Biogeosciences, 10, 5349–5365, 2013
www.biogeosciences.net/10/5349/2013/
doi:10.5194/bg-10-5349-2013

Biogeosciences
Open Access

Impact of western Siberia heat wave 2012 on greenhouse gases and trace metal concentration in thaw lakes of discontinuous permafrost zone

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Received: 28 February 2013 – Published in Biogeosciences Discuss.: 24 April 2013
Revised: 1 July 2013 – Accepted: 2 July 2013 – Published: 9 August 2013

Abstract. During the anomalously hot summer in 2012, surface air temperatures in Western Siberia were 5 to 15 °C higher than those observed during the previous period of > 30 yr. This unusual climate phenomenon provided an opportunity to examine the effects of short-term natural heating of water in thermokarst ponds and lakes in discontinuous permafrost zones and compare these observations to previous field results obtained when the temperature was normal during the summer of 2010 in the same region. In 2012, thermokarst bodies of water shrank significantly, water levels dropped approximately 50 cm in large lakes and small (< 10–100 m^2) ponds, and shallow soil depressions disappeared. Based on samples from ∼ 40 bodies of water collected previously and in 2012, first-order features of changes in chemical composition in response to increased water temperatures (from 14.1 ± 2.2 to 23.8 ± 2.3 °C in 2010 and 2012, respectively) were established. In these thermokarst bodies of water that covered a full range of surface areas, the average conductivity and pH were almost unchanged, whereas dissolved organic carbon (DOC), Cl^- and SO_4^{2-} concentrations were higher by a factor of ∼ 2 during summer 2012 compared to periods with normal temperatures. Similarly, most divalent metals and insoluble trivalent and tetravalent elements were more concentrated by a factor of 1.7–2.4 in the summer of 2012 than normal periods. The average concentrations of dissolved CO_2 and CH_4 during the hot summer of 2012 increased by factors of 1.4 and 4.9, respectively. For most of the trace elements bound to colloids, the degree of colloidal binding decreased by a factor of 1.44 ± 0.33 (for an average of 40 elements) during the hot summer of 2012 compared to normal periods. Increases in CO_2 and CH_4 concentrations with the decreasing size of the body of water were well-pronounced during the hot summer of 2012. The concentrations of CO_2 and CH_4 rose by factors of 5 and 150, respectively, in small ($\leq 10^2$ m^2) compared to large ($\geq 10^4$ m^2) thermokarst (thaw) lakes. Taken together, these trends suggest that, for a conservative scenario of lake size distribution, lake water warming at high latitudes will produce (1) a significant increase in methane emission capacity from thaw lake surfaces; (2) decreased molecular sizes of trace element complexes and potential bioavailability of metal micronutrients in water columns; and (3) relatively conservative responses by CO_2, DOC and trace element concentrations.

1 Introduction

Observations during field studies of thermokarst (also called thaw) lake dynamics in an actively developing permafrost system are of crucial importance for quantitative and predictive modeling of greenhouse gas (GHG) emissions from these lakes to the atmosphere (van Huissteden et al., 2011), which is one of the most significant environmental threats of permafrost warming at high latitudes (Schuur et al., 2008; O'Connor et al., 2010). Previously, the two main methods of predicting permafrost system evolution under climate warming scenarios were (i) substituting “space for time” by considering ecosystem changes along a latitude or landscape profile, for example, from sporadic to continuous permafrost (Frey et al., 2007) or corresponding to different degrees of permafrost coverage (Petrone et al., 2006), and (ii) artificial soil heating experiments (Melillo et al., 2002; Kirschbaum, 2004) or water table level manipulation (Blodau et al., 2008b; Reiche et al., 2009). Although these approaches are certainly useful for making straightforward predictions of the evolution of river – ocean and soil – atmosphere fluxes during climate warming, it is impossible to apply these two methods to model the main landscape features of arctic and subarctic wetlands, i.e., thermokarst (thaw) lakes and soils subsidences in permafrost regions. In contrast to these permafrost regions, boreal and glacial aquatic systems received much more attention due to the existence of long term data series that made it possible for researchers to observe trends in chemical compositions and predict future changes in aquatic systems (Granberg et al., 2001; Thies et al., 2007; Lepistö et al., 2008; Jankowski et al., 2006; Huser et al., 2011). Unfortunately, analogous time series are not available for major aquatic systems at high latitudes such as permafrost (thaw) lakes (cf. Smol and Douglas, 2007). However, natural weather perturbation phenomena, such as local droughts induced by the anomalously hot summer in 2012 in western and northern Siberia, provide opportunities to examine the effects of surface water heating on lake hydrochemistry and GHG exchange with the atmosphere. This natural short-term experiment offers a possibility for the straightforward assessment of summertime climate warming on permafrost thaw, lake drainage and water column chemical composition. Therefore, the first objective of this study was to quantify changes in thaw lake chemical composition during the anomalously hot summer of 2012 and compare these results to the normal period investigated during summer 2010 in the same region (Shirokova et al., 2013).

During recent years, significant progress was made in describing the evolution of thermokarst lakes under climate warming scenarios, mainly via the development of hydrological models of lake formation and drainage and biogeochemical models of GHG exchange with the atmosphere (Riordan et al., 2006; Anisimov et al., 2007; Jones et al., 2011; van Huissteden et al., 2011; Belshe et al., 2012). However, the smallest water bodies (< 0.01 ha), which are most subject to thawing and transformation (Pokrovsky et al., 2011), fall below the resolution threshold of these models, and these water bodies are not present on available topographic maps or detected by remote techniques. These small aquatic systems, which are not yet included in the global database, potentially make a large overall contribution to the hydrological balance (Lehner and Doll, 2004; Downing et al., 2006). Similar to small boreal lakes that regulate C stocks and accumulation rates in permafrost-free regions (e.g., Ferland et al., 2012 and references therein), small thaw ponds in western Siberia represent important stocks of dissolved and colloidal organic carbon (OC) and trace elements (TE) and contribute significantly to fluxes of CO_2 and CH_4 in the atmosphere (Shirokova et al., 2013). Examining patterns of dissolved gases and organic carbon in the smallest bodies of water undergoing thermokarst development, in view of their importance to overall gas exchange with the atmosphere, constituted the second objective of this study.

Finally, the third objective of this study was to characterize the concentration and colloidal properties of trace elements, which are still very poorly understood, in water columns of permafrost (thaw) lakes. On one hand, the characteristics of trace metals may reveal the sources of dissolved components in these lakes and differentiate contributions from groundwater, soil/peat leaching and atmospheric deposition. On the other hand, certain TE (B, Mn, V, Cu, Ni, Co, Zn, Fe, Mo, ...) may act as limiting nutrients for aquatic biota, and the role of these elements is particularly important given the highly oligotrophic/dystrophic status of thermokarst lakes. In this study, we aimed to assess concentrations and colloidal properties of over 40 major and trace elements during the anomalously hot summer of 2012 and to compare our observations with data from periods with normal temperatures. The main outcome of our measurements was to predict the consequences of lake water warming for trace element concentration, speciation and delivery to the Arctic Ocean through lake drainage to hydrological networks.

We addressed our objectives via concerted biogeochemical sampling of 40 thaw lakes in a pristine region of western Siberia where a heat wave occurred in June–July 2012, unprecedented over several decades of available meteorological records. The results obtained in 2012 were compared with our previous measurements in the same region during a summer with normal temperatures. On the basis of this comparison, we proposed conclusions about the chemical evolution of Siberian aquatic ecosystems and GHG exchange with the atmosphere under surface water warming scenarios.

2 Methods

2.1 Study site description

Our study site, which is located in the central part of Western Siberia (63.5° N, 75.4° E, 20 km from the Khanymey settlement), lies on a discontinuous permafrost tundra over Neocene sand and clay deposits that are covered by a layer of peat that is 1–2 m thick (Fig. 1 and ground photos in the Electronic Supporting Information, ESM-1). All of the bodies of water in this study were located at watershed divides between adjacent rivers in the Khanymey region, previously studied in 2010 (Shirokova et al., 2013). The locations of these bodies of water differed from those of other studies of thermokarst lakes in Siberia, Canada, and Alaska, which were situated in river plains and terraces, sea coastal zones, or river deltas (cf. van Huissteden et al., 2005; Emmerton

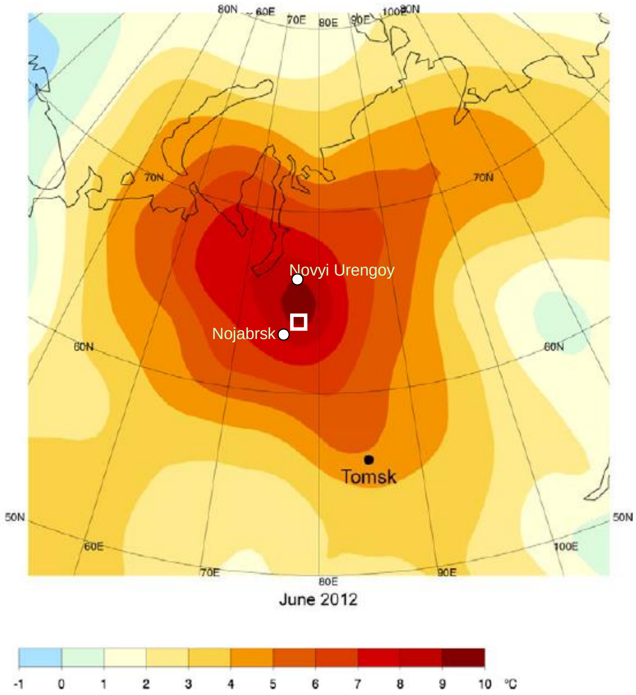

Fig. 1a. Localization of study site in 2010 and 2012 (white rectangular) shown on a map of air temperature anomalies in the western part of Siberia in June 2012 (Haeseler, 2012). Reference period: mostly 1961–1990.

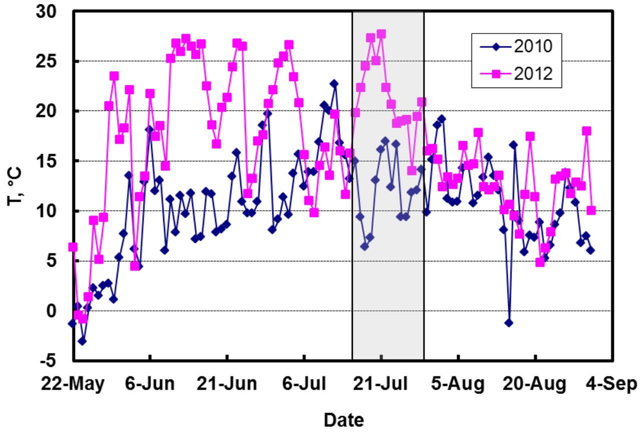

Fig. 1b. Mean daily temperatures of Tarko-Sale meteostation (the closest to Khanymey study area). The period of 2010 can be considered as normal year for the region. The sampling period of 2010 and 2012 is shown by grey field.

et al., 2007; Bouchard et al., 2011; Lougheed et al., 2011). Soil depressions, ponds, lakes and drainage basins in this study are originated from permafrost melt (soil subsidence). The typical sequence of thermokarst thawing and lake formation in the north of Western Siberia consist in the following events (Kirpotin et al., 2011; Pokrovsky et al., 2011). First, a crack appears in the lichen cover of the surface of the frozen mound; this decreases the albedo of the surface and leads to further peat degradation (example photo Z-4 of the ESM-1). The palsa depression is then filled by the water from the thawing. The size of the depression increases forming a shallow round lake characterized by intensive peat abrasion at the border. Eventually, the lake border is stabilized, and water becomes less acidic and less organic. The final stage of the ecosystem development consists of lake drainage into another larger water system or into the hydrological network, and a subsequent formation of the lake's dry bottom (khasyrey) with a small water body remaining in the center of the drained lake. All studied bodies of water ranged from 10 m to several km in diameter with a similar depth of 1.0 ± 0.5 m under normal precipitation/evaporation conditions.

In summer 2012, a heat wave impacted western Siberia, producing mean daily temperatures that were the highest measured since the beginning of the 20th century. The epicentre of ground heating in June 2012 was almost at the territory chosen for this study (Fig. 1a) and previously monitored in 2010 during a normal summer shown by white rectangular. Plotted in Fig. 1b are mean daily temperatures during summer season in 2010 and 2012 recorded at the nearest meteo-station of Russian Hydrometeorological Service. A systematic shift of ca. 10 °C between summer 2012 and 2010 also pronounced for both daily minimal and daily maximal temperatures (not shown) is clearly observed. The majority of samples collected in 2012 are from the Khanymey region located on the watershed devide tundra zone with large amount of thermokarst lakes (Fig. 1c). Exactly the same region was also sampled in July 2010 (Shirokova et al., 2013). We collected samples during the middle of July 2012, when the epicentre of the heat shifted toward the Yamal peninsula. However, anticyclonic conditions persisted over the whole month of July 2012, and the average surface water temperature (23.7 ± 2.4 °C, $n = 40$) remained approximately 10 °C higher than during summer 2010 (14.1 ± 2.2 °C, Shirokova et al., 2013). As a result of this extreme drought, water levels in large lakes decreased by ca. 0.3–0.5 m. Small thermokarst lakes and ponds shrank significantly due to evaporation (Fig. 1d). During this drought, surface areas of most bodies of water ($< 1000\,\mathrm{m}^2$, ≤ 0.5 m depth) decreased by a factor between 2 and 5, and many small soil depressions and ponds completely disappeared, leaving dry bottoms covered by mosses or organic-rich sediments (see photos in ESM-1).

2.2 Sampling, analyses and statistics

A list of water bodies sampled in 2012 and their main hydrochemical characteristics is presented in Table 1. The sampling, filtration, and dialysis methods used in this study, as well as the chemical analysis techniques, are very similar to those utilized in our previous studies (Pokrovsky et al., 2010, 2011, 2012a; Shirokova et al., 2013). Samples were

Table 1. General physical and hydrochemical parameters of studied water bodies. The sampling period is 16–18 July 2013.

No	N	E	Description	Depth, m	S, m^2	T, °C	O$_2$, mg L^{-1}	O$_2$, % sat	Cond, µ S cm^{-1}	pH	DIC, ppm	DOC, ppm	UV$_{280}$ nm	Cl, ppm	SO$_4$, ppm	CH$_4$, µmol L^{-1}	CO$_2$, µmol L^{-1}
Z-1	63°48′29.3″	75°29′43.6″	Growing lake	0.5	1000	18.5	8.2	90	16.4	4.50	0.428	16.8	0.364	0.2087	0.4543	4.16	88.71
Z-2	63°48’29.9″	75°29′43.1″	Fast growing pond, a lot of zooplankton	0.4	150	19.5	8	80	75	6.16	1.657	106.2	4.04	0.6116	0.4696	46.59	439.1
Z-3	63°48′38.5″	75°30′10.4″	Crack in moss coverage	0.2	14	19.9	8.5	92	30	4.27	0.531	19.9	0.544	0.0948	0.2174	30.12	190.4
Z-4	63°48′40.5″	75°30′13.9″	Depression over the peat crack	0.1	6	19.5	6	60	41.6	4.03	1.07	112.7		1.1787	1.5382	47.48	778.3
Z-5	63°48′44.9″	75°30′15.0″	mesotrophic lake	0.4	375	19.5	4.5	50	34.4	4.26	0.491	42.2	0.99	0.2147	0.3594	2.75	183.0
Z-6	63°48′53.8″	75°30′17.3″	large stable lake	0.5	7500	19.5	8.9	95	19.7	4.51	0.436	23.2	0.669	0.0931	0.0389	0.29	68.9
Z-7	63°48′58″	75°30′13.5″	Growing peat lake	0.4	1600	23.5	8.6	100	41.1	3.95	0.472	55.6	1.42	0.4170	0.2180	1.67	84.4
Z-8	63°49′04.0″	75°30′14.0″	Small lake	0.3	300	23.9	8.6	100	34.4	4.10	0.628	49.1	1.31	0.0434	0.1498	2.73	107.5
Z-9	63°49′06.7″	75°30′12.7″	Depression over the peat crack (moss on bottom)	0.4	100	24.8	8.5	105	53.4	3.79	0.409	56.8	1.42	0.0409	0.2388	36.11	319.3
Z-10	63°49′07″	75°30′12.1″	Coalescent ponds in an elongated depression	1.0	2000	21.4	8.1	95	12.9	4.62	0.470	18.7	0.6846	0.2675	0.0749	3.55	159.2
Z-11	63°49′15.0″	75°30′31.2″	Drying pond irregular shape	0.2	800	22.2	8.8	95	44.7	3.85	0.380	57.4		0.0223	0.2336		150.5
Z-12	63°49′12.1″	75°30′42.3″	classic t/k pond	0.5	2100	22.2	8.8	100	28.5	4.38	0.524	46.8	1.57	0.2348	0.1268		
Z-13	63°49′10.5″	75°30′48.4″	classic peat pond	0.4	300	24.9	7.9	95	32.1	4.31	0.403	69.0	2.046	0.2951	0.3305	2.44	97.4
Z14	63°49′01.7″	75°30′56.8″	thermokarst lake	0.5	750	24.8	8.3	98	20.5	4.21	0.355	28.1	0.6229	0.0318	0.1783		
Z15	63°48′34.3″	75°30′16.8″	Shallow pond covered by mosses	0.3	102	25.7	8.2	94	31.9	4.00	0.346	45.4	0.76	0.0799	0.3857	0.57	68.4
Z-16	63°48′34.3″	75°30′16.8″	1st stage, depression	0.3	2.0	25.8	8.4	98	50	3.76	0.749	42.8	1.00	0.5378	1.1985		100.6
Z-17	63°47′24.6″	75°37′57.1″	Lake of Khanumey 2010, N 34	0.75	40 000	21.3	8	92	10	4.49	0.370	14.1	0.2987	0.0975	0.4236	0.25	49.5
Z-18	63°47′29.1″	75°38′08.7″	Lake of Khanumey 2010 site,	0.6	20 000	21.9	7.8	91	24	3.97	0.529	28.3	0.675	0.0219	0.1826	3.56	57.1
Z-19	63°47′23.1″	75°38′23.6″	site of PP-2010 (N33)	0.75	20 000	21.8	8.1	95	23.5	4.16	0.345	25.2	0.7272	0.3230	0.5238	0.03	53.1
Z-20	63°47′19.1″	75°38′40.3″	N30 of 2010 Chernoe Lake	0.5	500	22.2	8.5	96	36.9	5.01	0.652	66.4	2.0989	0.1928	0.1037	1.07	159.5
Z-21	63°48′06.3″	75°33′37.2″	middle of the Khasyrey	0.4	500	22.4	7.8	92	10.8	4.40	0.394	12.3	0.2395	0.0361	0.9042	0.12	60.6
Z-22	63°48′03.7″	75°33′45.2″	Thermokarts pond, round	0.5	320	25.9	7.8	90	17.8	4.91	0.351	36.0	1.23	0.0352	0.1924	0.86	79.8
Z-23	63°48′04.4″	75°33′56.0″	classic t/k pond	0.4	5000	21.8	7.4	80	16.6	4.31	0.697	26.3	0.912	0.1318	0.1313	0.95	124.5
Z-24	63°48′10.5″	75°34′25.0″	large stable lake	0.85	4 000 000	21.9	8.7	100	7.4	6.04	0.464	33.3	0.30	0.2599	0.3702	0.23	114.8

Table 1. Continued.

No	N	E	Description	Depth, m	S, m^2	T, °C	O$_2$, mg L^{-1}	O$_2$, % sat	Cond, µ S cm^{-1}	pH	DIC, ppm	DOC, ppm	UV$_{280}$ nm	Cl, ppm	SO$_4$, ppm	CH$_4$, µmol L^{-1}	CO$_2$, µmol L^{-1}
Z-26	63°48′30.2″	75°34′59.7″	Large stable lake;	0.75	15 000 000	23.8	9.1	95	12.9	4.38	0.383	25.7	0.3606	0.6767	0.9142	0.05	48.3
Z-27	63°48′33.5″	75°35′18.0″	Classic t/k pond, round	0.4	300	23.2	9.0	100	20.3	3.98	0.303	28.3	0.764	0.1307	0.1167	1.25	63.2
Z-28	63°48′37.8″	75°35′28.6″	Pond with sphagnum, partially shrunk	0.5	400	24.2	8.8	95	20	3.97	0.365	21.1	0.4317	0.0250	0.3888	0.74	63.2
Z-29	63°48′41.5″	75°35′21.2″	Elongated shrunk pond (40–50 cm), × 14 times surface decrease	0.1	1000	25	8.7	90	19	4.61	0.450	27.6	0.8268	0.5601	1.3470	0.50	102.8
Z-25	63°48′23.5″	75°34′56.0″	Lake Kuropatochie, 40 cm shrinkage	0.6	1500	25.4	8.3	95	27.7	3.93	0.329	20.7	0.586	0.0094	0.9456	0.11	63.6
Z-30	63°48′41.8″	75°35′21.9″	“Meteorite” crater, shrunk pond	0.2	100	25	8.5	90	25.4	5.81	1.25	46.6	0.88	0.4364	0.5844	5.33	246.2
Z-31	63°48′19.1″	75°30′53.8″	Biofilm trap Lake	0.8	7000	24.8	7.8	100	21.1	4.31	0.325	36.3	1.22	0.4946	0.0114	2.02	108.7
Z-32	63°48′20.2″	75°31′11.3″	Oval pond, shrunk	0.2	700	27.0	7.9	99	33.3	4.08	0.440	68.2	2.2	0.2710	0.3025	8.61	142.6
Z-33	63°48′20.1″	75°31′09.7″	Shrunk pond	0.1	500	29	7.2	93	38.1	3.76	0.356	57.2	1.23	0.1581	0.1201	1.01	91.0
Z-34	63°48′24.2″	75°31′33.1″	Round pond	0.5	8000	26	8.5	102	22	3.97	0.333	28.7	0.5791	0.1090	0.3885	0.11	49.2
Z-35	63°48′24.7″	75°31′36.5″	Shrunk pond, of initial stage	0.3	250	29.6	4.9	60	22	4.12	0.504	46.9	1.596	0.3085	0.1928	2.68	173.3
Z-36	63°48′44.4″	75°32′14.7″	Elongated shrunk pond	0.4	500	26.9	8.4	100	20.9	4.03	0.385	32.1	0.88	0.1825	0.0094	2.79	63.9
Z-37	63°48′45.5″	75°32′21.2″	Large mature Lake, no stratification at 80 cm bottom	0.8	6 500 000	24	8.3	100	11.6	4.51	0.329	19.7	0.431	0.5250	0.8775	0.65	61.7
Z-38	63°48′51.2″	75°32′28.2″	Lake Plyazhnoe	0.9	15 896 250	24.3	8.7	100	12	4.70	0.262	19.6	0.298	0.5552	0.7967	0.04	42.6
Z-39	63°48′02.8″	75°32′39.2″	Lake at the border of Khasurey	0.8		29.3	7.1	94	11.7	4.20	0.332	25.0	0.435	0.3715	0.1650	1.39	73.7
Z-40	63°49′12.2″	75°32′52.3″	Shrunk lake with grass island in the middle (60 % of the surface)	0.8	625	27.5	7.8	99	22.4	3.98	0.266	19.6	0.3892	0.2011	0.6251	0.61	69.3
Z-41	63°48′04.4″	75°32′03.1″	Lake of the Khanumey road	0.6	4500	26.6	8.2	103	17.2	4.19	0.298	27.6	0.5272	0.5344	0.0270	3.04	82.1
Z-42			River Pyakopur next to Khanumey bridge						55.6	6.75	6.67	7.0	0.1756	1.9817	0.4467		

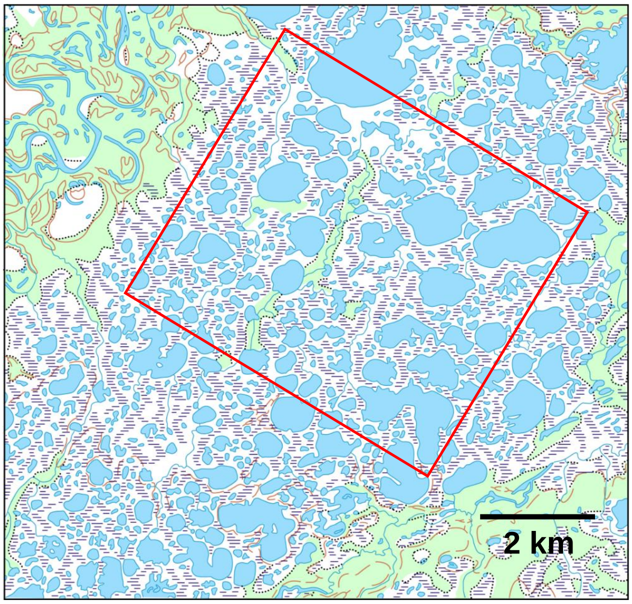

Fig. 1c. Detailed map of the Khanymey study site investigated in this work and sampled in July 2010 (Shirokova et al., 2013).

Fig. 1d. A photo of shrunk thaw lake.

filtered on-site, stored in HDPE bottles and refrigerated. For TE analysis, samples were acidified to $pH = 2$ with double distilled HNO_3. An ultraclean sampling procedure was used for all manipulations in the field (Shirokova et al., 2010). Water samples were taken from the middle of the pond or lake using a wide-mouth polypropylene, bottle attached to a non-metallic stick. Water samples were immediately filtered through sterile single-use Minisart® filter units (Sartorius, acetate cellulose filters) with a pore size of 0.45 µm. The first 100 ml of filtrate was discarded. Dissolved oxygen, pH, and Eh were measured on-site with uncertainties of 5 %, 0.02 units, and 2 mV, respectively, using a WTW® oximeter with a polarographic sonde and a Hanna® portable pH meter with an Eh/pH electrode.

Major anion concentrations (Cl^- and SO_4^{2-}) were measured by ion chromatography (HPLC, Dionex ICS 2000) with an uncertainty of 2 %. DOC was analyzed using a Carbon Total Analyzer (Shimadzu TOC 6000) with an uncertainty better than 3 %. Aqueous silica concentrations were determined using the molybdate blue method with an uncertainty of 2 % and a detection limit of 0.2 µM. Levels of Ca, Mg, Na, K and trace elements (TE) were determined without preconcentration with an ICP-MS Agilent 7500 CE, routinely used in our laboratory for the analysis of samples from boreal organic-rich lakes (cf. Pokrovsky et al., 2012a). Indium and rhenium were used as external standards. The international geostandard SLRS-4 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was used to check the accuracy and reproducibility of each analysis (Yeghicheyan et al., 2001). We obtained good agreement between replicate measurements of SLRS-4 and certified values (relative difference $< 10\,\%$ SD for repeated measurements), except for B and P (30 %). In addition to TE analysis using the Agilent 7500 CE instrument, approximately 30 undiluted samples were processed with an ultrasensitive Element XR ICP-MS instrument operated in a low and medium resolution mode. Using this ICP-MS greatly increased the detection limits of a number of elements and improved the precision of the analyses while avoiding interferences. The uncertainty of the Element XR analysis was $\leq 5\,\%$, while its detection limit was a factor of 100 lower than the traditional (Agilent) instrument. The average agreement between the two ICP-MS instruments for the majority of the TE was 10–15 %.

In situ dialysis experiments were performed by directly placing 20–50 ml pre-cleaned dialysis bags in water. The duration of this dialysis procedure was 72–96 h, which was based on previous dialysis equilibrium kinetic experiments for DOC, Si, and trace elements in other thermokarst (Pokrovsky et al., 2011) and boreal organic-rich waters (Pokrovsky et al., 2012a). For dialysis experiments, Spectra-Por 7® dialysis membranes made of regenerated cellulose with a pore size of 1 kDa were cleaned in EDTA to remove trace metals and thoroughly washed in 0.1 M double-distilled HNO_3 and ultrapure water. The dialysis membranes were filled with ultrapure Milli-Q deionized water and placed in natural water. The minimum volume of the external reservoir (soil depression or thaw pond) was 10 L, corresponding to an almost infinite ratio of external/internal reservoirs, an important prerequisite for dialysis procedure. The efficiency of the dialysis procedure was evaluated by comparing the concentrations of major anions or neutral species (e.g., Cl^- and H_4SiO_4) not associated with colloids in a dialysis bag with their concentrations in the external solution. These concentrations were always identical within ±20 %, suggesting an equilibrium distribution of dissolved components.

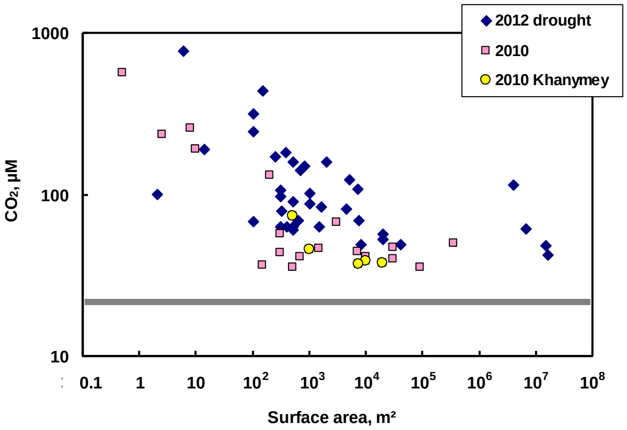

Fig. 2. CO_2 concentrations as a function of water body surface area. Blue diamonds and pink squares represent the data of draught 2012 and normal summer 2010, respectively. The permafrost subsidencies and thaw lakes sampled in 2010 in the Khanymey region are shown by yellow circles. Here and below the pink squares represent the adjacent sites of thermokarst lake development shown by white rectangular in Fig. 1a and sampled in 2010 (Shirokova et al., 2013). The grey line represents the equilibrium with the atmosphere. The symbol size reflects the value of the uncertainty.

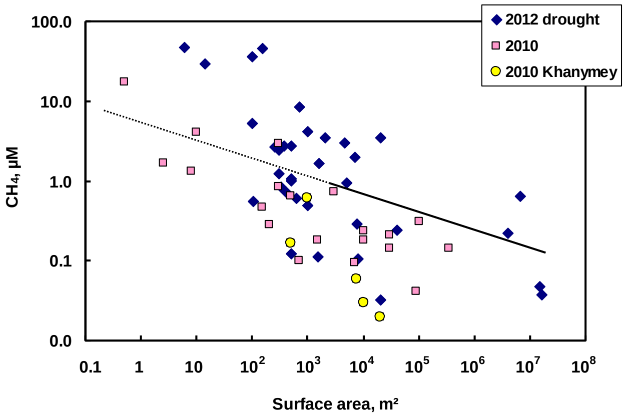

Fig. 3. CH_4 concentrations as a function of water body surface area. Blue diamonds and pink squares represent the data of draught 2012 and normal summer 2010, respectively. The permafrost subsidencies and thaw lakes sampled in 2010 in the Khanymey region are shown by yellow circles. The solid line represents the dependence recommended by Bastviken et al. (2004) for northern boreal and temperate lakes, and the dashed line represents the extrapolation of this dependence to smaller water bodies. The symbol size reflects the value of the uncertainty.

The colloidal fraction of a component was assessed as the difference between the filtrated and the dialyzed fractions, and normalized with respect to the total dissolved concentration according to

$$\%_{\text{colloidal}} = \frac{[<\ 0.45 \mu\text{m}] - [<\ 1\,\text{kDa}]}{[<\ 0.45\ \mu\text{m}]} \times 100\,\%$$

For the CO_2 and CH_4 analyses, 60 mL of bubble-free water was collected at a depth of 0.1–0.5 m with a 60 mL polypropylene syringe. Approximately 30 mL of the sample was injected from the syringe into a serum bottle previously flushed with nitrogen. As a preservative, 0.2 mL of saturated $HgCl_2$ was added. Two or three 0.5 mL replicates of the equilibrated headspace were analyzed for concentrations of CH_4 and CO_2 using a gas chromatograph (GC) equipped with a flame ionization detector. A column was used for separation at 60 °C with hydrogen and air carrier gases. Pressures of hydrogen and air were 20 psi and 5 psi, respectively. After 10 samples were analyzed, the detectors were calibrated using Air Liquide gas standards ($CH_4 = 100$ ppmv and $CO_2 = 1000$ ppmv). Duplicate injections of samples showed that results were reproducible within ±5 %. The specific gas solubility of CH_4 (Yamamoto et al., 1976) and CO_2 (Weiss, 1974) was used to calculate the total CH_4 and CO_2 content in each vial.

Element concentrations and speciation data were analyzed with best fit functions based on the method of least squares, Pearson correlation and one-way ANOVA with STATISTICA version 6 (StatSoft Inc., Tulsa, OK). Regressions and power functions were used to examine relationships between element concentrations and lake surface areas. Correlation coefficients were calculated to elucidate relationships between organic carbon or Fe and TE concentrations in lakes. The ANOVA method was used to test the differences in average TE concentrations and DOC parameters as well as concentration – lake surface regression slopes for two years of observations. The ANOVA test was carried out with a one-way analysis of variance by using the Dunn's method due to the different number of samples for each year (SigmaPlot version 11.0/Systat Software, Inc). In this method, $P < 0.05$ means the difference in the median values is important and statistically significant. On the other hand, $P > 0.05$ means that the differences in the median values are not statistically significant and they may stem from random sampling variability. In addition, a Sign test adopted from Rijsbergen (1979) was used to assess global differences in all averages of lake water composition parameters measured during two different years.

3 Results

3.1 Dissolved carbon dioxide and methane

All of the bodies of water in this study were in equilibrium with atmospheric oxygen (100 ± 10 % saturation). In small soil depressions, 70–60 % of the oxygen saturation was observed at the interface with the sediment. None of the large lakes in this study exhibited measurable temperature and oxygen stratification between the surface (0 m) and the bottom (max. 1 m) horizons. In the full range of studied surface

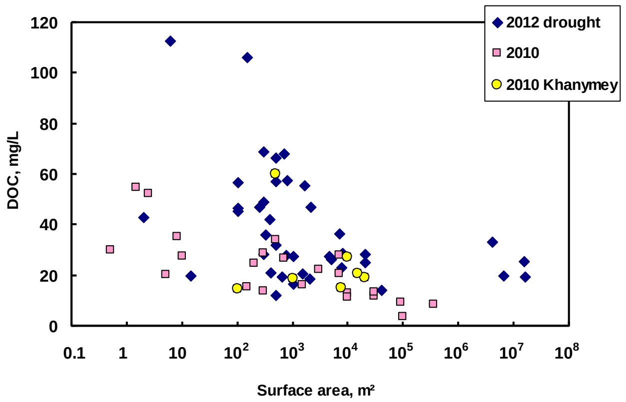

Fig. 4. Total dissolved ($< 0.45\,\mu m$) organic carbon concentration as a function of water body surface area. Blue diamonds and pink squares represent the data of draught 2012 and normal summer 2010, respectively. The permafrost subsidence's and thaw lakes sample din 2010 in the Khanymey region and shown by yellow circles. Uncertainties ($\pm 2\sigma$) are the same or smaller than symbol sizes unless otherwise labelled.

areas, the ponds and lakes were strongly supersaturated with respect to atmospheric CO_2 and CH_4 and thus likely acted as GHG sources during the sampled period. A plot of CO_2 and CH_4 concentrations as functions of water surface area (Figs. 2 and 3, respectively) revealed an increase of these GHG concentrations with the decrease of the water surface area at $S < 10^4\ m^2$ and quasi-constant concentration levels in larger ponds and lakes with surface areas ranging from 10^4 to $10^7\ m^2$. There was almost an order of magnitude increase in CO_2 concentration in the smallest ($< 10^2$–$10^3\ m^2$) bodies of water compared to the larger ponds and lakes (Fig. 2), and the relative increase of CH_4 concentration ranged between 10 and 50 times (Fig. 3). A power function $[CH_4] = A \times S^n$, where A and n are empirical constants and S is the surface area of the water body, adequately described the concentration – S dependence ($r^2 = 0.6$, not shown). The parameters A and n were equal to 4.34 and -0.365, respectively, for normal summertime temperate conditions in 2010. The values of A and n were 18.3 and -0.354, respectively, during the hot summer of 2012.

The CO_2 concentration in the water samples of the hot summer of 2012 was higher by a factor of 1.44 relative to the normal summer of 2010, whereas the methane concentration in summer 2012 was a factor of 4.9 times higher than in 2010. These differences are statistically significant, as the Sign test for the averages of 32 and 40 samples from 2010 and 2012, respectively, was highly significant and the ANOVA test yielded $P = 0.002$ and < 0.001 for CH_4 and CO_2 concentrations, respectively.

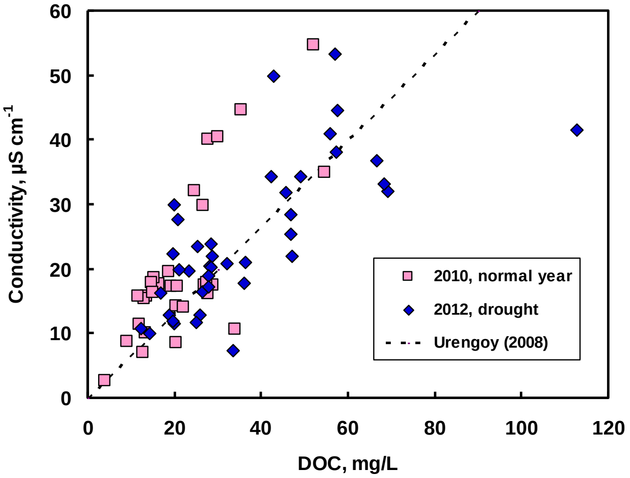

Fig. 5. Conductivity of the water samples as a function of DOC concentration for depressions, ponds, and lakes measured during the normal year 2010 (Shirokova et al., 2013) and during 2012 drought (this study). The dashed line represents the data from continuous permafrost zones (Urengoy region, Shirokova et al., 2009). Uncertainties ($\pm 2\sigma$) are the same or smaller than symbol sizes.

3.2 Dissolved organic carbon and major elements

For the sequence of thaw ponds and lakes, which ranged from local permafrost subsidences and shallow depressions to large, kilometer-sized lakes, we observed a systematic decrease of the total dissolved ($< 0.45\,\mu m$) OC concentration as a function of the surface areas of the bodies of water (Fig. 4). The general trend observed for samples taken during the period of high temperatures was similar to the trend reported during the normal period. However, the arithmetic and geometric averages of the DOC concentration of 40 ponds and thaw lakes in July 2012 were higher than those in 2010 by factors of 1.7 and 1.5, respectively. This difference is statistically significant with $P < 0.001$. In all studied lakes, ponds, depressions, and rivers in this study, we observed good correlation between DOC ($< 0.45\,\mu m$) and UV absorption at 280 nm ($R^2 = 0.88$, not shown). The average slope of [DOC]–A_{280} dependence measured in 2012 (0.0346) was statistically similar to that measured during the normal summer of 2010 (0.0324).

The decrease in the DOC concentration from the small depressions to the ponds and lakes correlated ($r^2 = 0.65$) with the decrease in solution conductivity (Fig. 5). This relationship was in general agreement with the relationship established for thaw lakes from continuous permafrost zones of western Siberia (e.g., Novy Urengoy region, Shirokova et al., 2009; Pokrovsky et al., 2011) and the Nojabrsk and Khanymey regions measured during the normal summer 2010 (Shirokova et al., 2013). The lake water pH did not depend strongly on the size of the body of water and remained essentially unchanged during the hot summer of 2012 compared to the normal summer of 2010 (4.35 ± 0.44 and 4.40 ± 0.80, respectively), as also proven by both Sign and ANOVA tests. Concentrations of major anions such as Cl^- and SO_4 were higher by factors of 2.3 and 1.5, respectively, during the 2012 drought compared to the normal year. While for Cl^- this difference is significant ($P = 0.012$), it is not statistically significant for SO_4 ($P = 0.176$) as shown by the ANOVA test.

3.3 Dissolved and colloidal trace elements

Similar to other western Siberia acidic thermokarst water bodies on frozen peat, concentrations of dissolved, low-mobility trace elements such as Fe and Al, which are among the major components of lake and pond waters, were comparable to those of Mg, K, Na, and Ca and significantly higher than those of Si (Table 1 and Table ESM-2). Although the highest and the lowest concentrations of Fe, Al and other insoluble elements were observed in small permafrost depressions and large lakes, respectively, the dissolved Fe concentration did not decrease systematically as the surface area increased in the chronosequence of permafrost thaw from peat depressions to thaw ponds and thermokarst lakes (not shown).

Calculations of correlation coefficients for DOC, Fe and TE concentrations distinguished between 2 groups of elements on the basis of their affinities: (i) affinity for Fe rather than DOC, with $r^2_{\mathrm{TE,\,Fe}} > r^2_{\mathrm{TE,\,DOC}}$: B, Al, Ti, V, Cr, Co, Ni, Cu, Ga, Ge, As, Rb, Sr, Zr, Cs, REEs, Hf, Pb, Th and U, and (ii) affinity for DOC rather than Fe, with $r^2_{\mathrm{TE,\,Fe}} < r^2_{\mathrm{TE,\,DOC}}$ such as Mg, Ca, Mn, Zn, Cd, and Ba. Finally, Na, K, Mo and Sb did not exhibit statistically significant correlations with DOC or Fe ($r^2 < 0.4$). Correlation coefficients for rare earth elements with Fe progressively decreased from light REE (0.71 and 0.64 for La and Ce, respectively) to heavy REE (0.38 for Yb). Statistical treatments of average annual concentrations using the Sign test (Rijsbergen, 1979) demonstrated significantly higher concentrations of 40 major and trace elements in 2012 than in 2010 with $p = 4.3 \times 10^{-13}$ at a threshold of 0.001. For 50 major and trace elements including DOC, the ratios of arithmetic and geometric average concentrations in 2012 and 2010 were equal to 2.42 ± 0.86 and 2.35 ± 0.80, respectively. Only Co, Mo, La, Pr, Sm and Th yielded statistically similar average concentrations in 2010 and 2012 as follows from the Sign test. The ANOVA test yielded the variations between two years for Si, K, Ca, V, Cu, Rb and Th as not statistically significant.

To assess the size fractionation of elements in thermokarst lakes, we calculated the percentage of colloidal OC, major and trace elements. Among the major elements, chloride and sulfate concentrations were the least influenced by dialysis. Other components, however, were strongly affected by the dialysis procedure, demonstrating significant proportions of colloidal forms. This is illustrated in the stack diagram in Fig. 6. For most of the insoluble trace elements and DOC, the dominant form (> 50 %) was colloidal, while Ca, Mg, Ni, Mn, Co, Cu, Cr, Cd, Zn, Cs and Sr were present (between 30 and 50 %) in colloidal forms, and only Na, K, Rb, Si, Mo, and Sb truly dissolved with < 1 kDa species (≥ 90 %). Figure 6 shows that the anomalously hot summer of 2012 yielded systematically smaller colloidal forms of most major and trace elements. This decrease was statistically significant as demonstrated by both ANOVA and Sign test. The ratio of the average proportion of colloids in 2010 to that in 2012 ranged from 1 to 1.8 with arithmetic and geometric means equal to 1.66 ± 0.33 and 1.30 ± 0.52, respectively. The elements whose speciation was most affected by the water temperature increase were K, Rb, Cs, Ca, Mg, Sr, Mn, Ni and Co. More importantly was the increase of the proportion of the $\mathrm{LMW}_{< 1\,\mathrm{kDa}}$ fraction for most elements during the hot summer of 2012. For six typical metal micronutrients capable to limit aquatic biota such as Ni, Cr, Zn, Mn, Co and Fe, this increase was equal to factors of 2.2, 1.5, 1.5, 2.3, 6.6 and 2.8, respectively.

4 Discussion

4.1 CO_2, CH_4 and DOC of thaw lakes in a warmer and drier climate

It is fairly well established that climate warming at high latitudes triggers enhanced GHG emissions to the atmosphere. Thus, in predicted future scenarios of a warmer and drier climate (Porcal et al., 2009; White et al., 2007), lake water levels may fall and expose previously stored organic sediments to greater aeration (see Fig. 1d), which would release more CO_2 into the atmosphere. In the present study, we evaluate the consequences of this scenario for vast wetland areas over permafrost in the central and northern parts of Western Siberia. Although fluxes of CO_2 or CH_4 from lake surfaces to the atmosphere were not assessed in our study, the relative increase of aqueous GHG concentrations during the anomalously hot summer of 2012 provided evidence of the great vulnerability of northern permafrost-controlled aquatic systems. Concentrations of major and trace inorganic element increased by factors of 1.7 to 2.4, respectively, during the hot summer of 2012 relative to the normal summer of 2012. These results for inorganic elements can be considered as conservative because a factor of ∼ 2 concentration increase may merely reflect water evaporation. Moreover, this degree of evaporation coincided with our field evaluations of water levels that decreased by between 20 and 50 cm, which constituted a factor of 2 given the typical depth of thaw lakes and ponds from 0.5 to 1.0 m (Pokrovsky et al., 2011; Shirokova et al., 2013). This is further confirmed by a good correlation between DOC concentration and conductivity (Sect. 4.1, Fig. 5) suggesting that these components may be controlled by similar processes such as peat leaching at the lake border following by progressive consumption of DOM by heterotrophic

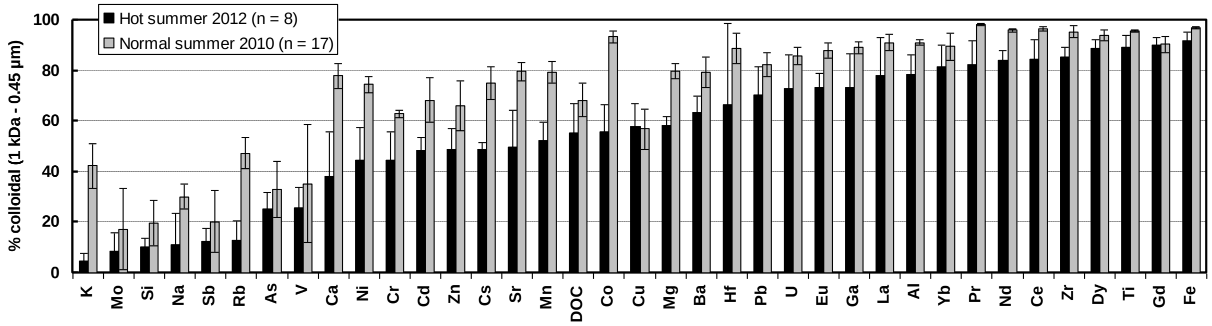

Fig. 6. A stack diagram of the proportion of colloidal forms (Eq. 1) measured using in-situ dialysis during normal summer 2010 and anomalously hot summer 2012.

bacterioplankton producing CO_2 flux to the atmosphere and metal deposition in the lake sediments (cf., Pokrovsky et al., 2011; Audry et al., 2011; Shirokova et al., 2009, 2013). Therefore, according to results from natural short-term water heating experiments, most major and trace components, including DOC, may behave conservatively following the evaporation line with a maxim concentration increase given by a factor of 2.

The situation was different for CO_2 that underwent a concentration increase by a factor of 1.44 during the hot summer of 2012. The CO_2 cannot be regarded as a conservative component whose concentration increases only by evaporation due to its very short residence time in thermokarst bodies of water. An increase in temperature by 10°, from 14 to 24 °C, should produce a factor of 1.35 decrease in CO_2 solubility in water, according to thermodynamic calculations using vMinteq code (Gustafsson et al., 2011). This decrease in solubility would certainly lead to faster CO_2 release from warmer lakes. Elevated CO_2 concentrations in lake water during the hot summer of 2012 should therefore be linked to internal processes in lake water columns or sediments rather than equilibrium exchange with external reservoirs (atmosphere, ice gas hydrates at lake bottoms over glacial substrates).

Results of the present study suggest that short-term consequences of heating of thaw lakes and ponds may include an almost five-fold increase in methane flux from lake surfaces to the atmosphere and less than a two-fold increase in CO_2 flux. This decoupling of two GHG fluxes most likely stems from the greater sensitivity to the temperature increase of methanogenesis compared to heterotrophic respiration of DOC by aerobic bacterioplankton, which are the main cause of CO_2 supersaturation in water columns of boreal (Kortelainen et al., 2000; Cole et al., 2004) and thermokarst (Blodau et al., 2008a) lakes and ponds. An additional cause of increases in methane concentration (and its flux to the atmosphere) may be a two-fold decrease of the depth of thaw ponds and lakes, which shortens the transit of methane from anoxic sediment layers (Audry et al., 2011) to the atmosphere. Because the full water columns of Western Siberia thermokarst lakes are oxygenated (Audry et al., 2011; Shirokova et al., 2013), the degree of methanotrophy may decrease significantly in response to the thinning of oxygenated water column depths, similar to behavior observed in littoral zones of temperate lakes (Bastviken et al., 2008).

4.2 Geochemistry of trace elements and their speciation changes: decrease of colloidal fractions in response to temperature increase

The particular bodies of water studied in western Siberia, compared to other known Arctic ponds and thermokarst lakes in Eastern Siberia or Canada, are characterized by very low total dissolved solid content, high DOC, low pH and relatively high Fe and Al concentration. For example, the mean conductance of high Arctic ponds that shrank significantly due to evaporation was between 100 and 400 $\mu S\,cm^{-1}$ (Smol and Douglas, 2007), an order of magnitude higher than the conductance of thaw lakes and ponds in western Siberia. Much lower ionic strengths and higher concentrations of allochthonous dissolved organic matter originating from peat leaching are the most likely causes of high proportions of colloidal metals, including even alkaline earth elements, in western Siberia water bodies developed on discontinuous permafrost.

Although western Siberian thermokarst waters are rich in Fe relative to major cations, the average value of the molar ratio $(Fe/C_{org}) \times 1000$ is equal to 1.7 ± 0.9 ($n = 40$). This value is significantly lower than values reported for boreal subarctic and temperate surface waters (5 to 50, Ilina et al., 2013), Alaskan rivers (3 to 5, Stolpe et al., 2013) and various European subarctic creeks and bog waters (5 to 20, Vasyukova et al., 2010, 2013). The most likely cause for this difference in Fe level is the lack of groundwater feeding of thermokarst water bodies that receive all of their dissolved components from surface peat leaching and atmospheric deposits. In contrast, boreal riverine Fe-rich colloids in the permafrost-free zone are formed during mixing of anoxic Fe(II)-bearing fluids with surface organic-rich waters within riparian or hyporheic zones of streams (Pokrovsky et al., 2012b). Although contributions of hyporheic exchange in the peat streams cannot be excluded (e.g., Greenwald et al., 2008), the contributions of groundwater feeding to isolated shallow bodies of water should be very limited. Indeed, the primary source of dissolved major and trace elements in ponds and lakes is peat leaching from surface soil horizons, followed by heterotrophic mineralization of DOM in water columns (cf., Shirokova et al., 2009; Audry et al., 2011). This is strongly supported by the absence of correlations between lake surface areas and TE concentrations. One may expect that the degree of deep groundwater discharge at the bottom of a lake increases with lake size and watershed area and enriches the lake water with dissolved solutes (e.g., Ca, Mg, Si, Sr, and Fe) that originate from water-rock interactions. However, this behavior was not observed in a large number of pond and lakes in this and other similar studies in Western Siberia (Pokrovsky et al., 2011; Shirokova et al., 2013).

Our results for [TE]–[Fe] or [DOC] correlations (Sect. 3.3) suggest that the majority of insoluble trivalent and tetravalent trace elements are associated with Fe rather than DOC. This proposal is in general agreement with size fractionation results from other boreal regions and suggests that organo-ferric colloids have an important role in TE transport in surface water (cf., Ingri et al., 2000; Pokrovsky et al., 2006; Bauer and Blodau, 2009; Stolpe et al., 2013).

Changes in TE size fractionation in response to the hot summer recorded in the present study allows us to hypothesize that water warming will bring about an increase in the lability of OC and TE and, most likely, their bioavailability. Indeed, $\mathrm{LMW}_{<1\,\mathrm{kDa}}$ species are potentially bioavailable because pore sizes of cell wall transport channels, which are 10–30 Å in bacteria and 35–50 Å in plant cells (Carpita et al., 1979; Trias et al., 1992), and 1 kDa dialysis membranes (1–2 nm) are comparable. This assumption may be true only for passive (diffusional) transport of metals through biological membranes. The increase of the bioavailability of TE micronutrients may impact the probability of phytoplankton bloom in lakes and adjacent rivers but also stimulate the activity of heterotrophic aerobic bacterioplankton. At the same time, the decrease of the colloidal proportion of most trace elements during the hot summer of 2012 appears counterintuitive because the main source of colloids – dissolved organic matter – almost doubled in average concentration compared to the normal year of 2010. However, several naturally occurring factors may drive the size fractionation of OC and TE towards low molecular weight fractions as discussed below.

One possible mechanism of $\mathrm{LMW}_{<1\,\mathrm{kDa}}$ increase during a period of increasing water temperature is the activity of heterotrophic aerobic bacteria capable of respiring DOM of allochthonous origin, which is well documented in various boreal and subarctic settings (i.e., Roehm et al., 2009; Karlsson et al., 2010; Ask et al., 2012). Higher temperatures can certainly increase both bacterial metabolic rates (Pomeroy and Wiebe, 2001) and secondary production (Kirchman and Rich, 1997), which is known from studies of Arctic (Adams et al., 2010) and temperate (Simon and Wunsch, 1998; Vrede, 2005) lakes. Therefore, given that DOC degradation rates are temperature-dependent (Cabaniss et al., 2005), DOM mineralization will be enhanced significantly by elevated water temperatures and will lead to production of $\mathrm{LMW}_{<1\,\mathrm{kDa}}$ organic fractions that can bind trace elements, thus decreasing relative proportions of colloidal fractions compared to the normal summer season.

The second possible mechanism for $\mathrm{LMW}_{<1\,\mathrm{kDa}}$ increase is photo-induced degradation of DOM, which is accelerated by rising temperatures especially in acidic lake water (Gennings et al., 2001; Molot et al., 2005). Photo-oxidation of DOM, strongly pronounced in Arctic surface waters, is capable of producing LMW organic ligands in large lakes (Molot and Dillon, 1997; de Haan et al., 1993) and breaking down HMW chromophoric fractions of DOM (Cory et al., 2007). This process can be especially important in thermokarst surface waters due to oxygen saturation in water columns, low pH, high DOC concentrations and dark waters, being further promoted by strong insolation due to Arctic summers, absence of forests and shallow waters (< 0.5–1.0 m).

Finally, the increase of temperature, solar radiation (anticyclone conditions) and nutrient concentrations during the hot summer of 2012 could also lead to the increase of phytoplankton biomass and primary productivity. Cyanobacterial blooms linked to climate warming in temperate and boreal systems are fairly well known (Paerl and Paul, 2012; Kosten et al., 2012). Phytoplankton exometabolites of low molecular weight, capable of strongly binding trace metals, are also capable of decreasing the proportion of colloidal (1 kDa–0.45 µm) forms at the expense of dissolved (< 1 kDa) fractions, as was recently demonstrated during the phytoplankton bloom in a boreal humic lake (Pokrovsky and Shirokova, 2013).

In addition to autochthonous (intra-water column) processes responsible for the increase of $\mathrm{LMW}_{<1\,\mathrm{kDa}}$ concentrations, such as bio-and photodegradation and phytoplankton exometabolites activity, allochthonous process are also capable of enriching lake water in $\mathrm{LMW}_{<1\,\mathrm{kDa}}$ fractions. Indeed, the LMW DOC is a very labile fraction of DOC in soil moisture (van Hees et al., 2005), and this source of LMW DOC could be particularly important in small thaw depressions. Moreover, LMW carbon compounds of terrestrial origin are important for bacterial growth in boreal lakes (e.g., Berggren et al., 2010). A strong correlation between [DOC] and $A_{280\,\mathrm{nm}}$ corresponds to a high level of humification or aromaticity (Summers et al., 1987; Weishaar et al., 2003; Helms et al., 2008) and suggests allochthonous origin (i.e., peat soil leaching) of dissolved OM from the beginning of permafrost thaw until the mature ecosystem stage. However, given the similarity of the slopes of $\mathrm{UV}_{280\,\mathrm{nm}}$–[DOC] dependencies in 2010 and 2012 (Sect. 3.2), we suggest that the allochthonous input of CDOM to lake water was not significantly affected by the temperature increase and drought conditions.

4.3 Consequences for surface water warming in Western Siberia

Similar to other natural weather perturbation phenomena that allow researchers to investigate possible effects of environmental changes on ecosystem function (cf., Schreader et al., 1998; IPCC, 2012; Hansen et al., 2012; Yuan et al., 2013), the anomalously hot summer of 2012 offered a unique opportunity to quantify the consequences of that most extreme climate warming scenario. It followed from results of our observations in Western Siberia during summer 2012 that the short-term heating of thaw lakes and ponds may bring about almost 50 % increase in CO_2 flux and a five-fold increase in methane fluxes from the lake surface to the atmosphere.

Western Siberia, which contains 26 % of the total peat reserves on this planet (Smith et al., 2004; Kirpotin et al., 2011) and represents as much as 10 % of the total annual Eurasian terrestrial C sink (Beilman et al., 2009), is likely to be most vulnerable territory with respect to climate change. In this century, peatlands may respond quickly to on-going warming by losing labile organic carbon from soil during dry periods (Ise et al., 2008; Yi et al., 2007). According to simulations, a temperature increase of 4 °C causes a 40 % loss of organic carbon from the shallow peat and an 86 % loss from deep peat (Ise et al., 2008). Thermokarst lakes in the permafrost context will further accentuate this loss due to lake surface-atmosphere exchanges of CO_2 and CH_4 (Laurion et al., 2010). Under climate warming scenarios in western Siberia, not only peat soil but also lake and wetland surfaces that now occupy between 30 and 80 % of watershed areas (Zakharova et al., 2009) may release GHG to the atmosphere and increase the potential for CO_2 and methane emissions by a factor between 2 and 5. This is a very conservative scenario that does not take into account the increase in the number of small (< 0.01 ha) thermokarst ponds with CO_2 and CH_4 concentrations 5 to 10 times higher than thaw ponds and lakes (Shirokova et al., 2013). Contributions of small lakes to total CO_2 summertime emissions from thermokarst areas are very high (cf., Repo et al., 2007; Abnizova et al., 2012). The difficulty of evaluating true GHG fluxes in permafrost-affected wetlands is that these small bodies of water were not considered in modeling predictions until now (cf., Smith et al., 2005; van Huissteden et al., 2011; Karlsson et al., 2012). Similar to other circumpolar regions, permafrost thaw in Western Siberia should bring about the drainage of large thermokarst lakes and the appearance of small (< 0.01 ha) thaw ponds and permafrost subsidences, especially in the sporadic/discontinuous permafrost zones (Sannel and Kuhry, 2011). Indeed, these authors demonstrated that elevation of the mean annual temperature caused a significant increase in the number of small (60–140 m^2) lakes in peat plateaus in the sporadic permafrost zone.

Results from this and previous studies indicate that if thermokarst bodies of water are connected to the hydrological network, then thermokarst water will become an important source of DOC and related TE in rivers. Therefore, accelerated warming in Western Siberia will certainly bring about a short-term increase of DOC and TE concentrations in rivers. Our observations strongly support increasing DOC releases from western Siberian catchments subject to permafrost thaw (cf., Frey et al., 2007) that is similar to DOC emission in the European zone (Olefeldt and Roulet, 2012). Several processes may control the degree and direction of the response of aquatic ecosystems to prolonged warming of the water column. The evaporative concentration is certainly capable of increasing DOC and metal dissolved concentration which can be at maximum a factor of 2 given the shallow depth of studied thaw ponds and lakes. This is not the case for dissolved CO_2 and CH_4 whose concentration is determined by chemical and microbiological processes occurring in the sediments and in the water column. Given that studied water bodies receive no input from surface streams draining adjacent soils and groundwaters, accelerated soil respiration or plant growth under climate warming should not affect directly thermokarst lake chemical composition. In contrast, for CO_2, the heterotrophic respiration of DOM in the water column and CO_2 production in the sediments should both respond positively to the rising water temperatures. The impact on methane concentration will be even stronger given the decrease of oxygenated water depth, enhanced O_2 uptake by heterotrophic respiration in the water column and intensification of methanogenesis in the sediments.

For DOC, major cations and trace metals the increased rate of C_{org} (in the form of DOM) leaching from the peat outcrop at the border of the lake may bring about an increase of the input flux by a factor of 3 for 10 °C heating, given the typical activation energy of solid material dissolution in water. It follows that for the case of Khanymey lakes studied in this work, despite an almost 10 °C increase in water temperature during more than 2 months of drought, heterotrophic respiration of dissolved organic carbon could not overcome enhanced peat leaching and physical evaporation, which are apparently more important factors that drive higher DOC in ecosystems with higher CO_2 and water levels under short-term climate warming scenarios.

Higher proportion of low molecular weight (< 1 kDa) fractions of TE at higher water temperatures may have an important implication for climate change feedback. At present it is unclear whether the trace elements are limiting in this region unlike P and N that are typically limiting for primary production in other freshwater systems. Several issues however, allow this possibility to be considered. First, aquatic systems investigated in this study cannot be considered similar to other freshwater systems: these are dystrophic, acidic waters, with high DOC and very low total dissolved solid concentration. A km-size permanently existing lakes have specific conductance of 10 to 15 $\mu S\,cm^{-1}$, which is an order of magnitude lower than that in other known pristine freshwater systems. At these conditions, not only N and P but also trace metals such as Fe, Mn, Zn, Co may become limiting. Second, there is virtually no phytoplankton and primary productivity in studied water bodies including large thermokarst lakes (Shirokova et al., 2009, 2013). The limitation of heterotrophic bacterioplankton by trace metals is at present unknown. And third, similar to oligotrophic coastal waters, it is not excluded that metal micronutrients such as Fe become limiting at certain conditions of thermokarst lakes.

The greater bioavailability of limiting metal micronutrients in thaw lake waters may (1) enhance the frequency and magnitude of phytoplankton bloom, and (2) facilitate aerobic mineralization of peat-originated humic and fulvic acids by heterotrophic bacterioplankton. These two processes have opposite effects on CO_2 fluxes from the lake water to the atmosphere: CO_2 uptake by phytoplankton and CO_2 release by heterotrophic bacterioplankton due to DOM respiration. However, it is reasonable to assume much higher biomass production by phytoplankton, especially in blooms, compared to the mineralization capacity of allochthonous OC by heterotrophic aerobic bacterioplankton. More important consequences of TE speciation changes for climate change feedback are linked to metal micronutrient delivery to oceans. In the estuary of the Arctic Ocean, LMW fractions of Fe and other metals are subject to much less coagulation than colloidal (1 kDa–0.22 µm) fractions (i.e., Dai and Martin, 1995; Pokrovsky et al., 2012b). The increase of metal micronutrients delivery in the form of LMW fractions to coastal waters may enhance the primary productivity and amplify the CO_2 uptake by phytoplankton in the coastal zones. Therefore, the overall effect of TE speciation change due to Western Siberia lake water warming is very likely to increase atmospheric CO_2 removal capacities of aquatic systems at high latitudes.

5 Conclusions

A study of permafrost depressions, thaw ponds, and thermokarst lakes conducted in discontinuous permafrost zones during the anomalously hot summer of 2012, when the water temperature increased approximately 10 °C above its normal average, revealed statistically significant increase of the concentration of organic and inorganic components and dissolved gases in thermokarst water bodies relative to previously studied normal summer 2010. The factors for these concentration increases are approximately 2–1.5 for most trace metals, DOC and CO_2, and as high as 5 for dissolved CH_4 in the full range of investigated surface areas, from soil depressions of 1–10 m^2 to mature lakes. When the temperature was elevated, the intensity of methanogenesis increased more significantly than the heterotrophic mineralization of DOM and was further accentuated by the decrease of methanotrophy in shrunk ponds and lakes. During both seasons, there is a systematic increase of dissolved CO_2, CH_4 and DOC with decreasing surface area of bodies of water, with approximate factors of 5, 100 and 3, respectively between small ($< 100\,m^2$) thaw ponds and large (> 1 ha) thermokarst lakes, respectively.

Enhanced peat leaching from lake borders to water columns and the prevalence of evaporation over precipitation may be responsible for a two-fold increase of major and minor dissolved components during periods when water temperatures are elevated. All major divalent cations and insoluble trace elements exhibited significant affinity to colloids (1 kDa–0.45 µm). However, despite the increase of DOC concentration during the anomalously hot summer of 2012, the proportion of colloidal forms of some major (Ca, Mg, K) and most trace elements decreased at the expense of the $LMW_{<1\,kDa}$ fraction. It is possible that enhanced heterotrophic respiration of organo-mineral colloids, photo-destruction of allochthonous dissolved organic matter and production of phytoplankton exometabolites contributed to the enrichment of $LMW_{<1\,kDa}$ fractions in thaw lakes when water temperatures increased compared to normal summer periods. Given that elevated air and water temperatures during summertime will thaw the permafrost in Western Siberia, this will bring about the drainage of large thermokarst lakes and the appearance of small (< 0.01 ha) thaw ponds and permafrost subsidences. Regardless of the water temperatures, this small water bodies exhibit CO_2 and CH_4 concentrations and fluxes from lake surfaces to the atmosphere a factor of 5 to 10 higher than those of the large thermokarst lakes, which is not included in current climate and hydrological models.

Supplementary material related to this article is available online at: http://www.biogeosciences.net/10/5349/2013/bg-10-5349-2013-supplement.pdf.

Acknowledgements. We thank two anonymous reviewers for their constructive comments. Yves Auda and Aridane Gonzalez are thanked for the help with statistics. This work was supported by the Mega-grant 220 of Russian Ministry of Education and Research and Tomsk State University "BIO-GEO-CLIM" No 14.B25.31.0001, ANR "Arctic Metals", GDRI "Carbon in Wetlands of Siberia", Programs of Presidium RAS (No 12-P-5-1021) and UroRAS (No 12-Y-5-1034).

Edited by: P. Stoy

The publication of this article
is financed by CNRS-INSU.

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