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Chemical composition of aquatic dissolved organic matter in five boreal forest catchments sampled in spring and fall seasons

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Abstract The chemical composition and carbon isotope signature of aquatic dissolved organic matter (DOM) in five boreal forest catchments in Scandinavia were investigated. The DOM was isolated during spring and fall seasons using a reverse osmosis technique. The DOM samples were analyzed by elemental analysis, FT-IR, solid-state CP-MAS ^{13}C -NMR, and C-1s NEXAFS spectroscopy. In addition, the relative abundance of carbon isotopes (^{12}C , ^{13}C , ^{14}C) in the samples was measured. There were no significant differences in the chemical composition or carbon isotope signature of the DOM sampled in spring and fall seasons. Also, differences in DOM composition between the five catchments were minor. Compared to reference peat fulvic and humic acids, all DOM samples were richer in O-alkyl carbon and contained less aromatic and phenolic carbon, as

shown by FT-IR, ^{13}C -NMR, and C-1s NEXAFS spectroscopy. The DOM was clearly enriched in ^{14}C relative to the NBS oxalic acid standard of 1950, indicating that the aquatic DOM contained considerable amounts of organic carbon younger than about 50 years. The weight-based C:N ratios of 31 ± 6 and the $\delta^{13}\text{C}$ values of $-29 \pm 2\text{‰}$ indicate that the isolated DOM is of terrestrial rather than aquatic origin. We conclude that young, hydrophilic carbon compounds of terrestrial origin are predominant in the samples investigated, and that the composition of the aquatic DOM in the studied boreal forest catchments is rather stable during low to intermediate flow conditions.

Keywords Dissolved organic matter · Boreal forest catchment · Flow condition · Reverse osmosis · Spectroscopy · Carbon isotopes

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Introduction

Natural organic matter (NOM) occurs in nearly all aquatic environments including lakes, rivers, oceans, soil water and groundwater (Schnitzer 1991). In rivers and lakes, NOM is mainly present as dissolved organic matter (DOM), but it can also be associated with colloidal particles. Average concentrations of DOM, expressed as dissolved organic carbon (DOC), range from about 0.1 mg l^{-1} in groundwater to 33 mg l^{-1} in peat bogs (Perdue and Ritchie 2004).

Transport of NOM in rivers is an important flux component within the global carbon cycle. Furthermore, it plays an important role in the biogeochemical cycling, transport of nutrients and contaminants, and bioavailability of metals (e.g., Al, Fe, Cu), which can form stable complexes with organic functional groups of NOM (Buffle et al. 1987; Tipping et al. 2002).

On average, freshwater DOM has an elemental mass composition of $49.5 \pm 3.3\%$ C, $5.0 \pm 1.0\%$ H, $43.0 \pm 4.1\%$ O, $1.7 \pm 1.0\%$ N, and $2.0 \pm 1.3\%$ S (Perdue and Ritchie 2004). The reported average molecular weight varies considerably, with typical values ranging from less than 1 kDa to more than 100 kDa, depending on differences in the composition and the aggregation state, but also in part on the different techniques applied (Leenheer and Croue 2003). For size exclusion chromatography, Perdue and Ritchie (2004) report a median value of 1.7 kDa for the weight-averaged molecular weight of 37 DOM samples. On average, more than 80% of aquatic DOM can be isolated by resins either as hydrophobic or hydrophilic acid fractions, which are often present in a ratio of about 2:1 (Perdue and Ritchie 2004). The hydrophobic acid fraction typically consists of fulvic acids and smaller amounts of humic acids. Less than 20% of DOM consists of hydrophilic bases and neutral compounds. Amounts of identifiable biomolecules, such as amino acids ($\sim 1.8\%$), sugars ($\sim 3.0\%$) and lignin-derived phenols ($\sim 0.6\%$) are typically small (Perdue and Ritchie 2004).

Surface waters in the cold and wet boreal climatic zones in the northern hemisphere are often particularly rich in DOM. Under boreal forest and bog vegetation, the soil cover is often dominated by Podzols and Histosols, respectively. Low Ca and Mg concentrations (soft water) in these soils along with high precipitation and low temperatures favor leaching of DOM into the rivers (Lobbjes et al. 2000). The aquatic NOM in these oligotrophic rivers seems to be of terrestrial origin rather than aquatic phytoplankton (Hedges and Oades 1997). Thus, riverine NOM may reflect the properties of the surrounding soils as well as the vegetation and climate of the region (Lydersen 1995).

Changes in hydrological conditions have been shown to affect DOM concentrations in freshwaters of boreal forest catchments. Skjelvåle et al. (2001) and Hongve et al. (2004) reported that fluctuations in

the amount and intensity of precipitation are the main reason for the observed changes in DOM concentrations in Scandinavia. In addition, changes in atmospheric deposition and land use are believed to have significant effect on the amount and quality of NOM (Vogt et al. 2004). Large variations in freshwater chemistry have also been reported for spring flood periods in boreal catchments, affecting pH and concentrations of inorganic and organic compounds (Vogt et al. 1990; Bishop et al. 2000; Stepanauskas et al. 2000; Hruška et al. 2001). The variations during spring floods may be largely controlled by the hydrological conditions in the catchments during the snowmelt period such as e.g., the groundwater level and the soil temperature, as well as by the depth-dependent distribution of water-soluble inorganic and organic compounds in the soils (Bishop et al. 2004; Laudon et al. 2004b). Seasonal variations of surface water DOM in boreal catchments during low to mean flow conditions, reflecting rather the influence of climatic fluctuations, have only been investigated in few studies (Heikkinen 1994; Moran and Zepp 1997).

Compared to riverine DOM, more detailed studies have been conducted on the dynamics of DOM in soil leachates, which may be a major source of aquatic DOM. In general, a decrease of DOM concentrations with depth is observed in soils, which may be primarily caused by adsorption of DOM to mineral surfaces (Kalbitz et al. 2000). As hydrophobic DOM compounds are preferentially adsorbed in soils (Jardine et al. 1989), relative amounts of hydrophilic compounds in soil DOM are increased by adsorption processes. In contrast, hydrophilic DOM tends to be more easily biodegradable than hydrophobic DOM (Kalbitz et al. 2003; Marschner and Kalbitz 2003). The observation that relative amounts of hydrophilic DOM compounds often increase with depth in subsoils implies that adsorption is the dominant process controlling amounts and composition of DOM in mineral subsoils (Kalbitz et al. 2000). Consequently, DOM of surface waters may exhibit a high percentage of hydrophilic compounds in case leachates from mineral subsoils represent the main source of DOM in the catchment. In addition, the seasonal variability of DOM in subsoil waters is expected to be minor generating a rather uniform input of DOM into surface waters (Solinger et al. 2001; Porcal et al. 2004; Yano et al. 2004), especially in case of coniferous forest catchments (Hongve 1999; Hongve et al. 2000).

In this study, we have characterized a set of ten aquatic DOM samples from five forested catchments in Scandinavia (Vogt et al. 2001, 2004) isolated by reverse osmosis under low to intermediate flow conditions during spring and fall seasons. The DOM samples were analyzed by elemental analysis, FT-IR spectroscopy, CP-MAS ^{13}C -NMR spectroscopy, synchrotron-based C-1s NEXAFS spectroscopy, and radiocarbon (^{14}C) analysis. Our objectives were (i) to study the composition of the DOM in five catchments, which differ in climate and exhibit some variations in soil types and vegetation, and (ii) to explore to which extent the chemical composition of aquatic DOM varies with respect to the sampling season and the sampling site.

Materials and methods

Sampling sites

Five catchments in Norway, Sweden and Finland were selected within the framework of a larger project on NOM in the Nordic countries (Vogt et al. 2001). The locations of the five sampling sites are depicted in Fig.1. Table 1 summarizes some key properties of the sites, which differ in climate, dominating soil type, and vegetation (Gjessing et al. 1999; Vogt et al. 2001). The annual average temperature ranges from 0 to 7 °C and the average annual precipitation from 590 to 2500 mm. All sampling sites are forested predominantly by

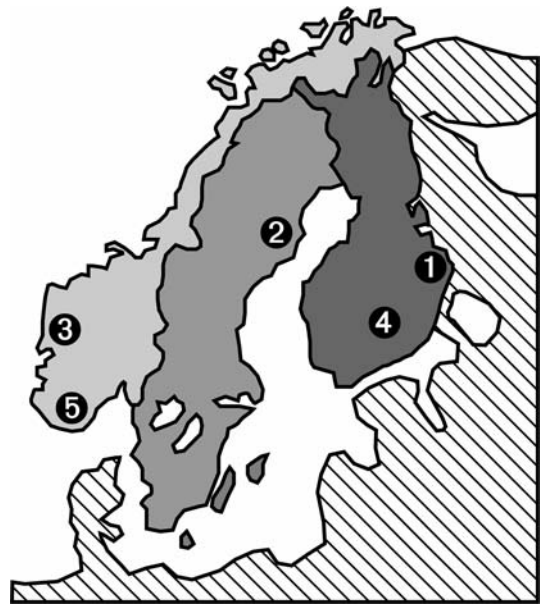


Fig. 1 Location of sampling sites: (1) Valkea-Kotinen, Finland, (2) Svartberget, Sweden, (3) Skjervatjern, Norway, (4) Hietajärvi, Finland, (5) Birkenes, Norway

Scots pine (*Pinus sylvestica* L.) and Norway spruce (*Picea abies* (L.) Karst.) on soils developed on glacial till. The soils in the catchments are acidic soils and the dominant soil types are dystric Cambisols and Podzols. In addition to these soil types, large areas of peatland are present in all catchments, with Histosols contributing between 13% and 45% of the total terrestrial area (Table 1).

Table 1 Geographic characteristics of the five selected sample sites (Vogt et al. 2001, 2004)

Sampling site	Valkea-Kotinen #1	Svartberget #2	Skjervatjern #3	Hietajärvi #4	Birkenes #5
Country	Finland	Sweden	Norway	Finland	Norway
Phytogeographic zone	Boreal	Boreal	Boreal-coastal	Boreal	Boreal-nemoral
Forest type	Spruce	Spruce	Pine	Pine & Spruce	Spruce
Bedrock	Gneiss & Granodiorite	Gneiss & Schist	Gneiss	Gneiss & Granodiorite	Granite
Dominant soil type	Dystric Cambisol	Ferric Podzol	Gleyic Podzol	Haplic Podzol	Humic Gleysol
Histosol coverage [%]*	25	16	42	45	13
Elevation [m a.s.l.]	150	235	136	165	190
Mean temperature [°C]	3.1	0.0	5.5	2.0	6.6
Precipitation [mm yr ⁻¹]	618	720	2560	592	1500
Evapotranspiration [mm yr ⁻¹]	432	395	NA	176	300
Discharge [mm yr ⁻¹]	186	325	NA	416	1200

NA denotes not available

*Values are given as percentages of the total soil coverage in the catchment

Isolation of DOM

DOM was isolated from surface water collected at all five sites between September 30 and October 13, 1999 (fall samples) and between April 26 and May 26, 2000 (spring samples), respectively. During water sampling, low to intermediate flow conditions predominated in all catchments except for the spring sampling at Svartberget (Table 2). Records on temperature, precipitation and discharge from Svartberget indicate that the elevated discharge in the Svartberget catchment during the spring sampling was caused by a rainfall event (17 mm) on soils still saturated to field capacity by melt-water. For DOM isolation, 500 to 1100 l of surface water was processed through a mobile reverse osmosis (RO) unit (PROS/2S, RealSoft, Kansas City, MO, USA) as described by Serkiz and Perdue (2004). Briefly, the surface water was passed through a pre-filter into a reservoir, from where it was pumped through a sodium-saturated cation exchange resin (Dowex 50, Dow Chemical Comp., Michigan, MI, USA) to prevent precipitation of insoluble salts. The water was then passed through the RO membranes with pores of about 150 Å. In the RO membranes, the water was separated into a permeate solution, containing virtually no solutes and a retentate solution that contained nearly all of the dissolved inorganic and organic material. The permeate solution was discharged and the retentate solution was recycled back into the reservoir. At the end of the RO treatment, 25 l of concentrated solution were filtered through a 0.45 µm filter (Nucleopore) and further concentrated by a rotary evaporator at 30°C to a volume of about 5 l and then freeze-dried (Vogt et al. 2001).

Elemental analysis

The freeze-dried, solid-state RO isolates were analyzed for total C, H, N, and S contents using a micro-CHNS analyzer (CHNS-932, Leco, St. Joseph, MI, USA). Five replicates were analyzed for each sample, using 2 mg subsamples. Inorganic cations and anions were analyzed after dissolving 1 mg of the freeze-dried RO isolates in 10 ml deionized water. The concentrations of SO_4^{2-} , NO_3^- , and Cl^- were measured by ion chromatography (761 Compact IC, Metrohm, Appenzell, Switzerland). The concentrations of Na, Ca, Mg, K, Al, Fe, Mn, and Si were analyzed by ICP-OES (Vista-MPX, Varian, Darmstadt, Germany) after acidifying the solutions with ultra-pure nitric acid. All concentrations were corrected for the moisture content of the samples, which was determined gravimetrically after drying the samples at 105°C during 24 h.

FT-IR spectroscopy

Transmission mode Fourier-transform infrared (FT-IR) spectra were collected in ambient air at room temperature using 300 mg KBr pellets containing 0.5 mg of freeze-dried RO isolate (Spectrum One, Perkin Elmer, Fremont, CA, USA). For each sample, 20 scans were collected from 500 to 4000 cm^{-1} with a resolution of 4 cm^{-1} , background corrected, and averaged.

Solid-state CP-MAS ^{13}C -NMR spectroscopy

The RO isolates were analyzed by solid-state cross polarization magic-angle spinning ^{13}C nuclear

Table 2 Flow characteristics of the five selected catchments. Maximum, average, and median values of daily discharge were derived from daily records during the years 1999 and 2000

Sampling site	Valkea-Kotinen #1	Svartberget #2	Skjervatjern #3	Hietajärvi #4	Birkenes #5
Maximum discharge [mm d^{-1}]	4.33	11.09	NA	3.53	59.36
Mean discharge [mm d^{-1}]	0.50	1.13	NA	0.97	4.45
Median discharge [mm d^{-1}]	0.36	0.33	NA	0.88	1.81
Date of fall sampling	5.10.1999	10.10.1999	13.10.1999	7.10.1999	30.9.1999
Discharge during fall sampling [mm d^{-1}]	0.00	0.09	NA	0.58	3.55
Date of spring sampling	26.5.2000	21.5.2000	28.4.2000	24.5.2000	26.4.2000
Discharge during spring sampling [mm d^{-1}]	0.28	3.22	NA	1.57	1.80

NA denotes not available

magnetic resonance (CP-MAS ^{13}C -NMR) spectroscopy (DSX 200, Bruker, Rheinstetten, Germany). The NMR spectra were collected at a resonance frequency of 50.3 MHz, using a magic-angle spinning speed of 6.8 kHz and a contact time of 1 ms. A pulse delay of 400 ms was used. A ramped ^1H pulse decreasing was used in order to avoid spin modulations of Hartmann–Hahn conditions (Peersen et al. 1993). The number of scans for each sample varied from 18,000 to 20,000. For quantitative analysis, each spectrum was divided into six chemical shift regions which were assigned to alkyl carbon (0–45 ppm), O-alkyl carbon (45–110 ppm), aromatic carbon (110–160 ppm), phenolic carbon (140–160 ppm), carboxyl carbon (160–185 ppm), and carbonyl carbon (185–20 ppm), respectively. The relative intensity of these peaks was determined by numerical integration of the spectral regions.

C-1s NEXAFS spectroscopy

Near edge X-ray absorption fine structure (NEXAFS) spectra at the C-1s edge were measured using the Stony Brook Scanning Transmission X-ray Microscope (STXM) at the NSLS beamline X-1A (National Synchrotron Light Source, Upton, N.Y.). The STXM was operated inside a helium-purged enclosure at room temperature and atmospheric pressure. A detailed description of the instrument can be found in Jacobsen et al. (1996). For specimen preparation, 2 mg of freeze-dried RO isolate were dissolved in 500 μl deionized water. A droplet of this solution was deposited onto a X-ray transparent Si_3N_4 window (Silson Ltd., Northampton, UK) and air-dried, resulting in a 50–200 nm thick film of organic carbon. On each specimen, absorbance spectra were collected from 280 to 310 eV at 25 different spots on the dry film and averaged. At least four spectra of the clean Si_3N_4 window were collected, averaged, and used for background correction of the C-1s NEXAFS spectra. For comparison of the spectra of different films, which can vary in thickness, the averaged spectra were normalized relative to their absorbance at 310 eV. The normalized NEXAFS spectra were deconvoluted by fitting the spectral region between 280 and 310 eV with seven Gaussian peaks representing the main $1s\text{-}\pi^*$ and $1s\text{-}\sigma^*$ transitions and one arctangent function for the ionization step at around 290 eV (Schumacher et al. 2005). For quantification,

the fitted areas of the peaks at 285 eV, 286.5 eV, 288.5 eV, 289.5 eV, and 290.5 eV were converted into percentages of carbon bound as aromatic, phenolic, carboxyl, O-alkyl, and carbonyl carbon, respectively, using empirical correlation functions based on C-1s NEXAFS and ^{13}C -NMR data of five humic acid samples, four fulvic acid samples, and two freshwater NOM samples (Schumacher 2005).

Carbon isotope analysis

All samples were analyzed for the carbon isotopes ^{12}C , ^{13}C , and ^{14}C . For the graphitization of the samples, the method described by Vogel et al. (1984) was applied. Carbon isotope measurements of the graphite materials were performed at the PSI/ETH compact accelerator mass spectrometry (AMS) facility in Zurich, Switzerland, which contains a 6 MV EN tandem accelerator (Synal et al. 1997). Details on sample preparation and the instruments specifications are reported elsewhere (Synal et al. 1997; Hajdas et al. 2004). From the AMS results, $\delta^{13}\text{C}$ values were calculated for each sample and the reference material PDB (Stuiver and Polach 1977). Compared to conventional mass spectrometry, the uncertainty range of $\delta^{13}\text{C}$ values obtained with AMS is at $\pm 1\text{‰}$ (Bonani et al. 1987). The conventional ^{14}C age and the percent modern carbon (pmC) were determined relative to the NBS oxalic acid standard from 1950 (Stuiver and Polach 1977). All ^{14}C age and pmC values were corrected for isotope fractionation using the $\delta^{13}\text{C}$ values (Stuiver and Polach 1977).

Results and Discussion

Elemental composition

The RO isolates contained between 29 and 66% inorganic material (ash) (Vogt et al. 2001), which is typical for RO isolates (Serkiz and Perdue 1990; Gjessing et al. 1999). The ash consisted mainly of sodium sulfates and chlorides. In addition, small amounts of calcium, magnesium and silicate were identified. The large amounts of sodium in the samples resulted from the use of a sodium-saturated cation exchange resin for the RO sample isolation. The sulfate content in the re-dissolved RO samples was low compared to the amount of carbon,

especially at the sites with minor anthropogenic S deposition and high levels of DOC (i.e. Skjervatjern and Svartberget). Instead, these three samples exhibited the highest contents of silicates compared to the other samples.

The elemental analysis data of the RO isolates, corrected for ash and water contents (Table 3), revealed that the carbon content of the DOM was rather constant ($543 \pm 18 \text{ g kg}^{-1} \text{ C}$) and that the median value ($547 \text{ g kg}^{-1} \text{ C}$) was in good agreement with the median carbon content ($496 \text{ g kg}^{-1} \text{ C}$) of freshwater DOM samples compiled by Perdue and Ritchie (2004). The differences between the carbon contents of the DOM samples isolated in spring and fall were remarkably small and statistically not significant. Furthermore, the contents of hydrogen and nitrogen were in good agreement with values published by Alberts and Takács (1999), who carried out elemental analysis of eight RO samples of DOM from Norwegian sites (i.e., NOM-typing project, Gjessing et al. 1999).

Calculated weight-based C:N ratios range from 25 to 42 (Table 3). Lowest values were obtained for the Birkenes samples and highest values for the Skjervatjern site. A similar range of C:N ratios, namely 26–56, was found for RO isolates from surface waters at sites in Southern Norway including the Birkenes and the Skjervatjern site (Gjessing et al. 1999). Consistent differences between fall and spring

samples were not observed for our samples, indicating that site-specific differences between C:N ratios seem to dominate over seasonal variations.

Values of C:N ratios are often used as indicator for the source of the organic material. Typically, average weight-based C:N ratios range below 10 for plankton, from about 10 to 25 for aquatic macrophytes, from less than 10 to about 20 for organic matter in mineral soils, and exceed 15 for terrestrial plant material (Stevenson 1994; Kendall et al. 2001). Litter of coniferous trees exhibits typical C:N ratios of 40–80 (Smolander et al. 1996; Moore et al. 2005). Comparison of our C:N ratios with values given in the literature indicates that terrestrial material may be the major source of aquatic DOM in the studied boreal forested catchments.

FT-IR spectroscopy

The normalized FT-IR spectra of all RO isolates (Fig. 2) exhibit the absorption bands (e.g. by $-\text{CH}_2-$, $-\text{COOH}$ etc.) typically found in spectra of natural organic matter and humic substances (Clapp et al. 1994; Stevenson 1994). In addition, also inorganic constituents of the RO isolates contribute to the FT-IR spectra. For example, Si–O bonds in silicates may contribute to a small extent to the absorption bands at 1270 cm^{-1} and 780 cm^{-1} , respectively (Orlov 1992; Haberhauer and Gerzabek 1998). More

Table 3 Total organic carbon (TOC) contents of original water samples and elemental composition as well as percent modern carbon (pmC) of isolated DOM. The values for the

elemental composition are corrected for ash contents. Organic nitrogen (N_{org}) was calculated as difference of total nitrogen and inorganic nitrogen. SD = standard deviation

		TOC* (mg l^{-1})	C (g kg^{-1})	H (g kg^{-1})	N_{org} (g kg^{-1})	C: N_{org} (g g^{-1})	pmC (%)
Birkenes	Fall	5	545	50	22	25	109.3
	Spring	4	569	61	22	26	107.4
Hietajärvi	Fall	6	526	53	15	35	116.4
	Spring	5	561	57	20	28	114.8
Skjervatjern	Fall	10	527	44	13	40	113.8
	Spring	6	553	46	13	42	114.1
Svartberget	Fall	11	549	58	20	28	104.5
	Spring	19	518	46	16	32	116.4
Valkea-Kotinen	Fall	9	523	51	20	26	121.8
	Spring	11	555	53	20	27	117.3
Mean±SD	Fall	8 ± 3	534 ± 12	51 ± 5	18 ± 4	31 ± 6	113.2 ± 6.6
Mean±SD	Spring	9 ± 6	551 ± 20	53 ± 7	18 ± 4	31 ± 7	114.0 ± 3.9
Mean±SD	Total	9 ± 5	543 ± 18	52 ± 6	18 ± 3	31 ± 6	113.6 ± 5.1

*From Vogt et al. (2001)

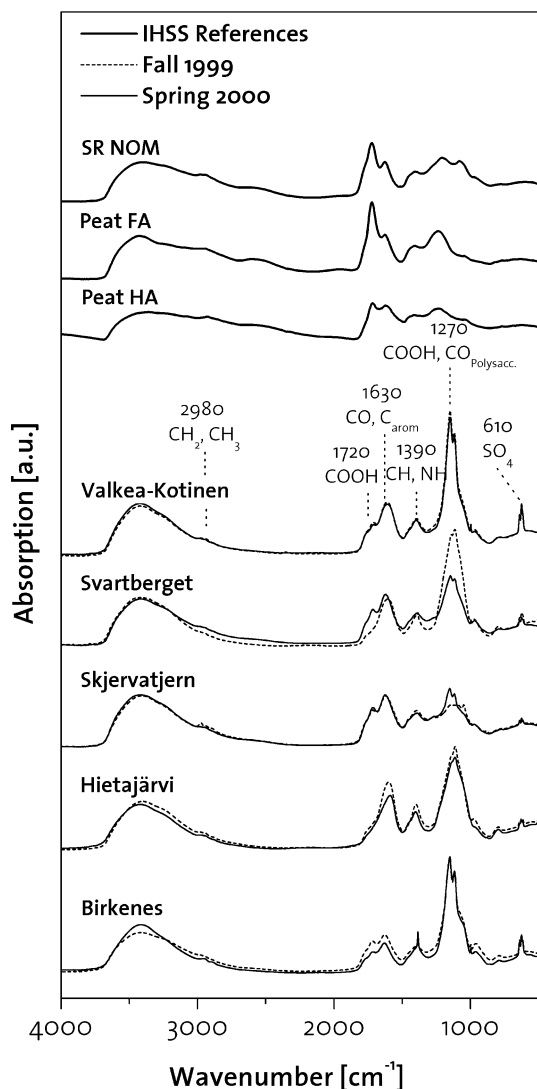


Fig. 2 FT-IR spectra of the DOM samples and selected IHSS reference materials (Suwannee river NOM, peat fulvic acid, and peat humic acid). Spectra from samples taken in fall 1999 and spring 2000 are plotted with dotted and solid lines, respectively

importantly, sulfate may contribute to the absorption band at 1270 cm^{-1} , as sulfate has several absorption bands between 1110 cm^{-1} and 1280 cm^{-1} (Nakamoto 1997; Smidt et al. 2002). The influence of sulfate may be responsible for the observation that the absorption bands between 1110 cm^{-1} and 1280 cm^{-1} are smaller for both samples from Skjervatjern and for the spring sample from the Svartberget site than for all other samples. As mentioned in the previous section, these three samples have low sulfate contents compared to their amounts of carbon. Figure 2 also

shows the FT-IR spectra of three reference materials, the Suwannee river NOM (IHSS 1R101N), peat fulvic acid (IHSS 1R103F), and peat humic acid (IHSS 1R103H), respectively. Compared to the fulvic and humic acids, the DOM samples gave a much stronger absorption band near 1270 cm^{-1} , which is probably due to high contents in polysaccharides.

The most striking feature of the FT-IR spectra is the similarity between the spring and fall samples, all of which were collected during low to intermediate flow conditions. Larger differences between spring and fall samples were only observed for the Svartberget catchment, which may mainly be related to their differences in the inorganic constituents caused by strongly different flow conditions between fall and spring sampling at Svartberget.

Solid-state CP-MAS ^{13}C -NMR spectroscopy

For the CP-MAS ^{13}C -NMR spectra, the differences between the spring and fall samples from each site were minor (Fig. 3). Note, that this was also true for the Svartberget site, which exhibited the largest differences in FT-IR spectra. This result supports our interpretation that differences in FT-IR spectra between the Svartberget fall and spring samples are mainly due to inorganic components. The quantitative evaluation of the ^{13}C -NMR spectra is summarized in Table 4, together with average values and standard deviations for the fall samples, the spring samples, and the total sample set. All ten ^{13}C -NMR spectra exhibited strong peaks in the chemical shift region assigned to O-alkyl carbon including alcohols, ethers and hemiacetals (45–110 ppm) and the region assigned to carboxyl carbon (160–185 ppm). On average, the DOM samples contained 42% O-alkyl carbon, which is slightly higher than the median O-alkyl carbon content of freshwater DOM reported in the literature (Perdue and Ritchie 2004). The DOM samples had an average carboxyl carbon content of 11%, which is comparably low. Perdue and Ritchie (2004) reported that the median carboxyl carbon content of freshwater DOM was 19% of the total carbon as estimated from ^{13}C -NMR data. The average content of total aromatic carbon in our DOM samples was 15%, which is lower than the median contents of freshwater NOM reported in the literature (Abbt-Braun and Frimmel 1999). The average contents of carbonyl carbon (6%) and alkyl carbon (26%)

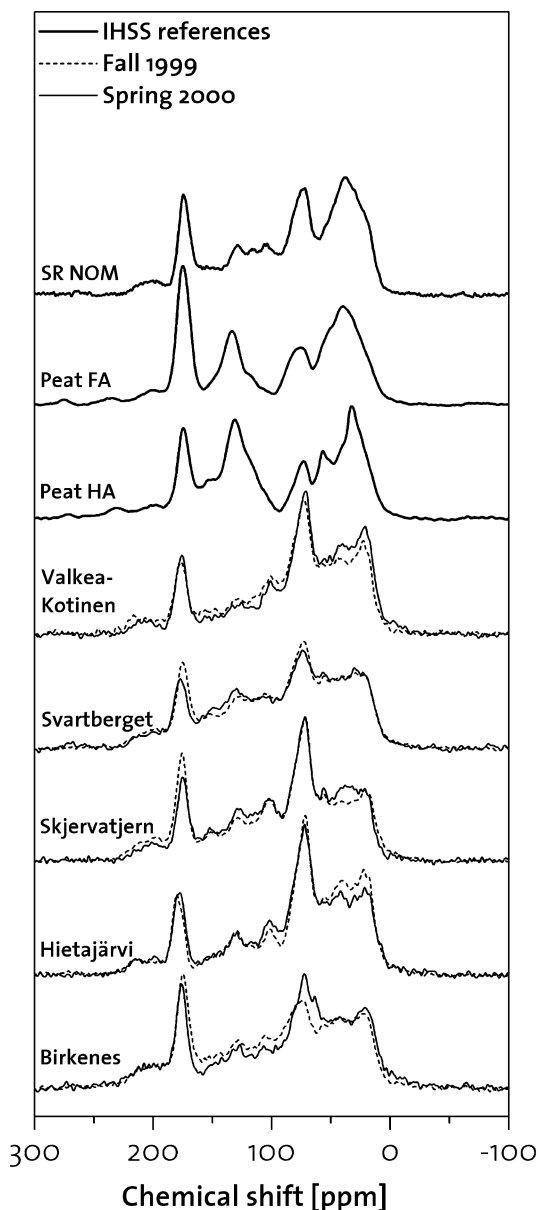


Fig. 3 Solid-state CP-MAS ^{13}C -NMR spectra of the DOM samples and selected IHSS reference materials (Suwannee river NOM, peat fulvic acid, and peat humic acid). Spectra from DOM samples taken in fall 1999 and spring 2000 are plotted with dotted and solid lines, respectively

were very similar to literature median values (Abbt-Braun and Frimmel 1999; Perdue and Ritchie 2004).

When comparing the composition of DOM from the five sampling sites, some small differences between sites can be observed. The Birkenes and Svartberget DOM, which are both sampled in stream

water, contained slightly less O-alkyl carbon. In addition, the samples from Birkenes, the catchment with the highest S deposition, exhibited slightly higher contents of carbonyl carbon than the DOM from the other sites. The DOM from Svartberget had the highest content of total aromatic carbon, while the Hietajärvi and Valkea-Kotinen samples had the lowest contents of total aromatic carbon. However, the differences in aromaticity are relatively small, particularly when comparing the values with the average composition of DOM reported in the literature (Perdue and Ritchie 2004). Again, no significant differences were observed between the samples collected during the spring and fall seasons (Table 4).

Comparison of the ^{13}C -NMR spectra obtained for our DOM samples with peat fulvic and humic acid (IHSS 1R103F and IHSS 1R103H) and a Suwannee river NOM sample (IHSS 1R101N) reveals that our DOM samples possess higher contents of O-alkyl carbon and lower contents of aromatic and alkyl carbon. Compared to peat fulvic acid our material also showed lower contents of carboxyl carbon (Fig. 3). This finding indicates that the DOM samples are more hydrophilic than the reference fulvic and humic acid samples. The clear differences between DOM samples and IHSS references materials suggest that although Histosols cover up to 45% of the terrestrial catchment area, the major part of the DOM found in the surface waters at low to intermediate flow conditions consists of leachates from mineral soil horizons rather than of leachates from humus layers or humic top soil horizons.

C-1s NEXAFS spectroscopy

In addition to ^{13}C -NMR spectroscopy, C-1s NEXAFS spectroscopy was carried out to probe the chemical bonding environment of carbon in the DOM samples. The spectral differences between the fall and spring samples were again extremely small and statistically not significant (Fig. 4). Only for the Svartberget fall and spring sample, the C-1s NEXAFS spectroscopy revealed differences in all functional groups, showing slightly higher contents of aromatic, phenolic, and O-alkyl carbon and slightly lower carboxyl and carbonyl carbon contents for the fall sample (Table 5).

The C-1s NEXAFS spectra of DOM samples from the five catchments were also similar to one another, although some minor differences were observed. The

Table 4 Carbon distribution as derived from integrated solid-state CP-MAS ^{13}C -NMR spectra. Values are given as percentages. SD = standard deviation

Functional group Spectral region [ppm]		Alkyl C 0–45	O-Alkyl C 45–110	Aromatic C* 110–140	Phenolic C 140–160	Carboxyl C 160–185	Carbonyl C 185–220
Birkenes	Fall	23	37	11	6	15	8
	Spring	27	39	7	4	13	8
Hietajärvi	Fall	27	45	10	3	10	5
	Spring	30	43	9	3	9	6
Skjervatjern	Fall	22	42	11	5	13	7
	Spring	22	44	12	5	11	6
Svartberget	Fall	24	40	14	7	10	5
	Spring	23	40	13	6	12	6
Valkea-Kotinen	Fall	26	45	9	4	10	6
	Spring	31	44	8	3	10	4
Mean \pm SD	Fall	24 \pm 2	42 \pm 3	11 \pm 2	5 \pm 2	12 \pm 2	6 \pm 1
Mean \pm SD	Spring	27 \pm 4	42 \pm 2	10 \pm 3	4 \pm 1	11 \pm 2	6 \pm 1
Mean \pm SD	Total	26 \pm 3	42 \pm 3	10 \pm 2	5 \pm 1	11 \pm 2	6 \pm 1

*Without phenolic carbon

amounts of aromatic and phenolic carbon were slightly elevated for the Svartberget and Skjervatjern sites, which is consistent with our NMR results and the findings by Vogt et al. (2004). In addition, DOM from the Svartberget and Skjervatjern sites tended to have lower carbonyl carbon contents. However, no clear differences or trends between the DOM from the five catchments were found by C-1s NEXAFS spectroscopy. This finding is in good agreement with the FT-IR and ^{13}C -NMR results and the elemental composition of the samples. In addition, C-1s NEXAFS spectra confirmed the clear differences between RO isolates and humic and fulvic acid as seen in the ^{13}C -NMR spectra (Fig. 4).

Comparison of quantitative results obtained by ^{13}C -NMR and C-1s NEXAFS spectroscopy shows that the values agree well for aromatic and carbonyl carbon (Tables 4 and 5). For phenolic, and carboxyl carbon, quantitative values derived from C-1s NEXAFS spectra tend to slightly exceed values derived from ^{13}C -NMR spectra. The largest deviations were found for O-alkyl carbon, where the estimated values derived from C-1s NEXAFS spectra were slightly lower than the values determined by ^{13}C -NMR spectroscopy. This may be due to the relative low response of the $1s\text{-}\sigma^*$ transition of O-alkyl carbon in C-1s NEXAFS spectra. Since the quantitative results of ^{13}C -NMR and C-1s NEXAFS spectroscopy are in good agreement for aromatic, phenolic, carboxyl, and carbonyl carbon, we

conclude that for NOM samples, reasonable estimates for these carbon types can be derived from C-1s NEXAFS spectra using the fitting scheme and the empirical correlation functions reported by Schumacher (2005).

Carbon isotope analysis

AMS measurements revealed that all samples were enriched in ^{14}C compared to the 1950 oxalic acid standard, which is reflected by the percent modern carbon values (Table 3). This result implies that most organic compounds in the samples are young (<50 years). In contrast, soil fulvic and humic acids often exhibit radiocarbon ages of several hundred to a few thousand years. Based on these findings, we conclude that the DOM samples contain significant amounts of young (<50 years) organic carbon, but only small amounts of refractory organic carbon compounds.

The $\delta^{13}\text{C}$ values derived from AMS measurements ranged from -25‰ to -32‰ for our DOM samples. For different kinds of organic materials, typical ranges for $\delta^{13}\text{C}$ values were found (Stuiver and Polach 1977; Szidat et al. 2004). Since the reported ranges widely overlap, it is difficult to reason the source of the organic material from $\delta^{13}\text{C}$ values alone (Kendall et al. 2001; Glaser 2005). In case of plant materials, the range of values additionally depends on the type of metabolism used for photosynthetic CO_2 fixation.

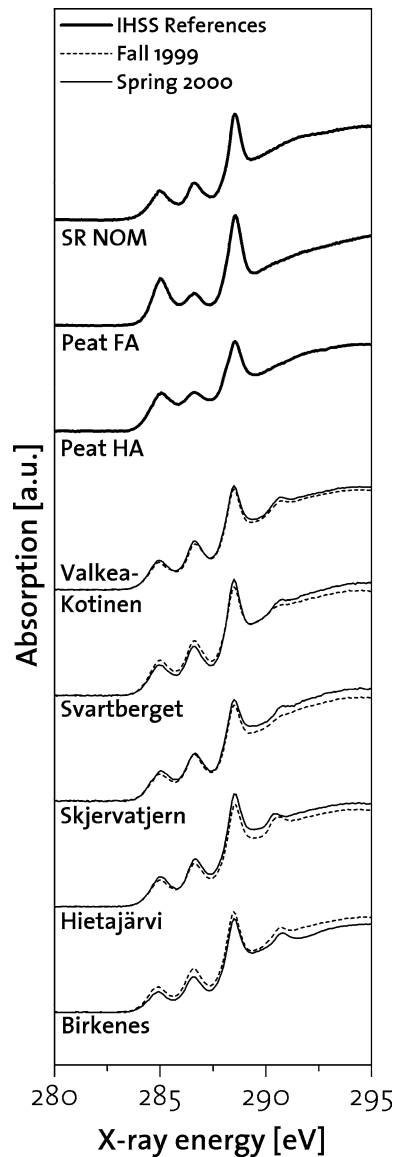


Fig. 4 C-1s NEXAFS spectra of the DOM samples. Spectra of samples taken in fall 1999 and spring 2000 are plotted with dotted and solid lines, respectively. Spectra of IHSS peat fulvic (FA), IHSS humic acid (HA), and IHSS Suwannee river NOM are plotted for comparison

For C3 plants, an average $\delta^{13}\text{C}$ value of -27‰ (range -22 to -32‰) is reported (Kendall et al. 2001; Glaser 2005). The C:N ratios of our DOM samples indicated a terrestrial origin of the sample material. As most plant material in the studied forested boreal catchment originates from C3 plants such as e.g., Norway spruce and Scots pine, the range of the $\delta^{13}\text{C}$ values derived from the AMS measure-

ments is in line with the results on elemental composition.

Conclusion

The striking similarity of the DOM samples from the five catchments indicates that the differences in climate, dominating soil type, and vegetation between the five sampling sites did not strongly affect the DOM composition in the surface waters. From our characterization results, we conclude that the investigated DOM isolated from surface waters in boreal forested catchments mainly consists of young, terrestrial, hydrophilic organic matter. A relative enrichment of hydrophilic compounds may be expected for the water-soluble fraction of organic matter when migrating from terrestrial environments into surface waters (Suominen et al. 2003) as adsorption of DOM is thought to be the key factor controlling the dynamics of DOM in mineral soils (Kalbitz et al. 2000). In addition, oxidative biodegradation of hydrophobic acids may lead to a further increase of hydrophilic acids (Guggenberger and Zech 1994). In summary, sorption and transformation processes occurring during the migration of organic matter through mineral soils into surface waters may explain why water-extractable DOM of humus layer and mineral top soils exhibits a high proportion of hydrophobic acids, while hydrophilic compounds are the major fraction of DOM in surface waters.

Comparison of DOM samples isolated at low to intermediate flow during the fall and spring seasons in five boreal forested catchments suggests that variations in DOM composition are negligibly small. However, major changes in freshwater chemistry are known to occur during high-flow conditions in boreal forested catchments as e.g., during spring floods (Laudon et al. 2004a). The ^{13}C NMR results from this study show that the DOM composition of the Svartberget spring sample, which was taken at the end of the spring flood period, was very similar to the fall sample taken under extremely low-flow conditions. These findings suggest that even though the amount of riverine DOM may be strongly affected by hydrological conditions in boreal catchments, the chemical composition may be rather stable unless larger amounts of humic materials are flushed out from surrounding peatlands and forest floors during flood periods.

Table 5 Carbon functional group distribution calculated from C-1s NEXAFS spectra. For the quantification of C-1s NEXAFS spectra, peak areas of the respective spectral regions were converted into percentages of carbon bound asaromatic, phenolic, carboxyl, O-alkyl, or carbonyl carbon applying the correlation of C-1s NEXAFS and ^{13}C -NMR data given by Schumacher [2005]. SD = standard deviation

Functional group		Aromatic C*	Phenolic C	Carboxyl C	O-Alkyl	Carbonyl C
Spectral region [eV]		285.0 ± 0.1	286.5 ± 0.1	288.5 ± 0.1	289.5 ± 0.2	290.5 ± 0.1
Birkenes	Fall	9	8	16	31	9
	Spring	6	6	17	39	11
Hietajärvi	Fall	9	7	15	33	11
	Spring	10	7	15	33	9
Skjervatjern	Fall	11	9	14	37	5
	Spring	12	9	13	36	7
Svartberget	Fall	13	10	13	31	6
	Spring	11	8	16	30	8
Valkea-Kotinen	Fall	10	8	15	34	8
	Spring	10	8	14	33	10
Mean ± SD	Fall	10 ± 2	8 ± 1	15 ± 1	33 ± 2	8 ± 2
Mean ± SD	Spring	10 ± 2	8 ± 1	15 ± 2	34 ± 3	9 ± 2
Mean ± SD	Total	10 ± 2	8 ± 1	15 ± 1	34 ± 3	8 ± 2

* Without phenolic carbon

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