Chemical water quality in Selenge River Basin in Mongolia: spatial-temporal patterns and land use influence

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Dissertation content

This doctoral thesis consists of a general introduction and four papers. The papers will be referred to by their Roman numbers (Papers I-IV). The published papers are reprinted by permission from the respective copyright holders.

I. Pfeiffer, M., Batbayar, G., Hofmann, J., Siegfried, K., Karthe, D., Hahn-Tomer, S. (2015). Investigating arsenic (As) occurrence and sources in ground, surface, waste and drinking water in northern Mongolia Environ. Earth Sci. 73 (2), 649 – 662.
II. Batbayar, G., Pfeiffer, M., von Tümpling, W., Kappas, M., Karthe, D. (2017). Chemical water quality gradients in the Mongolian sub-catchments of the Selenga River basin Environ. Monit. Assess. 189 (8), art. 420.
III. Karthe, D., Chalov, S., Moreido, V., Pashkina, M., Romanchenko, A., Batbayar, G., Kalugin, A., Westphal, K., Malsy, M., Flörke, M. (2017). Assessment of runoff, water and sediment quality in the Selenga River basin aided by a web-based geoservice Water Resour. 44 (3), 399 – 416.
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Author contributions

The contributions from listed authors are divided as follows for each article:

I. MP and GB led the writing with the help of all co-authors. GB, MP, JH, DK, KS acquired spatial and temporal data. All co-authors contributed to the data analysis and the design of the study. The writing was assisted by all co-authors. The study and related methods were designed by KS with help of MP and JH. The field data were collected by GB, MP, KS, and JH.

II. GB, MP and DK led the writing with the help of all co-authors. GB acquired the spatial and temporal data. Data analysis was done by GB and MP. The writing was assisted by all co-authors. The study methods were designed by GB, MP, WT and DK.

III. DK led the writing and all co-authors compiled the datasets and all co-authors did the data analysis. The water quality data analysis and chapter writing was done by GB and KW. The study and related methods were designed by all co-authors. All co-authors contributed to the field data collection.

IV. GB and MP collected the field data and statistical analysis was done by GB and MP. Sub watershed delineation was done by GB and land use data was obtained by MOMO project. The study and related methods were designed by all co-authors. Writing was led by GB.

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Chapter1. General introduction

Water is essential for life and for all human activities but also for preserving the environment and its resources. Rapidly growing population, intensification of agriculture, industrialization, urbanization, development of any kind and climatic factors are the main reasons for water pollution and scarcity conditions in many countries of the world (Tsihrintzis et al 2013, WWAP 2018).

1.1 Study region

The study region comprises the Mongolian part of the Selenga River Basin with a particular focus on the Kharaa, Tuul, Orkhon and their sub-basins, which are comparable with regard to the physical environment and socio-economic development (Karthe et al. 2013). The Selenga River itself has a transboundary catchment which is shared by two countries, Mongolia and Russia. Originating in Mongolia, it is the largest inflow of Lake Baikal with over 60 % of annual water amount contribution (UNOPS 2013). The delta of Selenga River is included in the list of Ramsar Wetlands of international importance because of its significant role as a habitat for flora and fauna as well as its role in functioning as a water filter against pollution flowing into Lake Baikal (UNOPS 2013). In Mongolia the Selenga River has a water catchment of 299,690 km^2 (67 %) and is divided into six sub-basins, while the catchment area in Russia is about 147,370 km^2 (33 %) (UNOPS 2013). The river plays an important role because 19 % of the total land area of Mongolia is located in its catchment, including the capital, important centers of industry and large farming areas (Nadmitov et al. 2015, Chalov et al. 2015).

The Tuul, Kharaa and Orkhon River Basins are home to Mongolia's three largest cities (Ulaanbaatar, Darkhan and Erdenet, respectively) and to more than half of the country's population. Moreover, the three river basins constitute important centers of agriculture, industry and mining (in particular for gold and copper). This does not only lead to a concentration of consumption but also of contamination risks. At the same time, water pollution in this region may harm a relatively large exposed population (Chalov et al. 2013).

The northern part of Mongolia is characterized by a highly continental climate with wide variations of annual, monthly and daily temperatures. The mean annual temperature is just below freezing, and annual precipitation ranges between 250-400 mm. Winters are long-lasting (monthly mean temperatures are 0°C or below between October and March) and very cold (temperatures frequently drop below -25°C), while summers are not only warm, but also the time of the main rainy period from June to August, when about 70 % of the annual precipitation falls (Hülsmann et al. 2015; Menzel et al. 2011).

Water availability is naturally limited due to low precipitation and high evaporation rates. Even though only 20% of the annual precipitation falls during the winter months, and sublimation losses are above 80%, the melting of snow and river icings produce a first considerable peak in river discharge around May (Minderlein & Menzel 2014). Because of a concentration of rainfall during the summer months, more than half of the annual runoff occurs during the months of July, August and September, albeit with a large interannual variability (Batimaa et al. 2005; Berezhnykh et al. 2012; Hülsmann et al. 2014). While open grasslands dominate low-lying regions, mountainous regions (particularly in the rivers' headwater areas) are typically forested and play a key role in runoff formation (Menzel et al. 2011).

1.2 Context and summaries of the papers

In the last two decades, Mongolia has experienced through a major political and economic transition. Much of the economic growth could attribute to the exploitation of natural resources. One of the major consequences of Mongolia's rapid economic growth over the last decade is urbanization. More than 70 percent of the population lives in urban areas with the majority in the Ulaanbaatar city (MEGD 2013). Due to the population growth and increasing demands on water resources, policy makers are facing with several major challenges regarding more sustainable water resource management at regional scale as follows:

1. The scarcity of environmental data, including water quality data, complicates planning processes;

2. The dynamic reform process of Mongolia's water sector and integrated water resources management, environmental legislation is only beginning to show positive results;

3. Due to mining, industrialization and population growth water resources will soon reach their limits especially in Ulaanbaatar city.

Regarding the longitudinal water quality pattern along the Selenga and its tributaries, this covers a region that is highly diverse, ranging from almost Virgin Mountain zones to densely urbanized areas and mining zones. These contrasts have a strong impact on rivers and their ecosystems. While headwater regions typically had a very good water quality status, wastewater from urban areas and impacts from mining were found to be main pollution sources in the tributaries (Karthe et al. 2015a, Batbayar et al. 2017, Pfeiffer et al. 2015).

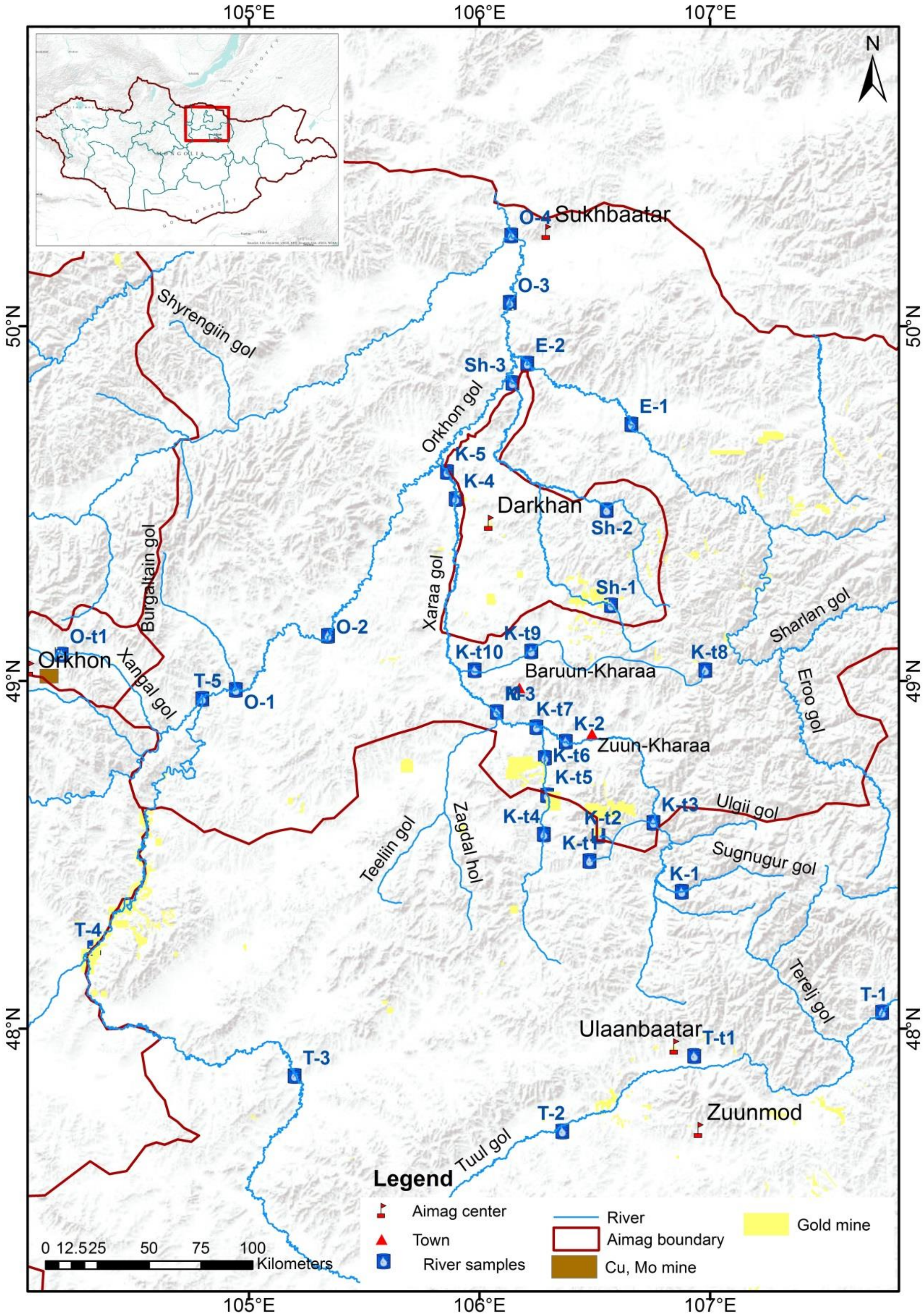

Figure 1 Map of the study area, indicating sampling locations and mining areas

Nevertheless a comprehensive quality monitoring for ground, surface and drinking water in Mongolia is still in its infancy, elevated levels of arsenic have recently been documented in surface water, groundwater, soils/sediments and urban vegetation for several locations in northern Mongolia. They appear to be mostly related to mining activities and the combustion of coal containing traces of arsenic (Hofmann et al. 2010; Kasimov et al. 2011a; Kasimov et al. 2011b; Inam et al. 2011; Murao et al. 2011, Thorslund et al. 2012; Batbayar 2012).

Gold mining and processing are also known to enhance the release of arsenic and its uptake by humans and livestock (Keshavarzi et al. 2012). Most of the gold mines are concentrated in northern Mongolia with a high environmental impact on local rivers, which all drain into the Selenga River: the Zaamar goldfield is located in the Tuul River Basin and two large open pit gold mines are situated at Boroo and Gatsuurt River, respectively. The placer gold mining at the Zaamar site has been estimated to increase total arsenic load of Tuul River by 30 tons per year (Thorslund et al. 2012). An arsenic content of 46,986 mg kg-1 was determined in rocks collected from Gatsuurt gold mine (Tsetsegmaa et al. 2009) and arsenic concentrations in artificial ponds of that mine have been measured to be 121 µg L-1 (Gandoljin et al. 2010). The average arsenic content in the tailing dam sediment of Boroo gold mine was determined at 4,419 mg kg-1, thus posing a potential source for future environmental contamination (Inam et al. 2011).

Besides the Arsenic problem, the highest nutrient concentrations in the catchment were found in Tuul River, and severely elevated concentrations of trace elements (As, Cd, Cu, Cr, Fe, Mn, Ni, Pb, Zn), nutrients (NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}) and selected major ions (SO_4^{2-}) were found in the main tributaries of Selenga River. Moreover, trace element concentrations during spring 2015 (a time when many mines had not started operation yet) were markedly lower than in summer 2014, indicating that the additional metal loads measured in summer 2014 were related to mining activities. Nevertheless, all water samples taken in 2014 and 2015 from the main channel of the Mongolian Selenga River complied with the Mongolian standard (MNS 4586:98) for the investigated parameters (Pfeiffer at al 2015).

Based on the chemical water quality, finding the interaction between land use characteristics and water quality is relevant for managing land use based pollution at sub catchment scale. However, it is not easy to explore how land use categories influence on water quality because of the large number of parameters and the complexity of the processes involved (Selle et al. 2013; Carey et al. 2013; Baker 2006; Allan 2004).

Watershed management and catchment scale studies have become more and more relevant in determining the impact of anthropogenic influences on water quality. Effective analytical tools, such as geographical information systems (GIS) and multivariate analysis that are able to deal with spatial data and complex interactions, are coming into common usage in watershed management (Sliva et al 2001). Therefore we used geographical information systems (GIS) and multivariate analyses (Principal component analysis (PCA), Redundancy analysis (RDA) and non-metric multidimensional scaling (NMDS) to investigate links between land use pattern and chemical water quality in the KRB.

In particular, vegetation cover, soil properties, intensity of land exploitation and distribution of settlement areas significantly affect runoff processes and transport of solids and solutes in catchments (e.g. Miller et al., 2011; Tu, 2011; Reimann et al., 2010; Kroll et al., 2009; Xie et al., 2005; Tomer and Burkart, 2003; Meisinger et al., 1991) and in groundwater (Lerner and Harris, 2009).

There is extensive research on chemical water quality and anthropogenic influences on surface water quality in Kharaa River Basin (KRB) (Batimaa et al 2013MOMO 2009, Javzan et al 2015, Batbayar et al 2017, Daniel et al 20156, Hofmann et al 2015, Zandaryaa et al 2015). However, little has been reported about the interactions between land use characteristics and water quality in KRB.

The landscape characteristics impact instream water quality. The most powerful predictors of river water quality were found to be forest, settlements, cropland and sub-basin size. In particular, this was true when instead of full sub-basins riparian buffer zones (3 km) were considered. From a management perspective, this implies that the protection of riparian zones should be a priority in the basin of the Kharaa and similar river basins in Mongolia and Central Asia. Because of its positive effects on water quality, forest protection should be closely coupled with river basin management. On the other hand, any further expansion of settlements, agricultural land use and mining should be avoided in the Kharaa's floodplains (Batbayar et al 2018 submitted).

Chapter2. Investigating arsenic (As) occurrence and sources in ground surface, waste and drinking water in northern Mongolia

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Investigating arsenic (As) occurrence and sources in ground, surface, waste and drinking water in northern Mongolia

2.1 Abstract

Elevated levels of arsenic in drinking water are found in several parts of Asia. Prolonged intakes of even low concentrations typically have serious health effects. This research paper integrates results of various studies on arsenic contamination of ground, surface, waste and drinking water in north-central Mongolia. Samples were analyzed with the ARSOlux biosensor and the Arsenator field test kit as well as different spectrometric methods (ICP-MS, ICP-OES). Altogether 309 samples were tested for their arsenic concentration, 44 of them with more than one technique.

In the study region, the enrichment of heavy metals in surface waters is often linked to mining and coal combustion. The highest concentration of arsenic (As) was detected in the effluent of a gold mine (up to 2,820 µg L^{-1}) and in the ash basin of a thermal power plant (up to 1,170 µg L^{-1}). Five of 54 drinking water samples and 16 of 184 river samples were found to contain As levels above the World Health Organization (WHO) maximum permissible limit (10 µg L^{-1}), with a maximum of 300 µg L^{-1} As. Additionally elevated levels of uranium were detected.

The degree and extent of As concentrations exceeding WHO standards was previously unknown and demonstrates the necessity for a more intensive screening as well as possible interventions concerning the intake of arsenic contaminated drinking water. Preliminary results indicate that the ARSOlux biosensor technology is well suited for a precise quantification of arsenic content at low detections limits in regions where access to central laboratories is difficult.

Keywords: arsenic pollution, drinking water, gold mining, Mongolia, upper Selenga River Basin

2.2 Introduction

Mongolia is a landlocked country located in the heart of Asia between China and Russian Siberia. There are about 210 rivers flowing through Mongolia into Russia and China. Large rivers originate in the country's mountainous northern and western area while very few surface streams are found in the south. The upper basin of the Selenga River, which is the main artery feeding Lake Baikal in Russia, forms the study region of this investigation. Located in Mongolia, it encompasses several major rivers including the Orkhon, which has the Tuul and Kharaa as important tributaries. Since more than half of Mongolia's population and a considerable part of the country's mining and industrial activities are concentrated in the Tuul and Kharaa river basins, they are of particular relevance in the context of water resources management in the transboundary Selenga River Basin (Karthe et al. 2013; Chalov et al. 2013).

While a comprehensive quality monitoring for ground, surface and drinking water in Mongolia is still in its infancy, elevated levels of arsenic have recently been documented in surface water, groundwater, soils/sediments and urban vegetation for several locations in northern Mongolia. They appear to be mostly related to mining activities and the combustion of coal containing traces of arsenic (Hofmann et al. 2010; Kasimov et al. 2011a; Kasimov et al. 2011b; Inam et al. 2011; Murao et al. 2011, Thorslund et al. 2012; Batbayar 2012). The Public Health Institute in Ulaanbaatar conducted extensive well-water surveys and clinical examinations (MOH 2004). In seven of 21 aimags the mean arsenic concentration of the water samples exceeded the maximum tolerable level for drinking water of 10 µg L-1 (WHO 2011) and altogether 100,000 people are probably exposed to arsenic contamination in drinking water. Analyses of urine, hair and nails in a study group of 91 persons found evidence of arsenicosis in 16.5% of the study group (MOH 2004), and further studies from northern Mongolia also demonstrated high arsenic content up to 11 mg kg-1 in human hairs (n = 21) (Murao et al. 2004, 2011).

Three recent studies (Unurtsetseg et al. 2012, Olkhanud 2012, Nriagu et al. 2013) point to the fact that drinking water in many parts of the Mongolian Gobi provinces is contaminated with arsenic from natural and industrial origin. The Mongolian Ministry of Health selected 62 sums from five Gobi provinces as research sites. Elevated arsenic concentrations were present in 106 of 142 samples, existing arsenic concentrations in 15.4 % of the samples were 1 to 6 times higher than the drinking water standard of Mongolia (MNS 900:2005) and the WHO (2011) guideline for drinking water of 10 µg L-1 (Unurtsetseg et al. 2012). In Dornod Gobi Aimag 202 water samples were taken by an American-Mongolian research team. These samples ranged in arsenic content from 0.075 to 154 µg L-1, with 20% of wells exceeding the WHO guideline for arsenic in drinking water (Nriagu et al. 2013). In Southern Gobi region 237 water samples were taken to explore water ressources near Oyu Tolgoi mine, where 33% (78) of all samples showed concentrations higher than 10 µg L-1 arsenic and 3% of wells had concentration of higher than 50 µg L-1 up, ranging up to a maximum of 159 µg L-1 (Olkhanud 2012).

For the Kharaa River Basin in northern Mongolia, where a comprehensive survey on the state of water resources was carried out (MoMo Consortium 2009; Karthe et al. 2014, Hofmann et al. 2014), heavy metal concentrations showed an enrichment as compared to natural background levels although they were usually below or near maximum permissible limits. A first survey including arsenic (Hofmann et al. 2010) found surface water concentrations mostly between 1 and 10 µg L-1 while reaching up to 31 µg L-1. A highly elevated level (up to 1,170 µg L-1 As) was detected in the ash basins of the thermal power plant in Darkhan. The concentration in nearby drainage trenches was about 78 µg L-1 As. This suggests that the combustion of coal is one localized source of arsenic in water bodies (Hofmann et al. 2010) as well as in soils (Kasimov et al. 2011a). In central Mongolia including the capital Ulaanbaatar, the main sources of coal are the deposits in Baganuur, Nalaikh and Chulut, all of which have elevated arsenic contents (Kasimov et al. 2011b). Arsenic concentrations in coal from Baganuur and Nalaikh typically exceed 100 mg kg-1, a level at which toxicity of combustion byproducts is considered to be of serious environmental and human health concern (MOH 2004). Moreover elevated levels of arsenic have been detected in plant material from Ulaanbaatar, possibly derived from air pollution (Kasimov et al. 2011b).

Gold mining and processing is also known to enhance the release of arsenic and its uptake by humans and livestock (Keshavarzi et al. 2012). Recently gold mining has emerged as one of the most dynamic sectors of the Mongolian economy. Most gold mines are concentrated in northern Mongolia with a high environmental impact on local rivers, which all drain into the Selenga River: the Zaamar goldfield is located in the Tuul River Basin and two large open pit gold mines are situated at Boroo and Gatsuurt River, respectively. The placer gold mining at the Zaamar site has been estimated to increase total arsenic load of Tuul River by 30 tons per year (Thorslund et al. 2012). An arsenic content of 46,986 mg kg-1 was determined in rocks collected from Gatsuurt gold mine (Tsetsegmaa et al. 2009) and arsenic concentrations in artificial ponds of that mine have been measured to be 121 µg L-1 (Gandoljin et al. 2010). The average arsenic content in the tailing dam sediment of Boroo gold mine was determined at 4,419 mg kg-1, thus posing a potential source for future environmental contamination (Inam et al. 2011).

This paper summarizes the results of extensive testing for arsenic, which has been conducted in northern Mongolia with different methods and by various teams between May 2007 and 2013 and included ground, surface, waste and drinking water sources. We assess the existing contamination and identify potential sources of arsenic contamination which may have negative impact on the water quality of this area in the future.

2.3 Material and Methods

2.3.1 Study Region

The study region comprises the Mongolian part of the Selenga River Basin with a particular focus on the Kharaa, Tuul and Orkhon subbasins, which are comparable with regard to the physical environment and socio-economic development (Karthe et al. 2013). A highly continental climate with very cold winters and short but warm summers is characteristic for this landlocked Central Asian region. Water availability is naturally limited due to low precipitation and high evaporation rates. Even though only 20% of the annual precipitation falls during the winter months, and sublimation losses are above 80%, the melting of snow and river icings produce a first considerable peak in river discharge around May (Minderlein & Menzel 2014). Because of a concentration of rainfall during the summer months, more than half of the annual runoff occurs during the months of July, August and September, albeit with a large interannual variability (Batimaa et al. 2005; Berezhnykh et al. 2012; Hülsmann et al. 2014). While open grasslands dominate low-lying regions, mountainous regions (particularly in the rivers' headwater areas) are typically forested and play a key role in runoff formation (Menzel et al. 2011). The Tuul, Kharaa and Orkhon River Basins are home to Mongolia’s three largest cities (Ulaanbaatar, Darkhan and Erdenet, respectively) and to more than half of the country’s population. Moreover, the three river basins constitute important centers of agriculture, industry and mining (in particular for gold and copper). This does not only lead to a concentration of consumption but also of contamination risks. At the same time, water pollution in this region may harm a relatively large exposed population (Chalov et al. 2013).

2.3.2 Sampling Procedure

Shallow and deep groundwater wells, lakes, rivers and artificial ponds, as well as wastewaters from mining and industry were sampled in the northern part of Mongolia between May 2007 and May 2013 in the context of different monitoring projects and expeditions. A total of 309 water samples were collected for chemical analysis in Mongolia and Germany.

Routinely, water samples were taken with a 10L bucket from water sources. At wells water was pumped for two minutes and discarded before collecting a sample. On site determinations of water quality included measurements of temperature and pH, total dissolved solids (TDS), electrical conductivity (EC), and dissolved oxygen (DO) by a multi parameter tester (WTW, Multi 3430 SET G, Weilheim, Germany). Water samples for chemical analyses were collected in 50 ml vials and were acidified in the field with 1 mM H_3PO^4 for stabilization (Daus et al. 2006). A part of these samples were filtered with a 0.45 µm cellulose acetate filter (see Table 1 for different methods). Whenever arsenic was to be determined using the Arsenator field test kit, samples were not filtered. In the field samples were stored in a cooler box at about 10 °C before laboratory analysis at the Central Geologic Laboratory of Mongolia or shipment to Germany.

Table 1 Description of testing methods.

Method	Description
A	Unfiltered samples, stabilized by 10 mM H_3PO_4, tested by ICP-MS at UFZ Magdeburg
B	Unfiltered samples, stabilized by 1% HNO_3, tested by ICP-MS at FUGRO CONSULT GmbH Berlin
C	Unfiltered samples, stabilized by 1% HNO_3, tested by ICP-MS at KIWA Control GmbH Berlin
D	Unfiltered samples, stabilized by 10 mM H_3PO_4, tested by ICP-MS at Central Geological Laboratory, Ulaanbaatar
E	Filtered samples, stabilized by 10 mM H_3PO_4, tested by HPLC, ICP-MS and ICP-OES, at UFZ Leipzig
F	Filtered samples, stabilized by 10 mM H_3PO_4, tested by ICP-MS at Central Geological Laboratory, Ulaanbaatar
G	Filtered samples, tested by the ARSOlux biosensor test kit at the National University of Mongolia
H	Unfiltered samples, tested by the Arsenator test kit on site

2.3.3 Chemical Analyses

This paper integrates the findings of several studies which were carried out independently from each other and therefore used different methods for assessing arsenic concentrations. A short description of the testing methods is found in Table 1. Even though different testing methods imply some limitations in comparability, the added value of this data compilation lies in providing the currently most comprehensive picture of arsenic occurrence in water for north-central Mongolia. Besides different certified laboratory methods such as ICP-MS (method A-F, Tab. 1), we also used the two field test kits, namely the ARSOlux biosensor (UFZ, Leipzig, Germany) and Arsenator (Wagtech, Palintest, London, U.K).

The ARSOlux biosensor field kit (method G, Tab. 1) contained lyophilized (freeze-dried) bioreporter bacteria (Siegfried et al. 2012). Before the measurement of a sample lot the Junior 9509 luminometer (Berthold Technologies, Bad Wildbad, Germany) device of the kit was calibrated individually with standards of known concentrations of arsenite prepared by dilution of a 1,000 µg L^{-1} $NaAsO_2$ stock solution in demineralized water. Calibration series included four concentrations ranging from 5 to 200 µg L^{-1} arsenite as $NaAsO_2$ (Fig. 8). A 1-mL portion of arsenite standard or water sample was filled into a plastic syringe and injected into a bioreporter vial by penetrating the stopper. Three replicate vials were filled this way. The vials were shaken five times by hand and kept at a temperature of 30 °C in an incubator. Water samples were occasionally 10-fold diluted prior to incubation to identify arsenite toxicity on the bioreporter cells, which would result in false-negative low bioluminescence. After exactly two hour incubation, the vials were inserted into the battery-driven luminometer to measure integrated bioluminescence over a 10 s interval. Arsenic concentrations in groundwater were inferred by comparison of luminescence values with those in the calibration series by using an automated logarithmic regression, and are thus expressed as arsenite equivalent concentration. Bioreporter bacteria were killed by application of a 6% H_2O_2 solution followed by autoclaving of used vials and syringes.

The Arsenator test kit (method H, Tab. 1, Wagtech, Palintest, London, U.K.) detects total arsenic concentration in water samples by the well established Gutzeit method. The speciations As (III) and As (V) are both chemically transformed into arsine gas. Upon contact of the gas with a reagent on a test stripe, colored mixed arsenic/mercury halide compounds are formed. The intensity of a yellow to brown colored spot on the stripe is compared to a semi-quantitative color scale. For a more accurate differentiation of very light yellowish signals induced by arsenic concentration lower than 100 µg L^{-1}, the Arsenator test kit also includes a small portable photometer. The test was conducted according to the instruction manual. The reliability of the field kit results of total arsenic was tested by comparison with spectrometric methods. Inductively coupled plasma optical emission spectrometry (ICP-OES; ARCOS, Spectro A.I.), and inductively coupled plasma quadrupole mass spectrometry (ICPqMS; ELAN DRC-e, Perkin-Elmer) were applied for concentrations of arsenic above and below 100 µg L^{-1}, respectively. Total concentrations of chromium, copper, iron, manganese, antimony and uranium were measured with ICPqMS while sodium, potassium and chloride concentrations were detected semi quantitatively with ICP-OES. By coupling high-performance liquid chromatography (HPLC) online with ICPqMS, the arsenic species As (III) and As (V) could be differentiated (Mattusch et al. 2000).

2.3.4 Data Analysis

Data were compiled in an Excel data sheet and analyzed with STATISTICA 7.1. Nonparametric Whitney-Mann U tests and Spearman Rank Correlations were performed on the data. Cross comparison of different analytical methods for arsenic detection was performed by linear regression using the software Microsoft Excel 2010. Results were compared with the Mongolian National Standard (MNS 900:2005) and the WHO (2011) guidelines for drinking water quality.

2.4 Results

2.4.1 Overview

From 2008 to 2013 a total of 309 water samples were collected from 130 sample points in northern Mongolia during routine monitoring and specific expeditions. The results could be categorized into 14 sample types, including different kind of surface and ground waters, drinking water for humans and livestock, various types of waste water and other sorts of technically used water. Eight major types of samples that comprised 297 water tests are shortly described as follows (Fig. 3): rivers (n = 184) were most often sampled and showed relatively low median concentration of arsenic of 2.5 µg L^{-1} (range: 0.7 - 190 µg L^{-1}), salt lakes were the second natural water source investigated, but only sampled twice with median arsenic concentrations of 19 µg L^{-1} (range: 18.7 - 19.0 µg L^{-1}). Drinking water wells (n = 54) had a median concentration of 2.5 µg L^{-1} (range: 0.9 - 300.0 µg L^{-1}), while herders' wells (n = 6) showed a median concentration of 2.7 µg L^{-1} (range: 0.05 - 330.0 µg L^{-1}) of the metalloid (Fig. 3). Effluents from waste water treatment plants (n = 19) had even lower arsenic concentrations averaging 2 µg L^{-1} (0.9 - 3.2 µg L^{-1}). The highest concentration of arsenic was measured in two types of artificial ponds: settling ponds of coal power plants, which serve as deposit for ashes (median: 372µg L^{-1}, range: 1.9 - 1,170.0 µg L^{-1}, n = 19), and mine waste water ponds (median: 105 µg L^{-1}, range: 5.4 - 221.0 µg/ L^{-1}, n = 7). However, while settling ponds of coal power plants work with a closed water circulation, ponds for mining operation are often drained into natural river systems. Particularly gold mining effluents in some cases carry high loads of arsenic in median 288 µg L^{-1} (49.0 - 2820.0 µg L^{-1}, n= 4).

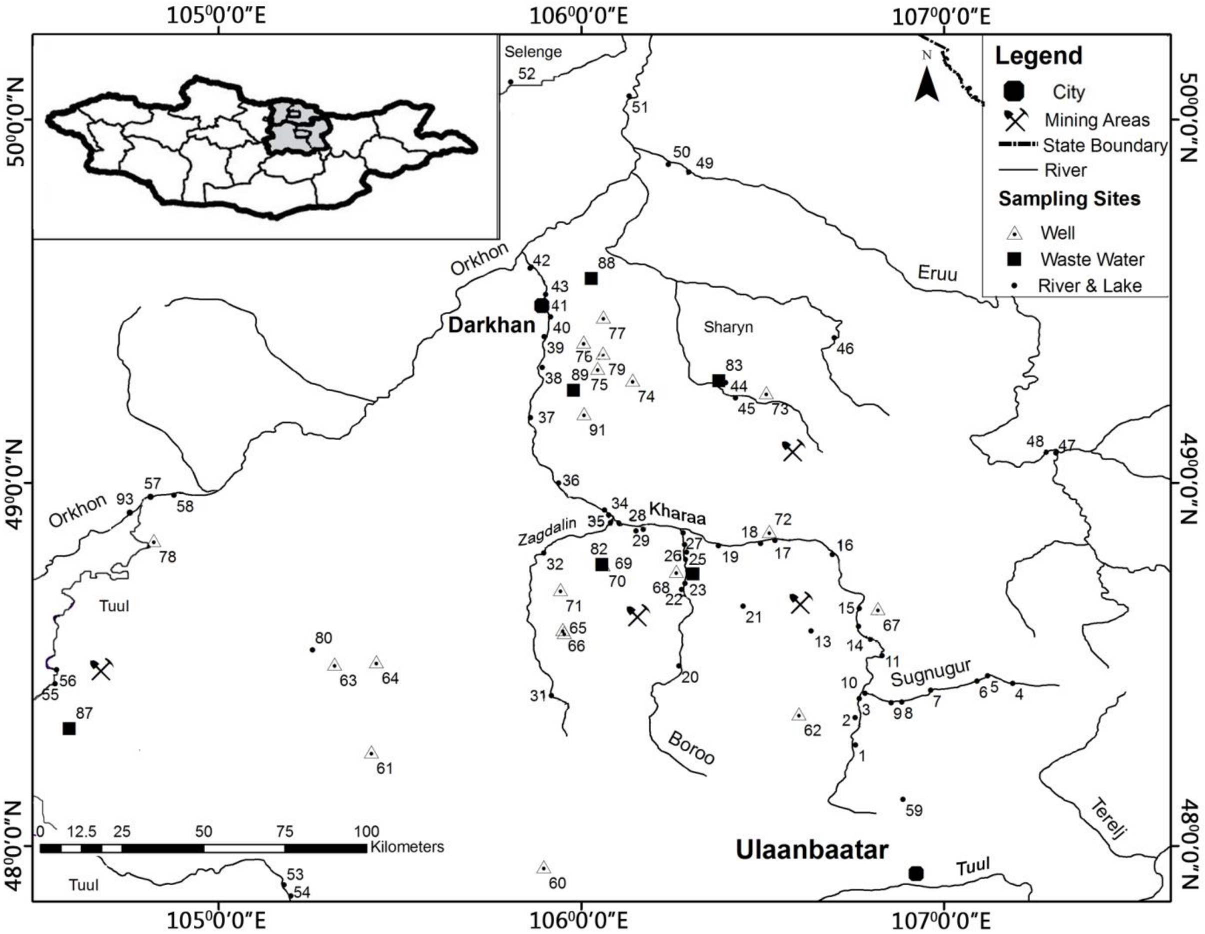

Figure 2 Map showing the geographic location of the sample sites of this study in northern Mongolia. Sample sites comprise ground, surface and drinking water resources in the Selenge, Tuv, Darkhan Uul and Bulgan Aimags (provinces) that are shaded in the inserted map of whole Mongolia

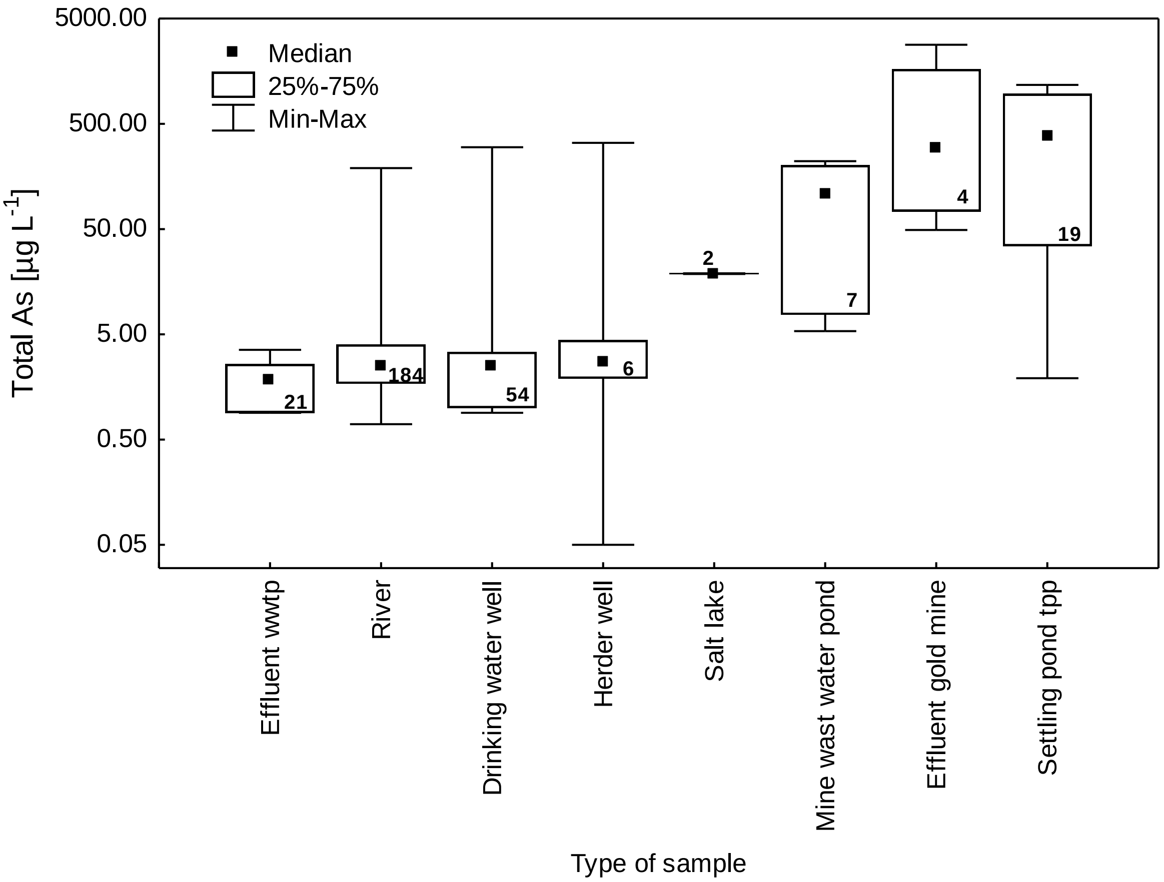

Figure 3 Sample types for 297 water samples taken in the course of this study. The figure shows the eight major groups of samples. Numbers refer to the n of the sample type. Mind the logarithmic scaling of the y-axis. Abbreviations: wwtp = wastewater treatment plant; tpp = thermal power plant

2.4.2 Rivers

Although the arsenic concentration in northern Mongolian rivers was mainly low, it exceeded the 10 µg L^{-1} WHO threshold for drinking water in 16 cases, which made 8.7% of all measurements, in Bayangol, Boroo, Gatsuurt, Kharaa and Orkhon River (Fig. 4, 5). The maximum concentration of arsenic was measured in an Orkhon River sample with 190 µg L^{-1} (Fig. 5a). In Gatsuurt River 9 of 10 measurements were above this threshold (Fig. 3, 5d). A detailed presentation of data from sites along the rivers clearly demonstrates a fluctuation of arsenic content downstream (Fig. 5), which may be caused by spatial-temporal variation of arsenic input and/or sedimentation and binding and subsequent leaching of arsenic in river sediments. Moreover, our data exhibit discharge of arsenic at certain river sections, viz. peaks of arsenic concentration were found downstream river junctions of Orkhon-Tuul (Fig. 5a) and Boroo-Kharaa (Fig. 5b). For Boroo River our data shows fluctuations of arsenic up to 400% of the measurement upstream the river, with an increase in arsenic concentration downstream (Fig. 5c), while in Orkhon (Fig. 5a) and in Gatsuurt River (Fig. 5d) a continuous dilution of arsenic concentration downstream mining area was observed.

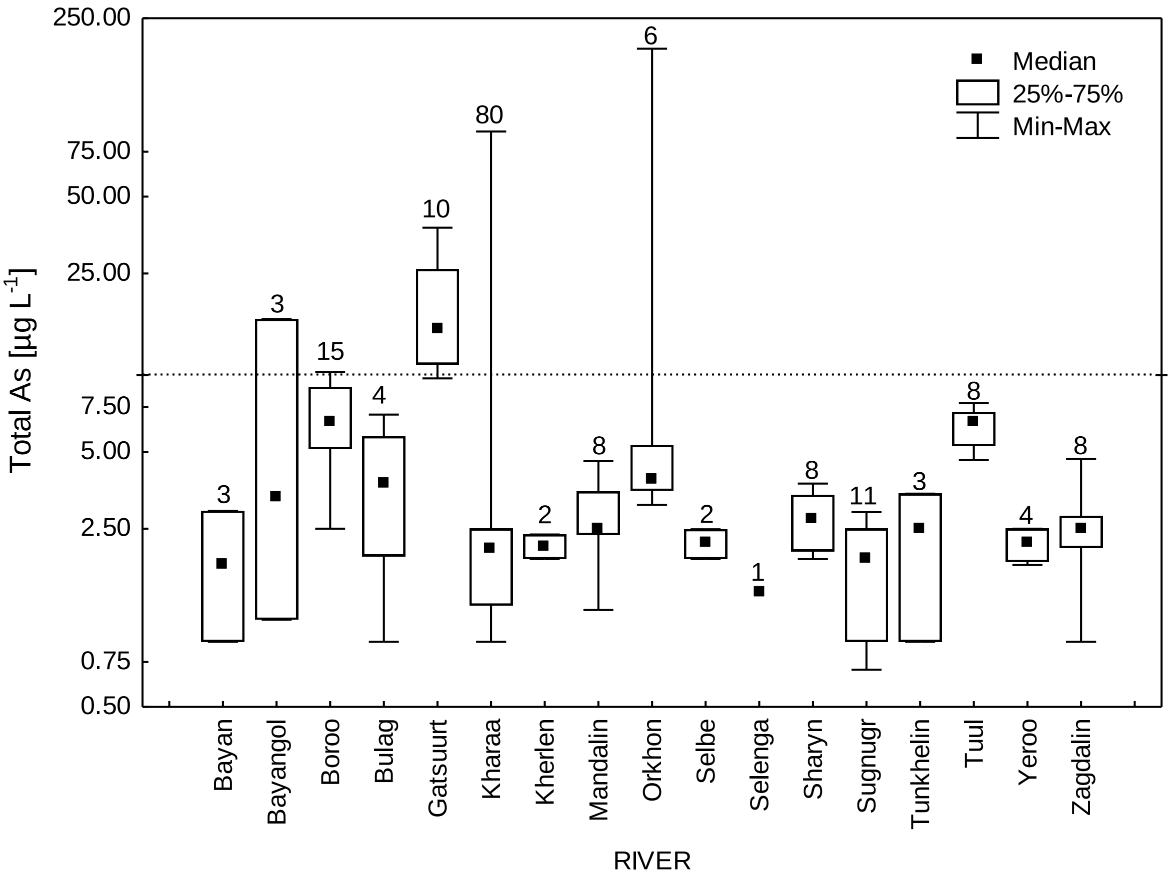

Figure 4 Arsenic content of rivers in northern Mongolia during our study from May 2007 to May 2013. Mind the logarithmic scaling of the y-axis. The dotted line gives the WHO guideline value for drinking water of 10 µg L^{-1}. Numbers show the number of samples (n) per river. Maximum values above the threshold were measured for Bayangol (16.6 µg L^{-1}), Boroo (10.2 µg L^{-1}), Gatsuurt (37.8 µg L^{-1}), Kharaa (90 µg L^{-1}) and Orkhon River (190 µg L^{-1})

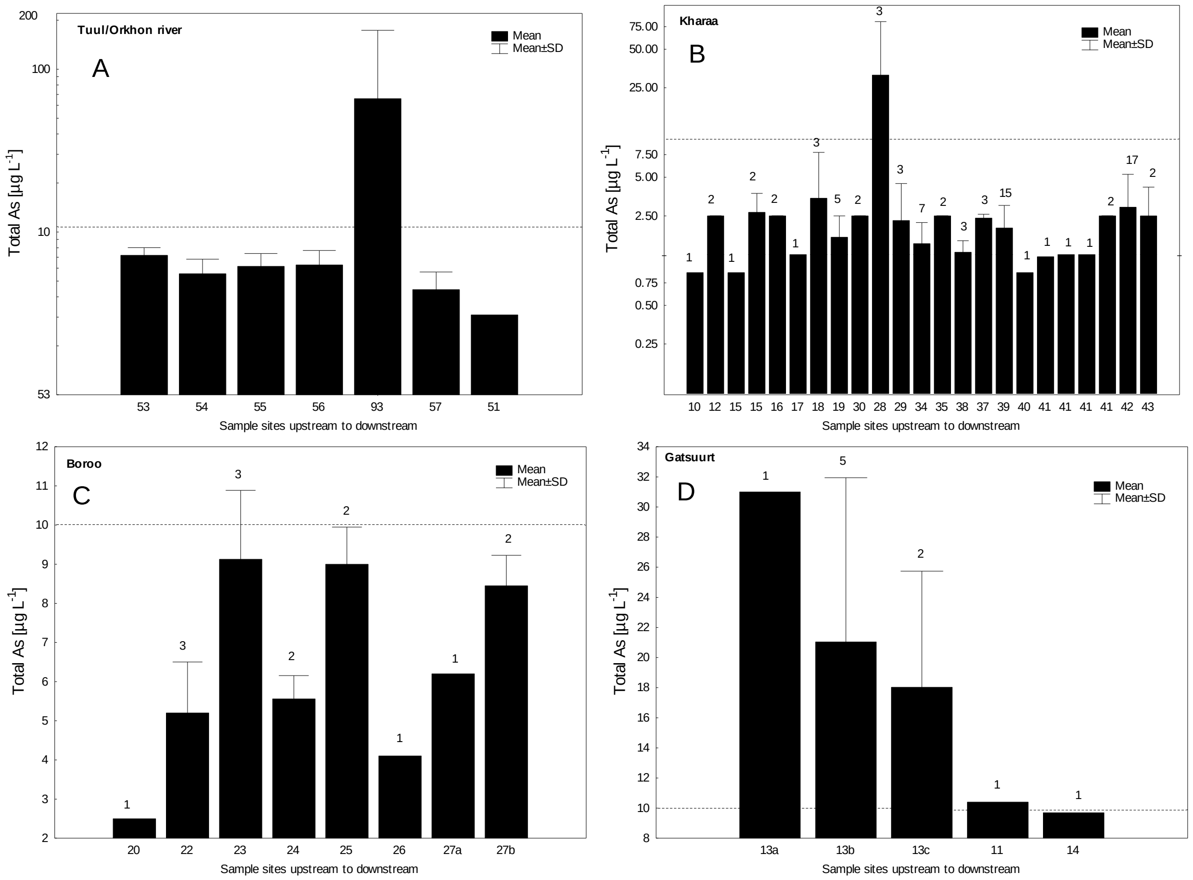

Figure 5 Changes in arsenic concentration along rivers. Shown is the distribution of arsenic concentration at samples size ordered from upstream (left) to downstream (right). Mind the different scaling and start value of the y-axis (Fig. a,b with logarithmic scaling). The dotted lines mark the WHO guideline value for drinking water of 10 µg L^{-1}. Sample sites are given according to Fig. 1, with each column representing a distinct samples site, while numbers are adjusted to optimal presentation in the map. 4 a) Tuul/Orkhon River. Site 53 to 56 Tuul River (Lun to downstream Zamar mines), Site 93 Orkhon River downstream Erdenet, Site 57downstream Tool-Orkhon junction. 4 b) Kharaa River. This sample site was investigated most thoroughly. Site 28 is downstream the Boroo-Kharaa River junction, with higher arsenic load coming from the mining areas at Boroo River. 4 c) Boroo River. Samples were taken upstream, midstream and downstream of the Boroo Gold mining area, with site 25 downstream an influx channel for mining effluents. 4 d) Arsenic content in different distance from Gatsuurt Gold Mine. Site 13a is taken immediately near the mining site; downstream sample sites are further remote from that area

2.4.3 Wells

Arsenic concentration higher than 10 µg L^{-1} was measured in 9.3% of all 54 samples, so in five cases altogether (Fig. 6). These extreme values showed concentrations up to 94 µg L^{-1} and 300 µg L^{-1} for Zuunkhaara deep well and Borewell 3, respectively. In six samples from herder wells we found one outlier of 330 µg L^{-1} arsenic for a well, otherwise measurements were below 5 µg L^{-1}.

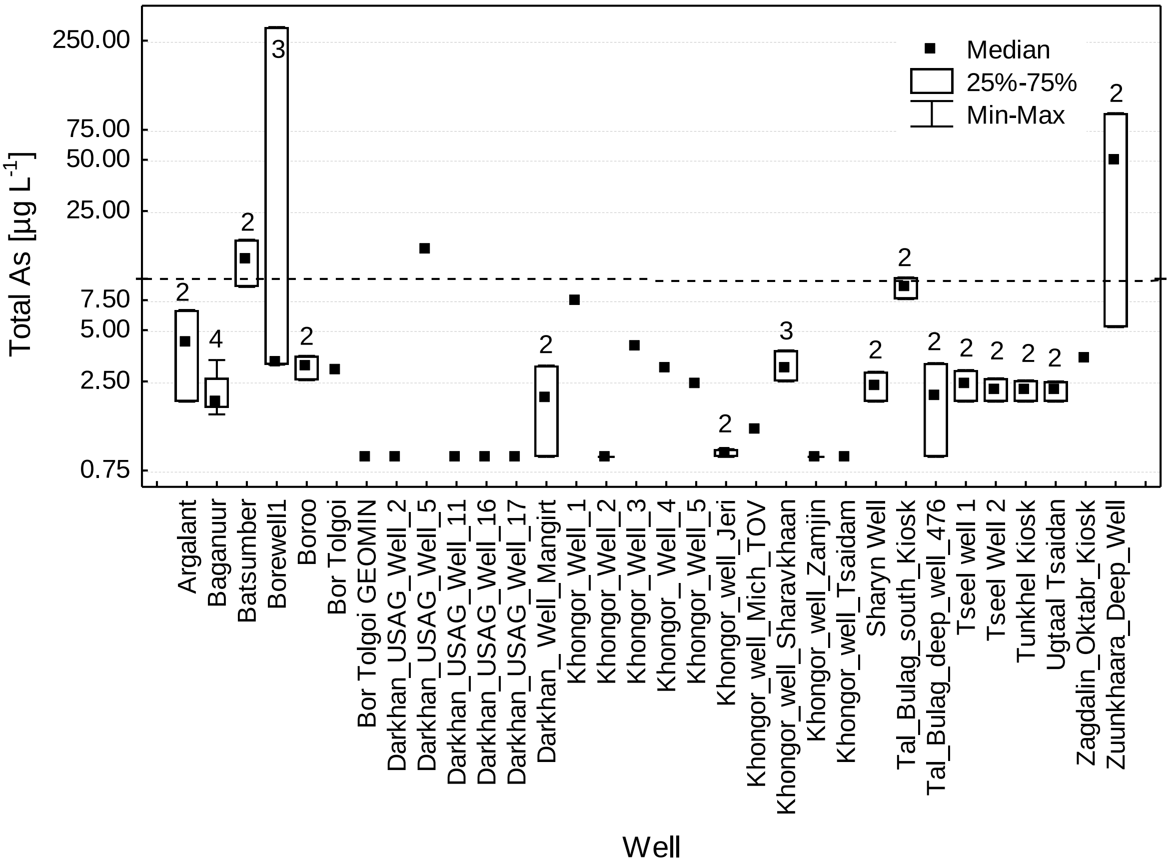

Figure 6 Arsenic concentration in 32 drinking water wells in our survey area. The numbers refer to the number of measurements (n). Maximum values above thus threshold were measured for Batsumber (17.0 µg L^{-1}), Borwell 3 (300.0 µg L^{-1}); Darkhan USAG Well 5 (14.8 µg L^{-1}), Tal Bulag South Kiosk (10.2 µg L^{-1}) and Zuunkhaara deep well (93.9 µg L^{-1}).The broken line gives the WHO guideline value for drinking water of 10 µg L^{-1}. Mind the logarithmic scaling of the y-axis

2.4.4 Artificial Ponds for Waste and Processing Water

The highest concentrations of arsenic were found in artificial ponds for waste and processing water of gold mining operations and coal fired power plants (Fig. 3). Arsenic concentration ranked up to 221 µg L^{-1} in mining waste water ponds and was especially high in mining effluents with a maximum of 2,820 µg L^{-1} arsenic found in the mining effluent of Bor Tolgoi gold mine, exceeding the Mongolian standard for waste water (MNS 4943 2011) 282 times. These high concentrations demonstrated that gold mining may dramatically influence arsenic concentration in surface waters. In Kharaa River arsenic concentration peaked at Kharaa-Boroo junction (Fig. 5b), presumably influenced by mining effluence from gold mining operations in the upstream catchment area of the Boroo River. At the Boroo River we found effluent small scale mining operation where water from a waste water pond drained directly into a small creek and subsequently into the Boroo river with gradually diminished arsenic concentrations (mean As concentration of 73 µg L^{-1}) (Fig. 7).

A maximum arsenic concentration of 1,170 µg L^{-1} was found in the settlement pond of the Darkhan coal power plant. A high mean content of arsenic of about 450 µg L^{-1} suggest a considerable impact on the environment, although measurements were highly variable over time. While samples from autumn (n= 7) showed a very high arsenic concentration (median

1,050 µg L^{-1}), samples that were taken in spring (n = 9) had a significantly lower arsenic concentration (median 59.37 µg L^{-1}, Mann-Whitney U-Test U = 5.00 Z = 2.81, p = 0.005).

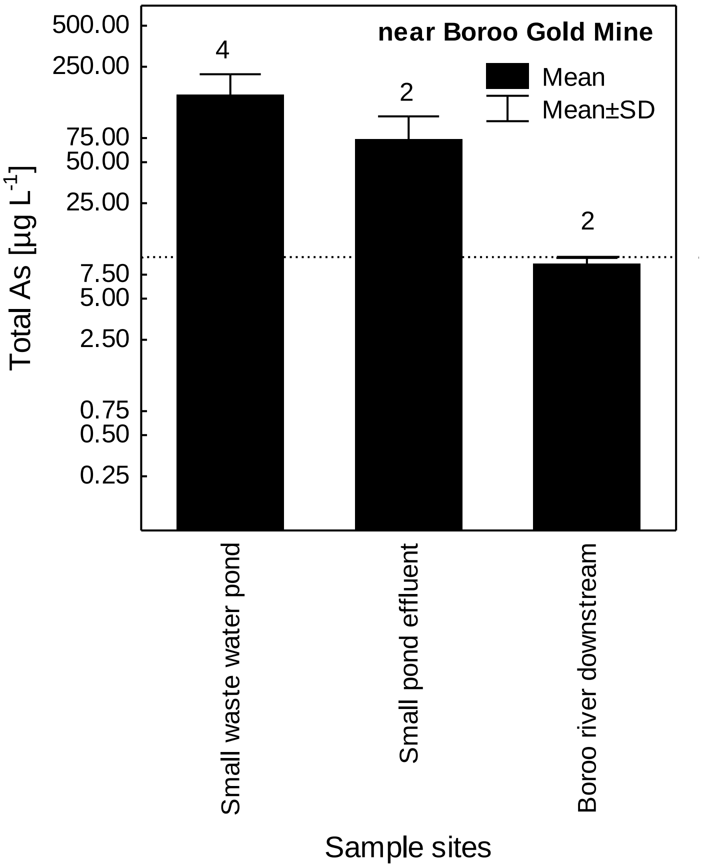

Figure 7 Arsenic concentration of samples collected at surface water ponds ca. 1 km beneath the tailing dam of Boroo gold mine in comparison with river water of Boroo Gol

2.4.5 Correlation of the Arsenic concentration and Environmental data

Arsenic content of water samples was highly significantly ($p < 0.001$) positively correlated (Spearman rank correlation, SRC) with water temperature (R = 0.32), ph value (R = 0.25) and total dissolved solids (R = 0.26) (Table 2). Moreover, arsenic concentration in water samples was found to be highly significantly correlated (SRC, $p < 0.001$) with concentration of sodium (R = 0.57), chloride (R = 0.49) and uranium (R = 0.41). More results are given in Table 3.

Table 2. Spearman rank order correlation of environmental descriptors with arsenic content of water samples (n= 309, ICP-MS methods A-E). Given are coefficients of Spearman rank order correlations for the factors water temperature, pH, electric conductivity/total dissolved solids, oxygen and the depth of the well in case of ground water samples. Bold correlations are significant at $p < 0.05$. Higher significances are marked as $p < 0.01$ **, $p < 0.001$ ***. Total n for descriptors are given in brackets in the first column, units are given in the second row, and for calculation missing data were pairwise deleted. See Appendix 1 for the data.

Table 2 Spearman rank order correlation of the concentration of different elements with the arsenic content of water samples (n= 43). Given are coefficients of Spearman rank order correlations for the concentrations of chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), antimony (Sb), uranium (U) sodium (K), potassium (Na) and chloride (Cl) with pH and electric conductivity/total dissolved solids of the samples, as well as with concentrations of total arsenic (As), the arsenic species As (III) and As (V) and –for comparison– with uranium (U). All samples were measured by method E only (see Tab. 1). Bold correlations are significant at $p < 0.05$. Higher significances are marked as $p < 0.01$ **, $p < 0.001$ ***. Data are given in Appendix 2.

	pH	EC/TDS [µs/cm]/mg/L	As [µg/L]	As(III) [µg/L]	As(V) [µg/L]	U [µg/L]
Cr [µg/L]	0.25	0.02	0.12	-0.18	0.29	**0.49*** **
Cu [µg/L]	0.01	0.06	0.24	-0.06	0.24	0.24
Fe [µg/L]	-0.08	-0.20	0.01	-0.04	-0.14	-0.08
Mn [µg/L]	-0.07	0.23	**0.32***	0.29	0.07	-0.02
Na [µg/L]	0.08	0.91	0.37	0.27	0.38	0.59
Sb [µg/L]	0.03	0.13	**0.38***	0.14	**0.35***	0.14
U [µg/L]	**0.37***	**0.57*** **	**0.41*** **	0.22	**0.51*** **	1.00

	Water temp. [C°]	pH	EC/TDS [µs/cm]/mg/L	Oxygen [mg/L]	Depth of well [m]	Total As [µg/L]
Water temp. (246)	1.00	**0.46*** **	**-0.14**	-0.12	0.31	**0.32*** **
pH (207)	**0.46*** **	1.00	0.13	**0.25*** **	**0.61****	**0.25*** **
EC/TDS (282)	**-0.13**	0.13	1.00	-0.04	**-0.50**	**0.26*** **
Oxygen (229)	-0.12	**0.25*** **	-0.04	1.00	0.36	0.11
Depth of well (24)	0.31	**0.61****	**-0.50**	0.36	1.00	-0.23

K [mg/L]	**0.36***	**0.57*** **	**0.57*** **	**0.44****	**0.58*** **	**0.63*** **
Na [mg/L]	0.08	**0.92*** **	**0.38***	0.26	**0.39***	**0.57*** **
Cl [mg/L]	0.24	**0.79*** **	**0.49*** **	**0.35***	**0.53*** **	**0.68*** **

2.4.6 Laboratory Data from ICP-MS and ICP-OES

To check the accuracy of arsenic detection methods, concentration data in field samples collected in spring 2013 (n=44) were determined with three different spectrometric methods (A, E, F) in the Central Geological Laboratory in Ulaanbaatar, Mongolia (ICP-MS) and the laboratory of the Department Analytical Chemistry of the UFZ in Leipzig, Germany

(HPLC-ICPqMS, ICP-OES). The results were in good agreement, but slightly lower arsenic concentration levels were detected for some specific samples by HPLC-ICPqMS and ICP-OES in Germany (Fig. 8B) compared to the data determined in Mongolia.

2.4.7 Performance of the ARSOlux Biosensor and Arsenator Field Test Kits

The results for arsenic concentration detected by the ARSOlux biosensor and Arsenator field test kits were in good quantitative agreement with the results of laboratory measurements (Fig. 8C, Table 4). The concentrations detected in unfiltered samples by the Arsenator were slightly higher than the data measured by ARSOlux in filtered samples.

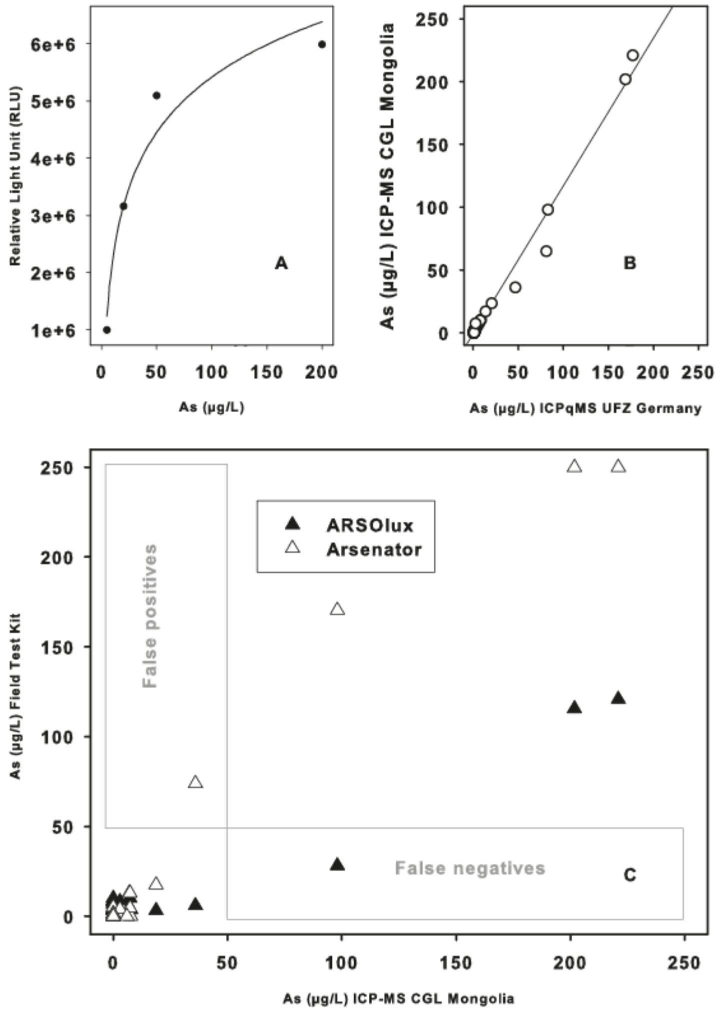

Figure 8 Calibration curve of the ARSOlux biosensor (a), Cross-analysis of ICPqMS data from UFZ Germany and ICP-MS results of the Central Geological Laboratory in Ulaanbaatar, Mongolia (n=44, b). Cross comparison of arsenic results measured by ICP-MS in the Central Geological Laboratory in Ulaanbaatar, Mongolia and data measured with the arsenic field test kits ARSOlux biosensor and Arsenator (n = 22, c)

Table 3 Arsenic concentrations detected with different analytical methods (total n=42). Given are averages with minimum and maximum values. Letters in square brackets refer to methods described in Table 1.

Method	ARSOlux [G]	ICP-MS (Mongolia)[F]	ICPqMS (Germany)[E]	HPLC-ICPqMS (Germany) [E]	
Unit	Total As µg L^{-1}	Total As µg L^{-1}	Total As µg L^{-1}	As (III) µg L^{-1}	As (V) µg L^{-1}
Rivers (n = 21)	6 (3-12)	4 (0-23)	4 (1-21)	0	5 (2-13)
Drinking water wells (n = 12)	7 (3-26)	2 (0-17)	2 (0-14)	0 (0-5)	3 (2-7)
Mining effluent	67 (4-121)	132 (8-221)	108 (5-177)	0	64 (5-104)

(n = 4)					
Industrial & municipal waste (n = 5)	16 (6-10)	23 (3-65)	21 (2-81)	0	14 (2-59)
All (n = 42)	13 (3-121)	18 (0-221)	16 (0-177)	0 (0-5)	12 (2-104)

2.5 Discussion

Our research comprises samples that were taken over a time span of five years in northern Mongolia. While most other comprehensive studies from Mongolia focused on monitoring of ground and drinking water (MOH 2004, Hofmann et al. 2010, Batbayar 2012, Olkhanud 2012, Unurtsetseg et al. 2012, Nriagu et al. 2013) our investigation also includes an assessment of river- and process water from industrial and mining activities to check for the reasons of arsenic pollution. The aggregated results draw the most comprehensive picture of arsenic contamination in north-central Mongolia available to this date.

2.5.1 Impact of Gold Mining on Arsenic Load of Rivers

Gold mining has been spotted as a frequent source for high arsenic loads in many regions of the World (Ravenscroft et al. 2009, Keshavarzi et al. 2012), and our results corroborate these findings. Besides gold the bedrock contains high concentrations of arsenic (Tsetsegmaa et al. 2009), which is solved during the gold washing and extracting process. At Gatsuurt gold mine Gandoljin et al. (2010) measured mining effluents with a concentration of 121 µg L^{-1} arsenic, while Enkhdul et al. (2010) reported 136 mg/kg arsenic for the sediment of Gatsuurt mid river. The present study revealed high arsenic concentrations in artificial ponds for mining processing water and in mining effluent, e.g. in the case of the artisanal small scale mining site Bor Tolgoi (ca. 9 km WNW of Boroo gold mine) direct measurement of the arsenic concentrations in mining waste water ponds and the effluent discharge revealed values of up to 2,820 µg L^{-1} that will contaminate the upper groundwater layer.

In contrast to small scale mining the big facilities have different operation procedures. Thus the Boroo gold mine waste water pond has been designed as a zero discharge facility; that is, supernatant water from the dam is stored in a tailing reservoir and will not be discharged to the environment. However, high concentrations of arsenic in the tailing dam sediment of Boroo gold mine were already measured by Inam et al. (2011), who also tracked underground flows of heavy metals (including As) from the dam to monitoring wells situated downhill. Mining waste water in that study showed arsenic concentrations of 1,746 µg L^{-1}, while a maximum of 46 µg L^{-1} was measured at the monitoring wells that all were above the Mongolia water quality standard for As. The highly fluctuating arsenic concentrations in Boroo river water presented here (Fig. 5C) may have been influenced by underground flows from mining areas. The enrichment of arsenic in tailing deposits, contaminated leachate and its accessibility by livestock, birds and other wildlife is a major point of concern. Moreover, in case of dam destruction and release of tailing deposits and water of the tailing reservoir itself a serious impact to the environment may occur.

As a consequence of the distribution of pollution sources arsenic concentration varied strongly along rivers (Fig. 5) with an overall trend of reduced concentration downstream, where larger water volumes led to dilution of the arsenic concentration, which is a common effect in large river systems (Mueller et al. 2008). In terms of mass flow contributions the river loads of arsenic have been investigated by Thorslund et al. (2012) for the Tuul River as the most polluted river in Mongolia. During the period 2005 to 2008 the average net increase for dissolved mass flows downstream of Zamaar gold field was 9 tons yr^{-1} arsenic and reached about 30 tons yr^{-1} in 2008. Therefore this mining area has been identified as a major contributor of heavy metal and arsenic influxes into the Selenga river system (Chalov et al. 2012, Thorslund et al. 2012). Interestingly, perhaps due to seasonal effects, we measured only low arsenic concentration in Tuul River downstream the Zaamar goldfield in May 2013. Recent investigations by Hofmann et al. (2013) also state increasing arsenic river loads at the outlet of Kharaa river basin, reaching 1.7 tons yr^{-1} arsenic in 2011 and 3.3 tons yr^{-1} in 2012. Arsenic concentration in Tuul River near Ulaanbaatar originates from natural and anthropogenic resources and was found strong enough to cause adverse aquatic biological effects (Dalai & Ishiga 2013). In contrast our measurements in Tuul River at Lun Bridge more than 200 km downstream revealed low arsenic concentrations, thus pointing towards spatial variation of arsenic load, possibly caused by binding of arsenic to the river sediment. These contrasting results demonstrate a lack of knowledge regarding the seasonal impact of mining areas on arsenic loads of rivers in steppe regions and identify some issues for further research in Mongolia: 1) identification of major dischargers and of probable occurrence areas of heavy metals (see also Rodríguez-Lado et al. 2013), 2) monitoring seasonal and spatial effects on arsenic load in rivers and sediments, 3) modeling discharge and sedimentation of arsenic along the rivers and within the course of the years (see also Brumbaugh et al. 2013, Chalov et al., 2014). Since groundwater recharge is mainly fed by bank infiltration from rivers and most of the drinking water extraction sites of the cities of Darkhan and Ulaanbaatar are situated in the river floodplains, the groundwater quality is already affected by increasing levels of arsenic and other heavy metals (see Dalai & Ishiga 2013).

2.5.2 Threats for the Ground Water

Still samples of well water in northern Mongolia ranked mostly well below the WHO maximum permissible limit for arsenic of 10 µg L^{-1}; however, 10% of the wells exceeded that limit with a maximum load of arsenic of 330 µg L^{-1} in herder wells and 300 µg L^{-1}for drinking water wells, five of which surpassed WHO level. It can be summarized that drinking water seems less affected by arsenic pollution than in other parts of the country, viz. in Dornogobi Aimag, where 20% of the wells were contaminated (Nriagu et al. 2013), or in Southern Gobi with 16.4% of the boreholes above the recommendation threshold (Olkhanud 2012). In 2004 nationwide 10.3% of 867 water samples contained arsenic with an average arsenic content of 14 ± 3 µg L^{-1} (MOH 2004); however, due to intensified mining activities all over Mongolia, arsenic pollution may have increased since that time.

While the Mongolian Ministry of Health' survey accounts for coal and mineral deposits in the vicinity of the wells as a latent cause of danger (MOH 2004), our study points towards gold mining sludge, ash deposits and settling ponds of power plants as further potential pollution sources. In fact up to 1,170 µg L^{-1} of arsenic were detected in the settling pond of Darkhan coal power station, and the total of 19 samples for all settling ponds showed a median arsenic concentration of 372 µg L^{-1}. These high loads of arsenic in the processing water pose a serious threat to the surrounding ground water and the population that uses it. Darkhan USAG Well 5 is in only 3.8 km distance from the power station and had an elevated arsenic concentration (14.8 µg L^{-1}), indicating a potential pollution by underground flow of contaminated process water (see also Inam et al. 2011, as discussed above). Seasonal changes of weather conditions may impact the arsenic concentration of the source pool, e.g. by higher dilution of processing water because of pronounced precipitation in spring and early summer, or increasing concentration in autumn after summer drought periods, as indicated by our results and in literature (Bhattacharya et al. 2011, Aguilar-Muniz et al. 2013).

Interestingly, high arsenic concentration was positively correlated with high concentration of uranium in 43 of our samples. This points towards another element that is frequently detected in Mongolian water samples and poses an additional danger to human health: 11 of 33 samples taken from rivers or drinking water wells had uranium concentrations above the provisional WHO drinking water guideline of 15 µg L^{-1}, with Ugtaal tsaidan and Tseel No. 2 drinking water wells both at levels ≥ 60 µg L^{-1}. These results corroborate findings from Ulaanbaatar (Nriagu et al. 2012), Dornogobi Aimag (Nriagu et al. 2013) and eastern Mongolia (Linhoff et al. 2011, lake water) where even higher values have been documented.

2.5.3 Arsenic Pollution as a General Threat in Mongolia

It can be summarized that arsenic pollution is a serious and increasing threat for water quality in northern Mongolia and several research results confirm enhanced uptake of arsenic by Mongolian villagers (Murao et al. 2004, 2011). Uptake of arsenic by humans may not only occur with drinking water; as Mongolian coal has high arsenic content (MOH 2004) and coal firing during the harsh winters produces high levels of air pollution, arsenic concentration in soil and plant material from Ulaanbaatar (UB) is unusually high (Batjargal et al. 2010, Kasimov et al. 2011a,b) and similarly livestock from Tuv Aimag (UB region) showed higher arsenic contents (0.06 mg kg^{-1}) in tissue of liver and parenchyma than livestock from other Mongolian regions (Šimoník 2012). Serious human health problems may result from long time uptake of arsenic as it is known from Inner Mongolia (Guo et al. 2007, Lamm et al. 2006, Wade et al. 2009, Xia et al. 2009). For the future, the natural geogenic arsenic background has to be considered in risk assessments of (anthropogenic) water pollution for whole Mongolia. For Kharaa river basin a first estimate for natural geogenic background conditions of groundwater is given by Hofmann et al. (2014). A better knowledge of the geological background is needed to improve decisions of water engineers and mining operators. A promising approach has been recently conducted in China with a statistical risk model to classify safe and unsafe areas with respect to geogenic arsenic contamination and the related probability of arsenic concentrations exceeding the 10 mg L^{-1} threshold in ground waters (Rodriguez-Lado et al. 2013).

2.5.4 Bacterial Biosensors – a Promising Option for Arsenic Screening in Mongolia

Major obstacles for extensive arsenic monitoring are the limited reliability or practicality, and/or the relatively high costs of existing analytical methods. Microbial reporter technologies (bacterial biosensors) have been proposed as an alternative, rapid, and cost-effective method to detect chemical species in aquatic samples (Harms et al. 2005, Siegfried et al. 2012). The bioreporter bacteria or biosensors in some cases consist of genetically modified bacteria that produce a reporter protein in response to the presence of a target chemical. Luminescent bacterial biosensors responding to arsenite and arsenate (Stocker et al. 2003, Trang et al. 2005) have been applied in the present study. The genetically modified (GMO) bioreporter bacteria included in the ARSOlux test kit remain in sealed vials throughout shipping, storage, application, disinfection and autoclaving. The Central Commission on Biologic Safety of the German Federal Office of Consumer Protection and Food Safety has stated in a risk assessment report (ZKBS 2013) that the application of the present ARSOlux biosensor field kit does not present a potential hazard to humans, animals and the environment. The risk assessment was prepared after a request of the Biosafety Committee of the Mongolian Ministry of Environment and Green Development. The Biosafety Committee of Mongolia permitted the import of the GMO ARSOlux biosensor for contained use. Biosensors such as ARSOlux could offer a cost-effective and environmentally friendly alternative to the cumbersome and expensive methods currently used for detection of arsenic and other contaminants.

2.6 Conclusions

To avoid the further contamination of groundwater and surface water resources in Mongolia with heavy metals the implementation of a set of measures is necessary. These include mitigation procedures in mining areas, containment of existing dump sites and processing water ponds, and search for save drinking water wells (see Zhang 2013), as well as capacity development of Mongolian institutions and the implementation of a monitoring system combined with effective analytical tools (Hofmann et al. 2010).

Acknowledgments

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Chapter3. Chemical water quality gradients in the Mongolian sub-catchments of the Selenga River basin

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Chemical water quality gradients in the Mongolian sub-catchments of the Selenga River basin

3.1 Abstract

Even though the Selenga is the main tributary to Lake Baikal in Russia, the largest part of the Selenga River basin is located in Mongolia. It covers a region that is highly diverse, ranging from almost virgin mountain zones to densely urbanized areas and mining zones. These contrasts have a strong impact on rivers and their ecosystems. Based on two sampling campaigns (summer 2014, spring 2015), we investigated the longitudinal water quality pattern along the Selenga and its tributaries in Mongolia. While headwater regions typically had a very good water quality status, wastewater from urban areas and impacts from mining were found to be main pollution sources in the tributaries. The highest nutrient concentrations in the catchment were found in Tuul River, and severely elevated concentrations of trace elements (As, Cd, Cu, Cr, Fe, Mn, Ni, Pb, Zn), nutrients (NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}) and selected major ions (SO_4^{2-}) were found in main tributaries of Selenga River. Moreover, trace element concentrations during spring 2015 (a time when many mines had not yet started operation) were markedly lower than in summer 2014, indicating that the additional metal loads measured in summer 2014 were related to mining activities. Nevertheless all taken water samples in 2014 and 2015 from the main channel of the Mongolian Selenga River complied with the Mongolian standard (MNS 4586:98) for the investigated parameters.

Keywords: Arsenic, central Asia, heavy metals, nutrients, seasonal variation

3.2 Introduction

In Mongolia, a small and nomadic population ensured a sustainable utilization of natural resources like water until the beginning of the 20th century (Neupert 1999). This has changed considerably over the past 100 years due to two processes: (1) population growth and urbanization and (2) more recently, economic growth with a boom in the mining sector.

In 1918, the total population of Mongolia was about 648,000 inhabitants and since then it has increased more than fourfold (Spoorenberg 2015). An over proportional population growth occurred in Mongolia’s cities which are relatively young. Ulaanbaatar had a population of about 403 thousands inhabitants in 1979 (Brinkhof 2015) and since then has grown rapidly by a combination of migration and relatively high birth rates. Today nearly half of the Mongolian people live in the metropolitan region of Ulaanbaatar (1.3 mill inhabitants; Census 2010) which is located at the Tuul River. Other important cities like Erdenet at the Orkhon River and Darkhan at Kharaa River were built with assistance of the Soviet Union after the Second World War and were typically founded as centers of mining or industry (Gardemann and Stadelbauer 2012). One problem that is frequently associated with urban areas in Mongolia is outdated or insufficient urban waste water collection and treatment. This typically results in the discharge of poorly treated or even untreated domestic wastewater. This wastewater is a major source of nutrients in rivers, particularly around areas of urbanization (Hofmann et al. 2011, 2015; Itoh et al. 2011; Karthe et al. 2016).

In the early 1990s, the collapse of the Soviet Union forced the Mongolian state to undergo an economic transition from a centralized, command economy to a decentralized, market oriented economy. This initially led to an economic decline, and Mongolians were coerced to think about alternative methods of sustaining themselves, including nomadic pastoralism and a turn to small-scale mining (Avlyush 2011). Economic growth and a gradual opening of the country to international investors led to a massive mining boom (Sandmann 2012). Although the mining sector had become a key source of employment, foreign exchange and a large percentage of the national GDP, it is also the cause of many environmental and social problems. Water plays a key role, because mining operations require large amounts of processing water that become severely polluted. For example, an average 4.1 tons of water are used to extract the up to 2.83 g gold from 1 ton of ore (Javzan et al. 2004). A state inventory for surface water in Mongolia conducted in 2003 (Batsukh et al. 2008) showed that even though most rivers were in relatively pristine condition, at least 23 rivers in eight provinces were morphologically changed or polluted due to the mining activities (Stubblefield et al. 2005, , Karthe et al. 2014). Surface and ground water contamination with heavy metals and arsenic have the potential to affect aquatic biota and human health (Avlyush 2011, Nadmitov et al. 2015). In particular, mining operations were shown to negatively impact surface water quality in the Selenga River and its tributaries through increased loads of heavy metals and arsenic (Batbayar et al. 2015, Chalov et al. 2015, Hoffman et al. 2015, Karthe et al. 2015a, Nadmitov et al. 2015, Pfeiffer et al. 2015).

Currently there are several major challenges for a more sustainable management of the region’s water resources: (1) the scarcity of environmental data, including water quality data, complicates planning processes (Karthe et al. 2015c), (2) the dynamic reform process of Mongolia’s water sector and environmental legislation is only beginning to show positive results (Regdel et al. 2012), and (3) due to mining, industrialization and population growth Mongolian water resources will soon reach their limits. This study provides an overview of chemical water quality gradients along the Mongolian part of the Selenga River and its tributaries and offers a systematic assessment of the role that urban and mining areas play for water contamination. It focuses on nutrients, heavy metals and arsenic and incorporates own measurements from all sub-basins.

3.3 Materials and methods

3.3.1 Study area

The northern part of Mongolia is characterized by a highly continental climate with wide variations of annual, monthly and daily temperatures. The mean annual temperature is just below freezing, and annual precipitation ranges between 250-400 mm. Winters are long-lasting (monthly mean temperatures are 0°C or below between October and March) and very cold (temperatures frequently drop below -25°C), while summers are not only warm, but also the time of the main rainy period from June to August, when about 70 % of the annual precipitation falls (Hülsmann et al. 2015; Menzel et al. 2011).

The Selenga River itself has a transboundary catchment which is shared by two countries, Mongolia and Russia. Originating in Mongolia, it is the largest inflow of Lake Baikal with over 60 % of annual water amount contribution (UNOPS 2013). The delta of Selenga River is included in the list of Ramsar Wetlands of international importance because of its significant role as a habitat for flora and fauna as well as its role in functioning as a water filter against pollution flowing into Lake Baikal (UNOPS 2013). In Mongolia the Selenga River has a water catchment of 299,690 km^2 (67 %) and is divided into six sub-basins (see Table 4 for a detailed description), while the catchment area in Russia is about 147,370 km^2 (33 %) (UNOPS 2013). The river plays an important role because 19 % of the total land area of Mongolia is located in its catchment, including the capital, important centers of industry and large farming areas (Nadmitov et al. 2015, Chalov et al. 2015). In the last few decades water quality has deteriorated due to rapid urbanization, insufficient wastewater treatment systems, and fast mining developments in several sub-basins in the upper part of Selenga River basin (Table 4). Thus, the ecological mismanagement of this river became considered as one of the important regional pollution issues in Northeast Asia (Nadmitov et al. 2015, Karthe et al. 2015a, and KEI 2010). Gold deposits of ground and placer types occur in many valleys, especially in the Eroo, Kharaa, Tuul and Orkhon River basin. A large copper deposit is exploited in Erdenet, in the Orkhon River basin.

For the water quality investigation six sub basins the river basins of Tuul (TRB), Kharaa (KRB), Orkhon (ORB), Sharyn (SHRB), Eroo (ERB) and Selenga (SRB) were selected. In total 88 water samples were taken from rivers (n = 79), mine ponds (n = 4) and waste water (n = 5) at 59 sampling points in two seasons, namely in TRB (n = 16), KRB (n = 40), ORB (n = 18), ERB (n = 5), SHRB (n= 7), and SRB (n = 2). In the first expedition the water samples were collected in summer (between May to July 2014) were intensive mining activities had been observed. During the second campaign in spring between March and May 2015 (see Fig. 9) most of the samples have been taken under ice cover. In order to prevent sample pollution by the gasoline auger, a hand ice auger was used for ice drilling. Deep samples were taken by an inertial pump. At that period the open mining companies had stopped their operations.

Table 4 Detailed description of the Mongolian sub-catchments of Selenga River Basin, including name, length and area of the catchment, as well as annual discharge, ecological threats and scientific references

Sub basins	Length km	Catchment area km^2	Annual mean discharge m^3/s^{-1}	Pressures	References
Selenga	1024	447	68	urban settlement	KEI 2010
Orkhon	1124	129,7	101 (max 891) at Sukhbaatar gauging station, 13.3 at Kharkhorin gauging station	Erdenet city, urban settlement, mine activities, industries, TPPs	Javzan 2011, Karthe et al. 2016, MEGD 2012
Tuul	704	49,8	26.6 (max 1580) at UB gauging station	UB city, urban settlement, mine activities, industries, TPPs	Dalai et al. 2013, Altansukh 2008, MEGD 2012
Kharaa	362	14,5	12	Darkhan city, urban areas, mine activities, industries, TPPs	Hofmann et al. 2015, Karthe et al. 2015a
Eroo	320	11,8	25	mine activities	Avlyush 2011
Sharyn	97	897	N/A	urban settlement, mine activities	Karthe et al. 2016

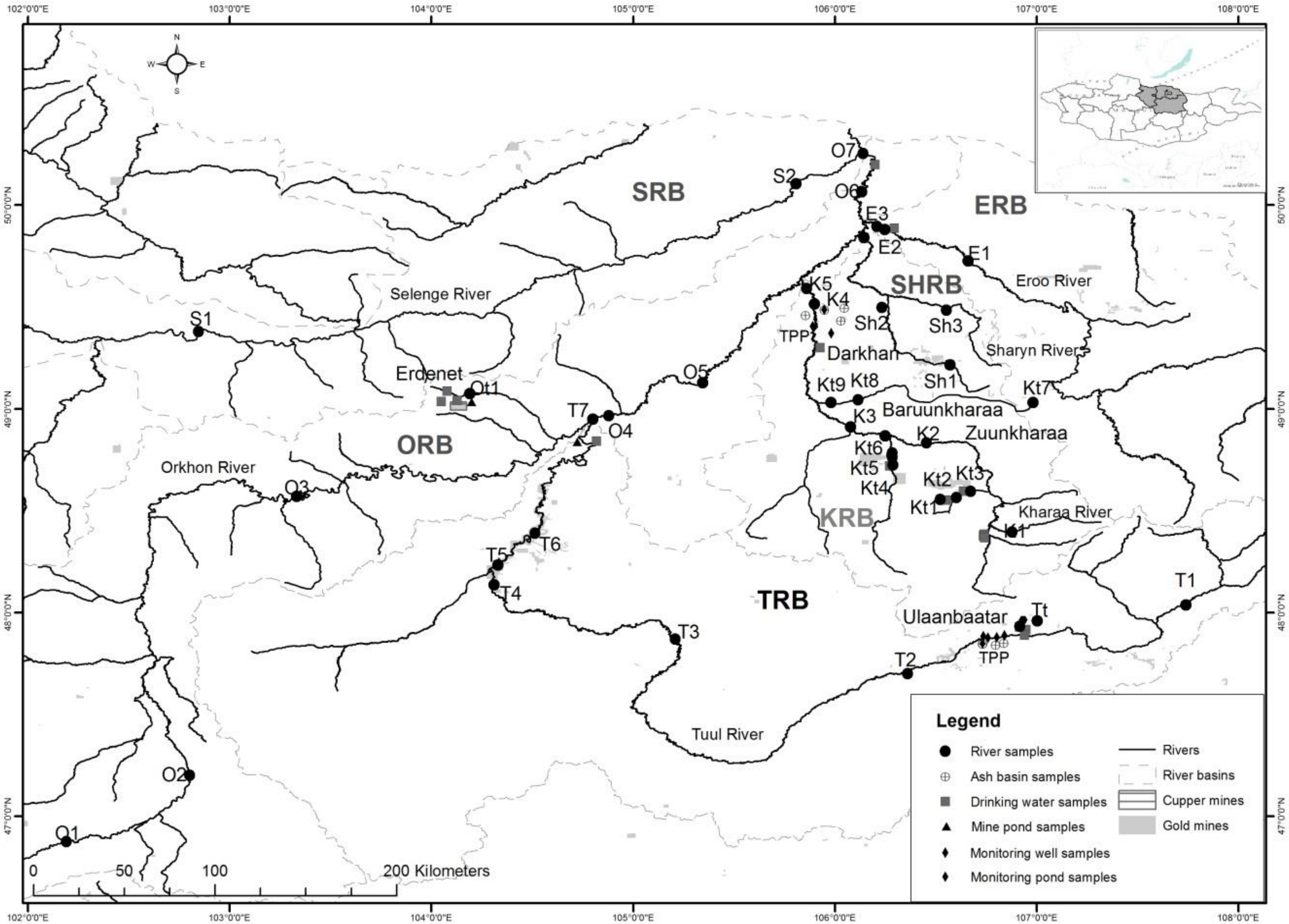

Figure 9 Map of the study area, spatial pattern of water sampling locations in six different sub basins (SRB- Selenga River Basin, ORB-Orkhon River Basin, TRB-Tuul River Basin, KRB-Kharaa River Basin, SHRN-Sharyn River basin, ERB-Eroo River Basin)

The main parameters such as water temperature, pH and electrical conductivity were measured on site using a calibrated and validated digital pocket meter MultiLine® Multi 3630 IDS from WTW GmbH, Germany. To determine the total concentration of the trace elements, the water samples were preserved with high purity nitric acid (HNO_3, pH < 2). The water samples for the nutrients filtered through Minisart® cellulose acetate filters with pore size of 0.45 µm in the field. Afterwards all water samples were filled bubble-free into brown glass and Sarstedt® tubes. At the laboratory the filtered samples were stored in a refrigerator at 4 °C. Most investigated elements were determined using inductively coupled plasma mass spectrometry (ICP-MS), Agilent 7500c, Santa Clara, USA, inductively coupled plasma optical emission spectrometry (ICP-OES), Perkin Elmer 2100 DV, Überlingen, Germany or cold vapor atomic absorption spectrometry (CV-AAS), Perkin Elmer 4100 ZL, Überlingen, Germany (Table 5). An ion chromatograph spectrometer (ICS), ICS-3000 Dionex, Waltham, USA was used to determine the Cl^- and SO_4^{2-}concentrations. Organic carbon was determined after acidification for the discrimination of inorganic carbon (IC) as total concentration (TOC) and after filtration as dissolved fraction (DOC) using a carbon analyzer (Dimatoc®; Dimatec Essen, Germany). Total nitrogen, ammonia, nitrate, nitrite and soluble phosphorus were determined using continuous flow analysis (CFA; Skalar Analytical B.V., Breda, Netherlands). For total P and total N analysis, we stored water samples in 30 ml HDPE (high density poly ethylene) bottles and preserved them with 350 µl H_2SO_4 (1 : 4). For quality assurance, all used methods had been validated before application according to the guide line of the federal environmental protection agency of Germany (Wellmitz and Gluschke 2005) based on the IUPAC Technical Report (2002).

Table 5 Water analysis methodology and parameters with detection limits

Laboratory	Methodology	Parameters with detection limits (lower limit of quantification)
Helmholtz Center for Environmental Research, Magdeburg, Germany	ICP-MS	Ba (<10 µg/L), Be (<1 µg/L), Li, Rb (<0.2 µg/L), Sr, B (<10 µg/L), Al (<0.02 mg/L), As (<0.5 µg/L), Cd (<0.2 µg/L), Co (<0.4 µg/L), Cu (<0.5 µg/L), Cr (<0.5 µg/L), Pb (<0.5 µg/L), Sn (<1 µg/L), Bi (<0.8 µg/L), Mo (<0.7 µg/L), Sb (<0.3 µg/L), Ag (<0.1 µg/L), Tl (<0.1 µg/L), Ti (<1 µg/L), V (<0.3 µg/L), U (<0.5 µg/L)
	ICP-OES	Ca^{2+}, K^+, Mg^{2+} , Na^+, Fe (<0.01 mg/L), Mn (<0.008 µg/L), Ni (<0.5 µg/L), Zn (<0.01 µg/L)
	ICS-3000	Cl^- (<1 mg/L), $SO_4{}^{2-}$
	Carbon analyzer	TOC (<0.5 mg/L), DOC
	Continuous flow analysis	Total P (<0.006 mg/L), Total N, NH_4^+(<0.01 mg/L), NO_2^- (<0.006 mg/L), NO_3^-(<0.047 mg/L), SRP (<0.003 mg/L)

	Atomic fluorescence	Hg (<0.002 µg/L)

3.3.2 Data analysis

Data were compiled in an Excel data sheet and analyzed with Origin Pro 9. In order to evaluate the trace element pollution of the river samples, the concentration factor (CF) was used for the parameters and chemical elements which were not considered in the standards. The concentration factor is used here as the ratio of the river water metal content at a given sampling location and the reference value (natural background value at a location that is not influenced by human impact) of the respective river. The reference value (BC) was measured in the headwaters of the respective rivers (T1 for TRB, O1 for ORB, K1 for KRB, Sh1 for SHRB, E1 for ERB, S1 for SRB) before mining and industrial activities could influence the water quality (Table 6). The concentration factor (CF) is expressed as:

$$CF = \frac{C_o}{C_b}$$

where C_o is the mean concentration of a given element in the water samples, C_b is the reference value for the respective element. The concentration factor was classified into four groups according to Hokanson (1980) and Pekey et al. (2004): CF < 1 for low contamination; 1 ≤ CF < 3 for moderate contamination; 3 ≤ CF < 6 for considerable contamination; and CF ≥ 6 for very high contamination (Samhan et al. 2013).

To evaluate the degree of pollution the water quality index (Wqi) was used for surface water quality. The Wqi is defined as a simple expression of a more or less complex combination of a several parameters which serve as a measure for water quality. It is estimated by the following equation:

$$W\mathrm{qi} = \frac{\sum \mathrm{i}\left(\frac{C_i}{Pl_i}\right)}{n}$$

Where C_i is concentration of i^{th} pollutant, Pl_i is the maximum permissible level of i^{th} pollutant in accordance with the National Standard Agency of Mongolia (4586: 98), and n is the total number of pollutants (Table 6).

Table 6 Water quality index classification which is indicating the degree of pollution of surface water quality

Water Quality Classification	Water Quality Index
Very Clean	<0.3
Clean	0.3-0.89
Slightly polluted	0.9-2.49
Polluted	2.5-3.99

Very polluted	4-5.99
Dirty	6-9.99
Very dirty	≥10

3.3.3 Statistical analysis

We used the statistical software package STATISTICA Version 13 (Dell Inc., 1984-2015) to calculate the non-parametric paired samples Wilcoxon test to compare single element's concentration means for samples conducted in different years at the respective sample sites, as well as Spearman rank correlation coefficient for the investigated element concentrations in relation to distance from source, which are the statistic proofs for these patterns.

3.3.4 Principal component analysis (PCA)

To reveal the general structure of the river pollution a principal component analysis of the sample data was performed with R package *vegan* (Oksanen et al. 2013). Ward clustering of the sites into four clusters using the environmental data was performed with squared Euclidean distance after standardizing the variables.

3.3.5 Cluster Analysis of river samples using a Model of Self-Organizing Maps (SOMs)

Self-organizing map (SOM) was used to analyze the longitudinal patterns of the water chemistry parameters of river water samples. The SOM approach is based on a learning algorithm in an artificial neural network and approximates the probability density function of the input data. The learning process of the SOM was applied using the SOM toolbox package developed by the Laboratory of Information and Computer Science in the Helsinki University of Technology for Mat lab ver. 6.1. with the purpose to represent the major features of the data along a reduced number of axes. Different variables were clustered together according to the similarity of chemical compositions. To evaluate the relations between chemical patterns, the classified variables were visualized by a color map (Wehrens and Buydens 2007).

3.4 Results

3.4.1 Water quality in Selenga River basin according to standards and limits – General overview

In general it can be stated, that in the main channel of the Selenga River, all taken water samples complied with the Mongolian standard (MNS 4586:98) for the investigated parameters. The same is observed for the medians (50 % values) of the investigated samples from the tributaries.

Nevertheless based on primary statistical analysis, the following parameters of one or more investigated water samples from the tributaries of Selenga River exceed given national and or international limits: concentration of heavy metals (Al, Cu, Mn, Ni), metalloid (As), cation (Na^+), anions (Cl^-, SO_4^{2-}) and/or nutrients (NH_4^+, PO_4^{3-}, NO_2^- and NO_3^-) (see Table 7).

Table 7 Primary statistical results of River water samples in comparison with following standards MNS 4586:98 Mongolian standard for Aquatic ecosystem quality indicators. Russian standard for surface water quality RNS 2010 and National Recommended Water Quality Criteria - Aquatic Life Criteria Table US EPA 2006. Values in bold indicate a standard exceedance

	Number of samples	Mean	SD	Min	Max	MNS 4586: 98	RNS 2010	US EPA 2006
Antimony (Sb) total µg/L	79	0.34	0.13	0.3	1.2			
Uranium (U) total µg/L	79	8.7	9.5	0.5	58.3			
Bismuth (Bi) total µg/L	79	0.82	0.16	0.79	2.2			
Magnesium (Mg^{2+}) mg/L	79	11.35	7.43	0.83	45.1			
Natrium (Na^+) mg/L	79	15.2	13.78	1.09	82.1			
Potassium (K^+) mg/L	79	3.09	1.88	0.6	9.56			
TOC mg/L	79	5.92	4.64	0.94	28.3			
DOC mg/L	79	5.02	4.27	0	21.3			
Chromium (Cr) total µg/L	79	4.21	5.91	0.5	**29.3**	50	1	11
Aluminum (Al) total mg/L	79	2.64	4.3	0.02	21.1			
Arsenic (As) total µg/L	**79**	7.53	27.17	0.5	**243**	10	5	150
Barium (Ba) total µg/L	79	45.06	33.36	5	172			
Cadmium (Cd) total µg/L	79	0.21	0.06	0.2	**0.7**	5	5	0.25
Cobalt (Co) total µg/L	79	1.28	1.6	0.4	8.1	10		
Copper (Cu) total µg/L	**79**	9.47	36.16	0.5	**316**	10	1	10
Iron (Fe) total mg/L	**79**	2.53	4.15	0.01	**19.7**		0.1	1
Mercury (Hg) µg/L	79	0.01	0.01	0	0.08	0.1		
Manganese (Mn) total mg/L	**79**	0.17	0.43	0.01	**2.81**	0.1	0.01	
Molybdenum (Mo) total µg/L	79	6.13	16.44	0.4	138	250		
Nickel (Ni) total µg/L	**79**	3.86	4.05	0.6	**20.5**	10	10	52
Lead (Pb) total µg/L	79	1.64	1.88	0.5	**7.79**	10	6	2.5
Rubidium (Rb) total µg/L	79	4.87	7.33	0.2	38.6			
Strontium (Sr) total µg/L	79	275.9	211.9	30	1610			
Vanadium (V) total µg/L	79	7.21	9.44	0.3	46.5			
Zinc (Zn) total mg/L	**79**	0.02	0.02	0.01	**0.16**	0.01	0.01	0.15
TNb mg/L	79	1.72	1.95	0.26	15.2			
Chlorine (Cl-) mg/L	79	8.29	11.25	0.99	77.1	300		
Sulfate (SO_4^{2-}) mg/L	**79**	28.14	45.99	2.66	**332**	100		
Calcium (Ca^{2+}) mg/L	79	33.88	18.55	4.3	131			
Lithium (Li) total µg/L	79	8.2	6.46	1	37			
Thallium (Tl) total µg/L	79	0.58	0.46	0	1.4			
Titan (Ti) total µg/L	79	124.25	204.79	1	1010			
Bor (B) total µg/L	79	23.04	21.47	5	98			

Silver (Ag) total µg/L	79	0.54	0.45	0.1	1			
Ammonium-N mg/L	**79**	0.41	2.06	0.01	**18.1**	0.5		
Total-Phosphate-P mg/L	**79**	0.17	0.22	0.01	**1.55**	0.1		
NO_2^- mg/L	**79**	0.06	0.46	0.01	**4.15**	0.02		
NO_3^- mg/L	**79**	0.47	0.65	0.02	**3.6**	9		
SRP mg/L	79	0.04	0.12	0	0.87			

Based on the CF results of the most downstream sample sites of each sub-basin, U, Ca^{2+}, and Li in Tuul River basin, U, Mg^{2+}, Sr, Ca^{2+} and SRP in Kharaa River basin, Ba, Rb, V, Li, Ti, Ag and DOC in Orkhon River basin were present at levels that indicate a very high contamination (Table 8).

The degree of pollution was significantly higher in summer than in early spring for 19 parameters (Ag, Al, As, Co, Cr, Cu, Fe, Hg, Li, Tl, U, V, TNb, TOC, B, Na^+, Cl^-, SO_4^{2-}, PO_4^{3-}) that were tested with the Wilcoxon Matched Pairs Test ($n = 27$, all $p < 0.01$ except Tuul River sampling point T2, see Fig. 10). During the summer campaign ($n = 20$) the concentration of pollutants increased downstream. The statistically highly significant Spearman rank correlation coefficients (r_s) for the investigated element concentrations in relation to distance from source are the statistic proof for this pattern (e.g. for As $r_s = 0.84$, $p < 0.001$; Cu $r_s = 0.78$, $p < 0.001$; Pb $r_s = 0.82$, $p < 0.001$).

Table 8 The concentration factors (CF) with reference value of different river basins in Selenga River basin. Bold numbers indicate very high contamination (BC is indicating the background concentration under natural condition. River catchments are abbreviated as follows: TRB- Tuul River Basin, KRB-Kharaa River Basin, ORB-Orkhon River Basin, ERB-Eroo River Basin, SHRB-Sharyn River basin, SRB-Selenga River Basin). The second raw of the table indicates the focus sites, where the respective measurements took place, these were the most upstream sites for measurement of BC and the most downstream sites of the sub-basins for the calculation of CF

Parameters	**BC**	**TRB**	**BC**	**KRB**	**BC**	**ORB**	**BC**	**ERB**	**BC**	**SHRB**	**BC**	**SRB**
Focus site	**T6**	**T6**	**K5b**	**K5b**	**O6a**	**O6a**	**E3b**	**E3b**	**Sh4b**	**Sh4b**	**S2**	**S2**
CF-Uranium (U) total µg/L	0.5	**48**	2.9	**7.5**	1.3	2.3	0.9	4	7.1	1	4	1
CF-Bismuth (Bi) total µg/L	0.8	1	0.8	1	0.8	1	0.8	1	0.8	0.9	0.8	1
CF-Magnesium (Mg2+) mg/L	1	**20**	0.8	**14**	4.3	2.3	2.5	2.2	4.3	2.5	9.1	1
CF-Potassium (K+) mg/L	0.6	5	1	2.8	2.1	2.3	1.3	0.9	1.4	2.1	1.3	1.1
CF-TOC mg/L	7.4	0.4	10	0.26	1.2	**7.9**	6.6	0.1	7.4	0.3	1.1	0.3
CF-DOC mg/L	7.7	0.2	14	N/A	2	2.3	3.2	N/A	8.3	0.5	1.5	0.3
CF-Barium (Ba) total µg/L	11	4.5	12	2.41	5	**24.8**	18	0.9	21	1.3	25	0.9
CF-Rubidium (Rb) total µg/L	0.7	0.3	0.8	1.75	0.7	**32.2**	0.4	0.2	1.9	0.8	0.2	1.5
CF-Strontium (Sr) total µg/L	54	**9.2**	30	**7.63**	104	2.7	61	2.1	113	1.6	276	1.1
CF-Vanadium (V) total µg/L	0.6	1.3	0.4	5.3	0.9	**33**	0.3	0.2	2.1	1	0.5	1.8
CF-TNb mg/L	0.7	1.3	0.7	1.9	1.3	1.8	1	1.3	0.5	2.8	0.8	1
CF-Calcium (Ca2+) mg/L	7.1	**8.8**	4.3	**6.8**	15	2	11	1.6	18	1.3	37	1
CF-Lithium (Li) total µg/L	1	**6.1**	6	1.05	2	**7.5**	3	0.6	21	0.2	1.5	1.6
CF-Titan (Ti) total µg/L	1	0.07	7	4.2	3.8	**168**	7.1	0.2	40	1.2	1	3.1
CF-SiLber (Ag) total µg/L	1	0.1	0.1	0.1	0.1	**10**	0.1	0.1	0.1	0.1	0.1	1
CF-SRP mg/L	0.006	0.5	0	**19**	0	3.6	0	1	0	**15**	0	1

*CF <1 for low contamination; 1≤CF<3 for moderate contamination; 3≤CF<6 for considerable contamination; and CF≥6 for very high contamination

* BC Background concentration

3.4.2 Water quality in the Tuul River basin

Reference conditions (quasi natural) that met with the surface water quality guidelines and standards have been observed in 2014 and 2015 at the water sampling point at Bosgo Bridge, Tuul River (T1) located upstream of Ulaanbaatar and other major settlements as well as upstream of all mining operations (all data for Tuul River in Table 9).

Downstream of T1, the Tuul River passes the central parts of Mongolia's capital. The Selbe River (Tt) a tributary of the Tuul River enters it midstream of Ulaanbaatar (UB) city. At the tributary sampling point Tt the concentration of NO2- (0.03 mg/L) slightly exceeded the Mongolian standard MNS 4586:98 in both observation years. This indicates the direct influence of untreated waste water from the "ger"-settlements (peri-urban residential districts in Mongolian cities that are characterized by simple houses or "gers" (felt tents) and the absence of sewage infrastructures).

Water quality declined further downstream the Tuul River. The investigation results from sampling point T2, which is located downstream of Ulaanbaatar, give an impression about the impacts of the poorly working waste water treatment plant (WWTP). Compared to the MNS 4586:98 standard, the concentration of following parameters exceeded the limits: NH_4^+ was 1.8 times higher (0.9 mg/L) in 2014 summer, 36.2 times higher (18.1 mg/L) in 2015 spring; PO_4^{3-} 1.9 times higher (0.19 mg/L) in 2014 summer, 15.5 times higher (1.55 mg/L) in 2015 spring; Mn 2 times higher (0.2 mg/L) in 2014 summer and 27.7 times higher (2.77 mg/L) in 2015 spring.

The reason of water quality deterioration in spring time at Tuul River sampling point (T2) is waste water discharge from the central WWTP of Ulaanbaatar city just upstream of the Tuul River sampling point (T2), where water is mostly frozen during the winter and spring. Therefore, there is a reduced waste water dilution as compared to summer conditions when there is greater discharge.

The sampling point T3 was located in the middle between the UB city and the Zaamar mining area. Compared to the sampling point T2, the concentrations of Al (2.17 mg/L in 2014), Mn (0.136 mg/L in 2014, 0.352 mg/L in 2015) and PO_4^{3-} (0.18 mg/L in 2014) were slightly lower, indicating sedimentation and self-purification of the river.

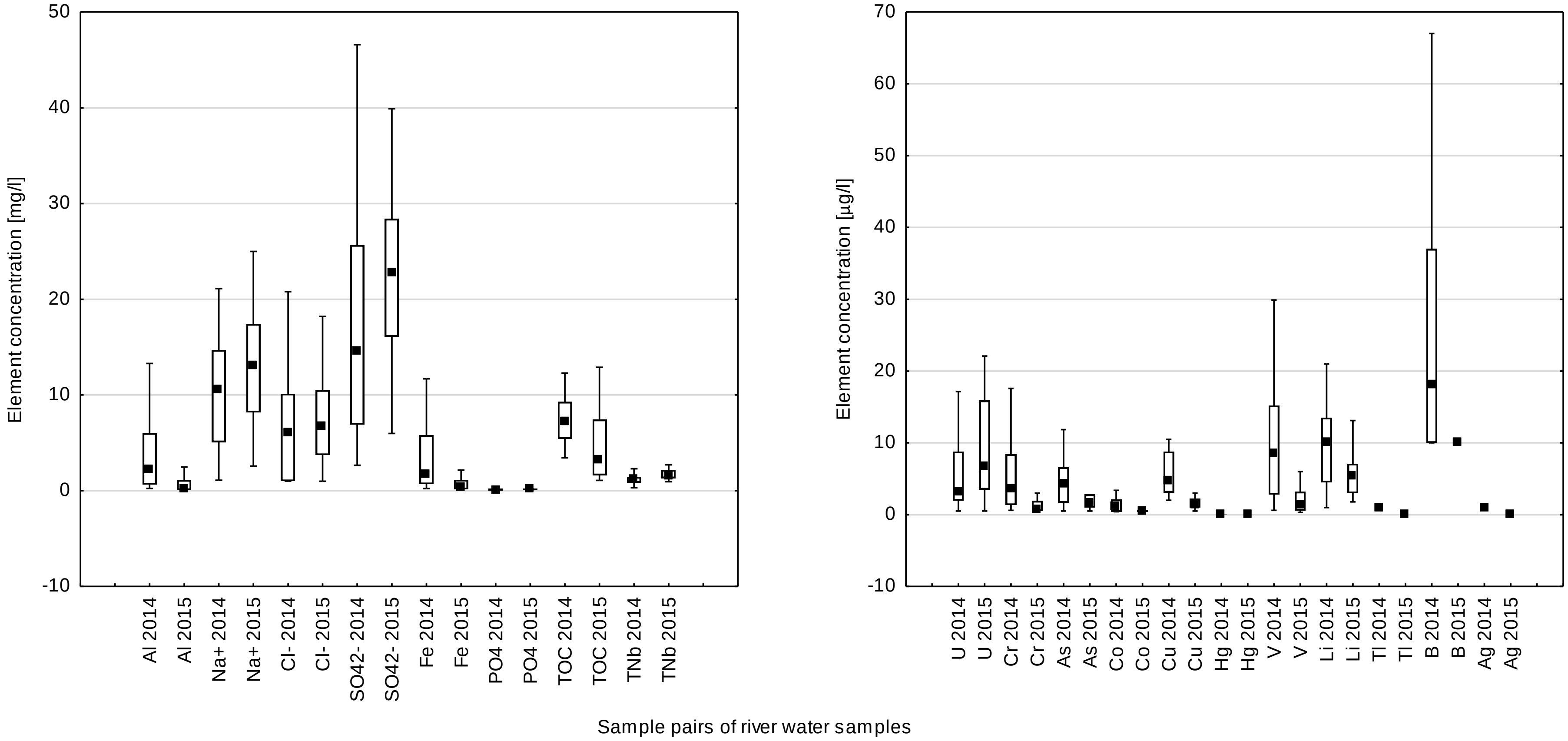

Figure 10 Contaminant loads in summer (2014) and spring (2015) at 27 samples sites in Selenga River Basin. Shown are pairs of samples of different pollutants. a) Macro elements. All pairs differed highly significantly in a Wilcoxon Matched Pairs test. b) Trace elements. All pairs differed highly significantly in a Wilcoxon Matched Pairs test

Subsequent samples from points T4 to T7 were taken downstream of mining activities in the Zaamar gold mining area (Fig. 11). This catchment between T4 and T5 is characterized by activities of large and small mining companies. Most of the major mines work with closed water circulation systems. But in contrast, small mines often discharge their waste water without treatment into the receiving waters. High concentrations of pollutants were found at sampling point T4, exceeding the Mongolian standard (MNS 4586:98) for As 1.55-fold (15.5 µg/L), Mn 28.1-fold (2.81 mg/L), SO_4^{2-} 1.12-fold (112 mg/L) and NH_4^+ 4.8-fold (2.4 mg/L) and PO_4^{3-} 6.6-fold (0.66 mg/L).

Around 100 km downstream of T4, at T5 the Al concentration reached 5.9 mg/L in summer 2014, whereas Mn (0.192 mg/L in 2014, 0.303 mg/L in 2015) slightly increased as compared to the measurements at T3. The concentration of NH_4^+ was 3.98-fold (1.99 mg/L) in 2015, of PO_4^{3-} 2.46-fold (0.246 mg/L) in 2014, and 5.73-fold (0.573 mg/L) in 2015, while NO_2^- was 2.65-fold (0.053 mg/L in 2015) higher than the standard value (MNS 4586:98), respectively. Location T7 marks the junction of Tuul and Orkhon Rivers.

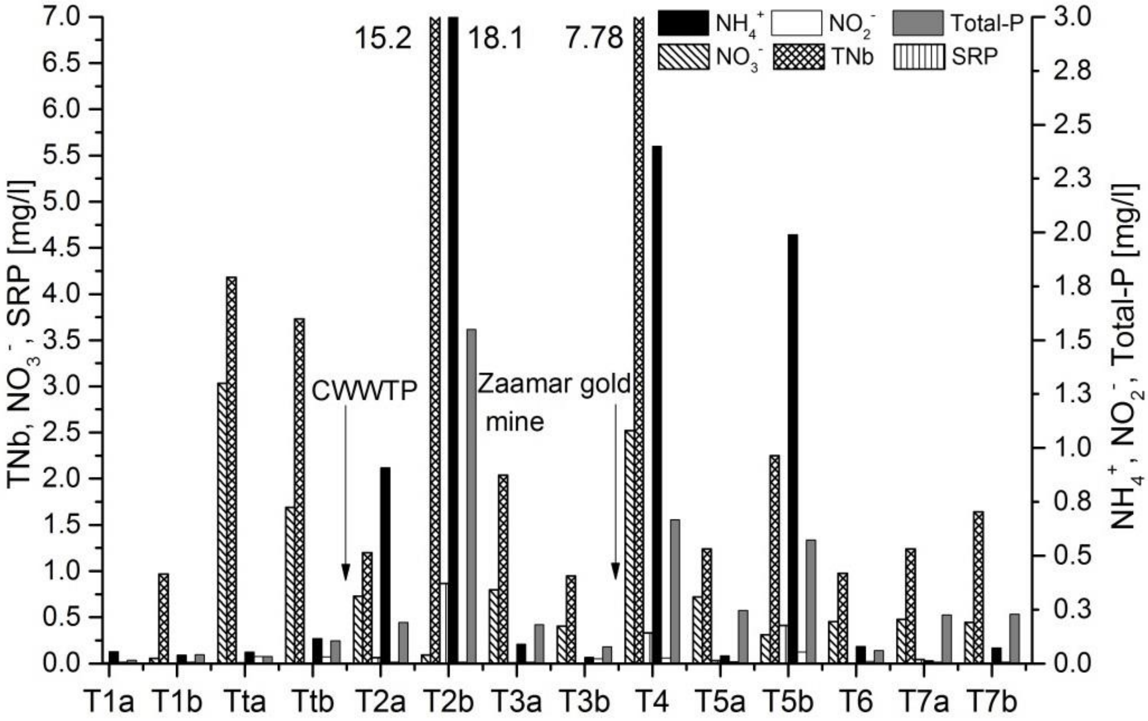

Figure 11 Changes of nutrient concentrations along the Tuul River. The flow direction is left to right. TNb is total nitrogen bound and SRP is soluble reactive phosphorus. CWWTP is indicating central waste water treatment plant in Ulaanbaatar

Table 9 Chemical water quality of Tuul River water samples from upstream to downstream. Comparison of observed concentrations in relation to standard value MNS 4586: 1998 (first row). Bold numbers are indicating concentrations higher than the standard

Names	ID	Year	Cr µg/l	As µg/l	Cd µg/l	Co µg/l	Cu µg/l	Hg µg/l	Mn mg/l	Mo µg/l	Ni µg/l	Pb µg/l	Zn mg/l	Cl^- mg/l	SO_4^{2-} mg/l	NH_4^+ mg/l	PO_4^{3-} mg/l	NO_2^- mg/l	NO_3^- mg/l	TOC mg/l	WQI	Al mg/l
MNS 4586:98			50	10	5	10	10	0.1	0.1	250	10	10	0.01	300	100	0.5	0.1	0.02	9			0.5*
Tuul_Bosgo_bridge	T1a	2014	0.6	0.5	0.2	0.4	2.0	0.01	0.01	0.7	0.9	0.5	0.01	1.0	3.6	0.06	0.02	0.01	0.1	7.4	0.08	0.24
Tuul_Bosgo_bridge	T1b	2015	0.5	0.5	0.2	0.4	0.5	0.00	0.03	0.4	1.0	0.5	0.01	1.1	5.9	0.04	0.04	0.01	0.06	8.2	0.09	0.08
Selbe_river	Tta	2014	1.5	1.5	0.2	0.6	4.2	0.07	0.03	1.6	2.6	1.3	0.01	13	28	0.05	0.03	**0.03**	3	9.3	0.2	0.45
Selbe_river	Ttb	2015	0.7	1.0	0.2	0.4	3.0	0.00	0.05	1.8	2.1	1.0	0.01	12	22	0.1	**0.1**	**0.03**	1.6	2.0	0.2	0.47
Tuul_Altanbulag	T2a	2014	7.7	2.2	0.2	1.1	5.1	0.01	**0.2**	1.0	2.9	2.7	**0.03**	7.4	11	**0.9**	**0.1**	0.01	0.7	5.5	0.4	**2.33**
Tuul_Altanbulag	T2b	2015	21	2.1	0.2	0.6	1.3	0.01	**2.7**	3.3	1.8	0.6	0.01	60	57	**18**	**1.6**	0.01	0.09	8.2	**4.8**	0.12
Tuul-Lun bridge	T3a	2014	4.5	3.0	0.2	0.9	5.1	0.01	**0.1**	1.5	3.1	1.5	**0.06**	7.8	11	0.09	**0.1**	0.01	0.8	6.2	0.3	**2.17**
Tuul-Lun bridge	T3b	2015	0.5	2.3	0.2	0.4	0.5	0.00	**0.3**	2.4	1.7	0.5	**0.03**	9.0	16	0.03	0.08	**0.02**	0.4	1.1	0.3	0.02
Tuul-Zaamar bridge	T4	2015	1.3	**15.5**	0.2	1.6	8.1	0.00	**2.8**	11	4.5	0.7	**0.03**	77	**112**	**2.4**	**0.66**	**0.03**	2.5	-	**2.7**	0.24
Tuul-Zaamar	T5a	2014	8.4	4.6	0.2	1.9	6.9	0.01	**0.2**	1.8	5.4	2.8	0.01	7.6	24	0.04	**0.2**	0.01	0.7	7.3	0.4	**5.90**
Tuul-Zaamar down	T5b	2015	0.5	8.2	0.2	0.4	2.2	0.01	**0.3**	7.4	1.2	0.5	0.01	16	66	**2.0**	**0.6**	**0.05**	0.3	1.4	**1.0**	0.02
Tuul River down	T6	2015	2.4	2.4	0.2	0.4	0.5	0.00	**0.4**	6.5	1.1	0.5	0.01	28	92	0.08	0.06	0.01	0.4	2.8	0.4	0.02
Orkhon Tuul junction	T7a	2014	9.4	5.2	0.2	2.9	8.8	0.01	**0.2**	3.3	7.6	3.5	0.01	6.1	6.8	0.01	**0.2**	0.01	0.4	10.1	0.4	**7.58**
Orkhon Tuul junction	T7b	2015	7.6	2.8	0.2	2.6	**10**	0.00	**0.1**	5.2	6.7	4.2	**0.02**	6.7	30	0.07	**0.2**	0.01	0.4	3.1	0.4	**8.14**

Note: * MNS 900:2005 Environment health protection, safety, drinking water, hygienically requirements, assessment of the quality and safety

3.4.3 Water quality of Orkhon River basin

The Orkhon is Mongolia's longest river and the most important tributary of the Selenga. The upstream area of the Orkhon River (O1) is characterized by near-natural conditions. Regarding the change in chemical water quality, the first relevant tributary is the Khangal River. Even though it is only a minor river, it drains the area around Erdenet, Mongolia's second largest city, including a major copper-molybdenum mine. Somewhat further downstream Tuul River is the major left tributary of Orkhon River. The most downstream tributaries of Orkhon River are the Kharaa, Eroo and Sharyn River which originate from the Khentii Mountains. Gold mining activities are present in the Tuul, Kharaa, Eroo and Sharyn River sub-basins. Moreover, one of Mongolia's largest coal mines is located on the Sharyn River.

The most polluted tributary of the Orkhon River was the Khangal River (Ot1), where we recorded high concentration of Cu, Mn, Mo, SO_4^{2-} as well as nutrients (Fig. 12). The reason for high pollution levels presumably include emissions from industrial and mining activities of the Erdenet urban region, the discharge of poorly treated urban waste water and low water flux (discharge of about 3.5 m^3/sec at the time of sampling). Highest values for NH4+ were reached at Orkhon-Tuul junction (O4) with 0.84 mg/l, almost 60% higher than MNS 4586:98.

Maximum concentrations of nickel occurred in the downstream sections of Orkhon River (, O7) after the confluences with the Kharaa (near K5), Sharyngol (near Sh4) and Eroo (near E3). An important pollution source is the Sharyn River (Sh4) which is influenced by mining activities. The concentrations of Fe, Cu, Ni, Mn, Zn and PO_4^{3-} increased in downstream direction thus showing a similar trend. The maximum concentration of nutrients and trace elements occurred in Khangal (Ot-1) and (O6) after the K5, Sh4, E3 confluences. The concentration of TNb and NO_3-N were high in the downstream part of the Sharyn River. A reduction of $N0_3^-$ by dilution or denitrification occurred along the Orkhon River between O6 and O7, following the confluences of its tributaries below Ot1, K5, Sh4 and E3, respectively. At sampling point Orkhon River (O6), the concentration of ammonium was slightly elevated after the confluence of Kharaa River (K5), Sharyn River (Sh4) and the Eroo River (E3). The concentration of soluble reactive phosphorus (SRP) was slightly elevated on Khangal River (Ot-1), but showed decreasing values along the longitudinal profile of the river.

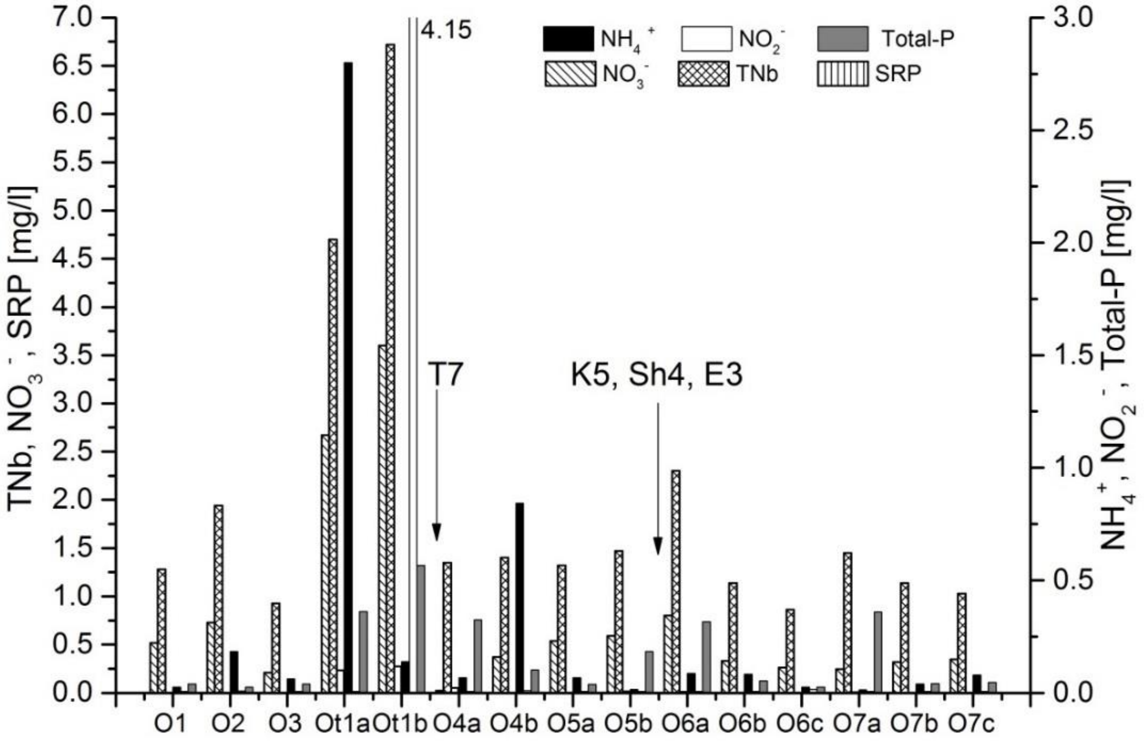

Figure 12 Changes of nutrient concentrations along the Orkhon River. The flow direction is left to right. TNb is total nitrogen bound and SRP is soluble reactive phosphorus

3.4.4 Water quality of Kharaa River basin

The Kharaa River is one of the main tributaries of the Orkhon River. Water quality data (Table 10) from the upstream sampling site (K1) reflect the very limited human impact in this sub catchment. While its upstream section is not much affected by anthropogenic activities, its midstream section falls into an area of agriculture and gold mining activities, most of them with closed water cycle. The Gatsuurt River is one of the tributaries of the Kharaa River which passes through the Gatsuurt gold mining area. During water sample collection, mining was not ongoing, but we found indicator pollutants for mining processes. Downstream of the Gatsuurt mine (Kt3b), the concentrations increased: Al up to 1.88 mg/L, PO_4^{3-} up to 0.4 µg/L, NO_2^- up to 0.1 mg/L and Zn up to 0.05 mg/L.

Zuunkharaa is a small town located below the confluence of the Gatsuurt River into Kharaa River. Here, water samples were taken downstream of the municipal waste water treatment plant. Not surprisingly, nutrient concentrations in this sample were elevated, but indicator parameters of mining activity showed signs of dilution which can be explained by the relatively high discharge of Kharaa River. The concentration of Al decreased up to 0.48 mg/L in summer (during mining operation), and 0.05mg/L in spring (no mining operation), Mn up to 0.04 mg/L in summer, 0.379 mg/L in spring, NH_4^+ 1.35mg/L in spring, PO_4^{3-} 0.218 mg/L in spring and NO_2^- 0.064 mg/L in spring 2015. But concentrations increased after the junction of the small tributary Boroo River, where one of the biggest Mongolian gold mining areas is located. The mining companies often discharge their waste water into the river. Beyond that, high concentrations of Al, As, Zn, U, Fe, PO_4^{3-} and NO_2^- were detected at the mine ponds (Table 13).

Compared to the reference (“background”) concentrations the values of Al (up to 2.86 mg/L), Mn (up to 0.084 mg/L) and PO_4^{3-} (up to 0.2 mg/L) were increased downstream of the Boroo river due to mining activities. Midstream of the Boroo River, a small gold mine discharges waste water directly into the river. At this location, elevated As concentrations of up to 243 µg/L, Cu (up to 10.9 µg/L), Mn (up to 0.1 mg/L) and PO_4^{3-} (up to 0.3 mg/L) were measured. Water quality complied with the Mongolian standard (MNS 4586:98) except for As and PO_4^{3-}. However, the concentrations of arsenic and PO_4^{3-} were diluted along the Boroo River before discharging into Kharaa River (Table 8).

The water quality at Baruunkharaa town (sampling site K3) met the standard expect for the Al concentration (0.917 mg/L) and the Zn concentration (0.02mg/L). Below Baruunkharaa town, the small tributary Bayangol empties into Kharaa River. At that sampling point the concentrations of Al (up to 14.3 mg/L), Cu (up to 16.4 µg/L), Mn (up to 0.23 mg/L), Ni (up to 16.8 µg/L) and PO_4^{3-} (up to 0.347 mg/L) were high, presumably due to gold mining activities.

The concentrations of ammonium and phosphorus were slightly elevated after the small town Zuunkharaa (K2), Baruunkharaa (K3) and Darkhan city (K5), respectively. Compared to the K1 (upstream) values the following sampling sites showed elevated values for NO_3^- (K4, K5) and slightly elevated values for TNb (K3 to K5, see Fig. 13).

Darkhan, Mongolia’s third largest city and an important center of industry, is located at the lower Kharaa River. According to the standard of Mongolia (MNS 4586:98), concentrations were elevated for Mn (up to 0.169 mg/L), Zn (up to 0.02mg/L), PO_4^{3-} (up to 0.5 mg/L) and Al (up to 4.8 mg/L), at Darkhan city (K4). The water quality at Buren-tolgoi station (K5) was comparable to Darkhan city, but the NO_2^- value was higher than the value before the Kharaa River discharges to Orkhon River. The reason for the elevated NO_2^- and Zn can be seen in the discharge of effluent water from Darkhan city.

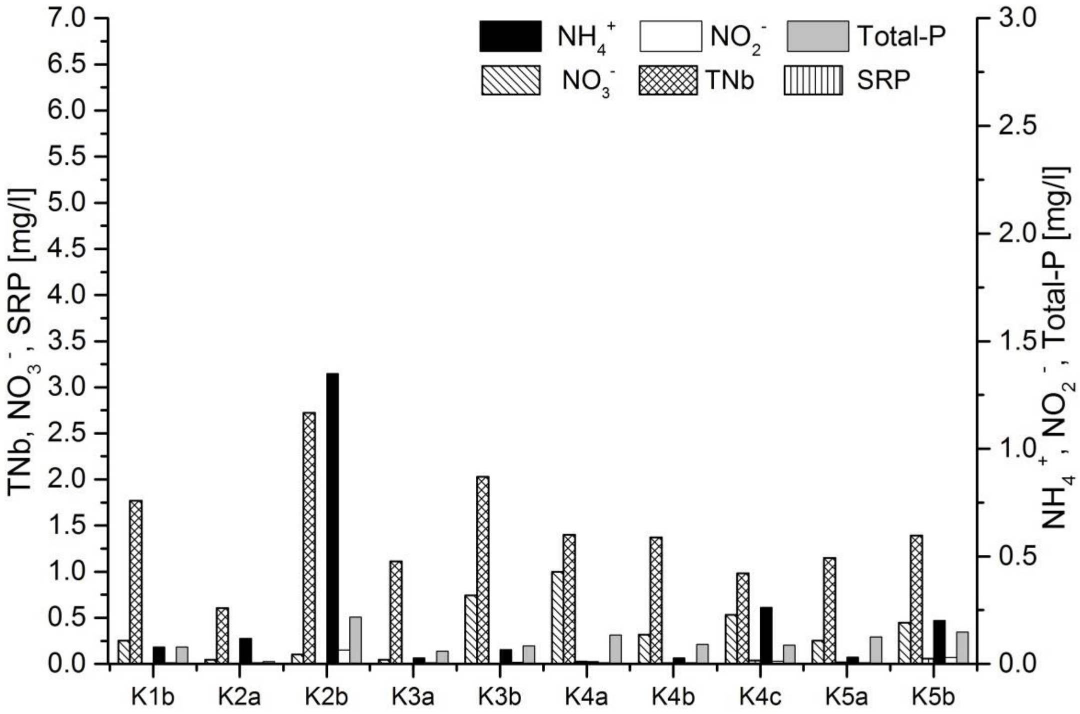

Figure 13 Changes of nutrient concentrations along the Kharaa River. The flow direction left to right. TNb is total nitrogen bound and SRP is the soluble reactive phosphorus

Table 10 Chemical water quality of Kharaa river water samples from upstream to downstream. Comparison of observed concentrations in relation to standard value MNS 4586: 98. Bold numbers are indicating concentrations higher than the standard

Names	**ID**	**Year**	**Cr µg/l**	**As µg/l**	**Cd µg/l**	**Co µg/l**	**Cu µg/l**	**Hg µg/l**	**Mn mg/l**	**Mo µg/l**	**Ni µg/l**	**Pb µg/l**	**Zn mg/l**	**Cl^- mg/l**	**SO_4^{2-} mg/l**	**NH_4^+ mg/l**	**PO_4^{3-} mg/l**	**NO_2^- mg/l**	**NO_3^- mg/l**	**TOC mg/l**	**WQI**	**Al mg/l**
MNS 4586:98			**50**	**10**	**5**	**10**	**10**	**0.1**	**0.1**	**250**	**10**	**10**	**0.01**	**300**	**100**	**0.5**	**0.1**	**0.02**	**9**			**0.5***
Sugnugur river	K1a	2014	0.8	0.5	0.2	0.4	2.6	0.01	0.01	0.7	1.3	0.5	0.01	1	2.6	0.03	0.01	0.01	0.05	12	0.08	0.26
Sugnugur river	K1b	2015	0.5	1.2	0.2	0.4	1.1	0.01	**0.1**	1.3	2.4	0.5	0.01	2	9.4	0.08	0.08	0.01	0.25	11	0.18	0.14
Gatsuurt up stream	kt1a	2014	1.4	**27**	0.2	0.4	2.6	0.01	0.04	4.7	1.35	0.6	0.01	1	5.4	0.04	0.04	0.01	0.05	3.5	0.26	**0.8**
Gatsuurt up stream	kt1b	2015	1.3	6.2	0.2	0.5	1	0.00	0.04	2.4	1.7	0.9	**0.07**	0.9	8.7	0.06	**0.1**	0.01	0.05	3.4	0.28	**0.52**
Gatsuurt mid-stream	kt2b	2014	34	**14**	0.2	1.1	4.7	0.01	0.08	2.1	3.4	1.4	0.01	7	17	0.02	**0.1**	0.01	0.43	4.3	0.29	**2.58**
Gatsuurt down stream	kt3a	2014	2	**11**	0.2	0.65	3.35	0.01	0.04	2.2	2.2	0.8	**0.03**	6	19	0.03	0.03	0.01	0.67	3.4	0.14	0.44
Gatsuurt down stream	kt3b	2015	0.5	1.5	0.2	0.4	0.7	0.00	0.08	2.2	0.9	0.5	**0.05**	9	28	0.1	**0.4**	**0.1**	0.91	3.6	0.76	**1.88**
Kharaa Zuunkharaa	K2a	2014	1	1.3	0.2	0.4	2.7	0.01	0.04	1	1.4	0.5	0.01	2	11	0.1	0.01	0.01	0.05	7.7	0.11	0.48
Kharaa Zuunkharaa	K2b	2015	0.5	2.2	0.2	0.6	2	0.00	**0.3**	1.1	3.1	0.5	**0.03**	4	16	**1.3**	**0.2**	**0.06**	0.1	5.0	0.76	0.05
Boroo up stream	kt4a	2014	3.2	7	0.45	1.3	4.2	0.05	0.06	6.4	3.6	1.6	**0.02**	10	25	0.1	**0.1**	0.01	0.17	6.9	0.37	**4.8**
Boroo up stream	kt4b	2015	12.4	6.4	0.2	3.3	7.8	0.00	**0.1**	4.9	9.4	6	**0.02**	10	27	0.06	**0.5**	0.01	0.63	2.0	0.67	**1.12**
Bortolgoi mine (Boroo mid-stream)	ktm	2014	2.9	**54**	0.2	0.9	4.1	0.01	0.06	9.9	3.4	1.1	**0.02**	10	27	0.06	**0.1**	0.01	0.15	3.3	0.75	**4.05**
Boroo mid-stream	kt5a	2014	3	7.2	0.2	1	4.75	0.03	0.06	6.6	3.6	1.3	**0.03**	10	25	0.05	**0.1**	0.01	0.2	4.6	0.3	**1.97**
Boroo mid-stream	kt5b	2015	1.5	5.6	0.2	0.4	1.2	0.00	0.02	3.4	2.3	0.7	0.01	7.6	21	0.08	**0.2**	0.01	0.36	3.1	0.24	**1.77**
Boroo down stream	kt6a	2014	3.6	5.4	0.2	1.1	4	0.02	0.06	6.2	3.4	1.3	0.01	10	25	0.03	**0.1**	0.01	0.19	5.3	0.23	**1.71**
Boroo down stream	kt6b	2015	3	6.7	0.2	1	2.2	0.01	0.06	3.5	3.5	1.9	0.01	7.4	20	0.07	**0.2**	0.01	0.48	4.5	0.28	**2.86**

Kharaa-Baruunkharaa	K3a	2014	1.7	2	0.2	0.5	3	0.01	0.05	2	2.1	0.6	0.01	3.6	15	0.03	0.06	0.01	0.05	5.7	0.15	**0.92**
Kharaa-Baruunkharaa	K3b	2015	0.7	1.2	0.2	0.4	1.3	0.00	0.05	2.5	2.4	0.5	**0.02**	6.5	23	0.07	0.08	0.01	0.74	1.6	0.17	0.09
Bayangol up stream	kt7	2014	15.3	5.7	0.2	4.8	**13.4**	0.03	**0.2**	2.8	**13**	6.4	**0.05**	2.7	5.6	0.01	**0.3**	0.01	0.04	16	0.63	**10.9**
Bayangol mid-stream	kt8	2014	16.7	6.1	0.2	5	**14.5**	0.01	**0.2**	3	**14**	6.7	**0.03**	1.6	7.4	0.05	**0.3**	0.01	0.12	9.9	0.65	**12.5**
Bayangol down stream	kt9	2014	20	6.6	0.2	5.9	**16.4**	0.02	**0.2**	3.1	**16**	7.8	**0.04**	2.8	8.7	0.01	**0.3**	0.01	0.09	4	0.73	**14.3**
Kharaa River Darkhan station	K4a	2014	7.3	3.6	0.2	2	6.3	0.01	**0.1**	3.4	5.5	2.4	**0.02**	2.7	21	0.01	**0.1**	0.01	1	5.5	0.35	**4.8**
Kharaa River Darkhan station	K4b	2015	1.2	1.3	0.2	0.45	1.75	0.00	0.04	4.6	1.4	0.7	**0.08**	6.5	24	0.1	0.09	0.01	0.43	5.3	0.17	**1.12**
Kharaa Buren tolgoi	K5a	2014	5.8	3	0.2	1.6	5.3	0.01	**0.**	3.6	4.5	1.8	**0.03**	7.3	21.2	0.03	**0.1**	0.01	0.25	4.2	0.29	**3.62**
Kharaa Buren tolgoi	K5b	2015	1.8	1.7	0.2	0.4	1.2	0.00	0.07	4.4	1.9	0.7	0.01	14	34.9	0.2	**0.1**	**0.03**	0.45	5.1	0.31	**0.68**

Note: * MNS 900:2005 Environment health protection, safety, drinking water, hygienically requirements, assessment of the quality and safety

3.4 5 Water quality of Sharyn and Eroo River basin

The Sharyn and Eroo Rivers are downstream tributaries of the Orkhon River. The upstream area of the Sharyn River is morphologically modified by mining activities. Further downstream, there is a potential impact by the little town of Sharyngol, which discharges its wastewater into the river, and a major coal mining operation. The Eroo River leads through mostly unpopulated areas, except some minor gold mining operations in its upstream section.

We found elevated concentrations of mine indicator elements in Sharyn River basin (Table 11). The Al-concentration in the upstream section of the Sharyn River was 0.9 mg/L. Further downstream Al concentrations showed values up to 21.1 mg/L (summer 2014 with operational mine), but Al concentration in spring time (with no mining operation) was around 0.9 mg/L. This shows that mining activities have a direct influence on the river water quality. Cu, Mn, Ni and Zn concentrations were high in the downstream part of the river (Table 11). The downstream area of the Sharyn River is highly influenced by mine activities. The concentration of PO_4^{3-} increased upstream to downstream from 0.02 mg/L to 0.45 mg/L. In addition NO_2^- concentration rose downstream to 0.024 mg/L behind the Sharyn Gol district.

Especially the concentrations of TNb, NH_4^+ and Total-P were high in the downstream of the Sharyn River. The concentrations of NO_2^- and PO_4^{3-} were particularly high behind the Sharyn Gol district (Fig. 14). Furthermore the concentrations of Fe (up to 19.7 mg/L), Mn (up to 0.3 mg/L) and Tl (up to 1.4 µg/L) increased along the river. Compared to the Sharyn River, Eruu River was less affected by mining activities (Fig. 14).

The Fe and Al concentrations were elevated in mid- and downstream area of the Eroo River (Table 12). The Al concentration was elevated both in the upstream (0.6 mg/L) and downstream area (0.8 mg/L) in summer 2014. The results from the water samples in spring 2015 complied with the Mongolian standards. Upstream the Fe-concentration was around 0.6 mg/L, but further downstream it increased to 0.94 mg/L. The Tl-concentration showed no differences between up- and downstream areas, but it was 5 times higher than the standard.

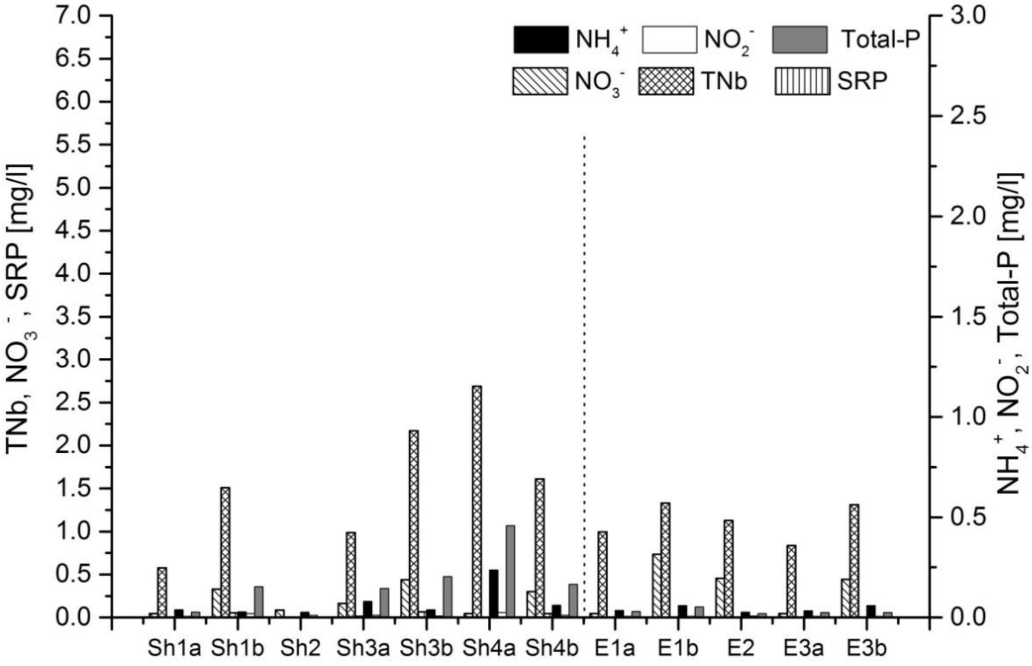

Figure 14 Changes of nutrient concentrations along the Sharyn and Eroo River. The flow direction left to right. TNb is total nitrogen bound and SRP is soluble reactive phosphorus

Table 11 Chemical water quality of Sharyn river water samples from upstream to downstream. Comparison of observed concentrations in relation to standard value MNS 4586: 98. Bold numbers are indicating concentrations higher than the standard

Names	ID	Year	Cr µg/l	As µg/l	Cd µg/l	Co µg/l	Cu µg/l	Hg µg/l	Mn mg/l	Mo µg/l	Ni µg/l	Pb µg/l	Zn mg/l	Cl$^-$ mg/l	SO$_4^{2-}$ mg/l	NH$_4^+$ mg/l	PO$_4^{3-}$ mg/l	NO$_2^-$ mg/l	NO$_3^-$ mg/l	TOC mg/l	WQI	Al mg/l
MNS 4586:98			50	10	5	10	10	0.1	0.1	250	10	10	0.01	300	100	0.5	0.1	0.02	9			0.5 *
Sharyn gol up stream	Sh1a	2014	1.8	0.8	0.2	0.4	3.3	0.02	0.02	3.3	2.4	0.5	0.01	1	6.3	0.04	0.03	0.01	0.05	12	0.12	**0.98**
Sharyn gol up stream	Sh1b	2015	1.1	0.8	0.2	0.4	1.8	0.01	0.10	5.6	1.8	0.5	0.01	6.6	22	0.03	**0.1**	0.02	0.33	7	0.26	**0.79**
Sharyn gol mid-stream	Sh2	2015	0.5	1.1	0.2	0.4	6.9	0.00	0.06	3.5	2.6	0.5	0.01	8.5	29	0.03		0.01	0.09	1	0.16	0.03
Sharyn gol Khuiten station	Sh3a	2014	8.1	3.7	0.2	2.1	7.3	0.03	0.09	1.8	5.8	2.3	0.01	1.0	8.4	0.08	**0.1**	0.01	0.17	8	0.34	**6**
Sharyn gol Khuiten station	Sh3b	2015	0.5	1.2	0.2	0.4	2.2	0.00	0.08	2.4	1.4	0.5	0.01	2.5	19	0.04	**0.2**	0.01	0.44	9	0.25	0.2
Sharyn gol Jimst station	Sh4a	2014	29	6.2	0.2	8.1	**21**	0.04	**0.3**	4.8	**20**	7.5	**0.05**	11.9	46	0.24	**0.4**	**0.02**	0.05	9	**1.06**	**21.1**
Sharyn gol Jimst station	Sh4b	2015	1.2	1.7	0.2	0.5	2.1	0.00	0.09	5.1	1.7	0.7	0.01	4.1	21	0.06	**0.1**	0.01	0.3	4	0.25	**0.89**

Note: * MNS 900:2005 Environment health protection, safety, drinking water, hygienically requirements, assessment of the quality and safety

Table 12 Chemical water quality of Eroo river water samples from upstream to downstream. Comparison of observed concentrations in relation to standard value MNS 4586: 98. Bold numbers are indicating concentrations higher than the standard

Names	ID	Year	Cr µg/l	As µg/l	Cd µg/l	Co µg/l	Cu µg/l	Hg µg/l	Mn mg/l	Mo µg/l	Ni µg/l	Pb µg/l	Zn mg/l	Cl- mg/l	SO42- mg/l	NH4+ mg/l	PO43- mg/l	NO2- mg/l	NO3- g/l	TOC mg/l	WQI	Al mg/l
MNS 4586:98			50	10	5	10	10	0.1	0.1	250	10	10	0.01	300	100	0.5	0.1	0.02	9			0.5 *
Eroo-Eroo	E1	201	1.0	1.2	0.2	0.4	4.3	0.00	0.02	0.9	4.6	0.5	**0.06**	1.0	4.2	0.04	0.03	0.01	0.05	6.6	0.1	0.5

station	a	4																				
Eroo-Eroo station	E1b	2015	0.5	0.6	0.2	0.4	0.5	0.00	0.05	0.9	1.3	0.5	0.01	1.7	10	0.06	0.05	0.01	0.7	3.6	0.1	0.09
Eroo mid stream	E2	2015	0.5	0.7	0.2	1.5	4.6	0.00	0.08	1.8	2.4	0.5	0.01	1.7	13	0.03	0.02	0.01	0.46	2.2	0.1	0.02
Eroo-Dulaankhaan	E3a	2014	1.3	1.7	0.2	0.4	3.1	0.00	0.06	1.4	1.4	0.5	0.01	1.0	6.9	0.03	0.02	0.01	0.05	7.2	0.1	**0.8**
Eroo-Dulaankhaan	E3b	2015	0.6	0.6	0.2	0.4	1.4	0.00	0.06	1.4	0.9	0.5	0.01	1.5	11	0.06	0.03	0.01	0.4	1.2	0.1	0.06

Note: * MNS 900:2005 Environment

Table 13 Water quality of mining ponds and monitoring wells, drinking water samples in comparison with Mongolian drinking water standard MNS 900:2005 and mind pond water samples in comparison with Mongolian effluent treated waste water general requirement MNS 4943:2011

Location description	**Sample class**	**Year**	**U [µg/l]**	**Mg^{2+} [mg/l]**	**Al [mg/l]**	**As [µg/l]**	**Fe [mg/l]**	**Mo [µg/l]**	**Sr [µg/l]**	**Ca^{2+} [mg/l]**
MNS 4943:2011			**50**		**0.5**	**10**	**1**	**500**	**2000**	**100**
MNS 900:2005			**15**	**30**	**0.5**	**10**	**0.3**	**70**	**2000**	**100**
Bortolgoi	mine pond	2014	15.6	19	**1.8**	**389**	**1.5**	10	397	31
Bortolgoi	drinking water	2015	13.4	16.5	0.04	1.3	0.1	3.5	328	50
Bortolgoi	drinking water	2014	**25.5**	23.1	0.07	1.8	0.09	3.9	526	75
Erdenet	mine pond	2015	28.2	89.1	0.04	1.4	0.2	916	**2470**	**219**
Erdenet	mine pond	2014	2.3	6	0.4	7.2	0.04	**353**	1210	**276**
Erdenet 1	drinking water	2015	2.9	8.8	0.02	0.5	0.02	2.3	247	38
Erdenet 1	drinking water	2014	5.7	**52**	0.06	0.6	0.1	8.3	1500	**140**
Erdenet 2	drinking water	2015	5.9	**33**	0.04	0.6	0.03	4.5	845	87
Erdenet 2	drinking water	2014	3.2	**34**	0.03	1.3	0.08	4.9	1030	86
Erdenet 3	drinking water	2015	6.9	**47**	0.03	0.6	0.02	5	1210	**125**
Erdenet 3	drinking water	2014	3.7	**34**	0.02	0.5	0.04	4.5	1010	87
Zaamar	mine pond	2014	21	**30**	**5**	6.8	**3.6**	9.9	583	31
Zaamar	drinking water	2014	0.7	1.98	**0.5**	0.7	**0.4**	0.5	95	11
Zaamar	drinking water	2014	2.8	25	0.0617	0.5	0.08	3.4	1220	46

3.4.6 Multivariate analysis

In order to get a more general overview about the differences among samples we used a combination of clustering and PCA as multivariate statistical method for all measured parameters. As a result of the PCA four meaningful factors with a cumulative explanation of 73 % of the variance were extracted. Eigenvalues of the first two axes (54 % explained variance) were 12.0 and 8.1, respectively. Factor loadings are given in Appendix Table 14. Factor one can be defined as the influence of mining and the second factor describes the influence of urban waste waters.

Four groups of samples were discriminated (Fig. 13 and Fig. 14): Cluster 1 (most of them headwater sites) comprises the samples that were either very low in nutrients or low in trace elements.

Cluster 2 consists of the river samples (Ktma, Ktm2, Kt3a, Kt3b, Kt2b, Ktmc, Tta, Kt4b, Kt2a, K4a, K5a, Kt4a, Kt4c, Kt5a, Kt5b, Kt6a, Kt6b, Ktmb, O5b, Sh3a, T5a, T7a, T7b) with medium trace element concentration as well as high concentration of following elements (Sb, Bi, As, Cd, Hg, Tl, B and Ag) which are indicator elements for gold mining in relation to other clusters.

The cluster 3 (Ot1a, Ot1b, T2b and T4) contains river samples for which high concentrations were observed in the following parameters: (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, Cu, Mn, Mo, Sr, DOC, TNb, NH_4^{+}, NO_2^{-}, NO_3^{-}, SRP, PO_4^{3-}). This typical pattern is indicating the influence of the cupper molybdenum mine and the city of Erdenet to a small tributary of Khangal River in relation to other three clusters. T2b is the river sample directly after the central WWTP UB. In spring 2015, the T2b sampling site water was flowing by discharge from the waste water of the central WWTP UB. Otherwise river water is mostly frozen during the winter and spring.

Cluster 4 (Kt6, Kt7, Kt8, O4a, O6a, O7a, Sh4a) contains sampling points with pollution by different heavy metals like Cr, Al, Ba, Co, Fe, Ni, Rb, Pb, V, Li, Ti. TOC as well as DOC are further parameter with high concentrations and an indicator for the urbanization near the mines or high concentrations may be also originate from erosion processes within the mining area. The reason for the high element concentrations at the samples can be seen in gold mining activities. For example O4 is located after the Zaamar mine area as well as at the junction with Orkhon River downstream Erdenet mining. High TOC and DOC values are an indication for the urban waste water influence of Erdenet.

Through the learning process of the Self Organizing Maps (SOMs), the samples were arranged by similarity in a SOM map in a “bee cluster” (Fig. 17) according to the distribution patterns of the examined pollutants (Appendix Fig. 1 b). The outcome was similar to our ward cluster result, with the four groups arranged in the different corners of the map. Cluster 1 and 2 at the upper part of the map comprised samples from the head water regions, while Cluster 3 comprised samples with high concentration of trace elements and Cluster 4 those with high nutrition concentration. Chemical parameters differed clearly between groups (Fig. 18).

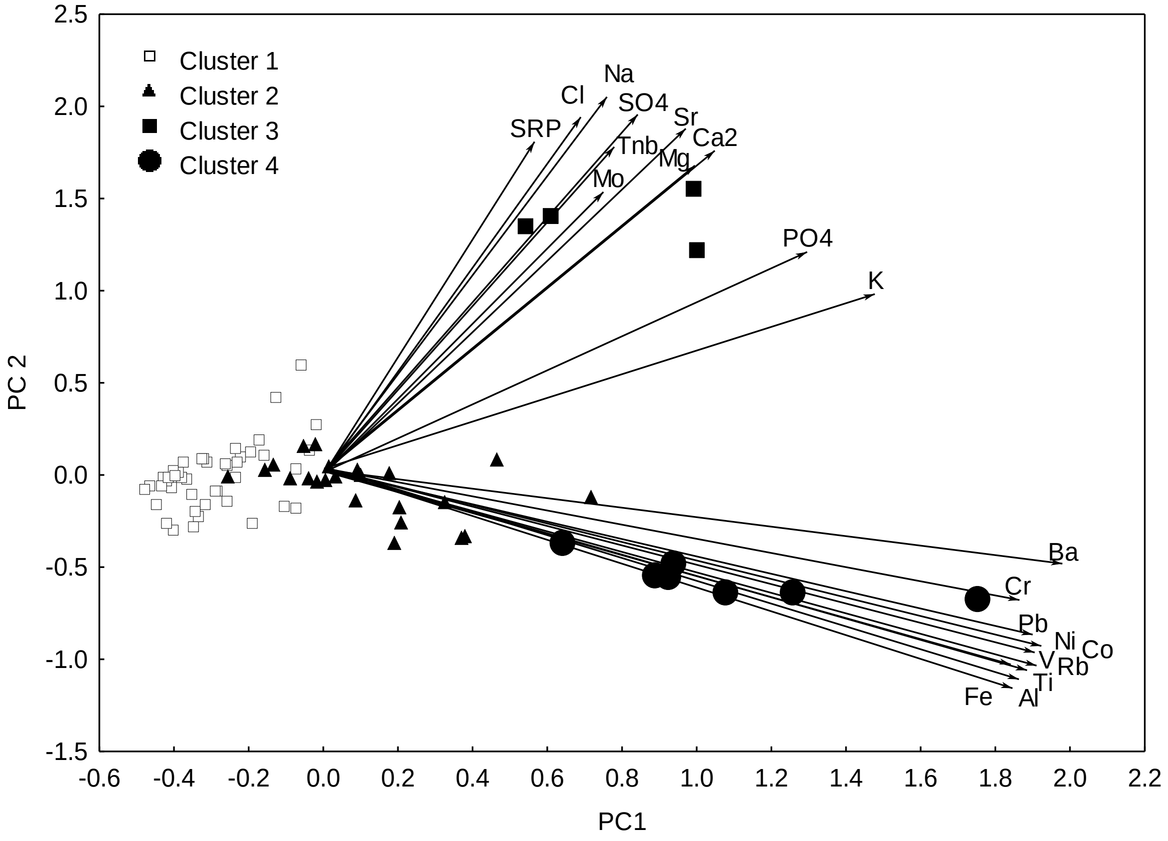

Figure 15 PCA and clustering of river sample sites. Arrows show environmental parameters that can be interpreted with confidence. Clustering produced 4 groups of sample sites that differed in chemical parameters. Cluster 1 in opposition to the direction of the arrows, included sites that were either very low in nutrition (headwaters) or low in trace elements. Cluster 2 was slightly impacted by trace elements. Cluster 3 included sites with mainly higher nutritional content: Ot1a, Ot1b, T2b,T4 and cluster 4 comprised sites with higher levels of (heavy) metals: kt6,kt7,kt8,O4a,O6a, O7a, Sh4a. For the full cluster dendrogram see Fig. 8

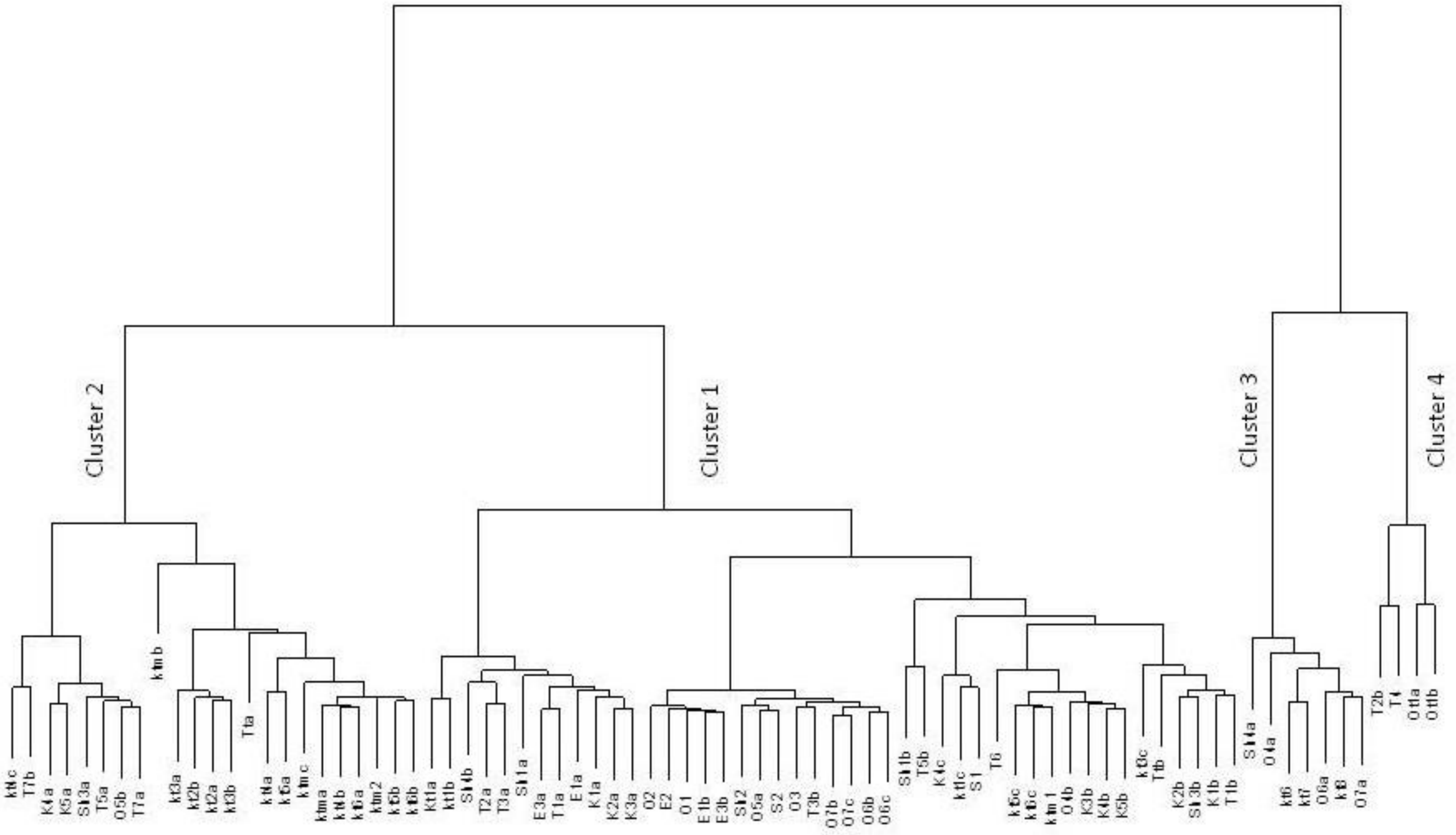

Figure 16 Cluster dendrogram used for grouping in the PCA (Fig. 2). We used four clusters to mark groups of different water quality. Cluster 1 included sites that were either very low in nutrition (headwaters) or low in trace elements. Cluster 2 was slightly impacted by trace elements. Cluster 3 included sites with mainly higher nutritional content: Ot1a, Ot1b, T2b,T4 and cluster 4 comprised sites with higher levels of (heavy) metals: kt6,kt7,kt8,O4a,O6a, O7a, Sh4a

3.5 Discussion

Our study is based on a recent compilation of data on water quality from the Mongolian part of Selenga River basin. They allow a characterization and quantification of the pollution load in the investigated catchment. A comparison of data from summer and spring seasons provides first insights into the pollution dynamics of this river system. Most measurements from spring time that took place on water samples collected under ice cover and in conditions when mining in Mongolia has been stopped showed much lower loads of pollution with metals and other contaminants. Especially concentrations of Al, As, B, Cr, Co, Cu, Fe, TOC, Tl, Li, V and Ag were low. Interestingly Na^+, Cl^-, SO_4^{2-}, TNb and U were high in spring 2015 relative to summer 2014 (Fig. 11). Waste waters from urban region and roads could be the reason. In urban areas, Uranium may be released into the environment by the combustion of coal during winter.

According to the water quality index, nearly 60 % of all river water samples showed a very clean status. Out of the remaining samples, 30.3 % were clean, 5.06 % slightly polluted (Ktmb, O7a, T5b, Sh4a), 2.53 % polluted (Ot1a, T4), 1.26 % very polluted (T2b) and 1.26 % very dirty (Ot1b), respectively (Fig 15. As demonstrated by PCA, clustering and SOM methods our samples could be grouped according to different pollution sources and loads according to human impact that differed in head waters and downstream of pollution sources. Taken together water quality in Selenga River basin can be considered as deteriorated by nutrients downstream of urban areas (due to deficient waste water treatment facilities) as well as by heavy metals and arsenic loads from mining activities.

This study focused on different surface water quality standards in order to evaluate water quality in a river system that is transboundary. The water quality standards of Mongolia and Russia are quite strict compared to the other standards (US EPA 2006, environmental quality norms according to the WFD). However, there are considerable differences between the Mongolian and Russian water quality guidelines. The Russian standard RNS 2010 is stricter than the Mongolian standard MNS 4586:98. For example, the tolerable value for Cr is 1 µg/L in the Russian standard, 11 µg/L in the US EPA standard, but 50 µg/L according to the Mongolian norm. Regarding As concentrations, the Russian standard (5 µg/L) is also stricter than the other standards. Regarding Nickel, Mongolian and Russian standards (10 µg/L) were stricter than other international standards. When compared to the Russian standard (RNS 2010), the parameters Cr, Fe and Pb occasionally exceeded the maximum limits. These differences should be taken into account in a transboundary management cooperation of the Selenga River basin between both countries (Nadmitov et al. 2015).

So far, only a few publications focused on water quality in the SRB area. According to a study of Nadmitov et al. (2015), Zn exceeded the Russian standard in half of the samples and Mn, Cr, Cu and As were identified as problematic dependent on their occurrence and concentration. Water samples were taken in 2007-2009. Our results are consistent with Nadmitov et al. (2015) except for chromium. The highest concentrations were observed in

Darkhan and downstream of the Sharyn River and Kharaa River for Mn, Cu, As and Cd in the Mongolian part of the Selenga River. They found Zn and Fe in Mongolian-Russian border. Through these three years of surveys, most rivers showed severe pollution by Fe, Zn and Mn. On the other hand Ni, Pb and Cd were found to be the least contaminating groups of metals across the upstream to downstream regions when compared to the water quality guidelines of Mongolia (MNS 4586:98) and (RNS 2010). In this study, Fe, Pb, Ni were exceeded the river samples compared to the Russian guideline (RNS 2010). However Cadmium met with the threshold value for both guidelines (MNS4586:98, RNS 2010).

The toxicity of aluminum to fish depends on the pH values of the river water. Previous studies (Zdenka et al. 1993) have found elevated levels of Al to be problematic for different species of fish, with greater Al toxicity under more acidic pH. The pH of the river water samples described here ranged between 7 and 8.5, which agrees with the findings of Thorslund et al. (2016), who investigated heavy metal transport processes under such non-acidic conditions.

The Al concentrations ranged from 0.02 to 21.1 mg/l. Concentrations that are toxicologically relevant for fish were found in the Tuul River, the Orkhon River and one of its tributary, the Kharaa River and several of its tributaries.

While the Mongolian part of the Selenga River fulfilled the Mongolian surface water quality guideline (MNS 4586:98), this was not true for the Tuul, Orkhon, Sharyn and Eroo Rivers which failed to meet surface water quality standards for some trace elements and nutrients (As, Cd, Cu, Cr, Fe, Mn, Ni, Pb, Zn, NH_4^+, NO_2^-, NO_3^-, PO_4^{3-},SO_4^{2-}), especially in their downstream parts.

3.6 Conclusion

The Mongolian part of the Selenga River basin plays a significant role for discharge generation into Lake Baikal. Over the past few decades, increasing pollution levels in the Selenga tributaries have led to growing concerns about potential effects on public health and aquatic biota (Karthe et al. 2015b, Kaus et al. 2016), and fears that pollutants from the Selenga could negatively impact the unique ecosystems of the Selenga Delta and Lake Baikal in the future (Chalov et al. 2016).

The Selenga River system in Mongolia is characterized by strong environmental gradients. All tributaries originate in regions that are characterized by very low population densities and an almost pristine natural environment. Therefore, they are well suited for the derivation of natural reference conditions. Further downstream, many of the Selenga's tributaries flow through more densely populated areas, including the three largest urban settlements of Mongolia, and regions where mining of various natural resources plays a significant role. Downstream of these areas, significant changes in chemical water quality could be observed, with several parameters exceeding national or international surface water quality standards.

The highest concentrations of nutrients were recorded in or downstream of urban areas and mining regions (Tuul directly downstream of Ulaanbaatar WWTP and downstream of Zaamar gold mining area; Khangal River downstream of Erdenet city; Kharaa downstream of Darkhan city). Several heavy metals and arsenic were found in elevated concentrations, including As (up to 54.2 µg/l in the Boroo River downstream of Bortolgoi mine, as compared to a maximum of 10 µg/l according to MNS 4586:98), Cu (up to 360.0 µg/l in the Khangal River downstream of the Erdenet copper-molybdenum mining complex, as compared to a maximum of 10 µg/l according to MNS 4586:98), Ni (up to 20.5 µg/l in the Sharyn River downstream of both coal and gold mining areas, as compared to a maximum of 10 µg/l according to MNS 4586:98) and Mn (up to 380 µg/l also in the Sharyn River downstream of both coal and gold mining areas, as compared to a maximum of 100 µg/l according to MNS 4586:98).

Despite the research done over the past decade, the basin of the Selenga remains a relatively data-scarce region (Karthe et al. 2015c). This study confirms the available evidence from other research in the region (e.g., Hofmann et al. 2011; Inam et al. 2011; McIntyre et al. 2016; Nadmitov et al. 2015; Pfeiffer et al. 2015) that waste water discharge from urban areas and mining have a significant impact on water quality along the Selenga and its tributaries. While generally corroborating previous results on nutrient and trace element pollution in the mid- and downstream sections the rivers, this paper also demonstrated the strong contrasts in water quality between relatively pristine headwater regions and more strongly impacted downstream sites as well as seasonal changes of water quality in six sub catchments. This comprehensive overview of water quality (which is based on samples analyzed in a certified laboratory in Germany) is also a good base for future studies.

In the future, additional research will be needed to monitor water quality development in this rapidly developing region. Moreover, a more detailed assessment of the links between urban waste water discharges and the various forms of mining on the one site and surface water quality on the other is still needed. This could not only help to better quantify individual pollution sources, but also aid to prioritize water management policies.

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Appendix

Table 14 Factor loadings for the PCA.

Var	PC1	PC2
SB	1.102364e-04	1.044278e-04
U	1.011030e-02	8.519891e-03
Mg2.	2.567313e-02	1.410778e-02
Na.	3.680297e-02	3.063571e-02
K.	4.693442e-03	-1.618307e-03
TOC	3.082217e-03	-1.013466e-02
DOC	2.359777e-03	-4.072374e-03
Cr	1.296429e-02	-2.166653e-02
Al	1.038166e-02	-1.777365e-02
As	1.333104e-02	5.113953e-03
Ba	1.048764e-01	-1.075363e-01
Co	4.043206e-03	-6.201636e-03
Cu	1.203619e-01	5.791488e-02
Fe	9.443654e-03	-1.707985e-02
Hg	1.634985e-05	-7.866833e-06
Mn	4.305551e-04	1.693374e-04
Mo	5.553553e-02	3.638419e-02
Ni	1.046360e-02	-1.509407e-02
Pb	5.084298e-03	-6.938891e-03
Rb	1.737563e-02	-3.014209e-02
Sr	8.201992e-01	5.031300e-01
V	2.405352e-02	-3.598855e-02
Zn	7.406568e-06	-2.001359e-05
TNb	3.275884e-03	1.943423e-03

Cl.	2.080683e-02	1.871874e-02
SO42.	1.651476e-01	1.090028e-01
Ca2.	6.857690e-02	3.680290e-02
Li	1.248328e-02	-1.194278e-02
Tl	3.625014e-04	-5.751549e-04
Ti	5.114898e-01	-8.432623e-01
B	2.778828e-02	2.889656e-02
Ag	3.951310e-04	-6.389302e-04
NH4	9.789594e-04	1.816100e-03
PO4	4.317886e-04	-1.243703e-04
NO2	8.596794e-04	2.389664e-04
NO3	1.666263e-03	1.198715e-03
SRP	1.506575e-04	1.604998e-04

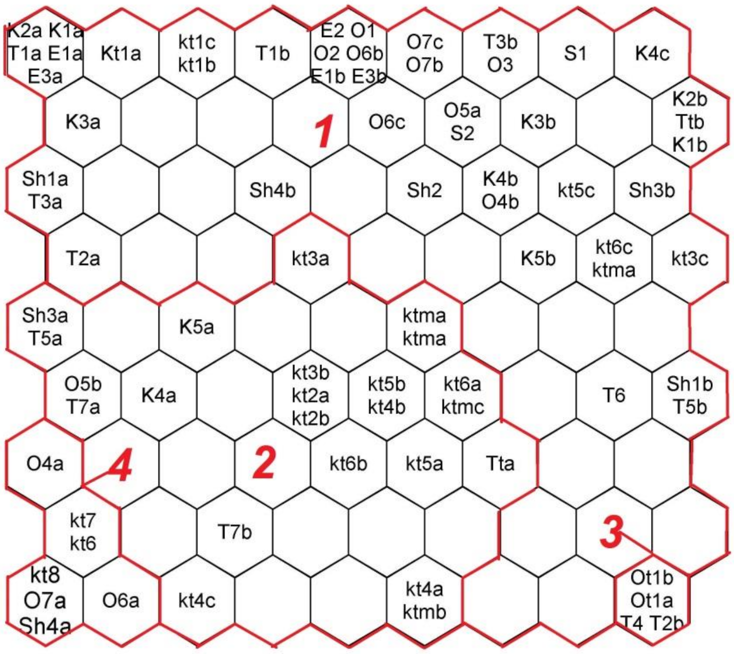

Figure 17 Self-organizing map (SOM) in relation to river water samples names. Unpolluted samples were put to the upper part of the map, while water samples with high concentrations were located in the lower part with the samples of high metal content to the left and high nutrient content to the right

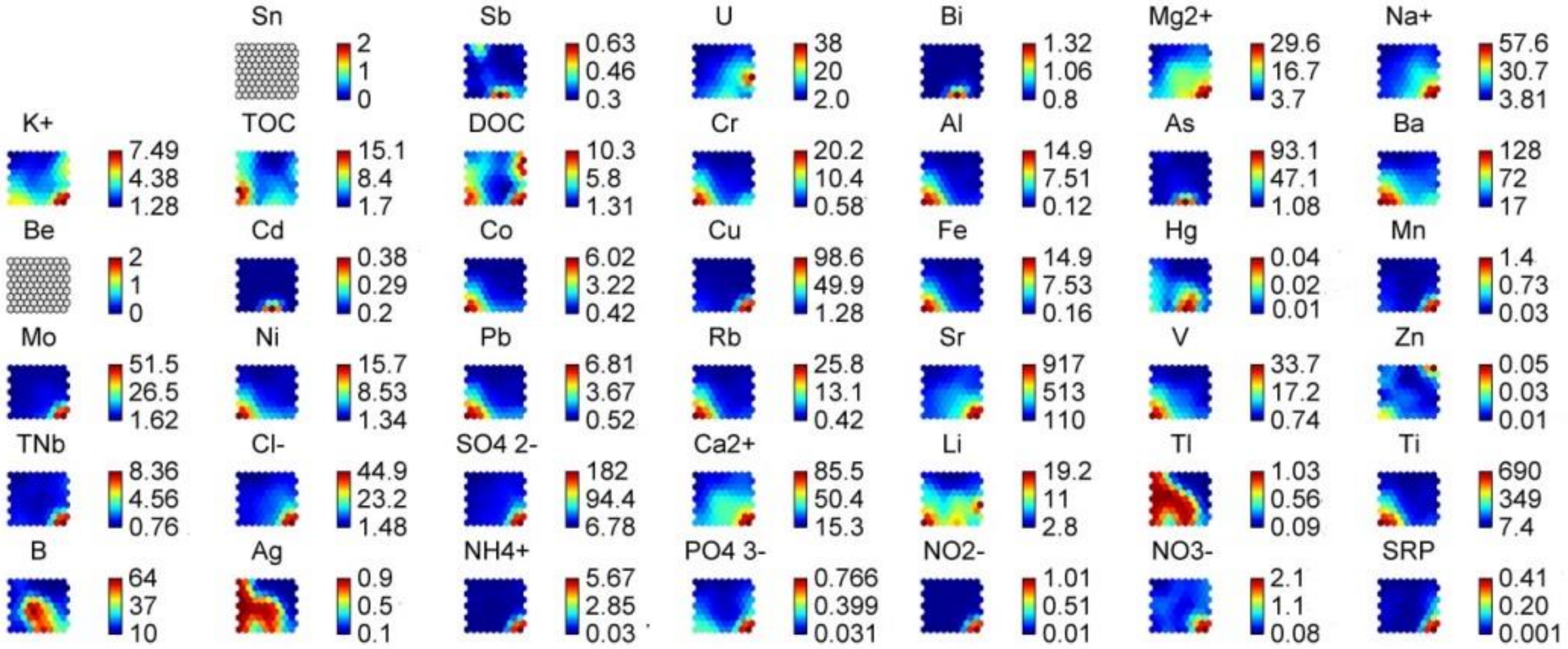

Figure 18 Self-organizing map (SOM) showing the longitudinal patterns of the water chemistry parameters of river water samples. Red color regions in the map indicate high values, whereas blue color regions indicate low values

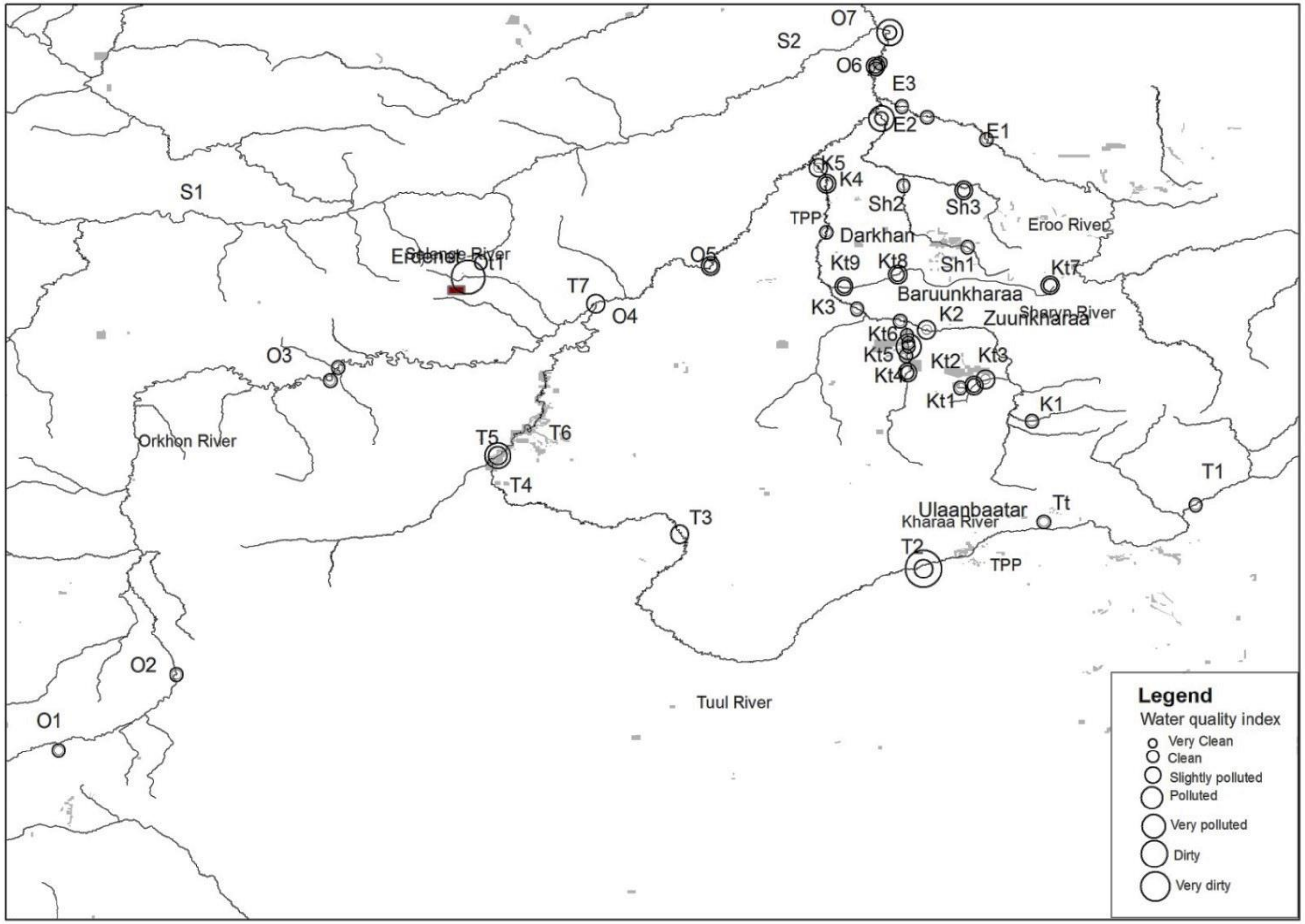

Figure 19 The map is showing the spatial pattern of the water quality index in the Mongolian part of Selenga river basin and its tributaries at one site in 2014 and 2015. The circles are indicating water quality from very clean (smallest circle) to very dirty (biggest circle). Concentric rings in one location indicate different water quality in both years

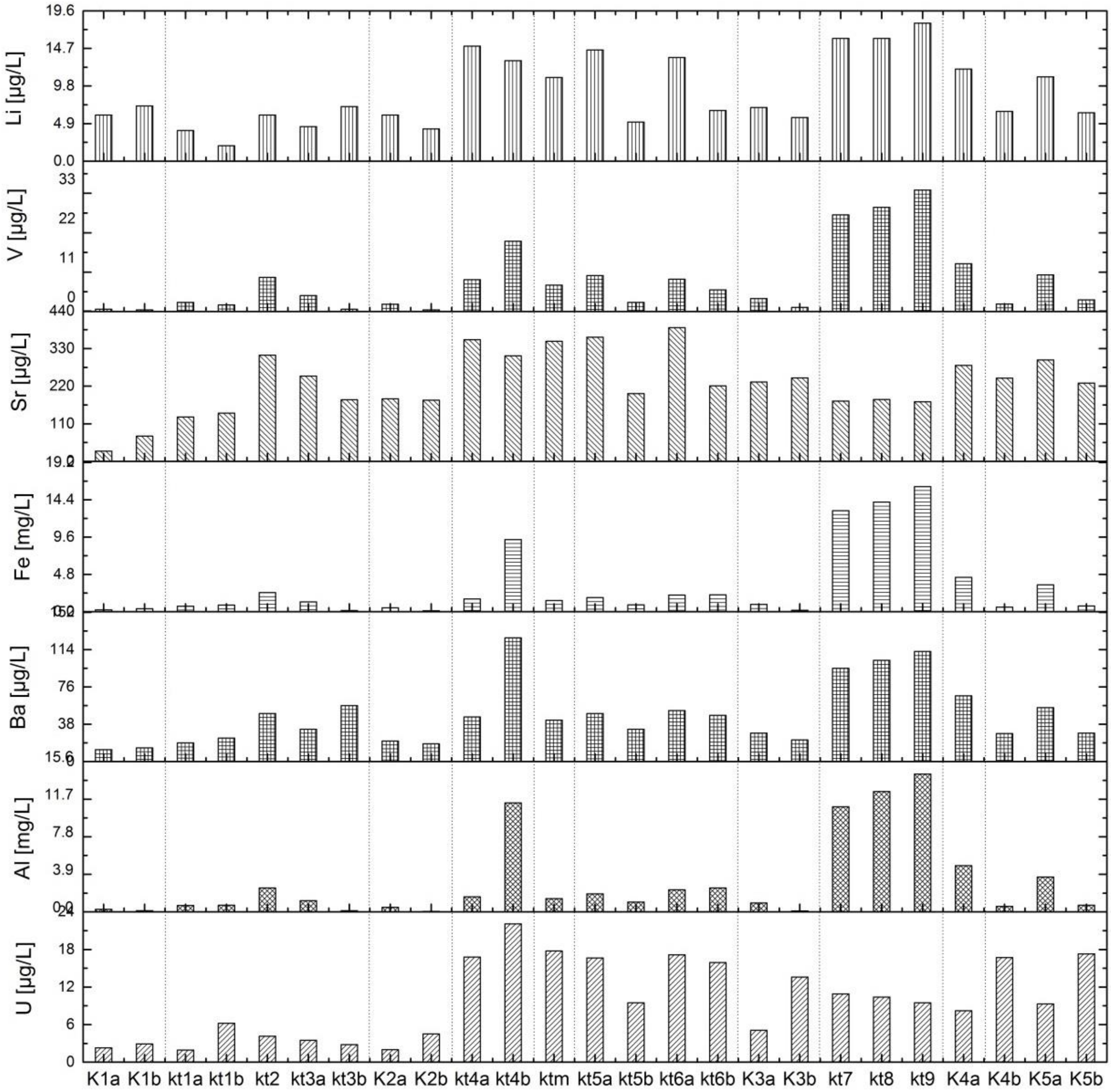

Figure 20 Changes of trace elements concentrations along the Kharaa River. The flow direction left to right. Sampling point Kt1 to Kt3b is Gatsuurt River which is left tributary of Kharaa River. Kt4a to Kt6b is Boroo River which is left tributary of Kharaa River. Ktm is located in along the small mine (Bor tolgoi). Kt7 to Kt9 is right tributary of Kharaa River (Bayan gol)

Chapter4. Assessment of Runoff, Water and Sediment Quality in the Selenga River Basin aided by a Web-Based Geoservice

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Assessment of Runoff, Water and Sediment Quality in the Selenga River Basin aided by a Web-Based Geoservice

4.1 Abstract

The Selenga River is the main artery feeding Lake Baikal. It has a catchment of ~450.000 km^2 in the boundary region between Northern Mongolia and Southern Siberia. Climate, land use and dynamic socioeconomic changes go along with rising water abstractions and contaminant loads originating from mining sites and urban waste water. In the future, these pressures might have negative impacts on the ecosystems of Lake Baikal and the Selenga River Delta, which is an important wetland region in itself and forms the last geobiochemical barrier before the Selenga drains into Lake Baikal.

Our study aims to assess current trends in hydrology and water quality in the Selenga-Baikal basin, identify their drivers and to set up models (WaterGAP3 framework and ECOMAG) for the prediction of future changes. Of particular relevance for hydrological and water quality changes in the recent past were climate and land use trends as well as contaminant influx from mining areas and urban settlements. In the near future, additional hydrological modifications due to the construction of dams and abstractions/water diversions from the Selenga’s Mongolian tributaries could lead to additional alterations.

Keywords: Selenga river system, Lake Baikal, water quality assessment, Transboundary Rivers, geodatabase

4.2 Introduction

Lake Baikal’s most important tributary is the Selenga River, which contributes about 50% to 60% of the surface water influx (Chalov et al. 2015; Opp 1994; Törnqvist et al. 2014). North of the Buryatian capital Ulan Ude, the Selenga River branches into the largest freshwater inland delta in the world (Logachev 2003). The associated wetland constitutes a unique ecosystem (Гармаев & Христофоров 2010) and acts as the final geobiochemical barrier before the Selenga discharges into Lake Baikal. Because of its sheer size and unique ecological characteristics, Lake Baikal and the Selenga river system form an ecoregion of global relevance that is being exposed to numerous anthropogenic stressors (Batuev et al. 2015, Karthe et al. 2015b). The Selenga river system, which drains a 447.060 km^2 watershed or 82% of the Lake Baikal Basin (Nadmitov et al. 2014) plays a key role in this regard:

Various mining activities are found in the Selenga River Basin, including the exploitation of coal, gold, copper, molybdenum and wolfram (Sandmann 2012; Thorslund et al. 2012). As a consequence, elevated levels of heavy metals and other mining-related pollutants (cyanides, phosphorus) have been detected in the water and sediments of the Selenga and its tributaries, as well as floodplain soils and groundwater (Brumbaugh et al. 2013; Chalov et al. 2015; Inam et al. 2011; Nadmitov et al. 2014; Pavlov et al. 2008, Pfeiffer et al. 2015; Stubblefield et al. 2005; Thorslund et al. 2012). Even though contaminant transport towards the Selenga delta does take place (Chalov et al. 2015; Khazeeva et al. 2004, 2006, Thorslund et al. 2012), it should be noted that contaminations so far have the largest effects in local hot spots (Hofmann et al. 2010, Inam et al. 2011, Pfeiffer et al. 2015). Currently, there are different views regarding their impacts on Lake Baikal (Chebykin et al. 2010, Pavlov et al. 2008). However, bioaccumulation and toxicological effects observed in aquatic biota ranging from insects to fish already indicate that water quality deterioration in the Selenga river system does have an ecological impact (Avlyush 2011, Kaus et al. 2016, Komov et al. 2014).

A considerable part of the Selenga River Basin's population is concentrated in four cities. The three largest cities of Mongolia (Ulaanbaatar, Erdenet and Darkhan) as well as Ulan Ude, the capital of the Republic of Buryatia in Russia, are located on the Tuul, Orkhon, Kharaa and Selenga Rivers, respectively. These urban areas have multiple impacts on the region's water resources. Firstly, per capita water consumption in urban areas is considerably higher than in peri-urban or rural regions (Scharaw & Westerhoff 2011, Sigel et al. 2012). Secondly, poor wastewater treatment infrastructures lead to nutrient inputs (Hofmann et al. 2010, 2011, Karthe et al. 2016) and microbiological contamination of rivers (Sorokovikova et al. 2013). Thirdly, urban areas in the Selenga River Basin are characterized by a concentration of pollutants originating from the combustion of fuels and various industries (Dalai & Ishiga 2013, Kasimov et al. 2011, Opp et al. 2007, Pfeiffer et al. 2015, Sorokina et al. 2013), some of which enter the water cycle directly or via atmospheric deposition.

Land use change, which is currently more pronounced in the Mongolian than the Russian part of the Selenga River Basin, is primarily driven by mining and the expansion of agricultural land (Mun et al. 2008, Priess et al. 2011). The conversion of forests and natural grasslands into pastures and fields has implications for both hydrology (Minderlein & Menzel 2015) and water quality, particularly by stimulating erosion processes (Priess et al. 2015, Theuring et al 2013, 2015).

Present and expected hydrological changes in the Selenga River Basin are caused by three processes: land use changes (Karthe et al. 2015c, Minderlein & Menzel 2015), the impacts of global climate change on precipitation and evaporation (Hampton et al. Karthe et al. 2013, Magnuson et al. 2000, Malsy et al. 2015, Törnqvist et al. 2015) and permafrost (Moore et al. 2009, Törnqvist et al. 2015), and increasing water withdrawals (Malsy et al. 2013, Priess et al. 2011). The latter are related to the expansion of agriculture and rising irrigation needs in the context of global warming (Malsy et al. 2015, Priess et al. 2011) and in the future, potentially due to water diversions into mining areas in the South Gobi (Sorokovikova et al. 2013).

For many of the above mentioned developments, evidence on the ecological consequences does not only exist from the Selenga Baikal Basin but from several other Central Asian river basins (Karthe et al. 2015a). The protection of Lake Baikal depends to a considerable degree on developments and conservation measures in the Selenga River Basin as well as a good understanding of the current state and functioning of the delta's ecosystem and the geo- and biochemical processes taking place in it (Chalov et al. 2016, Opp 1994, 2007).

For the assessment of past and future changes in hydrology, water and sediment quality we have combined data and model-driven approaches. The aims of the paper include the following: (a) assembling all currently accessible data on river discharges, sediment and water quality in the Selenga River Basin in an online geodatabase; (b) characterizing contemporary changes in the hydrology and contaminant loads due to climatic and human impacts and (c) assessing different hydrological and water quality models (particularly WaterGAP3, SedNet and EcoMag) with regard to their suitability to predict future trends in hydrology and water and sediment quality.

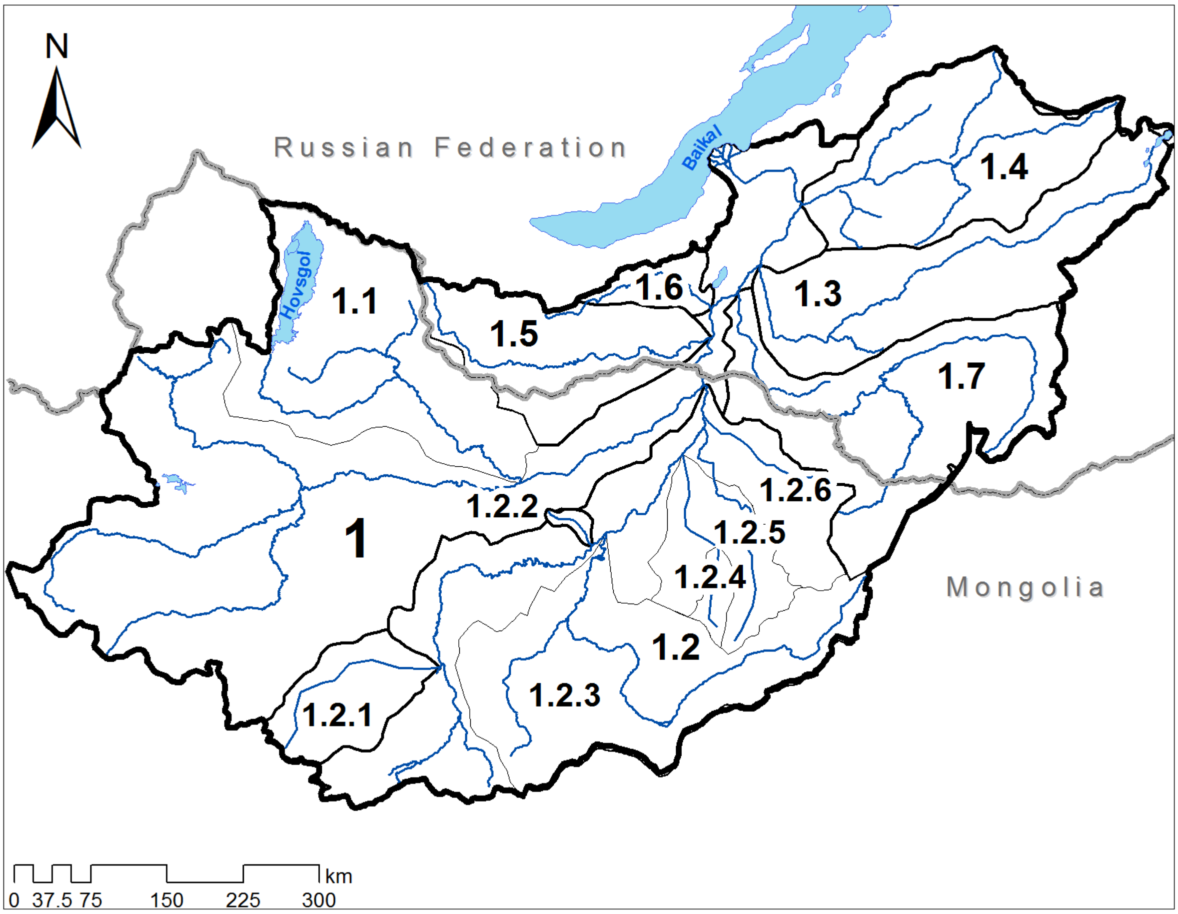

Figure 21 Geographic overview of the Selenga River Basin and key sub-catchments recognized as a responsible for the in-catchment discrepancies of water and sediment flow.

4.3 Data Compilation and Geodatabase Setup

We collected hydrological and water quality data from external sources and own projects carried out in the Selenga-Baikal Basin. While the discharge data are based on gauges operated by the hydrometeorological services of Mongolia and the Russian Federation and a few additional measurements performed by the project scientists, the situation is vastly different for water quality data for which there is no exhaustive database to this date. Therefore, we had to rely on (a) data published in scientific papers and (b) data collected by our own projects. Most of this data is from individual field campaigns rather than from regular monitoring, and therefore only available for limited periods of time. To facilitate the systematization of all collected information and provide access to all project's counterparts we set up a web-based geographical information system. We used the Geomixer.ru web GIS developed by Scanex company of Russia (www.geomixer.ru). It allows for multi-user spatial data upload and demonstration on several base maps, such as physical maps, elevation models, administrative maps (e.g. OpenStreetMap), or satellite imagery. Furthermore, the Geomixer.ru allows to export or access data via the WMS (web map service) functionality of desktop GIS products.

The uploaded data comprised

- general information on the Selenga, its basin and tributaries (e.g. river courses, lakes, government monitoring stations locations)
- daily time series of air temperature, air humidity and precipitation
- catchment parameters of the Selenga River and its tributaries (over 50 variables of topography (USGS Hydrosheds), vegetation and soil cover properties, permafrost distribution, land use and land cover characteristics, population, climatic variables)

water and sediment quality information from literature and sampling campaigns conducted by the authors and their research teams.

All of the working groups were provided with the access to the GIS system to upload the available data. Further applications of the system are described below.

provides an overview of published and own data used in the context of this study. Data were considered "usable" when they fulfilled at least the following characteristics: all sampling points had to be clearly described by geographic coordinates, and the methodology of data collection and laboratory analysis had to be documented.
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- water and sediment quality information from literature and sampling campaigns conducted by the authors and their research teams.

All of the working groups were provided with the access to the GIS system to upload the available data. Further applications of the system are described below.

Table 15 Data on water quality in the Selenga River Basin used for this study

Reference / Author	No. of sampling points	Measured parameter	Date of measurement	Short description
GEMS Database	2	DO, pH, water temperature NH_3, BOD, Cl, SiO_2	1990-2003, 2010	Monthly data for basic water quality data
Altansukh et al. 2012	15	SS, DO, BOD5 Cations: Ca^{2+}, K^+ , Mg^{2+}, Na^+, NH_4^+ Anions: Cl^-, HCO_3^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	1998-2008	Investigation of spatial and temporal trends of water quality in the Tuul River
Brumbaugh et al. 2013	15	Ag, As, Ca, Cd, Cl, Co, Cr, Cu, Hg, K, Ni, Mn, Mo, Pb, Rb, Sb, Se, Sn, Sr, Ti, V	2010	Elemental analysis of streambed sediment and subsurface floodplain soil in the Tuul and Orkhon River Basin
KEI 2008	28 (16 Mongolia, 12 Russia)	DO, hardness, EC, mineralization, pH, SPM concentrations, TDS, turbidity, water temperature As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn Anions: CO_3^{2-}, HCO_3^-, Cl^-, $SO4^{2-}$, NO_2^-, NO_3^- Cations: Na^++ K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, NH_4^+ Chlororganic pesticides: DDD, DDE, DDT, HCB, HCCH alipatic hydrocarbons, PCB; PAH;	2007	Identification of distribution of pollution sources to estimate the degree of water pollution in the Selenga River Basin

		Phenols; POP		
KEI 2009	37 (23 Mongolia, 14 Russia)	DO, hardness, EC, mineralization, pH, SPM concentrations, TDS, turbidity, water temperature As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn Anions: CO_3^{2-}, Cl^-, HCO_3^-, NO_2^-, NO_3^-, $SO4^{2-}$ Cations: Ca^{2+}, Fe^{2+}, Fe^{3+}, K^+, Mg^{2+}, Na^+, NH_4^+ Chlororganic pesticides: DDD, DDE, DDT, HCB, HCCH PCB; PAH	2008	Identification of distribution of pollution sources to estimate the degree of water pollution in the SRB water management system analysis, analysis of driving forces and pressure on the system
KEI 2010	30 (19 Mongolia, 11 Russia)	COD, DO, hardness, EC, mineralization, pH, SS, TDS, turbidity, water temperature As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn Anions: CO_3^{2-}, Cl^-, HCO_3^-, NO_2^-, NO_3^- , SO_4^{2-} Cations: Na^++ K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, NH_4^+ TN, TP, PO_4-P, NO_3-N, NO_2-N, NH_3-N	2009	Assessment of environmental state of SRB as a prerequisite for IWRM planning
Inam et al. 2010	14 (groundwater)	pH, SS NO_3, SO_4, PO_4 Al, As, B, Ca, Cd, Cl, Cu, F, Fe, Mg, Mn, Ni, Pb, Se, U, Zn	2009	Environmental impact assessment of Boroo Gold Mine. No coordinates of sampling points.

Mongolian Aquatic Insect Survey	30	DO, EC, turbidity, water temperature PO_4^{3-}, TN, NO_2^-, NO_3^-, NH_3	2006	Water quality investigation in the Selenga River
Nadmitov et al. 2014	76	As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	2007 - 2009	Assessment of metal pollution in river water in the Selenga River Basin. Based on the studies described in KEI 2008-2010.
Nriagu et al. 2011	129	Al, As, Cd, Co, Mn, Pb, Se, U, Zn	2011	Assessment of groundwater quality in Ulaanbaatar. No coordinates of sampling points.
Sorokovikova et al. 2013		Cations: Ca^{2+}, K^+, Mg^{2+}, Na^+ Anions: Cl^-, HCO_3^- , SO_4^{2-} TP, P_{inorg}, TN, TOC, NO_3^--N, NH_4 PAH Total coliforms, enterococci	2010	Assessment of Selenga River water quality near the Russian-Mongolian border
Thorslund et al. 2014		Al, As, Cu, Fe, Mn, Pb, Zn		Data for water quality in the Tuul and Orkhon rivers, compiled from different data sources
Own Data				

UFZ Magdeburg, Germany	52	As	2011	As screening using the ArsoLux biosensor system (partially with ICP-MS controls) in the Kharaa, Eroo and Orkhon River Basins.
UFZ Magdeburg, Germany	50	TP, TN, TOC Dissolved elements: Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Rb, Sr, Ti, Tl, U, V, Zn	2013	26 samples for water quality plus 24 samples for sediment quality, taken in the Tuul, Kharaa, Orkhon and Selenga River Basins
Batbayar 2012	47	As	2011-2012	As screening using the ArsoLux biosensor system (partially with ICP-MS controls) in the Tuul, Kharaa and Orkhon River Basins
UFZ Magdeburg, Germany (partly published in Batbayar et al. 2015)	94	TN, TP, TOC, DOC Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, Ti, Tl, V, U, Zn	2014 - 2015	Assessment of water quality in the Mongolian part of the Selenga River Basin

		Cations: Ca^{2+}, K^{+}, Mg^{2+} , Na^{+} Anions: Cl^{-}, SO_4^{2-} Organic matter and nutrients: DOC, TOC, TN, TP		
Pfeiffer et al. 2015	309	As For some samples: Cl, Cr, Cu, Fe, K, Mn, Na, Sb, U; pH, EC, TDS	2007-2013	As survey along the Kharaa, Orkhon, Tuul, Sharyn and Eroo rivers in Mongolia
Moscow State University field campaigns: July-August 2011 June 2012 September 2013 August 2014 March 2015	 56 55 35 53 22	Cations: Ca^{2+}, K^{+}, Mg^{2+}, Na^{+} Anions: Cl^{-}, HCO_3^{-},SO_4^{2-} pH, DOC, POC Concentrations in bottom sediments and in suspended and dissolved loads: Li, Be, B, Na, Mg, Al, Si, Psum., S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Iu, Pt, Au, Tl, Pb, Bi, Th, U TP, mineral P, Si SPM concentrations (g/m3), SL(t/day), SPM in the certain classes	2011-2015	Tuul River, Orkhon River, Eg River, Eroo River, Khangal River, Selenga River, Kharaa River Dzhida, Temnik, Chikoy, Hilok, Orongoy,Uda, Itantsa, Kiran, Kudara, Zheltura, Udunga , Suhara, Tugnui, Menza , Buy, Bryanka, Ilka, Chelutay, Kurba, Kodun, Kizhinga, Ona

Explanations:

TN = total nitrogen; TOC = total organic carbon; DOC = dissolved organic carbon; TP = total phosphorus; SPM– suspended particulate matter; SL = sediment loads; TDS = total dissolved solids

4.4 Water runoff modelling

To assess the variability of water resources in the Selenga river basin we used the ECOMAG model developed in the Water Problems Institute of the Russian Academy of Sciences (Motovilov 1999, Motovilov and Gelfan 2013). The ECOMAG is a semi-distributed physical process-based watershed hydrological model. The model accounts for watershed parameters taken from GDB, such as elevation, slope, aspect, land use, soil type, stream network and meteorological stations locations for weather variables distribution. The parameters are spatially distributed by partitioning the watershed into units called elementary basins. Each elementary basin accounts for different combinations of the parameters by computing the fraction of these combinations within it. In each elementary basin the processes of snow accumulation and melt, soil freezing and thawing, water infiltration into unfrozen and frozen soil, evapotranspiration, thermal and water regime of soil, overland, subsurface and channel flow are described. The water balance is computed in each elementary basin on a daily time step. The basin response is routed to the outflow point through a calculated river network.

The model is calibrated against streamflow measurements and, if available, measurements of the internal basin variables (snow characteristics, soil moisture, groundwater level, etc.). The ECOMAG model is driven by daily time series of surface air temperature, air humidity and precipitation. The model has been extensively tested in various types of catchments around the world (see Motovilov et al. 1999, Motovilov and Gelfan 2013, and Gelfan et al. 2015). The model was set up using the spatial data stored in the web-GIS, namely digital elevation model USGS HydroSheds (Lehner, et al, 2008), land cover database GLCC2000 (Bartholomé & Belward, 2005) and soil type database from FAO HWSD (Fischer et al. 2008), and river gauging stations locations.

For the initial parameters estimation, the ECOMAG model for the Selenga basin was driven by daily weather time-series from the ERA-Interim dataset (Dee et al. 2011) for the period of 1996 – 2005 on a 0.5° by 0.5° spatial grid and calibrated against the observed flow discharges from the most downstream gauge of Kabansk. The estimated Nash-Suttcliffe model efficiency criteria for daily discharges reached 0.85, which shows a good agreement between the modelled and the observed streamflow. Linear correlation coefficient between observed and simulated annual runoff volumes reached 0.72.

4.5 Sediment load modelling

Despite recent progress in setting up hydrodynamical models to predict sediment loads and in-channel processes at the level of single channel reaches (along the mined reaches of Tuul river by Pietron et al. 2015; and within reaches of almost 300 km of the Tuul and Orkon river by Chalov et al. 2015) there is still a need to link the sediment loads to the catchment characteristics. In this study we were aimed at developing a basinwide sediment model for each particular hydrological season. Data for 50 subcatchments was taken from the geodatabase for the periods of Moscow State University field campaigns: July-August 2011; June 2012; September 2013; August 2014; March 2015 (table 15).

Each season was characterized by the set of variables which was linked with SSC, daily sediment load and SPM grain size compositions. We tested the full data bank to find correlations between sediment load and catchment parameters. A step-forward procedure was used. On the first stage simple linear correlations (Pearson's r) were computed to explore relationships among sediment loads / characteristics and catchment properties: $r_{xy}= C(x, y)/\sigma_x\sigma_y$ for those properties which yielded significant correlations ($|r_{xy}| > 0, 5$, ($r_{xy}= C(x, y)/\sigma_x\sigma_{y)}$, mixed model analysis using STATISTICA V. 8.0 (StatSoft, 2008) was used. Linear regression model SelengaStatistic based on multivariate analysis ($y_i= b_1x_1+b_2x_2+ \ldots + b_nx_n +b_0 + c_i$), was developed for each hydrological season.

In addition, the sediment budget model SedNet was used to estimate the SS budget in the main subcatchments (fig. 21) of the Selenga River. The model applicability was tested in a cold semi-arid region before (Theuring et al, 2013). The model uses spatial data layers on land use, soil properties, precipitation and topography (DEM), focusing on the spatial patterns in sediment generation and movement. DEM derived stream network is divided with the help of linked stream node points, and the catchment is divided into subcatchments and river reaches. Each link extends between adjacent stream junctions or nodes and has a subcatchment that drains into the link between its upper and lower nodes. This allows the construction of the sediment budget for each section of the river network by calculating sediment delivery, transport and floodplain deposition. For this purpose, SedNet calculates surface and bank erosion, as well as floodplain deposition with separate submodels. The model calculates the sediment delivery following a load by source approach, calculating contributions from surface riverbank and gully erosion as separate sources (Rustomji et al., 2010). The sediment load output at each stream junction node is calculated by taking the difference between the supply of sediment from the internal subcatchment and tributary streams and the loss of sediment by deposition on the floodplain and in the channel. Surface erosion sediment supply is calculated on the basis of the revised universal soil loss equation (RUSLE) soil loss estimation (Renard, 1997, Priess et al. 2014).

4.6 Water quality modelling

The trend in water quality in terms of organic pollution was calculated with the WaterGAP3 modelling framework for the entire river basin for the time period 1990-2010. The model framework operates on a 5 arc minute global grid and includes a large-scale hydrology model, five sectoral water use models and a water quality model (WorldQual). Based on time series of daily climatic data, the hydrology model calculates the daily water balance for each grid cell, taking into account physiographic characteristics like soil type, vegetation, slope, and aquifer type. Runoff generated on the grid cells is routed to the catchment outlet on the basis of a global drainage direction map (Lehner et al. 2008), taking into account the extent and hydrological influence of lakes, reservoirs, dams, and wetlands. Spatially distributed sectoral water withdrawals and consumption are simulated for the five most important water use sectors: irrigation, livestock based agriculture, industry, thermal electricity production, and households and small businesses. Countrywide estimates of water use in the manufacturing and domestic sectors are calculated based on data from national statistics and reports and are then allocated to grid cells within the country based on the geo-referenced population density and urban population maps (Flörke et al. 2013). Irrigation and livestock water uses are calculated on the grid cells. As part of the model framework, the large-scale water quality model WorldQual calculates loadings to rivers on the basis of sectoral wastewater volumes and return flows as calculated by the water use models as well as the resulting in-stream concentrations based on the hydrological information simulated by WaterGAP3 following the standard equations of water quality dynamics. Up to now the model has been used to simulate biochemical oxygen demand (BOD5), faecal coliform bacteria (FC), total phosphorus (TP), total nitrogen (TP) and total dissolved solids (TDS) (Malve et al. 2012; Voß et al. 2012; Reder et al. 2013; Reder et al. 2015; Williams et al. 2012). All models are soft-linked and communicate through fluxes on a monthly temporal resolution.

The climate input for the hydrology and irrigation models consists of precipitation, air temperature and solar radiation. Here we make use of the WATCH data set (Water and Global Change) applied to ERA-Interim data (WFDEI) for the time period 1979-2010 (Weedon et al. 2014). The climate data have a temporal resolution of one day, and a spatial resolution of 0.5° by 0.5° (latitude and longitude, respectively) downscaled to the 5 arc minute grid cells.

Time series of domestic, manufacturing and cooling water use for the time period 1990-2010 were used from Flörke et al. (2013), livestock water use was calculated according to the approach in Alcamo et al. (2003) but with data on livestock numbers from FAO (FAOSTAT 2015).

The WaterGAP3 modelling framework was used to estimate organic pollution loads generated within the river basin from different point and diffuse sources. Based on the pollution loads the in-stream concentrations are calculated for each grid cell and routed through the river network. Sectoral loadings considered in the modeling approach are domestic-sewered, domestic-non sewered, irrigation, animal wastes, urban surface runoff, fertilizer, and background concentration. Non-conservative substances are reduced by decay and decomposition, e.g. solar radiation, and sedimentation.

4.7 Results and Discussion

4.7.1 Catchment Characterization

The Selenga River is the receiving water body for several tributaries from Mongolia and Russia that vary vastly with regard to their catchment size and characteristics. Based on GDB, the features of the key parameters are listed in the Table 15.

In Mongolia, the largest tributary is the Orkhon which itself is fed by several larger but also some much smaller rivers. The Tuul, Khangal and Kharaa pass by the cities of Ulaanbaatar, Erdenet and Darkhan respectively. These three cities concentrate almost half of the country’s population and the major part of industrial activities. While the Tuul directly passes to large areas of gold mining, the Khangal is situated downstream of the copper-molybdenum mining complex of Erdenet. The Kharaa river basin is also home to several gold mines. Gold mining is also found on Eroo and Sharyn River. Moreover, the latter also flows through the coal mining town of Sharyngol. The Khangal and Sharyn are the two river basins with the largest share of land degraded by mining activities. The river basins of the Eg and the Eroo are characterized by a mountainous terrain and forest covers of more than 50%, whereas all other Mongolian subbasins of the Selenga are predominantly covered by grassland that is typically used as pasture and has locally been transformed into large plots of agricultural land. (Seasonal) permafrost is present only in the most upstream subbasins.

The basins of the Russian tributaries of the Selenga have a much higher degree of forest cover than their Mongolian counterparts, but are typically free from seasonal permafrost. They tend to receive a slightly higher precipitation. Major settlements in the Russian part of the Selenga River Basin include the Buryatian capital of Ulan Ude and the mining town of Zakamensk which is located on the Dzhida River.

Table 16 Environmental Characteristics of the Selenga River Basin and Sub-Catchments (based on GDB)

No.	Basin / Subbasin	(Sub-) Catchment size [km²]	Average elevation [m]	Forest cover [%]	Degraded land from mining [km² / 1000 km²]	Seasonal Permafrost [km²]	Average Precipitation [mm]
1	Selenga	447.000	1406	37,5		9,5	314
1.1	Eg	42.412	1653	50,8	0,02	0	333
1.2	Orkhon	129.711	1422	14,08	0,92	36	285
1.2.1	Tamir	12.965	1966	12,36	0,01	85	322
1.2.2	Khangal	910	1220	22,8	36	0	129
1.2.3	Tuul	48.573	1375	5,05	0,75	34	243
1.2.4	Kharaa	16.310	1191	21,04	1,14	0	296

1.2.5	Eroo	11.555	1255	65,98	0,55	0	362
1.2.6.	Sharyn	897	1639	28,85	3,32	0	299
1.3.	Khilok	38.303	998	80,27	0,79	0	316
1.4.	Uda	35.088	952	81,71	0,17	0	290
1.5.	Dzhida	25.159	1292	71	0,6	0	327
1.6.	Temnik	5.844	1222	54,2	1,92	0	262
1.7.	Chikoy	44.914	1226	82,79	0,54	0	390

4.7.2 Water runoff modelling and projections

According to Törnqvist et al. (2015), who compared projections of future climate changes in the Selenga basin using a number of CMIP5 carbon emission scenarios, this area is expected to experience a significant increase in both annual air temperature and precipitation amount. To assess the variability extent of the Selenga river annual runoff under changing conditions we conducted several ECOMAG model runs with the weather forcing altered by a possible change in air temperature and precipitation amount. This approach to assess the hydrological system response to altered climate is known as “the delta change” method (Hay et al., 2000). The changes were applied to the same ERA-Interim reanalysis time-series as used for model calibration. The results are given Table 17. The experiments showed that the significant increase of annual temperature by 3°C leads to small changes in annual runoff, while the change in precipitation amount by 20% may result in runoff increase almost by half. In case of a decrease in annual precipitation (which was not projected by any of the above mentioned scenarious), the runoff would also decrease.

Table 17 Changes in Selenga’s annual runoff volume under different climate forcings

Forcings		Changes in mean annual air temperature, °C				
		-1	0	+1	+2	+3
Changes in annual precipitation amount, %	-10	-20.2	-19.9	-20.3	-20.8	-21.6
	0	-0.28	0	-0.33	-1.2	-2.0
	+10	21.3	21.7	21.3	20.5	19.5
	+20	44.2	44.7	44.4	43.5	42.3

4.7.3 Sediment load modelling

Water runoff changes both land use impacts induced comprehensive response of the river system. There has been a substantial decline in sediment yield of Selenga River (from 5832 t/day to 3015 t/day) and its main tributaries in the Russian part of the river basin since 1996 (Chalov et al, 2015). In the upper part of the basin where an absence of routine monitoring of sediment loads precludes statistical analyses of the sediment trends, the assessment of the sediment yield decrease was based on the comparison between SPM concentrations measured during the campaigns of 2011-2014 and historical field campaigns of 1934-1936 (Chalov et al., 2015).

The calculated eroded sediment yields using SedNet model (fig. 22) range from 5 to over 1000 t/year km^2 with an 470 t/year km^2 average throughout a catchment which is in line with large scale sediment budget modeling for Kharaa river system (Theuring et al, 2013). The calculation of the budget resulted in a suspended sediment export of 2.6 mln t/year for the whole Selenga catchment, thus fitting well with recent estimates of 2.5 mln t/year which are based on the Selenga's outlet monitoring station (Chalov et al, 2015). The spatial distribution of the erosion potential based on RUSLE application follows mostly orographic drivers, with little relation to human impact. Anthropogenic pressure could be seen only within small impacted catchments. The highest annual SPM concentrations were predicted for the Khangal (139 t/year km^2) and Modonkul Rivers (114 t/year km^2), which corresponds to the observed increase of sediment and pollutants fluxes (Chalov et al, 2015) below a large copper-molybdenum mine-mill complex and wolfram-molybdenum mining and processing factory respectively. In certain catchments, an underestimation of the present anthropogenic conditions could be seen but not incorporated in the model at its present stage. This particularly includes the heavy pollution with sediments due to insufficient wastewater treatment in Ulaanbaatar which explains over 90 % of the sediment yield in the Tuul downstream (Pietron et al., 2015).

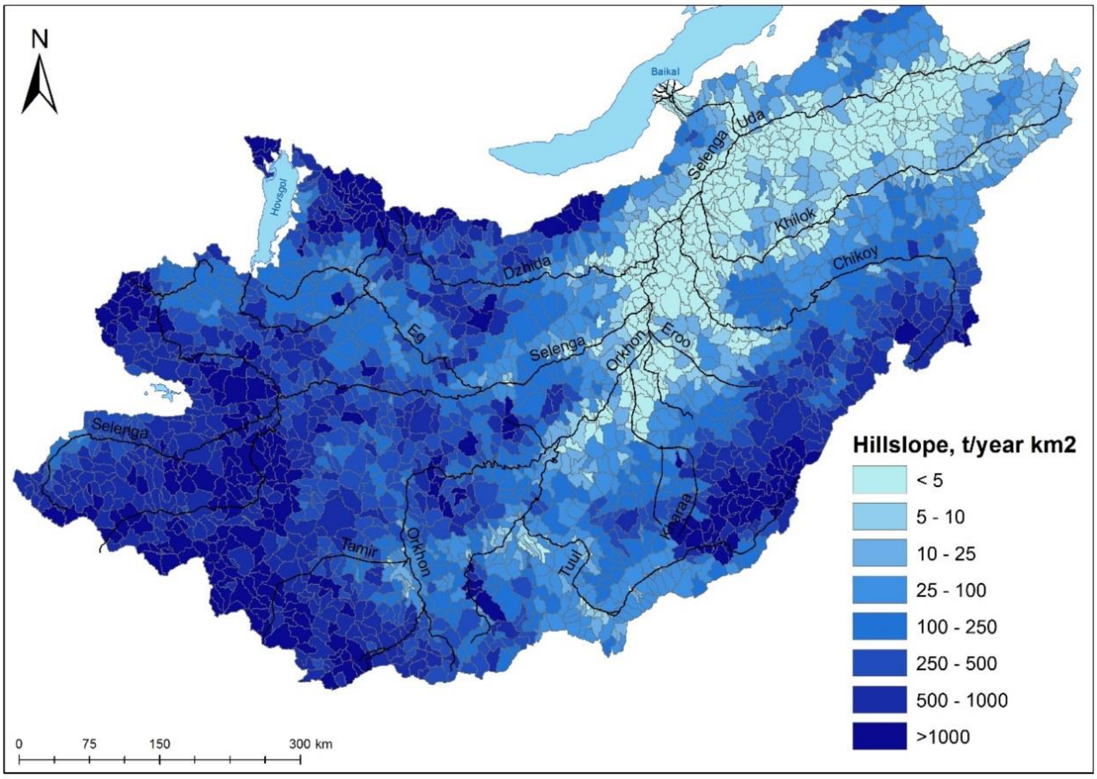

Figure 22 Modeled eroded sediment yields (B) in the Selenga River, t/year km2

The mostly environmental drivers of the sediment loads formation are also evidenced by the basinwide multivariate model SelengaStatistic. Among the monthly SPM concentration almost all were related to catchment vegetation (ТР – tundra, % of the catchment area; ГЛ – mountain forests, % of the catchment area; РС – flat steppes, % of the catchment area), permafrost (SM – seasonal permafrost, % of the catchment area; НВУ – areas with nearsurface permafrost, % of the catchment area) and glaciers (ВЛ – glaciers, % of the catchment area) or topology (I – slope) with an exception of types of pastures (ПСТБ - % of the catchment area), which were the only land use drivers in the basinwide model:

S(July)=0.55СМ+0.44ТР-0.12ВЛ-63.9

S(September)=0.68РС-0.02ГЛ+0.22I-0.51СГ+22.8

S(August)=0.46РС+0.33КП+0.17ДР+0.14Л+0.24ПНР-0.17I-9.4 (1)

S(March)=1.2ПН+0.11I+0.46ГЛ+0.36НВУ+0.62ПСТБ-55.2

These results indicate that in future hydroclimatic and associated environmentaltrends and variations will remain the main the driver of sediment and contaminants fluxes over the river system. Taking into account the expected change in temperature and precipitation, shifts in sediment transport patterns are particularly likely during extraordinary meteorological events. Among the main driving forces of the sediment transport are permafrost thaw and shifts in soil temperature and moisture which exert a strong control on soil aggregate stability, and thus on soil erosion intensity.

4.7.4 Analysis of trends in organic pollution

Figure 23 Annual BOD loadings in the Selenga - Baikal River Basin between 1990 and 2010

Between 1990 and 2000 a rapid decrease in total annual BOD loadings from 24,573 t/a to 18,623 t/a could be detected. This was followed by an increase to 22,208 t/a in 2010 (see figure 23). The first period (1990 to 2000) is clearly influenced by the collapse of the Soviet Union, while the second period (2000 to 2010) reflects Mongolia's progress in the political and socioeconomic transformation to a market economy. Nevertheless, for all three time steps domestic waste water is by far the most important contributor (65-80 %), especially waste water from sewered areas (≈55 %). The importance of the manufacturing sector dropped by nearly two-thirds (64 %) from 1990 to 2000, but subsequently doubled before 2010. Other contributors like animal wastes and urban surface runoff play only a minor role (2.5 – 4 %).

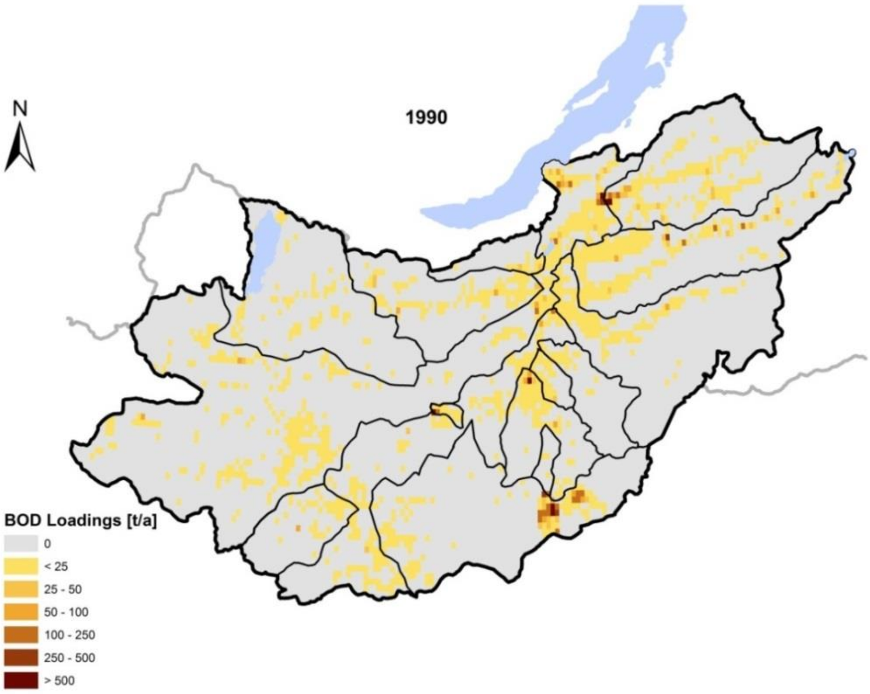

Figure 24 Spatial distribution of annual BOD loadings in the Selenga Baikal River Basin (1990)

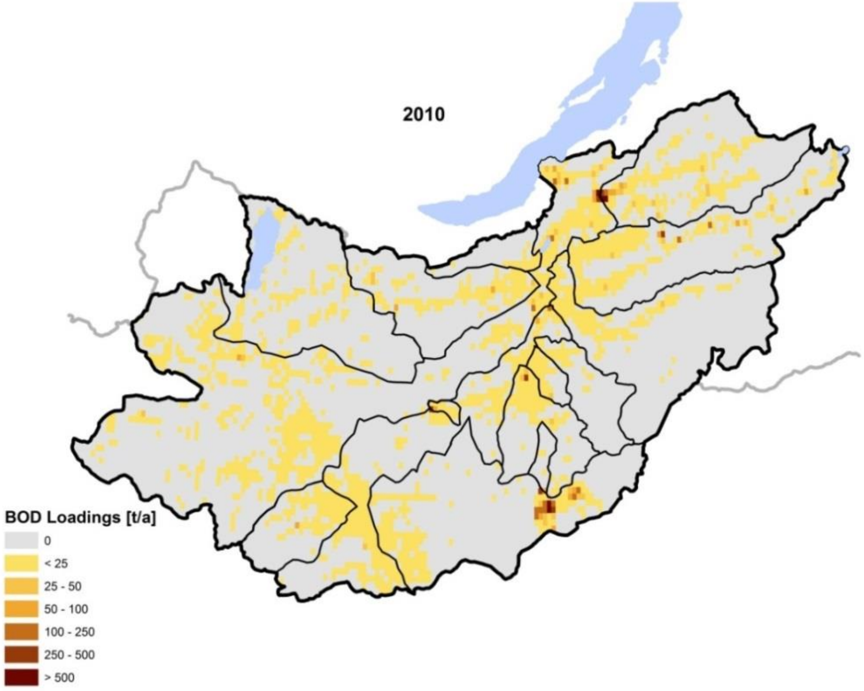

Figure 25 Spatial distribution of annual BOD loadings in the Selenga Baikal River Basin (2010)

The spatial distribution of BOD loadings (see Figure 24, 25) shows hotspots around the major settlements, especially Ulaanbaatar and Ulan-Ude. These two regions together accounted for more than 50 % of the total loadings in 2010 and may therefore be considered regional loading hotspots. The years 1990 and 2000 show a very similar picture in terms of spatial pattern, but differ in the total amount of BOD loadings, in particular around urbanized areas.

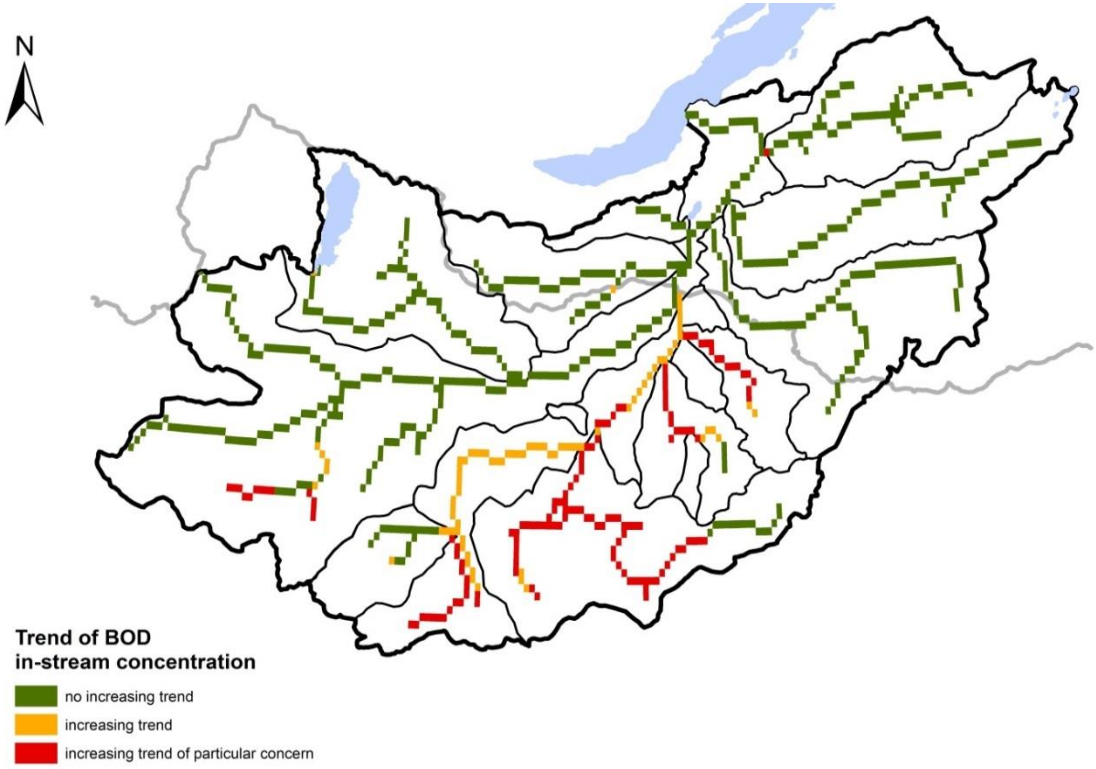

Figure 26 Change of mean annual BOD concentrations between 1990s and 2010s

According to international guidelines (e.g. DWA 1996, CPCB 2007-2008) three classes of BOD concentration were used to categorize organic pollution in the Selenga-Baikal River Basin (low: <4 mg/l, moderate: 4 – 8 mg/l, and severe >8 mg/l). In some parts of the Selenga river system, in-stream concentrations rose from the low class in 1990 to the moderate class in 2010 ('increasing trend' category in Figure 26). In other cases, the simulated in-stream concentration reached the severe class (> 8 mg/l) in 2010, or remained in this class but further increased by 2010 ('increasing trend of particular concern' in Figure 26). The strongest increases were observed in the Orkhon River Basin, with an increasing trend of particular concern in three of its subbasins (Kharaa, Eroo, and Tuul) and near Ulan-Ude (see Figure 26). By contrast, in most of the western and northern part of the Selenga River Basin, no shift to higher classes could be observed even though in-stream concentrations increased in large areas (but without class change).

4.7.5 Further Water Quality Problems

Anthropogenic water quality impairments in the Selenga River Basin show spatial pattern that are to a large degree related to the location of urban and mining areas (Batbayar et al. 2015, Koshaleva et al. 2015). They are of relevance both locally and in the context of contaminant transport towards the Selenga River Delta and Lake Baikal. In order to come to a comprehensive assessment of current water quality issues in the Selenga River Basin, we compiled data from literature and our own fieldwork. Table 17 provides a detailed overview about the currently known water (and sediment) quality problems in the subbasins of the Selenga. However, for the interpretation of the results it is important to keep in mind that environmental monitoring in the region has so far been quite limited (Karthe et al. 2015d), with very strong variations between different subbasins.

Table 18 Water Pollution Problems the Selenga River Basin and Sub-Catchments

No.	River	Characterization of Water Quality	Sources
1	Selenga	Mongolian Part	Nadmitov et al. 2014
		- elevated Fe and Pb concentrations (with Fe exceeding WHO drinking water guidelines) - elevated concentrations of Al, As, Cu, Fe, Mn and Ni downstream of the outlet of the Orkhon river	Sorokovikova et al. 2013, Thorslund et al. 2012; Own data
		Russian Part	
		- recent increase in sulfate and nutrient concentrations near the Russian-Mongolian border - among the most polluted Russian rivers in its downstream section, with elevated concentrations of As, Cd, Cu, Fe, Mn, Zn (particularly near Ulan Ude); concentration factors of 1 to 2 times for As, Cr, V, U; 3 to 4 times for Co, Fe Mn, Ni, V, Zn; and 5 to 10 times for Cu and Pb below Ulan-Ude - PAHs occasionally exceed the maximum allowable concentrations for drinking and surface waters - microbial pollution (E. coli, enterococci) is problematic during low flow situations	
1.1	Eg	- close to natural background conditions	Own data
1.2	Orkhon	- elevated levels of Al, As, Ca, Cu, Fe, Mo, Mn, Mg, Ni, U as well as SO_4^{2-} and nutrients documented along the Orkhon - very high As concentrations (190µg/L in one sample) just upstream of the confluence of Tuul and Orkhon - contaminant concentrations (Al, As, Cu, Fe, Mn, Pb and Zn) typically below the levels found in the Tuul - elevated Cu concentrations in sediments downstream the outlet of the Khangal river - high levels of metal contamination downstream of Darkhan city (frequently exceeding Mongolian surface water guidelines) - elevated concentrations of As in surface and drinking water in various parts of the Orkhon river basin	Brumbaugh et al. 2013, Nadmitov et al. 2014, Thorslund et al. 2012; Own data
1.2.1	Tamir	- close to natural background conditions	Own data
1.2.2	Khangal	- high concentrations of Cu in the upper part (near the Erdenet Cu-Mo mine) - elevated nutrient concentrations; - massively elevated levels of Ca^{2+}, K^+, Mg^{2+}, Na^+ and Cl^- , HCO_3^-, SO_4^{2-} (by two orders of magnitude vs. natural background conditions)	Brumbaugh et al. 2013; Own data

1.2.3	Tuul	- elevated concentrations of Al, As, Cu, Fe, Mn, Mo, Ni, Pb, U, V, Zn as well as Na$^+$, Cl$^-$ and SO$_4^{2-}$ documented along the river - Selbe river (tributary to the Tuul in Ulaanbaatar): elevated Pb, Zn and high nutrient levels; - most polluted river in Mongolia (in terms of metals exceeding guidelines) near Ulaanbaatar; Al, Cu, Fe, Mn, Mo, V, Zn below Ulaanbaatar increase from 3 to 9 times at low water period and from 9 to 52 times at summer flood period - 50 to 100 times increase in nutrient levels levels below Ulan-Baatar during winter - highest concentrations of Fe, Mn and Zn near Ulaanbaatar and Zaamaar mining area - dissolved concentrations of Al, As, Cu, Fe, Mn, Pb and Zn typically increase below Zaamar - TP concentrations double to triple downstream of Zamaar - elevated U levels detected in groundwater, sometimes exceeding the WHO drinking water guidelines - As levels in the Tuul are close to the limits of WHO drinking water guideline	Brumbaugh et al. 2013 Nadmitov et al. 2014, Nriagu et al. 2011, Stubblefield et al. 2005, Thorslund et al. 2012; Own data
1.2.4	Kharaa	- elevated concentration of Al, As, Cd, Cu, Fe, Mn, Ni, Pb, U, Zn documented along the river - Al, As, Cu, Fe, Mn, Pb, U and Zn higher than the maximum allowable concentration in the monitoring and heap leach wells around Boroo gold mine; Boroo (tributary to the Kharaa): elevated As and Hg concentrations, with elevated levels of As in the Kharaa downstream of the Boroo confluence (90µg/L in one sample) - most polluted sections near Darkhan City, with high concentrations of As, Cd, Cu and Mn (frequently exceeding the MNS (1998) guidelines) - increasing levels of N and P since 2000, with a clear longitudinal trend (highest concentrations downstream of Darkhan) - elevated As concentrations downstream of mining sites, in the ash basin of Darkhan's thermal power station and in drinking water of Khongor Soum	Brumbaugh et al. 2013, Hofmann et al. 2010, Inam et al. 2011, Nadmitov et al. 2014; Own data
1.2.5	Eroo	- elevated levels of Al, Fe and nutrients (TN, TP) measured in the downstream section	Stubblefield et al. 2005; Own data
1.2.6.	Sharyn	- elevated concentrations of Al, As, Cd, Cu, Fe, Mn, Ni, U in the downstream section (partly exceeding the MNS (1998) guidelines) - elevated nutrient levels in the downstream section	Nadmitov et al. 2014; Own data
1.3.	Khilok	- elevated concentrations of As, Cd in suspended sediments	Nadmitov et al. 2014; Own data
1.4.	Uda	- High levels of Zn near Ulan Ude; - elevated levels of suspended As, Cd, Mo, W in the downstream part	Nadmitov et al. 2014; Own data
1.5.	Dzhida	- elevated concentrations of Cd, Mn, Pb in the upstream reaches, indicating an independent source of metals originating in Russia - considerable heavy metal pollution around Zakamensk	Nadmitov et al. 2014; Own data

1.5.1	Modonkul	- total concentrations of Cd, Cu, Mn, Pb, Zn exceed permissible levels by one to two orders of magnitude - elevated levels of SPM in comparison with baseline values during low water season: Be (780x), Cd (650x), Cu (450x), Pb (100x), Zn (300x) - elevated levels of dissolved Be (90x), Cd (450-650x), Zn (80x), Cu, Mo, W (10x)	Own data
1.6.	Temnik	- Zn concentration exceed water quality guidelines	Nadmitov et al. 2014; Own data
1.7.	Chikoy	- no reported water quality problems	Nadmitov et al. 2014; Own data

Despite the differences regarding the water and sediment quality parameters measured and methodologies used in the studies included, their synopsis is an important step towards an integrated assessment of the current state of water quality in the Selenga River Basin. As shown by Table 17, a few tributaries that were investigated were found to be in a relatively pristine condition, including the Eg and Tamir rivers in Mongolia and the Chikoy River in Russia. On the other hand, all rivers passing by urban and mining areas show clear and multiple signs of water contamination, including elevated levels of nutrients and mining-related metals. According to present knowledge, at least the following elements (for which an elevation beyond natural background levels was detected in at least one sampling location) are of potential concern for surface water quality in (parts of) the Selenga River Basin: Al, As, Be, Cd, Cr, Co, Cu, Fe, Hg, Mn, Mo, Ni, Pb, U, V, W, and Zn. Even though not all of these elements are enriched in the Selenga's water, elevated levels for the underlined elements have been found in the Selenga's main channel.

4.8 Conclusions

The Selenga-Baikal Basin is a very sparsely settled region by international standards, but is characterized by significant and globally relevant changes in hydrology and water quality. Firstly, this highly continental region is affected by strong climate change signals and currently faces major land use changes due to the conversion of forests and steppe into agricultural land and mining areas. Mining is not only an important backbone of the regional economy, but also a major water user and polluter. Urban areas are limited to a few centers, but also represent hotspots of water withdrawals and water contamination.

Even though the discharge of the Selenga and many of its tributaries has been below long-term averages for most years since 1995, climate change which is predicted to lead to rising temperatures but also increasing precipitation will most likely lead to an increase in surface water discharge in the Selenga River and its tributaries. However, rising abstractions and a planned water diversion project from the Orkhon River may in the future counteract this positive trend. In the recent past, lower mean discharge rates resulted in reduced total sediment loads. However, it is important to understand both long-term and seasonal sediment transport variations, which have important implications for contaminant transport regimes and the morphodynamics of the Selenga river delta, the final biogeochemical barrier before the Selenga drains into Lake Baikal.

Water quality in the Selenga River system is strongly linked to discharge, but also shows clear spatial pattern that are largely determined by mining sites and urban areas. One important consequence are significant differences in water quality in the Selenga River Basin. Through the discharge of poorly treated waste water, urban areas constitute key sources of nutrients, BOD loadings and microbiological contamination. On the other hand, mining areas which exploit coal, Au, Cu, Mb and W resources are the sources of various heavy metal emissions. These are of localized concern when they affect drinking water resources or lead to bioaccumulation in fish, but are similarly relevant for regions further downstream including the Selenga Delta (where they are largely removed from the water but accumulated in the delta sediments) and ultimately Lake Baikal.

A good understanding of hydrological trends and changes in water quality in the Selenga River and its tributaries is an important prerequisite for water management. Science-based environmental management concepts in the region are the needed for at least three reasons: (1) to solve localized water-related challenges in the Selenga River Basin that show a strong spatial variation; (2) to ensure the protection of the Selenga delta’s and Lake Baikal’s unique ecosystems, and (3) to overcome disputes in transboundary water management between the riparian states, Mongolia and the Russian Federation.

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Chapter5. GIS based impact assessment of land use impacts on water quality in case of Kharaa River Basin

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GIS based impact assessment of land use impacts on water quality in case of Kharaa River Basin

5.1 Abstract

Watershed management and catchment scale studies are relevant to determining the impact of anthropogenic influences on water quality.

Effective analytical tools, such as geographical information systems (GIS) and multivariate analysis, help to deal with spatial data and complex interactions and are coming into common usage in watershed management. For the study region of this manuscript, the Kharaa River Basin (KRB), extensive research on chemical water quality has been conducted. However, a systematic analysis of the links between land use characteristics and water quality has been lacking to this date. This study investigated the relevance of landscape characteristics for water quality in KRB using GIS and multivariate analysis. In order to evaluate the impact of land use on chemical water quality, the whole catchment and sub catchments in relation to each sampling point were delineated and assessments of the water quality over three seasons were compared for 2014 (summer), 2015 (spring) and 2016 (autumn).

Keywords: Central Asia, land use, GIS, water quality

5.2 Introduction

Finding interactions between land use characteristics and water quality is relevant for managing land use based pollution in the sub catchment scale. However, it is not easy to explore how land use categories influence on water quality because of the large number of parameters and the complexity of the processes involved (Allan 2004; Baker 2006; Carey et al. 2013; Hofmann et al. 2015; Selle et al. 2013).

Generally, surface water can be contaminated by anthropogenic impacts in two ways: first, by point sources, such as waste water treatment discharge (Sliva et al.2001). Typical contaminants in this case include nutrients, pathogens and organic substances (Batbayar et al.2017). The second pathway involves typical non-point sources such as runoff from urban and agricultural areas. Non point sources are especially difficult to detect since they generally encompass large areas in drainage basins and involve complex biotic and abiotic interactions (Pfeiffer et al.2015; Solbe et al. 1986; Sliva et al. 2001). Mining is often considered as a mixed source because it may involve a direct discharge of wastewater but also more diffuse pollution which may for example originate from large mine tailings (Bayliss et al. 2012; Mighanetara et al. 2009).

Watershed management and catchment scale studies have become more and more relevant in determining the impact of anthropogenic influences on water quality. Effective analytical tools, such as geographical information systems (GIS) and multivariate analysis that are able to deal with spatial data and complex interactions, are coming into common usage in watershed management (Li et al. 2015; Sliva et al. 2001). In particular, vegetation cover, soil properties, intensity of land exploitation and distribution of settlement areas significantly affect runoff processes and transport of solids and solutes in catchments (e.g. Kroll et al.2009; Meisinger et al.1991; Miller et al.2011; Reimann et al.2010; Tomer and Burkart 2003; Tu 2011; Xie et al.2005).

Extensive research on chemical water quality and anthropogenic influences on surface water quality has been conducted in the KRB. Research findings include not only information on water quality pattern in the system of the Kharaa river and its tributaries (Batbayar et al.2017; Hofmann et al. 2015; Zandaryaa et al.2015), but also the identification of important pollutant sources (e.g. Karthe et al. 2016, Pfeiffer et al. 2015) and assessments of the ecological relevance of water pollution (Karthe et al. 2015; Kaus et al. 2017). However, a systematic analysis of the impacts of land use characteristics on water quality has been lacking so far.

In this study we used geographical information systems (GIS) and multivariate analyses (Principal component analysis (PCA), Redundancy analysis (RDA) and non-metric multidimensional scaling (NMDS) to investigate links between land use pattern and water quality in the KRB. For all sampling points along the Kharaa River, both the entire upstream catchments and the most intermediate sub-catchments were delineated. Statistical links were then investigated using water quality data collected for three different seasons.

5.3 Materials and Methods

5.3.1 Study area

The northern part of Mongolia is characterized by a highly continental climate with wide variations of annual, monthly and daily temperatures. The mean annual temperature is just below freezing and annual precipitation ranges between 250-400 mm. Winters are long-lasting (monthly mean temperatures are 0°C or below between October and March) and very cold (temperatures frequently drop below -25°C), while summers are not only warm, but also the time of the main rainy period from June to August, when about 70 % of the annual precipitation falls (Hülsmann et al. 2015; Menzel et al. 2011).

The KRB is the one of the sub-basins of the transboundary Selenga river basin (SRB), which is located between latitudes 47.883° and 49.633° N and longitudes 105.316° and 107.366° E and drains into Lake Baikal. The KRB is characteristic for many of the environmental changes occurring not only in the SRB (Kasimov et al. 2017, Malsy et al. 2017) but also larger parts of Central Asia (Karthe et al. 2017). Recently, this previously data-scarce region (Karthe et al. 2015) has been intensively studied, in particular with regard to mining-related water pollution (Batbayar et al. 2017; Inam et al. 2011; Kasimov et al. 2016; Lychagin et al. 2016; McIntyre et al. 2016). Similarly, significant pollution has been documented for the urban environment of Mongolia’s major cities (Fan et al. 2016; Karthe et al. 2016; Kasimov et al. 2016), a fact which comes particularly relevant in the light that most towns and cities are at least partly located within riverine floodplains.

The KRB covers an area of 14,534 km^2, which is situated north of Mongolia’s capital city of Ulaanbaatar. The Kharaa River’s tributaries originate from several relatively pristine valleys of the Khentii Mountains. In the midstream section, the Kharaa flows through an area with intensive agricultural usage (including large pastures), several small towns and gold mining activities. Finally, along its downstream section, agricultural areas are occasionally interspersed with larger settlements and some industry (Hofmann et al. 2015, Menzel et al. 2011). Downstream of Darkhan, the Kharaa discharges into the Orkhon River, which is the main tributary of the Selenga that feeds Lake Baikal. The long-term average discharge of the Kharaa River is approximately 12 m^3/s. The total population of the KRB is 147,000 (census data as of 2010, mean population density around 10 inhabitants km^2), with most of the inhabitants living in the city of Darkhan (about 75,000 inhabitants).

5.3.2 Field work

In total 52 river water samples were taken from the 12 sub-watersheds of KRB during three different seasons. Sampling sites were selected so that they represent natural background conditions as well as impacts by mining, agriculture/pastureland, and urban areas. During a first expedition, the water samples were collected in summer (between May and July 2014) when intensive mining activities were observed. During the second campaign in spring between March and May 2015, most of the samples were taken below ice cover. The last expedition was conducted in September 2016, which represents Mongolian autumn (more detailed information on the sampling procedure can be found in Batbayar et al.2017).

During the field work, water temperature, pH value, electric conductivity and dissolved oxygen were measured using a digital multimeter (MultiLine® Multi 3630 IDS, WTW GmbH, Germany). Sampling locations (coordinates and altitudes) were recorded by GPS (GPSMap 64, Garmin, USA).

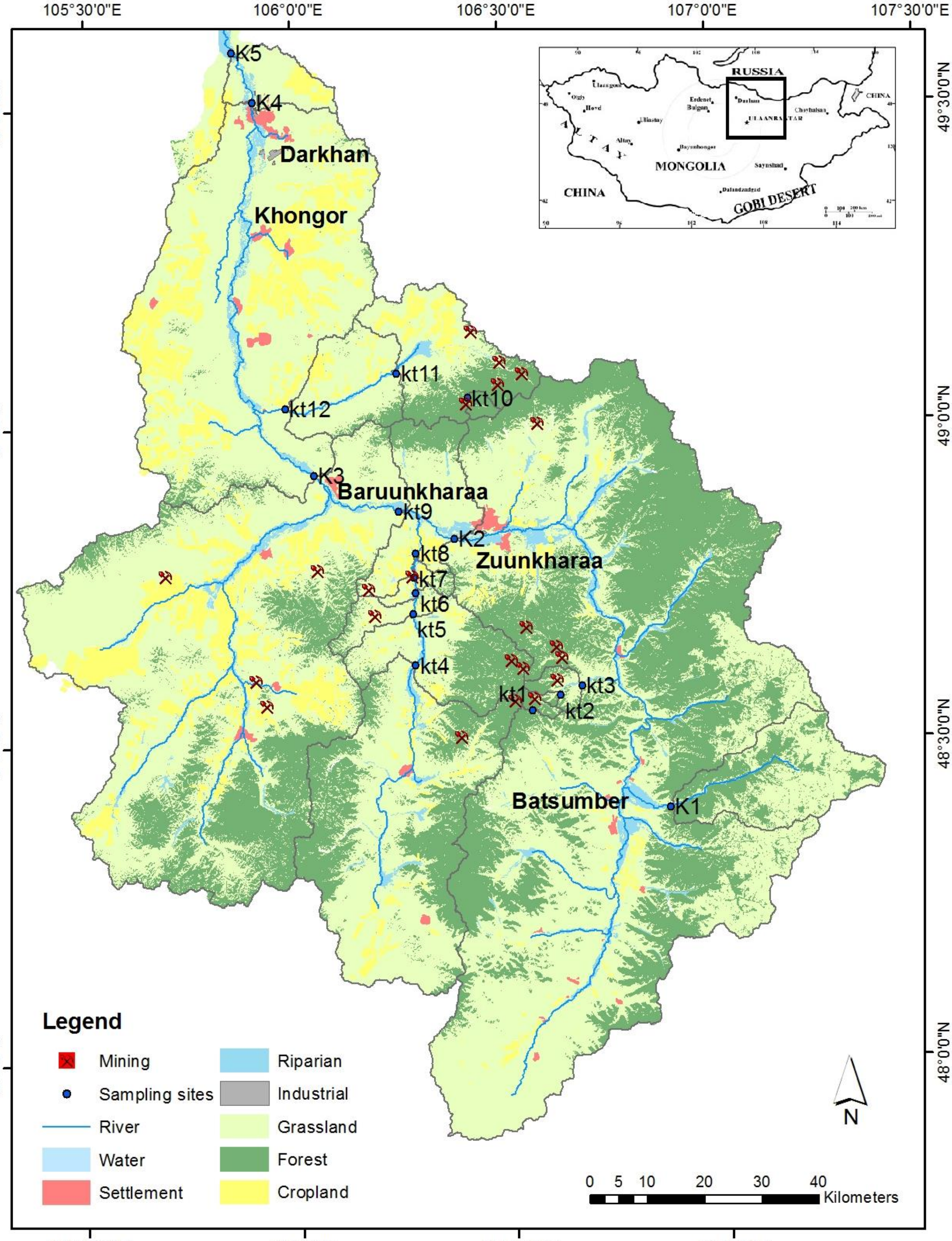


Figure 27 The map showing the sub-watersheds (grey border) for individual sampling sites in Kharaa River Basin.

Figure 28 Landuse, as seen here in the Mongolian capital Ulaanbaatar, can have a decisive impact on water quality (Photo: André Künzelmann).

5.3.3 Water quality analysis

In the first expedition the water samples were collected in summer (between May to July 2014) when intensive mining activities had been observed. During the second campaign in spring between March and May 2015 (see Fig. 27) most of the samples have been taken under ice cover. In order to prevent sample pollution by the gasoline auger, a hand ice auger was used for ice drilling. Deep samples were taken by an inertial pump. At that period the open mining companies had stopped their operations.

To determine the total concentration of trace elements, water samples were preserved with high purity nitric acid (HNO_3, pH < 2). The water samples for the nutrients were filtered through cellulose acetate filters with pore size of 0.45 µm (Minisart®, Sartorius, Göttingen, Germany) in the field. Afterwards all water samples were filled bubble-free into brown glass and Sarstedt® tubes. At the laboratory filtered samples were stored in a refrigerator at 4 °C. Most investigated elements were determined using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500c, Santa Clara, USA), inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer 2100 DV, Überlingen, Germany) or cold vapor atomic absorption spectrometry (CV-AAS, Perkin Elmer 4100 ZL, Überlingen, Germany). An ion chromatograph spectrometer (ICS, ICS-3000 Dionex, Waltham, USA) was used to determine the Cl^- and SO_4^{2-}concentrations. Organic carbon was determined after acidification for the discrimination of inorganic carbon (IC) as total concentration (TOC) and after filtration as dissolved fraction (DOC) using a carbon analyzer (Dimatoc®; Dimatec Essen, Germany). Total nitrogen, ammonia, nitrate, nitrite and soluble phosphorus were determined using continuous flow analysis (CFA; Skalar Analytical B.V., Breda, Netherlands). For total P and total N analysis, we stored water samples in 30 ml HDPE (high density poly ethylene) bottles and preserved them with 350 µl H_2SO_4 (1:4). For quality assurance, all used methods had been validated before application according to the guideline of the federal environmental agency of Germany (Wellmitz and Gluschke 2005). All data were compiled for each of the sample sites and are further referred to as WQ data.

5.3.4 GIS analysis

The Arc Map 10.5 software was used to determine the composition of the land use for each sub-watershed based on the landcover map published in Hofmann et al. 2015. For each water sampling site, sub-watershed boundaries were delineated using Arc Hydro Tools. In order to compare the land use impacts on water quality data 3 km buffer zones around river stretches in all sub-watersheds, the ArcGIS Spatial analysis/ buffer tool was used to extract land use data. The land use composition along with the sub-watershed area was calculated using tools incorporated into ArcGIS. In order to determine the area of the ongoing gold mining at sub-basin level, we used satellite images and Google Earth. As a result we provided two land use data sets: LU.a for the whole sub-watershed areas and LU.b for the buffer sites.

5.3.5 Statistical analysis of data

In order to analyze the basic characteristics of land uses and water quality parameters, descriptive statistics were used (STATISTICA version 13, Dell Inc. 2015). To reveal the general structure of the chemical water quality parameters and land cover data, principal component analysis (PCA) was performed with R studio *vegan* package (Oksanen et al. 2013). We used multiple regression to explore the general relationship between the land use and chemical water quality and regressed WQ-PCAs 1 and 2 on single landuse parameters of LU.a and LU.b.

Further relationships between water quality and land uses categories were drawn from a Redundancy Analysis (RDA) which enabled us to consider the water quality parameters due to land use categories related processes. For the calculation of the RDA we used R 3.4.0. (The R Foundation for Statistical Computing, 2017) according to instructions presented in Borcard et al. (2011). We tested different approaches: 1) including LU.a or LU.b or using both data sets as explanatory data, and 2) using all data or only summer/spring data (2014 and 2016). As additional explanatory geophysical variables (GEO) we included altitude (*alt*) and X°- and Y°- coordinates of the sampling point, size of sample basin, river km to the sample point before (*distance*), total river km of sampling site (*river km*), year (*season*) of sampling, water temperature (*t*°) and pH value measured during sampling. After a first calculation of the model we checked the variance inflation factor (VIF) and deleted in consecutive trials all used parameters with VIFs >10 (VIFD). The remaining parameters were included in the general RDA model. In a second approach we used forward selection of parameters (R library *packfor*) to select those parameters with the highest explanatory value. Models were qualitatively evaluated after VIFD by percentage of constrained inertia, adjusted r^2 and F-values. All models were tested with and without z-standardization. The six best models are presented as results to discuss landuse impact. In another attempt we used partial RDA to assess the impact of LU.a and LU.b on the WQ data set as whole, while at the same time holding the GEO parameters constant. Cluster analysis was used to separate samples according to their chemical loads into three groups for visualization in figures.

To evaluate the degree of pollution the water quality index (Wqi) was used for surface water quality. The Wqi is defined as a simple expression of a more or less complex combination of several parameters which serve as a measure for water quality. It is estimated by the following equation:

$$Wqi = \frac{\sum i\left(\frac{Ci}{Pli}\right)}{n}$$

Where C_i is concentration of i^{th} pollutant, Pl_i is the maximum permissible level of i^{th} pollutant in accordance with the National Standard Agency of Mongolia (4586: 98), and n is the total number of pollutants (Fig 34).

5.4 Results

5.4.1 Landcover composition at selected sub-basin levels

Based on the delineation of sub-catchments draining into individual sampling points (see Table 19), we calculated land use compositions (see Fig. 29). Forest and grassland were the most common land uses at the KRB scale. Other land uses such as cropland and riparian vegetation were relatively minor components of the sub basins. Only some sub basins (K2, K4, kt4, kt6, kt7, kt8, kt9 and kt11) had ongoing or recent mining activities. The sub-watersheds considered here are characterized in Table 19, figure 29 and additionally by the following characteristics:

- ***K1*** is located in the upstream parts of the KRB and not much affected by anthropogenic activities. Dominant land covers include grassland (59.2%) and forest (32.5%), whereas the percentage of riparian vegetation is only 1.2%. Samples taken in K1 complied with the Mongolian standard (MNS 1998) for surface water quality.
- **K2** is located in midstream parts of the KRB, with its terminal point at Zuunkharaa town. The total area of the K2 sub-watershed is 5454 km^2, most of which is covered by grassland (51.7%), forest (41.2%), riparian vegetation (3.59%), and cropland (2.1%). Mining areas (0.73%), and urban settlements (0.57%) exist.
- **K3** is also located in the midstream parts of the KRB, with its terminal point near Baruunkharaa town. The total area of the K3 sub-watershed is 3240 km^{2}and landcover consists mostly of grassland (57.5%), forest (21.4%), cropland (16.6%), and riparian vegetation (2.4%). Mining (1.16%) and urban settlements (0.47%) are present.
- **K4** is located in downstream parts of the KRB, with a terminal point at Darkhan city. The total area of the K4 sub-watershed is 2196 km^2. The K4 watershed is covered by 69.4% grassland, 22.4% cropland, 3.1% riparian vegetation, 1.95% forest, 1.89% settlement, 0.95% mining land and 0.19 % industrial land use.
- **K5** is located in downstream section of the KRB, with its outlet at Buren Tolgoi gauging and water quality monitoring station downstream of Darkhan. The total area of the K5 sub-watershed is 7353 km^2 and landcover consists of 97.9% forest, 1.49% grassland, 0.41% cropland.
- **Kt1-Kt3** sub-watersheds areas of gold mining activities along the Gatsuurt River, a left-side tributary of the Kharaa River. The Kt1-Kt3 sub-catchments are dominated by forest and grassland, and less than 5% are covered by mining and industrial area.

- **Kt4-Kt9** are the next left tributaries of the Kharaa River. One of the biggest gold mines, Boroo, is located in the mid-stream section of the river, as is a small mine named Bor-tolgoi. The grassland is the dominant landcover in these sub-catchments (Table 19, Fig.29).
- **Kt10-Kt12** are parts of the Bayangol River sub-catchment, around a right-side tributary of the Kharaa River upstream of Darkhan city. Upstream parts are dominated by forest whereas mid and downstream parts are dominated by grassland.

Table 19 Detailed description of the sub catchment of Kharaa River basin, including ID, name spatial information and industrial, settlement and gold mining area

ID	Name	Y [°degree]	X [°degree]	Altitude [m]	Sub catchments area km²	Industrial, km²	Settlement, km²	Gold mining, km ²
K1	Sugnugur	48.3961	106.8774	1153	440	0	0	0
K2	Zuun-kharaa	48.8328	106.4522	859	5454	0.32	31.3	1.4
K3	Baruun-Kharaa	48.9117	106.0750	796	3241	0	15.5	0.4
K4	Darkhan	49.5914	105.8591	663	2197	4.3	41.7	1.7
K5	Buren-tolgoi	49.5914	105.8591	663	7354	1.8	0.5	0.5
Kt1	Gatsuurt-up	48.6272	106.6515	1138	19	0	0	0
Kt2	Gatsuurt-mid	48.5932	106.6548	1104	6	0	0	0
Kt3	Gatsuurt-down	48.5947	106.7542	1028	49	1.1	0	0.4
Kt4	Boroo-up	48.7239	106.2864	877	1370	0	6.9	0
Kt5	Boroo up mine	48.7624	106.2839	865	420	0	0	0
Kt6	Boroo mid mine	48.7732	106.2824	860	100	0	0	0.5
Kt7	Boroo mine	48.7732	106.2824	860	29	0	0	0.1
Kt8	Boroo down mine	48.7832	106.2832	855	24	0	0	0.05
Kt9	Boroo down	48.8682	106.2469	824	375	0	2.2	4.4
Kt10	Bayangol up	49.0309	106.9794	1071	19	0	0	0
Kt11	Bayangol mid	49.0445	106.1146	825	417	0	0	0.54
Kt12	Bayangol down	49.0309	105.9794	787	2	0	0	289

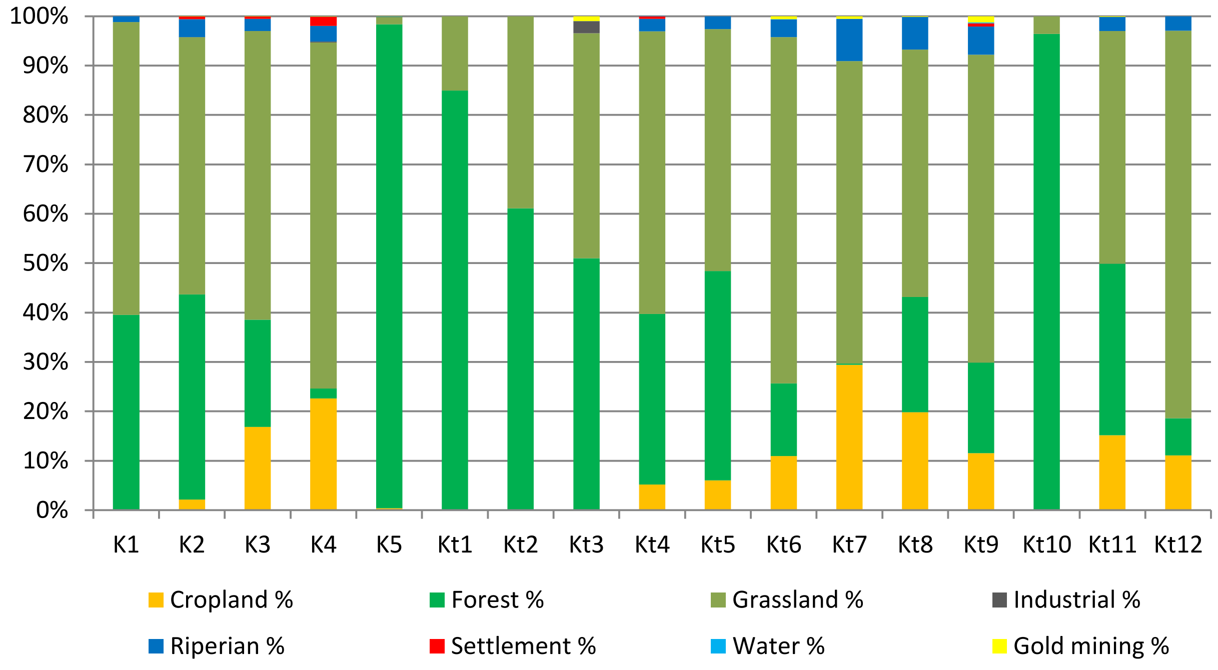


Figure 29 Landcover at the level of sub-catchments

As sub-basins for the single sample points were in part quite large (Table 19) and exceeded the river valley, we also calculated a subset for each of them, this time restricting the size of the area to a 3 km buffer zone directly along the river (Fig. 30).

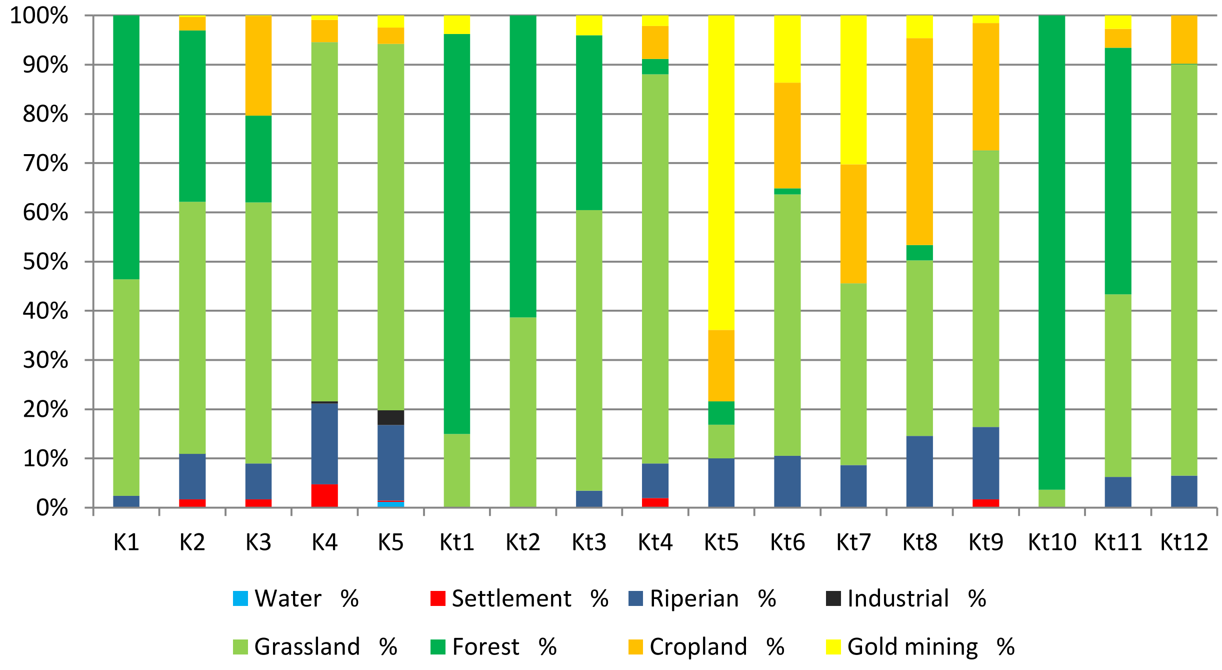


Figure 30 Landcover for 3 km buffer zones upstream of sampling points

Figure 31 Drone view of the Kharaa River and its confluxes (Photographs: Martin Pfeiffer (left side), André Künzelmann (right side).

5.4.2 Seasonal variation of chemical water quality

Variations of water quality for three seasons were compared using Kruskal-Wallis test. Many water quality parameters were not_significantly different for the three seasons. Silver (Ag), Arsenic (As), Copper (Cu) and Cadmium (Cd) were found to be indicator elements for mining and industrial activities. In case of silver, significant differences were found for the three seasons, but surprisingly, arsenic concentrations did not differ in the same way (Fig. 32). Copper concentrations were significantly different for summer and winter, and cadmium was significantly different for autumn as contrasted with summer or winter. TNb and PO_4^{3-} showed significant seasonal differences, but ammonium, nitrate and the water quality index did not exhibit significant differences (Fig 32). An overview of all measured water quality parameters over the three study seasons is given in Batbayar et al. 2017.

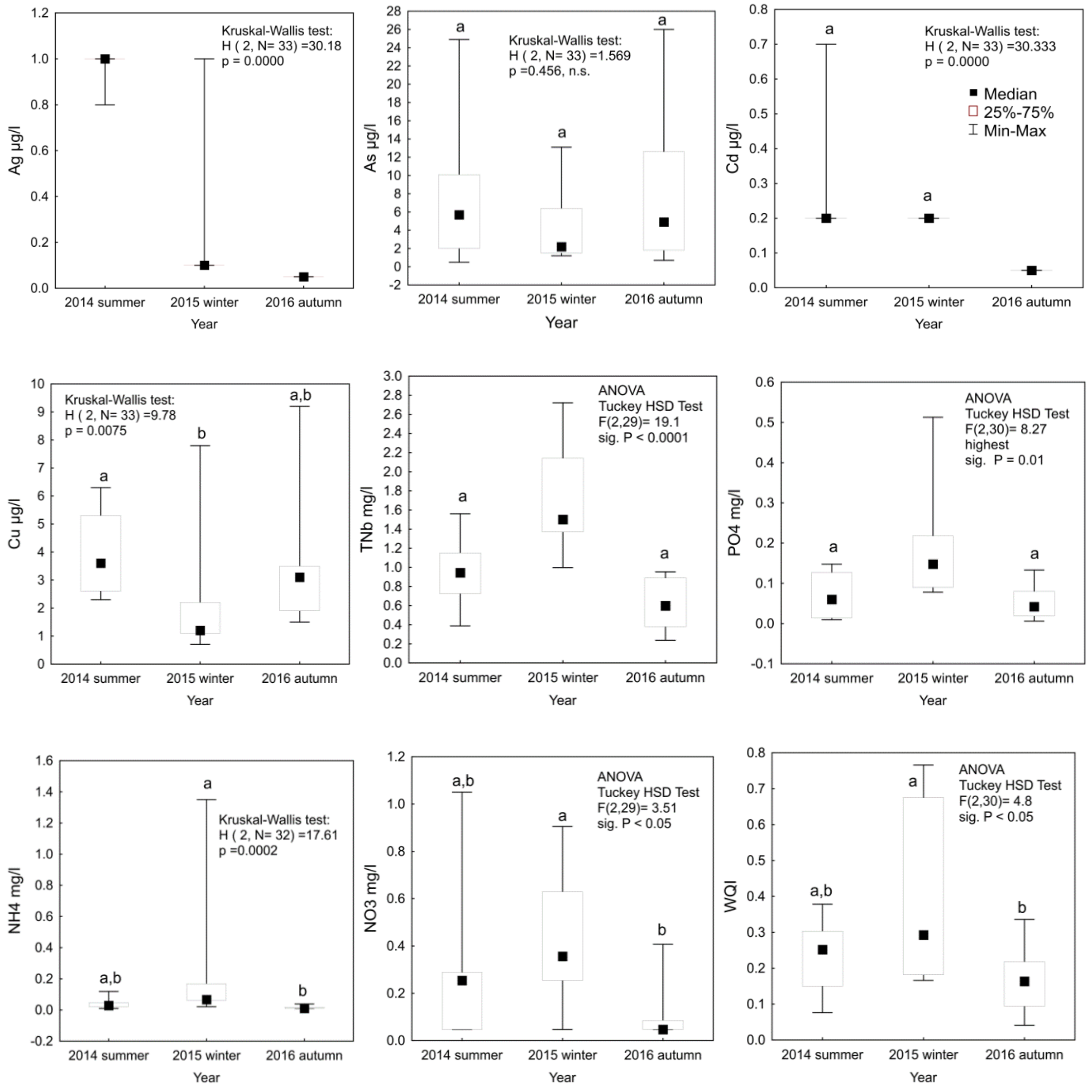


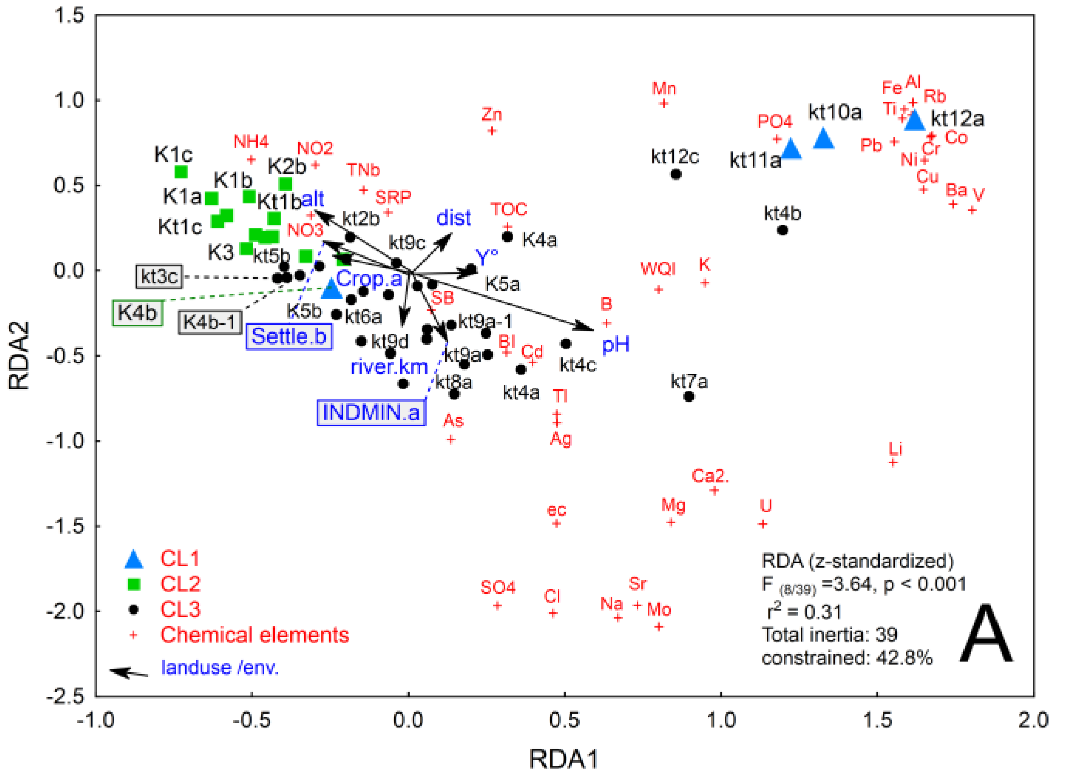
Figure 32 Seasonal variation of selected elements, nutrients and indices. Given are median, minimum and maximum, as well as lower and upper quartile of silver (Ag), arsenic (As), cadmium (Cd), copper (Cu), total nitrogen (TNb), total phosphate (PO43-), ammonium (NH4+), nitrate (NO3-) and water quality index (WQI). Seasons marked with the same letter did not significantly differ. Test results are given inside the figures. Data include 11 sites that have been sampled in all of the three seasons. An overview about the complete data set is given in the Table 19.

5.4.3 Relationship between land use and chemical water quality

As a first assessment of land use impact on water quality we extracted principle components (PCAs) from water quality data (WQ) and checked the impact of the landuse compositions LU.a and LU.b on PCA1 and PCA2 of WQ by multiple regression. WQ-PCA1 was highly impacted by eight LU parameters (Crop.a, b; Forest.a, b; Grass.a, b; SETTLE.a, WATRIP.b; Mult. Regr. F (8, 39) =5.067, adj. r^2 = 0.41, p < 0.001), while WQ-PCA2 was governed by six parameters (Crop.a, b; Grass.a, b; Forest.b; SETTLE.b, Mult. Regr. F (6, 41) =8.409, adj. r^2 = 0.49, p < 0.0001). Although true r^2 might be smaller due to overlapping of LU parameters of both data sets, these results corroborate a high impact of LU on WQ.

We used RDA models to evaluate the impact of landuse and environmental factors on the chemical composition of our samples in detail. Six models with different starting configuration and forward selection of significant variables explained 30 to 63 % of the model variation, while the models constrained 45 to 72% of the total variation in the data (Table 20, Fig. 33). Models A, C and E used the full set of sample data including the winter period 2015. They constrained less variance (44 to 53%) and explained less variance (r^2 = 30 to 44%) than models B, D, F that excluded winter time (r^2= 48% to 63%). One pair of the models used landuse data from the full range of the sample basin (LU.a), another one only the buffer area data (LU.b), but results were comparable, with the buffer models providing both the lowest and highest r^2 after forward selection (models C: 30% vs. D: 63%). Model E and F, however, used both datasets LU.a and LU.b as explanatory data, additionally to the GEO data, which was used by all of the models.

The best model explained 63% of the variation in chemical water quality among other factors by landuse patterns *settlement.b*, *forest.b* and *cropland.b*, as well as *basin size*, thus substantiating our hypothesis that landuse plays a major role in water quality. *Settlement* variable (n=5) played the largest role for water quality, while forest was selected in three models, grassland (n=1) and cropland were only chosen once (n = 1). Although the mining variable *INDMIN* was part of all data sets and contributed to their r^2 for the full model, it wasn't selected in any of the forward selected models. Variables from the GEO dataset were also good to explain water quality and chosen by forward selection: altitude of sample point (alt, n=6), northern location (Y°, n = 6), distance to spring (river.km, n=5), distance to next upstream sample point (dist, n=4), size of the full sample basin (size, n=1), water temperature (n=3) and pH (n= 2). Many of these measures overlap in their explanatory value and underline the fact that water quality changes from upstream to downstream due to contaminant accumulation on the one hand and river self-purification on the other hand.



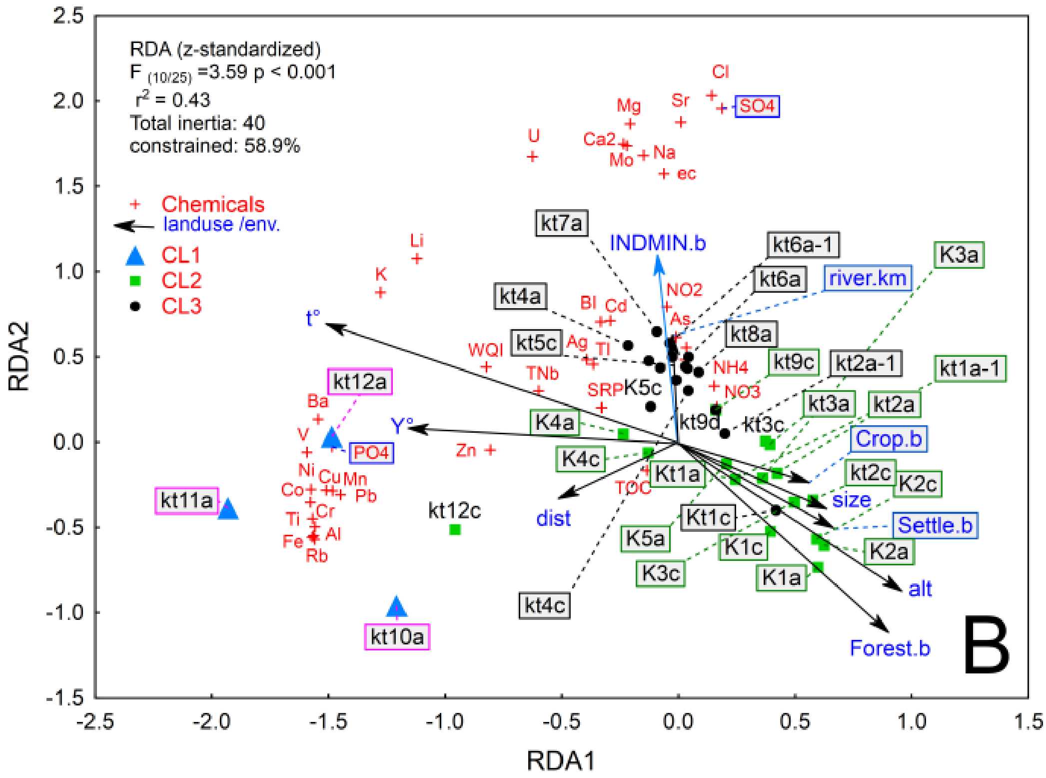


Figure 33 RDA models confirm the impact of landuse and environmental factors on the chemical composition of water samples from river sections along the Kharaa River in northern Mongolia. Arrows show valid constraining variables (variance inflation factors < 10). Samples are sorted in three clusters according to their chemical composition. Centroids of chemical elements are given in red. Explanatory landuse and environmental data are in blue. INDMIN variable was not selected in forward selection, but added to general explanation and is given for information. Abbreviations: .a= full area; alt = altitude, .b = buffer area, Crop = cropland, dist = distance to next sample point upstream, INDMIN = industry and mining, river km = distance to well, Settle = Settlements, size = size of sample basin, t° = water temperature, Y°= northern latitude. For clear figure structure water chemistry data have been z-standardized before RDA; the original results are given in Table 20. A. Samples from 2014-16, corresponding to model E, with a double data set of landuse data (buffer + whole basin) + environmental data (env) for explanation. B. Samples from 2014 and 2016 only, excluding the winter data of the 2015 expedition, with buffer data of landuse +env (Model D).

Table 20 Contrast of RDA models on the influence of landuse and environmental variables on chemical composition of water samples. While model A and B used the full size of the sample basin, model C and D used only data of a buffer zone along the river for assessment of landuse impact. Models E and F used both data sets simultaneously. Models B, D and F used a subset of the data, without sample data from winter (2015 data). Given are total inertia (variance) in the data, constrained variance for the full model after VIR (reduction of variables with variance inflation factors > 10), and number of variables that had been selected by forward selection procedure. For the reduced models further results are given: constrained inertia, eigenvalues of RDA axes, degrees of freedom for model, model variance, F-value and significance, number of significant axes (tested by ANOVA with 1000 runs), adjusted r2 for the selected variables and their names. Abbreviations: pH = pH value, alt = altitude of sample point, distance = distance to next sample point upstream, river km = distance to spring, Y° = Y coordinate, t°= water temperature at sample time, basin size = size of the sample basin, Settle.a = size of settlement land use in full sample basin, Settle.b = size of settlement land use in buffer zone, Forest.a = size of forest land use in full sample basin, Forest.b = size of forest land use in buffer zone, Grass.a = size of grassland land use in full sample basin, Crop.b = size of the cropland in buffer zone. VIFD: Deletion of variables with variance inflation factors >10.

Model properties	Model A	Model B	Model C	Model D	Model E	Model F
Full range of sample basin	X	X			X	X
Buffer zone			X	X	X	X
2014-16, with winter	X		X		X	
2014 u. 2016, no winter		X		X		X
Total inertia	58550	64660	58550	64660	58550	64660
Constrained inertia % after VIR	0.453	0.542	0.51	0.7248	0.514	0.683
Adjusted R2 for whole model	0.305	0.479	0.378	0.594	0.414	0.538
Forward selected variables	7	6	5	9	6	6
Constrained inertia %	0.53	0.562	0.441	0.722	0.514	0.576
Eigenvalue RDA1	15165	18332	13912	26100	15055	22219
Eigenvalue RDA2	13604	15930	10602	17230	12860	12328
DF Model /residual	7/39	6/29	5/42	9/26	7/40	6/29
Model Variance	31045	36360	25801	46695	30074	37225
F	6.45	6.21	6.618	7.509	6.035	6.558
P-Value (ANOVA, 1000 steps)	0.001	0.001	0.001	0.001	0.001	0.001
No. Significant axes	2	2	2	2	2	2
Final adj R2 cum for sel. Vars.	0.448	0.472	0.374	0.626	0.4287	0.488
No.1	alt	alt	alt	alt	alt	alt
No.2	Grass.a	Settle.a	Forest.b	Settle.b	Settle.b	Settle.a
No.3	river km	river km	river km	river km	river km	Y°
No.4	Y°	Y°	Y°	Y°	distance	Forest.a
No.5	distance	t°	distance	t°	Y°	Forest.b
No.6	Settle.a	distance		distance	pH	t°
No.7	pH			Forest.b		
No.8				basin size		
No.9				Crop.b		

Table 21 Primary statistical results of river water samples in comparison with following standards MNS 1998 Mongolian standard for aquatic ecosystem quality indicators; Russian standard for surface water quality RNS 2010 and National Recommended Water Quality Criteria—Aquatic Life Criteria Table US EPA 2006. Values in bold indicate a standard exceedance

Parameters	2014			2015			2016			MNS 4586: 98	RNS 2010	US EPA 2006
	Min	Max	Median	Min	Max	Median	Min	Max	Median			
Antimony (Sb) total µg/L	0.3	1.2	0.3	0.3	0.7	0.3	0.1	0.5	0.3			
Uranium (U) total µg/L	1.6	20.8	10.4	2.8	22.1	11.55	1.3	21.1	8.5			
Bismuth (Bi) total µg/L	0.8	2.2	0.8	0.8	0.8	0.8	0.1	0.8	0.1			
Magnesium (Mg2+) mg/L	0.834	20.5	14.7	3.14	20	11.5	0.909	19.1	9.88			
Natrium (Na+) mg/L	1.09	54.9	13.4	4.1	25	12.8	2.46	26.8	10.1			
Potassium (K+) mg/L	1.02	4.96	2.9	1.62	7.47	3.36	0.677	5.18	2.02			
TOC mg/L	3.35	20	5.25	0.94	12.9	3.6	1.9	101	4.29			
DOC mg/L	0	15.2	1.31	1.45	14.5	4.37	2.07	71.9	4.97			
Chromium (Cr) total µg/L	0.6	**20**	**3.1**	0.5	**12.4**	**1.4**	0.4	**11.7**	**1.1**	50	1	11
Aluminum (Al) total mg/L	0.246	14.3	1.71	0.022	11.3	0.689	0.0704	8.68	0.29			
Arsenic (As) total µg/L	0.5	**243**	**6.1**	0.9	**13.1**	1.95	0.7	**26**	**5.8**	10	5	150
Barium (Ba) total µg/L	12	112	46	14	126	30	5	99	31			
Cadmium (Cd) total µg/L	0.2	**0.7**	0.2	0.2	0.2	0.2	0.05	0.2	0.05	5	5	0.25
Cobalt (Co) total µg/L	0.4	5.9	0.9	0.4	3.3	0.45	0.1	3.1	0.3	10		
Copper (Cu) total µg/L	**2.3**	**16.4**	**4.1**	0.7	**7.8**	**1.25**	**1.5**	**10.9**	**3.1**	10	1	10
Iron (Fe) total mg/L	**0.23**	**16.1**	**1.68**	0.01	**9.28**	**0.7835**	**0.103**	**7**	**0.311**		0.1	1
Mercury (Hg) µg/L	0	0.08	0.01	0	0.01	0	0	0	0	0.1		
Manganese (Mn) total mg/L	0.007	**0.259**	**0.058**	**0.018**	**0.37**	**0.06**	0.007	**0.11**	**0.02**	0.1	0.01	
Molybdenum (Mo) total µg/L	0.7	15.2	3.7	1.1	5.3	2.95	0.9	9.6	3.1	250		
Nickel (Ni) total µg/L	1.2	**16.8**	3.2	0.9	9.4	2.25	0.9	9.9	2	10	10	52
Lead (Pb) total µg/L	0.5	**7.8**	1.2	0.5	**6**	0.7	0.3	**6.9**	1.3	10	6	2.5
Rubidium (Rb) total µg/L	0.5	24.5	3.1	0.2	19.2	1.95	0.3	16.9	0.8			
Strontium (Sr) total µg/L	30	456	297	74	309	225	33	510	286			
Vanadium (V) total	0.6	33.	8.8	0.4	19.	2.15	0.3	23.	4			

µg/L		9			6			8				
Zinc (Zn) total mg/L	0.009	**0.05**	0.009	0.009	**0.158**	**0.019**	0.009	**0.06**	**0.016**	0.01	0.01	0.15
TNb mg/L	0.256	1.67	0.977	0.982	2.72	1.54	0.237	1.5	0.635			
Chlorine (Cl-) mg/L	1	11.8	8.03	0.994	14.7	7.22	0.8	11	6.7	300		
Sulfate (SO42-) mg/L	2.66	35.8	21.2	8.74	34.9	22.65	2.66	24.1	15.9	100		
Calcium (Ca2+) mg/L	4.3	52.7	40.6	11.1	50.3	30.95	5.38	54.3	33.6			
Lithium (Li) total µg/L	4	18	12	2	13.1	6.15	2.8	19.4	8.1			
Thallium (TI) total µg/L	1	1	1	0.1	1	0.1	0.1	0.1	0.1			
Titan (Ti) total µg/L	9	617	73	1	581	44	6	308	35			
Bor (B) total µg/L	10	98	42	10	89	10	4	153	32			
Silver (Ag) total µg/L	0.2	1	1	0.1	1	0.1	0.05	0.1	0.05			
Ammonium-N mg/L	0.01	0.172	0.029	0.021	**1.35**	0.07	0.01	0.066	0.01	0.5		
Total-Phosphate-P mg/L	0.01	**0.347**	0.085	0.078	**0.513**	**0.13**	0.006	**0.313**	0.048	0.1		
NO2- mg/L	0.006	0.015	0.006	0.006	**0.128**	0.009	0.006	0.013	0.006	0.02		
NO3- mg/L	0.035	1.05	0.074	0.047	0.905	0.402	0.047	0.475	0.047	9		
SRP mg/L	0.003	0.027	0.007	0.003	0.313	0.0235	0.003	0.072	0.003			
WQI	0.076	1.89	0.25	0.16	0.76	0.25	0.04	0.49	0.171			
pH	6.45	9.54	8.72	7.11	8.16	7.81	7.12	8.64	8.4			
ec µs/cm	131	497	363	123.7	453	351	20	966.6	333.3			

5.5 Discussion and Conclusions

5.5.1 Water quality patterns in individual clusters

According to the RDA results, water quality is changing from upstream to downstream which can be explained by the combined effects of contamination accumulation and river self-purification processes. Samples were sorted in three clusters with regard to their chemical composition, different pollution sources and loads and human impacts. The reasons for water quality deterioration in mid and downstream sampling points is include deficient waste water treatment facilities in settlement areas (Karthe et al. 2016, Pfeiffer et al. 2015) as well as trace elements and arsenic loads originating from mining activities (Batbayar et al. 2017, Pfeiffer et al. 2015). Compared to the national (MNS1998) and international surface water quality standards (RNS 2010, US EPA 2006), the highest concentrations and most frequent water quality standard exceedances were observed in Darkhan and around the mining areas (Table 19).

As a result of the RDA B (Fig. 33), three clusters were discriminated: **cluster one** comprises the samples from the mining-affected Bayangol river (Kt10, Kt11, Kt12) in the northern part (predictor: Y^0) of the catchment. In this small stream, the following elements were high compared to cluster two and three: Al, Ba, Co, Cu, Cr, Mn, Ni, Pb, Ti, Fe, V and Rb.

Cluster two comprises samples K1a, K1c, K2a, K2c, K3a, K3c, K4a, K4c, K5a, kt1a, kt2c, kt3a, kt1a-1, kt9ь and kt12c, which originated from sub-basins with a large degrees of coverage by forest and high mountains. Altitude, forest, catchement size and settlements were the dominant predictors of instream water quality in this cluster.

The Cluster 3 consists of samples that were taken in the proximity of a major gold mining area (samples Kt7a, Kt4a, Kt5c, Kt6a-1, kt6a, kt8a, kt2a-1, kt4c, K5c and kt9d). The following elements were high: As, Cd, Ag, Ti...etc. (Fig. 33). The distance to spring and the pH value were identified as the main predictors of water quality in this cluster.

5.5.2 Comparison of buffer zones vs. entire catchment

The role of buffer zones as compared to whole catchments has emerged as an important topic not only for research on chemical water quality (Brogna et al. 2018), but also for river basin management planning (Heldt et al. 2017, Tockner et al. 2010)). Current perceptions on protection/buffer zone widths vary enormously – for the Nordic and Baltic regions of Europe alone, for example, protection policies range from 1m to several hundred meters and even 5km for coastal waters (Ring et al 2017). Riparian buffer zones between streams and agricultural, urban, industrial and mining areas can effectively reduce contamination input from non-point source pollution. Our results with high R^2 in RDA (Table 20, Model D) showed that the riparian 3km buffer zone has a high impact on sub catchment water quality. Other authors have looked at more narrow belts; for example, Brogna et al. 2018 found strong correlations between instream water quality and land use in 200 m riparian buffer zones.

This study identified as the strongest predictor of water quality not mining, but settlements, forest, cropland, and general geographical characteristics, particularly with regard to riparian zones. Landuse by industry and mining contributed to overall variability, but was never selected as major predictor in forward selection procedure. One factor to explain for that can be the small size of the mining areas, which may have diminished their mathematical impact even in the buffer zone data. Interestingly, the arrows for mining (IndMin) and river km point in the same direction or even overlap, thus indicating that both factors, on site pollution and accumulation of pollutants along the river, lead to a higher concentration of the same elements in river water. The relevance of forests for water quality that were documented by the studies of Martyn et al.2016 and Brogna et al. 2017 could be confirmed here. On the other hand, RDA results in our study also demonstrated that settlements within riparian zones negatively impacted stream water quality.

5.6 Conclusions

The main objective of this study was to analyze links between water quality and landscape characteristics in KRB using GIS and multivariate analysis at individual sub-catchments scales and the riparian zones therein. Our findings confirmed that landscape characteristics influence instream water quality. The most powerful predictors of river water quality were found to be forest, settlements, cropland and sub-basin size. In particular, this was true when instead of full sub-basins riparian buffer zones (3 km) were considered. From a management perspective, this implies that the protection of riparian zones should be a priority in the basin of the Kharaa and similar river basins in Mongolia and Central Asia. Because of its positive effects on water quality, forest protection should be closely coupled with river basin management. On the other hand, any further expansion of settlements, agricultural land use and mining should be avoided in the Kharaa's floodplains.

In the future, further studies should focus on pollutant loadings in addition to concentrations, because concentrations depend not only on pollutant influxes but also at the river system's dilution capacity, which tends to vary substantially between seasons, but also inter annually. Moreover, analyses incorporating riparian zone soil characteristics would be meaningful in order to assess whether different soil types and textures should be considered for the dimensioning of riparian buffer zones. Ultimately, it would be beneficial to look beyond instream water quality to aquatic ecology, e.g. macroinvertebrates communities, and its dependence on riparian zone land cover.

Appendix

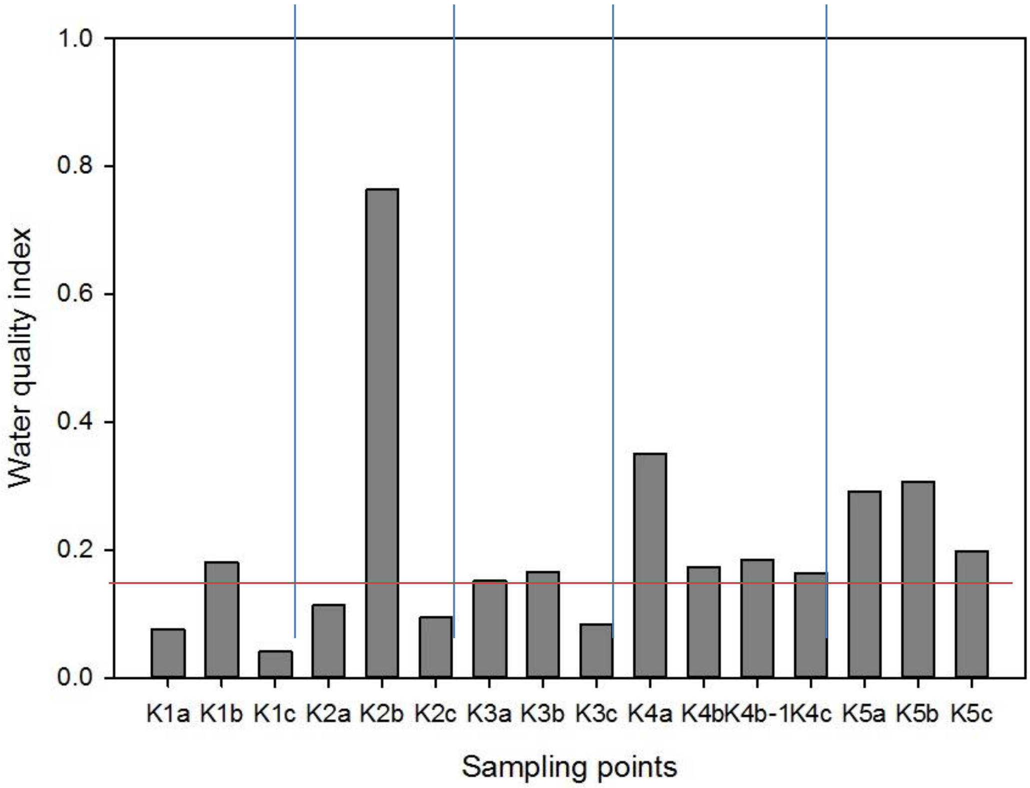


Figure 34 Water Quality index of the Kharaa River at different stations and in different seasons (a-summer 2014, b-spring 2015, c-autumn 2016)

Chapter6. General discussion and conclusions

This section provides an overview of the results and implications:

- To avoid the further contamination of heavy metals in both groundwater and surface water resources in Mongolia with heavy metals the implementation of a set of measures is necessary. These include mitigation procedures in mining areas, containment of existing dump sites, processing water ponds, and search for safe drinking water wells, capacity development of Mongolian institutions and the implementation of a monitoring system combined with effective analytical tools as well.
- The highest concentrations of nutrients were recorded in the downstreams of urban areas and mining regions (Tuul directly downstream of Ulaanbaatar WWTP and downstream of Zaamar gold mining area; Khangal River downstream of Erdenet city; Kharaa downstream of Darkhan city). Several heavy metals and arsenic were found in elevated concentrations, including As (up to 54.2 µg/l in the Boroo River downstream of Bortolgoi mine, as compared to a maximum of 10 µg/l according to MNS 4586:98), Cu (up to 360.0 µg/l in the Khangal River downstream of the Erdenet copper-molybdenum mining complex, as compared to a maximum of 10 µg/l according to MNS 4586:98), Ni (up to 20.5 µg/l in the Sharyn River downstream of both coal and gold mining areas, as compared to a maximum of 10 µg/l according to MNS 4586:98) and Mn (up to 380 µg/l also in the Sharyn River downstream of both coal and gold mining areas, as compared to a maximum of 100 µg/l according to MNS 4586:98).
- Water quality in the Selenga River system is strongly linked to discharge and also shows clear spatial patterns that are largely determined by mining sites and urban areas, resulting in significant changes in water quality in the SRB. Through the discharge of poorly treated waste water, urban areas constitute key sources of nutrients, BOD loadings and microbiological contamination. On the other hand, mines that exploit natural resources are the mian sources of various heavy metal emissions including Au, Cu, Mb and W. A good understanding of hydrological trends and changes in water quality of Selenga River and its sub-catchment scale is an important prerequisite for water management. Science-based environmental management concepts in the region are needed for at least three reasons: (1) to solve localized water-related challenges in the Selenga River Basin that show a strong spatial variation; (2) to ensure the protection of the Selenga river basin ecosystems, and (3) to overcome disputes in transboundary water management between the riparian states, Mongolia and the Russian Federation
- In the future, additional research will be needed to monitor water quality development in this rapidly developing region. Moreover, a more detailed assessment of the links between urban waste water discharges and the various

forms of mining on the one site and surface water quality on the other is still needed. This could not only help to better quantify individual pollution sources, but also aid to prioritize water management policies.

- The landscape characteristics influence instream water quality. The most powerful predictors of river water quality were found to be forest, settlements, cropland and sub-basin size. In particular, this was true when instead of full sub-basins riparian buffer zones (3 km) were considered. From a management perspective, this implies that the protection of riparian zones should be a priority in the KRB and similar river basins in Mongolia and Central Asia. Because of its positive effects on water quality, forest protection should be closely coupled with river basin management. On the other hand, any further expansion of settlements, agricultural land use and mining should be avoided in the Kharaa's floodplains.
- In the future, further studies should focus on pollutant loadings in addition to concentrations, because concentrations depend not only on pollutant influxes but also at the river system's dilution capacity, which tends to vary substantially between seasons, but also inter annually. Moreover, analyses incorporating riparian zone soil characteristics would be meaningful in order to assess whether different soil types and textures should be considered for the dimensioning of riparian buffer zones. Ultimately, it would be beneficial to look beyond instream water quality to aquatic ecology, e.g. macroinvertebrates communities, and its dependence on riparian zone land cover.
- In order to make a fact based decision making and good practice for water management, it's important to improve the quality assured database and scientific understanding of water resources. As well as data should be shared between relevant institutions and stakeholders. Expanding water resources monitoring activities and water resource assessments are required.
- Follow the legal framework, standarts and regulations including integrated water resource management plan for river basins. Encourage the polluter pays principle, and improve the environmental investment system which is including water usage fee, water service charge and waste water fee. It was introduced in the water law 2012. But most of the regulations haven't implemented at the field and enforcement of existing regulations is weak. There is no standard on effluent and waste water reuse. Therefore urgent action is needed.

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