Quantification of DOC concentrations in relation with soil properties of soils in tundra and taiga of Northern European Russia

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Abstract

Potential mobilization and transport of Dissolved Organic Carbon (DOC) in subarctic river basins towards the oceans is enormous, because 23–48% of the worlds Soil Organic Carbon (SOC) is stored in northern regions. As climate changes, the amount and composition of DOC exported from these basins are expected to change. The transfer of organic carbon between soils and rivers results in fractionation of organic carbon compounds. The aim of this research is to determine the DOC concentrations, its fractions, i.e. humic (HA), fulvic (FA), and hydrophilic (HY) acids, and soil characteristics that influence the DOC sorptive properties of different soil types within a tundra and taiga catchment of Northern European Russia. DOC in taiga and tundra soil profiles (soil solution) consisted only of HY and FA, where HY became more abundant with increasing depth. Adsorption of DOC on mineral phases is the key geochemical process for release and removal of DOC from potentially soluble carbon pool. We found that adsorbed organic carbon may desorb easily and can release DOC quickly, without being dependent on mineralization and degradation. Although Extractable Organic Carbon (EOC) comprise only a small part of SOC, it is a significant buffering pool for DOC. We found that about 80–90% of released EOC was previously adsorbed. Fractionation of EOC is also influenced by the fact that predominantly HA and FA adsorbed to soil and therefore also are the main compounds released when desorbed. Flowpaths vary between taiga and tundra and through seasons, which likely affects DOC concentration found in streams. As climate changes, also flowpaths of water through soils may change, especially in tundra caused by thawing soils. Therefore, adsorptive properties of thawing soils exert a major control on DOC leaching to rivers. To better understand the process of DOC ad- and de-sorption in soils, process based soil chemical modelling, which could bring more insight in solution speciation, mineral solubility, and adsorption reactions, is appropriate.
1 Introduction

Potential mobilization and transport of Dissolved Organic Carbon (DOC) in subarctic river basins towards oceans is enormous, because 23–48% of the world's Soil Organic Carbon (SOC) is stored in the high latitude regions (Guo and Macdonald, 2006). Currently about 11% of the global DOC is released from the total Arctic drainage basin (about $24 \times 10^6 \text{ km}^2$) and exported to the ocean (Lobbes et al., 2000). It has been reported that about 10–40 g DOC/m$^2$ are transported annually from the organic surface layer into the mineral soil horizons in temperate forests (Michalzik et al., 2001), with only slightly lower amounts (4–17 g DOC/m$^2$) in the continuous permafrost zone of Siberia (Prokushkin et al., 2005). This implies that about 10–25% of annual C input to the organic surface layer with litter is leached from the organic surface layers. As climate changes, the amount and chemical composition of DOC exported from these basins are expected to change. Recent evidence from Northern Europe about increased DOC concentrations in surface waters draining upland areas and wetlands (Freeman et al., 2001; Frey and Smith, 2005), highlights the importance of understanding the transfer of C between soil and freshwater systems. The transfer of organic carbon between soils and freshwater systems involves a discrepancy between DOC concentrations in soil and rivers, which is the result of the selective removal of organic carbon compounds.

Major sources of organic carbon that replenish the pool of potentially soluble organic carbon are e.g. plant litter, root exudates, SOC, and microbial biomass. The release of carbon to the potentially soluble organic carbon pool is controlled by decomposition, leaching and formation of soluble humic substances (Kalbitz et al., 2000). Adsorption of DOC on mineral phases is the key geochemical process for the release and removal of DOC from this potentially soluble carbon pool (McDowell and Likens, 1988). Most DOC leached from organic horizons is adsorbed and retained in the subsoils (Kaiser and Guggenberger, 2000; Kalbitz et al., 2000, 2005). The adsorption depends much on the content of sesquioxides and amount of carbon previously accumulated in soils (Kaiser et al., 2000). Besides adsorption of DOC by Al and Fe oxides (Tipping, 1981;
Moore et al., 1992) also DOC adsorption by clay minerals occurs (Jardine et al., 1989; Kaiser et al., 1996; Stevenson, 1982). Furthermore, polyvalent metal ions in solution, such as Al and Ca, can cause precipitation of DOC (Temminghoff et al., 1998; Weng et al., 2002; Scheel et al., 2007). Along with the decrease of DOC concentrations on its passage through mineral soil, there are major biogeochemical alterations of DOC composition. Hydrophobic compounds (humic – HA – and fulvic – FA – acids), of high molecular weight and that are rich in acidic functional groups and aromatic compounds, adsorb most strongly (Kaiser et al., 2000). Also, there is an introduction of new substances to soil solution in subsoil due to desorption of humified material and the release of hydrophilic products (Kaiser and Zech, 1998b; Kaiser et al., 1996). These hydrophilic (HY) compounds can contribute to DOC adsorption but are also easily desorbed because of the weaker bonding strength (Kaiser and Guggenberger, 2000).

There is a large uncertainty about how effectively different soil types that are distributed throughout the subarctic area retain DOC. Moreover, there is a need for better understanding of controls on DOC dynamics in soils of climate zones other than the temperate area (Kalbitz et al., 2000). In this perspective, the area of Northern European Russia is underexposed compared to other parts of the Arctic drainage basin like Siberia, Canadian High North and Alaska, even though the area is an important source of terrestrial organic carbon for the Arctic Ocean.

The aim of this paper was to characterise the DOC concentrations, its fractions (HA, FA, and HY), and the soil characteristics that influence the DOC concentrations and fractionation of different soil types within a tundra and taiga catchment of Northern European Russia. We sampled pore water and soil samples from different soils and soil horizons along a transect. Also, we sampled stream water from several locations along the stream. Samples were analysed for DOC and inorganic elements as well as for the different carbon fractions of DOC. By extracting soil samples with water we get an indication of the potentially Extractable Organic Carbon (EOC), which is used as a measure for the easily soluble organic carbon pool. Similar to Ros et al. (2009) for DON, we consider EOC as the sum of DOC plus extra organic compounds that
solubilise during extraction (Fig. 1). Besides giving basic understanding of DOC interactions in northern conditions, the current gradients in climatic, soil, and hydrological conditions may be representative of changes as a function of time in northern regions and enable to predict DOC balance changes due to climate changes.

2 Materials and methods

2.1 Site description and sampling strategy

This study was carried out in two catchments in the Komi Republic of European Northern Russia: a tundra (67° N/62° E) and a taiga (62° N/50° E). The tundra study area is located close to the city of Vorkuta in the zone of discontinuous permafrost, the taiga study area is located close to the city of Syktyvkar in the permafrost free zone (Fig. 2). Mean annual air temperature is −5.7 °C in Vorkuta and 1.0 °C in Syktyvkar. Mean temperature in July is 12.8 °C in Vorkuta and 16.9 °C in Syktyvkar. Mean annual precipitation is 457 mm in Vorkuta and 599 mm in Syktyvkar (Komi Republican Center for Hydrometeorological and Environmental Monitoring).

Fieldwork was carried out during the months June and July in 2008. In each catchment a transect with 5 soil profiles was lay out (Fig. 3). The transect was selected to represent the major soil types present in the catchment. Furthermore, the transect represents the flow path of water flowing from the hillslopes to the stream, covering both the upslope and riparian zone areas. Soil profiles were selected based on distinctive differences in vegetation and morphology. In tundra, soil profiles were excavated until the permafrost, wherever that was possible. In all other situations, soil profiles were excavated until no change in soil profile was noticed for about 30 cm.

Soil solution was collected using Rhizon samplers with 0.5 µm porous membrane (Rhizosphere Research Products, Wageningen, The Netherlands) connected to 30 ml syringes. These were installed in each soil horizon of every soil profile along the transect. Soil solution samples were stored in 10 ml tubes (Greiner Bio-One) with 10 µl
1 M NaN₃ (0.001 M final concentration) to prevent microbial degradation. Soil samples were taken from the same soil horizons at which Rhizon samplers were installed in every soil profile along the transect. About 250 g soil of each horizon was sampled and stored in polyethylene twist and seal bags (VWR). Stream water samples were collected at several locations going downstream along the stream (tundra \( n = 5 \), taiga \( n = 7 \)). They were filtered over 0.45 µm and stored in 50 ml tubes (Greiner Bio-One) containing 50 µl 1 M NaN₃ (to prevent microbial degradation). All liquid samples were analyzed for pH in the field. Samples were stored cool where possible until transport to the laboratory.

### 2.2 Chemical analysis

Easily Extractable Organic Carbon (EOC) was created from subsamples of the field moist soil extracted with water in 1:10 solid/solution ratio by gently shaking end-over-end (9 rpm) for 2 h before centrifugation (3000 g, 10 min) and filtration over 0.45 µm. pH was measured in each sample before centrifugation. EOC samples were stored in 50 ml tubes with 50 µl of 1 M NaN₃. Remaining soil samples were dried at 40 °C for 48 h and sieved over 2 mm for samples storage. Subsamples were dried at 105 °C for 24 h to determine moisture content of field moist and air-dry samples. Total carbon content \((C_T)\) of the soils was determined on finely ground subsamples of dry soil samples by dry combustion (C/N analyser). Effective Cation Exchange Capacity (CEC) of the soils was determined using BaCl₂ based on method of Hendershot and Duquette (1986). All major exchangeable cations (Al, Fe, Ca, K, Mg, Mn, Na) were determined using ICP-AES (Varian, Vista Pro). The CEC was calculated by summation of all exchangeable cations, assuming a charge of 3 for Al and Fe. Ammonium oxalate is used as a selective reagent for dissolution of amorphous Al and Fe (Schwertmann, 1964). Dithionite-citrate is used as a selective reagent for dissolution of crystalline and amorphous Fe (Fe₃DCB) (Holmgren, 1967). Amounts of extracted Al and Fe were determined using ICP-AES (Varian, Vista Pro).
All liquid samples were analyzed for organic carbon with SFA-TOC (Skalar SK\textsuperscript{12}) and cations (Al, Fe, Ca, K, Mg, Mn) with ICP-AES (Varian, Vista Pro). Humic, fulvic and hydrophilic acid fractions of all liquid samples were analyzed according to a rapid batch method (van Zomeren and Comans, 2007). In brief, samples were acidified to pH 1 with 6 M HCl to precipitate Humic Acids (HA). A subsample of the remaining solution was analyzed for organic carbon (FA+HY) with SFA-TOC (Skalar SK\textsuperscript{12}). To the remaining solution DAX-8 resin (Amberlite) was added (1:10 s/s ratio) to adsorb Fulvic Acids (FA). A subsample of the remaining solution was analyzed for organic carbon (HY) with SFA-TOC.

3 Results and discussion

3.1 Field description

Soils in tundra consist of an organic top layer, varying from 2 cm on mineral grounds to 20 cm peaty material in lower areas. Beneath, a structureless glacial till (silt-loam) was found. Soils in tundra are classified according to the World Reference Base (WRB) (Table 1). Soils in tundra can also be distinguished as podburs (USSR classification) based on soils described by Rusanova and Deneva (2006). The tundra landscape is characterised by circular polygons with a well developed channel network. Vegetation in tundra is dominated by willow bushes and dwarf birch with herbs, lichen, and mosses in the ground cover. Wet areas are covered with willow shrubs, Sphagnum, and sedges.

Soils in taiga consist of an organic top layer, varying in thickness from 3 cm on slopes to 8 cm in lower areas. Beneath, well developed weathering soils were found. Soils in taiga are classified according to WRB (Table 1). Soils in taiga can also be distinguished as podzols based on soils described by Rusanova and Deneva (2006). The taiga landscape is characterised by steep slopes near the stream but a pronounced microrelief is absent. Vegetation in taiga is dominated by spruce forest with herbs and lichens in
the ground cover. Closer to the stream, birch forest is found with herbs, mosses, and ferns in the ground cover.

3.2 Soil properties

3.2.1 Organic carbon

Largest part of the organic carbon stored in soils of taiga and tundra is found in the upper (organic) soil layers (150–570 g C/kg soil). The upper layer of both taiga and tundra soils contain quite comparable amounts of organic carbon ($C_T$) (Table 2). The amount of organic carbon stored in taiga soils, however, decreases sharply with increasing depth. The sharp decrease in $C_T$ that is found in taiga soils reflects the typical eluvial layer found in podzols and albeluvisols. Along the transect, in the downslope direction, the amount of organic carbon stored in especially the upper layer of both taiga and tundra soils decreases. Similar $C_T$ amounts have been found by Rusanova and Deneva (2006), whereas Zolotareva et al. (2009) found smaller amounts of $C_T$ (2–50 g C/kg soil) for podburs.

3.2.2 Sesquioxides

From literature, we know that the interaction of SOC with sesquioxides (Al and Fe) plays a major role in the stability of organic carbon in soils (Kaiser and Guggenberger, 2000; von Lützow et al., 2006; Gu et al., 1994; Kaiser and Zech, 1998a; Kalbitz et al., 2000). The amount of oxalate- and dithionite-citrate-bicarbonate extractable Al and Fe in the soil are important indicators for the size of the reactive surface area on which organic carbon can adsorb (Kögel-Knabner et al., 2008). Amorphous minerals differ from crystalline forms in their greater ability to adsorb dissolved organic functional groups as they have more reactive hydroxyl groups (McBride, 2000). $Fe_{DCB}$ is generally considered to represent both crystalline and amorphous Fe oxides, and $Al_{DCB}$ represents Al substituted in Fe oxides as well as Al originating from the partial dissolution
of poorly ordered Al-(oxy)hydroxides. Acid oxalate is supposed to extract Al and Fe from amorphous aluminosilicates, ferrihydrite and Al- and Fe-humus complexes. The Fe activity ratio (Fe\textsubscript{OX}/Fe\textsubscript{DCB}) reflects the amorphous fraction of total Fe oxides (Kaiser et al., 1996). Substracting Fe\textsubscript{OX} from Fe\textsubscript{DCB} represents the more or less crystalline Fe oxides.

We found increasing amount of sesquioxides (Al\textsubscript{OX} and Fe\textsubscript{DCB}) with increasing depth in soils of taiga and tundra (Table 2). The typical eluvial layer, with small Al and Fe oxide amounts, is clearly visible in taiga soils classified as podzols and albeluvisols, but is not present in the soils downslope in the taiga transects. In the near stream soil profiles of both taiga and tundra, the Al and Fe oxides decrease with increasing depth. Also in contrast to the general trend with depth, we found larger amounts of Al oxides in Ah horizons than in the deeper C horizons of tundra soil profiles. Above all, tundra soils contain more sesquioxides than soils in taiga. Mostly the sesquioxides found in soils of taiga and tundra comprise of Fe oxides. Compared to results found for Siberian forest tundra soils by Kawahigashi et al. (2006), our soils have considerable higher Al and Fe oxides content. For comparison, Kawahigashi et al. found for a Gleysol between 4–11 mmol/kg Al\textsubscript{OX} and between 16–27 mmol/kg Fe\textsubscript{DCB}.

Concentrations of amorphous Fe oxides (Fe\textsubscript{OX}) in tundra soil profiles were larger than of crystalline Fe oxides (Fe\textsubscript{DCB}-Fe\textsubscript{OX}) and followed the same trend to increase with increasing depth as total free Fe (Fe\textsubscript{DCB}) (Table 2). Only the near stream soil profile in tundra had a reversed trend, with amorphous Fe oxides decreasing with depth. There was a trend towards higher concentrations of crystalline Fe oxides (Fe\textsubscript{DCB}-Fe\textsubscript{OX}) with increasing depth in nearly all taiga soil profiles except for the near stream soil profiles, together with a trend towards higher crystallinity of total Fe oxides (lower Fe\textsubscript{OX}/Fe\textsubscript{DCB}) in the mineral soil layers. Higher concentrations of active Al (Al\textsubscript{OX}), generally representing amorphous aluminosilicates, interlayer Al, exchangeable Al and humus Al, were found in the mineral soil layers compared to organic soil layers of both taiga and tundra soil profiles. Because the amount of Al\textsubscript{OX} increased with depth, while the amount of C\textsubscript{T} decreased with depth suggests that most of the Al in the deeper layers is of amorphous
origin. Moreover, we can conclude that the tundra soil profiles contain more total free Fe ($\text{Fe}_{\text{DCB}}$) but also more amorphous minerals ($\text{Fe}_{\text{OX}}+\text{Al}_{\text{OX}}$) than taiga soil profiles and therefore tundra soil profiles have likely a greater ability to adsorb organic carbon.

Earlier we mentioned that several studies support the importance of amorphous minerals for OC stabilization. Surprisingly, regression analysis showed that total carbon $C_T$ content is neither related to total free Fe ($\text{Fe}_{\text{DCB}}$) ($r^2$ is 0.3 for tundra and <0.1 for taiga) nor to amorphous minerals ($\text{Fe}_{\text{OX}}+\text{Al}_{\text{OX}}$) ($r^2$ is 0.1 for tundra and <0.1 for taiga) (Fig. 4). The lack of a relationship means that although amorphous minerals are abundant, the amount of $C_T$ preserved in the soil is not dependent on the available sesquioxides, which are assumed to largely contribute to the soils adsorption capacity. Therefore, other processes such as cation (e.g. calcium) and proton binding should be considered as important for adsorption of organic carbon.

### 3.2.3 Cation exchange capacity

The Cation Exchange Capacity (CEC) of a soil is a measure of the available sites on soil surfaces, primarily clay and organic matter surfaces, that can retain positively charged ions (cations) by electrostatic forces. Cations retained electrostatically are easily exchangeable with other cations in the soil solution. Therefore, as CEC increases, also the pool of multivalent cations in soil increases and this favours the preservation of organic carbon in soils. Recently Ross et al. (2008) mentioned that the decrease of CEC with increasing depth is associated with the decreasing number of surface sites of organic carbon ($C_T$), which also decreases with depth. We found decreasing CEC with increasing depth in soils of taiga and tundra (Table 2), but the decrease was sharpest for taiga soil profiles. Therefore, tundra soil profiles have more easily exchangeable cations available that can compete with cations in soil solution and consequently influence the adsorption/coagulation of DOC (Kaiser, 1998; Kaiser et al., 2008). Along the transect, in the direction of the stream, the CEC in taiga soils increased, however, in soils along the tundra transect this trend was not visible. Regression analysis showed
that total carbon (C_T) is positively related to CEC for tundra soils (r^2=0.6) but not for taiga soils (r^2=0.2). When leaving out the highest CEC found in the upper layer of the near stream soil profile, taiga soils also showed a positive relationship between CEC and C_T (r^2=0.7). The near stream soil profile is exposed to seasonal flooding with fine material being deposited. The improved relationship suggests that, especially near the stream, the finer clay fraction contributes more to CEC than the organic carbon.

Not only does CEC differ between taiga and tundra, but also the composition of the exchange complex. Remarkably, in taiga, Al and Fe are the major exchangeable cations whereas in tundra Ca and Mg are the major exchangeable cations (Fig. 5). The difference in major exchangeable cations can be explained by the different degree of weathering between taiga and tundra soils. The taiga soils are more affected by weathering than tundra soils, which results in the release of Al and Fe. As mentioned before cations retained electrostatically are easily exchangeable with other cations in the soil solution. Especially Ca is known to neutralize the hydrophobic fraction of organic carbon which makes it possible to have more organic carbon adsorbed (Weng et al., 2005). Therefore, as there is more easily exchangeable Ca, this could favour the adsorption of hydrophobic organic carbon in soils.

### 3.3 Soil solution chemistry

#### 3.3.1 DOC concentrations

Soil solution of taiga soils have larger DOC concentrations than tundra soils (Table 3), despite that both have comparable total organic carbon. This difference can be attributed to different sources of plant litter and of climatic conditions, which can both affect DOC concentrations. Thus, mosses and lichen, which are the dominant vegetation type in tundra, produce litter that gives poorer quality SOC than vascular plants (Hob- bie et al., 2000). Furthermore, lower temperatures and wetter conditions adversely decrease the rate of organic carbon decomposition and therefore decrease DOC production.
Whereas taiga topsoils contain more DOC in solution, the concentration decreases rapidly with increasing depth and this decrease is more pronounced than for tundra soils. Also regarding the topographic gradient the trend in DOC concentrations differs for taiga and tundra. Whereas for taiga, DOC decreases in the downslope direction, this is not clearly the case for the tundra transect. Carey (2003) found DOC concentrations in soil profiles from the Yukon that are comparable to DOC concentrations we found in our tundra soil profiles. DOC concentrations found by Carey ranged from 24–40 mg/l in organic layers to around 5 mg/l in mineral layers. In Norwegian forest soils Michalzik et al. (2003) found DOC concentrations between 10–300 mg/l, which is in comparison with DOC concentrations found in our taiga soil profiles.

3.3.2 DOC retention

Except for the slower decomposition rates under colder temperatures and more recalcitrant plant material (mosses) in tundra, which lead to lower DOC concentration leaching from the upper organic layers, also the mineral soil layers in tundra have a larger capability of adsorbing DOC than taiga soil. Therefore, DOC in tundra soil solution being able to leach downward in the soil profile has lower DOC concentrations compared to taiga, but at the same time is also exposed to soils being more favourable for adsorption. Above, we concluded that the tundra soil profiles have a greater ability to adsorb organic carbon because they contain more amorphous minerals than taiga soil profiles. Therefore they can retain more DOC, which also explains the lower DOC concentrations found in the mineral soil layers of the tundra soil profiles. Despite the fact that we did not find a relationship between total organic carbon (C_T) and the amorphous minerals, regression analysis showed that DOC and C_T have a good correlation ($r^2=0.8$ for taiga and 0.7 for tundra) (Fig. 6). The trend of decreasing DOC concentrations in the downslope direction as described for taiga corresponds well with the increase of amorphous minerals and available sites for retaining cations (CEC). Previously, we suggested that CEC increased in downslope direction in taiga caused by the presence of clay minerals. Besides adsorption, polyvalent metal ions in solution,
such as Al and Ca, can cause coagulation (precipitation) of DOC (Temminghoff et al., 1998; Weng et al., 2002). Because we found a larger amount of exchangeable Ca in tundra soil compared to taiga soils, the easily exchangeable Ca could contribute to the coagulation of DOC in soil solution of tundra soils. Coagulation occurs for concentrations of about 0.1 mmol/l Al and 3 mmol/l Ca (Temminghoff et al., 1998). We found total metal concentrations in soil solution of mineral layers of taiga and tundra soils between 0.001–1.3 mmol/l, which suggest that coagulation does not occur in the soil solution of our taiga and tundra soils.

3.3.3 DOC fractions

Besides the decrease of DOC concentrations when leaching downward through mineral soil, there are major chemical alterations of DOC composition. The adsorption of DOC leads to fractionation of DOC: hydrophobic compounds (Humic Acids – HA – and Fulvic Acids – FA) are removed selectively from the soil (Jardine et al., 1989) and hydrophilic (HY) substances are released into the soil solution.

DOC in taiga and tundra soil profiles consist only of HY and FA carbon compounds, were HY carbon becomes more abundant with increasing depth (Table 3). Regression analysis has showed that DOC concentrations in soil solution of both taiga and tundra is related to HY carbon fraction ($r^2=0.7$ in tundra and 0.9 in taiga). Slow decomposition of relatively difficult decomposable organic carbon leads to the formation of mainly hydrophobic (HA and FA) carbon compounds. In soil solution of tundra soil profiles we clearly find a higher affinity of DOC with FA ($r^2=0.7$) compared to DOC in soil solution of taiga soil profiles ($r^2=<0.1$). It is expected that under warmer taiga conditions organic carbon turnover is more rapid compared to cooler tundra conditions, which would favour the rapid decomposition of the smallest and easily decomposable hydrophilic (HY) molecules. Surprisingly the HY substances are more abundant than FA which suggests that a large part of the FA is converted into HY. Also competition of HY carbon compounds with HA and/or FA for binding sites can result in the displacement of HY (Kaiser et al., 1996). Wickland et al. (2007) found for Alaskan boreal...
forest that HA and FA are the dominant DOC fraction accounting for even more than 50% of DOC. Also for more temperate forest Qualls and Haines (1991) found that the composition of DOC often shows higher concentrations of HA and FA than HY.

We have shown that the decrease in DOC concentrations is accompanied by a change in DOC composition, with a general preferential decrease in hydrophobic DOC. Therefore, HY becomes the most abundant DOC fraction with increasing depth.

3.4 Soil solution leaching to streams

There are several differences in runoff hydrology between permafrost affected tundra regions and the more temperate taiga regions. For example, snowmelt is an important hydrological event in tundra (Carey and Woo, 1998). Furthermore, deep drainage is restricted where permafrost is present, enhancing near-surface water tables (Carey and Woo, 1999). Matrix bypass mechanisms such as inter-hummock channel flow (Quinton and Marsh, 1999) may transport significant amounts of water during the melt period and wet conditions. Because we have shown that taiga and tundra soils have different DOC concentrations along the topographic gradient and we know that the pathways of water towards the streams also differ for taiga and tundra, the DOC release into surface water should be strongly fingerprinted by the pathway.

Stream water in taiga has larger DOC concentrations than stream water in tundra (Fig. 7). This is supported by the fact that we also found higher DOC concentrations in soil solution of taiga soils. We found decreasing DOC concentrations in the downstream direction of taiga and tundra streams, but the decrease was stronger for the taiga stream. Soils in the source area of the streams are rich in organic carbon (peat), which contribute largely to the DOC concentrations found in the upstream parts of the streams. Further downstream dilution and mixing with water that has been in contact with mineral soil layers or that is of less organic carbon rich origin takes place, which decreases the DOC concentrations found in the downstream parts of the streams. In-stream processes such as decomposition and coagulation can also decrease DOC concentrations in the downstream direction. Although cation
concentrations in the streams are not high enough to let coagulation take place (sum of cations <1–2.5 mmol/l) we did find a trend towards lower DOC concentrations with increasing cation concentrations in streams ($r^2 = 0.7$ for tundra with Ca and Mg and 0.9 for taiga with Al and Fe) (Fig. 8).

The topographic location of the histic gleysols emphasizes that this soil types may be important for the DOC concentrations found in the streams. The histic gleysols are found in the riparian zone of taiga and the inter-hummock channels of tundra. The soil solution in taiga is flowing down the hillslope to the riparian zone with histic gleysols, before the soil solution is entering the stream. The shallow active layer in tundra causes most of the water to be transported through inter-hummock channels.

When we compare the DOC concentrations found in soil solution of these soil types (Table 2) with the DOC concentrations found in the streams (Fig. 7), we notice that, except for the upstream parts of the streams, the soil solution DOC concentrations of the histic gleysols correspond well with the DOC concentrations found in the streams.

Besides the trend of decreasing DOC concentrations in the downstream direction we also found for tundra streams different DOC concentrations as a function of time during summer. This decrease in DOC concentrations as a function of time can be attributed to a change in flowpath. In spring there is a large supply of melt water flowing through the organic rich topsoils. This melt water contains relatively large amounts of DOC in comparison with soil solution from the melting active layer. We found that tundra stream water in June (end of melting season) reflects more shallow flow paths with higher DOC concentrations and lower cation concentrations than stream water in July (early summer) (Fig. 7). Especially further downstream, where there is no direct inflow of water from the peat soils, the DOC concentrations of tundra stream water in July decreased, whereas the cation concentrations increased. The melting of the active layer causes that tundra stream water DOC concentrations becomes more representative for DOC leached from mineral layers. This is because gradually more water from mineral sources is entering the stream when going in the downstream direction. The decreasing stream water temperature as a function of time also confirmed that the
water derived from the melting active soil layer increased. Our results are supported by Carey (2003) who found DOC concentrations in a tundra stream decreasing from 24 mg/l after stream flow began to 2–3 mg/l in base flow. Also Prokushkin et al. (2005) reported that thawing of active layer during the growing season led to decreasing concentration of DOC in stream from June to September.

In contrast to what we found in soil solution, HY carbon compounds are not the dominant carbon fraction contributing to DOC in taiga and tundra stream water. Stream water DOC in taiga and tundra mainly consists of FA. Regression analysis have showed that DOC concentrations in stream water of both taiga and tundra is related to FA carbon fraction \( r^2 = 0.9 \) in tundra and in taiga). Upstream in the catchments, organic carbon rich soils are the major sources of DOC to stream water, and therefore, organic carbon rich soils can contribute to a large input of FA. Further downstream, especially under the warmer taiga conditions, in-stream decomposition of the most easily degradable carbon compounds (HY) can result in low HY fractions and consequently a larger abundance of FA carbon compounds. Furthermore, we found for the decrease of DOC concentrations as a function of time in tundra that particularly the FA fraction decreases. With the increasing input of melting active layer when the spring season proceeds, the leaching of mineral soil layers with much lower DOC concentrations and predominantly HY carbon compounds also the stream water DOC composition becomes less rich in FA.

Summarizing, pathways vary between taiga and tundra and through seasons, and this affects the DOC concentration. The flow path of soil solution will largely determine the concentration of DOC in streams. The soil type that the soil solution is in contact with finally before entering the stream is the soil type that largely determines the DOC concentration in the stream. DOC composition is altered by in-stream processes, making FA the most abundant carbon fraction in streams.
3.5 Potentially soluble organic carbon

Desorption or dissolution from potentially soluble organic carbon controls the release of DOC into the soil solution (Fig. 1). Largest part of the Extractable Organic Carbon (EOC) stored in soils of taiga and tundra is found in the upper soil layer (0.3–1.3 g C/kg soil; see Table 2). The upper soil layer of both taiga and tundra soils contain quite comparable amounts of EOC. The amount of EOC stored in taiga and tundra soils, however, decreases sharply with increasing depth. Surprisingly, EOC does not increase as a function of depth as may be expected from soils with a reasonable adsorption capacity. Nevertheless, EOC from upper layers is only a very small percentage (0.1–0.5%) of the total carbon (C_T) stored in these layers, whereas in mineral soil layers EOC is between 1–5% of the total carbon stored. Our results are supported by several others (Jandl and Sollins, 1997; Uhlirova et al., 2007; Guo et al., 2007; Xu et al., 2009) who also found that up to 2% of arctic soil organic carbon stock could be potentially released into solution. In contrast, Rennert et al. (2007) found that water extractable OC from B horizons of German forest soils was approximately 0.4% of C_T.

Furthermore, the mineral soil layers of tundra soils contain slightly larger amounts of EOC than mineral soil layers of taiga soils. Earlier, we concluded that the tundra soil profiles have a greater ability to adsorb organic carbon because they contain more amorphous minerals than taiga soil profiles. Therefore it is plausible that they retain/release more EOC than taiga soils. However, regression analysis showed that EOC is not related to amorphous minerals, like we also found for C_T. Although we did not find a relationship between EOC and the amorphous minerals, however, regression analysis showed that EOC and C_T have a good correlation (r^2=0.8 for both taiga and tundra) (Fig. 9). Along the transect, in the downslope direction, the amount of EOC stored in especially the upper soil layer of taiga soils decreases. The trend of decreasing EOC in downslope direction as described for taiga contradicts with the increase of amorphous minerals and available sites for retaining cations (CEC), which could result in more available easily extractable organic carbon.
3.6 Potentially soluble organic carbon and DOC

To be able to compare potentially soluble organic carbon (EOC) with the current DOC concentrations in soil solution, we expressed EOC content as concentration (mg/l) available in soil solution. The largest EOC concentrations in taiga are found in the upper layers (100–1227 mg/l), whereas in tundra soils highest EOC concentrations are found in the mineral layers (172–920 mg/l). Hence, taiga soils contain larger EOC concentrations than tundra soils (Table 3). Earlier, we already found that soil solution of taiga soils also contains higher DOC concentrations than soil solution of tundra soils. This suggests that taiga soils have higher SOC carbon turnover than tundra soils. Regression analysis, however, showed that EOC concentrations are not well related to DOC concentrations for tundra soils ($r^2=0.3$) and for taiga soils ($r^2=0.2$). The lack of correlation means that there is not a straightforward relationship between organic carbon in solution and soluble organic carbon. From literature, we know that adsorption/desorption processes performed in laboratory experiments can be well described by Langmuir isotherms (Gu et al., 1994; Kothawala et al., 2008). Several others have successfully describe DOC binding with a surface complexation model, which also included e.g. pH and ionic strength affects and Ca binding (Weng et al., 2006; Filius et al., 2003; Lumsdon et al., 2005). Therefore, the process of adsorption/desorption, which plays a key role in the release of DOC from our soils, is suitable for process based soil chemical modelling and could bring more insight in the processes of solution speciation, mineral solubility, and adsorption reactions.

Also regarding the topographic gradient the trend in EOC concentrations differ for taiga and tundra. Whereas for taiga, EOC concentrations decreases in the downslope direction, this is not clearly the case for the tundra transect. We found EOC concentrations in taiga soils near the stream that are considerably lower than EOC concentrations further upslope in the transect. Adsorption of EOC can be stronger in the near stream soil profiles because they have larger amounts of amorphous minerals and available
sites for retaining cations (CEC) resulting in lower EOC concentrations, although we did not find a clear relationship between EOC and the available binding sites.

The enormous increase of organic carbon in soil solution when all potentially soluble organic carbon available in soils will dissolve suggests that organic carbon not only adsorbs rapidly when in contact with soil mineral compounds but can also desorb easily and contribute to organic carbon in soil solution and ultimately in streams. For example, in mineral layers of tundra soils, DOC is only 1–5% of the potentially soluble organic carbon pool, which means that about 80–90% of the released EOC was previously adsorbed.

It appears that desorption is the main process of influence on the release of organic carbon from the soil. Consequently, the composition of EOC is also influenced by the fact that predominantly hydrophobic compounds are adsorbed to the soil and will therefore also be the main compounds released when desorbed. Because of the slower decomposition and more recalcitrant plant material in tundra compared to taiga, the EOC in tundra is expected to be more hydrophobic than in taiga. EOC of upper soil layers in taiga and tundra soil profiles mainly consist of FA (60–70%). The contribution of FA to the composition of EOC decreased with depth (Table 3). In tundra soil profiles, however, the contribution of HA to the composition of EOC increased with depth. Regression analysis showed a strong relationship between EOC and FA for taiga ($r^2 = 0.8$) and between EOC and HA for tundra ($r^2 = 0.9$). Earlier we showed that tundra mineral layers have higher CEC and contain more exchangeable Ca than taiga soils. The negative charge of the HA can be neutralized by Ca which makes it possible to have more HA adsorbed (Weng et al., 2005). Our results are supported by Jandl and Sollins (1997) who also found that around 60% of the EOC in organic layers was hydrophobic acids. For mineral layers they found that 40% of EOC was hydrophobic acids (HA and FA). Similar results have been reported by Kalbitz et al. (2003) who found that 45–70% of EOC was FA.
4 Conclusions

We have shown that different soil types within a tundra and taiga catchment in Northern European Russia differ with respect to DOC concentrations and its chemical composition as well as the DOC adsorptive properties of these soils. Our results show that DOC in taiga and tundra soil profiles consisted only of hydrophilic (HY) and fulvic (FA) carbon compounds, however, HY carbon became more abundant with increasing depth. We demonstrated that on the short term the chemical process of adsorption and desorption are important for the release of DOC from these soils. Our results indicated that adsorbed organic carbon may desorb easily and in this way can release DOC quickly, without being dependent on mineralization and degradation.

In view of how climate change could affect stream DOC concentrations, it might be important that DOC concentrations are significantly controlled by adsorption and desorption processes, as a direct translation of expected changes of mineralization and degradation into DOC levels becomes disputable. Although EOC amounts comprise only a small fraction of soil organic carbon, it is a significant buffering pool for DOC. We found that about 80–90% of the released EOC was previously adsorbed. The composition of EOC is also influenced by the fact that predominantly hydrophobic compounds (HA and FA) adsorbed to the soil and will therefore also be the main compounds released when desorbed. Because of the slower decomposition and more recalcitrant plant material in tundra compared to taiga, the EOC in tundra is expected to be more hydrophobic than in taiga. The enormous increase of organic carbon in soil solution when all potentially soluble organic carbon available in soils would dissolve suggests that organic carbon not only adsorbs rapidly when in contact with soil mineral compounds but can also desorb easily and contribute to organic carbon in soil solution and ultimately in streams. We know that pathways vary between taiga and tundra and through seasons, and that this is likely to affects the DOC concentration found in streams. Hence, it is plausible, that DOC adsorption or desorption along the flowpaths from the catchment into the stream will control DOC release into the streams.
We showed that the soil type that the soil solution is in contact with finally before entering the stream, i.e. riparian zone or inter-hummock channels, is the soil type that largely determines the DOC concentration in the stream.

When using current taiga conditions as an analogy for future tundra conditions, we conclude that the implications for the release of DOC are still difficult to predict. Although the production and release of DOC from the upper organic soils is supposed to be greater in warmer soils, the deeper active layer increases the contact with mineral soils and thus the likelihood of DOC adsorption, allowing for C stabilization in soil. Especially under wetter climate conditions more DOC can be transported into the subsoil, and the retention of DOC in mineral horizons becomes of great importance for the fate of DOC leached from upper organic soils. Therefore, the adsorptive properties of thawing soils distributed across the subarctic area exert the major control on DOC leaching to rivers. To better understand the process of DOC adsorption/desorption in soils, process based soil chemical modelling, which could bring more insight in the processes of solution speciation, mineral solubility, and adsorption reactions, would be appropriate.

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Table 1. Soil types and coverage (% of the catchment) of the soil profiles in the transects of taiga and tundra.

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<th>Taiga</th>
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</tr>
<tr>
<td>B Albeluvisol Abruptic (20%)</td>
<td>Histic Gleysol (21%)</td>
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<tr>
<td>C Histic Albeluvisol (44%)</td>
<td>Folic Cambisol (14%)</td>
</tr>
<tr>
<td>D Gley Histic Podzol (5%)</td>
<td>Folic Cambisol Turbi Gelic (20%)</td>
</tr>
<tr>
<td>E Histic Gleysol (1%)</td>
<td>Folic Stagnic Cambisol (6%)</td>
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Table 2. Soil characteristics of the soil profiles in the transects of taiga and tundra

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Table 3. Humic (HA), fulvic (FA) and Hydrophilic acid (HY) fractions of Dissolved Organic Carbon (DOC) and Extractable Organic Carbon (EOC) of the soil profiles in the transects of taiga and tundra.

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<th>FA (%)</th>
<th>HY (%)</th>
<th>EOC (mg/l)</th>
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<th>FA (%)</th>
<th>HY (%)</th>
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Fig. 1. Conceptual relationships between SOC, EOC and DOC. The pool size of both DOC and EOC can vary due to soil properties (denoted by black arrows).
Fig. 2. Field locations in taiga and tundra of European Northern Russia. Blue shading from dark to light: continuous, discontinuous, sporadic and isolated permafrost. Map source: UNEP/GRID-Arendall and arcgisonline.com.
Fig. 3. Transect with soil profiles (soil sample locations) in taiga (a) and tundra (b).
Fig. 4. Relationship between total organic carbon content ($C_T$) and amorphous minerals for soil samples of taiga and tundra.
Fig. 5. Contribution of exchangeable cations – (a): Ca+Mg and (b): Al+Fe – to Cation Exchange Capacity (CEC) for soil samples of taiga and tundra.
Fig. 6. Relationship between dissolved organic carbon (DOC) and total organic carbon (CT) for soil samples of taiga and tundra.
Fig. 7. Dissolved Organic Carbon (DOC), total cation concentrations and temperature of stream water at different locations along the stream in taiga (a) and tundra – (b): June, (c): July.
Fig. 8. Relationship between dissolved organic carbon (DOC) and cations – (a): Ca+Mg, (b): Al+Fe – for stream water of taiga and tundra.
Fig. 9. Relationship between (a): Extractable Organic Carbon (EOC) and total organic carbon ($C_T$) and (b): EOC and amorphous minerals for soil samples of taiga and tundra.