MOORS FOR THE FUTURE PARTNERSHIP

MONITORING THE BIODIVERSITY AND ECOSYSTEM SERVICE IMPACTS OF RESTORATION OF DEGRADED BLANKET BOG SITES

CHAPTER 6: WATER CHEMISTRY

MoorLIFE 2020

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Monitoring the biodiversity and ecosystem service impacts of restoration of degraded blanket bog sites

Chapter 6: Water Chemistry

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1. Summary

Application of lime to bare peat restoration sites caused short-term spikes in calcium concentration and elevated pH. These chemical shifts were associated with short-term reductions in Dissolved Organic Carbon (DOC) concentration but long-term patterns of DOC concentration and flux were unaffected. Similarly, calcium concentrations recovered to baseline within 48 months of the final lime application. There is no long-term trajectory of pH associated with the treatment, up to 11 years after initial treatment.

The data indicate that the direct chemical impact of the restoration intervention was rapidly flushed from the system and that dissolved carbon fluxes were not significantly modified by the restoration activity beyond an immediate short-term impact. It seems likely that water table drawdown associated with the deep gully systems, the morphology of which cannot be fully restored, was a more important control on DOC concentration than surface processes.

On the single species dominated sites, data collected over the period of the study suggested that planting *Sphagnum* may have had an impact on chemistry of water leaving the catchments. Small decreases in electrical conductivity (EC) and DOC concentrations were observed, although the majority of these were not statistically significant. Planting *Sphagnum* had no statistically significant impact on the character of DOC in the water during the monitoring period, although small, non-significant changes in E4:E6 and specific absorbance ($SUVA_{254}$) were observed. Planting *Sphagnum* did not change the pH.

The gully blocking on the *Calluna* site 'SphaGB' catchment had no statistically significant effect on EC, DOC concentration or DOC character, although small (non-significant) changes were observed (increased EC, DOC concentration and E4:E6; decreased $SUVA_{254}$). No change was observed in the pH of the water leaving the catchment.

Planting *Sphagnum* at lower densities (4 plugs m^{-2}) has the potential to decrease DOC concentrations in overland flow and soil solution. The DOC concentration appeared to decrease in all four intervention catchments after low density *Sphagnum* planting, although changes were small and not all were statistically significant.

Planting *Sphagnum* at high densities (100 plugs m^{-2}) has the potential to decrease DOC concentrations in overland flow and soil solution. At the *Calluna* site there were apparent decreases in DOC concentrations in overland flow and soil solution, although these changes were not statistically significant. At the *Eriophorum* site, no clear changes in DOC concentration were observed. At the *Molinia* site small increases in DOC concentrations were observed (some but not all changes were statistically significant).

The DOC flux from *Calluna* and *Molinia* catchments appeared to be decreased by planting *Sphagnum*, but conversely there was found to be no clear change in DOC flux after planting in *Eriophorum* catchment.

All results from the sites dominated by single species are from the first 2.5 years following intervention – during this time any expected effects of treatment would be small, so these findings should be treated with caution and viewed only as possible early indications of future trajectories of change. Further monitoring is required to assess the medium and long-term effects of treatment.

2. Introduction

Historic degradation of peatlands across the South Pennines led to large areas of bare peat, severe erosion, lowering of water tables and dominance of single vegetation species, as described in the introductory annex of this report. This degradation, as well as restoration methods used on these peatlands, may have implications for water chemistry.

2.1. Peatland degradation

As discussed in Spencer and Evans (2016), a combination of human and natural influences has led to severe degradation of peatlands in the uplands of the South Pennines and Peak District (Tallis, 1998). Widespread erosion caused loss of vegetation cover and generated large expanses of bare peat and deeply incised gully networks. Subsequent drying of the peat mass restricted the possibility of vegetation recovery and increased rates of erosion. This contributes to increased concentrations of dissolved and particulate organic carbon and other nutrients or pollutants in the waters draining from these headwater catchments (Bussell *et al.*, 2010), with financial implications for utility companies removing these substances from drinking water supplies (Wallage *et al.*, 2006), as well as environmental impacts on the global carbon cycle including fluvial conversions of dissolved and particulate organic carbon (DOC and POC) to carbon dioxide (CO_2) (Evans *et al.*, 2013).

During and since the Industrial Revolution, rates of deposition of industrial pollutants including sulphur and nitrogen have been high. While nitrogen stimulates Net Primary Productivity (NPP) in plants, the acidification of the peat surface by the sulphur has historically negated this effect. However, since the 1970s, rates of sulphur deposition have declined, due to efforts to reduce human-driven atmospheric pollution. With the resulting increase in soil pH, combined with possible changes in climate, the historically deposited nitrogen store is being activated, causing an increase in NPP, and therefore DOC (Monteith *et al.*, 2015).

2.1.1. Dissolved organic carbon (DOC)

DOC is a complex group of organic carbon-containing compounds, including aromatic, phenol and carboxyl groups. These compounds contain other elements – usually hydrogen, oxygen and nitrogen. The composition (elemental and structural) varies based on site characteristics (e.g. soil and vegetation cover, land management, peat depth), weather, climate and location. DOC in peatland waters is derived from humic substances, and contains humic and fulvic acids. Absorbance at different parts of the spectrum ('colour' of the water) can give some indications about the ratio of humic to fulvic components of DOC; the E4:E6 ratio is the absorbance at 465 nm divided by 665 nm (Peacock *et al* 2014). Higher E4:E6 ratios indicate more fulvic DOC.

The structure of compounds in DOC is important for water treatment processes, and for natural photo- and biodegradation of DOC (the processes by which DOC is converted to smaller molecules or CO_2). Specific UV absorbance ($SUVA_{254}$: absorbance at 254 nm divided by DOC concentration) is considered a proxy for the aromatic carbon content of the water – studies have shown correlation between $SUVA_{254}$ and aromatic carbon compounds when analysed by ^{13}C NMR (Weishaar *et al* 2003). Highly aromatic DOC has a higher molecular weight, is more sensitive to changes in pH (Pschenyckyj *et al* 2020), and is generally derived from terrestrial sources (rather than produced in the water). Highly aromatic DOC compounds react differently during chlorination and coagulation to compounds with lower aromatic content, and can form disinfection by-products during water treatment (Williams *et al* 2019).

2.2. Peatland Restoration and Potential Impacts on Water Quality

Peatland stabilisation has been undertaken at the landscape scale on extensive areas of bare and eroding peat in the South Pennines, as detailed in Buckler *et al.* (2013). Work has focused on:

- Stabilising the large contiguous areas of bare and eroding peat through establishing and subsequently diversifying vegetation cover through the application of heather brash, amenity/local grass and heather seeds, granulated lime and fertiliser (three annual summer applications by helicopter-suspended hopper, see Table 1), *Sphagnum* mosses and other moorland species plug plants.
- Rewetting the peat mass and slowing the flow (and therefore reducing the erosional force) of storm-water from the headwaters to the river networks by blocking gullies and grips using stone, timber, plastic or peat dams.
- Planting *Sphagnum* mosses to encourage carbon sequestration, enhance the temporary water storage capacity of the vegetation canopy and increase hillslope surface roughness to reduce overland flow velocities.
- Improving footpaths to reduce erosion due to high footfall on popular walking routes.

Table 1: Typical lime and fertiliser components and application rates used by MFFP (Pilkington, 2015)

	Granulated lime components	**Application rate**	**Granulated fertiliser components**	**Application rate**
Year 1	98% Ca, 0.5% Mg, 1% Si_2	1000 kg/ha	40 N : 120 P_2O_5 : 60 K_2O	361 kg/ha
Year 2	98% Ca, 0.5% Mg, 1% Si_2	1000 kg/ha	40 N : 60 P_2O_5 : 60 K_2O	278 kg/ha
Year 3	98% Ca, 0.5% Mg, 1% Si_2	1000 kg/ha	40 N : 60 P_2O_5 : 60 K_2O	278 kg/ha

Granulated lime and fertiliser are applied to bare peat treatment sites to create soil conditions in which the nurse crop species can survive. Pre-treatment soil conditions are characterised by very low pH (2.5–3) and nutrient levels (Buckler *et al*., 2013). Caporn *et al.* (2007) found that lime and fertiliser are required in combination with each other to promote successful plant establishment and development at degraded bare peat sites. The calcium and magnesium components of lime were in the form of calcium carbonate and magnesium carbonate respectively.

These works may have a range of implications for water quality. Whilst some studies have suggested restoration may lead to short and/or longer-term reductions in DOC and water colour (Evans *et al*., 2015, Wallage *et al*., 2006), others report increases (Strack *et al*., 2011). Additionally, some studies suggest that DOC production is increasing in UK upland catchments, regardless of specific restoration works (Monteith *et al*., 2015).

The application of lime and fertiliser has been shown to result in short-term increases of pH and fluvial concentrations of the components of these treatment products, but the longer-term impacts, and the residency times of these components in the headwater streams are, as yet, unclear. The increase in pH could lead to interactions with metal pollutants stored in the peat mass and the organic materials that produce DOC (Rothwell *et al*., 2007; Stimson, 2015).

This study extends datasets previously reported in Spencer and Evans (2016), where five years of data were presented, including 18 months of data after the final application of lime. The current study adds an additional five years of data, providing important new evidence of the impacts on water chemistry of bare peat restoration techniques.

In addition to presenting extended bare peat restoration data, this study examines the impacts of *Sphagnum* introduction on water quality in areas dominated by a single species: *Calluna vulgaris*, *Eriophorum vaginatum* and *Molinia caerulea*. *Sphagnum* species are important for peatland carbon storage, and introducing *Sphagnum* to areas of land dominated by vascular plants can increase carbon storage. However, studies that demonstrate significant change in surface water quality as a result of *Sphagnum* planting are scarce (Ritson *et al,* 2017), despite several studies showing that the type of vegetation on a peatland can influence the production and release of DOC (Armstrong *et al,* 2012).

The water chemistry at three sites dominated by the species listed above, were monitored over a four year period, in order to examine the impact of planting *Sphagnum* moss plugs at varying densities across mini-catchments.

3. Methodology

3.1. Data collection

3.1.1. Bare peat sites

Water samples were collected at field lab sites F (bare peat control), O (revegetated), N (revegetated, gully-blocked and *Sphagnum*-planted) and P (intact reference) from 2011–2020. All samples were collected in 30 ml plastic sampling tubes from stream discharge flowing through the v-notch weir at each mini-catchment. All sample tubes were triple-rinsed in stream water before sampling. If there was no flow (during dry periods), samples were not collected. All samples were then stored in an opaque bag while on site and refrigerated until they were analysed in the laboratory.

Samples were collected during routine visits to the field labs. Frequency of sampling visits varied (from fortnightly to monthly) through the monitoring period. Samples were collected in a range of flow conditions but none from high-flow events; the majority were from baseflow.

3.1.2. Species dominated sites

On each site visit (approximately monthly) between 2018 and 2021, water samples were collected from every piezometer, crest stage tube and weir (a maximum of 448 water samples collected, if there was water present in all sampling locations). All samples were collected in pre-rinsed 50 ml plastic tubes. All samples were then stored in an opaque bag while on site and refrigerated until they were analysed in the laboratory. See the Introduction chapter of this report for further details on sample collection procedure.

Due to analysis constraints, these samples were amalgamated into a smaller number of samples per catchment for analysis, as shown in Table 2.

Table 2. The number of water samples collected from each species dominated site and catchment per visit.

Vegetation	Catchment	Location	Surface water (weir)	Overland flow (0 cm)	5 cm soil water	10 cm soil water	Samples collected	Samples analysed
CAL	**Con**	Weir (WE)	1				1	1
		Cluster (CL)		15	15	15	45	3*
		Intensive (IN)		6	6	6	18	3*
	Spha	WE	1				1	1
		CL		15	15	15	45	3*
		IN		6	6	6	18	3*
	SphaGB	WE	1				1	1
		CL		15	15	15	45	3*
		IN		6	6	6	18	3*
ERI	**Con**	WE	1				1	1
		CL		15	15	15	45	3*
		IN		6	6	6	18	3*
	Spha	WE	1				1	1
		CL		15	15	15	45	3*
		IN		6	6	6	18	3*
MOL	**Con**	WE	1				1	1
		CL		15	15	15	45	3*
		IN		6	6	6	18	3*
	Spha	WE	1				1	1
		CL		15	15	15	45	3*
		IN		6	6	6	18	3*
TOTAL	**7**						**448**	**49**

On one occasion before, and one after catchment intervention (*Sphagnum* planting and gully blocking), the water samples collected from the catchments were not amalgamated, and so the number of samples analysed was the same as the number of samples collected (n = 448, Table 2). These samples were analysed in order to look at the spatial variation in the water chemistry. This was carried out in January 2019 (before intervention) and November 2019 (after intervention).

3.2. Water chemistry analysis

3.2.1. Bare peat sites

At the laboratory, samples were filtered at 0.45 microns. From 2011-2014, samples were analysed colorimetrically using a Hach spectrophotometer. Absorbance was measured at 254 nm, 400 nm, 465 nm and 665 nm; absorbance at 400 nm was used as a proxy for DOC in 2011. From 2012 onwards DOC was also measured directly, as non-purgeable organic carbon (NPOC) via UV-persulphate oxidation on a Shimadzu TOC analyser. Water chemistry was analysed by ICP-OES and Ion chromatography to provide contextual data.

3.2.2. Species dominated sites

The pH and conductivity of the amalgamated routine water samples were measured by Moors for the Future Partnership as soon as possible after collection. The absorbance at eight wavelengths (665, 470, 465, 436, 400, 360, 265 and 254 nm) was measured by UV-Vis spectrophotometry at the University of Leeds. Before intervention, the DOC concentration of the water samples was measured in order to calculate a relationship between the absorbance and carbon concentration (Equation 1; Equation 2; Equation 3). The DOC concentration was measured on samples collected in September 2019 in order to check the relationship between absorbance and carbon concentration. The DOC concentration was measured on all samples taken for the spatial survey.

3.3. Data processing and analysis

3.3.1. Bare peat sites

Results from previous studies of the 2011–2014 data (Evans *et al* 2015; Spencer & Evans 2016) highlighted the need for further monitoring to focus on dissolved organic carbon (DOC), pH and calcium.

3.3.1.1. Dissolved organic carbon (DOC)

2011 data were converted from absorbance to DOC, primarily using Abs_{400} data. Data from all four wavelengths were tested using the Kruskal-Wallis independent samples test for treatment effect to see whether the DOC:Absorbance relationship was affected by treatment (application of lime may affect pH which may, in turn affect the type of DOC – and therefore the absorbance at different wavelengths – as well as the amount). Where a significant effect was noted, these wavelengths were excluded before a multiparameter model was fitted in cases where this significantly increased the fit above using 400nm alone. 2012 data onwards did not need processing in this way as they were from direct measurements. The different method used in the pre-treatment year could be a possible source of error in the analysis.

Preliminary analysis of the 2011–2020 DOC data suggested no relative change in DOC concentration between control (F) and treatment (O, N) sites but that discharge had changed (see the Stream Discharge chapter of this report). Therefore, it was possible that DOC load may have changed – if it were static, an increase in discharge would cause a dilution in concentration. DOC instantaneous load (mg/s) was calculated by multiplying daily mean discharge from the day of sampling (l/s) by DOC concentration (mg/l).

DOC instantaneous load data from field labs F, O and N were compared using a paired BACI design. This reduced the available dataset due to the requirement to have both DOC and discharge data from all three sites for any one datapoint. Initial applications of lime started in autumn 2011 so data were only available for the baseline year from January to July. To avoid bias in post-treatment data, August-December data were excluded from all years, further reducing the size of the dataset.

DOC instantaneous load data were not calculated for field lab P due to gaps in the stream discharge dataset. DOC concentration data were available and were processed to provide context for DOC concentration data from field labs F, O and N.

Where data were available, relative DOC instantaneous load and concentration (treatment-control) was calculated to isolate any effects on DOC of the treatment itself.

3.3.1.2. Calcium and pH

Calcium concentration and relative calcium concentration (treatment-control) were calculated to isolate any effects of the treatment itself; data from intact reference P provided context for results. The Kruskal-Wallis test was used to test for differences in calcium concentration between all four field labs for 2017–2020 (following the likely cessation of any short-term effect of the application of lime).

pH data were analysed for directional trends at each field lab; the Kruskal-Wallis test was used to test for differences between the field labs in 2017–2020 (following the likely cessation of any short-term effect of the application of lime).

3.3.2. Species dominated sites

The water chemistry data were analysed to answer three main questions:

1. Was there a difference in water chemistry at the catchment outlet between the control and intervention catchments?
2. How did different *Sphagnum* planting densities impact water chemistry?
3. How much carbon was lost from the catchments during the experiment?

Statistics were carried out where the box and whisker plots indicated there might be significant differences. Non-parametric, one-way Mann-Whitney U statistics were used to compare the 'before' (BACI year 0) to the 'after' (BACI year 1, 2 and 3 combined) relative metrics (Spha relative to Con, or SphaGB relative to Con).

3.3.2.1. Dissolved organic carbon (DOC)

The DOC concentrations were used to calculate a flux estimate for each weir. The total daily water discharge over each weir was calculated from the continuous logger records (L day^{-1}). The DOC concentrations were measured or modelled from water collected approximately every month, so these values were used to model a daily DOC concentration with a simple 45 day moving average. This resulted in 736 days with discharge and DOC concentration data at the *Calluna* site, 777 days at *Eriophorum*, and 816 days at *Molinia*. In order to compare fluxes, the catchment areas (Table 3) were used to calculated flux as grams of Carbon per day per m^2.

Table 3. Species dominated catchment areas (hectares)

Catchment name	Area (hectares)
Cal Con	0.74
Cal Spha	0.49
Cal SphaGB	0.59
Eri Con	0.73
Eri Spha	1.21
Mol Con	1.19
Mol Spha	2.52

The modelled DOC concentrations were compared to the measured DOC concentrations, and a paired t-test was carried out to see if the modelled and measured values were significantly different. The residual DOC values (the difference between the measured and modelled DOC concentrations) were plotted against the measured DOC concentrations, so see how the modelled values compared over the range of measured values.

3.3.2.2. *Calluna* site absorbance and colour

The calculated DOC concentration was modelled using all water samples taken from the CAL sites before intervention (including the spatial survey samples). The best model was found using three wavelengths (265, 360 and 400 nm):

$$DOC_{CAL} = 5.44 + (3.12 * abs_{400}) - (2.57 * abs_{360}) + (0.52 * abs_{265})$$

Equation 1: the modelled DOC concentration at CAL. N = 227; R^2 = 0.8592, adjusted R^2 = 0.8573

3.3.2.3. *Eriophorum* site absorbance and colour

The calculated DOC concentration was modelled using absorbance at four wavelengths: 470, 360, 265 and 254 nm:

$$DOC_{ERI} = 1.77 + (10.28 * abs_{470}) - (9.83 * abs_{360}) + (13.44 * abs_{265}) - (10.02 * abs_{254})$$

Equation 2: the modelled DOC concentration at ERI. N = 166, R^2 = 0.7442, adjusted R^2 = 0.7378

3.3.2.4. *Molinia* site absorbance and colour

The calculated DOC concentration was modelled using absorbance at three wavelengths: 465, 400 and 360 nm:

$$DOC_{MOL} = 4.08 - (5.79 * abs_{465}) + (9.07 * abs_{400}) - (2.74 * abs_{360})$$

Equation 3: the modelled DOC concentration at MOL. N = 168, R^2 = 0.8195

4. Results

4.1. Bare peat sites

4.1.1. Dissolved organic carbon (DOC)

The distribution of DOC concentration and load (raw and relative) were the same in all years at F and N. The distribution of DOC concentration (raw and relative) was the same in all years at O. DOC load was significantly higher than baseline (2011) at O in 2013 (test statistic = -23.00, p=0.005) and 2020 (test statistic = -25.50, p=0.003). It is possible that this difference was driven by changes in discharge. The distribution of relative DOC load was the same in all years at O. The distribution of DOC concentration (raw and relative) was the same in all years at intact reference field lab P.

An annual pattern in DOC concentration was evident at all four field labs, with higher concentrations in the summer than in the winter.

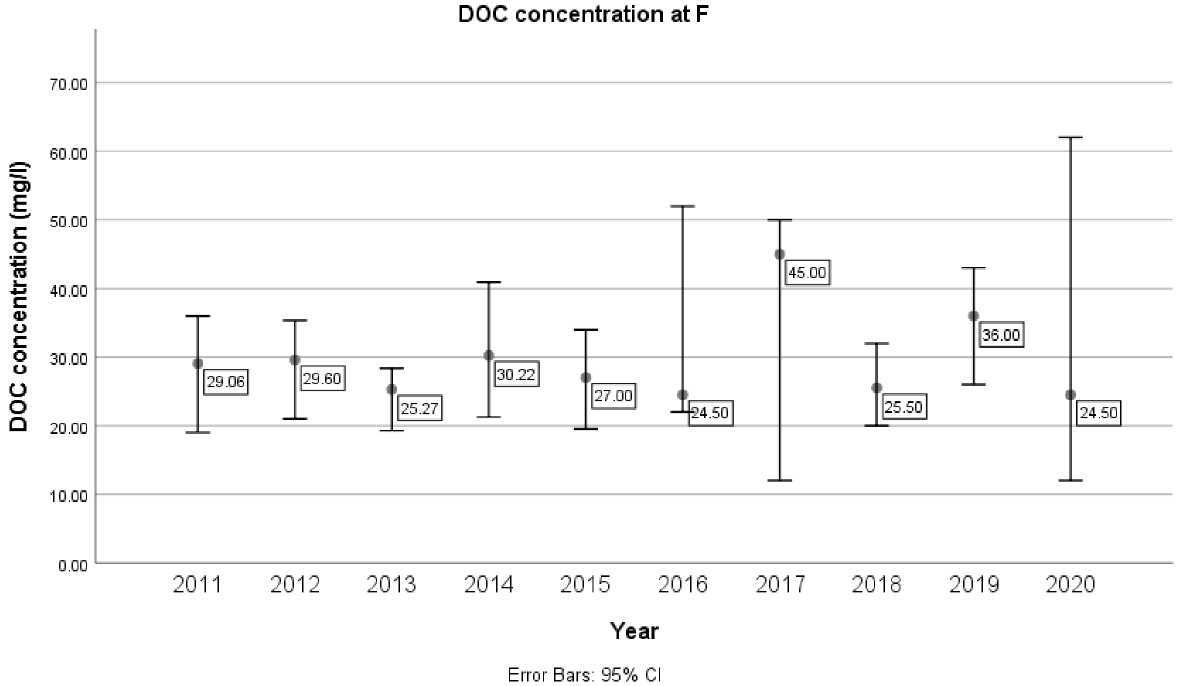

Figure 1: DOC concentration at F (bare peat control) showing annual median values and 95% confidence intervals

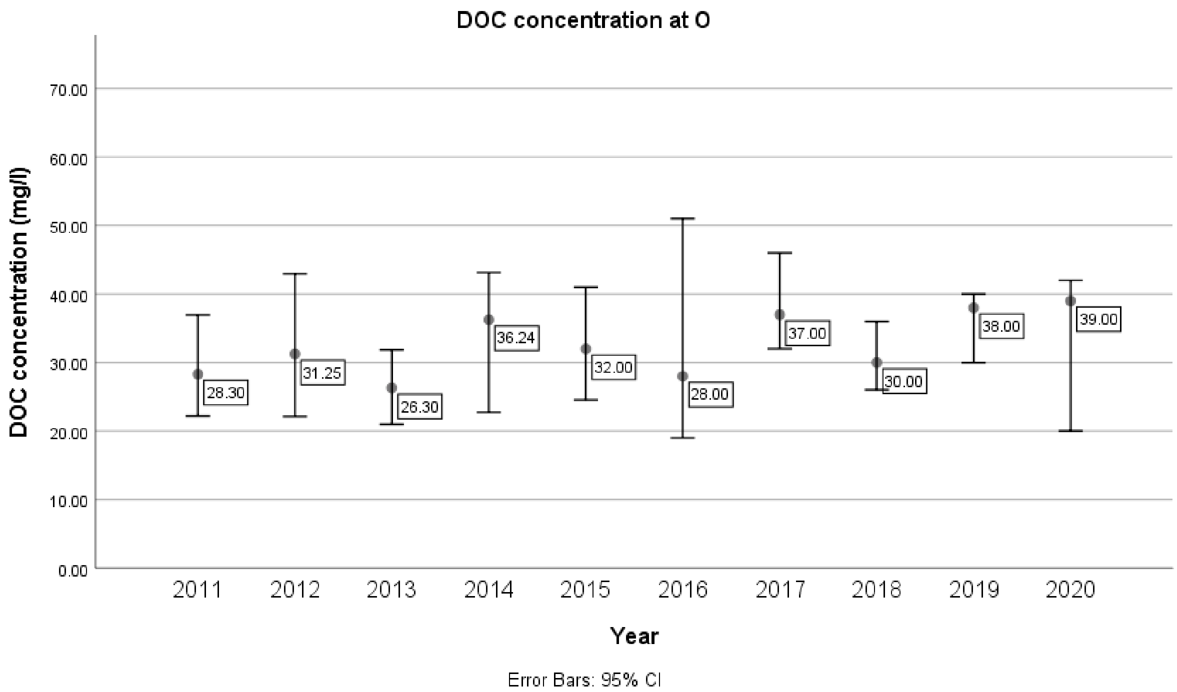

Figure 2: DOC concentration at O (revegetated site) showing annual median values and 95% confidence intervals

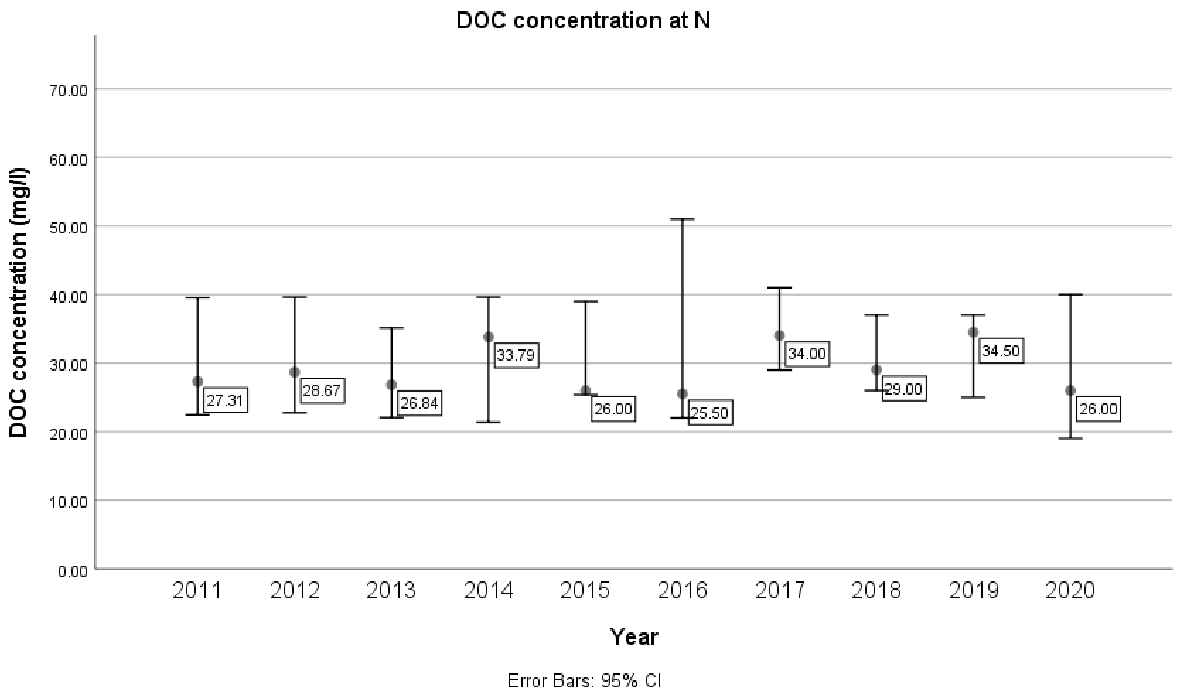

Figure 3: DOC concentration at N (revegetated, gully-blocked and *Sphagnum*-planted site) showing annual median values and 95% confidence intervals

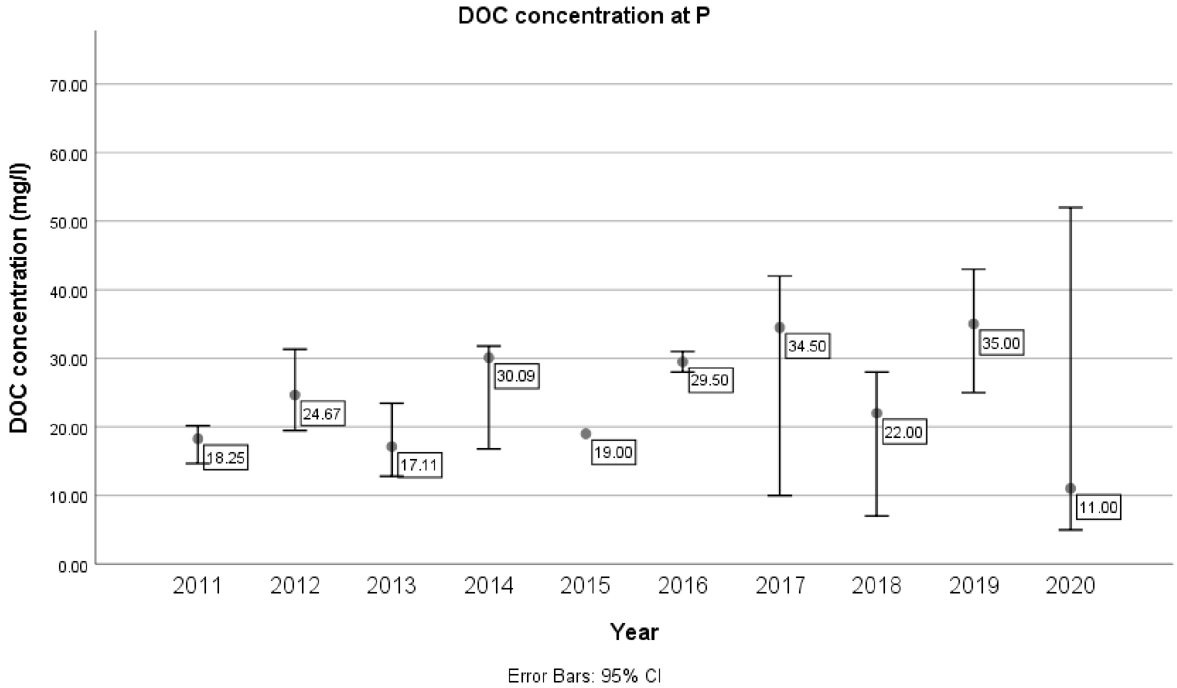

Figure 4: DOC concentration at P (intact reference) showing annual median values and 95% confidence intervals

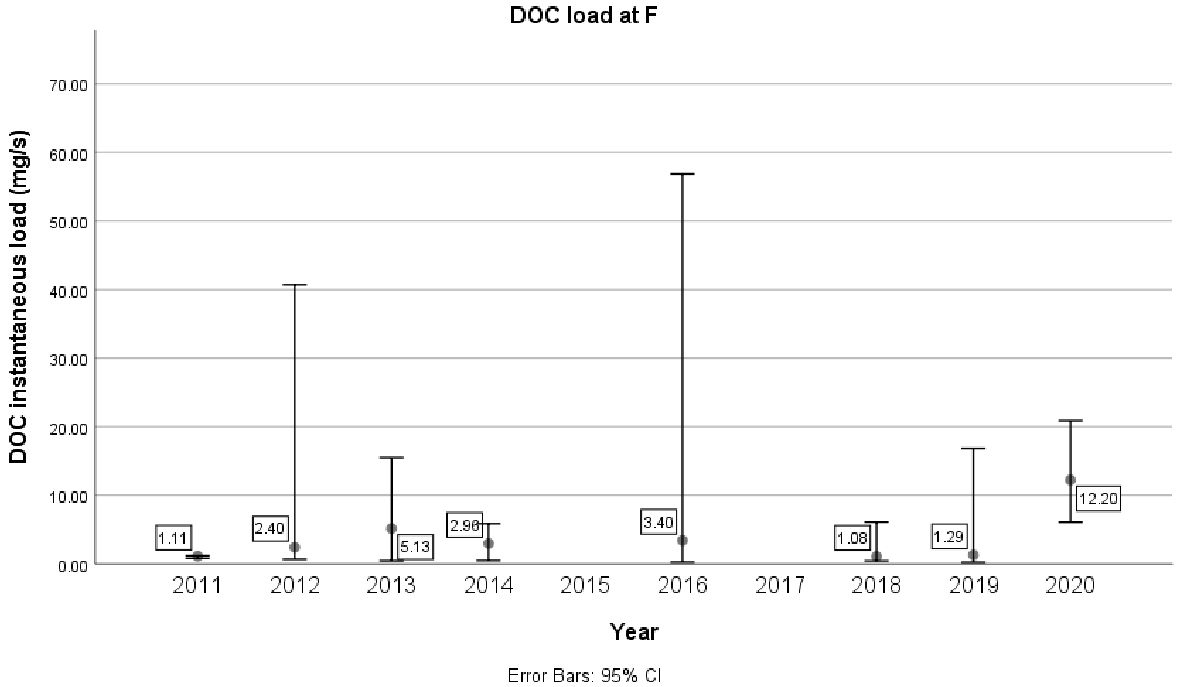

Figure 5: DOC instantaneous load at F (bare peat control) showing annual median values and 95% confidence intervals

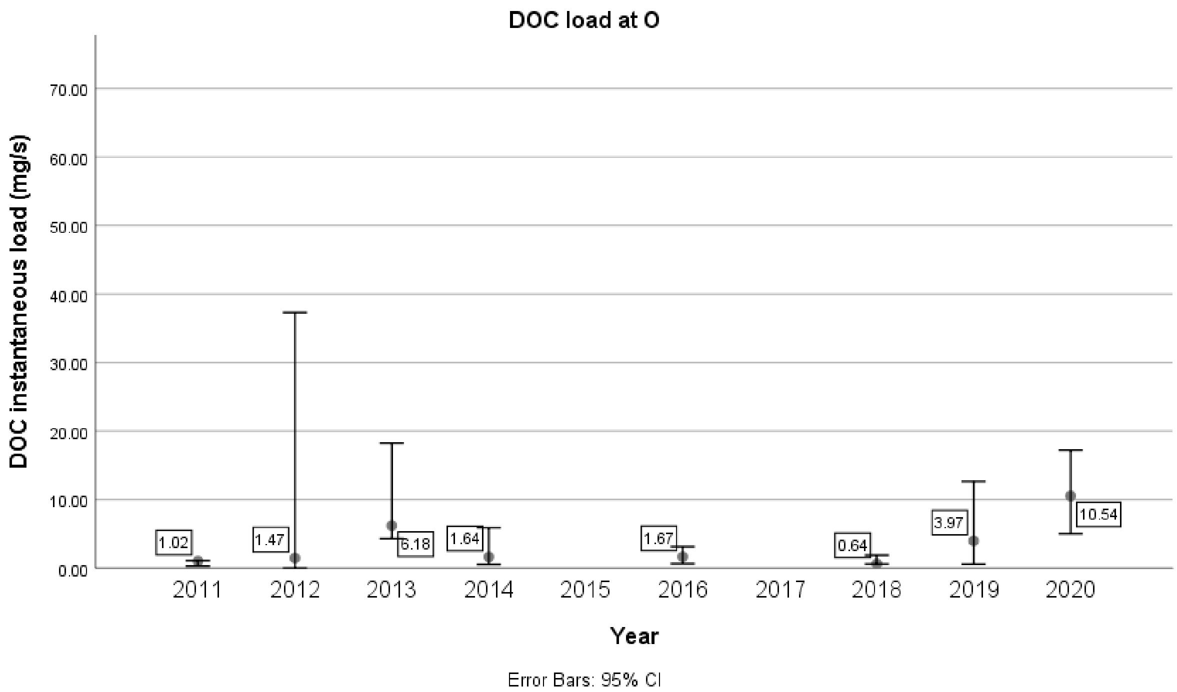

Figure 6: DOC instantaneous load at O (revegetated site) showing annual median values and 95% confidence intervals

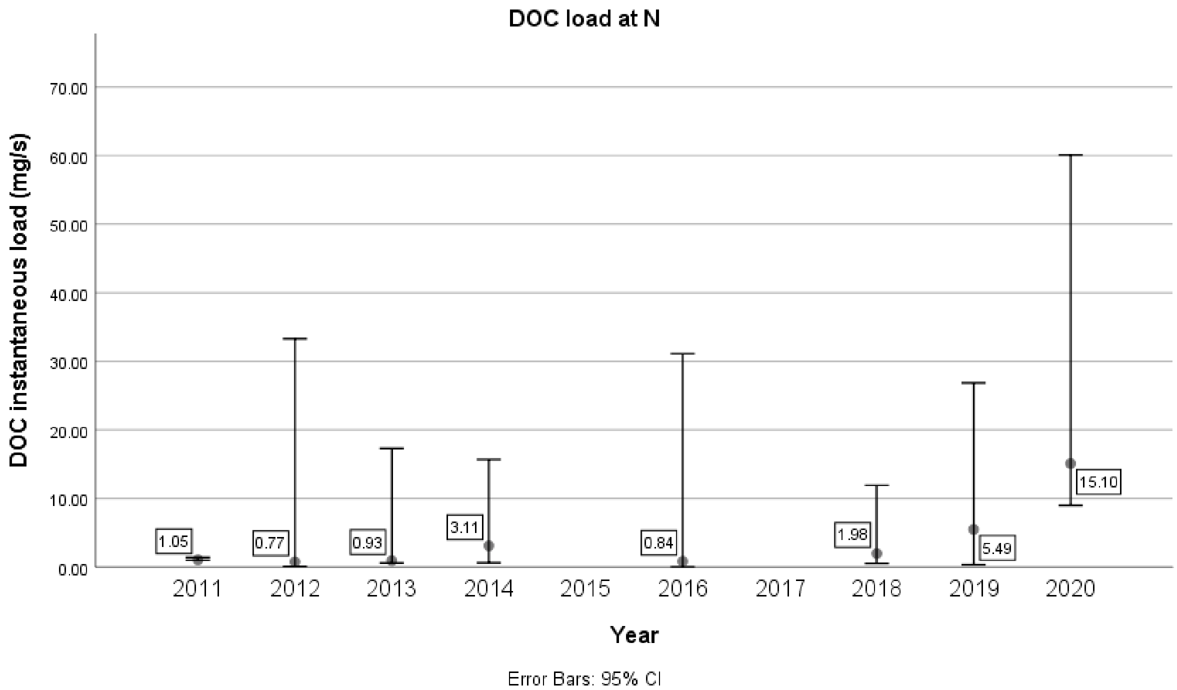

Figure 7: DOC instantaneous load at N (revegetated, gully-blocked and *Sphagnum*-planted site) showing annual median values and 95% confidence intervals

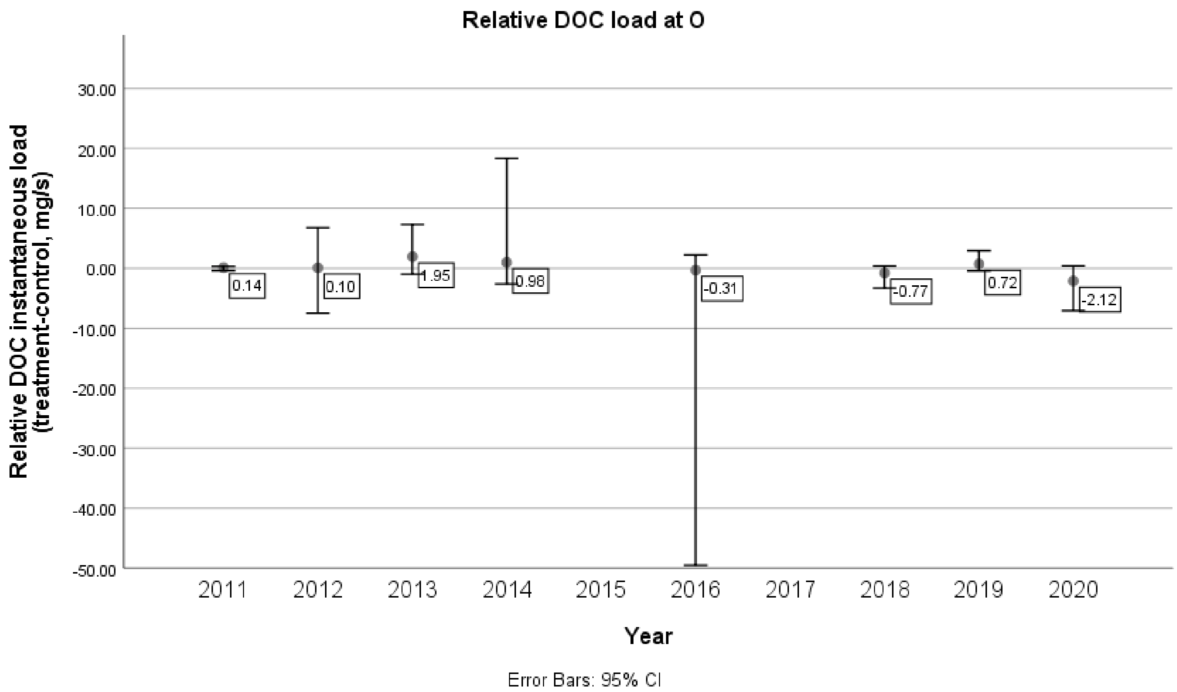

Figure 8: Relative (treatment-control) DOC instantaneous load at O (revegetated site) showing annual median values and 95% confidence intervals.
Positive values indicate higher DOC load at treatment than at control

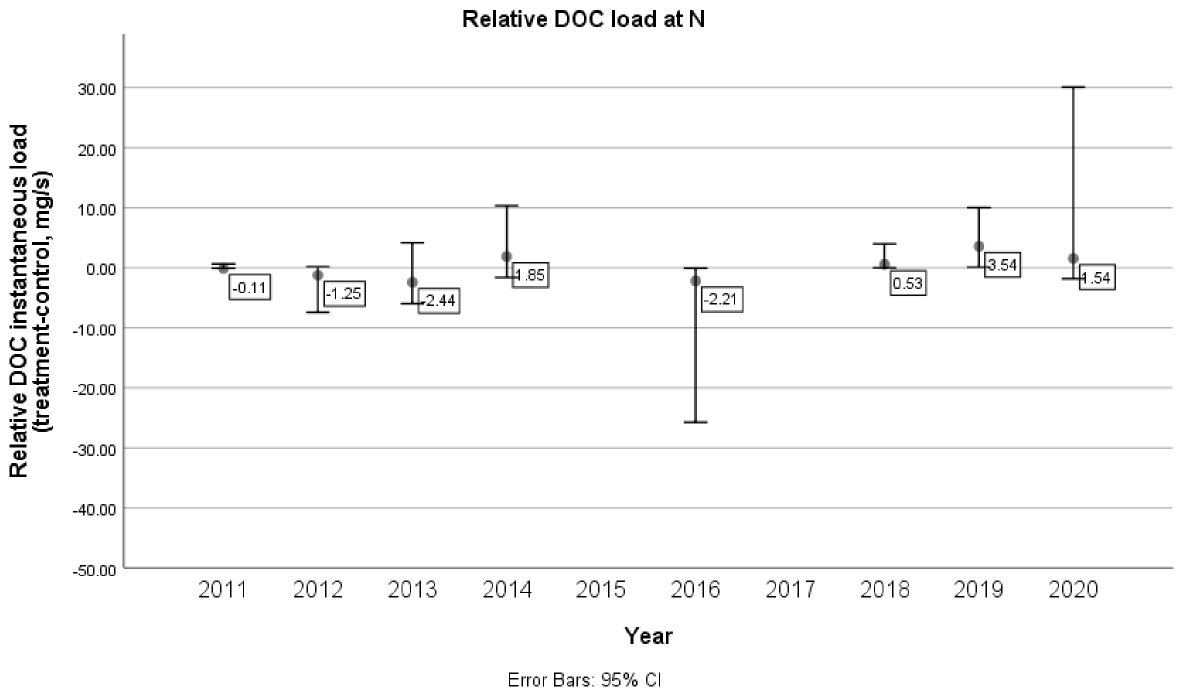

Figure 9: Relative (treatment-control) DOC instantaneous load at N (revegetated, gully-blocked and *Sphagnum*-planted site) showing annual median values and 95% confidence intervals.
Positive values indicate higher DOC load at treatment than at control

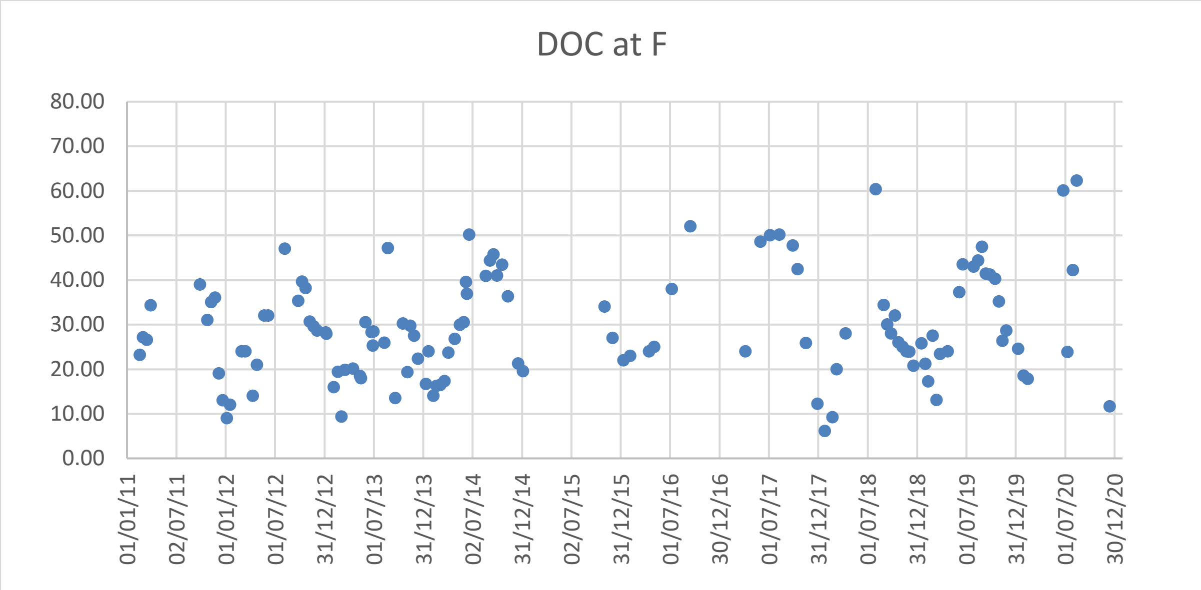

Figure 10: DOC concentration at F (bare peat control) showing all individual samples

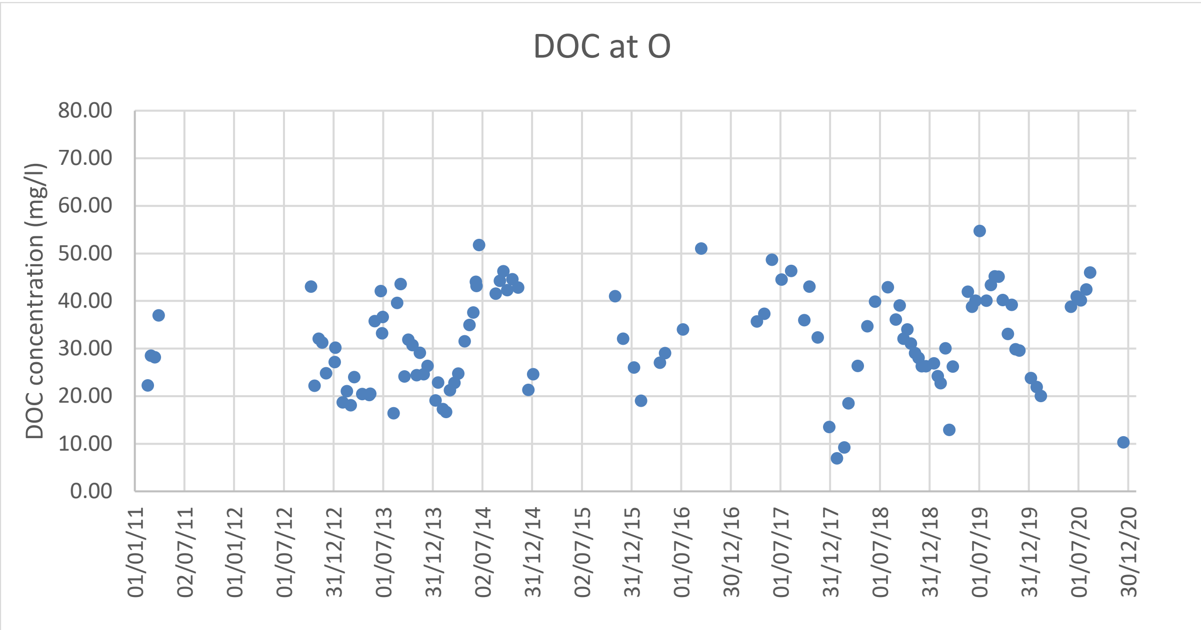

Figure 11: DOC concentration at O (revegetated site) showing all individual samples

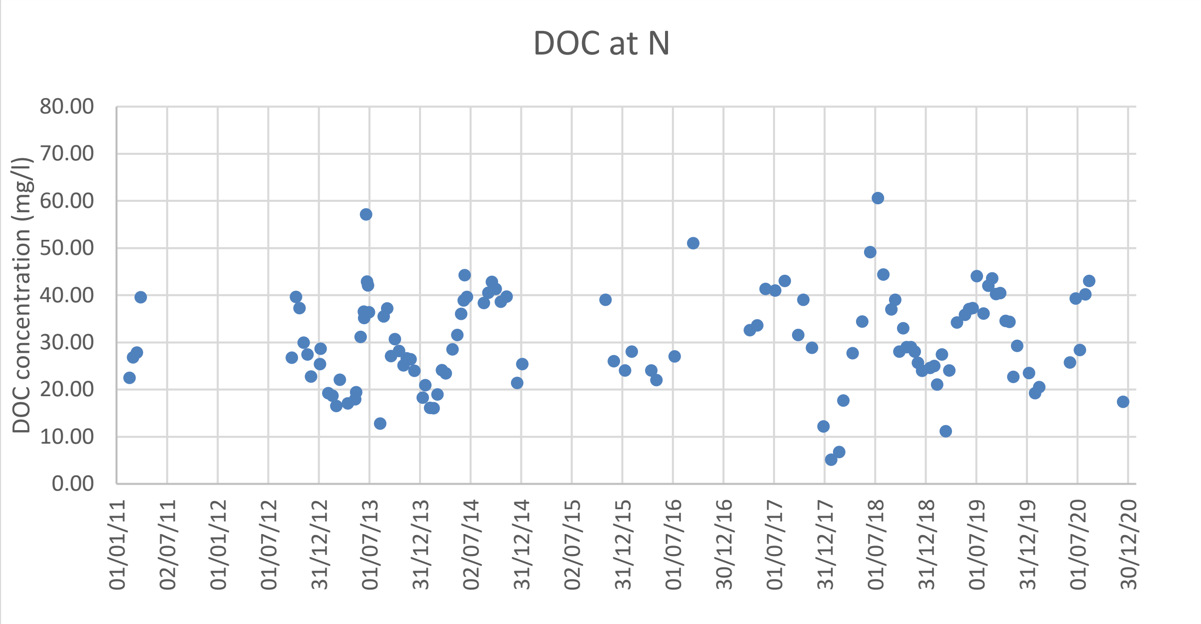

Figure 12: DOC concentration at N (revegetated, gully-blocked and *Sphagnum*-planted site) showing all individual samples

4.1.2. pH

pH increased at all four field labs between 2012 (the first year it was monitored) and later years, before stabilising from 2016–2020.

At F, pH significantly increased between 2012 (first year with data) and later years of 2014 (test statistic = -28.18, p= 0.010) and 2018 (test statistic = -48.21, p< 0.001). Median pH increased from 3.48 in 2012 to 3.90 by 2020.

At O, pH significantly increased between 2012 (first year with data) and later years of 2013 (test statistic = -25.63, p=0.001) and 2014 (test statistic = -32.14, p< 0.001). Median pH increased from 3.83 in 2012 to 4.21 by 2020.

At N, pH significantly increased between 2012 (first year with data) and later years of 2013 (test statistic = -35.56, p< 0.001) and 2014 (test statistic = -43.93, p< 0.001). Median pH increased from 3.88 in 2012 to 4.23 by 2020.

At P, pH significantly increased between 2012 (first year with data) and later years of 2013 (test statistic = -33.52, p=0.039) and 2014 (test statistic = -55.49, p< 0.001). Median pH increased from 3.72 in 2012 to 4.27 by 2020.

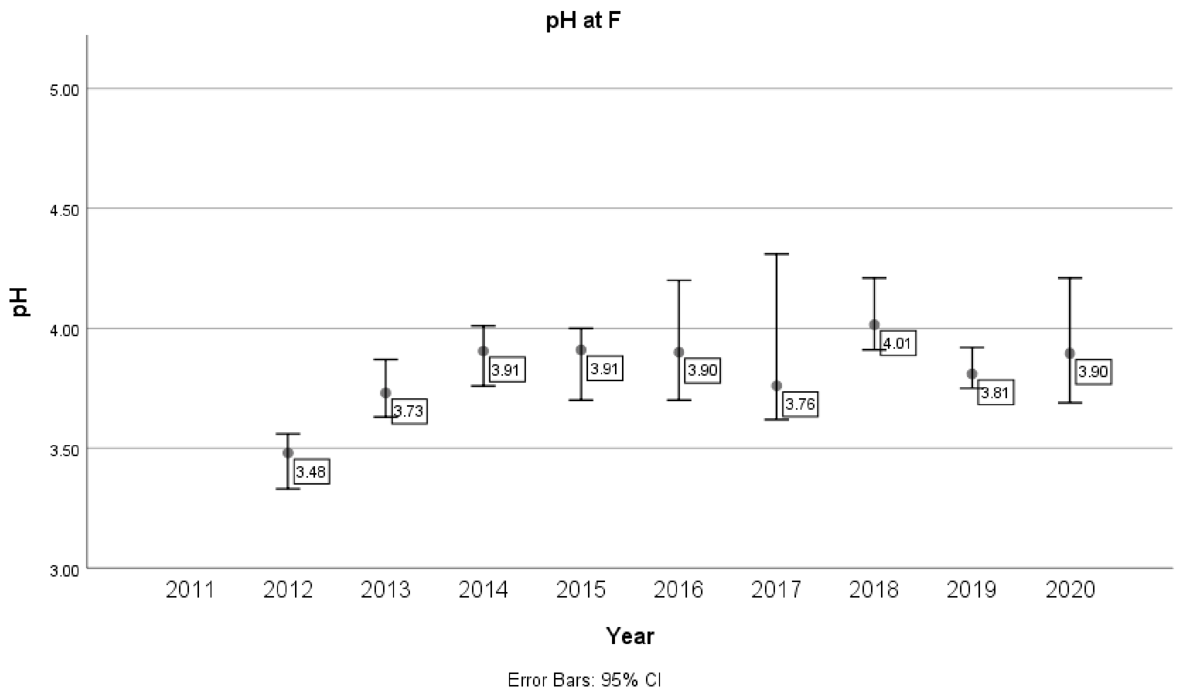

Figure 13: pH at F (bare peat control) showing annual median values and 95% confidence intervals

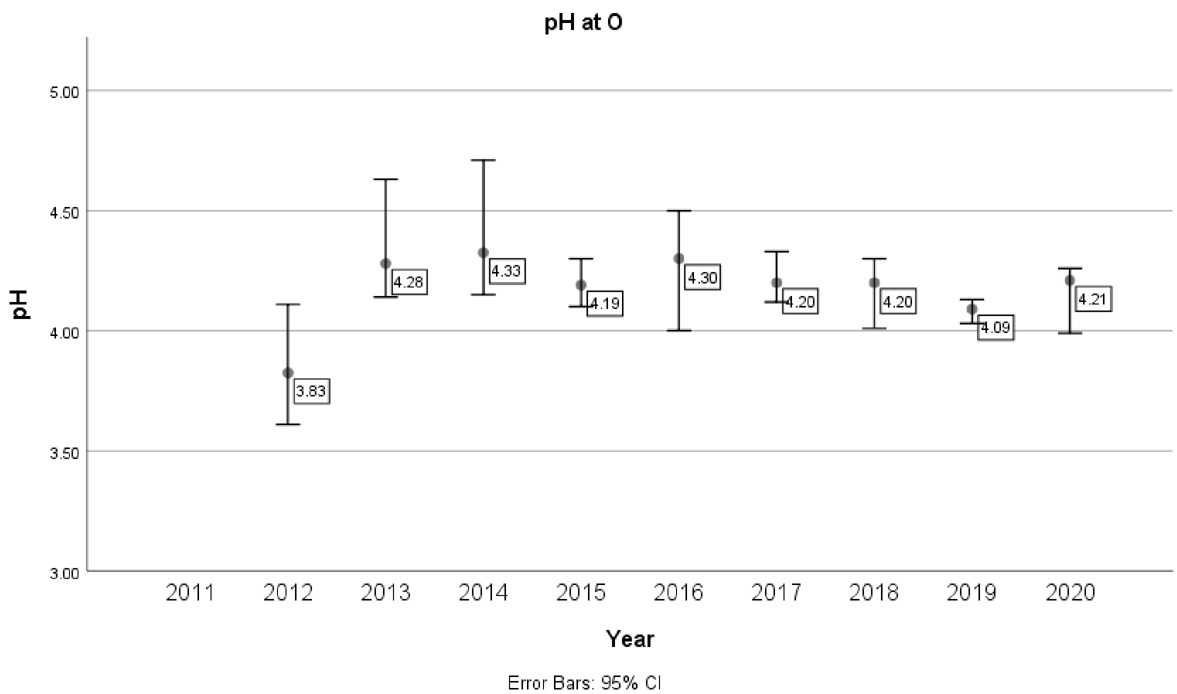

Figure 14: pH at O (revegetated site) showing annual median values and 95% confidence intervals

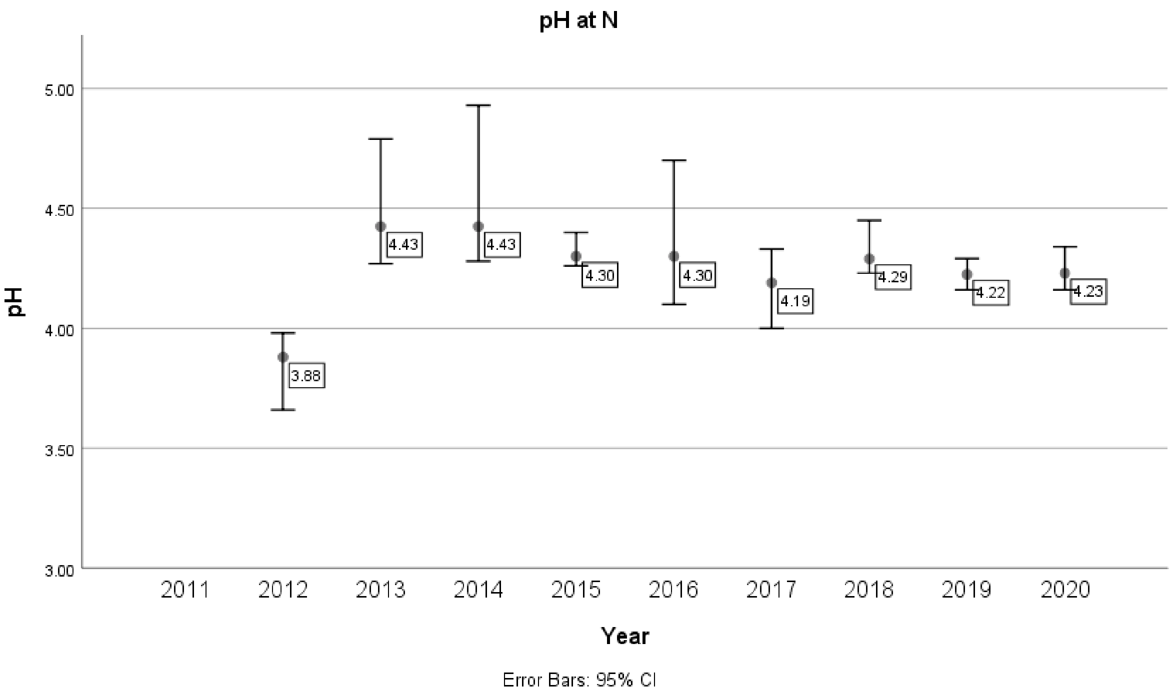

Figure 15: pH at N (revegetated, gully-blocked and *Sphagnum*-planted site) showing annual median values and 95% confidence intervals

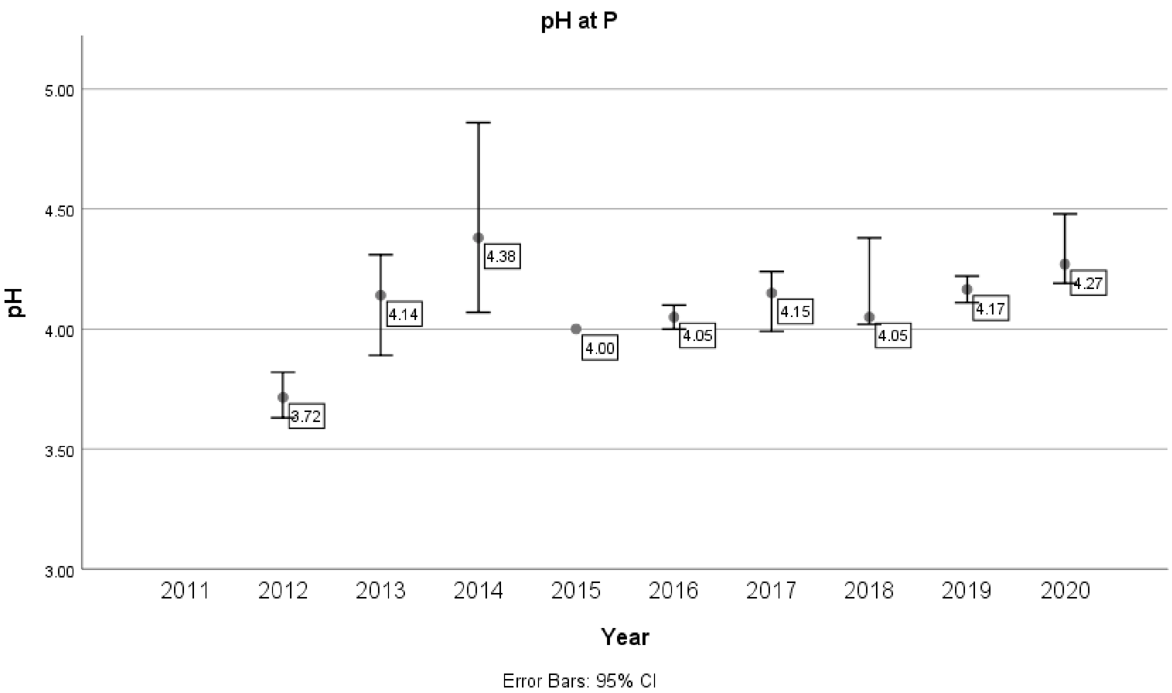

Figure 16: pH at P (intact reference) showing annual median values and 95% confidence intervals

4.1.3. Calcium

Calcium concentration data were not available from before the first application of lime. The available data at treatment field labs O and N showed elevated concentrations in 2011–2014 which reduced significantly from 2011 to 2018 (O: test statistic = 66.49, $p<0.001$; N: test statistic = 67.38, $p<0.001$) and then did not vary significantly. Median calcium concentration at O reduced from 3.85mg/l in 2011 to 0.11mg/l in 2018; median calcium concentration at N reduced from 2.67mg/l in 2011 to 0.11mg/l in 2018.

Calcium concentrations at F and P also declined significantly (but by smaller amounts than at O or N) from 2011 to 2018 (F: test statistic = 71.58, p<0.001; P: test statistic = 57.29, p<0.001) despite no applications of lime at either field lab. Median calcium concentration at F reduced from 0.57mg/l in 2011 to 0.04mg/l in 2018; median calcium concentration at P reduced from 1.24mg/l in 2011 to 0.09mg/l in 2018. It is possible that a small amount of lime was dropped accidentally on both of these areas while helicopters were travelling to nearby restoration areas.

Relative calcium concentration (treatment-control) declined at field labs O and N from 2011 to 2018 (O: test statistic = 56.16, p=0.001; N: test statistic = 51.11, p=0.005). Relative calcium concentration (intact reference-control) declined at P from 2011–2019 (change from 2011–2018 not significant): test statistic = 44.58, p=0.001).

When years 2017–2020 were grouped, the distribution of calcium concentration was higher at O, N and P than at F (O: test statistic = -50.69, p<0.001; N: test statistic = -61.48, p<0.001; P: test statistic = -37.15, p=0.011). There was no difference in distribution of calcium concentration between O, N and P for these years.

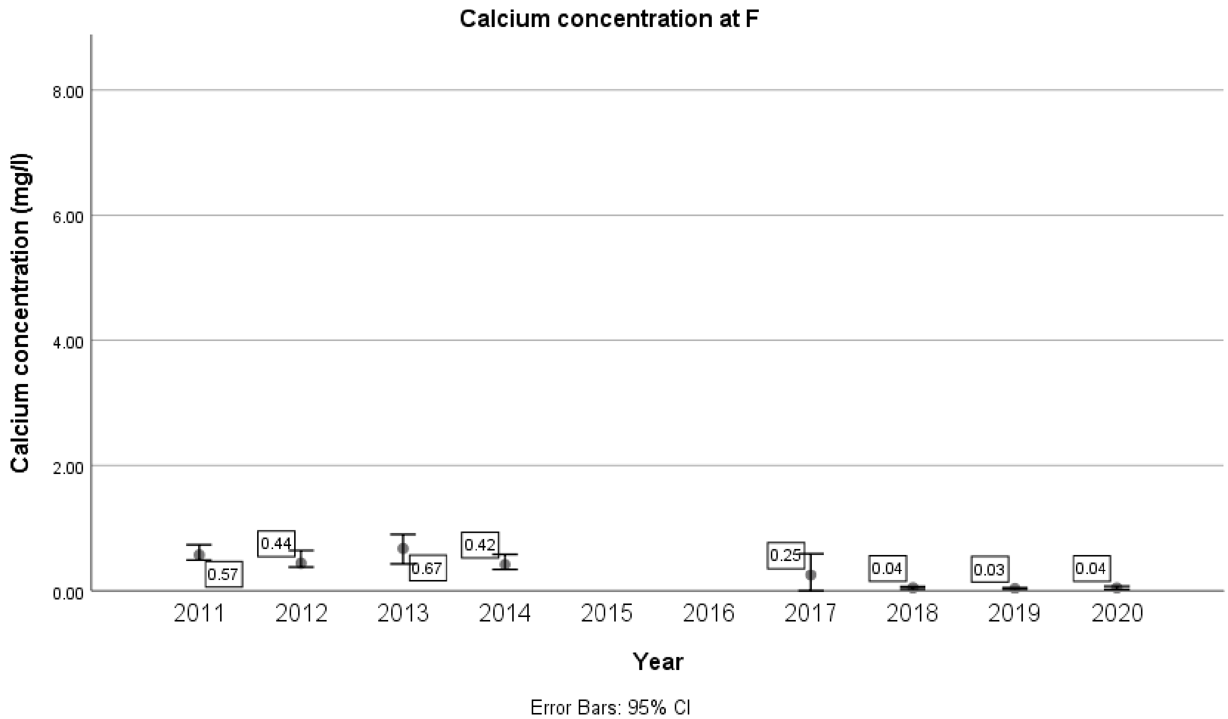

Figure 17: Calcium concentration at F (bare peat control) showing annual median values and 95% confidence intervals

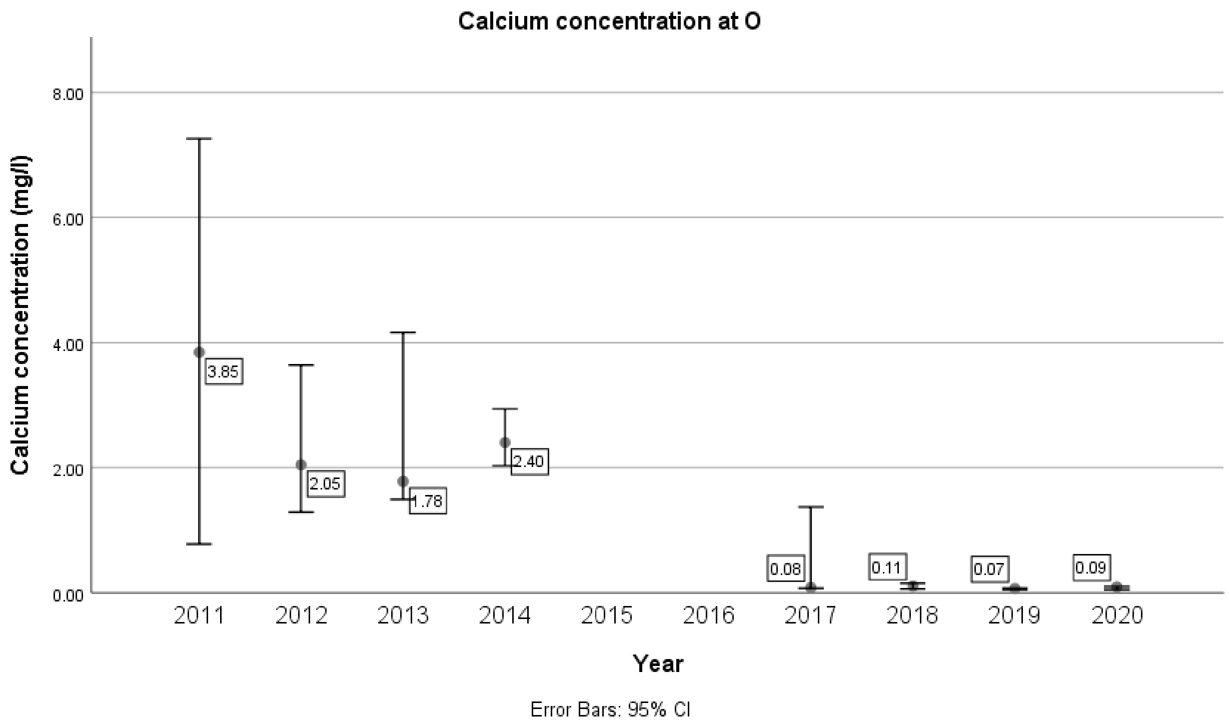

Figure 18: Calcium concentration at O (revegetated site) showing annual median values and 95% confidence intervals

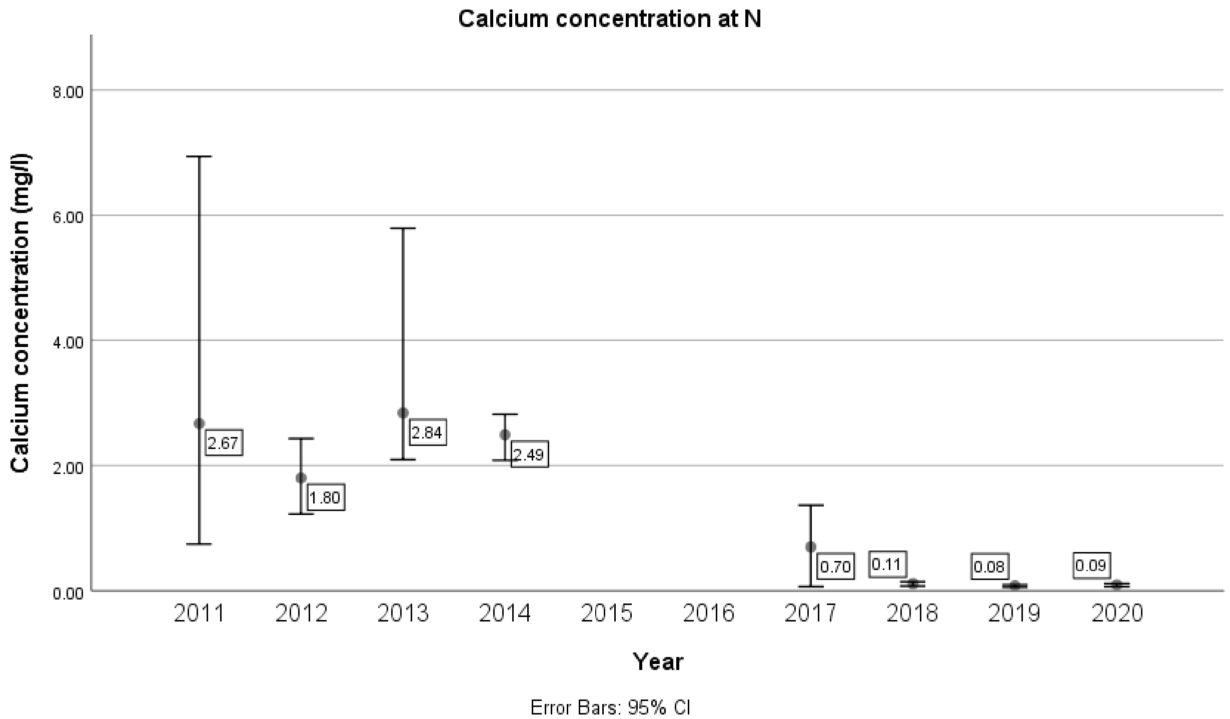

Figure 19: Calcium concentration at N (revegetated, gully-blocked and *Sphagnum*-planted site) showing annual median values and 95% confidence intervals

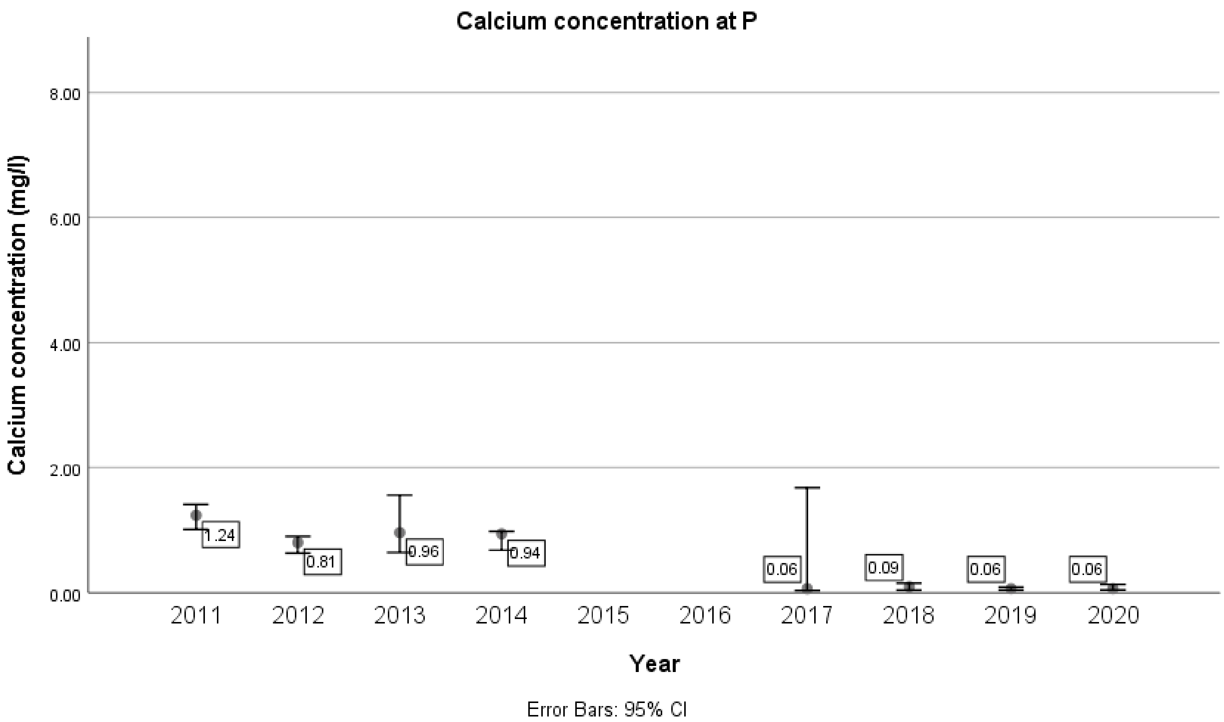

Figure 20: Calcium concentration at P (intact reference) showing annual median values and 95% confidence intervals

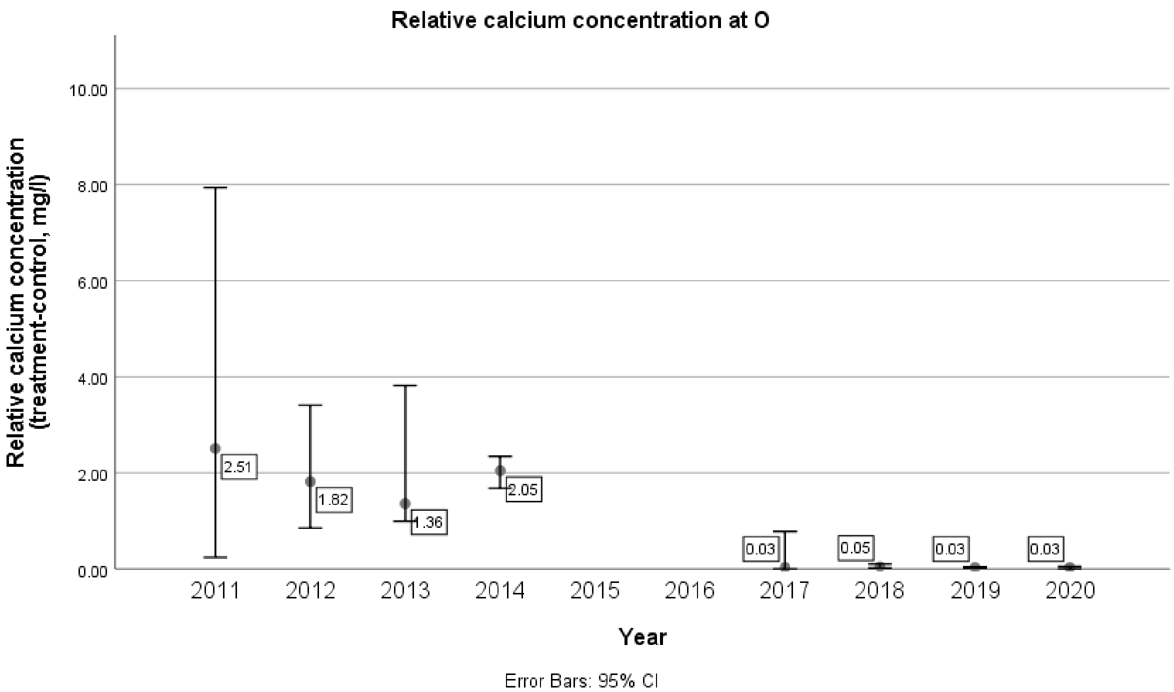

Figure 21: Relative (treatment-control) calcium concentration at O (revegetated site) showing annual median values and 95% confidence intervals

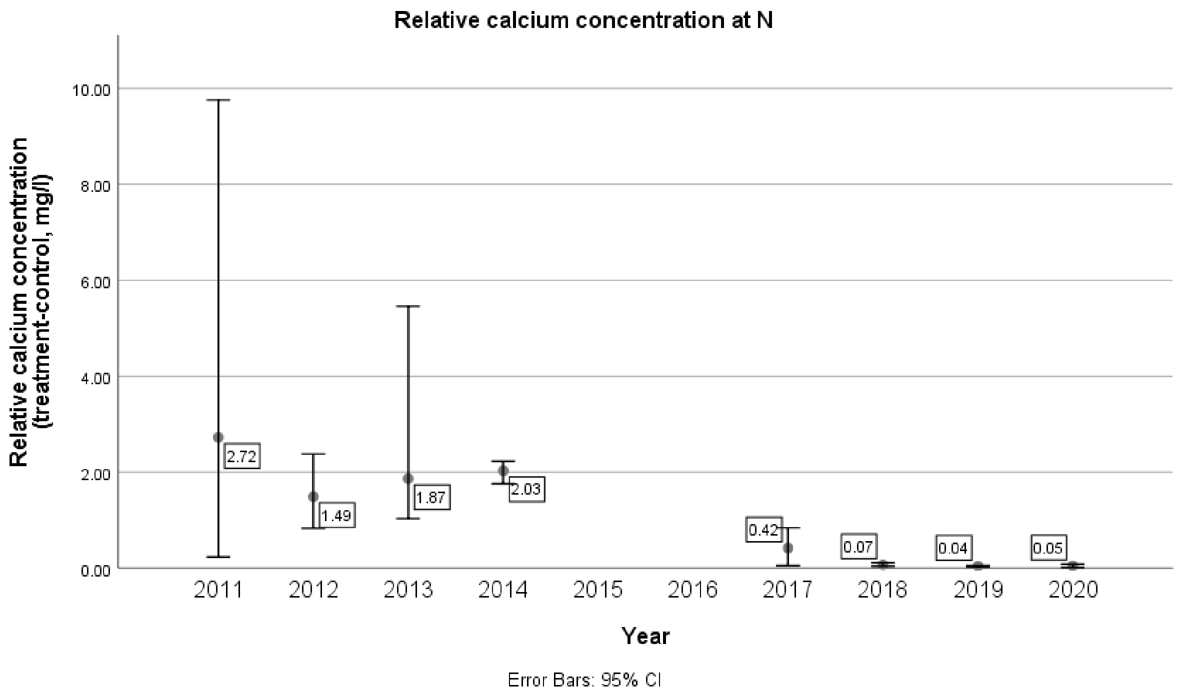

Figure 22: Relative (treatment-control) calcium concentration at N (revegetated, gully-blocked and *Sphagnum*-planted site) showing annual median values and 95% confidence intervals

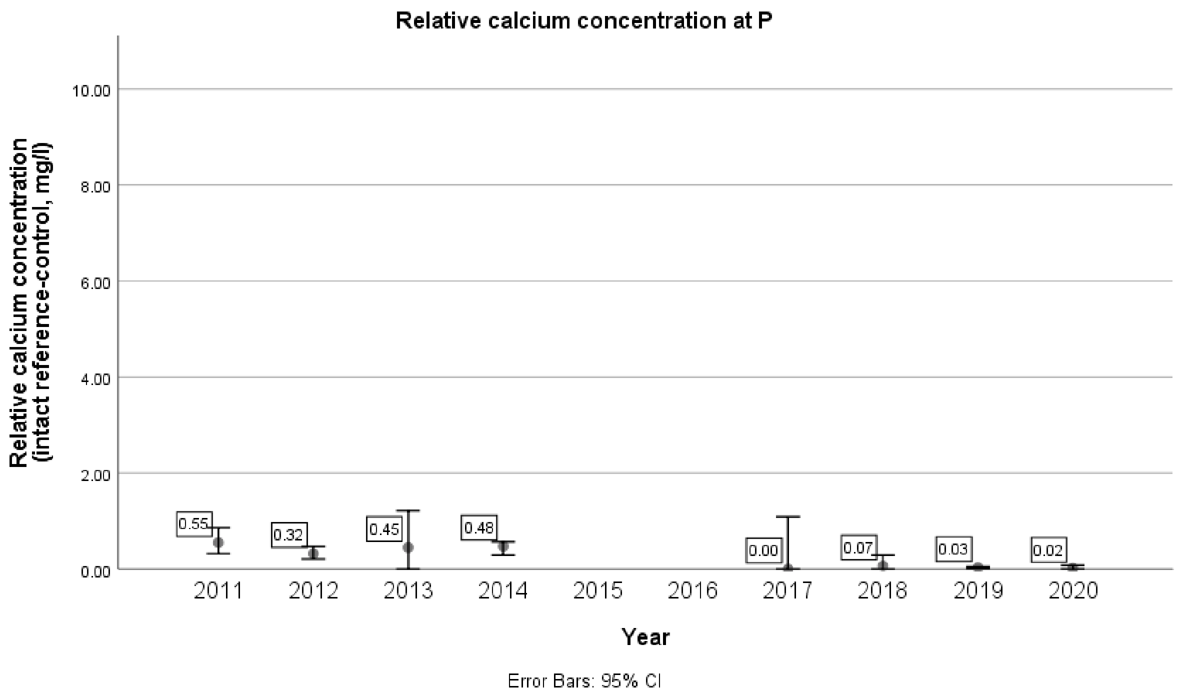

Figure 23: Relative (intact reference-control) calcium concentration at P (intact reference) showing annual median values and 95% confidence intervals

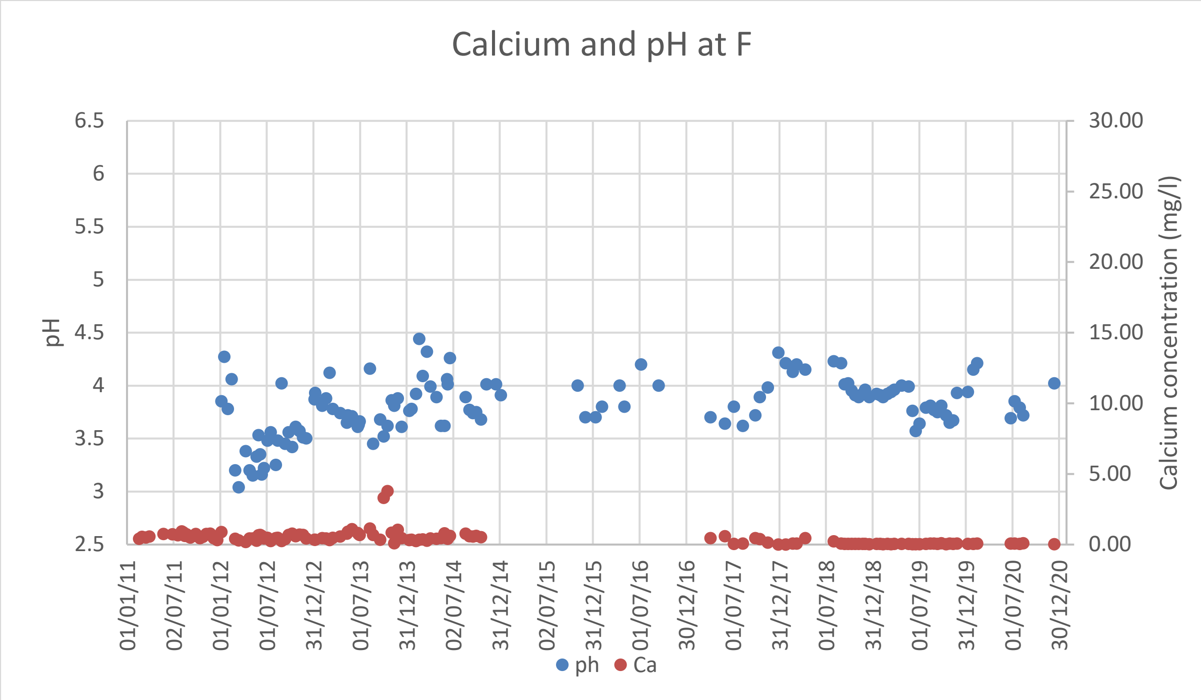

Figure 24: Calcium concentration and pH at F (bare peat control) showing all individual samples. pH is not driven by calcium concentration

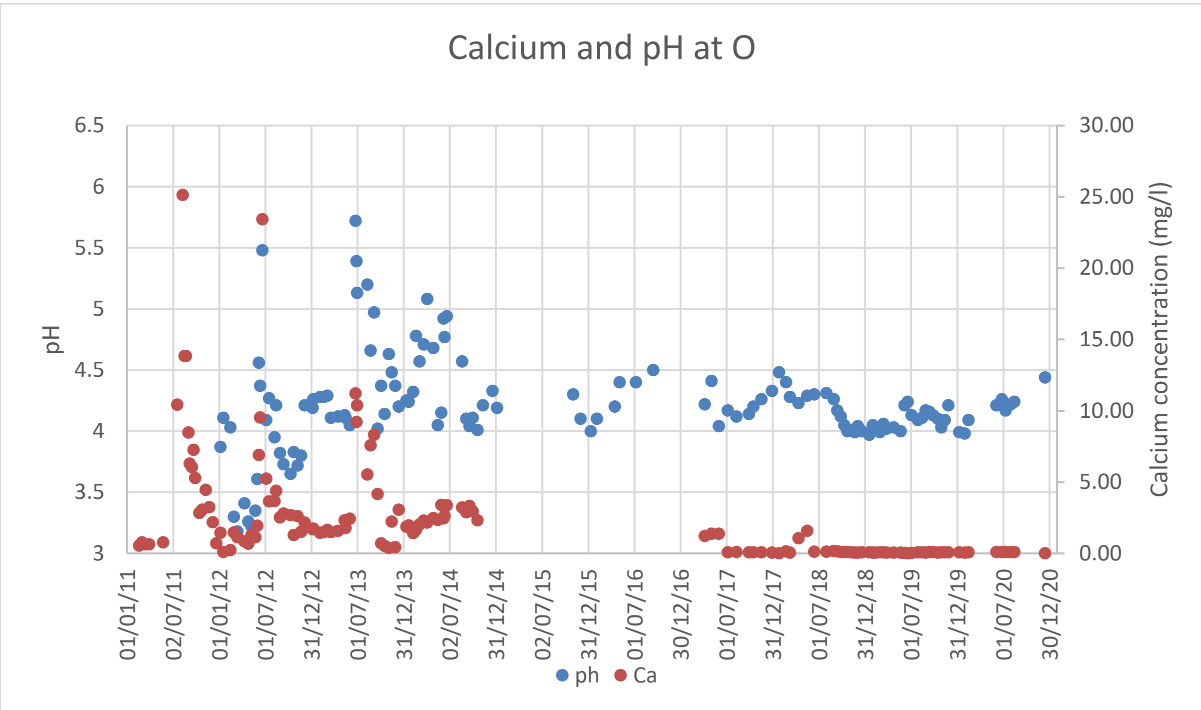

Figure 25: Calcium concentration and pH at O (revegetated site) showing all individual samples. pH variability is initially driven by calcium concentration due to lime applications in 2011, 2012 and 2013; subsequent pH variability is not driven by calcium concentration

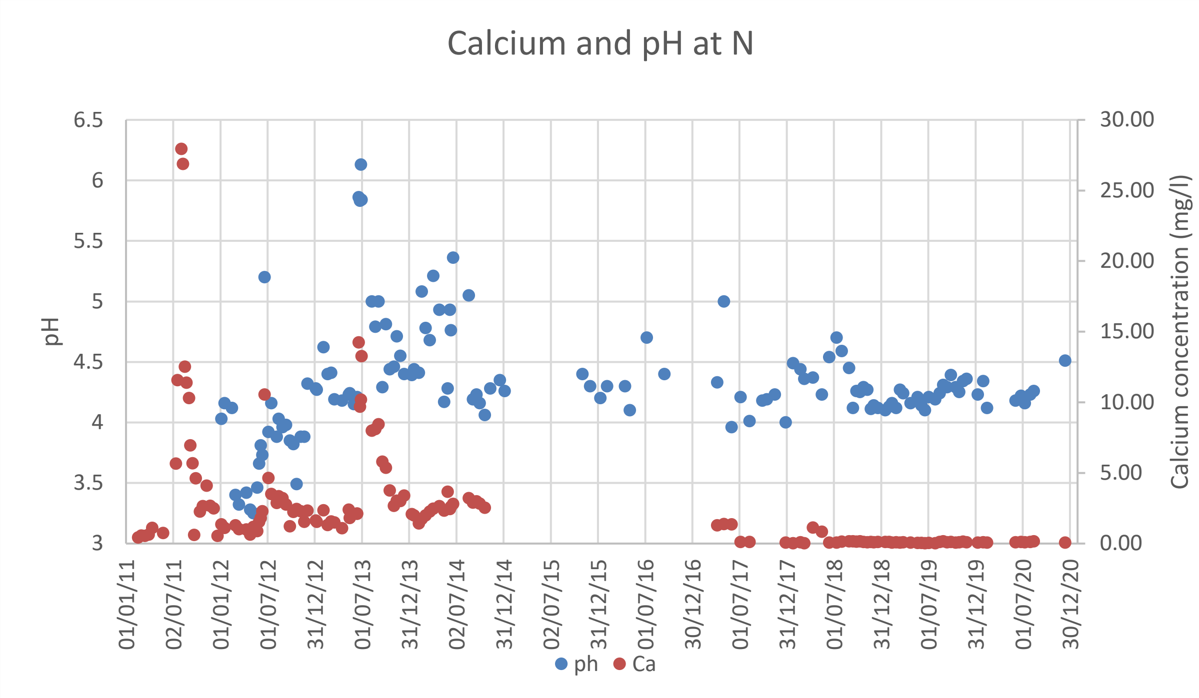

Figure 26: Calcium concentration and pH at N (revegetated, gully-blocked and *Sphagnum*-planted site) showing all individual samples.
pH variability is initially driven by calcium concentration due to lime applications in 2011, 2012 and 2013; subsequent pH variability is not driven by calcium concentration

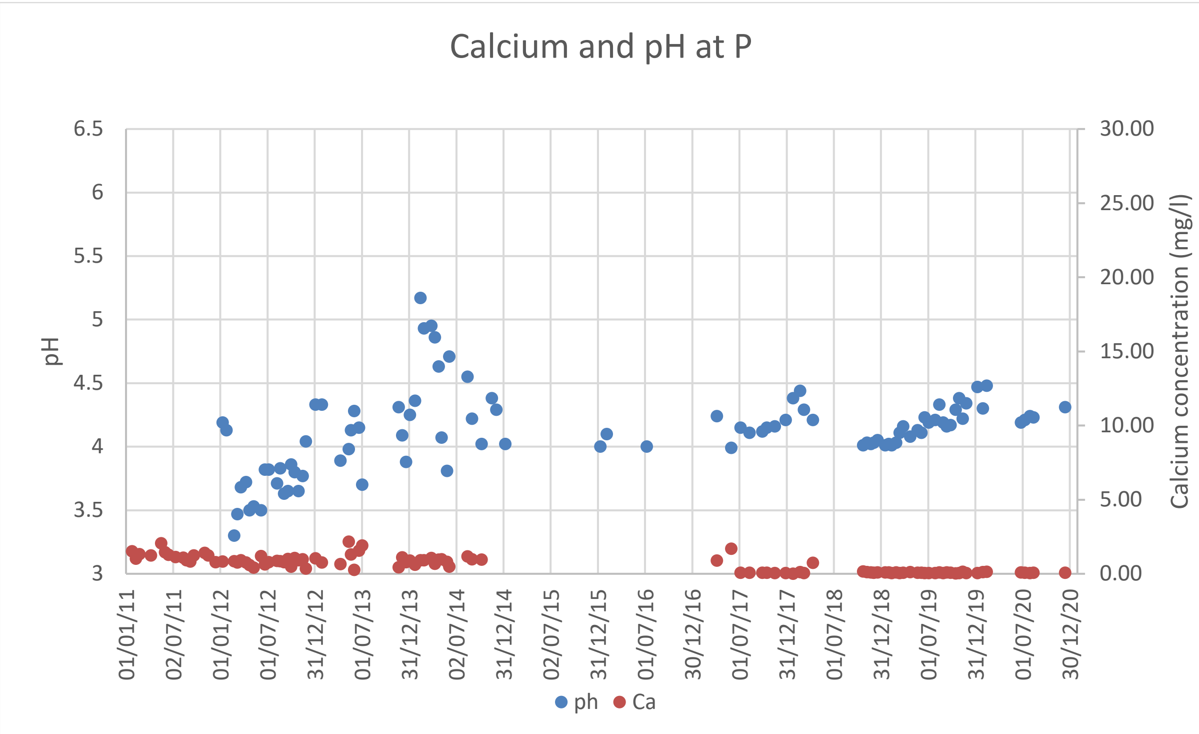

Figure 27: Calcium concentration and pH at P (intact reference) showing all individual samples.
pH is not driven by calcium concentration.

4.1.4. Other determinands

No trends were observed in the data for any other determinands, beyond what has already been reported elsewhere (Evans *et al*, 2015; Spencer & Evans, 2016).

4.2. Species dominated sites

There were 1,887 samples collected as part of the routine sampling campaign between 05/11/2018 and 31/08/2021. Of these, 178 were taken before catchment interventions were applied. There was a short break in sampling from 17/03/2020 to 16/06/2020, due to Covid-19. There were 448 samples collected in each spatial survey: 448 in January 2019 (before intervention) and 448 in November 2019 (after intervention). Including both spatial and routine samples, there were 2,783 water samples collected and analysed from the seven mini-catchments.

4.2.1. Measured vs modelled DOC

There were 633 water samples from *Calluna* that had both DOC and absorbance measured (Figure 28). The average modelled DOC concentration was 49.08 mg L^{-1}; the measured DOC concentration average was 45.98 mg L^{-1}. There were no significant differences between the modelled and measured DOC concentrations (paired t-test, $p=0.14$).

The residual DOC values were higher at higher measured DOC concentrations, suggesting the model had more realistic DOC concentrations when they were lower than 100 mg L^{-1} (Figure 28). As the majority of measured DOC concentrations were lower than 100 mg L^{-1} (only 35 of 633 samples used in this analysis were more than 100 mg L^{-1}), equation 1 was used to model DOC in water samples from the *Calluna* site.

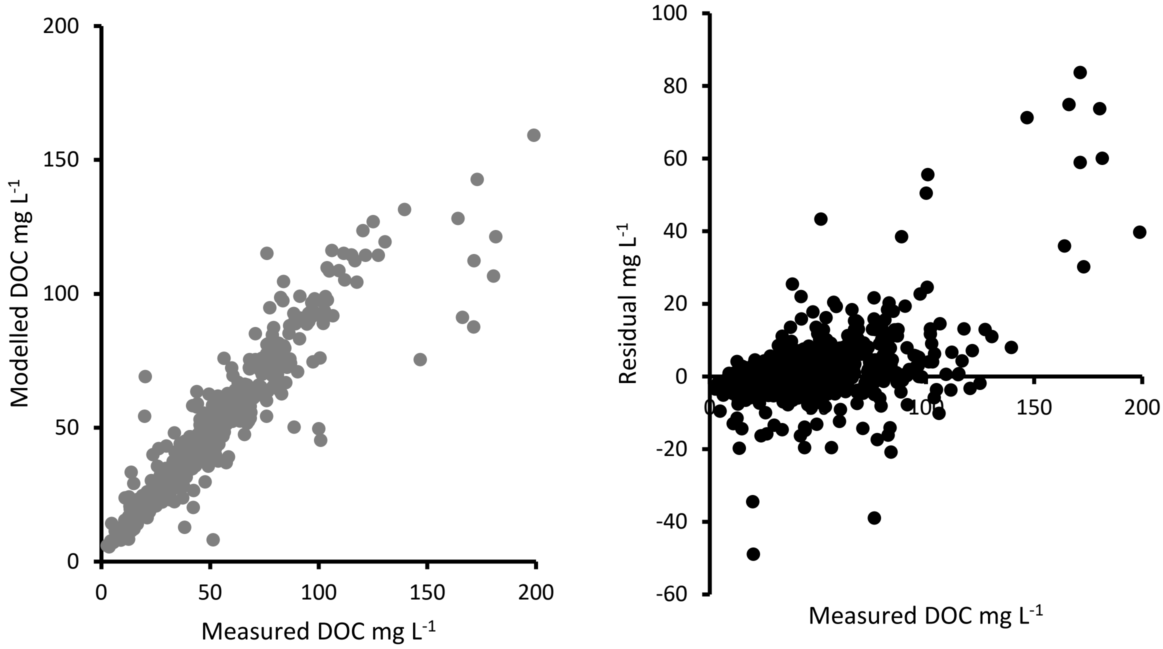

Figure 28. *Calluna* site measured and modelled DOC

There were 453 water samples from *Eriophorum* that had both DOC and absorbance measured (Figure 29). The average modelled DOC concentration was 40.30 mg L^{-1}; the measured DOC concentration average was 38.48 mg L^{-1}. There were no significant differences between the modelled and measured DOC concentrations (paired t-test, $p=0.90$).

The residual DOC values were higher at higher measured DOC concentrations, suggesting the model had more realistic DOC concentrations when they were lower than 100 mg L^{-1} (Figure 29). As the majority of measured DOC concentrations were lower than 100 mg L^{-1} (only 15 of 453 samples used in this analysis were more than 100 mg L^{-1}), equation 2 was used to model DOC in water samples from *Eriophorum*.

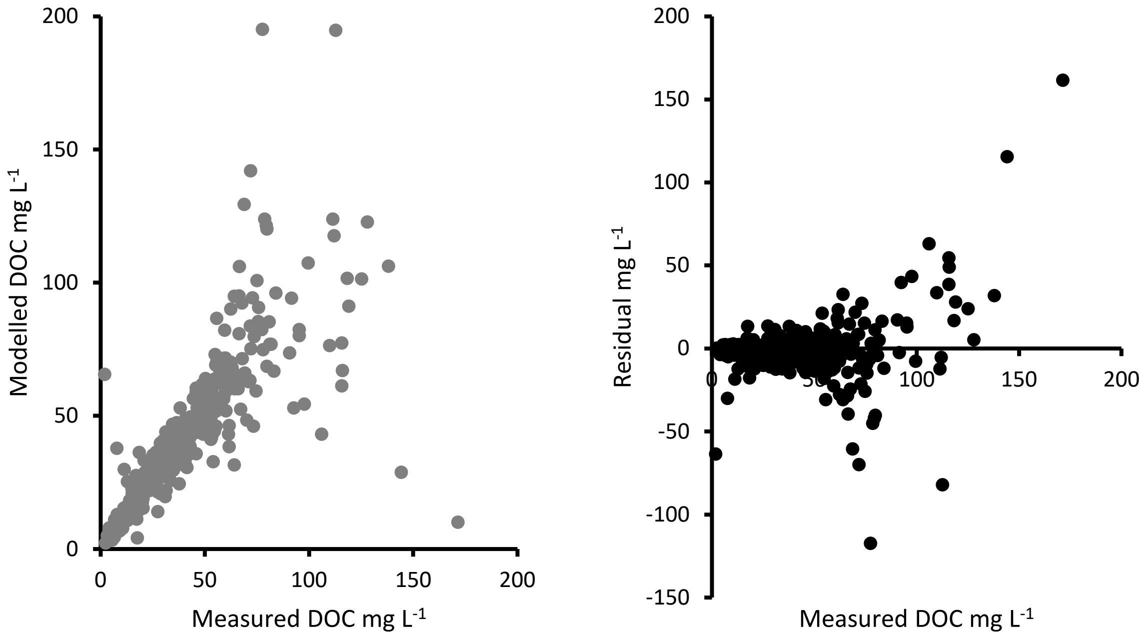

Figure 29. *Eriophorum* site measured and modelled DOC

There were 429 water samples from *Molinia* that had both DOC and absorbance measured (Figure 30). The average modelled DOC concentration was 16.25 mg L^{-1}; the measured DOC concentration average was 19.27 mg L^{-1}. There were no significant differences between the modelled and measured DOC concentrations (paired t-test, p=0.07).

The residual DOC values were higher at higher measured DOC concentrations, suggesting the model had more realistic DOC concentrations when they were lower than 60 mg L^{-1} (Figure 30). As the majority of measured DOC concentrations were lower than 60 mg L^{-1} (only 27 of 429 samples used in this analysis were more than 60 mg L^{-1}), equation 3 was used to model DOC in water samples from *Molinia*.

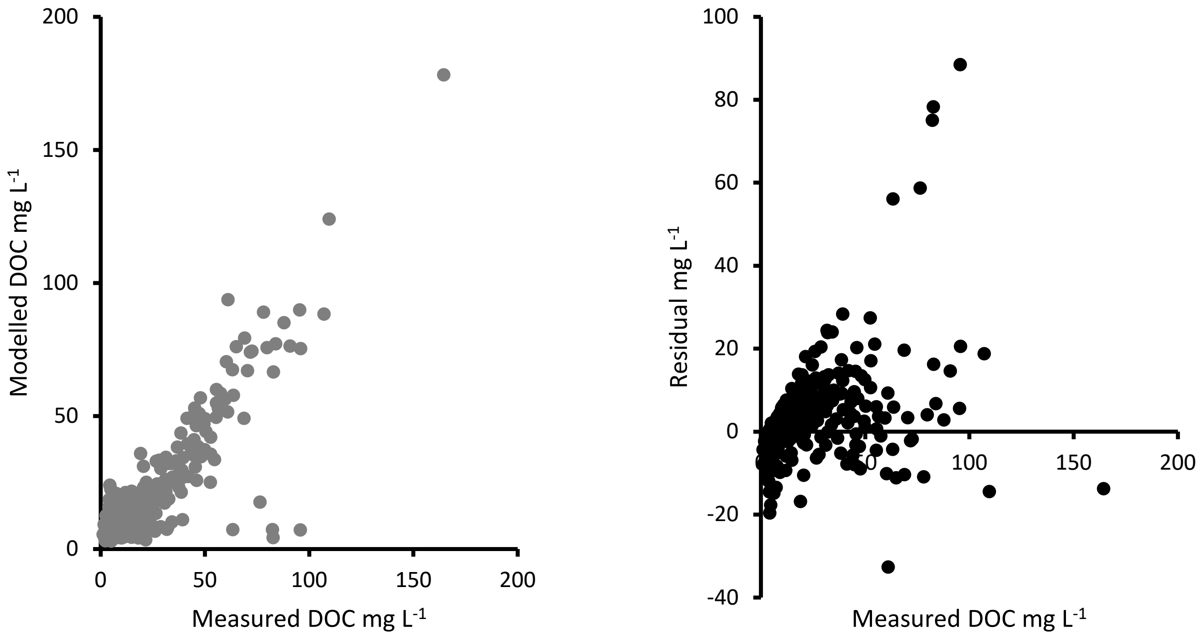

Figure 30. ***Molinia*** **site measured and modelled DOC**

4.2.2. Effect of treatment on water chemistry at catchment outlets

In order to assess impacts of planting *Sphagnum* at catchment outlets (weirs), the water chemistry variables in the *Sphagnum* (Spha) catchment were calculated relative to the concentrations in the Control (Con) catchment. At the *Calluna* sites, the impact of *Sphagnum* planting alone (Spha versus Con), *Sphagnum* planting and gully blocking (SphaGB versus Con) and of gully blocking alone (SphaGB versus Spha) were assessed. The closer the value is to 0 the more similar the concentrations at the two sites.

The pH, conductivity, DOC concentration, and two proxy measures of DOC composition (E4:E6 and $SUVA_{254}$) were analysed.

The majority of the catchment interventions were applied in March 2019 (apart from the *Sphagnum* planting at the intensive plots) and so the BACI design used for analysis of water at catchment outlets (weirs) uses the following timings:

- BACI year 0 – start of water sample collection (Nov 2018) to before intervention (March 2019)
- BACI year 1 – the 12 months from March 2019 to March 2020
- BACI year 2 – the 12 months from March 2020 to March 2021 (including a sampling break due to covid-19)
- BACI year 3 – the 6 months from March 2021 to September 2021

Table 4. Indicative summary of the direction of change in DOC concentration, pH, EC, $SUVA_{254}$ and E4:E6 at *Calluna* (CAL), *Eriophorum* (ERI) and *Molinia* (MOL) sites.
Arrows show the direction of change. One-way Mann-Whitney U test results are shown with: NS = not significant; * = p < 0.05; ** p < 0.01; and *** p < 0.001.

Vegetation	Location	Impact of treatment	Direction of change after catchment intervention				
			pH	EC	DOC	E4:E6	$SUVA_{254}$
CAL	Weir	Spha (Spha – Con)	- NS	↓ NS	↓ *	↑ NS	↑ NS
CAL	Weir	GB (SphaGB – Spha)	- NS	↑ NS	↑ NS	↑ NS	↓ NS
CAL	Weir	Spha&GB (SphaGB – Con)	- NS	↓ NS	↓ NS	↑ NS	- NS
ERI	Weir	Spha (Spha – Con)	- NS	↓ NS	↓ NS	- NS	↓ NS
MOL	Weir	Spha (Spha – Con)	- NS	↓ *	↓ NS	↓ NS	↓ NS

The main findings for each vegetation type and variable are summarised in Table 4. Most observed metrics showed no statistically significant change. The pH of the water was unaffected by planting *Sphagnum*, although several sites showed a small potential increase over time, perhaps a recovery from past acidification. In general, the electrical conductivity (EC) of the water decreased after planting, although this was generally not significant. The DOC concentration appeared to decrease after *Sphagnum* planting at most sites, however, the impact of gully blocking alone caused the DOC concentration to increase. Most of these changes were not significant. The E4:E6 ratio increased after planting, and the $SUVA_{254}$ decreased, suggesting the DOC was becoming more fulvic and less aromatic in character, however these changes were not significant.

4.2.2.1. *Calluna* site

4.2.2.1.1. pH

In BACI year 0 (before intervention), the mean pH at the Control site was 3.74. The pH was steadily increasing over time; in BACI year 2 it was 3.98 (mean). In the first six months of BACI year 3, the mean pH value was 3.94. A similar trend was found at the *Sphagnum* site, where the BACI year 0 mean pH was 3.77, and increased to 3.97 in year 2. There was only one pH value available in the first six months of year 3, so it is not known if this upward trajectory would continue. At the *Sphagnum* and gully blocked site, the mean pH was 3.82 in BACI year 0, and increased to 4.07 in BACI year 3. These were all marginal increases, but could be the beginning of a trend towards less acidic water leaving the catchment.

The *Sphagnum* site in BACI year 2 and year 3 had a lower pH than the Control catchment, but generally the water from the *Sphagnum* and *Sphagnum* and gully block weirs was less acidic than the Control catchment. However, there was no trend over time relative to the Control catchment.

These results show that planting *Sphagnum* and blocking the drainage gullies has not had a clear impact on the pH of water leaving the catchments at the weirs in the first 2.5 years after catchment interventions.

4.2.2.1.2. Electrical conductivity

The electrical conductivity (EC) of the water leaving the Control catchment was highest in BACI year 1 (mean 104.3 $\mu S\ cm^{-1}$), and decreased to its lowest point during year 2 (mean 65.9 $\mu S\ cm^{-1}$). The BACI year 3 mean EC was 80.2 $\mu S\ cm^{-1}$, showing a downward trend in EC during the monitoring period. The EC of the water leaving the *Sphagnum* catchment showed a similar trend. It was highest in BACI year 0 (mean 101 µS cm^{-1}), then decreased to its lowest point in year 2 (mean 67.3 µS cm^{-1}), before increasing slightly in year 3 (mean 82 µS cm^{-1}). The EC at the *Sphagnum* and gully blocked catchment was lower than the Control and *Sphagnum* catchments, but followed the same pattern of yearly increases and decreases: it was highest in BACI year 0 (mean 90.8 µS cm^{-1}), then decreased to its lowest point in year 2 (mean 60.2 µS cm^{-1}), before increasing slightly in year 3 (mean 69.3 µS cm^{-1}).

The EC of the Control and *Sphagnum* sites were relatively similar over the whole experiment, suggesting that the *Sphagnum* planting had no impact on the EC in the 2.5 years of monitoring. There were larger differences in the EC between the Control and the *Sphagnum* and gully blocked catchments – mean EC was lower at the SphaGB site than the Control site in years 0, 1, 2 and 3. The magnitude of the difference was greatest in BACI year 1, showing a large decrease in EC immediately after catchment intervention. The EC from the *Sphagnum* and gully blocked catchment was, on average, 13.53 µS cm^{-1} lower than the Control site, after intervention. Comparing the *Sphagnum* and gully blocked site with the *Sphagnum* only site showed that it was the gully blocks rather than the *Sphagnum* planting causing the changes in EC – there were large differences in the EC between the two sites.

4.2.2.1.3. Dissolved organic carbon

DOC concentration at all three catchment weirs followed an approximate seasonal pattern: the concentrations were low in winter and high in autumn (Figure 31). The mean DOC concentrations in BACI year 0 were low (32, 34, 33 mg L^{-1} at Con, Spha and SphaGB respectively); they were collected during the winter and early spring before catchment intervention. The average DOC concentration after intervention (BACI years 1–3) had higher concentrations overall than year 0, but there was a difference between the three *Calluna* catchments – the mean DOC concentration was lower at the Spha and SphaGB catchments (43 mg L^{-1} at both) than the Control catchment (48.3 mg L^{-1}).

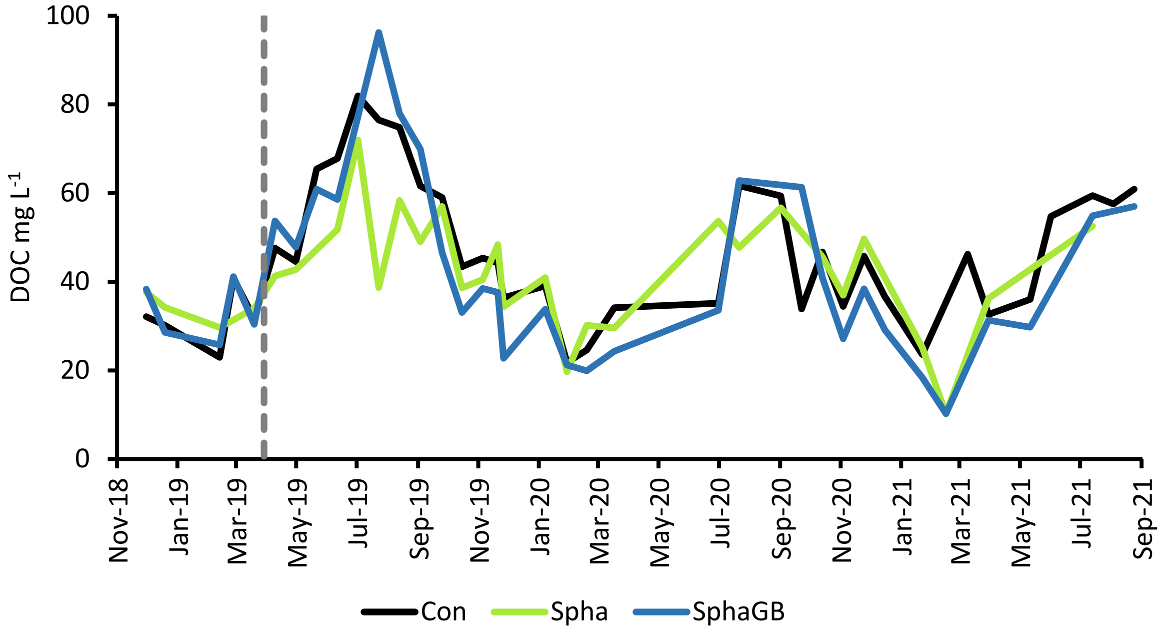

Figure 31. DOC concentration in water collected from the weir at the Control (Con), *Sphagnum* (Spha) and *Sphagnum* and gully blocked (SphaGB) *Calluna* catchments.
The vertical dotted line shows the date of catchment interventions.

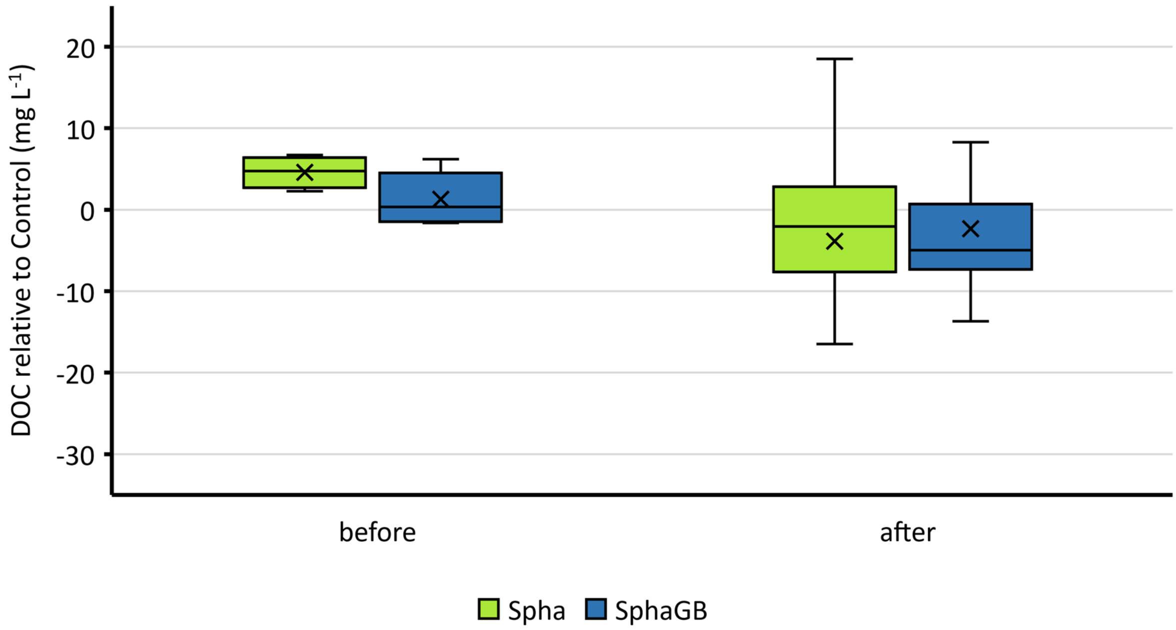

Figure 32. DOC concentration in water collected from the weir at the *Sphagnum* (Spha) and *Sphagnum* and gully blocked (SphaGB) *Calluna* catchments, relative to the Control catchment, before and after treatment intervention.

Before catchment intervention, there was a negligible difference in DOC between the catchments (Figure 32). After intervention, the average relative DOC values were: -3.85 (Spha), -2.35 (SphaGB) and 0.36 (GB). Comparing the *Sphagnum* to the Control site, the main decrease in DOC was observed at the *Sphagnum* site in the first year after intervention, mostly in the first 6 months. After that, the relative DOC concentration was closer to zero (indicating smaller or no differences in the DOC concentration between the Control and *Sphagnum* catchments). There was a significant difference in the relative DOC concentration – it was significantly lower after restoration (one-way Mann-Whitney U $p = 0.02$). Towards the end of BACI year 2, and in BACI year 3, DOC concentration was lower at the *Sphagnum* site than at the Control site, suggesting that as the *Sphagnum* plants grow, they may be decreasing the DOC concentration in the water leaving the catchment. It should be noted that the effect size was small in the context of annual variability of DOC concentration.

Comparing the *Sphagnum* and gully block treatment to the Control site shows that there was a significant, short-term increase in DOC concentration at the *Sphagnum* and gully blocked site following treatment. This increase occurred at all three mini-catchments (including untreated control), suggesting a seasonal effect. The increase at the Spha.GB site was greater than at the other two mini-catchments, but only for one water sampling date so this could be an anomaly. DOC concentration returned to levels comparable to the other two catchments within 6 months after treatment. This additional short-term increase in DOC concentration, if real, was likely due to the disturbance of installing the gully blocks into the peat, increasing the particulate organic carbon (POC) load in the water. POC can readily degrade to DOC in water.

Overall, the relative DOC concentration at the *Sphagnum* and the *Sphagnum* and gully blocked sites were lower than at the Control site in the two years after intervention, indicating that catchment interventions may have lowered the DOC concentrations. The effect size was small compared to annual variability, however, so future monitoring is required to establish whether any long-term change is maintained.

4.2.2.1.4. DOC composition

The E4:E6 ratio (absorbance at 465 nm divided by 665 nm) indicates the fulvic to humic ratio of the DOC. Higher E4:E6 ratios indicate more fulvic DOC. At the Control site, the E4:E6 ratio decreased from BACI year 0 to year 2, then was almost as high in year 3 as year 0. At the *Sphagnum* site the E4:E6 decreased from year 0 to year 2, then was highest in year 3. The E4:E6 in the water from the *Sphagnum* and gully blocked catchment did not follow the same pattern – it was low in year 0 and year 2, and higher in year 1 and year 3.

The water draining from the *Sphagnum* catchment had higher E4:E6 ratios than the Control and *Sphagnum* and gully block catchments over the whole experiment. These results indicate that planting *Sphagnum* and blocking gullies appeared to marginally increase the fulvic nature of DOC leaving the catchments.

The specific absorbance at 254 nm ($SUVA_{254}$, absorbance at 254 nm divided by DOC concentration) is considered a proxy for the aromatic carbon content of the water. Higher $SUVA_{254}$ values indicate higher aromaticity of the DOC. The water draining from the three *Calluna* catchments had no consistent patterns in the $SUVA_{254}$ values over the course of the experiment. The average values were lower after catchment interventions at the SphaGB catchment than before, whereas the $SUVA_{254}$ increased after *Sphagnum* planting in the *Sphagnum* catchment (Table 4). Planting *Sphagnum* had no consistent impact on the aromaticity of DOC in water at the weirs.

4.2.2.2. *Eriophorum* site

4.2.2.2.1. pH

In BACI year 0 (before intervention), the mean pH at the Control site was 3.84. This increased through the monitoring period; in BACI year 3 the mean value was 4.13. A similar trend was found at the *Sphagnum* site, where the BACI year 0 mean pH was 3.78, and increased to 4.00 in year 2, and 3.94 in year 3. These are all marginal increases, but could be the beginning of a trend towards less acidic water leaving both catchments.

The *Sphagnum* site had lower average pH values than the Control site in all BACI years; generally the water from the *Sphagnum* weirs was more acidic than the Control catchment. However, there was no trend over time relative to the Control catchment. These results show that planting *Sphagnum* has not had a clear impact on the pH of water leaving the catchments at the weirs in the first 2.5 years after catchment interventions.

4.2.2.2.2. Electrical conductivity

The electrical conductivity (EC) of the water leaving the Control catchment was highest in BACI year 0 (mean 92 $\mu S\ cm^{-1}$), and decreased to its lowest point during year 2 (mean 57 $\mu S\ cm^{-1}$). In BACI year 3 mean EC was 60 $\mu S\ cm^{-1}$, showing a downward trend in EC during the monitoring period. The EC of the water leaving the *Sphagnum* catchment showed a similar trend. It was highest in BACI year 0 (mean 110 $\mu S\ cm^{-1}$), then decreased to its lowest point in year 2 (mean 60 $\mu S\ cm^{-1}$), before increasing slightly in year 3 (mean 62 $\mu S\ cm^{-1}$).

The EC of the Control and *Sphagnum* sites were similar throughout the experiment; the largest difference was observed in BACI year 0, before intervention (mean difference of 18 $\mu S\ cm^{-1}$). After intervention, the EC values were much closer; the largest mean difference was only 3 $\mu S\ cm^{-1}$. These results suggest that while there has not been a large change in EC as a result of *Sphagnum* planting, the values are much more similar to those at the Control site after planting, so there may have been some impact of *Sphagnum* planting on the EC of water at the weirs.

4.2.2.2.3. Dissolved organic carbon

DOC concentration at both weirs followed an approximate seasonal pattern: the concentrations were low in winter and high in autumn (Figure 33). The mean DOC concentrations in BACI year 0 were low (22 and 30 mg L^{-1} at Con and Spha respectively); they were collected during the winter and early spring before catchment intervention. The DOC concentration at the Control weir water was lowest in year 0, and highest in year 3.

Before catchment intervention, there was the largest mean difference between the Spha and Con catchments – Spha was 8 mg L^{-1} higher than Con (Figure 34). After intervention, the range of relative DOC concentrations was larger than before intervention. However, the median and mean relative DOC concentrations were closer to 0, showing there had been a decrease in DOC concentrations at the Spha weir after intervention. The DOC concentrations were still higher than the Control catchment, but there was an apparent decrease after *Sphagnum* planting. It should be noted that the effect size was small compared to annual variability in DOC concentration at both weirs.

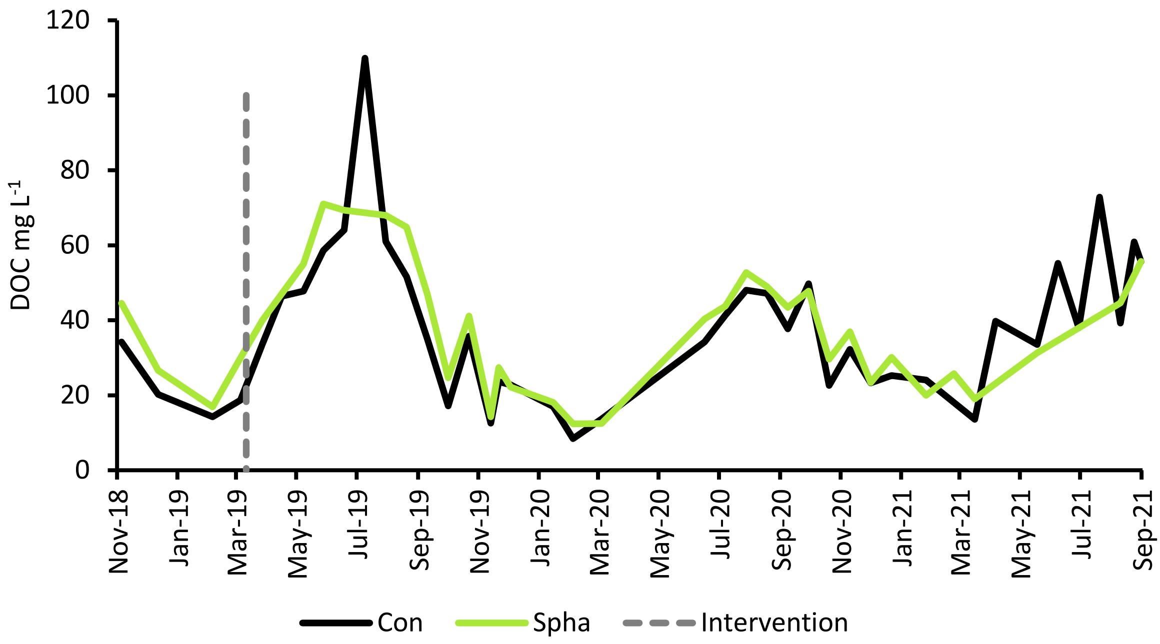

Figure 33. DOC concentration in water collected from the weir at the Control (Con) and *Sphagnum* (Spha) *Eriophorum* catchments.
The vertical dotted line shows the date of catchment interventions.

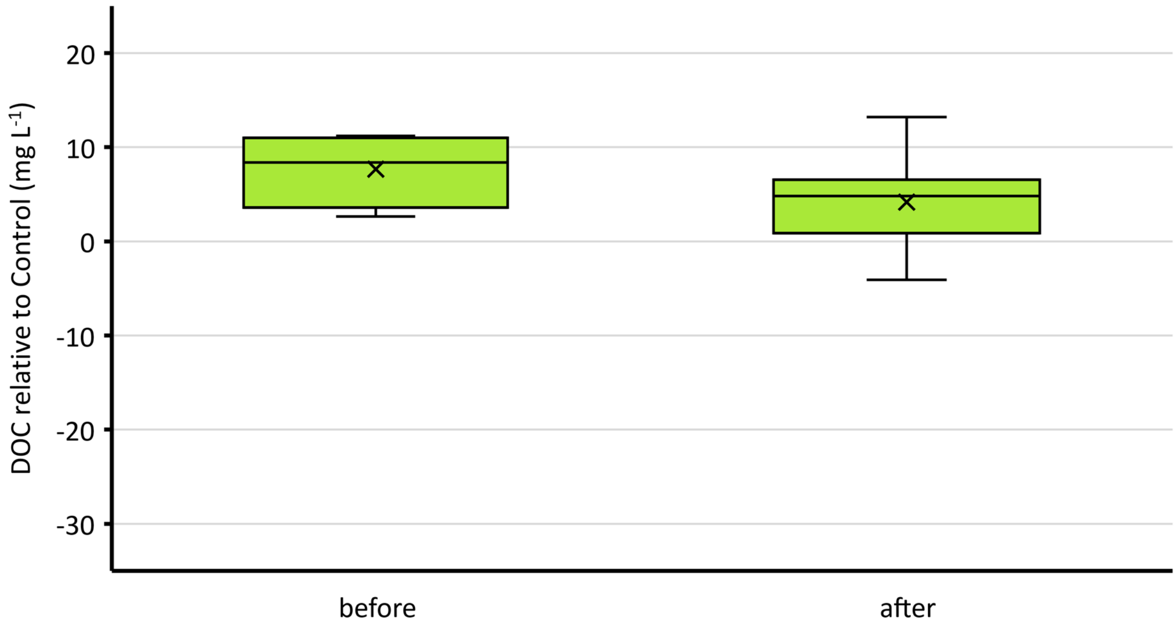

Figure 34. DOC concentration in water collected from the weir at the *Sphagnum* (Spha) *Eriophorum* catchment, relative to the Control catchment, before and after treatment intervention.

4.2.2.2.4. DOC composition

At the Control site, the E4:E6 ratio decreased from BACI year 0 to year 3. At the *Sphagnum* site the E4:E6 decreased from year 0 to year 2 and then increased slightly in year 3. The water draining from the *Sphagnum* catchment had higher E4:E6 ratios than the Control catchments throughout the monitoring period. The mean relative E4:E6 values were approximately 1 in all BACI years, indicating that the difference between the Control and *Sphagnum* catchment was consistent throughout the experiment. These results suggest that the DOC from both sites may have been becoming less fulvic over time, but there was no impact of *Sphagnum* planting.

The water draining from both catchments had similar $SUVA_{254}$ values during the monitoring period. Before intervention, the *Sphagnum* weir had slightly higher $SUVA_{254}$ values than the Control site, and in BACI year 3, the Control weir had slightly higher values than the *Sphagnum* site. These results suggest that planting *Sphagnum* may have lowered the aromaticity of DOC in water leaving the catchment. It should be noted that the effect size was small; future monitoring is required to establish whether this apparent change is maintained.

4.2.2.3. *Molinia* site

4.2.2.3.1. pH

In BACI year 0 (before intervention) the mean pH at the Control site was 3.67. This increased steadily during the monitoring period; in BACI year 3 the mean value was 4.33. A similar trend was found at the *Sphagnum* site, where the BACI year 0 mean pH was 3.71, and increased to 4.29 in year 3. These are all marginal increases, but could be the beginning of a trend towards less acidic water leaving both catchments.

The *Sphagnum* site had higher average pH values than the Control site in BACI years 0 to 2, and lower in BACI year 3. However, there was no trend over time relative to the Control catchment. These results show that planting *Sphagnum* has not had a clear impact on the pH of water leaving the catchments at the weirs in the first 2.5 years after catchment interventions.

4.2.2.3.2. Electrical conductivity

The electrical conductivity (EC) of the water leaving the Control catchment was highest in BACI year 0 (mean 112 µS cm^{-1}), and decreased to its lowest point during year 2 (mean 57 µS cm^{-1}). In BACI year 3 mean EC was slightly higher (74 µS cm^{-1}), but in general the results show a downward trend in EC over the experiment. The EC of the water leaving the *Sphagnum* catchment showed a similar downward trend. It was highest in BACI year 0 (mean 129 µS cm^{-1}), then decreased to its lowest point in year 2 (mean 58 µS cm^{-1}), before increasing slightly in year 3 (mean 60 µS cm^{-1}). The mean relative EC was highest in year 0; the largest difference between the two catchments was before intervention. After intervention, the *Sphagnum* site was significantly lower than the Control site (one-way Mann-Whitney U $p = 0.04$; BACI year 1–3 average 7 µS cm^{-1}). These results suggest that planting *Sphagnum* may have decreased the EC of water leaving the catchment.

4.2.2.3.3. Dissolved organic carbon

DOC concentration at both weirs followed an approximate seasonal pattern: the concentrations were low in winter and high in autumn (Figure 35). Mean DOC concentrations in BACI year 0 were low (10 and 6 mg L^{-1} at Con and Spha respectively); they were collected during the winter and early spring before catchment intervention. DOC concentration at the Control weir during BACI year 1 was very high; out of a total 42 Control weir water samples, only five had DOC concentrations over 40 mg L^{-1}, all collected between June and September in BACI year 1.

Before catchment intervention, the Control site DOC concentration was almost double the *Sphagnum* weir DOC concentration, and it was higher than the *Sphagnum* weir DOC concentration in all 3 BACI years (Figure 36). The largest difference was in BACI year 1 (due to very high Control DOC concentrations). However, there were still differences in DOC concentration in BACI years 2 and 3, where the *Sphagnum* weir DOC concentration was on average 8 and 3 mg L^{-1} lower than the Control. These results suggest that planting *Sphagnum* may have lowered the DOC concentration of water leaving the catchment, although the effect size was small. Future monitoring is required to establish whether this apparent change is real and maintained.

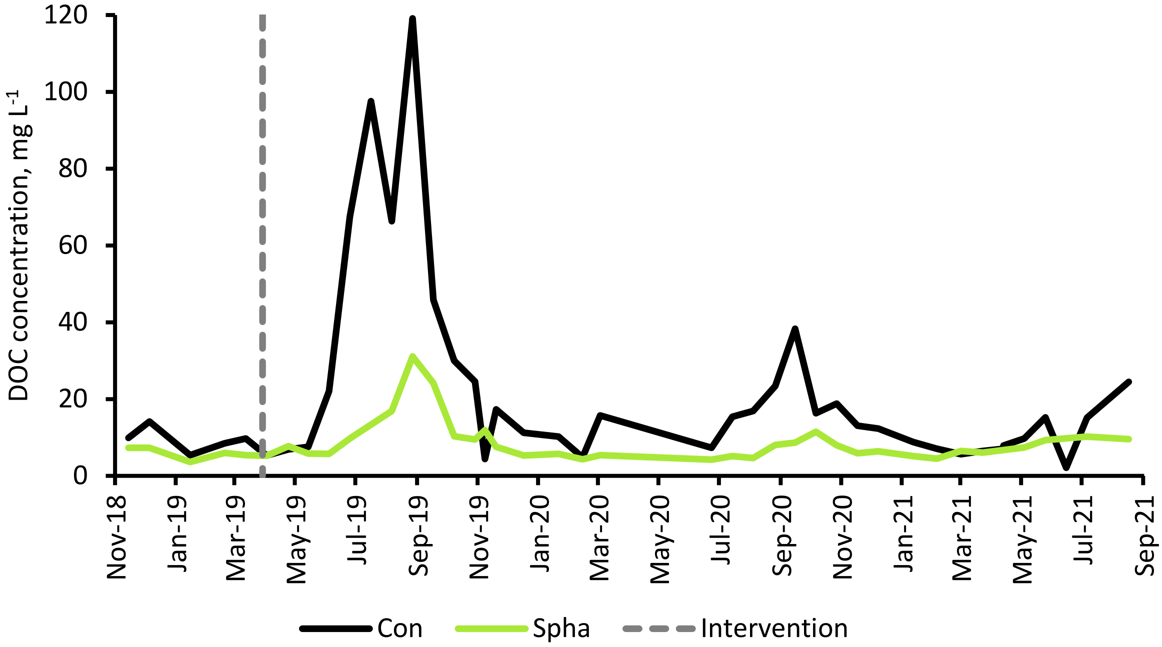

Figure 35. DOC concentration in water collected from the weir at the Control (Con) and *Sphagnum* (Spha) *Molinia* catchments.
The vertical dotted line shows the date of catchment interventions.

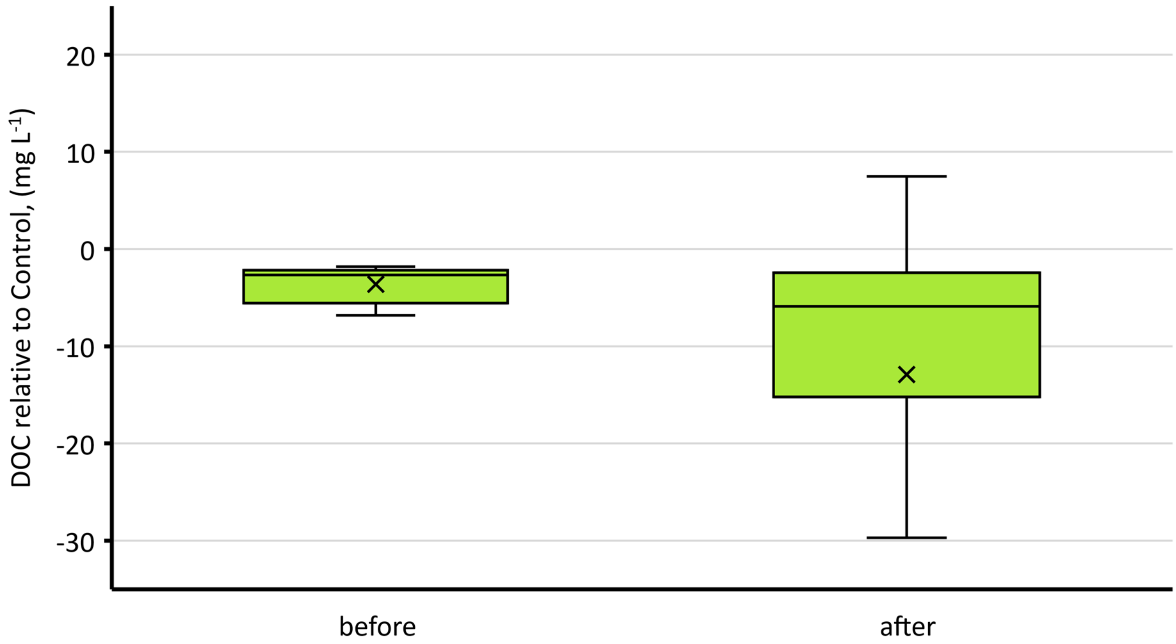

Figure 36. DOC concentration in water collected from the weir at the *Sphagnum* (Spha) *Molinia* catchment, relative to the Control catchment, before and after treatment intervention.

4.2.2.3.4. DOC composition

At the Control site, the E4:E6 ratio decreased from BACI year 0 to year 3. At the *Sphagnum* site the E4:E6 was high in year 0 and 3 and low in year 1 and 2. The water draining from the *Sphagnum* catchment had higher E4:E6 ratios than the Control catchment in BACI year 0, 2 and 3; the DOC in the water was generally more fulvic than humic in composition. The relative E4:E6 values showed no consistent trend over the experiment – there was a large difference in years 0 and 3. The average of all 'after' data (BACI years 1–3) showed a smaller difference than in year 0, suggesting that the DOC in the *Sphagnum* catchment was becoming more similar to the Control catchment. These results show that the fulvic and humic characteristics of DOC from both sites were variable, with no clear trend as a result of planting *Sphagnum*.

The water draining from both catchments had similar $SUVA_{254}$ values over the course of the experiment. At the Control site, the $SUVA_{254}$ increased from BACI year 0 to year 2, before returning to a similar value in year 3 as in year 0. At the *Sphagnum* site, the $SUVA_{254}$ values were low in year 0 and 3, and slightly higher in years 2 and 3.

Before intervention, the *Sphagnum* weir had slightly higher $SUVA_{254}$ values than the Control site (average 3.2 and 3.5 in Con and Spha, respectively). The largest difference was in year 2, where the average $SUVA_{254}$ were 4.4 at the Control site and 3.8 at the *Sphagnum* site – the DOC was more aromatic at the Control site. Overall, the average 'after' values (BACI years 1–3) were lower at the *Sphagnum* site than the Control site (average 4.1 and 3.9 in Con and Spha, respectively). Although small, these changes show that the aromaticity of DOC from the Control site varied more over the experiment, whereas DOC from the *Sphagnum* site had a more consistent aromaticity.

4.2.3. Effects of *Sphagnum* planting densities on water chemistry

In order to assess the impact of the two *Sphagnum* planting densities, water chemistry variables in the overland flow (0 cm), and soil water (5 and 10 cm depths) from the cluster (4 plugs m^{-2}) and intensive (100 plugs m^{-2}) plots in the catchments with *Sphagnum* planting were compared to the water from the Control catchment (0 plugs). If values are close to 0 this indicates that the concentrations were similar at the two sites. Samples collected as part of the routine and spatial sampling were included in this analysis. The DOC concentration was analysed at all sites and depths, and E4:E6 ratios, and $SUVA_{254}$ values were also analysed in the overland flow water from the intensive plots.

The cluster and intensive plots in the *Calluna Sphagnum* gully blocked cluster catchment were also included in this analysis, even though it was unlikely that the water chemistry of these areas would have been directly impacted by the gully blocking.

Due to the different planting times of the cluster and intensive plots, the water chemistry from these areas could not be directly compared. However, the *Sphagnum* cluster (lower density planting) water chemistry was compared to the Control cluster, and the *Sphagnum* intensive plots (high density planting) water chemistry was compared to the Control intensive plots. For the low density planting comparisons, the BACI design was the same as outlined in the Methodology section of this chapter, whereas the high density planting BACI timing was:

- BACI year 0 – start of water sample collection (Nov 2018) to before intervention (end of August 2019)
- BACI year 1 – the 12 months from September 2019 to August 2020
- BACI year 2 – the 12 months from September 2020 to August 2021

Table 5. The indicative direction of change after catchment intervention in DOC concentration of overland flow, and 5 and 10 cm soil water collected from *Calluna* (CAL), *Eriophorum* (ERI) and *Molinia* (MOL) cluster and intensive plots.
Results are shown as direction of change relative to the Control site, so if the DOC concentration increased, if the increase was smaller than the increase at the Control site, this would be shown as a decrease relative to Control. OLF = overland flow. One-way Mann-Whitney U test results are shown with NS = not significant; * = $p < 0.05$; ** $p < 0.01$; and *** $p < 0.001$.

Veg.	Location	Impact of treatment	Direction of change after catchment intervention		
			OLF DOC	5 cm soil DOC	10 cm soil DOC
CAL	Cluster	Spha (Spha – Con)	↓ ***	↓ NS	↓ *
CAL	Cluster	Spha & GB (SphaGB – Con)	↓ NS	↓ NS	↓ *
CAL	Intensive	Spha (Spha – Con)	- NS	- NS	- NS
CAL	Intensive	Spha & GB (SphaGB – Con)	↓ NS	↓ NS	↓ NS
ERI	Cluster	Spha (Spha – Con)	↓ **	↓ *	↓ ***
ERI	Intensive	Spha (Spha – Con)	- NS	↓ NS	↑ NS
MOL	Cluster	Spha (Spha – Con)	↓ *	↓ NS	↓ **
MOL	Intensive	Spha (Spha – Con)	↑ *	- NS	↑ *

Table 6. Indicative direction of change after catchment intervention in E4:E6 and $SUVA_{254}$ ratios in overland flow water collected from *Calluna* (CAL), *Eriophorum* (ERI) and *Molinia* (MOL) cluster plots. Results are shown as direction of change relative to the Control site. OLF = overland flow. Increases in E4:E6 indicate the DOC is becoming more fulvic in character, and increases in $SUVA_{254}$ indicate the DOC is becoming more aromatic in character. One-way Mann-Whitney U tests showed there were no significant differences in relative E4:E6 or relative $SUVA_{254}$ in overland flow between samples taken before and after restoration.

Veg.	Location	Impact of treatment	Direction of change after catchment intervention	
			OLF E4:E6	**OLF $SUVA_{254}$**
CAL	Intensive	Spha (Spha – Con)	↑ NS	↓ NS
CAL	Intensive	Spha & GB (SphaGB – Con)	↓ NS	↓ NS
ERI	Intensive	Spha (Spha – Con)	↑ NS	↓ NS
MOL	Intensive	Spha (Spha – Con)	↓ NS	↑ NS

To compare the low density to the high density (cluster vs intensive plots) planting, the DOC concentration of samples taken during the final 6 months of the experiment were compared (March to September 2021). The *Sphagnum* plants had been in the cluster for 2 years (planted in March 2019) and in the intensive plots for 1.5 years (planted in September 2019). This analysis avoids including times when the cluster had been planted but the intensive plots had not. As this was an approximate comparison, the *Calluna Sphagnum* and *Sphagnum* and gully blocked catchments were considered as replicates, rather than analysed separately.

4.2.3.1. *Calluna* site

4.2.3.1.1. DOC (lower density planting)

At the Control site, the mean DOC concentration in the overland flow and 5 cm soil solution increased each year (from 23 to 51 mg L^{-1} in overland flow; 35 to 55 mg L^{-1} in 5 cm soil solution). The DOC concentration in the 10 cm soil solution water from the Control cluster was lowest in BACI year 0 (39 mg L^{-1}), and higher in BACI years 1, 2 and 3 (mean 68 mg L^{-1}).

The relative DOC concentration in overland flow was significantly lower at the *Sphagnum* site (Spha) after intervention in year 1, 2 and 3 (one-way Mann-Whitney U, $p < 0.001$; Figure 37). The relative DOC concentration in the 5 cm soil solution was higher at Spha in BACI year 0, 1 and 2, but was lower than the concentration at the Control site in BACI year 3. The relative DOC concentration in the 10 cm soil solution was higher at Spha in BACI year 0, 1 and 3, however it was significantly lower after catchment intervention (one-way Mann-Whitney U, $p < 0.05$). These results suggest that planting *Sphagnum* may have decreased the DOC concentration in the overland flow to below concentrations at the Control site, and may be starting to have an impact on the 5 and 10 cm soil solution, but has not yet lowered them to below the Control site. However, given the low planting density (and resultant cover) of *Sphagnum*, a significant effect on DOC concentration would not necessarily be expected, so future monitoring is required to establish whether a consistent effect is emerging.

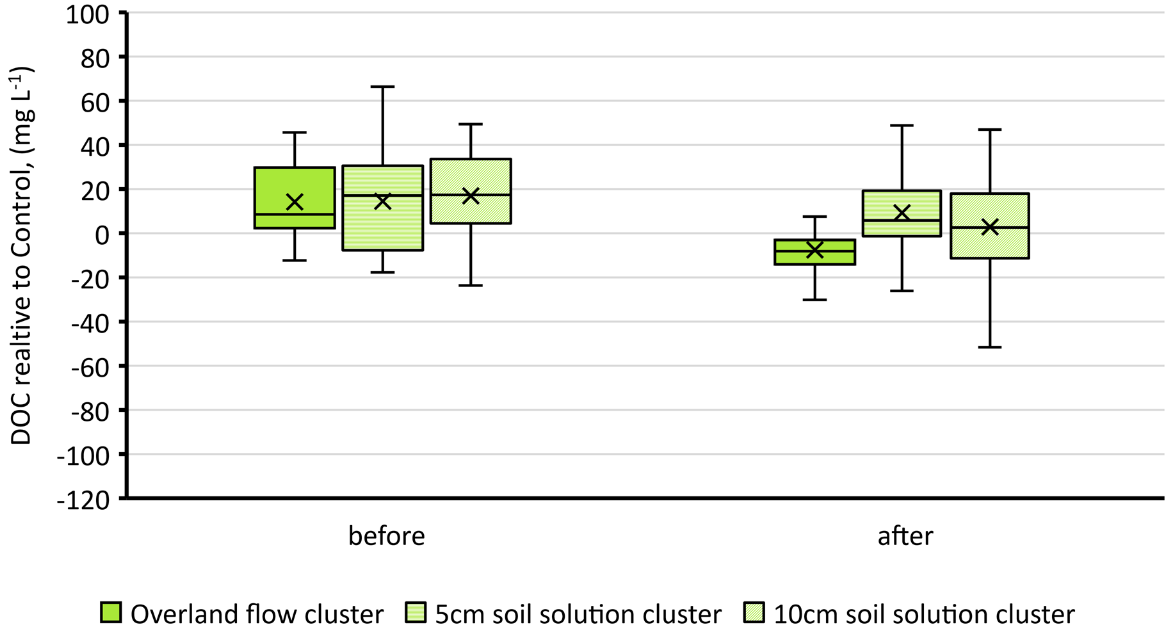

Figure 37. Relative DOC concentration in water collected from the *Calluna* Spha cluster (lower density planting) before and after *Sphagnum* planting.

The DOC concentration in overland flow was higher at the *Sphagnum* and gully blocking site (SphaGB) than at the Control site before catchment intervention and increased each year (from average 34 to 56 mg L^{-1}). In the 5 cm soil solution at SphaGB, DOC concentration increased each year (from average 46 to 53 mg L^{-1}), but the increase was smaller than the increase measured at the Control site. In the 10 cm soil solution at SphaGB, DOC concentration increased over time (from average 49 to 56 mg L^{-1}), and the highest average concentrations were in year 1 and 2 (75 and 60 mg L^{-1}). All increases in DOC concentration in the SphaGB cluster were smaller than the increase measured at the Control site, and so the relative DOC concentration was lower after catchment intervention than before, but this change was only significant at 10 cm (one-way Mann-Whitney U, $p < 0.05$; Figure 38). These results suggest that planting *Sphagnum* may have decreased the DOC concentration in the overland flow, and 5 cm and 10 cm soil solution. However, given the low planting density (and resultant cover) of *Sphagnum*, a significant effect on DOC concentration would not necessarily be expected, so future monitoring is required to establish whether a consistent effect is emerging.

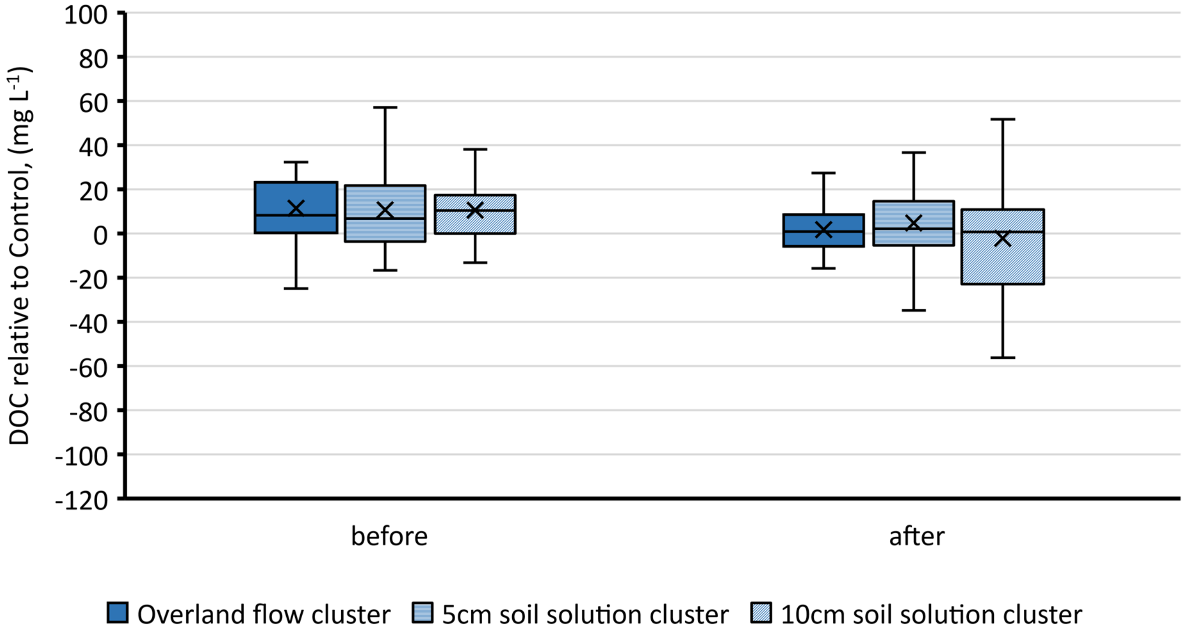

Figure 38. Relative DOC concentration in water collected from the *Calluna* SphaGB cluster (lower density planting) before and after *Sphagnum* planting.

4.2.3.1.2. DOC (higher density planting)

The mean DOC concentration in overland flow in the *Calluna* intensive plots was lower in BACI year 1 than in year 0 and 2 (51, 43 and 51 mg L^{-1}, respectively). In the Control intensive plots 5 cm soil solution, the DOC concentration was highest in year 0, then decreased in year 1 and 2 (from 49 to 40 mg L^{-1} in year 0 and year 2). The DOC concentration was highest in year 1 in the 10 cm soil solution in the Control intensive plots.

The DOC concentration in the overland flow, 5 cm and 10 cm soil solution was lower from the *Sphagnum* catchment than the Control catchment, both before and after intervention (Figure 39). There were no statistically significant changes in relative DOC concentrations in overland flow, 5 cm or 10 cm soil solution after intervention, suggesting that high density *Sphagnum* planting in intensive plots did not have a clear impact on DOC concentration at any depth during the monitoring period.

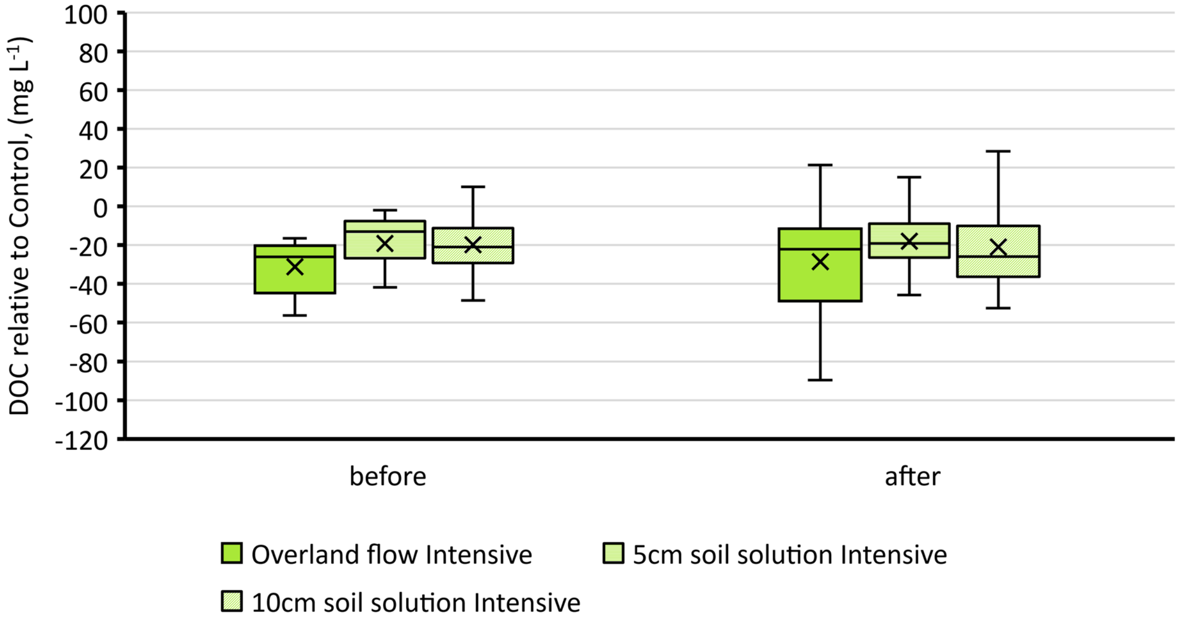

Figure 39. Relative DOC concentration in water collected from the *Calluna* Spha intensive plots (higher density planting), before and after *Sphagnum* planting.

The average DOC concentration in overland flow, and 5 and 10 cm soil solution from the *Sphagnum* and gully-blocked site (SphaGB) intensive plots were higher than those measured in the Control intensive plots in all BACI years. However, the SphaGB DOC concentrations were lower in year 2 than year 0, and decreased relative to the Control (Figure 40). These results suggest that planting *Sphagnum* may have decreased the DOC concentration in the water draining from the SphaGB intensive plots, however the DOC concentrations remained higher than those from the Control intensive plots. The reductions were not statistically significant and the effect size was small, so future monitoring is required to establish whether a consistent effect is emerging.

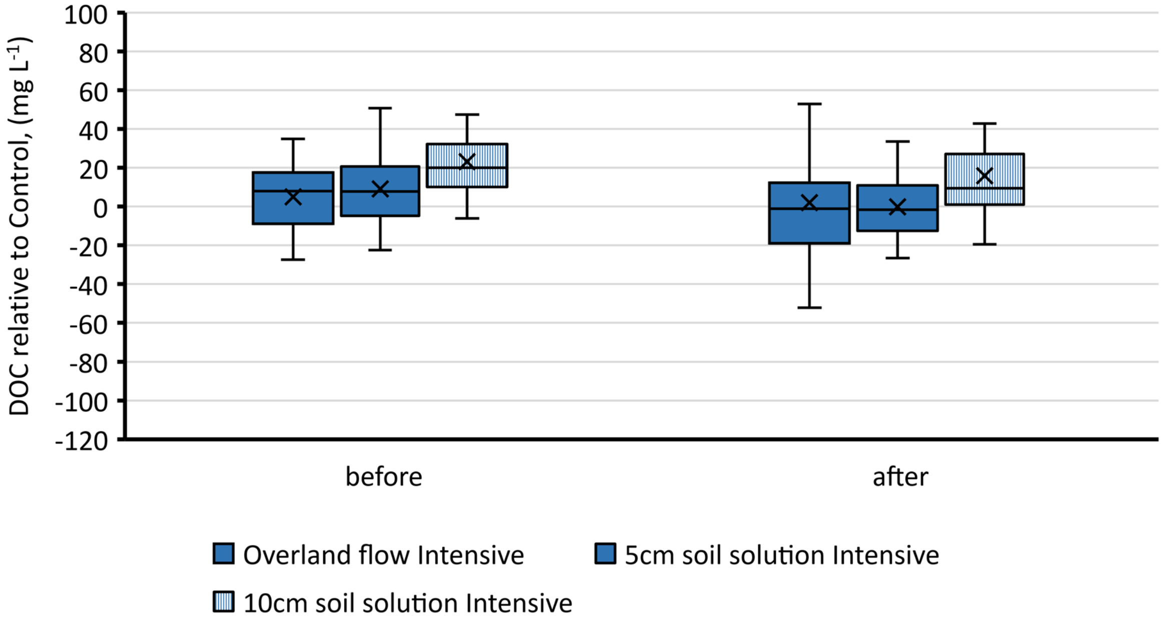

Figure 40. Relative DOC concentration in water collected from the *Calluna* SphaGB intensive plots (higher density planting), before and after *Sphagnum* planting

Comparing the low and high density planting in the *Calluna* catchments (using BACI year 0 and the final 6 months of the experiment only) showed that the relative DOC concentrations appeared to be lower after planting in both the low and high density plots – however these differences were generally not statistically significant and were within expected annual variability.

4.2.3.1.3. DOC composition (high density planting)

The mean E4:E6 ratio of water from overland flow from Control intensive plots was highest in BACI year 0, then lowest in year 1, and intermediate in year 2. At the *Sphagnum* site (Spha), the mean E4:E6 ratio was lowest in BACI year 0, highest in year1 and intermediate in year 2. At the *Sphagnum* and gully blocking site (SphaGB) site, the mean E4:E6 ratio was intermediate in BACI year 0, highest in year1 and lowest in year 2. Relative to the Control site, E4:E6 ratios at the Spha site were lower before planting (mean relative E4:E6 -1.28), and remained lower after planting (slight increase, mean relative E4:E6 -1.13). Relative to the Control site, E4:E6 ratios at the SphaGB site were lower before planting (mean relative E4:E6 -1.04), and decreased after planting (mean relative E4:E6 -1.24). Neither of these changes were statistically significant. These results suggest that that there was no consistent change in the E4:E6 ratio as a result of Sphagnum planting at high density.

$SUVA_{254}$ values were consistently decreasing in overland flow in all three catchments, although not significantly. The mean values in year 0 were 4.2, 3.2 and 4.2 in the Con, Spha and SphaGB catchments, and were 3.7, 2.7 and 3.6 in year 2. Relative to the Control site, $SUVA_{254}$ values in the Spha overland flow from intensive plots were lower before intervention, and decreased after intervention. Relative to the Control site, $SUVA_{254}$ values in the SphaGB overland flow from intensive plots were lower before intervention, and decreased after intervention. Neither of these changes were statistically significant. These results suggest that planting *Sphagnum* may reduce the aromaticity of DOC; future monitoring is required to establish whether this possible change becomes significant.

4.2.3.2. *Eriophorum* site

4.2.3.2.1. DOC (lower density planting)

At the Control site, the mean DOC concentration in the overland flow increased each year (from 15 to 30 mg L^{-1}). The DOC concentration in the 5 cm soil solution water from the Control cluster did not vary much in BACI years 0–3 (average 33, 38, 36 and 39 mg L^{-1} in year 0, 1, 2 and 3). The DOC concentration in the 10 cm soil solution water from the Control cluster was lowest in BACI year 0 (42 mg L^{-1}), and higher in BACI years 1, 2 and 3 (mean 67 mg L^{-1}).

The relative DOC concentration in overland flow and 5 cm soil solution was lower at the *Sphagnum* site after intervention (compared to before intervention), but was still higher than the Control cluster (Figure 41). The DOC concentration in the 10 cm soil solution was higher at the *Sphagnum* site in BACI year 0 and 1, but lower than the Control cluster in year 2. The relative DOC concentration was significantly lower at all three depths after catchment intervention (one-way Mann-Whitney U, OLF $p < 0.01$; 5 cm $p < 0.05$; 10 cm $p < 0.001$). These results suggest that planting *Sphagnum* may have decreased the DOC concentration in the overland flow and soil solution over time. The effect size was small and future monitoring is required to establish whether this change is maintained in future years.

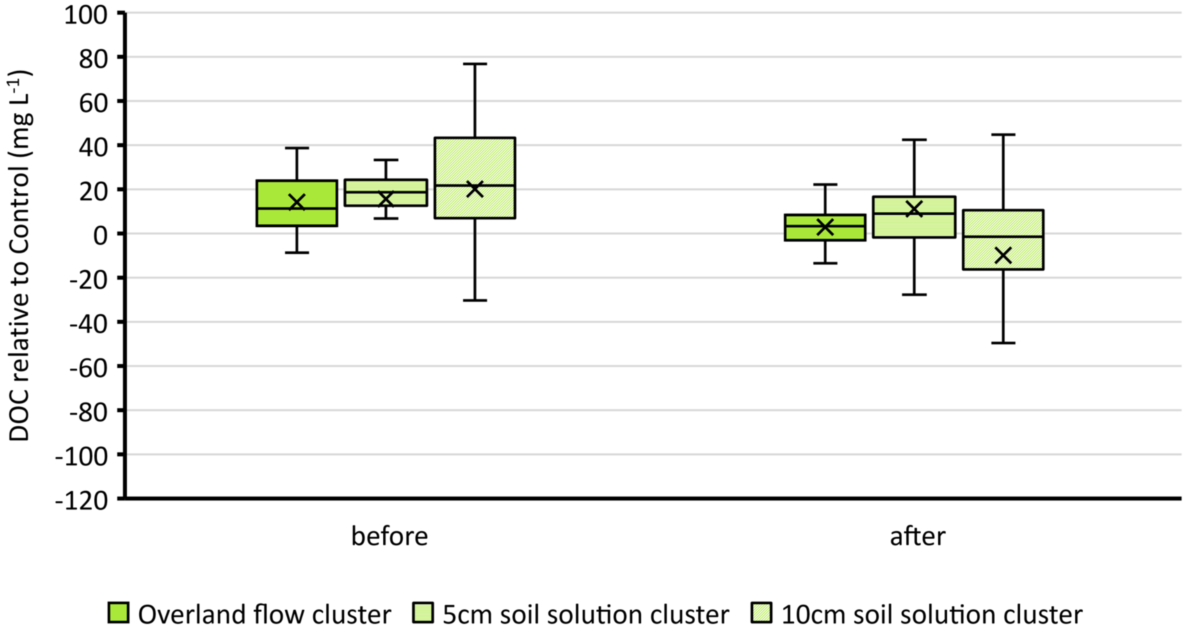

Figure 41. Relative DOC concentration in water collected from the *Eriophorum* cluster (lower density planting), before and after *Sphagnum* planting.

4.2.3.2.2. DOC (higher density planting)

In the *Eriophorum* Control intensive plots, the mean DOC concentration was higher in BACI year 0 than years 1 or 2 in overland flow, whereas it was lowest in year 0, then rose in year 1 and again in year 2 in the 5 cm soil solution (small increases, from 42 to 46 mg L^{-1}). The DOC concentration was higher in the 10 cm soil solution, and highest in year 1 (47 mg L^{-1} in year 1, compared with 41 and 43 mg L^{-1} in year 0 and year 2).

Relative DOC concentrations in overland flow were similar before and after intervention, and were higher after intervention in 10 cm soil solution (due to high DOC concentrations at *Sphagnum* site in year 1). The largest change was seen at 5 cm depth, where the *Sphagnum* DOC concentration was higher than Control in year 0, similar in year 1, then lower than the Control in year 2. These results suggest that planting *Sphagnum* had little to no impact on DOC concentrations in overland flow, but may have increased the DOC in the 10 cm soil solution, and may have decreased the DOC concentrations at 5 cm depth, however the differences were not statistically significant.

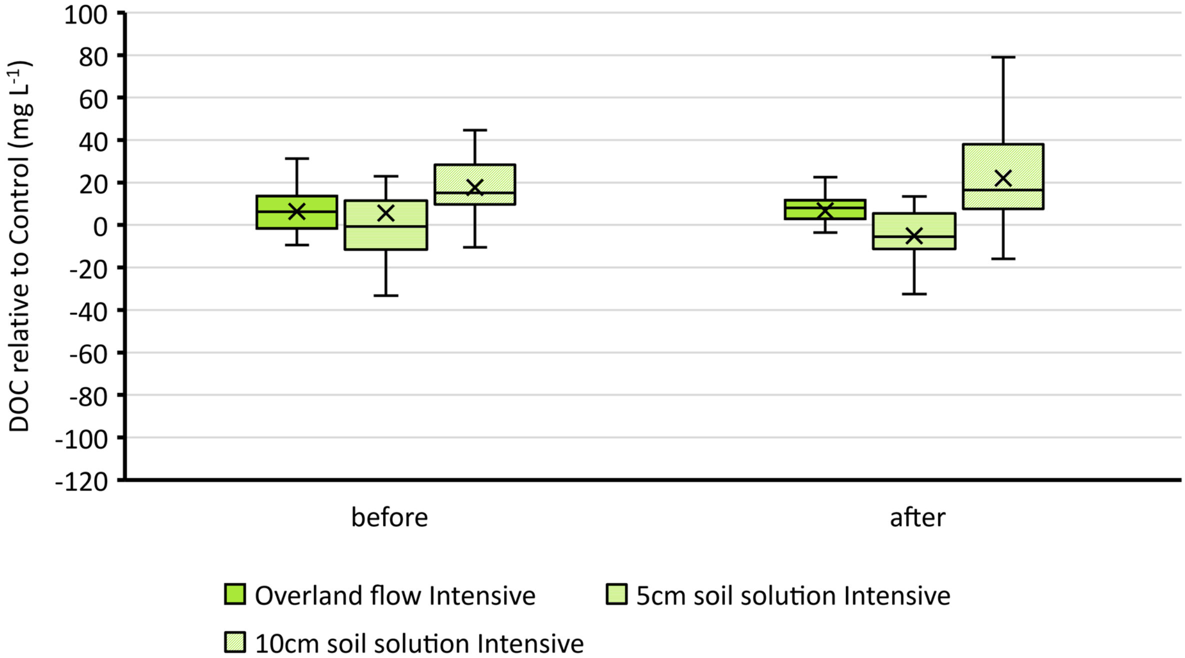

Figure 42. Relative DOC concentration in water collected from the *Eriophorum* intensive plots (higher density planting), before and after *Sphagnum* planting.

4.2.3.2.3. DOC composition (high density planting)

In BACI year 0, the mean E4:E6 ratio was high, then decreased in year 1 and was intermediate in year 2 at the Control catchment intensive plots. In the Spha catchment, the mean values were similar in year 0 and 2, and low in year 1.

The E4:E6 ratio of water in the overland flow was lower (more humic) in the Spha intensive plots than the Control before planting. However, after planting, the E4:E6 values from Spha site increased, becoming more similar to those in the Con catchment. The DOC character appeared to have become slightly more fulvic after planting *Sphagnum*, but the change seen was not statistically significant.

The $SUVA_{254}$ values in the Control catchment intensive plots overland flow decreased each year (mean 3.5 in year 0, 2.9 in year 2). In the Spha catchment, the values were highest in year 0, lowest in year 1 and intermediate in year 1 (mean 3.7, 3.1 and 3.4 in year 0, 1 and 2).

Relative to the Control catchment, the Spha catchment $SUVA_{254}$ values were higher before planting, and more similar to, but still higher than, the Con catchment after planting. The Spha $SUVA_{254}$ values, and therefore the aromaticity of the DOC, decreased slightly after planting, but not significantly.

4.2.3.3. *Molinia* site

4.2.3.3.1. DOC (lower density planting)

At the Control site, the mean DOC concentrations followed a similar pattern in the overland flow and soil solutions (both 5 and 10 cm depth). The concentration was lowest in year 0, then higher in year 1, low again in year 2 (but not as low as year 0), then highest in year 3.

The relative DOC concentration in overland flow, 5 cm and 10 cm soil solution was lower after catchment intervention (one-way Mann-Whitney U, OLF $p < 0.05$; 5 cm NS; 10 cm $p < 0.01$; Figure 43). The largest change was at 10 cm depth, were the relative DOC concentration was reduced on average by ~20 mg L^{-1} lower at the *Sphagnum* site than the Control site. These results suggest that planting *Sphagnum* may have decreased the DOC concentration in the overland flow and soil solution. DOC concentration was considerably more variable at the Control site than the *Sphagnum* site.

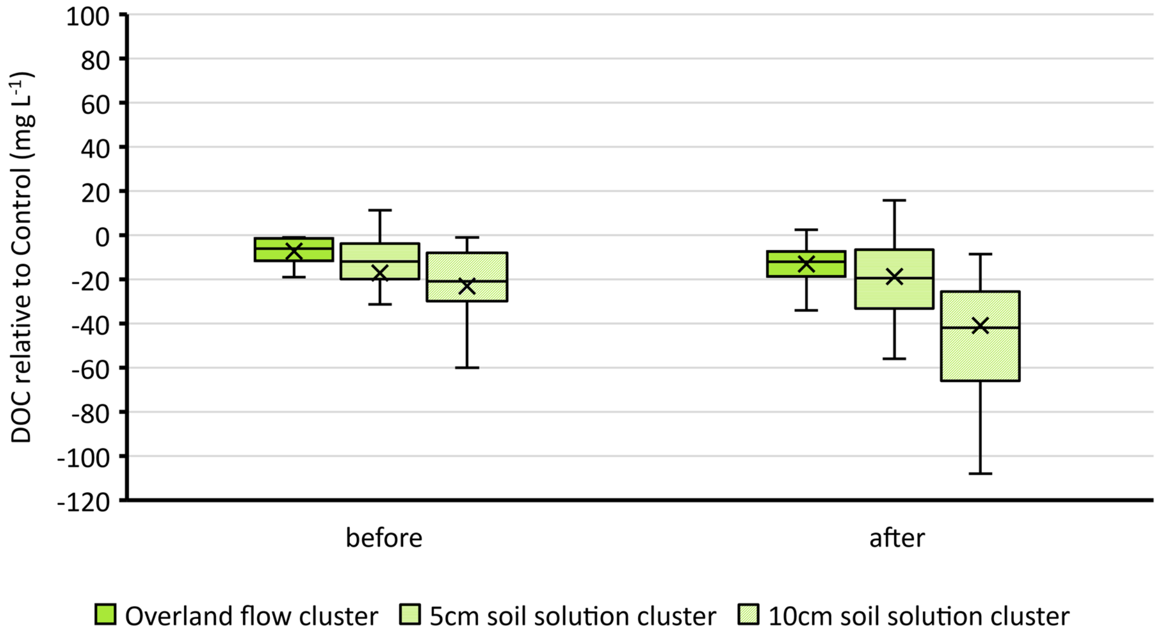

Figure 43. Relative DOC concentration in water collected from the *Molinia* cluster (low density planting), before and after *Sphagnum* planting.

4.2.3.3.2. DOC (higher density planting)

The mean DOC concentration in overland flow from the intensive plots in the *Molinia* Control catchment were lowest in year 1, and slightly higher in year 0 and 2 (8 mg L^{-1} in year 1, and 13 and 12 mg L^{-1} in year 0 and 2). The 5 and 10 cm soil solution mean DOC concentrations were higher than overland flow, and both were highest in year 0, and decreased in year 1 and 2 (5 cm: 20, 14, 13 mg L^{-1} in year 0, 1 and 2; 10 cm: 48, 22, 20 mg L^{-1} in year 0, 1 and 2).

Relative DOC concentrations increased in the overland flow, 5 and 10 cm soil solution after *Sphagnum* planting (one-way Mann-Whitney U, OLF $p < 0.05$; 5 cm NS; 10 cm $p < 0.05$; Figure 44). These results suggest that high density *Sphagnum* planting in intensive plots did not decrease DOC concentrations at any depth.

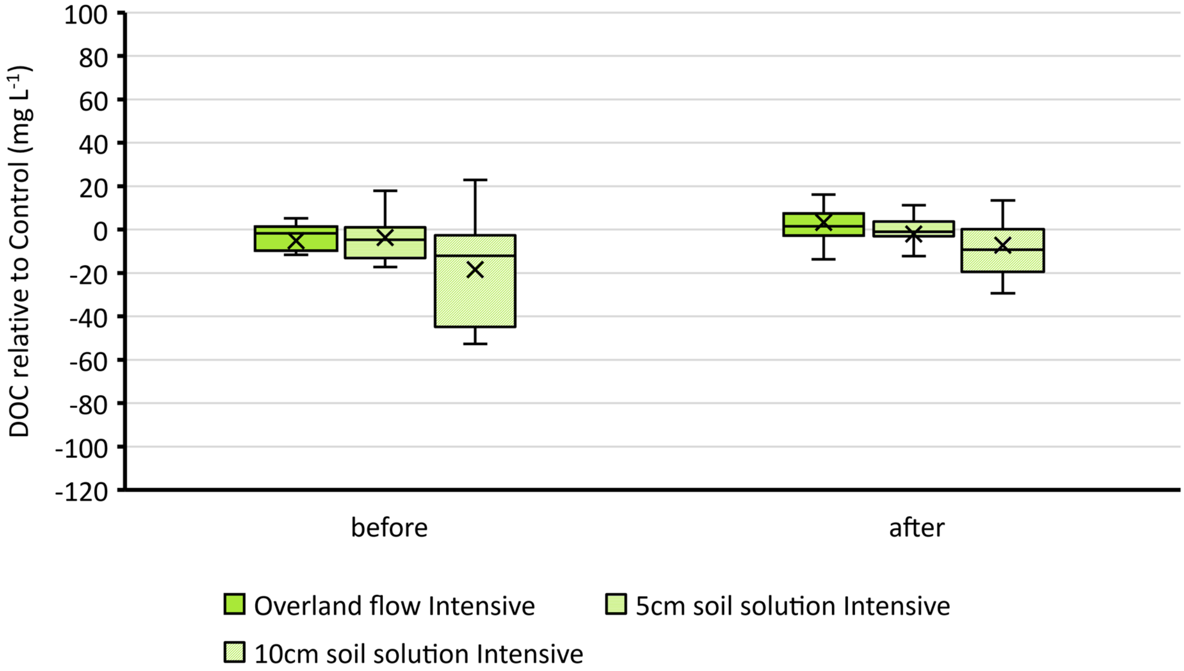

Figure 44. Relative DOC concentration in water collected from the *Molinia* intensive plots (higher density planting), before and after *Sphagnum* planting.

4.2.3.3.3. DOC composition (higher density planting)

In the Control catchment overland flow from the intensive plots, the E4:E6 ratio was highest in year 0, lowest in year 1 and intermediate in year 2 (mean 6.7, 6.0 and 6.2 in year 0, 1 and 2). At the Spha site, the E4:E6 ratio was high in year 0, lower in year 1, and still low in year 2 (mean 8.1, 4.8 and 5.7 in year 0, 1 and 2). Relative to the Control catchment, the Spha E4:E6 ratio appeared to be reduced following planting although this change was not significant.

The $SUVA_{254}$ values in the Control catchment were highest in year 0, and low in year 1 and 2. At the Spha catchment, the values were highest in year 0, and lower in year 1 and 2. Relative to the Control catchment, the Spha $SUVA_{254}$ values were higher before *Sphagnum* planting, and were still higher after planting. The values fell further at the Con catchment than at the Spha site, so the Spha site $SUVA_{254}$ values appeared to increase relative to the Control site, although this change was not significant.

4.2.4. DOC flux estimates

4.2.4.1. *Calluna* site

The DOC flux was estimated for each weir, using the DOC concentrations measured throughout the experiment, and the weir discharge data. Values are reported as total amount of carbon lost at each weir.

At the *Calluna* site, the DOC flux was highest in the second half of the year (July to December), and lowest in the Spring (April to June) at all three mini-catchments in both 2019 and 2020.

The mean flux was highest in 2018 from the Control site (3.97 g day^{-1}), 2020 from the Spha site (2.79 g day^{-1}) and 2019 from the SphaGB site (2.99 g day^{-1}). Relative to the Control site, the fluxes from both the Spha and SphaGB sites appeared to be reduced following catchment intervention, but further monitoring is required to establish whether this change is maintained in future years (Table 7, Figure 45, Figure 46).

Taking catchment area into account, the DOC fluxes from the Control catchment were 0.37 and 0.52 mg C day^{-1} m^{-2} (before and after intervention); 0.41 and 0.54 mg C day^{-1} m^{-2} from the *Sphagnum* catchment; and 0.31 and 0.44 mg C day^{-1} m^{-2} from the *Sphagnum* and gully blocked catchment.

Table 7. Mean DOC flux, in g day^{-1}, from the *Calluna* weirs, in each calendar year, and before and after catchment intervention.

Average DOC, g day^{-1}	**Con**	**Spha**	**SphaGB**
2018 (32 days)	3.97	2.78	2.54
2019 (327 days)	3.88 (1270 g yr^{-1})	2.41 (787 g yr^{-1})	2.99 977 g yr^{-1})
2020 (288 days)	3.43 (987 g yr^{-1})	2.79 (802 g yr^{-1})	2.06 (593 g yr^{-1})
2021 (89 days)	3.71	2.29	1.96
Before	2.74	2.03	1.85
After	3.85	2.65	2.59
Relative to CON, before		-0.71	-0.89
Relative to CON, after		-1.21	-1.26

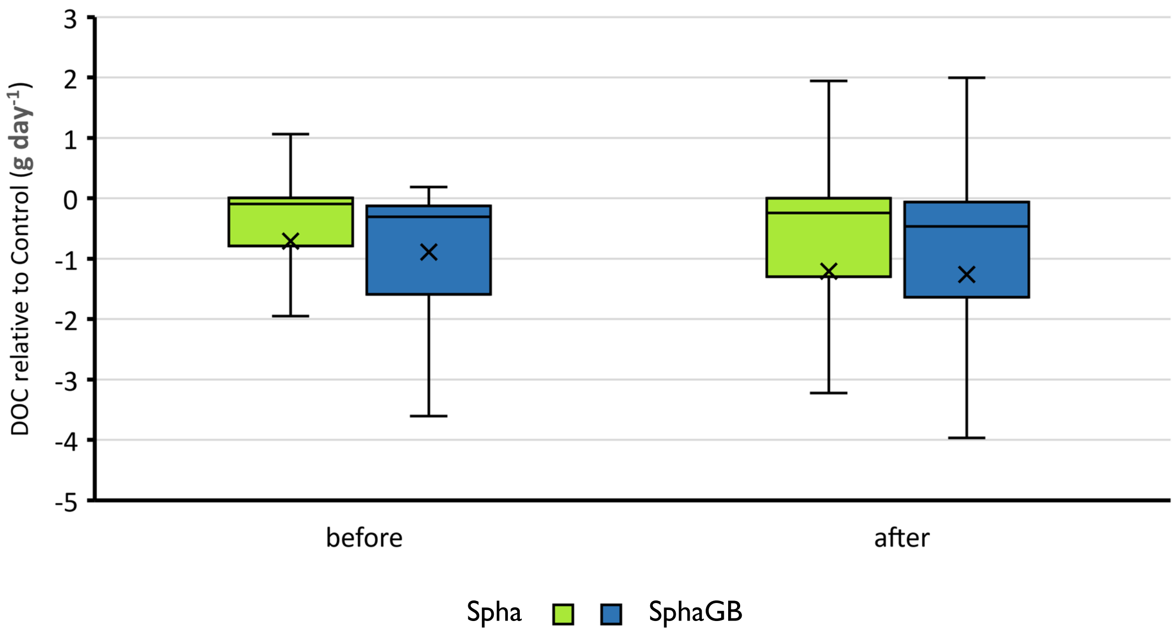

Figure 45. DOC flux relative to control at the *Calluna* Spha and SphaGB catchments, before and after intervention.

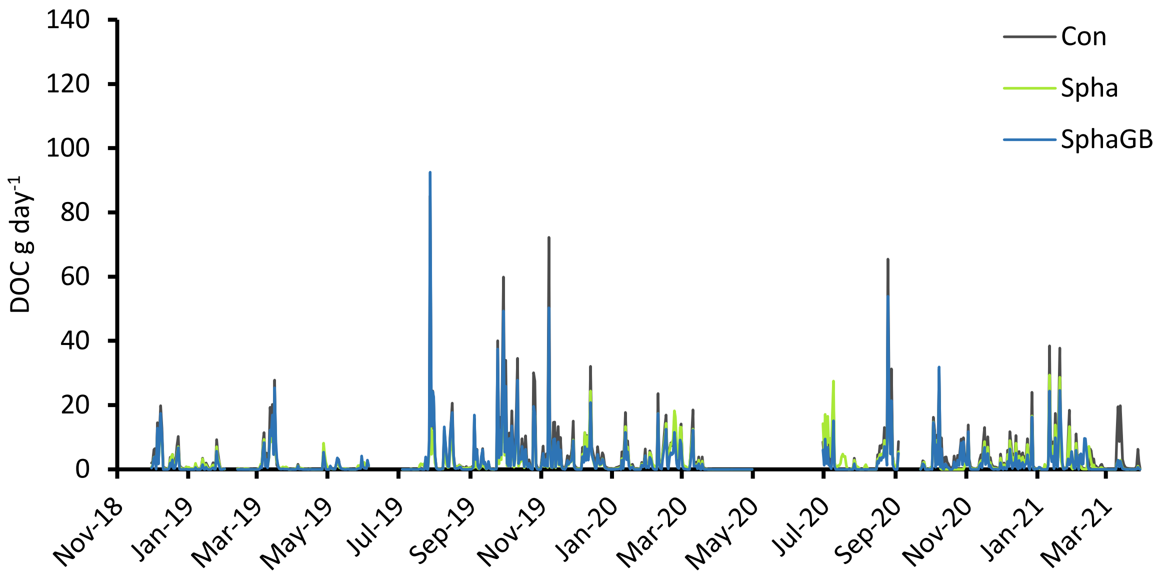

Figure 46. The flux of DOC (g day^{-1}), from the *Calluna* weirs.

4.2.4.2. *Eriophorum* site

At the *Eriophorum* site, the DOC flux was highest in the second half of the year (July to December), and lowest in the Winter (January–March) at both sites in 2019 and 2020. The mean flux was highest in 2018 from both the Control site (2.54 g day^{-1}), and the Spha site (8.87 g day^{-1}). Relative to the Control site, the flux from the Spha catchment appeared to be reduced following intervention, but further monitoring is required to establish whether this change is maintained in future years (Table 8, Figure 47).

Taking catchment area into account, the DOC fluxes from the Control catchment were 0.28 and 0.36 mg C day^{-1} m^{-2} (before and after intervention); and 0.48 and 0.50 mg C day^{-1} m^{-2} from the *Sphagnum* catchment.

Table 8. Mean DOC flux, in g day^{-1}, from the *Eriophorum* weirs, in each calendar year, and before and after catchment intervention.

Average DOC, g day^{-1}	Con	Spha
2018 (56 days)	3.15	8.87
2019 (355 days)	2.80 (994 g yr^{-1})	6.26 (2220 g yr^{-1})
2020 (258 days)	2.41 (621 g yr^{-1})	5.23 (1350 g yr^{-1})
2021 (108 days)	1.91	5.01
Before	2.07	5.73
After	2.66	5.97
Relative to CON, before		3.66
Relative to CON, after		3.31

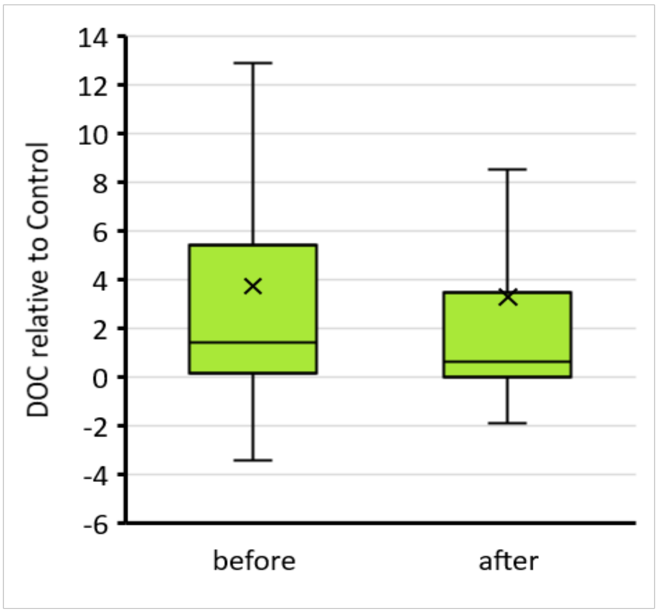

Figure 47. DOC flux relative to control (g day^{-1}) at the *Eriophorum* Spha catchment, before and after intervention.

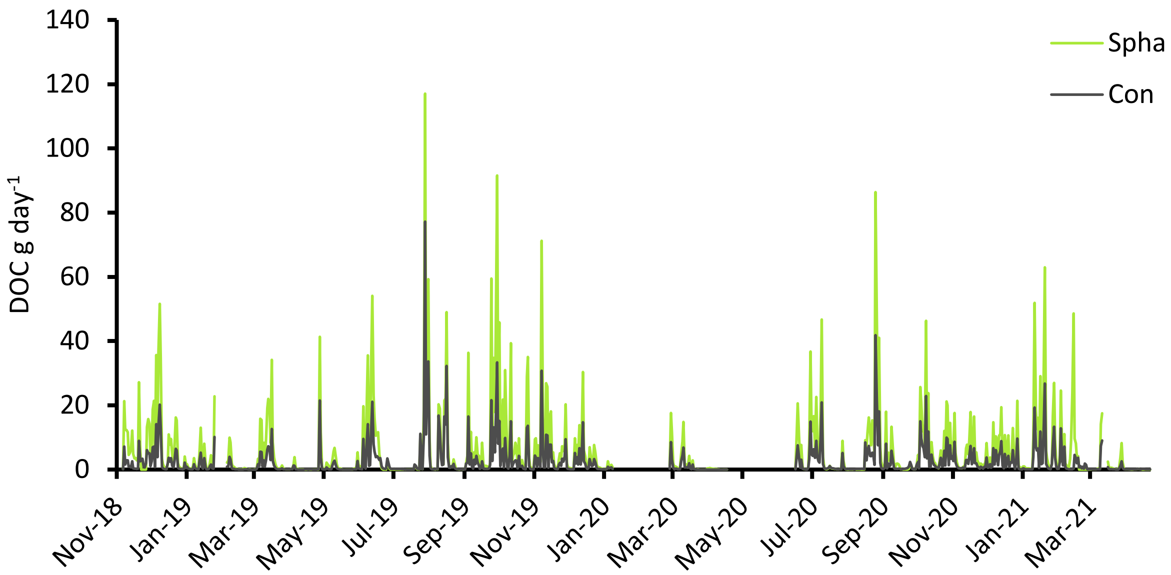

Figure 48. The flux of DOC (g day^{-1}), from the *Eriophorum* weirs.

4.2.4.3. *Molinia* site

At the *Molinia* site, the DOC flux was highest in the second half of the year (July to December), and lowest in Spring (April to June) at both catchments in 2019. In 2020, the DOC flux was highest in the last three months of the year, and lowest in the Spring (April to June) at both catchments. The mean flux was highest in 2019 from both the Control site (4.32 g day^{-1}), and the Spha site (1.34 g day^{-1}). Relative to the Control site, the flux from the Spha catchment appeared to be reduced following intervention, but further monitoring is required to establish whether this change is maintained in future years (Table 9, Figure 49).

Taking catchment area into account, the DOC fluxes from the Control catchment were 0.11 and 0.27 mg C day^{-1} m^{-2} (before and after intervention); and 0.03 and 0.05 mg C day^{-1} m^{-2} from the *Sphagnum* catchment.

Table 9. Mean DOC flux (g day^{-1}) from the *Molinia* weirs, in each calendar year, and before and after catchment intervention.

Average DOC, g day^{-1}	Con	Spha
2018 (48 days)	1.79	0.97
2019 (365 days)	4.32 (1580 g yr^{-1})	1.34 (491 g yr^{-1})
2020 (299 days)	1.88 (561 g yr^{-1})	0.88 (262 g yr^{-1})
2021 (103 days)	1.40	0.81
Before	1.31	0.73
After	3.23	1.15
Relative to CON, before		-0.58
Relative to CON, after		-2.08

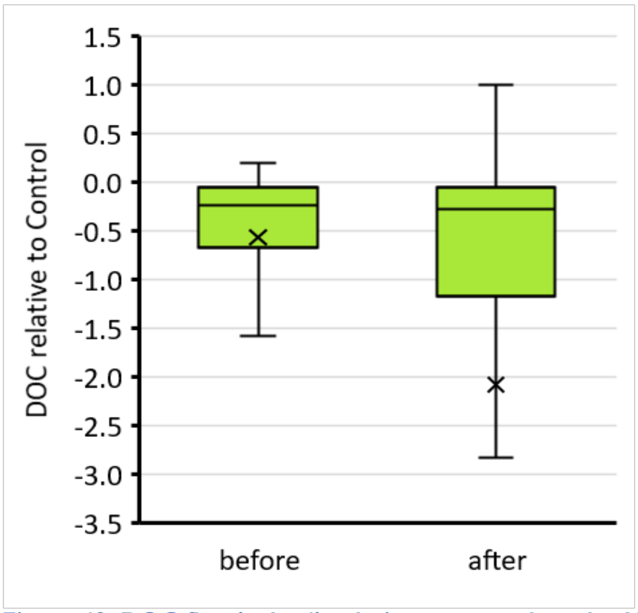

Figure 49. DOC flux (g day^{-1}) relative to control, at the *Molinia* Spha catchment, before and after intervention.

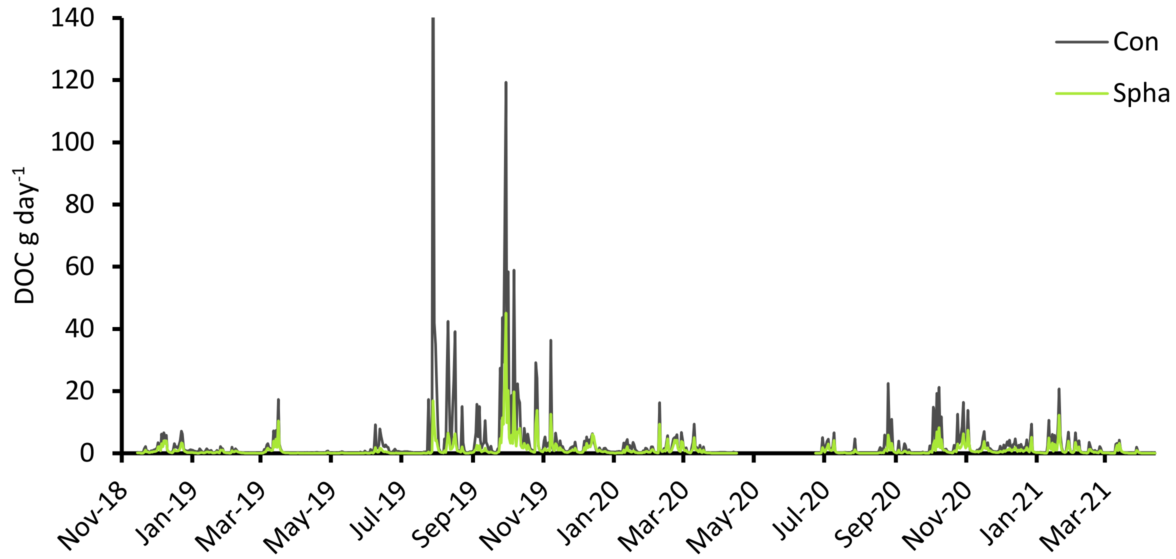

Figure 50. The flux of DOC (g day^{-1}), from the *Molinia* weirs.

5. Discussion

5.1. Bare peat sites

5.1.1. Dissolved organic carbon (DOC)

Previous work on the data from the first five years of monitoring has demonstrated short term reductions (up to 6 months) in DOC concentration at the treatment sites associated with the application of lime which is hypothesised to relate to the flocculating effect of calcium ions (Stimson *et al.* 2017). At the longer timescale assessed through the ML2020 monitoring no consistent long term change in DOC load was observed at any of the field labs during the monitoring period, including at untreated bare peat and intact reference sites and sites which had undergone restoration through a combination of revegetation, application of lime and fertiliser, gully-blocking and *Sphagnum* planting. At the revegetated site O, temporary changes in load were driven by changes in runoff which is a pattern reported elsewhere (Worrall *et al.* 2008). It is, however, possible that restoration has effected changes in the generation, mobilisation and flushing of DOC, but with multiple processes confounding each other and resulting in no overall change. Possible mechanisms for these changes following restoration include (in an approximate order of likely effect size):

Table 10: Possible mechanistic processes affecting DOC generation and transport following restoration work

Mechanism	Effect on DOC concentration
Dilution of existing sources of DOC due to altered hydrology. Increased overland flow could produce rapid flow of more dilute surface water which can reduce concentrations during storms.	Decrease
Higher pH leading to increased solubility of weak organic acids in DOC	Increase
Re-establishment of vegetation adding labile sources of DOC through senesced biomass and root exudates	Increase
Decomposition of mulch/litter layer adding labile source of DOC	Increase
Fertiliser increasing microbial decomposition of peat, therefore generation of DOC (this is normally P limited)	Increase (temporary)
Less POC generation and therefore less conversion of POC to DOC in the water column	Decrease
Higher water tables decrease decomposition of peat, and thus generation of DOC	Decrease
Longer residence time of water in the dammed channel increasing microbial and photolytic processing. This may be partially offset by increased opportunity for algal additions of DOC in the water column, meaning changes in DOC characteristics more likely than DOC quantity.	Decrease/change in characteristics not quantity

It is also important to note that the deep gullies across these sites are the macro scale control on water table for gully edge sites (Allott *et al* 2009) and that this is relatively unaffected by gully blocks the height of which is only circa 20% of gully depth. The restoration results seen in this work produce excellent restoration of the moorland vegetation but these are still modified systems. So whilst all the processes above are expected to be influenced by restoration it is likely that lowered water tables at gully edges are still the dominant control on DOC concentration so that there is no discernible trend in the observed data.

It should also be noted that the data presented in this study are from water samples collected during routine visits to the field sites, generally in low flow conditions. It was therefore not possible to assess any impacts of treatment on DOC generation in high flow conditions, when accumulated DOC may be 'flushed' from the system.

5.1.2. pH and calcium

pH and calcium levels are of particular interest in an acidic bog environment where lime has been added as part of the restoration process. Application of lime would be expected to raise pH at the treatment sites. It appears that there was an increasing trend in pH data in the early years of the experiment at all sites but this was driven by depressed pH in 2012 at all sites. Measurements before this dip were consistent with the main trend of later years.

At O and N short term spikes in pH coincide with peaks in calcium related to aerial applications of lime in 2011, 2012 and 2013. Increases in pH were also observed from 2012 to 2013 at the two untreated control sites (P and F), although the increases were smaller than at the treated sites. It is possible that this increase was caused in part by the depressed pH values observed at all sites in 2012, and also by contamination of the control sites. F is downwind of O and N; P is downstream of a helicopter lift site used for restoration. However, only very slightly elevated calcium levels were recorded at the control sites so that any lime contamination was minor and the pH changes were not well correlated with the calcium signal. At the treatment sites high calcium concentrations associated with the lime applications were evident for the first five years of the experiment. By 2017 (4 years post the final application), levels had returned to baseline. The calcium alone seems unlikely to explain fully the observed changes in pH at F and P. Further work is required to explore the drivers for the depressed pH in 2012 but the observation of this pattern at all sites suggests it may have been unrelated to the restoration process. Previous work has linked low pH episodes to periods of temporary drought (Clark *et al* 2005) and so it may be that the pH minimum is synoptically driven; it may relate to changes in atmospheric acid deposition, or it may relate to an undetected systematic error in pH readings.

5.2. Species dominated sites

Laboratory experiments have shown low concentrations of DOC from peat cores and incubations of *Sphagnum*. Water from cores dominated by *Sphagnum* had lower DOC concentrations than *Calluna*, *Juncus* or *Molinia*-dominated cores (Ritson *et al* 2017). Vegetation type also significantly impacted pH and $SUVA_{254}$ of water samples. In incubation experiments, *Sphagnum* moss tissue was shown to release DOC more slowly, at a constant rate, than other organic matter such as leaves of other plant species (Moore and Dalva 2001). *Sphagnum* and feather mosses released the least DOC, compared to peat, ericaceous shrubs, herbaceous plant and straw, in a series of incubation experiments (Strack *et al* 2011).

Field surveys of peatland sites including restored areas have shown lower concentrations of DOC from areas of peatland covered in *Sphagnum*. Soil solution from *Sphagnum* areas had lower DOC concentrations than *Calluna* and sedges, but higher than *Molinia* spp. in a survey of peatlands in the UK (Armstrong *et al* 2012). The same survey found high DOC concentrations in drains in *Calluna* areas. Introducing *Sphagnum* moss altered the pore water chemistry at a restoration site in Quebec, lowering the pH and $SUVA_{254}$, but increasing the DOC concentration (Strack *et al* 2015). The natural site (not restored or damaged) had the highest moss cover, the highest water table and lowest pH and DOC concentration.

These results are supported by the findings of this study – that planting *Sphagnum* may affect the DOC concentration in surface and soil water, as well as impacting on the DOC character (changing the fulvic and humic nature, or the aromaticity of DOC).

Small changes in DOC character were observed in the water at the weirs and in overland flow, although no changes were statistically significant. Increased E4:E6 would indicate water becoming more fulvic and less humic, and decreased $SUVA_{254}$ would indicate a decrease in aromaticity of DOC – this could indicate a change in the dominant production pathways of DOC from terrestrial (humic and highly aromatic DOC) to aquatic (more fulvic and less aromatic DOC) sources. Large or significant changes in the character of DOC could have an impact on water treatment processes downstream.

Plants affect the hydraulic conductivity of peat and the rate of evapotranspiration; they intercept rainfall and change the surface roughness of the peat; therefore they impact the water table depth (Armstrong *et al* 2012). Peat under plants such as shrubs and sedges (such as *Calluna* and *Eriophorum*) may have lower water tables and *Sphagnum* moss may have higher water tables. Areas with higher water tables may have lower DOC concentrations; areas with lower water tables may have higher DOC concentrations (Armstrong *et al* 2012; Strack *et al* 2015).

An increase in DOC concentrations after *Sphagnum* planting and/or gully blocking could be a result of disturbance – planting *Sphagnum* may disturb the peat surface, causing increased losses of POC, which can break down in water to become DOC. Restoration pools (formed as a result of blocking gullies) have been shown to have high DOC concentrations, and highly fulvic and aromatic DOC, compared to natural pools in the same area (Chapman *et al* 2022). Blocked and re-profiled drainage ditches on the Migneint blanket bog in Wales showed no significant changes in DOC concentration compared to open ditches (Peacock *et al* 2018). There were very small, but statistically significant, differences in DOC character (E4:E6 and $SUVA_{254}$) in the ditch water between the different ditches (open, blocked and re-profiled), although these were smaller than the temporal fluctuations observed. Also in Wales, blocking drains around Lake Vyrnwy decreased pH and EC in drain water (Wilson *et al* 2011). E4:E6 and DOC concentration increased, and $SUVA_{254}$ decreased after drain blocking. Both POC and DOC annual DOC flux estimates decreased after drain blocking. Wilson *et al* (2011) suggested that blocking the ditches caused slower transit times, decreased the pH and decreased the connectivity between rainwater and deep peat/mineral layers (as evidenced by decreased EC), creating a more suitable habitat for peat-forming species, such as *Sphagnum* mosses. They also show that while DOC concentrations increased initially, this was likely a short-term result, and the overall trend and annual flux estimates were decreasing after drain blocking.

Results from the study at the *Calluna* site found that blocking the gully may have increased the EC and DOC concentration, and changed the character of DOC (increased E4:E6 and decreased $SUVA_{254}$) although these effects were small and not statistically significant. No change was found in the pH of the water leaving the catchments. It is possible that other impacts of blocking the gully were either very short lived (therefore not evident in monthly sampling) or will take longer than 2.5 years to show.

Literature on the impact of different *Sphagnum* planting densities on water chemistry is scarce. Search results are dominated by studies of the planting densities of trees, such as Sitka spruce, on peat soils. However, there are a small number of studies of restoration planting densities. Models of CH_4 production pathways in mire complexes showed that moss planting density impacts the leaf area, soil temperature, soil moisture content and surface energy balance, but did not impact the standing water (water table depth; Chang *et al* 2019). Revegetation of bare coastal peat using *Juncus buffonius* (toad rush) and *Spartina pectinata* (prairie cordgrass) found no biological advantage of high density planting over lower density planting (Breathnach and Rochefort 2008). A survey of restoration projects of coastal wetlands found that using planting designs based on forestry science to reduce competition between planted propagules, was not necessarily the best strategy for growth. Changing the planting configuration from dispersed to clumped increased positive interactions between plants, and increased plant survival and density (Silliman *et al* 2015).

This study observed some small changes water chemistry in overland flow, soil solution and catchment outlet water after *Sphagnum* planting in both low and high densities, and over the whole catchment. In *Calluna* and *Eriophorum* dominated sites there was an apparent small decrease in DOC concentration, while on the *Molinia* dominated site there was an apparent small increase. However, the majority of observed changes were not statistically significant; future monitoring is required to determine if these changes are maintained in future years. The observed changes in DOC concentration, EC, E4:E6 and $SUVA_{254}$ were all small, and often only evident when intervention catchment data was compared to the control catchments. Considering the timescales of the experiment, any changes in water chemistry are interesting, and the small changes could become larger and significant with time.

5.2.1. Limitations

On 11/08/2020 portions of the *Calluna* site including both control and treatment catchments were subjected to a light aerial application of lime pellets unintentionally distributed by a helicopter applying the pellets to an adjacent site. This overspill was identified on the day of occurrence, and with no rain occurring overnight, steps were taken to mitigate the issue during the following day. A team manually removed the pellets from within all vegetation quadrats affected, including the intensive plots. It is thought that a high proportion of the lime was removed from these areas and what remained was so minimal as to be unlikely to contribute to any significant changes in vegetation or water chemistry within these areas. However, it was not possible to remove all pellets from whole catchments. The even distribution and light covering across both control and treatment catchments mean that the effects of this incident are likely to be minimal, and indeed the incident could not be detected in the water samples gathered immediately after the incident, or any samples gathered subsequently.

6. Conclusions

6.1. Bare peat sites

The restoration process involved the application of lime to the peatland surface; measurement of calcium concentrations in runoff from the experimental sites clearly demonstrated short-term changes related to the application. In response to three applications of lime between 2011–2014 calcium concentrations were elevated for the first five years of the project. pH levels at the treatment sites spiked in response to lime application, but recovered within six months. Previous work has reported short-term shifts in DOC concentration related to these applications of lime (Stimson *et al*. 2017) but long-term DOC concentration and flux were unaffected. Similarly, the longer-term pattern suggested a stable pH signal across the restored sites and the control sites. The dramatic habitat restoration achieved by the project has not led to divergence of water chemistry between the two control sites and the treatment sites. Over the five years of MoorLIFE 2020 without further application of lime, calcium concentrations have returned to background levels (four years post the final lime application) and DOC and pH are stable. It is likely that this represents a flushing of lime from the catchment and longer-term control of DOC which related to wider drawdown of water tables across the eroded peatland driven by gully morphology.

6.2. Species dominated sites

Data collected over the four years of the study suggested that planting *Sphagnum* may have had an impact on chemistry of water leaving the catchments. Small decreases in electrical conductivity (EC) and DOC concentrations were observed, although the majority of these were not statistically significant. Planting *Sphagnum* had no statistically significant impact on the character of DOC in the water during the monitoring period, although small, non-significant changes in E4:E6 and specific absorbance ($SUVA_{254}$) were observed. Planting *Sphagnum* did not change the pH.

The gully blocking on the *Calluna* site 'SphaGB' catchment had no statistically significant effect on EC, DOC concentration or DOC character, although small (non-significant) changes were observed (increased EC, DOC concentration and E4:E6; decreased $SUVA_{254}$). No change was observed in the pH of the water leaving the catchment.

Planting *Sphagnum* at low densities (4 plugs m^{-2}) has the potential to decrease DOC concentrations in overland flow and soil solution. The DOC concentration decreased consistently in all four intervention catchments after low density *Sphagnum* planting, although changes were small and not all were statistically significant.

Planting *Sphagnum* at high densities (100 plugs m^{-2}) has the potential to decrease DOC concentrations in overland flow and soil solution. At the *Calluna* site there were apparent decreases in DOC concentrations in overland flow and soil solution, although these changes were not statistically significant. At the *Eriophorum* site no clear changes in DOC concentration were observed. At the *Molinia* site small increases in DOC concentrations were observed (some but not all changes were statistically significant).

The DOC flux from *Calluna* and *Molinia* catchments appeared to be decreased by planting *Sphagnum*, but conversely there was found to be no clear change in DOC flux after planting in *Eriophorum* catchment.

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MoorLIFE 2020

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