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Critical Loads and Dynamic Modelling
Optional activity B:

A regional water and soil quality survey of the North York Moors

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SUMMARY

An extensive survey of surface waters in the North York Moors was undertaken during March 2005. The character of this upland area, proximity to major emission sources and limited pre-existing data all suggested that the region might be subject to significant acidification. The data collected appear to confirm this, and indeed show levels of acidity (extremely low pH and ANC, and high aluminium) that are unmatched by any previous survey of UK waters. Acidification appears in almost all cases to be driven by very high concentrations of sulphate, with nitrate making a minor contribution at the moorland sites; soil C/N ratios also suggest that nitrogen saturation is not greatly advanced in the typically deep, organic-rich moorland soils. Forest streams, by contrast, generally have much higher levels of nitrate leaching, and are significantly more acidic than comparable moorland streams. In addition, for a given ANC, aluminium concentrations are proportionately higher in forest versus moorland streams. Coniferous forestry in the region therefore appears likely to have intensified both the chemical and biological impacts of acid deposition.

Overall, the data suggest that surface waters in the North York Moors are among the most acidified in the UK, and that this acidification may extend across virtually the entire geologically-sensitive area of the National Park. Available evidence suggests that this has caused significant biological damage, including loss of economically important fish populations. Application of the MAGIC model will be used to ascertain whether recovery to acceptable chemical conditions is likely to be achieved under currently planned emissions reductions, or whether further reductions would be required. Limited further sampling might be beneficial in establishing whether the results of this one-off survey are representative of long-term conditions across the region. Ideally, this would extend to the full monitoring of a stream in the region.

INTRODUCTION

Over the last decade, CEH and the Macaulay Institute have undertaken regional surveys of surface water chemistry for many of the major acid-sensitive regions of the UK. These data, collected under Defra and other research programmes (e.g. GANE, Welsh Acid Waters Survey), underpin UK freshwater dynamic modelling activities, providing the basis for most of the 320 surface water MAGIC applications submitted to the February 2005 call for data of the UNECE Coordination Centre for Effects. Their inclusion in the FAB dataset has also substantially enhanced the spatial coverage of UK freshwater critical load sites. Although most key regions have now been sampled, a number of potentially sensitive areas remain for which surface water data are sparse or absent. Among these, the North York Moors was identified as the largest, and potentially most impacted, area; the National Park contains extensive areas of moderate-to-high elevation heathland and forest on poorly buffered bedrock, and is close to major emissions sources. Limited data from the CLAG survey suggested substantial acidification, with 5 out of 12 sites (sampled 1991-4) having ANC $\leq$ -50 µeq/l. Many of these sites were small, shallow hilltop ponds, however, and it was unclear to what extent these were representative of the larger population of surface waters (almost all streams) present in the sensitive upland area. Monitoring of one such stream, undertaken by a local voluntary group, shows pH levels consistently below 4.0, with no evidence of recovery since 1990 (Chadwick, 2001). To fill a potential gap in current knowledge of the status of surface water acidification in the UK, therefore, a regional survey was undertaken in March 2005, supported by Defra as an optional activity under the Critical Loads and Dynamic Modelling contract.

STUDY AREA AND BACKGROUND

The North York Moors National Park comprises an area of 1436 km^2, of which 34% (490 km^2) is moorland and 22% woodland, mainly coniferous plantation forest. The moorland area predominantly consists of heathland, the largest such area in England and Wales, most of it managed for grouse shooting and sheep farming. Most of the heathland area (440 km^2) has been designated as the North York Moors Special Area of Conservation. The upland area, on which most of the heathland occurs, rises to a maximum elevation of 450m and receives an annual rainfall of around 1m. The geology of this area is mainly base-poor Jurassic sandstones and shales, with well-buffered limestones and clays at lower elevations to the south of the Park. Of the two major rivers draining the upland area, the Esk (to the north) is the only river in Yorkshire to support salmon and sea trout, and as such represents an economically important fishery. However the fishery has been in decline since the 1960s (North York Moors National Park Authority, 2001). The Esk and the Derwent (draining the southeast of the National Park) support five threatened/declining species listed in the UK Biodiversity Action Plan: otter, water vole, kingfisher, dipper and freshwater pearl mussel. According to the River Esk Regeneration Programme (North York Moors National Park Authority, 2001), biological water quality in some headwater streams is in Environment Agency classes D-F (Fair to Bad), but this is attributed in part to ‘natural flushes of acidity from the moorland’.

Unlike most of the other acid-sensitive upland areas of the UK, the North York Moors are close to industrial areas, and downwind of several major emissions sources; three large coal-fired power stations (Drax, Ferrybridge and Eggborough) are located within 70 km to the south of the Moors. To the north (around 25 km), the industrial area of Teesside includes steel works and chemical plants. Estimated non-marine S deposition to moorlands in the region (based on 1998-2000 CEH Edinburgh estimates) is around 0.76 keq/ha/yr. In combination with the low rainfall volumes, this equates to very high effective rainfall SO_4 concentrations when compared to most other upland regions. Total N deposition to moorland areas is around 1.56 keq/ha/yr, divided equally between reduced and oxidised forms.

Despite strong evidence that the North York Moors are both acid sensitive, and subject to very high levels of acid deposition, remarkably little research has been carried out into the potential impacts on soils or waters in the region. The UK Freshwater critical loads survey dataset (CLAG, 1995) includes just 11 sites within the National Park, of which five are on non-sensitive geology (pH 6.7 or higher). The remaining six comprise three streams and three moorland pools, were all acidic, with pH from 3.9 to 5.1, and ANC from -383 to -49 μeq/l. Sulphate concentrations were extremely high (284 to 505 μeq/l), but nitrate concentrations were close to zero at all six sites. McNish et al. (1997) undertook a study of two acid-sensitive streams within the Esk catchment, and observed relatively high pH conditions under baseflow conditions (6.5 or higher) but severe pH depressions during high flows, down to minima below pH 4.0. Finally, a local voluntary group, Environet, has been undertaking regular pH sampling of rainfall, and of two headwater streams and one pond since 1990 (Chadwick, 2001). Rainfall had a mean pH of 4.5 between 1990 and 2000, with no clear temporal trend. The two streams and pond had mean pH values of 3.7, 4.4 and 4.5 respectively, with pH at the most acid stream, Danby Beck, falling as low as 3.0 during high flows. Again there is no evidence of recovery in pH since 1990; if anything, pH at the two streams actually declined in the early 1990s.

SURVEY DESIGN AND SAMPLING

GIS datasets describing geology, soils and land-cover were used to screen those areas likely to be sensitive to acidification, and Ordnance Survey 1:25,000 maps were used to identify suitable catchments within the screened area. Catchments chosen were located on sandstones or shales, one of five major acid-sensitive soil associations (Winter Hill, Onecote, Maw, Anglezarke, Belmont) and either moorland or forest land-use. As far as could be ascertained, any catchment containing significant areas of agriculturally improved land was excluded. Sites were distributed across the sensitive upland area as far as possible (within the constraints of site accessibility) and the range of water bodies chosen reflected the character of the region, which is dominated by streams, with very few standing waters.

All samples were collected between March 1st and March 4th 2005. The survey coincided with a large accumulation of snow across most of the region, with up to a metre of snow on the highest ridges, and about 5 to 20cm at lower elevations. Snowfall ended on the first day of sampling, and with temperatures close to zero throughout the week, there was little evidence of significant melting during the sampling period. Consequently, streams remained at a fairly uniform, moderately low flow, and the impact of snow on stream chemistry appears to have been limited (this is discussed further below). The snow did have some impact on site selection though, with some roads and footpaths impassable, requiring some alteration to the sampling plan. In particular, most forest tracks had not been cleared, and lack of access limited the number of forest streams that could be sampled.

A total of 51 surface waters were sampled, comprising 47 streams, three ponds and one reservoir. Seven of the stream catchments contained significant coniferous forestry. The locations of sites, and summary physical and chemical data, are given in Table 1 and Figure 1. One sample from each site was filtered in the field, and analysed for base cations (calcium, Ca; magnesium, Mg; sodium, Na; potassium, K); ammonium (NH_4); mineral acid anions (sulphate, SO_4; chloride, Cl; nitrate, NO_3); dissolved organic carbon (DOC); total aluminium (Al); and total nitrogen, used to calculate dissolved organic nitrogen (DON) by subtracting NO_3 and NH_4. Gran alkalinity and pH were measured on a separate unfiltered sample. Charge balance Acid Neutralising Capacity (ANC) was calculated as the difference between base cations and mineral acid anions. All analyses were undertaken at CEH Bangor according to standard protocols.

A small number of soil samples were collected as part of the survey, to obtain representative chemistry data for the major soil and vegetation types present; the number of samples collected was constrained in part by the difficulty of identifying soils types beneath deep snow. At 14 locations, a bulked sample of the full soil profile (maximum 1m depth) was collected using soil corers, and analysed for exchangeable base cations and acidity at CEH Bangor. A separate sample of the surface organic horizon (to a maximum of 10cm) was sampled at these locations, plus 3 additional sites, and analysed for %C and %N by NRM Laboratories, Bracknell.

Figure 1. The North York Moors, showing areas of acid sensitive moorland soils, coniferous forest, and sampled catchments (site numbers correspond to those in Table 1)

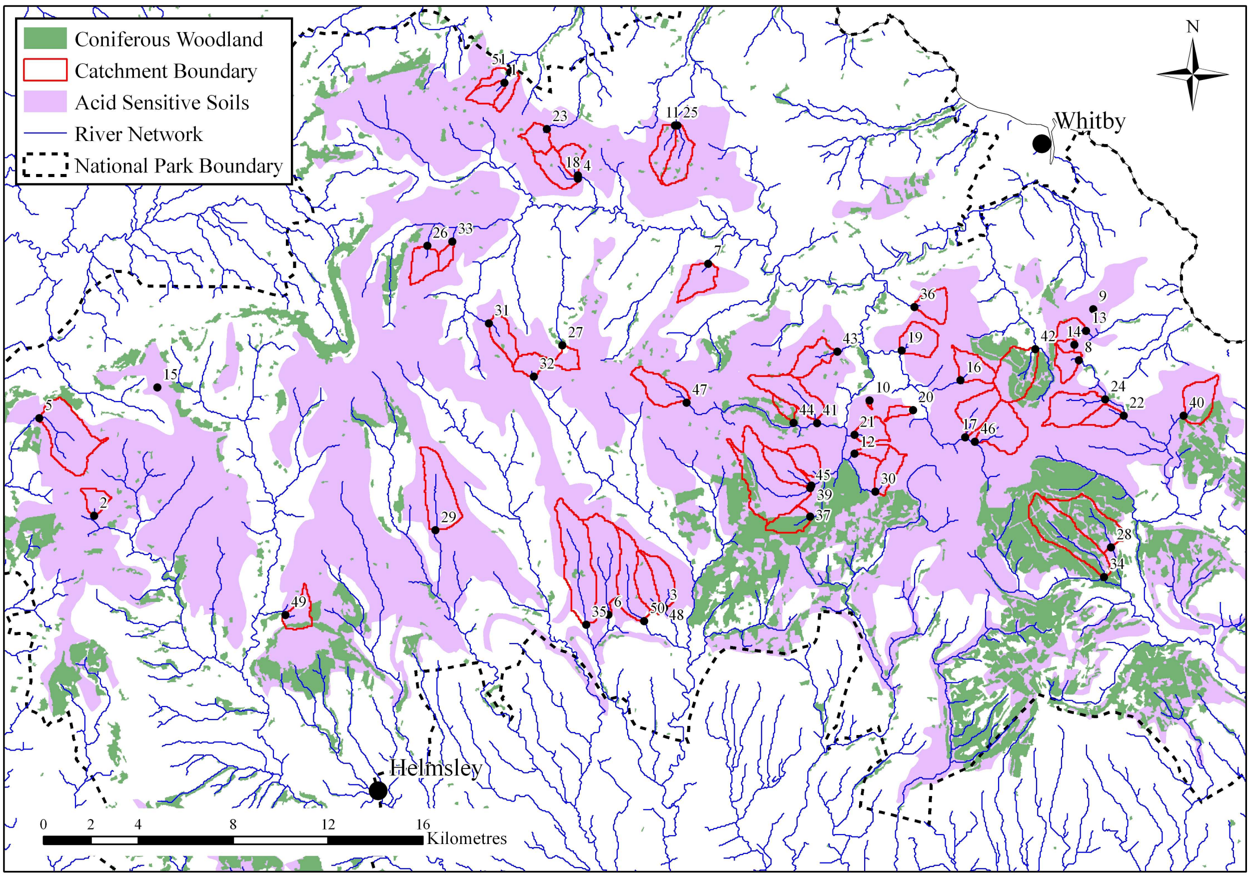


Table 1. The North York Moors, showing areas of acid sensitive moorland soils, coniferous forest, and sampled catchments (site numbers

No.	Name	Easting	Northing	Type	Forest %	Catchment altitude m	Dominant soil	pH	ANC μeq/l	Aluminium μg/l	Sulphate μeq/l	Nitrate μeq/l
1	Lockwood Beck	466820	513580	Stream	0	260	Peaty gley	6.84	193	110	241	8
2	Cringle Ing Slack	449520	495300	Stream	10	292	Peaty gley	4.38	-107	660	204	41
3	Gain Beck	473570	491420	Stream	0	208	Peaty podzol	4.25	-98	380	183	12
4	Haw Rigg Slack	469920	509520	Stream	1	242	Peaty gley	4.53	-58	210	165	3
5	Crab Dale Beck	447200	499420	Stream	1	282	Peaty gley	6.59	130	120	232	15
6	Loskey Beck	471210	491120	Stream	0	255	Peaty gley	6.62	97	60	210	14
7	Busco Beck	475420	505930	Stream	0	242	Peaty gley	4.21	-115	380	211	1
8	Biller Howe	491060	501870	Stream	0	210	Peaty gley	4.21	-104	200	165	2
9	Graystone Hills	491670	504020	Pond	0	204	Peaty gley	3.86	-127	130	174	0
10	The Tarn	482230	500170	Pond	0	216	Gley	4.35	-95	330	180	6
11	Bog House Beck	474020	511780	Stream	5	235	Podzol	6.10	19	90	193	12
12	Howl Moor Dike	481590	497920	Stream	0	229	Peaty gley	4.22	-139	370	173	4
13	Kirkmoor Beck	491370	503110	Stream	0	209	Peaty gley	4.11	-163	410	176	1
14	Grey Heugh Slack	490880	502520	Stream	0	209	Gley	4.10	-119	220	157	1
15	Brians Pond	452180	500710	Pond	0	335	Peaty podzol	3.84	-110	40	105	10
16	Brocka Beck	486070	501020	Stream	0	255	Peaty gley	4.18	-141	420	146	8
17	Sliving Sike	486270	498620	Stream	0	252	Peaty gley	4.28	-117	430	130	1
18	Ewe Crag Beck	469930	509670	Stream	1	238	Peaty gley	4.66	-75	290	219	1
19	Darn Holme	483590	502270	Stream	0	226	Peaty gley	7.51	667	50	712	11
20	Moss Dike	484060	499770	Stream	0	202	Peaty gley	4.35	-151	180	194	5
21	Hunt House	481590	498720	Stream	0	226	Peaty gley	4.11	-132	480	129	8
22	The Island	492960	499520	Stream	0	200	Peaty gley	4.33	-120	340	209	3
23	Haw Beck	468620	511620	Stream	0	253	Peaty gley	4.45	-115	310	156	1
24	Hullin Gill	492170	500220	Stream	0	226	Peaty gley	4.13	-126	480	127	4
25	Bella Dale Beck	474120	511770	Stream	6	241	Peaty gley	4.92	-81	210	208	9
26	Great Hograh Beck	463570	506690	Stream	0	343	Peat	4.06	-151	430	170	8
27	Danby Beck	469270	502500	Stream	0	398	Peat	4.08	-108	290	165	21
28	Hipperley Beck	492420	493980	Stream	75	192	Peaty podzol	5.21	-16	280	401	31
29	Ousegill Beck	463920	494700	Stream	0	332	Peaty gley	4.53	-81	400	211	16
30	Simon Howe Moss	482470	496320	Stream	1	239	Peaty gley	4.16	-111	410	193	8
31	Clough Gill	466170	503420	Stream	2	369	Peaty gley	4.39	-103	430	257	16
32	River Seven	468070	501180	Stream	1	400	Peaty gley	4.83	-77	180	327	23
33	Little Hograh Beck	464620	506870	Stream	0	324	Peat	4.18	-127	230	199	1
34	Stockland Beck	492120	492720	Stream	78	196	Peaty podzol	4.46	-128	780	400	50
35	Hutton Beck	470270	490710	Stream	2	248	Peaty gley	4.78	-52	320	180	15
36	Spa Hill Slack	484120	504110	Stream	0	262	Peaty gley	4.26	-132	470	228	4
37	Keys Beck	479720	495270	Stream	78	256	Peaty gley	4.16	-248	1730	344	84
38	Sod Fold Slack	480160	497020	Stream	0	228	Peaty gley	4.21	-100	480	141	7
39	Black Rig Beck	479770	496570	Stream	0	248	Peaty gley	4.25	-102	500	147	3
40	Helwarth Gains	495490	499520	Stream	17	217	Peaty gley	4.12	-172	510	288	4
41	Collier Gill	480020	499220	Stream	1	267	Peaty podzol	3.99	-77	280	160	9
42	May Beck	489220	502330	Stream	59	242	Peaty gley	4.67	-148	1350	375	67
43	Oakly Beck	480870	502220	Stream	3	238	Peaty gley	4.26	-110	380	191	2
44	Wheeldale Plant	479030	499230	Stream	40	263	Peaty podzol	3.93	-317	1880	376	95
45	Rutmoor Beck	479720	496480	Stream	16	258	Peaty gley	4.27	-116	490	175	12
46	Little Eller Beck	486670	498430	Stream	0	263	Peaty gley	4.32	-109	390	145	4
47	Bluewath Beck	474510	500070	Stream	0	363	Peat	3.96	-165	400	185	9
48	Tranmire Beck	473530	491370	Stream	1	209	Peaty gley	4.36	-84	410	198	20
49	Tod Hill Slack	457580	491110	Stream	16	255	Peaty podzol	4.14	-123	440	198	9
50	Hole Beck	472720	490860	Stream	0	223	Podzol	4.66	-50	260	177	29
51	Lockwood Res.	467070	514020	Reservoir	1	241	Gley	7.21	500	30	288	11

RESULTS

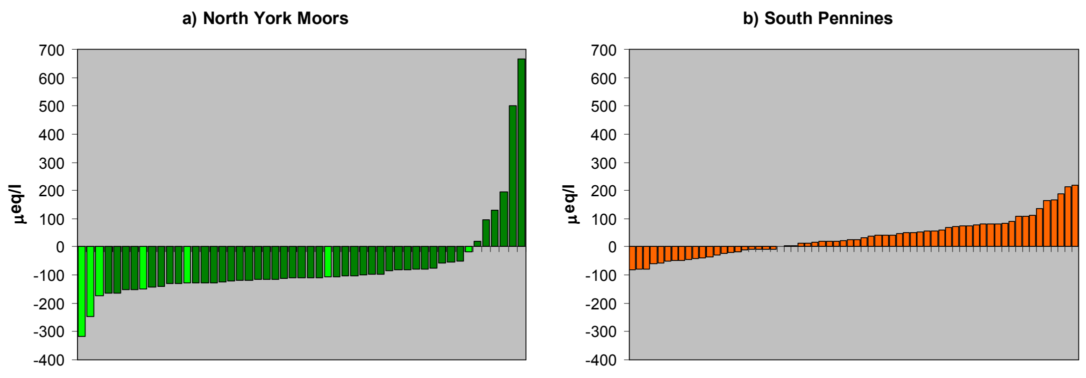
Surface Waters

The stream chemistry data are remarkably acidic. Out of 51 sites, 44 have a pH below 5.0, and 45 have a negative ANC (Table 2). Of these, 33 had an ANC of -100 μeq/l or below, and many had extremely high Al concentrations (max 70 μmol/l). Figure 2 shows measured ANC by site, ranked from lowest to highest, for the North York Moors dataset, and for the South Pennines sites to which MAGIC has been applied. The South Pennines represent the most acidic region currently included in the modelling dataset, and have previously been considered the most acidified region in the UK (e.g. Evans et al., 2000). Although there are some differences in terms of site characteristics (e.g. all reservoirs in the South Pennines, mostly streams in the present study), these data clearly suggest that the effects of acid deposition have been at least as severe in the North York Moors as in the South Pennines, and in all likelihood more severe. The very small number of high-ANC sites in the North York Moors survey appear to be those in which all or part of the catchment extends into more weatherable geology, and the data thus strongly suggest that all streams draining unimproved (mainly heathland and forest) land located on sensitive sandstone are strongly acidified. This equates to a total area of around 700 km^2, almost 50% of the National Park. It is also worth noting that the three streams with the lowest ANC all drained afforested catchments; this is discussed further below.

Table 2. Summary surface water chemistry data

	pH	Alkalinity μeq/l	ANC μeq/l	Na μeq/l	K μeq/l	Ca μeq/l	Mg μeq/l	Al μg/l	NH4 μeq/l	Cl μeq/l	NO_3 μeq/l	SO_4 μeq/l	xSO_4 μeq/l	DOC mg/l
Minimum	3.84	-100	-317	219	10	31	65	30	0	272	0	105	56	0.9
10th percentile	4.06	-85	-151	257	11	40	73	110	0	330	1	145	95	3.3
25th percentile	4.15	-82	-128	276	13	46	87	215	0	382	3	165	114	3.9
Median	4.27	-64	-110	355	19	75	104	380	0	471	8	193	147	4.8
75th percentile	4.60	-20	-79	429	23	124	135	435	1	562	15	224	178	6.6
90th percentile	6.10	69	19	507	28	310	187	510	2	718	31	344	284	8.6
Maximum	7.51	805	667	709	42	1161	356	1880	18	878	95	712	621	27.5

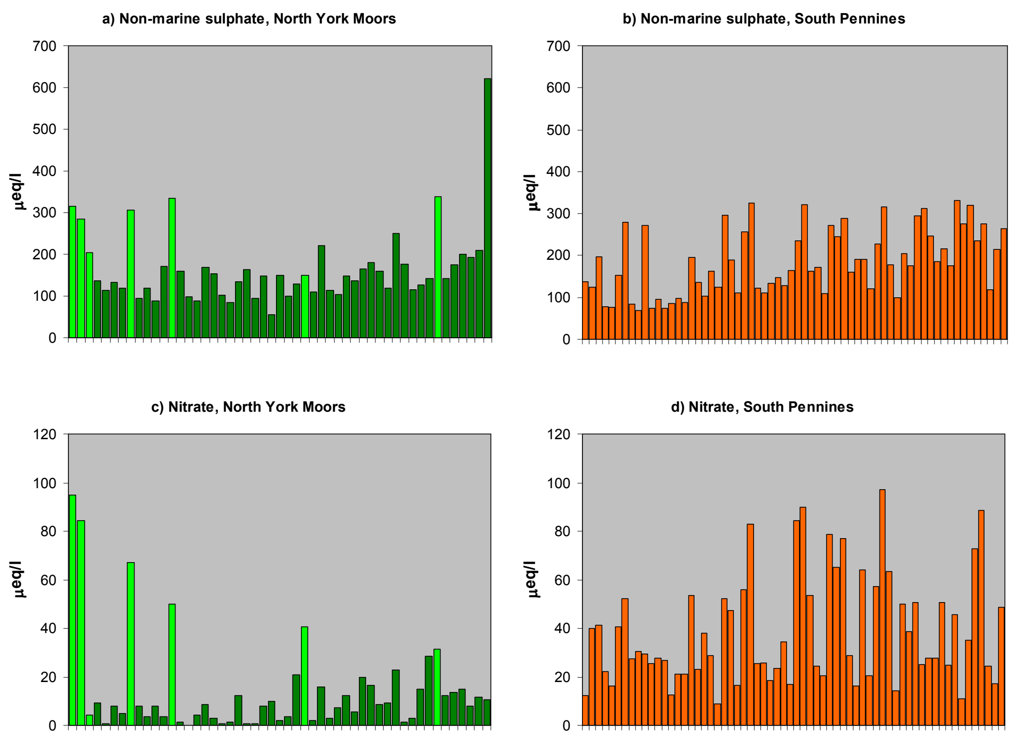
Figure 2. Observed ANC (ranked from lowest to highest) for a) the North York Moors survey, and b) the South Pennines sites to which MAGIC has been applied (in this and subsequent figures, streams draining wholly or partially afforested catchments in the North York Moors are highlighted in light green)



The major ion data clearly show that SO_4 is the major acidifying anion. Excluding the most alkaline site, Darnholme, which had an ANC of 667 μeq/l and a non-marine sulphate (xSO_4) of 621 μeq/l (likely to derive from agricultural or geological S sources), xSO_4 concentrations lie in the range 56 to 338 μeq/l (Figure 3). Median concentration (147 μeq/l) is slightly lower than for the South Pennines, although a number of catchments in the latter are thought to receive some input from geological sources. Six catchments containing significant areas of plantation forest all clearly had elevated xSO_4 concentrations, suggesting a combination of increased S deposition due to forest canopy filtering, and increased evaporative concentration.

By contrast, median NO_3 concentrations are low (8 μeq/l), suggesting that for most catchments, almost all N deposition continues to be retained (NH_4 is close to zero for almost all sites). Regional mean total N deposition (1.6 keq/ha/yr, based on CEH Edinburgh mean 1998-2000 data for a box containing the survey sites) is somewhat lower than for the survey sites in the South Pennines (2.2 keq/ha/yr) or indeed Snowdonia (1.7 keq/ha/yr), and the major soil types (peaty gleys and peats) contain a large amount of organic matter, likely to have a high N storage capacity (Evans et al., in press). However, the forested catchments provide a striking exception to this general pattern, with NO_3 concentrations elevated at all but one of these streams, with concentrations at the other streams in the range 31 to 95 μeq/l. These concentrations are sufficient to have having a major negative impact on ANC at these sites, which include the two lowest-ANC streams.

Figure 3. Observed non-marine sulphate and nitrate (ranked from lowest to highest ANC, as in Figure 2) for the North York Moors and South Pennines survey sites.



Cl concentrations are high in all catchments, with a median of 471 μeq/l (Figure 4). Since the region is likely receives intermediate loadings of seasalt deposition, these concentrations may be explained by a high evapotranspiration rate (for a UK upland area). Evaporative concentration will affect all ions, and the magnifying effect of this physical process may in part explain the extremely low ANC values observed in some streams. Although somewhat higher, Cl concentrations for the forested catchments are not as clearly elevated as those of xSO_4, suggesting that evaporative concentration is secondary to canopy filtering of pollutant S as a cause of elevated xSO_4 concentrations.

Base cations concentrations are variable, with Ca concentration providing the strongest correlation with both ANC and Gran alkalinity (Figure 5a). Again the effect of forestry is evident, with forested sites in general having a much lower alkalinity and ANC for a given Ca concentration. If the forested sites are omitted then, as in other surveyed regions such as the South Pennines (Evans et al., 2000), variations in catchment Ca (and to a lesser extent Mg) buffering largely control spatial variations in the extent to which acid deposition causes surface water acidification. It is noticeable, however, that with the exception of a small number of well-buffered sites, most have fairly uniformly low Ca concentrations, reflecting the base poor, and fairly homogeneous, nature of the geology.

Figure 4. Observed chloride, calcium, aluminium and hydrogen ion (ranked from lowest to highest ANC, as in Figure 2) for the North York Moors and South Pennines survey sites.

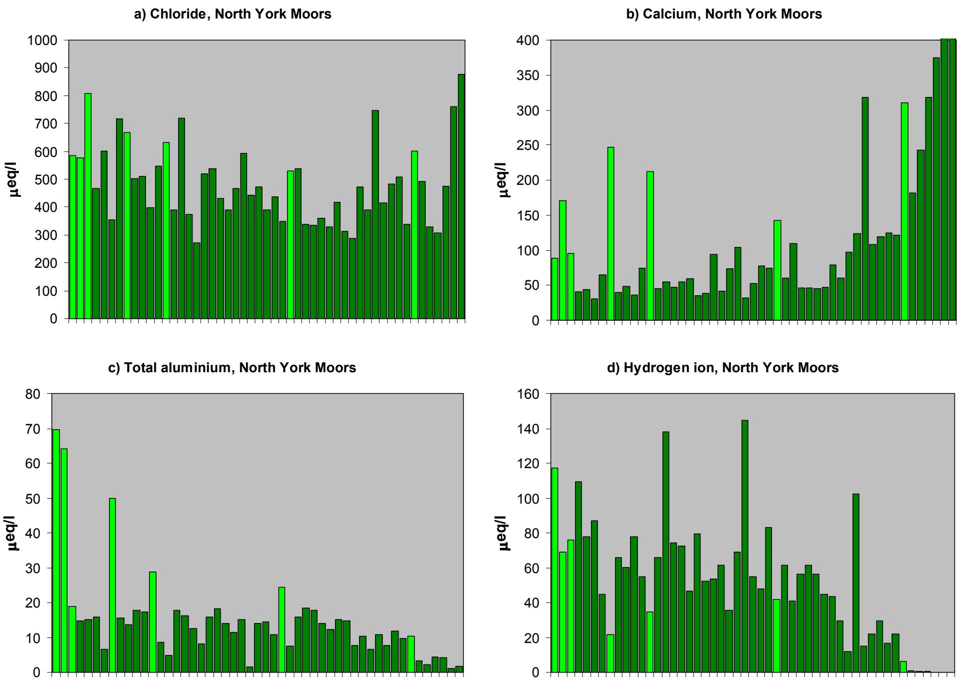
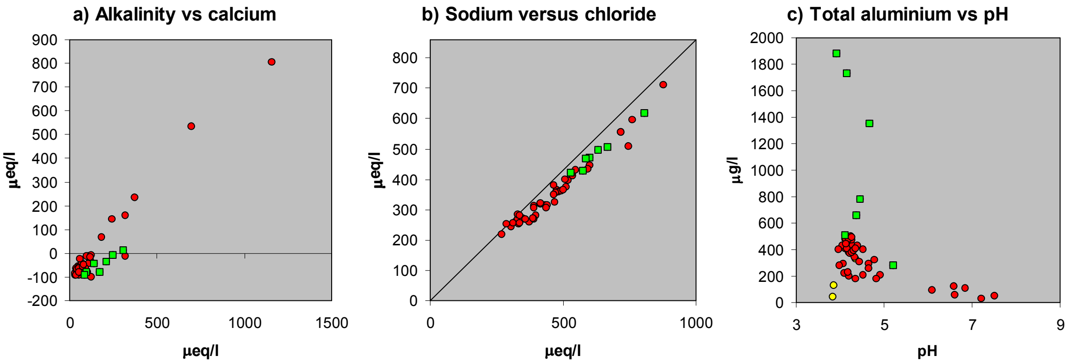


Figure 5. Observed relationships between a) Gran alkalinity and calcium concentration, and b) sodium and chloride concentrations. Forest catchments in all plots are shown in green, moorland pools in c) are shown in yellow. Line in b) indicates the relationship between Na and Cl that would be expected if both ions were present at sea-salt ratios.



Sodium concentrations are closely related to those of Cl (Figure 5b), but there is a clear deviation from the line that would be expected if sea-salt were the sole source of these ions (in other words, calculated non-marine Na is negative at most sites). There are two possible explanations for this deviation. The first is that, with higher sea-salt inputs during winter, some Na was being temporarily retained in the soil (the 'sea-salt effect') at the time of sampling. This process has an acidifying impact (e.g. Wright et al., 1988; Evans et al., 2001) and might indicate that observed ANC values are likely to be somewhat below the annual mean value. Similar problems were encountered at many sites in the UK Freshwater critical loads database sampled during spring, especially in NW Scotland (CLAG, 1995). An alternative explanation, however, is that a part of the total Cl input is from non-marine sources; HCl emitted by combustion and industrial processes is usually deposited close to source, and hence has a limited impact on more remote acid-sensitive regions. CEH Edinburgh deposition estimates suggest some non-marine Cl input, but this is small (< 1% of estimated marine Cl deposition). However significantly higher non-marine Cl deposition is estimated for nearby industrial areas, and the proximity of the North York Moors to major power generation and industrial sources may make an acidifying input from HCl a possibility.

Apart from the small number of high-pH sites, total Al concentrations were very high (> 200 µg/l at 75% of sites). With the exception of a small number of highly organic sites, DOC concentrations were moderate (10^{th} – 90^{th} percentile range 3 to 9 mg/l), suggesting that although some of this Al may be present in (less toxic) organic complexes, most is likely to be in toxic inorganic forms. Inorganic Al solubility is generally considered to be inversely related to pH, and this is largely supported by the North York Moors data, particularly for the moorland streams (Figure 5c). Two of the ponds sampled appear as outliers, and it is likely that at these sites, located within basins of deep peat, limited contact between the highly acid water and mineral soils prevents Al mobilisation from occurring. The second, very striking group of outliers, occurs among those streams draining forested catchments. In at least five of these, Al concentrations are much higher than the pH would indicate. This is also apparent in Figures 4c and 4d where, for a given (negative) ANC, far more of the total acid cation concentration is present as Al, rather than hydrogen ion. This difference in the balance of Al and H between forest and moorland streams has implications in terms of the biological impact of a given ANC (suggesting it may be higher in forest streams) and for which the application of MAGIC, since it implies that a higher Al solubility

(‘Gibbsite’) constant may be required for forest streams. The mechanism explaining greater Al mobilisation from forests is not entirely clear, although it may be related to greater soil acidification beneath forests.

Soils

Full analysis of soil exchangeable cations has not yet been completed, and consequently the results presented here are for organic soil C and N only (Table 3). The proportion of samples collected from different soil and vegetation types largely reflects the character of the upland area, which is heavily dominated by managed heathland, and by stagnohumic gley and humic podzol soils. Excluding the single sample of the Belmont series (collected under acid grass), median C/N ratios for the remaining soil series are consistent with the expectation that C/N will be higher in more organic-rich soils (Evans et al., in press), in the sequence peats > stagnohumic gleys > humus-ironpan stagnopodzol > humo-ferric podzol. However, with limited sample numbers and high scatter within the two better-sampled soil types, it is impossible to draw firm conclusions. Classed according to vegetation type, the single sample under grassland clearly has a lower C/N than the samples under heathland and conifer, but these are not clearly differentiated. Overall, the data are broadly consistent with the assessment by Rowe et al. (in prep.) of the relationship between soil C/N and N leaching, which shows a strong dependence of soil C/N on vegetation type, with soils under grassland having a lower characteristic C/N. The C/N ratio of most heathland soils was greater than the estimated threshold of NO_3 leaching (about 30 g/g) identified for heathland and forests by Rowe et al. The conifer soil C/N ratios were also above this threshold, although the strong variations in forest N cycling, and N leaching, as a function of stand age make it difficult to define such a threshold reliably for UK plantation forests. The single grassland sample is at or slightly below the threshold for NO_3 leaching estimated by Rowe et al.

Table 3. Organic soil C/N ratios (g/g) classified by a) soil type and b) vegetation type.

a) Samples classified by soil type

Soil Type	Series	C/N Min	C/N Median	C/N Max	Samples
Humo-ferric podzol	Anglezarke	-	28.1	-	1
Humus-ironpan stagnopodzol	Maw	30.4	33.1	57.0	6
Ironpan stagnopodzol	Belmont	-	14.9	-	1
Stagnohumic gley	Onecote	20.5	36.8	54.1	5
Blanket peat	Winter hill	42.0	59.1	76.3	2

b) Samples classified by vegetation type

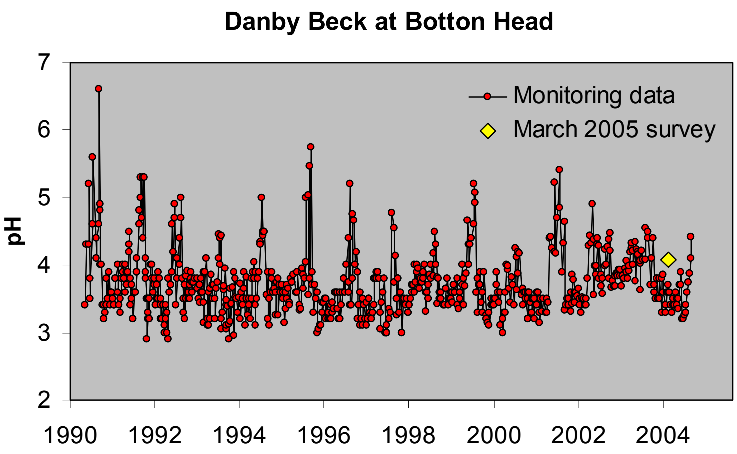
Vegetation type	C/N Min	C/N Median	C/N Max	Samples
Heathland	20.5	35.3	65.4	13
Grassland	-	14.9	-	1
Conifer	31.0	33.9	36.8	2

DISCUSSION

Representativeness of data

Given that the water quality data are based on a single survey, and that the survey took place during unusual conditions following a large snowfall, some caution is required in interpreting the results. In particular, it is uncertain to what extent observed surface water concentrations are representative of annual means (as is assumed, for example, when applying FAB or MAGIC). The evidence in the field was that stream flows were neither anomalously low (e.g. due to freezing) or high (due to snowmelt, which did not begin across most of the area until sampling was completed). Further evidence is provided by a comparison to long-term pH data collected at one of the sampled sites, Danby Beck (Figure 6; Chadwick, 2001). In the context of these long-term data, the March 2005 sample does not appear anomalous. The observed pH of 4.08 is within the range of observed variation in the stream, and in fact slightly higher than both the long-term mean of 3.70, and measurements made during the month either side of sampling. This could indicate less acid conditions on the day of sampling, or some CO_2 degassing from the sample prior to pH measurement. McNish et al. (1997) also monitored pH at Brocka Beck during 1995 and 1996, and found considerable temporal variation, with pH values considerably higher than the value of 4.18 observed in the current survey during summer baseflow, but falling as low as 3.7 during some high flows. Overall, the survey data do not appear obviously anomalous, but the Brocka Beck data do suggest that some streams may be subject to quite large episodic variability. Further sampling of a subset of streams over a year would assist in establishing whether the survey provides a representative indication of average surface water chemistry for the region.

Figure 6. Long-term pH data (from Chadwick, 2001 and T. Chadwick, pers. comm.), and March 2005 survey pH, for Danby Beck.



Probable impacts on aquatic biota

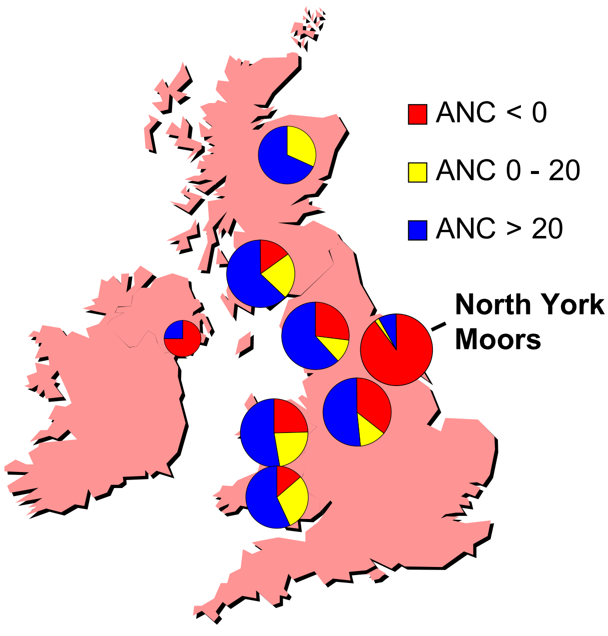
No biological data were collected for this survey, and it is impossible to accurately predict aquatic biological status across the region on the basis of a single set of chemistry data. Nevertheless, observed conditions were so acid (ANC < -100 μeq/l at most sites, median total Al 380 μg/l) that it is highly doubtful whether many of these waters could sustain viable populations of salmonid fish, or of many acid-sensitive macro-invertebrate species (e.g. Lien et al., 1996). The extremely high Al concentrations in forested streams (median 780 μg/l) suggest that aquatic biological damage may be most acute in, and downstream of, areas of conifer plantation.

The available information supports the conclusion that stream biota have been affected by acidification. Chadwick (2001) reports a general decline in salmonid fish catches in the River Esk, which drains much of the northern moorland area, with the near-disappearance of brown trout populations in headwater streams. Chadwick (2001) also describes a fish kill that occurred during a September 1993 high flow event in Botton Pond, in the upper Esk catchment, following stocking with brown trout in 1992. Conversations with local gamekeepers during fieldwork provided also provided anecdotal evidence that streams draining the upland area are generally fishless, and one reported similar fish kills in the first high flow after a drought period at a number of streams. It is likely that post-drought acid episodes such as these are caused by SO_4 pulses, generated by re-oxidation of stored sulphur in organic soils under aerobic conditions. Extreme autumn acid pulses caused by this mechanism have been observed in acidified parts of Canada (e.g. Dillon et al., 1997), and in peatland areas of Wales (Hughes et al., 1997) and Northern England (Adamson et al., 2001; Bottrell et al., 2004).

Implications for UK freshwater critical loads and target loads

It is apparent from this study that surface waters in the North York Moors have been very severely acidified. Until now they have been completely unrepresented in the coverage of MAGIC model applications used to derive target loads for submission to the CCE call for data. The model has yet to be applied to the North York Moors, but the present-day ANC status of the region, when compared to those to which MAGIC was applied for the last call for data (Figure 7) provides some indication of the likely significance of this additional region to the overall assessment.

Figure 7. Present-day ANC status of surface waters sampled in the North York Moors survey, compared to seven other regions (Cairngorms, Galloway, Lake District, South Pennines, North and South Wales, and the Mourne Mountains) to which MAGIC has been applied previously.



Although a small number of sites in the North York Moors are included in the freshwater critical loads dataset, some are outside the geologically sensitive area, and the combined ecosystem area these represent (particularly as many are hilltop ponds with very small catchment areas) is very small. The inclusion of the current dataset would therefore be expected to provide more representative coverage of this region, and to significantly increase the overall area of critical load exceedance. It is noteworthy that, although a reliable comparison between two single surveys 14 year apart cannot be undertaken, the general range of xSO_4, pH and ANC values observed in spring 2005 is very close to that which was observed in spring 1991. This tends to support the pH monitoring data that appear to show little evidence of recovery since 1990.

FURTHER WORK AND RECOMMENDATIONS

- Data will be submitted to the UK Freshwater Critical Load database, the FAB model used to calculate critical loads. The sites should be added to future critical load submissions to the CCE.

- MAGIC will be applied to all sites. Again, model outputs including target loads should be submitted to the next CCE call for data.

- Consideration will be given to possible publication of these results in the peer-reviewed literature. This could also include the results of the MAGIC application.

- Further sampling of a subset of sites could be considered, as a means to establish the temporal representativeness of existing data.

- As the UK upland region closest to major emission sources, and possibly also the most acidified, the lack of representation of the North York Moors within the Acid Waters Monitoring Network is unfortunate. Although the financial constraints on the network are recognised, it would be of great benefit to establish a monitoring site in the region. The existence of a pH record from 1990 at Danby Beck could be of value in this regard.

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