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Effect of permafrost thawing on organic carbon and trace element colloidal speciation in the thermokarst lakes of western Siberia

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Abstract. To examine the mechanisms of carbon mobilization and biodegradation during permafrost thawing and to establish a link between organic carbon (OC) and other chemical and microbiological parameters in forming thermokarst (thaw) lakes, we studied the biogeochemistry of OC and trace elements (TEs) in a chronosequence of small lakes that are being formed due to permafrost thawing in the northern part of western Siberia. Twenty lakes and small ponds of various sizes and ages were sampled for dissolved and colloidal organic carbon, metals and culturable heterotrophic bacterial cell number. We observed a sequence of ecosystems from peat thawing and palsa degradation due to permafrost subsidence in small ponds to large, km-size lakes that are subject to drainage to, finally, the khasyrey (drained lake) formation. There is a systematic evolution of both total dissolved and colloidal concentration of OC and TEs in the lake water along with the chronosequence of lake development that may be directly linked to the microbial mineralization of dissolved organic matter and the liberation of the inorganic components (Fe, Al, and TEs) from the organo-mineral colloids.

In this chronosequence of lake development, we observed an apparent decrease in the relative proportion of low molecular weight <1 kDa (1 kDa $\sim$ 1 nm) OC concentration along with a decrease in the concentration of total dissolved (<0.45 µm) OC. This decrease was accompanied by an increase in the small size organic ligands (probably autochthonous exometabolites produced by the phytoplankton) and a simultaneous decrease in the proportion of large-size organic (humic) complexes of allochthonous (soil) origin. This evolution may be due to the activity of heterotrophic bacterioplankton that use allochthonous organic matter and dissolved nutrients originating from peat lixiviation. Most insoluble TEs demonstrate a systematic decrease in concentration during filtration (5 µm, 0.45 µm) exhibiting a similar pattern among different samples. At the same time, there is an increase in the relative proportion of large size particles over the <1 kDa fraction for most insoluble elements along the chronosequence of lake evolution. TEs are likely to be bound to colloidal OC and coprecipitate with the mineral (Fe, Al) part of the colloids. Upon progressive consumption of dissolved OC by the heterotrophic bacteria, there is liberation of Fe, Al, and insoluble TEs in the water column that may be subjected to coagulation in the form of particles or large-size mineral colloids.

1 Introduction

Thawing permafrost and the resulting microbial decomposition of previously frozen organic carbon are among the most significant processes that provide positive feedback to a warming climate (Schuur et al., 2008). Ongoing processes of permafrost thawing in western Siberia are likely to increase the surface of water bodies via the formation of the alleged thermokarst lakes, mobilizing the organic carbon (OC) from the soil pool to the rivers and, eventually into the ocean, thus modifying the fluxes of methane (CH_4) and CO_2 in the atmosphere (Smith et al., 2005; Walter et al., 2006, 2007). The overall potential of carbon loss from yedoma (permafrost) soils under a scenario of continued warming is estimated at 1 Gt C yr^{-1} or $\sim$40 Gt C in the next four decades (Dutta et al., 2006), while 100 Gt C could be released from thawing

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permafrost by 2100 (Gruber et al., 2004). A significant part of this carbon flux will be mediated by active hydrological systems because microbial decomposition of organic matter (OM) is strongly limited by water abundance. In addition, thermokarst (thaw) lakes that are formed due to ground surface subsidence caused by the thawing of ice-rich permafrost may cause a significant and abrupt acceleration of the carbon mobilization process, which may be more important than the one occurring in the soils. This acceleration is due to the large surface and volume of water available for microbial processing of allochthonous OM and larger periods of liquid (unfrozen) water persistence in the lakes as compared to that in the soils. Moreover, it has been known for a long time that the boreal lakes and rivers yield a net annual CO_2 evasion into the atmosphere (referred to as the net heterotrophy) and that between 30% and 80% of the total OC that enters the freshwater ecosystems is lost in lakes via the mineralization and subsequent CO_2 emission into the atmosphere (Cole et al., 1994, 2007; Hope et al., 1996; Kelly et al., 2001; Sobek et al., 2003; Teodoru et al., 2009; Tranvik et al., 2009). Up until now, however, all measurements of this flux used direct (chambers) or indirect (isotopes, $p\mathrm{CO_2}$ values) techniques to assess the concentrations of CO_2 in the boundary air or the liquid phase (e.g., Kling et al., 1991), whereas the chemical and microbiological mechanisms of this process in the water column remained poorly understood. By drawing an analogy with the non-permafrost affected environments (Tranvik, 1988; Kritzberg et al., 2004), the net heterotrophic status of thermokarst lakes may be attributed to the bacterial utilization of allochthonous OC originating from peat erosion.

Small thermokarst lakes located between the Ob and Yenissey Rivers in the northern part of the western Siberian Plain present a unique opportunity to test this hypothesis by studying lake formation and drainage within the chronosequence of ecosystem development (e.g., Kirpotin et al., 2007, 2008a, b, 2009; Shirokova et al., 2009). There are only a few detailed studies of thaw lakes located in the subarctic zone. Zimov et al. (1997) investigated methane concentration and fluxes in permafrost lakes located on the Kolyma lowland (yedoma complex), but the information on OC, bacterioplankton, and dissolved major and trace elements (TEs) was not collected. The thermokarst depressions (alases) of central Yakutia have been extensively studied over the past decade (Desyatkin, 2008; Desyatkin et al., 2009); however, specific lithological and glacial contexts of this region do not allow a direct comparison with the western Siberian Palsa. The thaw lakes of northern Canada and Alaska have been investigated since the early 1970s (Prentki et al., 1980), but only recently, systematic characteristics of lakes hydrochemistry and microbiology have become available (Pienitz et al., 2008; Breton et al., 2009). A thorough study by Laurion et al. (2010) assessed the main hydrochemical and hydrobiological characteristics of ~50 lakes and ponds located in the forest-tundra and tundra zones of Canada. Most shallow (2–5 m) lakes were strongly stratified during summer with the average dissolved organic carbon (DOC) concentration of 5 to 12 $\mathrm{mg\,L^{-1}}$ and pH values ranging from 6.2 to 9.6. Additionally, most lakes exhibited net heterotrophy (supersaturation with respect to atmospheric CO_2). Together with reliable data on the hydrochemistry of lakes located in south Canada and northern Europe, the results of that study potentially allow for the extrapolation of the existing information onto the whole boreal zone. However, the vast area of western Siberia containing the largest peat resources in the world, dominated by discontinuous permafrost and thus being potentially the most vulnerable part of the boreal permafrost-bearing zone, remains poorly understood. In contrast to several studies on the western Siberian rivers (Frey and Smith, 2005; Frey et al., 2007; Frey and McClelland, 2009; Gordeev et al., 2004), lakes and Arctic ponds of eastern and central Siberia (Semiletov et al., 1996; Zimov et al., 1997; Blodau et al., 2008), the lakes of western Siberia remained virtually unexplored, both from the viewpoint of OC and bacterioplankton concentration as well as the trace element (TE) speciation and colloidal status. In consideration of the very high proportion of newly formed lakes in western Siberia (up to 48% of the surface area) (Zimov et al., 1997; Hinkel et al., 2003; Riordan et al., 2006) and as high as 60–80% in the Pur Taz and Nadum river basins (Zakharova et al., 2009), there is little doubt that the western Siberian thermokarst lakes are likely to act as an important source of CO_2 in the atmosphere.

Based on this rationale, our objective was to test the hypothesis that thermokarst lakes are efficient mediators of carbon flux from the soil to the atmosphere via bacterial decomposition of dissolved OM. In consideration of the extremely high concentration of DOC reported in the lakes of western Siberia that developed on the peat deposits, the largest part of the total dissolved carbon along with trace and other major elements is likely to be colloidal. To improve our understanding of carbon and related element biogeochemistry in shallow thermokarst lakes, we aimed to address the following specific issues: (1) assess the variations in TE and OC concentrations along with the chronosequence of lake development; and (2) characterize the colloidal status of TEs and distinguish between the relative proportion of organic and organo-mineral colloids.

2 Methods

2.1 Study site description

The study site is located in the northern part of western Siberia (65.5–66° N) between the rivers Nadym and Pur, within the tundra and forest-tundra landscapes developed on continuous permafrost ≤100 m depth over the Neocene sand and clay deposits covered by a 1–2 m thick peat layer (Fig. 1). Although the area was subjected to multiple glaciations during the Pleistocene age (Arkhipov et al., 1986), all studied lakes were of permafrost melting origin (soil subsidence) that

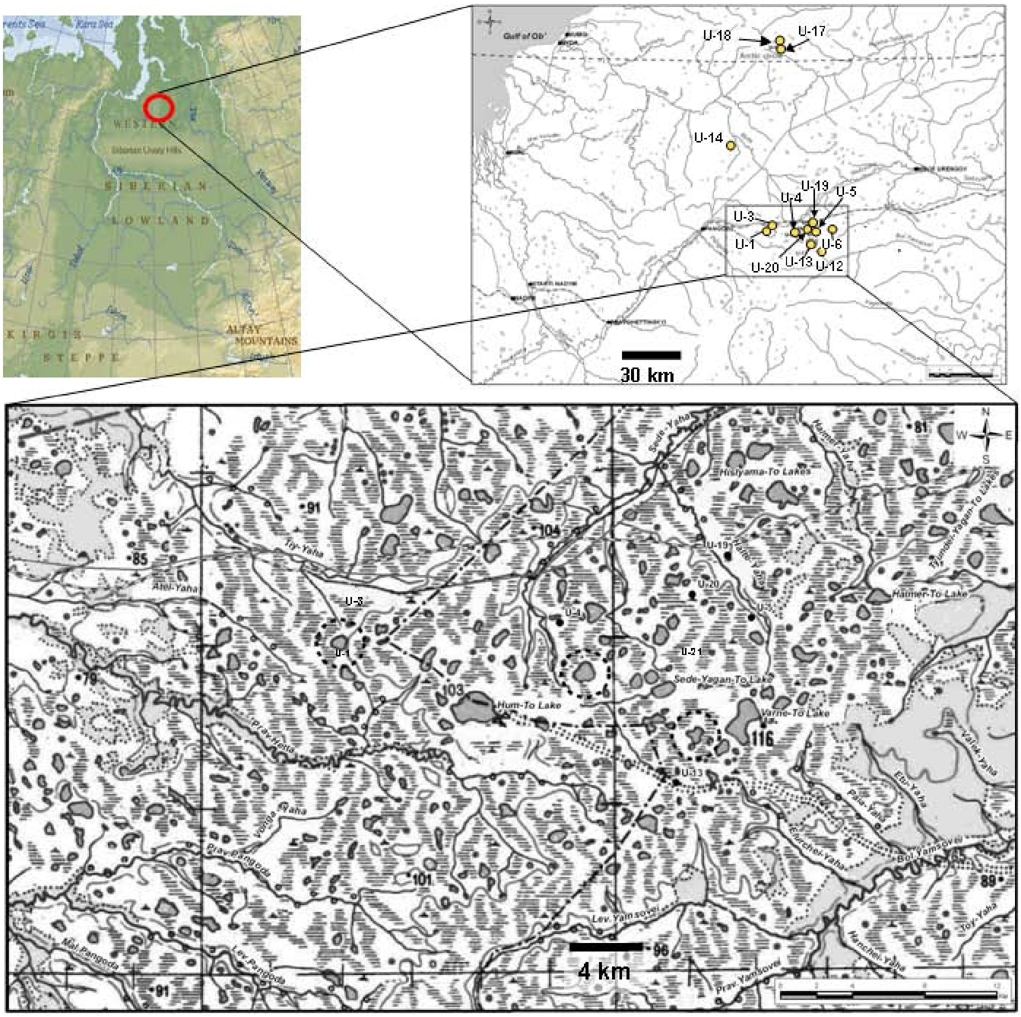

Fig. 1. Schematic map of the studied area.

occurred via cyclical events of peat palsa development as illustrated in photos 1 to 5 of the Supplement (ESM-1). This chronosequence of ecosystem evolution from peat thawing and palsa degradation due to permafrost subsidence in small ponds to large, km-size lakes subject to drainage to, finally, the khasyrey (drained lake) formation revealed in recent studies based on ground and remote sensing observations (Kirpotin et al., 2007, 2008a, b, 2009; Shirokova et al., 2009) is illustrated in Fig. 2 and briefly discussed below. 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. 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. At this stage of the system development, the water is acidic (pH value ranging from 3 to 4) and rich in DOC (20 to 80 mg L^{-1}). Eventually, the lake border is stabilized, and water becomes less acidic and less organic. At this mature stage of development, the lake has a pH value in the range of 5 to 6 and a DOC concentration of approximately 10–15 mg L^{-1}. 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. During this period, the lake becomes productive and there is a presence of aquatic plants, phytoplankton and zooplankton. In this study, we have only qualitative data on the presence of phytoplankton and zooplankton in mature lakes and khasyreys. The old khasyrey initiates a new stage of frozen mound degradation enabling the formation of the new pond. The lakes and ponds are typically glaciated from October to May. Their shallow depths (0.5 to 1.5 m), location within the tundra and strong winds favor thick ice coverage in winter and intensive wave mixing in the summer.

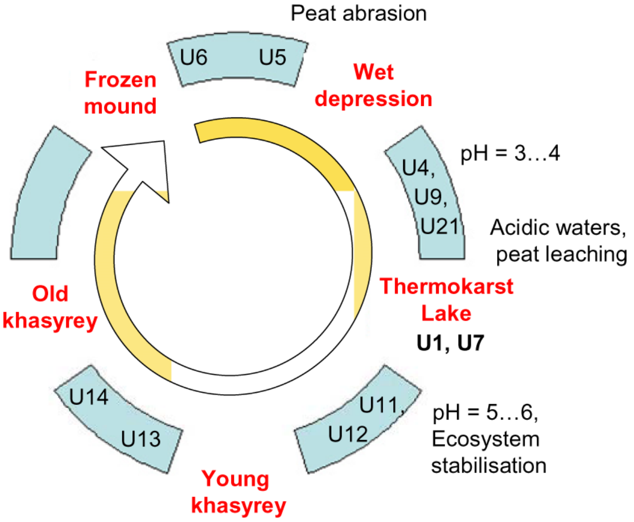

Fig. 2. Scheme of cyclic succession of thermokarst lakes and khasyrey development from flat and mound bogs. The numbers from U1 to U21 correspond to some of the water samples collected in this study at various stages of lake development (Table 1 and Fig. 1).

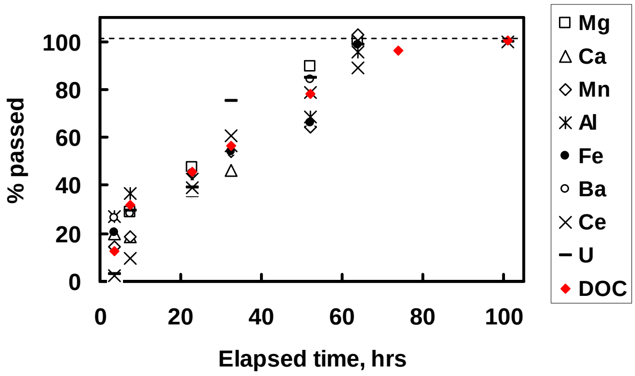

Fig. 3. Percentage of element passed through 1 kDa dialysis membrane as a function of time. Element concentration in the <1 kDa after 100 h exposure is taken as 100%.

2.2 Sampling and analyses

The list of the sampled objects together with the main hydrochemical characteristics is presented in Table 1. The sampling, filtration, and dialysis as well as the chemical analyses techniques are very similar to those used in our previous studies (Pokrovsky and Schott, 2002; Pokrovsky et al., 2006, 2010; Vasyukova et al., 2010). Ultraclean sampling procedure was used throughout all manipulations in the field (Shirokova et al., 2010). Sampling of ∼20 ponds, lakes and streams was performed in August 2008, and for several large lakes, sampling was performed in March 2010. The water samples were taken from a PVC boat from the central part of the lake and immediately filtered through sterile, single-use Minisart® filter units (Sartorius, acetate cellulose filter) with pore sizes of 5 or 0.45 µm. The first 100 ml of the filtrate was systematically discarded. Because the lakes were completely frozen to the bottom in March, filtration through 0.45 µm pore sizes only was performed for these samples after melting the entire ice block sampled approximately 0.5 m above the bottom. Dissolved oxygen and pH were measured on-site with an uncertainty of 5% and 0.02 units, respectively.

In August 2008, in-situ dialysis experiments were performed using 20–50 ml precleaned dialysis bags placed directly in the lake. The duration of this dialysis procedure was between 72 and 96 h. The exposure time was selected based on the kinetic experiments of dialysis equilibrium attainment for DOC, Si and trace metals as illustrated in Fig. 3. For the dialysis experiments, EDTA-cleaned trace-metal pure SpectraPor 7® dialysis membranes made of regenerated cellulose having pore sizes of 10, 3.5 and 1 kDa were thoroughly washed in 0.1 M double-distilled HNO_3 and ultrapure water, then filled with ultrapure MilliQ deionized water and finally placed in the lake water. The efficiency of the dialysis procedure was evaluated by comparing the concentration of the major anion or neutral species (e.g., Cl^-, $H_4SiO_4^0$) not associated with the colloids between the dialysis bag and the external solution. These concentrations were always identical within ±20%, suggesting an equilibrium distribution of dissolved components. To assess the mass balance during the dialysis procedure, concentrations of major and trace elements and OC were measured in the external solution and internal compartments, and compared with <0.45 µm filtrates. In all the cases, better than 95% recovery for the major elements, namely OC, Al, and Fe, and 90% recovery for the selected TEs (Ti, Sr, Y, Ba and Zr) was achieved, indicating that the adsorption of colloids and associated TEs onto and inside the thin Spectra Por 7 membrane was negligible.

Concentrations of DOC, Cl, SO_4, Alk, cations and TEs were measured using the methods routinely used in our laboratory for analysis of boreal organic-rich water samples (Vasyukova et al., 2010; Pokrovsky et al., 2010). Filtered and dialyzed samples were stored at 4–5 °C in the dark before the analysis. The storage temperature was reduced to decrease the coagulation and bacterial production in the experimental samples (Chen and Buffle, 1996; Wilkinson et al., 1997).

For culturable heterotrophic bacteria enumeration, samples were collected in sterile 250-mL flasks and stored at 6–8 °C in the dark for less than 3 h before culturing. The inoculation for culturing was performed in a prepared laboratory space sterilized by a UV lamp near an open flame. Blanks were always run for the sterile control. Two duplicates of different volumes of lake water (normally 0.5, 1 and 5 mL) were inoculated on Bacto agar nutrient media for the enumeration of eutrophic bacteria. The number of colony-forming units (CFU) was evaluated by the optical counting of colonies on the agar plate after 5 days of incubation at

Table 1. Physical and hydrochemical characteristics of studied ponds and lakes.

Sample	Description	Sampling depth, m	Water surface area	N	E	T, °C	O_2, mg L^{-1}	pH	Cond., µS	Alk, M	Cl, ppm	SO_4, ppm	DOC, ppm	A 280 nm	Bacteries CFU/mL
U-1	Lake Shirokoe surface	0.5	0.6 km^2	65°49′56.90″	75°10′11.17″	11.9	9.5	3.70	47.7	<d.l.	0.237	2.973	10.6	0.22	2350
U-2	Lake Shirokoe bottom	1.25	0.6 km^2	65°49′56.90″	75°10′11.17″	11.6	9.2	3.26	53.1	<d.l.	0.489	3.066	10.7	0.25	2410
U-3	Brook from thawing mound	surface	N.D.	65°50′59.5″	75°10′51.6″	12.6	7.9	4.13	9.3	<d.l.	0.081	0.376	14.0	0.42	348
U-4	Actively growing lake	surface	300 m^2	65°50′20″	75°11′13″	12.9	9.9	3.26	20.3	<d.l.	0.135	0.274	29.8	0.71	88
U-5	Small pond	surface	3 m^2	65°50′26″	75°11′25″	13.5	2.3	3.67	27.9	<d.l.	0.260	0.114	75.9	1.66	2760
U-6	Peat abrasion	surface	2 m^2	65°50′35″	75°11′34″	13.6	8.1	4.30	96.9	<d.l.	0.272	22.3	118.6	4.22	6912
U-7	Lake Shirokoe surface	0.5	0.6 km^2	65°49′56.90″	75°10′11.17″	12.5	8.0	3.48	N.D.	<d.l.	0.243	N.D.	10.5	0.23	N.D.
U-8	Lake Shirokoe bottom	1.3	0.6 km^2	65°49′56.90″	75°10′11.17″	12.4	9.5	3.82	N.D.	<d.l.	0.235	3.046	N.D.	N.D.	N.D.
U-9	Growing lake surface	0.5	20 000 m^2	65°49′54.51″	75°11′16.59″	12.1	10.3	4.33	18.8	<d.l.	0.280	0.516	33.9	1.23	2272
U-10	Growing lake bottom	1.5	20 000 m^2	65°49′54.51″	75°11′16.59″	12.1	10.3	4.33	18.7	0.000022	0.306	0.519	31.3	1.22	2010
U-11	Lake Yamsovey 1, stabilized border	surface	0.4 km^2	65°47′25.89″	75°28′00.98″	11.9	11.4	5.01	N.D.	0.000022	0.203	0.439	10.3	N.D.	N.D.
U-11	Lake Yamsovey 1	0.5	0.4 km^2	65°47′25.89″	75°28′00.98″	11.5	10.5	5.10	6.50	0.000014	0.204	0.439	12.0	N.D.	280
U-11	Lake Yamsovey 1	1.25	0.4 km^2	65°47′25.89″	75°28′00.98″	11.3	10.6	5.07	6.45	0.000014	0.210	0.441	10.2	0.29	120
U-12	Lake Yamsovey 2, stable borders	surface	1 km^2	65°44′51.8″	75°30′52.3″	11.4	9.6	5.59	8.50	0.000014	0.390	0.733	11.6	0.31	100
U-13	Lake Khasyrey, surface	0.5	1000 m^2	65°45′31.5″	75°31′03.0″	11.7	9.8	5.72	4.50	0.000015	0.090	0.165	7.6	0.16	20
U-13	Lake Khasyrey, water column	1.25	1000 m^2	65°45′31.5″	75°31′03.0″	11.5	9.5	5.65	N.D.	0.000016	0.091	0.167	8.8	0.14	80
U-13	Lake Khasyrey, bottom	1.5	1000 m^2	65°45′31.5″	75°31′03.0″	11.5	8.8	5.59	N.D.	0.000011	0.180	0.183	9.2	0.10	N.D.
U-14	Lake with stable border, macrophytes	surface	0.2 km^2	66°12′15.9″	74°00′41.0″	12.4	N.D.	5.56	4.0	0.0000093	0.179	0.433	4.9	0.10	N.D.
U-15	Mature lake	surface	0.3 km^2	66°13′05.86″	74°02′56.12″	12.5	9.3	6.24	10.0	0.000044	0.445	0.512	8.4	0.28	N.D.
U-16	Stabilized lake	surface	0.2 km^2	66°18′03.25″	74°04′23.36″	12.2	N.D.	5.58	8.8	0.000041	0.237	0.194	11.6	N.D.	N.D.
U-17	Tundra lake surrounded by bog	surface	0.15 km^2	66°36′35.7″	74°36′35.7″	11.5	7.8	6.76	55.5	0.000660	0.685	0.004	10.9	0.24	N.D.
U-18	Youngkhasyrey, macrophytes	surface	300 m^2	66°38′02″	74°19′51″	12.9	10.5	6.60	9.9	0.000033	0.038	0.060	17.1	N.D.	2
U-19	Small spring, 2 km length	surface	N.D.	65°52′18″	75°07′27″	9.0	10.2	5.10	14.9	0.000087	0.387	1.907	4.9	0.12	40
U-20	River Yamsovey, 10 km length	surface	N.D.	65°51′09″	75°23′11″	12.3	9.7	5.09	12.0	0.000047	0.187	1.357	9.1	0.21	40
U-21	Lake formed after palsa retreat	surface	2000 m^2	65°51′59″	75°16′96″	12.3	9.7	4.02	13.9	0.000016	0.556	0.160	23.4	0.48	35
U-11*	Lake Yamsovey 1, melted ice	0.5 m ice	0.4 km^2	65°47′25.7″	75°28′01″	N.D.	N.D.	4.65	5.50	<d.l.	0.317	0.1465	7.03	0.11	N.D.
U-12*	Lake Yamsovey 2, melted ice	0.5 m ice	1 km^2	65°44′52″	75°30′50″	N.D.	N.D.	5.49	8.10	N.D.	0.4894	0.712	13.06	N.D.	N.D.
U-13*	Lake Khasyrey, melted ice	0.5 m ice	1000 m^2	65°45′31.5″	75°31′03.0″	N.D.	N.D.	5.74	4.40	N.D.	0.0787	0.1197	3.03	0.05	N.D.

N.D. stands for non-determined;
* stands for sampling in March 2010.

25 °C in the dark. Previous studies have shown that culturable bacteria may represent only a small proportion of the species present (the ones that respond well to culture conditions), not necessarily the ones that have an important function in situ, with a possible bias toward rare species (e.g., Pedrós-Alió, 2006). We think that the heterotrophic aerobic bacteria growing on nutrient-rich agar yield the closest culturable approximation to the natural consortia of bacteria present in organic-rich well oxygenated waters of the thermokarst lakes. Culturing bacteria on other types of nutrient media, such as 10% diluted Nutrient agar and minimal nutrient Bacto oligotrophic agar, yielded similar trends of bacterial number evolution along the chronosequence of lake development (Shirokova et al., 2009).

3 Results and discussion

3.1 Evolution of dissolved organic carbon, eutrophic bacteria and major cations in the sequence of lake development

The list of sampled lakes and ponds is provided in Table 1, and their location is shown in Fig. 1. Trace element concentration is given in the Supplement (ESM-2). We did not find

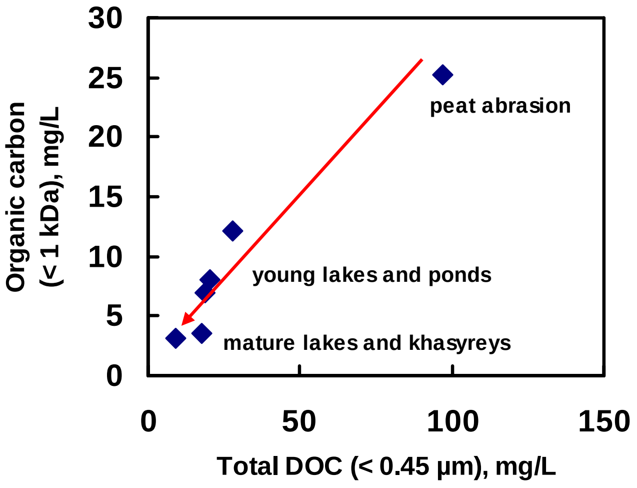

Fig. 4. Concentration of LMW fraction (<1 kDa) of organic carbon as a function of total DOC (<0.45 µm).

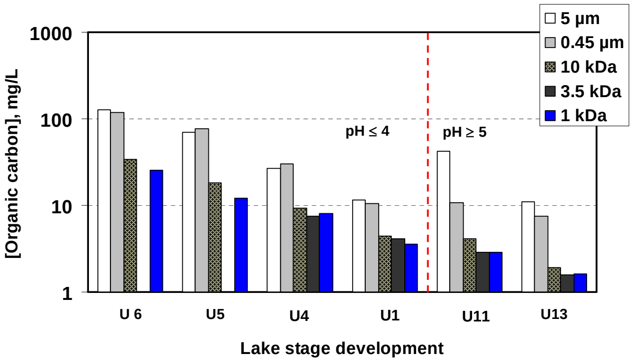

Fig. 5. Concentration of different size fractions of organic carbon (logarithmic scale) in the chronosequence of lake stage development.

any measurable chemical and thermal stratification in any of the studied shallow lakes (0.5–1.5 m depth). All lakes were close to equilibrium with atmospheric oxygen and values of pH, temperature, concentrations of O_2, DOC, and major and trace elements and were not subject to variation between the surface and bottom horizons (Table 1 and ESM-2). The presence of the anoxic bottom layer was not evident within the resolution of our measurements by the submersible oxygen sensor (±10 cm). However, our unpublished data on sediments and their pore waters composition for the three lakes of this study (U-1, U-11 and U-13) suggest the presence of a reduced interface at the first 0.5–1.0 cm of the lake bottom sediments.

The observed chronosequence of the lake ecosystem evolution starts from peat thawing and palsa degradation due to permafrost subsidence in small depressions, continues to shallow ponds and large, km-size lakes and results in the khasyrey (drained lake) formation. Accordingly, there is a systematic decrease of both total (<0.45 µm) and truly dissolved low molecular weight (<1 kDa) OC concentrations in the sequence of thermokarst development (Fig. 4). We observed a strong correlation ($r^2 = 0.95$) between the DOC (<0.45 µm) and UV absorptions at 280 nm, which is considered to be an indicator of humification or aromaticity (Summers et al., 1987; Weishaar et al., 2003; Helms et al., 2008). This correlation strongly suggests a dominantly allochthonous origin (peat soil leaching) of dissolved organic matter at all stages of lake development.

Detailed analysis of OC size fractionation in the course of thermokarst lake development demonstrates a general decrease in the concentration of all fractions of OC (5 µm, 0.45 µm, 10 kDa, 3.5 kDa and 1 kDa) as illustrated in Fig. 5. The decrease of the smallest fractions (3.5 kDa and 1 kDa) is more pronounced than that of the larger fractions of DOC; an increase in the 0.45–5 µm OC fraction at the mature lake stage corresponding to ecosystem stabilization in samples U-12 (data not shown in Fig. 5) and U-13 was observed. This increase may be linked to the coagulation and flocculation of organic colloids during bacterioplankton activity known to process colloidal allochthonous OM (e.g., Tranvik et al., 1988) or the experimental biases of filtration through large pore size filters and sample storage. In addition, the increase in the 0.45–5 µm OC fraction may stem from the degradation of large planktonic cells, which produce cell fragments in this size range. Exopolymeric substances from phytoplankton and bacteria may also contribute to this increase (Chin et al., 1998; Wilkinson et al., 1997). Finally, the abiotic process of self-organization of dissolved organic matter to micelle-like micro particles with a diameter of 0.4–0.8 µm, which are known to occur in the temperate rivers in autumn (e.g., Kerner et al., 2003), may be responsible for the observed OC size distribution change at these latest stages of lake evolution.

The relative proportion of LMW dissolved OC as a function of conventional DOC (<0.45 µm) concentration demonstrates two distinct ranges and increases from 15 to 20% at the stage of peat abrasion/young ponds and lakes to 28 ± 5% for most mature lakes and khasyrey (Fig. 6). We may tentatively attribute this increase to the appearance of small-size autochthonous OC in the form of phytoplankton exometabolites associated with the consumption of allochthonous soil-derived OM by heterotrophic bacterioplankton. In addition to exometabolites production, the higher proportion of LMW carbon in the larger and mature lakes can be a result of the decreasing input of soil and peat-derived organic matter to these lakes, mostly due to a large water-body in relation to the length of the shoreline. Therefore, the average residence time of the allochthonous organic macromolecules in these lakes is longer, exposing them to degradation by the bacterioplankton for a longer time (e.g., Amon and Benner, 1996a, b). As a result, forming macromolecules are smaller in size as compared to those in the smaller, young lakes. Simultaneously, in mature lakes and at the khasyrey stage, the proportion of

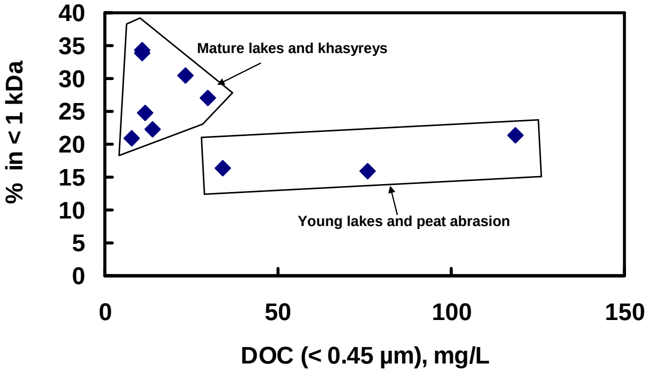

Fig. 6. Proportion of small-size dissolved organic carbon (<1 kDa) as a function of conventional DOC concentration (<0.45 µm). Note that at the mature stage of lake development and khasyreys, proportion of small size organic colloids does not depend on total DOC and for most studied lakes it is equal to 27 ± 5%.

small sized organic macromolecules does not depend on the total DOC and the lake trophic status and can therefore be considered as a representative value for the whole region.

The possible use of small-size organic molecules by the heterotrophic bacterioplankton in growing lakes is illustrated by a plot of LMW (<1 kDa) OC concentration as a function of the number of eutrophic bacteria that exhibits a r^2 value of 0.91 (Fig. 7a). This relationship is also maintained for conventional dissolved (<0.45 µm) organic carbon (Fig. 7b) although the correlation coefficient is smaller ($r^2 = 0.82$). This evolution can be explained by the use of allochthonous OM and dissolved nutrients originating from peat lixiviation by the heterotrophic microbial community of the lake water column. It should be noted that for mature lakes and khasyreys, there is a certain contribution of LMW OM from the phytoplankton that results in producing fresher OM as compared to the refractory soil-derived fraction that is easily respired by the bacterioplankton. In addition to the pelagic respiration of DOC, benthic respiration and dissolved organic matter (DOM) photolysis are known to be important factors in controlling OM degradation and CO_2 release into the atmosphere by the boreal lakes (e.g., Jonsson et al., 2001, 2008) with even the much larger contribution of benthic respiration occurring in shallow ponds (Kortelainen et al., 2006). However, given similar depth of all studied lakes, we do not expect significant variations in the relative intensity of benthic respiration over the course of lake chronosequence development. In contrast, the longer residence time of water in large lakes may increase the photodegradation of OM at the latest stage of lake development. In addition, water column transparency to solar radiation will also increase with a decrease in DOM concentration (and color). It is important to note that the values of bacterial respiration in all of the studied lakes measured using dark bottle incubation are close to 1 µM C hr^{-1} (Shirokova et al., 2009), which is of the same order of magnitude as the rate of DOC photo-oxidation in organic-rich and peat waters (1 to 4 µM C hr^{-1}, De Haan, 1993; Amon and Benner, 1996b). Given that photochemical processes degrade a part of the refractory pool of DOM that is not readily available to bacteria (Amon and Benner, 1996b), the importance of photodegradation in thermokarst lakes deserve further investigation.

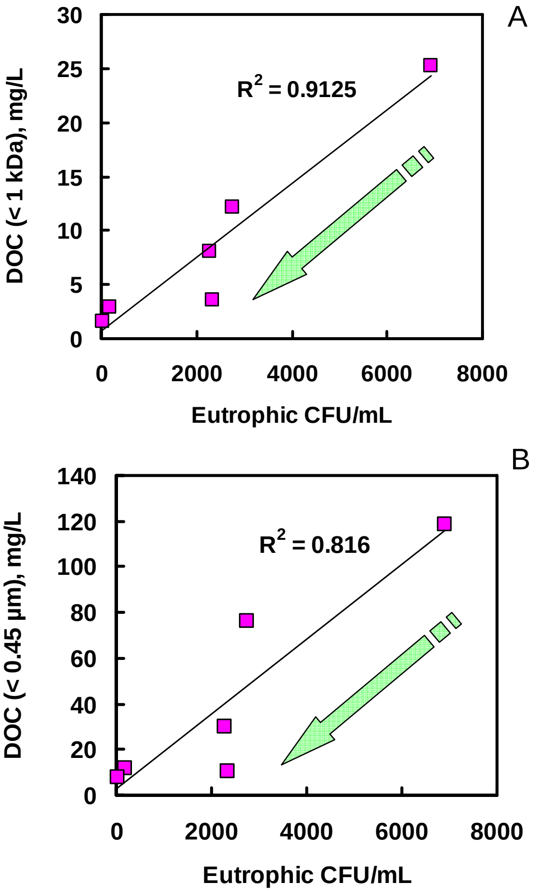

Fig. 7. Concentration of LMW fraction (<1 kDa; **A**) and conventionally dissolved (<0.45 µm; **B**) organic carbon as a function of active culturable heterotrophic bacteria (Colony Forming Units/mL). Arrow indicates the lake stage evolution, from peat abrasion, young lakes and ponds to mature lakes and khasyreys.

A specific and unique feature of the studied systems is that dissolved "trace metals" such as Al and Fe are the major components of western Siberian thermokarst lakes. Plotted in Fig. 8 are the correlations of Fe and Al with DOC in the <0.45 µm fraction ($r^2 = 0.835$ and 0.837, respectively). As shown in this figure, the typical concentrations of these metals range from 0.1 to 1 mg L^{-1}, which is higher than the concentration of other major elements, such as Mg, K, and Si (cf. Table ESM-2). These concentrations are much higher as compared to the following: (1) typical river and lake water metal concentrations all over the world (Gaillardet et al., 2003); (2) Al, Mn and Fe concentrations in the water column

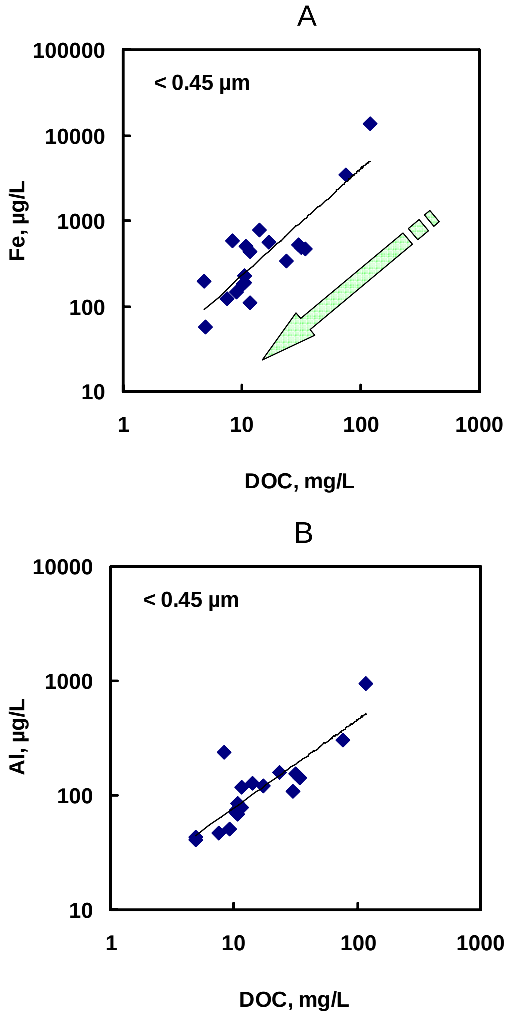

Fig. 8. Concentration of Fe **(A)** and Al **(B)** as a function of Dissolved Organic Carbon (DOC) in <0.45 µm fraction of various lakes and ponds. Arrow indicates the lake stage evolution, from peat abrasion, young lakes and ponds to mature lakes and khasyreys.

of the Imandra Lake of the Kola Peninsula (8, 10–22, and 17 µg L^{-1}, respectively, Ingri et al., 2011); (3) metal concentrations in the lakes of Canada's Northwestern Territories (Pienitz et al., 1997a, b; Rühland and Smol, 1998; Lim et al., 2005; Côté et al., 2010), the Canadian High Arctic (Lim et al., 2001; Michelutti et al., 2002a, b; Antoniades et al., 2003) and arctic Alaska (Kling et al., 1992); and (4) the chemical composition of lakes in central Yakutia (Kumke et al., 2007; Wetterich et al., 2008) and northern Eurasia (Duff et al., 1999; Solovieva et al., 2005). We propose that the observed composition of the lake water stems from the weathering of significantly altered Neogene sands underlying the podzols and acid peat soils that are poor in Na, Ca and Mg, and enriched in Al and Fe. Additional factors responsible for enhanced Fe and Al mobility in the studied waters were the presence of Al and Fe in partially ionic forms at low pH and a high concentration of DOM-stabilizing Fe and Al colloids at an elevated pH. This high mobility of usually "immobile" elements is further illustrated by a comparison of dissolved and colloidal element concentration ratios (Fe/Al, 3 to 10; Ca/Al, 2 to 7; Ti/Al, 0.01 to 0.03, and Zr/Al, 0.001 to 0.003) to those measured in the soil profile of unfrozen peat (Fe/Al, 1.5–3.5; Ca/Al, 0.5 to 1.5; Ti/Al, 0.05 to 0.07, and Zr/Al, 0.002 to 0.003). The similarity of these ratios demonstrates relatively low fractionation of chemical elements between the surface fluids and the source material. Unlike rivers draining the mineral bedrock, the water in the lakes and ponds located within the frozen peat terrain is unlikely to bear a signature of mineral horizons, being completely dominated by the dissolution of peat organic material.

Similar to OC, there is a systematic decrease of Fe and Al concentration from the beginning of lake formation toward mature ecosystems. According to their affinity to Fe, Al or DOC, several groups of major and trace elements can be distinguished. There are elements whose concentrations are indifferent to the stage of lake development. Typical elements of this group are anions, such as Cl^{-}, SO_4^{2-}, Mo, Sb, and As, and elements present in the form of neutral molecules, such as Si, Ge, alkali (Li, Na, K, Cs) and alkaline earth metals (Mg, Ca), that do not exhibit any correlation with Fe or DOC. Significant correlation with DOC is observed only for Cu, Pb, and Cd, whereas most insoluble trace metals are better correlated with Fe or Al than with the DOC: V, Cr, Mn, Co, Ni, Sr, Ba, Ga, Y, REEs, Zr, Hg, Th, and U. Examples of these correlations are illustrated in Fig. ESM-3 of the Supplement. Most lakes exhibit extremely high concentrations of insoluble and immobile elements, such as Ti and Zr (1–10 and 0.1–1 µg L^{-1}, respectively). These values are at least two orders of magnitude higher than the average concentration of these elements in continental waters and Siberian rivers (Gaillardet et al., 2003; Pokrovsky et al., 2006). Such high concentrations of insoluble TEs stem from the following: (1) low pH, especially at the beginning of lake formation, which stabilizes trivalent ions in the form of free ions in accordance with the well-known correlation between REE concentration and solution acidity (Johannesson and Zhou, 1999; Johannesson et al., 2004); and (2) high DOC and Fe concentration rendering these elements to the form of organo-mineral colloids as shown by the size-separation procedure and discussed in the following sections. A good correlation maintained over two orders of magnitude between Co and Mn concentration in all the studied lakes and ponds had a r^2 value of 0.861 (Fig. 9). This value may reflect a functional dependence of the adsorbed and coprecipitated Co scavenging with Mn oxy(hydr)oxides in the water column as it is known for stratified temperate lakes (Hamilton-Taylor et al., 2005). In thermokarst lakes, this functional relationship may be linked to the mineralization of organic material by heterotrophic bacterioplankton at the young stage of lake development and/or diffusion of Mn from the sediments to the water column at the mature stage, followed by the

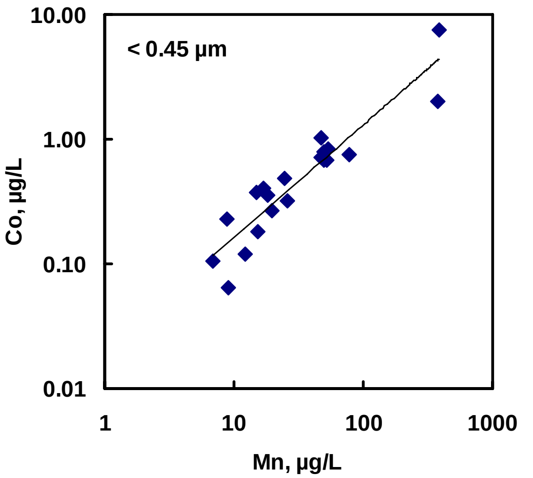

Fig. 9. Concentration of Co as a function of Mn concentration in <0.45 µm fraction of various lakes and ponds.

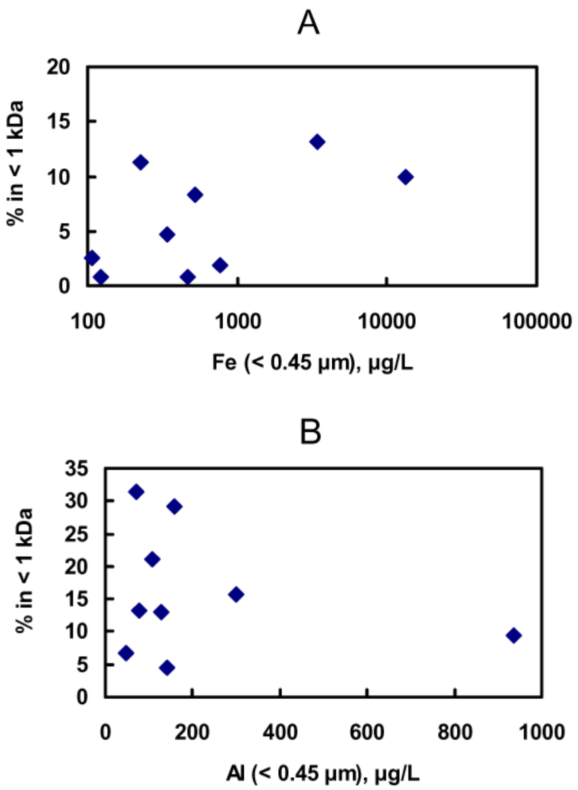

Fig. 10. Relative proportion of LMW of Fe **(A)** and Al **(B)** as a function of total dissolved (<0.45 µm) metals in all lakes and ponds. The average concentration of <1 kDa fraction is equal to 6±4% and 14±6% for Fe and Al, respectively.

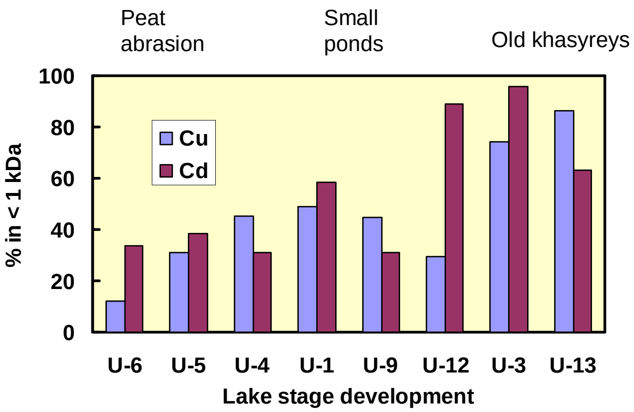

Fig. 11. Stack diagram of Cu and Cd proportion in the form of small-size complexes and ions (<1 kDa) in lakes and ponds along the chronosequence of lake development. There is an increase of small size organic ligands binding divalent metals produced by the phytoplankton at the mature stage of ecosystem development at the expense of bacterioplankton mineralization of large colloidal size allochthonous humic and fulvic complexes.

oxidation at the oxic front of bottom water horizons. In non-permafrost lakes, the biological precipitation of dissolved Mn, and the sedimentation and mineralization of the non-detrital Mn phase in the lake sediments resulting in a steady increase of dissolved Mn concentration is fairly well known (e.g., Pontér et al., 1992).

3.2 Proportion of organic carbon and trace elements in "truly dissolved" LMW (<1 kDa) fraction

The dialysis procedure employed in the present study allowed for a quantitative assessment of the proportion of colloidal (1 kDa–0.45 µm) and "truly dissolved" LMW (<1 kDa) element concentration in order to establish a link between these parameters and major solution parameters, such as [DOC] and pH. We found that the proportion of LMW Fe and Al do not depend on the lake stage development or the concentration of these metals in the <0.45 µm fraction as shown in Fig. 10a, b. The average proportion of the <1 kDa Fe and Al fraction is equal to 6±4 and 14±6%, respectively. Such an independence of the proportion of the <1 kDa LMW fraction on lake stage development (or the <0.45 µm element concentration) is observed for most trace metals except those that are strongly bound to biological ligands, such as Cu and Cd. For these elements, there is a general increase in the small-size fraction (<1 kDa) with lake stage evolution, from peat abrasion and small ponds to mature lakes and old khasyreys as illustrated in the form of a stack diagram in Fig. 11. We tentatively interpret this evolution as being related to an increase in the proportion of small size organic ligands produced by phytoplankton at the expense of large-size organic (humic and fulvic) complexes of allochthonous origin, which are being mineralized by the

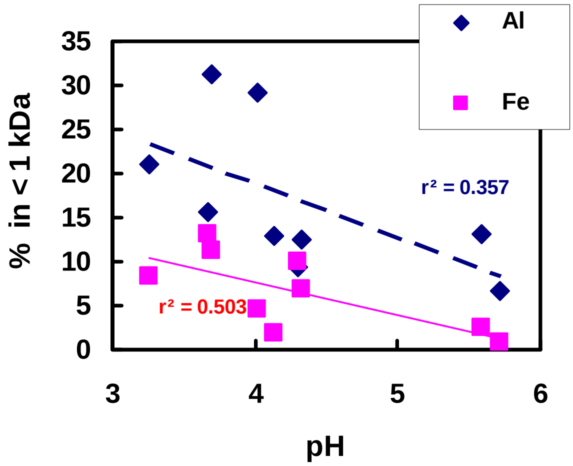

Fig. 12. Relative proportion of small-size fraction of Fe **(A)** and Al **(B)** as a function of solution pH in lakes and ponds.

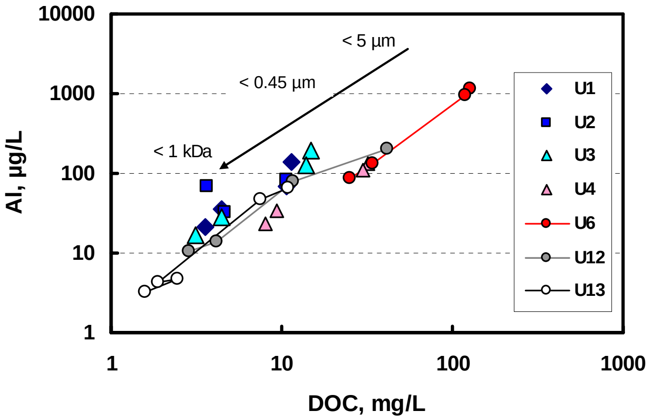

Fig. 13. Correlation between Al and DOC in filtrates and dialysates of various samples shown by different symbols (see Table 1 for description). In each series, the first (highest) point corresponds to filtration through 5 or 0.45 µm and the lowest point represents dialysis through 1 kDa.

heterotrophic bacterioplankton. However, such small-size strong ligands are fairly known for Cu in freshwaters and are most likely related to phytoplankton (e.g., Xue and Sigg, 1993; Wu and Tanoue, 2001). Simultaneously, because fulvic acids are only a few nm in size (e.g., 1.5–2.5 nm, Lead et al., 2000), significant parts of soil-derived organic matter are found in the 1 kDa dialysate. The divalent metals such as Cd and Cu form strong complexes with LMW ligands and, thus, do not follow the pattern of colloidal Fe and Al oxy(hydr)oxides similar to other insoluble TEs. Photoreduction is another possible reason for the appearance of small organic ligands. Undeniably, in this type of water (oxygen saturation, low pH, high Fe and DOC concentration), photoreduction of organic bound Fe (III) should be important for the following reasons: (i) strong insulation due to the Arctic summer and the absence of forests; and (ii) shallow depths of all the studied lakes (0.5–1.5 m).

We found that solution pH exerts certain control on the Fe and Al fractionation between colloidal and conventionally dissolved (<1 kDa) pools. This is illustrated in Fig. 12 where the percentage of Fe and Al in the <1 kDa fraction is plotted as a function of pH. There is a decreasing tendency of truly dissolved metals in proportion to the pH. Although Fe is less affected by pH change as compared to Al (slopes equal to 3.7 and 6.1, respectively), the correlation coefficient is larger for Fe as compared to Al (0.503 and 0.357, respectively). These positive correlations may reflect an increase in the complexation of metals with large-size organic ligands during their progressive deprotonation in the course of pH increase. The opposite tendency is the competition of hydroxyl ions with organic colloids for metal binding at pH >4–5, which should increase the proportion of small-size ions and molecules. Some strongly-bound organic ligands may be present in the <1 kDa fraction in which the OC concentration is between 15 and 35% of that in the <0.45 µm fraction.

3.3 Size fractionation of major and trace elements during filtration and dialysis

Major and trace element concentration in the filtrates and dialysates of all samples are listed in Table ESM-2 of the Supplement. Similar to DOC, concentrations of Fe and Al decrease drastically during the size separation procedure. Fe and Al are present in the form of large-size colloids (0.45 µm–10 kDa), and they are essentially removed from the solution before dialysis through 10 and 1 kDa membranes, as only 10 to 30% of these metals are concentrated in the <1 kDa fraction. Figure 13 presents an example of the filtration and dialysis patterns of Al in various lakes and ponds along with the stages of chronosequence. As shown in this figure, all samples are clustered within the same trend line as defined by the decreasing pore size from <5 µm fraction to <1 kDa fraction.

Among the major elements, dissolved silica concentration is least influenced by the filtration and dialysis procedures. Within the uncertainty of 10%, we could not detect any difference between the Si concentrations in various filtrates from 5 µm to 1 kDa, even at the beginning of lake formation (peat abrasion) in an organic-rich pond (DOC ~120 mg L^{-1}). This result indicates the absence of small-sized phytolithes, clays or silica-rich organic debris in these waters and suggests that most of the aqueous silica is not associated with colloids. Concentrations of alkali (Li, Na, K, Rb) do not change by more than 20–30% between size fractions ranging from 0.45 µm kD to 1 kD. At the same time, it is noteworthy that significant proportions of colloidal Ca, Sr, and Ba are present at all stages of lake evolution, from 30 to 50% (Table ESM-2). Colloidal alkaline earth metals in organic-rich surface boreal waters have been reported by Dahlqvist et al. (2004) and recently confirmed by Pokrovsky et al. (2010).

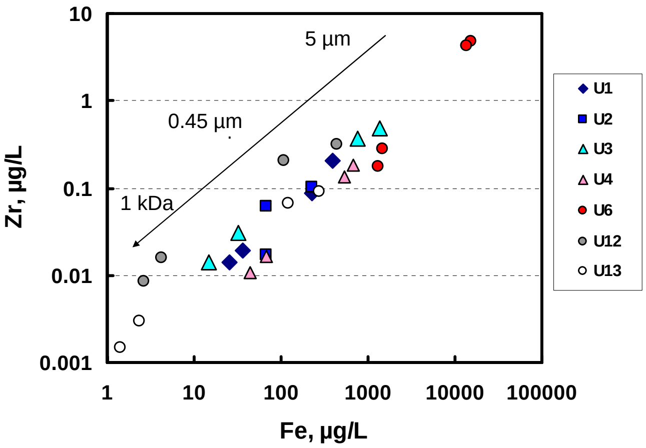

Fig. 14. Correlation between Zr and Fe in filtrates and dialysates of various samples shown by different symbols. In each series, the first (highest) point corresponds to filtration through 5 or 0.45 µm and the lowest point represents dialysis through 1 kDa.

Concentrations of V, As, Se, Nb, Mo, Sn and Sb remain stable during the filtration and dialysis procedures and do not exhibit a clear correlation with dissolved Fe or DOC. Concentrations of divalent transition metals decrease during filtration and dialysis in parallel with that of DOC as illustrated for Mn in the Supplement (ESM-4) (Fig. ESM-4C). In fact, more than 90% of Mn^{2+} is in the form of 1 kDa–0.45 µm organic colloids. This finding may explain the progressive decrease of Mn concentration along the sequence of lake development accompanied by a ten-fold decrease in [DOC] (Fig. 4). Trivalent, tetravalent elements and uranium exhibit a strong affinity for colloidal fraction in sampled waters. Typically, more than 80% of REEs are concentrated in the >1 kD fraction, and more than half of these elements are associated with large-size colloids (10 kDa to 0.45 µm). The relative proportion of heavy REE in the <1 kDa versus the <0.45 µm fraction is a factor of 2 to 3 higher than that of light REE (Table ESM-2). This finding is consistent with previously studied granite and basalt-dominated catchments (Ingri et al., 2000; Pokrovsky and Schott, 2002; Pokrovsky et al., 2006), tropical watersheds (Dupré et al., 1999; Eyrolle et al., 1996) and groundwater (Dia et al., 2000) and most likely linked to the preferential affinity of light REE, such as La, to colloidal organo-mineral surfaces and the tendency of heavy REE, such as Yb, to form stable solution complexes (i.e., Sholkovitz, 1995; Johannesson et al., 2004).

Insoluble tetravalent elements (Ti, Zr, Hf and Th) systematically decrease their concentration upon dialysis and filtration, exhibiting a good positive correlation between [TE^{4+}] and [Fe] ($0.93 \le R^2 \le 0.99$) as illustrated for Zr in Fig. 14. It is important to note that along with the filtration and dialysis patterns, all samples demonstrate the same slope between the concentrations of TEs and Fe or DOC. This slope is approximately 1 and 0.5 for Fe and DOC, respectively.

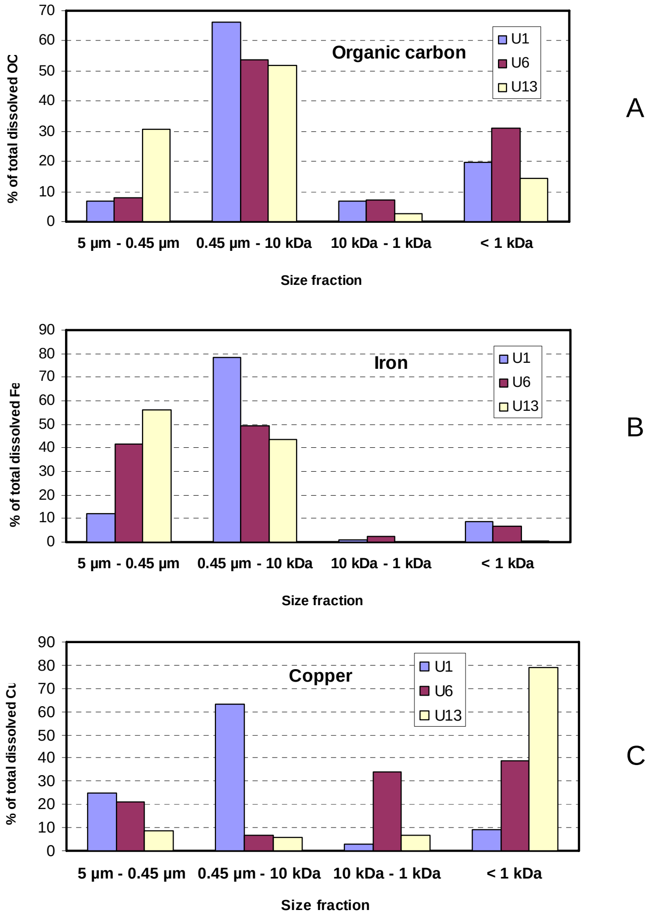

Fig. 15. Size fractionation of OC **(A)** , Fe **(B)** and Cu **(C)** among main colloidal and subcolloidal fractions in typical samples reflecting three main stages of thaw lake development: U-6, U-1 and U-13 corresponding to peat abrasion, large growing lake and final (khasyrey stage) of the lake.

To better illustrate the size fractionation scheme for the different elements, we present a histogram of OC, Fe and Cu distribution between the following four colloidal and sub colloidal fractions: 5–0.45 µm, 0.45 µm–10 kDa, 10 kDa–1 kDa, and <1 kDa for the three principal stages of lake development (Fig. 15a–c). It can be seen that for Fe, large-size particles (between 5 and 0.45 µm) and colloids (0.45–10 kDa) are the main constituents of the dissolved load. Similar size fractionation is observed for Al and other insoluble trivalent and tetravalent elements. In contrast, at the late mature stage of lake development or khasyrey (sample U-13), small size colloidal and truly dissolved fractions (1–10 kDa, <1 kDa) become significant for Cu, which may be strongly affected by the phytoplankton exometabolites or LMW complexes with fulvic acids (Fig. 15c).

Further insights on sub-colloidal versus truly dissolved (LMW) fraction evolution among different types of the studied ecosystems can be assessed from the analysis of the ratio [5–0.45 µm] fraction to [<1 kDa] fraction (Fig. 16).

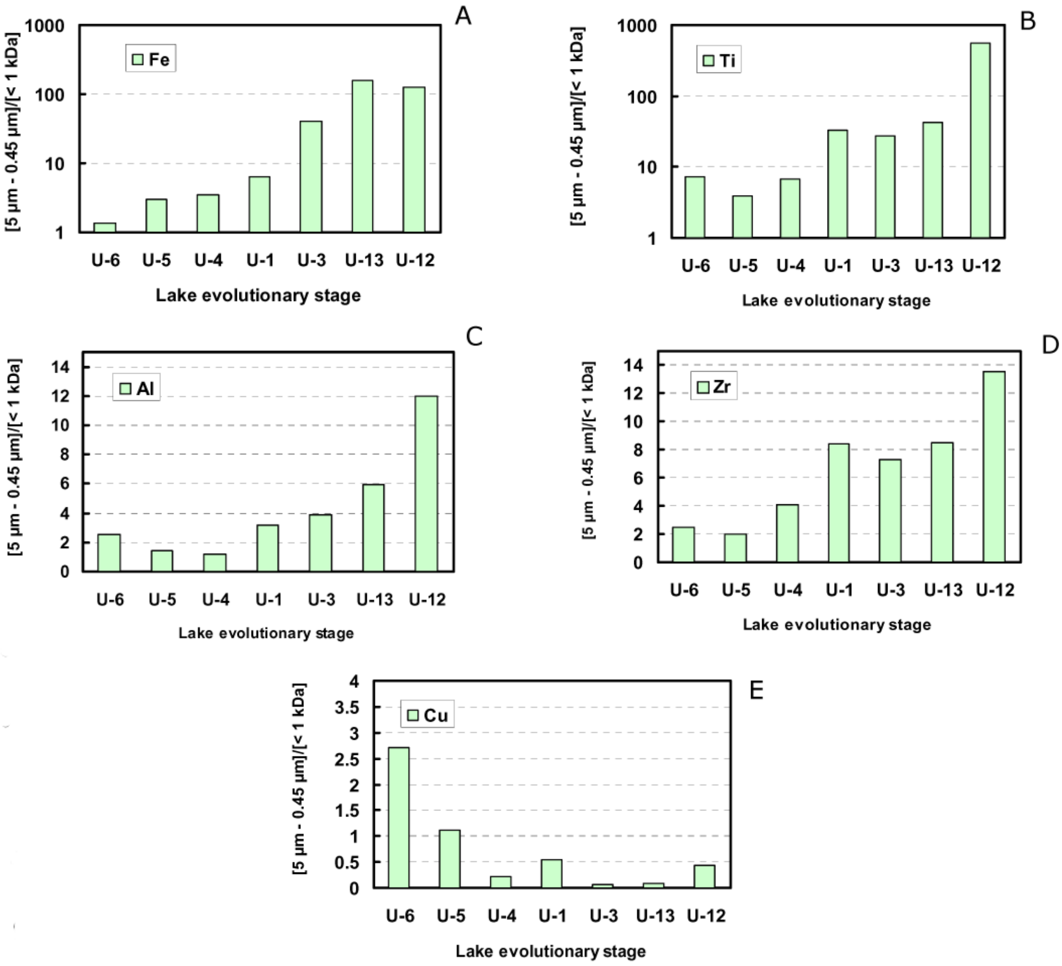

Fig. 16. Colloidal reorganization in the course of lake evolution: the increase of the relative proportion of large-size Fe(Al) sub-colloids/particles with lake chronosequence development. It is possible that the heterotrophic bacteria uptake DOC (<0.45µm), liberate Fe **(A)**, Al **(C)** mineral colloids that are aggregating in subcolloidal/particles thus tranforming size dsitribution of related trace elements: Ti **(B)**, Zr **(D)** and Cu **(E)**.

This ratio reflects the relative contribution of the suspended, non-silicate (particulate) fraction to the truly dissolved (low molecular weight) element fraction. There is a systematic increase in the ratio of particulate to LMW fraction along the chronosequence of lake stage development, from peat abrasion to mature ecosystems. We tentatively interpret this evolution as a process of on-going colloidal coagulation linked to the activity of heterotrophic bacterioplankton. Heterotrophic bacteria consume colloidal (<0.45 µm) and dissolved (<1 kDa) organic carbon (Fig. 7) as shown by the net heterotrophic status of all the lakes (Shirokova et al., 2009), thus liberating Fe, Al, mineral colloids and associated insoluble metals. In the course of progressive coagulation of large-size Fe-Al colloids, we observed a systematic increase in their relative proportion in the water column (Fig. 16a, c). Insoluble elements such as Ti or Zr carried by the Fe-Al colloids and particles follow this tendency (Fig. 16b, d). In contrast, for Cu, which may be strongly linked to small-size microbial and phytoplankton exudates, the relative role of LMW species increases over the course of lake stage development (Fig. 16e). For this element, the ultra filterable (<3 kDa) organic ligand stability constants are reported to be significantly stronger than those of 0.40 µm filterable fraction of freshwater (Hoffmann et al., 2007), thus confirming the high affinity of Cu to small-size organic ligands. This finding is also in agreement with the results of size fractionation in temperate rivers (Stolpe et al., 2010). The increase in the fraction 0.45–5 µm organic matter along the ecosystem stabilization trend may stem from the appearance of biopolymers and other organic matter from phytoplankton, which could further contribute to the coagulation of colloidal Fe and Al (Wilkinson et al., 1997; Perret et al., 2000).

3.4 Colloidal speciation modeling

Considering the high concentrations of Fe and Al in <0.45 µm fraction observed in the studied lakes, it is reasonable to assume that these metals are the major mineral constituents of colloids. Trace metals, notably trivalent and tetravalent elements, and uranium associated with these organo-mineral colloids may be present in the following three forms: (i) complexed with organic ligands of the organic part of the colloids, (ii) adsorbed at the surface of colloidal particles, and (iii) incorporated in the bulk of Fe(Al)-rich colloids stabilized (coated) by OM as reported in previous studies (Ingri et al., 2000; Dia et al., 2000; Andersson et al., 2006). The results of the present study corroborate recent research on colloidal size fractionation in temperate rivers and coastal waters that show the presence of small 0.5–3 nm spherical organic-matter colloids and 5–40 nm large size inorganic Fe oxy(hydr)oxides colloids (e.g., Stolpe and Hassellöv, 2007, 2010; Stolpe et al., 2010).

Complexation of trace metals with organic ligands of natural waters can be assessed using the available computer programs We used the geochemical program Visual MINTEQ (Gustafsson, 1999), version 2.52 for Windows, a recent adaption of the original code written by Allison et al. (1991) (see Unsworth et al., 2006 for vMINTEQ application example) in conjunction with a database and the NICA-Donnan humic ion binding model (Milne et al., 2003; Benedetti et al., 1995). Note that significant proportions of the data used to create this database represent soil humic and fulvic acids, and all aquatic FA and HA originated from temperate rivers and lakes, which may be quite different from the boreal subarctic waters studied in this research. Speciation calculations were performed for divalent metals, such as Ca, Mg, Mn, Co, Ni, Cu, Zn, Sr, Cd, Ba, Pb, Fe, Al, Dy, and $\mathrm{Th^{IV}}$, and $\mathrm{U^{VI}O_2}$ for the following three typical samples of the lake chronosequence: U-6, U-1 and U-13 corresponding to peat abrasion, active growing lake and lake drainage (khasyrey) stage, respectively. Similar to the results of a previous study on the European part of the boreal zone (Vasyukova et al., 2010), calculated proportion of divalent metals bound with organic ligands was comparable (±30%) with the proportion of colloidal (1 kDa–0.45 µm) fraction. However, a significant proportion (>80%) of elements was concentrated in large-size (10 kDa–0.45 µm) colloidal fraction, which was not accounted for by the vMINTEQ model, notably for insoluble trivalent and tetravalent elements. There are several possible reasons for this discrepancy. First, organic ligands that complex TEs are smaller than the minimal cut-off (1 kDa) of dialysis as shown by Pédrot et al. (2008); hence, these ligands are not detectable by the size-separation procedure. Indeed, using the in-situ dialysis procedure, we showed that between 15 and 35% of conventional DOC is concentrated in the fraction <1 kDa (Fig. 6). Second, stability constants of soil-derived humic and fulvic acids present in the model database are not necessarily good proxies for the aquatic dissolved organic matter subject to permafrost action. Finally, the speciation of TEs in colloids may be controlled by the interaction with Fe oxy(hydr)oxides rather than the DOC.

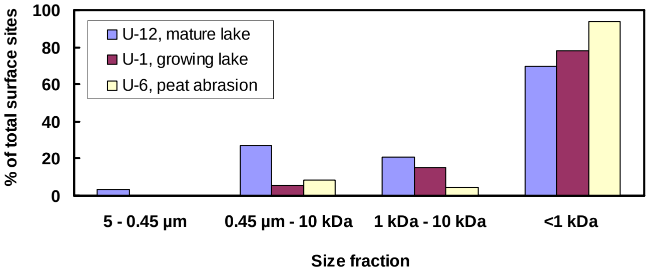

Fig. 17. Percentage of Fe colloids surface sites present in various size fractions for three typical stages of lake development. Total concentration of $>\mathrm{FeOH^o}$ surface sites in samples is the following: U-6, 23 µmol $\mathrm{L^{-1}}$; U-1, 0.5 µmol $\mathrm{L^{-1}}$; U-12, 0.07 µmol $\mathrm{L^{-1}}$.

To evaluate the capacity of TEs to adsorb on the surface of organo-mineral colloids, we calculated the surface areas for the following fractions: 5–0.45 µm, 0.45 µm–10 kDa, 10 kDa–1 kDa and <1 kDa assuming that (i) the average diameters of colloids and particles are equal to 2.5, 0.1, 0.002 and 0.001 µm, respectively, (ii) the colloids have a spherical shape, (iii) the surface site density is 10 µmol $\mathrm{m^{-2}}$, and (iv) the iron hydroxide density is 4 g $\mathrm{cm^{-3}}$ (Fig. 17). Despite a significant amount of Fe present in the colloidal fraction, the main contribution to the total number of surface sites is provided by the smallest fraction (<1 kDa). The fraction 0.45 µm–10 kDa, concentrating more than 90% of the total dissolved Fe and insoluble trace metals contribute to less than 20–30% to the total number of surface sites and, hence, cannot accommodate all the insoluble trivalent and tetravalent metals present in the <0.45 µm filtered fraction on the surface.

Therefore, we should consider, in addition to complexation with DOM and adsorption of TEs on the surface, the incorporation of TEs inside the colloids. For a quantitative assessment of TE distribution between the liquid phase and the bulk of colloids adsorbed on the surface, we calculated the iron-normalized TE partition coefficient (K_d) between conventionally dissolved (<1 kDa) and colloidal (1 kDa–0.45 µm) fractions assuming Fe is the main mineral component of the colloids defined as:

$$K_\mathrm{d} = (\mathrm{TE/Fe})_\mathrm{colloidal} / (\mathrm{TE/Fe})_\mathrm{dissolved}$$

The typical values ranged from 0.2 to 3.5 as illustrated for several insoluble elements in Fig. 18 for the three main stages of lake development, peat abrasion, active growth and mature (khasyrey) stage. These values are within the range reported in the earlier studies of boreal river waters (Pokrovsky et al., 2006; Vasyukova et al., 2010). There is a systematic decrease of K_d in the chronosequence of ecosystem development suggesting a progressive decrease in the role of mineral (Fe-rich) colloids in element binding in <0.45 µm fraction. Consistent

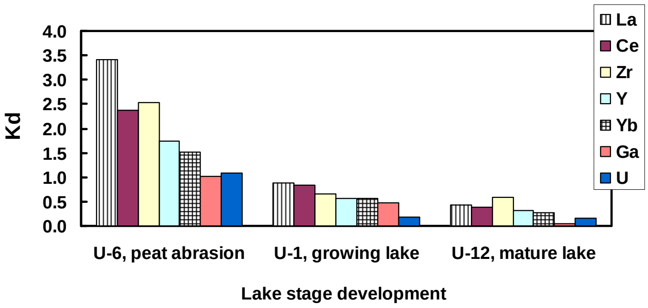

Fig. 18. Coefficients of trace element coprecipitation with colloidal Fe(III)oxy(hydr)oxides for three main stages of lake development, from the initial (peat abrasion) stage to the terminal (mature lake and khasyrey) stage.

with other observations presented above, it may be linked to the heterotrophic bacterial activity, which destabilizes colloids via selective consumption of organic substances, thus removing Fe from the system and decreasing the proportion of TEs linked to the mineral part of the colloids. A schematic cartoon demonstrating different types of colloidal aggregates and their evolution in the course of organic matter consumption is presented in the Supplement (ESM-5).

4 Conclusions and applications of permafrost thawing

In this study, we attempted to link the heterotrophic processes occurring in shallow, non-stratified thaw (thermokarst) lakes to the geochemistry of OC and major and trace elements. We observed a systematic decrease in the culturable heterotrophic bacteria, DOC, Fe, Al and TE concentrations along the chronosequence of ecosystem development, from permafrost subsidence to mature and drained lakes.

High concentration of DOC and normally insoluble elements (Fe, Al, trivalent and tetravalent elements) is a typical feature of all studied thermokarst lakes. Most TEs are essentially present in colloidal large-size fraction (0.45 µm–10 kDa), whereas some divalent metals (Cu, Cd) exhibit high affinity to small-size (<1 kDa) colloidal fraction. We hypothesized that upon progressive consumption of OM by the different types of bacteria and photodegradation in the course of lake development, there is a systematic decrease in both DOC and dissolved metal concentrations.

In addition, bacterioplankton consumption of both truly dissolved (<1 kDa) and colloidal (1 kDa–0.45 µm) OM may destabilize organo-mineral colloids leading to a significant reorganization of colloidal and particulate size fraction distribution. There is an increase in small size organic ligands binding divalent metals produced by the phytoplankton at the mature stage of ecosystem development at the expense of bacterioplankton mineralization of large colloidal size allochthonous humic and fulvic complexes. Alongside the sequence of lake evolution, we observed a steady decrease in the relative proportion of the "truly dissolved" (<1 kDa) fraction over sub-colloidal, particulate fraction (5 µm–0.45 µm), for most insoluble trivalent and tetravalent elements.

The systematic evolution of concentration and size fractionation of organic carbon and related trace elements in the course of thermokarst lake development may have important consequences on the speciation and bioavailability of the TEs in the water column, their flux to the rivers and the oceans during the high flooding period as well as the metals and carbon preservation in the sediments. In particular, we may notice an increase in potential bioavailability of metals in lake water during the evolution: the LMW complexes (<1 kDa) or conventionally dissolved species are potentially bioavailable as the pore sizes of the cell walls transport channels (10–30 Å in bacteria, 35–50 Å in plant cells (Carpita et al., 1979; Trias et al., 1992; Colombini et al., 1980) and are comparable to that of the 1 kDa dialysis membrane (1–3 nm). This may not be true for organic carbon whose bioavailability decreases as its size decreases (Amon and Benner, 1996a, b), with the LMW fraction in Arctic rivers being more refractory than the colloidal (1 kDa–0.45 µm) fraction (Guo and MacDonald, 2006).

The observed trend of DOC concentration decreasing with the increase in lake age and size signifies that at the beginning of massive permafrost thawing, the DOC level in the lakes and draining rivers will increase following the appearance of new palsa subsidence, small ponds and peat abrasion, whereas in the course of system stabilization, the DOC level in the rivers draining the mature thermokarst lakes will decrease.

On a global scale, the increase of DOC concentration in surface waters due to global warming observed in the Nordic countries, British Isles, and northern and eastern United States (by approx. 10% over 10 yr, Evans et al., 2005), is likely to be compensated by the decrease in DOC concentration in the course of existing thermokarst lake growth and drainage. The CO_2 flux from the lake surface to the atmosphere associated with microbial degradation of organic matter is estimated to be $107 \pm 50\,\mathrm{t\,C\,km^{-2}\,yr^{-1}}$ (Shirokova et al., 2009), which is approximately one order of magnitude higher than the organic carbon flux in the rivers of the northern part of western Siberia (4–6 $\mathrm{t\,km^{-2}\,yr^{-1}}$, Maltseva et al., 1987). The CO_2 flux is within the range reported for other boreal and temperate lakes in permafrost-free environments (175 $\mathrm{t\,km^{-2}\,yr^{-1}}$, Casper et al., 2000; 28 $\mathrm{t\,km^{-2}\,yr^{-1}}$, Teodoru et al., 2009) but significantly lower than that observed in the boreal ponds on peatlands (300–1000 $\mathrm{t\,C\,km^{-2}\,yr^{-1}}$, Hamilton et al., 1994) or boreal streams (1140 $\mathrm{t\,km^{-2}\,yr^{-1}}$, Teodoru et al., 2009).

Despite the average increase in thermokarst lake surface coverage by 4–6% during the last 36 yr in the northern part of western Siberia documented within the zone of continuous permafrost (Kirpotin et al., 2008a, b), the decrease in DOC concentration during lake maturation (a factor of 2 to 5) will certainly overweigh the contribution of surface area increase. Therefore, the total stock of DOC and dissolved metals in thermokarst lakes will progressively decrease. This decrease will be accompanied by a relative increase in aquagenic OM (water column derived biopolymers and polysaccharides) versus pedogenic fulvic acids, probably with the same trend as that observed for temperate lakes (from April to July, Wilkinson et al., 1997).

The typical warming scenario in the Yukon River and other Artic river basins suggests an increase in the export flux of terrestrial OC into the ocean because old OC stored in Arctic peatlands and permafrost will be transported in a particulate phase (Guo and MacDonald, 2006) of low bioavailability (Benner et al., 2004). Small rivers may deliver their particulate OM load to newly-formed thermokarst lakes where it will be buried in the sediments instead of entering the hydrological network. In contrast to the rivers, in thermokarst lakes, the proportion of the particulate phase is likely to be small, and most OC present in the colloidal state is subject to significant bacterial and photodegradation, which is likely to intensify under warmer conditions. Therefore, organic carbon present in the thermokarst lake may be much more reactive and susceptible for exchange with the atmosphere as compared to the OC of rivers and soils, further increasing the positive feedback of permafrost systems' response to the warming of the climate.

Overall, the thermokarst lakes of western Siberia represent an important site for the degradation and deposition of released terrestrial permafrost OC, thus corroborating the conclusion achieved in a recent study of the Kolyma paleoriver transect that the positive feedback of global warming from the degradation of permafrost carbon may be geographically displaced (Vonk et al., 2010). Further studies on lake biogeochemistry in the region of discontinuous and permafrost-free environments of western Siberia are needed to predict the net response of the boreal zone to the on-going environmental changes.

Supplementary material related to this article is available online at: http://www.biogeosciences.net/8/565/2011/bg-8-565-2011-supplement.pdf.

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