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The role of catchment soils and land cover on dissolved organic matter (DOM) properties in temperate lakes

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ABSTRACT

Dissolved organic matter (DOM) is a critical component in freshwater ecosystem functioning. The main sources of DOM in lakes are allochthonous inputs from the catchment and autochthonous in-lake production. This study focused on the role of catchment characteristics on the qualitative and quantitative properties of DOM in small temperate lakes along a gradient of alkalinity. We examined DOM properties based on the optical absorbance and fluorescence measurements of water from 34 Estonian lakes. The content and composition of DOM were highly diverse in the lakes studied, e.g. the dissolved organic carbon (DOC) concentrations varied from 3.2 to 53.0 mg L^{-1}. Land cover, soil, and catchment hydrology and geology had substantial effects on DOM in lakes. Stock of soil organic carbon (SOC) in the catchment and water exchange rate (a descriptor of catchment hydrology, reciprocal of water residence time) had major positive effects on DOC concentrations. The aromaticity and molecular weight of DOM, i.e. the relative abundance of humic substances, and the dominance of allochthonous DOM increased with the drainage ratio (catchment area/lake area) and the percentages of bogs, and Dystric and Fibric Histosols (peat soils in transitional mires and bogs, respectively) in the catchments. Dominance of non-humic over humic substances and autochthonous over allochthonous DOM in lakes corresponded to calcareous catchments and higher percentages of Gleyic Rendzinas (thin soils on calcareous rock), Sapric Histosols (peat soils in mires) and open spaces (areas with little vegetation). Our results showed that soil variables had in general a greater effect than land cover and were more informative for describing the role of catchment characteristics on DOM in lakes. Patterns in DOM quantity and quality found in our study were similar to patterns found in other temperate lakes; therefore, our results have important implications for understanding catchment-lake interactions across the temperate region.

1. Introduction

Dissolved organic matter (DOM) is the largest pool of biologically available organic carbon in aquatic environments and a critical component in freshwater ecosystem functioning (Hessen and Tranvik, 1998). DOM influences directly and indirectly a wide variety of physical (optical and thermal properties, e.g. Morris et al., 1995; Fee et al., 1996), chemical (transport and fate of metals and organic pollutants, e.g. Haitzer et al., 1998; Yamashita and Jaffé, 2008), and biological (plankton ecology, e.g. Steinberg, 2003) processes. On the other hand, the structure, composition, and relative abundance of DOM are controlled by many of these processes. The biogeochemistry of DOM is closely linked to the global carbon cycle as DOM contributes to greenhouse gas emissions from inland waters (Bastviken et al., 2011; Raymond et al., 2013) and acts as an energy source and cellular building material for heterotrophic microorganisms (Tranvik, 1988; del Giorgio and Williams, 2005). The bioavailability of DOM (the fraction of DOM pool available for rapid microbial degradation) is influenced by its composition, e.g. molecular weight and aromaticity (Tulonen et al., 1992; Wickland et al., 2007).

In freshwater lakes, the dynamics of DOM are driven by allochthonous inputs from the surrounding catchment and atmosphere, autochthonous in-lake production and losses through sedimentation, degradation and outflow. The allochthonous DOM from the catchment originates mainly from the decay of terrestrial plant material and subsequent leaching of partial decomposition products. These processes are influenced by the amount of precipitation (e.g. Schindler et al., 1992), water residence time (e.g. Schindler et al., 1997), catchment area (e.g. Kortelainen, 1993), vegetation, land use, soil cover, and geology (e.g. Li et al., 2015). High levels of DOM in unpolluted lakes originate predominantly from the catchment (Thurman, 1985). Water bodies with high DOM concentrations are typical of regions rich in swamps or bogs

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and with peat soils, thus it is generally believed that DOM in surface waters is derived from peats. However, a high proportion of agricultural land in the catchment can result in high levels of DOM as well (Mattsson et al., 2005) and also forests are important contributors to DOM export (Hongve, 1999), while coniferous and mixed forests provide a greater DOM input to lakes than deciduous forests (Cronan and Aiken, 1985). Catchment characteristics are often linked to anthropogenic pressure because changes in land use influence strongly DOM in lakes, e.g. clear-cutting may significantly increase the export of DOM (Nieminen, 2004). Autochthonous DOM is produced within the lake itself and connected to the lake trophic status (Williamson et al., 1999).

A high content of organic matter has an impact on surface water quality causing, for example, oxygen depletion (Robards et al., 1994) and light limitation (von Einem and Granéli, 2010). Organic enrichment due to pollution by oxygen-consuming substances is reported to affect 13% of lakes in the European Union (EU; EEA, 2012). The most important European policy document on water quality, the EU Water Framework Directive (WFD; EC, 2000), aims at improving the ecological status of all European surface waters and thus obligates monitoring, planning and control of water quality. However, about half of the EU countries do not measure lake OM in their surveillance monitoring programmes (Sepp et al., 2018). WFD stipulates *inter alia* estimation of land use patterns to provide information about the type and magnitude of the significant anthropogenic pressures on surface water bodies (EC, 2000).

DOM transported into and out of lakes is important for the biogeochemistry of inland waters. Examining the biogeochemical response of DOM in lakes provides insight into how different ecosystems may respond to future changes in climate and land use. However, only a small proportion of lakes can be included in monitoring programmes each year. Therefore, models are needed to provide estimates of DOM quality and loading to lakes based on land use and catchment hydrology. This study focuses on the role of catchment characteristics, i.e. catchment hydrology and percentages of land cover and soil types, on DOM in small temperate lakes along a gradient of alkalinity, the latter used as a proxy for catchment geology. We used GIS to describe the catchment characteristics of entire drainage basins, whereas absorbance and fluorescence properties of DOM yielded information about the molecular weight, aromaticity, relative measures of humic and fulvic acids, and origin of DOM. Specific objectives of this study were to: (1) estimate how the DOM quantity (measured as dissolved organic carbon (DOC) concentration) and quality in freshwater lakes are influenced by catchment characteristics; (2) assess the relative importance of allochthonous and autochthonous DOM sources. This study is part of a larger effort to understand the functioning of lake food webs and carbon metabolism across gradients of catchment alkalinity and climate.

2. Material and methods

2.1. Study sites

34 small lakes located all over Estonia were sampled under the national monitoring programme in 2015 and 2016 (Fig. 1). Limnological types of the lakes indicated in Table 1 are in accordance with the Estonian Environmental Register (register.keskkonnainfo.ee/).

The percentages of land cover types within the lake catchments were calculated using Estonian Base Map from Estonian Land Board (www.maaamet.ee/). Applied land cover types were bog (ombrotrophic), mire (minerotrophic), forest (forest, young forest, shrub), open space (area with little or no vegetation), agricultural area (arable land, pasture), grassland (natural grassland), and other (other land cover types together). Land cover types are in accordance with the Estonian Base Map (Estonian Land Board, 2018). Land cover varied greatly among the studied catchments, some being dominated by bogs or largely forested and some dominated by agricultural areas and grasslands (Table 1).

We differentiated 15 soil types in the studied catchments (Table 2) in accordance with the World Reference Base for Soil Resources (WRB; FAO, 2014). Some soil groups were combined together and taken into account as one type. The percentages of soil types within the catchments (Table 3) were calculated using Estonian Soil Map (mapping scale 1:10,000) from Estonian Land Board. GIS analysis was performed using MapInfo Professional, version 12.5 (Bitney Powes, 2014, www.pitneybowes.com). The soil organic carbon (SOC) stocks (Mg ha^{-1}) for the catchments were calculated based on the areal distribution of various soil types and their mean SOC stock obtained from Kõlli et al. (2009). The mean SOC content of Estonian soils is higher than in most European countries, is similar to that in Finnish soils whereas only Ireland and Sweden have higher SOC averages (Aksoy et al., 2016). Peat soils (Histosols) found mainly in colder, wetter regions in western and northern Europe were present in all of the catchments studied and dominated over mineral soils in 1/3 of them.

Three variables – the drainage ratio (CA/LA; catchment area/lake area), the water exchange rate (WE, the reciprocal of water residence time; times per year) (Table 1; data from the Estonian Environmental Register), and the mean lake alkalinity (Table 5) – were considered in the analysis as hydrogeological characteristics. We used alkalinity as a proxy for catchment geology considering values ≤ 1 meq L^{-1} typical for lakes with organic or siliceous catchment and > 1 meq L^{-1} for lakes with mixed or calcareous catchment (EC, 2009).

2.2. Water sampling, chemical and spectroscopic analyses

Surface water samples were collected under the Estonian small lake monitoring programme in May, July, August and September either in 2015 or 2016, while 11 lakes (Endla, Kooru, Nohipalo Mustjärv, Nohipalo Valgõjärv, Pühajärv, Rõuge Suurjärv, Suurlaht, Tänavjärv, Uljaste, Viitna Pikkjärv and Ähijärv) were sampled in both years. Alkalinity (as HCO_3^-, meq L^{-1}) was determined from unfiltered samples by titration with 0.05 M HCl using a potentiometric titrator TitroLine 6000 (SI Analytics, Germany). All samples were filtered within 24 h through Whatman GF/F glass microfiber filters previously washed with 500 mL of ultrapure water (Milli-Q). DOC concentrations (mg L^{-1}) of the filtrates were determined by TOC-V_{CPH} analyzer (Shimadzu, Japan). This method conforms to the European standard method (EN 1484, 1997).

In addition, absorbance and fluorescence of the water samples were measured to obtain different spectral parameters (Table 4), hereafter named DOM parameters. Absorbance spectra of filtered samples at wavelengths ranging from 200 to 800 nm were measured in a 1-cm quartz cuvette at 1 nm intervals using a UV–Vis spectrophotometer UV-1700 (Shimadzu, Japan). Absorbance ratios A_{250}/A_{365}, A_{254}/A_{436}, A_{365}/A_{465} and A_{465}/A_{665} were calculated from absorbance intensities (A, m^{-1}) at particular wavelengths. The specific ultraviolet absorbance ($SUVA_{254}$ and $SUVA_{285}$, L mg^{-1} m^{-1}) values were calculated by dividing, respectively, A_{254} or A_{285} by DOC concentration and the specific colour absorbance ($SCOA_{436}$, L mg^{-1} m^{-1}) by dividing A_{436} by DOC. Fluorescence was measured from filtered samples using a fluorescence spectrophotometer F-2500 (Hitachi, Japan). The fluorescence intensity was measured at excitation wavelengths (λ_{ex}) ranging from 220 to 380 nm and at emission wavelengths (λ_{em}) ranging from 220 to 520 nm, fluorescence reading intervals were 5 nm for excitation and 1 nm for emission. We calculated the fluorescence index (FI) using the ratio of intensities at λ_{em} 450 and 500 nm at an λ_{ex} of 370 nm, and the freshness index (β: α) as the ratio of intensities at λ_{em} 380 nm and the λ_{em} maximum between 420 and 435 at an λ_{ex} of 310 nm.

2.3. Statistical analysis

Spearman's Rank Order correlation was used to find the relationships between DOC and DOM parameters, and catchment

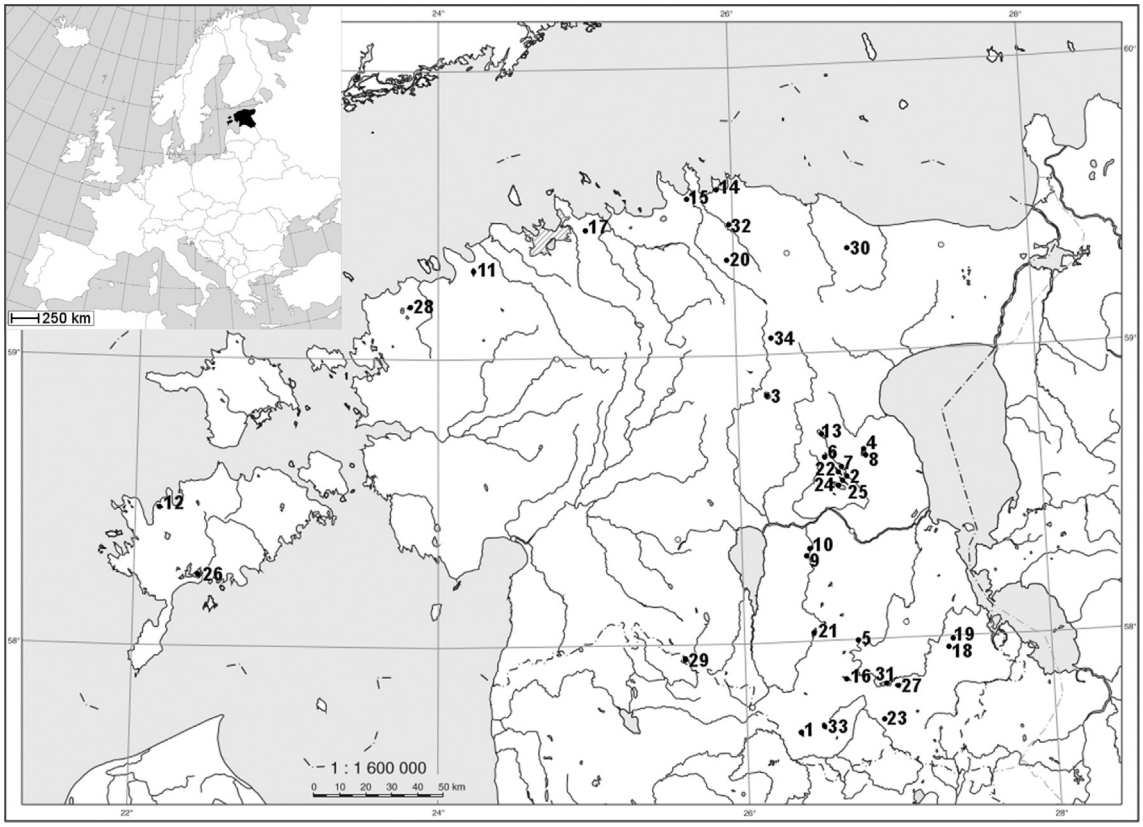

Fig. 1. Locations of studied lakes. Numbers marking the lakes are the same as in Table 1.

characteristics; $p < 0.05$ was accepted as significant. All measured values of DOC concentrations and DOM parameters were used in the analysis. Correlations were considered moderate if coefficients of the Spearman correlation (r) were ≥0.4–0.7. Correlation analysis was performed using R, version 3.4.2 (The R Foundation for Statistical Computing, 2017, https://www.r-project.org/), package pspearman, function spearman.test.

Variables of catchment characteristics (percentages of land cover and soil types in the catchments, CA/LA, WE, alkalinity, and SOC stocks) were included in multiple linear regression models predicting values of DOC and DOM parameters. Parameters, whose values were predicted by models, were A_{250}/A_{365} (reflecting the average molecular weight of DOM), $SUVA_{254}$ (reflecting the aromaticity of DOM) and FI (reflecting the origin of DOM). These parameters were chosen for the models as they had the strongest correlations with catchment characteristics and were not strongly correlated to each other. All measured values of DOC concentrations, A_{250}/A_{365}, $SUVA_{254}$, and FI were used in the analysis. Models were built using a mixed stepwise algorithm, which selects a model by Akaike information criterion (AIC). In addition, $p < 0.05$ was used as the condition for including a variable in the model. Models were checked for multicollinearity, only models with all variance inflation factors (VIF) < 5 were selected. Final models were checked for spatial autocorrelation. In order to examine the patterns of spatial autocorrelation the residuals of the models were plotted against the X and Y coordinates (planar rectangular coordinate system L-EST) of studied lakes using correlograms. Residuals were evenly distributed for all models, i.e. there were no apparent spatial autocorrelation in the models. Final models were also checked for homoscedasticity, all of the models conformed to this assumption. Linear regression analysis was performed using function lm in R, function step was used for model selection and package spatial, function correlogram was used for checking the spatial autocorrelation of the final models. Scatterplots describing the relationships between DOM parameters and variables of catchment characteristics used in the final models are shown on Figs. A.1 and A.2.

3. Results

3.1. DOC concentrations and spectroscopic properties of DOM

DOC concentrations ranged from 3.2 to 53.0 $mg\,L^{-1}$, being lowest in alkalitrophic and oligotrophic lakes and highest in dystrophic and acidotrophic lakes (Table 5). The values of DOM parameters did not vary remarkably in any of the lakes during the study period. The mean A_{250}/A_{365} values (range 3.8–10.5) and A_{254}/A_{436} values (range 8.7–31.9) were lowest in dystrophic Lake Ohepalu and highest in halotrophic Lake Suurlaht. The mean A_{365}/A_{465} values ranged from 3.2 to 6.0. The mean A_{465}/A_{665} values were < 5 in 19 lakes, 5–6 in 7 lakes and ≥6 in the rest of the lakes. The majority of mean $SUVA_{254}$ values varied between 1.4 and 3.7 $L\,mg^{-1}\,m^{-1}$ and were < 3 $L\,mg^{-1}\,m^{-1}$ in 20 lakes. The values were higher (> 4 $L\,mg^{-1}\,m^{-1}$) in lakes Ohepalu and Nohipalo Mustjärv (acidotrophic lake). The mean $SUVA_{285}$ values varied between ≥1 and < 2.0 $L\,mg^{-1}\,m^{-1}$ in 19 lakes. In the rest of the lakes, the values ranged from 2.0 to 3.2 $L\,mg^{-1}\,m^{-1}$, and in Lake Suurlaht, the value was < 1 $L\,mg^{-1}\,m^{-1}$. The majority of the mean $SCOA_{436}$ values varied between 0.05 and 0.2 $L\,mg^{-1}\,m^{-1}$, being higher only in lakes Nohipalo Mustjärv and Ohepalu (0.3 and 0.5 $L\,mg^{-1}\,m^{-1}$, respectively). The mean freshness index (β: α) values were lowest (0.4) in lakes Nohipalo Mustjärv and Ohepalu, highest in Lake Suurlaht (0.9) and varied between 0.6 and 0.8 in the rest of the lakes. The mean FI values ranged from 1.2 to 1.6 and were ≤1.4 in 11 lakes.

3.2. DOM relationships with catchment hydrology, geology, and land cover types

Water exchange (WE) had the strongest positive correlation with

Table 1
Limnological types, drainage ratios (catchment area/lake area; CA/LA) and water exchange rates (times per year; WE) of studied lakes, catchment geology types and percentages of land cover types in the catchments (%).

No	Lake	Limnological Type	WE	CA/LA	Catchment Geology	Bog	Mire	Forest	Open space	Agricult. area	Grass-land	**Other**
1	Aheru	Hard-water eutrophic	1.5	21.3	Calcareous	1.7	6.7	73.3	1.6	6.6	7.0	3.4
2	Elistvere	Macrophytic	11.3	67.1	Calcareous	0.3	1.1	35.3	1.0	53.4	4.5	4.2
3	Endla	Macrophytic	31	25.7	Mixed	20.5	2.9	46.6	2.1	20.6	3.0	4.6
4	Jõemõisa	Macrophytic	29	299.1	Calcareous	0.7	3.1	67.3	1.3	20.6	4.7	2.3
5	Jõksi	Hard-water eutrophic	2.6	77.9	Calcareous	4.2	1.8	43.7	2.1	37.5	7.7	3.0
6	Kaarepere Pikkjärv	Macrophytic	4.4	41.7	Calcareous	0	0.1	43.6	1.9	48.2	3.4	2.8
7	Kaiavere	Hard-water eutrophic	3.0	35.1	Calcareous	0.3	1.2	35.6	0.9	52.3	4.9	4.5
8	Kaiu	Hard-water mixotrophic	13.5	159.3	Calcareous	0.7	3.1	67.3	1.3	20.6	4.7	2.3
9	Karijärv	Hard-water eutrophic	0.59	18.6	Calcareous	0.1	2.3	38.9	2.3	44.5	8.8	3.2
10	Keeri	Hard-water eutrophic	30	294.6	Calcareous	0.2	3.4	44.9	2.1	35.9	7.9	5.6
11	Klooga	Macrophytic	0.68	4.7	Mixed	12.1	19.2	24.0	18.8	15.3	1.6	9.1
12	Kooru	Halotrophic	37	41.9	Calcareous	0	8.1	74.4	6.4	6.4	2.9	1.9
13	Kuremaa	Hard-water eutrophic	0.26	2.6	Calcareous	1.2	0.1	40.8	1.0	47.6	5.5	3.8
14	Käsmu	Soft-water mixotrophic	4.4	34.4	Siliceous	0	0.1	86.4	0.7	4.4	7.0	1.4
15	Lohja	Soft-water mixotrophic	2.4	18.7	Siliceous	2.7	0.4	78.1	3.4	10.3	3.7	1.6
16	Lõõdla	Hard-water eutrophic	0.48	6.2	Calcareous	0	4.5	38.0	2.4	37.2	13.2	4.3
17	Maardu	Hard-water mixotrophic	1.0	6.6	Siliceous	0	0	29.8	16.3	29.2	14.2	10.6
18	Nohipalo Mustjärv	Acidotrophic	2.9	42.4	Organic	44.0	0.5	54.8	0.1	0	0.5	0.2
19	Nohipalo Valgõjärv	Oligotrophic	0	13.1	Siliceous	0	2.2	97.6	0	0	0	0.2
20	Ohepalu	Dystrophic	3.7	10.5	Organic	28.2	4.1	22.6	2.0	35.7	6.1	1.6
21	Pühajärv	Hard-water eutrophic	0.95	12.2	Calcareous	0.1	6.4	56.7	3.3	18.8	7.2	7.5
22	Raigastvere	Hard-water eutrophic	2.8	40.3	Calcareous	0	0.6	37.8	1.3	52.6	4.3	3.5
23	Rõuge Suurjärv	Hard-water eutrophic	4.0	173.0	Calcareous	0.2	3.4	59.7	4.7	17.5	10.3	4.1
24	Saadjärv	Hard-water eutrophic	0.13	3.9	Calcareous	0	0.5	33.6	0.6	54.4	3.9	7.1
25	Soitsjärv	Macrophytic	1.5	31.0	Calcareous	0	3.6	22.7	0.6	65.6	3.9	3.5
26	Suurlaht	Halotrophic	5.0	8.5	Calcareous	0	0	58.6	23.2	7.8	7.6	2.8
27	Tamula	Hard-water eutrophic	0.39	2.1	Calcareous	0	1.2	52.4	6.3	16.2	5.0	19.0
28	Tänavjärv	Semidystrophic	0.54	6.2	Organic	85.6	1.2	12.5	0.9	0	0	0
29	Tündre	Hard-water eutrophic	0.5	3.0	Calcareous	6.3	2.8	80.1	1.0	6.6	2.6	0.7
30	Uljaste	Semidystrophic	0.2	10.2	Organic	46.9	0.4	30.1	2.0	18.2	0.1	2.3
31	Vagula	Hard-water eutrophic	4.9	6.2	Calcareous	1.5	1.9	55.2	2.7	27.8	6.8	3.9
32	Viitna Pikkjärv	Oligotrophic	0.5	79.2	Siliceous	0	0.4	96.7	2.9	0	0	0
33	Ähijärv	Hard-water eutrophic	0.5	3.0	Calcareous	1.2	4.1	74.4	1.6	13.2	4.5	1.0
34	Äntu Sinijärv	Alkalitrophic	7.0	7.1	Calcareous	0	0	98.5	0.3	0	0	1.2
	Average		**6.1**	**72.1**		**7.6**	**2.7**	**53.3**	**3.5**	**24.3**	**4.9**	**3.7**

Table 2
Soil types in the studied catchments and their stocks of soil organic carbon (SOC). SOC stock values of soil types are from Kõlli et al. (2009) and additional explanations are from FAO (2014).

Abbreviation	Soil type	Additional explanation	Mean SOC stock (Mg ha^{-1})
RZ	Rendzinas (Leptosols and Calcaric Cambisols)	Very thin soils on calcareous rock	74.9
BS	Brown soils (Mollic Cambisols and Luvisols)	Fertile soils with brownish coloration, used intensively for agriculture	97.9
AB	Albeluvisols (Retisols)	Fertile soils suitable for a wide range of agricultural uses	67.1
AB-ha	Haplic Albeluvisols	Acid soils with low nutrient levels occurring mainly under forest	70.0
PZ	Podzols	Acid soils on siliceous rock and under coniferous forest	45.7
RZ-gl	Gleyic Rendzinas	Very thin soils on calcareous rock (with gleyic properties)	122.5
CM-gl LV-gl	Gleyic Cambisols & Gleyic Luvisols	Fertile soils used for agriculture, temporarily wet (groundwater influence)	125.2
AB-st GL-sd	Stagnic Albeluvisols & Spodic Gleysols	Permanently or temporarily wet soils (groundwater influence)	90.5
AB-gl GL-um	Gleyic Albeluvisols & Umbric Gleysols	Permanently or temporarily wet soils (groundwater influence)	90.5
PZ-gl	Gleyic Podzols	Acid soils on siliceous rock and under coniferous forest (with gleyic properties)	114.5
HS-sa	Sapric Histosols	Peat soils occurring mainly in mires	333.2
HS-dy	Dystric Histosols	Peat soils in transitional mires, not suitable for agriculture	210.0
HS-fi	Fibric Histosols	Peat soils in bogs, not suitable for agriculture	139.4
RG-er	Eroded Regosols	Very weakly developed soils in unconsolidated materials, extensive in eroding lands	37.6
RG-co	Colluvic Regosols	Very weakly developed soils in unconsolidated materials, extensive in accumulation zones	105.3

DOC (r = 0.50, Fig. 2). Among land cover types, the percentage of bogs had the strongest correlations with DOM parameters: positive correlations with $SUVA_{254}$ (r = 0.51), $SUVA_{285}$ (r = 0.52) and $SCOA_{436}$ (r = 0.53), and negative correlation with A_{250}/A_{365} (r = −0.47), β: α (r = −0.67) and FI (r = −0.60). Land cover type "other" had moderate positive correlation with A_{250}/A_{365} (r = 0.41) and A_{254}/A_{436} (r = 0.40), alkalinity with A_{254}/A_{436} (r = 0.40) and A_{365}/A_{465} (r = 0.43), and both had moderate positive correlation (r ≥ 0.4) with FI. CA/LA correlated positively with A_{465}/A_{665} (r = 0.41), $SUVA_{254}$ and $SUVA_{285}$ (r = 0.54) and $SCOA_{436}$ (r = 0.42), and negatively with β: α (r = −0.45). Correlations of mire, forest, agricultural area, and open space with DOC, and correlations of WE, mire, forest, agricultural area, and open space with DOM parameters were weak or non-significant.

A combination of land cover variables and hydrogeological characteristics explained 21.2%, 47.3%, 26.5% and 54.6% of the variance in the values of DOC, A_{250}/A_{365}, $SUVA_{254}$ and FI, respectively (Table 6). Among land cover types, forests, mires and grasslands did not contribute significantly to the abovementioned DOM models. An

Table 3
Percentages of soil types (%) and stocks of soil organic carbon (SOC, Mg ha^{-1}) in the catchments of studied lakes. Abbreviations of soil types as in Table 2.

Lake	AB	AB-st GL-sd	AB-ha	AB-gl GL-um	PZ	PZ-gl	HS-fi	HS-dy	HS-sa	BS	CM-gl LV-gl	RZ	RZ-gl	RG-er	RG-co	SOC
Aheru	14.7	1.9	10.0	1.8	9.9	1.7	2.0	2.6	31.9	1.7	4.8	0.7	0	5.5	8.3	161.5
Elistvere	16.6	4.5	1.9	1.0	0	0	0.7	0.5	24.4	20.5	26.8	0.6	0	0.2	1.7	157.3
Endla	2.8	0.2	3.7	1.0	1.3	0.5	6.5	3.3	17.5	32.9	13.2	14.2	1.9	0	0.1	143.8
Jõemõisa	14.3	15.6	5.6	6.4	5.4	5.1	1.4	2.0	19.5	2.7	20	0	0	0.2	0.3	142.5
Jõksi	32.2	6.1	11.9	1.2	0.5	1.1	3.2	6.3	9.4	3.6	5.4	0.9	0	5.9	11.0	113.2
Kaarepere Pikkjärv	10.4	0.5	0.2	0	0	0	0	0.4	19.6	27.2	39.4	0.7	0	0.1	1.3	151.7
Kaiavere	22.0	6.7	2.4	1.0	0	0	0.7	0.7	25.3	14.4	24.0	0.7	0	0	0.8	156.9
Kaiu	7.0	17.9	5.2	7.4	6.8	7.4	2.0	2.3	20.2	1.9	19.5	0	0	0.3	0.4	146.5
Karijärv	21.1	0.9	5.7	2.0	0.4	0.2	0.2	1.0	19.0	13.8	8.3	1.2	0	8.6	17.3	133.3
Keeri	18.6	2.1	7.0	1.1	1.4	0.2	0.3	0.6	18.8	14.6	11.6	3.4	0	7.3	11.1	133.5
Klooga	0	0	0.6	0.3	3.1	2.5	11.8	5.2	7.9	1.1	11.3	18.0	29.5	0	0	127.3
Kooru	0	0	1.2	0.2	1.4	0.3	0	0	7.5	2.9	24.0	24.1	36.0	0	0	123.3
Kuremaa	28.8	9.2	1.7	0.1	0	0	2.6	1.7	30.1	7.4	16.4	0.6	0	0	0.5	166.1
Käsmu	0.7	0	7.6	15.5	22.6	12.6	0.1	4.9	10.6	3.2	12.4	8.6	1.2	0	0.1	116.8
Lohja	0.2	0.2	5.9	7.0	8.8	35.5	2.6	11.6	5.5	0.2	20.2	1.2	0.1	0	0	128.8
Lõõdla	9.4	1.8	6.9	0.9	0.3	0	0	0	14.1	16.0	8.6	3.1	0	15.6	22.4	120.0
Maardu	0	0.7	0	2.7	0	1.4	0.5	0.5	16.8	18.0	46.2	3.0	6.4	0	0	150.0
Nohipalo Mustjärv	4.2	1.3	1.5	4.5	23.1	11.2	40.2	11.2	2.3	0	0.3	0	0	0	0	120.3
Nohipalo Valgõjärv	3.8	13.8	2.7	7.6	29.2	23.0	0	18.4	1.5	0	0	0	0	0	0	107.1
Ohepalu	0.9	1.2	6.6	0.1	0.4	0.1	32.5	6.6	1.1	20.6	17.0	10.6	0.9	0	0	120.8
Pühajärv	22.9	2.6	5.7	0.3	1.4	0	0.2	0.4	21.9	9.5	5.3	1.0	0	14.3	13.4	134.3
Raigastvere	9.7	0.7	1.0	0.2	0	0.1	0	0.3	18.2	31.0	34.4	0.6	0	0.2	3.3	147.1
Rõuge Suurjärv	18.3	2.6	11.1	1.6	0.5	0.1	0.1	1.5	12.6	12.2	6.7	1.1	0	10.7	19.9	116.1
Saadjärv	13.4	5.6	0.7	1.2	0	0	0	0.1	22.5	24.1	31.0	0.1	0	0.5	0.7	154.3
Soitsjärv	12.8	3.2	0.5	0.3	0	0	0	0.1	29.3	27.6	24.6	0.3	0	0.3	1.0	169.0
Suurlaht	0	0	0	0.1	0	0	0	0	2.7	6.9	27.0	7.0	51.4	0	0	120.6
Tamula	5.7	0.2	12.5	2.4	23.1	6.0	0	4.3	22.2	5.6	3.6	0.5	0	4.2	8.4	137.7
Tänavjärv	0	0	0	0	5.5	10.7	78.2	5.6	0	0	0	0	0	0	0	135.5
Tündre	12.1	8.2	6.2	1.8	13.0	6.4	8.0	6.2	26.5	0.5	5.5	0	0	1.4	4.2	159.7
Uljaste	6.0	1.9	17.4	1.5	10.6	2.3	44.0	7.7	1.9	0	3.5	2.7	0	0	0	117.4
Vagula	21.9	7.9	14.9	3.2	6.9	2.2	1.0	2.6	11.4	5.0	7.6	0.4	0	4.9	7.5	112.9
Viitna Pikkjärv	0	0	7.5	1.5	79.2	1.3	0	9.3	0.1	0	0	0	0	0	0	65.5
Ähijärv	9.2	1.2	20.2	1.5	16.9	1.3	0.9	4.3	23.8	9.0	2.8	0.1	0	2.0	4.8	141.6
Äntu Sinijärv	0	0	16.2	2.5	0	0	0	0	4.6	19.2	3.1	54.4	0	0	0	92.5
Average	**10.0**	**3.5**	**6.0**	**2.4**	**8.0**	**3.9**	**7.1**	**3.6**	**14.7**	**10.4**	**14.2**	**4.7**	**3.7**	**2.4**	**4.1**	**133.1**

examination of the sums of squares associated to each variable in the multiple regression models allows to determine the relative influence of different catchment characteristics on DOC, A_{250}/A_{365}, $SUVA_{254}$ and FI (Fig. 3). Land cover variables and hydrogeological characteristics had a similar importance in predicting DOC values, explaining 10.8% and 10.4% of the variability, respectively. For DOM parameters, land cover variables were more important, explaining 36.9%, 21.7% and 47.4% of the variance in the values of A_{250}/A_{365}, $SUVA_{254}$ and FI, respectively. For DOC and FI, the most important land cover variable was the percentage of bogs, explaining even 37.1% of the variance in the FI values. For A_{250}/A_{365} and $SUVA_{254}$, the most important land cover variable was the percentage of open spaces.

Table 4
Description of applied spectral parameters.

Parameter (unit)	Correlative characteristics	Additional explanation	References
A_{250}/A_{365}	Molecular weight, aromaticity	Increases with decreasing molecular weight and aromaticity	Barreto et al., 2003 Peuravuori and Pihlaja, 1997 Obernosterer and Herndl, 2000
A_{254}/A_{436}	Molecular weight	Increases with decreasing molecular weight Indicates the intensity of UV-absorbing functional groups compared to the coloured ones	Uyguner and Bekbolet, 2005
A_{365}/A_{465}	Molecular weight of humic acids	Increases with decreasing molecular weight of humic acids	Uyguner and Bekbolet, 2005
A_{465}/A_{665}	Humification, aromaticity	< 5.0: humic acids 6.0–8.5: fulvic acids Increases with decreasing aromaticity	Chen et al., 2002 Peuravuori and Pihlaja, 2007
$SUVA_{254}$ (L mg^{-1} m^{-1})	Aromaticity, molecular weight, hydrophobicity and hydrophilicity	> 4: macromolecular aromatic hydrophobic compounds < 3: low-molecular weight hydrophilic compounds poor in aromatics	Uyguner and Bekbolet, 2005 Peuravuori and Pihlaja, 2007
$SUVA_{285}$ (L mg^{-1} m^{-1})	Fulvic acids	≤1.0: domination of aliphatic compounds from primary production ≥2.0: relatively high share of fulvic acids	Rostan and Cellot, 1995 Barreto et al., 2003
$SCOA_{436}$ (L mg^{-1} m^{-1})	Quinone and ketone functional groups	Increases with increasing contribution of quinonic and ketonic structures	Abbt-Braun and Frimmel, 1999 Barreto et al., 2003
Fluorescence index (FI)	Origin of dissolved organic matter (DOM)	1.3–1.4: terrestrially derived DOM Higher values: microbially derived DOM	McKnight et al., 2001
Freshness index (β: α)	Autochthonous origin of DOM	Ratio of β fluorophore (characteristic of autochthonous production) and α fluorophore (humic substances) Increases with increasing contribution of internally produced DOM	Huguet et al., 2009, Köhler et al., 2013

Table 5
Mean values and range of DOC (mg L^{-1}), mean values of alkalinity (HCO_3^-, meq L^{-1}), absorbance ratios (A_{250}/A_{365}, A_{254}/A_{436}, A_{365}/A_{465}, A_{465}/A_{665}), and $SUVA_{254}$, $SUVA_{285}$ and $SCOA_{436}$ (L mg^{-1} m^{-1}), and freshness index (β: α) and fluorescence index (FI) in studied lakes.

Lake	HCO_3^-	DOC Avg	DOC Range	A_{250}/A_{365}	A_{254}/A_{436}	A_{365}/A_{465}	A_{465}/A_{665}	$SUVA_{254}$	$SUVA_{285}$	$SCOA_{436}$	β: α	FI
Aheru	2.6	20.0	18.3–23.5	6.5	23.5	5.9	6.8	3.4	2.2	0.1	0.6	1.4
Elistvere	3.9	18.1	15.5–20.2	6.5	22.2	5.4	5.5	3.2	2.1	0.1	0.6	1.5
Endla	3.9	24.3	19.3–33.0	5.8	19.5	5.4	6.7	3.5	2.4	0.2	0.6	1.4
Jõemõisa	2.6	20.8	20.1–21.3	6.4	22.3	5.5	6.0	3.3	2.2	0.2	0.6	1.4
Jõksi	3.5	11.5	10.4–12.2	5.0	15.0	4.6	5.7	3.7	2.6	0.2	0.6	1.4
Kaarepere Pikkjärv	4.5	21.7	19.3–27.7	6.4	23.1	6.0	11.1	3.4	2.3	0.2	0.6	1.5
Kaiavere	3.9	17.7	14.3–21.6	6.4	22.4	5.9	8.2	3.3	2.2	0.2	0.6	1.5
Kaiu	2.8	21.3	20.3–21.7	6.3	21.4	5.4	6.3	3.3	2.2	0.2	0.6	1.4
Karijärv	4.6	10.6	10.3–11.0	8.0	25.9	5.1	3.1	2.4	1.5	0.1	0.8	1.5
Keeri	5.2	9.2	7.7–11.6	6.2	19.4	4.6	3.6	2.7	1.8	0.1	0.7	1.5
Klooga	1.6	13.5	12.4–14.6	8.0	20.8	3.6	2.5	1.8	1.1	0.1	0.8	1.5
Kooru	2.5	15.2	12.5–17.8	9.4	30.7	5.1	4.2	1.8	1.1	0.1	0.7	1.5
Kuremaa	3.2	14.1	13.4–15.2	7.9	27.7	5.7	4.7	2.8	1.7	0.1	0.7	1.5
Käsmu	0.5	12.6	12.0–12.9	6.8	21.2	4.8	3.0	2.6	1.7	0.1	0.7	1.5
Lohja	1.0	20.7	19.2–21.7	5.7	18.6	5.0	5.4	3.4	2.3	0.2	0.6	1.4
Lõõdla	3.0	8.0	7.3–8.7	8.3	23.4	4.3	2.2	1.9	1.1	0.1	0.8	1.6
Maardu	1.0	11.9	10.2–15.4	8.2	20.5	3.3	1.7	1.8	1.1	0.1	0.8	1.6
Nohipalo Mustjärv	0	49.7	45.0–53.0	4.5	13.7	4.4	6.4	4.4	3.1	0.3	0.4	1.3
Nohipalo Valgõjärv	0.1	5.9	5.1–6.7	5.4	12.8	3.2	2.6	1.5	1.0	0.1	0.8	1.5
Ohepalu	0.1	39.2	33.7–43.3	3.8	8.7	3.3	5.1	4.2	3.2	0.5	0.4	1.2
Pühajärv	2.9	9.4	8.6–10.3	7.9	25.0	4.7	3.3	2.4	1.5	0.1	0.7	1.5
Raigastvere	4.3	16.6	15.0–18.8	6.8	24.7	5.8	6.1	3.2	2.1	0.1	0.7	1.5
Rõuge Suurjärv	4.4	6.7	4.7–8.9	6.2	19.1	4.8	5.7	2.7	1.8	0.1	0.7	1.5
Saadjärv	2.6	9.4	9.2–9.8	9.3	28.4	4.6	3.1	2.1	1.3	0.1	0.8	1.5
Soitsjärv	2.4	16.5	16.0–16.8	8.2	28.4	5.5	4.8	2.4	1.5	0.1	0.7	1.5
Suurlaht	2.1	17.6	16.2–19.6	10.5	31.9	4.6	3.4	1.4	0.9	0.05	0.9	1.5
Tamula	3.6	8.5	8.2–9.0	8.1	25.4	4.4	3.3	2.4	1.5	0.1	0.8	1.5
Tänavjärv	0.2	12.8	10.2–14.3	6.0	16.5	3.8	2.7	1.7	1.2	0.1	0.6	1.4
Tündre	1.5	17.1	16.2–18.2	5.8	19.0	5.1	5.9	3.5	2.4	0.2	0.6	1.4
Uljaste	0.2	8.7	7.7–10.7	5.4	15.4	4.2	4.4	2.8	1.9	0.2	0.6	1.4
Vagula	3.5	9.2	8.1–10.5	6.2	19.9	5.1	5.2	3.0	2.0	0.2	0.6	1.5
Viitna Pikkjärv	0.1	5.7	5.2–6.3	5.3	13.3	3.7	2.8	1.7	1.1	0.1	0.8	1.5
Ähijärv	2.7	9.5	8.9–9.9	8.8	28.6	4.9	4.4	2.0	1.2	0.1	0.8	1.5
Äntu Sinijärv	5.2	4.6	3.2–5.4	6.8	17.9	3.7	2.8	1.8	1.3	0.1	0.7	1.5

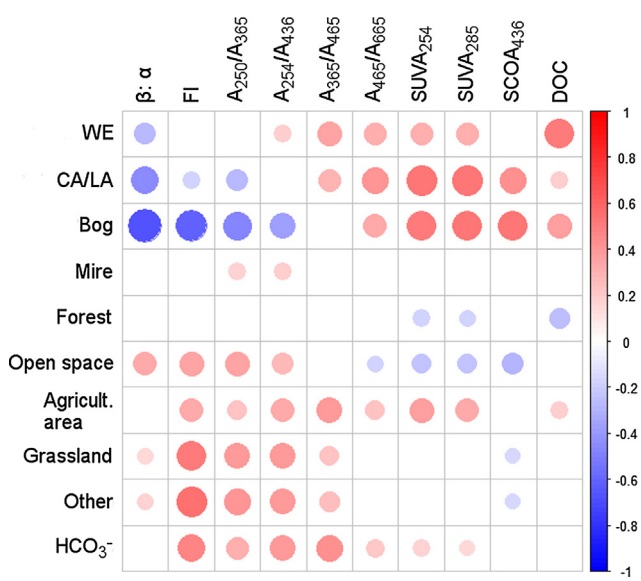

Fig. 2. Coefficients of Spearman correlation (r) between DOM parameters and the percentages of land cover types in the catchments, lake alkalinity (HCO_3^-), drainage ratio (CA/LA), and water exchange (WE). Empty cells denote statistically non-significant correlations ($p > 0.05$). β: α – freshness index, FI – fluorescence index.

3.3. DOM relationships with soil types

SOC stocks and the percentages of Gleyic Cambisols & Gleyic Luvisols and Fibric Histosols had the strongest positive correlations with DOC (r = 0.53, 0.48 and 0.40, respectively), and Haplic Albeluvisols the strongest negative correlation (r = −0.47; Fig. 4). Dystric Histosols and Fibric Histosols had moderate correlations with DOM parameters: positive with $SCOA_{436}$ (r = 0.53 and 0.51, respectively), and negative with A_{250}/A_{365} (r = −0.70 and −0.44, respectively), A_{254}/A_{436} (r = −0.69, only Dystric Histosols), β: α (r = −0.40 and −0.66, respectively) and FI (r = −0.58 and −0.59, respectively). Podzols and Gleyic Podzols had moderate negative correlations ($r \leq -0.4$) with A_{250}/A_{365}, A_{254}/A_{436} and FI. We found moderate positive correlations ($r \geq 0.4$) of (1) Albeluvisols and Fibric Histosols with $SUVA_{254}$ and $SUVA_{285}$; (2) Gleyic Cambisols & Gleyic Luvisols and Sapric Histosols with A_{250}/A_{365}, A_{254}/A_{436} and A_{365}/A_{465}; (3) SOC

Table 6
Multiple linear regression models predicting the values of DOC (mg L^{-1}), A_{250}/A_{365}, $SUVA_{254}$ and fluorescence index (FI). Estimates of coefficients are given for selected variables: the percentages of land cover types in the catchments, alkalinity (HCO_3^-), drainage ratio (CA/LA) and water exchange (WE). Variables were included in the model if $p < 0.05$ and variance inflation factors (VIF) < 5. The corresponding R^2 values are shown and n = 180 for all models.

Variable	DOC Coefficient	A_{250}/A_{365} Coefficient	$SUVA_{254}$ Coefficient	FI Coefficient
Bog	0.1272	−0.0158	0.0081	−0.0014
Agricultural area	0.1341		0.0117	
Open space		0.1435	−0.0451	0.0030
Other				0.0029
HCO_3^-	−1.9906	0.3064		0.0172
CA/LA		−0.0084	0.0028	−0.0002
WE	0.2891	0.0226		
Intercept	13.826	5.9663	2.3262	1.4180
R^2	0.212	0.473	0.265	0.546

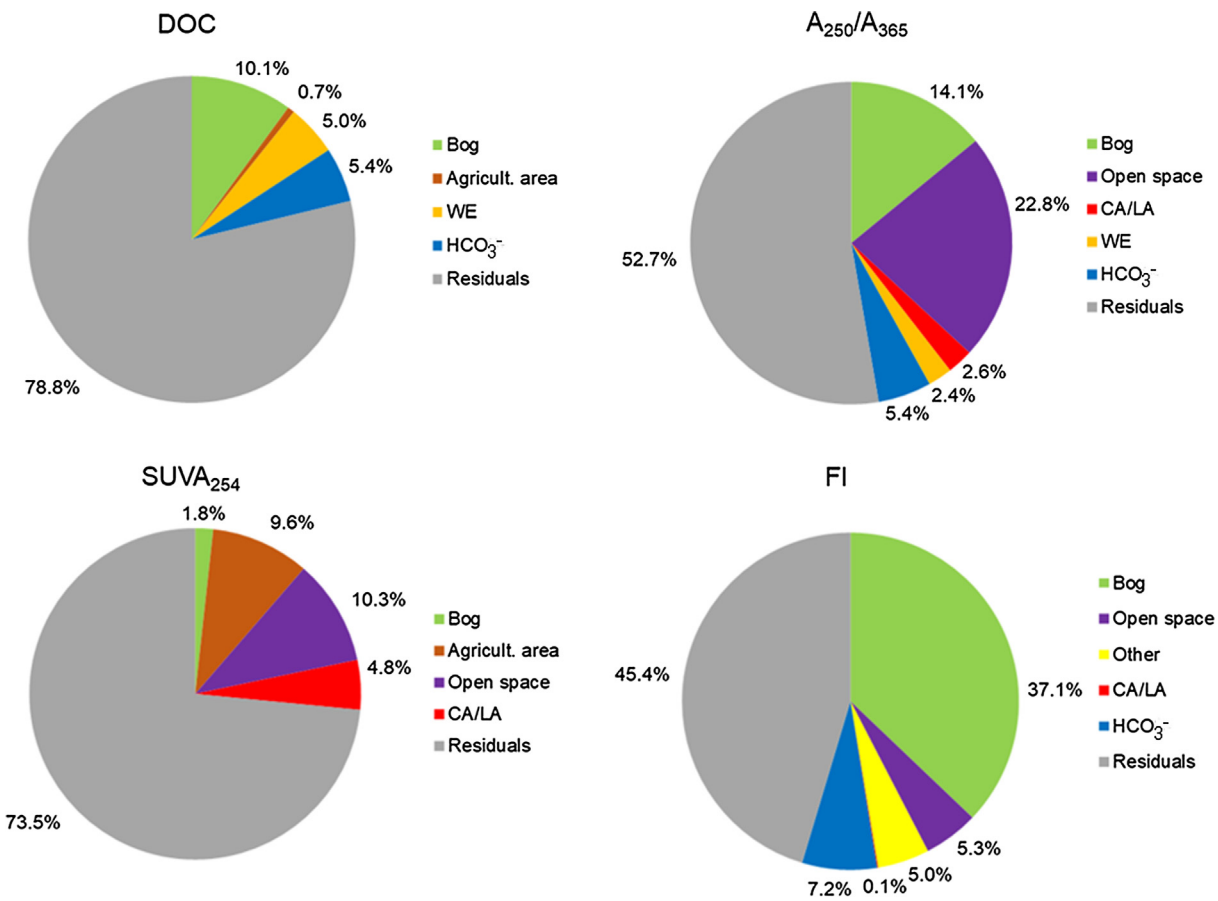

Fig. 3. Variance partitioning in the multiple linear regression models of DOC, A_{250}/A_{365}, $SUVA_{254}$ and FI, showing the percentage of the variability explained by each land cover type and hydrogeological characteristic and the residuals unexplained by the models. Abbreviations as in Table 6.

stocks with A_{254}/A_{436} and A_{365}/A_{465}; (4) Sapric Histosols and Brown soils with FI, and (5) Brown soils also with A_{254}/A_{436}. Correlations of Rendzinas, Gleyic Rendzinas, Stagnic Albeluvisols & Spodic Gleysols, Gleyic Albeluvisols & Umbric Gleysols and Eroded Regosols with DOC and DOM parameters were weak or non-significant.

A combination of soil variables and hydrogeological characteristics explained 37.2% of DOC, 66.7% of A_{250}/A_{365}, 43.0% of $SUVA_{254}$ and 59.3% of FI variance (Table 7), whereas alkalinity, Brown soils and Sapric Histosols did not contribute significantly to the predictions of DOC and DOM parameters. Soil variables were more important than the hydrogeological characteristics explaining 32.9% of DOC, 57.6% of A_{250}/A_{365}, 30.2% of $SUVA_{254}$, and 54.2% of FI variability (Fig. 5). For $SUVA_{254}$, WE explained 12.9% of the variability; for DOC, A_{250}/A_{365}, $SUVA_{254}$ and FI, hydrogeological characteristics explained much smaller proportions of the variability. For DOC, the most important soil variables were the percentage of Haplic Albeluvisols and SOC stock, explaining 12.8% and 12.7% of the variability, respectively. For A_{250}/A_{365} and $SUVA_{254}$, the most important soil variable was the percentage of Gleyic Rendzinas, and for FI, the percentage of Fibric Histosols.

4. Discussion

4.1. DOC concentrations and properties of DOM

The range of DOC concentrations measured by us in 34 Estonian lakes (Table 5) was comparable with that reported for lakes in Finland (Kortelainen, 1993), Sweden (von Einem and Granéli, 2010) and Latvia (Klavins et al., 2012), but slightly higher than those found in Irish (Aherne et al., 2002; Burton and Aherne, 2012) and Norwegian lakes (Hagman et al., 2015; Finstad et al., 2016).

According to DOM properties, the studied lakes could be divided into two groups by their limnological types. The first group comprising clear and dark water lakes with low nutrients (oligotrophic, semi-dystrophic, acidotrophic and dystrophic lakes) had greater contributions of humic substances with higher molecular weight, indicated by the low values of A_{250}/A_{365}, A_{254}/A_{436} and A_{365}/A_{465} (Tables 4 and 5). Low values of FI (≤ 1.4) and β: α (< 0.7) in these lakes (except oligotrophic ones) and two mixotrophic lakes showed predominantly terrestrial sources of DOM and a low autochthonous component. Humic substances with higher aromaticity had the highest relative contribution in dark water lakes (Nohipalo Mustjärv and Ohepalu) reflected by $SUVA_{254}$ values $> 4\,L\,mg^{-1}\,m^{-1}$. A_{250}/A_{365} values close to 4 in these lakes were characteristic of strongly coloured waters and higher $SCOA_{436}$ values compared to other studied lakes showed greater contribution of quinonic and ketonic structures.

The second group including most of the light-coloured eutrophic lakes (hard-water eutrophic, macrophytic and halotrophic lakes) had a relatively high share of low-molecular weight organic compounds from primary production, indicated by high values of A_{250}/A_{365}, A_{254}/A_{436} and A_{365}/A_{465}. Low $SUVA_{254}$ values ($< 3\,L\,mg^{-1}\,m^{-1}$) in these lakes reflected also a rather low aromaticity of DOM, and high values of FI (> 1.5) a greater contribution of internally produced DOM.

Humic acids had a greater contribution than fulvic acids in dystrophic, semidystrophic, mixotrophic and oligotrophic lakes, as evidenced by A_{465}/A_{665} values < 5 or near to it. Fulvic acids had a relatively high share only in 7 hard-water eutrophic, macrophytic or acidotrophic lakes, as indicated by A_{465}/A_{665} values of 6–8.5 and $SUVA_{285}$ values ≥ 2.

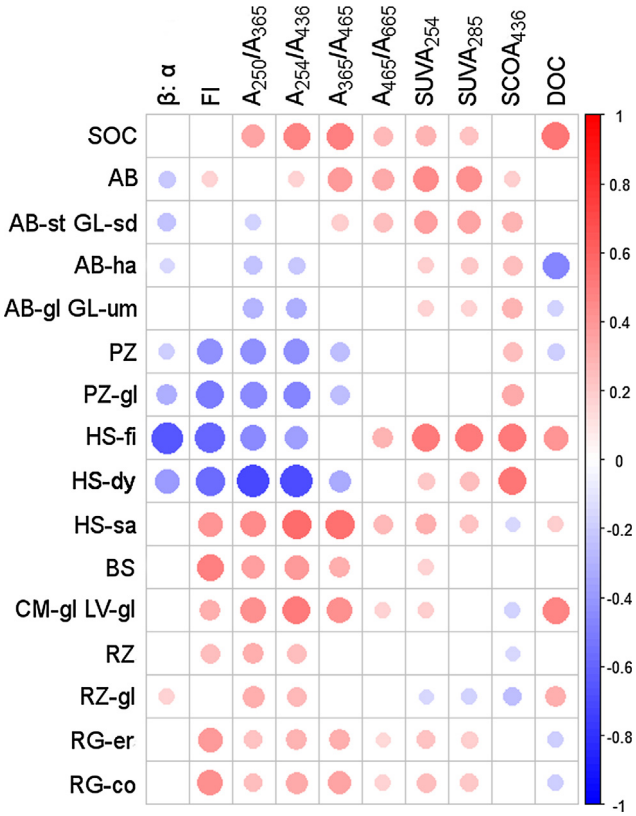

Fig. 4. Coefficients of the Spearman correlation between DOM parameters and the percentages of soil types in the catchments. Empty cells denote statistically non-significant correlations ($p > 0.05$). Abbreviations of soil types as in Table 2, β: α – freshness index, FI – fluorescence index.

Table 7
Multiple linear regression models predicting the values of DOC (mg L^{-1}), A_{250}/A_{365}, $SUVA_{254}$ and fluorescence index (FI). Estimates of coefficients are given for selected variables: the percentages of soil types in the catchments, soil organic carbon (SOC) stocks, drainage ratio (CA/LA) and water exchange (WE). Variables were included in the model if $p < 0.05$ and variance inflation factors (VIF) < 5. The corresponding R^2 values are shown and n = 180 for all models.

Variable	DOC Coefficient	A_{250}/A_{365} Coefficient	$SUVA_{254}$ Coefficient	FI Coefficient
Albeluvisols (AB)			0.0611	−0.0031
Stagnic Albeluvisols & Spodic Gleysols (AB-st GL-sd)	−0.9193	0.0879	−0.0636	
Haplic Albeluvisols (AB-ha)	−0.5504	0.0452		
Gleyic Albeluvisols & Umbric Gleysols (AB-gl GL-um)			0.0521	
Podzols (PZ)		0.0177		−0.0007
Gleyic Podzols (PZ-gl)	−0.3948	0.0847		
Fibric Histosols (HS-fi)			0.0143	−0.0030
Dystric Histosols (HS-dy)	1.5493	−0.3411	0.0806	−0.0096
Gleyic Cambisols & Gleyic Luvisols (CM-gl LV-gl)			0.0315	−0.0021
Rendzinas (RZ)				−0.0016
Gleyic Rendzinas (RZ-gl)		0.0692	−0.0208	
Eroded Regosols (RG-er)		0.0512		
Colluvic Regosols (RG-co)	−0.3339			
SOC	0.2142			
CA/LA	0.0546	−0.0089		
WE			0.0327	−0.0018
Intercept	−12.222	7.0960	1.1606	1.6056
R^2	0.372	0.667	0.430	0.593

4.2. The effect of catchment characteristics on DOC concentrations

The qualitative and quantitative properties of DOM in our study depended substantially on land cover and soil types in the catchments, and catchment hydrology and geology, showing that DOM originated predominantly from the catchment in many of the studied lakes. In general, soil variables were much more important than land cover variables and hydrogeological characteristics (WE, CA/LA and alkalinity) in determining DOC concentrations (Figs. 3 and 5). We have not found studies examining variables of catchment soil cover in relation to DOM in lakes, which makes us believe that our study is the first to find connections between organic carbon in catchment soils and lake water.

Soil organic carbon (SOC) stock in the catchment showed the strongest positive correlation with DOC concentrations in lakes (Figs. 2 and 4) and explained the greatest proportion of DOC variation among land cover and soil variables. Billett et al. (2006) also found a strong positive correlation between downstream changes of DOC in a Scottish stream and catchment SOC pool that was related to the percentage of peat soils (Histosols) in the catchment; however, the relationship between SOC and stream DOC weakened downstream as other processes (e.g. lower SOC inputs from minerals soils and in-stream processing of DOC) became more important.

SOC stocks are soil-type specific and depend mainly on soil carbonate and clay content, moisture regime, and method of soil management (Kõlli et al., 2009). Our results showed that agricultural soils with highest SOC stock among mineral soils in Estonia (Gleyic Cambisols & Gleyic Luvisols) had a strong positive effect on DOC concentrations in lakes and forest soils with low SOC content (mainly Haplic Albeluvisols) a negative effect. However, SOC storage does not directly equate to DOC leaching as SOC retaining capacity of soil types is different, e.g. Podzols, unlike Histosols, have a significant capacity to retain DOC within the soil profile by physicochemical adsorption (Lundström et al., 2000).

DOC concentrations in lakes increased, in addition, with the percentages of bogs and peat soils dominating in bogs (Fibric Histosols). The effect of bogs (peatlands) on DOC in lakes has been observed, for example, in Finnish lakes (Kortelainen, 1993; Rantakari et al., 2004; Mattsson et al., 2005; Arvola et al., 2016) and the role of peatlands as a major source of DOC has been confirmed for boreal catchments in general (e.g. Dillon and Molot, 1997).

Hydrogeological characteristics showed different effect on DOC concentrations in lakes. DOC increased with the water exchange (WE) and catchment area (drainage ratio; CA/LA) and DOC values were lower in lakes with calcareous catchment (light-coloured eutrophic lakes). Similar relationships with CA/LA have been observed in Finnish lakes (Kortelainen, 1993) and with WE in Finnish lakes (Vuorenmaa, 2006) and Swedish lakes (Köhler et al., 2013). Higher WE restricts in-lake DOC removal processes (e.g. sedimentation, microbial decomposition and photo-oxidation) and causes an increase in DOC concentrations (Schindler et al., 1992, 1997).

4.3. The effect of catchment characteristics on the properties of DOM

Catchment characteristics had a stronger effect on DOM properties than on its concentration as seen from linear models that explained more variance in A_{250}/A_{365}, $SUVA_{254}$ and FI values than in DOC concentrations (Figs. 3 and 5). Catchment characteristics explained more than half of the variability in A_{250}/A_{365} (66.7%) and FI (59.3%) while somewhat less in $SUVA_{254}$ (43.0%). Soil variables were more important than land cover variables in determining the properties of DOM in lakes. Soil variables together with hydrogeological characteristics explained a much greater proportion of the variability in average molecular weight, aromaticity and origin of DOM than land cover variables with hydrogeological characteristics.

The aromaticity and molecular weight, relative contribution of fulvic acids, quinonic and ketonic structures, and terrestrial origin of

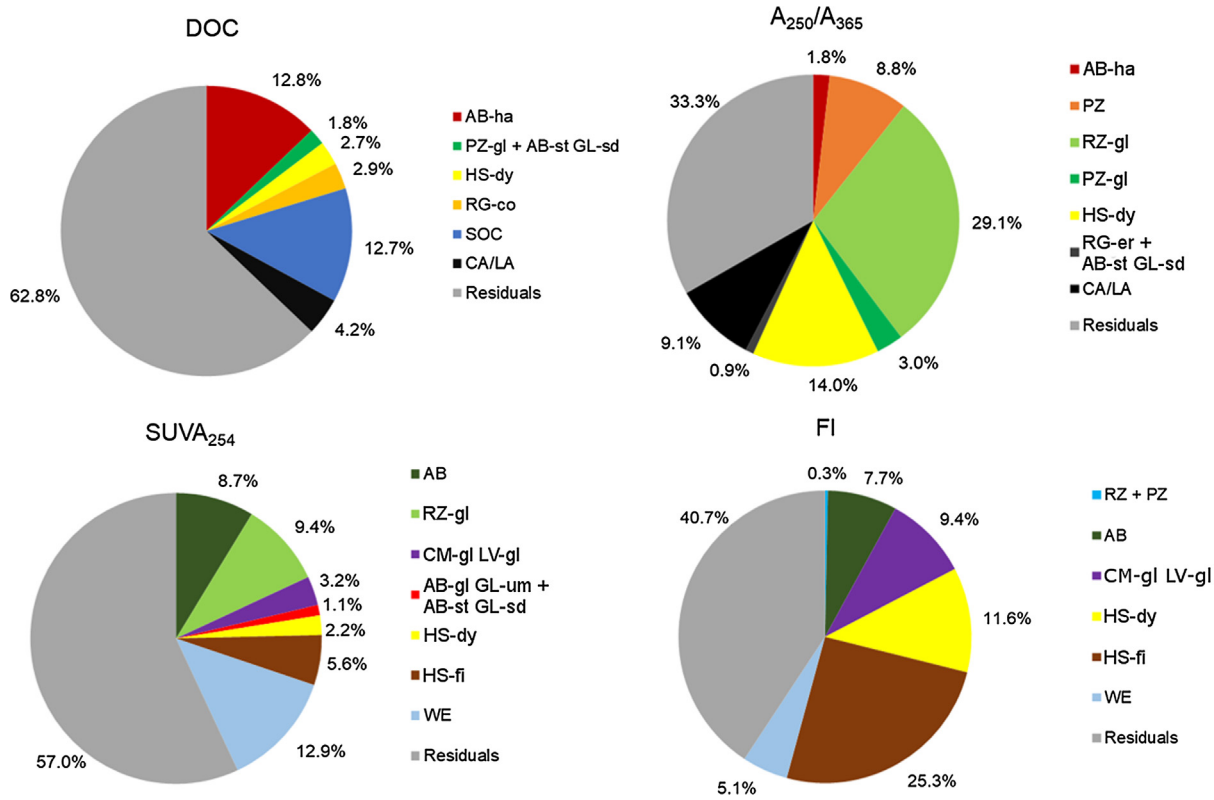

Fig. 5. Variance partitioning in the multiple linear regression models of DOC, A_{250}/A_{365}, $SUVA_{254}$ and FI, showing the percentage of the variability explained by each soil type and hydrogeological characteristic and the residuals unexplained by the models. Abbreviations as in Table 7.

DOM increased with CA/LA and the percentages of bogs and Dystric Histosols and Fibric Histosols (peat soils dominating in transitional mires and bogs, respectively) in the catchments (Figs. 2 and 4, Tables 6 and 7). This showed that the export of allochthonous DOM to the studied lakes was greater from larger catchments and confirmed the role of peatlands as a major source of DOM. Dependence of DOM aromaticity and molecular weight on catchment peatland cover has been found also in Finnish (Arvola et al., 2016) and Swedish catchments (Olefeldt et al., 2013). As described by Vogt et al. (2004), Histosols produce and release DOM with high quinone content and that explained the positive effect of Dystric and Fibric Histosols on the contribution of quinonic and ketonic structures.

According to the correlation analysis, Podzols and Gleyic Podzols (soils formed underneath coniferous forests) had a similar relationship with the molecular weight and origin of DOM as Dystric and Fibric Histosols; however, linear models did not confirm it. Billett et al. (2006) found a relationship between the percentage of Podzols in the catchment and stream DOC in Scotland, suggesting that the DOM in stream water originated at least partially from Podzols. Forests, especially coniferous forests, have been found to be an important sources of humic substances to lakes (Hongve, 1999). Our results did not confirm the effect of forests as a land cover type, maybe since it did not differentiate between deciduous, mixed and coniferous forests; and forests grow on many different soils types in Estonia (Kõlli et al., 2009). Moreover, DOM export from forested catchments is tightly linked to the catchment hydrology and local precipitation (Diodato et al., 2016) and forests in different catchments can have a different effect.

Aromaticity of DOM increased also with higher WE and with the percentages of agricultural areas and Albeluvisols (fertile agricultural soils). Similar relationship between WE and DOM aromaticity was found in Lake Mälaren, one of the largest lakes in Sweden (Köhler et al., 2013), and in other Swedish lakes (Kellerman et al., 2014), where the share of terrestrially derived DOM decreased with lower WE. Agricultural land was found to be an important source of DOM export in Finnish catchments (Mattsson et al., 2005). Other fertile agricultural soils (Gleyic Cambisols & Gleyic Luvisols and Brown soils) showed different effect on DOM properties. Molecular weight of DOM decreased with the percentage of Gleyic Cambisols & Gleyic Luvisols and Brown soils. Also the contribution of autochthonous DOM increased with the percentage of Brown soils, but our results did not confirm the same for Gleyic Cambisols & Gleyic Luvisols. Relationships between DOM in water bodies and organic carbon in soils are more complex and not so strong in the catchments where mineral soils are spatially more important than peat soils (Billett et al., 2006).

Contribution of low-molecular weight and autochthonous DOM increased also with the percentage of Sapric Histosols (peat soils dominating typically in mires). Research conducted in Norwegian lakes showed similarly very poor relationships between percentage of mires in the catchments and humic substances in lakes (Hongve, 1999). One explanation for the opposite effect of Sapric Histosols on DOM properties compared to other peat soils could be different land use – Fibric and Dystric Histosols are not used for agriculture in Estonia, yet Sapric Histosols are (Kõlli et al., 2009). Our results showed that Sapric Histosols had a similar effect on DOM properties than some agricultural soils (e.g., Brown soils). In addition, Sapric Histosols are part of heterogeneous catchments in our study sites, even if being the dominating soil type, and runoff from these soils can interact with mineral soils. This most likely causes the decrease in DOM aromaticity and molecular weight because of the substantial and selective absorption of hydrophobic DOM while passing through mineral soils (Kaiser and Zech, 1998). If bogs and Fibric Histosols dominate in the catchment in our study sites, the catchment soil cover is quite homogeneous with low percentage of mineral soils and runoff probably does not interact with mineral soils before reaching the lake.

Dominance of non-humic over humic substances and autochthonous over allochthonous DOM in lakes corresponded most strongly to calcareous catchments, higher percentages of Gleyic Rendzinas (thin soils on calcareous rock), and higher percentages of land cover types “open

space" (areas with little or no vegetation) and "other" (other land cover types together). In Estonia, Gleyic Rendzinas are common on land cover other than forest, arable land or grassland (Kõlli et al., 2009), i.e. land cover types "open space" and "other" used in our study both belong to this category. All the studied lakes with calcareous catchment are light-coloured eutrophic lakes and our results indicated a greater contribution of internally produced DOM in these types of lakes. The role of catchment characteristics in determining DOM properties was not so clear in eutrophic lakes because the contribution of autochthonous DOM is determined by the trophic status of a lake (Williamson et al., 1999). Increased nutrient loads from the catchment may increase the in-lake production of DOM and the relative importance of autochthonous over allochthonous DOM (Tranvik et al., 2009). In these lakes, catchment characteristics have an indirect effect on DOM properties.

5. Conclusions

The results of our study showed that catchment characteristics had a stronger effect on DOM properties than on DOC concentrations, explaining up to 66.7% of the variability in spectral parameters. In nutrient-poor clear and dark water lakes DOM was represented predominantly by humic substances originated from the catchment, whereas in light-coloured eutrophic lakes internally produced non-humic substances had a greater contribution. Catchment characteristics (land cover, soil, and catchment hydrology and geology) had substantial effects on DOM, especially in acidotrophic, dystrophic, semi-dystrophic and mixotrophic lakes. We can conclude that larger catchments and intensive water exchange resulted in higher levels of DOM in lakes and soil variables had in general a greater effect than land cover. Soil types provide more detailed information about organic carbon in the catchment and therefore are better predictors of DOM loading than general land cover types. Our study confirmed the role of peatlands as a major source of DOM to lakes; however agricultural lands with Albeluvisols and coniferous forests with Podzols and Gleyic Podzols were also important DOM sources. In eutrophic lakes with relatively high share of autochthonous DOM, catchment characteristics had an indirect and less clear impact on DOM. Patterns in DOM quantity and quality found in our study were similar to patterns found in temperate lakes in general. Our study sites do not represent all temperate catchments, especially regarding hydrological conditions (e.g. Estonian mean annual precipitation is lower than in several Western European countries) and soil variables (e.g. the mean SOC content of Estonian soils is higher than in most European countries). However, our results could still be expanded with some caution to other catchments and have important implications for understanding catchment-lake interactions across the temperate region.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jhydrol.2019.01.012.

References

Abbt-Braun, G., Frimmel, F.H., 1999. Basic characterization of Norwegian NOM samples – similarities and differences. Environ. Int. 25, 161–180. https://doi.org/10.1016/S0160-4120(98)00118-4.

Aherne, J., Kelly-Quinn, M., Farrell, E.P., 2002. A survey of lakes in the Republic of Ireland: hydrochemical characteristics and acid sensitivity. AMBIO 31, 452–459. https://doi.org/10.1579/0044-7447-31.6.452.

Aksoy, E., Yigini, Y., Montanarella, L., 2016. Combining soil databases for topsoil organic carbon mapping in Europe. PLOS ONE 11, e0152098. https://doi.org/10.1371/journal.pone.0152098.

Arvola, L., Äijälä, C., Leppäranta, M., 2016. CDOM concentrations of large Finnish lakes relative to their landscape properties. Hydrobiologia 780, 37–46. https://doi.org/10.1007/s10750-016-2906-4.

Barreto, S.R.G., Nozaki, J., Barreto, W.J., 2003. Origin of dissolved organic carbon studied by UV-vis spectroscopy. Acta Hydrochim. Hydrobiol. 31, 513–518. https://doi.org/10.1002/aheh.200300510.

Bastviken, D., Tranvik, L.J., Downing, J.A., Crill, P.M., Enrich-Prast, A., 2011. Freshwater methane emissions offset the continental carbon sink. Science 331, 50. https://doi.org/10.1126/science.1196808.

Billett, M.F., Deacon, C.M., Palmer, S.M., Dawson, J.J.C., Hope, D., 2006. Connecting organic carbon in stream water and soils in a peatland catchment. J. Geophys. Res.: Biogeosci. 111, G02010. https://doi.org/10.1029/2005JG000065.

Burton, A.W., Aherne, J., 2012. Changes in the chemistry of small Irish lakes. AMBIO 41, 170–179. https://doi.org/10.1007/s13280-011-0177-x.

Chen, J., Gu, B., LeBoeuf, E.J., Pan, H., Dai, S., 2002. Spectroscopic characterization of the structural and functional properties of natural organic matter fractions. Chemosphere 48, 59–68. https://doi.org/10.1016/S0045-6535(02)00041-3.

Cronan, C.S., Aiken, G.R., 1985. Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York. Geochim. Cosmochim. Acta 49, 1697–1705. https://doi.org/10.1016/0016-7037(85)90140-1.

del Giorgio, P.A., Williams, P.J. le B., 2005. The global significance of respiration in aquatic ecosystems: from single cells to the biosphere. In: del Giorgio, P.A., Williams, P.J. le B. (Eds.), Respiration in Aquatic Ecosystems. Oxford University Press, Oxford, pp. 267–303.

Dillon, P.J., Molot, L.A., 1997. Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments. Water Resour. Res. 33, 2591–2600. https://doi.org/10.1029/97WR01921.

Diodato, N., Higgins, S., Bellocchi, G., Fiorillo, F., Romano, N., Guadagno, F.M., 2016. Hydro-climatic forcing of dissolved organic carbon in two boreal lakes of Canada. Sci. Total Environ. 571, 50–58. https://doi.org/10.1016/j.scitotenv.2016.07.112.

EN 1484, 1997. Water analysis – guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC).

Estonian Land Board, 2018. Legend of Estonian basic map 1:10 000 (color). https://geoportaal.maaamet.ee/docs/pohikaart/pk_legend.png?t=20180131092133, Accessed date: 3 May 2018.

European Commission (EC), 2009. Water Framework Directive Intercalibration technical report. Part 2: Lakes. Office for Official Publications of the European Communities, Luxembourg.

European Community (EC), 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Official J. Eur. Communities: Legislation 327, 1–73.

European Environment Agency (EEA), 2012. European waters – assessment of status and pressures. EEA report No 8. Office for Official Publications of the European Union, Luxembourg.

Fee, E.J., Hecky, R.E., Kasian, S.E.M., Cruikshank, D.R., 1996. Effects of lake size, water clarity, and climatic variability on mixing depths in Canadian Shield lakes. Limnol. Oceanogr. 41, 912–920. https://doi.org/10.4319/lo.1996.41.5.0912.

Finstad, A.G., Andersen, T., Larsen, S., Tominaga, K., Blumentrath, S., de Wit, H.A., Tømmervik, H., Hessen, D.O., 2016. From greening to browning: Catchment vegetation development and reduced S-deposition promote organic carbon load on decadal time scales in Nordic lakes. Scientific Rep. 6. https://doi.org/10.1038/srep31944.

Food and Agriculture Organization of the United Nations (FAO), 2014. World reference base for soil resources 2014: international soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports 106. FAO, Rome.

Hagman, C.H.C., Ballot, A., Hjermann, D.Ø., Skjelbred, B., Brettum, P., Ptacnik, R., 2015. The occurrence and spread of Gonyostomum semen (Ehr.) Diesing (Raphidophyceae) in Norwegian lakes. Hydrobiologia 744, 1–14. https://doi.org/10.1007/s10750-014-2050-y.

Haitzer, M., Höss, S., Traunspurger, W., Steinberg, C., 1998. Effects of dissolved organic matter (DOM) on the bioconcentration of organic chemicals in aquatic organisms – a review. Chemosphere 37, 1335–1362. https://doi.org/10.1016/S0045-6535(98)00117-9.

Hessen, D.O., Tranvik, L.J., 1998. Aquatic Humic Substances. Springer, Berlin.

Hongve, D., 1999. Production of dissolved organic carbon in forested catchments. J. Hydrol. 224, 91–99. https://doi.org/10.1016/S0022-1694(99)00132-8.

Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J.M., Parlanti, E., 2009. Properties of fluorescent dissolved organic matter in the Gironde Estuary. Org. Geochem. 40, 706–719. https://doi.org/10.1016/j.orggeochem.2009.03.002.

Kaiser, K., Zech, W., 1998. Rates of dissolved organic matter release and sorption in forest soils. Soil Sci. 163, 714–725. https://doi.org/10.1097/00010694-199809000-00005.

Kellerman, A.M., Dittmar, T., Kothawala, D.N., Tranvik, L.J., 2014. Chemodiversity of dissolved organic matter in lakes driven by climate and hydrology. Nat. Commun. 5. https://doi.org/10.1038/ncomms4804.

Klavins, M., Kokorite, I., Eglite, L., Rodinov, V., 2012. Natural organic matter export from boreal catchments (the Salaca River basin, Latvia) and its influencing factors. Hydrol. Res. 43, 330. https://doi.org/10.2166/nh.2012.112.

Köhler, S.J., Kothawala, D., Futter, M.N., Liungman, O., Tranvik, L., 2013. In-lake processes offset increased terrestrial inputs of dissolved organic carbon and color to

lakes. PLoS ONE 8, e70598. https://doi.org/10.1371/journal.pone.0070598.
Kölli, R., Ellermäe, O., Köster, T., Lemetti, I., Asi, E., Kauer, K., 2009. Stocks of organic carbon in Estonian soils. Estonian J. Earth Sci. 58, 95–108. https://doi.org/10.3176/earth.2009.2.01.
Kortelainen, P., 1993. Content of total organic carbon in Finnish lakes and its relationship to catchment characteristics. Can. J. Fish. Aquatic Sci. 50, 1477–1483. https://doi.org/10.1139/f93-168.
Li, M., del Giorgio, P.A., Parkes, A.H., Prairie, Y.T., 2015. The relative influence of topography and land cover on inorganic and organic carbon exports from catchments in southern Quebec, Canada. J. Geophys. Res.: Biogeosci. 120, 2562–2578. https://doi.org/10.1002/2015JG003073.
Lundström, U., van Breemen, N., Bain, D., 2000. The podzolization process. A review. Geoderma 94, 91–107. https://doi.org/10.1016/S0016-7061(99)00036-1.
Mattsson, T., Kortelainen, P., Räike, A., 2005. Export of DOM from boreal catchments: impacts of land use cover and climate. Biogeochemistry 76, 373–394. https://doi.org/10.1007/s10533-005-6897-x.
McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, P.T., Kulbe, T., Andersen, D.T., 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol. Oceanogr. 46, 38–48. https://doi.org/10.4319/lo.2001.46.1.0038.
Morris, D.P., Zagarese, H., Williamson, C.E., Balseiro, E.G., Hargreaves, B.R., Modenutti, B., Moeller, R., Queimalinos, C., 1995. The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon. Limnol. Oceanogr. 40, 1381–1391. https://doi.org/10.4319/lo.1995.40.8.1381.
Nieminen, M., 2004. Export of dissolved organic carbon, nitrogen and phosphorus following clear-cutting of three Norway spruce forests growing on drained peatlands in southern Finland. Silva Fennica 38, 123–132.
Obernosterer, I., Herndl, G.J., 2000. Differences in the optical and biological reactivity of the humic and nonhumic dissolved organic carbon component in two contrasting coastal marine environments. Limnol. Oceanogr. 45, 1120–1129. https://doi.org/10.4319/lo.2000.45.5.1120.
Olefeldt, D., Roulet, N., Giesler, R., Persson, A., 2013. Total waterborne carbon export and DOC composition from ten nested subarctic peatland catchments-importance of peatland cover, groundwater influence, and inter-annual variability of precipitation patterns. Hydrol. Processes 27, 2280–2294. https://doi.org/10.1002/hyp.9358.
Peuravuori, J., Pihlaja, K., 1997. Molecular size distribution and spectroscopic properties of aquatic humic substances. Anal. Chim. Acta 337, 133–149. https://doi.org/10.1016/S0003-2670(96)00412-6.
Peuravuori, J., Pihlaja, K., 2007. Characterization of freshwater humic matter. In: Nollet, L.M.L. (Ed.), Handbook of Water Analysis, second ed. CRC Press, Boca Raton, pp. 435–448.
Rantakari, M., Kortelainen, P., Vuorenmaa, J., Mannio, J., Forsius, M., 2004. Finnish lake survey: the role of catchment attributes in determining nitrogen, phosphorus, and organic carbon concentrations. Water Air Soil Pollut.: Focus 4, 683–699. https://doi.org/10.1023/B:WAFO.0000028387.61261.96.
Raymond, P.A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Dürr, H., Meybeck, M., Ciais, P., Guth, P., 2013. Global carbon dioxide emissions from inland waters. Nature 503, 355–359. https://doi.org/10.1038/nature12760.
Robards, K., McKelvie, I.D., Benson, R.L., Worsfold, P.J., Blundell, N.J., Casey, H., 1994. Determination of carbon, phosphorus, nitrogen and silicon species in waters. Anal. Chim. Acta 287, 147–190. https://doi.org/10.1016/0003-2670(93)E0542-F.
Rostan, J.C., Cellot, B., 1995. On the use of UV spectrophotometry to assess dissolved organic carbon origin variations in the Upper Rhone River. Aquatic Sci. 57, 70–80. https://doi.org/10.1007/BF00878027.
Schindler, D.W., Bayley, S.E., Curtis, P.J., Parker, B.R., Stainton, M.P., Kelly, C.A., 1992. Natural and man-caused factors affecting the abundance and cycling of dissolved organic substances in precambrian shield lakes. Hydrobiologia 229, 1–21. https://doi.org/10.1007/BF00006987.
Schindler, D.W., Curtis, P.J., Bayley, S.E., Parker, B.R., Beaty, K.G., Stainton, M.P., 1997. Climate-induced changes in the dissolved organic carbon budgets of boreal lakes. Biogeochemistry 36, 9–28. https://doi.org/10.1023/A:1005792014547.
Sepp, M., Kõiv, T., Nõges, P., Nõges, T., 2018. Do organic matter metrics included in lake surveillance monitoring in Europe provide a broad picture of brownification and enrichment with oxygen consuming substances? Sci. Total Environ. 610–611, 1288–1297. https://doi.org/10.1016/j.scitotenv.2017.08.179.
Steinberg, C.E.W., 2003. Ecology of Humic Substances in Freshwaters. Springer-Verlag, Berlin.
Thurman, E.M., 1985. Organic Geochemistry of Natural Waters. Martinus Nijoff/Dr W. Junk Publishers, Dordrecht.
Tranvik, L.J., 1988. Availability of dissolved organic carbon for planktonic bacteria in oligotrophic lakes of differing humic content. Microbial Ecol. 16, 311–322. https://doi.org/10.1007/BF02011702.
Tranvik, L.J., Downing, J.A., Cotner, J.B., Loiselle, S.A., Striegl, R.G., Ballatore, T.J., Dillon, P., Finlay, K., Fortino, K., Knoll, L.B., Kortelainen, P.L., Kutser, T., Larsen, S., Laurion, I., Leech, D.M., McCallister, S.L., McKnight, D.M., Melack, J.M., Overholt, E., Porter, J.A., Prairie, Y., Renwick, W.H., Roland, F., Sherman, B.S., Schindler, D.W., Sobek, S., Tremblay, A., Vanni, M.J., Verschoor, A.M., von Wachenfeldt, E., Weyhenmeyer, G.A., 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnol. Oceanogr. 54, 2298–2314. https://doi.org/10.4319/lo.2009.54.6_part_2.2298.
Tulonen, T., Salonen, K., Arvola, L., 1992. Effects of different molecular weight fractions of dissolved organic matter on the growth of bacteria, algae and protozoa from a highly humic lake. Hydrobiologia 229, 239–252. https://doi.org/10.1007/BF00007003.
Uyguner, C.S., Bekbolet, M., 2005. Implementation of spectroscopic parameters for practical monitoring of natural organic matter. Desalination 176, 47–55. https://doi.org/10.1016/j.desal.2004.10.027.
Vogt, R.D., Akkanen, J., Andersen, D.O., Brüggemann, R., Chatterjee, B., Gjessing, E., Kukkonen, J.V.K., Larsen, H.E., Luster, J., Paul, A., Pflugmacher, S., Starr, M., Steinberg, C.E.W., Schmitt-Kopplin, P., Zsolnay, A., 2004. Key site variables governing the functional characteristics of Dissolved Natural Organic Matter (DNOM) in Nordic forested catchments. Aquatic Sci. 66, 195–210. https://doi.org/10.1007/s00027-004-0710-0.
von Einem, J., Granéli, W., 2010. Effects of fetch and dissolved organic carbon on epilimnion depth and light climate in small forest lakes in southern Sweden. Limnol. Oceanogr. 55, 920–930. https://doi.org/10.4319/lo.2010.55.2.0920.
Vuorenmaa, J., Forsius, M., Mannio, J., 2006. Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003. Sci. Total Environ. 365, 47–65. https://doi.org/10.1016/j.scitotenv.2006.02.038.
Wickland, K.P., Neff, J.C., Aiken, G.R., 2007. Dissolved organic carbon in Alaskan Boreal forest: sources, chemical characteristics, and biodegradability. Ecosystems 10, 1323–1340. https://doi.org/10.1007/s10021-007-9101-4.
Williamson, C.E., Morris, D.P., Pace, M.L., Olson, O.G., 1999. Dissolved organic carbon and nutrients as regulators of lake ecosystems: resurrection of a more integrated paradigm. Limnol. Oceanogr. 44, 795–803. https://doi.org/10.4319/lo.1999.44.3_part_2.0795.
Yamashita, Y., Jaffé, R., 2008. Characterizing the interactions between trace metals and dissolved organic matter using excitation-emission matrix and parallel factor analysis. Environ. Sci. Technol. 42, 7374–7379. https://doi.org/10.1021/es801357h.