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Water quality and the biodegradability of dissolved organic carbon in drained boreal peatland under different forest harvesting intensities

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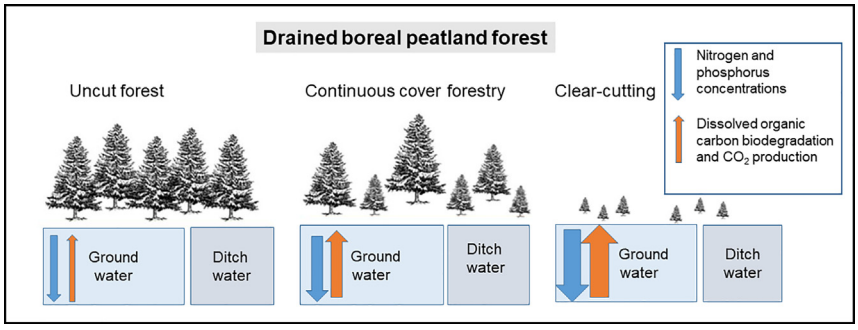
HIGHLIGHTS

- Forest harvesting intensity affects water quality and aquatic CO_2 emissions.
- Biodegradability of dissolved organic carbon increases with harvesting intensity.
- Continuous cover forestry can cause less environmental drawbacks than clear-cutting.

GRAPHICAL ABSTRACT



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ABSTRACT

Boreal peatlands are major sources of nitrogen (N), phosphorus (P) and dissolved organic carbon (DOC) to downstream aquatic ecosystems, and forest harvesting generally further increases the loading of DOC and nutrients. Continuous cover forestry (CCF) is proposed to be an environmentally more sustainable management option for peatland forests than conventional even-aged clear-cutting. However, the impacts of CCF on water quality, the biodegradability of DOC and consequent CO_2 emissions from inland waters are poorly known. We studied the concentrations of N, P and DOC, the quality of DOC, and the mineralization of DOC to CO_2 in ground water and ditch water in clear-cut, partially harvested, i.e. CCF, and uncut drained forests in Finland. Groundwater total N, NH_4-N and PO_4-P concentrations were significantly lower in CCF and uncut forest than in the clear-cut forest. Groundwater DOC concentrations were often highest in the clear-cut forest, where the water table was closer to the soil surface. Ditch water DOC and N concentrations were lowest next to the clear-cut area. DOC aromaticity in ground water was higher in the uncut forest than in the clear-cut and CCF, whereas ditch water aromaticity did not differ between the treatments. The biodegradation of DOC was studied by incubating water (at 15 °C for 24 h) 1, 3, 7 and 21 days after sampling. The results indicated that the majority of the CO_2 production took place during the first three days, and CO_2 fluxes were considerably higher from the ditch water than from the groundwater. The CO_2 emissions were lower in summer than in the other seasons. Ditch water and groundwater CO_2 production were generally significantly higher in the clear-cut than in the uncut forest. The results suggest

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that CCF can decrease the nutrient concentrations as well as CO_2 emissions from inland waters compared to conventional clear-cutting.

1. Introduction

Peatlands cover 15% of boreal regions and contain one third of the world's soil carbon (C) stock (Settele et al., 2014). Peatlands are also a major source of dissolved organic matter (DOM) entering streams, lakes and rivers in boreal catchments (Mattsson et al., 2005; Asmala et al., 2019). The annual organic C export loads from drained peatlands are have been reported to range from 80 kg ha^{-1} to 160 kg ha^{-1} in Finland (Finér et al., 2021). DOM consists of various sizes of organic molecules including for example humic, fulvic, amino and fatty acids and organic nutrients (Schumacher et al., 2006). Total or dissolved organic C (TOC or DOC, respectively) concentrations are generally used as a proxy for DOM. DOM affects transparency, temperature, biogeochemical processes, food webs and ecosystem productivity of surface waters (Solomon et al., 2015; Kritzberg et al., 2020). In addition, DOM may exacerbate eutrophication and hypoxia in aquatic ecosystems, and cause problems in drinking water treatment processes (Ledesma et al., 2012; Kritzberg et al., 2020). This lateral C flux from terrestrial to aquatic ecosystems is an important component of the global C cycle (Drake et al., 2018; Tranvik et al., 2018; Gómez-Gener et al., 2021), and DOC mineralization to CO_2 in inland waters markedly contributes to C emissions to the atmosphere (Raymond et al., 2013; Marx et al., 2017; DelSontro et al., 2018; Karlsson et al., 2021). In boreal catchments, up to 10-30% of the net C uptake is transported in DOC out of the forests (Juutinen et al., 2013; Wallin et al., 2013; Drake et al., 2018).

Increased DOC concentrations and brownification have been observed in boreal water bodies during the past decades and it has been attributed to climate change and decreased acid deposition (Kritzberg et al., 2020). Furthermore, especially in northern Europe, large-scale drainage of peatlands and intensive forest management have a significant impact on water quality (Finér et al., 2021). In the Baltic Sea drainage basin, about half of the total 19.5 Mha peatland area has been drained for forestry (Finér et al., 2021). Drained peatlands are long-term hot spots for the export of nitrogen (N), phosphorus (P) and DOC to water courses (Finér et al., 2021), and clear-cutting of peatland forests can further increase C and nutrient leaching (Schelker et al., 2013; Nieminen et al., 2017).

Continuous cover forestry (CCF) is thought to be an environmentally more sustainable management option for peatland forests than conventional even-aged clear-cutting (Nieminen et al., 2018). CCF has been suggested to cause less nutrient export to watercourses than clear-cutting because it reduces the need for ditch network maintenance and soil preparation, diminishes the amount of logging residues and maintains higher nutrient uptake and evapotranspiration (Nieminen et al., 2018). Water table (WT) in a partially harvested forest is lower than in clear-cut forest but higher than in mature uncut forest (Leppä et al., 2020). Thus, partial harvesting may decrease nutrient leaching caused by redox reactions compared to clear-cutting, whereas oxidation and mineralization of deep peat layers can be smaller than in uncut forest because of higher WT (Nieminen et al., 2018). So far, little is known about the impacts of CCF on water quality, or in general, the effects of forest harvesting on the quality and biodegradability of DOC. Forest harvesting alters soil temperature, WT, water transportation routes, runoff, soil microbial communities, vegetation and the amount of root exudates (Schelker et al., 2013; Leppä et al., 2020; Kritzberg et al., 2020), which in turn may change the release and transportation of DOC and nutrients (Kreutzweiser et al., 2008; Schelker et al., 2013; Nieminen et al., 2015, 2017), as well as DOC quality (Saari et al., 2009; Hribljan et al., 2014) and mineralization to CO_2 in water courses (Kawahigashi et al., 2004; Kazmiruk et al., 2021). Studies on the effects of forest harvesting on DOC quality are scarce and the results are variable. In some studies, DOC quality (aromaticity, molecular weight) in stream water has been significantly different between harvested and uncut forest catchments (Yamashita et al., 2011; Lee and Lajtha, 2016), whereas in other studies no differences have been observed (Cawley et al., 2014; Thieme et al., 2019). Klaus et al. (2018), in turn, found that CO_2 emissions from boreal streams and headwater lakes remained unchanged after forest harvesting.

DOC biodegradation is influenced by its quality, especially the structure of C compounds, which range from a labile, low molecular weight, easily biodegradable fraction to a larger, recalcitrant fraction resistant to biodegradation (Kalbitz et al., 2003; Kiikkilä et al., 2006; Mann et al., 2012; Pinsonneault et al., 2016). Vegetation affects DOC quality, which in *Sphagnum*-dominated peatlands is generally of low biodegradability compared to areas dominated by vascular plants (Tfaily et al., 2013). Clear-cutting may stimulate DOC biodegradation by increasing nutrient availability and altering vegetation which can enrich DOC with low molecular weight compounds (Pinsonneault et al., 2016; Robroek et al., 2016; Mastný et al., 2018). The half-life of the labile DOC is few days, while the half-life of the recalcitrant fraction ranges from months to years (Kalbitz et al., 2003). Therefore, the distribution of DOC between the labile and recalcitrant fractions is a key factor determining in which phase of the transportation path extending from groundwater to ditchwater and further to water course, the DOC disintegrates and releases the CO_2 emission. The quality of DOC can be investigated e.g. with UV–Vis spectroscopy at specific wavelengths. The specific ultraviolet absorbance at 254 nm normalized for DOC concentrations ($SUVA_{254}$) is positively correlated with complex macromolecular DOC rich in aromatics (Peacock et al., 2014). In contrast, the ratio of absorbance at 250 and 365 nm (E2:E3) is inversely related to DOC aromaticity and molecular weight (Peuravuori and Pihlaja, 1997).

The objectives of this study were: 1) to compare the biodegradability of DOC in groundwater and ditch water collected from clear-cut forest, CCF management (partially harvested forest) and uncut forest, and 2) to study experimentally the relationship between DOC concentration, DOC quality and CO_2 production, and 3) to investigate the effect of different forest harvesting intensity on DOC, N and P concentrations in ground water and ditch water. Water quality and the biodegradability of DOC were studied in a boreal peatland in Finland throughout a year to get an understanding of the seasonal variations. We hypothesize that clear-cutting increases DOC and nutrient concentrations and DOC biodegradability compared to CCF and uncut treatment.

2. Material and methods

2.1. Setting area and water sampling

Paroninkorpi study area (Fig. 1) locates in Janakkala in southern Finland (61.01°N, 24.75°E). The long-term (1990-2019) mean annual temperature for the area is 4.7 °C and the amount of precipitation is 638 mm. The effective temperature sum is 1460 degree days (sum of daily mean temperature exceeding +5 °C) and the average length of the growing season is 175-185 days. The site is a drained, herb-rich type (Laine, 1989) Norway spruce (*Picea abies* (L.) Karst.) dominated forest. The preharvest basal area in the study area varied from 22 to 31 m^2 ha^{-1}, of which 98% was Norway spruce and 2% birch (*Betula pubescens* Ehrh.). The dominant height of the trees was 21.15 m. The *Carex* peat layer is >1.5 m thick. The main ditches were dug in the

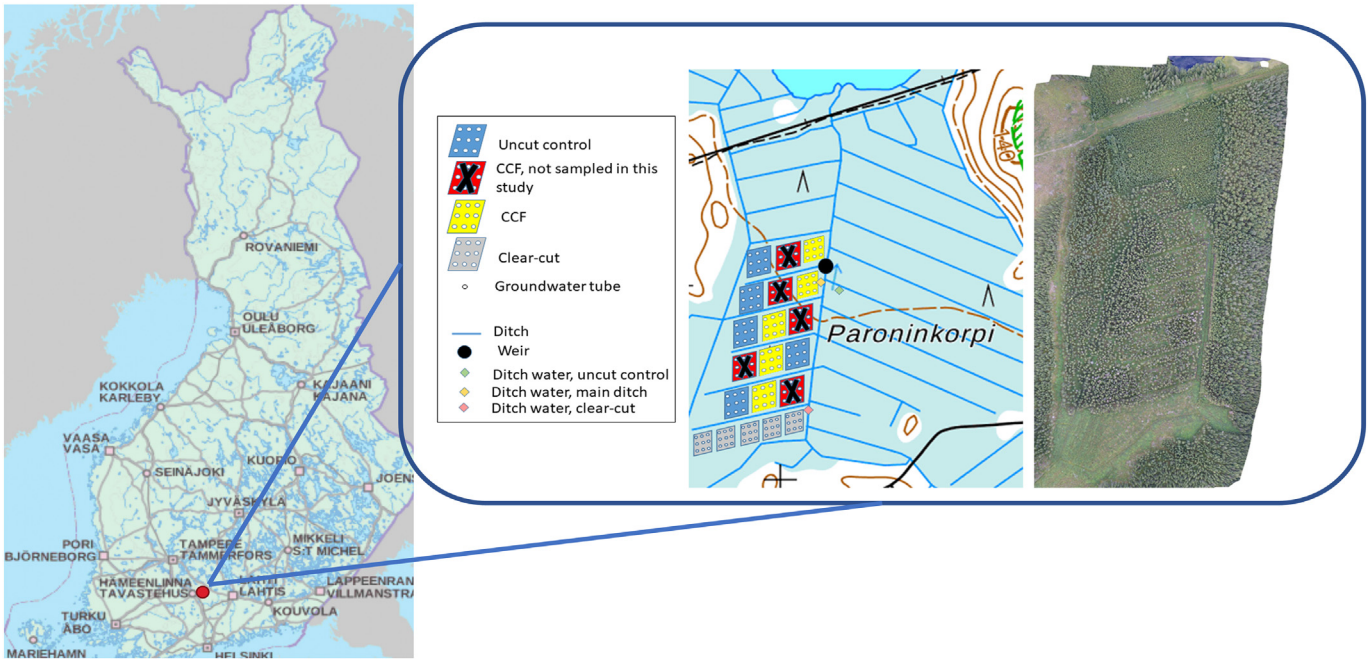

Fig. 1. Location of the study site in Finland. Schematic presentation and aerial photograph of the experimental setup in the study area. Ground water samples were collected from the uncut forest, continuous cover forest management (CCF, the basal area 12 m^2 ha^{-1}) and clear-cut area. The ditch water samples were collected from the main ditch flowing through the study area, from the ditch next to the clear-cut area and from a ditch collecting water from an uncut forest. The aerial photograph is taken by John Loehr.

1940s and ditch network was complemented in the beginning of the 1960s. Ditches are spaced at 65-70 m intervals and they are 0.6–0.7 m deep. The size of the catchment area is 0.035 km^2.

The study site had three treatments: 1) clear-cutting, 2) uneven-aged, continuous cover forest management (CCF), where the basal area of the stand was 12 m^2 ha^{-1} and 3) uncut forest, where the basal area of the stand was 25 m^2 ha^{-1} (Fig. 1). Harvesting was carried out in February 2017, two years before the start of our measurements. Continuous cover management was carried out in such a way that the upper half of the stand diameter at breast height distribution was removed, retaining the suppressed and understory trees and some of the largest trees. In August 2020, the vegetation in the clear-cut area consisted mainly of birch (*Betula* sp.; 54% of dry biomass), grasses (14%), mosses (12%) and raspberry (*Rubus idaeus* L.; 10%), whereas CCF was dominated by mosses (55%) and dwarf shrubs (38%), and the uncut controls by mosses (78%) and grasses (10%). There were five replicate plots (1600 m^2) in each treatment, thus 15 study plots in total (Fig. 1).

Each plot had 9 groundwater tubes (Fig. 1) that were installed in a form of a regular grid (3 × 3). The tubes were perforated (3 mm holes) from the bottom to a height about 10 cm below the peat surface and were installed down to 1 m depth. WT was monitored manually, and 100 mL of ground water was collected from each tube with a hose and a syringe in June, July, August, September, October and November in 2019 and February, April and May in 2020. The ditch water samples (2000 mL) were collected from three locations: i) from the main ditch flowing through the study area, ii) from the ditch next to the clear-cut area and iii) from a ditch collecting water from an uncut control site next to the study site (Fig. 1). Water samples were collected in June, July, August, September, October and November in 2019 and February, April and May in 2020. In August 2019, the ditch next to the clear-cut area had dried up and it was not possible to collect water.

2.2. Laboratory analyses and incubation experiment

Water samples were filtered through glass fiber filters with diameter of 47 mm and pore size 0.7 μm (Whatman Inc., USA). Dissolved organic carbon (DOC) and total nitrogen (TN) concentrations were determined with Multi N/C® 2100 (Analytik Jena AG, Jena, Germany) or with TOC-VCPH and TNM-1 (Shimadzu, Kyoto, Japan). The concentrations of nitrate (NO_3^-) and nitrite (NO_2^-) nitrogen (hereafter referred to as NO_3^--N) and ammonium nitrogen (NH_4^+-N) were determined colorimetrically applying the methods by Miranda et al. (2001) and Fawcett and Scott (1960), respectively. DOC quality (aromaticity) was studied by determining specific ultraviolet absorbance (SUVA) at 254 nm ($SUVA_{254}$) and E2:E3-ratio at 250 and 365 nm with a Shimadzu UV-1700 instrument (Suzhou Instruments Manufacturing Co., Ltd., China).

The biodegradation of DOC to CO_2 was studied in the incubation experiment. For the incubations, 20 mL aliquots of the filtered ground water were poured into 100 mL glass bottles, and 200 mL of the filtered ditch water were poured into 500 mL glass bottles. The experiments consisted of incubation cycles that were repeated 1, 3, 7 and 21 days after the onset of the experiment. Incubations were done in three replicates for each of the 15 plots. In the beginning of each incubation cycle, bottles were capped outdoors with septa and aluminum screw caps, and 20 mL and 40 mL of outdoor air was injected into the groundwater and ditch water bottles, respectively. The bottles were shaken in an orbital shaker (3 min, 80–100 rpm), after which 25 mL gas samples were taken from the headspace of each bottle with a syringe and a needle and injected into a pre-evacuated 12 mL Exetainer vials (Labco, UK). Then the bottles were placed into a 15 °C incubator for 24 h, after which the bottles were shaken again and sampled for gases similarly to the beginning of the incubation cycle. At other times, the bottles without caps were sealed with perforated aluminum foil and stored in the incubator at +15 °C. The gas samples were analyzed with an Agilent Gas Chromatograph (GC 7890A Agilent Technologies, USA). The analyses were performed with a flame ionization detector (FID) using helium as a carrier gas, and synthetic air (450 mL min^{-1}) and hydrogen (40 mL min^{-1}) as flame gases. In addition, nitrogen gas (5 mL min^{-1}) was used as the make-up gas for the FID standard. The carbon dioxide (CO_2) concentrations were measured using a 4-point calibration curve determined with 433, 750, 1067 and 1500 ppm standard gas concentrations (Oy AGA Ab, Espoo, Finland). The analyser's oven temperature was set to 60 °C with the detector temperature being 300 °C.

2.3. Calculations and statistical analyses

The solubility of CO_2 in water ($K_H(T)$) as mol kg^{-1} bar^{-1} was calculated according to the Henry's law as follows:

$$K_H(T) = K_H^{\circ}\, e^{[C \cdot (\frac{1}{T} - \frac{1}{298.15})]} \quad (1)$$

where K_H° is Henry's law constant (0.034 mol kg^{-1} bar^{-1}) for solubility for CO_2 in water at 298.15 K (mol kg^{-1} bar^{-1}), C is temperature dependence constant (2400) and T is water temperature (K) in bottles.

The amount of CO_2 dissolved in water (CO_{2W} mol L^{-1}) was calculated as follows:

$$CO_{2W} = \left(K_H(T) \cdot 10^{-5}\right) \cdot \left(PCO_2 \cdot 10^{-6}\right) \cdot P_{atm} \cdot V \quad (2)$$

where, $K_H(T)$ is the solubility of CO_2 in water converted to mol L^{-1} Pa^{-1}, PCO_2 is the measured CO_2 concentration as ppm converted to percentage, P_{atm} is the gas partial pressure under 1 atm (1.0135×10^5) above the boundary of a solution, and V is the water volume (L) in the bottle.

The amount of CO_2 released in the air space of the bottle (CO_{2A} mol L^{-1}) was calculated based on the ideal gas law as follows:

$$CO_{2A} = \frac{0.001 \cdot P_{atm} \cdot \left(PCO_2 \cdot 10^{-6}\right) \cdot V}{R \cdot T} \quad (3)$$

where 0.001 is the coefficient for converting gas volume from m^3 in to L, P_{atm} is the partial pressure of the CO_2 under 1 atm (1.0135×10^5), PCO_2 is the measured CO_2 concentration as ppm converted to percentage ($PCO_2 \times 10^{-6}$), V is the air volume (L) in the bottle, R is the universal gas constant (8.3145 J mol^{-1} K^{-1}) and T is the temperature (K).

The CO_2 production rate (mol L^{-1} day^{-1}) in the bottle during these 24 h incubations is the combination of CO_2 dissolved in water and released in the air:

$$CO_{2=CO_{2W}+CO_{2A}} \quad (4)$$

CO_2 production per DOC amount was calculated by dividing the CO_2-C emitted per day by the DOC amount in the bottle. By assuming first order decay the CO_2-C production per DOC amount corresponds to decay rate (k day^{-1}), which can be converted to half-life as follows: ln (2)/k (unit days).

Analysis of variance (ANOVA) was used to explore the differences in DOC and nutrient (TN, NO_3^--N, NH_4^+-N and PO_4-P) concentrations, WT level, and DOC quality parameters ($SUVA_{254}$, E2:E3-ratio) and the production of CO_2 in the groundwater of the clear-cut, CFF, and control forest as well as in the ditch water (main ditch, clear-cut, control). ANOVA was performed in conjunction with Tukey's test or Games-Howell post hoc analysis. Levene's test was used for assessing the homogeneity of variances. The significance level (p) for the statistical tests was set at 0.05. Monthly-wise statistical comparisons in ditch water quality between the treatments could not be done because only one water sample was taken from the ditch in each sampling occasion. Differences in ditch water quality between the treatments were studied by combining the measurements of different seasons in the statistical analyses. The statistical analyses were done with IBM SPSS Statistics software, version 26 (SPSS Inc. Chicago, IL, USA).

3. Results

3.1. DOC, N and P concentrations and WT

The DOC concentrations in the groundwater varied from 45 to 105 mg L^{-1} (Fig. 2a). When the treatments were compared, the highest

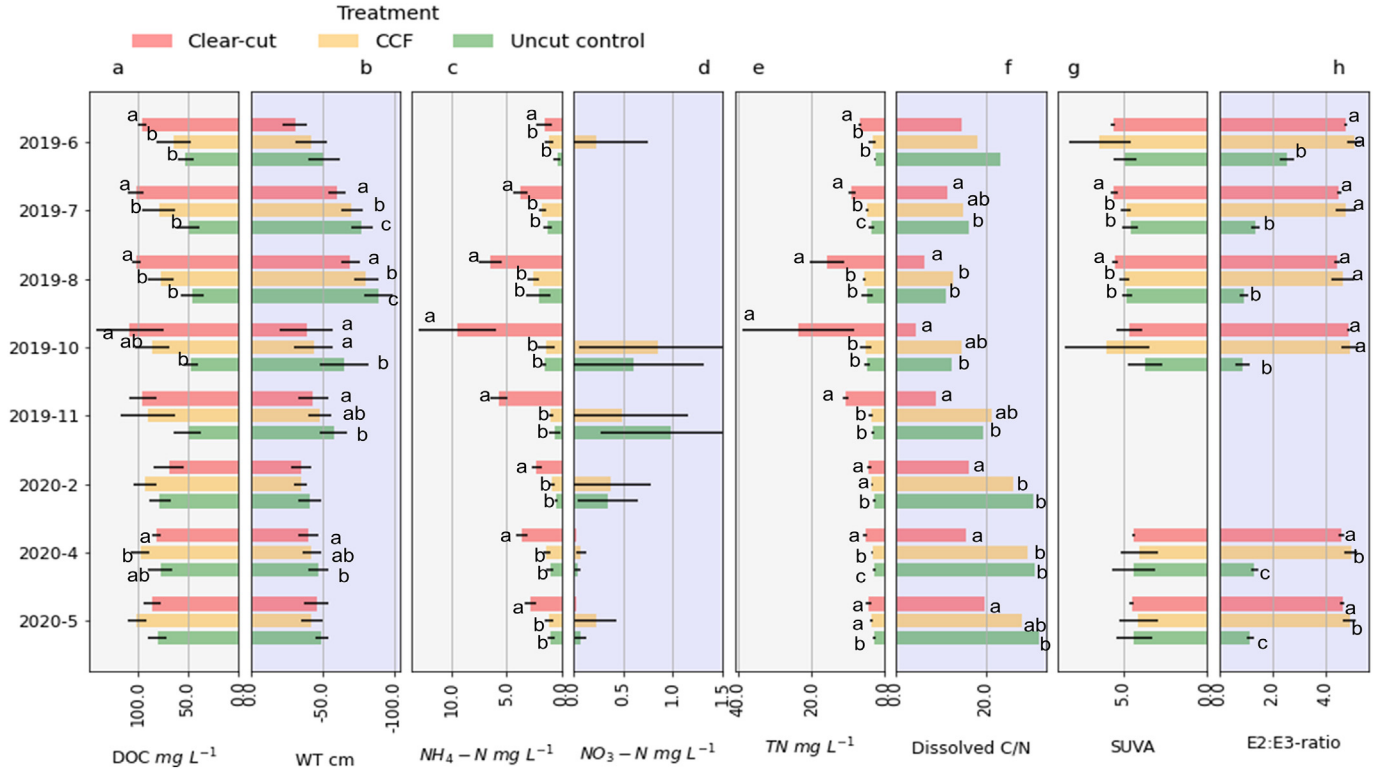

Fig. 2. (a) Dissolved organic carbon concentration, (b) water table, (c) ammonium, (d) nitrate, (e) total nitrogen concentrations, (f) DOC to total nitrogen ratio, (g) specific ultraviolet absorbance (SUVA) at 254 nm, and (h) E2:E3-ratio in ground water during the monitoring period extending from June 2019 to May 2020. Different letters (a-c) indicate statistically significant ($p < 0.05$) differences among treatments.

DOC concentrations were found in the groundwater of the clear-cuts in June-August 2019 ($p < 0.05$). However, this pattern changed, and during the following winter and spring the DOC concentrations did not differ significantly between the clear-cut and control sites (Fig. 2a). The groundwater DOC concentrations followed the WT, which varied from 31 to 89 cm (positive down), and was in general lowest in the uncut control plots (Fig. 2b).

The groundwater NH_4-N concentrations were always highest, i.e. between 1.5 and 9.4 mg L^{-1}, in the clear-cut ($p < 0.05$), whereas the NH_4-N in the CCFs and uncut controls did not differ from each other (0.9-2.5 and 0.4-2.0 mg L^{-1}, respectively; Fig. 2c). Groundwater NO_3-N was low, i.e. below 1 mg L^{-1}, and did not differ between the treatments, but the dissolved TN followed the pattern of NH_4-N being in general highest (4.2-23.8 mg L^{-1}) in the groundwater of the clear-cut area (Fig. 2d). The C:N ratios were lower in the clear-cuts than in CCF or control forests (Fig. 2f). PO_4-P was analyzed only in April and May 2020, and was significantly higher in the clear-cut (0.59 mg L^{-1}) than in CCF (0.21 mg L^{-1}) and control (0.05 mg L^{-1}) plots in April, and higher in clear-cut (0.42 mg L^{-1}) than in control (0.04 mg L^{-1}) in May.

Ditch water DOC concentrations were lowest next to the clear-cut area (Fig. 3a, $p < 0.05$), whereas the DOC concentrations did not differ between the main ditch and the uncut control. The dissolved TN was significantly higher ($p < 0.05$) in the main ditch than next to the clear-cut area or in the uncut control (Fig. 3d), but the NH_4-N, NO_3-N and PO_4-P concentrations or the C:N ratios did not differ between treatments in the ditches (Fig. 3b, c, e).

3.2. DOC quality

The $SUVA_{254}$ concentrations (L mg^{-1} m^{-1}) were relatively high (3.5-5.5) and similar in ground and ditch water indicating high relative content of macromolecular compounds rich in aromatics in both environments. Groundwater $SUVA_{254}$ differed between the treatments only in July and August (Fig. 2g), but the E2:E3-ratios were clearly lowest in the uncut controls throughout the study (Fig. 2h; $p < 0.05$). The low E2:E3-ratios indicate higher DOC aromaticity in the uncut forests than in the clear-cut or CCF. However, similar results were not obtained from ditch water, where neither $SUVA_{254}$ nor E2:E3 -ratio differed between the sampling sites (Fig. 3f, g).

3.3. CO_2 production

Groundwater incubations under constant temperature showed that the majority of the CO_2 production takes place during the first three days (Fig. 4). There were clear seasonal differences in CO_2 production. Outside the growing season, the initial CO_2 flux during the incubation was higher and ceased earlier than in the summer (Fig. 4). In June and July, the CO_2 production in the groundwater was low, only from 10 to 60 μg L^{-1} day^{-1}, whereas in autumn and winter months CO_2 was produced at a rate of 100-120 μg L^{-1} day^{-1} (Fig. 4a, c, e). The highest CO_2 flux in groundwater, up to 350 μg L^{-1} day^{-1}, was observed in the incubations in May.

There were statistically significant differences in the CO_2 production in the groundwater between the treatments (Fig. 4). CO_2 production per groundwater volume (μg L^{-1} day^{-1}) was generally significantly higher in the clear-cut than in the uncut forest and/or CCF (Fig. 4a, c, e). When the groundwater CO_2 production was considered in relation to the amount of DOC (μg CO_2-C DOC^{-1} day^{-1}), the differences between the treatments were more variable (Fig. 4b, d, f). It was significantly smaller in the clear-cut than in the uncut forest in July and November, whereas the opposite was true in February and May. In August and April, in turn, the CO_2 production in the first incubation day was lower in the clear-cut than in the uncut forest, but in the third day, CO_2 production was higher in the clear-cut than in the uncut forest.

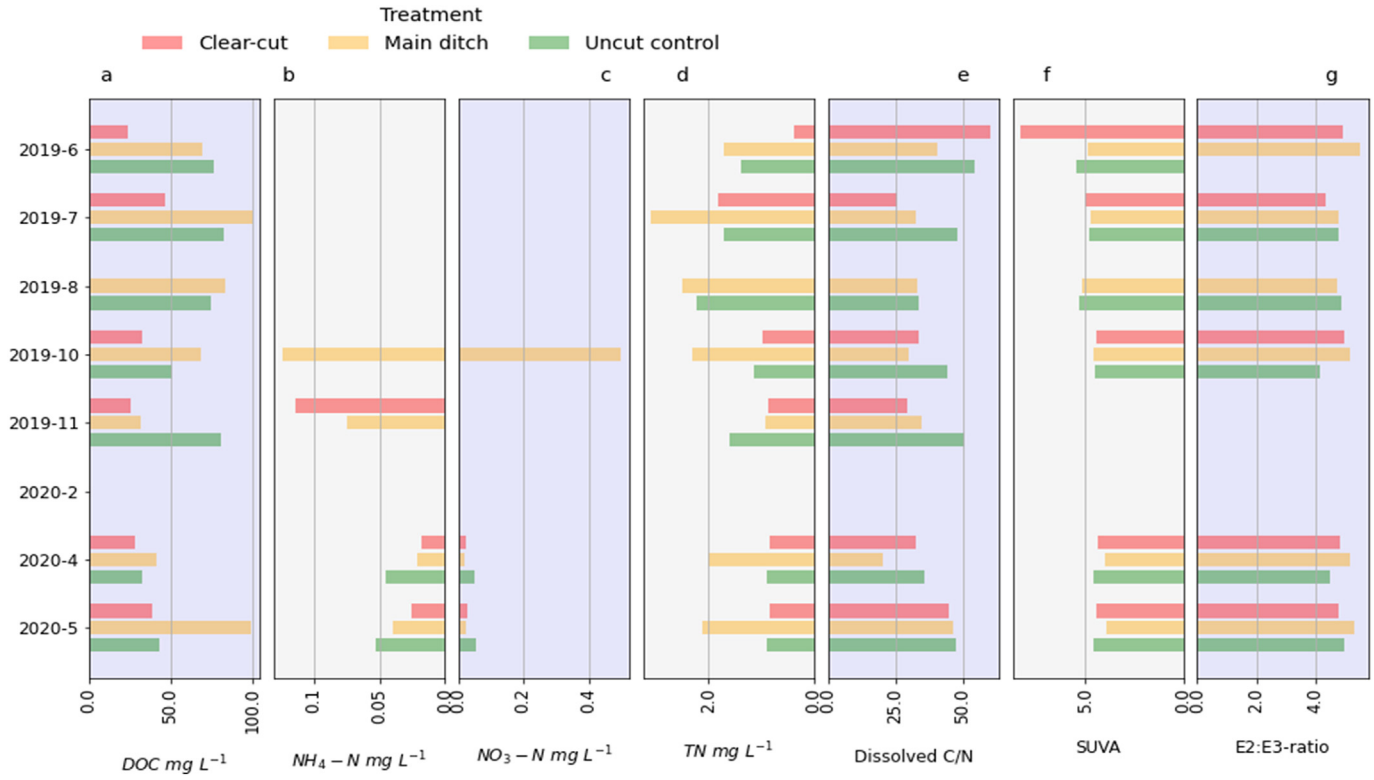

Fig. 3. (a) Dissolved organic carbon concentration, (b) ammonium, (c) nitrate, (d) total nitrogen concentrations, (e) DOC to total nitrogen ratio, (f) specific ultraviolet absorbance (SUVA) at 254 nm, and (g) E2:E3-ratio in ditch water during the monitoring period extending from June 2019 to May 2020.

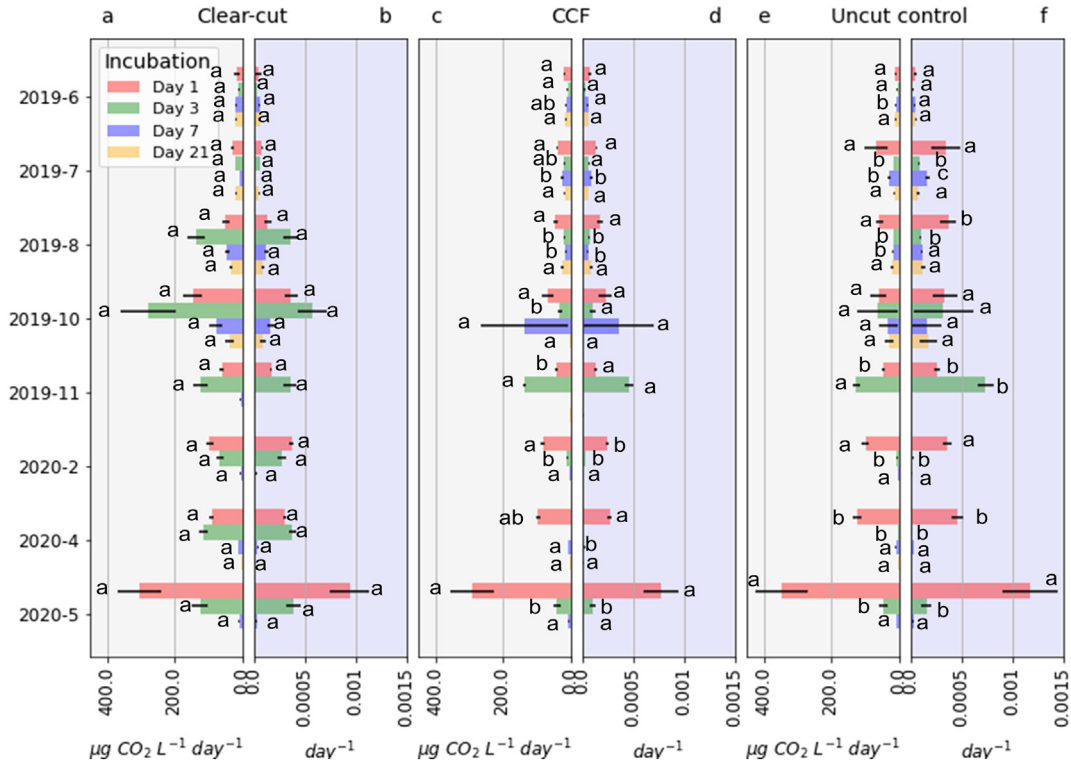

Fig. 4. CO_2 production in ground water collected from clear-cut area, continuous cover forest management (CCF) and uncut forest in different seasons (from June 2019 to May 2020) during the 21 days incubation. In panels a, c, and e the CO_2 production is expressed as mass CO_2 per water volume and in panels b, d, and f, the CO_2 production is expressed as a share from the DOC. Different letters indicate statistically significant ($p < 0.05$) differences among treatments.

The CO_2 production was considerably higher from the ditch water than from the groundwater (Figs. 4 and 5). Like in the groundwater, the majority of the CO_2 production took place during the first three days in the ditch water. Furthermore, the ditch water had a similar seasonal dynamics in CO_2 production than in the groundwater with considerably lower CO_2 flux in summer than in other months of the

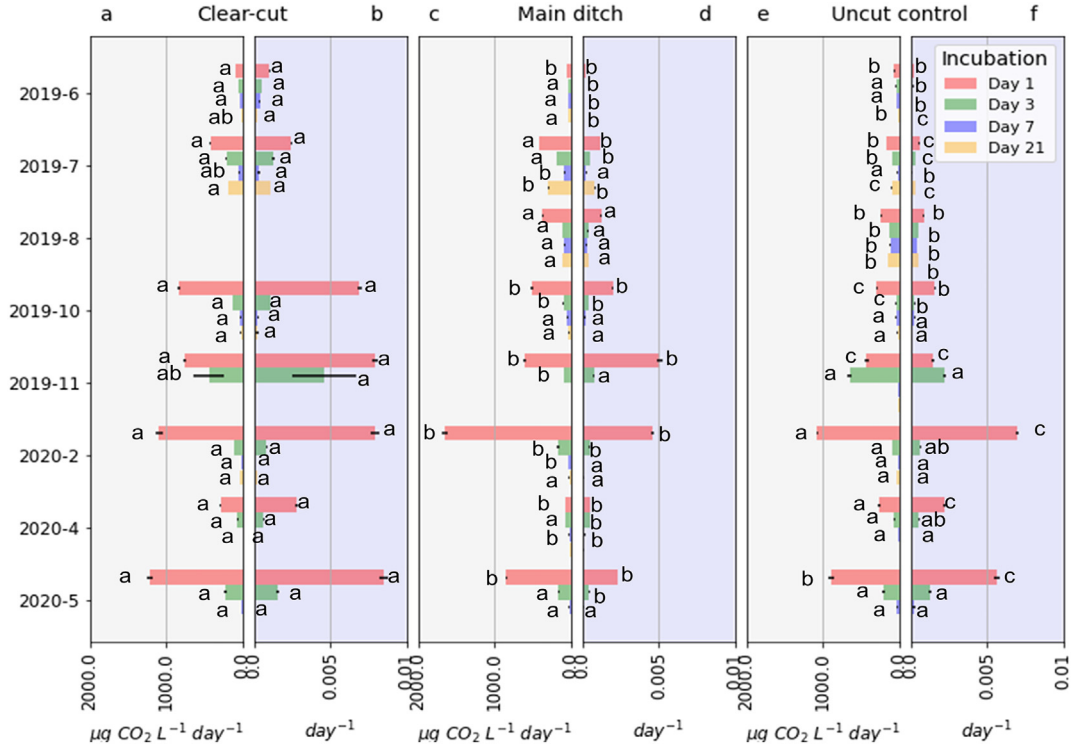

Fig. 5. CO_2 production during the 21 days incubation in ditch water collected from clear-cut area, main ditch and uncut forest in different seasons (from June 2019 to May 2020). In panels a, c, and e the CO_2 production is expressed as mass CO_2 per water volume and in panels b, d, and f, the CO_2 production is expressed as a share from the DOC. Different letters indicate statistically significant ($p < 0.05$) differences among treatments.

year. Summertime CO_2 flux was only 50-400 μg L^{-1} day^{-1}, whereas in other seasons, the fluxes were more than 1000 μg L^{-1} day^{-1} at the beginning of the incubation.

In many cases (June, July, October, November, May), CO_2 production per ditch water volume (μg L^{-1} day^{-1}) was significantly higher in the clear-cut than in the uncut forest (Fig. 5a, c, e). The CO_2 production was often (July, August, October, November, February) also higher from the main ditch which flows through the study area, than in the ditch water of the uncut forest (Fig. 5c, e). Ditch water CO_2 production in relation to the amount of DOC (μg CO_2-C DOC^{-1} day^{-1}), was always significantly higher in the clear-cut than in the main ditch or uncut forest (Fig. 5 b, d, f).

3.4. Correlations between water quality and CO_2 production

The correlations between the ground water quality variables and CO_2 production differed between the first incubation day and the later measurements (day 3, 7 and 21; Fig. 6). In the first incubation day, the CO_2 production correlated most strongly with $SUVA_{254}$ and C:N-ratio. From the third day onwards, CO_2 production correlated positively with the NH_4-N, PO_4-P and TN concentrations, and negatively with the C:N-ratio. The correlations between CO_2 production and the E2:E3-ratios were not statistically significant.

In the ditch water, the CO_2 production correlated most strongly with $SUVA_{254}$ (negative correlation) and NH_4-N (positive correlation) in the first incubation day, whereas in the later phases (from day 7 onwards; Fig. 7) the CO_2 production correlated positively with TN, PO_4-P, and DOC concentrations. There was a weak negative but non-significant correlation between the CO_2 production and C:N ratio and E2:E3-ratio.

4. Discussion

We detected the highest groundwater DOC, TN, NH_4-N and PO_4-P concentrations in the clear-cut plots, whereas the DOC and nutrient concentrations did not differ in general between the CCFs and the uncut control plots. These results suggest that the partial harvesting used in CCF may cause smaller nutrient export than the conventional clear-cutting in drained peatland forests.

The differences between the forest management practices were less pronounced in ditch water than in groundwater (Figs. 2 and 3). Ditch water chemistry data can be noisier than the groundwater data, because the water residence time in the ditch is considerably shorter than in groundwater (Haahti et al., 2017). Consequently, groundwater gradually integrates in time the changes caused by the stand management, whereas the ditch water changes quickly and the contribution of water input sources, i.e. surface runoff and groundwater from different depths of the peat profile and source areas, can differ depending on the hydrological conditions and WT (Koivusalo et al., 2008; Bernard-Jannin et al., 2018).

DOC aromaticity can be estimated using $SUVA_{254}$ and E2:E3-ratios calculated from the absorbance of shorter wavelengths into water (Peacock et al., 2014). Our $SUVA_{254}$ values (Figs. 2g, 3f) were in the upper end of the range (3.5-5.5 L^{-1} mg^{-1}) reported for boreal peatland waters (Hribljan et al., 2014; Dieleman et al., 2016; Menberu et al., 2017; Harris et al., 2020) indicating that our groundwater and ditch water samples had rather high aromaticity. In ground water, $SUVA_{254}$ was negatively correlated with the CO_2 production in the first incubation day (Fig. 6) showing that lower aromaticity favors DOC biodegradation. Comparison among the clear-cuts, CCFs and uncut controls revealed that the E2:E3-ratios were clearly lowest in the uncut plots (Fig. 2h). This indicates higher aromaticity and higher molecular weight in the uncut control plots, which further reflects as lower production of CO_2 in the uncut controls than in CCFs or clear-cuts (Fig. 4). It also implies that a larger proportion of DOC is in a more stable form in CCFs compared to clear-cuts (Lorenz et al., 2007).

The high DOC biodegradability in clear-cuts reflects the changes in vegetation. The clear-cutting had taken place two years before the onset of our study, and birch seedlings, grasses, and raspberries already had covered the clear-cut plots. The leaf litter is easily biodegradable compared e.g. to *Sphagnum* litter (Tfaily et al., 2013; Mastný et al., 2018), and it has been shown to release significant amounts of DOC and nutrients during the early stage of decomposition (Mastný et al., 2018), which could explain the high DOC, TN, NH_4-N and PO_4-P concentrations in the groundwater of the clear-cut plots. As expected, WT was higher in the clear-cut plots (Fig. 2b) due to decreased evapotranspiration. The higher WT was linked to elevated DOC concentrations (Fig. 2a,

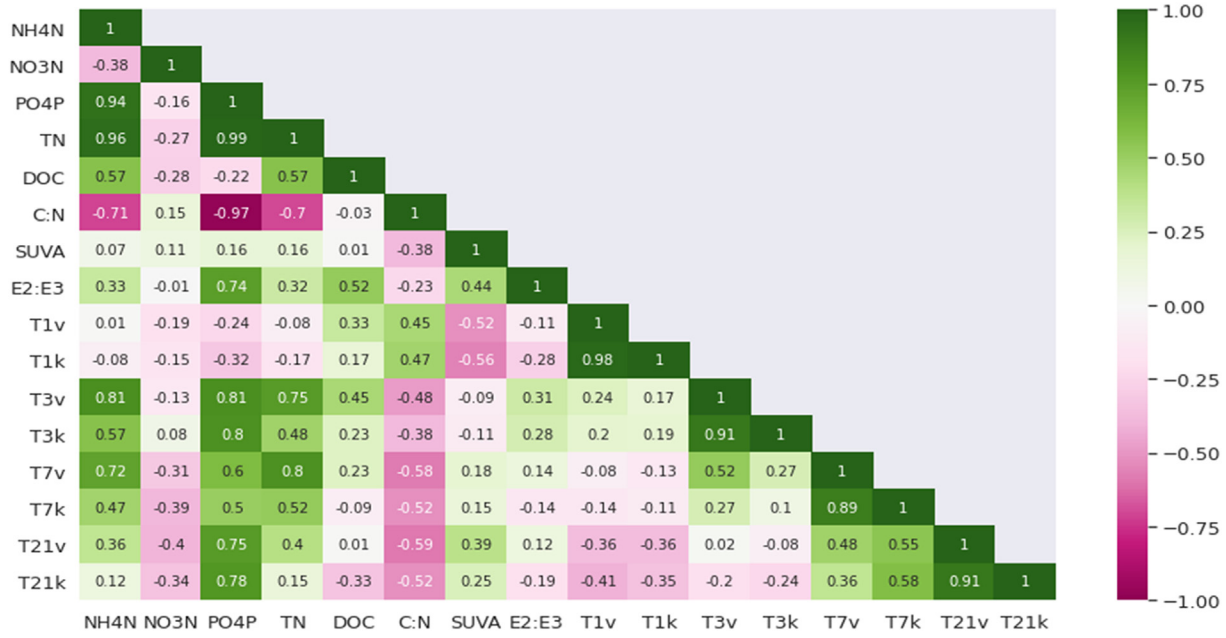

Fig. 6. Correlations between nutrient (NH_4-N, NO_3-N, PO_4-P and TN) and DOC concentrations, DOC quality parameters ($SUVA_{254}$, E2:E3-ratio), C:N-ratio, and the production of CO_2 on Day 1 (T1v = μg CO_2 L^{-1} day^{-1}; T1k = CO_2-C DOC^{-1} day^{-1}), Day 3 (T3v = μg CO_2 L^{-1} day^{-1}; T3k = CO_2-C DOC^{-1} day^{-1}), Day 7 (T7v = μg CO_2 L^{-1} day^{-1}; T7k = CO_2-C DOC^{-1} day^{-1}), Day 21 (T21v = μg CO_2 L^{-1} day^{-1}; T21k = CO_2-C DOC^{-1} day^{-1}) in groundwater. Correlations are statistically significant at $p < 0.05$ when $|r| > 0.47$ for $SUVA_{254}$ and E2:E3 ($n = 18$), $|r| > 0.82$ for PO_4-P ($n = 6$) and $|r| > 0.42$ ($n = 23$) for others.

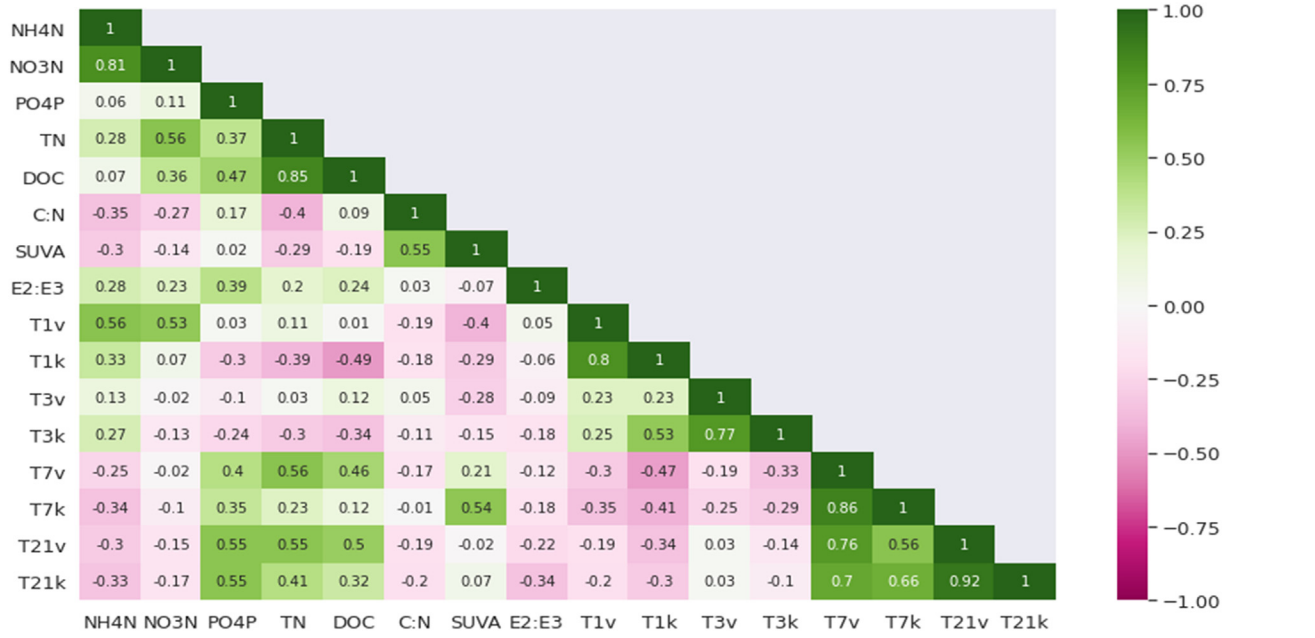

Fig. 7. Correlations between nutrient (NH_4-N, NO_3-N, PO_4-P and TN) and DOC concentrations, DOC quality parameters ($SUVA_{254}$, E2:E3-ratio), C:N-ratio, and the production of CO_2 on Day 1 (T1v = μg CO_2 L^{-1} day^{-1}; T1k = CO_2-C DOC^{-1} day^{-1}), Day 3 (T3v = μg CO_2 L^{-1} day^{-1}; T3k = CO_2-C DOC^{-1} day^{-1}), Day 7 (T7v = μg CO_2 L^{-1} day^{-1}; T7k = CO_2-C DOC^{-1} day^{-1}), Day 21 (T21v = μg CO_2 L^{-1} day^{-1}; T21k = CO_2-C DOC^{-1} day^{-1}) in ditch water. Correlations are statistically significant at $p < 0.05$ when $|r| > 0.49$ for $SUVA_{254}$, E2:E3 ($n = 17$), and PO_4-P ($n = 17$), and $|r| > 0.42$ ($n = 23$) for others.

b). This supports the previous findings that high WT contributes to DOC release from fresh plant litter and top peat layer, which contains more easily biodegradable organic matter than the deeper layers of the peat profile (Blodau et al., 2004; Clark et al., 2008; Bernard-Jannin et al., 2018). In addition, higher soil temperature in open clear-cut area may have contributed to the release of labile DOC (Laurén et al., 2019).

The chemical composition of DOC significantly affects it's biodegradation in aquatic ecosystems (Mann et al., 2012; Wickland et al., 2012). DOC consists of labile and recalcitrant fractions, which have distinctly different biodegradability. The half-life of the labile fraction is typically only a few days, while the half-life of the recalcitrant fraction ranges from 0.2 to 9 years (Kalbitz et al., 2003). In forest litter, the share of labile DOC can exceed 60%, while in peat it can be less than 5% (Kalbitz et al., 2003). Even though the share of the labile DOC in peat water is low, it can be concluded on the basis of the half-life that labile DOC strongly dominates the CO_2 production in our 21 days of incubation. In the situation where the labile DOC content is low, the used DOC quality indicators, i.e. $SUVA_{254}$ and E2:E3-ratio, are dominated by the abundant recalcitrant DOC fraction. To illustrate this, if the share of labile DOC increases from 3% to 6%, CO_2 efflux would likely double, but at the same time only marginal decrease in the recalcitrant DOC pool from 97% to 94% can be observed. Thus, the relationships between DOC biodegradation and the $SUVA_{254}$ and E2:E3-ratio, are not straightforward and universal, and are influenced by the share of labile and recalcitrant DOC and to what degree it has already been microbially processed (Burd et al., 2020). Therefore, if the share of labile DOC is small it can be difficult to detect correlations between biodegradation and $SUVA_{254}$ and E2:E3-ratios (Peacock et al., 2014).

In our study, the CO_2 production rate in groundwater ranged from 0.0001 day^{-1} to 0.001 day^{-1} (Fig. 4), which corresponds to half-lives of 6930 to 693 days, while in ditch water the CO_2 production rate (Fig. 5) was an order of magnitude higher 0.001 day^{-1} to 0.01 day^{-1} (half-life from 693 to 69 days). The observed daily CO_2 production from groundwater (Fig. 4) corresponded well with the values reported for labile (0.11-0.31 day^{-1}) and recalcitrant (0.0002-0.0005 day^{-1}) DOC extracted from peat and forest floor of spruce stands (Kalbitz et al., 2003; Kiikkilä et al., 2006). In boreal rivers and streams, the CO_2 production rates have been reported to be 0.03-0.05 for labile and 0.003-0.008 for recalcitrant DOC, respectively (Kawahigashi et al., 2004; Kaiser et al., 2017; Kazmiruk et al., 2021). The reason for the higher CO_2 production in the ditch water than in the groundwater can be explained by decomposing material, water flow paths and residence times: Surface runoff extracts labile DOC from the fresh litter, logging residues and surface peat, and ends up in the ditches in a rather short time (Bernard-Jannin et al., 2018). However, in groundwater, the large part of labile DOC is likely decomposed during the transport, because the hydraulic conductivity in the deeper peat layer can be orders of magnitude smaller than in the top peat layer leading to a longer residence time (Koivusalo et al., 2008; Laurén et al., 2021). In addition, the labile DOC can originate also from the ditch banks, which are potential, but unstudied, DOC hotspots with favourable aeration, temperature and moisture conditions for decomposition (Laurén et al., 2021). Inputs of labile DOC may also enhance the mineralization of the recalcitrant DOC and thus increase the CO_2 emissions from ditch water through the priming effect (Guenet et al., 2010).

The CO_2 production correlated positively with NH_4-N, TN and PO_4-P concentrations in groundwater (Fig. 6) indicating that the higher nutrient availability in the clear-cut plots compared to CCFs or uncut forest may have led to a higher rate of CO_2 production (Fig. 4). In the ditch water, the CO_2 production was controlled by the DOC quality ($SUVA_{254}$) and nutrient concentrations. High N and P levels have been found to correlate positively with biodegradability of DOC also in several other studies (Holmes et al., 2008; Kiikkilä et al., 2011; Mann et al., 2012; Wickland et al., 2012; Räsänen et al., 2014; Mao et al., 2017; Burd et al., 2020).

We found considerably lower CO_2 production rates in summer than in other seasons (Figs. 4 and 5). This may reflect the temperature dependency of DOC decomposition (Freeman et al., 2001; Laurén et al., 2019). Outside the growing season it is likely that labile DOC has accumulated in groundwater and ditch water, because DOC decomposition is slow under low temperatures (Freeman et al., 2001, Laurén et al., 2019). Therefore, it is possible that the decomposition of this labile DOC causes a burst of CO_2 emission when the water samples are incubated at a higher temperature in the laboratory. Marked seasonal variation in

DOC biodegradability has been found also in other studies. In boreal streams and rivers DOC biodegradability has been found to be high in winter and spring and decrease progressively through the summer (Holmes et al., 2008; Mann et al., 2012; Wickland et al., 2012; Vonk et al., 2013). Seasonal and event-scale variation in DOC biodegradation depends on several factors such as WT fluctuations, water residence time and flowpaths, vegetation, temperature, and nutrient concentrations in the water (Wickland et al., 2012; Campeau et al., 2019; Laurén et al., 2019; Rosset et al., 2020), and it deserves further study.

5. Conclusions

Our results indicated that in drained boreal peatlands, the biodegradation of DOC is higher for ground water than for ditch water. The biodegradability of DOC varies in different seasons, being the smallest in summer. Forest harvesting affects lateral C fluxes by changing the quality and biodegradability of DOC. Our results suggest that partial harvesting used in CCF reduces the concentrations of DOC and nutrients in watercourses, decreases DOC biodegradability, and therefore the aquatic CO_2 emissions compared to clear-cutting in drained peatland forests. Thus, CCF can cause less environmental drawbacks than conventional clear-cutting.

CRediT authorship contribution statement

Marjo Palviainen: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Visualization, Writing – original draft, Writing – review & editing. **Elina Peltomaa:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Ari Laurén:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Supervision, Visualization, Writing – original draft, Writing – review & editing. **Niko Kinnunen:** Data curation, Methodology, Writing – review & editing. **Anne Ojala:** Funding acquisition, Methodology, Project administration, Resources, Writing – review & editing. **Frank Berninger:** Funding acquisition, Resources, Writing – review & editing. **Xudan Zhu:** Data curation, Writing – review & editing. **Jukka Pumpanen:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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