

Annex 4

Water quality trajectories on bare peat stabilisation sites



Prepared by



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Water Quality Trajectories on Bare Peat Stabilisation Sites



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1. Summary

The aim of this report is to analyse water quality survey data collected by Moors for the Future Partnership (MFFP) from stabilised bare peat blanket bog sites in the South Pennines in order to assess any trajectories of change as a result of treatment works. Analysis of six years of data suggests that treatment works (gully-blocking and application of lime, seed and NPK fertiliser) may not have significant impacts on water quality in the short to medium term. Calcium (Ca), contained in the lime, was still present in headwater streams at elevated concentrations up to 18 months after the final application. This was accompanied by increased pH levels, but it is not yet clear whether, and to what extent, pH will return to pre-treatment levels once Ca has returned to pre-treatment concentrations. Dissolved Organic Carbon (DOC) concentrations do not change as a result of treatment, and long-term changes to the composition of DOC are not clearly evident. Longer-term monitoring is required to create statistically significant trajectories of change as a result of restoration works, as data from during the treatment period are affected by the initial impacts of the treatment products, and insufficient data are available from after the cessation of restoration work. Post-treatment data extend to a maximum of three years following the cessation of treatment (and to a maximum of 18 months for some determinands); this is therefore the current limit to the timeframe of the trajectories of change it is possible to create.

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2. Introduction

2.1. Peatland Degradation

A combination of human and natural influences has led to severe degradation of peatlands in the uplands of the South Pennines and Peak District (Tallis, 1998). Widespread erosion caused loss of vegetation cover and generated large expanses of bare peat and deeply incised gully networks. Subsequent drying of the peat mass restricted the possibility of vegetation recovery and increased rates of erosion. This contributes to increased concentrations of dissolved and particulate organic carbon and other nutrients or pollutants in the waters draining from these headwater catchments (Bussell *et al.*, 2010), with financial implications for utility companies removing these substances from drinking water supplies (Wallage *et al.*, 2006), as well as environmental impacts on the global carbon cycle including fluvial conversions of dissolved and particulate organic carbon (DOC and POC) to carbon dioxide (CO₂) (Evans *et al.*, 2013).

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

Degradation may also lead to increased fluvial loads of heavy metal pollutants deposited on the peatlands as a result of industrial activity in the surrounding conurbations during and following the Industrial Revolution (Rothwell *et al.*, 2007, Shuttleworth *et al.*, 2015).

2.2. Peatland Restoration and Potential Impacts on Water Quality

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

- stabilising the large contiguous areas of bare and eroding peat through establishing and subsequently diversifying vegetation cover through the application of heather brush, amenity/local grass and heather seeds (see Table 1), granulated lime and fertiliser (three annual summer applications by helicopter-suspended hopper, see Table 2), *Sphagnum* mosses and other moorland species plug plants
- rewetting the peat mass and slowing the flow (and therefore reducing the erosional force) of storm-water from the headwaters to the river networks by blocking gullies and grips using stone, timber, plastic or peat dams
- improving footpaths to reduce erosion due to high footfall on popular walking routes.

Seed mix plant species		Application rate (kg/ha)
Browntop Bentgrass	<i>Agrostis castellana</i>	4.00
Sheep's Fescue	<i>Festuca ovina</i>	14.00
Fine-leaved Sheep's Fescue	<i>Festuca longifolia</i>	10.00
Wavy-Hair Grass	<i>Deschampsia flexuosa</i>	1.00
Perennial Rye Grass	<i>Lolium perenne</i>	21.00
Heathers	<i>Calluna vulgaris</i> / <i>Erica tetralix</i> (90:10)	0.65

Table 1: Species composition of a typical seed mix used by MFFP (Buckler *et al.*, 2013)

	Granulated lime components	Application rate	Granulated fertiliser components	Application rate
Year 1	98% Ca, 0.5% Mg, 1% Si ₂	1000kg/ha	40 N : 120 P ₂ O ₅ : 60 K ₂ O	361kg/ha
Year 2	98% Ca, 0.5% Mg, 1% Si ₂	1000kg/ha	40 N : 60 P ₂ O ₅ : 60 K ₂ O	278kg/ha
Year 3	98% Ca, 0.5% Mg, 1% Si ₂	1000kg/ha	40 N : 60 P ₂ O ₅ : 60 K ₂ O	278kg/ha

Table 2: Typical lime and fertiliser components and application rates used by MFFP (Pilkington, 2015)

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

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

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

The amount of particulate organic carbon (POC) suspended in headwater catchment stream-water has been shown to reduce significantly following the revegetation of eroded catchments (Pilkington and Crouch, 2015; Shuttleworth *et al.*, 2015).

3. Aims

The aims of this study are to:

- Investigate the impact of land management works at bare peat stabilisation sites (re-vegetation and gully blocking) on water quality both during and following treatment.
- Create temporal trajectories for the impact of land management works on water quality to predict potential impact of future works of a similar nature.

4. Data Sources

4.1. Bare peat sites

This study is based on water quality datasets collected and supplied by the MFFP on peatland restoration sites across the South Pennines between 2010 and 2016. Datasets were selected from the full range provided according to the following requirements:

- 1) There should be available data from a bare peat control site comparable to the restoration site, preferably with samples collected from treatment and control sites on the same day.

- 2) Sufficient data are available pre-restoration.
- 3) Sufficient data are available post-restoration.
- 4) Suitable notes are available to fully assess the viability of data sets.

Project name	Selection criteria			
	(1)	(2)	(3)	(4)
Making Space for Water	✓	✓	✓	✓
Kinder Catchment	✓	✓	X	✓
Woodhead Gully Blocking Monitoring	✓	✓	X	✓
MoorLife	✓	X	X	✓
The Peatland Restoration Project	X	X	X	✓

Table 3: Data made available and their suitability to this study

Table 3 summarises the available data sources and whether they meet the above criteria. Data from the Kinder Catchment and Woodhead Gully Blocking Monitoring projects do not meet all of the conditions required; while there was a period of pre-restoration data collection, no data were available from after the end of the restoration works in any of the datasets (criterion 3). Data available from the MoorLife project do not meet criteria 2 or 3, as no data were available from pre-restoration or post-restoration periods. Catchment Restoration Fund data also were not available from pre or post restoration periods, and suitable bare peat control data were also not available. All datasets which include pre-restoration data may provide valuable information in the future if monitoring is continued post restoration.

Therefore, this study focuses on data from the Making Space for Water (MSW) project. To date, the MSW dataset spans six years (2011-2016) and includes 8 months of pre-restoration data (December 2010 to July 2011). Data collected from the start of the study until 2014 were originally processed for use in a Before-After-Control-Impact analysis in Evans *et al.* (2015), and were readily available. In this study these existing data are combined with newly processed raw data collected in 2015 and 2016 to assess the possibility of constructing trajectories of change through time following restoration at the two MSW headwater micro-catchments (O and N). The restoration works for these sites are outlined in Table 4, and used the treatment products and application rates detailed in Table 1 and Table 2 and . Site O was revegetated; site N was revegetated and gully-blocked. Data were available for a third treatment site (B, revegetated, monitored as part of the Kinder Catchment Project), although only from 2011 to 2014. While this dataset therefore does not include data from after the cessation of restoration works, it does include two years of pre-restoration data. The MSW monitoring programme also includes two control sites: an intact reference (P) and a bare peat control (F), which have not been subject to any restoration treatments.

Site	Application 1 of seed, lime and fertiliser	Application 2 of lime and fertiliser	Application 3 of lime and fertiliser	Installation of gully blocks
O	July 2011	May 2012	June 2013	X
N	July 2011	May 2012	June 2013	November 2011 – April 2012
B	June 2013	June 2014		X

Table 4: Restoration dates at study micro-catchments

5. Methodology

5.1. Sample Collection

Water samples were collected from the four main study catchments (O, N and F on the Kinder Scout plateau and from site P on the neighbouring Bleaklow plateau) on an approximately fortnightly basis between 1/12/2010 and 5/1/2015, and subsequently on a monthly basis between 2/11/2015 and 14/9/2016. Water samples were collected from an additional catchment on the Kinder Scout plateau (site B) between 15/10/2011 and 5/1/2015. In total there were 110 sampling visits. Water samples were collected from the water flowing over the v-notch weir installed at each site for the purpose of monitoring flow. Where there was no flowing water samples were not collected. Total numbers of samples collected are indicated in Table 5.

Site	Treatment	Number of samples (n)
O	Revegetated (2011)	101
N	Revegetated and gully-blocked (2011)	108
B	Revegetated (2012)	56
F	Bare peat control	100
P	Intact reference	65

Table 5: Study sites, treatments and sample size

Water samples were returned to the laboratory and filtered at 0.45 microns prior to analysis. Samples collected in the first sampling period were analysed for content of DOC and a range of metals, as well as for pH (from January 2012 onwards) and absorbance at wavelengths of 254, 400, 465 and 665nm. Samples collected in the second sampling period (November 2015 onwards) were analysed for DOC and POC content, pH and water colour (in units of Hazen). Analysis methods are summarised in Table 6.

Determinand	Machine / analysis method
DOC	TOC-V analyser (Shimadzu)
POC	TOC-V analyser (Shimadzu)
pH	pH meter
Absorbance (254, 400, 465 and 665 nm)	Spectrophotometer (Hach DR 5000)
Aluminium (Al)	ICP/OES
Calcium (Ca)	ICP/OES
Copper (Cu)	ICP/OES
Iron (Fe)	ICP/OES
Potassium (K)	ICP/OES
Lithium (Li)	ICP/OES
Magnesium (Mg)	ICP/OES
Manganese (Mn)	ICP/OES
Sodium (Na)	ICP/OES
Nickel (Ni)	ICP/OES
Lead (Pb)	ICP/OES
Zinc (Zn)	ICP/OES

Table 6: Details of laboratory analysis of water samples for this study. ICP/OES = inductively coupled plasma optical emission spectrometry

5.2. Data processing

All data from treatment sites (O, N, B) were processed to calculate change relative to bare peat control (F), by calculating the deviation from F data for each determinand at each site, using samples collected on the same day (or as close as possible). This minimises the effects of variables other than the treatment works, such as weather, climate and seasonal variation, as it is assumed that these factors will affect all sites (treatment and control) equally.

5.2.1. Procedure

Data were processed as follows, for all determinands at study sites O, N, B and P:

1. Match data from study site to data from bare peat control (F) from the same day where possible, or from the most temporally proximal F sample where same-day samples were not available (maximum allowable separation = 5 days; this was only ever necessary for sites P and B)
2. Assess comparability of study site data to bare peat control data for the period before the start of treatment. If not comparable, before-after-control-impact analyses may not be viable.
3. Calculate change as a result of treatment (= deviation from F data for each determinand in each sample)
4. Separate change data into annual datasets (2011, 2012 etc)
5. Remove data from July-November for each year (or from the date of treatment in each year, if earlier than July. For treatment years this is to remove the immediate influence of treatment; for subsequent years the same period of each year was used in order to minimise the influence of seasonal variation on change data)
6. Calculate median and range values for each year subsample
7. Standardise data so that the median value is zero in year 0 (the year before start of treatment), allowing direct comparison between sites of any trajectories of change during subsequent years
8. Test the viability of constructing linear trajectories of change over time (calculate p and r^2 values, and slope formulae for any trajectories constructed). Where linear relationships are strong, calculate 95% confidence intervals about the annual median values
9. Assess statistical significance at 95% confidence of difference between all year subsamples using the Kruskal-Wallis one-way ANOVA H-test (to allow analysis of significant influence of treatment during/after treatment, and the identification of any step-changes, as opposed to linear trajectories)
10. Assess statistical significance at 95% confidence of difference between year zero and final year subsamples using the Mann-Whitney U-test

The data were found to be non-normally distributed and sample sizes for each year were small, especially once data from the periods immediately following treatment were removed. It was therefore appropriate to use median values as opposed to mean values (to reduce the influence of outliers), and non-parametric tests for the purposes of statistical analyses.

5.2.2. Additional analyses

The origins and composition of DOC within water samples may be assessed using absorbance data (Wallage *et al.*, 2006). In this study, Colour:Carbon (C:C) and E4:E6 ratios were calculated for every sample where data were available, and then processed according to the procedure described above. The C:C ratio, which is the ratio of Abs_{400} : DOC, indicates the proportion of the DOC present in the sample which consists of coloured, humic substances (humic and fulvic acids), as opposed to relatively uncoloured non-humic substances. High C:C ratios may indicate high levels of microbial activity (soil organisms metabolise the small molecule, non-humic, uncoloured compounds in preference to the larger molecule, humic, coloured compounds) and/or low rates of new carbon production by vegetation in the form of carbohydrates from root exudates. The E4:E6 ratio, which is

the ratio of $Abs_{465} : Abs_{665}$, indicates the relative proportions of humic to fulvic acids in the coloured, humic substances within the DOC present in the sample, and can be used to measure the degree of humification.

5.2.3. Variations from procedure

No data were available for 2015 (year 4 after start of treatment). In order to provide some context for the final year of data (2016), data from 20/8/2014 to 5/1/2015 were used in place of year 4 data. It should be noted that this may introduce the influence of seasonal variation, and any interaction that that may have with the different hydro-chemical processes which may occur at revegetated sites as compared to bare peat sites. However, the availability of bare peat control data allows the minimisation of the influence of external factors such as weather, climate and generic seasonal variation. It was therefore deemed that the replacement 2014 data were appropriate for inclusion. For determinands where 2016 data were not available, these 2014 data were also used as the ‘final year’ values, for analysis of overall change.

DOC data were not available for 2012 for any MSW sites. In Evans *et al.* (2015), DOC values were estimated using absorbance at 400nm (Abs_{400}) data, following analysis that showed a strong correlation between DOC and Abs_{400} for samples where both values were available. In this study, given that DOC data were available for 2011, 2013, 2014 and 2016, while Abs_{400} data were not available in 2016, it was not deemed necessary to replace raw DOC data with estimated DOC values, although estimated DOC were used for comparison. As in Evans *et al.* (2015), strong correlations were observed between DOC and Abs_{400} , as shown in Figure 1.

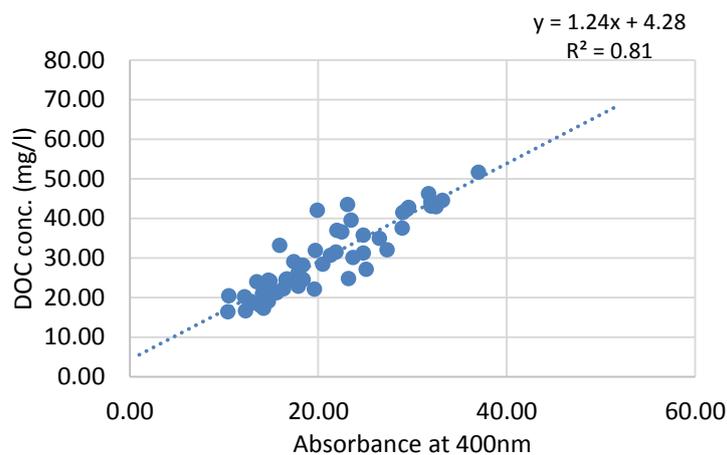


Figure 1: Linear relationship observed between DOC concentration and absorbance at 400nm, at study site O.

pH data were not available for 2011 (year 0). 2012 data were therefore used as the initial values. This may therefore lead to underestimations in overall changes in pH from pre-restoration level as a result of treatment works.

6. Results

6.1. Assessment of reliability of F as a control site

Pre-treatment data were compared between treatment sites (O, N) and the bare peat control (F), to assess the reliability of site F as a control for the treatment sites. While concentrations of determinands were not equal at the different sites, they were observed to vary 'in parallel', as shown in Figure 2. Site F is therefore considered to provide valid control data to assess the impacts of restoration works at study sites.

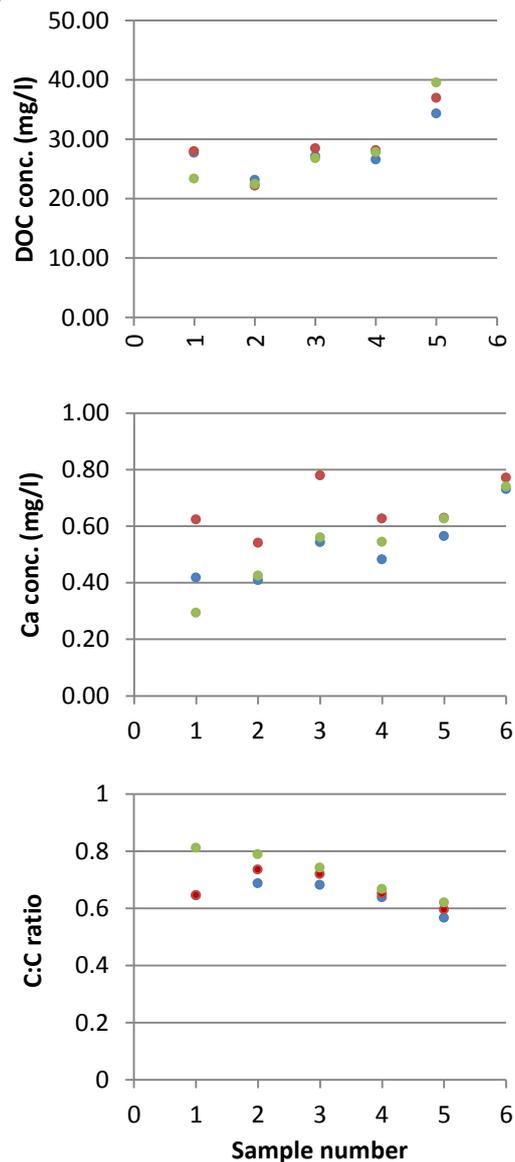


Figure 2: Comparison of bare peat control site (F) to treatment sites (O and N).

• = F, • = O, • = N. Pre-treatment concentrations of DOC and calcium, and the colour/carbon ratio (Abs_{400}/DOC) in pre-treatment water samples are shown to vary between samples comparably at all three sites

6.2. Immediate impacts of treatment

Restoration works undertaken at study sites O and N included the application of lime (98% Ca, 0.5% Mg and 1% Si₂ in 2011, 2012 and 2013) and fertiliser (N 11 : P 33.5 : K 16 in 2011; N 14.5 : P 21.5 : K 21.5 in 2012 and 2013). As detailed in Stimson (2015), data from the first water samples collected following each of these applications show noticeably elevated concentrations of the components in both products. These concentrations then tend to decrease over the following months, returning to 'baseline' levels within 4-6 months. An example of this is the time series of Ca concentrations at MSW sites O and N relative to equivalent samples at bare peat control site F shown in Figure 3.

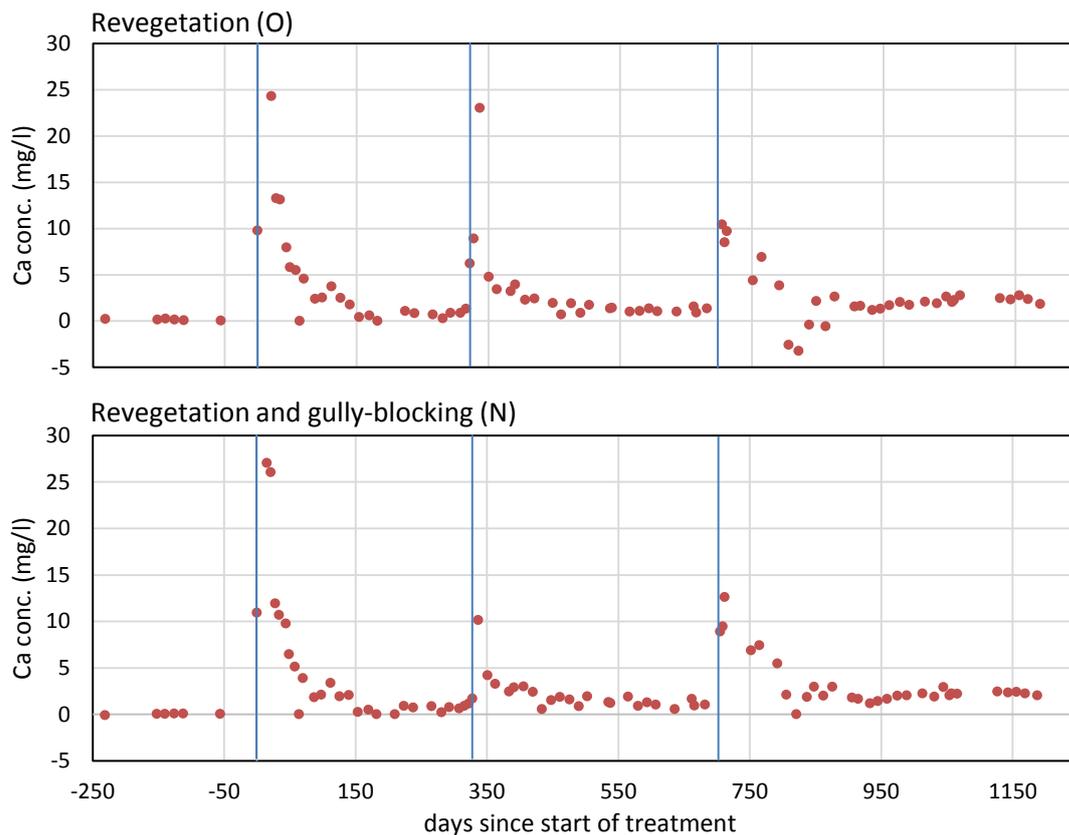


Figure 3: Calcium (Ca) concentrations as a result of treatment at MSW sites O and N.

● = difference between concentration at study site and bare peat control site for each sample. | = treatment date (application of lime).

The purpose of this report is to assess the longer-term impacts of restoration works. For this reason, the data from these initial periods following each application of lime and fertiliser have essentially been considered as noise, and have been discarded, in order to assess any underlying trends.

6.3. Post-treatment impacts

All data presented in the following sections are those from the periods deemed to be outside the immediate effects of restoration works (see section 5.2.11.1). All data presented are relative to equivalent data from the bare peat control site (i.e. the difference between the raw value at the study site and the raw value from the same day at the bare peat control site), in order to reduce the impact of factors other than restoration, such as seasonal or climatic variability. All data have been standardised such that all series start with difference to bare peat control = 0. Suitable data were available and analysed for the following determinands:

6.3.1. Dissolved Organic Carbon (DOC)

No statistically significant change in DOC concentration was recorded at any site up to five years following the start of treatment (see Figure 4). All potential impacts observed were small, and ranges in all years overlapped with range in pre-restoration data. An apparent increase in DOC concentration at site intact reference site P was recorded, with median values increasing by approximately 2.5 mg/l/year, but the change was not statistically significant.

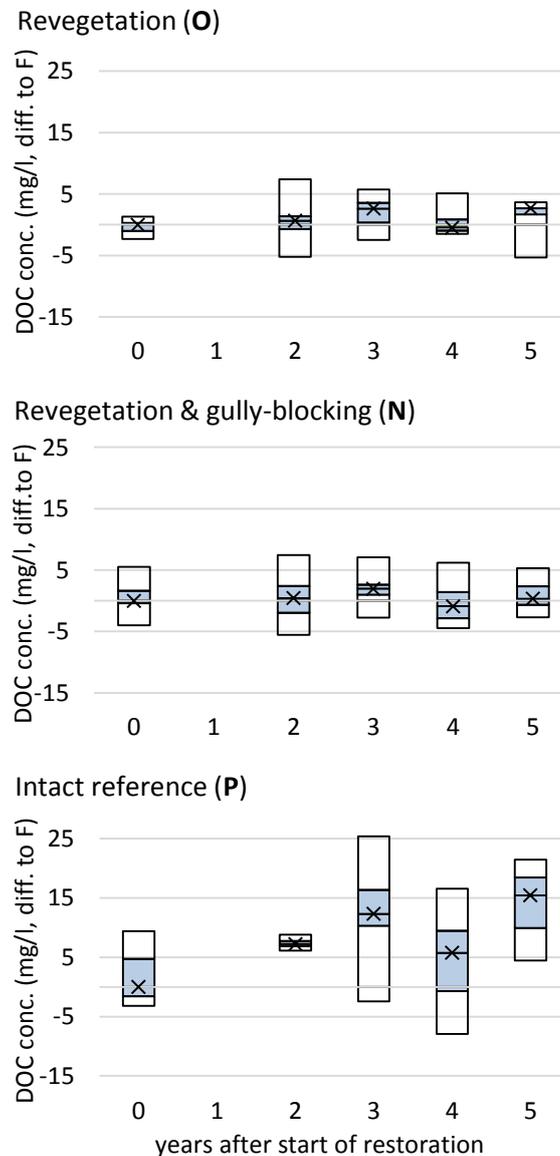


Figure 4: DOC concentration at two restored sites (O and N) and intact reference site P, relative to bare peat control site F.

X = annual median; = interquartile range; = range

6.3.3. DOC Qualities/Origins

6.3.3.1. Colour:Carbon (Absorbance at 400nm:DOC) Ratio

Increased variance was observed in Colour:Carbon (C:C) ratio at sites O and N during treatment years (see Figure 5). Difference between years was significant at both sites O ($H=13.28$; $n_1=5$, $n_2=10$, $n_3=11$, $n_4=8$; $p<0.01$) and N ($H=16.57$; $n_1=5$, $n_2=10$, $n_3=11$, $n_4=8$; $p<0.01$). However, no statistically significant linear trajectories of change in C:C ratio were observed at any sites up to four years following the start of treatment.

On comparison of pre-treatment data with data from after the cessation of treatment works a significant decrease in median C:C ratio of 0.07 after four years was observed at site N ($U=35$; $n_1=5$, $n_2=8$; $p<0.01$). No statistically significant change in the C:C ratio was observed at site O. At both sites, observed effect size was small.

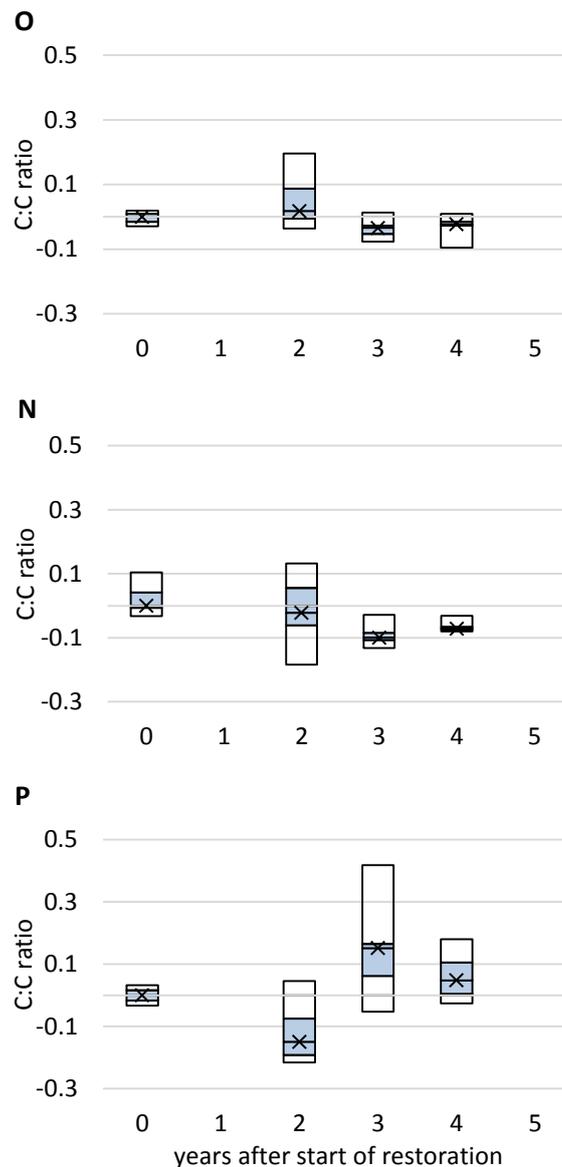


Figure 5: Colour/Carbon ratio at two restored sites (O and N) and intact reference site P, relative to bare peat control site F.

X = annual median; = interquartile range; = range

6.3.3.2. E4:E6 (Absorbance at 465nm: Absorbance at 665nm) Ratio

As shown in Figure 6, slightly increased variance in E4:E6 ratio was observed at MSW sites O and N during the first year following treatment (2012).

No statistically significant change in E4:E6 ratio was observed at any sites up to four years following the start of treatment. On comparison of pre-treatment data with data from after the cessation of treatment works a decrease in median E4:E6 ratio of 2.41 after 4 years was observed at site O, although not quite statistically significant ($U=28$; $n_1=5$, $n_2=7$; $p=0.07$). No statistically significant change in E4:E6 ratio was observed at site N. Four years after intervention, there is no clear impact of treatment. By comparison, an increase in median E4:E6 ratio of 2.65 after four years was observed at intact reference site P, although not statistically significant ($U=1$; $n_1=2$, $n_2=4$; $p=0.12$).

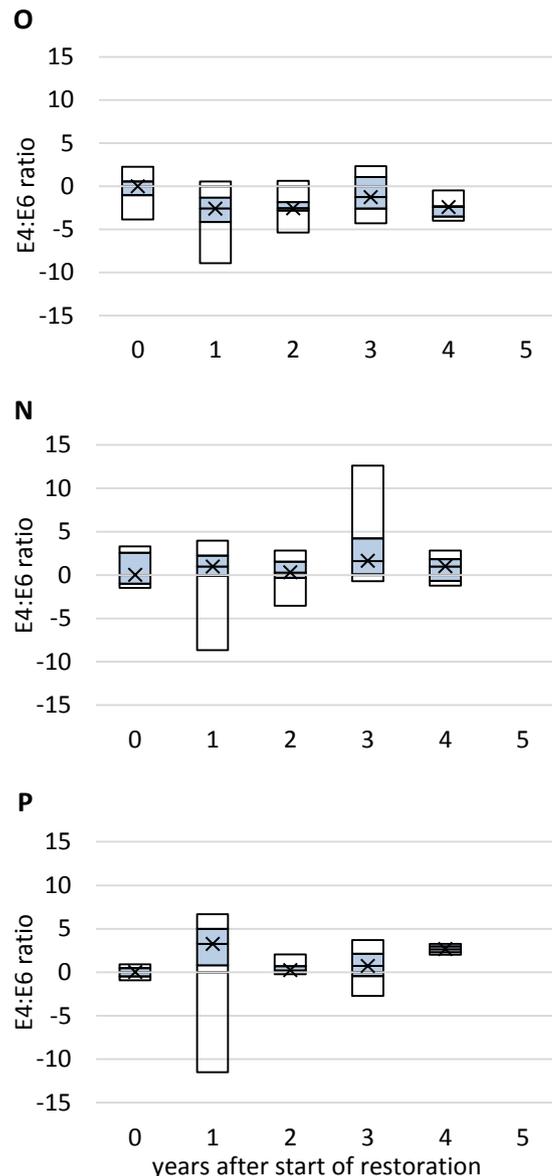


Figure 6: E4:E6 ratio at two restored sites (O and N) and intact reference site P, relative to bare peat control site F.

X = annual median; = interquartile range; = range

6.4. pH

Increased variance in pH values was observed at all sites during treatment years (see Figure 7). At sites O and N, pre-treatment data were not available but consistent increases in pH were recorded during treatment (years 1 and 2). Post treatment, pH did not continue to increase, but did not decrease to initial levels, up to 18 months following the cessation of treatment. Overall, median pH increased significantly from year 1 to post-treatment at both sites O (increase=0.27; $U=0$; $n_1=9$, $n_2=7$; $p<0.001$) and N (increase=0.4; $U=0$; $n_1=9$, $n_2=7$; $p<0.001$). Difference between years was statistically significant at both sites O ($H=27.38$; $n_1=9$, $n_2=10$, $n_3=11$, $n_4=8$, $n_5=7$; $p<0.001$) and N ($H=27.24$; $n_1=9$, $n_2=10$, $n_3=11$, $n_4=8$, $n_5=7$; $p<0.001$). The behaviour of pH at these sites may be considered as a step-change, dividing the time series into two discrete sections (during treatment: years 1-2; and post-treatment: years 3-5).

By comparison, no statistically significant change in pH was observed at intact reference site P, although an apparent increase in values was recorded in years 1-2.

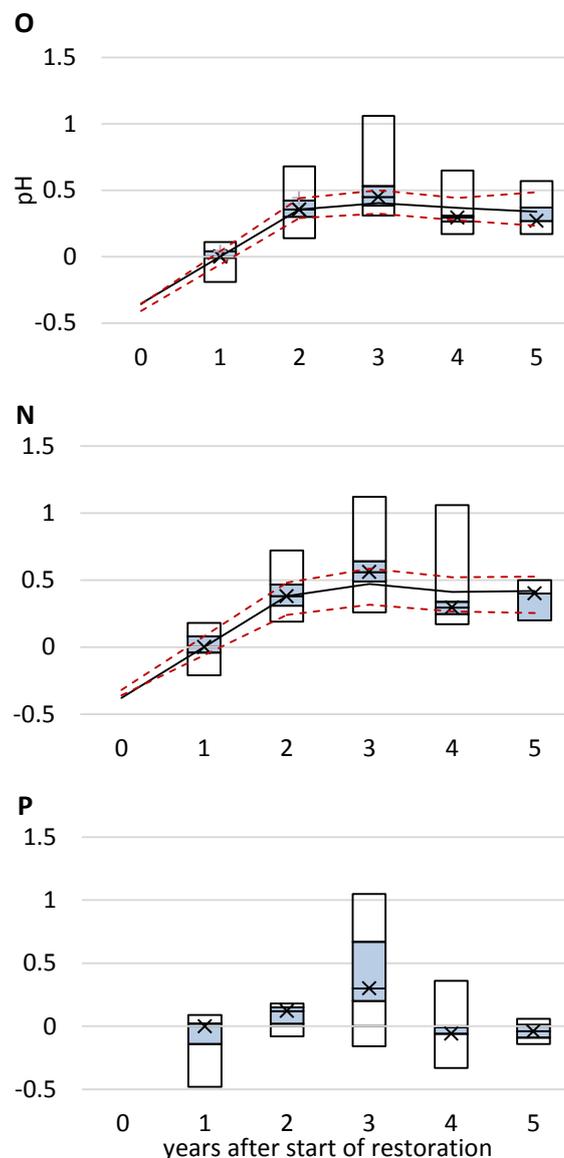


Figure 7: pH at two restored sites (O and N) and intact reference site P, relative to bare peat control site F.

X = annual median; — = line of best fit (annual median); - - - = 95% confidence interval about the annual median where appropriate; ■ = interquartile range; □ = range

6.5. Calcium (Ca)

Increased variance in Ca concentration was observed during treatment years at both sites O and N (see Figure 8). Statistically significant positive linear trajectories of change were recorded at sites O and N using linear regression, with increases in median values of approximately 0.53mg/l/year ($p < 0.001$) and 0.57 mg/l/year ($p < 0.001$) respectively, continuing 18 months beyond the end of treatment. By comparison, a possible slight, non-significant decrease in median values of Ca concentration was recorded at intact reference site P ($p = 0.23$). The increase from pre- to post-treatment concentration was significant at both sites O (increase=2.21 mg/l; $U = 0$; $n_1 = 6$, $n_2 = 5$; $p < 0.01$) and N (increase=2.29 mg/l; $U = 0$; $n_1 = 6$, $n_2 = 5$; $p < 0.01$).

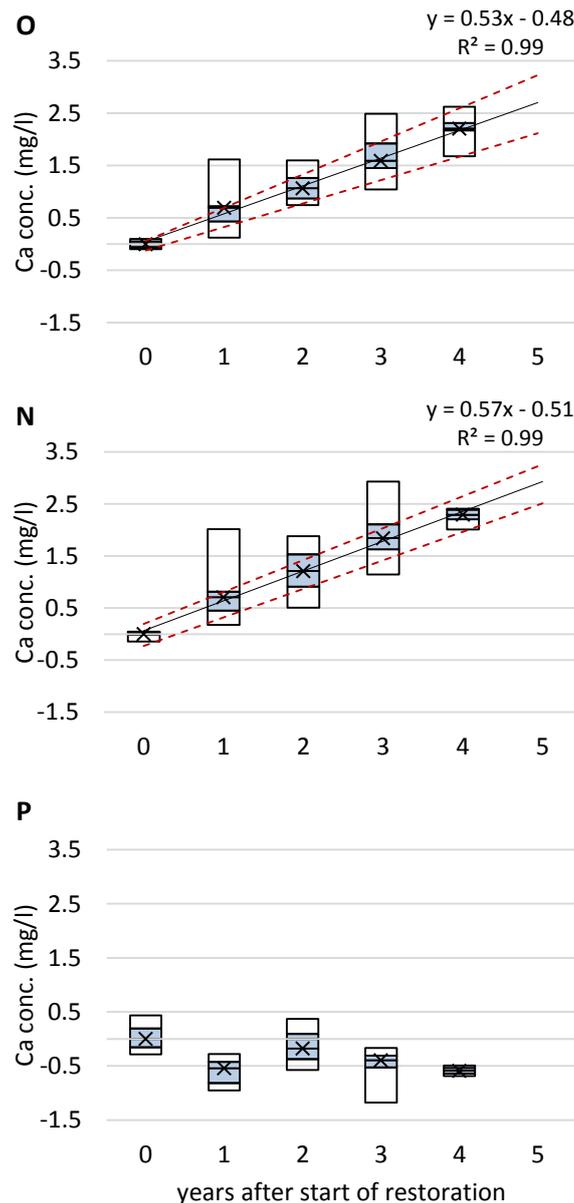


Figure 8: Calcium concentration at two restored sites (O and N) and intact reference site P, relative to bare peat control site F.

X = annual median; — = line of best fit (annual median); - - - = 95% confidence interval about the annual median where appropriate; ■ (shaded) = interquartile range; □ (white) = range

6.6. Magnesium (Mg)

Increased variance in Mg concentration was observed during treatment years at both sites O and N, although no statistically significant change was observed at either site (see Figure 9) up to four years following the start of treatment. By comparison, median values of Mg concentration decreased by 0.31mg/l over four years at intact reference site P, although the change was not quite statistically significant ($U=8$; $n_1=4$, $n_2=2$; $p=0.06$).

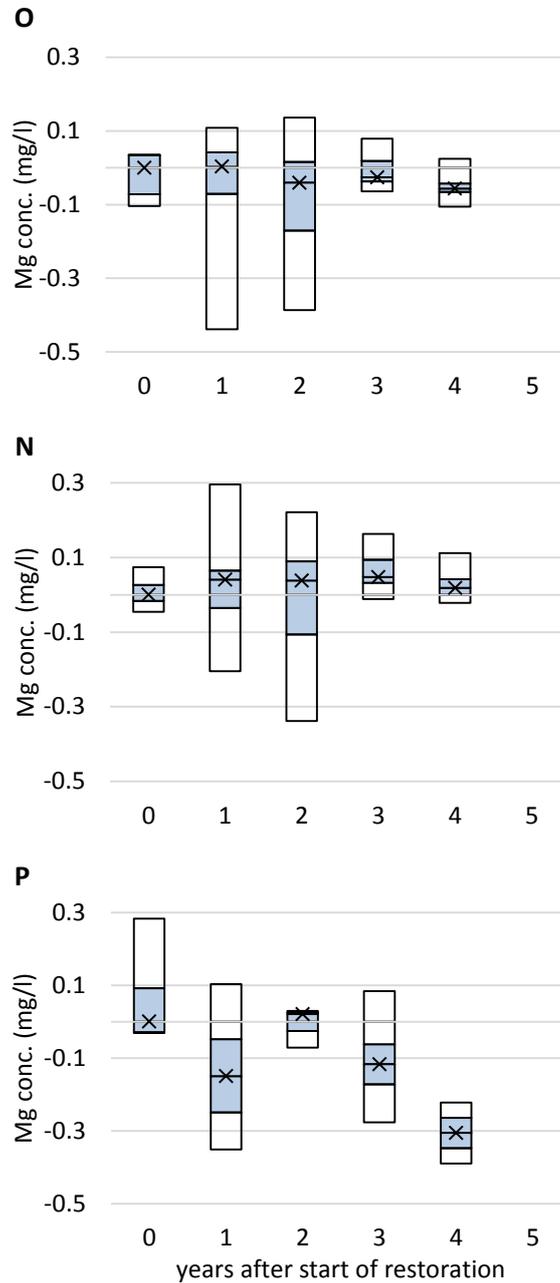


Figure 9: Magnesium concentration at two restored sites (O and N) and intact reference site P, relative to bare peat control site F.

X = annual median; = interquartile range; = range

6.8. Potassium (K)

Increased variance in K concentration was observed during treatment years at both sites O and N (see Figure 10). No significant linear trajectories of change were recorded up to four years following the start of treatment. A statistically significant increase of 0.26mg/l in median K concentration from pre- to post-treatment (18 months following the cessation of treatment) was recorded at site N ($U=3$; $n_1=6$, $n_2=5$; $p<0.05$). No statistically significant change was observed at site O. By comparison, median values of K concentration decreased by 0.29mg/l during the same period of time at intact reference site P, although the change was not quite statistically significant ($U=8$; $n_1=4$, $n_2=2$; $p=0.06$).

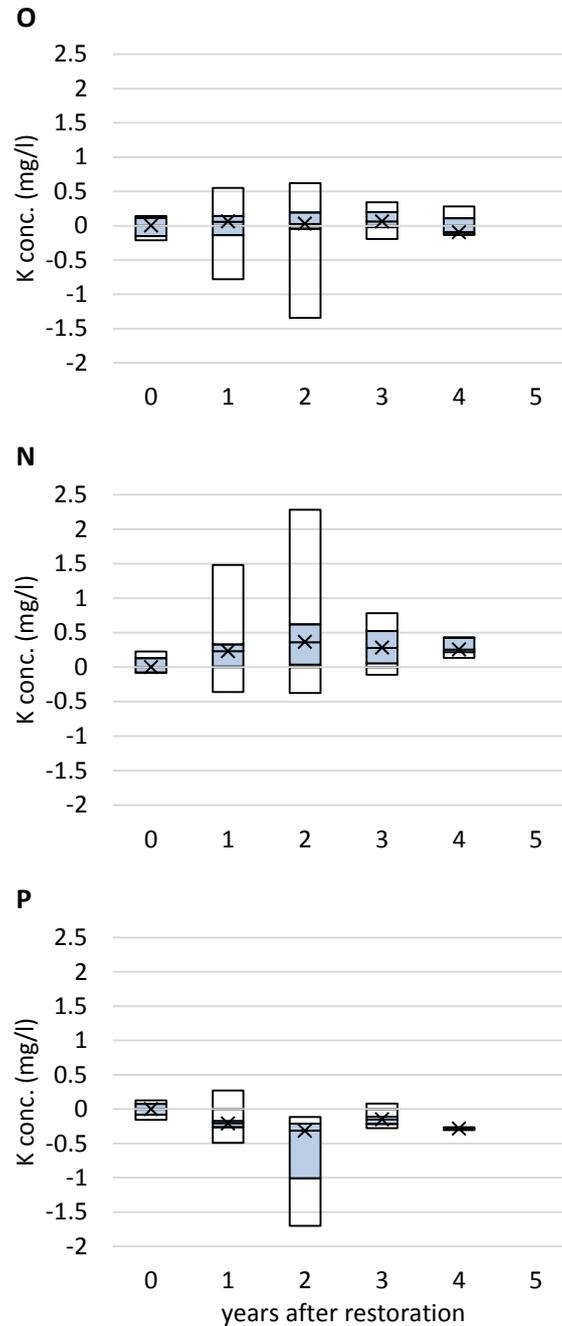


Figure 10: Potassium concentration at two restored sites (O and N) and intact reference site P, relative to bare peat control site F.

X = annual median; = interquartile range; = range

6.9. Heavy Metals

Soil and streamwater concentrations of heavy metals associated with industrial pollution are relatively high in the degraded peatlands of the South Pennines, following deposition of pollutants during and following the Industrial Revolution. Streamwater concentrations of these metals may be affected by changes in acidity and DOC/POC concentration (Rothwell *et al.* 2007; Shuttleworth *et al.*, 2015). It is therefore of particular interest to establish whether treatment works impact on concentrations of these metals. Results where significant or near-significant effects were recorded are presented here.

6.9.1. Lead (Pb)

Increased variance in Pb concentration was observed during treatment years at both sites O and N (see Figure 11). A very small, but statistically significant, positive linear trajectory of change was observed at site O, with an increase in median values of approximately 0.001mg/l/year ($p=0.04$), continuing 18 months beyond the end of treatment. The overall increase in concentration (0.005mg) from pre- to post-treatment was not significant ($U=7.5$; $n_1=6$, $n_2=5$; $p=0.16$). No other statistically significant changes were observed at any sites.

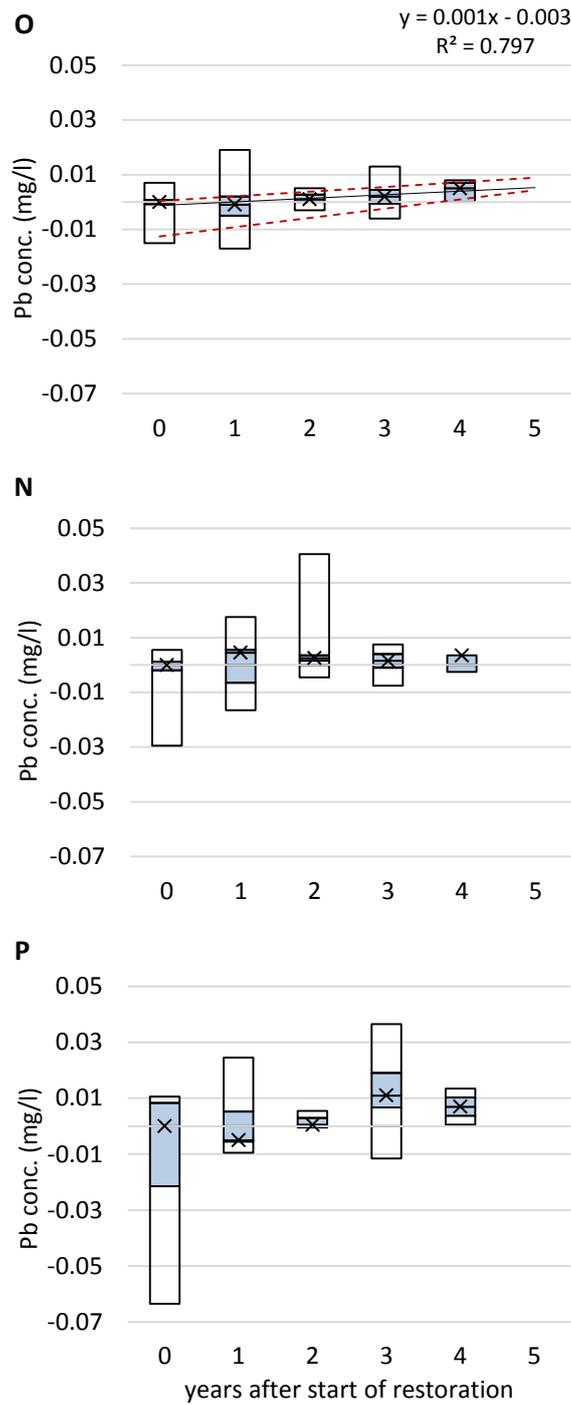


Figure 11: Lead concentration at two restored sites (O and N) and intact reference site P, relative to bare peat control site F.

X = annual median; / = line of best fit (annual median); - - = 95% confidence interval about the annual median where appropriate; ■ = interquartile range; □ = range

6.9.3. Zinc (Zn)

Increased variance in Zn concentration was observed during treatment years at both sites O and N, as well as at intact reference site P, most notably in the second year after the start of treatment (see Figure 12). No statistically significant trajectories of change were observed at any sites up to four years following the start of treatment. Very small increases in median concentrations were recorded at sites O and N from pre- to post-treatment (18 months after the cessation of treatment; 0.005 mg/l and 0.001 mg/l respectively). The increase was significant at site O ($U=0$; $n_1=6$, $n_2=5$; $p<0.01$) but not quite at site N ($U=5$; $n_1=6$, $n_2=5$; $p=0.07$).

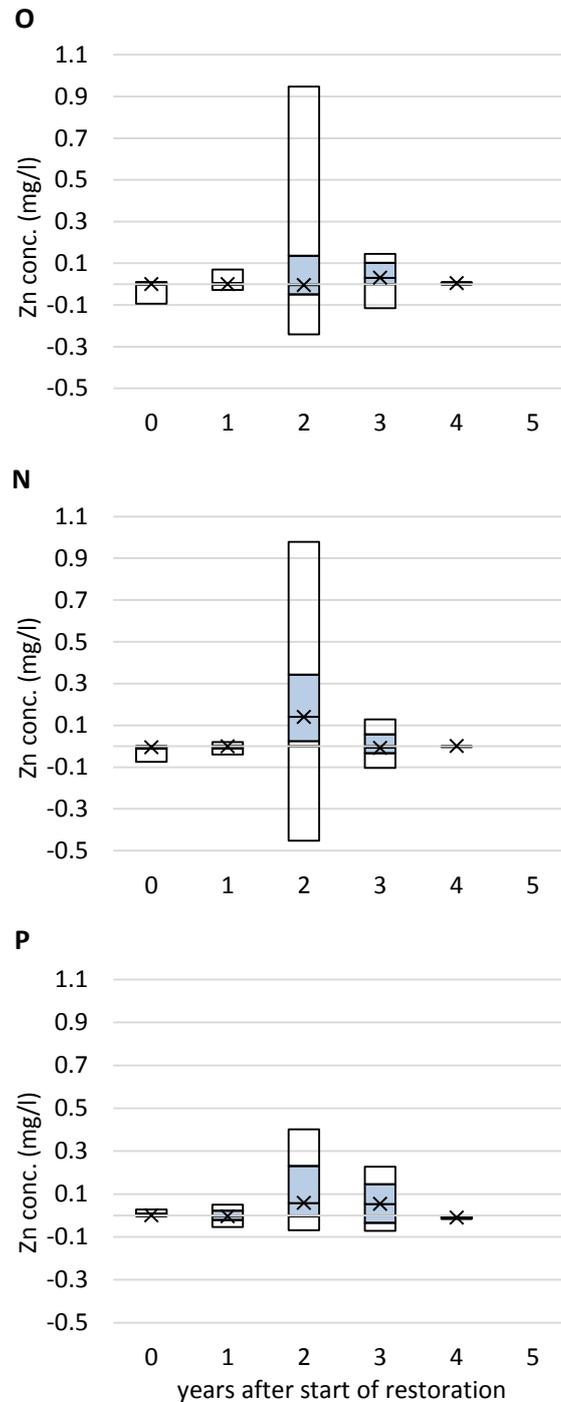


Figure 12: Zinc concentration at two restored sites (O and N) and intact reference site P, relative to bare peat control site F.

X = annual median; = interquartile range; = range

6.10. Particulate Organic Carbon (POC)

Data relating to dry weight of POC were not available for MSW sites. Large reductions in dry weight have been observed at sites O and N in previous studies as a result of restoration works. POC trapped in gully-bottom sediment traps at sites O and N reduced by 97% and 99% respectively after two years (Pilkington and Crouch, 2015).

Data relating to POC were available for WGBM sites, and no significant changes were observed. It is likely that the majority of POC released into fluvial systems from peatland headwater catchments is mobilised during heavy rainfall events. Routinely collected water samples are generally collected in relatively low flow conditions, and are therefore unlikely to capture the behaviour of POC in high flow events.

6.11. Other

Data were available for MSW sites for the following determinands: aluminium (Al), copper (Cu), iron (Fe), manganese (Mn), sodium (Na) and nickel (Ni). No statistically significant changes in concentration were observed for any of these substances.

Results of statistical tests are presented in Table 7, Table 8 and Table 9.

7. Discussion

The analyses performed for this study suggest that, for the majority of determinands assessed, treatment works have not had statistically significant impacts up to five years following treatment. The most notable impact was a linear increase in Ca concentration over four years following the initial treatment of lime, seed and fertilizer in year 0, and two subsequent maintenance treatments of lime and fertilizer in years 1 and 2. The most likely origin of Ca is directly from the lime in the treatments, which is composed mainly of calcium carbonate (CaCO_3). Likely as a result of this, statistically significant increases in pH were also recorded at treatment sites. Significant, but small increases in heavy metal concentrations (Pb and Zn) were also recorded at some treatment sites. Discussion of results for each determinand assessed is presented below.

For all determinands, insufficient data were available to construct reliable trajectories of change to assess the long-term impacts of treatment beyond the cessation of works. Further monitoring is required in future years to extend these trajectories.

As discussed in section 5.2.3, no data were available for 2015. Data from August 2014 – January 2015 were used in their place, in order to assess for overall differences between pre- and post-treatment conditions. This variation from the standard procedure, as well as shortening the overall length of the study period, also introduces an additional variable, in the form of seasonal variation, as all other annual datasets used are from the period January-June for each year. While all data used in this study are relative to bare peat control data, thereby minimising external influences such as season and weather, any conclusions drawn from these results should be treated with a degree of caution and require verification by future monitoring.

7.1. DOC

No statistically significant change in DOC concentration was observed at either MSW treatment site up to four years following the start of treatment. Increases in DOC concentration may have been expected, due to increased Net Primary Production (NPP) from increased vegetation cover, and because increases in DOC have been linked to re-wetting of previously drained peat. The findings of this study are consistent with those of Evans *et al.* (2015), where DOC was observed to be suppressed following the application of lime. While the cause of this effect is still not clear, it is

hypothesised that it may be due to decreased DOC solubility and flocculation due to Ca binding with humic substances (Valeur *et al.*, 2000). Ca concentrations have remained higher than before the start of treatment, and this may be causing a sustained suppression of DOC concentration. Longer-term monitoring is required to establish whether this will continue in future years.

By comparison, an increase in DOC relative to the bare peat control was observed at intact reference (P), although the increase was not statistically significant. This increase may be part of a longer-term trend as a result of declining rates of sulphur deposition from atmospheric pollution, combined with legacy deposits of nitrogen, allowing increased rates of NPP and therefore DOC production (Monteith *et al.*, 2015).

7.2. DOC Qualities/Origins

7.2.1. Colour:Carbon ratio

No statistically significant trajectories of change were observed as a result of restoration work up to four years following the start of treatment. Increased variation during treatment may be due to perturbation in carbon cycling, as reported in Evans *et al.* (2015). The decrease in C:C ratio values observed at site N represents a relative decrease in coloured, humic substances as compared to the content of colourless, non-humic substances. The mechanisms driving this change are not clear as many changes may be occurring following restoration works, but one possibility is that there is an increase in young labile and colourless carbon production due to increases in vegetation cover in the form of carbohydrates from root exudate. Alternatively, or in combination, higher water tables may be leading to lower production of coloured carbon.

7.2.2. E4:E6 ratio

Restoration work appears to have had no lasting statistically significant impact on the ratio of humic:fulvic acids in the humic substance component of DOC, up to four years following the start of treatment.

7.3. pH

A step-change was observed as result of restoration work, with pH levels stabilising approximately 0.3 pH units higher than the first monitored values, and remaining at these levels up to 18 months following the cessation of treatment. It should be noted that no pre-treatment pH data were available, meaning that this increase may well be an underestimation. These results were compared to data from site B (Kinder Catchment Project), and sites S3 DS, S3 HW and S4 DS (Woodhead Gully Blocking Project), where pre-treatment and during-treatment data (one year after start of treatment) were available. Significant increases in pH were observed at all sites (eg. at site B, increase=0.46; U=0; $n_1=17$, $n_2=5$; $p<0.01$). If these sites conform to the patterns observed at sites O and N, these increases would not be expected to continue post-treatment. Post-treatment data were not available for these sites, rendering them unsuitable for assessment of long-term change to any determinands as a result of treatment.

The sustained higher pH values, recorded at MSW sites O and N up to 18 months beyond the end of treatment works, are likely linked to the sustained increases in Ca concentration beyond the end of the treatment period. If these elevated pH levels are maintained in the long-term, there may be implications for rates of microbial activity, DOC production and mobilisation into the fluvial system of metals and other nutrients in the peat surface.

7.4. Calcium

Ca concentration was observed to continue increasing up to 18 months beyond the end of the restoration work period. Calcium carbonate (CaCO_3) represents 98% of the lime product used in the restoration process, and so large quantities have been applied to the peat surface. These findings suggest that the residency time of Ca following application of CaCO_3 is longer than the period of data availability following the cessation of treatment works (18 months). Elevated Ca levels may be driving higher pH, as discussed above. Further monitoring of Ca is required at these study sites to assess how long this effect will continue.

7.5. Magnesium

Variation in Mg concentrations increased during treatment works. This is likely a direct result of lime application, as MgCO_3 is a component in this product. No statistically significant effects of treatment were observed at any study sites up to four years following the start of treatment.

7.6. Potassium

Variation in K concentrations increased during treatment works. This is likely a direct result of fertiliser application, as K is a component in this product. No statistically significant trajectories of change were observed at any study sites, although an overall increase of 0.26 mg/l was observed at site N 18 months after the end of treatment work, as compared with pre-treatment levels. This increase is likely a lasting effect of the fertiliser application. Future monitoring is required to determine how long this effect will be sustained.

7.7. Lead

A statistically significant linear trajectory of increasing Pb concentration was recorded at treatment site O, continuing up to four years after the start of treatment. The increase recorded was extremely small, and is therefore assumed not to have major implications for water quality. A mechanism which could potentially contribute to increased metal concentrations is higher water tables, as a result of restoration works, leading to increased dissolution of metals in the surface layer of the peat (the section of the peat profile where atmospherically deposited pollutants are stored). However, water table rise during the monitoring period was not sufficiently significant to be likely to have caused this effect (Evans and Shuttleworth, 2016). Additionally, no statistically significant increase was recorded at site N, where treatment works included gully-blocking as well as revegetation, whereas at site O no gullies were blocked. The cause of the increase in Pb concentration at site O is not known and requires further investigation.

Increases in DOC have been linked to increases in fluvial lead (Pb) concentrations (Rothwell *et al.*, 2007), which may be of relevance in these catchments in future years, if the current suppression of DOC concentrations reduces as a result of declining Ca levels.

7.8. Zinc

Variation in Zn concentrations increased during treatment works. This may be as a result of disturbance to the upper peat layer, and/or temporary changes in soil chemistry following lime and fertiliser applications. No lasting, statistically significant effects of treatment were observed at any study sites up to 18 months following the cessation of treatment.

8. Conclusions

Water quality data have been assessed from a range of study sites across the South Pennines, from projects monitoring the impacts of restoration work at bare peat sites. The Making Space for Water (MSW) datasets met the suitability criteria for this study and have been analysed, with results presented above. The Kinder Catchment Project (KCP) and Woodhead Gully Blocking Monitoring (WGBM) datasets met some of the criteria and have been analysed for the purposes of comparison with results from MSW. Due to the differences in restoration works between sites, as well as differences in quality of the datasets, it has not been appropriate to combine any potential trajectories across sites.

8.1. Trajectories of change

No statistically significant trajectories of change relating to DOC or DOC qualities/origins were observed at any sites, up to five years following the start of treatment.

A significant positive step-change was observed in pH as a result of treatment, after which no significant change was recorded up to 18 months following the cessation of treatment. Further monitoring is required to determine whether pH will return to pre-treatment levels, remain as at the end of this study, or increase further in future years.

Statistically significant positive linear trajectories were observed at sites O and N relating to calcium concentrations, and have been presented with 95% confidence intervals. Although these trajectories extended 18 months beyond the end of treatment, it is hypothesised that they are a result of slow transit of liming products from the peat surface into the fluvial system. This would suggest that levels may decrease in future years, and these trajectories may not continue. Further monitoring is required to verify this.

No other statistically significant trajectories of change were observed where the amount of overall change was large enough to be considered important up to four years following the start of treatment, although small increases in lead were observed at site O.

The changes observed (increases in Ca concentration and pH) are impacts of products applied as part of restoration. There is no evidence that the basic function of the bog and its impact on water quality is changing. This may be, in part, because changes in water table height as a result of gully-blocking and revegetation are, as yet, relatively small.

8.2. Recommendations for extending trajectories of change

Increased variance in results was observed during the treatment period for Colour:Carbon ratio, E4:E6 ratio, pH, calcium, magnesium, potassium, lead and zinc, all due to direct and/or indirect effects of treatment work. This increased variance may limit the potential for construction of trajectories of longer-term changes as a result of treatment works, given the overall temporal extent of the current datasets. Monitoring of these determinands at MSW, KCP and WGBM sites on a monthly (or, ideally, fortnightly) basis over future years would allow trajectories to be constructed beyond the immediate impacts of treatment works. While the current KCP and WGBM datasets are too limited to assess any impacts after treatment, the availability of pre-treatment data suggest that, if monitoring is continued, they may provide a valuable comparison for the MSW data.

Data from intact reference site P provide valuable context for data from study sites, and it is recommended that water quality monitoring continues at this site, ideally with samples collected on the same day as at the other sites.

8.3. Recommendations for new monitoring programmes

The Before-After-Control-Impact design of the MSW, KCP and WGBM studies has enabled direct evaluation of the impacts of restoration works on water quality, although the sample size of the pre-treatment data is small for most sites, weakening the reliability of estimations of pre-treatment median values. It is recommended that this setup is replicated for future water quality monitoring projects. Suitable control sites should be identified, where pre-treatment conditions are comparable to study sites, and where treatment work will not be undertaken, and these sites should be monitored, synchronistically with study sites, for a full year prior to the start of restoration works. Laboratory tests should include those for all determinands which may be of interest, consistently throughout the monitoring programme, to avoid gaps in the datasets. This study design may be applied to a range of contexts, including bare peat stabilisation, diversification of single-species-dominated habitats, and clough woodland planting.

8.4. Impact of restoration on water quality

In the short-term, bare peat restoration results in perturbation in carbon cycling, and increases in fluvial concentrations of ingredients of lime and fertiliser products. DOC concentration is seemingly unaffected by the restoration treatments applied up to five years after the start of treatment. For assessment of longer-term impacts of restoration on water quality, further monitoring is required.

9. References

- Buckler, M., Proctor, S., Walker, J.S., Wittram, B., Straton, P. and Maskill, R.M., (2013) Moors for the Future Partnerships restoration methods for restoring bare peat in the South Pennines SAC: evidence-based recommendations. Moors for the Future Partnership, Edale.
- Bussell, J., Jones, D., Healey, J., Pullin, A. (2010). How do draining and re-wetting affect carbon stores and greenhouse gas fluxes in peatland soils. *CEE Rev.* 08-012.
- Caporn, S., Sen, R., Field, C., Jones, E., Carroll, J., Dise, N. (2007). Consequences of lime and fertiliser application for moorland restoration and carbon balance Research report to Moors for the Future, Edale.
- Evans C, Allott T, Billett M, Burden A, Chapman P, Dinsmore K, Evans M, Freeman C, Goulsbra C, Holden J, Jones D, Jones T, Moody C, Palmer S, Worrall F (2013). Greenhouse gas emissions associated with non gaseous losses of carbon from peatlands – Fate of particulate and dissolved carbon. Final Report to the Department for Environment, Food and Rural Affairs, Project SP1205. Centre for Ecology and Hydrology, Bangor.
- Evans, M., and Shuttleworth, E. (2016). *Annex 4: Peatland Restoration and Trajectories of Water table Change*. In *Trajectories for SSSI condition status of upland blanket bogs*
- Evans, M., Stimson, A., Allott, T., Pilkington, M., Shuttleworth, E., Holland, N., Spencer, T., Walker, J. (2015). Annex 4: *Dissolved Organic Carbon concentrations*. In Pilkington M.G. *et al.* (2015) *Restoration of Blanket bogs; flood risk reduction and other ecosystem benefits*. Final report of the Making Space for Water project: Moors for the Future Partnership, Edale.
- Monteith, D.T., Henrys, P.A., Evans, C.D. *et al.* (2015). Spatial controls on dissolved organic carbon in upland waters inferred from a simple statistical model. *Biogeochemistry* (2015) 123: 363.

- Pilkington, M.G. (2015). *Annex 1: Background, location, design and restoration*. In Pilkington M.G. et al. (2015) *Restoration of Blanket bogs; flood risk reduction and other ecosystem benefits*. Final report of the Making Space for Water project: Moors for the Future Partnership, Edale
- Pilkington, M.G. & Crouch, T. (2015). *Annex 3: Particulate organic carbon*. In Pilkington M.G. et al. (2015) *Restoration of Blanket bogs; flood risk reduction and other ecosystem benefits*. Final report of the Making Space for Water project: Moors for the Future Partnership, Edale.
- Rothwell, J.J., Evans, M.G., Daniels, S.M., Allott, T.E.H. (2007). Baseflow and stormflow metal concentrations in streams draining contaminated peat moorlands in the Peak District National Park (UK). *Journal of Hydrology*. 341, 90–104.
- Shuttleworth, E. L., Evans, M.G., Hutchinson, S.M., Rothwell, J.J. (2015). Peatland restoration: controls on sediment production and reductions in carbon and pollutant export. *Earth Surface Processes and Landforms* 40.4 (2015): 459-472.
- Stimson, A., G. (2015). Fluvial carbon dynamics in degraded peatland catchments. PhD thesis submitted to the University of Manchester.
- Strack, M., Tóth, K., Bourbonniere, R., Waddington, J.M. (2011). Dissolved organic carbon production and runoff quality following peatland extraction and restoration. *Ecol. Eng.* 37, 1998–2008.
- Tallis, J.H. (1998). Growth and degradation of British and Irish blanket mires. *Environ. Rev.* 6, 81–122.
- Valeur, I., Andersson, S., Nilsson, S.I. (2000). Calcium content of liming material and its effect on sulphur release in a coniferous forest soil. *Biogeochemistry* 50, 1–20.
- Wallage, Z.E., Holden, J., McDonald, A.T. (2006). Drain blocking: An effective treatment for reducing dissolved organic carbon loss and water discolouration in a drained peatland. *Sci. Total Environ.* 367, 811–821.

10. Appendices

10.1. Significance of apparent trends in annual median data

Determinand	Site	Regression equation y =	p-value of x coefficient	Average 95% confidence intervals about the median	Rate of change
Ca	O	0.531x – 0.480	<0.001	+0.214, -0.336	0.531mg/l yr ⁻¹
Ca	N	0.572x – 0.505	<0.001	+0.21, -0.344	0.572mg/l yr ⁻¹
Mg	O	-0.014x + 0.019	0.054	+0.054, -0.093	-0.014mg/l yr ⁻¹
K	P	-0.052 – 0.038	0.08	+0.087, -0.395	-0.052mg/l yr ⁻¹
Pb	O	0.001x – 0.003	0.041	+0.002, -0.007	0.001mg/l yr ⁻¹

Table 7: Rate of change in relative concentrations (treatment-control) of determinands, derived from linear trend lines through annual median data. Positive slope represents trajectory of increase relative to bare peat control; negative slope represents trajectory of decrease relative to bare peat control. Only data where p-value of x coefficient < 0.1 are included. p-values < 0.05 indicate significant correlation at 95% confidence.

10.2. Significance of difference between years

Determinand	Site	Sample size for each year	Test statistic (H)	p
pH	O	9,10,11,8,7	27.38	<0.001
pH	N	9,10,11,8,7	27.24	<0.001
pH	B	8,9,7,5	24.16	<0.001
Ca	O	6,7,10,11,5	32.1	<0.001
Ca	N	6,7,10,11,5	31.59	<0.001
Ca	B	6,9,7,3	19.76	<0.001
Ca	P	4,6,3,10,2	10.17	0.038
Mg	B	6,9,10,11,5	2.146	0.002
Mg	P	6,9,10,11,5	4.16	0.039
K	B	6,7,10,11,5	1.39	0.004
K	P	6,7,10,11,5	5.09	0.08
Pb	O	6,7,10,11,5	4.14	0.388
Zn	O	6,7,10,11,5	6.04	0.197
Zn	N	6,7,10,11,5	7.2	0.126
E4:E6	O	5,9,10,11,7	6.6	0.088
C:C	O	5,10,11,8	13.28	0.004
C:C	N	5,10,11,8	16.57	0.001
C:C	B	5,9,7,5	11.21	0.011

Table 8: results of Kruskal-Wallis one-way ANOVA tests for difference between all annual sub-samples. p-values < 0.05 indicate significant difference at 95% confidence.

Determinand	Site	Overall positive/ negative change in annual median values, relative to bare peat control (1 st – final years)	Sample size for each year	Test statistic (U)	p
pH	O	+0.27	9,7	0	0.001
pH	N	+0.4	9,7	0	0.001
Ca	O	+2.21mg/l	6,5	0	0.006

Ca	N	+2.29mg/l	6,5	0	0.006
Ca	P	-0.59mg/l	4,2	8	0.064
Mg	P	-0.31mg/l	4,2	8	0.064
K	P	-0.29mg/l	4,2	8	0.064
Zn	O	+0.005mg/l	6,5	0	0.006
Zn	N	+0.001mg/l	6,5	5	0.068
E4:E6	O	-2.41	5,7	28	0.088
C:C	O	-0.02	5,8	30	0.143
C:C	N	-0.07	5,8	35	0.005

Table 9: results of Mann-Whitney U tests for difference between pre-treatment and final year annual sub-samples. p-values<0.05 indicate significant difference at 95% confidence.