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Dissolved organic matter in small streams along a gradient from discontinuous to continuous permafrost

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Abstract

The Yenisei river passes every type of permafrost regime, from south to north, being characterized by increasing continuity of the permafrost and by decreasing thickness of the active layer. We used that situation to test the hypothesis that amounts and properties of dissolved organic matter (DOM) in small streams draining forested catchments respond to different permafrost regimes. Water samples were taken from eight tributaries along the Yenisei between 67°30′N and 65°49′N latitude. The samples were analysed for dissolved organic carbon (DOC) and nitrogen (DON) and DOM was characterized by its chemical composition (XAD-8 fractionation, sugars, lignin phenols, amino acids, protein, UV and fluorescence spectroscopy), and its biodegradability. Most properties of the tributary waters varied depending on latitude. The higher the latitude, the higher were DOC, DON and the proportion of the hydrophobic fraction of DOC. The contribution of hexoses and pentoses to DOC were higher in southern tributaries; on the other hand, phenolic compounds were more abundant in northern tributaries. Mineralizable DOC ranged between 4% and 28% of total DOC. DOM in northern tributaries was significantly ($P < 0.05$) less biodegradable than that in southern tributaries reflecting the differences in the chemical properties of DOM. Our results suggest that the differences in DOM properties are mainly attributed to differences of permafrost regime, affecting depth of active layer, soil organic matter accumulation and vegetation. Soil organic matter and vegetation determine the amount and composition of DOM produced in the catchments while the depth of the active layer likely controls the quantity and quality of DOM exported to streams. Sorptive interactions of DOM with the soil mineral phase typically increase with depth. The results imply that a northern shift of discontinuous permafrost likely will change in the long term the input of DOM into the Yenisei and thus probably into the Kara Sea.

Keywords: active layer, biochemical compounds, biodegradation, dissolved organic carbon, dissolved organic nitrogen, hydrophilic organic matters, hydrophobic organic matters, permafrost, phenols, sugars

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Introduction

Dissolved organic matter (DOM) in terrestrial forest ecosystems consists of lignin-derived degradation products, polysaccharides, uronic acids, low-molecular-weight organic acids, phenolic compounds and sugar monomers (Guggenberger *et al.*, 1994; Hongve *et al.*, 2000; Kaiser *et al.*, 2001; Kawahigashi *et al.*, 2003). Acidic compounds, especially those derived from lignin degradation, are typically retained in the soil due to sorption to minerals while neutral carbohydrates pass the mineral soil to a large extent (Guggenberger & Zech, 1994; Kaiser *et al.*, 2004). However, these latter compounds may be partly biodegraded (Kalbitz *et al.*,

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2003; Marschner & Kalbitz, 2003). Thus, the amount and composition of DOM exported from terrestrial to aquatic ecosystems is likely to be the result of a combination of sorption by minerals and biodegradation (Kalbitz *et al*., 2000) depending on soil depth (Johnson *et al*., 2000; Pabich *et al*., 2001).

Since permafrost prevents deep percolation, retention of DOM in soil should be limited (MacLean *et al*., 1999; Stottlemyer, 2001; Carey, 2003). This results in large concentrations of dissolved organic carbon (DOC) in arctic soil (MacLean *et al*., 1999) and surface waters (Lara *et al*., 1998; MacLean *et al*., 1999; Lobbes *et al*., 2000). The export of DOC from terrestrial ecosystems comprises much larger portions of the net primary production in arctic than in temperate regions (Judd & Kling, 2002). Due to the low net production in arctic surface waters (Miller *et al*., 1986; Peterson *et al*., 1986), terrestrial input is the major source of DOM in these aquatic systems (Lobbes *et al*., 2000). Consequently, DOM seems to be of greater relevance in arctic ecosystems than in others. When investigating the effects of global warming on permafrost distribution, DOM retention and release should be considered a primary indicator.

Carey (2003) proposed that discontinuous permafrost favours percolation and retention of DOM in deeper mineral soil layers because sorption of DOM is controlled by soil depth and the content of sesquioxides. These factors vary with the permafrost distribution (Guggenberger *et al*., 2001). Sorption of DOM results in its fractionation because hydrophobic compounds will be preferentially sorbed (Kaiser *et al*., 1996). Thus, in soils with a deep mineral soil layer, fairly small amounts of DOM with a large portion of hydrophilic components should be translocated into ground and surface waters. We hypothesize that in arctic regions, the permafrost regime and thus the thickness of the active layer, which is the seasonally frozen mineral soil layer above the permafrost layer, affect not only the amount but also the chemical composition and biodegradability of DOM exported from soil. In turn, the amount and composition of DOM in subarctic streams should reflect the permafrost regime underlying the catchments they drain.

The Yenisei is the longest river (4800 km) with the second largest basin area (2.5×10^6 km^2) in Siberia and has the largest discharge of all rivers in the arctic region. On its way to the Arctic Ocean, the Yenisei runs through every type of permafrost, which is sporadic, discontinuous and continuous permafrost from south to north (Kotlyakov & Khromova, 2002) giving excellent conditions to study the effects of changes in the permafrost regime on DOM dynamics. We sampled tributaries on the eastern bank that drain forested catchments along a gradient from south to north, from discontinuous to continuous permafrost and with decreasing depth of the active layer. Concentrations and properties of stream DOM were analysed (i) to relate amounts and properties of DOM to latitude and (ii) to estimate the potential impact of DOM in the aquatic environment. The latter was also addressed by testing the biodegradability of stream DOM.

Material and methods

Site description

The permafrost characteristics closely follow the temperature gradient. The depth of the active layer increases from 0.6 to 2 m in the north to >3 m in the south (Karpov & Baranovskij, 1998, personal communication). Concurrently, the thickness of the permafrost decreases from about 100 to <50 m with increasing discontinuity in the south. The area is further characterized by a transition of the eastern Siberian permafrost, which is in equilibrium with the present climatic conditions and the partly relictic western Siberian Permafrost (Astakhov & Isajeva, 1985). According to Jershov *et al*. (1988) the permafrost temperatures are within the range of −0.1 to −2.5 °C, with higher temperatures usually measured in the south (Baranovskij and Kasanskij, 1998, personal communication). These comparably high permafrost temperatures indicate a high susceptibility of the permafrost to climate change.

Parent materials in the study area are Quaternary sediments, primarily derived from the Zyryansk stage (122–59 kyr BP) and the Karginskaya interstage (59–24 kyr BP) of the last glaciation (Sachs, 1948). The tributaries all drained small catchments (<2 km^2 in size) of the Karginskaya terrace that is of glaciofluvial to glaciolimnic genesis. The Karginskaya terrace follows the Yenisei river from Turuhansk to the mouth of the river and is composed of a homogeneous coarse silty to fine sandy substrate. The catchments were covered with *Larix sibirica*, *Picea obovata* and *Pinus sibirica* stands, becoming less dense to the north. Towards the north, mosses become more abundant. Mean annual temperature varies between −7.4 (Igarka) and −6.8 °C (Turuhansk). Total precipitation is around 500 mm with about 50% of it during the growing season (Lieth *et al*., 1999).

Development of soils in the study area strongly depends on the permafrost regime. All soils showed thick mor-type forest floors. In the southern part, Guggenberger *et al*. (2001) found distinct weathering and enrichment of secondary Fe oxides in Bw horizons. To the north, the weathered horizons become less pronounced and finally disappear. Concurrently, there is a transition from only weak stagnic properties in the deep active layer of the southern soils to strong gleyic properties in the shallow active layer of the northern pedons. With higher permafrost table and decreasing evapotranspiration, there appears to be a transition from well developed Dystrocryepts to Cryaquepts and Cryaquents to Aquorthels (Soil Survey Staff, 1998) from south to north (Guggenberger *et al.*, 2001). However, within this zonal arrangement of soils, Histels occur throughout the whole area in small bogs.

Samples

The water samples were collected from eight small tributaries between Turuhansk and north of Igarka located at approximately 65°49′ to 67°30′ latitude, along the east shore of Yenisei (Fig. 1). Time of sampling was mid-August 2002, when the discharge of Yenisei was similar to the mean annual monthly discharge and well after peak flow during snowmelt (June–July). Surface water samples were collected at the outlet of the small tributaries using 2 L polyethylene bottles and transported cooled to the laboratory within 7 days. After filtrating through 0.7 μm glass-fibre filters (GF/F, Whatman Int. Ltd, Maidstone, UK) prerinsed distilled water, the water samples were stored frozen at −20 °C until analyses.

Analyses of general properties of tributary waters and DOM

Total carbon, dissolved inorganic carbon (DIC) and total nitrogen were determined by high temperature oxidation (High-TOC, Elementar Analysensysteme GmbH, Hanau, Germany). DOC was calculated by difference between DIC and total carbon. Nitrate and ammonium were determined by ion chromatography (DX-500, Dionex Corp., Sunnyvale, CA, USA) and photometrically (FIA-LAB II, MLE GmbH, Dresden, Germany), respectively. Because of inorganic nitrogen (NO_3^--N plus NH_4^+-N) being below the detection limit ($<0.02\,mg\,N\,L^{-1}$), dissolved organic nitrogen (DON) was equal to total nitrogen. Even when considering the detection limits for inorganic N, DON contributed to more than 90% to total nitrogen. The small concentrations of inorganic nitrogen are in agreement with results from other studies. Among the world's rivers, those of the arctic regions are reported to have the smallest concentrations of inorganic nutrients (Dittmar & Kattner, 2003). During the largest run-off in June, concentrations of NO_3^--N and NH_4^+-N in the Yenisei were $<0.02\,mg\,L^{-1}$ (Holmes *et al.*, 2001). Low microbial activity and therefore small ammonification and nitrification rates are responsible for small concentrations of NH_4-N and NO_3-N at low temperature and low pH (Atokin, 1996).

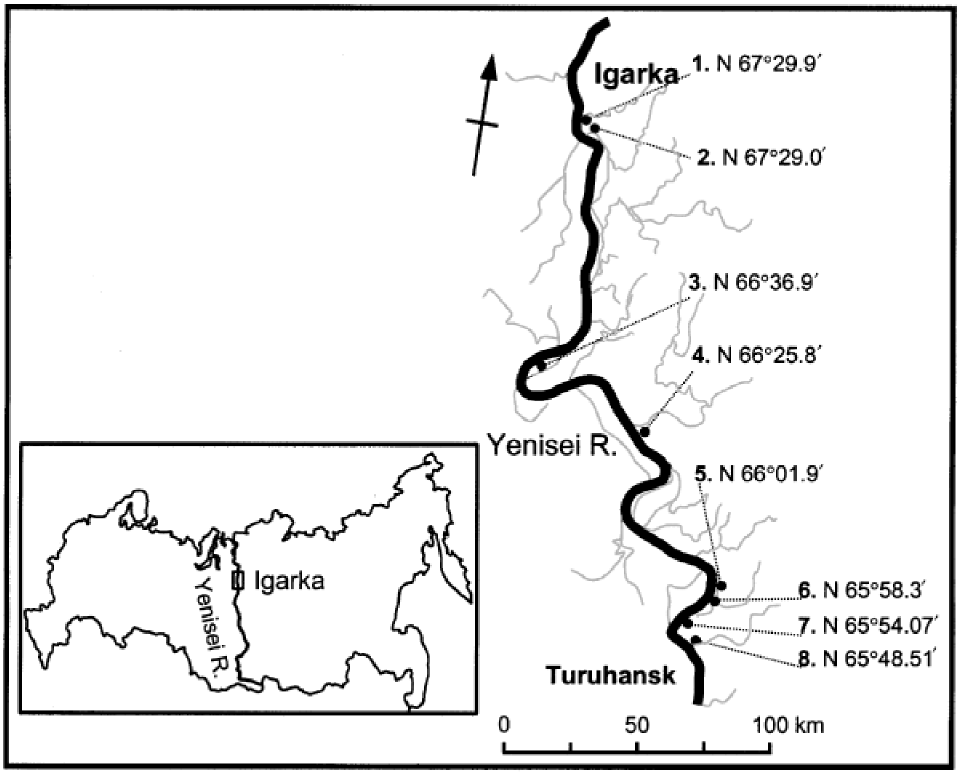

Fig. 1 Location of the sampling sites on east bank of the Yenisei river.

Concentrations of hexoses and pentoses were determined using anthrone-sulphate acid and orcinol-ferric chloride hydrochloric acid, respectively (Fukui, 1990). Amino acids were analysed using ninhydrin reagent (Joergensen & Brookes, 1993) and protein, using Bradford reagent (Bradford, 1976). Phenols were measured with the Folin–Ciocalteu method (Swain & Hillis, 1959). Concentrations of the organic compounds were normalized to the DOC concentrations.

Absorbance of UV light at 280 nm (UVIKON 930, Bio-Tek Instruments Inc., Highland Park, VT, USA) of the water sample was used to estimate the aromaticity of DOM (Chin *et al*., 1994). Synchronous and emission fluorescence spectra (SFM 25, Bio-Tek Instruments) were recorded for determination of humification indices (Zsolnay *et al*., 1999; Kalbitz & Geyer, 2001). The humification index deduced from synchronous spectra (HIX-syn) was calculated by the ratio of intensities at 460–345 nm and the humification index deduced from emission spectra (HIX-em) was calculated by the ratio of the area of fluorescence intensity from 430 to 480 nm to the area of fluorescence intensity from 300 to 345 nm after excitation at 254 nm. These humification indices are related to the aromaticity and complexity of organic molecules. For spectral analysis, the DOC concentration was adjusted to 3.5 mg L^{-1} and the reaction of the water samples to pH 2.0.

DOM was fractionated using glass columns filled with Amberlite XAD-8 (Rohm & Haas Corp., Philadelphia, PA, USA) macroreticular resin after acidification of the samples to pH 2 with 1 M HCl (Aiken & Leenheer, 1993; Raastad & Mulder, 1999). The effluent from the columns, typically termed the hydrophilic fraction, was collected and the acidic portion of the adsorbing DOM, typically referred to as the hydrophobic fraction, was eluted with 0.1 M NaOH. The portion of DOM adsorbing to XAD-8 not eluted by NaOH was $<5\%$. The hydrophobic fraction was protonated with a strongly acidic cation exchanger (AG-MP 50, BioRad Laboratories, Richmond, CA, USA). The bulk sample, the hydrophilic fraction and the portion of the hydrophobic fraction eluted were analysed for DOC and organic components. DOC in the hydrophobic fraction was calculated by the difference between total DOC and the DOC in the column effluents.

Biodegradability

Biodegradability of DOM was estimated by determination of CO_2 evolution through 97 days' liquid incubation experiment (Kalbitz *et al*., 2003). We used CO_2 instead of DOC analysis to avoid errors in the determination of biodegradable DOM due to formation of organic colloids and particles (Kalbitz *et al*., 2003). Their removal from solution by filtration before DOC analysis may result in an overestimation of the biodegradable DOC by 100% as compared with the determination of the CO_2 evolved (Schwesig *et al*., 2003). We aimed to estimate the potential biodegradability of DOM depending on its properties. Therefore, a uniform microbial community was chosen. An inoculum was prepared containing microorganisms with broad diversity by extracting organic layers from two forests and the A horizon of one upland arable and of one wetland soils with 4 mM $CaCl_2$ and combining the extracts (Kalbitz *et al*., 2003). The extraction was done the day the incubation started. The inoculum contained about 2.5×10^5 cells mL^{-1}. Water samples with more than 15 mg DOC L^{-1} were diluted before incubation to avoid overgrowth of microorganisms (Hongve *et al*., 2000) and to minimize concentration effects on DOM biodegradation (Zsolnay, 2003). Water samples low in DOC were directly incubated without dilution. Five replicates (incubation flasks with 120 mL) were filled with 56 mL of sample water and 0.56 mL of the inoculum. Four 25×25 mm pieces of glass-fibre filter, prerinsed with distilled water, were added to each flask to promote microbial growth. Biodegradation in this study was quantified as mineralization of organic carbon (Kalbitz *et al*., 2003, Marschner & Kalbitz, 2003). In order to facilitate mineralization rather than to stimulate the build-up of microbial biomass, no nutrients were added. The flasks were sealed and incubated in the dark at 20 °C. Three replicates were used to monitor the dynamic of mineralization whereas two replicates were acidified to pH <2 immediately after sealing the flasks in order to determine the carbonate-derived CO_2 at the beginning of the experiment (see below). The flasks were gently shaken by hand every day. Air in the head space of the flasks was sampled by a syringe and analysed for CO_2 using a gas chromatograph with thermal conductivity detector (HP 6890, Agilent Technologies Inc., Palo Alto, CA, USA). CO_2 was measured at short intervals (between 1 and 3 days) at the beginning of the experiment and at long intervals (between 1 and 3 weeks) at the end. Before starting the incubation, 8 mL of air was applied to each flask to maintain a pressure of about 100 hPa for proper sampling of the headspace. The CO_2 in the flasks was calculated using the general gas equation for the gas phase concentration, and from solubility constants and the pH measured for the liquid phase concentration. At the end of the incubation all flasks were acidified to pH <2.0 and total CO_2 concentration was measured.

Mineralization of DOC (% of initial DOC) was determined by the difference of CO_2 concentration of acidified (pH <2.0) samples before and after the incubation. In one case (the sample taken at 65°49′), the difference was negative due to evolution of large amounts of CO_2 from carbonate and therefore the sample was excluded from further analyses. The CO_2 concentration in the headspace of the incubation bottles represents CO_2 originating from DOC and DIC. So, the cumulative mineralization of DOC was estimated by multiplying the ratio of mineralized DOC to the total CO_2 concentration at the 97th incubation day with the CO_2 concentrations measured during the incubation. The cumulative mineralization of DOC was fitted to a double exponential model consisting of two different terms representing a rapidly mineralizing (labile) fraction and a slowly mineralizing (stable) fraction:

$$\text{DOC mineralized (\% of total DOC)} = (100 - a)(1 - \mathrm{e}^{-k1t}) + a\,(1 - \mathrm{e}^{-k2t}),$$

where $100-a$ and a are the proportion of labile DOC (%) and stable DOC (%), respectively, $k1$ and $k2$ are the mineralization rate constants of labile DOC and stable DOC, respectively, t is the incubation time (days) (Kalbitz *et al.*, 2003).

Half-life and mean residence time of labile and stable DOC were calculated based on $k1$ and $k2$.

$$\text{Half-life of labile and stable DOC} = \ln 2/(k1\ \text{and}\ k2),$$

$$\text{Mean residence time of labile and stable DOC} = 1/(k1\ \text{and}\ k2).$$

Statistical calculations

Statistical analysis was performed using SPSS 10.0 J for Windows. Relationships between latitude and properties of DOM as well as among DOM properties were analysed for linear correlations. The difference between mineralized DOC (%) of tributary waters were compared by one-way analysis of variance (ANOVA) at the $P = 0.05$ significance level.

Results

DOC, and especially DON concentrations, increased with increasing latitude (Fig. 2) and were significantly ($P < 0.01$) correlated to each other ($r = 0.92$). The ratio of DOC to DON ranged from 12 to 39 with the highest value observed at 66°26′ (Fig. 2). The proportions of DOC in the hydrophobic fraction were largest in northern samples at 67°30′, 67°29′ and 66°26′ where it comprised >60% of the DOC (Fig. 3).

Spectral properties also showed some differences between samples (Table 1). Absorbance at 280 nm ranged from 0.021 to 0.033 with the largest values observed for samples from the two most southern sites. Both humification indices (HIX-syn and HIX-em) obtained from fluorescence spectra were higher for samples from the northern tributaries at 67°30′, 67°29′ and 66°26′ compared with the other samples.

About 34–93% of the DOC can be assigned to classes of biomolecules with the wet-chemical methods used. The yield of DOC being identified decreased from south to north (Fig. 4). Hexoses and pentoses ranged from 1.7 to 3.3 mg C L^{-1} and from 1.3 to 2.8 mg C L^{-1}, respectively. Those concentrations significantly ($P < 0.05$) increased from south to north ($r = 0.72$ for hexoses; $r = 0.81$ for pentoses). However, the contribution of sugars to DOC was larger in southern streams than in the northern streams (Fig. 4). Large amounts of phenols were found in samples taken at 67°30′, 67°29′ and 66°26′, whereas no phenols were detectable at 66°02′ and 65°49′. The concentrations of phenols were correlated with latitude ($r = 0.87$, $P < 0.01$). The contribution of phenols to DOC tended to increase from south to north. There were significant correlation between hexoses and pentoses ($r = 0.79$, $P < 0.05$) and between sugars and phenols ($r = 0.92$ for hexoses; $r = 0.85$ for pentoses, $P < 0.01$). All samples contained small amounts of amino acids (0.3–5.8% of DOC; 2.5–14.5% of DON). Protein was found only at 67°30′, 67°29′ and 66°26′. The contribution of classes of biomolecules

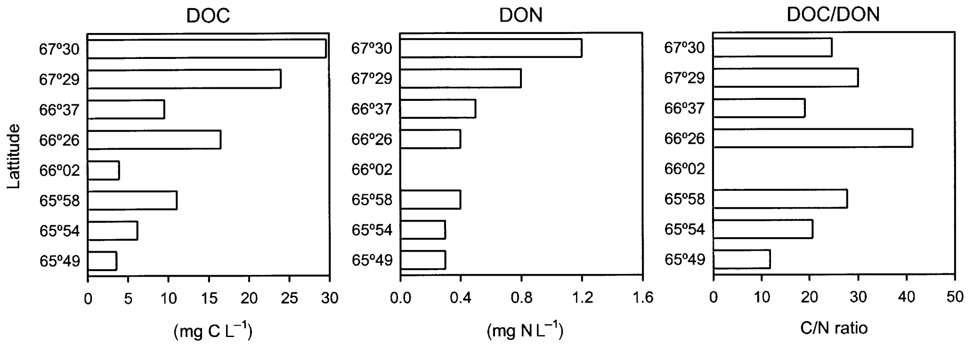

Fig. 2 Concentrations of dissolved organic carbon and nitrogen (DOC and DON) and the ratios of DOC to DON in the sampled stream waters.

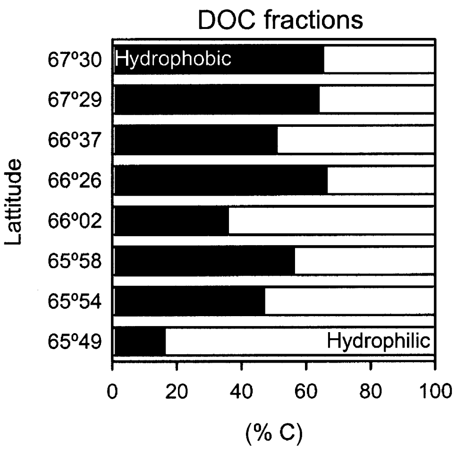

Fig. 3 Proportions of hydrophilic and hydrophobic organic fractions in the sampled stream waters.

Table 1 Spectral properties of Siberian tributary waters

Site	A 280[a] (L mg C^{-1} cm^{-1})	HIX-syn[b]	HIX-em[c]
67°30′	0.0263	0.36	7.9
67°29′	0.0283	0.43	8.4
66°37′	0.0234	0.30	4.8
66°26′	0.0286	0.47	8.4
66°02′	0.0211	0.31	4.5
65°58′	0.0260	0.33	6.5
65°54′	0.0309	0.32	6.7
65°49′	0.0326	0.29	5.5

[a] Specific absorbance at 280 nm.

[b] Humification index using synchronous fluorescence spectra (band ratio of intensities: 460/345 nm) (Kalbitz & Geyer, 2001).

[c] Humification index using emission fluorescence spectra (ratio of areas: 435–480 nm/300–345 nm) (Zsolnay *et al.*, 1999).

to the hydrophobic and hydrophilic fractions differed strongly (Fig. 5). Hydrophilic fractions were rich in hexoses, while the hydrophobic fractions were characterized by high contents of pentoses and phenols. Protein occurred only in hydrophobic fractions.

After 97 days' incubation, 4–28% of the initial DOC was mineralized (Table 2). The proportion of mineralized carbon was significantly ($P<0.05$) larger for samples from 66°02′, 65°58′ and 65°49′ than for samples from 67°30′ to 66°26′. Here, despite the largest concentrations, most DOC (>90%) was not biodegradable under the study conditions. Large mineralization rates were observed during the first 4 days after starting the incubation (Fig. 6). Later, the mineralization rate decreased. The exponential increase in CO_2 evolution without a lag phase during initial stage of biodegradation means that the experimental conditions were suitable for microbial growth and activity (Kalbitz *et al.*, 2003). The mineralization rate constants of labile DOC were similar for all samples (~ 0.3 days). On the other hand, the half-life of stable DOC ranged from 3 to 9 years, the longest for the sample at 66°37′. However, high contents of DIC affected the biodegradability assays. In the sample from 65°49′, the course of DOC mineralization could not be monitored due to the small percentage of CO_2 derived from DOC and in turn, the large DIC concentration. In the sample from 65°54′, the large concentration of DIC-derived CO_2 prevented even an estimation of the portion of mineralizable DOC (Table 2). Mineralization rate constants were negative for the samples from 67°30′ to 67°29′ because of slightly decreasing CO_2 concentrations at an already low level.

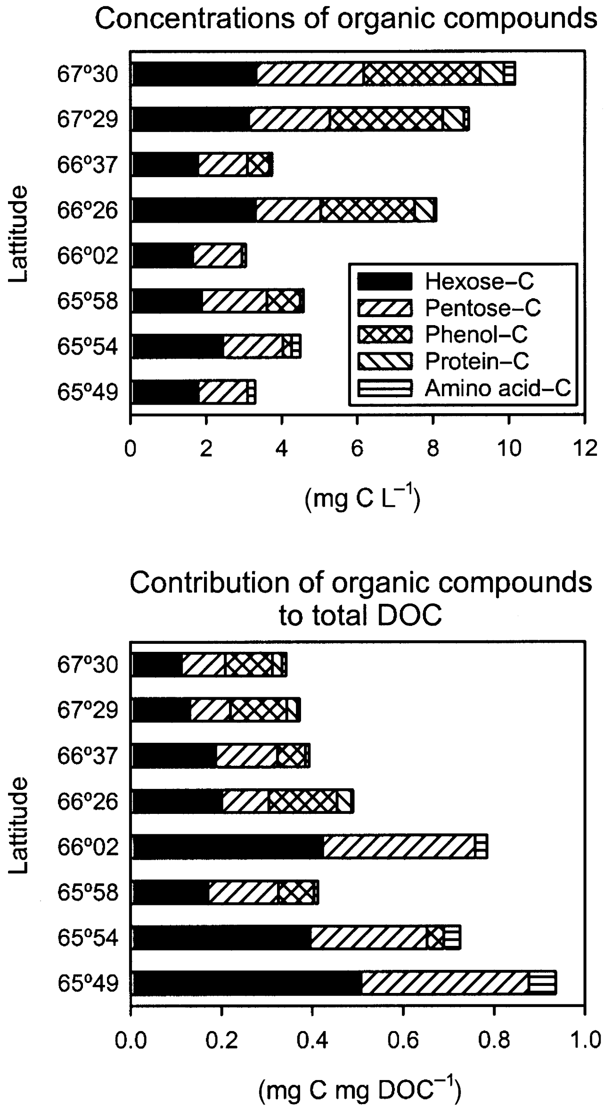

Fig. 4 Concentrations and distributions of organic compounds in the sampled stream waters.

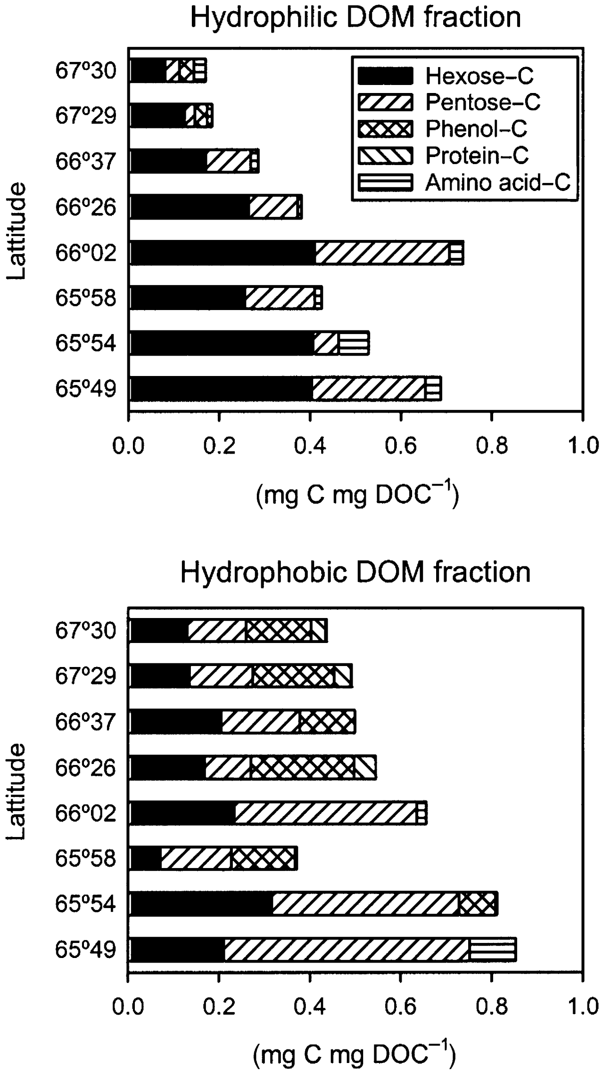

Fig. 5 Contribution of classes of biomolecules to hydrophobic and hydrophilic fractions of dissolved organic matter in the sampled stream waters.

Discussion

Soil processes in catchments controlling the export of DOM

The increase in DOC and DON with the latitude ($r = 0.92$, $P < 0.01$) likely reflects the depths of the permafrost in the catchments drained by the tributaries sampled. Typically, most DOM that enters the soil system is retained, most likely by sorption to soil minerals (McDowell & Likens, 1988) since microbial degradation of soil DOM is slow (Kalbitz *et al.*, 2003). The extent of the DOM retention in the soil relates to active minerals, especially Al and Fe hydrous oxides (Kaiser *et al.*, 1996), and the thickness of the soil and the vadose zone (Johnson *et al.*, 2000; Pabich *et al.*, 2001). In the study area, soil depth and reactive Al and Fe hydrous oxides increase southwards with the thickness of the active layer increasing from about 0.6 to >3 m (Guggenberger *et al.*, 2001). Export of DOM from soils to streams in permafrost regions, therefore, appears to be controlled by the thickness of the active layer (MacLean *et al.*, 1999). Because of inaccessibility we have no detailed data about the thickness of the active layer in the catchments drained by the studied tributaries.

During the passage through soil, not only the concentrations but also the composition and properties of DOM change because of selective sorption of the hydrophobic fraction rich in lignin degradation products (Guggenberger & Zech., 1994; Kaiser *et al.*, 2004). The small proportions of DOC in the hydrophobic fractions and the small concentrations of phenolic constituents in the southern tributaries can therefore be attributed to the greater depth of the active layer as well. In turn, towards the north, the proportion of DOC in the hydrophobic fraction and the concentration of phenols increase, suggesting weaker retention of the strongly sorbing lignin-derived compounds because of shallow active layers. Concurrently with the increase of phenols and of the hydrophobic fraction with latitude, the concentrations of pentoses increased. This indicates that in the north, larger proportions of plant-derived compounds, probably lignocellulose, enter the streams. Vice versa, the proportions of carbon in hexoses increased from north to south, suggesting larger contributions of microbial products (Guggenberger & Zech, 1994).

The low humification indices of DOM in the southern streams, indicating molecules with little complexity and few aromatic structures, agree well with composition of DOM as analysed by the wet-chemical methods. The larger proportion of DOC in the hydrophobic fraction and of phenols towards the north is also reflected by higher humification indices. The HIX-em relates closely to hydrophobic fraction ($r = 0.74$, $P < 0.05$) and phenols ($r = 0.88$, $P < 0.01$).

Ratios of DOC to DON in most of the small streams sampled were much lower than those in large Siberian rivers (29–69; Lobbes *et al.*, 2000; Dittmar & Kattner, 2003). Also, the contribution of sugars to DOC was larger in the small streams as compared with the rivers (Dittmar & Kattner, 2003). We therefore conclude that diagenetically young molecules contribute, to a larger extent, to DOM in small streams than in the large Siberian rivers.

Implications for in-stream processes

The amount and composition of DOM in streams of the northern and southern sampling area differed

Table 2 Quantitative measures of the biodegradation of DOC after incubation: percentage of mineralized DOC, proportions of the labile and stable DOC, mineralization rate constants and half-life for the labile (*k*1) and the stable (*k*2) DOC

	% of total DOC							
Site	Mineralized DOC	Labile DOC	Stable DOC	*k*1 (days^{-1})^{a}	*k*2 (days^{-1})^{b}	r^2	Half-life of labile DOC (days)	Half-life of stable DOC (years)
67°30′*	5.7^{ab} (0.3)							
67°29′	6.1^{ab} (0.4)							
66°37′	4.4^{a} (0.2)	1.9	98.1	1.997	0.000211	0.95	0.3	9.0
66°26′	7.3^{ab} (0.2)	6.2	93.9	1.833	0.000245	0.92	0.4	7.8
66°02′	16.3^{c} (3.1)	9.2	90.8	2.155	0.000557	0.76	0.3	3.4
65°58′	13.3^{bc} (0.5)	6.5	93.5	2.514	0.000673	0.95	0.3	2.8
65°54′**								
65°49′***	27.6^{d} (5.9)							

Samples represent the means of three replicates.

*All parameters except for mineralized DOC could not be analysed because of CO_2 concentrations slightly decreasing after fourth day incubation of samples from 67°30′ and 67°29′.

**No parameters on biodegradation could be determined for the sample from 65°54′ because of large evolution of CO_2 originating from dissolved inorganic carbon.

***Determination of CO_2 concentrations were terminated for the sample from 65°49′ because of large evolution of CO_2 originating from dissolved inorganic carbon.

r^2, coefficient of determination of the double exponential equation.

Standard errors of mineralized DOC are in parentheses. Different letters after mineralized DOC indicate significant differences among sites at $P<0.05$.

*Mineralization rate constant of the labile DOC pool (double exponential model).

†Mineralization rate constant of the stable DOC pool (double exponential model).

DOC, dissolved organic carbon.

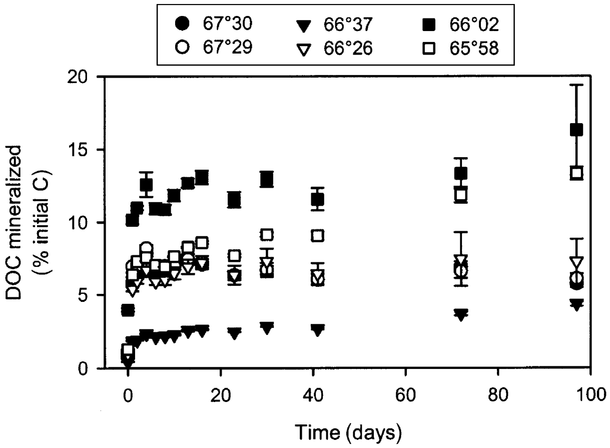

Fig. 6 Temporal pattern of C mineralized during 97 days' incubation of stream waters. Error bars represent the standard error of three replicates.

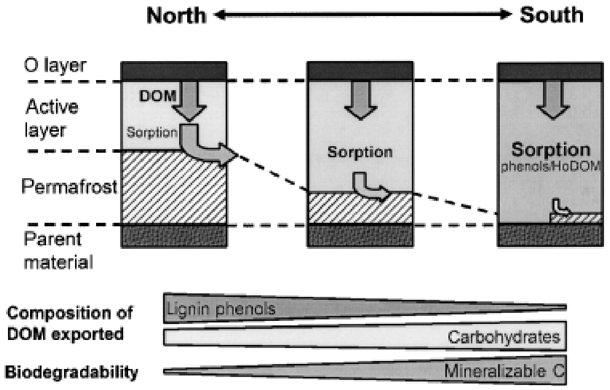

Fig. 7 Schematic illustration of flux, composition and biodegradability of DOM depending on depth of the active layer and distribution of permafrost.

remarkably. Microbial products seem to make up the majority of DOM in the southern part with the hexoses of the hydrophilic fraction being the most important constituents. The large proportions of sugars are likely the reason for the relative high portion of biodegradable carbon found for samples taken from the most southern streams (Volk *et al.*, 1997; Kalbitz *et al.*, 2003). However, the overall degradability (13–28% of total DOC) was less than of easily degradable organic matter from forest floor Oi and Oe horizons (Kalbitz *et al.*, 2003) and maize-cropped soils (Gregorich *et al.*, 2003) in temperate ecosystems but also of stream waters from arctic Alaska in spring (Michaelson *et al.*, 1998).

The decomposition rates of the labile portion of organic matter at 66°37′ to 65°58′ were much higher than those of DOM from stream water, mineral soils and organic layers under forests (Qualls & Haines, 1992; Kalbitz *et al*., 2003). Gregorich *et al*. (2003) found similar decomposition rates of labile organic matter in arable soils cropped with maize. However, the major part of DOM (91–98%) degraded with a minimum half-life of 2.8 years. Hence, the major part of DOM flushed into the Yenisei in the southern sampling area may survive in-stream degradation and be transported into the Arctic Ocean.

DOM in streams at the northern sampling sites was less degradable than DOM of the southern tributaries. This can be attributed to the smaller portions of the hydrophilic DOM fraction rich in hexoses and larger proportions of lignin-derived phenols in the hydrophobic fraction. According to Qualls & Haines (1992), the latter fraction seems to represent the most refractory DOM components. The low degradability of DOM from the northern sites compares well with that of DOM from peat horizons and other strongly decomposed organic matter (Kalbitz *et al*., 2003). Towards the north, the half-life of refractory DOM tends to increase. The large concentrations of hardly degradable DOM rich in lignin-derived phenols in the northern streams suggest that the northern basins of high latitude rivers, underlain by continuous permafrost with shallow active layers, are the major source for the large inputs of terrigenous DOM into the Arctic Ocean (Opsahl *et al*., 1999; Lobbes *et al*. 2000). However, not all of the lignin-derived compounds may reach the ocean but may partly degrade due to photooxidation (Opsahl & Benner, 1998).

Inputs of DOM from terrestrial ecosystems are considered to drive life cycles in surface waters of arctic regions because of their small net production (Miller *et al*., 1986; Peterson *et al*., 1986). The small portions of easily degradable DOM, especially in the northern tributaries sampled, suggest that DOM exported from soils in the Yenisei basin is not in favour of microbial growth serving as energy source for well prospering aquatic life. However, this may be compensated by the large inputs of DOM.

Conclusion

Most chemical properties of small tributaries of the Yenisei river changed with latitude due to the shift of discontinuous to continuous permafrost regime and the decrease in the depth of the active layer from south to north. Changes included increasing concentrations of hydrophobic DOM high in phenolic compounds, which are also expressed by increasing humification indices. The relative large proportion of lignocellulose decomposition products in the northern tributaries explain the low biodegradability of DOM in these waters. The chemical composition and the functional characteristics of tributary DOM seems to be controlled by the properties of the soils that developed in the active layer above the permafrost. Figure 7 illustrates the hypothetical control of depth of the active layer and distribution of permafrost on flux, composition and biodegradability of DOM in Siberian soils.

We assume the DOM input into the Yenisei river to change with the expected northern shift of the degradation of continuous permafrost. The increase in depth of the active layer may promote the retention of lignin-derived DOM in soil and favour the export of microbial hexoses over plant-derived pentoses. Such changes will have consequences for the aquatic food web and the export of organic matter into the Arctic Ocean. Periodical monitoring of the chemical properties of tributaries depending on latitude will therefore help gain information on the permafrost distribution and northern shift of the permafrost border due to its degradation under the present climatic conditions.

However, it should be kept in mind that the present situation represents almost steady-state conditions. Hence, any conclusions on changes in ecosystem processes derived from such a comparative study could be valid only for a perspective of a long-time scale when the new steady-state equilibrium is achieved, i.e. after the permafrost belts have been shifted to the north. During this shift, the response of the permafrost-affected terrestrial ecosystems with regard to DOC losses may be different.

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