Hydrological spreading of metal pollution and wetlands as nature-based solutions

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Abstract

The quality of the Earth's water resources have deteriorated due to human impacts. A key scientific challenge is to understand, quantify and predict the water-borne spreading of pollutants at relevant scales for freshwater management and water quality restoration programs. However, understanding the natural processes controlling large-scale hydrological transport of pollutants may be masked by river regulation schemes (in the form of dams and reservoirs), which are common in many large rivers. The main objective of this thesis is to increase the current knowledge regarding large-scale spreading of metals in hydrological systems. This objective is addressed through studying net impacts of mining (a main contributor to global metal pollution) on the spreading of metals in water systems and through investigating the mitigation opportunities of wetlands across the landscape. The main study region of this thesis is the Lake Baikal basin of Russia and Mongolia, which includes the large unregulated Selenga River and its delta-wetland areas. In addition, a set of global wetland sites are also studied. A multi-method approach is used in the four studies of this thesis. The methods include field-measurements, data synthesis, metal mass flow and water flow-path quantifications, as well as geochemical modelling. Results show that mining in the upstream part of the Lake Baikal basin is a significant contributor to riverine mass flows of several metals. The mass flows increased by an order of magnitude over the mining site. The observed speciation between dissolved (more bioavailable) and suspended (less bioavailable) phases could be well predicted for some metals (Fe, V, Pb and Zn) using a geochemical equilibrium model. However, the model failed to reproduce the speciation of other metals (Cr, Cu, Mn and Mo). In these cases, non-equilibrium processes may need to be considered, and adsorption databases may need to be developed, in order to make dependable predictions. Results also suggest that the concentration of dissolved organic carbon, which exhibits seasonal variability and long-term increasing trends due to climate change effects in the Arctic, can have a large impact on metal pollution transport. Further, observations showed that individual wetlands of the Selenga River delta locally retained between 77-99 % of incoming metal loads. However, a systematic analysis of current knowledge showed that large-scale net effects can differ considerably from the functions observed at individual wetlands on smaller scales. Along large-scale flow-paths, through which wetlands are connected with each other as well as with the larger landscape, key processes which can considerably contribute to such scale differences in function may occur. A survey of the current wetland research showed that relatively few studies have considered the larger scales at which key pollutant pressures and water quality changes take place. This thesis highlights the need for more research on large-scale wetland systems, which can aid in evaluating net pollution effects at landscape scales. This in turn can facilitate evaluations of how and when wetland systems may function as large-scale nature-based solutions.

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Abstract

The quality of the Earth's water resources have deteriorated due to human impacts. A key scientific challenge is to understand, quantify and predict the water-borne spreading of pollutants at relevant scales for freshwater management and water quality restoration programs. However, understanding the natural processes controlling large-scale hydrological transport of pollutants may be masked by river regulation schemes (in the form of dams and reservoirs), which are common in many large rivers. The main objective of this thesis is to increase the current knowledge regarding large-scale spreading of metals in hydrological systems. This objective is addressed through studying net impacts of mining (a main contributor to global metal pollution) on the spreading of metals in water systems and through investigating the mitigation opportunities of wetlands across the landscape. The main study region of this thesis is the Lake Baikal basin of Russia and Mongolia, which includes the large unregulated Selenga River and its delta-wetland areas. In addition, a set of global wetland sites are also studied. A multi-method approach is used in the four studies of this thesis. The methods include field-measurements, data synthesis, metal mass flow and water flow-path quantifications, as well as geochemical modelling. Results show that mining in the upstream part of the Lake Baikal basin is a significant contributor to riverine mass flows of several metals. The mass flows increased by an order of magnitude over the mining site. The observed speciation between dissolved (more bioavailable) and suspended (less bioavailable) phases could be well predicted for some metals (Fe, V, Pb and Zn) using a geochemical equilibrium model. However, the model failed to reproduce the speciation of other metals (Cr, Cu, Mn and Mo). In these cases, non-equilibrium processes may need to be considered, and adsorption databases may need to be developed, in order to make dependable predictions. Results also suggest that the concentration of dissolved organic carbon, which exhibits seasonal variability and long-term increasing trends due to climate change effects in the Arctic, can have a large impact on metal pollution transport. Further, observations showed that individual wetlands of the Selenga River delta locally retained between 77-99 % of incoming metal loads. However, a systematic analysis of current knowledge showed that large-scale net effects can differ considerably from the functions observed at individual wetlands on smaller scales. Along large-scale flow-paths, through which wetlands are connected with each other as well as with the larger landscape, key processes which can considerably contribute to such scale differences in function may occur. A survey of the current wetland research showed that relatively few studies have considered the larger scales at which key pollutant pressures and water quality changes take place. This thesis highlights the need for more research on large-scale wetland systems, which can aid in evaluating net pollution effects at landscape scales. This in turn can facilitate evaluations of how and when wetland systems may function as large-scale nature-based solutions.

Svensk sammanfattning

Kvaliteten på jordens vattenresurser har försämrats på grund av mänsklig påverkan. En viktig vetenskaplig utmaning är att förstå, kvantifiera och förutsäga den vattenburna spridningen av föroreningar, på skalor som är relevanta för vattenresursförvaltning och åtgärdsprogram. De underliggande, naturliga processer som styr storskalig hydrologisk föroreningstransport kan dock maskeras av att de flesta stora floders flöden är reglerade med hjälp av dammar och reservoarer. Målet med den här avhandlingen är att öka kunskapen kring storskalig hydrologisk spridning av metaller. Detta görs genom att studera nettoeffekter av gruvverksamhet (en viktig källa till globala metallföroreningar) på metallers spridning i vattensystemet, samt att undersöka våtmarkers möjligheter att rena förorenade flöden i landskapet. Avhandlingens huvudstudieområde är Bajkalsjön och dess tillrinningsområde (i Ryssland och Mongoliet), vilket inkluderar den oreglerade Selengafloden och dess delta-våtmarksområden. Även en grupp av globala våtmarksområden har studerats. Flera metoder användes i de fyra studierna som ingår i denna avhandling, inklusive fältmätningar, datasyntes, massflödes- och flödesvägskvantifieringar, samt geokemisk modellering. Resultaten visar att gruvdrift i uppströms-delar av Bajkalsjöns tillrinningsområde bidrar betydligt till förhöjda halter av flera metaller i flodsystemen. Massflödenena ökade en storleksordning över gruvområdet. Den observerade metall-specieringen mellan lösta (mer biotillgängliga) och partikulära (mindre biotillgängliga) faser kunde modelleras väl för vissa metaller (Fe, V, Pb och Zn) med en geokemisk jämviktsmodell. Modellen lyckades dock inte reproducera specieringen av andra metaller (Cr, Cu, Mn och Mo). I dessa fall kan icke-jämviktsprocesser behöva beaktas, och adsorptions-databaser kan behöva utvecklas för att förbättra prediktionerna. Resultaten visar också att koncentrationen av upplöst organiskt kol, som uppvisar stora årstidsvariationer samt långsiktigt ökande trender på grund av klimatpåverkan i Arktis, kan ha stor inverkan på metallföroreningars transport. Observationer visade också att enskilda våtmarker i Selengafloden lokalt kunde minska inkommande massflöden av metaller med 77 till 99 %. En systematisk genomgång av aktuellt kunskapsläge visade dock att storskaliga nettoeffekter kan skilja sig mycket från de funktioner som observeras vid enskilda våtmarker på mindre skalor. Längs storskaliga flödesvägar, genom vilka flera våtmarker är kopplade till varandra och till det större landskapet, kan viktiga processer ske, vilket avsevärt kan bidra till sådana skal-skillnader i funktion. En genomgång av aktuell våtmarksforskning visade att relativt få studier beaktade dessa större skalor där föroreningsspridning och vattenkvalitetsförändringar sker. Denna avhandling belyser behovet av ökat forskningsfokus på storskaliga våtmarkssystem. Detta kan hjälpa till att förstå föroreningars nettoeffekter på landskapsskalor, vilket underlättar vid bedömning av hur och när våtmarkssystem fungerar som storskaliga, så kallade naturbaserade lösningar.

Thesis content

This doctoral thesis consist of a summary and four Papers. The Papers are referred to as Papers I-IV in the thesis and are appended at the end of the thesis. The published Papers are reprinted by permission from the copyright holder.

I **Thorslund, J**., Jarsjö, J., Chalov, S.R., Belozerova, E.V., 2012. Gold mining impact on riverine heavy metal transport in a sparsely monitored region: the upper Lake Baikal Basin case. Journal of Environmental Monitoring 14, 2780–2792, doi: 10.1039/c2em30643c.

II **Thorslund, J**., Jarsjö, J., Wällstedt, T., Mörth, C.M., Lychagin, M.Y., Chalov, S.R., 2017. Speciation and hydrological transport of metals in non-acidic river systems of the Lake Baikal basin: Field data and model predictions. Regional Environmental Change 17, 2007-2021, doi: 10.1007/s10113-016-0982-7.

III Chalov, S., **Thorslund, J**., Kasimov, N., Aybullatov, D., Ilyicheva, E., Karthe, D., Kositsky, A., Lychagin, M., Nittrouer, J., Pavlov, M., Pietroń, J., Shinkareva, G., Tarasov, M., Garmaev, E., Akhtman, Y., Jarsjö, J., 2017. The Selenga River delta: a geochemical barrier protecting Lake Baikal waters. Regional Environmental Change 17, 2039-2053, doi:10.1007/s10113-016-0996-1.

IV **Thorslund, J**., Jarsjö, J., Jaramillo, F., Jawitz, J., Manzoni, S., Basu, N.B., Chalov, S., Cohen, M., Creed, I., Goldenberg, R., Hylin, A., Kalantari, Z., Koussis, A., Lyon, S., Mazi, K., Mård, J., Persson, K., Pietroń, J., Prieto, C., Quin, A., Van Meter, K., Destouni, G., 2017. Wetlands as large-scale nature-based solutions: status and challenges for research, engineering and management. Ecological Engineering, doi:10.1016/j.ecoleng.2017.07.012.

Author and co-authorship

I I led the writing and did the data synthesis and analysis, with the main help and support of J. Jarsjö who I also developed the idea of the paper with. All co-authors contributed to the field data collection, result analysis and the overall design of the study.

II I led the writing and performed the model simulations. Research ideas, including field preparations, measurements and modelling approach were developed in collaboration by me, J. Jarsjö and S. R. Chalov. T. Wällstedt was responsible for the modelling aspects, including the parameter settings. C.M. Mörth was responsible for the analytical methods, sample handling and analysis. M.Y. Lychagin contributed to the geochemical interpretation.

III S. R. Chalov led the writing and was assisted by all co-authors. We all contributed to the field data collection and result interpretation. I was, together with J. Jarsjö, responsible for metal sampling design and result interpretations regarding metal pollution.

IV I led the writing and result synthesis and interpretation, assisted mainly by J. Jarsjö and G. Destouni. All co-authors contributed to the paper idea and contributed with expert knowledge for each of the investigated 21 sites.

For all of the four papers of this thesis, my co-authors have had input regarding research ideas, data collection, result interpretations, and overall comments on language and flow, which have been very valuable for the publication of our works.

List of relevant co-authored papers, not included as part of this thesis

1. Fischer, S., Pietroń, J., Bring, A., **Thorslund, J**., Jarsjö, J., 2017. Present to future sediment transport of the Brahmaputra River: reducing uncertainty in predictions and management. Regional Environmental Change 17, 515-526. doi:10.1007/s10113-016-1039-7

2. Jarsjö, J., Chalov, S.R., Pietroń, J., Alekseenko, A., **Thorslund, J**., 2017. Patterns of soil contamination, erosion, and river loading of metals in a gold mining region of Northern Mongolia. Regional Environmental Change 17, 1991-2005. doi: 10.1007/s10113-017-1169-6

3. Lychagin, M., Chalov, S.R., Kasimov, N., Shinkareva, G., Jarsjö, J., **Thorslund, J**., 2017. Surface water pathways and fluxes of metals under changing environmental conditions and human interventions in the Selenga River system. Environmental Earth Sciences, doi:10.1007/s12665-016-6304-z

4. **Thorslund, J**., Chalov, S.R., Karthe, D., Jarsjö, J., 2016. Impacts of hydroclimate and mining on arsenic contamination of groundwater and surface water systems in Central Asia. In: Arsenic Research and Global Sustainability, (Eds) Bhattacharya, P., Vahter, M., Jarsjö, J., Kumpiene, J., Ahmad, A., Sparrenbom, C., Jacks, G., Donselaar, M.E., Bundschuh, J., Naidu, R. Tylor & Francis Group, London. ISBN: 978-1-138-02941-5

5. Chalov, S.R., Jarsjö, J., Kasimov, N.S., Romanchenko, A.O., Pietroń, J., **Thorslund, J**., Promakhova, E.V., 2015. Spatio-temporal variation of sediment transport in the Selenga River Basin, Mongolia and Russia. Environmental Earth Sciences 73, 663–680. doi: 10.1007/s12665-014-3106-z

6. Törnqvist, R., Jarsjö, J., **Thorslund, J**., Rao, P.S.C., Basu, N.B., Destouni, G., 2015. Mechanisms of Basin-Scale Nitrogen Load Reductions under Intensified Irrigated Agriculture. PLOS ONE 10, e0120015. doi:10.1371/journal.pone.0120015

7. Chalov, S.R., Zavadsky, A.S., Belozerova, E.V., Bulacheva, M.P., Jarsjö, J., **Thorslund, J**., Yamkhin, J., 2012. Suspended and Dissolved Matter Fluxes in the Upper Selenga River Basin. Geography, Environment, Sustainability 5, 78–94. doi:10.24057/2071-9388-2012-5-2-78-94

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1 Introduction

1.1 Background and Problem description

The pollution of freshwater resources is a global problem that is growing, for instance due to population increase and associated increasing pressures from industry, agriculture and domestic water use. These activities currently use more than 30 % by volume of the world's renewable freshwater resources (Schwarzenbach et al. 2010) and often cause various degrees of water pollution (e.g. Van Meter et al. 2017; Rivera-Utrilla et al. 2013). Various substances can also reach potentially hazardous concentrations in water systems due to natural erosion of soil, or mobilization of natural soil constituents related to human land-use impacts or impacts of hydroclimatic change. The spreading of pollutants from land-based source zones to aquatic systems can occur via atmospheric precipitation, wind or hydrological runoff. Once within the aquatic system, the water-borne spreading of pollutants to recipients can take different pathways; through groundwater, rivers, lakes and wetlands. Most pollutants are further influenced by transformation and retardation processes along the transport flowpaths, which may contribute to natural attenuation of pollution loads (e.g. Tesoriero et al. 2007; Schirmer et al. 2006). These processes include dispersion, sorption, dissolution–precipitation, and chemical reactions.

Achieving freshwaters of good water quality, by restoring polluted water systems and limiting on-going water quality deterioration, is a major scientific and societal challenge. Solving such a challenge requires an understanding of how pollutants are released into, and transported and transformed within the hydrological system, both today and in the future. With projected global net increases of water withdrawals with 62 to 75 % of current withdrawals in river basins by year 2050 (Alcamo et al. 2007), it is not hard to imagine that the pollution pressures on global water resources will further increase. For example, mining is today counted as a main contributor to metal pollution of local and regional aqueous systems (Schwarzenbach et al. 2010) and has been shown to increase the global river-borne heavy metal fluxes considerably (Meybeck and Vörösmarty 2005; Razo et al. 2003). In mining operations, metals are exposed to the environment due to excavation of rock or fluvial sediments. The release of metals into water systems can then occur due to exposure of the mined areas, during smelting and metal refinement of the mined material, and due to leaching from waste heaps or tailing dam failures (e.g. Younger and Wolkersdorfer 2004). The non-degradable nature and high toxicity of many heavy metals make this group of pollutants of particularly high concern (Wasim Aktar et al. 2010). Additionally, impacts of mining activities can result in pollution of both water, sediments and soils, with impacts at both local and regional scales (e.g. Serfor-Armah 2006; Yanguo et al. 2003).

Although local impacts from mining activities in many cases are relatively well understood, catchment scale impacts of such local land-use changes are usually not (e.g. McIntyre et al. 2016). This is due to increasing process complexity as scales increase, and the difficulties of comparing water quality impacts against natural variability and background levels (e.g. Schirmer et al. 2012). For the ability to attribute water quality impacts/ and or changes to a particular source zone, multi-method approaches will be needed. Further, to test hypotheses that could explain more specifically how and why mining impacts differ between regions of different hydrogeologic, geochemical and hydroclimatic conditions (even if source conditions are similar; e.g. Montaño-Ley et al. 2008), systematic observations are needed from several different regions (e.g. Nilsson et al. 2013). This is because a relative wealth of observational data can be required to distinguish trends from random fluctuations in environmental datasets. Preferably, within the regions, observations should be made at multiple locations with different degrees of mining disturbance. However, in comparison with laboratory observations of metal

leaching (Zheng et al. 2012; Jurjovec et al. 2002), and local field studies at mining sites (e.g. Kitula et al. 2006; Ogola et al., 2002), the large-scale transport of metals in hydrological systems are underexplored (Pandey et al. 2014; Mayes et al. 2010).

Further, predicting the partitioning and chemical forms of metals, hereafter referred to as speciation, is key for determining their mobility and toxicity. Geochemical models make it possible to investigate and predict speciation and its controls to great detail (Magu et al. 2016). Several widely used speciation models, including PHREEQC (Parkhurst and Appelo 1999), Visual MINTEQ (Gustafsson 2010) and WHAM (Tipping 1994) have been successful for predicting metal speciation in small-scale and well-defined laboratory environments (e.g. Caruso et al. 2008; Almås et al. 2007). However, field conditions such as spatio-temporal variability in hydro-climatic and geochemical characteristics can be inconsistent with basic model assumptions, such as that of equilibrium conditions (Keating and Bahr 1998). This may or may not introduce unacceptable prediction errors in the model output. Since there is a lack of large scale studies comparing model predictions of field conditions with independent data, the capacity of models to predict metal speciation under such complex and less well-defined conditions is relatively unknown.

The remoteness and sparse population of many mining areas make them particularly inaccessible and difficult to monitor (Paull et al. 2006). Additionally, many global river basins are ungauged and there are decreasing trends in funding being spent on up keeping of those that are monitored (Sivapalan et al. 2003). In order to understand and predict (downstream) impacts of mining, knowledge of metal loads (i.e. mass flows of metals) is a prerequisite. Quantifications of mass flows, defined as the product of concentration and water discharge, ideally need simultaneous observations of both of these quantities. However, whereas many observational studies contain relevant and detailed accounts of metal concentrations, hydrologic data on (riverine) water discharges at the time of such concentration observations is frequently lacking for mining regions (e.g. Ali et al. 2016; Islam et al. 2015). Because of this, the overall consequences of many of the world's mining regions for downstream recipients remain unclear. More generally, this data-mismatch problem is relevant for many different contaminants in various regions of the world (Azcárate et al. 2013).

Further, many large river basins are today extensively modified by river impoundments. On a global scale, more than 45 000 large dams (>15 m high) were constructed during the last century (Poff et al. 2007). As an example, the Connecticut River alone has about 3000 dams (Zimmerman et al. 2010). Such impoundments have changed natural flows of sediment and water in many river systems and has dampened the spatio-temporal dynamics, making systems more homogenous. In combination with a lack of monitoring data in naturally flowing river systems (Burn 2008), such river regulation constructions make process understanding and dynamics of natural flow regimes more and more difficult to establish. This in turn can make it more complex to distinguish cause-effect relationships (for example from mining and climate changes) on hydrological pollutant transport (Vörösmarty et al. 2003). To improve process understanding of the transport and transformation of pollutants, for example in response to seasonality and hydrological events, it is thus of central importance to study unregulated river basins.

Another central scientific and management challenge related to large-scale pollution issues is to assess potential mitigation opportunities. Nature-based solutions (NBS), which use nature's own features (e.g., biogeochemical natural attenuation or physical sedimentation processes), have potential to be among the most cost-efficient ways of addressing global environmental and social challenges (Maginnis et al. 2016), including pollution issues (Barbier 2013; Temmerman et al. 2013). Wetlands may have a particularly high potential to be used as cost-effective NBS. This potential arises from the well-known capacity of wetlands to mitigate polluted loads, for example through phytoremediation (Weis and Weis 2004), storage and

sedimentation, as well as through bioattenuation (Sheoran and Sheoran 2006). More generally, the global ecosystem services provided to humans by wetlands have been valued among the top three biomes in the world, for instance exceeding the total value of terrestrial forests and coral reefs (Costanza et al. 2014).

Traditionally, and still today, mitigation decisions are typically made at the scale of individual wetlands, and engineering solutions as well as management and policy decisions are often based on understanding isolated parts of the water system (Destouni et al. 2015; Borer et al. 2014). Although extensive research results at the scale of individual wetlands have been crucial for enhancing our understanding of fundamental wetland functions (e.g. Perry et al. 2004; Drexler and Bedford 2002), recent findings show that many landscape services emerge from the aggregated effects of wetland networks and their interactions with the surrounding larger landscape (e.g. Cohen et al. 2016). For example, even if individual wetlands may show high retention capacity for inflowing polluted water, a main question is whether such net retention will be achieved at larger landscape scales. To understand the potential usefulness and services of wetlands as larger-scale nature-based solutions, there is a need to understand the coupling between wetlands and their surroundings, hereafter referred to as wetlandscapes (illustrated in Fig. 1).

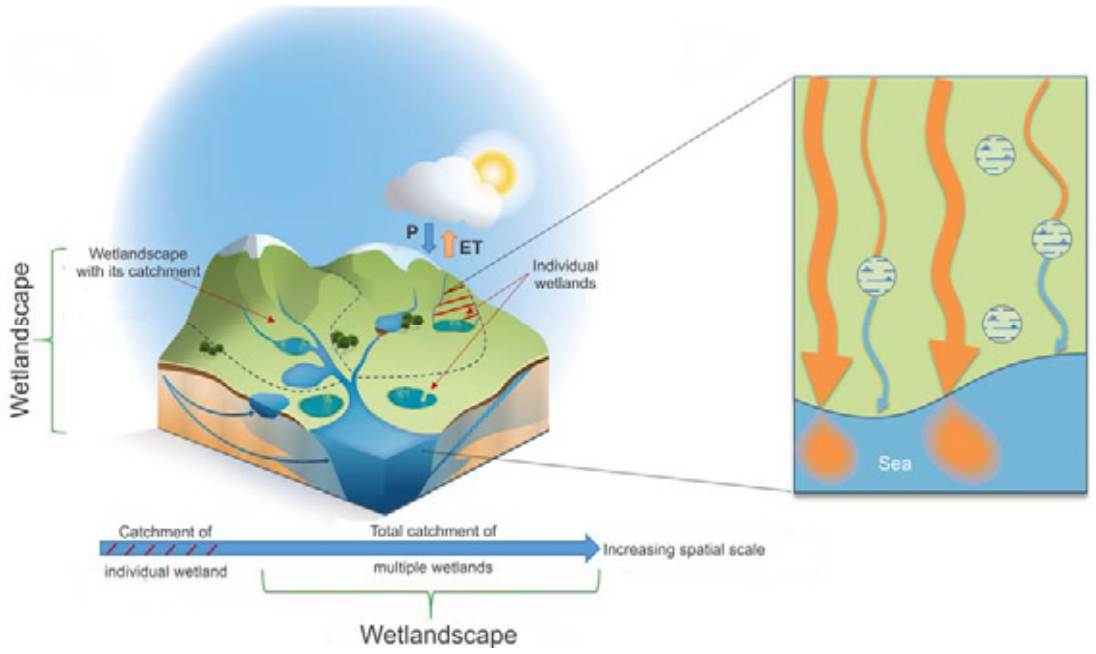

Figure 1. Conceptual sketch of a whole wetlandscape (a) with a zoom in on flow-path distributions across a section of the wetlandscape, shown as arrows, which width indicates the flow magnitude and the color indicates the water quality level (orange more polluted, blue less polluted). A wetlandscape consists of multiple wetlands that are hydrologically connected within an associated larger hydrological catchment than that of an individual wetland. The associated large-scale water flows, through precipitation (P), evapotranspiration (ET), runoff (R) and groundwater (GW) are represented by arrows in the landscape. A wetlandscape and its associated total catchment is not a static unit but can be defined at and represent various spatial scales (exemplified by dashed lines) (Modified from Fig. 1 and 3 in Paper IV: Thorslund et al. 2017).

This thesis targets some of the challenges described above, regarding the large-scale release, spreading and fate of metals in water systems. The Lake Baikal basin has been used as a main study site, for several reasons. Firstly, the upper parts of the Lake Baikal basin, in Mongolia, is known for its extensive mining, and comprises one of the world's largest gold mining site by annual production. Its expansion since the 1990s (McIntyre et al. 2016) has not only led to

local environmental concerns, but also to regional ones, not least due to the potential downstream transport of metals to the unique ecosystem of the Lake Baikal in Russia. The Lake Baikal hosts a wide variety of endemic species and encompasses a huge fresh-water resource (Granina 1997), making it valuable from both ecological and socio-economic perspectives (Brunello et al. 2006). Understanding processes controlling metal spreading and fate within the Lake Baikal basin is hence of key significance for managing its ecosystems under current to future conditions.

From a scientific perspective, the extensive mining source zones in the considered Lake Baikal basin increase the possibilities of tracing various mining impacts at different downstream distances and in different water systems (e.g., groundwater, surface waters and wetlands). This likely also increases the possibilities of testing hypotheses regarding the governing transport processes. Additionally, the Lake Baikal basin comprises one of few large rivers (the Selenga River; drainage basin of 447 000 km^2) in the world, which is not impacted by human flow regulations, such as dams and reservoirs. This decreases process complexity and allows for increased understanding of different natural processes, for instance the impact of hydrological events, which are otherwise in regulated basins at least partially masked. Finally, the Selenga River delta at the inlet of Lake Baikal is a good example of a wetlandscape. The delta's extensive wetland-channel networks enables investigations of its possible large-scale barrier functions (Lisitzin 1999) for pollutants entering the Lake Baikal (e.g. Ozersky et al. 2017). Such investigations can increase knowledge on the potential of wetland networks in supporting nature-based solutions for decreasing metal loads to downstream recipients.

1.2 Thesis objectives

This thesis takes on the scientific challenge of understanding cause-and-effect relations on large-scale pollutant spreading and fate. This is done through quantifications of hydrological and geochemical processes, and their impact on metal transport from upstream sources to downstream recipients, including large-scale functions of wetlands across the landscape. More specifically, the main objectives of this thesis are to:

A. Quantify the net impact of mining activities on metal transport to adjacent groundwater and surface water systems in an unregulated river basin.

B. Investigate to which extent, and in which cases the speciation of different metals can be predicted and explained, using assumptions common for state-of-the-art geochemical models.

C. Investigate the function of wetland networks for decreasing metal loads to downstream recipients.

D. Identify knowledge gaps regarding the functions of and impacts on wetland networks, considering their potential use as nature-based solutions.

These objectives are addressed in Papers I-IV, according to the following structure:

1. Paper I-II considers the headwaters of the Selenga River basin, and in particular the Tuul River in Mongolia (marked in Fig. 2) to address objective A. This is done using reported as well as field-based estimates of concentrations and mass flows of multiple metals upstream of, downstream of, and at mining areas in the Tuul River basin.

2. Paper II addresses objective B, by comparing predictions of the geochemical equilibrium model Visual Minteq (Gustafsson 2010) to measured metal partitioning of multiple metals in the Tuul River, investigating their detailed geochemical speciation and controls.

3. Paper III considers the downstream Selenga river delta at Lake Baikal, to address objective C. This is done using a combination of direct observations, GIS data and remote sensing data to investigate flow-path distributions and metal removal efficiency of the delta's wetland-channel networks.

4. Paper IV addresses objective D, by synthesizing results from active research projects among a global set of wetland sites, with a specific focus on large-scale functions and impacts on such systems. This synthesis is complemented by and compared with a survey of general wetland literature.

2 Study areas

An overview map of the study areas of this thesis, and corresponding focus regions for Paper I-IV, are shown in Fig. 2. More details about these sites are described in section 2.1 and section 2.2 below.

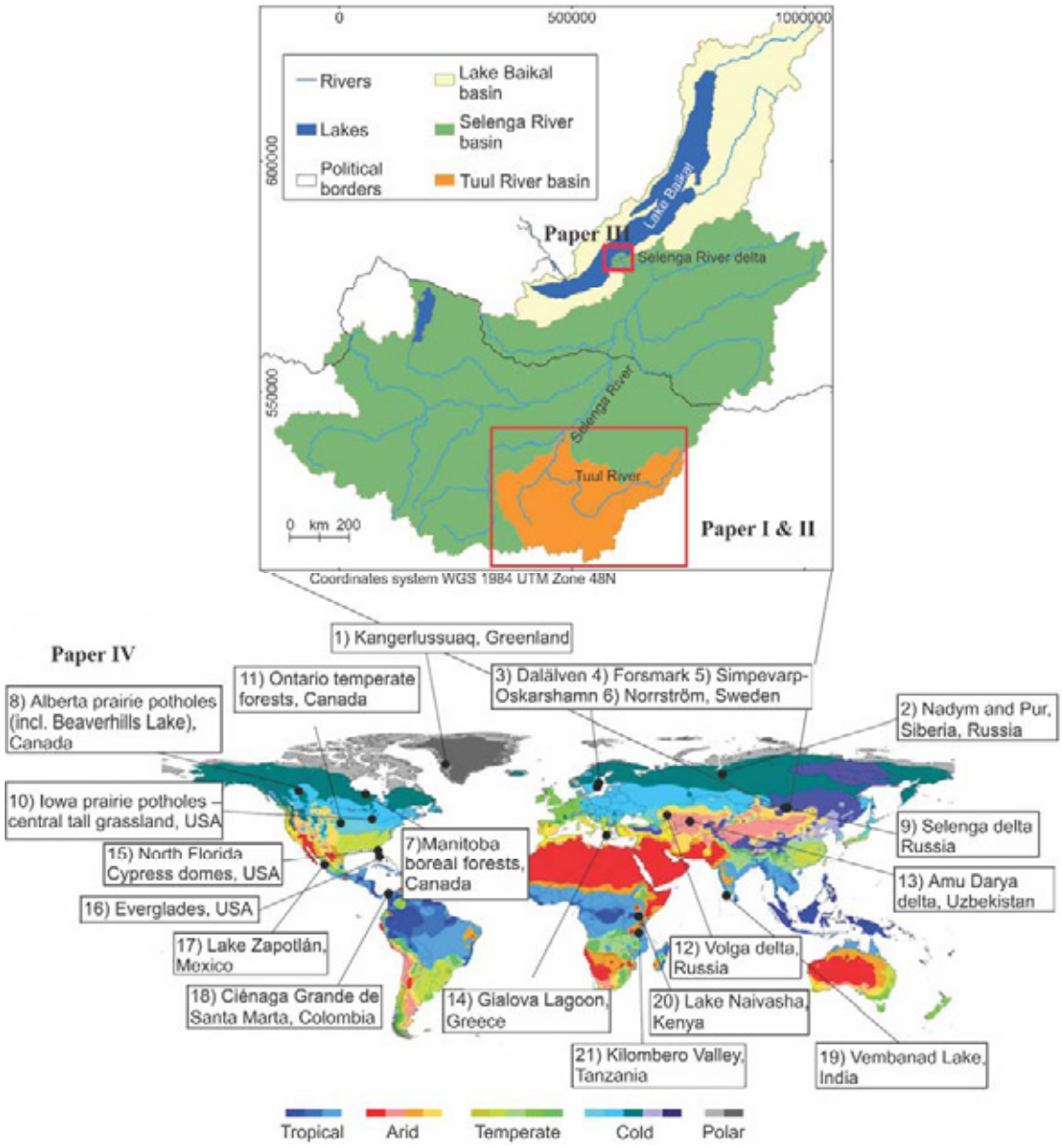

Figure 2. Overview map of the thesis study sites from Papers I-IV. Paper I-II considers the upstream part of the Lake Baikal basin (Tuul River Basin), Paper III considers the Selenga wetlandscape in the downstream part of the Lake Baikal basin and Paper IV considers a set of twenty-one globally distributed wetlandscapes. The locations of the wetlandscapes are shown on a background map of the Köppen-Geiger climate classification system, as updated by (Peel et al. 2007) and numbered according to Latitudinal position (Modified from Fig. 2 in Paper IV: Thorslund et al. 2017).

2.1 The Lake Baikal basin, including the Selenga wetlandscape (Paper I-IV)

The Lake Baikal basin is a transboundary basin (area of 576 500 km^2), located between Mongolia and Southern Siberia, in Russia, and with the majority of the basin located in Mongolia (63 %). The Lake Baikal is the deepest, largest and oldest freshwater body on earth, with a depth of about 1600 m, a volume of about 23 000 km^3 and an age of 25 million years (Granina 1997). It is included on the UNESCO World Heritage list, partly because of its very unique ecosystem, with many endemic species, including the only freshwater seal. The climate of the region is continental to subarctic (Brunello et al. 2006) and a large part of the basin is underlain by various degrees of permafrost (Törnqvist et al. 2014). The landscape of the basin is manly dominated by steppe and mountainous taiga and the geology is varied, including metamorphic, sedimentary and igneous rocks. The region overall has strong connections between groundwater aquifers and surface waters, due to large alluvial unconfined aquifers (Zandaryaa et al. 2008). The region is also naturally rich in calcium bicarbonate (Altansukh and Davaa 2011). The Lake Baikal is located in the upstream part of the Yenisey River system and its only outflowing river; the Angara River, eventually discharges into the Arctic Ocean. Inflowing rivers are the upper Angara River, the Barguzin River and the Selenga River. The main river flowing into the lake is the Selenga River, which has a basin area of 447 000 km^2. The Selenga River is an important contributor of both water and sediments into the delta-Lake Baikal system, discharging about 30 km^3 of water and 3.5 million tonnes of sediments per year. Long-term analyzed trends in hydroclimate of this region show that temperature has increased by 1.6 °C (1938-2009), but with relatively small changes in precipitation (P), evapotranspiration (ET) and runoff (R) for the same period. There are however noted decreases in runoff during since the 1990s (Törnqvist et al. 2014).

Although the Lake Baikal has a huge volume, reports of pollution, for example heavy metal accumulation in seals, have been reported (Ozersky et al. 2017; Boyle et al. 1998). There are many potential pollution sources within the basin, including pulp and paper mill industries in the Russian part of the basin and coal and gold mining industries in the Mongolian part of the basin, as well as the Mongolian capital of Ulan Bator. Mongolia's gold production and mining industries has expanded rapidly since the 1990s. The Tuul River basin, in the upstream part of the Selenga River basin, is where the largest gold production of Mongolia occurs; within the Zaamar Goldfields (Farrington 2000). The main type of mining performed here is placer mining, which is mining of alluvial sediments in the river bed. With many different mining companies and expanding production, resulting land-use changes have had a visual large impact on at least the local environment. The Tuul River, that has an area of 50 000 km^2 and long term (1945-2007) annual average discharge of 27 m^3s^{-1}, is a tributary of the Selenga River. The downstream part of the Selenga River ends with the Selenga Delta, which is the largest delta system in East Siberia (area of 600 km^2). The delta has an elevation of about 2 m above that of the average level of Lake Baikal and most parts of its system is swamped. The delta contains three main flow distributary systems (sectors): the Selenginskiy channel system (left), the Sredneustievskiy channel system (central), and the Lobanovskiy channel system (right). The Selenga delta-wetlandscape also contains numerous small channels and wetland networks, which may act as a critical retention filter for pollutants flowing towards Lake Baikal.

2.2 A set of global wetlandscapes (Paper IV)

To move beyond the Selenga delta wetlandscape and to compare detailed knowledge at this focus study site to other wetlandscapes, investigations on a set of 21 globally distributed wetlandscapes were also investigated (Fig. 2). These wetlandscapes include a range of different wetland types, including marine, estuarine, lacustrine, riverine, and palustrine wetlands. These sites are located in tropical, arid, temperate, cold and polar climatic zones and are thus subject to different regional hydroclimatic conditions and changes (Table 1 and Fig. 3). Although these sites are heterogeneous, both within and across sites, they share common traits such as containing multiple wetlands and the sites have been exposed to both hydroclimatic and human land-use changes. For example, large-scale hydroclimatic changes have occurred at many of the sites, for both surface temperature (Fig. 3b) and water fluxes (Fig. 3d, f, h), over the last century. The largest temperature changes have occurred at the relatively cold, northern boreal and temperate sites with mean annual temperature less than around 10°C (sites 1-13). The greatest hydrologic changes from 1901-1957 to 1958-2014 occur for annual average runoff (Fig. 3h), with increases at most of these wetlandscapes. For sites where changes so far have been relatively small, climate change projections indicate greater future changes (Sarukhán and Whyte 2005).

Table 1. Summary of main climatic, wetland-type and land-use/landscape setting characteristics of the 21 in-depth investigated wetlandscape sites (see Fig. 2) for site names and corresponding site numbers). Climate regimes are divided according to the Köppen-Geiger climate classification system, as updated by (Peel et al. 2007), and wetland types are classified according to the Cowardin system, established by the U.S Fish and Wildlife Service (Cowardin et al. 2013). (Table A1 in Paper IV: Thorslund et al. 2017)

Site number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Climate regime																					
Temperate			x	x	x	x	x	x		x											
Dry													x	x						x	
Tropical															x	x	x	x	x		x
Cold and polar	x	x							x		x	x									
Wetland type																					
Marine														x		x		x			
Estuarine														x		x		x			
Lacustrine								x			x	x	x			x	x		x	x	x
Riverine	x	x	x	x	x				x									x	x		x
Palustrine	x	x					x		x	x					x	x					
Land use/landscape setting																					
Forest/natural/peat	x	x	x	x	x	x	x	x	x		x	x						x	x		x
Agriculture	x	x				x	x	x		x		x	x	x	x	x	x		x	x	x
Urban			x	x	x	x		x		x				x	x	x	x	x	x	x	
Industry	x	x	x	x	x	x		x		x	x	x							x	x	x
Coastal			x	x	x	x								x		x		x	x		

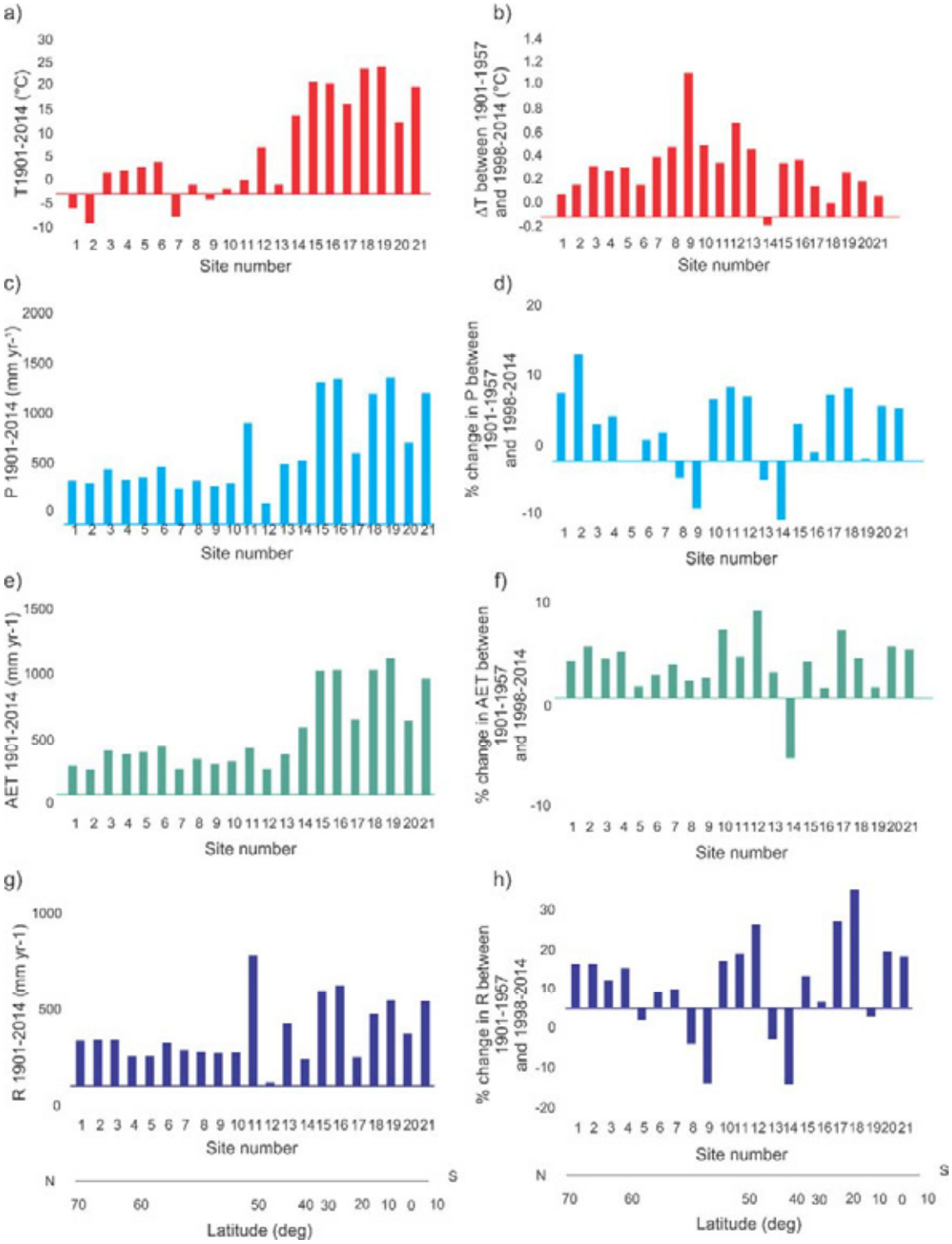

Figure 3. Long term average (1901-2014) hydroclimatic conditions (a, c, e, g) and changes (between 1901-1957 and 1958-2014: b, d, f, h), for the investigated 21 wetlandscape sites (name and numbers in Fig. 2). Parameters include temperature (T, in °C), precipitation (P, in mm yr^{-1}), actual evapotranspiration (AET, in mm yr^{-1}) and runoff (R, in mm yr^{-1}). For more details regarding data sources and methods, see section 3.2 and Appendix A.2 in Paper IV. (Modified from Fig. 2 in Paper IV: Thorslund et al. 2017).

3 Methods

3.1 Analysis of water quality (Paper I, II, III and IV)

For Paper I, II and III of this thesis, field sampling campaigns were conducted in various regions of the Lake Baikal basin, with in-situ measurements of hydrological and geochemical parameters. For Paper I, snapshot measurements of basic hydrogeochemical conditions from a novel field campaign (July 2011) was combined with a synthesis of riverine metal(loid) concentrations reported from autumn and summer periods of previous years (October 2005, June 2006 and July 2008), along river reaches upstream of the Zaamar mining site, at the mining site, and downstream of the mining site (in the Tuul-Orkhon-Selenga rivers). Additionally, concentration data from a publically available long-term monitoring station (June, July, October 1998-2003) in downstream Selenga River (near its delta at Lake Baikal) was gathered. The selection of metals for Paper I was based on metals commonly associated with mining activities (e.g. Weng et al. 2012; Nordstrom 2011; Jain and Sharma 2006), in combination with considerations regarding data availability, i.e. preferentially selecting metals having reported concentrations for all considered sampling locations, as well as having concentrations above detection limits. These selection criteria resulted in the following seven metals: Al, As, Cu, Fe, Mn, Pb and Zn of focus in Paper I.

For Paper II, the dataset was expanded, by own measurements conducted during two field campaigns (June 2012 and September 2013). From these campaigns, repeated measurements at the same locations as in Paper I was done (in Tuul River, upstream, downstream, and at the mining site, Fig. 4). The selection of metals was here expanded to a total of 11 metals (Al, As, Cd, Cr, Cu. Fe, Mn, Mo, Pb, V and Zn), hence including all of the selected metals of Paper I. In addition to metals, sampling for measurements of major ions, pH, alkalinity and total and dissolved organic carbon (TOC and DOC) was also conducted.

For the 2013 campaign, also groundwater and wastewater ponds in the vicinity of the mining site was sampled. These additional points were included to investigate pathways of pollution spreading, as well as for gathering further geochemical data needed as input parameters for geochemical modeling (see section 3.3 below). For Paper III, the focus was on the downstream part of the basin, with sampling for metal analysis conducted in over 30 locations of the Selenga delta. For all of the metal samples, both total and dissolved fractions (filtered using 0.45 μm pore membranes) were analyzed and suspended fractions were estimated as the difference between total and dissolved concentrations. Further details on sampling procedures and analysis methods are found in the methods sections, as well as in the supplementary information of Paper I-III.

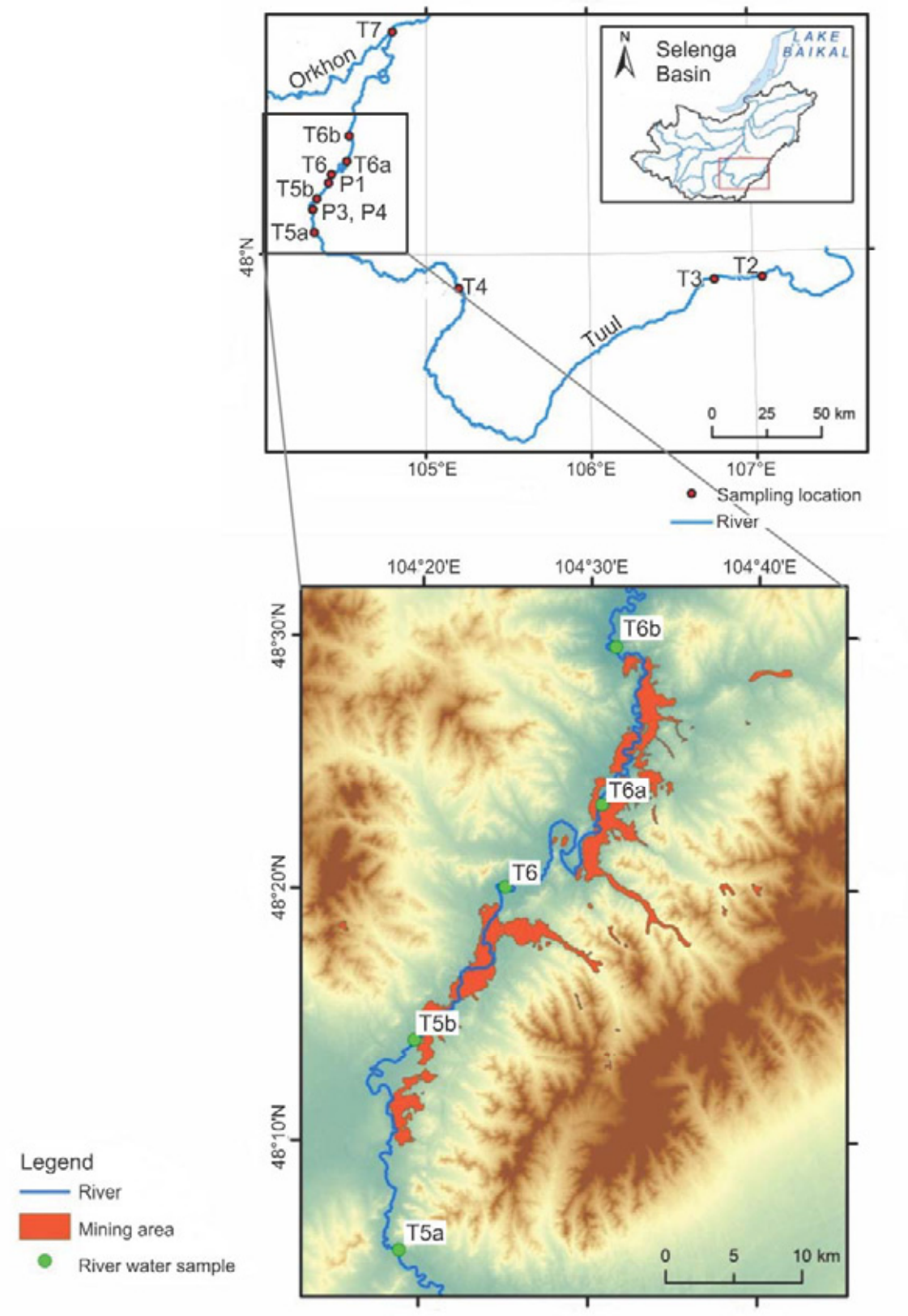

Figure 4. Location of the sampling points of Paper I-II in the mining region along the Tuul River, in the upstream part of the Lake Baikal basin, in Mongolia (Modified from Fig. 1 in Paper II: Thorslund et al. 2017).

3.2 Mass flow analysis (Paper I and II)

Mass flows estimations were done based on multi-location measurements, in the Tuul River, upstream of, downstream of, and at the mining site. This made it possible to evaluate net mass flow changes over the mining site, which is a measure of total mass input of metals due to mining activities over the considered river stretch. In this way, also contributions from diffuse sources, such as input from the groundwater system, can be detected.

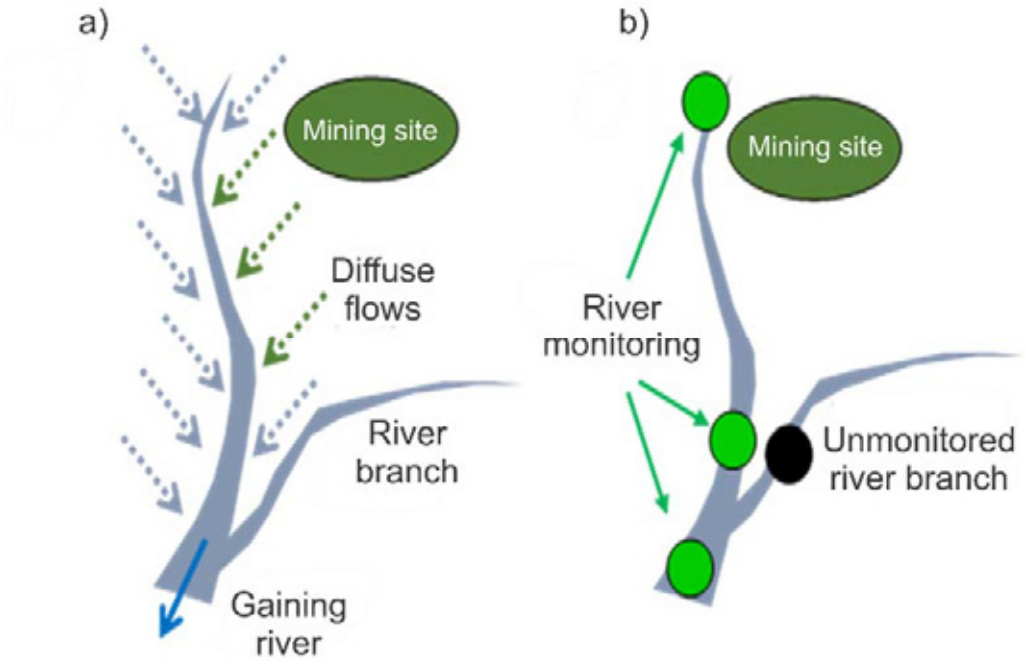

Figure 5. A schematic illustration of a mining site and its input of pollutants to riverine mass flows (a) as well as suitable monitoring locations to capture the net impact of the source zone (b). By applying conservation of mass, pollutant mass cannot be lost to other rivers. By monitoring upstream and downstream of the mining area the relative importance of point sources versus diffuse pollution sources can be evaluated (Modified from Fig. 1 in Paper I: Thorslund et al. 2012).

More specifically, simultaneous snap-shot measurements of riverine concentrations (C) of substances and water discharge (Q) were conducted, which allowed for mass flows quantifications according to

$$Mf = C_i \cdot Q_i \qquad (1)$$

where C_i is the pollutant concentration and Q_i is the water discharge at a given river cross section for a given time t_i.

These measurements were repeated in several field campaigns, covering different hydroclimatic conditions and seasons (Paper II). The snap-shot measurements were combined with a synthesis of previously reported data, to evaluate long-term characteristics (Paper I). By considering multiple measurements of C and Q over a defined time period (e.g. a month), eqn. 1 can be modified (eqn. 2) to approximately represent average mass flows over the selected time period, even if C and Q were not measured simultaneously:

$$Mf \approx \bar{C} \cdot \bar{Q} = \left(\frac{1}{n}\sum_{i=1}^{n} C_i\right)\left(\frac{1}{m}\sum_{j=1}^{m} Q_j\right) \quad (2)$$

where C_i and Q_j are the instantaneous values of concentration and discharge respectively, representative of the considered time period and n is the number of concentration samples, which may or may not differ from the number of discharge measurements, m, but obtained during the same considered time period (Paper I). The standard deviation of mass flows was also calculated (see section 2 of Paper I). Further details on sampling procedures and analysis methods are found in the method sections of Paper I-II, as well as in supplementary information.

3.3 Analyses of geochemical controls and model predictability (Paper II)

Speciation modelling can be used to test whether or not different hydrogeochemical processes can explain the observed metal partitioning between dissolved and suspended phases, given also the independently observed basic geochemical conditions of the river system. The model Visual Minteq, version 3.0 (Gustafsson 2010) was here used to investigate to which extent different geochemical processes and basic geochemical conditions in the mining region could be used to reproduce the observed speciation of metals in the studied region. Visual Minteq is a geochemical equilibrium model that can be used to calculate chemical equilibrium processes including dissolution-precipitation partitioning, sorption processes and organic and inorganic complexation. The model was chosen in particular because of its well-known developed sub-models for organic material, making it possible to model metal-organic complexation, which in many cases have been seen to have important controls on metal spreading (e.g. Weng et al. 2002). It is also valued for its extensive equilibrium constants database, which can be modified by the user, making it possible to adapt the model to a specific system (e.g. Gustafsson 2010; Zhang et al. 2008).

To test in which cases model predictions agree (i.e., considering different metals and different possible geochemical reactions) with the actual measurements in the Tuul River system, linear correlation analyses were performed. From the coefficient of determination (r^2), metals could be categorized according to model performance and thus give indications on the degree of each metal's governance by equilibrium geochemistry. The analysis was performed comparing modelled and observed dissolved metal fractions (expressed in percent of the total concentration). The dissolved fraction was chosen because of the increased toxicity and bioavailability of most metals in this phase (e.g. Boenigk et al. 2005), which could then be most relevant to predict under current and changing conditions. Further details on the correlation analysis, as well as used modeling parameters, assumptions and procedures are found in methods and supplementary information of Paper II.

3.4 Analysis of the function of wetlandscapes (Paper III and IV)

For the ability of assessing the potential of using wetlands as large-scale NBS, a key question for wetland-related research is whether wetland functions, interactions (among wetlands and with their surroundings), associated services, and regional-global change impacts on these are currently evaluated at relevant scales. To investigate the current knowledge regarding wetlandscapes, this thesis analyzed research results from 21 study sites of global wetlandscapes (section 2.2), including the present focus study site of the Selenga River delta. The analysis consisted of (i) a synthesis of functional differences between individual wetlands and wetlandscapes; (ii) an expert survey on wetlandscapes and their changes, as well as (iii) a general wetland literature survey.

For (i), results were obtained from measurements of Paper III, as well as from on-going and published research across the 21 wetlandscape study sites, as synthesized in Paper IV. Quantifications of flows and flow-path distribution were used in combination with analyses of retention capacity of individual wetlands and wetland networks (Paper III and IV and conceptually illustrated in Fig. 1b). Methods used for these analyses include analytical model development (Quin et al. 2015; Törnqvist et al. 2015), spatially distributed runoff quantifications using catchment-scale PCRaster-based Polflow type of models (de Wit 2001), as well as field-measured (Chalov et al. 2017) and synthesized data on discharge and contaminant concentrations (Quin et al. 2015; Törnqvist et al. 2015; Thorslund et al. 2012).

As an example, a detailed map is shown below (Fig. 6) of the sampling locations used in the Selenga River delta, addressing its role in pollution mitigation. Sampling of metal concentrations in various parts of the delta was combined with discharge measurements and quantifications of flow-partitioning between the different delta sectors (left, central and right). In particular, focus was on sampling both large distribution channels, as well as smaller channels with wetlands. More details on sampling and analyses for this site can be found in the methods-section of Paper III. More details regarding quantification methods and analysis of the other investigated wetlandscapes can be found in methods and Appendix (mainly Table A1-A2 and references therein) of Paper IV.

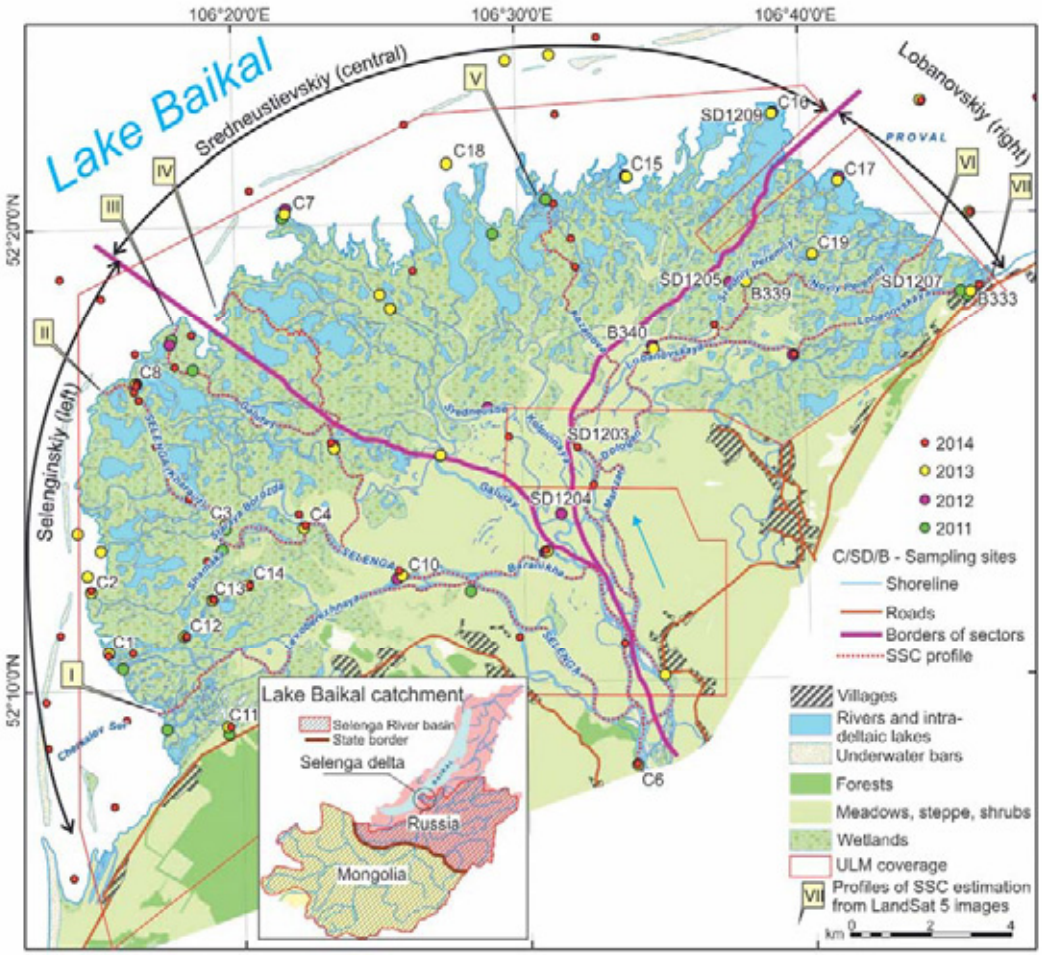

Figure 6. Location of the sampling points and different sectors (left, central, right) in the Selenga River Delta, by the inlet of the Lake Baikal, analyzed and sampled for Paper III (Modified from Fig. 1 in Paper III: Chalov et al. 2017).

Regarding (ii), the authors of Paper IV; a group of eco-hydrological researchers working within a global wetland network (http://www.gwennetwork.se/), held a designated workshop in Greece (April 30th – May 1st, 2015). The author group are all involved in active research projects across the considered global set of wetlandscapes (Fig 2). The overall objective of the workshop was to identify and discuss the large-scale functions of and impacts on wetlandscapes (Paper IV). The collective expertise and knowledge of the involved group of researchers were synthesized at the workshop and in a follow-up survey. Additionally, consistently documented site descriptions and published results from previous and ongoing research projects were available for these sites. Together with the expert survey, this was the basis for the synthesis of knowledge regarding wetlandscape functions and their changes. Further details regarding the survey can be found in Appendix Table A1 and A2 of Paper IV.

Lastly, in order to investigate the general wetland literature (iii), in particular with regard to the relative frequency of small-scale versus large-scale studies, a comprehensive general survey of the published scientific literature on the considered wetland functions and change drivers was conducted. The Web of Science™ Core Collection (WoS) was used, and the search was directed to include all wetland related publications (a total of 20 997 published papers), published until the search date (May 3rd, 2017). Further details regarding the literature analysis can be found in Appendix A3 and Table A3 of Paper IV.

4 Results

4.1 Source zone pollution and mass transport of metals

The average pH conditions in the Tuul River along the Zaamar mining site is, in contrast to many mining areas, alkaline: ranging between pH 7.2 -9 (data from 2011-2013 Paper I and II). Local mining water ponds are in the same range, with an average pH value of 8.7, whereas groundwater measurements show pH values in the range of 7.5 to 7.8 (data from 2013, Paper II). Similarly as pH, alkalinity and turbidity are also high, with values of up to 8.5 meq L^{-1} for alkalinity and ranging between 85.5 and 493 NTU for turbidity. The organic material fraction is dominated by DOC throughout the region, with values ranging between 7.6 and12 mg C L^{-1} (data from 2013, Paper II).

Fig. 7 shows a selection of metals (Al, As, Fe och V) from the set of the eleven analyzed metals in 2012 and 2013, and their concentrations across the mining site (Paper II). For all of these metals, concentrations are higher in the downstream location (T6a) compared to the upstream locations (T5), relative to the mining site. Al (Fig. 7a) and Fe (Fig. 7c) have overall highest concentrations, with total concentrations reaching levels of 6020 μg L^{-1} and 3180 μg L^{-1} respectively. Their dissolved concentrations reach levels of 89 μg L^{-1} and 74 μg L^{-1}, respectively. Dissolved concentrations dominate fractions for As (Fig. 7b) with levels reaching 13 μg L^{-1}. Concentrations of V (Fig. 7d) shows varying behavior, with highest dissolved and total concentrations of 8 μg L^{-1} and 12.9 μg L^{-1} respectively. In line with the results shown here (Fig. 7), concentrations of most of the metals (the groups of seven and eleven analyzes metals for Paper I respectively Paper II) in the Tuul River for all measurement campaigns increase over the mining site, with observed net higher concentrations downstream compared to upstream of the mining area . This trend is consistent for both dissolved and total concentrations, but with total concentrations reaching generally up to one order of magnitude higher compared to dissolved concentrations (Paper I and II). For example, in Paper II, five of the investigated metals (Al, Fe, Mn, Pb, Zn) are dominated by their suspended phase. Two of the metals (Cr and V) show varying domination of dissolved versus suspended concentrations. The remaining three metals (As, Cd, and Mo) are dominated by their dissolved phases.

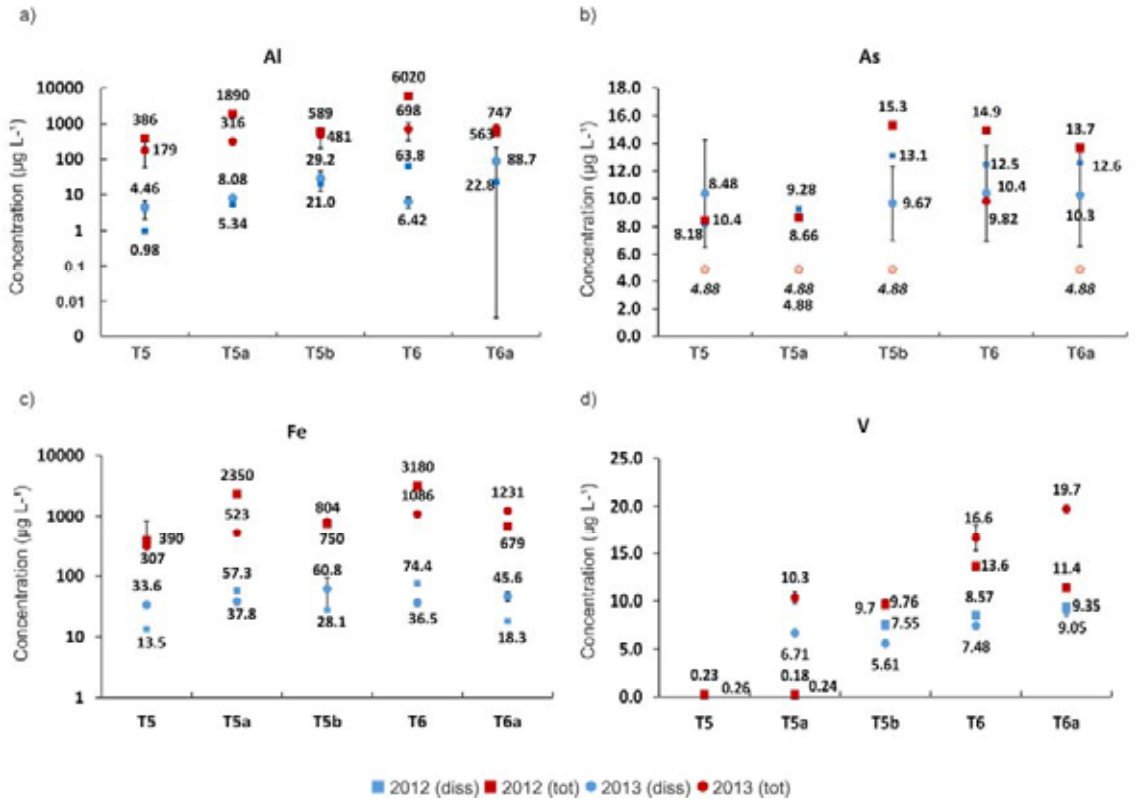

Figure 7. A selection of four of the total set of eleven analyzed metal concentrations along the Tuul River reach. Locations represent upstream (T5-T5a), at site (T5b-T6) and downstream (T6b) of the mining site. Dissolved concentrations are shown in blue, total concentrations are shown in red, for the year 2012 (squares) and 2013 (circles) (Figure modified from Fig. 2 in Paper II: Thorslund et al. 2017).

The metals As and Mn exceed WHO health risk-based guideline values at multiple locations and times in the Tuul River, with their highest concentrations reaching 13.1 µg L^{-1} (June 2012; WHO guideline value: 10 µg L^{-1}) and 413 µg L^{-1} (July 2008; WHO guideline value: 400 µg L^{-1}, WHO 2006) respectively (Paper I and II). Except for these metals, dissolved concentrations do not generally exceed WHO's guideline values. For comparison, Fig. 8 illustrates the dissolved concentrations in groundwater and waste ponds, relative to the dissolved concentrations in the Tuul River, for the same measurement periods (June 2012 and September 2013). A seen in these results, the concentrations of Mo and Zn were clearly elevated (with ratios at and above 4) in the groundwater-waste pond system, whereas concentrations of Cr, Cu and Pb were slightly elevated (ratios between 1 and 2). These concentrations represent diffuse inflow sources; from (many) small ponds distributed along the Tuul river as well as extensive groundwater systems (down to 70 m depth).

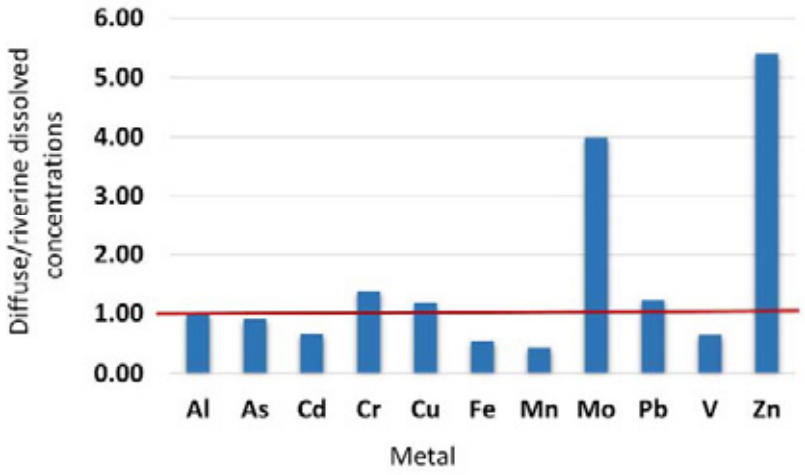

Figure 8. Figure showing the ratio between averages of dissolved concentrations of diffuse sources (groundwater and ponds) and river water concentrations (average of 2012 and 2013 data). The red line indicates where concentrations of diffuse sources and the river are the same. Values below and above the red line thus represent lower respectively higher diffuse concentrations compared to the river water concentrations.

Further, riverine mass flows of metals were quantified at upstream locations (T5, T5a), over the mining site (T5b, T6) and at downstream locations (T6a). The mass flow graphs for all sampled and synthesized years are found in Paper I (Fig. 3) and Paper II (S2: Fig. 3). Generally, most metals show net increasing mass flows over the mining site for all sampling campaigns and years, reflecting a clear mass input of metals from the mining activities to downstream river reaches. In line with concentration results, suspended mass flows dominate the overall transport for Al, Fe, Mn, Pb, and Zn, whereas As, Cd, Cu and Mo are dominated by dissolved transport and Cr and V show varying behavior (Paper II). In particular for Al, Fe and Mn, the total transport were consistently much higher (up to two orders of magnitudes) compared to dissolved flows, considering different locations and years; Paper I and II).

As a summary example, Fig. 9 shows net mass flow increases of Al, As Cu, Fe, Mn, Pb and Zn over the site (T5-T6a), for the years of 2005, 2006 and 2008 (Paper I). On average, dissolved mass flows of the considered metals increase six-fold over the mining area, whereas the total mass flows increased 4-fold. Although dissolved mass flows increase more relative total mass flows, the absolute net increase in transport is much larger for total mass flows. The total mass flows are generally dominated by transport of metals in suspension. For total mass flows, they were quantified to be in 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 (Fig. 9). For dissolved mass flows, the overall largest net increase in dissolved transport occurred for Al and Fe, but with Mn showing the overall greatest increase of around 1900 tonnes per year in 2008. The overall lowest net increases are found for Pb, on average increasing dissolved mass flows with 1.5 tonnes per year over the studied years.

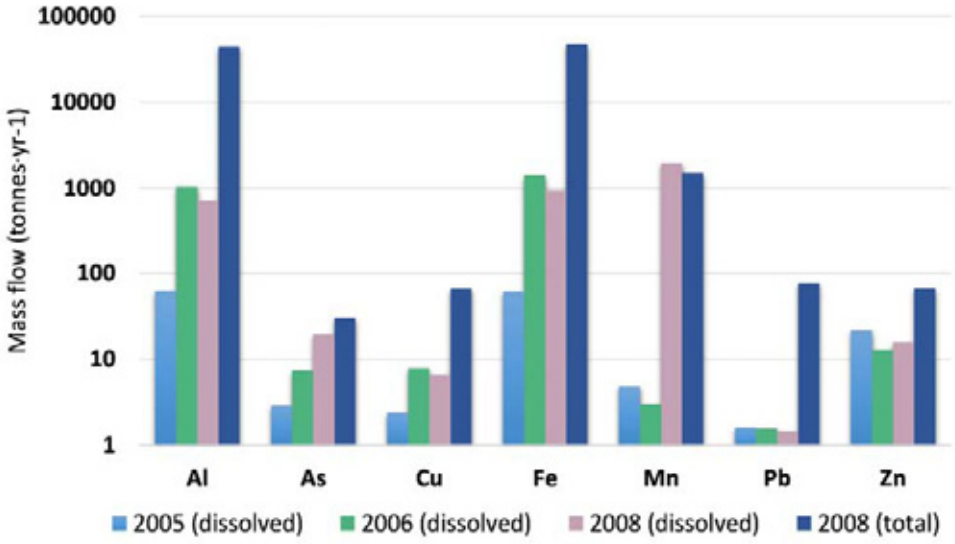

Figure 9. Figure showing the net increase in metal loads (in tonnes/year) over the mining site, in the Tuul River, for the set of the seven metals analysed in Paper I (years 2005, 2006, 2008). The net increase is estimated as the downstream load minus the upstream load, relative to the mining source zone location.

4.2 Impact of hydrogeochemical processes on metal speciation and transport

Fig. 10 shows measured versus modelled dissolved fractions (in percent of the total mass), considering data from the 2013 campaign. There is a significant correlation between measured and modelled fractions for six out of the total set of the eleven investigated metals (Al, As, Fe, Pb, V and Zn). These metals can further be divided into two groups: group 1, showing strong significant correlations ($r^2 \geq 0.45$, $p < 0.05$: Fe, Pb, Zn and V) and group 2 showing weak, but significant correlations ($r^2 < 0.45$, $p < 0.05$: Al and As). Hence, for all of these metals, the model can reproduce the observed partitioning to some degree (further results details are given in Supplementary materials S6, Paper II). The strong reproducibility of model predictions for group 1 metals suggests that they are governed to by equilibrium processes, in accordance with basic model assumptions. The weaker correlations of metals in group 2 indicate possible influence of non-equilibrium processes, non-represented equilibrium processes, and/ or inaccurate values of equilibrium constants.

Detailed model speciation results for the six metals with statistically significant correlations, considering conditions along the Tuul River reach (T5a-T6b), are shown in Fig. 11. The main processes keeping several metals in suspension were precipitation of gibbsite (an aluminum mineral) and ferrihydrite (an iron mineral) and associated sorption processes. Specifically, the observed high ratio of suspended to total levels of Fe and Al were predicted to be controlled to 96 -100 % by precipitation of ferrihydrite and gibbsite respectively. These solids were further predicted to limit the solubility of V, Pb and Zn, through the formation of sorption complexes between these metals and both ferrihydrite and gibbsite. Ferrihydrite was the main solid controlling V and Pb (on average 52 % and 45 %, respectively, of their total concentration were associated with sorption complexes), whereas Zn sorbed to both of these solids (on average by 50 %), but with predominant sorption to gibbsite at higher pH (>8).

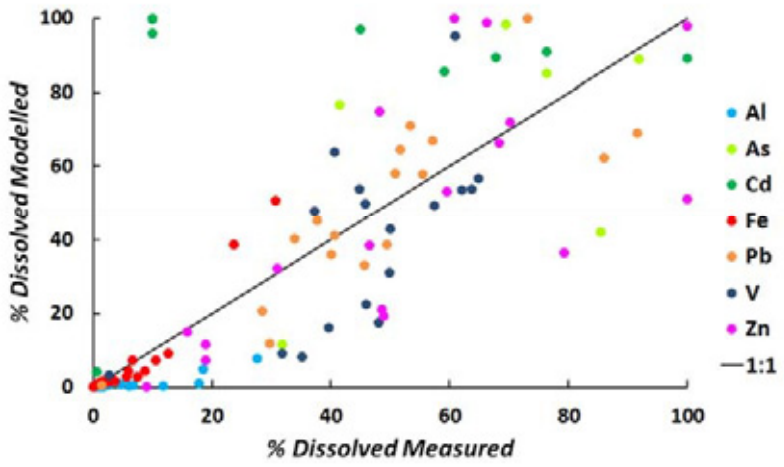

Figure 10. Comparison between the measured and modelled dissolved fraction results (percentage) of all metals in 2013, Paper II. The 1:1 line represent 100 % agreement between model prediction and measured results (Modified from Fig. 3 in Paper II: Thorslund et al. 2017).

Dissolved inorganic fractions were predicted to dominate the speciation of As (85 % of its total concentration) and also be considerable in the speciation of V (48 % of its total concentration). Further, dissolved organic fractions are according to model predictions important for Pb and Zn, forming soluble complexes with DOC to an average extent of 55 % respectively 38 % of their total concentrations. More generally, when DOC was omitted as a model parameter in sensitivity tests, model predictability compared to measurements significantly decreased, indicating its significance for overall predictive capacity of metals in this system. Furthermore, increasing the DOC levels with 50 % in a model run (to test parameter sensitivity) increased the average predicted solubility of Fe, Pb and Zn by 65 %, 40 % and 30 %, respectively.

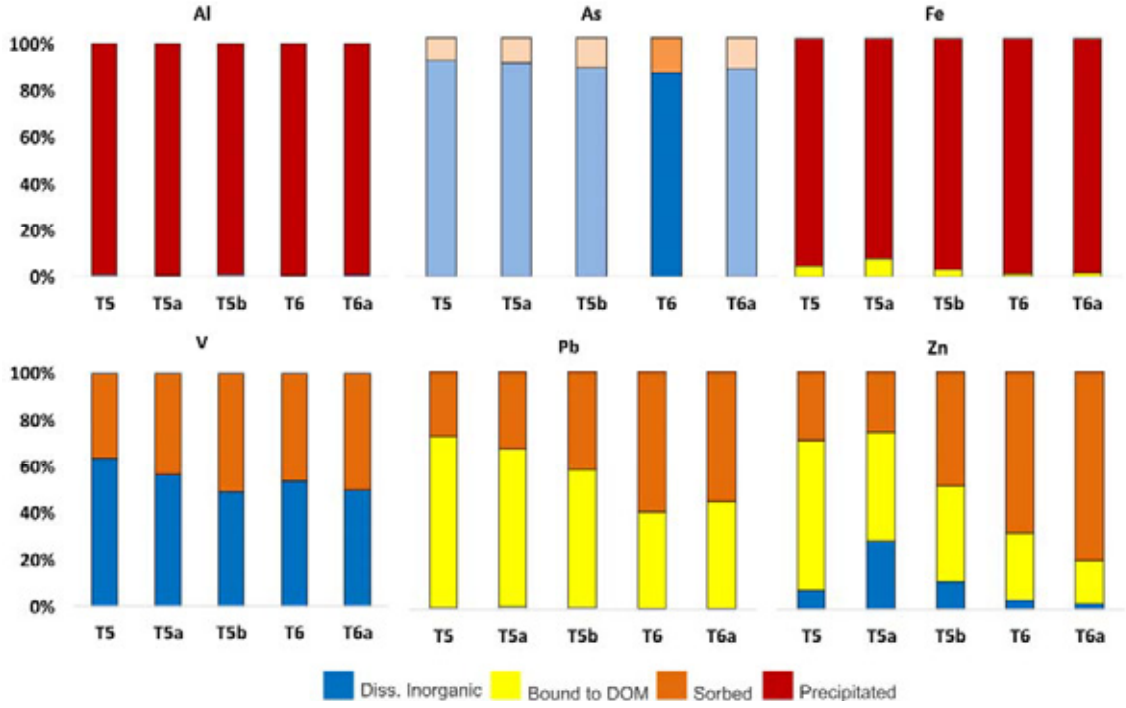

Figure 11. Detailed modelled speciation ('dissolved inorganic', 'bound to DOM', 'sorbed' or 'precipitated') of the metals governed by geochemical equilibrium in the 2013 campaign, across the mining region, in Tuul River. Lighter colours indicate that measured concentrations were <DL (Modified from Fig. 4 in Paper II: Thorslund et al. 2017).

4.3 The role of wetlandscapes in mitigating pollutant loads

As pollutants get transported downstream, the wetlandscape of the Selenga River delta (a wetland-delta system) may act as an important control on metals, for instance by providing filtering functions before metal loads discharge into Lake Baikal. Most metals entering the delta are dominated by suspended concentrations and mass flows (Paper III), as previously seen for upstream regions (Paper I and II). Total concentrations of multiple metals along different channels and regions of the Selenga River delta, during low flow condition and high flow conditions are shown in Fig. 12 respectively Fig. 13. Metal retention in the channels is reflected in decreasing total concentrations in the river water along the flow direction (i.e., negative slopes of the lines in Figure 12-13). As indicated here, such retention of metals flowing through smaller wetland-dominated regions of the delta (Fig. 12b and Fig. 13c) seem to generally be up to orders of magnitudes higher than the retention of metals transported through the larger channels without wetlands (Fig. 12a, b, d and Fig. 13a, note the logarithmic scale of the y-axes). Most metals show no, or slightly negative retention in the large channels, suggesting on-going metal re-suspension and/ or re-dissolution along these transport pathways. The decreasing total concentrations along the wetland dominated flow-paths was consistently observed during both low and high flow conditions, but with slightly higher retention of most metals during low flow conditions. During high flows, total metal concentrations of Al, Mn and Fe decreased the most after passing through wetland regions (Fig. 12c; decrease by 97.3, 97.0 and 95.5 % respectively). Overall, these quantifications show that individual wetlands of the delta locally can retain between 77-99 % of incoming total metal loads (based on total concentrations and assuming constant Q along the small channel reach). During low flows, total metal concentrations of Al, Pb and Zn decreased the most of all measured metals, after passing through wetland regions (Fig. 13b; decrease by 99.2, 97.4 and 90.8 %, respectively).

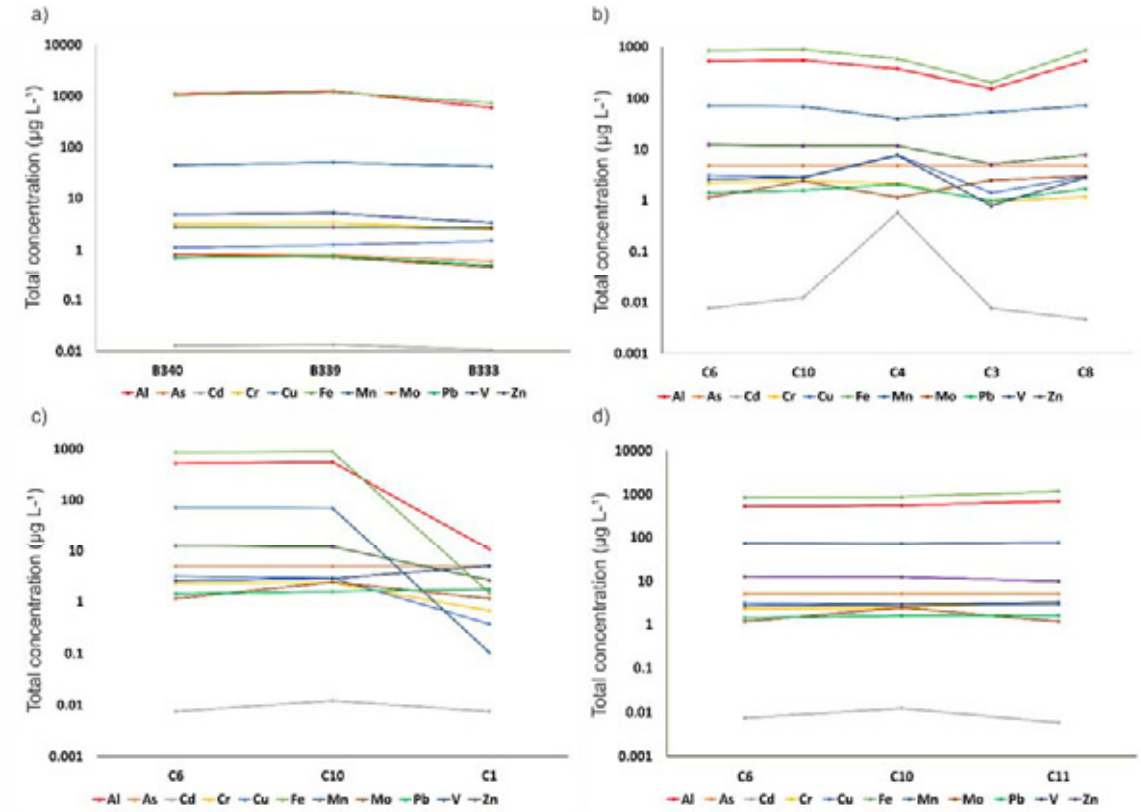

Figure 12. Total concentrations (upstream-downstream) of Al, Cr, Cu, Fe, Mn, Pb, V and Zn along (a) the large Lobanovskaja channel (sampling points: B340, B339, B333), (b) the large Selenga (Kharauz) channel (sampling points: C6, C10, C4, C3, C8) (c) the smaller and wetland-dominated Shamanka region (sampling points: C6, C10, C1) and (d) the large Levoberezhnaya channel (sampling points: C6, C10, C11), sampled during high flow conditions in 2013. Note, for As, the concentrations were under the measureable detection limit in graphs (b-d) **(**Fig. S4 in Paper III: Chalov et al. 2017).

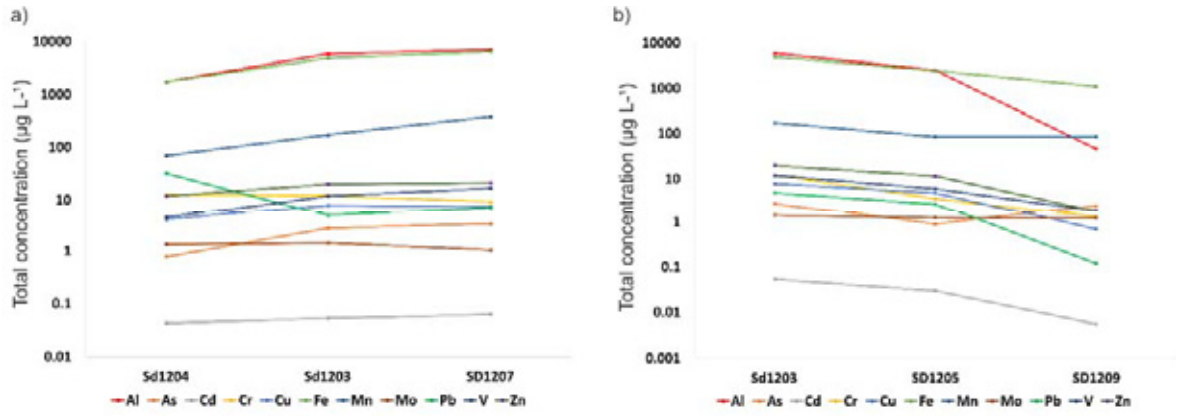

Figure 13. Total concentrations (upstream-downstream) of Al, Cr, Cu, Fe, Mn, Pb, V and Zn along (a) the large Lobanovskaja channel (sampling points: SD1204, SD1203, SD1207) and (b) the smaller and wetland-dominated Sredniy Peremoy region (sampling points: SD1203, SD1205, SD1209), sampled during low flow conditions in 2012 (Fig. S3 in Paper III: Chalov et al. 2017).

However, our quantifications across the larger Selenga wetlandscape shows that most flow-paths through the delta's distribution channels did not pass through sections dominated by wetland and small channels at the time of investigations. Only up to 30 % of total flows, and at times as low as 5–10%, are passing wetland abundant regions (Paper III). As most of the polluted flows thus pass along large channels with limited retention capacity, the resulting net retention effect is limited, despite the fact that smaller channels and wetlands can have a high retention capacity. Such domination of larger channels at the investigated period could explain observations of sediment plumes sometimes reaching the inlet of the Lake Baikal (Fig 14 a and b). Results from the Selenga delta (Paper III) shows that flowpath distributions have shifted over time (period between 1952-1998), due to changes in the delta morphology, resulting in more domination of central and right sections of the delta compared to the left sections (which used to dominate total flows-paths in the 1970s). More recent results (from measurements in 2012-2014) additionally indicate impact of seasonality, with flow partitioning differing between low and high flow conditions. During lower flows (Q = 992-1482 m^3s^{-1}) a higher percentage of total flows were conveyed through the left section (45-48 %) compared to the central and right sections. During higher flows (Q = 1697-2794 m^3s^{-1}) most of the flow was conveyed through the right section (48-52 %) (for more details, see Table 1, Paper III).

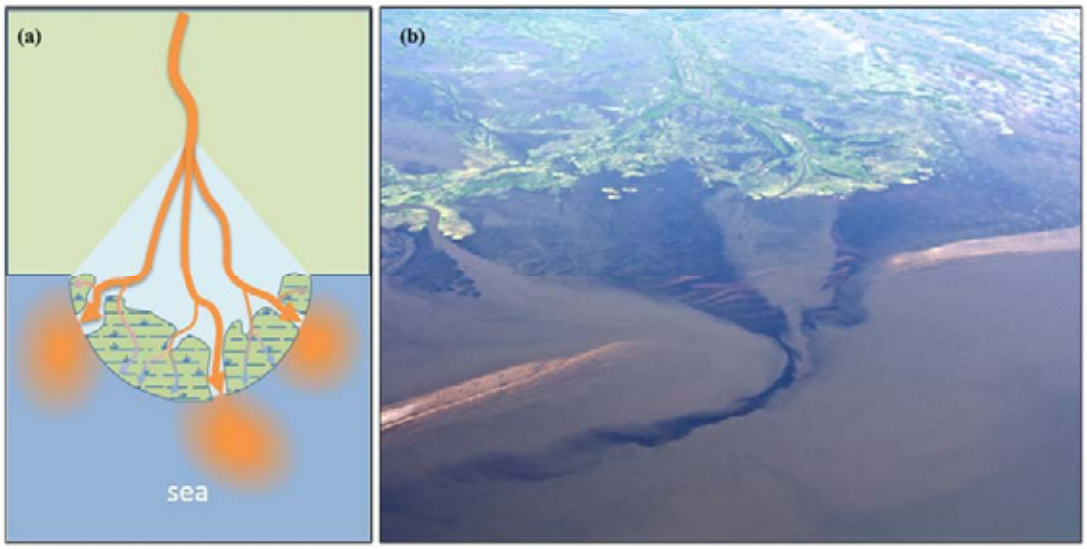

Figure 14. Conceptual illustration (a) and flight photograph (b) of the Selenga wetlandscape. In (a), flow-pathways are shown as arrows, which width indicates flow magnitude and the color indicating water quality level (orange more polluted, blue less polluted). In (b), examples of polluted sediment plumes from the wetlandscape into Lake Baikal is shown. (Modified from Fig. 3 in Paper IV: Thorslund et al. 2017 and Fig. 5 in Paper III: Chalov et al. 2017, photograph in (b) from ULM Russian-Swiss project in 2012-2013, re-used with permission from S. Chalov).

Similar net effects as in the Selenga wetlandscape were also quantified at two Swedish wetlandscapes (Fig. 2: site 5-6). Results showed that although local wetlands had a high capacity of retaining pollutants (in this case investigated for nutrients), their large-scale coastal protection function was undetectable for water entering the Baltic Sea. Spatially distributed hydrological modelling indicated that a main reason was that only a small fraction of flow-paths through the landscape intersected these wetlands, whereas most of the polluted flows did not. Thus, the landscape-scale contribution of investigated wetlands to coastal protection was not achieved (Paper IV and further described in Quin et al., 2015). In contrast, results from the highly managed Amu Darya River basin (ADRB, site 13, Fig. 2), including its delta near the former shoreline of the Aral Sea in Uzbekistan, showed high net retention capacity of the larger wetlandscape. Under conditions of expanding agricultural activities and increasing nutrient

inputs to the system, decreasing concentrations and loads by factors between three and six were observed in the downstream regions (Paper IV). Model results showed that this net effect was achieved due to increasing water diversion over time, from the main river to agricultural fields. Such diversions increased the net flow-path lengths and re-circulation of polluted flows to and from the irrigated fields of the wetlandscape, thus increasing net retention effects (Paper IV; further described in Törnqvist et al. 2015).

Taken together, these results (Paper III and IV) all show feedbacks between multiple, interconnected wetlands and their surroundings and an emerging, aggregated process complexity at the scales of wetlandscapes, with flow-path distribution variability that can vary over shorter (seasonal) and longer (yearly) timescales. Although expert survey results from the global set of investigated wetlandscapes show a high consensus on the relevance of these larger interconnected scales, understanding of many large scale processes at such scales emerged as largely unknown (Paper IV). Particularly, impacts from many large-scale drivers (e.g. hydroclimatic change and irrigation) on the pollutant and nutrient retention capacity of wetlandscapes were dominated by knowledge gaps (Fig. 5 in Paper IV). Similarly, the survey of the global wetland literature showed that the number of studies addressing local or individual wetlands was much higher than the number of studies addressing large wetlandscape scales (Fig. 15). For instance, results showed that although the absolute number of publications addressing retention functions of wetlands was high (2563 Papers) compared to most other wetland functions, 80 % of those papers focused on individual wetlands. These results hence provide strong indications of remaining essential research gaps for a range of water-related drivers of global change and their relations to the large-scale function and service potential of wetlandscapes (Paper IV).

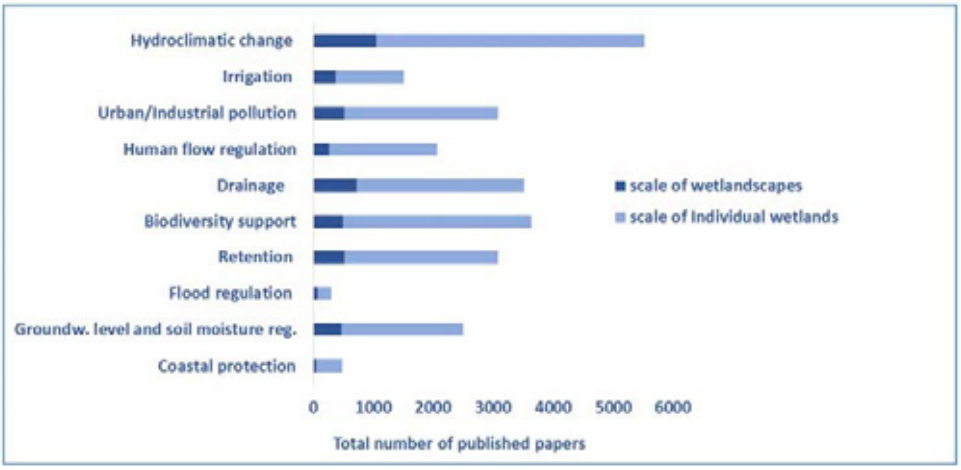

Figure 15. Result summary of the general literature survey, showing the distribution between the number of published articles considering only individual wetlands (light blue) and those considering larger-scale wetlandscapes (dark blue). (Modified from Fig. 5 in Paper IV: Thorslund et al. 2017).

5 Discussion

5.1 Release of metals from mining areas

This thesis has identified the upstream mining activities to significantly contribute to the release and transport of metals within the transboundary Lake Baikal basin (Paper I and II). The observed riverine mass flows of many metals downstream of the mining sites were about an order of magnitude higher than under natural conditions, upstream of the mining sites (considering total transport of both dissolved and suspended phases, and correcting for the upstream influence of the capital city of Ulan Baator; Paper I). Parallel studies in this region support the thesis results of mining being the main driver to increasing metal loads, particularly those transported with suspended sediments (Chalov et al. 2017; Pietroń et al. 2017). Support that such increasing loads over the mining region actually are caused by the mining activities and not by natural erosion processes are found in Jarsjö et al. (2017). Modelling results of this study showed that natural erosion of metal-rich soil at the mining sites played a minor role to the here observed load increases of metals, suggesting that they must enter the Tuul River through other pathways, such as with turbid waste waters from the mining operations. Although such wastewater input can be expected to be relatively independent of weather conditions, once metals are in the river, observations show that the turbidity and metal loads increase during high-flow events, and in particular during peak flow events following heavy rain (Chalov et al. 2015; Pietroń et al. 2015). This may be explained by in-channel processes which mobilize sediment, particularly metal rich fine particles, stored in the river bed (Pietroń et al. 2017). Long term monitoring data from the downstream parts of the Selenga River, just before its delta, shows that dissolved mass flows of Fe and Pb constitute 1 and 3 % respectively of globally transported flows of these metals from rivers to the oceans (Viers et al. 2009). Given that the Selenga River basin only covers 0.4% of earth's ocean drained land area, its mass flow contribution of these metals are a significant compared to other regions of the world.

Compared to other mining regions of the world, the here estimated total loads (tonnes/year) of Fe, Mn and Pb in the Tuul River (Paper I) were 87, 21 and 4.3 times higher than the contribution of historical mining activities in the UK (Mayes et al. 2010). Considering Arctic mining regions, load estimations from mining activities in the Murmansk region of Russia show transport of 120 tonnes of Cu, 19 tonnes of Zn and 0.78 tonnes of Pb, over a period of 60 years (Dauvalter 2003). These loads are lower than what is estimated along the Tuul River. Gold mining is also a reported problem in the Khaara River basin of Mongolia, with elevated metal concentrations and loads as a result of mining operations (Hofmann et al. 2014; Pfeiffer et al. 2014). Although mass flows of metals in the Tuul River are of the same order of magnitude for several metals, they can reach up to an order of magnitude higher than reported values for the Khaara River (Hofmann et al. 2013). Additionally, the concentration of several metals measured in the Tuul River are of the same order of magnitude as around the Norilsk mining industry (Taymyr Peninsula in the Russian Arctic), which is considered to be one of the most polluted industrial regions, not only in Russia but in the world (e.g. Zhulidov et al. 2011; Mudd 2010).

Regarding metal concentrations in the mining region, dissolved levels of As were measured to be above heath-based guideline values in the Tuul River, with net increases over the mining site (Paper I). Furthermore, groundwater samples taken near the Tuul River showed relatively high As levels (Paper II). Speciation results showed that As should exist in soluble inorganic forms or organic complexes (Paper II), which are of toxic concern due to their high bioavailability (e.g. Boenigk et al. 2005). Results of Thorslund et al. (2016), Hoffman et al. (2014), Pfeiffer et al. (2014) and Inam et al. (2011) show that the problem is not restricted to the Tuul river basin; they report increasing groundwater pollution of As as a result of mining

in both the adjacent Kharaa River basin and the Sharyngol River basin, as well as in the Selenga River delta (Thorslund et al. 2016). The highest reported As concentrations reached 300 µg L^{-1} in the Kharaa River basin (Pfeiffer et al. 2014). Although As may be naturally occurring in this region, observed net increases over the mining site indicate that these activities contribute to mobilization of As sources. More generally, this is supported by the anthropogenic 'industrial age' arsenic contamination, as assessed by Han et al. (2003), which showed that at the start of the 21st century, 4.5 million tonnes of arsenic have been produced by anthropogenic industrial activities. They identify mining as the number one producer, followed by coal and petroleum production.

5.2 Processes controlling local to regional metal pollution

Present results show that most of the investigated metals in the Tuul River are primarily transported in suspended phases (Paper I and II), either as precipitated solids or as sorption complexes (Paper II). The main factor limiting dissolution is the prevailing alkaline pH conditions. Some studies have suggested that the dissolved metal concentrations are usually below health-risk based guideline values in non-acidic mining regions (Žák et al. 2009; España et al. 2006). However the current knowledge on non-acidic systems (such as the Tuul River) is much more limited than, e.g., metal behavior in acid mine drainage systems, although metal pollution in non-acidic systems is common (e.g. Grosbois et al. 2009). Notably, diffuse inputs from alkaline groundwater in unconfined porous aquifers of the region (Hoffman et al. 2015; AATA 2008), which potentially receive infiltration water from hundreds of open waste heaps in the valley of the Tuul River, may considerably contribute to the detected increasing dissolved riverine metal loads downstream of the source zone. Such groundwater loading of rivers with metals has been shown to be important in the vicinity of the Pacific Mine in Utah (Lachmar et al. 2006) as well as in other mining regions of the world (e.g. Coynel et al. 2007).

Further, on-site groundwater flow inputs may not only impact dissolved phases, but could also increase suspended phase concentrations. This is due to the gradient in oxygen levels between groundwater and surface waters. Since oxygen concentrations are usually low in groundwater, oxygen-rich environments of the river can oxidize redox-sensitive metals that enter through groundwater diffuse flows, making them precipitate or sorb onto particles found in suspension. This process has been recognized as important in many mining systems (Aleksander-Kwaterczak and Ciszewski 2016; Cidu et al. 2009; Viers et al. 2009), including a gold mining site in South Africa, where sediments were enriched with metals due to groundwater inputs to the river (Winde et al. 2004). Such potential on-site processes may contribute to metal enrichment of bottom sediments, which combined with e.g. on-going dredging activities could contribute both to enriching and re-suspending sediments of the Tuul River system.

Present modeling results suggest that ferrihydrite control the riverine concentrations of several of the investigated metals, through formation of sorption complexes (Paper II). This is for instance consistent with geochemical investigations in the Lena River, which showed Ferrihydrite to be the main Fe-bearing particle, often found in association with organic material and accounting for about 70 % of total suspended loads of Fe (Hirst et al. 2017). More generally, sorption processes are known to be important controls on metal solubility in non-acidic natural systems (e.g. Zhao et al. 2011; Espana et al. 2006). The current data-supported predictions (Paper II) however show considerable sorption to ferrihydrite under even higher pH conditions than in previous studies. Taken together, the thesis results and independent studies support the use of equilibrium models for predicting the speciation of several (but not all) key metals in natural systems, under a range of pH conditions. Further, organic material, in particular DOC, may also have a large influence on metal dissolved complexation, with predicted increasing solubility of Al, As, Cu, Fe, Mn and Zn in the Tuul River (Paper II) and in other surface waters of Mongolia (Szopińska et al. 2016). More generally, these results are

supported by several studies showing a high impact of organic matter on metal transport and fate (e.g. Hagedorn et al. 2000; Sauvé et al. 2000; Christensen et al. 1996), which may increase the solubility of some metals as much as up to two orders of magnitude (e.g. Weng et al. 2002). For metals that could not be readably predicted, results suggest that the phosphate mineral Hydroxyapatite may act as a key sorption site (Paper II). Model predictions indicated that it would precipitate if added as a possible mineral. This is because on-site concentrations of this mineral's main components: particulate calcium and phosphorous, were observed to be high. However, in the currently used model, an adsorption database for hydroxyapatite is yet unavailable. Developing such a database might increase the general model capability to predict the speciation and sorption of for instance Cr, Cu and Mo, which showed relatively large differences between observed and modelled concentrations in the present comparison. Several studies converge on showing the relevance of hydroxyapatite for governing metal partitioning under different non-acidic conditions (e.g. Bazargan-Lari et al. 2014; Rajiv-Gandhi et al. 2011), including pH conditions of up to pH 11 (Asgari et al. 2012).

5.3 Impacts of changing environmental conditions on metal spreading and fate

Since the transport of metals in the Tuul and Selenga rivers largely occurs in association with suspended sediments, impacts of changes in such sediment transport dynamics can be profound. For instance, in recent decades, hydroclimatic changes of the Selenga River basin have resulted in decreased annual maximum flows and increased annual minimum flows (Kasimov et al. 2017; Pietroń et al. 2017; Törnqvist et al. 2014). Since a large part of the annual riverine sediment transport occurs during high flow events (Pietroń et al. 2015), the observed hydroclimatic changes has thus far contributed to decreasing the annual sediment budgets. Consequently, significant long-term declines in sediment fluxes to the downstream parts of the Selenga River have already been seen (Chalov et al. 2017). Under current conditions, incoming suspended sediment flows have been measured at about 3000 tonnes/day in the downstream regions of the Selenga delta (Chalov et al. 2017). However, although sediment transport due to erosion of in-channel material decrease during low flows, sediment input from the mining area is still high during such conditions (Pietroń et al. 2017). Taken together, there are still considerable knowledge gaps regarding the net effects of projected future changes in hydro-climatic and land-use conditions on the transport of sediment and sediment-bound metals over the full extent of the transboundary basin. Changing conditions (hydroclimatic and land-use) were however seen to impact the net function of the Selenga wetlandscape in retaining metals. Quantifications showed that the overall retention effect of the Selenga wetlandscape decreased during low flow conditions, due to less flow routing towards wetland dominated regions (Paper III).

Changing geochemical conditions may also have a large impact on metals transported with suspended sediments. For example, changing pH conditions from dominantly alkaline, as measured upstream in the mining region, to more acidic conditions, could increase the dissolution and bioavailability of metals (e.g. Lourino-Cabana et al. 2011; Tarras-Wahlberg 2001). Measurements show that such a pH gradient exist in the Selenga River basin (Paper I). In line with these results, independent studies report on high dissolved concentrations of several metals in downstream regions of the Lake Baikal basin (e.g. Khazheeva et al. 2006), including accumulation of metals in biota (Ozersky 2017; Watanabe et al. 1998). More generally, the Arctic region, in which the Lake Baikal basin is located, not least from a hydrogeochemical perspective is particularly vulnerable to changes in both climate and carbon cycling (e.g. Hirst et al. 2017). Many regions of the Arctic are extremely carbon rich (Schuur et al. 2015) and DOC concentrations (Dai et al. 2012) have already been seen to increase over time in many locations (e.g. Monteith et al. 2007). Since DOC is important for metal soluble complexation, for instance acting to increase the dissolved fractions of several metals in the Tuul River (Paper

II), changing spatial or temporal DOC concentrations may thus have a large influence on metal pollution. Since the warming of the Arctic region is known to be faster than any other region globally (e.g. Hinzman et al. 2005), and the Selenga River basin is no exception (Törnqvist et al. 2014), there will also be associated increases in permafrost degradation (e.g. Jorgenson et al. 2006). Permafrost thawing could substantially change surface water chemistry. When permafrost is melting, the depth of the active layer will increase, which has already been quantified for permafrost soils in this region (Zhang 2005). This could mobilize considerable amounts of previously frozen organic matter (Tarnocai et al. 2009), which could then form soluble complexes with several metals of toxic concern (Paper II). Projections for permafrost degradation impacts on surface waters in general and particularly for the here studied region of Mongolia and Russia are still few (Szopinska et al. 2016). However, some predictions suggest that riverine DOC concentrations can increase with up to 700 % in Siberia over the next century (Frey and Smith 2005).

5.4 Using wetlands as large-scale NBS: identified knowledge gaps and their implications

Individual wetlands are well known for their capacity of metal retention (e.g. Huang et al. 2017; Hafeznezami et al. 2012; Arroyo et al. 2007) and are often used as an abatement measure downstream of industries and mines (e.g. Baresel et al. 2006). This thesis has however shown that a scientific understanding of aggregated wetland functions and changes needs to be developed in order to rationally use wetlands as a NBS to mitigate large-scale pollution impacts. Key questions are when, how and to what extent wetlands connect to the larger landscape and downstream or downgradient waters. Although cause-effect relations are known at the local scale, survey results including opinions of experts working at large wetlandscape sites, as well as conducted topical surveys of the scientific literature, indicate a frequent lack of knowledge about critical linkages between wetlands and their surroundings (Paper IV).

This thesis shows evidence that the function of wetlands as mitigation solutions to pollutant loads is largely controlled by large-scale parallel and circular flow-paths, which connects multiple wetlands in the landscape (Paper IV). Circular flowpaths may for instance arise as water is diverted from rivers and used and re-circulated in catchments with (irrigated) agriculture, industry and/ or urban developments. Impacts of such circular flowpaths have previously been studied only at small plots or at laboratory scales (e.g. Hitomi et al. 2006; Feng et al. 2004). In line with the example of the Amu Darya wetlandscape site near the Aral Sea in Uzbekistan (Paper IV; Törnqvist et al. 2015), decreasing downstream loads of nutrients with increased water use and water re-circulation have been observed in several regions of the world (e.g., Brown et al. 2011; García-Garizábal and Causapé 2010), in spite of increasing upstream nutrient inputs at agricultural sites. Further, at least on smaller scales, effects of re-circulation of water have also been seen to impact for example suspended sediment concentrations and loads (Hama 2012). Combining those results with the here seen large-scale retention impacts suggests that suspended metals loads, could potentially be decreased by large-scale water re-circulation. However, systematic investigations at the scale of wetlandscapes, beyond the here studied examples, are still missing (Paper IV).

The here identified lack of scientific basis on large-scale effects of wetlands may impact their legal protection. This is for instance the case for geographically isolated wetlands within the US, which is a wetland type that lacks surface water connections to their surroundings. These types of wetlands are frequently occurring in the US but currently excluded from legal protection by the ‘the clean water act’ until it can be proved that they have significant impact on the water quality or quantity of navigable waters (e.g. Calhoun et al. 2017; Golden et al. 2017; Cohen et al. 2016). The lack of large-scale quantifications of landscape-wetland interaction may also result in construction of wetlands in non-ideal locations of the landscape,

e.g. with limited potential for useful ecosystem services. Taken together, such uninformed decisions may put additional stress on wetland ecosystems and lead to delays or failures in reversing the on-going rapid global wetland loss (e.g. Mitsch and Gosselink 2015; Davidson 2014).

In face of additional pressures on wetlands and wetlandscapes from future hydro-climatic change, it is essential to understand their large-scale functions both under current and expected future conditions. If not, possibilities to predict functions changes due to various aspects of global change will be limited. This thesis (Paper IV) identified essential research gaps for a range of water-related drivers of global change, including changes in climate, water use, land use, and their relations to the largescale function and service potential of wetlandscapes. Improving such knowledge may be critical for developing a broader understanding of the generality of the function of wetlandscapes, including retention of metals, nutrients and other pollutants (Jarsjö et al. 2017).

6 Conclusions

This thesis has identified and quantified impacts of mining activities on local to regional metal pollution and assessed the potentials and current limitations for using wetland networks for mitigating pollutant loads across the landscape. Specific conclusions for each objective are outlined below.

Objective A:

- Mining activities in the upstream part of the Lake Baikal basin considerably contributes to elevated riverine metal mass flows downstream of the mining region, with a net increase in mass flows over the mining site by up to an order of magnitude.
- The transport of Al, Fe, Mn, Pb and Zn are dominated by suspended phases, while As, Cd, Cu and Mo are dominated by dissolved phases, under a relatively wide range of hydrological conditions.
- The high transport of suspended metals to downstream areas are shown to increase substantially under the influence of hydrological storm events, which may increase in frequency under future predicted hydro-climatic changes.
- Regarding dissolved concentrations, those of As are of particular concern, due to measured concentrations that were above health-risk based guideline values in many locations, including deep parts of the groundwater system.

Objective B:

- The geochemical partitioning of several metals observed in the Tuul River (Fe, Pb, V and Zn) could be well predicted using simplifying assumptions of the Visual MINTEQ model, and are thus governed by equilibrium geochemistry under studied conditions.
- Precipitation of ferrihydrite and gibbsite and associated sorption complexes were predicted to limit dissolved phases of several metals, explaining the high impact of suspended relative to total transport that was independently observed in this system.
- Speciation modeling of metals that could not be well predicted by the geochemical model (Al, As, Cr, Cu, Mn, Mo) could likely benefit by developing an adsorption database for the phosphate mineral Hydroxyapatite.
- The solubility of several metals was predicted to increase considerably with increasing DOC concentrations; such changes are likely to happen in the Tuul-Selenga basin (and other Arctic basins) over time, due to seasonality, permafrost degradation and land-use changes, which resulting large impact on metal spreading and fate.

Objective C:

- Individual wetlands of the Selenga River delta showed high potential for filtering incoming pollutants, with between 77 to 99 % retention for key metals under different flow conditions.
- Evidence from the Selenga wetlandscape, and from several of the other investigated wetlandscapes, however suggests that the large-scale function of wetlands as mitigation

solutions to pollutant loads is largely controlled by their degree of interaction with the larger landscape through parallel and/ or circular flow-paths.

- In the Selenga case, such wetland-flowpath interactions were quantified to account for 30 % or less (during low-flows as low as 5-10 %) of total flows across the whole wetlandscape, resulting in contaminated plumes sometimes reaching the Lake Baikal.

- Projected future hydroclimatic changes, with low-flow conditions becoming more frequent in the Selenga – Lake Baikal region, may potentially decrease such wetland-flowpath interactions and the function of the delta in decreasing metal loads.

Objective D:

- Beyond the Selenga wetlandscape and a few other detailed site examples, expert knowledge on the function of and impacts on the large-scale pollution retention of wetlandscapes emerge as largely unknown.

- In addition, only around 20 % of the analyzed global wetland literature addressed change drivers and impacts on whole wetlandscapes, which suggests that there is an urgent need to increase the research focus on large scales.

- These identified knowledge gaps imply that critical linkages between wetlands and their surroundings may be overlooked, adversely affecting the realization of wetland capacity, sustainability and potential as nature-based solutions.

- To better realize the pollutant retention functions of wetlandscapes as a nature-based solution, there is a demand for improved quantifications of water flow pathways and fluxes through whole wetlandscapes, including parallel hydrogeochemical monitoring of both groundwater and surface water components.

7 Future research perspectives

During my Ph.D. studies and thesis work, several knowledge gaps and future research needs have been identified. Some ideas on future research areas that would benefit from further scientific attention are outlined below.

It would be valuable to focus future investigations on understanding, to a larger degree, pollution and interactions of coupled groundwater-surface water systems. Although groundwater and surface waters are being increasingly recognized as a joint resource, there is still a lack of studies that focus on this coupled system (e.g. Destouni et al. 2015). Further, since there is a general lack of groundwater monitoring (Gleick and Cain 2004) and groundwater is used for drinking water in many parts of the here considered Lake Baikal basin (Hofmann et al. 2015; Nriagu et al. 2012) despite, measurements are needed to clarify present groundwater quality status. This was emphasized by the results of the present thesis, showing that some metals reach high groundwater concentrations in the upstream parts of the Lake Baikal basin (Paper II). For increasing the understanding (and facilitate models testing) of contaminant spreading, useful monitoring efforts would include groundwater concentrations at various depths, as well as further quantifications of diffuse (and potentially polluted) groundwater inputs into river systems.

Additionally, research focusing on the coupling between permafrost degradation and hydrogeochemical changes would be highly relevant for the Lake Baikal basin in particular, as well as for Arctic regions in general. With melting permafrost, changes in both organic carbon and transport pathways are expected to occur (e.g. Keller et al. 2010; Pokrovsky et al. 2006). Results from Paper II indicate that increasing levels of DOC may substantially increase dissolution of several metals, at least under conditions prevailing in the Lake Baikal basin. However, there is a lack of information, data and similar sensitivity studies on metal concentrations of other regions in relation to permafrost occurrence and changes (Barker et al. 2014). More studies are thus needed that focus on investigating the role of DOC for metal speciation in thawing permafrost areas. For this, synthesizing data on simultaneous change in both permafrost extent, DOC levels and metal concentrations could be a valuable start for investigating correlations and causation. The here used equilibrium model (Paper II), or similar geochemical models, could then be applied to test the sensitivity of the speciation of metals to reported historical or projected future DOC changes.

The limits and potential for using geochemical equilibrium models in predicting metal speciation under actual, field-scale conditions should be further explored. This is emphasized by results from Paper II showing a lack of predictive model capability for several metals including As, which is of great toxic concern in the Lake Baikal basin and many other regions. For improved model speciation capacity, oxide and humic material interactions, equilibrium constants, and the possible influence of non-equilibrium conditions should be investigated. In particular, developing sorption databases for minerals (such as the here identified phosphate mineral Hydroxyapatite) that may govern the speciation of several metals could be an important contribution.

Finally, there is a great need for studies that target identified research gaps regarding the use of wetlands as large-scale NBS. To do this, as outlined in Paper IV, more focus needs to be put on cross-regional collaborations and measurements, and development of analytical tools and modelling approaches that capture the aggregated functions of whole wetlandscapes. Such efforts will most likely include a combination of methods, such as hydrological and hydrochemical monitoring in downstream locations, thus targeting the whole landscape, including the land-coast interface. Useful tools include analytical quantifications and statistical

approaches (Quin et al. 2015; Törnqvist et al. 2015), conservative solutes (e.g. Abbott et al. 2016), as well as GIS and remote sensing (e.g. Queiroz et al. 2015; Settele and Wiemers 2015). These tools and approaches can be combined with existing modeling and assessment frameworks (e.g. Mazi et al. 2016; Mazi et al. 2013; Koussis et al. 2012) to evaluate large-scale interactions between wetlands and the larger surrounding landscape. Scientific advances in this field could significantly improve our capacity for using wetlands in addressing a range of societal challenges, including the here discussed pollution issues, but also extending to other highly-valued ecosystem services such as coastal protection and biodiversity support.

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