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1 **Regional trends in soil acidification and exchangeable metal concentrations in relation**

2 **to acid deposition rates**

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14 **Abstract**

15 The deposition of high levels of reactive nitrogen (N) and sulphur (S), or the legacy of that

16 deposition, remain among the world's most important environmental problems. Although

17 regional impacts of acid deposition in aquatic ecosystems have been well documented,

18 quantitative evidence of wide-scale impacts on terrestrial ecosystems is not common. In this

19 study we analysed surface and subsoil chemistry of 68 acid grassland sites across the UK

20 along a gradient of acid deposition, and statistically related the concentrations of

21 exchangeable soil metals (1 M KCl extraction) to a range of potential drivers. The deposition

22 of N, S or acid deposition was the primary correlate for 8 of 13 exchangeable metals

23 measured in the topsoil and 5 of 14 exchangeable metals in the subsoil. In particular,

24 exchangeable aluminium and lead both show increased levels above a soil pH threshold of

25 about 4.5, strongly related to the deposition flux of acid compounds.

1

2   Capsule   2

3   S and N deposition contribute to regional-scale soil acidification and metal mobilisation.

4

5   Keywords – Acidification, aluminium, lead, nitrogen deposition, sulphur deposition

1 **Introduction**

2 Deposition of reactive sulphur (S) and nitrogen (N) resulting from industrial and agricultural

3 emissions has been implicated in numerous environmental problems throughout the

4 industrialised world, including soil and water acidification, forest decline, local species

5 extinctions and damage to structures and monuments (NEGTAP, 2001). Deposition of S

6 compounds has declined considerably over the last 30 years in North America and Europe,

7 however this period has seen either no change, or a slight increase in the deposition of N

8 compounds (NEGTAP, 2001). Over the same period, S and N deposition have greatly

9 increased in many areas of Asia due rapid industrialisation (Kim and Cho, 2003). S and N

10 deposition acidify the soil by a number of processes, including the direct deposition of acids

11 in precipitation, the oxidation of dry-deposited compounds, loss of basic cations through ion

12 exchange, and plant uptake and nitrification of ammonium. Increasing soil acidity can

13 increase the solubility of potentially toxic metals, impact nutrient cycling, reduce or shift the

14 populations of soil microbes and fauna, change vegetation community composition and

15 reduce vegetation species diversity (Johnston et al., 1986; Falkengren-Grerup, 1995; Stevens

16 et al., 2004).

17

18 Re-surveys of previously-studied sites in Europe have documented declines in soil pH of

19 between 0.2 and 2 units over time periods ranging from 17 to 110 years, including forest and

20 heathlands in south Sweden (Falkengren-Grerup et al., 1987; Hallbäcken and Tamm, 1986),

21 and grasslands, forests and heathland in Great Britain (Blake et al., 1999; Kuylenstierna and

22 Chadwick, 1991, Farmer, 1995, Adamson et al., 1996). Jönsson et al. (2003) also observed

23 reductions in calcium, potassium and magnesium concentrations in southern Sweden between

24 1988 and 1999, which they related to acid deposition.

25

1   There is some evidence from regional surveys that these changes in soil pH and chemical

2   constituents are occurring at a large, perhaps continental, scale. In Värmland, Sweden, a

3   survey of forests found significantly lower soil pH (B horizon) in the south, where there are

4   relatively high levels of anthropogenic acid deposition, than in the north, which is far less

5   impacted by acid deposition (Lundström et al., 1998). In Scotland, Skiba et al. (1989) found

6   a significant correlation between soil pH and total acid deposition on peat soils. Dise et al.

7   (2001) demonstrated that even on a European scale, despite wide differences in climate,

8   vegetation and geology, a significant relationship between the level of acid deposition and the

9   flux of Al^{3+} can be detected in forests.

10

11   The bio-availability, mobility and speciation of most metals in soils are affected by pH (Tyler

12   and Olsson, 2001). Acid deposition mobilises metals in ionic form such as Al^{3+}, which can

13   interfere with root function or be taken up by plants creating chemical stress (Kabata-Pendias

14   and Pendias., 1991). Al is released into solution at a pH below 5 by the hydrolysis of both

15   Al-hydroxides and silicates on clay mineral surfaces, and Al complexed with soil organic

16   matter (Ashman and Puri, 2002). Pb, Fe and a number of other heavy metals behave in a

17   similar manner to Al, becoming more biologically available in the soil below a pH of

18   approximately 5. Once mobilised into solution, there is greater potential for metals to reach

19   watercourses where they can be toxic to macro-invertebrates and fish and increase water

20   treatment costs of drinking water supplies. The base cations (including Na, Mg and Ca) are

21   commonly found at higher levels in higher pH soils and are the first to leach from the soil as

22   pH declines. A decline in base saturation is symptomatic of soil acidification.

23

24   Although several studies have demonstrated links between the regional level of acid

25   deposition and soil pH or selected metals, few, if any have considered the full range of metals

1   in soil that may be influenced by chronically elevated sulphur or nitrogen deposition, and no

2   study to our knowledge has investigated all of the major factors that may influence

3   exchangeable metal concentrations on a regional scale over a range of soil types.   In this

4   study we use a transect across Great Britain to investigate relationships between acid

5   deposition, soil pH, climate and other driving variables, and the concentration of KCl-

6   extractable metals in the soil of acid grasslands.   High ionic strength salt extractions such as

7   this are considered to release the 'exchangeable' fraction of the metal pool from the surfaces

8   of clay or organic fractions (Peverill et al. 1999), and we will refer to the metals as

9   exchangeable throughout the paper (recognising that the actual fraction released is a topic of

10 continuing debate). The habitat we investigate, acid grassland, is particularly sensitive to

11 atmospheric deposition (Stevens et al., 2004) and variants of it occur throughout Europe,

12 Australia and North America, where it is economically important pastureland.   Great Britain

13 is an excellent region for such a study since acid deposition there covers the major range of

14 ambient annual deposition in most parts of the industrialised world and because vegetation

15 community composition is extremely well documented.

16

17 **Materials and Methods**

18 **Site selection**

19 This study focussed on the acid grassland community U4 *Festuca ovina-Agrostis capillaris-*

20 *Galium saxatile* grassland (Rodwell, 1992) (closely allied to the *Violion caninae* association

21 described in Swickerath, 1944).   Using information supplied by Natural England,

22 Countryside Council for Wales and Scottish Natural Heritage, a database of all recorded U4

23 grasslands in the British Isles was compiled. This consisted primarily of protected areas

24 including Sites of Special Scientific Interest (SSSI), National Nature Reserves (NNR) and

25 National Parks. None of the grasslands had a history of fertilisation. This information was

1   entered into the Geographical Information System package ArcInfo (ESRI, 1999). A map of

2   total nitrogen deposition was then overlaid to allow a nitrogen deposition value to be assigned

3   to each of the potential field sites. Sixty-eight sites were randomly selected to cover the

4   range of nitrogen deposition in the UK (Figure 1). The correlation of N deposition with S

5   deposition means that the range of acid deposition is also covered. A full description of each

6   site was made, including location (latitude/longitude) and altitude determined using a global

7   positioning system (GPS). Aspect, slope and grazing intensity were also estimated, and the

8   presence of enclosures was noted. In addition to N deposition, the 68 sites covered the UK

9   range in sulphur deposition and a wide variety of physical and chemical site characteristics

10 (Table 1).

11

12 Deposition of inorganic N (oxidised and reduced) and sulphate-S were modelled by the

13 Centre for Ecology and Hydrology (CEH), Edinburgh using the CEH National Atmospheric

14 Deposition Model (Smith et al., 2000). This provides values for both wet and dry deposition

15 and oxidised and reduced deposition at a 5 km resolution. Total inorganic N deposition

16 ranged from 44.0-259 $mmol_c$ m^{-2} y^{-1} (6.2–36.3 kg N ha^{-1} y^{-1}) and sulfate deposition ranged

17 from 41.2-179.0 $mmol_c$ m^2 y^{-1} (6.6-28.7 kg S ha^{-1} y^{-1}) (Table 1). Acid deposition was

18 calculated from the molar equivalents of reactive N and S (NO_3^- + NH_4^++ SO_4^{2-}, $mmol_c$ m^{-2} y^-

19 ^{1}). Heavy metal deposition data (Cu, Ni, Pb and Zn) were also provided by CEH Edinburgh

20 based on the DEFRA funded Heavy Metals Monitoring Network, giving total deposition to

21 grasslands at a 5 km resolution (Fowler et al., 2006). Data on mean annual rainfall, actual

22 evapotranspiration, potential evapotranspiration and soil moisture deficit were obtained from

23 the MORECS database (Thompson et al., 1981). Temperature data averaged for the years

24 1971-2000 were obtained from the UK Meteorological Office (UK Met. Office, 2004).

25

1   All of the sites were surveyed during the summers of 2002 and 2003, beginning in the south

2   of England and moving north. Full details of the field sites are given in Stevens (2004).

3

4   **Chemical analyses**

5   Soil samples were taken from five randomly placed 2×2m quadrats. Topsoil samples were

6   collected from two opposing corners of the quadrat; these were bulked to give five samples

7   per site. Topsoil samples were taken from the A horizon or, where there was no A horizon

8   present, samples were taken from the O horizon below the root mat. Subsoil samples were

9   taken from the centre of the quadrat at a depth of 30-40 cm using a Dutch auger. Soil

10 samples were kept cool in plastic bags until they could be returned to the laboratory. All

11 topsoil and subsoil samples were dried in an oven at $40^{o}C$ and ground to <2 mm prior to

12 analysis. Samples were thoroughly mixed to ensure homogeneity.

13

14 Eighteen soil chemical constituents were measured, most both in topsoil and subsoil: pH, %C

15 (topsoil only), %N (topsoil only), %P (topsoil only), and KCl-extractable Na^{+}, Ca^{2+}, Mg^{2+},

16 Li^{+}, Al^{n+}, Si^{n+}, Cr^{2+}, Mn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ba^{2+}, and Pb^{2+}. The molar Ca:Al ratio in

17 the extractant and the C:N by mass of the topsoil were derived. Soil K^{+} was not measured as

18 it was used for the extraction.

19

20 For pH, 10 g of air-dried soil was placed into a 50 ml beaker. 10 ml of distilled water was

21 added using a pipette and this was stirred for 30 minutes (Thomas, 1996). pH was

22 determined using an Acumet AR20 pH meter calibrated with pH 4 and 7 buffers every 20

23 samples and with every tenth sample replicated. For metal analyses, bulked air-dried, ground

24 soil samples for each site were made up using 2 g of topsoil from each quadrat to give a total

25 of 10 g. The soil was placed in an acid-washed leaching tube and leached with 100 ml 1M

1   KCl. The extracted solution was diluted to 1 in 50 with deionised water and acidified using

2   0.2 ml of concentrated nitric acid. Concentrations of major and trace metals were determined

3   using an Agilent 7500a Inductively Coupled Phase Mass Spectrometer (ICP-MS). Soil total

4   carbon and nitrogen were measured on a LECO element analyser, and soil plant-available P

5   was measured using an Olsen extract and colorimetric analysis (ADAS, 1986).

6

7   **Statistical analyses**

8   Stepwise multiple regression was used to identify the most significant relationships between

9   soil chemical constituents and potential environmental drivers. Regression analysis

10   quantifies the amount of variation in a dependent variable that is explained by one or several

11   correlates. Stepwise regression builds a model from those variables that together explain the

12   most variability in the dependent variable, but are themselves statistically independent. The

13   dependent variables used in the stepwise regression included all of those that would be

14   expected to influence soil chemistry, including climate, site geomorphology, and deposition

15   chemistry (table 2). Metal deposition (Cu, Ni, Pb, Zn) was also used as independent

16   variables for the analyses of the corresponding soil exchangeable metals. Some variables,

17   such as soil pH, were used as both dependent and independent variables (although never in

18   the same regression). The level of significance was set at $p<0.05$ for all statistical analyses.

19

20   Principal components analysis (PCA) was used to identify the major axes of variability in the

21   metals data and the most closely related variables in the full dataset. PCA condenses the data

22   into a smaller number of variables accounting for the maximum variation. This allowed us to

23   group metals in terms of their response. Using a correlation matrix, comparisons of the

24   principal components could also be made to the environmental variables. Topsoil metals only

25   were used for the PCA.

1

2   **Results**

3   The mean and range of exchangeable metals for topsoil and subsoil samples are given in

4   Table 3. The independent variables that explained the most amount of variation in each of

5   the soil chemical constituents (the first identified in each stepwise regression), and the r^2

6   value for each of these, are shown in Table 4. If two or more independent variables gave the

7   same r^2 value (i.e. exclusion of one results in a stepwise regression where the other emerges

8   first with an equal r^2), both are shown. Since latitude and longitude integrate many

9   environmental variables that are impossible to separate (e.g. climate, deposition, parent

10   material), in cases where either latitude or longitude emerge as the most significant predictors

11   the model was rerun without them to determine if combinations of other variables creates a

12   satisfactory model.

13

14   Of 22 independent predictor variables (table 2), topsoil pH was most closely related to the

15   level of acid deposition (negative relation). Acid deposition explained 42% and 31% (not

16   shown) of the variation in topsoil and subsoil pH, respectively (table 4, figure 2a).   After acid

17   deposition, the most important predictor variables in the topsoil pH stepwise regression were

18   topsoil C:N, (negative relation), latitude, and slope (negative relation). Together these

19   variables explained 59% of the variation in topsoil pH.   Separating the different components

20   of acid deposition, deposition of oxidised and reduced N showed higher correlations to

21   topsoil pH ($r^2 = 0.33$ for each, as well as combined as total N deposition, figure 2b) than S

22   deposition ($r^2 = 0.22$), but all were clearly less correlated to soil pH separately than NH_4^+,

23   NO_3^- and SO_4^{2-} deposition combined. Subsoil pH, on the other hand, was most closely

24   correlated to total inorganic N deposition ($r^2 = 0.33$, figure 2b), with reduced and oxidised N

25   accounting for about equal amounts of variation in pH (0.29 and 0.26 respectively). %C

1 (negative relation), slope (negative relation), latitude, and altitude also contributed to

2 explaining a total of 55% of the variability in subsoil pH.   When these variables were

3 included in the stepwise regression, sulphate deposition did not contribute to the model.

4

5 Of the metals for which deposition data were available (Cu, Ni, Pb and Zn) only Pb showed a

6 significant correlation between the flux in deposition and the concentration of the

7 corresponding exchangeable metal in the soil (topsoil r^2=0.24, p<0.001; subsoil r^2=0.35,

8 p<0.001). There was also a significant correlation between acid deposition and Pb deposition

9 (r^2=0.46, p<0.01). Deposition of other metals was not significantly related to N deposition.

10

11 The deposition of either reduced N, total N, sulphate-S or acid deposition was the primary

12 correlate for eight metals in the topsoil and five metals in the subsoil, as well as for the molar

13 Ca:Al ratio in both top- and subsoil. Topsoil Cr, Mg and Ni were negatively correlated to

14 reduced N deposition, Li and Na were negatively correlated to total N deposition, Cu was

15 positively correlated to S deposition in both topsoil and subsoil, and Al in both topsoil and

16 subsoil and Pb in topsoil showed positive relationships to acid deposition (figure 3) (topsoil

17 Al equally with C:N). In the subsoil, Li (negative) and Na (negative) were most strongly

18 correlated to reduced N deposition, and Mg was negatively related to acid deposition. Pb in

19 subsoil was most closely related to Pb deposition, but showed almost as strong a relationship

20 with acid deposition (r^2=0.31). The Ca:Al ratio showed negative relationships with acid

21 deposition in topsoil, and oxidised N deposition in the subsoil (equally with %C). Stepwise

22 regressions for Al and Pb consistently showed soil carbon concentration (C:N or %C) to be a

23 significant secondary variable in models that included the deposition flux of acids, with

24 exchangeable Al negatively correlated to carbon content and Pb positively correlated.

25

1   Of the remaining significant variables showing at least an r^2 of 0.10, the topsoil nutrients %N,

2   %C and C:N were all negatively correlated to topsoil pH, with C:N a stronger correlate than

3   either of the organic nutrients separately. Soil %P, on the other hand, was uncorrelated to

4   either topsoil or subsoil pH but was most strongly related to %N. Also related to topsoil pH

5   were topsoil Ca and Fe (negative). Ba (topsoil and subsoil) and Si (subsoil) were both

6   positively related to subsoil pH.   Of all of the topsoil and subsoil metals measured, only

7   topsoil Si was most strongly related to a driver other than acid deposition (N, S or combined),

8   pH or soil carbon (%C, C:N); altitude is the first variable to emerge from the stepwise

9   regression of topsoil Si.

10

11   Some exchangeable metals may show nonlinear relationships to acid (or N or S) deposition

12   flux – increasing, for example, at a higher rate in the soil as N or S deposition increases

13   linearly.   We tested this hypothesis with simple regressions using $\log_{(10)}$-transformed soil

14   exchangeable metal concentrations as the dependent variable and either N, S or acid

15   deposition as the independent variable.   This produced improved correlations with deposition

16   fluxes for a number of soil exchangeable metals (Table 4), in particular for topsoil Cr, Li and

17   Pb.

18

19   Principal Components Analysis (figure 4 and table 5) gave 5 axes of variation with

20   eigenvalues greater than one, accounting in total for 0.73 of the variation in the 14 major and

21   trace metals measured in topsoil. The first principal component (PC1) accounted for 0.27 of

22   the variation (eigenvalue = 3.83) with strong negative loadings from Cr, Ni, Na, Mg and Li

23   and positive loadings from Pb and Al. Regressing environmental variables (table 2) against

24   PC1 shows that the strongest correlation for this group is with N deposition ($r^2 = 0.63$;

25   p<0.001). PC2 accounted for 14.4% of variation in the data (eigenvalue = 2.01) with strong

1   negative loadings from Al, Fe, Pb, and Cu, and a positive loading for Ca.   Plotting

2   environmental variables against PC2 shows that the strongest correlation for this group is

3   with topsoil pH ($r^2 = 0.50$; $p<0.001$). When plotted against pH, exchangeable Al, Pb and Fe

4   show thresholds at pH 4.5-5, above which levels of the metals are low for all or nearly all

5   sites, and below which a significant number of sites show elevated exchangeable metal

6   levels. This is consistent with known distribution coefficient values for these metals. The

7   groupings of the metals in the PCA diagram reflect similar geochemical behaviour, with base

8   cations grouped towards the top of the ordination and metals expected to be found at higher

9   concentrations with increasing pH on the opposing side of the diagram where Pb, Cu, Fe, Al

10   and Mn are clustered. These metals all show a similar geochemical behaviour within this pH

11   range (Tyler and Olsson, 2001).

12

13

14   **Discussion**

15   In this study we consider the relationship between soil metal levels and important drivers,

16   including the deposition of nitrogen, sulphate and metals.   We believe that relationship

17   between deposition chemistry and the most important soil parameters we measured (e.g. pH,

18   exchangeable Al and Pb) primarily reflects the response to many years of chronically

19   elevated N, S or metal deposition. Evidence for this comes from long-term field

20   manipulation studies of N and S at realistic levels, which consistently show a very slow

21   response of soil chemistry in relation to other pools (e.g. Gundersen et al. 1998).   As with

22   other such regional gradient studies, we assume that the current pattern of deposition

23   chemistry is broadly similar to the long-term pattern.

24

1   For the statistical analyses, we included all of the variables that would be expected to

2   influence exchangeable metal concentrations for which data were readily available (Table 2);

3   the stepwise regression builds models of combined independent variables that best explain

4   the variability in the dependent variable. Since differences in soil chemistry among sites are

5   only partly due to differences in deposition chemistry, a model containing soil pH rather than

6   (or in addition to) acid deposition would suggest that non-acid deposition-related soil pH

7   (due, for example, to differences in geology or land use) of the site is important.   Some

8   important variables, however, such as previous site history, soil type, and local sources of

9   metals, are not explicitly included. These remain part of the unexplained variability in the

10   analyses.

11

12   Within the UK, as with other industrialised regions of the world, the distribution of NO_x, NH_y

13   and SO_4^{2-} fluxes overlap, with some areas of high deposition for nitrogen also areas of high

14   sulphur deposition. However, due to the importance of agriculture as a source of N but not S,

15   there is a much closer spatial correlation between SO_4^{2-} and NO_x deposition ($r^2=0.72$, $p<0.05$)

16   than SO_4^{2-} and total N deposition ($r^2=0.49$, $p<0.05$). Thus, when considering the impact of

17   acid deposition on natural ecosystems, each of these components must be considered

18   separately.

19

20   Despite the large geographic scale and wide range in climate, site morphology, soil

21   chemistry, and other drivers (e.g. Table 1), more than 40% and 30% of the variability in soil

22   pH in topsoil and subsoil, respectively, can be explained by the current flux of acid

23   deposition.   N deposition consistently explains more of the variability in soil pH than S

24   deposition: indeed, for subsoil, S deposition is not significant in a regression containing N

25   deposition alone. This probably reflects both nitrification of NH_4^+ (producing hydrogen ions)

1 and the movement of NO_3^- through soils (depleting exchange sites of basic cations). The

2 lower overall r^2 in subsoil probably reflects the increasing influence of non-deposition factors

3 on soil pH, such as soil parent material. The lack of correlation between subsoil pH and

4 atmospheric sulphate deposition may be due to this overall higher variability masking

5 relatively subtle differences between the signals of oxidised forms of N and S. This

6 indicates that N deposition is at least as important as S deposition for soil acidification.

7

8 The results from this large-scale study of grasslands augment smaller-scale studies

9 conducted in peatlands (Skiba et al., 1989) and forests (Lundström et al., 1998) which

10 showed correlations between the deposition of acidifying substances and soil pH but did not

11 consider as wide a geographical region or as comprehensive a set of predictor variables as

12 this study. They also support the findings of long-term soil pH measurements (Blake et al.,

13 1999) and studies that have made repeat measures of soil pH after a number of years (Farmer,

14 1995; Kuylenstierna and Chadwick, 1991) where pH changes have been attributed to acid

15 deposition.

16

17 The PCA and the stepwise regressions complement each other in identifying both the

18 dominant correlates to exchangeable metal concentrations and the major groups of metals that

19 show similar responses. Al and Pb show a positive loading on PC1 (N deposition) as well as

20 a strong negative loading on PC2 (soil pH). The multi-factor stepwise regressions for Al and

21 Pb indicate that acid deposition, soil pH, and soil carbon all play a role in determining the

22 release of these metals onto the soil exchange complex. This is also consistent with the

23 wedge-shaped relationship between these metals and both acid / N deposition and soil pH,

24 indicating that multiple factors drive exchangeable metal concentrations.

25

1   The mobilisation of Al at high acid deposition and low pH is consistent with its known

2   solubility from experimental acidification of soils (Tyler and Olsson, 2001; Kanata-Pendias

3   and Pendias, 1992; Ulrich, 1991). This effect is also seen with Pb but is complicated by the

4   correlation between Pb deposition and acid deposition.   The increased mobilisation of

5   aluminium with increasing N deposition and fertilisation is well recorded in both

6   manipulation experiments and correlative studies along deposition gradients (e.g. Blake et al.,

7   1999; Dise et al., 2001; Emmett et al., 1995; Mulder and Stein, 1994). The binding of these

8   metals to exchange sites on organic matter is an additional control on their bio-availability in

9   the soil (Tippling et al., 2003). The different behaviour between the two metals with relation

10   to soil carbon content may reflect their sources: Al is primarily derived from the soil mineral

11   matrix, whereas the main source of Pb is atmospheric, with deposited Pb complexed on

12   organic carbon and thus preferentially retained in carbon-rich soils.

13

14   Cr, Ni, Na and Mg were strongly negatively related to PC1 (N deposition), and all showed

15   reduced N deposition as the most significant (negative) correlate in stepwise regressions. It is

16   likely, however, that most or all of these are spurious correlations.   Cr and Ni are very

17   closely correlated (r^2 = 0.94 topsoil; 0.97 subsoil), and their negative relationship to reduced

18   N deposition is driven by high values in two topsoils and four subsoils in low N-deposition

19   sites. It is likely that local sources are responsible for the behaviour of these metals.

20   Exchangeable Na and Mg similarly are influenced by 4-5 relatively remote grasslands, with

21   high levels again most likely due to local sources, including in some cases the sea.   Of these

22   four metals, only Na still showed a weak significant negative relationship with reduced N

23   deposition when the high outliers are removed (and thus may truly reflect some exchange of

24   soil Na^+ for NH_4^+ in high N-deposition areas). In contrast, the sources of metals such as Pb

1   and Cu are primarily atmospheric, from fossil fuel combustion and smelting, leading to a

2   regional-scale distribution.

3

4   Of the other metals that cluster in the negative region of PC1, levels of exchangeable Ba are

5   driven by a single high value, and Si levels (strongest regression correlations with altitude

6   and pH) may reflect broad differences in parent material between upland and lowland parts of

7   the UK and are thus probably driven by geological / weathering reactions. In contrast, Li does

8   show an overall negative trend with increasing levels of reduced N deposition, even when

9   several high outliers are removed. Like Na, this may reflect an exchange of Li^+ for NH_4^+ in

10   regions receiving elevated N deposition.

11

12   Cu and Fe showed strong loadings to PC2 (soil pH) but not PC1 (N deposition). The

13   stepwise regressions also show that soil pH is the strongest predictor of exchangeable Fe,

14   although the relationship is fairly weak, and only in the topsoil.   Of all the metals, Cu alone

15   showed the most significant relationship to sulphate deposition in stepwise regressions.

16   Calcium showed a positive loading to PC2, as also reflected in significance of soil pH in the

17   stepwise regressions. Calcium is found in generally low levels in these acid soils and levels

18   are very variable. The weak relationship between calcium and other drivers considered in

19   this study, including pH, suggests that levels of Ca are also significantly influenced by factors

20   we have not considered, such as site history, management, and soil parent material.

21

22   Finally, exchangeable Mn shows no relation to either axis of the PCA, and in regressions is

23   also not closely related to acid deposition or pH, but shows the strongest (negative)

24   relationships with soil C:N.   Like aluminium, this suggests a mineral soil source and binding

1 to organic exchange sites. However, the release of Mn may be more controlled by soil drying

2 / wetting cycles and redox levels than by soil acidity.

3

4 **Conclusion**

5 A large number of sites across a wide geographical gradient can provide insight into long-

6 term controls over the mobilisation of metals. The impacts of acidification, particularly N

7 deposition, can be inferred from the significant relationships (regression and PCA) between

8 acid deposition and high concentrations of exchangeable lead and aluminium in soils of acid

9 grasslands in Great Britain at levels of acid deposition above about 200 $mmol_c$ m^{-2} y^{-2}. Soil

10 pH and the binding of metals by organic exchange sites on carbon-rich soils modifies the

11 response to acid deposition.   The results presented here show the impacts of cumulative

12 deposition over many years and, although levels of acid deposition are declining in Europe

13 (NEGTAP, 2001), they are increasing in other parts of the world. Even where acid

14 deposition is declining, the effects are likely to be seen for a long time to come in both the

15 soil and plant communities.

16

17

1

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1 **Table 1.** Range of physical variables across the 68 sites investigated in this study

2   23

Variable	Range
Total inorganic N deposition ($mmol_c$ m^{-2} y^{-1})	44.0 - 258.8
SO_4^{2-} – S deposition ($mmol_c$ m^{-2} y^{-1})	41.2 - 179.0
Acid Deposition (Total N + SO_4^{2-}-S) ($mmol_c$ m^{-2} y^{-1})	87.1 - 413.1
Altitude (m)	15 - 692
Slope (°)	0 - 60
Mean annual temperature (°C)	6.6 – 10.6
Mean annual precipitation (mm)	594 - 3038
Topsoil pH	3.7 - 5.5
Subsoil pH	3.3 - 5.7
Soil % N	0.12 - 1.57
Soil % C	2.90 - 40.6
Soil C:N	13.1 - 30.5

3

1 **Table 2.** Independent variables used in statistical analyses. Metal deposition (Cu, Ni, Pb,
2 Zn) used as independent variables for the analyses of the corresponding soil exchangeable
3 metals only.
4

Variable	Unit
Deposition variables	
Total inorganic N deposition	$mmol_c\ m^{-2}\ y^{-1}$
Oxidised N deposition	$mmol_c\ m^{-2}\ y^{-1}$
Reduced N deposition	$mmol_c\ m^{-2}\ y^{-1}$
Sulphate-S deposition	$mmol_c\ m^{-2}\ y^{-1}$
Acid deposition	$mmol_c\ m^{-2}\ y^{-1}$
Total Cu deposition	$g\ ha^{-1}\ yr^{-1}$
Total Ni deposition	$g\ ha^{-1}\ yr^{-1}$
Total Pb deposition	$g\ ha^{-1}\ yr^{-1}$
Total Zn deposition	$g\ ha^{-1}\ yr^{-1}$
Site physical characteristics	
Latitude	decimal
Longitude	decimal
Altitude	m
Aspect	^{o}
Slope	^{o}
mean annual temperature	^{o}C
Mean annual precipitation	mm
Potential evapotranspiration	mm
Actual evapotranspiration	mm
Soil moisture deficit	mm
Grazing intensity	(visual inspection, scale 1-3)
Enclosure	(presence or absence)
Soil variables	
Topsoil Carbon (C)	% by mass soil DW
Topsoil Nitrogen (N)	% by mass soil DW
Topsoil C:N	Ratio by mass
Topsoil P (Olsen)	$mg\ kg^{-1}$ soil DW
Litter cover	% (visual inspection)
pH (topsoil and subsoil; 1:1 water)	

5

1   Table 3. Mean and range of topsoil and subsoil KCl-extractable metal concentrations (mg

2   100g^{-1} DW soil).   25

KCl-extractable metal	Topsoil (mg 100g^{-1})		Subsoil (mg 100g^{-1})	
	Range	Mean	Range	Mean
Al	1.2 - 131.9	36.1	0.5-162.4	42.9
Ba	0.3 - 15.7	2.2	0.3-39.7	2.5
Ca	2.8 - 354.7	75.1	2.7-355.6	40.5
Cr	0.0 - 1.7	0.1	0.0-6.3	0.2
Cu	0.0 - 0.26	0.05	0.0-0.2	0.02
Fe	1.1-29.5	4.9	0.7-26.7	3.0
Li	0.02-2.4	0.2	0.0-2.9	0.2
Mg	1.1-61.4	11.9	1.1-107.7	8.4
Mn	0.2-19.5	3.1	0.2-9.9	2.2
Na	4.6-61.0	11.8	2.5-25.5	7.0
Ni	0.0-1.8	0.1	0.0-5.1	0.3
Pb	0.0-6.2	1.3	0.0-3.7	0.8
Si	0.0-6.0	1.8	0.0-11.7	2.9
Zn	Not measured		0.1-2.7	0.6

1   **Table 4.** Independent variables (from Table 2) that explain the most variation in each of the

2   soil chemical constituents (the first identified in each stepwise regression), and the r^2 value

3   (p<0.05). Negative correlations are shown as (-); a double dash (--) shows no significant

4   correlations with measured variables. For variables that explain the same amount of variation

5   in a dependent variable, both are given. Soil independent variables were excluded from

6   regression analyses where autocorrelations would occur, and only soil variables in the same

7   soil layer were regressed against each other.   Deposition correlates to log-transformed soil

8   constituents are shown where the r^2 value is higher than for untransformed values (acid

9   deposition, total N deposition and S deposition only considered).

Dependent variable	Topsoil	r^2	Subsoil	r^2
Non-metal soil variables				
pH	Acid Dep. (-)	0.42	N Dep. (-)	0.33
% C	Topsoil pH (-)	0.14	Not measured	
% N	Topsoil pH (-)	0.06	Not measured	
C:N	Topsoil pH (-)	0.21	Not measured	
%P	% N (+)	0.23	Not measured	
Metals				
Al	Acid Dep. (+)	0.12	Acid Dep.	0.27
	C:N (-)	0.12		
Log Al			*Acid Dep*	*0.39*
Ba	Subsoil pH (+)	0.17	Subsoil pH (+)	0.13
Ca	Topsoil pH (+)	0.11	Subsoil pH (+)	0.09
Cr	Reduced N Dep. (-)	0.20	--	
Log Cr	*Total N Dep (-)*	*0.40*	*Acid Dep (-)*	*0.06*
Cu	Sulphate Dep. (+)	0.12	Sulphate Dep. (+)	0.14
Fe	Topsoil pH (-)	0.10	--	
Log Fe			Sulphate Dep. (+)	0.06
Li	Total N Dep. (-)	0.26	Reduced N Dep. (-)	0.15
Log Li	*Total N Dep (-)*	*0.45*		
Mg	Reduced N Dep. (-)	0.20	Acid Dep. (-)	0.09
Log Mg			*Acid Dep. (-)*	*0.16*
Mn	C:N (-)	0.15	C:N (-)	0.17
Na	Total N Dep. (-)	0.30	Reduced N Dep. (-)	0.31
Log Na	*Total N Dep (-)*	*0.36*		
Ni	Reduced N Dep (-)	0.16	--	
Log Ni	*Total N Dep (-)*	*0.23*	*Total N Dep (-)*	*0.08*
Pb	Acid Dep. (+)	0.32	Pb Dep. (+)	0.35
Log Pb	*Total N Dep (+)*	*0.51*	*Pb Dep. (+)*	*0.44*
Si	Altitude (+)	0.10	Subsoil pH (+)	0.12
Zn	Not measured		C:N (+)	0.06
Ca:Al	Acid Dep. (-)	0.22	Oxidised N (-)	0.12
			%C (+)	0.12

1

1   **Table 5.** Factor loadings for metals on axes 1 and 2 of the principal components analysis.

	Factor 1	Factor 2
Al	0.273	-0.691
Ba	-0.475	-0.241
Ca	-0.183	0.301
Cr	-0.870	-0.212
Cu	-0.206	-0.551
Fe	0.011	-0.662
Li	-0.637	0.002
Mg	-0.599	0.145
Mn	-0.003	-0.110
Na	-0.776	0.067
Ni	-0.863	-0.235
Pb	0.367	-0.614
Si	-0.597	-0.001

2

1   **Figure Captions**

2   **Figure 1.** Map showing sites visited in this investigation and total inorganic N deposition

3   (kg N ha^{-1} y^{-1}). Closed circles represent sites surveyed in 2002 and open circles sites

4   surveyed in 2003. Data supplied by CEH Edinburgh (Smith, 2000).

5

6   **Figure 2.** Decreasing topsoil (open circles, dashed line) and subsoil (closed circles, solid

7   line) pH with (**A**) increasing total acid deposition (**B**) increasing inorganic N deposition, both

8   in mmol$_c$ m^2 y^{-1}

9

10   **Figure 3.** Concentration of (**A**) aluminium and (**B**) lead in topsoil (open circles) and subsoil

11   (closed circles) with increasing total acid deposition.

12

13   **Figure 4.** Projection of variables for principle component analysis factors one and two.

14

15