

# The chemistry of river–lake systems in the context of permafrost occurrence (Mongolia, Valley of the Lakes). Part I. Analysis of ion and trace metal concentrations

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## abstract

This study provides a description of water chemistry in river–lake systems located in central Mongolia, at the border-line of permafrost occurrence. The analysis involved water samples collected from two river–lake systems: Baydrag River–Böön Tsagaan Lake system, and Shargalyuut/Tuyn Rivers–Orog Lake system. In the water samples, ions and trace elements were detected and quantified. Additionally, the parameters of pH, electrical conductivity (SEC), total dissolved solids (TDS) and total organic carbon (TOC) were determined. Principal Component Analysis (PCA) was performed on the sample results. Water chemistry is mostly influenced by geochemical and hydrometeorological processes. Permafrost thawing could increase the concentration of nitrogen ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ) as well as  $\text{Na}^+$  and  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ . However, it may also be an effect of other factors such as livestock farming. Seasonal drying out of lakes (e.g., Lake Orog) may also influence water chemistry by deflation of evaporites from exposed lake beds and, at the same time, with lower concentration of chemical compounds in water. The PCA shows that water samples can be divided into two groups. The first group contains lake samples, where water chemistry is shaped by prevailing evaporation processes, whereas the second includes samples from rivers and springs. Water chemistry of the latter is predominantly influenced by geochemical and hydro-meteorological processes.

Keywords: Mongolia, River–lake systems Water, inorganic chemistry Trace, elements Permafrost

## 1. Introduction

Hydrological processes in permafrost regions are controlled by thickness of the active layer and total thickness of the underlying permafrost (White et al., 2007). The presence of permafrost can greatly affect the geochemistry of Northern Hemisphere watersheds, changing the seasonal fluxes of nutrients including carbon and nitrogen (e.g., Carey, 2003; O'Donnell and Jones, 2006; Petrone et al., 2006; Frey et al., 2007; Frey and McClelland, 2009; Keller et al., 2010; Bagard et al., 2011; Cheng and Jin, 2012; Douglas et al., 2013; Larouche et al., 2015; Manasyrov et al., 2015). Recent monitoring observations indicate widespread permafrost degradation in the Northern Hemisphere (Christiansen et al., 2010; Romanovsky et al., 2010; Smith et al., 2010; Zhao et al., 2010; Slater and Lawrence, 2013). Rapid changes of permafrost have also been observed at the southern range of permafrost appearance (Zhang et al., 2008; Schaefer et al., 2011). The interaction between permafrost degradation and watershed hydrological changes

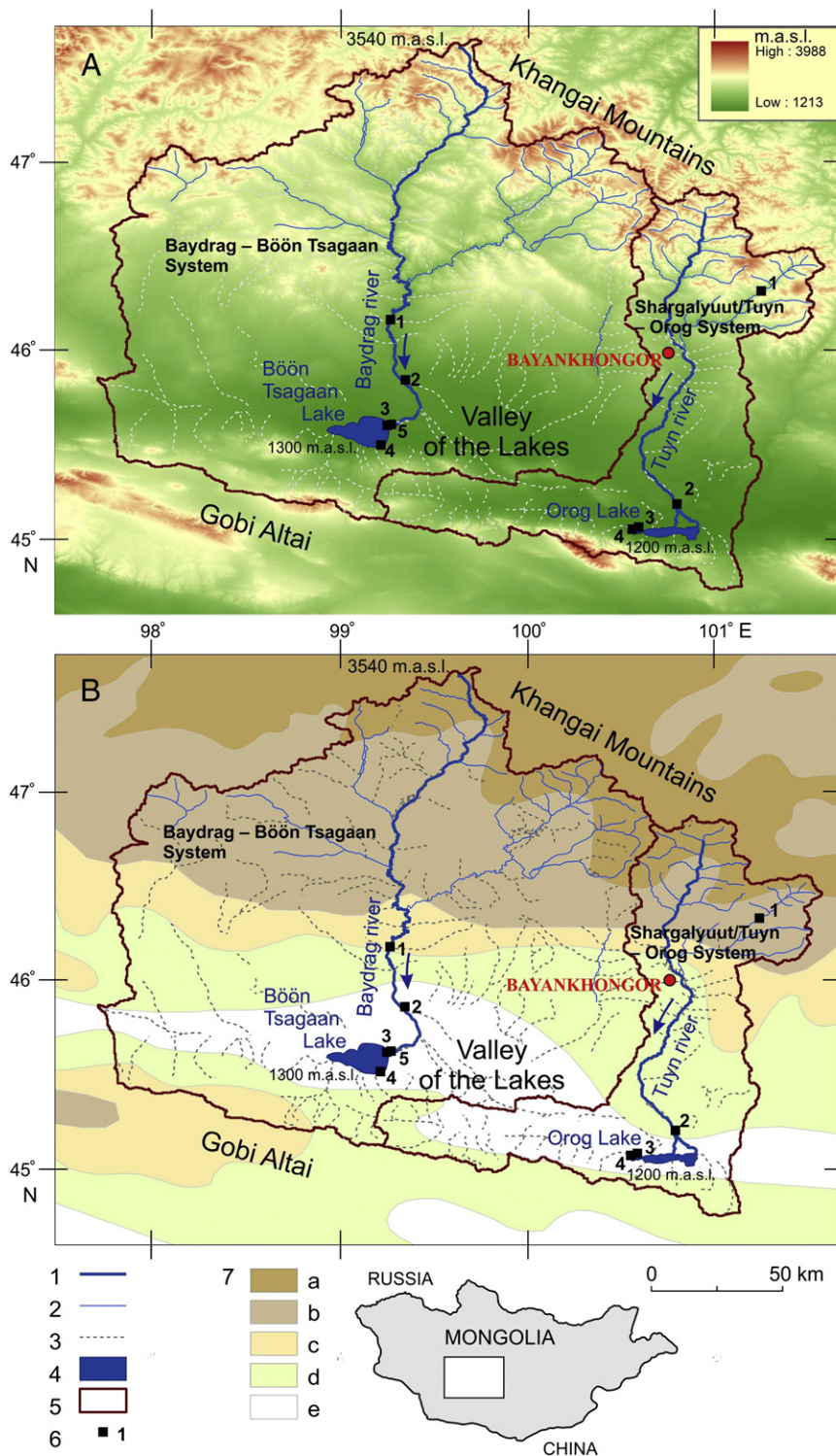
can help us predict the response of aquatic ecosystems to climate changes (McClelland et al., 2007; Koch et al., 2013; Abbott et al., 2015). As temperatures increase at higher latitudes, large amounts of carbon, nitrogen and other chemical compounds stored in permafrost may start to become available for transport to aquatic ecosystems. There is a growing understanding of the potential effects of permafrost degradation on aquatic biogeochemical cycles in Arctic regions such as Alaska (Petrone et al., 2006; McClelland et al., 2007; Douglas et al., 2013), Canada (Zhang et al., 2008; Kokelj et al., 2009; Stotler et al., 2009; Olefeldt et al., 2014), and Russia (Frey et al., 2007; Bagard et al., 2011; Manasyrov et al., 2015). However, there is no information concerning surface water chemistry (in the context of permafrost occurrence) in Mongolia.

Detailed hydrological and hydrochemical investigations have been carried out in individual regions of Mongolia (e.g., Ma et al., 2003; Lange et al., 2015). Only a few hydrological and hydrochemical studies have covered the entire country (Glazik, 1995; Davaa et al., 2007; Batsukh et al., 2008; Davaa and Oyunbaatar, 2012; Demeusy, 2012). A significant issue is the impact of strip mining in river valleys on water chemistry and volume of water resources (Farrington, 2000;

Stubblefield et al., 2005; Thorslund et al., 2014). However, the chemical status of lakes and rivers still constitutes an understudied element of the environment of Central Mongolia.

This paper aims at defining chemical features of water within the river–lake systems located in Central Mongolia, at the boundary of permafrost occurrence (Fig. 1): Baydrag river–Böön Tsagaan Lake system (the Baydrag–Böön Tsagaan System) and Shargalyuut/Tuyn Rivers–

Orog Lake system (the Shargalyuut/Tuyn–Orog System). The main aim of the research involved establishing relationships between rivers, their sources and lake water chemistry. The source of all rivers is located in the continuous and discontinuous permafrost zones. Both lakes (Böön Tsagaan and Orog) constitute terminal parts of rivers. The river mouths – lakes – are located in an area where permafrost is absent and where evapotranspiration over infiltration (both in the aqueous



**Fig. 1.** Location of the research area against the background of (A) digital elevation model (DEM) and (B) permafrost occurrence in Mongolia. Locations: 1 – the Baydrag and the Tuyn rivers, 2 – perennial tributaries of main rivers, 3 – intermittent streams, 4 – researched lakes, 5 – watersheds of the Baydrag and the Tuyn basins, 6 – sampling points, 7 – zones of: (a) continuous and discontinuous, (b) insular, (c) sparsely insular, (d) sporadic permafrost occurrence, (e) seasonally frozen ground (DEM based on Jarvis et al., 2008, 1–5 and 7 based on Sharkhuu, 2000; Sodnom and Yanshin, 2005; Lehner et al., 2008).



and land environment) is significant. This study investigates the influence of permafrost on river water chemistry and the role of evapotranspiration in terms of lake water chemistry characteristics.

## 2. Study area

### 2.1. Hydrological setting

The two analysed rivers – Baydrag and Tuyn – have their source zones in the Khangai mountains and flow to the south, across uplands to the Valley of the Lakes, where they feed two large lakes (Fig. 1). The basins of the river–lake systems cover an area of 45,020 km<sup>2</sup> and 14,929 km<sup>2</sup> for the Baydrag–Böön Tsagaan system and the Tuyn–Orog system, respectively (Lehner et al., 2008). Permafrost occurrence is related to altitude, and is continuous in the Khangai mountains, whereas at the southern slopes of the Khangai, permafrost occurs in patches and disappears in a southward direction (Sharkhuu, 2000; Sodnom and Yanshin, 2005) (Fig. 1).

The Khangai mountains has a total precipitation in the range of 300–350 mm and continuous and discontinuous permafrost occurrence (Davaa and Oyunbaatar, 2012; Kwadijk et al., 2012). Annual specific runoff decreases southwards with the river course and ranges from 2.5 to 3.0 L s<sup>-1</sup> km<sup>-2</sup> in the vicinity of the Khangai slope to less than 1.0 L s<sup>-1</sup> km<sup>-2</sup> in the Valley of the Lakes (Glazik, 1995; Batsukh et al., 2008; Davaa and Oyunbaatar, 2012). The primary sources of Baydrag and Tuyn river water are from rainfall, groundwater and snow melting. In the Tuyn river basin rainfall constitutes 46% of annual runoff, groundwater 36% and snow melting 16% (Davaa and Oyunbaatar, 2012). The Böön Tsagaan and Orog Lakes represent a declining stage of a former lake (Komatsu et al., 2001). The surface area of the lakes amounts to 252 km<sup>2</sup> in the case of Böön Tsagaan, and 140 km<sup>2</sup> for Orog Lake, volume of 2.355 km<sup>3</sup> and 0.42 km<sup>3</sup>, and mean depth of 10 m and 3 m respectively (Davaa et al., 2007). At present the lakes are relatively shallow (Böön Tsagaan 10 m, Orog Lake 5 m). Due to the fact that the lakes are located at the border between an arid steppe and a semi-desert, the water bodies are characterised by marked water table fluctuations. Lake Orog is subject to annual groundwater fluctuation. Groundwater supply of Orog Lake is from springs located in the western part of the basin. Seasonal increase in supply causes the basin to slowly fill up (usually from spring to autumn), and later in autumn and winter the water level tends to drop. In 1989 and between 2006 and 2011, Orog Lake dried out, which may have significantly affected the chemical status of water. Satellite images of June and July 2005 indicate a shorter period of disappearance of Orog Lake, leading to deflation of the surface layer of bed sediment along with precipitation at chemical compounds (Szumińska, 2016). The surface area and water tables of both lakes have decreased since the 1970s, by 14% for Böön Tsagaan Lake, and 51% for Orog Lake (Szumińska, 2016).

### 2.2. Geological setting

The source areas of sediments for both rivers and lakes mainly consist of granitic rocks of Paleozoic age (alkali feldspar granites to tonalities). In the southern part of the study area (the Valley of the Lakes), the rivers flow through a Neogene system of sedimentary and volcanic rocks with clastics and basic volcanites (mainly basalts) (Tomurtogoo, 2004).

In the basin of the Baydrag river there are hydrothermal Au–Cu veins, Au (in alluvial deposits), Au, Ag, Cu deposits (related to hydrothermal polymetallic veins), magnesite, iron and brown coal. In the Shargalyuut and Tuyn rivers are Sn–W (related to felsic rocks greisenisation), polymetallic Au–W–Mo (related to granites), deposits of Zn–Pd (hydrothermal veins), fluorite (hydrothermally altered weathering waste) and brown coal (Dejidmaa et al., 2001). There are no operating mines, and thus mining is not an important factor of water use and pollution. Large-scale illegal gold mining is common in

most districts and the use of heavy metals for recovery processes could lead to water and soil pollution.

## 3. Methodology

### 3.1. Sampling design

Samples for the analyses were collected in August and September 2013. The sites of samples collection are marked in Fig. 1 and represent areas of different extent of permafrost coverage. On the Baydrag River–Böön Tsagaan Lake (the Baydrag–Böön Tsagaan System), samples were collected at the terminal mountain reach of the Baydrag river (sample 1), at the border of Khangai and the Valley of the Lakes (sample 2), and at the river mouth of Böön Tsagaan (sample 3). A sample was taken from the Böön Tsagaan Lake (sample 4) and spring that supplies the river (sample 5). On the Shargalyuut/Tuyn rivers–Orog Lake system (the Shargalyuut/Tuyn–Orog System), samples were collected from the Shargalyuut river – tributary of the Tuyn (sample 1), from the Tuyn river at the border of the Khangai and the Valley of the Lake (sample 2), from Orog Lake (sample 3) and the lake-supplying springs (sample 4).

Sampling sites 1 within both systems are located where permafrost occurs (in the case of the Baydrag–Böön Tsagaan System – at the border between sparsely insular and sporadic permafrost, in the case of the Shargalyuut/Tuyn–Orog System at the border between discontinuous and insular permafrost). Sample 2 from both systems represent the zone where permafrost occurs in the form of sparsely insular or sporadic. Sample 3 in the case of the Baydrag–Böön Tsagaan System was collected at the terminal reach of the river flowing through an area of seasonally frozen ground.

Based on climate data for the Bayankhongor station in 1974–2013 ([www.ogimet.com/gsocd.phtml](http://www.ogimet.com/gsocd.phtml)), in 2013 the mean annual temperature was 1.5 °C (Fig. 2B), which was higher than the mean for the entire period (–0.3 °C). Total annual precipitation in 2012 and 2013 was lower than the long term mean (205 mm) at 187 mm and 186 mm respectively. In the time preceding sampling (July, August), average daily temperatures reached 15–20 °C, however maximum daily temperatures at the beginning of July were up to 30 °C (Fig. 2A). It rained from June to the second half of August, however, total daily precipitation amount did not exceed 20 mm (Fig. 2A). Several years before 2013 featured low total precipitation (apart from years 2010 and 2011) and high air temperatures (Fig. 2B).

### 3.2. Analytical methods

The concentrations of organic and inorganic compounds (total organic carbon – TOC, metals and ions) in water samples were determined by Analyzer TOC-VCSH/CSN (method of catalytic combustion (oxidation) with the use of NDIR detector), inductively coupled plasma mass spectrometry Thermo XSERIES 2 ICP-MS (Thermo Fischer Scientific, Bremen, Germany) and DIONEX 3000 chromatograph (DIONEX, USA), respectively. Physicochemical parameters such as pH and electrolytic conductivity (SPC) were determined by the electrochemical method with the application of a microcomputer pH/conductometer CPC-411 by Elmetron, electrode type EPS-1, and conductivity sensor EC 60. Total dissolved solid (TDS) was obtained using gravimetric method. Linear calibration curves were obtained for each method. Limit of detection (LOD) was calculated based on standard deviation of response (*s*) and the slope of the calibration curve (*b*) according to the formula: LOD = 3.3 (*s* / *b*). Limit of quantitation (LOQ) was calculated based on the standard deviation of response (*s*) and the slope of the calibration curve (*b*) according to the formula: LOQ = 10 (*s* / *b*). Standard deviation of the response (*s*) was calculated based on ten method blank replicates. All blanks were analysed in the same setup as for the samples, using the same reagents, in deionised water which has shown levels below detection limit for TOC, selected ions and trace elements. Limit of detection was

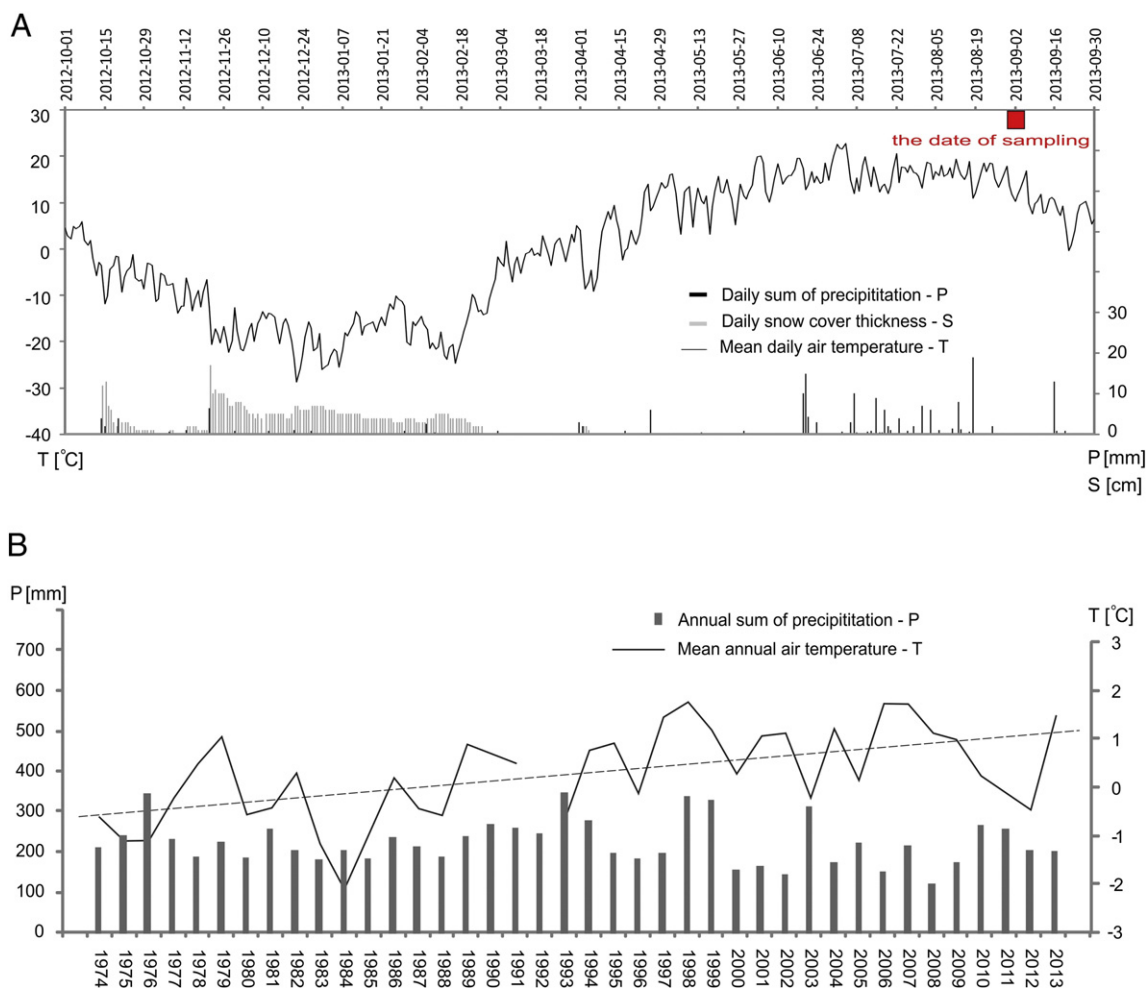


Fig. 2. Weather conditions (A) in the study area (1 October 2012–30 September 2013) and (B) long-term climate data at the Bayankhongor station. Based on data from [www.ogimet.com/gsocd.phtml](http://www.ogimet.com/gsocd.phtml), and Harris et al. (2014).

from  $0.003 \mu\text{g L}^{-1}$ ,  $0.01 \text{ mg L}^{-1}$  and  $0.03 \text{ mg L}^{-1}$  for metals, ions and TOC concentration, respectively. Resolution of the pH microcomputer/Elmetron CPC-411 conductometer was 0.01 for pH 956 S  $\text{cm}^{-1}$  conductivity. Technical specifications, reagents for determining selected parameters and analyte contents in water samples and basic validation parameters of the analytical procedures are summarized in Appendix A1.

### 3.3. Statistical methods

Pearson's correlation coefficients ( $r$ ) were calculated to detect pairwise relationships among the metals and TOC concentration in the investigated water samples. Correlation coefficients were considered as statistically significant at the level of significance  $p < 0.05$ . To identify patterns in all physicochemical data Principal Component Analysis (PCA) was performed. Both PCA and Pearson's correlation coefficients were computed with the software package STATISTICA 6.1 (StatSoft Inc., Tulsa, OK, USA).

## 4. Results

### 4.1. Basic inorganic chemical analysis

Major chemical properties of the studied water samples are listed in Table 1. The river-lake systems are different in terms of mineral properties, with TDS ranging from  $0.15$  to  $6.38 \text{ g L}^{-1}$  and from  $0.07$  to  $1.71 \text{ g L}^{-1}$  for the Baydrag–Böön Tsagaan System and the Shargalyuut/Tuyn–Orog System, respectively. In the sampling area where permafrost

occurs, values of TDS in river waters range from  $0.15$  to  $0.22 \text{ g L}^{-1}$  and from  $0.07$  to  $0.17 \text{ g L}^{-1}$  in Baydrag river and Shargalyuut/Tuyn rivers, respectively. All water samples range from neutral to alkaline but these values differ across the sampling area.

Ion concentrations give quantitative information regarding chemical water composition (Table 1). However, the percentage of ion distribution in the sample (% meq) is required to determine the exact chemical water characterisation in detail (Fig. 3). Concentrations of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  anions in the Baydrag river tend to decrease down the river. This appears to be reversed in the Shargalyuut/Tuyn–Orog System.  $\text{NO}_2^-$  concentrations in these samples were under the detection limit.  $\text{PO}_4^{3-}$  notably decreases down the river from  $12.9 \text{ meq L}^{-1}$  to  $0.77 \text{ meq L}^{-1}$  in samples 1 and 2, respectively.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  increased in both river–lake systems.

To evaluate correlations between individual groups of ions in each sample, a trilinear diagram was prepared (Fig. 3). The figure represents (a)  $\text{Mg}^{2+} + \text{Ca}^{2+}$  – ions, which shape water hardness; (b)  $\text{Na}^+ + \text{K}^+$  – ions typical for lakes located in arid zones, where evaporation exceeds the supply of water; (c)  $\text{NH}_4^+$ , and (d)  $\text{NO}_2^- + \text{NO}_3^- + \text{PO}_4^{3-}$  – ions, which can be used as an indicator of the organic matter's mineralization grade and/or as an indicator of fertilizer usage; (e)  $\text{Cl}^- + \text{F}^-$  – ions indicate salinity (mainly  $\text{Cl}^-$ ), and (f)  $\text{SO}_4^{2-}$  – effect of the dissolution of minerals in sedimentary rocks. The percentage share in individual cation groups under is similar in samples collected from rivers and springs. In the lake water the percentage of  $\text{Na}^+ + \text{K}^+$  in total cations is high, which is largely accounted for by high  $\text{Na}^+$  values. In the case of anions, these are almost all chlorides ( $\text{Cl}^-$ ) and

**Table 1**  
Major chemical properties in Mongolian water reservoirs.

Analyte or parameter:		TDS	pH	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Li <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	F <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	Br <sup>-</sup>	Ref.	
Area	Sampling place	g L <sup>-1</sup>	—	mg L <sup>-1</sup>														
Unit																		
Gobi region	Böön Tsagaan Lake <sup>a</sup>	—	—	1530	—	40	170	—	—	1170	1680	—	—	—	—	—	Egorov (1993)	
	Orog Lake <sup>a</sup>	—	—	1800	—	20	410	—	—	16900	6250	—	—	—	—	—		
	Hyargas Lake <sup>a</sup>	—	—	2380	—	10	0.30	—	—	1350	2220	—	—	—	—	—		
	Uvs Lake <sup>a</sup>	—	—	5470	—	10	840	—	—	6150	4930	—	—	—	—	—		
	Dorgon Lake <sup>a</sup>	—	—	1410	—	<LOD	160	—	—	560	1110	—	—	—	—	—		
Khangai-Khentei region	Sangiwyin	—	—	1180	—	10	090	—	—	1140	290	—	—	—	—	—		
	Dalay Lake <sup>a</sup>	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—		
	Oygon Lake <sup>a</sup>	—	—	9200	—	30	550	—	—	7690	8300	—	—	—	—	—		
	Arhel Lake <sup>a</sup>	—	—	6820	—	40	680	—	—	2770	11,000	—	—	—	—	—		
	Tsagan Lake <sup>a</sup>	—	—	5660	—	10	170	—	—	1620	7260	—	—	—	—	—		
	Darday Lake <sup>a</sup>	—	—	7170	—	10	050	—	—	3070	4990	—	—	—	—	—		
Altai mountains region	Dzugny Lake <sup>a</sup>	—	—	980	—	20	100	—	—	890	0460	—	—	—	—	—		
	Talmen Lake <sup>a</sup>	—	—	1800	—	10	370	—	—	1430	1780	—	—	—	—	—		
Khangay and Gobi region	Ureg Lake <sup>a</sup>	—	—	1010	—	10	520	—	—	740	2040	—	—	—	—	—		
	Duro Lake <sup>a</sup>	—	—	1410	—	<LOD	160	—	—	560	1110	—	—	—	—	—		
	Baydrag-Böön Tsagaan System	Baydrag river (a)	0.15	8.10	6.02	7.05	5.46	0.57	<LOD	7.46	12.1	12.0	5.80	5.23	0.67	<LOD	5.40	Our research
	Baydrag river (b)	0.22	8.18	6.80	5.16	8.49	0.65	<LOD	7.26	9.63	30.7	4.65	4.66	0.34	<LOD	<LOD		
	Baydrag river (b)	0.32	8.07	7.97	8.07	8.14	0.91	<LOD	8.97	24.3	44.3	2.03	0.34	0.50	<LOD	<LOD		
	Böön Tsagaan Lake (b)	6.38	9.40	451	1031	235	40.4	<LOD	14.1	1329	1661	2.03	<LOD	13.7	31.8	<LOD		
	Supply spring (b)	0.20	7.85	7.56	10.6	11.3	0.76	<LOD	7.20	16.1	9.42	2.59	2.69	0.07	13.7	4.00		
	Shargalyuut-tributary Tuyn (c)	0.08	7.91	11.9	2.26	6.63	0.60	<LOD	4.31	7.65	13.7	5.42	<LOD	0.88	12.9	<LOD		
	Tuyn river (d)	0.18	8.10	8.58	8.67	10.2	0.72	<LOD	7.14	11.3	24.1	6.64	<LOD	4.77	0.77	0.838		
Yabulai Mountains	Orog Lake (b)	1.71	9.20	27.8	368	13.6	16.5	0.22	7.90	318	230	2.07	<LOD	25.8	<LOD	<LOD		
	Supply spring (b)	0.12	8.10	6.96	8.58	7.21	1.20	<LOD	6.90	9.62	24.2	9.69	0.30	4.54	<LOD	<LOD		
	Lake <sub>1</sub>	353	9.8	7073	128,700	<0.01	29	<0.01	—	180,953	30,993	6	—	5	12.4	—	Yang (2006)	
Northern Mongolia	Lake <sub>2</sub>	125.52	8.9	3393	41,335	62	1809	19.00	—	58,758	18,341	14	—	8	<0.04	—		
	Lake <sub>3</sub>	17.18	9.7	282	5766	4	294	0.35	—	6679	2587	1	—	6	0.06	—		
Shargaljuut	Inlet streams to Lake Hövsögöl <sup>b</sup>	—	7.4–8.0	16–23	166–302	278–532	215–389	—	0.5–3	10–51	95–281	0.5–3	—	—	—	—	Puntsag et al. (2010)	
	Hot springs <sup>c</sup>	120–140	8.2–8.7	1.1–1.9	62.5–88.2	1.6–2.4	<0.1	0.47–0.53	—	0.1	0.7–1.0	—	0.06–0.67	0.04–0.05	—	—	Bignall et al. (2003)	
Inner Mongolia	Warm springs <sup>c</sup>	130–150	8.4	1.7–1.8	74.7–89.3	1.7–1.9	<0.1	0.51–0.54	—	0.1–0.6	0.8–5.6	—	—	0.22–1.37	—	—	Williams (1991)	
	Dalatulu Lake	—	—	0450	42,000	—	30	—	—	26,500	25,700	—	—	—	—	—		
Badain Jaran Desert (Inner Mongolia)	Hadat Lake	—	—	3210	85,300	—	130	—	—	49,700	19,500	—	—	—	—	—		
	Wudu Lake	—	—	3480	127,900	—	130	—	—	78,000	36,000	—	—	—	—	—		
	Aledante Lake	—	—	—	142,100	—	10	—	—	73,300	47,700	—	—	—	—	—		
	Baoritelegai Lake	1.2	7.79	0.01	0.296	0.1	0.03	0.02	<0.05	0.318	0.33	—	—	—	<0.05	—	Yang and Williams (2003)	
	Badain Lake	1.8–398.2	86,800–10,600	30–7620	590–147,000	10	3–80	30–560	380–2000	0.46–112,000	280–42,900	—	—	—	22,000	—		
	Maoertu Lake	380	10,180	13,900	136,000	4	58	320	<LOD	169,000	4900	—	—	—	6000	—		
Central Mongolia	Sumujilin Lake	127.8–167	10,500–10,600	3930–4000	48,400–71,400	0.007	81–143	20–100	540–15,500	39,500–40,500	14,100–25,700	—	—	—	1100–2400	—		
	Nuoertu Lake	89.8	10,300	2860	42,600	<LOD	347	300	<LOD	33,600	13,900	—	—	—	—	—		
	Yindeertu Lake	242.5	10,500	—	90,600	<LOD	152	110	<LOD	—	24,300	—	—	—	—	—		
	Huhejilin Lake	109	10,500	3380	40,800	8	109	240	2550	28,100	11,600	—	—	—	1100	—		
Khangay region	Tuul river at Ulaanbaatar	—	—	0.7	9.5	1.1	2.4	—	—	4.5	—	—	3.1	—	3.1	—	Chalov et al. (2012)	
	Orkhon river at Kharkhorin	—	—	1.59	9.3	1.9	1.3	—	—	5.3	—	—	—	—	—	—		

(—) not determined.

<LOD – below limit of detection.

List of abbreviation – zones of: (a) sparsely insular permafrost, (b) seasonally frozen ground, (c) insular permafrost, (d) sporadic frozen ground (Fig. 1).

<sup>a</sup> K<sup>+</sup> and Na<sup>+</sup> determined like sum of each one.

<sup>b</sup> Concentration of ions in μmol L<sup>-1</sup>.

<sup>c</sup> Analytes and parameter TDS determined in unit mg kg<sup>-1</sup>.

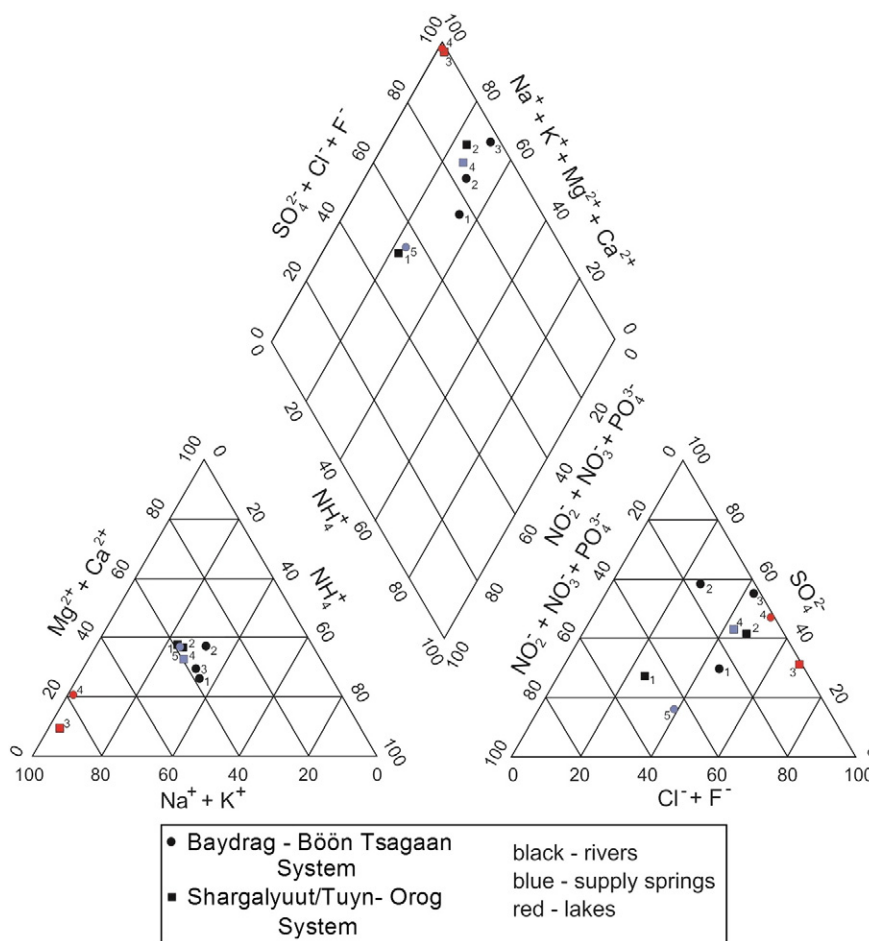


Fig. 3. Trilinear diagram for the both river–lake systems. Diagram indicates major ions concentrations in % meq.

sulphates ( $\text{SO}_4^{2-}$ ) (likely in the form of sodium sulphate combined with  $\text{Na}^+$ , which prevails among the cations). In most studied samples the percentage of  $\text{Cl}^- + \text{F}^-$  with  $\text{SO}_4^{2-}$  is 75–89%, and  $\text{NO}_2^- + \text{NO}_3^- + \text{PO}_4^{3-}$  reach 50% of total anions (Fig. 3). Chemistry of lake water is distinctly different to rivers and streams, hence a Thielker diagram can be used to describe and compare in the ion chemistry of both lakes. As indicated in Fig. 4, the values of anions and cations in Bööen Tsagaan are distinctively higher than those in Orog Lake, but with very similar distributions of individual ions.

#### 4.2. Trace metal analysis in the context of TOC concentration

For the initial characterisation of metals in the analysed water samples, metals were ranked depending on concentration levels (Appendix B1). From highest to lowest, there are: silicon, strontium (high and medium ranges of metal concentration) and barium, aluminium, scandium and lithium (medium range of metal concentration). In springs and lakes, the most significant trace metal is uranium. Total organic carbon concentration (TOC) can be compared with the concentration of metals (Appendix B2). Significant positive correlations were found in the metal group of Cu, Fe, Mn, Al, Zn, Ni, U, V, Li, and As, and in the group of Ga, Rb, Ba, Sr, Se, Co, Cr, Si, and Sc. Scandium and silicon shows a negative correlation with all variables, but a positive correlation with one another ( $r = 1.00$ ). Moreover, very strong correlations ( $0.8 < |r| \leq 1$ ) were found between TOC and Li, Co, As, Se, Rb, Sr, Ba, Si and Sc. The level of occurrence of heavy metals in water is closely determined by the chemical environment (pH) (Naseem et al., 2014). Ficklin introduced the concept of water classification in the form of relationship between total base metal (Zn, Cu, Pb, Cd, Ni, Co) content ( $\mu\text{g L}^{-1}$ ) and water pH

(Naseem et al., 2014). The initial analysis involved a selection of base metals such as Zn, Cu, Pb, Cd, Ni, and Co. However, in all of the analysed samples, Pb concentration was below the limit of detection and Cd concentration was determined only in lake water. A modified Ficklin diagram was used, with As, Fe and Cr (instead of Pb and Cd) as heavy metals can be used to analyse metal concentration in this particular environment. Therefore, the relationship between the sum of heavy metals ( $\text{Cr} + \text{Co} + \text{Ni} + \text{Cu} + \text{Zn} + \text{As} + \text{Fe}$ ) and pH was obtained (Fig. 5). Significant differences in metal occurrence are seen in river and lake waters. At pH values of 9.2–9.4, the sum of heavy metals amounts to  $40.9 \mu\text{g L}^{-1}$  and  $81.8 \mu\text{g L}^{-1}$  for the Bööen Tsagaan Lake and Orog Lake, respectively. At lower pH (7.85–8.18), the sum of selected metals is  $1.0$ – $9.2 \mu\text{g L}^{-1}$ . These values correspond to the river and spring water samples (Fig. 5).

#### 4.3. Entire chemistry analysis – application of Principal Component Analysis

In this paper PCA considered the hydrogeochemical variables (36) common to all samples taken from both river–lake systems. Variables include major ions, metals, pH, SPC and TOC. The correlations among the variables were used to estimate Principal Components (PCs) and their loadings. Three principal components were identified. PCs 1 and 2 represent 81.93% of the variance. PC1 represents the majority of variables and is strongly negatively correlated with Si and Sc, and strongly positively correlated with pH, SPC, TOC,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , Li, V, Co, As, Se, Rb, Sr, and Ga. PC2 is positively correlated with Al, V, Mn, Cu, U, Fe, Ni, and Zn. Based on the projection of each data point on the plane of the two principal components (Fig. 6), the

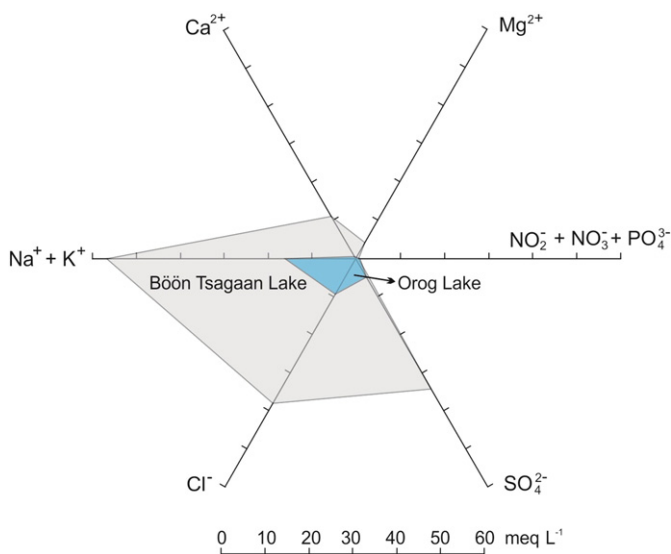


Fig. 4. Thicket diagram for both researched lakes.

water samples can be distinguished into two groups, represented by lake water, and river and spring water.

## 5. Discussion

Water chemistry may be affected by numerous factors, including permafrost occurrence, geology and climate.

### 5.1. Permafrost impact

Permafrost environments have highly variable physical, biological and geochemical conditions. The distribution of frozen ground and taliks, as well as the freeze–thaw processes of aquifers exert influence on the hydrogeological conditions of rivers and lakes (e.g., Petrone et al., 2006; Frey and McClelland, 2009; Bagard et al., 2011, Douglas et al., 2013; Larouche et al., 2015; Manasyrov et al., 2015). Degradation of permafrost and changes in snow cover dynamics have considerably

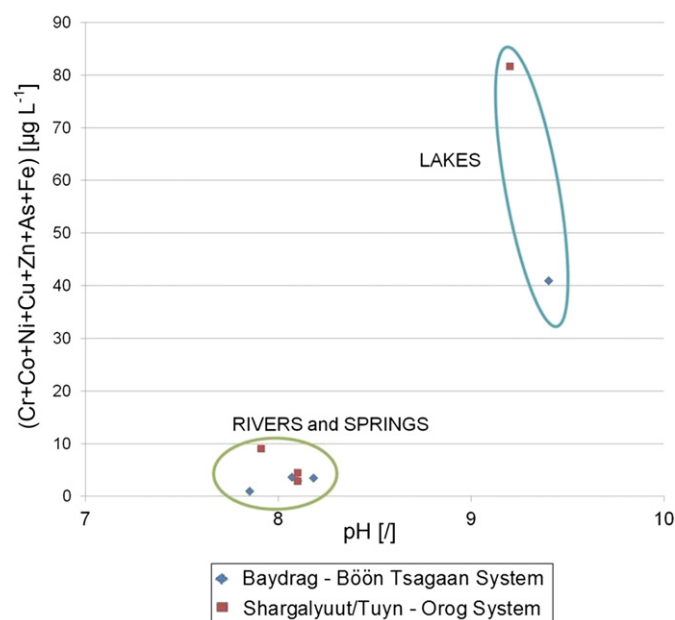


Fig. 5. Relationships between metal concentration and pH values in both river–lake systems.

altered cold-region hydrological and hydrogeological environments (Cheng and Jin, 2012). Since the late 20th century, the thermal state of shallow permafrost has changed in Mongolia (Batimaa et al., 2008; Bayasgalan et al., 2009).

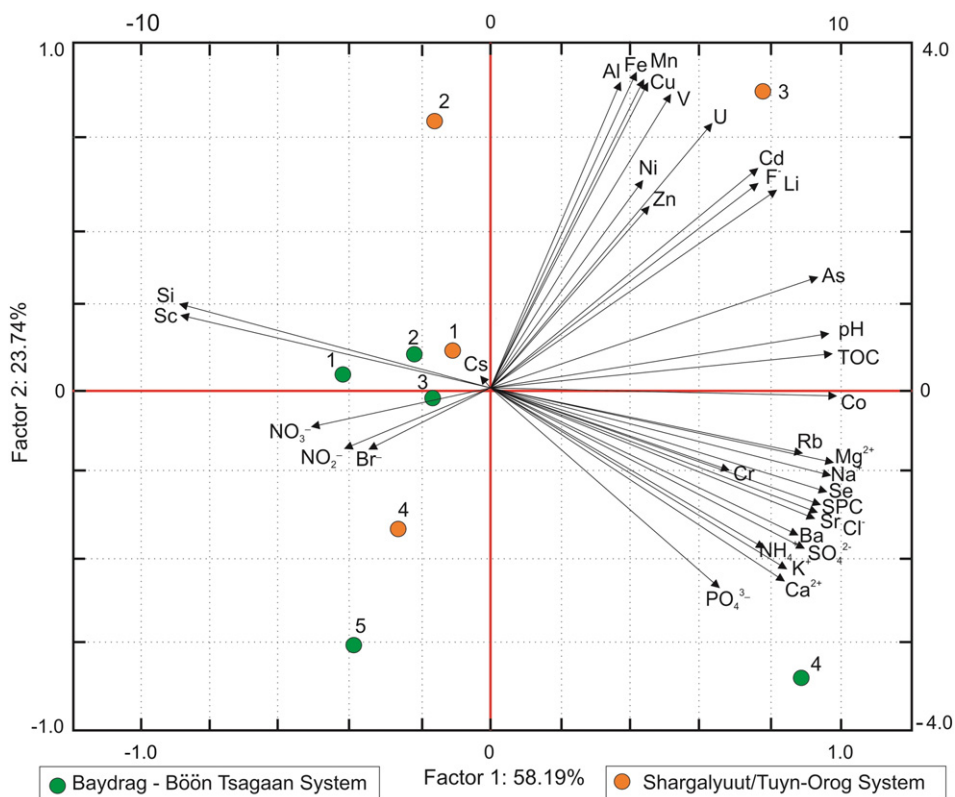
River valleys in Mongolia have unconfined aquifers (Thorslund et al., 2014), which provide favourable conditions for ion exchange, except in areas with continuous and discontinuous permafrost. Since the water samples were collected in summer, it is difficult to say whether the active layer of permafrost affected water mineralisation in any significant way. During summer rivers are supplied mostly by precipitation, while water from the thawing permafrost cover is, almost all subject to evapotranspiration (e.g., Glazik, 1995). The thawing of permafrost could increase the concentration of nitrogen ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ), as well as  $\text{Na}^+$  and  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , since increased soil temperature improves nitrogen mineralisation and nitrogen availability (Yang et al., 2010). However, it may also be the effect of livestock grazing, which results in a loss of topsoil and riparian vegetation. Trampling of riparian zones by animals further increases the suspended load in water (Demeusy, 2012). An increase in Sr between samples 1 and 2 in both rivers (Table 1) may reflect soil erosion and rock weathering, hence, this element may be more strongly retained by permafrost in higher reaches than in the lower reaches.

The relationship between inorganic solute concentrations and permafrost distribution was also observed across western Siberia (in summer) (Frey et al., 2007). These results do not indicate a release of compounds as a result of permafrost degradation. Frey et al. (2007) concluded that inorganic solutes (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ) are more concentrated in water in permafrost-free watersheds than in areas affected by permafrost. Despite this, Frey et al. (2007) pointed out that climate warming and potential permafrost degradation can increase dissolved solid concentration in watersheds. Furthermore, they observed that the concentration of Si remains unaffected by permafrost. This, however, can be a result of the overall low silicate mineral content in the area (Frey et al., 2007). Abbott et al. (2015) discussed the potential effects of permafrost collapse (thermokarst) on aquatic biochemical cycles. The authors concluded that upland thermokarst (across the foothills of the Brooks Range, Alaska) causes significant increases to the concentration of inorganic nitrogen and other solutes (e.g.,  $\text{SO}_4^{2-}$ ) in surface water bodies. In our research we also observed an increase in the concentration of nitrogen ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ),  $\text{Na}^+$  and  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  downstream in the Tuyn river, which may possibly be a consequence of permafrost degradation. Abbott et al. (2015), in accordance with Frey et al. (2007), underline the increasing impact of permafrost changes on aquatic ecosystems, which can occur with global temperature rise.

### 5.2. Geology impact

In many places, water chemistry is controlled by chemical weathering of sediments, dissolution of secondary carbonates and ion exchange between water and clay minerals. Most minerals dissolve slowly, thus higher TDS water should occur in those areas where the water is in contact with more soluble minerals for longer periods of time (e.g., Fitts, 2002). Due to the highly variable lithology, there is the possibility of contamination of surface water with various elements and compounds. The content of minerals, such as  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , and metals such as Fe, Li, Mn, Cr, Ni, Rb, Co, Cs and Si in the study area is mostly related to long-term dissolution of minerals from the local igneous rocks, post-magmatic veins and sedimentary rocks.

In the Shargalyuut river, geology influenced water chemistry in a considerable way. There is a higher content of Fe, Cr, Ni, Rb, Co, Cs, Ga and actinide elements in comparison with Baydrag and Tuyn river waters. Furthermore, silicon content in samples taken from the upper river reaches of the Baydrag and Shargalyuut rivers is particularly high. This is also a result of weathering of acid igneous rocks and post-magmatic chalcedony veins. In the middle reaches of the rivers,



**Fig. 6.** PCA biplot for data set. Projection of environmental variables (bottom X axis and left Y axis) and cases – sampling points (upper X axis and right Y axis) on the plane of two principal components.

sample 2 from the Tuyn river has slightly higher lithium, silicon and higher heavy metals than the sample taken from the Baydrag river (sample 3). This is related to the lithological enrichment of lithium minerals (e.g., lepidolite). The supply springs are characterised by low mineral content. Enrichment of lake water (with  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions) from evapotranspiration processes can also affect the supply spring chemistry.

Extended information regarding geological influence on river and spring water chemistry is available in Appendix C.

### 5.3. Climate impact

Waters of both lakes are highly mineralised and constitute an outlet for all elements that naturally occur in flowing water. Seasonal and multi-annual fluctuations in water level cause the elements flowing down with river waters to concentrate in the lake basins. River waters in Mongolia transport during heavy rainfall large amounts of suspended sediments (e.g., Chalov et al., 2012; Thorslund et al., 2014), which further enriches mineral content of water in a given lake. It results from rapid surface runoff caused by sparse vegetation and the occurrence of permafrost, which prevents infiltration. In arid periods, lakes are subject to intense evaporation, when chlorides (in particular) and sulphates increase their concentration as water volume decreases (Williams, 1991), which leads to precipitation of evaporates, mostly plaster stones and halite.

There is a clear difference between chemistry of lakes and of other waters under analysis (Table 1, Figs. 3–6). High TDS and high amounts of ions in the lake water originate from intensive evaporation: precipitation (50–150 mm; Davaa and Oyunbaatar, 2012) is much smaller than potential evaporation (800–1000 mm; Davaa and Oyunbaatar, 2012) on the water surface. A higher total content of cations in the lakes arises from a markedly higher content of  $\text{Na}^+$ , compared to samples from rivers and supply springs (Table 1). Similar results were presented by Egorov (1993). Deflation of precipitated compounds

from dry lake beds and changes in water chemical composition in lakes under fluctuating lake levels reflect seasonal and annual climate changes.

### 5.4. Two river–lake systems – similarities and differences

Despite widespread occurrence of saline lakes in Mongolia, their chemistry has not been well studied. Ion chemistry of water collected from desert lakes is subject to considerable changes depending on the region. All Mongolian lakes are of continental origin, and have ionic compositions dominated by  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ . In the river–lake systems under study, one may also indicate the prevalence of  $\text{Ca}^{2+}$  (Table 1). Si, Sr and Ba, Al, Sc and Li represent the most significant contribution in water chemistry in the studied samples (Appendix B1).

The water samples collected from Mongolian river–lake systems show different pH values for rivers and supply springs (7.85–8.18) and lakes (9.2–9.4). However, both are located in the near-neutral zone, which is related to low metal content (Fig. 5). Hence, at high pH values, metal content (apart from alkaline metals and alkali soils) in rivers and springs is not particularly high. However, organic matter (as measured by TOC) plays an important role in the adsorption of heavy metals. There were significant strong positive correlations between TOC and Li, Co, As, Se, Rb, Sr and Ba (Appendix B2) which increases the adsorption of these metals. Solubility of metals increases with TOC content as a result of metal ion complexation in the form of ions with organic ligands. The presence of organic matter in waters can also change the hydrogeochemical cycles of trace elements by the means of redox reactions, peptisation and sorption. Permafrost may play an active role in TOC storage (e.g., Koch et al., 2013). Organic matter availability depends on thickness of the active layer (Yang et al., 2010). The increase in the depth of active layer (degradation of permafrost) can make considerable amounts of otherwise frozen organic matter bio-available (Yang et al., 2010).



Two extracted PCs indicate two different influences on water chemistry. PC1 is strongly correlated with pH, SPC, TOC, F<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Li, V, Co, As, Se, Rb, Sr, Ga, and Cd (positive correlation) and Si and Sc (negative correlation). This can indicate that water chemistry is modified by groundwater supply and evaporation processes. PC2 is positively correlated with Al, V, Mn, Cu, U, Fe, Ni, and Zn. This may indicate limited transport of these elements in this environment, which can occur for example due to oxidation–reduction reactions. Moreover, based on Fig. 6, the water samples can be grouped into (1) lakes samples, where water chemistry is shaped by dominated evaporation processes, and (2) river and spring waters. Water chemistry of these samples is mostly influenced by geochemical and hydro-meteorological processes.

## 6. Conclusions

This work presents the first comprehensive chemical inorganic analysis of the Baydrag River–Böön Tsagaan Lake system and the Shargalyuut/Tuyn Rivers–Orog Lake system. The rivers and their sources are characterised by low mineralization and constitute “background” for the lake water chemistry, which in turn is strongly modified by evapotranspiration. Moreover, one must take into consideration seasonal drying out of the lakes, which leads to deflation of evaporites from exposed lake beds. Water samples from lakes that periodically dry out have lower concentrations of chemical compounds (e.g., ions). This means that lakes that periodically dry out cannot be compared with lakes with relatively stable water tables.

Factors affecting the state of water chemistry in the regions of the Central Mongolia are complex by nature and involve the following:

- permafrost occurrence in the upper reaches of the rivers,
- increased element concentration resulting from cyclical evaporation processes and rapid surface runoff during snow melt and rainfall,
- deflation of evaporites from exposed lake beds, causing relatively lower concentration of elements in these lakes,
- infiltration of elements from evaporates found in exposed lake beds into groundwater, and
- anthropogenic factor (agriculture).

Factors affecting the status of water chemistry recommended for further investigation include influence of permafrost, especially in the upper reaches of rivers, and the impact of grazing on water chemistry characteristics.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.sedgeo.2016.03.004>.

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