Spatial variation in water quality within the water bodies of a Peak District catchment and the contribution of moorland condition

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Executive summary

Introduction

Uplands provide over 70% of fresh water in Great Britain (Bonn *et al.* 2010; Watts *et al*. 2001). However, the blanket peat moorlands which characterise these upland areas are ombrotrophic (Shotyk, 2002, cited in Rothwell et al., 2007a); therefore, peatlands in close proximity to industrial or urban areas can be highly contaminated with anthropogenically derived, atmospherically deposited pollutants, such as heavy metals (Rothwell et al., 2005; Rothwell et al., 2007b). Heavy metals are stored in the near-surface layer of peat soils (Rothwell et al., 2005; Rothwell et al., 2007b). Processes such as leaching and erosion of soils and sediments may release these pollutants into the aquatic environment (Shotbolt et al., 2008) and consequently represent a threat to both aquatic ecosystems and drinking water supplies, threats that are regulated by the Water Framework Directive (WFD) and the Drinking Water Inspectorate (DWI) respectively.

Aims and Objectives

This project is funded by the Environment Agency (EA) and Severn Trent Water Ltd. (STWL) in response to known issues relating to WFD and Drinking Water Standards (DWS). There are two aims of this project: the first aim is to identify spatial and temporal variability of water quality within the Bamford Water Treatment Works (WTW) catchment; the second aim is to assess the contribution of moorland condition to water quality within the Bamford WTW catchment. Overall, this project is intended to provide evidence of the potential impacts of moorland restoration and management on downstream water quality and DWS and WFD objectives.

Study Site and Methods

The Bamford WTW catchment is located in the Upper Derwent Valley, Derbyshire. It is 20,159 ha in size, of which 12,302 ha (61%) is classified as moorland. The catchment consists of two main systems; the Upper Derwent River to the north (eight sub-catchments), and the River Noe to the south (three sub-catchments). Eight sub-catchment sample sites were chosen based on the existing sample sites used by the EA and / or STWL, and eight moorland edge sample sites were chosen to represent different peat conditions (bare peat, early stage restoration, vegetated, heather burn and 'intact' reference). Water samples were collected fortnightly for one year, and were analysed by Scientific Analysis Laboratories (SAL) Ltd. for dissolved organic carbon (DOC), particulate organic carbon (POC), total organic carbon (TOC), colour, pH, total hardness and a suite of heavy metals, including copper (Cu), zinc (Zn) and iron (Fe).

Results

The EA requested fortnightly analysis of DOC, pH, total hardness, dissolved Cu and total Zn. Severn Trent Water Ltd (STWL) requested monthly analysis of colour and total Fe. The results for DOC, pH, Cu, and Zn are considered in relation to the WFD ‘good’ standard; and the results for colour and Fe are considered in relation to the DWS.

Across sub-catchments, water quality relative to DWS and WFD objectives was variable.

Water quality within the Bamford WTW catchment. Red = fails condition; green = meets condition.

Sub-catchment	Code	pH	Copper	Zinc	Colour	Iron
		WFD	WFD	WFD	DWS	DWS
Abbey Brook	AB					
Ladybower Brook	LB					
River Alport	RAL					
River Ashop	RAS					
River Derwent	RD					
River Noe lower	RNL					
River Noe upper	RNU					
River Westend	RW					

Across moorland edge catchments, water quality relative to DWS and WFD objectives was generally poor, failing DWS and WFD objectives. All moorland catchments failed on pH, copper, zinc and colour.

Water quality from moorland edge catchments. Red = fails condition; green = meets condition.

Moorland catchment	Code	Peat condition	pH	Copper	Zinc	Colour	Iron
			WFD	WFD	WFD	DWS	DWS
Fair Brook	FB	Un-restored					
Upper Red Brook	URB	Early stage restoration					
Devils Dike	DD	Degraded					
Upper North Grain	UNG	Degraded					
Green Clough	GC	Heather burn					
Within Clough	WC	Heather burn					
Ashop Head	AH	Intact reference					

In general, water draining moorland catchments is not achieving DWS or WFD objectives and moorland condition has a significant impact on all of the determinands identified by the EA and STWL. Overall the impact of moorland condition, when condition is summarised as either 1) degraded (five catchments); 2) heather burn (two catchments); and 3) intact (one catchment), was consistent across the determinands – stream water concentration of focal determinands were greatest for degraded catchments and lowest for the intact catchments; for pH, acidity was highest for degraded sites and lowest for the intact site. Heather burn catchments were placed between unrestored catchments and the intact catchment. Iron did not show a clear relationship with moorland condition.

Summary of the relative impact of moorland condition on water quality. Red = relatively high concentrations; yellow = relatively low concentrations; orange = concentrations between high and low.

	Degraded	Heather Burn	Intact reference
DOC			
POC			
Colour			
Copper			
Zinc			
Iron			
pH			

Discussion

This project was carried out during a year of atypical weather, i.e. below average rainfall from January to March, followed by an exceptionally wet summer and above average rainfall for the autumn and December. The results presented in this report must be viewed in the context of sampling taking place during a year of unusual weather conditions.

There are significant water quality issues across the sub-catchments of the Bamford WTW catchment. These are variable in space (between the sub-catchments) and in time. In terms of spatial difference a major distinction within the Bamford WTW catchment is that the catchment essentially comprises two distinct systems, the River Derwent and River Noe. There are similar water quality issues between the two systems in relation to WFD and DWS; however, there are also distinct differences in terms of the magnitude of determinand concentrations. The Noe system has lower mean annual concentrations of DOC, pH, colour and iron than the Derwent system, but has higher zinc concentrations and is the only catchment that does not meet the WFD standard for chromium. Additionally, within the Noe catchment there is relatively little moorland compared with the Derwent system and the composition and management of the non-moorland areas of the catchments (e.g. rough grazing and in-bye) may have a significant influence on fluvial water quality. The high concentrations of zinc within the lower River Noe sub-catchment, but low concentrations in the upper River Noe catchment, suggests that in this system zinc input from non-moorland land management is significant. An understanding of the contribution of moorland and non-moorland inputs to fluvial chemistry loadings is essential to formulate plans to address water quality across the Bamford WTW catchment.

Of the sub-catchments within the River Derwent system, the Ladybower Brook sub-catchment potentially represents the most significant issues as, relative to other sub-catchments, it has the highest annual mean concentrations of DOC, zinc, colour and iron. The Abbey Brook sub-catchment (that neighbours Ladybower) also has relatively high concentrations of DOC, colour and iron. The Ashop and Alport sub-catchments, similarly, in terms of the magnitude of loadings above WFD and DWS, represents significant issues within the Bamford WTW catchment for DOC, copper and iron (and level of acidity with Westend and Derwent sub-catchments).

The condition of moorland catchments had a significant impact on the quality of the fluvial water flowing from them. Bare peat, degraded, and eroded / eroding catchments had significantly lower water quality than moorland 'heather' catchments that were managed by burning, while the 'best' water quality was recorded from the 'intact' reference site (Ashop Head). Intact is relative within the moorlands of the Peak District / South Pennines, the intact catchment in this project comprised ~3.5 % bare peat and contains some gullies. Although the water quality from this catchment was better than the other moorland catchments in this study, it nevertheless still failed WFD standards for pH, copper and zinc and DWS for colour and iron, and some restoration intervention on this catchment to reduce the extent of bare peat and gullies would be beneficial for water quality.

In the short-term, results from an 'early stage restoration' catchment suggest that moorland restoration does not significantly improve water quality compared with unrestored moorland in terms of DOC and heavy metal loadings. In the short term, the water quality benefits of bare peat stabilisation and gully blocking are significantly lower peaks in the concentration of POC compared with unrestored sites.

Within the Ashop sub-catchment, the concentration of focal determinands from moorland edge catchments, while variable across different moorland conditions, was on average twice as high as at the bottom of the Ashop sub-catchment. An understanding of the contribution of moorlands to sub-catchment water quality is required in order to assess the impact of moorland land management on sub-catchment scale water quality. Addressing moorland catchment condition should have significant impacts on water quality at the sub-catchment scale.

The relationship between the focal determinands was also investigated. Significant relationships between the following determinands were found: DOC and colour at sub-catchment and moorland edge sites; DOC and pH at moorland edge sites; colour and pH at moorland edge sites; DOC and Cu at moorland edge sites; DOC and Fe at sub-catchment sites; colour and Cu at moorland edge sites; colour and Fe at sub-catchment sites; and pH and Cu at moorland edge sites. DOC and colour are positively correlated because the humic and fulvic acids that make water appear coloured also make up 50 to 75% of DOC (Watts et al., 2001). This provides a link between the issues raised by the EA and STWL. DOC and Cu are positively correlated because some metals can complex with DOC. pH is negatively correlated with DOC and Cu. This is because metal complexation is dependent on pH (Stumm and Morgan, 1996, cited in Rothwell et al., 2007a). Therefore, a reduction in surface water acidification and DOC export may lead to a reduction in metal export. Fe is also positively correlated with DOC and colour (sub-catchment sites). In addition to complexing with DOC, water table fluctuations and redox cycling have been used to explain increased Fe in surface waters (Rothwell et al., 2010).

Conclusions

This study of spatial variation in water quality within the water bodies of a Peak District catchment and the contribution of moorland condition has shown that:

1. DOC, pH and heavy metal concentrations of sub-catchment and moorland edge sites are spatially and temporally variable.
2. A number of sub-catchment sites are failing to achieve the WFD 'good' standard for pH, Cu and Zn.

3. All moorland edge sites are failing to achieve the WFD 'good' standard for pH, Cu and Zn.
4. All sub-catchment sites are failing to achieve the DWS for colour and Fe (except RW), and half are failing to achieve the DWS for Al.
5. All moorland edge sites are failing to achieve the DWS for colour, Fe (except FB) and Al.
6. DOC is significantly positively correlated with Cu (moorland edge sites) and Fe (sub-catchment sites). This is because some metals can complex with DOC. pH is negatively correlated with DOC and Cu. This is because metal complexation is dependent on pH. Therefore, a reduction in surface water acidification and DOC export may lead to a reduction in metal export.
7. DOC is significantly positively correlated with colour (sub-catchment and moorland edge sites). This is because the humic and fulvic acids that make water appear coloured also make up 50 to 75% of DOC. This provides a link between the issues raised by the EA and STWL.
8. Fe is significantly positively correlated with DOC and colour (sub-catchment sites). In addition to complexing with DOC, water table fluctuations and redox cycling have been used to explain increased Fe in surface waters.
9. Differences between moorland edge sites are significant. DOC, colour, Cu and Zn is significantly higher and pH is significantly lower in streams draining more degraded moorland sites than in those draining less degraded sites. Therefore, DOC, colour, Cu and Zn may be reduced by returning sites to a less degraded state.
10. Differences between moorland edge sites are also significant for Fe and Al. However, there is no obvious pattern and it is not particularly clear if / how moorland condition affects Fe and Al concentration. It is possible that there are other factors affecting Fe and Al concentration that were not investigated in this report, e.g. fluctuations in water table depth and redox cycling.

1. Introduction

Upland locations are significant water supply sources, providing over 70% of fresh water in Great Britain (Bonn *et al.* 2010; Watts *et al*. 2001). However, blanket peat moorlands, which characterise many upland locations in the UK, are ombrotrophic, i.e. they receive inputs solely from the atmosphere (Shotyk, 2002, cited in Rothwell et al., 2007a). Therefore, peatlands in close proximity to industrial or urban areas can be highly contaminated with anthropogenically derived, atmospherically deposited pollutants, such as heavy metals (Rothwell et al., 2005; Rothwell et al., 2007b). These pollutants are the by-products of fossil fuel combustion, iron and steel manufacture, and vehicle emissions (Rothwell et al., 2005 and references therein).

Heavy metals are stored in the near-surface layer (top 15 cm) of peat soils (Rothwell et al., 2005; Rothwell et al., 2007b), and while accumulating peat soils may act as sinks for large quantities of these pollutants, e.g. lead (Pb) (Rothwell et al., 2007c), processes such as leaching and erosion of soils and sediments could be releasing them into the aquatic environment (Shotbolt et al., 2008). For example, a study by Rothwell et al. (2005) found that erosion of the upper peat layer is potentially releasing large quantities of Pb into the fluvial system.

The peatlands of the Peak District, Southern Pennines are amongst the most contaminated in the world. This is due to their location between the cities of Manchester and Sheffield, the heartland of the 19th century English Industrial Revolution (Rothwell et al., 2005). These peatlands are also the most severely eroded in Britain, with sediment yields for eroding peat catchments exceeding 100 t km^2 a^{-1} (Labadz et al., 1991; Hutchinson, 1995; Evans et al., 2006, cited in Rothwell, 2008a). Therefore, erosion of the upper peat layer could be releasing atmospherically derived contaminants into the fluvial system, representing a threat to both aquatic ecosystems (see Rhind, 2009) and drinking water supplies. These threats are regulated by the Water Framework Directive (WFD) and the Drinking Water Inspectorate (DWI) respectively - see below.

Restoration of the peatlands of the south Pennines has been a major conservation concern for several decades. Since 2003 the Moors for the Future Partnership (MFFP) have been restoring the large areas of bare peat found throughout this area, using a range of techniques to stabilise and revegetate bare peat and block gullies (Moors for the Future Partnership, 2012). This has been successful in reducing sediment, POC and contaminants, e.g. lead, to levels comparable to intact sites (Shuttleworth et al., 2011).

1.1 Water Framework Directive

The Water Framework Directive (WFD) establishes a legal framework to protect and restore clean water across Europe and ensure its long-term, sustainable use. Under the directive, water management is based on river basins, and specific deadlines are set for Member States to protect aquatic ecosystems. The directive applies to inland surface waters, transitional waters, coastal waters and groundwater (European Commission, 2008).

One of the aims of the WFD is to ensure that all of Europe's water bodies are of good ecological quality by 2015. Aquatic ecosystems which are part of modified water bodies may not be able to meet this standard; therefore, the directive allows Member States to designate some of their surface waters as heavily modified water bodies or artificial water bodies. Heavily modified water bodies will need to meet the "good ecological potential" criterion rather than "good ecological status". However, artificial and heavily modified bodies will still need to achieve the same low level of chemical contamination as other water bodies (European Commission, 2008).

There are 11 River Basin Districts (RBD) in England and Wales (Environment Agency, 2012). The Bamford WTW catchment is located within the Humber RBD. This is the second largest RBD in England and Wales, covering an area of 26, 109 km^2 (Environment Agency, 2009a).

Table 3.6 lists the WFD threshold values for the determinands included in this report. For full details of WFD requirements see *The River Basin Districts Typology, Standards and Groundwater threshold values* (WFD, 2010).

1.2 Drinking Water Inspectorate

The Drinking Water Inspectorate (DWI) was formed in 1990 to provide independent reassurance that public water supplies in England and Wales are safe and drinking water quality is acceptable to consumers and meets the standards set down in law. The legal standards for drinking water are set down in national regulations and come directly from European law. The health based standards are based on expert global opinion and World Health Organisation guidelines (DWI, 2013).

Table 6 lists the Drinking Water Standards (DWS) for the determinands included in this report. For full details of the DWS see *The Water Supply (Water Quality) Regulations 2000* (Water Supply Regulations, 2000).

2. Aims and Objectives

There are two aims of this project. The first aim is to identify spatial and temporal variability of water quality within the Bamford Water Treatment Works (WTW) catchment (see section 3.1). This will be achieved by one year of fortnightly spot sampling at eight of the tributaries into the reservoir system. The second aim is to assess the contribution of moorland condition to water quality within the Bamford WTW catchment. Similarly, this will be achieved by one year of fortnightly spot sampling at eight moorland streams. Overall, this project is intended to provide evidence of the potential impacts of moorland restoration and management on downstream water quality and DWS and WFD objectives.

3. Methods

3.1 Study area

The Bamford WTW catchment is located in the Upper Derwent Valley, Derbyshire. It is 20,159 ha in size, of which 12,302 ha (61%) is classified as moorland. The catchment consists of two main systems; the Upper Derwent River to the north (Rivers: Derwent, Westend, Alport and Ashop), and the River Noe to the south. The Bamford WTW catchment is located within the Humber RBD, and contains 11 water bodies. The current overall potential for all 11 water bodies is moderate, with five aiming to achieve good ecological status by 2027, and six aiming to achieve good ecological potential by 2027 (Table 3.1), due to being designated as heavily modified. The justification for not achieving good status by 2015 includes disproportionate expense and technical infeasibility (Environment Agency, 2009b).

Table 3.1: Sub-catchments within the Bamford WTW catchment.

Site ID	River	EA water body name	EA water body ID	Area/ ha	Moorland area/ ha	Current status	Status objective
1	River Derwent	River Derwent: Source to R Westend	GB104028057960	1850	1761	Moderate	Good ecological status by 2027
2	River Westend	River Westend: Source to R Derwent	GB104028057950	1465	1254	Moderate	Good ecological status by 2027
3	River Alport	River Alport: Source to River Ashop	GB104028057940	1127	940	Moderate	Good ecological status by 2027
4	River Ashop	River Ashop: Source to R Alport	GB104028057930	2705	2406	Moderate	Good ecological status by 2027
5	River Noe upper	River Noe: Source to Peakshole Water	GB104028057890	3515	2013	Moderate	Good ecological potential by 2027
6	Peakshole Water	Peakshole Water: Source to R Noe	GB104028057860	1263	127	Moderate	Good ecological status by 2027
7	River Noe lower	River Noe: Peakshole Water to R Derwent	GB104028057850	2269	137	Moderate	Good ecological potential by 2027
8	River Noe	River Derwent: R Ashop to R Wye	GB104028057880	758	187	Moderate	Good ecological potential by 2027
9	Ladybower Brook	Highshore Clough Catchment (trib of R Derwent)	GB104028057900	987	908	Moderate	Good ecological status by 2027
10	Abbey Brook	River Derwent: R Westend to R Ashop	GB104028057920	2647	1663	Moderate	Good ecological potential by 2027
11	River Ashop Lower	River Ashop: R Alport to R Derwent	GB104028057910	999	380	Moderate	Good ecological potential by 2027

3.2 Sub-catchment site selection

Eight sub-catchment sample sites were chosen (Table 3.2 and Figure 3.5) based on the existing sample sites used by the EA and / or STWL. This is because these are the most appropriate sample sites for characterising the water quality in each of the sub-catchments. As stated above, the Bamford WTW catchment consists of two main systems; the Upper Derwent River (eight sub-catchments) and the River Noe (three sub-catchments). Six 'Derwent' sub-catchments were sampled; those that were not included were essentially the Ladybower reservoir and sub-catchment immediately downstream. Sample sites for Abbey Brook and the River Noe upper sampled only a proportion of the sub-catchment they were within; see Figure 3.5. Apart from the River Noe upper sample site that monitored water quality from the southern Kinder plateau, the River Noe system was sampled from a site at the bottom of the three River Noe sub-catchments; the rationale for this is that there is very little moorland within these sub-catchments.

Table 3.2: Sub-catchment sample sites.

Site ID	Site name
AB	Abbey Brook
LB	Ladybower Brook
RAL	River Alport
RAS	River Ashop
RD	River Derwent
RNL	River Noe lower
RNU	River Noe upper
RW	River Westend

3.3 Moorland edge site selection

Moorland edge sites were located on deep peat soils at the edge of moorland plateaus. Seven sample sites (catchments) were chosen (Table 3.3 and Figure 3.5) to represent different peat conditions; these included bare peat (severely degraded and eroding), early stage restoration, vegetated but eroding (gullied), heather burn and an 'intact' reference site. These sites were initially chosen using relevant GIS layers and verified in the field by a site walk-over. Landscape Audit data (Chapman *et al.* 2010) and other relevant GIS datasets (i.e. gullies and heather burn areas) held by the MFFP were used to calculate the area in hectares and as a percentage of the catchment of land cover and management activities (see Table 3.4 and Table 3.5). An additional sample site (Nether Red Brook) was adopted at the end of April in response to low water flows at Upper Red Brook resulting in it not always being possible to collect a water sample. Like Upper Red Brook this sample site represents an early stage restoration peat condition.

Table 3.3: Moorland edge sample sites.

Site ID	Site name	Peat condition
FB	Fair Brook	Un-restored severely degraded (bare peat and gullies) (see Figure 3.1)
NRB	Nether Red Brook	Early stage (2 years) post restoration of bare peat and gullies (see Figure 3.2)
URB	Upper Red Brook	Early stage (2 years) restoration of bare peat and gullies
DD	Devils Dike	Un-restored degraded moorland - Low vegetation cover / low gullies
UNG	Upper North Grain	Un-restored degraded moorland - High vegetation cover / high gullies
GC	Green Clough	Heather burn (high area of burn)
WC	Within Clough	Heather burn (low area of burn) (see Figure 3.3)
AH	Ashop Head	Intact reference (high vegetation, low gullies) (see Figure 3.4)


Figure 3.1: Un-restored severely degraded (bare peat and gullies).


Figure 3.2: Early stage (2 years) post restoration of bare peat and gullies.


Figure 3.3: Heather burn.


Figure 3.4: 'Intact' reference.

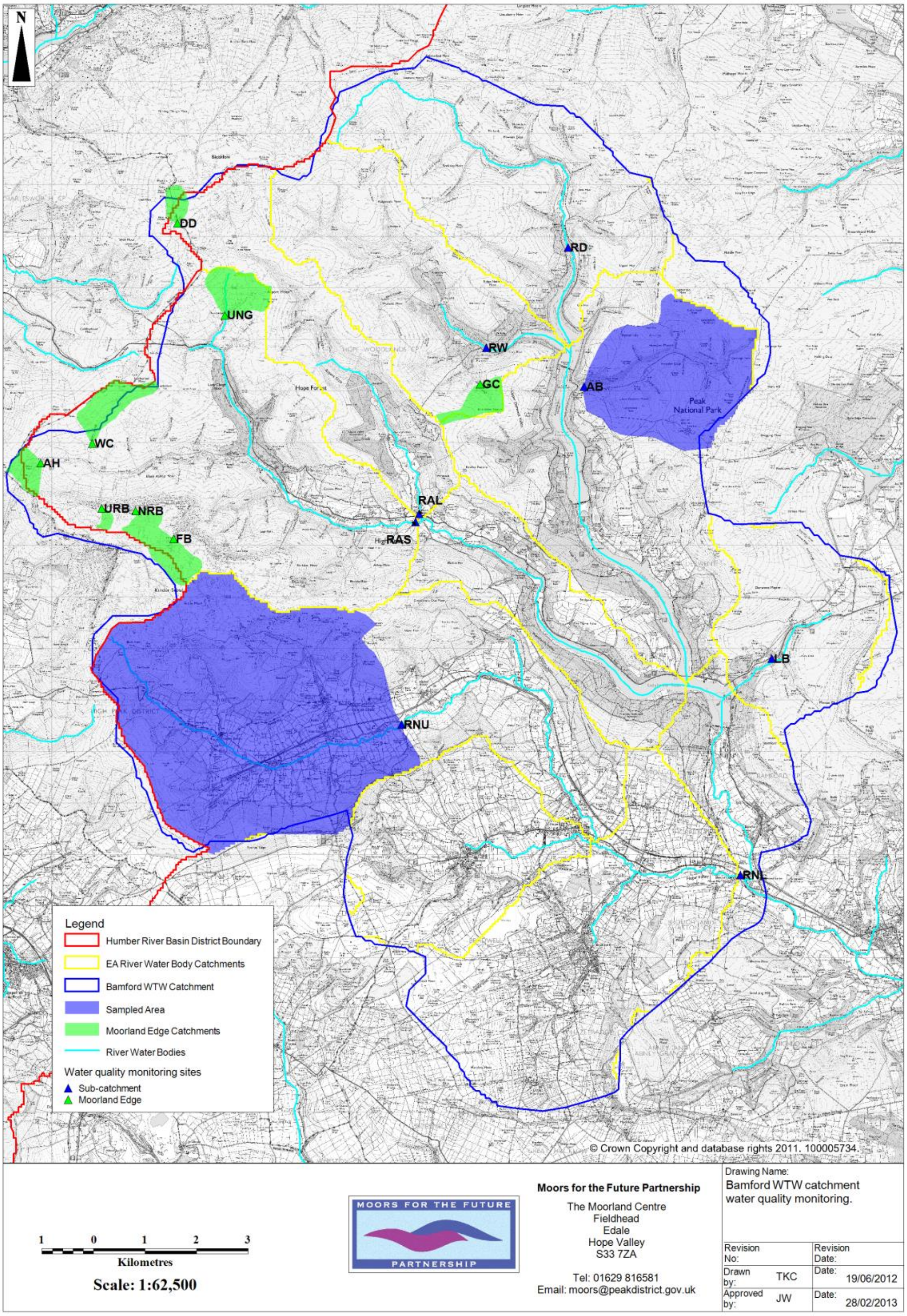

Figure 3.5: The Bamford WTW catchment showing moorland edge catchments and sample sites.

Table 3.4: Composition of land cover / management (ha) within moorland edge catchments (based on 2005 aerial imagery (Chapman et al. 2010)).

	Area / hectares										
Site	Area	Bare peat	Mineral soil	Bilberry	Bracken	Cotton grass	Grasses	Heather	Rushes	Heather burn	Gullies / km
FB	60.9	31.8	7.1	4.7	0.3	14.7	1.0	0.0	1.2	0.0	10.4
NRB	31.3	12.0	7.0	1.0	0.1	9.7	0.1	0.1	1.2	0.0	5.3
URB	8.3	3.2	0.8	0.0	0.0	3.8	0.0	0.4	0.1	0.0	1.7
DD	25.5	13.2	1.3	2.7	0.2	6.2	0.2	0.0	1.6	0.0	3.2
UNG	86.3	5.0	1.6	8.8	2.3	37.6	16.8	1.0	13.2	0.0	10.3
GC	54.4	0.9	0.4	2.1	1.6	3.4	1.4	42.7	1.9	52.0	2.7
WC	78.8	1.1	0.8	8.7	0.8	30.4	2.7	28.3	6.1	12.8	3.2
AH	38.4	1.3	0.8	8.6	0.5	11.5	4.4	1.0	10.3	0.0	3.0

Table 3.5: Composition of land cover / management (%) within moorland edge catchments (based on 2005 aerial imagery (Chapman et al. 2010); gully length = extent (length) of gullies per km^2.

		Area / %									
Site	Area / ha	Bare peat	Mineral soil	Bilberry	Bracken	Cotton grass	Grasses	Heather	Rushes	Heather burn	Gullies
FB	60.9	52.3	11.6	7.8	0.5	24.1	1.6	0.0	2.0	0.0	17.0
NRB	31.3	38.2	22.4	3.3	0.4	31.0	0.2	0.3	4.0	0.0	17.0
URB	8.3	38.0	9.2	0.1	0.2	45.9	0.0	5.3	0.6	0.0	19.9
DD	25.5	51.6	5.1	10.7	0.7	24.3	0.8	0.2	6.4	0.0	12.5
UNG	86.3	5.7	1.8	10.2	2.7	43.6	19.5	1.2	15.3	0.0	11.9
GC	54.4	1.7	0.7	3.8	3.0	6.2	2.5	78.5	3.5	95.6	5.0
WC	78.8	1.3	1.0	11.0	1.0	38.6	3.4	35.9	7.7	16.3	4.1
AH	38.4	3.5	2.1	22.3	1.4	29.9	11.3	2.7	26.8	0.0	7.8

3.4 Fieldwork

A year long programme of fortnightly spot sampling began on 9 January 2012 and was completed on 4 January 2013. Samples were generally collected in the same order between Monday and Wednesday of the same week. All stream water was collected using sterile 1000 ml storage bottles that were pre-rinsed with stream water three times. Samples were refrigerated within seven hours of collection. The acceptable temperature range for the sample storage environment is 1-8 °C. However, for most analytical purposes best practice is to keep the samples at a constant temperature of not more than 5 °C (Environment Agency, 2010). Samples were collected by Scientific Analysis Laboratories (SAL) Ltd. within 5 days of sampling. SAL has a maximum turnaround time of 10 days; therefore, samples were always analysed within 16 days, as recommended by SAL for Dissolved Organic Carbon (DOC), Particulate Organic Carbon (POC) and Total Organic Carbon (TOC). Analyses requested by the EA included pH, total hardness, DOC, copper (dissolved) and zinc (total) and were analysed fortnightly. Analyses requested by STWL included colour and iron (total) and were analysed monthly. In addition to the analyses requested by the EA and STWL, water samples were also analysed for a number of other determinands as part of the analysis suite (see Table 3.6 for a full list of analyses (those requested by EA and STWL are shown in bold)). In addition, stream temperature was recorded using an electronic thermometer (Hanna Instruments HI-8751) and rainfall was measured using a tipping-bucket rain gauge (Skye Instruments ARG 100/1) connected to a data logger (Skye Instruments SDL 5200 DataHog2) which automatically records the total number of tips in every 10 minute period.

Figure 3.6: Volunteer Simon Cunningham collecting a water sample from Fair Brook.

Table 3.6: Water sample analyses, level of detection (LOD), technique, accreditation, DWS and WFD objectives.

Determinand	LOD	Unit	Technique	Accreditation	DWS	WFD
Colour	**1**	**Hazen**	**Colorimetry**	**None**	**20 HU**	
pH			**Probe**	**UKAS**		**5.2**
Total hardness ($CaCO_3$)	**10**	**mg/l**	**ICP/OES**	**None**		
Dissolved Organic Carbon	**1**	**mg/l**	**OX/IR**	**None**		
Particulate Organic Carbon	1	mg/l	Calc	None		
Total Organic Carbon	1	mg/l	OX/IR	UKAS		
Arsenic	0.2	µg/l	ICP/MS (Filtered)	UKAS	10 µg/l	50 µg/l*
Barium	1	µg/l	ICP/MS (Filtered)	UKAS		
Beryllium	0.05	µg/l	ICP/MS (Filtered)	UKAS		
Cadmium	0.02	µg/l	ICP/MS (Filtered)	UKAS	5 µg/l	
Chromium	1	µg/l	ICP/MS (Filtered)	UKAS	50 µg/l	3.4-4.7 µg/l*
Copper	**0.5**	**µg/l**	**ICP/MS (Filtered)**	**UKAS**	**2 mg/l**	**1-28 µg/l***
Lead	0.3	µg/l	ICP/MS (Filtered)	UKAS	25 µg/l	
Mercury	0.05	µg/l	ICP/MS (Filtered)	UKAS	1 µg/l	
Nickel	1	µg/l	ICP/MS (Filtered)	UKAS	20 µg/l	
Selenium	0.5	µg/l	ICP/MS (Filtered)	UKAS	10 µg/l	
Vanadium	2	µg/l	ICP/MS (Filtered)	UKAS		
Zinc	2	µg/l	ICP/MS (Filtered)	UKAS		
Arsenic	0.2	µg/l	ICP/MS (Total)	UKAS	10 µg/l	
Barium	1	µg/l	ICP/MS (Total)	UKAS		
Beryllium	0.05	µg/l	ICP/MS (Total)	UKAS		
Cadmium	0.02	µg/l	ICP/MS (Total)	UKAS	5 µg/l	
Chromium	1	µg/l	ICP/MS (Total)	UKAS	50 µg/l	
Copper	0.5	µg/l	ICP/MS (Total)	UKAS	2 mg/l	
Lead	0.3	µg/l	ICP/MS (Total)	UKAS	25 µg/l	
Mercury	0.05	µg/l	ICP/MS (Total)	UKAS	1 µg/l	
Selenium	0.5	µg/l	ICP/MS (Total)	UKAS	10 µg/l	
Vanadium	2	µg/l	ICP/MS (Total)	UKAS		
Zinc	**2**	**µg/l**	**ICP/MS (Total)**	**UKAS**		**8-125 µg/l***
Aluminium	0.02	mg/l	ICP/OES (Total)	UKAS	200 µg/l	
Boron	0.01	mg/l	ICP/OES (Total)	none	1 mg/l	
Iron	**0.01**	**mg/l**	**ICP/OES (Total)**	**none**	**200 µg/l**	

* Annual mean

3.5 Laboratory analysis

To determine the concentration of DOC samples are filtered (SAL, 2013), then analysed using a UKAS accredited IL550 (Lianne Bromiley, personal communication). This instrument converts the organic carbon in the sample to CO_2 by catalytic combustion. The CO_2 produced is then measured directly using an infrared detector to determine the concentration of TOC. POC is calculated by subtracting DOC from TOC (SAL, 2013). To determine colour a filtered sample is analysed using a UV-visible spectrophotometer. Colour is interpreted in terms of the platinum-cobalt scale (Hazen units (H.U.)) by comparison to known PtCo standards (Lianne Bromiley, personal communication). A pH meter is used to measure the pH. Two analytical procedures were used to determine the concentration of metals; Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) for the determination of Arsenic, Barium, Beryllium, Cadmium, Copper, Lead, Mercury, Nickel, Selenium, Vanadium and Zinc, and

Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) for the determination of Aluminium, Boron and Iron. The level of detection (LOD) is dependent upon the specific metal; ICP-MS is capable of a lower LOD than ICP-OES; therefore it was the preferred method for the determination of most metals. However, not all metals could be determined using this method, e.g. Iron; therefore ICP-OES was also used. ICP-OES was also used to determine total hardness ($CaCO_3$). For more detailed method statements see SAL (2013).

3.6 GIS

Existing Environment Agency (EA) data was used to delineate the Humber river basin district boundary, EA river water body catchments and river water bodies. Existing STWL data was used to delineate the Bamford WTW catchment. Water body catchments for the moorland edge sites were delineated manually using MapInfo Professional 11.0. There is some disparity between these boundaries / catchments which is presumably due to the different methods of boundary / catchment delineation used.

3.7 Statistical analyses

All statistical tests were carried out in SPSS 17.0. One-way analysis of variance (ANOVA) was used to investigate differences between moorland edge sites in the concentration of DOC and Zinc. This method assumes that data are normally distributed. In addition, Fisher's LSD test was used to identify between which sites the differences occurred. In cases where the data was not normally distributed the non-parametric Kruskal-Wallis test was used. Non-normal data occurred for the following determinands: pH, colour, copper, iron, aluminium and chromium. Boxplots were used to identify between which sites the differences occurred. Spearman's rank order correlation was used to investigate the relationships between the various determinands.

4. Results

The Environment Agency requested fortnightly analysis of dissolved organic carbon (DOC), pH, total hardness, dissolved copper (Cu) and total zinc (Zn). Severn Trent Water Ltd (STWL) requested monthly analysis of colour and total Iron (Fe). In addition to the analyses requested by the EA and STWL, water samples were also analysed for a number of other determinands as part of the analysis suite (see Table 3.6 for a full list of analyses). Of particular interest are the results for total aluminium (Al) (analysed monthly) and dissolved chromium (Cr) (analysed fortnightly). The results for DOC, pH, total hardness, Cu, Cr and Zn are considered in relation to the Water Framework Directive (WFD) ‘good’ standard; and the results for colour, Al and Fe are considered in relation to the Drinking Water Standards (DWS). The WFD ‘good’ standard is generally specified as an annual mean concentration; therefore, the following results are presented as an annual mean for each site and a mean for sub-catchment and moorland edge sites for each sample week. In the following text, all determinands are referred to as concentrations. Data on rainfall and water temperature was also recorded to provide contextual information. Summary statistics for all determinands are presented in section 9.1.

4.1 Rainfall

Rainfall data was collected under the MFFP's Defra / EA funded Making Space for Water project. Mean total rainfall was calculated from three weather stations (one located on Bleaklow and two located on Kinder Scout). No data was available for January and February. Of the available data, rainfall ranged from 39 mm in March to 309 mm in June (Figure 4.1). The period from April to June is the wettest recorded for the UK (Met Office, 2012).

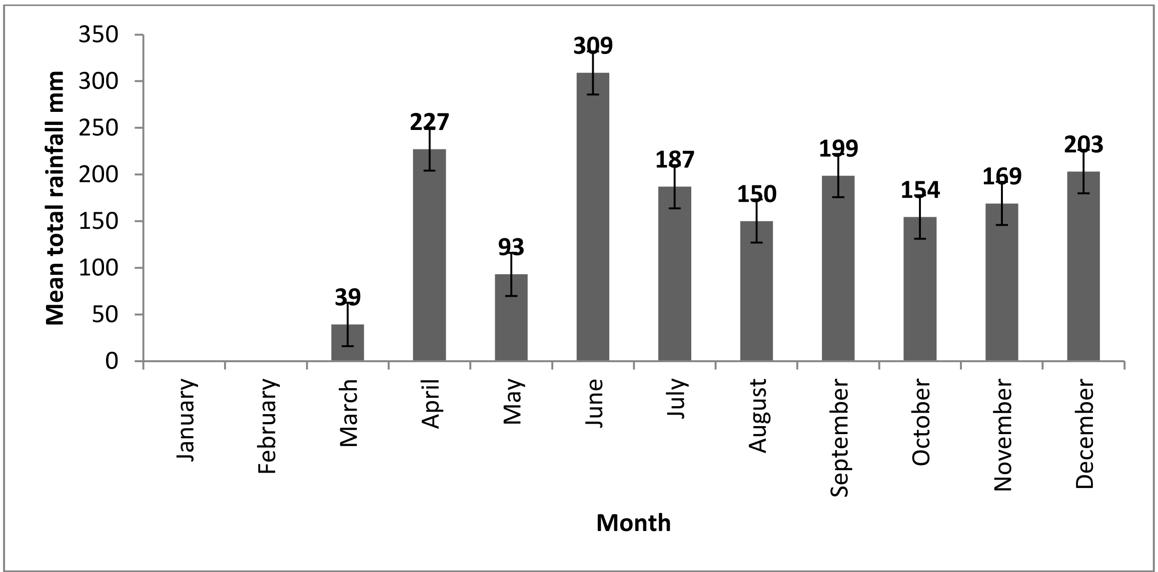

Figure 4.1: Mean total monthly rainfall for 2012.

4.2 Water temperature

Mean water temperature across all sampling locations ranged from 2.5 °C to 14.3 °C (Figure 4.2).

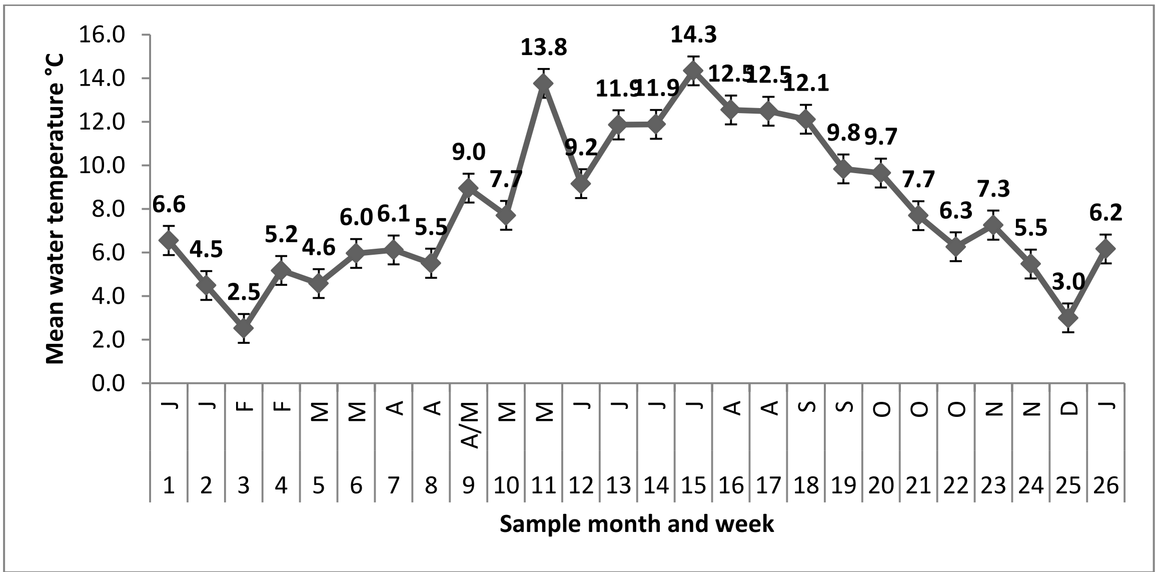

Figure 4.2: Mean water temperature for all sites within the Bamford WTW catchment.

4.3 Dissolved Organic Carbon

The annual mean DOC for sub-catchment sites is 8 mg/l. This ranges from 4 mg/l at the River Noe lower to 12 mg/l at Ladybower Brook (Figure 4.3). Annual mean DOC for moorland edge sites is 20 mg/l. This ranges from 9 mg/l at Ashop Head to 29mg/l at Upper Red Brook (Figure 4.4). There is no DWS (Water Supply Regulations, 2000) or WFD 'good' standard for DOC (WFD, 2010).

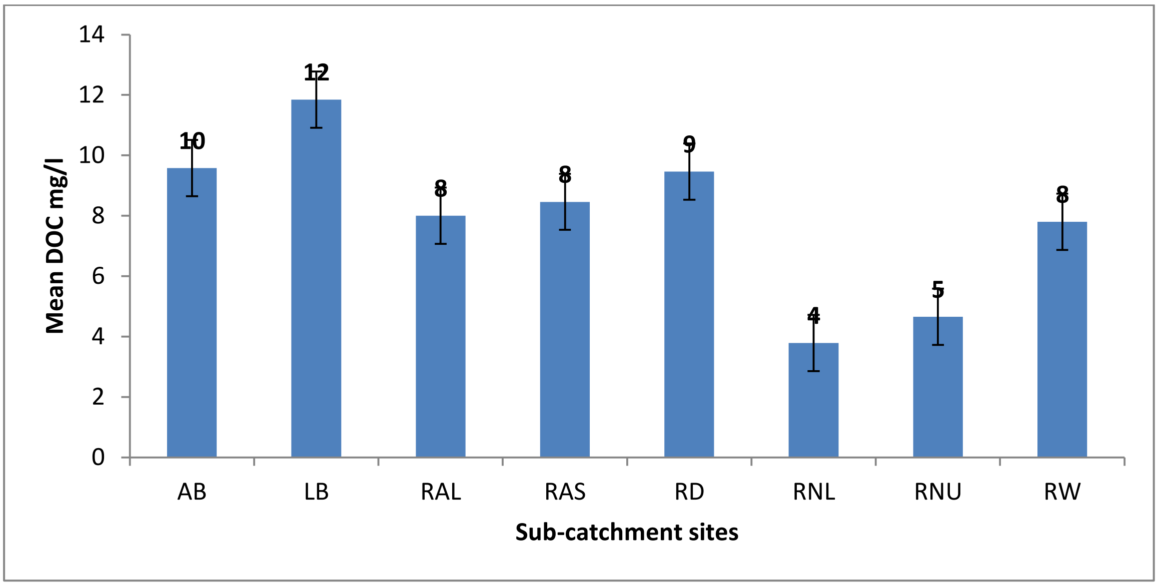

Figure 4.3: Annual mean DOC at eight sub-catchment sites within the Bamford WTW catchment.

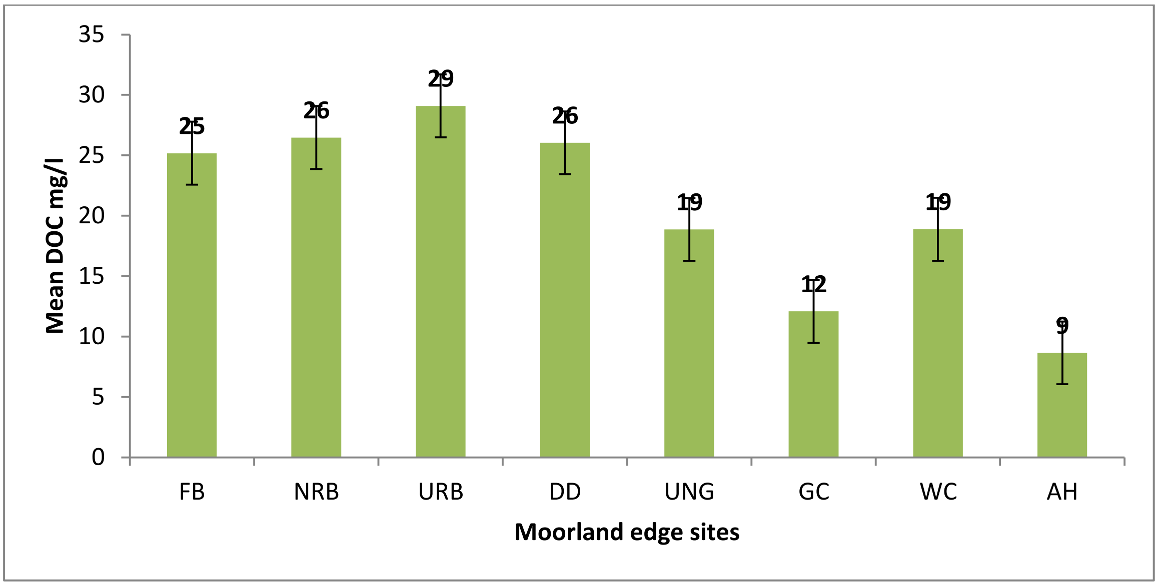

Figure 4.4: Annual mean DOC at eight moorland edge sites within the Bamford WTW catchment (sites displayed along a gradient from unrestored (FB) to intact reference site (AH).

One-way ANOVA was used to look for differences in the concentration of DOC between moorland edge sites. There are significant differences in the concentration of DOC between the moorland edge sites ($F_{(7,178)} = 17.24$; $P < 0.001$). Fisher's LSD post hoc test showed where differences exist (see Table 4.1). FB, NRB, URB and DD have a significantly higher mean concentration of DOC than UNG, GC, WC and AH; and UNG and WC have a significantly higher mean concentration of DOC than GC and AH. This shows that the mean concentration of DOC is significantly higher at the more degraded moorland sites and significantly lower at the less degraded sites (see Table 3.3).

Table 4.1: Post hoc (Fisher's LSD test) for differences in the concentration of DOC between moorland edge sites.

	NRB	URB	DD	UNG	GC	WC	AH
FB	0.64	0.13	0.73	0.01*	0.00***	0.01*	0.00***
NRB		0.35	0.86	0.01**	0.00***	0.00***	0.00***
URB			0.24	0.00***	0.00***	0.00***	0.00***
DD				0.00***	0.00***	0.00***	0.00***
UNG					0.01**	0.99	0.00***
GC						0.01**	0.15
WC							0.00***

(Significance levels: * 0.05, ** 0.01, *** 0.001)

At the sub-catchment scale the mean DOC ranged from 3 mg/l to 17 mg/l (Figure 4.5). At the moorland edge scale the mean DOC ranged from 3 mg/l to 33 mg/l (Figure 4.6).

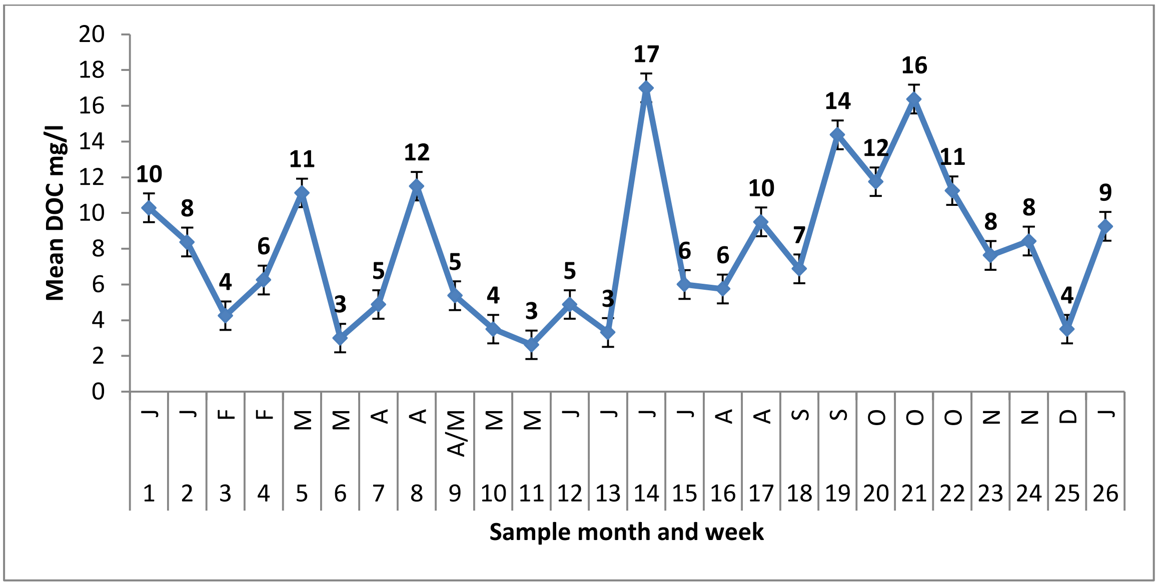

Figure 4.5: Mean DOC for sub-catchment sites within the Bamford WTW catchment over time.

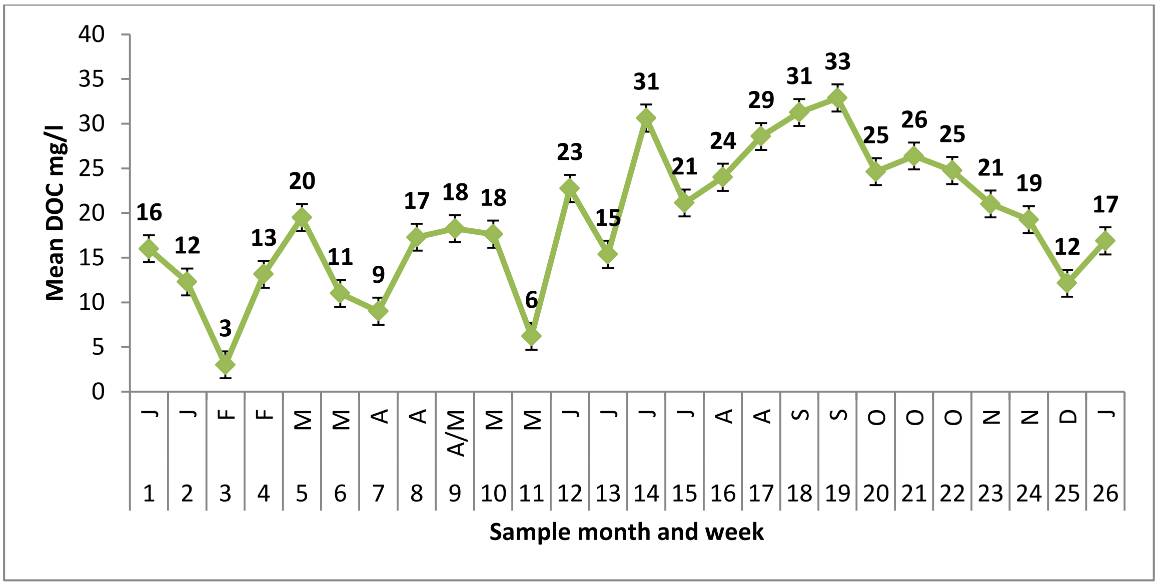

Figure 4.6: Mean DOC for moorland edge sites within the Bamford WTW catchment over time.

4.4 Particulate Organic Carbon

4.4.1 POC concentrations across sub-catchments

POC concentrations > 1 mg/l were recorded during 37 of 208 (18 %) sampling events; samples with the minimum level of detectable POC (1 mg /l) comprised 46 % of these POC positive events (Figure 4.7). The maximum level of POC recorded was 6 mg/l; this was only recorded on two sampling occasions, in the same sampling week (start October) at the Rivers Derwent and Westend.

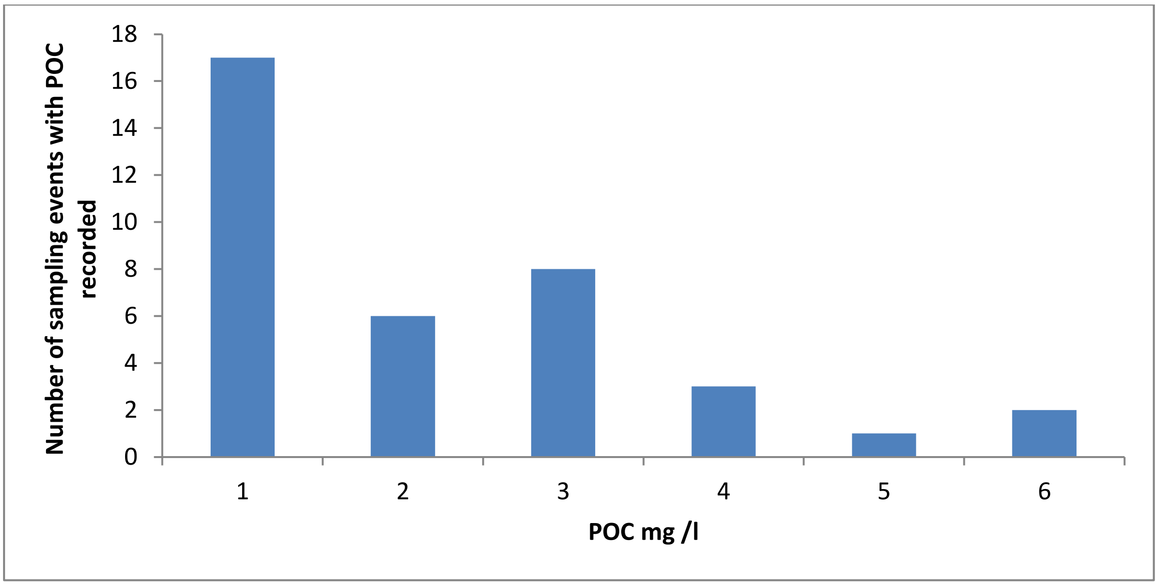

Figure 4.7: Number of sampling events that recorded POC concentrations ≥ 1 mg/l.

POC concentrations above the level of detection were recorded within catchments between 3 (12 %) and 8 (31 %) times during the 26 event sampling programme. At the sub-catchment scale Ladybower Brook and the River Derwent recorded the greatest number of POC positive sampling events (Figure 4.8).

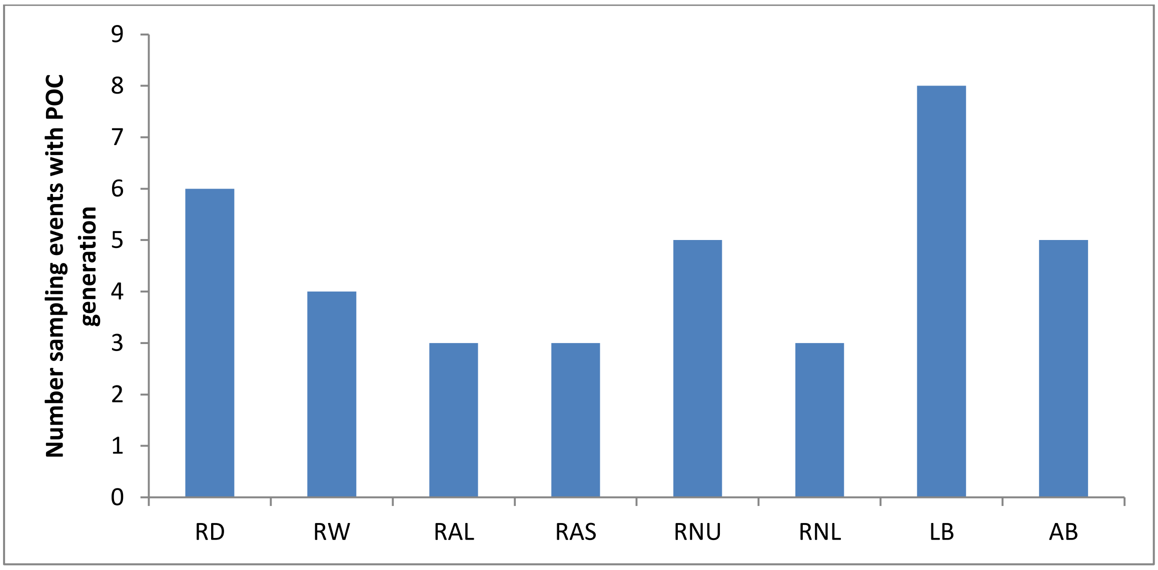

Figure 4.8: Number of sampling events recording POC ≥ 1mg/l across sub-catchments.

There are a number of occasions when POC positive sampling events are recorded (Figure 4.9). During 2012, in weeks 10 (mid May) and 20 (start October) all catchments, except the Rivers Ashop and Noe, recorded POC, with further 'spikes' in weeks 8 (mid April) and 15 (end July).

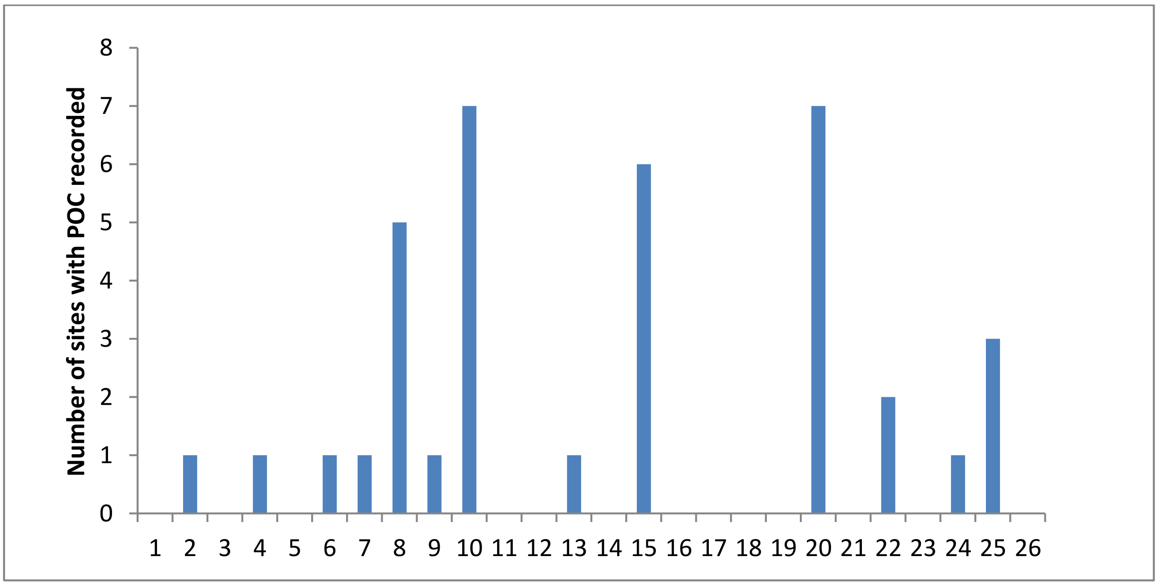

Figure 4.9: Temporal pattern of POC concentrations.

4.4.2 POC concentrations across moorland peat catchments

At moorland edge catchments, 65 of the 208 sampling events (31%) recorded POC concentrations ≥ 1 mg/l (Figure 4.10). Moorland edge catchments were classified into four groups un-restored, early stage restoration, heather burn and intact reference. There was no significant difference between the number of sampling events that were recorded as POC positive between these categories (G_{adj} = 4.90, df = 3, P = 0.179).

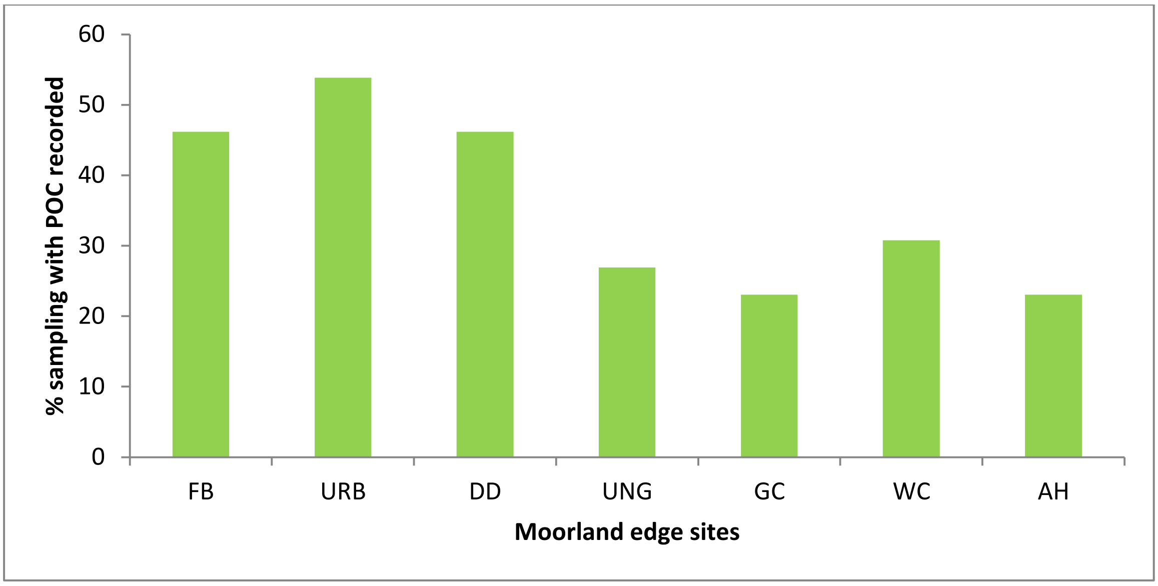

Figure 4.10: Proportion of sampling events across moorland edge catchments that recorded positive POC concentrations.

There is temporal variation in POC concentration across catchments, with peaks in weeks 9 and 10 (start May) and week 20 (start October) – POC was recorded from all moorland catchments in these weeks, except WC, a heather burn catchment (Figure 4.11). Other periods when POC generation was widespread across moorland catchments was week 6 (end March), weeks 14-15 (end June) and week 25 (December).

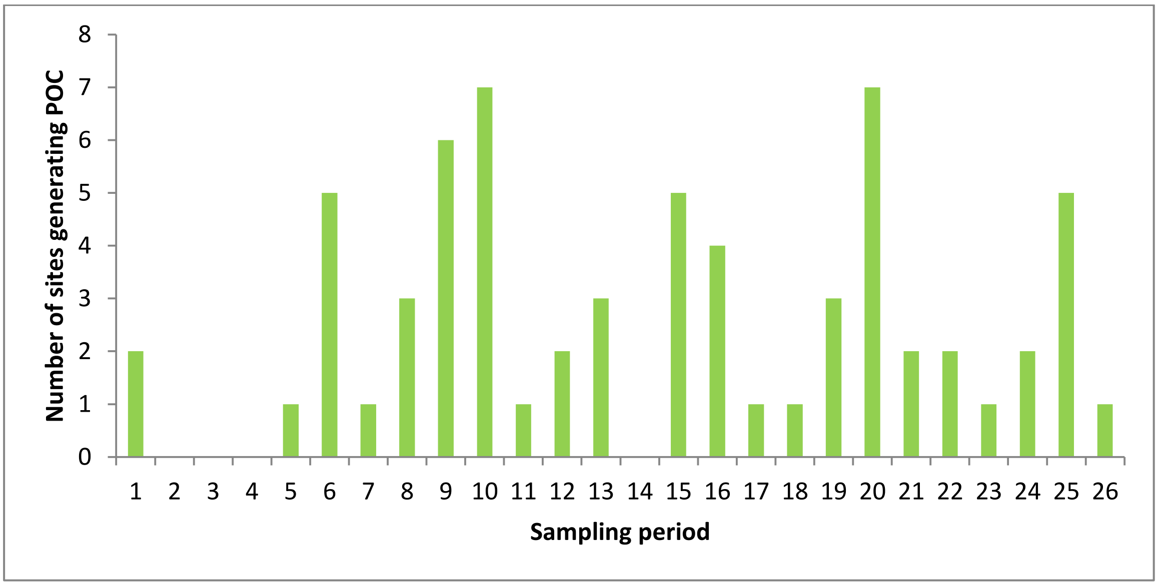

Figure 4.11: POC generation (number of sites generating POC) over the fortnightly sampling programme in 2012.

Thirty-eight percent of the (65) sampling events when concentrations of POC ≥ 1 mg/l were recorded were the minimum detectable (1 mg/l). Samples with 'extremely' high POC (18.5, 19 and 27 mg/l) were only recorded during three sampling events (weeks 5, 10 and 13); the former from UNG the latter two records from DD – both unrestored sites (Figure 4.12).

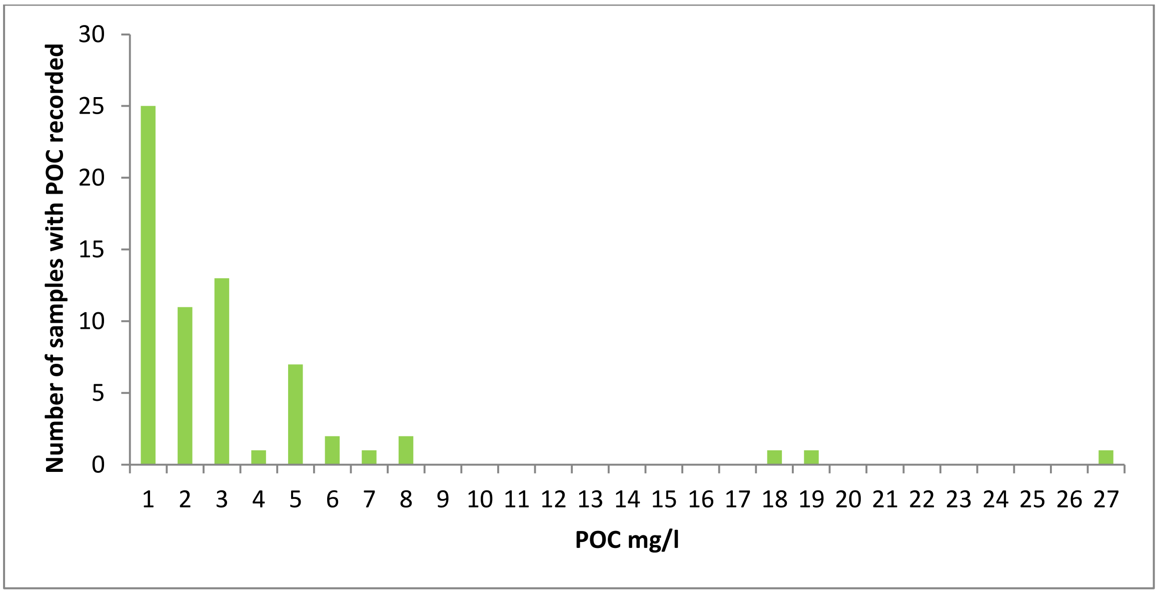

Figure 4.12: Level of concentration of POC from moorland edge sites during POC positive events.

When POC above 1 mg/l was recorded, higher, more extreme, levels of POC were recorded significantly more frequently from unrestored moorland catchments than other moorland conditions (G = 12.59, df = 6, P < 0.05) (Figure 4.13).

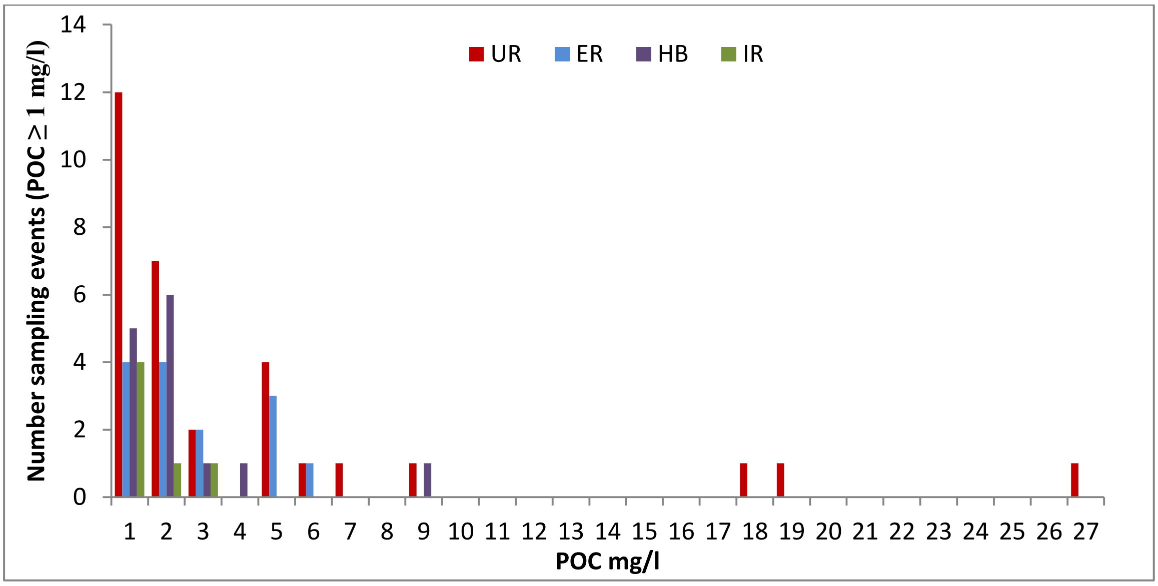

Figure 4.13: Level of POC concentration in water samples between moorland catchment 'conditions' (red = un-restored; blue = early stage restoration, purple = heather burn; green = intact reference).

4.5 pH

The WFD 'good' standard for pH is between 6 (as a 5 percentile) and 9 (as a 95 percentile) (Suzanne Haldane, personal communication; WFD, 2010). The annual mean pH for sub-catchment sites is 6.8. This ranges from 6.5 at the Rivers Alport, Derwent and Westend to 7.8 at the River Noe lower (Figure 4.14). The annual mean pH for moorland edge sites is 5.1. This ranges from 4.1 at Fair Brook to 6.5 at Ashop Head (Figure 4.15). At the sub-catchment scale all sites have an annual mean pH between 6 and 9; however, due to the way in which pH is assessed only the River Ashop, Noe upper and Noe lower are achieving the WFD 'good' standard (see Appendix 9.2). Similarly, at the moorland edge scale Green Clough and Ashop Head have an annual mean pH between 6 and 9; however no sites are achieving the WFD 'good' standard (see Appendix 9.2).

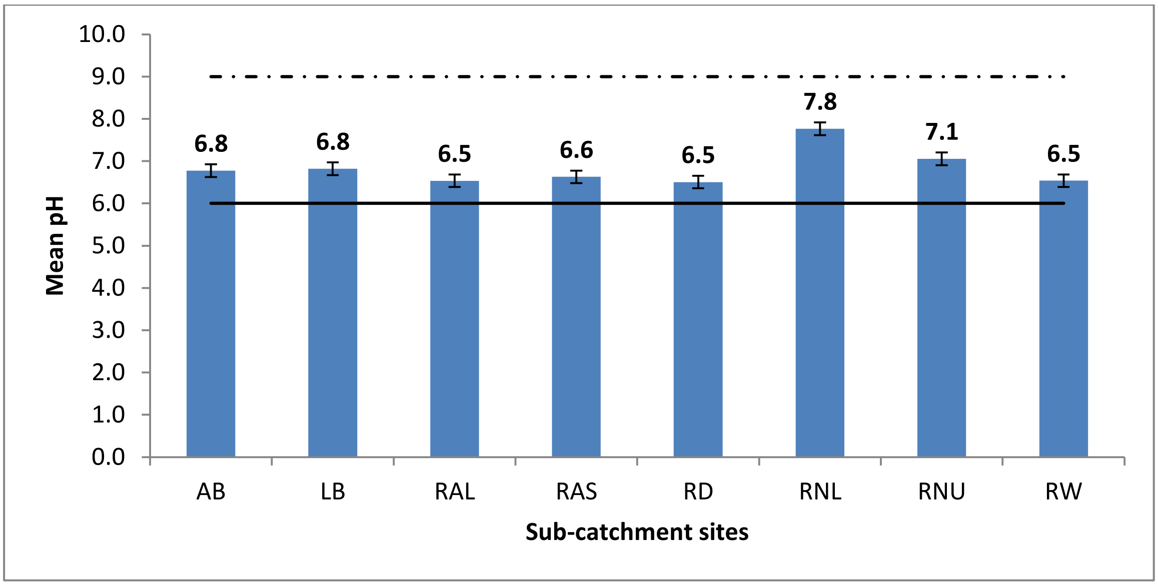

Figure 4.14: Annual mean pH at eight sub-catchment sites within the Bamford WTW catchment (black solid line = WFD lower limit; black dash line = WFD upper limit).

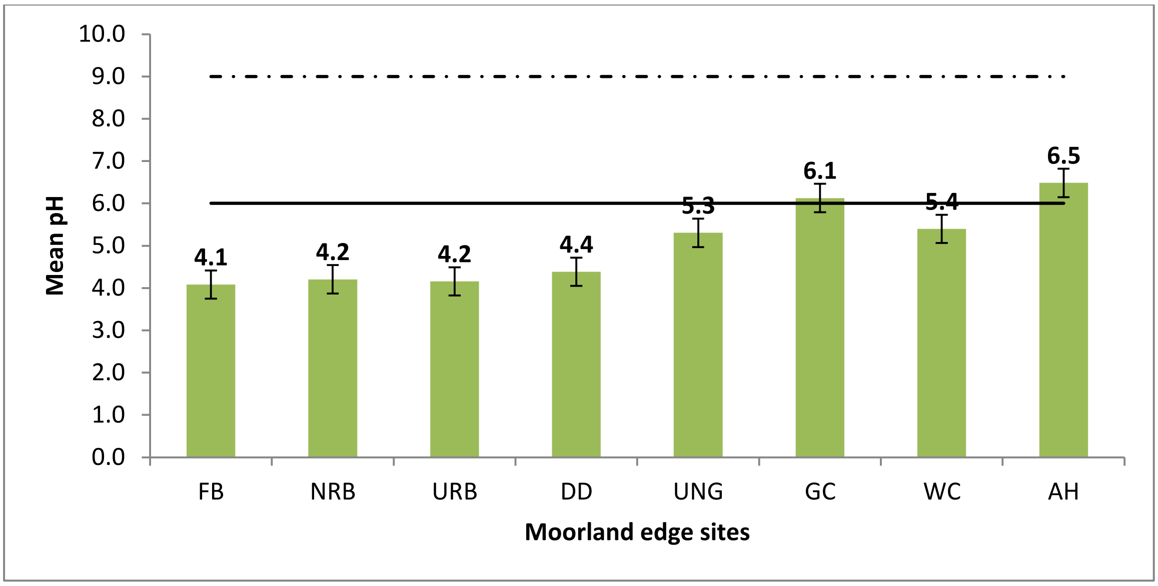

Figure 4.15: Annual mean pH at eight moorland edge sites within the Bamford WTW catchment (sites displayed along a gradient from un-restored (FB) to intact reference site (AH); black solid line = WFD lower limit; black dash line = WFD upper limit).

There are significant differences in pH between moorland edge sites ($\chi^2 = 123.41$, d.f. = 7, $P < 0.001$; Figure 4.16). FB, NRB, URB and DD have a significantly lower median pH than UNG, GC, WC and AH. This shows that the median pH is significantly lower at the more degraded moorland sites and significantly higher at the less degraded sites (see Table 3.5).

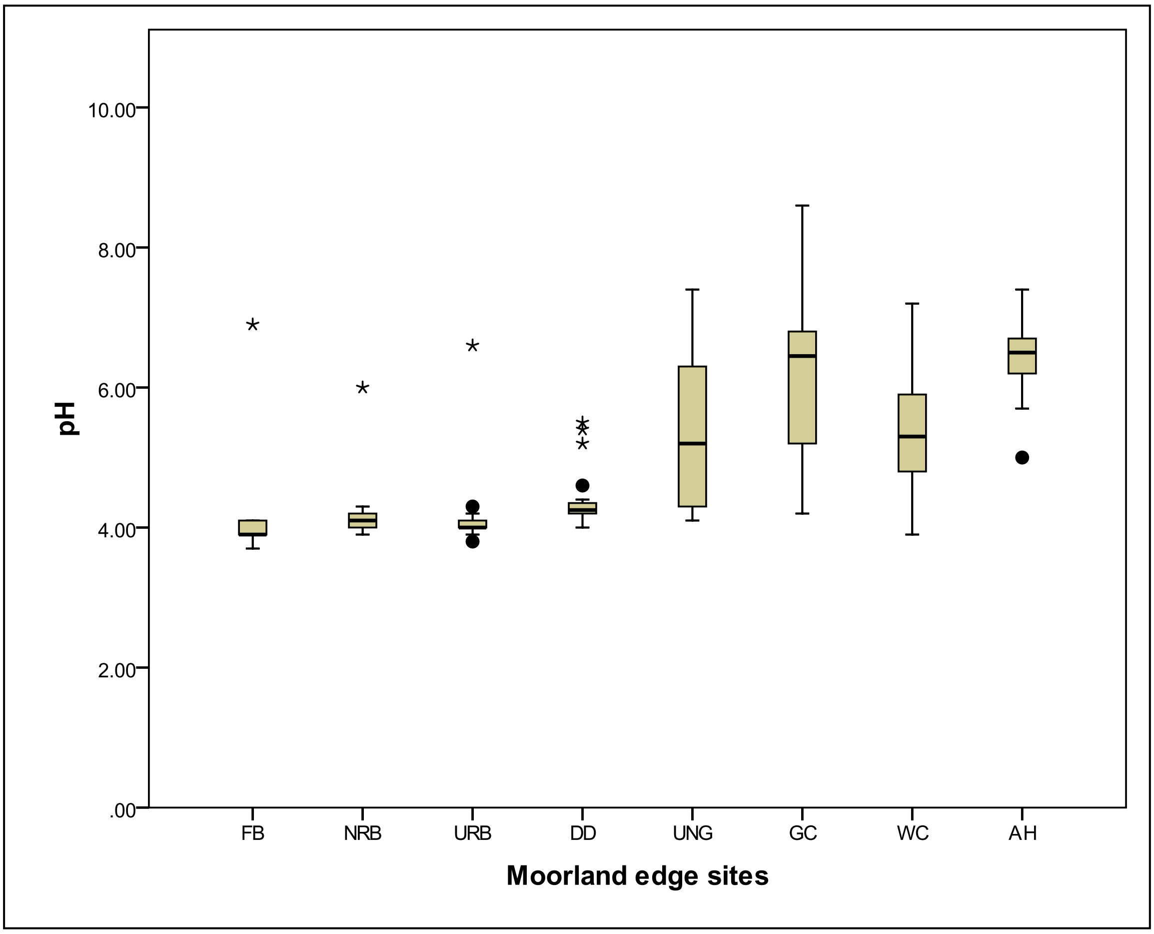

Figure 4.16: Boxplot showing differences in pH between moorland edge sites.

At the sub-catchment scale the mean pH ranged from 5.8 to 7.6 (Figure 4.17); therefore, the WFD 'good' standard for pH is being achieved at 90 % of sampling events. At the moorland edge scale the mean pH ranged from 4.5 to 7.0 (Figure 4.18) therefore, the WFD 'good' standard is being achieved only at 12 % of sampling events.

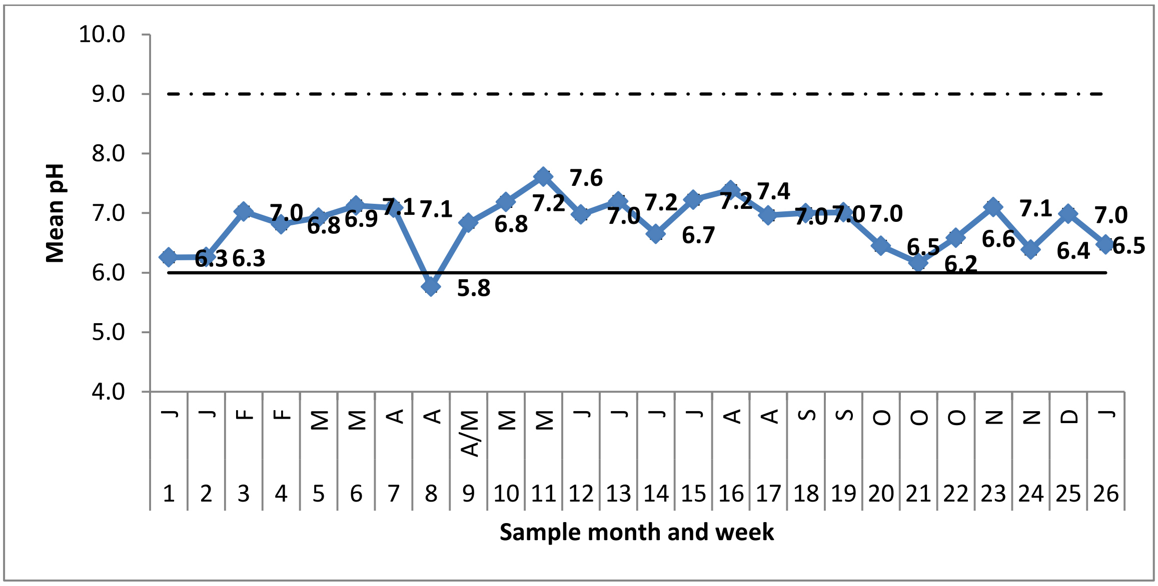

Figure 4.17: Mean pH for sub-catchment sites within the Bamford WTW catchment over time (black solid line = WFD lower limit; black dash line = WFD upper limit).

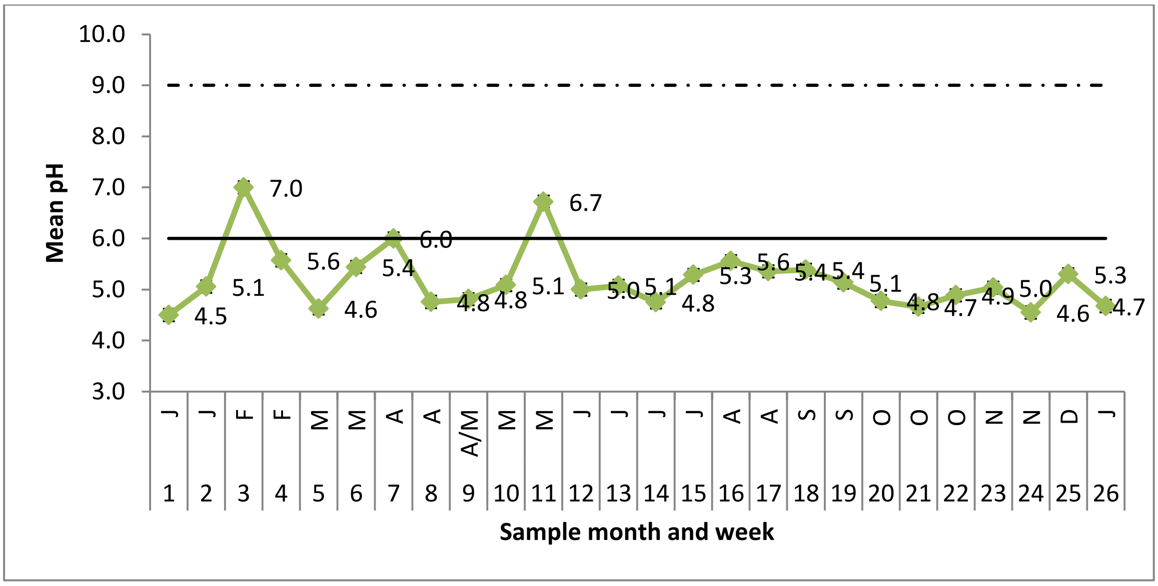

Figure 4.18: Mean pH for moorland edge sites within the Bamford WTW catchment over time (black solid line = WFD lower limit; black dash line = WFD upper limit).

4.6 Total hardness (expressed as $CaCO_3$)

The annual mean $CaCO_3$ for sub-catchment sites is 42 mg/l. This ranges from 16 mg/l at the River Derwent to 172 mg/l at the River Noe lower (Figure 4.19). The annual mean $CaCO_3$ for moorland edge sites is 11 mg/l. This ranges from 5 mg/l at Devils Dike to 22 mg/l at Ashop Head (Figure 4.20). There is no DWS or WFD 'good' standard for $CaCO_3$; however, the concentration of $CaCO_3$ does have implications for the WFD 'good' standards for Cu and Zn – see sections 4.7 and 4.8 (WFD, 2010).

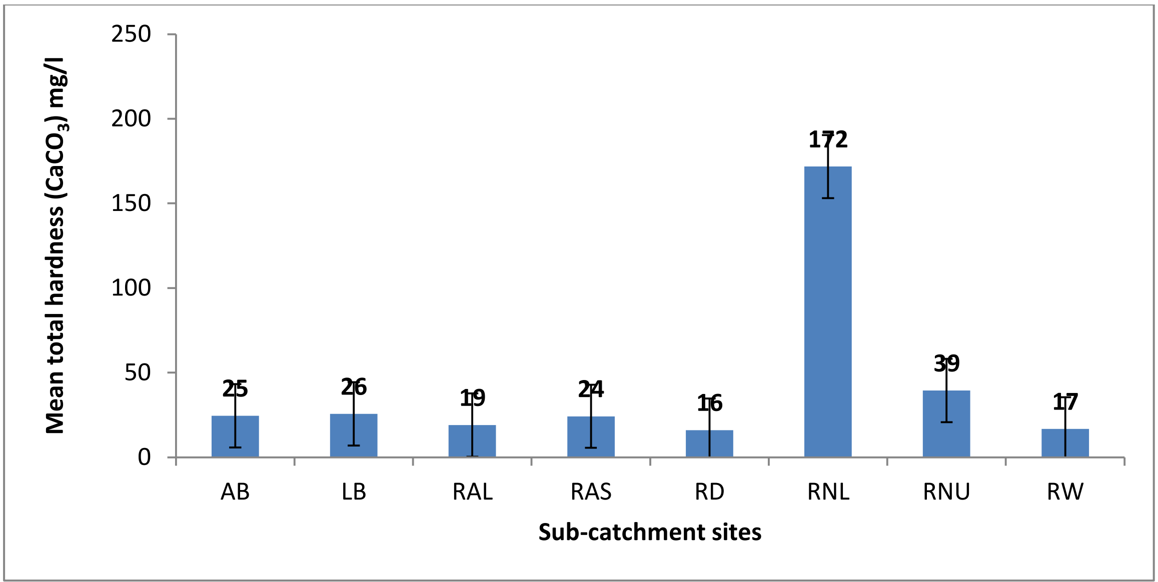

Figure 4.19: Annual mean $CaC0_3$ at eight sub-catchment sites within the Bamford WTW catchment.

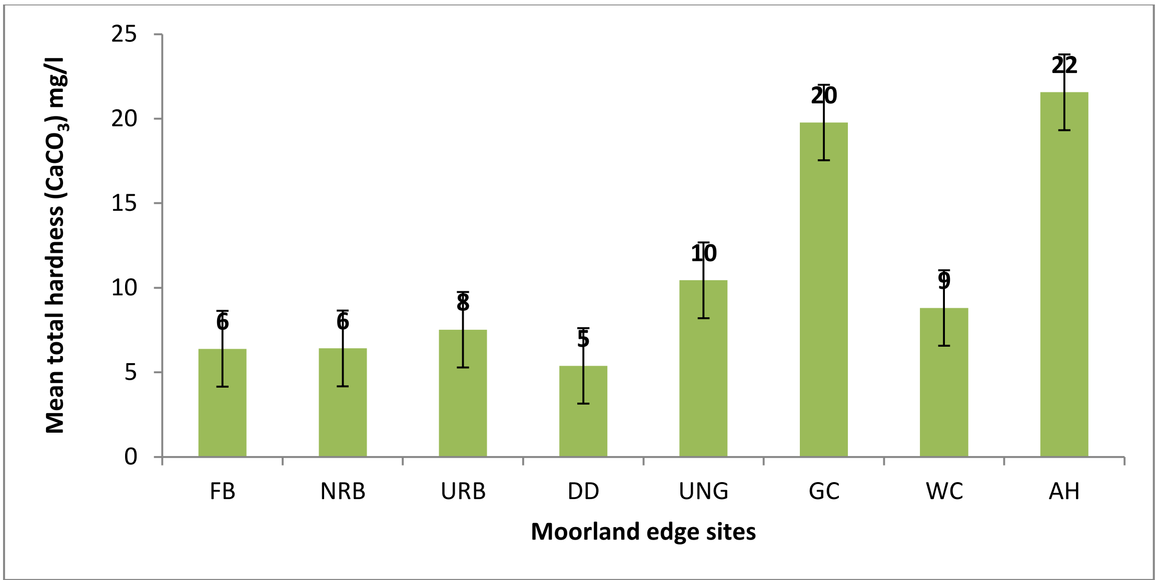

Figure 4.20: Annual mean $CaC0_3$ at eight moorland edge sites within the Bamford WTW catchment (sites displayed along a gradient from un-restored (FB) to intact reference site (AH).

At the sub-catchment scale the mean $CaCO_3$ ranged from 29 mg/l to 54 mg/l (Figure 4.21). At the moorland edge scale the mean pH ranged from 6 mg/l to 27 mg/l (Figure 4.22).

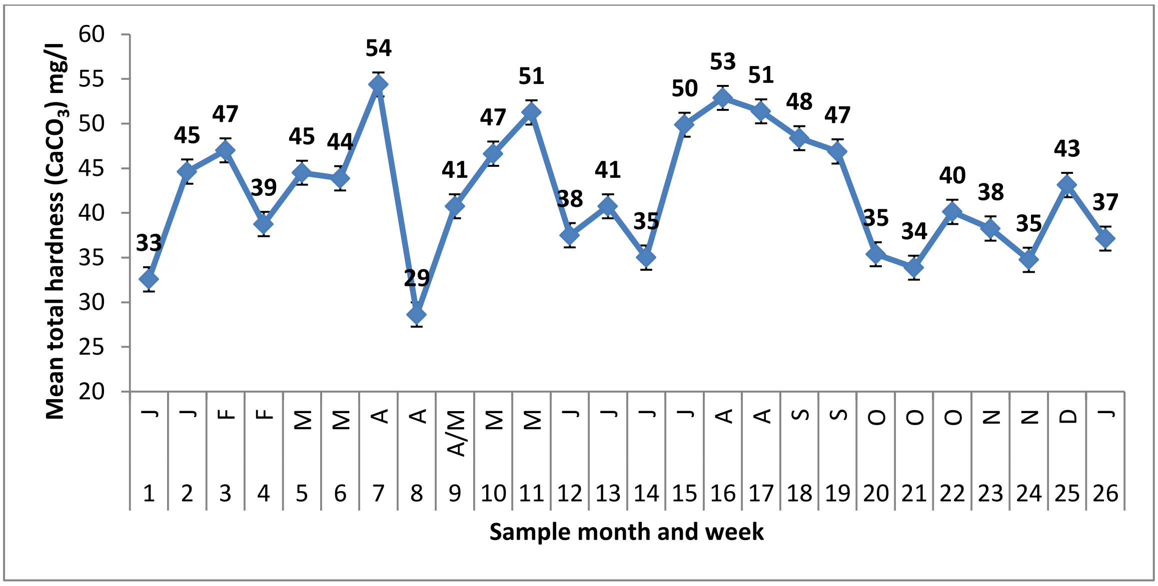

Figure 4.21: Mean $CaC0_3$ for sub-catchment sites within the Bamford WTW catchment over time.

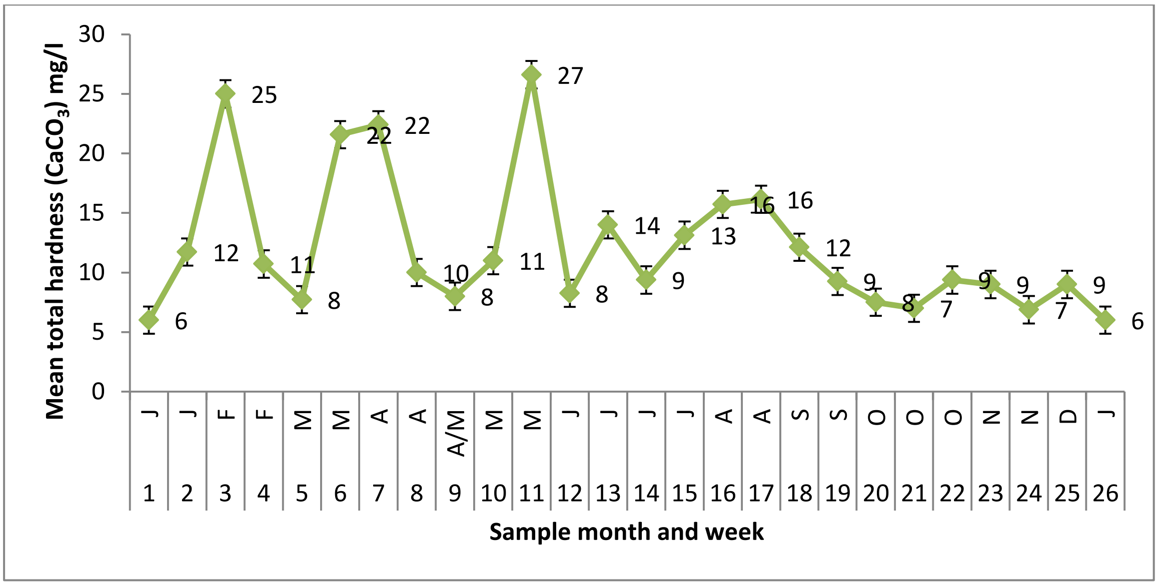

Figure 4.22: Mean $CaC0_3$ for moorland edge sites within the Bamford WTW catchment over time.

4.7 Copper dissolved

The annual mean Cu for sub-catchment sites is 1.3 µg/l. This ranges from 1.0 µg/l at Abbey Brook to 1.6 µg/l at the River Alport (Figure 4.23). The annual mean Cu for moorland edge sites is 2.1 µg/l. This ranges from 1.2 µg/l at Green Clough to 3.0 µg/l at Fair Brook (Figure 4.24). The WFD 'good' standard is between 1 and 28 µg/l (annual mean) of dissolved Cu. This is dependent upon the concentration of $CaCO_3$ [1] (WFD, 2010). All sites, except the River Noe lower, have low levels of $CaCO_3$ (annual mean < 50 mg/l – see Figure 4.19); therefore, the WFD 'good' standard for these rivers is 1 µg/l. Due to its higher level of $CaCO_3$ the WFD 'good' standard for the River Noe lower is 10 µg/l; therefore, only Abbey Brook and the River Noe lower are achieving the WFD 'good' standard for dissolved Cu. There is no DWS for Cu.

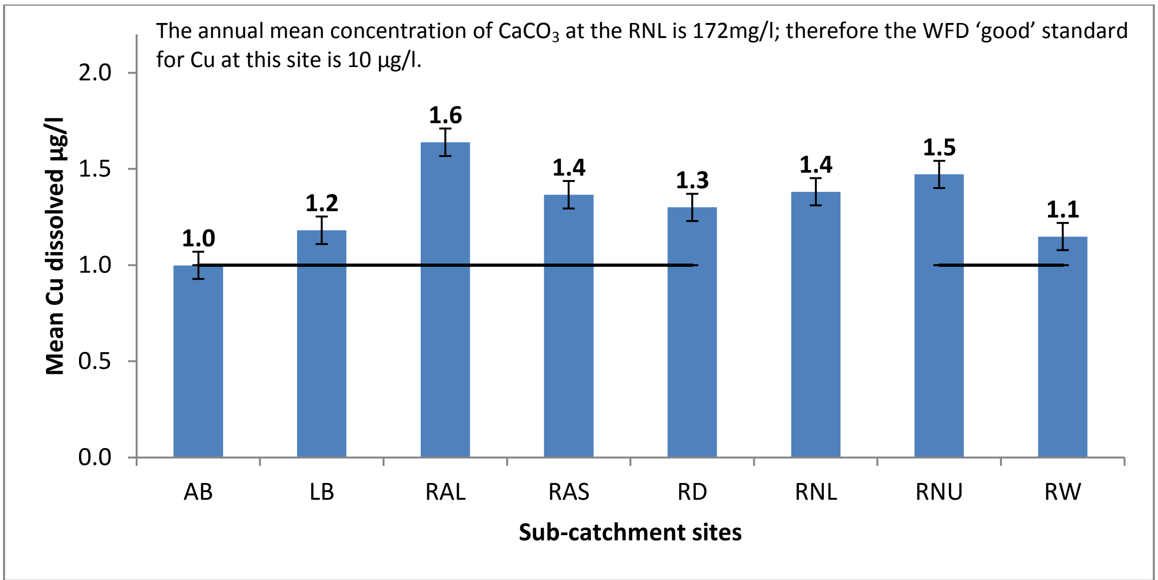

Figure 4.23: Annual mean copper dissolved at eight sub-catchment sites within the Bamford WTW catchment (black line = WFD when 0-50 mg/l $CaC0_3$).

1

Environmental standards for copper (WFD, 2010)	
Water hardness bands to which the corresponding river and freshwater lake standards apply	'Good' water standards for rivers and freshwater lakes
Annual mean concentration of $CaCO_3$ (mg/ l)	Annual mean concentration (µg/ l) of dissolved copper
0-50	1
50-100	6
100-250	10
>250	28

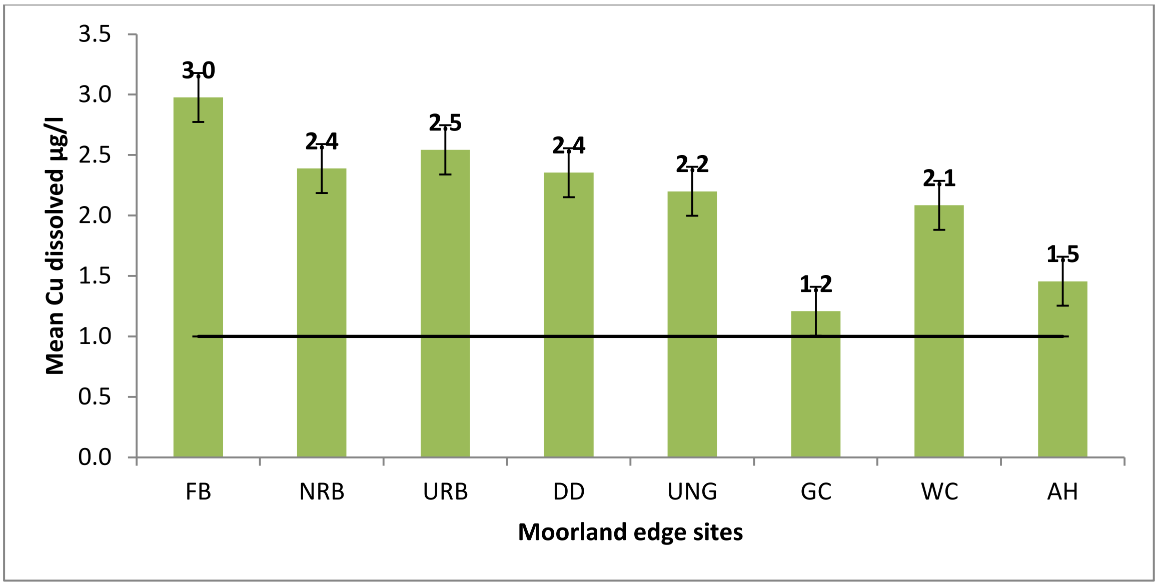

Figure 4.24: Annual mean copper dissolved at eight moorland edge sites within the Bamford WTW catchment (sites displayed along a gradient from un-restored (FB) to intact reference site (AH); black line = WFD when 0-50 mg/l $CaC0_3$).

The Kruskal-Wallis test was used to look for differences in the median concentration of Cu between moorland edge sites. There are significant differences in the concentration of Cu between moorland edge sites (χ^2 = 46.68, d.f. = 7, P < 0.001). GC and AH have lower concentrations of Cu than FB, NRB, URB, DD, UNG, and WC (Figure 4.25). Although this does not provide a particularly clear picture of the effect of moorland condition on Cu, it does show that concentrations of Cu are lower at two of the less degraded sites.

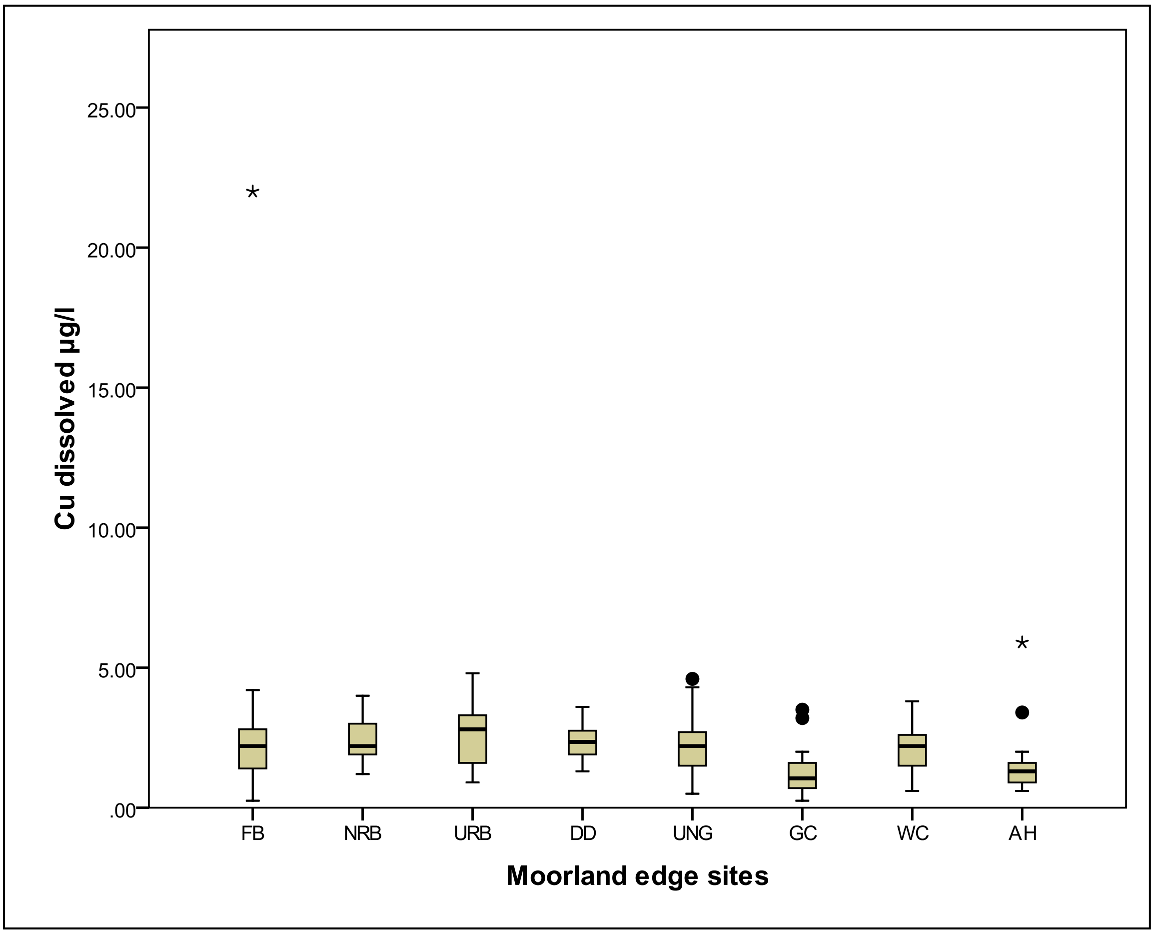

Figure 4.25: Boxplot showing differences in the concentration of Cu between moorland edge sites.

At the sub-catchment scale the mean dissolved Cu ranged from 0.4 µg/l to 2.6 µg/l (Figure 4.26); fifteen weeks did not achieve the WFD 'good' standard. At the moorland edge scale the mean dissolved Cu ranged from 0.7 to 5.5 µg/l (Figure 4.27); 24 weeks did not achieve the WFD 'good' standard.

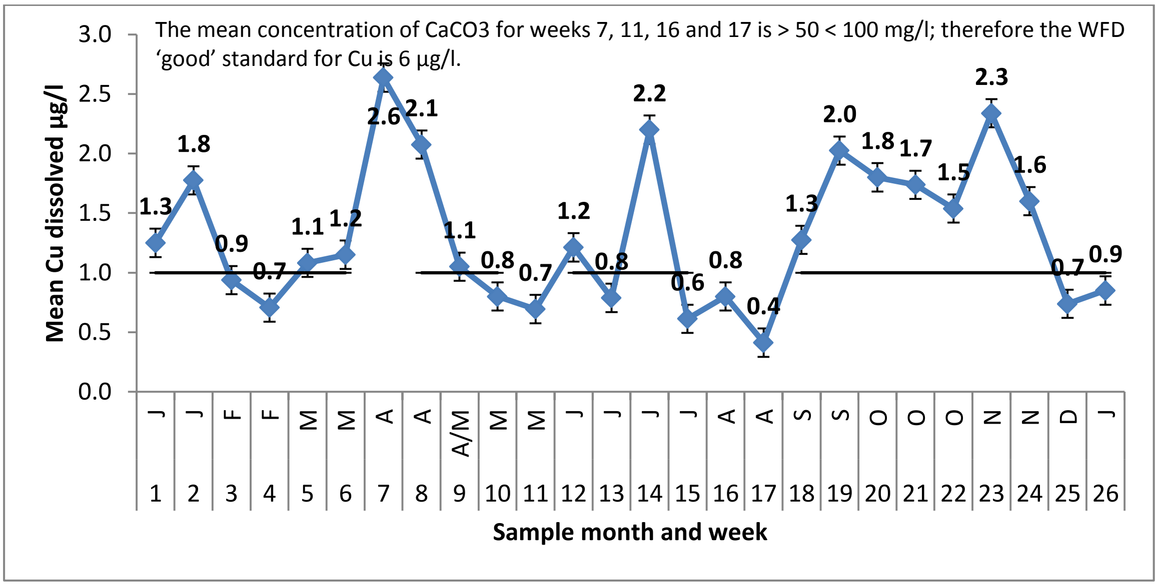

Figure 4.26: Mean copper dissolved for sub-catchment sites within the Bamford WTW catchment over time (black line = WFD when 0-50 mg/l CaC03).

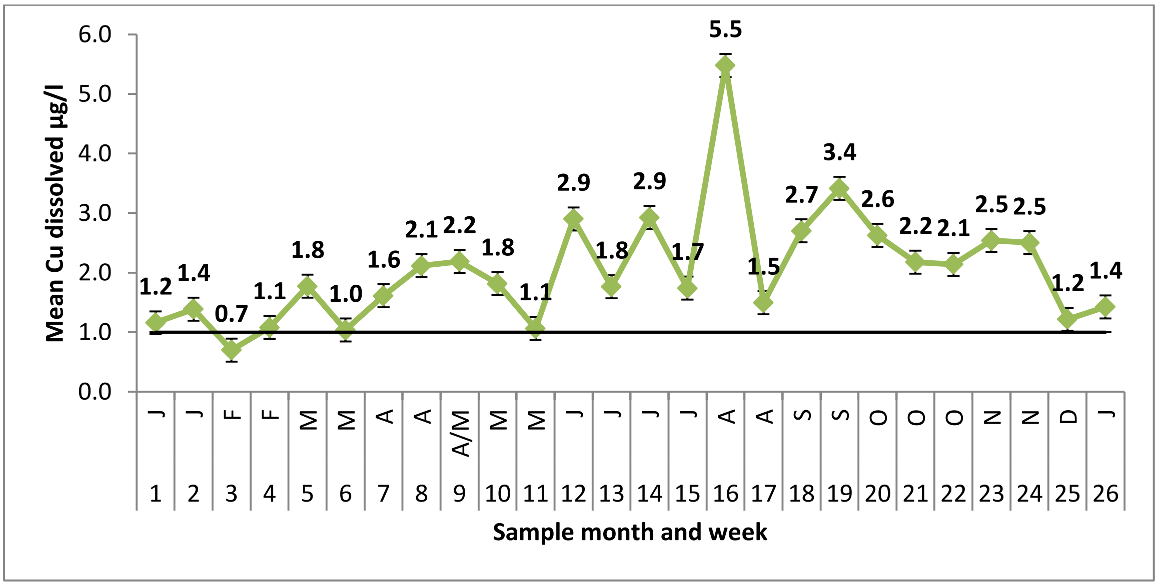

Figure 4.27: Mean copper dissolved for moorland edge sites within the Bamford WTW catchment over time (black line = WFD when 0-50 mg/l CaC03).

4.8 Zinc total

The annual mean Zn for sub-catchment sites is 9 µg/l. This ranges from 6 µg/l at the River Noe upper to 22 µg/l the River Noe lower (Figure 4.28). The annual mean Zn for moorland edge sites is 20 µg/l. This ranges from 11 µg/l at Ashop Head to 25 µg/l at Upper North Grain (Figure 4.29). The WFD 'good' standard for Zn is between 8 and 125 µg/l. This is dependent upon the concentration of $CaCO_3$ [2] (WFD, 2010). Most sites have low levels of $CaCO_3$ (< 50 mg/l – see Figure 4.21); therefore, the WFD 'good' standard for zinc in these rivers is 8 µg/l. Only two sites are achieving this: River Derwent and River Noe upper. Due to its higher level of $CaCO_3$ the WFD 'good' standard for Zn for the River Noe lower is 75 µg/l; therefore, this site is also achieving the WFD 'good' standard. There is no DWS for Zn.

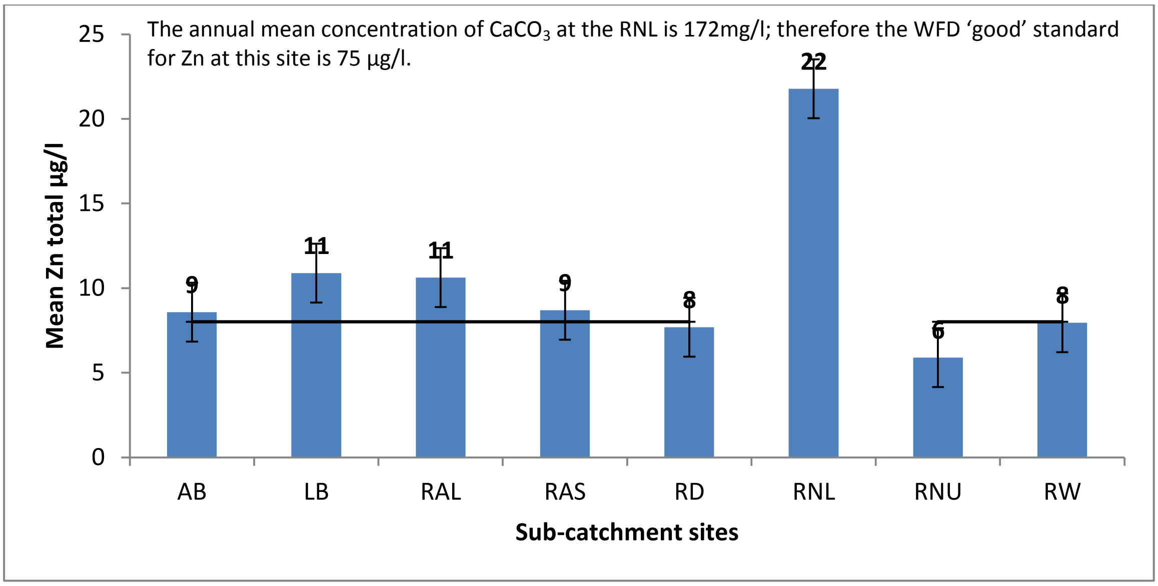

Figure 4.28: Annual mean zinc total at eight sub-catchment sites within the Bamford WTW catchment (black line = WFD when 0-50 mg/l $CaC0_3$).

2

Environmental standards for zinc (WFD, 2010)	
Water hardness to which the corresponding river and freshwater lake standards apply	'Good' standards for rivers and freshwater lakes
Annual mean concentration of $CaCO_3$ (mg/ l)	Annual mean concentration (µg/ l) of total zinc
0-50	8
50-100	50
100-250	75
>250	125

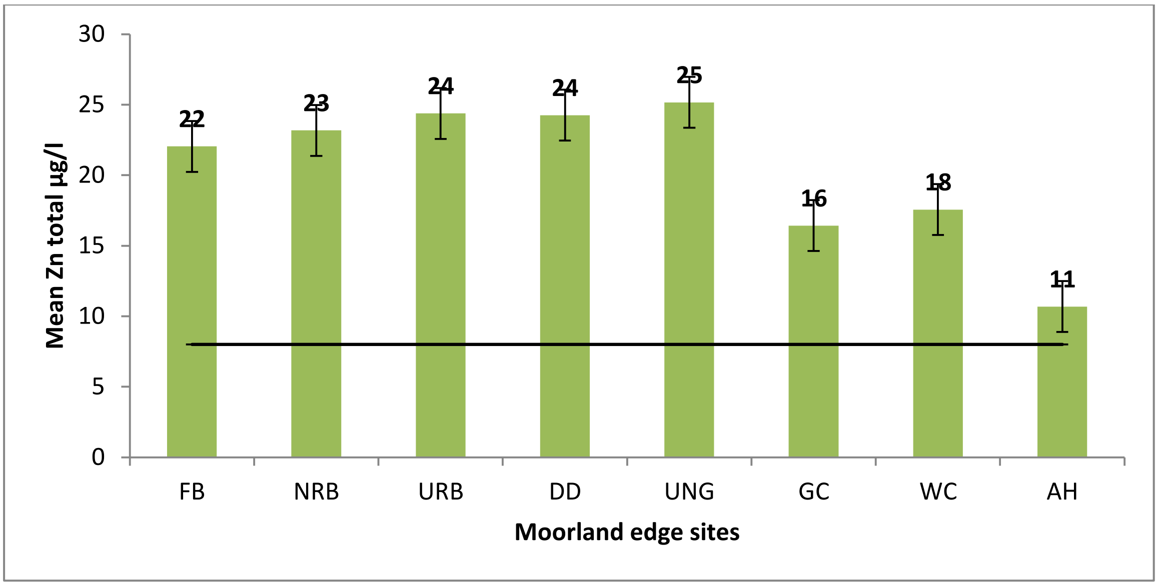

Figure 4.29: Annual mean zinc total at eight moorland edge sites within the Bamford WTW catchment (sites displayed along a gradient from un-restored (FB) to intact reference site (AH); black line = WFD when 0-50 mg/l CaC03).

There are significant differences in the mean concentration of Zn between the moorland edge sites ($F_{(7, 178)} = 5.76$, $P < 0.001$). Fisher's LSD post hoc test (see Table 4.2) showed that FB has a significantly higher mean concentration of Zn than AH; NRB has a significantly higher mean concentration of Zn than GC and AH; URB, DD and UNG have significantly higher mean concentrations of Zn than GC, WC and AH; GC and WC have significantly higher mean concentrations of Zn than AH. This shows that the mean concentration of Zn is significantly higher at the more degraded moorland sites and significantly lower at the less degraded sites (see Table 3.5).

Table 4.2: Post hoc (Fisher's LSD test) for differences in the concentration of Zn between moorland edge sites.

	NRB	URB	DD	UNG	GC	WC	AH
FB	0.74	0.46	0.47	0.30	0.06	0.14	0.00***
NRB		0.73	0.75	0.55	0.04*	0.09	0.00***
URB			0.97	0.80	0.01**	0.03*	0.00***
DD				0.76	0.01**	0.03*	0.00***
UNG					0.00***	0.01**	0.00***
GC						0.70	0.05*
WC							0.02*

(Significance levels: * 0.05, ** 0.01, *** 0.001)

At the sub-catchment scale the mean Zn ranged from 5 to 20 µg/l; fifteen weeks did not achieve the WFD 'good' standard. At the moorland edge scale the mean total Zn ranged from 12 to 45 µg/l (Figure 4.31); therefore the WFD 'good' standard was not achieved.

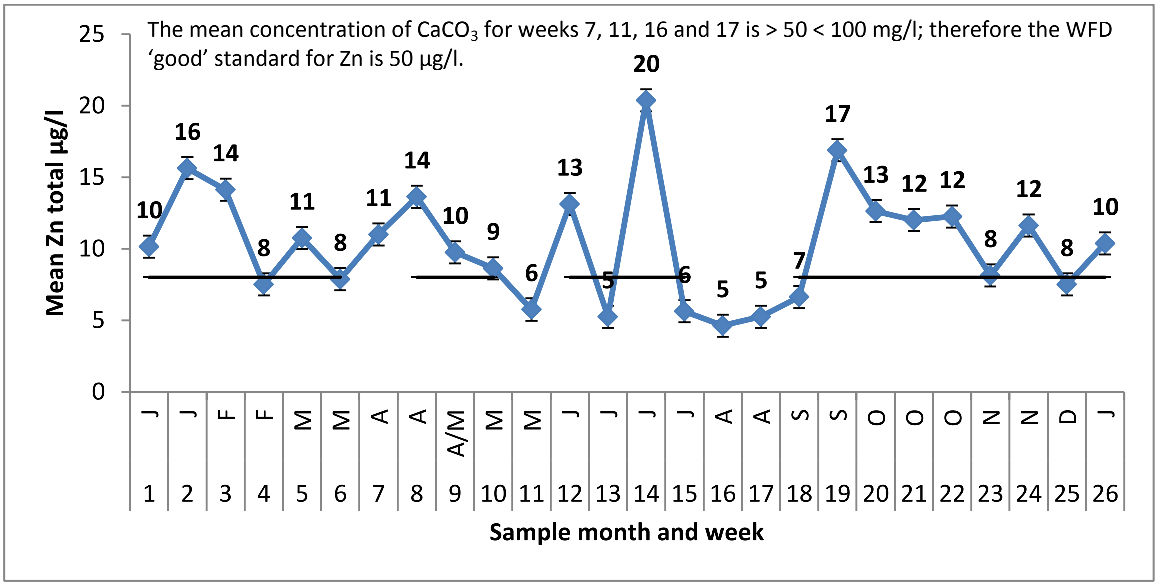

Figure 4.30: Mean Zn total for sub-catchment sites within the Bamford WTW catchment over time (black line = WFD when 0-50 mg/l $CaC0_3$).

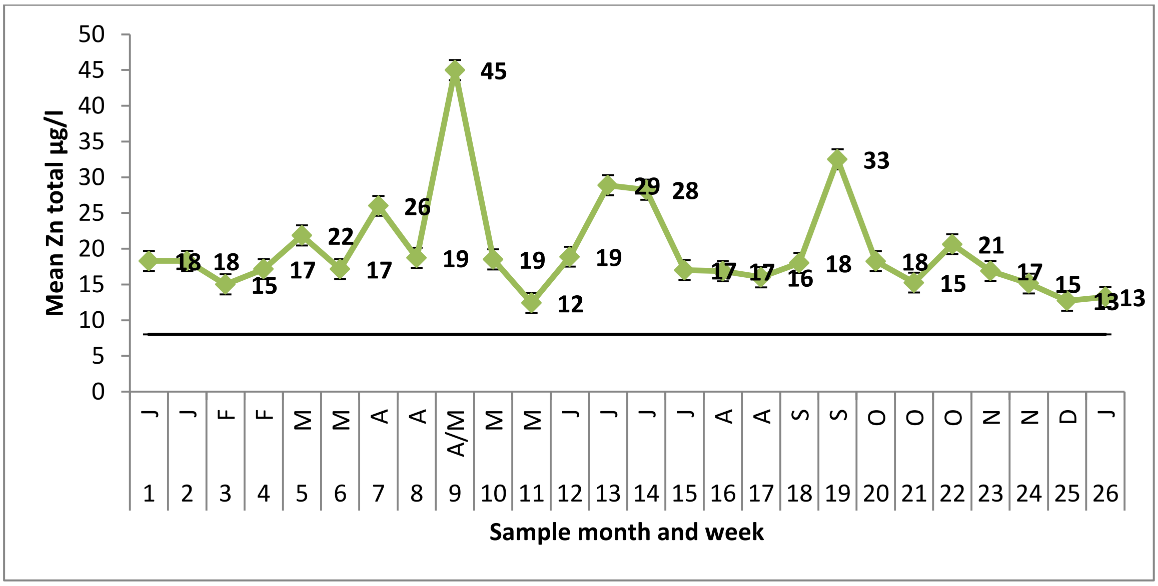

Figure 4.31: Mean Zn total for moorland edge sites within the Bamford WTW catchment over time (black line = WFD when 0-50 mg/l $CaC0_3$).

4.9 Chromium dissolved

The annual mean Cr for sub-catchment sites is 1.6 µg/l. This ranges from 0.8 µg/l at the River Alport to 4.9 µg/l at the River Noe lower (Figure 4.32). The annual mean Cr for moorland edge sites is 1.0 µg/l. This ranges from 0.8 µg/l at Green Clough to 1.2 µg/l at Upper North Grain (Figure 4.33). The WFD 'good' standard for Cr III is 4.7 µg/l and for Cr VI is 3.4 µg/l (WFD, 2010); therefore, the River Noe lower is not achieving the WFD 'good' standard for Cr. There is no DWS for Cr.

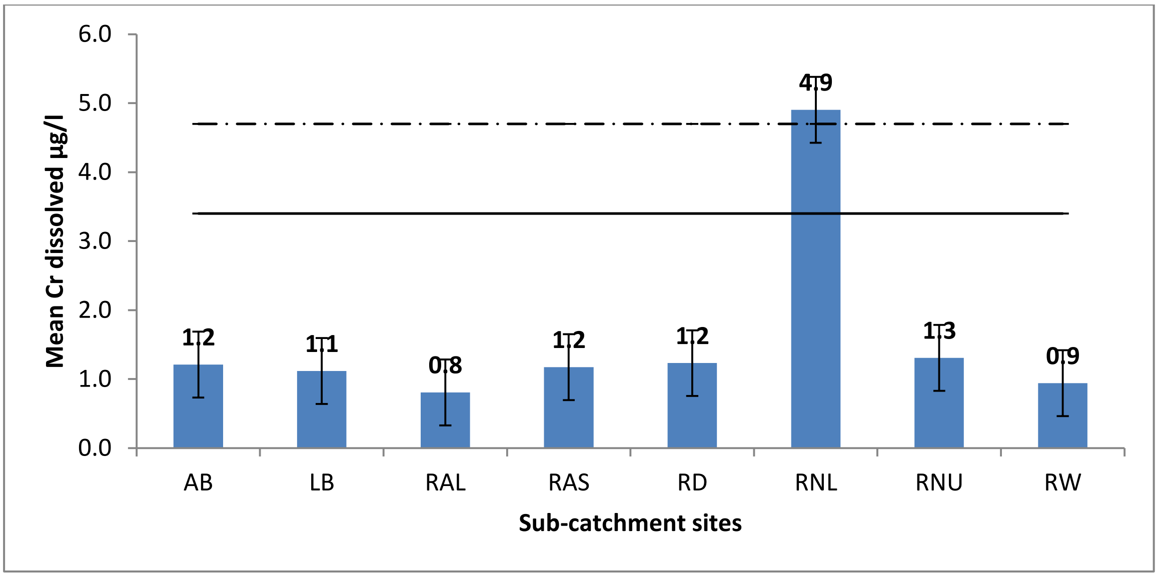

Figure 4.32: Annual mean Cr dissolved at eight sub-catchment sites within the Bamford WTW catchment (black solid line = WFD 'good' standard for Cr VI; black dash line = WFD 'good' standard for Cr III).

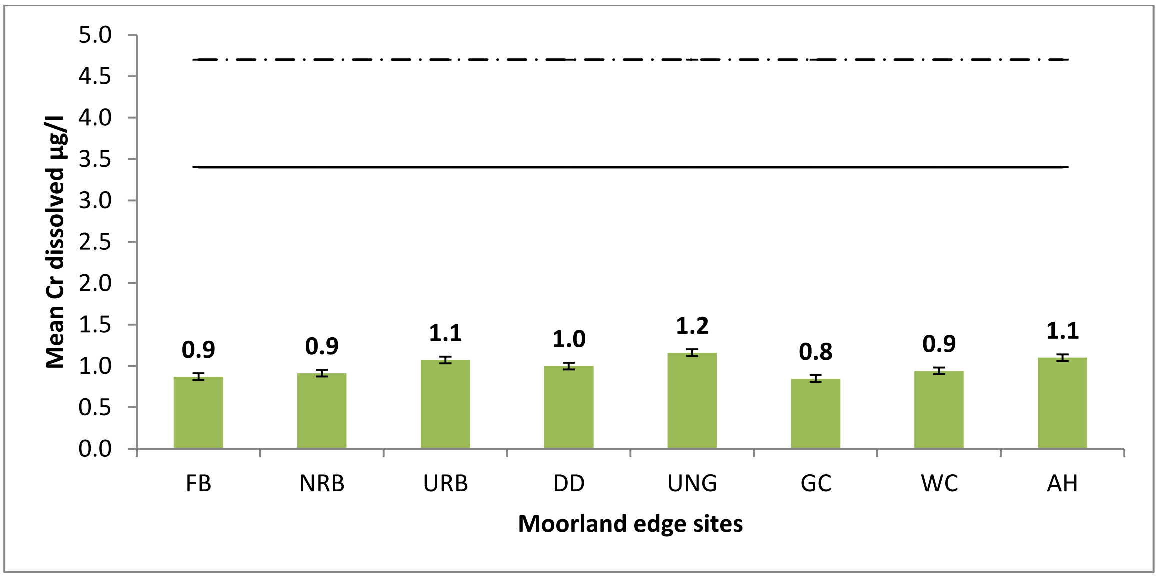

Figure 4.33: Annual mean Cr dissolved at eight moorland edge sites within the Bamford WTW catchment (sites displayed along a gradient from un-restored (FB) to intact reference site (AH); black solid line = WFD 'good' standard for Cr VI; black dash line = WFD 'good' standard for Cr III).

At the sub-catchment scale the mean Cr ranged from 0.5 to 4.1 µg/l (Figure 4.34); three weeks did not achieve the WFD 'good' standard. At the moorland edge scale the mean Cr ranged from 0.5 to 2.6 µg/l (Figure 4.35). All sites were within WFD threshold during all sampling events.

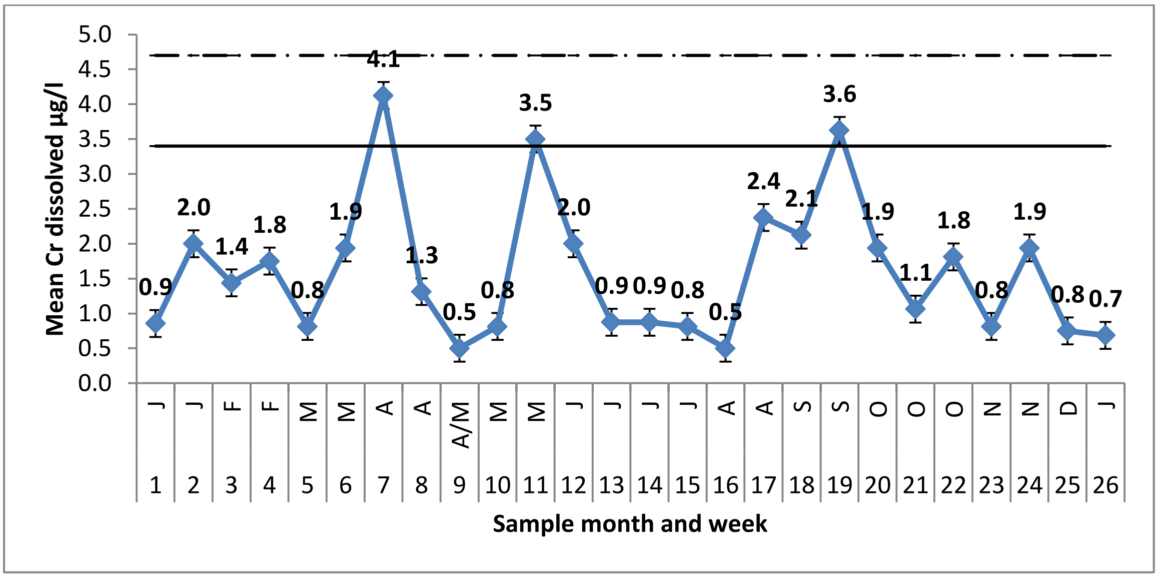

Figure 4.34: Mean Cr dissolved for sub-catchment sites within the Bamford WTW catchment over time (black solid line = WFD 'good' standard for Cr VI; black dash line = WFD 'good' standard for Cr III).

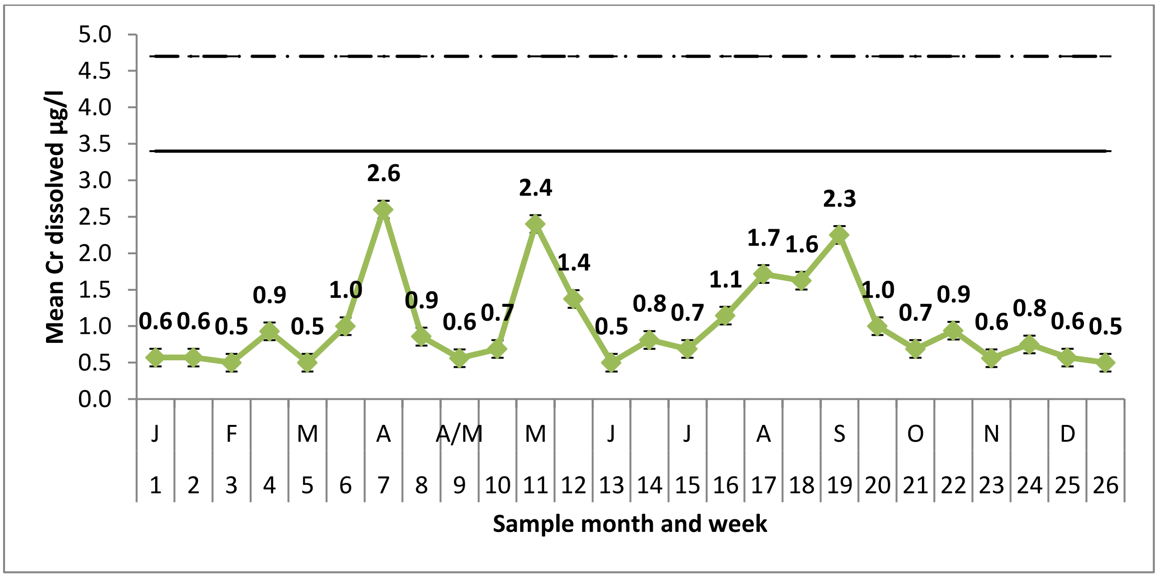

Figure 4.35: Mean Cr dissolved for moorland edge sites within the Bamford WTW catchment over time (black solid line = WFD 'good' standard for Cr VI; black dash line = WFD 'good' standard for Cr III).

4.10 Colour

The annual mean colour for sub-catchment sites is 142 H.U. This ranges from 48 H.U. at the River Noe lower to 246 H.U. at Ladybower Brook (five times higher than the Noe; Figure 4.36). The overall annual mean colour for moorland edge sites is 471 H.U. This ranges from 191 H.U. at Ashop Head to 717 H.U. at Devils Dike (Figure 4.37). The DWS for colour is 20 H.U (Water Supply Regulations, 2000); none of the sub-catchment or moorland edge sites achieve this. Sub-catchment sites are between ~ 2.5 and 12.5 times the DWS, while moorland edge sites are between ~ 9.5 and 36 times the DWS. There is no WFD 'good' standard for colour.

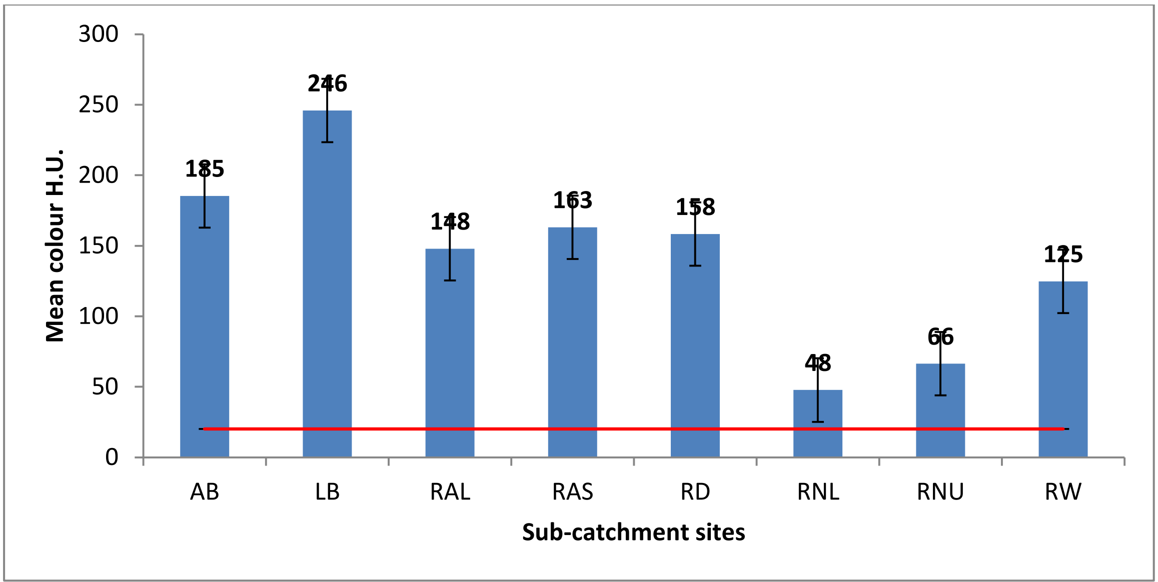

Figure 4.36: Annual mean colour at eight sub-catchment sites within the Bamford WTW Catchment (red line = DWS).

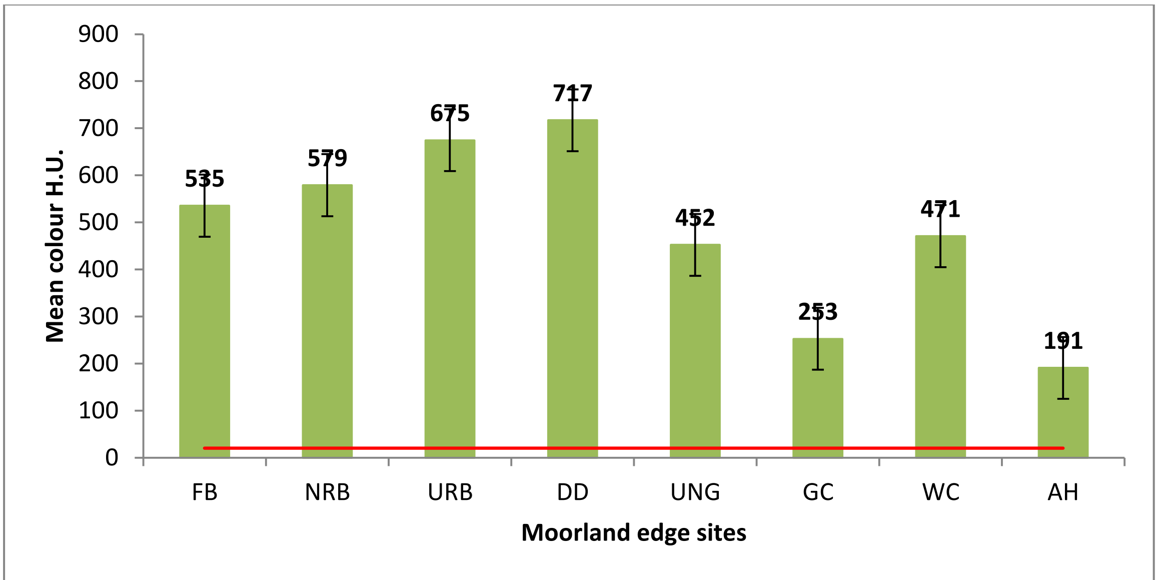

Figure 4.37: Annual mean colour at eight moorland edge sites within the Bamford WTW catchment (sites displayed along a gradient from un-restored (FB) to intact reference site (AH); red line = DWS).

There are significant differences in colour between moorland edge sites (χ^2 = 40.26, d.f. = 7, P < 0.001; Figure 4.38). FB, NRB, URB and DD have a significantly higher median colour than UNG, GC, WC and AH; and UNG and WC have a significantly higher median colour than GC and AH. This shows that the median colour is significantly higher at the more degraded moorland sites and significantly lower at the less degraded sites.

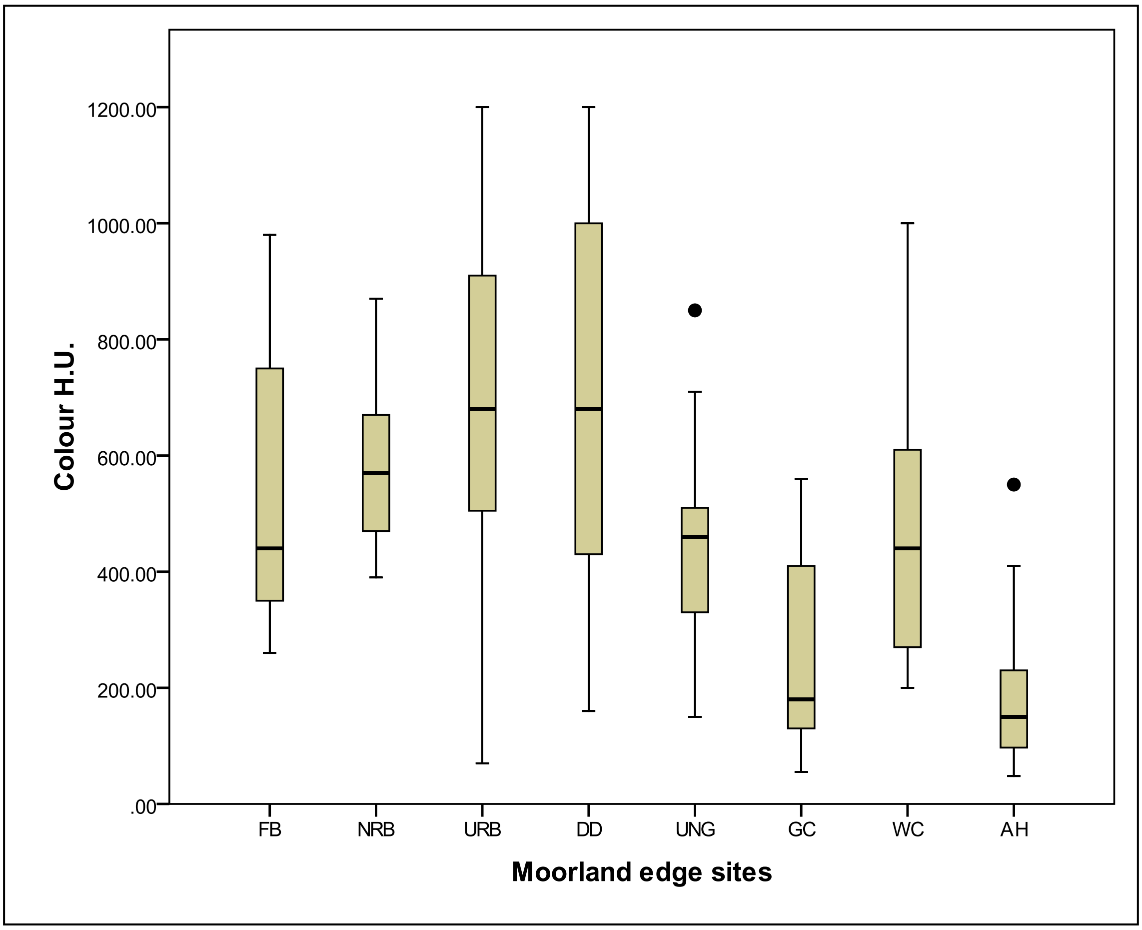

Figure 4.38: Boxplot showing differences in colour between moorland edge sites.

At the sub-catchment scale the mean colour ranged from 32 H.U. to 356 H.U. (Figure 4.39). At the moorland edge scale the mean colour ranged from 214 to 771 H.U. (Figure 4.40). The DWS was not achieved at the sub-catchment or the moorland edge scale at any of the 26 sampling events during 2012.

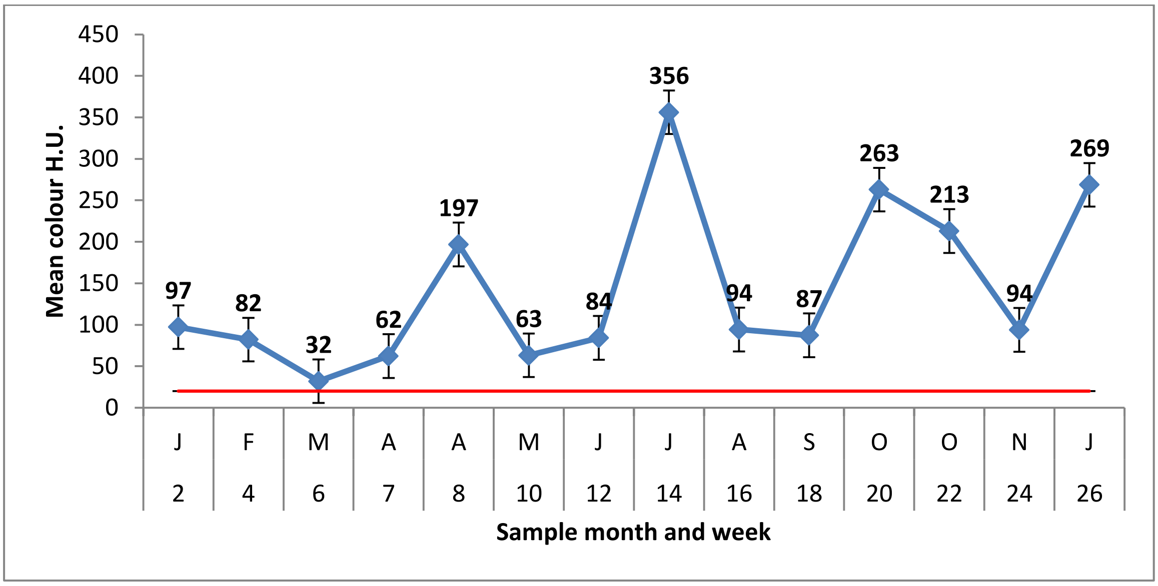

Figure 4.39: Mean colour for sub-catchment sites within the Bamford WTW Catchment over time.

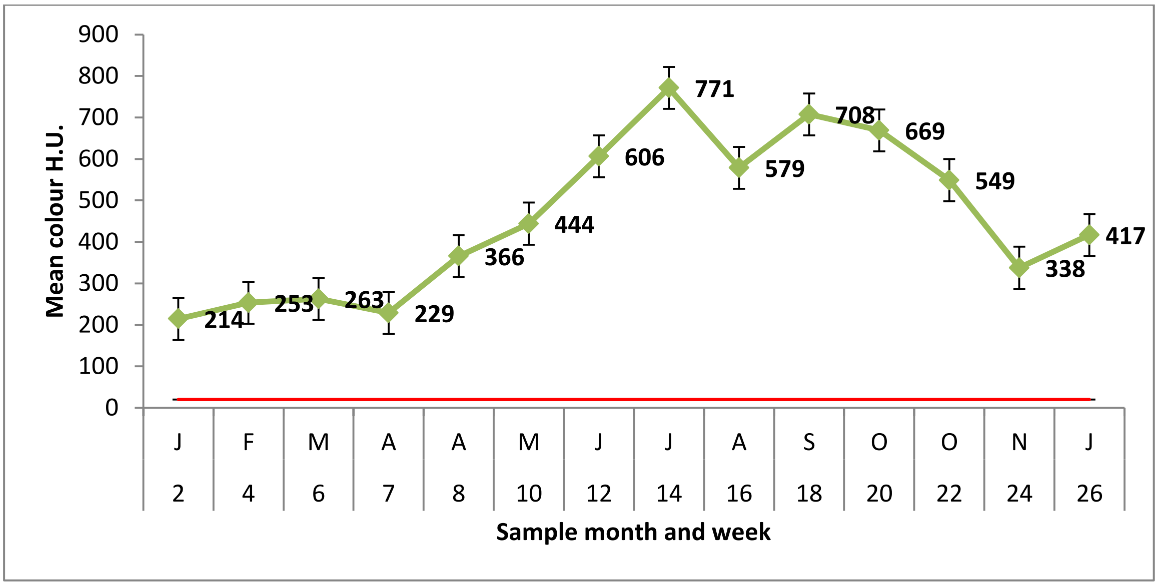

Figure 4.40: Mean colour for moorland edge sites within the Bamford WTW Catchment over time.

4.11 Iron total

The annual mean Fe for sub-catchment sites is 0.45 mg/l. This ranges from 0.20 mg/l at the River Westend to 0.99 mg/l at Ladybower Brook (Figure 4.41). The overall annual mean Fe for moorland edge sites is 1.07 mg/l. This ranges from 0.20 mg/l at Fair Brook to 1.91 mg/l at Devils Dike (Figure 4.42). The DWS for Fe is 0.20 mg/l (Water Supply Regulations, 2000); therefore, only the River Westend (sub-catchment scale) and Fair Brook (moorland edge scale) are achieving the DWS for Fe. The WFD 'good' standard is based on dissolved Fe (1 mg/l), not total Fe (WFD, 2010); therefore, Fe is not considered in relation to the WFD in this report.

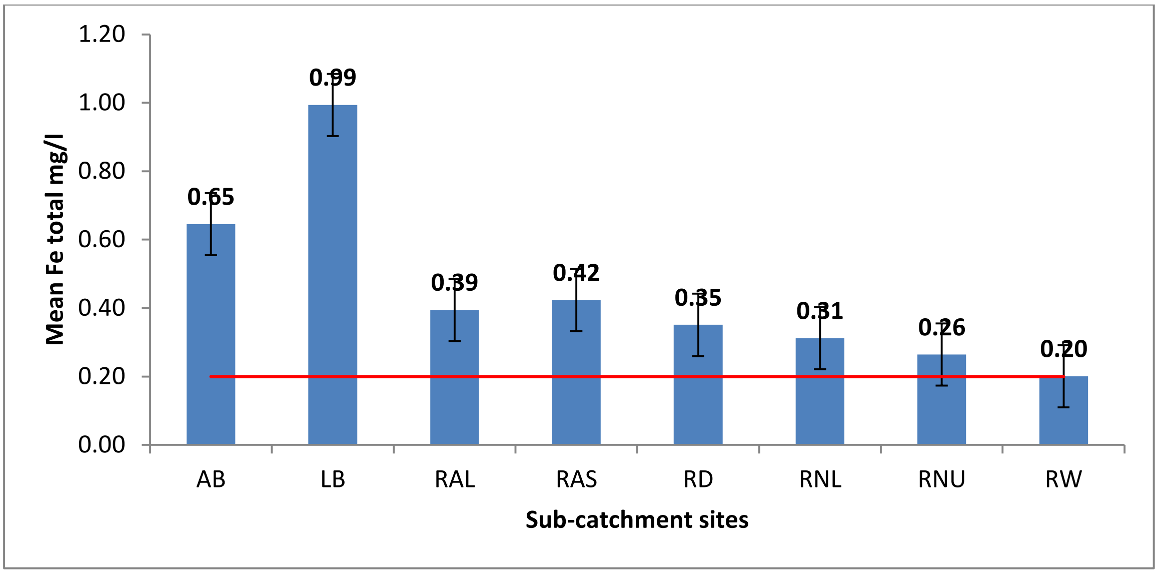

Figure 4.41: Annual mean iron total at eight sub-catchment sites within the Bamford WTW Catchment (red line = DWS).

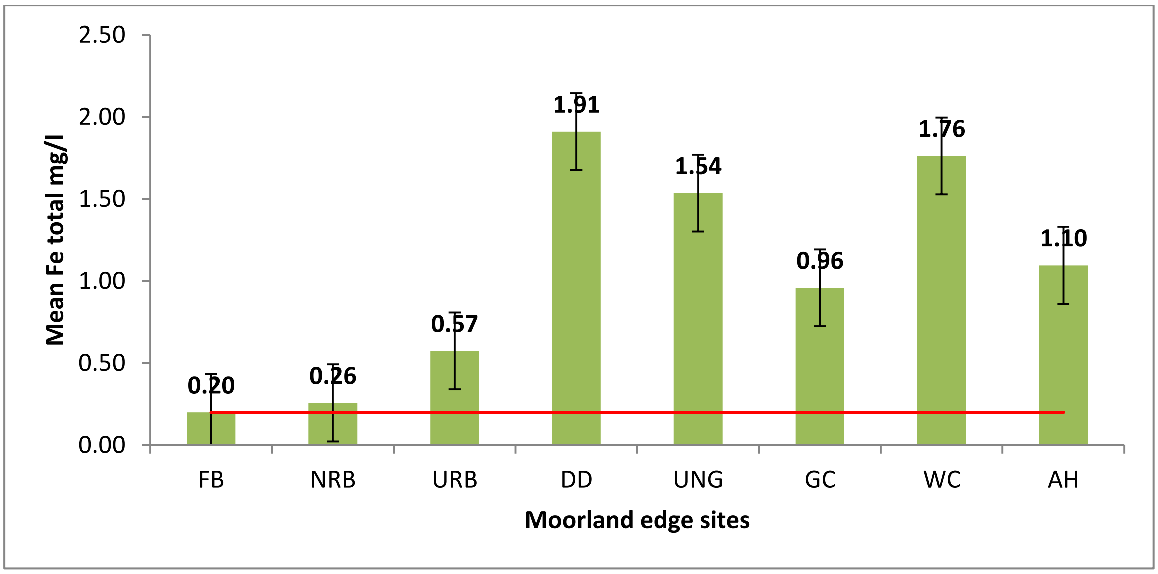

Figure 4.42: Annual mean total iron at eight moorland edge sites within the Bamford WTW Catchment (sites displayed along a gradient from un-restored (FB) to intact reference site (AH); red line = DWS).

There are significant differences in the concentration of Fe between moorland edge sites (χ^2 = 63.90, d.f. = 7, P < 0.001; Figure 4.43). FB, NRB and URB have significantly lower median concentrations of Fe than DD, UNG, GC, WC and AH; and GC and AH have significantly lower median concentrations of Fe than DD, UNG and WC. However, it is not particularly clear if / how moorland condition effects the median concentration of Fe.

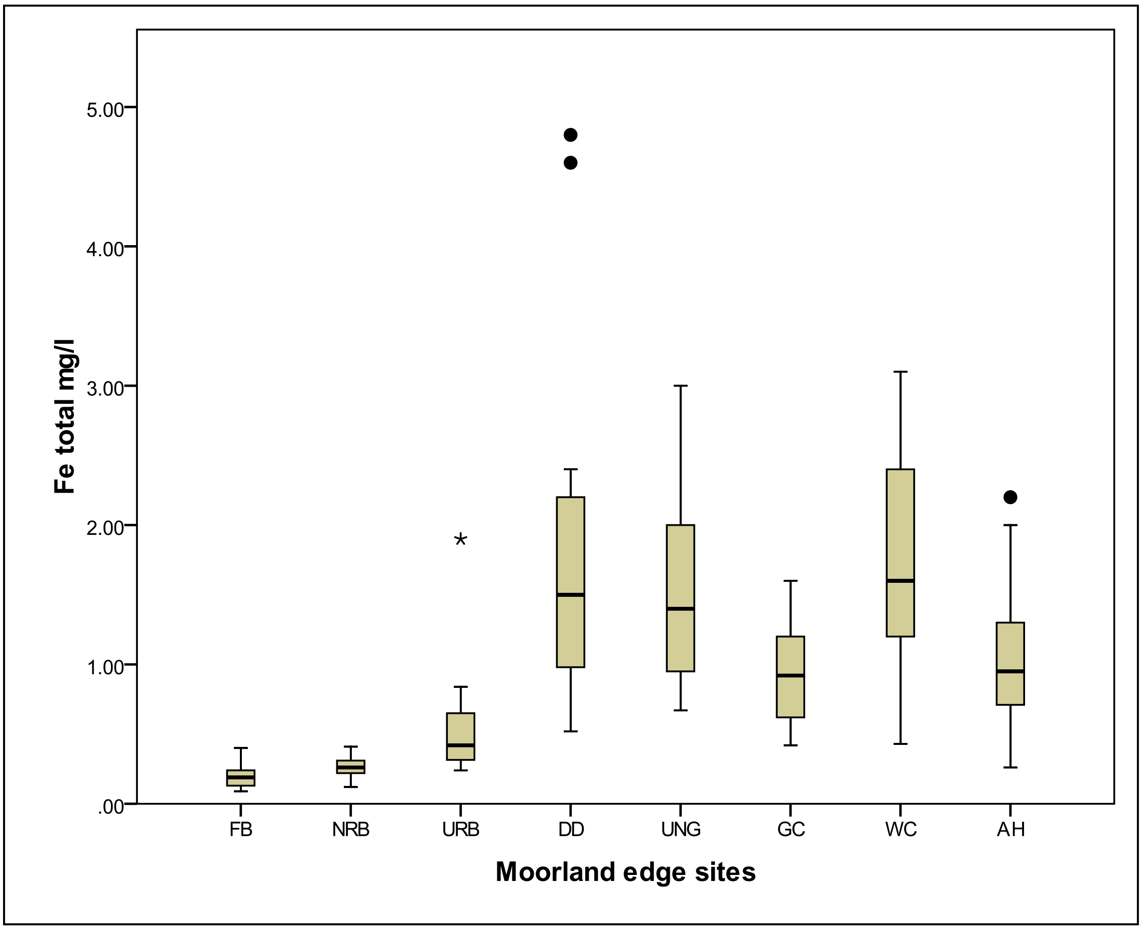

Figure 4.43: Boxplot showing differences in the concentration of Fe between moorland edge sites.

At the sub-catchment scale the mean for Fe ranged from 0.2 mg/l to 1.0 mg/l (Figure 4.44); eight weeks did not achieve the DWS. At the moorland edge scale the mean for Fe ranged from 0.6 mg/l to 2.0 mg/l (Figure 4.45); no weeks achieved the DWS.

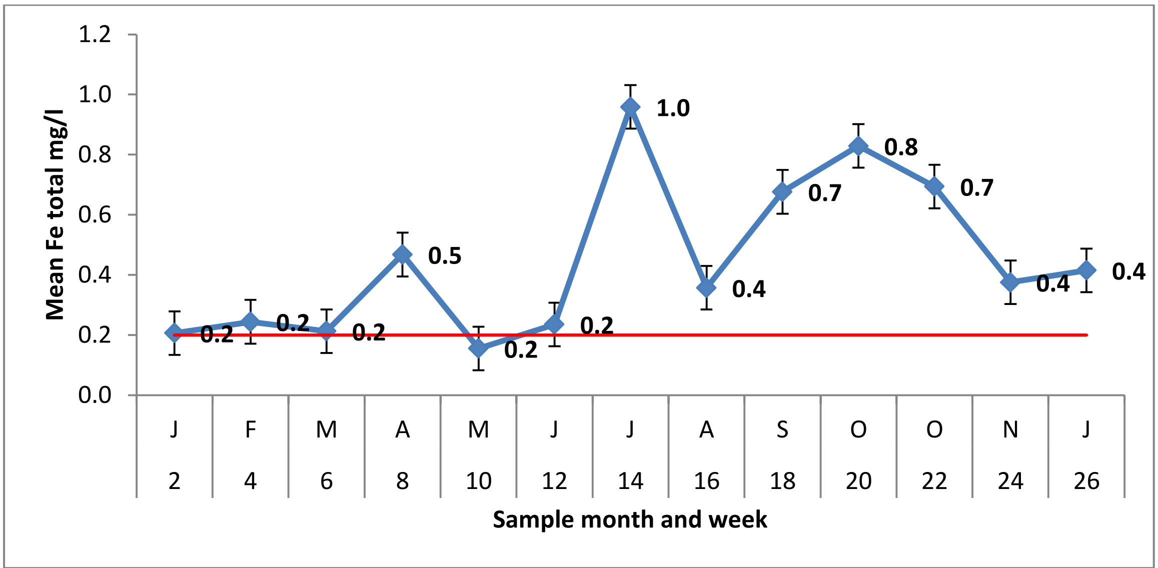

Figure 4.44: Mean iron total for sub-catchment sites within the Bamford WTW catchment over time (red line = DWS).

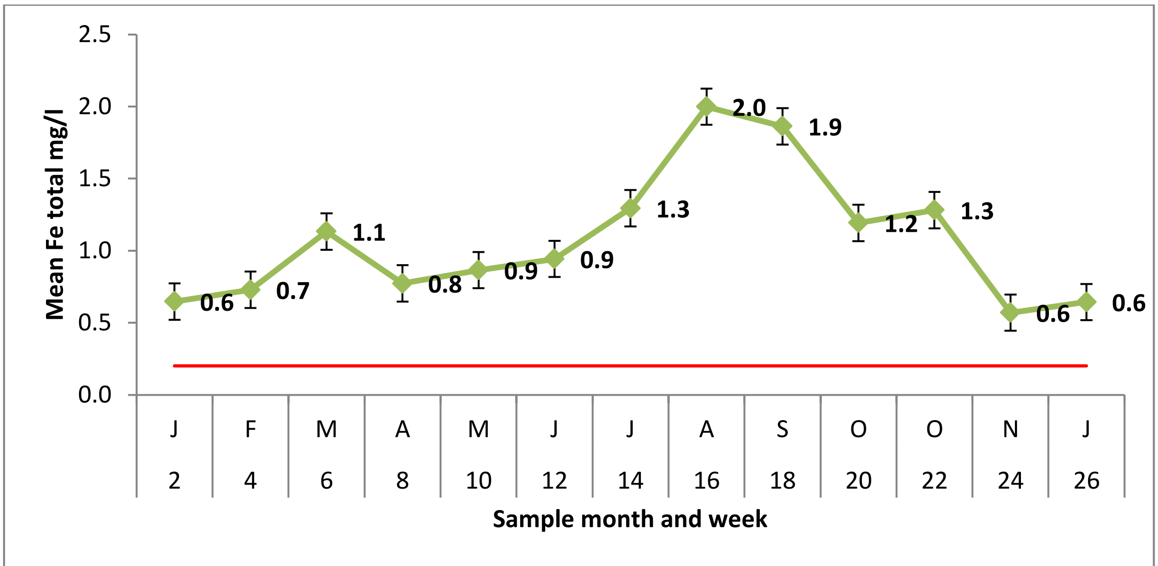

Figure 4.45: Mean iron total for moorland edge sites within the Bamford WTW Catchment over time (sites displayed along a gradient from un-restored (FB) to intact reference site (AH); red line = DWS).

4.12 Aluminium total

The overall annual mean Al for sub-catchment sites is 0.23 mg/l. This ranges from 0.19 mg/l at Abbey Brook to 0.29 mg/l at the River Alport (Figure 4.46). The annual mean Al for moorland edge sites is 0.41 mg/l. This ranges from 0.21 at Ashop Head to 0.72 mg/l at Withins Clough (Figure 4.47). The DWS for Al is 0.20 mg/l (Water Supply Regulations, 2000); therefore, only four of the sub-catchment sites are achieving the DWS. There is no WFD 'good' standard for Al; pH is used as a proxy (Alan Roe, personal communication) (see section 4.5).

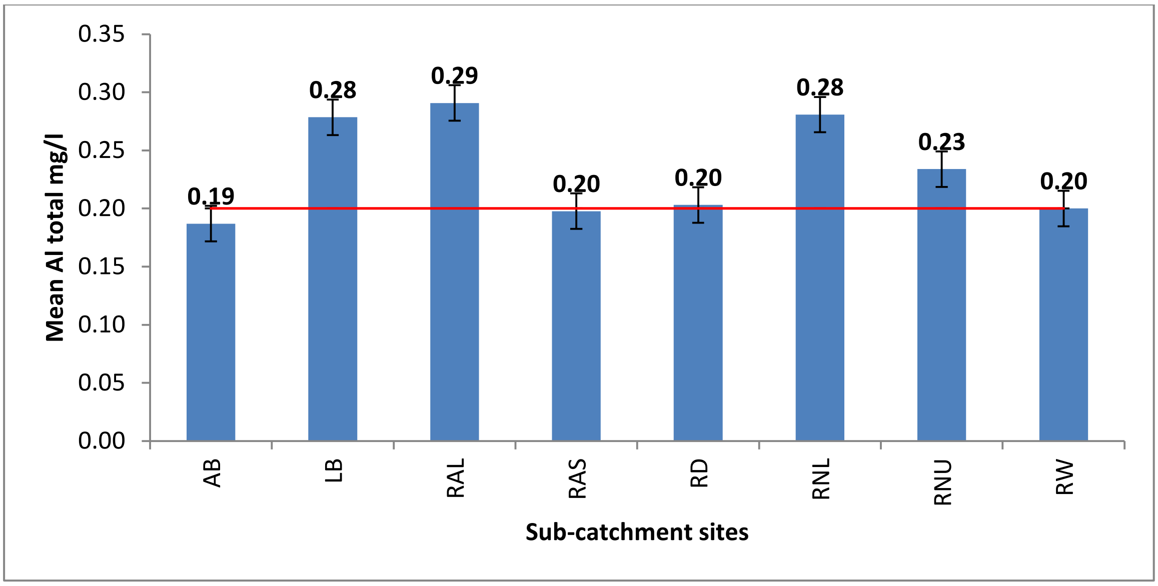

Figure 4.46: Annual mean aluminium total at eight sub-catchment sites within the Bamford WTW Catchment.

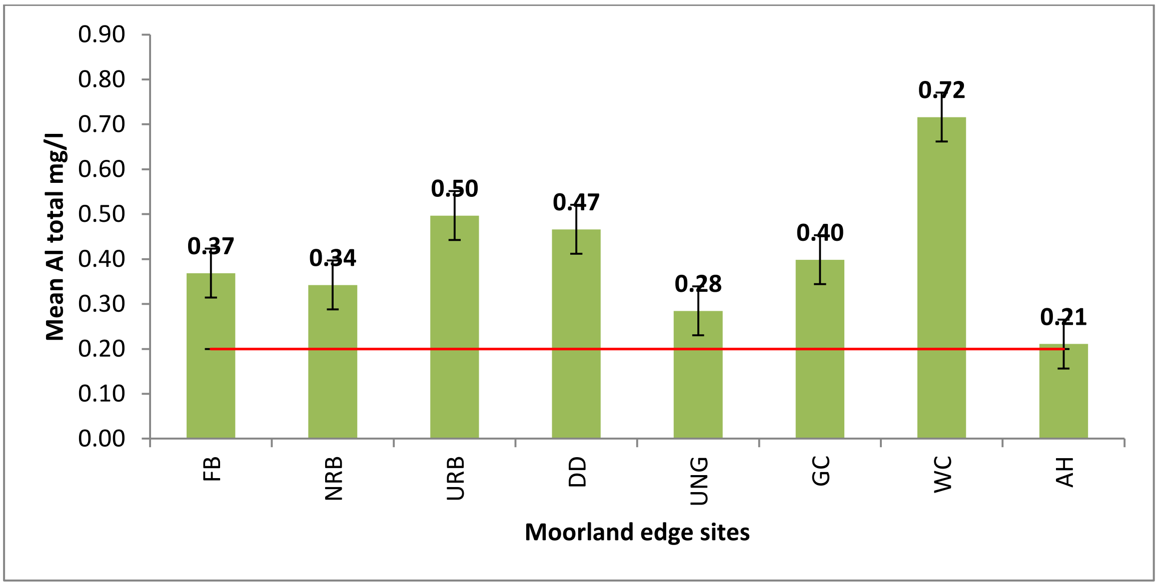

Figure 4.47: Annual mean aluminium total at eight moorland edge sites within the Bamford WTW Catchment (sites displayed along a gradient from un-restored (FB) to intact reference site (AH)).

There are significant differences in the concentration of Al between moorland edge sites ($\chi^2 = 25.53$, d.f. = 7, $P < 0.001$; Figure 4.48). AH has a significantly lower median concentration of Al than all other sites. However, it is not particularly clear if / how moorland condition effects the mean concentration of Al.

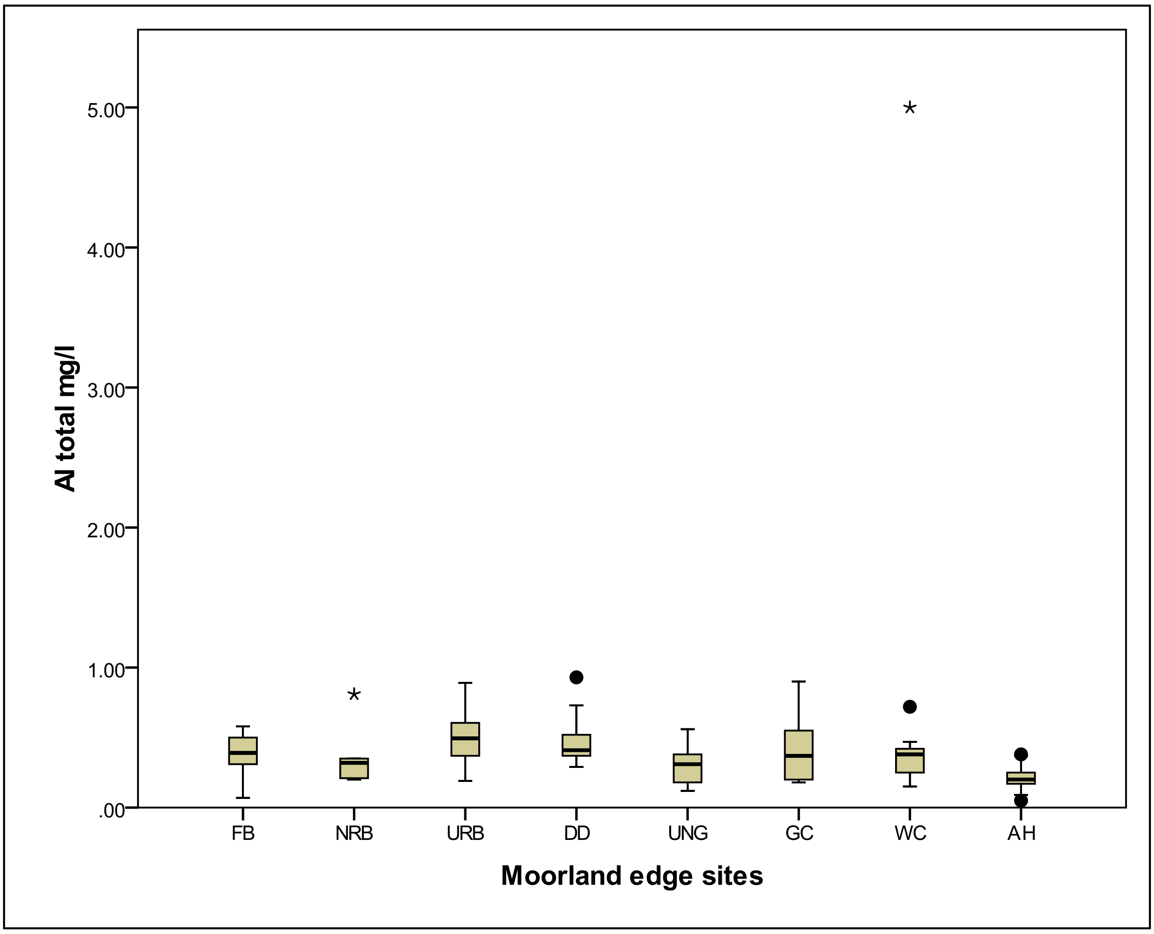

Figure 4.48: Boxplot showing differences in the concentration of Al between moorland edge sites.

At the sub-catchment scale the mean Al ranged from 0.02 mg/l to 0.41 mg/l (Figure 4.49); seven weeks did not achieve the DWS. At the moorland edge scale the mean Al ranged from 0.29 mg/l to 0.94 mg/l (Figure 4.50); no weeks achieved the DWS.

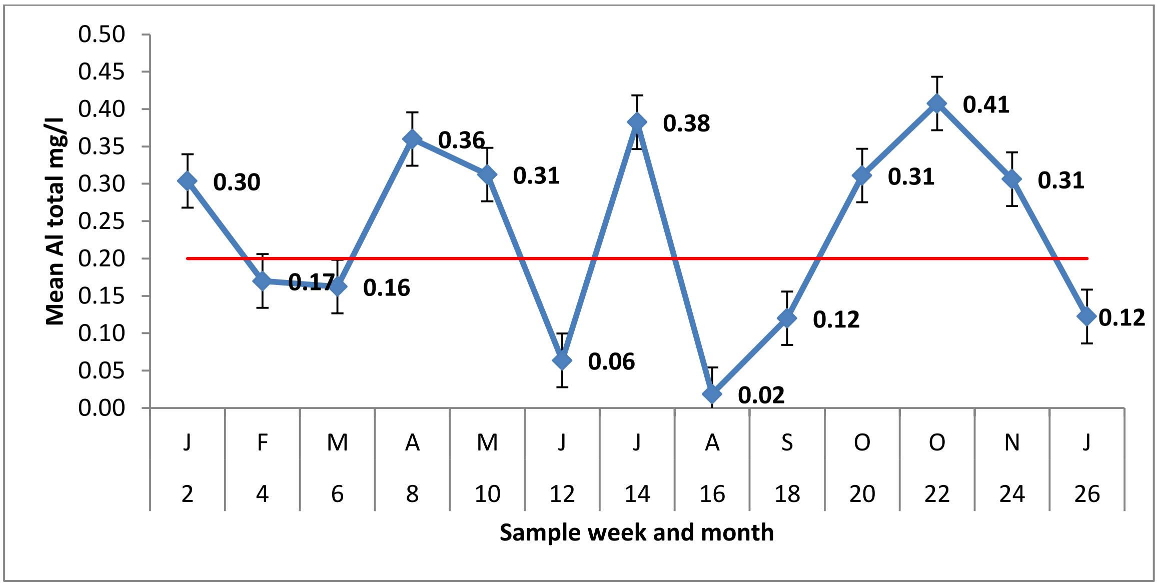

Figure 4.49: Mean aluminium total for sub-catchment sites within the Bamford WTW Catchment over time.

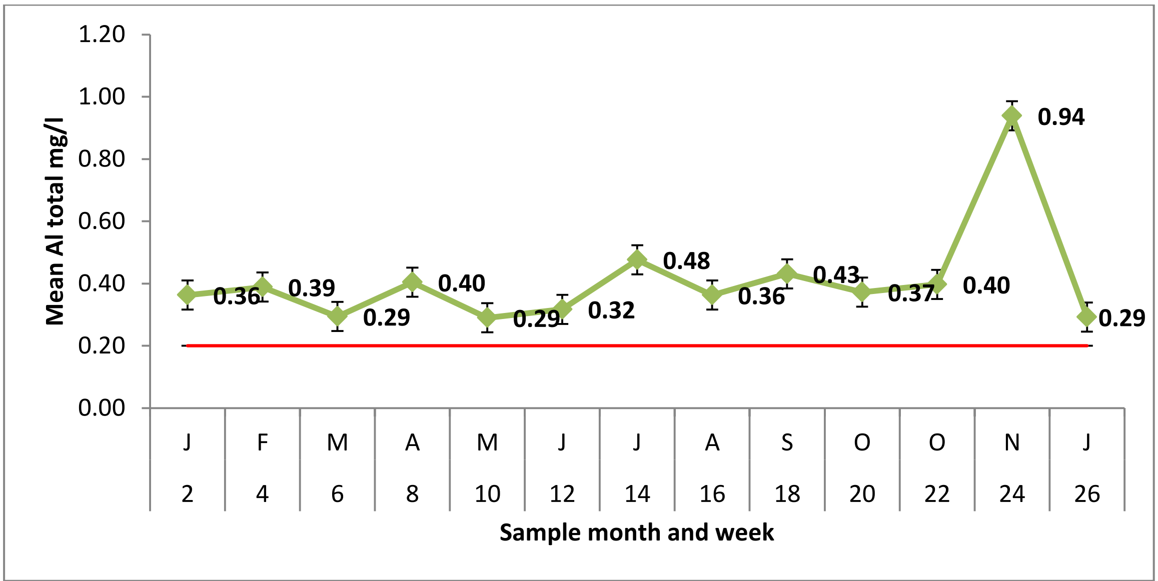

Figure 4.50: Mean aluminium total for moorland edge sites within the Bamford WTW Catchment over time.

4.13 Relationship between moorland edge and sub-catchment sites

The concentration of six determinands (DOC, pH, Cu, Zn, colour, Fe) in stream water flowing off five moorland edge sites in the River Ashop catchment was investigated. Their concentration was also recorded at the bottom of this sub-catchment. Concentrations of all determinands were between 1.6 and 3.0 times greater (average 2.2 times greater) at the moorland edge than at the bottom of the sub-catchment; pH was 23 % lower at moorland edge sites than at the bottom of the sub-catchment. For this subset of determinands there is high input from moorland deep peat catchments but these loadings are significantly reduced through the Ashop system by a process of dilution, deposition and / or transformation.

Table 4.3: Relationship between water quality at the moorland edge and at the bottom of the River Ashop sub-catchment. Five moorland catchments are included: Fair Brook (degraded: un-restored), Upper Red Brook (early stage restoration), Upper North Grain (degraded: vegetated with gullies) and Ashop Head (intact reference).

	Mean concentration		Ratio (Edge : sub-catchment)		
	Moorland Edge	Ashop sub-catchment	Minimum	Maximum	Mean
DOC	18.0	6.1	1.4	3.9	3.0
pH	5.1	6.6	0.6	1.0	0.8
Copper	2.3	1.4	1.1	2.1	1.6
Zinc	20.2	9.0	1.1	3.3	2.2
Iron	1.0	0.4	0.5	4.2	2.5
Colour	465	163	1.2	4.1	2.9

4.14 Summary of spatial results

4.14.1 Sub-catchment summary

Across sub-catchments, water quality relative to DWS and WFD objectives was variable (see Table 4.4). The relative magnitude of the concentrations of these determinands across the sub-catchments of the Bamford WTW catchment are presented below (see Figure 4.51 - Figure 4.56).

Table 4.4: Water quality within the Bamford WTW catchment. Red = fails condition; green = meets condition.

Sub-catchment	Code	pH	Copper	Zinc	Colour	Iron
		WFD	WFD	WFD	DWS	DWS
Abbey Brook	AB					
Ladybower Brook	LB					
River Alport	RAL					
River Ashop	RAS					
River Derwent	RD					
River Noe lower	RNL					
River Noe upper	RNU					
River Westend	RW					

pH is an issue within the Upper Derwent system (Figure 4.52), with only the River Ashop achieving the WFD ‘good’ standard.

Copper is an issue in both the Upper Derwent and Noe systems (Figure 4.53). In the Derwent system, concentrations were particularly high within the Alport, Ashop and Derwent sub-catchments.

Zinc is a particular issue within the lower River Noe sub-catchments (Figure 4.54) but not in the upper River Noe catchment. Within the Upper Derwent system, Ladybower Brook and the River Alport recorded the highest concentrations of zinc.

Colour and iron were significantly correlated (see section 5 and Figure 5.7). These two determinands, included by STWL, correspondingly have similar spatial maps, with Ladybower Brook, Abbey Brook and the River Ashop having the highest concentrations of these determinands (Figure 4.55 and Figure 4.56).

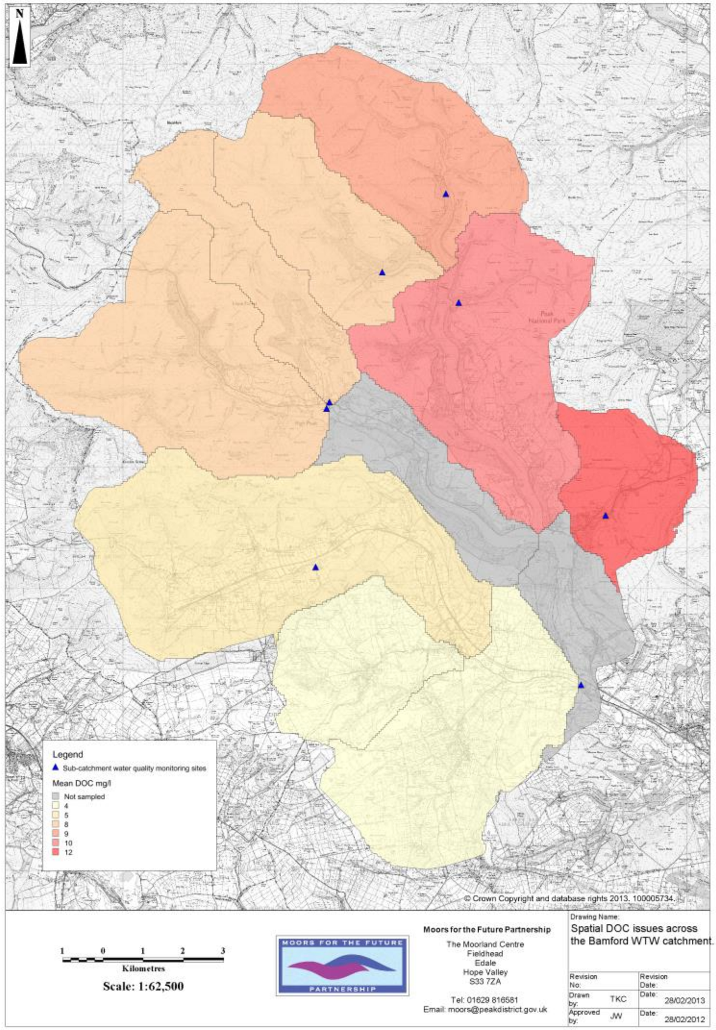

Figure 4.51: Spatial DOC across the Bamford WTW catchment (NB. sample sites for AB and RNU sampled only a proportion of the sub-catchment they were within – see Figure 3.5).

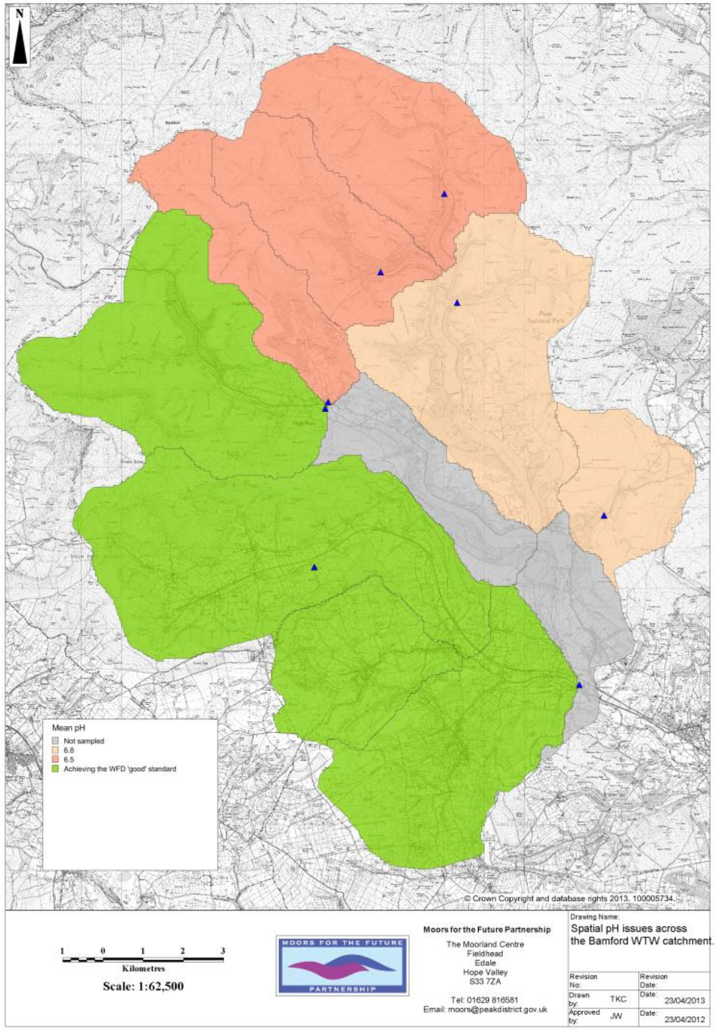

Figure 4.52: Spatial pH issues across the Bamford WTW catchment.

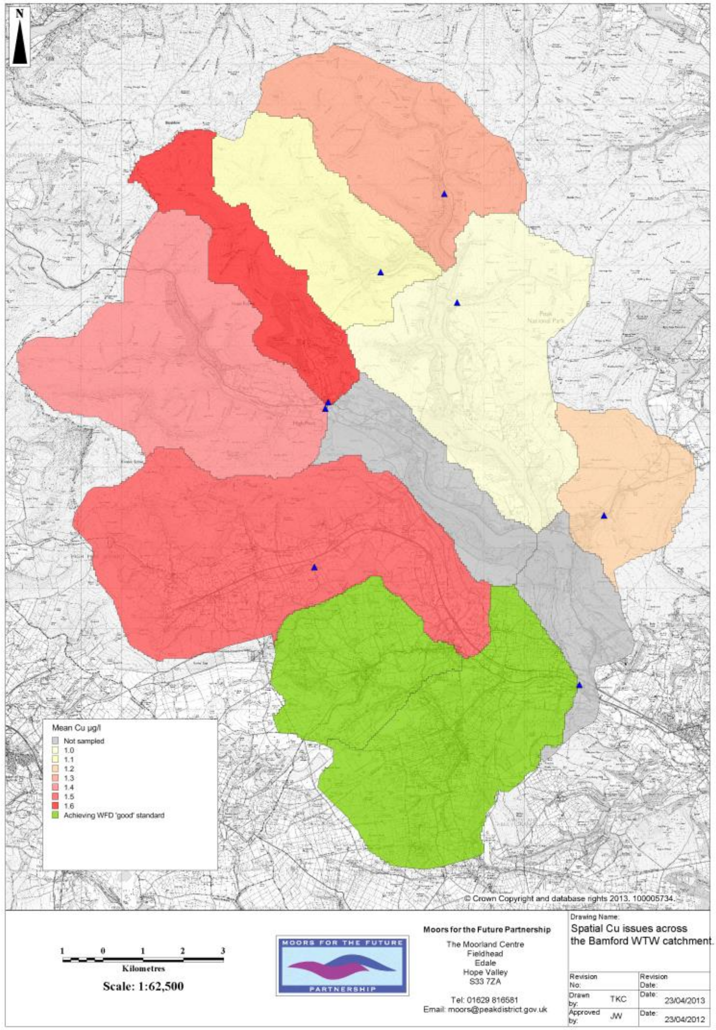

Figure 4.53: Spatial copper issues across the Bamford WTW catchment.

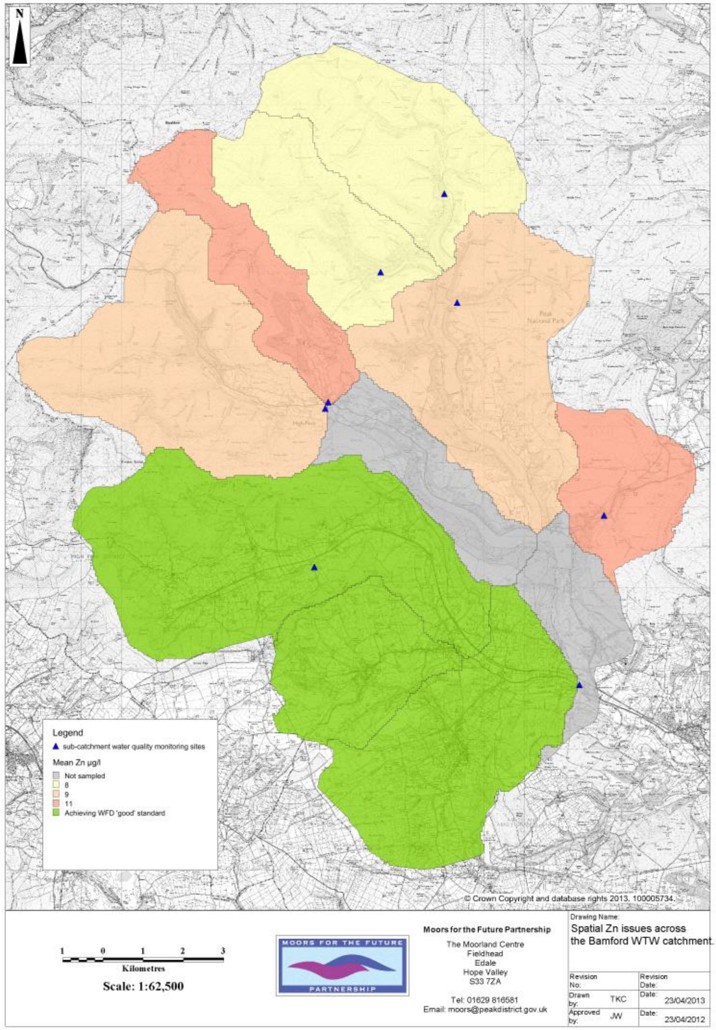

Figure 4.54: Spatial zinc issues across the Bamford WTW catchment.

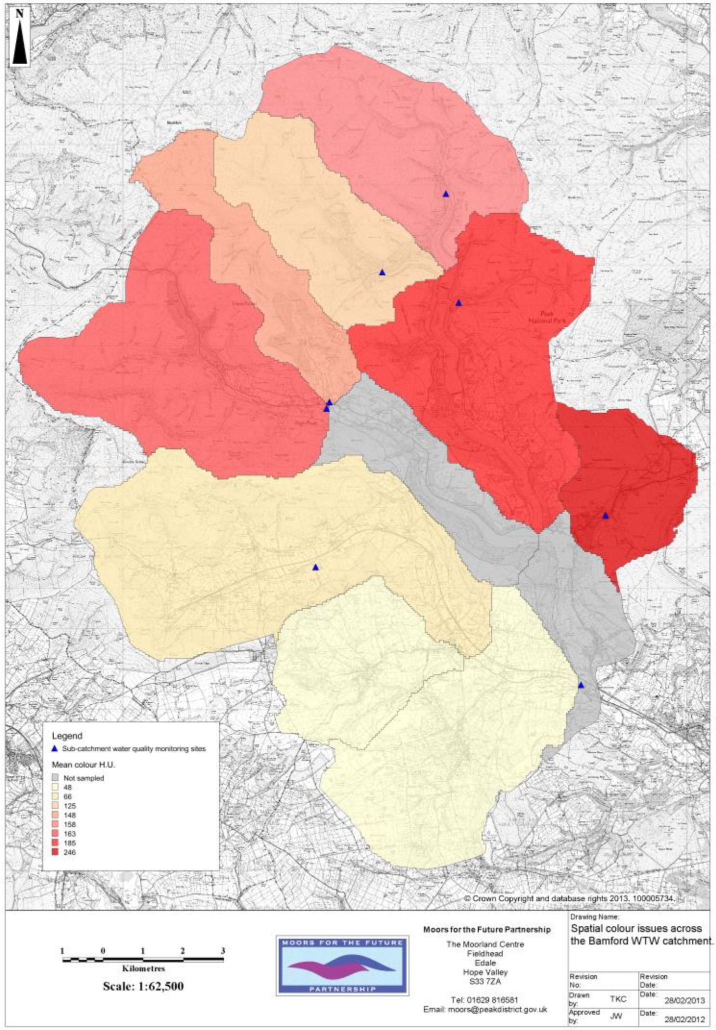

Figure 4.55: Spatial colour issues across the Bamford WTW catchment.

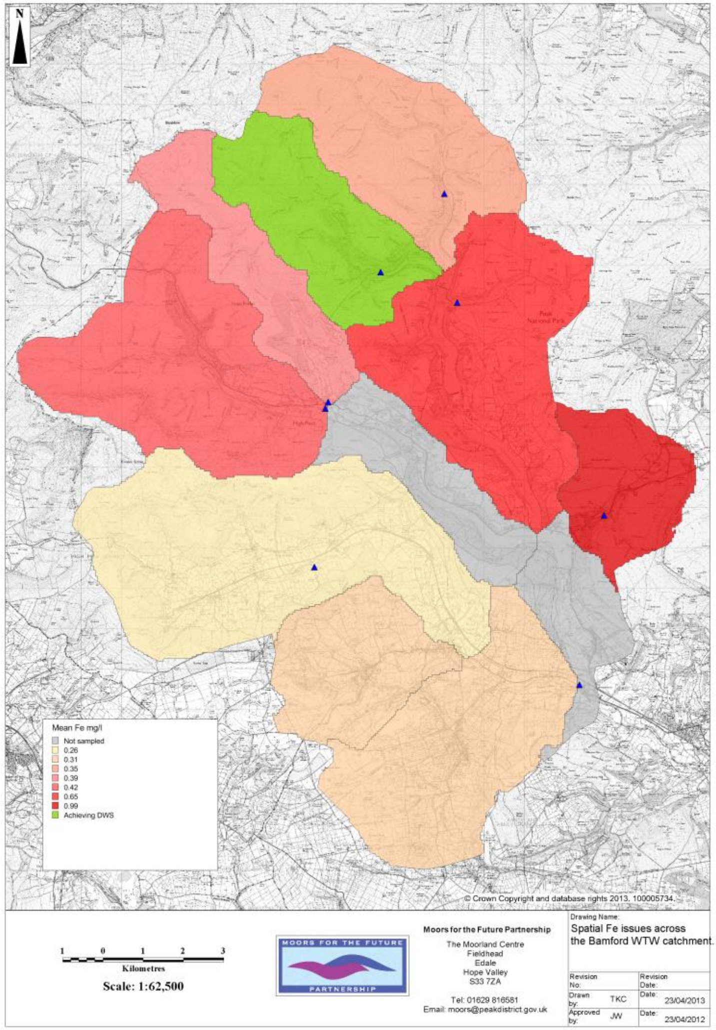

Figure 4.56: Spatial iron issues across the Bamford WTW catchment.

4.14.2 Moorland edge summary

The water quality from moorland edge catchments is generally poor, failing DWS and WFD objectives for the determinands of focus in this report (see Table 4.5). All moorland catchments failed on pH, copper, zinc and colour.

Table 4.5: Water quality from moorland edge catchments. Red = fails condition; green = meets condition.

Moorland catchment	Code	Peat condition	pH	Copper	Zinc	Colour	Iron
			WFD	WFD	WFD	DWS	DWS
Fair Brook	FB	Un-restored					
Upper Red Brook	URB	Early stage restoration					
Devils Dike	DD	Degraded					
Upper North Grain	UNG	Degraded					
Green Clough	GC	Heather burn					
Within Clough	WC	Heather burn					
Ashop Head	AH	Intact reference					

In general, water draining moorland catchments is not achieving DWS or WFD objectives and moorland condition has a significant impact on all of the determinands identified by the EA and STWL (see Table 4.6). Overall the impact of moorland condition, when condition is summarised as either 1) degraded (five catchments); 2) heather burn (two catchments); and 3) intact (one catchment), was consistent across the determinands – stream water concentration of focal determinands were greatest for degraded catchments and lowest for the intact catchments; for pH, acidity was highest for degraded sites and lowest for the intact site. Heather burn catchments were placed between unrestored catchments and the intact catchment. Iron did not show a clear relationship with moorland condition.

Table 4.6: Summary of the relative impact of moorland condition on water quality. Red = relatively high concentrations; yellow = relatively low concentrations; orange = concentrations between high and low.

	Degraded	Heather Burn	Intact reference
DOC			
POC			
Colour			
Copper			
Zinc			
Iron			
pH			

5. Relationship between determinands

Spearman's rank-order correlation was used to look for relationships between determinands across sub-catchment sites (Table 5.1) and moorland edge sites (Table 5.2). There are significant relationships between the following determinands: DOC and colour at sub-catchment and moorland edge sites (Figure 5.1); DOC and pH at moorland edge sites (Figure 5.2); colour and pH at moorland edge sites (Figure 5.3); DOC and Cu at moorland edge sites (Figure 5.4); DOC and Fe at sub-catchment sites (Figure 5.5); colour and Cu at moorland edge sites (Figure 5.6); colour and Fe at sub-catchment sites (Figure 5.7); and pH and Cu at moorland edge sites (Figure 5.8).

Table 5.1: Level of significance of correlations between determinands across sub-catchment sites.

	Colour	pH	Cu	Zn	Fe	Al	Cr
DOC	0.00**	0.41	0.10	0.10	0.04*	0.45	0.23
Colour		0.58	0.22	0.80	0.00***	0.46	0.34
pH			0.86	0.53	0.89	0.71	0.02*
Cu				0.79	0.59	0.06	0.80
Zn					0.24	0.15	0.88
Fe						0.98	0.64
Al							0.70

(* correlation is significant at the 0.05 level; ** 0.01 level; *** 0.001 level)

Table 5.2: Level of significance of correlation between determinands across moorland edge sites.

	Colour	pH	Cu	Zn	Fe	Al	Cr
DOC	0.00***	0.01*	0.01**	0.06	0.59	0.27	0.82
Colour		0.03*	0.03*	0.09	0.96	0.18	0.95
pH			0.00***	0.15	0.15	0.65	0.92
Cu				0.14	0.26	0.67	0.71
Zn					0.76	0.80	0.18
Fe						0.57	0.48
Al							0.40

(* correlation is significant at the 0.05 level; ** 0.01 level; *** 0.001 level)

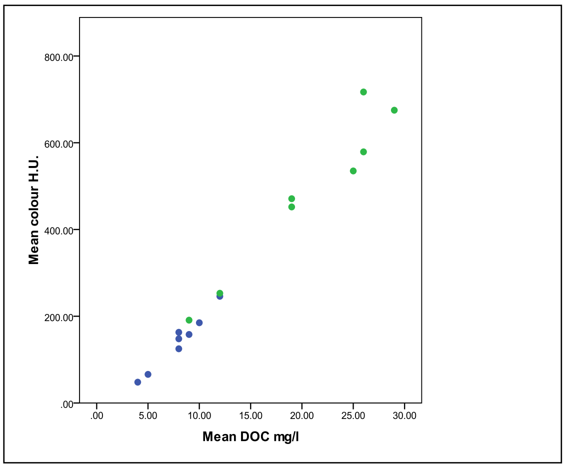

Figure 5.1: DOC and colour (blue = sub-catchment sites; green = moorland edge sites).

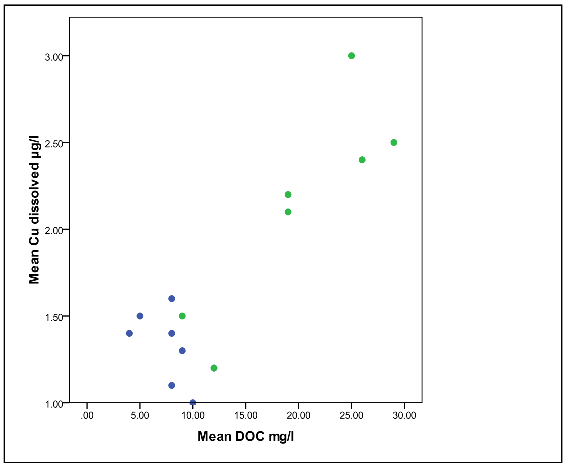

Figure 5.4: DOC and copper (blue = sub-catchment sites; green = moorland edge sites).

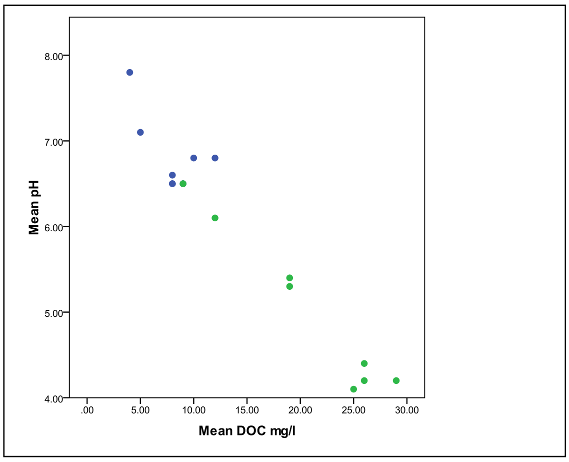

Figure 5.2: DOC and pH (blue = sub-catchment sites; green = moorland edge sites).

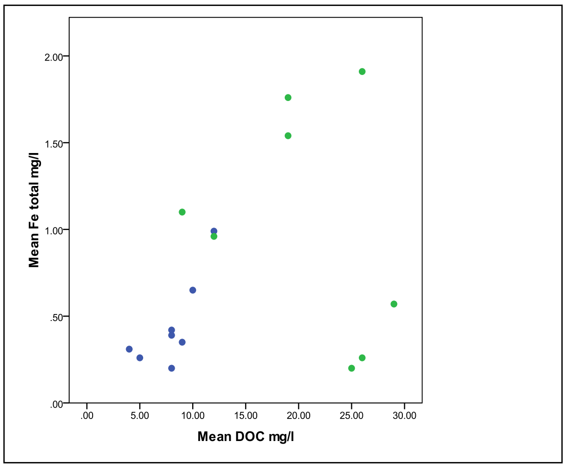

Figure 5.5: DOC and iron (blue = sub-catchment sites; green = moorland edge sites).

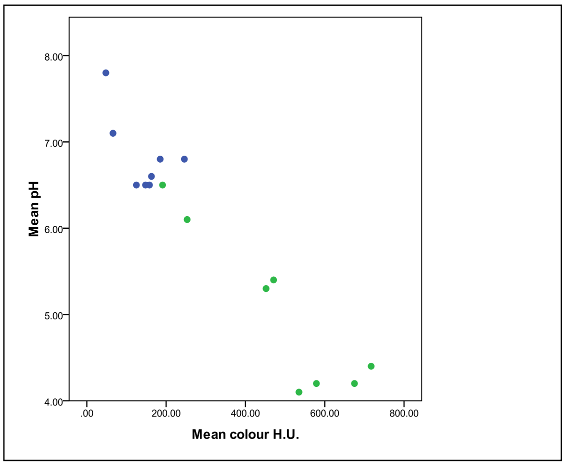

Figure 5.3: Colour and pH (blue = sub-catchment sites; green = moorland edge sites).

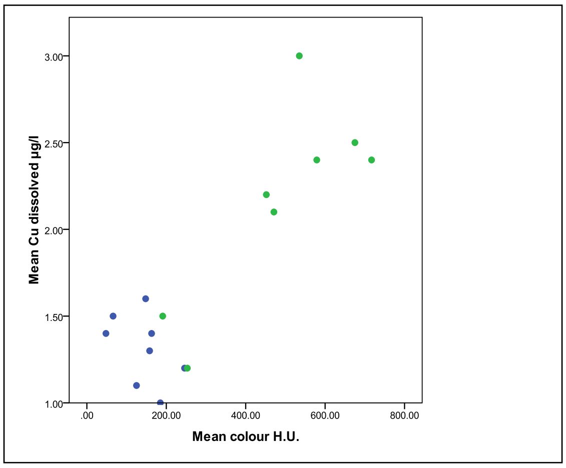

Figure 5.6: Colour and copper (blue = sub-catchment sites; green = moorland edge sites).

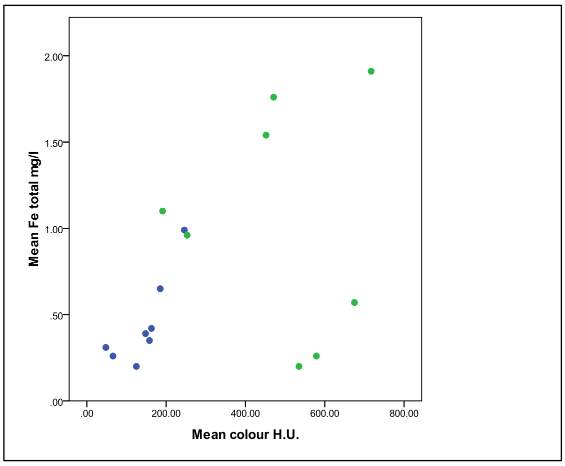

Figure 5.7: Colour and iron (blue = sub-catchment sites; green = moorland edge sites).

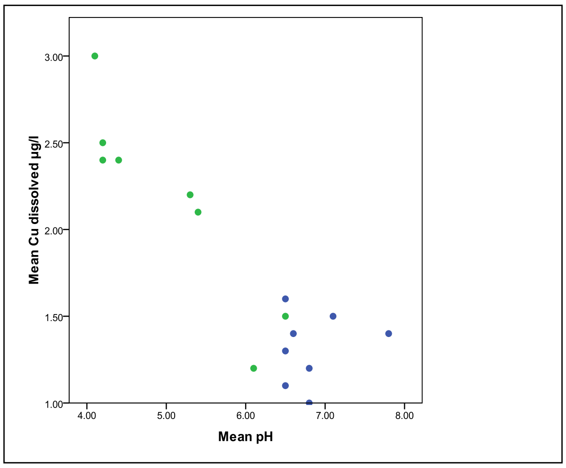

Figure 5.8: pH and copper (blue = sub-catchment sites; green = moorland edge sites)

6. Discussion

The results of the annual water quality monitoring programme across the Bamford water treatment works catchment was carried out during a year of atypical weather (see Figure 6.1). The Met Office summary for 2012[3] describes a year of dramatic contrast. The year began with concerns over long-term drought heightened by a relatively dry January to March (March 2012 was the third warmest on record for the UK) but an abrupt shift in weather patterns brought an exceptionally wet period for most of the country from April lasting through much of the summer. April and June were the wettest in the England and Wales since 1766, while summer (June, July, August) was the wettest since 1912. Rainfall totals for autumn and December remained well above average.

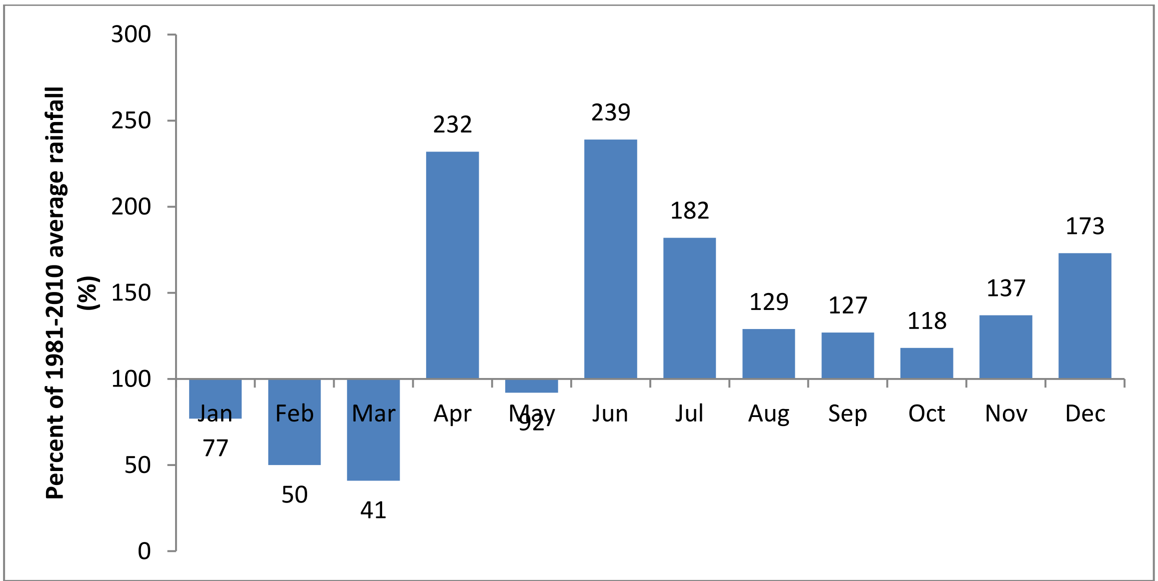

Figure 6.1: Rainfall anomalies for 2012 compared to average rainfall in England during proceeding 30 year period (1981-2010). Data taken from Met Office: http://www.metoffice.gov.uk/climate/uk/anomalygraphs/.

The water quality results presented in this report and spatial and temporal patterns must be viewed in the context of sampling taking place during a year of unusual weather conditions; although whether such conditions actually become more typical as a result of climate change remains to be seen.

A manual spot sampling campaign across the catchment, while providing a reliable baseline of some parameters of water quality measured in this study of the sub-catchments within the Bamford WTW catchment will invariably under record the peak concentrations generated, particularly those during storm events, especially at the end of summer / early autumn (the so called 'autumn flush'). A number of storm events have been sampled during this project; however, generally accessing remote moorland sites and sampling rivers during storm events is not possible for obvious health and safety reasons. Automated water sampling is possible, which would enable sampling during rainfall conditions and at locations not safe for fieldworkers to access / work out in; although auto-sampling at the scale and duration of this project would require significant resources. A programme of storm sampling would be highly informative; particularly to investigate the relative impact / effect storm

[3] http://www.metoffice.gov.uk/climate/uk/2012/annual.html

events, across different moorland ‘conditions’ as different moorland conditions / land covers may be differentially affected by storm events.

6.1 Moorland condition and water quality

The condition of moorland catchments had a significant impact on the quality of the fluvial water flowing from them. Degraded, bare peat and eroded / eroding catchments had significantly lower water quality than moorland ‘heather’ catchments that were managed by burning, while the ‘best’ water quality was recorded from the ‘intact’ reference site (Ashop Head) used in the study. Intact is relative within the moorlands of the Peak District / South Pennines, the intact catchment in this project comprised ~3.5 % bare peat and contains some gullies. Although the water quality from this catchment was better than the other moorland catchments in this study, it nevertheless still failed WFD standards for pH, copper and zinc and DWS for colour and iron, and some restoration intervention on this catchment to reduce the extent of bare peat and gullies would be beneficial for water quality.

In the short-term, however results from an ‘early stage restoration’ catchment suggest that moorland restoration does not significantly improve water quality compared with unrestored moorland in terms of DOC and heavy metal loadings. Water quality benefits, in the short-term of bare peat stabilisation and gully blocking was significantly lower peaks in POC concentrations compared with unrestored sites which supports previous evidence of the benefit of restoration on POC flux (Evans et al 2009, PAA 2010). The longer term impacts are being monitored by the Moors for the Future Partnership and other moorland restoration projects e.g. SCaMP (United Utilities).

Within the Ashop sub-catchment the water quality (for the focal determinands) from moorland catchments monitored, while variable across the different moorland conditions and parameters, overall contributed high concentration / values compared to those recorded at the bottom of the Ashop sub-catchment. On average, concentrations are twice as high at the moorland edge as they are at the bottom of the Ashop sub-catchment. High(er) DOC concentrations are generated from extensive peat catchments than non-peat catchments and so high DOC / colour is as expected at the moorland edge scale (and for copper which was positively correlated with DOC in this catchment). This has significance as there will be a gradient of pollutant concentration through sub-catchments, and at a finer spatial resolution pollutant loadings and ‘condition status’ may vary significantly down the sub-catchments with unknown potential impact on wildlife at this scale. What is required is an understanding of the contribution of moorlands to sub-catchment water quality, the contribution of water quality to the impact of in-stream processes on water chemistry down to the sub-catchment scale to formulate and assess the impact of moorland land management on sub-catchment scale water quality. Addressing moorland catchment condition should have significant impacts on water quality at the sub-catchment scale.

6.2 Water Quality within the Bamford WTW catchment

There are significant water quality issues across the sub-catchments of the Bamford WTW catchment. These are variable in space (between the sub-catchments) and in time. In terms of spatial difference a major distinction within the Bamford WTW catchment is that the catchment essentially comprises two distinct systems, the River Derwent and River Noe. There are similar water quality issues between the two systems in relation to WFD and DWS; however, there are also distinct differences in terms of the magnitude of determinand concentrations within the systems. The Noe system has lower mean annual concentrations of DOC, pH, colour, iron than the Derwent system, but has higher zinc concentrations and is the only catchment that does not meet the WFD standard for Chromium. The River Noe catchments differ from the rest of the catchments in that the southern slopes of the catchment mark the transition of underlying geology from Millstone Grit to the north to Limestone (with Subordinate Sandstone And Argillaceous Rocks; BGS[4] 2013). Additionally, within the Noe catchment there is also relative little moorland compared with the Derwent system while the composition and management of the non-moorland areas of the catchments (e.g. rough grazing and in-bye) may have a significant influence fluvial water quality. The high concentrations of zinc within the lower River Noe sub-catchment, but low concentrations in the upper River Noe catchment, suggests that in this system zinc input from non-moorland land management is significant. Again, an understanding of the contribution of moorland and non-moorland inputs to fluvial chemistry loadings is essential to formulate plans to address water quality across the Bamford WTW catchment.

Of the sub-catchments within the River Derwent system, in terms of meeting DWS and WFD objectives, the Ladybower Brook sub-catchment potentially represents the most significant issues as, relative to other sub-catchments, it has the highest annual mean concentrations of DOC, zinc, colour and iron. The Abbey Brook sub-catchment (that neighbours Ladybower Brook) also has relatively high concentrations of DOC, colour and iron. The Ashop and Alport sub-catchments, similarly, in terms of the magnitude of loadings above DWS and WFD objectives, represents significant issues within the Bamford WTW catchment for DOC, copper and iron (and level of acidity with Westend and Derwent sub-catchments).

[4] http://mapapps.bgs.ac.uk/geologyofbritain/home.html; accessed 04.03.2013

6.3 Discussion of individual determinands

The following section discusses the results for each determinand in relation to the recent literature.

6.3.1 Dissolved organic carbon

Dissolved organic carbon (DOC) is an important component of soils and natural waters. However, over the last three decades, DOC concentrations have increased in surface waters draining semi-natural ecosystems in many areas. In the United Kingdom, DOC concentrations have approximately doubled since the 1980s in areas dominated by organic soils. This represents issues for both the aquatic ecosystem, in terms of energy supply and light regime, and drinking water supplies, in terms of DOC removal and the associated health risks through trihalomethane formation. Increases in DOC have previously been attributed to climate change, land management (e.g. moorland burning and draining), and atmospheric deposition (Evans et al., 2012). More recently, Evans et al. (2012) suggest that decreasing acid deposition represents a highly plausible driver of increased surface water DOC. According to Evans et al. (2012), the Peak District has seen around a threefold reduction in sulphur deposition since 1970, meanwhile DOC concentrations in nearby surface waters have increased by a factor of 2.94. Furthermore, Rothwell et al. (2007a) suggest that high DOC concentrations in the southern Pennines can be explained by a lower water table position. This allows DOC production to increase due to an increase in oxygenation of organic matter (Holden et al., 2004, cited in Rothwell et al., 2007a). This is supported by higher stream water DOC concentrations in artificially drained peatlands than in intact peatland systems (Wallage et al., 2006, cited in Rothwell et al., 2007a).

Humic substances are major complexing agents in natural waters and control the behaviour and mobility of many metals in fluvial systems (Gao et al., 1999). In blanket peats, the onset of rainfall causes the water table level to rise in the acrotelm (Holden and Burt, 2003, cited in Rothwell et al., 2007a). Near-surface acrotelm drainage flushes accumulated stores of DOC into peatland fluvial systems, resulting in elevated DOC concentrations during high flow (Worrall et al., 2002, cited in Rothwell et al., 2007a). Under stormflow conditions, the acidity of waters draining blanket peat catchments also increases (Worrall et al., 2003, cited in Rothwell et al., 2007a). This is due to the flushing of organic acids from the acrotelm and the export of H^+ ion rich waters, due to cation exchange in the peat (Chapman et al., 1993; Gorham et al., 1984, cited in Rothwell et al., 2007a). Therefore, acidic, DOC-rich waters draining the contaminated top few centimeters of the peat layer have the potential to release dissolved metals to receiving surface waters (Rothwell et al., 2007a).

This study found that the concentration of DOC varies spatially between and within sub-catchment and moorland edge sites. The differences between moorland edge sites are significant and demonstrate that that the concentration of DOC is significantly higher in streams draining more degraded moorland sites than in those draining less degraded sites. For example, FB (un-restored) has an annual mean DOC concentration of 25 mg/l compared with 9 mg/l at AH (intact reference site). This demonstrates the potential reduction in DOC that may be achieved by returning sites to a less degraded state. NRB and URB (early stage restoration) have higher annual mean DOC concentrations than the FB (un-restored);

however, this may be due to reduced soil acidity through the application of lime (a phase of bare peat restoration), and is likely to be a short term phenomenon. The concentration of DOC also varies in time; this appears to be related to rainfall, for example, some of the highest concentrations of DOC were recorded during sample week 14 (July) following very high rainfall in June (309 mm – see Figure 4.1). Furthermore, there are a few peaks in DOC which are followed by three to four weeks of decreasing DOC. This may demonstrate an exhaustion of DOC, similar to that demonstrated by Worrall et al. (2002, cited in Rothwell et al., 2007a) for the autumn period. DOC is significantly and positively correlated with colour (sub-catchment and moorland edge sites); this is because the humic and fulvic acids that make water appear coloured also make up 50 to 75% of DOC (Watts et al., 2001). DOC is also significantly and positively correlated with Cu (moorland edge) and Fe (sub-catchment) and significantly and negatively correlated with pH (moorland edge). This is because DOC can form dissolved complexes with dissolved metals in fluvial systems. Furthermore, metal complexation is dependent on pH (Stumm and Morgan, 1996, cited in Rothwell et al., 2007a); therefore, variations in pH and the type and amount of DOC influence the spatial variability in metal concentrations in peatland fluvial systems (Lawlor and Tipping, 2003, cited in Rothwell et al., 2007a).

6.3.2 pH

The concentration of pH varies spatially between and within sub-catchment and moorland edge sites. The differences between moorland edge sites are significant and demonstrate that pH is significantly lower in streams draining more degraded moorland sites than in those draining less degraded sites. This demonstrates the potential increase in pH that may be achieved by returning sites to a less degraded state. NRB and URB have marginally higher pH (0.1) than FB; this supports the theory that reduced soil acidity may be causing higher DOC at early stage restoration sites, compared to un-restored sites. The pH also varies in time; this variation is greater for moorland edge sites (pH 4.5 – 7.0) than for sub-catchment sites (pH 5.8 – 7.6). There is a significant negative relationship between pH and DOC, colour and Cu (moorland edge sites). Rothwell et al. (2007a) also found a significant negative relationship between pH and DOC at Upper North Grain.

6.3.3 Copper

The concentration of Cu varies spatially between and within sub-catchment and moorland edge sites. The differences between moorland edge sites are significant and demonstrate that the concentration of Cu is significantly higher at FB (un-restored) than at AH (intact reference site). There is a significant positive relationship between DOC and Cu (at moorland edge sites); as a result, the concentration of Cu follows a similar pattern to that of DOC, whereby it is higher in streams draining more degraded moorland sites than in those draining less degraded sites. This demonstrates that Cu, in addition to DOC, may be reduced by returning sites to a less degraded state. The concentration of Cu also varies in time; this appears to be more variable for sub-catchment sites than for moorland edge sites. Cu is also significantly and positively correlated with colour and significantly and negatively correlated with pH.

6.3.4 Zinc

The concentration of Zn varies spatially between and within sub-catchment and moorland edge sites. There are significant differences between some of the moorland sites, i.e., FB has a significantly higher mean concentration of Zn than AH; NRB has a significantly higher mean concentration of Zn than GC and AH; URB, DD and UNG have significantly higher mean concentrations of Zn than GC, WC and AH; and GC and WC have significantly higher mean concentrations of Zn than AH. This shows that the mean concentration of Zn is significantly higher at the more degraded moorland sites and significantly lower at the less degraded sites. The concentration of Zn also varies in time. For sub-catchment sites, the highest concentration of Zn recorded for sub-catchment sites was for sample week 14 (July) following high rainfall in June (309 mm – see Figure 4.1). However, this does not seem to apply to moorland edge sites.

Rothwell et al. (2007a) investigated baseflow and stormflow dissolved metal concentrations in streams draining contaminated blanket peat catchments in the peak district, including Upper North Grain. They found that under baseflow and stormflow conditions previously deposited heavy metals, including Cu and Zn are leached from blanket peats into the fluvial system. Rothwell et al. (2007a) found no significant relationship between DOC and Cu or DOC and Zn under baseflow conditions and only a weak significant relationship under stormflow conditions. It is suggested that Cu is not effectively complexed by DOC in this upland region under baseflow conditions due to sorption of Cu with abundant dissolved mineral phases in the soil-water system. The lack of any relationship between DOC and Zn under baseflow is because Zn is poorly complexed to organic matter in acidic peatland systems (Tipping et al., 2003, cited in Rothwell et al., 2007a). However, in a lab based mixing experiment, Rothwell et al. (2008b) demonstrates that stream water Zn concentrations are increased when contaminated peat is mixed with acidic stream water (Rothwell et al. (2008b).

6.3.5 Water colour

Water colour varies spatially between and within sub-catchment and moorland edge sites. The differences between moorland edge sites are significant and demonstrate that water colour is significantly higher in streams draining more degraded moorland sites than in those draining less degraded sites. However, this is not as clear a picture as that for DOC because some of the colour is due to Fe. For example, DD has lower DOC but higher colour than FB, NRB and URB. This difference is due to a higher Fe concentration at DD, for example at DD colour consists of 93 % DOC and 7 % Fe compared with 99 % DOC and 1 % Fe at FB (see Table 6.1). Water colour also varies in time; as with DOC, this appears to be related to rainfall, with the highest concentrations of water colour recorded during sample week 14 (July) following very high rainfall in June (309 mm – see Figure 4.1). Water colour is significantly and positively correlated with DOC (sub-catchment and moorland edge sites), Cu (moorland edge sites), and Fe (sub-catchment sites) and significantly and negatively correlated with pH (moorland edge sites).

Increased water colour is generally attributed to increased concentrations of DOC; this is supported by the strong correlation between DOC and water colour. However, according to

Kritzberg and Ekström (2012), water colour has often increased significantly more than organic matter, suggesting that organic matter content alone is not sufficient to explain the increase in water colour. A number of studies (Kritzberg and Ekström, 2012 and references therein) suggest that both organic matter and Fe contribute to colour. This is supported here by a weak but significant relationship between colour and Fe at sub-catchment sites. Increasing Fe concentrations have been reported for upland waters in the UK (Neal et al., 2008) and surface waters in Sweden (Kritzberg and Ekström, 2012). While, an important pathway for Fe into surface waters is leaching from soils in complex with DOC, this may not be the sole explanation for increasing Fe. Kritzberg and Ekström (2012) speculate that increasing iron can be caused by changes in redox conditions, which mean more anoxic water with high concentrations of FeII are feeding into surface waters.

Table 6.1: Contribution of DOC and iron to water colour for moorland edge sites.

Site ID	% DOC	% Fe
FB	99	1
NRB	99	1
URB	98	2
DD	93	7
UNG	93	7
GC	93	7
WC	92	8
AH	89	11

6.3.6 Iron

Iron concentrations have doubled over the past 20 years (~3.7 µg yr^{-1} for moorland). Generally Fe correlates well with DOC (Neal et al., 2008); with the greatest rates of Fe increase coinciding with those for DOC. According to Neal et al. (2008), Fe increases for surface waters are associated with increased microparticulate Fe (III) due to stabilisation against aggregation by binding of dissolved organic matter (DOM) to its surface.

The mean concentration of Fe varies spatially between and within sub-catchment and moorland edge sites. The differences between moorland edge sites are significant. However, there is no obvious pattern and it is not particularly clear if / how moorland condition effects Fe concentration. However, Fe is a redox sensitive metal (Rothwell et al., 2010); therefore the variability could be related to specific processes such as fluctuations in water table depth and redox cycling. For example, Rothwell et al. (2010) showed that short-term fluctuations in water table depth and redox cycling have led to the accumulation and precipitation of Fe just below the peat surface. Fe also varies in time; for sub-catchment sites, the highest concentration of Fe recorded for sub-catchment sites was for sample week 14 (July) following high rainfall in June (309 mm – see Figure 4.1). As with Zn, this does not seem to apply to moorland edge sites. Fe is significantly and positively correlated with DOC and water colour (sub-catchment sites).

6.3.7 Aluminium

The mean concentration of Al varies spatially between and within sub-catchment and moorland edge sites. The differences between moorland edge sites are significant; however, there is no obvious pattern and it is not particularly clear if / how moorland condition effects Al concentration. Al also varies in time; for sub-catchment sites, the highest concentration of Al recorded for sub-catchment sites was for sample week 14 (July) following high rainfall in June (309 mm – see Figure 4.1). However, this does not seem to apply to moorland edge sites.

6.3.8 Chromium

The mean concentration of Cr for sub-catchment sites is 1.6 µg/l; however, this is biased by the high contribution from the RNL (4.9 µg/l). Excluding the RNL, the mean concentration of Cr for sub-catchment sites is 1.1 µg/l. This is higher than the mean concentration of Cr for moorland edge sites of 1.0 µg/l. This demonstrates that Cr is not a moorland issue and for that reason it is not discussed further. Moreover, there is no significant relationship between Cr and DOC, nor Cr and water colour.

7. Conclusions

This study of spatial variation in water quality within the water bodies of a Peak District catchment and the contribution of moorland condition has shown that:

1. DOC, pH and heavy metal concentrations of sub-catchment and moorland edge sites are spatially and temporally variable.
2. A number of sub-catchment sites are failing to achieve the WFD 'good' standard for pH, Cu and Zn.
3. All moorland edge sites are failing to achieve the WFD 'good' standard for pH, Cu and Zn.
4. All sub-catchment sites are failing to achieve the DWS for colour and Fe (except RW), and half are failing to achieve the DWS for Al.
5. All moorland edge sites are failing to achieve the DWS for colour, Fe (except FB) and Al.
6. DOC is significantly positively correlated with Cu (moorland edge sites) and Fe (sub-catchment sites). This is because some metals can complex with DOC. pH is negatively correlated with DOC and Cu. This is because metal complexation is dependent on pH. Therefore, a reduction in surface water acidification and DOC export may lead to a reduction in metal export.
7. DOC is significantly positively correlated with colour (sub-catchment and moorland edge sites). This is because the humic and fulvic acids that make water appear coloured also make up 50 to 75% of DOC. This provides a link between the issues raised by the EA and STWL.
8. Fe is significantly positively correlated with DOC and colour (sub-catchment sites). In addition to complexing with DOC, water table fluctuations and redox cycling have been used to explain increased Fe in surface waters.
9. Differences between moorland edge sites are significant. DOC, colour, Cu and Zn is significantly higher and pH is significantly lower in streams draining more degraded moorland sites than in those draining less degraded sites. Therefore, DOC, colour, Cu and Zn may be reduced by returning sites to a less degraded state.
10. Differences between moorland edge sites are also significant for Fe and Al. However, there is no obvious pattern and it is not particularly clear if / how moorland condition affects Fe and Al concentration. It is possible that there are other factors affecting Fe and Al concentration that were not investigated in this report, e.g. fluctuations in water table depth and redox cycling.

8. References

Bonn, A., Holden, J., Parnell, M., Worrall, F., Chapman, P.J., Evans. C.D., Termansen, M., Beharry-Borg, N., Acreman, M.C., Rowe, E., Emmett, B., Tsuchiya, A. (2010) Ecosystem services of peat – Phase 1. Report to Defra (project code: SP0572). http://randd.defra.gov.uk/Default.aspx?Menu=Menu&Module=More&Location=None&Completed=0&ProjectID=15990

Chapman, D.S., Bonn, A., Kunin, W.E., Cornell, S.J. (2010) Random Forest characterization of upland vegetation and management burning from aerial imagery. *Journal of Biogeography* 37: 37–46.

DWI (2013) Drinking Water Inspectorate (on-line). http://dwi.defra.gov.uk/. Accessed 6 March 2013.

Environment Agency (2009a) *River Basin Management Plan Humber River Basin District* (on-line). http://www.environment-agency.gov.uk/research/planning/124803.aspx. Accessed 22 March 2012.

Environment Agency (2009b) *Annex B: Water body Status objectives* (on-line). http://publications.environment-agency.gov.uk/PDF/GENE0910BSQT-E-E.pdf. Accessed 22 March 2012.

Environment Agency (2010) *Supplementary briefing note 4: Temperature control of samples during transportation* (on-line). http://www.environment-agency.gov.uk/static/documents/Business/bn4_samples_during_transportation.pdf. Accessed 23 March 2012.

Environment Agency (2012) *Find out about your River Basin District* (on-line). http://www.environment-agency.gov.uk/research/planning/33112.aspx. Accessed 23 March 2012.

European Commission (2008) *Water Note 4 Reservoirs, Canals and Ports: Managing artificial and heavily modified water bodies* (on-line). http://ec.europa.eu/environment/water/waterframework/pdf/water_note4_reservoirs.pdf. Accessed 23 March 2012.

Evans, C.D., Jones, T.G., Burden, A., Ostle, N., Zieliński, P., Cooper, M.D.A., Peacock, M., Clark, J.M., Oulehle, F., Cooper, D., Freeman, C. (2012) Acidity controls on dissolved organic carbon mobility in organic soils. *Global Change Biology* 18: 3317-3331.

Evans, M.G., Pawson, R., Daniels, S. , Yang, J., Wilkinson, R. Rowson,J., Worrall,F. (2009) Carbon Flux from Moorland Restoration Sites: Interim Report - Year 2. Moors for the Future Report No 19.

Kritzberg, E.S., Ekström, S.M. (2012) Increasing iron concentrations in surface waters – a factor behind brownification? *Biogeosciences* 9: 1465-1478.

Met Office (2012) Met Office confirms wettest June in over a century (on-line). http://www.metoffice.gov.uk/news/releases/archive/2012/wettest-June. Accessed 11 February 2013.

Moors for the Future Partnership (2012) Repairing Bare Peat (on-line). http://www.moorsforthefuture.org.uk/repairing-bare-peat. Accessed 12 July 2013.

Neal, C., Lofts, S., Evans, C. D., Reynolds, B., Tipping, E., Neal, M. (2008) Increasing iron concentrations in UK upland waters. *Aquatic Geochemistry*, 14, 263-288.

Penny Anderson Associates (2010) SCaMP Sustainable Catchment Management Programme; Monitoring Progress Report Year 4. PAA, Buxton.

Rhind, S.M. (2009) Anthropogenic pollutants: a threat to ecosystem sustainability? *Phil. Trans. R. Soc. B* 364: 3391-3401.

Rothwell, J.J., Robinson, S.G., Evans, M.G., Yang, J., & Allott, T.E.H. (2005) Heavy metal release by peat erosion in the Peak District, southern Pennines, UK. *Hydrological Processes*, 19, 2973-2989.

Rothwell, J.J., Evans, M.G., Daniels, S. M., Allott, T.E.H. (2007a). Baseflow & stormflow metal concentrations in streams draining contaminated peat moorlands in the Peak District (UK). *Journal of Hydrology*, 341, 90-104.

Rothwell, J.J., Evans, M.G., Allott, T.E.H. (2007b). Lead contamination of fluvial sediments in an eroding blanket peat catchment. *Applied Geochemistry*, 22, 446-459.

Rothwell, J.J., Evans, M.G., Liddaman, L.C., Allott, T.E.H. (2007c). The role of wildfire & gully erosion in particulate PB export from contaminated peatland catchments in the southern Pennines, UK. *Geomorphology*.

Rothwell, J.J., Evans, M.G., Daniels, S.M., Allott, T.E.H. (2008a). Peat soils as a source of lead contamination to upland fluvial systems. *Environmental Pollution*, 153, 582-589.

Rothwell, J.J., Evans, M.G., Allott, T.E.H. (2008b). In-stream processing of sediment-associated metals in peatland fluvial systems. Water Air Soil Pollut, 187, 53-64.

Rothwell, J.J., Taylor, K.G., Chernery, S.R.N., Cundy, A.B., Evans, M.G., Allott, T.E.H. (2010). Storage and behaviour of As, Sb, Pb and Cu in ombrotrophic peat bogs under contrasting water table conditions. *Environ. Sci. Technol.*, 44, 8497-8502.

SAL (2013) Method statements (on-line). http://www.salltd.co.uk/about_us/methods#navbar. Accessed 21 November 2012.

Shotbolt, L.A., Rothwell, J.J., Lawlor, A.J. (2008). A mass balance approach to quantifying Pb storage and fluxes in an upland catchment of the Peak District, north-central England. *Earth Surface Processes and Landforms*, 33, 1721-1741.

Shuttleworth, E.L., Evans, M.G., Rothwell, J.J. (2011). Impacts of erosion and restoration on sediment flux and pollutant mobilisation in the peatlands of the Peak District national Park. The University of Manchester.

Water Framework Directive (2010) *The River Basin Districts Typology, Standards and Groundwater threshold values (Water Framework Directive) (England and Wales) Directions 2010* (on-line). http://archive.defra.gov.uk/environment/quality/water/wfd/documents/2010directions.pdf Accessed 29 March 2012.

Water Supply Regulations (2000) *The Water Supply (Water Quality) Regulations 2000* (on-line). http://www.legislation.gov.uk/uksi/2000/3184/pdfs/uksi_20003184_en.pdf. Accessed 29 March 2012.

Watts, C.D., Naden, P.S., Machell, J. and Banks, J. (2001) Long term variation in water colour from Yorkshire catchments. *The Science of the Total Environment*, 278, 51-72.

9. Appendices

9.1 Appendix 1: Summary statistics

Colour H.U.						
Site name	Site ID	N	Mean	Std Dev	Min	Max
Abbey Brook	AB	14	185	126	39	390
Ladybower Brook	LB	14	246	188	27	600
River Alport	RAL	14	148	141	27	580
River Ashop	RAS	14	163	175	23	720
River Derwent	RD	14	158	106	24	330
River Noe lower	RNL	14	48	41	3	150
River Noe upper	RNU	14	66	49	3	160
River Westend	RW	14	125	86	24	270
Sub-catchment site total		**112**	**142**	**135**	**3**	**720**
Fair Brook	FB	13	535	229	260	980
Nether Red Brook	NRB	9	579	150	390	870
Upper Red Brook	URB	11	675	326	70	1200
Devils Dike	DD	13	717	350	160	1200
Upper North Grain	UNG	14	452	176	150	850
Green Clough	GC	14	253	164	55	560
Withins Clough	WC	14	471	230	200	1000
Ashop Head	AH	14	191	140	48	550
Moorland edge sites total		**102**	**471**	**285**	**48**	**1200**

Organic Carbon														
		DOC mg/l					**POC mg/l**				**TOC mg/l**			
Site name	Site ID	N	Mean	Std Dev	Min	Max	Mean	Std Dev	Min	Max	Mean	Std Dev	Min	Max
Abbey Brook	AB	26	10	6	2	23	1	1	1	4	9	6	1	20
Ladybower Brook	LB	26	12	7	2	25	1	1	1	4	11	6	1	27
River Alport	RAL	25	8	6	2	25	1	1	1	5	7	5	1	23
River Ashop	RAS	26	8	6	3	31	1	1	1	3	7	6	1	29
River Derwent	RD	26	9	6	2	23	1	1	1	6	8	6	1	22
River Noe lower	RNL	26	4	2	1	7	2	6	1	30	4	6	1	32
River Noe upper	RNU	26	5	3	1	13	1	1	1	4	4	3	1	11
River Westend	RW	25	8	5	2	21	1	1	1	6	6	5	1	20
Sub-catchment site total		**206**	**8**	**6**	**1**	**31**	**1**	**2**	**1**	**30**	**7**	**6**	**1**	**32**
Fair Brook	FB	23	25	8	15	44	2	2	1	6	26	7	15	41
Nether Red Brook	NRB	17	26	7	17	39	1	2	1	7	26	7	12	37
Upper Red Brook	URB	21	29	11	6	54	2	2	1	6	31	11	5	52
Devils Dike	DD	24	26	11	5	51	4	7	1	31	28	11	10	47
Upper North Grain	UNG	25	19	9	1	35	1	1	1	5	19	8	5	39
Green Clough	GC	26	12	9	2	34	1	1	1	3	12	8	1	34
Withins Clough	WC	25	19	7	6	36	1	2	1	8	19	7	5	31
Ashop Head	AH	25	9	5	2	25	1	1	1	3	8	5	2	21
Moorland edge sites total		**186**	**20**	**11**	**1**	**54**	**1**	**3**	**1**	**31**	**20**	**11**	**1**	**52**

pH						
Site name	Site ID	N	Mean	Std Dev	Min	Max
Abbey Brook	AB	26	6.8	1.0	3.9	9.5
Ladybower Brook	LB	26	6.8	0.6	5.3	7.7
River Alport	RAL	26	6.5	0.4	5.6	7.4
River Ashop	RAS	26	6.6	0.4	5.7	7.4
River Derwent	RD	26	6.5	0.8	4.5	7.6
River Noe lower	RNL	26	7.8	0.3	7.2	8.3
River Noe upper	RNU	26	7.1	0.3	6.5	7.6
River Westend	RW	25	6.5	0.6	5.0	7.5
Sub-catchment site total		**207**	**6.8**	**0.7**	**3.9**	**9.5**
Fair Brook	FB	23	4.1	0.6	3.7	6.9
Nether Red Brook	NRB	17	4.2	0.5	3.9	6.0
Upper Red Brook	URB	21	4.2	0.6	3.8	6.6
Devils Dike	DD	24	4.4	0.4	4.0	5.5
Upper North Grain	UNG	25	5.3	1.1	4.1	7.4
Green Clough	GC	26	6.1	1.1	4.2	8.6
Withins Clough	WC	25	5.4	0.8	3.9	7.2
Ashop Head	AH	25	6.5	0.5	5.0	7.4
Moorland edge sites total		**186**	**5.1**	**1.2**	**3.7**	**8.6**

Total hardness (expressed as CaCO3 mg/l)						
Site name	Site ID	N	Mean	Std Dev	Min	Max
Abbey Brook	AB	26	25	10	5	42
Ladybower Brook	LB	26	26	9	5	42
River Alport	RAL	26	19	4	13	26
River Ashop	RAS	26	24	28	12	160
River Derwent	RD	26	16	6	5	25
River Noe lower	RNL	26	172	41	25	250
River Noe upper	RNU	26	39	8	27	57
River Westend	RW	25	17	5	5	25
Sub-catchment site total		**207**	**42**	**53**	**5**	**250**
Fair Brook	FB	23	6	7	5	37
Nether Red Brook	NRB	17	6	5	5	24
Upper Red Brook	URB	21	8	6	5	25
Devils Dike	DD	24	5	2	5	14
Upper North Grain	UNG	25	10	9	5	36
Green Clough	GC	26	20	10	5	40
Withins Clough	WC	25	9	5	5	21
Ashop Head	AH	25	22	9	11	41
Moorland edge sites total		**186**	**11**	**9**	**5**	**41**

Aluminium (Al) mg/l							
		Total					
Site name	Site ID	N	Mean	Std Dev	Min	Max
Abbey Brook	AB	13	0.19	0.17	0.01	0.53
Ladybower Brook	LB	13	0.28	0.17	0.01	0.56
River Alport	RAL	13	0.29	0.21	0.01	0.69
River Ashop	RAS	13	0.20	0.14	0.03	0.53
River Derwent	RD	13	0.20	0.14	0.02	0.45
River Noe lower	RNL	13	0.28	0.25	0.01	0.69
River Noe upper	RNU	13	0.23	0.31	0.01	1.20
River Westend	RW	13	0.20	0.14	0.02	0.45
Sub-catchment site total		**104**	**0.23**	**0.20**	**0.01**	**1.20**
Fair Brook	FB	13	0.37	0.16	0.07	0.58
Nether Red Brook	NRB	9	0.34	0.19	0.20	0.81
Upper Red Brook	URB	12	0.50	0.19	0.19	0.89
Devils Dike	DD	13	0.47	0.18	0.29	0.93
Upper North Grain	UNG	13	0.28	0.13	0.12	0.56
Green Clough	GC	13	0.40	0.23	0.18	0.90
Withins Clough	WC	13	0.72	1.29	0.15	5.00
Ashop Head	AH	13	0.21	0.10	0.05	0.38
Moorland edge sites total		**99**	**0.41**	**0.50**	**0.05**	**5.00**

Arsenic (As) µg/l										
		Dissolved					**Total**			
Site name	Site ID	N	Mean	Std Dev	Min	Max	Mean	Std Dev	Min	Max
Abbey Brook	AB	26	0.8	0.5	0.2	2.0	0.7	0.4	0.1	1.8
Ladybower Brook	LB	26	1.0	0.5	0.3	2.9	0.9	0.4	0.1	2.2
River Alport	RAL	26	0.6	0.4	0.2	1.6	0.5	0.3	0.2	1.6
River Ashop	RAS	26	0.7	0.4	0.3	1.7	0.6	0.4	0.2	1.8
River Derwent	RD	26	0.9	0.8	0.3	4.1	0.7	0.4	0.2	1.6
River Noe lower	RNL	26	0.6	0.5	0.2	2.8	0.6	0.5	0.1	2.5
River Noe upper	RNU	26	0.5	0.4	0.1	1.7	0.4	0.3	0.1	1.7
River Westend	RW	25	0.7	0.4	0.3	1.7	0.6	0.3	0.1	1.6
Sub-catchment site total		**207**	**0.7**	**0.5**	**0.1**	**4.1**	**0.6**	**0.4**	**0.1**	**2.5**
Fair Brook	FB	23	1.6	0.8	0.6	4.2	1.7	0.8	0.4	3.6
Nether Red Brook	NRB	17	3.6	1.2	1.7	5.5	3.6	1.4	1.1	6.8
Upper Red Brook	URB	21	4.5	2.0	0.3	8.8	4.6	2.5	0.5	12.0
Devils Dike	DD	24	1.7	0.5	0.6	2.5	1.7	0.6	0.7	2.7
Upper North Grain	UNG	25	1.1	0.4	0.5	1.9	1.2	0.5	0.6	2.5
Green Clough	GC	26	0.8	0.5	0.2	2.0	0.9	0.5	0.1	2.1
Withins Clough	WC	25	1.3	0.6	0.6	3.1	1.4	0.7	0.7	3.9
Ashop Head	AH	25	0.6	0.4	0.1	2.0	0.6	0.4	0.1	1.8
Moorland edge sites total		**186**	**1.8**	**1.5**	**0.1**	**8.8**	**1.8**	**1.6**	**0.1**	**12.0**

Barium (Ba) µg/l										
		Dissolved					Total			
Site name	Site ID	N	Mean	Std Dev	Min	Max	Mean	Std Dev	Min	Max
Abbey Brook	AB	26	12	3	6	16	12	3	5	23
Ladybower Brook	LB	26	22	5	6	34	22	6	6	34
River Alport	RAL	26	13	2	9	15	13	2	11	17
River Ashop	RAS	26	18	21	10	120	18	19	9	110
River Derwent	RD	26	13	2	10	19	14	2	11	18
River Noe lower	RNL	26	118	41	15	270	129	63	20	410
River Noe upper	RNU	26	64	16	38	96	67	18	40	100
River Westend	RW	25	6	2	4	10	7	2	5	13
Sub-catchment site total		**207**	**34**	**40**	**4**	**270**	**35**	**46**	**5**	**410**
Fair Brook	FB	23	6	3	2	18	6	3	2	19
Nether Red Brook	NRB	17	8	4	4	22	8	5	3	26
Upper Red Brook	URB	21	10	5	4	29	11	6	4	35
Devils Dike	DD	24	7	3	3	13	7	2	3	10
Upper North Grain	UNG	25	13	7	4	33	14	7	5	31
Green Clough	GC	26	7	5	4	32	7	5	4	31
Withins Clough	WC	25	5	2	3	10	5	2	3	12
Ashop Head	AH	25	6	1	5	10	7	1	5	10
Moorland edge sites total		**186**	**8**	**5**	**2**	**33**	**8**	**5**	**2**	**35**

Beryllium (Be) µg/l										
		Dissolved					Total			
Site name	Site ID	N	Mean	Std Dev	Min	Max	Mean	Std Dev	Min	Max
Abbey Brook	AB	26	0.04	0.04	0.03	0.18	0.05	0.03	0.03	0.13
Ladybower Brook	LB	26	0.07	0.05	0.03	0.23	0.07	0.04	0.03	0.17
River Alport	RAL	26	0.06	0.04	0.03	0.20	0.06	0.04	0.03	0.15
River Ashop	RAS	26	0.04	0.04	0.03	0.19	0.05	0.05	0.03	0.25
River Derwent	RD	26	0.05	0.04	0.03	0.18	0.05	0.04	0.03	0.17
River Noe lower	RNL	26	0.04	0.03	0.03	0.12	0.04	0.03	0.03	0.16
River Noe upper	RNU	26	0.04	0.04	0.03	0.18	0.05	0.04	0.03	0.19
River Westend	RW	25	0.05	0.04	0.03	0.20	0.05	0.04	0.03	0.21
Sub-catchment site total		**207**	**0.05**	**0.04**	**0.03**	**0.23**	**0.05**	**0.04**	**0.03**	**0.25**
Fair Brook	FB	23	0.04	0.05	0.03	0.23	0.05	0.04	0.03	0.19
Nether Red Brook	NRB	17	0.06	0.05	0.03	0.17	0.06	0.05	0.03	0.17
Upper Red Brook	URB	21	0.05	0.04	0.03	0.16	0.05	0.04	0.03	0.16
Devils Dike	DD	24	0.07	0.05	0.03	0.18	0.08	0.05	0.03	0.24
Upper North Grain	UNG	25	0.06	0.03	0.03	0.16	0.07	0.04	0.03	0.21
Green Clough	GC	26	0.07	0.03	0.03	0.16	0.08	0.04	0.03	0.19
Withins Clough	WC	25	0.05	0.04	0.03	0.18	0.06	0.04	0.03	0.16
Ashop Head	AH	25	0.04	0.03	0.03	0.16	0.06	0.05	0.03	0.23
Moorland edge sites total		**186**	**0.06**	**0.04**	**0.03**	**0.23**	**0.06**	**0.05**	**0.03**	**0.24**

Boron (B) mg/l						
		Total				
Site name	Site ID	N	Mean	Std Dev	Min	Max
Abbey Brook	AB	13	0.01	0.00	0.01	0.02
Ladybower Brook	LB	13	0.01	0.00	0.01	0.02
River Alport	RAL	13	0.01	0.01	0.01	0.03
River Ashop	RAS	13	0.01	0.01	0.01	0.03
River Derwent	RD	13	0.01	0.01	0.01	0.04
River Noe lower	RNL	13	0.01	0.01	0.01	0.02
River Noe upper	RNU	13	0.01	0.01	0.01	0.03
River Westend	RW	13	0.01	0.01	0.01	0.03
Sub-catchment site total		**104**	**0.01**	**0.01**	**0.01**	**0.04**
Fair Brook	FB	13	0.01	0.00	0.01	0.02
Nether Red Brook	NRB	9	0.01	0.00	0.01	0.01
Upper Red Brook	URB	12	0.01	0.00	0.01	0.01
Devils Dike	DD	13	0.01	0.00	0.01	0.01
Upper North Grain	UNG	13	0.01	0.00	0.01	0.01
Green Clough	GC	13	0.01	0.00	0.01	0.01
Withins Clough	WC	13	0.01	0.00	0.01	0.01
Ashop Head	AH	13	0.01	0.01	0.01	0.02
Moorland edge sites total		**99**	**0.01**	**0.00**	**0.01**	**0.02**

Cadmium (Cd) µg/l										
		Dissolved					**Total**			
Site name	Site ID	N	Mean	Std Dev	Min	Max	Mean	Std Dev	Min	Max
Abbey Brook	AB	26	0.07	0.05	0.01	0.20	0.07	0.04	0.02	0.19
Ladybower Brook	LB	26	0.12	0.06	0.04	0.26	0.11	0.05	0.03	0.22
River Alport	RAL	26	0.20	0.13	0.08	0.59	0.21	0.11	0.09	0.53
River Ashop	RAS	26	0.09	0.06	0.03	0.25	0.09	0.05	0.02	0.27
River Derwent	RD	26	0.20	0.59	0.02	3.10	0.08	0.05	0.02	0.18
River Noe lower	RNL	26	0.24	0.09	0.03	0.50	0.33	0.11	0.04	0.55
River Noe upper	RNU	26	0.12	0.06	0.01	0.27	0.13	0.07	0.04	0.36
River Westend	RW	25	0.07	0.04	0.01	0.16	0.08	0.05	0.01	0.20
Sub-catchment site total		**207**	**0.14**	**0.23**	**0.01**	**3.10**	**0.14**	**0.11**	**0.01**	**0.55**
Fair Brook	FB	23	0.17	0.15	0.03	0.77	0.14	0.05	0.04	0.24
Nether Red Brook	NRB	17	0.17	0.09	0.06	0.41	0.18	0.12	0.05	0.58
Upper Red Brook	URB	21	0.17	0.09	0.07	0.41	0.17	0.09	0.05	0.49
Devils Dike	DD	24	0.12	0.06	0.05	0.29	0.12	0.05	0.05	0.30
Upper North Grain	UNG	25	0.15	0.06	0.09	0.36	0.15	0.04	0.10	0.24
Green Clough	GC	26	0.18	0.06	0.09	0.35	0.19	0.05	0.10	0.28
Withins Clough	WC	25	0.11	0.04	0.04	0.20	0.11	0.06	0.03	0.26
Ashop Head	AH	25	0.10	0.06	0.03	0.29	0.10	0.04	0.05	0.23
Moorland edge sites total		**186**	**0.15**	**0.08**	**0.03**	**0.77**	**0.14**	**0.07**	**0.03**	**0.58**

Chromium (Cr) µg/l											
		Dissolved					Total				
Site name	Site ID	N	Mean	Std Dev	Min	Max	Mean	Std Dev	Min	Max	
Abbey Brook	AB	26	1.2	1.1	0.5	5.0	0.9	0.7	0.5	3.0	
Ladybower Brook	LB	26	1.1	0.8	0.5	3.0	1.0	0.6	0.5	2.0	
River Alport	RAL	26	0.8	0.8	0.5	4.0	0.7	0.4	0.5	2.0	
River Ashop	RAS	26	1.2	1.4	0.5	6.0	1.3	2.0	0.5	10.0	
River Derwent	RD	26	1.2	1.0	0.5	4.0	0.8	0.5	0.5	2.0	
River Noe lower	RNL	26	4.9	3.1	0.5	11.0	4.7	2.8	0.5	9.0	
River Noe upper	RNU	26	1.3	0.9	0.5	3.0	1.3	1.3	0.5	7.0	
River Westend	RW	25	0.9	0.7	0.5	3.0	0.7	0.6	0.5	3.0	
Sub-catchment site total		**207**	**1.6**	**1.9**	**0.5**	**11.0**	**1.4**	**1.9**	**0.5**	**10.0**	
Fair Brook	FB	23	0.9	0.6	0.5	3.0	1.2	1.1	0.5	5.0	
Nether Red Brook	NRB	17	0.9	0.5	0.5	2.0	1.0	0.6	0.5	2.0	
Upper Red Brook	URB	21	1.1	0.6	0.5	2.0	0.9	0.5	0.5	2.0	
Devils Dike	DD	24	1.0	0.6	0.5	2.0	1.6	1.5	0.5	8.0	
Upper North Grain	UNG	25	1.2	1.0	0.5	5.0	2.1	4.4	0.5	23.0	
Green Clough	GC	26	0.8	0.6	0.5	3.0	1.1	0.8	0.5	4.0	
Withins Clough	WC	25	0.9	0.5	0.5	2.0	1.1	0.9	0.5	4.0	
Ashop Head	AH	25	1.1	1.2	0.5	6.0	1.1	1.0	0.5	4.0	
Moorland edge sites total		**186**	**1.0**	**0.8**	**0.5**	**6.0**	**1.3**	**1.9**	**0.5**	**23.0**	

Copper (Cu) µg/l										
		Dissolved					Total			
Site name	Site ID	N	Mean	Std Dev	Min	Max	Mean	Std Dev	Min	Max
Abbey Brook	AB	26	1.0	0.6	0.3	2.2	1.0	0.6	0.3	2.0
Ladybower Brook	LB	26	1.2	0.6	0.3	2.4	1.2	0.8	0.3	3.6
River Alport	RAL	26	1.6	0.7	0.8	3.5	1.8	0.8	0.7	4.3
River Ashop	RAS	26	1.4	1.8	0.3	9.2	1.1	0.9	0.3	3.7
River Derwent	RD	26	1.3	1.3	0.3	7.0	1.0	0.6	0.3	2.3
River Noe lower	RNL	26	1.4	0.7	0.3	2.8	1.7	0.8	0.3	4.0
River Noe upper	RNU	26	1.5	0.8	0.3	3.1	1.5	0.7	0.3	3.3
River Westend	RW	25	1.1	0.7	0.3	2.7	1.0	0.7	0.3	3.3
Sub-catchment site total		**207**	**1.3**	**1.0**	**0.3**	**9.2**	**1.3**	**0.8**	**0.3**	**4.3**
Fair Brook	FB	23	3.0	4.2	0.3	22.0	2.4	1.2	0.3	5.8
Nether Red Brook	NRB	17	2.4	0.8	1.2	4.0	2.3	0.7	1.0	3.5
Upper Red Brook	URB	21	2.5	1.1	0.9	4.8	2.6	1.1	1.1	4.6
Devils Dike	DD	24	2.4	0.7	1.3	3.6	2.5	0.9	1.2	4.5
Upper North Grain	UNG	25	2.2	1.0	0.5	4.6	2.4	1.1	0.5	5.8
Green Clough	GC	26	1.2	0.8	0.3	3.5	1.2	0.6	0.3	2.6
Withins Clough	WC	25	2.1	0.8	0.6	3.8	2.1	0.9	0.7	4.5
Ashop Head	AH	25	1.5	1.1	0.6	5.9	1.7	1.4	0.7	7.4
Moorland edge sites total		**186**	**2.1**	**1.8**	**0.3**	**22.0**	**2.1**	**1.1**	**0.3**	**7.4**

Iron (Fe) mg/l						
		Total				
Site name	Site ID	N	Mean	Std Dev	Min	Max
Abbey Brook	AB	13	0.65	0.43	0.10	1.30
Ladybower Brook	LB	13	0.99	0.67	0.17	2.00
River Alport	RAL	13	0.39	0.27	0.16	1.20
River Ashop	RAS	13	0.42	0.36	0.18	1.50
River Derwent	RD	13	0.35	0.19	0.11	0.62
River Noe lower	RNL	13	0.31	0.28	0.01	1.00
River Noe upper	RNU	13	0.26	0.13	0.08	0.61
River Westend	RW	13	0.20	0.11	0.03	0.34
Sub-catchment site total		**104**	**0.45**	**0.41**	**0.01**	**2.00**
Fair Brook	FB	13	0.20	0.09	0.09	0.40
Nether Red Brook	NRB	9	0.26	0.09	0.12	0.41
Upper Red Brook	URB	12	0.57	0.46	0.24	1.90
Devils Dike	DD	13	1.91	1.37	0.52	4.80
Upper North Grain	UNG	13	1.54	0.74	0.67	3.00
Green Clough	GC	13	0.96	0.39	0.42	1.60
Withins Clough	WC	13	1.76	0.88	0.43	3.10
Ashop Head	AH	13	1.10	0.59	0.26	2.20
Moorland edge sites total		**99**	**1.07**	**0.93**	**0.09**	**4.80**

Lead (Pb) µg/l										
		Dissolved					**Total**			
Site name	Site ID	N	Mean	Std Dev	Min	Max	Mean	Std Dev	Min	Max
Abbey Brook	AB	26	1.3	1.0	0.2	4.3	1.5	1.2	0.2	4.4
Ladybower Brook	LB	26	2.0	1.3	0.3	5.6	2.3	1.6	0.3	5.2
River Alport	RAL	26	0.8	0.8	0.2	3.8	1.0	0.8	0.2	4.1
River Ashop	RAS	26	1.1	1.0	0.2	4.8	1.4	1.3	0.2	6.0
River Derwent	RD	26	1.7	1.4	0.2	6.1	1.8	1.4	0.2	5.8
River Noe lower	RNL	26	0.9	0.5	0.2	2.1	3.0	1.9	0.2	9.0
River Noe upper	RNU	26	0.4	0.3	0.2	1.3	0.6	0.6	0.2	2.6
River Westend	RW	25	1.5	1.5	0.2	6.6	1.4	1.2	0.2	4.2
Sub-catchment site total		**207**	**1.2**	**1.2**	**0.2**	**6.6**	**1.6**	**1.5**	**0.2**	**9.0**
Fair Brook	FB	23	5.1	2.5	0.2	11.0	5.2	2.3	0.5	9.2
Nether Red Brook	NRB	17	5.4	1.5	2.9	8.2	5.4	1.4	2.7	8.2
Upper Red Brook	URB	21	6.2	2.9	0.4	11.0	6.4	3.0	0.5	11.0
Devils Dike	DD	24	5.3	2.1	1.8	9.5	5.9	2.4	1.5	9.3
Upper North Grain	UNG	25	4.2	2.2	0.7	9.4	4.8	2.7	1.0	12.0
Green Clough	GC	26	2.8	2.2	0.4	9.4	3.1	2.2	0.7	8.1
Withins Clough	WC	25	3.4	1.5	0.8	7.2	3.9	1.9	1.2	9.3
Ashop Head	AH	25	0.9	0.9	0.2	4.1	1.2	1.0	0.3	4.7
Moorland edge sites total		**186**	**4.0**	**2.6**	**0.2**	**11.0**	**4.4**	**2.7**	**0.3**	**12.0**

Mercury (Hg) µg/l										
		Dissolved					**Total**			
Site name	Site ID	N	Mean	Std Dev	Min	Max	Mean	Std Dev	Min	Max
Abbey Brook	AB	26	0.03	0.01	0.03	0.09	0.03	0.02	0.03	0.11
Ladybower Brook	LB	26	0.03	0.02	0.03	0.11	0.03	0.03	0.03	0.17
River Alport	RAL	26	0.03	0.01	0.03	0.08	0.03	0.04	0.03	0.25
River Ashop	RAS	26	0.03	0.02	0.03	0.12	0.03	0.01	0.03	0.09
River Derwent	RD	26	0.04	0.05	0.03	0.25	0.10	0.39	0.03	2.00
River Noe lower	RNL	26	0.03	0.02	0.03	0.12	0.03	0.05	0.03	0.28
River Noe upper	RNU	26	0.03	0.02	0.03	0.11	0.03	0.01	0.03	0.10
River Westend	RW	25	0.03	0.01	0.03	0.09	0.03	0.03	0.03	0.17
Sub-catchment site total		**207**	**0.03**	**0.02**	**0.03**	**0.25**	**0.04**	**0.14**	**0.03**	**2.00**
Fair Brook	FB	23	0.04	0.04	0.03	0.20	0.03	0.04	0.03	0.22
Nether Red Brook	NRB	17	0.03	0.00	0.03	0.03	0.04	0.07	0.03	0.31
Upper Red Brook	URB	21	0.03	0.03	0.03	0.14	0.03	0.03	0.03	0.14
Devils Dike	DD	24	0.03	0.00	0.03	0.03	0.04	0.05	0.03	0.27
Upper North Grain	UNG	25	0.03	0.00	0.03	0.03	0.03	0.02	0.03	0.13
Green Clough	GC	26	0.03	0.02	0.03	0.12	0.03	0.03	0.03	0.17
Withins Clough	WC	25	0.03	0.02	0.03	0.10	0.03	0.03	0.03	0.18
Ashop Head	AH	25	0.03	0.02	0.03	0.11	0.08	0.27	0.03	1.40
Moorland edge sites total		**186**	**0.03**	**0.02**	**0.03**	**0.20**	**0.04**	**0.11**	**0.03**	**1.40**

Nickel (Ni) µg/l						
		Dissolved				
Site name	Site ID	N	Mean	Std Dev	Min	Max
Abbey Brook	AB	26	1	1	1	4
Ladybower Brook	LB	26	2	1	1	3
River Alport	RAL	26	3	1	1	4
River Ashop	RAS	26	1	1	1	4
River Derwent	RD	26	1	1	1	3
River Noe lower	RNL	26	4	1	1	7
River Noe upper	RNU	26	3	1	1	4
River Westend	RW	25	1	1	1	2
Sub-catchment site total		**207**	**2**	**1**	**1**	**7**
Fair Brook	FB	23	1	1	1	2
Nether Red Brook	NRB	17	1	0	1	1
Upper Red Brook	URB	21	1	2	1	7
Devils Dike	DD	24	1	1	1	4
Upper North Grain	UNG	25	1	1	1	3
Green Clough	GC	26	3	1	1	4
Withins Clough	WC	25	1	1	1	3
Ashop Head	AH	25	3	1	1	6
Moorland edge sites total		**186**	**2**	**1**	**1**	**7**

Selenium (Se) µg/l										
		Dissolved					**Total**			
Site name	Site ID	N	Mean	Std Dev	Min	Max	Mean	Std Dev	Min	Max
Abbey Brook	AB	26	0.3	0.1	0.3	0.6	0.3	0.0	0.3	0.5
Ladybower Brook	LB	26	0.3	0.1	0.3	0.7	0.3	0.1	0.3	0.6
River Alport	RAL	26	0.3	0.2	0.3	1.3	0.3	0.1	0.3	0.6
River Ashop	RAS	26	0.3	0.1	0.3	0.8	0.3	0.1	0.3	0.6
River Derwent	RD	26	0.4	0.4	0.3	1.9	0.3	0.1	0.3	0.6
River Noe lower	RNL	26	0.8	0.3	0.3	1.9	0.8	0.2	0.3	1.2
River Noe upper	RNU	26	0.3	0.2	0.3	0.9	0.3	0.1	0.3	0.6
River Westend	RW	25	0.3	0.3	0.3	1.7	0.3	0.1	0.3	0.7
Sub-catchment site total		**207**	**0.4**	**0.3**	**0.3**	**1.9**	**0.3**	**0.2**	**0.3**	**1.2**
Fair Brook	FB	23	0.4	0.2	0.3	0.9	0.5	0.2	0.3	0.9
Nether Red Brook	NRB	17	0.5	0.2	0.3	0.8	0.4	0.2	0.3	0.8
Upper Red Brook	URB	21	0.5	0.3	0.3	1.0	0.4	0.3	0.3	0.9
Devils Dike	DD	24	0.4	0.2	0.3	0.8	0.4	0.2	0.3	0.8
Upper North Grain	UNG	25	0.4	0.2	0.3	0.8	0.4	0.2	0.3	0.8
Green Clough	GC	26	0.3	0.1	0.3	0.6	0.3	0.1	0.3	0.6
Withins Clough	WC	25	0.3	0.1	0.3	0.6	0.3	0.2	0.3	0.7
Ashop Head	AH	25	0.3	0.1	0.3	0.5	0.3	0.0	0.3	0.3
Moorland edge sites total		**186**	**0.4**	**0.2**	**0.3**	**1.0**	**0.4**	**0.2**	**0.3**	**0.9**

Vanadium (V) µg/l										
		Dissolved					**Total**			
Site name	Site ID	N	Mean	Std Dev	Min	Max	Mean	Std Dev	Min	Max
Abbey Brook	AB	26	1	0	1	3	1	0	1	3
Ladybower Brook	LB	26	1	1	1	4	1	0	1	3
River Alport	RAL	26	1	1	1	4	1	0	1	2
River Ashop	RAS	26	1	1	1	5	1	0	1	2
River Derwent	RD	26	2	2	1	11	1	0	1	2
River Noe lower	RNL	26	1	1	1	4	1	1	1	4
River Noe upper	RNU	26	1	1	1	3	1	0	1	3
River Westend	RW	25	1	1	1	6	1	0	1	2
Sub-catchment site total		**207**	**1**	**1**	**1**	**11**	**1**	**0**	**1**	**4**
Fair Brook	FB	23	1	1	1	4	1	1	1	3
Nether Red Brook	NRB	17	1	1	1	3	1	1	1	3
Upper Red Brook	URB	21	2	1	1	4	1	1	1	3
Devils Dike	DD	24	2	1	1	3	1	1	1	3
Upper North Grain	UNG	25	1	1	1	4	1	1	1	3
Green Clough	GC	26	1	0	1	2	1	1	1	8
Withins Clough	WC	25	1	0	1	3	1	1	1	3
Ashop Head	AH	25	1	0	1	3	1	0	1	3
Moorland edge sites total		**186**	**1**	**1**	**1**	**4**	**1**	**1**	**1**	**8**

Zinc (Zn) µg/l										
		Dissolved					**Total**			
Site name	Site ID	N	Mean	Std Dev	Min	Max	Mean	Std Dev	Min	Max
Abbey Brook	AB	26	8	6	1	26	9	6	2	27
Ladybower Brook	LB	26	11	5	4	24	11	7	3	30
River Alport	RAL	26	9	4	2	19	11	7	1	32
River Ashop	RAS	26	9	5	2	22	9	5	1	23
River Derwent	RD	26	9	4	1	17	8	4	1	16
River Noe lower	RNL	26	16	6	5	34	22	7	3	33
River Noe upper	RNU	26	5	3	1	13	6	3	1	13
River Westend	RW	25	8	5	1	18	8	6	1	23
Sub-catchment site total		**207**	**9**	**6**	**1**	**34**	**10**	**7**	**1**	**33**
Fair Brook	FB	23	22	12	1	58	22	12	8	64
Nether Red Brook	NRB	17	24	11	12	51	23	13	11	63
Upper Red Brook	URB	21	30	21	11	100	24	14	10	79
Devils Dike	DD	24	25	12	11	75	24	11	11	69
Upper North Grain	UNG	25	24	8	11	49	25	10	12	52
Green Clough	GC	26	14	7	7	39	16	9	7	52
Withins Clough	WC	25	15	8	6	41	18	9	9	40
Ashop Head	AH	25	10	4	5	24	11	4	5	25
Moorland edge sites total		**186**	**20**	**13**	**1**	**100**	**20**	**11**	**5**	**79**

9.2 Appendix 2: Compliance with the WFD ‘good’ standard for pH.

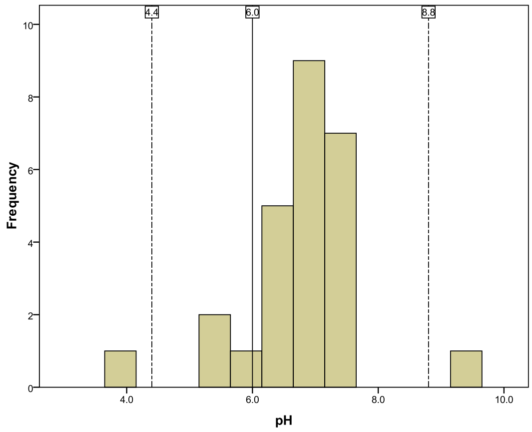

Figure 9.1: Histogram of pH at Abbey Brook (black dash line = 5 and 95 percentile values; black solid line = WFD lower limit for pH.

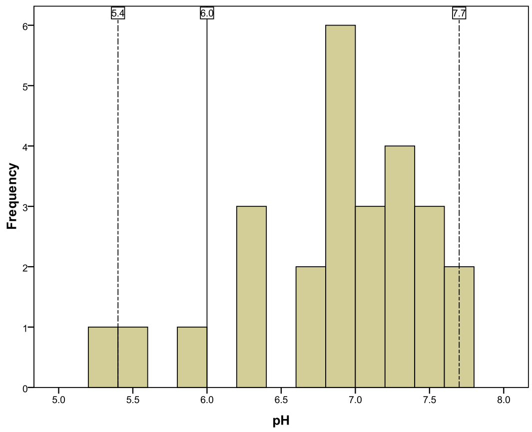

Figure 9.2: Histogram of pH at Ladybower brook (black dash line = 5 and 95 percentile values; black solid line = WFD lower limit for pH.

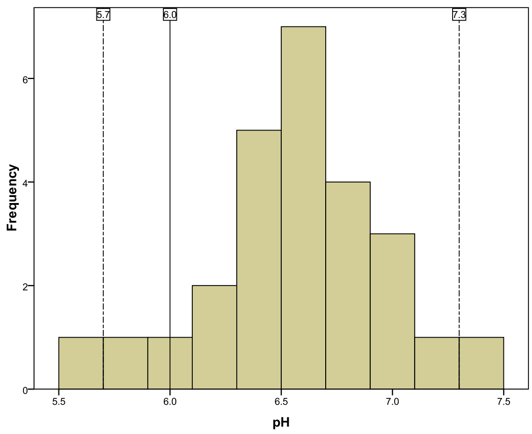

Figure 9.3: Histogram of pH at the River Alport (black dash line = 5 and 95 percentile values; black solid line = WFD lower limit for pH.

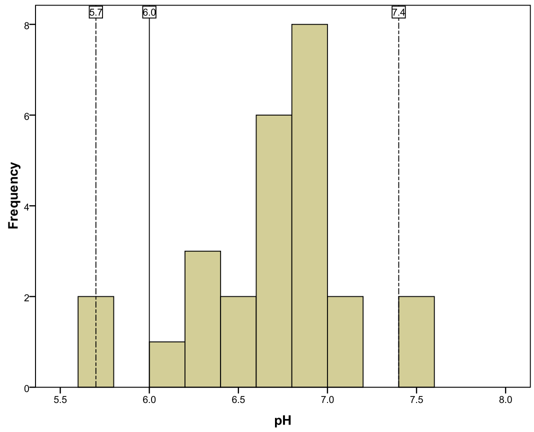

Figure 9.4: Histogram of pH at the River Ashop (black dash line = 5 and 95 percentile values; black solid line = WFD lower limit for pH.

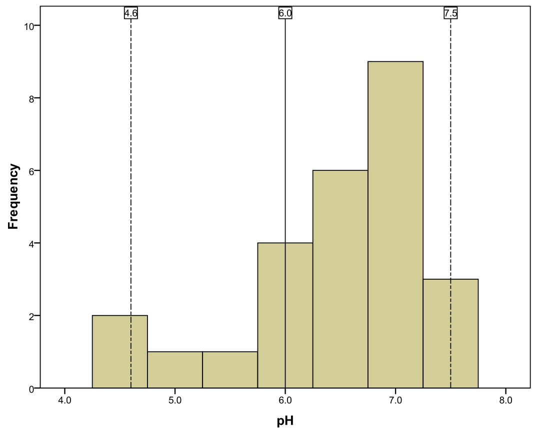

Figure 9.5: Histogram of pH at the River Derwent (black dash line = 5 and 95 percentile values; black solid line = WFD lower limit for pH.

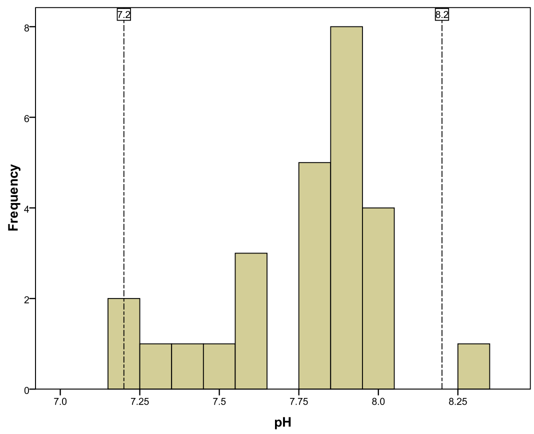

Figure 9.6: Histogram of pH at the River Noe lower (black dash line = 5 and 95 percentile values.

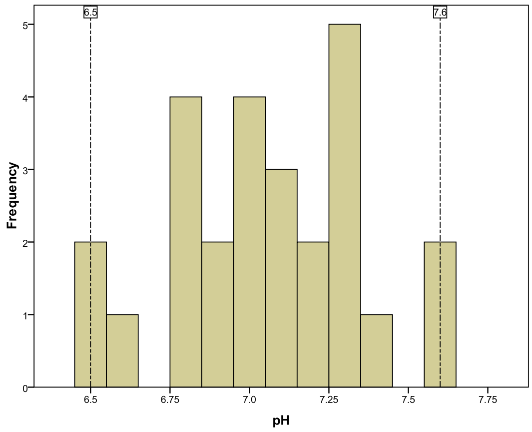

Figure 9.7: Histogram of pH at the River Noe upper (black dash line = 5 and 95 percentile values.

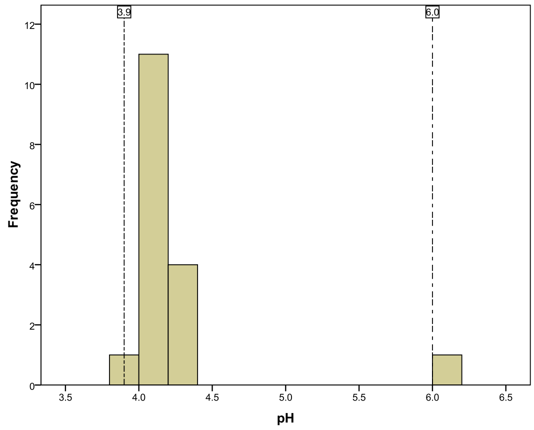

Figure 9.10: Histogram of pH at Nether Red Brook (black dash line = 5 and 95 percentile values.

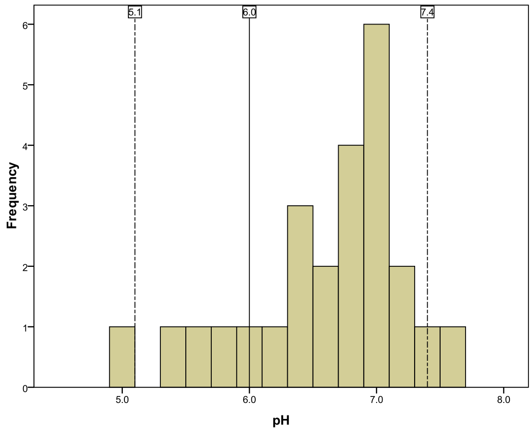

Figure 9.8: Histogram of pH at the River Westend (black dash line = 5 and 95 percentile values; black solid line = WFD lower limit for pH.

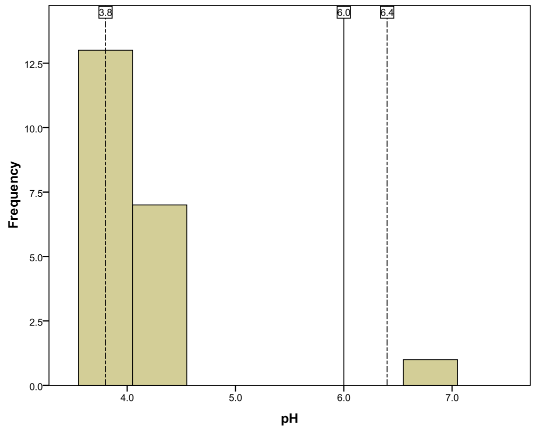

Figure 9.11: Histogram of pH at Upper Red Brook (black dash line = 5 and 95 percentile values; black solid line = WFD lower limit for pH.

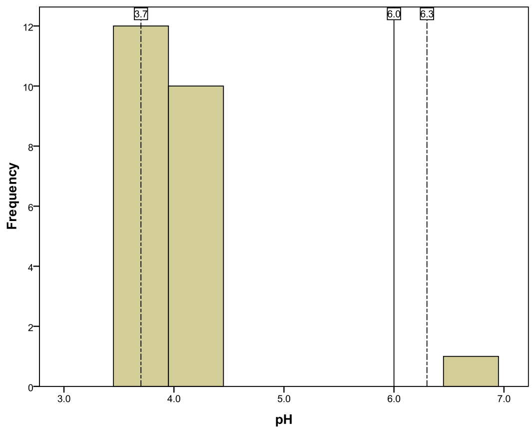

Figure 9.9: Histogram of pH at Fair Brook (black dash line = 5 and 95 percentile values; black solid line = WFD lower limit for pH.

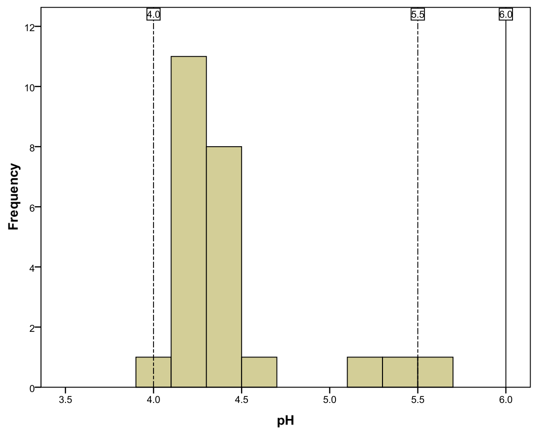

Figure 9.12: Histogram of pH at Devils Dike (black dash line = 5 and 95 percentile values; black solid line = WFD lower limit for pH.

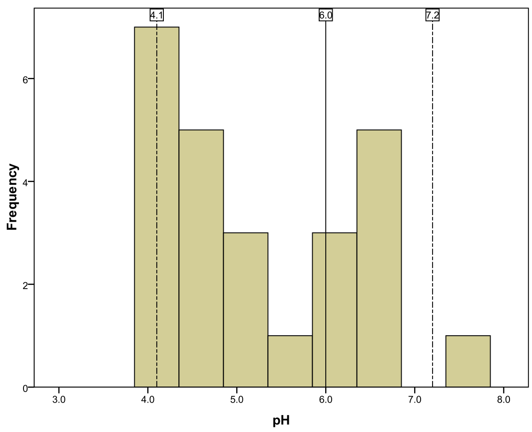

Figure 9.13: Histogram of pH at Upper North Grain (black dash line = 5 and 95 percentile values; black solid line = WFD lower limit for pH.

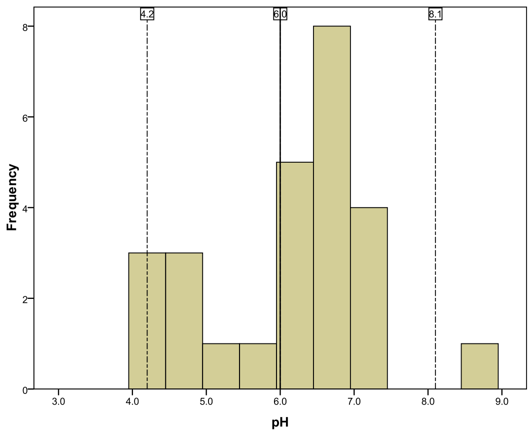

Figure 9.14: Histogram of pH at Green Clough (black dash line = 5 and 95 percentile values; black solid line = WFD lower limit for pH.

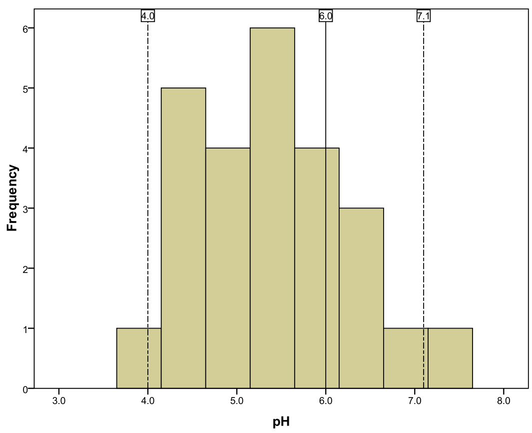

Figure 9.15: Histogram of pH at Withins Clough (black dash line = 5 and 95 percentile values; black solid line = WFD lower limit for pH.

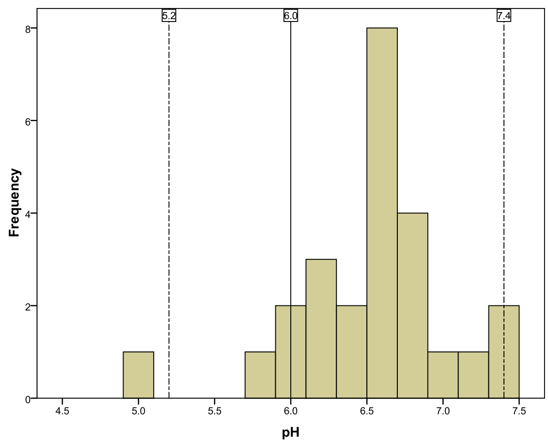

Figure 9.16: Histogram of pH at Ashop Head (black dash line = 5 and 95 percentile values; black solid line = WFD lower limit for pH.

9.3 Appendix 3: Ratio between water quality variables at moorland edge sites and at the bottom of the sub-catchment for the Rive Ashop catchment. **Mean = average concentration within catchment, Ashop = average concentration for River Ashop sub-catchment; ratio = Mean / Ashop.**

HU	Mean	Ratio	Ashop
FB	535	3.3	
URB	675	4.1	
AH	191	1.2	163
WC	471	2.9	
UNG	452	2.8	
Mean	464.8	2.9	
DOC	Mean	Ratio	Ashop
FB	22.3	3.7	
URB	23.5	3.9	
AH	8.3	1.4	6.1
WC	18.2	3.0	
UNG	17.6	2.9	
Mean	18.0	3.0	
pH	Mean	Ratio	Ashop
FB	4.1	0.6	
URB	4.2	0.6	
AH	6.5	1.0	6.6
WC	5.4	0.8	
UNG	5.3	0.8	
Mean	5.1	0.8	
Cu	Mean	Ratio	Ashop
FB	3	2.1	
URB	2.5	1.8	
AH	1.5	1.1	1.4
WC	2.1	1.5	
UNG	2.2	1.6	
Mean	2.3	1.6	
Fe	Mean	Ratio	Ashop
FB	0.2	0.5	
URB	0.57	1.4	
AH	1.1	2.6	0.42
WC	1.76	4.2	
UNG	1.54	3.7	
Mean	1.0	2.5	
Zn	Mean	Ratio	Ashop
FB	22	2.4	
URB	30	3.3	
AH	10	1.1	9
WC	15	1.7	
UNG	24	2.7	
Mean	20.2	2.2	