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Recovery of acidified surface waters from acidification in the United Kingdom after twenty years of chemical and biological monitoring (1988-2008)

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Abstract

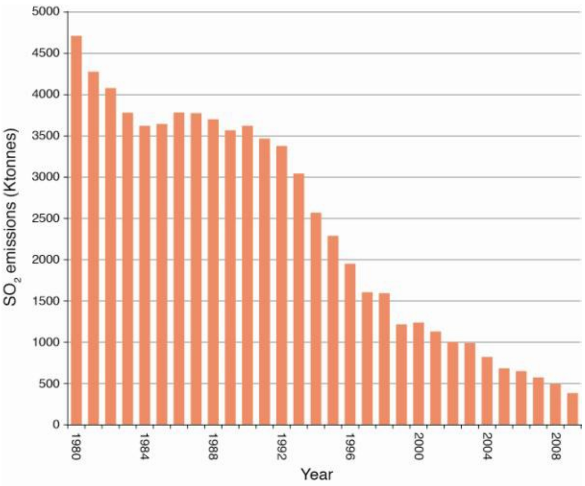
In this special issue we present papers based on data from the UK's Acid Waters Monitoring Network (UK AWMN) and other UK acid waters. The AWMN was set up in 1988. It was designed to monitor the chemical and biological response of acidified surface waters in the UK to the planned reduction in the emission of acidic sulphur and nitrogen gases as required by the UNECE Convention on Long Range Transboundary Air Pollution. Most papers in the volume are concerned with the changes that have taken place at the 22 AWMN sites during 20 years of monitoring from 1988 to 2008. They show that significant changes in deposition chemistry, in water chemistry and, to a lesser extent, in biology have taken place, consistent with a recovery from acidification. However, when compared with pre-acidification conditions inferred from lake sediment records, the extent of biological recovery so far is shown to be quite limited. The volume also contains papers on other aspects of surface water acidification in the UK. They include evidence for persistent highly acidic conditions of streams in the North York Moors, data from Scotland showing how afforestation is modifying recovery from acidification and the results of chemical speciation modelling in explaining the relationship between acidification and macroinvertebrate species richness at AWMN and other sites in the UK. The final papers are concerned with projections for the future and the extent to which acidified sites will continue to improve. They conclude that recovery will continue albeit slowly during this century but that other pressures principally from climate and land-use change are likely to alter the recovery pathways towards novel ecological endpoints potentially quite different from past baselines.

Keywords

Monitoring, surface water acidification, hydrochemistry, macroinvertebrates, salmonid fish, lake sediments, afforestation.

1. Introduction

Lake sediment records demonstrate that Upland Waters in the UK have been in receipt of atmospheric pollutants from the combustion of fossil fuels for over 200 years (Rippey, 1990). In addition, the analysis of diatom remains from sediments reveals that many upland lakes, specifically those situated in catchments in areas of high acid deposition and with low acid neutralising capacity, became severely acidified during the nineteenth century and early part of the twentieth century (Battarbee et al., 1988). However, despite Gorham's prescient concern about "whether the effects of the industrial age upon air chemistry have as yet seriously influenced the ecology of the Lake District…." (Gorham, 1958), surface water acidification was not recognised as a problem in the UK until the late 1970s following a chemical and biological survey of Galloway lakes and streams by Wright et al. (1980) in 1979. At the time the UK Government was not convinced by the evidence for fossil fuel combustion as the ultimate cause of acidification. It was consequently reluctant to accept responsibility for the problem, either in the UK or indeed in Scandinavia where long-range transported air pollutants from the UK and other industrial countries had also been blamed for acidification and loss of fish populations (Almer et al., 1974). Nevertheless, by 1986, the UK accepted the research evidence that conclusively demonstrated a clear correspondence between acid deposition and the acidification of low alkalinity surface waters both in the UK and Scandinavia (Mason, 1990). The UK consequently signed up to the UNECE Convention on Long Range Transboundary Air Pollution (LRTAP) aimed at controlling the emission of S and N gases to the atmosphere. As a result, over the last three decades there have been sustained reductions in the emissions of acidic gases across the UK and across Europe as a whole. By 2010 levels of S and oxidised N emissions in the UK had declined by approximately 94% and 58% respectively relative to 1970 (RoTAP, 2012) (Figure 1).



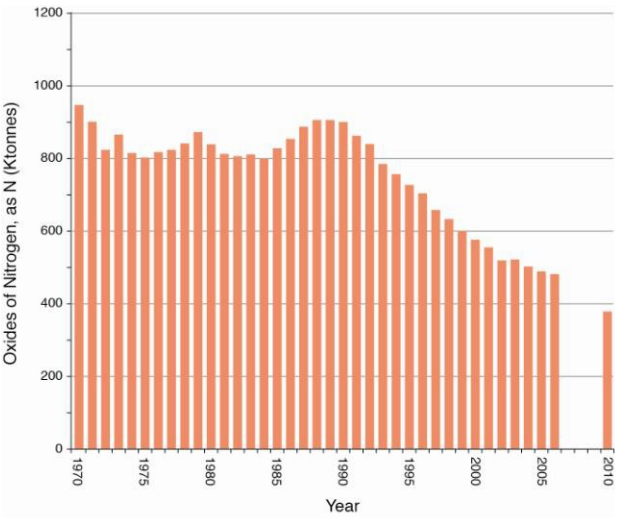


Figure 1. Trends in UK emissions of (a) SO_2 and (b) NO_x (modified from RoTAP 2012).

The UK Acid Waters Monitoring Network (AWMN) was established by the UK Department of Environment (now Defra) in 1988 to assess the chemical and biological response of acidified lakes and streams in the UK to the planned reduction in emissions following the recommendations of the UK Acid Waters Review Group (AWRG, 1987).

The Network comprised 22 lake and stream sites across upland regions of the UK (Figure 2, Table 1). Figure 2 shows 24 sites as Loch Coire nan Arr was replaced in 2007 by Loch Coire Fionnaraich and Danby Beck (Site 24) was added to the Network in 2012. Hydrochemical analysis is undertaken monthly from streams and quarterly from lake outflows. Biological monitoring involves annual surveys of diatoms, macroinvertebrates, salmonid fish and stream aquatic macrophytes, with lake aquatic macrophytes surveyed bi-annually. The design of the Network, sampling methodology and analytical protocols are described by Patrick *et al*. (1995) and Monteith & Evans (2000) and further information is available on the AWMN website (awmn.defra.gov.uk).

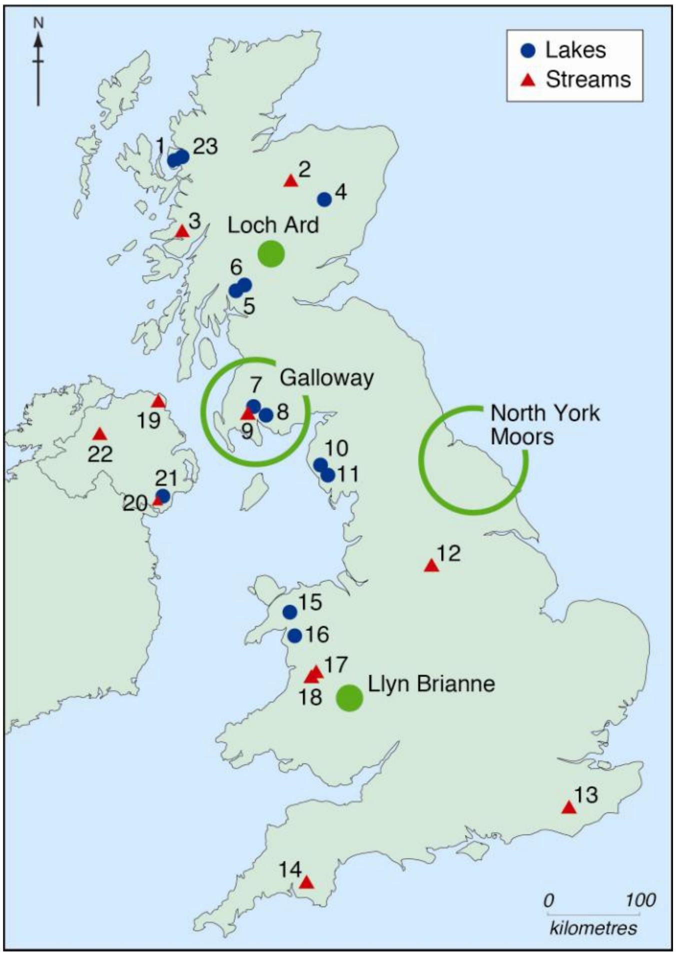


Figure 2. Map of UK Acid Waters Monitoring Network sites and other sites included in the this Special Issue. Sites: 1. Loch Coire nan Arr; 2. Allt a'Mharcaidh; 3. Allt na Coire nan Con; 4. Lochnagar; 5. Loch Chon; 6. Loch Tinker; 7. Round Loch of Glenhead; 8. Loch Grannoch; 9. Dargall Lane; 10. Scoat Tarn; 11. Burnmoor Tarn; 12. River Etherow; 13. Old Lodge; 14. Narrator Brook; 15. Llyn Llagi; 16. Llyn Cwm Mynach; 17. Afon Hafren; 18. Afon Gwy; 19. Beagh's Burn; 20. Bencrom River; 21. Blue Lough; 22. Coneyglen Burn; 23. Loch Coire Fionnaraich; 24. Danby Beck.

The Network has evolved since its inception. In 1995, following recognition of nitrogen deposition as a secondary driver of surface water acidification, total dissolved nitrogen and total dissolved phosphorus were added to the suite of measured chemical determinands. At the same time monitoring of one of the AWMN sites in north-east Scotland, Lochnagar, was expanded to include mercury in atmospheric deposition, water and aquatic plants. In 1999, in response to concerns about the potential role of climate change, shallow sub-surface and deep-water temperature began to be monitored at all lake sites using thermistor-based temperature dataloggers. A weather station was installed at Lochnagar in 2002 and an automatic hydro-meteorological monitoring buoy equipped with a thermistor chain and water quality sensors was deployed at the Round Loch of Glenhead in 2005. Temperature dataloggers have been installed at all sites and there are plans to complete the installation of conductivity and stage (loch and river) recorders throughout the Network to assess the impacts of climate variability especially with respect to changing storminess and the magnitude of sea-salt episodes). It will also allow hydrochemical data to be expressed as fluxes as well as concentrations.

A unique feature of the AWMN is the use of sediment traps emptied annually in the lake sites and used to monitor changes in diatom assemblages and trace metals. These complement sediment core data (Juggins et al., 1996) and allow changes in diatom assemblages to be tracked back continuously to the pre-acidification reference period in the early 19th century.

The AWMN database now holds over 20 years of chemical and biological data and provides the basis for a new assessment of the chemical and biological trends that are occurring in the UK uplands following earlier reviews after five (Patrick et al., 1995), ten (Monteith and Evans, 2000) and fifteen years (Monteith and Evans, 2005). The length of the time series now allows a more detailed statistical analysis of trends including the use of additive modelling to allow for non-linear temporal trends in hydrochemical data and a variety of ordination-based techniques for multivariate biological data. Taken together, the greater quantity of data and advances in statistical analyses enables the extent of the recovery to be assessed more definitively than hitherto.

Data from the Network are made available to other national and international long-term monitoring programmes including the UK Environmental Change Network (ECN), the International Cooperative Programme on Assessment of Rivers and Lakes (ICP Waters) for which the AWMN provides all six UK sites (e.g. Garmo *et al.*, 2011) and the Programme on Integrated Monitoring (ICP IM).

In addition to the intrinsic value of the long-term AWMN data-sets many of the sites also fulfil key roles in national scale experimental programmes and in the calibration, testing and application of biogeochemical and ecological models to upland waters. AWMN sites have been the focus of catchment based experimental or modelling studies on the biogeochemistry of carbon (Clark *et al.*, 2010; Dawson *et al.*, 2008; Evans *et al.*, 2012; 2008) and nitrogen (Curtis *et al.*, 2006; 2005; 2011; 2012; Evans *et al.*, 2006; 2008). Detailed algal ecology, ecological modelling and food-web studies have built on biological and chemical monitoring data (Layer et al., 2011; 2010; Ledger and Hildrew, 2005; Woodward and Layer, 2007; Yang and Flower, 2012). Understanding and modelling the speciation and toxicity of heavy metals have been the focus of several studies using AWMN data (e.g. Neal *et al.*, 2011; Rippey *et al.*, 2008; Tipping and Carter, 2011). Climate change impacts on upland waters have also been modelled for AWMN sites (e.g. Evans, 2005; Futter *et al.*, 2009; Thompson, 2012).

2. Paper synopses

This Special Issue presents the results of the analyses of the 20-year AWMN time-series data-sets together with other studies on low alkalinity waters in the UK subject to or recovering from problems of acidification. The first papers deal with deposition chemistry and hydrochemistry, the second section is concerned with biological change and the last section places the 20-year observational record into a longer time context, both past and future. The volume concludes with a synthesis and a look to the future.

2.1 Trends in acid deposition and hydrochemistry

The first four papers in the volume present mainly chemical data describing how the reduction in the emission of acidic gases (Figure 1) has been reflected by changes in the chemistry of deposition and by changes in surface water chemistry at AWMN sites and at other long-term study sites in the UK.

Curtis and Simpson (this issue) use **a**n additive model to show trends in both concentrations and bulk acid deposition loads at the 12 Acid Deposition Monitoring Network (ADMN) sites most closely associated with sites in the UK AWMN. The results indicate significant increasing trends in rainfall pH, significant decreasing trends in non-marine sulphate concentration but no significant trend in N concentration at most sites. However, non-marine chloride concentrations decline significantly at nine sites showing that chloride reductions are acting alongside sulphate reductions in explaining the increasing pH of bulk deposition across the country.

Monteith et al. (this issue) used both linear and non-linear statistical modelling to assess changes in the hydrochemistry of the 22 lakes and streams in the AWMN over the twenty year period from 1988-2008. Concentrations of non-marine sulphate fell in line with reductions in non-marine sulphur deposition, although concentrations in recent samples from the most acidified sites remain several times higher than those in the most remote, low-deposition regions of the UK. Nitrate concentrations also declined slightly at several sites in northern England and Wales but increased in some Scottish sites. A combination of unusually high rainfall and sea-salt inputs in the early years of monitoring, gradual long-term reductions in hydrochloric acid deposition, and later, more substantial reductions in sulphur deposition, mainly account for the relatively linear increases in Acid Neutralising Capacity (ANC) across the network with time. In the most acidified waters, the response in acidity to reductions in acid deposition was dominated initially by large reductions in inorganic aluminium concentrations whilst a substantial proportion of the deposition-driven increase in ANC at several sites is accounted for by increases in concentrations of Dissolved Organic Carbon (DOC). For the non-acidified, but acid-sensitive, waters in the far north and west of the UK, changes in DOC represent the only clear response to the small changes in sulphur deposition that have taken place. In a comparison of sites with afforested and moorland catchments, consistently higher levels of inorganic aluminium concentration and lower ANC provide clear evidence that the afforested sites are, and remain, more acidified than moorland sites, although it is suggested they are recovering at a similar rate.

Evans et al. (this issue) present data from the North York Moors National Park in Northeast England, a region located immediately downwind of major sulphur and nitrogen emission sources but one not formally represented by an AWMN site. Instead the acidification status of surface waters in the region is assessed by the authors from a unique 20 year stream pH record from Danby Beck, a stream site in the north of the Park, and from a snapshot survey of 51 surface waters draining moorland and conifer plantations. The Danby Beck data show that extremely acidic conditions have prevailed over the length of the 20 year data-set, with recovery only evident in the last few years. The survey data confirmed that extreme acidification of the moorland area is widespread: out of 37 moorland streams sampled, 32 had an acid neutralising capacity (ANC) below −50 μeq/l. Sulphate was found to be the dominant cause of acidification, and sulphur isotope analysis confirmed that the sulphur was derived primarily from atmospheric deposition. The data also indicate that conifer planting has exacerbated acidification, leading to fivefold higher nitrate and threefold higher aluminium concentrations in afforested sites compared to the moorland sites. The authors argue that the slow recovery of surface waters in the North York Moors is due to the release of a legacy of stored sulphur from the surrounding peatlands during droughts and they recommend the addition of a formal monitoring site representing the region to the AWMN.

In an assessment of the effect of plantation forestry on the recovery of surface waters from acidification, Malcolm et al. (this issue, a) use long term data (1976–2009) from eight streams with contrasting catchment land-use in the Loch Ard area of Central Scotland. Streams ranged from highly acidic (median annual pH 4.1) to circumneutral (pH 7.1). The data show that significant reductions in non-marine sulphate (NM-SO_4) concentrations closely match reductions in S deposition resulting in significant increases in pH and ANC and reductions in toxic inorganic labile aluminium (L-Al). Streams draining large areas of mature or second phase forestry were characterised by greater NM-SO_4 and L-Al concentrations and lower pH and ANC than sites with a modest forestry influence or with moorland vegetation. Chemical recovery at sites with a strong forestry influence was greater than observed for the moorland catchment, but relative inter-site differences persisted, indicating the continued influence of forestry on hydrochemical conditions under contemporary conditions and the legacy of forestry effects from previous decades. Non-linear temporal trends in the composition of macroinvertebrate assemblages consistent with ecological recovery from acidification were detected in all streams, regardless of their absolute chemical status. The authors stress the need to understand the recovery process better with respect, especially, to the complexity of chemical and biological interactions, the non-linear nature of change, the potential for hysteresis to occur and the definition of recovery endpoints.

2.2 Biological response to changing hydrochemistry

The marked increase in acid neutralising capacity that has occurred at acidified lakes and streams has led to more muted but nevertheless significant changes in biota across the UK, most clearly seen by changes in diatom epilithon and by the appearance of aquatic plant taxa previously thought to have been lost (Kernan et al., 2010). In this volume we describe the changes to macroinvertebrate and fish populations that have occurred over the last 20 years and the principal factors controlling those changes.

Murphy et al. (this issue) analyse the 20-year (1988–2008) record of macroinvertebrate data from the AWMN and demonstrate significant temporal changes in community structure at 12 of the 22 sites. Acidification indices suggest that macroinvertebrate recovery from acidification is taking place at five stream sites and five lake sites. However there is no evidence for macroinvertebrate recovery at a further seven sites that show a significant increase in ANC. The authors argue that this mismatch is evidence that biological recovery is delayed compared to the chemistry and that the macroinvertebrate changes observed are modest with most sites still showing signs of acid stress. They conclude that the limited recovery is due to continuing unfavourable chemical conditions and/or to ecological inertia in the reassembly of acid-sensitive faunas.

Stockdale et al. (this issue) use the chemical speciation model, WHAM-FTOX, to predict the impact of proton and metal mixtures (including Al) on the species richness of macroinvertebrate assemblages from upland surface waters in the UK (including AWMN sites) and Norway recovering from acidification and they compare their results with direct observations from time-series data. Model results compare well with observed trends of chemical and biological improvement at some sites, indicating that chemistry is often the principal factor controlling species richness. At other sites additional (un-modelled) factors appear to account for further suppression of diversity. They conclude that the model gives a good indication of the relative importance of chemical toxicity and other un-modelled factors in limiting the recovery response of macroinvertebrate communities.

Malcolm et al. (this issue, b) assess evidence for the recovery of salmonid fish populations from the effects of acidification using data from the AWMN. The effects of different chemical determinands on brown trout fry and parr populations were assessed alone and in combination. Significant positive temporal trends in fish presence were observed at two of the most acidified sites in the network indicating that limited recovery is occurring where favourable chemical conditions have now been attained. Fry were found to be substantially more sensitive to water quality than parr and labile monomeric aluminium (L-Al) concentration was the best single chemical determinand for predicting fry presence. The authors suggest that chemical thresholds for the probability of occurrence of brown trout populations should be derived from L-Al - fry response relationships and that monitoring of L-Al should become standard practice in acidified areas of the UK.

2.3 Recovery and future threats

Despite evidence of recovery from acidification provided by the 20 year AWMN chemical and biological data, the extent of recovery as judged against past baselines is as yet limited. Moreover, a full recovery is threatened by new pressures from climate change and land-use change and their uncertain interaction with pollutants stored in catchment soils.

Battarbee et al. (this issue) address the issue of recovery using the combined data from sediment cores and sediment traps to track changes in diatom assemblages in the 11 AWMN lakes from pre-acidification times (prior to ca. 1850 AD) to the present (2008 AD). They show that the degree of recovery from acidification varies amongst sites but in all cases its extent is limited when compared with the pre-acidification reference. In most cases the recovery, although slight, is characterised by a decline in acid tolerant taxa and a return towards taxa that occurred previously at each respective site. In a few cases, however, the floristic composition of recent samples is different from those that occurred during and before the acidification phase. The reasons for this are not yet clear but it is possible that nutrient enrichment from atmospheric N deposition and/or climate change is beginning to play a role in driving water quality as acidity decreases. The authors maintain that diatom samples from annually exposed sediment traps when combined with sediment core data provide a high resolution and continuous record of environmental change and provide a unique method of comparing recovery endpoints with past reference conditions.

In the next two papers Helliwell et al. (this issue, a & b) use the dynamic hydrogeochemical model MAGIC to simulate the chemical response of catchment soils and surface waters to future changes in atmospheric pollution and land use at UK AWMN and other sites. In the first paper the authors hindcast acid neutralising capacity (ANC) for the 22 AWMN sites and show that, with the exception of Blue Lough, all sites had modelled ANC values above 20 μeq/l in 1860 AD. During the subsequent period of acidification from 1860 to 1970 modelled ANC declined to <20 μeq/l at 14 of the sites. After 1970, despite significant reductions in sulphur and to a lesser extent nitrogen deposition the simulated soil base saturation at all sites either continued to decline or remained stable until the late 1980s, with marginal recovery detected at some sites thereafter in the past decade. On the basis of planned emission reduction scenarios for 2020 under the Gothenburg protocol and land use scenarios for 2050 under approved Forestry Commission plans at the five afforested sites in the

AWMN, model predictions indicated that surface water acid status will continue to improve during the next decade and beyond primarily due to the projected significant decline in sulphate concentrations. The contribution of nitrate leaching to the total acid status of surface water in 2020 was small but predicted to increase slightly by the end of the century (2100 AD) and likely therefore to have a small confounding influence on the rate of chemical recovery at most sites in the network. There was no evidence from the model predictions that afforested sites will follow a different recovery trajectory to moorland sites. Planned reductions in coniferous forest cover amounting to approximately 13% across the five afforested sites are projected to result in a slight increase in ANC and pH.

The second modelling paper (Helliwell et al.) (this issue, b) focusses on forestry and its role in the acidification of soils and surface waters of five sites with varying forest cover from 0 to 65% in Galloway, South-west Scotland. A 'no forestry' scenario was compared to future 'Forest Design Plans' provided by the Forestry Commission. In the model conifer planting enhanced pollutant scavenging and increased base cation uptake but did not strongly impede the widespread chemical recovery of surface waters from the mid 1980s to the present day. Current ANC values are above the critical ANC threshold of 20 µeq/l at all five sites and >50 µeq/l at three of the four forested sites. However, ecological surveys show that the response of fish and aquatic invertebrates has generally been small. For the future, continued chemical recovery was predicted in response to planned reductions in acid deposition to 2020 but thereafter the recovery rate was much slower with no site expected to return to the conditions of 1860 by 2100. There were only small differences in the ANC response post 2010 between the planned forest cover scenario and the 'no forest' scenario based on the underlying assumptions and calibration of the model suggesting that future changes in forest cover are unlikely to have a major impact on the recovery process and that future emissions reductions, rather than land-use change, may therefore be required to promote further biological recovery in affected catchments.

The final paper (Curtis et al., this issue) provides an overview of the pressures facing upland waters in the UK both now and in the future. It maintains that the threat from acid deposition has declined sharply since the 1980s but its legacy remains a major concern. Although recovery is taking place a complete recovery is unlikely as projected pressures from climate change increase. UK upland waters are likely to become warmer, summer streamflows lower, winter streamflows higher and the occurrence and influence of snowfall and lake ice-cover will decrease. Expansion of forest planting, changing grazing regimes and land management practices are also likely to take place under the influence of socio-economic as well as climate pressures leading to the modification of catchment biogeochemistry, surface water quality and freshwater biodiversity. The authors conclude that the reference condition concept may not be appropriate in setting ecological restoration targets and stress the importance of high quality integrated monitoring of upland waters to underpin decision making in the future.

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Site	**Code**	**UK Grid Reference**	**Type**	**Altitude Range (m)**	**Geology**	**Soils**	**Catchment area (ha)**	**Forest area (%)**	**Lake area (ha)**	**Lake max. depth (m)**
1. Loch Coire nan Arr	ARR	NG 808422	Lake	125 – 896	Sandstone	Podzol, gley, peat	897	-	12	12
2. Allt a' Mharcaidh	MHAR	NH 881045	Stream	325 – 1111	Granite	Podzol, peat	998	-	-	-
3. Allt na Coire nan Con	ANCC	NM 793688	Stream	10 – 756	Schist, gneiss	Peaty gley	790	48	-	-
4. Lochnagar	NAG	NO 252859	Lake	785 – 1155	Granite	Alpine podzol	92	-	10	27
5. Loch Chon	CHN	NN 421051	Lake	100 – 600	Schist, grits	Podzol, gley	1470	56	100	25
6. Loch Tinker	TINK	NN 445068	Lake	420 – 700	Schist, grits	Peat	112	-	11	10
7. Round Loch of Glenhead	RLGH	NX 450804	Lake	295 – 531	Granite	Peat, peaty podzol	95	-	13	14
8. Loch Grannoch	LGR	NX 542700	Lake	210 – 601	Granite	Gley, podzol, peat	1290	70	114	21
9. Dargall Lane	DARG	NX 449786	Stream	225 – 716	Shale, greywackes	Peaty podzol	210	-	-	-
10. Scoat Tarn	SCOATT	NY 159104	Lake	602 – 841	Volcanics	Peaty ranker	95	-	5	20
11. Burnmoor Tarn	BURNMT	NY 184044	Lake	252 – 602	Volcanics, granite	Ranker, podzol, peat	226	-	24	13
12. River Etherow	ETHR	SK 116996	Stream	280 – 633	Millstone grit	Peat	1300	-	-	-
13. Old Lodge	LODGE	TQ 456294	Stream	94 – 198	Sandstone	Brown podzol, gley	240	-	-	-
14. Narrator Brook	NART	SX 568692	Stream	225 – 456	Granite	Podzols	475	-	-	-
15. Llyn Llagi	LAG	SH 649483	Lake	380 – 678	Slate, shale, dolerite	Peaty podzol, peat	157	-	6	17

16. Llyn Cwm Mynach	MYN	SH 678238	Lake	285 – 680	Cambrian sedimentary	Rankers, peat	152	55	6	11
17. Afon Hafren	HAFR	SN 844876	Stream	355 – 690	Shale, gritstone	Peaty podzol, peat	358	50	-	-
18. Afon Gwy	GWY	SN 842854	Stream	440 – 730	Shale, gritstone	Peaty podzol, peat	210	-	-	-
19. Beagh's Burn	BEAH	D 173297	Stream	150 – 397	Schist	Peat	273	-	-	-
20. Bencrom River	BENC	J 304250	Stream	140 – 700	Granite	Peat	298	-	-	-
21. Blue Lough	BLU	J 327252	Lake	340 – 703	Granite	Peat	42	-	2	5
22. Coneyglen Burn	CONY	H 641884	Stream	230 – 562	Schist	Peat	1410	15	-	-
23. Loch Coire Fionnaraich	VNG9402	NG 945498	Lake	236 – 933	Sandstone, quartzite	Peat, peaty podsols	550	-	9	14

Table 1. Selected characteristics of the UK AWMN sites