A CRITICAL LOAD EVALUATION OF THE PEAK DISTRICT MOORLAND STREAM NETWORK

A thesis submitted to the University of Manchester for the degree of Master of Science in the Faculty of Science & Engineering

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THE UNIVERSITY OF MANCHESTER

ABSTRACT OF THESIS submitted by Simon David Barber for the degree of Master of Science and entitled ‘A Critical Load Evaluation of the Peak District Moorland Stream Network’. Submitted 09/2004.

Critical loads of acidity have been calculated and evaluated for 36 moorland streams in the Peak District National park, under baseflow conditions. Two different models were implemented, the Steady-State Water Chemistry model, and the Empirical Diatom model. Over a third of the streams sampled exceeded their critical loads using the Steady-State Water Chemistry model, indicating that the moorland habitats of the Peak District are acidified in many places. The cause of this acidification has been attributed to atmospheric deposition from nearby industrial areas. An even higher proportion of sites were found to exceed their critical loads using the more cautious Empirical Diatom model, suggesting that this acidification is widespread. Uncertainty analysis in the form of a ‘Monte Carlo’ simulation showed the Steady-State Water Chemistry to have good precision. Coupled with a sensitivity analysis of the model input variables, this proved the results of the Steady-State Water Chemistry model to be relatively stable. This study thus provides a ‘best case scenario’ for the critical load status of the Peak District moorland stream network, however the results imply extensive acidification with few signs of a recovery.

DECLARATION

I declare that no portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any university of other institute of learning.

SIMON BARBER

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1. Introduction

1.1 The Critical Load Concept

A critical load is ‘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 can be used in reference to soils or surface waters. By providing a value above which acid deposition is detrimental to the ecology of an environment, critical loads can document areas where this value is being exceeded, thus helping policy-makers develop strategies for reductions in acid deposition (Curtis *et al.* 2001). The critical loads concept has been widely accepted across Europe, where it has been adopted for use by the United Nations Economic Commission for Europe (UNECE) convention on Long-range Transboundary Air Pollution (LRTAP) (Henriksen and Posch 2001).

There are three commonly used models for the calculation of critical loads in surface waters. The Steady-State Water Chemistry (SSWC) model and the Empirical Diatom model are both empirical, and allow the calculation of current freshwater critical loads of acidity, and their exceedances. The First-order Acidity Balance (FAB) model also allows the calculation of critical loads of acidifying S- and N-deposition and their exceedances; however this process-orientated model requires more catchment data. This study, like other similar surface water chemistry surveys (e.g. Aherne *et al.* 2002, Henriksen *et al.* 1992, and CLAG 1995) will primarily employ the SSWC model, but in addition will also investigate the results of the Empirical Diatom model.

1.2 The Peak District National Park

The Peak District National Park is situated in the centre of England at the southern end of the Pennine range, and is 1438km^2 in size. This area has often been shown to be one of the most susceptible areas to acid deposition, with high exceedances of critical loads picked out by previous nationwide studies (e.g. Harriman *et al.* 1995). These high values of exceedances are mainly due to the fact that this area receives some of the highest concentrations of Sulphur deposition in the United Kingdom. This was observed as early as 1990 by the UKGAR report (documented by Allott *et al*. 1995). These high concentrations can be accredited to the industrial centres west of the Peak District, namely Greater Manchester and Merseyside, from where prevailing winds tend to come from. In addition, the Peak District is also surrounded by large industrial settlements to the North and East, namely Huddersfield and Sheffield respectively. The Peak District has therefore been subject to atmospheric pollution from these industrial areas for the last 250 years. Prior to this, the mining and smelting of lead in the Peak District also provided small amounts of localised atmospheric pollution to the area (Lee 1981). High amounts of acid deposition are harmful to the moorland ecology, and are thought to result in clear vegetational changes. For example, Tallis (1964) ascribed the probable cause of the massive decline in *Sphagnum* in the Peak District over the last 200 years to atmospheric deposition. Although spatial studies of Peak District water chemistry have been carried out (e.g. Evans *et al*. 2000) a detailed study of the critical load exceedances of the area has not yet been done.

This study aims to provide a thorough evaluation of the critical loads of the Peak District moorland stream network. These streams are often ignored by wider studies as they may be remote and feed larger, more accessible rivers. The Acid Water Monitoring Network (AWMN) do have one site in the Peak District, the River Etherow, however one site cannot be used to draw assumptions about an area as large as the Peak District. The study, carried out over a dry summer's week, will provide a snapshot of the moorland stream baseflow conditions. Chemical conditions in streams in the Peak District are hugely variable, for example the river Etherow has shown ranges in pH from >7.0 at baseflow to <4.0 at high flow (Evans and Monteith 2002). The study will thus provide a conservative evaluation of the chemistry and critical load status of these streams.

2. Methods

2.1 Sampling Methods

A total of 37 sites were sampled in the study, as shown in figure 1. These were based on a pseudo-random selection of predominantly third order streams

(Strahler 1957), as observed from an Ordnance Survey 1:63,360 map, draining the "Section 3 moorland" areas of the Peak District National Park. The park was split into 5 distinct areas ('Black Hill and Wessenden', 'Bleaklow, Hope and Derwent', 'Kinder', 'Eastern moors and North West', and the 'South West moors') and at least six sites were sampled within each area. Although 40 sites were originally selected for sampling, five sites were inaccessible because of problems gaining permission. In addition, a further two sites were added whilst sampling in the field because of ease of sampling (see appendix for full list of sites).

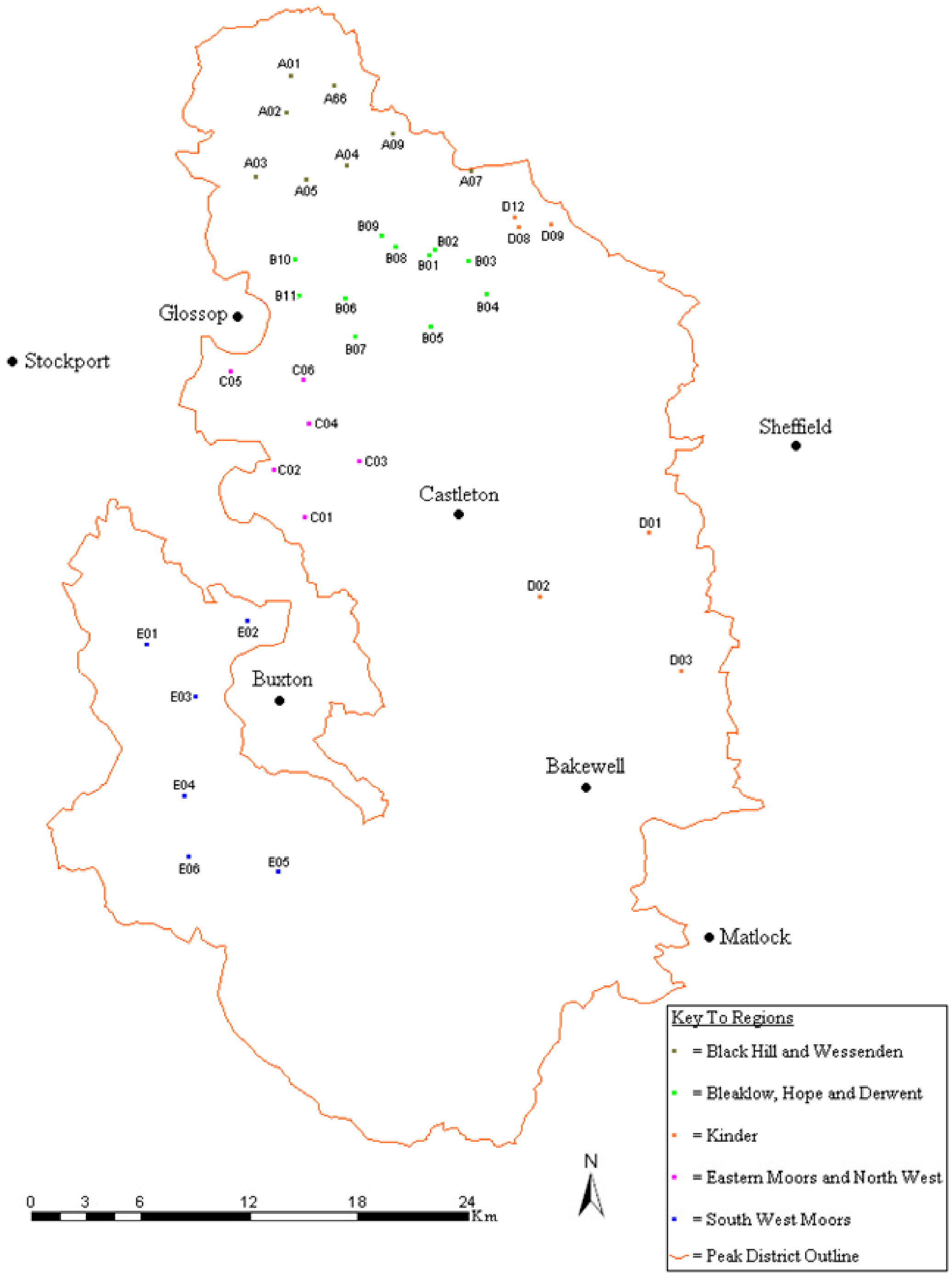
At each site, two 500ml Nalgene sampling bottles were filled with water from a flowing part of the stream. Photographs were taken of each sampling site, and the position was accounted for using a Global Positioning Signal (GPS) where possible to allow the survey to be repeated in the future. The water samples were then taken back to the School of Geography, University of Manchester and stored in a refrigerator at 3°C. The sampling process took place in late May, and lasted a week. Precipitation over this period was negligible.

2.2 Sample Analysis

Shortly after arriving at the laboratory, all samples were filtered using Whatman 0.45µm cellulose nitrate membrane filters. Following this, two 25ml samples were sent to the Department of Earth Sciences, University of Manchester, for assessment of anions and cations using methods of Ion Chromatography (IC) and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) respectively.

Conductivity and pH were both measured at room temperature in the laboratory soon after the samples had been collected. Conductivity was measured using a Jenway 4310 meter and pH was measured using a Jenway 3320 meter. Alkalinity was then measured using a "dual end-point" titration technique (HMSO 1981). Samples above pH 4.5 were titrated using 4.5 and 4.2 as the dual end points, whilst samples below pH 4.5 were titrated using 2.9 and 2.6 as the end points, and gave negative values of alkalinity. Hydrochloric acid (0.02M) was used as the titrant. A rodwell magnetic stirrer was used to homogenise the solutions being measured at all times. In addition, Total Organic Carbon (TOC) was measured using an aqueous carbon analyser (Shimadzu TOC-V CPN) and Colour was measured in Pt-Co units using a spectrophotometer (HACH DR/4000U).

Figure 1. Map of the Peak District National Park, showing sampling sites used in this study.



2.3 Calculating Critical Loads

2.3.1. Sea Salt Corrections

Sea salt corrections were applied to the measured concentrations of calcium, magnesium, potassium, sodium, sulphate and chloride (equations 1 to 6 respectively). This ensured that changes in atmospheric deposition did not include ions originating from sea salt spray. The sea salt corrections used are the same as those documented by Henriksen and Posch (2001) and assume that all sea salt components are transported and deposited in the same ratio as found in seawater. In addition, it was assumed that all chloride in the water originates from sea salt spray. Where sea salt adjusted values were negative, a value of zero was recorded (as documented by Harriman and Christie 1995).

$$[Ca^*] = [Ca] - 0.037.\ [Cl] \qquad (1)$$

$$[Mg^*] = [Mg] - 0.198.[Cl] \qquad (2)$$

$$[K^*] = [K] - 0.018.[Cl] \qquad (3)$$

$$[Na^*] = [Na] - 0.858.[Cl] \qquad (4)$$

$$[SO_4^*] = [SO_4] - 0.103.[Cl] \qquad (5)$$

$$[Cl^*] = 0 \qquad (6)$$

2.3.2 The SSWC Model

The SSWC model can be applied to firstly calculate the critical load of acidity of a surface water, and secondly to calculate the exceedance that atmospheric deposition is causing. First devised by Henriksen *et al.* (1986), the theory behind the model is based on the present balance between sea-salt adjusted base cations (BC^*_t, as calculated in equation 7) and acidic anions (AN^*_t, as calculated in equation 8), which is summarised as the acid neutralising capacity (ANC), as shown in equation 9. Fluxes are more commonly used through the modelling process, and are simpler to use than concentrations; hence all values referred to in the model are fluxes. Concentrations were converted into fluxes using runoff values. A default figure of 85% of precipitation was used to calculate runoff, as this calculation has previously been used in moorland areas of Scotland by White *et al.* (2000). The precipitation values used were average annual precipitation figures derived from the Met. Office (from 1971 to 2001). The only available format that these figures were in was a map, so the mean value of a rainfall range was used for each site.

An ANC limit (ANC_{limit}) is set for the surface waters being studied, which relates to the probability of harm to biological populations within the surface water. The most commonly used value for this limit is 20 μeq L^{-1}, however, in the UK a limit of 0 μeq L^{-1} is often used so as not to wrongly show the large number of naturally acid waters in the UK to be exceeding their critical loads (Harriman & Christie 1995). The critical load of a surface water (equation 10) is thus determined by subtracting the ANC_{limit} from the base cation flux prior to acidification (BC^*_o). As this is unknown, it must be estimated through a calculation (equation 11).

The calculation of BC^*_o subtracts the difference between the acid anion flux currently found in the surface water and the acid anion flux prior to acidification, from the current base cation flux. The acid anion flux prior to acidification (AN^*_o) is calculated as in equation 12. The value of pre-acidification nitrate ($NO_3{}^*_o$) is usually assumed to be zero, whilst the value of pre-acidification sulphate can be calculated using a simple regression formula (equation 13). A number of regression formulae have been calculated from empirical data. The constants used in this study are those estimated by Brakke *et al.* (1989), as this is the regression formula that has previously been applied in the UK by other studies such as CLAG (1995). This study estimated the value of 'a' to be 15 and that of 'b' to be 0.16, however constants derived from other studies will be investigated. The difference in acid anion concentration is however multiplied by the F-factor (F) in an attempt to relate the long-term changes in inputs of non-marine acid anions to the present day excess production of base cations (Henriksen & Posch 2001) and is described as shown in equation 14. The value of S within this calculation is the base cation flux at which F = 1 and is usually set at 400μeq L^{-1}. Hence where the base cation flux is greater than S, F is set to 1.

Finally, exceedance of the critical load of acidity is calculated by subtracting the critical load of acidity from the sum of sulphur deposition ($SO_4{*}_{dep}$) and nitrate leaching ($NO_{3\ Leach}$) as shown by equation 15. Nitrate leaching is determined from the sum of the measured concentrations of nitrate and ammonia in runoff. Where this figure is positive, exceedance of the critical load is occurring, and where it is negative, exceedance of the critical load is not occurring.

$$BC{*}_t = Ca{*}_t + K{*}_t + Mg{*}_t + Na{*}_t \qquad (7)$$

$$AN{*}_t = SO_4{*}_t + NO_3{*}_t \qquad (8)$$

$$ANC = BC{*}_t - AN{*}_t \qquad (9)$$

$$CL(A) = BC{*}_o - ANC_{limit} \qquad (10)$$

$$BC{*}_o = BC_t{*} - F(AN{*}_t - AN{*}_o) \qquad (11)$$

$$AN{*}_o = SO_4{*}_o + NO_3{*}_o \qquad (12)$$

$$SO_4{*}_o = a + b.BC{*}_t \qquad (13)$$

$$F = \sin(\pi.BC{*}_t/2.S) \qquad (14)$$

$$EX(A) = SO_4{*}_{dep} + NO_{3\ Leach} - CL(A) \qquad (15)$$

2.3.3 The Empirical Diatom Model

The empirical diatom model does not rely on the fixing of a threshold ANC value, but instead utilises palaeolimnological data from UK lake cores to identify the first point of biological change in response to acidification. Battarbee *et al.* (1996) developed a model based on a ‘dose response’ function that can be used to set critical load values for a site from a knowledge of the ratio of Ca^{2+} of the water (sensitivity) to modelled S deposition (loading) at the site. This ‘critical ratio’ is normally set at 94:1 to calculate the critical load of sulphur, or at 89:1 to calculate the critical load of acidity. The critical load is then calculated by dividing a pre-acidification value of calcium (Ca^*_o) by the critical ratio (equation 16). The value of Ca^*_o is calculated in a similar way to the calculation of BC^*_o in the SSWC model with the use of an F factor (equations 17 and 18). The value of S_{Ca} was fixed at 400ueq L^{-1}, and where BC^*_t values exceeded this value; an F factor of 1 was used.

To calculate critical load exceedance (equation 19), the critical load was subtracted from the sum of sulphur deposition (S_{dep}) and the fraction of nitrogen deposition contributing to acidification ($a_N.N_{dep}$). The value of a_N was calculated from the differences between the ratios of sulphate/nitrate in the water and in the deposition at the site (Henriksen & Posch 2001) as shown in equation 20. This model is generally perceived to be more cautious than the SSWC model because it predicts the loading at the time when the diatom communities first respond to changes water chemistry, thus generating lower critical loads (Harriman et al. 1995).

$$CL(A) = Ca^*_o/89 \tag{16}$$

$$Ca^* = Ca^*_o - F_{ca}(SO_4{}^*_t + NO_3{}^*_t - SO_4{}^*_o - NO_3{}^*_t) \tag{17}$$

$$F_{ca} = \sin(\pi.Ca^*_t/2.S_{Ca}) \tag{18}$$

$$EX(A) = S_{dep} + a_N.N_{dep} - CL(A) \tag{19}$$

$$a_N = (S^*_{dep}/N^*_{dep})/(SO_4{}^*_t/NO_3{}^*_t) \tag{20}$$

2.4 Uncertainty and Sensitivity Analysis

Uncertainty analysis of the SSWC model was carried out through a ‘Monte Carlo’ simulation. This method computes a large number of output values from the model by using values drawn at random from the distribution of each input (Morgan and Henrion 1990). By producing a random sample from the probability distributions of the input variables, the precision of the output distribution can be estimated using standard statistical techniques (Morgan and Henrion 1990). This technique has previously been utilised by Aherne & Curtis (2003).

The distributions of input parameters of the SSWC model (base cations, nitrate, sulphate, and discharge) were assessed prior to creation of the 'Monte Carlo' simulation. Discharge and base cations were distributed in normal distributions, and hence when modelling these parameters, the inverse of the normal cumulative distribution for the specified mean and standard deviation was determined using the probability of a randomly generated number. Nitrate, sulphate, ammonium and sulphate deposition on the other hand, all showed a lognormal distribution, and this was determined by modelling the inverse of the lognormal cumulative distribution for the specified mean and standard deviation, again using the probability of a randomly generated number. In order to be true to the original model, formulae for the F factor and other associated modelled variables were calculated, and in the case of the F factor, wherever the base cation flux was greater than 400μeq L^{-1}, an F factor of 1 was used. A total of 10,000 parameter sets were used in this analysis, and these were then used to calculate critical load values. The distribution of the critical load values was then analysed using descriptive statistics, and compared to that of the original sample population to get an estimate of precision.

The aim of carrying out the sensitivity analysis was to determine how receptive and responsive the model was to changes in certain parameters with particular emphasis on how this affected the number of streams exceeding their critical loads. By varying some of the parameters of the model, it could be seen which parameters the model was most sensitive to. Although previous studies have looked at the sensitivity of the SSWC model to changes in the different parameters (e.g. Henriksen, Dillon and Aherne 2002, Aherne and Curtis 2003), it was still considered important to see if the sample population was particularly susceptible to changes in certain parameters. The input parameters that were investigated were BC^*_o, $SO_4{}^*_o$ and the ANC_{limit}. BC^*_o was tested by varying the amount that was input into the model, $SO_4{}^*_o$ was tested by implementing three different regression equations, and ANC_{limit} was tested by inputting four different values into the model.

3. Results

3.1 Acid Status & Water Chemistry

The stream water chemistry of the sites sampled showed noticeable variation between sites; however obvious patterns can be seen from the data (table 1). The pH of the streams was predominantly acidic, with values lower than 4.5 were recorded in some peat dominated catchments. Alkalinity was generally low, and even negative in some cases. Specific Conductivity was also extremely low (as low as 41.4) in some of the sampled sites. TOC and colour both showed that the water was very clear in some streams, with little dissolved carbon, however in some of the peat dominated catchments the colour of the water was much darker due to an increased amount of organic carbon. This was especially apparent at one site, Hoar Clough. Base cations showed a wide range of variation, however in more acidic upland streams, the sum of base cations was low, and it was only in some of the streams in the moorland fringe areas that base cation sums reached high levels. Similarly, anions ranged from negligible values to reasonably high values and were highest in the moorland fringe areas. The moorland streams of the peak district can therefore be characterised as acidic, with low values of base cations and acidic anions, often resulting in a negative ANC. These characteristics become more variable on moorland fringe areas.

Table 1. Descriptive Statistics for chemical variables throughout the sample population (n = 37).

		Min	Max	Mean	ST dev
General chemistry	pH	4.29	7.94	6.69	1.11
	Alkalinity (ueq/l)	-1030.00	2860.00	543.24	732.83
	Conductivity (µs/cm)	41.40	234.00	97.89	45.02
	Colour (Pt-Co units)	4.00	171.00	29.54	28.56
	TOC (mg/l)	-2.02	10.066	1.224	2.018
Analytes	Flouride (ueq/l)	1.58	6.32	2.97	1.16
	Chloride (ueq/l)	131.18	656.45	228.34	127.60
	Nitrate (ueq/l)	1.29	101.46	24.93	21.51
	Sulphate (ueq/l)	78.39	707.66	257.46	128.06
	Ammonium (ueq/l)	1.66	51.01	9.05	8.06
Catalytes	Aluminium (ueq/l)	0.56	22.79	6.02	5.03
	Calcium (ueq/l)	10.03	1275.80	238.10	242.97
	Iron (ueq/l)	0.00	14.00	3.41	3.54
	Potassium (ueq/l)	10.97	48.81	26.72	9.35
	Magnesium (ueq/l)	26.50	579.41	212.88	120.59
	Manganese (ueq/l)	0.00	3.42	0.92	0.91
	Silica (ueq/l)	0.00	0.06	0.01	0.01
	Sodium (ueq/l)	121.41	533.06	264.17	94.62
	Zinc (ueq/l)	0.00	0.95	0.09	0.17

3.2 Critical Loads Models For Acidification Status

The mean critical load of acidity determined using the SSWC model was 3.79 keq ha^{-1} yr^{-1} (n = 36), however values ranged from 0.06 keq ha^{-1} yr^{-1} to 14.26 keq ha^{-1} yr^{-1} (see table 2). In total, 13 sites (36%) were had low critical loads (<2 keq ha^{-1} yr^{-1}) as shown in table 3, 16% more than the Critical Loads Advisory Group (CLAG) found in their nationwide study (1995). In comparison to the CLAG study of 1995, a higher percentage of sites were also found to be in critical load classes 4 and 5, showing that not only do more sites in this study have lower critical loads of acidity than would be expected, but more sites have very low critical loads of acidity than would be expected (see table 3). Using the SSWC model, a total of 14 sites (39%) were determined to be exceeding their critical load. When compared to the results of CLAG (1995), the percentage of sites exceeding their critical load is 25% higher. Of these sites, 14% were found in the highest exceedance class (5), suggesting that where exceedance is occurring it is often severe (table 3). Of the sites exceeding their critical loads, all were sites where low critical loads had been documented. In addition, no sites were found to be exceeding their critical load where a low critical load was not observed.

Table 2. Descriptive statistics of the results of the two critical loads model implemented and the 'Monte Carlo' simulation.

	SSWC Model	Empirical Diatom Model	'Monte Carlo' CL(A)
Sample size	36	36	10000
Mean CL(A) (keq ha^{-1} yr^{-1})	3.79	1.34	3.97
Median CL(A) (keq ha^{-1} yr^{-1})	3.45	0.62	3.55
Standard Deviation CL(A) (keq ha^{-1} yr^{-1})	3.25	2.33	4.40
Minimum CL(A) (keq ha^{-1} yr^{-1})	0.06	0.00	-16.14
Lower Quartile CL(A) (keq ha^{-1} yr^{-1})	1.15	0.23	0.82
Upper Quartile CL(A) (keq ha^{-1} yr^{-1})	5.21	1.42	6.83
Maximum CL(A) (keq ha^{-1} yr^{-1})	14.26	12.82	21.35
Skewness CL(A) (keq ha^{-1} yr^{-1})	1.28	3.91	0.19
Kurtosis CL(A) (keq ha^{-1} yr^{-1})	1.70	17.67	0.58
% exceeding CL(A)	36.11%	69.44%	32.85%
Exceedance class 1	63.89%	30.56%	67.15%
Exceedance class 2	2.78%	5.56%	1.86%
Exceedance class 3	5.56%	5.56%	3.25%
Exceedance class 4	13.89%	25.00%	5.38%
Exceedance class 5	13.89%	33.33%	22.36%

Table 3. Proportions of sites in the 5 critical load and exceedance classes of this study (n = 36) compared with a nationwide study by CLAG (n = 2712).

		SSWC Model Results		Diatom Model Results	
Critical loads class	Critical load (keq ha-1 yr-1)	This Study	CLAG (1995)	This study	CLAG (1995)
1	>2	63.9%	79.7%	13.9%	75.3%
2	>1 and <=2	19.4%	7.5%	25.0%	6.6%
3	>0.5 and <=1	8.3%	6.9%	13.9%	7.4%
4	>0.2 and <=0.5	5.6%	4.0%	27.8%	7.6%
5	<=0.2	2.8%	1.9%	19.4%	3.1%
Exceedance Class	Exceedance (keq ha-1 yr-1)				
1	Not Exceeded	63.9%	89.6%	30.56%	85.0%
2	>0 and <=0.2	2.8%	2.7%	5.56%	3.3%
3	>0.2 and <=0.5	5.6%	3.8%	5.56%	4.6%
4	>0.5 and <=1.0	13.9%	1.8%	25.00%	4.2%
5	> 1.0	13.9%	2.1%	33.33%	2.9%

The mean critical load of acidity determined using the diatom model was 1.34 keq ha^{-1} yr^{-1} (n = 36), with values ranging from 0 keq ha^{-1} yr^{-1} to 12.82 keq ha^{-1} yr^{-1} (as shown in table 2). Out of the 36 sites sampled, 31 (86%) were shown to have low critical loads (<2 keq ha^{-1} yr^{-1}). As shown in table 3, this figure is 61% more than CLAG found in their nationwide study (1995), and ominously, 20% of the sites sampled had extremely low critical loads (class 5). Not surprisingly, most of the sites sampled exceeded their critical loads (69%). The CLAG study of 1995 found only 15% of nationwide sites to be exceeded using the diatom model.

When the 5 regions were compared for differences in the number of sites where critical loads of acidity were exceeded, it was clear there were obvious disparities. Over half of the sites in regions A and B were exceeded, whereas exceedance was less common in regions D and E and was not documented at all in region C (see table 4). Although region A had more sites which exceeded their critical load of acidity than region B, in region B exceeded sites were in the higher exceedance classes, implying that exceedance was more severe here.

Table 4. Numbers of sites in regional exceedance classes.

		Exceedance Class				
Region	% exceeded	1	2	3	4	5
A	62.50%	3	1	1	2	1
B	54.55%	5	0	0	3	3
C	0.00%	6	0	0	0	0
D	20.00%	4	1	0	0	0
E	16.67%	5	0	0	0	1

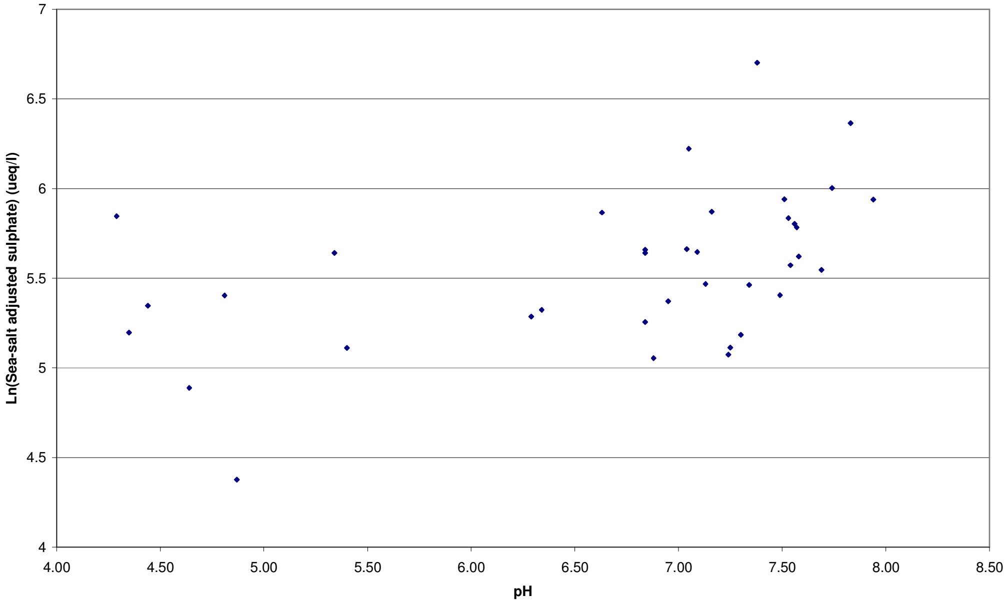
4. Discussion

4.1 Acidity & Acidification

An important question to answer is whether the moorland streams that exceed their critical loads document acidity or acidification. There are three possible causes for acidity in the moorland streams of the Peak District, namely past mining activity, organic carbon dissolved in the streams, and atmospheric deposition. It is therefore important to quantify which of these factors are affecting the acidity of the moorland streams in this study.

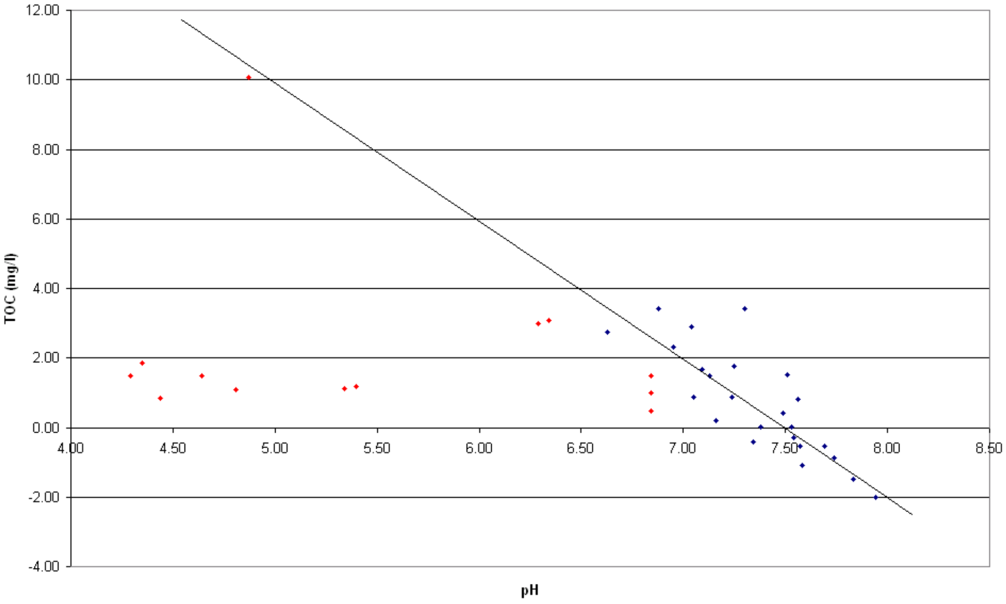
Lead mining was widespread in the Peak District until the mid 19th century. The lead ore of the Peak District is the common mineral galena, lead sulphide (Ford and Rieuwerts 1968); hence if past mining activities influence stream acidity, one would expect a strong negative relationship between sulphur and pH. In fact, the opposite has been found during this study, with a positive relationship (Pearson correlation coefficient, $R^2 = 0.47$ being observed (significant at the 0.01 level) as shown in figure 2 between the lognormal of sulphate and pH. This would suggest that previous mining activities do not affect the acidity of these moorland streams, implying that differences in sulphur are simply due to different catchment weathering rates. In one particular case however, it is likely that past mining activities have and are influencing the water chemistry of the stream. Bretton Clough (D02) is located in an area littered with mineral veins according to Ford and Rieuwerts (1968) and has a very high value for sulphate. For this site, it is likely that the acid status of the stream is not due to atmospheric deposition, and hence this site is not included in the analysis of critical loads.

Figure 2. A comparison of pH values and sea-salt adjusted sulphate fluxes (n = 37).



Where areas of peat are drained, acidity can be affected by influxes of organic matter. Such influxes can lead to high levels of dissolved organic carbon, and hence increase the acidity of the water. If this were the case, one would expect a negative correlation between TOC and pH in the moorland streams studied. Such a relationship was found with a weak (Pearson correlation coefficient $R^2 = 0.20$), but significant (at the 0.01 level) correlation (as shown in figure 3). This relationship is interesting as most of the values showed a very good linear relationship, however the relationship broke down in most of the highly acid streams. When a line was drawn through the sites which appear to follow the linear relationship, it was observed that all of the sites above the line did not exceed their critical loads (see figure 3). Of the sites below this line, those closest to the line did not exceed their critical loads; however the probability of exceedance increased with distance from this line. The sites which were nowhere near this line are clearly unnaturally acidic; however those closest to the line probably display some degree of natural acidity, although they may have also been further acidified by atmospheric deposition. The further from the line the point lies, the more likely this is to be a factor.

Figure 3. A comparison of pH values and TOC values (n = 37). Sites with a red point are those which exceed their critical load. Sites with are blue point do not. An inferred 'natural' linear relationship between the two variables has been added. Equation of line is TOC = 30 – 4.pH.



To investigate the causes of acidity further, the relationship between base cations and pH was examined. A strong positive relationship (Pearson $R^2 = 0.56$) significant at the 0.01 level was clear between the total base cation flux and pH (see figure 4); however it was noticeable that again this relationship was weaker in the more acid streams. Where pH is above 6.5, there is a very strong positive relationship between the two variables, however below this point there appears to be a uniform relationship where decreases in pH bring about little or no change in the base cation flux. Interestingly, the pattern of these points is almost identical to that of the sulphate points suggesting that the sulphate and base cation flux are strongly related at low pH values. The greater range and variability of base cations compared to sulphate means that where weathering rates increase, the proportion of base cations in comparison to sulphate increases and hence so does the neutralising effect. This is exemplified by the relationship between the ratio of sulphate to base cation flux, and pH (figure 5). Where the weathering rate is low, this neutralising effect is small making sites with low weathering rates highly susceptible to acidification through atmospheric deposition. This was investigated further, and it was found that the ratio of sulphate to base cations was an excellent predictor of the critical load. Where a power relationship was assumed ($CL = 1.0644.(SO_4:BC)^{-0.6221}$) an R^2 value of 0.90 was obtained. Similar observations of a relationship between sulphate and base cations were made by Evans *et al*. (2000) in their study of reservoirs in the Southern Pennines.

Acidified sites can be therefore be characterised as having low pH and low TOC, and are unnaturally acidic because of a lack of base cations in these systems to buffer the acidic inputs of atmospheric deposition. Seven of the sites in this study are clearly of this nature and are unnaturally acid. It remains uncertain whether the remaining six sites which exceed their critical loads are naturally acid, however as an ANC_{limit} of 0 has been used in the study to reduce the possibility of labelling naturally acid sites as acidified, these sites would appear to be acidified. Further evidence of acidification in these six sites comes from the fact that these sites have low amounts of base cations.

Figure 4. A comparison of pH values and total sea-salt adjusted base cation fluxes (n = 37).

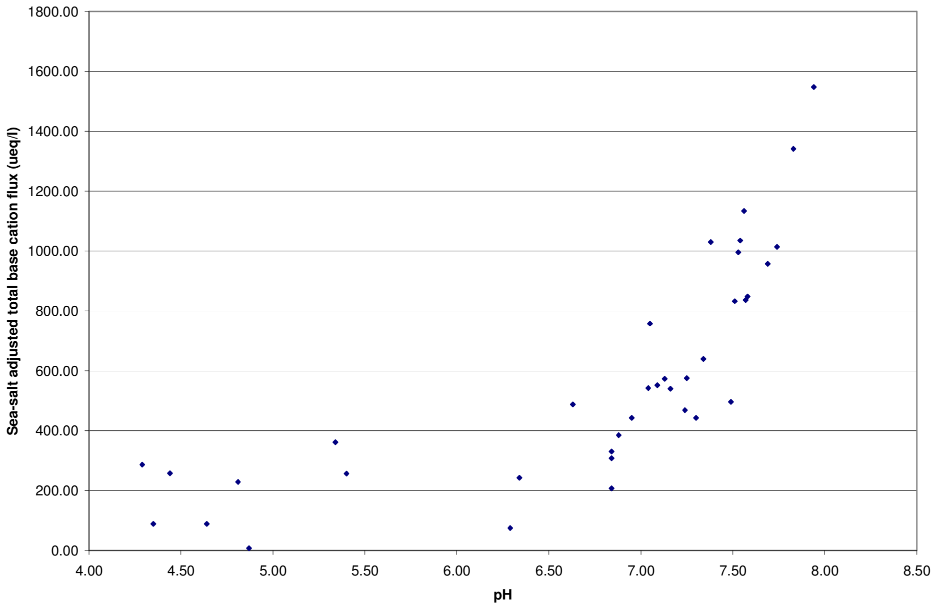
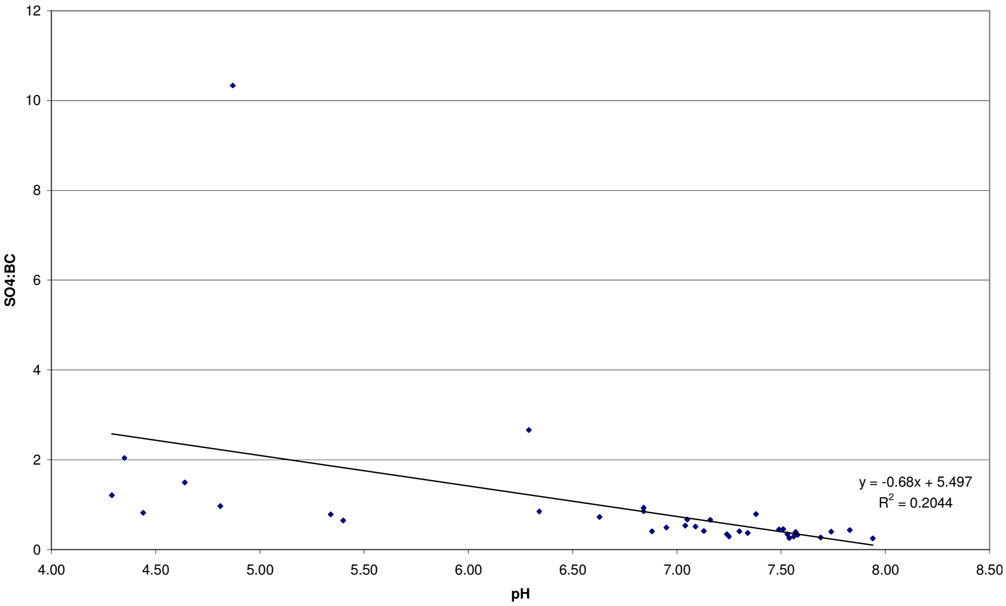


Figure 5. Relationship between the ratio of sulphate to base cations, and pH (n = 37).



4.2 Assumptions & Uncertainties

The ‘Monte Carlo’ analysis provided a large dataset of simulated values. These values were found to have a very similar distribution to the observed values which this simulation was based on (table 2). Although the standard deviation of the simulated data set was larger than that of the original dataset, the mean (3.97 keq ha^{-1} yr^{-1} compared with an observed value of 3.79 keq ha^{-1} yr^{-1}) and median (3.55 keq ha^{-1} yr^{-1} compared with 3.45 keq ha^{-1} yr^{-1}) of the two distributions were similar. Other statistics show that the two distributions were alike, such as the skewness, and the upper and lower quartiles. Importantly, the percentage of sites exceeding their critical load was fairly similar with just a 3.5% difference between the two. However there were discrepancies in the distribution of the exceedance classes, with a higher proportion of the simulated values falling in exceedance class 5. Overall, this would suggest that the uncertainty associated with the model was small, and that the results of the critical loads modelling of the original dataset are well-founded. These results are particularly good when considering the small size of the observed dataset. The results of the simulation inspire confidence in the application of the SSWC model to the moorland streams of the Peak District by indicating that the model results have good precision. The ability to simulate the results of this model analysis suggests that that the model is robust in these sites.

Four different values of ANC_{limit} were input into the SSWC model. These values were 0 μeq L^{-1}, the value commonly used in the UK, 20 μeq L^{-1}, the value commonly used elsewhere, and 40 μeq L^{-1}, and -20 μeq L^{-1}, two more extreme values. Changing the ANC_{limit} values had a minor effect on the number of sites which exceeded their critical load, and even less of an effect on the number of sites that had low critical loads (see table 5). However, there were noticeable shifts in the number of sites in the higher classes of exceedance and critical load status. This suggests that most of the sensitivity to changes in the ANC_{limit} is amongst the values that exceed their critical load. Therefore, the precaution of using a lower than usual ANC_{limit} of 0 μeq L^{-1} to ensure that naturally acidic waters are not calculated to exceed their critical loads appears to be redundant in this study. In addition, problems can be encountered if the ANC_{limit} is set too low as acidified waters may not display critical load exceedances (Battarbee *et al.* 1996). Again, this does not appear to be the case in this study.

Table 5. Number of sites in different exceedance and critical load classes using different values for the ANC_{limit}.

		ANC_{limit}			
		-20	0	20	40
Exceedance Class	keq ha^{-1} yr^{-1}				
1	Not exceeded	25	23	23	22
2	>0 and <= 0.2	1	1	0	1
3	>0.2 and <=0.5	1	2	2	0
4	>0.5 and <=1.0	7	5	2	3
5	>1.0	2	5	9	10
Critical Load Class	keq ha^{-1} yr^{-1}				
1	>2	23	23	22	22
2	>1 and <= 2	8	4	2	1
3	>0.5 and <=1.0	4	6	7	7
4	>0.2 and <=0.5	1	2	2	1
5	>0.2	1	1	4	6

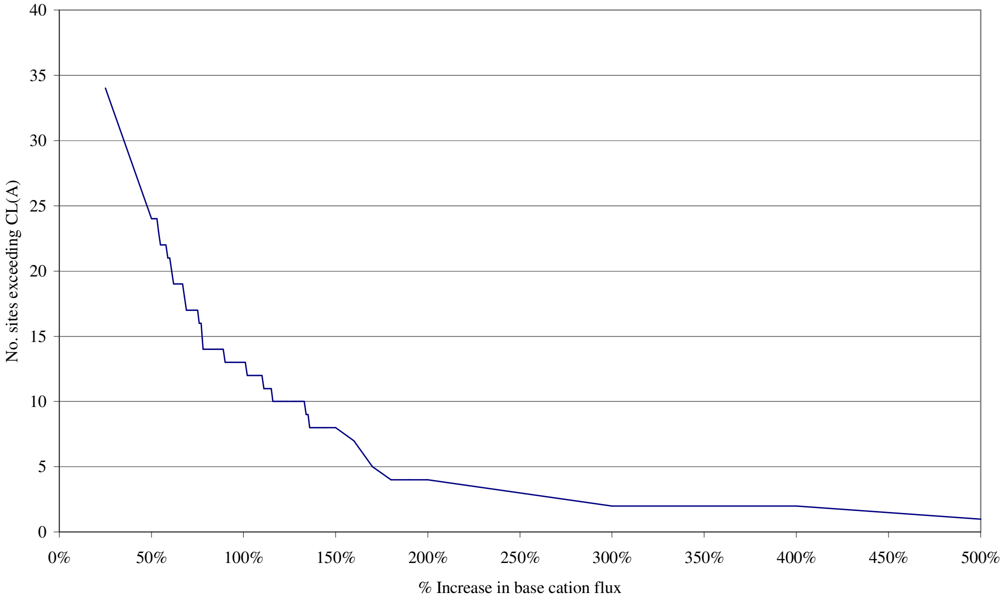
Three different regression equations to determine pre-acidification non-marine sulphate levels were input into the model to investigate how susceptible the model was to changes in the parameters of this equation. The three equations used are documented in table 6. Using the three equations the same number of sites were found to be exceeding their critical loads. In addition, variation in the distribution of the sites among the exceedance classes was small. Different sites appeared to be effected differently by a change in the equation. For example B02 has the same exceedance value using all three equations; however two sites changed their exceedance class due to changes in the equation used. As shown by table 6, none of the equations have particularly strong correlation coefficients, so it is important to be aware that this part of the model could bring in some level of uncertainty. In addition, all three of the equations were developed using data from Scandinavia, not the UK. The equation used predominantly in this study is that of Brakke *et al.* (1989), and this equation appears to be the most conservative of the three tested. This maintains the ‘best case scenario’ approach to this study.

Table 6. Different regression curves for calculating $SO_4{*}_o$ and the number of sites that exceeded their critical loads using these relationships.

		Brakke et al. (1989)	Posch et al (1993)	Posch et al. (1997)
a		15	14	19
b		0.16	0.10	0.08
Correlation coefficient (r)		0.38	0.29	0.66
No. of samples		143	61	251
Exceedance Class	keq ha^{-1} yr^{-1}			
1	<=0	23	23	23
2	>0 and <= 0.2	1	1	1
3	>0.2 and <=0.5	2	1	1
4	>0.5 and <=1.0	5	5	5
5	>1.0	5	6	6

The sea-salt adjusted base cation flux was varied between 25% and 500% to determine how sensitive the model was to changes in base cation inputs in the study sites. Where the base cation flux was increased, the critical load of acidity increased, and the number of sites exceeding these loads decreased. This was at first fairly sensitive, with 3 sites no longer exceeding their critical load after a 20% increase. However this sensitivity became less and less as the input change was increased. Where the base cation flux was decreased, the critical load of acidity decreased and hence more sites exceeded their critical loads. The sensitivity of the model to decreases in the base cation flux was at first low, with just one additional exceeding site after the base cation flux was decreased by 20%. However, after this point the model became highly sensitive to changes in the base cation flux, with an additional 10 sites exceeding their critical loads within a 50% decrease. This is documented in figure 6. These results therefore show that the base cation flux can distort the results of the model if it is incorrectly measured; however this susceptibility is not great directly around the measurement, especially if the base cation flux is underestimated. The base cation flux therefore has the most potential to lead to uncertainties in the model results through its sensitivity. This sensitivity comes from two main components, the value of S, and the F factor, which have been the subject of many previous sensitivity analyses (e.g. Henriksen *et al.* 2002). This sensitivity has however been noted as being small in sensitive sites (Harriman *et al.* 1995) such as the Peak District.

Figure 6. Cumulative distribution curve for the number of sites exceeding their critical loads using the SSWC model, based on variations in the base cation flux.



4.3 Implications

The critical load values and their exceedances in this study show a ‘best case scenario’ for the Peak District moorland stream network as the sampling was undertaken at baseflow conditions. As the streams were at baseflow conditions, the survey is expected to provide the highest possible critical load values, and therefore the number of sites exceeding these loads is expected to be at a minimum. The fact that over a third of the streams sampled exceeded their critical loads in these conditions suggests that when baseflow conditions do not prevail, this proportion is greater. These implications are realised by the results of the diatom model, which provides more cautious values for the critical loads of acidity and hence displays more incidents of exceedance of critical loads. In this study, the diatom model generated much lower critical loads than the SSWC in this study, with the difference between the means of the two model results being greater than 1.5 keq ha^{-1} yr^{-1}.

The results suggest that recovery from acidification in the moorland catchments of the Peak District still has a long way to go, and is a significant environmental problem in the area. The acidity of several streams has been shown in this study to be largely down to atmospheric deposition. The Peak District is one of the worst places for this in the UK because of its close proximity to large industrial settlements of the past and present, and perhaps this is the reason why recovery from acidification in the Peak District appears to be slower than in other parts of the United Kingdom, where recovery from acidification has been clearly documented. There are however some signs of recovery. Region C, Kinder, had no sites which exceeded critical loads of acidity under the SSWC model. The reason for this is uncertain, but it may be linked to efforts made by the National Trust to restore the degraded moorland of the Kinder estate. The reintroduction of moorland vegetation and reductions in sheep grazing (documented by Wilson 1995) may be helping to stabilise the moorland system, leading to a subsequent stabilisation of the freshwater chemistry. This offers hope that other moorland restoration efforts may lead to further recoveries from acidification.

The results of this survey must however be approached with some degree of caution. All of the sites used in the study were streams as there are no freshwater lakes in the areas being studied. Lakes provide a better signal for critical load determination as temporal variations are a less of an issue. Although there are plenty of reservoirs in the Peak District, streams were sampled in this study to give results indicative of moorland areas, and to enable samples to be taken higher up the systems. However this does mean that the results only represent the critical loads of the streams under certain conditions. Nevertheless this study is still of environmental importance as it gives a baseline for the least amount of critical load exceedance in these systems

5. Conclusions

This study evaluated freshwater critical loads for moorland streams in the Peak District National Park. In these streams, critical loads were found to be low, and cases of exceedance were high. In addition, this exceedance was in places high confirming that atmospheric deposition has led to acidification in a substantial number of moorland streams in the area. These results are a ‘best case scenario’ as sampling occurred at baseflow, it is inferred that the extent of this acidification is widespread and severe, and shows few signs of a reversal despite decreasing deposition. In many cases, the critical load is so low due to catchment weathering processes that even small amounts of anthropogenically induced acidic atmospheric deposition will cause exceedance of critical loads. Some of the streams were found to document natural acidity; however a more in depth study into the relationship between TOC and pH would have to be carried out to clarify this. A regression curve between these two variables could be derived to enable acidified sites to be distinguished in future studies.

The uncertainty analysis carried out through a ‘Monte Carlo’ simulation showed the results of the SSWC model to be relatively stable, providing a similar distribution amongst the output values as that observed in the original sample population. In addition, sensitivity analysis was carried out on several parameters of the SSWC model, and these findings again confirm that the results of this study are well-founded. Some of the sensitivity analysis even showed that the results of the original model were conservative compared to the possible use of different pre-acidification sea-salt adjusted sulphate equations and various values of ANC_{limit}. The results of this study therefore highlight the acidified state of moorland streams in the Peak District National Park. Nevertheless, there are areas of the Park where acidification appears to be less apparent, and these sites offer hope of a future recovery from acidification in other areas of the Park.

Acknowledgments

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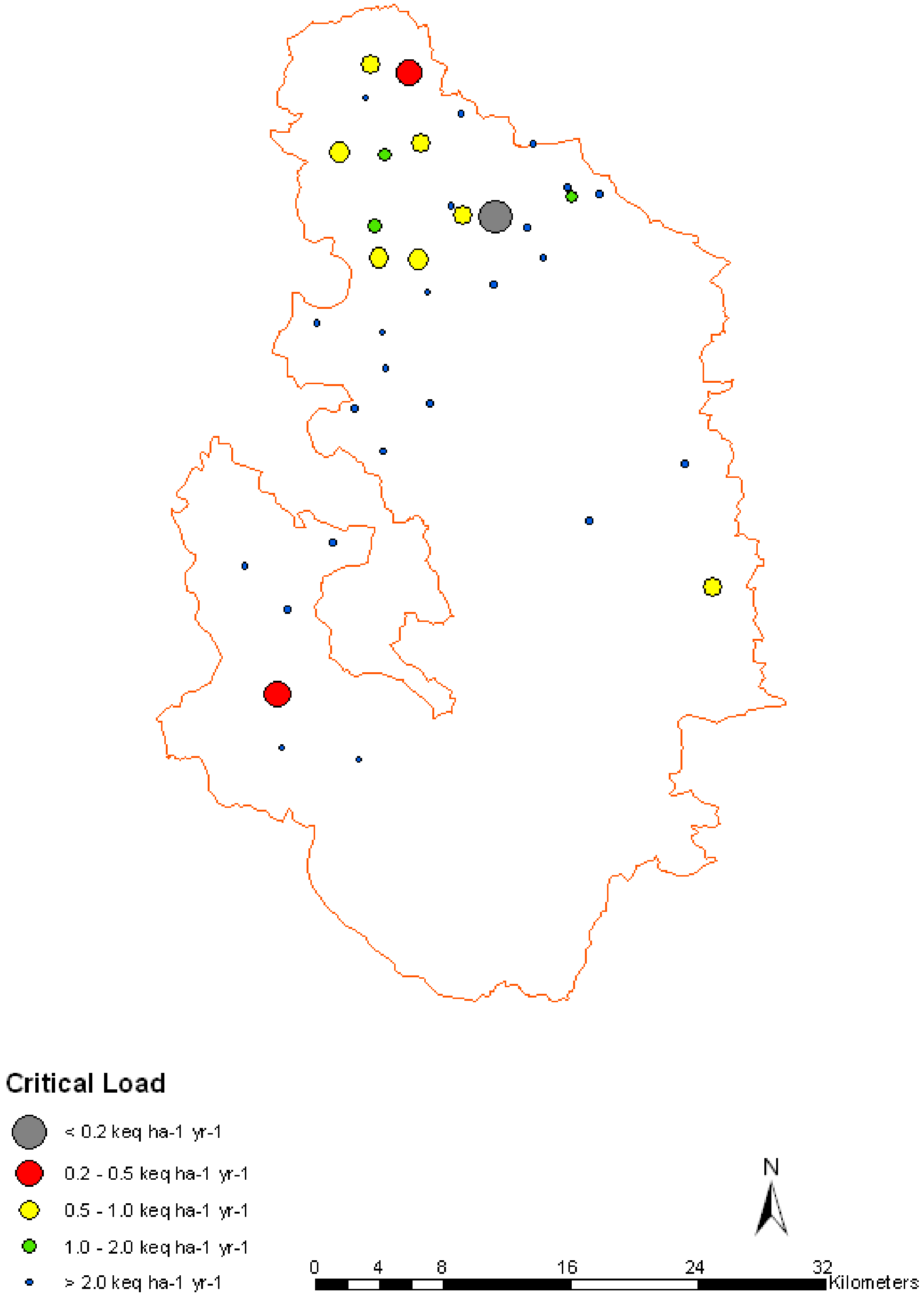
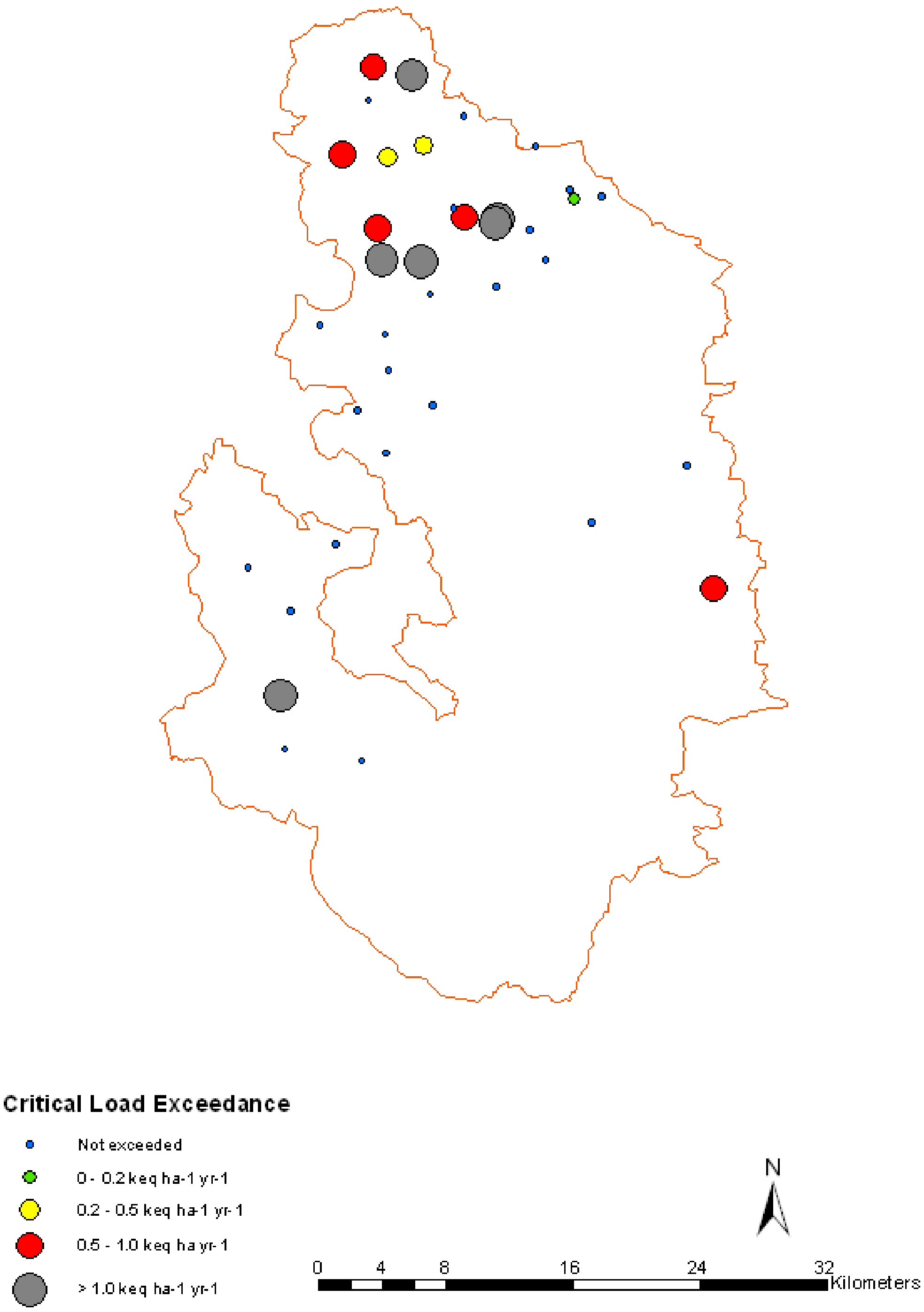
Appendix A. List of all the sites used in the study, giving their geographic location and stream order.

Sample No.	Name	Sample X	Sample Y	Stream Order (from OS 1:63,360 scale)
A01	Shiny Brook	406457	407462	2
A02	Holme Clough	406134	405374	3
A03	Black Chew Grain	404500	401950	3
A04	Heyden Brook	409575	402521	3
A05	Crowden Little Brook	407350	401800	3
A07	Ramsden Clough	412124	404333	3
A09	Long Grain	416650	402450	3
A66	Marsden Clough	408850	406950	3
B01	River Derwent	414100	397650	3
B02	Hoar Clough	414300	397875	3
B03	Stainery Clough	416286	397207	3
B04	Cranberry Clough	417300	395346	3
B05	Black Clough	414187	393619	3
B06	Hern Clough	409450	395230	2
B07	Upper North Grain	410016	393150	3
B08	Far Black Clough	412200	398000	3
B09	Middle Black Brook	411500	398600	3
B10	Torside Clough	406727	397315	3
B11	Yellowslacks Brook	406948	395322	3
C01	Roych Clough	407205	383165	3
C02	River Sett	405450	385850	3
C03	Crowden Brook	410190	386187	3
C04	River Kinder	407400	388400	3
C05	Long Clough	403050	391200	3
C06	River Ashop	407200	390650	1
D01	Burbage Brook	426200	382400	2
D02	Bretton Clough	420200	378800	3
D03	Bar Brook	427900	374650	2
D08	Mickelden Beck	419107	399174	3
D09	Thickwoods Brook	420834	399328	3
D12	Porter	418833	399713	4
E01	Todd Brook	398550	375955	3
E02	Upper Meveril	404100	377450	3
E03	River Goyt	401250	373250	3
E04	River Dane	400600	367800	3
E05	Oakenclough Brook	405700	363700	3
E06	Black Brook	400850	364450	3

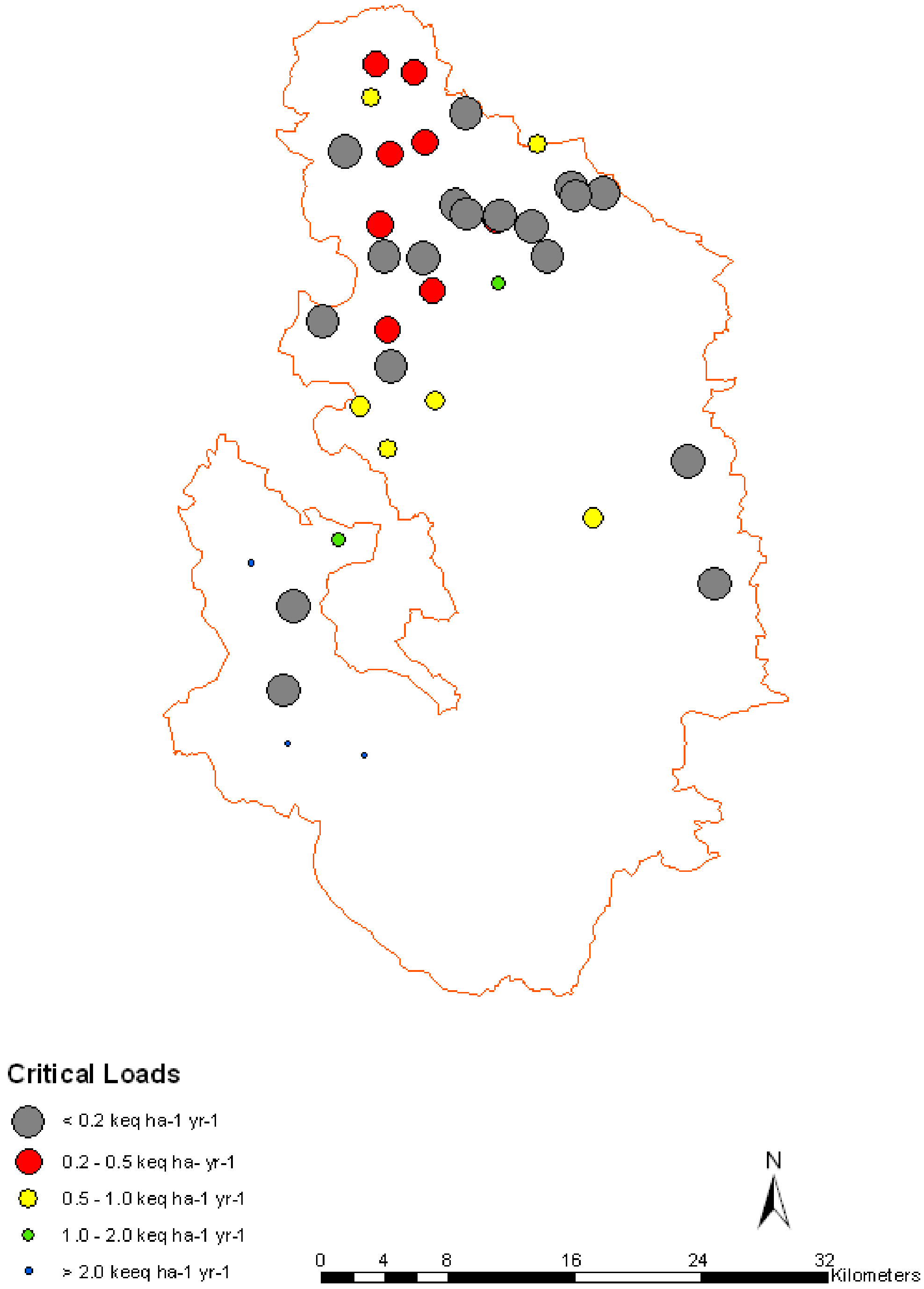
Appendix B. Map of critical loads across the Peak District moorland stream network computed using the SSWC model.



Appendix C. Map of critical load exceedances across the Peak District moorland stream network computed using the SSWC model.



Appendix D. Map of critical loads across the Peak District moorland stream network computed using the Empirical Diatom model.



Appendix E. Map of critical load exceedance across the Peak District moorland stream network computed using the Empirical Diatom model.