**Biogeosciences
Discussions**

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

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Abstract

In order to understand the mechanisms of carbon mobilization and biodegradation during permafrost thawing and to establish the link between the organic carbon (OC), and other chemical and microbiological parameters in forming thermokarstic (thaw) lakes,
5 we studied biogeochemistry of OC and trace elements (TE) in a chronosequence of small lakes that are being formed due to permafrost thawing in the northern part of Western Siberia. About 20 lakes and small ponds of various sizes and ages were sampled for dissolved and colloidal organic carbon and metals and culturable heterotrophic bacterial cell number. We observed a sequence of ecosystem stages corresponding to
10 the evolution from peat thawing and palsa degradation due to permafrost subsidence in small ponds to large, km – size lakes subject to drainage and, finally, the khasyrey (drained lake) formation. There is a systematic evolution of both total dissolved and colloidal concentration of OC and TE in the lake water along the chronosequence of lake development that may be directly linked to microbial mineralization of dissolved organic
15 matter and liberation of the mineral part (Fe, Al, TE) from organo-mineral colloids.

In this chronosequence of lake development, we observe a clear decrease of the relative proportion of <1 kDa (1 kDa~1 nm) OC concentration along with concentration of total dissolved (<0.45 μm) OC. This is accompanied by an increase of the small size organic ligands (probably autochtonous exometabolites produced by the phyto-
20 plankton) and a concomitant decrease of the proportion of large-size organic (humic) complexes having allochtonous (soil) origin. This evolution may be due to the activity of heterotrophic bacterioplancton that uses allochtonous organic matter and dissolved nutrients originated from the peat lixiviation. Most insoluble TE demonstrate a systematic decrease of concentration during filtration (5 μm, 0.45 μm) exhibiting a similar pattern
25 among different samples. At the same time, there is an increase of the relative proportion of large size particles over <1 kDa fraction for most insoluble elements along the chronosequence of lake evolution. TE are likely to be bound to colloidal OC but also coprecipitated with the mineral (Fe, Al) part of colloids. Upon progressive consumption

of dissolved OC by heterotrophic bacteria, there is a liberation of Fe, Al, and insoluble TE 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 resulting microbial decomposition of previously frozen organic carbon is one of the most significant terrestrial ecosystem positive feedback to a warming climate (Schuur et al., 2008). Ongoing processes of the permafrost thawing in Western Siberia are likely to increase the surface of water bodies via forming so-called thermokarst lakes, mobilizing the organic carbon (OC) from the soil pool to the rivers and, finally, to the ocean, and thus modifying the fluxes of methane (CH_4) and CO_2 to the atmosphere (Smith et al., 2005; Walter et al., 2006, 2007). The overall potential of carbon loss from yedoma (permafrost) soils under scenario of continuing warming is estimated as $1 \, Gt \, C \, yr^{-1}$ or $\sim 40 \, Gt \, C$ in the next four decades (Dutta et al., 2006), and $100 \, Gt \, C$ could be released from thawing permafrost by 2100 (Gruber et al., 2004). 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 this regard, thermokarst (thaw) lakes, formed due to ground surface subsidence caused by thaw of ice-rich permafrost may cause significant and even abrupt acceleration of carbon mobilization which may be more important than that occurring in soils. This is due to both large surface and volume of water available for microbial processing of allochtonous OM and larger period of liquid (unfrozen) water persistence in lakes compared to that in soils. Indeed, it is known for long that the boreal lakes and rivers yield net annual CO_2 evasion to the atmosphere (so-called net heterotrophy) and between 30% and 80% of the total OC that entered the freshwater ecosystems is lost in lakes via mineralization and subsequent CO_2 emission to 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 to present time, however, all measurements of this flux

dealt used direct (chambers) or indirect (isotopes, pCO$_2$ values) techniques to assess the concentrations of CO$_2$ in the boundary air or in the liquid phase (e.g., Kling et al., 1991) whereas the chemical and microbiological mechanisms of this process remained poorly understood. It can be suggested, that, by analogy with non-permafrost affected environments (Tranvik, 1988; Kritzberg et al., 2004), the net heterotrophic status of thermokarst lakes can be due to bacterial utilization of allochtonous OC originated from the peat erosion.

Small thermokarst lakes located between the Ob and Yenissey Rivers of the northern part of Western Siberia Plain present a unique opportunity to test this hypothesis via studying lake formation and drainage within the chronosequence of ecosystem development (e.g., Kirpotin et al., 2008a, b, 2009; Shirokova et al., 2009). There are only a few detailed studied 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, dissolved major and trace element (TE) was not collected. The thermokarst depressions (alases) of Central Yakutia have been extensively studied over the pas decade (Desyatkin, 2008; Desyatkin et al., 2009); however, specific lithological and glacial context of this region do not allow direct comparison with Western Siberia Palsa. The thaw lakes of Northern Canada and Alaska have been investigated since early 70th (Prentki et al., 1980), but only recently systematic characteristics of lakes hydrochemistry and microbiology became available (Pienitz et al., 2008; Breton et al., 2009). A thorough study of Laurion et al. (2010) allowed assessing the main hydrochemical and hydrobiological characteristics of ~50 lakes and ponds located in forest-tundra and tundra zone of Canada. Most shallow (2–5 m) lakes turned out to be strongly stratified during summer with the average dissolved organic carbon (DOC) concentration of 5 to 12 mg L^{-1} and pH from 6.2 to 9.6. Most lakes exhibited net heterotrophy (supersaturation with respect to atmospheric CO$_2$). Together with reliable data on hydrochemistry of lakes located in South Canada and Northern Europe, this potentially allows extrapolating the existing information to the whole boreal zone. However, the vast area of the Western Siberia containing

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the largest peat resources on the planet, dominated by discontinuous permafrost and thus being potentially the most vulnerable part of boreal permafrost-bearing zone, remains poorly understood. In contrast to several studies of Western Siberia rivers (Frey and Smith, 2005; Frey et al., 2007; Frey and McClelland, 2009; Gordeev et al., 2004) and 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 and from the trace element (TE) speciation and colloidal status. Bearing in mind very high proportion of newly formed lakes in the 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 Siberia thermokarst lakes are likely to act as an important source of CO_2 to the atmosphere.

Based on this rationale, we intended in this work to test the hypothesis of thermokarst lakes being an efficient mediators of carbon flux from soil to the atmosphere via bacterial decomposition of dissolved OM. Towards the general goal of improving our understanding of carbon and related element biogeochemistry in shallow thermokarst lakes, we aimed to address the following specific issues: 1) Assess the variation of TE and OC concentration along the chronosequence of lake development; 2) Characterize the colloidal status of TE and distinguish between the relative proportion of organic and organo-mineral colloids. Given extremely high concentration of DOC reported in lakes of Western Siberia developed on the peat deposits, the largest part of total dissolved carbon but also trace and some major elements is likely to be colloidal. As such, microbial transformation of aquatic organic and organo-mineral colloids should be the main mechanism of soil allochtonous OM processing by aquatic biota in the course of thermokarst lake development.

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2 Methods

2.1 Study site description

The study site is located in the North of Western Siberia, between the Nadym and the Pur Rivers within the tundra and forest-tundra landscape developed on continuous permafrost ≤100 m depth over the Neocene sand and clay deposits, covered by 1–2 m thick peat layer (Fig. 1). Although the area was subjected to multiple glaciations during Pleistocene (Arkhipov et al., 1986), all studied lakes are of permafrost melting origin (soil subsidence) that occurs via cyclic events of peat palsa development as illustrated in photos 1 to 5 of the Electronic Supporting Information 1 (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 and, finally, the khasyrey (drained lake) formation as it was revealed in recent studies based on ground and remote sensing observations (Kirpotin et al., 2008a, b, 2009; Shirokova et al., 2009) is illustrated in Fig. 2 and briefly discussed below. First, a crack appears in the lichen coverage of the surface of frozen mound, this decreases the albedo of the surface and leads to further peat degradation; the palsa depression is being filled by thawed water. The size of the depression increases forming a shallow lake of round shape characterized by intensive peat abrasion at the border. At these stages of the system development, waters are acidic (pH 3 to 4) and rich in DOC (20 to 80 mg L^{-1}). Eventually, the lake border is stabilized; water becomes less acidic and less organic. At this mature stage of development the lake has a pH of 5 to 6 and DOC concentration is typically around 10–15 mg L^{-1}. The final stage of the ecosystem development consist of lake drainage to another, larger water system or to the hydrological network and formation of dry bottom of the lake (khasyrey) with some small water body remaining in the center of the drained lake. At this terminal stage of the ecosystem development the lake becomes productive, and there is a presence of aquatic plants and phyto- and zooplankton. The old khasyrey initiates the new stage of frozen mound degradation and the new pond can be formed. The lakes and ponds

are typically glaciated from October to May. Their shallow depth (0.5 to 1.5 m), tundra context and strong winds favor thick ice coverage in winter but intensive wave mixing in summer.

2.2 Sampling and analyses

The list of sampled objects together with 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, in March 2010. The water samples were taken from a PVC boat in the middle part of the lake and immediately filtered through sterile, single-use Minisart® filter units (Sartorius, acetate cellulose filter) with pore sizes of 5 and 0.45 µm. The first 100 ml of the filtrate was systematically discarded. Because in March the lakes were completely frozen to the bottom, only filtration through 0.45 µm was performed for these samples, after melting of entire ice block sampled approx 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 or the pond water. The duration of this dialysis procedure was between 72 and 96 h. This exposure time was selected based on kinetic experiments of dialysis equilibrium attainment for DOC, Si and trace metals as illustrated in Fig. 3. For dialysis experiments, EDTA-cleaned trace-metal pure SpectraPor 7® dialysis membranes made of regenerated cellulose and having pore sizes of 10, 3.5 and 1 kDa were thoroughly washed in 0.1 M double-distilled HNO_3, ultrapure water, filled with ultrapure MilliQ deionised water and then placed into natural water. The efficiency of the dialysis procedure was evaluated by comparing concentration of

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major anion or neutral species (e.g., Cl^-, $H_4SiO_4^°$) not associated with colloids between the dialysis bag and the external solution. These concentrations were always identical to within $\pm 20\%$, suggesting an equilibrium distribution of dissolved components. To assess the mass balance during dialysis procedure, concentrations of major and trace

5 elements and OC were measured in the external solution and internal compartments and compared with $<0.45\,\mu m$ filtrates. In all cases, better than 95% recovery for major elements, OC, Al, Fe and 90% recovery for selected TE (Ti, Sr, Y, Ba and Zr) was achieved indicating that the adsorption of colloids and associated TE onto inside the thin Spectra Por 7 membrane was negligible.

10 Concentrations of DOC, Cl, SO_4, Alk, cations and TE were measured using methods routinely used in our laboratory for analysis of boreal water samples (Vasyukova et al., 2010; Pokrovsky et al., 2010).

For culturable heterotrophic bacteria enumeration, samples were collected in sterile 250-mL flasks and kept at 6–8 °C in the dark during less than 3 h before culturing. The

15 inoculation for culturing was performed in a prepared laboratory space sterilized by a UV lamp near an open flame. Blanks were always run for sterile control. Two duplicates of different volumes of the lake water (normally 0.5, 1 and 5 mL) were inoculated on three types of agar nutrient media (nutrient Bacto agar, 1:10 diluted nutrient agar, and Difco nutrient-poor agar, for enumeration of eutrophic (E), facultatively oligotrophic

20 (FO) and oligotrophic (O) bacteria, respectively). The number of colony-forming units (CFU) was evaluated by optical counting of colonies on the agar plate after 5, 10 and 30 days of incubation at 25°C in the dark for E, FO, and O-type bacteria, respectively.

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 given in Table 1 and their location is shown in Fig. 1. Trace element concentration is given in the Electronic Supporting Information 2 (ESM-2). In none of the studied shallow lakes (0.5–1.5 m depth) we found measurable chemical and thermal stratification. All lakes are close to equilibrium with atmospheric oxygen and values of pH, temperature, concentrations of O_2, DOC, major and trace elements are not subjected to variation between the surface and the bottom horizons (Table 1 and ESM-2).

Observed chronosequence of 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 ends up by the khasyrey (drained lake) formation. Accordingly, there is a systematic decrease of both total (<0.45 μm) and truly dissolved (<1 kDa) OC concentration in this sequence of thermokarst development (Fig. 4). Detailed analysis of OC size fractionation in the course of thermokarst lake development demonstrates general decrease of 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 large fractions of DOC; note an increase of <5 μm DOC at the mature lake stage corresponding to ecosystem stabilization (samples U-12, U-13). This may be linked to coagulation and flocculation of large-size organic colloids during bacterioplankton activity that is known to process colloidal allochtonous OM (e.g., Tranvik et al., 1988) or the experimental biases of filtration through large pore size filters. Relative proportion of small-size dissolved OC as a function of conventional DOC concentration demonstrates two distinct ranges and increases from 15 to 20% at the stage of peat abrasion/young ponds and lakes to 23±5% of most mature lakes and khasyrey (Fig. 6). We may tentatively attribute this increase to the appearance of small-size allochtonous OC in the

form of phytoplankton exometabolites concomitant to the consumption of allochtonous soil-derived OM by heterotrophic bacterioplankton. At the same time, in mature lakes and at the khasyrey stage, proportion of small size organic does not depend on total DOC and the lake trophic status and can therefore be considered as a representative value for the whole region.

The preferential use of small-size organic molecules by the heterotrophic bacterioplankton in growing lakes is illustrated by a plot of DOC (<1 kDa) concentration as a function of the number of eutrophic bacteria with r^2=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 allochtonous OM and dissolved nutrients originated from the peat lixiviation by heterotrophic microbial community of the lake water column. In addition to pelagic respiration of DOC, benthic respiration and dissolved organic matter (DOM) photolysis are known to be important factors controlling the CO_2 supersaturation in boreal lakes (e.g., Jonsson et al., 2001, 2008) with even much larger contribution of benthic respiration occurring in shallow ponds (Kortelainen et al., 2006). However, given similar depth of studied lakes, we do not expect significant variations of the relative intensity of these processes along the lake chronosequence development, although both benthic respiration and DOM photolysis of shallow lakes and ponds of Western Siberia deserve a special study.

Specific and probably unique feature of the studied systems is that usual dissolved "trace metals" such as Al and Fe are the major components of Western Siberia thermokarst lakes. Indeed, it can be seen from Fig. 8 which presents the correlation of Fe and Al with DOC in <0.45 μm fraction (r^2=0.835 and 0.837, respectively) that typical concentrations of these metals range from 0.1 to 1 mg L^{-1} which is even higher than the concentration of other major elements such as Mg, K, Si. Similar to OC, there is a systematic decrease of Fe and Al concentration from the beginning of lake formation to 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

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concentrations are indifferent to the stage of lake development. Typical elements of this group are anions Cl^-, SO_4^{2-}, MoO_4^{2-}, and elements present in the form of neutral molecules such as Si, Ge, Sb, As, alkali (Li, Na, K, Cs), and alkali-earth metals (Mg, Ca) that do not exhibit any correlation with Fe or DOC. Significant correlation with DOC
5 is observed only for Cu, Pb, and Cd, where as most insoluble trace metals are better correlated with Fe or Al than with DOC: V, Cr, Mn, Co, Ni, Sr, Ba, Ga, Y, REEs, Zr, Hg, Th, U. Examples of these correlations are illustrated in Figs. ESM-3 of the Electronic Supporting Information 3. Most lakes exhibit extremely high concentrations of usually insoluble and immobile elements such as Ti and Zr (1–10 and 0.1–1 $\mu g\,L^{-1}$, respec-
10 tively). These values are at least two orders of magnitude higher than the average concentration of these elements in continental waters and in Siberian rivers (Gaillardet et al., 2003; Pokrovsky et al., 2006). Such high concentrations of insoluble TE are likely to stem from the combination of following factors determining their elevated mobility in water: (1) pH<4, especially at the beginning of the lake formation, which stabilizes
15 trivalent ions in the form of free ions, as also follows from 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 size-separation procedure and discussed in the next sections. Note a good correlation, maintained over two
20 orders of magnitude, between Co and Mn concentration in all studied lakes and ponds with $r^2 = 0.861$ (Fig. 9). This may reflect a functional dependence of Co scavenging in the form of adsorbed and coprecipitated Co with Mn oxy(hydr)oxides in the water column known for stratified temperate lakes (Hamilton-Taylor et al., 2005). In thermokarst lakes, this functional relationship may be linked to mineralization of organic material
25 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 oxidation at the oxic front in deep water horizons. In the non-permafrost lakes, the biological precipitation of dissolved Mn and sedimentation and mineralisation of the non-detrital Mn phase in lake sediments resulted in a steady increase of the dissolved

Mn concentration is fairly well known (e.g., Ponter et al., 1992).

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

Dialysis procedure employed in the present study allowed quantitative assessment of the proportion of colloidal (1 kDa–0.45 µm) and "truly dissolved" (<1 kDa) element concentration in order to establish the link of these parameters with major solution parameters such as [DOC] and pH. We found that the proportion of truly dissolved Fe and Al depend neither on the lake stage development nor on the concentration of these metals in the <0.45 µm fraction as shown in Fig. 10a, b. The average proportion of <1 kDa Fe and Al fraction is equal to 6±4 and 14±6%, respectively. Such an independence of the proportion of <1 kDa fraction on lake stage development (or the <0.45 µm element concentration) is observed for most trace metals except those strongly bound to biological ligands such as Cu and Cd. For these elements, there is a general increase of the small-size fraction (<1 kDa) with the lake stage evolution, from peat abrasion and small ponds to mature lakes and old khasyreys as illustrated in the form of stack diagram in Fig. 11. We interpret this evolution as the increase of proportion of small size organic ligands produced by phytoplankton at the expense of large-size organic (humic and fulvic) complexes of allochtonous origin which are being mineralized by heterotrophic bacterioplankton. Indeed, such small-size strong ligands are fairly known for Cu in freshwaters being most likely related to phytoplankton (e.g., Xue and Sigg, 1993; Wu and Tanoue, 2001).

We noted that solution pH exerts certain control on 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 <1 kDa fraction is plotted as a function of pH. There is a tendency of decreasing of proportion of truly dissolved metals with pH and Fe being less affected by pH change than Al (slopes equal to 3.7 and 6.1, respectively). These positive correlations may reflect the increase of 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 the hydroxyl ions with organic colloids for metal binding at pH>4–5 which should increase the proportion of small-size ions and molecules. Note also that some strongly-bound organic ligands may be present in the <1 kDa fraction in which the OC concentration is between 15 and 30% of that in the <0.45 µm fraction.

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

Primary data on major and trace element concentration in the filtrates and ultrafiltrates and dialysates of all samples are given in Table ESM-2 of the Electronic Supplementary Material 2. Similar to DOC, the concentrations of Fe and Al decrease strongly during ultrafiltration. Fe and Al are present in the form of large-size colloids (0.45 µm–10 kDa) and they are essentially removed from solution before filtration through 10 and 1 kD membranes, as only 10 to 30% of these metals is concentrated in <1 kDa fraction. Figure 13 presents an example of filtration and dialysis patterns of Al in various lakes and ponds along the stages of chronosequence. It can be seen that all samples are clustered within the same trend line defined by decreasing of colloidal size from <5 µm fraction to <1 kDa fraction.

Among major elements, dissolved silica concentration is the least influenced by filtration and dialysis procedure: within the uncertainty of 10%, we could not detect difference between Si concentration in various filtrates, from 5 µm to 1 kDa, even at the beginning of lake formation (peat abrasion) in organic-rich pond (DOC~120 mg L^{-1}). This 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 a significant proportion of colloidal Ca, Sr, and Ba is present at all stages of lake evolution, from 30 to 50% (Table ESM-2). Colloidal alkali-earth metals in organic-rich surface boreal waters have been reported by Dahlqvist et al. (2004) and recently confirmed by Pokrovsky et al. (2010).

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 in filtrates or ultrafiltrates. Concentrations of divalent transition metals decrease during filtration and dialysis in parallel with that of DOC as illustrated for Mn in the Electronic Supplementary Information 4 (Fig. ESM-4C). Trivalent, tetravalent elements and uranium exhibit a strong affinity for colloidal fraction in sampled waters. Typically, more than 80% of REEs is concentrated in the >1 kD fraction and more than half of these elements are associated with the large-size colloids (10 kDa to 0.45 μm). The relative proportion of heavy REE in <1 kDa versus <0.45 μm fraction is a factor of 2 to 3 higher than that of light REE (Table ESM-2). This 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 groundwaters (Dia et al., 2000) and most likely linked to the preferential affinity of light REE such as La to colloidal organo-mineral surfaces and tendency of heavy REE such as Yb to form stable solution complexes (i.e., Sholkovitz, 1995; Johannesson et al., 2004).

All 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] ($0.93 \leq R^2 \leq 0.99$) as it is illustrated for Zr in Fig. 14. It is important to note that in the log scale, all samples exhibit similar functional or correlation dependence between trace metal and Fe(Al) or DOC concentration.

In order to better illustrate size fractionation scheme for different elements, we present a histogram of OC, Fe and Cu distribution between four main colloidal and subcolloidal fractions: 5–0.45 μm, 0.45 μm–10 kDa, 10 kDa–1 kDa, <1 kDa for 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 U13) small size colloidal and truly dissolved fractions

(1–10 kDa, <1 kDa) become significant for Cu which is strongly affected by the phytoplankton exometabolites (Fig. 15c).

Further insights on sub-colloidal versus truly dissolved fraction evolution among the 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). This ratio reflects the relative contribution of suspended, non-silicate (particulate) fraction to truly dissolved (potentially bioavailable) element fraction. It can be seen that there is a systematic increase of the ratio of particulate to truly dissolved fraction along the chronosequence of lake stage development, from peat abrasion to mature ecosystem. We 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 also proven by strongly heterotrophic status of all the lakes (Shirokova et al., 2009) and thus liberate Fe, Al and mineral colloids and associated insoluble metals. In the course of progressive coagulation of large-size Fe–Al colloids we observe a systematic increase of their relative proportion in the water column (Fig. 16a,c). Insoluble elements such as Ti or Zr carried by 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 truly dissolved species increases in the course of lake stage development (Fig. 16e). Indeed, for this element, the ultrafilterable (<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 high affinity of Cu to small-size organic ligands.

3.4 Colloidal speciation modeling

Considering high concentrations of Fe and Al in <0.45 µm fraction observed in 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 three main forms: (i) complexed with organic ligands of the organic part of 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 it was already reported in previous works (Ingri et al., 2000; Dia et al., 2000; Andersson et al., 2006). Complexation of trace metals with organic ligands of natural waters can be assessed using available computer codes. We used geochemical program Visual MINTEQ (Gustafsson et al., 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 proportion of data used to create this database represents soil humic and fulvic acids, and all aquatic FA and HA originate from temperate rivers and lakes which may be quite different from boreal subarctic waters studied in this work. Speciation calculations were performed for divalent metals Ca, Mg, Mn, Co, Ni, Cu, Zn, Sr, Cd, Ba, Pb and Fe, Al, Dy, Th^{IV} and $U^{VI}O_2$ for three typical samples of the lake chronosequence: U6, U1 and U13 corresponding to peat abrasion, active growing lake and lake drainage (khasyrey) stage, respectively. Similar to results of previous work on the European part of boreal zone (Vasyukova et al., 2010), calculated proportion of divalent metals bound with organic ligands is comparable ($\pm$ 30%) with the proportion of colloidal (1 kDa–0.45 µm) fraction. However, significant proportion (>80%) of elements is concentrated in large-size (10 kDa–0.45 µm) colloidal fraction which is not accounted for by vMINTEQ model, notably for insoluble trivalent and tetravalent elements. There are several possible reasons for this discrepancy. First, organic ligands that complex TE are smaller than the minimal cut-off (1 kDa) of dialysis as also shown by Pédrot et al. (2008), so these ligands are not detectable by the size-separation procedure. Indeed, we show using in-situ dialysis procedure that between 15 and 35% of conventionally 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 aquatic dissolved organic matter subjected to permafrost action. And finally, the speciation of TE in colloids may be controlled by interaction with Fe oxy(hydr)oxides rather than DOC.

In order to evaluate the capacity of TE to be adsorbed on the surface of organo-mineral colloids, we calculated surface areas for fractions 5–0.45 µm, 0.45 µm–10 kDa, 10 kDa–1 kDa and <1 kDa assuming (i) average diameters of colloids and particles equal to 2.5, 0.1, 0.002 and 0.001 µm, respectively, (ii) spherical shape for colloids, (iii) surface site density of 10 µmol m^{-2}, and (iv) iron hydroxide density of 4 g cm^{-3} (Fig. 17). Despite significant amount of Fe present in 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 total dissolved Fe and insoluble trace metals contribute less than 20–30% to the total number of surface sites and as such can not accommodate on the surface all the insoluble trivalent and tetravalent metals present in the <0.45 µm filtered fraction.

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

$$K_d = (\text{TE}/\text{Fe})_{\text{colloidal}}/(\text{TE}/\text{Fe})_{\text{dissolved}}$$

The typical values range from 0.2 to 3.5 as illustrated for several insoluble elements in Fig. 18 for three main stages of lake development, peat abrasion, active growth and mature (khasyrey) stage. These values are within the range reported in 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 progressive decrease of the role of mineral (Fe-rich) colloids in element binding in aqueous solution. Consistent with other observations presented above, it may be linked to heterotrophic bacterial activity which destabilizes colloids via selectively consuming organic substances thus removing Fe from the system and decreasing the proportion of TE linked to the mineral part of colloids. A schematic cartoon demonstrating different types of colloidal aggregates and their evolution in the course of organic

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matter consumption is presented in the Electronic Supporting Information 5 (ESM-5.ppt file).

4   Conclusions and applications to permafrost thawing

In this work we attempted to link the heterotrophic processes occurring in shallow, non-stratified thaw (thermokarst) lakes to geochemistry of OC, major and trace elements. We observe a systematic decrease of culturable heterotrophic bacteria, DOC, Fe, Al and TE concentration 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 TE are present essentially 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. Upon progressive consumption of OM by bacteria in the course of lake development, there is a systematic decrease of both DOC and dissolved metal concentrations.

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

The systematic evolution of both concentration and size fractionation of organic carbon and related trace element in the course of thermokarst lake development may have important consequences on the speciation and bioavailability of TE in the water column, their flux to the rivers and to the ocean during high flooding period as well

as metals and carbon preservation in the sediments. In particularly, we may notice the increase of potential bioavailability of metals in the lake water during evolution: the small-size complexes (<1 kDa) or conventionally dissolved species are potentially bioavailable since the pore sizes of cell wall transport channels (10–30Å in bacteria, 35–50Å in plant cells (Carpita et al., 1979; Trias et al., 1992; Colombini et al., 1980) and that of 1 kDa dialysis membrane (1–3 nm)) are comparable.

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

On a global scale, the increase of DOC concentration in surface waters due to climate warming as it is observed in Nordic Countries, British Isles, and Northern and Eastern United States (by approx. 10% over 10 years, Evans et al., 2005) is likely to be compensated by the decrease of 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 $107 \pm 50\,t\,C\,km^{-2}\,y^{-1}$ (Shirokova et al., 2009) which is at least one order of magnitude higher than the organic carbon flux in rivers of Northern Western Siberia (4–$6\,t\,C\,km^{-2}\,y^{-1}$, Maltseva et al., 1987). This flux is within the range reported for other boreal and temperate lakes in the permafrost-free environments ($175\,t\,C\,km^{-2}\,y^{-1}$, Casper et al., 2000; $28\,t\,C\,km^{-2}\,y^{-1}$, Teodoru et al., 2009) but significantly lower than that observed in boreal ponds on peatlands ($300–1000\,t\,C\,km^{-2}\,y^{-1}$, Hamilton et al., 1994) or boreal streams ($1140\,t\,C\,km^{-2}\,y^{-1}$, Teodoru et al., 2009).

Note that despite the average increase of thermokarst lake surface coverage by 4–6% during last 36 years in the northern part of Western Siberia documented within the zone of continuous permafrost (Kirpotin et al., 2008a, b), the decrease of DOC concentration during lake maturation (a factor of 2 to 5) will certainly overweight the contribution of surface area increase. As such, the total stock of DOC and dissolved

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

Supplementary material related to this article is available online at: http://www.biogeosciences-discuss.net/7/8041/2010/ bgd-7-8041-2010-supplement.pdf.

References

Allison, J. D., Brown, D. S., and Novo-Gradac, K. J.: MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: version 3.0 user's manual, EPA/600/3-91/021, http://www.epa.gov/ceampubl/mmedia/minteq/, last access: 29 October 2010, 1991.

Andersson, K., Dahlqvist, R., Turner, D., Stolpe, B., Larsson, T., Ingri, J., and Andersson, P.: Colloidal rare earth elements in a boreal river: changing sources and distributions during the spring flood, Geochim. Cosmochim. Ac., 70, 3261–3274, 2006.

Arkhipov, S. A., Isayeva, L. L., Bespaly, V. G., and Glushkova, O.: Glaciation of Siberia and Northeast USSR, Quaternary Sci. Rev., 5, 463–474, 1986.

Benedetti, M., Milne, C., Kinniburgh, D., van Riemsdijk, W., and Koopal, L.: Metal ion binding to humic substances: application of the non ideal competitive adsorption model, Environ. Sci. Technol., 29, 446–457, 1995.

Blodau, C., Rees, R., Flessa, H., Rodionov, A., Guggenberger, G., Knorr, K.-H., Shibistova, O., Zrazhevskaya, G., Mikheeva, N., and Kasansky, O. A.: A snapshot of CO_2 and CH_4 evolution in a thermokarst pond near Igarka, Northern Siberia, J. Geophys. Res.-Biogeo., 113, G03023, doi:10.1029/2007JG000652, 2008.

Breton, J., Vallières, C., and Laurion, I.: Limnological properties of permafrost thaw ponds in Northeastern Canada, Can. J. Fish. Aquat. Sci., 66, 1635–1648, 2009.

Carpita, N., Sabularse, D., Montezinos, D., and Delmer, D.: Determination of the pore size of cell walls of living plant cells, Science, 205, 1144–1147, 1979.

Casper, P., Maberly, S. C., Grahame, H., Hall, G. H., and Finlay, B. J.: Fluxes of methane and carbon dioxide from a small productive lake to the atmosphere, Biogeochemistry, 49, 1–19, 2000.

Cole, J. J., Caraco, N. F., Kling, G. W., and Kratz, T. K.: Carbon dioxide supersaturation in the surface waters of lakes, Science, 265, 1568–1570, 1994.

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J., and Melack, J.: Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget, Ecosystems 10, 171–184, 2007.

Colombini, M.: Pore size and properties of channels from mitochondria isolated from Neurospora crassa, J. Membrane Biol., 53, 1432–1424, 1980.

Dahlqvist, R., Benedetti, M. F., Andersson, K., Turner, D., Larsson, T., Stolpe, B., and Ingri, J.: Association of calcium with colloidal particles and speciation of calcium in the Kalix and Amazon rivers, Geochim. Cosmochim. Ac., 68, 4059–4075, 2004.

Desyatkin, R. V.: Soil formation in thermokarst basin – alases of cryolithozone, Novosobirsk, Nauka, 1, 43–52, 2008.

Desyatkin, A. R., Takakai, F., Fedorov, P., Nikolaeva, M. C., Desyatkin, R. V., and Hatano, R.:

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CH$_4$ emission from different stages of thermokarst formation in Central Yakutia, East Siberia, Soil Sci. Plant Nutr., 55, 558–570, doi:10.1111/j.1747-0765.2009.00389, 2009.

Dia, A., Gruau, G., Olivié-Lauquet, G., Riou, C., Molénat, J., and Curmi, P.: The distribution of rare earth elements in groundwaters: assessing the role of source-rock composition, redox changes and colloidal particles, Geochim. Cosmochim. Ac., 64, 4131–4151, 2000.

Dupré, B., Viers, J., Dandurand, J.-L., Polvé, M., Benezeth, P., Vervier, P., and Braun, J.-J.: Major and trace elements associated with colloids in organic-rich river waters: ultrafiltration of natural and spiked solutions, Chem. Geol., 160, 63–80, 1999.

Dutta, K., Schuur, E. A. G., Neff, J. C., and Zimov, S. A.: Potential carbon release from permafrost soils of Northeastern Siberia, Glob. Change Biol., 12, 2336–2351, 2006.

Eyrolle, F., Benedetti, M. F., Benaim, J. Y., and Février, D.: The distributions of colloidal and dissolved organic carbon, major elements, and trace elements in small tropical catchment, Geochim. Cosmochim. Ac., 60, 3643–3656, 1996.

Evans, C., Monteith, D., and Cooper, D.: Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts, Environ. Pollut., 137, 55–71, 2005.

Frey, K. E., Siegel, D. I., and Smith, L. C.: Geochemistry of West Siberian streams and their potential response to permafrost degradation, Water Resour. Res., 43, W03406, doi:10.1029/2006WR004902, 2007.

Frey, K. E. and Smith, L. C.: Amplified carbon release from vast West Siberian peatlands by 2100, Geophys. Res. Lett., 32, L09401, doi:10.1029/2004GL022025, 2005.

Frey, K. E. and McClelland, J. W.: Impacts of permafrost degradation on arctic river biogeochemistry, Hydrol. Process., 23, 169–182, 2009.

Gaillardet, J., Viers, J., and Dupré, B.: Treatise on Geochemistry, 5, edited by: Holland, H. D. and Turekian, K. K., in: Surface and Ground Water, Weathering, and Soils, edited by: Drever, J. I., Elsevier-Pergamon, Oxford, 225–272, 2003.

Gordeev, V. V., Rachold, V., and Vlasova, I. E.: Geochemical behaviour of major and trace elements in suspended particulate material of the Irtysh River, the main tributary of the Ob River, Siberia, Appl. Geochem., 19, 593–610, 2004.

Gruber, N., Friedlingstein, P., Field, C. B., Valentini, R., Heimann, M., Richey, J. E., Romero-Lankao, P., Schulze, D., and Chen, C.-T. A.: The vulnerability of the carbon cycle in the 21st century: an assessment of carbon-climate-human interactions, in: The Global Carbon Cycle: Integrating Humans, Climate, and the Natural World, edited by: Field, C. B. and

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Raupach, M. R., Island Press, Washington D.C., 45–76, 2004.

Gustafsson, J.: WinHumicV for Win95/98/NT, avialable at: http://www.lwr.kth.se/English/OurSoftware/vminteq/ last access: 29 October 2010, A Windows version of MINTEQA2 website, Gustafsson, J., 1999.

Hamilton, J. D., Kelly, C. A., Rudd, J. W. M., Hesslein, R. H., and Roulet, N. T.: Flux to the atmosphere of CH_4 and CO_2 from wetland ponds on the Hudson Bay Lowlands (HBLs), J. Geophys. Res., 99(D1), 1495–1510, 1994

Hamilton-Taylor, J., Smith, E. J., Davison, W., and Sugiyama, M.: Resolving and modeling the effects of Fe and Mn redox cycling on trace metal behavior in a seasonally anoxic lake, Geochim. Cosmochim. Ac., 69, 1947–1960, 2005.

Hinkel, K. M., Eisner, W. R., Bockheim, J. G., Nelson, F. E., Peterson, K. M., and Dai, X.: Spatial extent, age, and carbon stoks in drained thaw lake basins on the Barrow Peninsula, Alaska, Arct. Antarct. Alp. Res., 35, 291–300, 2003.

Hoffmann, S. R., Shafer, M. M., and Armstrong, D. E.: Strong colloidal and dissolved organic ligands binding copper nd zinc in rivers, Environ. Sci. Technol., 41, 6996–7002, 2007.

Hope, D., Kratz, T. K., and Riera, J. L.: The relationship between pCO_2 and dissolved organic carbon in the surface waters of 27 Northern Wisconsin lakes, J. Environ. Qual., 49, 1442–1445, 1996.

Ingri, J., Widerlund, A., Land, M., Gustafsson, O., Andersson, P. S., and Öhlander, B.: Temporal variations in the fractionation of the rare earth elements in a boreal river; the role of colloidal particles, Chem. Geol., 166, 23–45, 2000.

Johannesson, K. H. and Zhou, X.: Origin of middle rare earth element enrichments in acid waters of a Canadian High Arctic lake, Geochim. Cosmochim. Ac., 63, 153–165, 1999.

Johannesson, K. H., Tang, J., Daniels, J. M., Bounds, W. J., David, J. and Burdige, D. J.: Rare earth element concentrations and speciation in organic-rich blackwaters of the Great Dismal Swamp, Virginia, USA, Chem. Geol., 209, 271– 294, 2004.

Jonsson, A., Aberg, J., Lindroth, A., and Jansson, M.: Gas transfer rate and CO_2 flux between an unproductive lake and the atmosphere in Northern Sweden, J. Geophys. Res., 113, G04006, doi:10.1029/2008JG000688, 2008.

Jonsson, A., Meili, M., Bergstrom, A.-K., and Jansson, M.: Whole-lake mineralization of allochthonous organic carbon in a large humic lake (Ortrasket, N. Sweden), Limnol. Oceanogr., 46, 1691–1700, 2001.

Kelly, C. A., Fee, E., Ramlal, P. S., Rudd, J. W. M., Hesslein, R. H., Anema, C., and

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Schindler, E. U.: Natural variability of carbon dioxide and net epilimnetic production in the surface waters of boreal lakes of different sizes, Limnol. Oceanogr., 46, 1054–1064, 2001.

Kirpotin, S. N., Naumov, A. V., Vorobiov, S. N., Mironycheva-Tokareva, N. P., Kosych, N. P., Lapshina, E. D., Marquand, J., Kulizhski, S. P., and Bleuten, W.: Western-Siberian peatlands: indicators of climate change and their role in global carbon balance, in: Climate Change and Terrestrial Carbon Sequestration in Central Asia, chapt. 33, edited by: Lal, R., Suleimenov, M., Stewart, B. A., Hansen, D. O., and Doraiswamy, P., Taylor and Francis, Amsterdam, Holland, 453–472, 2007.

Kirpotin, S. N., Polishchuk, Yu. M., and Bryksina, N. A.: Dynamics of thermokarst lakes areas in continuous and discontinuous cryolithozones of Western Siberia under global warming, Vestnik Tomsk State Univ., 311, 185–189 (in Russian), 2008a.

Kirpotin, S., Polishchuk, Yu., Zakharova, E., Shirokova, L., Pokrovsky, O., Kolmakova, M., and Dupre, B.: One of possible mechanisms of thermokarst lakes drainage in West-Siberian North, Int. J. Environ. Stud., 65, 631–635, 2008b.

Kirpotin, S. N., Berezin, A., Bazanov, V., Polishchuk, Y., Vorobiev, S., Mozgolin, B., Aakerman, E., Mironycheva-Tokareva, N., Volkova, I., Dupré, B., Porkovsky, O. S., Koiraev, A., Zakharova, E., Shirokova, L., Viers, J., and Kolmakova, M.: West Siberian wetlands as indicator and regulator of climate change on the global scale, Int. J. Environ. Stud., Special Issue "Western Siberia", 66(N4), 409–421, doi:10.1080/00207230902753056, 2009.

Kling, G. W., Kipphut, G. W., and Miller, M. C.: Arctic lakes and streams as gas conduits to the atmosphere: implications for tundra carbon budgets, Science, 251, 298–301, 1991.

Kortelainen, P., Rantakari, M., Huttunen, J. T., Mattsson, T., Alm, J., Juutinen, S., Larmola, T., Silvola, J., and Martikainen, P. J.: Sediment respiration and lake trophic state are important predictors of large CO_2 evasion from small boreal lakes, Glob. Change Biol., 12, 1554–1567, 2006.

Kritzberg, E. S., Cole, J. J., Pace, M. L., Granéli, W., and Bade, D. L.: Autochtonous versus allochtonous carbon sources of bacteria: results from whole-lake ^{13}C addition experiments, Limnol. Oceanogr., 49(2), 588–596, 2004.

Laurion, I., Vincent, W. F., MacIntyre, S., Retamal, L., Dupont, C., Francus, P., and Pienitz, R.: Variability in greenhouse gas emissions from permafrost thaw ponds, Limnol. Oceanogr., 55, 115–133, 2010.

Maltseva, A. V., Tarasov, M. N., and Smirnov, M. P.: Discharge of organic substances from the USSR territory, Gidrokhimicheskie Materialy, 102, 1–118 (in Russian), 1987.

Organic carbon and trace elements in thermokarst lakes

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Milne, C. J., Kinniburgh, D. G., van Riemsdijk, W. H., and Tipping, E.: Generic NICA-donnan model parameters for metal-ion binding by humic substances, Environ. Sci. Technol., 37(5), 958–971, 2003.

Pédrot, M., Dia, A., Davranche, M., Coz, M. B., Henin, O., and Gruau, G.: Insights into colloid-mediated trace element release at the soil/water interface, J. Colloid Interf. Sci., 325, 187–197, 2008.

Pienitz, R., Doran, P. T., and Lamoureux, S. F.: Origin and geomorphology of lakes in the Polar regions, in: Polar Lakes and Rivers – Limnology of Arctic and Antarctic Aquatic Ecosystems, edited by: Vincent, W. F. and Laybourn-Parry, J., Oxford University Press, Oxford, 25–41, 2008.

Pokrovsky, O. and Schott, J.: Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia), Chem. Geol., 190, 141–179, 2002.

Pokrovsky, O. S., Schott, J., and Dupré, B.: Trace element fractionation and transport in boreal rivers and soil porewaters of permafrost-dominated basic terrain in Central Siberia, Geochim. Cosmochim. Ac., 70, 3239–3260, 2006.

Pokrovsky, O. S., Viers, J., Shirokova, L. S., Shevchenko, V. P., Filipov, A. S., and Dupré, B.: Dissolved, suspended, and colloidal fluxes of organic carbon, major and trace elements in Severnaya Dvina River and its tributary, Chem. Geol., 273, 136–149, 2010.

Pontér, C., Ingri, J., and Boström, K.: Geochemistry of manganese in the Kalix River, Northern Sweden, Geochim. Cosmochim. Ac., 65, 1485–1494, 1992.

Prentki, R. T., Miller, M. C., Barsdate, R. J., Alexander, V., Kelley, J., and Coyne, P.: Chemistry, in: Limnology of Tundra Ponds, Barrow, Alaska, US/IBP synthesis series, vol. 13, edited by: Hobbie, J. E., Dowden, Hutchinson and Ross, Stroudsburg, PA, 76–178, 1980.

Riordan, B., Verbyla, D., and McGuire, A. D.: Shrinking ponds in subarctic Alaska based on 1950–2002 remotely sensed images, J. Geophys. Res., 11, G04002, doi:10.1029/2005JG000150, 2006.

Semiletov, I. P., Pipko, I. I., Pivovarov, N. Ya., Popov, V., Zimov, S. A., Voropaev, Yu. V., and Daviodov, S. P.: Atmospheric carbon emission from North Asian Lakes: a factor of global significance, Atmos. Environ., 30, 1657–1671, 1996.

Schuur, E. A. G., Bockhein, J., Canadell, J. P., Euskirchen, E., Field, C. B., Goryachkin, S. V., Hagemann, S., Kuhry, P., Lafleur, P. M., Lee, H., Mazhitova, G., Nelson, F. E., Rinke, A., Romanovsky, V. E., Shiklomanov, N., Tarnocai, C., Venesy, S., Vogel, J. G., and Zimov, S. A.:

Vulnerability of permafrost carbon to climate change: implications for the global carbon cycle, BioScience, 58, 701–714, 2008.

Shirokova, L. S., Pokrovsky, O. S., Kirpotin, S. N., and Dupré, B.: Heterotrophic bacterio-plankton in thawed lakes of northern part of Western Siberia controls the CO_2 flux to the atmosphere, Int. J. Environ. Stud., Special Issue "Western Siberia", 66(N4), 433–445, doi:10.1080/00207230902758071, 2009.

Shirokova, L. S., Pokrovsky, O. S., Viers, J., Klimov, S. I., Moreva, O. Y., Zabelina, S. A., Voro-bieva, T. Y., and Dupré, B.: Diurnal variations of trace elements and heterotrophic bacteri-oplankton concentration in a small boreal lake of the White Sea Basin, Ann. Limnol. Int. J. Lim., 46, 67–75, doi:10.1051/limn/2010011, 2010.

Sholkovitz, E. R.: The aquatic chemistry of rare earth elements in rivers and estuaries, Aquat. Geochem., 1, 1–34, 1995.

Smith, L. C., Sheng, Y., McDonald, G. M., and Hinzman, L. D.: Disappearing Arctic lakes, Science, 308, 1429, 2005.

Sobek, S., Algesten, G., Bergstrom, A.-K., Jansson, M., and Tranvik, L. J.: The cathcment and climate regulation of pCO_2 in boreal lakes, Glob. Change Biol., 9, 630–641, 2003.

Teodoru, C. R., del Giorgio, P. A., Prairie, Y. T., and Camire, M.: Patterns in pCO_2 in boreal streams and rivers of Northern Quebec, Canada, Global Biogeochem. Cy., 23, GB2012, doi:10.1029/2008GB003404, 2009.

Tranvik, L. J.: Availability of dissolved organic carbon for planktonic bacteria in oligotrophic lakes of differing humic content, Microbial. Ecol., 16, 311–322, 1988.

Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., Dil-lon, P., Finlay, K., Fortino, K., Knoll, L. B., Kortelainen, P. L., Kutser, T., Larsen, S., Laurion, I., Leech, D. M., McCallister, S. L., McKnight, D. M., Melack, J. M., Overholt, E., Porter, J. A., Prairie, Y., Renwick, W. H., Roland, F., Sherman, B. S., Schindler, D. W., Sobek, S., Trem-blay, A., Vanni, M. J., Verschoor, A. M., von Wachenfeldt, E., and Weyhenmeyer, G. A.: Lakes and reservoirs as regulators of carbon cycling and climate, Limnol. Oceanogr., 54, 2298–2314, 2009.

Teodoru, C. R., del Giorgio, P. A., Prairie, Y. T., and Camire, M.: Patterns in pCO_2 in boreal streams and rivers of Northern Quebec, Canada, Global Biogeochem. Cy., 23, GB2012, doi:10.1029/2008GB003404, 2009.

Trias, J., Jarlier, V., and Benz, R.: Porins in the cell wall of mycobacteria, Science, 258(5087), 1479–1481, 1992.

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Vasyukova, E. V., Pokrovsky, O. S., Viers, J., Oliva, P., Dupré, B., Martin, F., and Candaudaup, F.: Trace elements in organic- and iron-rich surficial fluids of the boreal zone: assessing colloidal forms via dialysis and ultrafiltration, Geochim. Cosmochim. Ac., 74, 449–468, 2010.

5 Vonk, J. E., Sánchez-García, L., Semiletov, I., Dudarev, O., Eglinton, T., Andersson, A., and Gustafsson, Ö.: Molecular and radiocarbon constraints on sources and degradation of terrestrial organic carbon along the Kolyma paleoriver transect, East Siberian Sea, Biogeosciences, 7, 3153–3166, doi:10.5194/bg-7-3153-2010, 2010.

Walter, K. M., Zimov, S. A., Chanton, J. P., Verbyla, D., and Chapin III, F. S.: Methane bubbling
10 from Siberian thaw lakes as a positive feedback to climate warming, Nature, 443, 71–75, 2006.

Walter, K. M., Smith, L. C., and Chapin, F. S.: Methane bubbling from northern lakes: present and future contributions to the global methane budget, Philos. T. R. Soc. A, 365, 1657–1676, doi:10.1098/rsta.2007.2036, 2007.

15 Wu, F. and Tanoue, E.: Isolation and partial characterization of dissolved copper-complexing ligands in streamwaters, Environ. Sci. Technol., 35, 3646–3652, 2001.

Xue, H. B. and Sigg, L.: Free cupric ion concentration and Cu(I1) speciation in a eutrophic lake, Limnol. Oceanogr., 38, 1200–1213, 1993.

Unsworth, E. R., Warnken, K. W., Zhang, H., Davison, W., Black, F., et al.: Model predictions of
20 metal speciation in freshwaters compared to measurements by in situ techniques, Environ. Sci. Technol., 40, 1942–1949, 2006.

Zimov, S. A., Voropaev, Y. V., Semiletov, I. P., Davidov, S. P., Prosiannikov, S. F., Chapin III, F. S., Chapin, M. C., Trumbore, S., and Tyler, S.: North Siberian lakes: a methane source fueled by Pleistocene carbon, Science, 277, 800–802, 1997.

25 Zakharova, E. A., Kouraev, A. V., Kolmakova, M. V., Mognard, N. M., Zemtsov, V. A., and Kirpotin, S. N.: The modern hydrological regime of the northern part of Western Siberia from in situ and satellite observations, Int. J. Environ. Stud., 66, 447–463, doi:10.1080/00207230902823578, 2009.

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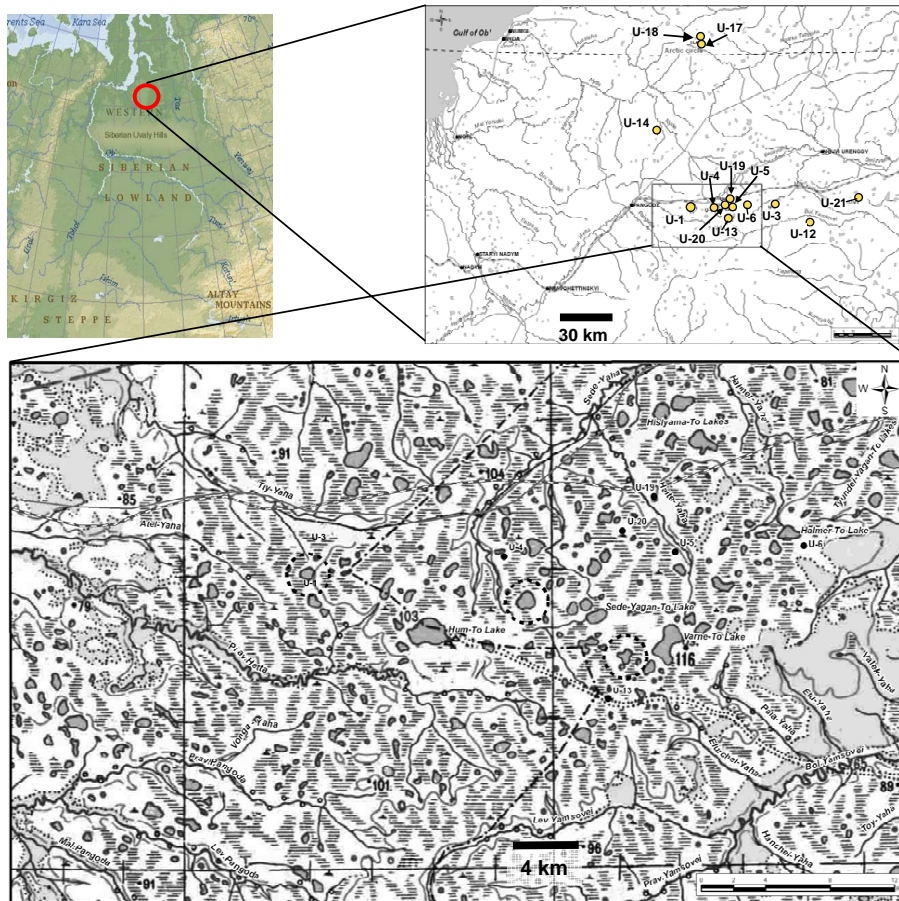Full Screen / Esc

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Organic carbon and trace elements in thermokarst lakes

O. S. Pokrovsky et al.

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	pH	Cond., µS	Alk, M	Cl, ppm	SO4, ppm	DOC, ppm	Bacteria, CFU/mL E	FO	O
U-1	Lake Shirokoe surface	0.5	0.6 km²	65°49'56.90	75°10'11.17	11.9	9.5	3.70	47.7	< d.l.	0.237	2.973	10.6	2350	2360	2780
U-2	Lake Shirokoe bottom	1.25	0.6 km²	65°49'56.90	75°10'11.17	11.6	9.2	3.26	53.1	< d.l.	0.489	3.066	10.7	2410	2690	2870
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	348	809	860
U-4	Actively growing lake	surface	300 m²	65°50'20	75°11'13	12.9	9.9	3.26	20.3	< d.l.	0.135	0.274	29.8	88	91	95
U-5	Small pond	surface	3 m²	65°50'26	75°11'25	13.5	2.3	3.67	27.9	< d.l.	0.260	0.114	75.9	2760	2800	2950
U-6	Peat abrasion	surface	2 m²	65°50'35	75°11'34	13.6	8.1	4.30	96.9	< d.l.	0.272	22.3	118.6	6912	4480	5890
U-7	Lake Shirokoe surface	0.5	0.6 km²	65°49'56.90	75°10'11.17	12.5	8.0	3.48	N.D.	< d.l.	0.243	N.D.	10.5	N.D.	N.D.	N.D.
U-8	Lake Shirokoe bottom	1.3	0.6 km²	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.	N.D.
U-9	Growing lake surface	0.5	20,000 m²	65°49'54.51	75°11'16.59	12.1	10.3	4.33	18.8	0.000022	0.280	0.516	33.9	2272	690	448
U-10	Growing lake bottom	1.5	20,000 m²	65°49'54.51	75°11'16.59	12.1	10.3	4.33	18.7	0.000022	0.306	0.519	31.3	2010	580	560
U-11	Lake Yamsovey 1, stabilized border	surface	0.4 km²	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.	N.D.
U-11	Lake Yamsovey 1	0.5	0.4 km²	65°47'25.89	75°28'00.98	11.5	10.5	5.10	6.50	0.000014	0.204	0.439	12.0	280	340	650
U-11	Lake Yamsovey 1	1.25	0.4 km²	65°47'25.89	75°28'00.98	11.3	10.6	5.07	6.45	0.000014	0.210	0.441	10.2	120	700	950
U-12	Lake Yamsovey 2, stable borders	surface	1 km²	65°44'51.8	75°30'52.3	11.4	9.6	5.59	8.50	0.000014	0.390	0.733	11.6	100	200	300
U-13	Lake Khasyrey, surface	0.5	7000 m²	65°45'31.5	75°31'03.0	11.7	9.8	5.72	4.50	0.000015	0.090	0.165	7.6	20	2000	3500
U-13	Lake Khasyrey, water column	1.25	7000 m²	65°45'31.5	75°31'03.0	11.5		5.65	N.D.	0.000016	0.091	0.167	8.8	80	100	120
U-13	Lake Khasyrey, bottom	1.5	7000 m²	65°45'31.5	75°31'03.0	11.5	8.8	5.59	N.D.	0.000011	0.180	0.183	9.2	N.D.	N.D.	N.D.
U-14	Lake with stable border, macrophytes	surface	0.2 km²	66°12'15.9	74°00'41.0	12.4		5.56	4.0	0.0000093	0.179	0.433	4.9	N.D.	N.D.	N.D.
U-15	Mature lake	surface	0.3 km²	66°13'05.86	74°02'56.12	12.5	9.3	6.24	10.0	0.000044	0.445	0.512	8.4	N.D.	N.D.	N.D.
U-16	Stabilized lake	surface	0.2 km²	66°18'03.25	74°04'23.36	12.2		5.58	8.8	0.000041	0.237	0.194	11.6	N.D.	N.D.	N.D.
U-17	Tundra lake around swamps	surface	0.15 km²	66°36'35.7	74°36'35.7	11.5	7.8	6.76	55.5	0.000660	0.685	0.004	10.9	N.D.	N.D.	N.D.
U-18	Remained water of Khasyrey, plants	surface	300 m²	66°38'02	74°19'51	12.9	10.5	6.60	9.9	0.000033	0.038	0.060	17.1	2	20	45
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	40	200	350
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	40	820	960
U-21	Lake formed after palsa retreat	surface	2000 m²	65°51'59	75°16'96	12.3	9.7	4.02	13.9	0.000016	0.556	0.160	23.4	35	300	600
U 11*	Lake Yamsovey 1, melted ice	0.5 m ice				N.D.	N.D.	4.65	N.D.		0.317	0.1465	7.03	N.D.	N.D.	N.D.
U 12*	Lake Yamsovey 2, melted ice	0.5 m ice				N.D.	N.D.	5.49	N.D.		0.4894	0.712	13.06	N.D.	N.D.	N.D.
U 13*	Lake Khasyrey, melted ice	0.5 m ice				N.D.	N.D.	5.74	N.D.		0.0787	0.1197	3.03	N.D.	N.D.	N.D.

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

Fig. 1. Schematic map of the studied area.

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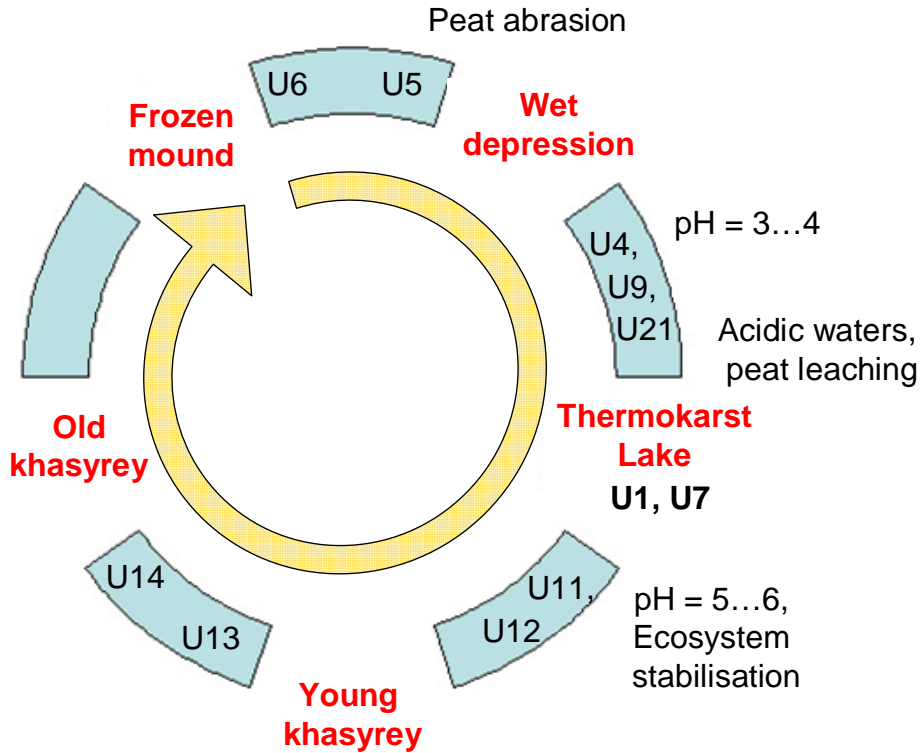
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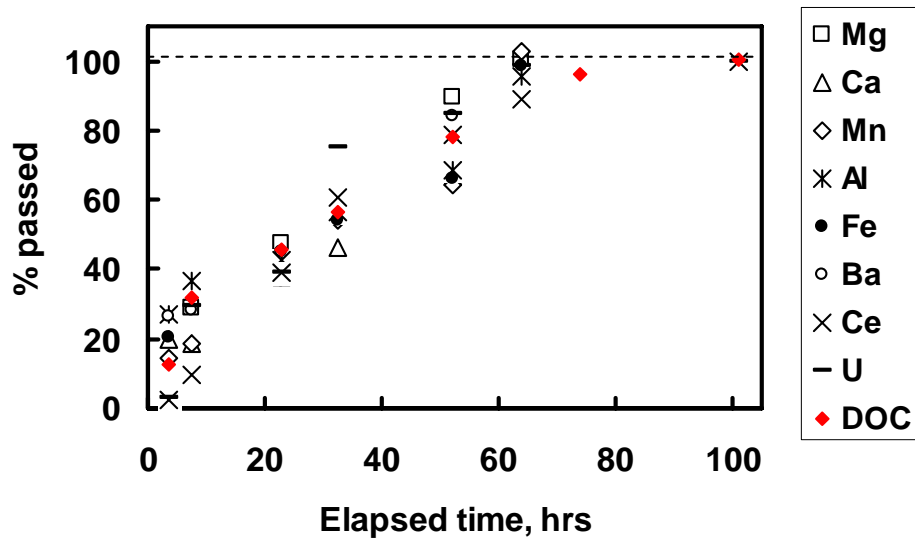
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Fig. 2. Scheme of cyclic succession of thermokarst lakes and khasyrey development from flat and mound bogs. The numbers from U1 to U21 correspond to some of the water samples collected in this study at various stages of lake development (Table 1 and 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%.
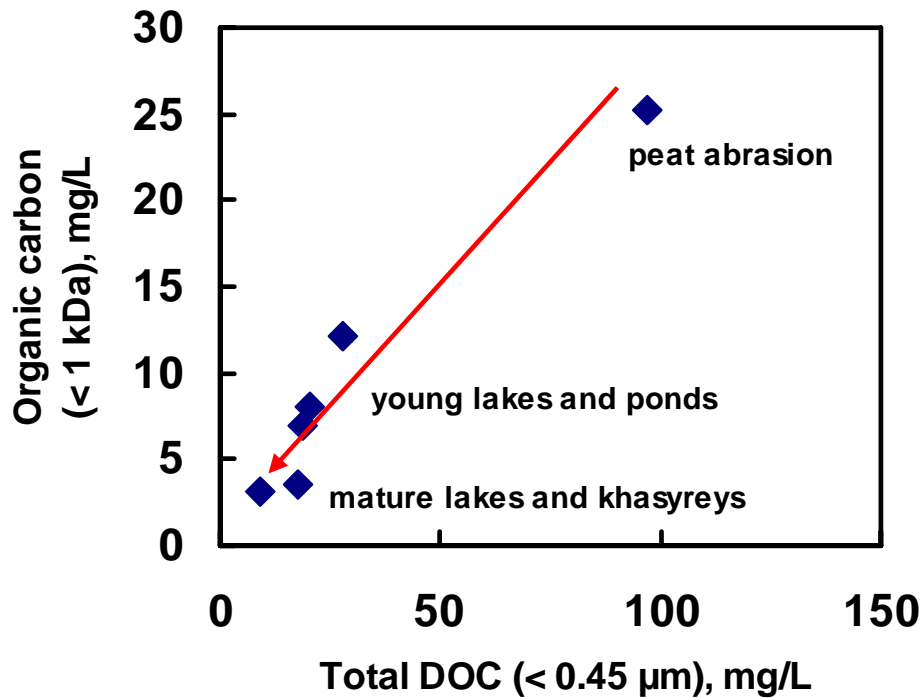
Fig. 4. Concentration of potentially bioavailable (<1 kDa) organic carbon as a function of total DOC (<0.45 μm).
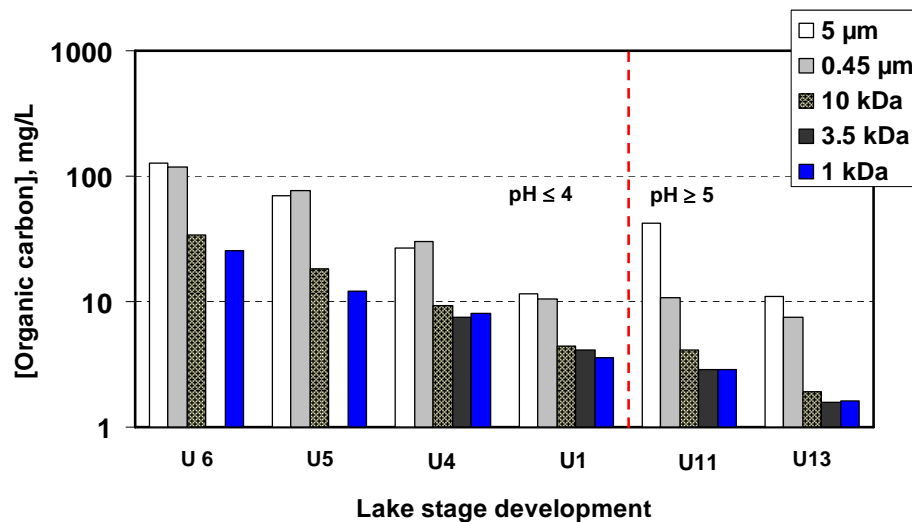
Fig. 5. Concentration of different size fractions of organic carbon in the chronosequence of lake stage development.

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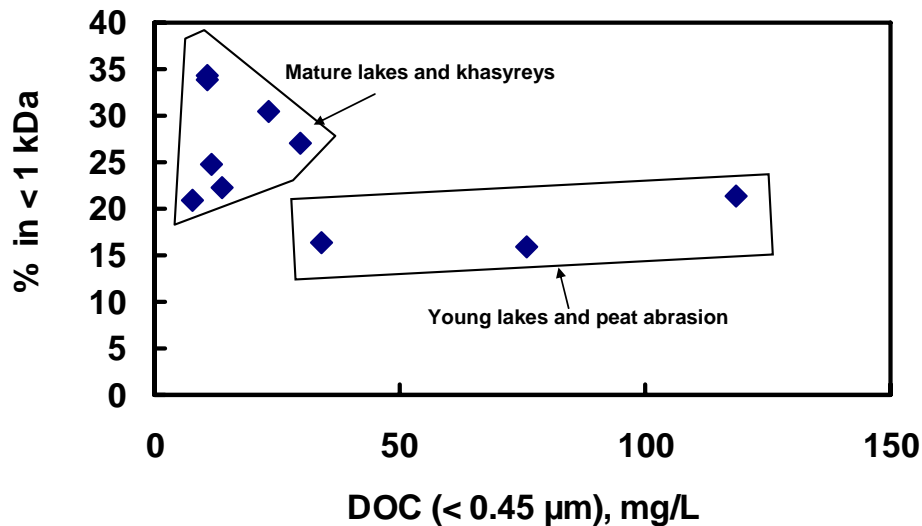
Fig. 6. Proportion of small-size dissolved organic carbon (<1 kDa) as a function of conventional DOC concentration (<0.45 µm). Note that at the mature stage of lake development and khasyreys, proportion of small size organic colloids does not depend on total DOC and for most studied lakes it is equal to 27±5%.
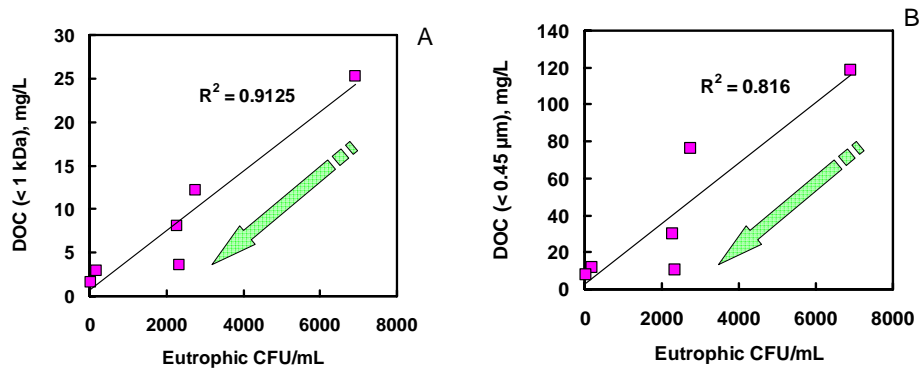
Fig. 7. Concentration of potentially bioavailable (<1 kDa; **(A)** and conventionally dissolved (<0.45 μm); **(B)** organic carbon as a function of active culturable heterotrophic bacteria (colony forming Units/mL). Arrow indicates the lake stage evolution, from peat abrasion, young lakes and ponds to mature lakes and khasyreys.
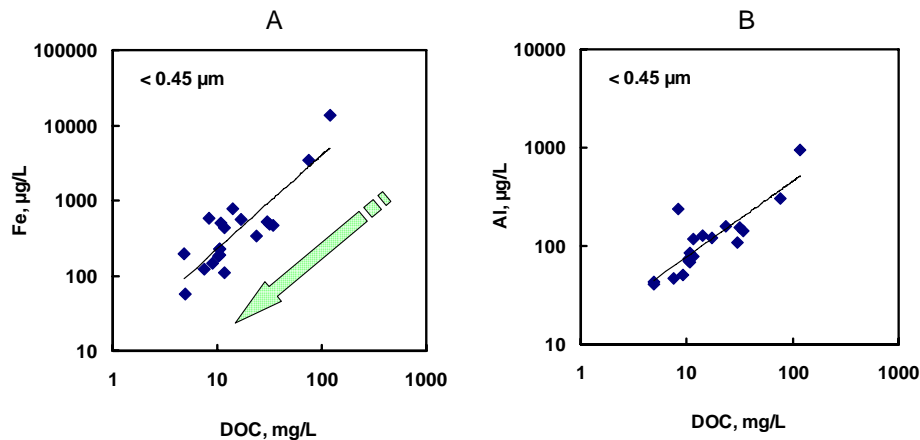
Fig. 8. Concentration of Fe **(A)** and Al **(B)** as a function of Dissolved Organic Carbon (DOC) in <0.45 µm fraction of various lakes and ponds. Arrow indicates the lake stage evolution, from peat abrasion, young lakes and ponds to mature lakes and khasyreys.

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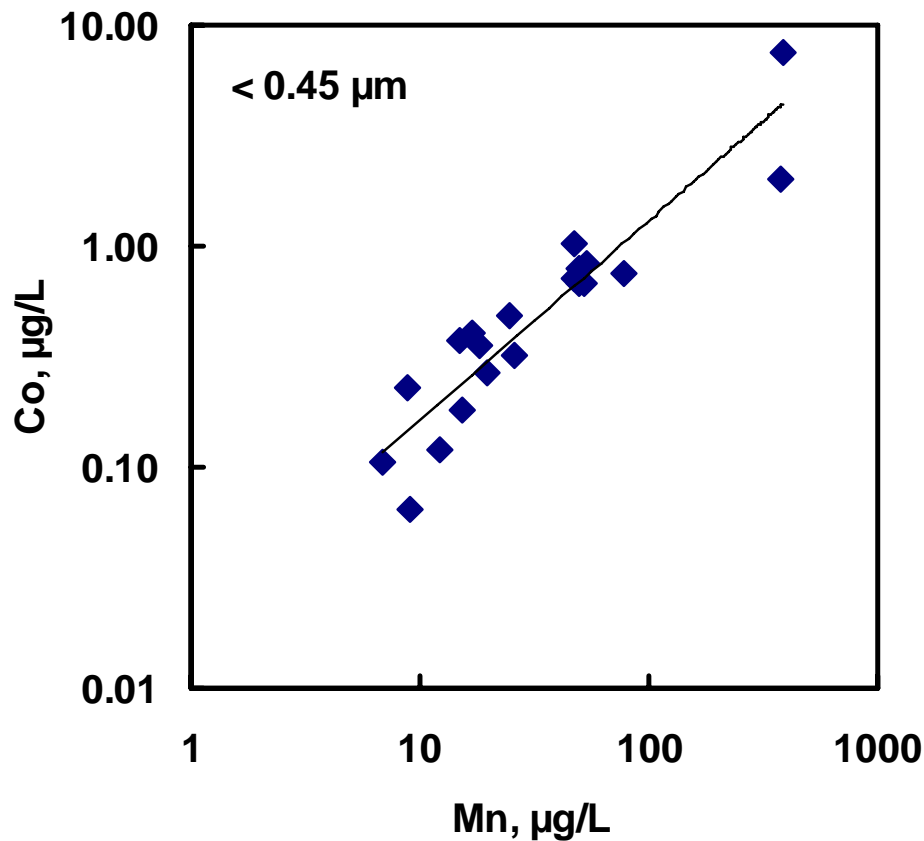
Fig. 9. Concentration of Co as a function of Mn concentration in <0.45 μm fraction of various lakes and ponds.
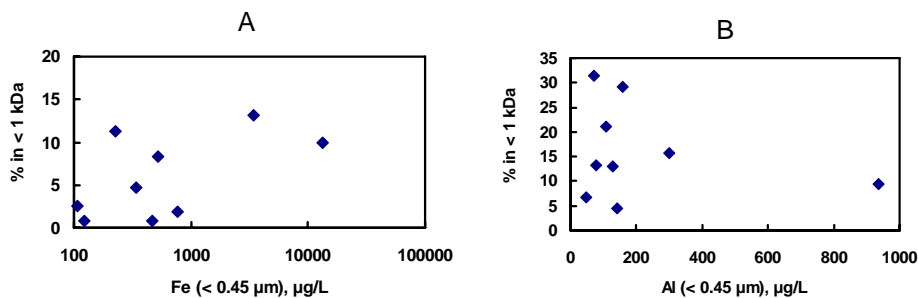
Fig. 10. Relative proportion of small-size fraction of Fe **(A)** and Al **(B)** as a function of total dissolved ($<0.45\,\mu$m) metals in all lakes and ponds. The average concentration of $<1\,$kDa fraction is equal to $6 \pm 4\%$ and $14 \pm 6\%$ for Fe and Al, respectively.
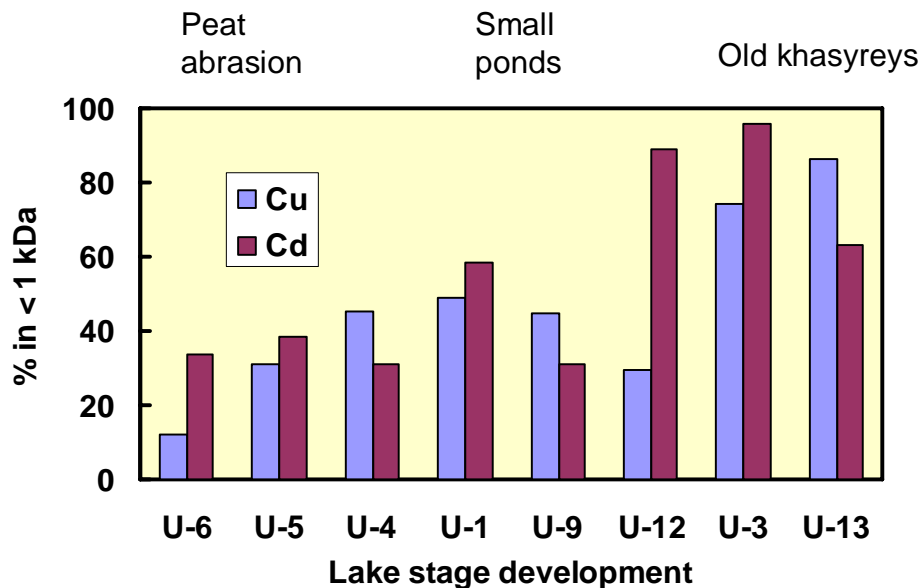
Fig. 11. Stack diagram of Cu and Cd proportion in the form of small-size complexes and ions (<1 kDa) in lakes and ponds along the chronosequence of lake development. There is an increase of small size organic ligands binding divalent metals produced by the phytoplankton at the mature stage of ecosystem development at the expense of bacterioplankton mineralization of large colloidal size allochtonous humic and fulvic complexes.
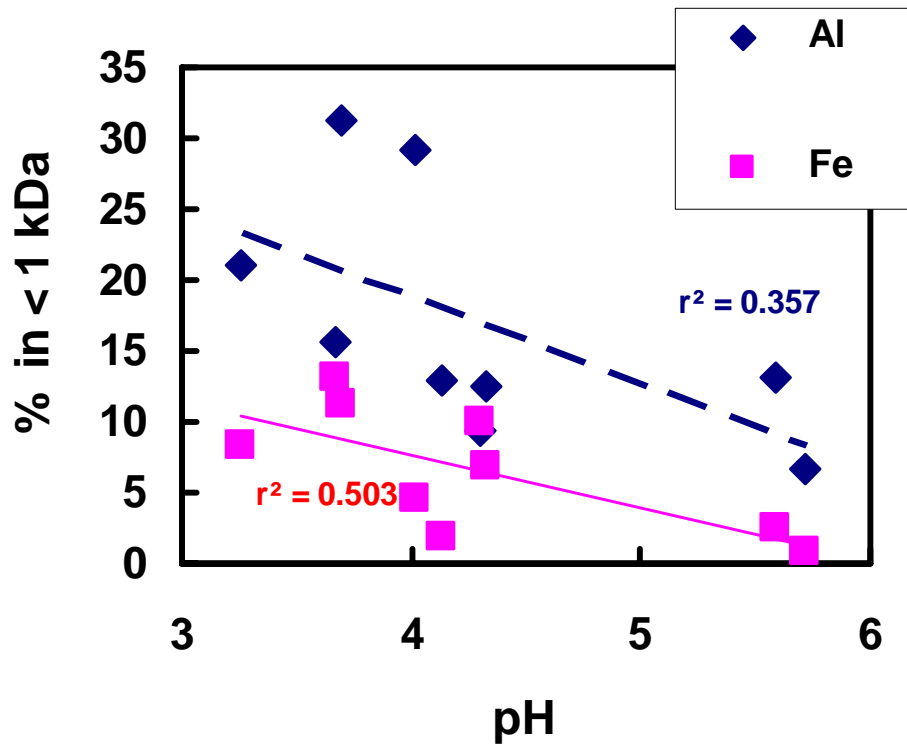
Fig. 12. Relative proportion of small-size fraction of Fe **(A)** and Al **(B)** as a function of solution pH in lakes and ponds.
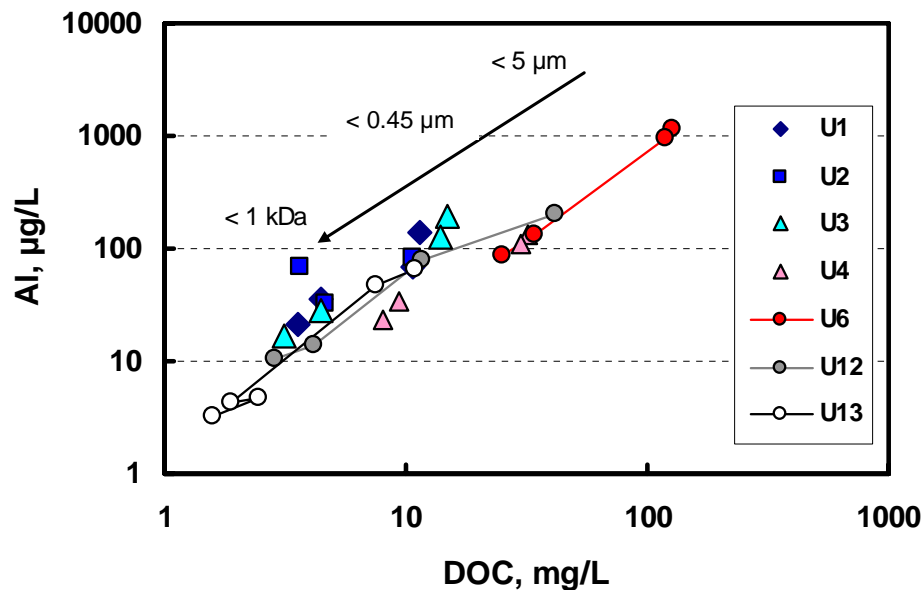
Fig. 13. Correlation between Al and DOC in filtrates and dialysates of various samples shown by different symbols (see Table 1 for description). In each series, the first (highest) point corresponds to filtration through 5 or 0.45 µm and the lowest point represents dialysis through 1 kDa.

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.

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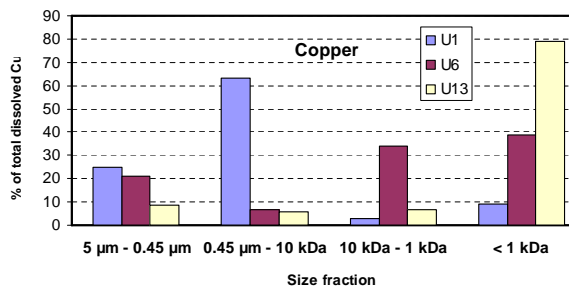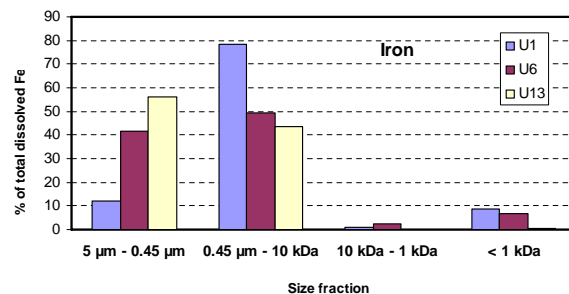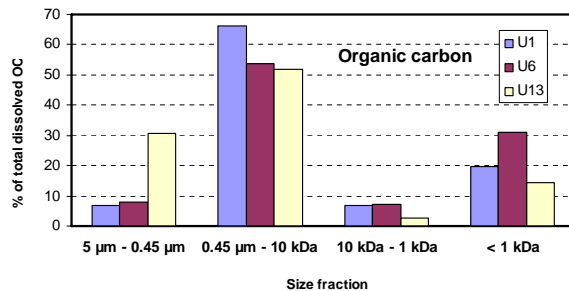
Fig. 15. Size fractionation of OC **(A)**, Fe **(B)** and Cu **(C)** among main colloidal and subcolloidal fractions in typical samples reflecting three main stages of thaw lake development: U6, U1 and U13 corresponding to peat abrasion, large growing lake and final (khasyrey stage) of the lake.

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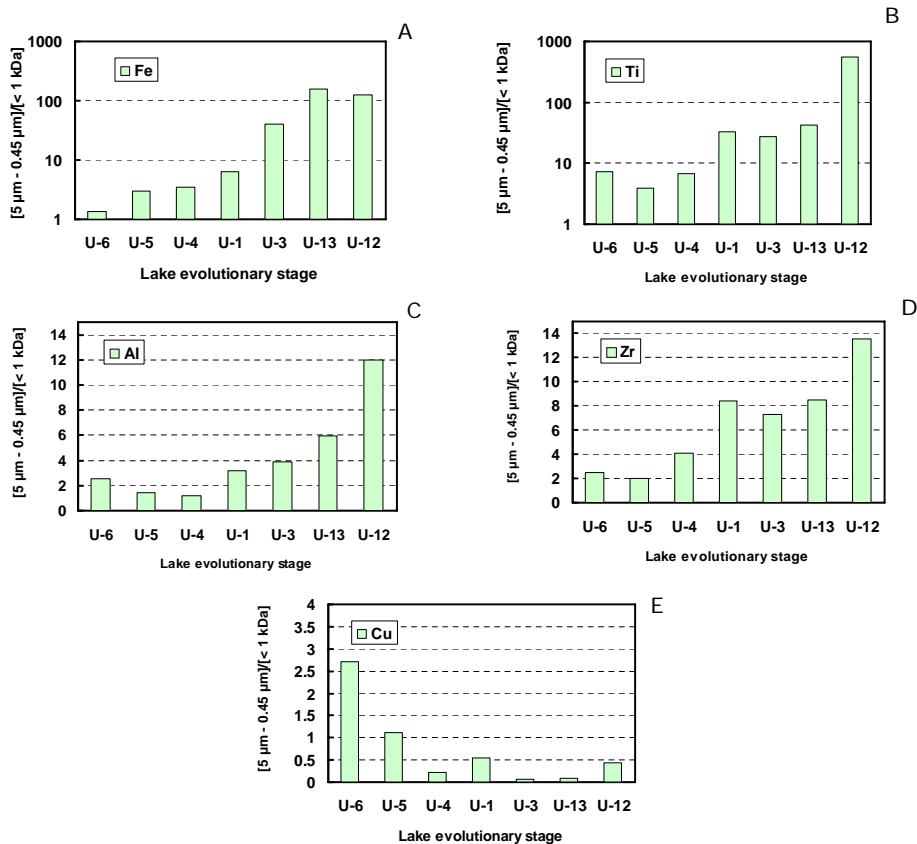
Fig. 16. Colloidal reorganization in the course of lake evolution: the increase of the relative proportion of large-size Fe(Al) sub-colloids/particles with lake chronosequence development. It is possible that the heterotrophic bacteria uptake DOC (<0.45 μm), liberate Fe **(A)**, Al **(C)** mineral colloids that are aggregating in subcolloidal/particles thus tranforming size dsitribution of related trace elements: Ti **(B)**, Zr **(D)** and Cu **(E)**.
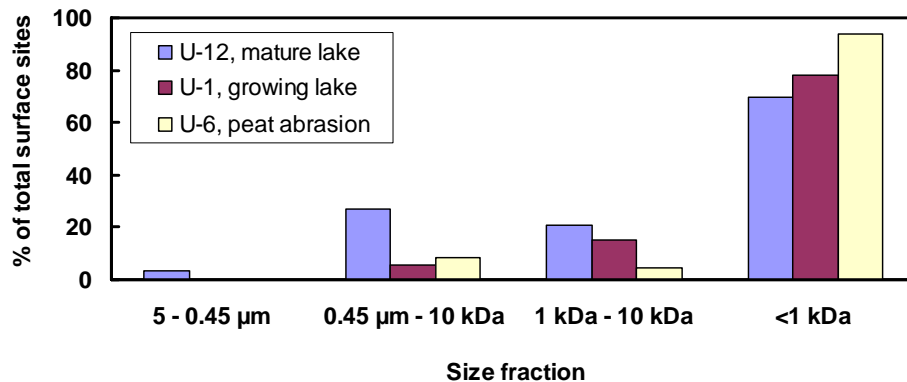
Fig. 17. Percentage of Fe colloids surface sites present in various size fractions for three typical stages of lake development. Total concentration of >FeOH° surface sites in samples is the following: U-6, 23 μmol L^{-1}; U-1, 0.5 μmol L^{-1}; U-12, 0.07 μmol L^{-1}.

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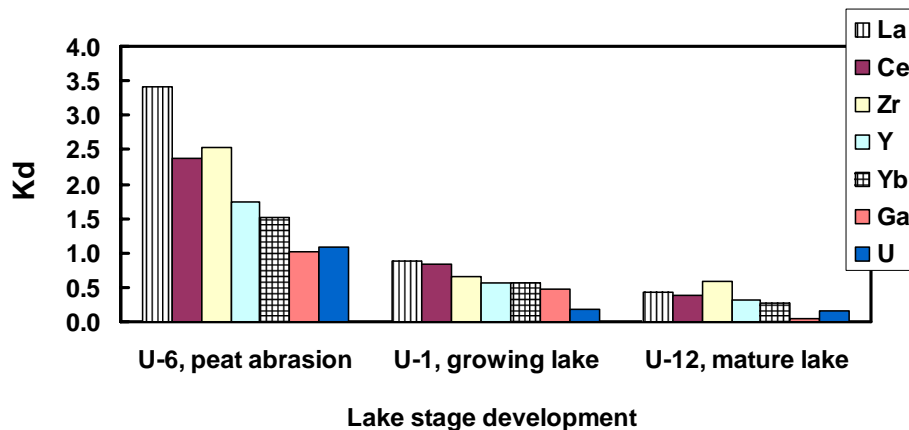
Fig. 18. Coefficients of trace element coprecipitation with colloidal Fe(III)oxy(hydr)oxides for three main stages of lake development, from the initial (peat abrasion) stage to the terminal (mature lake and khasyrey) stage.