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The chemistry of river–lake systems in the context of permafrost occurrence (Mongolia, Valley of the Lakes) Part II. Spatial trends and possible sources of organic composition

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a b s t r a c t

The chemistry of river–lake systems located in Central Mongolia near the southern border of permafrost occur-rence has not been well studied. The main aim of this paper is to summarize patterns in water chemistry in supply springs, rivers and lakes in relation to permafrost occurrence, as well as other natural and anthropogenic impacts. The analyses involved water samples taken from two river–lake systems: the Baydrag River–Böön Tsagaan Lake system and the Shargalyuut/Tuyn Rivers–Orog Lake system. Total organic carbon (TOC) and polycyclic aromatic hydrocarbons (PAHs) were detected and quantified. Other organic compounds, such as organic halogen com-pounds, phthalates, and higher alkanes were also noted. The main factors which influence differences in TOC con-centrations in the water bodies involve permafrost occurrence, mainly because compounds are released during active layer degradation (in the upper reach of the Tuyn river), and by intensive livestock farming in river valleys and in the vicinity of lakes. In relation to the concentrations of PAHs, high variability between samples (N300 ng L^{-1}), indicates the influence of thermal water and local geology structures (e.g., volcanic and sedimen-tary deposits), as well as accumulation of suspended matter in lakes transported during rapid surface runoff events. The monitoring of TOC as well as individual PAHs is particularly important to future environmental stud-ies, as they may potentially reflect the degradation of the environment. Therefore, monitoring in the Valley of the Lakes should be continued, particularly in the light of the anticipated permafrost degradation in the 21st century, in order to collect more data and be able to anticipate the response of river–lake water chemistry to changes in permafrost occurrence.

Keywords: Mongolia, River–lake systems, Organic compounds, PAHs, Permafrost, Volcanism

1. Introduction

Permafrost is widespread in the Arctic and boreal regions of the Northern Hemisphere (e.g., Petrone et al., 2006; Frey et al., 2007; McClelland et al., 2007; Kokelj et al., 2009; Stotler et al., 2009; Douglas et al., 2013; Olefeldt et al., 2014; Manasypov et al., 2015), including China and Mongolia (Yang et al., 2010) and several mountain regions (e.g., Cheng and Dramis, 1992; Zhao et al., 2010; Dobinski, 2011). The distribution of permafrost is controlled by air temperature and, to a minor extent, by vegetation and soil properties (Schaefer et al., 2011). As temperature rises, permafrost degradation can be identified as one of the key cryosphere indicators of global climate change (Yang et al., 2010). The extent of permafrost degradation is indirectly reflected in the changes in freshwater conditions. The hydrochemical status of fresh water in the Northern Hemisphere is believed to be greatly affected by permafrost degradation. This phenomenon is observed as seasonal fluxes of nutrients and carbon (e.g., Petrone et al., 2006; Frey et al., 2007; McClelland et al., 2007; Zhang et al., 2008; Kokelj et al., 2009; Stotler et al., 2009; Bagard et al., 2011; Douglas et al., 2013; Olefeldt et al., 2014; Manasypov et al., 2015).

The study area (Valley of the Lakes, Mongolia) is located at the border of permafrost occurrence, which reaches its southernmost latitude in the Northern Hemisphere. According to predictions, climate in Mongolia will continue to change over the 21st century (Dagvadorj et al., 2009), with an increase in annual temperatures from 3.5 to 4 °C across Mongolia over the next 100 years (Christensen et al., 2007), which may lead to significant permafrost degradation over a consider-able area (Lawrence and Slater, 2005; Guo et al., 2012). We can assume that in the southern range of permafrost occurrence, changes will be most severe and will eventually lead to complete degradation of the permafrost. Hence, the better thermal characterization and spatial distribution of permafrost degradation in this region would greatly contribute to improving the prediction of global climate change impacts.

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Thus far relatively few studies have investigated the chemistry of Mongolian reservoirs (e.g., Williams, 1991; Egorov, 1993; Bignall et al., 2003; Puntsag et al., 2010; Hofmann et al., 2015). Moreover, only a few papers attempted to provide a description of water chemistry and organic components (e.g., Baek et al., 2013; Free et al., 2014). The characteristics of inorganic chemistry of two studied river–lake systems in the Valley of the Lakes (the Baydrag River–Böön Tsagaan Lake system and the Shargalyuut/Tuyn Rivers–Orog Lake system) was discussed by Szopińska et al. (2016). Overall findings of this study suggest that the rivers and their sources have low mineralization and constitute a "background" for the lakes' water chemistry. Moreover lake water is considerably modified by evapotranspiration as well as by seasonal drying out of the lakes (e.g., Lake Orog). Based on Szopińska et al. (2016), two categories of factors that affect water chemistry can be distinguished: natural factors, such as permafrost occurrence, intensive water evaporation and mineralogical background; and anthropogenic factors, including agriculture. These factors can also potentially influence the spatial trends and shape of organic composition in both river–lake systems.

The main aim of this paper is to summarize patterns at organic composition variation (mainly total organic carbon – TOC, and polycyclic aromatic hydrocarbons – PAHs) of rivers located in the vicinity of permafrost occurrence. TOC was selected as a priority parameter to indicate general changes in water organic composition. PAH determination and identification of volatile and semi-volatile organic compounds were used to offer a precise description of water chemistry. Permafrost degradation may mainly affect the organic solute chemistry of upper river reaches (Baydrag, Shargalyuut and Tuyn). Volcanic and sedimentary deposits as well as hydrothermal minerals can also contain dispersed bituminous materials enriched with PAHs (Geptner et al., 2005). Hence, volcanic deposits and numerous hot springs (near the Shargalyuut river) in the study area can potentially affect PAH levels. Moreover, the impact extent of the volcanic factor on water chemistry in river–lake systems could be better understood, if we compare the chemical characteristics of water samples taken from an area subject to the influence of earlier volcanic activity with water chemistry of the lake formed in a volcanic caldera (Togo volcano area).

2. Study area

2.1. Hydrological setting

The study involved two river lake systems located in the Valley of the Lakes: the Baydrag River–Böön Tsagaan Lake system (Baydrag–Böön Tsagaan System) and Shargalyuut/Tuyn Rivers–Orog Lake system (Shargalyuut/Tuyn–Orog System) (Fig. 1A). The basins of the analyzed river–lake systems cover an area of 45,020 km^2 and 14,929 km^2 for the Baydrag–Böön Tsagaan system and the Tuyn–Orog system, respectively (Lehner et al., 2008). Both rivers have their source zones in the Khangai mountains (one of the Mongolian "runoff-forming areas") (Davaa and Oyunbaatar, 2012; Kwadijk et al., 2012), flow to the south, across the uplands to the Valley of the Lakes, where they feed two large lakes (Fig. 1A).

Total precipitation in the study area decreases southwards, from 300 to 350 mm in the Khangai mountains, where the river source zones are found, to 50–150 mm in the Valley of the Lakes, where they flow into the lakes of Böön Tsagaan and Orog (Davaa and Oyunbaatar, 2012; Kwadijk et al., 2012). Mean sum of annual precipitation in the analyzed basins in the years 1974–2013 was 205 mm and mean annual temperature was −0.3 °C (Fig. 2A).

In this region river runoff is shaped by rainfall, groundwater and snowmelt (Davaa and Oyunbaatar, 2012). Groundwater resources in both basins are spatially varied, but more than 90% of the area is characterized by scarce groundwater resources with a yield at less than 0.3 L s^{-1} km^{-2} (Jadambaa and Batjargal, 2012). Annual specific runoff in the Baydrag and Tuyn basins tends to decrease southwards with the river course and ranges from 2.5–3.0 L s^{-1} km^{-2} in the vicinity of the Khangai slope to less than 1.0 L s^{-1} km^{-2} in the Valley of the Lakes (Glazik, 1995; Batsukh et al., 2008; Davaa and Oyunbaatar, 2012). Data collected at two gauges in Tuyn (1970–2008) show a downstream decrease in specific runoff from 1.22 L s^{-1} km^{-2} for the Tuyn in Bayankhongor to 0.302 L s^{-1} km^{-2} for the Tuyn in Bogd (Davaa and Oyunbaatar, 2012).

The lakes of Böön Tsagaan and Orog constitute remnants of a former larger lake that covered the greater part of the Valley of the Lakes (Komatsu et al., 2001). The surface area of the lakes in the middle of the 20th century amounted to 252 km^2 in the case of Böön Tsagaan, and 140 km^2 for Lake Orog, with a volume 2.355 km^3 and 0.42 km^3, and mean depth at 10 m and 3 m, respectively (Davaa et al., 2007). However, the surface area of both lakes decreased in the period 1974–2013 by 14% in the case of the Böön Tsagaan Lake and 51% in the case of Lake Orog. Due to the fact that the lakes are located at the border between an arid steppe and a semi-desert, the water bodies are characterized by marked water table fluctuations. Lake Orog is subject to considerably greater fluctuation, both on an annual and interannual bases (Szumińska, 2016), which is a result of three times smaller discharges in the Tuyn river in comparison to the Baydrag river (Davaa and Oyunbaatar, 2012). In 1974–2013, Lake Orog dried out on several occasions (in 1989 and later between 2006 and 2011), which may have significantly affected the current chemical status of the lake water.

2.2. Weather conditions at the time of sampling

Samples were collected in late August and early September 2013. Average daily temperatures in that period ranged from 10 to 17 °C (Fig. 2B). It rained from June to the second half of August, but total daily precipitation did not exceed 20 mm. Average daily temperatures in July and August reached 15–20 °C, however the maximum daily temperatures at the beginning of July were up to 30 °C. Data analysis shows that several consecutive years before 2013 featured low total precipitation (apart from the years 2010 and 2011) and high air temperatures (Fig. 2A). The most dominant directions of wind in the research area are northeast (40% — NE, NNE) north (10–15%) and northwest (25% — NW and NNW) (Fig. 2C).

2.3. Permafrost occurrence and geological conditions

Permafrost occurrence in the research area tends to diminish to the south, hence in the Khangai mountains permafrost is variously continuous and discontinuous, at the southern slopes of the Khangai it is insular or sparsely insular and disappears completely further down south (Sharkhuu, 2000; Sodnom and Yanshin, 1990) (Fig. 1). The Valley of the Lakes is classified as a zone with seasonally frozen ground, where the depth of freezing ranges from 2.0 to 4.5 m (Sodnom and Yanshin, 1990).

The researched basins have highly varied lithology and tectonics, which may potentially be a reason of considerable contamination of surface water with different elements and compounds. The source areas of sediments for both river–lake systems mainly consist of Paleozoic granites, Khangai flysch clastic rocks, exposed fragments of Early Proterozoic basement, and Precambrian Bayankhongor ophiolite with a complex of ultrabasic rock formations, mélange of volcano–sedimentary complexes (basaltoids, sandstones, mudstones, metasedimentary shales, limestones), and criss-crossed with quartz and chalcedony veins (Tomurtogoo et al., 2002; Tomurtogoo, 2004; Machowiak and Stawikowski, 2012). Furthermore, Central Mongolia features numerous volcanic areas of Miocene, Pliocene, Pleistocene and Holocene ages (Chuvashova et al., 2007; Yarmolyuk et al., 2007) (Fig. 1). Some well-preserved volcanic cones include the Togo volcano (Pleistocene) and the Khorgo volcano (Holocene). In the watershed zones and southern part of the study area, the Baydrag and Tuyn rivers flow through a Neogene system of sedimentary–volcanic rocks with the prevalence of

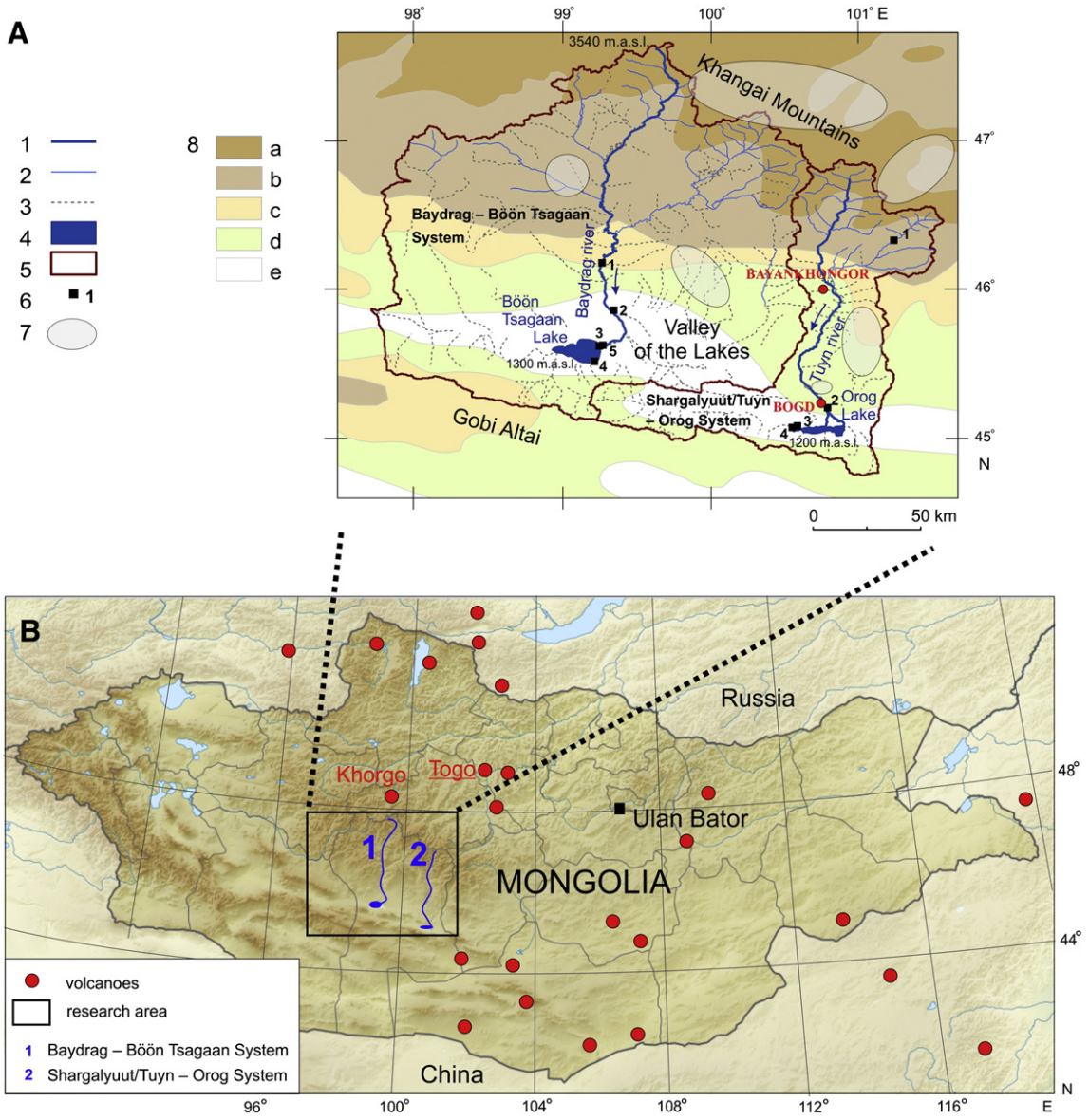

Fig. 1. (A) Research area against the background of permafrost occurrence (based on: Sharkhuu, 2000; Sodnom and Yanshin, 1990; Yarmolyuk et al., 2007, Lehner et al., 2008), (B) volcanoes location in Mongolia (www.bgs.ac.uk/vogripa, 15 June 2015). Symbols in (A) are: 1 the Baydrag and Tuyn rivers, 2 perennial tributaries of main rivers, 3 intermittent streams, 4 researched lakes, 5 watersheds of the Baydrag and the Tuyn basins, 6 sampling points, 7 schematic location of lava fields in the Khangai and Orkhon volcanic areas, 8 zones of (a) continuous and discontinuous, (b) insular, (c) sparsely insular, (d) sporadic permafrost occurrence, and (e) seasonally frozen ground.

clastics and basic volcanites (mainly basalts) (Fig. 1A). The Valley of the Lakes lower watershed is covered by Pleistocene and Holocene river alluvium and proluvial-talus deposits (Tomurtogoo et al., 2002; Tomurtogoo, 2004).

2.4. Anthropogenic activity — livestock farming

As precipitation decreases southwards, vegetation cover diminishes, and only minor fragments of the northern parts of the study area (mountains) are forested. Most of the surface is covered by steppe and semi-desert and is used as pastures (more than 90%), however due to unfavorable dry climatic conditions their productivity is relatively low (Demeusy, 2012; Khishigsuren, 2012). Climate changes tend to reduce the areas used by herders and increase the concentration of livestock around the surface water bodies. Most of the former pastures are degraded and subject to desertification, especially in the southern part of the basins (Khishigsuren, 2012).

3. Methodology

3.1. Sampling design

Two river–lake systems in the Valley of the Lakes were investigated: the Baydrag River–Böön Tsagaan Lake system (Baydrag–Böön Tsagaan System) the Shargalyuut /Tuyn Rivers–Orog Lake system (Shargalyuut/Tuyn –Orog System). The sampling points are shown in Fig. 1A. Samples were taken from sparsely insular and sporadic permafrost (Baydrag–Böön Tsagaan System — sample 1); at the border between discontinuous and insular permafrost (Shargalyuut/Tuyn–Orog System — sample 1); at the border of sporadic permafrost and seasonally frozen ground (Shargalyuut/Tuyn–Orog System sample 2); and in the area of seasonally frozen ground (Baydrag–Böön Tsagaan System — samples 2–5; Shargalyuut/Tuyn–Orog System — samples 3, 4) (Fig. 1). It should be noted that the conditions prevailing in a given cross-section of a river are affected by the entire area above this point (from that cross-section

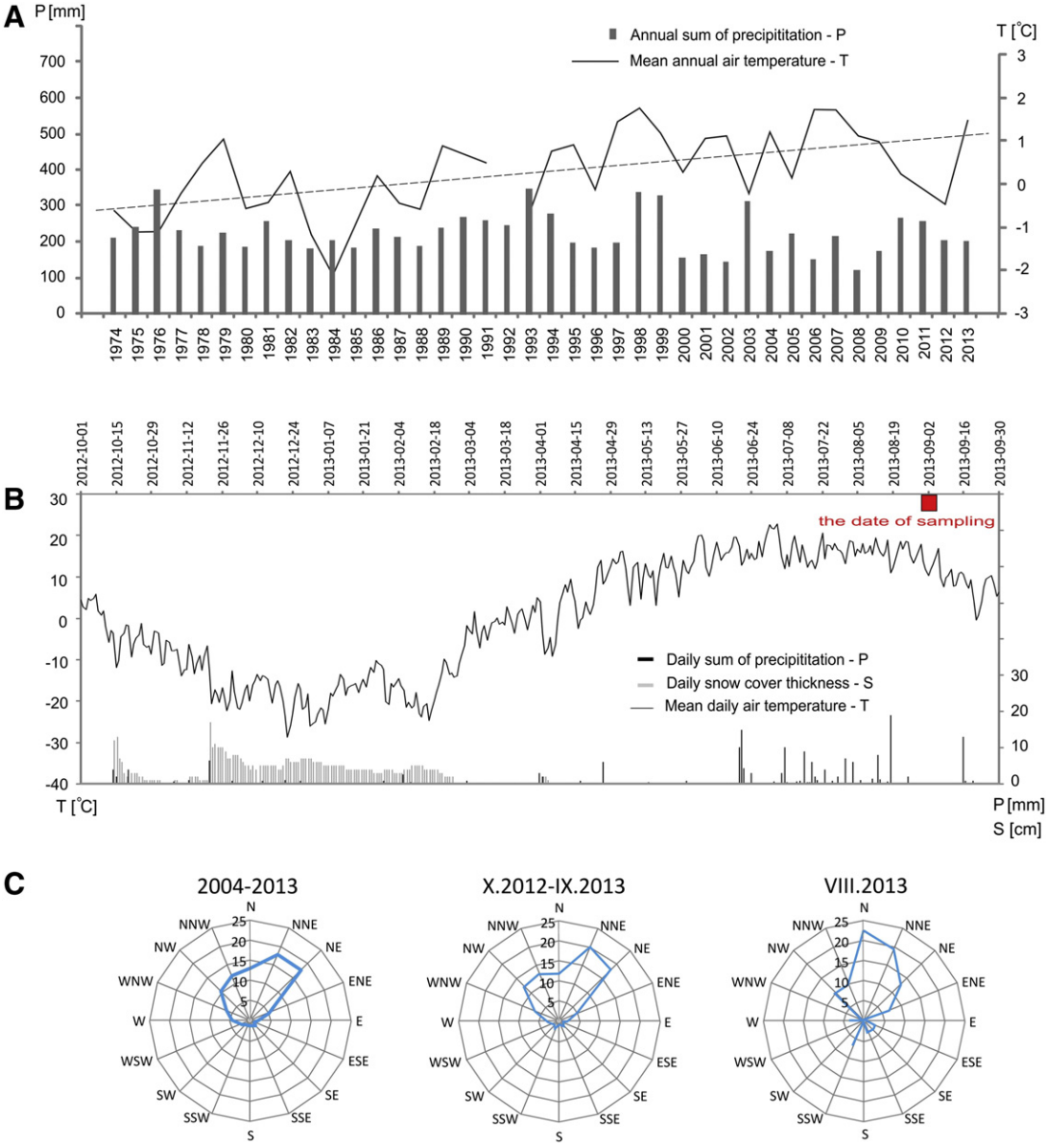

Fig. 2. Climate conditions in the research area: (A) long-term climate record; (B) weather conditions in the period from October 1st 2012 to September 30th 2013, and (C) wind directions in the period of 2004–2013 and from September 2012 to October 2013 (based on NOAA data on www.ogimet.com/gsodc.phtml, at the Bayankhongor station).

to the river source). Samples were collected manually in a volume of 1 L each, and stored at a temperature of 4 °C. Total number of samples was n = 10. The general view of the sampling area is presented in Fig. 3.

3.2. Analytical methods

Technical specifications, reagents for determining selected parameters, analyte contents in water samples and basic validation parameters of the proposed analytical procedures are summarized in Appendix A1. The concentration of total organic carbon (TOC, mg L^{-1}) was determined with the TOC-VCSH/CSN analyzer — a method of catalytic combustion (oxidation) with the use of an NDIR detector. Polycyclic aromatic hydrocarbons (PAHs, ng L^{-1}) and the main group of organic compounds in water samples were identified with the use of gas chromatography coupled with mass spectrometry (GC–MS) and ultra two-dimensional gas chromatograph with time-of-flight mass spectrometer (2D GC–TOF-MS), respectively.

All data were subject to strict QC procedures. Milli-Q deionized water was used during the determination of various target analyte groups. All sampling materials (tubes, beakers, pipettes, etc.) were cleaned rigorously after sampling to avoid potential cross-contamination between samples. Linear calibration curves were prepared. Limit of detection (LOD) was calculated on the basis of standard deviation of the 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 standard deviation of the 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 analyzed in the same setup as the samples, using the same reagents, in deionized water featuring levels below detection limit for total PAHs and TOC reported in this paper. This way, the background level present in the reagents and analytical containers used during the analytical procedure could be eliminated. PAH concentration was tested by injecting standard mixtures of the analytes in the measured range of concentrations and for checking column performance, peak height and resolution. For both chromatographic methods (PAH determination and screening analysis of organic compounds), after every 10 analyses of the

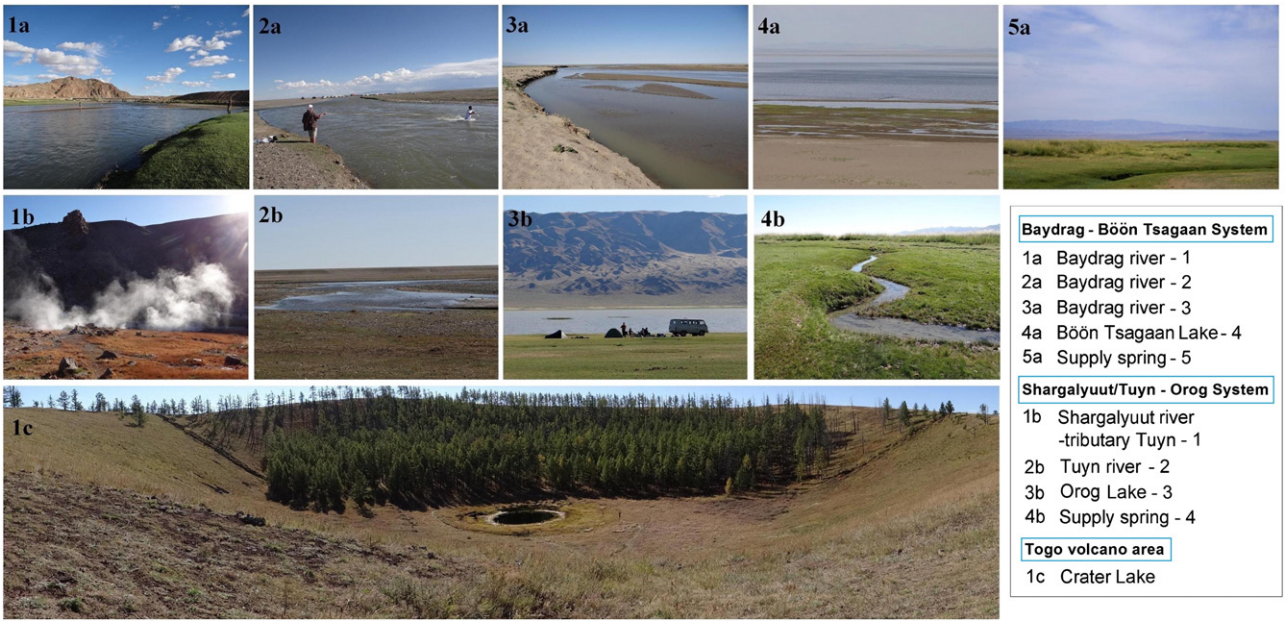

Fig. 3. General view of the study area. Symbols are: (1a–5a) sampling points in Baydrag–Böön Tsagaan System; (1b–4b) sampling points in Shargalyuut/Tuyn–Orog System; and (1c) Crater Lake.

environmental samples a blank analysis was provided to eliminate potential contamination from preceding analysis and to verify the proper working order of the chromatograph. Limit of detection was from 0.05 ng L^{-1} and 0.03 mg L^{-1} for PAHs and TOC concentration, respectively. Measurement range was 0.05–100 ng L^{-1} and 1–200 mg L^{-1} in the case of PAHs and TOC concentration, respectively.

In relation to the part of the studies performed with the 2D GC–TOF-MS technique, it should be noted that the duplicate analysis was applied in order to confirm the quality of the results obtained in terms of reproducibility. The data acquisition rate of 125 spectra s^{-1} and the detection of ions in the range of m/z 40–400 was applied to detect compounds at ultra-trace level with high similarity factor (over 90%). The use of comprehensive two dimensional gas chromatography coupled with time-of-flight mass spectrometry (2D GC–TOF-MS) ensures a very high peak capacity. The power of separation and detection in this system makes it possible to identify many more compounds in comparison with one dimensional gas chromatography coupled with mass spectrometry. The identification was performed by means of comparing mass spectrum obtained from the experiment and the one included in the NIST 2011 library.

Detailed analytical procedure used for identifying the main group of organic compounds and detailed analytical procedure for PAH determination can be found in Appendix A (A1–A4).

4. Results

4.1. TOC distribution in river–lake systems

The values of dissolved organic matter measured as total organic carbon (TOC) are shown in Fig. 4. Samples taken from the area of permafrost occurrence, in the upper segment of the Baydrag river (Fig. 4, sample 1) are characterized by higher organic matter content (30.80 mg L^{-1}) than in the lower reach of the river (Fig. 4, samples 2, 3) and the determined concentrations ranged between 19.85 mg L^{-1} and 20.32 mg L^{-1}. An increase in TOC concentration is noted in the Shargalyuut/Tuyn–Orog System down the river course: from 15.41 mg L^{-1} to 30.51 mg L^{-1} in Shargalyuut river–tributary Tuyn (sample 1) and Tuyn river (sample 2) respectively. The highest TOC concentrations in both systems were recorded in the lakes: 145.7 mg L^{-1} and 119.3 mg L^{-1} for the Böön Tsagaan Lake and Orog Lake, respectively.

4.2. Main groups of organic compounds — screening analysis

Organic halogen compounds (organochlorides, organobromine and organoiodine compounds) were identified in each sampling point (Table 1). Among the identified compounds we can highlight single compounds, such as: dibutyl phthalate, bis-(2-methylpropyl)-1,2-

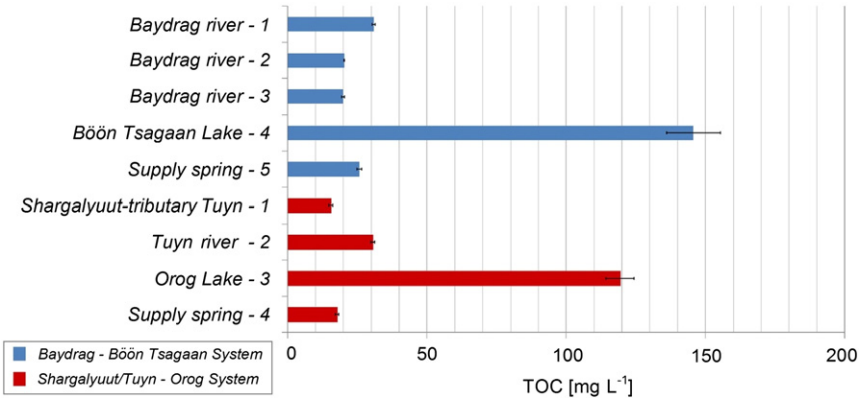

Fig. 4. TOC spatial trends in both river–lake systems. Error bar reflects uncertainty.

Table 1
List of compounds identified in the samples using 2D GC–TOF-MS.

No.	Identified compounds	Baydrag–Böön Tsagaan system					Shargalyuut/Tuyn–Orog system				Crater Lake (Togo volcano area)
		Baydrag river — 1	Baydrag river — 2	Baydrag river — 3	Böön Tsagaan Lake — 4	Supply spring — 5	Shargalyuut river-tributary Tuyn — 1	Tuyn river — 2	Orog Lake — 3	Supply spring — 4	
1	Sum of organic halogen compounds	+++	+++	+++	+++	+++	+++	++	+++	+++	+++
2	Dibutyl phthalate	+++	++	+++	+++	+++	−	+++	+++	+	+++
3	1,2-Benzenedicarboxylic acid-bis (2-methylpropyl) ester	++	+++	++	++	+++	+	++	++	+++	++
4	Tetrachloroethene	++	++	++	++	++	++	++	++	++	+
5	Nonane	−	+	+	++	+	+	+	++	+	−
6	1,3-Dimethylbenzene (m-xylene)	+	++	+	++	++	+	++	+	+	−
7	Propanoic acid-2-methyl-3-hydroxy-2,4,4-trimethylpentyl ester	−	−	−	−	−	+	++	+++	++	+
8	Pentadecane						+	−	+	+	+
9	Tridecane	+	−	−	++	−	−	−	−	−	−
10	Heptadecane	−	−	−	++	−	−	−	−	−	−
11	6-Methyl-1-octene	−	−	−	++	−	−	−	−	−	−
12	n-Octyl ether	+	−	+	++	+	−	−	−	−	−
13	2-Furaldehyde (furfural)	−	++	−	+	−	−	−	−	−	−
14	2-Furancarboxaldehyde	−	−	−	−	−	+	+	++	+	−
15	Propanoic acid-2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester	−	−	−	−	−	−	+	+	+	−
16	Octadecanoic acid butyl ester	−	−	−	−	−	−	−	+	+	−
17	Hexadecanoic acid butyl ester	−	−	−	−	−	−	+	+	+	−

Intensity description for Baydrag–Böön Tsagaan system and Shargalyuut/Tuyn–Orog system: +++, ++ and + are respectively more than 5%, in the range of 1–5% and less than 1% of total sum of peak areas calculated regarding lakes' chromatogram in each system; − is below LOD of 2D GC–TOF-MS system.
Intensity description for Crater Lake: +++, ++ and + are respectively more than 30%, in the range of 10–20% and less than 1% of total sum of peak areas calculated regarding Crater Lake chromatogram; − is below LOD of 2D GC–TOF-MS system.

benzenedicarboxylic acid ester (diisobutyl phthalate), tetrachloroethene, and higher alcanes, e.g. nonane, tridecane, pentadecane, heptadecane. The presence of these compounds was confirmed with a control sample (blank). Some of the peaks were found in the blank, nevertheless, their quantity and intensity were negligible in comparison with the amount and intensity of the peaks detected in the studied water samples.

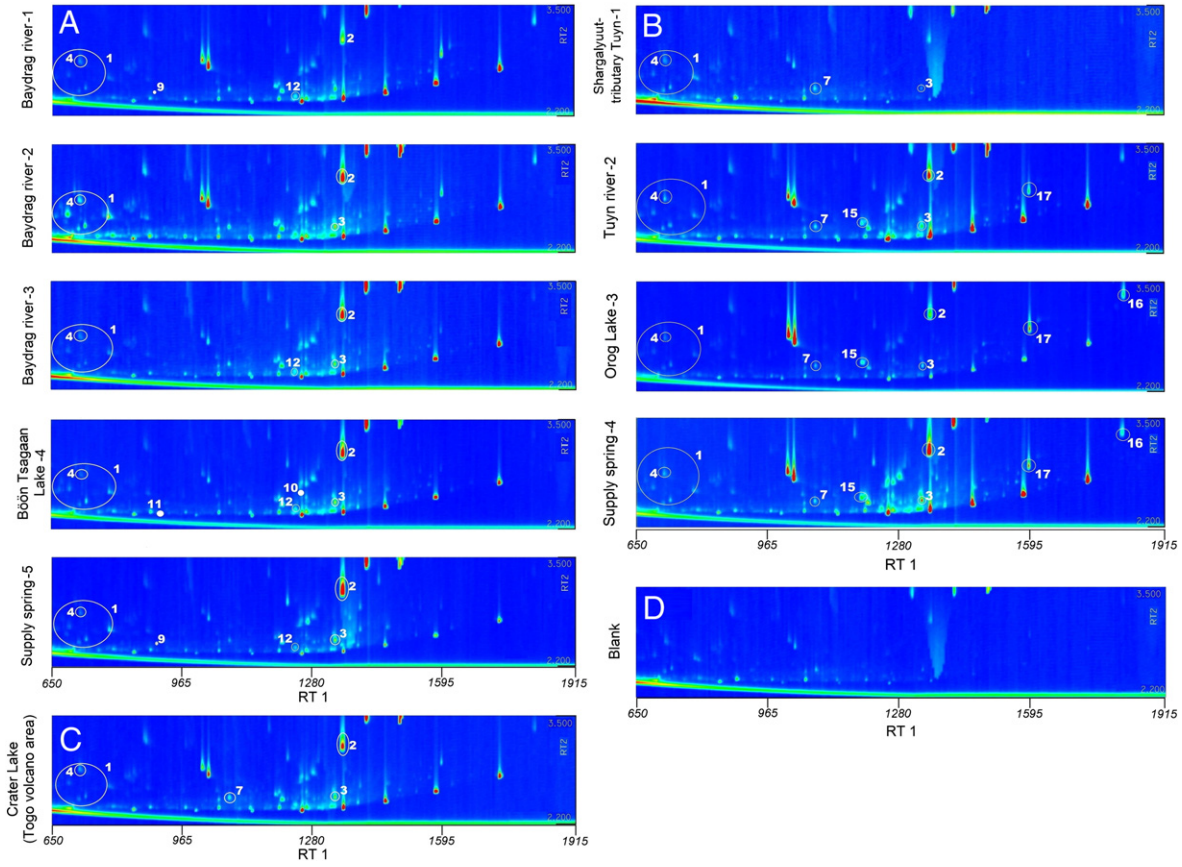

Fig. 5. 2D GC–TOF-MS chromatograms of the dichloromethane extracts, of the samples taken from following areas: (A) Baydrag–Böön Tsagaan System; (B) Shargalyuut/Tuyn–Orog System; and (C) Caldera Lake. Fig. 5D is related to the blank. The thermochromic scale codes intensity. Retention times are given in seconds. Each number presented on chromatograms corresponds to the number of compounds listed in Table 1. Abbreviations: RT1 — retention time in the first dimension, RT2 — retention time in the second dimension.

Table 2
Concentrations of PAHs in water and aerosol samples taken from Mongolia and other regions reported in literature.

Analyte		NP	ACY	ACE	ANT	FL	PHE	FLA	PYR	BaA	CHY	BbF	BkF	BaP	IcdP	DahA	BghiP	Total PAHs	Lit
Sampling area	Unit																		
Mongolia (water)		ng L^{-1}																	
Baydrag–Böön Tsagaan system	Baydrag river — 1	23	<LOD	<LOD	0.66	6.2	1.0	1.6	0.63	1.4	<LOD	<LOD	1.1	<LOD	<LOD	<LOD	<LOD	35	Our research
	Baydrag river — 2	27	<LOD	1.3	1.4	18	0.38	1.6	2.1	4.5	<LOD	<LOD	2.7	<LOD	<LOD	<LOD	<LOD	59	
	Baydrag river — 3	25	<LOD	0.71	0.86	8.1	0.37	0.84	1.1	1.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	39	
	Böön Tsagaan Lake — 4	83	16	9.4	15	77	48	49	13	3.6	5.7	8.1	5.2	5.1	7.1	<LOD	5.7	350	
	Supply spring — 5	82	16	10	16	74	42	43	13	4.1	4.5	8.1	5.3	<LOD	4.2	<LOD	5.9	328	
Shargalyuut/Tuyn–Orog system	Shargalyuut–tributary Tuyn — 1	85	17	9.5	16	87	48	50	14	3.8	4. 7	11	5.0	5.0	4.2	<LOD	3.4	363	
	Tuyn river — 2	19	<LOD	<LOD	0.59	7.8	1.3	1.8	0.60	1.4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	33	
	Orog Lake — 3	28	2.5	6.8	2.6	28	14	16	7.1	3.1	<LOD	<LOD	3.1	<LOD	<LOD	<LOD	<LOD	111	
	Supply spring — 4	28	<LOD	0.83	1.0	10	0.42	0.98	0.60	1.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	43	
Crater Lake (Togo volcano area)		36	0.71	2.9	2.7	27	1.4	2.0	4.0	6.8	1.0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	84	
Mongolia (air)		ng m^{-3}																	
Sainshand[a] (atmospheric aerosols of the Gobi Desert)		–	–	–	0.32	0.24	0.20	0.24	0.16	0.11	0.19	0.51	0.67	0.36	0.26	–	0.58	3.01	Zhamsueva et al. (2015)
China (water)		ng L^{-1}																	
Lake Taihu[b] (urban area)		1154	72	–	nd	122	153	44	30	5	12	nd	nd	nd	nd	nd	nd	1592	Zhang et al., 2011
Luan River (mixed urban and non-urban areas)[b]		15.8	4.6	4.4	4.3	16.7	35.0	8.6	6.1	2.0	1.1	0.4	0.1	0.3	0.1	0.1	0.3	99.4	Cao et al. (2010)
Songhua River Basin (urban area)[b]		–	0.78	2.6	2.36	3.7	11.3	4.66	3.07	0.47	0.65	1.05	0.52	2.79	nd.	nd.	nd.	33.9	Ma et al. (2013)
China (air)		ng m^{-3}																	
Beijing Normal University (urban area)		–	–	–	–	–	–	6.47	3.85	1.29	2.39	1.84	0.86	0.83	3.15	2.47	3.33	26.48	Hou et al. (2006)
Shanghai (urban area)		–	–	–	–	–	–	0.92	0.51	0.25	0.76	0.87	0.35	0.81	0.76	0.24	0.87	6.34	
Miyum (suburban area)		–	–	–	–	–	–	1.58	0.81	0.15	0.55	0.37	0.11	0.19	0.24	0.13	0.33	4.45	
Island (water)		ppb (ng L^{-1})																	
Öxarfjörður[c] (groundwater, 97–102 °C)		–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	**235–505**	Geptner et al. (2005)

PAH abbreviations: naphthalene (NP), acenaphthylene (ACY), acenaphthene (ACE), anthracene (ANT), fluorene (FL), phenanthrene (PHE), fluoranthene (FLA), pyrene (PYR), benzo(a)anthracene (BaA), CHRYSENE (CHY), Benzo(b)fluoranthren (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IcdP), dibenzo(a,h)anthracene (DahA), and benzo (g,h,i)perylene (BghiP).
Other abbreviations: <LOD — below limit of detection (LOD values available in Appendix A1; nd — not detected.
[a] The highest concentration.
[b] The mean concentration.
[c] Concentration range.

Fig. 5(A–C) features chromatograms divided into three sampling regions: the Baydrag–Böön Tsagaan system, the Shargalyuut/Tuyn–Orog system and the Crater Lake. Fig. 5D focuses on the blank sample. Chromatograms can be seen as a profile of the volatile fraction, which allows for a general assessment and comparison of the chemical profile of water samples collected in different geographical regions. The retention time ranges and peak intensity integration were performed to offer an objective comparison of these profiles.

4.3. Polycyclic aromatic hydrocarbon distribution in the entire study area

The results of PAH analytical data analysis are summarized in Table 2. A range of total PAHs is 36–365 ng L^{-1} and 43–363 ng L^{-1} for Baydrag–Böön Tsagaan system and Shargalyuut/Tuyn–Orog System, respectively. Naphthalene, fluorene and phenanthrene constitute compounds that have a significant input in the total sum of PAHs in both systems. Total PAHs for the Crater Lake amount to 84 ng L^{-1} and are enriched mainly by naphthalene, fluorene and benzo(a)anthracene. The highest concentration of an individual PAH (fluorene, 87 ng L^{-1}) was found in a sample taken from the Shargalyuut river–tributary Tuyn.

Percentage distribution of PAHs in each sample is shown in Fig. 6 and show two kinds of distributions. The Baydrag river (samples 1–3), the Tuyn river (sample 2), spring (sample 4) as well as the Crater Lake (the Togo volcano area) water samples have similar distribution of PAH content. A characteristic feature is the large percentage of naphthalene in the samples (in a range from 43 to 65%). Another group with a very similar percentage of individual PAHs involves water samples from the Böön Tsagaan Lake (sample 4) supply spring (sample 5), the Shargalyuut river (sample 1) and Lake Orog (sample 3). In this case the analysis showed lower (compared with the first group) percentage of naphthalene (in a range from 24% to 26%), with a significant contribution of fluorene, phenanthrene and fluoroanthrene.

5. Discussion

The river–lake systems are located in an area featuring a very complex geological structure (e.g., Buchan et al., 2002), which makes it susceptible to surface water contamination by different types of chemical compounds (e.g., trace metals, PAHs). Furthermore, this part of Mongolia is exposed to contemporary volcanic influence and anthropogenic activity, including livestock farming and industry from remote regions.

5.1. Permafrost and climate influence on water chemistry characteristics

The summary parameters, such as TOC and specific groups of compounds (e.g., PAHs), are of great importance when estimating the state of natural environment. They allow for obtaining data during one measuring cycle. The hydrological study assumes that chemical composition of a river at its measurement point is predominantly determined by conditions in the area (basin) above that point. Olefeldt et al. (2014) indicates that permafrost may have an influence on the organic composition of lowland catchments in Canada because of the capacity of permafrost to store organic matter. Organic matter availability during permafrost degradation depends on the thickness of the permafrost active layer (Yang et al., 2010) and this organic matter can enrich the composition of rivers and lakes. This phenomenon (water enrichment with TOC) is clearly visible in the Baydrag–Böön Tsagaan System sample 1 (Fig. 4). The Shargalyuut/Tuyn–Orog System research shows a visible storage of TOC in permafrost. Distinctly lower concentration of TOC is observed in the Shargalyuut river–tributary Tuyn (sample 1; 15.41 mg L^{-1}), than in the lower part of the Tuyn river (sample 2; 30.51 mg L^{-1}). Sample 1 of the Shargalyuut/Tuyn–Orog System was collected from an area under a strong influence of continuous and discontinuous permafrost, and thus shows no release of TOC (as opposed to the Baydrag–Böön Tsagaan System, sample 1). A higher concentration of TOC observed in sample 2 from Tuyn River can be a result of both release of TOC from permafrost degradation and grazing, which is common in the area (Demeusy, 2012). Animals use the rivers as sources of drinking water, which significantly affect TOC availability. Moreover, grazing results in a loss of topsoil and riparian vegetation. This can intensify erosion and consequently increase the amount of suspended load in water (Demeusy, 2012). Diminishing of vegetation cover constitutes yet another cause of permafrost degradation (Sharkhuu and Sharkhuu, 2012), resulting in a release of TOC.

Mongolian rivers transport a large amount of suspended particular matter, especially during rapid runoff events (Chalov et al., 2012; Thorslund et al., 2014; Lange et al., 2015). It shapes the chemical composition of water in the lakes which constitute outlets for rivers. That is why there is a substantially higher concentration of total organic matter in the lakes (Fig. 4) in comparison to its concentration in rivers and supply springs. Additionally, the dissimilarity of the Böön Tsagaan Lake (145.7 mg L^{-1}) and the Orog Lake (119.3 mg L^{-1}) occurs due to differences in seasonal and long-term fluctuations of water level. Research shows that even a short period of lowered water table in Orog Lake causes deflation of the surface layer of bed sediment along with any precipitated chemical compounds (Szumińska, 2016). Moreover, TOC

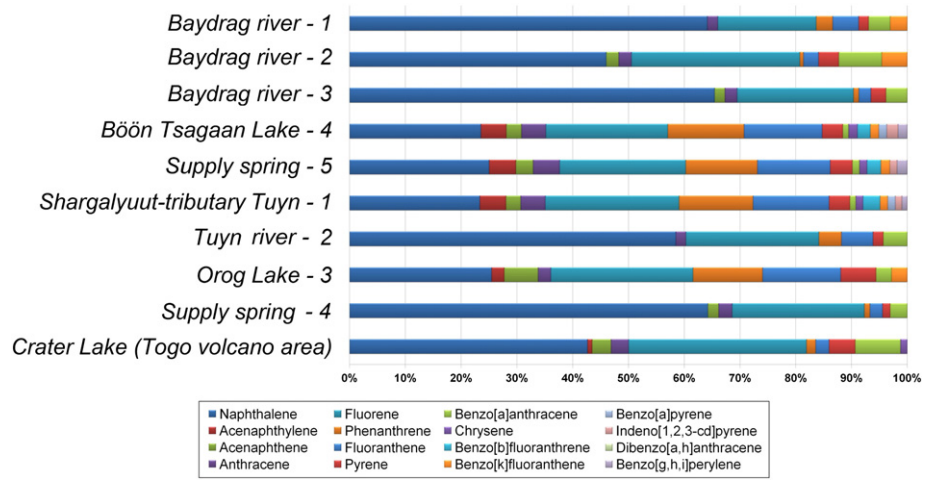

Fig. 6. PAH distribution (in %) in each sample.

concentration in the supply springs (25.75 mg L^{-1} for sample 5 from Baydrag–Böön Tsagaan System and 17.66 mg L^{-1} for sample 4 from Shargalyuut/Tuyn–Orog System) also affected the differences in TOC concentration in the lakes.

5.2. Influence of human activity on water chemistry characteristics

A detailed analysis of volatile and semi-volatile organic compounds was possible owing to 2D-GC–TOF-MS (Fig. 5). The identified compounds, such as phthalate, BTEX (benzene, toluene, ethylbenzene, and xylenes) are of anthropogenic origin. Phthalate and BETEX compounds are used in the production of plastic materials (Al-Saleh et al., 2011; Srijata and Pranab, 2011). Free et al. (2014) quantified pelagic microplastics and shoreline anthropogenic debris in the Hovsgol Lake in Mongolia. It was the first evaluation of the amount, distribution, and composition of pelagic microplastic pollution in a large, remote mountain lake. Hence, there is a possibility that similar contaminants may also be present in the studied river–water systems. The identified phthalates could have been extracted from materials such as PET — polyethylene terephthalate, PS — polystyrene or PP — polypropylene (Al-Saleh et al., 2011). However, no microplastic pollution has been observed during fieldwork, hence the presence of these compounds can potentially be a result of long-range atmospheric transport (Net et al., 2015). The conducted analysis also indicated the presence of esters and aldehydes in the area and their concentrations were different in each river system. In the Shargalyuut/Tuyn–Orog System propanoic acid-2-methyl-3-hydroxy-2,4,4-trimethylpentyl ester; octadecanoic acid butyl ester and hexadecanoic acid butyl ester as well as 2-furancarboxaldehyde have been identified (Table 1, Fig. 5). However, none of these compounds were found in the Baydrag–Böön Tsagaan system. On the other hand, 6-methyl-1-octene and n-octyl ether have been identified in the Baydrag–Böön Tsagaan system but not in the Shargalyuut/Tuyn–Orog system (Table 1). The presence of fatty acids can be seen as a useful tool in bacterial taxonomy (Řezanka et al., 2003). The presence of identified esters, which can be transformed from fatty acid molecules by cyanobacteria (Liu and Shi, 1998), may indicate water blooming. However, during fieldwork this phenomenon was not observed, hence higher bacterial activity in the Orog Lake in comparison with the Böön Tsagaan Lake can be a result of changes in water table fluctuation and drying out that entails different microbiological activities. Moreover, the presence of propanoic acid esters in the Shargalyuut/Tuyn–Orog system can indicate grazing impacts on organic water chemistry. Propanoic acid as well as other acid compounds (e.g., butyric acid, isovaleric acid) are typically found as the dominant components in the air at livestock production facilities (Susaya et al., 2011). Thus, it can be indicated that those components can be found in the analyzed water samples due to livestock farming, which is common in the Shargalyuut/Tuyn–Orog system (Krylov et al., 2011). In the Baydrag–Böön Tsagaan system (samples 2,4) derivative of furan-2-furaldehyde (commonly known as furfural) has been identified. A major source of this compound involves the operation of the oil industry (Risk Assessment Report, SCHER, 2008), biomass burning, and food processing. Moreover, BETEX compounds are degraded to furans by OH radical reactions in the atmosphere (Krause et al., 2014). However only a few measured concentrations of furfural in water have been reported (Risk Assessment Report, SCHER, 2008; Krause et al., 2014). Hence, it can be concluded that furfural may be potentially transported by long-range atmospheric transport from remote industrial regions.

While the sources of PAHs may vary depending on the region being considered (Zhang and Tao, 2009), incomplete combustion of carbonaceous materials in industrial processes and energy production is considered their main source (Stogiannidis and Laane, 2015). The majority of anthropogenic emissions of PAHs into the atmosphere comes from biomass burning, coal and petroleum combustion, as well as coke and metal production (Zhang and Tao, 2009; Liu et al., 2012). Compounds from the PAH group are easily absorbed on the surface of particulate matter (PM_{10}, $PM_{2.5}$) (Cretney et al., 1985). This means that PAHs can be transported from distant areas, such as China (Zhang et al., 2007; Table 3). Zhamsueva et al. (2015) argue that anthropogenic pollution comes to Mongolia primarily from the south and southeast, again hinting at China as their source.

5.3. Volcanism as a significant factor determining water chemistry characteristics

Due to high wind velocity (Elliott et al., 2001) there is capacity for sediment transport from the Khangai mountains and Gobi Altai. These areas, covered by volcanic rocks (Fig. 1), make up a supply area, while the valleys in Central Mongolia, including the Valley of the Lakes (Grunert and Lehmkuhl, 2004), may be places of accumulation. The study area shows susceptibility to water and aeolian erosion. It is mainly due to scarce vegetation cover, as well as extreme temperature differences, which accelerates the destruction and breaking down of rocks. Grunert and Lehmkuhl (2004) pointed out that whereas sand can only be transported horizontally by strong winds over relatively short distances, silt-sized particles can be transported both horizontally and vertically, thus being the major source for long-range transport. The latter supports long-range atmospheric transport. The analyzed systems can therefore also be an accumulation of organic halogen compounds (identified in the water samples across the entire sampling area, Table 1). It may occur only locally, but also at long distances and together with volcanic dust. Apart from volcanic lava cover in the Baydrag and Tuyn basins indicated in Fig. 1, there is a significant accumulation of volcanic tracks in south-eastern Mongolia, northern China and Korea (www.bgs.ac.uk/vogripa, 15 June 2015). The most common directions of wind in the Valley of the Lakes are northwest and north (Hempelmann, 2010). However, based on the NOAA data obtained from www.ogimet.com/gsodc.phtml (Fig. 2B) northeast direction has also been very common over the last ten years. Therefore, for the most part of a year, the main source of aeolian sediment may be the Khangai Mountain. Summer features three wind directions of the same frequency: northwest, north and southeast, hence, also the Gobi Desert and the Altai Mountains can be considered supply areas (Hempelmann, 2010) (Fig. 2).

As previously mentioned, organic compounds can be released to the watersheds as a result of permafrost degradation processes. It should be noted that the area is surrounded by volcanoes, hence some of the compounds released from permafrost may also be of volcanic origin. It is possible that PAHs occur in the volcanic sediments in the study area, especially of Pleistocene and Holocene ages. The numerous basalt fields may have enriched weathered debris and soils in PAHs (Geptner et al., 2005) and, as a result of water erosion and transport of matter, they may cause high PAH concentrations in the lakes. PAHs may have been also introduced to the lakes and river systems through the deposition of particulate matter from the atmosphere. Moreover, nearby volcanic activity can also affect PAH composition (long-range atmospheric transport). Thus, spatial distribution of PAHs may be related to two types of volcanism: contemporary volcanic activity (outside Mongolia, Appendix B) and volcanic sediment background of young Pleistocene and Holocene in Mongolia (Fig. 1), as well as anthropogenic activity in remote areas (Cretney et al., 1985; Stogiannidis and Laane, 2015).

Total PAH concentration in the upper part of the Baydrag–Böön Tsagaan system is not particularly high (36–59 ng L^{-1}), however its concentration in the Böön Tsagaan Lake and its supply spring is ten times higher (328 ng L^{-1} and 350 ng L^{-1}, respectively). Because of their hydrophobic characteristics, PAHs tend to adsorb to particulate organic matter (e.g., in sediments or soots) rather than dissolve in water (Stogiannidis and Laane, 2015). Hence, the presence of PAHs in the lakes can be a result of local surface erosion (e.g., during the snow melt in spring) as well as river transport of suspended load and bed load. The accumulation in suspended particular matter in bottom sediments of lakes constitutes the secondary source of PAH, due to their

Table 3
PAH indicator ratios for research water samples and the potential sources of emission of these compounds.

PAH indicator ratio[a]	NP/PHE	PHE/ANT	FLA/PYR	FL/(FL + PYR)	BaA/CHY	ΣLMW/ΣHMW
Sampling area						
Baydrag river — 1	22	1.6	2.6	0.9	–	6.5
Baydrag river — 2	71	0.3	0.8	0.9	–	4.4
Baydrag river — 3	68	0.4	0.8	0.9	–	10
Böön Tsagaan Lake — 4	1.7	3.2	3.8	0.9	0.6	2.8
Supply spring — 5	2	2.6	3.3	0.9	0.9	3.1
Shargalyuut–tributary Tuyn — 1	1.8	3	3.6	0.9	–	2.8
Tuyn river — 2	15	2.2	3	0.9	–	7.6
Orog Lake — 3	2	5.4	2.3	0.8	–	2.8
Supply spring — 4	67	0.4	1.6	0.9	–	14
Crater Lake (Togo volcano area)	26	0.5	0.5	0.9	6.8	5.1
Source						
Pyrogenic (combustion)	>1[b]	<4–10[c]	>1.5[c]	>0.5[d]	>0.5–1[c]	<1[e]
Petrogenic	<1[b]	>15–30[c]	<0.5[c]	<0.5[d]	<0.25–0.5[c]	>1[e]
Result	Pyrogenic (combustion)					Petrogenic

[a] ΣLMW — sum of low molecular weight PAHs (two and three-ring PAHs); ΣHMW — sum of high molecular weight PAHs (four and five ring PAHs. Other PAH abbreviations are available in the description of Table 2.
[b] Ravindra et al. (2008a).
[c] Stogiannidis and Laane (2015).
[d] Ravindra et al. (2008b); >0.5 — diesel emissions (pyrogenic); <0.5 petrol emissions (petrogenic).
[e] Zhang et al. (2008).

subsequent re-emission into the environment in consequence of desorption processes (Barnier et al., 2014). High concentration of PAH in supply springs also enriches the lake water with compounds from this group. Ground water is modified by permafrost occurrence. This means that it may indicate emission of PAH compounds from permafrost during the sampling period. However, in the case of the Shargalyuut/Tuyn–Orog system, in the upper course of the Shargalyuut river (tributary Tuyn), a higher total concentration of PAHs (363 ng L^{-1}) is observed, as opposed to samples taken from the rivers. This can be a result of hot spring influence (see level of total PAH concentrations determined in hot springs in Table 2). It cannot be associated with the release of these compounds into the environment resulting from permafrost thawing, as we do not observe any increase in TOC within the area.

On the basis of Fig. 6 we can distinguish two groups with similar (%) PAH distribution in each sample: (1) the Baydrag–Böön Tsagaan system samples 1–3; the Shargalyuut/Tuyn–Orog system sample 2 and Crater Lake water, and (2) the Baydrag–Böön Tsagaan system samples 4 and 5; the Shargalyuut/Tuyn–Orog System samples 1 and 3. The first group is related to a low sum of PAH content in the studied waters, and the second group corresponds to the sum of PAHs exceeding 300 ng L^{-1} (Table 2). The composition of PAH in Crater Lake resembles that at flowing water rather than other lakes. Water in the Crater Lake is mainly fed by precipitation (negligible impact of surface runoff). Hence, it may suggest an influence of suspended particular matter transport by water surface runoff.

5.4. Environmental risks related to the presence of PAHs

Although PAHs are not among the “dirty dozen” of the Stockholm Convention on Persistent Organic Pollutants (http://chm.pops.int/, 20 February 2016), the global atmospheric emissions of 16 PAHs are listed as priority pollutants by the United States Environmental Protection Agency (US EPA) and the European Union. The group is known for its adverse effects on human health (Zhang and Tao, 2009) and has been long considered an environmental concern as a carcinogenic constituent (Straif et al., 2006). The determination and risk assessment of PAHs have gained considerable attention in recent years mostly because of their capacity for bioaccumulation in living organisms, their toxicity and mutagenicity (Yang et al., 2015). According to the Water Framework Directive of European Union (Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy) and Environmental Quality Standards (Priority Substance No. 28), PAH concentrations in all surface waters should exceed 0.002 μg L^{-1} for 6-ring PAHs (IcdP&BghiP), 0.03 μg L^{-1} for 5 ring PAHs (BbF&BkF) and 0.05 μg L^{-1} for BaP.

Owing to PAH toxicity and widespread distribution, identification of the sources of PAHs is extremely important (Saha et al., 2009). The initial step in source identification is differentiation between petrogenic and pyrogenic sources. Petrogenic substances are defined as substances that originate from petroleum, including crude oil and petroleum products, such as kerosene, gasoline, fuels, and asphalt (Saha et al., 2009; Stogiannidis and Laane, 2015). Pyrogenic substances constitute organic substances produced from incomplete combustion of fossil fuels and organic matter (e.g., coal, wood). Recently, diagnostic ratios have been used as a tool for identifying pollution emission sources of PAHs. The ratios help distinguish the origin of PAH pollution between petrogenic and pyrogenic (combustion). There are many indexes for identifying contribution of PAH sources (e.g., NP/PHE; PHE/ANT; BaA/CHY; FLA/PYR; BbF/BkF) (Polkowska et al., 2011; Stogiannidis and Laane, 2015). Almost all of the presented PAH ratios (NP/PHE; PHE/ANT; FLA/PYR; FL/(FL + PYR)); BaA/CHY indicate combustion (pyrogenic origin) as the source of this group of compounds (Table 3). As far as the ΣLMW/ΣHMW ratio is concerned (sum of low molecular weight PAHs/sum of high molecular weight PAHs), the source of PAHs can be of petrogenic origin. Considering the limited number of samples (n = 10), the obtained results can be treated as preliminary. In order to distinguish each PAH's source clearly, the compounds should be subject to long-term monitoring.

Fig. 6 shows that naphthalene represents the greatest contribution in chemical composition across the studied water samples. Naphthalene has been classified as possibly carcinogenic to humans and animals (Group 2B) by The International Agency for Research on Cancer (IARC) (http://www.iarc.fr/, 17 June 2015). Its origin can be a result of atmospheric deposition of natural combustion products (PAH indicator ratio NP/PHE for both systems are in a range of 1.7–71). However the increasing anthropogenic activity in the last few years (since 1991) (Warburton et al., 2013) may also, to some extent, have an impact on PAH origin. Moreover a significant contribution of fluorene, phenanthrene and fluoroanthrene across the study area is also visible. Although PAH concentrations have not reached the critical value set in the 2000/60/EC Directive, all 16 EPA PAHs should be monitored. Due to the bioaccumulation properties, chronic exposure even to its small concentration can affect organisms of the lower part of the food chain. Hence we agree with Warburton et al. (2013) that there is clearly an urgent need for amplification of environment research on pollution in Mongolia.

6. Conclusions

This paper summarizes the description of watershed chemistry characteristics in the Valley of the Lakes (Mongolia). Spatial distribution of permafrost occurrence varies across the area, which translates into differences in water chemistry in individual parts of the watersheds. In an area of continuous permafrost, organic compounds (including contaminants) can be largely retained. On the other hand, permafrost thawing may indicate a release of organic matter, which can then become available for aquatic transport, particularly in spring and summer. Hence, any shifts of permafrost boundaries can indirectly be observed through the changes concerning the chemistry of aquatic environments. Moreover, number of other water chemistry-shaping factors should be also taken into account. Therefore, in the region of Central Mongolia we can distinguish the following factors affecting the organic chemistry composition:

- permafrost: retention of organic matter in the area of continuous and discontinuous permafrost occurrence and release of organic matter into the environment due to permafrost degradation (visible in the lower parts of the rivers),
- transport of suspended particular matter into lakes as a result of rapid surface water runoff,
- microorganism activity in waters,
- location of the river–lake systems in the volcanic area, which can cause an increase in the concentration of PAHs,
- long-range atmospheric transport of volcanic dust from remote areas, and
- anthropogenic factors (livestock farming, long-range atmospheric transport of pollution from remote industrial areas).

Monitoring of concentration levels of individual PAHs as well as chlorinated compounds should be especially taken into consideration in future environmental studies. These two groups can be treated as potential contaminants that may affect the formation (degradation) of the environment in Central Mongolia. Moreover, monitoring of TOC and PAHs would provide information on changes taking place at the periphery of permafrost occurrence, as the compounds could have potentially been accumulated in the deeper layers of permafrost during earlier volcanic activity.

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