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Carbon concentrations in natural and restoration pools in blanket peatlands

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Abstract

Open-water perennial pools are common natural features of peatlands globally, and peatland restoration often results in new pool creation, yet the concentrations of different forms of aquatic carbon (C) in natural and artificial restoration pools are not well studied. We compared carbon concentrations in both natural pools and restoration pools (4–15 years old) on three blanket peatlands in northern Scotland. At all sites, restoration pools were more acidic and had mean dissolved organic carbon (DOC) concentrations in restoration pools of 23, 22, and 31 mg L^{-1} compared with natural pool means of 11, 11 and 15 mg L^{-1} respectively across the three sites. Restoration pools had a greater fulvic acid prevalence than the natural pools and their DOC was more aromatic. Restoration pools were supersaturated with dissolved CO_2 at around 10 times atmospheric levels, whereas for natural pools, CO_2 concentrations were just above atmospheric levels. Dissolved CH_4 concentrations were not different between pool types, but were ~200 times higher than atmospheric levels. Regular sampling at one of the peatland sites over 2.5 years showed that particulate organic carbon (POC) concentrations were generally below 7 mg L^{-1} except during the warm, dry summer of 2013. At this regularly-sampled site, natural pools were found to process DOC so that mean pool outflow concentrations in overland flow were significantly lower than mean inflow DOC concentrations. Such an effect was not found for the restoration pools. Soil solution and pool water chemistry, and relationships between DOC and CO_2 concentrations suggest that different processes are controlling the transformation of C, and therefore the form and amount of C, in natural pools compared to restoration pools.

KEYWORDS
aquatic, carbon dioxide, dissolved organic carbon, methane, particulate organic carbon, ponds, rehabilitation, wetland

1 | INTRODUCTION

Northern peatlands store around 500–600 gigatonnes of carbon (C), which accumulated during the Holocene (see e.g., Yu, 2012). Peatlands form in locations of poor drainage or plentiful rainfall. In actively-forming peatlands, C inputs from plant production exceed the outputs of C to the atmosphere and in runoff to water bodies. Measurements of gaseous C fluxes in peatland ecosystems show that they are generally a net sink for carbon dioxide (CO_2) and a net source of methane (CH_4) although there can be high variability across different microforms (e.g., Pelletier et al., 2011; Waddington & Roulet, 1996), sites (Billett et al., 2010; Webster et al., 2018) and between years (Dinsmore et al., 2010; Mikhaylov et al., 2019; Roulet et al., 2007). While much focus has been on peatland terrestrial C concentrations and fluxes, less attention has been paid to the factors controlling the processing of aquatic C in peatland water bodies and the potential for evasion of that C to the atmosphere.

Open-water pools are a common feature of peatlands, particularly in maritime systems (Glaser, 1998). The number and surface area of pools relative to vegetated surfaces in Arctic peatlands is increasing due to climate warming (Jorgenson et al., 2001; Swindles et al., 2015; Vonk et al., 2015). In some locations, where peatland restoration has been undertaken, pools have been created. These "restoration pools" have most commonly occurred when drainage ditches or gullies have been blocked with dams and artificial pools have formed behind each dam (Goudarzi et al., 2021; Holden et al., 2017; Parry et al., 2014). Expansion of the number of peatland pools could be of importance for the peatland C cycle because pools may be large sources of both CO_2 and CH_4 to the atmosphere (Hamilton et al., 1994; Pelletier et al., 2014). The presence of pools may also influence the concentration and forms of aquatic C, with downstream impacts on water quality and drinking water treatment of key importance in some regions (Xu et al., 2018; Xu et al., 2020).

Although inland waters have been recognized as important components of the global C cycle, actively processing the organic matter derived from the terrestrial ecosystem and releasing CO_2 and CH_4 to the atmosphere (Bastviken et al., 2011; Chmiel et al., 2020; Cole et al., 2007; Tranvik et al., 2009), most previous research has been focused on larger water bodies, such as lakes or large river systems. Peatland pools represent an interface between a C-rich terrestrial system and an aquatic system and are a potential hotspot for organic matter processing. Data that enable the extent of this processing to be quantified are sparse (e.g., Hamilton et al., 1994; Pelletier et al., 2014; Radomski, 2020). In addition, the factors that control the fate of terrestrially-derived organic matter in peatland pools is poorly understood, but the fate is likely to be affected by the physical and chemical properties of the pool (e.g., water residence time, pH), the form of organic C (dissolved versus particulate), and the quality of the C because this affects rates of microbial respiration and photochemical degradation, which in turn influence dissolved CO_2 concentrations (Cory et al., 2007; Cory et al., 2014). For example, in lakes, a number of studies have reported that variability in dissolved CO_2 can be explained by variation in dissolved organic carbon (DOC)

concentrations (e.g., Hope et al., 1996; Roehm et al., 2009). Pelletier et al. (2014) observed a positive relationship between dissolved CO_2 and DOC concentrations in one of the five peatland pools they studied in Quebec while they found a negative relationship in another of the pools.

Here we differentiate pools (which could also be termed 'ponds') from lakes by noting that the main water inputs for peatland pools are from precipitation and flows either over or through the surrounding peat, rather than from streams. Lakes tend to be located in a geological depression whereas peatland pools are features within the peatland that are often located irrespective of the form of the underlying geology. In natural peatlands, pools are discrete bodies of open water that form, often in high-density clusters, within the peat matrix, developing after the peat has accumulated (Belyea & Lancaster, 2002). They are shallow (<0.6 m deep), range in surface area from <1 m^2 to tens of thousands of m^2 and are typically steep sided. Their main source of water is from precipitation and flows either over or through the surrounding peat during storm events. Thus, unlike lakes, peatland pools have no permanent inflow (stream or spring) or outflow, although individual pools may become connected to adjacent pools by overland flow during rainfall events, or via subsurface piping (Holden & Burt, 2002). Restoration pools created through ditch blocking on blanket peatlands are also shallow (<0.5 m deep) but tend to be much smaller with a surface area of <10 m^2 and during storms they can receive water from the old ditch channel as well as directly from precipitation and flows over and within the surrounding peat. Pools can be permanent and seasonal.

As pools are components of peatlands, C cycling within pools should be considered along with C cycling in the peat to understand overall peatland C processing. Pools are recipients of C in runoff from the surrounding peat, but little is known about the form or amount of C entering and leaving peatland pools, particularly for POC, which has been poorly studied in comparison to DOC. While there is some information on the different C forms and their concentrations in peatland pools, studies have usually focused on a few natural pools and sampling has often been limited to a few occasions. For example, Abnizova et al. (2012) sampled two permafrost peatland pools over a 6 week period in northeastern Siberia and recorded low DOC concentrations (means of 4.2 and 6.8 mg L^{-1}). Pelletier et al. (2014) sampled DOC from five Canadian peatland pools on five occasions between May and October 2012 with concentrations ranging between 8 and 25 mg L^{-1}, observing no temporal pattern. In contrast Billett and Moore (2008), observed a seasonal pattern in DOC concentrations for one Canadian pool sampled in 2005, with concentrations peaking at 64.1 mg L^{-1} in July. Arsenault et al. (2018) also found seasonal variations in DOC concentrations among nine pools sampled in a raised bog in eastern Canada between May and October 2016. In their study, shallower pools showed the largest seasonal contrasts, with concentration peaks in October. In a snapshot study (one-off sampling) of 66 pools across three regions of the UK, Turner et al. (2016) reported that DOC concentrations ranged between 3.1 and 20.4 mg L^{-1}, but were significantly lower in one of the regions. Data on pool water particulate organic C (POC) is limited to the study of

Turner et al. (2016), who reported that concentrations were generally <6 mg L^{-1}. Although a few pool studies (Arsenault et al., 2018; Pelletier et al., 2014; Turner et al., 2016) have included information on DOC quality in the form of specific UV absorbance (SUVA$_{254}$) that gives an indication of the aromaticity of DOC (Weishaar et al., 2003), there is generally a lack of such data from peatland pools.

Furthermore, the forms and concentrations of C are even less well characterized in pools created from ditch blocking undertaken as part of peatland restoration schemes, particularly for "restoration pools" that have been in place for several years. Worrall et al. (2007) measured outflow from blocked peatland drains containing restoration pools for a 10-month period in the immediate aftermath of blocking, finding that DOC concentrations and water colour were significantly greater for blocked drains than unblocked drains. However, Peacock et al. (2018) found no meaningful differences (no significance, or very small effect sizes) in outflow DOC concentrations or quality from blocked peatland drains in the first 4 years after blocking compared to nearby open drains. Neither of these studies sampled water from the restoration pools directly. Taken together, all these findings suggest that there is still an important knowledge gap regarding the spatial and temporal variability of C forms and concentrations in peatland pools, including restoration pools.

Without a better understanding of the forms, concentrations and factors controlling the fate of organic C in peatland pools, we are unable predict the impact of climate change or management on the peatland C cycle and greenhouse gas fluxes. Therefore, the aims of this study were to: (1) determine whether C concentrations and forms in restoration pools are different from those in natural pools, and establish whether these differences were the same across three sites in northern Scotland, (2) determine how C concentrations and forms in peatland pools vary over time; and (3) examine potential controls on C concentrations and forms and whether these controls differ between pool type.

2 | METHODS

2.1 | Study sites

Three separate sites within the Flow Country of northern Scotland, the largest blanket peatland in Europe (c. 4000 km^2), were used in this study (Figure 1). These sites each provided paired areas of natural and restoration pools. At each site, the two pool types were in different sub catchments from each other. The sites were Cross Lochs (CL: 58° 22'N, 03° 57'W, 211 m altitude), Loch Leir (LL: 58° 23'N, 03° 46'W, 185 m altitude) and Munsary (M: 58° 23'N, 03° 20'W, 105 m altitude). At each site, six natural and six restoration pools were sampled (see Table S1 for information on their surface area and depth). The six pools in each case were sampled within a 9 ha area. The restoration pools were created in locations where ditch drainage had occurred in the 1970s. Such peatland drainage had been previously grant aided by government across the UK prior to the early 1980s. In the Flow Country, some drainage also occurred on areas that were deemed potential sites for conifer plantations. At our sites, there had been no plantation forestry, although at all sites there was plantation forestry in nearby subcatchments. In recognition of the importance of conserving peatland habitats and their associated ecosystem services, peatland restoration through blocking of ditches has been undertaken in the UK since the mid-1990s. At our sites, the ditch blocking had occurred in 2002 (CL), 1998 (LL), and 2009 (M), forming pools behind
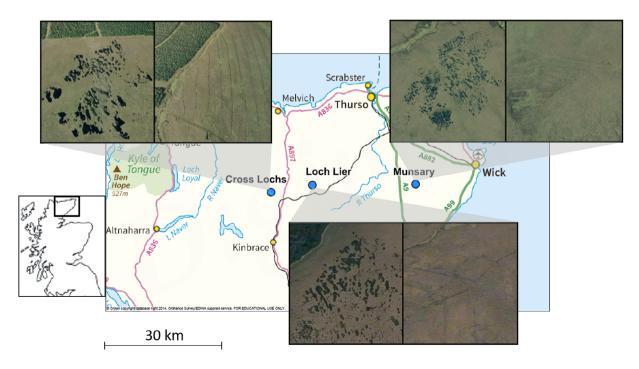

FIGURE 1 Location of study sites in northern Scotland. Aerial imagery from GetMapping, Edina Digimap

evenly-spaced peat dams along the course of the ditches (see e.g., Armstrong et al., 2009).

The UK climate is classified as temperate maritime, and ice cover of pools is generally limited to surface freezing for brief periods during the winter (i.e., days or weeks rather than months or seasons). The long-term (1981–2010) mean annual precipitation, mean daily minimum temperature and mean daily maximum temperature were 970.5 mm, 3.3°C and 11.4°C, respectively, at the Kinbrace hatchery meteorological station (World Meteorological Organization station #3044), approximately 9 km south of Cross Lochs, located 103 m above mean sea level. During the study (June 2013 to December 2015), the season with the lowest precipitation was the dry summer of 2013 with 111 mm recorded at CL whereas 250 mm and 143 mm (second lowest total for any season in the study) occurred in summers 2014 and 2015, respectively (Holden et al., 2018).

Natural pool vegetation at all three sites was broadly limited to aquatic Sphagna (*Sphagnum cuspidatum* Ehrh. ex Hoffm. and *S. auriculatum* Schimp.), the sedge *Eriophorum angustifollium* Honck., and bog bean (*Menyanthes trifoliata* L.). Terrestrial vegetation at all three sites comprised a mosaic of typical blanket bog species including *Sphagnum* mosses, (*S. papillosum* Lindb., *S. tenellum* (Brid.) Bory, *S. capillifolium* (Ehrh.) Hedw.), sedges (*E. angustifollium*, *Eriophorum vaginatum* L., *Trichophorum cespitosum* [L.] Hartm.), ericacous shrubs (*Calluna vulgaris* [L.] Hull, *Erica tetralix* L.), bog asphodel (*Narthecium ossifragum* [L.] Huds.) and the locally common Purple Spoonwort (*Pleurozia purpurea* Lindb.). Distinct hummocks were commonly dominated by woolly fringe-moss (*Racomitrium lanuginosum* Brid.).

2.2 | Sample collection and chemical analysis

All pools were sampled at least once in each of five consecutive seasons between autumn 2013 and autumn 2014, where autumn is September, October and November, winter is December, January and February, spring is March, April and May and summer is June, July and August. In addition, at CL the six natural (P1–P6) and six restoration pools (P7–P12) were sampled every 2 weeks between July 2013 and December 2014 and then monthly until December 2015. Water temperature, pH (corrected to 20°C), dissolved oxygen, and electrical conductivity were recorded in situ using a handheld Hach-Lange HQ40D multi meter at ~10 cm water depth. At CL only, overland flow was collected using PVC crest-stage tubes (Burt & Gardiner, 1984) with holes flush to the peat surface, and PVC piezometers were used, 1.5 m from pool edges, to collect shallow subsurface flow (hereafter referred to as soil solution) through the peat over a 5 cm depth range with mid points at 5, 10, 20, and 50 cm depth. Overland flow was collected upslope and downslope of each pool to sample inflow and outflow water. The soil solution samples from the four sampling depths were bulked for DOC analysis until February 2015, after which the samples from each depth were analysed separately.

A 500 ml water sample was collected from each pool approximately 10 cm below the water surface and 1 m from the pool edge for analysis of DOC and POC. At CL, a second water sample was taken from just above the sediment layer at the base of the water column from October 2013 onwards. All water samples were stored in the dark at ~4°C. DOC was determined (after filtration at 0.45 μm) using an Analytik JenaMulti N/C 2100S combustion Total Organic Carbon analyser (detection limit: 1.06 mg L^{-1}). Absorbance at 254 (abs$_{254}$), 465 and 665 nm was determined using a Jasco V-630 UV–Vis spectrophotometer. Absorbance readings were converted to standardized water colour measurements of absorbance units per metre (au m^{-1}). The two dominant components of DOC, humic and fulvic acids, absorb light in different amounts and at different wavelengths. As a result, the ratio of abs$_{465}$ to abs$_{665}$, known as the E4 to E6 ratio (hereafter E4:E6), gives an indication of the proportion of humic and fulvic acids, and hence the degree of humification, because humic acids are more mature than fulvic acids. Thurman (1985) observed that humic acids from soils had E4:E6 values of 2–5, whereas fulvic acids had E4:E6 values of 8–10. Specific UV absorbance (SUVA, L mg^{-1} m^{-1}) was calculated as abs$_{254}$ divided by DOC concentration, as an indicator of DOC aromaticity and hydrophobicity (Weishaar et al., 2003).

Pool water samples were filtered through pre-ashed, pre-weighed Whatman GF/F 0.7 μm filter papers for POC analysis, which was calculated using loss-on-ignition (Ball, 1964). Sediment traps, of 9.5 cm diameter, as designed by Teodoru et al. (2013), were installed just above the pool floor using an anchor weight and buoys to maintain an upright position, in all 12 pools at CL on 7 February 2014. The traps were emptied on 1 July 2014 and the water and sediment were filtered through pre-combusted and pre-weighed 0.7 μm Whatman GF/F glass-fibre filters. The filters were then dried at 105°C for 24 h and re-weighted to determine the dry-weight of the filtered material, hereafter referred to as the suspended sediment content. Subsequently, the filters were ashed at 375°C for 16 h in a muffle furnace to burn off the organic matter and re-weighed when cool to determine POC, which was calculated using loss-on-ignition (Ball, 1964). Suspended sediment and POC collected by the traps were expressed as a deposition rate in g m^{-2} day^{-1}.

Dissolved CO_2 and CH_4 concentrations in the pools were calculated using the headspace technique (Billett et al., 2004; Kling et al., 1991). A 40 ml water sample was equilibrated with 20 ml ambient air at pool temperature by shaking underwater for 1 min. The equilibrated headspace was then transferred to a pre-evacuated 12 ml Exetainer® vial (Labco, Lampeter, UK). Headspace samples were analysed on a Hewlett Packard HP5890 Series II gas chromatograph (detection limits: CO_2 7 ppmv; CH_4 4 ppbv) with electron capture (ECD) and flame ionization detectors (with attached methaniser). Concentrations of gases dissolved in the pool water were calculated from the headspace and ambient concentrations using Henry's Law (e.g., Hope et al., 1995).

At CL, Holden et al. (2018) continuously gauged all of the pool water levels and also monitored water-table depths within the peat at a distance of 1 m from the edge of each pool. These hydrological data are used in this paper to provide background information on site hydrological functioning and to aid interpretation of the pool water carbon data.

2.3 | Statistical analysis

The seasonal (five seasons) pool water data were analysed using a fixed-effect, repeated-measures ANOVA, with pool type (natural or restoration) and site (CL, LL, MU) and the interaction of pool type and site as factors. The associated overall factor p values are reported in the text. While the three sites provide some replication within a region, site was included as a factor because earlier peatland work has suggested pool chemistry may vary with region (Turner et al., 2016) but it is unclear whether there is also significant variability within regions. For CL, where more intensive sampling took place, time series of pool water chemistry variables were plotted and in most cases, there was little overlap between natural and restoration pool values and thus further statistical analysis was deemed redundant. As pool is a replicate in the analysis, soil solution data for each pool were analysed as mean values in a two-way ANOVA to include pool type (and depth for data after February 2015) and the interaction between pool type and depth, as factors. Data were tested for normality using Kolmogorov–Smirnov tests, and log_{10}-transformed if necessary. Where significant results were found, post hoc least significant difference (LSD) tests were used to determine which factors or interactions were responsible. Least-squares means were used to calculate effect size, so a proportion of the variance could be attributed to each factor or interaction in the ANOVA.

For both the seasonal data from the three sites and the routine data for CL, linear regression models were used to examine relationships between (i) carbon forms (DOC, POC, CO_2 and CH_4, as we expect the gases to be produced as a result of the decomposition of DOC and POC), (ii) carbon forms and other water chemistry variables (e.g., pH, conductivity, abs_{254}, as we expect the water chemistry to control decomposition rates) and (iii) carbon forms and site characteristics (e.g., pool size, as we expect decomposition to be influenced by geomorphology). Forwards stepwise regressions were used in multivariate analyses, where each variable was added to the model, and retained if significant, or removed if insignificant (at $p < 0.05$). The variables included: CH_4, DO and DOC concentrations, water-table depth, and water temperature. The adjusted r^2 of the model, and the variance inflation factor values of the variables, were used to determine the best models. All statistical analyses were carried out using SAS 9.4.

3 | RESULTS

3.1 | Seasonal sampling across all sites

3.1.1 | Pool water pH, conductivity and dissolved oxygen

The pH of the natural pools was significantly different to that of the restoration pools ($p < 0.001$) and also varied between sites ($p = 0.01$), with the pools at CL and MU generally more acidic than at LL (Table 1). The pH was lowest in autumn 2013 and greatest in autumn 2014 for the restoration pools at all sites, while for the natural pools it was lowest at MU in autumn 2013 and lowest at CL in winter but there was little seasonal difference for natural pools at LL. The electrical conductivity of the restoration pools was significantly different ($p = 0.03$) to that in the natural pools (Table 1). Conductivity varied between the sites ($p < 0.001$), with means following a gradient MU > CL > LL. Conductivity was greatest in autumn 2013 and least in autumn 2014 for both restoration and natural pools at all sites except CL where lowest conductivity was observed in summer 2014. The dissolved oxygen concentration of the natural pools was significantly different to that in the restoration pools ($p < 0.001$) with higher mean values in natural pools. Dissolved oxygen concentration was lowest in the summer and highest in the winter in both pool types and at all sites.

3.1.2 | Pool water POC and DOC

Overall, DOC concentrations and abs_{254} values were lowest in winter and highest in summer. At all sites and in all sampling periods the DOC concentrations were larger in restoration pools than in natural pools (Figure 2a), with mean DOC concentration in restoration pools more than twice that in natural pools (Table 1). The range in DOC was also much larger for restoration pools (4.94–57.3 mg L^{-1}) than for natural pools (2.0–31.6 mg L^{-1}). In addition, mean abs_{254} in restoration pools was over three times that of natural pools (Table 1). DOC concentrations and abs_{254} also varied significantly ($p < 0.001$) between sites. The composition of DOC varied between pool type, with both SUVA and E4:E6 being significantly larger in restoration pools than in natural pools ($p < 0.001$; Figure 2b and c; Table 1). Both SUVA and E4:E6 were highest in the winter. In contrast, concentrations of POC were not significantly different between pool type, site or season (Table 1).

3.1.3 | Pool water dissolved CO_2 and CH_4

All pools were supersaturated in dissolved CO_2 and CH_4, relative to the atmosphere (Table 1). Both CO_2—C and CH_4—C concentrations were highest in the summer and lowest in the winter. Concentrations of CO_2—C were significantly greater ($p < 0.001$) in restoration pools than natural pools, whereas CH_4—C concentrations did not vary significantly between pool type (Figure 2e–f; Table 1).

For each pool type, at each site, CO_2 concentration could be predicted using CH_4 concentration, and DOC concentration or water temperature, with up to 60% of the variation explained by a combination of two of these three variables (forwards stepwise regressions; Table 2). The relationship between dissolved CO_2 and CH_4 concentration was significant at all sites, and it was positive in all except at LL in the restoration pools (parameter estimate −0.036, Table 2). When the three sites were analysed separately, DOC concentration (but not water temperature) was significant in all three models of dissolved CO_2 in the restoration pools. The water temperature (but not DOC

TABLE 1 Mean, minimum and maximum for each water chemistry variable by site and pool type. Ep CO_2 and CH_4 indicate the concentrations relative to the atmosphere

Values shown as mean / minimum / maximum.

	Cross lochs Restoration	Cross lochs Natural	Loch Lier Restoration	Loch Lier Natural	Munsary Restoration	Munsary Natural	Repeated measures ANOVA p value Quarter	Site	Pool type
pH	4.26 / 4.09 / 4.6	4.37 / 3.59 / 4.66	4.3 / 3.77 / 4.72	4.56 / 4.33 / 4.83	4.19 / 3.78 / 4.54	4.48 / 4.09 / 5.11	<0.001 ***	0.011 *	<0.001 ***
DO (mg L^{-1})	7.34 / 3.51 / 12.06	10.19 / 5.48 / 13.33	9.24 / 3.94 / 13.44	14.05 / 5.34 / 104.8	8.8 / 1.62 / 12.46	11.06 / 9.4 / 12.91	0.053 NS	0.117	0.005 **
Conductivity (µS cm^{-1})	72.72 / 34.1 / 112.3	74.33 / 53.9 / 102.8	67.2 / 35.1 / 91	65.92 / 30.6 / 102.6	97.38 / 50.6 / 139.9	90.82 / 47.6 / 117.5	<0.001 ***	<0.001 ***	0.025 *
DOC (mg L^{-1})	22.69 / 6.15 / 42.28	11.49 / 4.89 / 31.61	22.07 / 4.94 / 36.5	10.91 / 2 / 30	31.45 / 10.17 / 57.3	14.29 / 6 / 27.8	<0.001 ***	<0.001 ***	<0.001 ***
abs$_{254}$ nm (m^{-1})	61.95 / 50.83 / 84.38	13.69 / 6.02 / 25.94	84.47 / 22.01 / 153.82	30.05 / 5.53 / 92.21	118.52 / 36.92 / 212.84	37.34 / 18.26 / 61.63	<0.001 ***	<0.001 ***	<0.001 ***
SUVA (L mg^{-1} m^{-1})	2.32 / 0.17 / 4.52	0.96 / 0.15 / 1.79	3.42 / 1 / 5.21	2.83 / 1.05 / 6.17	3.23 / 0.8 / 5.01	2.47 / 1 / 4.76	<0.001 ***	0.0352 *	<0.001 ***
E4:E6	15.72 / 7.17 / 31.92	7.02 / 2.71 / 12.4	14.13 / 8.51 / 24.1	7.96 / 3.56 / 15	17.06 / 8.56 / 36.9	7.96 / 2.15 / 16	<0.001 ***	0.2237 NS	<0.001 ***
POC (mg L^{-1})	2.79 / 0.21 / 16.34	3.41 / 1.09 / 8.7	2.19 / 0.15 / 23.98	1.32 / 0.49 / 3.35	1.07 / 0.08 / 4.33	1.57 / 0.67 / 7.07	0.079 NS	0.063 NS	0.266 NS
CO_2—C (mg L^{-1})	3.11 / 0.91 / 7.76	0.58 / 0.23 / 1.43	2.03 / 0.62 / 4.56	0.49 / 0.33 / 0.81	2.02 / 0.61 / 6.32	1.18 / 0.21 / 8.1	<0.001 ***	0.239 NS	<0.001 ***
CH_4-C (µg L^{-1})	15.56 / 0.72 / 58.61	5.06 / 0.16 / 25.3	7.54 / 0.19 / 60.11	7.48 / 0.32 / 27.72	15.54 / 1.52 / 85.75	16.38 / 0.56 / 96.08	0.009 **	0.029 *	0.557 NS
ep CO_2	10.04 / 1.63 / 25.63	1.79 / 0.95 / 5.02	7.09 / 1.98 / 16.84	1.61 / 1 / 3.23	7.53 / 1.92 / 27.51	3.37 / −0.08 / 20.46	<0.001 ***	0.2802 NS	<0.001 ***
ep CH_4	211.82 / 7.52 / 716	79.15 / 1.64 / 303.6	145.09 / 3.4 / 1274	142.62 / 5.49 / 585.49	302.83 / 32.44 / 1849	304.92 / 10.4 / 1460	0.001 ***	0.032 *	0.646 NS

Note: Results from a repeated measures ANOVA examining differences between pool type (restoration and natural) and site (CL, LL and M) across the five seasons are indicated by *** = $p < 0.001$, ** = $p < 0.01$, * = $p < 0.05$, NS, no significant difference.

concentration) was significant in the natural pool models at CL and LL, but not at MU. The adjusted r^2 values were higher for models developed for individual sites than for a larger model including site as an independent variable. Analysing the three sites separately explained between 41 and 60% of the variance in dissolved CO_2 concentrations, whereas a lower proportion of the variance was explained by CH_4, DOC and water temperature when modelling all restoration or natural pools together (42% for restoration, 46% for natural pools).

3.2 | Routine sampling at cross lochs

3.2.1 | Pool water POC and DOC

Data from the intensive routine sampling at CL showed that restoration pools were more coloured, had higher SUVA and E4:E6 values and lower temperatures than natural pools (Table 3). Concentrations of DOC were higher in the restoration pools than the natural pools, particularly during the summer months; a strong seasonal cycle occurred for DOC in both pool types with concentrations peaking in the summer (Figure 3). The mean DOC concentration was 19.4 and 22.0 mg L^{-1} for the base and surface of restoration pools and 10.4 and 11.6 mg L^{-1} for the base and surface of natural pools where the mean pool depth was 40 cm and 39 cm respectively (Table S1). Mean concentrations of POC were 3.2 and 2.9 mg L^{-1} for restoration and natural pools respectively (Table 3), and were highest in the summer of 2013, particularly in the restoration pools, but during 2014 and 2015 all mean concentrations from each sampling visit were below 7 mg L^{-1} (Figure 3). The high POC concentrations in 2013 contributed to a significant positive relationship being observed between POC and DOC concentrations (both at the surface and base of the pool) in both the natural and restoration pools ($p < 0.001$), but only a small proportion of the variation in DOC concentration could be explained by POC variation ($r^2 = 0.06$ to 0.11). For the period that pool floor sedimentation was monitored (February to July 2014), mean sedimentation rates were larger for natural pools (2.43 g m^{-2} day^{-1} total sediment; 1.25 g m^{-2} day^{-1} POC) than for restoration pools (0.72 g m^{-2} day^{-1} total sediment; 0.35 g m^{-2} day^{-1} POC).

As pool volume, depth and area increases, DOC concentrations decreased in the natural pools ($p < 0.001$; all weakly negative, highest $r^2 = 0.11$ for pool depth), but not for the restoration pools. There was a significant positive relationship between pool water temperature and pool surface water DOC concentration (Figure 4), and there was a significant difference in the gradient of the relationship for restoration and natural pools ($p < 0.001$) (but not for intercept, $p = 0.45$). For every 1°C increase in water temperature the surface water DOC concentration increased, on average (± standard error), by 1.95 (± 0.10) mg L^{-1} in the restoration pools and by 0.71 (± 0.08) mg L^{-1} in the natural pools (Figure 4).

Surface water DOC concentration at both the restoration and natural pools increased as water-table depth (the distance from the peat surface to the water table) increased in the peat adjacent to the pools ($p < 0.001$ at both, $r^2 = 0.15$ and 0.29 respectively). In the

restoration pools, surface water DOC concentration, abs254, SUVA and E4:E6 were greater when the pool surface water level (height of water above the base of the pools) was shallowest ($p < 0.01$). Variations in pool surface water level over time explained a quarter of the variation in the DOC concentration and abs$_{254}$, but only 6% of the variation in SUVA and E4:E6. The relationship between pool surface water level and the surface DOC concentration was also significant in the natural pools ($p < 0.001$, $r^2 = 0.18$). However, DOC composition variables for natural pools were not significantly explained by the pool surface water level. The intercept of the relationship between the surface DOC concentration and both pool surface water level and depth to water table was much higher in the restoration pools than the natural pools. For example, when the pool surface was level with the peat surface (the pool was 'full') mean DOC concentration in the restoration pools was 8.46 mg L^{-1}, but only 0.51 mg L^{-1} in the natural pools.

3.2.2 | Pool water dissolved CO_2 and CH_4

Dissolved CO_2 concentrations in restoration pools were on average 10 times higher than atmospheric levels while those in natural pools were typically only just above atmospheric equilibrium. For both pool types, dissolved CO_2 concentrations showed strong seasonal patterns with concentrations higher in the summer than the winter (Figure 3). During a period of very low pool water levels (shallow water above the pool base) during summer and autumn 2013 (Figure 3g), the concentrations of dissolved CO_2 were extremely high (Figure 3e) being on average 41.38 mg L^{-1} and 31.85 mg L^{-1} (484 and 319 times atmospheric) for restoration and natural pools respectively. Dissolved CH_4 concentrations were similar between pool types (Figure 3) typically between 100 and 200 times higher than atmospheric levels (Table 3) but in summer/autumn 2013 they were 1200 and 2300 times atmospheric (98.7 μg L^{-1} and 219.5 μg L^{-1}) for restoration and natural pools respectively (Figure 3f).

Significant bivariate relationships between dissolved CO_2 and pool variables are listed in Table S2. When several explanatory variables are included together, a stepwise regression for natural pools ($n = 111$) showed dissolved CO_2 concentration was best predicted ($p < 0.001$, adjusted $r^2 = 0.63$) as: $CO_2 = 1.01 + 0.01*CH_4 + 0.02*DOC - 0.04*DO - 0.04*T$, where DO is dissolved oxygen and T = water temperature. A stepwise regression for the restoration pools ($n = 287$) suggested that CO_2 concentration was best predicted ($p < 0.001$, adjusted $r^2 = 0.81$) with: $CO_2 = 5.86 + 0.04*CH_4 - 0.41*DO + 0.09*WTD$, where WTD is water-table depth in the peat.

3.2.3 | Overland inflow and outflow

Overland inflow samples were available at all 12 CL pools simultaneously on 29 sampling days. The mean inflow DOC concentration was 19.1 mg L^{-1} and 17.4 mg L^{-1} for restoration and natural pools respectively. However, the mean inflow DOC concentration tended
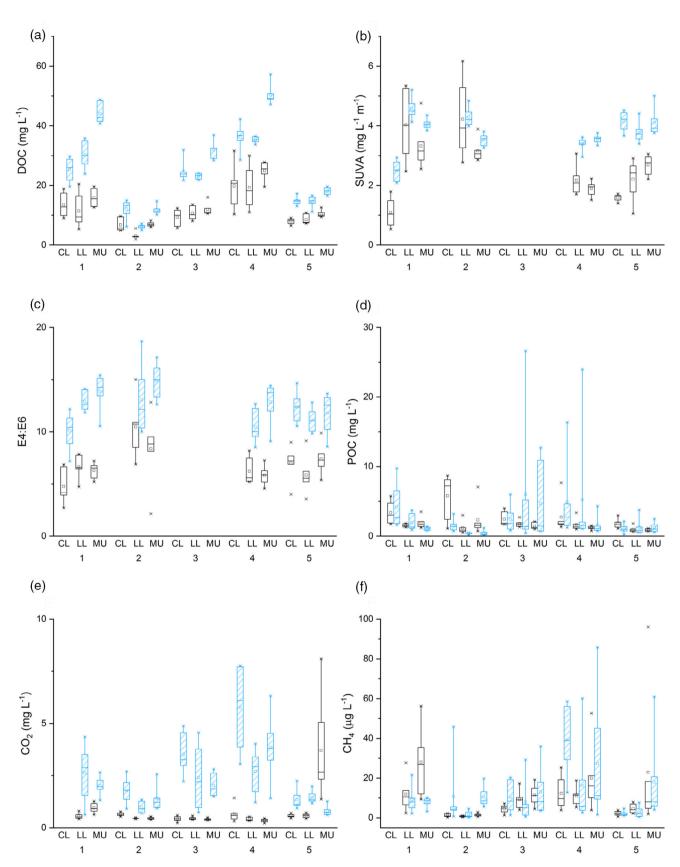
FIGURE 2 Box plots of: (a) DOC, (b) SUVA₂₅₄, (c) E4:E6, (d) POC, (e) CO₂ and (f) CH₄ for each site (CL, LL and MU) and season (season 1 = autumn 2013, 2 = winter 2013/2014, 3 = spring 2014, 4 = summer 2014, 5 = autumn 2014). Natural pools = black; restoration pools = blue

TABLE 2 Predictions of dissolved CO_2 from forward stepwise regressions using dissolved CH_4 and DOC concentrations, and water temperature, for seasonal sampling for each pool type at the three study sites

Site	Pool type	Parameter	r^2	p	Intercept	CH_4	DOC	Temp
CL	Restoration	CH_4 DOC	0.60	<0.001	0.067	0.032	0.116	
CL	Natural	CH_4 temp	0.54	<0.001	0.653	0.036		−0.022
LL	Restoration	CH_4 DOC	0.41	<0.001	0.505	−0.036	0.082	
LL	Natural	CH_4 temp	0.56	<0.001	0.527	0.016		−0.016
MU	Restoration	CH_4 DOC	0.58	<0.001	−0.096	0.018	0.060	
MU	Natural	CH_4 DOC	0.49	<0.001	1.711	0.058	−0.107	
All	Restoration	CH_4 temp	0.42	<0.001	0.370	0.021		0.174
All	Natural	CH_4 DOC	0.46	<0.001	0.846	0.056	−0.054	

Note: Three variables (CH_4 and DOC concentrations, and water temperature) were entered into the forward stepwise regression; however, only two variables were found to be significant in predicting the CO_2 concentrations at each site and pool type. The CH_4 concentration was significant in all models, combined with either DOC concentration or water temperature, but never both. Reported r^2 values are the adjusted r^2.

to be much higher than the outflow DOC for the natural pools, whereas this was not the case for the restoration pools, suggesting that DOC is more likely to be consumed within the natural pools than the restoration pools (Figure 5). Discounting natural Pool 1 (P1 in Table S1), for which data for both overland inflow and outflow were only available on two sampling dates, the two largest pools by volume (P2 and P4) were also the largest net consumers of DOC. Two of the restoration pools and one of the natural pools were net producers of DOC on average across the study period (P6, P7 and P11).

3.2.4 | Soil solution

For bulked soil solution data before February 2015 (28 sampling dates, data not available for P3), the soil solution DOC concentrations were higher in the proximity of the restoration pools (mean = 26.3 mg L^{-1}) than around the natural pools (mean = 17.6 mg L^{-1}). The mean abs$_{254}$ and SUVA were both higher in the bulked soil solution near the restoration pools than for the natural pools (Table 3). A two-way ANOVA indicated that both DOC and abs$_{254}$ in soil solution was higher near the restoration pools ($p < 0.001$) and increased significantly with depth ($p < 0.001$). Mean DOC was 15 mg L^{-1} at 5 cm depth and 23 mg L^{-1} at 50 cm depth. The interaction between soil solution depth and pool type was not significant. The soil solution DOC concentrations at 5, 10 and 20 cm depth, the overland flow water concentrations, and the pool water concentrations for restoration pools had mean values within 3.1 mg L^{-1} of each other. For the natural pools, DOC concentration in soil solution was larger than that measured in the pool water, except for at P6. Mean SUVA was 3.8 L mg^{-1} m^{-1} in the restoration pool water and 4.0 L mg^{-1} m^{-1} in the restoration bulked soil solution, but much lower in the natural pool water (2.3 L mg^{-1} m^{-1}) than in the nearby soil solution (3.0 L mg^{-1} m^{-1}). Mean E4:E6 was 10.1 and 11.0 for restoration pool water and the soil solution respectively, while being much lower in the natural pool water (4.7 L mg^{-1} m^{-1}) compared to the nearby soil solution (7.7 L mg^{-1} m^{-1}).

4 | DISCUSSION AND CONCLUSIONS

4.1 | Comparison between restoration pool water and natural pool water

At all three sites, we found differences in pool water chemistry between restoration and natural peatland pools, despite the restoration pools having been in place for several years prior to sampling (11 years at CL, 4 years at M, and 15 years at LL). These differences suggest that full recovery in peatland functioning following pool creation through ditch blocking may not be achievable over decadal timescales without further intervention, or changes in the method of ditch blocking and design of restoration pools. Restoration pools were more acidic and had significantly higher DOC, water colour, SUVA, E4:E6, dissolved CO_2—C concentrations and water temperature, and lower dissolved oxygen concentrations than natural pool waters. Even where restoration had led to the creation of pools more than 15 (LL) and 11 (CL) years prior to sampling, DOC concentrations in restoration pools were around double those of natural pools. The DOC composition ratios (SUVA, E4:E6) suggest that restoration pools had a greater fulvic acid prevalence than the natural pools and that the DOC was more aromatic (Korshin et al., 1997).

When pool water surface levels fell and water tables within the peat were deep, DOC concentrations tended to be greater in the pool water and the soil solution, reflecting increased DOC production in the more aerobic peat (Clark et al., 2009) or simply a concentration effect due to evaporation and lack of rainfall dilution. Holden et al. (2018) found that mean peat water-table depths were 4.7 cm for the peat around the natural pools sites and 3.7 cm for the peat around the restoration pools at CL but much more variable over time around restoration pools, possibly due to a lower bulk specific yield. We found a relationship that suggested that even when pools were full to the peat surface, DOC concentrations in restoration pools were likely to be much higher than in natural pools. It is likely that pool size plays a role in controlling DOC concentrations: restoration pools were all smaller than natural ones. Pool size and depth also appear to be important controls on DOC concentrations in natural

TABLE 3 Mean, median, maximum, minimum and interquartile range for each parameter by pool type for the cross lochs routine sampling data. Surface = pool water collected just below the pool surface; base = pool water collected just above the sediment layer in the pool; inflow = overland flow samples from upslope of the pools; outflow = overland flow samples from downslope of the pools; bulk = bulked soil solution samples from 5, 10, 20 and 50 cm piezometers, otherwise the soil solution sampling depth is indicated

		Restoration					Natural				
	n	Mean	Med	Max	Min	IQR	Mean	Med	Max	Min	IQR
Pool pH	551	4.2	4.2	4.9	3.7	0.2	4.4	4.5	5.6	3.5	0.2
Pool DO (mg L^{-1})	488	7.7	7.2	68.6	0.9	4.6	9.8	9.4	96.6	3.0	3.5
Pool conductivity (µS cm^{-1})	551	83.0	79.0	268.0	13.9	31.0	81.7	78.0	136.0	50.0	30.0
Pool water temperature	544	9.5	9.7	18.8	0.7	7.1	10.9	10.7	24.3	0.1	9.1
Pool POC (mg L^{-1})	555	3.2	1.4	95.0	0.2	1.7	2.9	1.80	158.0	0.3	1.5
DOC pool surface (mg L^{-1})	563	22.0	22.4	52.3	2.1	16.2	11.6	9.0	57.6	1.6	9.7
DOC pool base (mg L^{-1})	509	19.4	18.5	46.4	2.2	13.6	10.6	8.5	40.7	1.6	7.7
DOC inflow (mg L^{-1})	442	19.1	16.5	79.1	2.1	14.5	17.4	13.6	139.1	1.6	13.6
DOC outflow (mg L^{-1})	391	18.5	17.0	82.6	1.4	13.4	12.8	10.0	87.6	1.7	11.3
DOC bulk soil solution (mg L^{-1})	343	26.3	23.6	62.0	5.6	22.2	17.6	13.5	71.4	1.1	15.7
DOC 5 cm (mg L^{-1})	134	18.3	13.9	42.0	2.3	16.9	11.9	9.8	29.4	1.6	13.4
DOC 10 cm (mg L^{-1})	174	19.3	16.6	41.0	2.5	19.4	12.9	9.7	36.2	1.6	13.4
DOC 20 cm (mg L^{-1})	186	20.8	20.9	42.4	2.3	20.7	14.3	10.8	38.8	2.0	13.5
DOC 50 cm (mg L^{-1})	172	28.4	28.1	57.0	2.4	26.9	18.2	18.6	44.2	3.0	17.4
abs$_{254}$ pool surface (abs m^{-1})	240	72.9	75.5	140.3	6.1	62.5	20.0	18.1	98.0	2.1	14.3
abs$_{254}$ bulk soil solution	55	74.1	64.9	162.0	23.9	64.8	45.6	33.5	129.3	9.2	42.9
abs$_{254}$ 5 cm	114	66.8	54.3	150.3	2.6	71.5	32.6	25.0	111.4	3.2	33.2
abs$_{254}$ 10 cm	149	72.7	71.6	159.0	2.3	85.0	40.7	27.1	145.2	1.8	50.2
abs$_{254}$ 20 cm	164	84.5	93.2	193.7	8.6	86.3	50.8	32.6	165.7	2.0	49.2
abs$_{254}$ 50 cm	151	105.9	91.1	241.2	4.9	124.2	60.6	51.1	169.3	3.8	68.8
SUVA pool surface	240	3.8	3.8	4.7	0.9	0.7	2.3	2.1	21.1	0.6	0.7
SUVA bulk soil solution	55	4.0	3.8	6.6	2.4	1.1	3.0	2.9	5.4	1.4	1.2
SUVA 5 cm	114	3.7	3.9	6.7	1.1	1.1	2.7	2.8	4.2	0.7	1.1
SUVA 10 cm	149	3.8	4.0	8.4	0.8	1.2	3.0	3.0	6.3	0.8	1.3
SUVA 20 cm	164	4.1	4.1	18.6	1.7	0.9	3.3	3.2	20.4	0.8	1.5
SUVA 50 cm	150	3.8	3.9	14.9	0.8	1.2	3.1	3.2	4.6	0.7	1.3
E4:E6 pool surface	199	10.1	9.8	37.0	0.8	5.3	4.7	4.0	40.0	<0.1	4.0
E4:E6 bulk soil solution	49	11.0	10.3	27.0	2.8	7.9	7.7	6.0	30.0	1.0	7.9
E4:E6 5 cm	96	9.5	9.1	40.5	1.1	6.0	7.6	5.5	31.0	1.0	8.8
E4:E6 10 cm	119	9.8	10.3	22.5	1.0	6.4	8.4	7.0	26.5	1.0	7.2
E4:E6 20 cm	141	9.6	9.7	24.0	1.0	3.9	6.7	6.6	15.5	0.2	6.0
E4:E6 50 cm	137	9.4	8.2	73.0	1.5	2.5	7.7	6.7	33.0	1.5	4.0
Pool CO$_2$ (mg L^{-1})	553	3.3	2.4	14.1	0.3	2.9	0.8	0.4	11.3	0.1	0.2
Pool ep CO$_2$	553	10.2	8.2	41.4	0.7	11.7	2.5	1.5	34.3	0.3	1.0
Pool CH$_4$ (µg L^{-1})	553	18.5	20.0	319.7	0.3	40.5	10.1	9.9	429.9	0.2	11.2
Pool ep CH$_4$	553	275.9	123.0	4126.3	3.1	291.8	133.4	65.0	4826.3	1.6	91.0

pools, as DOC decreased as pool depth increased, a relationship that was also reported for natural pools in Canada by Arsenault et al. (2018). However, it is likely that a legacy of peatland degradation, disturbance and more variable pool levels and water tables around restoration pools (Holden et al., 2018) contributed to enhanced DOC production in the surrounding peat. There may also have been a greater relative contribution of DOC from vegetation turnover within the restoration pools.

Restoration pools tended to be supersaturated in CO_2 (~10 times higher than atmospheric levels) whereas natural pools tended to have values just above what would be expected if the water were in equilibrium with atmospheric concentrations. Turner et al. (2016) also
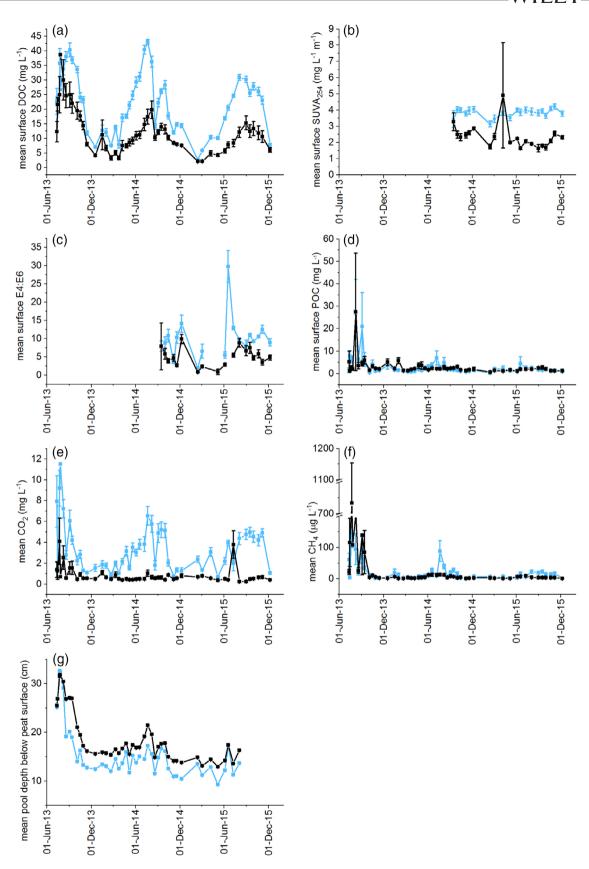
FIGURE 3 Mean and standard errors of (a) DOC, (b) SUVA$_{254}$, (c) E4:E6, (d) POC, (e) CO$_2$, (f) CH$_4$ for pool samples taken near the pool surface and (g) pool water depth for each pool type at cross lochs over time. Natural pools = black; restoration pools = blue. The standard errors of the mean pool depth below peat surface were small; therefore, the error bars are masked by marker symbols
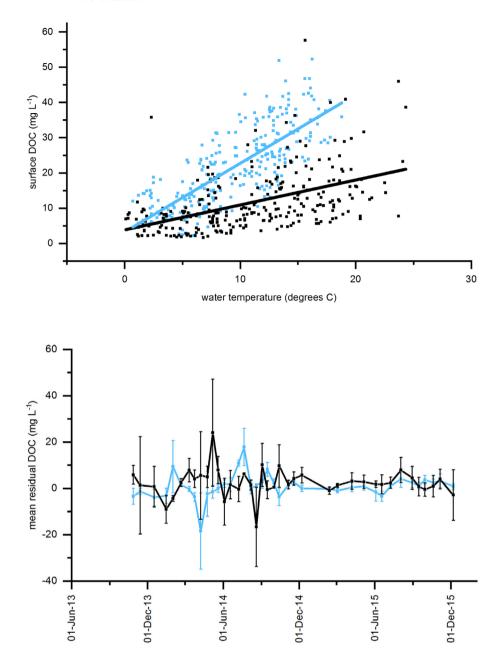
FIGURE 4 Scatter plot of pool water temperature versus surface DOC concentration. Natural pools = black; restoration pools = blue. DOC in surface water of natural pools = 0.71 * (pool water temperature) + 3.84, $r^2 = 0.25$; DOC in surface water of restoration pools = 1.95 * (pool water temperature) + 3.25, $r^2 = 0.59$

FIGURE 5 Mean and standard error of residual DOC (inflow minus outflow) of the overland flow. Natural pools = black; restoration pools = blue

observed dissolved CO_2 levels only slightly above atmospheric equilibrium in natural peatland pools in southwest Scotland and Northern Ireland. The difference in CO_2 concentrations between the pool types may be because:

i. Soil and root respiration was greater in the peat surrounding restoration pools than natural pools (peat water-table depth was a predictor of pool CO_2 concentration in a stepwise regression for restoration pools but not for natural pools). Additionally, smaller pools have a greater soil-water interface proportional to their volume.

ii. In-pool respiration by aquatic plants and heterotrophic respiration of organic matter is greater in the restoration pools than the natural pools, as suggested by the observed inverse relationship between dissolved CO_2 and DO in the restoration pools only. Plant biomass

appeared to be proportionately greater per unit pool volume in restoration pools than natural pools, although we did not directly measure biomass. Many of the restoration pools were dominated by *Sphagnum* sp. which are known to host methanotrophs which consume methane and oxidize it to CO_2 (Kip et al., 2010), whereas the natural pools had larger areas of open water.

iii. The residence time of water in the restoration pools was smaller thereby reducing time for CO_2 equilibration. Peacock et al. (2013) noted that water residence times in restoration pools studied in Wales were relatively short. Holden et al. (2018) calculated, using pool catchment areas, volume, rainfall and evaporation that the natural pools at CL would have a median of 9 times their volume of water flushed out of them per year, compared to 54 times their volume for the studied restoration pools.

iv. Atmospheric exchange may be greater for natural pools as they are generally larger than the restoration pools, subject to greater wind speeds and wave action and thus more turbulent which promotes CO_2 evasion from the pool surface and equilibration with atmospheric CO_2 concentrations (Read et al., 2012; Vachon & Prairie, 2013). Restoration pools tended to be more sheltered within former ditches with simple shapes and smaller perimeters, thereby allowing build-up of dissolved CO_2.

v.   Pool water pH may have influenced the proportion of inorganic C that was present as CO_2. However, given the maximum pH across both groups was only 5.6, this influence is likely to be minor.

4.2 | Impacts of a dry summer

The dry summer and autumn of 2013 was associated with a long lasting pool level drawdown to around 30 cm below the peat surface at CL (Holden et al., 2018). We found that this summer period was associated with the highest DOC concentrations for the natural pools, but for the restoration, pools the same period produced DOC concentrations in line with those observed in the other two summers sampled during the study. Mean POC concentrations from each site visit were below 7 mg L^{-1} except during summer 2013 when desiccation may have loosened peat material (Li et al., 2018) on the upper levels of exposed pool side walls, and existing suspended sediment became more concentrated due to evaporative loss of water. The large concentrations of dissolved CH_4 and CO_2 in pool waters during summer 2013 highlight potential future risks of climate change and summer droughts on peatland C cycling. The translation of high dissolved CH_4 concentrations into emissions from the pool surface will, however, depend upon vegetative cover in pools. Whereas pools with high coverage of *Eriophorum angustifolium* may facilitate CH_4 evasion through their aerenchyma (Cooper et al., 2014; Marinier et al., 2004), *Sphagnum sp.* are known to have symbiotic relationships with methanotroph assemblages and have been associated with an enhanced C sink strength (Raghoebarsing et al., 2005). However, the high aquatic CH_4 values need to be taken into account when modelling landscape-scale responses to stressors such as climate change. While the largest CH_4 release from peatlands is often associated with the wettest conditions (Abdalla et al., 2016), the driest periods were when dissolved CH_4-C concentrations in pool waters were at their greatest. Mean CH_4-C concentrations in summer 2013 were typically over 100 µg L^{-1}, and on one sampling occasion for natural pools, mean values were over 800 µg L^{-1}. However, for all other periods, including summers 2014 and 2015 when pool levels dropped to ~15–20 cm below the peat surface, CH_4-C concentrations were never above 40 µg L^{-1}. Since the peat at CL had median permeability at 30 and 50 cm depths of 1.5×10^{-5} cm s^{-1} and 1.4×10^{-6} cm s^{-1} respectively (Holden et al., 2018), there may have been little flow into and out of the pools through the main peat mass during summer 2013. The high summer 2013 CH_4 concentrations may have been due to a combination of warm temperatures (MacDonald et al., 1998), a lack of water turnover

in the pools, and reduced water pressure on the pool floor, which may have allowed trapped CH_4 bubbles below the pool floor to expand and be released. McEnroe et al. (2010) found CH_4 fluxes from pools to increase with decreasing pool depth. As bubbles move through the pool water column, they may be partly stripped of their CH_4 causing a rise in dissolved CH_4 concentrations in pool water.

4.3 | Transformation of DOC

At CL, DOC concentrations in outflows from natural pools were lower than the DOC flowing into them suggesting that DOC was being processed within the pools. The two largest natural pools by volume (P2 and P4; Table S1) were also the two pools where most DOC was consumed (inflow DOC >outflow DOC). Enhanced UV photodegradation and biological turnover (Moody & Worrall, 2017) likely account for these differences, but pool-size effects require further testing. Pool surface area across the natural pool site as a whole was more than 10 times that of the pool surface area at the restoration pool site (Holden et al., 2018). There was a much stronger relationship between DOC and dissolved CO_2—C concentrations for restoration pools than natural pools (Figure S1), possibly because a greater proportion of the DOC in larger natural pools had been transformed by photo decay (Pickard et al., 2017). It was also notable that mean rates of POC deposition onto pool floors (per m^2) were more than three times greater for natural pools than for restoration pools. It is possible that flowing water between restoration pools within ditches was sufficient to keep more of the sediment in suspension. Alternatively, higher dissolved oxygen concentrations in natural pools may have been conducive to enhanced algal growth, which may have contributed to the accumulation of pool floor POC. However, the higher proportion of humic fractions of DOC in natural pools suggest that flocculation of DOC (Asmala et al., 2014; Eckert & Sholkovitz, 1976) may have more readily occurred in natural pools than in restoration pools. Thus, DOC may be acting as a precursor of POC in natural peatland pools, as observed in boreal lakes by von Wachenfeldt and Tranvik (2008). Attermeyer et al. (2018), reported that microbial degradation rates of POC were approximately 15 times higher than those of DOC for a range of inland waters, including surface peat water. A faster degradation rate for POC than DOC implies that a constant replenishment must occur to sustain POC concentrations. Thus, Attermeyer et al. (2018) suggested that degradation of aquatic organic matter occurs, to a large extent, via transition of DOC into more rapidly cycling POC. Degradation of POC was not investigated in this study, but warrants further investigation, particularly to determine whether rates of degradation vary between natural and restoration pools.

If more DOC can be transformed by creating larger pools during peatland restoration projects, and more POC is trapped or degraded by natural pools, then this may lead to improved water quality downstream, thereby reducing water treatment costs at potable water works. However, such effects should not be overstated because soil water around natural peatland pools was also much lower in DOC

concentration, SUVA, and E4:E6, compared with soil water around restoration pools, showing that there was potentially a peatland degradation legacy from drainage inherent in the biogeochemical functioning at the CL restoration site.

When DOC concentrations in soil solution and nearby pool water were compared (Table 3), the natural pool water had lower mean concentrations for all soil solution depths. For the restoration pool water, the DOC concentrations were greater than soil solution at 5 cm, 10 and 20 cm depth with only 50 cm depth soil solution having greater DOC than the pool water. These data suggest restoration pool water is sourced from deeper peat layers than natural pool water, in line with the greater water-table and pool-level variability at the restoration pool site shown by Holden et al. (2018). P6 was the only natural pool that had larger DOC concentrations in pool water than overland inflow water. For P6, the DOC concentrations were similar to those in the deepest soil solution water suggesting that the pool may have deeper water sources, perhaps entering via pipeflow, which can be an important aquatic C pathway in blanket peatlands (Dinsmore et al., 2011; Holden et al., 2012). Overall, there was little difference in soil solution and pool water SUVA or E4:E6 at the restoration pool site, whereas the differences were large at the natural pool site (Table 1), further suggesting that the dominant processes controlling the form and concentration of C were different for the two pool types. The fact that the SUVA for natural pool water was lower than the SUVA in soil solution surrounding the natural pools, suggests that sustained sunlight-induced DOC photodegradation occurred in the natural pool water (Waiser & Robarts, 2004). Several studies have shown that photochemical oxidation leads to the loss of aromatic DOC (e.g., Spencer et al., 2009), and thus the reduction in SUVA as well as the production of CO_2. Arsenault et al. (2019) also observed that DOC concentration and SUVA were lower in natural pool water than in soil solution from the surrounding peat, and attributed this to photodegredation occurring in the pools. Streamwater DOC concentrations downslope of the natural pool site were reported by Gaffney et al. (2020) (as an undamaged 'bog control' in their study) for the same time period as our study and showed similar values and temporal patterns to those we found in the natural pool water in this study. This finding suggests that, where natural pools are present within a catchment, they may play an important role in controlling downstream aquatic carbon chemistry.

4.4 | Overview

There was clear evidence that concentrations of DOC and dissolved CO_2 were greater in restoration pools than natural pools at all three study sites. We found clear seasonal patterns in pool C concentrations and a dry summer in 2013 was associated with the highest concentrations of DOC, POC and dissolved CH_4 and CO_2. Overall, the concentration, form and cycling of C in natural pools appears to be linked most strongly to pool water level and size, and light penetration (photodegredation), as highlighted by lower SUVA in pools than the surrounding peat and the strong differences in inflow and outflow DOC. For restoration pools, in contrast, temperature, pool size (reducing exposure to turbulence so that CO_2 does not readily escape), pool water level, peat-pool linkages and substrate decomposition (as shown by low DO, and higher DOC and CO_2 production) appear to be more important controls on C form and concentration.

Peatland restoration is increasingly seen as an essential element of global climate change mitigation strategies (Evans et al., 2021; Leifeld & Menichetti, 2018). In our study, restoration pools were in effect a by-product of restoration of drained peatlands and some of their characteristics appear related to a lack of recovery of biogeochemical processing. It will be important to understand whether small restoration pools are transient but dynamic features of restored peatlands (e.g., Peacock et al., 2013), but going forward, there might be opportunities to consider how the design and management of restoration pools may support peatland functioning, while also supporting biodiversity objectives (Beadle et al., 2015).

DATA AVAILABILITY STATEMENT
Carbon concentration data associated with this manuscript are available at the NERC Environmental Information Data Centre at https://eidc.ac.uk.

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