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Quantifying Dissolved Organic Carbon Efflux from Drained Peatlands in Hemiboreal Latvia

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Abstract: This study evaluated the impact of different land use types on groundwater dissolved organic carbon (DOC) concentrations and annual DOC efflux from drained peatlands to catchment runoff, providing insights into the mechanisms of carbon stock changes in peatland soils. We measured groundwater chemical properties and various environmental variables, and calculated daily runoff and evapotranspiration for 2021 to estimate monthly and annual DOC efflux and analyzed main affecting factors in different peatland land use types. The highest DOC concentrations in groundwater were found in Scots pine forests and active peat extraction sites, with values of 113.7 mg L^{-1} and 109.7 mg L^{-1}, respectively, and the lowest in silver birch forests and croplands, at 51.9 mg L^{-1} and 18.6 mg L^{-1}, respectively. There were statistically significant correlations, including a strong negative correlation between DOC concentrations and several groundwater chemical properties, such as pH, electrical conductivity (EC), Ca, Mg, and K concentrations. The concentrations of DOC in the groundwater of drained peatland showed significant variation between different land use types. The highest annual DOC efflux was observed in active peat extraction sites, at 513.1 kg ha^{-1} y^{-1}, while the lowest was in grasslands, at 61.9 kg ha^{-1} y^{-1}, where Ca and Mg concentrations, as well as EC, were the highest. Continuous monitoring of these concentration patterns is essential.

Keywords: dissolved organic carbon; runoff; evapotranspiration; groundwater; peatland

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Citation: Meļņiks, R.N.; Upenieks, E.M.; Butlers, A.; Bārdule, A.; Kalēja, S.; Lazdiņš, A. Quantifying Dissolved Organic Carbon Efflux from Drained Peatlands in Hemiboreal Latvia. *Land* **2024**, *13*, 790. https://doi.org/10.3390/land13060790

Academic Editors: Oskars Purmalis and Marios Drosos

Received: 26 April 2024
Revised: 27 May 2024
Accepted: 31 May 2024
Published: 3 June 2024

1. Introduction

Under wet soil conditions, the production of soil organic matter exceeds decomposition; thus, organic material accumulation can occur [1,2]. Areas where a layer of peat has naturally formed are called peatlands, which are of fundamental ecological importance, being the most efficient carbon (C) sinks among other terrestrial ecosystems [3,4]. These large C sinks in peatlands are ensured by the wet conditions—natural peatlands are always wetlands [5]. Most peatland areas can be found in the temperate zone of North America and Eurasia, and they cover [6] roughly 2.8% of the world's land area; furthermore, they hold between one-third and one-half of the world's soil carbon (C) stock. Nonetheless, these vital ecosystems are under considerable risk from the dual challenges of heavy land use and drainage on a global scale. Studies also suggest that global atmosphere warming in temperate and boreal zones can indeed lower groundwater levels and impact carbon accumulation in wetlands [6–8]. Lowering the water table by drainage is a prerequisite for peatland forestry, use for agriculture, and peat extraction in most countries [9,10]. These practices are also common in Latvia, where more than 10% of the total area is covered by peatlands [11,12]. As a result, the hydrological regime of the peatlands is altered, and mineralization of peat is promoted, resulting in increased gross C losses. After drainage, the peat initially begins to decompose rapidly, which can cause the greenhouse gas (GHG) emissions to increase. However, both natural and drained peatlands can experience significant mineralization, particularly during dry summer conditions [13–15].

On-site emissions occur locally, but off-site emissions occur when waterborne organic matter (including DOC) is transported outside peatland areas and further emitted as CO_2 or CH_4 due to biological or chemical transformation [16]. Over the course of the past 30 years, increasing concentrations of DOC have been observed in surface waters in several parts of Europe and North America, which implies an increased release of dissolved organic matter from soils [17]. DOC is mostly defined as organic molecules that can pass through a filter with a pore size of 0.45 µm. It is formed during the decomposition of organic matter and transported by water [18]. Forest floor, ground vegetation, litter, and wood debris are considered important sources of DOC and comprise different substrates that produce different volumes of DOC with varying complexity [19]. DOC fluxes are an important source of carbon in most ecosystems and facilitate the transfer of nutrients from terrestrial to aquatic ecosystems [20]. C emissions from water can make up to 15–50% of total GHG emissions, and DOC accounts for most of them [16]. However, the share of human-induced DOC influx to surface waters due to peatland drainage is not known.

The concentration of DOC and efflux tends to correlate with precipitation. DOC concentrations in rainwater are generally very low, but they increase as water encounters canopies and forest floor [21]. Additionally, certain physical and chemical soil water properties, such as the pH level and basic ion and phosphate concentrations, can significantly influence the DOC content [22]. DOC fluxes increase with higher carbon contents in soils, as well as with more wetlands within the watershed [23].

DOC fluxes can also be affected by evapotranspiration, which plays an important role in the water cycle, being responsible for a significant proportion of water removal from the ecosystem. In summary, evapotranspiration is affected by weather, vegetation characteristics, management, and environmental factors [24]. As a result of afforestation, the tree stand affects the groundwater level through evapotranspiration. An effective drainage system in the first years after ditching increases runoff and reduces evapotranspiration. If ditches are maintained, as the stand biomass increases, runoff decreases but transpiration increases [25]. Lower runoff may therefore result in lower DOC efflux, which would reduce off-site emissions [16,26]. Therefore, it is necessary to ensure proper management, which can mitigate climate change while also preventing the degradation of land and conserving biodiversity [4].

In this study, we assessed the DOC concentration in groundwater and monthly and annual DOC efflux from drained peatlands with different land use types through ditches and catchment runoff out of peatlands. To estimate monthly and annual runoff, and to evaluate the factors affecting DOC concentration, in addition to groundwater sampling, measuring environmental variables and GHG concentrations, we calculated 7-day and monthly runoff and evapotranspiration.

2. Materials and Methods

2.1. Research Sites

This study was carried out across 14 sites in drained hemiboreal peatlands in Latvia, representing former peat extraction sites with different current land use types (Figure 1). The research was conducted during the 2021 season. The meteorological conditions in Latvia in 2021 were characteristic for the area, with no notable anomalies observed [27]. The mean annual precipitation in Latvia for 2021 was 676 mm, which is 1% less than the typical annual mean of 685 mm. The annual mean air temperature recorded was 7.0 °C, with the coldest monthly mean temperature being −5.2 °C in February 2021 and the warmest monthly mean temperature reaching 21.5 °C in July 2021. The year 2021 experienced a mean air temperature that was 0.2 °C higher than the climatic norm for the period 1991–2020, making it the ninth consecutive year of exceeding temperatures, and the fourth consecutive year with precipitation less than the climatic norm.

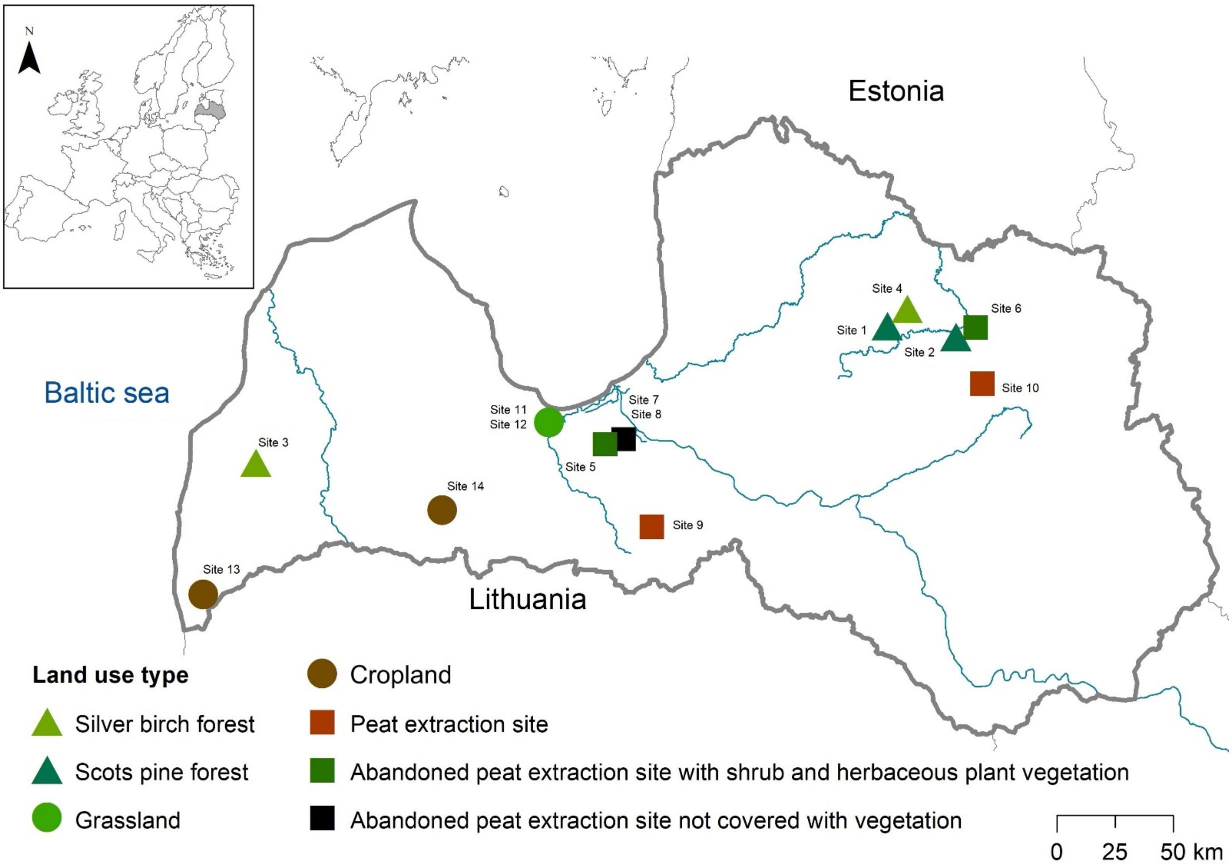

Figure 1. Location and land use type of the research sites in Latvia.

Each land use type was represented by two research sites. Four of the sites were in the forest land—two Scots pine (*Pinus sylvestris* L.) and two silver birch (*Betula* spp.). The main characteristics of these forest stands are represented in Table 1. In addition to forested peatlands, research sites were established in active peat extraction sites, former peat extraction sites, which are abandoned with or without vegetation or are currently managed as cropland and grassland, where the current land use type in each site has been practiced for more than 20 years (Table 2). In all study sites, the soil type was Histosol and the peat layer depth was at least 1 m.

Table 1. Main parameters of the forest stands (Mean ± S.E.).

Land Use Type, Tree Specie	Research Site	Number of Trees ha^{-1}	Tree Diameter at Breast Height, cm	Tree Height, cm
Scots pine forest	Site 1	2060	21.3 ± 0.9	18.8 ± 1.3
Scots pine forest	Site2	3920	7.9 ± 0.4	8.6 ± 0.5
Silver birch forest	Site3	800	14.2 ± 0.8	13.7 ± 1.4
Silver birch forest	Site4	1940	15.3 ± 0.3	16.8 ± 0.7

Table 2. Characterization of the research sites.

Land Use Type	Research Site	Ditch Catchment Area, ha	Ditch Width, cm	Ditch Depth, cm	Coordinates (EPSG: 4326) X	Y
Scots pine forest	Site1	192	205	31	25.9943	57.2681
	Site 2	96	212	54	26.4794	57.2165
Silver birch forest	Site 3	21	260	57	21.5200	56.7274
	Site 4	192	269	52	26.1401	57.3312

Table 2. *Cont.*

Land Use Type	Research Site	Ditch Catchment Area, ha	Ditch Width, cm	Ditch Depth, cm	Coordinates (EPSG: 4326) X	Y
Abandoned peat extraction site with shrub and herbaceous plant vegetation	Site 5	95	153	75	23.9802	56.8246
	Site 6	81	207	69	26.6256	57.2494
Abandoned peat extraction site with bare peat	Site 7	131	133	57	23.9773	56.8259
	Site 8	41	196	38	24.1085	56.8453
Active peat extraction site	Site 9	137	142	90	24.3058	56.5041
	Site 10	240	144	122	26.6558	57.0322
Grassland	Site 11	52	232	46	23.5818	56.9108
	Site 12	66	255	70	23.5951	56.9129
Cropland	Site 13	48	166	52	21.1897	56.2119
	Site 14	55	205	51	22.8384	56.5644

2.2. Data Collection and Measurements of Environmental Variables

Groundwater samples were collected every month in the period from January to December 2021. Water samples were collected from groundwater wells next to the ditches. At each research site, we installed three groundwater wells 50 cm from the ditches, 3 m apart from each other. These wells were constructed from 5 cm wide and 150 cm long polyvinyl chloride (PVC) pipes with a covered top to block direct precipitation. The pipes were perforated to allow groundwater to enter and were lined with geotextile to filter out soil particles and organisms.

A vacuum pump was used to collect water from the wells, which connected the water in the well and the glass bottle with plastic tubes. During each measurement session, we also recorded a set of environmental variables. These included the groundwater (GW) level, where positive values indicate flooding and water level in ditch, but negative values indicate water levels below the surface. Additionally, we measured soil and air temperatures using a Comet data logger (COMET SYSTEM, s.r.o., 756 61 Roznov pod Radhostem, Czech Republic) [28] equipped with Pt1000 temperature probes. Atmospheric pressure readings were measured using the Gasmet DX4040 instrument (Gasmet Technologies Oy, Mestarintie 6, Vantaa FI-01730 FINLAND) [29]. Additionally, the presence of water in the drainage ditches was monitored manually, noting that a zero value indicated an absence of water.

GW samples were gathered and transported to the Latvian State Forest Research Institute "Silava" laboratory, accredited according to the LVS EN ISO 17025:2018 [30], for subsequent analysis. Analysis conducted on these samples included pH measurement according to the LVS ISO 10523:2012 [31]; electrical conductivity (EC) in accordance with the LVS EN 27888:1993 [32]; as well as total nitrogen (TN) and dissolved organic carbon (DOC) concentrations, which were determined using a FORMACS^{HT} TOC/TN Analyzer with an ND25 nitrogen detector (Skalar Analytical B.V. Tinstraat 12, 4823 AA Breda The Netherlands) [33] according to the LVS EN 12260:2004 [34] and LVS EN 1484:2000 [35], respectively. Concentrations of potassium (K), calcium (Ca), and magnesium (Mg) were quantified using an iCE3500 flame atomic absorption spectrometer (Thermo Fisher Scientific (Asheville) LLC, 275 Aiken Road, Asheville, NC 28804 USA, Serial No: AA05191115) [36] according to LVS EN ISO 7980:2000 [37] and LVS ISO 9964-3:2000 [38]. Notably, water samples were not collected from the ditches due to their predominantly dry condition throughout the year.

In addition to the collection of GW samples and environmental variables, measurements of GHG (CO_2, CH_4, and N_2O) concentrations from drainage ditches were conducted during each measurement session, for correlation analysis. We used a closed-type GHG flux measurement chamber to record GHG fluxes across the full cross-section of a drainage ditch, including the ditch bed or water surface and its slopes. This chamber spans the ditch's width, perpendicular to its longitudinal axis, ensuring GHG flux data collection from the cross-sectional area of the ditches ranging in size from 0.65 m^2 to 1.32 m^2. Metal construction covered the surface of the drainage ditch, with plastic film pressed against the ditch profile by a stainless steel chain placed around the perimeter of the gas exchange chamber. The chamber's 50 cm width was kept constant during the study. A small ventilator was placed inside the chamber to continuously circulate the air, aiding in the accurate measurement of GHG levels. GHG concentrations were measured using a portable Gasmet DX4040 gas analyzer [29], which utilizes Fourier transform infrared (FTIR) spectroscopy. This setup facilitated the monitoring of changes in the levels of GHG within the chamber, capturing the average atmospheric content of these gasses over 2 min intervals across a 30 min duration, resulting in 15 individual measurements per chamber for each measurement period. These measurements were documented using "Calcmet Lite v2.0" software [29], Calcmet Lite v2.0. The GHG data processing and emission calculation methodology in our research sites is described more in depth in the study published by Vanags-Duka et al. (2022) [39].

2.3. Evapotranspiration and Runoff Estimation

To assess the annual DOC efflux from the peatlands, we used daily meteorological data to calculate monthly and annual DOC efflux for each land use type. Initially, we assessed 7-day precipitation and calculated actual evapotranspiration to estimate how much water from the area goes through the runoff. This is performed by subtracting 7-day potential evapotranspiration (Equation (1)) from the 7-day total precipitation. In this study, we assumed that the precipitation water which fed the aquifers was zero. The DOC efflux was determined by multiplying the measured monthly GW DOC concentrations with the calculated water runoff in millimeters. Runoff and efflux were then quantified from L m^{-2} to kg ha^{-1} based on DOC concentration. We obtained monthly and annual values.

$$Q = P - ET \tag{1}$$

where Q is the water runoff, mm; P is the precipitation, mm; and ET is the evapotranspiration, mm.

We calculated potential evapotranspiration (ET_o) using the R package 'evapotranspiration', with the Penman–Monteith equation (Equation (2)) [24,40]. The input data required, including precipitation, for the calculations were taken from the Latvian Environment, Geology and Meteorology Centre (LEGMC) database using data from the closest meteorological station for each research site. The parameters required for the calculations were the daily maximum and minimum air temperature, maximum and minimum air humidity, and the solar radiation.

$$ET_o = (0.408\Delta(Rn-G) + \gamma\ (900/(T + 273))\ u_2\ (e_s - e_a))/(\Delta + \gamma\ (1 + 0.34u_2)) \tag{2}$$

where ET_o is the reference evapotranspiration, mm day^{-1}; Rn is the total solar radiation, MJ m^{-2}, d; G is the soil heat flux, MJ m^{-2}, d; T is the daily mean air temperature at 2 m height from ground, °C; u_2 is the wind speed, 2 m height, m s^{-1}; e_s is the saturated vapor pressure, kPa; e_a is the water vapor pressure, kPa; e_s–e_a is the saturated vapor pressure deficit, kPa; Δ is the vapor pressure curve, kPa $°C^{-1}$; and γ is the psychometric constant, kPa $°C^{-1}$.

Initial output data of Equation (2) were the reference evapotranspiration, which provides information on a default area with grassland vegetation covering the entire area. To obtain representative data on potential evapotranspiration, it was necessary to apply the correction coefficients for each land use type in this study. Equation (3) was used to transform the reference evapotranspiration into the evapotranspiration corresponding to the vegetation using the Food and Agriculture Organization of the United Nations (FAO) correction coefficients.

$$ET_c = K_c \cdot ET_o \tag{3}$$

where ET_c is the actual evapotranspiration, mm; K_c is the vegetation specific coefficient (Table 3); and ET_o is the reference evapotranspiration, mm.

Table 3. Adjusted FAO correction coefficient values for each land use type using Allen et al. [24].

Land Use Type	$K_{c\ ini}$	$K_{c\ mid}$	$K_{c\ end}$
Scots pine forest	1	1	1
Silver birch forest	0.5	1.2	0.95
Abandoned peat extraction site with shrub and herbaceous plant vegetation	0.6	1.05	0.7
Abandoned peat extraction site with bare beat	0.5	0.65	0.55
Active peat extraction site	0.5	0.65	0.55
Grassland	0.6	1	0.9
Cropland	0.3	1.05	0.3

Table 3 presents the FAO K_c values, adjusted for our study case from the study by Allen et al. [24], for various agricultural crops, including deciduous trees and conifers [41]. These K_c values are influenced by vegetation characteristics, soil evaporation, and the vegetative growth period. The coefficients are categorized into three distinct phases, $K_{c\ ini}$, $K_{c\ mid}$, and $K_{c\ end}$, each corresponding to specific intervals before, within, or after the vegetation period, respectively (Table 3). The coefficient value transitions from $K_{c\ ini}$ to $K_{c\ mid}$, linearly interpolated from the onset of the vegetation period to the first day of active vegetation growth, with the value increasing incrementally each day. The $K_{c\ mid}$ value is then applied throughout the entire active vegetative growth period. Between $K_{c\ mid}$ and $K_{c\ end}$, the coefficient value is linearly interpolated from the final day of active vegetation growth to the last day of the vegetation period. Following the $K_{c\ end}$ period, the coefficient value for each day gradually decreases until it reverts to the $K_{c\ ini}$ value, beginning from the first day the mean diurnal air temperature falls below zero. This value remains constant for the remainder of the period. The coefficient values used for ET_o correction vary, reflecting the specific vegetation present. If the daily mean air temperature is below 0 °C, precipitation accumulates and releases linearly when the air temperature is positive.

2.4. Statistical Analysis

All statistical analyses were performed using R software [42]. A comparison of the DOC concentration and efflux among different land use types was conducted. The comparison included monthly mean DOC concentrations and runoff, as well as the annual total DOC runoff under different land use types. The Kruskal–Wallis rank sum test, along with pairwise comparisons via the Wilcoxon rank sum test, were used to identify differences in the mean values of DOC concentrations and environmental variables, including groundwater chemistry, across various peatland land use types, using ('stats') package [35]. For all analysis we used a significance threshold of 0.05. Correlations between DOC concentrations and environmental variables were compared using Spearman's correlation ('corrplot') [43]. The function cor() from ('ggpmisc') [44] was used to calculate the significance levels for Spearman correlations. Using correlation analysis, DOC concentrations were compared with groundwater chemical properties (pH, EC, K, Ca, Mg, and TN concentration), soil and air temperatures, water levels (WLs) in wells and ditches, precipitation, and GHG (CO_2, CH_4, and N_2O) emissions from ditches. We explored the factors affecting DOC concentrations in GW using a five-component partial least squares (PLS) model. In the analysis, environmental parameters (denoted as X) were analyzed to explain variations in DOC concentrations (denoted as Y) in GW employing the PLS regression method. The computation of the PLS regression was conducted using the 'mdatools' package [45], which prioritizes the X variables based on their importance on explaining the variation in Y, a process quantified through variables important for projection (VIP) values. In addition to PLS regression and correlation analysis, we performed non-linear regression analysis between the most important variables according to PLS regression, explaining DOC concentrations individually.

For each research site, the catchment area was calculated using a LiDAR-derived digital elevation model (DEM), which was included in the correlation analysis, to detect the impact of catchment area on DOC concentrations. We used Latvian Geospatial Information Agencies LiDAR data (Latvian Geospatial Information Agency (LGIA), Latvia, Riga, Ojara Vaciesa street 43) and GRASS GIS 8.3.1. tool "r.terraflow" for this task. Data visualization was performed using ArcMap 10.8 for spatial data and maps, but figures were created using R package 'ggplot2' [46].

3. Results

3.1. Variation in DOC Concentration in Groundwater

Mean DOC concentrations in GW varied between land use types. In general, the mean DOC concentration for all studied land use types was 74.9 ± 15.9 mg L^{-1}. We observed the highest mean concentration in Scots pine forests (113.7 ± 3.3 mg L^{-1}), followed by active peat extraction sites (109.7 ± 11.5 mg L^{-1}), abandoned peat extractions sites with shrub vegetation (94.9 ± 3.1 mg L^{-1}), and with bare peat (91.8 ± 6.1 mg L^{-1}). In silver birch forests, DOC concentrations were significantly lower than in Scots pine forests (51.9 ± 1.4 mg L^{-1}), while in cropland (14.5 ± 0.6 mg L^{-1}) and grassland (18.6 ± 1.3 mg L^{-1}), they were the lowest from all studied land use types (Figure 2, Table 4).

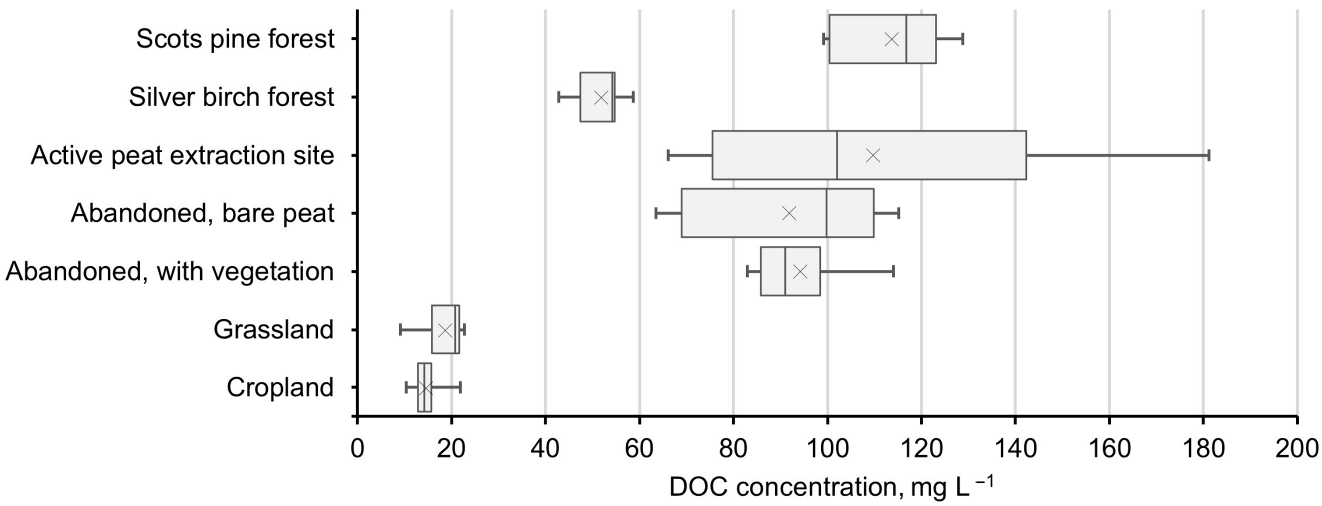

Figure 2. Variation in monthly mean DOC concentration in groundwater by land use type (*n* = 24 for each land use type). Rectangles fall within the first to third quartile range. The intercepts fall within the zeroth to fourth quartile range. The rectangles are divided by the median. "x" represents the arithmetic mean value. Abandoned means abandoned peat extraction site.

Table 4. Variations in monthly mean values (±S.E.) of environmental variables in different land use types. Superscript numbers show statistically significant ($p < 0.05$) differences between mean values across land use types (*n* = 24 for each land use type). Abandoned means abandoned peat extraction site.

Parameter	Cropland (1)	Grassland (2)	Silver Birch Forest (3)	Scots Pine Forest (4)	Abandoned with Vegetation (5)	Abandoned without Vegetation (6)	Active Peat Extraction Site (7)
DOC, mg L^{-1}	14.17 ± 1.63 2, 3, 4, 5, 6, 7	18.62 ± 1.26 3, 4, 5, 6, 7	51.86 ± 8.06 4, 5, 6, 7	113.71 ± 4.41 5, 6	94.23 ± 3.56	91.81 ± 5.37	109.72 ± 14.14
ET, mm	49.59 ± 13.0	51.08 ± 14.28	63.99 ± 12.52 6, 7	58.81 ± 9.88 6, 7	53.97 ± 11.19	32.34 ± 5.43	32.34 ± 5.43
pH	7.81 ± 0.04 3, 4, 5, 6, 7	7.71 ± 0.06 3, 4, 5, 6, 7	7.18 ± 0.1 4, 5, 6, 7	5.47 ± 0.2 7	5.63 ± 0.21 7	5.22 ± 0.17 7	6.29 ± 0.12

Table 4. *Cont.*

Parameter	Cropland [(1)]	Grassland [(2)]	Silver Birch Forest [(3)]	Scots Pine Forest [(4)]	Abandoned with Vegetation [(5)]	Abandoned without Vegetation [(6)]	Active Peat Extraction Site [(7)]
EC, μS cm^{-1}	465.57 ± 13.56 [3, 4, 5, 6, 7]	533.82 ± 31.26 [3, 4, 5, 6, 7]	285.13 ± 20.39 [4, 5, 6, 7]	68.58 ± 6.49 [6, 7]	82.28 ± 8.42 [6, 7]	50.17 ± 4.06 [7]	114.96 ± 13.11
K, mg L^{-1}	1.6 ± 0.17 [3, 4, 5, 6]	1.3 ± 0.41	1.0 ± 0.08 [4, 5, 7]	0.41 ± 0.02 [5, 6, 7]	0.67 ± 0.05 [6, 7]	0.9 ± 0.06 [7]	1.96 ± 0.18
Ca, mg L^{-1}	96.74 ± 2.56 [2, 3, 4, 5, 6, 7]	108.75 ± 3.78 [3, 4, 5, 6, 7]	59.03 ± 3.26 [4, 5, 6, 7]	18.53 ± 1.84 [6]	16.4 ± 1.78 [6]	10.11 ± 1.17 [7]	18.54 ± 1.9
Mg, mg L^{-1}	18.09 ± 0.98 [2, 3, 4, 5, 6, 7]	25.55 ± 0.64 [3, 4, 5, 6, 7]	11.48 ± 1.19 [4, 5, 6, 7]	0.83 ± 0.08 [5, 6, 7]	1.3 ± 0.07 [6, 7]	0.62 ± 0.02 [7]	4.45 ± 0.42
TN, mg L^{-1}	6.62 ± 1.61 [2, 4]	1.74 ± 0.66 [3, 5, 6, 7]	3.75 ± 0.72 [7]	2.7 ± 0.21 [5, 7]	4.04 ± 0.2 [6, 7]	3.35 ± 0.27 [7]	8.11 ± 0.68
GW, cm	−29.63 ± 7.1 [2, 4, 5]	−5.25 ± 5.01 [3, 5, 7]	−47.54 ± 8.06 [4, 6, 7]	−11.18 ± 3.53 [5, 7]	−55.94 ± 9.47 [6, 7]	−16.92 ± 3.05 [7]	−28.13 ± 3.94
WL in ditch, cm	11.3 ± 2.35 [2, 3, 5, 6, 7]	19.49 ± 2.2 [3, 4, 6]	2.81 ± 1.27 [5, 6, 7]	5.75 ± 2.23 [5, 6, 7]	38.55 ± 9.59	37.49 ± 7.01	24.13 ± 5.42

The dynamics of DOC concentration in groundwater varied and did not show consistent patterns across different land use types. In active peat extraction sites, DOC concentrations increased from April to October, but in abandoned sites without vegetation, they increased starting from June. In vegetated areas, the concentrations were more stable year-round, staying close to the mean value. Conversely, the most notable fluctuations in DOC concentration were observed in non-vegetated areas, including active peat extraction sites and abandoned sites without vegetation (Figure 3).

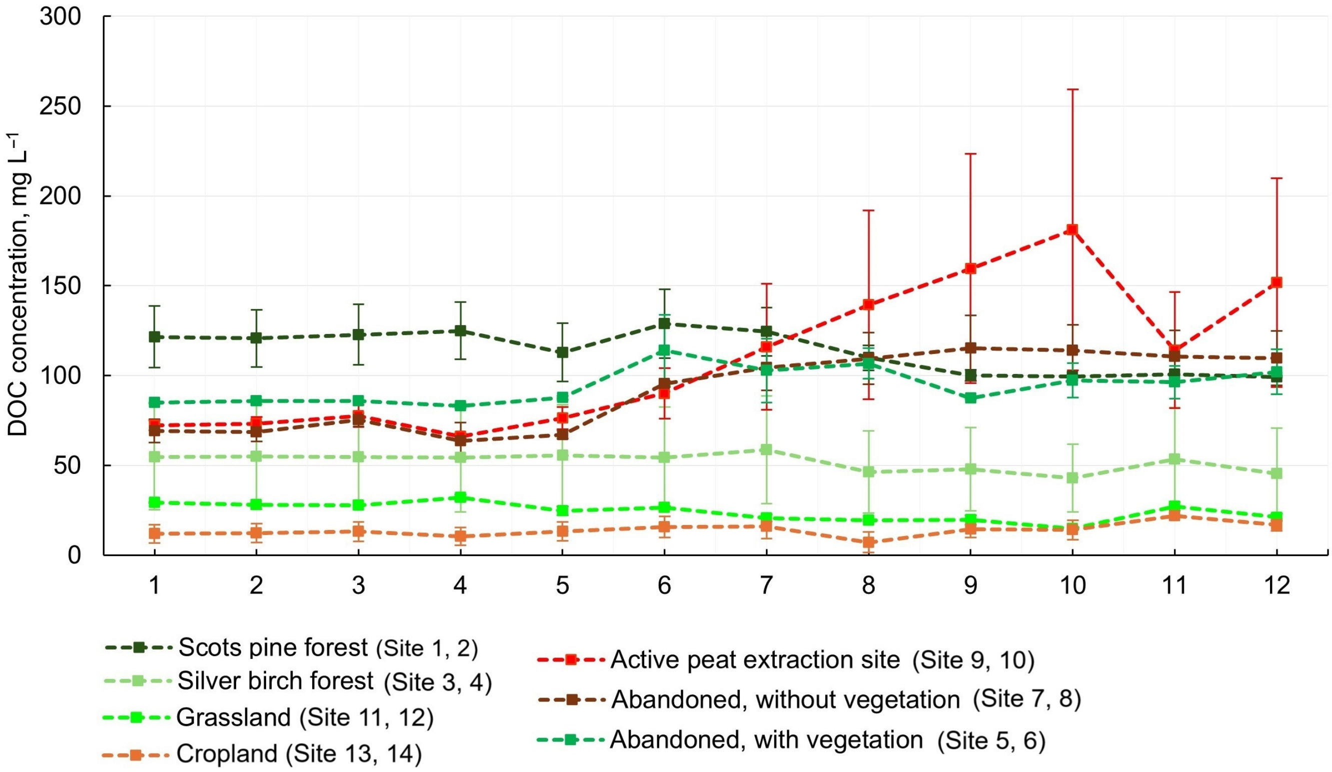

Figure 3. Mean monthly DOC concentrations in groundwater in different land use types. Abandoned means abandoned peat extraction site.

In active peat extraction sites, the mean DOC concentration is highly influenced by Site 10, where it increased from June to October. In contrast, in Site 9, the DOC concentration remained steady throughout the year. Additionally, in abandoned sites without vegetation, Site 7 affected the mean DOC concentration in this land use type, where the DOC concentration significantly increased starting in June. In Site 8, the concentration remained comparatively steady throughout the year.

3.2. Runoff and Evapotranspiration

The highest monthly mean precipitation within all research sites was observed in August (134 mm, Figure 4), which resulted in runoff rates from 37 mm in silver birch forests to 87 mm in active peat extraction sites. The lowest monthly mean precipitation within all research sites was observed in February, with 13 mm, and runoff rates, from 4 mm in Scots pine forests to 9 mm in croplands and abandoned peat extraction sites with vegetation.

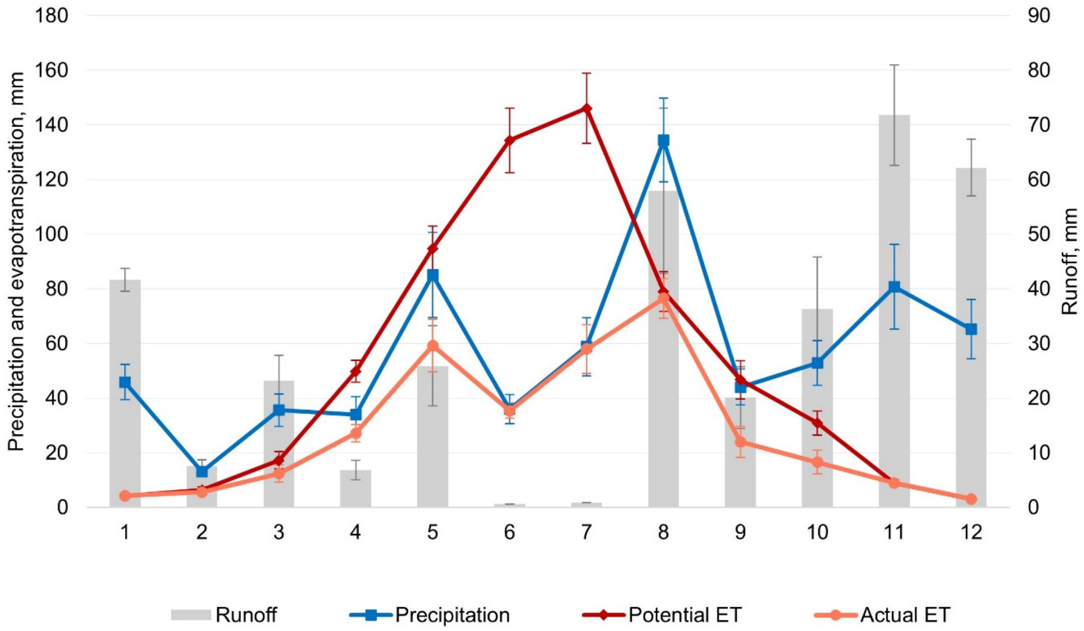

Figure 4. Monthly mean precipitation, potential evapotranspiration, actual evapotranspiration, and runoff rates in all research sites (n = 2190).

In June and July, in all research sites, potential evapotranspiration exceeded precipitation significantly, resulting in 0 mm runoff. The exceptions were active peat extraction sites and abandoned peat extraction sites without vegetation, where runoff was similar (4 mm and 5 mm in June and July, respectively). Potential evapotranspiration rates between different land use types did not vary significantly, except active and abandoned peat extraction sites without vegetation compared to other land use types (Figure 5). We estimated the highest potential annual evapotranspiration in silver birch and Scots pine forests (767 ± 61 mm y^{-1} and 705 ± 47 mm y^{-1}, respectively), whereas the lowest was in active peat extraction sites and abandoned peat extraction sites without vegetation (388 ± 26 mm y^{-1} and 395 mm y^{-1}, respectively).

The highest annual runoff was observed in active peat extraction sites and abandoned peat extraction sites and croplands (423 ± 27 mm y^{-1}, 418 ± 25 mm y^{-1} and 392 ± 26 mm y^{-1}, respectively), followed by abandoned peat extraction sites with vegetation and grasslands (349 ± 22 mm y^{-1} and 347 mm y^{-1}, respectively). We estimated the lowest annual runoff in Scots pine and silver birch forests to be 307 mm y^{-1} in both forest types.

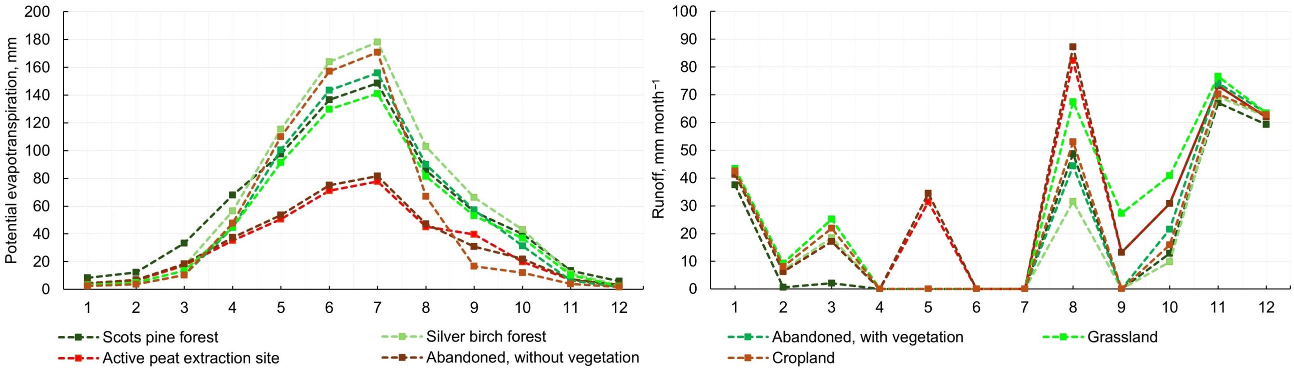

Figure 5. Monthly potential evapotranspiration (**left**) and runoff (**right**) rates in all research sites. Abandoned means abandoned peat extraction site.

3.3. DOC Efflux from Peatlands

Similarly to monthly mean DOC concentrations in groundwater, the mean monthly DOC efflux generally showed similar patterns, when comparing different land use types. Overall, for all studied land use types, the mean monthly DOC efflux was 23.5 ± 6.0 kg ha^{-1} month^{-1}. The highest DOC efflux was observed in active peat extraction sites (42.7 ± 11.6 kg ha^{-1} month^{-1}), followed by abandoned sites without vegetation (34.5 ± 9.1 kg ha^{-1} month^{-1}), Scots pine forests (27.3 ± 6.9 kg ha^{-1} month^{-1}), and abandoned sites with shrub vegetation (27.2 ± 6.9 kg ha^{-1} month^{-1}). In silver birch forests, the DOC efflux was significantly lower than in Scots pine forests (12.8 ± 3.3 kg ha^{-1} month^{-1}), while the lowest was observed in cropland (6.4 ± 1.5 kg ha^{-1} month^{-1}) and grassland (5.1 ± 1.3 kg ha^{-1} month^{-1}, Figure 6). Compared to the overall mean value of monthly DOC efflux (23.5 ± 6.0), the most noticeable differences in DOC efflux occurred in active peat extraction sites and abandoned peat extraction sites without vegetation, which showed the highest mean monthly DOC efflux. However, while Scots pine forests exhibit the highest DOC concentrations, the greater runoff in areas without vegetation resulted in a higher DOC efflux despite their lower DOC concentrations. This increased runoff is due to lower evapotranspiration in areas without vegetation cover, which, in turn, leads to elevated DOC efflux.

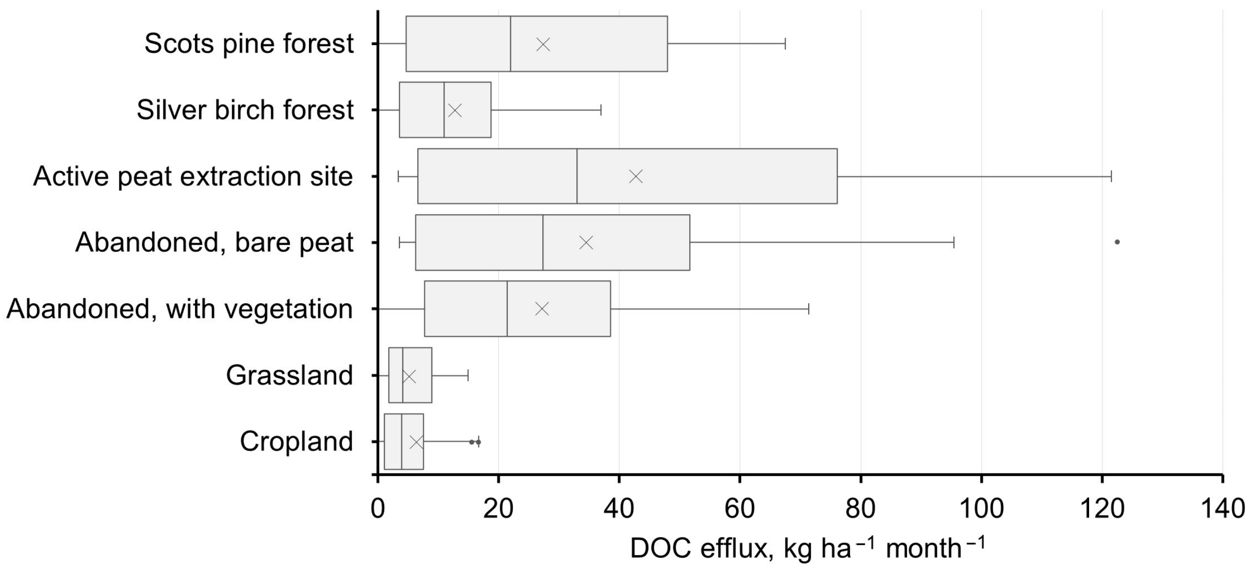

Figure 6. Mean monthly DOC efflux by land use type, each represented with 24 measurements (n = 168). The rectangles are located within the first to third quartile range. The intercepts range from the zeroth to fourth quartile. Dots represent extremes. The rectangles are divided by the median. "x" represents the arithmetic mean value. Abandoned means abandoned peat extraction site.

The highest annual DOC efflux values (Figure 7) were observed in areas without vegetation—active peat extraction sites (513.1 ± 38.7 kg ha^{-1} y^{-1}) and abandoned peat extraction sites without vegetation (413.9 ± 30.3 kg ha^{-1} y^{-1}). Comparatively high DOC efflux was also observed in Scots pine forests (328.3 ± 23.1 kg ha^{-1} y^{-1}) and in abandoned peat extraction sites with shrub vegetation (326.1 ± 22.9 kg ha^{-1} y^{-1}). In the silver birch forests, annual DOC efflux was comparatively low (153.6 ± 11.2 kg ha^{-1} y^{-1}), but the lowest was in croplands (62.1 ± 5.0 kg ha^{-1} y^{-1}) and grasslands (61.9 ± 4.4 kg ha^{-1} y^{-1}).

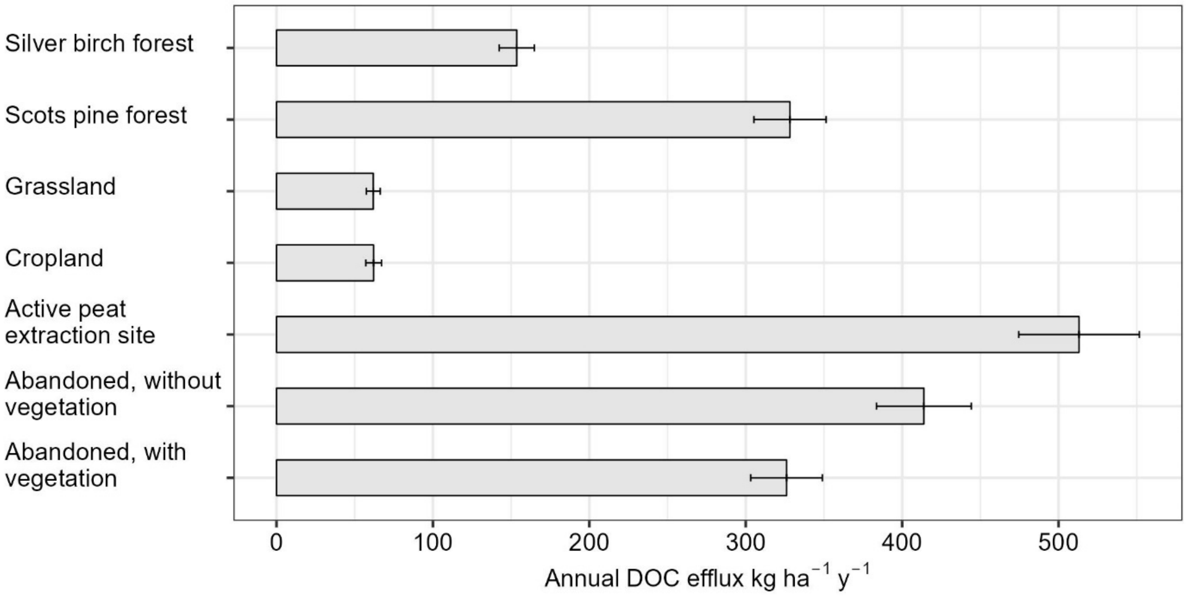

Figure 7. Estimated annual DOC efflux from each land use type, each represented by 24 concentration measurements and runoff estimates (n = 168). Whiskers indicate S.E. Abandoned means abandoned peat extraction site.

3.4. Evaluation of Affecting Factors

The monthly mean DOC concentration was correlated with several physical and chemical variables of groundwater (Figure 8). Statistically significant ($p < 0.05$) correlations for DOC concentrations were observed with groundwater pH (ρ = −0.65), EC (ρ = −0.73), Ca (ρ = −0.70), and Mg (ρ = −0.73) concentrations. Although weak (ρ = 0.22), a statistically significant ($p < 0.05$), positive correlation between DOC concentration and WL in the ditch was observed. The other parameters did not show a significant correlation with DOC concentrations.

The explanatory power (R^2 = 0.67) of the PLS model revealed that different factors affect DOC concentration levels and the usefulness of PLS model. VIP scores calculated from the model elucidated the relative importance of the predictors. Notably, water chemical properties—specifically EC, Mg, Ca, and pH—emerged as the most critical variables, with VIP scores of 1.84, 1.83, 1.79, and 1.65, respectively, when analyzing our dataset with all land use types. These scores, which are inter-related, affirm the significant influence of water chemical composition, including acidity on DOC concentrations. Additional variables, such as K, TN, and the WL in the ditch, also showed substantial influence depending on the land use type.

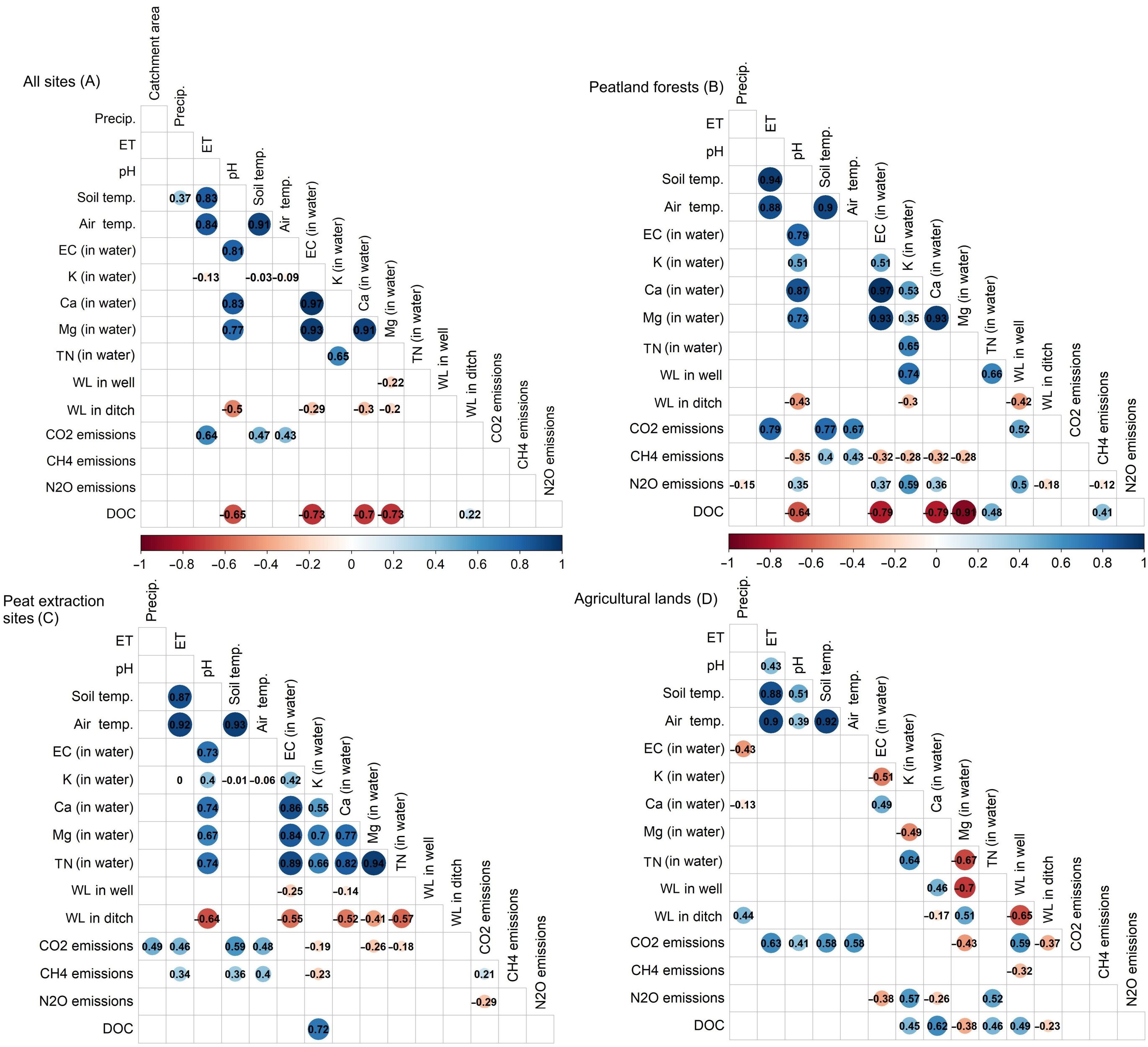

Figure 8. Correlation matrix for each land use type group. All sites (**A**) consist of all research sites, Peatland forests (**B**) consist of Scots pine forests and silver birch forests; peat extraction sites (**C**) consist of active peat extraction sites and abandoned peat extraction sites with and without vegetation; and agricultural lands (**D**) consist of croplands and grasslands. Red indicates negative correlation; blue indicates positive correlation; blank indicates insignificant correlation ($p > 0.05$).

In peatland forests, DOC concentrations in groundwater were negatively correlated with water pH (ρ = −0.64), EC and Ca concentration (ρ = −0.79), and Mg concentration (ρ = −0.91), while positively correlated with instantaneous CH_4 emissions from drainage ditches (ρ = 0.41), as well as with TN concentrations in groundwater (ρ = 0.48). A PLS model (R^2 = 0.74) revealed that the most influential parameters on CH_4 emissions are water pH, EC, Ca, and Mg concentrations, with VIP scores >1.5, but CH_4 emissions from drainage ditches and TN concentration in groundwater showed VIP scores 0.9 and 1.05, respectively.

DOC concentrations in peat extraction sites were significantly and strongly positive correlated with K concentration (ρ = 0.72) and PLS model was weak (R^2 = 0.34).

In agricultural lands (grasslands and croplands), the analysis revealed slightly different correlations compared to other land use types; DOC was positively correlated with Ca concentration (ρ = 0.62), WL in wells (ρ = 0.49), TN (ρ = 0.46), and K concentration (ρ = 0.45), and negatively correlated with the Mg concentration (ρ = −0.38) and WL in ditches (ρ = −0.23). The PLS model (R^2 = 0.54) revealed that variation was mostly explained by Ca, K, and TN concentrations and the WL in wells, with VIP scores of 1.6, 1.4, 1.3, and 1.1, respectively.

In all research sites, the most important variable was EC in water (R^2 = 0.54); however, excluding one outlier (research Site 10), the coefficient increased significantly (R^2 = 0.71). In peatland forests, the most important affecting variable was the Ca concentration in groundwater (R^2 = 0.76), but in peat extraction sites, the K concentration in groundwater showed the highest non-linear relationship (R^2 = 0.74, Figure 9).

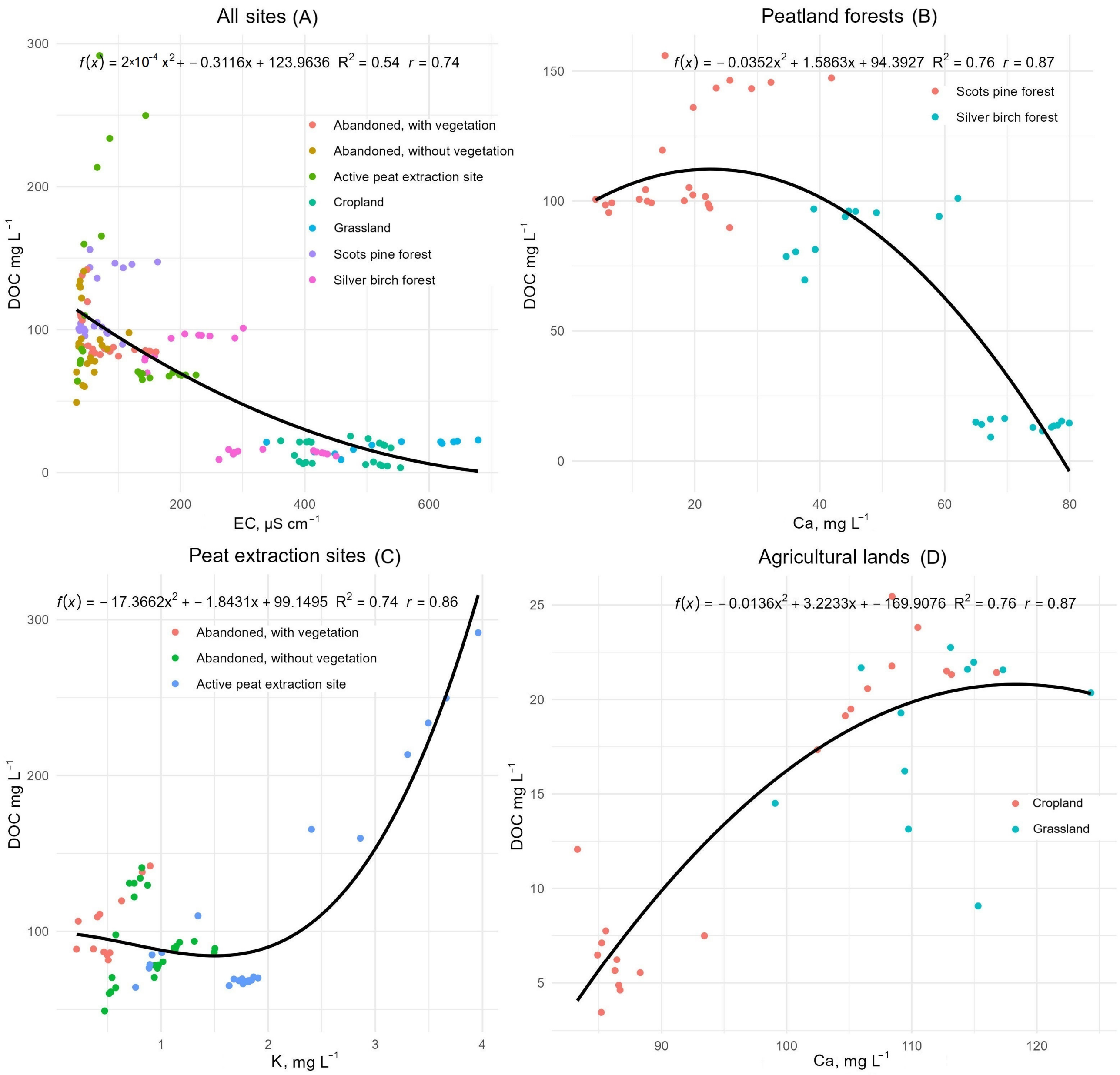

Figure 9. Most significant individual regressions between monthly mean DOC concentrations and different parameters of groundwater chemical composition in different types of land use. All sites (**A**) consist of all research sites, Peatland forests (**B**) consist of Scots pine forests and silver birch forests; peat extraction sites (**C**) consist of active peat extraction sites and abandoned peat extraction sites with and without vegetation; agricultural lands (**D**) consist of croplands and grasslands. Abandoned means abandoned peat extraction site.

4. Discussion

4.1. DOC Efflux and Affecting Factors

Comparing our results to other studies—for example, a large-scale study [47] that examined 62 sites across the globe (51 boreal and temperate peatlands and 11 tropical peatlands) and revealed that annual DOC efflux from peatlands may vary between 14 and 948 kg ha^{-1} y^{-1}, averaging 244 ± 219 kg ha^{-1} y^{-1}—it can be concluded that our results are similar and comparable to the results from temperate and boreal climate zones. The amount of DOC efflux increases from colder to tropical climates, and it is influenced by thermal gradient, which contributes to other large studies [16,48]. Across both drained and natural sites, peatlands in boreal (137 kg ha^{-1} y^{-1}), temperate (242 kg ha^{-1} y^{-1}), and tropical regions (579 kg ha^{-1} y^{-1}) showed significantly different amounts of DOC efflux. Disturbed sites had significantly higher annual DOC efflux than those from undisturbed naturally wet sites, showing means of 307 ± 231 and 185 ± 193 kg ha^{-1} y^{-1}, respectively [16,48]. Our results revealed that among all studied land use types of peatlands, the mean annual DOC efflux varied from 61.9 ± 4.4 kg ha^{-1} y^{-1} in grasslands to 513.1 ± 38.7 kg ha^{-1} y^{-1} active peat extraction sites. Silver birch (153.6 ± 11.2 kg ha^{-1} y^{-1}) and Scots pine forests (328.3 ± 23.1 kg ha^{-1} y^{-1}) are common in Latvia, where more than 10% of the total area is covered by peatlands [11,12]. The DOC efflux from Scots pine forests and all peat extraction sites coincided with values from the temperate climate zone, while efflux from silver birch forests, croplands, and grasslands were more comparable to the results from the boreal zone, which contributes to previous findings about the thermal gradient impact.

The default DOC efflux factor in naturally wet temperate and boreal peatlands is provided by the Intergovernmental Panel on Climate Change (IPCC) guidelines [49]. Tier 1 is 210 and 80 kg C ha^{-1} y^{-1}, respectively, and the impact of drained organic soils is expressed with a default coefficient of 0.6 to be used as a 60% increase compared to naturally wet peatlands. Those coefficients were obtained from a range of studies conducted in different boreal peatlands in Scandinavian countries and Canada (37–159 kg C ha^{-1} y^{-1}), and in temperate zones (53–360 kg C ha^{-1} y^{-1}, [49]). In our study, the mean annual DOC efflux from drained peatlands with different land use types was 265.5 ± 66.6 kg C ha^{-1} y^{-1}. Our mean drained peatland DOC efflux value is comparable to the value provided by the IPCC guidelines for temperate climate zones. In Scots pine forests and abandoned peat extraction sites with vegetation, this value fell within the guidelines; however, in active peat extraction sites and abandoned sites without vegetation, DOC efflux was higher. Moreover, in silver birch forests, the DOC efflux of croplands and grasslands was significantly lower. This indicates that the emission factors provided in the IPCC guidelines for temperate climate zones characterize DOC emissions in Latvia incompletely and, depending on the land use type of peatland, emissions may be lower (Table 5).

Table 5. Comparison of the annual DOC efflux in different types of land use estimated within this study with IPCC default DOC emission factors for temperate climate zone. Δ DOC is proportional increase (1 + Δ DOC) in DOC flux from drained peatlands relative to naturally wet peatlands.

Land Use Type	IPCC DOC Efflux (Natural) (kg C ha^{-1} y^{-1})	IPCC ΔDOC (Drained)	IPCC DOC Efflux (Drained) (kg C ha^{-1} y^{-1})	DOC Efflux in Our Research Sites (kg C ha^{-1} y^{-1})	ΔDOC (Drained) in Our Research Sites
Scots pine forest	210 (170–260)	0.6	340 (270–420)	328.3 ± 23.1	0.56
Silver birch forest				153.6 ± 11.2	-
Active peat extraction site				513.1 ± 38.7	1.44
Abandoned extraction site with vegetation				326.1 ± 22.9	0.55
Abandoned extraction with bare peat				413.9 ± 30.3	0.97
Grassland				61.9 ± 4.39	-
Cropland				62.1 ± 5.0	-
Mean				265 ± 66.6	-

Our findings indicate that our applied methodology for calculating runoff, evapotranspiration and, accordingly, DOC efflux using a calculation of the total ecosystem water balance provides comparable results to the values obtained using other modeling and direct measurements. The advantage of such a methodology is the possibility to calculate the total runoff of the ecosystem and catchment area, compared to direct runoff measurement methods by measuring surface stream runoff; it is also possible to calculate the runoff of smaller catchments without direct measurements. However, the disadvantages of such an approach should also be considered, such as the challenges of including various physical parameters of the catchment in the calculation [50], and an uncertainty of soil moisture and the variety of evapotranspiration correction coefficients [51]. Some studies [52,53] have highlighted how soil properties, such as the degree of soil organic matter decomposition, soil pH, and texture, affect DOC composition and biodegradability.

4.2. DOC Concentrations and Affecting Factors

In Finland, Rasilo et al. [54] also studied DOC efflux from mixed forest peatland catchment and obtained similar yet higher DOC concentrations in GW compared to our study, ranging from 43 mg L^{-1} in spring to 123.0 mg L^{-1} in autumn, pointing to seasonal differences, which we did not observed in our case. Only one research site (Site 10), which was an active peat extraction site, showed a similar trend, with significantly increasing DOC concentrations from August to October. In a study conducted in Canada, Thompson et al. [55] estimated slightly lower runoff, 80–213 to 164–236 mm y^{-1}, respectively, compared to our estimations, where the annual runoff varied from 307 mm in silver birch forests to 423 mm in active and abandoned peat extraction sites without vegetation.

A recent study in Finland [56] identified several factors influencing variations in DOC concentrations, with stream sulfate (SO_4) concentrations standing out as the predominant driver. This aligns with findings that decreasing SO_4 concentrations significantly impact long-term increases in DOC trends, acting as a primary control mechanism. This conclusion is supported by previous research in Krycklan, Sweden, which examined the DOC and SO_4 relationship in soil water, as reported by Ledesma et al. [57]. That study also noted that concentrations of Ca, Mg, and other basic cations significantly influence DOC concentrations. Laudon et al. [58] further mentioned that drops in basic cation concentrations, linked with decreases in SO_4 concentrations, influence water acidity, leading to higher DOC solubility and pH drops [59].

Negative correlations between the DOC concentration and Ca and Mg concentrations have been observed in several other studies. For example, prior research in drained soils in Canada found a negative correlation between DOC concentrations in groundwater and pH values, attributing this trend to pH levels [60]. Elevated DOC concentrations under acidic conditions are associated with the dissociation of hydrogen atoms from carbonic acids, which become hydrogen ions. As pH levels drop below the pKa value of organic materials, DOC sorption in groundwater increases, leading to higher concentrations [61,62]. Although sulfur compounds were not analyzed in our study, we found a significant negative correlation between pH and DOC. These findings suggest that basic cations such as Ca and Mg play a crucial role in regulating pH and electrical conductivity (EC) in water, which in turn affects DOC solubility and concentrations.

In our case study, the annual mean DOC concentration in different land use types showed a statistically significant relationship with Ca and Mg concentrations. The mean Ca concentration in GW across all research sites was 42 mg L^{-1}, while for Mg it was 7.6 mg L^{-1}. The mean Ca and Mg concentrations are considerably higher in cropland (averaging 97.2 mg L^{-1} Ca and 17.9 mg L^{-1} Mg), grasslands (108.7 mg L^{-1} and 25.6 mg L^{-1}, respectively) and silver birch forests (59.03 mg L^{-1} Ca and 11.48 mg L^{-1} Mg). Higher concentrations of Ca and Mg in those land use types were accompanied with significantly higher pH values (7.18–7.81) compared to Scots pine forests and all peat extraction sites (pH 5.22–6.29). In croplands and grasslands, this can be attributed to historical liming practices common in Latvian agriculture and higher peat decomposition levels [63,64].

Liming with Ca- and Mg-containing fertilizers, such as wood ash or dolomite lime, is used to increase soil pH for favorable agricultural conditions [63,65,66].

Silver birch forests, where the mean Ca and Mg concentrations were also significantly higher, may be receiving basic cations from groundwater, providing a higher concentration of these nutrients accordingly [67]. In Scots pine forests, the Ca and Mg concentrations were low (averaging 18.5 mg L^{-1} Ca and 0.8 mg L^{-1} Mg), similar to active peat extraction sites and abandoned extraction sites. An increasing DOC concentration was paralleled by a statistically significant decrease in Ca and Mg concentrations, indicating increasing DOC in groundwater, being less bound to soil, influenced by Ca and Mg sorption in the soil [60,68]. Differences in DOC and Ca and Mg concentrations in our research sites may also be influenced by bedrock material, on which peatland has developed [69]. In Latvia, bedrock and groundwater are mostly neutral or slightly alkaline [70]. Even though these factors, such as bedrock material, were not considered in our study, they may have influenced peat chemical properties due to capillary effects, plant uptake, and litter input.

5. Conclusions

DOC concentrations in groundwater in drained peatlands vary significantly depending on land use types; it is necessary to continue to monitor patterns of these concentrations. Patterns of DOC concentrations and their affecting factors did not fluctuate significantly within the year, except in active peat extraction sites, which showed that peat extraction is of fundamental importance to DOC concentrations. Croplands and grasslands were the most insignificant sources of DOC; the main drivers of lower DOC concentrations were the availability of nutrients compared with other sites, which is affected by pH. In peatland forests, the DOC concentration was mostly explained by concentrations of Ca and Mg, but in peat extraction sites, the K concentration in water had the highest influence. We did not identify an impact of water level in the ditches and the groundwater level on DOC concentrations. DOC efflux was mostly influenced by DOC concentration and evapotranspiration in different land use types. The study results indicate that peat extraction site afforestation with silver birch can reduce DOC efflux from peatland, but sites with active peat extraction and abandoned peat extraction sites without vegetation are significant sources of DOC. It is necessary to improve runoff and evapotranspiration estimates, as well as catchment area characterization, using elevation and satellite data to obtain more site-specific runoff and DOC efflux data. The obtained DOC efflux depending on land use type can be considered when selecting the most suitable peatland restoration techniques, and can be included in national calculations of a C stock changes and GHG emissions.

Author Contributions: Conceptualization, A.L.; methodology, R.N.M. and A.L.; software, R.N.M. and E.M.U.; validation, A.B. (Aldis Butlers), A.B. (Arta Bārdule) and A.L.; formal analysis, R.N.M.; investigation, R.N.M., S.K. and A.B. (Aldis Butlers); resources, A.L.; data curation, A.L.; writing—original draft preparation, R.N.M.; writing—review and editing, A.B. (Aldis Butlers), A.B. (Arta Bārdule); visualization, R.N.M. and E.M.U.; supervision, A.L.; project administration, A.L.; funding acquisition, A.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Forest Sector Competence Center Project No. 5.1.1.2.i.0/1/22/A/CFLA/007, "Prototype and datasets of the Carbon-Binding Forestry Planning Program", and Fundamental and Applied Research Program Project No. LZP-2021/1-0137, "Evaluation of factors affecting greenhouse gas (GHG) emissions from surface of tree stems in deciduous forests with drained and wet soils".

Data Availability Statement: Data are available on request made to the corresponding author Raitis Normunds Meļņiks.

Acknowledgments: R.M.'s contribution was supported by the European Regional Development Fund project "Evaluation of factors affecting greenhouse gas (GHG) emissions reduction potential in cropland and grassland with organic soils" (1.1.1.1/21/A/031) and doctoral grant project (No. 8.2.2.0/20/I/006). A.L.'s contribution was funded by the European Regional Development Fund project, No. 1.1.1.1/19/A/064, "Development of greenhouse gas emission factors and decision support tools for management of peatlands after peat extraction".

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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