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A CRITICAL APPRAISAL OF FIELD EVIDENCE FROM A REGIONAL SURVEY FOR ACID DEPOSITION EFFECTS ON SCOTTISH MOORLAND PODZOLS

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Samples have been collected from major horizons of 34 podzol profiles distributed throughout Scotland, all developed from granite or granitic tills and under *Calluna* moorland. The pH in water and calcium chloride pastes, exchangeable cations and cation exchange capacity, and extractable aluminium of the soils collected have been measured, and the results studied in relation to reported atmospheric deposition of H⁺, non-marine sulphur and nitrate. For all horizons, significant positive correlations were found between soil pH and rainfall mean pH, as might be expected when the critical load of H + deposition isexceeded. Acidifying pollutant deposition also apparently increased soil extractable aluminium concentrations in the B and **C** horizons. However, exchangeable base cation concentrations tended to increase, rather than decrease, with increasing precipitation acidity. This effect was attributed to increases in biogeochemical cycling of base cations, increases in leaching inputs of base cations from overlying **A/E** horizon soils, and increases in the inputs of base cations leached from upslope. The results suggest that the simple steady state mass approach to the quantification of critical loads, as often applied, may be an oversimplification.

KEY WORDS: Granite, acid deposition, mineral weathering, biogeochemical cycling, critical load, peaty podzols.

INTRODUCTION

Links between acid deposition and ecosystem acidification throughout Europe and America have been clearly established in a number of studies (e.g. Skiba and Cresser, 1989; Cresser *et al.,* 1989; Clayton *et al.,* 1991, Reuss and Johnson, 1986). Despite the increased awareness of this connection and the apparent decrease in sulphur emissions over recent years, the effect of acid deposition on soil acidification remains a major problem (Hedin *et al.,* 1994). Indeed, acidification is thought to be so widespread that acidity has become one of the most widely discussed and most commonly studied properties of soils. In spite of this, there have been few reports in the UK of observations on a regional scale of acidification of soils attributable to acid deposition. Exceptions are studies for peat soils (Skiba *et al.,* 1989; Smith *et al.,* 1993; Sanger *et al.,* 1994a, 1995) and, for the B horizons only, of *Calluna* moorland podzols (Barton *et al.,* 1994).

The inputs of nitric and sulphuric acids to soils result in short term shifts in ion exchange equilibria, leading to enhanced leaching of base cations. The rate at which, and the extent to which, these cations are replaced on the soil exchange sites depend on the type, quantity and particle size of the minerals present, which, in turn, are determined by the soil/parent material, the state of soil evolution and long-term leachate composition. The decline over time in base status for the soil profile depends predominantly on mineralogy and precipitation quantity and quality. If the base cations leached from cation exchange sites are subsequently replenished by geochemical weathering, the pH and base saturation of the soil will not fall. Some soils may be strongly buffered against pH change for many years. If, however, a soil is naturally low (or already highly depleted) in readily weatherable minerals, there is a reduction in the base saturation, and potentially toxic aluminium is mobilised (Ulrich, 1991). In such base-poor soils, base cation inputs *viu* precipitation and dry deposition become increasingly important in offsetting soil acidification. Thus, the risk of acidification of moorland podzol B horizon soils in Scotland has been found to be strongly dependent on bedrock and soil type (Barton *et d.,* 1994), with areas of acidic and intermediate acidic hard rocks, such as granites, gneisses, sandstones and quartzites being most sensitive.

The critical loads concept, defined by Nilsson and Grennfelt (1988) as "a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge", was devised in an effort to quantify the resistance of soils to effects of acidifying pollution. It has gained wide international acceptance over recent years and is important as a potentially useful tool for quantifying the advantages of specific strategies for abatement of nitrogen and sulphur deposition. Bull (1992) has discussed the problem in detail in relation to the efforts made by various specialist groups to find acceptable definitions for sensitive receptors which might serve as indicators of "harmful effects". Critical loads can be assigned to mineral soils according to the known or estimated weathering rates of their mineral components (Nilsson and Grennfelt, 1988).

Most sensitive podzolic soils in Scotland contain quartz, feldspars and mica, all poor in base materials. Soils evolved from granites are sometimes shallow and poorly buffered, and therefore at risk of acidification. In addition, the mineral matrix in many Scottish soils has been exposed to chemical weathering since the last glaciation, which ended some ten thousand years ago (Hall, 1992). Accordingly, it should be assumed that the production of cations in the soil by weathering will follow weathering kinetics appropriate for this stage in the soil's evolution, and the initial dissolution kinetics of fresh minerals may be no longer relevant. The critical loads approach currently adopted in the UK, however, groups together all soils derived from granites or granitic tills, regardless of the extent of weathering (Hornung *et al.*, 1995). This makes precise prediction of probable exceedance effects on soil chemistry difficult. The additional features of high rainfall, low temperatures and, in some cases, steep slopes, make granite- or granitic till-derived Scottish soils particularly susceptible to soil acidification and sensitive to episodes of low pH river runoff.

The concept of "damage" to soils, as applied when quantifying critical loads, is not clearly defined in chemical terms. The most precise definition to date is that based on reduction in [Ca+Mg]/[Al] ratio in soil solution, which is, in turn, related to adverse effects upon plant growth (Critical Loads Advisory Group, 1994). However, it is not immediately obvious what statistically significant correlations might be expected

between amounts or concentrations of deposited acidifying pollutants and soil solid phase physico-chemical properties, such as pH or exchangeable cation concentrations.

The objective of the present study was to look for evidence of chemical damage to soils, as reflected in selected soil physico-chemical characteristics, over a range of pollution loads, which could be interpreted as indicating "harmful effects", for example pH reduction or increased aluminium mobilisation in soils that are already very acidic. Due to their expected sensitivity to acid deposition, moorland podzol soils derived from granitic parent material of Scottish uplands were located, and sampled on a regional basis, and statistical analysis was used to identify the key factors involved in the acidification of these soils by atmospheric pollution. In Scotland, the critical loads of many sensitive soils are "exceeded", which implies that such soils are, by definition of critical loads, being damaged in some way. Wet deposited $H⁺$ alone ranges from < 0.2 to < 0.6 keq ha⁻¹ yr⁻¹ in Scotland, so that even in the absence of dry deposition of acidifying pollution, the critical load for soils derived from granites, 0.5 keq ha^{-1} yr⁻¹, would be exceeded at many sites (Critical Loads Advisory Group, 1994).

METHODOLOGY

Sampling Techniques and Sites

This regional survey was based on soil map units used in the 1:250,000 soil maps compiled by the Soil Survey of Scotland, which are based upon soil type, soil association, landforms and information on associated vegetation and land use. Specific attention was paid to parent material. So that soil chemistry could be related to pollution climate, the sampling programme was based on the Ordinance Survey 20 km square grid used by the UK Review Group on Acid Rain (UKRGAR, 1990). The dominant parent material for these grids has been shown in maps presented elsewhere (Barton *et ul.,* 1994).

Having identified the granite dominant areas, two or three sites which satisfied the following constraints were selected from each grid square:

At each site in October/November 1993, the surface vegetation was removed using secateurs, the major root fragments were discarded and a soil sample of approximately 1 kg was collected from each horizon. Composite samples were taken for the L/F/H and **A/E** horizons. The soils were placed in sealed polythene bags. The site locations are shown in Figure 1. At some of the sites, the C horizon was unattainable due to excessively stony terrain.

Figure 1 The **sites** chosen for regional survey of granite podzols in Scotland.

Soil Preparution and Analysis

Soil samples were sieved and then analysed for moisture content, pH, exchangeable cations $(Ca^{2+}, Mg^{2+}, Na^{+}$ and K^{+}), cation exchange capacity (CEC), and KCl- extractable (primarily exchangeable) aluminium. All measurements were carried out on < 2 mm fractions of field moist soils.

Soil pH was measured in both water and 0.01 M CaCl,, after equilibrating a soil: solution paste (1:5 ratio) for 1 hour using a low conductivity combined glass calomel electrode. For exchangeable base cation and base saturation measurements, the soil was extracted with 1 M (CH₃COONH₄) using a soil: solution ratio of 1:100 and this extract was analysed for exchangeable sodium, potassium, calcium and magnesium. The residual soil was then washed with 80% ethanol and subsequently leached with 250 ml of acidified 1 M NaCl. The amount of ammonium in this final wash was determined and the result was used to calculate the soil CEC. Subsamples of the soils were also extracted using 1 M KCl solution (1:5, soil: solution ratio) and the extracts analysed colorimetrically for exchangeable aluminium (Hesse, 1971, Royset, 1986).

Deposition Data

Deposition was not measured at the sites, and therefore modelled estimates were used. All the estimates were provided on a grid square basis, and in each case the value applied to each site was the average value for the grid square into which the site fell. Wet deposition was estimated from interpolated rainfall composition measurements from 1986-88 (UKRGAR, 1990), by multiplying the interpolated concentration field by interpolated Met. Office rainfall measurements **(S.M.** Gammack, pers. comm.). Geostatistical interpolation by kriging (Webster *et al.,* 1991) was performed using the computer package Unimap. Total (wet $+$ dry $+$ cloud) deposition of oxidised nitrogen species for 1986-88 (as published in UKRGAR, 1990, p.61) on a 20 km grid was supplied by G.W. Campbell (pers. comm.). Dry deposition estimates for 1987 were made on a 50 km grid basis (R. Derwent, pers. comm.). Seeder-feeder enhanced and cloud (occult) deposition values for sulphate for 1986-88 were modelled on a 20 km grid (D. Fowler, pers. comm.). Total acid deposition was estimated as the sum of dry H+, seeder-feeder H⁺, cloud H⁺ (all estimated by assuming that $H^+ = 2SO_1 + 1NO_2 + 1NH_x$), and wet H^+ (from rain pH).

Annual evaporation estimates (40 km grid) for the years 1986-88 were obtained from the Meteorological Office Rainfall and Evaporation Calculation System (MORECS). Runoff ("effective rainfall") was calculated by subtracting the evaporation estimates from interpolated Met. Office rainfall measurements (S.M. Gammack, pers. comm.).

RESULTS AND DISCUSSION

As stated in the introduction, a primary aim of this study was to seek, for moorland podzol soils evolved from granites or granitic tills, evidence for soil chemical "damage" attributable to atmospheric acidifying pollutant inputs. It was thought that this would be reflected by trends in soil physico-chemical characteristics, especially in the relative amounts of aluminium, base cations and $H⁺$ on the cation exchange complex at various depths in the soil profile. The proportion of the cation exchange sites occupied by any specified cation (subsequently termed, when expressed as a percentage of total CEC, as the saturation % for that cation) depends upon several interactive processes (Billett and Cresser, 1992); these include biogeochemical weathering, mineralisation of organically bound elements, three dimensional movement of solute in drainage water, biological uptake and secondary mineral formation.

In the present context, it is appropriate to consider the probable consequences if most of the mineral soil horizons in the podzol profiles studied were in the aluminium buffering range, as postulated by Ulrich (1991). It would follow that there would be strong positive relationships between H^+ deposition flux or precipitation pH and soil exchangeable aluminium and/or aluminium saturation, because ultimately H^+ inputs would result in dissolution of mineral aluminium, which would raise the aluminium $\%$ saturation of the exchange complex. It would follow, since the soils would be acidified beyond the ion exchange buffering range, that no significant negative relationships would be expected between H^+ and soil exchangeable base cations or base saturation. Under these conditions, atmospheric deposition of base cations could become more important than mineral weathering-derived base cation inputs.

Table I shows how effective rainfall amount, rainfall mean volume-weighted pH and effective concentrations of H^+ , non-marine sulphur, or nitrate correlate with soil exchangeable aluminium. Figure 2 shows plots of the relationships of exchangeable aluminium with rainfall mean pH values, the latter values calculated from mean H^+ concentrations. Effective H^+ ion concentration was calculated by dividing the total wet and dry H⁺ deposition by runoff (Smith et al., 1993), effective acidifying sulphur concentration by dividing the sum of non-marine sulphate-S and **SO,-S** by runoff, and

Table I Correlation coefficients between rainfall **pH,** effective concentrations of H', non-marine *S* and NO; or effective rainfall amount and the exchangeable aluminium concentrations in the LIFIH, **ME,** B and **C** soil horizons **for** moorland podzol profiles derived from granites and granitic tills.

	Aluminium				
	LIFIH	AIE.	B	C	
Rainfall pH	$-0.375*$	-0.017	$-0.614***$	$-0.541*$	
H_{eff}^{+}	0.233	-0.005	$0.551***$	$0.555*$	
	0.254	-0.052	$0.344*$	$0.662**$	
S_{eff} NO _{3 eff}	0.274	-0.003	$0.564***$	$0.550*$	
$Rainfall_{\text{eff}}$	-0.079	-0.015	-0.207	-0.341	

*,** and *** denote significance levels of 95, 99 and 99.9% respectively; The subscript "eff" denotes an effective value, calculated by dividing the combined wet and dry non-marine deposition fluxes (for H⁺, S and NO₃) by runoff. Rainfall_{eff} is equal to estimated runoff (deposition-evapotranspiration).

effective nitrate concentration calculated by dividing the sum of wet-deposited nitrate-N and dry NO_x -N deposition loads by runoff.

As might be expected, rainfall pH gave stronger correlations generally with exchangeable aluminium in the L/F/H horizon than did the effective concentrations of individual acidifying pollutants. However, effective nitrate concentration gave the most significant correlation with exchangeable aluminium of all the concentration parameters tested in the B horizon soils. This, and the less significant correlation for effective sulphur concentration, may well reflect the consequences of strong sulphate adsorption in the B horizon soils. In the C horizon soils, however, effective sulphur concentration gave the most significant correlation.

The results suggest that many of the B and some of the C horizon soils are indeed in the aluminium buffering range, although the distribution of points in Figure 2 for the B and C horizon soils suggest that weathering and ion exchange buffering may still play a role in these soils when rainfall pH is at or above pH **4.7.** The relationships appear not to be simple linear ones, and volume-weighted mean rain pH values below *ca.* 4.7 seem necessary to initiate increases in exchangeable aluminium. These results perhaps are to be expected, since only 46 and 11% of the B and C horizon soils, respectively, were below pH 4.2, the threshold value postulated by Ulrich (1991) for mineral soil pH to be regulated by aluminium. Thus it is to be expected that the relationships between rainfall acidity and extractable aluminium would be more significant for the B horizon soils than for the *C* horizon soils.

It is important to consider, briefly, possible alternative explanations for the apparent link between rainfall acidity and exchangeable soil aluminium, especially since pollution gradients in the UK are often associated coincidently with climatic gradients. However, Table I also shows no indication of any relationship between effective rainfall and exchangeable aluminium, so the observed effect cannot be attributed to a precipitation gradient effect. Temperature effects have been minimised by the imposition of altitude range constraints on sampling site selection, as in the previous study by Barton *et al.* (1994). Thus volume-weighted precipitation pH remains the most probable cause for the relationships. In this study, effects of rainfall pH and effective H^+ concentration were significant, unlike those of total $H⁺$ load.

Figure 2 Relationships between rainfall pH and soil exchangeable **A1** for the four major soil horizons of the granite-derived profiles.

The lack of any significant relationships in Table I for the A/E horizon soils probably reflects the extensive aluminium leaching that has taken place during podzolization of the profiles. It may also reflect differences in the CEC values of these horizons between sites. The results for the L/F/H horizon soils may well reflect the consequences of accelerated biogeochemical cycling of aluminium, although for the present this suggestion must be regarded as speculative.

For peat soils, strong negative correlations are found between precipitation pH and exchangeable base cations, because the chemistry of the exchange complex in peat is regulated entirely by ion exchange reactions *i.e.* no weathering (Skiba and Cresser, 1989: Sanger *et al.,* 1995). However, if many of the soils are in the aluminium buffering range, as postulated above, strong negative correlations between acidifying pollutant deposition and exchangeable base cations in the soils would not be expected. In practice, any correlations found with $H⁺$ concentration were positive rather than negative (Table II). Correlations between % saturation values for individual base cations, especially for sodium, and effective rainfall, effective $H⁺$ concentration or rainfall mean pH were almost always weaker than those with individual base cation concentrations, so only the latter correlation coefficients are shown. While the lack of negative correlation between effective H^+ concentrations and base cation concentrations is in accord with the supposition that the soils are still above the aluminium buffering range, the occurrence of positive correlation warrants further comment.

There was clear evidence for a sea-salt effect on the **pH** of all the horizons studied. The pH values of soil pastes in calcium chloride were significantly correlated with rainfall effective concentrations of sodium, magnesium and chloride at the 95% level for the L/F/H, **A/E** and C horizon soils (Figure **3),** and at 99% for the B horizon soils. Moreover, when the relationships were plotted, the similarities between the plots for sodium, magnesium and chloride were immediately apparent. Thus, regardless of any acidifying effect of high levels of H^+ deposition, areas of high sea-salt deposition tended to have higher soil pH throughout the podzol soil profile. This might be expected as a consequence of sea-salt episodes in the production of acid pulses in surface water

	Sodium			
	LIFIH	A/E	\boldsymbol{B}	C
Rainfall pH	$-0.811***$	$-0.395*$	$-0.774***$	$-0.724***$
H^*_{eff}	$0.656***$	$0.530**$	$0.707***$	$0.702***$
$Rainfall_{\rm eff}$	$-0.422*$	$-0.599**$	$-0.537***$	$-0.539*$
	Potassium			
	LIFIH	A/E	\boldsymbol{B}	C
Rainfall pH	$-0.478**$	0.172	-0.257	$-0.527*$
H_{eff}^+	$0.395*$	0.198	0.052	$0.528**$
Rainfall _{eff}	-0.261	$-0.411*$	0.035	-0.177
	Calcium			
	LIFIH	A/E	B	\mathcal{C}
Rainfall pH	-0.229	0.183	$-0.354*$	$-0.610**$
$\rm H_{eff}^{+}$	0.082	-0.141	$0.511**$	$0.746***$
Rainfaller	0.015	0.190	-0.310	$-0.571*$
	Magnesium			
	LIFIH	A/E	B	\overline{C}
Rainfall pH	0.038	0.264	$-0.344*$	-0.427
H^*_{eff}	-0.125	-0.154	$0.426*$	$0.689**$
Rainfalleff	0.260	0.131	-0.234	$-0.615**$

Table II Correlation coefficients between rainfall pH, effective H⁺ and rainfall deposition and exchangeable base cation concentrations in the LIFIH, **AIE,** B and **C** soil horizons.

Significance levels and subscripts are as in Table **^I**

Figure 3 Relationships between soil **pH,** measured using pastes in CaCI, solution, and wet Na, Mg and **CI** deposition for the L/F/H and *NE* horizons.

(Langan, 1989), since displacement of H⁺ from exchange sites by Na⁺ and Mg²⁺ is associated with retention of the base cations.

It must be stressed, however, that this effect is not merely the result of simple competition between $H⁺$ and marine-derived base cations in soil horizons where weathering-derived inputs of those cations are negligible. If it was, positive, if weak, relationships between sodium inputs and soil exchangeable sodium and between magnesium inputs and soil exchangeable magnesium might still be expected. No such positive correlations were found.

There are several potential mechanisms worthy of consideration to explain the observation that the soils from areas of high sea-salt deposition tended to have low concentrations of exchangeable sodium but relatively high pH values. Exchangeable sodium was significantly negatively correlated with runoff for all four horizon groupings, at 95% for the L/F/H and *C* horizon soils and at **99%** for the A/E and **B** horizon soils. Areas of high sea-salt deposition flux may not necessarily be areas with high seasalt concentrations in precipitation, and the relationships above might suggest a dilution effect, since concentration rather than flux would tend to regulate the exchange complex sodium concentration. However, effective volume-weighted mean sodium concentration in precipitation was not positively correlated significantly with exchangeable sodium in the A/E and C horizon soils, and only weakly, and still negatively, correlated for the other two soil horizons. Thus the low exchangeable sodium concentrations in regions of high sea-salt deposition flux are not simply the result of a dilution effect. This suggests that exchangeable sodium is influenced by factors other than sea salt and H^+ influx effects on cation exchange equilibria.

It may be postulated that sustained high inputs of maritime salts over hundreds or thousands of years have had an inhibitory effect upon mineral weathering, as might be anticipated from application of the law of mass action, and thus upon the extent of the podzol profile acidification. This could explain the higher soil pH values in areas of high sea-salt deposition, since soil pH falls naturally where weathering is more advanced. Why such soils do not have increased exchangeable sodium concentrations at the present phase of their evolution may be a consequence of a retained capacity to release other base cations by weathering, which then compete with sodium for the exchange sites.

It is also probable that variability in biogeochemical recycling of base cations from sub-surface mineral soils, arising partly as a consequence of variability in granite mineralogy, may outweigh more direct effects of atmospheric inputs. Moreover, enhanced pollution-derived mobile anion concentrations at depth could result in increased rates of biogeochemical cycling and contribute to enhanced exchangeable base cation concentrations in surface horizons. Enhanced concentrations of base cations leached from upslope as a consequence of acidifying pollutant deposition might have a similar effect. Both of these mechanisms could explain positive correlations between precipitation H+ concentrations and exchangeable soil base cation concentrations. **A** further effect might be enhancement in the biogeochemical cycling of non-marine base cations following their displacement down the profile as a result of sea-salt inputs,

Sanger *et al.* (1994b) demonstrated that soils developed on upper slopes have a limited sulphate adsorption capacity and that soils on lower slopes have a much greater capacity. Furthermore, Barton *et al.* (1994) showed that the amount of clay and fine silt present was a key factor and higher sulphate adsorption capacity is found in

	LIFIH	A/E	В	
Rainfall pH vs	$0.344*$	0.206	$0.355*$	$0.566*$
Soil pH _(water) Rainfall pH vs Soil $pH_{(cal,j)}$	$0.559***$	$0.576***$	$0.526**$	0.449

Table I11 Correlation coefficients between rainfall **pH** and soil pH values and calcium chloride pastes in the L/F/H, AIE, **B** and C soil horizons.

Significance levels and subscripts are as in Table I

generally finer textured soils downslope. Sulphate adsorption leads to a corresponding amount of base cation retention and reduces runoff acidification in the short term. In the longer term, once equilibrium is attained for any given deposition sulphate concentration, soil sulphate saturation leads to sulphate and base cation leaching and soil acidification. Laterally-flowing drainage water produced from such sensitive upper slope soils may, therefore, be significantly modified by physico-chemical reactions in lower slopes before reaching watercourses (Billett and Cresser, **1992).** These modifications, exaggerated by higher acid deposition on the upper slopes, may explain the positive correlations that exist between the acid deposition and the soil exchangeable base cation status of the lower altitude soils.

In spite of the trends found in the relationships between soil base cation saturation values and rainfall pH and effective H^+ concentration, as discussed above, there were still significant correlations for all horizons between soil pH values and precipitation pH (Table 111). Such a relationship was reported by Barton *et al.* **(1994)** in a regional survey confined to moorland podzol B horizon soils. For the C horizon soils, the correlation was better when the pH was measured in water, rather than calcium chloride. This suggests that for the C horizons the greater mobile anion effect associated with greater acid deposition enhances the soil acidification effect. The pH effect for soils is to be expected, bearing in mind the significant trends already found for exchangeable aluminium.

CONCLUSIONS

Critical load corresponds to an $H⁺$ flux at which damage will start to occur. Once exceeded, the implication is that geochemical weathering and atmospheric base cation deposition will be insufficient to balance biomass uptake and acceptable leaching loss. At any given site, this might be expected to result in a decrease in exchangeable base cations and, for mineral soils, an increase in exchangeable aluminium. However, the composition of the mixture of cations on the cation exchange complex will then depend upon competitive dynamic equilibria between base cations, ammonium and H' inputs for the exchange sites. Thus, even for soils derived entirely from granites, there will be considerable variation between sites in the proportional occupancy of the exchange complex by any specified base cation. On a regional scale, a significant negative correlation between H^+ deposition flux or concentration and exchangeable base cation concentrations should not necessarily be expected. The positive correlations observed for the **B** and C horizons probably reflect increases in base cation inputs in laterally flowing and upwelling water in response to $H⁺$ deposition.

For exchangeable aluminium, the situation is more straightforward, since atmospheric aluminium inputs are negligible, and less variability might be expected between sites for exchangeable aluminium than for exchangeable base cations. Therefore, exchangeable aluminium increases significantly in B and C horizon soils with concentration of H+ in precipitation, reflecting a dissolution effect on aluminium mineral species. The relationship is with concentration, rather than flux of H^+ , because the effective pH for the dissolution process will depend upon soil pH and upon total mobile anion concentration. The latter is linked to deposited $H⁺$ concentration. Thus exchangeable aluminium appears to be the most appropriate single indicator of soil damage, provided soils are grouped according to parent material and land use, as in this study.

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