



Article (refereed) - postprint

Battarbee, Richard W.; Shilland, Ewan M.; Kernan, Martin; Monteith, Donald T.; Curtis, Chris J.. 2014. **Recovery of acidified surface waters from acidification in the United Kingdom after twenty years of chemical and biological monitoring (1988–2008) [in special issue: Threats to upland waters]**

Copyright © 2014 Elsevier B.V.

This version available <http://nora.nerc.ac.uk/503769/>

NERC has developed NORA to enable users to access research outputs wholly or partially funded by NERC. Copyright and other rights for material on this site are retained by the rights owners. Users should read the terms and conditions of use of this material at

<http://nora.nerc.ac.uk/policies.html#access>

NOTICE: this is the author's version of a work that was accepted for publication in *Ecological Indicators*. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in *Ecological Indicators*, 37 B. 267-273. [10.1016/j.ecolind.2013.10.011](https://doi.org/10.1016/j.ecolind.2013.10.011)

www.elsevier.com/

Contact CEH NORA team at
noraceh@ceh.ac.uk

The NERC and CEH trademarks and logos ('the Trademarks') are registered trademarks of NERC in the UK and other countries, and may not be used without the prior written consent of the Trademark owner.

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

3

4 **Richard W. Battarbee^a, Ewan M. Shilland^a, Martin Kernan^a, Don Monteith^b, Chris J. Curtis^{a,c}**

5

6 ^aEnvironmental Change Research Centre, University College London, Gower St., London WC1E 6BT,
7 UK

8 ^bNERC Centre for Ecology & Hydrology, Lancaster Environment Centre, Library Avenue, Bailrigg,
9 Lancaster, LA1 4AP, UK

10 ^cSchool of Geography, Archaeology and Environmental Studies, University of the Witwatersrand,
11 Private Bag 3, Wits 2050, Johannesburg, South Africa.

12

13

14 **Abstract**

15

16 In this special issue we present papers based on data from the UK's Acid Waters Monitoring Network
17 (UK AWMN) and other UK acid waters. The AWMN was set up in 1988. It was designed to monitor
18 the chemical and biological response of acidified surface waters in the UK to the planned reduction
19 in the emission of acidic sulphur and nitrogen gases as required by the UNECE Convention on Long
20 Range Transboundary Air Pollution. Most papers in the volume are concerned with the changes that
21 have taken place at the 22 AWMN sites during 20 years of monitoring from 1988 to 2008. They show
22 that significant changes in deposition chemistry, in water chemistry and, to a lesser extent, in
23 biology have taken place, consistent with a recovery from acidification. However, when compared
24 with pre-acidification conditions inferred from lake sediment records, the extent of biological
25 recovery so far is shown to be quite limited. The volume also contains papers on other aspects of

26 surface water acidification in the UK. They include evidence for persistent highly acidic conditions of
27 streams in the North York Moors, data from Scotland showing how afforestation is modifying
28 recovery from acidification and the results of chemical speciation modelling in explaining the
29 relationship between acidification and macroinvertebrate species richness at AWMN and other sites
30 in the UK. The final papers are concerned with projections for the future and the extent to which
31 acidified sites will continue to improve. They conclude that recovery will continue albeit slowly
32 during this century but that other pressures principally from climate and land-use change are likely
33 to alter the recovery pathways towards novel ecological endpoints potentially quite different from
34 past baselines.

35

36

37 **Keywords**

38

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

41

42

43 **1. Introduction**

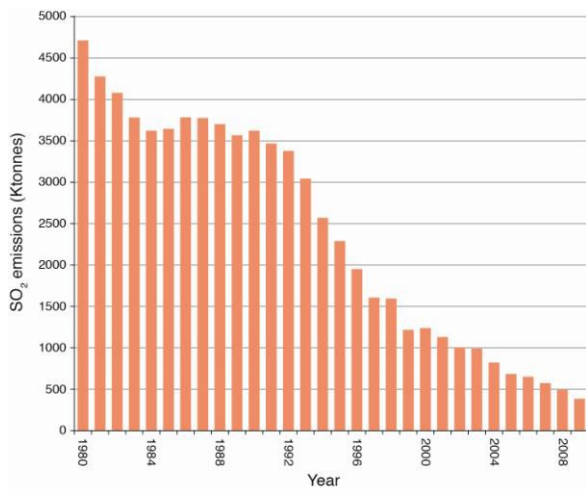
44

45 Lake sediment records demonstrate that Upland Waters in the UK have been in receipt of
46 atmospheric pollutants from the combustion of fossil fuels for over 200 years (Rippey, 1990). In
47 addition, the analysis of diatom remains from sediments reveals that many upland lakes, specifically
48 those situated in catchments in areas of high acid deposition and with low acid neutralising capacity,
49 became severely acidified during the nineteenth century and early part of the twentieth century
50 (Battarbee et al., 1988). However, despite Gorham's prescient concern about "whether the effects

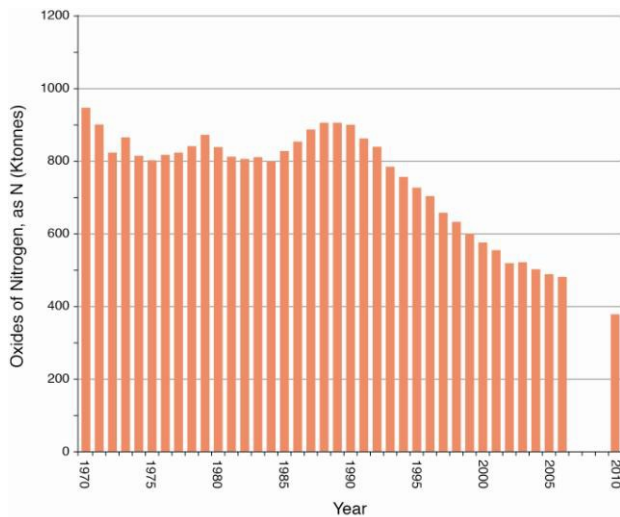
51 of the industrial age upon air chemistry have as yet seriously influenced the ecology of the Lake
52 District....” (Gorham, 1958), surface water acidification was not recognised as a problem in the UK
53 until the late 1970s following a chemical and biological survey of Galloway lakes and streams by
54 Wright et al. (1980) in 1979. At the time the UK Government was not convinced by the evidence for
55 fossil fuel combustion as the ultimate cause of acidification. It was consequently reluctant to accept
56 responsibility for the problem, either in the UK or indeed in Scandinavia where long-range
57 transported air pollutants from the UK and other industrial countries had also been blamed for
58 acidification and loss of fish populations (Almer et al., 1974). Nevertheless, by 1986, the UK accepted
59 the research evidence that conclusively demonstrated a clear correspondence between acid
60 deposition and the acidification of low alkalinity surface waters both in the UK and Scandinavia
61 (Mason, 1990). The UK consequently signed up to the UNECE Convention on Long Range
62 Transboundary Air Pollution (LRTAP) aimed at controlling the emission of S and N gases to the
63 atmosphere. As a result, over the last three decades there have been sustained reductions in the
64 emissions of acidic gases across the UK and across Europe as a whole. By 2010 levels of S and
65 oxidised N emissions in the UK had declined by approximately 94% and 58% respectively relative to
66 1970 (RoTAP, 2012) (Figure 1).

67

68



69



70

71

72 Figure 1. Trends in UK emissions of (a) SO₂ and (b) NO_x (modified from RoTAP 2012).

73

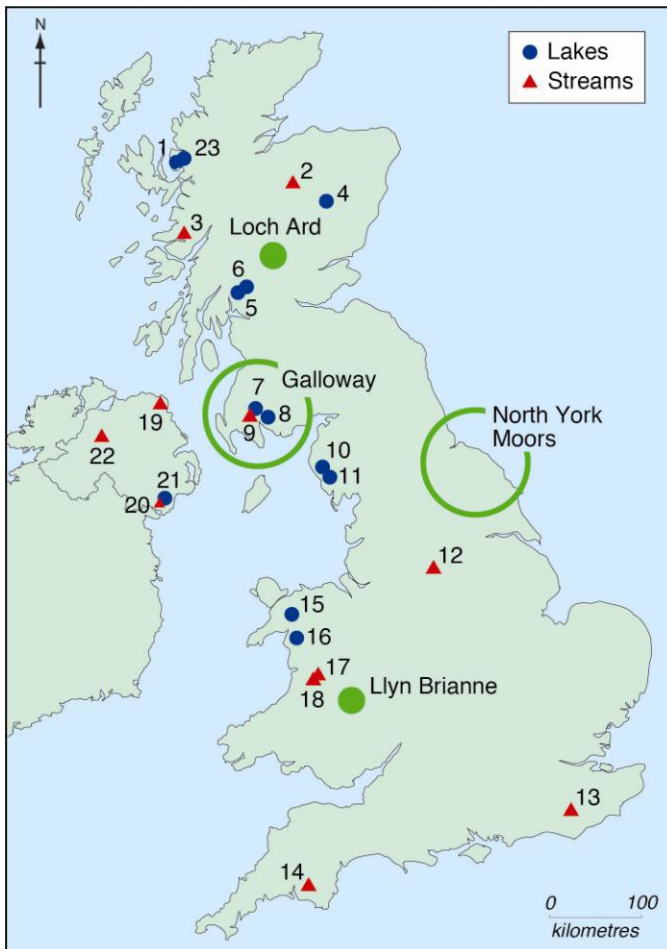
74 The UK Acid Waters Monitoring Network (AWMN) was established by the UK Department of
 75 Environment (now Defra) in 1988 to assess the chemical and biological response of acidified lakes
 76 and streams in the UK to the planned reduction in emissions following the recommendations of the
 77 UK Acid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

78

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

87

88



89
90
91
92
93
94
95
96
97
98

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 Llgi; 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.

99

100 The Network has evolved since its inception. In 1995, following recognition of nitrogen deposition as
101 a secondary driver of surface water acidification, total dissolved nitrogen and total dissolved
102 phosphorus were added to the suite of measured chemical determinands. At the same time
103 monitoring of one of the AWMN sites in north-east Scotland, Lochnagar, was expanded to include
104 mercury in atmospheric deposition, water and aquatic plants. In 1999, in response to concerns about
105 the potential role of climate change, shallow sub-surface and deep-water temperature began to be
106 monitored at all lake sites using thermistor-based temperature dataloggers. A weather station was
107 installed at Lochnagar in 2002 and an automatic hydro-meteorological monitoring buoy equipped
108 with a thermistor chain and water quality sensors was deployed at the Round Loch of Glenhead in
109 2005. Temperature dataloggers have been installed at all sites and there are plans to complete the
110 installation of conductivity and stage (loch and river) recorders throughout the Network to assess
111 the impacts of climate variability especially with respect to changing storminess and the magnitude
112 of sea-salt episodes). It will also allow hydrochemical data to be expressed as fluxes as well as
113 concentrations.

114

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

119

120 The AWMN database now holds over 20 years of chemical and biological data and provides the basis
121 for a new assessment of the chemical and biological trends that are occurring in the UK uplands
122 following earlier reviews after five (Patrick et al., 1995), ten (Monteith and Evans, 2000) and fifteen
123 years (Monteith and Evans, 2005). The length of the time series now allows a more detailed

124 statistical analysis of trends including the use of additive modelling to allow for non-linear temporal
125 trends in hydrochemical data and a variety of ordination-based techniques for multivariate biological
126 data. Taken together, the greater quantity of data and advances in statistical analyses enables the
127 extent of the recovery to be assessed more definitively than hitherto.

128
129 Data from the Network are made available to other national and international long-term monitoring
130 programmes including the UK Environmental Change Network (ECN), the International Cooperative
131 Programme on Assessment of Rivers and Lakes (ICP Waters) for which the AWMN provides all six UK
132 sites (e.g. Garmo *et al.*, 2011) and the Programme on Integrated Monitoring (ICP IM).

133
134 In addition to the intrinsic value of the long-term AWMN data-sets many of the sites also fulfil key
135 roles in national scale experimental programmes and in the calibration, testing and application of
136 biogeochemical and ecological models to upland waters. AWMN sites have been the focus of
137 catchment based experimental or modelling studies on the biogeochemistry of carbon (Clark *et al.*,
138 2010; Dawson *et al.*, 2008; Evans *et al.*, 2012; 2008) and nitrogen (Curtis *et al.*, 2006; 2005; 2011;
139 2012; Evans *et al.*, 2006; 2008). Detailed algal ecology, ecological modelling and food-web studies
140 have built on biological and chemical monitoring data (Layer *et al.*, 2011; 2010; Ledger and Hildrew,
141 2005; Woodward and Layer, 2007; Yang and Flower, 2012). Understanding and modelling the
142 speciation and toxicity of heavy metals have been the focus of several studies using AWMN data
143 (e.g. Neal *et al.*, 2011; Rippey *et al.*, 2008; Tipping and Carter, 2011). Climate change impacts on
144 upland waters have also been modelled for AWMN sites (e.g. Evans, 2005; Futter *et al.*, 2009;
145 Thompson, 2012).

146

147

148 **2. Paper synopses**

149

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

156

157 *2.1 Trends in acid deposition and hydrochemistry*

158

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

162

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

170

171 Monteith et al. (this issue) used both linear and non-linear statistical modelling to assess changes in
172 the hydrochemistry of the 22 lakes and streams in the AWMN over the twenty year period from
173 1988-2008. Concentrations of non-marine sulphate fell in line with reductions in non-marine sulphur

174 deposition, although concentrations in recent samples from the most acidified sites remain several
175 times higher than those in the most remote, low-deposition regions of the UK. Nitrate
176 concentrations also declined slightly at several sites in northern England and Wales but increased in
177 some Scottish sites. A combination of unusually high rainfall and sea-salt inputs in the early years of
178 monitoring, gradual long-term reductions in hydrochloric acid deposition, and later, more substantial
179 reductions in sulphur deposition, mainly account for the relatively linear increases in Acid
180 Neutralising Capacity (ANC) across the network with time. In the most acidified waters, the response
181 in acidity to reductions in acid deposition was dominated initially by large reductions in inorganic
182 aluminium concentrations whilst a substantial proportion of the deposition-driven increase in ANC at
183 several sites is accounted for by increases in concentrations of Dissolved Organic Carbon (DOC). For
184 the non-acidified, but acid-sensitive, waters in the far north and west of the UK, changes in DOC
185 represent the only clear response to the small changes in sulphur deposition that have taken place.
186 In a comparison of sites with afforested and moorland catchments, consistently higher levels of
187 inorganic aluminium concentration and lower ANC provide clear evidence that the afforested sites
188 are, and remain, more acidified than moorland sites, although it is suggested they are recovering at
189 a similar rate.

190
191 Evans et al. (this issue) present data from the North York Moors National Park in Northeast England,
192 a region located immediately downwind of major sulphur and nitrogen emission sources but one not
193 formally represented by an AWMN site. Instead the acidification status of surface waters in the
194 region is assessed by the authors from a unique 20 year stream pH record from Danby Beck, a
195 stream site in the north of the Park, and from a snapshot survey of 51 surface waters draining
196 moorland and conifer plantations. The Danby Beck data show that extremely acidic conditions have
197 prevailed over the length of the 20 year data-set, with recovery only evident in the last few years.
198 The survey data confirmed that extreme acidification of the moorland area is widespread: out of 37

199 moorland streams sampled, 32 had an acid neutralising capacity (ANC) below $-50 \mu\text{eq/l}$. Sulphate
200 was found to be the dominant cause of acidification, and sulphur isotope analysis confirmed that the
201 sulphur was derived primarily from atmospheric deposition. The data also indicate that conifer
202 planting has exacerbated acidification, leading to fivefold higher nitrate and threefold higher
203 aluminium concentrations in afforested sites compared to the moorland sites. The authors argue
204 that the slow recovery of surface waters in the North York Moors is due to the release of a legacy of
205 stored sulphur from the surrounding peatlands during droughts and they recommend the addition of
206 a formal monitoring site representing the region to the AWMN.

207
208 In an assessment of the effect of plantation forestry on the recovery of surface waters from
209 acidification, Malcolm et al. (this issue, a) use long term data (1976–2009) from eight streams with
210 contrasting catchment land-use in the Loch Ard area of Central Scotland. Streams ranged from highly
211 acidic (median annual pH 4.1) to circumneutral (pH 7.1). The data show that significant reductions in
212 non-marine sulphate (NM-SO₄) concentrations closely match reductions in S deposition resulting in
213 significant increases in pH and ANC and reductions in toxic inorganic labile aluminium (L-Al). Streams
214 draining large areas of mature or second phase forestry were characterised by greater NM-SO₄ and
215 L-Al concentrations and lower pH and ANC than sites with a modest forestry influence or with
216 moorland vegetation. Chemical recovery at sites with a strong forestry influence was greater than
217 observed for the moorland catchment, but relative inter-site differences persisted, indicating the
218 continued influence of forestry on hydrochemical conditions under contemporary conditions and the
219 legacy of forestry effects from previous decades. Non-linear temporal trends in the composition of
220 macroinvertebrate assemblages consistent with ecological recovery from acidification were detected
221 in all streams, regardless of their absolute chemical status. The authors stress the need to
222 understand the recovery process better with respect, especially, to the complexity of chemical and

223 biological interactions, the non-linear nature of change, the potential for hysteresis to occur and the
224 definition of recovery endpoints.

225

226 *2.2 Biological response to changing hydrochemistry*

227

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

234

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

244

245 Stockdale et al. (this issue) use the chemical speciation model, WHAM-FTOX, to predict the impact of
246 proton and metal mixtures (including Al) on the species richness of macroinvertebrate assemblages
247 from upland surface waters in the UK (including AWMN sites) and Norway recovering from

248 acidification and they compare their results with direct observations from time-series data. Model
249 results compare well with observed trends of chemical and biological improvement at some sites,
250 indicating that chemistry is often the principal factor controlling species richness. At other sites
251 additional (un-modelled) factors appear to account for further suppression of diversity. They
252 conclude that the model gives a good indication of the relative importance of chemical toxicity and
253 other un-modelled factors in limiting the recovery response of macroinvertebrate communities.

254

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

265

266 *2.3 Recovery and future threats*

267

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

272

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

286
287 In the next two papers Helliwell et al. (this issue, a & b) use the dynamic hydrogeochemical model
288 MAGIC to simulate the chemical response of catchment soils and surface waters to future changes in
289 atmospheric pollution and land use at UK AWMN and other sites. In the first paper the authors
290 hindcast acid neutralising capacity (ANC) for the 22 AWMN sites and show that, with the exception
291 of Blue Lough, all sites had modelled ANC values above 20 $\mu\text{eq/l}$ in 1860 AD. During the subsequent
292 period of acidification from 1860 to 1970 modelled ANC declined to $<20 \mu\text{eq/l}$ at 14 of the sites.
293 After 1970, despite significant reductions in sulphur and to a lesser extent nitrogen deposition the
294 simulated soil base saturation at all sites either continued to decline or remained stable until the late
295 1980s, with marginal recovery detected at some sites thereafter in the past decade. On the basis of
296 planned emission reduction scenarios for 2020 under the Gothenburg protocol and land use
297 scenarios for 2050 under approved Forestry Commission plans at the five afforested sites in the

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

307
308 The second modelling paper (Helliwell et al.) (this issue, b) focusses on forestry and its role in the
309 acidification of soils and surface waters of five sites with varying forest cover from 0 to 65% in
310 Galloway, South-west Scotland. A 'no forestry' scenario was compared to future 'Forest Design
311 Plans' provided by the Forestry Commission. In the model conifer planting enhanced pollutant
312 scavenging and increased base cation uptake but did not strongly impede the widespread chemical
313 recovery of surface waters from the mid 1980s to the present day. Current ANC values are above
314 the critical ANC threshold of 20 $\mu\text{eq/l}$ at all five sites and $>50 \mu\text{eq/l}$ at three of the four forested sites.
315 However, ecological surveys show that the response of fish and aquatic invertebrates has generally
316 been small. For the future, continued chemical recovery was predicted in response to planned
317 reductions in acid deposition to 2020 but thereafter the recovery rate was much slower with no site
318 expected to return to the conditions of 1860 by 2100. There were only small differences in the ANC
319 response post 2010 between the planned forest cover scenario and the 'no forest' scenario based on
320 the underlying assumptions and calibration of the model suggesting that future changes in forest
321 cover are unlikely to have a major impact on the recovery process and that future emissions

322 reductions, rather than land-use change, may therefore be required to promote further biological
323 recovery in affected catchments.

324
325 The final paper (Curtis et al., this issue) provides an overview of the pressures facing upland waters
326 in the UK both now and in the future. It maintains that the threat from acid deposition has declined
327 sharply since the 1980s but its legacy remains a major concern. Although recovery is taking place a
328 complete recovery is unlikely as projected pressures from climate change increase. UK upland
329 waters are likely to become warmer, summer streamflows lower, winter streamflows higher and the
330 occurrence and influence of snowfall and lake ice-cover will decrease. Expansion of forest planting,
331 changing grazing regimes and land management practices are also likely to take place under the
332 influence of socio-economic as well as climate pressures leading to the modification of catchment
333 biogeochemistry, surface water quality and freshwater biodiversity. The authors conclude that the
334 reference condition concept may not be appropriate in setting ecological restoration targets and
335 stress the importance of high quality integrated monitoring of upland waters to underpin decision
336 making in the future.

337

338 **Acknowledgements**

339

340 We gratefully acknowledge funding support for the Acid Waters Monitoring Network (now the
341 Upland Waters Monitoring Network) from the principal funder, the UK Department for Environment
342 Food and Rural Affairs (DEFRA), and also from other funders, the Department of the Environment
343 (Northern Ireland), the Welsh Government, Natural Resources Wales (NRW), the Environment
344 Agency (EA), the Forestry Commission (FC) and Scottish Natural Heritage (SNH). Significant support
345 in kind has been provided by the NERC Centre for Ecology and Hydrology (CEH), the Scottish
346 Government through Marine Scotland Pitlochry, Queen Mary, University of London and ENSIS Ltd. at

347 the Environmental Change Research Centre, University College London. We thank all our staff and
348 countless volunteers for their help with field sampling since the inception of the Network in 1988.
349 We also thank those cited above for funding the work presented by several papers in this Special
350 Issue that are not specifically concerned with the AWMN. Additional funders include the Agri-Food
351 and Biosciences Institute (Northern Ireland), the Biotechnology and Biological Sciences Research
352 Council, the Defence Science and Technology Laboratory, the Freshwater Biological Association,
353 Natural England, the Natural Environment Research Council, the Northern Ireland Environment
354 Agency, the Scottish Environment Protection Agency, Trent University Ontario and the Rural and
355 Environment Science and Analytical Services Division (RESAS) of the John Hutton Institute. We are
356 grateful to Iain Malcolm and Rachel Helliwell for constructive comments on this manuscript and to
357 Miles Irving for producing the figures.

358

359 **References**

360

- 361 Almer, B., Dickson, W., Ekström, C., Hörnström, E., Miller, U., 1974. Effects of acidification
362 on Swedish lakes. *Ambio* 3, 30-36.
- 363 AWRG, 1987. Monitoring acidity in United Kingdom freshwaters: recommendations of the
364 UK Acid Waters Review Group. Department of the Environment, London.
- 365 Battarbee, R.W., Anderson, N.J., Appleby, P.G., Flower, R.J., Fritz, S.C., Haworth, E.Y., Higgitt,
366 S., Jones, V.J., Kreiser, A., Munro, M.A.R., Natkanski, J., Oldfield, F., Patrick, S.T., Raven, P.J.,
367 Richardson, N.G., Rippey, B., Stevenson, A.C., 1988. Lake acidification in the United Kingdom
368 1800-1986: Evidence from analysis of lake sediments. ENSIS Ltd, London, p. 68.
- 369 Battarbee, R.W., Simpson, G.L., Shilland, E.M., Flower, R.J., Kreiser, A., Yang, H., Clarke, amp,
370 Gina, Recovery of UK lakes from acidification: An assessment using combined
371 palaeoecological and contemporary diatom assemblage data. *Ecological Indicators*.
- 372 Clark, J.M., Bottrell, S.H., Evans, C.D., Monteith, D.T., Bartlett, R., Rose, R., Newton, R.J.,
373 Chapman, P.J., 2010. The importance of the relationship between scale and process in
374 understanding long-term DOC dynamics. *Science of the Total Environment* 408.
- 375 Curtis, C.J., Emmett, B.A., Reynolds, B., Shilland, J., 2006. How important is N₂O production
376 in removing atmospherically deposited nitrogen from UK moorland catchments? *Soil Biology
377 & Biochemistry* 38, 2081-2091.

378 Curtis, C.J., Evans, C., Helliwell, R.C., Monteith, D.T., 2005. Nitrate leaching as a confounding
379 factor in chemical recovery from acidification in UK upland waters. *Environmental Pollution*
380 137, 73-82.

381 Curtis, C.J., Evans, C.D., Goodale, C.L., Heaton, T.E.H., 2011. What have stable isotope
382 studies revealed about the nature and mechanisms of N saturation and nitrate leaching
383 from semi-natural catchments? *Ecosystems* 14, 1021-1037.

384 Curtis, C.J., Heaton, T.E.H., Simpson, G.L., Evans, C.D., Shilland, J., Turner, S., 2012.
385 Dominance of biologically produced nitrate in upland waters of Great Britain indicated by
386 stable isotopes. *Biogeochemistry* 111, 535-554.

387 Curtis, C.J., Simpson, G.L., Trends in bulk deposition of acidity in the UK, 1988–2007,
388 assessed using additive models. *Ecological Indicators*.

389 Dawson, J.J.C., Soulsby, C., Tetzlaff, D., Hrachowitz, M., Dunn, S.M., Malcolm, I.A., 2008.
390 Influence of hydrology and seasonality on DOC exports from three contrasting upland
391 catchments. *Biogeochemistry* 90, 93-113.

392 Evans, C.D., 2005. Modelling the effects of climate change on an acidic upland stream.
393 *Biogeochemistry* 74, 21-46.

394 Evans, C.D., Chadwick, T., Norris, D., Rowe, E.C., Heaton, T.H.E., Brown, P., Battarbee, R.W.,
395 Persistent surface water acidification in an organic soil-dominated upland region subject to
396 high atmospheric deposition: The North York Moors, UK. *Ecological Indicators*.

397 Evans, C.D., Chapman, P., Clark, J., Monteith, D.T., Cresser, M., 2006. Alternative
398 explanations for rising dissolved organic carbon export from organic soils. *Global Change*
399 *Biology* 12, 2044-2054.

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

403 Evans, C.D., Monteith, D.T., Reynolds, B., Clark, J.M., 2008. Buffering of recovery from
404 acidification by organic acids. *Science of the Total Environment* 404, 316-325.

405 Futter, M.N., Helliwell, R.C., Hutchins, M., Aherne, J., 2009. Modelling the effects of
406 changing climate and nitrogen deposition on nitrate dynamics in a Scottish mountain
407 catchment. *Hydrology Research* 40, 153-166.

408 Garmo, O.A., Skjelkvale, B.L., Colombo, L., Curtis, C.J., Dubokova, I., Folster, J., Hoffmann, A.,
409 Hogasen, T., Jeffries, D., Keller, B., Majer, V., Paterson, A., Rogora, M., Rzychon, D., Srybny,
410 A., Steingruber, S., Stoddard, J.L., Talkop, R., Vuorenmaa, J., de Wit, H.A., Worsztynowicz, A.,
411 2011. Trends in surface water chemistry in Europe and North America 1990-2008, Trends in
412 precipitation chemistry, surface water chemistry and aquatic biota in acidified areas in
413 Europe and North America from 1990 to 2008. NIVA, Oslo, pp. 19-46.

414 Gorham, E., 1958. The influence and importance of daily weather conditions in the supply of
415 chloride, sulphate and other ions to fresh waters from atmospheric precipitation.
416 *Philosophical Transactions of the Royal Society of London Series B-Biological Sciences* B 241,
417 147-178.

418 Helliwell, R.C., Aherne, J., MacDougall, G., Nisbet, T.R., Lawson, D., Cosby, B.J., Evans, C.D.,
419 Past acidification and recovery of surface waters, soils and ecology in the United Kingdom:
420 Prospects for the future under current deposition and land use protocols. *Ecological*
421 *Indicators*.

422 Helliwell, R.C., Aherne, J., Nisbet, T.R., MacDougall, G., Broadmeadow, S., Sample, J.,
423 Jackson-Blake, L., Doughty, R., Modelling the long-term response of stream water chemistry
424 to forestry in Galloway, Southwest Scotland. *Ecological Indicators*.

425 Juggins, S., Flower, R.J., Battarbee, R.W., 1996. Palaeolimnological evidence for recent
426 chemical and biological changes in UK Acid Waters Monitoring Network sites. *Freshwater*
427 *Biology* 36, 203-219.

428 Kernan, M., Battarbee, R.W., Curtis, C.J., Monteith, D.T., Shilland, E.M., 2010. UK Acid
429 Waters Monitoring Network 20 Year Interpretative Report. ENSIS Ltd, Environmental
430 Change Research Centre, University College London, London.

431 Layer, K., Hildrew, A.G., Jenkins, G.B., Riede, J.O., Rossiter, S.J., Townsend, C.R., Woodward,
432 G., 2011. Long-term dynamics of a well-characterised food web: four decades of
433 acidification and recovery in the Broadstone Stream model system. *Advances in Ecological*
434 *Research* 44, 69-117.

435 Layer, K., Hildrew, A.G., Monteith, D.T., Woodward, G., 2010. Long-term variation in the
436 littoral food web of an acidified mountain lake. *Global Change Biology* 16, 3133-3143.

437 Ledger, M.E., Hildrew, A.G., 2005. The ecology of acidification and recovery: changes in
438 herbivore-algal food web linkages across a stream pH gradient. *Environmental Pollution*
439 137, 103-118.

440 Malcolm, I.A., Bacon, P.J., Middlemas, S.J., Fryer, R.J., Shilland, E.M., Collen, P., Relationships
441 between hydrochemistry and the presence of juvenile brown trout (*Salmo trutta*) in
442 headwater streams recovering from acidification. *Ecological Indicators*.

443 Malcolm, I.A., Gibbins, C.N., Fryer, R.J., Keay, J., Tetzlaff, D., Soulsby, C., The influence of
444 forestry on acidification and recovery: Insights from long-term hydrochemical and
445 invertebrate data. *Ecological Indicators*.

446 Mason, B.J., 1990. *The Surface Waters Acidification Programme*. Cambridge University
447 Press, Cambridge.

448 Monteith, D.T., Evans, C.D., 2000. United Kingdom Acid Waters Monitoring Network 10 Year
449 Report. Analysis and Interpretation of Results, April 1988 - March 1998, in: Monteith, D.T.,
450 Evans, C.D. (Eds.). ENSIS Ltd, London, pp. 1-364.

451 Monteith, D.T., Evans, C.D., 2005. The United Kingdom Acid Waters Monitoring Network: a
452 review of the first 15 years and introduction to the special issue. *Environmental Pollution*
453 137, 3-13.

454 Monteith, D.T., Evans, C.D., Henrys, P.A., Simpson, G.L., Malcolm, I.A., Trends in the
455 hydrochemistry of acid-sensitive surface waters in the UK 1988–2008. *Ecological Indicators*.

456 Murphy, J.F., Winterbottom, J.H., Orton, S., Simpson, G.L., Shilland, E.M., Hildrew, A.G.,
457 Evidence of recovery from acidification in the macroinvertebrate assemblages of UK fresh
458 waters: A 20-year time series. *Ecological Indicators*.

459 Neal, C., Rowland, P., Neal, M., Jarvie, H.P., Lawlor, A., Sleep, D., Scholefield, P., 2011.
460 Aluminium in UK rivers: a need for integrated research related to kinetic factors, colloidal
461 transport, carbon and habitat. *Journal of Environmental Monitoring* 13, 2153-2164.

462 Patrick, S.T., Monteith, D.T., Jenkins, A., 1995. UK Acid Waters Monitoring Network: The first
463 five years. Analysis and interpretation of results, April 1988 - March 1993. ENSIS Publishing
464 London, pp. 1-320.

465 Rippey, B., 1990. Sediment chemistry and atmospheric contamination. *Philosophical*
466 *Transactions of the Royal Society of London*. B 327, 311-317.

467 Rippey, B., Rose, N., Yang, H., Harrad, S., Robson, M., Travers, S., 2008. An assessment of
468 toxicity in profundal lake sediment due to deposition of heavy metals and persistent organic
469 pollutants from the atmosphere. *Environment International* 34, 345-356.

470 RoTAP, 2012. Review of Transboundary Air Pollution: Acidification, Eutrophication, Ground
471 Level Ozone and Heavy Metals in the UK. Centre for Ecology & Hydrology, p. 292.

472 Stockdale, A., Tipping, E., Fjellheim, A., Garmo, Ø.A., Hildrew, A.G., Lofts, S., Monteith, D.T.,
473 Ormerod, S.J., Shilland, E.M., Recovery of macroinvertebrate species richness in acidified
474 upland waters assessed with a field toxicity model. *Ecological Indicators*.

475 Thompson, J.R., 2012. Modelling the impacts of climate change on upland catchments in
476 southwest Scotland using MIKE SHE and the UKCP09 probabilistic projections. *Hydrology*
477 *Research* 43, 507-530.

478 Tipping, E., Carter, H.T., 2011. Aluminium speciation in streams and lakes of the UK Acid
479 Waters Monitoring Network, modelled with WHAM. *Science of the Total Environment* 409,
480 1550-1558.

481 Woodward, G., Layer, K., 2007. Pattern and process In the Lochnagar food web, in: Rose,
482 N.L. (Ed.), *Lochnagar - The natural history of a mountain lake*. Springer, Dordrecht, pp. 231-
483 252.

484 Wright, R.F., Harriman, R., Henriksen, A., Morrison, B., Caines, L.A., 1980. Acid lakes and
485 streams in the Galloway area, south-western Scotland, in: Drabløs, D., Tollan, A. (Eds.),
486 *Ecological impact of acid precipitation. Proceedings of an international conference,*
487 *Sandefjord, Norway*, pp. 248-249.

488 Yang, H., Flower, R.J., 2012. Effects of light and substrate on the benthic diatoms in an
489 oligotrophic lake: a comparison between natural and artificial substrates. *Journal of*
490 *Phycology* in press.

491

492

493

494

495

496

497

498

499

500

501

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