

Restoration of Blanket bogs; flood risk reduction and other ecosystem benefits

Annex 4. Dissolved Organic Carbon concentrations

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SUMMARY

- 1) This section examines the evidence from the MS4W experimental catchments in order to assess the impact of the peatland restoration programme on water quality, specifically on measures of water colour and dissolved organic carbon.
- 2) The controlled experimental design of the study has allowed a careful assessment of the potential impact of the restoration treatments. Water samples were collected approximately fortnightly from the treated catchments and three control catchments and analysed for water colour (Absorbance at 400nm), Dissolved Organic Carbon (DOC), and water chemistry.
- 3) The results indicate high water colour and DOC concentration from all the catchments consistent with previous work on degraded headwater sites. The data demonstrate a clear impact of the lime/seed/fertiliser applications on measured water colour at the treatment sites and only limited impacts on DOC quality (E4:E6 ratio - ratio - a proxy where higher values are less humic) so that the changing water colour is strongly correlated with changes in concentrations of DOC. Water colour and DOC are suppressed after initial restoration treatment for a period of up to 6 months. The magnitude of this depression is up to 10 mg/l of DOC. The evidence for the impact of subsequent maintenance applications of lime and fertiliser after the initial treatment is less clear with further suppression of DOC concentration at only one of the three treatment sites. There is no evidence for long term changes in water colour and DOC concentration in response to restoration in this dataset. This is largely because the before treatment data are limited and because the magnitude of the perturbation in the Carbon (C) system induced by the treatments makes it difficult to discern long term changes without further monitoring.
- 4) The implications of these findings are that concerns over whether the restoration treatments might increase water colour and DOC concentration are not justified in the short term and in fact there may be short term water colour benefits. However, because of the ongoing nature of the restoration treatments insufficient time has elapsed post-treatment to assert that there are no longer term impacts. Further monitoring will be required to assess the long term trajectory of water colour and DOC in response to the peatland restoration process.

1. INTRODUCTION

The main aim of the MS4W study was to consider the impact of restoration on the quantity and timing of runoff. However the regular monitoring visits to the site and the controlled experimental setup also offered a unique opportunity to consider impacts of the restoration process on water quality. The main focus of this work was assessing water colour/DOC which is a major water quality concern in areas of degraded peatland. Because liming is an important part of the restoration process alongside application of fertiliser and seed there is a potential risk that rates of C turnover will increase under conditions of increased pH (Ivarsson, 1977). Lime addition to peat bog soils has been demonstrated experimentally to increase rates of peat decomposition and CO₂ flux associated with increased bacterial populations (Ivarsson 1977; Filep et al 2003). Water colour associated with high DOC concentration is a significant and increasing water quality issue in UK upland peatland catchments (Evans et al 2005).

The main aim of this element of the work is therefore to assess the impact of the restoration process, in particular the liming, on water colour and DOC concentrations in the study catchments.

2. METHODS

Water samples were collected from the five main study catchments (O, N and F on Kinder Scout and from site P) on an approximately fortnightly basis between 1/12/2010 and 5/1/15. Water samples were collected from an additional catchment on Kinder Scout (site B) between 15/10/11 and 5/1/15. In total there were 102 sampling visits. Water samples were collected from the water flowing over the weir at each site. Where there was no flowing water samples were not collected. Total numbers of samples collected are indicated in Table 1

Water samples were returned to the laboratory and filtered at 0.45 microns. All samples were analysed colorimetrically using a Hach spectrophotometer. Absorbance was measured at a wavelength of 400 nm which is a common proxy for dissolved carbon concentrations. In the second half of the study period (From October 2012) samples were also analysed for Total organic carbon content using a Shimadzu TOC-V analyser. From January 2012 sample pH was also measured. Water chemistry was analysed by ICP-OES and Ion chromatography to provide contextual data.

3. RESULTS

Mean values of absorbance at 400 nm measured across the whole monitoring period and mean values of DOC concentration measured in the period September 2012 until January 2015 are presented in tables 3 and 4. These demonstrate that mean DOC concentrations for Site J (10 years restored on Bleaklow) are the highest and that Site P (intact control, Bleaklow) and Site B (treatment, Kinder Scout) are the lowest Sites. F, N, and O are the bare peat control and the two main treatment sites on Kinder Scout, respectively. Overall mean values for treatment sites are however potentially affected by the treatment and trend data is most informative for these sites. For the three control sites the lowest values are observed at the intact control (P), followed by the bare

peat (F) with the highest values at the 10 year restored site (J). At each of these sites DOC concentrations above 20 mg/l are very high consistent with previous observations in headwater peatlands (eg. Pawson et al., 2012). Values at site J significantly exceed the remaining sites suggesting that site specific factors may be important. Consequently the focus in the subsequent analysis is on the intact (P) and bare peat (F) control sites.

3.1 Trends in absorbance

The water colour data from this study (measured as absorbance at 400nm) do not show a clear trend of increasing DOC over the period of lime application (Fig. 1). In fact the overall pattern is controlled primarily by the seasonal pattern of DOC production with peak absorbance measured in late summer and autumn. This pattern is common in upland peatlands (e.g. Koehler et al 2009) with higher rates driven by enhanced decomposition in warmer drier conditions. The data in Fig. 1 clearly demonstrate that variation at synoptic and seasonal timescales significantly exceeds any difference between treatments and across the four years of the study. In order to simplify the dataset and assess the impact of the treatments the data has been expressed below as the deviation from estimated absorbance at the control catchment P. Estimated absorbance was calculated by simple interpolation between the measured ABS 400 values at P to derive continuous Abs 400 estimates for the site. Differencing these values from measured Abs 400 at the other sites potentially removes the main seasonal and synoptic patterns. It also normalises for between site variance in average absorbance so that remaining variance should be primarily influenced by differences in site treatment.

Fig. 2 demonstrates that even normalising to a control site water colour is still significantly variable. However what becomes clear is that some of this variation is systematically associated with the application of the lime and fertiliser treatment to the catchments. In Fig. 2 a and b it is apparent that the two treatment sites N and O have Abs₄₀₀ values significantly depressed below the control site after the initial treatment. This pattern is not seen in the bare peat control site F. This impact remains apparent in the record for 20-24 weeks with gradual recovery to values equivalent to the control site F over this period. The suppression of Abs₄₀₀ below the bare peat control site is not apparent for the two subsequent annual applications of lime and fertiliser to the catchment. These observations are further apparent in Fig. 3 which compares site O and N directly to site F.

Fig. 2c presents comparable data for site B which was treated later than sites O and N. There is a similar pattern observed of suppression of the Abs₄₀₀ below the bare peat site although the magnitude of change is smaller than at sites O and N. At site B this effect is also observed during the subsequent maintenance application of lime and fertiliser.

The implication of these data is that there is a transient effect of the lime, seed and fertiliser treatment on water colour in the catchments causing a reduction in water colour in comparison to the control site for up to 6 months after the initial application.

3.2 Patterns of DOC concentration

Direct monitoring of DOC spans the full treatment period for site B but for the remaining sites begins after the second treatment. Measured DOC concentrations are shown in Fig. 4. Unsurprisingly the patterns of variation seen in these data are similar to those in the absorbance data with seasonal and synoptic variability very high. Table 4 presents summary data on the DOC data showing highest

mean DOC concentrations at site J with the three untreated sites ordered $J > F > P$ as with the water colour data.

Fig. 5 plots the DOC data as deviation from the intact control site P to remove the seasonal effects. Again the patterns reflect the water colour data and the treatment effect is apparent in Fig. 5b as a depression of DOC concentration below control site F for a period of 14-20 weeks after treatment. The magnitude of this effect is approximately a depression of 10 mg/l of DOC and so approaches 50% of the long term mean concentration for the catchment.

The direct measurement of DOC also allows us to address the question of whether the absorbance data available for the full period of the study are a suitable proxy to study DOC concentration in this context. This requires the answer to two questions 1) is Absorbance at 400 nm well correlated with DOC concentration and 2) are there changes in DOC quality associated with treatment that might affect this relationship.

In order to answer the first of these questions Fig. 6 plots Abs_{400} against DOC concentration for all samples where DOC data are available. These data are after the treatment period and so the limed samples and control sites are plotted separately. Best fit lines through the two datasets have very similar slope and R^2 values. Mean values of the Abs_{400} :DOC ratio by site are presented in Table 5 which shows that the ratio is comparable across all sites both treatment and control with the exception of site J. The implication of these data is that the changes in absorbance observed in the full data set reflect changes in DOC concentration rather than changes in DOC quality. In order to further assess this Fig. 7 plots the ratio of absorbance at 465 and 665 nm, the E4:E6 ratio (Wallage, 2006) for each site over time. What Fig. 7. indicates is that variation in E4:E6 is relatively small across the 5 years with no significant trend either within or between sites. The one exception to this pattern is a short term response to initial treatment at sites N and O with ratios significantly elevated above the control sites for a period of up to 60 days after the treatment.

4. WHAT MIGHT BE CAUSING THESE EFFECTS?

Suppression of DOC concentrations in response to the treatments is counter to the hypothesis that increased pH will enhance DOC solubility and increase DOC levels. Clearly in these systems another mechanism is important. Two potential mechanisms identified in the literature could produce the observed effects.

Initial short term chemical hydrolysis of organic matter (impact of lime - 2-4 weeks) (cf Marschner 1993) or short term pH changes impacting DOC solubility

Decreased DOC solubility and flocculation due to Ca binding with humic substances (Valeur et al 2000, Romkens et al 1996)

The first of these mechanisms is plausible but the magnitude of the effects seen in this experiment exceeds the time frame reported by Marschner et al. (1993). Fig. 8 plots the time series of calcium ion concentrations over the treatment periods which indicate peaks in calcium for periods of up to 6 months after initial application of lime to the catchments. These time periods are consistent with the suppression of DOC seen at the treatment catchments and provide some support for the second

potential mechanism. However calcium ion peaks are seen after each treatment and DOC suppression occurs only after initial treatment at sites N and O. Fig. 9 plots pH in runoff waters. pH monitoring began after the initial treatment but shows significant pH response to subsequent treatments. The liming of the treatment catchments has led to significant increases of pH from values around pH 3.5 to values approaching pH 4.5. The most significant rises occur immediately after treatment but the overall trend in pH is upward across the period. pH at the treatment sites N and O remains above that at the control sites (F and J) through the entire treatment and post-treatment period. The increases in E4:E6 observed after initial treatment are consistent with short term decreases in humic content of DOC.

The catchment scale data presented here are not sufficient to identify the mechanism driving suppression of DOC but the data point to a mechanism which is associated with increasing calcium ion concentrations and increased pH and potentially with temporary reductions in humic content. Further experimental work is required to investigate the combined effects of changes in pH and calcium ion concentration on DOC solubility in these systems.

5. LONG TERM CHANGE IN RESPONSE TO TREATMENT

The initial concern in this study was the potential that the lime/seed/fertiliser treatment, and in particular the liming of the catchments might lead to increases in DOC concentration and water colour in runoff waters. The magnitude of the perturbation of the system through the treatment effects is such that simple analysis of trend in the dataset is not appropriate. An alternative would be to consider before-after comparisons of DOC or Abs₄₀₀. Table 6 shows mean values of Abs₄₀₀ at sites O and N expressed as deviations from the control site F. Mean values are presented for the period before the treatments and the period after day 1037 after which pH has stabilised in the catchments (Fig. 8). These data show a small reduction in absorbance at site N and a small increase at site O. However the quantity of data in the before period is very small (n = 5 and 9) because this was a dry summer period when the sites only occasionally had flowing water. There is therefore no basis to confidently undertake a statistical comparison of before and after data. Qualitative assessment of the trends expressed in Fig. 2 indicates that there is no gross long term trend in Abs₄₀₀. Comparison of the three control sites however indicates that the 10 year restored site J has the highest Abs₄₀₀ and DOC values of any of the sites. This may be a site specific factor. Site J has higher slope than the other study catchments which may drive lower water tables and higher DOC production. However, the data here cannot exclude the possibility that there is a longer term impact of the restoration process. Further, the pH data in Fig. 9 indicate that the pH in the treatment catchments remains above the control sites so that the treatment catchments may not have fully equilibrated after the lime application. The current dataset has included 577 days of monitoring post the final intervention. Further monitoring to extend this to a 5 year interval is required to further assess whether there is a long term impact of the treatment on DOC and water colour.

6. CONCLUSIONS

- Fluvial carbon flux and water colour from the headwater peatland catchments is highly variable on seasonal and synoptic timescales. Average concentrations are high in line with previous work on similar systems.
- The restoration treatment (Lime/Seed/Fertiliser) causes significant perturbation to carbon cycling in the system
- The initial restoration treatment causes a reduction in water colour and DOC concentrations for a period of up to 6 months
- There is evidence that subsequent ‘treatments’ have limited additive effect. This may be due to a stabilisation of pH at higher levels.
- There is little evidence of changes in DOC quality associated with the treatments.
- Because the perturbation caused by the treatment is significant, and because the monitoring in the pre-restoration period was limited it is not possible to fully assess the longer term impact of the restoration on water colour and DOC concentration in these systems. Initial evidence is that the effects are limited.
- Because of the need to separate the short term perturbation from the longer term impacts of re-establishing vegetation a longer period of post restoration monitoring is required.

7. REFERENCES

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8. TABLES

Table 1. Study catchment treatments and sample sizes.

Site	Treatment	Sample n
P	Intact Control	62
J	Restored 2003	65
F	Bare peat Control	92
N	Restored 2011 and gully blocked	100
O	Restored 2011	93
B	Restored 2012	56

Table 2. Dates of restoration treatments (days after day 0 (1/12/10)).

Year	Lime		Fertiliser		Seed	
	Day	Dates	Day	Dates	Day	Dates
a. Kinder North Edge (sites O and N)						
2011	231	20/7	232	21/07	232	21/07
2012	546-567	30/5-20/6	565-567	18/6-20/6	None	None
2013	922-962	10/6-20/7	919-950	07/6-8/7	None	None
2014	None	None	None	None	None	None
b. Kinder West and Central (site B)						
2011	None	None	None	None	None	None
2012	None	None	None	None	None	None
2013	922-962	10/6-20/7	919-950	07/6-8/7	None	None
2014	1267-1300	21/5-23/6	1302	25/06	573-579	26/6-2/7

Dates shown are the range of days quoted by the contractors as to when applications were made. When multiple dates are given it is difficult to be precise about exactly when a given site received an application due to the ad hoc nature of the flying regime).

Table 3. Mean Absorbance at 400nm (au m^{-1}) for the period Dec 2010 - Jan 2015.

Site	Sample n	Mean Abs ₄₀₀ au m^{-1}	Standard deviation
P	62	17.82	8.19
J	65	30.70	10.83
F	92	20.74	8.07
N	100	18.69	6.77
O	93	19.21	7.78
B	56	19.26	10.82

Note: the period for site B was Oct 2011 – Jan 2015

Table 4. Mean DOC measured at all sites in the period Sept 2012 – Jan 2015.

Site	Sample n	Mean DOC mg/l	Standard deviation	Max	Min
P	36	22.30	8.07	40.45	9.12
J	35	35.78	11.53	55.44	13.81
F	53	27.94	9.57	50.13	9.38
N	61	29.90	9.46	57.14	12.79
O	57	30.70	9.56	51.69	16.40
B	35	22.96	10.00	49.92	10.93

Table 5. Values of Abs₄₀₀:DOC ratio by site.

Site	Sample n	Mean Abs 400:DOC	Standard deviation
P	35	0.71	0.15
J	35	0.78	0.16
F	52	0.69	0.09
N	61	0.67	0.12
O	57	0.69	0.10
B	35	0.71	0.21

Table 6. Comparison of Abs₄₀₀ values at the treatment sites before treatment and after the end of the main treatment period.

Site	Before Treatment			After Treatment		
	Abs ₄₀₀ difference from site F	Standard Deviation	n	Abs ₄₀₀ difference from site F	Standard Deviation	n
N	2.19	7.33	9	0.21	9.52	30
O	1.31	5.11	5	3.05	5.72	30

9. FIGURES

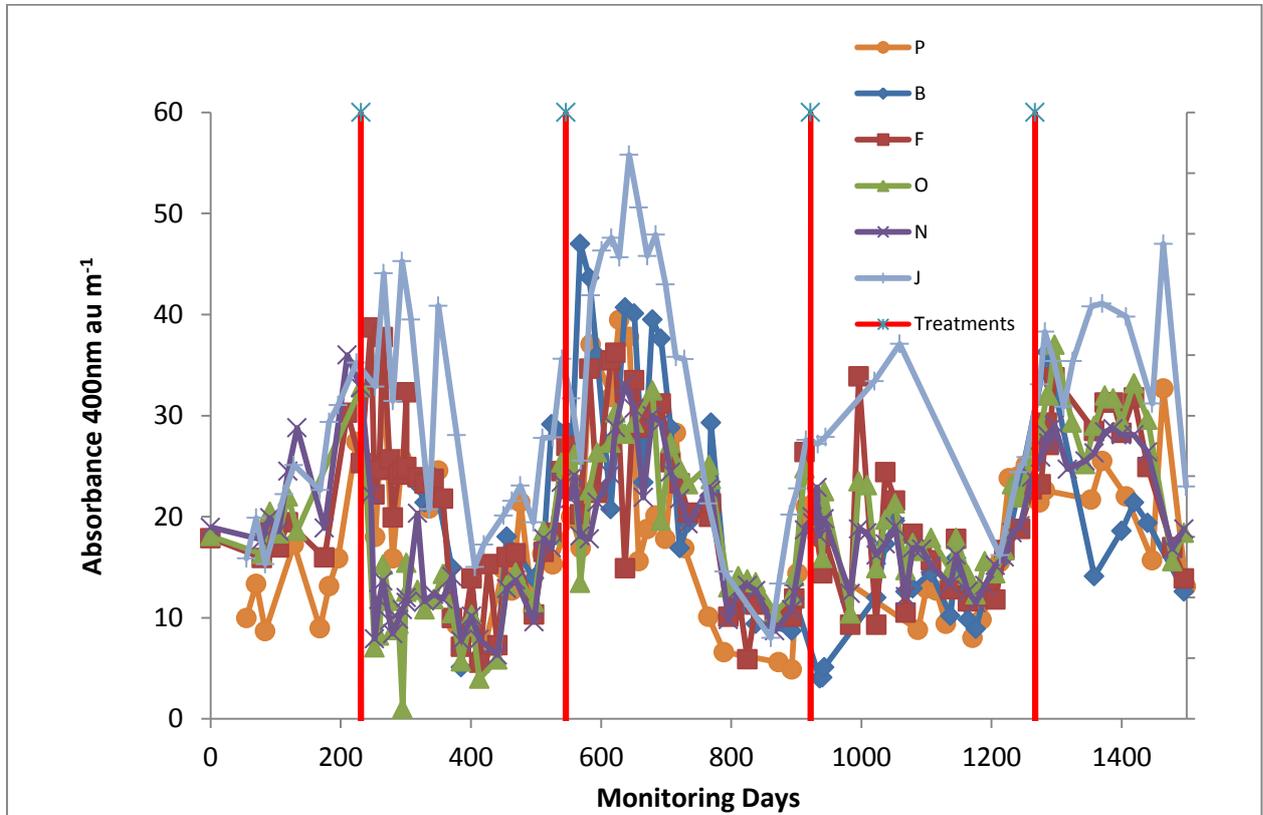
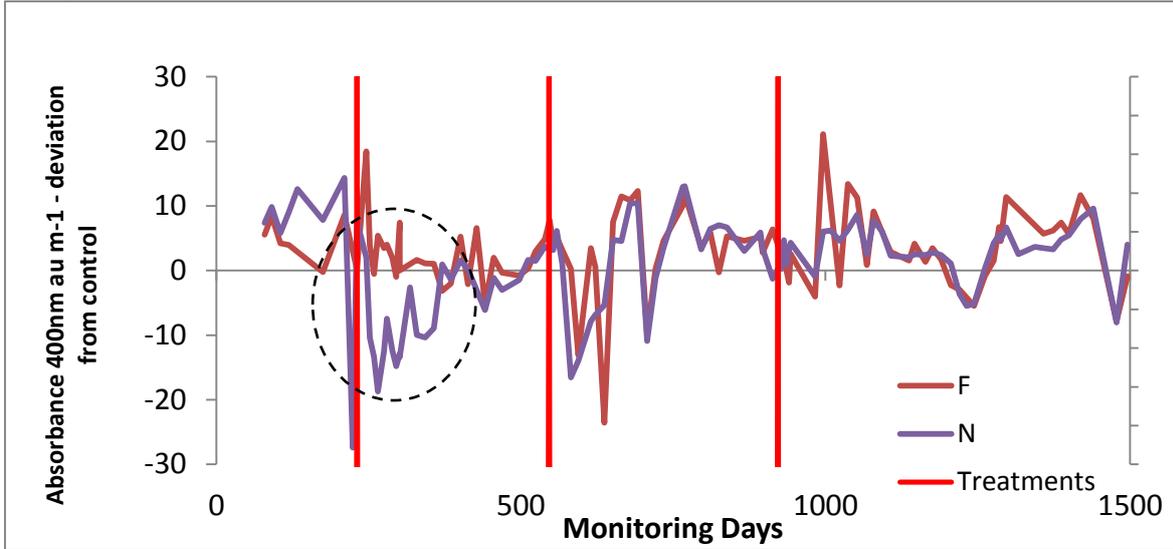


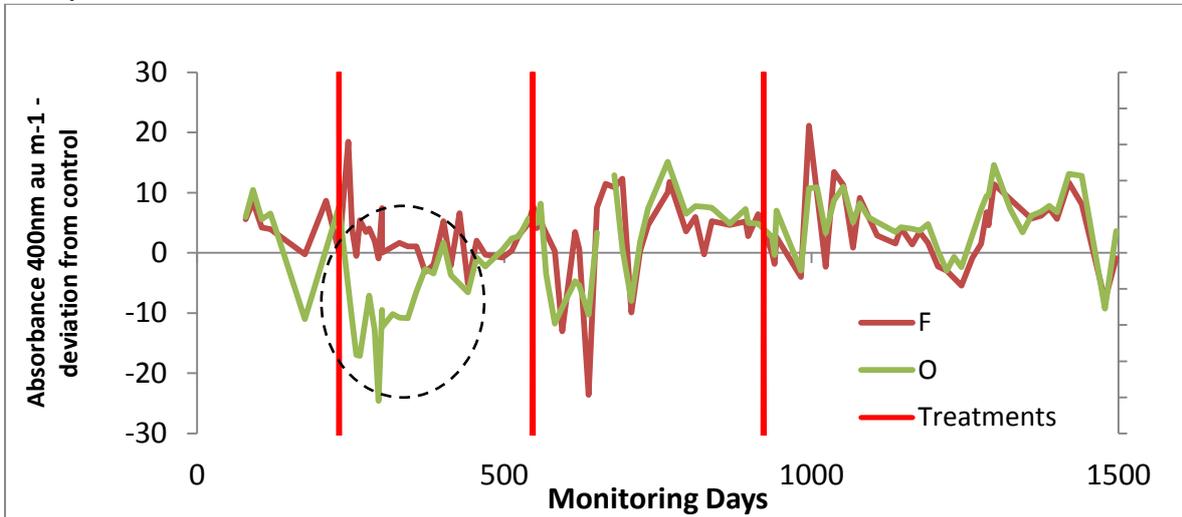
Fig. 1. Absorbance data for all samples at all sites.

Lime/Seed/Fertiliser applications are indicated by the red lines. Note that the regime at site B differed in that the final application was only at site B and the first two applications were not applied to site B (see table 2)

a) Abs. 400 deviation from control site P at Sites F and N



b) Abs. 400 deviation from control site P at Sites F and O



c) Abs. 400 deviation from control site P at Sites F and B

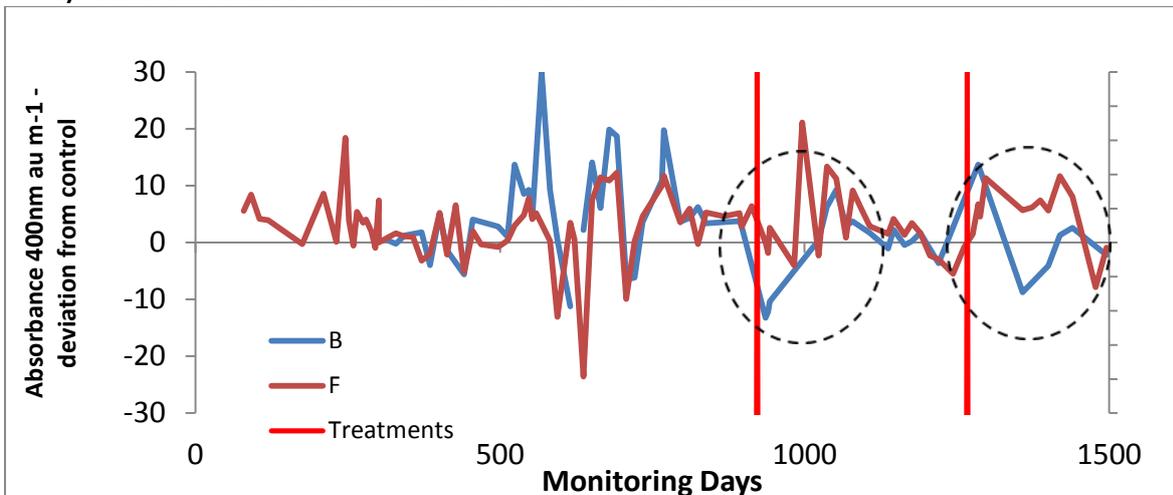


Fig. 2. Deviation of measured Absorbance at 400 nm from estimated values at control site.

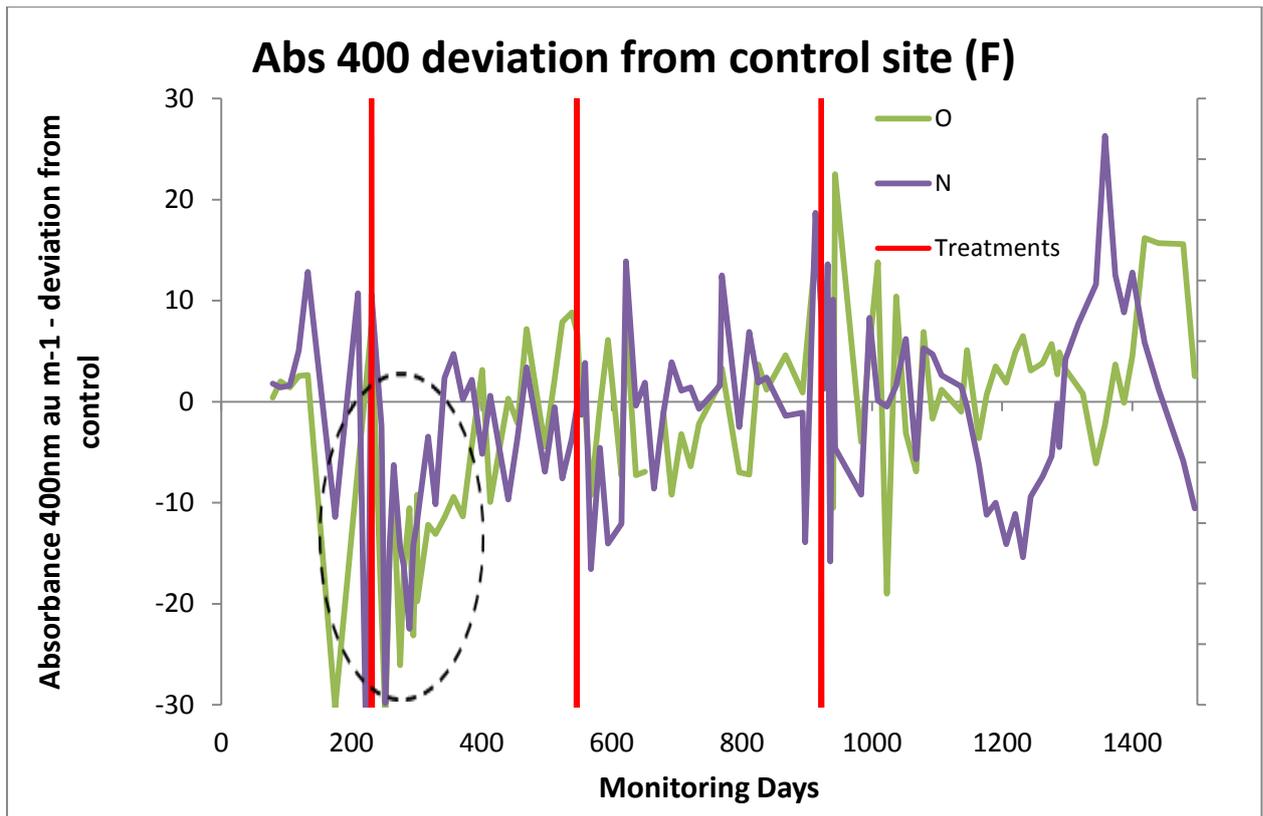


Fig. 3. Direct comparison of Abs₄₀₀ at sites O and N (treatment) to site F bare peat control.

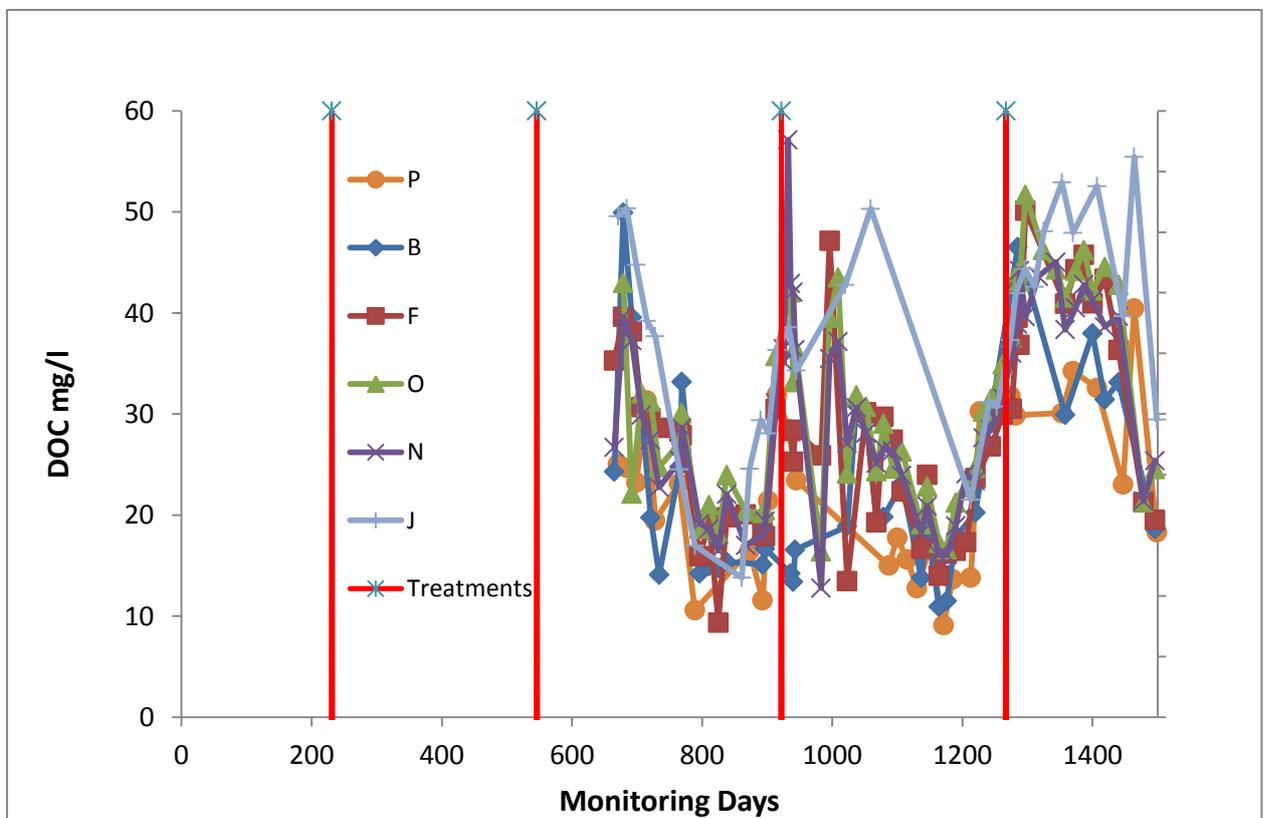
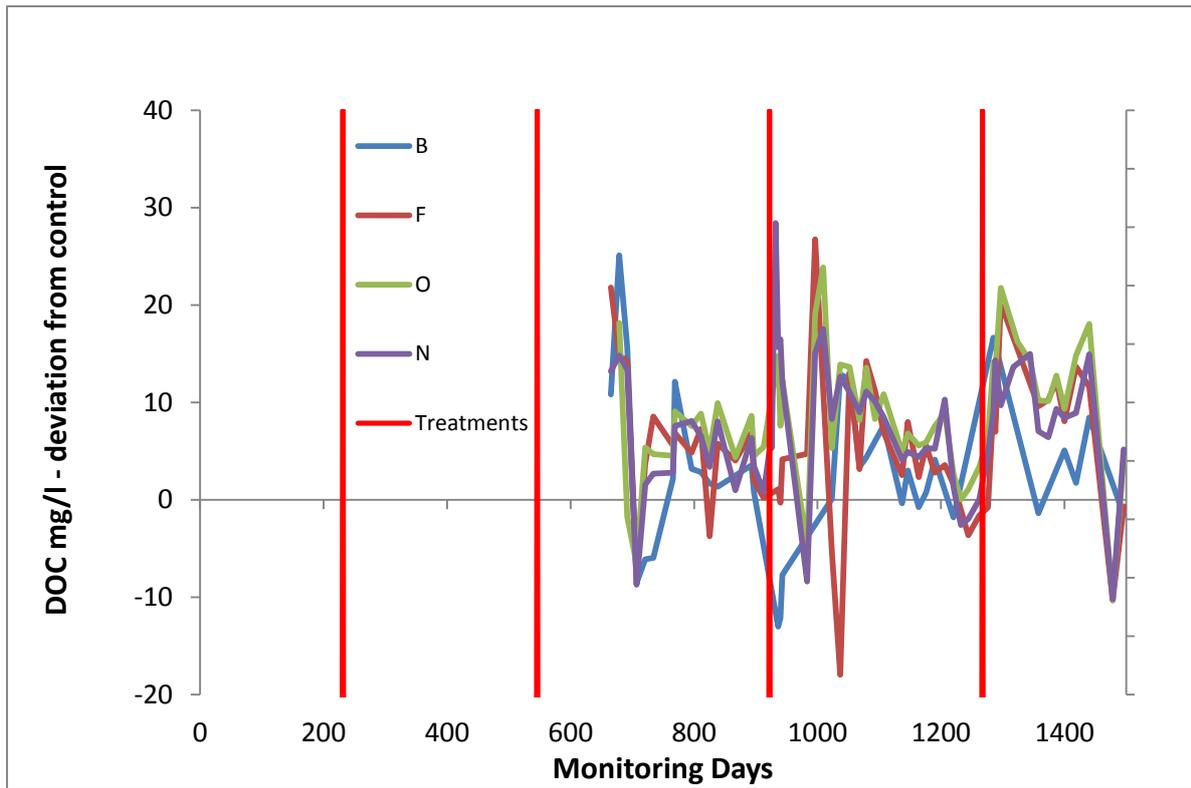


Fig. 4. Measured DOC concentrations at all sites.

All Sites



a) Site B and F

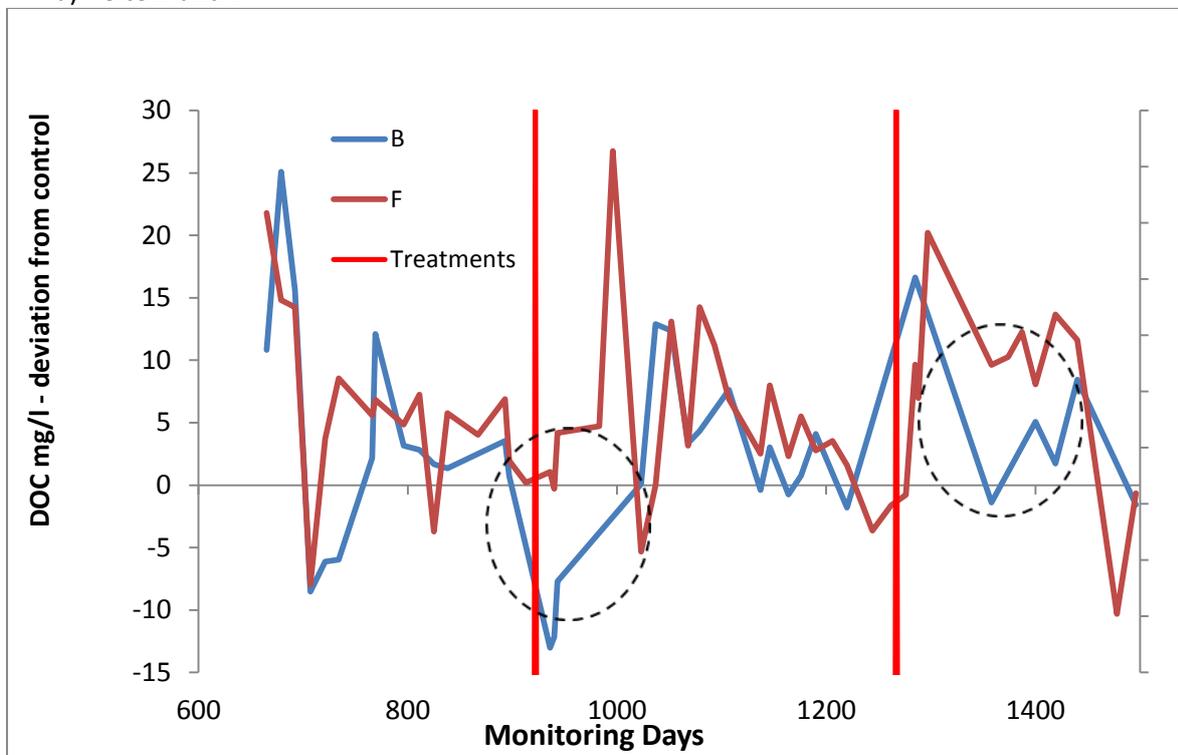


Fig. 5. DOC concentrations expressed as deviation from the intact control (Site P).

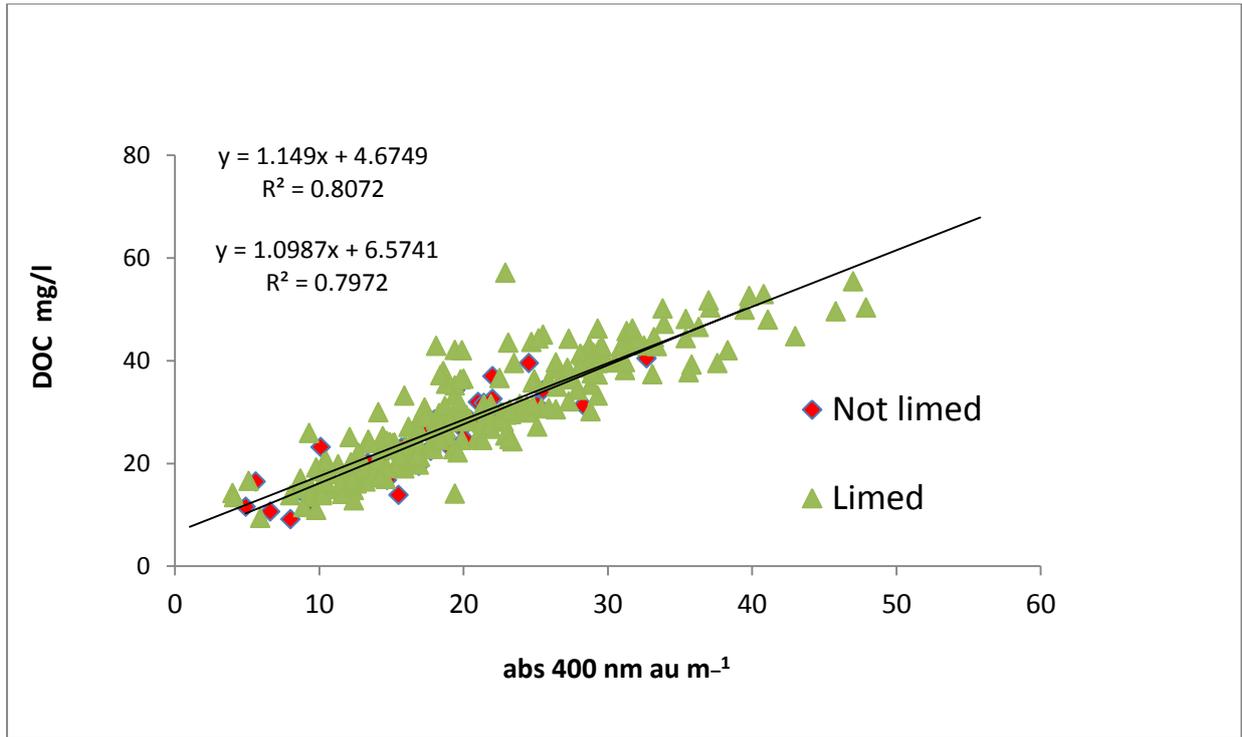


Fig. 6. Abs₄₀₀ vs DOC concentration for treated and untreated sites.

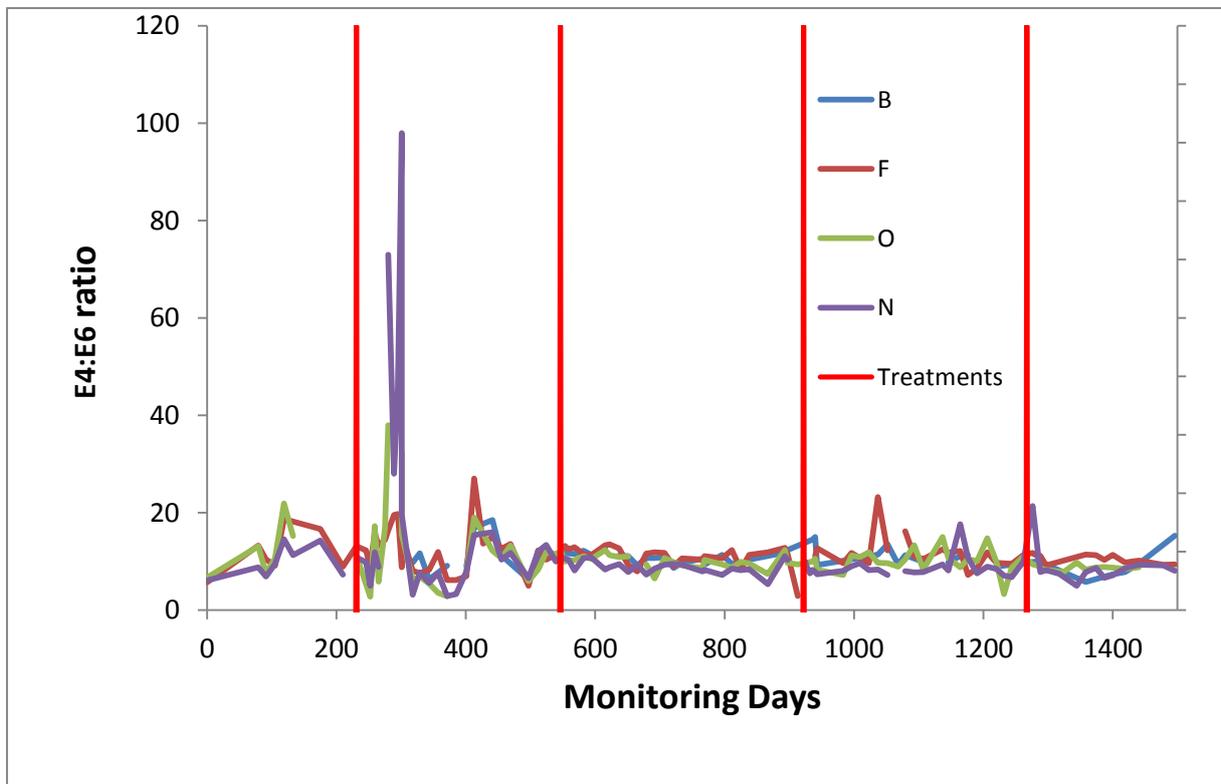


Fig. 7. E4:E6 ratio for Kinder Scout sites and intact control.

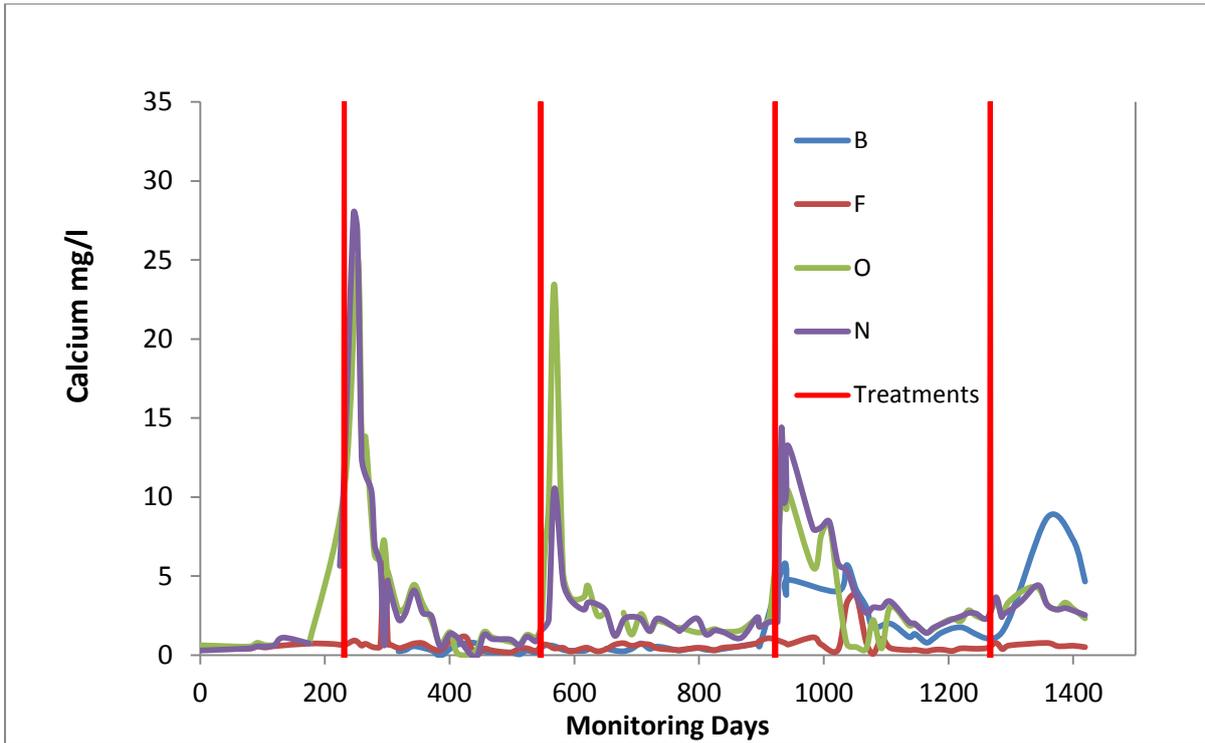


Fig. 8. Calcium ion concentration measured in runoff waters at all sites.

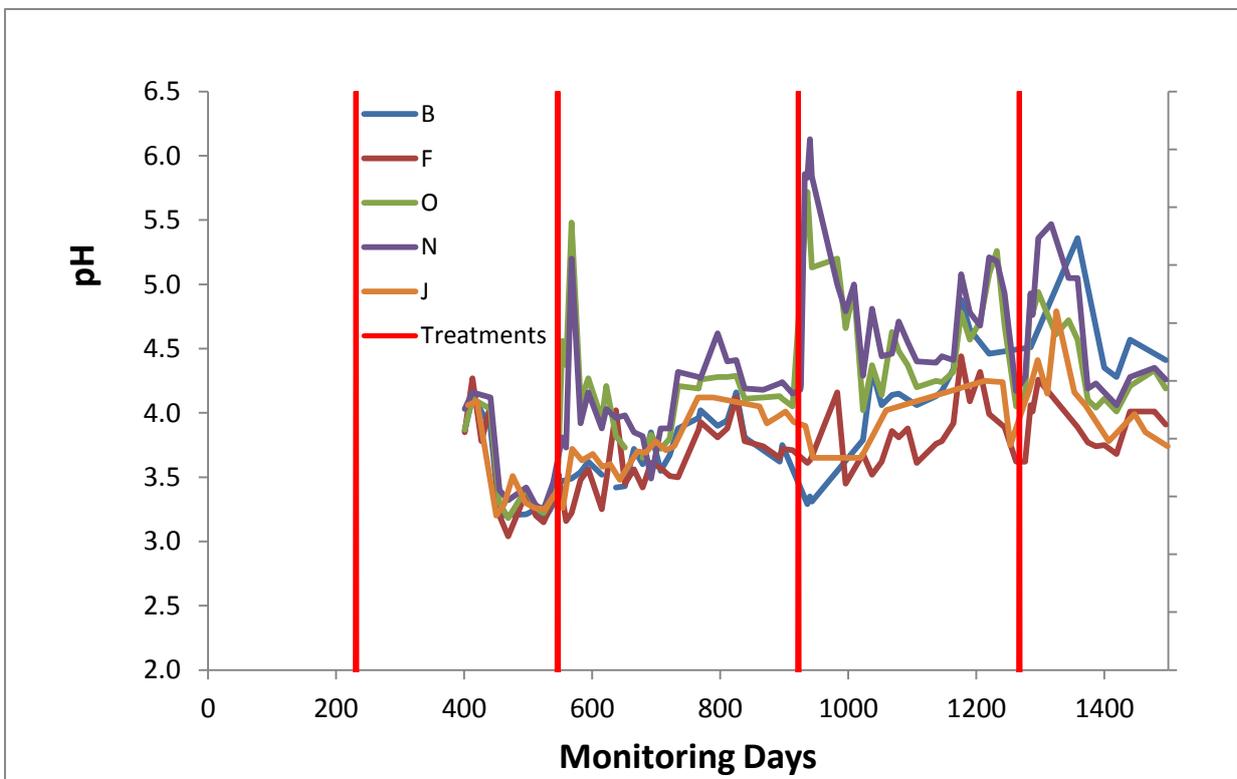


Fig. 9. pH of runoff waters recorded at all sites.