**Sustained biogeochemical impacts of wildfire in a mountain lake catchment**

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**ABSTRACT**

Wild and prescribed fires can cause severe deterioration in water quality, including increases in sediment, nutrients and dissolved organic carbon (DOC). Due to the unpredictability of wildfires, few studies have been able to employ before-after, control-intervention experimental designs, or to evaluate fire-induced water quality changes in the context of long-term datasets. Here, we present data from a lake draining a moorland catchment in the United Kingdom, part of a 22 site, 25 year monitoring network, which experienced a major wildfire in 2011. The main water quality response was a large, sustained increase in nitrate concentrations, sufficient to raise acidity and aluminium concentrations, effectively reversing over a decade of recovery from the effects of acid deposition. Concurrently, we observed a clear reduction in DOC concentrations, contrasting with prescribed fire studies from similar ecosystems (none based on before-after studies) that have suggested that burning causes DOC to increase. However data from a downstream water supply reservoir do suggest a fire-induced change in DOC quality towards more soil-derived aromatic organic compounds, and lake sediment data suggest a large increase in particulate organic carbon. We conclude that the biogeochemical responses to wildfire in our moorland catchment were broadly similar to those observed in forest ecosystems elsewhere, but that historically high nitrogen deposition has made the ecosystem particularly susceptible to nitrate leaching and (re-)acidification. The observed reduction in DOC concentrations casts some doubt on the widely held view that prescribed burning in moorland systems has contributed to long-term DOC increases.

**INTRODUCTION**

Wildfires are important drivers of ecological and biogeochemical change. Although fires are a natural phenomenon, human activities have significantly increased both their frequency and severity. In North America, the area affected by wildfires has increased due to a combination of climatic changes, accumulation of combustible material following decades of fire suppression, and increased human presence in forests (Smithwick and others, 2005; Bladon and others, 2014). In the boreal zone, wildfire frequency is predicted to double by the end of the century due to climate change (Flannnigan and others, 2009). Wetter ecosystems such as peatlands become susceptible to fire when dry conditions expose normally waterlogged organic matter to oxygen, and drainage therefore greatly increases both fire risk and severity (Dikici and Yilmaz, 2006; Turetsky and others, 2011). Smouldering peat fires can last for weeks or months and, given the large carbon (C) stores in organic soils, generate very large CO2 emissions (Turetsky and others, 2015; Page and others, 2002). Other impacts of wildfires include destruction of habitat and property, increased air pollution and visibility loss, loss or degradation of soils, accelerated erosion, and hydrological changes including reductions in transpiration following loss of vegetation, leading to increased total runoff, overland flow and peak flows (e.g. Wright, 1976; Carignan and others, 2001; Shakesby and Doerr, 2006).

Wildfires also have wide-ranging impacts on water quality. Smith and others (2011) and Bladon and others (2014) identify elevated fluvial suspended (inorganic and organic) sediment concentrations as a consistent fire response, associated with increased erosion of bare or partly combusted soils, and transport of particle-associated pollutants such as phosphorus (P) and heavy metals (e.g. Petticrew and others, 2006). Nitrogen (particularly as nitrate, NO3-) increases are also widely recorded; Smith and others (2011) report 3 to 250 times higher NO3- concentrations in burned versus unburned catchments across a range of studies. Increased NO3- losses after fire are associated with two key processes: pyrolysis of soil and plant organic matter, leading to an accumulation of ammonium (NH4+) in the soil (Smithwick and others, 2005); and reduced plant and microbial uptake, allowing this NH4+ (as well as ongoing atmospheric N inputs) to be nitrified and leached as NO3- (Ranalli, 2004). Many studies also show post-fire peaks in sulphate (SO42-), chloride (Cl-) and/or base cation concentrations (e.g. Bayley and others, 1992; Carignan and others, 2000; Mast and Clow, 2008; Bladon and others, 2014). Again, peaks in these solutes can be attributed to their release via pyrolysis from biomass and soil organic matter, and to after-effects of fire such as soil drying and cracking. Soil modifications may be particularly important in organic soils, where elements such as sulphur (S) are stored in reduced form, and therefore susceptible to oxidation and leaching. The effects of these solute losses on freshwater acidity depend on the relative balance of base cation and acid anion leaching. In Canadian lakes studied by Carignan and others (2000), increases in NO3-, SO42- and Cl- were counterbalanced by increases in base cations, so that alkalinity and pH were unaffected. However Bayley and others (1992) found evidence of post-fire acidification in the same region, and a study of acid-sensitive lakes in Norway recorded severe short-term acidification during the first few months post-fire (Lydersen and others, 2014).

One of the least predictable water quality responses to wildfire is that of dissolved organic matter (DOM). Although dissolved organic nitrogen (DON) leaching has been found to increase alongside those of mineral N (Bladon and others, 2008; Pilkington and others, 2007), the behaviour of dissolved organic carbon (DOC) appears more variable. Studies in the Western US have shown small/variable increases (Minshall and others, 2001; Emelko and others, 2011) or no change (Mast and Clow, 2008), despite large increases in other solutes. Similarly, in higher-latitude (typically peatier) ecosystems, DOC has been reported to increase (McEachern and others, 2000), decrease (Betts and Jones, 2009; Lydersen and others, 2014) or remain unchanged after wildfires (Carignan and others, 2000; Marchand and others, 2009; Olefeldt and others, 2013a).

Whilst wildfires can be considered – to varying degrees – natural ecological processes, in many parts of the world controlled (prescribed) burning has been used as a component of land-management for millennia (Russell-Smith and Thornton, 2013; Davies et al., 2016). In dry forest areas, prescribed fires are used to reduce the risk of more severe wildfires by reducing the “fuel load” of combustible biomass (e.g. Beche and others, 2005; Rocca and others, 2014). In UK moorland ecosystems, managed burning is widely used to sustain mixed-age heather (*Calluna vulgaris*) moorland for rearing red grouse (*Lagopus lagopus*), a commercially important game bird (Holden and others, 2007). Prescribed fires resemble wildfires in that they remove much of the above-ground vegetation, but differ in that (provided they remain under control) they should not burn into the organic soil. Thus, water quality responses associated with loss of vegetation cover, such as pyrolysis of plant biomass, reduced nutrient uptake or reduced transpiration, might be expected to be common to both types of fire, whereas those associated with soil combustion or structural damage, such as S oxidation or mineral soil erosion, might not. Worrall and others (2007) suggested that reduced transpiration following prescribed burning might increase soil moisture, decrease organic matter decomposition and enhance ecosystem C storage. However, even low temperature burns are likely to alter vegetation cover (e.g. by reducing the cover of peat forming species; Holden and others, 2007), and to reduce albedo where dark soil surfaces are exposed, which may result in higher soil temperatures and microbial activity (Smithwick and others, 2005). Reported water quality responses to prescribed fires broadly resemble those for wildfires, including increases in suspended sediments, NO3-, SO42-, Cl-, base cations and total P, but tend to be smaller and of shorter duration (e.g. Williams and Melack, 1997; Stephens and others, 2004; Pilkington and others, 2007; Ramchunder and others, 2013). The ecological impacts of prescribed burning have been particularly controversial in the UK (e.g. Davies and others, 2016), where it has been claimed that expansion of managed burning in upland areas is responsible for observed DOC increases in drinking water supplies, and associated treatment problems (e.g. Yallop and others, 2010).

It is now widely recognised that extreme events can trigger major ecological changes in ecosystems subject to lower-intensity, long-term pressures, and that such extreme events may also delay or even halt the recovery of ecosystems from past anthropogenic disturbances. However, these interactions between chronic and acute pressures are often hard to observe under real-world conditions, and particularly challenging to capture in the case of wildfire impacts, where full before-after, control-intervention (BACI) studies are extremely rare. The random nature of wildfires also makes it difficult to place their impacts into a longer-term context; for example, their significance relative to decadal-scale water quality trends is poorly quantified. In this study, we evaluate the impact of wildfire on the chemistry of a UK mountain lake with over 20 years of pre-fire monitoring data. Our objectives were to: 1) evaluate the effects of the fire on lake water quality, focusing particularly on organic C, N and acidity-related responses; 2) quantify the magnitude and ecological significance of fire-induced water quality changes relative to observed long-term trends; 3) determine the extent of downstream impacts on drinking water quality; 4) quantify fire effects on lake sediment and carbon accumulation rates; and 5) consider the relevance of our results to the ongoing debate about prescribed fire impacts on water quality, particularly in relation to DOC.

**METHODS**

**Site Descriptions**

Blue Lough

Blue Lough is a small (1.9 ha, maximum depth 5 m, volume 36,000 m3) mountain lake in the Mourne Mountains of Northern Ireland, UK (Monteith and Evans, 2000; <http://uwmn.defra.gov.uk/sites/site_21.php>). It is located close to a drainage divide between two mountains, at an altitude of 340 m. The 48 ha catchment drains the slopes of one of these mountains, Slieve Lammagan, which has a maximum altitude of 703 m. The catchment is on granite bedrock, with bare rock and scree on steeper slopes and peaty podzols, peaty gleys, and deep peat on shallower slopes. Vegetation comprises dwarf shrubs (predominantly *Calluna vulgaris*) and rough grasses. Land-use is restricted to low-intensity sheep grazing. Annual rainfall is 1600 mm, and mean lake water residence time 23 days. On May 1st 2011 the entire Blue Lough catchment was affected by a severe wildfire (Figure 1), combusting most above-ground biomass and burning into the organic soil in some areas. The fire followed an extended dry spring period, and was one of a spate of fires that affected over 10,000 ha of land in Northern Ireland during this period, many of which were started deliberately (Climate Northern Ireland, 2013).

The UK Upland Waters Monitoring Network

Blue Lough forms part of the UK Upland Waters Monitoring Network (UWMN), a set of acid-sensitive moorland and forest monitoring catchments distributed across the UK (Monteith and Evans, 2005). The catchments vary in acidity from circumneutral to severely acidified; Blue Lough is among the most N and S polluted sites in the network (Curtis and others, 2005). Most sites have shown substantial chemical recovery from acidification since monitoring began in 1988 (Monteith and others, 2014) and some sites have shown signs of biological recovery (e.g. Malcolm and others 2014). Almost all sites have experienced large (approximately two-fold) DOC increases during the monitoring period (Evans and others, 2008). Most of the UWMN catchments are not thought to have been affected by fires during the monitoring period. The two exceptions are the River Etherow (Northern England) where about a third of the catchment is subject to rotational burn management (on an estimated 10-15 year cycle), and the Round Loch of Glenhead (Southwest Scotland) where around 25% of the catchment was affected by wildfire in April 2007.

The Mourne Water Supply Network

Blue Lough falls within a large (36 km2) drinking water catchment, operated by Northern Ireland Water, which supplies the city of Belfast and surrounding areas. The outlet of the Lough drains to the Annalong River, from which water is abstracted via a 3.6 km tunnel to feed the Silent Valley Reservoir. This reservoir also receives water from two upstream reservoirs, one of which, the Bencrom Reservoir, drains an area immediately to the west of the Blue Lough catchment and was also partly affected by the 2011 fires (although overall burn extent was not determined). Water from Silent Valley is then transferred to the Drumaroad Water Treatment Works (WTW) where it forms the majority of the water supply. Both Silent Valley Reservoir and the Drumaroad WTW intake water are monitored routinely by Northern Ireland Water (see below).

**Water quality data**

The UWMN was initiated in 1988, and Blue Lough added to the network in 1990. All 11 UWMN lakes are sampled quarterly and concurrently (at the start of March, June, September and December), whilst the 12 streams, which have higher short-term variability, are sampled monthly. Water samples are sent directly to laboratories at the Centre for Ecology and Hydrology (CEH) and Marine Scotland’s Freshwater Fisheries Laboratory, Pitlochry. Unfiltered samples are analysed for pH and alkalinity by dual endpoint titration using a Metrohm Titrando. Samples filtered through pre-rinsed Whatman 0.45 m cellulose nitrate filters are analysed for SO42-, NO3- and Cl- by ion chromatography on a Dionex ICS1000. DOC and total N are measured colorimetrically on a Skalar San++ continuous flow analyser. Base cations (calcium, Ca2+; magnesium, Mg2+; sodium, Na+; potassium, K+) are analysed on field-filtered and acidified samples using a Perkin Elmer Optima DV7300 Inductively Coupled Plasma Optical Emission Spectrometer. Aluminium (Al) is speciated into organic (Alorg) and inorganic (Alinorg) fractions using an ion exchange resin following the method of Driscoll (1984) and analysed using the Catechol violet method of Dougan and Wilson (1974). Acid Neutralising Capacity (ANC) is calculated using the ‘alkalinity-based’ method in order to reduce short-term noise associated with the charge-balance method in areas of high Na+ and Cl- concentrations (Evans and others, 2001) as:

ANC = Alkalinity + 5x DOC – 3x Alinorg (1)

Where ANC and alkalinity are in eq l-1, DOC in mg l-1 (assigned a charge density of 5 eq mg-1 at the alkalinity titration endpoint) and Alinorg in mol l-1 (assigned a valency of 3+ at the titration endpoint). Ultraviolet absorbance at 254 nm (Abs254) is used to determine specific UV absorbance (SUVA254), calculated as Abs254/DOC, widely considered to indicate the degree of aromaticity of DOC (e.g. Weishaar and others, 2003).

The Silent Valley Reservoir is sampled approximately monthly by Northern Ireland Water, and analysed for a range of water quality determinands including pH and NO3-, following similar methods to the UWMN. Intake water at the Drumaroad WTW is analysed weekly for a wider range of determinands, including total organic carbon (TOC) by infrared measurement of CO2 following UV and sodium persulphate oxidation, visible colour (absorbance at 400 nm, Abs400) and Abs254. Given that turbidity levels in the samples were low (mean 0.8 mg l-1, data not shown), we assumed for the purposes of comparison between sites that TOC ≅ DOC. Data from Silent Valley and Drumaroad were provided by Northern Ireland Water for the period 2009 to 2015.

**Sediment data**

Sediment traps have been deployed at Blue Lough since 1992. These comprise arrays of three tubes attached to the corners of triangular plastic frames. The internal diameter of each tube is 5.2 cm with an aspect ratio (length:diameter) of >7 to maximise trapping efficiency (Bloesch and Burns, 1980). Each array is made buoyant with high density Styrofoam, maintaining the trap approximately 1 m above the sediment-water interface. Two arrays are deployed to reduce risk of loss, both of which are anchored in the sediment in the profundal zone. Upon retrieval, traps are immediately emptied into pre-weighed sealable plastic bags, cleaned and re-deployed. The retrieved sediment is allowed to settle, supernatant water removed and samples freeze-dried. The dry weight of each tube sample is determined, providing triplicate measurements of sediment flux measurement per array. Samples from 2002 onwards have been analysed for C content at the UCL Bloomsbury Environmental Isotope Facility (as part of a broader suite of isotopic measurements, not reported here) using a Flash Elemental Analyser (1112 series; Thermo-Finnigan) coupled to a Finnigan Delta V IR-mass spectrometer, and calibrated against a graphite standard (USGS-24).

**Data analysis**

Annual mean concentrations of a range of determinands at Blue Lough were calculated as unweighted arithmetic means of quarterly measurements for each full calendar year of monitoring. The same approach was applied to other lakes in the network, whilst for streams means were calculated from the 12 monthly samples. One discontinued site (Loch Coire nan Arr) was omitted from the analysis, along with several sites that were added to the network in recent years, in order to provide a complete and consistent dataset for between-site analysis. Annual data were then standardised by subtracting the mean concentration for the first 10 years of Network operation (1989-1998) and dividing by the standard deviation for the same period. This approach provides a standardised ‘Z score’, with a mean of zero and a standard deviation of 1 for the first 10 years of monitoring. Deviations from a Z score of zero in the years since 1998 are thus indicative of long-term changes or shorter-term perturbations in water chemistry relative to this baseline period. The approach is effective for comparing underlying temporal patterns across sites with differing sampling frequencies, absolute solute concentrations and/or short-term variability, and previous analyses of UWMN data have demonstrated high underlying temporal coherence among sites (Davies and others, 2005; Evans and others, 2010). Similar coherence has been identified in other regional water quality datasets using the same approach (Watmough and others, 2004; Erlandsson and others, 2008; Oulehle and others, 2013; Futter and others, 2014).

We applied the Z score method in a BACI-type analysis, whereby the Blue Lough fire represented the intervention, and all of the other UWMN sites were treated as controls. Despite some rotational burning in the Etherow, and a wildfire in part of the Round Loch catchment in 2007, we did not find clear evidence of divergent water chemistry at these sites when compared to other sites in the network, and they were therefore retained within the control group (by utilising a large set of control sites, the sensitivity of the analysis to short-term disturbances at any one site is minimised). Pre-fire, annual Z scores at Blue Lough were compared to median, 10th and 90th percentile Z scores for the control group, to assess whether Blue Lough was behaving similarly to other sites during this period. Post-fire, we considered deviations in Blue Lough Z scores outside the 10th-90th percentile range for the control group to be indicative of fire effects on water quality. We also calculated the change in Z score (Z) during the 20 year pre-fire period, calculated as the difference between the means of the first three years of data (1991-1993) and of the last three pre-fire years (2008-2010). This was compared to the Z values following the fire, calculated as the difference between the means of the first three post-fire years (2012-2014) and the pre-fire 2008-2010 period. Comparison of these Z values provided an indication of the direction and magnitude of fire responses relative to long-term trends at the site. Again, these changes were compared to Z values for the other UWMN sites.

**Results**

*Pre-fire water quality trends at Blue Lough*

Untransformed water quality data from Blue Lough are shown in Figure 2. At the outset of monitoring, Blue Lough was among the most acidified sites in the UWMN, with mean 1991-1995 pH 4.67, alkalinity -24 eq l-1, ANC -42 eq l-1 and Alinorg 308 μg l-1, well above the toxicity threshold for salmonid fish (Malcolm and others, 2014). Nitrate concentrations of 26 eq l-1 were, along with those at the nearby Bencrom River, the highest in the network apart from the highly polluted River Etherow, which is located close to major emission sources in Northern England, and affected by peatland erosion and managed burning as noted above. Mean non-marine sulphate (xSO42-) concentration for this period was 67 eq l-1, again among the highest in the network. Since that time, Blue Lough has, along with most other sites in the UWMN, shown clear signs of recovery from acidification, although it still remains comparatively acidic; for the five years prior to the fire (2006-2010) mean pH was 4.98, alkalinity -9 eq l-1, ANC 4 eq l-1, and Alinorg 153 g l-1. Concentrations of xSO42- were less than half those of the early 1990s (26 eq l-1), and NO3- was also lower (16 eq l-1). DOC concentrations increased steadily from 1990 to 2007, but stabilised thereafter, whilst SUVA254 decreased until 2006 (consistent with observations from sites in Scotland; Dawson and others, 2009) before increasing slightly to 2010.

Comparing Z score time series it is apparent that the direction of chemical changes at Blue Lough were similar to those for other UWMN sites during the pre-fire period (Figure 3), although rates of change tended to be larger than average. For pH, Z scores during 2005-2010 were at or above the 90th percentile value for the rest of the network, and Alinorg Z scores at or below the 10th percentile. These above-average rates of chemical change are also highlighted by Z values (Figure 4a) which show proportional changes in SO42-, Ca2+ and DOC were similar to the UWMN median, but proportional changes in pH, alkalinity and Alinorg were larger by a factor of 2-3, and changes in NO3- larger by a factor of around five. The implication of these results is that, prior to 2011, Blue Lough was recovering more rapidly from the effects of acid deposition than the network average.

*Fire Impacts on water quality at Blue Lough*

Following the May 2011 fire, Blue Lough underwent profound changes in water quality. Nitrate concentrations rose rapidly in the latter part of 2011 and have remained high thereafter. A peak NO3- concentration of 111 eq l-1 was recorded in March 2013, and the 2012-13 mean of 82 eq l-1, is approximately five times pre-fire values. Although a similar pulse of SO42- did not occur, the increase in NO3-, which acts as a “mobile anion” by transporting cations, including hydrogen ion (H+), from soils to surface waters. This mechanism was sufficient to depress mean 2012-13 pH to 4.78, alkalinity to -16 eq l-1, and ANC to -23 eq l-1, with continuously negative measured values recorded since September 2011. Inorganic Al rose to a post-fire mean of 236 g l-1. Concentrations of Ca2+ and Mg2+ also rose, to levels typical of the early monitoring period. In contrast, DOC concentrations declined sharply, to a 2012-13 mean of 4.1 mg l-1, around two thirds of pre-fire values. SUVA254 did not change in the first year post-fire, but then declined to the lowest value recorded at the site (1.45 l mg C-1 m-1) in June 2013, before rising to 5.03 l mg C-1 m-1 by April 2014.

The Z score data (Figure 3) highlight the extent to which post-fire changes at Blue Lough diverged from general chemical trends across the rest of the UWMN. The peak NO3- Z score at Blue Lough (6.0 in 2013) was far above the UWMN 90th percentile (1.2 in the same year), and the large positive post-fire Z value (Figure 4b) contrasts with a marginal decrease elsewhere. The post-fire NO3- increase also far exceeded (by a factor of 8) the decrease in concentrations measured during the preceding 20 years (compare Figures 4b and 4a). The pre-fire seasonal pattern of autumn NO3- minima and spring maxima appears to have been approximately retained post-fire, albeit at a much higher concentration level.

For SO42-, a similar divergence in trends between Blue Lough and the rest of the UWMN occurred after the fire (Z +0.49 versus a median of -0.78 for the other sites), but this increase was far smaller relative to the 20-year pre-fire decrease in SO42- concentrations (Z = -4.3). Furthermore, annual post-fire Z scores for SO42- at Blue Lough did not fall outside the 10th-90th percentile range for the rest of the UWMN (Figure 3b). This was also true for pH and alkalinity, but in both cases mean Z scores fell from the UWMN 90th percentile value back to the median value, implying that the fire was sufficient to change Blue Lough from one of the fastest-recovering sites to approximately the network average. This re-acidification is also evident in the sharp divergence of post-fire Z values for Blue Lough when compared to UWMN median in the post-fire period (Figure 4b). Increases in Alinorg at Blue Lough were sufficient to shift Z scores from the 10th to the 90th percentile for the UWMN, and a similar shift was observed for Ca2+. DOC shifted from Z score values typically close to the 90th percentile in 2004-2010 to values close to the 10th percentile in 2012-13.

*Fire impacts on pre-treatment drinking water quality*

Data for the Silent Valley Reservoir and Drumaroad WTW intake are shown in Figure 5. Given the similarity in NO3- and pH for the two datasets, we infer that the (more frequent) data from Drumaroad provide a reasonable proxy for water quality in Silent Valley. Prior to the 2011 fire, NO3- concentrations in Silent Valley were similar to those in Blue Lough at around 20-30 eq l-1. The reservoir data show a small (range ~10 µeq l-1) but consistent seasonal cycle, with peak concentrations in early summer. Following the fire, reservoir NO3- concentrations showed a similar but more damped response to Blue Lough, rising to a peak of 60 eq l-1 in the summer of 2013, and declining steadily thereafter. The pH of the reservoir is higher than Blue Lough, ranging from 6 to 7 before the fire. Following the fire, reservoir pH fell at a similar rate to Blue Lough, reaching a minimum of around 5.6 in summer 2013. TOC concentrations at Silent Valley were lower than DOC at Blue Lough during the pre-fire period, with an apparently lagged seasonal cycle peaking in autumn. Following the fire, TOC concentrations at Silent Valley declined, reaching a minimum in summer 2013 coincident with peaks in NO3- and acidity. The TOC decrease at Silent Valley was less pronounced than that of DOC at Blue Lough, as a result of which the two sites have had similar concentrations since 2012. SUVA254 data for Silent Valley (from Drumaroad WTW only, based on TOC) show a clear decrease from pre-fire levels (2010 mean 4.06 l mg C-1 m-1) to lower values in the immediate aftermath of the fire (2011 mean 3.80 l mg C-1 m-1), followed by a sustained increase to levels exceeding the pre-fire baseline (2014 mean 4.45 l mg C-1 m-1).

*Fire impacts on sediment accumulation rates*

Annual Blue Lough sediment accumulation rates are shown in Figure 6. The pre-fire (1992-2010) mean accumulation rate was 0.8 g cm-2 yr-1, with a maximum (in 1999) of 2.0 g cm-2 yr-1. Since the fire, sediment accumulation has approximately tripled, with a 2012-2015 mean rate of 2.4 g cm-2 yr-1, and a maximum value of 3.0 g cm-2 yr-1 recorded during the last year of data collection. The C concentration of the sediment (measured on annual samples since 2002) varies from 21.2% to 26.6%, with no clear changes post-fire (pre-fire mean 23.4%, post-fire mean 23.9%). Based on these data, the mean C accumulation rate in the sediment traps was 0.19 g C cm-2 yr-1 pre-fire, and 0.57 g C cm-2 yr-1 post-fire.

**Discussion**

*The effects of wildfire on lake water quality*

Despite differences in catchment characteristics, we observed strong similarities between wildfire effects on the chemistry of Blue Lough, draining a moorland catchment, and those reported elsewhere, primarily in forested landscapes. In particular, the sharp increase in NO3- concentrations corresponds to those seen in many previous wildfire studies. Indeed, NO3- loss appears to be among the most consistent responses to many forms of major ecological disturbance leading to loss of, or damage to, above- and/or below-ground biota, such as forest felling, insect attacks (e.g. Oulehle and others, 2013), drought (e.g. Watmough and others, 2004), and soil freezing (e.g. Monteith and others, 2000; Callesen and others, 2007). The severity of this disturbance-induced terrestrial N loss appears related to the extent of prior N-enrichment of the ecosystem, for example due to atmospheric N deposition; Pilkington and others (2007) observed much higher soil NO3- leaching following a (prescribed) fire at heathland plots that had been exposed to experimentally elevated N inputs over a 10 year period, relative to low-addition or control plots. In this respect, the high ambient N deposition levels at Blue Lough, and correspondingly high pre-fire NO3- concentrations (Figure 2), suggest that the terrestrial ecosystem was already N-enriched. This may explain why, when biotic (i.e. plant and microbial) demand for N was disrupted by the fire, NO3- concentrations rose to very high levels; the maximum observed concentration of 108 eq l-1 exceeds most peak concentrations reported in previous wildfire studies, despite the damping effect of lake mixing. The extended duration of the NO3- peak at Blue Lough (at least 3 years) is typical of previous studies in forest catchments, suggesting elevated concentrations for 4-5 years (e.g. Hauer & Spencer, 1998; Mast and Clow, 2008; Mast, 2013). However some studies have shown shorter (e.g. Bladon and others, 2008; Carignan and others, 2000) or longer peaks (Bayley and others, 1992). Smithwick and others (2005) suggest that modifications to the ecosystem N cycle can extend for decades after major fires.

In contrast to the large NO3- response, and unlike a number of previous studies, we observed relatively modest effects of the fire on SO42-, and none on Cl-. The reasons for this are unclear, although compared to more continental areas Blue Lough is subject to high rates of marine ion deposition, which may mask biotic SO42- or Cl- responses to wildfire. Carignan and others (2000) noted the importance of pollutant S deposition and soil S storage at their study sites, but despite high historical S deposition to Blue Lough we did not observe a similar release of SO42-. On the other hand, we did observe increases in Ca2+, as well as similar increases in other base cations (data not shown) which appear largely consistent with previous work (Carignan and others, 2000; Mast and Clow, 2008; Bladon and others, 2014). These increases, which can be explained by co-transport of base cations along with NO3-, effectively returned base cation concentrations to levels last seen at Blue Lough in the early 1990s (Figure 2g).

The overall impact of the ionic changes following wildfire at Blue Lough was strongly acidifying. This was almost entirely attributable to increased export of NO3-, acting as a mobile anion for the transport of H+ and Alinorg from the soil. This mechanism was sufficient to reverse the long-term rising trend in ANC and pH, returning the lake to acidity levels last recorded in the 1990s. The increase in Alinorg generated peak concentrations last recorded in 1996. Such high H+ and Alinorg concentrations might be expected to have significant detrimental impacts on lake biota, or to delay the recovery of an ecosystem still affected by the legacy of acid deposition. The flush of base cations into the lake following the fire, whilst partially buffering the short-term acidifying effects of NO3- leaching, implies some depletion of soil base cation stocks, with possible detrimental consequences for future lake acidity. Comparing the effects of wildfire at Blue Lough to those reported elsewhere, it appears that the acidity response of an ecosystem depends strongly on its pre-existing susceptibility. In relatively well-buffered catchments, increases in acid anion concentrations following wildfire appear to be balanced, or even outweighed, by increases in base cation concentrations (e.g. Minshall and others, 2001), but in poorly buffered catchments base cation increases may be insufficient to offset increases in NO3- and/or SO42- leaching, resulting in an acidification response (e.g. Lydersen and others, 2014; Bayley and others, 1992).

Although suspended sediment concentrations were not measured directly, sediment trap data from Blue Lough clearly indicate a sharp increase in sediment inputs to the lake following the 2011 fire. This suggests an increase in catchment POC export, consistent with previous work (Smith and others, 2011). In contrast, the negative impact of wildfire on DOC concentrations at Blue Lough seems clear, but somewhat at odds with recent reviews suggesting risks to downstream ecosystems and water supplies of DOC increases following wildfire (Ranalli, 2004; Smith and others, 2011; Bladon and others, 2014), and with the substantial body of literature on prescribed burning and DOC (discussed below). Amongst reviews of wildfire impacts, it is notable that the primary evidence for DOC increases appear limited to just three studies. Of these, Minshall and others (2001) observed significant differences between stream DOC concentrations for two burned/unburned catchment pairs, but one had higher DOC concentrations in the fire-affected stream, and the other the reverse, suggesting that these differences perhaps existed pre-fire. Emelko and others (2011) recorded higher median DOC concentrations in burned versus unburned catchments, but concentrations remained fairly low and differences were small (median 3 mg l-1 in burned versus 1-2 mg l-1 in reference catchments in the first year post-fire; 95th percentile 3.8 versus 4.6 mg l-1 over a four year period; maximum 7.9 versus 8.1 mg l-1). The one study reporting a large, positive effect on surface water DOC concentrations was that of McEachern and others (2000), who sampled 14 lakes draining unburned catchments and 15 lakes draining burned catchments in Northern Alberta. Our re-analysing the data presented in this study, however, shows a strong inverse relationship between DOC concentration and lake volume (DOC = 37.4 – 2.41 ln[lake volume], R2 = 0.50, p < 0.001) spanning both burned and unburned catchments. Because the unburned lakes were on average almost an order of magnitude larger than the fire-affected lakes (mean volumes 15,100 m3 versus 1,820 m3) it appears that most if not all of the differences in DOC between burned and unburned catchments may be explained by differences in lake size, rather than fire. This conclusion is supported by other data presented by McEachern and others (2000) showing no difference in DOC concentrations in water leaving burned and unburned fens, and slightly lower DOC concentrations in burned versus unburned stream catchments.

To our knowledge, there has only been one previous paired (burned/unburned) catchment wildfire study with substantial pre-fire data, by Betts and Jones (2009). This study, like ours, observed a significant negative effect on DOC concentrations two years after the fire. Our results are also consistent with the interpretation of Lydersen and others (2011), albeit based on post-fire data only, that DOC solubility in burn-affected catchments was suppressed by high acidity during the early post-fire period. Betts and Jones (2009), Lydersen and others (2011) and Carignan and others (2000) all attributed the lack of DOC increases at their sites to some combination of loss and/or modification of soil organic matter, reduced soil microbial activity, and/or a reduction in seasonal litter inputs. Radiocarbon evidence that a high proportion of DOC in runoff from both peatland and forest catchments normally derives from recent litter inputs (e.g. Schiff and others, 1997; Palmer and others, 2001; Evans and others, 2007) suggests that loss of vegetation and surface litter, together with damage to soil decomposer communities, may be important in explaining lower DOC export from burned catchments. It is also possible that the observed re-acidification of Blue Lough by high NO3- leaching had the effect of reducing DOC export from the soil via the suppressive effect of elevated H+ on organic matter solubility (Evans and others, 2012). Intriguingly, the simultaneous increase in NO3- and decrease in DOC is also consistent with the widely observed inverse spatial and temporal relationship between these two water quality determinands (e.g. Goodale and others, 2005; Evans and others, 2006a; Taylor and Townsend, 2010), which has been interpreted in terms of stoichiometric constraints on N versus C availability (Kopaček and others, 2013).

*The effects of wildfire on downstream drinking water quality*

Emelko and others (2011) and Bladon and others (2014) have suggested that more frequent and severe wildfires present a significant risk to the quality of drinking water supplies in many regions. Our results support these conclusions in relation to sediment and nutrient loads, and demonstrate the potential for effects to extend downstream into reservoirs and distribution networks, and to persist for several years after the fire. On the other hand, our results reinforce the conclusion of Smith and others (2011) that post-fire peak concentrations of most substances are unlikely to breach drinking water guidelines. For example, peak NO3- concentrations observed at Blue Lough (108 eq l-1) and at the intake of the Drumaroad treatment works (60 eq l-1), although exceptionally high for upland waters, remain far below the European Union limit for NO3- in drinking water of 50 mg l-1 (3570 eq l-1; EU, 1991). Nevertheless, increased nutrient loadings to lakes and reservoirs do have the potential to increase algal growth, and therefore to have indirect detrimental impacts on water supplies.

With regard to DOC, we found that concentrations in water supplies decreased following the fire (Figure 5c). Nevertheless, it is possible that the quality, if not the quantity, of organic matter in drinking water supplies may have been detrimentally affected by the wildfire, for example by increasing its disinfection by product (DBP) formation potential. Wang and others (2013) measured lower extractable DOC concentrations in burned (ash) versus unburned (forest floor) materials following a forest fire, and reduced production of DBP precursor compounds. Olefeldt and others (2013b) measured lower extractable DOC concentrations in burned versus unburned forest and peatland soils, with DOC from burned soils having higher SUVA254, lower biodegradability and higher photodegradability. In a chronosequence study, Clay and others (2012) found that colour (but not DOC) levels were elevated at recently burned peatland sites. Our SUVA254 data, from Blue Lough and Silent Valley Reservoir, provide somewhat contrasting evidence. At Silent Valley, reduced SUVA254 during the initial post-fire period could indicate flushing of UV-transparent plant-derived material. The subsequent increase in SUVA254 to above-background levels suggests either the mobilisation of more aromatic, soil-derived organic matter or (given the overall reduction in DOC concentrations) a reduction in plant-derived DOC. At the smaller Blue Lough, temporal variability in SUVA254 was higher both pre- and post-fire, and there was little evidence of a reduction in the first post-fire year. However, there was a very marked reduction in SUVA254 during summer 2013, to the lowest values recorded at the site. Long-term meteorological data from the nearby Armagh monitoring station (<http://www.metoffice.gov.uk/pub/data/weather/uk/climate/stationdata/armaghdata.txt>) show that the three warmest summers in the UWMN monitoring period were 1995, 2006 and 2013, all of which were associated with summer reductions in SUVA254 (Figure 2h). This could indicate enhanced photo-bleaching of DOM by UV radiation, together with extended water residence times, during hot dry summers. It is also possible that water flow through deeper soil layers reduced leaching of UV-absorbent DOM, or that warm conditions enhanced rates of UV-transparent algal DOM production in the lake. In the latter case, increased NO3- supply following the fire (maximum concentrations were recorded in March 2013; Figure 2a), together with possible release of P from sediment eroded into the lake (Figure 6), could have contributed to the size of the algal bloom, and thus to the particularly large SUVA254 reduction during summer 2013. However, Silent Valley Reservoir data suggest that short-term changes in DOM quality observed at Blue Lough were not replicated at the larger catchment scale (Figure 5d). Overall, it appears that changes in quantity and quality of DOM entering raw water supplies following the Mourne Fire were relatively minor, and insufficient to cause problems for either colour removal or DBP formation.

*Implications of wildfire for fluvial carbon fluxes*

The sediment trap data from Blue Lough provide clear evidence of increased total and organic sediment accumulation rates following the fire, suggesting an increase in POC export from catchment soils. If we assume that all additional organic C accumulation in the sediment following the fire (3.8 kg C m-2 yr-1) derived from terrestrial POC export, and that the lake effectively trapped all incoming sediment, this would imply a fire-induced POC flux from the catchment of 150 g C m-2 yr-1. This is similar to fluvial POC loss from actively eroding blanket bogs (e.g. Worrall and others, 2011) and around one third of the C typically lost through biomass combustion during prescribed moorland burns (Worrall and others, 2013). This suggests that erosional losses over a three year post-fire period could lead to similar rates of terrestrial C loss as the fire itself. However, it is also possible that a proportion of the organic matter accumulated in the sediment traps was produced through autochthonous production. In this case, the increased flux following the fire could, as discussed above, represent an increase in aquatic primary production due to elevated nutrient inputs to the lake. In either case, the continuously high levels of sediment C accumulation in the years following the fire suggest a sustained effect.

Because discharge measurements are unavailable, we were not able to quantify fire-induced changes in water flux, or therefore DOC flux, from Blue Lough. However, given that DOC concentrations declined by around one third following the fire, it would be necessary for runoff to have increased by the same proportion simply to maintain a constant rate of DOC loss. Whilst runoff increases of this magnitude have been reported from dry, forested catchments in North America as a result of reduced evapotranspiration (e.g. Wright, 1976; Carignan and others, 2000) this mechanism could not have the same effect at Blue Lough where long-term average evaporative loss (UK Meteorological Office Rainfall and Evaporation Calculation System; Hough and Jones, 1997) is only 25% of precipitation. Thus changes in transpiration rates in response to change in vegetation cover, no matter how drastic, are unlikely to have much influence on runoff. On this basis, we infer that fluvial DOC fluxes probably declined as a result of the wildfire, although further data would be required to confirm this.

Even without a change in DOC flux, the observed shift in DOM quality may indicate a transition towards overall C loss from the ecosystem. As noted earlier, radiocarbon measurements from intact ecosystems typically show DOC to be derived from recent plant and litter material, but DOC from ecosystems disturbed through drainage, agriculture and other human activities typically has an older radiocarbon value, indicating loss of stored soil C (Evans and others, 2014; Butman and others, 2015). Peatlands affected by burning and erosion have been shown to export particularly old DOC in both the UK and Southeast Asia (Evans and others, 2014). Based on this evidence, we infer that the Mourne fire likely triggered a shift from an ecosystem in approximate C balance, with low POC losses and DOC export derived from recently sequestered CO2, to one in which photosynthetic CO2 uptake has been reduced due to the loss of plant cover, POC loss has increased as a result of soil erosion, and an increased proportion of DOC exports derived from the mobilisation of old, stored soil organic C.

*Relevance of this study for prescribed moorland burning*

In the UK, although wildfires are reasonably common, prescribed fires occur more extensively as part of moorland management, and have been invoked as a cause of deteriorating drinking water quality. Controlled, catchment-scale data on prescribed fire impacts are scarce (Holden and others, 2012) and there are no previous UK studies in which the effects of fire (prescribed or wild) can be assessed in the context of long-term pre-burning data. Davies and others (2016) argue that conflation of prescribed fire and wildfire studies has led to misrepresentation of the impacts of prescribed fire, and we recognise the need for caution when interpreting the results of our study in this context. However, as noted earlier, prescribed fire studies in other regions have shown very similar directional changes in water quality (e.g. elevated NO3-, SO42-, Cl-, base cations) to those observed following wildfire studies, including our own. Large increases in stream NO3- concentrations observed by Cresser and others (2004) following prescribed moorland burning are also consistent with our observations at Blue Lough. On this basis, we argue that the direction (if not the magnitude) of water quality changes may be fundamentally similar for different fire types.

In light of this conclusion, it is surprising that the DOC decreases observed at Blue Lough are apparently so inconsistent with the prevailing view that moorland burning causes DOC leaching to increase. However, as highlighted by Holden and others (2012), almost every study connecting higher DOC concentrations to prescribed burning has been based on spatial correlations with burn extent at the catchment scale (Mitchell and McDonald, 1995; Yallop and others, 2010; Clutterbuck and Yallop, 2010; Grayson and others, 2012; Ramchunder and others, 2013). In contrast, chronosequence studies (Clay and others, 2012) and plot-scale experiments (Clay and others, 2009; Ward and others, 2007; Helliwell and others, 2010) have shown unchanged or even decreasing DOC concentrations following prescribed fire. In Alaska, Shibata and others (2003) recorded decreased DOC concentrations in the organic horizon of a catchment subject to prescribed fire, consistent with observed decreases in DOC at the nearby, wildfire-affected catchment studied by Betts and Jones (2011). The long-term DOC increases attributed by Yallop and others (2010) to increased moorland burning extend well beyond areas (and indeed countries) where prescribed burning occurs, and can be better explained by decreases in acidic deposition (Evans et al., 2006b; Monteith and others, 2007; Chapman and others, 2010). The spatial extent of prescribed burning may itself be linked to other factors, such as peat cover (Chapman and others, 2010) or vegetation community (Holden and others, 2012) that better explain spatial variations in DOC concentration. Consequently, given: i) the finding from this and several previous studies that DOC did not increase following wildfire (and in some cases, including this one, actually decreased); ii) the similar direction of response in other water quality variables to wildfires and prescribed burns; iii) the lack of a single plot-scale prescribed burning experiment in which DOC leaching has increased; and iv) the lack of *any* catchment-scale BACI studies, the view that prescribed burning causes surface water DOC to increase seems questionable. Whilst we certainly cannot rule it out based on our study, or any previous studies, we support the conclusion of Holden and others (2012) that further focused work is required, and specifically highlight the need for rigorously designed catchment-scale experimental studies that exclude other potential explanatory factors.

**Conclusions**

To our knowledge, this is the first detailed study of wildfire impacts on water quality in a UK moorland catchment, and the only study of any ecosystem where it has been possible to evaluate these impacts in the context of both a multi-decadal pre-fire monitoring dataset, and a large number of reference sites. This highlights the importance of consistently operated, multiple-site long-term monitoring networks for the detection, quantification and correct attribution of ecological responses to extreme events. The large and sustained fire responses observed bear a close resemblance to those observed elsewhere, despite differences in soil (organic versus mineral) and vegetation (moorland versus forest). The large peak in NO3 leaching suggests that the long history of high N deposition at Blue Lough, and resulting accumulation of N in catchment soils, have predisposed it to disturbance-induced N loss, in this case due to wildfire. Similarly, despite strong recovery from acidification in the decades prior to the fire, our results indicate that Blue Lough, and potentially many other catchments subject to historically high acid deposition, remain vulnerable to re-acidification as a consequence of extreme events such as wildfire, possibly because the base cation buffering capacity of the soil has yet to be replenished. We found clear evidence of increased particulate C loss, as well as changes in the quality of DOC indicative of a shift towards loss of older soil C. Whilst a large body of literature has suggested, largely from spatial surveys, that burning leads to a DOC increase, our results from a before-after, control-intervention wildfire study showed a clear DOC decrease.

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**Figure Captions**

**Figure 1a)** The Blue Lough catchment on May 8th 2011, seven days after the fire, viewed from the south-west; **b)** Detail of the Blue Lough catchment and Slievelamagan on May 3rd 2011, two days after the fire, viewed from the south (both images courtesy of Charles McRobert).

**Figure 2.** Quarterlymeasured concentrations of a range of water chemistry variables at Blue Lough from 1990 to 2014. Samples collected before the May 2011 fire are denoted by grey circles, those from after the fire by black circles.

**Figure 3**. Mean annual Z scores for Blue Lough (thick black line) compared to the median (grey solid line) and 10th-90th percentile range (grey dashed lines) of mean annual Z scores for all other continuously monitored sites in the UWMN. Zero line represents the mean 1980-1998 concentration, vertical line shows the date of the wildfire at Blue Lough (other UWMN sites have not been subject to similar fires during the monitoring period)**Figure 4**. Calculated changes in standardised concentrations (Z) of a range of water chemistry variables a) during the 20 year period before the Blue Lough fire, and b) between the last three years and the first three years after the Blue Lough fire. Error bars represent 10th and 90th percentile Z values for the UWMN sites.

**Figure 5**. Measured nitrate, pH, DOC and SUVA254 (where measured) for Silent Valley Reservoir (open circles), raw intake water at the Drumaroad Water Treatment Works (filled circles) and Blue Lough (triangles) from 2009 to 2015. Vertical line indicates the date of the fire, which affected all of the Blue Lough catchment as well as adjacent areas within the larger Silent Valley supply catchment.

**Figure 6**. Annual sediment accumulation rates measured in Blue Lough from 1992 to 2015 (light grey bars pre-fire, dark grey bars post-fire). Note that samples are collected in late summer of the year shown on the x axis, and the accumulation rate thus refers to the preceding 12 month period rather than the calendar year. Data for 2007 are missing.

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**b)**

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