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Empirical Critical Loads Modelling for Freshwater Ecosystems

A Report of the Environmental Diagnostics Freshwater Critical Loads Project to the National Power-Powergen-Eastern Generation Joint Environment Programme (contract PA 82932)

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1. Introduction

In the UK various critical load models have been used to derive maps based on the national grid for developing sulphur and nitrogen abatement strategies as required by the UNECE. However many features of the current models and maps are inappropriate for management tool purposes. Freshwaters need to be managed on a catchment, not a grid, basis and management needs to regard the whole biological system, not just target species. Moreover, exceedance calculations at a catchment scale need to be based on deposition fluxes of high spatial resolution, and response models must incorporate the heterogeneous nature of hydrological flows in space and time.

The project addresses these issues. A range of sophisticated numerical techniques have been used to model the relationships between catchment characteristics, flow pathways, water chemistry and biology, with special attention being paid to uncertainty analysis. During this integrated three-year integrated project a new critical loads methodology specifically for the management of catchments of all sizes throughout the UK has been developed. Nine separate research institutions, have been involved each with an international reputation in freshwater acidification and critical loads research. Existing datasets have been used for the most part, with new data generation where appropriate. The project was structured according to a number of inter-related modules addressing key scientific issues.

Module 1: Developing and evaluating a catchment scale approach to critical loads and exceedance predictions

This module attempts (i) to improve the spatial resolution of deposition data and evaluate the uncertainty in applying low resolution deposition data to individual catchments and (ii) to improve predictive models for critical loads.

Work Unit 1A: Improving spatial resolution and evaluating uncertainty in atmospheric deposition inputs

Field studies have been undertaken to provide fine-scale deposition data to examine the spatial variability in wet deposition in an area of complex mountainous terrain. The area selected for experimental study was a 20 x 20 km grid square in western Snowdonia. Work has focussed on a statistical evaluation of uncertainty in critical loads and exceedances calculated using high and low resolution deposition data.

Work Unit 1B: Improving the accuracy and spatial resolution of critical loads predictions using GIS and spatial statistics

The purpose of this work unit was to develop a new, more rigorous, approach to the prediction of freshwater critical loads by exploring i) the use of high resolution data to produce catchment critical loads models and sensitivity maps at a river catchment scale and ii) the use of alternative statistical methods for predicting critical loads from catchment attributes.

Module 2: Interpreting critical loads exceedance in terms of biological status and change

In this module the primary objective is to test the hypothesis that critical loads exceedance is related to biological change or "damage" in a simple dose-response relationship using contemporary (space) and historical (time) data and evaluate factors which could modify the relationship.

Work Unit 2A: Assessing the relationship between exceedance and biological change using contemporary field data

Research here has utilized the Welsh Acid Waters Surveys (WAWS) dataset to evaluate the relationship between critical loads exceedance and biological status and change. The objective is to assess long-term changes between 1984 and 1995 in critical load exceedance and biological status, and identify factors which modify response, including base-cation depletion and land-use.

Work Unit 2B: Validating critical loads exceedances using historical data

Data from c.60 sites with full diatom data and ^{210}Pb dating, distributed across various regions of the UK were used to estimate changes in diatom assemblages since 1850. Assemblage changes were quantified using a diatom-chemistry transfer function to reconstruct changes in lake water acidity. The magnitude of the diatom-floristic changes are quantified in terms of species turnover. These parameters are compared to current critical loads, exceedances and catchment characteristics to assess the degree to which exceedance reflects chemical change and biological damage.

Module 3: Evaluating the influence of episodicity on critical loads assessments

This module seeks (i) to develop and validate dynamic modelling approaches to the assessment of seasonal and episodic response, and (ii) to evaluate the influence of episodicity on biological response to critical loads exceedances.

Work Unit 3A: Dynamic modelling at seasonal and episodic scales.

New critical load assessment methodologies have been developed which realistically incorporate the effects of heterogeneity for catchment-scale impact assessment and associated uncertainty, and represent both seasonal and episodic effects. Several detailed datasets (e.g. Acid Waters Monitoring Network Sites, long-term experimental sites at Plynlimon) have been used for spatial analysis and for model development and validation.

Work Unit 3B: Influence of episodicity on biological response to critical loads exceedances

This work unit addresses the modifying effects of episodicity on biological response to critical loads exceedance using new field data from Scotland and existing data from the WAWS.

SCOPE OF REPORT

The work summarised above is being carried out by the Environmental Diagnostics Freshwater Critical Loads Consortium (ED-FCL) under contract to NERC ('Biological Significance and Uncertainty Analysis of Critical Load Exceedance for Freshwaters at the Catchment Scale' - Contract No. GST/02/1572). The project recieved additional financial support from the National Power-Powergen-Eastern Generation Joint Environment Programme, the Forest Authority and the Scottish Environmental Protection Agency. The final results will be included in a NERC report in July 2000 which will also be made available to the National Power-Powergen-Eastern Generation Joint Environment Programme. This report presents four studies on empirical critical loads modelling undertaken as part of this wider ED-FCL programme:

(i) A reformulation of the steady-state water chemistry (SSWC) model - Curtis *et al.*.

(ii) An exploration of the use of empirical statistical models to predict critical loads using nationally available datasets by Kernan *et al.*. This forms part of Work Unit 1B;

(iii) An preliminary evaluation of lake acidification in Wales by Allott *et al.*, which forms part of Work Unit 2B;

(iv) A stand-alone software application to allow the calculation of critical loads based on the empirical steady state water chemistry (SSWC) and diatom (DCL) models. This software is still being developed and a final version will be available with a final NERC report in July 2000.

2. The link between the exceedance of acidity critical loads for freshwaters, current chemical status and biological damage: a re-interpretation.

Curtis, C.J, Reynolds, B., Allott, T.E.H. and Harriman, R.

Introduction

For several years critical loads have been employed by policymakers to aid in the development of strategies for acid deposition abatement. The most widely used definition of a critical load is that of Nilsson and Grennfelt (1988):

"a quantitative estimate of the loading of one or more pollutants below which significant harmful effects on specified sensitive elements of the environment are not likely to occur according to present knowledge."

Critical loads therefore provide an effects-based approach whereby a pollutant flux (in this case of acid deposition) greater than the critical load (known as critical load exceedance) implies that significant harmful effects on a selected target organism will occur. For freshwater ecosystems, the target organism is often salmonid fish or macroinvertebrates, and the most widely used critical chemical parameter is acid neutralizing capacity (ANC), which has been empirically shown to act as a good indicator of biological damage (Lien *et al.*, 1992). Implicit in this approach are two assumptions: first, the exceedance of a critical load will harm the target organism, and second, the severity of biological impact is related to the magnitude of exceedance.

Critical loads of total acidity for freshwater ecosystems have been defined using various models including the Steady State Water Chemistry (SSWC) model (Henriksen *et al.*, 1992) and the First-order Acidity Balance (FAB) model (Posch *et al.*, 1997). These models provide the national freshwaters critical loads contributions to international protocol negotiations, and were used in negotiations for a multi-pollutant, multi-effect protocol under the UNECE Convention on Long Range Transboundary Air Pollution. The basis of both of these models is the definition of the pre-industrial (assumed to be sustainable) leaching rate of base cations which provides buffering against the adverse effects of acidification. The significance of this term forms the basis of this paper, which aims to describe the relationships between critical load exceedance values calculated with the SSWC model and biological damage. While previous authors have attempted to find links between critical load exceedance and the biological status of water bodies (e.g. Allott *et al.*, 1995; Harriman *et al.*, 1995a; Turnbull *et al.*, 1995) their efforts have been confounded by the disparity between current conditions and the SSWC model output, which is a notional future steady-state condition. A reformulation of the SSWC model is proposed which forms a more direct link with present biological response.

Methods: model description and application

ANC: THE CRITICAL CHEMICAL PARAMETER

The critical chemical parameter ANC is widely used because it has been found in other studies to be the best single indicator of biological response in acid-sensitive systems (Lien *et al.*, 1992) and is relatively simple to model. Logistic regression of species presence/absence data against ANC can provide a quantitative dose-response function which indicates the probability of occurrence of an organism for a given value of ANC (e.g. Figure 2.1; Juggins *et al.*, 1995). For freshwater critical loads in the United Kingdom, a critical chemical value of ANC = 0 μeql^{-1} is used, and is assumed to represent a fifty percent probability of damage to brown trout populations (Lien *et al.*, 1992). The selection of the critical chemical value is an arbitrary decision; a lesser risk of damage to brown trout populations could be chosen by opting for a value of ANC greater than zero. Similarly, a required probability of occurrence could be chosen for any organism for which the dose-response function is known and the corresponding ANC value used to determine critical loads.

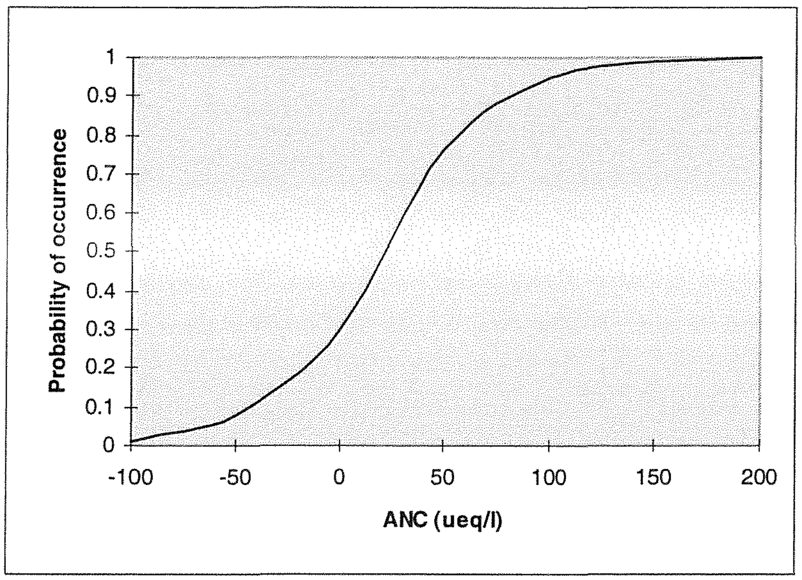

Fig. 2.1: Response curve derived using logistic regression showing the relationship between probability of occurrence of the diatom *Achnanthes minutissima* and ANC. (Redrawn from Juggins *et al.*, 1995).

ANC is operationally defined as the sum of base cations minus the sum of acid anions (Henriksen *et al.*, 1992), but since critical loads relate to acid deposition inputs it is first necessary to quantify and remove the proportion of ions deriving from neutral sea-spray inputs so that the definition of ANC becomes:

$$ANC = [BC]_t^* - [AA]_t^* \qquad \textbf{(Equation 1)}$$

where $[BC]_t^*$ is the current, measured sum of non-marine base cation concentrations (= $Ca^* + Mg^* + K^* + Na^*$) and $[AA]_t^*$ is the sum of non-marine acid anion concentrations (= $SO_4^* + NO_3$). It is assumed that all chloride is derived from marine sources; * denotes the non-marine component whereby the marine contribution of each ion is subtracted as a proportion of measured chloride concentration from the known ratios of these ions in seawater.

THE SSWC MODEL

The equation defining ANC forms the basis of the freshwater modelling approach: empirical relationships are invoked to determine the pre-industrial concentration of base cations ($[BC]_0^*$), and this effectively sets the long term critical load because it represents the only source of base cations over the long term. Given a pre-selected critical ANC value, then the freshwater critical load is simply the input flux of acid anions from atmospheric deposition which gives the critical ANC when subtracted from the pre-industrial flux of base cations (Henriksen *et al.*, 1992):

$$\text{Critical load} = ([BC]_0^* - [ANC_{crit}]).Q \qquad \textbf{(Equation 2)}$$

Concentrations are multiplied by runoff (Q) from the site to convert them into fluxes. The critical load is therefore a critical flux of non-marine acid anions.

Given that the critical ANC concentration is selected on an arbitrary basis to provide the desired level of protection for a target organism, the models have only to provide the pre-industrial flux of base cations from the catchment in order to set the critical load. However, this cannot be done by simply measuring base cation concentrations in runoff because acid deposition actually increases the leaching of base cations through ion-exchange within catchment soils.

It is crucial at this point to distinguish between *weathering* and *leaching* of base cations. Weathering is assumed to be a relatively constant process driven largely by the reaction of CO_2 with primary minerals in the soils and bedrock. It is assumed to be unaffected by acid deposition *per se*, and therefore to provide base cations at a constant rate over a very long time period. Leaching is the removal of base cations in solution from a catchment, which can occur at lesser or greater rates than the weathering supply. Soils contain a "store" of adsorbed base cations (measured as base saturation) which are derived from weathering but have accumulated over millenia throughout the period of soil formation, until eventually a condition of notional "steady-state" was achieved, whereby the supply of base cations from weathering was in approximate equilibrium with the removal of base cations by rainwater, itself in equilibrium with the atmosphere. In pre-industrial times, with atmospheric chemistry relatively unaffected by human activity, it is assumed that soil base saturation had reached a steady state, so that weathering and leaching were balanced and there was no net gain of base cations in the soil.

The effect of acid deposition is to deplete the soil store of base cations through ion-exchange, and the leaching of base cations is therefore elevated. Dynamic models of soil and freshwater acidification using intensive chemical and deposition data, for example the Model of Acidification of Groundwater in Catchments, or MAGIC (Cosby *et al.*, 1985), have been used to illustrate the theoretical change in soil base saturation through time, which may reach steady state with deposition over timescales ranging from decades to more than a century. However, soil base saturation represents a finite store of base cations and so this extra leaching component, which provides additional buffering against the acidification of surface waters over a finite timescale, is excluded from the definition of long term critical load. The critical load is therefore grounded in the concept of "sustainability". According to the assumptions of the SSWC model, under a constant acid load a new steady-state will be achieved, where base cation leaching is in equilibrium with base cation supply. The key to the interpretation of the SSWC model is the concept that when the critical load is exceeded, base cation leaching exceeds supply to the soils and base saturation declines until no more ion-exchange occurs, when base cations are leached at the pre-industrial supply rate.

The SSWC model employs certain assumptions and empirical relationships in order to determine the "permanent" buffering provided by the pre-industrial base cation concentration ($[BC]_0^*$) which is the sum of weathering ($[BC_w]$) supply plus base cation deposition ($[BC^*_{dep}]$) if it is assumed that base cation deposition has not significantly changed since pre-industrial times. The first step is to quantify the proportion of measured base cation leaching which is derived from transient ion-exchange processes (BC_{ex}) and is proportional to the load of acid anions. This proportion is represented in the SSWC model by the term "F", calculated according to the methodology of Brakke *et al.* (1990):

$$F = \sin\left(\frac{\pi}{2}\frac{[BC]_t^*}{S}\right)$$ **(Equation 3)**

where $[BC]_t^*$ is measured non-marine base cation concentration and S is a constant which varies regionally according to geology, but from empirical studies is taken as 400 μeql^{-1} (Harriman and Christie, 1995). This constant determines the measured non-marine base cation concentration which represents a catchment likely to be unaffected by acid deposition; when $[BC]_t^* = S$, F=1 and base cation leaching is increased by exactly the value of the acid anion load, resulting in no change in the ANC of runoff. For values of $[BC]_t^*$ greater than S (400 μeql^{-1}) F is set to 1 (it would otherwise decrease again with $[BC]_t^*$ according to the sine function).

F is then used to calculate the pre-industrial base cation concentration according to the following equation (Henriksen *et al.*, 1992):

$$[BC]_0^* = [BC]_t^* - F([AA]_t^* - [AA]_0^*)$$ **(Equation 4)**

where $[AA]_0^*$ is the pre-acidification concentration of non-marine acid anions from weathering and natural atmospheric sources and the measured leaching rate of non-marine base cations ($[BC]_t^*$) represents the sum of weathering, non-marine deposition and ion-exchange sources (BC_{leach}: Figure 2.2). Data from near-pristine lakes in northern Scotland indicate that "background" concentrations of nitrate are close to zero, while "background" concentrations of sulphate are determined from empirical relationships between base cations and sulphate in near-pristine Scandinavian lakes (see Henriksen *et al.*, 1990, 1992).

Since $[BC]_0^*$ is now known, the critical load can be defined by Equation 2. If the critical load of acid deposition is exceeded, then when BC_{leach} has declined to the concentration $[BC]_0^*$ the ANC of the water body will cross the threshold concentration $[ANC_{crit}]$. The magnitude of critical load exceedance, expressed as a flux of acid anions, provides the theoretical ANC of the water body when BC_{leach} has declined to $[BC]_0^*$ (Figure 2.3). Critical load exceedance for total acidity is calculated from sulphur deposition and nitrate leaching (Kämäri *et al.*, 1992):

$$\text{Exceedance} = S^{*}_{dep} + [NO_3^-].Q - \text{Critical Load} \qquad \textbf{(Equation 5)}$$

where S^{*}_{dep} is non-marine sulphur deposition. Nitrate deposition cannot be treated in the same way because in general, only a small proportion of it is leached into surface waters; most is retained within the terrestrial part of the catchment. Measured nitrate concentration is therefore converted into an exceedance flux (using runoff) to represent the quantity of N deposition which is contributing to exceedance (Kämäri *et al.*, 1992).

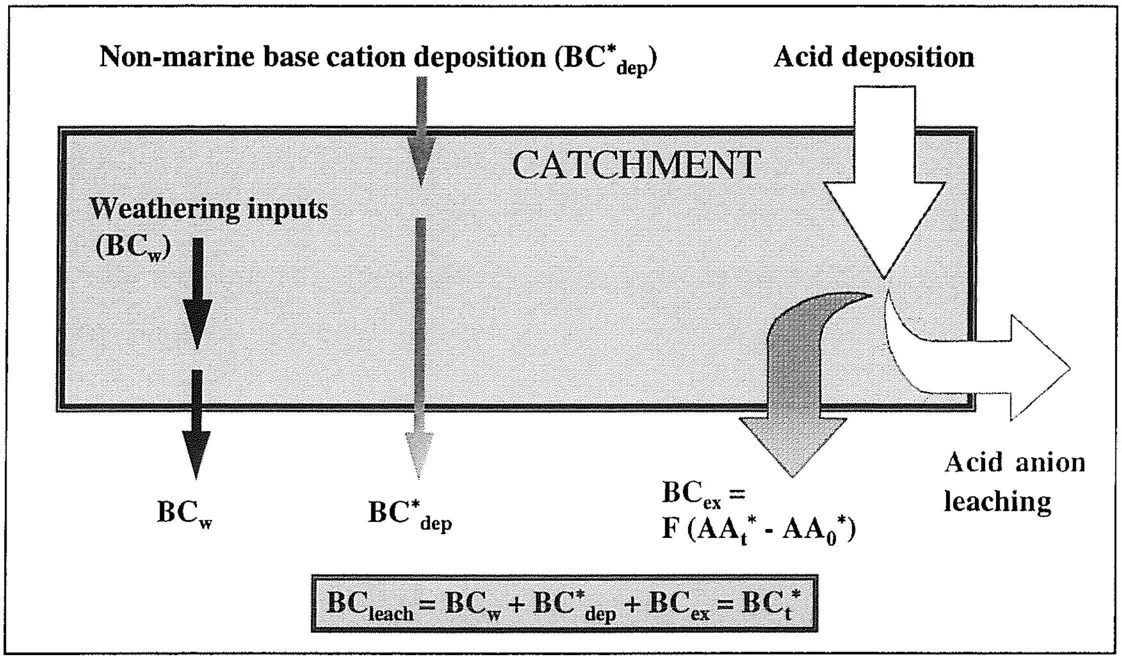

Fig. 2.2: Current (measured) base cation fluxes represented in the SSWC model

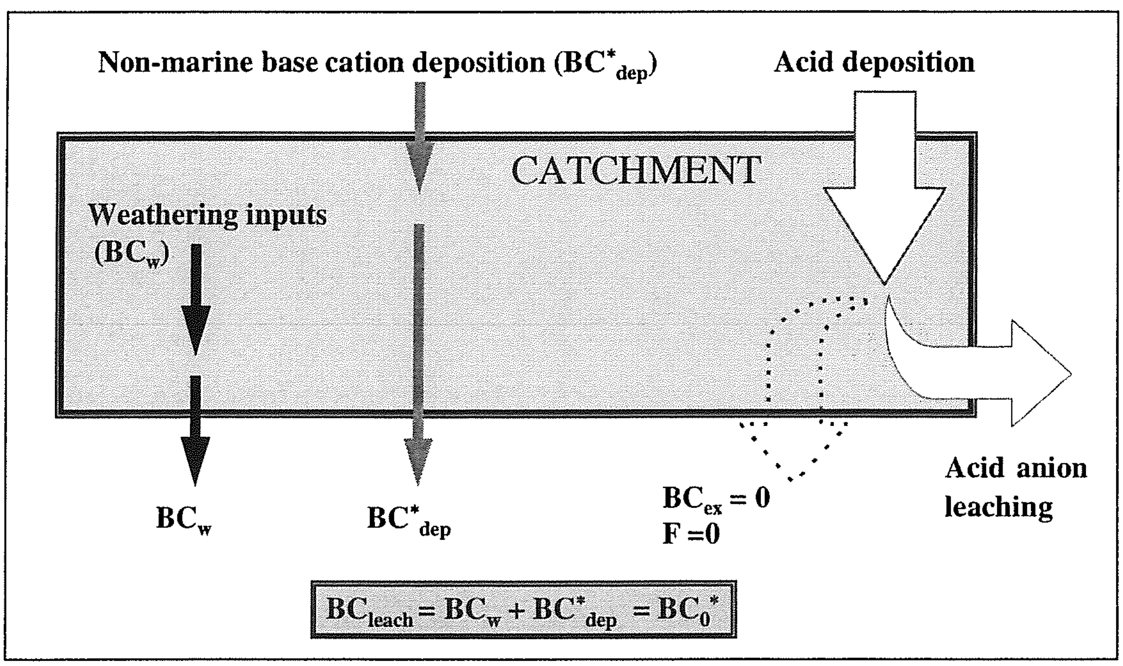

Fig. 2.3: Modelled base cation fluxes under steady-state with acid deposition greater than the critical load (i.e. with exceedance)

The predicted, steady-state ANC concentration ([ANC_{pred}]) for a site experiencing critical load exceedance is given in an analogous way by:

$$[ANC_{pred}] = [BC]_0^* - (S^*_{dep}/Q) - [NO_3^-] \qquad \textbf{(Equation 6)}$$

which is equivalent to the derivation of exceedance (Equation 5) but converts fluxes into concentrations using runoff.

It is therefore possible to provide a prediction of future ANC concentration which could be linked to a predicted biological response. However, critical load exceedance calculated in this way provides no information on the current chemical status of the water body, because current base cation leaching (and hence ANC) is elevated by the ion-exchange reactions in the soil. Measured and predicted ANC values for a national freshwaters dataset in Britain are shown in Figure 2.4. The sites (n=1470) were sampled once for water chemistry during the period 1992-93. Critical loads, exceedances and predicted ANC were calculated using mean runoff and sulphur deposition data for 1992-94 as described above.

The effect of ion-exchange driven increases in base cation leaching under acid deposition load can be clearly seen in Figure 2.4. Measured ANC values (Figure 2.4a) are negative (less than [ANC_{crit}]) at many sites (n=156) and there is a distinct regional pattern overall. In these sites the threshold for biological damage has been exceeded, meaning in this case that the probability of damage to brown trout populations is greater than 50% (see section 1). However, it is not possible to ascertain from measured ANC alone whether the damage is due to acid deposition, because no account has been taken of the deposition load.

The ANC concentration predicted by the SSWC model, which does incorporate the effects of acid deposition, shows a very similar regional pattern to the measured ANC values (Figure 2.4b). Note that a predicted negative value indicates critical load exceedance by definition, since the critical chemical value for ANC was set at zero. There are two very significant features of the predicted ANC values. The first is that the great similarity between the two maps shows that the negative ANC values measured in the field occur at sites where the critical load is exceeded, providing strong evidence that the SSWC model has successfully identified the most vulnerable sites. The second feature is that predicted ANC values are generally lower than measured values, and there is a greater distribution of sites with a predicted negative ANC; 277 compared with 156 measured negative values. These differences are due to the current, enhanced concentrations of base cations which are caused by finite ion-exchange processes and leaching from the soil. As Brodin and Kuylenstierna (1992) pointed out, it may take many decades of an excess of deposition over critical loads before harmful effects occur, so the geographical distribution of critical load exceedance will not necessarily correlate with current damage patterns. However, where high levels of acid deposition have been occurring over a long period as in parts of the UK, some effects are likely to be apparent at the present time, and this is reflected in the similarities between maps of sites with measured negative ANC and predicted negative ANC.

The current biological status of the sampled water bodies is linked to the measured ANC value (Figure 2.4a), while the potential biological status is linked to the predicted value (Figure 2.4b). The discrepancy between the two maps illustrates the problem of trying to link biological effects directly to critical load exceedance. There are 121 more sites where the critical load is exceeded and therefore negative ANC is predicted than there are sites with currently measured negative ANC. In fact at sites with critical load exceedance, there is likely to be a continuous distribution of impacts depending on local factors, from sites where acid deposition has at present caused little change in ANC to sites where severe ANC decline and biological damage have already occurred.

While there is great interest in assessing the current biological effects of acid deposition, it is obvious that the SSWC model in its current formulation is not appropriate for this purpose, because the model output is a prediction of a steady-state condition and does not link deposition directly to current water chemistry. However, it is possible to reformulate the model to provide a direct link between deposition and water chemistry and to quantify a new critical load value which is related to the current chemical status of the water body. Under this reformulation, a critical load exceedance indicates that the critical chemical threshold value is exceeded at the present time.

THE REFORMULATED SSWC MODEL

The SSWC model can be reformulated to take account of the effect of extra leaching of base cations on current water chemistry. The buffering provided by current base cations is the sum of the "background" (pre-industrial) concentration $[BC]_0^*$ (= $[BC_w]+[BC^*_{dep}]$) and the ion-exchange supply $[BC_{ex}]$ (Figure 2.2). While $[BC]_0^*$ is constant, $[BC_{ex}]$ is proportional to acid deposition, and is linked by F.

Substitution of Equation 1 into Equation 4 gives:

$$[BC]_t^* = [BC]_0^* + F([BC]_t^* - [ANC]_t - [AA]_0^*)$$

$$\Rightarrow \quad [BC]_t^* - F.[BC]_t^* = [BC]_0^* - F([ANC]_t + [AA]_0^*)$$

$$\Rightarrow \quad [BC]_t^* = \{[BC]_0^* - F([ANC]_t + [AA]_0^*)\} / (1-F)$$ **(Equation 7)**

Therefore, if we require a critical load for which the critical ANC (ANC_{crit}) is exceeded by the current acid load, then the base cation concentration at critical load $[BC_{crit}]$ is given by:

$$[BC_{crit}] = \{[BC]_0^* - F([ANC_{crit}]+ [AA]_0^*)\} / (1-F)$$ **(Equation 8)**

The reformulated critical load substitutes $[BC_{crit}]$ into Equation 2 in place of $[BC]_0^*$ and becomes:

$$\text{Critical Load} = ([BC_{crit}] - [ANC_{crit}]).Q$$ **(Equation 9)**

Therefore when F = 0 (no soil acidification, all freshwater acidification):

$$C.L. = ([BC]_0^* - [ANC_{crit}]).Q$$ **(Equation 10)**

which is the original SSWC equation, and when F approaches 1 (only soil acidification, no freshwater acidification), the reformulated critical load approaches infinity because of the division by zero in Equations 8 and 9. In either case, exceedance is calculated as for the standard SSWC model (Equation 5).

The derivation for the reformulated critical load, which can be considered the "current damage" critical load, uses a similar approach to that employed by Shaffer *et al.* (1991) and described in Holdren *et al.* (1993), although these authors were comparing different critical loads models for sulphur rather than looking at the immediate effects of total acidity.

The "current damage" critical load will now provide the load of acid deposition which will cause ANC to fall to the critical value, so that if it is exceeded, measured ANC should be less than the critical value. This can be tested by a large scale application of the model.

Results and discussion

Critical load exceedance maps generated with the standard and "current damage" SSWC models are presented in Figure 2.5. The standard exceedance map (Figure 2.5a) shows a greater distribution of exceeded sites (n=277, Figure 2.5a) than the "current damage" exceedance map (n=190, Figure 2.5b), and at sites which are exceeded according to both models, the standard SSWC model generates a greater exceedance value as would be expected, since it represents the exceedance when base cation leaching has declined from present values to pre-industrial levels.

Since the exceedance maps use sulphur deposition data at a 20km grid scale to determine the theoretical sulphate concentration in the surface water (CLAG Freshwaters, 1995), uncertainties are introduced into the comparison with measured data. The "current damage" exceedance map (Figure 2.5b) does however match closely with the map of sites with negative measured ANC values (Figure 2.4a), which demonstrates that the model reformulation is reproducing current conditions reasonably well.

Another measure of the success of the "current damage" model in identifying sites where the critical ANC threshold (0 μeql^{-1}) has been crossed is provided by maps of sites with positive measured ANC values but which show critical load exceedance (Figure 2.6). With the standard SSWC model, exceedance does not necessarily mean that ANC is already negative, and Figure 2.6a does indeed show that a large proportion of exceeded sites (n=130, or 47% of exceeded sites) still have a positive ANC. At these sites, enhanced base cation leaching rates are still sufficiently high to maintain a positive ANC, but both will in theory decline over time until steady-state is achieved and ANC reaches the negative values in Figure 2.4b. Using the "current damage" model, there are very few sites with both a critical load exceedance and positive ANC (n=63, or 33%) except in Western Scotland and the northernmost islands (the Shetlands). In these regions, high levels of marine inputs are known to affect critical load calculations due to ion exchange displacement effects (Harriman *et al.*, 1995b), which might explain the spurious "current damage" exceedances modelled.

The reformulation of the SSWC model can be applied with any selected value for ANC_{crit}. In the above examples, a critical ANC value of 0 μeql^{-1} was used, but a similar outcome is obtained with a more stringent value. For example, using ANC_{crit} = 20 μeql^{-1} (which represents a probability of damage to brown trout populations of c.15%; Lien *et al.*, 1992) the standard SSWC model indicates that 390 of the 1470

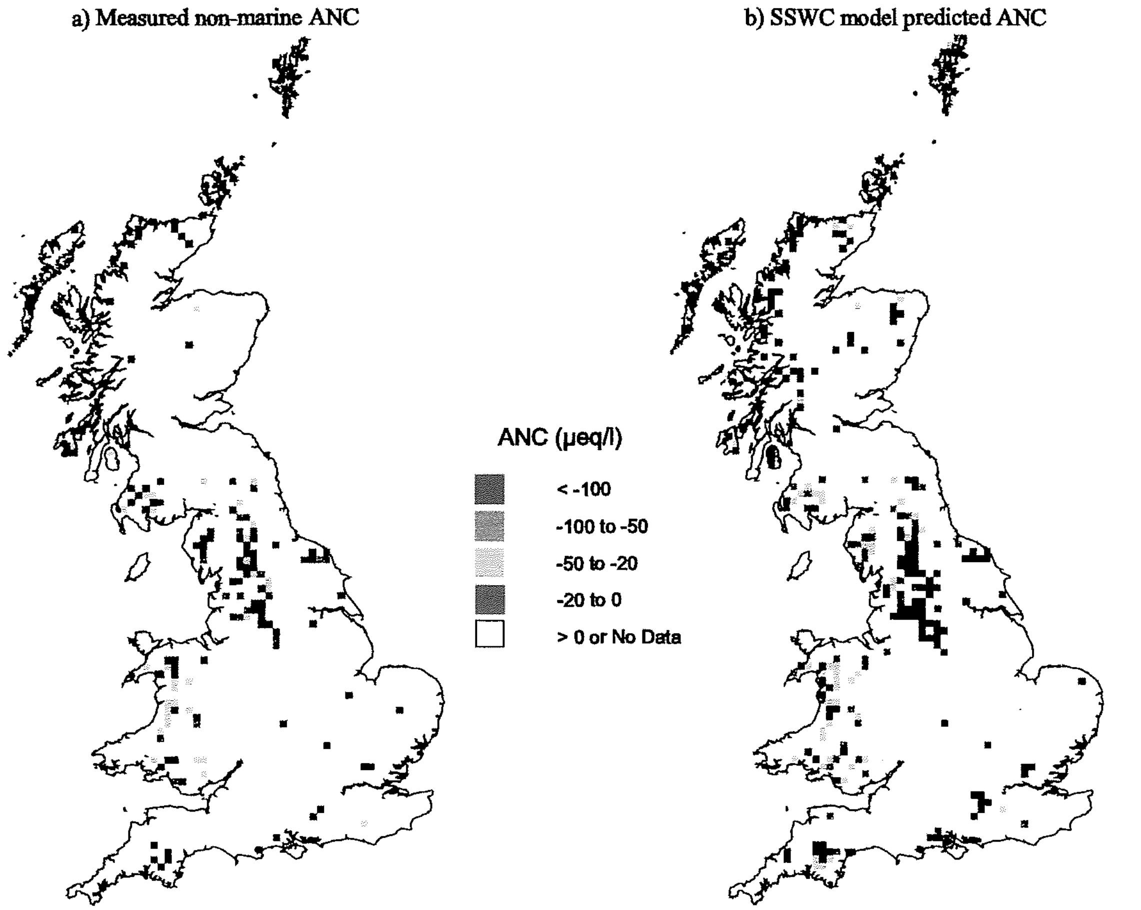

Fig 2.4: Measured and SSWC modelled ANC concentrations in the British freshwaters mapping dataset.

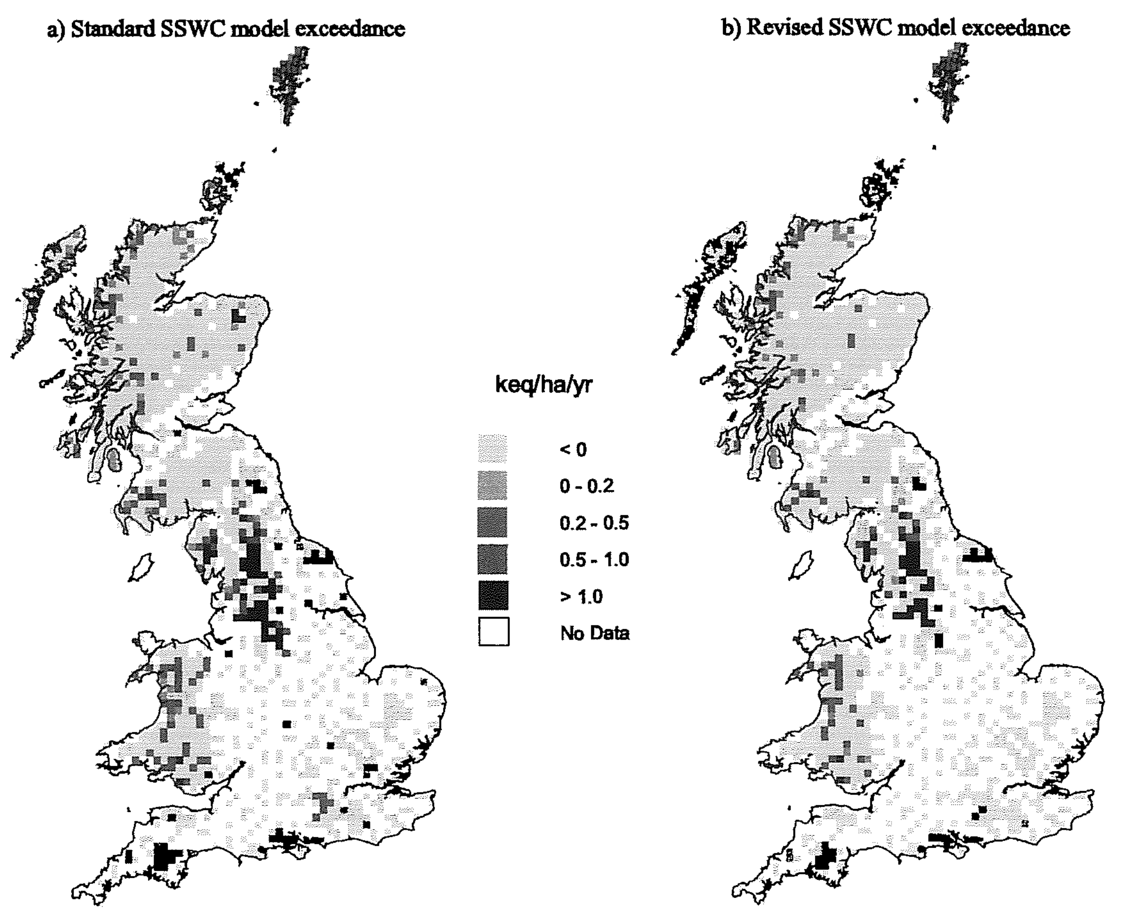

Fig 2.5: Critical load exceedance maps using standard and "current damage" SSWC models.

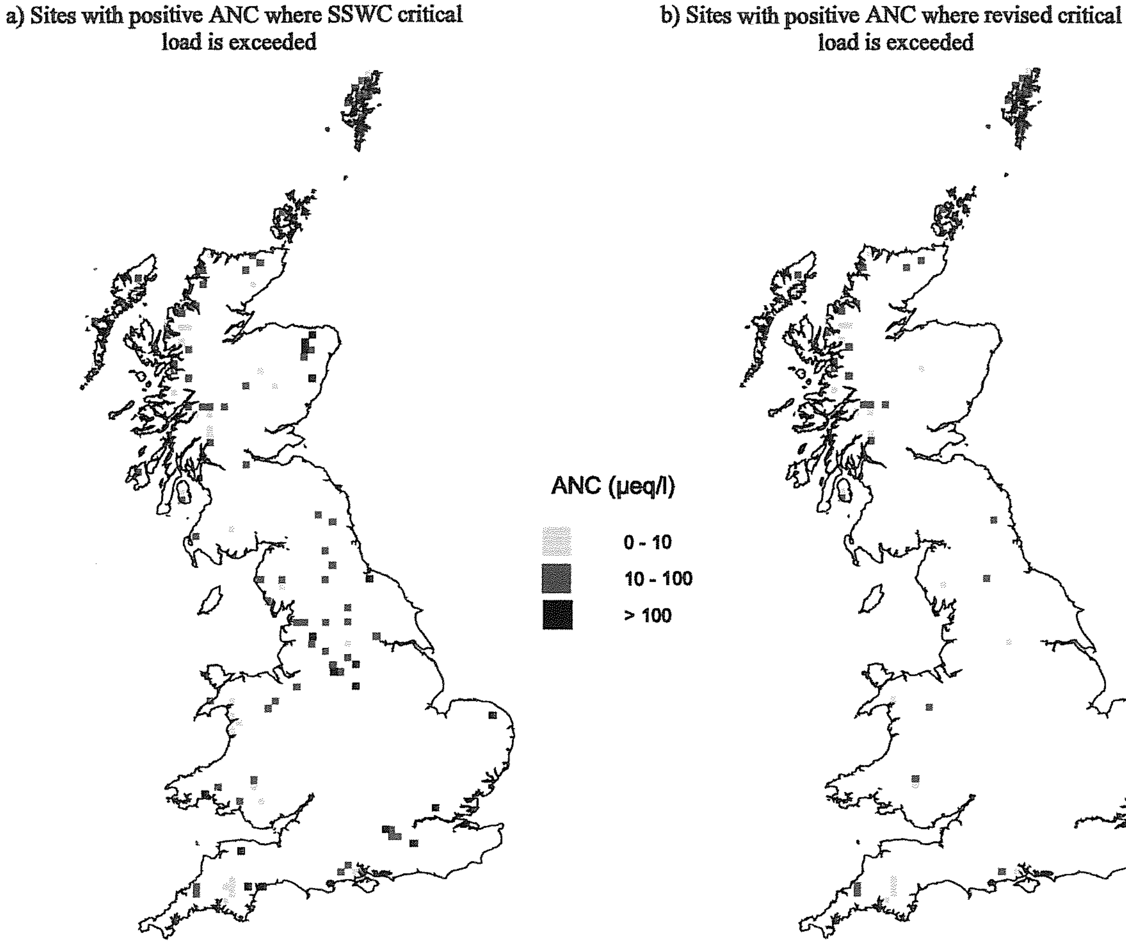

Fig 2.6: Sites with critical loads exceedance according to standard and revised SSWC model applications for which measured ANC is greater than $[ANC_{crit}]$ (i.e. > 0 μeql^{-1})

British sites exceed their critical loads, while 281 are already exceeding the critical chemical threshold according to the "current damage" formulation.

The problem of attempting to link biological status to critical load exceedance using the standard SSWC model is illustrated in Figures 2.4 and 2.6a. While most sites with negative measured ANC values do also show critical load exceedance, predicted ANC is often lower than measured (Figure 2.4). Furthermore, almost half of exceeded sites still have a positive ANC value. It is therefore highly unlikely that any close correlation between biological status and critical load exceedance would be found in Great Britain. The "current damage" version of the SSWC model should provide a much greater indication of the current biological impact of acid deposition, since it is more closely related to measured chemical conditions. Unfortunately the biological data are currently lacking at this national scale, but future work will aim to test model performance in this respect. Of course there are many other potential confounding factors related to the unknown distributions of target organisms and historical changes which might have occurred, especially given the decline in acid deposition in the UK over the last 20 years (RGAR, 1997).

Conclusions

The potential for the standard SSWC model to predict future, steady-state ANC concentrations has been demonstrated, and this could in turn be used to generate predictions of biological response if the relationships between ANC and biology are known (e.g. via logistic regression of presence/absence data against measured ANC, see Figure 2.1). However, attempts to quantify the current biological effects of acid deposition expressed as critical load exceedance are confounded by the lack of a steady-state between acid deposition and water chemistry at many British freshwater sites. The discrepancy between current conditions and predicted conditions is a function of "F" (see Equation 8). Since the SSWC model does not attempt to describe current chemical conditions, there is no reason to expect a strong relationship between critical load exceedance and measured biological damage unless "F" is very small.

While measured water chemistry can be used to predict biological status from known chemical-biological relationships, it cannot directly be used to determine where acid deposition is responsible for biological damage. The "current damage" version of the SSWC model presented here provides this theoretical link between contemporary acid deposition, surface water chemistry and biological response. It serves to test the assumptions regarding base cation exchange which are central to the SSWC model, and further work is now required in this area.

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3. Predicting freshwater critical loads from catchment characteristics using national datasets

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Introduction

Maps of critical loads of freshwater acidity provide a guide to the spatial distribution of acid sensitive lakes and streams across the UK (CLAG Freshwaters, 1995). These are presented on a 10 km grid with a single spot sample defining the critical load for that grid square (Kreiser *et al.*, 1993). The aim was to sample the most acid sensitive site within each square so that, theoretically, these were maps of the lowest freshwater critical load in each square. As such, they do not provide any information about the spatial variability of the surface water critical loads within the square (Curtis *et al.*, 1995). The calculation of freshwater critical loads requires the water chemistry of the lake or stream of interest to be determined. However, water chemistry data are not readily available for all surface waters and where the sensitivity of a large number of catchments across a wide geographical area needs to be assessed, the water sampling programmes required to generate the appropriate critical loads data can be expensive and logistically difficult. An alternative means of characterising the sensitivity of sites for which no (or limited) water chemistry data exist would provide scope for undertaking extensive, catchment based critical loads assessments without undertaking costly field surveys. This would also enable regional and national assessments of the sensitivity and stock at risk of populations of lakes to be made.

The various catchment mechanisms and attributes influencing the sensitivity of surface waters to acidification are well documented (e.g. Reuss and Johnson, 1986; Hornung *et al.*, 1990; Sverdrup *et al.*, 1992) and include the nature of soils, geology, hydrology, land use and precipitation. These do not act independently but form part of a highly integrated system, which can exacerbate or ameliorate the impact of acid deposition on surface waters. All these potentially important factors are mapped, at varying resolutions, with comprehensive coverage across the whole of Great Britain.

Previous attempts have been made, based on the relationships between catchment attributes and surface water chemistry, to identify where acid waters may occur at regional and national levels (Edmunds and Kinniburgh, 1986; UKAWRG 1988; Langan and Wilson 1992, Hornung *et al.*, 1995). From these analyses, maps of potentially sensitive areas were produced. These did not focus on individual catchments.

At the catchment scale, other studies have related surface water chemistry to soil (Rees *et al.*, 1989) geology (Duarte and Kalff, 1989) and land use (Hunsaker *et al.*, 1991) separately, or using an integrated approach (Lynch and Dise, 1985; Kernan *et al.*, 1998). This work has been undertaken at a variety of spatial scales, using data at different spatial resolutions and the response of surface waters has been characterised using a variety of water quality indicators. Previous attempts to relate critical loads to catchment characteristics at a national scale have used national sensitivity maps to predict critical load class (Hall *et al.*, 1995) or explain variation in critical loads (Kernan, 1995; Kernan *et al.*, 1998). This paper explores the potential for predicting critical loads for individual catchments across the whole of Great Britain using a wide range of variables representing catchment attributes, all available at the national scale. Initially a global model is developed (i.e. one that is applied to all sites across Great Britain). However, the nature of the relationships between explanatory and response variables can vary across attribute and geographic space. To assess the performance of the model when reduced environmental gradients are considered, the 'global' model developed for all sites is applied to sites at higher altitude and to sites with little or no arable land. To examine whether these relationships vary spatially the model is applied on a regional basis. This enables between region comparisons of the predictive potential of the model to be made. Following this comparison, individual models are developed both for the environmental and regional sub-sets to examine how model performance is affected when gradient- or region-specific models are used in preference to global models. The emphasis here is on exploring the predictive potential of this approach rather than developing validated models for this purpose.

Data

To calibrate the model, a range of national datasets is employed. The response dataset comprises Diatom Critical Load values (Battarbee *et al.*, 1996) for 1467 lake and stream sites sampled as part of the UK Department of Transport and the Regions critical loads mapping programme (Kreiser *et al.*, 1993). These were calculated from spot samples taken from each site. To parameterise the independent side of the model a data collation exercise was undertaken which identified a number of national datasets providing a series of variables representing the key catchment attributes governing freshwater sensitivity to acidification. These catchment variables are summarised in Table 3.1 and comprise a range of digital datasets containing variables relating to soil, geology, land cover, hydrology, and deposition. Catchment boundaries for each sample site have been digitised from 1:25,000 Ordnance Survey (OS) maps using a Geographic Information System (GIS). These have been overlaid onto the digital datasets listed in Table 3.1 enabling the catchments to be characterised according to each of the catchment attributes.

The location (Easting and Northing) and topographical variables (site and maximum catchment altitude) were derived from 1:25,000 OS maps. Catchment and lake size and lake to catchment ratio (where applicable) were determined using a GIS. Rainfall and runoff values for each catchment were estimated for each site by overlaying the digital catchment boundaries onto the 1 km digital maps of rainfall and runoff held by the Institute of Hydrology. Rainfall and runoff values were spatially weighted according to pixel coverage within the catchment to provide a single value for each catchment. Sulphur and nitrogen deposition values were determined for each catchment in the same way using data provided by the Institute of Terrestrial Ecology although the resolution of the digital deposition maps is much lower at 20 km. The 25 m resolution digital land cover map of UK (Fuller *et. al.,* 1994) was used to provide land cover information. The catchment boundaries were overlaid onto this dataset enabling the percentage of each land cover class in each catchment to be specified.

Those classes with no (or negligible) variance were omitted from the analysis. The remaining classes are described in Table 3.1. A digital map of groundwater sensitivity to acidification (Edmunds and Kinnbiburgh, 1986) was used to characterise.

TABLE 3.1:
Catchment data used for empirical critical loads model

Code	Variable	Source	Min.	Max.	Mean	Explanation
Easting	Site Easting	1	-	-	-	-
Northing	Site Northing	1	-	-	-	-
L_area	Lake area (km^2)	1	0	2.01	.005	-
C_area	Catchment area (km^2)	1	0.01	76.3	2.3	-
L:C	Lake to catchment ratio	1	0	0.75	.06	-
Lcov5	% Land Cover Class 5	2	0	71	2.4	Grass heath
Lcov8	% Land Cover Class 8	2	0	67	1.7	Rough / Marsh grass
Lcov9	% Land Cover Class 9	2	0	90	11.0	Moorland grass
Lcov10	% Land Cover Class 10	2	0	99	21.7	Open shrub moor
Lcov11	% Land Cover Class 11	2	0	86	6.4	Dense shrub moor
Lcov12	% Land Cover Class 12	2	0	67	1.9	Bracken
Lcov13	% Land Cover Class 13	2	0	37	.7	Dense shrub heath
Lcov15	% Land Cover Class 15	2	0	98	5.3	Deciduous woodland
Lcov16	% Land Cover Class 16	2	0	96	4.5	Coniferous woodland
Lcov17	% Land Cover Class 17	2	0	51	3.6	Upland bog
Lcov22	% Land Cover Class 22	2	0	89	2.7	Inland Bare Ground
Lcov24	% Land Cover Class 24	2	0	61	.36	Lowland bog
Lcov25	% Land Cover Class 25	2	0	70	2.0	Open shrub heath
Arable	% arable	2	0	100	27	Tilled land, pasture, meadow
Wt_rain	Rainfall (mm/yr)	5	547	4460	1461	Catchment weighted rainfall
Wt_runoff	Runoff (mm/yr)	5	205	4152	1042	Catchment weighted runoff
Wt_ndep	Nitrogen deposition (keq $H^+ ha^{-1} yr^{-1}$)	2	.28	2.66	1.1	Catchment weighted N deposition
Wt_sdep	Sulphur deposition (keq $H^+ ha^{-1} yr^{-1}$)	2	.25	2.49	.86	Catchment weighted S deposition
Alt_site	Site altitude (m)	1	0	1000	227	Altitude at sampling point
Alt_max	Maximum altitude (m)	1	30	1130	514.7	Highest point in the catchment
Geol1	% Geological sensitivity class 1	3	0	100	47.5	Granite and igneous rock, most medasediments, grits, quartz sandstones and decalcified sandstones, some Quaternary sands
Geol2	% Geological sensitivity class 2	3	0	100	18.5	Intermediate igneous rocks, metasediments free of carbonates, impure sandstones and shales, coal measures
Geol3	% Geological sensitivity class 3	3	0	100	14.6	Basic and ultrabasic igneous rocks, calcareous sandstones, most drift and beach deposits, mudstone and marlstones
Geol4	% Geological sensitivity class 4	3	0	85.8	16.0	Limestones, chalk, dolomitic limestones and sediments
Peat	% Peat	4	0	100	14	-
Bfsoil	% Brown forest soils	4	0	100	20.5	-
Humirpd	% Humic iron podsols	4	0	100	4.1	-
NCGely	% Non-calcareous gleys	4	0	100	10.6	-
Peatygle	% Peaty gleys	4	0	100	17.5	-
Peatypod	% Peaty podsols	4	0	100	14.8	-
Subalpin	% Subalpine soils	4	0	100	5.4	-
Rankers	% Rankers	4	0	100	2.6	-
Pelosols	% Pelosols	4	0	100	2.2	-
BFI	Base flow index	5	.09	1.0	.49	BFI of dominant HOST class in catchment
SRP	Standard % runoff	5	2	60	44.6	SRP of dominant HOST class in catchment

Legend:
Key to sources: 1 = GIS/OS Map; 2 = ITE Monks Wood; 3 = Kinniburgh and Edmunds (1986); 4 = MLURI and SSLRC national soil inventories; 5 = Institute of Hydrology;

the catchments according to their underlying geology. This ascribes a sensitivity class to each of the geological formations on the 1:625,000 geological map of Great Britain. These range from highly sensitive (Class 1) including granite and igneous rock to non-sensitive (Class 4) such as limestone and chalk. The percentage of each of these classes present in each catchment was calculated. The digitised soil map of Scotland (1:250,000 scale) held at the Macaulay Land Use Research Centre and the equivalent for England and Wales held at the Silsoe Soils Survey and Land Research Centre were used to determine the percentage of each soil type in each catchment. These were aggregated into generic soil types and a procedure was adopted to harmonise the taxonomic equivalents between soils categorised in the Scottish classification system with those identified in England and Wales. All soil types in the UK are identified by a code and, for the most part, these have equivalents in both classification systems. Lithosols in Scotland (Code 1.1), for example have similar morphological and physico-chemical properties as raw skeletal soils (Code 130) in England and Wales (J. Gauld, personal communication). By establishing common links between the Scottish and English/Welsh classification systems it was possible to aggregate soil types across both systems. To assess the hydrological status of each catchment the Hydrology of Soil Types (HOST) database was used. This describes a hydrological classification of soils based on physical properties and substrate hydrogeology (Boorman *et al.*, 1995). A HOST class is allocated to each soil map unit from the Scotland and England and Wales classifications. Each class is also associated with a particular Standard Percent Runoff (SPR) value and a Base Flow Index (BFI). The former is the percentage of rainfall that produces a short-term increase in flow and provides an indication of the 'flashiness' of the catchment. The latter is the long-term average proportion of flow that occurs as baseflow (Boorman *et al.*, 1995). In these analysis the SPR and BFI values used are associated with the dominant soil map unit in each of the catchments.

The explanatory dataset thus comprises 40 variables (Table 3.1) selected to act as surrogates for the catchment attributes and mechanisms which determine sensitivity to acidification. These data are available at a variety of resolutions and their utility may depend on the resolution. However, the key issue here is that all these variables are available at national coverage (with the exception the Geology variables which have no coverage in the Shetlands and Orkney) and can therefore be used for any catchment.

Methodology

There are several stages involved in this exploratory analysis. Initially a Redundancy analysis (RDA) (Van den Wollenburg, 1977) is carried out on the full dataset (i.e. all sites and all variables) to enable the synoptic relationships between the variables representing catchment characteristics and the Diatom Critical Load (DCL) to be examined. Redundancy analysis (RDA) can be considered as a multivariate form of regression analysis. The response data (DCL) are modelled as a function of one or more ordination axes that are constrained to be linear combinations of the explanatory data. With a single response variable there is only one constrained ordination axis which, in this instance, can be said to represent DCL.

The second stage is to reduce the number of independent variables in accordance with the principle of parsimony so that the model is simplified, collinearity among explanatory variables is eliminated and spurious explanation is reduced (Økland and Eilertson, 1994). For this purpose an RDA with forward selection was undertaken to find a statistically significant subset of the explanatory variables which account for almost as much variation in DCL as the full dataset. Forward selection is a stepwise procedure whereby explanatory variables are selected sequentially to maximise extra fit. The significance at each iteration can be tested using Monte Carlo Permutation tests (ter Braak, 1990).

Having identified this statistically significant sub-set, the variables are regressed onto DCL in a multiple regression to gauge their predictive potential. This model is applied to all sites in the dataset and is termed the 'global' model. To compare model performance across attribute and geographical space, a series of multiple regressions are undertaken, using the same predictors as the global model, to a number of subsets of the full dataset, representing reduced environmental and spatial gradients. Sites at higher altitude bands (>300 m and >600 m) and with reduced levels of arable land (<10%, <5% and 0%) are analysed. To examine spatial variation the observations are regionalised by creating a number of 'pseudo-regions' based on the 100 km grid squares of the UK national grid. Where there are insufficient numbers of sites some grid squares were amalgamated. Comparisons are made between the explanatory power of the global model when it is applied to all sites and when it is used across these reduced environmental and geographical gradients. Regression analysis is used in this context primarily in an exploratory, descriptive sense. It is not the intention to compare directly the predictive power of each model as this will depend to some extent on the nature and distribution of the critical load in each specific region.

The fourth analytical step is undertaken to assess whether the relationships between critical load and catchment characteristics are stronger at regional scales and across reduced environmental gradients if region-specific 'local' models are employed. Backward stepwise regression is used to identify those catchment variables that best explain variation in DCL for specific regions and across the reduced environmental gradients. In backward stepwise regression the independent variables are removed from the analysis iteratively, based on their partial correlation until the "best" regression model is obtained.

Results

EXPLORATION OF SYNOPTIC RELATIONSHIPS USING REDUNDANCY ANALYSIS

Following Redundancy analysis on all sites, the interset correlations between each of the catchment variables and the first ordination axis were examined. Given that RDA with a single response variable produces a single constrained axis, the interset correlations provide a guide to the relationships between DCL and the catchment characteristics. The magnitude and direction of the interset correlations are illustrated by Figure 3.1, which shows the interset correlation for each variable, sorted from the highest negative correlations on the left to the highest positive correlations to the right. Thus high values of variables with strong negative correlations are associated with more sensitive freshwaters (low DCL values) whereas high values of variables to the right of the bar chart are associated with well buffered surface waters. Variables with correlations at or near 0 are poorly related to DCL across this national gradient.

Those variables with the highest negative interset correlations include runoff (Wt_runoff), rainfall (Wt_rain) and both measures of altitude (Alt_max and Alt_site). The standard percent runoff (SPR) also exhibits a negative interset correlation. The strength of these relationships is due to the dilute nature of the waters draining catchments in areas of high precipitation with high levels of surface run off. These are often at higher altitudes where catchments have thinner soils and steeper slopes with a limited ability to buffer incoming acid deposition. The percentage of the most sensitive geology class (Geol1) also has a high negative interset correlation reflecting the sensitive nature of freshwaters in catchments underlain by poorly weathered rocks such as granite and gneiss. In terms of soil cover, catchments with high proportions of peaty gleys, peats, subalpine soils and rankers are also associated with more sensitive freshwaters with lower critical loads. Catchments dominated by peat have a low buffering capacity as percolating waters have limited contact with soil mineral horizons. Rankers and subalpine soils are thin, poorly developed soils and are characterised by slow weathering rates, reduced cation exchange capacity and a limited ability to assimilate deposited nitrogen. The land cover types with negative interset correlations are mostly associated with upland/moorland systems including open shrub moor (Lcov10), upland bog (Lcov17), moorland grass (Lcov9), dense shrub moor (Lcov11) and bare ground (Lcov22). These are mainly found at high altitudes and are often underlain by poorly buffered soil and geology. The nature of the catchment dataset is such that there is a high degree of collinearity between many of the variables. This reflects the combination of catchment attributes, which result in surface waters that are sensitive to incoming acid precipitation. Poorly buffered soils and geology are often coincident with high rainfall and runoff regimes in catchments at higher altitudes dominated by moorland vegetation or with large areas of exposed bare rock. The negative relationship between Northing and DCL shows that these catchment types are predominantly found in Northern Britain.

The variable with the highest positive interset correlation is percentage arable land. Surface waters in catchments dominated by arable land are not sensitive to acidification. These catchments are likely to be located in lowland areas on relatively base rich soils. Additionally, lime is routinely added in agricultural areas to maintain soil pH and calcium. This further buffers surface waters against the effects of acid deposition in these catchments. The influence of more base rich soils on surface water sensitivity is reflected by the high positive interset correlations exhibited by percentage pelosols, non calcareous gleys (Ncgley) and brown forest soils (Bfsoil). Similarly, the buffering capacity of calcareous bedrock can provide catchments with protection against the most intense acid loading, hence the strong positive relationship between DCL and percentage geology class 4 (Geol4). Figure 3.1 also shows that high critical loads are associated with a high base flow index (BFI). Systems where a high proportion of catchment surface water is derived from base flow sources are likely to be well buffered as the percolating water will have come into contact with mineral buffering layers in the deeper soil horizons. The positive relationship between Easting and DCL stems from the concentration of lowland agricultural catchments in eastern England (and, to a lesser degree, Scotland). As with those variables exhibiting an inverse relationship with DCL, there is substantial collinearity between those variables whose high values are associated with high critical loads. Agricultural catchments are likely to be underlain by well buffered base rich soils which in turn, usually overlie calcareous, non-sensitive bedrock. Further, there are high levels of collinearity between those variables which are positively related to DCL (e.g. Arable, Geol4) and those with inverse relationships (e.g. Alt_site, Geol1).

The purpose of this section has been to illustrate the structure of the relationships between the catchment variables and DCL by examining, synoptically, the correlations between them. This analysis appears to separate well buffered arable catchments in the lowlands, with base rich soils and well weathered geology from upland moorland systems overlying thin, acid soils and poorly weathered bedrock. The strong correlations suggest that these variables can be used for predictive purposes and the subsequent sections explore this possibility.

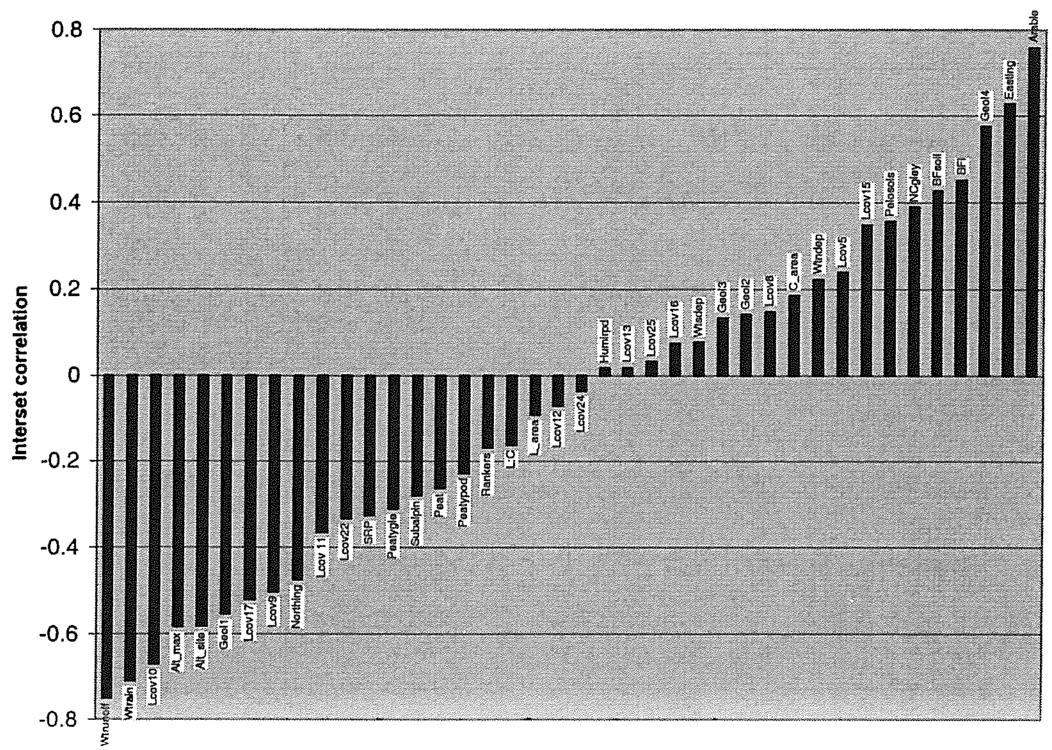

Fig 3.1: Bar chart showing interset correlations for each explanatory variable. This provides a measure of the magnitude and direction of the relationship between these variables and DCL. Variables with high negative interset correlations with DCL are to the left and those with high positive correlations lie to the right (See Table 3.1 for codes).

DATA REDUCTION

The catchment variables used to parameterise the global regression model were determined by undertaking RDA with forward selection, in tandem with Monte Carlo Permutation tests. This enabled the reduction from a large number of variables to a statistically significant sub-set. Table 3.2 shows which variables were chosen to go forward into the regression analysis together with the extra (conditional) variance added by their inclusion in the model. Approximately 74% of the variation in DCL can be explained by the 7 variables highlighted in Table 3.2. This compares with 76% when all variables are included in the analyses. Reducing the number of explanatory variables in the model from 40 to 7 results in a 2% loss of explanatory power. The lack of a substantial reduction in explanatory power is due to the high collinearity between the catchment variables. The variation in DCL can thus be represented by a few key variables. These comprise the variables with the highest interset correlations (Wt_runoff and arable), variables representing extremes of geological sensitivity (Geol1 and Geol4), sensitive soils (peat) and altitude (Alt_site) and catchment area (C_area). The significance of catchment size is likely to be due to hydrological factors.

(Wt_runoff and arable), variables representing extremes of geological sensitivity (Geol1 and Geol4), sensitive soils (peat) and altitude (Alt_site) and catchment area (C_area). The significance of catchment size is likely to be due to hydrological factors. Larger catchments tend to exhibit greater buffering potential as there is a greater chance that the surface waters will be derived from base flow. For lake systems these are also likely to have longer water residence times. These variables encapsulate the nature of catchments at either end of the sensitivity spectrum.

TABLE 3.2
Results of forward selection on full catchment dataset

Variable added	Cumulative variance explained
Arable	.50
Wt_runoff	.58
Geol4	.62
C_area	.62
Geol1	.63
Peat	.64
Alt_site	.64

GLOBAL REGRESSION MODEL

Regression analysis was applied to the full 1467 site dataset using the reduced sub-set of seven explanatory variables. Table 3.3 shows the regression diagnostics for this model. The adjusted R^2 is .64 (adjusted for degrees of freedom) with a standard error of .31. The standard error of the estimate provides a measure of the spread of the residuals and indicates, in this instance, a fairly wide scatter. This is to be expected given the size and complexity of the data. The standardised (to 0 mean and unit standard deviation) Beta and non-standardised (raw) (B) regression coefficients are also shown together with their respective standard errors. The magnitude of the standardised Beta coefficients allows comparison of the relative contribution of each independent variable to the predictive model. The t and p values indicate that these variables are all statistically significant with the magnitude of t also providing a guide to the relative importance of each variable in the model. Those variables with high t values drive the overall model. Thus, confirming the results of the exploratory work in the previous two sections, those variables which best explain critical load variation are % arable land, runoff and the sensitive (Geol1) and non-sensitive (Geol4) geology classes. At the national scale this distinguishes between those sites in lowland agricultural Britain overlying calcareous geology from those in upland areas with high runoff and poorly weathered acid igneous bedrock. These results suggest that, at this national scale, there is considerable potential for predicting critical loads from national datasets.

To examine whether there are any spatial patterns in terms of model fit, the standardised residuals of this global model are mapped (Figure 3.2) to allow the spatial trends within the relationships to be assessed and the areas where the model over- or under-predicts critical loads to be identified. Generally, given that the ideal value for a residual is as close to zero as possible, at the national scale the model is well fitted, particularly in Wales and Scotland. However, there are clusters of sites where the fit is poor. In south east England there are numerous sites where the negative residual values indicate that the model is under-predicting critical load (i.e. the observed values are considerably greater than the predicted). This region is characterised by very high critical load values that may cause instability at this extreme end of the critical load gradient. The model is over-fitted in Orkney (i.e. the model is predicting critical loads much higher than those observed). In the Pennines, model performance is affected both by under and over-fitting. This is an area of very high deposition which may be influencing the surface water chemistry to such an extent that the relationships between the critical load and catchment characteristics are atypical.

TABLE 3.3
Regression diagnostics for global model

Regression summary for Dependent variable: Diatom Critical Load						
$R = .80$ $R^2 = .64$ Adjusted $R^2 = .64$						
F (8, 1458) = 332.28 p<0.0000 Standard Error of estimate: .319						
	Beta	St. Err of Beta	B	St. Err. of B	t(1458)	p-level
Intercept			1.42	0.151	9.77	0.0000
C_area	0.101	0.016	0.080	0.013	6.28	0.0000
Arable	0.309	0.024	0.047	0.003	12.84	0.0000
Wt_runoff	-0.248	0.026	-0.436	0.046	-9.51	0.0000
Alt_site	-0.073	0.021	-0.001	0.002	-3.37	0.0001
Peat	-0.077	0.017	-0.025	0.005	-4.64	0.0000
Geol1	-0.128	0.018	-0.030	0.005	-6.47	0.0000
Geol4	0.202	0.019	0.063	0.006	10.64	0.0000

This analysis of the entire dataset shows that it is possible to differentiate between sensitive and non-sensitive sites using these techniques across a wide gradient of sensitivity.

APPLICATION OF GLOBAL MODEL TO SCREENED AND REGIONAL SUB-SETS

To assess whether the global model (as applied using all sites) has the same explanatory power when applied to reduced environmental and spatial gradients, the same model was applied to a number of sub-sets of the data. The environmental gradients assessed here are altitude and %arable. The model was applied separately to sites above 300 m and 600 m to establish whether the relationships at the national level would hold when the altitude gradient was shortened. Similarly, the model was applied to sites with less than 10% arable land, less than 5% arable land and no arable land to assess how downweighting or removing the variable which seems to drive the national model influences the strength of the model. To examine regional differences a series of arbitrary 'pseudo-regions' were defined based on the 100 km grid squares from the national grid.

The results of applying the global regression model to the screened and regional sub-sets are summarised in Table 3.4. The adjusted R^2 (R^2_{adj}) values for each

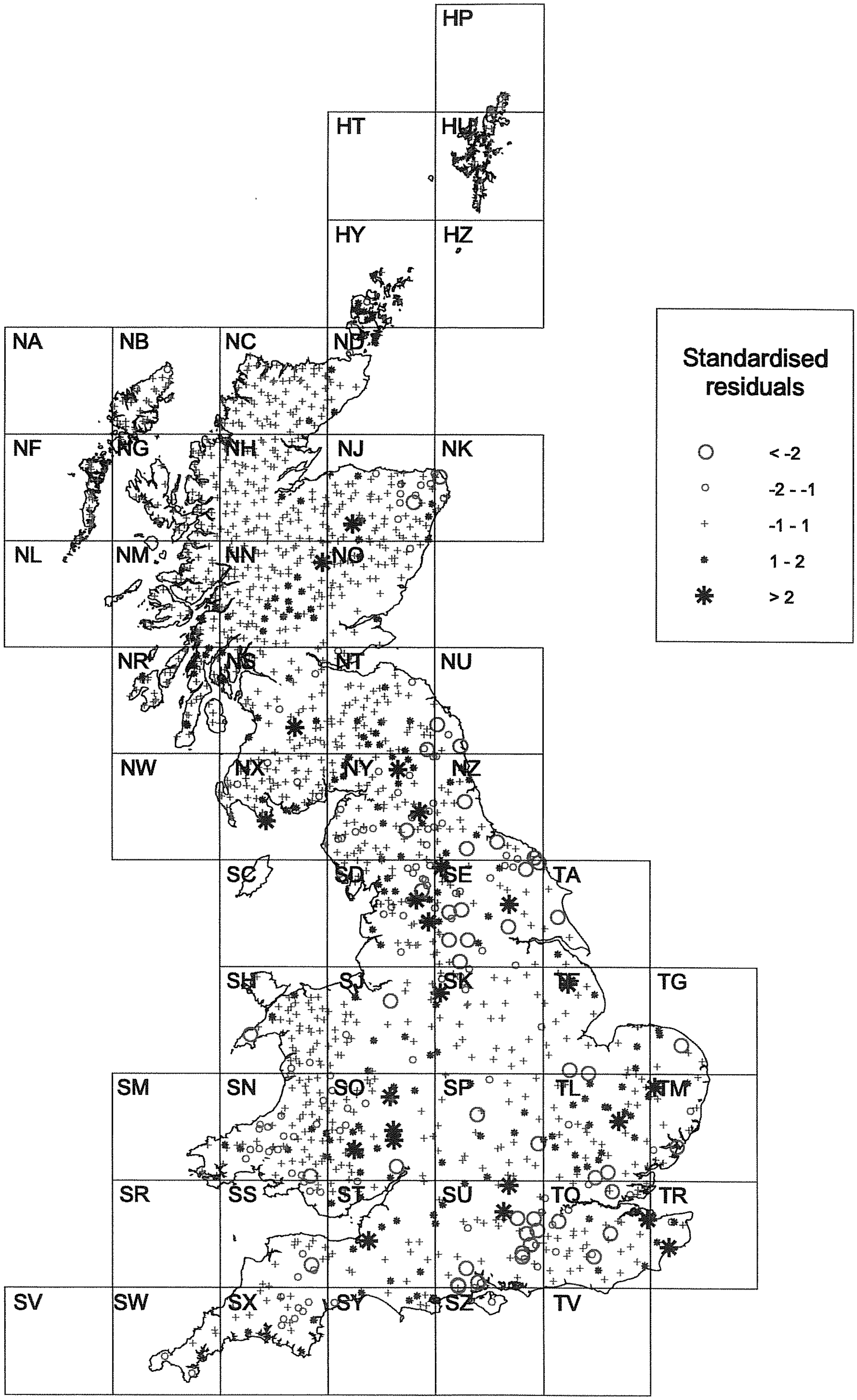

Fig. 3.2: Map showing spatial distribution of standardised residuals from global regression model

analysis, the standard error of the estimate and the variables which maintain significant beta values are included in the table. There is substantial variation with R^2_{adj} values both across the environmental gradients and between the arbitrarily defined regions. With a reduced arable gradient the R^2_{adj} is much lower. When the analysis is restricted to sites with no arable land, R^2_{adj} falls to .21 and only runoff, catchment area and geology class 4 have significant beta values. Thus, once the dominant driving variable (the amount of arable land in the catchment) is removed, the distinction between sensitive and non-sensitive freshwaters is based on catchment size, geology and runoff levels. The standard error is similar for each of the three reduced arable classes but is less than that for the global application, despite the higher R^2_{adj} value for the latter. The reduced arable gradient is likely to be characterised by a concomitant reduction in the range of DCL as the highest critical loads are to be found in lowland catchments with high proportions of arable land. With the extremely high DCL values eliminated, the scatter of the residuals is reduced and this is reflected by the lower standard errors.

Similar effects on model performance are apparent when the altitude gradient is shortened. When the response data are constrained so that only sites above 300m are included the model performs less well (R^2_{adj} = .26) and fewer of the explanatory variables have significant beta values. The reduction of the altitude gradient results in a reduced critical load variance as these sites will generally tend to be more sensitive. Thus the explanatory power of the model (parameterised for the global case) is diminished. With the altitude gradient narrowed further (sites above 600 m) model performance is even more attenuated (Adj. R^2 = .03). With the sensitivity gradient reduced by this altitude constraint the variables used to parameterise the global model explain very little of DCL variation with only catchment area exhibiting a significant beta value. Here again the standard errors have not increased despite the reduced R^2_{adj} values, a reflection of the reduced DCL variance.

With regard to the regional subsets, the R^2_{adj} varies substantially from .05 with no significant predictors (NG - Skye and west coast of Scotland) to .80 (HP/HY/HU - Shetland and Orkney). The standard error varies between 0.1 (NB/NF - Outer Hebrides) to .47 (SE - Pennines). Generally the higher standard errors are associated with lower R^2_{adj} values although this relationship is not straightforward and there are some pseudo-regions with low R^2_{adj} values and low standard errors (e.g. NB/NF and NG). Additionally, there are some high R^2_{adj} values associated with high standard errors (e.g. SO/SP - West Wales and the Midlands and SJ/SK - NE Wales and North Midlands). The standard error is positively associated with the DCL variance in each case. In each pseudo-region the distribution of DCL values is likely to have a significant effect on both explanation and prediction, with outliers potentially confounding the relationships identified in the global model.

In some of these pseudo-regions the variables used to parameterise the global model explain DCL variation fairly well. Those regions with the highest R^2_{adj} are likely to exhibit the full range of catchment sensitivity with concomitant variation in terms of catchment characteristics. Within the pseudo-region (HP/HU/HY) sites on the Shetlands are dominated by peat coverage whereas arable land is prominent in sites on Orkney. Thus this 'region' is characterised by variables having either strong positive or strong negative correlations with DCL. Similarly in NW/NX (the Galloway region) the most important predictor is Geol1, the most sensitive geology class which underlies sites draining the granitic plutons in central Galloway. These contrast with the agricultural catchments in the central lowlands. Grid square NO (Fife and Perthshire) contains high altitude catchments in the Cairngorms and arable farming in the Fife lowlands. Thus, when applying a model calibrated for the global dataset, success with regard to explanation and prediction will depend to a large extent on how the region is defined. If the response gradient and catchment variation in the region mirrors that found nationally then the model is likely to perform well. However, if there is little variation in critical load (i.e. most sites are highly sensitive or non-sensitive) then the model will perform poorly.

TABLE 3.4
Application of the Global Regression Model to screened and regional sub-sets of the data

Subset (no. of sites)	Adj. R^2	Stand. error	Variables with significant Betas
Global Model	.65	.32	Arable, Wt_runoff, Geol4, Geol1, C_area, , Alt_site, Peat
Arable <10% (724)	.31	.24	Wt_runoff, C_area, Peat, Geol4, Geol1, Arable, Peat
Arable <5% (618)	.26	.22	Wt_runoff, C_area, Peat, Geol4, Geol1, Arable
Arable 0% (423)	.21	.20	C_area, Wt_runoff, Geol4, C_area
Alt>300m (376)	.26	.22	Wt_runoff, C_area, , Geol1, Peat, Arable
Alt>600m (73)	.03	.13	C_area
HP/HU/HY (43)	.80	.22	Arable, Peat (NB: No Geology classes)
NB/NF (45)	.28	.10	Peat, C_area
NC/ND (75)	.73	.15	Arable, C_area, Wt_runoff, Peat
NG (45)	.05	.14	None significant
NH (80)	.67	.11	Wt_runoff, Arable
NJ/NK (70)	.29	.28	Peat
NM (39)	.52	.14	Wt_runoff,
NN (93)	.35	.17	Wt_runoff, Alt_site
NO (43)	.79	.15	Wt_runoff, C_area, , Arable, Geol1
NR (42)	.44	.23	Arable
NS (54)	.61	.21	C_area, Arable, Peat
NT (60)	.56	.23	Arable, Geol4
NW/NX (57)	.69	.22	Geol1
NY (77)	.50	.33	Arable, C_area
NU/NZ (33)	.19	.52	Arable
SD (50)	.56	.32	Alt_site, Arable
SE (43)	.30	.47	None significant
TA/TF/TG (33)	.21	.44	Geol4
SH (39)	.40	.23	Arable
SJ/SK (65)	.66	.33	Arable, Geol4
SN/SM (64)	.22	.27	Wt_runoff
SO/SP (81)	.66	.32	Alt_site, C-Area, Geol1
TL/TM (62)	.16	.39	Wt_runoff, C_area
SS/SW/SX (43)	.62	.24	Alt_site, Arable
ST/SU/SY/SZ (81)	.45	.42	Geol4, Arable,
TQ/TR (50)	.26	.36	Arable

BACKWARD STEPWISE REGRESSION

This section develops a 'local' regression model whereby variables more suited to the environmental gradients of interest or local situations are used to explain and, ultimately, predict critical loads. For this purpose, backward stepwise regression was undertaken using the same screened and regional sub-sets as the global regression. The results of these analyses are shown in Table 3.5 which shows, for each model, the adjusted R^2 , the standard error of the estimate, together with those variables selected by the stepwise regression procedure. The direction of the relationship between each individual variable and the DCL is also indicated. Using this approach, the 'best' model produced for the full national dataset produces an R^2_{adj} of .66 which is similar to that using the variables input into the analysis following forward selection in RDA. Several additional variables also exhibit significant beta values including N deposition, percent open shrub moor, percent dense shrub heath and percent inland bare ground which all display inverse relationships with DCL. Additionally, geology class 3 (which include basic and ultrabasic igneous rocks) and percent brown forest soils are also significant predictors but exhibit positive relationships with DCL.

When backward stepwise regression is applied to the subsets with reduced environmental gradients there is considerable improvement in R^2_{adj} values compared to those in section 4.3.1. For sites with no arable land, R^2_{adj} increases from .21 to .39, an improvement brought about through model utilisation of those variables which are better at explaining DCL variation across this narrower gradient than those variables used to parameterise the 'global' model. With the removal of the ameliorating influence of arable land the significant predictors positively related to DCL comprise percent brown forest soils, catchment area, non-sensitive geology and percent peaty podsols. The model also incorporates a number of variables inversely related to DCL including rainfall, percent upland bog and percent inland bare ground. Thus, although in comparison with the national regression, model performance is diminished across these narrower environmental gradients, the gradient specific paramaterisation offers considerable improvement over applying the global parameters. For sites above 300m and 600m gradient-specific parameterisation improves R^2_{adj} substantially over those achieved by using the global parameters, particularly in the latter instance where an increase from .03 to .34 is evident. The use of iterative selection procedures allows those variables in a dataset which most account for response variation to be highlighted. For sites above 600 m the model-explained DCL variation is driven by catchment area and percent dense shrub moor (Lcov10) both positively related to DCL. The importance of Lcov10, which covers marginal hill grazing land in northern and western Britain, may be due to a differentiation at high altitude between catchments where this land cover is abundant and those where bare rock dominates, the latter exhibiting a greater sensitivity due to the lack of buffering associated with such systems.

The region-specific models generally perform better than the global parameterisation. There is still a wide range of R^2_{adj} values reflecting both the range of variation and the nature of the catchments within each of these pseudo-regions. Although the variables used to parameterise the global model remain significant in a number of the regions, in many instances other variables that better explain region-specific variation in DCL are selected. Clearly the DCL variation within each subset remains the same thus, for the most part, the standard errors for each are similar to those generated using variables from the global model.

Discussion

Many of the variables acting as surrogates for catchment characteristics exhibit strong statistical relationships with the diatom critical load, particularly at the national

TABLE 3.5

Results of backward stepwise regression on screened and regional sub-sets of the data

Subset (no. of sites)	Adj. R^2	Stand. error	Stepwise selections (in order of beta values and with direction of relationship)
Great Britain (1467)	.66	.31	Arable (+), Wt_runoff (-), Geol4 (+), C_area (+), Wt_ndep (-), Lcov10 (-), Geol1 (-), Lcov22 (-), Peat (-), Bfsoil (+), Geol3 (+)
Arable <10% (724)	.37	.23	C_area (+),Wt_runoff (-),Bfsoil (+),Peat (-), Lcov22 (-), Geol4 (+), L_area (-)
Arable <5% (618)	.39	.20	Wt_sdep (-),Lcov22 (-),C_area (+), Bfsoil (+),Geol4 (+), L_area (-), Northing (-), Peatypod (+), Geol1 (-), Peat (-)
Arable 0% (423)	.39	.17	Bfsoil (+), C_area (+), Wt_rain (-), Geol4 (+), Lcov17 (-), L_area (-), Lcov22 (-), Peatypod (+)
Alt>300m (376)	.35	.21	C_area (+), Geol3 (+), L_area (-), Bfsoil (+), Peatypod (+), Wt_rain (-)
Alt>600m (73)	.34	.11	Lcov11 (+), C_area (+)
HP/HU/HY (43)	.85	.19	Arable (+), Lcov10 (+), Bfsoil (+), Peat (-)
NB/NF (45)	.41	.09	Peat (+), L:C (-)
NC/ND (75)	.76	.14	Arable (+), Lcov11 (+), C_area (+)
NG (45)	.58	.09	Lcov11 (+), Wt_ndep (+), Alt_max (-)
NH (80)	.75	.09	Wt_runoff (-), Wt_rain (+) Geol2 (-), Lcov8 (+), C_area (-), Ncgley (-), L_area (-)
NJ/NK (70)	.25	.29	Lcov25 (+)
NM (39)	.57	.13	Bfsoil (+)
NN (93)	.44	.16	Northing (-), Wt_sdep (-), L:C (-)
NO (43)	.80	.15	Lcov 13 (-), Lcov11 (-), Alt_max (-), Lcov5 (+), Lcov22 (-), Lcov9 (-)
NR (42)	.25	.29	Lcov5 (+)
NS (54)	.57	.22	Wt_runoff (-), C_area (+)
NT (60)	.70	.19	Arable (+), Lcov12(+), Alt_max (-), Wt_ndep (-), Geol2(+)
NW/NX (57)	.68	.23	Northing (-), Wt_ndep (-), Geol1 (-)
NY (77)	.52	.32	Wt_runoff (-), Lcov11 (-), C_area (+)
NU/NZ (33)	.45	.43	Lcov22 (-), Lcov24 (-), L_area (+)
SD (50)	.62	.30	Alt_max (-), Arable (+)
SE (43)	.58	.40	Arable (+), Geol3 (+), Lcov5 (-)
TA/TF/TG (33)	.47	.37	Lcov22 (-)
SH (39)	.64	.17	Alt_max (-), Northing (+)
SJ/SK (65)	.65	.33	Arable (+), Geol3 (+)
SN/SM (64)	.18	.28	Easting (-)
SO/SP (81)	.64	.33	Alt_site (-), Wt_runoff (-), Alt_max (+), C_area (+)
TL/TM (62)	n/a	n/a	No variables significant
SS/SW/SX (43)	.62	.24	Alt_site (-), BFI (+)
ST/SU/SY/SZ (81)	.55	.38	Peatypod (-), Geol4 (+), Humirpd (-)
TQ/TR (50)	.52	.29	Lcov15 (-), Lcov12 (-), Peatypod (-)

scale. With process studies having demonstrated that soil, geology and land cover determine freshwater sensitivity this is not surprising. The broad spatial patterns displayed by digital geology, land cover and soil maps reflect similar patterns in the sensitivity of surface waters. The resolution and accuracy of the catchment data do not appear problematic at the national scale and these national datasets allow differentiation between sensitive and non-sensitive sites along broad gradients of sensitivity. Key explanatory variables (e.g. %arable, runoff, geology class and % peat) are associated with catchments at both extremes of this sensitivity spectrum. The wide range of DCL values increases the explanatory capacity of those independent variables with which it is strongly correlated. However, the large variance and extreme values associated with DCL across this gradient results in a relatively high standard error.

However, when parameters from this 'global' model are applied across more restricted attribute and geographical space, the explanation offered by the model is substantially reduced. Clearly the ability of the global parameters to explain critical load is potentially reduced when some of the key environmental variables driving sensitivity (e.g. % arable land and altitude) exhibit less variance. It may be that across these gradients there is insufficient DCL variance to allow prediction (using national datasets) to be viable. Evidently, in some instances the variables used to parameterise the global model are inappropriate at the regional and sub-regional scale. At sites above 600 m different processes and mechanisms will dictate freshwater sensitivity to those operating across the full altitude range. Different soils and land cover types are found at these higher elevations and the influence of variables such as arable land are negligible. It may not be possible to reflect variations with these high altitude processes using national datasets and it may be that higher resolution data will be required to develop this further. When region- and gradient-specific models are applied, model performance, in terms of explanation, generally improves. Different variables become important in different areas of geographical and attribute space as the driving mechanisms vary within these areas. Evidently the global model parameterised in the national context should not be applied regionally, or if specific catchment types are being examined. The potential success of these parameters for prediction at a regional level will depend on how the regions are defined and therefore the extent to which both critical load and those variables acting as surrogates for the driving mechanisms vary. The success of the regional approach will depend on how the regions are defined and the heterogeneity of that region. Even using the region specific model there are some regions where model performance is poor. There may be little inherent variability in these regions. As with the global model, it may be that inappropriate data are being used and that more high resolution data are required. It may simply be a case that the available data are inadequate surrogates for the main driving mechanisms.

6. Conclusions

These analyses have comprised an exploration of the relationships between variables acting as surrogates for catchment characteristics and freshwater critical load. The results demonstrate the potential for predicting DCL using national datasets. However, it is also shown that the parameters used in the global model are not necessarily useful across all areas of attribute and geographical space. Ideally, region- or gradient-specific models should be developed. However, the differences in the standard error, even for models with similar Adj. R^2 values suggests that, even if there is a reasonable level of explanation, this may not be matched by the potential for prediction. This may be due to the presence of extreme values or outliers within specific pseudo-regions exerting a disproportionate influence on the results of the analysis. Further work is required on model validation using these data. To further develop the model's predictive capability there is a need to examine more closely the structure of the response data across the reduced environmental and geographical gradients. The removal of spurious outliers will potentially reduced the standard error thus increasing the potential for these models to be used in a predictive capacity. Additionally, where the national data exhibit very poor relationships with DCL, the use of higher resolution data should be explored, both spatial and temporal (i.e. using mean chemistry). This may be the major constraint when moving from national to regional scale modelling. Another potential area where this work could be further developed is through the application of Geographically Weighted Regression (GWR) models (Brunsden *et al.*, 1998) which fit regression models at any location using proximity weighted data and identify location specific regression parameters. These techniques offer some scope for applying the critical loads approach to populations of sites rather than limiting it to those for which chemistry data exist.

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4. How many lakes in Wales have acidified? A preliminary evaluation using critical loads models and palaeolimnology

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Introduction

Wales has been a major focus for research on surface water acidification over the past two decades, and numerous studies have demonstrated the significant impact of acid deposition on the chemistry and biology of Welsh lakes (e.g. Battarbee *et al.* 1988, Fritz *et al.* 1990, Ormerod and Gee 1990, Rimes *et al.* 1994, Patrick *et al.* 1996, Stevens *et al.* 1997, Jenkins *et al.* 1997). National water chemistry surveys (e.g. CLAG 1995, Stevens *et al.* 1997) indicate that acidified surface waters are widespread across the uplands of Wales, which are highly sensitive to acid deposition (Hornung *et al.* 1995). However, in contrast to other regions affected by acidification (see for example Forsius *et al.* 1990 and Cumming *et al.* 1992) there has been no direct quantification of the number, or proportion, of Welsh lakes impacted by acid deposition.

Critical loads models can potentially be used to quantify the regional extent of lake acidification. For example, Henriksen *et al.* (1992) and Posch *et al.* (1997) have used critical loads models to quantify the extent of lake acidification in Scandinavia. Critical loads assessments have also been made for UK surface waters (CLAG 1995, Curtis *et al.* 1998). However, these UK applications were based on a national dataset of water chemistry in which sites were systematically sampled from the most sensitive water body within each 10 x 10 km grid square (Kreiser *et al.* 1995). Although this approach allows grid squares containing acidified sites to be identified, it does not provide an estimate of the number or proportion of impacted lakes within a region.

In this paper we present data from a water chemical survey of randomly selected Welsh lakes undertaken in 1995 as part of the wider North European Lake Survey (Henriksen *et al.* 1998). The application of critical loads models to the chemical dataset allows the number of lakes in Wales showing a critical load exceedance, and therefore predicted to have been impacted by acid deposition, to be estimated for the first time. However, a feature of the critical loads methodology is that the relationship between critical load exceedance and chemical and biological change is not well established, and there is significant uncertainty in the interpretation of exceedance data. We therefore also use palaeolimnological data (see Battarbee *et al.* 1988) to validate the predictions of acidification provided by the critical loads models.

Methods

THE 1995 WELSH LAKE SURVEY

Ordinance Survey maps at 1:50,000 scale were used to identify all standing waters in Wales with a surface area >4ha. This size cut-off was used to define lakes as opposed to the smaller ponds and pools which proliferate in the Welsh landscape, and is consistent with the approach of the Northern European Lake Survey. A total of 255 lakes and reservoirs were identified. A sub-set of 52 lakes and reservoirs was selected for chemical sampling using a stratified random procedure, with stratification by size class (see Henriksen *et al.* 1998). The spatial distribution of this subset reflects the distribution of lakes and reservoirs in Wales, with the largest concentrations of sites found in the uplands of mid- and north Wales (Figure 4.1). Water samples were taken from these 52 lakes in November and December 1995 following autumn overturn (Table 4.1). Water chemistry was analysed at the SOAFD Freshwater Fisheries Laboratory within two days of sampling using standard methodologies (Harriman *et al.* 1990). Acid neutralising capacity was determined according to Cantrell *et al.* 1990.

CRITICAL LOADS MODELLING

Two empirical critical loads models were employed to predict acidification status from the chemical data; the steady state water chemistry (SSWC) model (Henriksen *et al.* 1992) and the diatom model (DCL) (Allott *et al.* 1995a, Battarbee *et al.* 1996). Although both models are empirical and use measurements of water chemistry to calculate critical loads of total acidity, they differ in approach. The SSWC model relates the critical load to a pre-defined concentration of ANC (ANC_{crit}). ANC_{crit} is selected as a chemical criterion for sensitive indicator organisms. For example, in Norway few fish populations are damaged at ANC concentrations above 20 μeq l^{-1} (Lien *et al.* 1996), and this value has been adopted as ANC_{crit} for critical loads modelling in Scandinavia (Henriksen *et al.* 1992, Posch *et al.* 1997). However lakes in sensitive regions can naturally have ANC <20 μeq l^{-1}, resulting in negative critical loads when ANC_{crit} is set at this level. For this reason applications of the SSWC model in the UK have set ANC_{crit} to zero (CLAG 1995). In this study SSWC model critical loads were calculated with $ANC_{crit} = 0$.

In contrast to the SSWC model, critical loads calculated using the DCL model predict the deposition above which diatom assemblages will respond to lake-water acidification (Battarbee *et al.* 1996). The DCL is not directly linked to ANC, it indicates in theory the first point of change for a site whatever ANC threshold is crossed. As diatoms are amongst the most sensitive ecological indicators of water chemistry change, the DCL model provides a baseline critical load. An important feature of the DCL model is that it can be directly validated, as exceedances are effectively a prediction that diatom assemblages will have responded to acidification. These predictions can be validated using palaeolimnological techniques (see below).

Critical load exceedance data were calculated for both models using national 1992-94 deposition data (sulphur and nitrogen) at a 20 x 20 km scale.

PALAEOLIMNOLOGICAL EVALUATIONS OF ACIDIFICATION

Ten of the sites within the survey dataset have been the focus of palaeolimnological studies (Table 4.1). Fossil diatom data from sediment cores are therefore available for

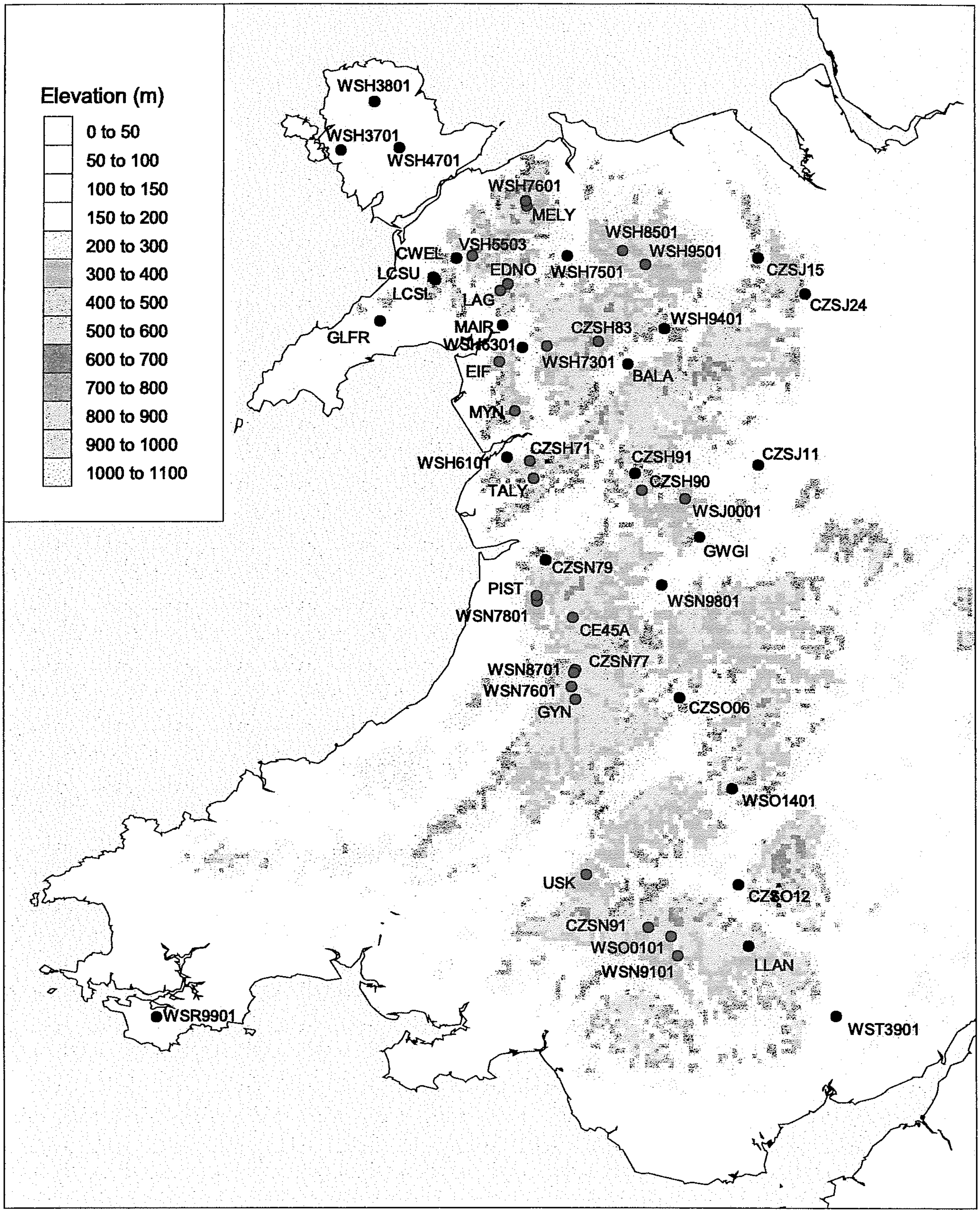

Fig. 4.1: Location of 1995 Welsh lake survey sites

Table 4.1
Site details for the 1995 Welsh lake survey, indicating sites with palaeolimnological data and water sampling dates

Sitecode	Site	Palaeolimnological Study	Grid Reference	Sampling Date
BALA	LLYN TEGID (BALA LAKE)	Bennion *et al.* (1998)	SH 907334	25.11.95
CE45A	LLYNNOEDD IEUAN	Simpson (1998)	SN 795814	13.12.95
CWEL	LLYN CWELLYN	Bennion *et al.* (1997)	SH 559549	23.11.95
CZSH71	LLYN-Y-GADAIR	-	SH 708135	26.11.95
CZSH83	LLYN ARENIG FAWR	-	SH 847382	26.11.95
CZSH90	LLYN GWYDDIOR	-	SH 934074	27.11.95
CZSH91	LLYN COCH-HWYAD	Clarke (1999)	SH 922110	27.11.95
CZSJ11	LLYN DU	-	SJ 173127	27.11.95
CZSJ15	LLYN GWERYD	-	SJ 172550	22.11.95
CZSJ24	CAE LLWYD RES	-	SJ 269479	22.11.95
CZSN77	LLYN FYRDDON FACH	-	SN 796701	28.11.95
CZSN79	LLYN CONACH	-	SN 740931	13.12.95
CZSN91	CANTREF RESERVOIR	-	SN 993159	11.12.95
CZSO06	LLYN GWYN	-	SO 012649	21.11.95
CZSO12	LLANGORSE LAKE	Bennion *et al.* (1997)	SO 131265	21.11.95
EDNO	LLYN EDNO	-	SH 662497	25.11.95
EIF	LLYN TRAWSFYNDD	-	SH 693367	25.11.95
GLFR	LLYN GLASFRYN	-	SH 402421	23.11.95
GWGI	GWGIA	-	SO 053979	13.12.95
GYN	LLYN GYNON	Battarbee *et al.* (1988)	SN 799646	28.11.95
LAG	LLYN LLAGI	Battarbee *et al.* (1988)	SH 649482	25.11.95
LCSL	LLYNNAU CWM SILYN (LOWER)	-	SH 512508	23.11.95
LCSU	LLYNNAU CWM SILYN (UPPER)	-	SH 514505	23.11.95
LLAN	LLANGYNIDR RESERVOIR	-	SO 152140	11.12.95
MAIR	LLYN MAIR	-	SH 652412	24.11.95
MELY	MELYNLLYN	-	SH 701656	24.11.95
MYN	LLYN CWM-MYNACH	Battarbee *et al.* (1988)	SH 678238	26.11.95
PIST	LLYN CRAIGYPISTYLL	-	SN 721858	12.12.95
TALY	TAL-Y-LLYN LAKE	-	SH 716099	26.11.95
USK	USK RES	-	SN 821286	21.11.95
VSH5503	LLYN FFYNNON-Y-GWAS	-	SH 591553	23.11.95
WSH3701	LLYN TRAFFWLL	-	SH 325769	22.11.95
WSH3801	LLYN ALAW	-	SH 392867	22.11.95
WSH4701	CEFNI RES	-	SH 443774	22.11.95
WSH6101	LLYNNAU CREGENNEN (LOWER)	Clarke (1999)	SH 661143	26.11.95
WSH6301	LLYN EIDDEW-MAWR	-	SH 646338	25.11.95
WSH7301	LLYN HIRAETHLYN	Clarke (1999)	SH 743370	26.11.95
WSH7501	LLYN ELSI RES	-	SH 783553	24.11.95
WSH7601	DULYN RES	-	SH 700665	24.11.95
WSH8501	LLYN ALWEN	-	SH 897565	24.11.95
WSH9401	LLYN CAER-EUNI	-	SH 982406	26.11.95
WSH9501	ALWEN RES	-	SH 943537	24.11.95
WSJ0001	LLYN HIR	-	SJ 023058	27.11.95
WSN7601	LLYN EGNANT	-	SN 792672	28.11.95
WSN7801	LLYN SYFYDRIN	-	SN 722847	12.12.95
WSN8701	LLYN FYRDDON FAWR	-	SN 800707	28.11.95
WSN9101	YSTRADFELLTE RESERVOIR	-	SN 947178	11.12.95
WSN9801	LLYN EBYR	-	SN 976881	13.12.95
WSO0101	LLWYN-ON RESERVOIR	-	SO 007119	11.12.95
WSO1401	LLAN BWCH-LLYN LAKE	-	SO 119463	22.11.95
WSR9901	UN-NAMED(WEST ORIELTON LAKE)	-	SR 950994	12.12.95
WST3901	LLANDEGFEDD RESERVOIR	-	ST 330996	11.12.95

these sites, allowing estimates of recent pH change to be made which are independent of the critical load assessments. Diatom samples of modern and pre-industrial assemblages for each site were downloaded from the AMPHORA database at the Environmental Change Research Centre. Modern samples represent the uppermost sample from each core. The pre-industrial samples were taken from sediments dating to c.1800 AD. Where dating was not available the pre-industrial samples were taken from the core base, typically at 20-30 cm depth. Sediment accumulation rates in UK upland lakes are generally <1.5 mm yr^{-1} (Battarbee *et al.* 1988, so the assumption that basal sediments from these cores represent pre-industrial assemblages is relatively secure. The diatom assemblages were harmonised according to Surface Water Acidification Project (SWAP) taxonomy (Stevenson *et al.* 1991) and diatom-inferred pH (DpH) calculated for each sample by weighted average calibration using the SWAP training set (Birks *et al.* 1990). Comparison of the modern and pre-industrial DpH values was used to provide a measure of recent (e.g. post -1800 AD) pH change (δDpH).

Results

CHEMICAL STATUS OF WELSH LAKES

The distribution of key chemical determinands across the survey lakes is summarised in Tables 4.2-4.7. A large proportion of the lakes are acidic; over 60% have pH less than 6.5 and 35% have pH less than 5.5. Alkalinity is also generally low, with 42% of the lakes having values less than 20 μeq l^{-1}. Twenty-one percent of the sampled lakes have labile aluminium concentrations greater than 20 μg l^{-1}. The data also demonstrate the importance of sea salts deposition to these systems, as reflected by high measured chloride concentrations, and the nutrient-poor status of most Welsh lakes. Sixty-five percent of the lakes have total phosphorus concentrations less than 10 μg l^{-1} and can be classified as oligotrophic. Although the dataset does also include well buffered lowland systems, these observations emphasise the numerical importance of nutrient poor, acid-sensitive upland systems to the Welsh lake population.

CRITICAL LOADS AND CRITICAL LOAD EXCEEDANCES

The distributions of critical load and exceedance data across the survey dataset are shown in Tables 4.8-4.11 and Figures 4.2 and 4.3. An important feature of the SSWC critical loads data (Table 4.8) is that few sites have very low critical loads. Indeed, only one site has a SSWC critical acidity load of less than 1 keq ha^{-1} yr^{-1}. This is likely to be a product of the generally high measured non-marine base cation concentrations (Table 4.2) and high runoff values for Wales. In contrast 48% of the lakes have DCL model critical acidity loads less than 1 keq ha^{-1} yr^{-1} (Table 4.9 and Figure 4.2). These between-model differences in critical load values are reflected in the exceedance data. According to the SSWC model 9.6% of the sites have exceeded their critical load (Table 4.10). This compares with 62% of the sites showing an exceedance according to the DCL model (Table 4.11 and Figure 4.3) . The DCL model also shows a significant proportion of sites (40%) with exceedances greater than 0.5 keq ha^{-1} yr^{-1}.

Table 4.2
Summary of distributions of key chemical determinands in the 1995 Welsh lake survey samples

Determinand	Minimum	25 percentile	50 percentile	75 percentile	Maximum
pH	4.50	5.35	6.21	6.80	7.86
Alkalinity ($\mu eq\ l^{-1}$)	-35	0	30	322	2565
ANC ($\mu eq\ l^{-1}$)	-3	17	67	393	2588
Non-marine base cations ($\mu eq\ l^{-1}$)	63	116	191	541	10652
Chloride ($\mu eq\ l^{-1}$)	129	178	218	334	1501
Non-marine sulphate ($\mu eq\ l^{-1}$)	36	61	86	152	5470
Nitrate ($\mu eq\ l^{-1}$)	1	8	12	24	453
Labile aluminium ($\mu g\ l^{-1}$)	0	1	4	15	163
Total organic carbon ($mg\ l^{-1}$)	0.9	3.5	5.9	10.0	19.0

Table 4.3
Distribution of pH in the 1995 Welsh lake survey samples

pH class	<5.0	5.0-5.5	5.5-6.0	6.0-6.5	6.5-7.0	>7.0
Number of sites	7	11	5	10	9	10

Table 4.4
Distribution of alkalinity in the 1995 Welsh lake survey samples

Alkalinity class	<0	0-20	20-50	50-200	>200
Number of sites	12	10	7	8	15

Alkalinity is expressed in $\mu eq\ l^{-1}$

Table 4.5
Distribution of labile aluminium (Al-L) in the 1995 Welsh lake survey samples

Al-L class	<10	10-20	20-30	30-40	>40
Number of sites	32	9	4	2	5

Aluminium is expressed in $\mu g\ l^{-1}$

Table 4.6
Distribution of total phosphorus (TP) in the 1995 Welsh lake survey samples

TP class	<10	10-30	30-100	>100
Number of sites	34	11	5	2

Total phosphorus is expressed in $\mu g\ l^{-1}$

Table 4.7

Distribution of acid neutralising capacity (ANC) in the 1995 Welsh lake survey samples

ANC class	<0	0-20	20-50	50-200	>200
Number of sites	1	13	11	11	16

ANC is expressed in $\mu eq\ l^{-1}$

Table 4.8

Distribution of steady state water chemistry (SSWC) model criticalloads in the 1995 Welsh lake survey samples

Critical load class	<0.2	0.2-0.5	0.5-1.0	1.0-2.0	2.0-4.0	>4.0
Number of sites	0	0	1	18	17	16

Critical loads are expressed in keq $ha^{-1}\ year^{-1}$

Table 4.9

Distribution of diatom (DCL) model critical loads in the 1995 Welsh lake survey samples

Critical load class	<0.2	0.2-0.5	0.5-1.0	1.0-2.0	2.0-4.0	>4.0
Number of sites	0	12	13	10	4	13

Critical loads are expressed in keq $ha^{-1}\ year^{-1}$

Table 4.10

Distribution of steady state water chemistry (SSWC) model critical load exceedances in the 1995 Welsh lake survey samples

	Non-exceeded sites		*Exceeded sites*			
Exceedance class	<-0.5	-0.5-0.0	0.0-0.2	0.2-0.5	0.5-1.0	>1.0
Number of sites	39	8	3	1	1	0

Critical load exceedances are expressed in keq $ha^{-1}\ year^{-1}$

Table 4.11

Distribution of diatom (DCL) model critical load exceedances in the 1995 Welsh lake survey samples

	Non-exceeded sites		*Exceeded sites*			
Exceedance class	<-0.5	-0.5-0.0	0.0-0.2	0.2-0.5	0.5-1.0	>1.0
Number of sites	18	2	6	5	17	4

Critical load exceedances are expressed in keq $ha^{-1}\ year^{-1}$

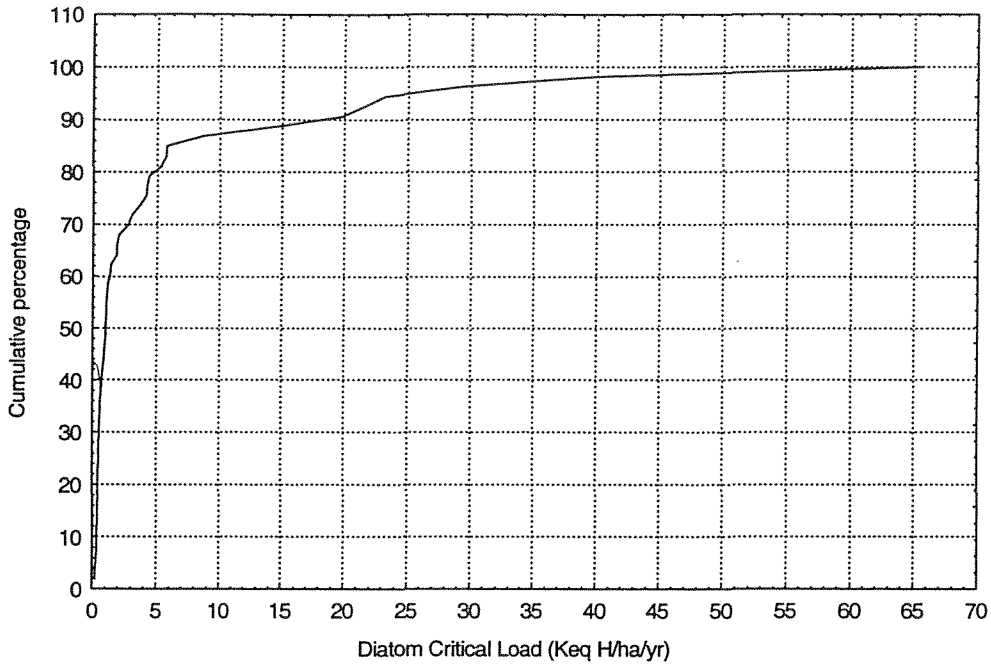

Fig. 4.2: Cumulative frequency distribution of the diatom (DCL) model critical acidity load for the 1995 Welsh lake survey

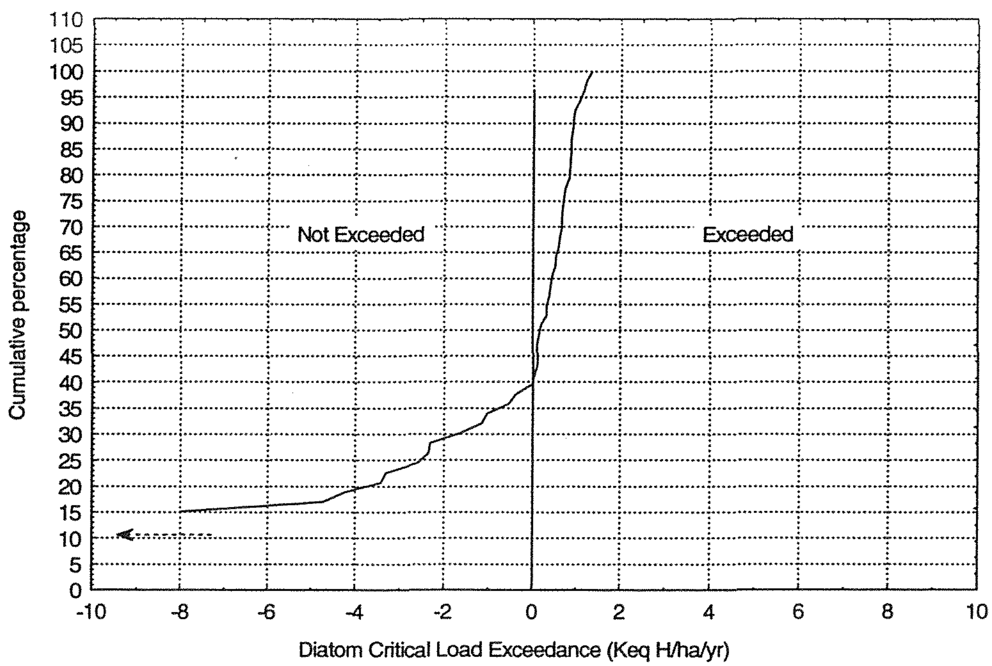

Fig. 4.3: Cumulative frequency distribution of exceedance of the diatom (DCL) model critical acidity load for the 1995 Welsh lake survey

PALAEOLIMNOLOGICAL VALIDATION OF EXCEEDANCE DATA

Diatom-based pH reconstructions are available for 10 of the 52 sites in the survey (Tables 4.12-4.14). DCL model critical loads are exceeded at eight of these sites. The diatom-inferred pH (DpH) data indicate that post-1800 pH decline (acidification) has occurred at seven of the eight exceeded sites. Bala Lake (Llyn Tegid) is the only site with a DCL exceedance where there is no decline in DpH. This site is known to have suffered recent nutrient enrichment (Bennion *et al.* 1998) and the primary diatom response is to changing nutrient status. Bennion *et al.* (1998) found no evidence of recent lake acidification in the palaeolimnological record. It should be noted that the declines in DpH at three of the exceeded sites (Llyn Cwm Mynach, Llyn Gynon and Llyn Coch-Hywad) are within the error of the pH reconstruction technique (Birks *et al.* 1990). However, at the former two sites analysis of full stratigraphy has demonstrated consistent trends in diatom assemblages and DpH representing recent acidification (see Battarbee *et al.* 1988, Fritz *et al.* 1990). The two non-exceeded sites according to the DCL model either show no change in post-1800 DpH (Llynnau Creggennen) or a significant increase in DpH associated with recent nutrient enrichment (Llangorse Lake; Bennion *et al.* 1997). The palaeolimnological data therefore support the predictions of the DCL model exceedance data at nine of the ten sites. In contrast, there is much weaker correspondence with the SSWC model exceedance data. Although seven of the sites show declines in DpH only one site (Llynnoed Ieuan) is exceeded on the basis of the SSWC model (4.14), although it is interesting to note this site shows the largest decline in DpH.

Table 4.12

Diatom-based palaeolimnological reconstructions of pH change from ten of the 1995 Welsh lake survey sites. Sites are presented in order of DCL exceedance. DpH = diatom inferred pH.

Sitecode	Site Name	Data Source	Coring Date	DpH-c.1800	DpH-modern	δDpH
LAG	Llyn Llagi	Battarbee *et al.* (1988)	1985	5.90	4.79	-1.11
CE45A	Llynnoed Ieuan	Simpson (1998)	1997	5.92	4.78	-1.13
MYN	Llyn Cwm Mynach	Battarbee *et al.* (1988)	1985	5.64	5.41	-0.22
GYN	Llyn Gynon	Battarbee *et al.* (1988)	1985	5.57	5.40	-0.17
CZSH91	Llyn Coch-Hywad	Clarke (1999)	1999	6.30	6.14	-0.16
BALA	Llyn Tegid	Bennion *et al.* (1998)	1996	7.01	7.16	+0.14
CZSH7301	Llyn Hiraethlyn	Clarke (1999)	1999	6.64	6.02	-0.62
CWEL	Llyn Cwellyn	Bennion *et al.* (1997)	1995	6.54	5.96	-0.57
WSH6101	Llynnau Creggennen	Clarke (1999)	1999	6.39	6.44	+0.05
CZSO12	Llangorse Lake	Bennion *et al.* (1997)	1996	7.14	7.77	+0.63

Table 4.13

Summary chemical data for the ten sites in the 1995 Welsh lake urvey with palaeolimnological reconstructions.

Sitecode	**pH**	**Alkalinity ($\mu eq\ l^{-1}$)**	**Labile aluminium ($\mu g\ l^{-1}$)**	**Total organic carbon ($mg\ l^{-1}$)**	**Acid Neutralising Capacity (ANC) ($\mu eq\ l^{-1}$)**
LAG	5.35	2	18	3.7	17.9
CE45A	4.95	-10	42	8.5	26.6
MYN	5.34	2	34	2.9	14.5
GYN	4.72	-20	33	4.1	-2.4
CZSH91	5.58	15	2	16.0	83.8
BALA	6.41	99	0	4.4	117.9
CZSH7301	6.31	43	1	4.6	62.8
CWEL	6.23	30	1	2.0	38.6
WSH6101	6.84	186	0	3.1	199.0
CZSO12	7.95	2565	2	5.4	2588

Table 4.14
Critical load data for the ten sites in the 1995 Welsh lake survey with palaeolimnological reconstructions. Shaded cells indicate predictions of critical load exceedance.

SSWC-CL = *Critical load from steady state water chemistry model*
SSWC-EX = *Critical load exceedance from the steady state chemistry model*
DCL-CL = *Critical load from the diatom model*
DCL-EX = *Critical load exceedance from the diatom model*
δDpH = *Post-1800 change in diatom inferred pH*

Sitecode	SSWC-CL	SSWC-EX	DCL-CL	DCL-EX	δDpH
LAG	2.39	-0.67	0.63	1.15	-1.11
CE45A	1.01	0.03	0.28	0.74	-1.13
MYN	1.55	-0.14	0.72	0.71	-0.22
GYN	1.58	-0.45	0.42	0.68	-0.17
CZSH91	2.71	-1.36	0.93	0.40	-0.16
BALA	3.40	-1.45	1.81	0.20	+0.14
CZSH7301	2.50	-1.24	1.14	0.11	-0.62
CWEL	2.91	-1.55	1.07	0.06	-0.57
WSH6101	4.01	-2.93	2.71	-1.64	+0.05
CZSO12	18.19	-17.03	21.36	-28.20	+0.63

Discussion

The critical load data presented from the Welsh lake survey sites suggest that 9.6% and 60% of the sites have exceeded their critical acidity loads according to the SSWC and DCL models respectively. If the survey data are scaled up to the full population of Welsh lakes they indicate that SSWC model critical load exceedance occurs at 25 out of the 255 lakes in Wales, and DCL model exceedance at 157 lakes. The predictions made on the basis of the DCL model are supported by the palaeolimnological data. At nine of the ten survey sites for which palaeolimnological data are available the diatom-inferred pH changes match the predictions of the DCL model, increasing the confidence with which the data can be interpreted. The DCL exceedance data therefore suggest that the majority (60%) of Welsh lakes have undergone chemical and biological change as a result of acid deposition.

A key feature of the results is the large discrepancy between the predictions of the two models, in particular the much smaller number of critical load exceedances predicted by the SSWC model. The two models differ in approach and the DCL model is expected to generate more critical load exceedances than the SSWC model (see Allott *et al.* 1995b). This is because the SSWC model relates the critical load to a fixed ANC_{crit} (zero in this application), whereas diatom assemblage responses can occur at any ANC value. Nevertheless, in other studies the discrepancy in exceedances between the two models has not been as pronounced. For example, in a study of lake acidification in north-west Scotland, Allott *et al.* (1995c) found that, although the DCL model gave larger exceedance values, the number of exceeded sites was similar in both SSWC and DCL applications.

The relatively low number of SSWC model exceedances is a result of the high SSWC model critical loads. The Welsh lakes have high non-marine base cation concentrations in comparison to other regions affected by acidification (Table 4.2 and see Henriksen *et al.* 1998). Pre-industrial ANC levels are therefore also likely to have been high in Wales in contrast to other regions (e.g. Scotland, southern Norway). Although significant changes in water chemistry and biology due to acid deposition have occurred in Wales, as clearly evidenced by the DCL model results and other palaeolimnological studies (e.g. Battarbee *et al.* 1988, Fritz *et al.* 1990, Simpson 1998), relatively few sites are predicted by the SSWC model to have ANC < zero at steady state with current deposition. Indeed, current measured water chemistry shows only one of the survey sites with ANC < zero.

These considerations highlight a problem with using $ANC_{crit} = 0$ for sites, such as many of the Welsh lakes, where acid loadings and non-marine base cation concentrations are both relatively high. Background ANC levels will have been well above zero at these sites and significant ANC decline due to acid deposition, with corresponding biological changes, can have occurred without a SSWC model exceedance. Whereas $ANC_{crit} = 0$ is appropriate for highly sensitive lake sites, such as those found in the north-west of Scotland or Norway, uncritical application of this threshold in the SSWC model will lead to discrepancies between exceedance and biological change in regions such as Wales.

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5. Implications of the Research for Critical Load Applications

The results presented in this report represent only a part of the wider Environmental Diagnostics programme, which will report in full in August 2000. However the three studies do have some clear implications for critical loads modelling, in particular to the application of empirical critical loads models to UK surface waters.

Reformulation of the steady state water chemistry model

A critical load exceedance with the steady state water chemistry (SSWC) model does not necessarily indicate that the critical chemical threshold (ANC_{crit}) has been crossed. The geographical distribution of critical load exceedance will not therefore necessarily correlate with current damage patterns, and this can result in problems in linking biological effects directly to critical load exceedance.

A reformulation of the SSWC model is presented in this study which allows the model to provide a direct link between deposition and water chemistry. Under this reformulation, a critical load exceedance indicates that the critical chemical threshold value is exceeded at the present time. It is recommended that this reformulated SSWC model is used for UK critical load applications where a link to current chemical or biological status is required.

Empirical statistical modelling

This study has presented an empirical statistical approach to the prediction of critical loads using nationally available datasets representing a range of catchment characteristics. In particular, the approach is developed to demonstrate the importance of region- or gradient-specific models. Although this approach needs further development, it will contribute to ongoing work on the quantification of spatial representativeness, using related techniques (including GIS), to provide inventories of the population of ecosystems and to model the distribution of critical loads and exceedances among the whole population. .

Lake acidification in Wales

Application of critical loads models to the 1995 Welsh lake survey highlights differences between the diatom critical loads (DCL) model and UK applications of the SSWC model. The DCL model indicates that 62% of the sites have exceeded their critical load, whereas the SSWC model application indicates that 9.6% of the sites are exceeded. This discrepancy is largely due to the use of ANC_{crit} = zero in the SSWC model, and highlights the problem with use of this threshold value at sites such as the Welsh lakes where acid loadings and non-marine base cation levels are both relatively high. Significant chemical change has occurred at many of the Welsh which are non-exceeded according to the SSWC model application, and the use of ANC_{crit} = zero in UK applications requires re-appraisal.

6. CLCalc : Critical Loads Calculator Operators Manual

Introduction

The Critical Loads Calculator (CLCalc) is a Visual Basic application. It is used to calculate the Henriksen's and Diatom Critical Loads and Exceedances using rainfall, deposition and water chemistry data.

PC Requirements

CLCalc can be run on any PC using Microsoft Windows 3.1/95/98/NT or 2000.

Installation

In your system directory (e.g. c:\windows\system for Windows 3.1, 95 and 98 or c:\winnt\system for Windows NT) the files vbrun300.dll and vbdb300.dll should already be present. These are provided on the ClCalc disc if this is not the case. Files grid.vx and cmdialog.vbx may not be present (these are extra Visual Basic Modules) and should be copied into your system directory. ASK YOUR SYSTEM ADMINISTRATOR FOR HELP IF UNSURE. Now copy the application (clcalc.exe) and the test data file (testdata.csv) to a directory of your choice. Now run the clcalc.exe file by double-clicking.

Operation

STEP 1: SPECIFY INPUT FILE (File / Load File)

From the File menu select 'Load file'. The input file must be in comma separated (.csv) format and contain the following information:

Site Code, Na, K, Mg, Ca, Cl, NO3, SO4, Rainfall, Runoff, S*Dep, Ndep, BC*Dep

where:

Site Code is a unique code for each record. It can have a maximum of 10 characters.
Water chemistry determinands (Na, K, Mg, Ca, Cl, NO3 and SO4), must be in the units: μeql^{-1}.
Rainfall and runoff data must be a yearly mean measured in millimetres. If the user does not have measured runoff data, 0.85*Rainfall may be used as an approximate value.
S*Dep is the total non-marine sulphur deposition measured in $keq^{-1}ha^{-1}yr$.
NDep is the total nitrogen deposition measured in $keq^{-1}ha^{-1}yr$.
BC*Dep is the total non-marine base cation deposition (Mg + Ca) measured in $keq^{-1}ha^{-1}yr$.

for example:

site01, 113, 4, 38, 67, 116, 17, 45, 3426.65, 3147.59, 1.47, 1.85, 0.75
site02, 192, 14, 42, 48, 224, 7, 82, 2286.43, 1884.43, 1.19, 1.72, 0.5

Data must be present in all fields for the critical load and exceedance calculations to run successfully. Empty fields will be interpreted as having a value of 0. No header is necessary in the data file but ensure data fields are in the correct order.

STEP 2: CALCULATE CRITICAL LOADS (Tools / Calculate critical loads)

Select 'Calculate critical loads' from the Tools menu. Critical Loads and exceedances will be calculated for EACH record in the INPUT file. The table of values will be displayed. The program will produce a table of calculated values under the following headings:

Site Code	Unique Site Reference Code
HenCL_Ac	Henriksen critical load for total acidity (keq^{-1}ha^{-1}yr)
HenEx_Ac	Exceedance of Henriksen critical load for total acidity (keq^{-1}ha^{-1}yr)
DiatCL_Ac	Diatom critical load for total acidity (keq^{-1}ha^{-1}yr)
DiatEx_Ac	Exceedance of Diatom critical load for total acidity (keq^{-1}ha^{-1}yr)
HenCL_S	Henriksen critical load for total Sulphur (keq^{-1}ha^{-1}yr)
HenEx_S	Exceedance of Henriksen critical load for total Sulphur (keq^{-1}ha^{-1}yr)
DiatCL_S	Diatom critical load for total Sulphur (keq^{-1}ha^{-1}yr)
DiatEx_S	Exceedance of Diatom critical load for total Sulphur (keq^{-1}ha^{-1}yr)

STEP 3: EXPORT CRITICAL LOADS (Tools / Export critical loads)

The table of critical loads values can be exported as comma separated text. Comma separated format has been chosen as this imports directly into Microsoft Excel and Microsoft Access. Select 'Export critical loads' from the Tools menu and follow on-screen instructions.

The process (steps 1-3) can be repeated as many times as necessary. To exit select 'Exit' from the File menu.

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