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Comparison of different critical load approaches for assessing streamwater acid-sensitivity to broadleaf woodland expansion

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Abstract

Due to its potential adverse effects on freshwater acidification, risk assessments of the impacts of forest expansion on surface waters are required. The critical loads methodology is the standard way of assessing these risks and the two most widely used models are the Steady-State Water Chemistry (SSWC) and First-order Acidity Balance (FAB) models. In the UK the recommended risk assessment procedure for assessing the impact of forest expansion on freshwater acidification uses the SSWC model, whilst the FAB model is used for guiding emission policy. This study compared the two models for assessing the sensitivity of streamwater to acidification in 14 catchments with different proportions of broadleaf woodland cover in acid-sensitive areas in the UK. Both models predicted the exceedance of streamwater critical loads in the same catchments, but the magnitudes of exceedance varied due to the different treatment of nitrogen processes. The FAB model failed to account for high nitrogen leaching to streamwater, attributed to nitrogen deposition and/or fixation of nitrogen by alder trees in some study catchments, while both models underestimated the influence of high seasalt deposition. Critical load exceedance in most catchments was not sensitive to the use of different acid neutralising capacity thresholds or runoff estimates, probably due to the large difference between critical load values and acidic deposition loadings. However, the assessments were more sensitive to differences in calculation procedure in catchments where nitrogen deposition was similar to the availability of base cations from weathering and/or where critical load exceedance values were <1 keq H^+ ha^{-1} yr^{-1}. Critical load exceedance values from both models agreed with assessments of acid-sensitivity based on indicator macroinvertebrates sampled from the study catchments. Thus the methodology currently used in the UK appears to be robust for assessing the risk of broadleaf woodland expansion on surface water acidification and ecological status.

Keywords acid-sensitivity; acid neutralising capacity; broadleaf woodland; critical loads; First-order Acidity Balance model; Steady-State Water Chemistry model

1) Introduction

Freshwater acidification resulting from deposition of atmospheric sulphur (S) and nitrogen (N) has resulted in adverse impacts on aquatic ecology worldwide, most notably the depletion of salmonid fish (e.g. Driscoll et al., 2001; Stevens et al., 1997). The impact of freshwater acidification has been extensive in the UK, affecting thousands of km of river length in the 1980s and 1990s, resulting in estimated annual economic losses in fisheries of millions of pounds (Jenkins and Ferrier, 2000). To address these problems international agreements are in place to reduce atmospheric emissions of S and N. The critical load concept has been widely accepted as the basis for the development of air pollution control strategies in Europe (Gregor et al., 2001), and has been used for assessing the sensitivity of freshwaters to acidification in 24 countries in Europe and North America (UBA, 2004). The critical load of acidity for surface waters is “the highest deposition of acidifying compounds that will not cause chemical changes leading to long term harmful effects on ecosystem structure and function” (Nilsson and Grennfelt, 1988) and is calculated as the pre-acidification availability of base cations, estimated from present-day water chemistry, minus a required level of buffering or acid neutralising capacity (ANC) to maintain suitable conditions. An appropriate ANC threshold is selected to maintain acceptable conditions for specified aquatic organisms (usually fish). Surface waters that receive acid deposition greater than the critical load are termed “exceeded” and at risk of biological damage. Although emission reduction has led to significant chemical recovery in previously acidified waters (Davies et al., 2005), biological recovery has been more limited (Monteith et al., 2005). Acidification is still a serious issue in parts of the UK; e.g. 22% of rivers in the Wales/England cross-border Dee River Basin

District are at risk of failing to achieve good ecological status by 2015 due to acidification (Environment Agency, 2008).

Since one of the contributory factors to acidification is forestry, the Forests & Water Guidelines produced by the Forestry Commission (2003) require assessment of the risk of new planting or restocking of existing forests enhancing acidification in acid-sensitive catchments in the UK. The Forestry Commission has adopted the Steady-State Water Chemistry (SSWC) model (Henriksen et al., 1986) to assess freshwater acid-sensitivity, whilst the First-order Acidity Balance (FAB) model (Posch et al., 1997) is used in the UK to calculate freshwater critical loads to guide emission policy (UK National Focal Centre, 2004). The SSWC model was initially developed to address the impact of S deposition and is the simplest such model, requiring water chemistry measurements and annual runoff (usually estimated from annual rainfall since runoff data are rarely available) to calculate critical loads. The FAB model attempts to model explicitly the fate of incoming N deposition and leaching to waters and requires additional catchment data. In the UK different ANC thresholds to protect target sensitive freshwater organisms have been selected. The Forests & Water Guidelines have adopted an ANC threshold of 0 μeq l^{-1} whilst the National Focal Centre normally uses an ANC value of 20 μeq l^{-1}, although 0 μeq l^{-1} is applied if site-specific data suggest that the pre-industrial value was lower (UK National Focal Centre, 2003).

Due to differences in formulation and data requirements, assessments of freshwater acid-sensitivity may be affected by the choice of model and there is a need to examine the robustness of the Forestry Commission approach. This study focused on broadleaf woodland expansion which is encouraged by current policies in the UK but which may still exert a significant impact on the most acid-sensitive freshwaters (Alexander and Cresser, 1995). It compared the suitability of the SSWC and FAB models for assessing surface water acidification within acid-sensitive areas of the UK. The effects on calculated critical loads and exceedance values of different ANC thresholds and runoff estimates were also investigated as the latter reflect changes in catchment water yield related to woodland expansion and are thus particularly relevant to the Forestry Commission approach. Finally, since the purpose of critical load assessments is to protect freshwater ecosystems from acidification, the outputs from both models were compared with the current status of macroinvertebrate populations as an indicator of freshwater acidity status.

2) Materials and methods

2.1) Study catchments

Fourteen study catchments with varying proportions of broadleaf woodland cover and no other confounding land uses were selected from across the main acid-sensitive areas of the UK as defined by falling either within 10 km x 10 km critical load exceedance squares or adjacent squares. Exceedance squares are those in which modelled atmospheric deposition of non-marine S and N for 1995-1997 exceeded the critical load calculated with the SSWC model from the chemical analysis of water samples from the most sensitive water body, usually a lake, within each square (Curtis and Simpson, 2001). Due to the relatively coarse spatial resolution of this approach waters in squares adjacent to those in which critical loads are exceeded are also considered at risk in the Forests & Water Guidelines. The catchments ranged from Glen Arnisdale in north Scotland, Loch Katrine in central Scotland and Ullswater in north-west England to Yarner Wood and Narrator Brook (part of the UK Acid Waters Monitoring Network (AWMN, Evans et al., 2000)) in Devon, south-west England. The catchment characteristics are summarised in Table 1 and detailed in Gagkas (2007). Catchment geologies and soils were predominantly acid-sensitive. Vegetation cover comprised varying proportions of broadleaf woodland, acid grassland, blanket bog and fen communities; arable or improved grassland was not present. 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 to 37 years, ranged from 1010 mm (Ullswater area) to 2275 mm (Loch Katrine area) (British Atmospheric Data Centre, BADC).

Table 1

2.2) Streamwater sampling and chemical analysis

Although riparian zone geology has been shown to be a strong predictor of river water alkalinity in UK upland catchments (Smart et al., 2001), this study took a whole catchment approach to be consistent with the protocol within the Forests & Water Guidelines. Following this, 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 when streamwater is expected to be most acidic. All streamwater samples were collected in acid-washed polyethylene bottles and stored in the dark at 4 °C prior to analysis. Gran alkalinity was determined within 48 hours of sample collection by manual titration with 0.01 M HCl from pH 4.5 to 3.5 (Neal, 2001). Ca^{2+}, Mg^{2+}, Na^+ and K^+ were determined using a Unicam AA M Series flame atomic absorption spectrometer, Cl^- and SO_4^{2-} with a Dionex DX-500 liquid chromatography system and NO_3^- with a Bran & Luebbe AA3 continuous flow analyser. Standard laboratory quality assurance measures detailed in Gagkas (2007) provided confidence in the accuracy, precision and reproducibility of the analyses. Streamwater chemistry data were obtained from the AWMN for three samples collected in January-March 2005 at Narrator Brook. The ANC of each water sample was calculated in μeq l^{-1} as the difference between the sums of base cation (Ca^{2+}, Mg^{2+}, Na^+, K^+) and acid anion (SO_4^{2-}, NO_3^-, Cl^-) concentrations.

2.3) Critical load model calculations

2.3.1) The Steady-State Water Chemistry (SSWC) model

Although other versions of the SSWC model have been proposed (e.g. Henriksen and Posch, 2001), this study used the formulation in Henriksen et al. (1986) which has been adapted for UK conditions in the Forests & Water Guidelines (Forestry Commission, 2003). In the SSWC model the critical load of acidity for surface waters (CL(A), Eq. 1, in keq H^+ ha^{-1} yr^{-1}) is calculated as the difference between $[BC]_0^*$ (the pre-industrial concentration of non-marine base cations) and ANC_{crit} (the critical ANC value) multiplied by Q (the catchment annual runoff).

$$CL(A) = ([BC]_0^* - [ANC_{crit}]).Q \qquad \text{(Equation 1)}$$

$[BC]_0^*$ was estimated (Eq. 2) using measured streamwater chemistry in the study catchments.

$[BC]_0^* = [BC]_t^* - (F \times ([AA]_t^* - [AA]_0^*))$ (Equation 2)

In Eq. 2 [AA] represents the concentration of non-marine strong acid anions (NO_3^-, SO_4^{2-}). F is the fraction of present-day base cation leaching that is due to ion-exchange processes in soils, with lower values indicating acid-sensitivity and higher values well-buffered conditions (UK National Focal Centre, 2004). The superscript * refers to non-marine concentrations, calculated using published seasalt correction factors (UBA, 2004), and subscripts 0 and t refer to pre-industrial and present-day concentrations, respectively. For the UK, data from near-pristine lakes in northern Scotland indicate that pre-industrial concentrations of NO_3^- are close to zero and $[AA]_0^*$ is the pre-industrial concentration of SO_4^{2-} which is empirically related to base cations (Eq. 3).

$[AA]_0^* = (15 + (0.16 \times [BC]_t^*))$ (Equation 3)

The present-day exceedance of critical load, Ex(SSWC), was calculated as

$\mathrm{Ex(SSWC)} = S_{dep} + N_{leach} - \mathrm{CL(A)}$ (Equation 4)

where S_{dep} is estimated non-marine S deposition, generated in this study from the FRAME (Fine Resolution Atmospheric Multi-pollutant Exchange) Lagrangian atmospheric transport model (Singles et al., 1998) for 2002 at a grid resolution of 5 km. The Forests & Water Guidelines recommend the use of modelled S_{dep} for 1995-1997 although these values are higher than the FRAME 2002 data due to marked reductions in S deposition between the two dates (see Gagkas et al., 2008 for comparison of values and discussion). However, since the aim of this study was to compare different models and parameter values the FRAME 2002 data were used in all calculations. N_{leach} was calculated as the product of mean measured streamwater NO_3^- concentration and runoff (Q) at the catchment outlet.

2.3.2) The First-order Acidity Balance (FAB) model

Compared to the SSWC model, the FAB model contains a more detailed formulation of the acid anion budget for the catchment. The total critical load exceedance was calculated using the FAB model (Ex(FAB)) for the study catchments as

$$Ex(FAB) = (S_{dep} + N_{dep}) - (N_{imm} + N_{den}) - AA_{leach} \qquad \text{(Equation 5)}$$

where all units are in equivalents per unit area and time and:

S_{dep} = non-marine S deposition (as in the SSWC model)

N_{dep} = total N (oxidised and reduced) deposition

N_{imm} = long term immobilisation of N in catchment soils

N_{den} = N lost through denitrification in catchment soils

AA_{leach} = acid anion leaching from catchment

Some notations in this paper have been amended from the ones used by Posch et al. (1997) to make them consistent with notations used by the SSWC model. The FAB model terms for retention of N and S in lakes and the removal of N in harvested forest vegetation were omitted from Eq. 5 since the study catchments did not contain lakes and harvesting did not occur. Given a pre-selected ANC_{crit} value for the protection of selected biota, the leaching rate of acid anions (AA_{leach}) in the charge balance equates to the critical acid load to water which will depress ANC below the ANC_{crit} value. Hence AA_{leach} is equivalent to CL(A) calculated with the SSWC model (Eq. 1) using water chemistry data. Values of S_{dep} and N_{dep} were obtained from the FRAME model output for 2002. N_{imm} and N_{den} were estimated by multiplying fixed values for the appropriate soil types (Hall et al., 1998), which are independent of N deposition, by the relative proportion of the catchment covered by each soil type.

2.4) Macroinvertebrate sampling and analysis

To compare the critical load exceedance results with the freshwater ecological status, one to three macroinvertebrate samples were collected using a net and 3-minute kick sampling from riffle sections of 11 of the study catchments (GA2, GA3, GACON and the Loch Katrine area and the Ullswater area catchments) in low flow conditions in June 2005 (Newman, 2005). GA1 contained insufficient water for sampling. Samples were preserved in 60% alcohol and identified to species level. Macroinvertebrate species counts for five samples taken in NAR on 12 April 2005 were provided by the AWMN. The macroinvertebrate data were used to calculate various indices of acid-sensitivity. Based on the presence/absence of indicator macroinvertebrate families the catchments were allocated using the Rutt model (Rutt et al., 1990) to one of four groups, ranging from non-acidic to acidic. The RA Acid Family Index and combined evidence risk score, both components of the updated risk assessment for acidification in surface freshwaters in England and Wales (Environment Agency, 2007), were also calculated. The former is calculated from the numbers and presence/absence of indicator macroinvertebrate families and indicates the sensitivity to acidification. The combined evidence risk score for acidification is calculated for a waterbody from the RA Acid Family Index, chemical monitoring evidence and modelled CL exceedance.

3) Results

3.1) Streamwater chemistry

The streamwater chemistry results for the study catchments are summarised in Table 2. The low, and sometimes negative, Gran alkalinity and ANC concentrations showed that most of the catchments had a low buffering capacity to strong acidic inputs, apart from UL2 and ULCON which had mean ANC of 250 and 190 μeq l^{-1}, respectively. The highest mean streamwater NO_3^- concentrations were in UL1 and UL2 and have been attributed to nitrate leaching from the alder woodland in these catchments (Gagkas et al., 2008). The high Na^+ and Cl^- concentrations in the Glen Arnisdale catchments are evidence of seasalt inputs from precipitation (there was no influence of road salting on streamwater chemistry in the study catchments). These have probably affected ion-exchange processes in the catchment soils, resulting in particular in the retention of Na^+, leading to the lowest streamwater molar Na:Cl ratios in the study catchments of 0.71-0.76.

Table 2

3.2) Calculation of critical loads and exceedance with the SSWC and FAB models

Selected parameters for calculating streamwater critical loads (CLs) and exceedances for the study catchments using the SSWC and FAB models are given in Table 3.

Runoff was estimated from the most recent available local annual rainfall data from the BADC, assuming that for UK conditions catchment runoff is equivalent to 85% of the annual rainfall (Forests & Water Guidelines, 2003). Present-day streamwater non-marine base cation and acid anion concentrations ($[BC]_t^*$ and $[AA]_t^*$) exceeded estimated pre-industrial values ($[BC]_0^*$ and $[AA]_0^*$) in all the study catchments apart from those in Glen Arnisdale. The low $[AA]_t^*$ in these catchments is attributed to their distance from sources of anthropogenic N and S deposition and also to seasalt deposition which has been shown to condition soils to selectively retain non-marine pollutant SO_4^{2-} (Harriman et al., 1995a). Because of the low $[AA]_t^*$ in the Glen Arnisdale catchments calculated pre-industrial base cation concentrations $[BC]^*_0$ exceeded present day values $[BC]_t^*$ (see Eq. 2). The high $[AA]_t^*$ values in the Ullswater catchments and YAR and NAR are mainly attributed to historical high S_{dep} and N_{dep}, along with possible enhanced pollutant scavenging by woodland canopies and NO_3^- leaching as the result of N fixation by alder trees in UL1 and UL2 (Gagkas et al., 2008).

S_{dep} was highest in the Loch Katrine area and lowest in the Glen Arnisdale catchments. N_{dep} ranged from 0.13 to 1.28 keq H^+ ha^{-1} yr^{-1} and was lowest in the Glen Arnisdale catchments and highest in the Ullswater area catchments. However, the sum of S_{dep} and N_{dep} was similar in most of the catchments and ranged from 1.13 to 1.69 keq H^+ ha^{-1} yr^{-1}, apart from the Glen Arnisdale catchments where it was considerably lower at 0.22 keq H^+ ha^{-1} yr^{-1}. N_{imm} values were similar for most catchments, with the exception of ULCON which had the lowest value due to the high cover of leptosols (or "rankers" - shallow, poorly-developed soils) (Table 1) which have a low capacity for N immobilisation. N_{den} was more variable, with the lowest value occurring again in ULCON, and the highest in UL1 and UL2, resulting from the high % gleysol cover.

Table 3

3.3) Comparison of critical load exceedances calculated with the SSWC and FAB models

Table 4 shows the CL values, calculated for each catchment using critical ANC thresholds (ANC_{crit}) of 0 (CL_0) and 20 μeq l^{-1} (CL_{20}) for the SSWC and FAB models, respectively, and the resulting CL exceedances when compared to 2002 acid deposition inputs. CL_0 ranged from 0.40 to 2.64 keq H^+ ha^{-1} yr^{-1}, indicating moderate to high susceptibility of the study catchments to acidification. Both models showed CL_0 exceedances in the same three catchments (UL1, YAR and NAR), with the remainder protected from acidification. However, the magnitude of CL exceedance (and non-exceedance) for individual catchments differed between the two models. The SSWC CL_0 exceedance values were 0.01, 0.36 and 1.02 keq H^+ ha^{-1} yr^{-1}, compared with FAB model values of 0.46, 0.72 and 0.82 keq H^+ ha^{-1} yr^{-1} for NAR, YAR and UL1, respectively. Hence NAR was considered only marginally exceeded, whilst UL1 was impacted to the greatest extent, despite lying in a not-exceeded CL square (see Table 1).

Table 4

In eight of the study catchments (the Loch Katrine catchments, ULCON, YAR and NAR) the FAB CL_0 exceedance values were higher (less negative) than those derived from the SSWC model, but the opposite occurred for the Glen Arnisdale catchments, UL1 and UL2. Since the same modelled S deposition data were used in both models, these differences must be due to the different treatment of N deposition and calculation of N leaching. In the FAB model N leaching to streamwater (N_{output}) is calculated as the N deposition remaining after N immobilisation and denitrification in the soil. Soil processing of N is not directly considered in the SSWC model and N leaching (N_{leach}) is calculated as the product of measured streamwater NO_3^- concentration and runoff. Fig. 1 shows that the N_{leach} values were lower than N_{output} in the Loch Katrine area catchments and in ULCON, YAR and NAR, resulting in more positive CL_0 exceedance and less negative non-exceedance (more positive alkalinity surplus) values when these were calculated with FAB compared to the SSWC model (Table 4). Conversely, in the Glen Arnisdale catchments, UL1 and UL2, N_{output} was lower than N_{leach} (Fig. 1), explaining why CL_0 exceedance values were lower when calculated using FAB compared to the SSWC model (Table 4). The reasons for the different N leaching behaviour in these catchments are discussed later in section 4.1.

Figure 1

3.4) Sensitivity analysis of calculated critical loads

Table 4 also shows the effect on the CL values and the SSWC and FAB model exceedance values of using a higher ANC_{crit} (20 μeq l^{-1}). Since the CL value calculation includes catchment runoff (see Eq. 1), the differences between the CL_{20} and CL_0 values were smallest in the catchments near Ullswater (0.16 keq H^+ ha^{-1} yr^{-1}) and greatest in the Loch Katrine area catchments (0.48-0.49 keq H^+ ha^{-1} yr^{-1}) which have the lowest and highest annual runoff, respectively (see Table 3). Using an ANC_{crit} of 20 μeq l^{-1} resulted in more positive CL exceedance values for all catchments for both models, as expected. However, use of the higher ANC_{crit} value did not affect the overall pattern of CL exceedance in the study catchments. CLs were exceeded in the same three catchments as previously, NAR, YAR and UL1, by 0.25, 0.21 and 0.16 keq H ha^{-1} yr^{-1} more, respectively, than when an ANC_{crit} of 0 μeq l^{-1} was used.

To investigate the sensitivity of critical loads calculations to different runoff estimates, CL_0 and CL_0 exceedance values were re-calculated for both models (Fig. 2) using runoff estimates derived from the minimum, mean and maximum annual rainfall data available from the BADC for each study catchment. CL_0 values remained exceeded in catchments UL1 and YAR using all three runoff estimates for both models. However, in NAR CL exceedance occurred for all runoff estimates used in the FAB model, but only occurred with the SSWC model when minimum runoff was used. CLs were not exceeded in the remaining study catchments for the three different runoff estimates and for both models. As expected from the SSWC model formulation, increases in runoff produced higher CL_0 and N_{leach} values, resulting in lower exceedance/greater non-exceedance in nearly all of the study catchments. The only exception was UL1, where the SSWC CL exceedance increased with the amount of runoff because $[NO_3^-]$ exceeded the sum of non-marine pre-industrial base cations $[BC]_0^*$ in streamwater (110 vs. 50 μeq l^{-1}). Hence the effect of runoff on CL exceedance calculated for a catchment using the SSWC model depends upon the streamwater chemistry characteristics. CL exceedance increases with increasing runoff if $[NO_3^-] > [BC]_0^*$, but decreases with increasing runoff if $[NO_3^-] < [BC]_0^*$. With the FAB model, higher CL values arising from greater runoff estimates will always result in more negative CL exceedance (more positive alkalinity surplus) values because S and N deposition are estimated directly.

Figure 2

3.5) Comparison of catchment acid-sensitivity assessed from macroinvertebrates with calculated critical load exceedances

The total number of macroinvertebrate taxa found in the study catchments sampled was 72. These included Plecoptera (11 taxa), Ephemeroptera (8 taxa) and Trichoptera (14 taxa). The number of taxa found in individual catchments varied from 8 in UL1 to 41 in GACON (Table 5), and the mean number of taxa per catchment was 21. Taxon abundance excluding Gammarus spp. ranged from 18 in UL1 to 320 in NAR, with a catchment mean of 97. When NAR was excluded, the SSWC CL_0 and FAB CL_{20} exceedance values were significantly negatively correlated with taxon abundance (Spearman's rank correlation, n=11: r=-0.61, P=0.023; and r=-0.65, P=0.016, respectively), indicating that the magnitudes of acid-sensitivity calculated using the two different CL approaches compared here (SSWC CL_0 of the Forestry Commission and FAB CL_{20} of the UK National Focal Centre) were both reflected in the catchment ecological status. The lack of significant correlations when NAR data were included is attributed to the different timings of macroinvertebrate sampling. All catchments were sampled in summer low flow conditions, apart from NAR which was sampled in mid-April, which could have resulted in the observation of higher taxon abundance in NAR.

Table 5

The Rutt model classifications of the study catchments generally agreed with the catchment acid-sensitivity status determined with the CL methodology. Catchments in which CL values were not exceeded - the Loch Katrine area catchments, UL2, GA2 and GACON - were all classified in the non-acidic Groups 1 and 2, with the latter three catchments being in the least acidic Group 1. The exceeded status of UL1 agreed with its position in the most acidic Group 4. There was a poorer match with NAR which was classified as non-acidic even though both SSWC and FAB model calculations showed critical load exceedance. However, the SSWC CL_0 value for NAR was only just positive (0.01 keq H^+ ha^{-1} yr^{-1}) and was not exceeded when mean and maximum runoff estimates were used (see section 3.4). ULCON and GA3 were classified as acidic even though CL values were not exceeded. ULCON appears to be on the threshold of being acid-sensitive since critical load exceedances calculated with the FAB model were only just negative (-0.38 and -0.22 keq H^+ ha^{-1} yr^{-1} for ANC_{crit} of 0 and 20 μeq l^{-1}, respectively). Other evidence supports the classification of GA3 as more acidic than some of the other study catchments; it had considerably lower mean streamwater ANC and Ca concentrations than in the other Glen Arnisdale catchments and also the lowest Acid RA Family Index value (equal with LK1) of all the catchments sampled for macroinvertebrates.

The RA Acid Family Index values were low (≤ 2.0) for all the study catchments indicative of a high biological impact of acidification. The surprisingly high index value of 1.6 for UL1, which was classified as acidic by the Rutt model, is attributed to the low flow conditions at the time of sampling, resulting in a noted clustering of Gammarus in the stream beds of all the Ullswater area catchments. The combined evidence risk scores yielded similar assessments of catchment acid-sensitivity as the CL exceedance values, identifying UL1 and NAR as catchments with a high risk of acidification, UL2 and ULCON as low risk, and the other study catchments sampled for macroinvertebrates as at a moderate risk of acidification.

4) Discussion

4.1) Effect of N processes on assessing catchment acid-sensitivity using the critical load methodology

CLs were exceeded in the same study catchments (UL1, YAR, NAR) when the SSWC and FAB models were used, suggesting that both models were equally effective at identifying water bodies at risk of acidification. However, the magnitudes of CL exceedance differed due to the different treatment of N processes in the two models, which resulted in differences in calculated N leaching for the study catchments from the two models. N leaching estimates were lower for the SSWC model than in the FAB model for ULCON and the Loch Katrine area and Devon catchments, whilst for UL1 and UL2 and the Glen Arnisdale catchments, N leaching estimates for the SSWC model exceeded those for the FAB model. In UL1 and UL2 the high N leaching values calculated using the SSWC model are attributed to the high measured streamwater NO_3^- concentrations which were up to an order of magnitude higher than the other study catchments (see Table 2), probably because of the high % alder woodland cover. Although the presence of nitrogen-fixing alder trees can lead to enhanced NO_3^- leaching and cause soil and eventually streamwater acidification by depletion of base cations through the mobile ion effect, alder is unlikely to form a sizeable proportion of future woodland planting in the UK, which will comprise a mixture of different tree species (Reynolds, 2004). In the Glen Arnisdale catchments the N_{output} values calculated in the FAB model were negative even though very low NO_3^- concentrations (c.3.5 μeq l^{-1}) were measured in streamwater. This was probably because N retention in catchment soils was overestimated due to uncertainties in the default values of denitrification. Improved characterisation of N processes in critical load models, including plant-soil interactions and their effect on N leaching, are likely to be become more important for future assessments of acidification impacts in the UK (Curtis et al., 2005). Nevertheless, the expansion of broadleaf woodland is not expected to pose a significant risk of streamwater acidification in acid-sensitive catchments, unless the woodland cover exceeds about 30% of the catchment area (Gagkas et al., 2008).

4.2) Effect of seasalt deposition on assessing catchment acid-sensitivity using the critical load methodology

Since CL values calculated by both the SSWC and FAB models for the Glen Arnisdale area catchments were highly not exceeded, it was expected that these catchments would have streamwater ANC concentrations above the ANC_{crit} values used of 0 and 20 $\mu eq\ l^{-1}$. However, mean measured streamwater ANC was negative for three of the four catchments, indicating excess acid anion loads in streamwater which were attributed to the high loading of seasalts, resulting in temporary Na retention on soil ion exchange sites as reflected by the low Na:Cl ratios in streamwater. Steady state critical load models are known to have difficulty in dealing satisfactorily with such short term dynamics associated with seasalt events, which are common in north-west Scotland (Battarbee et al., 1992). However, whether this limitation in assessing the acid-sensitivity of catchments affected by seasalt events has an impact on their ecological status is unclear. In the Glen Arnisdale catchments episodic streamwater acidity driven by seasalt events is apparent which may potentially have an adverse impact on freshwater biota (Larssen and Holme, 2006) as demonstrated by the classification of GA3 as acidic by the Rutt model on the basis of its macroinvertebrate community. Nevertheless, studies of salmonid fish densities in north-west Scotland suggest that salmon populations in relatively pristine, acid-sensitive waters subject to heavy seasalt loadings have not been subject to significant acidification (Harriman et al., 1995b). Consequently caution is required when using the CL methodology to assess acid impacts in catchments affected by seasalt events and it has been argued that the methodology should be developed to take account of base cation inputs in seasalt events (Cresser, 2007).

4.3) Comparison of critical load model predictions

The SSWC and FAB models were found to be relatively insensitive to the use of different runoff estimates for the study catchments as the same acid-sensitivity classifications were obtained using mean, minimum and maximum runoff. The exception was NAR whose classification using the SSWC model changed from non-exceeded (alkalinity surplus), when minimum runoff was used, to exceeded when mean and maximum runoff were used. Since woodland establishment is widely associated with decreased catchment water yield (e.g. Van Dijk and Keenan, 2007) the effect of minimum runoff estimates on CL exceedances calculated using different models is of particular interest. The minimum runoff values were all a similar percentage of the mean long term estimated runoff for all the study catchments at 72-77%, apart from YAR where the minimum runoff was 62% of the mean. Plotting the differences between the SSWC and FAB model % exceedances of the CL for each of the study catchments when minimum runoff was used against the differences in % exceedances calculated using mean runoff (Fig. 3a) showed that the differences in the % exceedance of CL calculated using the two models were very similar for minimum and mean runoff in most of the study catchments. The deviation of UL1 and YAR from this pattern is attributed to the high streamwater [NO_3^-] relative to the sum of non-marine pre-industrial base cations in streamwater $[BC]_0^*$ in these catchments (already discussed for UL1 in section 3.4) which means that calculation of critical load exceedance is particularly sensitive to the different treatment of N leaching in the SSWC and FAB models. Therefore it appears that catchment acid-sensitivity assessments from SSWC and FAB models are relatively insensitive to different runoff estimates unless $[NO_3^-] \approx [BC]_0^*$.

Figure 3

The sensitivity analysis of the SSWC and FAB models using different ANC_{crit} values was conducted to evaluate the robustness of the Forestry Commission approach to CL calculations for assessing the effect of forestry on acidification (i.e. SSWC model with ANC_{crit} = 0 μeq l^{-1}) compared to the UK Focal Centre approach (i.e. FAB model with ANC_{crit} = 20 μeq l^{-1}). Although the two different approaches yielded differences in absolute exceedance/non-exceedance values, there was no difference in the acid-sensitivity classification of the study catchments (in Table 4 compare columns for SSWC CL_0 and FAB CL_{20} exceedances), despite the very different treatment of N processes in the two models. However, CL assessments for many of the study catchments were relatively insensitive to different calculation procedures due to the large relative size of the critical loads in relation to the deposition loading (compare values for N_{dep} and S_{dep} in Table 3 with CL_0 and CL_{20} values in Table 4), i.e. there was a sufficient gap between the two loadings to offset differences arising from the calculation procedures. To provide guidance for identifying catchments in which CL values may be sensitive to different calculation procedures, CL exceedance values from the study catchments for the two approaches were plotted against the relevant CL value (Fig. 3b). The very similar linear relationships and x-axis intercepts shown in Fig. 3b for the two approaches suggest that more detailed CL assessments, such as including more site-specific data (Heywood et al., 2007), may be required to determine the likely effects of broadleaf woodland expansion in catchments with CL values <1 keq H^+ ha^{-1} yr^{-1}.

Overall, the Forestry Commission approach appeared to give similar assessments of the effects of broadleaf woodland expansion on streamwater sensitivity to acidification as the UK Focal Centre approach. Although the latter approach yielded higher CL exceedances in this study which used 2002 FRAME-modelled deposition data, calculation of the SSWC exceedances using the higher 1995-97 S deposition data, as recommended in the Forestry Commission approach, will reduce the differences in the absolute exceedance values produced by the two approaches. Furthermore, the agreement between the assessments of catchment acid-sensitivity arising from the macroinvertebrate surveys and the CL exceedances calculated from streamwater chemistry data suggests that the Forestry Commission approach is robust in protecting freshwaters from acidification. However, this agreement may not be occurring because of the “correct” reasons; in particular the representation of N processes in the SSWC model is crude, yet N is becoming an increasingly important driver of acidification.

5) Conclusions

Assessments of the acid-sensitivity of 14 UK catchments using the SSWC and FAB critical models showed consistency in identifying the same catchments as being exceeded, but the magnitude of acid-sensitivity differed due to the different treatment of N leaching to streamwater. Whilst the FAB model tended to estimate greater exceedance of CL values than the SSWC model, the opposite was the case in around 40% of the catchments partly due to failing to account for enhanced N leaching, probably arising from plant-soil interaction associated with alder woodland. Whilst limitations were identified in the critical load methodology for assessing acid-sensitivity in catchments subject to high seasalt deposition and with additional N input from N-fixing tree species, these may have a limited impact on the assessment of ecological status. Apart from for one catchment, there were no changes in assessments of acid impact when a higher ANC critical value or different runoff estimates were used with both models, suggesting that the CL calculations were relatively insensitive to these variables in the study catchments. The critical load assessments of acid impact generally corresponded well with observed ecological status based on indicator macroinvertebrates, suggesting that the CL methodology is effective at identifying aquatic ecosystems at risk of acidification.

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References

Alexander CE, Cresser MS. An assessment of the possible impact of expansion of native woodland cover on the chemistry of Scottish freshwaters. Forest Ecol Manag 1995; 71: 1-27.

Battarbee RW, Allott TEH, Birks HJB, Bull K, Flower RJ, Jenkins A, Hall J, Harriman R, Juggins S, Kreiser A, Ormerod SJ, Patrick ST, Rose NL, Weatherley N. Critical loads and acid deposition for UK freshwaters, Interim report to the DoE from the Critical Loads Advisory Group (CLAG) Freshwaters sub-group, ECRC Research Paper 5. ECRC, University College London, London, 1992.

British Geological Survey. Digital Map of Solid and Quaternary Geology; scale 1:625 000. British Geological Survey, 1995.

Cresser MS. Why critical loads of acidity and N for soils should be based on pollutant effective concentrations rather than deposition fluxes. Water Air Soil Poll Focus 2007; 7: 407-412.

Curtis CJ, Simpson GL. Acidification of freshwaters: the role of nitrogen and the prospects of recovery. Environmental Change Research Centre Report 79. University College London, London, 2001.

Curtis C, Allot T, Hall J, Harriman R, Helliwell R, Hughes M, Kernan M, Reynolds B, Ullyett J. Critical loads of sulphur and nitrogen for freshwaters in Great Britain and assessment of deposition reduction requirements with the First-order Acidity Balance (FAB) model. Hydrol Earth Syst Sci 2000; 4: 125-140.

Curtis CJ, Evans CD, Helliwell RC, Monteith DT. Nitrate leaching as a confounding factor in chemical recovery from acidification in UK upland waters. Environ Pollut 2005; 137: 73-82.

Davies JJL, Jenkins A, Monteith DT, Evans CD, Cooper DM. Trends in surface water chemistry of acidified UK Freshwaters, 1988-2002. Environ Pollut 2005; 137: 27-39.

Driscoll CT, Lawrence GB, Bulger AJ, Butler TJ, Cronan CS, Eagar C, Lambert KF, Likens GE, Stoddard JL, Weathers KC. Acidic deposition in the Northeastern United States: Sources and inputs, ecosystem effects, and management strategies. BioScience 2001; 51: 180-198.

Environment Agency. Technical Method Risk Assessment, Water Category Rivers, Significant Pressure Acidification, River Basin Characterisation 2 Project. Environment Agency, 2007, 15 pp. http://www.environment-agency.gov.uk/static/documents/Research/rbc2_acid_rivers_1909601.pdf (visited May 2009)

Environment Agency. Dee River Basin District Draft Plan. Environment Agency, 2008, 52 pp. http://wfdconsultation.environment-agency.gov.uk/wfdcms/en/Dee/Intro.aspx (visited May 2009)

Evans CD, Monteith DT, Beaumont B, Flower R, Winterbottom J. Site summaries. In: Monteith DT, Evans CD, editors. UK Acid Waters Monitoring Network: 10 Year Report, Analysis and Interpretation of Results, April 1988 - March 1998. ENSIS Publishing, London, 2000, pp. 37-268.

Forestry Commission. National Inventory of Woodlands & Trees - Scotland. Forestry Commission, Edinburgh, 2001, 58 pp.

Forestry Commission. Forests & Water Guidelines, fourth edition. Forestry Commission, Edinburgh, 2003, 66 pp.

Gagkas Z. Effects of Broadleaf Woodland Cover on Streamwater Chemistry and Risk Assessments of Streamwater Acidification in Acid-sensitive Catchments in the

UK, PhD Thesis, The University of Edinburgh, Edinburgh, 2007, 294 pp. (Free access: http://hdl.handle.net/1842/2431)

Gagkas Z, Heal KV, Stuart N, Nisbet, TR. Effects of broadleaf woodland cover on streamwater chemistry and risk assessments of streamwater acidification in acid-sensitive catchments in the UK. Environ Pollut 2008; 154: 232-240.

Gregor H-D, Nagel H-D, Posch M. The UN/ECE International Programme on mapping Critical Loads and Levels. Water Air Soil Poll Focus 2001; 1: 5-19.

Hall J, Bull K, Bradley I, Curtis C, Freer-Smith P, Hornung M, Howard D, Langan S, Loveland P, Reynolds B, Ullyett J, Warr T. Status of UK Critical Loads and Exceedances, Part 1- Critical Loads and Critical Loads Maps. CEH Monks Wood, UK, 1998, 39 pp.

Harriman R, Anderson H, Miller JD. The role of seasalts in enhancing and mitigating surface water acidity. Water Air Soil Poll 1995a; 85: 553-558.

Harriman R, Bridcut EE, Anderson H. The relationship between salmonid fish densities and critical ANC at exceeded and non-exceeded stream sites in Scotland. Water Air Soil Poll 1995b; 85: 2455-2460.

Henriksen A, Posch M. Steady-state models for calculating critical loads of acidity for surface waters. Water Air Soil Poll Focus 2001; 1: 375-398.

Henriksen A, Dickson W, Brakke DF. Estimates of critical loads to freshwaters. In: Nilsson J, editor, Critical Loads for Sulphur and Nitrogen. Nordic Council of Ministers, Copenhagen, Denmark, 1986, pp. 87-120.

Heywood L, Skeffington R, Whitehead P, Reynolds B. Comparison of critical load exceedance and its uncertainty based on national and site-specific data. Water Air Soil Poll Focus 2007; 7: 391-397.

IUSS Working Group WRB. World Reference Base for Soil Resources, second edition, World Soil Resources Reports 103. FAO, Rome, Italy, 2006, 128 pp.

Jenkins A, Ferrier RC. Acidifying atmospheric pollutants. In: D'Arcy BJ, Ellis JB, Ferrier RC, Jenkins A, Dils R, editors. Diffuse Pollution Impacts - The Environmental and Economic Impacts of Diffuse Pollution in the U.K. Terence Dalton Publishers, 2000, pp. 105-111.

Larssen T, Holme J. Afforestation, seasalt episodes and acidification - A paired catchment study in western Norway. Environ Pollut 2006; 139: 440-450.

MISR. Digital Soil Map of Scotland; scale 1:250 000. Macaulay Institute for Soil Research, 1981.

Monteith DT, Hildrew AG, Flower RJ, Raven PJ, Beaumont WRB, Collen P, Kreiser AM, Shilland EM, Winterbottom JH. Biological responses to the chemical recovery of acidified fresh waters in the UK. Environ Pollut 2005; 137: 83-101.

Neal C. Alkalinity measurements within natural waters: towards a standardised approach. Sci Total Environ 2001; 265: 99-113.

Newman K. The Effect of Native Woodlands in Acid-sensitive Catchments on the Ecology of Macroinvertebrates. MSc Thesis, The University of Edinburgh, Edinburgh, 2005, 90 pp.

Nilsson J, Grennfelt P, editors. Critical loads for sulphur and nitrogen, UNECE/Nordic Council workshop report. Nordic Council of Ministers, Copenhagen, 1988, 15 pp.

NSRI. National Soil Map of England and Wales; scale 1: 250 000. National Soil Resources Institute, Cranfield University, 1984.

Posch M, Kämäri J, Forsius M, Wilander A. Exceedance of critical loads for lakes in Finland, Norway and Sweden: reduction requirements for acidifying nitrogen and nitrogen deposition. Environ Manage 1997; 21: 291-304.

Reynolds B. Continuous cover forestry: possible implications for surface water acidification in the UK uplands. Hydrol Earth Syst Sci 2004; 8: 306-313.

Rutt GP, Weatherley NS, Ormerod SJ. Relationships between the physicochemistry and macroinvertebrates of British upland streams: the development of modelling and indicator systems for predicting fauna and detecting acidity. Freshwater Biol 1990; 24: 463-480.

Singles R, Sutton MA, Weston KJ. A multi-layer model to describe the atmospheric transport and deposition of ammonia in Great Britain. Atmos Environ 1998; 32: 393-399.

Smart RP, Soulsby C, Cresser MS, Wade AJ, Townend J, Billett MF, Langan S. Riparian zone influence on stream water chemistry at different spatial scales: a GIS-based modelling approach, an example for the Dee, NE Scotland. Sci Total Environ 2001; 280:173-193.

Stevens PA, Ormerod SJ, Reynolds B. Final Report on the Acid Waters Survey for Wales. Institute of Terrestrial Ecology, Bangor, Gwynedd, UK, 1997.

UBA. Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads & Levels and Air Pollution Effects, Risks and Trends. Umweltbundesant, Berlin, Germany, 2004, 254 pp.

UK National Focal Centre. Status of UK Critical Loads - Critical Loads Methods Data & Maps. CEH Monks Wood, UK, 2003, 77 pp.

UK National Focal Centre. Update to: The Status of UK Critical Loads - Critical Loads Methods Data & Maps. CEH Monks Wood, UK, 2004, 41 pp.

Van Dijk AIJM, Keenan RJ. 2007. Planted forests and water in perspective. Forest Ecol Manage; 251: 1-9.

Figure captions

Fig. 1. Comparison of N output calculated in the FAB model and N leaching calculated in the SSWC model for the study catchments.

Fig. 2. CL_0 and CL_0 exceedance values calculated with the SSWC and FAB models using runoff estimated from (a) minimum, (b) mean and (c) maximum rainfall for each study catchment. Negative values indicate non-exceedance. The numbers beneath the catchment names in each figure are the annual runoff totals (in mm) calculated as 85% of the annual rainfall (data provided by the British Atmospheric Data Centre).

Fig. 3. Analysis of sensitivity of CL exceedances calculated for the study catchments with the SSWC and FAB models using FRAME 2002 deposition data. Each point represents a study catchment. (a) The effect of different runoff estimates: difference between % CL_0 exceedance calculated with the two models using minimum runoff vs. difference calculated using mean runoff. The line shows a 1:1 relationship. (b) The effect of different ANC_{crit} values and approaches: linear regression relationships between CL exceedance and CL values for the study catchments, calculated with the Forestry Commission (i.e. SSWC model with ANC_{crit} = 0 μeq l^{-1}) and the UK Focal Centre (i.e. FAB model with ANC_{crit} = 20 μeq l^{-1}) approaches. Negative values indicate non-exceedance.

Figure 1

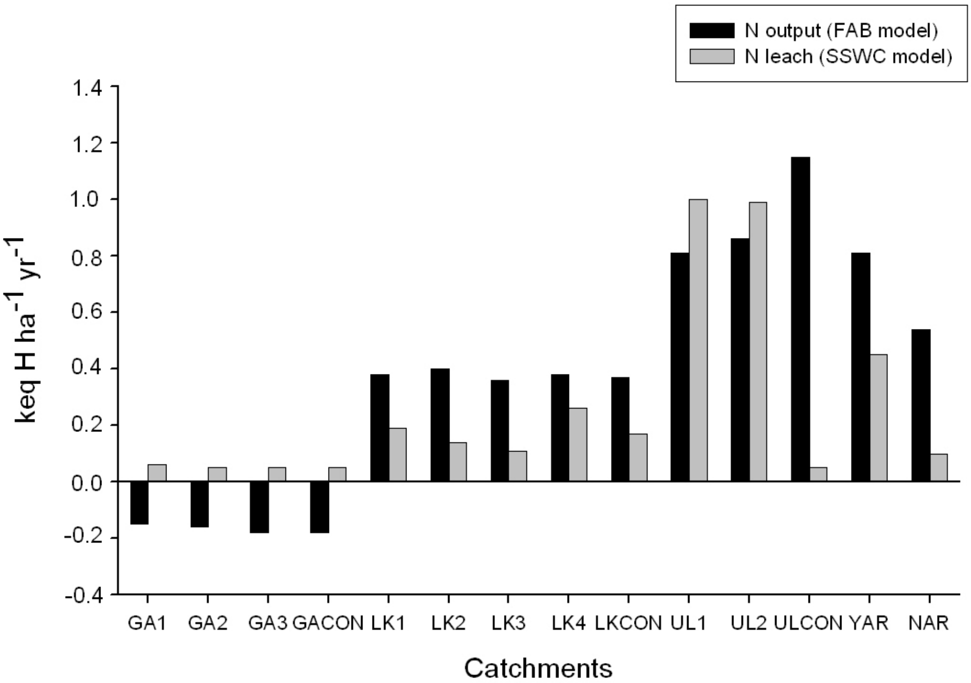

N output (FAB model)
N leach (SSWC model)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
keq H ha-1 yr-1
GA1
GA2
GA3
GACON
LK1
LK2
LK3
LK4
LKCON
UL1
UL2
ULCON
YAR
NAR
Catchments

Figure 2

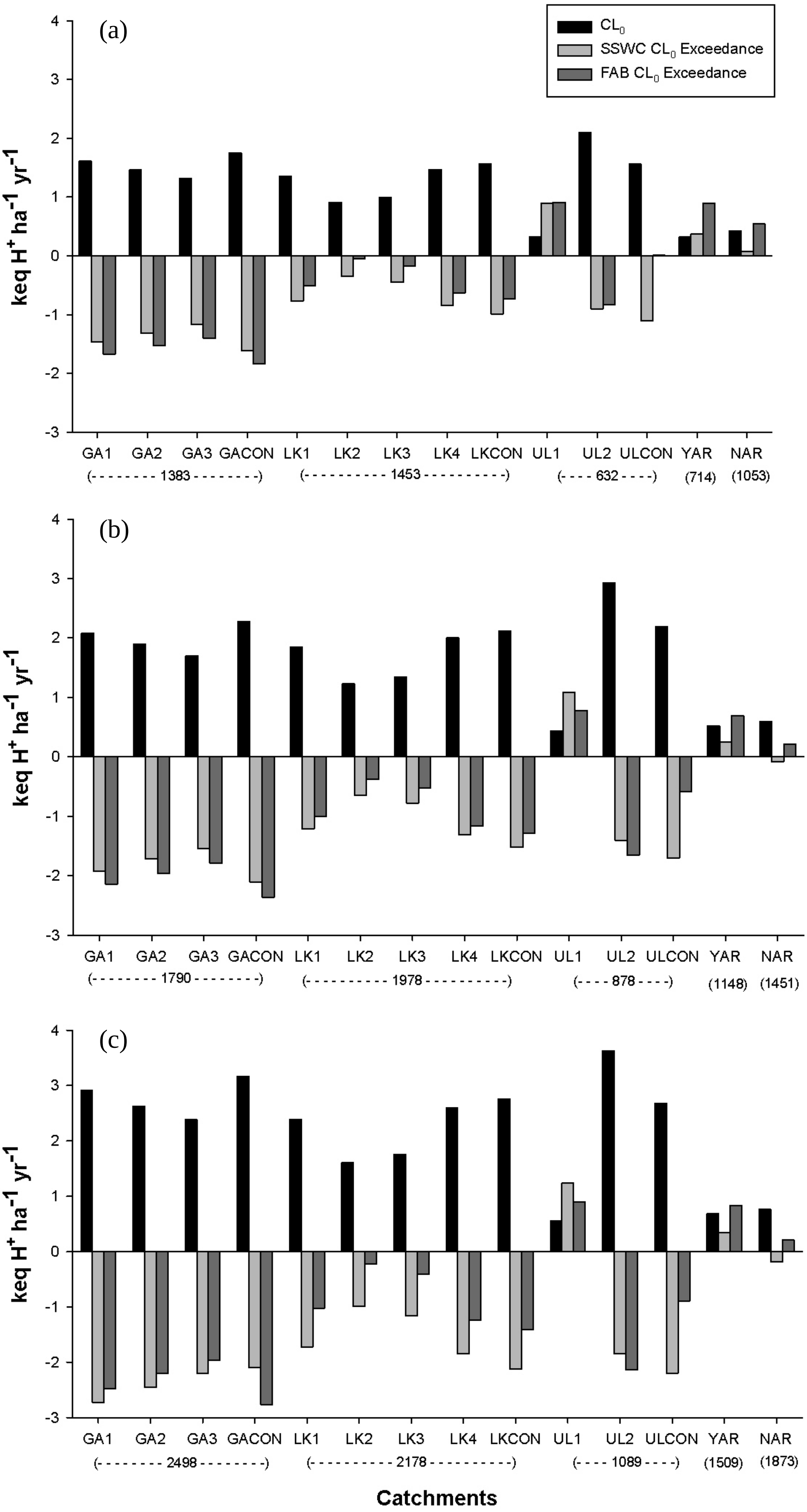
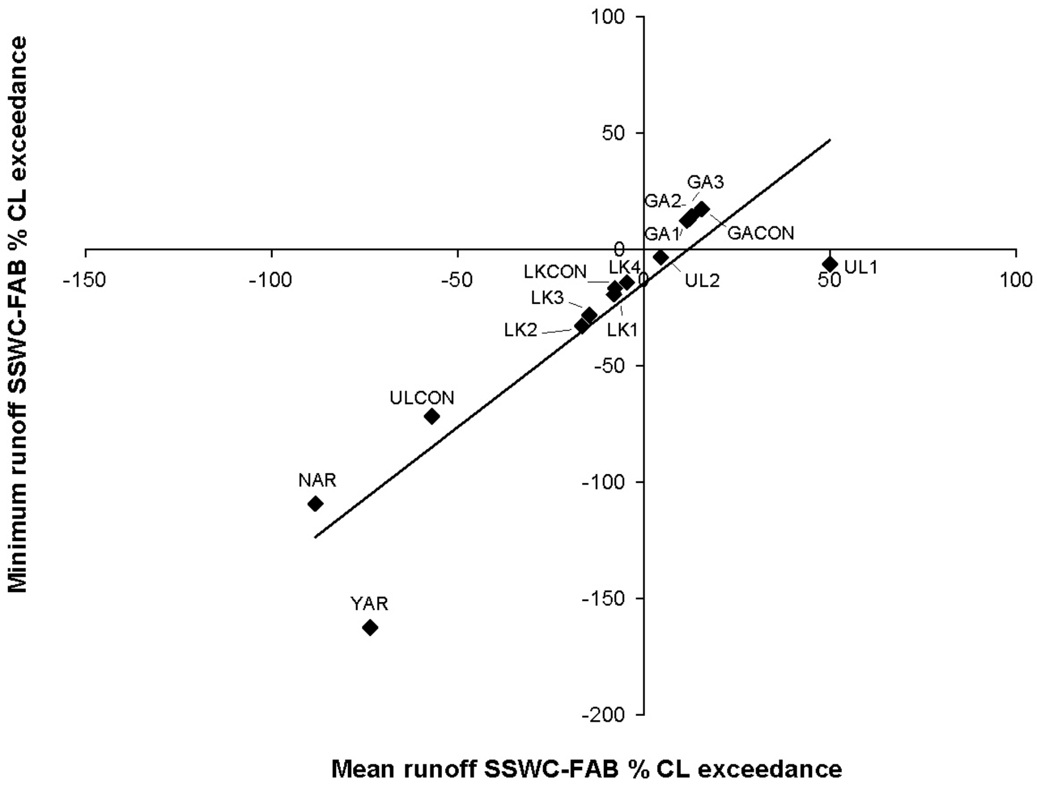

(a)
CL0
SSWC CL0 Exceedance
FAB CL0 Exceedance
keq H+ ha-1 yr-1
GA1 GA2 GA3 GACON LK1 LK2 LK3 LK4 LKCON UL1 UL2 ULCON YAR NAR
(- - - - - - - - 1383 - - - - - - - -) (- - - - - - - - - - 1453 - - - - - - - - - -) (- - - - 632 - - - -) (714) (1053)
(b)
GA1 GA2 GA3 GACON LK1 LK2 LK3 LK4 LKCON UL1 UL2 ULCON YAR NAR
(- - - - - - - - 1790 - - - - - - - -) (- - - - - - - - - - 1978 - - - - - - - - - -) (- - - - 878 - - - -) (1148) (1451)
(c)
GA1 GA2 GA3 GACON LK1 LK2 LK3 LK4 LKCON UL1 UL2 ULCON YAR NAR
(- - - - - - - - 2498 - - - - - - - -) (- - - - - - - - - - 2178 - - - - - - - - - -) (- - - - 1089 - - - -) (1509) (1873)
Catchments

Figure 3

(a)


Minimum runoff SSWC-FAB % CL exceedance
Mean runoff SSWC-FAB % CL exceedance
100
50
0
-50
-100
-150
-200
-150
-100
-50
50
100
GA3
GA2
GACON
GA1
UL1
UL2
LKCON
LK4
LK3
LK2
LK1
ULCON
NAR
YAR

(b)

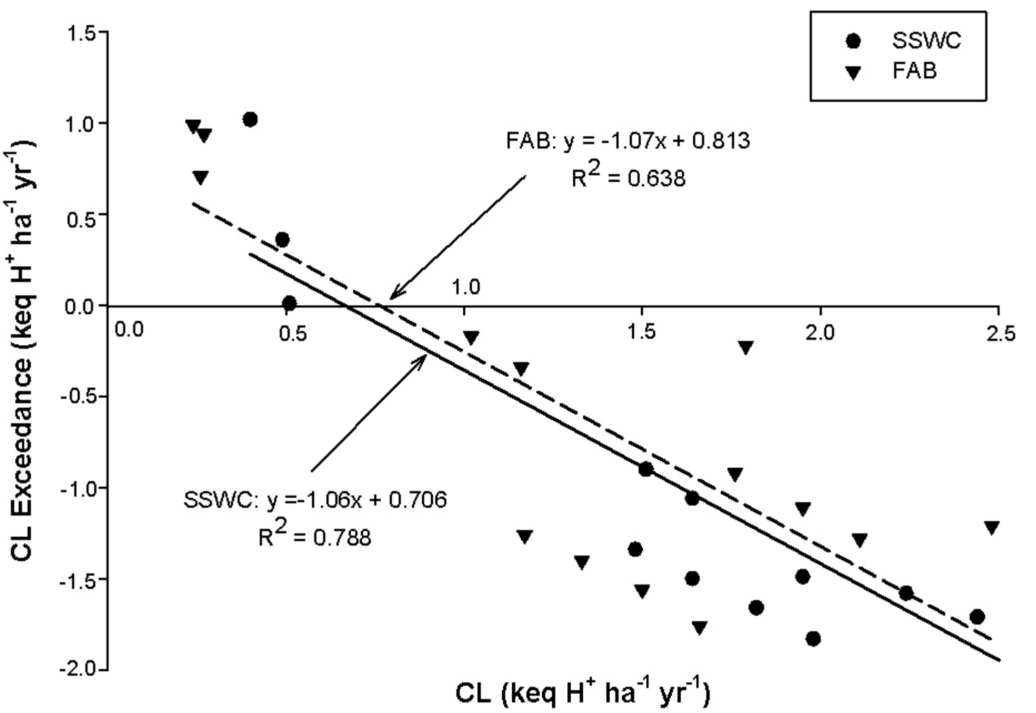

SSWC
FAB
FAB: y = -1.07x + 0.813
R^2 = 0.638
SSWC: y =-1.06x + 0.706
R^2 = 0.788
CL Exceedance (keq H^+ ha^{-1} yr^{-1})
CL (keq H^+ ha^{-1} yr^{-1})
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
0.0
0.5
1.0
1.5
2.0
2.5

Table 1. Characteristics of the study catchments in Glen Arnisdale (GA), Loch Katrine (LK), Ullswater (UL), Yarner Wood (YAR) and Narrator Brook (NAR). Broadleaf woodland cover calculated from Forestry Commission (2001), catchment geology from British Geological Survey (1995) and percentage cover of soil types from NSRI (1984) and MISR (1981). Tree species: downy birch (*Betula pubescens*), alder (*Alnus spp.*), sessile oak (*Quercus petraea*). Main soil types: PZ=podzols, GL=gleysols, LP=leptosols (after IUSS Working Group WRB, 2006). Critical load exceedance is from the 1995-97 dataset for UK freshwaters (see text for explanation).

Area	Geology of area	Main soil types of area	Catchment	Latitude (^{o}N), longitude (^{o}E) of catchment outlet	Land cover	Catchment area (ha)	Mean (min-max) altitude (m)	Mean slope (^{o})	Cover of main soils (%)	Critical load exceedance class (keq H^+ ha^{-1} yr^{-1})
Glen Arnisdale, north-west Scotland	Schists and gneisses of the Moine group	Histic podzols, histic gleysols, sapric histosols	GA1	57.123, -5.506	27% natural downy birch	66.0	444 (84-640)	29	PZ (53) GL (17)	0.0-0.2
			GA2	57.124, -5.516	25% natural downy birch	16.9	428 (53-611)	28	PZ (55) GL (19)	0.0-0.2
			GA3	57.123, -5.516	20% natural downy birch	53.5	338 (40-600)	29	PZ (37) GL (31)	0.0-0.2
			GACON	57.123, -5.528	Acid grassland, blanket bog	35.6	272 (9-489)	26	PZ (33) GL (32)	0.0-0.2
Loch Katrine, southern Highlands, Scotland	Dalradian schists, grits and shales	Osteinic albic folic and histic podzols	LK1	56.272, -4.597	29% natural downy birch	103	412 (128-683)	26	PZ (90) GL (2)	0.5-1.0
			LK2	56.289, -4.626	16% natural downy birch	132	461 (139-763)	23	PZ (81) GL (1)	0.5-1.0
			LK3	56.277, -4.604	20% natural downy birch	20.9	367 (185-556)	24	PZ (93) GL (7)	0.5-1.0
			LK4	56.292, -4.644	10% natural downy birch	39.6	502 (182-726)	26	PZ (89) GL (4)	0.5-1.0
			LKCON	56.284, -4.616	Purple moor grass, fen	47.6	407 (134-681)	24	PZ (91) GL (5)	0.5-1.0

Ullswater, north-west England	Ordovician slates and silicic tuffs	Histic gleysols, leptosols	UL1	54.595, -2.823	54% mature, semi-natural alder	8.56	306 (204-401)	9	GL (100)	Not-exceeded adjacent square
			UL2	54.595, -2.831	79% mature, semi-natural alder	17.0	265 (176-386)	10	GL (97) LP (3)	Not-exceeded adjacent square
			ULCON	54.589, -2.834	Wet heath, fen	8.99	313 (187-462)	22	LP (70) PZ (15) GL (15)	Not-exceeded adjacent square
Devon, south-west England	Upper Carboniferous sandstones and slates	Histic stagnic podzols, haplic dystric cambisols	YAR	49.967, -3.696	50% semi-natural/sessile oak	134	272 (108-411)	11	PZ (100)	0.2-0.5
	Granite		NAR	49.959, -3.979	2% oak woodland; acid grassland, blanket bog	255	366 (255-456)	18	PZ (67) GL (33)	0.2-0.5

Table 2. Summary of streamwater chemistry (to 2 significant figures) in samples collected at high flow in the study catchments. Concentrations ($\mu eq\ l^{-1}$) are mean values with min and max values shown in parentheses. Na:Cl ratios are molar. Catchment acronyms are given in Table 1.

Catchment	No. samples	Alkalinity	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	NO_3^{-}	Na:Cl ratio	ANC
GA1	2	34	120	110	340	18	530	57	3.7	0.73	-17
		(20-48)	(62-170)	(49-160)	(190-480)	(12-23)	(220-850)	(27-87)	(3.4-4.0)	(0.57-0.88)	(-99-66)
GA2	2	8.8	92	130	400	20	560	59	3.4	0.76	10
		(4.1-14)	(44-140)	(52-200)	(220-570)	(14-26)	(260-870)	(28-89)	(3.1-3.7)	(0.66-0.86)	(-23-43)
GA3	2	-13	68	160	430	29	650	64	3.5	0.71	-32
		(-20- -6.2)	(29-110)	(62-250)	(250-610)	(21-37)	(310-990)	(31-98)	(3.4-3.5)	(0.62-0.80)	(-80-15)
GACON	2	24	120	150	470	23	700	71	3.4	0.72	-13
		(18-31)	(57-180)	(60-250)	(240-690)	(16-31)	(290-1100)	(39-100)	(3.2-3.5)	(0.62-0.83)	(-67-41)
LK1	10	42	77	42	120	8.0	140	41	8.8	0.87	61
		(15-98)	(52-93)	(34-48)	(100-140)	(6.1-11)	(95-210)	(31-52)	(4.1-14)	(0.49-1.1)	(-12-87)
LK2	10	-11	44	37	110	6.7	120	34	6.6	0.91	36
		(-45-10)	(29-56)	(29-41)	(96-130)	(4.6-10)	(90-190)	(30-43)	(<0.30-12)	(0.52-1.1)	(-25-56)
LK3	10	2.5	54	37	120	6.9	130	39	5.34	0.90	40
		(-29-26)	(37-69)	(29-42)	(100-150)	(4.6-11)	(91-200)	(30-46)	(<0.30-12)	(0.53-1.1)	(-18-56)
LK4	10	37	79	45	110	6.8	120	41	11	0.90	66
		(17-61)	(57-95)	(36-51)	(95-140)	(5.1-9.0)	(91-190)	(33-50)	(5.5-17)	(0.51-1.1)	(0.41-95)
LKCON	9	32	71	45	110	8.2	120	40	7.1	0.97	75
		(-12-73)	(50-83)	(36-49)	(97-140)	(6.1-12)	(93-150)	(34-45)	(2.2-13)	(0.80-1.1)	(55-93)
UL1	5	-35	84	97	230	17	280	98	110	0.83	-76
		(-65- -1.4)	(57-120)	(77-140)	(190-270)	(11-19)	(190-340)	(76-120)	(12-180)	(0.69-1.1)	(-180--20)
UL2	5	280	250	200	300	13	280	100	110	1.1	250
		(170-380)	(140-350)	(120-300)	(220-360)	(11-15)	(240-310)	(92-120)	(30-170)	(0.86-1.5)	(100-290)
ULCON	5	140	140	110	180	6.2	160	84	5.0	1.3	190
		(120-160)	(130-160)	(69-140)	(130-210)	(0.46-11)	(56-230)	(40-120)	(<0.30-8.4)	(0.92-2.4)	(72-200)
YAR	8	16	42	84	280	17	330	80	41	0.85	-33
		(-34-38)	(26-59)	(58-110)	(250-310)	(15-22)	(280-450)	(72-92)	(32-47)	(0.66-0.96)	(-160-23)
NAR	3	15	31	63	210	18	250	83	7.8	0.84	-19
		(11-22)	(30-32)	(62-66)	(210-210)	(17-18)	(240-260)	(77-94)	(3.6-13)	(0.80-0.86)	(-31-0.99)

Table 3

Parameters for calculating streamwater critical loads (CLs) and exceedances for the study catchments using the SSWC and FAB models: mean high flow concentrations of calculated sums of non-marine pre-industrial base cations $[BC]_0^*$ and acid anions $[AA]_0^*$, non-marine present-day base cations $[BC]_t^*$ and acid anions $[AA]_t^*$, F, runoff (Q) estimated from the most recent available annual rainfall (year given in brackets), N leaching (N_{leach}), non-marine S (S_{dep}) and total N (N_{dep}) deposition generated by FRAME for 2002, catchment N immobilisation (N_{imm}) and denitrification (N_{den}) values. The derivation of parameter values is explained in sections 2.2 and 2.3. Catchment acronyms are given in Table 1.

Catchment	$[BC]_0^*$	$[BC]_t^*$	$[AA]_0^*$	$[AA]_t^*$	F	Runoff	N_{leach}	S_{dep}	N_{dep}	N_{imm}	N_{den}
	μeq l^{-1}				unitless	mm	keq H^+ ha^{-1} yr^{-1}				
GA1	116	106	32	6	0.40	1560 (*2003*)	0.06	0.09	0.13	0.17	0.11
GA2	105	96	30	4	0.37	1560 (*2003*)	0.05	0.09	0.13	0.18	0.11
GA3	95	90	30	16	0.35	1560 (*2003*)	0.05	0.09	0.13	0.17	0.14
GACON	127	119	34	18	0.45	1560 (*2003*)	0.05	0.09	0.13	0.17	0.14
LK1	93	95	30	35	0.36	2420 (*2005*)	0.19	0.47	0.66	0.20	0.08
LK2	62	63	25	28	0.25	2420 (*2005*)	0.14	0.47	0.66	0.19	0.07
LK3	68	69	26	30	0.27	2420 (*2005*)	0.11	0.47	0.66	0.21	0.09
LK4	101	104	32	39	0.40	2420 (*2005*)	0.26	0.47	0.66	0.20	0.08
LKCON	107	108	32	34	0.41	2420 (*2005*)	0.17	0.47	0.66	0.21	0.08

UL1	50	127	35	195	0.48	790 (*2005*)	1.00	0.41	1.28	0.20	0.27
UL2	333	443	85	197	1.00	790 (*2005*)	0.99	0.41	1.28	0.18	0.24
ULCON	246	261	57	74	0.85	790 (*2005*)	0.05	0.41	1.28	0.10	0.03
YAR	45	59	25	87	0.23	1090 (*2005*)	0.45	0.39	1.10	0.21	0.07
NAR	41	49	23	65	0.19	1090 (*2004*)	0.10	0.42	0.90	0.21	0.14

Table 4

CL and CL exceedance values (keq H^+ ha^{-1} yr^{-1}) calculated for each catchment with the SSWC and FAB models using ANC_{crit}= 0 (CL_0) and 20 μeq l^{-1} (CL_{20}). Negative values indicate non-exceedance.

Catchment	CL_0	SSWC CL_0 Exceedance	FAB CL_0 Exceedance	CL_{20}	SSWC CL_{20} Exceedance	FAB CL_{20} Exceedance
GA1	1.82	-1.66	-1.87	1.50	-1.35	-1.56
GA2	1.64	-1.50	-1.71	1.33	-1.18	-1.40
GA3	1.48	-1.34	-1.57	1.17	-1.02	-1.26
GACON	1.98	-1.83	-2.07	1.66	-1.52	-1.76
LK1	2.24	-1.58	-1.40	1.76	-1.10	-0.92
LK2	1.51	-0.90	-0.65	1.02	-0.41	-0.17
LK3	1.64	-1.06	-0.82	1.16	-0.58	-0.34
LK4	2.44	-1.71	-1.60	1.95	-1.23	-1.11
LKCON	2.59	-1.96	-1.76	2.11	-1.47	-1.28
UL1	0.40	1.02	0.82	0.24	1.18	0.99
UL2	2.64	-1.24	-1.36	2.48	-1.08	-1.21
ULCON	1.95	-1.49	-0.38	1.79	-1.33	-0.22
YAR	0.49	0.36	0.72	0.27	0.57	0.94
NAR	0.51	0.01	0.46	0.26	0.26	0.71

Table 5

Macroinvertebrate summary data, Rutt model classification, RA Acid Family Index values and Combined evidence risk scores for the study catchments based on sampling in June 2005, apart from NAR which was sampled by the UKAWMN in April 2005. GA1 and YAR were not sampled. The calculation of the indices is explained in section 2.4.

Catchment	No. samples	Total no. taxa	Taxon abundance (excl. Gammarus spp.)	Rutt model classification	RA Acid Family Index	Combined evidence risk score
GA1	0	---	---	---	---	---
GA2	6	21	145	Group 1 non-acidic	1.0	2 Moderate
GA3	2	14	40	Group 3 acidic	0.8	2 Moderate
GACON	6	41	184	Group 1 non-acidic	1.4	2 Moderate
LK1	3	13	31	Group 2 non-acidic	0.8	2 Moderate
LK2	3	20	76	Group 2 non-acidic	1.0	2 Moderate
LK3	3	24	87	Group 2 non-acidic	1.8	2 Moderate
LK4	3	25	89	Group 2 non-acidic	1.4	2 Moderate
LKCON	3	20	93	Group 2 non-acidic	1.8	2 Moderate
UL1	1	8	18	Group 4 acidic	1.6	1 High
UL2	2	12	35	Group 1 non-acidic	1.6	3 Low
ULCON	1	13	49	Group 3 acidic	2.0	3 Low
YAR	0	---	---	---	---	---
NAR	5	39	320	Group 2 non-acidic	1.0	1 High