

Organic matter mineralization and trace element post-depositional redistribution in Western Siberia thermokarst lake sediments

S. Audry¹, O. S. Pokrovsky¹, L. S. Shirokova^{1,2}, S. N. Kirpotin³, and B. Dupré¹

¹Observatoire Midi Pyrénées, UMR5563 GET CNRS, Université de Toulouse; 14 Avenue Edouard Belin, 31400 Toulouse, France

²Laboratory of Aquatic Ecosystems, Institute of Ecological Problems of the North, Russian Academy of Science Ural Branch Russian Academy of Science, Arkhangelsk, Russia

³Tomsk State University, 36, Lenina Prospekt, Tomsk, 634050, Russia

Received: 21 June 2011 – Published in Biogeosciences Discuss.: 30 August 2011

Revised: 2 November 2011 – Accepted: 7 November 2011 – Published: 16 November 2011

Abstract. This study reports the very first results on high-resolution sampling of sediments and their porewaters from three thermokarst (thaw) lakes representing different stages of ecosystem development located within the Nadym-Pur interfluvium of the Western Siberia plain. Up to present time, the lake sediments of this and other permafrost-affected regions remain unexplored regarding their biogeochemical behavior. The aim of this study was to (i) document the early diagenetic processes in order to assess their impact on the organic carbon stored in the underlying permafrost, and (ii) characterize the post-depositional redistribution of trace elements and their impact on the water column. The estimated organic carbon (OC) stock in thermokarst lake sediments of $14 \pm 2 \text{ kg m}^{-2}$ is low compared to that reported for peat soils from the same region and denotes intense organic matter (OM) mineralization. Mineralization of OM in the thermokarst lake sediments proceeds under anoxic conditions in all the three lakes. In the course of the lake development, a shift in mineralization pathways from nitrate and sulfate to Fe- and Mn-oxyhydroxides as the main terminal electron acceptors in the early diagenetic reactions was suggested. This shift was likely promoted by the diagenetic consumption of nitrate and sulfate and their gradual depletion in the water column due to progressively decreasing frozen peat lixiviation occurring at the lake's borders. Trace elements were mobilized from host phases (OM and Fe- and Mn-oxyhydroxides) and partly sequestered in the sediment in the form of authigenic Fe-sulfides. Arsenic and Sb cycling was also closely linked to that of OM and Fe- and Mn-oxyhydroxides. Shallow diagenetic enrichment of particulate Sb was observed in the less mature stages. As a result of au-

thigenic sulfide precipitation, the sediments of the early stage of ecosystem development were a sink for water column Cu, Zn, Cd, Pb and Sb. In contrast, at all stages of ecosystem development, the sediments were a source of dissolved Co, Ni and As to the water column. However, the concentrations of these trace elements remained low in the bottom waters, indicating that sorption processes on Fe-bounding particles and/or large-size organo-mineral colloids could mitigate the impact of post-depositional redistribution of toxic elements on the water column.

1 Introduction

Boreal and subarctic peat-accumulating wetlands are recognized as a major sink of organic carbon (OC) and are estimated to hold one-third of the global soil carbon stock (i.e. 390–455 Pg C; Gorham, 1991; Jenkinson et al., 1991). There are currently concerns about the destabilization of these wetlands under warmer climate conditions and the consequent increase of dissolved organic carbon (DOC) export to the rivers and methane (CH₄) and carbon dioxide (CO₂) release to the atmosphere (e.g. Zimov et al., 1997; Freeman et al., 2001, 2004; Smith et al., 2004; Laurion et al., 2010). Under recent and projected future climatic warming trend (ACIA, 2007), it is estimated that in areas such as Siberian permafrost, the overall carbon loss from thawing permafrost could reach up to 1 Gt C yr⁻¹ or ~40 Gt C in the next four decades (Dutta et al., 2006). Western Siberian peat-accumulating wetlands represent the world's most extensive peatlands and, according to the recent high-resolution GIS-based inventory of Sheng et al. (2004), contains as much as 70 Pg C. The region is submitted to increasing air temperatures that are rising more rapidly than the Arctic as a whole (Frey and Smith, 2003; Kirpotin et al., 2007). Western



Correspondence to: S. Audry
(stephane.audry@get.obs-mip.fr)

Siberian peatlands peculiarly comprise a myriad of lakes (>800 000; Ivanov and Novikov, 1976), which area and abundance have been reported shrinking (−13 % and −9 %, respectively) in the discontinuous permafrost zone due to permafrost thawing over the past four decades, while increasing (+12 % and +4 %, respectively) in the continuous permafrost zone (Smith et al., 2005). Western Siberian wetlands therefore represent highly reactive, sensitive and potentially unstable continental ecosystems that could play a pivotal role in the modification of the carbon cycle under future warmer climate conditions. Among Western Siberian lakes, thermokarst (thaw) lakes (that comprise up to 90 % of the lakes in the Russian permafrost zone; Walter et al., 2006) represent an ecosystem type following a highly dynamic life cycle of formation, expansion and drainage (Hinkel et al., 2003; Kirpotin et al., 2008). Thermokarst lakes are recognized as past and contemporary sources of atmospheric CH₄ (almost exclusively through ebullition at the water-atmosphere interface; Zimov et al., 1997; Walter et al., 2007). Methane production is fueled by early diagenesis processes (Froelich et al., 1979; Berner, 1980; Aller, 2004) that occur in lake sediments. These processes are responsible for post-deposition mineralization of organic matter (OM) and therefore play a pivotal role in OC transformation and mobilization. Additionally, as reported for marine (e.g. Shaw et al., 1990; Chaillou et al., 2002; Sundby et al., 2004) and freshwater (e.g. Widerlund et al., 2002; Audry et al., 2010; Couverture et al., 2010) environments, early diagenesis controls the post-depositional redistribution of trace elements through the destabilization of trace element-bearing phases and subsequent authigenic mineral precipitations.

There is a striking paucity of comprehensive studies of thermokarst lakes in the subarctic zone. To our knowledge, only one study reported sediment chemistry from shallow lakes in arctic zone (tundra ponds in Alaska; Prentki et al., 1980). And among the more recently published studies (e.g. Zimov et al., 1997; Duff et al., 1998; Walter et al., 2007; Smith et al., 2004; Blodau et al., 2008; Turner et al., 2010) none focused, or even reported data, on the sediment compartment and early diagenesis processes. Only some large and polluted lakes, located in subarctic, non-permafrost-affected zone, received recent attention from the view point of sediment geochemistry (e.g. Ingrid et al., 2011). However, these studies reported limited porewater data regarding redox species.

Accordingly, there is an important necessity to improve our understanding on the processes of OM mineralization in subarctic thermokarst lakes as these processes likely control (i) mechanisms such as CH₄ production, CO₂ evasion to the atmosphere, export of OC to rivers and eventually ocean that are involved in positive feedbacks to climate warming and (ii) the sedimentary transformation, mobilization/sequestration and bioavailability of trace metals and metalloids. The present study is based on the sampling of thermokarst sediments from three shallow lakes representing

three different stages of the life cycle of thermokarst lakes. The selected area of investigation is the Nadym-Pur interfluvium of the Northern part of Western Siberia plain whose lake sediments remain virtually unexplored regarding their biogeochemical behavior. The aim of the study was to document the oxidation-reduction processes occurring during early diagenesis in order to assess their impact on (i) OC previously sequestered in the underlying permafrost, and (ii) the post-depositional redistribution of Fe, Mn, and trace elements (Cd, Co, Ni, Cu, As, Sb, Zn, Pb) and their potential upward diffusive fluxes to the water column. The potential control of thermokarst lake development stage on the above issues and the prospective of permafrost thawing in Western Siberia were also investigated.

2 Study area and sampling sites

The investigations were conducted in the forest-tundra and tundra “palsa” landscape complex between the Nadym and Pur Rivers in the North of Western Siberia (Fig. 1). The study area is characterized by continuous permafrost (Kotlyakov and Khromova, 2002) covered by 1–2 m thick peat layer and overlying Neocene deposits of marine and lacustrine-alluvial genesis with sandy and loamy soils. In this region, mean annual temperature is −9.3 °C and the number of days with stable negative air temperature ranges between 200 and 240 (Ershov, 1989). During winter, precipitation is accumulated as snow as much as 100–200 mm yr^{−1} of water equivalent. The region’s flat relief greatly affects the hydrological network by favoring a myriad of interconnected and diversified ecosystems such as large and small rivers, floodplains, lakes, mires, etc. Among these ecosystems, 30 % (in surface area) are represented by thermokarst (thaw) lakes (Zimov et al., 1997) and the proportion of newly-formed lakes may be as high as 60–80 % in the Pur-Taz-Nadym River watersheds (Zakharova et al., 2009). Typically, thermokarst lakes develop as a result of ground subsidence triggered by permafrost thawing and subsequent loss of volume from melting ice (Czudek and Demek, 1970; Mackay, 1992). Water then accumulates in the depression and may coalesce with other water bodies to form lakes spanning on wide ranges of size and depth. Thermokarst lakes are known to follow a cycle of formation-expansion-drainage (Billings and Peterson, 1980; Hinkel et al., 2003). Based on ground and remote sensing observations (Kirpotin et al., 2007, 2008), the main features of the thermokarst life cycle in the studied region are as follows (Fig. 2): (i) following the cracking of the lichen cover on the surface of frozen mound, the subsequent decrease of albedo and further peat degradation, the palsa depression is being filled by thaw water. This constitutes the first stage of the thermokarst life cycle; (ii) the size of the depression increases forming an expanding shallow lake characterized by intensive peat abrasion and leaching at the border (2nd and 3rd stages) and eventual border stabilization (4th stage);

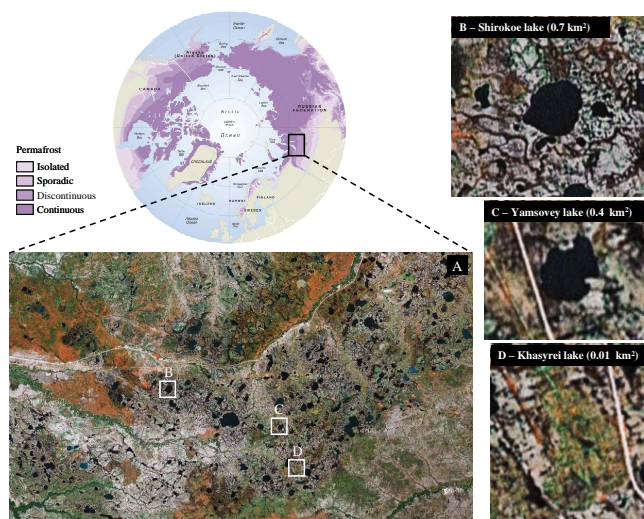


Fig. 1. Map of the study area (Nadym-Pur Interfluvium, Western Siberia Wetlands) showing the locations of the three studied lakes. Source for the map of permafrost distribution: International Permafrost Association (2003). Images A, B, C, D from GoogleEarth.

(iii) the final stage (5th stage) of the lake development consists of the drainage of the lake (locally named “khasyrei”) to a larger water body or the hydrological network. At the end of this stage, a small lake remains surrounded by a vegetated area representing the maximum of expansion of the former lake. At this stage, aquatic plants/macrophytes and phyto- and zooplankton is observed. From this fifth stage, the whole cycle starts over again. The chemical characteristics of the thermokarst lake’s water column evolve during the course of the life cycle with, from the first to the fifth stage, pH increase (from 3 to 6) and decrease of DOC (from 120 to 7 mg l⁻¹), electrical conductivity, sulfate, Fe and Mn concentrations (Shirokova et al., 2009; Pokrovsky et al., 2011). At all stages, the dominant form of dissolved OM is allochthonous fulvic and humic acids originating from peat soil leaching which are being mineralized in the water column by heterotrophic bacterioplankton (Pokrovsky et al., 2011). A peculiar feature to these lakes is that dissolved Fe and Al, present as large-size colloids (0.45 μm–10 kDa) are the major components of the water column, with concentrations ranging from 0.1 to 1 mg l⁻¹ and higher than that of the other major elements such as Mg, K and Si. This specific feature is likely the result of (i) the weathering of Na-, Ca-, Mg-poor and Al- and Fe-rich altered Neogene sand and acid peat soils, and (ii) the high concentrations of Fe and Al colloids stabilized by dissolved OM (Pokrovsky et al., 2011).

For the present study, sediments from three shallow (<1–1.5 m depth) non-stratified thermokarst lakes were sampled. Each sampled lake represents a different stage of the life cycle described above: (i) actively growing, young Lake Shirokoe (0.7 km²; Fig. 1b) for the third stage; (ii) mature Lake Yamsvey (0.4 km²; Fig. 1c) with stabilized border

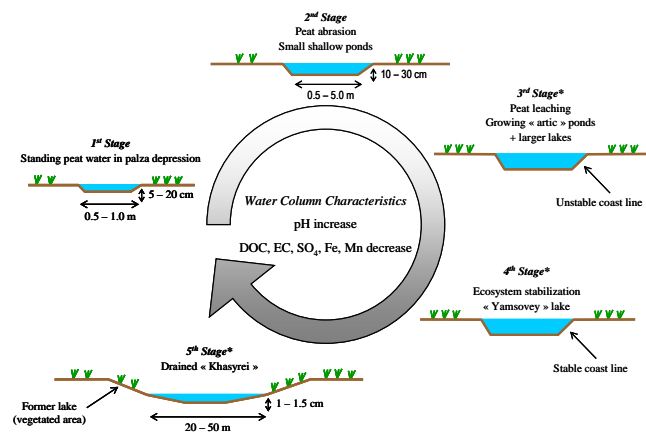


Fig. 2. Schematic representation of the life cycle (formation-expansion-drainage) of thermokarst lakes in the studied region. *Stages sampled in this study. POC, particulate organic carbon; EC, electrical conductivity.

for the fourth stage and (iii) remaining part of drained Lake Khasyrei (0.01 km² of water surface with a surrounding vegetated area of 0.8 km²; Fig. 1d) for the fifth stage (Fig. 1 and Table 1). These lakes are typically glaciated from October to May and may be frozen to the bottom at the winter’s end. According to the processes of thermokarst lake formation reported above, the sediments investigated in this study represent former peat soil flooded and degraded during lake expansion.

3 Material and methods

3.1 Sampling

Sampling of the three lakes was performed in August 2008 using an inflatable boat. Samples from the water column were retrieved and treated using protocols described in Pokrovsky et al. (2011). The water samples were taken in the middle part of the lake and immediately filtered through sterile, single-use Minisart[®] filter units (Sartorius, acetate cellulose filter) with pore size of 0.45 μm. The first 100 ml of the filtrate were systematically discarded. Dissolved oxygen and pH were measured on-site with an uncertainty of 5 % and 0.02 units, respectively.

One sediment core was collected for each three lakes using a Large Bore Interface Corer (Aquatic Research Instruments[®]) equipped with a polycarbonate core tube (60 cm length, 10 cm inner diameter). This corer enables sampling the uppermost decimetres of the sediments without any disturbance of the water-sediment interface (WSI). Immediately after recovery, the overlying bottom water was collected from the polycarbonate tube using a 10-ml syringe, filtered through disposable filter unit (0.22 μm porosity; Sartorius[®]) and divided into 3 aliquots for nutrient,

Table 1. Physical and water column hydrochemical characteristics of the studied thermokarst lakes. WSA, water surface area; EC, electrical conductivity; DOC, dissolved organic carbon; Alk, alkalinity.

Lake	Stage	Latitude	Longitude	WSA (km ²)	Depth (m)	T (°C)	O ₂ (mg l ⁻¹)	pH	EC (μs cm ⁻¹)	Alk (mM)	SO ₄ (μM)	DOC (mg l ⁻¹)	Fe (μM)	Mn (μM)
Shirokoe	3rd	65°49′56.90″ N	75°10′11.17″ E	0.7	0.5	11.9	9.50	3.70	17.70	<d.l.	31.0	10.6	4.07	0.87
Shirokoe	3rd	65°49′56.90″ N	75°10′11.17″ E	0.7	1.25	11.6	9.20	3.26	53.10	<d.l.	31.9	10.7	n.d.	n.d.
Yamsovey	4th	65°47′25.89″ N	75°28′00.98″ E	0.4	0.5	11.5	10.50	5.10	6.50	0.014	4.57	12.0	1.88	0.45
Yamsovey	4th	65°47′25.89″ N	75°28′00.98″ E	0.4	1.25	11.3	n.d.	5.07	6.45	0.014	4.59	10.2	n.d.	n.d.
Khasyrei	5th	65°45′31.50″ N	75°31′03.00″ E	0.01	0.5	11.7	9.80	5.72	4.50	0.015	1.72	7.60	1.66	0.12
Khasyrei	5th	65°45′31.50″ N	75°31′03.00″ E	0.01	1.25	11.5	8.80	5.59	n.d.	0.011	1.90	9.20	n.d.	n.d.

sulfate and metal analyses. Aliquots for nutrient analyses were kept frozen until analysis; aliquots for sulfate analysis were stored at 4 °C; aliquots for metals and metalloids measurements were acidified (pH~1; HNO₃ ultrapure double-distilled 1 %) and stored in acid-cleaned tubes at 4 °C. Subsequently, the cores were sliced in thin horizontal sections with a plastic cutter. A decreasing vertical resolution of slicing was applied: from 10-mm resolution below the WSI to 40-mm resolution down to the bottom of the core. The length of the cores ranged from 15 to 34 cm. All the samples were collected in acid-cleaned vials and centrifuged in the field at 4000 r.p.m. to retrieve porewater. For each sample, the supernatant (i.e. porewater) was processed and stored as for bottom water samples. The sediment samples were then sealed in double sampling-bags. In the laboratory, sediment samples were freeze-dried to constant weight and then powdered and homogenized with a manual agate mortar.

3.2 Analyses

Freeze-dried sediments were subjected to two different treatments. Total digestion was performed with HF+HNO₃+H₂O₂ using a high pressure microwave accelerated reaction system (MARS model of CEM Corporation[®]) equipped with an XP-1500 plus Liner system for 20 minutes at 150 °C following a modified digestion protocol from the US Environmental Protection Agency (EPA 3052). Each batch of samples included method blanks and digestion of certified international reference material (LKSD01 & LKSD03). Sediments were also subjected to selective extraction to extract Mn oxides and to separate the most reactive Fe oxide fraction (i.e. amorphous oxides) from crystalline Fe oxides, such as goethite, hematite and magnetite that are probably detrital and less reactive (Canfield, 1989). Manganese oxides and reactive Fe oxides were extracted by an ascorbate reagent consisting of a 5:5:2 sodium citrate/sodium bicarbonate/ascorbic acid mixture (e.g. Anschutz et al., 2000; Kostka and Luther III, 1994).

Alkalinity and DOC from the water column samples were analysed using methods routinely used in our laboratory for analysis of boreal organic-rich water samples (Pokrovsky et al., 2010; Vasyukova et al., 2010). Briefly, Alkalinity was measured by potentiometric titration with HCl by automated titrator (Metrohm 716 DMS Titrino) using a Gran method with a detection limit of 10⁻⁵ M and an uncertainty of 2 %. DOC was analysed using a Carbon Total Analyzer (Shimadzu TOC 5000) with an uncertainty better than 3 %. N-species (NO₂, NO₃), sulphate and phosphate in bottom and porewaters were measured by ion chromatography (HPLC, Dionex ICS 2000) with an uncertainty of 2 %. Element concentrations in bottom and porewater and from total digestion were measured using a quadrupole ICP-MS 7500ce (Agilent Technologies). Analytical drift was controlled and calibrated by an internal Re-In standard. Regardless of the digestion technique, accuracy was within 5 % of the certified values and the analytical error (relative standard deviation) was better than 5 % for concentrations 10 times higher than the detection limits. Iron and Mn concentrations from ascorbate extractions were measured by flame AAS (Perkin-Elmer Analyst 400) using calibration standards prepared with the same matrix as the extraction solution. Particulate organic carbon (POC) and total sulfur (S_{tot}) were measured directly from the dry, powdered and homogenized material using a carbon/sulfur analyzer (Horiba Jobin Yvon Emia-320V C/S Analyzer) and according to Cauwet et al. (1990). Method accuracy was determined by certified C and S certified reference materials HOR-007, JSS242-11 and HC16024. All analyses accuracy was within 2 % of the certified values and reproducibility generally better than 5 % r.s.d.

3.3 Diffusive fluxes calculation

Diffusive fluxes (J_{xi}) through the WSI in the three lakes were estimated using the Fick's first law:

$$J_{xi} = -\phi D_{sed} \left(\frac{\partial C}{\partial z} \right) \quad (1)$$

where, J_{xi} (μmol cm⁻⁴) is the diffusive flux, ϕ porosity, D_{sed} is the diffusive coefficient in sediment and $\partial C/\partial z$ is

the linear concentration gradient through the WSI. Porosity was estimated assuming an average particle density (ρ) of 0.2 g cm^{-3} and measured water content; ρ was estimated assuming that investigated sediments are mainly now-flooded former peat and using the simple linear regression model of Sheng et al. (2004). D_{sed} was corrected for temperature and tortuosity according to Boudreau (1997). However, D_{sed} was not corrected for any random transport mechanism such as biodiffusion, gas ebullition or wave-induced mixing. Regarding As and Sb, D_{sed} was estimated using the molecular self-diffusion coefficient (D_0) for the arsenate (Widerlund and Ingri, 1995) and antimonate species. Positive J_{xi} indicates an upward-directed flux (efflux from the sediment into the overlying water column) and negative J_{xi} indicates a downward-directed flux (influx from the water column into the sediment). Taking into account that the lakes' water column is frozen from mid-October to mid-May in the studied region, annual rates of diffusive transport through the WSI (expressed in $\mu\text{mol cm}^2 \text{ yr}^{-1}$) were integrated over the ice-free period of 152 days.

4 Results

4.1 Particulate phase

4.1.1 Particulate organic carbon and total sulfur

Particulate organic carbon concentrations range from 3.6 to 31 % and contribute at least for 95 % of the total carbon present in the investigated sediments (Fig. 3). The POC concentration-depth profile in actively growing Lake Shirokoe (3rd stage) exhibits a wide range of concentrations (3.6 % to 31 %) and can be divided in two parts: the 'organic' part of the sediment (the first 25 cm) with POC concentrations averaging 27.3 ± 4.1 % and the "mineral" part of the sediment (from 25 cm of depth to the bottom of the core) with POC concentrations drastically dropping to 3.6 % (Fig. 3a). The "organic" part of Lake Shirokoe's sediment likely represents the former and now-flooded peat. Its thickness is in agreement with peat depth as low as 25–30 cm reported in this region (Kremenetski et al., 2003) and our unpublished data from the chemical composition of a peat column sampled in a palsa site adjacent to Lake Shirokoe. Mature Lake Yamsovey (4th stage) and drained Lake Khasyrei (5th stage) show lower and less-variable POC concentrations (24.7 ± 0.9 % and 16.9 ± 2.1 %, respectively; Fig. 3b and c). The boundary between 'organic' and "mineral" sediments in both latter lakes is below the maximum depth of our sampling. Actively growing Lake Shirokoe (3rd stage) shows higher and more variable S_{tot} concentrations (0.58 ± 0.12 %; Fig. 3a) compared to both other lakes (0.23 ± 0.01 %; Fig. 3b and c). For all the three lakes, the S_{tot} profiles mimic relatively well the POC profiles, in agreement with the well-known association of sulfur with OM in freshwater sedi-

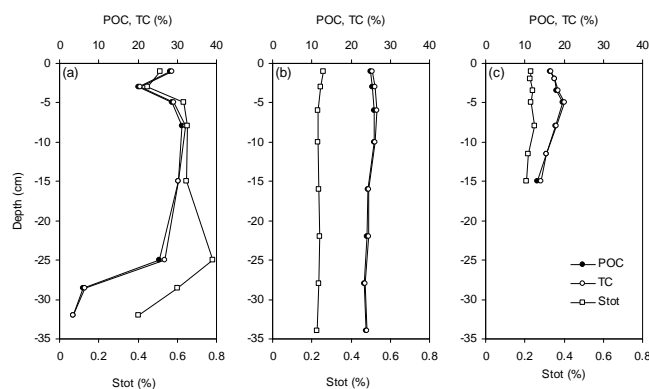


Fig. 3. Concentration-depth profiles of total carbon (TC) and sulphur (Stot), and particulate organic carbon (POC) in the sediments of (a) Lake Shirokoe (3rd stage of the thermokarst life cycle), (b) Lake Yamsovey (4th stage), and (c) Lake Khasyrei (5th stage).

ments (Holmer and Storkholm, 2001). However, the increase of S_{tot} from 0.68 % to 0.78 % observed in the 15–25 cm depth interval in Lake Shirokoe (Fig. 3a) is not mimicked by the POC profile and suggests an authigenic source of particulate sulfur (see Sect. 5.1. below).

4.1.2 Particulate Fe and Mn

Particulate Fe and Mn average concentrations increase from actively growing Lake Shirokoe (3rd Stage; Fe: $214 \pm 22 \text{ mmol kg}^{-1}$; Mn: $2.7 \pm 0.3 \text{ mmol kg}^{-1}$; Figs. 4a and 5a, Table 2) to mature Lake Yamsovey (4th Stage; Fe: $252 \pm 14 \text{ mmol kg}^{-1}$; Mn: $3.2 \pm 0.2 \text{ mmol kg}^{-1}$; Figs. 4b and 5b) and to drained Lake Khasyrei (5th Stage; Fe: $287 \pm 29 \text{ mmol kg}^{-1}$; Mn: $3.9 \pm 0.1 \text{ mmol kg}^{-1}$; Figs. 4c and 5c). The average Fe concentration in the three thermokarst lake sediments are two times higher than that reported for peat soils in Western Siberia (95 mmol kg^{-1} ; Moskovchenko, 2006), indicating a strong Fe enrichment in thermokarst lake sediment compared to peat soil. As for Mn, average concentrations in thermokarst lake sediments are similar to that typically observed in Western Siberia peat soils (3.3 mmol kg^{-1} ; Moskovchenko, 2006) but lower than that reported for river bottom sediments from the same region (8.6 mmol kg^{-1} ; Sorokina et al., 2006). The increase of average Fe and Mn particulate concentrations in the three thermokarst lake sediments in the course of the ecosystem development is accompanied by a decrease of the average contribution of ascorbate-extractable Fe (Fe_{asc}) and Mn (Mn_{asc}) from 37 % and 48 %, respectively, in Lake Shirokoe to 20 % (Fe_{asc}) and 34 % (Mn_{asc}) in Lake Khasyrei (Figs. 4 and 5). Mature Lake Yamsovey (4th stage) shows rather flat-shaped concentration-depth profiles for both Fe and Mn (Figs. 5b and 6b) while the two other lakes show more variable Fe and Mn concentrations. Iron shows contrasted behaviors in the first five centimeters below the WSI

Table 2. Average particulate concentrations (dry weight) and standard deviations of Fe and Mn (mmol kg^{-1}) and trace metals and metalloids ($\mu\text{mol kg}^{-1}$) in the sediments of Lake Shirokoe, Lake Yamsovey and Lake Khasyrei.

Lake	Fe	Mn	Co	Ni	Cu	Zn	As	Cd	Sb	Pb
Shirokoe	214 ± 22	2.7 ± 0.3	100 ± 15	252 ± 13	132 ± 22	380 ± 71	53 ± 9	1.3 ± 0.5	1.4 ± 1.0	35 ± 5
Yamsovey	266 ± 14	3.2 ± 0.2	109 ± 7	340 ± 22	217 ± 18	507 ± 69	49 ± 4	1.2 ± 0.1	2.2 ± 1.0	40 ± 2
Khasyrei	287 ± 29	3.9 ± 0.1	138 ± 11	408 ± 42	240 ± 28	549 ± 63	57 ± 8	1.3 ± 0.2	2.9 ± 1.1	50 ± 4

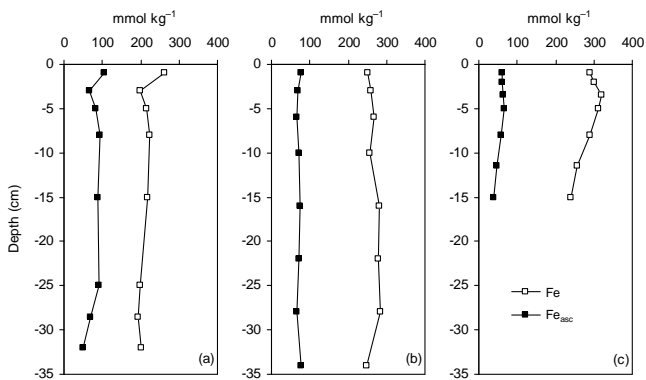


Fig. 4. Concentration-depth profiles of total Fe and ascorbate-extractable Fe (Fe_{asc}) in the sediments of (a) Lake Shirokoe (3rd stage), (b) Lake Yamsovey (4th stage), and (c) Lake Khasyrei (5th stage).

with a decrease (from 262 to 199 mmol kg^{-1}), accompanied with decreasing Fe_{asc} concentrations, in actively growing Lake Shirokoe (Fig. 4a) and an increase (from 288 to 321 mmol kg^{-1}) in drained Lake Khasyrei (Fig. 4c). Within the same depth interval, Mn shows increasing concentrations for both lakes (Fig. 5a and c). The “mineral” part of Lake Shirokoe sediments is characterized by decreasing both Fe_{asc} and Mn_{asc} concentrations and contributions (Figs. 4a and 5a). Total Fe is correlated to POC ($R^2 = 0.84$, $n = 7$) in Lake Khasyrei sediments but not in the two other lakes and total Mn does not show any correlation with POC in any of the three lakes.

4.1.3 Particulate trace metals and metalloids

Particulate trace metals and metalloids show increasing average concentrations (Table 2), with the exception of As and Cd that are more or less constant, from the third stage (actively growing Lake Shirokoe) to the fifth stage (drained Lake Khasyrei). These average particulate concentrations are 2–8 times higher than those reported for typical peat soils from Western Siberia (Co: 71.3 $\mu\text{mol kg}^{-1}$, Ni: 115.9 $\mu\text{mol kg}^{-1}$, Cu: 77.1 $\mu\text{mol kg}^{-1}$, Zn: 272.2 $\mu\text{mol kg}^{-1}$, Cd: 0.36 $\mu\text{mol kg}^{-1}$, Pb: 23.2 $\mu\text{mol kg}^{-1}$, As: 6.9 $\mu\text{mol kg}^{-1}$, Sb: 1.7 $\mu\text{mol kg}^{-1}$; Moskovchenko, 2006; Stepanova, 2011).

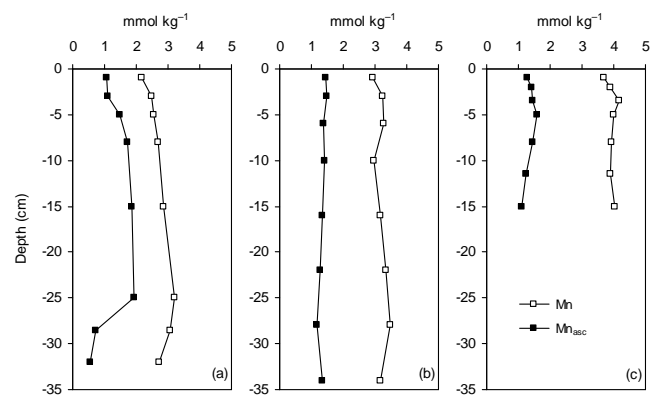


Fig. 5. Concentration-depth profiles of total Mn and ascorbate-extractable Mn (Mn_{asc}) in the sediments of (a) Lake Shirokoe (3rd stage), (b) Lake Yamsovey (4th stage), and (c) Lake Khasyrei (5th stage).

In Lake Shirokoe and Lake Yamsovey, particulate concentrations of Co, Ni, Cu, Zn and Pb do not show any pronounced trend with depth (Fig. 6a and b). Antimony profiles are similar in both lakes showing a concentration peak at 3-cm depth followed by more or less constant concentrations downward. Decreasing concentrations are observed for As (from 68 to 39 $\mu\text{mol kg}^{-1}$) and Cd (from 1.7 to 0.5 $\mu\text{mol kg}^{-1}$) in Lake Shirokoe while being fairly constant in Lake Yamsovey. In drained Lake Khasyrei (Fig. 6c), trace metals and metalloids can be divided in two groups: (i) Co, Ni, Cu, Zn and As showing concentration–depth profiles very similar to that of Fe with first an increase of concentrations in the three first centimeters below the WSI and then a decrease; (ii) Cd, Sb and Pb showing steady concentration decrease with depth, particularly Sb dropping from 5.1 $\mu\text{mol kg}^{-1}$ below the WSI to 1.8 $\mu\text{mol kg}^{-1}$ at the bottom of the core. From the young (3rd) to the final (5th) stage of lake development, an increasing number of trace elements are associated with Fe ($R^2 \geq 0.7$) (Table 3): Cu (actively growing Lake Shirokoe), Co, Ni, Cu (mature Lake Yamsovey), and Co, Ni, Cu, Zn and As (drained Lake Khasyrei). In contrast, only Co in Lake Shirokoe and Pb in Lake Yamsovey show significant association with Mn.

4.2 Porewater

4.2.1 Phosphate, N-species and sulfate

The sediments of the three lakes show similar convex-shaped profiles depicting the release of dissolved phosphate and nitrite in porewater (Fig. 7). A drastic decrease of nitrate concentration in the bottom water is observed from Lake Shirokoe (29.7 μM) to Lake Khasyrei (0.8 μM). Sharply decreasing nitrate concentrations (i.e. nitrate consumption) just below the WSI are observed in the former while increasing in Yamsovey and Khasyrei Lakes (Fig. 7). Dissolved sulfate concentration in the bottom water drops by one order of magnitude from actively growing Lake Shirokoe (30.8 μM) to mature Lake Yamsovey (4.0 μM). All the three lakes show concave-shaped sulfate profiles indicating first dissolved sulfate consumption below the WSI and production deeper in the sediment. According to diffusive fluxes calculation (Table 4), sediments of the three lakes are a sink of dissolved sulfate. In contrast, sediments are a source of nitrite (all three lakes) and nitrate (Yamsovey and Khasyrei) for the overlying water column. Only the sediments of actively growing Lake Shirokoe represent a sink of nitrate.

4.2.2 Dissolved Fe and Mn

Iron concentrations in bottom water are always higher than those observed in surface water (Table 1 and Fig. 7). All the three lakes show fairly similar profiles depicting first Fe production just below the WSI and Fe consumption deeper in the sediment. Manganese concentrations in bottom water decrease from Lake Shirokoe (0.9 μM) to Lake Khasyrei (0.2 μM). Manganese profiles are similar to that of Fe in Lake Yamsovey and Lake Khasyrei suggesting similar behavior in the sediment at the mature stage of lake development. In actively growing Lake Shirokoe, dissolved Mn behavior differs from that of Fe just below the WSI with decreasing concentrations while mimicking Fe behavior deeper in the sediment. In all the three lakes, the sediments are a source of dissolved Fe for the overlying water column (Table 4). Similarly, efflux of Mn from the sediment into the overlying water column is observed for mature Lake Yamsovey and drained Lake Khasyrei while the sediments of actively growing Lake Shirokoe represent a sink of dissolved Mn.

4.2.3 Dissolved trace metals and metalloids

Trace metals and metalloids in porewater show variable profiles between the three lakes. In actively growing Lake Shirokoe (Fig. 8a), trace metals and metalloids can be divided in two groups: (i) Cu, Zn, Cd, Sb and Pb that show sharply decreasing concentrations just below the WSI, and (ii) Co, Ni and As that are characterized by increasing (As and Ni) or nearly constant (Co) concentration below the WSI and then decreasing concentrations toward the bottom of the core. In mature Lake Yamsovey (Fig. 8b), Co and Ni are character-

ized by profiles very similar to that of Fe and Mn. The other trace elements show concentration peaks more (As) or less (Cd) pronounced and at different depths in the sediment. In drained Lake Khasyrei (Fig. 8c), and similarly to mature Lake Yamsovey, Co and Ni profiles mimic that of Fe and Mn. Trace metals and metalloids, exception made of Zn, show a peak at 5-cm depth, which is the same depth where the maximum Fe and Mn dissolved concentrations are observed (Fig. 7c). Diffusive transport through the WSI indicates that the sediments are either a source or a sink of dissolved trace metals and metalloids depending on both the considered element and lake (Table 4). For all the three lakes, there is an efflux from the sediment into the overlying water column of Co, Ni and As. The sediments of mature Yamsovey and drained Khasyrei are a source of dissolved Sb to the overlying column while being a sink of Sb in actively growing Lake Shirokoe. Zinc, Cd, Pb and Cu are characterized by influx from the water column into the sediments in the three lakes, except for Zn, Cd and Cu in mature Lake Yamsovey where the efflux from the sediment into the water column are observed for these three latter trace metals.

5 Discussion

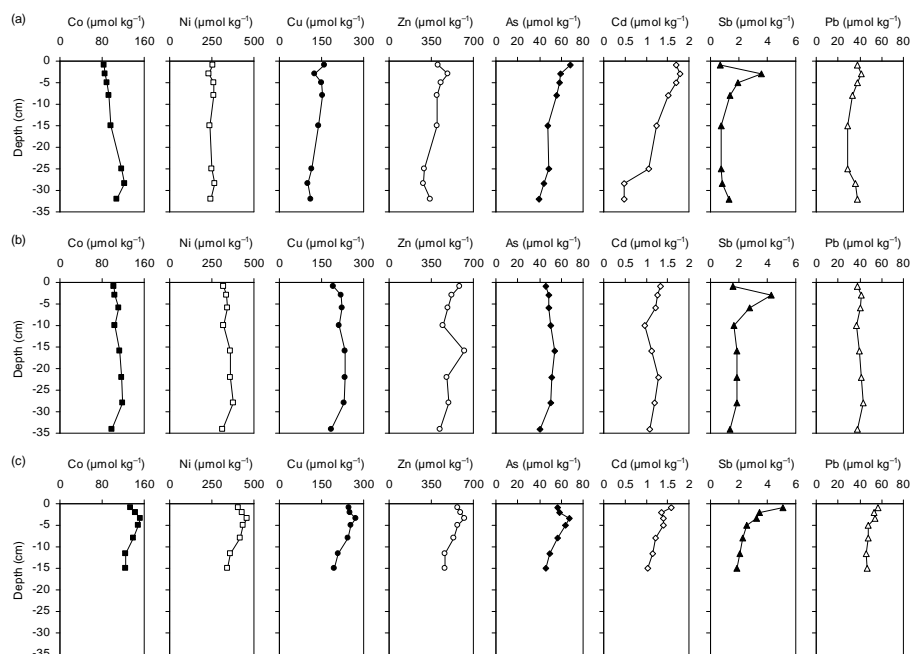
5.1 Carbon stock in the sediments

Peat organic material is characterized by carbon content typically of 52 %, regardless peat type and location: 51.8 ± 2.5 % in Western Siberian lowlands (Lapshina and Pologova, 2001) and 51.8 ± 4.7 % in Western Canada (Vitt et al., 2000). Mean POC concentrations observed in the sediments (i.e. former peat) investigated in this study are significantly lower (<30 %; Fig. 3). Taking into account a 25-cm thickness of organic sediment, a mean POC concentration of 27.3 ± 4.1 % and a dry density of the sediment of 0.2 g cm^{-3} (see Sect. 3.3), we roughly estimated the OC stock in the sediments of actively growing Lake Shirokoe to be $14 \pm 2 \text{ kg m}^{-2}$. This OC stock is significantly lower than that reported by Kortelainen et al. (2004) for Finnish boreal lakes ($\sim 40 \text{ kg m}^{-2}$) of size comparable to that of Lake Shirokoe and is rather similar to that exhibited by larger lakes with size up to 100 km^2 . It is also much more lower than the typical OC stock of 105 kg m^{-2} reported for peat soils from the same region (Sheng et al., 2004), therefore indicating that about 87 % of the OM previously sequestered in peat soil prior thawing and flooding has been mineralized at this stage of the thermokarst lake development. Additionally, we observed a significant decrease of mean POC concentration in the course of lake maturation (i.e. from the 3rd to the 5th stage), dropping as low as 17 % in the sediments of drained Lake Khasyrei, which corresponds to a rate of OC loss of ~ 70 % compared to the peat soil. This suggests the intense OM mineralization in the sediments during the course of lake development (maturation).

Table 3. Correlation coefficients (R^2) between particulate trace elements and Fe and Mn in the sediments of Lake Shirokoe, Lake Yamsovey and Lake Khasyrei.

Lake		Co	Ni	Cu	Zn	As	Cd	Sb	Pb
Shirokoe	Fe	0.43	0.05	0.71	0.13	0.51	0.3	0.09	<0.01
	Mn	0.76	<0.01	0.51	0.57	0.06	0.42	0.11	0.04
Yamsovey	Fe	0.91	0.96	0.82	0.10	0.64	0.02	<0.01	0.58
	Mn	0.54	0.59	0.35	0.06	0.04	0.09	0.07	0.89
Khasyrei	Fe	0.94	0.98	0.98	0.89	0.96	0.55	0.19	0.30
	Mn	0.17	0.06	0.01	0.02	0.11	0.13	0.34	0.09

$R^2 \geq 0.7$ in bold

**Fig. 6.** Concentration–depth profiles of trace metals and metalloids in the sediments of (a) Lake Shirokoe (3rd stage), (b) Lake Yamsovey (4th stage), and (c) Lake Khasyrei (5th stage).

5.2 Early diagenesis processes and organic matter mineralization pathways

In addition to the OM present in the former and now-flooded peat, early diagenesis processes in the thermokarst lake sediments investigated here are mainly fueled by OM inputs at the WSI from peat lixiviation in the lake's border. In the course of lake maturation, lake's border stabilization drastically decreases the OM inputs into the lake (Fig. 2), leaving early diagenesis processes to feed on OM originating from the weak primary production in the water column (Shirokova et al., 2009) and the (refractory) OM remaining in the sediments. In addition, with the increase of thermokarst lake size, there is a decreasing input of soil and peat-derived OM into the lake water due to a larger water body in rela-

tion to the length of the shoreline. Sediment redox stratification and early diagenesis processes, presumably driven by microbially-mediated OM mineralization, can be inferred from porewater concentration–depth profiles. In contrast to the water column of these thermokarst lakes, where aerobic respiration of heterotrophic bacterioplankton consumes the DOM, releasing CO_2 to the atmosphere (Shirokova et al., 2009; Pokrovsky et al., 2011), in the investigated sediments, OM mineralization proceeds mainly through anaerobic reactions. Sulfate reduction and reductive dissolution of Fe-oxyhydroxides are suggested by decreasing dissolved sulfate concentrations and increasing dissolved Fe concentrations just below the WSI in the three lakes (Fig. 7). In these sediments, microbial reductive dissolution of Fe-oxyhydroxides

Table 4. Diffusive transport through the water-sediment interface in the three studied lakes.

	NO ₃	NO ₂	SO ₄	Fe	Mn	Zn	Cd	Pb	Cu	Co	Ni	As	Sb
Shirokoe (3rd stage)													
D_{sed} (cm ² s ⁻¹)	4.18×10^{-6}	4.24×10^{-6}	2.25×10^{-6}	1.51×10^{-6}	1.48×10^{-6}	1.51×10^{-6}	1.51×10^{-6}	2.02×10^{-6}	1.56×10^{-6}	1.51×10^{-6}	1.46×10^{-6}	1.76×10^{-6}	1.27×10^{-6}
$\partial C/\partial z$ ($\mu\text{mol cm}^{-2}$)	2.47×10^{-2}	-5.13×10^{-4}	5.39×10^{-3}	-4.59×10^{-3}	2.60×10^{-4}	1.87×10^{-4}	2.49×10^{-6}	3.98×10^{-5}	3.33×10^{-5}	-1.52×10^{-6}	-6.45×10^{-6}	-1.62×10^{-5}	2.14×10^{-7}
J_{xi} ($\mu\text{mol cm}^{-2} \text{s}^{-1}$) ^a	-3.76×10^{-8}	7.95×10^{-10}	-4.43×10^{-9}	2.52×10^{-9}	-1.40×10^{-10}	-1.03×10^{-10}	-1.37×10^{-12}	-2.93×10^{-11}	-1.89×10^{-11}	8.39×10^{-13}	3.43×10^{-12}	1.04×10^{-11}	-9.92×10^{-14}
J_{xi} ($\mu\text{mol cm}^{-2} \text{yr}^{-1}$) ^b	-4.94×10^{-1}	1.04×10^{-2}	-5.82×10^{-2}	3.31×10^{-2}	-1.84×10^{-3}	-1.35×10^{-3}	-1.80×10^{-5}	-3.84×10^{-4}	-2.48×10^{-4}	1.10×10^{-5}	4.51×10^{-5}	1.37×10^{-4}	-1.30×10^{-6}
Yamsovey (4th stage)													
D_{sed} (cm ² s ⁻¹)	4.96×10^{-6}	5.04×10^{-6}	2.67×10^{-6}	1.79×10^{-6}	1.76×10^{-6}	1.79×10^{-6}	1.80×10^{-6}	2.39×10^{-6}	1.85×10^{-6}	1.80×10^{-6}	1.73×10^{-6}	2.09×10^{-6}	1.51×10^{-6}
$\partial C/\partial z$ ($\mu\text{mol cm}^{-2}$)	-2.22×10^{-3}	-2.30×10^{-3}	7.90×10^{-4}	-2.26×10^{-2}	-9.30×10^{-4}	-8.81×10^{-6}	-8.14×10^{-8}	3.00×10^{-6}	-2.58×10^{-6}	-2.11×10^{-5}	-2.28×10^{-5}	-3.04×10^{-5}	-2.83×10^{-8}
J_{xi} ($\mu\text{mol cm}^{-2} \text{s}^{-1}$) ^a	5.10×10^{-9}	5.37×10^{-9}	-9.78×10^{-10}	1.87×10^{-8}	7.56×10^{-10}	7.31×10^{-12}	6.77×10^{-14}	-3.32×10^{-12}	2.21×10^{-12}	1.75×10^{-11}	1.83×10^{-11}	2.95×10^{-11}	1.98×10^{-14}
J_{xi} ($\mu\text{mol cm}^{-2} \text{yr}^{-1}$) ^b	6.70×10^{-2}	7.05×10^{-2}	-1.28×10^{-2}	2.46×10^{-1}	9.93×10^{-3}	9.60×10^{-5}	8.89×10^{-7}	-4.37×10^{-5}	2.90×10^{-5}	2.30×10^{-4}	2.40×10^{-4}	3.87×10^{-4}	2.60×10^{-7}
Khasyrei (5th stage)													
D_{sed} (cm ² s ⁻¹)	4.22×10^{-6}	4.28×10^{-6}	2.27×10^{-6}	1.52×10^{-6}	1.49×10^{-6}	1.52×10^{-6}	1.53×10^{-6}	2.03×10^{-6}	1.57×10^{-6}	1.53×10^{-6}	1.47×10^{-6}	1.78×10^{-6}	1.28×10^{-6}
$\partial C/\partial z$ ($\mu\text{mol cm}^{-2}$)	-1.00×10^{-3}	-2.38×10^{-3}	3.43×10^{-3}	-1.73×10^{-2}	-6.70×10^{-4}	9.24×10^{-5}	9.70×10^{-8}	2.51×10^{-6}	4.19×10^{-6}	-2.00×10^{-5}	-3.03×10^{-5}	-4.44×10^{-5}	-2.33×10^{-8}
J_{xi} ($\mu\text{mol cm}^{-2} \text{s}^{-1}$) ^a	1.56×10^{-9}	-2.88×10^{-9}	-2.88×10^{-9}	9.75×10^{-9}	3.70×10^{-10}	-5.20×10^{-11}	-5.48×10^{-14}	-1.89×10^{-12}	-2.43×10^{-12}	1.13×10^{-11}	1.65×10^{-11}	2.93×10^{-11}	1.11×10^{-14}
J_{xi} ($\mu\text{mol cm}^{-2} \text{yr}^{-1}$) ^b	2.05×10^{-2}	4.95×10^{-2}	-3.79×10^{-2}	1.28×10^{-1}	4.86×10^{-3}	-6.83×10^{-4}	-7.19×10^{-7}	-2.48×10^{-5}	-3.20×10^{-5}	1.48×10^{-4}	2.16×10^{-4}	3.84×10^{-4}	1.45×10^{-7}

^a Diffusive fluxes were calculated using Fick's first law: $J_{xi} = -\phi D_{sed}(\partial C/\partial z)$, where D_{sed} is the diffusion coefficient corrected for temperature and tortuosity, ϕ is porosity (Shirokoe: 0.36; Yamsovey: 0.46; Khasyrei: 0.37) assuming an average sediment density of 0.2 g cm^{-3} and measured water content, and $\partial C/\partial z$ is the linear concentration gradient across the water-sediment interface. Positive J_{xi} indicates an upward-directed flux (efflux from the sediment into the overlying water column) and negative J_{xi} indicates a downward-directed flux (influx from the water column into the sediment).

^b Annual rates of diffusive transport were integrated over the ice-free 152 days.

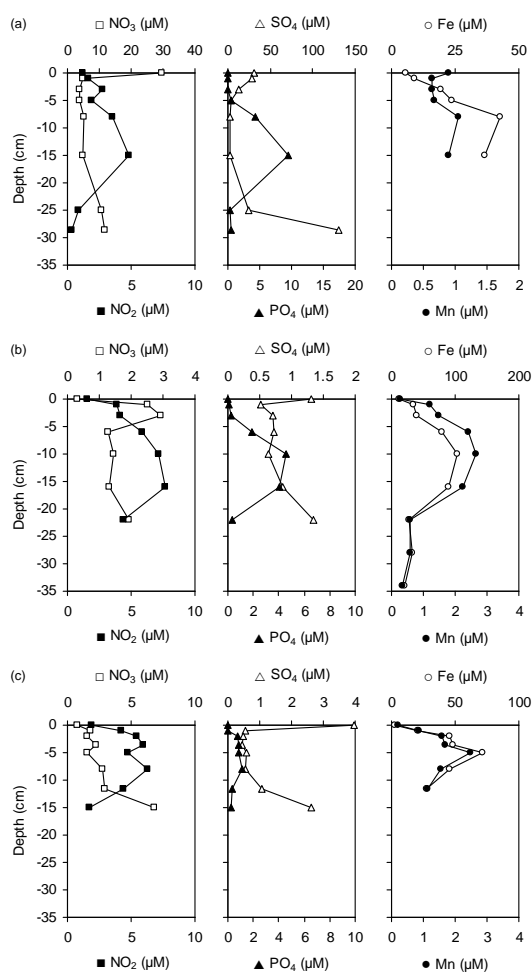


Fig. 7. Concentration–depth profiles for N-species, sulfate, phosphate, Fe and Mn in the porewater of Lake Shirokoe (a), Lake Yamsovey (b) and Lake Khasyrei (c).

is likely stimulated by humic matter (Jones et al., 2000; Thamdrup, 2000). Such humic compounds are likely abundant in the porewater as originated from the lixiviation of the lakes' border peat. Accordingly, Pokrovsky et al. (2011) observed high degrees of OC humification in the water column of these lakes. In the 3rd stage (actively growing Lake Shirokoe), there is no evidence of redox control on Mn chemistry as supported by the absence of dissolved Mn increase below the WSI (Fig. 7a). This result contrasts with the pivotal role of Mn on redox processes and element redistribution suggested for a large subarctic lake (Lake Imandra) by Ingri et al. (2011). Manganese behavior in Lake Shirokoe is in accordance with reported Mn behavior in acidic lakes ($\text{pH} < 5.5$; Huerta-Diaz et al., 1998). However, reductive dissolution of Mn-oxyhydroxides is suggested in the mature 4th (Lake Yamsovey) and the terminal, drained 5th (Lake Khasyrei) stages, by increasing dissolved Mn concentrations below the WSI. This is likely favored by water column higher pH compared to the 3rd stage (almost two pH units, see Table 1). Reductive dissolution of Fe- and Mn-oxyhydroxides is further supported by the observed decrease of Fe_{asc} and Mn_{asc} contribution in the course of thermokarst lake maturation (see above). As a result of reductive dissolution of Fe-oxyhydroxides and subsequent upward-directed diffusive transport (Table 4), dissolved Fe accumulates above the WSI of the three lakes, as evidenced by higher concentrations in bottom water than in surface water (Fig. 7 and Table 1). This could indicate that either the bottom water very close to the WSI is oxygen-depleted due to heterotrophic microbial respiration of OC (as reported for the same lakes by Shirokova et al. (2009) or Fe(III) remains in the colloidal phase, even in oxygenated bottom water, being stabilized by dissolved organic matter (Pokrovsky et al., 2011). Deeper in the sediments of the three lakes, dissolved Fe and Mn are removed from porewater (Fig. 7) most likely due to precipitation of authigenic Fe sulfides and/or adsorption on inorganic or organic

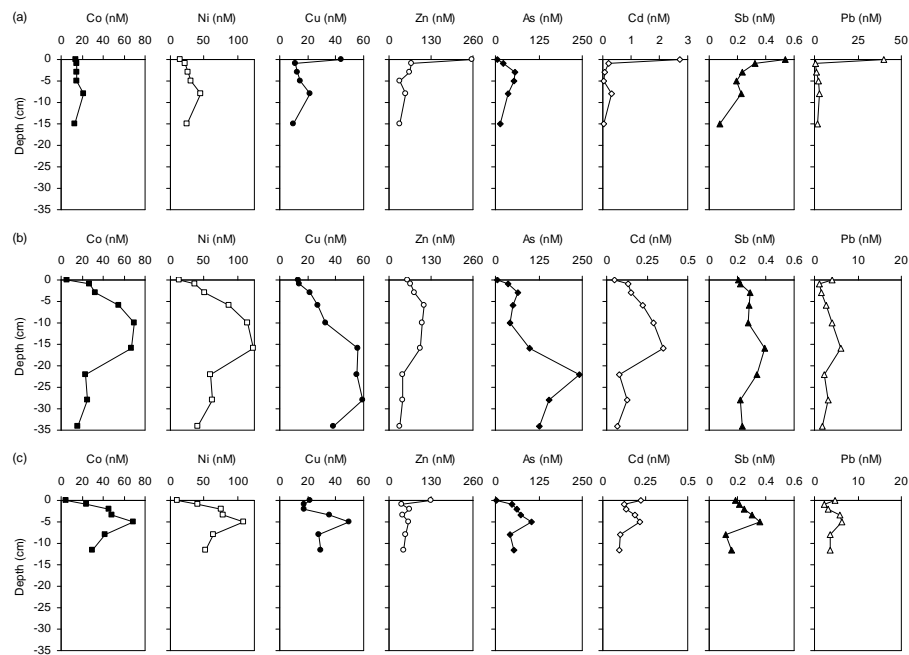


Fig. 8. Concentration–depth profiles for trace elements in the porewater of Lake Shirokoe (a), Lake Yamsvey (b) and Lake Khasyrei (c).

particulates as reported for other freshwater environments (Davison, 1993; Audry et al., 2010).

Denitrification, as evidenced by decreasing nitrate concentration below the WSI, also contributes to OM degradation, apparently only in the initial, 3rd stage of lake growth (Fig. 7a). In the 4th (mature) and 5th (drained) stages, denitrification is not evidenced (Fig. 7b and c). On the contrary, nitrate is produced (anaerobic nitrification), likely through the reduction of Mn-oxyhydroxides by ammonium (Hulth et al., 1999; Hyacinthe et al., 2001). While ammonium concentrations were not determined in this study, ammonium should likely be present in porewater as being produced by OM mineralization processes such as reductive dissolution of Fe-oxyhydroxides and sulfate reduction (Hyacinthe et al., 2001). It is therefore possible that little denitrification actually occurs in the 4th and 5th stages while being masked by higher rates of anaerobic nitrification. Slow anaerobic nitrification is suggested by the nitrate profile in the sediments of Lake Shirokoe (Fig. 7). This could be related to slow nitrification in relation to slow oxidation of ammonium at low pH (Mihelcic, 1999). Nitrite production is observed at depth in the three lakes and likely results from anaerobic ammonium oxidation mediated by Mn- and/or Fe-oxyhydroxides (Clément et al., 2005; Javanaud et al., 2011). Dissolved phosphate is produced at depth in the sediment of the three lakes (Fig. 7) as a by-product of OM mineralization being most likely released during reductive dissolution (Koretsky et al., 2006) of Fe-oxyhydroxides, for which it has a strong affinity (Dzombak and Morel, 1990).

All the above observations suggest a shift of OM degradation pathways in the course of the life cycle of thermokarst lakes driven by the progressive exhaustion of terminal electron acceptor pools. In the 3rd stage of actively growing lake, denitrification, reductive dissolution of Mn- and Fe-oxyhydroxides and sulfate reduction are likely the prevailing pathways of OM mineralization. In contrast, at the final, 5th stage, Fe- and Mn-oxyhydroxides dissolution becomes the dominant process. Electron acceptors such as nitrate and sulfate available at the WSI for OM mineralization mainly originate from peat lixiviation at the lake's borders. As the lake's border stabilizes during the transition from the 3rd stage to the 4th stage (Fig. 2), nitrate and sulfate inputs at the WSI drastically decrease, leading to the progressive exhaustion of these terminal electron acceptors until the final, 5th stage of lake evolution. Nitrification and sulfide oxidation caused by oxygenated surface or ground water circulation at depth (see Sect. 5.3 below) and the subsequent upward-directed diffusive transport of nitrate and sulfate (Table 4) are not sufficient to regenerate the depleted pools. Therefore, in the course of the life cycle of thermokarst lakes, reductive dissolution of Fe- and Mn-oxyhydroxides likely becomes the prevalent OM mineralization pathway. Accordingly, reactive Fe- and Mn-oxyhydroxides become progressively depleted, as evidenced by the decrease of Fe_{asc} and Mn_{asc} from the 3rd stage to the 5th stage (Fig. 4). This also suggests that the possible partial regeneration of the Fe- and Mn-oxyhydroxides due to oxygenated surface or ground water circulation at depth (see Sect. 5.3 below) is not enough to maintain such both pools during the course of the ecosystem maturation.

5.3 Transient redox conditions

Transient redox conditions, as evidenced, for instance, by significant Fe_{asc} and Mn_{asc} concentrations at depth in the anoxic sediment, are likely prevailing in the three lakes. These reactions are promoted by temporal change of element sources at the WSI: (i) decreasing allochthonous peat-derived OM fluxes due to lake's border stabilization; (ii) variable dissolved (OC, nutrients, Fe and Mn) and particulate (POC, Fe- and Mn-oxyhydroxides) input due to drainage of small and less-mature surrounding lakes, ponds and soil depressions towards larger lakes (Kirpotin et al., 2008); and (iii) seasonal ice and snow melting. In all the three lakes, transient redox conditions are likely to be further promoted by groundwater inputs at depth in the sediment. Boreal ponds and thermokarst lakes are typically influenced by groundwater lateral fluxes, shallow near-surface run-off and shallow water table (Price et al., 2005; Turner et al., 2010) that provide nutrient enrichment (Woo and Young, 2003). Particularly, sulfate enrichment could originate from pyrite weathering within the surrounding peat soils. While pyrite content in the peat soils surrounding the three thermokarst lakes was not determined, it has been reported that pyrite can be present in peat soils in fairly significant amounts (e.g. Dellwig et al. 2001). Therefore, the observed increase of dissolved sulfate and nitrate, along with a decrease of dissolved phosphate at depth in the three lakes (Fig. 7) are likely the consequence of the following groundwater-related processes: (i) direct inputs of dissolved nitrate and sulfate; (ii) oxidation of porewater and/or particulate sulfides by oxygenated groundwater; and (iii) dissolved phosphate dilution by phosphate-poor groundwater. Additionally, fast chemical oxidation of porewater dissolved sulfides by dissolved OM, as experimentally observed for organic-rich anoxic sediments by Heitmann and Blodau (2006), could also enhance the production of dissolved sulfate at depth in the sediment. Higher porewater sulfate enrichment in Lake Shirokoe compared to the two other lakes (Fig. 7) is in accordance with the likely higher pyrite weathering due to stronger lixiviation of the surrounding peat in this growing lake compared to the two other mature, non-growing lakes (see Sect. 2 and Fig. 2). Similarly, strong pyrite weathering and the associated production of sulfuric acid could partially explain the lower pH exhibited by Lake Shirokoe's water column compared to the two other lakes (Table 1). However, the concentration of H_2SO_4 in Lake Shirokoe's water column alone cannot explain the very low pH. Additional pH regulation is likely to be related to the concentration and the nature of DOC as evidenced from the study of the water column DOC along the chronosequence of thermokarst lake development (Pokrovsky et al., 2011).

5.4 Post-depositional redistribution of trace metals and metalloids

The early diagenesis processes discussed above prompt complex post-depositional redistribution of trace metals and metalloids through destabilization of carrier phases and eventually either mobilization or sequestration.

5.4.1 Cobalt and nickel

Pokrovsky et al. (2011) showed that in the water column of the three thermokarst lakes, Co and Ni are correlated with Fe and likely to be adsorbed and/or coprecipitated with Mn oxyhydroxides. Accordingly, in the sediments of the three lakes, the concentration-depth profiles of both dissolved trace metals mimic that of Fe and Mn, with the release of Co and Ni in the porewater occurring concomitantly to the release of Fe and Mn (Figs. 7 and 8). This strongly suggests that Co and Ni are delivered to the sediment being mainly associated with Fe- and/or Mn-oxyhydroxides particles. They are further released from these particles to the porewater when the carrier phases are reduced during OM mineralization. Deeper in the sediments, the removal of Co and Ni from the porewater concomitantly to Fe removal (Figs. 7 and 8) points to iron sulfide as a sink for Co and Ni. The link between Ni and Co cycles with that of Fe and Mn established in thermokarst lake sediment is in accordance with previous studies on temperate freshwater environments (Huerta-Diaz et al., 1998; Hamilton-Taylor et al., 2005).

5.4.2 Copper, zinc, cadmium and lead

The behavior of these four trace metals differs among the three lakes. In the actively growing Lake Shirokoe (3rd stage), the steep decrease of Cu, Zn, Cd and Pb dissolved concentrations just below the WSI (Fig. 8) suggests a sink for these trace metals at the depth of the sulfate reduction zone (i.e. dissolved sulfide production). The fact that this removal intervenes above the observed active layer (~8-cm depth) of Fe- and Mn-oxyhydroxides reductive dissolution (Fig. 7) points to the sequestration of Cu, Zn, Cd and Pb through the authigenic precipitation of their respective distinct sulfides rather than co-precipitation and/or sorption with iron sulfides. Such behavior was previously reported for other freshwater sediments (e.g. Huerta-Diaz et al., 1998). At depth, in the zone of dissolved Fe removal, the solubility of Cu, Zn, Cd and Pb is likely controlled by sorption and/or co-precipitation with iron sulfides. (Pokrovsky et al., 2011) reported association of Cu, Zn, Cd and Pb with DOC in the water column of Lake Shirokoe. Therefore, it is likely that release of these trace metals into the porewater occurs below the WSI during the mineralization of DOC. Similarly to actively growing Lake Shirokoe, authigenic precipitation of Cu-, Zn-, Cd- and Pb-sulfide is evidenced in the first centimeters of the sediments of drained Lake Khasyrei (Fig. 8c). In contrast, only

Pb seems to be involved in authigenic metal-sulfide precipitation in mature Lake Yamsovey (Fig. 8b). In both latter lakes (Fig. 8b and c), the observed zone of maximum porewater concentrations of Cu, Zn (except in Lake Khasyrei where no Zn release is observed), Cd and Pb is observed at the depth zone where Fe is also released. Mobilization of Cu, Zn, Cd and Pb is tentatively attributed to the destabilization of Fe-bounding particles (Fe sulfides or Fe-oxyhydroxides) during early diagenesis and the consequent release of the associated trace metals. The importance of this process is likely enhanced from the 3rd stage (actively growing Lake Shirokoe) to the final 5th stage (drained Lake Khasyrei) of lake development as the overall accumulation of Fe-bounding particles (and associated trace metals) at the WSI is likely increasing in the course of lake life cycle due to the progressive coagulation of Fe in the form of particles and large-size colloids (Pokrovsky et al., 2011). Similar to Co and Ni (see Sect. 5.4.1), removal of Cu, Zn, Cd and Pb at depth is assigned to adsorption and/or co-precipitation with Fe-sulfides. At the WSI, Cu, Zn, Cd and Pb are mainly associated with small-size microbial and phytoplankton exudates (small-size organic ligands), whose concentration increase from the 3rd to 5th stage of the lake development being linked to OM mineralization and increased phytoplankton activity in the water column (Pokrovsky et al., 2011). It is known that the DOC released by phytoplankton is highly prone to bacterial utilization (Chen and Wangersky, 1996). As a result, microbial degradation of metal-organic compounds in the sediments could facilitate the incorporation of these trace metals into Fe-sulfides during authigenesis. All this is consistent with the increased association of particulate Cu, Zn and Cd with Fe from the 3rd stage to the 5th stage (Table 3).

5.4.3 Arsenic and antimony

Iron- and Mn-oxyhydroxides and OM play a dominant role in the post-depositional redistribution of the metalloid elements As and Sb in the three studied lakes. Particulate As is likely to be provided to the WSI associated with Fe- and Mn-oxyhydroxides (Belzile and Tessier, 1990; Smedley and Kiniburgh, 2002) and phytoplankton debris (Seyler and Martin, 1989). Note the very low proportion (i.e. max. 10–15 %) of both As and Sb organic and mineral colloidal (1 kDa–0.45 μm) form in the water column of the three studied lakes (Pokrovsky et al., 2011). A shallow release ($\sim 3\text{-cm}$ depth) of As into porewater occurs above the suggested depth of reductive dissolution of Fe- and Mn-oxyhydroxides in actively growing Lake Shirokoe and mature Lake Yamsovey (Figs. 7 and 8). Masscheleyn et al. (1991) and Zobrist et al. (2000) reported from laboratory experiments that under reducing conditions part of As bound to Fe-oxyhydroxides was released before Fe implying reductive desorption from Fe-oxyhydroxides rather than reductive dissolution. Therefore, the shallow release of As in the sediments of Lake Shirokoe and Lake Yamsovey is attributed to both reductive des-

orption from Fe-oxyhydroxides and mobilization from OM upon oxidation. In drained Lake Khasyrei (5th stage), release of As is observed at the depth where reductive dissolution of Fe- and Mn-oxyhydroxides likely proceeds (Fig. 7 and 8c) and no shallow release of As is observed. The absence of As release into the dissolved phase above the Fe-oxyhydroxides reductive dissolution layer can be related to the progressive depletion in the course of the thermokarst lake life cycle of (i) labile OM and associated As and (ii) the As pool available for reductive desorption from Fe-oxyhydroxides. Therefore, in the more mature stages of the lake life cycle, Fe- and Mn-oxyhydroxides likely represent the main contributors for porewater As. Additionally, in all the three lakes, As release into porewater could be caused by reduction of As(V) to As(III) which is more soluble under reduced conditions. At depth, Fe-sulfides (amorphous and/or pyrite) likely play an important role in As sequestration by controlling its solubility as previously reported for other systems (Belzile, 1988; Couture et al., 2010). Evidence to that contention is the progressive association of particulate As with Fe from the 3rd to the 5th stage (Table 3). It is to note that in the three studied thermokarst lakes As concentrations in porewater remain below the micromole level. Under such conditions, as suggested by O'Day et al. (2004), As removal from porewater would be limited to sorption on the surface of sulfide minerals rather than co-precipitation with sulfides. The efficiency of As sequestration could be tempered in the most mature stages (4th and 5th) by decreased sorption of As onto mineral substrates due to the presence of competing anions (such as phosphate, OC and other sorbates; O'Day et al., 2004; Root et al., 2007) originated from near-surface run-off and shallow water table. Accordingly, higher dissolved As concentrations are observed in mature Lake Yamsovey and drained Lake Khasyrei sediments compared to actively growing Lake Shirokoe sediments (Fig. 8).

Antimony behavior contrasts to that of As in Lake Shirokoe (Fig. 8a) while being similar in the other two lakes (Fig. 8b and c). In Lake Shirokoe, porewater Sb shows decreasing concentrations just below the WSI while As concentration increases. The concave-shaped porewater Sb profile indicates that dissolved Sb, likely originating from mineralized OM (El Bilali et al., 2002), is consumed by early diagenetic reactions in the upper layers of the sediment. Evidence of authigenic formation of crystalline stibnite (Sb_2S_3) in natural sediments during early diagenesis has never been reported and owing to the low dissolved Sb concentration in porewater, it is unlikely such process can account for the Sb consumption observed here. Rather, under the anoxic conditions prevailing in the studied sediments, thioantimonite complexes (HSb_2S_5^- and $\text{Sb}_2\text{S}_6^{2-}$) are produced (Helz et al., 2002). These anionic S-coordinated complexes tend to condense to form large polymeric molecules (Filella et al., 2002). It is thus suggested that (part of) such large polymeric molecules are retained by the 0.2 μm -porosity filters and therefore included in the particulate phase. This contention

is supported by the particulate Sb enrichment observed at 5 cm depth in Shirokoe and Yamsovey sediments (Fig. 7a and b). The release of Sb into the porewater is likely to occur due to destabilization of Fe- and Mn-oxyhydroxides as host phases, as previously observed in other freshwater lakes (Chen et al., 2003). Such contribution is evidenced by: (i) maximum porewater Sb concentrations observed at the depth where Fe- and Mn-oxyhydroxides undergo reductive dissolution in Yamsovey (4th stage) and Khasyrei (5th stage) sediments (Figs. 7b, c, 8b and c); (ii) the slight increase in dissolved Sb concentration within an otherwise decreasing profiles at the very depth of Fe and Mn reductive dissolution in Shirokoe (3rd stage) sediments (Figs. 7a and 8a). At depth, and similarly to As, Fe-sulfides are likely controlling Sb removal from porewater and subsequent sequestration into the sediments, as reported for other freshwater lakes (Chen et al., 2003). In the most mature lake (drained Khasyrei), porewater Sb and As concentrations are highly correlated ($R^2 = 0.84$, $n = 7$), indicating the same source and sink for both metalloids.

6 Environmental significance and conclusions

In this study, the use of concentration-depth profiles of sediment and associated porewaters of three western Siberian thermokarst lakes representing different stages of ecosystem maturity development permitted to propose a comprehensive assessment of redox processes related to OM mineralization (Fig. 9). Intense mineralization of OM under anoxic conditions was suggested in the sediments, with up to 70 % of the POC previously sequestered in the peat mineralized in the most mature (drained) thermokarst lake. In the course of the life cycle of thermokarst lakes, a plausible shift in OM mineralization pathways was suggested with Fe- and Mn-oxyhydroxides likely representing the main terminal electron acceptors in the microbe-mediated early diagenetic reactions for the most mature (drained) stage. This shift is probably promoted by the diagenetic consumption of nitrate and sulfate and their gradual depletion in the water column due to progressively decreasing peat lixiviation at the lake's borders. Transient redox reactions prevail in these lakes as prompted by strong seasonal variations (related to ice and snow melting) of (i) OM inputs at the water-sediment interface, and (ii) the intensity of sub-surface water circulation and depth of the water table. Additionally, transient redox conditions at the timescale of the lake life cycle are favored by lake maturation-related changes such as decreasing OM, nutrients and sulfates supply to the water-sediment interface (Fig. 9).

Progressive decrease of DOC, Fe and Mn concentration in the water column in the course of thermokarst lake evolution was related to heterotrophic bacterial activity and the decrease of peat component supply from the border to the lake water (Pokrovsky et al., 2011). In this previous study,

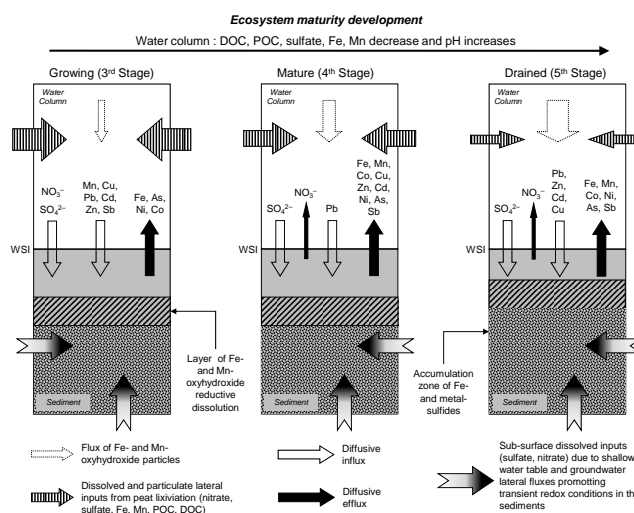


Fig. 9. Schematic conceptual model of early diagenesis-related processes and associated post-depositional redistribution of trace metals and metalloids during the thermokarst lake maturity development.

we show that aerobic heterotrophic bacterial activity in fully oxygenated water column consumes DOC leading to destabilization and coagulation of organo-mineral colloids and their transformation to subcolloidal particles (0.45–5 μm). This creates a flux of Fe-rich particles and associated trace elements from the water column to the WSI and progressive enrichment of the sediments in metals during the maturation of the lake ecosystem, encountered in the present study.

The early diagenetic reactions were shown to be responsible for strong post-depositional redistribution of trace metals (Cu, Zn, Cd, Pb, Co, Ni) and metalloids (As and Sb) as summarized in Fig. 9. These trace elements are mobilized from destabilized host particulate phase (OM and Fe- and Mn-oxyhydroxides) and partly sequestered at depth in the sediment with authigenic Fe-sulfides. For the early, actively growing (3rd) stage of lake development, shallow sequestration of the respective distinct sulfides of Cu, Zn, Cd and Pb was suggested. Arsenic and Sb cycling is also closely linked to that of OM and Fe- and Mn-oxyhydroxides, from which these metalloids are released at shallow depth. Sorption on, rather than co-precipitation with, Fe-sulfides was proposed as the main mechanism for As and Sb sequestration in the sediments. Shallow diagenetic enrichment of particulate Sb was thus observed in growing and mature (3rd and 4th) stages. As a result of authigenic sulfides precipitation at shallow depth, the sediments of the early stage of lake development (actively growing Lake Shirokoe) represent a sink for water column Cu, Zn, Cd, Pb and Sb (see Table 4). This result is in accordance with the progressive depletion of trace elements concentrations in the water column during the course of the lake maturation reported by Pokrovsky et al. (2011) for the same lakes. In contrast, regardless of

the development stage, the thermokarst lake sediments represent a source of dissolved Co, Ni and As to the overlying water column (see Table 4). However, the concentrations of these trace elements remain low in the bottom waters. This indicates that sorption processes on Fe-bounding particles and/or large-size ferric sub-colloids (5 μm to 0.45 μm), whose abundance increases along with the lake maturation degree (Pokrovsky et al., 2011), could mitigate the impacts on the water column of post-depositional redistribution of potentially toxic elements such as As. Given that sorption of As onto Fe-oxyhydroxides has a tendency to decrease in the presence of OM (Grafe et al., 2001; Redman et al., 2002; Bauer and Blodau, 2006), an increased sorption of upward-diffusing As onto Fe-bounding particles is expected in the course of the lake's life cycle due to decreasing DOC concentration in the water column.

At the scale of the Northern part of the Western Siberia peatlands (195 500 km^2 ; Sheng et al., 2004), we roughly estimated the OC stock in the region's lake sediments by extrapolating our OC stock in the actively growing Lake Shirokoe (i.e. $14 \pm 2 \text{ kg m}^{-2}$; see Sect. 5.1) over the whole region, and assuming a surface area represented by lakes of 30–60 % of the total peatland area (Kirpotin et al., 2009, 2011; Zakharova et al., 2009). This estimated OC stock ranges from 0.8 to 1.6 Pg C and represent from 4.5 to 8.7 % of the total OC stock of the region (50 Pg C; Sheng et al., 2004). While our estimated OC stock in lake sediments is much lower than that in peat soils, it represents a significant pool of potentially much more mobile OC compared to soils given that the thermokarst lakes act as permanent source of CO_2 to the atmosphere with a magnitude several times higher than that of OC flux by Siberian rivers (Shirokova et al., 2009). Smith et al. (2005) reported an increase of 12 % (13 300 ha) in total lake area over the last three decades in the continuous permafrost zone of Western Siberia. Extrapolating our results of POC mineralization in the mature, (but not drained) most typical Lake Yamsovey (4th stage) over the continuous permafrost zone suggests that the loss of organic carbon driven by OM mineralization in the lake sediments for the increased lake area would have been roughly equivalent to about 0.5 % of the total carbon stock (i.e. 7.8 Pg C; Sheng et al., 2004) estimated for this area. However, if recently observed trends of air temperature increase in Western Siberia (Frey and Smith, 2003) persist, amplified dissolved sulfates, micronutrients (such as Cu, Co, Fe, Mn, Ni, Zn) and highly labile DOC (Uhlířová et al., 2007) fluxes in Western Siberia streams are expected (Frey et al., 2007) due to permafrost degradation and increased water-rock interaction. This will be accompanied by an increased efficiency of OM mineralization in sediments promoted by sustained electron acceptors pools (sulfates, Fe- and Mn-oxyhydroxides). As a result, the share of the carbon stock in the Western Siberia continuous permafrost zone impacted by thermokarst lake dynamics is likely to drastically increase in the next decades. The increase of export fluxes of terrestrial organic carbon to

Table 5. Estimated stocks of trace metals and metalloids in lake sediments and their contribution to the total stocks of the Northern part of the Western Siberia peatlands. See text for the calculation details.

	Stock in lake sediments (Tg)	Contribution to the total stock (%)
Fe	36–72	12.0–21.4
Mn	0.4–0.9	4.5–8.5
Co	0.02–0.03	7.2–13.4
Ni	0.04–0.09	11.3–20.2
Cu	0.02–0.05	9.0–16.5
Zn	0.08–0.15	8.0–14.8
Cd	0.0005–0.001	19.9–33.1
As	0.012–0.025	32.2–48.7
Sb	0.0005–0.001	5.1–9.8
Pb	0.02–0.04	8.1–14.9

the ocean, as suggested by Guo and Macdonald (2006) for the Yukon River, could be first mitigated in Western Siberia by temporary sequestration of POC in thermokarst lake sediments. However, due to enhanced OM mineralization in the sediments, the major part of this additional organic carbon would be eventually released through CO_2 and CH_4 evasion to the atmosphere. As such, early diagenesis redox processes occurring in the thermokarst lake sediments play a pivotal role on the carbon cycle in Western Siberia.

As for trace elements and metalloids, we roughly estimated their stock in lake sediments over the Northern part of Western Siberia peatlands. First, the trace metal stocks in actively growing Lake Shirokoe were estimated following the same approach as for the OC stock estimation (see Sect. 5.1). Then, these estimates were extrapolated over the Northern part of the Western Siberia peatlands area assuming again a surface area represented by lakes of 30–60 % of the total area (Zakharova et al., 2009; Kirpotin et al., 2009). The resulting stocks of trace elements are reported in Table 5. In order to evaluate the contribution of the lake trace metal stocks to the regional stocks (Table 5), the trace metal and metalloid stocks in peat soils were estimated using typical mean concentrations in the peat soils of the Northern part of Western Siberia (see Sect. 4.1.3; Moskovchenko, 2006; Stepanova, 2011) and a total peat mass of 50 Pg (estimated using data from Sheng et al., 2004). While these rough estimates are impaired by large uncertainties they nevertheless indicate that peatland lakes from the Northern part of Western Siberia host significant pools of potentially more mobile trace metals than those sequestered in peat soils. While the response of thermokarst lakes to amplified fluxes of particulate and dissolved elements is highly complex owing the complicated network of interacting redox processes thermokarst lake sediments could mitigate the prospected enhancement of their export fluxes to the ocean due to permafrost degradation

through their authigenic sequestration in the form of sulfides. However, further studies of the Siberian thermokarst lakes in different states of development along a latitude profile are needed to quantify potential changes and responses to global warming of organic carbon and trace metals and metalloids fluxes and stocks in the boreal regions.

Acknowledgements. This work was supported by the French National Programme INSU (EC2CO Cytrix), GDR CAR-WET-SIB, by RFBR 08-05-92496-CNRS.a, 08-05-92497-CNRS.a, 08-0492495-CNRS.a, by Russian Governmental Program “Studies in the Earth Science and Ecology” (No. 2011-1.5-505-008) and the Russian Federal Program “Kadry”. We gratefully acknowledge the following colleagues for various aspects of the field and laboratory work: P. Besson, F. Candaudap, C. Causserand, A. Lanzanova, S. Mounic and C. Zouiten. Insightful comments from one anonymous reviewer and Johan Ingri are gratefully acknowledged.

Edited by: K. Ksel



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

References

- ACIA: Arctic Climate Impact Assessment, Scientific Report, ACIA Secretariat and Cooperative Institute for Arctic Research University of Alaska Fairbanks, available at: <http://www.acia.uaf.edu/pages/scientific.html>, 2007.
- Aller, R. C.: Conceptual models of early diagenetic processes: The muddy seafloor as an unsteady, batch reactor, *J. Mar. Res.*, 62, 815–835, 2004.
- Anschutz, P., Sundby, B., Lefrancois, L., Luther III, G. W., and Mucci, A.: Interactions between metal oxides and species of nitrogen and iodine in bioturbated marine sediments, *Geochim. Cosmochim. Ac.*, 64, 2751–2763, 2000.
- Audry, S., Grosbois, C., Bril, H., Schäfer, J., Kierczak, J., and Blanc, G.: Post-depositional redistribution of trace metals in reservoir sediments of a mining/smelting-impacted watershed (the Lot River, SW France), *Appl. Geochem.*, 25, 778–794, 2010.
- Bauer, M. and Blodau, C.: Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments, *Sci. Total Environ.*, 354, 179–190, 2006.
- Belzile, N.: The fate of arsenic in sediments of the Laurentian Trough, *Geochim. Cosmochim. Ac.*, 52, 2293–2302, 1988.
- Belzile, N. and Tessier, A.: Interactions between arsenic and iron oxyhydroxides in lacustrine sediments, *Geochim. Cosmochim. Ac.*, 54, 103–109, 1990.
- Berner, R. A.: *Early Diagenesis: A Theoretical Approach*, Princeton University Press, New York, 1980.
- Billings, W. D. and Peterson, K. M.: Vegetational Change and Ice-Wedge Polygons through the Thaw-Lake Cycle in Arctic Alaska, *Arctic Alpine Res.*, 12, 413–432, 1980.
- 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 CO₂ and CH₄ evolution in a thermokarst pond near Igarka, northern Siberia, *J. Geophys. Res.-Biogeo.*, 113, G03023, doi:10.1029/2007JG000652, 2008.
- Boudreau, B. P.: *Diagenetic models and their implementations: Modeling transport and reactions in aquatic sediments* Springer, Berlin, Heidelberg, Germany, New York, USA, 414 pp., 1997.
- Canfield, D. E.: Reactive iron in marine sediments, *Geochim. Cosmochim. Ac.*, 53, 619–632, 1989.
- Cauwet, G., Gadel, F., de Souza Sierra, M. M., Donard, O., and Ewald, M.: Contribution of the Rhone River to organic carbon inputs to the northwestern Mediterranean Sea, *Cont. Shelf Res.*, 10, 1025–1037, 1990.
- Chaillou, G., Anschutz, P., Lavaux, G., Schäfer, J., and Blanc, G.: The distribution of Mo, U, and Cd in relation to major redox species in muddy sediments of the Bay of Biscay, *Mar. Chem.*, 80, 41–59, 2002.
- Chen, W. and Wangersky, P. J.: Rates of microbial degradation of dissolved organic carbon from phytoplankton cultures, *J. Plankton Res.*, 18, 1521–1533, 1996.
- Chen, Y. W., Deng, T. L., Filella, M., and Belzile, N.: Distribution and Early Diagenesis of Antimony Species in Sediments and Porewaters of Freshwater Lakes, *Environ. Sci. Technol.*, 37, 1163–1168, 2003.
- Clément, J.-C., Shrestha, J., Ehrenfeld, J. G., and Jaffé, P. R.: Ammonium oxidation coupled to dissimilatory reduction of iron under anaerobic conditions in wetland soils, *Soil Biol. Biochem.*, 37, 2323–2328, 2005.
- Couture, R.-M., Shafei, B., Van Cappellen, P., Tessier, A., and Gobeil, C.: Non-Steady State Modeling of Arsenic Diagenesis in Lake Sediments, *Environ. Sci. Technol.*, 44, 197–203, 2010.
- Czudek, T. and Demek, J.: Thermokarst in Siberia and its influence on the development of lowland relief, *Quaternary Res.*, 1, 103–120, 1970.
- Davison, W.: Iron and manganese in lakes, *Earth-Sci. Rev.*, 34, 119–163, 1993.
- Dellwig, O., Watermann, F., Brumsack, H. J., Gerdes, G., and Krumbein, W. E.: Sulphur and iron geochemistry of Holocene coastal peats (NW Germany): a tool for palaeoenvironmental reconstruction, *Palaeogeogr. Palaeoclimatol.*, 167, 359–379, 2001.
- Duff, K. E., Laing, T. E., Smol, J. P., and Lean, D. R. S.: Limnological characteristics of lakes located across arctic treeline in northern Russia, *Hydrobiologia*, 391, 205–222, 1998.
- 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.
- Dzombak, D. A. and Morel, F. M. M.: *Surface Complexation Modeling: Hydrous Ferric Oxide*, Wiley-Interscience, New York, 393 pp., 1990.
- El Bilali, L., Rasmussen, P. E., Hall, G. E. M., and Fortin, D.: Role of sediment composition in trace metal distribution in lake sediments, *Appl. Geochem.*, 17, 1171–1181, 2002.
- Ershov, E. D.: *Geocryology of the USSR, The Western Siberia*, Moscow, 454 pp., 1989.
- Filella, M., Belzile, N., and Chen, Y.-W.: Antimony in the environ-

- ment: a review focused on natural waters: II. Relevant solution chemistry, *Earth-Sci. Rev.*, 59, 265–285, 2002.
- Freeman, C., Evans, C. D., Monteith, D. T., Reynolds, B., and Fenner, N.: Export of organic carbon from peat soils, *Nature*, 412, 785–785, 2001.
- Freeman, C., Fenner, N., Ostle, N. J., Kang, H., Dowrick, D. J., Reynolds, B., Lock, M. A., Sleep, D., Hughes, S., and Hudson, J.: Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels, *Nature*, 430, 195–198, 2004.
- Frey, K. E. and Smith, L. C.: Recent temperature and precipitation increases in West Siberia and their association with the Arctic Oscillation, *Polar Res.*, 22, 287–300, 2003.
- 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:03410.01029/02006WR004902, 2007.
- Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., and Maynard, V.: Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis, *Geochim. Cosmochim. Ac.*, 43, 1075–1090, 1979.
- Gorham, E.: Northern Peatlands: Role in the Carbon Cycle and Probable Responses to Climatic Warming, *Ecol. Appl.*, 1, 182–195, 1991.
- Grafe, M., Eick, M. J., and Grossl, P. R.: Adsorption of Arsenate (V) and Arsenite (III) on Goethite in the Presence and Absence of Dissolved Organic Carbon, *Soil Sci. Soc. Am. J.*, 65, 1680–1687, 2001.
- Guo, L. and Macdonald, R. W.: Source and transport of terrigenous organic matter in the upper Yukon River: Evidence from isotope ($\delta^{13}\text{C}$, $\Delta^{14}\text{C}$, and $\delta^{15}\text{N}$) composition of dissolved, colloidal, and particulate phases, *Global Biogeochem. Cy.*, 20, GB2011, doi:2010.1029/2005GB002593, 2006.
- 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.
- Heitmann, T. and Blodau, C.: Oxidation and incorporation of hydrogen sulfide by dissolved organic matter, *Chem. Geol.*, 235, 12–20, 2006.
- Helz, G. R., Valerio, M. S., and Capps, N. E.: Antimony Speciation in Alkaline Sulfide Solutions: Role of Zerovalent Sulfur, *Environ. Sci. Technol.*, 36, 943–948, 2002.
- Hinkel, K. M., Eisner, W. R., Bockheim, J. G., Nelson, F. E., Peterson, K. M., and Dai, X.: Spatial Extent, Age, and Carbon Stocks in Drained Thaw Lake Basins on the Barrow Peninsula, Alaska, *Arct. Antarct. Alp. Res.*, 35, 291–300, 2003.
- Holmer, M. and Storkholm, P.: Sulphate reduction and sulphur cycling in lake sediments: a review, *Freshwater Biol.*, 46, 431–451, 2001.
- Huerta-Diaz, M. A., Tessier, A., and Carignan, R.: Geochemistry of trace metals associated with reduced sulfur in freshwater sediments, *Appl. Geochem.*, 13, 213–233, 1998.
- Hulth, S., Aller, R. C., and Gilbert, F.: Coupled anoxic nitrification/manganese reduction in marine sediments, *Geochim. Cosmochim. Ac.*, 63, 49–66, 1999.
- Hyacinthe, C., Anschutz, P., Carbonel, P., Jouanneau, J.-M., and Jorissen, F. J.: Early diagenetic processes in the muddy sediments of the Bay of Biscay, *Mar. Geol.*, 177, 111–128, 2001.
- Ingri, J., Pekka, L., Dauvalter, V., Rodushkin, I., and Peinerud, E.: Manganese redox cycling in Lake Imandra: impact on nitrogen and the trace metal sediment record, *Biogeosciences Discuss.*, 8, 273–321, doi:10.5194/bgd-8-273-2011, 2011.
- Ivanov, K. E. and Novikov, S. M.: Mires of Western Siberia: their structure and hydrological regime, *Hydrometeoizdat, Leningrad*, 448 pp., 1976 (in Russian).
- Javanaud, C., Michotey, V., Guasco, S., Garcia, N., Anschutz, P., Canton, M., and Bonin, P.: Anaerobic ammonium oxidation mediated by Mn-oxides: From sediment to strain level, *Res. Microbiol.*, in press, doi:10.1016/j.resmic.2011.01.011, 2011.
- Jenkinson, D. S., Adams, D. E., and Wild, A.: Model estimates of CO₂ emissions from soil in response to global warming, *Nature*, 351, 304–306, 1991.
- Jones, C. A., Langner, H. W., Anderson, K., McDermott, T. R., and Inskeep, W. P.: Rates of Microbially Mediated Arsenate Reduction and Solubilization, *Soil Sci. Soc. Am. J.*, 64, 600–608, 2000.
- Kirpotin, S., Naumov, A., Vorobiov, S., Mironycheva-Tokareva, N., Kosykh, N., Lapshina, E., Marquand, J., Kulizhski, S., 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*, edited by: Lal, R., Suleimenov, M., Stewart, B. A., Hansen, D. O., and Doraiswamy, P., Taylor & Francis, 453–472, 2007.
- Kirpotin, S., Polishchuk, Y., Zakharova, E. A., Shirokova, L., Pokrovsky, O. S., Kolmakova, M., and Dupré, B.: One of possible mechanisms of thermokarst lakes drainage in West-Siberian North, *Int. J. Environ. Stud.*, 65, 631–635, 2008.
- Kirpotin, S. N., Berezin, A., Bazanov, V., Polishchuk, Y., Vorobiov, S., Mironycheva-Tokareva, N., Kosykh, N., Volkova, I., Dupre, B., Pokrovsky, O., Kouraev, A., Zakharova, E., Shirokova, L., Mognard, N., Biancamaria, S., Viers, J., and Kolmakova, M.: Western Siberia wetlands as indicator and regulator of climate change on the global scale, *Int. J. Environ. Stud.*, 66, 409–421, 2009.
- Kirpotin, S., Polishchuk, Y., Bryksina, N., Sugaipova, A., Kouraev, A., Zakharova, E., Pokrovsky, O. S., Shirokova, L. S., Kolmakova, M., Manassypov, R., Dupré, B.: West Siberian peatlands: distribution, typology, hydrology, cyclic development, present-day climate-driven changes and impact on CO₂ cycle, *Int. J. Environ. Stud.*, 68, 603–623, 2011.
- Koretsky, C., Haas, J., Miller, D., and Ndenga, N.: Seasonal variations in pore water and sediment geochemistry of littoral lake sediments (Asylum Lake, MI, USA), *Geochem. Trans.*, 7, 11, doi:10.1186/1467-4866-7-11, 2006.
- Kortelainen, P., Pajunen, H., Rantakari, M., and Saarnisto, M.: A large carbon pool and small sink in boreal Holocene lake sediments, *Glob. Change Biol.*, 10, 1648–1653, 2004.
- Kostka, J. E. and Luther III, G. W.: Partitioning and speciation of solid phase iron in saltmarsh sediments, *Geochim. Cosmochim. Ac.*, 58, 1701–1710, 1994.
- Kotlyakov, V. and Khromova, T.: Maps of permafrost and ground ice, in: *CD-ROM Land Resources of Russia*. Laxenburg, Austria: International Institute for Applied Systems Analysis and the Russian Academy of Science CD-ROM, edited by: Stolbovoi, V. and McCallum, I., distributed by the National Snow and Ice Data Center/World Data Center for Glaciology, Boulder, USA, 2002.
- Kremenetski, K. V., Velichko, A. A., Borisova, O. K., MacDonald, G. M., Smith, L. C., Frey, K. E., and Orlova, L. A.: Peatlands

- of the Western Siberian lowlands: current knowledge on zonation, carbon content and Late Quaternary history, *Quaternary Sci. Rev.*, 22, 703–723, 2003.
- Lapshina, E. D. and Pologova, N. N.: Carbon accumulation, in: *Carbon Storage and Atmospheric Exchange by West Siberian Peatlands*, edited by: Bleuten, W., and Lapshina, E. D., Utrecht, Netherlands, 50–72, 2001.
- 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.
- Mackay, J. R.: Lake stability in an ice-rich permafrost environment: examples from the western Arctic coast, in: *Aquatic Ecosystems in Semi-Arid Regions: Implications for Resource Management*, edited by: Robarts, R. D. and Bothwell, M. L., NHRI Symposium Series 7, Environment Canada, Saskatoon, Saskatchewan, 1–26, 1992.
- Masscheleyn, P. H., Delaune, R. D., and Patrick, W. H.: Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil, *Environ. Sci. Technol.*, 25, 1414–1419, 1991.
- Mihelcic, J. R.: *Fundamentals of Environmental Engineering*, John Wiley & Sons, New York, 352 pp., 1999.
- Moskovchenko, D. V.: Biogeochemical features of bogs of Western Siberia, *Geograph. Nat. Resour.*, 1, 63–70, 2006.
- O'Day, P. A., Vlassopoulos, D., Root, R., and Rivera, N.: The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions, *P. Natl. Acad. Sci. USA*, 101, 13703–13708, 2004.
- 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 the Severnaya Dvina River and its tributary, *Chem. Geol.*, 273, 136–149, 2010.
- Pokrovsky, O. S., Shirokova, L. S., Kirpotin, S. N., Audry, S., Viers, J., and Dupré, B.: Effect of permafrost thawing on organic carbon and trace element colloidal speciation in the thermokarst lakes of western Siberia, *Biogeosciences*, 8, 565–583, doi:10.5194/bg-8-565-2011, 2011.
- Prentki, R. T., Miller, M. C., Barsdate, R. J., Alexander, V., Kelley, J., and Coyne, P.: Chemistry, in: *Limnology of tundra ponds, Barrow, Alaska*, edited by: Hobbie, J. E., Dowden, Hutchinson & Ross, Stroudsburg, Pa., 514, 1980.
- Price, J. S., Branfireun, B. A., Michael Waddington, J., and Devito, K. J.: Advances in Canadian wetland hydrology, 1999–2003, *Hydrol. Process.*, 19, 201–214, 2005.
- Redman, A. D., Macalady, D. L., and Ahmann, D.: Natural Organic Matter Affects Arsenic Speciation and Sorption onto Hematite, *Environ. Sci. Technol.*, 36, 2889–2896, 2002.
- Root, R. A., Dixit, S., Campbell, K. M., Jew, A. D., Hering, J. G., and O'Day, P. A.: Arsenic sequestration by sorption processes in high-iron sediments, *Geochim. Cosmochim. Ac.*, 71, 5782–5803, 2007.
- Seyler, P. and Martin, J. M.: Biogeochemical processes affecting arsenic species distribution in a permanently stratified lake, *Environ. Sci. Technol.*, 23, 1258–1263, 1989.
- Shaw, T. J., Gieskes, J. M., and Jahnke, R. A.: Early diagenesis in differing depositional environments: The response of transition metals in pore water, *Geochim. Cosmochim. Ac.*, 54, 1233–1246, 1990.
- Sheng, Y., Smith, L. C., MacDonald, G. M., Kremenetski, K. V., Frey, K. E., Velichko, A. A., Lee, M., Beilman, D. W., and Dubinin, P.: A high-resolution GIS-based inventory of the west Siberian peat carbon pool, *Global Biogeochem. Cy.*, 18, GB3004, doi:10.1029/2003GB002190, 2004.
- Shirokova, L. S., Pokrovsky, O. S., Kirpotin, S. N., and Dupré, B.: Heterotrophic bacterio-plankton in thawed lakes of the northern part of Western Siberia controls the CO₂ flux to the atmosphere, *Int. J. Environ. Stud.*, 66, 433–445, 2009.
- Smedley, P. L. and Kinniburgh, D. G.: A review of the source, behaviour and distribution of arsenic in natural waters, *Appl. Geochem.*, 17, 517–568, 2002.
- Smith, L. C., MacDonald, G. M., Velichko, A. A., Beilman, D. W., Borisova, O. K., Frey, K. E., Kremenetski, K. V., and Sheng, Y.: Siberian Peatlands a Net Carbon Sink and Global Methane Source Since the Early Holocene, *Science*, 303, 353–356, 2004.
- Smith, L. C., Sheng, Y., MacDonald, G. M., and Hinzman, L. D.: Disappearing Arctic Lakes, *Science*, 308, p. 1429, doi:10.1126/science.1108142, 2005.
- Sorokina, E. P., Dmitrieva, N. K., Karpov, L. V., and Trikhulina, N. Y.: Differentiation of geochemical background of the environment based on landscape properties of the territory, *Geograph. Nat. Resour.*, 143–152, 2006 (in Russian).
- Stepanova, V. A.: Biogeochemical features of bog catena. In: *Western-Siberia Peatbogs and carbon cycle: past and future*, 3rd International Field Symposium, Khanty-Mansiisk, Tomsk, 195–197, 2011.
- Sundby, B., Martinez, P., and Gobeil, C.: Comparative geochemistry of cadmium, rhenium, uranium, and molybdenum in continental margin sediments, *Geochim. Cosmochim. Ac.*, 68, 2485–2493, 2004.
- Thamdrup, B.: Bacterial Manganese and Iron Reduction in Aquatic Sediments, in: *Advances in Microbial Ecology*, edited by: Schink, B., Springer, 41–84, 2000.
- Turner, K. W., Wolfe, B. B., and Edwards, T. W. D.: Characterizing the role of hydrological processes on lake water balances in the Old Crow Flats, Yukon Territory, Canada, using water isotope tracers, *J. Hydrol.*, 386, 103–117, 2010.
- Uhlířová, E., Santrúcková, H., and Davidov, S. P.: Quality and potential biodegradability of soil organic matter preserved in permafrost of Siberian tussock tundra, *Soil Biol. Biochem.*, 39, 1978–1989, 2007.
- Vasyukova, E. V., Pokrovsky, O. S., Viers, J., Oliva, P., Dupré, B., Martin, F., and Candaudap, 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.
- Vitt, D. H., Halsey, L. A., Bauer, I. E., and Campbell, C.: Spatial and temporal trends in carbon storage of peatlands of continental western Canada through the Holocene, *Can. J. Earth Sci.*, 37, 683–693, 2000.
- Walter, K. M., Zimov, S. A., Chanton, J. P., Verbyla, D., and Chapin III, F. S.: Methane bubbling from Siberian thaw lakes as a positive feedback to climate warming, *Nature*, 443, 71–75, 2006.
- Walter, K. M., Edwards, M. E., Grosse, G., Zimov, S. A., and Chapin III, F. S.: Thermokarst Lakes as a Source of Atmospheric CH₄ During the Last Deglaciation, *Science*, 318, 633–636, 2007.
- Widerlund, A. and Ingri, J.: Early diagenesis of arsenic in sediments of the Kalix River estuary, northern Sweden, *Chem. Geol.*, 125,

- 185–196, 1995.
- Widerlund, A., Roos, P., Gunneriusson, L., Ingri, J., and Holmstrom, H.: Early diagenesis and isotopic composition of lead in Lake Laisan, northern Sweden, *Chem. Geol.*, 189, 183–197, 2002.
- Woo, M.-K. and Young, K. L.: Hydrogeomorphology of patchy wetlands in the high arctic, polar desert environment, *Wetlands*, 23, 291–309, 2003.
- 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, 2009.
- Zimov, S. A., Voropaev, Y. V., Semiletov, I. P., Davidov, S. P., Prosiannikov, S. F., Chapin, 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.
- Zobrist, J., Dowdle, P. R., Davis, J. A., and Oremland, R. S.: Mobilization of Arsenite by Dissimilatory Reduction of Adsorbed Arsenate, *Environ. Sci. Technol.*, 34, 4747–4753, 2000.