REPORT

Effect of catchment land use and soil type on the concentration, quality, and bacterial degradation of riverine dissolved organic matter

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Abstract We studied the effects of catchment characteristics (soil type and land use) on the concentration and quality of dissolved organic matter (DOM) in river water and on the bacterial degradation of terrestrial DOM. The share of organic soil was the strongest predictor of high concentrations of dissolved organic carbon, nitrogen, and phosphorus (DOC, DON, and DOP, respectively), and was linked to DOM quality. Soil type was more important than land use in determining the concentration and quality of riverine DOM. On average, 5–9 % of the DOC and 45 % of the DON were degraded by the bacterial communities within 2–3 months. Simultaneously, the proportion of humic-like compounds in the DOM pool increased. Bioavailable DON accounted for approximately one-third of the total bioavailable dissolved nitrogen, and thus, terrestrial DON can markedly contribute to the coastal plankton dynamics and support the heterotrophic food web.

Keywords Terrestrial dissolved organic matter · Catchment characteristics · Bacterial degradation · DOM quality · Bioavailability

INTRODUCTION

Most of the terrestrial organic carbon entering the sea in the boreal zone is in dissolved form (Mattsson et al. 2005). Due to projected changes in climate and hydrology, the loads of dissolved organic carbon (DOC) have been predicted to increase in boreal and temperate areas (e.g., Freeman et al. 2001; Lepistö et al. 2008). A long-term increase in total organic carbon (TOC) concentrations has already been encountered in several headwater lakes and

streams in the northern midlatitudes as well as in large areas of the Northern Baltic Sea coastline (e.g., Lepistö et al. 2008; Pärn and Mander 2012; Fleming-Lehtinen et al. 2014). Terrestrial dissolved organic matter (TDOM) can also notably contribute to the transport of nutrients into coastal waters. For example, an average of 40 % of the total nitrogen load and 20 % of the total phosphorus load is in organic form in the Baltic Sea during summer (Stepanuskas et al. 2002).

TDOM can affect the planktonic growth of the receiving riverine and coastal waters in several ways. The chromophoric fraction of DOM (CDOM) reduces the penetration of light into the water body and modifies the transparency and heat budgets of surface waters. This DOM-induced change in the light and heat regime may affect primary production (Sandberg et al. 2004; Dupont and Aksnes 2013). The biologically available part of TDOM may be an important source of energy and nutrients for coastal heterotrophic bacteria (Sandberg et al. 2004), and provide nutrients for phytoplankton (Korth et al. 2012). The effect of utilized TDOM on the coastal plankton community and carbon (C) cycling is further determined by the partition of utilized DOC between bacterial biomass and respiratory losses or the bacterial growth efficiency (BGE). The quality of DOM substrates utilized by bacterial communities is important in determining BGE (del Giorgio and Cole 1998; Apple and del Giorgio 2007).

The catchment characteristics, including soil type and land use, affect the concentration and quality of TDOM entering water ecosystems. A high proportion of peatlands in the catchment has been linked to high TOC concentrations in river water (Laudon et al. 2004; Mattsson et al. 2005), whereas a long residence time (with lakes and reservoirs) can decrease TOC concentrations in river water

(Mattsson et al. 2005, 2009). Similarly, a high share of agricultural land has been reported to increase DOC concentrations in Central Europe (Graeber et al. 2012) and DON and DOP concentrations compared to forest-dominated catchments along the European climatic gradient (Mattsson et al. 2009). Contrastingly, agriculture did not affect DOC concentrations in the watersheds of North-eastern U.S. (Wilson and Xenopoulos 2008). The different patterns may occur due to differences in the history of agricultural land or the stream order (Graeber et al. 2012). The DOM originating from peat-dominated catchments typically has high aromaticity and low bioavailability (Asmala et al. 2013), whereas mineral soils under agricultural production are expected to export small-molecular-sized DOM with relatively high bioavailability (Seitzinger et al. 2002; Chantigny 2003). DOM originating from agricultural land may again lead to higher BGE in receiving aquatic systems (Apple and del Giorgio 2007; Asmala et al. 2013).

In areas with relatively high human population, most of the fertile soil suitable for agricultural production has been taken into cultivation. Agricultural fields are preferably on flat areas and the soil is fertile, fine-textured, and well-sorted, whereas forests are left to grow on coarse-textured and stony areas. Comparisons made between various land use types, such as agricultural and forested areas, therefore almost always include the effect of soil type. Also, in the context of land use types, peatlands are a form of land use aside with forests and agricultural land but peatlands can be taken into use for forestry or modified for cultivation. After the change in land use, they will still have a high soil organic matter content. To address the role of land use on the quantity and quality of riverine DOM, both soil type and land use should thus be taken into account. However, these kinds of studies are rare. Furthermore, how the catchment characteristics affect the fate of DOM in the receiving waters remains still poorly known.

The objective of our study was to investigate the effects of the catchment's main land use (forests and fields) and major soil type (organic, clay, and coarse mineral soils) to the quantity and quality of DOM in the receiving waters. We also investigated how the catchment characteristics affect the bacterial degradation of TDOM in river and coastal waters and the partition of utilized terrestrial organic carbon (TDOM) to bacterial biomass and respiratory losses. With these objectives in mind, we framed two research questions: (1) Do the quantity and quality of TDOM in river water differ between the soil types and the catchment land use types and if so, whether one of these characteristics is dominating over the other? (2) Do these differences have direct, measurable effects on the bacterial degradation of DOM?

MATERIALS AND METHODS

Study area

The water samples were taken from Vantaanjoki river and its tributaries (Fig. 1). Vantaanjoki river is located in southern Finland and flows into the Gulf of Finland in the Baltic Sea. The drainage basin is 1685 km² and covers some of the most densely inhabited areas of the country. Over 50 % of the drainage basin is forest, approximately 25 % is agricultural land and 17 % is urban land cover. Only 2 % of the area is covered by lakes (Räike et al. 2012). The soil in the Vantaanjoki river drainage basin is 40 % clay ground, 20 % moraine, 20 % sand, fine sand, and gravel, 10 % rocks, and 10 % peat (Hänninen 1997). In 2013, the annual nutrient load from Vantaanjoki river to the Baltic Sea was 66 t phosphorus (P) and 1370 t nitrogen (N) (Vahtera et al. 2014). The average annual TOC load is 6700 t (Räike et al. 2012).

Sampling and experimental design

Selection and catchment characteristics of the sampling sites

The study sites (14) were selected to represent a gradient along organic to mineral soil and forest to field land use with minimal correlation between land use and soil type. Geographic Information System (GIS) data were used for defining the areas of different land use and soil combinations. The selection criteria for the sampling site candidates were based on the prevalence of fields and forests, and organic soil and non-organic soil upon a visual overview of the data. Upstream locations were preferred to avoid overlapping between the sampling sites, and sites with large lakes or notable settlement in the catchment were excluded. The initial candidate locations were assessed on-site, and the final sampling coordinates were recorded based on the sites that were accessible. These coordinates were input into GIS, and the area forming the catchment for each point was estimated using a laser scan-derived digital elevation model (2 × 2 m) and TauDEM tools (Tarboton et al. 2012). The catchment polygons of the sampling sites were used to clip forest and swamp data from Corine2006 (EEA 2010), field data from the Information service of the Ministry of Agriculture and Forestry (TIKE) 2012, soil data from the Geological Survey of Finland (GTK), and lake data from the National Land Survey of Finland (NLS).

Organic soil was defined according to the soil classification of the Food and Agriculture Organization (FAO) of the United Nations (UN), and corresponds to the soil group 'histosols', that comprises soils formed in organic soil material (IUSS Working Group WRB 2014). Histosols are

Fig. 1 Study area and sampling sites with their subcatchments

characterized as soils with thick organic layers in the upper 80 cm of the soil profile, or as soils with an organic horizon in the soil surface 10 cm or more in thickness with a lithic or paralithic layer underneath. Mineral soils were divided into clay soils and coarse soils, with the latter including gravel, sand, fine sand, and silt. The calculated forest, field, and lake areas were then divided by the total surface area of each catchment to obtain the fractions of these land uses in each catchment draining to the sampling sites. Organic, clay, and coarse soil areas were similarly divided by the total surface area of each catchment to obtain the fractions of soil types in the catchments (Table 1).

Sampling and bioavailability incubations

The river water samples were collected from the selected upstream sites (Fig. 1) November 2012 and May 2013. Both sampling occasions coincide with late phases of the seasonal high flow periods (Fig. 2). The samples (15 l) were taken from flowing surface water, in the middle of the 2–4 m wide streams with an acid-washed plastic jug. They were filtered through three connected cartridge filters to

remove bacterivores, particulate matter, and most of the bacterial cells. The filters were (1) Sartopure-PP2 MidiCap (Sartorius Stedim Biotech), nominal cutoff 3 μm (2) Sartoclean-GF Sterile MidiCap (Sartorius Stedim Biotech) 3 + 0.8 μm , and 3) Sartobran 300 Sterile Capsule (Sartorius Stedim Biotech) 0.45 + 0.2 μm . About 1 l of Milli-Q (Millipore) water was run through the filters between each sample. The 0.2- μm filtrate was sampled for analyses of the initial DOC and DON concentrations and DOM quality (colored DOM; CDOM and fluorescent DOM; FDOM).

To investigate the biological availability of the DOM from different sources, the 0.2- μm filtered samples were inoculated with natural bacterial communities and incubated for 2–3 months. To widen the applicability of the bioavailability results, the experiments were conducted with differing experimental setups. In November 2012, TDOM degradability in the receiving river was tested by inoculating the samples with a natural bacterial inoculum from the river mouth. In May 2013, the TDOM degradability potential in receiving coastal water was tested by inoculating the samples with a natural bacterial inoculum from the open sea surface water 8 km from the shore off

Table 1 Catchment characteristics of the sampling sites. Exp I refers to samples taken in November 2012, while Exp II to samples taken in May 2013

Site N°	Experiment	Field %	Forest %	Organic soil %	Clay soil %	Coarse soil %	Area (ha)
1	Exp I	0	89	2	12	80	1331
	Exp II						
2	Exp I	4	71	5	10	70	27 357
	Exp II						
3	Exp I	50	39	0	74	17	1187
	Exp II						
4	Exp I	13	67	12	5	83	31 183
	Exp II						
5	Exp I	23	55	11	2	84	36 900
	Exp II						
6	Exp I	23	47	10	5	85	51 370
7	Exp I	17	62	19	7	72	81 555
8	Exp II	43	42	0	60	40	4606
9	Exp II	8	74	32	5	64	16 114
10	Exp II	19	60	11	4	82	52 001
11	Exp II	18	51	34	0	66	9470
12	Exp II	49	39	37	2	61	1555
13	Exp II	31	39	3	57	39	10 803
14	Exp II	35	46	0	40	60	2955

Helsinki in the Gulf of Finland, the Baltic Sea (10 l). The experiments will hereafter be referred to as Exp I and Exp II, respectively.

Preceding the incubation, the river samples in Exp II were treated with synthetic sea salt (TROPIC MARIN® Sea Salt, Dr. BienerGMBH, Wartenberg, Germany) to increase the salinity to 6.0 (salinity of the coastal bacterial inoculum). DOC, DON, CDOM, and FDOM samples were taken the next day to examine the possible salt-induced flocculation of DOM. These measurements also represent the initial DOC, DON, and DOP concentrations as well as the CDOM and FDOM parameters of the bioassays. Initial inorganic nutrient concentrations (NH_4^+ , $\text{NO}_3^- + \text{NO}_2^-$, and PO_4^{3-}) were also measured at this point. The samples in Exp II, where the higher temperature was expected to lead to a higher bacterial growth rate compared to Exp I, were treated with nutrients (NH_4^+ $10 \mu\text{mol N l}^{-1}$ and PO_4^{3-} $2 \mu\text{mol P l}^{-1}$) to ensure their sufficiency during incubation.

For both experiments, the inocula were filtered through Sartoclean-GF Sterile MidiCap (Sartorius Stedim Biotech) $3 + 0.8\text{-}\mu\text{m}$ filters, and concentrated 100-fold with ≤ 100 kD tangential flow filtration to minimize the addition of seawater DOM into the river water samples. The concentrated inocula were immediately divided into the river water samples (final bacterial concentration approximately 5 % of the original seawater sample).

The inoculated samples were siphoned into acid-washed 300-ml Duran-bottles and 100-ml oxygen bottles for incubation. To avoid contamination and dependence between the bottles, one Duran-bottle and one oxygen bottle per site were reserved for each sampling day. The samples were incubated in darkness at in situ temperature (3°C in Exp I and 15°C in Exp II). Measurements were made from designated bottles after 4, 7, 14, 32, and 103 days of incubation in Exp I and 7, 14, 27, and 59 days of incubation in Exp II. The incubation times were designed to be sufficiently long for the changes in TDOC concentration to level off. The lower temperature in Exp I was compensated with a longer incubation period. To take the dynamic nature of the biological and chemical processes into account, several samplings were conducted during the incubation.

All equipments were acid-washed before use as described in Lignell et al. (2008). Glass vials for DOC/DON, CDOM, and flagellate samples were also combusted in 400°C for 4 h.

Analyses

The subsamples for DOC, DON, inorganic nutrient, CDOM, and FDOM analyses were filtered with $<0.22\text{-}\mu\text{m}$ syringe filters (Millipore) at each sampling. The subsamples (3 replicates) for DOC and DON analyses were

Fig. 2 Flow and rainfall at river Vantaanjoki. Flow is based on water level measurements at two points near the outlet (Myllymäki and Keravanjoki), which are combined with the Oulunkylä observations. Daily rainfall data are from the Helsinki-Vantaa Airport observation station. The sampling dates and flow estimates are indicated on the map

acidified with HCl to pH 2.5 and kept frozen at -20°C until analysis. DOC and total dissolved nitrogen (TDN) concentrations were measured with high-temperature catalytic oxidation (HTCO) using a Shimadzu TOC-V CPH carbon and nitrogen analyzer. DON concentrations were calculated by subtracting inorganic nitrogen from TDN. Sub-samples (2 replicates) for $\text{NO}_3^- + \text{NO}_2^-$, PO_4^{3-} , and total dissolved phosphorus (TDP) measurements were stored at -20°C . Ammonium samples (2 replicates) were stored at $+4^{\circ}\text{C}$ and measured within 24 h from sampling. Inorganic nutrients were measured according to Grasshoff et al. (1983).

Dissolved oxygen concentration was measured using the Winkler titration method (Metrohm 848 Titrino Plus potentiometric titrator, Metrohm AG). Bacterial respiration was measured by converting the oxygen concentration decrease into a release of CO_2 with a respiratory quotient of 1.2 (Berggren et al. 2012).

Samples for flow cytometric determination of bacterial cell abundance were preserved with a mixture of

paraformaldehyde (AlfaAesar) (final concentration 1 %) and glutaraldehyde (final concentration 0.05 %, Sigma) (Marie et al. 1996), kept at room temperature for approximately 10 min and stored at -70°C . Bacterial cell counts were performed with a BD LSR II flow cytometer using a blue light (480 nm) emitting laser according to Gasol et al. (1999). The samples were colored with DNA-binding fluorescent SybrGreen stain (Sigma) and kept in the dark for 15 min. CountBright beads (Invitrogen) with a known concentration were added to each sample for determining bacterial concentration. At least 700 beads and 1500 bacterial cells were counted per sample. Results were analyzed using BD FACS Diva software. The bacterial biomass was calculated from cell abundance assuming an average cell carbon content of $0.12 \text{ pg C (cell } \mu\text{m}^3)^{0.7}$ (Norland 1993) and an average heterotrophic bacterial cell size of $0.06 \mu\text{m}^3$, previously measured in the Gulf of Finland (Lignell et al. unpublished).

The samples for a flagellate check were preserved with glutaraldehyde (Sigma) (final concentration 5 %), and

stored in glass vials at 4 °C. The samples were filtered on a polycarbonate filter (pore size 0.2 µm) and colored with proflavine according to Haas (1982). Any possible flagellates were counted using a Leitz Aristoplan epifluorescence microscope under a blue light.

The concentration of labile DOC (LDOC) was calculated from the decrease in DOC concentration during incubation. Another estimate for LDOC was derived from the bacterial carbon demand (BCD) during incubation. BCD was calculated as the sum of bacterial respiration and the increase in bacterial biomass. If heterotrophic flagellates were found from the sample, their biomass was also added. The BGE was calculated for first 2 weeks by dividing the increase in bacterial biomass with BCD (in samples with no flagellates).

The filtered CDOM and FDOM samples were stored at 4 °C and measured within 14 days. Spectrophotometric analyses of CDOM absorbance spectra were performed with a PerkinElmer Lambda 650 UV/VIS Spectrometer using a 1-cm quartz cuvette. Milli-Q (Millipore) water was used as a reference. Absorbance was measured with wavelengths of 200–800 nm and transformed to an absorption coefficient by dividing by the path length (cuvette size 0.01 m) and multiplying by 2.303. A slope coefficient for wavelength range 275–295 nm ($S_{275-295}$) was calculated as described in Stedmon et al. (2000). DOC-specific UV absorbance ($SUVA_{254}$) was calculated by dividing absorbance at 254 nm by DOC concentration (mg l^{-1}) (Weishaar et al. 2003).

Excitation–emission matrices (EEMs) of fluorescence were measured for the DOM samples in a 1-cm quartz cuvette in a Varian Cary Eclipse fluorometer (Agilent). Bandwidths were set to 5 nm for excitation and 4 nm for emission. A series of emission scans (280–600 nm) were collected over excitation wavelengths ranging from 220 to 450 nm in 5-nm increments. The fluorescence spectra were corrected for inner filter effects, which accounted for the absorption of both excitation and emission light by the sample in the cuvette (Mobed et al. 1996). This was done following the methods of McKnight et al. (2001). The FDOM spectra (excitation and emission) were also corrected for instrument biases using an excitation correction spectrum derived from a concentrated solution of oxazine 1 and an emission correction spectrum derived using a ground quartz diffuser. The fluorescence spectra were Raman calibrated by normalizing to the area under the Raman scatter peak (excitation wavelength of 350 nm) of a Milli-Q water sample, run on the same session as the samples. To remove the Raman signal, a Raman normalized Milli-Q EEM was subtracted from the sample data. As the measured signal was normalized to the Raman peak and excitation and emission correction spectra were used, all the instrument-specific biases were effectively removed.

Rayleigh scatter effects were removed from the dataset by not including any emission measurements made at wavelengths $\leq$ the excitation wavelength +20 nm. The fluorescence peaks C, A, M, and T were extracted from the EEM data (Coble 1996). Peak A is a primary fluorescence peak from dissolved humic substances; peak C is a secondary humic substance peak characteristic of terrestrially derived DOM; peak M is a secondary humic substance peak characteristic of marine-derived DOM; peak T is a peak attributable to fluorescence from the aromatic amino acid tryptophan (Coble 1996). As a precursor of humic-like properties of the DOM pool, peak C was chosen to represent the terrestrial signal of DOM. Fluorescence index is the ratio of emission intensity (450/500 nm) at 370 nm excitation (McKnight et al. 2001).

Statistical analyses

The effect of land use and soil in the catchment on the concentration and quality of DOM in the Vantaanjoki river was tested using redundancy analysis (RDA) in R (Vegan package). Correlation scaling (Scaling 2) was used to draw the graphs, which means that angles between the variable arrows should be interpreted. The environmental variables were the proportion of field, forest, organic soil, clay soil, and coarse mineral soil in the sub-catchments and the area of the sub-catchments. The level of collinearity between these variables was very high, and it was minimized by removing part of the environmental variables from the model (variance inflation factor ≤ 6). The selection of the environmental and response variables was based on the significance of the model. The response variables were the initial DOC, DON, and DOP concentrations, DOC:DON ratio, and CDOM parameters as well as bacterial respiration, growth in bacterial biomass, BGE, share of labile DOC and DON (LDOC and LDON, respectively), and the changes in CDOM and FDOM parameters during incubation. Model significance and individual axes were tested with permutation tests. The correlations between the variables were also tested with a regression analysis using IBM SPSS Statistics 22.

RESULTS

Initial conditions: concentrations of DOM and inorganic nutrients and DOM quality

The initial DOC concentrations were generally similar in both experiments and variation between sites was large (Exp I: average $1627 \pm 754 \mu\text{mol l}^{-1}$, Exp II: average $1576 \pm 1346 \mu\text{mol l}^{-1}$) (Table 2). In those sampling sites, which were repeated in both experiments, concentrations

Table 2 Initial concentrations of DOC, DON, and inorganic nutrients as well as initial DOC:DON ratio in the two experiments. DOP concentrations are only available for Exp II

Site	Experiment	DOC ($\mu\text{mol l}^{-1}$)	DON ($\mu\text{mol l}^{-1}$)	DOP ($\mu\text{mol l}^{-1}$)	DOC:DON	NH_4^+ ($\mu\text{mol l}^{-1}$)	($\text{NO}_3^- + \text{NO}_2^-$)- N ($\mu\text{mol l}^{-1}$)	PO_4^{3-} -P ($\mu\text{mol l}^{-1}$)
1	Exp I	835	16		51	2.2	7.8	0.20
	Exp II	752	19	0.23	39	1.3	3.5	0.16
2	Exp I	704	17		40	2.1	3.9	0.21
	Exp II	624	19	0.15	34	2.1	4.3	0.12
3	Exp I	1111	48		23	2.6	49.2	0.36
	Exp II	742	16	0.23	45	3.6	38.1	0.51
4	Exp I	2258	44		52	3.2	28.1	0.47
	Exp II	1562	35	0.32	45	3.1	22.4	0.27
5	Exp I	1906	71		27	3.4	54.2	0.48
	Exp II	1178	16	0.25	75	1.4	52.7	0.25
6	Exp I	1888	63		30	2.6	51.1	0.78
7	Exp I	2687	63		43	1.1	46.1	0.78
8	Exp II	880	25	0.36	35	1.7	31.0	0.74
9	Exp II	2316	45	0.39	52	2.4	21.7	0.86
10	Exp II	1634	36	0.39	45	4.9	35.0	0.40
11	Exp II	1847	37	0.44	50	10.0	41.4	0.73
12	Exp II	5517	132	1.38	42	61.4	0.4	5.34
13	Exp II	890	26	0.33	34	2.7	36.0	0.76
14	Exp II	971	17	0.35	57	1.9	50.0	0.53

Table 3 Initial CDOM and FDOM parameters in Exp I and II

Site ID	Experiment	$a_{\text{CDOM}(254)}$ (m^{-1})	$a_{\text{CDOM}(440)}$ (m^{-1})	SUVA_{254} ($\text{l mg}^{-1} \text{C m}^{-1}$)	$S_{275-295}$ (μm^{-1})	$S_{300-650}$ (μm^{-1})	Peak C (R.U.)	Index
1	Exp I	101.9	7.5	4.4	12.4	14.7	0.9	1.32
	Exp II	86.4	6.7	4.0	11.8	14.5	1.1	1.36
2	Exp I	78.7	5.2	4.0	13.5	15.1	0.8	1.26
	Exp II	65.1	4.4	3.8	13.1	15.2	1.0	1.33
3	Exp I	121.7	7.0	4.0	13.1	16.2	1.5	1.40
	Exp II	72.5	4.1	3.5	13.7	16.2	1.4	1.37
4	Exp I	270.5	18.4	4.3	12.2	15.2	2.4	1.27
	Exp II	194.5	14.7	4.5	11.8	14.6	2.5	1.40
5	Exp I	213.0	13.8	4.0	12.7	15.4	2.2	1.26
	Exp II	143.6	11.2	4.4	12.1	14.3	1.9	1.28
6	Exp I	216.2	14.1	4.1	12.4	15.5	2.3	1.30
7	Exp I	318.5	20.9	4.3	12.4	15.4	3.1	1.29
8	Exp II	102.1	6.7	4.2	12.7	15.4	1.5	1.39
9	Exp II	305.5	25.5	4.7	11.5	14.0	3.1	1.29
10	Exp II	204.3	14.7	4.5	12.3	14.8	2.7	1.27
11	Exp II	237.0	19.9	4.6	11.6	14.0	2.8	1.33
12	Exp II	695.0	36.7	4.5	12.9	16.6	10.1	1.38
13	Exp II	88.0	5.2	3.5	13.6	15.9	1.6	1.39
14	Exp II	114.2	7.8	4.2	12.4	15.2	1.7	1.38

were higher in Exp I than Exp II (average $1363 \pm 684 \mu\text{mol l}^{-1}$ and average $976 \pm 367 \mu\text{mol l}^{-1}$, respectively). Similarly, $a_{\text{CDOM}(254)}$ and $a_{\text{CDOM}(440)}$ were higher in Exp I than Exp II (Table 3). In Exp II, where salt was added to the samples, the addition decreased DOC concentration on average by $2 \pm 3 \%$, which falls within the measurement uncertainty (2.3 % Lignell et al. 2008). Thus, no significant flocculation was observed, and the concentrations in Exp II after salt addition were treated as initial.

Initial DON concentrations in Exp I were an average $46 \pm 22 \mu\text{mol l}^{-1}$ and an average $35 \pm 32 \mu\text{mol l}^{-1}$ in Exp II (Table 2). The shares of DON from TDN were an average 58 ± 8 and $50 \pm 20 \%$ in In Exp I and Exp II, respectively. Inorganic nitrogen concentrations were generally higher in Exp I than Exp II (average $39 \pm 23 \mu\text{mol l}^{-1}$ and average $21 \pm 8 \mu\text{mol l}^{-1}$, respectively). The DOP results from Exp II varied between 0.15 and $0.44 \mu\text{mol l}^{-1}$, except for site 12 where DOP was as high as $1.38 \mu\text{mol l}^{-1}$ (Table 2). Site 12 was exceptional in all parameters by having multifold DOC, DON, DOP, NH_4^+ , and PO_4^{3-} concentrations and one order of magnitude lower $\text{NO}_3^- + \text{NO}_2^-$ concentration.

Effects of catchment characteristics on initial DOM concentration and quality

Both RDA models testing the effect of the catchment characteristics on the initial conditions were statistically significant ($p \leq 0.05$) (Fig. 3). The first canonical axis (RDA1) in the RDA of Exp I (Fig. 3a) explained 62.9 % and the second axis (RDA2) explained 27.6 % of the variation, and both axes were statistically significant ($p \leq 0.05$). RDA1 in the RDA of Exp II (Fig. 3b) explained 49.1 % of the variation and was statistically significant ($p \leq 0.05$). RDA2 explained 11.4 % of the variation and had a p value of 0.14. Correlations along RDA2 should therefore not be interpreted.

The share of organic soil in the catchment in both experiments correlated positively with the DOC concentration in the river water (Fig. 3). This strong correlation was confirmed by regression analysis (correlation presented in Fig. 4a, b). In Exp I (Fig. 3a), the share of fields correlated negatively with the initial DOC:DON ratio but no relation to DOC concentrations was found. The latter finding was also shown by a regression analysis where the shares of field and forest did not affect the DOC concentration in Exp I (Fig. 4c, d). Variance homogeneity did not apply in an equivalent regression analysis of Exp II. The R^2 -values in the correlations between the share of field and DOC concentration and the share of forest and DOC concentration were in any case low (0.10 and 0.04, respectively). The DOC:DOP ratio was tested but did not show correlation with the environmental variables. The RDA

Fig. 3 Redundancy analysis on the effects of catchment characteristics on the DOM concentrations and DOC:DON ratios in the river water during the late phases of autumn (a) (Exp I) and spring (b) (Exp II) high flow periods. Blue arrows indicate the explanatory variables (shares of field, clay soil, and organic soil) and black arrows the response variables (DOC, DON, and DOP concentrations and DOC:DON ratio at the beginning of the experiment)

model also suggested a weak correlation of DON with the share of organic soil and the share of fields in Exp I. Both these correlations were significant in regression analysis when tested simultaneously ($R^2 = 0.83$, $p \leq 0.05$). In Exp II (Fig. 3b), the share of organic soil also correlated positively with the DOP and DON concentrations, and this correlation was stronger with DOP. The share of fine-textured clay soils correlated negatively with DOC concentrations, which was especially clearly seen in Exp II.

Fig. 4 Correlations between the share of organic soil and DOC concentration in Exp I (**a**) ($R^2 = 0.84$, $p \leq 0.05$) and Exp II (**b**) ($R^2 = 0.80$, $p \leq 0.05$), share of field and DOC concentration in Exp I (**c**) ($R^2 = 0.01$, $p = 0.79$), and share of forest and DOC concentration in Exp I (**d**) ($R^2 = 0.07$, $p = 0.55$)

The RDA model with initial CDOM and FDOM response variables was statistically significant ($p \leq 0.05$) in Exp I (Fig. 5a). RDA1 explained 45.6 % of the variation and was significant ($p \leq 0.05$). RDA2 was on the limit of being statistically significant ($p \leq 0.07$) and explained 27.4 % of the variation. The equivalent model for Exp II with initial CDOM and FDOM variables was significant ($p \leq 0.005$) and both RDA axes were also significant ($p \leq 0.05$) (Fig. 5b). RDA1 explained 68.5 %, and RDA2 8.4 %.

The share of organic soil in the catchment was the strongest predictor of initial $a_{\text{CDOM}(254)}$, $a_{\text{CDOM}(440)}$, and peak C values in both Exp I and Exp II (Fig. 5). The share of field in Exp I correlated positively with $S_{300-650}$, and the share of clay soil with FIndex (Fig. 5a). However, the arrows are projected on RDA2 ($p \leq 0.07$), and thus, these correlations should be interpreted cautiously. In Exp II, the catchment area and the share of organic soil correlated negatively with FIndex (Fig. 5b). The shares of forest and coarse soil also correlated negatively with $S_{275-295}$ and $S_{300-650}$. This also indicates a positive correlation between $S_{300-650}$ and the share of fields as seen in Exp I, since there

is a strong negative correlation between the shares of forest and field. SUVA_{254} correlated negatively with the share of clay soil in Exp I. Exp II RDA in turn shows a positive correlation between this parameter and the share of organic soil in the catchment.

Bacterial degradation of DOM

Bacterial growth and respiration

Bacterial biomass increased in all units in Exp I throughout the experiment, reaching $9.4\text{--}29.4 \mu\text{mol C l}^{-1}$ at the end of the 3-month incubation period (Fig. 6a). No flagellates were found in any of the samples. The bacterial biomass increase was higher in samples with $>10\%$ of organic soil in the catchment compared to ones with higher shares of mineral soil. It was lowest in samples with forest-dominated catchments and containing $<10\%$ of organic soil. In agriculture-dominated catchments, the role of soil type was less pronounced (Fig. 6a). Bacterial biomass in Exp II grew during the incubation and varied between 9.8 and $29.6 \mu\text{mol C l}^{-1}$ at the end of a 2-month incubation period

Fig. 5 Redundancy analysis on the effects of catchment characteristics on the CDOM and FDOM parameters in river water during the late phases of autumn (a) (Exp I) and spring (b) (Exp II) high flow periods. Blue arrows indicate the environmental variables (shares of field, clay soil, and organic soil) and black arrows the response variables (a_{254} , a_{440} , $SUVA_{254}$, $S_{275-295}$, $S_{300-650}$, Peak C, and FIndex as initial values). Parameters a_{254} and a_{440} refer to $a_{CDOM(254)}$ and $a_{CDOM(440)}$, respectively

(Fig. 7a). Bacterial biomass grew in all the samples during the first month of incubation, but this growth slowed down during the second month, and decreased in samples 9 and 14. Heterotrophic flagellates were found in sample 9 in the 2-month sample, and their biomass was $1.0 \mu\text{mol C l}^{-1}$. This explains the biomass decrease in sample 9 (approx. $5 \mu\text{mol C l}^{-1}$), as flagellate growth efficiency is $\sim 20 \%$

Fig. 6 Growth in bacterial biomass (a) and respiration (b) in different upstream samples during the 3-month incubation period in Exp I. Dotted line $>56 \%$ forest and $<22 \%$ field; solid line $>22 \%$ field and $<56 \%$ forest; black symbol $>10 \%$ organic soil and $<10 \%$ clay soil; white symbol $<10 \%$ organic soil and $>10 \%$ clay soil. Catchment characteristics of the samples are presented in Table 1

(Straile 1997). No flagellates were found in sample 14, and the biomass decrease could have been caused by viruses. During the first month, biomass growth was fastest in samples where catchments had the biggest shares of forest and organic soil (Fig. 7a).

Bacterial respiration in Exp I varied between 21.5 and $77.2 \mu\text{mol C l}^{-1}$ over the 3-month incubation period (Fig. 6b). In Exp II, this variation was 50.8 – $113.0 \mu\text{mol C l}^{-1}$ over the 2-month incubation period (Fig. 7b). In both experiments, samples with catchments with the largest shares of organic soil had the largest respiration rates. In Exp I, respiration was lowest in samples with forest-dominated catchments and containing $<10 \%$ of organic soil (Fig. 6b). Similar to bacterial biomass increase, in agriculture-dominated catchments, the role of soil type was less pronounced. In Exp II, land use did not have as clear an effect on respiration as it had on bacterial biomass growth (Fig. 7b).

BGE in Exp I averaged $60 \pm 13 \%$ for the first two incubation weeks. The share of fields seemed to negatively

Fig. 7 Growth in bacterial biomass (a) and respiration (b) in different upstream samples during the 2-month incubation period in Exp II. Dotted line >50 % forest and <25 % field; solid line >25 % field and <50 % forest; black symbol >10 % organic soil and <10 % clay soil; white symbol <10 % organic soil and >10 % clay soil. Catchment characteristics of the samples are presented in Table 1

Fig. 8 Boxplot showing the upper and lower quartiles of bacterial growth efficiency in Exp I, grouped according to the share of field in their catchment. Average values are denoted with dots and the error bars indicate the range

correlate with BGE for the first two incubation weeks (Fig. 8), but the correlation was not significant ($R^2 = 0.53$, $p = 0.062$). In Exp II, respiration results for day 14 were lost, and thus, the BGE could not be calculated.

Degradation of DOC and DON

The estimated BCD in Exp I averaged $70 \pm 21 \mu\text{mol C l}^{-1}$ within the 3-month incubation period, accounting for $5 \pm 1 \%$ of the respective initial DOC pools. The decrease in DOC concentration averaged $73 \pm 27 \mu\text{mol C l}^{-1}$ ($5 \pm 1 \%$ of initial DOC pool), correlating with the BCD-based values ($R^2 = 0.60$) (Table 4). DON concentrations were measured only at the start and end of the incubation. The change in DON concentrations falls within the measurement uncertainty (4.8 %, Lignell et al. 2008).

At the end of Exp II, BCD averaged $90 \pm 25 \mu\text{mol C l}^{-1}$, which accounted for $7 \pm 2 \%$ of the initial DOC pools. The decrease in DOC concentration was slightly higher, averaging $103 \pm 41 \mu\text{mol C l}^{-1}$ ($9 \pm 4 \%$) (Table 5). An average $12 \pm 6 \mu\text{mol N l}^{-1}$ DON was degraded during the first month, which accounted for an average $45 \pm 27 \%$ of the total DON, but DON concentrations increased back to original concentrations during the second month (Fig. 9). After 1 month of incubation, the ammonium and nitrate concentrations did not differ from initial levels, but $7 \pm 10 \mu\text{mol}$ of the nitrate was used after the second month.

The RDA models testing the effect of the catchment characteristics on the bacterial responses in the bioassays were statistically significant in both experiments ($p \leq 0.05$) (Fig. 10). The first canonical axis (RDA1) in Exp I explained 69.7 % of the variation and was statistically significant ($p \leq 0.05$). The second axis (RDA2) only explained 10.0 % of the variation and was not significant. Both axes were significant in the Exp II model ($p \leq 0.05$), explaining 48.6 and 17.9 % of the variation, respectively. In both models, the share of organic soil correlated positively with bacterial respiration and biomass. The share of fields in Exp II correlated positively with the LDON %.

Changes in DOM quality

The humic-like fluorescence (peak C; Coble 1996) decreased in both experiments during the first weeks of incubation (Fig. 11). In Exp I, peak C began increasing during the latter half of the experiment, whereas it generally continued to decrease in Exp II until the end of incubation. SUVA_{254} , on the other hand, increased during the first days of the experiments, after which average SUVA_{254} values remained relatively stable (Fig. 11). The decrease in fluorescence peak C during the first weeks of the experiment appeared to be bigger in clay-dominated catchments (Fig. 12), but was not affected by land use (data not shown). During the first incubation month, the share of fields in Exp I enhanced the increase in the aromaticity of the DOM pool (SUVA_{254}) (Fig. 12). No correlation between soil type and SUVA_{254} was detected (data not shown).

Table 4 Labile DOC (LDOC) concentrations and the shares of LDOC of the total DOC (%) in upstream samples from different sites in Exp I. LDOC was measured from bacterial carbon demand (BCD) and decrease in DOC concentrations after 1 and 3 months. Catchment characteristics of the samples in Table 1

Site ID	LDOC from BCD				LDOC from DOC decrease			
	1 month		3 months		1 month		3 months	
	$\mu\text{mol l}^{-1}$	%	$\mu\text{mol l}^{-1}$	%	$\mu\text{mol l}^{-1}$	%	$\mu\text{mol l}^{-1}$	%
1	21.8	2.7	34.7	4.2	33.6	4.2	30.7	3.8
2	17.6	2.5	45.4	6.4	79.0	11.2	34.9	4.9
3	38.8	3.6	68.0	6.1	45.9	4.2	88.9	8.1
4	48.2	2.2	88.5	3.9	95.6	4.4	106.0	4.8
5	37.9	2.0	72.8	3.8	171.4	9.1	103.2	5.5
6	46.4	2.5	79.4	4.2	98.9	5.3	78.8	4.2
7	56.5	2.2	105.9	3.9	84.7	3.3	81.6	3.1

Table 5 Labile DOC (LDOC) and labile DON (LDON) concentrations, and their shares of the total DOC and DON pools (%), respectively, and the LDOC:LDON ratios in upstream samples from different sites in Exp II. LDOC was measured from bacterial carbon demand (BCD) and decrease in DOC concentrations after 1 and 2 months incubation. LDON was only detected after 1 month incubation. Catchment characteristics of the samples in Table 1

Site ID	LDOC from BCD				LDOC from DOC decrease				LDON		LDOC:LDON		LDOC:LDON	
	1 month		2 months		1 month		2 months		1 month		1 month (from BCD)		1 month (from DOC decrease)	
	$\mu\text{mol l}^{-1}$	%	$\mu\text{mol l}^{-1}$	%	$\mu\text{mol l}^{-1}$	%	$\mu\text{mol l}^{-1}$	%	$\mu\text{mol l}^{-1}$	%				
1	52.7	7.0	68.9	9.2	92.6	12.31	109.6	14.6	3.3	17.4	16		28	
2	47.9	7.7	65.3	10.5	21.0	3.4	95.1	15.3	4.3	23.3	11		5	
3	42.6	5.7	67.5	9.1	93.0	12.5	65.9	8.9	11.2	67.8	4		8	
8	55.4	6.3	92.2	10.5	42.3	4.8	58.5	6.6	12.0	48.3	5		4	
9	95.5	4.1	130.7	5.6	162.1	7.0	199.2	8.6	8.2	18.3	12		20	
10	63.2	3.9	92.6	5.7	34.0	2.1	106.9	6.5	10.7	29.4	6		3	
4	78.4	5.0	97.2	6.2	86.3	5.5	125.8	8.1	8.1	23.2	10		11	
5	56.1	4.8	79.9	6.8	94.7	8.0	125.3	10.6	14.0	88.7	4		7	
11	81.8	4.4	119.5	6.5	45.2	2.4	126.7	6.9	17.1	46.1	5		3	
12	68.2	1.2	117.9	2.1	3.9	0.1	41.5	0.8	25.9	19.7	3		0	
13	39.6	4.4	60.0	6.7	72.6	8.2	97.5	11.0	15.9	61.3	2		5	
14	58.8	6.1	74.1	7.6	75.8	7.8	86.2	8.9	15.6	91.8	4		5	

DISCUSSION

Dependence of DOC and DON concentrations and river water quality on the catchment characteristics

DOC, DON, and DOP concentrations in the river water varied severalfold between the tributaries of the Vantaanjoki river, correlating significantly with the catchment characteristics. The share of organic soil in the catchment was the strongest predictor of DOM concentrations in the river water. A similar strong correlation was present between $a_{(\text{CDOM}254)}$ and $a_{(\text{CDOM}440)}$ values and the share of organic soil. The potential for DOM export was clearly

higher in soils of high organic matter content. In addition, DOM sorption is less effective in organic soils than mineral soils because of the lower amount of sorption sites (Kaiser et al. 1996; McDowell 1998). In accordance with our results, previous research has shown that catchments with a high share of peatlands and wetlands (known to have high soil organic matter content) are associated with elevated DOC concentrations in river water (Laudon et al. 2004; Kortelainen et al. 2006).

In our study, land use did not significantly affect DOC concentrations and DOM quality (CDOM and FDOM parameters as proxies). Similarly in south-central Ontario, the DOC concentrations in the river water were not different from agricultural and forested catchments (Wilson

Fig. 9 Changes in dissolved nitrogen during the 2 months of incubation in Exp II. Catchment characteristics of the sampling sites in Table 1

and Xenopoulos 2008). In contrast, land use was found to dominate over soil type in determining DOC concentrations in Central Europe where DOC concentrations from forest-dominated catchments were 5–8 times lower than those from wetland- and agriculture-dominated catchments (Graeber et al. 2012), being over 10-fold lower than the concentrations in Vantaanjoki river. Thus, in here, the dominating role of organic soil may have masked possible effects of land use on DOC concentrations or DOM quality. Mattsson et al. (2015) reported a positive correlation between TOC concentrations in the river mouth and the proportion of agricultural land in the catchment, except for March and April. In our study, the water samples for Exp II were taken in May 2013 after a snowy winter, suggesting that spring runoff may also have dissipated the possible land use-induced differences. The dominance of organic soil over the effects of land use highlights the importance of taking the soil type into account when analyzing the land use-induced changes in water quality. As fertile soil is likely taken into cultivation, comparisons made between forests and agricultural land almost always include the effect of soil type, and thus, the results should be interpreted with caution. To address the role of land use on the DOM load, smaller and more homogenous areas regarding soil type should be studied.

The share of fields and organic soil increased DON concentrations significantly in the water samples taken during autumn. Crop residues are the main sources of DON in agricultural land in addition to soil organic matter (Van Kessel et al. 2009). Nitrogen fertilization, reported to increase DON concentrations in soil leachates (Huang et al. 2011), increases the biomass production affecting the amount of residues incorporated in soil in the autumn.

Further, soil microbial activity may be stimulated as the autumn rains wet the soil (Mattsson et al. 2015). Thus, the higher DON concentrations in autumn detected in rivers from field-dominated catchments arise from the higher input of nitrogen and following the production of N-rich biomass, which is degraded in agricultural land in the autumn.

The DOC:DON ratios varied between 23 and 75, having a similar range as previously found from river mouths in the northern Baltic Sea area (21–60, Asmala et al. 2013; Stepanauskas et al. 2002). High DOC:DON ratio has been linked to humic-like, aromatic, and refractory DOM (McKnight et al. 2001). Lower DOC:DON ratios have been measured in the southern Baltic Sea area, where DOM is more autochthonous, fresh, and labile (Stepanauskas et al. 2002). In autumn, the DOC:DON ratios were inversely correlated with the share of fields. Lower DOC:DON ratios have also previously been reported in river water originating from agriculture-dominated catchments (Seitzinger et al. 2002; Mattsson et al. 2005; Asmala et al. 2013; Mattsson et al. 2015).

DON accounted for a major share (23–80 %, average 50 %) of the total dissolved N pool in the river water. DON shares of 4–41 % have been reported in the Horsens Fjord catchment in Denmark, where land use is dominated by agriculture, with lowest values (4–10 %) at sites most dominated by agriculture (Stedmon et al. 2006). Nitrogen fertilization increases the loss on inorganic nitrogen from fields through increased biomass production and following organic matter mineralization (Kirchmann et al. 2002), thus

Fig. 11 Boxplots showing changes in fluorescence peak C and SUVA_{254} in Exp I and II. Start of the experiment = 100 %. Whiskers indicate the minimum and maximum observations, lower and upper ends of boxes indicate lower and upper quartiles, and thick horizontal line is the mean value of the dataset. Circles denote outliers in the data. Notice the different axis values in Exp I and II

and del Giorgio 2007). Estimating bacterial production from the increase in bacterial biomass is likely to lead to underestimation of BGE when incubation time significantly exceeds bacterial turnover times. However, the BGE values measured in this study were at the higher end of the range previously obtained for bacterial communities in the Baltic Sea (5–60 %, reviewed in Hoikkala et al. 2015). In addition, using either increase in bacterial biomass or ^3H -thymidine and ^{14}C -leucine incorporation in estimating bacterial production led to similar BGE values in a long-term study by Asmala et al. (2013) conducted in the river estuaries in Finland. This indicates that in experiments where relatively small bacterial inoculum is added to energy and nutrient-rich samples that are free of grazers, estimating bacterial biomass production from increase in bacterial biomass can produce reliable BGE values even in longer (weeks-months) bioassays.

The share of fields in the catchment appeared to decrease BGE, suggesting that the nutritional quality of

TDOM from agricultural land was lower than that from forested areas. The low DOC:DON ratios, observed at sites with high field shares in the catchment, did thus not predict high BGE values. The same was also observed in a temperate salt marsh system (Apple and del Giorgio 2007). In the boreal region of Sweden, forest dominance in the catchment significantly increases BGE compared to mire-dominated catchments, which was attributed to the high nutritional quality of relatively young detrital matter drained from the surface soil (Berggren et al. 2007). Unlike the forests, fields under cereal production are harvested yearly, and a large share of the fresh biomass is removed from the site. Furthermore, in cultivated fields, the preferable route of excess water from the surface soil is to leach through the soil to the tile-drainage system, to prevent surface runoff. This enables sorption and the further microbial processing of DOM. These factors may contribute to the negative effect of agricultural land on BGE in our study. However, results showing that agricultural

Fig. 12 Change in humic-like fluorescence peak C and SUVA₂₅₄ after 14 days and 1 month incubation in Exp I and II, respectively. Data were categorized by soil type and land use as in Fig. 6 for Exp I and Fig. 7 for Exp II

impact in the catchment may lead to high BGE have also been published (Apple and del Giorgio 2007; Asmala et al. 2013). Despite significant correlations between the share of organic soil and the concentration and quality of DOM, no strong correlations occurred between soil type and BGE.

The share of LDON in total DON (LDON %) in the water samples taken in the spring (Exp II) correlated positively with the share of fields in the catchment. Similarly, Asmala et al. (2013) found that DON originating in field-dominated catchments was more labile than DON originating in peatland- and forest-dominated catchments. In Exp II, DON was the most preferable source of nitrogen for the heterotrophic bacteria during the most intensive growth, despite high concentrations of inorganic N. An average 45 % of DON was utilized during the first incubation month. The shares of LDON are high in summer in most rivers draining into the Baltic Sea, which was suggested to occur due to autochthonous production in the rivers (Stepanauskas et al. 2002). However, our samples were taken from the upstream and during high flow when

rivers in Finland transport terrestrial DOM and do not have any major role in producing microbial DOM (Mattsson et al. 2015). This is supported by our low fluorescence index values indicative of terrestrially derived substances (McKnight et al. 2001). DON accounted for approximately 1/3 of the bioavailable N in spring, when most of the discharge occurs, indicating that a significant share of annual riverine loads of bioavailable N can be in the form of DON. Moreover, due to the high DON content of the most labile DOM (utilized within a month), heterotrophic bacteria did not utilize inorganic forms. DOM utilized during the first incubation month had on average C:N ratios of 8.3, indicating that it contained extra N compared to bacterial demand, as bacterial C:N ratios range quite strictly between 4 and 5 (Goldman et al. 1987) and the respiration losses averaged ~80 % (leading to bacterial demand of C and N in ratio 20–25). Occurring in nature, this would benefit phytoplankton growth, as bacteria utilizing N-rich TDOM would not markedly compete with phytoplankton for the riverine inorganic nutrient loads.

During the second month of the incubation, DON concentrations increased back to nearly initial levels, coinciding with the uptake of NO_3^- and NO_2^- . The heterotrophic bacteria might have begun releasing DON after the first month, possibly reflecting the production of ectoenzymes or viral lysis. A similar increase in DON concentrations during bacterial enclosure experiments has been previously observed with samples from fresh and coastal waters (e.g., Kawasaki and Benner 2006; Lignell et al. 2008). Due to simultaneous degradation and production of DON, estimating LDON is challenging in incubation experiments. Thus, the LDON values obtained are likely to be underestimates, and hence, the significance of DON as a N source for heterotrophic bacteria in coastal shores may even be higher.

Changes in DOM quality by bacterial degradation

DOM quality changed during the incubations, indicated by the increasing aromaticity of the DOM pool (Fig. 11). The decrease in relative peak C indicates that a part of the humic-like fractions of the DOM pool can be utilized as a substrate by the bacterial community (Fig. 12). Further, the observed increase in SUVA_{254} values indicates that the aromatic DOM pool increased in relation to the whole DOM pool (Weishaar et al. 2003; Berggren et al. 2009; Asmala et al. 2013).

Kinetics of the humic-like fluorescence (Peak C) and the proxy for aromaticity, SUVA_{254} during the degradation experiments, reveal that the degradation of terrestrial DOM is a highly dynamic process, where the balance of production and consumption of different DOM compounds is constantly changing (Fig. 11). This may be the result of the bioavailability continuum of the DOM pool, where compounds with the highest energetic or catabolic value are utilized first (Vähätalo et al. 2010). Bacteria simultaneously excrete DOM as extracellular enzymes or metabolic by-products with similar properties as terrestrial DOM (Romera-Castillo et al. 2011; Jørgensen et al. 2014), which was indicated by the increase in humic-like fluorescence during the latter half of Exp I. Absorbance and fluorescence results further suggest that both land use and soil type can affect DOM quality (Fig. 12). The differences in the results between these two experiments encourage future studies on seasonal variation in TDOM degradation.

CONCLUSIONS

Our results revealed that in the catchments, which are heterogeneous in terms of land use and soil type, the share of organic soil is the most important predictor of the concentration and quality of riverine DOM. A high share

of organic soil increases DOC, DON, and DOP concentrations in river water and the humic-like, aromatic properties of the DOM pool. In the boreal zone where the organic soils are abundant, the possible effects of land use changes in mineral soils will be masked by the high relative importance of organic soil in determining the DOC concentrations in the catchment level. Despite the twofold differences in the share of bioavailable DOC, it was independent of land use and soil type. Thus, other factors, such as vegetation and hydrologic flow paths, may contribute to the biological availability of DOC and need to be studied further. DON was the preferred N source for coastal bacteria during the spring high flow period, and most labile TDOM (utilized within 1 month) provided coastal bacteria, a substrate with lower C:N ratios compared to the bacterial demand. It thus appears that during the spring flood, when most of the annual riverine discharge occurs, utilization of TDOM by coastal bacteria does not necessarily increase their demand for inorganic N or their competition for it with phytoplankton in the northern Baltic Sea. Altogether, labile terrestrial DON appears to be an important N substrate in the receiving coastal area, accounting for approximately one-third of the bioavailable dissolved N in upstream water. Agricultural land may increase both the concentrations of terrestrial DON in river water and its biological availability for heterotrophic bacteria.

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