

# Critical loads for soils and freshwaters; a comparison of methods at the Plynlimon catchments

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## Abstract

International agreements aimed at reducing sulphur deposition from the atmosphere are now focused on the 'critical loads' concept. This provides a distributed link between sources and receptors of acidic oxides and also links the level of reduction with biological recovery. Methods for calculating critical loads include simple classification (Level 0), mass-balance equilibrium models (Level 1) and dynamic hydrochemical models (Level 2). Here, examples of each method are applied to headwater catchments in Plynlimon, mid-Wales. The critical loads derived are compared and the utility of the critical loads concept as a tool for local pollution control and land management is assessed.

Differences in critical load methods for soils result from assumptions regarding biological receptors. Surface water critical loads are generally similar under all methods. As a local management tool, the dynamic model is most appropriate although it has a high data requirement. The utility of other methods depends upon detailed maps of soil and vegetation being available at an appropriate scale.

## Introduction

The increase in industrial emissions of sulphur (S) and nitrogen (N) oxides to the atmosphere since the Industrial Revolution of the mid-1800s (Mylona, 1993) has led to acidification of soils and surface waters across N America and NW Europe (Martin, 1986). There is now growing concern that ecosystems in other regions of the world, notably in SE Asia, are at risk from increasing acidification in the future (Grennfelt *et al.*, 1995). The role of S in the acidification process is well understood (e.g. Reuss *et al.*, 1987) and the rate of reversal of acidification depends largely upon the underlying geology, the vegetation, the degree to which the ecosystem has already been impacted and the continuing rate of acidic deposition. The role of N has been assessed more recently (Dise and Wright, 1995); its importance is stressed by the recognition of increased N leakage in surface waters (Traaen and Stoddard, 1995). This is the result of N deposition exceeding biotic demand, referred to as N saturation, and is reported for many areas of Europe and N America (Stoddard, 1994).

The long recognition of the problem of soil and surface water acidification has prompted a series of international negotiations aimed at decreasing the flux of atmospheric emission (Murlis, 1995). These negotiations have led to

agreements to reduce emission by up to 60% of 1980 levels from large combustion sources. In general, however, the 'blanket' reduction approach did not target the most sensitive areas and the most recent agreement, signed in Oslo in 1994, was based upon the concept of critical loads. A critical load for an ecosystem is defined as 'a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge' (Nilsson and Grennfelt, 1988).

Critical loads are estimated for different components of an ecosystem based upon the damage to, or loss of, a receptor. For soils and surface waters, the most commonly targeted receptors are coniferous trees and brown trout, respectively. Chemical criteria are defined as the level at which damage to the receptor occurs and the critical load describes the level of deposition at which these criteria are achieved; if deposition is above the critical load the chemical criteria will be exceeded and damage to the receptor will occur. For soils and surface waters, for example, commonly used chemical criteria are base cation: aluminium molar ratio of 1.0 in soil water and acid neutralising capacity of 0 ueq l<sup>-1</sup>, respectively. Given the wide range of receptors, the critical load for the ecosystem is that for the

most sensitive receptor. Furthermore, given that ecosystem sensitivity varies spatially as a function of geology, land use and deposition levels, as well as other biogeochemical catchment characteristics, maps of critical loads can be produced for wide areas and emission reductions can be targeted to produce maximum benefit through the application of atmospheric transport and deposition models.

The methods used to calculate critical loads vary depending on the biological receptor chosen and the availability of data required for model application. The simplest approach requiring least data is empirical (Level 0) and incorporates a classification scheme (Nilsson and Grennfelt, 1988). Of intermediate complexity and data requirement are the equilibrium models (Level 1) including the Steady State Water Chemistry model (SSWC, Henriksen *et al.*, 1992) and First-order Acidity Balance model (FAB, Posch, 1995) for surface waters and the Simple Mass Balance Equation (SMBE, Nilsson and Grennfelt, 1988) and PROFILE model (Sverdrup and Warfvinge, 1988) for soils. Dynamic models (Level 2) require detailed catchment data and include MAGIC (Cosby *et al.*, 1985), SAFE (Sverdrup *et al.*, 1995) and SMART (Posch *et al.*, 1993).

This paper describes the application of the three levels of critical load calculation for soils and surface waters at several headwater catchments in Plynlimon, mid-Wales. The detailed time series and spatial data available in this area offer a unique opportunity critically to assess and compare the different approaches. Furthermore, this case study provides for a unique assessment of the utility of the critical loads approach as a tool for local pollution control and land management.

## Empirical Critical Loads—The Level 0 Approach

The Level 0 empirical critical load approach for soil acidity is based on an allocation of soils to classes as a function of their mineralogy (Nilsson and Grennfelt, 1988); effectively, it sets the critical load equal to the estimated annual release of base cations by bedrock weathering. It makes no allowance for the acidity produced within the soil-plant system as a result of the net uptake of base cations, nor does it allow for the potential neutralising effect of atmospheric inputs of calcium (Ca) and magnesium (Mg).

Soils are divided into five classes, defined on the basis of their dominant weatherable minerals (Hornung *et al.*, 1993). Critical loads are then assigned to these classes according to the amount of acidity which can be neutralised by base cation production from mineral weathering. The critical load for a given soil can also be adjusted, within the range of values suggested for each class, by applying modifiers to allow for the influence of texture, drainage, elevation, rainfall, land use, etc on weathering

rate (Hornung *et al.*, 1993). For example, land improvement by addition of agricultural lime increases the pool of base cations available to neutralise incoming acidity, thereby increasing the critical load to the highest class ( $>4 \text{ keq H}^+ \text{ ha}^{-1} \text{ yr}^{-1}$ ).

A major weakness in the classification, as outlined at Skokloster (Nilsson and Grennfelt, 1988) is that it does not consider peat; these soils cannot be classified on the basis of mineralogy as they consist almost entirely of organic remains in various stages of decomposition (Cresser *et al.*, 1993) and the supply of base cations in the surface layers depends on atmospheric inputs. Critical load estimates for the UK, however, include this methodology for peats (CLAG, 1995).

Within the UK, the Level 0 approach has been used to produce a national critical loads map at 1km grid scale. The critical load assigned to each 1km square is that of the dominant soil within the square. However, there is a policy need to apply critical loads methodology at a much more local scale. The catchment-based assessments undertaken here provide an opportunity to identify the potential problems of such downscaling by comparing nationally available critical loads data with those derived at a much finer scale of resolution.

### APPLICATION TO PLYNLIMON

The soils of the Plynlimon catchments fall within 5 main Soil Series (Table 1) supplemented by complexes consisting of two or more Series. In addition to bare rock and soils, other surficial deposits consist of scree, valley alluvium and disturbed ground. A critical load was assigned to each soil series (Table 2) using the same approach as the UK national mapping exercise (Hornung *et al.*, 1993). The four Soil Series comprised of mineral soils were assigned to critical load class 4 ( $0.2\text{--}0.5 \text{ keq H}^+ \text{ ha}^{-1} \text{ yr}^{-1}$ ) whilst the deep peats (Caron Series) were placed in class 5 ( $<0.2 \text{ keq H}^+ \text{ ha}^{-1} \text{ yr}^{-1}$ ). The disturbed ground which results from historic mining activity and consists of calcite-rich mine waste was assigned to class 1 ( $>4.0 \text{ keq H}^+ \text{ ha}^{-1} \text{ yr}^{-1}$ ) although it occupies only 7.1% of the Nant Iago catchment and is, therefore, spatially insignificant. Large areas of the catchments are characterised by various complexes of the soil series. Since the exact proportions of peat forming the complexes were not known, they were all assigned the critical load range of  $0.2\text{--}0.5 \text{ keq H}^+ \text{ ha}^{-1} \text{ yr}^{-1}$ . The effect of upland improvement by liming within the Cyff and Nant Iago subcatchments was ignored, in line with the national mapping programme.

The distribution of soil series and critical loads within the catchments (Table 2) indicates that only in the cases of the Hafren and Gwy are the most sensitive soil types also the dominant ones. In other catchments, the most sensitive soil occupies a very large proportion of the catchment (30–40%) with the exception of the Cyff, where the proportion of peat is 10%. Thus, reducing acid deposition

Table 1. Soil series within the Plynlimon catchment (after Newson 1976).

Series	Description
CARON	peat generally exceeding 35 cm thickness, but including land from which peat has been eroded near hags.
DROSGOL	peaty podzolised soils usually with strongly developed thin iron pan. Sub-pan characters range from a dark brown humus-rich loam to strongly gleyed silty clay.
HIRAETHOG	peaty podzolised soils usually with well developed thin iron pan over a diffuse ochreous horizon of strongly silty clay loam.
MANOD	slightly podzolised acid brown soils.
YNYS	peaty gleyed soil.
VALLEY complex	includes alluvium and most of the soils of the region occurring in complex close to streams and associated with the steep sides of locally incised valleys.
Disturbed Ground	isused mines where the workings on the surface cover significant area.

Table 2. Distribution of soil series and Level 0 critical loads within the Plynlimon catchments.

Soil series	Critical load keq H <sup>+</sup> ha <sup>-1</sup> yr <sup>-1</sup>	Catchments (percentage of area)					
		Hafren	Hore	Tanllwyth	Cyff	Gwy	Nant Iago
CARON	<0.2	58.1	29.8	38.2	10.6	38.3	32.4
DROSGOL	0.2–0.5	2.9	2.0			1.2	
HIRAETHOG	0.2–0.5	21.3	30.2	41.8	35.1	20.7	50.9
MANOD	0.2–0.5				11.0	0.2	
YNYS <sup>1</sup>	0.2–0.5						
ALLUVIUM	0.2–0.5	9.7	6.9	12.9	11.5	9.7	0.4
DISTURBED GROUND	>4.0						7.1
COMPLEXES	0.2–0.5	8.0	30.5	7.1	31.7	29.6	9.1

<sup>1</sup> Only occurs as a complex with other soils

to the amount equivalent to the critical load of the dominant soil would leave 30–40% of the soils in the Tanllwyth, Hore and Nant Iago and about 10% of the Cyff soils unprotected and liable to continued acidification.

The local, catchment-based assessments have also been compared to empirical critical loads derived using data from the UK national 1km critical load map. To do this, the fraction of each grid square falling within each catchment boundary was aggregated by critical load class and summarised as a percentage of the total catchment area (Table 3). Comparison of the UK national and catchment scale critical loads shows that, with the exception of the Gwy, the national map identifies, correctly, the dominant critical load class within each catchment. In all cases, the national map makes no attempt to quantify the proportion of the most sensitive critical load class.

## Steady State Critical Loads—The Level 1 Approach

The level 1 approach to critical load calculation applies the mass balance equations to calculate the balance between sources and sinks of acidity in a catchment. The net result of this balance is related to the critical load which can then be set equal to the pollutant input at which the critical chemical value for a given receptor is not transgressed. Mass balance equations have been developed for both soils and water and incorporate both S and N.

### THE STEADY-STATE WATER CHEMISTRY (SSWC) METHOD

The SSWC method (Henriksen *et al.*, 1992) assumes a steady state situation between mean annual chemical input

Table 3. Level 0 critical loads for the Plynlimon catchments derived from the UK national 1 km critical loads map.

Critical load keq H <sup>+</sup> ha <sup>-1</sup> yr <sup>-1</sup>	Catchment (percentage of area) UK National 1 km critical loads map					
	Hafren	Hore	Tanllwyth	Cyff	Gwy	Nant Iago
<0.2	54	25	7	0	14	0
0.2–0.5	46	75	93	100	86	100
>0.4	0	0	0	0	0	0

Critical load keq H <sup>+</sup> ha <sup>-1</sup> yr <sup>-1</sup>	Catchment based estimates					
	Hafren	Hore	Tanllwyth	Cyff	Gwy	Nant Iago
<0.2	58	30	38	11	38	32
0.2–0.5	42	70	62	89	62	61
>4.0	0	0	0	0	0	7

and output fluxes. The basis of the method is that excess base cation production in the catchment should be equal to or greater than the acidic anion input, so maintaining ANC above the level selected for any receptor, such that:

$$CL = ([BC]_o^* - [ANC_{lim}]) \cdot Q - [BC]_d^* \cdot R$$

where:

- CL = critical load (meq m<sup>-2</sup>)
- \* = indicates non-marine component
- [BC]<sub>o</sub> = base cation concentration prior to acidification (ueq l<sup>-1</sup>)
- ANC<sub>lim</sub> = critical ANC concentration for a given receptor (ueq l<sup>-1</sup>)
- [BC]<sub>d</sub> = base cation concentration in precipitation (ueq l<sup>-1</sup>)
- Q = runoff (m)
- R = rainfall (m)

Simple empirical relationships are invoked to estimate the value of [BC]<sub>o</sub> (CLAG, 1995). Defined in terms of total acidity (S + N), the exceedance of the critical load is then given by:

$$EX_{AC} = S_{dep} + N_{leach} - CL$$

where:

- EX<sub>AC</sub> = exceedance of the critical load of acidity
- S<sub>dep</sub> = present day S deposition
- N<sub>leach</sub> = the mass balance of present day N deposition minus all N sinks within the catchment.

#### APPLICATION TO THE PLYNLIMON CATCHMENTS

Critical loads and exceedances have been calculated for the Cyff, Gwy, Hafren, Nant Iago, Hore and Tanllwyth catch-

ments using flow weighted annual mean stream water chemistry. For the Hore and Tanllwyth, data were selected to cover the pre-felling period because clear-felled areas are replanted again as part of normal forest-management practice and critical load methodology assumes a long-term, steady-state approach. Atmospheric inputs of non-marine S, total N and excess base cation concentrations in rain were estimated from 4 years of bulk precipitation data (Neal *et al.*, 1996) and annual rainfall and runoff amounts are the mean of 4 years of observation (1990–1994).

Critical loads of S (Table 4) are similar for the acid moorland Gwy catchment and the three forest streams although the Hafren is the most acid-sensitive stream and the closest to critical load exceedance. A bedrock Ca source is thought to account for the higher critical load in the Hore catchment compared to the Hafren, despite the former having a larger proportion of forest cover (c.70% as compared to c.54% in the Hafren). However, such factors cannot explain the relatively high critical load in the Tanllwyth which has 100% forest cover and is dominated by acid peaty gley soils. The high critical load in the Nant Iago results from the occurrence of calcite in the bedrock which buffers streamwater acidity (Reynolds *et al.* 1986). The presence of lead and zinc sulphide veins also provide a weathering source of S resulting in high pre-acidification excess SO<sub>4</sub> concentration compared to excess base cation concentration. In consequence, the critical load value is not as high as anticipated given the large present-day streamwater excess base cation concentration ([BC]<sub>t</sub><sup>\*</sup> = 209 μeq l<sup>-1</sup> in the Nant Iago compared to 60 μeq l<sup>-1</sup> in the Gwy). Within the Cyff catchment, the presence of calcite in the bedrock and agricultural liming combine to give base-rich streamwaters ([BC]<sub>t</sub><sup>\*</sup> = 109 μeq l<sup>-1</sup>) and a critical load approximately double that of the adjacent Gwy.

Table 4. Critical loads of S and total freshwater acidity and exceedance values calculated using the SSWC for the Plynlimon subcatchments.

Sulphur acidity	Cyff	Gwy	Nant Iago	Hore	Hafren	Tanllwyth
Critical load	2.00	1.00	3.26	1.10	0.65	1.14
Exceedance	0	0	0	0	0	0
Total acidity	Cyff	Gwy	Nant Iago	Hore	Hafren	Tanllwyth
Critical load	1.89	0.95	2.92	0.91	0.57	0.87
Exceedance	0	0	0	0.25	0.39	0.67

Calculated critical loads of total acidity (S + N) are slightly lower than for S alone (Table 4) since more base cations are lost due to the additional NO<sub>3</sub> leaching and, hence, the pre-acidification excess base cation concentration is reduced. The streams draining forested sites have lower critical loads for total acidity and higher NO<sub>3</sub> leaching than the streams draining the grassland catchments. Elsewhere in Wales, mature trees over 35 years old have a reduced demand for N, which results in greater rates of N leaching (Emmett *et al.*, 1995). Critical loads of total acidity are exceeded in the forest sites by the current wet deposition of S and N although S critical loads are not exceeded. The Gwy is close to exceedance for total acidity, but is not exceeded for S. These results indicate that N is important in the acidification of these systems, particularly for forests. It should also be remembered that only wet deposition data have been considered in the critical load and exceedance calculations. Dry and occult inputs enhance S and N deposition significantly, especially to the forest (Reynolds *et al.*, in press) and particularly for dry deposited ammonia. This is associated with a relatively small increase in non-marine base cation inputs through occult deposition and, consequently, critical load exceedances are likely to be greater than the values indicated here, especially in the forested streams.

## The First-Order Acidity Balance (FAB) Method

While the SSWC model assumes that current N leaching represents a steady-state condition, it is not known whether catchments have been subjected to elevated N deposition for a long enough period to achieve steady state. Alternatively the major potential sinks for N and S deposition in a catchment can be quantified and a critical load function for total acidity defined through a simple mass-balance equation, again assuming steady state conditions. Since the S and N components of acid deposition are affected by different catchment processes, they cannot be considered together when balancing inputs with sinks in calculating a critical load. Separate critical loads for N and S, therefore, have to be combined into the critical load

function. This approach forms the basis of the FAB model (Posch, 1995).

The formulation of the FAB model is adapted for application to streams assuming that denitrification is a function of N deposition. The charge balance for the stream and catchment is:

$$N_{\text{dep}} + S_{\text{dep}} = fN_{\text{upt}} + N_{\text{imm}} + N_{\text{den}} + BC_1 - ANC_1$$

$N_{\text{dep}}$  = total 'potentially acidifying' N deposition

$S_{\text{dep}}$  = total S deposition

$N_{\text{upt}}$  = net growth uptake of N by forest vegetation

$N_{\text{imm}}$  = immobilization of N in catchment soils

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

$BC_1$  = base cation leaching from catchment

$ANC_1$  = ANC leaching from catchment

$f$  = fraction of forested area in the catchment

All units are expressed in equivalents per unit area and time and it is assumed that any NH<sub>4</sub><sup>+</sup> deposition that is not retained in the soil/plant biomass is nitrified to NO<sub>3</sub><sup>-</sup> and, hence, is 'potentially acidifying' (Posch *et al.*, 1993).

### APPLICATION TO THE PLYNLIMON CATCHMENTS

The net growth uptake of N in forest biomass ( $N_{\text{upt}}$ ) is a sink for N in the long term and is removed during harvesting of the forest. The biomass removed per unit area is divided by the harvest cycle (in years) to provide average annual net flux of N out of the catchment. Emmett and Reynolds (1996) report a range of N removal rates in bolewood for Sitka spruce stands of Yield Class 6 to 24 (mean annual volume increment of stemwood in m<sup>3</sup> ha<sup>-1</sup>) and bolewood N concentrations from 0.06 to 0.10 per cent N, of 1.0–8.5 kgN ha<sup>-1</sup> yr<sup>-1</sup>. Assuming an average Yield Class of 10 for Sitka spruce at Plynlimon, a mid-range bolewood N concentration of 0.08 per cent and a harvest interval of 40 years, interpolation of the above figures gives a value for  $N_{\text{upt}}$  of 2.5 kgN ha<sup>-1</sup> yr<sup>-1</sup>. It is assumed that there is no net growth uptake over the long term in other 'non-harvested' vegetation types.

The long-term immobilization rate ( $N_{\text{imm}}$ ) is calculated from chronosequence studies in which the total amount of

accumulated N in a soil profile is divided by the assumed period of soil formation to give an annual figure. There are wide variations in estimates for this figure, from 0.5–1.0 kgN ha<sup>-1</sup> yr<sup>-1</sup> in certain natural systems, up to 3–10 kgN ha<sup>-1</sup> yr<sup>-1</sup> in aggrading systems and a working range of 2–5 kg ha<sup>-1</sup> yr<sup>-1</sup> has been proposed for critical load calculations (Posch *et al.*, 1995). As a result of elevated N deposition, shorter term studies have revealed immobilization rates which are higher than long-term rates, the upper value of this range (5 kgN ha<sup>-1</sup> yr<sup>-1</sup>) was selected for this study.

N immobilization and growth uptake are faster processes than denitrification (Posch, 1995) and assuming that denitrification is linearly related to the net input of N into the soil system:

$$N_{den} = f_{de} (N_{dep} - N_{imm} - fN_{upt})$$

where,  $f_{de}$  is the 'denitrification fraction', with a value between 0 and 1, ascribed to the catchment soils. The denitrification fraction is derived by interpolation of values reported for peat and non-peat soils (de Vries *et al.*, 1993) such that:

$$f_{de} = 0.1 + 0.7 f_{peat}$$

where,  $f_{peat}$  is the fraction of the catchment with a peat soil (Caron series) cover; this drives the denitrification term at Plynlimon.

The input data for application of the FAB model are the proportion of forest cover, the proportion of peat soils (Caron series), and the critical base cation leaching ( $L_{crit}$ ) defined by the SSWC model. The critical load function for freshwater is then constrained by:

$$CL(S) = L_{crit} \quad (\text{Critical load for S})$$

$$CL_{max}(N) = fN_{upt} + N_{imm} + (L_{crit} / (1 - f_{de}))$$

('Maximum' critical load for N)

$$CL_{min}(N) = fN_{upt} + N_{imm}$$

('Minimum' critical load for N)

If S deposition is greater than CL(S) then S alone will exceed the critical load and acidification will occur—likewise if total N deposition is greater than  $CL_{max}(N)$  then N alone will cause critical load exceedance and acidification. For levels of total N deposition below  $CL_{min}(N)$ , all N

deposition is either taken up by forest vegetation or immobilized in the soil microbial biomass. Where  $N_{dep} < CL_{max}(N)$  and  $S_{dep} < CL(S)$ , critical load exceedance (CL(EX)) is dependent on both  $N_{dep}$  and  $S_{dep}$  as defined by:

$$CL(EX) = (1 - f_{de})N_{dep} + S_{dep} - f(1 - f_{de})N_{upt} - (1 - f_{de})N_{imm} - L_{crit}$$

Application of the FAB model to the Plynlimon catchments defines a series of critical load functions (Table 5). The Afon Hafren is the most sensitive catchment with the lowest critical load constraints and comes closest to exceedance because of the very low value of pre-industrial base cation leaching. The Nant Iago catchment is the least sensitive, as indicated by the high values of  $CL_{max}(N)$  and  $CL(S)$ , which reflect the high base cation concentrations attributed to the presence of calcite veins in the bedrock.

#### THE SIMPLE MASS BALANCE EQUATION (SMBE) CRITICAL LOAD OF ACIDITY FOR SOILS

For soils, the Level 1 approach uses a simple mass balance equation to set the critical load with respect to a critical chemical limit within the rooting zone for a chosen biological indicator, generally fine roots (Sverdrup and de Vries, 1994). In the SMBE, the critical load of actual acidity (CL(A)) is defined by the available sources of alkalinity in the soil-plant system, independent of landuse and deposition such that;

$$CL(A) = BC_w - ANC_{Lcrit}$$

where  $BC_w$  = weathering rate of Ca+Mg+K (keq ha<sup>-1</sup> year<sup>-1</sup>) and the limiting ANC leaching term ( $ANC_{Lcrit}$ ) is defined by the maximum permitted leaching of H<sup>+</sup> and Al<sup>3+</sup>;

$$ANC_{Lcrit} = -H^+_{crit} - Al^{3+}_{crit}$$

where,  $Al^{3+}_{crit}$  = the critical or limiting inorganic aluminium flux (keq ha<sup>-1</sup> year<sup>-1</sup>) and  $H^+_{crit}$  = the critical or limiting H<sup>+</sup> flux (keq ha<sup>-1</sup> year<sup>-1</sup>). This definition is valid only for acid soils (soil solution pH < 5.0), where the concentration of bicarbonate is negligible. Furthermore, it is assumed that the concentration of organic acids is also negligible, as these will contribute to soil solution ANC.

Table 5. Constraints on the critical load function for the Plynlimon catchments.

Site:	CL <sub>max</sub> (N)	CL <sub>min</sub> (N)	CL(S)	N leaching	Exceedance
Cyff	2.94	0.36	2.13	0.04	0
Gwy	2.16	0.36	1.14	0.04	0
Hafren	2.06	0.45	0.79	-0.02	0
Hore	2.27	0.48	1.23	-0.04	0
Nant Iago	5.41	0.36	3.40	0.05	0
Tanllwyth	2.56	0.54	1.28	-0.06	0

All units in keq H<sup>+</sup> ha<sup>-1</sup> yr<sup>-1</sup>.

Given these assumptions,  $Al^{3+}_{crit}$  is commonly set with reference to the critical molar  $(Ca+Mg+K)/Al_{crit}$  ratio in the soil solution for the plant species of interest (Sverdrup and de Vries 1994). The critical concentration of  $Al^{3+}$  ( $[Al^{3+}_{crit}]$ ) can be determined from this ratio provided the concentration of available base cations in the soil solution within the rooting zone is known. The latter is determined by a mass balance of base cations derived from atmospheric deposition and weathering versus those taken up by the vegetation and those leached from the soil. The critical  $H^+$  concentration ( $[H^+_{crit}]$ ) is calculated using a Gibbsite equilibrium relationship and  $[Al^{3+}_{crit}]$ . The values of  $[Al^{3+}_{crit}]$  and  $[H^+_{crit}]$  are converted to fluxes by multiplying by the runoff volume.

A major difference between the Level 0 and Level 1 approaches for soils is that the latter permits a critical load to be set for a particular habitat type defined by a soil-vegetation combination. In principle, providing a critical  $(Ca+Mg+K)/Al_{crit}$  ratio can be specified for an indicator plant species within a chosen habitat, the critical load can be calculated given data on base cation weathering rates, net base cation uptake, water flux and leachate base cation concentration.

#### APPLICATION TO THE PLYNLIMON CATCHMENTS

The availability of detailed soils and vegetation data for Plynlimon means that CL(A) can be calculated for the main soil-vegetation combinations present within the catchments. To provide a manageable data set, some simplification of the vegetation map (Newson, 1976) was undertaken. Vegetation types were combined into; plantation forest, improved grassland, heath, mires (comprising mesotrophic mires and mesotrophic grass) and acidic grassland (comprising montane *Festuca* and acidic grass). Each vegetation group was assigned the  $(Ca+Mg+K)/Al_{crit}$  ratio of a characteristic or dominant plant species using data provided by Sverdrup and Warfvinge (1993). The forest area is dominated by Sitka spruce ( $(Ca+Mg+K)/Al_{crit} = 0.4$ ) whilst improved grassland is characterised by *Lolium perenne* ( $(Ca+Mg+K)/Al_{crit} = 0.5$ ). Heath refers to *Calluna* ( $(Ca+Mg+K)/Al_{crit} = 0.8$ ) dominated communities, *Juncus* ( $(Ca+Mg+K)/Al_{crit} = 0.3$ ) was used as the characteristic species for mire vegetation and acidic grassland was characterised by *Agrostis* ( $(Ca+Mg+K)/Al_{crit} = 1.0$ ). In reality, the acid grass in the Wye catchment is dominated by *Nardus-Festuca* species but, since the relevant  $(Ca+Mg+K)/Al_{crit}$  ratio for *Nardus str.* (Sverdrup and Warfvinge, 1993) is very high (10), it was rejected lest it refer to some different, very acid-sensitive ecotype.

Soil weathering rates were derived from the Level 0 critical loads, described previously, with each soil type being assigned a weathering rate equal to the midpoint of the Level 0 critical load class. In reality, this provides two groups; i) peat represented by a weathering rate of 0.1 keq

$H^+ ha^{-1} yr^{-1}$ , and; ii) all other soil associations and complexes with a weathering rate of 0.35 keq  $H^+ ha^{-1} yr^{-1}$ . The disturbed ground, which has a very high weathering rate, has been ignored since it occupies only a small proportion of the Nant Iago catchment. Peats were assigned a value of 0.1 keq  $H^+ ha^{-1} yr^{-1}$  rather than zero as in the UK national map so as to reflect the variable depth and mineral content of these soils at Plynlimon.

Modelled atmospheric deposition inputs to the Hafren, Cyff and Gwy catchments for the period 1987–88 incorporating, for base cations, seeder-feeder enhanced wet deposition and cloud water deposition plus, for sulphur, dry deposition of  $SO_2$ , were utilised (Reynolds *et al.*, in press). As this represents the best available estimate of deposition to these catchments, these data have been used as input to the SMBE. The non-marine component of base cation deposition was used in all CL(A) calculations and, in the case of the Hafren catchment only, different values for base cation deposition were used for forest and grass species to account for 'scavenging effects'.

Within the SMBE, other parameter values were assigned as follows. Net base cation uptake by the vegetation was assumed to be zero for semi-natural and improved grassland. For Sitka spruce, uptake was estimated from a regression relationship between Yield Class and base cation uptake (Miller *et al.*, 1993). This provided an uptake of 0.278 keq  $ha^{-1} yr^{-1}$  assuming an average Yield Class of 10 for Sitka spruce at Plynlimon. The annual soil water flux below the rooting zone was estimated as rainfall/1.15 (area-weighted mean annual rainfall for 1987–88) for the sites Hafren, Cyff and Gwy. To allow for a quantity of base cations within the rooting zone to be unavailable for plant uptake due to physiological limitations the SMBE includes a term here set to a default value of 2  $\mu eq l^{-1}$  (Sverdrup and deVries, 1994). The relationship between  $H^+$  and inorganic  $Al^{3+}$  is determined by a simple gibbsite equilibrium within the SMBE. The widely used default gibbsite equilibrium constant is  $K_{gibb} = 300 m^6 eq^{-2}$ , which corresponds to  $pK_{gibb} = -8.5$ .

Digital maps of soil weathering rates and vegetation groups were overlaid to produce a single map representing unique soil / vegetation combinations. The SMBE was then solved for each combination within the Hafren, Gwy and Cyff catchments as these had the best atmospheric input data. The SMBE was not solved for improved grassland since, due to the effects of liming,  $BC_w \gg 0.2$  keq  $H^+ ha^{-1} yr^{-1}$  and thus, the entire area of *Lolium pe.* was given a critical load of 4 keq  $H^+ ha^{-1} yr^{-1}$ . Excess S deposition was estimated for each catchment as an area-weighted average figure.

The critical loads for the soil-vegetation combinations in each catchment (Table 6) are very variable both within and between catchments. For example, within the Hafren, all vegetation types occur on both soil types (peat and other soil associations) and the lowest CL(A) is assigned only to a small proportion of peat covered with coniferous forest

(c. 16% of the total catchment area). The most acid-tolerant species, *Juncus*, is characterised by the highest critical load value. Complete protection for the entire soil/vegetation system within a specified area is achieved only if the critical load is set to the value of the most sensitive soil/vegetation combination. In this respect, the average excess S input to the Hafren catchment as a whole exceeds the SMBE critical loads values for the entire area under coniferous forest and for acid grass growing on the peat, which in total amounts to 73.1% of the catchment (Table 6). Complete protection would be achieved if the deposition of acidity was reduced to the critical load of the forest growing on the peat (16.1% of the total catchment area). However, this represents an extremely acid-sensitive combination which is probably not sustainable in terms of commercial forestry.

The entire Cyff catchment is protected with regard to

acidifying inputs of S. The smallest critical load value is for *Agrostis* species growing on the peat and occupying only 1.5% of the entire catchment. Similarly, the Gwy catchment is completely protected with the exception of a minor proportion of peat covered with forest (less than 1%). Neglecting this proportion, complete protection would require acid inputs to be no greater than CL(A) for *Agrostis* species growing on the peat (23.80% of the area).

#### DYNAMIC MODELLING OF CRITICAL LOADS—THE LEVEL 2 APPROACH

Dynamic models offer an opportunity to determine the level of deposition reduction required to achieve a given soil or water target chemistry, for example surface water ANC of zero  $\mu\text{eq l}^{-1}$ , within a given time scale. In this respect, the Level 0 and 1 approaches detailed earlier sim-

Table 6. CL(A) values for soil-vegetation combinations occurring within the Hafren, Cyff and Gwy subcatchments. The soil types are characterised by two weathering rates of 0.1 (denoted by \*) and 0.2  $\text{keqH}^+\text{ha}^{-1}\text{yr}^{-1}$  (denoted by #).

Catchment	Vegetation	Species	Critical Load $\text{keqH}^+\text{ha}^{-1}\text{yr}^{-1}$	Proportion of the catchment (%)	
Hafren	conifers	Sitka sp.*	0.10	16.1	
		Sitka sp.#	1.18	37.7	
	heath	<i>Calluna</i> *	1.55	17.8	
		<i>Calluna</i> #	1.86	2.17	
	acid grassland	<i>Agrostis</i> *	1.38	19.3	
		<i>Agrostis</i> #	1.65	1.18	
	mires	<i>Juncus</i> *	2.79	4.80	
		<i>Juncus</i> #	3.34	0.89	
	Cyff	acid grassland	<i>Agrostis</i> *	1.15	1.50
			<i>Agrostis</i> #	1.44	26.02
improved grassland		<i>Lolium</i> *	>3.5	3.30	
		<i>Lolium</i> #	>3.5	34.79	
acid heath		<i>Calluna</i> *	1.29	0.50	
		<i>Calluna</i> #	1.62	2.73	
mires		<i>Juncus</i> *	2.24	5.30	
		<i>Juncus</i> #	2.79	25.85	
Gwy	acid grassland	<i>Agrostis</i> *	1.18	23.80	
		<i>Agrostis</i> #	1.46	33.48	
	improved grassland	<i>Lolium</i> *	>3.5	2.10	
		<i>Lolium</i> #	>3.5	10.06	
	forest	Sitka sp.#	0.20	0.13	
		acid heath	<i>Calluna</i> *	1.31	4.90
	<i>Calluna</i> #		1.63	8.25	
	mires	<i>Juncus</i> *	2.27	7.50	
		<i>Juncus</i> #	2.84	10.7	



Table 7. A comparison of critical loads ( $\text{keq ha}^{-1} \text{yr}^{-1}$ ) calculated using each approach. The range of MAGIC critical loads at the Hafren reflect the two future afforestation scenarios.

	Level 0 Empirical	Level 1 SSMB	Level 1 SSWC (S)	Level 1 SSWC (Acidity)	Level 1 FAB (S)	Level 2 MAGIC (S)	
						Water	Soil
HAFREN	<0.2–0.5	0.1–1.86	0.65	0.57	0.79	0.54–0.97	0–0.7
HORE	<0.2–75		1.1	0.91	1.23		
TANLLWYTH	0.2–0.5		1.14	0.87	1.28		
CYFF	0.2–0.5	1.44–>3.5	2.0	1.89	2.13		
GWY	0.2–0.5	1.18–>3.5	1.0	0.95	1.14	1.02	0.74
IAGO	0.2–0.5		3.26	2.92	3.4		

ply relate critical load to some future predicted atmospheric deposition and yet soil and surface water acidity may not recover for many years following achievement of the critical load. Dynamic models can determine the time lag involved and quantify the degree of impact in areas where the critical load is predicted to continue to be exceeded. The MAGIC model (Cosby *et al.*, 1985) is applied to the two major sub-catchments at Plynlimon, the Hafren and the Gwy.

MAGIC is a dynamic, process-oriented model which utilises a lumped approach in that only the key chemical and biological processes which determine soil and surface water acidity are considered and the spatial heterogeneities of soil and vegetation characteristics are aggregated into one or two soil layers. The model is described fully in Cosby *et al.* (1985) and has been applied extensively in the UK (Jenkins *et al.*, 1994) and Europe (Jenkins *et al.*, 1997).

#### APPLICATION TO THE PLYNLIMON CATCHMENTS

The model has been applied to the Hafren and Gwy using a one soil-layer structure for surface water critical load and a two soil-layer structure for soil critical load. For the two layer calibration, the soil is lumped both spatially and with depth such that the upper layer represents the organic surface horizons and the lower layer represents the deeper B and C horizons. Model calibrations use the best available data on soils, vegetation history, deposition history and water chemistry (Jenkins *et al.*, 1997). Future land use policy is incorporated in the model at the Hafren by assuming that the forest is felled at age 50 years and replanted immediately. Critical loads are calculated for surface water and soil as the required change in S deposition, effected immediately, to achieve  $\text{ANC} = 0 \mu\text{eq l}^{-1}$  in surface water and a soil solution base cation aluminium molar ratio of 1.0 within 50 years, respectively. For the two layer structure, the soil critical load is calculated for the upper organic horizon. Nitrogen is incorporated in the model as

a simple net retention at each time step (zero order uptake) and this is assumed to continue at the present rate in the future. The critical loads calculated, therefore, are essentially for total acidity. If, on the other hand, the forest is not replanted, considerably higher critical loads are predicted (Table 7).

The dynamic response to S deposition reductions is shown in Figure 1. Under the MAGIC—calculated critical load and using the forest replanting scenario, ANC is stabilised into the future implying that the impact of the second rotation forest is compensated by the reduction in S deposition. Reduction in S deposition to the level prescribed by the SSWC critical load causes in a marked decrease in ANC with zero ANC ( $\mu\text{eq l}^{-1}$ ) predicted by 2020.

The predicted response of ANC under the most recently agreed emissions reduction strategy (the Oslo Protocol) is yet more pessimistic and implies severe acidification with ANC falling below zero ( $\mu\text{eq l}^{-1}$ ) by 2005. If, on the other hand, the alternative land management strategy is assumed, under the SSWC critical load, recovery is marked and rapid (Figure 1).

The calculated critical loads for the Hafren are lower than for the Gwy (Table 4) as a consequence of the commercial forest plantation which exerts an acidifying affect. The critical load of zero for the soil at the Hafren indicates that even if S deposition were reduced to pre-acidification levels, the soil would not recover to the chemical target within 50 years. This is due to the assumed reforestation and implies that in the long-term, commercial forestry at this site is not sustainable due to low base-cation weathering rates. This result requires more rigorous analysis and is the subject of a further study (Jenkins and Neal, in preparation).

## Discussion

Comparing the different critical load calculation methodologies is made difficult by the different assumptions

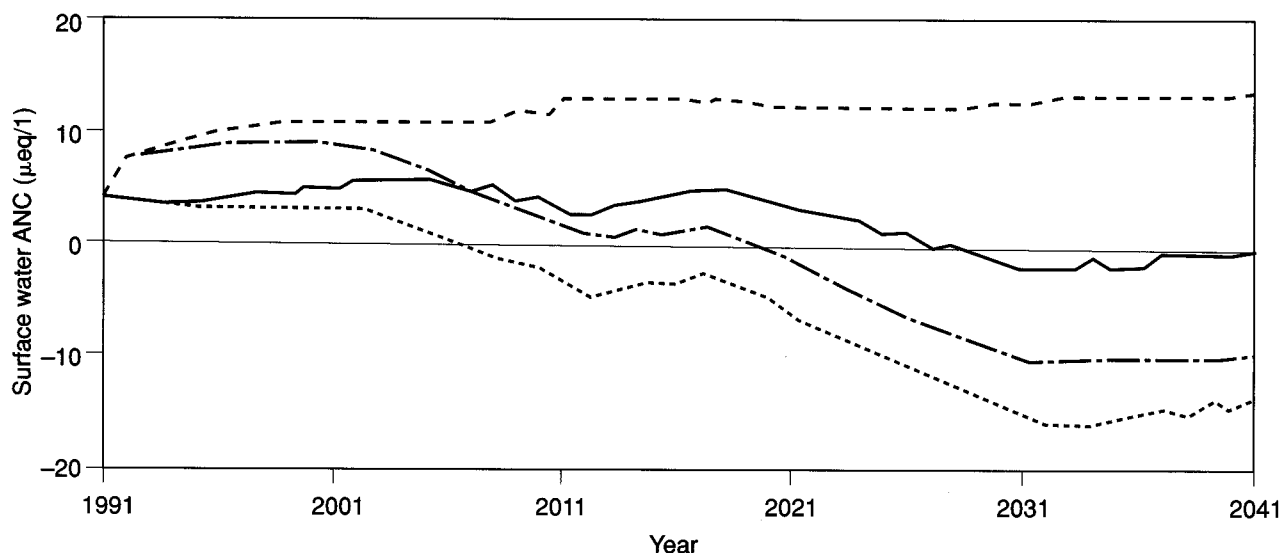


Fig. 1. The MAGIC predicted stream water (ANC ( $\mu\text{eq l}^{-1}$ )) under different S deposition loads and land use scenarios at the Afon Hafren; MAGIC calculated critical load to achieve ANC = 0 within 50 years under a second rotation forest (—); SSWC calculated critical load and second rotation forest (---); SSWC calculated critical load and no future planting (- · - · -); Oslo protocol deposition and second rotation forest (·····).

regarding steady state conditions, chemical targets and the way in which N is included. Nevertheless, it is clear that the soils level 0 approach produces the lowest critical loads but shows very little variation across the sites (Table 7). This inter-site variation is captured better by the water chemistry methods which produce critical loads that are consistent with the known geochemistry of the sites.

#### COMPARISON OF SOIL APPROACHES

Reducing acidic deposition to the national or locally derived Level 0 critical load will provide protection for all soil/vegetation combinations occurring within the studied sites according to the SMBE model. This is an inevitable consequence of the different methodologies and highlights a major conceptual difference in the two approaches. An underlying assumption of the SMBE is that the  $(\text{Ca}+\text{Mg}+\text{K})/\text{Al}_{\text{crit}}$  ratio must have a value which will result in  $\text{ANC}_{\text{Lcrit}}$  remaining negative. A consequence of this and of the definition of CL(A) is that the SMBE critical load will always be numerically greater than the weathering rate. The Level 0 classification for mineral soils allows no ANC leaching and the empirical critical load approximates closely to the weathering rate. By implication therefore, the SMBE critical load will always be greater than the Level 0 critical load. The Level 0 approach sets the critical load with reference to selected inherent chemical and physical properties of the soil to prevent chemical changes occurring within the soil in response to pollutant deposition. As such it represents a 'precautionary approach'. The SMBE adopts an 'ecosystem approach' by setting the critical load with respect to a critical chemical limit or threshold for a chosen target organism. Depending on the sensitivity of this target

organism, chemical changes in the soil and / or damage to other ecosystem components may occur before the critical chemical limit is transgressed.

The dynamic model is aimed at chemical targets in the soil but is apparently inappropriate at the Hafren due to the assumptions made regarding base cation uptake to the growing forest. At the Gwy, the MAGIC critical load is lower than that for level 1 but higher than that for level 0. This is probably due to the low N immobilisation used in MAGIC to match the high current leaching of N which is assumed to continue into the future.

#### COMPARISON OF SURFACE WATER APPROACHES

All three surface water approaches produce consistent results across the range of catchments (Table 7). The SSWC method for total acidity is consistently the lowest as a result of the assumptions relating to N leaching.

Because of the FAB-prediction of low  $\text{NO}_3$  leaching at these forested sites, none of the Plynlimon catchments shows critical load exceedance according to the FAB model for total acidity. This is in contrast with the SSWC model which indicates exceedance at the Hore, Hafren and Tanllwyth. This low prediction of nitrate leaching, may relate to either the deposition estimates or to the values attributed to the sink terms.

Since dry deposition of N is excluded from the input estimates to the catchments, it might be expected that  $\text{NO}_3$  leaching would be low even if the N sink terms could be quantified accurately. Nitrate leaching is predicted by the FAB model at the unafforested sites, so the N sinks are not large enough to retain all the wet deposited N and the inclusion of dry deposited N would increase the predicted leaching. However, dry and occult inputs of S are known

to be enhanced in the forest at Plynlimon (Reynolds *et al.*, in press) so the omission of dry and occult inputs of N will have a larger effect on the predicted leaching from the forested catchments.

Although the inclusion of dry and occult deposition would account, at least in part, for the predicted low NO<sub>3</sub> leaching, it is also possible that the values allocated to the sink terms are inaccurate. The negative values for N leaching at forested sites (Table 5) indicate that the assumed sinks for N are greater than the actual inputs, implying that the values used for N<sub>upt</sub>, N<sub>imm</sub> or N<sub>den</sub> are over-estimates. N<sub>imm</sub> may be too large because the higher value within the default range was selected, and indeed the leaching predicted at all the catchments does appear to be very low. However, denitrification values are assumed to be negative in forested areas and very low for unafforested areas, implying that the problem lies in the other sink terms and not N<sub>den</sub>. Since only the sites with forest cover within their catchments show negative values for N leaching, the N<sub>upt</sub> term may be too large. A possible explanation is the age of the forest stands at these sites: the mean net N uptake is calculated over the whole forest growth cycle, but uptake decreases with age and will, therefore, be lower than the mean when the forest is mature. This promotes enhanced NO<sub>3</sub> leaching with age which reduces the SSWC critical load for total acidity when calculated using present day chemistry.

The results from MAGIC are consistent with the steady state methods although they vary with land use assumptions. This similarity with the equilibrium time scale approaches indicates that considerable recovery will occur within a 50 year timescale, provided that reductions of deposition to the critical load are achieved immediately. This prediction of a rapid recovery immediately following a decrease in deposition is partly supported by field observations across the UK and Europe (Wright and Hauhs, 1991). The main advantages of the dynamic model over other approaches is the ability to assess changes in land use in conjunction with changes in deposition coupled with an assessment of the timescale over which recovery may be expected. In this respect, the MAGIC model provides an effective catchment management tool.

#### VALIDITY OF APPLICATION AT SMALL CATCHMENT SCALE

At small catchment scale, critical loads for surface waters represent a useful tool for assessing acid sensitivity. Drainage waters always represent the net characteristics of the soils, vegetation and bedrock geology within their contributing area. A more important consideration here is the choice of chemical criteria; it is inappropriate to utilise a criterion for protecting brown trout, if the stream has not supported them historically or is too small to support them.

With regards to soils, the scale of data availability becomes a key issue in the successful application and inter-

pretation of the critical loads. Comparison of the catchment-based assessments with the UK 1 km National Map shows that, except for the Gwy, the larger scale approach identifies the dominant critical load class within each catchment correctly. However, in all cases, the National Map underestimates the proportion of the most sensitive soil type with the largest discrepancies occurring in the Nant Iago, Tanllwyth and Cyff catchments. Thus, local applications of the Level 0 critical loads approach (e.g. for catchment management) must use data at a scale appropriate for the land area in question. A simple downscaling from the National Map may not be sufficiently accurate. Similarly, assessment of 'stock at risk' may also be in error for relatively small sites of high conservation value (e.g. nature reserves, SSSIs) using a 1 km<sup>2</sup> resolution 'dominant soil' approach.

Using the SMBE, the differences between CL(A) values for different vegetative species arise from the combined effects of the different base cation inputs, base cation uptake rates and critical chemical values. The result is a much more complex distribution of critical loads compared to the simple empirical map. This makes the issue of scaling much more acute, as quite small, but highly sensitive, areas emerge from the CL(A) maps. Site specific impact assessments and estimates of stock at risk will, therefore, generally require more detailed information than can be gleaned from 1km<sup>2</sup> resolution mapping.

Application of critical load methodologies at small catchment scale does, however, provide an important check on the European scale assessment used for the negotiation of transboundary pollution policies. They also provide an essential means by which the effects of these transboundary policies can be assessed at local scale. At a national scale, the determination of emission control policies also requires validation at small scale. However, at both national and international scales, whether the small catchments are representative of larger regions can always be questioned and a true policy validation can be achieved only if multiple 'small catchment' applications are carried out.

The most tempting use of a small scale approach lies in its contribution to land and catchment management, for example, determination of land which may not be suitable for afforestation on the grounds of acid sensitivity. In this case, the finest data resolution can be used for the assessment but the results will require interpretation with reference to the uncertainties in the databases used. In the present case, estimates of S and N deposition at small scale are most uncertain.

## Conclusions

This paper has focused on the application of current critical loads models in the catchment context, notwithstanding the shortcomings and weaknesses in the model formulations themselves (e.g. the validity of the BC/Al

ratio as a chemical indicator of plant response, the use of the gibbsite equilibrium expression, etc) but a critique of the models is beyond the scope of this paper. In relation to soils, readers are referred to: Cronan and Grigal (1995), and Hogberg and Jensen (1994), for waters Turnbull *et al.* (1995) and Tervet *et al.* (1995).

Operationally, the availability of GIS and related data manipulation techniques make the critical loads approach attractive as a catchment management tool, especially in defining areas vulnerable to acidification. The scale of available data becomes the limiting factor in the interpretation of sensitive or exceeded areas. It is clear that for small catchment application, the spatial resolution of the soils and vegetation data must be high.

For soils, the Level 0 approach provides an empirical classification of soil vulnerability to acidification. It is easily applied provided a catchment scale soil map is available. Simple downscaling from the national 1 km resolution critical loads map is likely to be misleading as small areas of vulnerable soils might not be identified. Being a soils-based approach, the Level 0 soil critical load cannot be interpreted from an ecosystem perspective. Although severely limited by data availability, the Level 1 approach provides critical load data which is directly applicable to ecosystem assessment. It is particularly useful in identifying small ecosystem areas vulnerable to acidification. Model applications must be at the catchment scale using the best available data; downscaling from a national map is again likely to be misleading.

With the exception of the SSWC, the Level 0 and Level 1 approaches require data about the soils and landuse in the catchment. This may provide a practical limitation as to their usefulness. The Level 2 approach is very demanding of data, but gives information on the timing of critical load exceedance, and may ultimately provide the most useful technique as a catchment management tool.

## Acknowledgements

This work was funded in part by the Department of the Environment, Transport and the Regions under the soils and water umbrella research projects.

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