Effects of broadleaf woodland cover on streamwater chemistry and risk assessments of streamwater acidification in acid-sensitive catchments in the UK

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Abstract

Streamwater was sampled at high flows from 14 catchments with different (0–78%) percentages of broadleaf woodland cover in acid-sensitive areas in the UK to investigate whether woodland cover affects streamwater acidification. Significant positive correlations were found between broadleaf woodland cover and streamwater NO3 and Al concentrations. Streamwater NO3 concentrations exceeded non-marine SO4 in three catchments with broadleaf woodland cover ≥50% indicating that NO3 was the principal excess acidifying ion in the catchments dominated by woodland. Comparison of calculated streamwater critical loads with acid deposition totals showed that 11 of the study catchments were not subject to acidification by acidic deposition. Critical loads were exceeded in three catchments, two of which were due to high NO3 concentrations in drainage from areas with large proportions of broadleaved woodland. The results suggest that the current risk assessment methodology should protect acid-sensitive catchments from potential acidification associated with broadleaf woodland expansion.

Keywords: Broadleaf woodland; Critical loads; Forests & Water Guidelines; Streamwater acidification

1. Introduction

Conifer afforestation has been associated with elevated streamwater acidity and aluminium concentrations (Ormerod et al., 1989) and contributing to the decline or complete loss of fish populations and other freshwater biota in acid-sensitive areas of the UK (Harriman et al., 1987). Forests contribute to surface water acidification in areas of high acid deposition due to the enhanced canopy capture of atmospheric pollutants (the scavenging effect) (Nisbet et al., 1995), especially by dry and occult deposition, as a result of increased turbulent air mixing (Fowler et al., 1989). Another factor is the accumulation and removal of base cations in harvested trees. Areas most affected by acidification have soils with small exchangeable base cation pools which are rapidly depleted in response to acidic deposition, resulting in the acidification of soils and freshwaters. Reducing emissions of acid pollutants has been recognised as the principal way of solving the problem of acidification. In the UK, it is estimated that sulphur (S) and nitrogen (N) emissions declined by 71% and 35%, respectively, between 1986 and 2001, while deposition of non-marine S declined by 60% over the same period (Fowler et al., 2005). Future reductions in S and N emissions have been determined by the Gothenburg Protocol, under the UNECE Convention on Long-Range Transboundary Air Pollution, which aims to facilitate the recovery of acidified terrestrial and aquatic ecosystems.
(Jenkins and Cullen, 2001). In the UK, this will involve reductions from 1990 levels of around 80% in S and 45% and 20% in oxidised and reduced N emissions, respectively, by 2010 (NEGATAP, 2001).

Despite the decline in emissions of acid pollutants and in conifer afforestation in the UK since the 1980s, there is concern that increasing forest cover from the expansion of broadleaf woodlands could delay the recovery of acidified surface waters, or even lead to further acidification, in the most sensitive areas. Planting of broadleaves has gradually increased since the 1970s, with more than 11 000 ha planted in the UK in 2005, as the result of policies and initiatives to restore native broadleaf woodlands and improve the conservation status and habitat value of forested ecosystems (Rollinson, 2000). Although pollutant deposition is less on broadleaf woodland than on the more aerodynamically rough conifer canopies (Robertson et al., 2000), large-scale broadleaf planting schemes may still exert a significant impact on the most acid-sensitive freshwaters where critical loads are likely to remain exceeded (Alexander and Cresser, 1995).

This study aimed to: (1) determine if there is an association between the proportion of broadleaf woodland cover within acid-sensitive catchments and various indicators of water acidification and; (2) assess the effectiveness of the critical loads methodology for identifying catchments at risk of acidification where broadleaf woodland is expanding.

2. Assessing the risk of freshwater acidification using the critical loads methodology

The critical loads methodology is used for assessing and mapping freshwater acid-sensitivity in 24 countries in Europe and North America (UBA, 2004). It has been incorporated into the Forests & Water Guidelines (Forestry Commission, 2003) which describe best practice for minimising the effect of forestry activities on the freshwater environment in the UK. The Guidelines use the provisional critical loads exceedance map for UK freshwaters shown in Fig. 1 to determine freshwater catchments where risk of acidification from the scavenging effect due to new woodland planting or restocking plans in acid-sensitive areas. The map was derived from calculating critical loads with the Steady-State Water Chemistry (SSWC) model (Henriksen et al., 1986) from the chemical analysis of water samples from the most sensitive water body, usually a lake, within each 10 km × 10 km grid square. These were then compared with the modelled atmospheric deposition of non-marine S and N for 1995–1997. When more than 10% of a catchment area is to be planted with conifers or more than 30% with broadleaves within a critical load exceedance square (i.e., in which modelled deposition exceeds the critical load value), or adjacent square, the Guidelines require a site-specific critical load assessment. This involves the chemical analysis of one to three water samples collected from the catchment outlet at high flows, preferably from January to March, when streamwater tends to be more acidic. Where the estimated pollutant deposition exceeds the critical load calculated for the specific catchment, approval of a planting grant or restocking plan is unlikely until pollutant emissions are reduced.

3. Materials and methods

3.1. Catchment selection

Catchments selected for the study lay within acid-sensitive areas of the UK and ranged in percentage cover of broadleaf woodland with no other confounding land uses. Study catchments were identified and characterised using digital spatial datasets in an ArcGIS (ESRI, CA, USA) Geographical Information System (GIS). The critical loads exceedance dataset utilised by the Forests & Water Guidelines (ECRC, 2001, 10 km grid) and the National Inventory of Woodlands and Trees-Interpreted Forest Type (Forestry Commission, 1:25 000) were used to select broadleaf woodland polygons lying within, or adjacent to, a critical load exceedance square. Catchment areas were delineated from digital elevation models (Ordinance Survey/EDINA, Land-Form PROFILE®), 1:10 000 and percentages of broadleaf woodland cover were calculated in each catchment. The underlying geology was determined from a digital 1:625 000 geology map (BGS, 1995) and the proportions of soil types calculated from the digital 1:250 000 National Soil Maps for England and Wales (NSRI, 1984) and for Scotland (MISR, 1981).

3.2. Catchment description

Following field visits, 10 forested catchments representative of acid-sensitive areas throughout the UK were selected in Scotland (Glen Arnisdale, three catchments, and the Loch Katrine area, four catchments) and England (two catchments near Ullswater in north-west England and the Yaner Wood catchment in Devon, south-west England) (Fig. 1). Three control catchments with no woodland cover were also selected, one adjacent to each group of catchments in Glen Arnisdale and the Loch Katrine and Ullswater areas. The control for the Yaner Wood catchment was the nearby (20 km) Narrator Brook catchment, which had only 2% broadleaf woodland cover and is part of the UK Acidic Waters Monitoring Network (AWMN, Evans et al., 2000).

The characteristics of the study catchments are summarised in Table 1 and detailed in Gagkas (2007). Catchment geologies and soils were mainly acid-sensitive. Broadleaf woodland covered from 10.3% to 78.7% of the forested catchments. Woodlands were dominated by open canopy, natural downy birch (Betula pubescens) in the Scottish catchments and by mature, semi-natural alder (Alnus glutinosa) and semi-natural and ancient sessile oak (Quercus petraea) in the Ullswater area and Yaner Wood catchments, respectively. The Scottish control catchments were covered by acid grassland and blanket bog, dominated by ericoid shrubs and grasses in Glen Arnisdale and by purple moor grass (Molinia caerulea) and patches of fen in the Loch Katrine area. The Ullswater area control catchment was covered by wet heath and fen communities and Narrator Brook by acid grassland and blanket bog dominated by Molinia caerulea. Catchments in Glen Arnisdale and the Loch Katrine area had an upland character while those near Ullswater and in Devon had a gentler relief and lower altitudes. Catchment distance from the nearest coast ranged from 2 km (Glen Arnisdale) to 57 km (Loch Katrine area). Mean annual rainfall, calculated from rainfall records spanning 29–37 years, ranged from 1010 mm (Ullswater area) to 2275 mm (Loch Katrine area) (British Atmospheric Data Centre, BADC).

3.3. Streamwater sampling and chemical analysis

Two to 10 streamwater samples were collected at the catchment outlets from January to April 2005 and November 2005 to March 2006 during high flow conditions. All streamwater samples were taken in acid-washed polyethylene bottles and stored in the dark at 4 °C prior to analysis at Edinburgh. Gran alkalinity was determined within 48 h of sample collection by manual titration with 0.01 M HCl from pH 4.5 to 3.5 (Neal, 2001). Ca, Mg, Na and K were determined using a Unicam AA M Series flame atomic absorption spectrometer, Cl and SO4 with a Dionex DX-500 liquid chromatography system and NO3 with a Bran & Luebbe AA3 continuous flow analyser. Al was determined
as total filtrable Al using a Perkin Elmer Optima 5300 inductively coupled plasma-optical emission spectrometer in water samples that had been passed through 0.45 μm cellulose nitrate membrane filters after collection and then acidified with 2 ml of concentrated HNO₃ to minimise loss through adsorption to the bottle and precipitation. Standard laboratory quality assurance measures detailed in Gagkas (2007) provided confidence in the accuracy, precision and reproducibility of the streamwater analyses. Streamwater chemistry data for three samples from Narrator Brook were obtained for January-March 2005 from the AWMN to compare as a control with samples from the Yarner Wood catchment.

3.4. Calculation of critical loads and exceedences

Non-marine solute concentrations were calculated using published seasalt correction factors (UBA, 2004). Streamwater acid neutralising capacity (ANC) was determined in μeq l⁻¹ as the difference between the measured streamwater base cation (Ca, Mg, Na, K) and acid anion (Cl, SO₄, NO₃) concentrations. Critical loads and exceedences were calculated according to the methodology of the Forests & Water Guidelines since this is the risk assessment approach currently used, even though alternative methods and new deposition data are available (UK National Focal Centre, 2004). Mean high flow streamwater chemistry was used in the SSWC model to calculate the critical loads (CL) for each catchment (Eq. (1)). CLs are based on the principle that the acid load to water should not exceed the long-term supply of neutralising base cations in the catchment, represented by the pre-industrial concentration of non-marine base cations ([BC₀*]) derived from weathering minus a critical buffer concentration, as shown in Eq. (1) (Henriksen et al., 1986),

$$ CL = \left( [BC₀^*] - [ANC_{crit}] \right) \cdot Q $$

where ANC_{crit} is the lowest concentration that does not damage selected biota. The Guidelines use a value of ANC_{crit} = 0 μeq l⁻¹, which provides a 50% probability of brown trout (Salmo trutta) populations being protected based
on mean chemistry (UK National Focal Centre, 2004), but is thought to provide complete protection at high flows. Catchment runoff ($Q$), calculated as 85% of the catchment annual rainfall, is used to convert concentrations to fluxes.

CL exceedance was calculated by comparing CL values with the estimated deposition of non-marine S ($S_{dep}$) and N ($N_{dep}$) (Eq. (2)).

\[
\text{Exceedance} = \left( S_{dep} + NO_3 \times Q \right) - CL
\]

N deposition was estimated for each catchment as the mean streamwater NO$_3$–N concentration measured at high flow converted to a flux using rainfall data for 2005 provided by the BADC. Two estimates of non-marine S deposition were used: (a) modelled data for 1995–1997 as recommended by the Forests & Water Guidelines and (b) the most recent (2002) data generated by the FRAME (Fine Resolution Atmospheric Multi-pollutant Exchange) model (Singes et al., 1998).

### 4. Results

#### 4.1. Streamwater chemistry

The streamwater chemistry results for the study catchments are summarised in Table 2. Mean high flow alkalinity in 12 catchments ranged from −35.3 to 41.6 μeq l$^{-1}$, and was 141 μeq l$^{-1}$ in ULCON. Streamwater in these catchments was therefore considered strongly and moderately acidic, respectively, in comparison with Neal’s (2001) definition of waters with alkalinity <200 μeq l$^{-1}$ as acidic. Catchment UL2 had a higher mean streamwater alkalinity (278 μeq l$^{-1}$) and appeared to be well buffered to acidic inputs, perhaps due to local outcrops of more base-rich geology. The acid-sensitive nature of the catchments, with the exception of UL2, is indicated by the negative and small positive mean streamwater ANC values. Mean streamwater concentrations of marine SO$_4$ and non-marine SO$_4$ (tSO$_4$) ranged from 34.4 to 101 μeq l$^{-1}$ and from 10.9 to 72.4 μeq l$^{-1}$, respectively, with the higher concentrations measured in the English catchments. The highest mean streamwater NO$_3$ concentrations were in the three forested English catchments and ranged from 41.4 to 107 μeq l$^{-1}$, with the greatest values in the forested Ullswater catchments (maximum concentration of 179 μeq l$^{-1}$ in UL1). Mean NO$_3$ concentrations were generally lower in the nine Scottish catchments and in the two English control catchments, ranging from 3.40 to 11.4 μeq l$^{-1}$. Mean streamwater AI concentrations were highest in catchment UL1 (3.27 μmol l$^{-1}$), while the lowest concentrations occurred in the Ullswater control catchment and some of the Loch Katrine area catchments. Calculated Na:Cl ratios in streamwater for many of the study catchments were close to the value for seawater of 0.86, indicating that seasalt inputs accounted for most of the Na in winter high flow samples. The maritime influence on streamwater chemistry was greatest in the Glen Arnisdale catchments (Na:Cl ratios in streamwater of 0.63–0.71), and least in LKCON, UL2 and ULCON (Na:Cl ratios in streamwater of 0.97–1.12).

#### 4.2. Effect of broadleaf woodland cover and other catchment characteristics on streamwater chemistry

Relationships between mean streamwater solute concentrations and catchment characteristics (percentage broadleaf.

<table>
<thead>
<tr>
<th>Area</th>
<th>Geology of area</th>
<th>Main soil types</th>
<th>Catchment characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glen Arnisdale, north-west Scotland</td>
<td>Schists and gneisses of the Moine group</td>
<td>Histic podzols, lateritic gleysols</td>
<td>Glen Arnisdale, Glen (GA)</td>
</tr>
<tr>
<td>Loch Katrine, southern Highlands, Scotland</td>
<td>Dalradian schists, grits and shales</td>
<td>Osteinic albic folic soils, leptosols</td>
<td>Loch Katrine, Loch (LK)</td>
</tr>
<tr>
<td>Ullswater, north-west England</td>
<td>Upper Carboniferous sandstones, clays and shales</td>
<td>Histic gleysols, leptosols</td>
<td>Ullswater, Lake (UL)</td>
</tr>
<tr>
<td>Devon, south-west England</td>
<td>Upper Carboniferous sandstones, clays and shales</td>
<td>Histic gleysols, leptosols</td>
<td>Devon, River (YAR)</td>
</tr>
<tr>
<td>Narrator Brook (NAR)</td>
<td>Ordovician slates</td>
<td>Leptosols</td>
<td>Narrator Brook, River (NAR)</td>
</tr>
</tbody>
</table>

Table 1. Characteristics of the study catchments in Glen Arnisdale (GA), Loch Katrine (LK), Ullswater (UL), Yarner Wood (NAR) and Narrator Brook (NAR).
woodland cover and percentage of gleysols and podzols) were investigated using correlation analysis (Spearman’s rank) in streamwater sampled at high flow in the study catchments (Table 3). As expected there were significant positive correlations between mean streamwater Gran alkalinity and Ca and between the marine-derived ions, Na and Cl. The other atmospherically derived ions, Mg and SO₄, were also significantly positively correlated with Na and Cl and all marine-derived ions were significantly negatively correlated with distance from the nearest coast. Gran alkalinity and Al were significantly negatively correlated indicating a greater occurrence of Al in poorly buffered waters. The percentage of gleysols was significantly positively correlated with Ca, Mg and Na. However, this relationship was not significant for non-marine Mg and Na concentrations ($r_s = 0.40, P > 0.05$ and $r_s = -0.27, P < 0.05$, respectively), suggesting that the presence of gleysols in the study catchments provides buffering mainly through release of Ca. Significant negative correlations occurred between the percentage area of podzolic soils in a catchment and Ca, Mg, non-marine Mg ($r_s = -0.51, P < 0.05$) and SO₄ ($r_s = -0.51, P < 0.05$), the latter suggesting SO₄ retention by podzolic soils.

Percentage broadleaf woodland cover was significantly positively correlated with mean streamwater NO₃ (Fig. 2a) and Al concentrations (Fig. 2b). Catchments with percentage broadleaf woodland cover less than 30% had mean streamwater NO₃ concentrations below 11.5 μeq l⁻¹, while the more heavily forested catchments YAR, UL1 and UL2 had the highest NO₃ concentrations. A significant positive correlation ($r_s = 0.82, P < 0.001$) also occurred between percentage broadleaf woodland cover and the nitrate index, the ratio of NO₃ to (xSO₄ + NO₃) when expressed in μeq l⁻¹ (Fig. 2c). The ratio provides an index of the influence of NO₃ on acidification status, assuming that both anions are derived from anthropogenic acid deposition (Curtis et al., 2005). Values above 0.5 indicate that NO₃ has a greater influence than xSO₄ on surface water acidification. Catchments with the highest percentage broadleaf woodland cover, YAR, UL1 and UL2, had the highest ratio values (0.48, 0.56 and 0.57, respectively, calculated as the mean values of water samples). There were no significant correlations between percentage broadleaf woodland cover and mean streamwater CI and SO₄ ($r_s = 0.28$ and $r_s = 0.29$, respectively).

### 4.3. Critical loads and exceedance

CL values ranged from 0.40 to 2.64 keq H ha⁻¹ year⁻¹, showing moderate to high catchment susceptibility to acidification (Fig. 3). Using the modelled S deposition data for 1995–1997 and estimated N deposition, CLs were found to be exceeded in three catchments, NAR, YAR and UL1 by 0.45, 0.81 and 1.74 keq H ha⁻¹ year⁻¹, respectively. NAR remained in the same CL exceedance class as its grid square, while YAR fell into a higher exceedance class and UL1 into the highest exceedance class (>1 keq H ha⁻¹ year⁻¹), despite lying in a not exceeded square (Table 1). CLs were not exceeded in the other catchments by 0.15–1.21 keq H ha⁻¹ year⁻¹. Compared to the provisional critical loads exceedance...
Table 3
Correlation (Spearman’s rank) matrix of r, values of mean streamwater high flow concentrations and selected catchment characteristics for the 14 study catchments

<table>
<thead>
<tr>
<th>Gran alkalinity</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>Cl</th>
<th>SO4</th>
<th>NO3</th>
<th>Al</th>
<th>% woodland cover</th>
<th>% gleysols</th>
<th>% podzols</th>
<th>Distance coast</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gran alkalinity</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.54*</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.15</td>
<td>0.63**</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>−0.13</td>
<td>0.38</td>
<td>0.86***</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>−0.33</td>
<td>0.03</td>
<td>0.63***</td>
<td>0.87***</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>−0.20</td>
<td>0.31</td>
<td>0.79**</td>
<td>0.97***</td>
<td>0.86***</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>SO4</td>
<td>0.17</td>
<td>0.41</td>
<td>0.72**</td>
<td>0.53*</td>
<td>0.30</td>
<td>0.52*</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO3</td>
<td>0.15</td>
<td>−0.17</td>
<td>−0.28</td>
<td>−0.44</td>
<td>−0.39</td>
<td>−0.42</td>
<td>0.28</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>−0.53*</td>
<td>−0.35</td>
<td>0.05</td>
<td>0.32</td>
<td>0.48*</td>
<td>0.46*</td>
<td>0.20</td>
<td>0.23</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% woodland cover</td>
<td>−0.07</td>
<td>0.08</td>
<td>0.18</td>
<td>0.25</td>
<td>0.19</td>
<td>0.28</td>
<td>0.29</td>
<td>0.51*</td>
<td>0.64**</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>% gleysols</td>
<td>−0.07</td>
<td>0.74**</td>
<td>0.72**</td>
<td>0.61*</td>
<td>0.38</td>
<td>0.53*</td>
<td>0.44</td>
<td>−0.19</td>
<td>−0.01</td>
<td>0.25</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>% podzols</td>
<td>−0.10</td>
<td>−0.81**</td>
<td>−0.67**</td>
<td>−0.43</td>
<td>−0.18</td>
<td>−0.40</td>
<td>−0.51*</td>
<td>0.10</td>
<td>0.06</td>
<td>−0.20</td>
<td>−0.87***</td>
<td>1.00</td>
</tr>
<tr>
<td>Distance coast</td>
<td>−0.19</td>
<td>−0.23</td>
<td>−0.76**</td>
<td>−0.80**</td>
<td>−0.90***</td>
<td>−0.90***</td>
<td>−0.48*</td>
<td>0.57*</td>
<td>−0.19</td>
<td>−0.05</td>
<td>−0.39</td>
<td>0.29</td>
</tr>
</tbody>
</table>

*P < 0.05, **P < 0.01, ***P < 0.001.

5. Discussion

5.1. Factors controlling streamwater chemistry in the study catchments

There was clear evidence of an effect of broadleaf woodland cover on high flow streamwater chemistry in the study catchments since NO3 and Al concentrations increased with % broadleaf woodland, despite significant variation in soil types and local pollutant deposition climate due to different distances from major pollutant sources. The catchments near Ullswater have been most impacted by acid deposition and lie within areas that received the highest measured deposition rates in the UK of 25 kg non-marine S and 25 kg total N ha−1 year−1 in 1997 (NEGTAP, 2001). On the other hand the remote Glen Arnisdale catchments in north-west Scotland have never experienced large amounts of anthropogenic pollutant deposition and the acid sensitivity of freshwaters in this area is mainly due to the low buffering capacity of soils for acidic inputs (Harriman et al., 2001). The pollution climate in the Loch Katrine area and Devon is intermediate between these two extremes.

Wet S deposition dominated the modelled total non-marine deposition inputs to all the study catchments. This may explain the similar streamwater SO4 and xSO4 concentrations in the forested and unforested catchments in most of the study areas since the scavenging effect of forest canopies mainly enhances dry and occult deposition of pollutants. Streamwater SO4 concentrations in the Devon and Loch Katrine area catchments could also have been influenced by SO4 retention in the Fe- and Al-rich horizons of the dominant podzolic soils (Barton et al., 1999). Streamwater Cl concentrations appeared to be influenced more by distance from the nearest coast than by woodland scavenging in the Glen Arnisdale and Loch Katrine area catchments, where there was no significant difference in Cl concentrations between forested (10–30% cover) and unforested catchments. Only in the two catchments with high percentage woodland cover near Ullswater was there evidence of enhanced Cl capture by the woodland canopy, with mean Cl streamwater concentrations significantly greater than those in the control catchment (P < 0.05, Kruskal–Wallis and non-parametric multiple comparison tests). Streamwater Ca and Mg concentrations appeared to be influenced by soil type and were generally higher in catchments with substantial percentages of gleysols (UL1, UL2 and Glen Arnisdale catchments) indicating possible contributions of Ca-rich water at depth even at high flows (Stevens et al., 1997).

5.2. Nitrate

The association between mean high flow streamwater NO3 concentrations and percentage woodland cover indicated
a “threshold” effect in which concentrations in the three heavily forested catchments (>50% cover) were substantially higher than in catchments with woodland cover below 30%. The high streamwater NO₃ concentrations in catchments YAR, UL1 and UL2 can be attributed to the high local N deposition inputs, enhanced by the scavenging effect of the trees and the type and extent of broadleaf woodland cover, leading to increased soil acidification and N leaching. N deposition remains relatively high in north-west and south-west England due to proximity to pollution sources such as nitrous oxides from industry and transport and ammonia emissions from livestock agriculture. Pollutant scavenging increases with the height and density of the woodland canopy, especially for dry and occult deposition (Nisbet et al., 1995). The higher aerodynamic roughness of the dense oak and alder woodlands in the YAR, UL1 and UL2 catchments is expected to result in greater pollutant scavenging than the more open canopy of the birchwoods in the Glen Arnsdale and Loch Katrine area catchments. Furthermore, the positive association reported between NO₃ in streamwater and forest age in monoculture Sitka spruce plantations in Wales (Stevens et al., 1994) suggests that the mature woodlands in the YAR, UL1 and UL2 catchments may release more NO₃ into streamwater than the birchwoods in the Scottish catchments where succession has probably been arrested due to the harsher climate and grazing by animals. The higher streamwater NO₃ concentrations in catchments UL1 and UL2 may also be influenced by enhanced N leaching resulting from symbiotic N fixation in the alder-dominated woodland (Verburg et al., 2001).

The strong relationship between percentage broadleaf woodland cover and streamwater NO₃ index values indicates the important role of NO₃ in streamwater chemistry in heavily wooded catchments subject to high N deposition. NO₃ is the dominant excess acid anion in streamwater from catchments UL1 and UL2 and almost of equal importance to SO₄ in YAR. Concentrations of reduced and oxidised N in rainfall currently exceed the non-marine S concentration by a factor of two in the UK (NEGTAP, 2001) and it is expected that the relative role of NO₃ in excess anion loads will probably increase in the future as SO₄ concentrations continue to decline. Therefore, it has been suggested that NO₃ leaching could impede the recovery of acidified freshwaters in the UK uplands (Curtis et al., 2005).

5.3. Aluminium

Measured streamwater alkalinity at high flow indicated that all study catchments, apart from UL2, were acid-sensitive as a result of the base-poor, slowly weathering soil parent materials present. If UL2 is excluded from Fig. 2b, due to greater buffering in this catchment, there is an even stronger association between Al and % woodland cover, with $r_s = 0.83$ ($P < 0.001$). The significant positive association between streamwater Al concentrations and percentage woodland cover can be attributed to the enhanced deposition of mainly N on woodland canopies and also NO₃ leaching from mature woodland stands, probably enhanced by the alder woodland in UL1. Both these processes cause Al displacement from the soil ion-exchange complex and subsequent leaching to streamwater. However, the toxicity of the increased Al concentrations in streamwater will depend on how much is present in the inorganic form (Lange et al., 2006).
5.4. CL exceedance

CLs were not exceeded in most of the study catchments by the modelled deposition inputs for both 1995–1997 and 2002. Modelled deposition was lower, and consequently non-exceedance of CLs was higher, with the 2002 dataset due to marked reductions in S emission, and subsequent deposition, as a result of international agreements. Long term trends in streamwater $\times$SO$_4$ in AWMN catchments indicate that as levels of atmospherically deposited S have declined, surface water concentrations of $\times$SO$_4$ have fallen accordingly (Davies et al., 2005). However, despite the decline of inland sources of SO$_2$, S emissions from shipping have increased and become a significant contributor to S deposition in western coastal areas, such as south-west England (Fowler et al., 2005). This could help to explain the relatively high $\times$SO$_4$ streamwater concentrations and CL exceedance in the YAR and NAR catchments. Small increases in N deposition have also been reported in western areas, although total N deposition in the UK has remained fairly constant. The high CL exceedance in catchment UL1 was probably due to a combination of low soil buffering capacity and relatively high S and N deposition, possibly coupled with high N leaching to streamwater caused by N fixing by alder. The fact that the UL1 catchment was assessed as highly acid-sensitive, despite lying within a not exceeded square, shows the high variability in freshwater chemistry present within each 10 km $\times$ 10 km critical load exceedance square and the necessity for also conducting streamwater assessments for woodland expansion plans in areas adjacent to exceeded squares, as recommended in the Forests & Water Guidelines. The Loch Katrine area catchments received high S and N loadings, predominantly as wet deposition, but streamwater concentrations of SO$_4$, $\times$SO$_4$ and NO$_3$ were relatively low probably due to dilution by high rainfall amounts and/or SO$_4$ retention by catchment soils. Thus, in these catchments, the calculated CL values exceeded the acid deposition load and positive values of streamwater ANC were maintained (Table 2). Pollutant deposition in the remote Glen Arnisdale catchments was very low and consequently CLs were not exceeded. However, mean high flow streamwater ANC was negative for three of the four catchments (Table 2), mainly due to high excess Cl concentrations arising from seasalt–soil interactions. Non-exceedance of CLs resulted largely from the low calculated non-marine SO$_4$ concentrations, probably due to selective retention of pollutant SO$_4$ in seasalt-conditioned catchment soils (Harriman et al., 1995). The SSWC model is known to have difficulty in dealing satisfactorily with streamwater chemistry influenced by high seasalt inputs, especially during storm events (Battarbee, 1992). The three forested Glen Arnisdale catchments are probably naturally acid-sensitive, with episodic streamwater acidity driven by soil ion-exchange and the release of organic acids during seasalt events, potentially having an adverse impact on freshwater biota (Larssen and Holme, 2006).

6. Conclusions

Broadleaf woodland appears to exert a significant influence on streamwater chemistry in acid-sensitive catchments, mainly due to pollutant scavenging and NO$_3$ leaching, but only when woodland covers a large proportion of the catchment area. Critical loads were not exceeded in most of the study catchments but atmospheric N deposition is of concern in those with very poor buffering and high woodland cover, where NO$_3$ was the principal acidifying ion and contributed to critical load exceedance. Almost all study catchments with woodland cover less than 30% had CL non-exceedance and positive, ANC values at high flows, suggesting that this is a sensible
threshold value for risk assessments of the effects of broadleaf woodland expansion, as recommended by the Forests & Water Guidelines to protect acid-sensitive freshwater biota. However, limitations were identified in the critical loads methodology for assessing the risk of acidification in catchments subject to high seasalt deposition.

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