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Biological Significance and Uncertainty Analysis of Critical Load Exceedance for Freshwaters at the Catchment Scale: A Progress Report

Environmental Diagnostics Freshwater Critical Loads Consortium.
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Introduction

This report briefly summarises progress during the NERC Environmental Diagnostics Freshwater Critical Loads (ED-FCL) project. This project receives additional financial support from the National Power-Powergen-Eastern Generation Joint Environment Programme, Forestry Authority and Scottish Environmental Protection Agency. The overall aim of the project is to develop and evaluate the critical loads approach for assessment of freshwater acidification at the catchment scale. The project involves nine different research institutes and six different work units.

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

Fowler, D.

The work programme for 1997-98 included work on:

1.interpretation and modelling the Autumn 1996 Snowdonia field measurements;

2. development of 5 km by 5 km dry deposition models for SO_2 and NO_2 to provide the fine scale deposition inputs in Snowdonia;

3. catchment specific deposition inputs to compare the annual deposition of considered species (SO_4^{2-}, Cl^-) with measured hydrochemistry.

1. Snowdonia experiment

The measurement campaign was designed to provide two transects of precipitation and cloud chemistry with approximately 1km horizontal resolution over the complex terrain of Snowdonia for airflow in a westerly sector. The transects run for between 20 and 30 km from the coast to Snowdon and downwind of the summit of Snowdon to a distance sufficient to measure the enhanced wet deposition due to wind-drift effects of falling rain through orographic cloud.

Objective: To produce and validate 5 km x 5 km wet deposition maps for the UK.

Experimental approach
Snowdonia:
A two transect study to examine the orographic effects on concentration and deposition over 20 km of the highest wet deposition area of Snowdonia.

Transect 1: (Moel Hebog) SW-NW
20 km from coast to Snowdon
16 rainfall collectors; 3 cloud collectors
2 automatic weather stations

Campaign dates 15 October 1996 - 1 November 1996
Approx. 100 mm precipitation at coast, 200 mm on high ground
9 collectors; 5 clear runs (3, 4, 5, 6 and 7)
6 additional rain collectors downwind of Snowdon (22 in all)

Transect 2: Snowdon
20 km transect from coast to Caernarfon to Snowdon
20 rain collectors; 3 cloud collectors
2 AWS one upwind (Plas-y celyn) one on Snowdon
Start 15 October 1996; stop 1 November 1996
10 collections in all, 6 clear runs (2, 4, 5, 6, 7 and 8)

Results

The results provide approximately 10 major precipitation events and a total precipitation at high elevation sites of 200 mm (roughly 10% of annual precipitation) in westerly air flow. The data show large enhancements in precipitation and Cl^-, NO_3^-, and SO_4^{2-} concentration with altitude over the three mountains in the SW transect and one on the NW transect. The detailed results are being analysed for publication and lie outside the summary here, however it is clear that for the major ions in precipitation and cloud that:

- Orographic enhancement caused precipitation at the high level sites to be approximately a factor of two greater than coastal values.
- Peak wet deposition occurs downwind (e.g. east) of Snowdon summit.
- Peak wet deposition of Cl^-, NO_3^-, SO_4^{2-} and NH_4^- exceed coastal values by a factor of 3.5.
- That for individual events there is evidence of washout of aerosol and cloud leading to appreciably smaller wet deposition of the major ions at the highest precipitation sites downwind of Snowdon.

The data are being used to test models of precipitation scavenging over complex terrain by colleagues at UMIST. The model uses observed meteorology and therefore is event specific. It is helpful to consider one such event as an example.

The rain event modelled took place between 00.00 and 03.15 on the 18th October 1996. The wind direction at this time was approximately 200°, i.e. south-westerly, and the wind speeds were low at only 3 m/s near the surface. The stratification type used for the purposes of modelling the wind field was neutral below an inversion with a constant buoyancy-frequency above. The inversion was at a height of 850 m. Parameters such as the heights of the cloud base and the cloud top were unknown. The figure for the cloud top of 1650 m was calculated by adding the height of the inversion to the height of the summit of Moel Hebog. Originally the cloud base was not specified and the model calculated it using the mixing ratios, but this produced a cloud base which was too low and caused the SO_4^{2-} to be scavenged at altitudes lower than observed. Therefore, the cloud base was raised to a height of 200 m, in order to produce a sensible pattern of SO_4^{2-}.

The rainfall rate used was 2.4 mm/hr, which was calculated using the AWS data as a guide to the length of the rainfall event and the rainfall volume in the bottle at the first site. As can be seen in the comparisons between the measured and modelled rainfall volumes, the predicted enhancement of the rainfall volume with altitude is only about half that observed. The peaks and troughs in the simulated rainfall volumes are in roughly the correct positions, which suggests that the wind speed and directions used in the model were accurate. Predicted SO_4^{2-} concentrations are shown for two values of the boundary layer loading as it was difficult to calculate the actual loading. When the boundary layer loading has a value of $1.79 \mu g\ m^{-3}$, the values of the predicted SO_4^{2-} concentrations are more than twice the observed values. When the boundary layer loading is $1.2\ \mu g\ m^{-3}$, the predicted SO_4^{2-} concentrations are still about 50% too high. The seeder rain concentration was $2.7 \mu mol\ l^{-1}$ in both cases. The predictions for the chloride concentrations were more accurate than those for SO_4^{2-}, in this case the boundary layer loading was $10\ \mu g\ m^{-3}$, and the seeder rain concentration was $89.94\ \mu mol\ l^{-1}$. The deposition plots show that the model under predicts the deposition for both SO_4^{2-} and chloride on Moel Hebog but becomes more accurate on Snowdon. The SO_4^{2-} deposition plot is for the case when the boundary loading is $1.79\ mg\ m^{-3}$.

In short the model reproduces the pattern of SO_4^{2-} and chloride concentration, precipitation and deposition quite well qualitatively, but the absolute values differ from observation, often by a factor of two or more.

Dry Deposition

The bulk of the work within this part of the project represents separate work for the DETR on deposition processes. However, the development of 5 km x 5 km estimates of dry deposition upwind by the other projects provides a means of calculating inputs on a similar spatial scale for the study areas within this Environmental Diagnostics project. The 5 km x 5 km dry deposition model is now operational and is being subject to test and checking prior to the supply of new high resolution maps. Example maps for SO_2 and NO_2 are attached.

2. Catchment specific input budgets

The application of catchment specific models of orographic enhancement of wet dry and cloud deposition provides a valuable opportunity to compare the models with observed hydrochemical outputs from suitable catchments and ions which may be considered to behave conservatively over the time scales of a year. This approach has been shown for sulphate and chloride in Plynlimon catchments to provide a close match between the observed input fluxes and the annual flux leaving the catchments. Similar work is planned for a number of UK sites. The first two are in Wales (Delyn and Cwm) as attached.

The focus during the next year in this aspect of the work will be to provide catchment specific inputs for those catchments which provide local precipitation (and if possible, orographic cloud) chemistry data to use as input for the model along with digital terrain, land use and where possible available local meteorological data. In this way a set of validation data will become available to test the model across a range of deposition values for both sulphate and chloride.

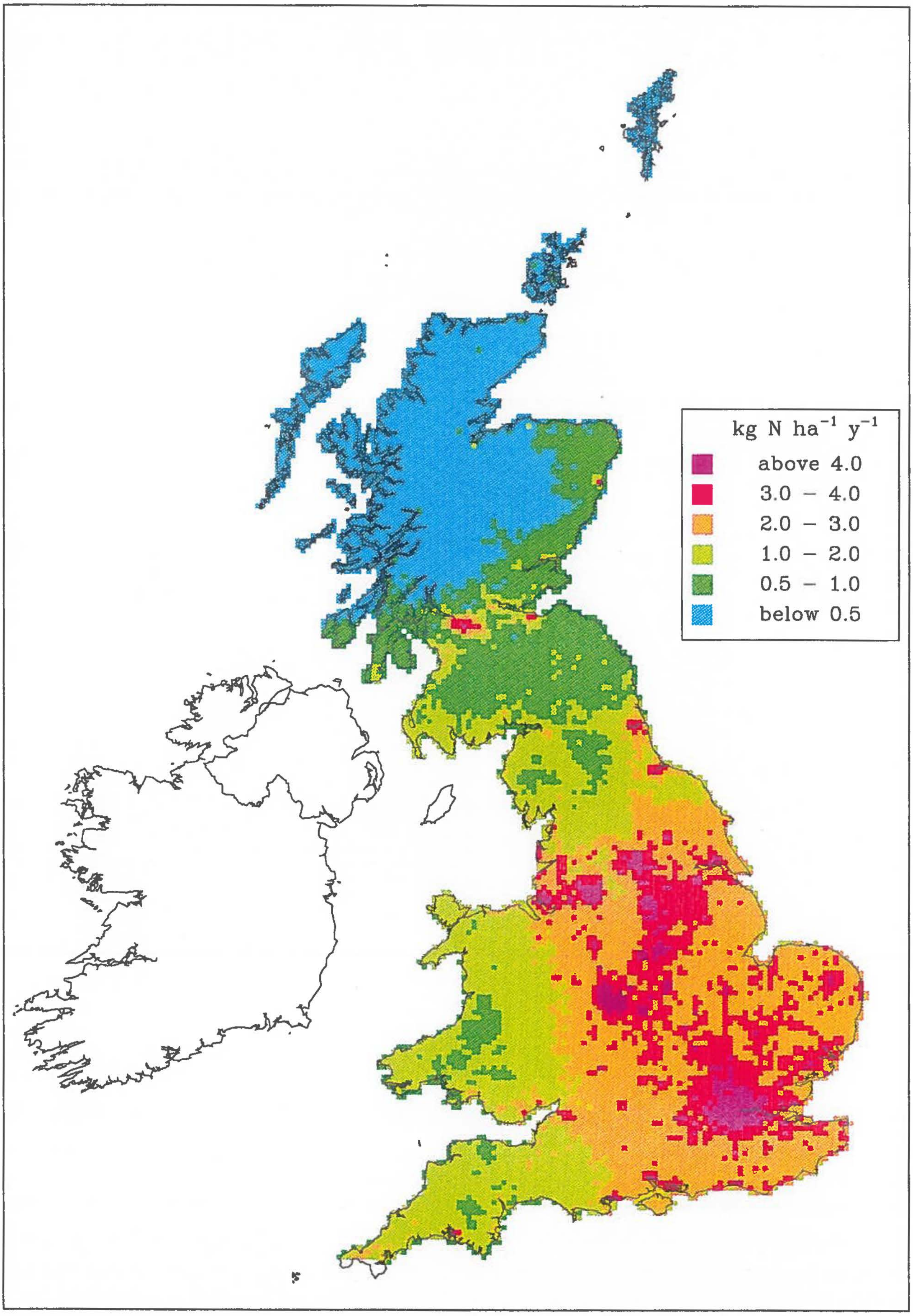
Table 1 Total deposition excluding sea-salt components (kg y^{-1})

Catchment	S	Ca	Mg	Cl	K
Cwm	3135	3007	3281	-1279	403
Cwm-moor	2348	1802	2125	102	295
Delyn	645	515	598	3.4	81

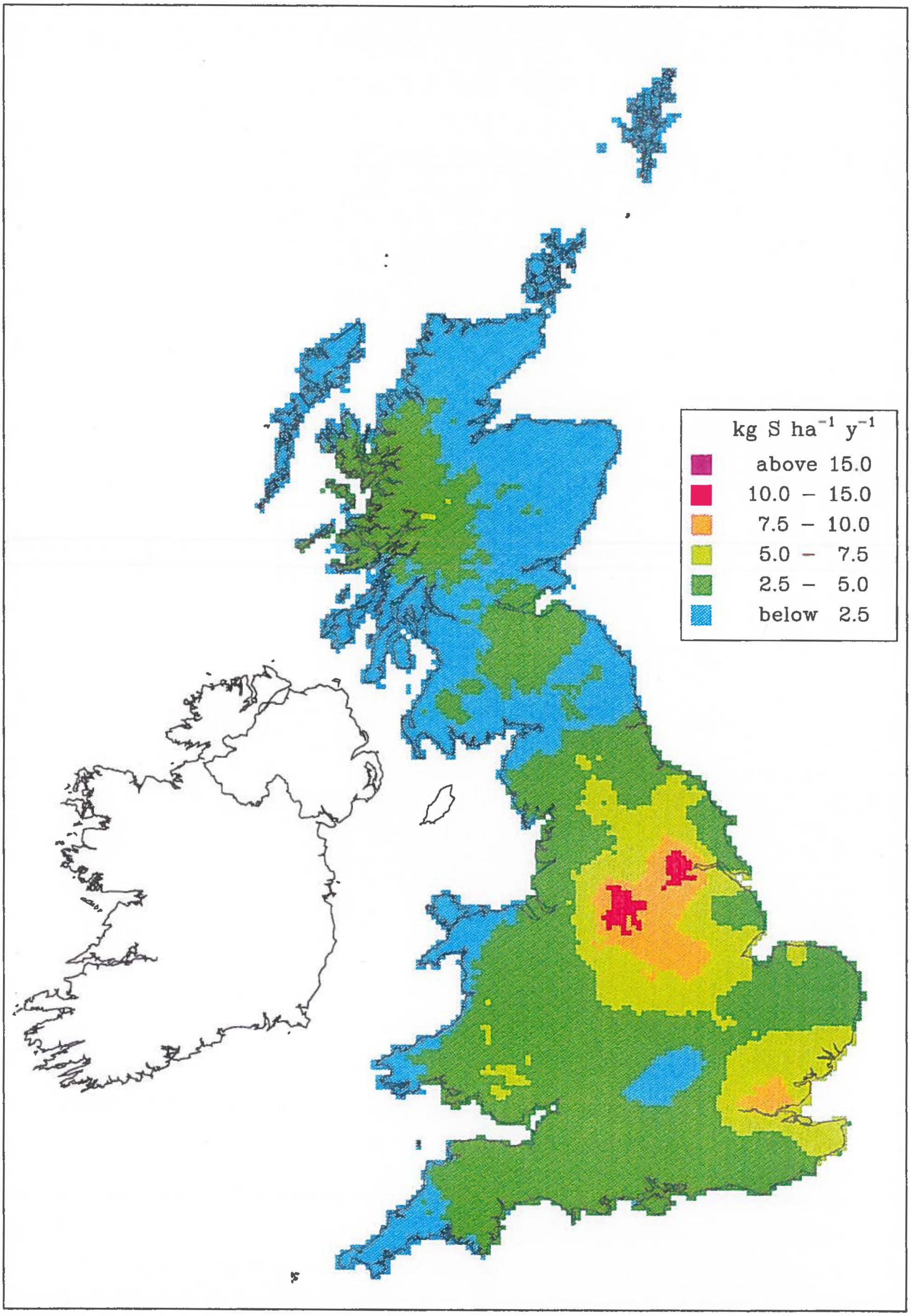
The table for the Delyn with an extra 250 mm rainfall is:

Catchment	S	Ca	Mg	Cl	K
Delyn	792	615	720	59	99

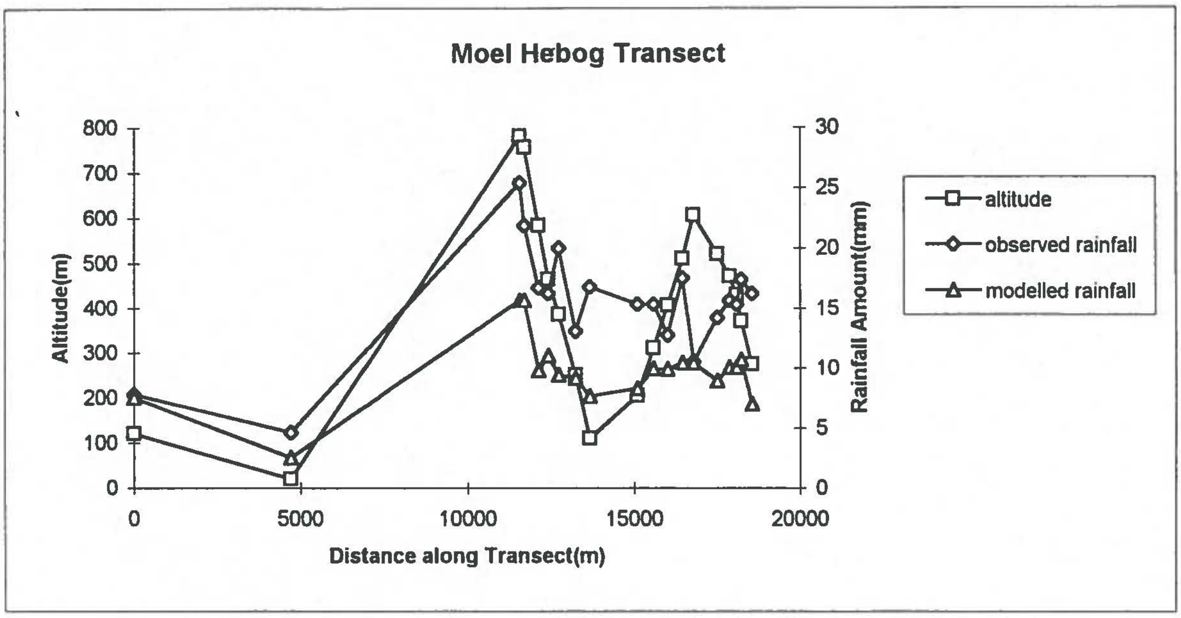
Dry deposition of NO_2 (92–94)

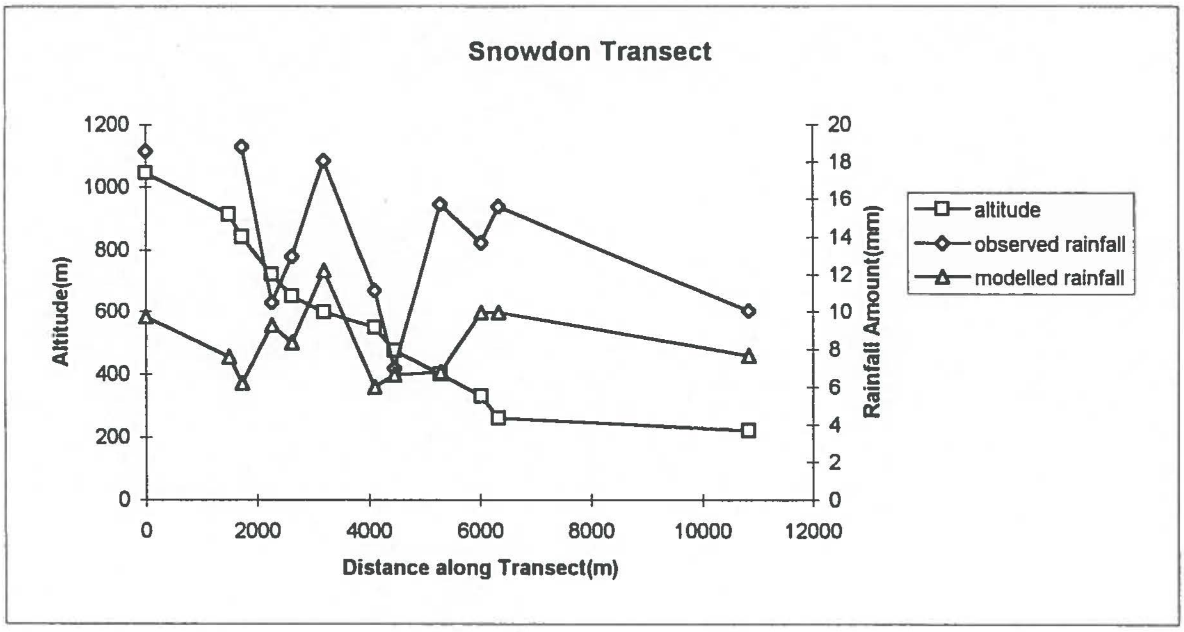


Dry deposition of Sulphur (92–95)



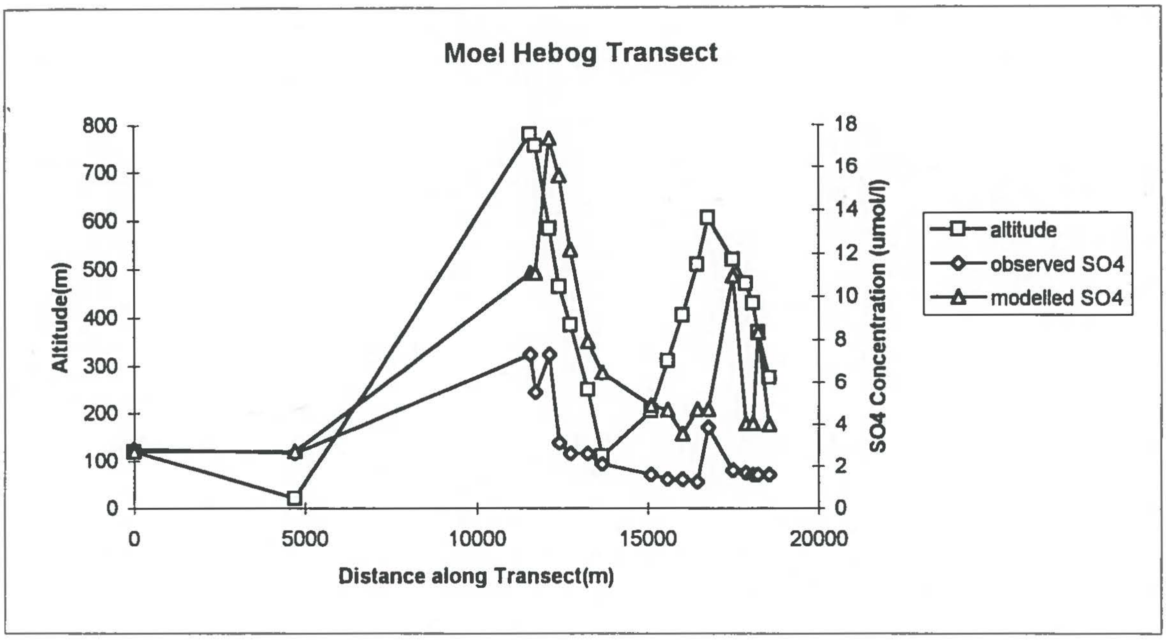
Comparison Between Modelled and Observed Rainfall Volumes

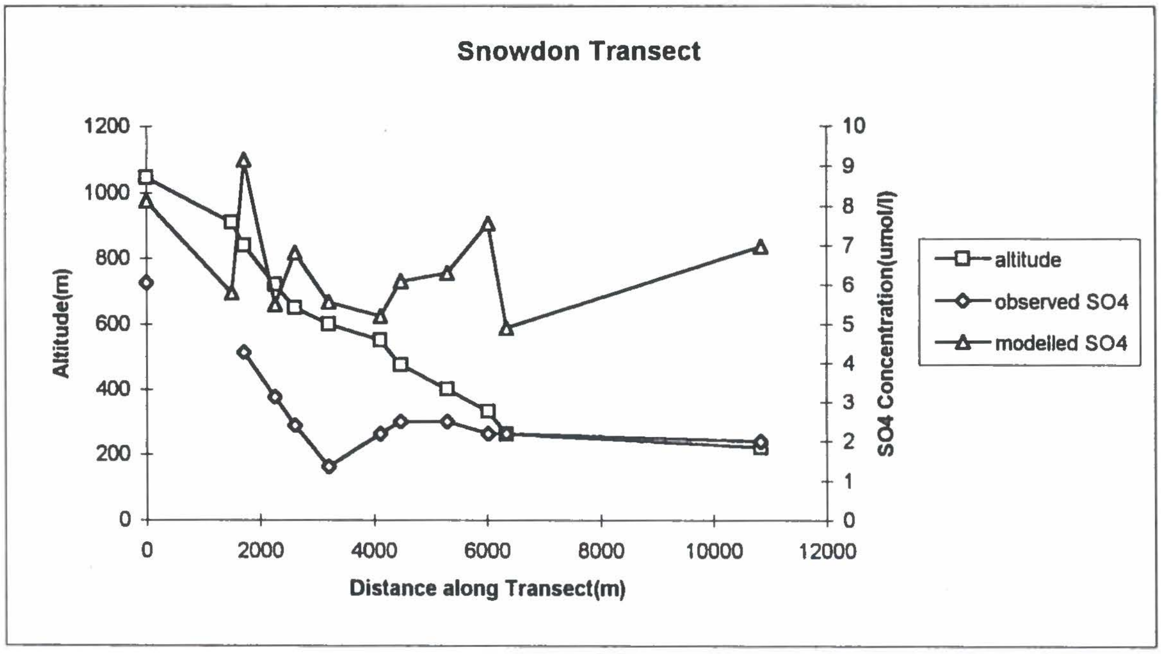




Rainfall Rate = 2.4 mm/hour
Cloud Base = 200m
Cloud Top = 1650m

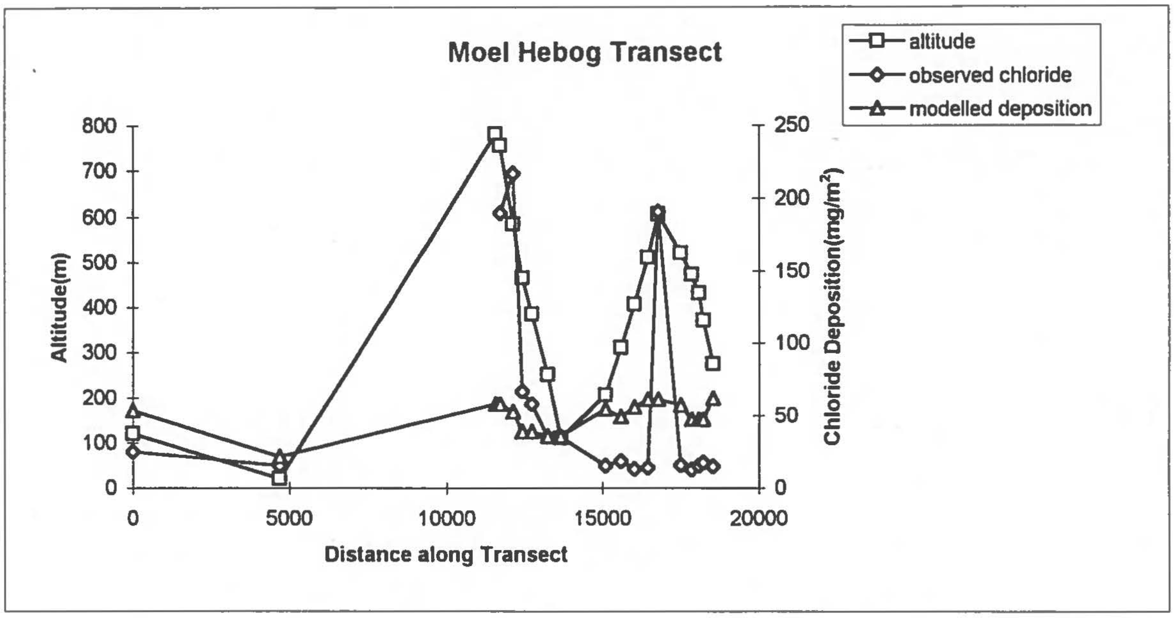
Comparison of Modelled and Observed SO4 Concentrations

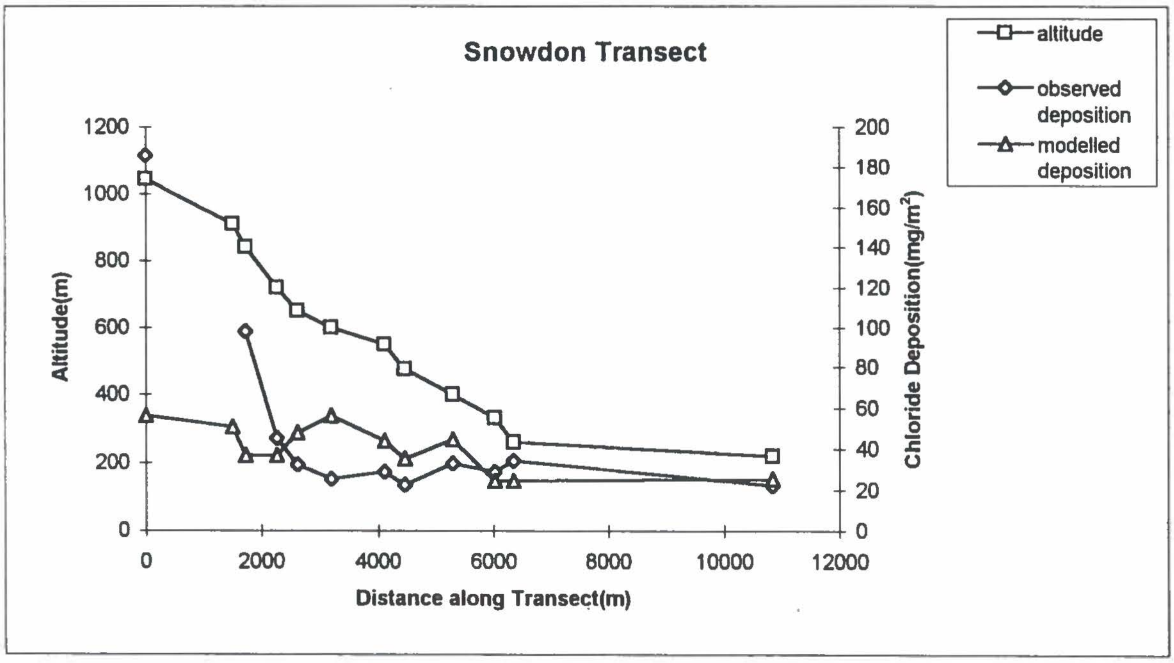




Seeder Rain SO4 Concentration = 2.7 umol/l
Boundary Layer SO4 Loading = 1.79 ug/cubic metre

Comparison Between Observed and Modelled Chloride Deposition





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

Kernan, M. & Hall, J.

This part of the programme examines critical loads predictions at two scales.

1. High resolution data are being used to develop catchment critical loads models and freshwater sensitivity maps at a catchment scale.

a) Multivariate statistical techniques will be applied to assess the potential for predicting freshwater critical loads using these high resolution catchment data (e.g. Kernan, 1995; Kernan *et al*, in press).

b) High resolution maps will be developed showing the sensitivity of surface waters to acidification.

2. Predictive models will also be applied nationally a) to assess the effects of using lower resolution data on predictive power and b), to enable regional variations in the relationships between catchment characteristics and freshwater critical loads to be identified.

1. Catchment scale model development

To calibrate the empirical model and provide data for the sensitivity mapping, a total of 38 sites were selected for sampling in the Glaslyn (Snowdonia) and Duddon (Lake District) catchments. Two sampling runs were planned, one during Autumn and one in the Spring to avoid the extremes of flow (and chemical composition) associated with Summer and Winter (and thus approximate mean chemical conditions). Samples were taken towards the end of October, 1997 and the sites are to be revisited in April, 1998. Table 1 presents summary statistics for the water chemistry following the October sampling run.

Catchment boundaries and stream networks have been digitised from 1:25,000 Ordnance Survey maps. A list of sites and their digitised catchment boundaries is attached (Figs. 1 and 2). Each catchment will be characterised according to a range of attributes derived from a number of existing digital datasets using ARC/INFO. These include;

Digital maps of soil association (1:250,000 at 100 m resolution) - each 100 m pixel contains the code for the soil association representing that grid cell.
Digital geology maps (1:250,000)
- raster versions of the polygon data have been generated at 100 m and 50 m for use with the soils data

These data have been imported into the GIS at ITE. The soil and geology data are currently held in their original classifications. Subsequently, the soils and geology data will be aggregated into the sensitivity classes used in the generation a UK map of acid sensitivity (Hornung et al., 1995).

Other data sets being collated include;

Digital geology maps at 1:50,000
Soil attribute (physical chemistry) data from soil profile database
HOST hydrology of soil types
Hydrogeological data
Fine scale deposition data for Snowdonia study (Work unit 1A)
Land cover data (25 m resolution)

Table 1: Summary statistics for water chemistry, October 1997.

	Mean	Minimum	Maximum	Range	Std. Dev.
pH	6.50	4.78	7.62	2.84	.72
Alkalinity	98.16	-17.00	486.00	503.00	114.95
Cond	44.39	27.00	83.00	56.00	13.31
Na	197.76	145.00	296.00	151.00	40.21
NH_4	.68	0.00	3.00	3.00	1.02
K	7.45	3.00	12.00	9.00	2.18
Mg	82.45	42.00	189.00	147.00	34.72
Ca	173.53	19.00	518.00	499.00	113.73
Cl	193.58	130.00	276.00	146.00	42.62
NO_3	16.17	2.60	42.00	39.40	8.74
SO_4	92.50	65.00	156.00	91.00	19.16
SiO_2	2735.53	1160.00	5240.00	4080.00	1039.73
PO_4	.32	0.00	9.00	9.00	1.47
TP	3.58	2.50	22.00	19.50	4.60
AL-TM	23.82	4.00	201.00	197.00	39.49
AL-NL	10.39	3.00	41.00	38.00	8.11
AL-L	13.42	0.00	186.00	186.00	37.69
ABS-250	.05	.01	.13	.12	.03
TOC	1.53	.30	2.90	2.60	.64

Work for year two;

- model calibration and validation using catchment characteristics to explain and predict critical load variation
- comparison of models using different techniques (multiple regression, Partial Least Squares regression, neural networks)
- comparison of models different spatial scales (1 km^2, catchment specific, 1:250,000, 1:50,000 etc.)
- production of freshwater sensitivity maps showing how critical loads change downstream

2. National applications of predictive models

The use of nationally available data to apply and validate predictive models at national level has not required the acquisition of primary data. Hitherto a number of datasets have been collated for input into the models which are currently being developed. These are listed below;

Geology (Kinniburgh and Edmunds sensitivity class, 1-4)
Freshwater Sensitivity Map class (1-5)
Three class buffering capacity class (1-3)
Soil critical Load class (1-5)
Land cover class (1-25)
Runoff
Rainfall
S and N deposition

Initially, modelling will focus on the relationships between critical loads and catchment characteristics at the national scale. However, for these models to perform well when predicting at scales other than those at which they have been calibrated, it is essential that the data exhibit spatial stationarity. If spatial stationarity can not be assumed, other methods are required to describe critical load-catchment relationships at different scales. To this end it is intended to use spatially-weighted regression, a technique that fits 'local' regression models which should give improved local estimates of critical loads. The use of geostatistical techniques within this context are also being explored.

A number of datasets are being used to undertake this study. These include;

Critical loads dataset for Scotland - comprising 613 sites with land cover and soil critical load data at 1 km resolution, rainfall (10 km resolution), altitude and freshwater critical loads data. These data have been mapped in a GIS. Exploratory data analyses have been undertaken. Figure 3 shows the distribution of residuals from a global regression of soil and land cover classes on critical load. The strong spatial structuring in the residuals suggest local regression methods will be more appropriate.

Snowdonia dataset - comprising water chemistry, land cover and altitude data from 76 lake sites in a 20 km grid square centred on Snowdonia national park. These data have been incorporated into a GIS and are being examined to assess their suitability in terms of geostatistical methods.

National critical loads data set - 1479 sites for which full water chemistry and a range of catchment characteristics are being calibrated (see above). These have been mapped using a GIS. Further work will proceed once critical loads and catchment data have been collated for these sites.

Work for Year 2

I. Apply predictive models used at catchment scale to national data
II. Compare predictive techniques using national data
III. Assess effects of scale on prediction of critical loads
IV. Identify regional differences in model efficacy, mapping parameter uncertainty, residuals etc.
V. Develop spatially-weighted regression and geostatistical approach with the above datasets.

References

Hornung, M., Bull, K.R., Cresser, M., Ullyett, J., Hall, J.R., Langan, S., Loveland, P.J. & Wilson, M.J. 1995. The sensitivity of surface waters of Great Britain to acidification predicted from catchment characteristics. **Env. Poll. 87, 207-214.**

Kernan, 1995. The use of catchment attributes to predict surface water critical loads: a preliminary analysis. **Water, Air and Soil Poll. 85, 2479-2484**

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Figure 1. Duddon catchment

Site Code	Site Name
D1	River Duddon
D10	Long House Gill
D11	Tarn Beck
D12	Gobling Beck
D13	Old Park Beck
D14	Sling Beck
D15	River Duddon
D16	Crosby Gill
D17	River Duddon
D18	Holehouse Gill
D19	Logan Beck
D2	Gaitscale Gill
D20	River Duddon
D3	River Duddon
D4	Moasdale Beck
D5	Dale Head Gill
D6	Castlehow Beck
D7	River Duddon
D8	Grassguards Gill
D9	Tarn Beck

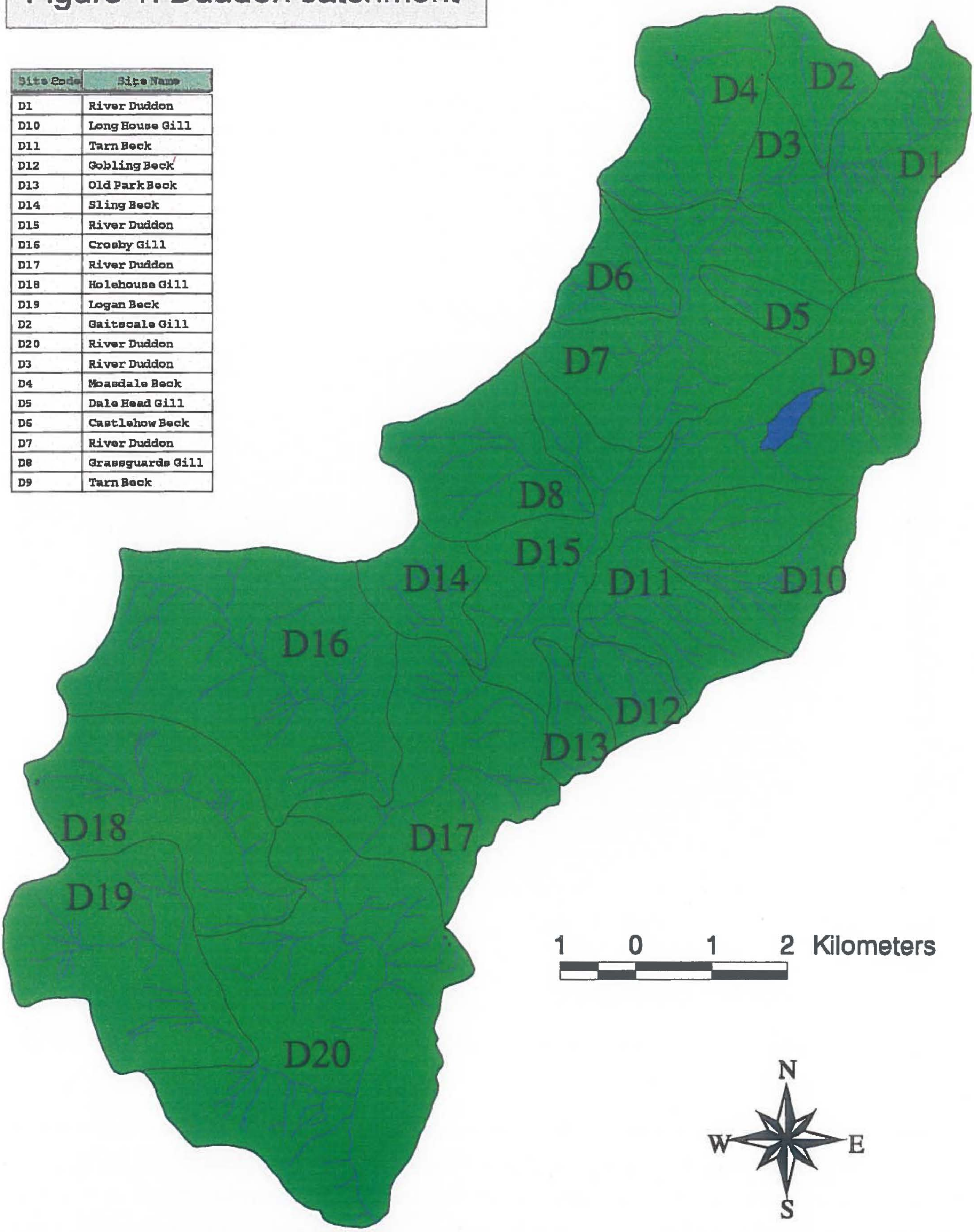


Figure 2. Glaslyn catchment

Site Code	Site name
SE1	Afon Glaslyn
SE10	Afon-y-cwm
SE11	Afon Glaslyn
SE12	Afon Glaslyn
SE2	Afon Trawsnant
SE3	Ceunant Mawr
SE4	Afon Glaslyn
SE5	Afon Merch
SE6	Afon Cwm Llan
SE7	Afon Llynedno
SE8	Afon Goch
SE9	Afon Glaslyn
SW1	Afon Colwyn
SW2	Afon Cwm-du
SW3	Afon Hafod-Ruffydd-isaf
SW4	Afon Colwyn
SW5	Afon Meillionen
SW6	Afon Glochig
SW7	Nant Cwmcloch
SW8	Afon Colwyn

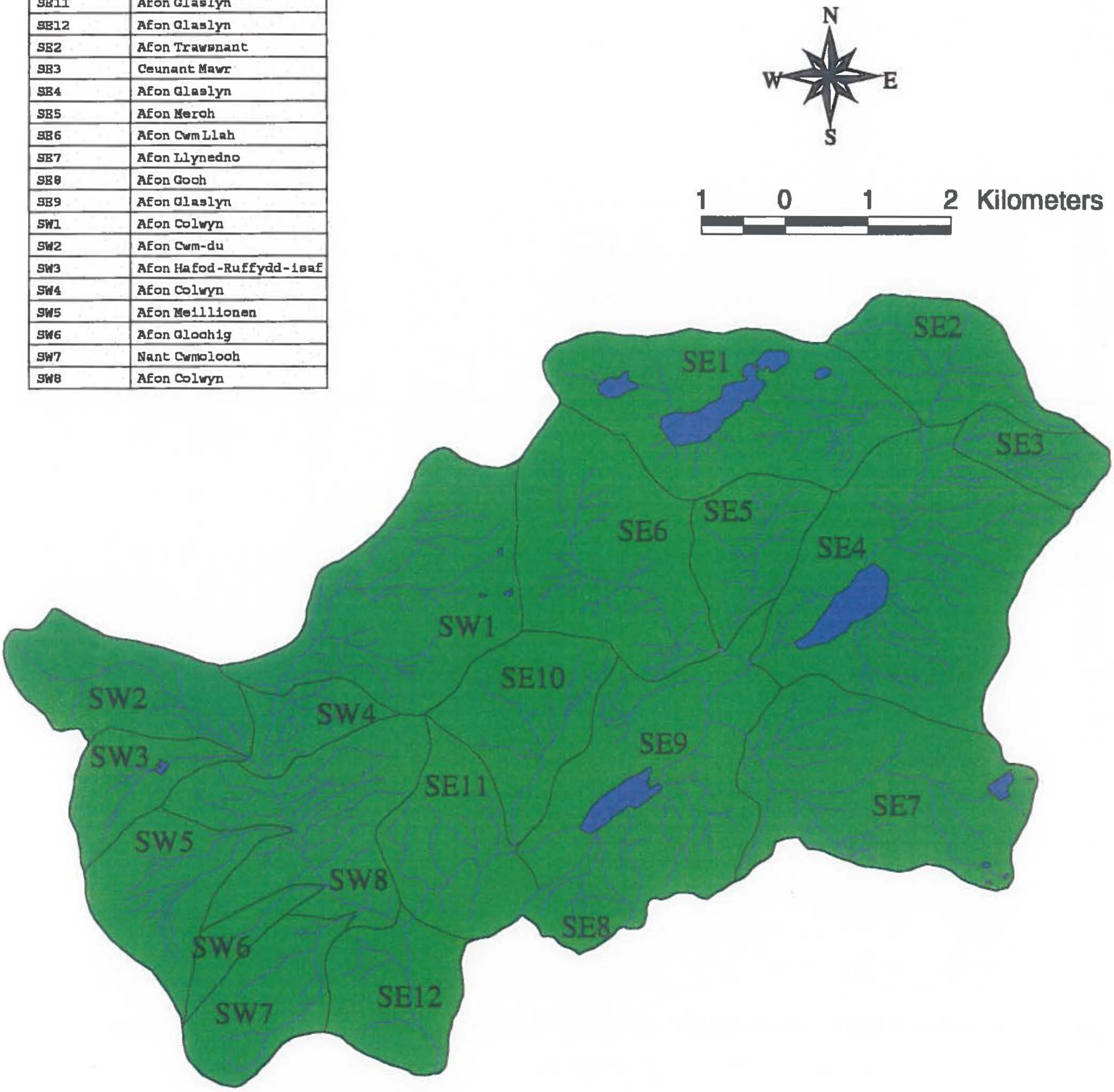
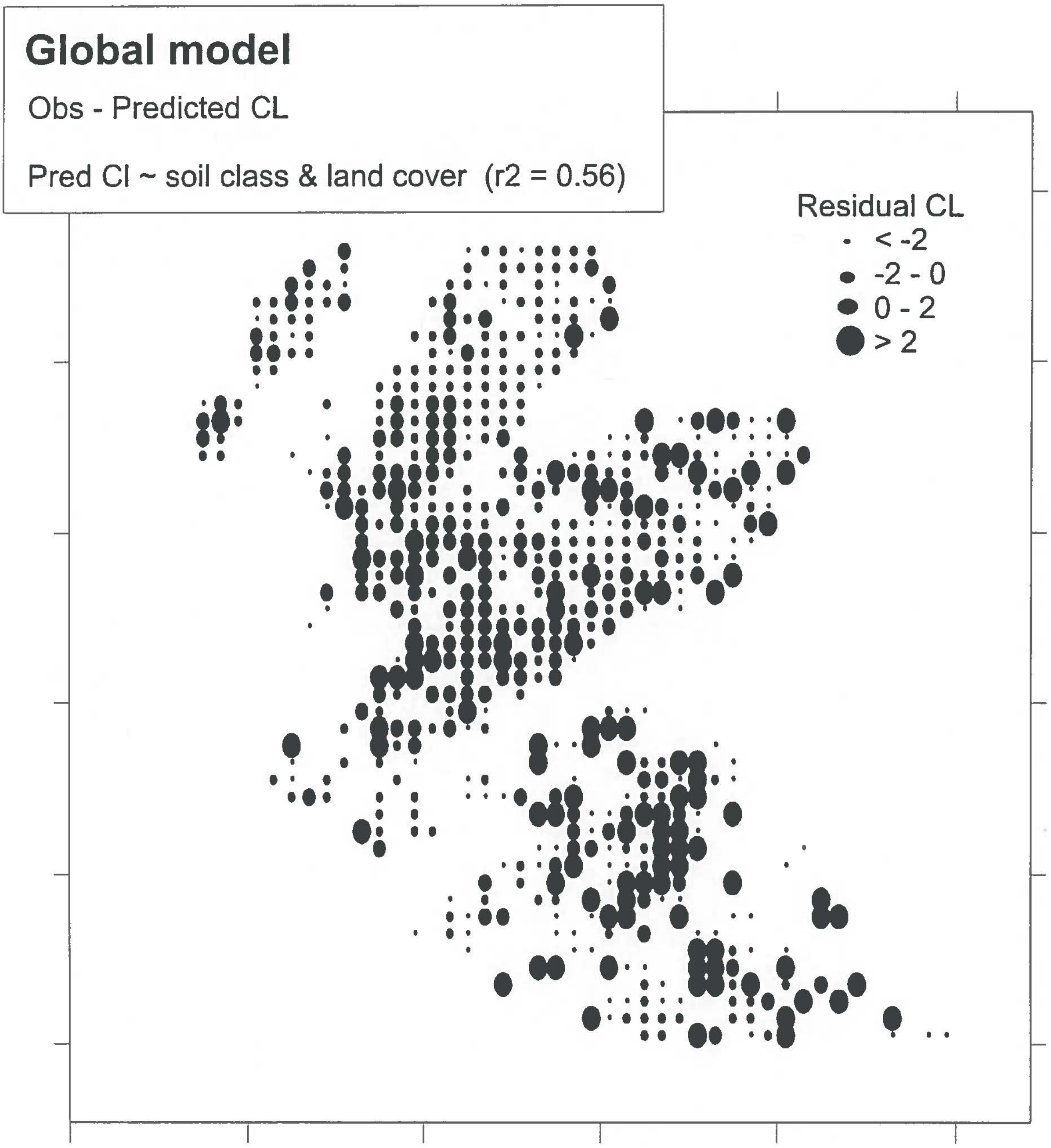


Figure 3. Distribution of residuals from a global regression of soil and land cover classes on critical load - Scottish critical loads dataset



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

Reynolds, B. & Norris, D.A.

The Welsh Acid Waters Survey (WAWS) has provided a unique chemical and biological data base with which assess the performance of steady state critical loads models against biological observations. The first part of the project has involved the calculation of critical loads and exceedance values for the 102 WAWS stream sites. The work has included a theoretical appraisal of the Henriksen Steady State Water Chemistry (SSWC) equation and an assessment of sensitivity of critical loads and exceedance values to variations in input data using the variety of data sets available for Wales.

1. The SSWC equation, base cation deposition and critical loads exceedance

The initial stages of this work unit revealed a discrepancy in approach concerning the inclusion of present-day non-marine (anthropogenic) base cation deposition in the exceedance calculation for the SSWC equation. The term is included in equations described in the current European mapping manual (UNECE 1996) and the Northern European Lake Survey report (NIVA 1997) but excluded from the UK formulation (CLAG 1995). The following is a derivation of the SSWC equation from first principles for the critical load of sulphur acidity and critical load exceedance.

1.1 Derivation of the SSWC equation

For a given catchment, the total load of base cations leaving the catchment is equal to the sum of all base cation sources minus any losses due to biological uptake:

$$BCt = BCt^* + BCm = BCw + BCd^*_0 + BCdm + BCi - BCu + BCdt^* \qquad (1)$$

Where:
BCt = present-day total base cation leaching loss
BCt^* = present-day non-marine base cation leaching loss
BCm = leaching loss of seasalt base cations
BCw = base cation weathering flux
BCd^*_0 = long-term, background non-marine base cation deposition
$BCdm$ = seasalt base cation deposition
BCi = release of base cations from ion exchange sites
BCu = net base cation uptake by vegetation
BCd^*_t = present-day anthropogenic (industrial) base cation deposition

Taking a long-term view, ie assuming steady state with respect to seasalt fluxes and net base cation uptake, then:

$$BCt^* = BCw + BCd^*_0 + BCi + BCd^*_t \qquad (2)$$

since $BCdm = BCm$ and $BCu = 0$.

From work by Henriksen (1984) and Brakke *et al.* (1990),

$$BCi = F.DSO4^* = F.(SO_4{}^*{}_t - SO_4{}^*{}_0) \qquad (3)$$

where:
F = the F factor

DSO_4^* = the difference between the present-day non-marine sulphate flux in stream water ($SO_4{}^*{}_t$) and the pre-industrial non-marine sulphate flux ($SO_4{}^*{}_0$).

Assuming BCw does not change with acid inputs and sulphate in runoff is in steady state with respect to sulphate deposition, then:

$$BCt^* = BC_0 + F.DSO_4^* + BCd^*_t \qquad (4)$$

where BC_0 = pre-industrial (long-term sustainable) base cation loss (= $BCw + BCd^*_0$)
re-arranging (4):

$$BC_0 = BC^*t - F.DSO_4^* - Bcd^*_t \qquad (5)$$

The critical load of acidity (CL(A)) is defined as the difference between the long-term alkalinity sources to the system and the critical alkalinity flux:

$$CL(A) = ANCw + ANCd_0 - ANClimit \qquad (6)$$

where:
ANCw = alkalinity flux from weathering (= BCw)
$ANCd_0$ = alkalinity flux from long-term, non-marine base cation deposition (= BCd^*_0)
ANClimit = critical ANC flux = [ANC]limit.Q
and:
[ANC]limit = critical ANC concentration
Q = runoff

Thus:

$$CL(A) = BC_0 - ANClimit \qquad (7)$$

or substituting (5)

$$CL(A) = BC^*_t - F.DSO_4^* - BCd^*_t - ANClimit \qquad (8)$$

1.2 Calculation of critical loads exceedance

At critical load, the long-term sustainable sources of alkalinity should equal the incoming net acidity. In terms of sulphur acidity, this equals the present day non-marine sulphate deposition minus the present day non-marine base cation deposition originating from industrial sources. Thus at critical load:

$$CL(A) = SO_4d^* - BCd^*_t \qquad (10)$$

or

$$BC^*_t - F.DSO_4^* - BCd^*_t - ANClimit = SO_4d^* - BCd^*t \qquad (11)$$

and exceedance equals:

$$Ex = SO_4d^* - BCd^*t - CL(A) \qquad (12)$$

where:
SO_4d^* = present day non-marine sulphate deposition

This has the effect of making critical load exceedance numerically independent of BCd*t as:

$$Ex = SO_4d^* - BCd^*t - BC^*_t + F.DSO_4^* + BCd^*_t + ANClimit \qquad (13)$$

or

$$Ex = SO_4d^* - BC^*_t + F.DSO_4^* + ANClimit \qquad (14)$$

Although this appears contradictory, it is the correct formulation as it accounts for the fact that (I) not all the sulphate in precipitation is balanced by hydrogen ions (ii) the incoming flux of anthropogenic base cations must appear in the stream if there is no net uptake within the catchment. If BCd*t is omitted from the deposition side of the exceedance calculation (equation 11), critical loads exceedance will be overestimated. This is illustrated by data from WAWS in Section X.3.3. Note also, that because BCi represents the gradual depletion of the ion exchange store of base cations (a source of stream water ANC), it is possible to have sites where the critical load is said to be exceeded but which have a stream water ANC greater than the critical limit. Thus the SSWC allows for acidification down to the critical load and will not necessarily preserve present-day conditions.

2. Calculation of SSWC critical loads for the WAWS sites

From the section above concerning the SSWC equation, the following input variables (Table 1) are required to solve the SSWC equation for individual sites. Alternative data sets were available for many of these variables and these are described in more detail below.

Table 1 Input variables for the SSWC equation applied to WAWS catchments.

Input variable	Data required
$BCt^* = [BCt^*].Q$	$[BCt^*]$ = stream water excess base cation concentration Q = catchment runoff
BC^*d	excess base cation deposition flux to catchment
$SO_4{}^*t = [SO_4{}^*{}_t].Q$	$[SO_4{}^*t]$ = present day stream water excess sulphate concentration
F factor	F = sin[90.([BCt*]/S)] from (Brakke *et al.* 1990); S was set to 400 meq l^{-1}.
$SO_4{}^*{}_0 = [SO_4{}^*{}_0].Q$	$[SO_4{}^*{}_0]$ = pre-industrial stream water excess sulphate concentration = 15+0.16.[BCt*] (CLAG 1995).
ANClimit = [ANClimit].Q	[ANClimit] = critical ANC value set at 20 meq l^{-1} (NIVA 1997).

2.1 Runoff data set

In the absence of runoff data for individual catchments, 1 km square resolution data supplied to the National Mapping Programme by the Institute of Hydrology were used. For each catchment, an area-weighted runoff was calculated from the 1 km squares included within the catchment boundary using a GIS. The SSWC equation was solved using both 30 year average and 1992-1994 average runoff values.

2.2 Stream water excess base cation and excess sulphate concentrations

For each catchment the SSWC was solved using annual, winter and summer geometric mean excess base cation and excess sulphate concentrations.

2.3 Excess base cation deposition

Modelled excess base cation deposition data were available at 20 km square resolution from the 1995 WAWS rain chemistry survey and from the UK 1992-94 national data set. In both cases, a GIS was used to calculate an area-weighted deposition value from the 20 km squares included within each catchment boundary. For the national data set, it was also possible to use the GIS to partition inputs according the proportions of forest and short (grass) vegetation within the catchments. The breakdown of inputs to according to vegetation type was not available from the WAWS data set.

2.4 Excess sulphur deposition

Modelled excess sulphur deposition data were available at 20 km square resolution from the 1995 WAWS rain chemistry survey, the UK 1992-94 national data set and from HARM predictions for present day and 2010. Two sulphur deposition data sets were available from WAWS; one with sulphur dioxide concentrations enhanced to allow for the effects of urban areas (version v1) and one which used rural background sulphur dioxide concentrations (version v2). The UK 1992-94 data used urban enhanced sulphur dioxide concentrations. In all cases, a GIS was used to calculate area-weighted deposition values from the 20 km squares included within individual catchment boundaries. For the national data set it was also possible to use the GIS to partition inputs according the proportions of forest and short (grass) vegetation within the catchments. The breakdown of inputs to according to vegetation type was not available from the WAWS data set.

2.5 Critical load and exceedance calculations

The critical loads and exceedance calculations were performed on Excel spreadsheets using data imported from the GIS and the WAWS chemistry data base. Twelve permutations of critical load values were calculated for each catchment.

3. SSWC critical loads and exceedance values

3.1 Comparison of data sets

The two estimates of catchment runoff agree closely (Figure 1) and choice of data set for this variable was not a large source of uncertainty in the SSWC equation. In contrast, estimates of BCd* for the catchments derived from the UK national data set were much larger than those from the WAWS data (Figure 2). Plotted against each other, there was no relationship between the two sets of values. The differences in the 20 km square deposition patterns (Figure 3) and partitioning the UK data according to vegetation canopy type will have both contributed to the differences in catchment inputs as a forest canopy will increase occult deposition of base cations to catchments (Reynolds *et al.* 1997).

3.2 SSWC equation critical loads

The results for the 12 sets of critical load calculations are summarised in Table 2. There was a wide variation in critical load depending on which combination of data was used to solve the equation. More variation occurred at lower values with 25%ile critical loads differing by a factor of 3.5 (0.40 to 1.40 keqH^+ ha^{-1} yr^{-1}) compared to 75%ile values which varied between 1.40 and 3.76 keqH^+ ha^{-1} yr^{-1}; a factor of 2.7 (Table 2). The choice of stream water chemistry data caused much larger variation in critical loads (Figure 4) compared to the choice of runoff and non-marine base cation deposition (Figure 5), indicating that the SSWC equation is relatively insensitive to these two variables. This is important, as they both used data which were extrapolated to the catchment from national grid-square values. Furthermore, there were considerable differences in BCd* depending on which regional data set was used. The sensitivity of the critical load to stream water chemistry can be resolved by careful sampling avoiding extreme flow conditions.

Table 2 25, 50 and 75%ile Henriksen sulphur acidity critical loads for 102 WAWS sites determined using annual, summer and winter geometric mean stream water chemistry.

			25 percentile critical load (keqH$^+$ h^{a-1} y^{r-1})		
	Runoff	92-94	30 yr avg.	92-94	30 yr avg.
	BCd*	WAWS (95)	WAWS (95)	UK (92-94)	UK (92-94)
Stream chemistry	Annual	1.08	0.89	0.85	0.67
	Summer	1.40	1.21	1.25	1.04
	Winter	0.73	0.65	0.52	0.40
			50 percentile critical load (keqH$^+$ h^{a-1} y^{r-1})		
	Runoff	92-94	30 yr avg.	92-94	30 yr avg.
	BCd*	WAWS (95)	WAWS (95)	UK (92-94)	UK (92-94)
Stream chemistry	Annual	1.62	1.46	1.37	1.15
	Summer	2.30	1.99	2.05	1.82
	Winter	1.15	1.10	0.91	0.78
			75 percentile critical load (keqH$^+$ h^{a-1} y^{r-1})		
	Runoff	92-94	30 yr avg.	92-94	30 yr avg.
	BCd*	WAWS (95)	WAWS (95)	UK (92-94)	UK (92-94)
Stream chemistry	Annual	2.56	2.39	2.41	2.08
	Summer	3.76	3.47	3.34	3.19
	Winter	1.80	1.69	1.55	1.40

3.3 Critical loads exceedance

There were large differences in the regional patterns of excess sulphur deposition in Wales between the UK 92-94 data and the other three data sets (Figures 6 and 7) which will have contributed to the variations in the frequency distributions of deposition for the WAWS catchments (Figure 8). As with excess base cation deposition, the UK national excess sulphur inputs were generally larger than the WAWS estimates reflecting both the influence of the different 20 km square data sets and the effects of partitioning inputs for forest and grass vegetation. Occult and dry sulphur deposition to catchments are increased substantially by the presence of tree canopies (Reynolds *et al.* 1997). The HARM model predicts intermediate amounts of deposition but with more sites in the range 0.8 to 1.0 keq ha^{-1} yr^{-1} compared to the other data sets.

From the permutations of critical load and sulphur deposition data, sixty critical loads exceedance values were calculated for each 102 sites using equation 12. As the critical load exceedance is independent of BCd*, only thirty different values were produced for each site and these are summarised as the percentage of exceeded sites in Table 3. Although the four present-day sulphur deposition patterns were different, this had a relatively small effect on the number of exceeded sites. The HARM and national sulphur deposition estimates resulted in a very similar proportion of exceeded sites which were about 6% more than from the WAWS estimates. Predictions to 2010 showed 5% or fewer sites where the critical load was exceeded. The main source of variability in the exceedance values derived from the choice of stream water chemistry used to calculate the critical loads. The range of exceedance values was large (4% to 48% of sites exceeded), with the most sites exceeded for winter chemistry and fewest for the summer. This demonstrates the difficulties of setting critical loads and calculating exceedance values for streams where the chemistry is much more dynamic compared to lakes. Catchment based critical loads assessments must take account of the large variability in stream chemistry, and its influence on the critical load and exceedance.

Table 3. Percentage of WAWS sites for which the SSWC critical load is exceeded where exceedance = S*dep - BCd* - CL(A).

	Stream water chemistry		
	Annual	Summer	Winter
UK S* dep 92-94 runoff	18	6	38
UK S* dep 30 yr runoff	22	12	44
WAWS v1 S* dep 92-94 runoff	11	4	26
WAWS v1 S* dep 30 yr runoff	16	8	34
WAWS v2 S* dep 92-94 runoff	11	4	28
WAWS v2 S* dep 30 yr runoff	15	6	36
HARM 94 S* dep 92-94 runoff	17	7	37
HARM 94 S* dep 30 yr runoff	24	12	48
HARM 2010 S* dep 92-94 runoff	2	0	5
HARM 2010 S* dep 30 yr runoff	2	0	5

Exceedance values were also calculated using the equation presented in CLAG (1995); ie with BCd* omitted from the right hand side of equation 12. In this case 60 exceedance values were calculated for each site and these are summarised in Figure 9 as the percentage of sites at which the critical load was exceeded. In this case, the numbers of exceeded sites were greater and there was much more variability with between 8 and 66% of sites exceeded depending on the combination of data used in the calculation.

The two calculation methods are compared in Figure 10 for critical loads calculated using the annual geometric mean stream chemistry. Excluding BCd* from the exceedance equation results in a larger proportion of exceeded sites in all cases and the range of exceedance values is greater.

4. Predicting nitrate leaching using the FAB (First-order Acidity Balance) model

The FAB model (Posch 1995), sets the critical load of acidity for freshwaters incorporating the major sources and sinks for sulphur and nitrogen. The acidity balance for lakes at critical load is thus:

$$\mathrm{Ndep} + \mathrm{Sdep} = \mathrm{fNupt} + (1-\mathrm{r})(\mathrm{Nimm} + \mathrm{Nden}) + \mathrm{rNret} + \mathrm{rSret} + \mathrm{BC^{*}l} - \mathrm{ANClcrit} \quad (15)$$

where:

Ndep = total N deposition
Sdep = total S deposition
Nupt = net growth uptake of N by forest vegetation (removal at harvest)
Nimm = long-term immobilisation of N in catchment soils
Nden = N lost through denitrification from catchment soils
Nret = in-lake N retention
Sret = in-lake S retention
BC*l = non-marine base cation leaching from catchment
ANClcrit = critical ANC leaching from catchment
f = fraction of forested area in catchment
r = lake:catchment area ratio

For a stream catchment, FAB simplifies to:

$$\mathrm{Ndep} + \mathrm{Sdep} = \mathrm{fNupt} + \mathrm{Nimm} + \mathrm{Nden} + \mathrm{BC^{*}l} - \mathrm{ANClcrit} \quad (16)$$

Applications of FAB to 13 catchments from the UK CLAG research programme have predicted much higher rates of N leaching than are currently measured in the surface waters (Curtis *et al.* in press). This implies either that present-day rates of N retention and / or denitrification in the catchments are much larger than the long-term values used in the model or that there is a large sink which has not been accounted for. The FAB model has therefore been applied to the WAWS stream sites to investigate whether predictions of nitrate leaching match observed data for a larger suite of sites.

4.1 Catchment nitrogen variables

Values for Nimm and Nden were assigned to each soil type within the catchment according to data presented by Hall *et al* (1997). The catchment total for each variable was calculated in the GIS using the areal proportion of each soil type. The uptake of N by coniferous forest was calculated from the forest fraction (f) in each catchment multiplied by the default Nupt figure of 0.279 keq ha^{-1} yr^{-1}, whilst moorland N uptake was calculated as (1-f) multiplied by the default value of 0.07 keq ha^{-1} yr^{-1} (Hall *et al.* 1997).

4.2 Nitrate leaching estimates

The observed nitrate leaching for each catchment was calculated from the annual geometric mean nitrate concentration multiplied by the catchment-area weighted runoff (Section x.2.1) derived either from the 30 year average or from the 1992-94 data sets. Nitrate leaching (Nle) predicted by FAB was calculated as:

$$\mathrm{Nle} = \mathrm{Ndep} - \mathrm{Nupt} - \mathrm{Nimm} - \mathrm{Nden} \quad (17)$$

Ndep was calculated using both the WAWS and the UK national deposition data sets (Section X.2.4).

4.3 Comparison of observed and predicted nitrate leaching

Estimates of observed N leaching calculated using the two different runoff data sets agreed closely (Figure 11) but N inputs to catchments were much larger when calculated using the UK 1992-94 data compared to WAWS data (Figure 12). As a result, catchment nitrate leaching predicted by FAB was in excess of observations for both estimates of nitrogen deposition while FAB predictions using the UK national deposition data were much greater and increased roughly in parallel with the observed leaching losses (Figure 13). In contrast, predictions using the WAWS deposition data tended to converge towards observed values at higher rates of N leaching. It is clear from Figure 13, that variations in the estimates of N deposition will contribute significantly to uncertainty in catchment-scale FAB predictions of N leaching losses. For the WAWS catchments, much of the variance in nitrate leaching can be explained by the amounts of conifer forestry within the catchment with significant positive relationships between nitrate leaching, area-weighted mean forest age and percentage catchment cover by conifer forestry (Stevens *et al.* 1997). Deposition to forested sites is likely to be underestimated using the WAWS data as it was not possible to partition inputs according to vegetation type. This was done for the UK data and probably explains the larger catchment N inputs as ammonia gas and occult deposition are increased significantly by forest cover (Reynolds *et al.* 1997). The convergence between N leaching predicted using WAWS deposition data and observed values may thus result from a progressive underestimate of N inputs with increasing forest cover.

5 Discussion

The work so far has revealed a number of sources of uncertainty in assigning SSWC critical loads and exceedance values to individual catchments and in predicting nitrogen leaching losses using FAB. One source of uncertainty relates to the estimates of catchment BCd*, S* and total-N deposition. Uncertainty arises because of (1) differences between the WAWS and UK 1992-94 national deposition data and (2) because the UK 1992-94 catchment inputs are partitioned according to vegetation cover within each catchment whereas the WAWS data are not. Considering firstly the two data sets, it is unlikely that the different collection periods (1992-94 and 1995) explain the difference in deposition patterns. However, WAWS deposition was modelled using bulk precipitation data from 25 collectors distributed throughout Wales in contrast to the UK national monitoring network which has only four collectors actually located in the Principality. Spatial averaging of the concentration field across the higher density Welsh network is likely to produce a different pattern compared to that from the whole of the UK, even though the same Kriging techniques were used in both cases. For BCd*, deposition is modelled entirely from bulk precipitation data while for S* the wet component dominates the deposition to most of Wales. Modelled wet deposition incorporates the process of seeder-feeder enhancement and occult deposition over high ground (RGAR 1997) which accounts for the larger inputs to the central Wales uplands, the mountains of Snowdonia in the north and the Brecon Beacons in the south (Figure 3, 6 and 7). However the differences between the two sets of maps for BCd* (Figure 3) and S* (Figure 6 and 7) suggest that this effect may have been over emphasised in the UK national map as much larger inputs were predicted to high ground. The total-N deposition maps are dominated by the reduced nitrogen component, particularly by ammonia dry deposition. As the same ammonia data were used for both the UK and the WAWS maps, deposition patterns for reduced nitrogen species and total-N are quite similar (Figures 14 and 15).

Partitioning atmospheric inputs according to the vegetation type or canopy roughness will contribute to differences in the WAWS and UK 1992-94 estimates of catchment inputs as discussed earlier. This effect has yet to be quantified, although a comparison with catchment estimates derived using the UK 1992-94 20 km square data aggregated across landuse types with the WAWS data would give a good indication of the importance of the effect.

The main source of uncertainty so far identified in SSWC critical loads is the choice of stream water chemistry input data. This has been noted previously (CLAG 1995), but the effect appears to be greater in this study. The SSWC equation appears to be relatively insensitive to variations in the values of BCd* or runoff, although a more systematic sensitivity analysis is required to confirm this.

Surprisingly, the variations in S* deposition estimates had a relatively small effect on the proportions of exceeded sites compared with the choice of chemistry data used in the critical loads calculation. It is important to resolve the practical question of whether to include BCd* in the exceedance calculation.

In common with earlier work (Curtis *et al.* in press), the FAB model predicts much larger nitrogen leaching rates than are currently observed. As stream water ammonium concentrations are generally negligible and nitrate is the dominant form of dissolved inorganic-N, the predicted increase in nitrogen losses will probably be in the form of nitrate. Assuming the UK 1992-94 data provide the best estimates of deposition, as they allow for vegetation type, the catchments are presently retaining an average of 87% of the incoming inorganic-N, although nitrate leaching generally increases with deposition (Figure 16). At steady state, assuming that nitrogen inputs remain constant at current values, FAB predicts that nitrogen retention will decline to an average of 24%. The corresponding increase in nitrate leaching amounts to an average of 16.5 kgN ha^{-1} yr^{-1}. Assuming there is no change in excess sulphur deposition, and all additional nitrogen is leached as nitrate accompanied by protons or aluminium, quite severe acidification will occur with 62% of sites having an annual average charge balance ANC less than zero, compared with 15% at present. This result points again to the urgent need to verify the steady-state FAB model and the values assigned to its variables.

6 References

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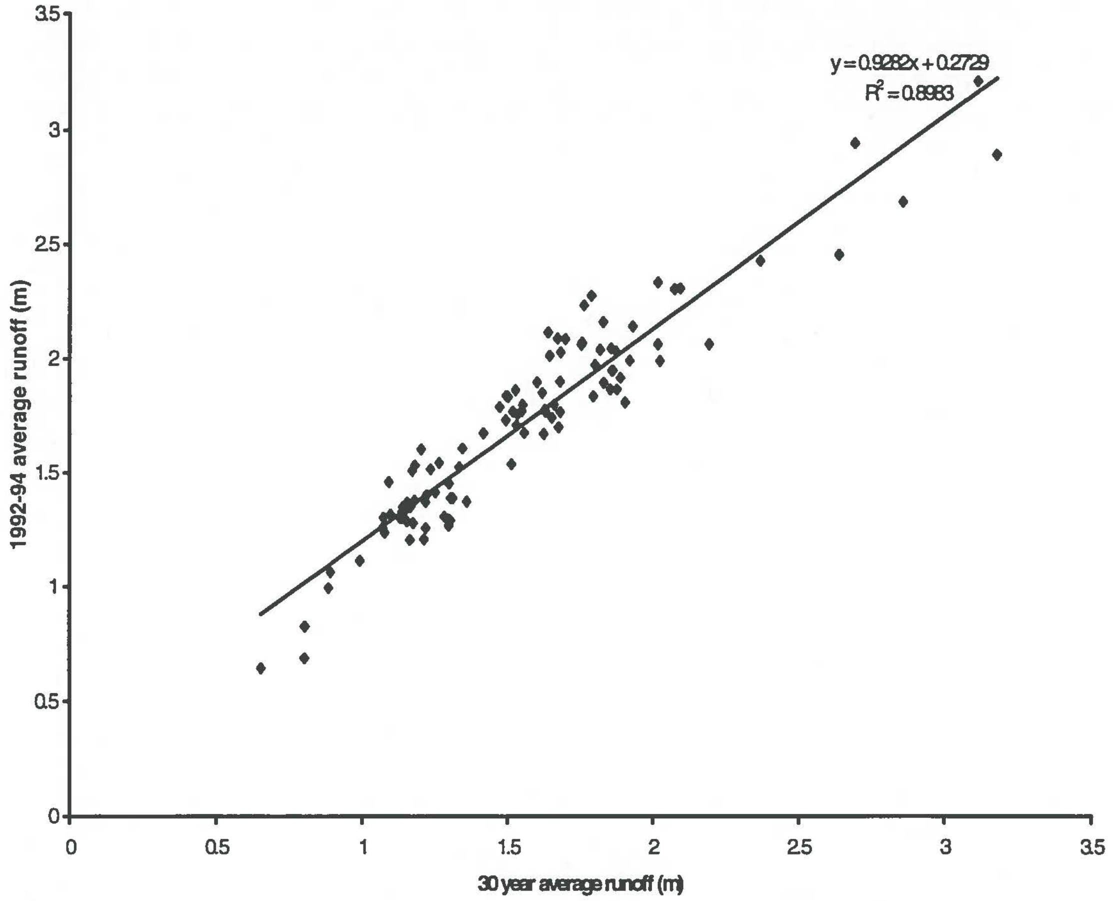


Figure 1. Plot of catchment runoff estimates derived from 30 year average and 1992-94 average 1 km square data.

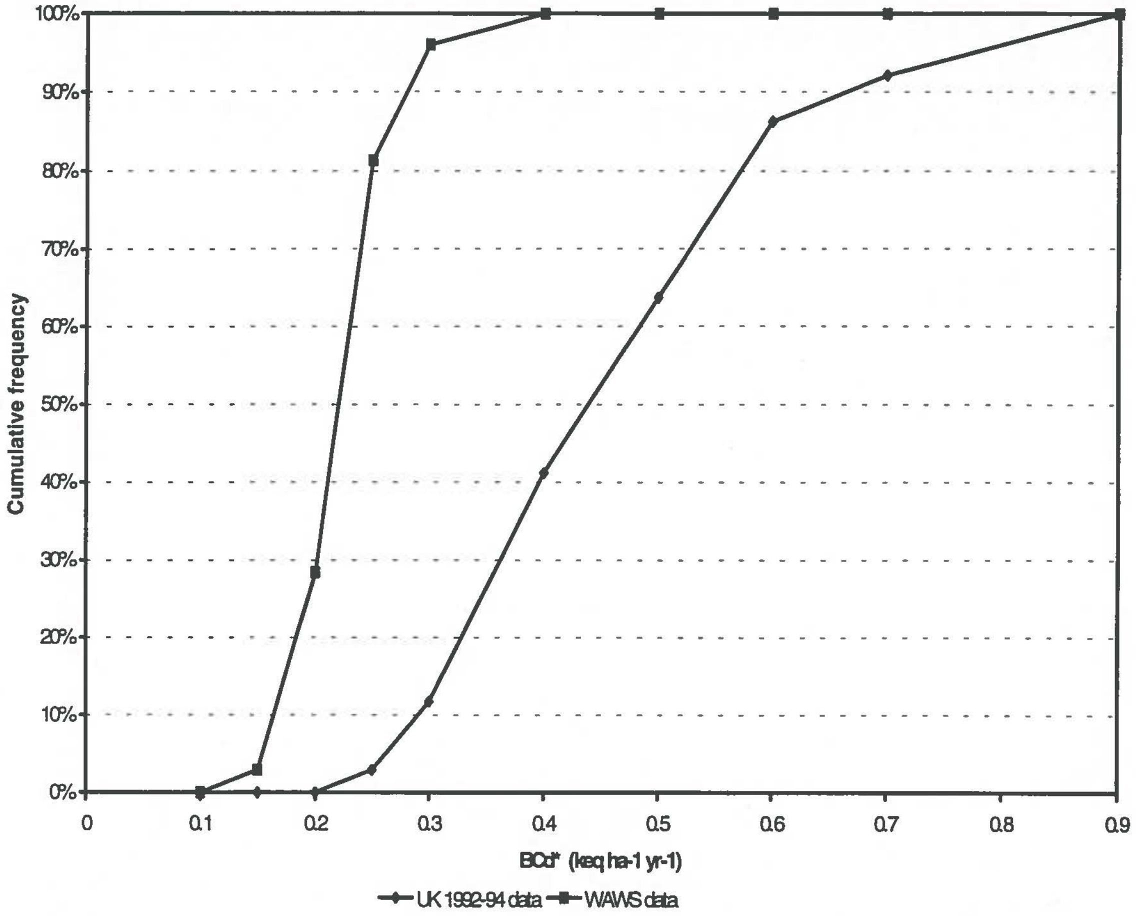


Figure 2. Cumulative frequency plot of catchment BCd* values calculated using UK 1992-94 and WAWS data.

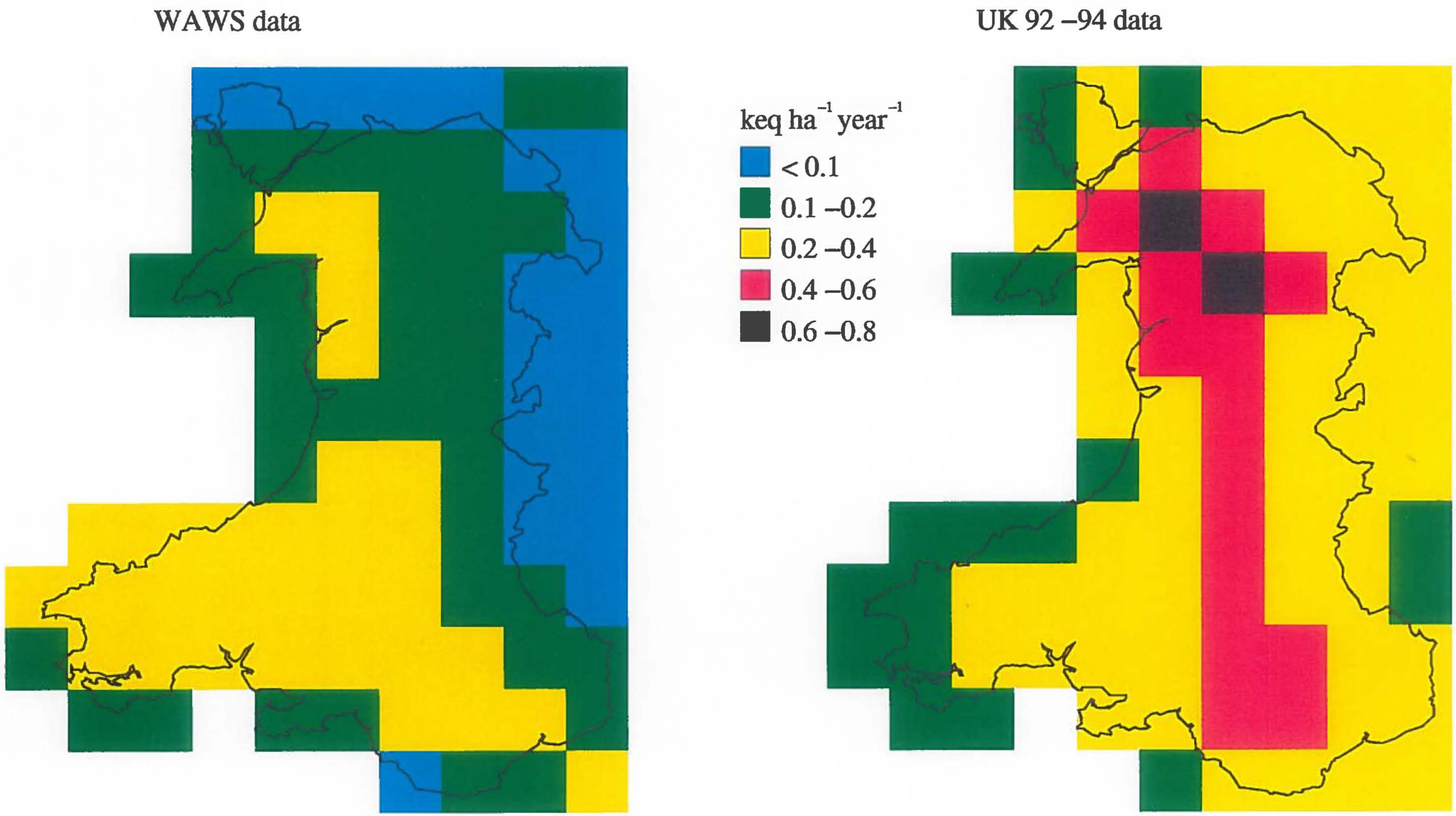


Figure 3 Total non marine base cation (Mg + Ca) deposition

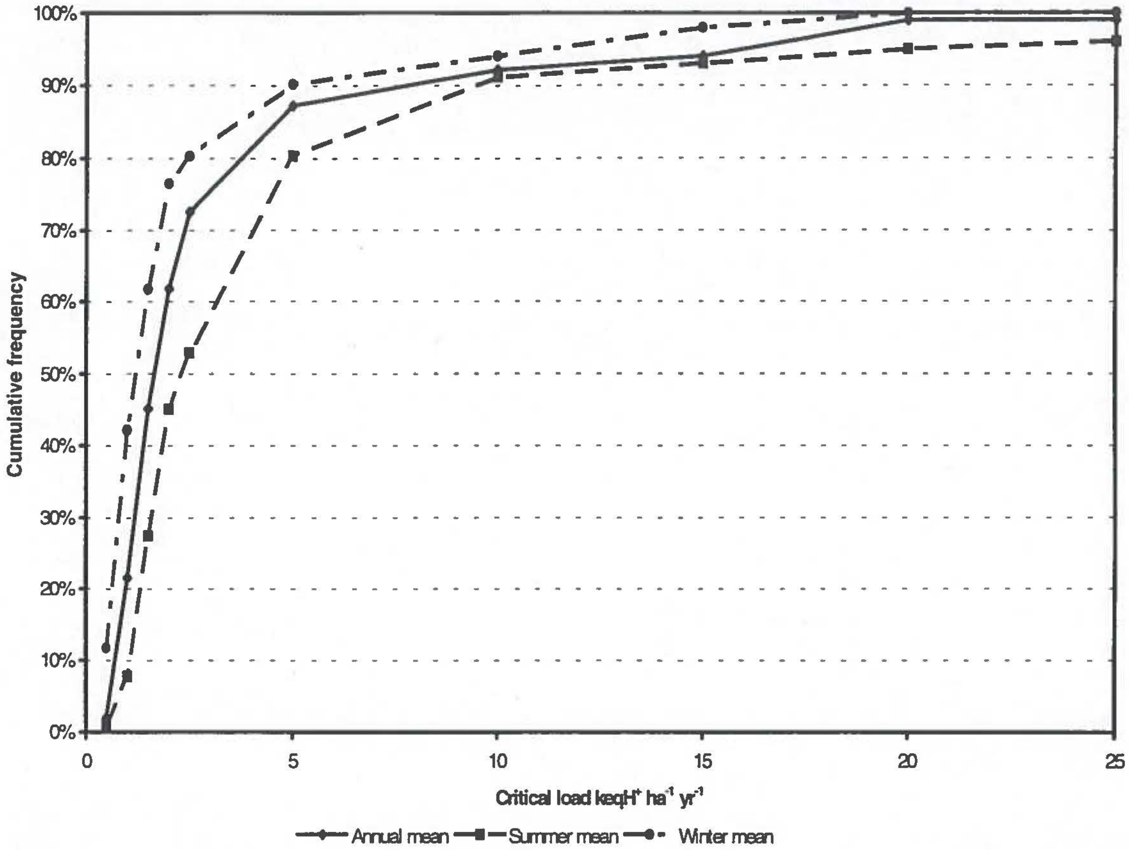


Figure 4. Cumulative frequency plots of critical loads calculated using annual, summer and winter geometric mean chemistry, 1992-94 runoff data and WAWS BCd* data.

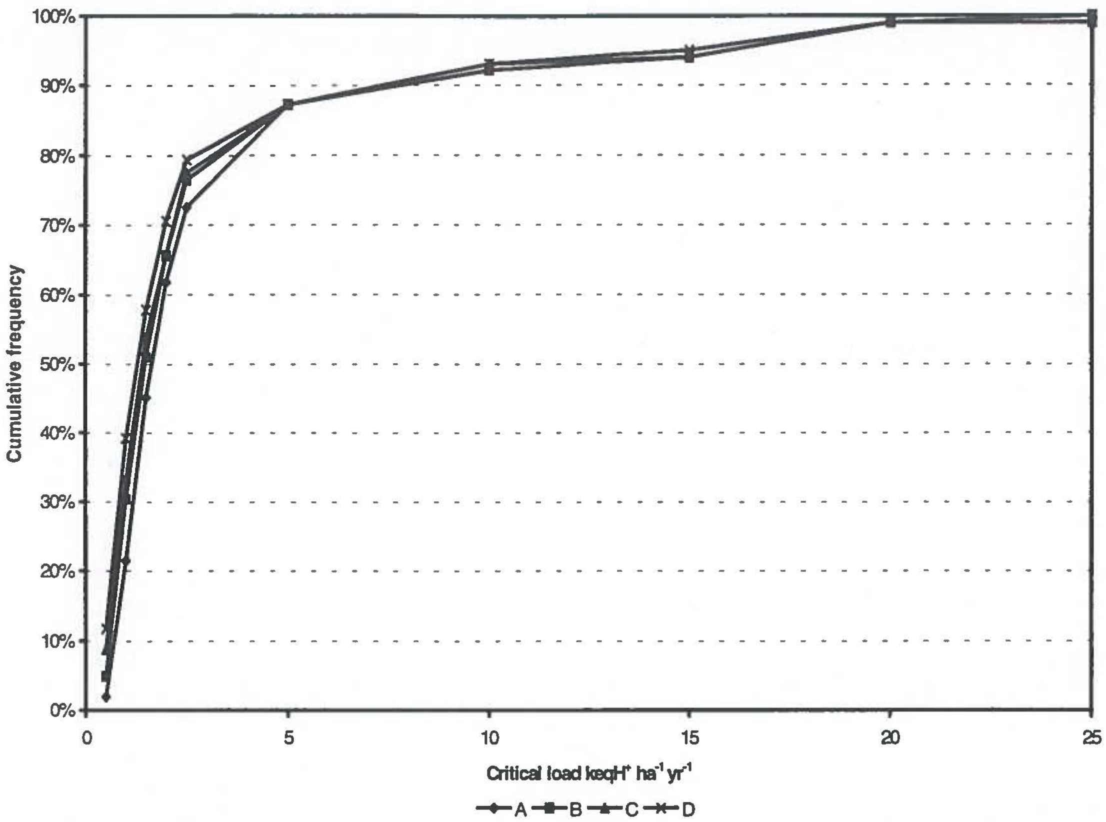
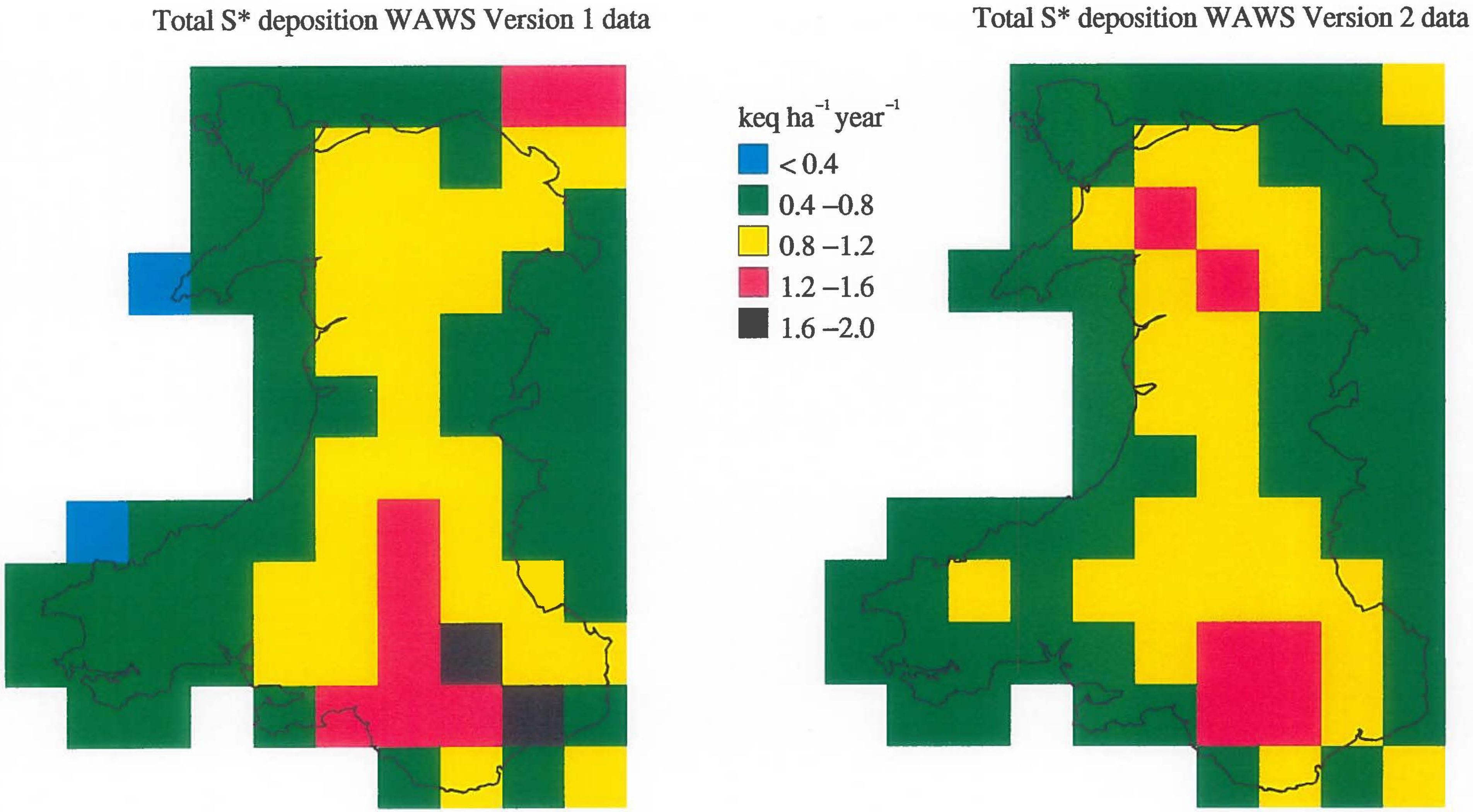
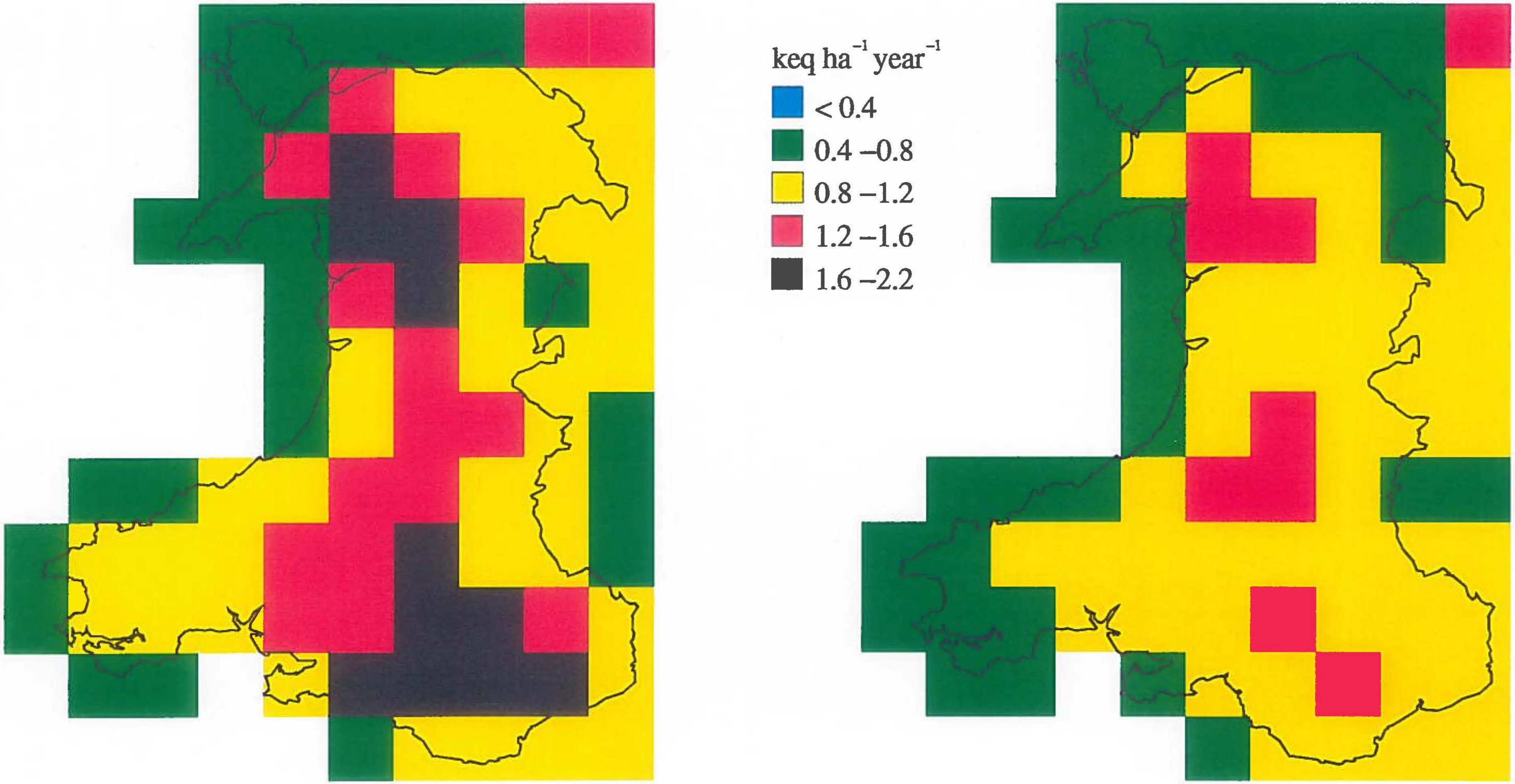


Figure 5. Cumulative frequency plots of critical loads calculated using annual geometric mean stream water chemistry and A: 1992-94 runoff and WAWS BCd* data; B: 30 year average runoff and WAWS BCd* data; C: 1992-94 runoff and UK 1992-94 BCd* data and D: 30 year average runoff data and UK 1992-94 BCd* data.


Total S* deposition WAWS Version 1 data

Total S* deposition WAWS Version 2 data

Figure 6 Total S* deposition


Total S* deposition UK 92 –94 data

Total S* deposition HARM 1994 data

Figure 7 Total S* deposition

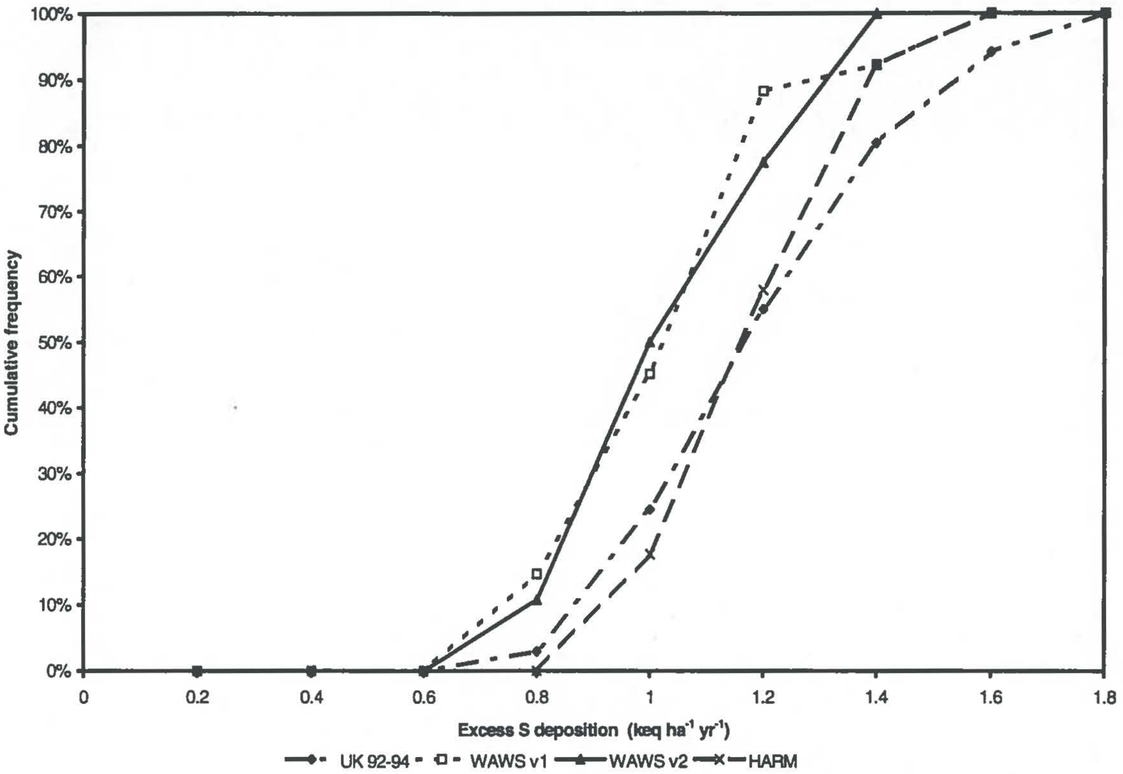


Figure 8. Cumulative frequency plots of catchment excess sulphur deposition derived from four different 20 km square data sets: UK 92-94; WAWS v1 using urban enhanced SO_2 concentrations; WAWS v2 using rural SO_2 concentrations; HARM present-day predictions.

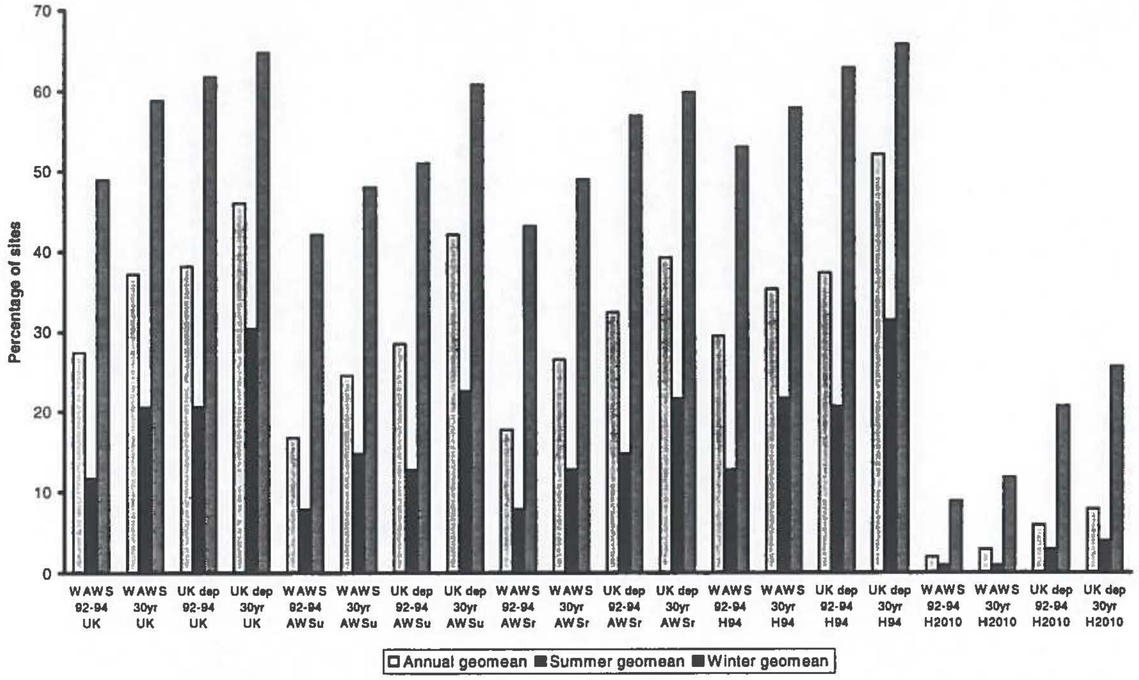


Figure 9. Percentage of sites at which SSWC critical loads exceeded where exceedance is calculated as: Ex(CL)=S*dep-CL(A).

Key: WAWS = BCd* from WAWS data; UKdep = BCd* from UK data
92-94 = 1992-94 runoff data; 30yr = 30 year average runoff
UK = UK S*deposition; AWSu = WAWS S*deposition with urban enhanced SO_2; AWSr = WAWS S* deposition with rural SO_2; H94 = HARM predicted S*deposition for 1992-94; H2010 = HARM predicted S* deposition for 2010.

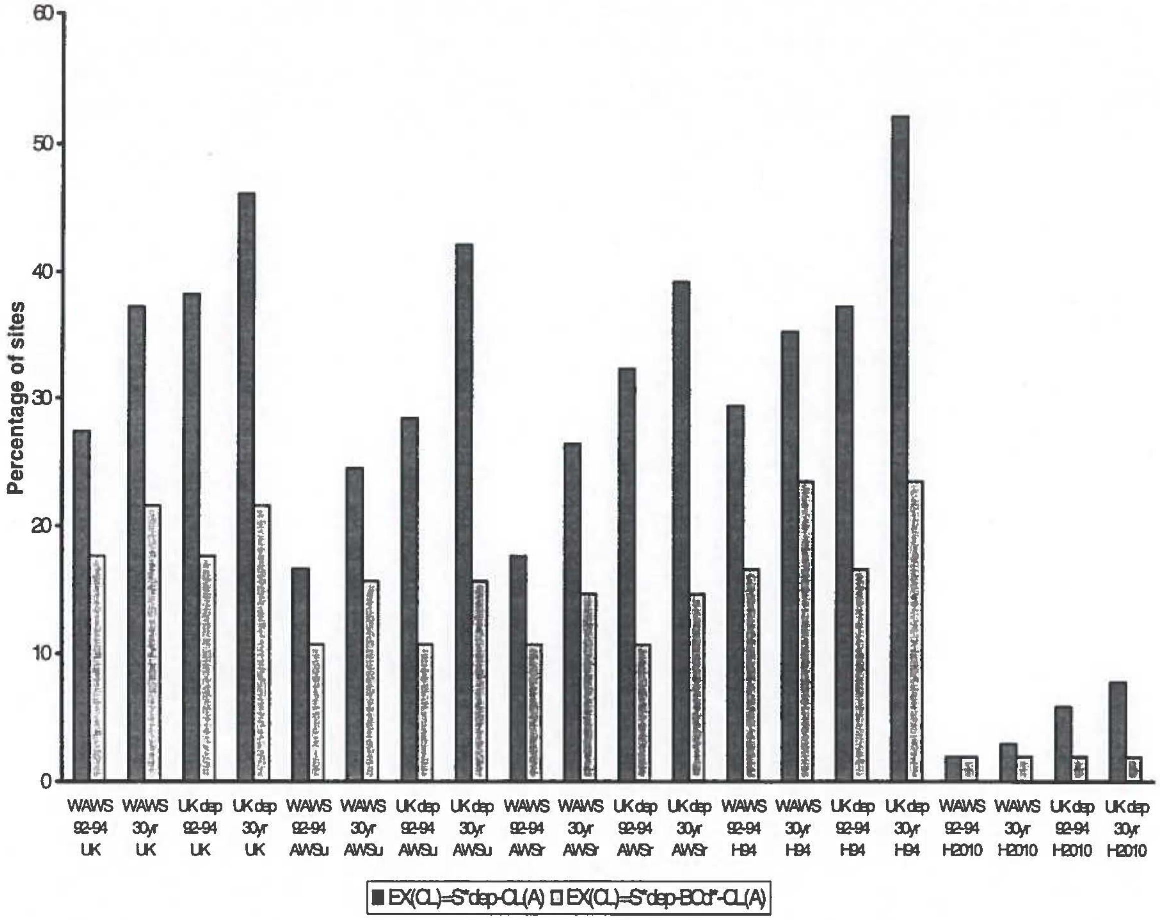


Figure 10. Percentage of sites at which the SSWC critical load is exceeded where the critical load is calculated using annual geometric mean stream water chemistry.

Key: WAWS = BCd* from WAWS data; UKdep = BCd* from UK data
92-94 = 1992-94 runoff data; 30yr = 30 year average runoff
UK = UK S*deposition; AWSu = WAWS S*deposition with urban enhanced SO_2; AWSr = WAWS S* deposition with rural SO_2; H94 = HARM predicted S*deposition for 1992-94; H2010 = HARM predicted S* deposition for 2010.

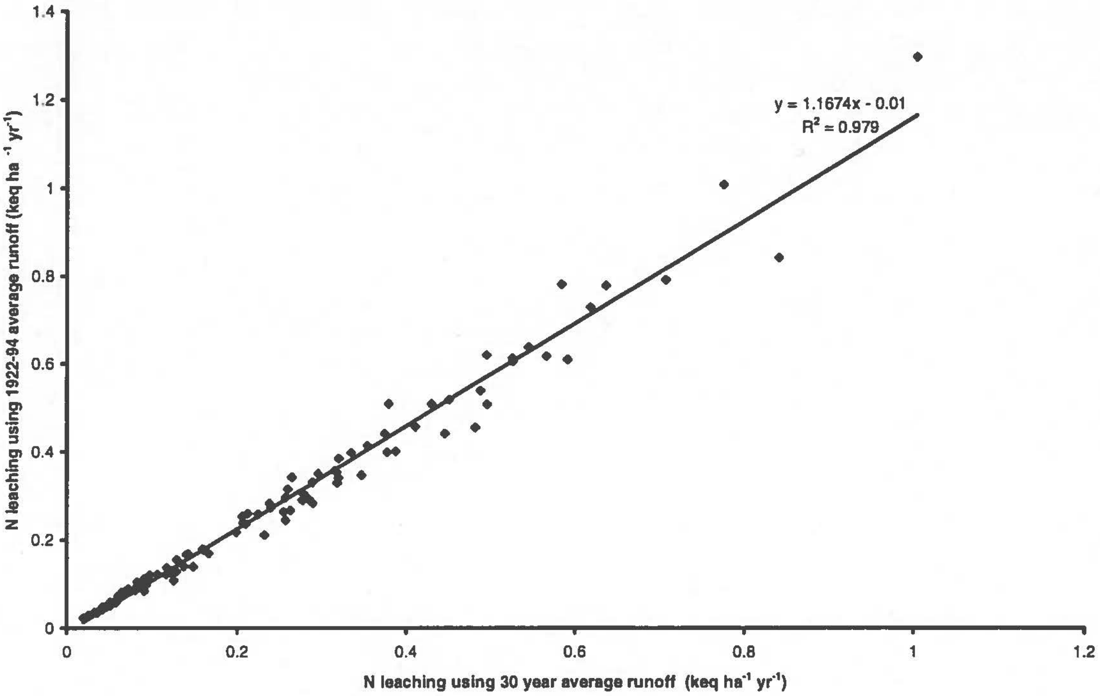


Figure 11. Comparison of observed N leaching calculated using annual geometric mean nitrate-N concentrations and catchment runoff derived from 1992-94 average and 30 year average data.

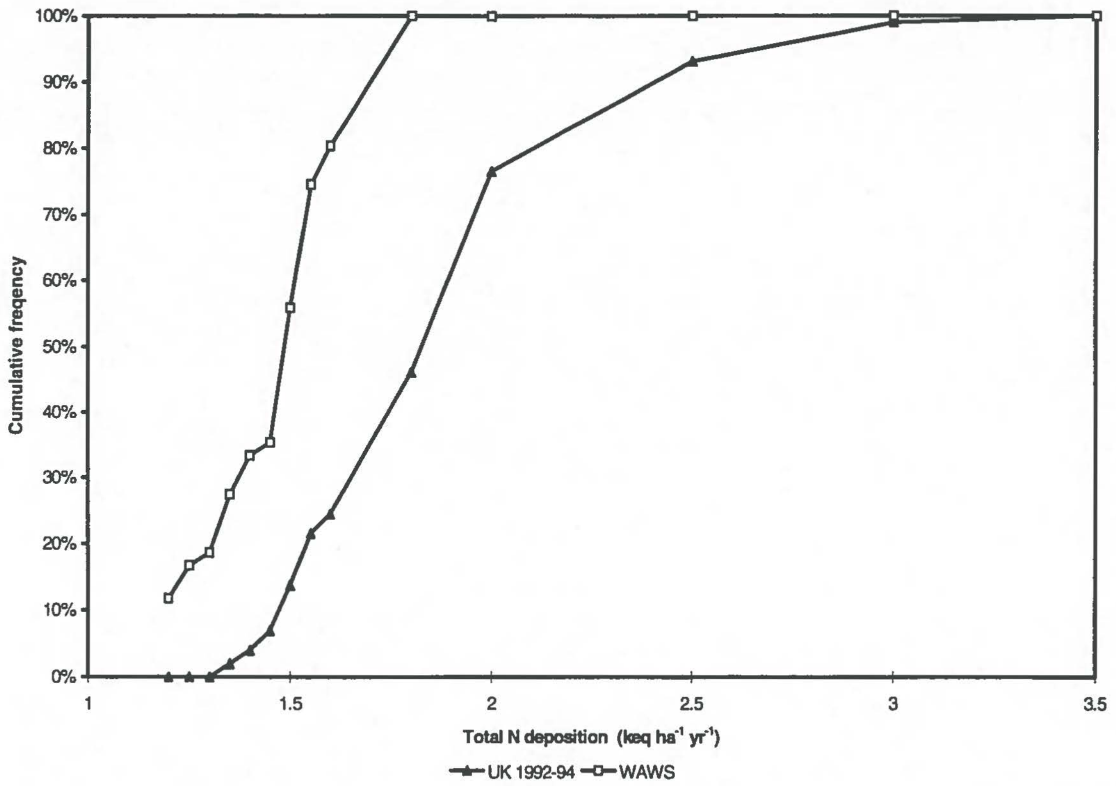


Figure 12. Cumulative frequency plots of catchment total nitrogen deposition derived from two different 20 km data sets: UK 1992-94 and WAWS.

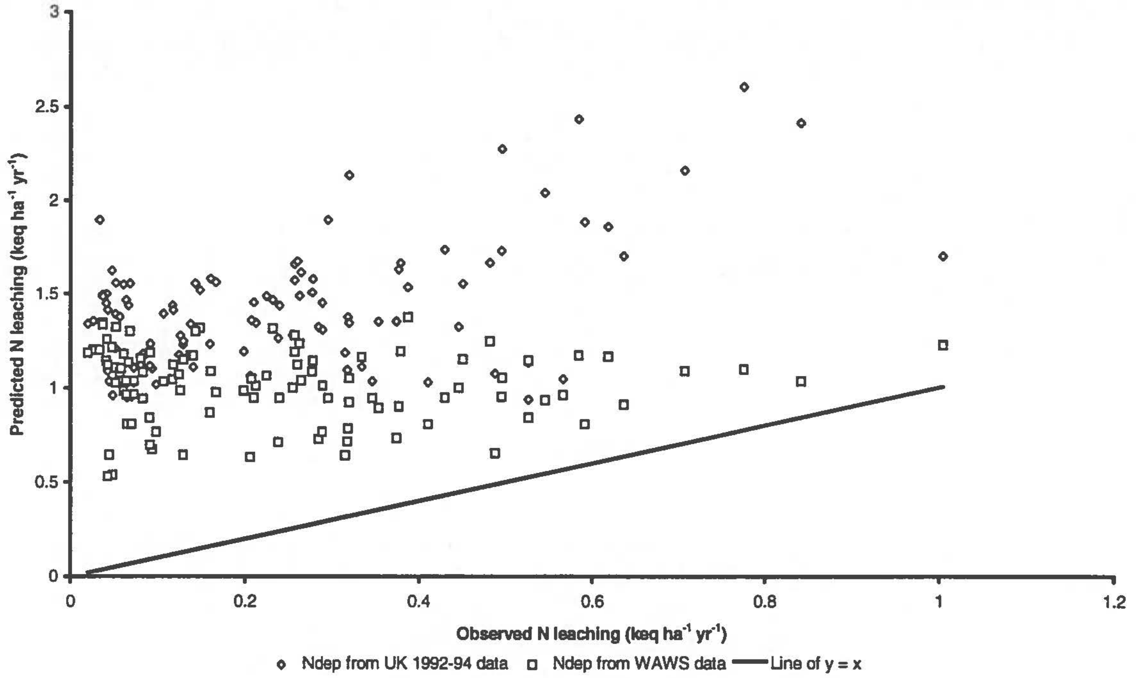
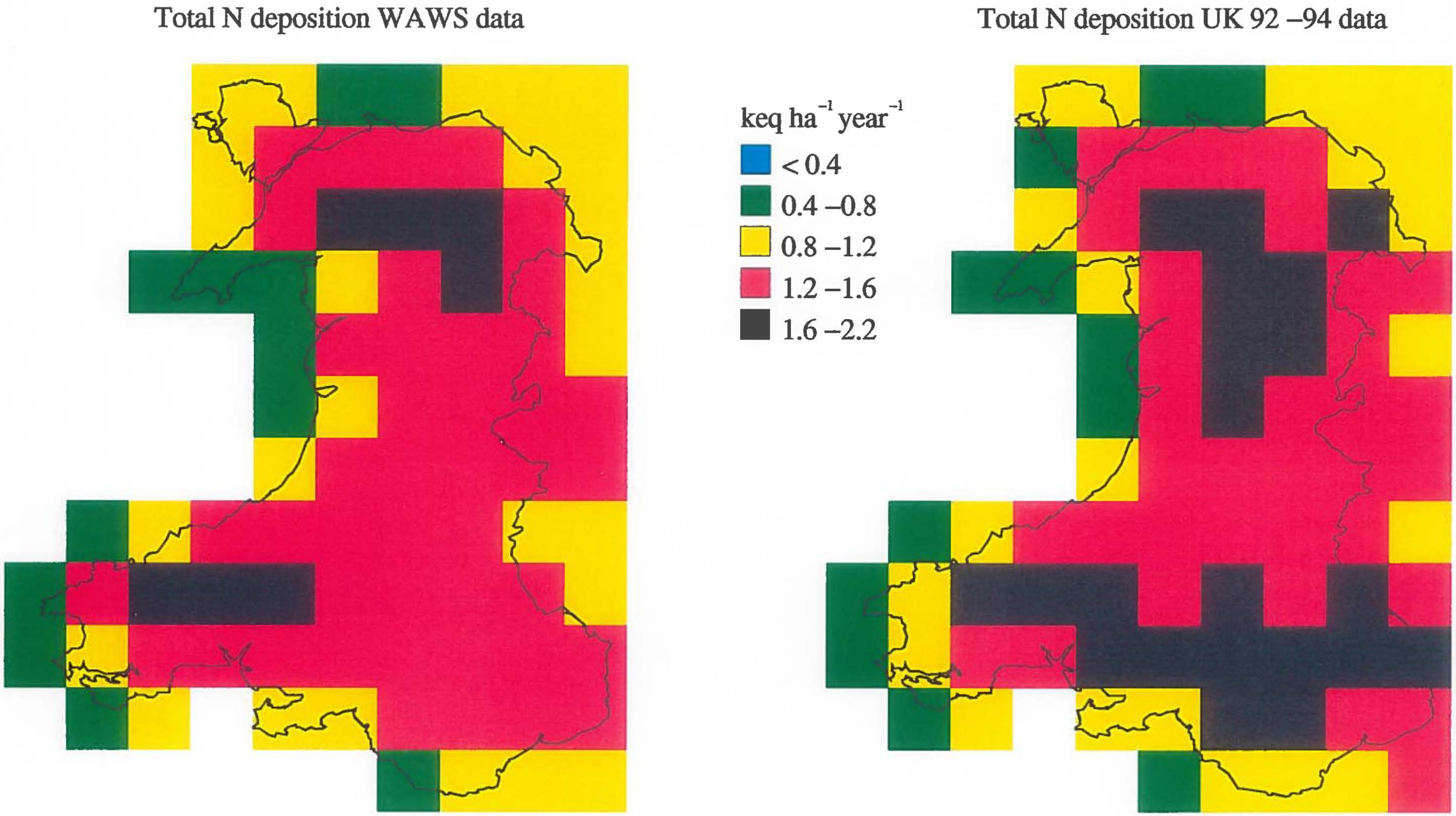


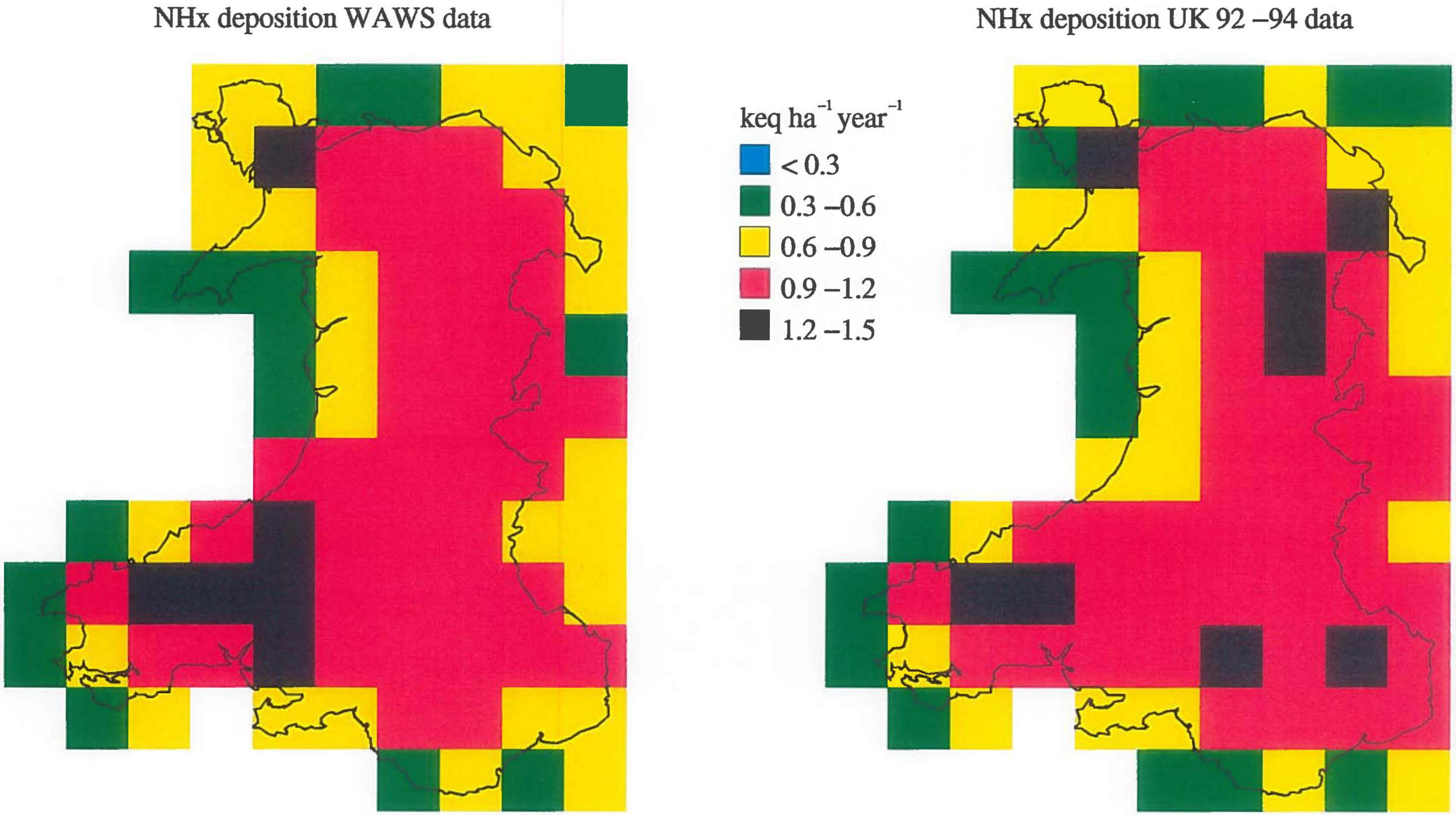
Figure 13. Plot of observed N leaching from WAWS catchments estimated using 30 year average runoff against N leaching predicted by the FAB model.



Total N deposition WAWS data

Total N deposition UK 92 –94 data

Figure 14 Total N deposition



NHx deposition WAWS data

NHx deposition UK 92 –94 data

Figure 15 Deposition of reduced nitrogen species

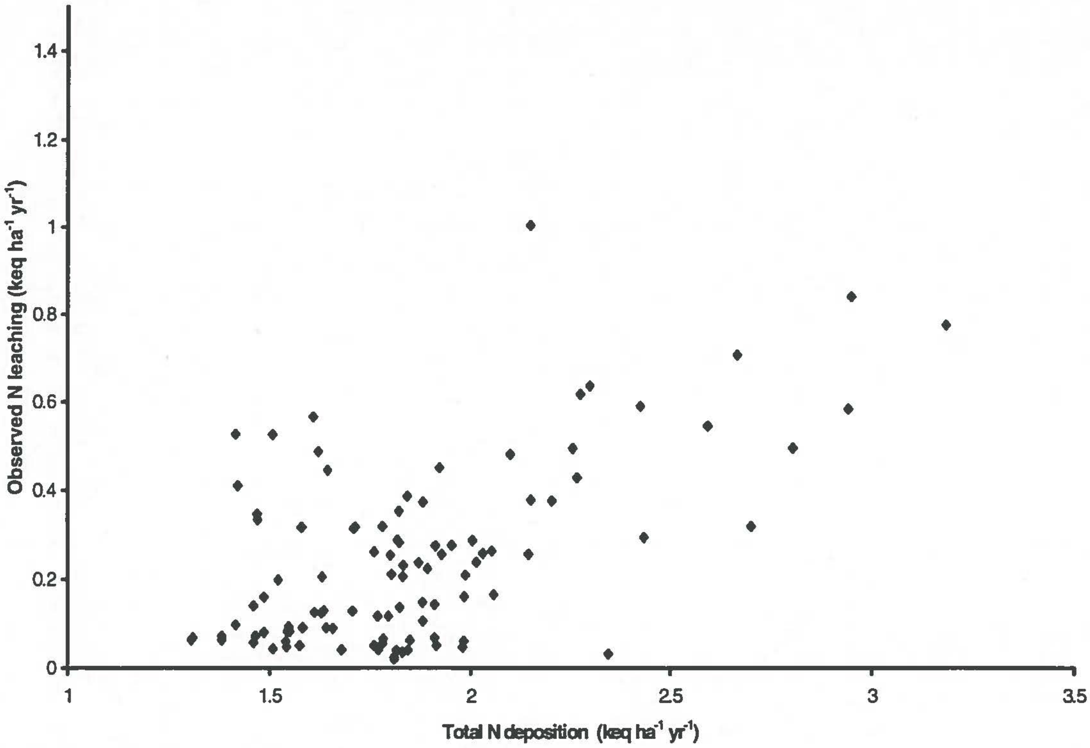


Figure 16. Comparison of atmospheric inputs and nitrate leaching losses from the WAWS catchments.

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

Allott, T.E.H. & Juggins, S.

The work programme in Year 1 has focused on the collation of data from palaeolimnological studies of acid sensitive lakes in Great Britain and Ireland, and the entry of these data onto relational databases. The final dataset includes 105 sites from which sediment core diatom data ares available (See Table 1).

The core data vary in terms of both the detail of stratigraphic diatom record available, and the technique used to provide chronological control. The majority of the sites (62) have a full stratigraphic diatom record, with at least 10 samples covering the post-1800 period. The remainder of the cores have either skeletal diatom records (>5 samples in the post-1800 period) or diatom assemblages available for core tops and bottoms only. These latter cores can be used to reconstruct current and pre-acidification conditions, but cannot be used to evaluate the timing or rate of any acidification trend.

The core data also vary in terms of chronological control. Over half the cores (55) have been dated using the Lead-210 technique, and generally a full core chronology is available for the last 150 years. The other technique used to date cores is the Spherical Carbonaceous Particle (SCP) method of Rose *et al.* (1995). Four cores have not been dated.

Diatom data arenow held on the AMPHORA database at the Environmental Change Research Centre.

Data has also been collated for each site on water chemistry and catchment characteristics. Critical loads have been calculated for each site using both the diatom and steady-state water chemistry models (see CLAG 1995).

The work programme in Year 2 will focus on analyses of the diatom data. The stratigraphic diatom assemblages will be used to calculate:

i) changes in diatom inferred pH (DpH) records for each core;
ii) diatom species turnover for each core.

The relationships between critical loads exceedances, catchment characteristics, pH change and diatom species turnover will be evaluated in Years 2 and 3 of the project.

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Table 1 **List of sites included in the palaeolimnological database, indicating nature of the diatom data and chronological control**

Sitecode	Site Name	Grid Reference	Diatom Data	Chronology
ARR	Loch Coire nan Arr	NG 808422	Full	210-Pb
BEIS	Loch na Beiste	NG 885943	Skeleton	SCP
BER	Llyn Berwyn	SN 743568	Full	210-Pb

BHAI	Loch Coire a'Bhaic	NC 247295	Top/Bottom	SCP
BHAR	Loch Bharranch	NG 977575	Skeleton	SCP
BLU	Blue Lough	J 327252	Full	210-Pb
BOGA	Loch nam Badan Boga	NH 100930	Top/Bottom	SCP
BRAC	Loch nam Brac	NC 179480	Full	210-Pb
BURNMT	Burnmoor Tarn	NY 18404	Full	210-Pb
CADH	Loch Dubh Cadhafuaraich	NC 682183	Skeleton	SCP
CE45A	Llynoedd Ieuan	SN 794812	Full	SCP
CFEA	Loch na Claise Fearna	NC 201468	Full	SCP
CHAM	Loch a'Cham Alltain	NC 283446	Top/Bottom	SCP
CHN	Loch Chon	NN 421051	Full	210-Pb
CLAI	Loch Clair	NG 999574	Full	210-Pb
CLYD	Llyn Clyd	SH 635597	Full	210-Pb
CON	Llyn Conwy	SH 780463	Full	210-Pb
COR	Loch Coire an Lochain	NH 943004	Full	210-Pb
CORN	Loch Bealach Cornaidh	NC 208282	Skeleton	SCP
CNAM	Loch Coire nan Cnamh	NG 974083	Skeleton	SCP
CUAR	Loch nan Cuaran	NC 292238	Skeleton	SCP
CULF	Loch Cul Fraioch	NC 025330	Top/Bottom	SCP
CUR	Loch na Curra	NG 823800	Skeleton	None
CRA	Loch Craggie	NC 625072	Skeleton	None
CRAN	Cranmer Pond	SU 794324	Full	210-Pb
CREI	Loch na Creige Duibhe	NC 005118	Top/Bottom	SCP
CRIC	Loch na Cric	NC 166 037	Skeleton	SCP
CWEL	Llyn Cwellyn	SH 560 549	Full	SCP
CZSN66	Llyn Eiddwen	SN 606670	Full	SCP
DALL	Loch Dallas	NJ 092475	Skeleton	SCP
DCAL	Loch Dubh Camas an Lochain	NG 871972	Top/Bottom	SCP
DEVOKE	Devoke Water	SD 163970	Full	210-Pb
DOI	Loch Doilet	NM 808678	Full	210-Pb
DUBH	Lochanan Dubha	NC 147055	Top/Bottom	SCP
DUH	Dubh Loch	NO 238828	Full	210-Pb
DUL	Llyn Dulyn	SH 662244	Full	210-Pb
EIB	Llyn Eiddew Bach	SH 646343	Full	210-Pb

ENO	Loch Enoch	NX 445851	Full	210-Pb
EOIN	Loch nan Eoin	NG 928517	Full	SCP
EUN	Loch nan Eun	NO 230854	Full	210-Pb
FEOI	Lochan Feoir	NC 229252	Top/Bottom	SCP
FHIO	Lochan Fhionnlaidh	NC 191103	Top/Bottom	SCP
FLE	Loch Fleet	NX 560697	Full	210-Pb
FLEO	Loch Fleodach Coire	NC 275248	Top/Bottom	SCP
FNOD	Llyn Fanod	SN 603643	Full	SCP
GAIN	Loch na Gaineimh	NC 765304	Skeleton	SCP
GLAS	Llyn Glas	SH 601547	Full	210-Pb
GREENT	Greendale Tarn	NY 146074	Full	210-Pb
GRUA	Loch na Gruagaich	NC 243158	Top/Bottom	SCP
GYN	Llyn Gynon	SN 800647	Full	210-Pb
HAIR	Loch na h'Airbe	NH 103924	Skeleton	SCP
HHHH	Un-named	NO 653909	Skeleton	SCP
HIR	Llyn Hir	SN 789675	Full	210-Pb
HOID	Loch na h'Oidhch	NH 154778	Skeleton	SCP
HUID	Loch Bealach a Bhurich	NC 262280	Skeleton	SCP
IDWA	Llyn Idwal	SH 645596	Full	SCP
IOIG	Loch Iain Oig	NG 792292	Skeleton	SCP
IRD	Llyn Irddyn	SH 630220	Full	210-Pb
KEMP	Loch Kemp	NH 470178	Full	210-Pb
LACH	Lochan Lairig Cheile	NN 558278	Skeleton	SCP
LAG	Llyn Llagi	SH 649483	Full	210-Pb
LAI	Loch Laidon	NN 380542	Full	210-Pb
LAMH	Loch a'Mhadaidh	NH 199732	Skeleton	SCP
LAR	Loch na Larach	NC 217583	Full	210-Pb
LDE	Loch Dee	NX 470790	Full	210-Pb
LGR	Loch Grannoch	NX 541691	Full	210-Pb
LOCH	Loch Toll an Lochain	NH 074833	Top/Bottom	SCP
LON	Long Loch of Dunnett Head	ND 204 759	Full	210-Pb
LOD	Lochan Dubh	NM 895710	Full	210-Pb
LOSG	Loch Bad an Losguinn	NH 158038	Skeleton	SCP
LOWT	Low Tarn	NY 163091	Full	210-Pb

MAAM	Lough Maam		Full	210-Pb
MAUM	Lough Maumwee		Full	210-Pb
MHIC	Loch Mhic Leiod	NJ 008347	Skeleton	SCP
MUCK	Lough Muck		Full	210-Pb
MUIG	Loch Muighbhlaraidh	NH 635830	Skeleton	SCP
MYN	Llyn Cwm Mynach	SH 678238	Full	210-Pb
NAME	Loch na Beiste	NC 004125	Top/Bottom	SCP
NAGA	Lochnagar	NO 252859	Full	210-Pb
NAHU	Loch Bealach na h-Uidhe	NC 264256	Top/Bottom	SCP
NARR	Loch Narroch	NX 453916	Full	210-Pb
NESS	Loch Ness	NH 535295	Full	210-Pb
NELD	Loch Neldriken	NX 440830	Full	210-Pb
NEUN	Loch na Eun	NC 232298	Top/Bottom	SCP
NIGH	Lochan Nigheadh	NC 182148	Skeleton	SCP
RLDN	Round Loch of the Dungeon	NX 466 846	Full	210-Pb
RLGH	Round Loch of Glenhead	NX 450805	Full	210-Pb
SAID	Loch Coire Saidhe Duibhe	NC 450360	Skeleton	SCP
SCOATT	Scoat Tarn	NY 159104	Full	210-Pb
SGAM	Loch Sgamhain	NH 100530	Skeleton	SCP
SION	Loch Sionascaig	NC 120140	Full	210-Pb
SKE	Loch Skirrow	NX 605682	Full	210-Pb
SLET	Loch Sletill	NC 965470	Skeleton	None
TANN	Loch Tanna	NR 921428	Full	210-Pb
TARF	Loch Tarff	NH 425100	Skeleton	SCP
TEAN	Loch Teanga	NF 818383	Full	210-Pb
TINK	Loch Tinker	NN 445068	Full	210-Pb
TOLL	Loch Tollaidh	NG 841785	Skeleton	None
UAI	Lochan Uaine	NO 001981	Full	210-Pb
UIS	Loch Uisge	NM 808550	Full	210-Pb
UN02	Un-named	NC 168478	Top/Bottom	SCP
URR	Loch Urr	NX 760845	Full	210-Pb
VAL	Loch Valley	NX 445817	Full	210-Pb
VEAG	Lough Veagh		Full	210-Pb
YBI	Llyn y Bi	SH 648564	Full	210-Pb

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

Collins, R., Jenkins, A., Lees, M., Foster, H., Chen, J. & Wheater, H.

Work Carried out at the Institute of Hydrology

Although critical loads are based upon mean annual water chemistry, seasonal leaching of nitrate has been observed at many sites across the UK. Simulation of mean annual chemistry may therefore be insufficient in the critical loads exercise since high levels of nitrate and hence, acidity, in winter may cause significant effects on freshwater biota whilst the mean chemistry indicates no cause for concern. The long term dynamic model MAGIC has previously been applied at an annual timescale to predict changes in mean chemistry given future changes in deposition loading. Modification of the model has been undertaken by IH to incorporate a monthly time step enabling the capture of the seasonal dynamics associated with a broad understanding of the ecosystem nitrogen cycle.

The model has been applied to the Afon Hafren catchment at Plynlimon for which sufficiently detailed monthly input-output chemistry and soils and vegetation data are available. A strong seasonal variation in stream nitrate concentration is observed at the Afon Hafren; increased uptake by vegetation during the summer months decreases stream nitrate concentrations causing an increase in stream pH; during the winter months, uptake is negligible, nitrate levels are therefore enhanced and drive a reduction in pH.

Hydrological and hydrochemical data, collected by IH since 1988, has been analysed to determine mean annual and mean monthly proportions of rainfall, runoff, deposition chemistry and net retention of nitrate. Net retention is calculated as the balance between the input flux in deposition and the output flux in streamwater and in reality represents a lumped value which accounts for plant uptake, retention within the soil and loss by gaseous processes. These values have been incorporated into MAGIC within a framework of ion and mass balance on both an annual and monthly timestep. The application has successfully reproduced the seasonal variations in stream nitrate, with concentrations in the summer months falling to below 5 μEq l^{-1} and increasing to > 30 μEq l^{-1} during the winter. Some discrepancy exists between observed and modelled nitrate values reflecting the variability associated with samples collected on a monthly basis. The nitrogen dynamics contribute to a seasonality in stream pH, reflected by both observed and modelled values. Typically pH is greater than 6 during summer, falling below 5 during winter.

Current research is focused upon the identification of seasonal trends in; base cation uptake by vegetation, the partial pressure of CO_2 in soil and stream, and the release of organic acids to streamwater (reflected by DOC concentrations). Utilisation of the results in the model is likely to further improve the prediction of stream pH on a monthly basis. Further modifications will include the incorporation of hydrological flow routing to provide the relative proportions of ground and soil water, two hydrochemically distinct water sources, to flow each month.

Future model applications will use observed monthly deposition chemistry over the last 10 years to drive the model, in addition, observed rainfall and runoff over this period can be incorporated. This approach is likely to improve model prediction by removing the smoothing effect caused by the use of mean monthly values. Once model prediction has been optimised the implications for critical loads of the seasonal nitrogen dynamics will be assessed.

Work carried out at Imperial College

Work in this unit officially started in June 1997 with the appointment of Dr. Jining Chen as a PDRA employed solely on the project. However, Helen Foster, who started a related NERC funded studentship in October 1996, carried out some valuable initial work.

An investigation into the availability of suitable episodic hydrochemical data was carried out, resulting in the decision to focus model development work on the Institute of Hydrology's (IH) Plynlimon catchments. A database containing over ten years of weekly streamwater/rainfall chemistry data and 3 years of 15 min sampled pH and conductivity data was obtained from Dr Colin Neal at IH Plynlimon. Daily stream chemistry is also available as the result of a 6 month sampling campaign carried out by a past IC research student.

Initial work investigated the dominant catchment controls on episodic hydrochemical response utilising the daily streamwater chemistry data. The effects of antecedent conditions, soil-type, land-use and groundwater and tributary inflow on stream episodic hydrochemical response were investigated for a range of spatial scales. The results clearly show that hydrological pathways influence stream chemistry, with soil water dominating streamflow during episodic events. First order ditches draining gley soils showed little chemical variation because the baseflow component was restricted by an impermeable clay layer, which left only the organic horizons as a source of water and caused the flow to be ephemeral. In contrast, ditches on podzols received a groundwater component, which increased stream alkalinity and enabled perennial flow. The chemistry of the major streams was intermediate between that of the first order ditches draining gleys and podzols, reflecting the mixture of contributing sources. Forestry affected chemistry by atmospheric scavenging and evapotranspiration and recently felled sites showed a flushing of some elements and the influence of biological processes from decomposition. This work has been written up and has been accepted for publication (Foster et al., 1998).

Work has recently started on the development of a new integrated episodic hydrochemical model that will be initially calibrated on the IH Plynlimon catchments. The modelling work will take a step-wise approach to model structure identification, rather than fixing the structure *a priori* according to perceived catchment processes. Since high frequency flow data are usually available, or can be relatively easily collected, the hydrological pathways will be determined first. Next, a chemical model for each pathway will be estimated resulting in an integrated episodic hydrochemical model. This step-wise approach to modelling is data led, with model complexity only being increased if a significant improvement in the model's predictive capability is demonstrated. Through this approach we hope to minimise model identifiability problems that have beset the application of previous models.

Ultimately, this model will be coupled to a long-term catchment acidification model such as the MAGIC-WAND model, which is being extended to include seasonal responses as part of this project. Thus, long-term scenarios of stream chemistry episodic response will possible, and when linked to work on the biological affects of episodic events, an improved method of assessing critical loads at a catchment (and sub-catchment) scale will be produced.

Output

Foster, H.J., Alexander, S., Locks, T., Wheater, H.S., Lees, M.J., and Reynolds, B. (1998) Scale Dependence of the Episodic Hydrochemical Response of Nested Catchments at Plynlimon, Wales, accepted for publication in Hydrological and Earth System Sciences.

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

Work Carried out at SOAEFD

Work began on Unit 3B in June 1997. The SOAEFD databases hold extensive information relating to chemical variables, salmonid populations and macroinvertebrate communities, at a large number of sites across Scotland. During the initial stages of research, the SOAEFD chemical and biological databases were examined, with the aim of identifying suitable study catchments. Stream sites were required which had similar mean ANC values, but differing values of key components, such as aluminium and total organic carbon, which contribute to ANC. The preliminary review highlighted four main watersheds, within which to locate field sites. These are the River Halladale in Sutherland, the River Dee in Aberdeenshire, the Loch Ard catchment in the Trossachs and the Water of Fleet in Galloway.

A desk study identified small streams within each main watershed, which according to geological and soils maps and existing data, would be likely to have either acid, intermediate or alkaline chemical characteristics. All sites downstream of standing water were rejected, as were sites at which salmonid stocking was known to occur and those where catchment disturbance, e.g. forestry activity, had occurred recently, or is likely in the next two years. A subsequent pilot field survey then collected water samples from each potential site for chemical analysis. Fish and invertebrate populations were also checked, at sites for which no previous data was available.

A final selection of field sites was made, based on the results of the pilot chemical survey and the suitability of each site for biological sampling. All sites are less than 10m wide, have boulder / cobble / pebble substrates and incorporate riffle habitat. A range of riparian cover types are represented in the selected sites, including deciduous woodland, coniferous forestry and moorland. Six streams, comprising two each of low ANC, intermediate ANC and high ANC, were chosen within each of the four main catchment areas. In addition, two other streams, within the River Bladnoch catchment in Galloway, were included at the request of SEPA. These sites do not comply with the original site selection criteria, in that one is stocked and the other downstream of a loch. They may, however, provide a valuable comparison with the other 24 sites, following data analysis. For the purposes of statistical analysis, the number of stream sites may be increased further at a later date, by the inclusion of comparable SOAEFD data.

Figure 1 shows the location of each of the main catchment areas in Scotland, together with site lists. Table 1 outlines the characteristics of each of the chosen field sites, based on data collected during the pilot field survey. The sites are presented in order of increasing alkalinity. Hydrological conditions varied between sampling dates, but none of the samples were taken at extreme high or low flows.

2. Programme of work for Year 2

During Year 2 the following monitoring will be conducted at each site:

- Stream chemistry - Dip samples will be collected at least once a month, with additional samples taken to obtain chemistry data at a wide range of flow conditions. Continuous pH data is available for a limited number of sites in the Loch Ard catchment.

- Episode sampling - Two automatic water samplers will be rotated between sites, in order to gather hourly samples throughout storm events at acidic and alkaline tributaries in each main catchment.

- Salmonid populations - Salmonid densities will be surveyed twice; in June, to estimate fry productivity, and in August / September once populations have stabilised.

- Macroinvertebrate communities - Quantitative Hess samples will be taken in April (5 per site). A kick sample will be collected on the same occasion, to provide a species diversity estimate.

- Habitat - Data relating to a range of catchment and instream habitat variables, known (from a literature review) to be biologically important, will be recorded throughout the year.

- Hydrology - Stage boards will be installed, in order to relate chemical variables to flow conditions at all sites. Where continuous stage or flow records are available, either from FFL or SEPA, relationships developed between chemical variables and flow will be used to produce estimates of the frequency and severity of episodic events.

- Deposition - Local deposition data is already available for Halladale and Loch Ard, therefore efforts will be concentrated on collecting new data for Galloway and the Dee catchment. This data will complement the 20km national deposition data already available.

Table 1. Chemical characteristics of field sites.

Site Name	Catchment	Grid Reference	Date	Alkalinity µeq l	pH	Al-L µg
Benmeal Burn	Water of Fleet	NX559658	08/01/98	-65	4.22	139
Craiglowrie Burn	Water of Fleet	NX553670	08/01/98	-51	4.3	213
Cardoon Burn	Water of Fleet	NX528647	08/01/98	-23	4.66	19
Carrouch Burn	Water of Fleet	NX548665	08/01/98	-22	4.69	79
Allt Dhaidh Beag	River Dee	NN979877	23/01/98	-11	4.92	11
Burn 11	Loch Ard	NS470988	29/10/97	-8	5.02	41
Allt Dhaidh Mor	River Dee	NN966878	23/01/98	-5	5.06	16
Polbae Burn	River Bladnoch	NX265726	08/01/98	-4	5.07	4
Bealach Burn East	River Halladale	NC906411	16/10/97	4	5.31	25
Burn 2	Loch Ard	NN388043	29/10/97	4	6.41	0
Burn 7	Loch Ard	NS451985	29/10/97	10	5.69	32
Beoch Burn	River Bladnoch	NX314713	08/01/98	26	5.75	0
Achridigill Burn	River Halladale	NC888628	16/10/97	72	6.41	9
Burn 6	Loch Ard	NS438989	29/10/97	81	6.66	2
Greendams Burn	River Dee	NO648900	01/10/97	86	6.92	7
Bealach Burn West	River Halladale	NC904411	16/10/97	119	6.62	3
Ewe Burn	River Halladale	NC893451	16/10/97	119	6.5	3
Castramont Burn	Water of Fleet	NX587615	08/01/98	142	6.98	2
Forsinain Burn	River Halladale	NC905485	16/10/97	146	6.86	3
Green Burn	Loch Ard	NS505943	29/10/97	148	6.8	8
River Halladale at gorge	River Halladale	NC913414	16/10/97	160	6.67	19
Pollagach Burn	River Dee	NO414961	29/08/97	205	6.96	1
Allt an t-Slugain	River Dee	NO156936	29/08/97	246	7.36	2
Manhole Burn	Loch					