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Key Points:

- We present old ^{14}C dates from waters draining eroded temperate peats, caused by deep C loss and low water tables in gullied peats
- Novel approaches to dissolved organic carbon source identification indicate that water table drawdown and the nature of peat erosion influence loss of old carbon
- Our method has potential as a rapid way to indicate peatland function and assess restoration success

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Carbon Loss Pathways in Degraded Peatlands: New Insights From Radiocarbon Measurements of Peatland Waters

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Abstract Peatland carbon stores are under widespread anthropogenic pressure, resulting in degradation and carbon loss. This paper presents $DO^{14}C$ (Dissolved Organic Carbon) dates from waters draining two eroded blanket peatland catchments in the UK. Both catchments are characterized by severe gully erosion but one additionally has extensive surface erosion on unvegetated surfaces. $DO^{14}C$ values ranged from 104.3 to 88.6 percent modern (present to 976 Before Present). The oldest DOC dates came from the catchment characterized by both gully and surface erosion and are among the oldest reported from waters draining temperate peatlands. Together with peat age-depth data from across the peatland landscape, the $DO^{14}C$ ages identify where in the peat profile carbon loss is occurring. Source depths were compared with modeled water table data indicating that in the catchment where gully erosion alone dominated, mean water table was a key control on depth of DOC production. In the system exhibiting both gully erosion and surface erosion, DOC ages were younger than expected from the age of surficial peats and measured water tables. This may indicate either that the old organic matter exposed at the surface by erosion is less labile or that there are modifications of hydrological flow pathways. Our data indicate that eroded peatlands are losing carbon from depth, and that erosion form may be a control on carbon loss. Our approach uses point measurements of $DO^{14}C$ to indicate DOC source depths and has the potential to act as an indicator of peatland function in degraded and restored systems.

Plain Language Summary Peatlands are the largest terrestrial soil carbon store, but are under widespread anthropogenic pressure, resulting in degradation and carbon loss. In this study of UK upland peatlands, we used radiocarbon dating of dissolved organic carbon (DOC) from waters draining eroded peatlands to identify the age of the carbon that has been lost. These dates are among the oldest reported from waters draining temperate peatlands. The dates combined with age-depth data from across the peatland landscape allowed us to model where in the peat profile the carbon loss was concentrated. We compared these results with water table data and found that in the systems we studied, the type of peatland erosion that the system had experienced was an important factor controlling the age of carbon lost. The close association between radiocarbon age of carbon and water table suggested that radiocarbon dating of DOC might be a useful catchment scale proxy for water table, a direct measurement of the locus of carbon loss from the peat, and an effective measure of the overall "health" of the peatland ecosystem. The approach therefore has potential as a rapid method of assessing stabilization and restoration of intact peatland function.

1. Introduction

Peatlands are the largest terrestrial soil carbon store, containing circa 620 Pg of carbon (Dargie et al., 2017; Page et al., 2011). Deep peat accumulations have been built up over at least Holocene timescales (Gorham et al., 2012; Harden et al., 1992), so that the long-term accumulation of organic matter represents an important component of the terrestrial carbon cycle. However, peatlands are under widespread pressure with stressors, such as plantation forestry and agriculture (Dommain et al., 2016), drainage (Pronger et al., 2014), nitrogen pollution (Payne, 2014), controlled and uncontrolled fires (Turetsky et al., 2015), overgrazing of seminatural areas, thawing of permafrost (Frey & Smith, 2005; Romanovsky et al., 2012; Schuur & Mack, 2018), and changing hydroclimate (Clark et al., 2010). This diverse set of issues has the potential to fundamentally alter the peatland carbon store with

most anthropogenic pressures leading to carbon loss (Page & Baird, 2016) and accelerating climate warming (Gallego-Sala et al., 2018).

Peatlands that have been subject to these pressures often feature low water tables, resulting in enhanced losses of old carbon from peatland storage as fluvial carbon in dissolved form, in addition to direct losses to the atmosphere through in situ oxidation of organic carbon. The primary control on decomposition rates in peatlands and so on gaseous and dissolved organic carbon (DOC) production is the availability of oxygen to support aerobic microbial decomposition, which is in turn significantly influenced by water table (Clymo, 1984; Strack et al., 2008). Globally, direct gaseous carbon emissions are enhanced by peatland degradation (e.g., an additional 1.30 $GtCO_2$/yr released to the atmosphere due to drainage in 2008; Joosten, 2010 and 0.2 Gt CO_2 eq/yr released due to peatland fires; van der Werf et al., 2010). Fluvial dissolved carbon losses in both pristine and degraded systems occur through the mobilization of soluble products of organic matter decomposition in the aerobic upper layers of the peat (typically the top 10–20 cm in intact peats). In peatland soils, there is commonly a rapid (often exponential) decline in hydraulic conductivity with depth (Fraser et al., 2001; Hoag & Price, 1995; Morris et al., 2015) so that near-surface flow paths dominate runoff (Holden & Burt, 2003a). Limited evidence suggests that fluvial carbon losses are increased by drainage and/or other activities that lower the water table and increase the depth of the oxic zone (Evans et al., 2016; Moore et al., 2013). Lower water tables may also modify the near-surface hydrology leading to matrix throughflow and macropore flow in deeper peats (Holden et al., 2006).

In heavily eroded systems, therefore, losses of DOC may occur much deeper in the peat profile. Loss of carbon from the peatland surface is associated with the turnover of surface vegetation and fresh litter, whereas carbon loss from deeper peats due to peatland drainage represents an additive transfer of carbon from the long-term peatland store to the atmosphere.

Peatland soils are cumulative deposits so that the age of the organic remains in the peat profile is correlated with depth. Aging carbon in runoff from degraded peatland systems therefore offers the potential to fingerprint where in the peat profile decomposition is occurring. Bulk radiocarbon dates from stream water reflect the age of a mixture of the organic material that has been leached into the fluvial system. Aged signals can therefore be diluted by modern contributions (turnover of litter), but old dates will definitively indicate significant contributions from the decomposition of old organic matter stored in the peat profile. DOC ages can also be dependent on water residence times (Dean, 2019) although this is unlikely to be a significant issue in the blanket peat systems. In these peatlands, water residence times are often short (minutes) as they tend to be hydrologically "flashy" systems (Shuttleworth et al., 2019), generating the majority of flow from surficial flow paths so that DOC from slow flow paths is a minor component of stormflow. Older DOC radiocarbon ages from waters draining degraded peatlands are an indicator of modified carbon cycling, and potentially accelerated, loss of stored carbon (Evans, Bonn, et al., 2014).

Despite the compilation of large data sets of dated fluvial DOC (e.g., Butman et al., 2015; Marwick et al., 2015), data from peatlands are relatively limited, particularly from heavily degraded peatlands. Dating of DOC in waters leaving intact temperate peatlands has usually produced modern radiocarbon dates, consistent with the diplotelmic model of peat soils (Evans et al., 2007; Raymond et al., 2007) and turnover of modern organic matter at the peatland surface. However, at a few drained and degraded peatland sites, much older radiocarbon dates have been recorded. Evans, Page, et al. (2014) have reported radiocarbon as old as 4,374 years Before Present (BP) (59.4% modern) for drained tropical peats. Northern hemisphere drained peatlands produced aged carbon typically in the range 100–300 years BP with one sample from the UK Peak District dated as 2006 years BP (Evans, Page, et al., 2014). Hulatt et al. (2014) have reported radiocarbon ages of up to 3,100 years BP from agricultural peatlands and peatland extraction sites in Finland.

In this paper, we have assembled radiocarbon ages on DOC samples from what are arguably the most severely eroded blanket peatlands in the world; the Peak District in the UK (Evans & Warburton, 2007). These include radiocarbon data from published and unpublished projects (Evans et al., 2013; Stimson et al., 2017) and some new data. By comparing dates from two sites with contrasting erosional characteristics, and further comparing DOC ages to measured and modeled water tables in these catchments, we aim to understand the controls on the age of DOC generated and exported from eroded peatland catchments. Furthermore, we aim to assess the implications for the use of ^{14}C as an indicator of deep peat stability and as a marker for restoration recovery. We test the

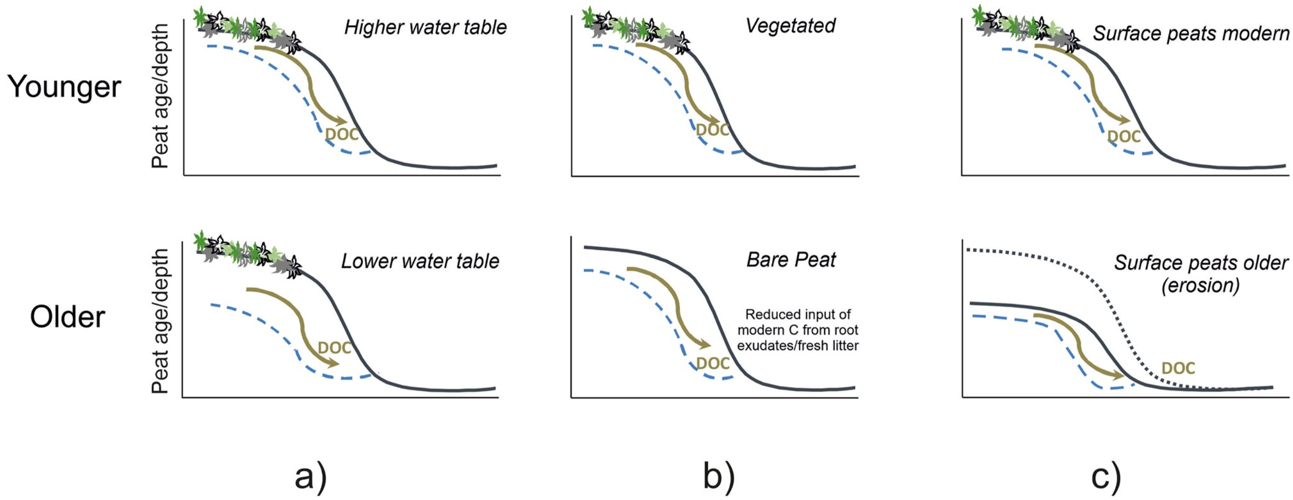

Figure 1. Hypotheses linking erosion and production of older dissolved organic carbon (DOC) from gullied peatlands. The blue line is the position of the water table and the brown arrow is the direction of the movement of DOC. The black line represents the gully profile and the surface of the peat. (a) Water table as the control: older DOC as water tables lowered; (b) supply of modern DOC from fresh litter and root exudates is the control: older DOC as this supply is removed; (c) presence of surficial erosion is the control: older DOC generated at the surface as younger peat is removed by erosion.

primary hypothesis that these degraded peatlands are losing carbon at depth. In addition, we will consider three hypotheses that could explain the production of old DOC from eroding peatland systems. These are (Figure 1):

1. That decomposition of older carbon is associated with lower water tables, which results from gully erosion of the peat (Figure 1a)
2. Extensive surface erosion can remove vegetation so that there is bare peat at the surface, which reduces supply of "modern" DOC from freshly degraded plant litter and root exudates erosion (Figure 1b)
3. Where there has been considerable depth of surface erosion, old peat at the surface might contribute old carbon even under relatively high water table conditions (Figure 1c).

2. Study Area and Methods

2.1. Study Site

In the UK, peatland carbon storage has been estimated at around 5 Gt C, which represents 52% of total UK soil carbon storage (Ostle et al., 2009). However, many UK peatlands are severely degraded with extensive gully erosion occurring in many parts of upland Britain (Evans & Warburton, 2007). The most severe erosion is seen in the southern Pennine region, which has been described as the "badlands of Britain" (Tallis, 1997). This description reflects their past history of relatively intensive land use, including grazing, drainage, and the widespread occurrence of prescribed burning and wildfires, as well as a history of acidifying atmospheric pollution resulting from their proximity to the major industrial cities of Northern England, which led to the loss of key peatland vegetation including Sphagnum mosses (Evans et al., 2006; Tallis, 1987). Previous dates on fluvial DOC have been reported in this region (Evans, Page, et al., 2014). Dates from an ungullied site and a re-wetted site were 99.12% and 101.43% modern, modeled as age equivalents of 399 and 291 years BP, respectively, while two dates from gullied sites were 95.11% and 81.14% modern, modeled as age equivalents of 655 and 2006 years BP (Evans, Page, et al., 2014).

This study focused on two degraded headwater peatland catchments in the Peak District National Park of the Southern Pennines. These blanket bogs are ombrotrophic mires that closely follow the underlying topography on flat surfaces or gentle slopes. The peats develop under specific climatic conditions, notably a minimum of 1,000 mm rainfall, mean temperatures of <15°C, and little seasonal variability (Lindsay et al., 1988). Blanket peats have distinctive flora and fauna, and their ecological functioning is intimately linked with their hydrology (Charman, 2002; Evans, Bonn, et al., 2014).

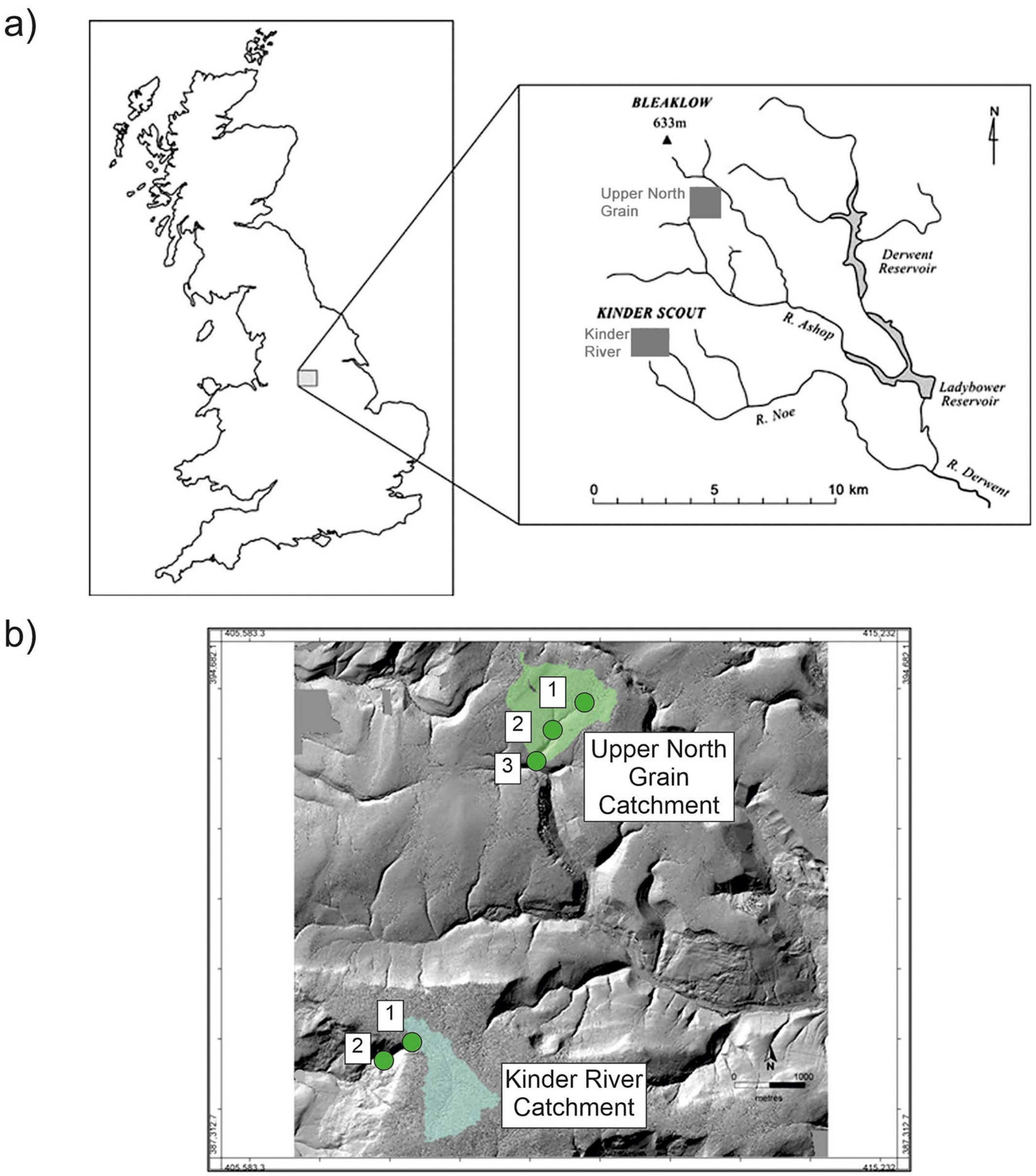

Figure 2. Study sites location and sampling points. (a) Location of Bleaklow Plateau and Kinder Scout in relation to the UK and each other. (b) Hillshade digital elevation model identifying the two study catchments and green dots representing the location of the sampling points.

The study sites are within a blanket mire complex, which span two upland plateaux about 5 km apart and which form the watershed dividing east and west flowing drainage in the southern Pennines (Figure 2). The Kinder River catchment drains the northern half of the Kinder Scout Plateau and the Upper North Grain stream catchment drains the southern flanks of the Bleaklow Plateau (Figure 2). Both catchments are areas of upland blanket peat at elevations between ~500 and 633 m (Shuttleworth, 2015; Stimson, 2015). Upper North Grain descends ~60 m (Goulsbra et al., 2014) before a confluence with the River Ashop, which eventually drains into Ladybower Reservoir, whereas the Kinder River headwaters descend almost 300 m into Kinder Reservoir (Stimson, 2015). These are small upland streams with stream depths less than a meter in high flow and maximum stream widths on the order of five m.

The mean annual temperature in the area is 6.9°C with a range of −8 to 22°C, over the period 2004–2013, and the mean annual rainfall is ~1,300 mm (Clay & Evans, 2017). The vegetation is dominated by wavy-hair grass

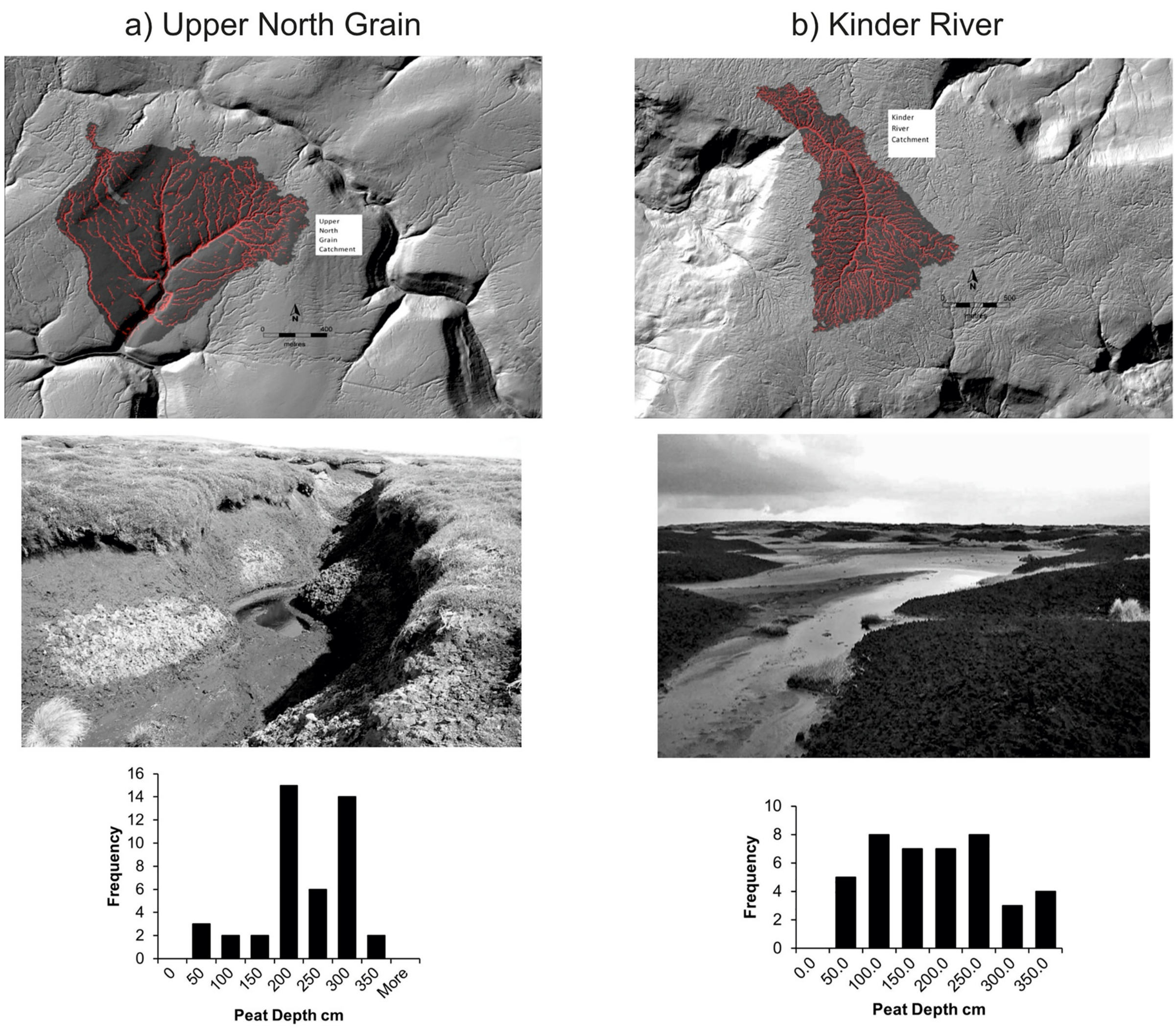

Figure 3. Hillshade Digital Elevation Model of study catchments with the gully network highlighted. Photos of the nature of erosion and peat depth distributions. (a) Gully erosion in the Upper North Grain (UNG) catchment. (b) Extensive bare peat and sheet erosion in the Kinder River catchment.

(*Deschampsia flexuosa*), cottongrass (*Eriophorum vaginatum*), heather (primarily *Calluna vulgaris*) bilberry (*Vaccinium myrtillus*), and crowberry (*Empetrum nigrum*). A number of native UK blanket bog forming species were historically depleted in the area due to its past pollution and management history, but key indicator species including bryophytes (e.g., peat-forming *Sphagnum* spp.) have seen improvements in coverage over the past 10 years as a consequence of restoration efforts in both areas (Alderson et al., 2019).

Stream waters were sampled for radiocarbon analysis of DOC at three sites in the Upper North Grain catchment and two sites in the Kinder River catchment (Figure 2). In the Kinder River system, one sample was taken at the outlet of the peat catchment and one further sample from a short distance downstream circa 500 m. Sampling sites in the Upper North Grain catchment were all within the study catchment. This study utilized available radiocarbon data from other projects and published works (Evans et al., 2013; Stimson et al., 2017 and unpublished data) and these studies suggest that there was no systematic downstream change in observed ^{14}C ages over short distances such as these.

Figure 3 shows each catchment in more detail, highlighting the differences in the nature of the erosion and peat depth data at each site. The distribution of peat depth data was based on manual probing of peat depth and derived from a wider peat depth database for the Bleaklow and Kinder Scout areas collected by Moors for the Future Partnership. The spacing of these data points at 100 m centers meant that a limited number of points fall within the study catchments. Therefore, representative peat depth distributions were derived for the local blanket peats

Table 1
Comparative Data for the Two Study Catchments

	Upper North Grain	Kinder River catchment
Area (km^2)	1.05	1.12
Gully Area (%)	15.1	25.9
Mean gully depth (m)	1.12	1.21
Gully length (km)	31.1	39.8
Bare peat (%)	7.3	Circa 15 (33.5 in 2008)
Peat Depth (cm)	208	161

Note. Gully data are calculated from gully maps of the catchment derived from the method of Evans and Lindsay (2010) based on 2 m resolution LiDAR-derived digital elevation data. Bare peat areas (areas where erosion has removed all surface vegetation) are derived from vegetation mapping based on a supervised classification of R-G-B-NIR aerial photography developed by Liddaman (2009). The lower figure for Kinder River incorporated revegetation work undertaken since 2,010. Peat depth data are the average of peat probe data for each catchment.

by incorporating additional sample points (within 2 km of the catchment) on Alport Moor (Upper North Grain) and the wider Kinder Scout Plateau (Kinder River) were included. For Kinder Scout, $n = 43$ and for Upper North Grain, $n = 45$. Peat depths from the Kinder River site were lower on average and more variable, consistent with extensive surface erosion in the catchment. On Kinder Scout, although gully erosion was extensive, there were also large expanses of bare peat on the interfluves (approximately 33% of the catchment: Table 1). These are areas where the surface vegetation has been completely removed and where considerable sheet erosion has occurred. As such, these areas of bare peat represented "fossil" surfaces where the surface peat was older than the surficial peat in the remainder of the catchment. In contrast, the Upper North Grain catchment was dominated by extensive gully erosion but the interfluves remained vegetated and surface erosion were minimal. Further comparative data on erosion in the two catchments are given in Table 1.

2.2. Derivation of Age-Depth Curve for South Pennine Peatlands

To use ^{14}C ages of DOC as a fingerprint of the locus of in the peat profile, an estimate of the average age-depth relation for catchment peats was required. Age and depth data were compiled from an extensive body of existing paleoecological data from the Bleaklow and Kinder Scout Plateaux (Conway, 1954; Livett et al., 1979; Tallis, 1964, 1994, 1995; Tallis & Livett, 1994; Tallis & Switsur, 1983, 1990). From these published data, 35 radiocarbon dates were derived and further age-depth data were obtained by combining these dates with established core correlations (based on pollen zoning) in the original literature. In this way, 128 separate dated horizons were identified in 43 peat cores from the Bleaklow and Kinder Scout plateaux. Radiocarbon dates (and associated error bounds) were calibrated using OxCal 4.2.4 and the IntCal 2,013 curve (Reimer et al., 2013). Linear regression was performed to create the age-depth curve.

2.3. Radiocarbon Dating of DOC

Water samples for radiocarbon analysis were collected between March 2012 and May 2014 in Nalgene bottles, which had been acid washed in the laboratory and then further washed three times in the streamwater before taking the samples. Samples were collected whilst in the falling stages of high flow events (sampling from the Kinder River on 6/9/13 and 12/5/14 and from Upper North Grain on 4/3/12, 15/5/13 and 7/3/14). Samples were filtered through pre-ashed Whatman GF/F filter papers and submitted to either the Natural Environment Research Council radiocarbon facility or to the Chrono laboratory at Queens University Belfast for dating of DOC. In each case, samples were acidified to remove carbonate prior to the analysis. In total, 11 samples were analyzed for DOC and further 8 samples were analyzed to determine the age of the particulate organic carbon (POC) retained on the filter papers.

Assigning a single "date" to DOC samples from peatlands is problematic since measurements pertain to a mixture of material of differing ages contributed from across the peat profile. Evans, Page, et al. (2014) developed a new approach to generating ages from ^{14}C data in these systems. This approach assumed that rather than representing a single "date," ^{14}C dates of DOC are the sum of a weighted average of the ^{14}C contribution of each year represented in the peat profile. The weighting assumed an exponential decline in the proportion of total DOC derived from each year class, which was justified on the basis that both peat decomposition rate (the source of the aged carbon) and hydraulic conductivity (controlling flux of soluble products from peatland soils) typically exhibit exponential decline with depth in peatland soils (Morris et al., 2015). DOC age is calculated as in Equation 1:

$$DO^{14}C = \sum_{t=1}^{t=10,000} \left({}_{14}CO_2 t \times \exp^{(-kt)} \right) \quad (1)$$

where $^{14}CO_2t$ is the atmospheric ^{14}C concentration in year t and the constant "k" is derived iteratively to fit the measured ^{14}C % modern value from the sample. The ^{14}C % modern contribution post-1950 was atmospheric

concentrations, whereas pre-1950, they were derived from the Intcal13 radiocarbon calibration curve (Reimer et al., 2013).

The Evans, Page, et al. (2014) approach was applied to determining the "age" of DOC from the study sites. The fitting process can produce two solutions for *k* for samples containing a substantial proportion of modern (post 1950s) material, and following Evans, Page, et al. (2014), the older date was used in these degraded systems. This method and the derived ages are subsequently referred to as Model 1, which takes a default approach and assumed that the full peat profile was present in the catchments. Model 1 was therefore used to calculate $DO^{14}C$ for both the Upper North Grain and Kinder River catchments. However, on Kinder Scout, extensive surface erosion means that this approach may not be accurate since the youngest peats may have been eroded from the catchment. The Evans, Page, et al. (2014) model was therefore adjusted for this site to allow for calculation of DOC ages based in areas where the old peat was exposed at the surface (Model 2).

The range of peat depths across the two sites (Figure 3: 0–350 cm) was consistent, which is to be expected given comparable basal ages and climate. Therefore, the reduced mean peat depth and increased variability observed on Kinder Scout may be reasonably assumed to be due to erosion of surficial peats observed in this catchment. In Upper North Grain, erosion was confined to gullies, and gully sites were not included in the peat depth measurements. The difference in mean depth between sites was 0.47 m, which was interpreted to represent the average depth of surface erosion in the Kinder catchment. The Model 2 version of the Evans, Page, et al. (2014) model was therefore modified for the Kinder catchment to model $DO^{14}C$ accounting for areas of surficial erosion in some areas of the catchment as follows.

The surface erosion in the Kinder River catchment was concentrated within bare peat areas, which represented 33% of the catchment area (Table 1); therefore, the depth of peat removed from these sites may be taken as 1.42 m (1/0.33 × 0.47 m), assuming that erosion is negligible on vegetated surfaces and so the catchment averaged erosion is concentrated on the bare peat locations. This depth was used in combination with the age depth relationship detailed in the results to calculate the likely age of surface peats in eroded areas, which was 3,577 years. Model 2 calculates the estimated age based on carbon sourced from two theoretical peat profiles. The first eroded peat profile (i.e., excluding years 0–3,577) represents the eroded third of the catchment, and the second intact peat profile represents the remaining two thirds of the catchment (excluding gullied areas where the complete peat profile has been removed). Model 2 iteratively calculates a revised single value for the exponent *k* (determining the depths from which DOC is sourced) assuming a 67% contribution of carbon from the intact peat profile and a 33% combination from the eroded profile.

Equation 1 remains the same but it is calculated separately for two peat columns and the results combined weighted by area (33% (eroded catchment) and 67% (uneroded catchment)) as indicated by Equation 2.

$$DO^{14}C = \left(\sum_{t=1}^{t=10,000} \left({}_{14}CO_2 t \times \exp^{(-kt)} \right) \times 0.67 \right) + \left(\sum_{t=3578}^{t=10,000} \left({}_{14}CO_2 t \times \exp^{(-kt)} \right) \times 0.33 \right) \tag{2}$$

The two versions of this model (1 for UNG and 1 and 2 for Kinder) were used to produce a single average DOC age for the study sites. The Evans, Page, et al. (2014) approach to determining the age of DOC in waters means that in addition to an estimated mean DOC age, an age distribution can be produced, which effectively represents the ages of the layers of decomposing peat thought to be contributing DOC to the measured waters. In this study, the age depth curve derived for the Bleaklow and Kinder Scout region allowed the conversion of these age distributions to depth distributions. This approach provided a basis for estimating the relative contribution of near-surface peat layers to DOC export.

The approach to modeling age of DOC rests on several assumptions. The core assumption of the Evans, Page, et al. (2014) model that the contribution of DOC from deeper layers declines exponentially is well supported by conventional understanding of vertical changes in hydraulic conductivity and decomposition in peatlands. Model 2 further assumes that we have accurately estimated the area of bare peat and the removal of surface peats in this area. In order to test these assumptions, a sensitivity analysis was undertaken to assess the degree to which error in these parameters would influence our results.

Model 2 was calculated 36 times varying both bare peat area (25%–50% in increments of 5%) and surficial erosion depth (20–60 cm in 10 cm increments). This led to a total of 36 iterations of Model 2. The model results

Table 2
Data Used for Water Table Model Testing

Date range	Measurements	n (wells per site)	Number of sites
11/06–10/08	23 (monthly)	3	2 sites
7/07–11/08	16 (monthly)	1–3	2 sites
2/11–12/13	35 (weekly September–December)	15	1 site
9/10–12/10 and 9/11–12/11	20 (weekly)	3–5	2 sites

were interpolated using the Origin software package to visualize the range of age outputs across this range of input variables in order to assess the potential error associated with these parameters. Model 2 also assumes that the eroded and intact areas contribute carbon in proportion to their areas.

2.4. Water Table Modeling

An empirical spatial model of median water table across the Bleaklow and Kinder Scout plateaux was derived based on regression of the relationship between topographic wetness index (WI) (calculated as the average WI value in a 30 m square based on a 2 m resolution LiDAR Digital Elevation Model (DEM), where WI = ln (a/s), a = upslope contributing area and s = slope) and median water table, measured at 12 sites across Kinder Scout and Bleaklow plateau (Allott et al., 2009). Water table was measured manually as depth below the peat surface in 15 dipwells (See Allott et al., 2009 for detailed methodology) in a 30 m diameter plot concurrently at each of these sites every two weeks between April and November 2008 (9 measurement intervals). Median water table for each site was derived by taking the mean of the 15 measurements at each site and further calculating the median site value across the nine measurement intervals.

Allott et al. (2009) reported water table drawdown in heavily gullied peats on the Bleaklow and Kinder Scout Plateaux. These results demonstrate that this was a very local phenomenon with drawdown limited to a 2 m distance from gully edges. As a consequence, all WI model training and test data were from vegetated interfluve sites away from gully edges. In order to incorporate gully edge effects into the empirical water table model, an additional 200 mm of water table depression was modeled for a 2 m (one pixel) buffer (Allott et al., 2009) around the gully system. Gully extent was derived from the gully maps presented by Evans and Lindsay (2010).

In order to validate the empirical model, it was tested against an additional independent water table data set as outlined in Table 2. The test data set is comprised of available data compiled from dipwells on the Bleaklow and Kinder Scout Plateau used for other projects. As such, it contains data from sites with different numbers of dipwells and with data collected at varying intervals and over changing time periods, which would introduce spatial and temporal variability into the WI versus. water table relationship. For this reason, these data were considered to provide a robust and conservative test of the empirical model.

The model was used to calculate average median water table depths for each catchment. The Kinder River catchment was modeled in two parts, thus taking into account the different types of erosion in the catchment; (a) areas where the surface was intact (vegetated areas with gully presence 67% of the catchment) and (b) combined gully and surface erosion (bare peat areas, 33% of the catchment).

3. Results

3.1. Radiocarbon Ages

^{14}C determinations for all DOC samples, and associated age estimates, are detailed in Table 3. The data from the Kinder River catchment show a tight clustering of ages between sampling sites and on for sampling periods with all samples showing aged DOC (range 88.6%–89.1% modern). This consistency supports the view that DOC age was controlled by the peatland catchment characteristics and that it was not a function of sample location downstream of the peatland catchment. Stimson et al. (2017) also report further data from a site downstream, which confirm these patterns but which are excluded from this analysis because of an intervening tributary.

Table 3
Radiocarbon Determinations for Dissolved Organic Carbon From Kinder River and Upper North Grain (UNG)

Publication code	Site	Date	^{14}C enrichment % modern ± 1s	Radiocarbon age (years BP)	Modeled ages (years before sampling date) kinder (model 1/Model 2)
Upper North Grain catchment					
UBA-20265	UNG1	4/3/12	99.26 ± 0.32	60 ± 26	393
UBA-20266	UNG3	4/3/12	97.94 ± 0.33	167 ± 27	467
UBA-23192	UNG1	15/5/13	102.58 ± 0.29	Modern	247
UBA-23193	UNG2	15/5/13	103.11 ± 0.34	Modern	228
UBA-23194	UNG3	15/5/13	104.27 ± 0.39	Modern	193
UBA-25463	UNG1	7/3/14	96.51 ± 0.43	285 ± 36	557
UBA 25464	UNG2	7/3/14	97.17 ± 0.41	231 ± 34	514
UBA-25465	UNG3	7/3/14	97.36 ± 0.34	215 ± 28	502
Kinder River catchment					
SUERC-50395	Kinder1	06/9/13	89.06 ± 0.41	931 ± 37	1,178/1,441
SUERC-50396	Kinder2	06/9/13	88.61 ± 0.40	972 ± 37	1,223/1,463
SUERC-54801	Kinder1	12/5/14	88.56 ± 0.41	976 ± 37	1,228/1,466

Note. BP: Before Present.

For Upper North Grain, a greater degree of variability between samples was observed. All samples from this catchment showed a greater degree of ^{14}C enrichment (range 96.5%–104.3% modern) than any of the samples collected from the Kinder catchment. Four of the samples returned modern radiocarbon ages, three of which related to a single sampling visit. There was no consistent spatial variation downstream in ^{14}C between the sampling sites within the catchment (Table 3).

Mean conventional radiocarbon ages (i.e., assuming that samples contained material of uniform age) for DOC in waters from the Kinder River site were 960 ± 62 BP ($n = 3$) and from Upper North Grain 96 ± 116 years BP ($n = 8$). Error ranges on these estimates were 95% confidence intervals of the mean age.

3.2. Peat Age Depth Curves

The age depth curve derived from published radiocarbon dates and correlated horizons on the Bleaklow and Kinder Scout plateaux is presented in Figure 4. Across the whole region, simple linear regression of the radiocarbon ages against centroid of depth produces a linear age-depth model over Holocene timescales with the age and peat depth relationship being $D = 0.03720$ A ($R^2 = 0.91$ $P < 0.0001$), where D is peat depth in cm and A is calibrated radiocarbon age in years. The data density was much greater in the most recent part of the Holocene. Multiple points representing the same age are indicative of varying depths of correlated horizons found in multiple cores.

3.3. Modeled Radiocarbon Ages

Application of the Evans, Page, et al. (2014) approach to determining age (Model 1), which considers DOC as a continuous mixture of ages, yielded older dates with average ages of 1,210 years BP for the Kinder River catchment and 388 years BP for Upper North Grain.

Model 2 calculated an average age of DOC from the Kinder River catchment of 1,457 years BP.

Mean radiocarbon levels and estimated ages for POC retained on filter papers are shown in Table 4. All POC samples had pre-bomb ^{14}C levels, and all were ^{14}C-depleted compared to DOC samples. Average radiocarbon ages were 2,761 (Kinder River $n = 1$) and 2,842 ± 507 (Upper North Grain $n = 5$). The model of Evans, Page, et al. (2014) was not applied because the underlying assumptions regarding the age distribution of material in the samples were unlikely to be valid for POC generated by spatially heterogeneous erosion processes.

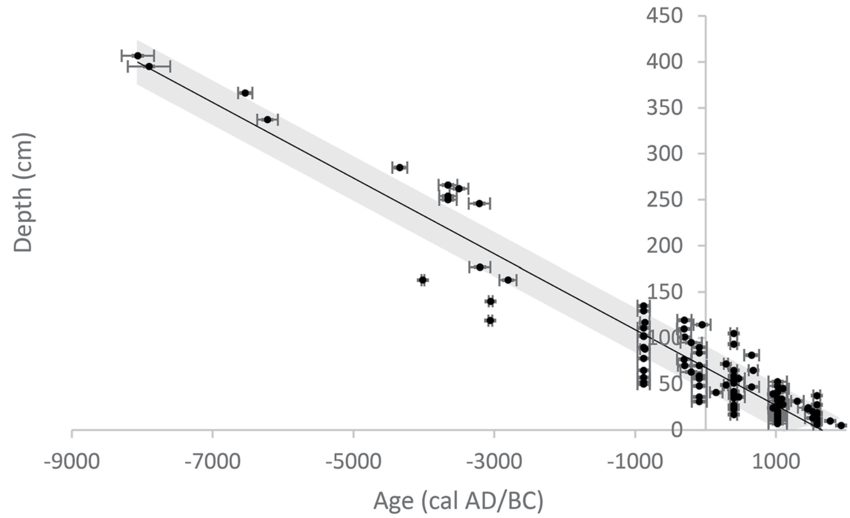

Figure 4. Peat Age-Depth relations for the Bleaklow Plateau and Kinder Scout area. Error bars for peat depth were not quantified. Error bars for age are the errors from OXCAL. The solid line represents the linear regression for the mean age produced from OXCAL; the shaded area is the standard error of the estimate from the linear regression (±24 cm). Original data from: Conway, 1954; Livett et al., 1979; Tallis, 1964, 1985, 1995; Tallis & Livett, 1994; Tallis & Switsur, 1983, 1990.

3.4. Modeling Source Depths of DOC

Figure 5 shows the estimated age distributions of DOC from the Evans, Page, et al. (2014) model, and those plots converted to depth distributions on the basis of the age depth relationships (Figure 4). Figure 5a describes the age and depth relationships at Upper North Grain. Figure 5b shows the age and depth relationships in the Kinder River catchment utilizing Model 1 (not accounting for surface erosion). Figure 5c presents the second approach (Model 2) to account for surface erosion in the Kinder River catchment, assuming that surface erosion was concentrated in one third of the catchment. The age profiles for Kinder River Model 2 are presented on two different scales (0–5,000 and 3,577–8,577), the former for the intact part of the catchment and the latter for the area of concentrated surface eroded section of the catchment. These curves are identical as k (Equation 1) was recalculated to take into account both areas of the catchment in their appropriate proportions.

The mean lower quartile, 50th percentile, and upper quartile are marked on Figure 5. Standard error of the mean was calculated for each quartile across the sites. The lower quartile, 50th percentile, and upper quartile, respectively, were at approximately 106 (±24), 237 (±42), and 497 (±42) years, or 4 (±0.80), 9 (±1.46) and 19 (±2.09) cm in the UNG catchment, whereas in the Kinder River catchment (Model 1), they were 358 (±5), 822 (±11), and 1,697 (±23) years, or at 13 (±0.17), 31 (±0.42), and 63 (±0.87) cm. The results clearly suggested that DOC was sourced from a greater range of depths in the Kinder River catchment Model 1 than in the Upper North Grain catchment. However, Kinder River Model 2 suggests source depths that are more comparable with UNG with

Table 4
Radiocarbon Determinations for Particulate Organic Carbon (POC) Samples From Kinder River and Upper North Grain (UNG)

Publication code	Site	Date	^{14}C enrichment % modern ± 1s	Radiocarbon age (years BP)
UBA-20262	UNG1	4/3/12	76.64 ± 0.28	2,137 ± 29
UBA-20263	UNG3	4/3/12	69.71 ± 0.26	2,961 ± 30
UBA-23189	UNG1	15/5/13	67.26 ± 0.26	3,187 ± 31
UBA-23190	UNG2	15/5/13	68.71 ± 0.24	3,014 ± 29
UBA-23191	UNG3	15/5/13	67.72 ± 0.25	2,913 ± 30
SUERC-54372	Kinder1	12/5/14	70.91 ± 0.37	2,761 ± 41

Note. BP: Before Present.

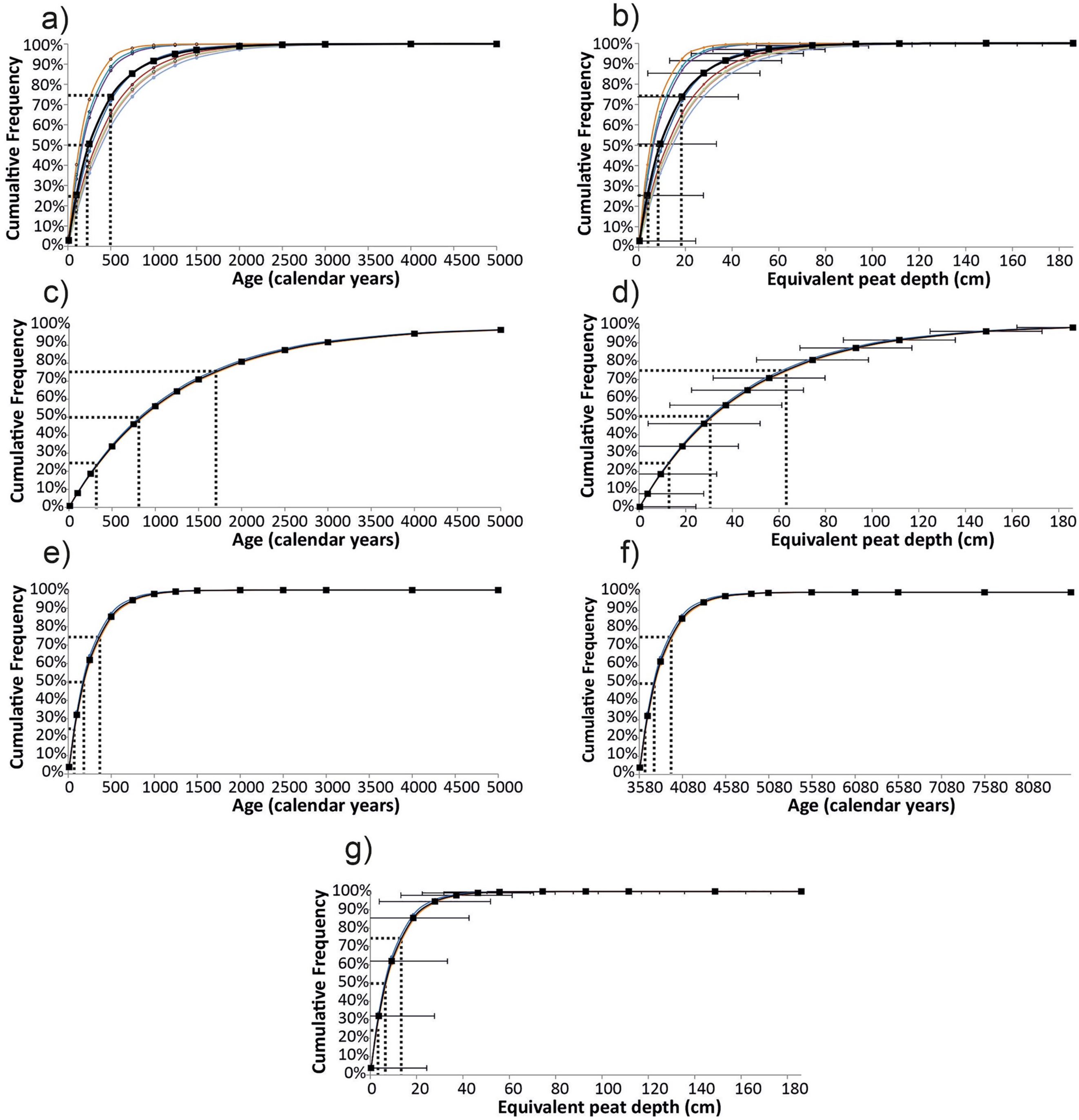

Figure 5. Modeled source ages and equivalent depths of dissolved organic carbon for all models. 25th, 50th, and 75th percentiles marked as dotted lines. The black line represents the mean and the colored lines represent each individual sample. There were 8 samples at Upper North Grain (UNG) and 3 at Kinder River. (a and b) UNG catchment; (c and d) Kinder River catchment Model 1; (e–g) Kinder River catchment Model 2. Age distributions presented both assuming that the surface begins at 0 years (e) and at 3,577 years (on the basis of calculations of the age of surface erosion as in Section 3.3). Error bars on the peat depth frequency plots represent one standard error of the estimate from Figure 4.

the lower quartile, 50th percentile, and upper quartile being 3,652 (±2), 3,756 (±6), and 3,933 (±11) (equivalent to 74, 179, and 358 years older than the surface date) or 3 (±0.09), 7 (±0.21), and 13 (±0.41) cm, respectively. Kinder River Model 1 implies peat loss throughout the profile, while Kinder River Model 2 has peat loss confined to the upper layers of the peat profile in common with UNG.

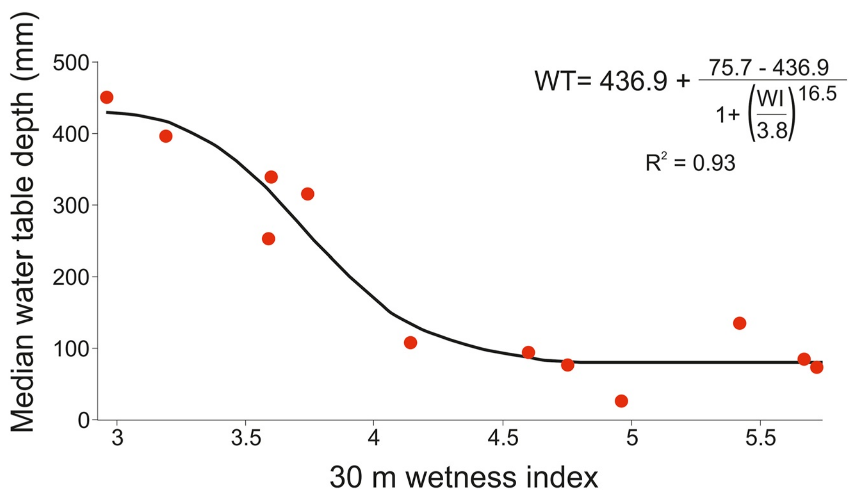

Figure 6. Relation between wetness index and median water table depth at 12 vegetated sites across the Kinder Scout and Bleaklow Plateau. The dashed line is line of best fit and the solid line is the 1:1 line.

3.5. Water Table Modeling

Figure 6 shows the relation between site WI derived from 2 m DEM data and median water table for 12 sites across Bleaklow and Kinder Scout. The empirical relationship implied that beyond WI values of around 5, median water table is approximately constant. This is consistent with physical understanding of peatland systems with a thin upper acrotelm layer of very high hydraulic conductivity where water table residence times are short (Holden & Burt, 2003b). The empirical model was validated against available water table data from other sites across Bleaklow and Kinder Scout and Figure 7 shows observed and predicted values. The test data are from smaller dipwell arrays and for a range of sample collection periods. This is a very conservative test of the model (as both conditions are likely to increase variability in water table relative to WI due to synoptic variability and the variability of peatland water tables; Allott et al., 2009). In this context, the model performance ($R^2 = 0.64$ SE 100.8 and the mean estimated = 0.89) gives confidence that the model adequately represents long-term average water table positions.

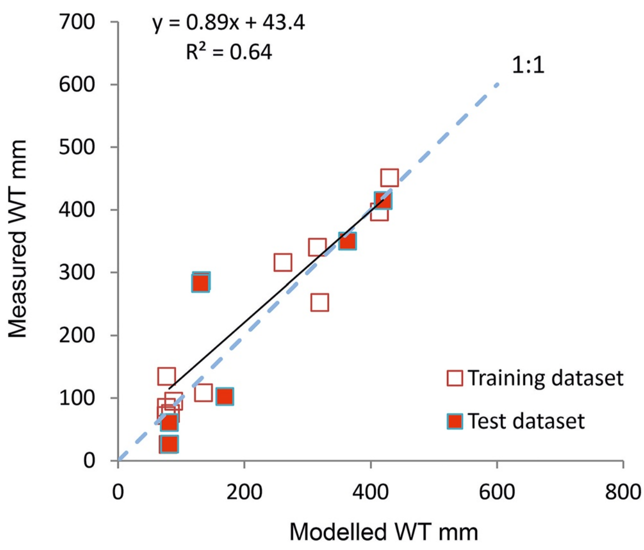

Figure 7. Observed and predicted water table for validation sites. The black regression line relates to the test data set only.

Modeled median water table for the two study catchments is presented in Figure 8. Mean median water table depth in Upper North Grain was 194 ± 45 mm and in the Kinder River catchment, it was 348 ± 45 mm. To complement the "Model 2" modeling of DOC ages for the Kinder catchment, water tables for Kinder Scout were also calculated separately for areas of surface erosion (~33% of the catchment) and vegetated areas (~67% of the catchment). These were modeled as 340 and 358 mm, respectively. Figure 9 presents the cumulative frequency distribution of water table depths in the two catchments indicating that near-surface water tables (<150 mm) were preserved in over 50% of the Upper North Grain catchment, whereas in the Kinder River catchment, this value was approximately 20%. The modeling of water table depths allows comparison of catchment average water table conditions with the depths from which the ^{14}C models suggest that DOC is being sourced.

3.6. Comparing Water Table Models and DOC Source Depths

Figure 10 compares the modeled mean 50th percentile source depths of DOC within the peat derived from the analysis in Figure 5 to mean modeled water table depth for the two catchments, derived from the analysis presented in Figure 8. To allow the comparison of the two Kinder River models, the water

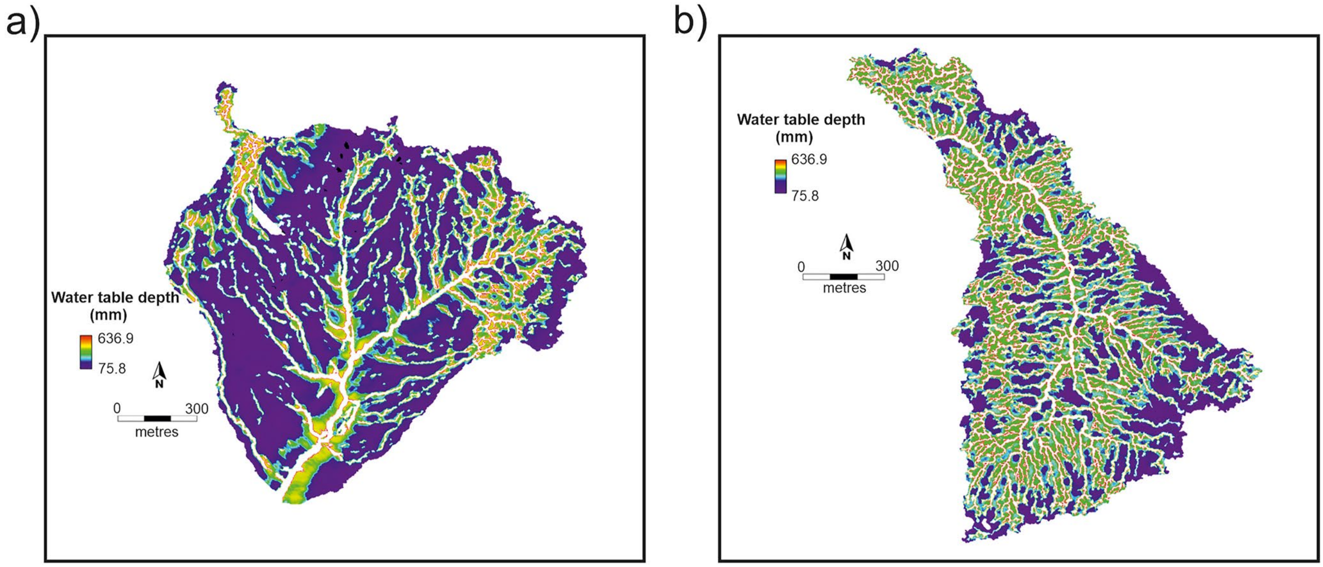

Figure 8. Modeled median water table depth for the two study catchments. (a) Upper North Grain and (b) Kinder River.

table depths presented are from the gullied (i.e., relating to Model 1) and gullied and surface eroded (i.e., relating to Model 2) portions of the catchment.

The modeled water table depths were consistently deeper than the modeled average ^{14}C depth although this was less apparent for Kinder Model 1. For both sites model 1, ^{14}C depth lies in the predicted range of water table although the median modeled water table was within the interquartile error range of the DOC data only for Kinder Model 1. There was a much larger discrepancy between the modeled water table depth and the modeled average ^{14}C depth for Kinder River Model 2.

3.7. Sensitivity Analysis

The influence of bare peat area and erosion depth assumptions on model 2 output is presented in Figure 11. Increasing both erosion depth and bare peat area increases the model age output linearly.

Modeling *a* ±25% proportional error in erosion depth (35–59 cm) and error in bare peat coverage (25%–41%) resulted in age outputs of 1,288–1,696 years BP and 1,369–1,564 years BP, respectively. The age outputs from the model are relatively insensitive to minor error in these parameters.

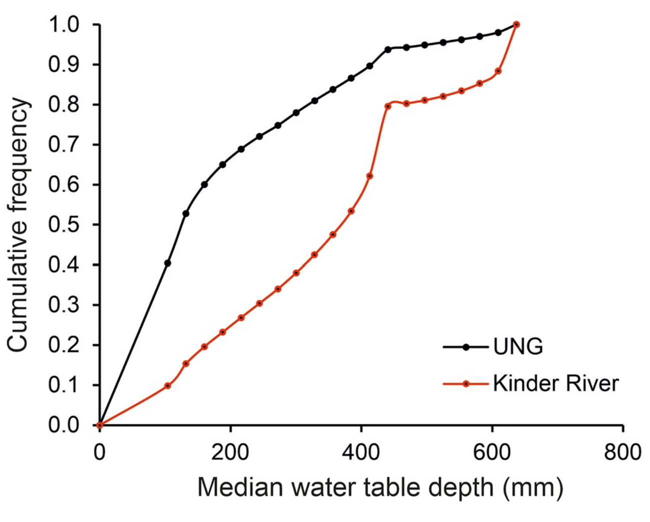

Figure 9. Modeled distributions of water table for the two study catchments.

4. Discussion

4.1. Radiocarbon Age of DOC in Runoff

The data presented here represent the most extensive suite of radiocarbon ages of DOC reported to date from heavily eroded peatlands in the UK. For both catchments studied, there was limited variability in DOC ages between sampling sites and no consistent change in DOC ages downstream. This result supports the idea that the catchment sources, rather than in-stream carbon transformations, govern the radiocarbon age of DOC at the headwater catchment scale. In the Upper North Grain catchment, younger (modern) ages were obtained from one sampling event, suggesting some temporal variability in the source of DOC as a function of hydrological conditions. This is consistent with other studies that have shown previous UK blanket bog studies that have shown higher levels of ^{14}C enrichment in DOC during periods

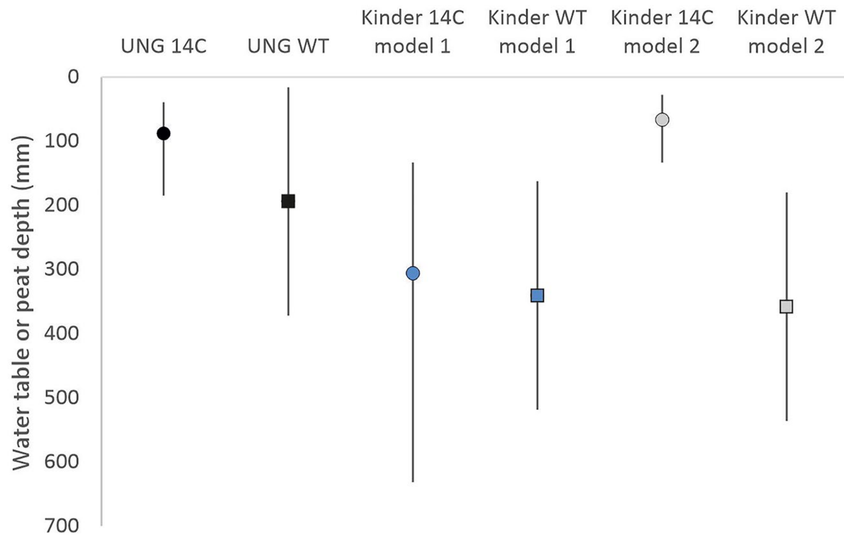

Figure 10. Comparison of modeled water table (squares) and depth of peat (circles) associated with the mean modeled ^{14}C age of dissolved organic carbon for each catchment, including both model versions for Kinder River. Error bars are 2 × RMSE of the water table model tested against the intact data set (Figure 7) (WT) and the interquartile range of the source depth distribution from the ^{14}C model.

of higher flow, when more DOC is sourced from shallower horizons (Evans et al., 2007; Tipping et al., 2010). However, higher resolution sampling would be required to substantiate this finding at the study sites used here.

Previously reported DOC dates from comparatively undisturbed UK peatlands have largely indicated modern or near modern ages, indicative of turnover of litter and decomposition of recently deposited peat (Billett et al., 2011; Evans, Page, et al., 2014; Palmer et al., 2001; Tipping et al., 2010). These dates are consistent with aerobic decomposition in the acrotelm layers of relatively intact peatland systems. In contrast, two dates on eroded southern Pennine systems have indicated older sources of carbon with conventional radiocarbon ages of 463 and 1763 years BP (Evans, Page, et al., 2014). The three dates from the Kinder River catchment presented here have produced age estimates from 931 to 976 years BP, which support the view that the single extreme date from Evans, Page, et al. (2014) is not an outlier. The data support the idea that in degraded UK peatlands, older ^{14}C ages indicative of decomposition of deeper peat layers are characteristic. These systems are therefore losing carbon at depth in a similar manner (although not to a similar degree) to the pattern reported for tropical peatlands in Evans, Page, et al. (2014) and for drained boreal agricultural peatlands by Hulatt et al. (2014). Eight dates from the less eroded Upper North Grain catchment ranged from modern to 285 years BP, and one included in Evans, Page, et al. (2014) (95.11% modern or ~403 years BP), similarly indicate decomposition of deeper peat layers, but to a lesser degree.

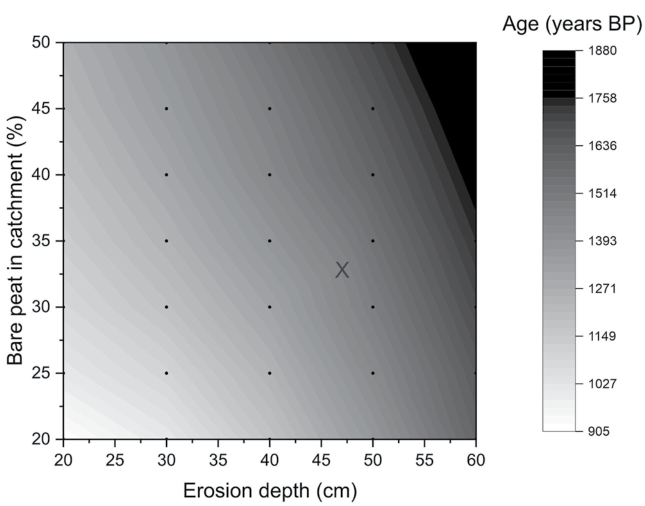

Figure 11. Sensitivity analysis for the major assumptions of Model 2. Contour analysis based on the age outputs of 36 iterations of Model 2. The age output from Model 2 of 1,457 years Before Present (BP) is marked with an X and other iterations as dots.

Applying the Evans, Page, et al. (2014) model resulted in the average modeled dates being consistently older than the average measured dates for both UNG (measured: 106; modeled: 388 years BP) and Kinder (measured: 1,014; modeled 1 and 2: 1,210/1,457 years BP). Since DOC is almost always composed of a broad range of compounds with variable ages, this age-continuum model likely provides a more realistic mean age estimate than the single-year conventional age model.

4.2. Controls on DOC Age in Degraded Peat Systems

One potential control in DOC ages measured in stream systems is in stream transformation of carbon (e.g., from POC: Brown et al., 2019). In the catchments studied here, POC ages were consistently much older than DOC ages.

$PO^{14}C$ average ages were 2,761 (Kinder River $n = 1$) and 2,842 ± 507 (Upper North Grain $n = 5$). The similarity in age between catchments indicates that POC to DOC transformation is not the explanation for varied DOC ages between catchments. The small catchments are of comparable scales and stream residence times in stormflow conditions are likely to be on the order of 20 min, so that in-stream DOC is expected to reflect carbon source rather than in-stream processes.

There is a distinct contrast in the age of DOC draining from the two study catchments with aged DOC being produced from both systems but older DOC from Kinder Scout. The ^{14}C modeling results allow us to address the three hypotheses relating erosion and the production of older DOC.

1. The water table data and the distributions of depth of peat decomposition derived in this study (Figure 10) allow us to assess the role of water table changes as drivers of deep peat decomposition in these degraded systems. Water table and predicted source depths for DOC were closer to the surface in Upper North Grain (Figure 10). More intense dissection of the Kinder Scout plateau produced lower median water tables (Figures 8 and 9) across the headwater peatlands of the Kinder River, and measured DOC ages indicated DOC sourced from deeper in the peat at this location when modeling the catchment using model 1 (assuming there had been no surface erosion) (Figure 10). For both catchments, the predicted DOC source depths were within the range of predicted water table depths. This result was consistent with water table control on DOC production (Figure 1a).
2. Where extensive erosion has removed vegetation so that bare peat is exposed at the surface, the supply of fresh DOC from litter is reduced. We can assess the relative importance of this mechanism (Figure 1b) with reference to Figure 5. Across both sites (UNG and Kinder Model 2), the proportion of DOC, which was derived from the material aged 0–9 years, was estimated at just 1.8%–5% so that the reduced supply of modern DOC is unlikely to be the primary cause of differences in the age of DOC exported from the two catchments.
3. Where there has been extensive surface erosion of bare peat, or fire-related peat loss (Evans, Page, et al., 2014), then much older peat from lower down the profile will be exposed at the surface, and DOC may be sourced from the older peat material that now lies within the upper aerobic zone (Figure 1c). In the Kinder River catchment, there is extensive bare peat. Model 2 that adapted the Evans, Page, et al. (2014) model to account for surface erosion in one third of the catchment predicted sourcing of DOC from a shallow zone (75% DOC from above 14 cm) at the surface of the peat profile, which was not consistent with the modeled water table depth (Figure 10). This is in contrast with the Upper North Grain results where the zone of production of the majority of DOC appeared to be within the range of the modeled WT. Applying the original Evans, Page, et al. (2014) model (Model 1) to the Kinder River data yielded a more widely distributed depth distribution of DOC production than UNG with some DOC production occurring in deeper peats consistent with deeper water tables modeled for this catchment. However, Model 1 did not account for surface erosion. Model 2 explicitly accounted for measured surface erosion but counterintuitively predicted DOC production limited to the shallow near surface. Model 2 assumed old surface peat across 33% of the catchment (circa 3.5ka). If DOC were sourced significantly from deep peat in these areas, a much older date than the observed ^{14}C date of 960 ± 62 years BP would be expected. The dominant control of erosion hypothesized in Figure 1c is therefore not supported.

Both the theory and the data from Upper North Grain support the idea that water table was controlling decomposition of the peat. The mismatch of water table and the modeled source depths for DOC in Model 2 for the Kinder Catchment suggested that in this case the assumptions of the modified Evans model break down. The sensitivity analysis indicated that the discrepancy between predicted and actual DOC age is unlikely to be driven by error in the erosion depths or percentage bare area, which were inputs to model 2. The implication therefore is that the DOC flux from older peats in areas of surficial erosion was reduced, compared to intact peat profiles, impacted by gully erosion. The apparent congruence of water table and DOC source depths predicted by model 1 suggests that the uneroded sites dominate DOC production.

Two possibilities arise: (a) that rates of decomposition, and so, of DOC production in eroded areas are reduced because the surficial peat is older and less labile or; (b) alternatively that the flow pathways in heavily eroded systems lead to reduced interaction of runoff and the peat matrix. Bare peat respiration rates at nearby sites in the Peak District have been shown to be low and show no seasonal change (Caporn et al., 2007), supporting hypothesis

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one. The second hypothesis is consistent with some evidence from drained systems that macropore flow (bypassing the peat matrix) is much more extensive in peatlands with lowered water tables (Holden et al., 2006).

4.3. Carbon Age and Carbon Flux

Dissolved carbon ages from both catchments indicate loss of deep peat such that it might be expected that absolute dissolved carbon fluxes from the systems are high. Previous research in the catchments supports this view. Pawson et al. (2012) report DOC flux from UNG of 27.5 MgC km^{-2} a^{-1}. For the Kinder River catchment, Stimson et al. report a flux of 8.6 MgC km^{-2} a^{-1} for the 3.9 km^2 catchment above the Kinder reservoir. However, only the upper portion of this catchment is peat covered (the 1.1 km^2 catchment considered in this study). If it is assumed that the DOC is sourced from the peat covered catchment, this gives a DOC flux of 29.9 MgC km^{-2} a^{-1}, which would be a maximum estimate for this system. These values exceed typical peatland fluvial DOC flux values reported by Aitkenhead and McDowell (2000) (5.7–8.6 MgC km^{-2} a^{-1}) and also values reported for eroded headwater peats in northern England (Worrall et al., 2006) (13.4–22.5 MgC km^{-2} a^{-1}). These results are therefore consistent with elevated dissolved carbon flux from degraded peats with carbon sourced from deep peat sources. However, the significantly older carbon derived from the Kinder River catchment is not matched by increased rates of carbon loss. It is possible that in extremely degraded systems, such as the Kinder Plateaux, reduced rates of microbial activity (implied by reduced soil respiration on bare peat such as seen at some Finnish peat extraction sites; Shurpali et al., 2008) and modifications of hydrological pathways act to moderate DOC loss. These results are relevant to other areas of expansive bare peat, such as extensive peat mining (e.g., Haghighi et al., 2018; Salm et al., 2012).

5. Conclusions

We observed deep carbon loss from degraded temperate peatland systems comparable to the results reported for a wider set of global peatlands by Evans, Page, et al. (2014). These UK upland peatlands are losing carbon that has been stored for timescales in excess of a millennium. A new approach to modeling the source of DOC has demonstrated that old DOC was sourced from greater depths in the peat profile, and the similarity of measured water tables to the areas of the peat profile, which is the source of this DOC, was consistent with water table drawdown as the primary control on DOC ages. The removal of the youngest layers of peat by surface erosion appeared to have a smaller than expected impact on the age of carbon exported from the system. This discrepancy needs further investigation, but potentially suggests that either (a) bare eroded peat is less biologically active due to a combination of the presence of recalcitrant materials and lack of plant mediated processes and input of fresh material to drive microbial processes or (b) the recognized expansion of macropore density in drained peats may be a limiting factor on deep carbon loss since a proportion of throughflow bypasses the peat matrix limiting DOC export.

This paper has demonstrated a clear link between gully erosion of peatlands, reductions in water table, and the loss of old carbon stored in the peat soils to the fluvial system. In these eroded peatlands, the form of peatland erosion appeared to have a significant impact. Gully erosion appeared to be more significant than surficial erosion as a factor in the loss of old DOC from eroded peats.

Across the globe, peatland drainage and degradation are widespread (Bonn et al., 2016) and threaten long-term carbon storage. A growing body of evidence indicates that loss of old organic carbon from peatlands is an indicator of deep decomposition linked to degradation. The approaches developed here if applied more widely at small catchment scales have the potential to explore the links between degradation and deep carbon loss across a range of peatland types. Similarly, the aim of many peatland restoration projects is to raise water table in order to reduce carbon losses from the peat store. The association between radiocarbon age of DOC and water table indicated here suggests that ^{14}C dating of DOC might be a useful catchment scale proxy for water table, a direct measurement of the locus of carbon loss from the peat, and an effective measure of the overall "health" of the peatland ecosystem. The approach therefore has potential as a rapid method of assessing stabilization and restoration of intact peatland function at landscape scale in comparison to intensive and expensive monitoring campaigns.

This paper has exploited the correlation between peat depth and peat age, which along with new approaches to interpreting radiocarbon ages of peatland waters has allowed us to identify where in the depth profile dissolved carbon is being sourced. There is a long history of study of the chronostratigraphy of peatlands, which can

potentially be utilized, together with new ^{14}C data on peatland waters to explore the interactions of peatland hydrology and carbon loss from these important terrestrial carbon stored.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Data sets for this research are available here https://doi.org/10.5281/zenodo.4548224.

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