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FURTHER DEVELOPMENT OF AN EFFECTS BASED APPROACH FOR CADMIUM, COPPER, LEAD AND ZINC

Annexes to the Final Report to Defra

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ANNEXE 1

DERIVING SOIL CRITICAL LIMITS FOR CU, ZN, CD, AND PB: A METHOD BASED ON FREE ION CONCENTRATION

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Deriving Soil Critical Limits for Cu, Zn, Cd, and Pb: A Method Based on Free Ion Concentrations

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We present a method to calculate critical limits of cationic heavy metals accounting for variations in soil chemistry. We assume the free metal ion concentration (M_{free}) to be the most appropriate indicator of toxicity, combined with a protective effect of soil cations (e.g., H^+, Ca^{2+}). Because soil metal cations tend to covary with pH, the concentration of M_{free} exerting a given level of toxic effect ($M_{\text{free,toxic}}$) can be expressed as a function of pH alone. We use linear regression equations to derive $M_{\text{free,toxic}}$ in toxicity experiments from soil pH, organic matter content, and endpoint soil metal. Chronic toxicity data from the literature, for plants, invertebrates, microbial processes, and fungi are interpreted in terms of an average log $M_{\text{free,toxic}}$ together with distributions of species sensitivity. This leads to critical limit functions to protect 95% of species, of the form $\log M_{\text{free,CRIT}} = \alpha \text{pH} + \gamma$. Appreciable effects of soil pH upon log $M_{\text{free,CRIT}}$ are found, with $\alpha = -1.21$ (Cu), -0.34 (Zn), -0.43 (Cd), and -0.83 (Pb). Critical limit functions in terms of the geochemically active soil metal ($M_{\text{soil,CRIT}}$), that pool of metal which controls the free ion concentration, have also been derived, with soil pH and organic matter content as variables. The pH effect on $M_{\text{soil,CRIT}}$ is relatively small, with slopes of 0.05 (Cu), 0.19 (Zn), 0.16 (Cd), and 0.20 (Pb), since the effect of pH on $M_{\text{free,CRIT}}$ is countered by the variation of M_{free} with pH.

Introduction

Environmental quality standards for heavy metals in soils are an important component of the environmental risk assessment process in many legislatures. There exist a number of approaches to deriving quality standards and to their application in risk assessment (e.g., refs *1* and *2*). Despite evidence that variability in soil chemistry affects the bioavailability and toxicity of metals to the biota, and that total soil metal includes nonbioavailable forms (*3*), standards are commonly expressed as a single value for all soils. Certain legislatures allow for distinct standards for different classes of soil (*4*), but beyond this there is no attempt to account systematically for variations in metal toxicity among soils of varying properties. Various chemical extractions of soils have been employed to identify a measurable metal fraction that correlates with toxic effect (*5*−*7*), but no consistent relationship has been found between any extracted metal fraction and either bioaccumulation or toxicity.

Studies of toxicity mechanisms in the aquatic environment have produced a considerable body of evidence to suggest that the speciation of metals in the aqueous medium has significant effects upon their toxicity. The free ion activity model (FIAM) (*8*) postulates that metal toxicity is related to uptake of specific metal species at the organism−water interface and that the free metal ion in solution ought to be a better predictor of toxicity than the total dissolved metal. This has led some researchers (*9*, *10*) to postulate that bioaccumulation and/or toxicity in soils may be related to the free ion concentration in the soil solution, at least for organisms for which the main uptake route for metals is via the pore water. Sauvé and co-workers (*9*) found statistically significant relationships between % inhibition in toxicity tests with Cu and Pb and the free ion concentration. However, as pointed out by Morel (*8*) and Campbell (*11*), variations in the concentrations of other solution ions such as H^+, Mg^{2+}, and Ca^{2+} must in principle be accounted for when applying the FIAM since uptake sites are expected to bind these ions in competition with the toxic metal. It has been shown in freshwaters that the free ion alone does not necessarily provide a consistent predictor of metal toxicity (*12*). More recently, the Biotic Ligand Model (BLM) (*13*, *14*) has provided a modeling framework to account for the effects of both solution speciation and protective effects of solution cations upon metal toxicity to selected freshwater organisms.

If a theory of the protective effects of cations on free metal ion (FMI) toxicity were applied to soils, we would expect to see variations in the apparent toxicity of the free ion with soil cation concentrations. This has been observed experimentally; Lexmond (*15*) related copper toxicity to maize in soil at a range of pH values to measured Cu^{2+} activities. The activity of the free ion was not a constant predictor of the metal toxicity; in contrast, the free ion activity corresponding to a given level of toxic effect increased as the pH increased. This is consistent with the theory of protective ions as a control on toxic effect, in this case the H^+ ion. Plette et al. (*16*) studied the variation of metal uptake by a number of soil species as a function of soil chemistry and concluded that uptake was a complex and species-specific function of metal chemistry and uptake characteristics of the species, in which the effects of pH and other porewater ions were important. Studies of metal toxicity as a function of soil chemistry, but not including measurement of free ion concentration, have been performed for single species. Spurgeon and Hopkin (*17*) measured mortality and cocoon production of *Eisenia fetida* exposed to zinc in artificial soils of pH 4−6 and percent organic matter 5−15. Generally, lower pH and lower organic matter increased zinc toxicity, although the trends seen were not completely consistent. Of recent note is the work of Lock and co-workers (*18*, *19*), who looked at the acute effects of Cu, Zn, Cd, and Pb on *Enchytraeus albidus* under varying soil conditions. They concluded that metal toxicity decreased with increasing soil pH and cation exchange capacity or percent organic matter and produced empirical models allowing prediction of toxicity in soils of different composition. A body of data where effects of soil chemistry on toxicity are explicitly studied is therefore developing. However, such studies still form a small proportion of the available toxicity data, and there is therefore a need to integrate other published data, if possible, into a

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TABLE 1. List of Symbols Used in the Text

symbol	explanation
A	coefficient of pH in linear regression predicting free metal ion concentration in soil
B	coefficient of log OM in linear regression predicting free metal ion concentration in soil
C	coefficient of log M_{soil} in linear regression predicting free metal ion concentration in soil
C_i	concentration of a free cation protecting against metal toxicity
EC_x	concentration of a chemical having an x% effect on an organism, relative to a control
D	constant term in linear regression predicting free metal ion concentration in soil
N	number of points in multiple species toxicological data set for a metal
n_i	number of toxicological datapoints in group i having common study, species, and effect
LC_x	concentration of a chemical causing x% lethality to an organism, relative to a control
LOEC	lowest concentration of a chemical having a statistically significant toxic effect on an organism
M_{soil}	concentration of geochemically active soil metal
$M_{soil,toxic}$	M_{soil} associated with a given level of toxic effect
$M_{soil,CRIT}$	critical value of M_{soil}
M_{free}	concentration of free metal ion
$M_{free,toxic}$	M_{free} associated with a given level of toxic effect
$M_{free,CRIT}$	critical value of M_{free}
NOEC	highest concentration of a chemical not having a statistically significant toxic effect on an organism
OM	% organic matter content of soil
Q	predicted variable in critical limit function; equals log M_{soil} + [b/c] log OM
w_i	weight assigned to grouped datapoints for regression and statistical analysis purposes
α	coefficient of pH in free ion−toxicity relation
β_i	coefficient of free cation Ci protecting against metal toxicity
δ	constant term in critical limit function for Msoil
ϵ	sum of y and d
ϕ	coefficient of pH in Msoil−toxicity relation
γ	constant term in free ion−toxicity relation
ψ	constant term in M_{soil}−toxicity relation

framework for calculating quality standards as a function of soil chemistry.

In this paper, we present a method to calculate environmental quality standards for chronic effects of Cu, Zn, Cd, and Pb as a function of soil chemistry. These values can be used in regulatory activities such as soil screening during risk assessment and in calculating critical loads of atmospherically deposited heavy metals to soils. In the critical loads approach, a key objective is to define a metal concentration in soil or soil solution above which long-term damage to the ecosystem is likely to occur. This concentration is termed the critical limit, and we will use this term here.

Our methodology draws on chemical first principles, based on the chemistry of the FMI, to quantify the influence of soil chemistry on single species end points. We then apply a statistical approach, related to the principle of the species sensitivity distribution (*20, 21*), to derive a function for the critical limit. The method aims to make the best use of existing single species toxicity tests where basic soil parameters (pH, percent organic matter) have been specified. Central to the method is the concept of the metal free ion as the best predictor of toxicity, modified by the protective effects of other cations in the soil solution.

Theory

A list of the symbols used in the text is given in Table 1 for reference.

Single Species Toxicity Tests and Critical Limit Calculation. In toxicological experiments, effect concentrations (e.g., LC_x, EC_x, LOEC, and NOEC) in soils are derived using an experimental setup where different doses of metal, as a salt, are added to portions of soil to which the test organisms are then exposed. The metal concentration at the chosen end point is expressed either as the concentration added to the soil prior to the test or as the concentration measured by chemical extraction of the soil after the test. The species sensitivity distribution (SSD) approach (*20, 21*), for calculating ecosystem critical limits, uses a data set of single species test results having comparable end point types. It assumes that the test organisms in the data set comprise a statistical sample of the soil ecosystem, to which a distribution (typically log−normal or −logistical) may be applied. The parameters of the distribution are then used to calculate the metal concentration that does not affect a chosen proportion of the ecosystem (5% is a typical proportion chosen). This concentration is the critical limit. However, if the data set does not follow any given statistical distribution, then the SSD approach will not provide the optimal estimate of the critical limit. Bootstrap methods, where no a priori assumption of distribution type is required, can be regarded as a more general alternative approach (*22*) to deriving critical limits, and we will use such an approach here.

Theoretical Critical Limit Function. In producing a theoretical function for soil metal toxicity, we draw on knowledge gained from detailed studies of aquatic metal toxicity (e.g., ref *23*). Such studies indicate that toxicity depends on the concentration of the FMI and of other free solution cations (H^+, Na^+, Ca^{2+} etc.). If the concentration of one free cation is increased while other concentrations are held constant, then the FMI concentration at which a given level of effect occurs also increases, in a log−log relation to the concentration of the varied free cation. This may be expressed mathematically as

$$\log M_{\mathrm{free,toxic}} = \alpha \mathrm{pH} + \Sigma\beta_i \log C_i + \gamma \qquad (1)$$

where C_i refers to solution concentrations of protective free ions; log $M_{free,toxic}$ is the FMI concentration producing a given toxic response; and α, β_i, and γ are empirical coefficients. The solution free cations exert a protective effect against the toxicity of the FMI.

In practice, soil solutions tend to exhibit negative covariance of pH and other solution cations since the pH is controlled by the concentrations of the other ions. Therefore, eq 1 may be approximated to

$$\log M_{\mathrm{free,toxic}} = \alpha \mathrm{pH} + \gamma \qquad (2)$$

The form of eq 2 does not imply that the H^+ ion alone exerts a protective effect but rather that the overall protective effect of all free cations may be expressed as a function of pH alone. Equation 2 cannot be applied directly to literature toxicological data because toxic end points have not been expressed, or measured, as FMI concentrations. Measurement of FMI concentrations in soil solution is possible but technically complex. Therefore, estimation of the FMI concentration from the quoted end point metal concentration must be done by modeling.

Prediction of Free Ion Concentrations. Several authors (*24–27*) have produced multivariate linear regression equations to predict FMI concentrations from bulk soil properties. Necessary variables in such regressions are the soil pH and the geochemically active soil metal, which is the metal bound to the soil that is able to exchange with the soil solution and hence controls the FMI concentration. In some cases, the organic matter content of the soil is included as a measure of the complexation ability of the soil. The following general expression may be formulated:

$$\log M_{\mathrm{free}} = a\mathrm{pH} + b \log \mathrm{OM} + c \log M_{\mathrm{soil}} + d \quad (3)$$

where OM is the percent organic matter content of the soil, and M_{soil} is the geochemically active soil metal (mol/g). Several analytical methods exist to estimate the geochemically active metal, largely based on the use of extractants that are believed to remove metal from the solid phase either by supplying an ion that outcompetes the metal for solid-phase binding sites (e.g., H^+ in the case of dilute acid extractants) or that are strong metal complexing agents able to remove metal from binding sites by chelation (e.g., EDTA).

Calculation of Critical Limit Functions. At the end point soil metal concentration in a toxicity test, eq 3 may be written

$$\log M_{\mathrm{free,toxic}} = a\mathrm{pH} + b \log \mathrm{OM} + c \log M_{\mathrm{soil,toxic}} + d \quad (4)$$

Combining this expression with eq 2 and rearranging gives

$$\log M_{\mathrm{soil,toxic}} + [b/c] \log \mathrm{OM} = \phi\mathrm{pH} + \psi \quad (5)$$

or

$$Q = \phi\mathrm{pH} + \psi \quad (6)$$

where ϕ and ψ are new coefficients, and Q represents [log $M_{\mathrm{soil,toxic}}$ + $[b/c]$log OM]. Given sufficient data, the coefficients would be derived by fitting the expression to a set of individual values of Q for a single organism end point in soils of varying chemical composition.

In practice, there are insufficient data sets for effects on single species under varying soil conditions, to allow derivation of sufficient functions of the form of eq 6 for the estimation of a critical limit for the whole ecosystem. Therefore, we have adopted an alternative approach that puts the available data to best use. By taking equivalent toxicological end points for different species and fitting eq 6 to the entire data set by median linear regression, we obtain an expression giving the best estimate for the median log $M_{\mathrm{soil,toxic}}$ for the whole soil community, under varying conditions of soil pH and OM. We assume the residuals in Q (i.e., the portion of Q that cannot be explained by the regression equation) to be due to intrinsic variations in species sensitivity to the metal. We then calculate the percentile of the residuals in Q corresponding to the desired proportion of species to be protected. To protect a given proportion p of species, we calculate the $100(1 - p)$th percentile of the residuals, which we term δ. This gives the following critical limit function for the ecosystem:

$$Q_{\mathrm{CRIT}} = \phi_{\mathrm{EC}}\mathrm{pH} + \psi_{\mathrm{EC}} + \delta \quad (7)$$

or

$$Q_{\mathrm{CRIT}} = \phi_{\mathrm{EC}}\mathrm{pH} + \epsilon_{\mathrm{CRIT}} \quad (8)$$

where ϵ_{CRIT} is the sum of ψ_{EC} and δ, the subscript EC refers to an ecosystem average value, and the subscript CRIT refers to a value in the critical limit function. The method of calculating δ will be discussed in the Derivation of $M_{\mathrm{soil,CRIT}}$ section.

Expanding the term Q and rearranging gives the critical limit function for log M_{soil}:

$$\log M_{\mathrm{soil,CRIT}} = \phi_{\mathrm{EC}}\mathrm{pH} + \epsilon_{\mathrm{CRIT}} - [b/c]\log \mathrm{OM} \quad (9)$$

Parametrization of eq 9 gives a critical limit function expressed as a concentration of geochemically active soil metal (mol/g). We may also express the critical limit as a function of the FMI concentration, by calculating values for the coefficients α and γ in eq 2

$$\log M_{\mathrm{free,CRIT}} = \alpha_{\mathrm{CRIT}}\mathrm{pH} + \gamma_{\mathrm{CRIT}} \quad (10)$$

where

$$\alpha_{\mathrm{CRIT}} = a + c\phi_{\mathrm{EC}} \quad (11)$$

and

$$\gamma_{\mathrm{CRIT}} = d + c\epsilon_{\mathrm{CRIT}} \quad (12)$$

Application

Toxicological Data. The critical limits to be derived were intended to relate to chronic, low level effects on soil organisms. The following criteria were set when collecting data:

(i) The exposure medium was soil. Tests carried out on extracted organisms in artificial media, e.g. agar, were not used. Neither were tests on plants grown in nutrient solutions.

(ii) The exposed organism was of a species living in intimate contact with and considered to take up metal directly from the pore water (e.g., earthworms and other soft-bodied invertebrates, plants, and soil microorganisms). We did not consider the possible influence of soil ingestion (e.g., ref *28*) upon metal availability and toxicity to soil animals, nor did we consider food chain effects.

(iii) The metal was added singly to the soil in a soluble form, for example, as a nitrate or sulfate salt. Insoluble metal forms, such as oxide salts, were not used.

(iv) The pH and organic carbon or organic matter content of the soil were quoted or referenced. Where organic carbon alone was quoted it was converted to organic matter by multiplying by two. Where multiple pH values were given (measured using different soil extractants, e.g., H_2O, KCl), the pH measured using H_2O was taken if quoted, otherwise the pH was measured using KCl, or the pH was measured using $CaCl_2$. Possible variations in the nature of the soil organic matter, for example, the use of sphagnum peat in artificial soils as compared with natural organic matter in field soils, were not considered.

(v) If chemical manipulation of the soil was done in an experiment, for example, by nutrient addition, such manipulations were identical for each dose of metal.

(vi) The end point effect was a chronic effect with clear consequences for the fitness of the organism (for plants and invertebrates) or the soil process (microorganisms). Survival and biomarker effect data were not used, and neither was bioaccumulation of metal without consideration of organism performance.

(vii) Ideally, all metal end point concentrations would be in terms of the geochemically active metal since it is this pool that controls the FMI. However, in most tests the end point metal was quoted in terms of the concentration added

TABLE 2. Summary of Ecotoxicological Data Sets for Copper, Zinc, Cadmium, and Lead

	copper	zinc	cadmium	lead
Plants				
studies	7	4	13	6
species/groups	8	5	18[a]	8
end points	30	11	35	16
Invertebrates				
studies	15	16	10	4
species/groups	12	6	4[b]	2
end points	33	59	22	8
Microbial Processes[c]				
studies	10	10	15	11
processes	5	5	8	9
end points	25	25	60	27
Total				
studies	32	30	38	21
species/processes	25	16	30	19
end points	88	95	117	51

[a] *Brassica rapa* cv. Italica (cauliflower) and *Brassica rapa* cv. Botrytis (broccoli) considered as separate species. [b] Includes a single end point for the entire community of nematodes. [c] Carbon mineralization and respiration are considered the same process, and all nitrogen transformations are considered as a single process. Microbial biomass effects are also considered under this heading.

in soluble salt form. Therefore, it was necessary to assume that the added metal constituted the added geochemically active pool over the course of the test. It is possible that over the course of a test some of the added metal is lost from the geochemically active pool by fixation processes (aging); however, this cannot be quantified for the data used here. The added metal concentration was therefore an upper estimate of the added geochemically active pool. Where the end point was expressed only as a metal concentration measured by chemical extraction following organism exposure (corrected for the background metal concentration), this value was taken instead. Suitable chemical extractions were considered to be those that would extract metal specifically bound to the soil (e.g., aqua regia, EDTA, DTPA, or dilute mineral acid). Weaker extractions (e.g., KCl, $CaCl_2$) were not considered suitable as they may not measure all of the geochemically active metal. Where both added metal and extracted metal were quoted as end points, the added concentration was taken for consistency since the majority of end points were quoted as the added metal.

(viii) End point concentrations of metals (NOEC, LOEC, EC_{10}) were either quoted in the paper, could be clearly extracted from tables of dose−response relationships, or in the case of EC_{10} values were calculable from tabulated or graphed dose−response data. For NOEC and LOEC end points, significant differences between organism response at the 95% confidence level only were considered.

The choice of end point type was determined according to a scheme similar to that used to select end points for EU Risk Assessment Guidelines (*29*); full details are given in the Supporting Information. A log−logistic dose−response model was used to calculate an EC_{10} value when required. A description of this model and example fits are given in the Supporting Information.

A summary of the toxicological data is given in Table 2. The numbers of species or microbial processes having suitable data were greatest for Cd and least for Zn, although more actual data points were found for Zn than either Cu or Pb, which both had greater numbers of species or processes. Of note was the large number of plant species with suitable data for Cd effects and the large number of invertebrate species with suitable data for Cu effects. By contrast, the invertebrate data for Pb were relatively sparse in both species and number of end points.

TABLE 3. Ranges of Chemical Parameters in Toxicological Test Soils[a]

metal	pH	%OM	$M_{soil,toxic}$ (mg/kg soil)
copper	3.3−8.2 (5.5)	0.5−96 (4.5)	2.0−3000 (109)
zinc	4.0−8.3 (6.0)	0.6−85 (5.0)	1.0−3000 (180)
cadmium	2.7−8.3 (5.7)	0.4−96 (4.5)	0.2−8077 (32)
lead	3.3−8.4 (6.0)	0.6−80 (3.4)	5−8000 (799)

[a] Range (median in parentheses).

Ranges of soil pH, percent organic matter, and end point metal in the toxicological experiments are given in Table 3. Approximately half of the points derived from tests were done in circumneutral or weakly acidic soils with low organic matter; 51% had a pH between 5 and 8 and organic matter less than 10%. Acid soils with pH less than 5 made up 30% of the data set. Alkaline soils with a pH greater than 8 were a small component of the data (2%).

Prediction of Free Ion Concentrations. The linear regression (eq 3) was parameterized using data sets for copper, zinc, cadmium, and lead from both high and low organic matter soils. For this purpose, we used soil data and associated measured free ion concentrations measured by Sauvé and co-workers (*25, 26, 30, 31*) for Canadian agricultural and urban soils and by Weng and co-workers (*32*) for Dutch agricultural soils. Soil properties and free ions estimated using the WHAM/Model VI model (*33*) for high organic matter soils of the UK uplands, described by Tipping et al. (*27*), were also used. Properties of the data sets used, calculated coefficients, and error measures are given in Table 4. MINITAB v13.32 (Minitab Inc., State College, PA) was used for statistical analysis. The values of the coefficients all accorded with the theory of soil−solution metal equilibria. The coefficients of pH were negative giving lower M_{free} with increasing pH, due to proton−metal competition for solid-phase binding. The coefficients of log OM were also negative, indicating lower M_{free} with increasing content of binding sites on organic matter. The coefficients of log M_{soil} were positive, indicating higher M_{free} with increasing content of soil-bound metal. Cu_{free} and Pb_{free} were predicted to be more sensitive to changes in pH and geochemically active metal than were Zn_{free} and Cd_{free}. Sensitivity to organic matter content was similar for all the metals.

Derivation of $M_{soil,CRIT}$. The desired method for calculating critical limit functions (eq 9) ought to account for sources of uncertainty in the input data:

(i) Uncertainty in Q due to the uncertainty in b and c.

(ii) Statistical uncertainty in the regression parameters ϕ_{EC}, ψ_{EC}, and δ due to scatter in Q.

We derived a bootstrapping method for deriving limit functions that accounted for both sources of uncertainty simultaneously. The method allows calculation of a critical limit that protects a given proportion of species and processes at a given confidence level. Here, we focus on critical limits to protect 95% of species and processes at a confidence level of 50%, which we refer to as median critical limits. The method involves the generation of populations of Q by repeated sampling from the whole data set, and their regression against pH to derive populations of ϕ_{EC}, ψ_{EC}, and thereby δ values, which may be used to generate critical limit functions to protect a given proportion of species in the ecosystem. By calculating many estimates of the critical limit function based on samples of the data, large populations of the parameters ϕ, ψ, and δ were generated, which were then used to derive limit functions with an associated confidence level.

TABLE 4. Summary of Input Data and Parameters for Linear Regressions Predicting Free Metal Ion from Soil Properties (Eq 3)

metal	n	pH[a]	OM[a]	log M_{soil} (mg/kg)[a]	log M_{free} (nM)[a]	a[b]	b[b]	c[b]	d[b]	SE[c]	R^2	ref
Cu	151	3.35–8.27 (4.99)	0.41–97.8 (15.7)	0.96–637 (13.0)	−3.96–4.24 (0.77)	−1.26 (0.035)	−0.63 (0.090)	0.93 (0.091)	4.99 (0.63)	0.61	0.90	27, 30, 32
Zn	145	3.35–8.28 (4.94)	0.41–97.8 (17.5)	0.19–2460 (15.6)	0.92–4.37 (2.69)	−0.45 (0.027)	−0.61 (0.077)	0.57 (0.071)	0.55 (0.62)	0.46	0.62	27, 31, 32
Cd	183	3.35–8.27 (5.37)	0.41–97.8 (12.8)	0.0098–44.9 (0.52)	−1.51–1.97 (0.37)	−0.52 (0.031)	−0.60 (0.076)	0.60 (0.062)	−0.14 (0.65)	0.53	0.62	26, 27, 32
Pb	200	3.35–8.28 (5.63)	0.41–97.8 (5.8)	1.24–14860 (120)	−4.36–3.85 (0.41)	−1.02 (0.032)	−0.69 (0.074)	1.05 (0.056)	4.33 (0.49)	0.60	0.85	25, 27, 32

[a] Range (median in parentheses). [b] Standard error in parentheses. [c] Standard error of prediction.

TABLE 5. Parameters for Critical Limits Expressed as Functions of the Added Soil Metal and of the Free Ion Concentration

	median critical limit parameters			
	log M_{soil} function (eq 9)		log M_{free} function (eq 10)	
metal	ϕ_{CRIT}	ϵ_{CRIT}	α_{CRIT}	γ_{CRIT}
Cu	0.05	−8.13	−1.21	−2.57
Zn	0.19	−9.06	−0.34	−4.66
Cd	0.16	−9.25	−0.43	−5.66
Pb	0.20	−8.85	−0.83	−4.83

Sampling and parameter selection were performed using a custom PC program written in Visual Basic 6.0 (Microsoft Corp., Redmond, WA). The following steps in the methodology were undertaken, for each metal:

(i) A set of normally distributed values of a, b, c, and d (eq 3) were calculated using the Box–Müller algorithm (*34*), assuming the standard errors of the parameters (Table 4) to be their standard distributions.

(ii) From the toxicological data, n sets of pH, log $M_{soil,toxic}$, and log OM values were obtained by sampling with replacement, where n was the number of points in the data set, and n values of Q were calculated.

(iii) The sampled values of Q were assigned weights prior to regression. Weighting was considered necessary to allow for equal emphasis on data sets for different species/effect combinations, without the need to lump end point data by averaging. Values of Q were grouped according to study, species, and effect. For a group I of n_I values, each value was given a weight w_I where

$$w_I = \frac{1}{n_I} \qquad (13)$$

Microbial process data were not weighted (i.e., all $w_I = 1$) since microbial processes occurring in soils of varying chemical composition may be considered to be due to different microbial species (*1*).

(iv) Pairs of ϕ_{EC} and ψ_{EC} values (eq 7) for the sample were calculated by weighted median linear regression of Q against pH.

(v) A value of δ (eq 7) was calculated iteratively, by minimizing the sum of the following error terms for each residual R in Q:

$$|R - \delta\ |w_I p \text{ for } R \geq \delta \qquad (14)$$

and

$$|R - \delta\ |w_I(1 - p) \text{ for } R < \delta \qquad (15)$$

where $(1 - p)$ is the desired proportion of species to be protected. Here, we have chosen to calculate limits to protect 95% of species, so $p = 0.05$. A value of ϵ_{CRIT} (eq 8) was obtained by summing ψ_{EC} and δ.

(vi) Steps 1–5 were repeated 10 000 times to generate 10 000 sets of ϕ_{EC} and ϵ_{CRIT} values.

(vii) The populations of ϕ_{EC} and ϵ_{CRIT} values were used to generate 10 000 values of Q_{CRIT} (eq 8) at each of a series of pH values spanning the range found in the toxicological tests.

(viii) The median critical limit function was derived by linear regression of the median Q_{CRIT} against pH. The calculated slope and intercept were termed ϕ_{CRIT} and ϵ_{CRIT}, respectively.

Values of ϕ_{CRIT} and ϵ_{CRIT} are given in Table 5. The slopes of the functions were all positive, resulting in limit functions where log $M_{soil,CRIT}$ (eq 9) increased with increasing pH.

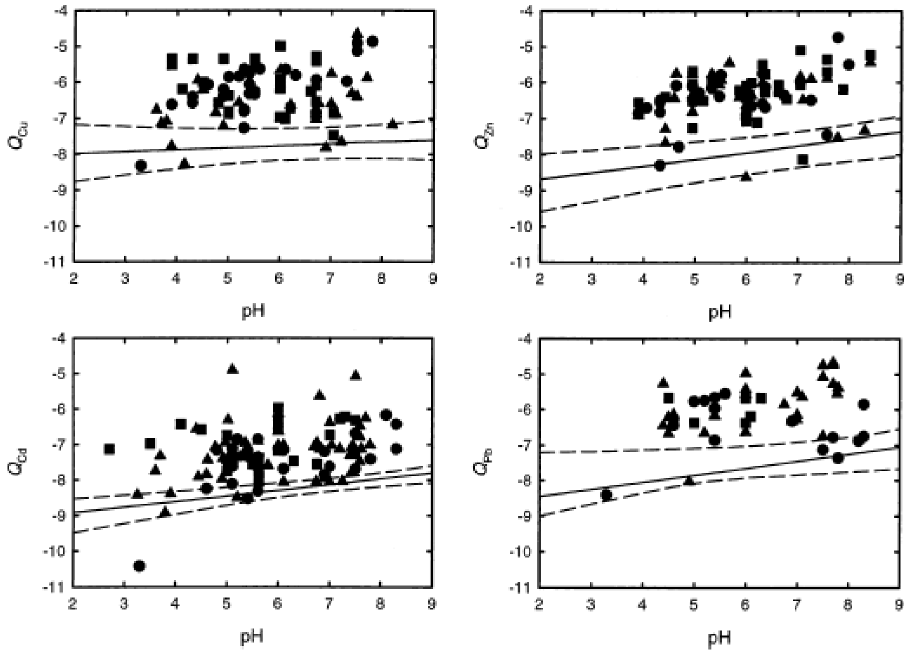

FIGURE 1. Plots of Q against pH (eq 6; Table 7) for Cu, Zn, Cd, and Pb. Circles: plant data; squares: invertebrate data; and triangles: microbial process data. Solid line: median critical limit function and dotted lines: 90% confidence limits on the median critical limit.

Plots of Q against soil pH, and calculated critical limit functions, are shown in Figure 1. Confidence intervals for the functions were obtained by plotting the fifth and 95th percentile values of Q_{CRIT}, from step 7, against pH. The confidence intervals were nonlinear functions of pH. The range of Q spanned by the confidence intervals was typically 1−2 orders of magnitude. In the cases of Zn, and particularly Pb, the confidence intervals were asymmetric about the median critical limit line. This was due to the presence of several outlying points representing low end points for these metals.

Derivation of log $M_{free,CRIT}$. Values of α_{CRIT} and γ_{CRIT} (eqs 11 and 12) were derived as follows:

(i) Each set of a, c, d, ϕ_{EC}, and ϵ_{CRIT} values from the Calculating Critical Limits section was used to generate 10 000 pairs of α_{CRIT} and γ_{CRIT} values.

(ii) A total of 10 000 values of log $M_{free,CRIT}$ (eq 10) were calculated at each of a series of pH values spanning the range found in the toxicological tests.

(iii) The median log $M_{free,CRIT}$ was found to vary linearly with pH, so the critical limit function for the free ion was derived by linear regression of median log $M_{free,CRIT}$ against pH. The parameters of the equation were denoted α_{CRIT} and γ_{CRIT}.

Parameter values are given in Table 5. For all the metals, $\alpha_{CRIT} > a$ due to ϕ_{EC} being consistently positive. Therefore, although the effect of pH upon log $M_{soil,CRIT}$ was relatively small (calculated ϕ_{CRIT} up to 0.19), the effect of pH upon log $M_{free,CRIT}$ was much more significant (calculated α_{CRIT} up to −1.21).

Critical limit functions for the free ion concentration are shown graphically in Figure 2, along with predicted end point FMI concentrations from the toxicological data. Over the range of pH found in the toxicological data, the critical FMI concentration spanned several orders of magnitude for log $Cu_{free,CRIT}$ and log $Pb_{free,CRIT}$. The effect of pH on $Zn_{free,CRIT}$ and $Cd_{free,CRIT}$ was smaller but remained clear.

Discussion

Methodology. The approach presented here allows for the calculation of a critical limit function of a given metal taking into account variations in soil pH and organic matter content. The complete set of end point concentrations for each metal is assumed to have a deterministic component (due to the effects of soil chemistry) and a distributed component (due to the range of sensitivities of species to the metal). This method first quantifies the deterministic effects of soil chemistry and then applies a percentile-based approach to analyze the distributed component. Linear regression (eq 3) provides an independently determined relationship between log $M_{soil,toxic}$ and soil organic matter. We can then describe the relationship between the mean log $M_{soil,toxic}$ and soil pH using a single regression and analyze residuals to obtain a critical limit function. The specific method was chosen to avoid the need to make assumptions about the statistical distribution of residuals in Q, in contrast to the SSD approach. The method of calculating δ retains an element of the SSD approach since the calculation of a percentile of the residuals is dependent upon all their values. Where the distribution of residuals approaches a normal distribution, the results will be similar to those obtained by SSD analysis assuming a normal distribution.

It was not possible using literature data to elucidate any protective effect of other solution cations independent of the overall effect of pH. To do so would require measurement or estimation of free cation concentrations, which was not possible due to the limitations of the available literature data. In principle, concentrations of free cations might be estimated by linear regression, as for FMI concentrations.

As explained in the Theory section, it is possible that the need to consider the effects of other cations implicitly rather than explicitly (eq 2) is not a source of significant uncertainty in the predicted functions. However, where free cations (especially Ca and Mg) are controlled by solid phases, an explicit consideration of their effect may be more appropriate.

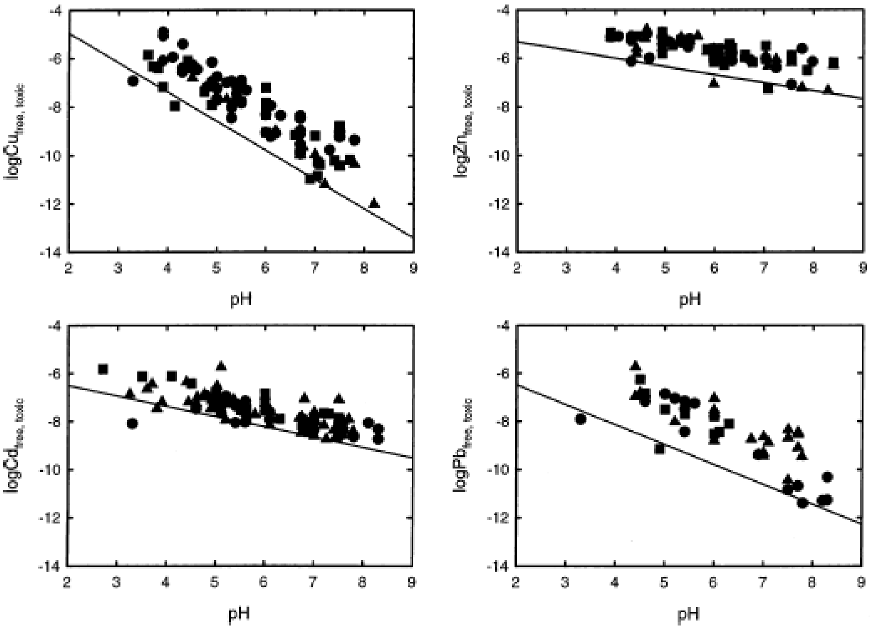

FIGURE 2. Critical limit functions of log M_{free} as a function of pH (solid lines) (eq 10; Table 7). Also shown for comparison are end point free ion concentrations in toxicological data, calculated using functions of free ion against soil properties (eq 3; Table 6). Circles: plant data; squares: invertebrate data; and triangles: microbial process data.

More work is needed to establish whether this is indeed the case.

A notable feature of the approach is that two critical limit functions are calculated, for the geochemically active soil metal and for the FMI. This provides versatility in applying the functions. For example, for routine comparison of metal levels in a given soil with the critical limit, the limit expressed as the geochemically active soil metals would be preferred. To calculate a critical load for a soil in steady state with respect to atmospheric metal inputs, the FMI critical limit may be used.

The approach also provides a context and framework for future ecotoxicological studies. Outlying end points that might exert a disproportionate effect on the critical limit function may be identified. The underlying theory suggests approaches to the design of toxicological studies to generate data suitable for analysis by the approach. Particularly desirable is the direct measurement of FMI in toxicological experiments. Given sufficient FMI end points, a critical limit function could be derived directly, taking eq 2 as a starting point. This is not strictly possible with the current data set since it would entail regressing log $M_{free,toxic}$, calculated as a function of pH, against pH itself. The approach presented here is algebraically equivalent but avoids regressing a function against one of its variables.

The linear regressions relating geochemically active soil metal to free ion are an important part of the complete method. They provide an alternative to the use of speciation modeling, requiring fewer soil chemistry variables. The use of the soil organic matter alone as a measure of the capacity of the soil to complex metal does not imply that other solid phases (e.g., clay, mineral oxides) are not significant in binding metal. Such phases might be important where organic matter is present at low concentrations, but existing data sets do not allow us to determine whether additional variables might be needed in the regression equations. An important assumption of the approach is the linear relationship between log M_{soil} and log M_{free} in the regressions. Given the relatively high effect concentrations encountered in the toxicity data, it is possible that saturation effects lead to nonlinearity in this relationship. Theoretical calculations using the WHAM/Model VI speciation model (*27, 33*) indicated at least the possibility of a nonlinearity at high metal loadings (> 1000 mg/kg). There is, therefore, a need to investigate the relationship at high metal loadings, preferably experimentally. The theoretical calculations should be treated with some caution since at high metal loadings the free ion activity might be controlled by precipitation of metal salts, which are not currently simulated by WHAM.

Impact of Metal-Sensitive Organisms on Critical Limits. The method of calculating the critical limit function is somewhat sensitive to especially low end point concentrations. This is particularly so for Zn and Pb, for which a number of relatively low end points were found (Figure 1). To determine how sensitive the critical limit functions were to such end points, critical limit functions were recalculated for each metal after first removing all the end points with log $M_{soil,toxic}$ values below the upper 95% confidence level of the critical limit function. Such a selection of points was necessarily subjective but should have demonstrated the sensitivity of the functions. The number of points removed was 7, 7, 11, and 6 for Cu, Zn, Cd, and Pb, respectively. The critical limits so calculated were reasonably similar to the originals for Cd_{soil}, calculated differences in log $M_{soil,CRIT}$ being around 0.1–0.5 orders of magnitude. Larger changes were seen for Cu_{soil}, Zn_{soil}, and Pb_{soil}, of between 0.5 and 1.4 orders of magnitude. In the case of Zn_{soil}, this was due to the relatively large number of outliers removed, whereas for Pb_{soil} the effect was largely due to removing two significant outliers in the pH range 3–5. Clearly outlying points can affect the critical limit function, particularly if they have an extreme value of soil pH as well as *Q*. Special scrutiny should be afforded to outliers to verify the validity of the data.

Effects of Soil Chemistry on Critical Limits. Critical limit functions for the FMI predict a strong pH effect. This is a fundamental tenet of the FIAM and BLM but one that is

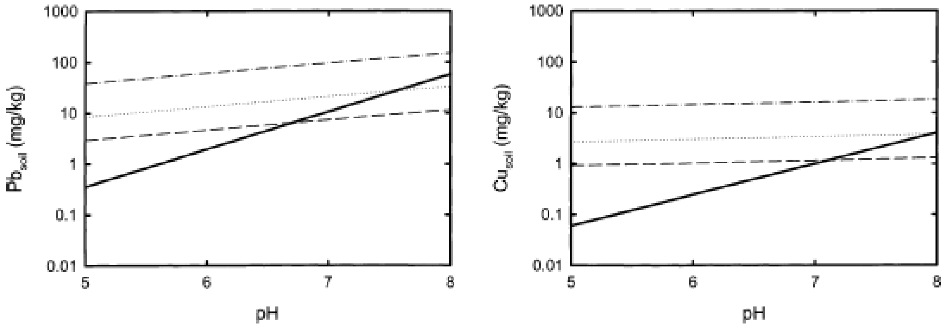

FIGURE 3. Plots of critical Cu and Pb, against pH, as predicted by the functions of Sauvé et al. (*8*) and in this paper. Solid line: function of Sauvé et al. for 10% inhibition of organism or process function. Dashed line: function of this paper for 95% protection of soil with 1% organic matter. Dotted line: function of this paper for 95% protection of soil with 5% organic matter. Dash−dot line: function of this paper for 95% protection of soil with 50% organic matter.

sometimes overlooked. An advantage of our approach is that the presence or absence of such an effect will become apparent on analysis of a data set, so we are not obliged to discount such an effect at the outset. By contrast, Sauvé et al. (*9*) assumed no effect of pH on FMI toxicity and produced expressions for inhibition of organism function as a function of the FMI alone. Although the limit functions given by Sauvé et al. (*9*) cannot be directly compared with the functions given here due to conceptual differences, trends, as shown in Figure 3, may be compared. Sauvé et al. calculated free Pb and Cu in toxicity tests using transfer functions that did not include organic matter terms, so the approach resulted in a function giving the critical soil metal as a function of pH and percent inhibition of organism function. The current approach gives critical soil metal as a function of pH and organic matter content, for a given proportion of species and processes adversely affected. The trend in the variation of critical soil metal with pH is the same using both methods, but the current approach predicts the critical limits to vary much less than does Sauvé's approach. Our method accounts for the effect of pH on metal toxicity directly from the data and therefore simultaneously considers both the effect of pH on the FMI concentration and the protective effect of pH against FMI toxicity. These two effects are predicted to cancel each other to a large degree resulting in limit functions with relatively small overall dependence on pH, although still potentially significant in risk assessment and management. By contrast, the approach of Sauvé et al. considers pH to affect only the free ion concentration resulting in significant trends of critical soil metal with pH.

Species Sensitivity Distributions under Field Conditions. Our approach focuses on drawing as much information as possible from current data. This has necessitated making some key assumptions. One important such assumption is that the distribution of species sensitivities for a given metal is the same across the entire pH range. In practice, different species and processes may exhibit different dependencies of toxicity on pH (i.e., species-specific α and ϕ values). Additionally, we would expect the composition of soil communities to vary naturally with pH and organic matter content, and ideally the test data ought to reflect these community variations. Clearly, it would be desirable to have test data for single species and processes in as many different soils as possible, allowing examination of organism-specific trends in toxicity.

Field Application of Critical Limit Functions. Application of the critical limit functions to the field must be done with care. The critical limits expressed as soil metal do not refer to the total metal in a soil as measured in the field but rather to the geochemically active soil metal concentration (i.e., the soil-bound metal that can exchange with the soil solution, and which determines the free ion concentration (cf. eq 3)). In toxicological tests where metal is added in soluble form, it can be considered to be present, initially at least, entirely in geochemically active form, and unless the background metal in the test soil is high, it usually approximates to the total metal in the soil. In field soils, however, a substantial portion of the metal present may not be geochemically active and therefore should not, as far as possible, be considered to contribute to the toxic metal in the soil. In measuring soil metal for comparison with critical limits, therefore, very strong extractions that measure total or pseudo-total metal (e.g., aqua regia), are not appropriate unless the non-geochemically active metal is small. Far more useful are extractions that directly estimate the geochemically active metal, such as EDTA and dilute mineral acids (*27*).

Also important to consider in applying critical limits to the field is the natural background concentration of metal. In this approach, we have used toxic end point data expressed relative to a control soil itself containing a certain level of metal. Effects have therefore been expressed relative to metal already present in the soil, and in applying, the limits in the field the geochemically active background metal (such as metal derived from natural rock weathering) should be discounted. Methods of determining background metals based on geochemical surveying and relationships with underlying rock type (e.g., refs *35*−*38*) appear to be the best option for calculation of background metal, although care must be taken to ensure that only the geochemically active forms are considered.

Acknowledgments

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Supporting Information Available

Description of the decision process for choosing toxic end points, the derivation of EC_{10} values from literature dose−response data, and a complete listing of all the toxicological data used. This material is available free of charge via the Internet at http://pubs.acs.org.

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Annexe 2.

Background Document contributed to the UNECE ICP Modelling and Mapping Meeting, Paris April 9-10 2003

Information and proposed methodology for determining critical loads of cadmium and lead; a UK contribution

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March 2003

PLEASE NOTE!

The information and ideas presented in this document are still in the process of development, and may require revision. The material should not be quoted outside the Modelling and Mapping Editorial Group.

1. Introduction

Critical loads methods for toxic metals are currently being developed within the United Nations Economic Commission for Europe (UN/ECE) Convention on Trans-boundary Air Pollution (CLRTAP), with a view to applying them in a revision of the Protocol on Heavy Metals in 2004/5. However, there are still major uncertainties about the most appropriate methodological approaches to be used when applying the critical load concept to metals, as opposed to acid deposition. This project aims both to contribute to the development of improved critical loads methods for application within UN/ECE and to develop improved tools to assess the effects of changing rates of atmospheric deposition on pools of metals in soils and freshwaters. It builds on previous research carried out both for DETR (under contracts EPG 1/3/144 and EPG 1/3/85) and as part of the NERC Environmental Diagnostics programme.

This Report arises from additional work, prompted by discussions of the Expert Group on Effect-based Critical Limits for Heavy Metals and Methods for their Application, held on 2 – 4 December 2002, in Berlin, Germany. The Meeting was attended by members of the Defra project (L.Shotbolt, D.Spurgeon, E.Tipping), and by a Defra representative (A.Irving). One outcome of the Meeting was the resolution to develop and publish, within a short time frame, recommended procedures for the calculation of steady-state critical loads for Cd and Pb. This was seen as an interim measure, the eventual aim being to move to a dynamic evaluation. Because the UK research team working on the present project (EPG 1/3/188) has contributed considerably to the Critical Loads Methodology, it was agreed to carry out additional work, funded by Defra, necessary to meet the needs of the steady state approach. The work was performed during the period January – March 2003.

2. Outline of the proposed approach to set steady state critical loads

The discussions in Berlin identified the solution concentration of free metal ion (Cd^{2+}, Pb^{2+}) as the key determinant of ecotoxicological effects, and also accepted the evidence for pH dependence of toxicity in soils, and dependence on pH, and possibly also alkalinity, in waters. Thus, a critical limit would be defined as a free metal ion concentration, dependent upon pH for soil, or pH and possibly alkalinity (or hardness) for waters. We therefore propose that steady state critical loads should be based on such critical limits.

2.1 Soils

Fig. 2.1 shows schematically the different forms of metal in a soil at steady state with respect to metal input and output. Since the system is in steady state, and the critical limit is defined in terms of $[M^{z+}]$, the solution concentration of M^{z+}, the metal content of the soil solids does not have to be known in order to calculate the critical load[*].

Fig. 2.2 shows how the critical load for a soil would be calculated. The key points are:

- Definition of the critical limits, i.e. $[Cd^{2+}]_{CLim}$ and $[Pb^{2+}]_{CLim}$, given the soil pH. See Section 5 for details.

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[*] But it is needed to estimate how long the system would take to reach steady state, i.e. for dynamic prediction. Knowledge of the relationship between the sorbed amount and $[M^{z+}]$ is used to derive critical limits for soils (Section 5). Knowledge of solid-soltuion partitioning may be used to estimate the erosional loss of metal (Sections 3 and 7).

- Calculation of the total dissolved concentrations of Cd and Pb corresponding to $[Cd^{2+}]_{crit}$ and $[Pb^{2+}]_{crit}$ respectively. This is done by application of the WHAM6 chemical speciation model, given knowledge of pH, [DOC], inorganic ligands (principally HCO_3^- and CO_3^{2-}], and concentrations of competing metals (principally Mg, Ca, Al and Fe(III)). See Section 3 for details.
- Combination of the total dissolved metal concentration with the throughput of water, to obtain the drainage load corresponding to the critical limit. This would be equal to the steady state atmospheric critical load, in the absence of other loads, e.g. export of metals by harvesting or erosion, or input of metals by weathering.
- Obtain the atmospheric critical load by taking account of other metal loads.

Thus, the data required for the calculation are:

(a) The critical limit
(b) The soil pH
(c) The soil type
(d) The concentration of DOC in soil drainage water
(e) The annual runoff
(f) Knowledge of other metal loads.

Illustrative calculations are presented in Section 7.

2.2 Surface waters

Calculating the critical load for a surface water is similar to the procedure for a soil. The key points are:

- Definition of the critical limits, i.e. $[Cd^{2+}]_{crit}$ and $[Pb^{2+}]_{crit}$, given the pH and possibly the hardness (i.e. the sum of Mg and Ca concentrations). See Section 5 for details.
- Calculation of the total dissolved concentrations of Cd and Pb corresponding to $[Cd^{2+}]_{crit}$ and $[Pb^{2+}]_{crit}$ respectively. As for soils, this is done by application of the WHAM6 chemical speciation model, given appropriate inputs. See Section 4 for details.
- Combination of the total dissolved metal concentration with the throughput of water, to obtain the drainage load corresponding to the critical limit.
- Take account of other metal loads.

Thus, the data required for the calculation are:

(a) The critical limit
(b) The water pH and possibly hardness.
(c) The water type
(d) The concentration of DOC
(e) The annual runoff
(f) Other metal loads.

Illustrative calculations are presented in Section 7.

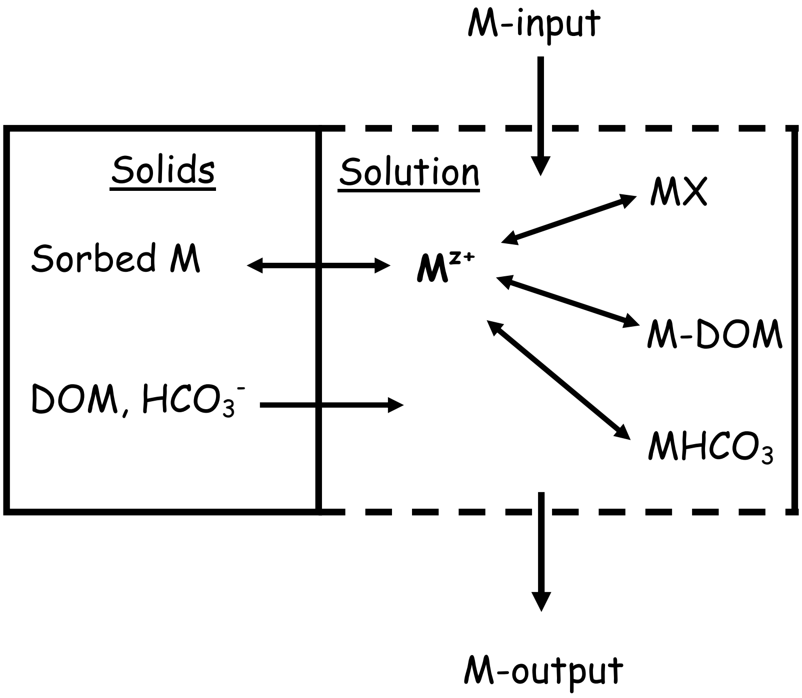


Fig. 2.1 Soil at steady state with respect to metal input and output.

- The input load is the sum of the atmospheric deposition and any other inputs & outputs (harvest, weathering, erosion etc).
- The output load is the total dissolved concentration × drainage water flux.
- The critical load is the output load corresponding to $[M^{z+}]_{crit}$.
- For a given value of $[M^{z+}]_{crit}$, the greater is the complexation with X, HCO_3^- and DOM occurs, the higher is the dissolved concentration, and the higher the critical load.
- The critical load does not depend upon the amount of metal sorbed to the soil, since *at steady state* this is dictated by $[M^{z+}]_{crit}$.

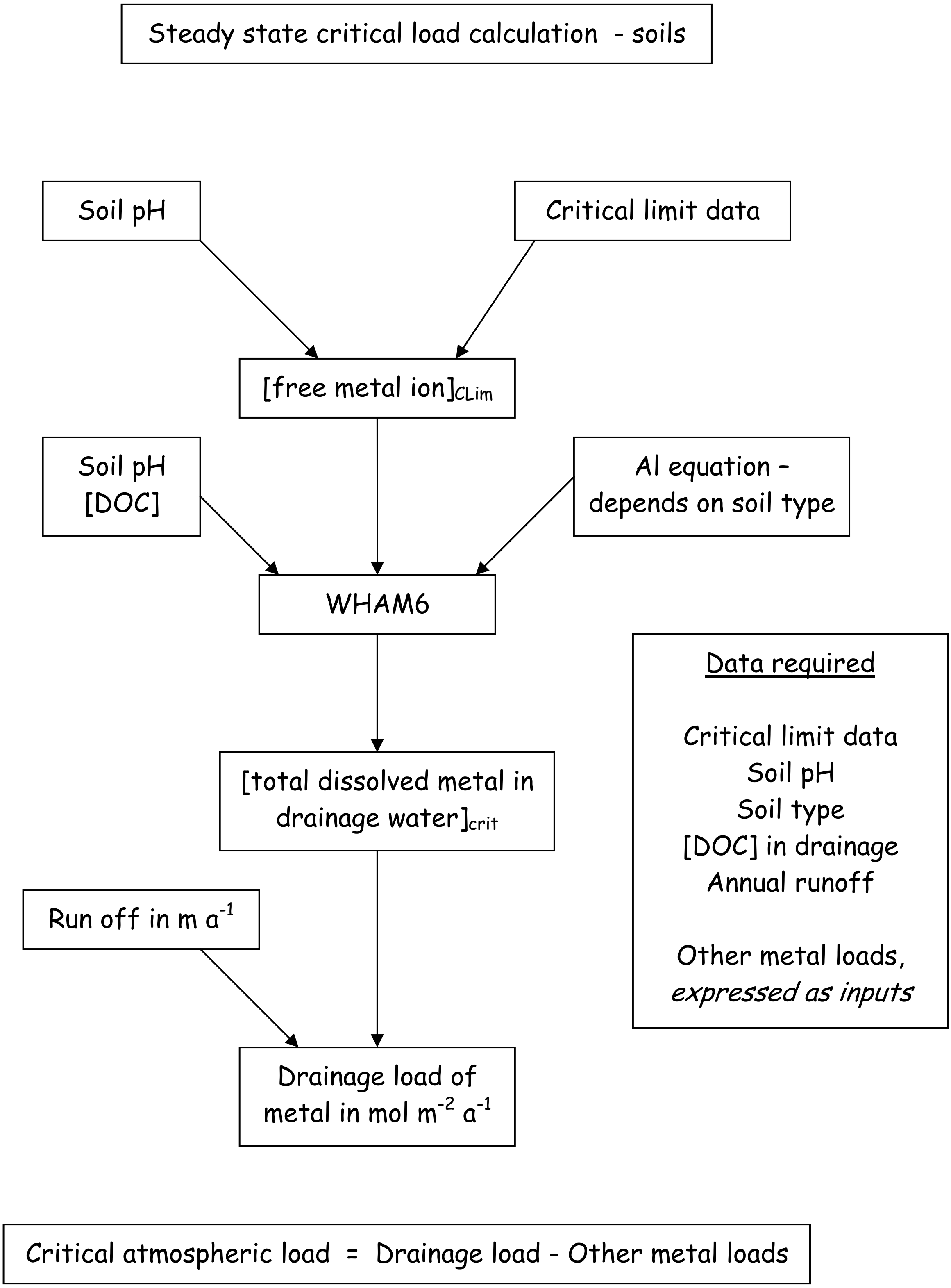


Fig. 2.2 Schematic explanation of the calculation of steady state critical loads for soils.

3. Chemical speciation calculations

For both soil waters and surface waters, the following species of dissolved Cd and Pb need to be taken into account:

- the free metal ions, Cd^{2+} and Pb^{2+} (used to express the critical limits)
- complexes with inorganic ligands, Cl^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}
- complexes with dissolved organic matter (DOM)
- metal sorbed by the soil solids

The solution concentrations of the different species can be calculated with a suitable chemical speciation model, given the appropriate input data. A good choice of model is WHAM6 (Tipping, 1998; WHAM6 website), which has been developed especially to take account of metal interactions with DOM. The input data required to calculate how the total dissolved metal is distributed among the different species are:

- total concentrations of Cd and Pb
- concentrations of major competing metals, i.e. Mg, Ca, Al, Fe(III)
- total concentrations of inorganic ligands
- DOC concentration
- pH
- ionic strength
- temperature

For the calculation of critical loads, the model would be used "in reverse", to calculate the total dissolved concentrations of Cd and Pb from the critical limit values of Cd^{2+} and Pb^{2+}.

3.1 Competing metals in soils and waters

Heavy metal interactions with ligands are reduced by competing metals, notably Mg, Ca, Al and Fe(III). These competition effects have to be taken into account in estimating how much of the heavy metal is complexed.

3.1.1 Mg and Ca

Competition effects by these two alkaline earth metals can be calculated from knowledge of their total dissolved concentrations, since they are largely uncomplexed. Because Mg and Ca behave similarly with regard to competition, it will usually be acceptable to lump them together, assuming them both to be Ca, since it is usually the dominant metal.

3.1.2 Fe(III)

In the case of Fe(III), it can be reasonably assumed that soils and freshwaters are in equilibrium with iron hydroxides, colloidal forms of which are ubiquitous in both environments. Therefore, the activity of Fe^{3+} - the key species for performing chemical speciation calculations – can be estimated from the solubility product of $Fe(OH)_3$.

3.1.3 Al

Aluminium presents greater difficulties because concentrations of Al^{3+} do not, in general, follow the pattern expected for solubility control by $Al(OH)_3$. Therefore, we assembled literature data for soils and waters, and derived empirical equations that can be used to estimate Al^{3+} activity as a function of pH. The data used for the analysis refer to temperatures close to 10^{o}C. We propose that Al activities are estimated as follows (CL = confidence limits, in log a 95% when regression, suggested when oxide control)

<u>Mineral soils</u>

$pH < 5.5$ $\log a_{Al3+} = 2.22 - 1.59\ pH$ CL ± 0.9

$pH \geq 5.5$ $\log a_{Al3+} = 10.0 - 3\ pH$ CL ± 1.0

<u>Organic soils</u>

$pH < 6$ $\log a_{Al3+} = -1.94 - 1.02\ pH$ CL ± 1.8

$pH \geq 6$ $\log a_{Al3+} = 10.0 - 3\ pH$ CL ± 1.0

<u>Surface waters</u>

$pH < 5.5$ $\log a_{Al3+} = 3.10 - 1.90\ pH$ CL ± 1.2

$pH \geq 5.5$ $\log a_{Al3+} = 9.5 - 3\ pH$ CL ± 1.0

<u>Bog waters</u>

pH 4-6, dissolved Al sufficiently low to be neglected.

3.2 Inorganic ligands

The most important inorganic complexing agents are carbonate species, the concentrations of which can be calculated from the pH and the known or assumed CO_2 partial pressure. Other ligands that could be taken into account include Cl^- and SO_4^{2-}, but their influence on heavy metal speciation is generally small.

3.3 Dissolved organic matter

This is a highly significant complexing agent of heavy metals. If the DOC concentration is known, the concentration of "active" (with respect to ion-binding) organic matter can be estimated by assuming 65% of the material to behave as isolated fulvic acid (see refs in Tipping et al., 2003). However, it is anticipated that DOC concentrations will often not be available. Therefore we have reviewed the literature to attempt to derive representative values (see Section 4).

3.4 pH and ionic strength

The soil or water pH is a vital input to the calculations. Knowledge of ionic strength is helpful to the WHAM calculations but in most cases it can be estimated.

3.5 Transfer functions

These are multiple regression equations that relate free ion activities or concentrations to amounts sorbed by the soil solids. We are collaborating with our Dutch colleagues to determine definitive versions of these functions. In the present work we used transfer functions in the derivation of critical limits (Section 5), for estimating soil metal contents (Section 6), and for estimating amounts of metal bound to suspended particulate matter (Section 7).

For mineral soils we used the following "Freundlich transfer functions", derived from data published by Sauvé and colleagues (Sauvé et al., 1998, 2000);

$$\log\left(\frac{\mathrm{Cd}_{soil}}{[\mathrm{Cd}^{2+}]^{0.72}}\right) = -5.00 + 0.56\mathrm{pH} \qquad \mathrm{SE} = 0.45$$

$$\log\left(\frac{\mathrm{Pb}_{soil}}{[\mathrm{Pb}^{2+}]^{0.55}}\right) = -5.24 + 0.54\mathrm{pH} + 0.45\log\%OM \qquad \mathrm{SE} = 0.37$$

The units of Pb_{soil} are mol g^{-1}.

For organic soils we used the following transfer functions, based on conventional K_D values (mol metal per gram soil / $[M^{2+}]$), published by Tipping et al. (2003);

Cd: $\log K_D = 0.71 \log\%LOI + 0.43\mathrm{pH} - 2.93$ $\qquad$ SE = 0.31

Pb: $\log K_D = 0.60 \log\%LOI + 1.13\mathrm{pH} - 4.36$ $\qquad$ SE = 0.44

The Sauvé equations were used for mineral soils (< 10% organic matter), and the Tipping equations for soils with organic matter contents of > 10%. This approach leads to some incompatibilities, because the equations have not yet been harmonised.

4. Dissolved Organic Carbon (DOC) levels

4.1 DOC concentrations in soil water

DOC strongly complexes many heavy metals, influencing metal partitioning between the soil and soil solution and metal leaching from the soil profile. DOC is, therefore, an essential parameter in the calculation of critical loads. Unfortunately, DOC is rarely measured in national soil surveys. As accurate DOC data is essential in the calculation of critical loads, a literature review has been carried out to determine typical DOC concentrations across a range of soils.

Different soil-water extraction procedures can result in marked differences in the concentrations of DOC. Studies reviewed were restricted to those that collected soil solution using zero-tension or tension lysimeters. Although no extraction procedure is without drawbacks, the advantage of this technique over others such as centrifuging soil samples or creating a soil-slurry through mixing with water is that the soil solution is obtained *in-situ* and can be continuously collected over a period of time.

39 studies in Europe and North America have been identified that have determined DOC in soil solutions collected in lysimeters. Within this dataset, 192 individual or bulked lysimeter results were obtained. These span a range of soil types, vegetation types (Table 4.1) and horizons (Table 4.2). The majority of studies included have measured DOC over a period of one or more years and DOC concentrations presented are mean annual concentrations. Also included are a number of studies that have only measured during the summer months, often due to snow cover or freezing during the winter.

Soil groups (WRB)	Number of samples	Vegetation	Number of samples
Acrisols	30	Coniferous forest	72
Andosols	3	Deciduous forest	56
Cambisols	29	Grassland communities	25
Gleysols	23	Sphagnum communities	13
Histosols	32	Carr (wooded wetlands)	8
Leptosols	2	Agricultural (cereal)	6
Podzols	57	Unspecified	12
Unspecified	15		

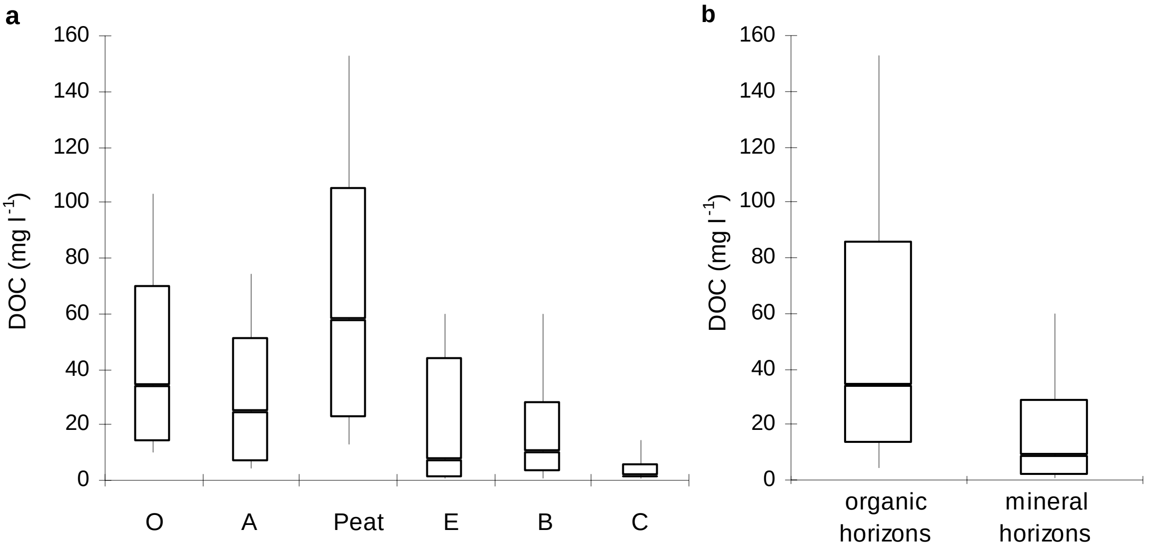
Table 4.1. Soil groups in the studies reviewed according to the World Reference Base for Soil Resources (FAO, 1998) and predominant vegetation type.

Samples from mineral soils were separated into major horizons (i.e. organic (O) horizons, mineral/organic (A) horizons, elluvial (E) horizons, illuvial (B) horizons and relatively unaltered (C) horizons) for analysis. Samples from deep peat profiles were also considered, though as a separate category. Sample distributions were positively skewed (particularly the E, B and C horizons) and therefore the median was considered the most appropriate average value. Median, 10th and 90th percentiles and range of DOC concentrations are shown below (Table 4.2 and Figure 4.1a).

Horizon	no. of samples	median DOC	min. DOC	max. DOC	10th percentile	90th percentile

O	30	33.6	10.0	103.2	14.0	70.0
A	26	24.8	4.6	74.2	6.6	51.2
Peat	32	57.4	12.8	152.8	22.2	104.9
E	16	7.1	0.6	60	0.9	44.3
B	66	9.9	1.0	60	2.9	28.1
C	11	1.5	0.4	14.41	0.5	5.9

Table 4.2. Summary statistics for DOC concentrations classified by soil horizon. Values are calculated from annual mean concentrations although some studies used only provide data during the growing season.



Figures 4.1. (a) median, 10th and 90th percentile and range of DOC concentrations in samples from major soil horizons; (b) median, 10th and 90th percentile and range of DOC concentrations in samples from organic and mineral horizons.

The range of DOC concentrations measured in the studies reviewed is considerable. However, clear differences between soil horizons are apparent (Figure 1a). The more organic soil horizons (O, A and Peat) produce higher concentrations of DOC than the mineral horizons (E, B and C). This suggests DOC export from organic soils will be considerably greater than from soils with mineral horizons. For the purposes of providing DOC data to input into steady state critical load calculations it is most appropriate to simply differentiate between organic and mineral horizons (Table 4.2 and Figure 4.1b).

Horizon	no. of samples	median DOC	min. DOC	max. DOC	10th percentile	90th percentile
Organic Horizons	89	34.0	4.6	152.8	12.8	86.0
Mineral Horizons	94	8.9	0.4	60	1.3	28.8

Table 4.2. Summary statistics for DOC concentration in mineral and organic soil horizons

Results from these horizons can be considered to represent typical DOC export from mineral and organic soils.

4.2 Waters

Information on DOC concentrations in surface waters draining temperate forests, grasslands and wetlands has been taken from the review by Hope et al. (1994). Fifty-six annual average DOC concentrations were obtained. The median [DOC] was 2.8 mg l^{-1}, and the 10- and 90-percentiles were 0.7 and 11.7 mg l^{-1} respectively.

5. Critical limits for Cd and Pb in soils and waters

The theoretical basis for calculating critical limits is that for organisms whose primary mode of metal uptake is directly from their surrounding medium (soil water in the case of soil organisms), the concentration of the free metal ion (Cd^{2+}, Pb^{2+}) provides the best guide to bioavailability and thereby toxic effects. However, it is also assumed that the bioavailability of the metal depends upon the concentrations of other cations, principally pH, but also possibly major metal cations (Na^+, Mg^{2+}, K^+ and Ca^{2+}). The same assumptions form the basis of the Biotic Ligand Model (BLM; Paquin et al., 2000), but whereas the BLM postulates a specific site of action for all the cations, our approach is completely empirical; we simply seek equations that describe limiting toxicity as a function of solution variables.

Chronic toxicity data for were collected from all possible literature sources. Data were collected for plants, soil animals, soil microbial processes, aquatic plants and aquatic animals. Acceptable endpoints for use were the NOEC, LOEC, EC_{10} and EC_{20}. Where more than one endpoint was quoted for the same species and effect/process, the following hierarchy was used to select a single endpoint for use: NOEC – EC_{10} – LOEC – EC_{20}. Sublethal population effects (i.e. reproduction, growth) were allowed, effects on physiology and/or behaviour were excluded. In waters, where a study explicitly found survival to be more sensitive than any sublethal effect, the survival endpoint was used.

Requirements of soil and water composition, necessary for the calculation of free ion concentrations, will be described separately for soils and waters below.

5.1. Soils

For the calculation of free metal ion concentrations, the soil pH and organic matter (%) were required. For each endpoint the toxic free ion concentration (denoted $[M^{2+}]_{tox}$) was calculated using the transfer functions given in Section 3.

Calculated values of $[M^{2+}]_{tox}$ are shown plotted against $\log[H^+]$ in Figs. 5.1 and 5.2. For each metal, considering all species and effects endpoints together, a significant ($P < 0.001$) correlation between $\log[M^{2+}]_{tox}$ and $\log[H^+]$ was seen. It was not possible with current data to determine any independent effects of Ca^{2+} or Mg^{2+} on $[M^{2+}]_{tox}$, therefore critical limits as the free ion were expressed as functions of $\log[H^+]$ only. This was done using a method which is intended to combine the species sensitivity distribution approach of Aldenberg and Slob (1991) with a description of the dependence of the critical limit, $[M^{2+}]_{crit}$, upon $\log[H^+]$. The method comprised two stages:

1. A weighted linear regression of $\log[M^{2+}]_{tox}$ against $\log[H^+]$. The weighting of data points was done to compensate for the differing number of data points from different studies. Data points from the same study which referred to the same species or effect were grouped together. Each point was assigned a weight n_{max}/n, where n was the number of data points within the group and n_{max} was the largest group size for that metal. The best fit regression line was found by minimising the sum of squares in the term $\Sigma[(\log[M^{2+}]_{tox} - \log[M^{2+}]_{tox,\ regression})^2 . n_{max}/n]$. For each metal this gave a best fit regression of the form

$$\log[M^{2+}]_{tox} = a.\log[H^+] + b \qquad (5.1)$$

2. The critical limit, $\log[M^{2+}]_{crit}$, was assumed to be a linear function with the form

$$\log[M^{2+}]_{crit} = a.\log[H^+] + b + B \qquad (5.2)$$

where a and b are the terms in Equation 5.1. The term B was calculated by assuming the residuals in $\log[M^{2+}]_{tox}$ to be log-logistically distributed, and applying the expression of Aldenberg and Slob(1991):

$$B = \mu - \beta . \log[(100 - p) / p] \qquad (5.3)$$

with $p = 95$. The value of B was found by optimising the variables μ and β, minimising the term $\Sigma\, [(p - p_{calc})^2 .\, n_{max}/n]$.

This procedure gave the following expressions for $\log[M^{2+}]_{crit}$:

$$\log[Cd^{2+}]_{crit} = 0.76\log[H^+] - 3.87 \qquad (5.4)$$

$$\log[Pb^{2+}]_{crit} = 0.66\log[H^+] - 5.47 \qquad (5.5)$$

Plots of $\log[M^{2+}]_{tox}$ against $\log[H^+]$, and distributions of residuals in $\log[M^{2+}]_{tox}$, are shown in Figures 5.1 and 5.2.

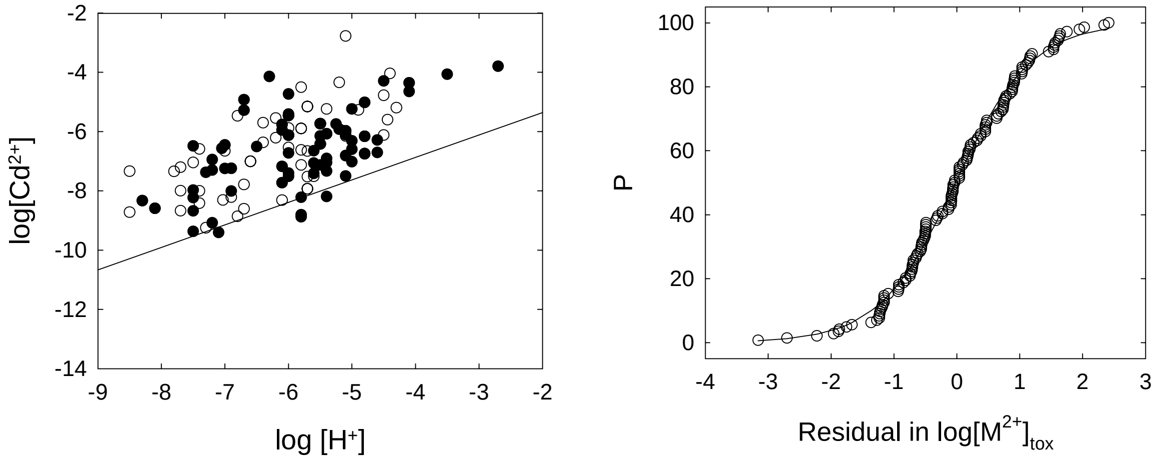


Figure 5.1. Left: $\log[Cd^{2+}]_{tox}$ plotted against $\log[H^+]$, showing the critical limit function (solid line) derived from weighted regression and the distribution of residuals in $\log[Cd^{2+}]_{tox}$ (right). Solid points in the left hand pane are for effects on plants and animals, open points are for effects on microbial processes. The critical limit function was calculated by combining the data on both types of effect.

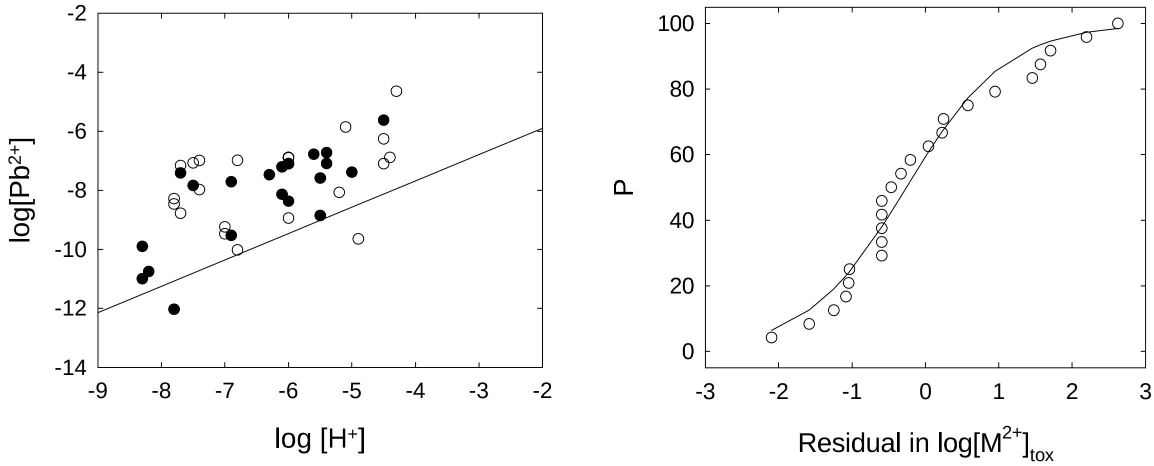


Figure 5.2. As Fig. 5.1 but for Pb.

5.2 Waters

Calculation of the free ion concentration in freshwater toxicity experiments was done using the WHAM6 speciation model (http://windermere.ceh.ac.uk/Aquatic_Processes/wham/). For the calculation of free ion concentration in a test medium, the ideal parameter set included, in addition to the total dissolved Cd or Pb at the toxic endpoint, the pH, the concentrations of Na, Mg, K, Ca, Cl, SO_4 and CO_3 and the amount of dissolved organic carbon (DOC) present. In practice it was usually necessary to accept a smaller data set. The minimum set of chemistry parameters required was pH, hardness (assumed to be Ca) and alkalinity (assumed to be CO_3). For some tests where natural waters were used as the medium, reference was made to USGS water quality databases (http://waterdata.usgs.gov/nwis/qw) for estimating missing concentrations.

In calculating Cd^{2+} or Pb^{2+} in the test medium, the issues of metal losses from solution and of metal complexation by DOC were also considered. Significant losses of metal to the vessel wall may occur during toxicity testing. Therefore, where only nominal concentrations of metal were quoted for a test, calculation of the free ion was done assuming both the quoted nominal concentration and a concentration half the nominal concentration, to give a rough estimate of losses. It was also assumed that in reconstituted test media without added DOC, excretion of organic matter by the test organisms might occur. Therefore, in these cases an additional calculation of the free ion concentration, assuming a DOC concentration of 2 mg/l, was done.

Compared to soils, fewer suitable endpoints covering a smaller number of species were found for aquatic toxic effects. Also, the range of pH covered in the tests was limited, with very few endpoints measured at pH < 6 and most points measured in the pH range 7–8. No significant effect of pH could be seen on values of $\log[M^{2+}]_{tox}$ when considering all species and effects together. The range of hardness covered was representative of natural waters ($\sim 10^{-4}$-10^{-2}M Ca + Mg). However, no significant effect of hardness on $\log[M^{2+}]_{tox}$ was seen. Also, the uncertainties about DOC and actual Cd or Pb concentrations in some test media introduced considerable uncertainity into some of the free ion concentrations. The uncertainty was greater for Pb due to its higher affinity for DOC than Cd.

In the light of these findings, we propose to apply the critical limits derived for soils to waters also. There are several reasons for adopting this approach:

1. There is no theoretical reason why the sensitivities of soil and water organisms to metals should not be similar, assuming that uptake of the free ion from the aqueous phase is the significant mechanism leading to toxicity.
2. There is overlap between $[M^{2+}]_{tox}$ values for soils and waters, for Cd (Figure 5.3). As Cd is not complexed greatly, uncertainties in the calculated free ion concentrations are not so great. Similar overlap between limits has also been found for Zn (data not shown).
3. There is also some overlap between the $[M^{2+}]_{tox}$ values for Pb (Figure 5.4). Although uncertainties in a number of the calculated free ion concentrations are large, inspection of the figure shows that the majority of the endpoints fall above the critical limit. The single value of $\log[Pb^{2+}]_{tox}$ which is below the critical limit line has a large uncertainty associated with possible DOC complexation.

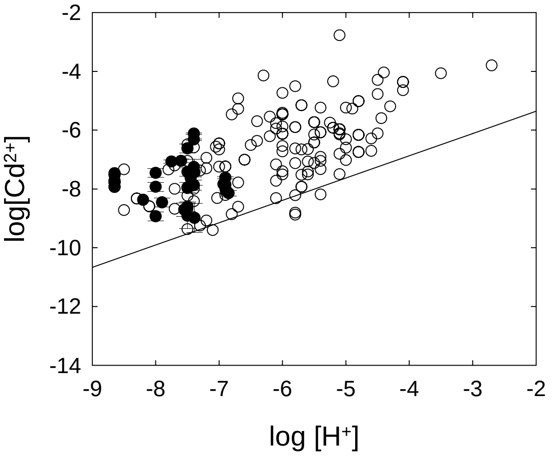


Figure 5.3. Critical values of log[Cd^{2+}] for soils (open symbols) and waters (closed symbols). Error bars for the aquatic critical values give the maximum and minimum log[Cd^{2+}]$_{tox}$ taking complexation by DOC and losses to the vessel wall into account. The solid line is the critical limit function for Cd based on the soil data.

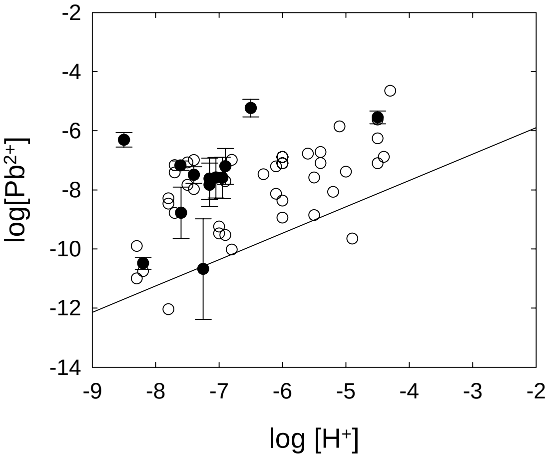


Figure 5.4. As Fig. 5.3 but for Pb.

6. Comparison with other critical limits

The critical limit values derived in Section 5 can be used to calculate more conventional critical limit values for soils and waters, permitting the methods to be compared.

6.1 Soils

Conventionally, critical limits for soils have been expressed in terms of metal soil content, typically in units of mg kg^{-1}. We calculated soil metal contents corresponding to the free ion critical limits derived in Section 5, using the transfer functions of Section 3. The calculated values are dependent upon pH and, except for Cd in mineral soils, soil organic matter content. The results are compared to conventional values (UK Environment Agency, 1997; Geotechnics and Contaminated Land Group, 1994; Eikmann & Kloke, 1991) in the following Tables.

Cadmium (mg kg^{-1})				
Conventional values : 0.8 – 3				
pH	**1% OM**	**10% OM**	**50% OM**	**100% OM**
3	2.0	2.0	29.3	48.0
4	2.1	2.1	13.7	22.4
5	2.1	2.1	6.4	10.5
6	2.2	2.2	3.0	4.9
7	2.3	2.3	1.4	2.3
8	2.3	2.3	0.7	1.1

Lead (mg kg^{-1})				
Conventional values : 85 – 500				
pH	**1% OM**	**10% OM**	**50% OM**	**100% OM**
3	4.0	11.2	8.2	12.5
4	6.0	16.8	24.3	36.8
5	9.0	25.3	71.7	109
6	13.5	38.0	212	321
7	20.3	57.1	624	946
8	30.4	85.8	1842	2790

The variations in the total soil critical limits with pH reflect the pH dependences of the free metal ion critical limits, and of the free metal ion concentration. Note that there are some inconsistencies in the trends with respect to soil organic matter content; these arise because the transfer functions for mineral and organic soils have not yet been harmonised (Section 3).

6.2 Surface waters

The free ion critical limit values were converted to total dissolved concentrations by applying WHAM6 as outlined in Section 6. The solutions considered vary in [DOC] and pH, the latter being related to calcium concentration. The conventional critical limit for Cd in the Netherlands (van de Plassche et al., 1997) is 0.34 µg l^{-1}, and for Pb 11µg l^{-1}. The following Table shows total dissolved metal critical limits, calculated from the free metal ion values.

[DOC] mg l^{-1}	pH	[Ca]mM	Cd_{crit} µg l^{-1}	Pb_{crit} µg l^{-1}
1	4	0	15	1.7
	5	0	2.6	0.4
	6	0.008	0.6	0.3
	7	0.07	0.1	0.8
	8	0.70	0.03	1.5
3	4	0	15	1.7
	5	0	2.7	0.5
	6	0.012	0.8	0.6
	7	0.076	0.2	2.2
	8	0.71	0.04	4.2
10	4	0	15	1.7
	5	0.007	3.0	0.7
	6	0.029	1.5	1.6
	7	0.097	0.5	7.0
	8	0.73	0.07	14
30	4	0	15	1.9
	5	0.032	3.7	1.5
	6	0.077	2.9	3.9
	7	0.16	1.1	19
	8	0.80	0.2	40

It is evident from the Table that toxic effects of Cd and Pb on aquatic organisms are expected to vary appreciably with solution conditions. For Cd the main effect is the pH dependence of toxicity, which means that higher concentrations can be tolerated at lower pH values. For Pb, this also applies, but complexation by dissolved organic matter counteracts the pH effect, so that the critical limit concentration passes through a minimum at pH 5-6. The values for Cd are generally higher than the conventional critical limit, while those for Pb are generally lower.

7. Example calculations of steady state Critical Loads

The example calculations here take account of atmospheric loads, and erosional export loads, but not loads due to harvesting ,weathering etc.

7.1 Soils

7.1.1 Basis of calculation

We assume here that steady state Critical Loads are to be calculated on the basis of the following information, for a given soil horizon:

- pH
- soil type (mineral or organic)
- annual runoff in mm
- the loss flux and LOI of particulates

The following assumptions are made about the soil solution:

- It has a pCO_2 of 20 times the atmospheric value, uncertainty being addressed by performing calculations also for 5 and 100 times (see e.g. Buckman & Brady, 1969; Freeze & Cherry, 1979 for information on soil pCO_2 values).
- Its inorganic solutes are Na^+ (1 mM), Cl^- (1 mM), carbonate species (concentrations determined by pH and pCO_2) and Ca^{2+}. The Ca concentration is obtained within the speciation calculation, by forcing a charge balance.
- For an organic soil horizon, the DOC concentration is 34.0 mg L^{-1}, uncertainty being addressed by assuming a lower limit of 12.8 mg L^{-1} and an upper one of 86.0 mg L^{-1}.
- For a mineral soil horizon, the DOC concentration is 8.9 mg L^{-1}, uncertainty being addressed by assuming a lower limit of 1.3 mg L^{-1} and an upper one of 28.8 mg L^{-1}.
- The activity of Al^{3+} is estimated from equations given in Section 3, depending upon soil type. Uncertainty is addressed as indicated by the confidence intervals in Section 3.
- The activity of Fe^{3+} is estimated from $\log K_{so,25°C} = 2.5$, with an uncertainty of ± 1.

The program takes the critical limit concentrations and back-calculates to total fluxes from the above information, providing a “best estimate” and lower and upper critical loads.

The calculation can be refined, and made more certain, if more detailed information about the soil solution can be supplied.

7.1.2 Example results

The following Table gives some example results. In all cases the annual runoff is 1000 mm. For the mineral soils, the eroded particulate matter is assumed to be 5% organic matter, while for the organic soils it is 90%.

Soil type	**pH**	**erosion $g\ m^{-2}\ a^{-1}$**	**Cd critical load $g\ ha^{-1}\ a^{-1}$**			**Pb critical load $g\ ha^{-1}\ a^{-1}$**		
			low	**medium**	high	low	**medium**	high
Mineral	**5**	**0**	26	**27**	42	4	**5**	18
	6	**0**	5	**8**	17	1	**5**	43
	7	**0**	1	**2**	4	2	**12**	110
	8	**0**	1	**1**	3	18	**40**	140
	6	***10***	*5*	***8***	*19*	*2*	***8***	*58*
Organic	**4**	**0**	150	**170**	330	17	**33**	190
	5	**0**	26	**48**	170	4	**29**	230
	6	**0**	6	**14**	43	3	**17**	260
	7	**0**	2	**3**	6	8	**37**	320
	5	***10***	*27*	***49***	*180*	*5*	***39***	*340*

For Cd, the critical load decreases with soil pH because the critical limit decreases and there is little compensation due to solution complexation. For Pb, complexation in solution, mainly due to DOC, counters the decrease with pH of the critical limit.

7.2 Waters

7.2.1 Basis of calculation

We assume here that steady state Critical Loads are to be calculated on the basis of the following information, for a given surface water:

- pH
- water type ("normal" or acid bog water)
- annual runoff in mm
- the areal flux of suspended particulates and their LOI

No differential effects of a lake and its catchment are considered, since at steady state the free ion metal concentration will be the same in streamwater, lakewater and soil water, as long as the evaporation rates from land and the lake water surface are assumed equal. Thus the calculated critical load refers to deposition per unit area of the total catchment.

The following assumptions are made about the surface water:

- It has a pCO_2 twice the atmospheric value.
- Its inorganic solutes are Na^+ (1 mM), Cl^- (1 mM), carbonate species (concentrations determined by pH and pCO_2) and Ca^{2+}. The Ca concentration is obtained within the speciation calculation, by forcing a charge balance.
- The DOC concentration is 2.8 mg L^{-1}, uncertainty being addressed by assuming a lower limit of 0.7 mg L^{-1} and an upper one of 11.7 mg L^{-1} (see Section 4.2).
- The activity of Al^{3+} is estimated from equations given in Section 3, depending upon water type. Uncertainty is addressed as indicated by the confidence intervals in Section 3.
- The activity of Fe^{3+} is estimated from $\log K_{so,25°C} = 2.5$, with an uncertainty of ± 1.

The program takes the critical limit concentrations and back-calculates to total fluxes from the above information, providing a "best estimate" and lower and upper critical loads.

As for soils, the calculation can be refined, and made more certain, if more detailed information about the surface water chemical composition can be supplied.

7.2.2 Example results

The following Table gives some example results. In all cases the annual runoff is 1000 mm. The critical load values follow similar trends to those for soils.

	Cd critical load g ha^{-1} a^{-1}			**Pb critical load g ha^{-1} a^{-1}**		
pH	low	**medium**	high	low	**medium**	high
No suspended solids						
4	147	**149**	155	16	**17**	21
5	26	**27**	44	4	**5**	23
6	5	**8**	29	1	**6**	49
7	1	**2**	8	2	**20**	246
8	0.2	**0.4**	1	5	**39**	273
Erosion of mineral soil 10 g m^{-2} a^{-1}						
4	147	**149**	157	17	**18**	28
5	26	**27**	45	4	**7**	33
6	5	**8**	30	2	**8**	64
7	1	**2**	10	3	**25**	269
8	0.3	**0.6**	3	6	**46**	308
Erosion of organic soil 10 g m^{-2} a^{-1}						
4	148	**151**	177	17	**20**	58
5	26	**28**	54	5	**16**	131
6	5	**8**	34	4	**38**	370
7	1	**2**	10	12	**115**	115
8	0.3	**0.5**	2	33	**319**	3066

8. Calculating critical limit exceedances

The critical limits derived in Section 5 can be used to determine whether soils and waters are currently impacted by Cd and Pb, i.e. to test for exceedance. For soils, the critical limit free ion concentrations can be inserted into the transfer functions of Section 3 to obtain total active soil metal (cf. Section 6), which can then be compared with measured values. Alternatively, soil waters may have been sampled, and the free metal ion concentrations either measured or estimated by chemical speciation calculation. For waters, the total dissolved metal can be computed (again see Section 6), and compared with the measured value, or possibly with measured free metal ion concentrations.

8.1 Data for upland UK organic soils

In the study of Tipping et al. (2003), soil solutions from 98 upland UK soils were sampled, analysed for total dissolved metal concentrations, and speciated by application of WHAM / Model VI to obtain free metal ion concentrations. Comparison with the critical limits of Section 5 showed that 14 of the soils exceeded the critical limit for Cd, and 63 for Pb. It should be noted however, that for Cd the data set included sites deliberately chosen because of their naturally high Cd levels. The majority of the Pb exceedances were in acid soils, whereas for Cd the exceeding soils were alkaline (pH > 7). The large number of exceedances for Pb can be attributed to widespread mining and smelting activities in the UK uplands in the past.

8.2 UK upland surface waters

Lawlor and Tipping (2003) reported free metal ion concentrations for upland waters in northern England. The results are shown in the following Table, together with critical limit values.

	pH	log $[Cd^{2+}]$	log $[Cd^{2+}]_{CLim}$	log $[Pb^{2+}]$	log $[Pb^{2+}]_{CLim}$
UDV D3	5.1	-9.2	-7.8	-8.7	-8.8
UDV D5	5.6	-9.2	-8.1	-9.0	-9.2
UDV D8	7.1	-10.0	-9.3	-10.7	-10.2
GDF X	4.9	-9.6	-7.6	-8.8	-8.7
Great Y	6.8	-9.7	-9.0	-10.0	-10.0

The waters are all below the critical limit for cadmium, but almost exactly on the critical limit for lead. Again, the high $[Pb^{2+}]$ values probably reflect localised mining and smelting activities in the past.

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WHAM6 Website http://windermere.ceh.ac.uk/Aquatic_processes/wham/

Annexe 3.

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Modelling Al competition for heavy metal binding by dissolved organic matter in soil and surface waters of acid and neutral pH

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Abstract

Published field data on the activity of Al^{3+} (a_{Al3+}) in temperate soil and surface waters of pH 3.3 to 7.1 have been assembled, and empirical equations describing the dependence of log a_{Al3+} on pH derived. For soils, two equations are necessary, one describing mineral, or high-Al, soils, and the other low-Al soils. In each case, the data at higher pH (> 5.5 or 6) can be described with a limiting relationship in which a_{Al3+}/a_{H+}^3 was constant, while at lower pH the a_{H+} exponent is smaller, 1.02 for low-Al soils, and 1.59 for high-Al soils. The majority of data for surface waters can be represented by a single equation, involving either a limiting a_{Al3+}/a_{H+}^3 value, or a quadratic expression. Exceptions are acid bog waters, which have appreciably lower values of a_{Al3+} than other waters. For each equation, estimates of uncertainty are derived. The equations have been used to estimate competition by Al^{3+} and $AlOH^{2+}$ for the binding of heavy metals (Cu, Zn, Pb) by dissolved fulvic acid under natural conditions, also taking into account competition by Ca and Fe(III) species. The simulations suggest that Al significantly decreases the extents of organic complexation of all three metals, but that the concentrations of Cu^{2+} and Pb^{2+} are substantially more sensitive to competition than is the concentration of Zn^{2+}.

Key words

Aluminium, chemical speciation, heavy metals, modelling, soil waters, surface waters

1. Introduction

The complexation of heavy metals by natural organic matter, especially humic substances, is an important process in natural waters, sediments and soils. Modelling of the interactions has improved significantly in recent years, as more data have been gathered, and comprehensive models developed (Tipping, 2002). An important factor has been the recognition of the presence of high affinity binding sites for metals in organic matter, present in comparatively small amounts. In laboratory experiments carried out in simple electrolyte solutions and with organic matter having been treated to remove interfering metals, such sites appear highly significant for metals present at trace concentrations (Benedetti et al., 1995). However, the role played by these sites in natural systems will be of less importance if competition effects are significant, the most likely candidates to exert such effects being major divalent cations (Mg^{2+} and Ca^{2+}) and Al^{3+} and Fe^{3+} and their hydrolysis products (Tipping et al., 2002).

In attempting to predict heavy metal speciation in soil and surface waters, using ion binding models for humic matter, ideally the activities of Al and Fe(III) species should be known, or the total truly-dissolved concentrations of the two metals. In the case of Fe(III), the competitive effect can be calculated by assuming the solutions to be in equilibrium with $Fe(OH)_3$ to obtain activities of the key competing ions such as Fe^{3+} and $FeOH^{2+}$. This is justified by the ubiquity of colloidal iron (hydr)oxides in freshwaters and soils. For Al however, the situation is less clear. Whereas some studies indicate that soil Al^{3+} activity is governed by mineral dissolution (Zysset et al., 1999; Gustafsson et al., 2001), others report pH - a_{Al3+} relationships that are inconsistent with such a control (Cronan et al., 1986, Tipping et al., 1995; van Hees et al., 2001). Similar inconsistency exists in the data for surface waters. Given the uncertainty with regard to Al^{3+} activity control, a more empirical approach may prove useful, and this is the basis of the work described here. The aim is to analyse available data for dissolved Al in soils and waters to establish empirical pH – a_{Al3+} relationships that can be used to predict the competitive effects of Al towards the binding of heavy metals by dissolved organic matter.

2. Speciation modelling

The calculations were performed using WHAM / Model VI, based on WHAM (Tipping, 1994), with Humic Ion Binding Model V replaced by Model VI (Tipping, 1998). Model VI uses a structured formulation of discrete, chemically-plausible, binding sites for protons, in order to allow the creation of regular arrays of bidentate and tridentate binding sites for metals. Metal aquo ions (Al^{3+}, Fe^{3+}, Cu^{2+} etc.) and their first hydrolysis products ($AlOH^{2+}$, $FeOH^{2+}$, $CuOH^+$ etc.) compete with each other, and with protons, for binding. The same intrinsic equilibrium constant is assumed to apply to the aquo ion and its first hydrolysis product. The intrinsic equilibrium constants are modified by empirical electrostatic terms, that take into account the attractive or repulsive interactions between ions and the charged macromolecule. Parameter values were given by Tipping et al. (2002). The humic ion-binding model is combined with an inorganic speciation model, the species list and constants for which were given by Tipping (1994). The inorganic reactions in this database are restricted to monomeric complexes of metals. Ionic strength effects on the inorganic reactions are taken into account using the extended Debye-Hückel equation. Temperature effects on reactions between inorganic species are taken into account using published or estimated enthalpy data, but in the absence of experimental information, reactions involving humic substances are assumed to be independent of temperature. Tipping (1998, 2002) showed that the model can account for the great majority of published data sets describing either proton binding by humic matter or the binding of individual metals. Results from laboratory experiments involving competition for binding between metal ions and protons, and between different metal ions, have also been successfully accounted for.

Previous use of the model to investigate the humic complexation of Al, Fe(III) and heavy metals in surface waters was described by Tipping et al. (2002). In the present work, the model was applied in two ways. Firstly, in analysing the published field data, it was used to estimate activities of Al^{3+}, given the total Al concentration, pH, and other solution variables. Secondly, in predicting competition effects, activities of Al^{3+} and Fe^{3+} were taken as input values, and the model used to calculate the total dissolved concentrations, notably including amounts of metal bound to humic matter. In the second case, speciation of Ca and heavy metals was computed from total dissolved concentrations.

3. Field data for Al^{3+} activity

Data for soil waters were collated from 15 published studies (Table 1). Most of the data were from field measurements obtained using lysimeters, but those from the two studies of Adams et al. (1999, 2001) were obtained by centrifugal separation of pore waters in the laboratory. All the studies refer to field sites in the temperate or boreal zones. In most cases, monomeric organic aluminium was measured using the method of Driscoll (1984), and monomeric inorganic Al determined from total by difference, but other techniques were used by Liator (1987), LaZerte (1989), Adams et al. (1999, 2001) and Maitat et al. (2000). The soil waters studied by Mulder et al. (1987) were sufficiently high in dissolved Al, and low in DOC, that organic complexation could be neglected. In 8 of the 15 studies, values of pH and Al^{3+} activity or concentration at field temperature were presented by the authors in the original publications. In two studies, total concentrations of Al^{3+} and its hydrolysis products were provided, and Al^{3+} activities were calculated using WHAM / Model VI. In four cases where concentrations of total inorganic Al were reported, Al^{3+} activities were again calculated with WHAM / Model VI, assuming a temperature of 10°C, but now taking into account Al complexation by sulphate and fluoride, either using total ligand concentrations provided by the authors, or in two cases (Nilsson and Bergkvist, 1983; Funakawa et al., 1993) assuming a total fluoride concentration of 2 μM. The data presented by LaZerte (1989) referred to speciation calculations performed for a temperature of 25°C; these were recalculated for 10°C using WHAM / Model VI. Furthermore, the data obtained by LaZerte (1989) were so numerous that individual values could not be derived from the published figures; therefore, representative pairs of pH and Al^{3+} activity were selected. The numbers of data points from each study shown in Table 1 refer to the product of the number of different sites and the number of soil horizons sampled at each site. In all cases the values are time-averaged or spatially-averaged, or refer to bulked samples, and therefore, although the data analysis presented here is based on 157 points, these actually represent some 2000 individual samples. A data set published by van Hees et al. (2001) was not used because it referred only to Swedish podzols and would therefore have biased the overall results; instead the data were used to test relationships derived from the main data. Similarly, Al^{3+} activities calculated by Tipping et al. (2003) for solutions obtained from upland organic UK soils were used for testing purposes.

Data for surface waters are summarised in Table 2. Again, the sites to which the data refer are in the temperate or boreal zones. As for the soil waters, the analytical speciation method of Driscoll (1984), or a related cation-exchange-based technique, was used in most cases. The exceptions were the study of LaZerte (1989) in which a dialysis technique was used, and the study of Urban et al. (1990), in which only total dissolved Al was determined, Al^{3+} activities being estimated for the present study by the use of WHAM / Model VI. Some of the data sets refer to samples taken from different waters, others to a number of samples from the same water at different times, others to a mixture of the two sampling schemes. The 12 studies provide a total of 302 points for analysis. In two cases (Driscoll et al., 1984; LaZerte, 1989) the data were too numerous for individual values to be extracted from the published figures, and so representative values were selected. For the Northern Appalachian streams and Adirondack lakes data sets of Sullivan and Cosby (1998), every second point was taken, to reduce bias in the overall data analysis.

4. Results

In the following, analytical results are assumed to refer to a temperature of 10°C, which can be considered representative of the field sites. All calculations are performed for this temperature.

4.1 Al^{3+} activities

Fig. 1 shows all the soil solution data, as a plot of log a_{Al3+} against pH. The plot also includes a line of slope –3, to indicate the expected behaviour if a_{Al3+} were controlled by dissolution and precipitation of $Al(OH)_3$. In previous work (Tipping et al., 2003) it was assumed that log $K_{so,25}$ (solubility product at 25°C) was 8.5, corresponding to a value of 9.5 at 10°C if an enthalpy reaction of -107 kJ mol^{-1} is assumed (Tipping et al., 2002). The present data in the higher pH range (> 5.5) suggest a somewhat higher value for the solubility product, although there is appreciable scatter in the data at pH > 6. It should be borne in mind that Al^{3+} activities estimated for the higher-pH soil waters may be unreliable, since degassing of CO_2 from such waters after sampling may lead to increases in pH without re-equilibration of Al with soil solid phases, leading to dissolved Al concentrations that are unrepresentatively high. It is not possible, from the presently available data, to derive a definitive value of log $K_{so,}$ but a value of 10.0 at 10°C can be tentatively proposed. With this value adopted, the issue becomes how to represent the observations at lower pH values.

Considering only the 132 data points for pH ≤ 5.5, the soils were placed into three categories, namely organic topsoils, mineral soils, and others. Organic topsoils (total = 33) were those classified as O horizons, and/or having organic matter contents greater than 10%. Mineral soils (total = 89) were those with organic matter contents of less than 10%, or classified as brown soils, or the B and C horizons of podzols. Into the "others" category (total = 10) were placed podzol A and E horizons, and one sample from a depth of 8 cm in a dystric cambisol.

Data for mineral soils are plotted together in Fig. 2. They can be fitted with the following linear equation

$$\log a_{\mathrm{Al3+}} = -1.59\,pH + 2.22 \qquad (1)$$

with $r^2 = 0.78$ and RMSD (root mean squared deviation) in log $a_{Al3+} = 0.44$. The number of data points is sufficiently large that the 95% confidence interval for prediction of log a_{Al3+} from pH is well-defined by taking ± 2 × RMSD, instead of the strictly-correct hyperbolic confidence bands. The figure also shows the plot of a_{Al3+} vs. pH for control by $Al(OH)_3$ with log K_{so} = 10 (at 10°C), which crosses the regression line at pH 5.5. Uncertainty in the log K_{so} value is set to ± 1 log unit.

The range of log a_{Al3+} values predicted by equation (1) at low pH, and by the solubility relation at higher pH, including the uncertainty range, includes 98% (205 out of 210 points) of the data given by van Hees et al. (2001) for the B and C (i.e. mineral) horizons of Swedish podzols.

Data for organic topsoils and for soils in the "others" category fall in the same range, and are plotted together in Fig. 3. The values are much more scattered than those for the mineral soils, and a strong trend does not emerge, although the slope is highly significant ($p < 0.001$). The two categories of soil are designated "low-Al" (and for consistency, the mineral soils are called "high-Al"). The combined data set of 43 points for the low-Al soils gave the following regression equation:

$$\log a_{\mathrm{Al3+}} = -1.02 pH - 1.94 \qquad (2)$$

with $r^2 = 0.28$ and RMSD in log $a_{Al3+} = 0.91$. The regression line crosses the line for log K_{so} = 10 at pH 6.0. The uncertainty range is large, covering ± 1.82 log units, and this reflects the high variability in these soils. Consequently, there is overlap in the predictions of equations (1) and (2), the upper 95% level of equation (2) exceeding the mean value of equation (1) for pH > 4.1. Equation (2) and its uncertainty bands, and the 10.0 solubility line, with a range of ± 1.0, include all the E horizon data (162 points) from van Hees et al. (2001) for Swedish podzols (see Section 3). The data of Tipping et al. (2003) for UK upland organic soils with pH ≤ 5.5 are also covered (63 out of 65 points).

Data for a_{Al3+} in surface waters are plotted in Fig. 4. For pH > 6, a limiting solubility product of 9.5 (at 10^{o}C) can reasonably be proposed, in agreement with the value of 8.5 at 25^{o}C chosen previously (Tipping et al., 2002). After omitting points with pH > 6 and the six low-pH, high DOC, outliers identified in the diagram, the remaining 263 points give the following regression line:

$$\log a_{\mathrm{Al3+}} = -1.83\mathrm{pH} + 2.73 \qquad (3)$$

for which $r^2 = 0.68$ and RMSD = 0.60. Equation (3) crosses the line for log K_{so} = 9.5 at pH 5.8. The value of –1.83 for the slope of equation (3) is at the lower end of the range of values (-1.82 to –2.34) reported by Sullivan and Cosby (1998) for north American study areas. An alternative way to describe the surface water data is to fit the whole data set, making no assumptions about mineral solubility control. As shown in Fig. 4B, a good fit is provided by the following quadratic curve:

$$\log a_{\mathrm{Al3+}} = -0.49\mathrm{pH}^2 + 3.26\mathrm{pH} - 10.27 \qquad (4)$$

with $r^2 = 0.83$ and RMSD = 0.61. In the pH range up to 7, equation (4) provides very similar results to those obtained with equation (3), combined with log Kso = 9.5. However, the two approaches give divergent results on extrapolation to higher pH; for example, at pH 8 equation (4) predicts log a_{Al3+} = -15.7, whereas the value from the solubility product is –14.5.

4.2 Heavy metal competition effects

The chemical compositions of soil and surface waters were simulated by assuming a background composition of 0.001 M NaCl / 0.00025 M HCl, different pH values being obtained by the inclusion of NaOH or $Ca(OH)_2$. The CO_2 partial pressure was taken to be the atmospheric value for surface water and ten times the atmospheric value for soil water. When Fe(III) solution species were present, their concentrations were calculated by assuming a_{Fe3+} to be controlled by $Fe(OH)_3$ with a log K_{so} of 2.5, which is typical for aged ferrihydrite (Tipping et al., 2002). Dissolved organic matter was represented by fulvic acid (FA), at a concentration of 10 mg l^{-1}.

Fig. 5 shows results for surface waters with Al^{3+} activity following the main trend of Fig. 4 (i.e. not including acid bog waters). The simulations are presented as binding isotherms at pH 4.5 and pH 7, comparing the competitive effects of Ca, Fe and Al on the binding of Cu, Zn and Pb. Activity of Al^{3+} was calculated using equation (3) for pH 4.5 and from K_{so} at pH 7, but nearly identical results were obtained with equation (4). The competitive effects can be gauged by comparing the free metal concentrations at a given value of ν (moles of metal bound per g FA); for example, at both pH 4.5 and pH 7, $[Cu^{2+}]$ for ν_{Cu} = 1 μmol g^{-1} is c. 10^3 times greater in the presence of Al, Ca and Fe than in their absence. In the case of Cu at low concentrations, binding is slightly more sensitive to Fe than Al, but this trend is reversed at higher Cu concentrations, because Al occupies the more abundant FA binding sites to a greater extent than does Fe. Calcium is a far weaker competitor than either Al or Fe. The binding of Zn by FA is most sensitive to Al at pH 4.5, whereas at pH 7 Ca has more effect. (The competition results for Ni and Cd, which also bind comparatively weakly to humic matter, are similar to those for Zn.) For Pb, Al is most important competitor at both pH 4.5 and 7. It can be concluded that competition effects are significant towards each of the three trace heavy metals, and that the contribution of Al is substantial.

Competition by Al is much less significant in acid bog waters, represented by the filled points in Fig. 4. Fig. 6 shows simulated free metal ion concentrations as a function of Al activity at pH 4. In these simulations, a_{Al3+} increases from values typical for the bog waters to values found in other freshwaters. Only when the Al activity reaches 10^{-7} M, which can be considered the transition between the two types of water, does competition become apparent.

Simulations for soil waters (Fig. 7) compare the combined competitive effects of Al, Ca and Fe with those of just Ca and Fe. The simulations were performed with a_{Al3+} calculated from equations (1) or (2), or from log K_{so} = 10.0 at higher pH. Trace heavy metals were assumed to be present at a total dissolved concentration of 10^{-8} M (~ 1 μg l^{-1}). The competitive effects are judged in terms of the concentration of free metal ion and ν. For Cu, there are quite small effects of Al on [Cu^{2+}] in a low-Al soil, and although the effects are larger in a high-Al soil, [Cu^{2+}] is not increased by as much as a factor of 10 at any pH. The effects of Al on ν_{Cu} are seen at low pH, since a very high proportion (close to 100%) of Cu is bound at higher pH. In the case of Zn, there are negligible effects on the free metal ion concentration, since relatively little of the metal is bound, but there are large effects on ν_{Zn} at acid pH. Similar results were obtained with Ni and Cd. Aluminium has appreciable effects on Pb binding at all pH values, increasing [Pb^{2+}] by more than a factor of 10 at higher pH. The effects on ν_{Pb} are again greatest at acid pH, because a high proportion of the metal is bound at higher pH. Very similar competitive trends were found when the calculations were performed for an FA concentration of 50 mg l^{-1}, again with a total trace heavy metal concentration of 10^{-8} M, although the free metal ion concentrations and values of ν were, of course, lower than for 10 mg l^{-1} FA.

Fig. 8 considers the effects of uncertainties in a_{Al3+}, for the two most sensitive of the variables considered in Fig. 7, namely [Pb^{2+}] and ν_{Zn}. In both cases, the greatest range of values is found for acid, low-Al soils, although the ranges at higher pH are also considerable.

5. Discussion

The plot of log a_{Al3+} vs. pH for mineral or "high-Al" soils has a slope of less than 3 at pH < 6 (Fig. 2), indicating that Al solubility is not generally controlled by a single mineral such as $Al(OH)_3$ with a constant solubility product. This does not rule out the possibility that such a control may operate in some soils. For example, Zysset et al. (1999) and Gustafsson et al. (2001) have recently provided convincing evidence for mineral solubility control in podzol B horizons; according to Gustafsson et al. (2001), the mineral in question is $Al(OH)_3$, whereas Farmer and Lumsdon (2002) claim it to be proto-imogolite allophane. However, in other high-Al soils, solution Al is thought to be controlled by complexation / adsorption reactions involving organic matter (e.g. Berggren and Mulder, 1995; Tipping et al., 1995). In general, we cannot tell, simply from the Al^{3+} activity and the pH, which control is operating. Thus, although equation (1) of the present work provides a reasonable description of Al^{3+} activity in a wide range of high-Al soils, this does not mean that a common solubility control mechanism applies. The equation should therefore be thought of only as a convenient means of summarising the available field data. It should also be noted that the equation is not claimed to predict a_{Al3+} - pH relationships that result from laboratory experiments in which a soil sample is titrated with acid or base; such relationships would be governed by the total, constant, amount of reactive Al in the system, whereas equation (1) summarises conditions generated by a range of different soils.

Equation (2) provides an approximate guide to Al solubility in low-Al soils, but there is wide variability in the prediction, probably because the loading of Al onto organic matter, responsible for controlling Al^{3+} activity by sorption / desorption reactions, can vary substantially, leading to a wide range of log a_{Al3+} - pH relationships. For such soils, prediction of a_{Al3+} is inevitably imprecise, unless additional information about the Al loading can be obtained (cf. Cronan et al, 1986).

Few of the available data for soil waters refer to pH values greater than 6, and for reasons given in Section 4, those data are considered the least reliable. Therefore the assumption has been made that $Al(OH)_3$ solubility control applies at the higher pH values. However, aluminosilicate minerals may also play a role in determining Al^{3+} activity. Soils of neutral pH have received little attention in recent research into environmental aluminium chemistry, where the focus has been on acid systems with high Al concentrations. Nonetheless, aluminium in neutral soils is evidently important with regard to competition effects with trace metals (Fig. 7), and there is a need for work to establish reliable values of a_{Al3+} for such soils. Whereas mineral control of a_{Al3+} seems reasonable for neutral soils, it may not operate for surface waters. Thus, although the available data (Fig. 4) can be described by assuming $Al(OH)_3$ control at pH > 6, just as good a description is provided by a continuous quadratic function (equation 4). However, the two models give divergent predictions for pH values greater than 7, and, as with soils, this highlights the need for the determination of Al^{3+} activities at higher pH.

The simulations of competitive effects with heavy metals (Section 4.2) suggest that Al contributes significantly for each of the three metals considered. The binding isotherms (Fig. 5) of Zn at low pH, and of Pb at both low and neutral pH, are especially sensitive to the presence of Al, while for Cu, Al exerts a similar effect to that of Fe(III). Consideration of the simulations of Fig. 7 shows that Al has appreciable effects on ν_{Cu}, ν_{Zn} and ν_{Pb}, more so for high-Al soils.

However, when competition is assessed in terms of pH variations in free metal ion concentration (Fig. 7), it is seen that Zn^{2+} is insensitive to competition effects, because relatively little of the total metal is organically complexed. Of the two strongly binding metals, Cu and Pb, the latter is more sensitive to Al competition. These conclusions also apply to surface waters.

In a previous study (Tipping et al., 2002), competition effects of Al towards trace metals in surface waters were assessed by assuming a_{Al3+} to be controlled by $Al(OH)_3$ with log $K_{so} = 9.5$ at 10°C. It is evident from the plots in Fig. 4 that this will have overestimated competition by Al, especially in the acid pH range, and even more so for acid bog waters, where Al has virtually no effect on trace metal free ion concentrations (Fig. 6). These considerations, and comparison of the simulated results for low- and high-Al soils, show that it is important to decide upon the Al status of a soil or surface water when using a chemical speciation program such as WHAM / Model VI to estimate trace metal speciation. In the absence of detailed chemical information on the composition of a soil or surface water, the equations for Al^{3+} activity presented here should provide a useful guide.

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Table 1 Summary of data for soil waters. The soil designations and horizons are as given in the original publications. [a] Number of data points.

Ecosystem type and location	**Soil type(s)**	**pH**	**- log a_{Al3+}**	**n[a]**	**Reference**
Forest, Sweden	Podzol	3.8 – 4.6	4.3 – 7.5	12	Nilsson and Bergkvist, 1983
Forest, New Hampshire, USA	Spodosol	3.6 – 5.2	5.4 – 7.1	10	Driscoll et al., 1985
Alpine meadow and forest, Colorado, USA	Spodosolic Cryochrept	5.5 – 6.9	5.3 – 9.1	6	Liator, 1987
	Typic Cryumbrept	5.4 – 6.1	5.7 – 6.6	6	
Forest, Netherlands	Haplaquept	3.4 – 4.5	3.2 – 5.1	4	Mulder et al., 1987
	Dystrochrept	3.3 – 4.0	3.2 – 3.9	5	
	Udipsamment	3.7 – 4.3	3.5 – 4.4	5	
Forest, Washington, USA	Spodosol	3.9 – 5.5	5.2 – 7.5	9	Dahlgren and Ugolini, 1989
Forest, Ontario, Canada	Podzol	4.1 – 5.7	4.9 – 8.0	16	LaZerte, 1989
Forest, Spain	Entic and Typic Haplumbrpet	4.8 – 5.6	6.0 – 8.4	6	Alvarez et al., 1992
Forest, Wales	Podzol	3.8 – 4.4	4.3 – 5.4	6	Reynolds et al., 1992
	Gley	3.7 – 4.3	4.4 – 5.4	6	
Forest, Japan	Podzol	3.9 – 5.1	4.6 – 5.5	6	Funakawa et al., 1993
	Brown forest soil	4.5 – 5.2	4.5 – 4.7	6	
Forest, Maine, USA	Spodosols	3.5 – 4.5	4.4 – 5.4	4	Lawrence and David, 1997
Pasture, New Zealand	Brown and recent soils	5.9 – 6.3	7.4 – 8.1	6	Adams et al., 1999
Forest, Sweden	Inceptisol	4.6 – 4.8	4	2	Berggren, 1999
	Spodosol	3.7 – 4.1	3.9 – 4.1	4	
Forest, Belgium	Dystric cambisol	3.6 – 6.7	5.1 – 10.9	6	Brahy et al., 2000
Forest, France	Podzol	3.5 – 7.1	5.5 – 10.2	3	Maitat et al., 2000
	Acid brown earth	4.0 – 4.6	4.5 – 4.9	3	
Grassland and forest, New Zealand	Brown soils	4.0 – 5.8	4.5 – 7.1	26	Adams et al., 2001

Table 2 Summary of data for surface waters

Location	**pH**	**-log a_{Al3+}**	**n**[a]	**Reference**
Québec lakes, Canada	4.5 – 7.0	5.7 – 13.5	18	Campbell et al., 1984
Adirondack lakes, USA	4.0 – 7.1	5.1 – 13.0	13	Driscoll et al., 1984
Falls Brook, New Hampshire, USA	4.7 – 6.3	5.0 – 10.1	34	Hooper and Shoemaker, 1985
De la Trinité River, Québec, Canada	4.4 – 6.9	6.0 – 10.3	16	Hansen and Campbell, 1987
Upland streams in northern England	3.9 – 6.0	5.2 – 8.4	34	Tipping et al., 1988
Lakes and streams, Ontario, Canada	4.3 – 6.9	5.3 – 10.6	17	LaZerte, 1989
Massachusetts streams, USA	4.2 – 5.5	4.9 – 7.5	34	McAvoy, 1989
Nova Scotia lakes, Canada	4.0 – 6.1	5.0 – 8.2	33	Urban et al., 1990
Forest streams in Wales	4.7 – 5.1	5.0 – 5.2	10	Reynolds et al., 1992
Northern Appalachian streams, USA	4.0 – 6.0	4.6 – 9.5	33	Sullivan and Cosby, 1998
Catskill Streams, USA	4.2 – 5.9	5.4 – 9.0	28	Sullivan and Cosby, 1998
Adirondack lakes, USA	4.4 – 5.9	5.4 – 9.0	32	Sullivan and Cosby, 1998

[a] Number of data points.

Figure captions

Fig. 1 Soil Al^{3+} activities as a function of pH. The line represents the solubility relationship for $Al(OH)_3$ with log K_{so} = 10.0.

Fig. 2 Data for mineral (“high-Al”) soils at pH ≤ 5.5. The solid line is the linear regression (equation 1); the dashed line represents the solubility relationship for $Al(OH)_3$ with log K_{so} = 10.0.

Fig. 3 Data for low-Al soils at pH ≤ 5.5. The solid line is the linear regression (equation 1); the dashed line represents the solubility relationship for $Al(OH)_3$ with log K_{so} = 10.0.

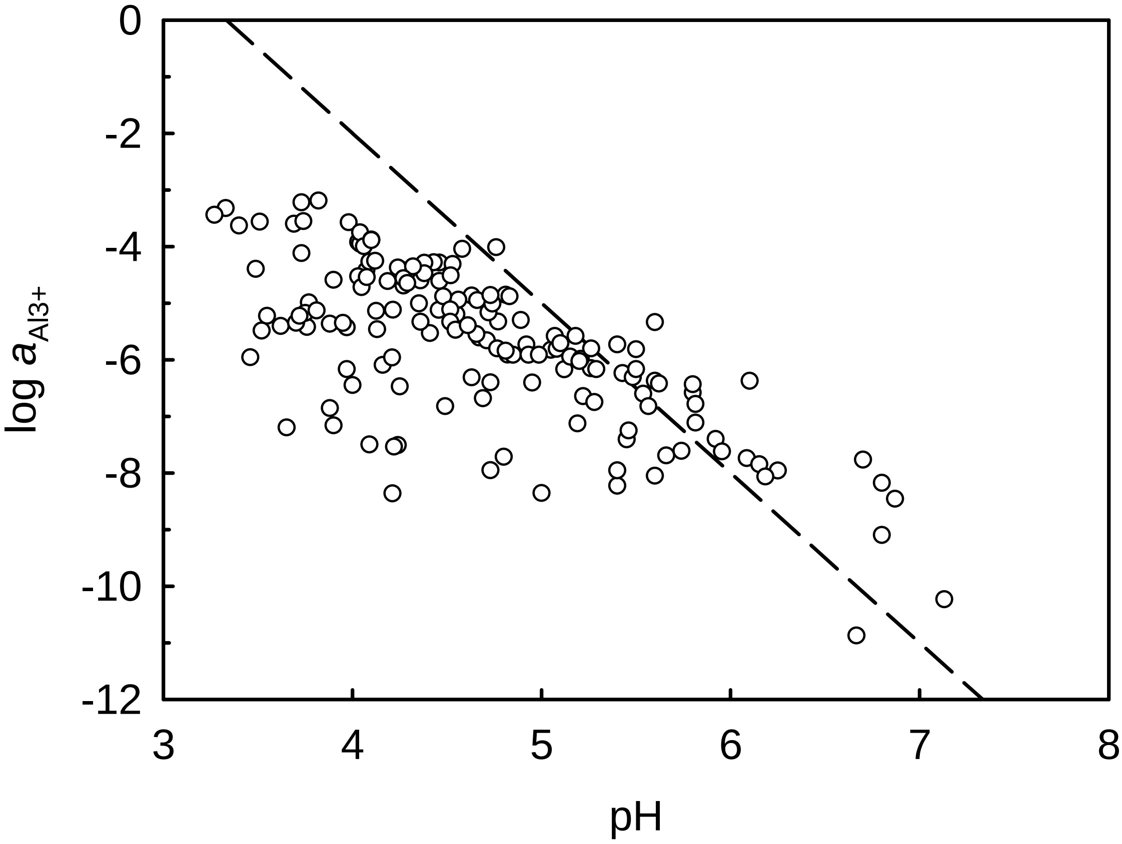
Fig. 4. Data for surface waters. In panel A, a linear regression (equation 3) represents the data at pH < 5.8, while at higher pH solubility control by $Al(OH)_3$ with log K_{so} = 9.5 is assumed. In panel B, the whole data set is fitted by equation (4). The six solid points represent acid bogwaters, and were not included in the fitting.

Fig. 5 Simulated binding of Cu, Zn and Pb by fulvic acid in surface waters (see Section 4.2). The ν of the y-axis is moles of metal bound per gram of fulvic acid. Each panel shows five binding isotherms; no competitors, competition by Ca, Al and Fe(III) individually, and competition by their combination.

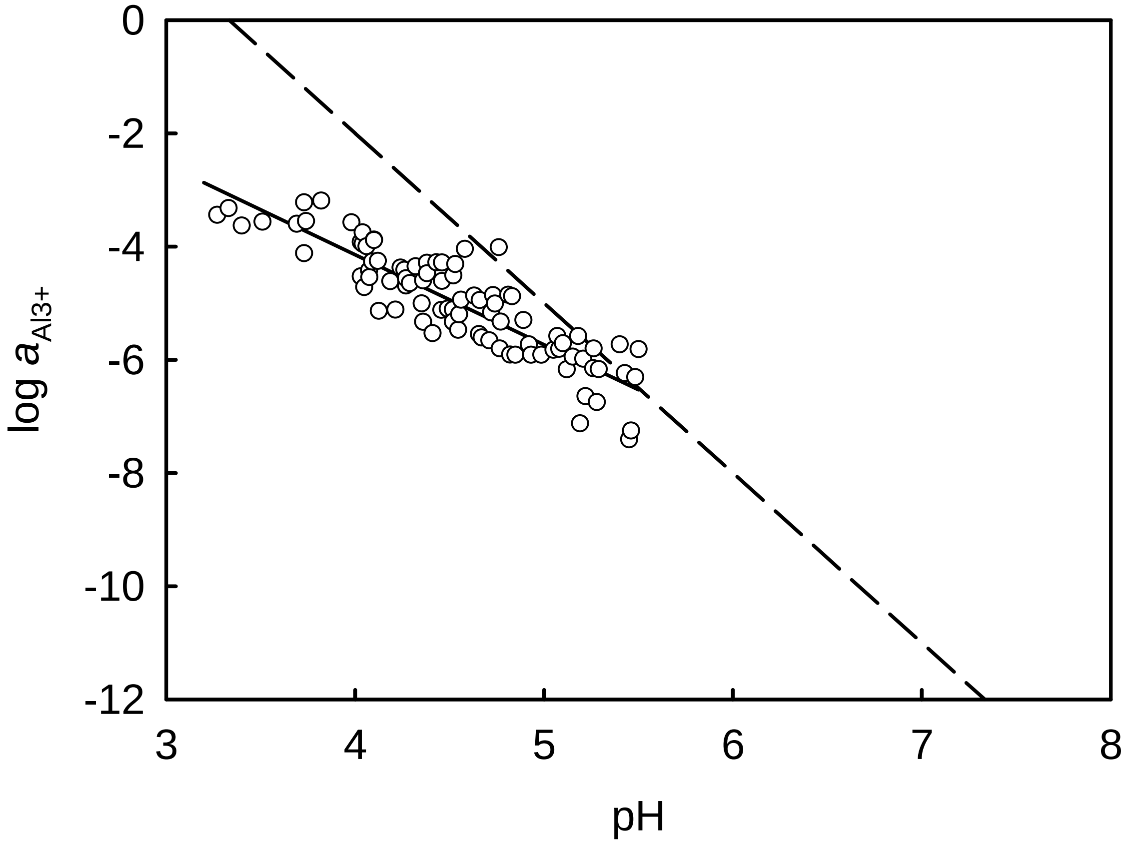
Fig. 6 Simulated concentrations of Cu^{2+}, Zn^{2+} and Pb^{2+} in a pH 4 water containing 50 mg l^{-1} fulvic acid, and different activities of Al^{3+}. Each trace metal is present at a total dissolved concentration of 10^{-8} M.

Fig. 7 Simulated concentrations of Cu^{2+}, Zn^{2+} and Pb^{2+} (left panels) and ν (right panels), in soil waters containing 10 mg l^{-1} fulvic acid and 10^{-8} M in each trace metal. The solutions contain increasing Ca with increasing pH, and are in equilibrium with $Fe(OH)_3$ (see text). In each panel, a plot is shown for zero Al absent, for Al activity in low-Al soil and high-Al soil, and for Al activity controlled by $Al(OH)_3$ with log K_{so} = 10.0.

Fig 8 Effects of uncertainties in Al^{3+} activity (Section 4.1) on predicted competition for trace metal binding. The results ($[Pb^{2+}]$ in the upper panel, ν_{Zn} in the lower panel) are for zero Al, Al^{3+} activity at the lower uncertainty limits in low-Al and high-Al soils, and Al^{3+} activity at the upper uncertainty limit in high-Al soils. The results for the upper Al^{3+} uncertainty limit in low-Al soils are virtually the same as those for the high-Al case.



Tipping / Fig. 1



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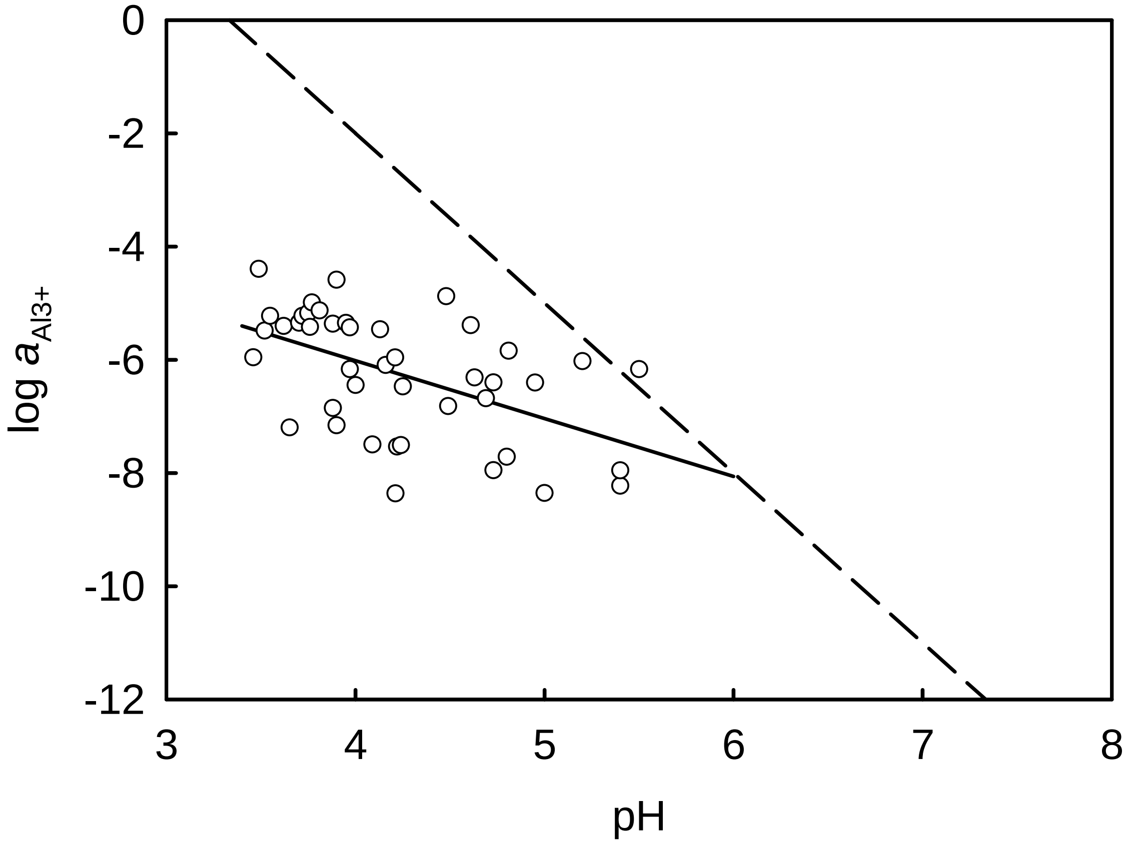

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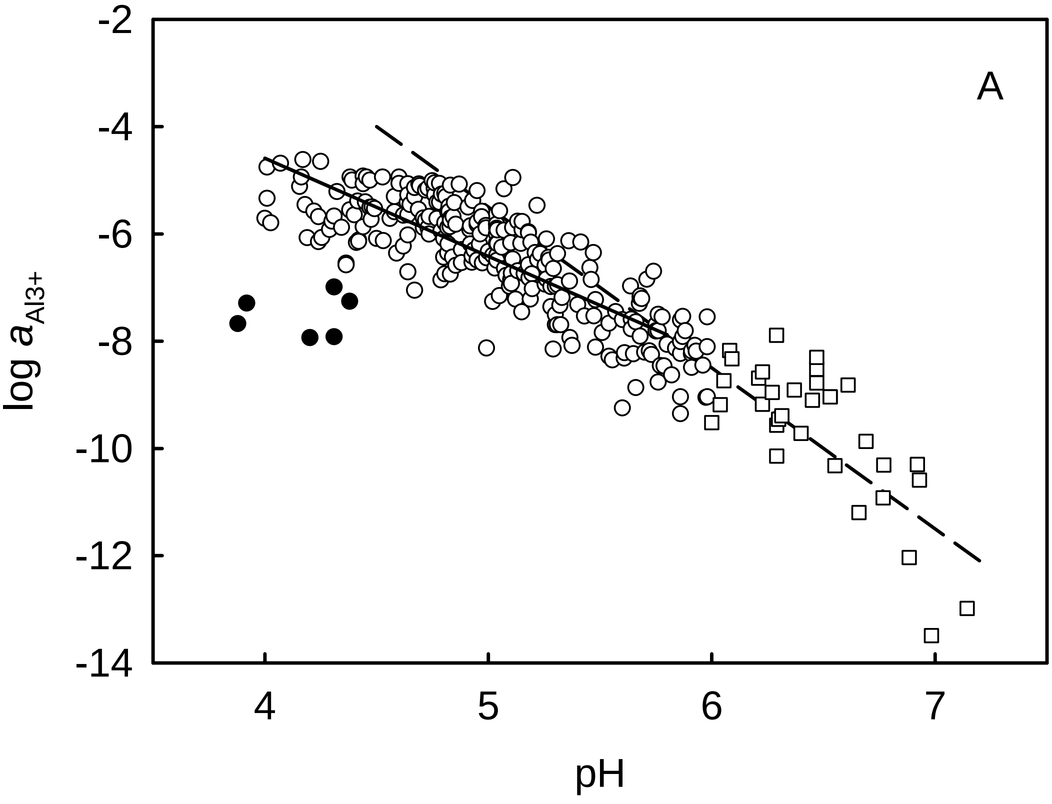

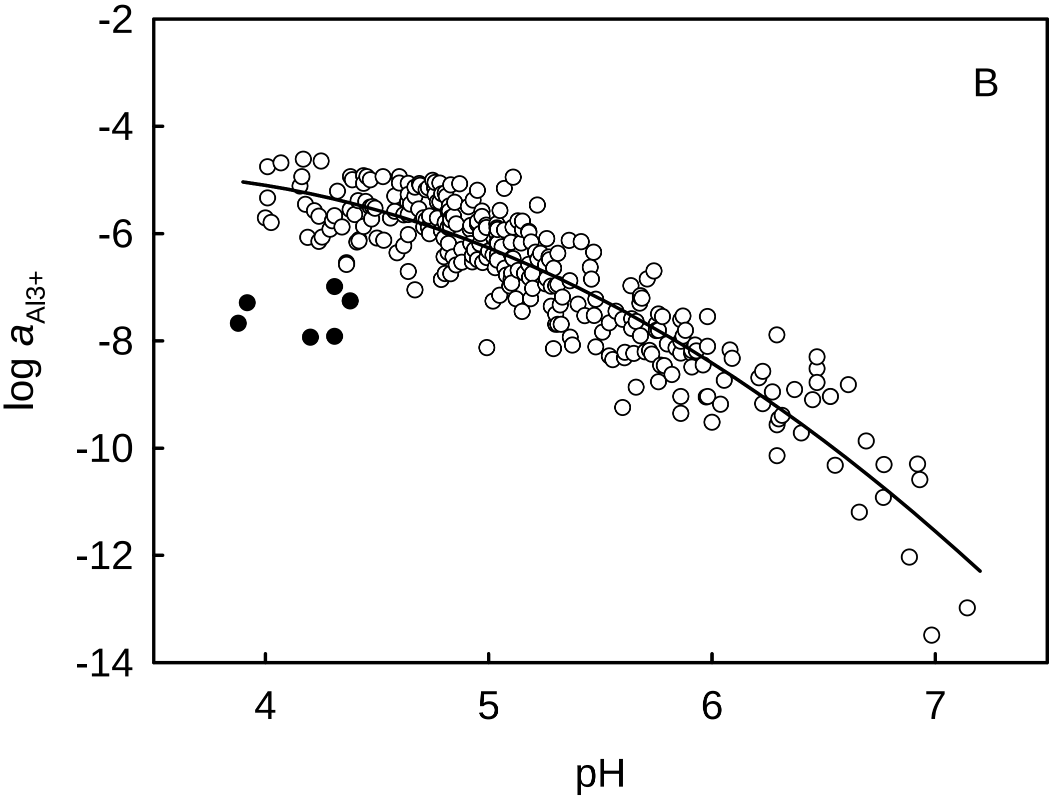

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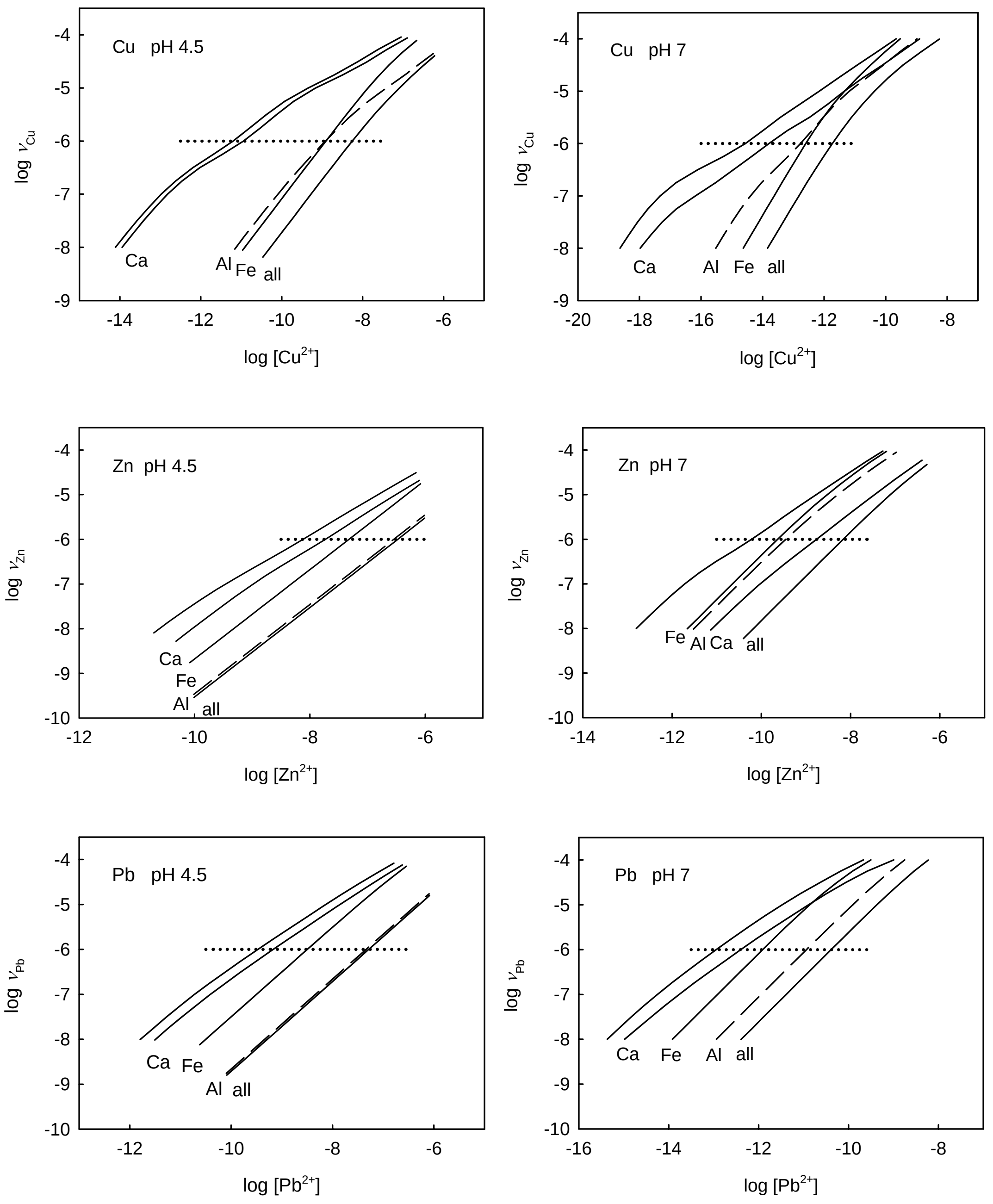

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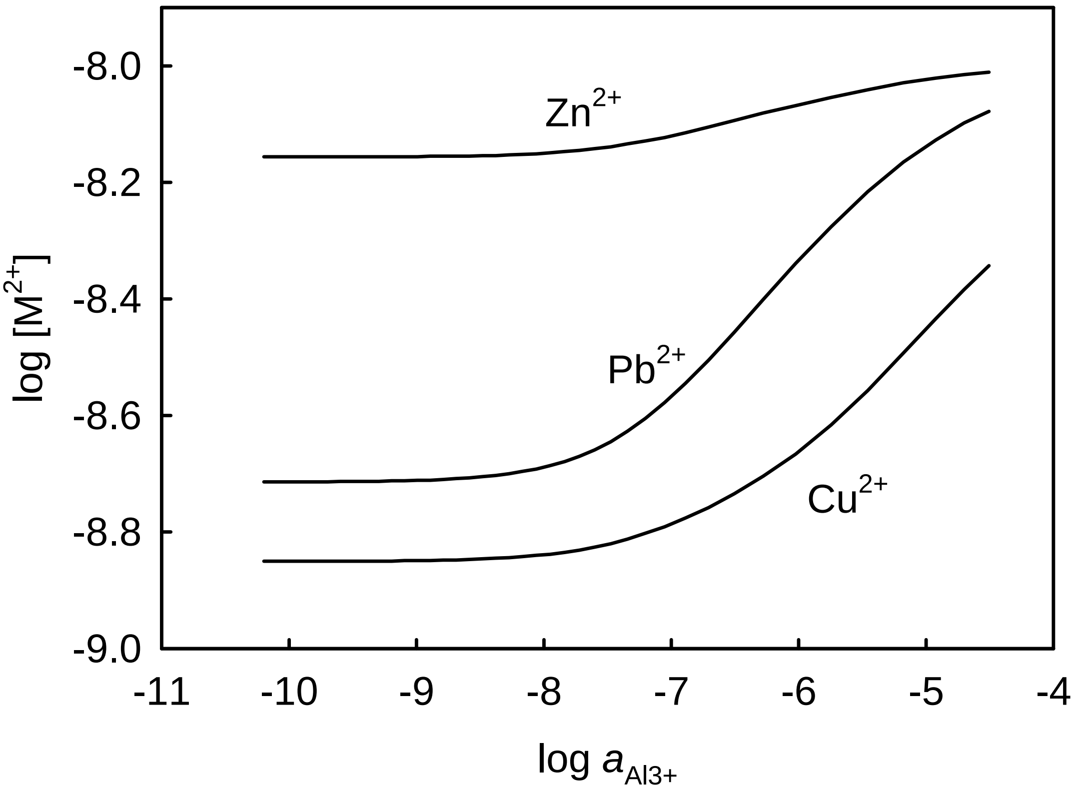

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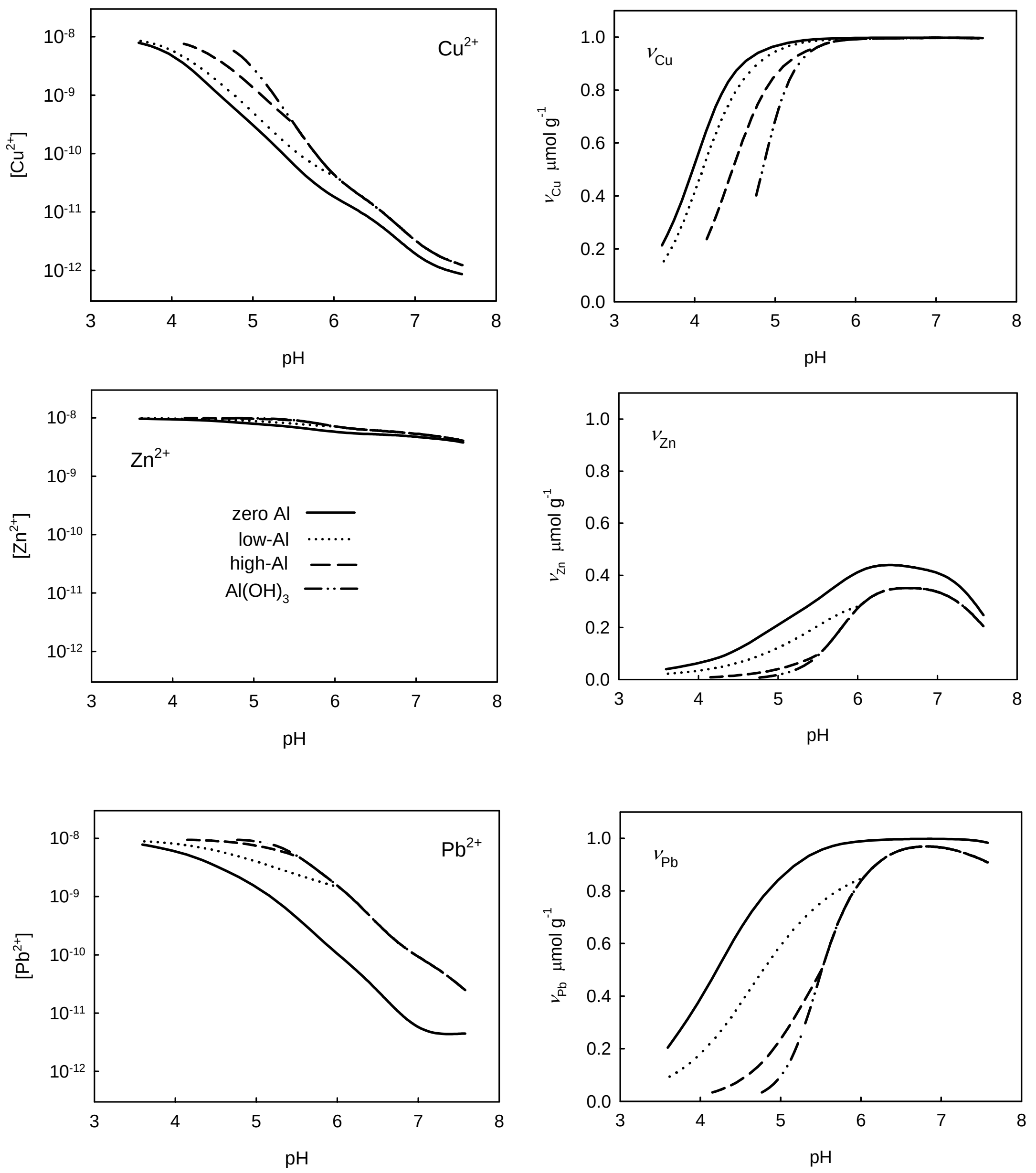
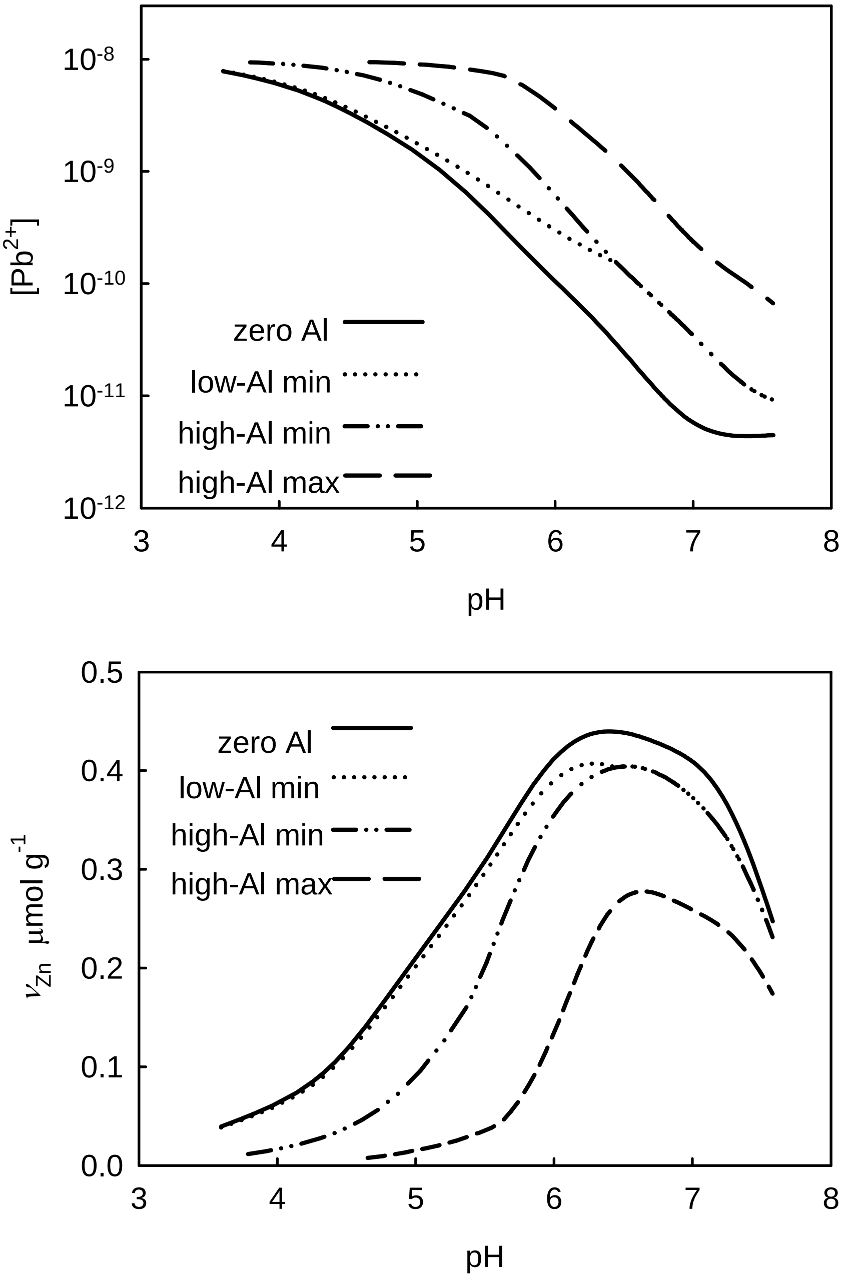


Tipping / Fig. 7



Tipping / Fig. 8

ANNEXE 4: ANALYTICAL METHODS USED IN DYNAMIC MODELLING STUDIES

A.J.Lawlor and E.Tipping

Metal deposition

Bulk deposition collectors consisted of a funnel (14 or 28 cm diameter) and a bottle (5 l), both made of polypropylene. For easy and efficient cleaning and acid washing, each funnel was welded onto, and cut off parallel to, the inside of a bottle lid (Just Plastics, London). Polyethylene inserts provided a watertight seal for the bottles and aided transport and preparation. Prior to deployment, the collectors and associated equipment were cleaned with 1 M hydrochloric and nitric acids to remove contaminating metals. Polyethylene gauze filters were placed in the funnels to prevent the collection of local debris (e.g. insects and grass seeds). Bulk deposition collectors were transported to the field sites triple-bagged, the outer two bags covering the entire apparatus and the inner (which had been acid-washed) only the funnel and debris filter. Duplicate collectors were placed on poles at a height of 1.5 m, away from potential sources of local contamination such as trees, buildings and roads, and within an enclosure to prevent disturbance by grazing animals. To minimise contamination, a strict protocol for changing the bulk deposition collectors was followed, based on that of Ross (1984). On return to the laboratory, the collection bottles were weighed to determine precipitation volume and then acidified with 0.2 % (v/v) nitric acid to pH <2. After sealing and re-bagging, the bottles were periodically inverted over a two-day period to release any adsorbed metal ions, then the acidified samples were transferred to acid-washed polyethylene bottles and stored at 4°C. Bulk precipitation samples collected using 28 cm diameter funnels were prepared to allow the analysis of “dissolved” and acid-recoverable metal fractions.

Sample preparation for metal analysis was carried out under ISO Class 5 conditions (Atlas, Pathfinder) using powder-free clean-room gloves. Double sub-boiling point distilled nitric acid (Baker, Ultrex II) and ultrapure Milli-Q water (Millipore) were used throughout. Surface water samples requiring the analysis of metal concentrations were prepared so that the acid-recoverable and “dissolved” (i.e. fulterable) fractions could be determined. The acid-recoverable fraction was determined after leaching with 1 % (v/v) nitric acid for a period of 24 hours and includes both particulate and “dissolved” forms. The “dissolved” fraction was operationally defined as that which passes through a 0.45 µm membrane filter. The filters (Puradisc PP 25, Whatman) were sealed polypropylene units, operated under positive pressure. Filtrates were acidified with 1 % (v/v) nitric acid as a preservative and stored in acid washed polyethylene bottles.

Metal concentrations in bulk precipitation were determined by Inductively Coupled Plasma Mass Spectrometry (ICPMS), using a PQ Eclipse (ThermoElemental) instrument. The ICPMS was routinely optimised using ^{115}In to give maximum response with good stability. Batches of samples (typically 60) were only analysed if the short-term stability was better than 5 % RSD for the analytical isotopes (^{27}Al, ^{55}Mn, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{114}Cd, ^{115}In and ^{208}Pb) at a concentration of 1 µg l^{-1}. Operating under standard conditions (i.e. using pneumatic nebulisation) the ICPMS was insufficiently sensitive to allow the analysis of Cd in bulk precipitation and some surface waters, and therefore we employed a desolvating nebuliser (Mistral, TJA Solutions) to allow better detection of this element. The accuracy and precision of the ICPMS method was extensively tested using a certified reference material (CRM), TMRAIN-95 from the National Water Research Institute, Environment Canada. Furthermore, quality control was achieved using this

CRM and an Analytical Quality Control sample (AQC) that consisted of the metals of interest at a concentration of 5 µg l-1 in 1 % (v/v) nitric acid. AQC solutions were prepared from Claritis PPT Instrument Check Standards (SPEX Industries) and analysed at a frequency of one every ten samples. An error of ±10 % was allowed; if the metal results for the AQC fell outside this range the analytical batch was repeated. The figures of merit (accuracy, precision, and detection limits) for the determination of metals by ICPMS are given in Table 1. Field blanks were also analysed on four occasions; 500 cm3 of Milli-Q water were carefully poured into the funnel of a bulk precipitation collector in the field and processed as normal. Results (µg l-1) were typically below the ICPMS method detection limits and were of the order, Mn: <0.3; Ni: <0.2; Cu: <0.2; Zn: <0.5; Sr: <0.1; Cd: <0.1; Ba: <0.2; Pb: <0.1.

Metals in streamwaters

Surface water samples were collected at weekly intervals during the year commencing April 1 1998. Three types of bottle were used: stoppered glass for pH determination, high-density polyethylene for major components (Na, Mg, K, Ca, NH_4, Cl, NO_3, SO_4, SiO_2, conductivity, DOC, and suspended particulate matter), and acid-washed high-density polyethylene for Al and minor metals. Bottles were filled upstream of the sampler to avoid any material disturbed from the streambed, and below the water surface to avoid floating material and the surface film. Samples taken for metal analysis were transported in sealed polyethylene bags to prevent contamination and all bottles were kept in a cool box. Analyses for metals were performed as described above for bulk deposition samples.

Soils

Soils were sampled by digging small pits down to bedrock or collections of large stones. Bulk densities of organic horizons were determined by weighing cut cuboids of known dimensions, and correcting for water content. Bulk densities of mineral horizons were determined by excavating known volumes of the soil pits, separating, weighing and correcting for water content material of particle size < 4mm, and determining the volume of material of particle size > 4 mm from its specific gravity. Carbon, H, N and S contents were determined by elemental analysis with a Universal CHNS-O Vario EL elemental analyser. Soil samples were extracted with 1 mM NaCl at a ratio of 10 g field moist solids to 25 cm^3 solution. The suspensions were shaken overnight, centrifuged (15,000 × g, 30 minutes), and the supernatants taken for the determination of pH (combination glass electrode).

At each catchment, 5 or 6 soil samples were taken, and the data were averaged to obtain a single idealised soil type. Two soil layers were defined (L1 and L2). In catchments with only organic soil (Great Dun Fell, R.Etherow) both were given the same properties, and were of equal thickness. In the other catchments, the upper layer was organic-rich and the lower contained more mineral matter.

Mineral dissolution experiments

Samples of local rocks or stones taken from the study catchments were split into approximate 1 cm cubes. Ten cubes with all fresh surfaces were selected from each sample, and washed ten times each by sonication for 15 minutes in de-ionised water, with three rinses between each sonication. They were then air-dried.

Experiments were performed in 500 ml Teflon bottles, acid washed and pre-weighed before use. The washed rock samples were placed in the bottles, which were reweighed and sample weight calculated. Approximately 250 ml Milli-Q water was added and the les weighed again to determine the total liquid volume. The solutions were then made 0.001 M with respect to HNO_3 by adding 0.156 M HNO_3. The bottles were incubated at 10°C with gentle shaking. Solutions were sampled after 5, 11 and 20 days. Sub-samples were taken for the determination of pH (5 ml), silicon (5 ml), major cations (10 ml) and heavy metals (10 ml). The sub-samples for metals (ICPMS) were acidified prior to analysis.

The samples from Cote Gill were treated separately because they were limestone, and dissolved very quickly. Three replicate samples of limestone rock from the Cote Gill catchment were completely dissolved in 1% HNO3 (Baker Ultrex II).

Solution compositions were determined by ICP-MS (trace metals), ICP-OES (Na, K, Ca, Mg, Fe and Al) and colorimetry (Si).

References

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ANNEXE 5: DESCRIPTION OF CHUM-AM

E.Tipping and S. Lofts

The model used in the present work is CHUM-AM (CHemistry of the Uplands Model – Annual, Metals). It is developed from CHUM (Tipping, 1996), but is simpler with respect to water movements, and takes account of additional biogeochemical processes. Fig. A2.2.1. summarises the model structure, inputs and outputs, and processes, as applied to stream catchments. The model considers a soil-rock profile consisting of three completely mixed layers (L1, L2, L3) through which water percolates, streamwater being drainage from L3. The model is run with annual average input data, and annual average outputs are reported. Some of the processes identified in the Figure are explicitly represented in the model, others are characterised by input data.

Atmospheric deposition

All atmospherically deposited elements and species are in solution on entering the plant-soil system. The dry-deposited gases NH_3, NO_2 and SO_2 dissolve in rainwater to form NH_4^+, NO_3^- and SO_4^{2-} respectively. Deposition of major solutes due to cloud water is taken into account by increasing the measured bulk concentrations by a constant factor.

Carbon cycle

The model does not include an explicit carbon cycling model; instead, the soil carbon contents are specified in the input file, either as steady-state (constant) values or as values for individual years. Elements (N,S, metals) associated with soil organic matter transfer from L1 to L2, to take into account mineralization and water transport losses of carbon from L2. This transfer is specified as an annual fraction. In a peat, where organic matter is transferred from the acrotelm to the catotelm as new organic matter is added to the soil surface, organic carbon is also considered to be lost from L2 (equated with the bottom part of the acrotelm) by downward transfer, along with associated elements.

Annual outputs of organic carbon from L1 and L2, as dissolved organic carbon (DOC) and particulate organic carbon (POC) in percolating water are also specified in an input file. All the organic matter comprises 50% C. The soil pCO_2 is specified either as a constant value or by year. Dissolved CO_2 in percolation water from L2 enters L3, where it may be supplemented by CO_2 from carbonate dissolution. Outgassing of CO_2 occurs in the stream, to a specified partial pressure.

Nitrogen cycle

The model simulates N uptake by, and release from, the plant-soil system in L1. Uptake (mol m^{-2} a^{-1}) is proportional to the combined annual input (mol m^{-2} a^{-1}) of NH_4^+ and NO_3^- :

$$\text{uptake to soil N} \;=\; k_{N1}\,(\text{NH}_4\text{ input} \;+\; \text{NO}_3\text{ input}) \qquad (1)$$

Release of NH_4^+ and NO_3^- (mol m^{-2} a^{-1}) depends upon the size of the pool of soil N (mol m^{-2}) and also on the N/C ratio (mol mol^{-1}) , according to the expression:

$$\text{release of inorganic N} \;=\; k_{N2}\ (\text{N/C})\ \text{soil N} \qquad (2)$$

Thus, the greater the N content of the soil organic matter, the greater is its tendency to release inorganic N. Inorganic N transformations in L1 are accounted for by specifying the fraction of released inorganic N that is NO_3^-, by the constant k_{N3}; the remainder is NH_4. Organic N is transported to and from L2 as dissolved and particulate organic nitrogen; the N/C ratios in DOM and POM are the same as those in bulk soil.

Sulphur cycle

Uptake of sulphur in L1 is proportional to the annual input of SO_4^{2-}, and release is proportional to the pool of soil S, according to the equations:

$$\text{uptake to soil S} \;=\; k_{S1}\ SO_4\ \text{input} \qquad (3)$$

$$\text{release of } SO_4 \;=\; k_{S2}\ (\text{S/C})\ \text{soil S} \qquad (4)$$

Organic S is transported to and from L2 as dissolved and particulate organic sulphur; the S/C ratios in DOM and POM are the same as those in bulk soil.

Hydrology

The volume of water falling onto the catchment in a given year is the total precipitation (P) minus the evaporation (E). Water falling directly onto bare rock is diverted onto the soil surface, so the volume entering the soil profile is given by the expression $(P - E)/(1 - f_R)$, where f_R is the areal fraction of the catchment that is bare rock. Water percolates at a constant rate from L1 to L2 to L3 and then to the stream. Each box is completely mixed; there are no macropores as postulated in the original CHUM. The available pore space in the soil layer is nearly completely emptied and refilled at each step. The number of steps is determined by dividing the annual input volume by the pore space and increasing the result to the next highest integer. At each water replacement step, the equilibrium distribution of chemical species is calculated, solutes are removed in drainage water, and new chemical species are added in input water, and from decomposition and weathering reactions.

Physical transport

The loss of POC from L1 and L2 is specified in the input file (see above), and this governs the transfer of POM, and associated elements, to the stream. Mineral particulates may also be transferred, and their fluxes are also specified as model inputs; however, they do not transport adsorbed elements.

Chemical equilibrium reactions

The chemical "master species", i.e. the inorganic species on which all the chemical reactions are based, are as follows;

Major cations:	H^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Fe^{3+}, NH_4^+
Trace cations:	Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}
Anions and neutral species:	OH^-, Cl^-, NO_3^-, SO_4^{2-}, F^-, CO_3^{2-}, $Si(OH)_4$

In L1 and L2, solutes may bind to organic matter (HA and FA) and to a mineral cation exchanger. The organic matter may be in the solid phase, in solution (DOM) or in suspension (POM). The interactions are described using the soil version of WHAM / Model VI (Tipping, 1998; Tipping et al., 2003a), in which the basic model is modified to treat the high effective concentrations of soil organic matter, as described by Tipping (1994). The model also takes account of reactions among inorganic species in solution. In addition, precipitation and dissolution of $Al(OH)_3$, $Fe(OH)_3$ and carbonates may occur. However, these phases in L1 and L2 are not considered to have active surfaces capable of interacting with solutes, because the natural organic matter has an overwhelming influence.

In L3, the same reactions as in L1 and L2 are possible, together with surface complexation at the surfaces of Al and Fe oxides. Surface complexation of cations is described with the model of Lofts and Tipping (1998). Since $Al(OH)_3$ and $Fe(OH)_3$ have similar surface complexation parameters, the mixed oxide phase in L3 is considered to have constant chemical properties, irrespective of the proportions of $Al(OH)_3$ and $Fe(OH)_3$, and the equilibrium constants used are averages of those derived by Lofts & Tipping (1998) for the individual pure phases. Adsorption of SO_4 and other inorganic anions by the oxides is ignored. Adsorption of FA is described with a Langmuir model. Although FA adsorption by amphoteric oxides in simple electrolyte media is pH dependent (Tipping, 1981; Davis, 1982), the dependence on pH is much reduced, and even reversed, in the presence of Ca^{2+} (Tipping, 1981; Tipping & Heaton, 1983), and presumably also by other multivalent cations including Al species. Moreover, calculated pH values for the L3 layers of the four field sites fell within quite a small range, 4.7 – 6.2 (see below). Therefore the simplifying assumption is made that FA adsorption by oxides in L3 is independent of pH. Thus, we obtain;

$$\mathrm{FA}_{\mathrm{ads}} = \frac{n_{FAOx} K_{FAOx} S_{Ox} [FA_{free}]}{1 + K_{FAOx} [FA_{free}]} \qquad (5)$$

where FA_{ads} is the FA adsorbed in g g^{-1} oxide, $[FA_{free}]$ is the concentration of FA in the aqueous phase (g l^{-1}), and S_{Ox} is the oxide surface area (m^2 g^{-1}). The Langmuir constants n_{FAOx} and K_{FAOx} are assigned values of 10^{-3} g m^{-2} and 10^3 l g^{-1} respectively, on the basis of data published by Tipping (1981). These constants are regarded as only representative, and are used to explore the possible influence of adsorbed FA on the chemistry of percolation water. The adsorbed FA is binds solutes exactly as does FA in solution.

In streamwater, the reactants are the inorganic components, together with DOM and POM. Again, precipitation and dissolution of $Al(OH)_3$, $Fe(OH)_3$ and carbonates may occur.

Chemical weathering

Weathering inputs of major and trace metals, and carbonate, are described with the following equation, based on that of Schnoor & Stumm (1986):

$$\text{weathering rate} = k_{\mathrm{w}}\, a_{\mathrm{H^+}}^{n_{\mathrm{w}}} \qquad (6)$$

The weathering rate is in mol m^{-2} a^{-1}, a_{H+} is the activity of H^+ and k_w and n_w are constants. Note that k_w is simply a calibration parameter, which includes the effects of mineral type and available surface area. Weathering inputs can occur in all three layers.

Removal of oxide surface in L3

The model permits accumulation of oxides to occur in L3, if the export rate of dissolved Al and/or Fe(III) in percolating water is smaller than the combined input rate from L2 and weathering in L3. However, this does not lead to an indefinite accumulation of reactive oxide surface, either because erosion will remove bulk oxide, or because the mineral surface is continually covered by freshly precipitated oxides. These two processes control the reactive oxide surface, and are represented by an annual fractional rate of removal of oxide surface from the system. The removal of Al and Fe is accompanied by removal of inorganic components of the oxide phase, including heavy metals, but not of adsorbed FA.

Uptake and release of metals by vegetation

A model with the same format as those for N and S uptake by the plant-soil system was used, i.e. with an uptake rate coefficient as a proportion of the total deposition, and a first-order release rate coefficient that relates metal loss to the pool of metal in the plant. This is a very simple model, aimed at obtaining some insight into the relative importance of metal sequestration by trees. A more realistic picture would include the uptake of metals from the soil as well as uptake of atemospherically-deposited metal.

Lake sediments

The incorporation of heavy metals into lake sediment was estimated from the following assumed processes;

Metal entry into the sediment by solute exchange from the water column, and adsorption to sediment solids

The chemical composition of the lakewater is calculated by keeping a budget of the total inputs of geochemically-active chemical components and water from the catchment and by direct deposition, and the outflow water. The sediment pore water composition is calculated using WHAM, and assuming the active sorbent in sediment solids to be humic acid. The sediment is assumed to be sufficiently reducing to convert Fe(III) to Fe(II), and sulphate to sulphide; these reactions cause the sediment pH to be higher than that of the overlying water. Solute exchange is described with a simple exchange coefficient.

Metal entry into the sediment by direct deposition to the lake surface of "inert" metal

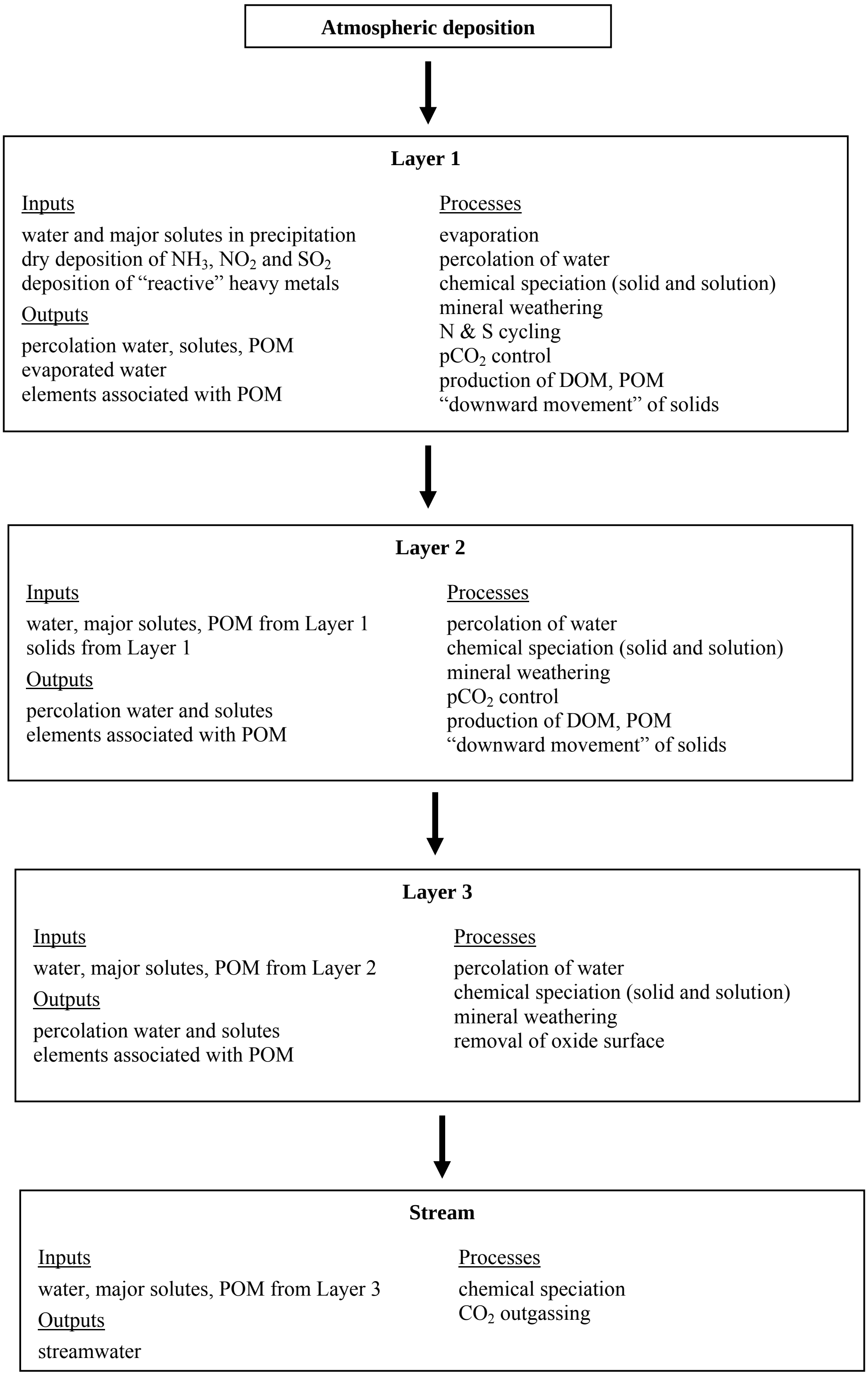
The conventional method of determining metals in deposition, i.e. extraction with 1% nitric acid, does not recover all the deposited metals, but provides an estimate of the "geochemically active" fraction, which may be about two-thirds of the total. In the present modelling work, the remaining metal is considered inert in the catchment soils. However, the method used by Dr Handong Yang to extract metal from the lake sediments involved a stronger extractant (hot, concentrated HNO_3), and this could release the "inert" metal from the sediment. Therefore it was assumed that the inert metal was delivered to the sediment in proportion to the deposition of active metal.

Metal entry into the sediment by release from eroded particles

The Lochnagar sediment contains considerable mineral matter, and this could release metals in the extraction scheme used by Dr Handong Yang. Because the atmospheric deposition of metals at Lochnagar is relatively low, this post-sedimentation weathering input could be significant. We estimated the metal inputs due to eroded mineral matter by assuming the granite at Lochnagar to have typical heavy metal contents (2, 13, 45, 0.06, 49 μg g^{-1} for Ni, Cu, Zn, Cd and Pb respectively), and further assuming that these metals were quantitatively released by the nitric acid extraction procedure.

Metal loss from the sediment by "burial" as the sediment accumulates

The model is used to compute the metal content of the surface sediment, and therefore account must be taken of sediment accumulation, which effectively causes the loss of particles, and associated metals, into the deeper part of the sediment column. This loss is taken into account when calculating the total metal in the surface sediment.



Atmospheric deposition

Layer 1

Inputs

water and major solutes in precipitation
dry deposition of NH_3, NO_2 and SO_2
deposition of "reactive" heavy metals

Outputs

percolation water, solutes, POM
evaporated water
elements associated with POM

Processes

evaporation
percolation of water
chemical speciation (solid and solution)
mineral weathering
N & S cycling
pCO_2 control
production of DOM, POM
"downward movement" of solids

Layer 2

Inputs

water, major solutes, POM from Layer 1
solids from Layer 1

Outputs

percolation water and solutes
elements associated with POM

Processes

percolation of water
chemical speciation (solid and solution)
mineral weathering
pCO_2 control
production of DOM, POM
"downward movement" of solids

Layer 3

Inputs

water, major solutes, POM from Layer 2

Outputs

percolation water and solutes
elements associated with POM

Processes

percolation of water
chemical speciation (solid and solution)
mineral weathering
removal of oxide surface

Stream

Inputs

water, major solutes, POM from Layer 3

Outputs

streamwater

Processes

chemical speciation
CO_2 outgassing

Fig. A2.2.1 Schematic representation of CHUM-AM.

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ANNEXE 6: CONSTRUCTION OF DEPOSITION SCENARIOS FOR THE UPPER DUDDON VALLEY

E.Tipping, L.Shotbolt and S.Lofts

Major chemical components

Long-term deposition scenarios were constructed by the following procedure:

1. Average rainwater concentrations (in equivalents) were calculated from measured recent values. For each year, the average of the total cation and total anion concentrations was calculated, then a charge balance was forced by multiplying each cation concentration by the ratio of total average charge to total cation charge, and performing the corresponding operation for the anions.
2. The overall ratio [Na] + [Mg] / [Cl] in charge-balanced rain was calculated. A value less than the value of 1.054 expected for seawater (Stumm & Morgan, 1996) was interpreted to mean that a contribution of Cl (never more than 5 % of the total) came from anthropogenic emissions, and all the Na and Mg were attributed to the marine source. Marine [K], [Ca] and [SO_4] were calculated from their seawater ratios to marine [Cl]. A ratio greater than 1.054 was taken to indicate the deposition of non-marine Na and Mg (again, only small amounts were required).
3. Following other workers (e.g. Reynolds, 1997, Jenkins & Cullen, 2001), non-marine SO_4 deposition in bulk deposition prior to the period of measurement was assumed to be proportional to S emissions in the UK. The ratio of non-marine [SO_4] to UK S emissions for the period of measurement was determined, and used to estimate [SO_4] in the past, by scaling to the emission data. It was assumed that up to 1600 there had been no excess S deposition, and that between 1600 and 1850 deposition increased linearly. The small amounts of non-marine Cl or non-marine Na and Mg were determined in the same way, i.e. taken to be proportional to S emissions.
4. Marine [Na], [Mg], [K], [Ca], [Cl] and [SO_4] for years before the period of measurement were assigned the average values for the period of measurement.
5. Both NH_4 and NO_3 were assumed to come from non-marine sources, and trends were based on data compiled by Pitcairn et al. (1995). It was assumed that until 1940 concentrations were one-fifth of the recent averages, and that they rose linearly from 1941 to 1970, after which they were constant at the present-day average values.
6. From the values obtained in steps 1 to 5, net acidity terms for each year were calculated as either $[Cl]_{nm} + [NO_3] + 2[SO_4]_{nm} - [NH_4]$, or $[NO_3] + [SO_4]_{nm} - [NH_4] - [Na]_{nm} - 2[Mg]_{nm}$ where the subscript nm indicates non-marine. From the present-day average data, the ratio of ions balancing the acidity term was found, and used to calculate the contributions balancing ions in years before the period of measurement.
7. Values for the dry deposition of NH_3, NO_x and SO_x to for 1992-1994, were taken from the UKRGAR (1997) report, and values for other years were scaled to the wet deposition values. Bulk deposition fluxes of major solutes to moorland were increased by 7%, and those to forest by 14%, to take into account the inputs associated with cloud water, based on the findings of Reynolds et al. (1997) for moorland sites in the Welsh uplands that are similar to those in the upper Duddon valley.

Heavy metal deposition

Measurements of heavy metal deposition have been made at Wraymires, ca. 12 km from the Duddon valley, since 1972 (Baker, 2001), and in the upper Duddon valley itself in 1998-9 (Lawlor & Tipping, 2003), and we use here further data for 2002. The measurements have been made after acidifying bulk deposition samples to pH < 2, using HNO_3, and therefore are reasonable estimates of "geochemically active" metal, i.e. the metal fraction that participates in solid-solution partitioning, solution complexation, and precipitation-dissolution reactions (Lawlor & Tipping, 2003; Tipping et al., 2003). The data reported by Baker (2001) show that, during the period 1972-2000, deposition of Zn fell by about threefold, and that of Pb by about fivefold.

Sediment core data from Blelham Tarn, a lake ca. 12 km from the Duddon Valley provide information on earlier metal deposition trends (Ochsenbein et al., 1983). We re-analysed the data by regressing sediment metal content against % mineral matter for the deeper part of the sediment, and then using the regression to "correct" the metal levels nearer to the surface for background metal derived from catchment minerals. This procedure yielded sediment metal profiles that could be attributed to variations in anthropogenic atmospheric metal deposition, either directly onto the lake surface or via the catchment soils. The corrections were greatest for Ni, most of which is derived from catchment minerals. The sediment profiles show that atmospheric deposition of Ni, Cu, Zn and Cd began to increase in around 1800, while that of Pb commenced earlier, in about 1600. For each metal, the sediment concentrations show upward curvature, with peaks being reached at around 1950-1970.

We made a simple model of metal deposition over time. Before the year when significant metal pollution begins (y_0), deposition is assumed constant at the background level (D_B). From y_0 to 1960, an increase in anthropogenic deposition (D_A) to a maximum value ($D_{A,\max}$) occurs, according to the equation

$$D_A = D_{A,\max}\left(\frac{y - y_0}{1960 - y_0}\right)^n$$

where y is the year and n is a constant. Anthropogenic deposition during the period 1960 to 1970 is assumed constant. After 1970, it declines linearly to the present day.

The metal deposition model was first applied to Pb. Linear regression of the data from 1972 to 2002 yielded total deposition values for 1970, by back-extrapolation, and for 2000. Background deposition (D_B) was assumed to be 3.0 μmol m^{-2} a^{-1}, i.e. 20% of the 2000 value, and $D_{A,\max}$ was obtained by subtracting D_B from the total for 1970. The value of n was found to be 3.5, by fitting the sediment core data, with $y_0 = 1600$. Then, given D_B and $D_{A,\max}$, deposition from 1600 to 1960 could be calculated. The same approach could be applied to Zn.

Long-term data on Ni and Cd deposition are not available for the Wraymires site. Therefore, data reported by Baker (2001) for Ni at two other UK rural sites (Chilton, Oxfordshire and Styrrup, Nottinghamshire) were averaged to estimate the trend since 1972; this procedure can be justified by the similarity in deposition of Zn and Pb at the three monitoring sites (i.e. Chilton, Styrrup, Wraymires). No long-term deposition data are available for Cd, but air concentrations have been reported, from 1979. It was assumed that the rate of decline in deposition was the same as that in air concentrations, and by scaling to recent deposition data, the absolute deposition of Cd from 1970 to the present was estimated. Results for Ni, Zn, Cd and Pb are given in Table A2.3.1.

Copper presented difficulties, firstly because the data reported by Baker (2001) for Wraymires show a substantial increase in deposition from 1991 to 1998, returning to the high values similar to those for the early 1970s. Our own estimate of Cu deposition at the Cockley Beck site in 1998 (Lawlor & Tipping, 2003) is only 4% of the value reported for Wraymires in the same year. In a first effort to resolve this issue, we ignored the Wraymires data after 1990. This appeared justified given that the Chilton and Styrrup sites showed approximately constant Cu deposition from 1990 onwards. Linear regression of the 1972-1998 Wraymires data , and fitting of the sediment core data, then gave the parameters shown in Table A2.3.1, for Cu-A. We compared the estimated values of $D_{A,max}$ estimated from the directly measured data with the lake sedimentation trends, by taking ratios of the deposition or sedimentation of the other metals to those of Pb. For the lake sediments, increases in metal sedimentation from background levels were used. The last two columns in Table A2.3.1 show that there is reasonably good agreement between the deposition and sedimentation ratios for Ni, Zn and Cd, but that the ratios for Cu differ markedly; whereas the sediment records indicate that anthropogenic Cu deposition has been about half that of Pb, the estimates based on the measured deposition records suggest that Cu deposition has been about four times greater than that of Pb. Given this large discrepancy, a second deposition scenario for Cu, Cu-B (Table A2.3.1), was constructed, based on an estimate of $D_{A,max}$ of 49 μmol m^{-2} a^{-1}, calculated by taking half the Pb value, and using the data for Cu deposition at Cockley Beck in 1998 (Lawlor & Tipping, 2003) and 2002 (present work). Scenario Cu-B gives an estimated deposition of 34 μmol m^{-2} a^{-1} in 1981-1983, in reasonable agreement with the value of 55 μmol m^{-2} a^{-1} reported by Hamilton-Taylor & Willis (1990) as the mean for two sites ca. 15 km to the east of the Upper Duddon Valley, and within 2 km of the Wraymires site. Hamilton-Taylor & Willis noted that their trace metal deposition estimates agreed with the data reported by Cawse (1980) for Wraymires in 1978 for all metals except Cu, for which there was an order-of-magnitude difference; the Cawse (1980) results were part of the data set reported by Baker (2001), referred to above.

To this point, the analysis of the deposition scenarios has been based on directly measured bulk deposition values. In previous work (Lawlor & Tipping, 2003), we proposed adding an additional 20% to take account of dry deposition, and cloud water effects. Therefore, for dynamic modelling we followed this procedure, i.e. the scenarios for modelling had the $D_{A,max}$ and D_B values of Table A2.3.1 increased by a factor of 1.2.

Table A2.3.1 Heavy metal deposition parameters (see section 2.4). Deposition (D_B, $D_{A,max}$) is in µmoles m^{-2} a^{-1}. The final column gives concentration ratios in lake sediments reported by Hamilton-Taylor (1979) and Ochsenbein et al. (1984) – see the text for full explanation.

	y_0	n	D_B	$D_{A,max}$	$D_{A,max}$ / $D_{A,max,,\mathrm{Pb}}$	ΔSed / $\Delta\mathrm{Sed}_{\mathrm{Pb}}$
Ni	1800	1.5	1.4	67	0.88	0.58
Cu-A	1800	2.5	15	290	3.8	0.50
Zn	1800	4.5	30	620	7.1	6.4
Cd	1800	3.5	0.12	2.3	0.071	0.036
Pb	1600	3.5	3.0	76	1.00	1.00
Cu-B	1800	2.5	3.0	49	0.50	0.50

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ANNEXE 7: HEAVY METAL DEPOSITION TRENDS IN FIVE UK CATCHMENTS: A RECONSTRUCTION BASED ON MONITORING, HISTORICAL AND ENVIRONMENTAL RECORDS

L.Shotbolt, M.R.Ashmore, E.Tipping.

Within the current project, a key objective is the development and testing of dynamic models of heavy metal accumulation in soils and waters. These models aim to interpret the current metal burden in soils and lake sediments, and to forecast the effects of changes in future emissions on soil and water metal concentrations. They are based on five rural catchments in the UK: Lochnagar, north-east Scotland; Cote Gill in the Yorkshire Dales, Castle How Beck in the Lake District; the River Etherow, Peak District; and Old Lodge in the south-east of England. An important input to these models is past heavy metal deposition.

Few long-term records of atmospheric heavy metal deposition exist. Past deposition scenarios must be reconstructed largely from other sources such as palaeo-environmental, monitoring and historical records. This report reviews the published literature for data on past metal deposition in the UK and reconstructs deposition histories for the five catchments from the best available data. Analysis of herbarium moss samples (see annexe 8) was then directed at confirming or refuting suggested deposition histories and filling any gaps in information.

1. Background and aims

The importance of anthropogenically-derived emissions to atmospheric aerosol metal concentrations has increased over the last few centuries to greatly surpass natural inputs (Nriagu, 1989). The UK has had a particularly long history of atmospheric heavy metal pollution. It has been a globally significant producer of metal ores over the last two millennia (Raistrick & Jennings, 1965; Blick, 1991) and from the mid 18th century (the start of the industrial revolution) heavy metal emissions from mining and smelting have been bolstered by other industrial emissions including metal refining, energy production, manufacturing processes, waste incineration and vehicular combustion (Nriagu, 1990). The range of metals used in manufacturing (Nriagu, 1990), our ability to disperse pollutants over a wide area and the intensity of emissions increased with population and energy consumption to peak in the late 1960s and early 1970s (Goodwin et al., 2002).

There are several important sources of heavy metal emissions in the UK. They can be considered in two groups:

1) *General sources.* Sources such as vehicular emissions, energy production and manufacturing occur across the UK. Although there is some concentration of emissions in areas with high population and industry, their widespread distribution means that all areas will be affected, to some degree, by these sources.

2) *Isolated sources.* Certain sources of heavy metal emissions, most importantly mining and smelting on orefields, occur in a few specific areas of the UK. Heavy metal pollution from

these sources will be concentrated in the immediate vicinity of these sites, although there may also be some regional and national impact.

Reconstructing trends in metal deposition at specific rural sites in the UK should take into account both categories of emitters. It is, therefore hypothesised that two deposition histories can be reconstructed for each catchment; one reconstructing deposition from ‘isolated sources’ i.e. local mining and smelting related inputs and one reconstructing deposition from ‘general’ UK-wide sources. These can then be combined to reconstruct trends in total deposition at each catchment.

2. ‘General’ deposition records

It will be assumed that the ‘general’ metal sources have resulted in UK wide deposition patterns for each metal that can be described by a single trend. This assumption is based on recent heavy metal monitoring data which shows that, since 1972, atmospheric heavy metal composition over rural England does not vary greatly spatially (Pierson and Cawse, 1979) although the concentrations of trace elements were found to vary by an order of magnitude between the most polluted and least polluted rural sites. The chemical uniformity suggests similarity of origin, long-distance transport or good atmospheric mixing. Whether this is a valid assumption for the past, particularly before the introduction of measures to more widely disperse pollutants by the first UK Clean Air act of 1956 is uncertain, but a necessary assumption for the purposes of this investigation.

A variety of data is available from which to reconstruct general deposition trends. Monitoring of heavy metal deposition at Styrrup (South Yorkshire), Wraymires (Lake District) and Chilton (Oxfordshire) provides valuable data on recent (post 1972) trends in deposition (Baker, 1999). Other useful data has been obtained from emissions estimates (Goodwin et al., 2002). Deposition and emissions data show similar trends for post 1972 heavy metal pollution in the UK.

Prior to 1972 there is no direct record of atmospheric heavy metal deposition. However, evidence from a range of other sources has been used to reconstruct trends in metal deposition. This includes data on metal concentrations in lake and peat records (e.g. Sugden, 1993; Eades et al., 2002; Yang et al., 2002; Rippey, 1990, Rose and Rippey, 2002; Weiss et al., 2002). Spheroidal carbonaceous particle (SCP) records of fossil fuel deposition in lake sediments are also useful as a surrogate for power station emissions (Rose et al., 1995). Estimates of global metal emission estimates (Nriagu, 1979; 1996) have also been considered.

Details of the key data used are provided in sections 2.1 to 2.4.

2.1 Heavy metal emissions and deposition data

Emission and deposition data for a range of heavy metals are available from which deposition since 1972 can be reconstructed.

Figures 1a to 1e show estimated UK emissions of heavy metals split into key sources (Goodwin *et al.,* 2001). Dominant sources of Cd, Cu, Ni, Pb and Zn include:

i) Industrial combustion (combustion for metal production, cement, ceramics and glass industries as well as power stations supplying industry only), which is a significant source of Cu and Ni.
ii) Public power generation (power stations, coke, gas, and nuclear fuel production, combustion in refineries, town gas and smokeless fuel production) which is a significant source of Cd, Cu and Ni.
iii) 'Other fuel combustion' (i.e. in accidental fires, agricultural, domestic combustion, etc), a source of Cd, Cu and Ni and some Pb.
iv) Road transport is the dominant source of Pb.
v) Waste incineration is a source of Cd, Zn and a small proportion of Cu.
vi) Iron and steel production is a major source of Zn and a small amount of Cd
vii) Non-ferrous metal production is a minor source of Zn (Goodwin *et al.,* 2001)

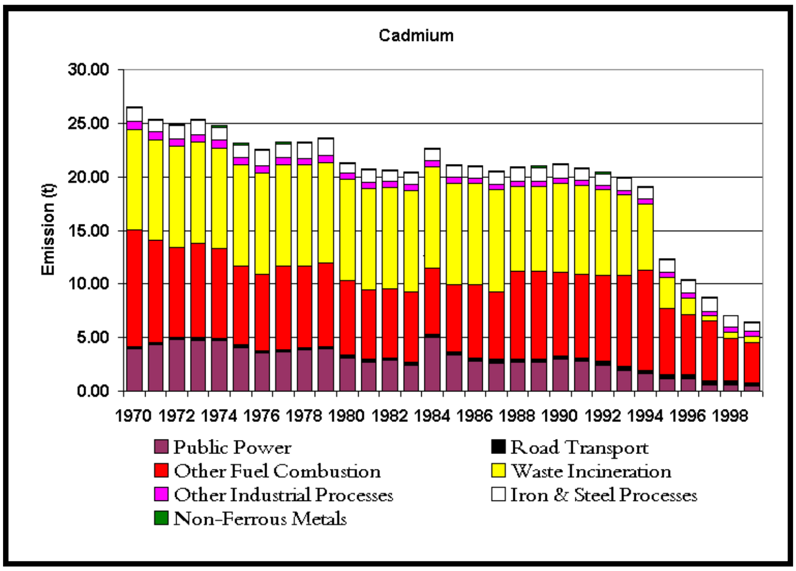


Figure 1a Emission estimates of Cd from 1970 to 1999 (Goodwin et al., 2001)

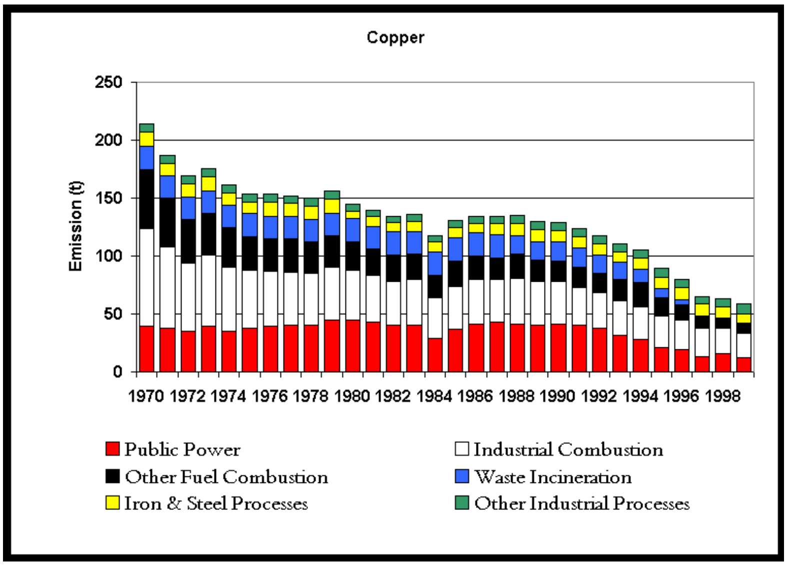


Figure 1b Emission estimates of Cu from 1970 to 1999 (Goodwin et al., 2001)

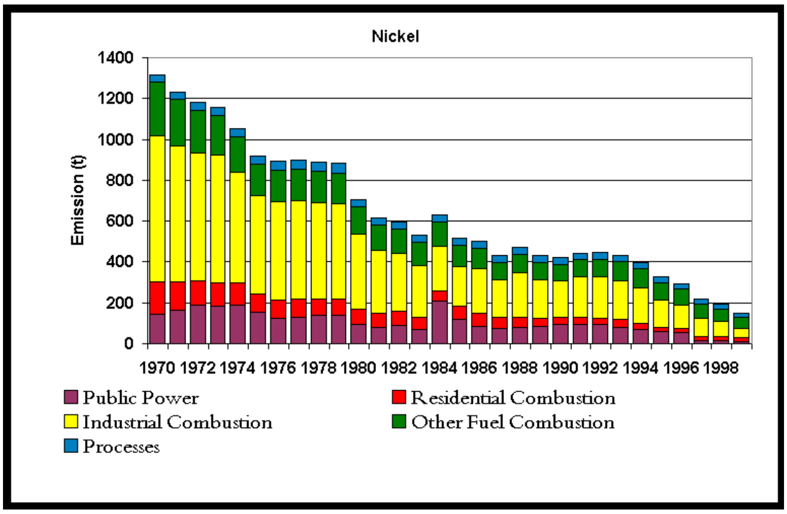


Figure 2c Emission estimates of Ni from 1970 to 1999 (Goodwin et al., 2001)

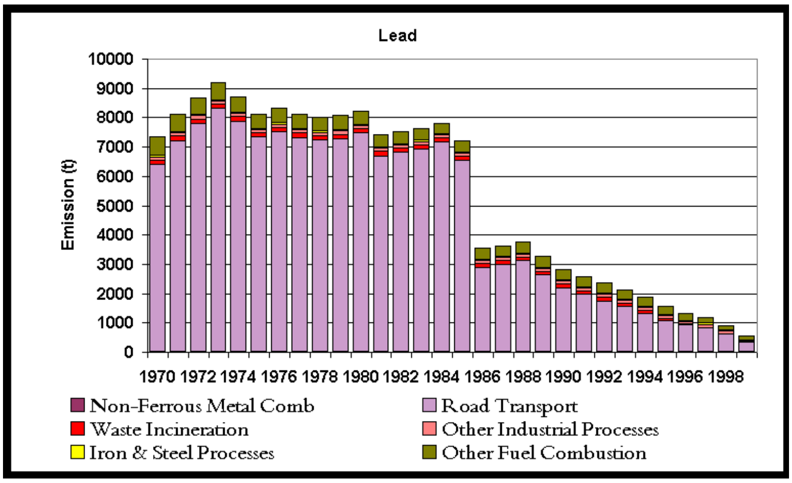


Figure 1d Emission estimates of lead from 1970 to 1999 (Goodwin et al., 2001)

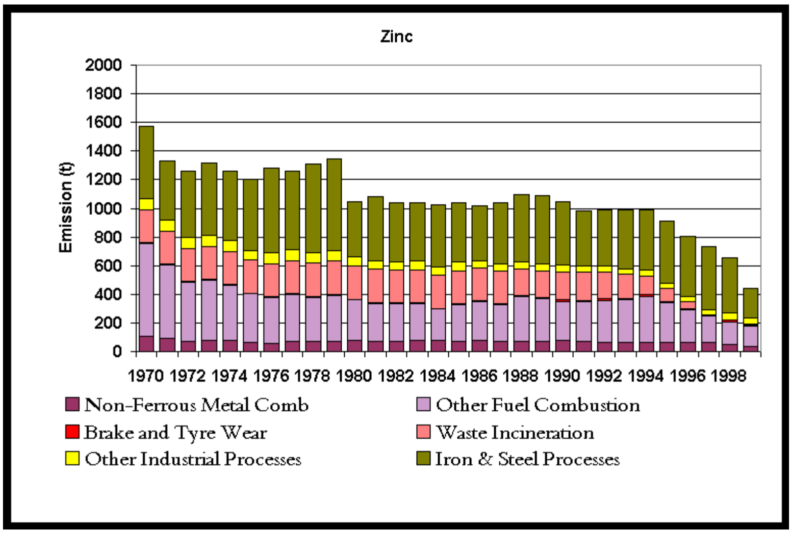


Figure 1e Emission estimates of zinc from 1970 to 1999 (Goodwin et al., 2001)

Estimated metal emissions are highest in 1970 (except Pb which peaks in 1973) and decline to present. All demonstrate major reductions (72-95%) over this period (Table 1). This trend is the result of numerous factors including past economic recession, improvements in emissions control and dispersion by taller stacks (Baker, 1999) as well as changing oil prices and the progressive removal of Pb added to petrol.

Table 1. Emission reductions based on estimated emissions between 1970 and 1999.

	1970 emissions (t)	1999 emissions (t)	% reduction
Cd	26.5	6.5	75
Cu	220	60	73
Ni	1320	160	88
Pb	9200 (in 1973)	500	95
Zn	1580	440	72

Heavy metal deposition has also been monitored since 1972 at three sites in South Yorkshire, Cumbria and Oxfordshire (NETCEN deposition monitoring network). 35 elements including Cu, Ni, Pb, Cd and Zn have been measured in particulates and 25 elements in rainwater as well as nitrate, sulphate and pH (Baker, 1999). Unfortunately monitored data is not available for Cd as this element has been consistently below detection limits.

A comparison of emission estimates to monitored air metal concentration confirms that estimates are translated into real reductions in metal levels in the atmospheric aerosol, and therefore, deposition (Table 2). Only Cu deposition at Wraymires appears to have declined significantly less than emission estimates suggest, due to an unexplained increase in the 1990s.

Table 2. Temporal change in air concentrations at rural locations: 1972-1997 (Baker, 1999).

		1972-79 (μg m^{-2})	1993-1997 (μg m^{-2})	% reduction
Cu	Chilton	9470	4320	54
	Styrrup	13400	3690	70
	Wraymires	1430	1080	25
Ni	Chilton	5170	826	84
	Styrrup	3340	992	70
	Wraymires	7170	Below l.o.d.	-
Pb	Chilton	18600	1590	91
	Styrrup	26000	2490	90
	Wraymires	14900	4360	71
Zn	Chilton	46700	15100	68
	Styrrup	81900	26700	67
	Wraymires	41200	15800	62

2.2 Global emission scenarios

Prior to 1970, emissions estimates of metals have only been made on a global scale (Nriagu, 1979; 1996). The global pattern pre-1970 is estimated to be one of exponentially increasing deposition for all metals except Pb which shows a more consistent rate of increase (Figure 2a & b).

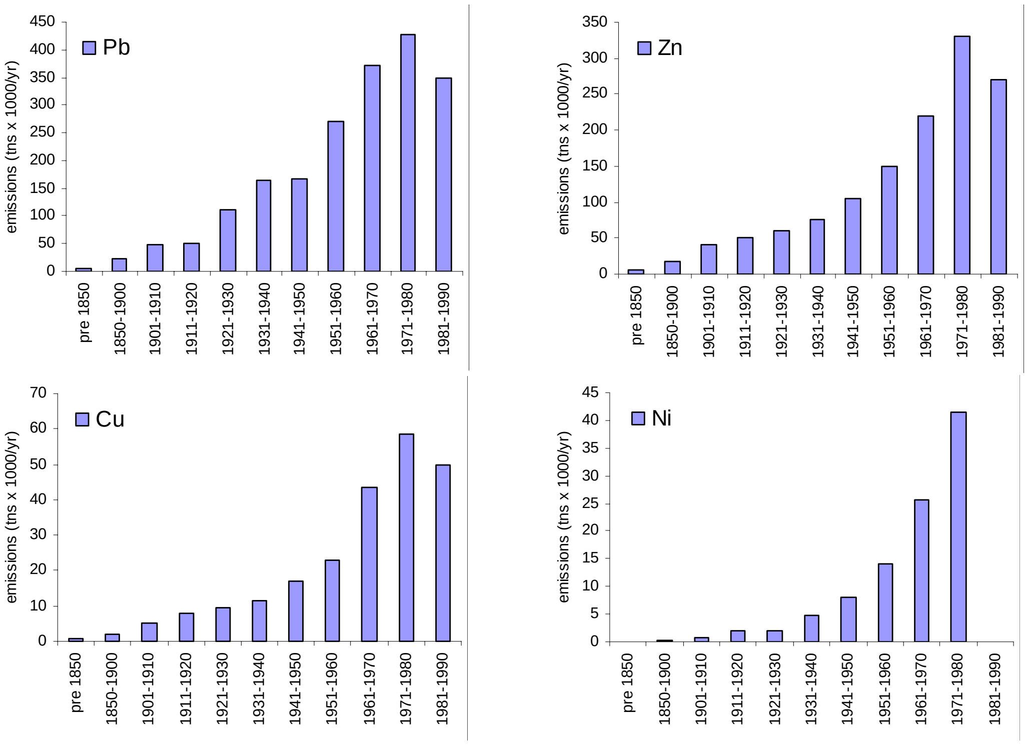


Figure 2a. Global lead, zinc, copper and nickel emission estimates (Nriagu, 1979; 1996). Pre-1850s annual emission estimated for all metals on the basis of constant deposition from 1400 to 1850.

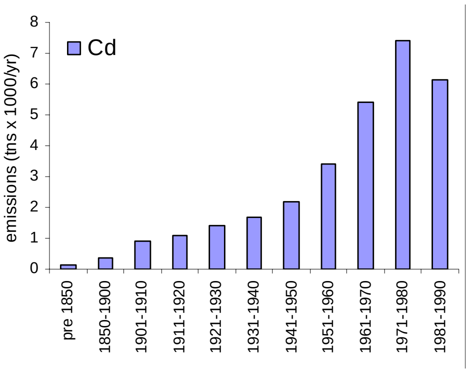


Figure 2b. Global cadmium emission estimates (Nriagu, 1996). Pre-1850s annual emission estimated for all metals on the basis of constant deposition from 1400 to 1850. Global cadmium emission estimates based on trends in zinc emissions.

2.3 Heavy metal concentrations in lake sediment and peat records.

Concentrations of metals in dated lake sediment and peat core profiles can be used to reconstruct trends in metal inputs through time. Figures 3a to 3e show lake sediment and peat core records of heavy metal inputs in areas largely remote from sources of mining and smelting.

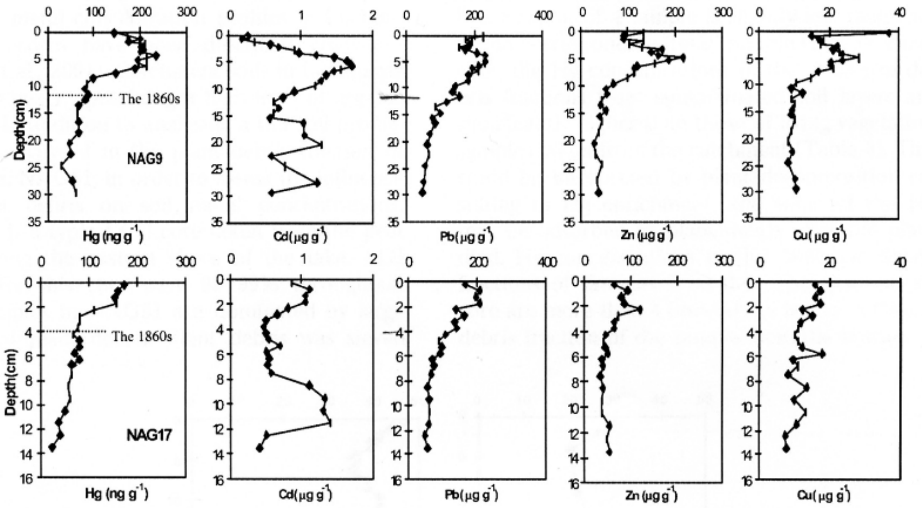


Figure 3a. Deposition in central cores from Lochnagar (Yang et al., 2002)

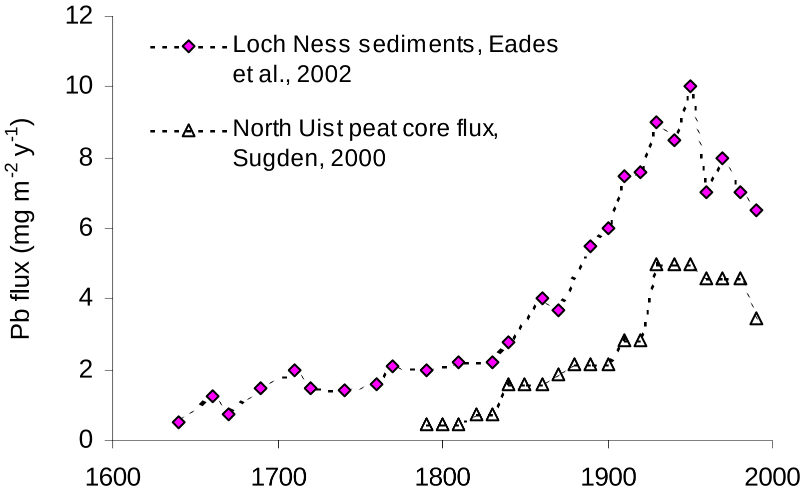


Figure 3b. Deposition in Loch Ness and a peat core from North Uist (Sugden, 2000; Eades et al., 2002)

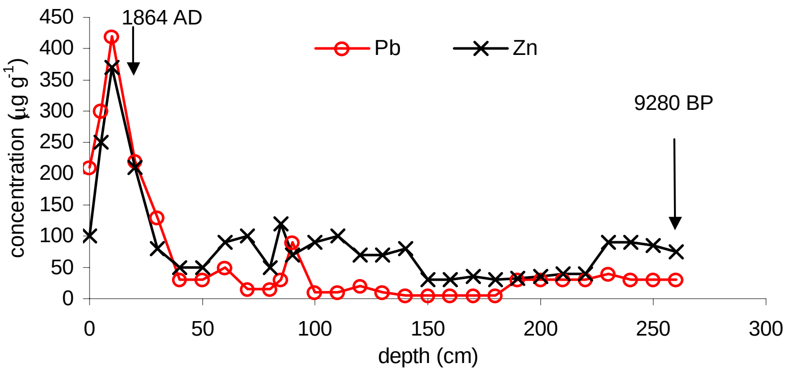


Figure 3c. Concentration of lead and zinc in sediments from the Round Loch of Glenhead, Galloway (redrawn from Rippey, 1990).

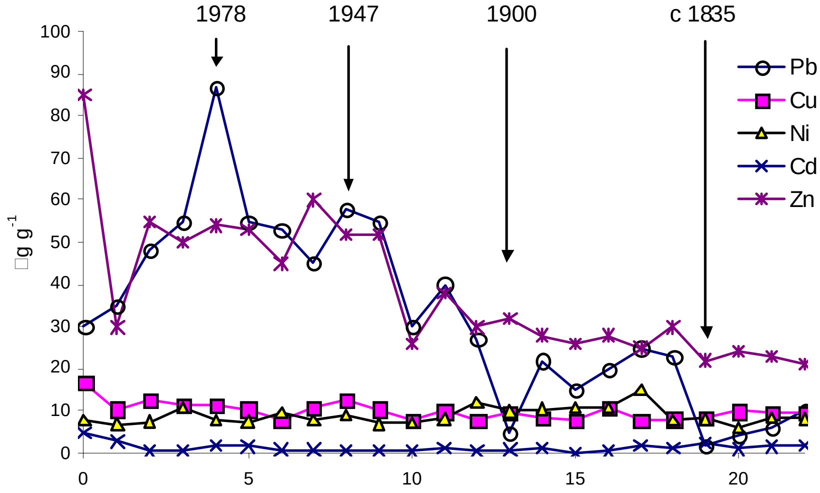


Figure 3d Concentrations of lead, zinc, copper, nickel and cadmium in Loch Coire nan Arr, redrawn from Rose and Rippey (2002)

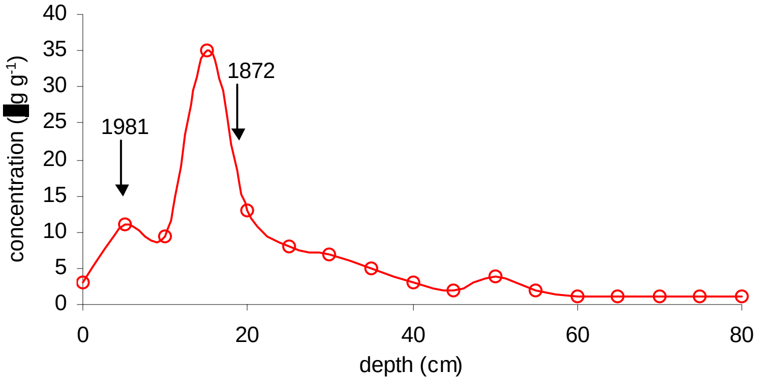


Figure 3e. Concentrations of lead in Loch Laxford, Northwest Scotland redrawn from Weiss et al. (2002)

In all these remote environmental records, there are clear indications of recent increase in metal concentrations, and often a sub surface peak. For Pb (the most commonly measured metal), where precise dating has been attempted (Sugden, 2000; Eades et al., 2002; Rose and Rippey, 2002) peak input appears to occur in the late 20th century.

2.4 Spheroidal carbonaceous particle records.

Although lake sediment records can be valuable records of past metal deposition, in some cases there are concerns over the mobility of some metals within the sediment column (particularly Zn and Cd) as well as the complicating influence of metals input from the catchment rather than via deposition directly onto the lake surface.

An alternative source of information in the lake sediment record is concentrations of spheroidal carbonaceous particles (SCP). SCP are elemental carbon particles produced only through high-temperature fossil fuel combustion. SCP are deposited onto lake surfaces and catchment soils, however, particles deposited onto soils are unlikely to reach lake sediments because the particles are physically very fragile and will not survive transportation through upland streams. SCP concentrations in lake sediments, therefore, are a conclusive indicator of industrial deposition (mostly from power generation), unaffected by any complicating catchment input.

SCP have been measured in lake sediments across the UK (Figure 4; Rose et al., 1995) and some general trends have emerged. SCP occur in measurable quantities from the latter half of the 19th century and increase slowly to around the 1950s. From the 1950s numbers rise sharply until the mid 1970s before declining to present. Although there is no direct link between SCP numbers in sediments and metal concentrations this does further corroborates the decline in industrial emissions indicated in section 2.1.

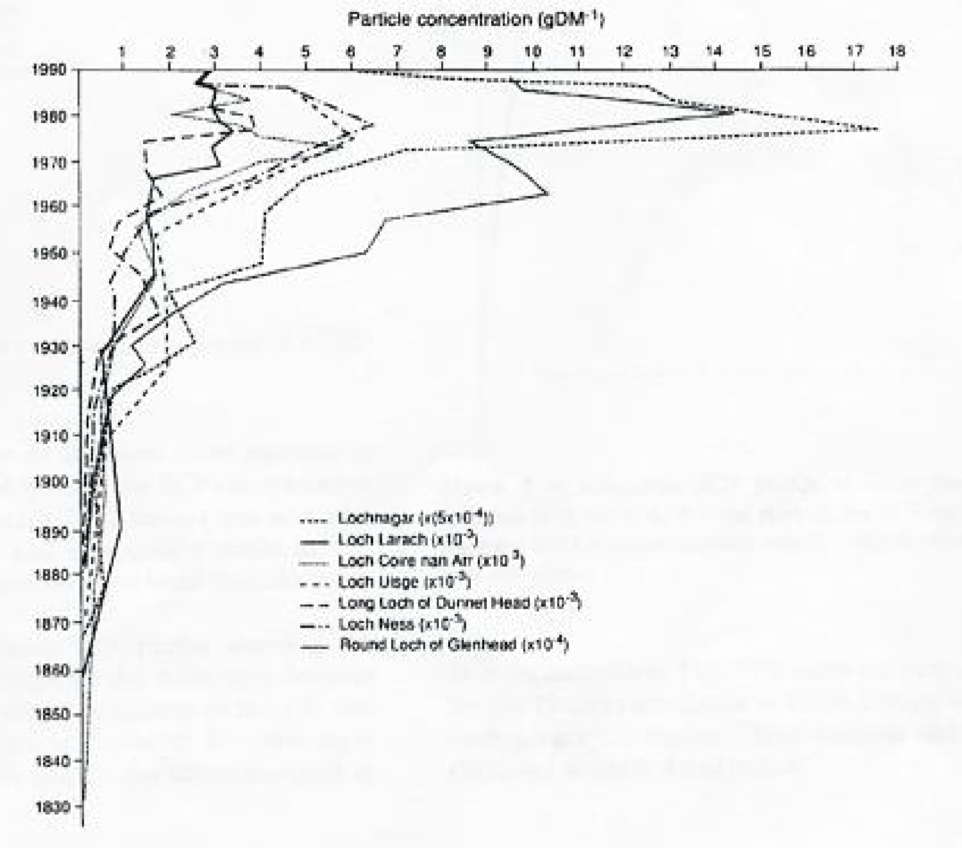


Figure 4. SCP concentrations in Scottish lakes (Rose et al., 1995).

2.5 Identifying the start of significant deposition by 'general' sources

Measurable numbers of SCP are first seen in the sedimentary records between about 1830 and 1880 (centred on the 1850s) (Rose *et al.,* 1995). There will certainly have been metal emissions unrelated to power generation prior to this, from the start of the industrial revolution (approximately 1750 in the UK (Ashton, 1997)) but the significance of early heavy metal emissions is uncertain. Thus 1830 represents the latest possible date to assign to the start of industrial heavy metal deposition.

In general Pb inputs to these lake and peat cores occur prior to the appearance of SCP (Loch Coire nan Arr may be an exception although the record does not extend back far enough to be certain of background Pb concentrations). Zinc records are less consistent, although the general picture is of a slightly later increase than Pb. For example, Zn (and Cu) first appear in measurable quantities around the mid 19th century in Lochnagar sediments although the difference between profiles from the two cores and pronounced subsurface peaks for these metals suggests some additional influence other than rates of deposition (i.e. post-depositional metal mobilisation).

It is possible that most of the pre-SCP metal input is the impact of long-distance mining and smelting rather than 'general' industrial deposition. Potential mining inputs will be taken into account in the mining and smelting related deposition profiles. Therefore the start of the Pb deposition record in remote lake sediments cannot easily be used to identify the start of the 'general' deposition record. This remains an area of uncertainty, although it can be constrained to between 1750 (start of the industrial revolution) and 1850 (approximate start of the SCP record). A lack of pre-1850 herbarium samples precludes resolution of this uncertainty through moss analysis.

2.6 Reconstructing the shape of heavy metal deposition trends from 'general' sources

A further area of uncertainty is the shape of the increase up to the 1970s peak. The SCP records demonstrate a broadly exponential increase, or more precisely, a slow increase until around 1950 followed by a more rapid increase to peak deposition in the mid 1970s. Prior to 1970, emissions estimates of metals have only been made on a global scale (Nriagu, 1979; 1996). The global pattern pre-1970 is estimated to be one of exponentially increasing deposition for all metals except Pb (Figures 2a & b). This is similar to trends indicated by SCP profiles in lake sediments. The relatively early increase in Pb and the trend (somewhere between an exponential increase and a straight line) is similar to trends in the UK Pb lake and peat core records (Figures 5a to e).

The exact form of metal increases to the 1970 peak is uncertain. It is certain that heavy metal emissions have increased up to the late 20th century peak. A rapid post-war increase preceded by a slower rise from a start date in the 19th century is plausible on the evidence of the lake and peat records.

2.7 General deposition scenarios

On the basis of the available information (sections 2.1 to 2.4) general metal deposition trends for Cd, Cu, Ni and Zn across the UK can be described as a slow increase from background around the start of the industrial revolution, a more rapid increase related to post WWII increases in consumption and a decrease from peak deposition in the early 1970s (Figure 5). A start date of around 1800 may be considered as a compromise between the beginning of industrialisation in the UK and the start of the SCP record. 1950 is suggested as a suiTable date for the start of a more rapid increase in deposition based on the SCP record (the metal increase from 1800 up to 1970 could equally be described as an exponential curve). 1970 is suggested as an approximate date for peak deposition based on a compromise between the continuing decline after this point indicated in the emissions inventories, and the slightly later date suggested by the SCP profiles for power station emissions (average UK lake sediment estimate of 1975). Lead deposition trends vary slightly from this. The higher resolution lake and peat records (Figure 3a and 3b) suggest a slow increase until around 1850. After which there is a more rapid increase than the other metals to peak in 1973 (Figure 5). However, a sharp peak is implied by the emissions inventory, which suggests that emissions in 1970 were only 80% of emissions in 1973. The magnitude of the post 1970s decline in all metals can most accurately be fixed from the emission estimates, but the shape of the decrease is estimated from the deposition record. These trends can be used to estimate past 'general' deposition by scaling to known deposition at any point on the profile.

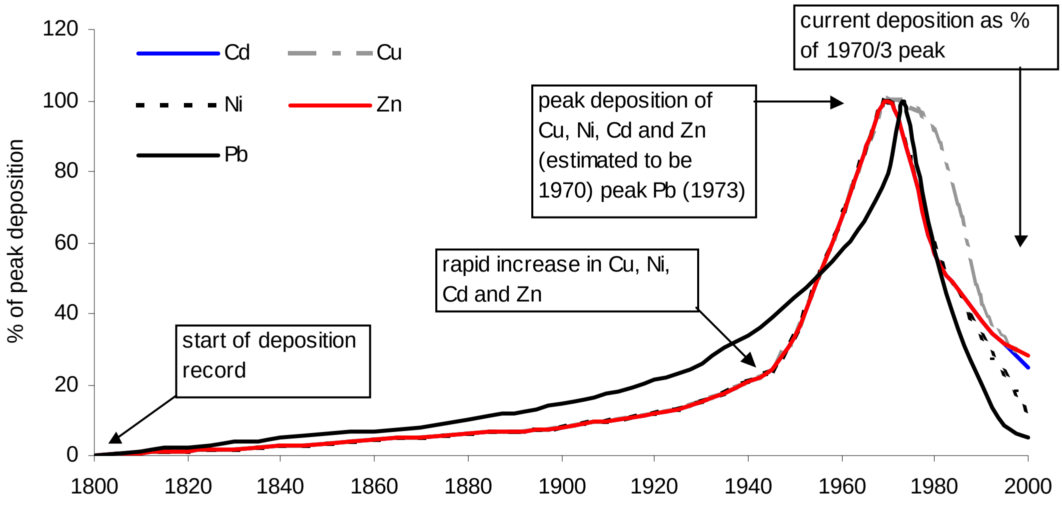


Figure 5 Estimated 'general' metal deposition profiles for the UK.

3. 'Isolated' sources of heavy metal emissions: mining-related deposition records

Mining of Pb, Zn and Cu have been important industries in the UK although neither Cd nor Ni have been mined to any significant extent. Mining-related deposition scenarios for each metal, and at each catchment are, therefore, required.

To reconstruct trends for the five catchments, sources of mining-related deposition in the vicinity of each catchment must first be identified (Section 3.1). The options for reconstructing trends in mining-related deposition will be considered in Section 3.2, in particular whether local deposition scenarios can be determined from nearby palaeo-records or whether a more generic national trend in deposition must be used. Section 3.3 will put forward UK wide mining-related deposition scenarios for each metal. Section 3.4 will reconstruct catchment specific deposition scenarios where possible and appropriate. Finally section 3.5 will make some concluding observations on the deposition scenarios.

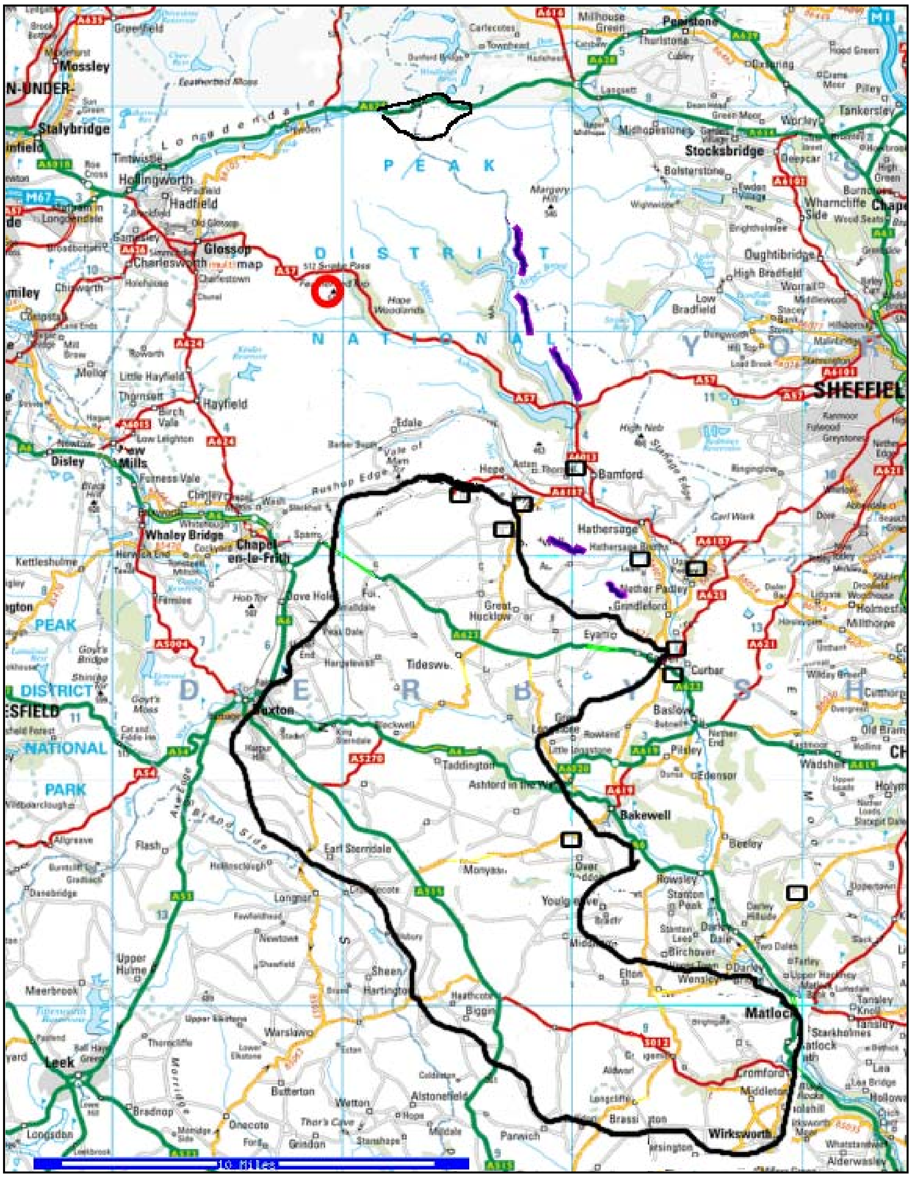
3.1 Mining around the five catchments

The key non-ferrous metal mining areas of the UK include Cornwall (Sn and Cu), the Yorkshire Dales (Pb), the North Pennines (Pb and Zn), the Lake District (Pb and Cu), Northern and Southern Wales (Cu and Pb), Southern and North-West Scotland (Pb) and the White Peak area of the Peak District (mainly Pb, small amounts of Zn). The Cote Gill, Etherow and Castle How Beck catchments are all close to old mining areas. Lochnagar and Old Lodge are, however, remote from mining-related sources of metal pollution.

3.1.1 The Etherow

The Etherow catchment is located between Manchester and Sheffield in the Dark Peak (Gritstone) area of the Peak District (Figure 6a). Lead mining has occurred in many areas of the White Peak (Limestone) to the south of the Etherow. The most important mines are found in two broad bands between Wirksworth and Matlock, and Eyam and Castleton as well as in areas centred on Youlgeave, Monyash, Carsington and Hartington (Wood, 2001). Zinc extraction has also occurred, although on a smaller scale than for Pb. Ford and Rieuwerts (1983) estimate that 3 to 6 million tons of Pb ores have been recovered since mining began in the Peak District. Zinc extraction is estimated at around 0.25 to 0.5 million tons. Copper mining has been historically important at Alderley Edge, Cheshire, which is about 50 km from the Etherow, but Cu mining within the Peak District has only been of minor importance, with around 4000 tons of Cu ore extracted (Ford and Rieuwerts, 1983).

Whether the Etherow catchment could have been directly affected by inputs of Pb and Zn generated by mining in the White Peak is debaTable. However, smelting of metals occurred primarily in the Dark Peak to utilise the wind or water-power required for early smelting techniques. Pre-17th century smelting occurred in low walled constructions on the Gritstone edges utilising strong winds to smelt the ore. 17th century smelting occurred in smelt mills located close to water and a supply of charcoal (Ford and Rieuwerts, 1983) (Figure 6a).



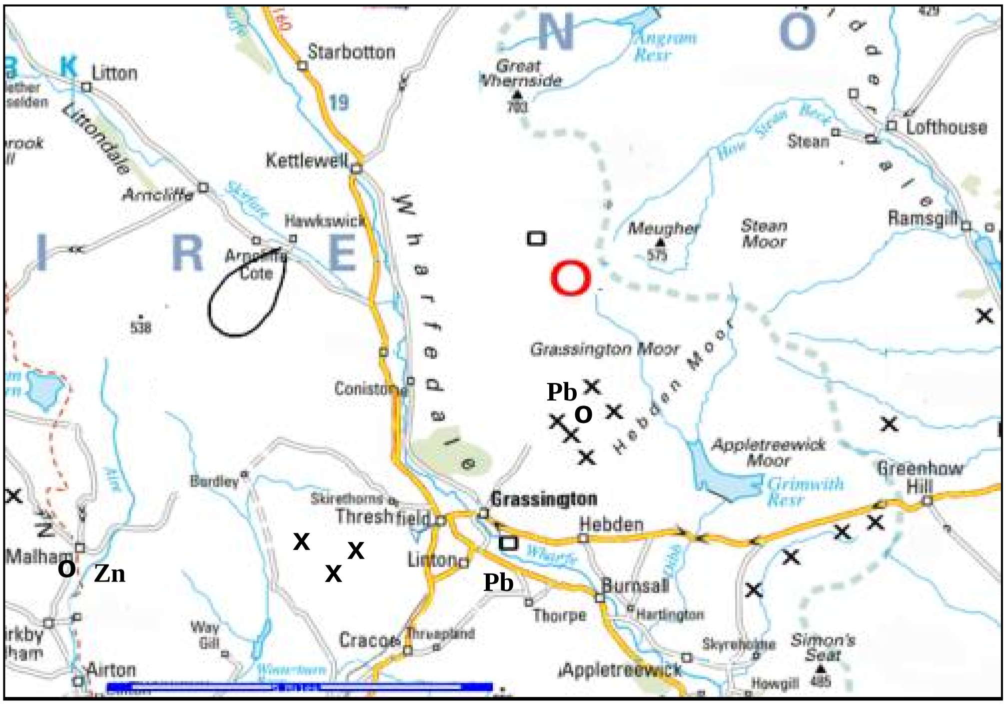
○ = site of Featherbed Moss peat core (Lee and Tallis, 1973)
〰 = bole smelting areas
◯ = major mining areas
□ = smelt mills
◯ = approx. area of catchment

Figure 6a. Mine and smelt sites around the Etherow catchment.

(Mine and smelting sites on this and the Yorkshire Dales and Lake District maps are simply those identified in the literature reviewed. There may be numerous others not included). In addition, Willies and Maskall (1995) have identified around 100 boles, mills and cupolas on and around the River Derwent and its tributaries of which only a few of the most northerly have been included).

3.1.2 Mining around the Cote Gill catchment

The Cote Gill catchment is close to Malham Moor, at which Zn (and a smaller amount of Pb) have been mined and smelted between 1790 and 1830 (Raistrick, 1947). It is also close to the Grassington Mines, which was an important Pb mining and smelting site (Figure 6b). Cote Gill is also south of the major Pb and Zn mining valleys of Wensleydale and Swaledale (not on the map), which contained over forty Pb smelting mills, the oldest operating from the late 16th century (Raistrick, 1975).



O = site of Grassington peat core (Livett et al., 1979)
X = mines
O = smelt mill
= approx. area of catchment

Figure 6b. Mine and smelt sites around the Cote Gill catchment

3.1.3 Mining around the Castle How Beck catchment

Most large mines in the Lake District were located considerably north of the Castle How Beck catchment. There are clusters on the Caldbeck Fells, in the Newlands Valley and around Blencathra and Helvellyn. Smelting occurred at some of the larger sites (Figure 6c). Zinc was produced mainly at the mines of Force Crag, Threlkeld and Thornthwaite. Lead was principally mined in the Helvellyn, Newlands and Caldbeck areas (Matheson and Jones, 2000). The copper mines of the Lake District were almost entirely on the Skiddaw slates, particularly in the Newlands Valley, but also Borrowdale (Fleming, 2000). In the southern Lake District the only major mine was the copper mine complex at Coniston. The Coniston copper mines extracted mainly Cu but also some Pb and Zn.

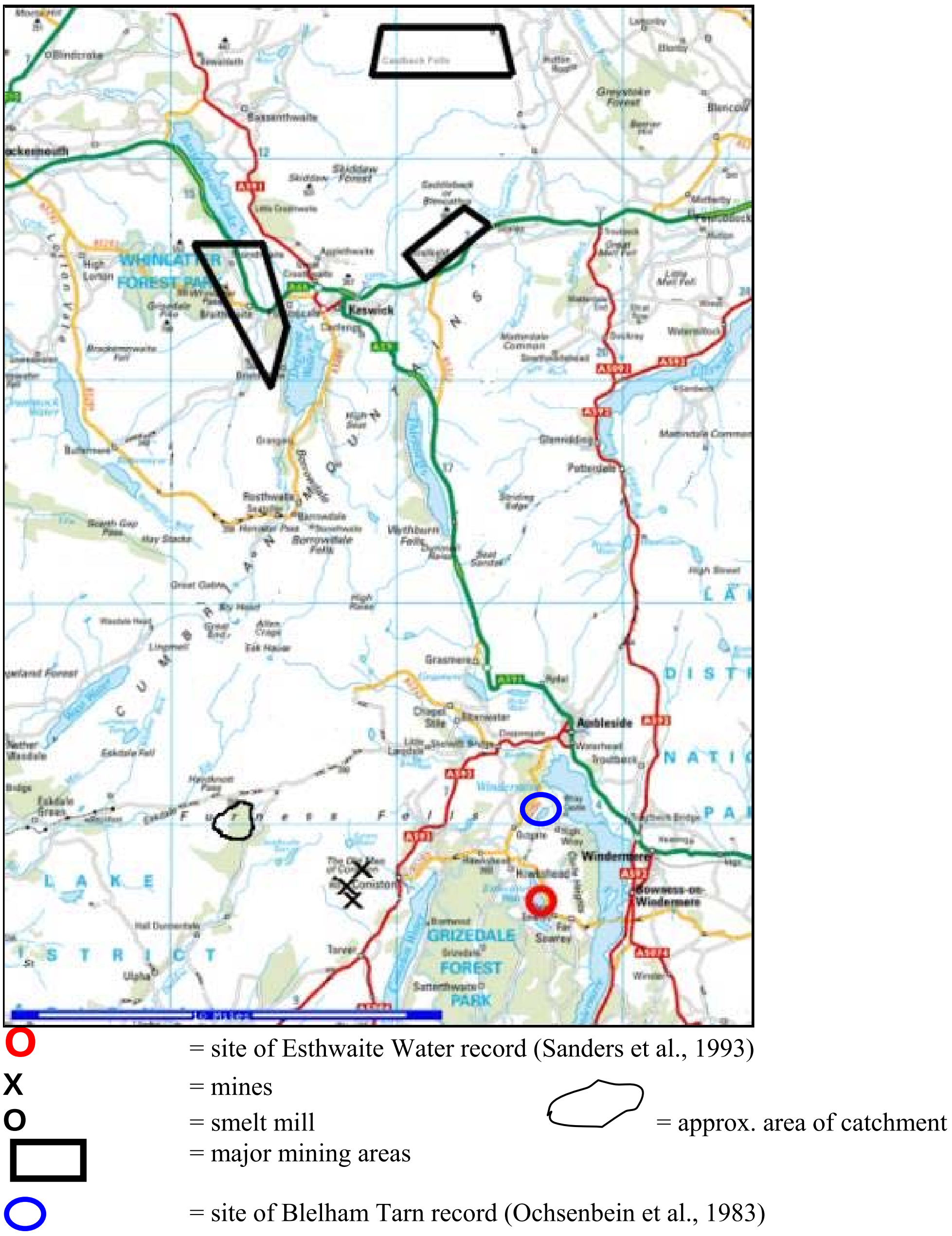


Figure 6c. Mine and smelt sites around the Castle How Beck catchment

The Lake District mines cannot be discounted as a major Pb producer in the past; however, the mines are largely in the north, at least 30 km from the Castle How Beck catchment. With the possible exception of Cu, the prevailing winds and upland topography may have limited any impact on the site.

3.1.4 Mining-related deposition at Lochnagar and Old Lodge

A mining-related heavy metal input to Lochnagar and Old Lodge cannot be discounted. The longer lake and peat records from Scotland show low-level Pb inputs prior to industrialisation (Figures 3a and 3b). There is a measurable Pb input into Lochnagar from before the 1860 dated horizon, possibly 1790 (Figure 3a) and Loch Ness from around 1650 (Figure 3b) that may indicate a long distance input of metals from mining-related sources. However, remote lake and peat records also show peak Pb deposition in the 20th century (Figure 3a to 3e). This is also true for Zn where records are available (Figure 3a, c & d) and Cu (Figure 3a). This indicates the dominance of industrial and vehicular deposition above mining-related inputs in these remote catchments.

3.2 Reconstructing trends in mining production: local or 'UK-wide' deposition scenarios?

The five catchments are located at varying distances from mining and smelting areas. One option for reconstructing past mining-related deposition at each catchment is to reconstruct a 'UK-wide' deposition trend based largely on national production trends appropriately scaled to account for distance from mining sources (further details in section 3.3, Figure 7). This may be most appropriate for reconstructing the small, mining-related input at the remote catchments. It could also be used for the other catchments where there are no good local records of mining-related deposition.

The use of national mining-related production trends is reasonable because major trends in ore production would have been determined by technological innovation and, to a certain extent, the existence of financers to back operations. For example, a period of growth in the first half of the 18th century was enabled due to the introduction of steam engines into Pb mines (the first introduced in 1715) (Burt, 1984). This would quickly have been introduced into mines across the country increasing production nationwide. Subsequently many large ore strikes occurred in the second half of this century (Raistrick, 1975). Although local differences (i.e. availability of ore) will occur, general economic and technological trends will have had a major influence not limited to specific regions. Regional differences are most likely to be important during early mine production.

However, a 'UK-wide' trend is not ideal. Deposition will be primarily influenced by the closest mine sources, and local differences in production trends do occur: there will have been differences in metal production in any given mine as ore deposits are discovered, exploited and finally depleted, even if the national economic and technological environment is an important influence. Where possible, it is more appropriate to base mining-related deposition trends on more local information such as peat core and lake sediment records.

3.3 National mining-related deposition trends.

3.3.1 Post-1700 metal production in the UK

Records of mining production in the UK have been collated by Schmitz (1979) from government sources and publications of international organisations (Figure 7). These data provide a starting point for reconstructing mine-related deposition of Pb, Zn and Cu, documenting trends in production from 1700 to present.

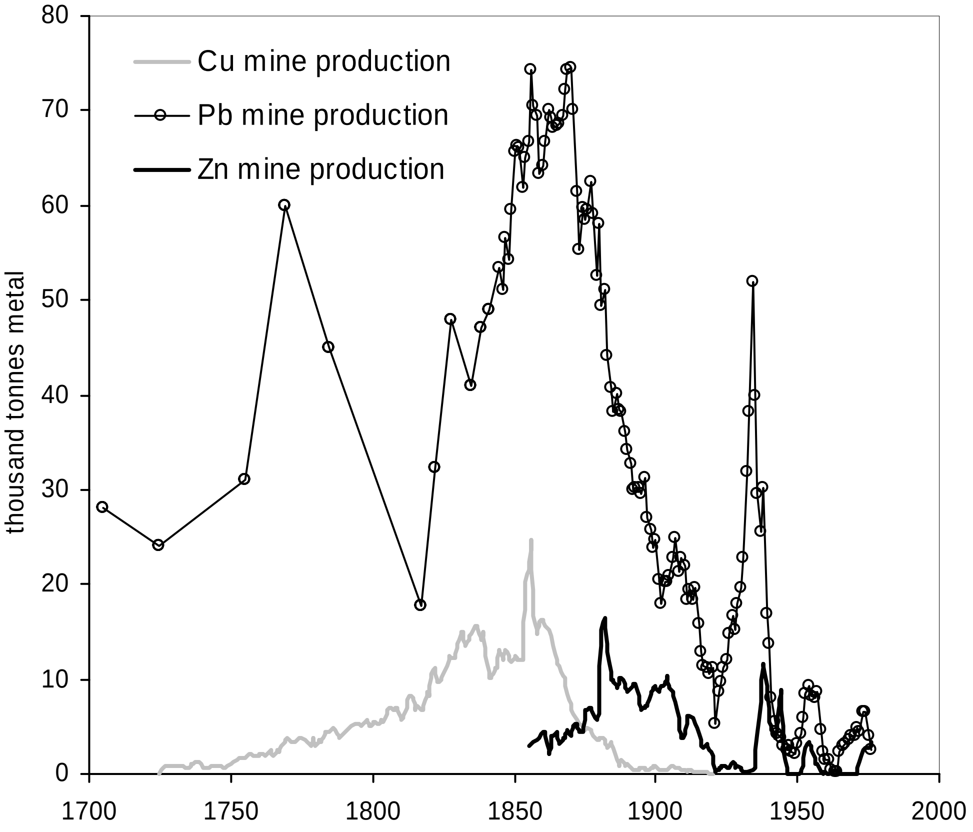


Figure 7. Lead, copper and zinc production in the UK (Schmitz, 1979).

There are some important uncertainties in the mine production data that should be considered. Firstly, the early part of the Cu record (1726-1818) is derived from data on public sales of Cu and Cu ores in Cornwall and Devon. This is thought to be a slight underestimation due to fluctuating amount of Cu ores obtained from Wales, the Lake District and elsewhere. Secondly, significant production of Pb occurred before 1700 for which there are no good records. In fact, few data on Pb production exist until about 1830: those between 1700 and 1770 are estimates based on trade in Pb.

Despite the uncertainties, the mine production record clearly highlights the importance of the Pb industry in the UK. From 1700, approximately 8 times more Pb has been extracted than Cu and 17 times more than Zn. This does not include the significant Pb production that occurred before records began. Production peaked between 1854 and 1871 before declining sharply to a low point in 1921. There is a secondary peak and decline between first and second world wars, but post 1947 there has been little Pb production in the UK

Significant Cu exploitation began in 1726. Production increased gradually until 1816 and then more rapidly to a first peak in 1837. Production then decreased slightly before rising to a larger peak in 1856. There followed a rapid decline until 1890 after which there was little Cu mining in the UK. The majority of all Cu production occurred in the south-west.

Zinc production began comparatively recently. The first recorded production was in 1855, however, there was clearly some production prior to this. Production rapidly increased to peak in 1882 after which there was an equally rapid decline until 1921. There was very little production throughout the 1920s and 30s although there was an increase in Zn production during the Second World War after which levels have remained low to present.

National trends in production indicate the dominance of Pb production and the potential importance of 19th century pollution from all three metals. However, while mining operations result in large amounts of waste material and dust affecting the immediate vicinity, it is metal smelting that has the potential to cause regional pollution. No similar records exist for smelting output, and the link between mining production records and metal emissions, though the best available, is uncertain.

3.3.1 Pre-1700 metal production and deposition

UK wide, mining-related deposition records can be based primarily on the production record shown in Figure 7. However, this does not cover the whole period during which Pb has been mined in the UK. In fact, globally, Pb has been extracted and smelted for at least 5000 years and Cu for around 6500 years (Patterson, 1971; Settle and Patterson, 1980; Tylecote, 1992).

Pre-industrial metal smelting techniques were initially highly inefficient. For example, Hong et al. (1996b) estimate that from 2500 BP to AD 1750 Cu emissions were 15% of production for sulphide ores. From AD 1750 to AD 1900 they estimate the emission factor decreases linearly from 15% to 1%. It is possible that early metal smelting, though a very small industry in comparison to that in the 19th century, may had a disproportionate polluting effect. It is, therefore, important to establish an estimate of early metal pollution.

Early lead pollution

The earliest significant extraction of Pb in the UK occurred during the Roman period. Pre-industrial Pb inputs can be clearly identified in Scandinavian lake sediments (Renberg et al., 1994; Renberg et al., 2002), much of which is likely to have originated in the UK (Figure 8). The four lakes sampled from northern Norway show Pb deposition from around 1000 AD (Renberg et al., 2002) (Figure 8). Lead levels rise from 1000 AD, with various peaks and troughs corresponding to documented changes in Europe, until the 1970s. These trends are corroborated by Renberg et al., (1994) who show similar trends for numerous Southern Swedish lakes. European emissions of Pb at this time were also extensive enough to reach Greenland ice core records (Hong et al., 1994), although were less 1 % of inputs in the 1960s (Boutron et al., 1995).

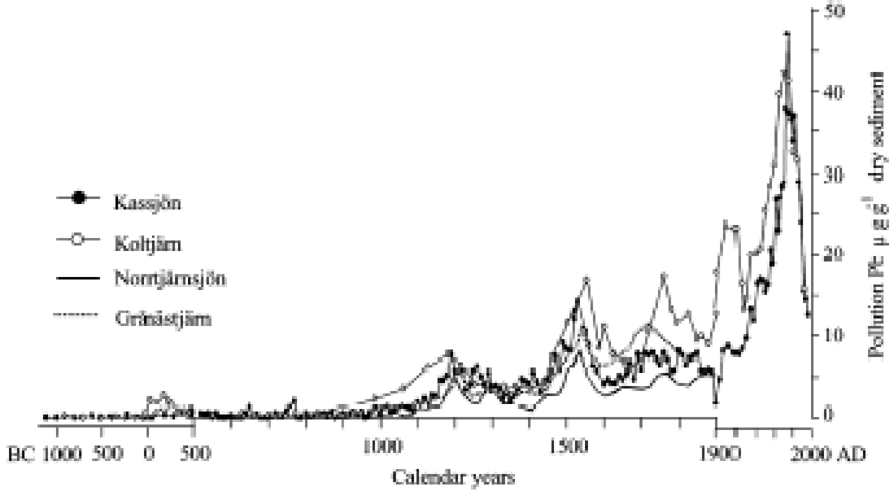


Figure 8. Varved lake sediment pollution lead concentrations. Pollution lead derived from the proportion of lead with a different isotopic ratio than local soils (determined by Pb-isotopes (Renberg et al., 2002)).

It is probable that there has been a significant pre-1700 contribution to Pb emissions and deposition. Brannvall *et al.* (1999) calculate that 50% of total Pb deposition onto Norway occurred before 1800 AD (from the lake inventories in Figure 8). Renberg *et al.,* (1994) concur stating deposition from 600 BC to 1800 AD was at least as large as the cumulative deposition during the industrial period (AD 1800 to present).

Significant early Pb deposition in parts of the UK is also indicated by a number of dated UK peat cores (Figure 9). These records are from peat cores collected close to extensively mined areas except for the records from Glenshieldaig and North Uist. The oldest samples (15th century) from cores from Grassington and Moor House show Pb levels considerably higher than background (around 100 µg/g). These early inputs are small in comparison to later inputs, but could be potentially significant if they extended over a long period. Early inputs to the Featherbed Moss core are lower (around 50 µg Pb g^{-1}), however, similar levels extend back for 2000 years, around 16% of the total Pb present in this core.

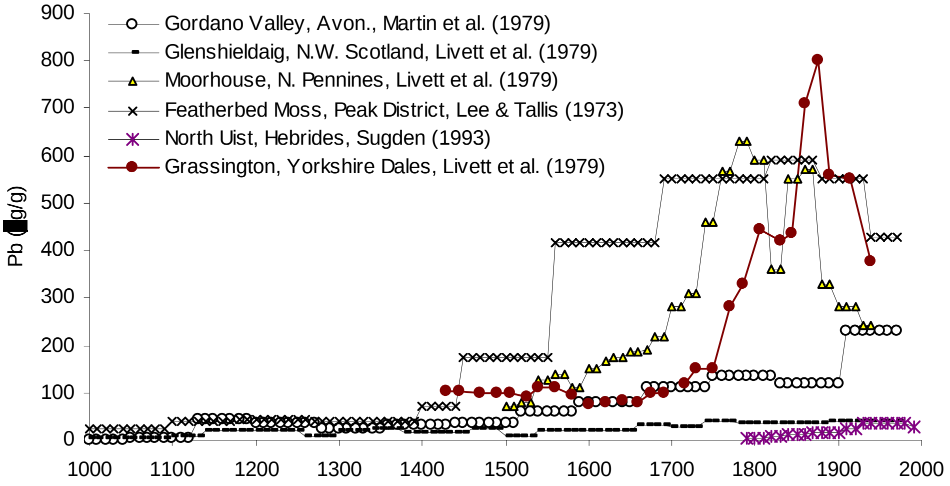


Figure 9. Lead concentrations in UK peat cores (Lee & Tallis, 1973; Livett et al., 1979; Martin et al., 1979; Sugden, 1993). The Featherbed Moss data is based on the few dated horizons shown in Lee & Tallis (1973) and a peak at 1850 as indicated in Livett (1988).

Early copper pollution

Copper also has a long history of mining and smelting. Like Pb, Roman use of Cu had an impact large enough to be measurable in Greenland ice cores (Hong *et al.,* 1996a). Nriagu (1979, 1996) estimates pre-1850 Cu emissions to be 15% of total global emissions compared to his estimate of 12 % for Pb. In the UK, it is likely that Cu was mined at Coniston and Alderley edge by the Romans (Matheson and Jones, 2000). Enough Cu was mined in the Lake District to justify the building of a smelter at Keswick in 1565 (Postlethwaite, 1889).

Despite the evidence of early Cu production, the Grassington record seems to largely agree with production records (Figure 7) of an early 18th century take-off point (Figure 10). Grassington is not close to any Cu mines, therefore, this might equally represent the start of the general industrial pollution record. At Moor House (Figure 10) pre-industrial inputs are similarly low at around 5 µg/g between 1500 and 1730, after which they rise slowly to peak around 30 mg/kg at the surface. There is perhaps some indication of pre-1730 increases in the Gordano Valley record, however, Cu has fluctuated between 0 and 10 µg/g back to the start of the record around 9000 BP so any increase within this range cannot definitely be ascribed to anthropogenic sources. There is, therefore, little evidence of significant Cu deposition prior to the early 18th century.

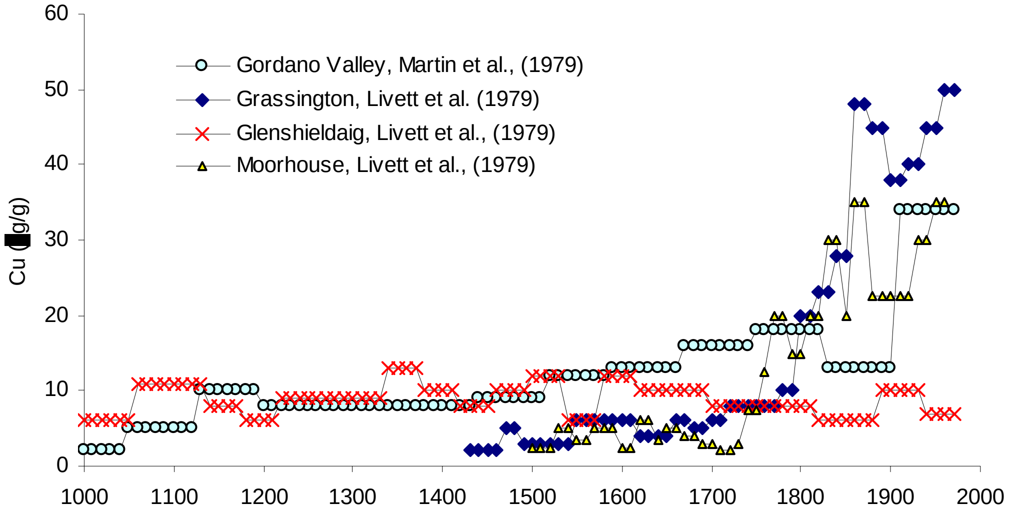


Figure 10. Copper concentration in UK peat cores (Livett et al., 1979; Martin et al., 1979).

Early zinc pollution

Recognition of Zn as a smelTable metal occurred relatively recently. Reduction of Zn from calamine was first reported in Germany in 1746. However, it is known that Zn was used to make brass probably as early as 4000 BP (Darling, 1990). It is also found in association with many Pb deposits and must 'accidentally' have been mined and smelted for much longer.

Ice core records from Greenland do not show any evidence of increased zinc deposition until the last 250 years (Hong *et al.,* 1997). However, natural background inputs of Zn are high enough to ensure anthropogenic inputs of Zn at the same order of magnitude as Pb and Cu would not easily be identifiable.

Zn production data goes back to 1855 (Schmitz. 1979), although, at 3200 tonnes, Zn production had clearly been in operation before this (Figure 7). In fact, there are records of Zn being recognised as valuable and extracted from old Pb slag heaps in the northern Pennines from 1794 to 1831 (ref). Unfortunately the peat records from Grassington, Moor House and the Gordano Valley cannot provide any information on pre 1700 Zn deposition as they are likely to be influenced by solubilisation and leaching processes (Figure 11).

Cadmium and nickel have not been mined in the UK to any significant degree.

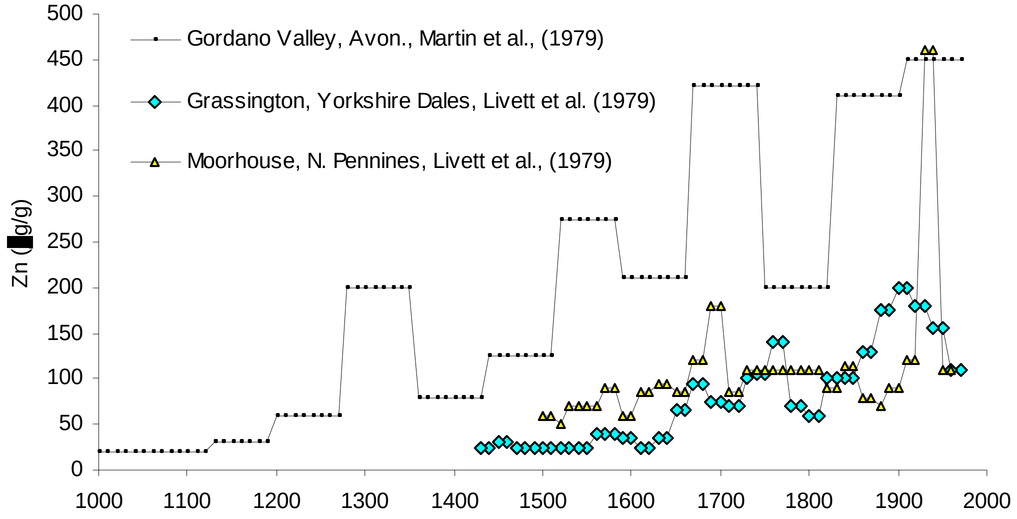


Figure 11 Zinc concentrations in UK peat cores (Livett et al., 1979; Martin et al., 1979)

3.3.2 UK-wide lead, copper and zinc deposition histories.

A suggested national deposition trend for Pb is shown in Figure 12. Trends post-1835 are based on the UK production data (an 11 yr running mean, Schmitz, 1979) and are therefore presumably a reasonably accurate reflection of trends. Trends between 1700 and 1835 are based on the trade records of Schmitz (1979) - the line is a best fit through the wide scatter of points suggested by the trade records (Figure 7). There are no records between 1000 and 1700. However, peat cores from the UK (Figure 9), Scandinavian lake sediment records (Figure 8) and ice core records all suggest a remarkably long history of Pb deposition. The general pattern determined from the remote paleo-records is of is a slow increase from around 1000 to 1400 followed by a more rapid increase until the 19th century.

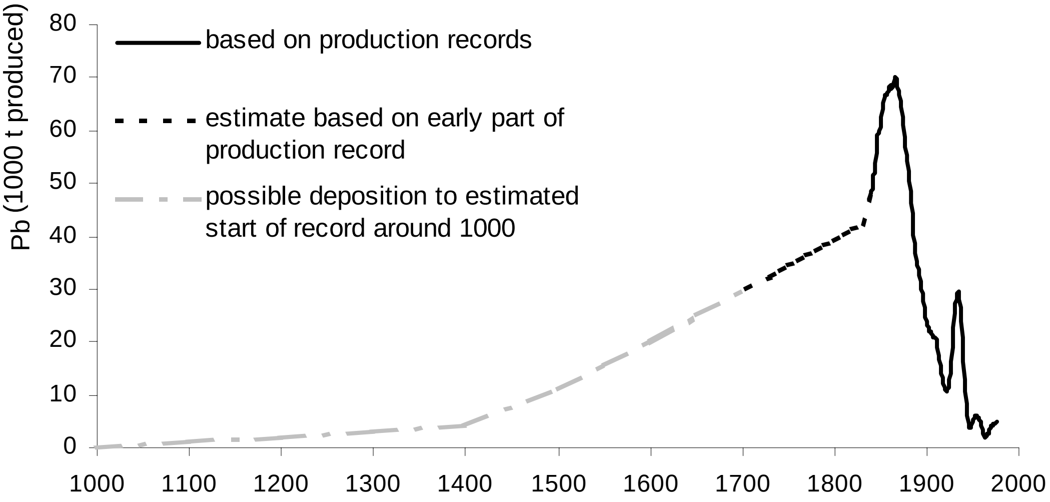


Figure 12. UK mining lead deposition trend based on production records.

Although Cu mining was in operation before 1726 (the date Cu production is first recorded (Schmitz, 1979) it is likely that outputs before 1726 were small scale. A nationally applicable deposition profile may be based entirely on the production records, as below (Figure 13). Production records, based on a reconstruction of Pb and Cu records in Figures 12 and 13 indicates UK Cu extraction may have been only 8% of Pb production which would account for the lack of evidence of early Cu deposition in remote lake sediments in addition to naturally higher background levels.

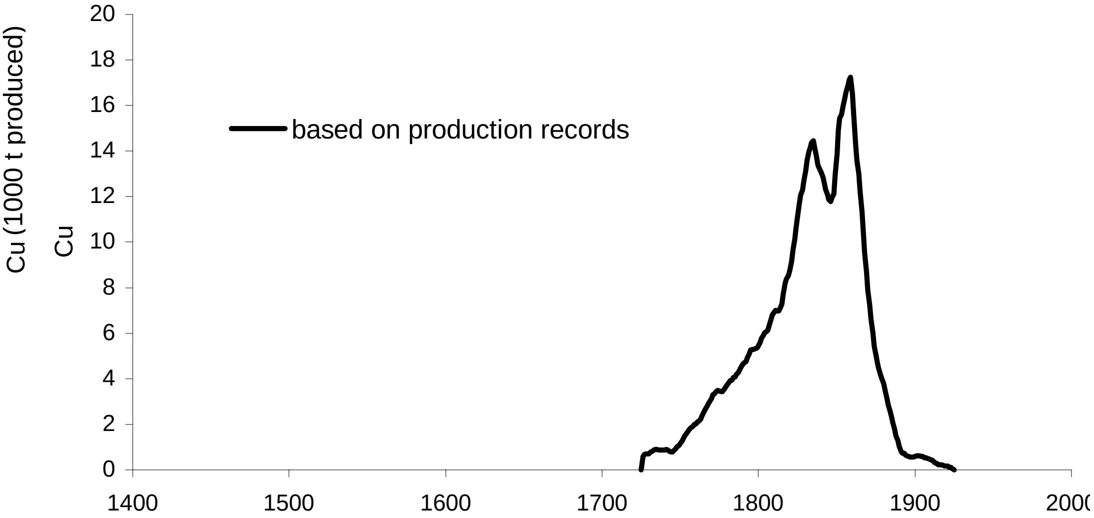


Figure 13. UK mining copper deposition trend based on production records (using an 11 year running mean).

Zinc production records extend back to 1855, however, the first part of the record appears to be missing (Figure 7). An exponential increase from 1800 to 1855 is suggested (Figure 14). Nationally, Zn production is only 4.5% of the Pb production.

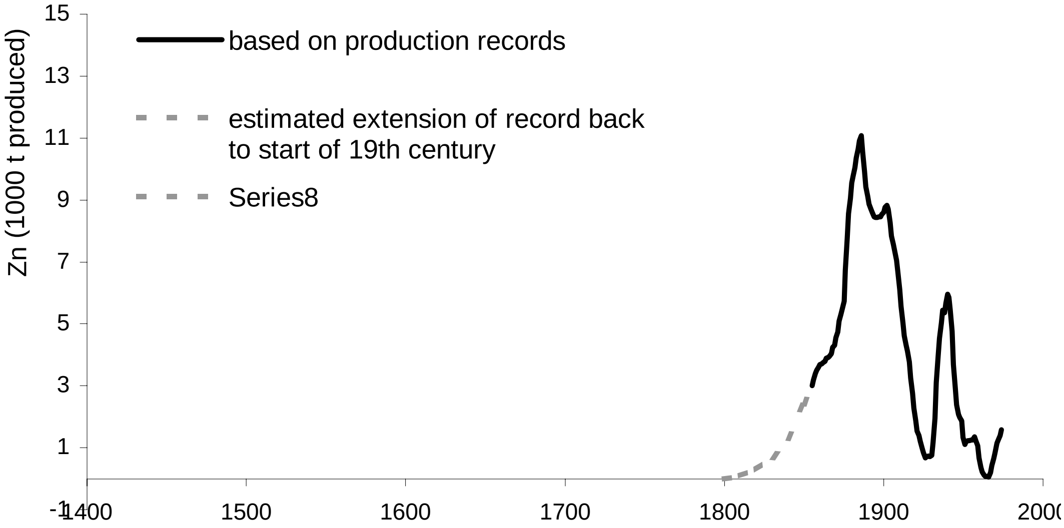


Figure 14. UK mining zinc deposition trend based on production records (using an 11 year running mean).

3.4 Catchment-specific deposition scenarios.

The above deposition scenarios (Figures 12 to 14) can be used for estimating the small, but important input from early mining to the catchments that are remote from mining and smelting. They will also be useful for the remaining catchments where there are no usable local records of metal deposition.

Where there are useful local records of metal deposition, however, these should be used. There are not detailed regional records of emissions, deposition or mine production. Thus the potential to reconstruct catchment-specific deposition scenarios will depend on the availability and reliability of local peat and lake sediment records.

3.4.1 The validity of using peat cores and lake sediment records to reconstruct deposition

Various authors have questioned the stability of heavy metals under the acid conditions in peat (Jones & Hao, 1993). Mobility of metals including Zn and Cd that are not strongly sorbed by organic matter is likely. Whether there will be any mobilisation of metals that are strongly sorbed by organic matter has not been fully resolved in the literature. The potential for Zn mobility means that reconstructing the history of Zn deposition must rely on national production records.

A further consideration is the accuracy of dating techniques and the low resolution of peat records. Livett et al. (1979) found peat accumulation at a number of sites in the UK to vary between 0 and 18 cm per century, which means a single sample may cover decades or more of deposition. Lake sediment records, though often higher resolution, may be difficult to interpret due to the complicating influence of heavy metals from the catchment as well as directly from the atmosphere. Catchment inputs can be estimated by normalising the record to concentrations in the oldest sediments, assuming that this represents background concentrations. This enables an estimated atmospheric concentration (or flux) to be determined. However, it does assume catchment inputs remain constant, which is likely not to be true as soil metal stores accumulate.

A final consideration is that, by using local palaeo-environmental records, reconstruction of past deposition will rely on a small number of sources. This will be peat cores from Grassington (8 km from Cote Gill) and Featherbed Moss (8 km from Etherow) (Figures 9 to 11) and lake sediment records from Blelham and Esthwaite Tarn (both about 14 km from Castle How Beck) (Figures 15 and 16). This does limit confidence in the resulting deposition scenarios, but is the best that can currently be achieved with the available information.

3.4.2 Trends in lead deposition onto the Cote Gill, Etherow and Castle How Beck catchments

The peat core from Featherbed Moss, close to the Etherow catchment shows increased lead inputs from around 1400 (Figure 9). The early Pb input plausibly reflects the impact of pre-17th century smelting on the nearby Gritstone Edges. Peak deposition in this core is difficult to pinpoint due to the low sampling resolution, but occurs in the 19th century, corresponding reasonably well with the national Pb mine production peak of 1870 (Schmitz, 1979).

Peak Pb deposition in the peat core from Grassington, close to the Cote Gill catchment, occurs around 1870 before declining to present (which matches closely the national production peak)

(Figures 7 & 9). This is slightly later than the decline in mine production at Grassington (Table 3) which declined rapidly from 1851. However, smelting continued at Grassington from 1605 to 1882 (Gill, 1993) and smelting is likely to have the bigger effect on deposition.

Table 3. Grassington: Ore production (Burt, 1984)

Date	Production (tonnes)
1851	2200
1861	1000
1871	200
1881	0

The Esthwaite Water sediment record indicates that the highest Pb inputs occurred around 1940 (Figure 15, Sanders et al., 1993). This record does not indicate any significant 19th century inputs. There is, however, some evidence of a relatively small, early Pb input to the more slowly accumulating Blelham Tarn sediments (Figure 16, Ochsenbein et al., 1983). A significant flux of Pb occurs from 1600 (and may extend even further back as it has been assumed the fairly constant input prior to 1600 (average of 47.5 µg/g) is the natural background input. There is also a peak in Pb inputs around the mid 19th century, about 20% of the size of the 1970s peak. This may be related to Pb mining in this sediment core.

The most significant mining in the Lake District occurred in the north of this region. The distance from these mines to the Castle How Beck catchment (and the lake sediment records) in the south Lakes, suggests no major input of metals can be expected. A small mining-related input is however, plausible, as some of the Lake District mines were very productive. For example, Greenside mine, Helvellyn, is thought to have produced in the order of 2,400,000 tons of Pb ore (Matheson and Jones, 2000).

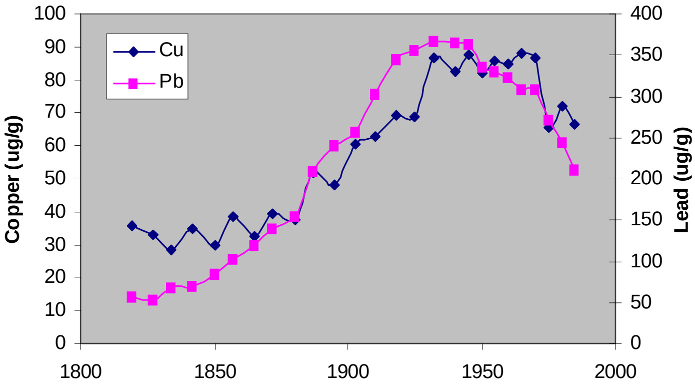


Figure 15 Copper and lead profiles from Esthwaite Water (Sanders et al., 1993)

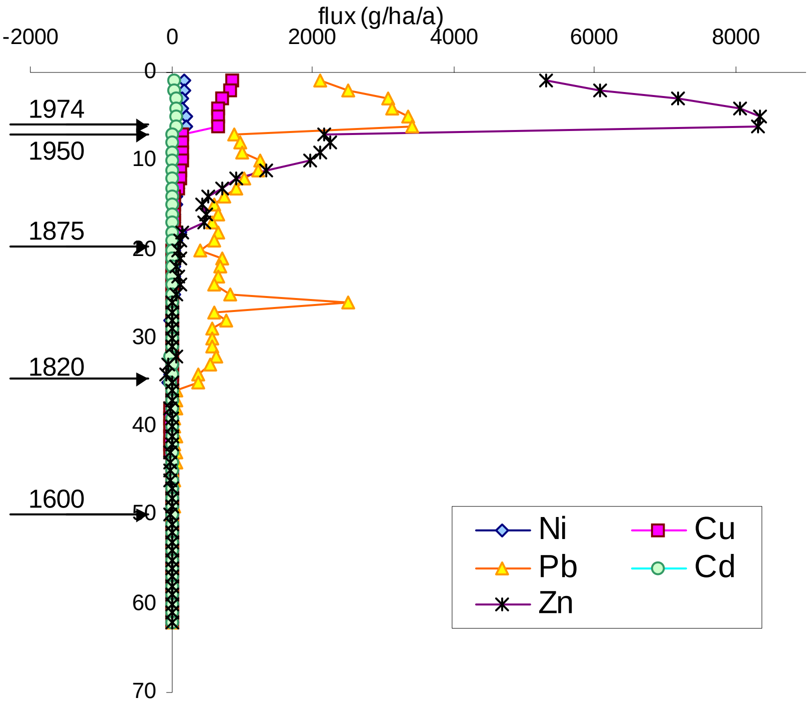


Figure 16. Estimated anthropogenic flux of metals in core from Blelham Tarn (data from Ochsenbein et al., 1983 normalised to pre-1600 sediments).

3.4.3 Trends in copper deposition onto the Cote Gill, Etherow and Castle How Beck catchments

Copper profiles from Grassington and Moorhouse peat cores show some similarity (Figure 10). Both show increased inputs from the early 18th century to a peak in the mid 19th century. There is then a decline in in both cores at about the point where employment figures indicate a major decline in Cu mining (from 1861, Burt, 1984: Figure 10 & 17). Levels then rise in the 20th century presumably due to ‘general’ industrial Cu inputs. Neither Grassington nor Moorhouse are close to significant Cu mining areas. It is therefore likely that Cu concentrations in the peat cores are related to long distance Cu emissions, first from mining and smelting and later from general industrial sources. The high late 18th and early 19th century Cu levels suggests the impact of Cu mining and smelting needs to be accounted for.

Unfortunately Cu profiles have not been published for the peatcore from Featherbed Moss, therefore, the extent of Cu deposition at the Etherow cannot be determined.

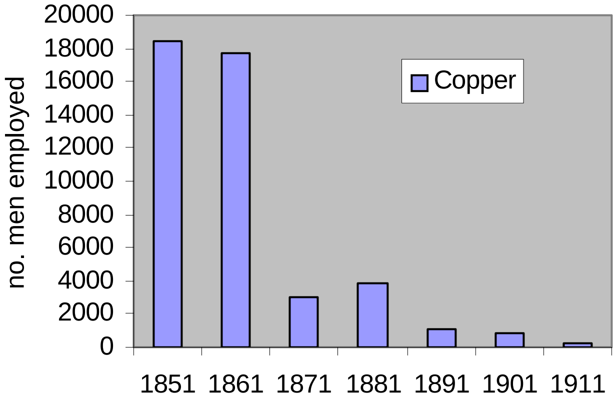


Figure 17 England and Wales employment figures for copper mining (Burt, 1984) census data.

Conversely, there is little evidence of any significant mining-related Cu input to Esthwaite or Blelham Tarns. Despite the proximity of the Coniston Copper mines. In Esthwaite Tarn, Cu concentrations peak around 1950 with lower concentrations before about 1880 (around 35 µg/g) (Figure 15). This does not correspond to the metal production history of the Coniston mines which peaks in 1856 and was in decline by 1860 (Fleming, 2000). The anthropogenic flux of Cu to Blelham Tarn increases from the mid to late 19th century (around 25 cm) again indicating no correspondence to the production record at the Coniston Copper mines (Figure 16).

3.4.4 Trends in zinc deposition onto the Cote Gill, Etherow and Castle How Beck catchments

Although the peat records are not suiTable for reconstructing Zn deposition, Zn mining and smelting on the nearby Malham Moor is likely to have had an impact on the Cote Gill catchment. Whether any impact from Zn mining in the Wharfedale and Swaledale valleys to the north of Cote Gill is possible, or similarly, whether Zn mining in the White Peak could have reached the Etherow is unresolved.

National production records may be the best option for reconstructing trends in mining-related deposition of zinc. The problem with using national production trends is that zinc production was concentrated in Wales, Cornwall and the Isle of Man (Table 4) and the amount produced in the Peak District and Yorkshire is relatively small. Although Cumberland will have included the Lake District, the relatively large amount of extraction will have been predominantly from the Northern Pennine mines.

A significant input of Zn to the Etherow and Castle How Beck catchments seems unlikely. It is possible that there has been a significant impact on Cote Gill from the Malham Moor mines; however, all that is known about these is that they were in operation between 1790 and 1830 (Raistrick, 1947).

Table 4. Zinc production in 1881 (Burt, 1984)

	Zn ore (tonnes)	Metal (tons)		Zn ore (tons)	Metal (tons)
Denbighshire	5602	2531	Cornwall	7792	3507
Flintshire	4233	1863	Isle of Man	7567	3480
Cardiganshire	3453	1544	**Cumberland**	1771	284
Anglesea	2305	632	Shropshire	196	107
Montgomeryshire	1414	610	**Scotland**	323	61
Carnarvonshire	792	291	**Derbyshire**	40	16
			Yorkshire	35	15

3.4.5 Lead deposition scenarios for the Etherow, Cote Gill and Castle How Beck catchments

Peat and lake sediment records from close to the catchments are used to describe trends in deposition until the late 19th century. After this point, the peat and lake core records will reflect the significant contribution from 'general' as well as 'mining-related' sources. For the latter part of the record, therefore, a history based on the production records is more appropriate. This is reasonable as the reduction in Pb mining was a UK wide phenomenon, at least partly due to the development of massive Pb reserved in the US and Australia and resulting cheap imports (Schmitz, 1979). Furthermore, census data show the beginning of a decline in Pb production and number of miners occurring between 1861 and 1871 in Derbyshire and Yorkshire and between 1871 and 1881 in the North Pennines (Burt, 1984).

A start date of 1000 AD has been estimated for national Pb deposition scenarios (Section 3.3.2) and is also considered an appropriate start point for the local deposition scenarios for Cote Gill and the Etherow, where the peat cores record a significant early Pb input. Figures 18a to c show estimated mining and smelting deposition trends for the Etherow, Cote Gill and Castle How Beck catchments.

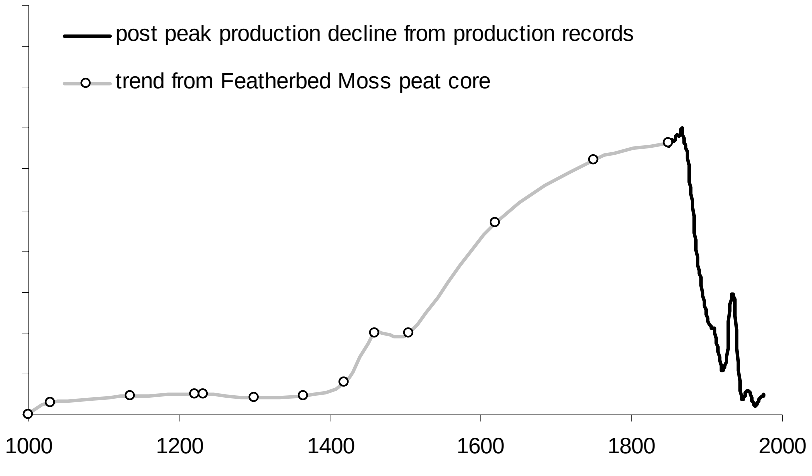


Figure 18a Suggested lead deposition trends for the Etherow based on peat core and production records.

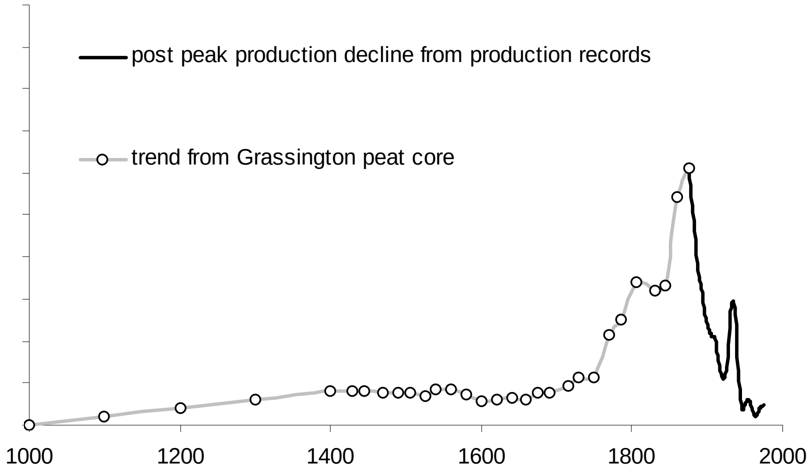


Figure 18b Suggested lead deposition trends for Cote Gill based on peat core and production records

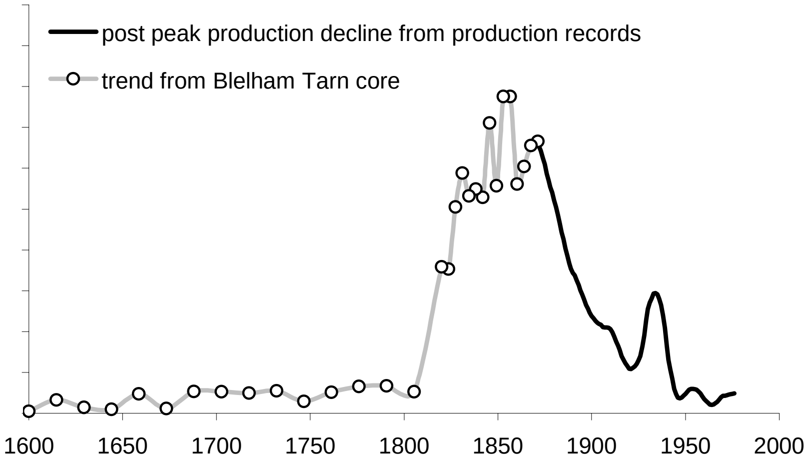


Figure 18c Suggested lead deposition trends for Castle How Beck based on lake sediment and production records

3.4.6 Copper deposition scenarios for the Castle How Beck, Cote Gill and Etherow catchments

Mining is a possible source of Cu to the Castle How Beck. It is close to the Coniston Copper mines, a major source of Cu. However, the Esthwaite Water and Blelham Tarn records do not show any significant increases before the mid to late 19th century. It must, therefore, be assumed that the topography may have prevented emissions reaching Castle How Beck.

There is no major source of Cu mining close to either the Etherow or Cote Gill. Despite the peat core records, which show Cu peaks in the late 19th century, it was decided that national deposition profiles should be used for these catchments due to concerns over the accuracy of there records, given the lack of Cu emission sources identified.

3.4.7 Zinc deposition onto the Cote Gill, Etherow and Castle How Beck catchments

Unfortunately, not enough is known about Zn mining and close to these catchments to reconstruct a useful deposition history. Neither are peat and lake sediment records of Zn reliable. A lack of information on Zn mining means that, where the Zn mining history is thought important, it must be based on the national trends as in Figure 17.

3.5 Conclusions on the estimated trends in mining-related deposition

Lead has been the only metal for which there is sufficient, locally-relevant data from which to reconstruct catchment-specific deposition scenarios. Lake sediment and peat records have been used to reconstruct catchment specific deposition histories for the period up to peak mining activity in the late 19th century. National production trends (Schmitz, 1979) have been used after this point due to the complicating inputs from general sources such as vehicular emissions and power stations.

These records reveal significant local differences in Pb deposition, justifying the use of local sources of deposition data. In particular, Pb smelting on the Gritstone Edges of the Dark Peak has led to a much greater pre-industrial (1400-1700) input of Pb to the Etherow catchment than to the other catchments. A significant drawback, however, of using these peat and lake sediment records is that the accuracy of the deposition scenarios becomes very dependent on the reliability and representitiveness of one or two sources.

For Cu and Zn, despite acknowledging that there will be local differences in deposition from mining and smelting, there is little local information on which to base deposition scenarios. Zn mobility in peat and lake sediments makes them potentially unreliable. For Cu, the peat record at Grassington could possibly be used to reconstruct deposition at Cote Gill, but there is no equivalent available at the Etherow. There is no evidence of any significant mining-related input of Cu in the Lake District lake sediment records. The national production trends of Schmitz (1979) remain the primary resource for reconstructing past mining-related deposition of these metals.

It is assumed that there is no mining-related deposition of Ni and Cd as these metals have not been mined in any significant quantity. However, there is some, unquantified potential for some pollution, particularly for Cd which does exist in association with some Pb and Zn ores. In general, the scarcity of suiTable data means that the accuracy and precision of the mining-related deposition scenarios is considerably less than that of the general deposition scenarios.

4. Reconstructing actual deposition rates for the five catchments

4.1. Determining relative importance of mining and general deposition at each catchment

Mining and general deposition scenarios for each catchment can be combined to produce an overall deposition history. To do this, and to establish absolute rates of deposition from these, largely, relative records, deposition at some points on the trend profiles must be known. Table 5 lists monitored and estimated (from peat and lake sediment records) rates of deposition at the late 19th century mining maximum, the 1960s/1970s general deposition maximum and current deposition. Accurate deposition data from the early 1970s to present is available from the NETCEN monitoring station data, but these sites are not close to the catchments. Peak mining-related deposition is best estimated from the flux to peat cores from Yorkshire and the Peak District (Livett, 1988) and cores from Blelham Tarn (Ochsenbein et al., 1983) (Table 5).

In addition, recent rates of metal deposition have been monitored as part of the current project at the 5 catchments (between 2002-2003) at all catchments and between 1999 and 2003 at Lochnagar (data from Yang and Rose) (Table 6).

Table 5 Deposition rates estimated from peat cores and anthropogenic input to lake sediments

		Deposition at mining peak	Deposition at industrial peak	Industrial peak as % of mining peak	Deposition at present
		$\mu g\ cm^{-2}\ yr^{--}$	$\mu g\ cm^{-2}\ yr^{--1}$		$\mu g\ cm^{-2}\ yr^{--1}$
Grassington[1]	Pb	3.6 (1870)	1.3 (approx. 1970)	36.1	
Featherbed Moss[1]	Pb	4.8 (1850)	3.5 (approx. 1970)	72.9	
Ringinglow Bog (nr Sheffield)[1]	Pb	6.5 (1930)	3.9 (approx (1970)	60.0	
Buxton[1]	Pb	3.0 (1880)	2.2 (approx. 1970)	73.3	
Glenshieldaig[1]	Pb		0.15 (approx. 1970)		
North Uist[2]	Pb	0.2 (1880)	0.46 (1952-75)		
Loch Ness[3]	Pb	0.4 (1860)	1.0 (approx. 1950)		0.65 (1990)
Fladdabister[1]	Pb		0.63 (approx. 1970)		
Loch Lomond[4]	Pb	4.0 (1860)	4.5 (1950-60)	110	
Blelham Tarn [5]	Pb	0.7 (1871)	3.4 (1974)	476.3	
Wraymires[6]	Pb		2.9 (1972)		0.37 (1994-
Styrrup[6]	Pb		3.8 (1972)		0.26 (1995-
Chilton[6]	Pb		2.8 (1972)		
Featherbed Moss[1]	Cu	0.9 (1890)	0.8 (approx. 1970)	88.9	
Buxton[1]	Cu	0.5 (1880)	0.4 (approx. 1970)	80.0	
Grassington[1]	Cu	0.23 (1850)	0.25 (approx. 1970)	90.0	
Glenshieldaig[1]	Cu		0.0 (approx. 1970)		
Fladdabister[1]	Cu		0.18 (approx. 1970)		
Blelham Tarn [5]	Cu		0.66 (1974 not peak)		
Wraymires[6]	Cu		1.7 (1972)		1.48 (1994-
Styrrup[6]	Cu		2 (1972)		0.48 (1994-
Chilton[6]	Cu		0.8 (1972)		
Grassington[1]	Zn	0.9 (1890)	0.42 (approx. 1970)	88.9	
Featherbed Moss[1]	Zn		1.7 (approx. 1970)		
Ringinglow Bog[1]	Zn	7.3 (1940)	4.4 (approx. 1970)	60.3	
Buxton[1]	Zn	0.9 (1880)	0.4 (approx. 1970)	44.4	
Fladdabister[1]	Zn	1.8 (1910)	0.9 (approx. 1970)		
Blelham Tarn[5]	Zn		8.4 (1974)		
Wraymires[6]	Zn		6.4 (1972)		1.83 (1994-
Styrrup[6]	Zn		18 (1972)		2.32 (1994-
Chilton[6]	Zn		3.8 (1972)		
Blelham Tarn[5]	Ni		0.22 (1974)		
Styrrup[6]	Ni		0.39 (1972)		
Chilton[6]	Ni		0.29 (1972)		
Blelham Tarn[5]	Cd		0.08 (1974)		

[1] ***Livett (1988) The date of 1970 is an estimate based on the date of publication of the original sources as date of core collection is not mentioned in Livett (1988)***

[2] ***Sugden (1993)***

[3] ***Eades et al. (2002)***

[4] ***Farmer et al. (1997)***

[5] ***Ochsenbein et al. (1983)***

[6] ***Baker (1999) soluble metal deposition.***

Table 6. Bulk deposition of heavy metals (μg cm^{-2} a^{-1}).

Site	dates	Ni	Cu	Zn	Cd	Pb
Castle How Beck	2002-2003	0.06	0.07	0.70	0.005	0.20
Old Lodge	2002-2003	0.02	0.04	0.34	0.003	0.08
River Etherow	2002-2003	0.06	0.11	0.76	0.006	0.30
Cote Gill	2002-2003	0.07	0.08	0.76	0.005	0.19
Lochnagar[1]	1999-2003	0.02	0.03	0.47	0.003	0.10

[1] data of Yang and Rose.

The NETCEN monitored Pb deposition in 1972 for Styrrup (just east of Sheffield) of 3.8 μg cm^{-2} yr^{-1} is very similar to that estimated in the early 1970s from the Featherbed Moss peat core of 3.5 μg cm^{-2} yr^{-1}, and Ringinglow Bog (just west of Sheffield) of 3.9 μg cm^{-2} yr^{-1}. This gives us confidence to the accuracy of the peat bog Pb deposition inventories. The Cu deposition at Styrrup in 1972 (2 μg cm^{-2} yr^{-1}) is twice that estimated from Featherbed Moss (0.8 μg cm^{-2} yr^{-1}) however, Zn estimates from the peat cores for 1970 (Featherbed Moss 1.7 μg cm^{-2} yr^{-1} and Ringinglow Bog 4.4 μg cm^{-2} yr^{-1}) are less than a quarter of the Styrrup deposition estimate (18 μg cm^{-2} yr^{-1}) probably reflecting the mobility of Zn in the peat profile and further indicating that Zn records in peat cannot be relied on.

The NETCEN monitored Pb deposition in 1972 at Wraymires is reasonably close to that estimated from the Blelham Tarn sediments in 1974 (2.9 μg cm^{-2} yr^{-1} in comparison to 3.4 μg cm^{-2} yr^{-1}). However, Cu concentrations measured at Wraymires are considerably higher than the flux to the tarn sediments. Zinc flux to the sediments at Blelham Tarn, despite concerns over post-deposition mobilisation, is only slightly higher than the deposition flux measured at Wraymires (8.4 μg cm^{-2} yr^{-1} in comparison to 6.4 μg cm^{-2} yr^{-1})

The relative concentration at peak mining and peak industrial deposition can be used to estimate the relative proportions of each contributing to Pb and Cu deposition at Cote Gill and Etherow. This can only be an approximate estimate as: i) the estimate must be based on data from only one peat core; ii) the peat cores are close to, but not from the catchments of interest; iii) although there can, perhaps be some confidence in the Pb record, Cu is less certain and this will not be possible for Zn. Nevertheless, this is currently the best option available for estimating past deposition.

Actual rates of deposition are determined by scaling the deposition trends to currently monitored rates of deposition at the five catchments.

4.2 Lead deposition scenarios

4.2.1 Lead deposition onto the Etherow catchment

Lead deposition in the 1970s, as measured by the Peak District peat cores is between 60 and 73% of peak mining deposition (Featherbed Moss (73%), Ringinglow Bog and Buxton). Deposition of 0.30 μg cm^{-2} a^{-1} has been measured at the Etherow catchment in 2002 to 2003.

Using the general deposition trends and the mining trends for the Etherow catchment (Figures 7, 18a) and scaling to the 2002/3 deposition (Table 6), an estimate for historical Pb deposition can be obtained (Figure 19a). The combined deposition estimate highlights the importance of historical smelting in this area. Although the input of Pb from 'general,' industrial and vehicular sources of pollution is higher than in the other catchments, it is of minor importance in comparison to the mining-related input.

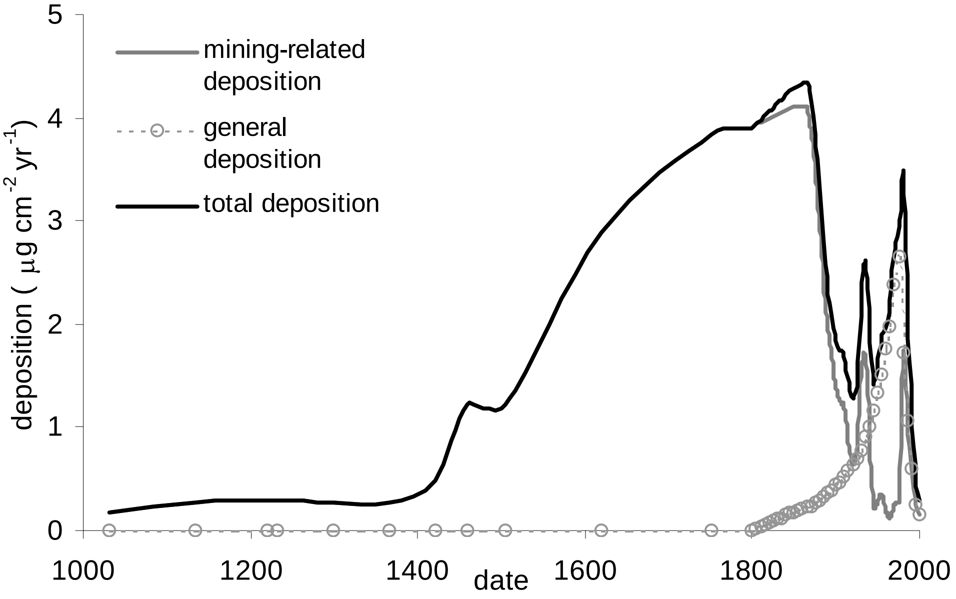


Figure 19a. Estimate for historical lead deposition onto the Etherow catchment.

4.2.2 Lead deposition onto the Cote Gill catchment

Lead deposition in the 1970s, as measured in the Grassington peat core is 36% of peak mining deposition. Deposition of 0.19 µg cm^{-2} a^{-1} has been measured at the Cote Gill catchment in 2002 to 2003.

Using the general deposition trends and the mining trends for the Cote Gill catchment (Figures 7, 18b) and scaling to the 2002/3 deposition (Table 6), an estimate for historical Pb deposition can be obtained (Figure 19b). Mining-related Pb inputs are relatively large to this catchment. Athough this is likely, as it is a very rural catchment, but close to historical mined areas, it should be noted that the Grassington peat core is nearer Pb mines than the Cote Gill catchment so there is a possibility that the mining peak may be overestimated.

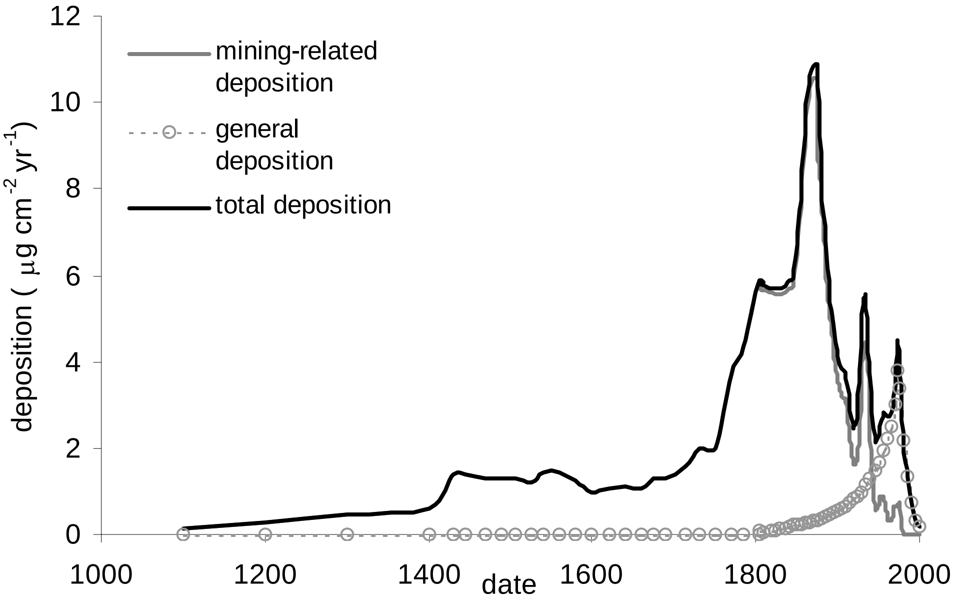


Figure 19b Estimate for historical lead deposition at Cote Gill.

4.2.3 Lead deposition at the Castle How Beck,

The Blelham profile suggests a minor mining-related Pb input, only 21% of the 1970s peak input (based on comparitive flux at 1880 and 1970, although the changing sedimentation rates and few dated horizons mean this is uncertain). Deposition of 0.20 µg cm^{-2} a^{-1} has been measured at the Castle How Beck catchment in 2002 to 2003. Using the general deposition trends and mining-related trends for the Castle How Beck catchment (Figures 7 and 18c) and scaling to the 2002 to 2003 deposition, an estimate for historical Pb deposition has been obtained (Figure 19c).

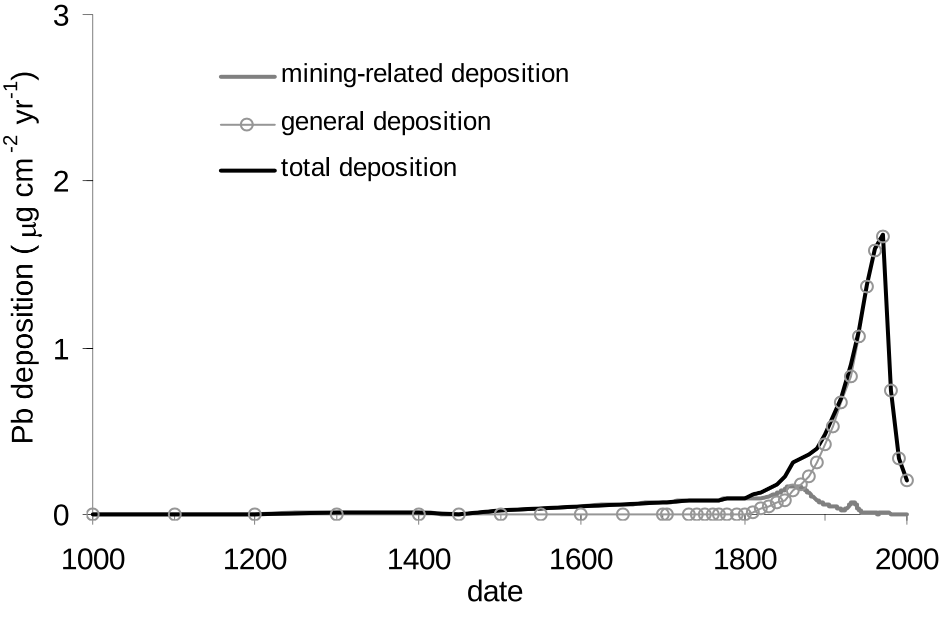


Figure 19c. Estimate for historical lead deposition estimated at Castle-How Beck.

4.2.4 Lead deposition at Lochnagar and Old Lodge.

Early inputs to remote lakes and peat bogs indicate some mining input is likely to these catchments. The flux of Pb to sediments in Loch Ness and a peat core from North Uist suggest that inputs in the late 19th century were around 40% of peak inputs in the late 20th century. This value seems high, especially in comparison to the estimate for the Lake District (although some of this will be from general deposition). However, it is the best available information on which to determine the relative mining and general contributions for Lochnagar and Old Lodge.

Deposition of 0.10 μg cm^{-2} a^{-1} has been measured at the Lochnagar catchment in 2002 to 2003 and 0.08 μg cm^{-2} a^{-1} at the Old Lodge catchment. Using the mining and general deposition trends determined (Figures 7 & 12) and scaling to the 2002 to 2003 deposition, an estimate for historical Pb deposition at these catchments can be obtained (Figures 19d & e).

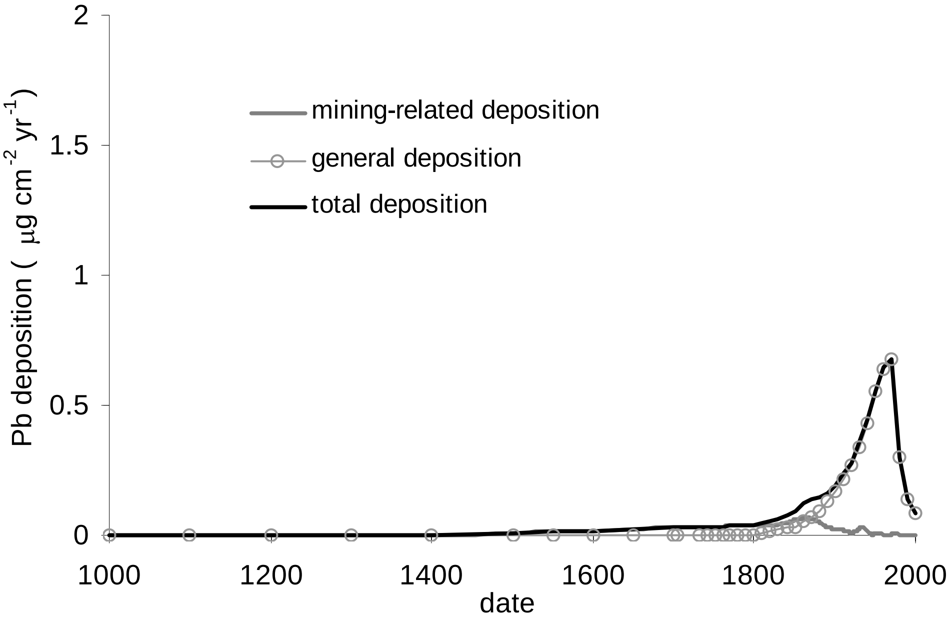


Figure 19d. Lead deposition at the Old Lodge catchment.

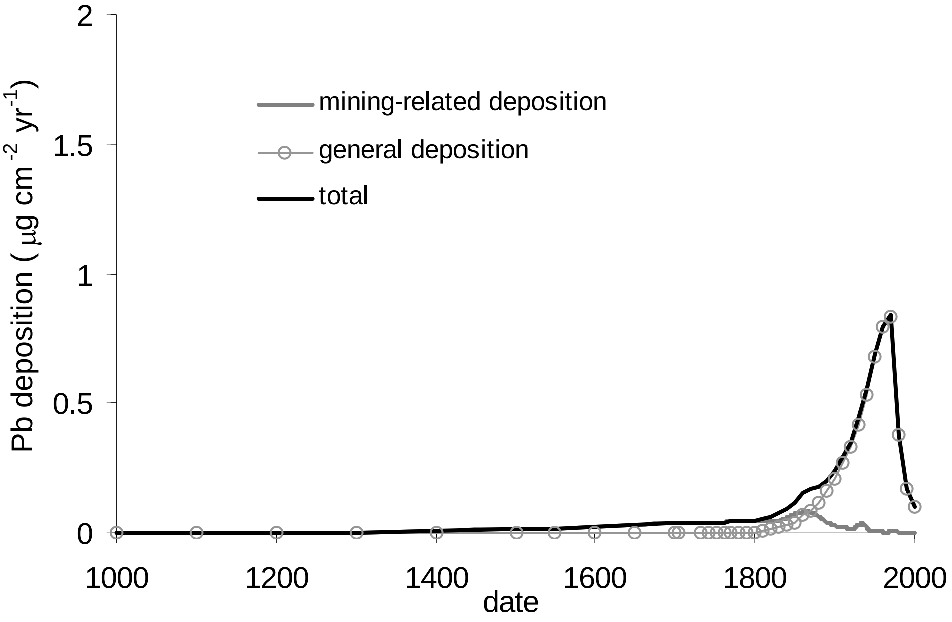


Figure 19e. Lead deposition at the Lochnagar catchment.

4.3 Copper deposition scenarios

4.3.1 Copper deposition at Cote Gill and the Etherow catchments

Reconstructing Cu deposition in the Cote Gill and Etherow catchments is problematic. The peat profile data suggests a mining-related input comparable with the levels in the 1970s. However, the lack of Cu mines in the vicinity of either catchments casts doubt on the peat profile data. If the peat core data is considered reliable, deposition profiles may be estimated as in Figure 20a and b.

Copper deposition in the 1970s, as measured in the Featherbed Moss core is 89% of peak mining deposition. In the Grassington peat core 1970s Cu deposition is 90% of of peak mining deposition. Deposition of 0.11 μg cm^{-2} a^{-1} has been measured at the Etherow catchment and 0.08 μg cm^{-2} a^{-1} at the Cote Gill catchment in 2002 to 2003.

Using the mining and general deposition trends (Figures 7 and 13) and scaling to the 2002 to 2003 deposition, estimates for historical Pb deposition have been obtained (Figures 20a & b).

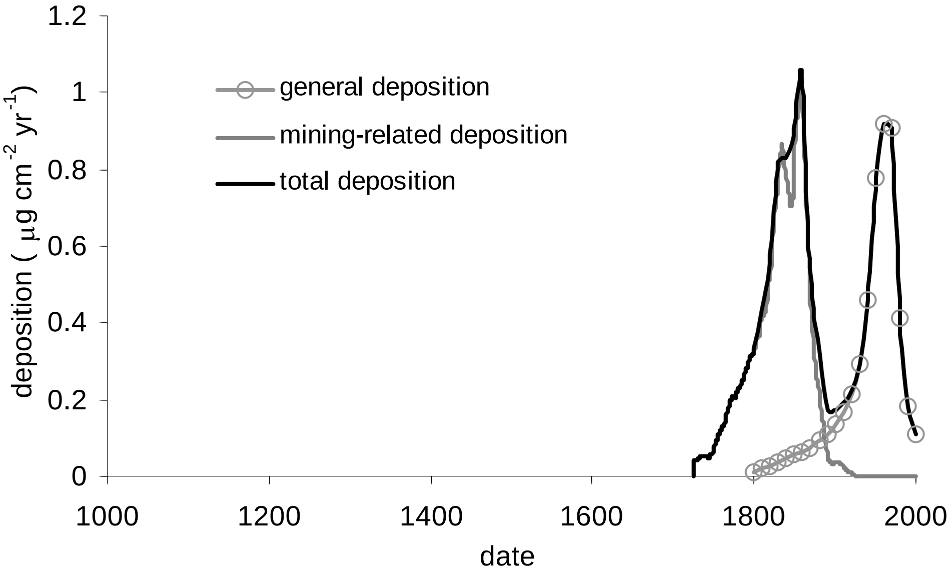


Figure 20a. *Estimate for historical copper deposition at the Etherow catchment, assuming the Cu profiles in nearby peat cores can be used to estimate the mining-related input.*

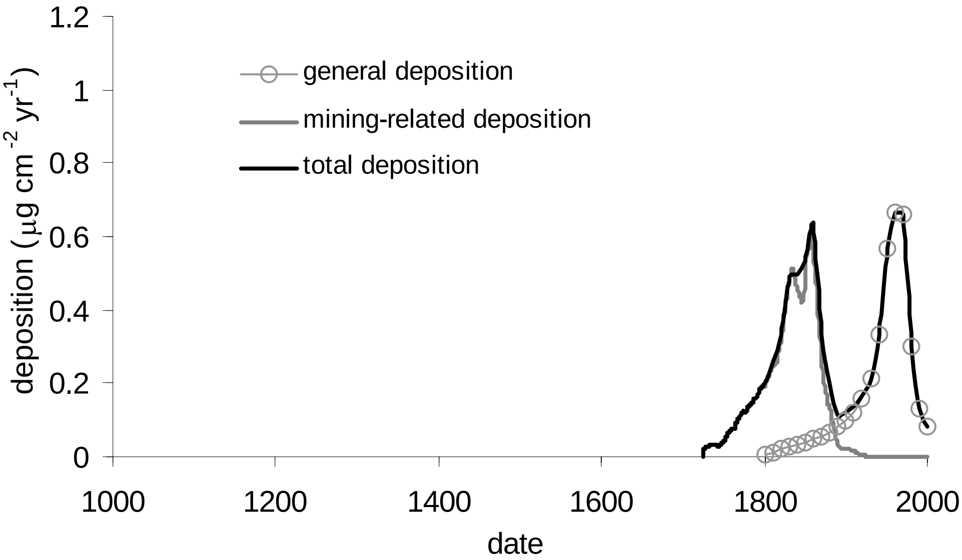


Figure 20b. *Copper deposition at the Cote Gill catchment assuming the Cu profiles in nearby peat cores can be used to estimate the mining-related input.*

If the peat record is considered unreliable (and there is nothing apart from the peat cores that suggests there should be high historical Cu deposition at these catchments) Cu deposition estimates may be based on the general deposition profile (Figure 7). Scaling this to the 2002 to 2003 deposition gives the following deposition scenarios (Figurew 21a & b). There is considerable difference between Figures 20a & b and Figures 21a & b.

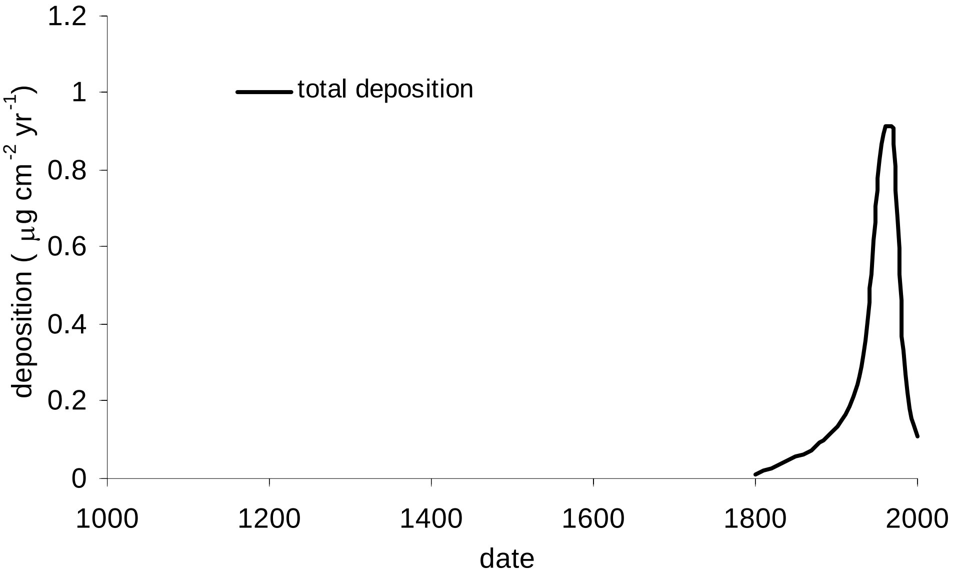


Figure 21a. Estimate for historical copper deposition at the Etherow catchment, assuming no significant mining-related input

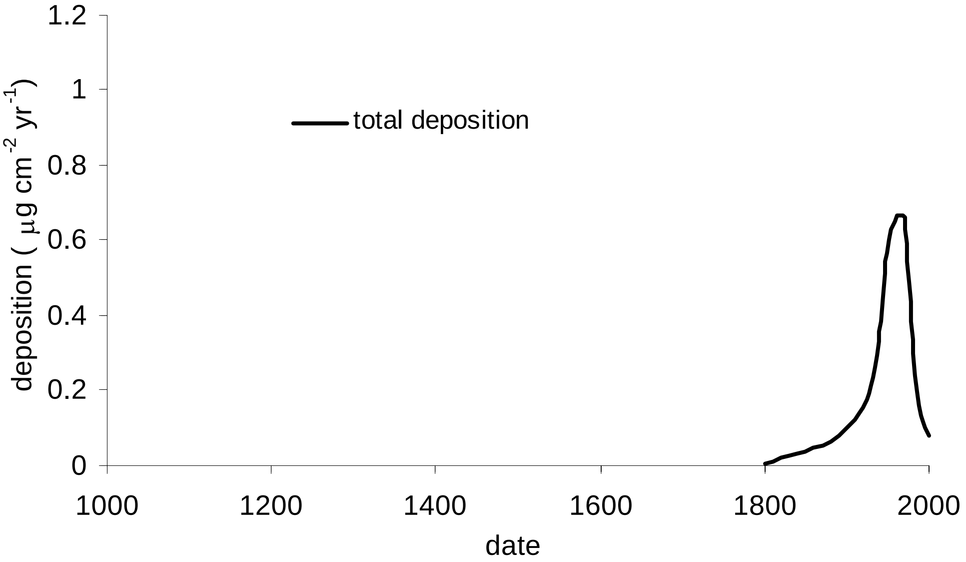


Figure 21b. Estimate for historical copper deposition at the Cote Gill catchment, assuming no significant mining related input

4.3.2 Copper deposition at Castle How Beck, Old Lodge and Lochnagar

There is no evidence of a mining-related Cu input to the Castle How Beck catchment from the nearby Blelham Tarn record, in fact Cu concentrations do not appear to increase above background until the late 19th century (Figure 16). Neither is there likely to have been a significant mining-related Cu input to the Old Lodge and Lochnagar catchments. Copper deposition estimates may, therefore, be based on the general deposition profile. Scaling this to the 2002 to 2003 deposition gives the following deposition scenarios (Figure 22).

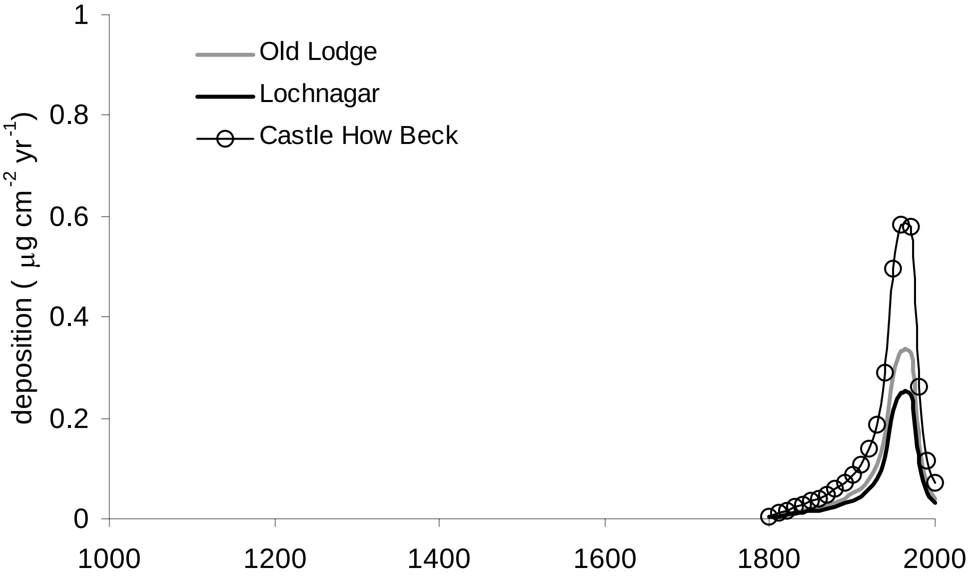


Figure 22. Estimated historical copper deposition onto the Castle How Beck, Lochnagar and Old Lodge catchments.

4.4 Zinc deposition scenarios

There is little reliable data on which to base Zn deposition histories. It is fairly certain that the Cote Gill catchment will have been influenced by deposition from local mining and smelting. It is also possible that the Etherow has been influenced to a small degree by Zn mining in the Peak District. It is, however, unlikely that the other catchments have been affected by any mining-related inputs.

4.4.1 Zinc deposition onto the Cote Gill catchment.

Reconstructing zinc deposition onto the Cote Gill catchment is problematic. There has almost certainly been a significant input of Zn from mining, however, we currently have no means by which to estimate this input. Analysis of herbarium moss samples from this region may provide an estimate for historical deposition.

4.4.2 Zinc deposition onto the Etherow, Castle How Beck, Lochnagar and Old Lodge catchments.

For the remaining catchments it can be assumed that the mining-related zinc input has been small in comparison to general sources of deposition (given the lack of close Zn mines or smelters and the relatively small amount of Zn exploitation in the UK in comparison to the Pb exploitation).

Zinc deposition estimates may, therefore, be based on the general deposition profile (Figure 7). Scaling this to the 2002 to 2003 deposition gives the following deposition scenarios (Figure 23).

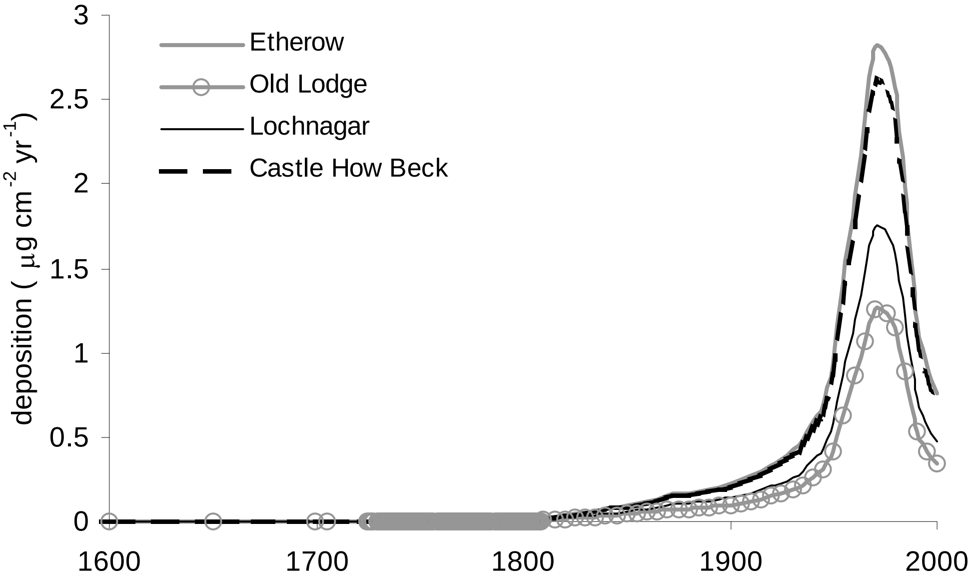


Figure 23. Estimated historical zinc deposition onto the Etherow, Castle How Beck, Lochnagar and Old Lodge catchments.

4.5 Cadmium and Nickel

Cadmium and Ni have not been mined in the UK, and therefore historical deposition scenarios can be approximated from the general deposition records in Figure 7 scaled to the 2000 to 2003 deposition in the five catchments (Figures 24 and 25).

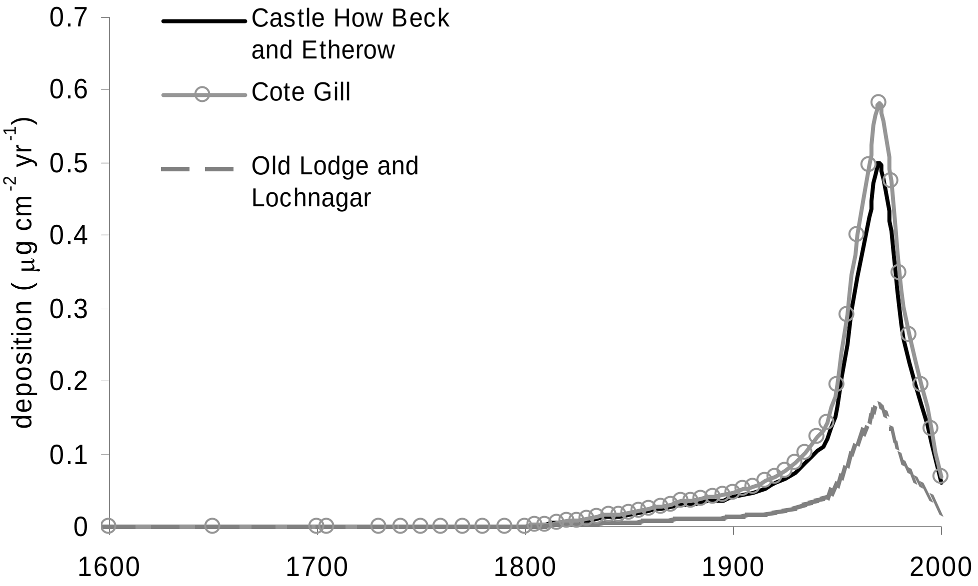


Figure 24. Estimated historical cadmium deposition onto the Etherow, Cote Gill, Castle How Beck, Lochnagar and Old Lodge catchments.

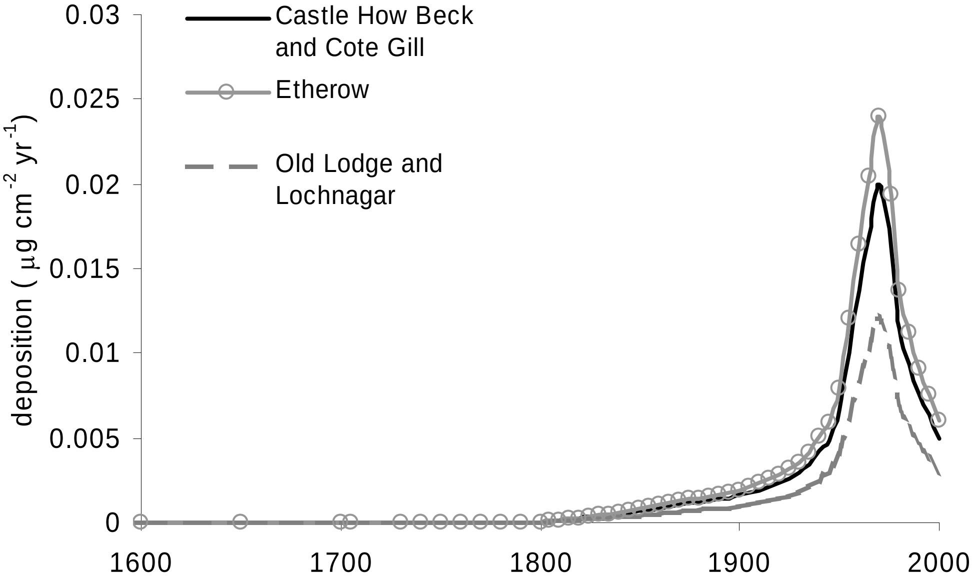


Figure 25. Estimated historical nickel deposition onto the Etherow, Cote Gill, Castle How Beck, Lochnagar and Old Lodge catchments.

5. Conclusions.

The UK has a long history of metal extraction and production and a relatively long history (in global terms) of general industrial and vehicular pollution. The division of heavy metal emission sources into ‘mining and smelting’ and ‘general’ sources allows regional differences in each to be accounted for.

5.1. Mining-related deposition scenarios

It has been possible to estimate UK wide trends in the deposition of Pb, Cu and Zn from mine production records (Schmitz, 1979). There are two key uncertainties with these trends: i) how mine production relates to emissions and deposition, as smelting will presumably have a much greater impact on deposition; and ii) the accuracy of the early part of the production record. The early part of the record is particularly important for Pb as the lake sediment records indicate early Pb deposition could be highly significant. Production from 1000 to 1700 is, therefore, estimated from general trends indicated in peat and lake sediment records. Pb production from 1700 to 1838 is estimated from the trade records. On this basis, Pb emissions from mining-related activity are shown to have been particularly significant in the UK: Pb production has been 12 times greater than Cu and 22 times greater than Zn production. Nickel and Cd have not been mined to any significant extent in the UK.

The long and intensive history of Pb production means that it has been most important to reconstruct mining-related deposition for this metal, and especially for the Cote Gill and Etherow catchments, areas that are close and downwind of mining and smelting sites. Peat core records from close to the Etherow and Cote Gill catchments indicate that deposition from mining and smelting has been more important that other industrial and vehicular deposition. Lead deposition fluxes determined from these peat cores (Livett, 1988) have been used to estimate the relative contributions of mining-related and ‘general’ deposition onto these catchments. Lake sediment records from Blelham Tarn in the southern Lake District have shown that mining-related inputs of pb are less important in this area, and have provided useful estimates of trends in Pb deposition onto the Castle How Beck catchment.

It is likely that the Lochnagar and Old Lodge catchments are sufficiently distant from mining sources to have been largely unaffected, however, the peat and lake sediment records from remote areas of the UK, Scandinavia and even Greenland suggest that there is a small long-distance effect of mining-related emissions. Lead flux to remote lake sediments and peat cores (from Loch Ness and North Uist) suggest deposition at the mining-related peak (around 1880) is 40% of that in the early 1970s general deposition peak.

Unfortunately, mining-related inputs of copper to the five catchments are uncertain. Peat cores close to the Etherow and Cote Gill catchments suggest an input comparable to that in the 1970s. However, the reliability of this record is questionable. Mining-related copper inputs to the other catchments are unlikely to be significant.

Mining-related inputs of zinc are likely to have been significant at Cote Gill close to many Zn mines in the Yorkshire Dales. Unfortunately there is no reliable data from which to estimate rates of deposition. Mining-related inputs of zinc to the other catchments are considered likely to be negligible.

Despite the general lack of data for many of the catchment-specific scenarios, the catchments that are most likely to have been affected by mining-related deposition (i.e. Pb at Cote Gill and Etherow) are the ones for which the deposition record is most readily reconstructed.

5.2. General deposition scenarios

Deposition from vehicles and general industrial sources has been reconstructed from a combination of post-1970 emissions estimates, post-1972 deposition monitoring, remote lake and peat sediment records and the global emission estimates of Nriagu (1979 & 1996). Post 1972 deposition monitoring at sites in South Yorkshire, Cumbria and the South East demonstrate clear UK-wide reductions in metal deposition, allowing us to be reasonably confident about this period of the deposition scenarios. A peak in metal deposition has been ascribed to 1970 based on the continuous decline in deposition since 1972 and the peak in SCPs measured in lake sediments which is centred on the mid 1970s. Peak Pb deposition can be more accurately dated to 1973 based on emission estimates (Goodwin *et al.,* 2001).

The “take-off point” for ‘general’ metal deposition is uncertain, but can be estimated at 1800, the mid point between 1750 (the estimated start of the industrial revolution) and 1850 (the start of the SCP record). Another uncertainty is the shape of the increase in metal deposition up to the 1970 peak. A slow increase in deposition until around the 1950s followed by a more rapid increase until 1970 is assumed, based on the SCP record (Rose *et al.,* 1995) and the global emission estimates (Nriagu, 1979; 1996). The only exception to this is Pb, which remote lake sediment Pb profiles and the global emission estimates suggest may increase more rapidly from around 1850.

5.3 Deposition estimates

Mining and general deposition scenarios have been combined to provide initial estimates of rates of deposition at the five catchments. The relative contributions from mining and general deposition have been determined from concentrations recorded in nearby peat and lake sediment records. Profiles have then been scaled to fit current deposition at the five catchments monitored in 2002 to 2003 as part of this project.

Key areas of uncertainty that may be (at least partly) resolved through analysis of herbaria moss samples include:

i) Analysis of mosses around the Cote Gill catchment may provide an indication of the influence of Zn mining.
ii) Determining the relative amounts of deposition at each catchment (for example, determining how much Cu is deposited at Castle How Beck as compared to Lochnagar could indicate whether there has been a significant mining-related Cu input to this catchment).
iii) Determining the relative amounts of each metal deposited at each catchment (for example determining the amount of Cu deposited compared to Pb in the Etherow catchment will allow approximate rates of Cu deposition to be determined (as Pb deposition is known from the peat profiles).
iv) Determining the importance of early (1850 to 1900) deposition onto the Lochnagar and Old Lodge catchment could indicate whether there is any mining-related input to these catchments.

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ANNEXE 8. HERBARIUM MOSS SAMPLE RECORDS OF HISTORICAL METAL DEPOSITION

L.Shotbolt, P.Büker, M.R.Ashmore.

1. Introduction

A key objective of the current project is the development and testing of dynamic models of heavy metal accumulation in soils and waters. These models aim to interpret the current metal burden in soils and lake sediments, and to forecast the effects of changes in future emissions on soil and water metal concentrations. They are based on five rural catchments in the UK: Lochnagar, north-east Scotland; Cote Gill in the Yorkshire Dales; Castle How Beck in the Lake District; the River Etherow, Peak District; and Old Lodge in the south-east of England. An important input to these models is past heavy metal deposition. To reconstruct past heavy metal deposition we have carried out an extensive literature review and developed deposition scenarios based on the available data (instrumental records, historical records and environmental records such as peat bogs and lake sediments – see Annexe 7). However, few records exist and there are major uncertainties associated with the deposition scenarios. To improve these scenarios and provide temporal records of historical metal deposition we have analysed metal content in herbarium moss samples collected over the last 150 years in the vicinity of the 5 study catchments. This report presents the results of the herbarium moss sample analysis.

1.1 Background

There have been few retrospective studies of heavy metal concentration in mosses. Most are listed in Table 1. In the UK there have been only two such studies: Farmer et al. (2002) investigated trends in Pb isotope deposition in Scotland, and Lee and Tallis (1973) compared Pb concentrations in herbarium samples to metal concentrations in surface peats in historically mined regions of the UK.

Table 1. Herbarium based studies of temporal changes in atmospheric heavy metal deposition

Authors	Metals	Method	Location	Findings
Farmer, et al. (2002)	Pb, Pb isotopes	188 samples from RB Garden, Edinburgh. 0.1 g samples used, dry ashed and digested in HNO_3. ICP-MS	Scotland	Presents Pb isotope results which compare well to other environmental records (peat bogs and lake sediments). 1830 to 2000.
Johansson and Rasmussen (1977)	Pb, V, Zn, Cd, Cr, Cu, Fe, Mn, Ni.	*Pterogonium gracile* collected from a single tree between 1944 and 1976 in Jutland. Un-washed prior to analysis. 1 g digested in 40 ml 50% HNO_3.	Jutland, Denmark	Only Pb, V and Zn showed significant and linear increase.
Hallingback (1992)		Comparison of species found today with herbarium species	Skane, Sweden	Decline in at least seven species including *Hy.sp,* suggests air pollution is the cause.
Herpin, Markert et al. (1997)	As, Cd, Cr, Cu, Pb, Ni, V, Zn	28 herbarium samples, all compared to 1991 levels. Not washed, dried at 40°C, ground and digested (400 μg) with 5 ml HNO_3.	Germany	(Samples from 1845-1974, 1991). Divided into 4 periods. Lowest concentrations between 1845 to 1901. Metal concentrations (median of 7) are compared to similar locations and species in 1991. As and

				Pb herbarium samples are higher than 1991. Cd and Zn generally higher. Ni and V however, are higher in 1991. Cr and Cu are less uniform.
Lee and Tallis (1973)	Pb	*H. cu.* Compared herbarium samples to contemporary (1972-1973) samples, close to original sites. Washed before analysis.	1850 to 1900 at 6 UK sites.	Some very high historical and contemporary moss concentrations. No significant temporal changes except Teesdale where dropped in response to cessation of industry from > 215 μgg^{-1} to 71 μgg^{-1}.
Penuelas and Filella (2002)	V, Cr, Ba, Sr, Al, Fe, Pb, Cd, Ti	3 bryophytes throughout 20th century	North and Eastern Spain.	V (proxy tracer of oil pollution) exponentially increased in latter 20th century. Other metals show recent decrease in 1985-1995.
Pott and Turpin (1996)	Pb, Cd, Cr, Ni, Zn, Mn	*Isothecium stoloniferum.* Used 0.1 g. Not washed, dried and digested in HNO_3.	Fraser Valley, Canada	Collected during three periods: 1960-1966, 1975-1980, 1993. Significant decrease in most metals except Mn.
(Rasmussen (1977)	Ca, Cd, Cr, Cs, Fe, K, Mg, Mn, Na, Ni, Pb V, Zn.	5 species collected from the same trees in Jutland in 1951, 1973, 1975. Pools results of 5 species to get mean for each year.	Jutland, Denmark	Cr, Cu, Fe, Ni, Pb, and V increased between 1951 and 1975. Short term variation may obscure long term trends in concentration under some circumstances.
Rao et al (1977)	Cu, Cd, Cr, Ni, Pb, Zn	1905-1971. Several species.	Montreal Canada	Increases in mean concentration of all metals except Cu.
Ruhling and Tyler (1968)	Pb	*Hy. sp; H. cu; Pl. sc.* Not washed. Dried at 37°C, digested with $HNO_3 + HClO_4$ (4:1).	Skane Sweden	20 μgg^{-1} in 1860-75, more than doubling between 1875 and 1900, not significantly changing in the first half of the 20th century (though wide range). Increased to 80 – 90 μgg^{-1} in 1968.
Ruhling and Tyler (1969)	Pb, Zn, Cu, Ni, Cr	*Hy. sp; H. cu; Pl. sc.* Not washed. Dried at 37°C, digested with $HNO_3 + HClO_4$ (4:1).	Sweden	Samples collated from between 1870 to 1968, split into 4 periods. Cu increase from the 1870-99 period to the 1900-1919 period, but not into the 20th century. Zn increased around 1900. Ni, in the 20th century. No change in Cr.
Sergio, Seneca et al. (1992)	Cd, Cu, Fe, Pb, Zn	Herbarium samples from 1924 and 1981	Northern Portugal.	
Weiss et al. (1999)	Pb, Pb isotopes	*Sphagnum species.* Used 0.25 to 0.8 g, washed, macerated and sonicated in HCl (diluted to pH 2.4), then digested with HNO_3 and HF (semi-sequential extraction)	Switzer-land	Pb isotope records show pollution records in good agreement with other archives from Switzerland (peat, sediment, ice). Very little Pb in the supernatant, no contamination.

Pl. sc = Pleurozium schreberi*; Hy. sp* = Hylocomium splendens*; H. cu* = Hypnum cupressiforme

Key issues for reconstructing records of past deposition raised in these studies are i) the possibility of contamination from storage in the herbarium; and ii) the variability of metal concentrations due to spatial variation in deposition. These two issues were considered in designing the sampling and analytical methodology.

2. Sample collection

Samples of four moss species, *Hylocomium splendens*, *Hypnum cupressiforme, Pleurozium schreberi* and *Rhytidiadelphus squarrosus*, were collected from herbarium collections. These species are thought to obtain nutrients and metals predominantly from the atmosphere and are therefore particularly useful for the study of atmospheric metal deposition. They have been used across Europe to monitor heavy metal deposition (Ruhling, 1987; 1996; Buse et al., 2003). The most recent UK survey of metal content in mosses (Ashmore et al., 2002) used these species and made an assessment of differences in metal uptake between species. While none of these species cover the whole of the UK, in combination they will provide the potential for doing so.

We aimed to produce a deposition history for five catchments:

- Old Lodge, Ashdown Forest, South of London (grid reference: TQ4529)
- River Etherow, Peak District (grid reference: SJ9892)
- Cote Gill, Yorkshire Dales (grid reference: SD9470)
- Castle How Beck, Lake District (grid reference: NY2300)
- Lochnagar, Scottish Highlands (grid reference: NO2586)

To reduce the impact of spatial variation mosses were collected within a suitable vicinity of the five target sites - at the most 50 km, dependent on source rock and landscape units but generally much less. Mosses were not collected from sites close to the sea (in order to exclude competition from sea-salt cations) or quarries (which could results in highly localised increases in dust and metal loading).

The following British herbaria have provided samples for this survey:

- The Manchester Museum
- The Natural History Museum, London (including the former herbarium of Kew Gardens)
- The National Museum of Wales, Cardiff
- The Royal Botanical Gardens Edinburgh

17 samples were obtained from London, 55 from Cardiff, 24 from Edinburgh and 47 from Manchester. 69 samples of *Hypnum cupressiforme* were collected, 31 of *Hylocomium splendens*, 29 of *Pleurozium schreberi* and 14 of *Rhytidiadelphus squarrosus.* In total 143 samples have been collected and analysed.

0.1 g of each sample were collected and stored in paper bags until analysis. Samples were not collected where there was insufficient material to allow the removal of 0.1 g, or where the sample had been glued onto sheets of paper since the chemical composition of the glue and consequently the potential influence on the heavy metal analysis was not known.

The five target sites were represented satisfactorily between 1850 and 2000 (Castle How Beck: 41 samples, Cote Gill: 39 samples, River Etherow: 25 samples, Lochnagar: 23 samples and Old Lodge: 15 samples), however, it was not possible to find specimens for the Old Lodge site for the time period from 1850 till 1900 (Figure 1).

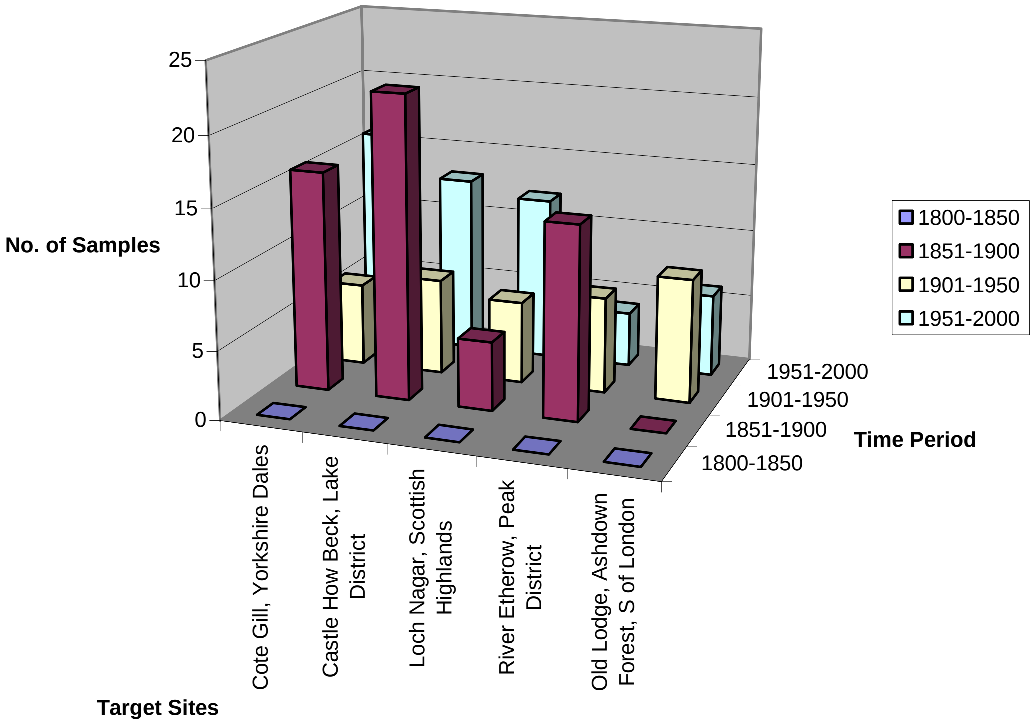


Figure 1. Distribution of moss samples between regions and time periods.

3. Analytical methods

Analysis of heavy metal concentrations in herbaria moss samples was adapted from the methods used in the 2000 moss survey. Key aims of the analysis were:

- To extract all metals held on and within the moss
- To produce results that can be compared to UK moss deposition survey data
- To identify samples that had been contaminated by soil or during storage in the herbarium, and to quantify the contamination.
- To produce results with a usable level of accuracy and precision

Some differences have been introduced to speed up the digestion process and also to account for the greater likelihood of contamination. The main variation introduced is the inclusion of a pre-digest sample washing step. The purpose of washing samples prior to digestion and analysis was to reduce any surface contamination by soil particles or rock fragments. This may also have the advantage of removing surface contaminants introduced in the herbarium including preserving treatments such as pesticides or through drying samples: Herpin *et al.* (1997) report that a common practice has been to dry and press samples between layers of newspaper. Although unproven, this could lead to contamination from metals such as Pb, Cr, Ba and Cd in the ink.

The washings were retained and analysed and the presence of high metal concentrations in the washings used to identify any contaminated samples. Washing samples has, however, been suggested to result in the loss of some more soluble metals. If the soluble component is significant and not thought to represent contamination, the retention and analysis of washings means that this could be accounted for.

Other differences include:

- the smaller weight of sample used (0.1 g in comparison to 1 g). Only small samples could be collected from the herbaria
- the larger amount of acid relative to the sample size
- the use of microwave digestion
- analysis of all metals using ICP-MS (previous method analysed base cations by ICP-AES).

3.1 Moss digestion

1. 0.1g of moss was weighed into a 50 ml acid washed centrifuge tube after removing any obvious soil, grass or other particles. Approx 10 mls of double distilled water was added and the sample shaken gently. The moss sample was then removed using plastic tweezers and rinsed thoroughly with DDW. Approximately 100 mls of washings were generated from this (two centrifuge tubes). A plastic sieve was used to retain any small pieces of moss.
2. The washings were evaporated at 70°C.
3. Washed moss samples were decanted into acid washed microwave digestion tubes. 5 mls of Primar nitric acid were added (used to wash any remaining sample from the centrifuge tubes if necessary) followed by 2 mls of DDW.
4. Samples (10 samples, 1 CRM or duplicate, 1 blank) were digested at full power for 30 minutes.
5. Extracts were transferred quantitatively to new 50 ml acid washed centrifuge tubes and made up to 25 mls.
6. 2 mls of 1000 ppb In was added as an internal standard.
7. Samples were diluted x10 prior to analysis by ICP-MS.
8. Washings from the same batch were analysed immediately after the moss samples, thus removing the necessity to thoroughly wash digestion tubes. 2.5 mls Primar nitric acid was added to the evaporated centrifuge tubes and shaken. This was poured into the digestion tubes and the process repeated with a further 2.5 mls HNO_3, then 2 sets of 2 ml DDW. (i.e. digest carried out on 5mls HNO_3 and 4 mls DDW).
9. The same digestion procedure was followed for the washings from this point (points 4,5,6 and 7).

3.2 Precision and accuracy assessment

Accuracy of the ICP-MS and accuracy of the whole analytical procedure was assessed. ICP-MS accuracy was determined through analysis of known standard solutions made up by the Analytical Centre at Sheffield (i.e. made up by a different operator than the standards used in the calibration). These standards were measured every 10 samples throughout the run. ICP-MS accuracy was found to be acceptable (Table 2), although Ni and As were consistently measured to be 9% and 11% higher than the known standard concentrations. No correction has been made for this at present.

Total analytical accuracy was assessed by the analysis of certified reference samples that had been digested and analysed alongside the moss samples. Measured concentrations were compared to the certified concentrations. Total analytical accuracy was found to be acceptable, although Ni appears to be slightly overpredicted and Cd underpredicted.

Table 2. *Accuracy assessment*

	Accuracy of the ICP-MS *	Mean measured	% extracted	Total analytical accuracy**	mean measured CRM	% extracted
Ni	5	5.44 ± 0.17	108.76	2.47± 0.07	2.90 ± 0.42	117.27
Cu	10	10.05 ± 0.13	100.50	7.03 ± 0.19	6.98 ± 0.67	99.33
Zn	50	51.95 ± 0.67	103.91	100.6 ± 2.2	108.52 ± 3.81	107.87
As	6	6.68 ± 0.14	111.34	0.85 ± 0.07	0.84 ± 0.04	99.11
Cd	5	5.07 ± 0.05	101.39	0.56 ± 0.02	0.5 ± 0.03	89.45
Pb	50	49.42 ± 0.26	98.84	40.9 ± 1.4	38.67 ± 0.70	94.55

± are 95% confidence limits

* Assessed using Analytical Centre Standard solutions, standards made up separately (and by different operator) from standards used in the calibration. Mean of samples measured at 10 sample intervals throughout the analysis.

** Assessed against a Certified Reference Material (BCR 482 (lichen)) thus incorporating any errors arising from sample preparation and instrumental analysis.

Precision of the ICP-MS, the digestion procedure and ICP-MS and the whole analyical procedure were also measured. The ICP-MS precision was assessed by determining variability in repeated measurement of an Analytical Centre standard solution. This was found to be excellent (confidence intervals of less than 4%). Analysis of the variability in the certified reference material enabled the precision of the digestion procedure and ICP-MS to be quantified. Although the digestion procedure introduced further loss of precision, particularly for Ni and Cu, overall precision remained acceptable. The greatest precision loss is introduced by sub-sampling (Table 3). This was assessed by analysis of the variability in duplicate samples. This is unavoidable due to the small sample size available from the herbaria. Subsampling errors may be overestimated slightly as, to gain duplicate samples, smaller amounts of material (down to 0.06g) was used. Nevertheless, this results in significant precision error and 95% confidence limits around the mean of up to 30%.

Table 3. Precision assessment

	Precision of the ICP-MS*		Precision of the digestion procedure and ICP-MS**		Precision of the whole procedure including sub-sampling, digestion and ICP-MS analysis***	
	mean	% CI	mean	% CI	Mean* (standardised)	% CI
i	5.44 ± 0.17	3.13	2.90 ± 0.42	15.83	1.20 ± 0.33	27.69
Cu	10.05 ± 0.34	3.39	6.98 ± 0.67	10.45	1.04 ± 0.18	16.93
Zn	51.95 ± 0.67	1.28	108.52 ± 3.81	3.84	0.90 ± 0.25	25.65
As	6.68 ± 0.17	2.54	0.84 ± 0.039	5.04	1.12 ± 0.28	24.67
Cd	5.07 ± 0.05	0.91	0.5 ± 0.032	6.90	1.27 ± 0.39	30.40
Pb	49.42 ± 0.26	0.52	38.67 ± 0.679	1.92	1.11 ± 0.21	19.20

± are 95% confidence limits

* precision assessed using Analytical Centre standard solutions

** precision assessed using CRM

*** precision assessed using standardised duplicates.

4. Assessment of contamination

Contamination of herbarium moss samples could occur through:

- Attachment of soil to moss samples.
- Use of pesticides or fungicides in herbaria or storage in newspaper
- During collection (e.g. collector smoking)
- At any stage of the analysis

No research could be found on possible sources of contamination to herbaria moss samples during storage. Although contamination could be through the application of insecticides or fungicides, it is likely that the main insecticides used were repellents such as naphthalene (mothballs) and paradichlorobenzene (a similar substance) rather than direct application to the sample. A further possibility is the contamination of samples from newspaper ink, which may have contained heavy metals in the past, although most black newspaper inks no longer contain heavy metals.

The greatest potential source of contamination, however, is from soil. To reduce the impact of this source of contamination, samples have been washed prior to analysis. However, washing samples introduces a real possibility of removing metals that we want to include – either metals from dry deposition, or possibly metals on exchange sites that could easily be desorbed. The proportion of metals removed during the washing process varies (Table 4). It is, however, 10% or less for four key elements of interest (Pb, Cd, Cu, Zn) indicating washing will not remove the majority of these metals. It is, however, 17% for As and 18% for Ni. Similar concentrations of Al, Th, Li, V and Ga are found in the washings to As and Ni – these are elements most likely to be from soil particles. Note also the very high concentrations of Na and K, elements that are particularly soluble and perhaps found largely at the surface of the mosses.

Table 4 Median concentration in washings as percentage of concentration in moss.

Element		Element		Element	
Fe	14%	Zr	25%	Sr	7%
Al	16%	Se	5%	Ca	6%
Th	20%	As	17%	Mg	2%
Cr	14%	Pb	4%	B	25%
Co	12%	Cu	10%	Ba	9%
Ni	18%	Sb	11%	Mn	10%
V	13%	Sn	12%	Na	76%
Li	18%	Zn	10%	K	65%
Ga	10%	Cd	9%		

4.1 Contamination during digestion and instrumental analysis

Analysis of blanks and other quality control data indicates very little contamination has been introduced during the digestion procedure (Table 5).

Table 5. *Analysis of instrumental and method blanks*

	instrumental blanks				method blanks		
	LOD (mean + 3*st.dev.)	mean	min	max	mean	min	max
Ni(PPB)	0.008	0.003	0.003	0.007	0.067	0.000	0.320
Cu(PPB)	0.053	0.026	0.009	0.049	0.123	0.000	1.100
Zn(PPB)	0.235	-0.086	-0.220	0.084	1.111	-0.270	3.087
As(PPB)	0.033	0.014	0.003	0.028	0.006	0.000	0.058
Cd(PPB)	0.008	0.003	0.003	0.010	0.016	0.000	0.068
Pb(PPB)	0.008	0.003	0.003	0.009	0.068	0.000	1.112

4.2 Identification of contaminated samples

We need to be concerned about samples where the washings contribute significantly to the overall metal concentration or have an unusually high proportion of pollutant metals. To identify such samples we have:

i) noted samples that either looked like there was soil on the moss, or had material remaining after digestion (resistant material may be mineral) (Table 6)

ii) noted samples where a large proportion of metals are found in the washings (greater than 50%)

iii) carried out ordination analysis to identify samples that have high scores for pollutant metals (Figure 2).

i) samples identified as potentially contaminated during analysis.

Table 6. Suspected contaminated samples

Sample	Location	Year	Comments	Species	Location
73	South East	1934	Washings cloudy. Digest and digested washings also cloudy	*Pleurozium*	Balcombe Tunnel
46	Yorkshire Dales	1957	Some material left after digest	*Hypnum*	Nr. Malham Tarn
217	South East	1954	A little material left after digest	*Hypnum*	Balcombe
215	Yorkshire Dales	1926	Soily but rid of most before washing	*Hypnum*	Chapel-le-Dale
208	Cairngorms	1967	A little material left after digest	*Hylocomium*	Glen Doll

ii) samples with high concentrations in the washings

There are a few samples with unusually high concentrations of metals in the washings and contamination may be responsible for this. Samples where metal concentration in the washings is greater than that in the actual moss were identified (Table 7).

Table 7. Samples with high metal concentrations in washings.

No.	Location	Year	Contam -inants	Species	Location	Notes
419	Cairngorms	1965	Zn	*Pleurozium*	Loch Brady	
353	Peak District	1903	As	*Hypnum*	Below High or Lightwood Reservoir	Stored in newspaper
73	South East	1934	Ni, Cd	*Pleurozium*	Balcombe Tunnel	
217	South East	1954	Cd	*Hypnum*	Balcombe	
7	South East	1923	Pb	*Hylocomium*	Worth Forest	Stored in a plastic bag
46	Yorkshire Dales	1957	Cu	*Hypnum*	Nr. Malham Tarn	
55	Yorkshire Dales	1898	Ni, Cd	*Hypnum*	Bank of R. Hodder	
324	Yorkshire Dales	1878	Zn, As, Cd	*Hypnum*	Skipton	
326	Lake District	1883	Ni	*Hypnum*	Witherslack, Westmorland	
346	Yorkshire Dales	1871	Cd	*Hypnum*	Craven	

This is a rather subjective method of identifying contaminated samples. As a less subjective method, principle components anlaysis has been utilised to identify samples with an unusually large contribution of pollutant metals in the washings.

ii) Principle Components Analysis

Ordination techniques aim to reduce a multidimensional data set to a few dimensions in order to visualise relationships between the data without losing important variability. A commonly used linear method of ordination is principle components analysis (PCA). Based on eigenanalysis (Pielou, 1984) a process of linear transformation of the original data extracts a new axis that summarises as much of the data as possible. The remaining unexplained data (residuals) is then subject to further analysis to extract a second orthogonal axis that explains as much of the remaining data as possible and so on. Each axis is described by an eigenvalue indicating the amount of variance summarised by each axis. Ordination techniques produce axes that explain much of the variation in a set of variables, but have no direct physical meaning and cannot, therefore, directly be used to directly relate the multivariate data set to external variables. However, we can determine how strongly each metal (factor) is associated with each axis (factor loadings – see table 8). By analysing a wide range of metals and determining how strongly each relates to the axes, it should be possible to draw some conclusions as to their source.

To carry out the PCA, the amount of each metal in the washings was expressed as a percentage of the metal concentration in the moss sample. Values were logged to bring sample distributions close to normal. The dataset was standardised by dividing each logged value by the log mean.

Principle components analysis was carried out in SPSS. Varimax rotation was used to simplify the explanation of factors (Table 8).

Table 8. Factor loadings for each element on the five principle factors identified by PCA. .

% washings

Eigen-values	5.53	4.00	3.74	1.79	1.35
% of variation explained	22.10	15.99	14.95	7.15	5.41
Factor loadings					
	1	2	3	4	5
Li	**0.83**	0.24	0.06	0.23	0.04
Al	**0.81**	0.23	0.33	0.01	0.01
Th	**0.80**	0.16	0.15	0.05	-0.01
Fe	**0.78**	0.33	0.39	-0.01	0.01
Co	**0.77**	0.31	0.20	0.30	-0.14
Zr	**0.73**	0.10	0.21	0.08	-0.03
V	**0.65**	0.41	0.44	-0.01	0.04
Sn	0.47	0.04	0.10	0.43	0.23
Zn	-0.01	**0.69**	0.23	0.42	0.26
Sb	0.30	**0.65**	0.17	-0.06	-0.08
As	0.45	**0.64**	0.21	-0.10	0.07
Pb	0.24	**0.63**	0.42	0.18	-0.09
Cr	0.42	**0.62**	0.19	0.02	0.13
Ni	0.34	**0.62**	-0.03	0.20	0.06
Cu	0.33	0.46	0.34	0.35	0.05
Cd	-0.05	0.46	0.21	0.25	-0.32
Mn	0.33	0.37	**0.62**	0.35	-0.02
Mg	0.32	0.06	**0.65**	0.19	-0.05
Ca	0.27	0.24	**0.71**	0.40	0.06
Sr	0.27	0.32	**0.73**	0.33	0.15
Ga	0.14	0.06	**0.69**	-0.28	0.13
Ba	0.19	0.41	0.56	0.15	-0.11
Na	0.11	0.13	0.15	**0.67**	-0.02
K	0.01	-0.14	0.00	0.13	**0.66**
B	-0.04	0.28	0.11	-0.09	**0.75**

Factor loading over 0.3 is generally considered the cut-off point, over 0.4 weak, 0.6 strong.

In the analysis above, much of the variation in the percentage of elements in washings is described by the first three factors. The first factor is dominated by elements that are most likely to be derived from local soil inputs (Al, Li, Th, Ga, Fe). The second factor however is dominated by elements (i.e. Zn, Sb, As, Pb, Cr, Ni, Cu, Cd) that may be more associated with atmospheric deposition. The remaining factors seem most influenced by elements such as Mg, B, Na, Sr, Ca that are probably derived from marine aerosols, but may also represent differences in uptake of nutrients by the mosses from adjacent vegetation or substrate.

For each sample a score can be derived that represents the importance of each factor in determining its composition. For example a high score on factor 2 means there is likely to be a high proportion of metals Zn, Sb, As, Cr, Ni and Pb in that sample. Figure 2 shows ranked sample scores on factors 1 and 2. For each factor there are 4 samples with an unusual influence (Figure 2). These are shown in Table 9.

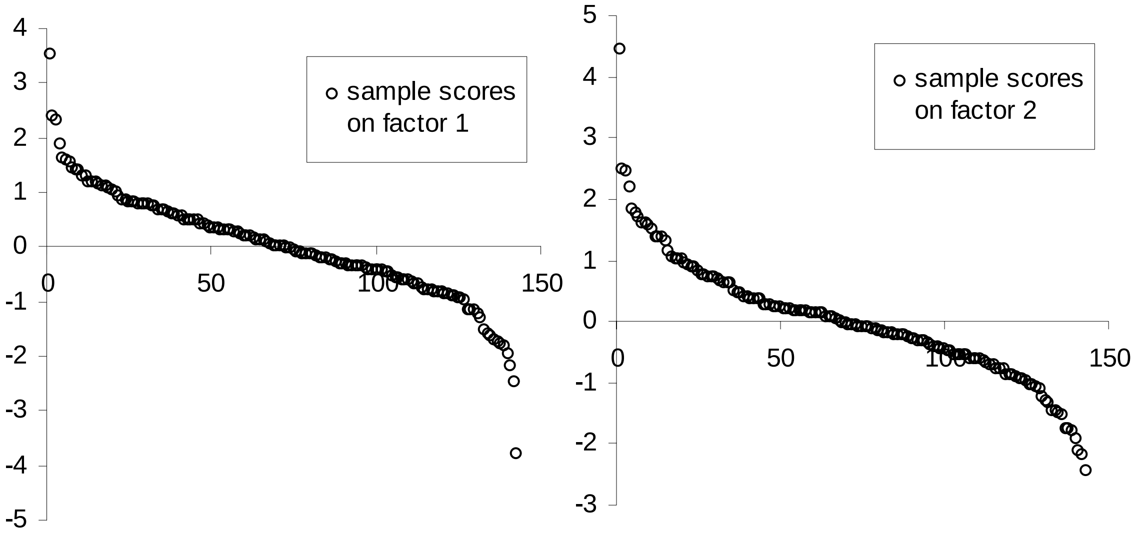


Figure 2. *Frequency distribution of sample scores on factors 1 and 2.*

Table 9. *Samples with either high (more than 2) or low (less than –2) scores on factors 1 and 2.*

	Factor 1	Factor 2
High (> 2)	412 (*Hylocomium*) Braemar, Cairngorms 367 (*Pleurozium*) Milnthorpe, Lake District 10 (*Hylocomium*) Crowborough, South East	324 (*Hypnum*) Skipton, Yorkshire Dales 55 (*Hypnum*) River Hodder, Yorkshire Dales 73 (*Pleurozium*) Balcombe Tunnel, South East 326 (*Hypnum*) Witherslack, Lake District
Low (< -2)	410 (*Hypnum*) Cairngorms 407 (*Hypnum*) Shap, Lake District 31 (*Hypnum*) Worth Forest, South East	405 (*Hypnum*) Braemar, Cairngorms 205 (*Hylocomium*) Cheedale, Peak District 423 (*Rhytidiadelphus*) Shap, Lake District

The samples identified as having material remaining after digestion do not correspond to those identified by ordination analysis (except sample 73). However, all the samples identified as having more than half of their metals in the washings are identified by the PCA. Samples with high loading on factor 2 (324, 55, 73 and 326) are considered most likely to be contaminated.

This will not definitely indicate contamination. High metal concentrations in the washings could be the result of the retention of dry deposition. However, contamination is likely and therefore these samples have been excluded from the concentration and deposition graphs shown in section 7.

4.3 Conclusions on contamination

Contamination cannot unequivocally be established, however, four samples are identified that are most likely to be affected. In fact, very few samples showed any positive indication of contamination. This does not rule it out, but perhaps indicates that this is not likely to be a significant factor.

For the purposes of further statistical analysis two datasets are analysed, firstly one including all samples and secondly with all the outlying samples identified in the PCA of the washings (positive and negative) removed. The analysis of the dataset with outlying samples removed is to determine if these will have any effect on the interpretation.

5. Assessment of sources of metals

In addition to the possible influence of contamination, a variety of factors mean that moss metal concentration may not be directly related to rates of atmospheric deposition.

The main reasons are:

- There may be an influence from marine cations. Competition effects may result in coastal moss samples having lower concentrations of heavy metals relative to rates of deposition than those out of the range of influence of marine aerosols.
- There may be some uptake of metals from non-atmospheric sources, either from substrate or from adjacent or decomposing vegetation.
- Differences in macro and micro-environmental conditions and possibly also the influence of pollution on growth rates which will influence the concentration of pollutants (i.e. a faster growing plant will have a lower pollutant concentration under the same deposition conditions).

Berg and Steinnes (1997a) and Berg et al. (1995) have used PCA to identify the factors influencing metal concentration in Scandinavian mosses. They found that the dominant factors extracted by the PCA represented the influence of long-range atmospherically transported elements (Bi, Pb, Sb, Mo, Cd, V, As, Zn, Tl, Hg, Ga), windblown mineral particles (Y, La, Al, Li, U, Th, Ga, Fe, V, Cr), three local emissions sources (Ni, Cu, As; Zn, Cd, Hg; Fe, Cr, Al), transport from the marine environment (Mg, B, Na, Sr, Ca) and contributions from higher plants (Cs, Rb, Ba, Mn). PCA may, similarly, be useful for identifying sources of metals to UK mosses.

Ordination analysis of the UK moss samples has, therefore, been used to identify the sources of metals and influences on metal concentration. As with the washings, samples were logged and standardised (although samples were multiplied by 100 in order not to create negative values when logging them and complicate interpretation). Analysis was carried out on moss concentrations including and excluding the contribution in the washings. In addition, a number of different runs were carried out on: the whole data set, individual areas, with all samples, with various possibly contaminated samples removed, with outliers identified by the PCA on the washings removed, on a correlation matrix (i.e. standardised variance), on a covariance matrix (not standardised variance), on individual moss species, on time periods, limiting the number of metals analysed.

Table 10 shows the principle factors for the whole dataset (including outliers) with and without washings. Results show:

- The first factor is dominated by Al, Li, Fe, Cr, Th, Co, Ni, V, Ga, Cr.
- The second factor is dominated by Pb, Cu, Sb, Sn, As. Zn and Cd have significant loading on this factor, but also on the 3rd factor.
- The third factor is dominated by Zn, Cd and Ba
- fourth and fifth factors are dominated by marine derived elements

Table 10. Factor loadings on whole dataset with and without washings.

A removed washings	1	2	3	4	5	**B** including washings	1	2	3	4	5
Eigen-values	7.95	3.84	1.97	1.89	1.86		7.81	3.71	2.06	1.91	1.38
% variation	31%	15%	8%	7%	7%		30%	14%	8%	7%	5%
Factor loadings											
AL	**0.92**	0.04	-0.08	0.02	-0.13	AL	**0.91**	0.08	-0.10	0.08	-0.04
LI	**0.91**	0.04	-0.04	0.17	0.04	LI	**0.83**	0.03	-0.04	0.08	0.09
FE	**0.91**	0.20	-0.06	0.11	-0.16	FE	**0.92**	0.22	-0.05	0.12	-0.09
CR	**0.90**	0.18	0.04	0.09	0.00	CR	**0.86**	0.16	0.18	0.10	-0.03
TH	**0.90**	0.05	-0.06	0.10	-0.04	TH	**0.89**	0.09	-0.10	0.11	-0.07
CO	**0.87**	0.14	0.04	0.08	-0.17	CO	**0.87**	0.16	0.03	0.16	0.03
NI	**0.82**	-0.03	0.25	-0.07	-0.03	NI	**0.80**	0.00	0.34	0.02	0.05
V	**0.79**	0.00	0.26	-0.03	0.07	V	**0.81**	0.02	0.20	-0.04	-0.13
GA	**0.76**	0.37	0.06	0.03	-0.06	GA	**0.77**	0.34	0.03	-0.01	-0.19
ZR	**0.66**	0.34	0.05	0.06	0.08	ZR	**0.69**	0.37	-0.05	0.05	-0.06
AS	0.52	**0.73**	-0.17	0.08	-0.21	AS	0.54	**0.71**	-0.06	0.08	-0.10
SE	0.36	0.16	0.06	0.11	0.12	SE	0.31	0.24	-0.19	0.12	0.00
SB	0.11	**0.84**	0.26	-0.03	0.02	SB	0.13	**0.83**	0.29	-0.04	0.02
CU	0.25	**0.79**	0.06	-0.06	0.02	CU	0.26	**0.78**	0.13	0.01	0.16
SN	-0.01	**0.78**	0.15	0.07	0.29	SN	0.00	**0.76**	0.24	-0.03	0.17
PB	0.23	**0.69**	0.23	-0.04	-0.27	PB	0.23	**0.73**	0.17	0.10	-0.14
ZN	0.05	0.45	**0.63**	0.09	0.25	ZN	0.08	0.37	**0.69**	0.19	0.14
CD	-0.02	0.36	**0.73**	0.05	0.18	CD	0.06	0.31	**0.74**	0.10	0.02
BA	0.30	0.09	**0.65**	0.17	-0.38	BA	0.33	0.14	0.47	0.39	-0.17
CA	0.03	0.11	0.04	**0.88**	0.13	CA	0.03	0.12	0.09	**0.80**	0.07
SR	0.16	-0.14	0.26	**0.80**	-0.15	SR	0.20	-0.09	0.11	**0.89**	-0.12
NA	0.02	0.06	-0.13	-0.13	**0.70**	NA	0.00	0.07	-0.14	0.06	**0.79**
B	-0.12	-0.03	0.33	0.19	**0.65**	B	-0.16	-0.08	0.25	0.04	0.08
K	-0.27	0.05	0.17	-0.48	0.47	K	-0.20	0.04	0.25	-0.13	**0.67**
MG	0.15	-0.36	-0.21	0.24	0.33	MG	0.21	-0.31	-0.45	0.36	0.25
MN	0.05	0.07	0.09	0.02	0.15	MN	0.08	0.04	0.04	0.04	-0.03

Factor loading over 0.3 is generally considered the cut-off point. Over 0.4 weak, 0.6 strong.

Interpretation of the meaning of factors is also assisted by plotting component scores on each factor against time (Figure 3).

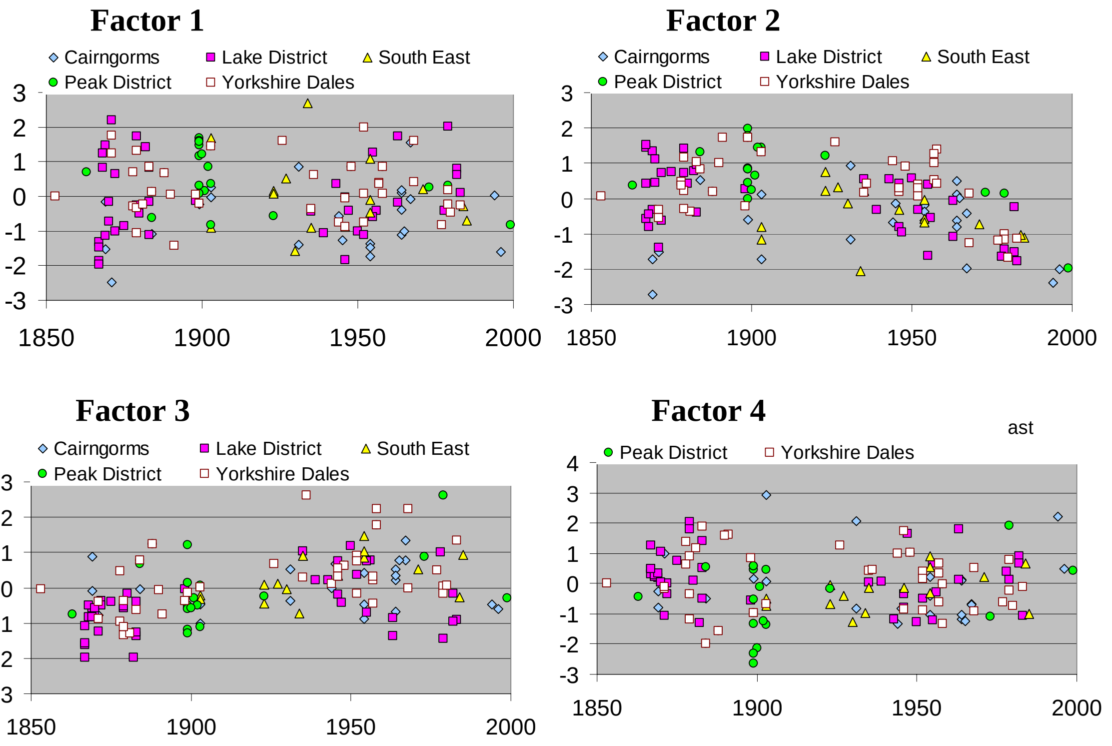


Figure 3. Component scores from analysis A (including washings) for first four factors identified by the PC) (graphs where washings excluded look very similar).

Factor 1. Berg and Steinnes (1997a) attribute a factor which contains Li, some Th, Fe and V to soil dust. Berg et al., (1995) attribute a factor containing high loadings of Li, Al, Ga, and Th to windblown dust (elements associated with mineral particles). Probably this is the case here, particularly as scores do not change through time (Figure 3). However, it might be worth considering that these are also elements that will be contained in coal and oil fired power station emissions (especially Al, V, Fe, Ba).

Nickel is predominantly associated with this factor, and As partially, suggesting Ni concentrations in mosses do not reflect deposition and As may only partly reflect deposition.

Factor 2 is dominated by Pb, As, Cu, Sb and Sn. Samples generally score highest in the late 19th century, and decrease recently. These metals are not (with the exception of As) at all associated with the first factor. Although there is a lot of scatter, the highest loading on this factor occur in the late 19th century before declining to present. This is consistent with the trends in mining-related heavy metal deposition that have been reconstructed in annexe 7 and possibly indicates that the variation in metal concentrations explained by factor 2 is influenced by historical heavy metal deposition, largely from mining-related sources.

Factor 3 is dominated by Cd, Zn and Ba. Although again there is a lot of scatter, scores indicate an increasing trend, at least up until about 1970. This factor may be better reflecting a 'general' heavy metal deposition trend which peaked in the 1960s/early 1970s (i.e. deposition of metals from non-mining sources such as other industry and energy production – see annexe 7). It is interesting that Cd and Zn are picked out.

Other factors. The remaining factors account for variation in Ca, Sr, Na, B, K, Mg and Mn. Inputs of these metals may be from marine aerosols, uptake from substrate or leaching from adjacent vegetation. Variation in concentration of these elements is unrelated to the pollutant metals such as Pb, Zn, Cu, Ni and Cd, and therefore there is no evidence of any influence of competing marine cations or uptake from soils on heavy metal concentrations.

There is no significant difference between trends with and without washings. The same analysis on the dataset with outlying samples removed creates some minor differences, although in general the patterns shown by the analysis are remarkably consistent.

Table 11. Factor loadings on dataset with 13 high or low samples removed (with and without washings)

C With washings but removed samples with unusual % of metals in washings						**D** Without washings but otherwise as C					
No of samples = 131						No of samples = 131					
Eigen-values	7.85	4.16	1.79	1.58	1.43		7.80	4.00	1.85	1.82	1.55
% variation	30.18	15.99	6.89	6.08	5.48		29.99	15.62	7.13	6.98	5.98
	1	2	3	4	5		1	2	3	4	5
FE	**0.91**	0.18	0.11	-0.17	0.01	FE	**0.91**	0.19	-0.18	0.10	0.06
AL	**0.90**	0.04	0.05	-0.20	0.04	AL	**0.89**	0.02	-0.22	0.03	0.09
TH	**0.89**	0.05	0.10	-0.06	-0.05	TH	**0.90**	0.04	-0.06	0.08	-0.01
CR	**0.87**	0.17	0.09	0.03	0.07	CR	**0.91**	0.17	0.03	0.08	0.03
CO	**0.86**	0.17	0.11	-0.16	0.13	CO	**0.84**	0.15	-0.18	0.09	0.21
NI	**0.83**	0.05	-0.05	0.10	0.21	NI	**0.80**	-0.01	0.07	-0.10	0.28
V	**0.81**	0.06	-0.04	0.25	0.13	V	**0.78**	0.03	0.30	-0.07	0.10
LI	**0.80**	0.06	0.10	-0.05	0.04	LI	**0.90**	0.06	-0.04	0.20	0.02
GA	**0.76**	0.36	-0.03	0.03	-0.03	GA	**0.77**	0.39	0.06	-0.04	0.01
ZR	**0.69**	0.40	0.05	0.05	-0.01	ZR	**0.67**	0.39	0.15	0.03	-0.07
SE	0.34	0.18	0.24	0.16	-0.22	SE	0.33	0.19	0.10	0.13	0.05
AS	0.55	0.68	0.10	-0.28	-0.14	AS	0.54	**0.70**	-0.27	0.10	-0.08
PB	0.27	**0.70**	0.05	-0.19	0.26	PB	0.24	**0.69**	-0.17	-0.03	0.37
CU	0.26	**0.78**	0.03	-0.08	-0.01	CU	0.23	**0.79**	-0.06	-0.02	0.06
SB	0.18	**0.86**	-0.02	0.11	0.11	SB	0.15	**0.86**	0.19	-0.04	0.09
SN	0.04	**0.83**	-0.01	0.23	-0.07	SN	0.01	**0.80**	0.30	0.02	-0.08
ZN	0.06	0.53	0.15	0.47	0.34	ZN	0.05	0.49	0.50	0.11	0.40
CD	0.05	0.45	0.08	0.51	0.39	CD	-0.02	0.40	**0.64**	0.03	0.38
SR	0.18	-0.08	**0.84**	-0.03	0.35	SR	0.13	-0.12	-0.01	**0.80**	0.44
CA	0.03	0.11	**0.84**	0.13	-0.04	CA	0.03	0.09	0.20	**0.87**	-0.09
MG	0.21	-0.43	0.35	-0.14	-0.22	MG	0.12	-0.42	-0.14	0.30	0.00
B	-0.14	-0.05	0.06	**0.80**	-0.13	B	-0.10	-0.05	**0.77**	0.12	-0.16
BA	0.32	0.19	0.21	-0.05	**0.75**	BA	0.27	0.14	0.02	0.11	**0.82**
MN	0.06	0.08	0.02	0.14	0.05	MN	0.06	0.07	0.14	0.02	0.06
NA	-0.03	0.09	0.11	0.12	-0.28	NA	-0.04	0.07	0.13	-0.01	-0.17
K	-0.24	0.10	-0.18	-0.03	0.27	K	-0.33	0.11	0.14	-0.41	0.10

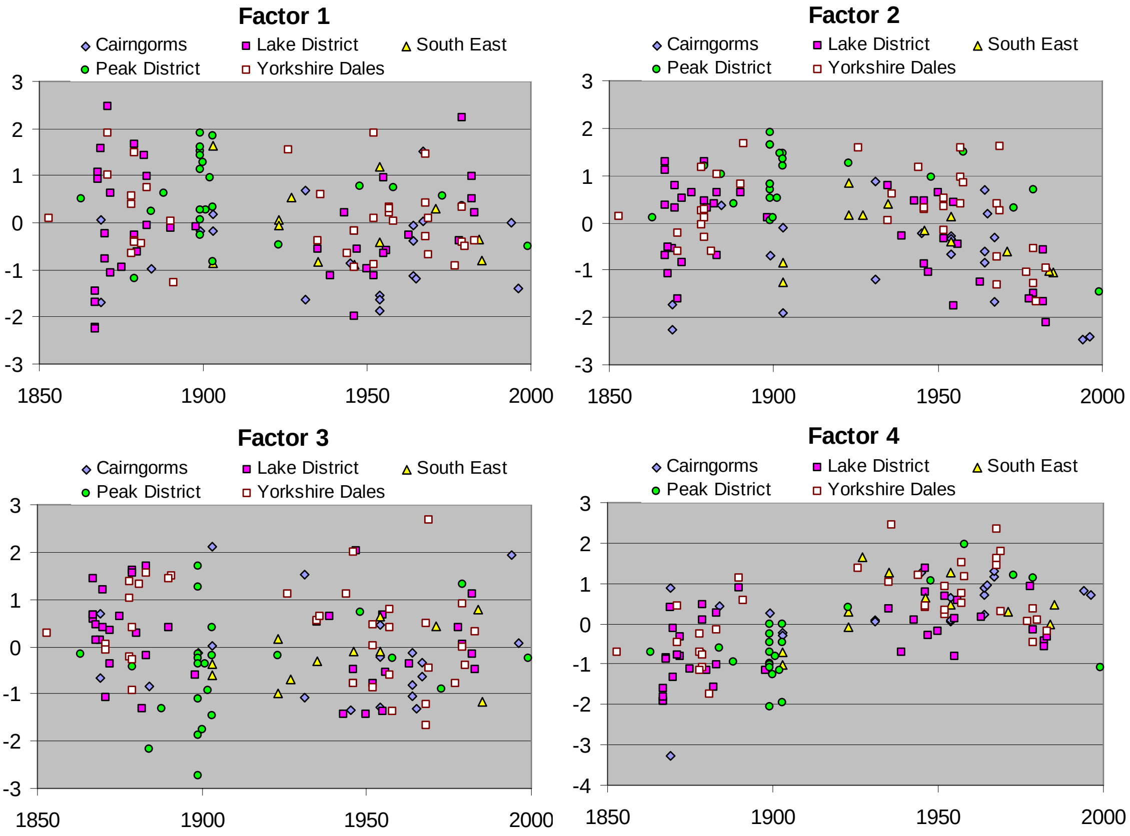


Figure 4. Component scores for analysis C (including washings), first four factors identified by the PCA.

The main difference occurs in the location of Zn and Cd. In the previous analysis, Zn and Cd were loading on Factor 3 with Ba, with a lower loading on Factor 2 with Pb, Cu, Sn and Sb. In this analysis Zn and Cd are loading on Factor 2 with Pb, Cu, Sn and Sb, on Factor 4 with B and Factor 5 with Ba and Sr (with washings). Without washings, Zn and Cd are associated approximately equally with Factor 2 (pollutant metals), Factor 4 (Sn and B) and Factor 5 (Ba and Sr). Factors 3 to 5 explain little variance in comparison to the first 2 factors. It is difficult to explain why Zn and Cd may be related to concentrations of these metals, but this does reintroduce the possibility that Zn and Cd are affected by something other than atmospheric deposition of these elements.

5.1 Conclusions on sources of metals

Principle components analysis of the dataset indicates that variation in sample metal concentrations can be largely explained by the first two factors. These factors probably represent inputs from soil or soil-derived dust, and from the atmospheric deposition of anthropogenically-derived emissions.

Concentrations of soil derived elements (factor 1) do not show any temporal trends. In contrast component scores on factor 2 (which is strongly influenced by Pb, Cu and As) are highest in the late 19th century coincident with peak mining production in the UK and decline to present. Component scores on factor 3 (which does not explain much variation, but is strongly influenced by Zn and Cd) increase from the 1850s to peak in the 1970s coincident with peak heavy metal deposition in the UK (Baker, 2002).

Nickel varies in a similar way to soil derived elements and it is likely that the largest Ni inputs to mosses are from this source. Analysis of moss Ni concentrations will not, therefore, provide any useful information on past rates of Ni deposition. Copper and lead concentrations are, however, largely associated with other pollutant metals and are thought, therefore to largely come from atmospheric deposition. Arsenic is most associated with atmospheric deposition, but has a significant soil-derived component.

Cadmium and zinc are partly associated with the other anthropogenically derived metals, but partly load on a third factor (sometimes fourth or fifth) that shows an increasing trend (at least until about 1970) and may be anthropogenic in origin, but may be influenced by an unknown factor. When the outlying samples were removed, variability in Zn and Cd is complicated, loading on three factors that are difficult to account for.

In summary, the source of lead and copper concentrations in mosses can confidently be attributed to atmospheric deposition. Cadmium and zinc are probably reflecting atmospheric inputs, do not reflect soil inputs, but there may be other factors involved. Arsenic concentrations are partly related to atmospheric inputs, but there may also be an input from soil dust. Nickel concentrations do not primarily reflect atmospheric deposition but are mainly derived from soil inputs.

6. Metal concentrations in mosses

The following figures show the concentrations of metals found in mosses around each of the five catchments. Concentrations with and without the contribution in washings are shown. Concentrations in samples collected from the same five areas as part of the 2000 moss survey are also shown for comparison. All samples are shown but samples with more than 50% of the total metal content found in the washings (and therefore possibly contaminated) are circled.

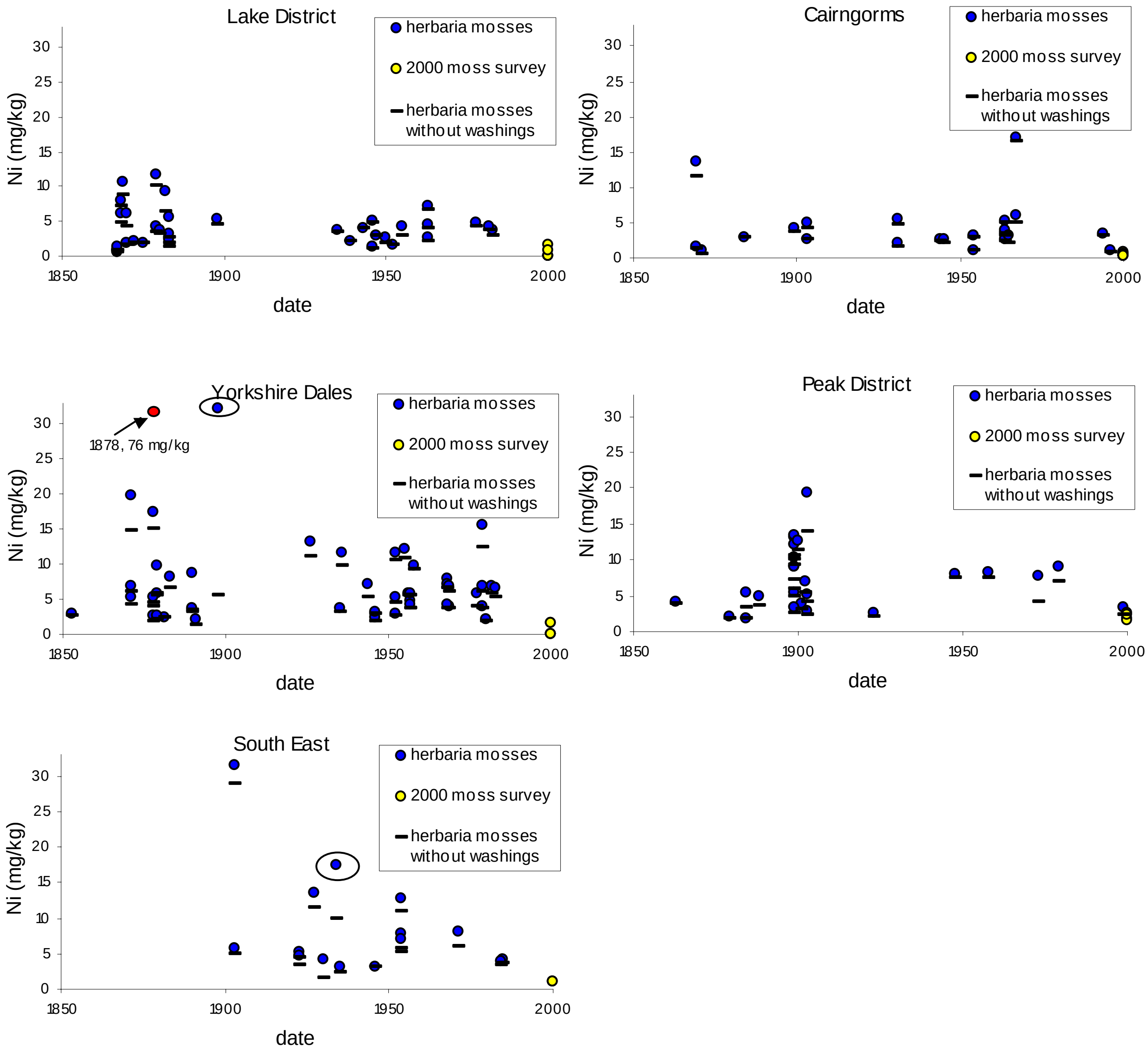


Figure 5. Nickel concentrations in herbaria moss samples

- Samples with relatively high concentrations in washings are circled
- Samples off the scale coloured red

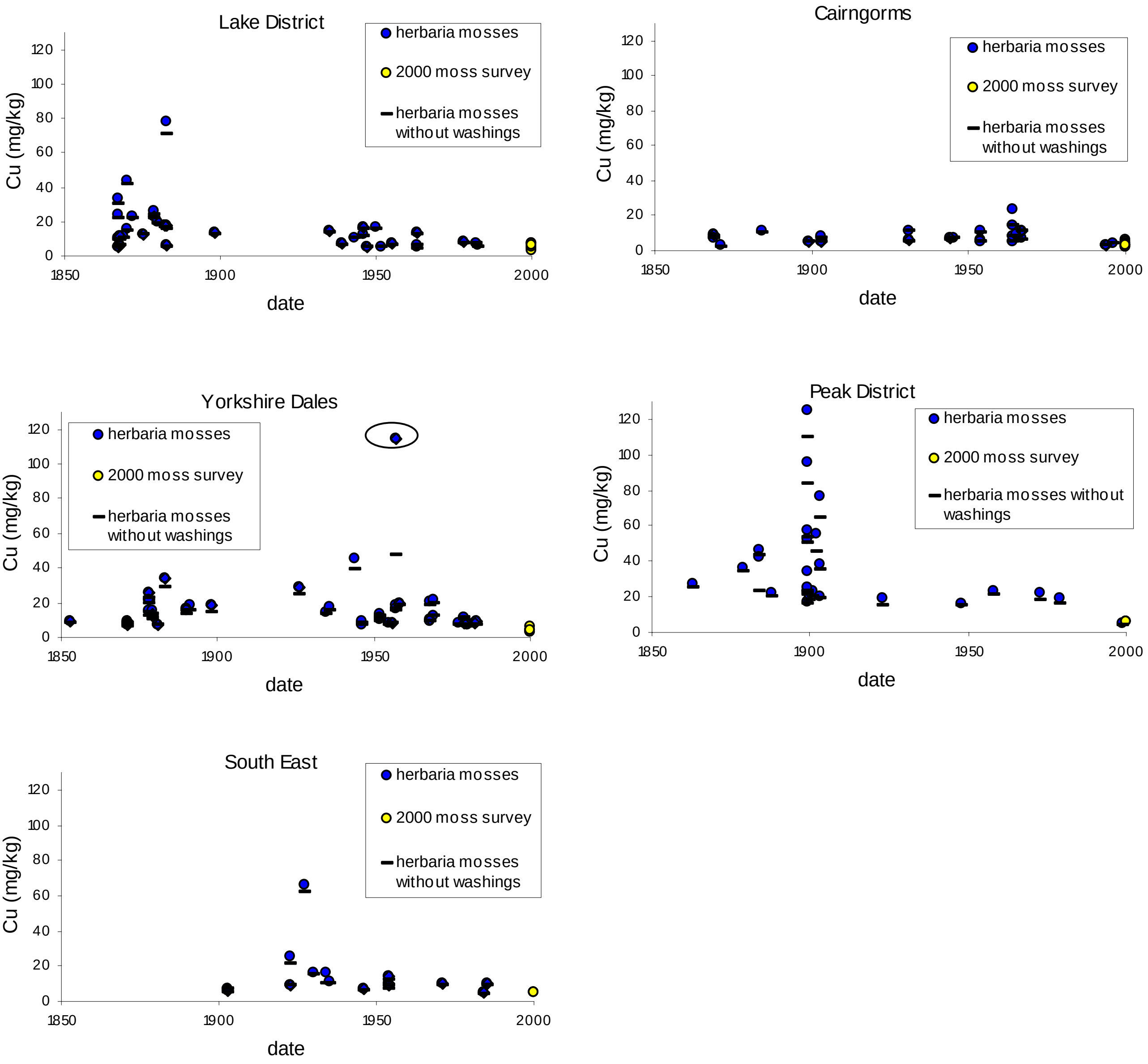


Figure 6. Copper concentrations in herbaria mosses

- Samples with relatively high concentrations in washings are circled
- Samples off the scale coloured red

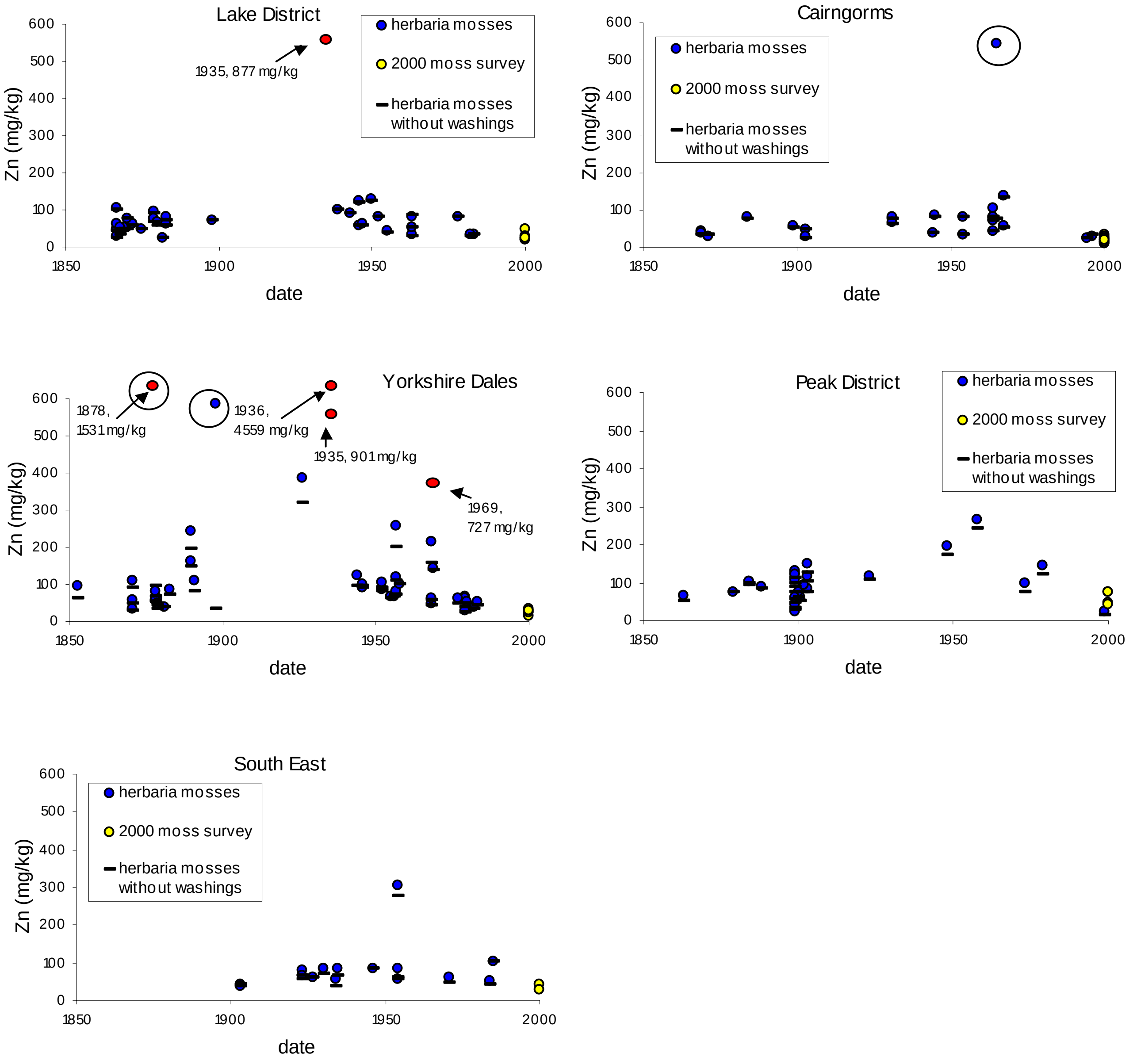


Figure 7. Zinc concentration in herbaria moss samples

- Samples with relatively high concentrations in washings are circled
- Samples off the scale coloured red

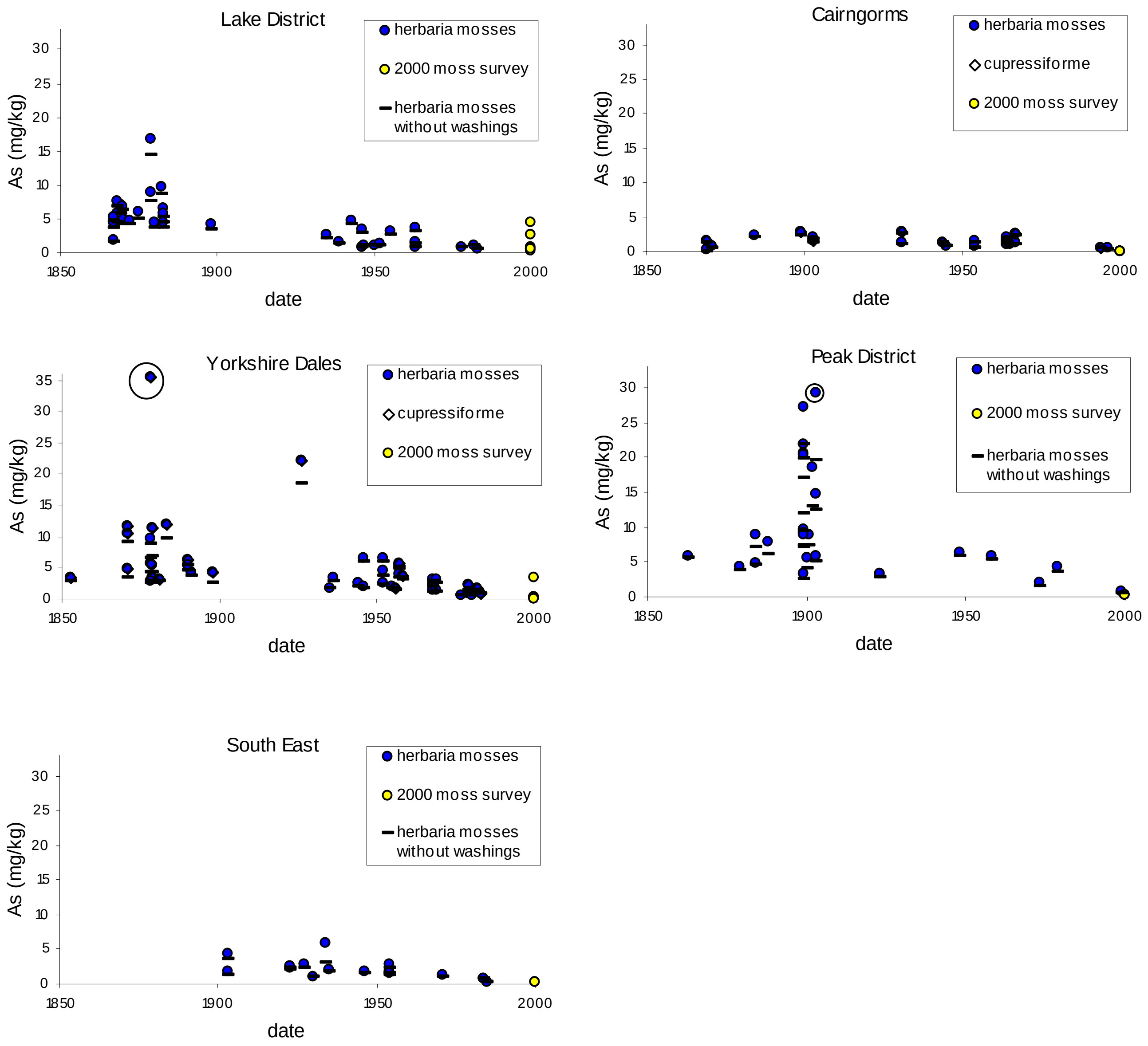


Figure 8. Arsenic concentration in herbaria mosses

- Samples with relatively high concentrations in washings are circled
- Samples off the scale coloured red

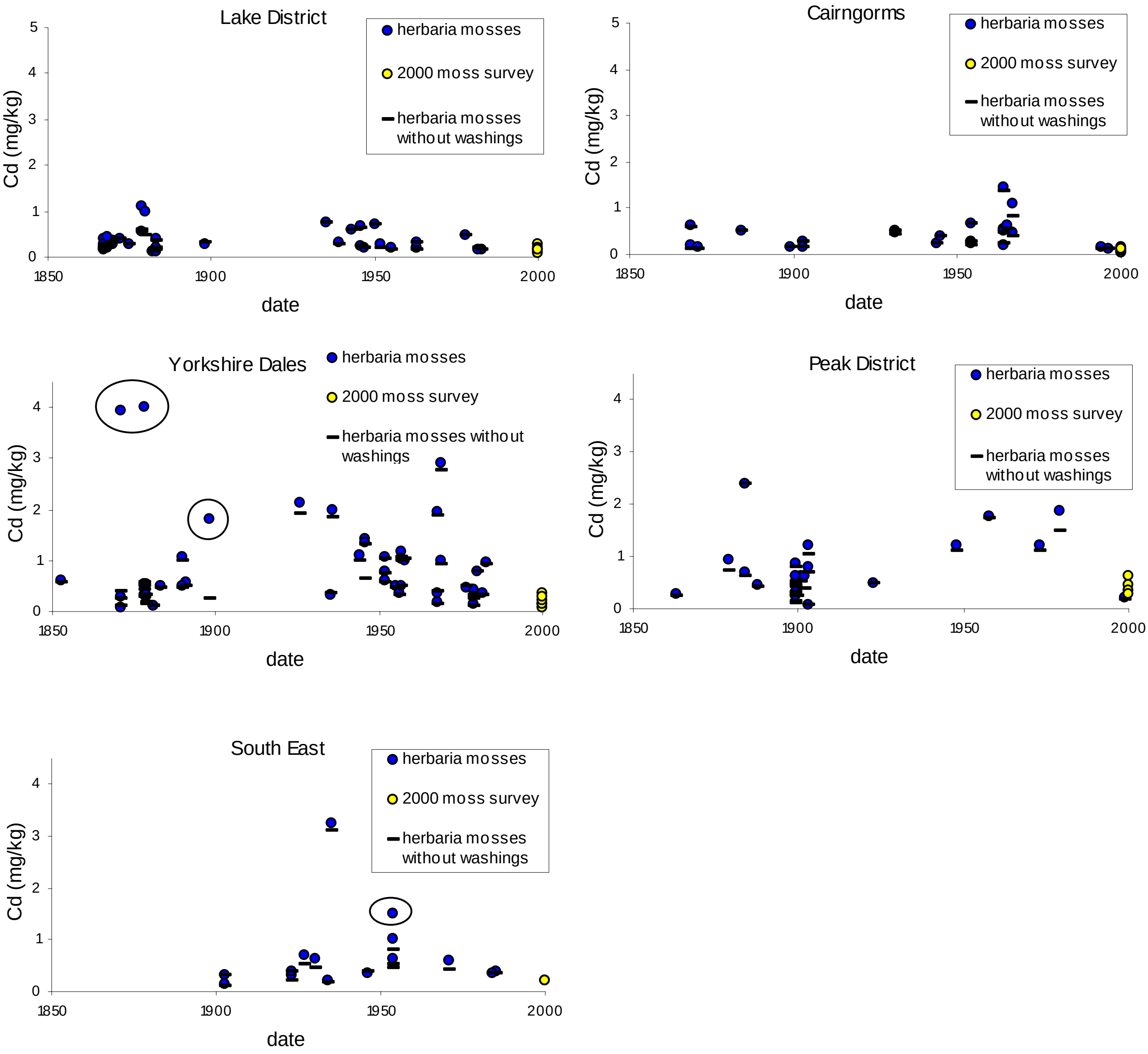


Figure 9. Cadmium concentration in herbaria moss samples

- Samples with relatively high concentrations in washings are circled
- Samples off the scale coloured red

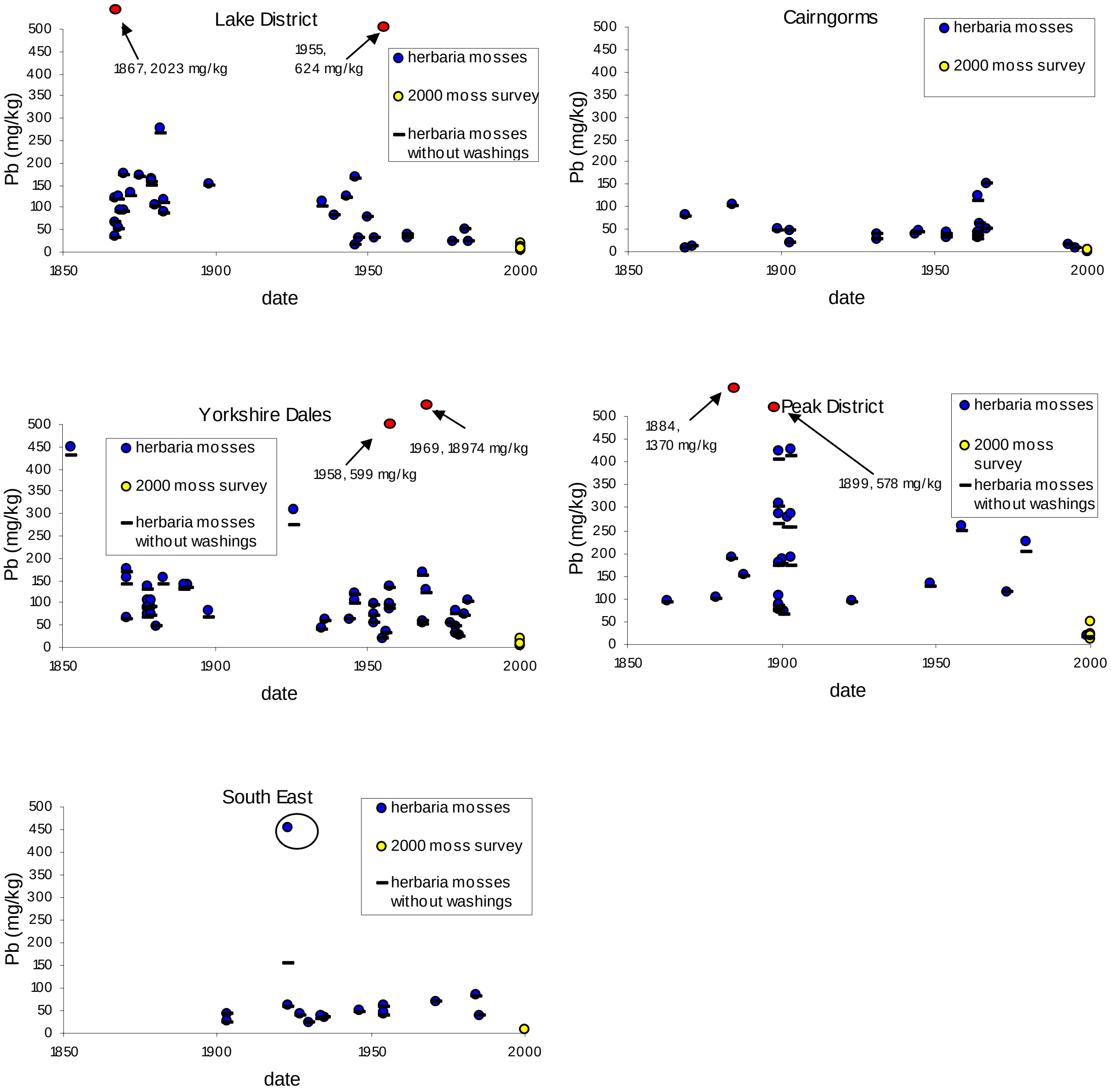


Figure 10. Lead concentration in herbaria moss samples.

- Samples with relatively high concentrations in washings are circled
- Samples off the scale coloured red

6.1 Trends in metal concentrations in mosses.

Nickel

Concentrations of Ni in the mosses are generally between 0 and 20 μg g^{-1}. It has already been established that Ni concentrations are primarily related to inputs from the soil rather than from deposition. This probably explains the lack of any temporal change in Ni concentrations in the mosses (although the Ni concentrations found in the 2000 survey mosses are low in comparison to levels in most of the herbarium samples). Neither are there major differences in concentrations between sites although there do appear to be generally slightly lower levels in the Cairngorms and Lake District than elsewhere.

Copper

Copper concentrations in the mosses are generally between 5 and 40 μg g^{-1}. Concentrations in the Cairngorms and South East are generally lower than in the Northern England sites. At these sites levels measured in mosses collected in 2000 as part of the moss deposition survey are low but comparable to historical levels. Some of the highest concentrations are also found in mosses from the late 19th and very early 20th century (e.g. Lake District, Peak District). In the Nothern England sites, current levels (2000) are low in comparison to historical deposition.

Zinc

Concentrations of zinc generally vary between around 20 and 150 μg g^{-1} although there are some samples with levels significantly higher than this. Concentrations are generally below 100 μg g^{-1} in the Lake District, Cairngorms and South East. Levels in the Yorkshire Dales are generally similar, but there are a significant number of moss samples with considerably higher Zn concentrations. As the Yorkshire Dales is a historical Zn mining area, these samples may be influenced by this. Some Peak District samples also have higher Zn concentrations – again this area has been subject to some Zn mining, although much less than in the Yorkshire Dales. In general, however, the highest levels do not occur (as they do for Cu, As and Pb) in the 19th century but around the mid 20th century.

Arsenic

Levels of arsenic generally vary between 0 and 15 μg g^{-1} although concentrations in the South East and Cairngorms remain below 5 μg g^{-1}. In the Northern England sites, the highest levels of As are found in the older samples (pre 1900). Levels then appear to decline to present, although there is considerable scatter.

Cadmium

Concentrations of cadmium are generally below 1 μg g^{-1}in the Lake District, Cairngorms and South East. Some higher levels are, however, found in the Yorkshire Dales and Peak District. There is little evidence of any clear temporal trends, although the higher concentrations tend to occur towards the mid 20th century. This is in contrast to As, Pb and Cu, where the highest levels are found in the 19th century. Inputs are, perhaps, less associated with historical mining and smelting, although the Yorkshire Dales does have some of the highest Cd concentrations.

Lead

Concentrations of lead are highly variable. Most samples from the Cairngorms and South East have concentrations below 150 μg g^{-1} but levels are often above this in the Northern England sites. Like As and Cu, some of the highest concentrations have been measured in the 19th century samples.

For all metals, there is significant variability in the concentrations. Part of this variability will be associated with the low analytical precision that has resulted from the use of very small subsamples of moss. Some variability may also result from differences in moss uptake under different climatic conditions and dilution by differing rates of growth. However, much of the variability is thought to be the result of spatial variation in deposition. This would be expected to be more significant in the older samples. 19th century smelt mills and other industrial sources would have been less concerned about the dispersal of pollutants than today. Also, sources would have been smaller but more numerous, resulting in greater spatial variability in deposition. The wide variability in moss concentration (and therefore deposition) is most clearly seen in the graph showing lead concentration in mosses from the Peak District (figure 6). Several samples were collected around 1900 and show highly variable Pb concentrations (between 50 and 500 μg g^{-1}).

Key results:

- Metal concentrations in moss samples collected as part of the 2000 moss survey are similar to concentrations in recent herbaria mosses (post 1990 samples exist in the Cairngorms and Peak District only). Concentrations in recently collected mosses are some of the lowest found since 1850.

- In general, metal concentrations are higher in the Northern England areas than in the Cairngorms and South East. This is particularly true for 19th century samples. Only nickel is similar, perhaps due to the soil input from this metal.

- Deposition in the late 19th century appears to have been very significant, particularly in the Northern England sites. In fact 19th century levels of Pb, As and Cu tend to be higher than 20th century in these areas.

7. Calculation of deposition from mosses.

7.1 Standardization to *Pleurozium*

In the most recent UK moss survey (Ashmore et al., 2002) samples of *Pleurozium schreberi, Hypnum cupressiforme, Hylocomium splendens and Rhytidiadelphus squarrosus* from the same locations were analysed to assess the relationship between metal concentrations in the different moss species. This allowed the calculation of regression equations to describe these relationships and allow calibration of all moss species to a '*Pleurozium* standard.' (summarised in Tables 12 to 14). In almost all cases, significant relationships were obtained between moss species although there were exceptions. No significant relationship could be found for Cu and As between *Pleurozium* and *Hypnum.* In most cases, the slopes of the regression lines between *Pleurozium* metal concentrations and those of the other mosses were close to unity. Deviations in slope from unity are indicative of differences in the relative efficiency of the different moss species for capturing metals from the atmosphere. For the majority of regressions, the intercept was not significantly different from zero. Where significant non-zero intercepts exist, this may indicate differences in the background accumulation of metal in the different moss species. For example, previous work (Berg et al., 1995; Rühling and Steinnes 1998) suggests that *Pleurozium* and *Hylocomium* contain a background quantity of 20-30 mg kg^{-1} of Zn even at pristine sites. This is attributed to a nutrient function of Zn in the moss.

Table 12. Summary statistics for regression equations to determine Pleurozium standardized metal concentrations (mg kg-1) from Hylocomium splendens (Ashmore et al., 2002).

Metal	**Constant1**	**Slope**	**r2**	**n**
Ni	-0.024	1.026	0.908***	27
Cu	1.020	0.708	0.690***	26
Zn	9.342	0.601	0.529***	27
As	-0.017	1.243	0.919***	26
Cd	0.042	0.754	0.420***	25
Pb	0.503	0.933	0.669***	28

** significant at P<0.001*

Table 13 Summary statistics for regression equations to determine Pleurozium standardized metal concentrations (mg kg-1) from Hypnum cupressiforme (Ashmore et al., 2002).

Metal	**Constant**	**Slope**	**r2**	**n**
Ni	-0.110	0.905	0.822***	15
Cu	3.129	0.293	0.072	17
Zn	15.277	0.346	0.524**	12
As	0.127	0.231	0.044	13
Cd	0.065	0.429	0.399**	15
Pb	1.323	0.506	0.764***	13

**** significant at p<0.001; ** significant at p<0.01; * significant at p<0.05*

Table 14. Summary statistics for regression equations to determine Pleurozium standardized metal concentrations (mg kg-1) from Rhytidiadelphus squarrosus (Ashmore et al., 2002).

Metal	**Constant**	**Slope**	**r2**	**n**
Ni	0.016	0.933	0.911***	14
Cu	-0.140	0.885	0.825***	13
Zn	-28.275	2.119	0.907***	14
As	0.024	0.971	0.729***	12
Cd	0.054	0.364	0.480**	14
Pb	0.933	0.577	0.885***	12

**** significant at p<0.001; ** significant at p<0.01; * significant at p<0.05*

The r^2 values for Cu and As to relate *Hypnum cupressiforme* to *Pleurozium schreberi* are very weak. Therefore the *Hypnum* samples for these metals could not be standardised. These are plotted separately, but are not removed from the analysis due to the large number of *Hypnum* samples in the dataset. Furthermore, as regression equations between *Hylocomium* and deposition as well as *Pleurozium* and deposition are available (Berg and Steinnes, 1997b) there is no need to standardise the *Hylocomium* samples.

7.2 Calculation of deposition from metal concentrations in herbaria moss samples

Linear relationships have been found between wet deposition and metal concentration in *Pleurozium* and *Hylocomium* at sites in Norway (Berg and Steinnes, 1997b, tables 15, figures 11 and 12). These relationships have been used to relate the concentration of metal in the *Pleurozium* and *Hylocomium* samples to deposition. These relationships have also been used to relate the concentration of metal in the *Hypnum* and *Rytiddiadelphus* samples that have been standardised to *Pleurozium* using the equations in tables 13 and 14. Where *Hypnum* samples could not be standardised (i.e. for Cu and As) the relationships in Table 5 are still used but we accept that this will limit the accuracy of the deposition estimate.

Table 15. Regression relationships to determine deposition from i) Pleurozium metal concentration and, ii) Hylocomium metal concentration

i) Pleurozium				ii) Hylocomium			
	a	b	r^2		a	b	r^2
Pb	1.758	-0.773	0.980	Pb	1.675	-1.112	0.984
Cd	1.581	0.017	0.884	Cd	2.568	-0.007	0.817
As	12.378	-0.365	0.845	As	9.057	0.006	0.949
Cu	1.191	1.757	0.351	Cu	1.243	-0.132	0.362
Zn	1.405	-24.892	0.479	Zn	1.276	-8.205	0.205
Ni	1.208	1.153	0.277	Ni	1.294	-0.476	0.308

$$\text{deposition (g ha a}^{-1}) = a*M\ (\mu\text{g g}^{-1}) + b$$

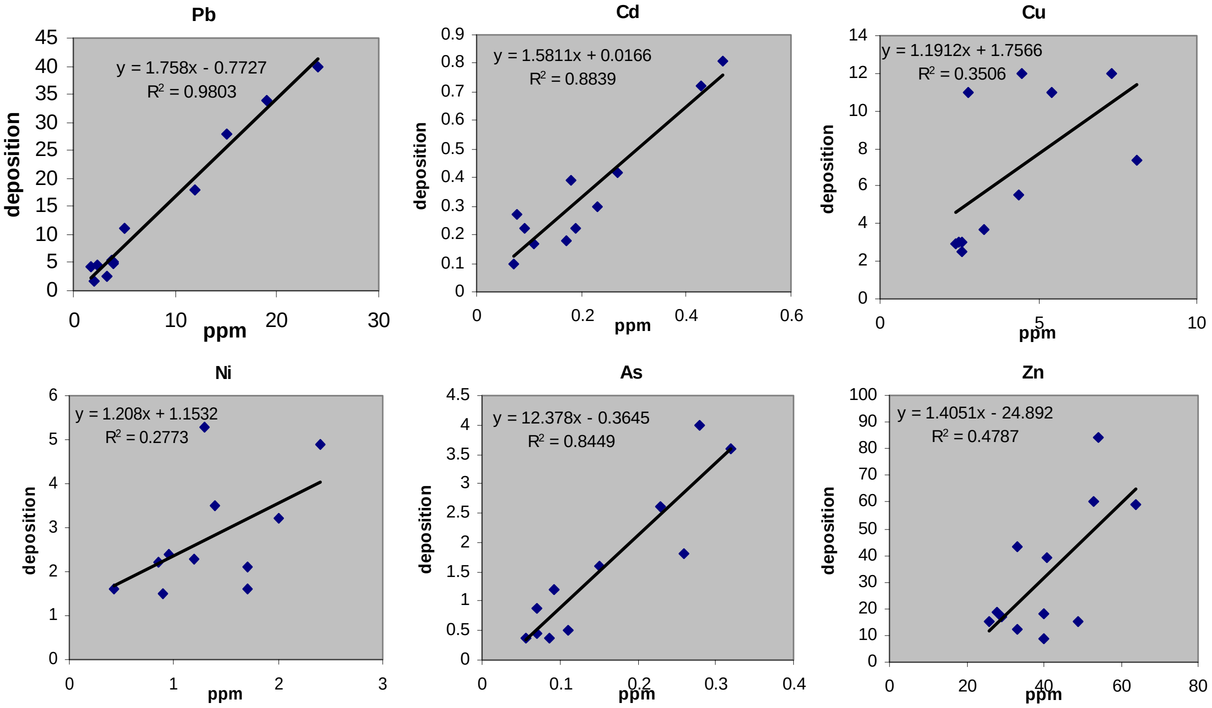


Figure 11. Relationship between metal content in Pleurozium and wet deposition data at 13 Norwegian sites (data from Berg and Steinnes, 1997)

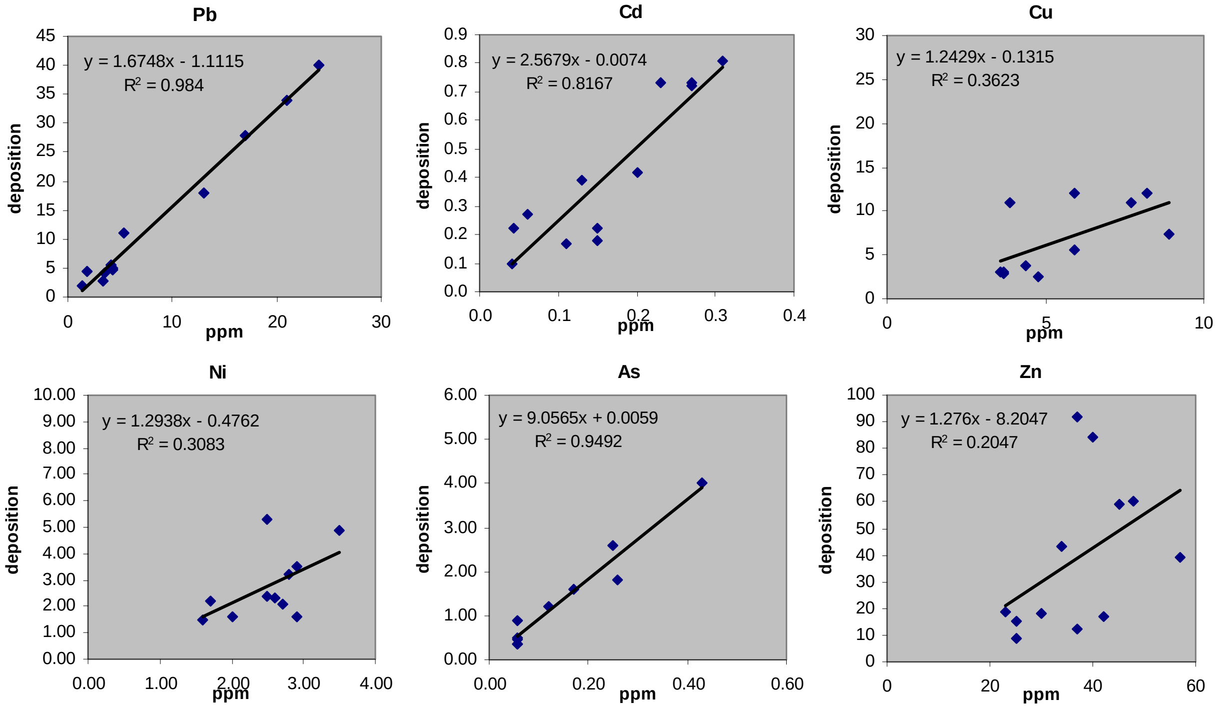


Figure 12. Relationship between metal content in Hylocomium and wet deposition data at 13 Norwegian sites (data from Berg and Steinnes, 1997)

The use of different species of mosses was necessary in order to provide enough samples. However, having to standardise to Pleurozium does introduce inaccuracy.

Figure 13 shows deposition estimated from UK Hylocomium samples using Berg and Steinnes direct regression equation (ii) shown in Table 15. This is compared to deposition estimated when the concentration in the Hylocomium samples is first standardised to Pleurozium and then converted to deposition using Berg and Steinnes regression equation (i) (Table 15). For all metals except Pb, there are significant differences in the deposition estimates.

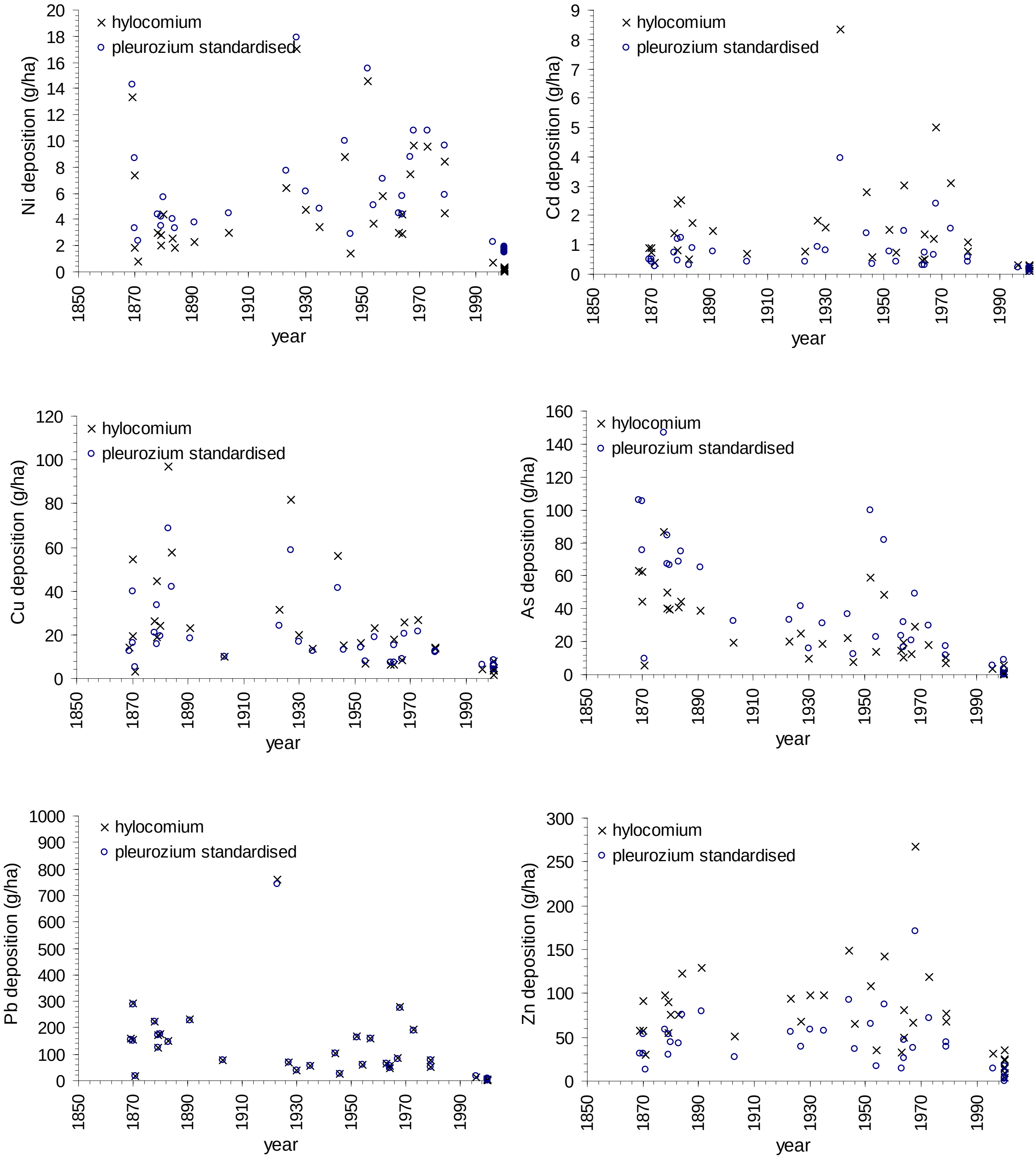


Figure 13. Comparison of deposition estimated from Hylocomium samples using i) the regression relationships between Hylocomium and wet deposition determined from Berg and Steinnes (1997) and ii) standardising to Pleurozium (Table 11) then using the regression relationship between Pleurozium and wet deposition (Table 14).

7.3 Conclusions on deposition calculations

- The basis for using lead concentration in mosses to reconstruct Pb deposition is good. There are strong correlations between *Pleurozium*, *Hylocomium* and deposition.

- The relationship between Cd and As concentration in mosses and deposition is strong, but some accuracy will be lost through difficulty standardising to *Pleurozium*.

- For Ni, a poor calibration to deposition has been achieved, probably because the main source of Ni is soil dust.

- For Cu and Zn, both standardisation to *Pleurozium* and calibration to deposition are poor (although standardisation only poor for *Hypnum*)

- Zn, Ni and Cu cannot, at present, be calibrated to deposition with any confidence, and should only be used as a relative record to demonstrate trends over time, and differences in rates of deposition between catchments.

7.4 Deposition estimates from mosses

Figure 14 show deposition estimated from moss metal concentrations. Deposition rates have been calculated for Cu, Zn and Ni but, due to uncertainties in the relationship between deposition and moss concentrations of these metals, must not be considered reliable.

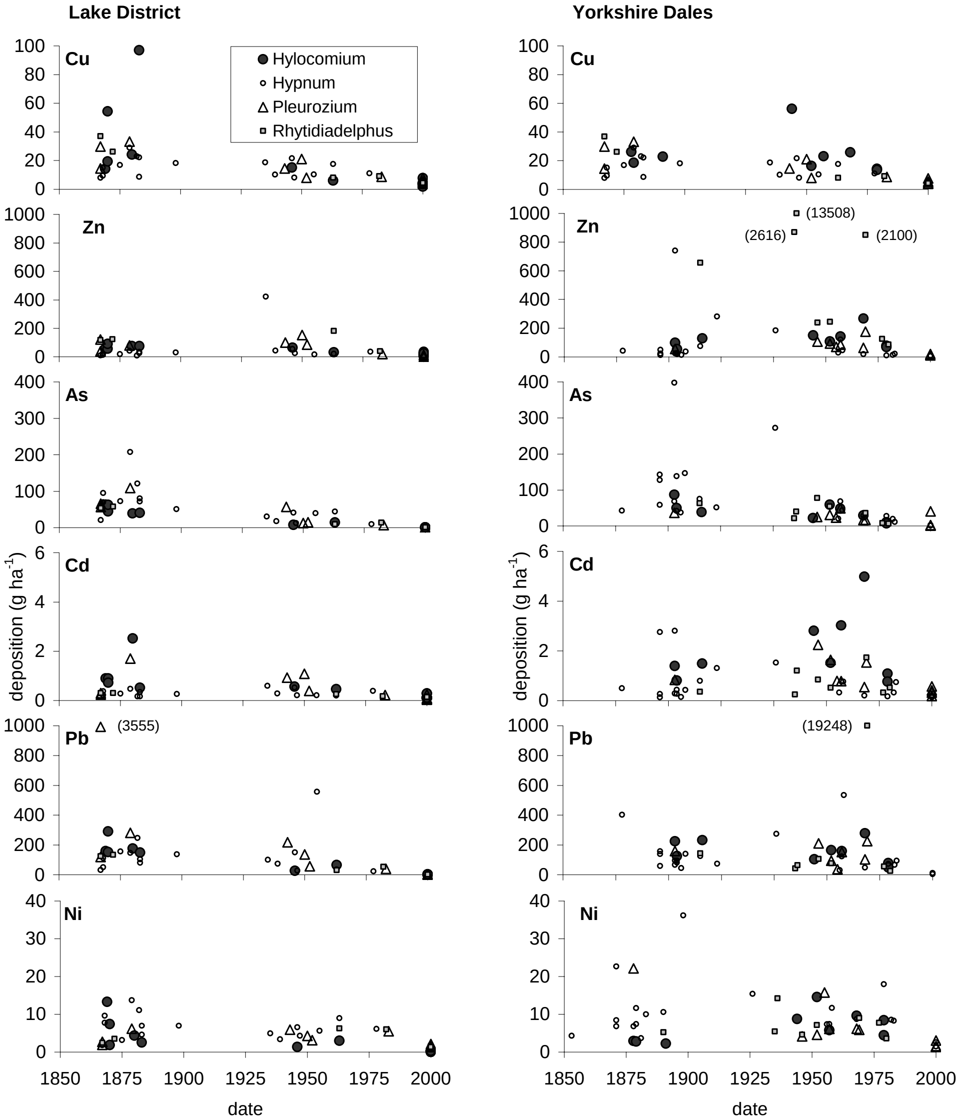
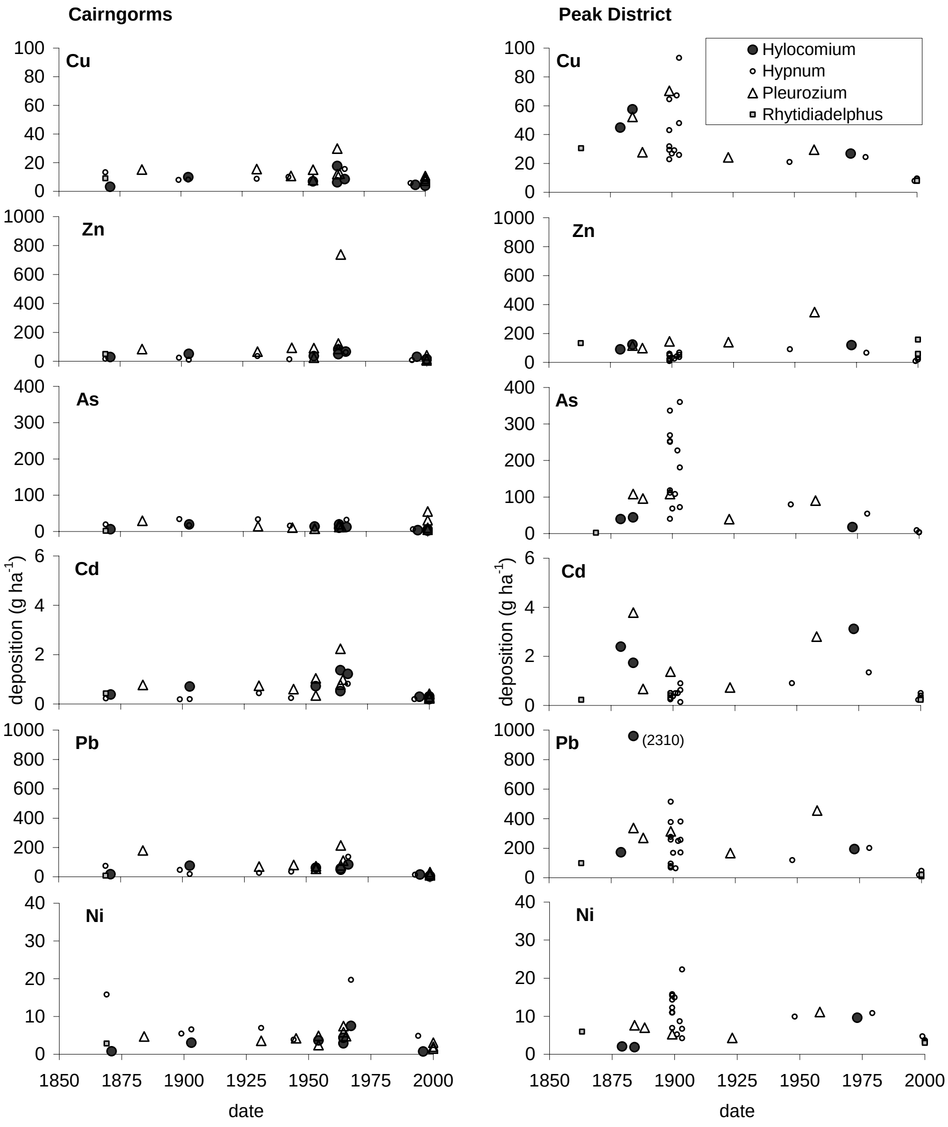


Figure 14 Deposition estimated from herbarium moss samples. *Pleurozium* and *Hylocomium* deposition estimates based on the equations of Berg and Steinnes (1997b), *Hypnum* and *Rytiddiadelphus* are standardised to *Pleurozium* where possible. As standardisation introduces some error these are shown as small symbols



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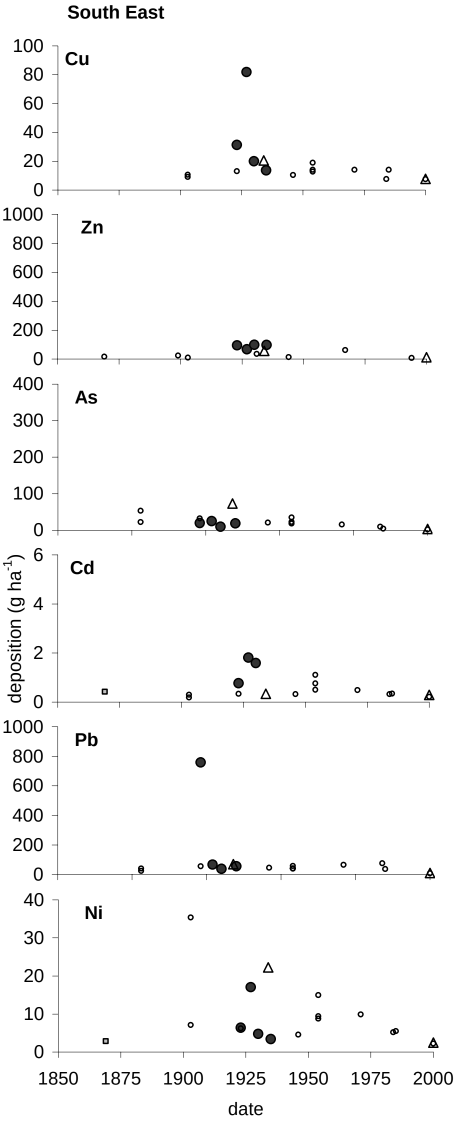

Figure 14 Deposition estimated from herbarium moss samples. *Pleurozium* and *Hylocomium* deposition estimates based on the equations of Berg and Steinnes (1997b), *Hypnum* and *Rytiddiadelphus* are standardised to *Pleurozium* where possible. As standardisation introduces some error these are shown as small symbols

8 Conclusions

Herbarium moss samples represent a valuable resource for reconstructing past heavy metal deposition. However, detailed analysis of 143 samples from 4 UK herbarium collections has revealed some significant difficulties.

The main problems encountered have been:

1) Samples are necessarily small. The variability in metal accumulation within each moss sample means that errors introduced by using such small sub-samples are significant.
2) The fact that mosses are distributed across a region means that deposition trends will be representative of a large area rather than a particular location (as is the case for peat or lake sediment cores). However, this introduces significant variability, particularly in historically mined regions. Therefore, trends can be difficult to distinguish due to sub-sampling and spatial variability in metal deposition.
3) Principle components analysis indicates that atmospheric deposition is the main source of Cd, Pb, Zn, Cu and As to mosses.
4) Principle components analysis indicated that soil or windblown dust is the dominant source of Ni and a significant source of As to mosses.
5) Different species of moss accumulate metals at different rates. Relationships established between species for some metals are currently poor, particularly for Cu and As. Further research into the different different rates of accumulation of metals by mosses would be useful.
6) While strong relationships between deposition of Pb, Cd and As and moss concentration have been found (Berg and Steinnes, 1997b) only poor relationships exist between Cu, Zn and Ni deposition and moss concentration. Further work to better quantify the relationship between deposition and moss concentrations would be useful for all metals, but necessary before Cu, Zn and Ni can be used to accurately estimate deposition.

Despite these difficulties, the reconstruction of *trends* in metal deposition has been reasonably successful. Few samples have been shown to be contaminated, and the main source of Pb, Cd, Zn, Cu and As in herbarium mosses has been demonstrated to be atmospheric deposition. Although there is significant scatter, as a result of subsampling errors, spatial variability and variation in metal accumulation between species, there are some clear trends:

1) In general, metal concentrations in mosses are higher in the Northern England regions than in the Cairngorms and South East. This is particularly true for 19th century samples and Pb, As, Cu and Zn.
2) 19th century levels of Pb, As, Cu and Ni tend to be higher than 20th century levels in the northern England sites.
3) Peak deposition of Cu, Pb and As occur earlier than Cd and Pb, which tend to be higher in the mid 20th century.
4) Current concentrations of metals are low in comparison to historical concentrations.

The reconstruction of *rates* of Pb deposition are thought to be accurate, due to the existence of strong relationships between uptake between species, and strong relationships to deposition (Berg and Steinnes, 1997b). Furthermore, deposition estimated from the mosses are similar to those estimated using a variety of historical, environment and monitored records. There is good agreement between the historical scenarios and the herbarium moss deposition estimates for this metal.

Deposition estimates of Cd and As are also thought to be accurate, although there is some loss of precision associated with standardizing *Hypnum* and *Rytiddiadelphus* concentrations to *Pleurozium*. Differences between the literature-based estimate of Cd deposition and the herbarium moss based estimate need further investigation.

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ANNEXE 9: EXTENSION OF CRITICAL LOADS MAPPING TO FORESTS AND LOWLAND VEGETATION: DERIVATION OF NEW TRANSFER FUNCTIONS

L.Shotbolt, M.R.Ashmore

1. Introduction

Transfer functions used in the previous mapping of critical loads were based on extensive sampling of non-forested upland soils (Ashmore et al., 2002; Tipping et al. 2003). To extend critical load mapping onto lowland soils and forested uplands, the applicability of these transfer functions has been tested.

2. Site selection

Five new land cover classes were identified. These are upland coniferous forest, lowland coniferous forest, deciduous forest, acid grassland and heathland.

Ten sampling locations were selected for each land cover class to provide:

- a geographical spread representative of the spread of each land cover class
- a range of cadmium, copper, lead, nickel and zinc concentrations representative of that experienced by each land cover class
- inclusion of sites currently monitored for critical loads or environmental change research.

Sampling locations for forested and non-forest land cover class were selected by different processes, which are explained in Sections 2.1 and 2.2. Sites selected are listed in Table 1.

2.1 Forested land cover classes

The Forestry Commission undertakes periodic environmental monitoring for two networks of forest sites in the United Kingdom. The UK programme for the intensive monitoring of forest ecosystems (Level II network), which has ten sites, is maintained to meet the FC's statutory responsibility under European regulations. The majority of the Level II sites were included in the new sampling locations to enable comparison and sharing of results between research programmes. Under UN/ECE initiatives, various national surveys were incorporated into a large-scale pan-European survey, the 'Level I' programme, with the major aim of monitoring crown condition changes over a long period of time in a large number of forest plots. Soil metal concentration data from level I Forestry Commission sites were supplied by the Forestry Commission (Kennedy, pers. comm.) and forestry sites included with a wide range of metal concentrations.

For upland coniferous forest, Castle How Beck was initially chosen as a site already included in the dynamic modelling work package of this research. A further nine sites were made up of the five Forestry Commission level II upland coniferous sites two Forestry Commission level I sites and two Level 1 forest health plots from sites in Northern Ireland, providing a range of metal concentrations.

For lowland coniferous forest, two Forestry Commission level II sites were chosen, along with six level I sites (five in Britain and one in Northern Ireland) and two National Nature Reserves experiencing a range of metal deposition loads.

For deciduous forest, Old Lodge was initially chosen as a site already included in the dynamic modelling work package of this research. A further nine sites experiencing a range of metal deposition loads comprised two Forestry Commission level II sites, five level I sites, one National Nature Reserve and one Forestry Commission site not monitored by the level 1 or 2 schemes.

2.2 Non-forested land cover classes

For lowland heathland and lowland acid grassland, maps of key natural areas of national importance for each land cover class were produced from the English Nature website (http://www.englishnature.gov.uk). Sampling sites were then chosen with a geographical spread representative of each land cover class' spread, and which also experienced a range of metal deposition loads. Lowland heathland sites comprised seven National Nature Reserves and two Natural Areas. Lowland acid grassland sites comprised seven National Nature Reserves and three Natural Areas. Sampling sites within each natural area were identified in consultation with the relevant English Nature, Scottish Natural Heritage or Countryside Council for Wales’s local team.

Table 1. Location of sample sites

Deciduous Woodland	
Forest of Dean	SO898134
Richmond Park NNR	TQ194708
Alice Holt Forest	SU795402
Grizedale	SD334915
Savernake	SU055888
Salcey	SP796522
Brandon, Thetford	TL793892
Dronley Wood, Tay	NO341368
Old Lodge LNR	TQ456294
Chaddersley Woods	***SO910735***
Hoddesden Woods	TL353086
Castle Eden Dene NNR	NZ429390
Heathlands	
FinglandRigg Woods NNR	NY274566
Linwood Warren	TF136874
Cannock Chase	SJ986164
Charnwood Lodge NNR	SK460149
Thetford Heath NNR	TL846801
Chobham Common NNR	SU966650
Kingston Great Common NNR	SU186038
Muir of Dinnet NNR	NO435986
Strensall Common	SE648616
Treffgarne Rocks	SM954249
Upland coniferous Forest	
Tummel	NN739613
Llyn Brianne	SN812485
Rannoch	NN599534
Coalburn	NY693781
Loch Awe	NM966107
Castle How Beck	NY234003
Llandovery	SN834271
Glenahulish, Lorne	NN044579
Moydamlaght Forest	H740990
Lough Braddan Forest	H250730
Acid Grasslands	
Gowk bank NNR	NY680737
Charnwood Lodge NNR	SK464157
Stiperstones NNR	SO363977
Thetford Heath NNR	TL848797
Richmond Park NNR	TQ193709
Kingston Common NA77	SU184039
Tregoss Moor NA95	SW977609
Cathkin Braes	NS609583
Cors Caron	SN685628
Sutton Park	SP091962
Lowland Coniferous Forest	
Thetford Forest	TL954832
Sherwood	SK162908
Hoddesdon Park Wood NNR	TL356098
Tentsmuir (Aberfoyle)	NO490280
Pelenna	SS803984
Stock Hill	ST548521
Torrachility (Loch Achility)	NH427561
Torridge	SS416019
Creggan Wood	H610790

3. Methods

A single, intact, block of soil, 16 x 12 x 7 cm, was collected from each site. The sample was stored in a cool box before returning to the laboratory. At five sites a replicate sample was collected at a distance of 10 m. In total, 56 soil samples were collected.

Samples were analysed for a range of soil and soil solution variables. Methods used on the upland soil samples have been replicated in order to provide a comparable dataset. Methods are listed at the end of this report.

4. Results and discussion

Under EPG 1/3/144 transfer functions were derived from 98 upland grassland soils. The new soils dataset of 56 samples from five key habitats introduces some differences in the distribution of soil parameters. In particular, the new dataset includes a greater proportion of acid soils, with only six samples of pH > 5 (Figure 1). It also includes more mineral soils and less peat soils. The dataset now includes soils with organic matter contents down to 5% (Figure 1).

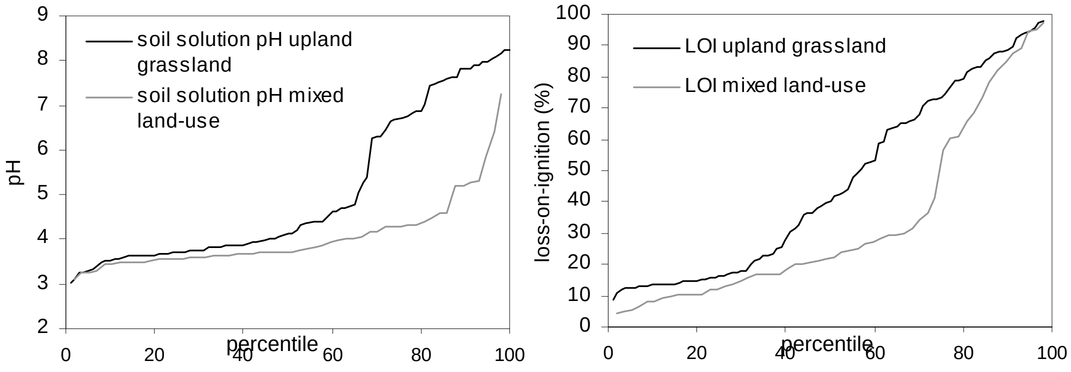

Figure 1. Cumulative frequency distributions of pH and loss-on-ignition in the upland grassland soils dataset and the mixed land-use soils dataset. Ordering is from lowest to highest and is different for each variable.

Trace metal concentrations in soil porewater are generally comparable to the uplands soils dataset (Figure 2). However, sample sites were specifically selected to represent background metal concentrations across the UK, therefore there are less highly contaminated sites, particularly by Pb and Zn. There are also a number of samples with lower Cd concentrations (Figure 2).

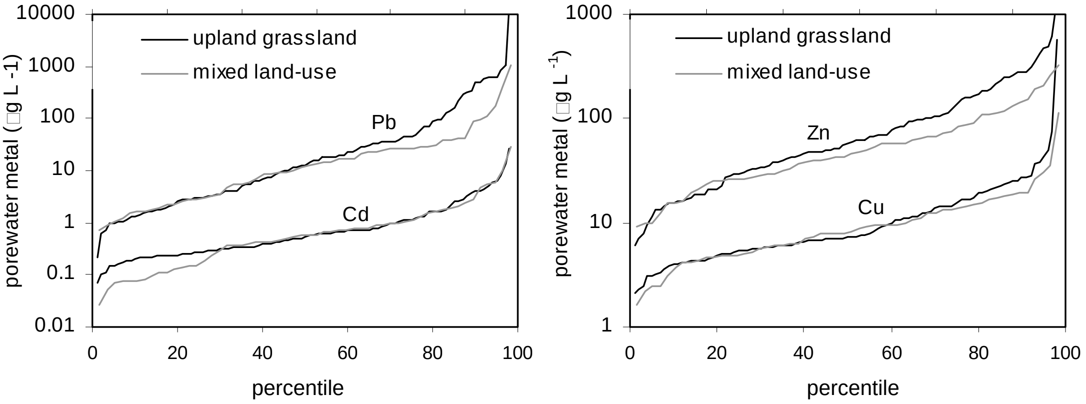

Figure 2. Cumulative frequency distributions of porewater metal concentrations in the upland grassland soils and the mixed land-use soils dataset.

There are, however, some significant differences in bulk soil metal concentrations. Pseudo-total metal analysis shows at least 20% of the samples to contain lower metal concentrations than found in the previous dataset (Figure 3). This is particularly noticeable with Cd, with almost half of the samples having lower Cd concentrations than any of the upland grassland samples. This probably reflects the influence of calcareous grasslands in the upland grassland dataset, which tend to have higher Cd concentrations. The generally lower metal concentrations are thought to be the result of extending the range of locations sampled, with heathland and coniferous forest sites (particularly those with low organic matter content) constituting the bulk of these 'low-metal' samples.

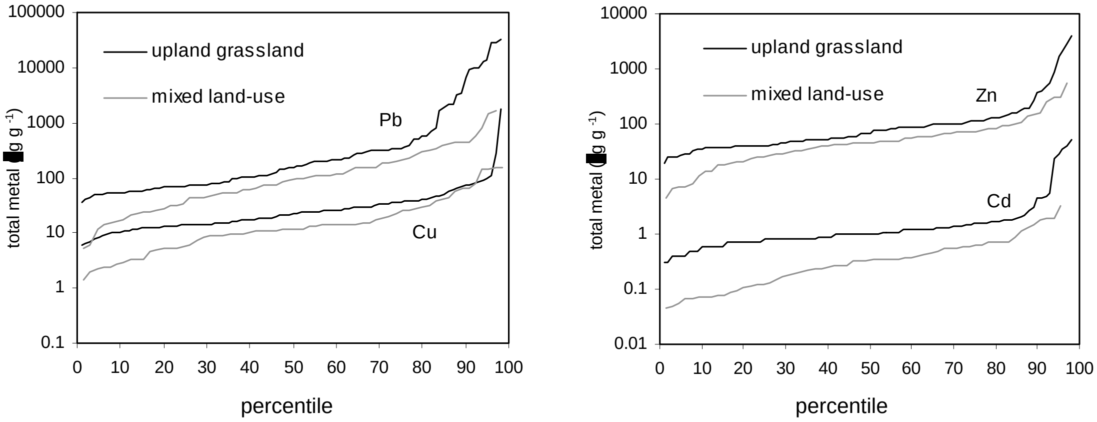

Figure 3. Cumulative frequency distributions of pseudo-total metal concentrations in the upland grassland soils and the mixed land-use soils dataset.

In addition to extending the range of metal concentrations below those in the previous dataset, we have also contributed data to the upper range. A small additional exercise is completed by a MSc project at Bradford University, in which soil samples have been analysed from three sites in the Northern Pennines contaminated by historical lead mining and smelting and three neighbouring uncontaminated sites. Metal concentrations of up to 40,000 µg Pb g^{-1}, 7170 µg Zn g^{-1}, 340 µg Cu g^{-1} and 15 µg Cd g^{-1} have been measured at the contaminated sites. This has allowed us to test the ability of transfer functions to predict metal pools over a wide range of soil metal levels as well as a greater range of habitats. Results are listed at the end of this report and are subsequently referred to as the 'historically mined' data.

4.1 Applicability of upland grassland transfer functions to new dataset.

The ability of transfer functions determined from regression analysis of the upland soils dataset under EPG 1/3/144 to predict soil metal pools in the 56 'mixed land use' samples and the 16 'historically mined' soils was tested. Transfer functions were recalculated as Freundlich partitioning coefficients (K_f) (Table 2). This type of transfer function is preferred (see section 4.5) as it enables us to use the same partitioning equation to calculate either free-ion or reactive soil metal (Römkens *et al.*, 2004). Furthermore, the non-linear Freundlich model allows us to take into account the tendency of binding strength to decrease as the amount of metal sorbed increases if necessary. In fact, only Cd prediction is improved by using the Freundlich model. Partitioning of the remaining metals is best explained by a linear relationship with soil parameters (n = 1, Table 12). K_f is related to soil properties such that:

$$\log K_f = a + b\ \mathrm{pH} + c \log \mathrm{LOI} \qquad [\text{where } K_f = Q_{reactive} / Q_{free}^{n}] \qquad (\text{Eq. 1})$$

Table 2. Regression coefficients for determining partitioning between reactive (edta) soil metal concentration and free-ion activity. Derived from the upland non-forested dataset under EPG 1/3/144.

	a	b	c	n	r^2	s.e.
log K_f Cu	-4.585	1.143	0.528	1	0.928	0.519
log K_f Zn	-4.006	0.406	1.171	1	0.650	0.394
log K_f Cd	-3.749	0.418	0.855	0.92	0.724	0.358
log K_f Pb	-4.270	1.134	0.695	1	0.902	0.599

Figure 4 illustrates the capacity of the upland transfer functions to predict free-ion metal activity on a wider range of soils and habitats. Predicted free-ion activity using the above regression equations is plotted against actual (modelled) free-ion activity. Transfer functions perform satisfactorily for Pb and Cu, however Zn free-ion activity is slightly over predicted and Cd is imprecisely predicted at the ends of the distribution.

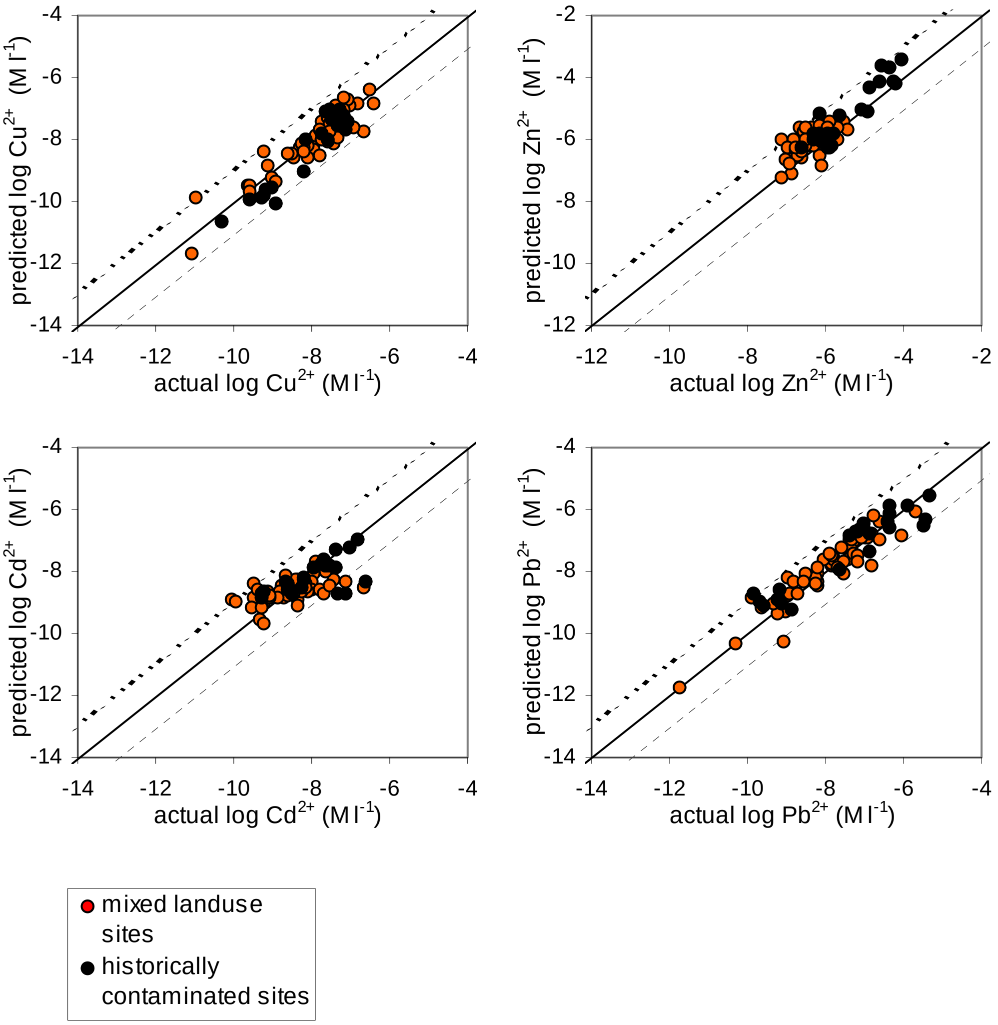

Figure 4. Predicted free-ion activity (M l^{-1}) from upland transfer functions compared to actual (modelled) free-ion activity at the mixed land use and historically contaminated sites.

4.2 Use of other transfer functions to predict soil metal pools across the UK

The performance of transfer functions derived from other soil datasets (Sauvé et al., 1998, 2000; Römkens et al., 2004) was tested on the mixed land use and historically mined soils.

4.2.1 Transfer functions - Römkens et al. (2004)

Römkens et al. (2004) have derived transfer functions on Dutch soils (summarised in Table 3). As shown in Figure 5, prediction of free-ion activity in UK soils is less accurate than using the upland UK transfer functions (Figure 4). There is also some over prediction of Ni, Zn and Pb. The historically mined data are not included as %clay was not determined.

Table 3. Regression coefficients for partitioning (K_f) between reactive (edta) soil metal concentration and free-ion activity. After Römkens et al. (2004)

	a	b	c	d	n	s.e.	r^2
log K_f Ni	-5.05	0.31	0.65	0.39	0.51	0.28	0.88
log K_f Cu	-3.55	0.16	0.48	0.18	0.47	0.35	0.62
log K_f Zn	-4.51	0.45	0.39	0.35	0.74	0.40	0.82
log K_f Cd	-4.85	0.27	0.58	0.28	0.54	0.33	0.79
log K_f Pb	-2.96	0.25	0.83	0.02	0.68	0.55	0.57

$$\log K_f = a + b\ \mathrm{pH} + c \log \mathrm{LOI} + d \log \%\ \mathrm{clay}\ [\text{where } K_f = Q_{\mathrm{reactive\ (M\ g^{-1})}} / Q_{\mathrm{free\ (mM^{-1})}}{}^{n}] \qquad \text{(Eq. 2)}$$

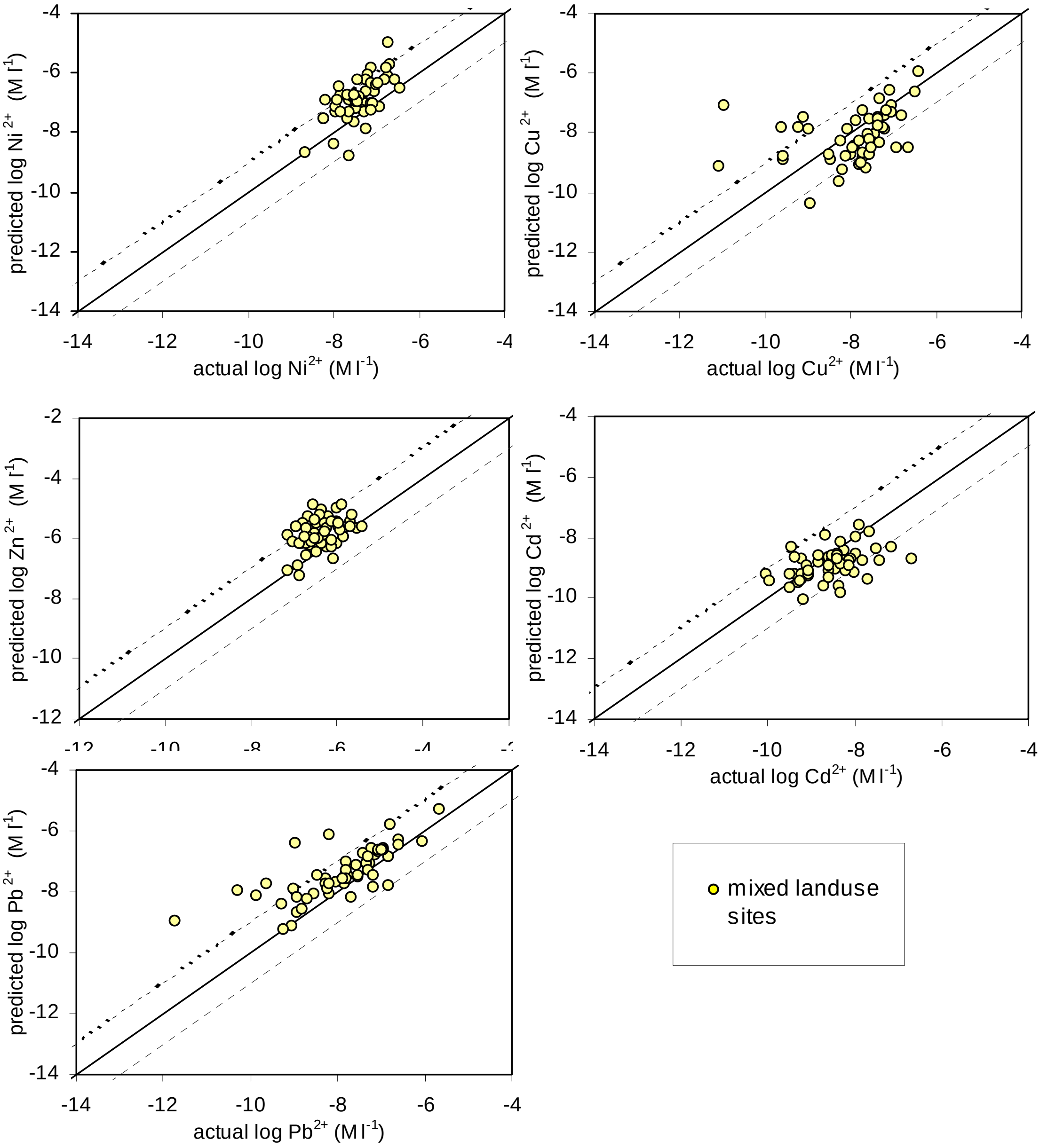

Figure 5. Predicted free-ion activity (M l^{-1}) using the transfer functions of Römkens et al. (2004).

4.2.2 Transfer functions - Sauvé et al. (2000)

Sauvé et al. (2000) derived transfer functions using data compiled from the literature on a range of contaminated soils (summarised in Table 4). These are also presented in Römkens et al. (2004). Figure 6 demonstrates that these transfer functions poorly predict free-ion activity in UK soils in both contaminated and uncontaminated soils.

Table 4. Regression coefficients for partitioning (K_d) between reactive (edta) soil metal concentration and free-ion activity. After Sauvé et al. (2000)

	a	b	c	s.e.	r^2
log K_f Ni	-4.16	1.02	0.80	0.61	0.76
log K_f Cu	1.75	0.21	0.51	0.55	0.42
log K_f Zn	-1.34	0.60	0.21	0.72	0.57
log K_f Cd	-0.65	0.48	0.82	0.62	0.61
log K_f Pb	1.19	0.37	0.44	0.59	0.56

$$\log K_d = a + b\,\mathrm{pH} + c \log \mathrm{LOI} \qquad [\text{where } K_d = Q_{\text{reactive (M g}^{-1})} / Q_{\text{free (M}^{-1})}\,] \qquad \text{(Eq. 3)}$$

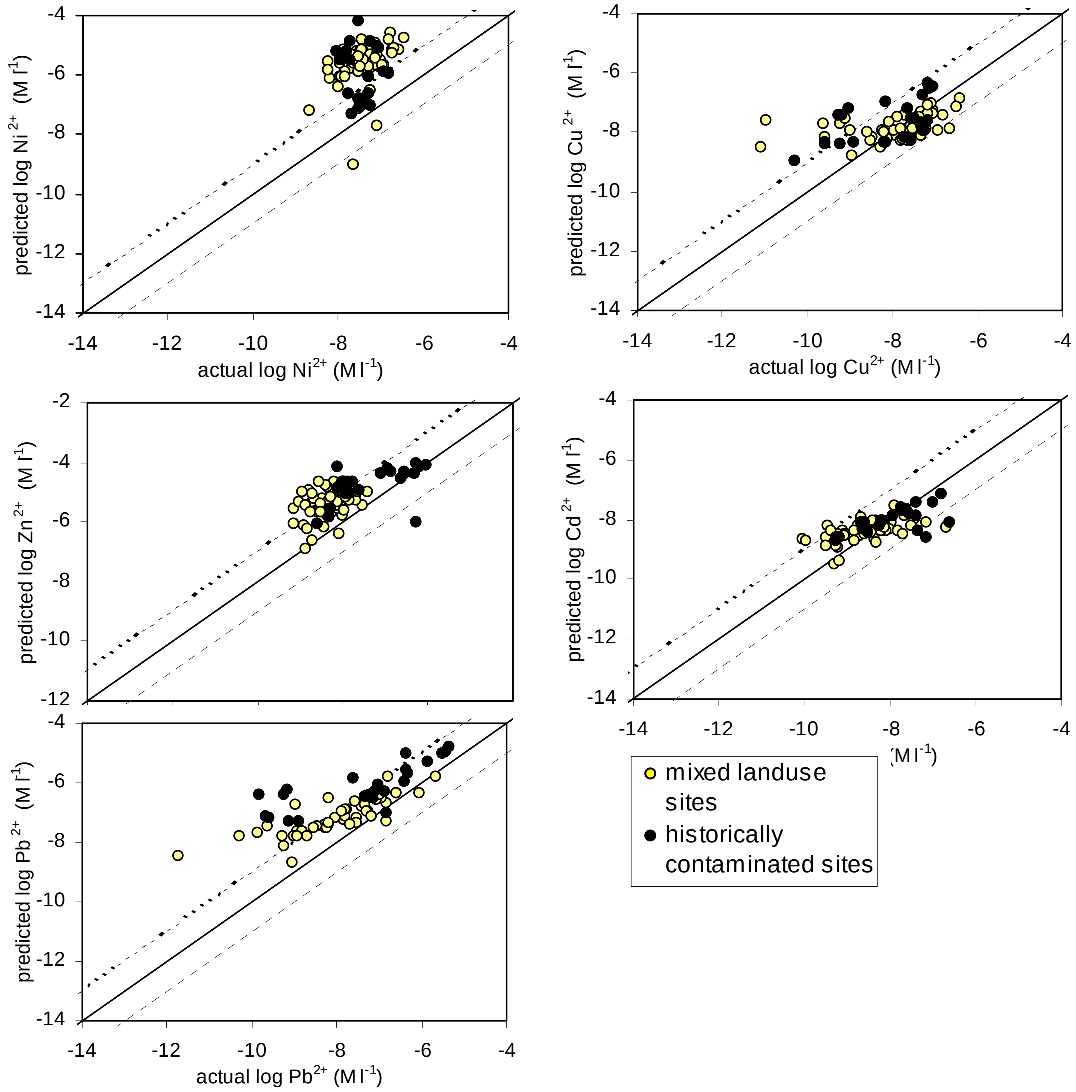

Figure 6. Predicted free-ion activity (M l^{-1}) using the transfer functions of Sauvé et al. (2000).

In general, both sets of transfer functions performed less well on the mixed land use and historically contaminated datasets than those derived under EPG 1/3/144. This probably results from methodological differences in the extraction of porewater and metals and the determination of pH. A possible contributing factor may also be that these functions, developed outside the UK, may be less suitable to the soil, vegetation and environmental conditions in the UK. As a result, only data from the UK were used to produce new transfer functions for use across the UK.

While the transfer functions developed under EPG 1/3/144 appear to predict metal speciation across a range of soil types and habitats in the UK reasonably well, Zn is slightly under predicted and Cd prediction is inaccurate at the ends of the distribution. There is, therefore, potential to improve on these functions by combining all UK data .

4.3 Transfer functions using all UK data. Comparison of transfer functions between total and free-ion metals and reactive and free-ion metals.

Previously, transfer functions have been derived between reactive metal concentrations and free-ion activity (Ashmore et al., 2002). These have been used to map reactive metal concentrations across the UK from the free-ion critical limits and derive critical loads. However, UK soil maps are actually presented as total soil metals. In the previous project two steps were, therefore, required: i) a transfer function to determine reactive metal from free-ion activity and; ii) a function to determine reactive metal concentrations from the presented total metal concentrations.

Ideally, therefore, transfer functions between total and free-ion metals are required. These would remove the necessity for using two functions, would be easier to use and could result in less uncertainty in the resulting critical limits and loads calculations. We have, therefore, derived and compared transfer functions between total and free-ion metal concentrations as well as reactive and free-ion metal concentrations. Tables 5 and 6 summarise these functions and Figures 7 and 8 show the quality of the predictions they provide.

4.3.1 EDTA to free-ion transfer functions.

Table 5 and Figure 7 show transfer functions developed using all available UK data. Unfortunately, Ni was not measured at the upland UK sites, therefore there were relatively few data points from which to determine Ni transfer functions. Furthermore, the range in Ni concentrations in the new UK data was small and therefore transfer functions derived were poor, explaining only 49% of the variation (Table 5). In an attempt to improve this function we obtained some further data on Ni (from Pampura et al., pers. comm. and Weng et al., 2002). The second transfer function for Ni in Table 5 is derived from the new UK mixed land use data, Russian forest soils (Pampura et al.) and Dutch agricultural soil samples (Weng et al., 2002). The inclusion of the Dutch and Russian data produces a very similar transfer function confirming the accuracy of the UK data. The greater range of data improves our confidence in the Ni transfer function, which now explains 71% of the variation. Only for Ni and Cd was the predictive power of the transfer functions improved by using the curvilinear Freundlich coefficients (i.e. $n < 1$).

Table 5. New UK transfer functions (based on EDTA extracted metals)

	a	b	c	n	r2	se
log K_f Cu	-5.174	1.169	0.781	1.00	0.921	0.472
log K_f Zn	-3.282	0.363	0.899	1.00	0.573	0.418
log K_f Cd	-5.852	0.392	0.951	0.68	0.681	0.357
log K_f Pb	-4.203	1.124	0.718	1.00	0.900	0.518
log k_f Ni$^+$	-4.836	0.305	0.928	0.70	0.491	0.331
log k_f Ni*	-4.850	0.353	0.952	0.73	0.708	0.339

$$\log(K_f) = a + b*\mathrm{pH} + c*\log\mathrm{LOI}\% \qquad [\text{where } K_d = Q_{\mathrm{reactive}\ (\mathrm{M\ g^{-1}})} / Q_{\mathrm{free}\ (\mathrm{M^{-1}})}{}^{n}] \tag{Eq. 4}$$

Log k_f Ni$^+$ = Ni transfer function using only UK data
Log k_f Ni* = Ni transfer function using UK, Russian and Dutch data.

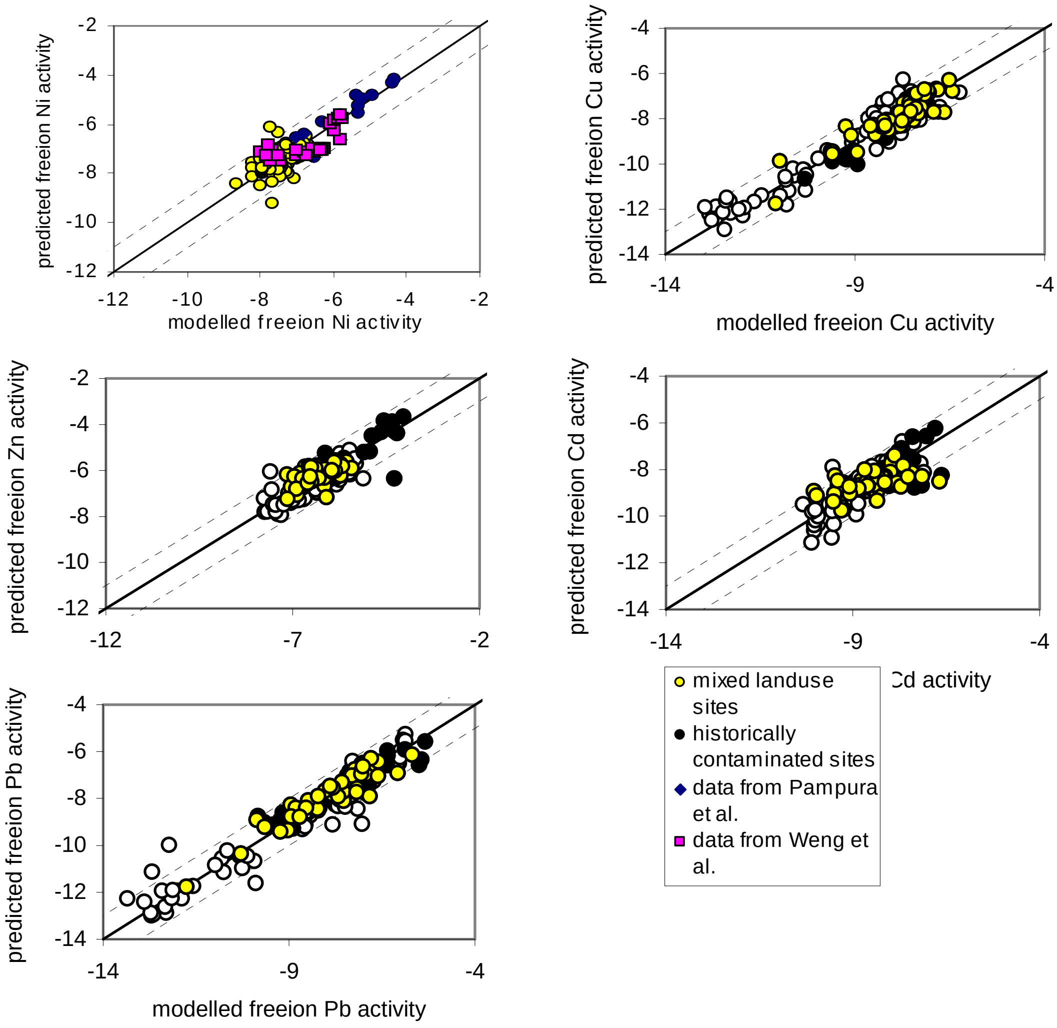

Figure 7. Predicted free-ion activity (M l^{-1}) using the new UK transfer functions (reactive to free-ion) .

The combined UK data predicts free-ion activity successfully across a wide range of soil types and habitats and a large contamination gradient (Figure 7).

4.3.2 Total metal to free-ion transfer functions

Table 6 and Figure 8 show transfer functions developed using all available UK data between total and free-ion metal pools.

Table 6. Transfer functions on all UK data between total and free-ion metals.

	a (int)	b (pH)	c (logLOI)	n	r2	se
log K_f Cu	-4.289	1.116	0.603	1.000	0.922	0.452
log K_f Zn	-2.573	0.324	0.121	0.830	0.588	0.381
log K_f Cd	-5.712	0.399	0.727	0.630	0.665	0.372
log K_f Pb	-4.191	1.175	0.763	1.000	0.919	0.483
log K_f Ni	*-4.031*	*0.246*	*0.337*	*0.570*	*0.278*	*0.333*

$\log(K_f) = a + b*pH + c*\log LOI\%$ [where $K_d = Q_{total\ (M\ g^{-1})} / Q_{free\ (M^{-1})}{}^{n}$] (Eq. 5)

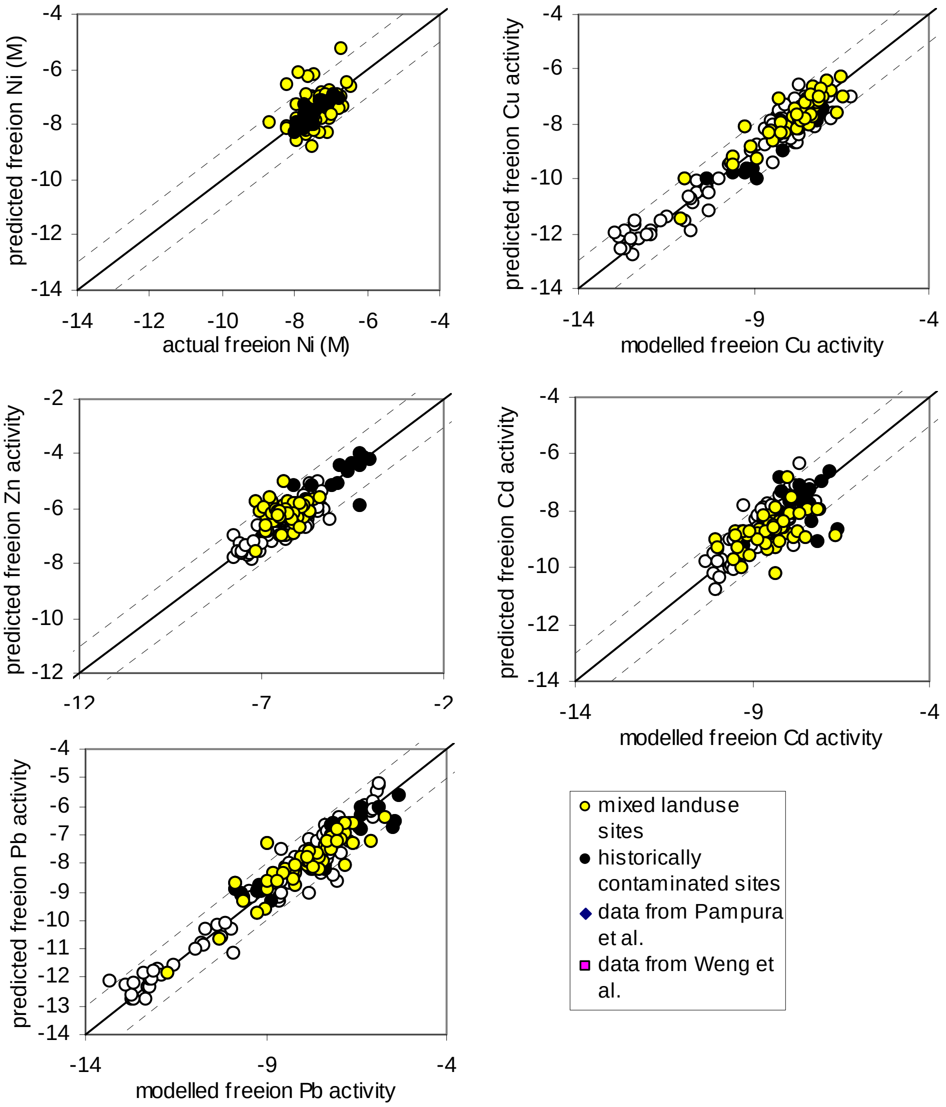

Figure 8. Predicted free-ion activity (M l^{-1}) using the new UK transfer functions (total to free-ion) .

The relationship between total metal concentrations and free-ion activity is good. The predictive power of the transfer functions is improved for Cd, Ni and now also Zn, by using the curvilinear Freundlich equations rather than linear regression. For Cu ad Pb both r^2 values and standard errors are lower using these relationships than using the reactive to free-ion transfer functions. While r^2 are very slightly lower for Zn and Cd and the standard error is higher for Cd, on balance, because it removes the necessity for two transfer functions, it is preferable to use the total to free-ion transfer functions.

The exception is Ni. Due to the lack of data, we have only been able to produce weak relationships between total and free-ion Ni concentrations. For this metal, therefore, two transfer functions - free-ion to reactive (Table 5) and reactive to total (Table 6) must be used. Reactive to total Ni transfer functions are shown below (a direct transfer function has been used as this was found to produce the slightly better prediction of speciation).

Table 6. Qc/cQ transfer functions for Ni based on UK data between total and reactive (edta) metals

	a	b	c	d	r2	se
Log edta Ni (M/g)	-4.351	-	0.663	0.628	0.558	0.249
Log total Ni (M/g)	-1.58	0.0066	0.484	0.626	0.534	0.252

Log edta Ni (M/g) = a + c log LOI + c log total Ni (M/g)
Log total Ni (M/g) = a + b pH + c log LOI + d log edta (M/g)

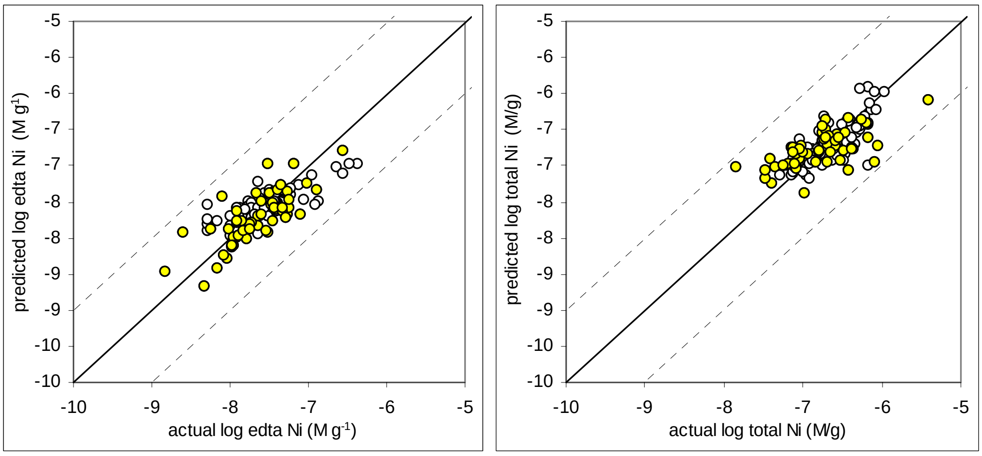

Figure 9. Predicted edta and total Ni using direct transfer functions

4.4 Comparison of direct and indirect transfer functions

Finally, there has been some debate as to whether it is better to use direct (cQ-Qc) transfer functions or indirect (K_f, K_d) partitioning functions. The following section compares the predictive power and accuracy of both sets of transfer functions.

Direct transfer functions relate the free-ion activity directly to the total concentration as well as soil parameters (i.e. pH and LOI). These are written in the form:

$$\log C_{metal} = a + b\,\mathrm{pH} + c\,\mathrm{LOI} + d \log Q_{metal}$$

Where C is the free-ion metal activity and Q is the total metal concentration.

In contrast the indirect functions, such as have been used throughout this report, are based on the derivation of an adsorption constant which is related to soil properties. This can either be based on a linear model (K_d) or a nonlinear model such as the Freundlich model (K_f). These are written in the form:

$\log(K_f) = a + b*pH + c*\log LOI\%$ [where $K_f = Q_{total\ (M\ g^{-1})} / Q_{free\ (M^{-1})}{}^{n}$] or

$\log(K_d) = a + b*pH + c*\log LOI\%$ [where $K_d = Q_{total\ (M\ g^{-1})} / Q_{free\ (M^{-1})}$]

The key advantage of the indirect approach is that only one equation is needed from which both free-ion and total metal concentrations can be derived. Two equations are needed with the direct approach. The nature of multilinear regression used to derive the equations means that the concentration of total metal predicted from free-ion metal will not necessarily be the same as the free-ion metal activity predicted from the total metal. However, if the indirect functions were significantly weaker than the direct functions, it may be more appropriate to use the direct method.

4.5.1 Comparison of r^2 and standard errors produced by direct and indirect approaches.

Tables 7 and 8 show r^2 and standard errors produced by calculation of total metal concentrations and free-ion activity using direct and indirect transfer functions (note these will be different from the values previously produced for the K_f prediction which were the r^2 and s.e. of the relationship between predicted and actual K_f, whereas these are the relationship between predicted and actual total metal concentrations, and predicted and actual free-ion metal concentrations).

Table 7. Prediction of total metal concentration. Comparison of Kf and cQ functions

	cQ		K_f	
	r^2	SE	r^2	SE
Cu	0.374	0.326	0.369	0.448
Zn	0.626	0.359	0.618	0.378
Cd	0.579	0.345	0.556	0.369
Pb	0.716	0.425	0.714	0.478

Table 8. Prediction of free-ion metal concentration. Comparison of Kf and Qc functions

	Qc		K_f	
	r^2	SE	r^2	SE
Cu	0.923	0.448	0.922	0.448
Zn	0.616	0.426	0.608	0.455
Cd	0.518	0.518	0.490	0.586
Pb	0.926	0.483	0.926	0.478

Both r^2 and standard error prediction are similar for both approaches but the relationships are consistently slightly weaker using the K_f approach. However, examination of the residuals generated from the direct transfer function prediction of total metal concentration shows that they are not independent (Figures 10 and 11). The transfer function leads to some underprediction of high values and over prediction of low values of Cu Cd, and Zn to a lesser extent. Residuals produced by the Qc prediction of free-ion metals are also biased for Cd and Zn (not shown).

Although the indirect approach results are slightly less precise, this method does not produce any of the bias that is evident using the direct approach. The indirect approach was, therefore, used throughout critical loads mapping and modelling.

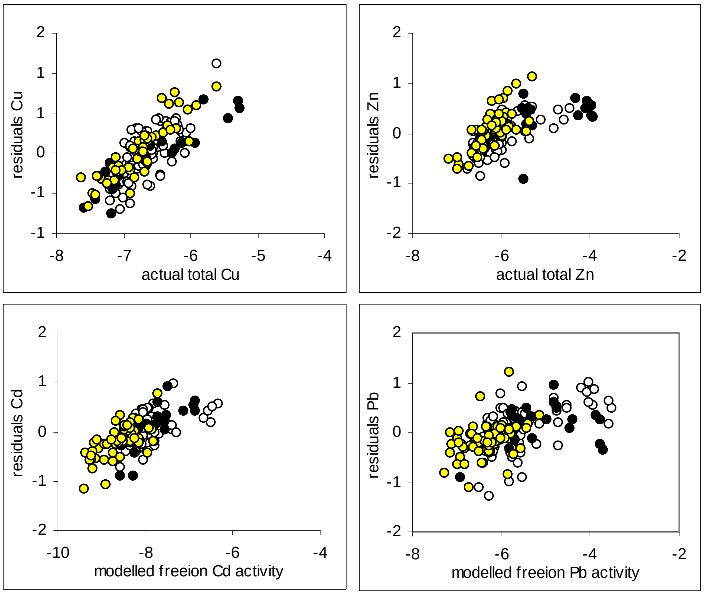

Figure 10. Residual plots generated from prediction of total metal concentrations using direct (cQ) transfer functions.

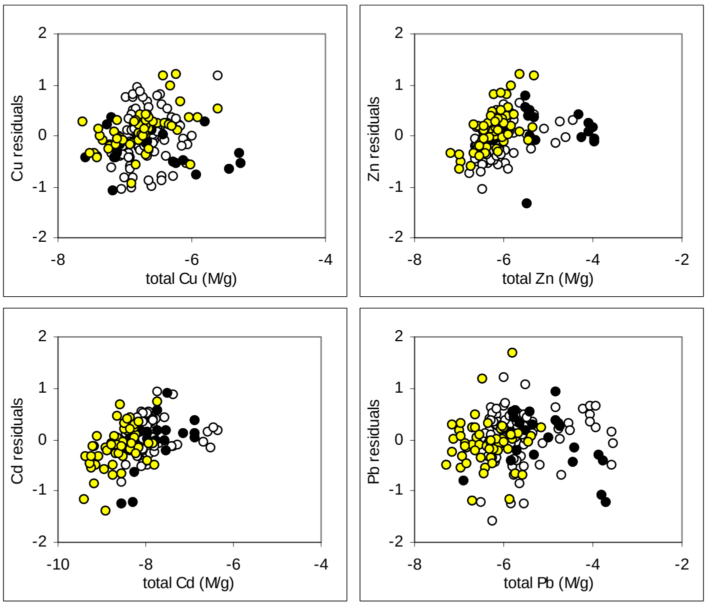

Figure 11. Residual plots generated from prediction of total metal concentrations using indirect (K_f) transfer functions.

4.5 Transfer functions used in critical loads mapping and modelling

The following transfer functions are, therefore, used in critical loads mapping and modelling.

Table 9. K_f transfer functions for Cu, Zn, Cd and Pb based on all UK data between total and free-ion metals.

	a (int)	b (pH)	c (logLOI)	n	r2	se
log K_f Cu	-4.289	1.116	0.603	1.000	0.922	0.452
log K_f Zn	-2.573	0.324	0.121	0.830	0.588	0.381
log K_f Cd	-5.712	0.399	0.727	0.630	0.665	0.372
log K_f Pb	-4.191	1.175	0.763	1.000	0.919	0.483

$\log(K_f) = a + b{*}pH + c{*}\log LOI\%$ [where $K_d = Q_{total\ (M\ g^{-1})} / Q_{free\ (M^{-1})}{}^{n}$]

Table 10. K_f **t**ransfer functions for Ni based on UK, Dutch and Russian data between reactive (edta) and free-ion metals.

	a	b	c	n	r2	se
log k_f Ni*	-4.850	0.353	0.952	0.73	0.708	0.339

$\log(K_f) = a + b{*}pH + c{*}\log LOI\%$ [where $K_d = Q_{reactive\ (M\ g^{-1})} / Q_{free\ (M^{-1})}{}^{n}$]

Table 11. Qc/cQ transfer functions for Ni based on UK data between total and reactive (edta) metals

	a	b	c	d	r2	se
Log edta Ni (M/g)	-4.351	-	0.663	0.628	0.558	0.249
Log total Ni (M/g)	-1.58	0.0066	0.484	0.626	0.534	0.252

Log edta Ni (M/g) = a + c log LOI + c log total Ni (M/g)
Log total Ni (M/g) = a + b pH + c log LOI + d log edta (M/g)

5. Conclusions

- Transfer functions were produced under Defra contract 1/3/144 for upland soils. When applied to a wider range of soils and habitats they predict metal partitioning satisfactorily for Pb and Cu, but less well for Zn and Cd.
- Transfer functions derived by Römkens et al. (2004) and Sauve et al. (2000) predict metal partitioning poorly in UK soils.
- The upland UK soil data were combined with data collected under the current contract across a wide range of UK soils and habitats to produce new transfer functions suitable for application for critical loads mapping and modelling in the UK.
- Relationships between total metal concentration and free-ion activity were found to be as strong as relationships between reactive metal concentration and free-ion activity. Therefore total to free-ion transfer functions are being used for mapping and modelling (as UK wide soil data is only available as total metal). Due to a lack of data for Ni, however, two transfer functions are necessary for this metal (free-ion to reactive Ni and reactive to total Ni).

- A comparison was made of direct (Qc-cQ) and indirect (K_f) transfer functions. Indirect transfer functions produced slightly weaker but unbiased relationships. Residuals produced by the direct transfer functions for Cd, Zn and Cu were not independent of metal concentration. Indirect functions are therefore used throughout critical loads mapping and modelling.

6. References

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Methods

Extraction of porewater

1. Soil is brought in from the field in Tupperware boxes, and stored at 4°C for no longer than 3 weeks.
2. Boxes are removed from store in batches of 10 to 15.
3. Boxes are wiped clean and holes are punched in the base of each box
4. Boxes are weighed.
5. Lid is removed and the box placed in onto the lid. DDW added gradually to the surface.
6. On first appearance of water from holes addition of water halted and contents of lid added to the surface
7. Water added until can take no more (i.e. field capacity). Boxes are reweighed to determine amount of water added.
8. Lids reattached and wrapped in Clingfilm returned to the store for 1 week to equilibrate.
9. After 1 week brought into the lab and left for 1 day at room temperature.
10. Cling film removed and a Rhizon samplers inserted into one of the holes (holes made first with thin stick)
11. Syringe is attached and plunger withdrawn to create a vacuum and porewater extracted until 30ml has been collected. This may take anywhere between a few hours and several days (though most are extracted within 24 hours). Where extraction takes longer than 6 hours, boxes are returned to the cold store for the remainder of the extraction.
12. Syringes are put into plastic bags to be used later to filter samples.
13. Extracted porewater is removed to plastic bottles, about 15 mls into a clean but not acid washed container for anion analysis and pH and the remaining 15 mls into an acid washed container (make note of total volume of solution removed).

Separation of sample into aliquots for heavy metal, anion, base cation, DOC and pH analysis.

DOC analysis

1. 5 ml of sample is removed from each acid washed storage bottle using a pipette into acid washed small plastic containers.
2. 5 ml DDW is added to make up to 10 mls.
3. Samples are analysed using a Dohrmann DC-190 TOC analyser

Heavy metal and base cation analysis

1. The remaining extract is filtered through 0.2 µm syringe filters into separate centrifuge tube. Run DDW through the filter first, then pour 2 mls of sample into the syringe filter and discard. Pour the remaining extract into the syringe and filter into a centrifuge tube.
2. 5 mls of filtered extract is then removed using a calibrated pipetter to another centrifuge tube for analysis of base cations and heavy metals by ICP-AES.
3. 5 mls of DDW are added to each sample
4. 0.2 mls of high grade HNO3 are added to each sample to acidify to approx 2%.
5. Standards are made up using same matrix.
6. Analysis carried out on ICP-AES

pH analysis

1. Approx 5 mls of sample is removed from the non-acid washed container into small clean but not acid washed plastic containers.
2. Analysed for pH.

Anion analysis

1. The remainder not used for pH (up to 10 mls) is kept for the analysis of anions by ion chromatography. Samples analysed using Dionex Ion Chromatography.

Soil Analysis

pH

1. A core of soil is removed from the Tupperware box using a cork corer and put into a small plastic container. Find weight of soil removed.
2. DDW is added to the soil at a ratio of 2 mls of water per gram of soil.
3. Mix thoroughly and leave to equilibrate for an hour
4. Stir then measure pH using a glass electrode.

Soil Homogenisation

1. Soil is weighed (must reweigh as water removed and soil for pH analysis) then dried in a fan oven at 40 C.
2. Soil remains in the oven until it is not losing any more water. Reweigh to determine air dry moisture content and dry bulk density
3. Air-dry soils are sieved to < 2 mm. Where soils are consolidated, light grinding in a pestle and mortar is used to break them up (or breaking up in a plastic bag).
4. Separate suitable quantities for CEC (4.g of < 1mm soil), total metal analysis <2mm (0.5 g) particle size analysis <2mm (50g) EDTA extractable metal analysis <2mm (1 g) and LOI < 2mm (10 g). Representative samples for each are obtained using a riffle sampler (which must be rinsed and dried between each sample).

Water content and LOI

1. Soil must first be oven dried to determine the difference between oven-dry and air-dry weight (which is the standard soil water content). Approx. 10 g of soil is weighed into a crucible and oven dried at 105oC. (weigh crucible then weigh with soil in it)
2. Crucibles are removed from the oven and placed in a desiccator to cool. Once cool they are weighed and the difference in weight used to determine the water content of the < 2 mm fraction.
3. Crucibles are then placed into the furnace. Furnace is heated to 450oC overnight.
4. Samples are removed (with tongs) placed into a desiccator to cool, and reweighed. % weight difference between oven dry and ignited soils is LOI.

Pseudo-total metal analysis

1. Weigh 0.5g milled air dried soil into a digestion tube (not forgetting replicates, blanks, CRMs)
2. Add 8 ml HNO_3 to each (70%)
3. Add 2 ml $HClO_3$ to each (60%)
4. Add caps and place in heating block and raise temperature to 50^oC. Samples with high organic matter react vigorously with nitric and perchloric, so best to leave heating block on at 50C overnight after the addition of acids. After at least 3 hours and preferably overnight raise temperature to 150^oC, leave at this temperature for 3 hours.
5. Increase temperature to 185^oC and leave for 18 hours (overnight). Next morning, remove caps and allow to evaporate at this temperature (will take approx 3 hours – sample is completely dry when the white fumes disappear).
6. Allow to cool. Add 2 ml HCl and 2 ml DDW to each test tube.
7. Heat to 60^oC and leave for one hour. Cool.
8. Add 4 ml water and mix.
9. Filter quantitatively using ashless, slow filters (Whatman 542) into 50 ml volumetrics.
10. Add 1 ml of this solution to an acid washed centrifuge tube. Add 10 mls water. Add 2ml ultrapure HNO3. Analyse on ICP-AES
11. Ensure COSHH form filled out and safety gear worn.

EDTA extraction

1. Make up 1litre of 0.1 M Na_2EDTA solution.
2. Weigh 1 g of air-dried, < 2 mm soils into large centrifuge tubes. Shake for an hour with 10 ml 0.1 M Na_2EDTA (Analar) on flask shaker.
3. Each tube is then centrifuged at 2000 rpm for 2 mins
4. 5ml of supernatant is removed to separate glass test tubes.
5. Add 4ml nitric acid (primar). Weigh tubes. Put glass balls on to prevent evaporation. Acid attack is then performed on the supernatant .
6. put into heating block and heat up to 100^oC for 6hrs.
7. Allow to cool. Reweigh to check no evaporation. Allow any remaining solids to settle.
8. pipette 0.3 mls into a acid washed centrifuge tube.
9. Add 10 mls DDW. Add 0.1 ml ultrapure HNO3.
10. Analyse on ICP-AES.

Cation Exchange Capacity

1. Make up 2 litre, 1 N Sodium acetate solution; 2 litre, 1 N Ammonium acetate solution. Weigh 4 g of < 1 mm soil into large centrifuge tubes (can do 12 at a time)
2. Add 33 ml NaAc solution to each sample. Shake on flask shaker for 5 minutes. Centrifuge at 2250 revs per min for 5 mins. Carefully decant supernatant.
3. Repeat step 2, 3 times.
4. Add 33 ml isopropyl alcohol (propan-2-ol). Shake, centrifuge and decant as above.

5. Repeat step 4, twice.
6. Add 33 ml NH_4Ac solution to each sample. Shake, centrifuge and decant into 100 ml volumetrics.
7. Repeat step 6, twice. Make up to 100 ml mark with spare NH_4Ac preferably or DDW.
8. Measure Na on ICP-AES./ICP-MS/Flame photometer

Particle size analysis

1. Dry soils to 350°C (reweigh)
2. In large beakers, add H_2O_2 in small quantities.
3. Heat once you think you might be able to without it overflowing
4. When no further reaction (may be a little residual bubbling due to carbonate attack but you should be able to tell from colour and lack of reaction when the organic matter is gone) dry in oven at 105°C (reweigh).
5. Sieve to get 63 micron fraction (weigh and determine % less than 63 microns)
6. Add 25 ml DDW to the less than 63 micron fraction. Add 1 ml of 1% calgon solution.
7. Shake on sieve shaker for 1 hr.
8. % clay determined using the settling and Stokes Law technique.

sample	grid ref	Vegetation	dry bulk density g/cm^3	solution pH	soil pH	DOC (mg/l)	LOI %	% clay	CEC (Meq 100g^{-1})	Chloride (mg/l)	Nitrate (mg/l)	Sulphate (mg/l)	Phosphate (mg/l)
Cathkin Braes	NS609583	Acid Grassland	0.6	4.6	5.0	57.6	20.1	4.7	22.9	0.3	1.1	7.2	0.1
Charnwood acid	SK464157	Acid Grassland	0.3	3.5	3.8	52.2	78.1	15.2	55.8	3.3	bdl	9.0	bdl
Cors Caron 1	SN685628	Acid Grassland	0.7	5.9	4.8	23.0	12.0	13.2	11.8	12.8	4.4	13.1	bdl
Cors Caron 2	SN685628	Acid Grassland	0.7	5.3	4.7	8.2	10.4	8.1	11.9	6.8	13.2	5.3	bdl
Gowk Bank	NY680737	Acid Grassland	0.1	3.8	4.2	52.6	87.2	13.6	58.5	4.0	bdl	18.6	0.2
Kingston Common acid	SU184039	Acid Grassland	0.1	4.3	4.2	56.1	82.0	10.3	60.2	3.9	bdl	1.6	bdl
Richmond Park acid	TQ193709	Acid Grassland	1.0	3.9	3.9	106.2	9.2	4.5	16.3	24.2	9.3	9.5	bdl
Stiperstones	SO363977	Acid Grassland	0.9	5.3	5.6	53.4	18.7	25.0	22.6	3.9	3.2	3.8	bdl
Sutton Park	SP091962	Acid Grassland	0.5	6.4	5.6	168.7	21.6	1.2	16.3	4.9	1.5	3.1	bdl
Thetford acid	TL846801	Acid Grassland	0.7	3.9	3.7	192.0	13.5	1.0	5.8	2.6	1.3	5.5	0.6
Tregoss	SW977609	Acid Grassland	0.5	3.7	3.9	17.7	24.9	14.7	19.9	32.3	bdl	30.2	bdl
Alice Holt	SU795402	Deciduous	0.7	4.3	4.4	43.9	17.1	10.9	20.7	16.6	0.9	3.3	bdl
Brandon	TL793892	Deciduous	0.8	3.3	3.7	148.6	10.2	0.4	8.8	10.7	41.4	13.2	5.4
Castle Eden Dene	NZ429390	Deciduous	1.0	4.3	4.6	73.9	9.6	17.5	14.0	28.5	1.5	23.6	bdl
Chaddersley	SO910735	Deciduous	0.6	3.3	3.5	38.3	16.6	11.8	15.9	4.8	150.5	13.2	bdl
Dronley Woods 1	NO341368	Deciduous	0.5	3.7	4.1	42.2	29.5	4.7	34.1	11.4	1.1	12.9	bdl
Dronley Woods 2	NO341368	Deciduous	0.4	3.8	4.1	62.7	29.6	2.2	30.0	5.0	1.4	7.7	bdl
Forest of Dean	SO898134	Deciduous	0.5	7.3	7.4	39.3	36.7	3.7	47.9	8.3	8.5	22.6	bdl
Grizedale	SD334915	Deciduous	0.6	3.6	3.8	17.9	20.6	1.9	24.9	4.6	88.9	1.6	bdl
Hoddesden deciduous	TL353086	Deciduous	0.2	3.5	3.8	162.3	73.6	13.4	51.7	10.3	17.2	22.2	bdl
Old Lodge	TQ456294	Deciduous	0.5	3.4	3.8	48.3	27.3	8.8	25.0	17.6	bdl	7.7	bdl
Richmond Park deciduous	TQ194708	Deciduous	0.6	4.0	4.2	49.6	24.0	3.0	11.2	8.8	58.4	16.5	2.6
Salcey	SP796522	Deciduous	0.9	4.5	4.4	30.8	10.6	12.7	12.7	10.9	43.3	15.5	bdl
Savernake	SU055888	Deciduous	0.7	4.2	3.9	20.1	22.3	24.6	23.3	4.6	51.7	2.3	bdl
Cannock Chase	SJ986164	Heathland	0.5	3.1	3.4	78.7	19.9	2.6	20.7	1.3	bdl	21.7	bdl
Charnwood heath	SK460149	Heathland	0.4	3.7	3.8	33.5	41.1	8.1	42.8	5.7	bdl	8.7	bdl
Chobham common 1	SU966650	Heathland	1.0	4.0	3.9	25.0	6.3	3.2	10.6	3.9	bdl	3.9	bdl
Chobham common 2	SU966650	Heathland	0.7	3.8	3.9	38.0	12.9	1.9	16.1	4.0	0.3	9.6	bdl
Finlandrigg Woods	NY274566	Heathland	0.4	3.7	4.0	56.2	30.1	3.9	30.3	8.1	3.4	7.0	bdl
Kingston Common	SU186038	Heathland	0.4	3.7	3.7	104.2	31.3	2.3	34.1	20.7	bdl	13.9	bdl
Linwood	TF136874	Heathland	0.8	3.7	3.8	65.5	8.3	0.5	8.9	2.0	bdl	7.1	bdl
Muir of Dinnet	NO435986	Heathland	0.8	4.2	4.5	33.6	15.9	1.6	24.0	11.5	37.5	6.9	bdl
Strensall	SE648616	Heathland	0.4	3.6	3.6	75.3	21.4	1.3	13.9	4.2	2.0	9.6	bdl
Thetford heath	TL954832	Heathland	1.1	3.6	4.1	84.3	5.1	0.9	5.7	5.8	25.3	7.6	bdl
Trefgarne	SM954249	Heathland	0.5	3.6	3.7	20.3	26.6	12.5	20.0	38.6	19.3	4.8	bdl
Cregan	274520E, 399	Lowland Coniferou	0.1	3.5	3.4	75.6	97.2	8.3	80.4	5.9	7.1	4.1	bdl
Hoddesden coniferous	TL356098	Lowland Coniferou	0.9	3.4	3.7	24.2	17.0	8.5	26.7	10.0	bdl	7.3	bdl
Pelenna 1	SS803984	Lowland	0.2	3.6	3.8	33.2	65.8	12.4	55.8	10.0	4.3	11.1	bdl
Pelenna 2	SS803984	Lowland	0.3	3.6	3.8	35.5	60.6	8.2	46.8	5.5	7.0	7.6	bdl
Sherwood forest	SK162908	Lowland	0.5	3.6	3.5	58.6	17.0	8.9	17.7	2.2	13.8	6.2	bdl
Stocks Hill	ST548521	Lowland Coniferou	0.3	3.6	3.7	65.5	56.5	6.9	40.2	5.6	12.8	5.1	bdl

sample	free ion activities (WHAM)					Pseudo-total metals					EDTA extractable metals				
	Ni (ug/l)	Cu (ug/l)	Zn (ug/l)	Cd (ug/l)	Pb (ug/l)	Ni (ug/g)	Cu (ug/g)	Zn (ug/g)	Cd (ug/g)	Pb (ug/g)	Ni (ug/g)	Cu (ug/g)	Zn (ug/g)	Cd (ug/g)	Pb (ug/g)
Cathkin Braes	0.4	0.0	4.6	0.0	0.0	38.2	23.6	146.0	0.3	67.6	1.8	4.9	16.1	0.1	20.4
Charnwood acid	1.5	5.5	66.9	0.6	14.7	9.6	39.2	43.8	0.5	331.2	3.2	19.9	22.0	0.5	338.4
Cors Caron 1	1.7	0.0	64.3	0.6	0.2	37.2	19.8	282.1	1.6	844.4	2.0	7.8	51.9	0.9	485.0
Cors Caron 2	3.2	0.1	181.9	1.2	1.2	32.4	16.6	240.0	1.3	736.2	2.2	7.8	56.4	1.0	516.8
Gowk Bank	1.2	0.6	37.9	0.2	3.4	4.8	10.0	41.4	0.7	151.3	2.0	3.2	32.1	0.6	139.2
Kingston Common acid	5.2	0.2	15.1	0.3	1.2	10.2	7.8	33.0	0.8	80.0	7.4	2.9	16.2	0.8	67.5
Richmond Park acid	11.1	1.2	125.2	1.2	3.2	11.4	10.5	44.2	2.1	52.4	1.8	4.7	12.6	0.1	43.1
Stiperstones	0.1	0.0	8.0	0.0	0.0	9.3	10.5	84.2	0.5	93.9	0.7	2.3	10.4	0.4	57.7
Sutton Park	4.8	0.0	9.5	0.1	0.0	11.6	30.7	98.7	0.8	109.2	3.1	20.0	49.4	0.7	84.6
Thetford acid	3.2	0.8	65.3	0.4	2.8	5.5	4.4	26.5	0.1	30.7	0.6	1.0	7.4	0.1	23.2
Tregoss	3.2	14.3	89.2	1.1	2.9	4.9	8.0	25.6	0.2	39.9	0.6	2.2	9.1	0.1	28.9
Alice Holt	1.7	0.7	28.9	0.5	1.3	13.9	7.7	45.1	0.1	60.1	1.3	2.1	8.5	0.1	28.4
Brandon	4.2	3.7	61.9	0.9	11.2	5.1	3.0	17.1	0.1	27.2	0.6	1.1	5.7	0.0	27.3
Castle Eden Dene	4.1	0.8	27.4	0.2	7.7	15.9	14.4	74.2	0.1	110.4	1.3	5.1	7.7	0.1	95.4
Chaddersley	20.5	9.8	244.4	4.3	29.6	15.4	13.1	68.0	0.3	85.5	1.5	4.8	8.2	0.1	63.7
Dronley Woods 1	3.8	1.7	40.7	0.3	22.0	12.2	13.1	41.7	0.6	250.1	3.3	5.8	13.4	0.2	214.3
Dronley Woods 2	3.2	1.9	22.0	0.2	173.9	11.7	10.1	35.0	0.2	288.1	2.1	2.2	11.8	0.1	319.7
Forest of Dean	1.3	0.0	8.6	0.1	0.0	19.8	13.0	143.6	1.3	105.8	1.9	3.8	33.3	0.8	43.7
Grizedale	15.5	3.8	125.5	23.6	23.5	24.1	12.0	62.6	0.1	154.9	1.5	4.3	6.3	0.1	130.2
Hoddesden deciduous	4.4	2.8	41.8	0.4	8.9	15.3	25.0	60.2	0.6	188.5	5.5	11.4	38.0	0.5	198.9
Old Lodge	2.0	2.3	34.5	0.8	12.1	10.9	10.0	39.3	0.2	172.2	2.8	3.1	13.8	0.2	179.7
Richmond Park deciduous	12.0	23.5	138.1	1.7	50.6	10.3	60.3	47.5	0.2	379.6	4.5	37.5	25.4	0.2	339.1
Salcey	5.5	0.5	35.0	0.7	1.1	22.0	11.2	109.5	0.3	47.6	3.0	3.7	7.8	0.2	26.5
Savernake	6.8	2.2	89.3	2.2	6.0	16.7	9.4	82.8	0.3	73.8	2.1	3.2	18.1	0.2	47.8
Cannock Chase	9.9	19.2	83.5	1.5	51.7	5.4	28.8	30.7	0.6	145.4	1.7	9.8	15.5	0.4	126.0
Charnwood heath	2.8	3.5	46.6	0.6	9.6	17.1	59.0	65.0	0.5	314.7	1.3	5.8	4.7	0.2	136.4
Chobham common 1	0.6	1.0	28.4	0.7	1.1	2.3	2.2	7.4	0.1	15.7	0.1	0.4	2.6	0.1	9.9
Chobham common 2	1.3	1.5	19.3	0.3	3.2	2.3	5.4	7.0	0.2	28.7	0.5	1.7	3.9	0.1	31.0
Finlandrigg Woods	2.9	1.2	36.4	0.4	10.5	2.6	5.1	22.6	0.3	122.3	0.7	1.2	9.2	0.2	64.1
Kingston Common heathland	1.6	1.2	29.0	2.5	30.3	5.2	5.8	43.7	0.6	39.5	1.1	1.3	27.4	0.6	29.0
Linwood	1.8	3.0	51.8	3.3	422.4	0.8	2.4	7.3	0.1	563.7	0.3	0.7	0.3	0.1	560.9
Muir of Dinnet	0.8	0.5	14.1	0.0	1.2	4.7	3.8	29.8	0.2	24.5	1.0	0.9	19.5	0.2	17.4
Strensall	2.2	3.0	51.0	0.5	13.7	3.8	43.7	14.5	0.6	63.3	0.6	8.2	7.1	0.2	32.2
Thetford heath	2.0	1.7	47.4	0.4	5.9	22.0	2.7	23.6	0.1	14.1	0.1	0.4	3.5	0.0	10.1
Trefgarne	0.3	1.8	46.3	0.3	1.9	3.3	12.7	18.4	0.2	51.3	0.7	2.8	6.1	0.1	28.9
Cregan	0.0	0.3	5.9	0.1	0.2	8.6	36.2	40.3	0.4	317.0	2.4	0.9	7.9	0.3	16.9
Hoddesden coniferous	8.8	5.8	73.6	0.5	17.7	11.3	12.7	49.6	0.1	108.8	2.1	6.0	6.8	0.1	101.5
Pelenna 1	1.3	7.6	12.6	0.1	13.6	46.4	157.0	75.4	0.4	434.3	3.5	95.6	8.9	0.2	403.2
Pelenna 2	0.7	5.3	10.2	0.1	10.2	52.9	77.7	93.6	0.4	304.3	3.8	30.5	21.3	0.1	253.2
Sherwood forest	4.5	4.4	29.3	0.3	18.0	6.6	11.6	26.2	0.1	100.1	0.9	6.7	6.0	0.1	110.7
Stocks Hill	1.2	1.0	26.4	0.1	33.3	18.7	14.4	319.3	0.4	1437.1	2.6	3.4	33.5	0.2	1448.0

	Porewater metals											
sample	Na (mg/l)	Mg (mg/l)	Al (mg/l)	K (mg/l)	Ca (mg/l)	Mn (µg/l)	Fe (mg/l)	Ni (µg/l)	Cu (µg/l)	Zn (µg/l)	Cd (µg/l)	Pb (µg/l)
Cathkin Braes	4.2	0.5	0.4	1.7	0.7	34.4	0.0	2.0	5.8	29.6	0.1	0.9
Charnwood acid	3.9	1.2	0.9	1.9	1.5	42.6	1.7	1.9	13.9	84.4	0.7	26.3
Cors Caron 1	7.1	0.8	0.2	0.3	3.3	1876.2	0.1	3.3	6.2	143.9	1.6	10.2
Cors Caron 2	6.2	0.9	0.1	-0.1	4.2	396.1	bdl	4.2	2.5	258.0	1.8	9.1
Gowk Bank	9.0	1.5	0.3	2.5	5.4	46.9	0.6	1.7	4.9	58.3	0.3	13.8
Kingston Common acid	18.0	2.8	0.7	3.4	2.2	27.3	0.8	7.8	7.9	25.0	0.5	8.7
Richmond Park acid	6.1	3.4	1.1	13.9	11.3	1300.6	0.6	17.3	19.7	209.5	2.1	16.3
Stiperstones	5.7	2.4	0.6	1.9	8.2	14.6	0.4	0.3	10.7	26.1	0.2	1.6
Sutton Park	7.5	3.1	1.1	1.1	40.1	2013.2	33.3	25.3	9.4	65.8	0.7	6.8
Thetford acid	4.3	3.7	1.7	3.7	14.7	945.8	1.1	5.7	18.0	130.4	0.9	22.5
Tregoss	24.1	4.8	0.5	7.7	3.9	40.2	bdl	4.2	30.0	118.1	1.6	4.8
Alice Holt	7.8	2.3	0.7	1.9	6.4	80.2	0.6	2.3	14.1	43.1	0.8	5.4
Brandon	5.7	3.7	1.3	4.7	35.0	3611.2	0.9	6.0	12.6	90.3	1.3	29.0
Castle Eden Dene	26.5	4.3	2.0	5.7	6.8	109.1	1.9	6.1	19.0	42.8	0.4	29.4
Chaddersley	6.7	7.8	4.2	15.3	15.6	2178.3	0.7	27.4	15.6	327.7	5.8	42.6
Dronley Woods 1	6.1	2.8	0.9	3.2	1.0	55.3	0.5	4.8	5.3	52.7	0.4	40.7
Dronley Woods 2	4.9	1.9	1.4	2.9	0.8	12.8	0.7	4.2	9.6	29.7	0.2	382.4
Forest of Dean	12.4	1.8	0.0	0.9	46.3	2.9	bdl	3.7	16.5	40.8	0.4	2.8
Grizedale	9.9	6.7	1.6	4.1	3.0	298.4	bdl	19.0	6.1	155.0	29.5	30.8
Hoddesden deciduous	9.1	3.4	1.1	10.1	7.5	150.7	0.6	7.4	17.7	73.9	0.8	40.0
Old Lodge	13.2	1.8	0.4	2.9	1.0	143.5	0.2	2.6	6.0	45.3	1.1	26.5
Richmond Park deciduous	7.0	3.9	1.2	18.0	22.7	1061.8	1.5	16.1	114.2	190.4	2.4	108.8
Salcey	8.3	2.6	0.6	1.6	26.5	77.0	0.2	7.5	9.5	49.9	1.1	3.4
Savernake	7.8	4.2	0.8	4.5	11.6	474.4	0.0	8.5	9.3	111.4	2.8	9.5
Cannock Chase	5.3	0.6	0.8	1.9	2.3	66.7	0.2	13.0	35.6	110.9	2.0	95.8
Charnwood heath	3.5	1.4	0.7	4.5	1.4	36.5	1.9	3.4	11.2	58.1	0.8	17.2
Chobham common 1	3.2	0.5	0.3	3.0	0.9	7.9	0.2	0.8	7.0	37.5	0.9	3.0
Chobham common 2	3.8	0.5	0.4	8.7	1.0	2.3	0.4	1.7	7.2	26.4	0.4	8.5
Finlandrigg Woods	8.2	1.2	1.1	6.2	0.7	9.0	2.4	3.7	4.7	47.3	0.6	21.6
Kingston Common heathland	9.1	1.3	0.8	2.8	1.6	11.9	0.7	3.2	12.4	62.5	5.6	174.0
Linwood	5.1	0.4	1.0	2.2	1.6	8.6	0.5	2.4	13.2	71.8	4.7	1020.8
Muir of Dinnet	2.3	0.2	1.0	0.4	0.5	2.1	0.6	1.5	4.7	26.9	0.1	3.5
Strensall	4.9	0.6	2.0	0.8	2.5	24.8	1.6	2.9	9.8	66.7	0.7	25.4
Thetford heath	5.2	3.1	1.4	15.2	7.2	429.5	0.7	2.6	8.3	65.2	0.6	14.4
Trefgarne	15.7	3.4	0.7	15.9	2.7	23.5	0.1	0.4	3.1	57.8	0.4	2.8
Cregan	9.7	0.7	0.1	0.2	0.4	1.9	0.4	bdl	1.6	9.9	0.1	1.0
Hoddesden coniferous	11.3	2.4	1.9	1.1	6.6	50.9	1.0	10.5	8.8	88.7	0.6	23.1
Pelenna 1	15.2	0.9	0.3	0.3	0.3	6.1	0.7	1.6	19.8	16.2	0.1	27.0
Pelenna 2	11.5	1.0	0.6	0.1	0.1	7.9	1.3	0.9	13.5	12.6	0.1	17.5
Sherwood forest	5.1	1.0	0.9	1.8	2.1	298.9	0.6	5.9	14.6	39.0	0.4	38.6
Stocks Hill	10.8	0.7	0.8	3.1	0.8	62.6	0.5	1.7	4.4	37.0	0.1	90.1

sample	grid ref	Vegetation	dry bulk density g/cm^3	solution pH	soil pH	DOC (mg/l)	LOI %	% clay	CEC (Meq 100g^{-1})	Chloride (mg/l)	Nitrate (mg/l)	Sulphate (mg/l)	Phosphate (mg/l)
Tentsmuir	NO490280	Lowland Coniferou	0.9	4.0	4.4	60.0	4.6	0.6	8.3	16.4	bdl	12.2	bdl
Thetford forest	TL848797	Lowland Coniferou	0.9	5.2	6.0	113.6	7.9	0.3	8.5	11.7	156.8	22.6	bdl
Torrachility	NH427561	Lowland Coniferou	0.2	3.7	3.8	76.9	94.7	7.0	51.7	1.4	bdl	0.7	bdl
Torridge	SS416019	Lowland	0.3	3.5	3.6	82.4	68.2	11.8	45.0	126.6	bdl	16.3	bdl
Castle HowBeck	NY234003	Upland Coniferous	0.3	3.3	3.6	23.7	34.1	6.0	40.2	5.3	58.9	8.0	bdl
Coalburn	NY693781	Upland	0.1	3.7	3.6	30.0	89.3	5.8	2.8	1.0	0.5	9.4	bdl
Glenahulish	NN044579	Upland Coniferous	1.0	5.2	5.4	21.6	5.6	0.4	8.0	4.2	0.5	2.9	bdl
Llandovery	SN834271	Upland	0.8	3.7	4.0	37.0	14.7	14.8	33.0	23.3	20.8	10.6	bdl
Llyn Brianne	SN812485	Upland	0.3	3.6	3.8	18.2	95.3	6.9	35.2	3.2	2.9	6.0	bdl
Loch Awe	NM966107	Upland	0.5	4.1	4.1	57.7	24.3	2.7	42.2	3.8	0.3	2.1	bdl
Loch Bradon	225020E, 373	Upland	0.1	4.4	5.7	54.7	84.9	19.4	60.2	14.5	1.1	2.7	2.2
Moydamlaght	274520E, 399	Upland	0.5	4.6	4.8	59.0	28.5	2.3	49.1	0.3	0.2	0.2	bdl
Rannoch	NN599534	Upland Coniferous	0.2	3.5	3.7	137.8	60.1	2.4	39.4	0.4	bdl	5.6	bdl
Tummel 1	NN739613	Upland Coniferous	0.8	4.3	4.8	53.0	10.1	1.6	15.7	3.1	8.0	5.1	bdl
Tummel 2	NN739613	Upland Coniferous	0.7	4.3	4.6	46.9	12.0	3.7	18.0	2.0	bdl	3.1	bdl
Old Mining sites													
BLAGILL SLOPE 1		Grassland		5.6		19.3	17.9		46.0	1.2	1.4	36.2	
BLAGILL SLOPE 2		Grassland		5.6		27.2	19.1		52.1	0.5	0.8	7.5	
BLAGILL SLOPE 3		Grassland		5.7		35.9	19.3		52.1	2.6	8.9	4.3	
BLAGILL SLOPE 4		Grassland		5.4		28.4	20.5		67.5	1.1	0.7	2.1	
BLAGILL FLOODPLAIN 1		Grassland		6.5		8.5	5.4		30.7	1.7	0.7	15.9	
BLAGILL FLOODPLAIN 2		Grassland		6.3		7.4	11.7		49.1	0.7	12.2	11.3	
BLAGILL FLOODPLAIN 3		Grassland		6.7		4.0	6.1		42.9	1.9	12.4	33.7	
BLAGILL FLOOD PLAIN 4		Grassland		6.2		6.2	5.0		35.3	3.0	9.8	32.1	
GUDHAM GILL 2		Grassland		3.7		7.6	28.8		85.9	2.8	2.1	12.4	
GUDHAM GILL 3		Grassland		3.5		10.7	58.1		104.3	1.2	1.5	20.3	
GUDHAM GILL 4		Grassland		3.8		10.2	51.9		92.0	1.0	2.8	21.0	
HILLTOP 1		Grassland		3.5		31.9	66.8		107.4	7.7	0.7	3.6	
HILLTOP 2		Grassland		3.2		36.9	46.2		88.9	12.4	0.8	12.6	
HILLTOP 3		Grassland		3.5		42.3	74.8		95.1	3.6	1.1	10.0	
HILLTOP 4		Grassland		3.5		39.4	42.0		101.2	3.2	1.6	4.4	
YARNBURY TIPS 1		Grassland		4.3		24.4	14.8		30.7	3.0	1.2	9.2	
YARNBURY TIPS 2		Grassland		5.4		12.8	15.3		47.5	0.9	1.0	40.6	
YARNBURY TIPS 3		Grassland		5.3		11.7	18.4		39.9	3.3	0.8	23.9	
YARNBURY TIPS 4		Grassland		5.1		11.1	16.2		49.1	0.5	1.4	32.0	
DUKE'S NEW ROAD 1		Grassland		3.5		29.7	77.6		119.6	1.4	1.6	24.1	
DUKE'S NEW ROAD 2		Grassland		3.5		39.5	82.6		119.6	1.1	0.7	11.9	
DUKE'S NEW ROAD 3		Grassland		3.4		21.6	83.0		119.6	0.5	0.9	9.8	
DUKES NEW ROAD 4		Grassland		3.3		59.6	85.1		116.6	4.4	0.7	19.4	

sample	Na (mg/l)	Mg (mg/l)	Al (mg/l)	K (mg/l)	Ca (mg/l)	Porewater metals Mn (µg/l)	Fe (mg/l)	Ni (µg/l)	Cu (µg/l)	Zn (µg/l)	Cd (µg/l)	Pb (µg/l)
Tentsmuir	13.2	2.2	1.2	0.6	2.2	197.8	0.3	8.8	2.2	107.2	0.4	2.2
Thetford forest	12.6	4.6	1.0	3.3	76.7	216.3	0.4	4.6	9.6	58.2	0.5	5.5
Torrachility	5.4	0.5	0.1	1.4	0.7	0.8	0.0	0.7	4.1	15.4	0.1	2.5
Torridge	73.5	6.2	0.3	2.2	3.2	59.4	0.0	2.9	5.7	21.1	1.0	14.4
Castle How Beck	18.7	2.2	1.5	2.0	0.8	17.7	0.2	2.5	3.8	40.0	1.0	26.7
Coalburn	4.9	0.3	0.4	0.3	0.5	1.5	0.6	2.1	8.0	15.2	10.4	11.2
Glenahulish	6.0	0.5	0.5	1.9	0.9	3.2	0.1	bdl	8.0	23.1	0.1	1.7
Llandovery	24.5	3.5	1.6	1.6	1.5	170.0	0.6	5.4	4.8	26.1	0.6	1.9
Llyn Brianne	5.2	0.2	0.1	0.1	0.2	2.8	1.0	bdl	2.5	10.0	0.1	5.9
Loch Awe	6.5	1.0	1.1	0.3	1.1	15.5	0.5	0.9	5.1	25.0	0.1	2.2
Loch Bradon	12.4	2.4	0.0	0.8	8.1	6.1	0.2	bdl	4.2	9.3	0.0	1.6
Moydamlaght	16.1	8.2	1.0	6.2	6.9	44.9	0.2	16.7	6.3	19.5	0.1	0.7
Rannoch	6.4	1.2	1.0	0.7	2.0	9.1	0.8	1.1	26.6	32.2	0.4	12.2
Tummel 1	7.0	1.0	0.9	0.3	6.4	73.2	0.3	1.0	4.9	32.6	0.1	1.2
Tummel 2	2.9	1.0	1.0	0.4	4.6	55.8	0.6	1.2	8.0	28.2	0.1	1.5
Old Mining sites												
BLAGILL SLOPE 1	3189.1	4608.7	10.1	1516.2	30085.9	2.7	6.2	2.6	3.4	5275.7	12.6	7.9
BLAGILL SLOPE 2	2931.6	665.7	139.6	253.4	3139.0	13.3	85.3	5.6	6.2	95.1	0.5	11.8
BLAGILL SLOPE 3	3831.8	1051.9	155.7	611.2	4708.8	12.6	118.3	2.9	11.5	197.4	0.2	5.8
BLAGILL SLOPE 4	3532.1	612.5	203.7	766.0	3519.1	8.3	74.9	5.7	20.4	106.2	0.3	11.6
BLAGILL FLOODPLAIN 1	3850.3	2657.9	38.8	1006.9	17427.2	17.1	65.3	2.9	6.4	2548.2	6.4	5.7
BLAGILL FLOODPLAIN 2	3570.2	2497.2	17.8	2352.5	12996.1	1.2	41.6	4.3	5.8	2156.8	3.3	2.9
BLAGILL FLOODPLAIN 3	3842.1	6264.9	4.1	1361.5	37893.3	1.0	26.4	2.5	2.6	4249.8	15.0	8.3
BLAGILL FLOOD PLAIN 4	3372.4	4742.6	86.1	1656.2	30642.1	2.1	26.4	4.1	6.5	8153.5	24.7	26.2
GUDHAM GILL 2	3611.4	896.8	224.5	626.7	2210.0	376.4	91.1	5.4	3.4	618.0	3.1	123.4
GUDHAM GILL 3	3906.0	1094.8	173.5	161.3	3596.4	339.8	50.3	3.9	6.7	586.5	2.4	130.5
GUDHAM GILL 4	3133.5	953.0	230.4	125.7	5439.0	515.8	27.1	6.4	3.3	937.4	3.3	361.8
HILLTOP 1	4310.8	586.2	296.6	260.2	566.4	235.3	978.1	0.8	1.0	89.7	6.1	16.4
HILLTOP 2	5869.1	1236.7	453.4	1593.6	1262.8	550.7	298.5	2.1	5.4	114.5	0.8	22.5
HILLTOP 3	5261.4	798.9	644.0	717.3	780.1	33.1	201.1	0.8	4.4	91.8	0.4	53.0
HILLTOP 4	3710.3	556.5	402.1	387.9	616.8	124.7	538.3	0.7	2.9	58.3	33.3	30.0
YARNBURY TIPS 1	2536.1	588.0	428.9	1403.9	6327.9	130.6	2.5	1.4	22.2	199.5	1.0	2230.5
YARNBURY TIPS 2	2715.3	389.8	873.2	117.4	4105.2	735.9	6.2	4.8	21.0	1168.8	1.7	176.3
YARNBURY TIPS 3	768.2	973.6	1752.6	95.6	11898.2	327.8	6.2	11.6	12.7	5065.5	5.9	948.6
YARNBURY TIPS 4	715.0	940.3	2612.7	224.3	9576.5	383.8	6.2	8.4	12.1	4303.3	4.1	1072.8
DUKE'S NEW ROAD 1	5083.3	1466.6	292.0	247.3	4327.7	25.3	108.0	1.4	6.2	144.7	0.9	144.3
DUKE'S NEW ROAD 2	3924.5	676.4	147.0	427.9	1169.1	1.9	90.7	0.9	8.9	73.9	0.4	45.7
DUKE'S NEW ROAD 3	7358.5	786.0	296.4	203.1	1485.9	2.1	109.4	1.0	2.7	97.7	0.3	41.5
DUKES NEW ROAD 4	5912.4	463.6	299.1	59.1	1510.6	5.0	478.1	0.9	7.9	88.7	0.4	33.7

sample	free ion activities (WHAM)					Pseudo-total metals					EDTA extractable metals				
	Ni (ug/l)	Cu (ug/l)	Zn (ug/l)	Cd (ug/l)	Pb (ug/l)	Ni (ug/g)	Cu (ug/g)	Zn (ug/g)	Cd (ug/g)	Pb (ug/g)	Ni (ug/g)	Cu (ug/g)	Zn (ug/g)	Cd (ug/g)	Pb (ug/g)
Tentsmuir	6.2	0.2	72.2	0.3	0.7	4.1	1.5	12.5	0.0	14.2	0.4	0.4	4.0	0.0	10.6
Thetford forest	2.0	0.0	23.1	0.2	0.2	4.4	2.5	19.3	0.2	21.5	0.5	0.7	6.1	0.1	17.6
Torrachility	0.4	0.4	7.2	0.0	0.3	4.7	9.4	56.8	0.5	48.2	1.5	1.5	25.2	0.2	21.5
Torridge	2.0	1.4	13.4	0.5	4.3	4.7	4.6	17.5	0.0	29.4	2.8	1.3	9.5	0.1	26.8
Castle How Beck	2.0	2.7	32.5	0.8	20.2	4.5	12.9	24.1	0.3	212.9	1.1	5.6	5.7	0.1	173.1
Coalburn	1.7	2.6	11.8	7.9	5.4	5.8	14.2	36.6	1.7	203.8	3.4	8.3	18.8	0.7	220.0
Glenahulish	0.0	0.1	12.2	0.1	0.2	24.3	16.6	30.5	0.0	5.5	0.3	1.7	1.9	0.0	1.6
Llandovery	4.3	1.9	20.6	0.4	1.2	13.2	3.7	24.2	0.2	21.4	0.8	1.6	2.9	0.2	16.8
Llyn Brianne	0.0	1.1	8.2	0.1	3.1	6.0	12.7	14.4	0.5	198.1	0.5	1.9	6.6	0.2	111.5
Loch Awe	0.6	0.4	16.5	0.0	0.6	12.1	8.7	58.5	0.1	45.6	0.7	2.3	5.2	0.1	19.5
Loch Bradon	0.0	0.1	4.7	0.0	0.1	1.9	1.9	4.5	0.4	10.4	0.7	0.6	4.3	0.4	10.3
Moydamlaght	11.0	0.1	11.6	0.1	0.1	230.6	65.6	106.0	0.1	45.3	16.1		12.9	0.1	16.6
Rannoch	0.6	4.3	17.5	0.2	2.6	2.0	31.3	33.0	0.8	59.8	1.0	24.9	38.6	0.6	68.8
Tummel 1	0.7	0.2	20.2	0.0	0.2	5.4	4.8	50.2	0.1	23.1	0.6	1.4	14.5	0.1	8.6
Tummel 2	0.8	0.4	19.1	0.1	0.4	4.4	4.9	41.5	0.1	22.6	0.6	1.6	6.5	0.1	8.9
Old Mining sites															
BLAGILL SLOPE 1	1.8	0.0	3396.5	7.9	0.0	14.4	5.4	208.9	0.6	329.0	3.2	1.7	22.2	0.5	187.6
BLAGILL SLOPE 2	1.2	0.0	15.7	0.1	0.1	14.4	4.0	194.3	0.5	351.0	1.1	0.4	21.7	0.4	157.8
BLAGILL SLOPE 3	1.0	0.1	31.3	0.1	0.3	16.1	4.3	237.3	0.8	301.5	6.6	1.8	42.6	0.6	139.3
BLAGILL SLOPE 4	1.7	0.0	32.7	0.1	0.1	14.8	4.4	254.6	0.6	276.0	2.1	1.3	51.2	0.4	108.7
BLAGILL FLOODPLAIN 1	2.2	0.1	1823.7	4.5	0.1	19.8	37.6	6653.1	8.0	3104.0	7.1	23.4	5065.7	8.7	1960.7
BLAGILL FLOODPLAIN 2	3.3	0.0	1549.6	2.3	0.0	28.7	32.8	3629.1	14.8	3062.0	8.3	19.3	2962.1	7.3	1778.5
BLAGILL FLOODPLAIN 3	1.8	0.0	3031.9	10.6	0.1	24.2	46.9	6919.1	15.2	3748.5	8.6	17.3	6016.5	12.1	1668.5
BLAGILL FLOOD PLAIN 4	3.0	0.4	5990.0	17.9	5.0	22.8	72.7	7169.1	14.5	7177.3	7.2	33.4	5496.0	11.0	3779.1
GUDHAM GILL 2	4.6	2.1	526.1	2.6	92.8	11.6	15.7	244.8	1.2	2093.0	3.7	6.2	102.1	0.9	1548.0
GUDHAM GILL 3	3.2	4.4	48.1	2.0	90.9	13.3	23.1	200.0	2.1	3538.5	5.3	6.7	138.7	1.4	2267.7
GUDHAM GILL 4	5.2	1.4	759.2	2.7	273.8	16.6	27.6	325.1	2.0	8111.5	6.7	20.5	195.6	1.6	5380.5
HILLTOP 1	0.6	0.4	73.6	4.9	9.0	4.4	3.4	36.9	0.6	25.2	1.2	1.1	12.1	0.2	250.6
HILLTOP 2	1.7	3.4	92.4	0.6	14.6	3.4	2.5	26.5	3.5	362.6	10.8	2.0	7.4	0.2	139.4
HILLTOP 3	0.7	1.7	72.1	0.3	28.6	4.5	4.8	42.2	0.3	412.5	1.6	1.4	44.1	0.2	390.7
HILLTOP 4	0.5	1.2	47.1	26.6	15.4	2.6	1.7	36.7	0.3	463.5	2.0	1.4	19.6	0.3	313.8
YARNBURY TIPS 1	1.1	3.1	153.8	0.7	941.3	11.7	101.0	308.3	2.1	27786.0	12.7	43.9	49.5	0.4	16773.7
YARNBURY TIPS 2	3.0	4.1	862.7	1.3	90.2	25.3	231.8	3054.8	3.3	35224.0	8.8	207.7	1118.8	2.0	24394.3
YARNBURY TIPS 3	9.4	4.8	4059.1	4.7	651.9	27.8	336.9	5077.9	3.2	39799.0	12.2	155.6	1713.7	2.2	25857.7
YARNBURY TIPS 4	6.7	5.6	3416.4	3.2	755.1	29.8	330.6	5354.4	3.1	33330.5	7.8	136.5	1544.5	1.8	22693.7
DUKE'S NEW ROAD 1	1.1	3.1	111.2	0.7	80.6	4.1	13.9	83.7	1.2	990.5	1.7	3.6	40.8	0.7	958.9
DUKE'S NEW ROAD 2	0.7	3.3	54.3	0.3	18.7	4.1	12.9	59.9	0.5	625.0	1.9	6.0	24.0	0.3	737.3
DUKE'S NEW ROAD 3	0.9	1.8	83.1	0.2	29.0	5.0	14.6	59.9	0.7	918.0	2.4	8.4	15.0	0.5	67.7
DUKES NEW ROAD 4	0.7	3.1	61.0	0.3	13.8	4.8	16.1	51.5	0.7	770.5	1.8	5.1	31.8	0.4	300.8

ANNEXE 10: DISSOLVED ORGANIC CARBON CONCENTRATIONS IN UK SOILS

L.Shotbolt, M.R.Ashmore

DOC strongly complexes many heavy metals, influencing metal partitioning between the soil and soil solution and metal leaching from the soil profile. DOC is, therefore, an essential parameter in the calculation of critical loads. Unfortunately, DOC is rarely measured in national soil surveys. As accurate DOC data is essential in the calculation of critical loads, a wide ranging review of the available data on DOC concentrations and fluxes in soils was carried out.

Studies reviewed were restricted to those that collected soil solution in the field using zero-tension or tension lysimeters. The advantage of lysimeter studies over others such as centrifuging soil samples or creating a soil-slurry through mixing with water is that the soil solution is obtained *in-situ* and can be continuously collected over a period of time. Restricting the dataset to lysimeter-based studies should also reduce variability in the data as different extraction techniques have been found to produce different DOC concentrations. Particularly marked differences have been observed between DOC concentrations measured in laboratory studies and those collected in the field (Kabitz et al., 2002). Lysimeters probably represent the technique most likely to obtain DOC data representative of concentrations in the soil profile.

Three sources of information were available and have been used to produce:

1. An analysis of data from published lysimeter-based DOC research
2. An analysis of DOC concentrations measured in lysimteres at ICP Forest sites
3. An analysis of DOC concentrations and fluxes measured in the UK (unpublished lysimeter studies mostly carried out at CEH Bangor).

1. Literature review of lysimeter studies

An extensive review of the published literature found 38 studies that have determined DOC in soil solutions collected in lysimeters. Within this dataset, 192 individual or bulked lysimeter results were obtained. These span a range of soil types, vegetation types (Table 1) and horizons (Table 2) and are predominantly from locations in Europe and North America. All studies included have measured DOC over at least several months and generally one or more years. DOC concentrations presented are mean annual concentrations.

Table 1. Soil groups in the studies reviewed according to the World Reference Base for Soil Resources (FAO, 1998) and predominant vegetation type. For many studies, soil classification was for a larger area than the lysimeter, leading to classifications such as 'cambisols to podzols.'

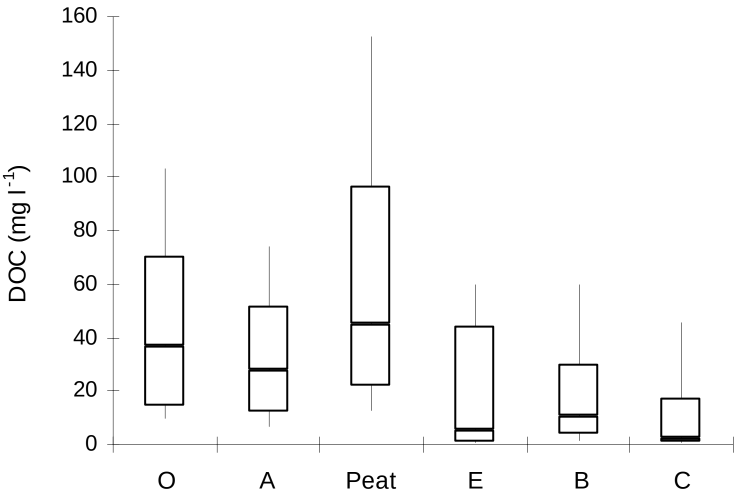
Soil groups (WRB)	Number of samples	Vegetation (most common in study area)	Number of samples
Acrisols	19	Coniferous forest	83
Acrisols to Cambisols	5	Deciduous forest	60
Cambisols	27	Grassland communities	24
Cambisols to Podzols	12	Moorland communities	12
Gleysols	31	Carr (wooded wetlands)	5
Histosols	27	Agricultural (cereal)	8
Histosols to Podzols	2		
Podzols	43		
Leptosols	3		
Unspecified	23		

Data points have been separated into major horizons (i.e. organic (O) horizons, mineral/organic (A) horizons, elluvial (E) horizons, illuvial (B) horizons and relatively unaltered (C) horizons). Samples from peat profiles were also considered, though as a separate category. Sample distributions were positively skewed (particularly the E, B and C horizons) and therefore the median was considered the most appropriate average value. Median, 10th and 90th percentiles and range of DOC concentrations are shown below (Figure 1 and Table 2).

Table 2. Summary statistics for DOC concentrations classified by soil horizon. Values are calculated from annual mean concentrations.

Horizon	no. of samples	median DOC (mg l^{-1})	min. DOC (mg l^{-1})	max. DOC (mg l^{-1})	10th percentile	90th percentile
O	30	36.75	10.0	103.2	13.97	69.97
A	25	28.00	7.0	74.2	11.60	51.44
Peat	25	45.00	12.8	152.8	21.56	96.38
E	15	4.97	0.6	60.0	0.84	44.04
B	51	10.10	1.5	60.0	3.54	30.00
C	10	2.28	0.6	45.7	0.69	17.54
Groundwater	1	0.39				
Stream	7	2.16	0.8	10.0	0.78	8.80
Unclassified	28					

The range of DOC concentrations measured in the studies reviewed is considerable. However, clear differences between soil horizons are apparent. The upper soil horizons (O, A and also horizons from peat profiles) produce higher concentrations of DOC than the lower horizons (E, B and C) reflecting the greater DOC production in the surface horizons.



Figures 1 Median, 10th and 90th percentile and range of DOC (mg l^{-1}) concentrations in samples from major soil horizons

DOC concentrations are clearly highly variable. There are many factors involved in determining DOC concentrations, but climate (in particular rainfall and temperature) is thought to be important. Therefore the use of data from widely varying climatic regions across Europe and North America for determining average DOC concentrations in UK soils may not be advisable. To test this, we compared DOC concentrations measured at ICP forest sites in the UK to concentrations across the rest of Europe.

2. DOC concentrations in ICP forest soils

Figure 2 shows DOC concentrations in soils from coniferous and deciduous forests across Europe (data collected as part of the ICP Forests monitoring programme, de Vries pers comm..).

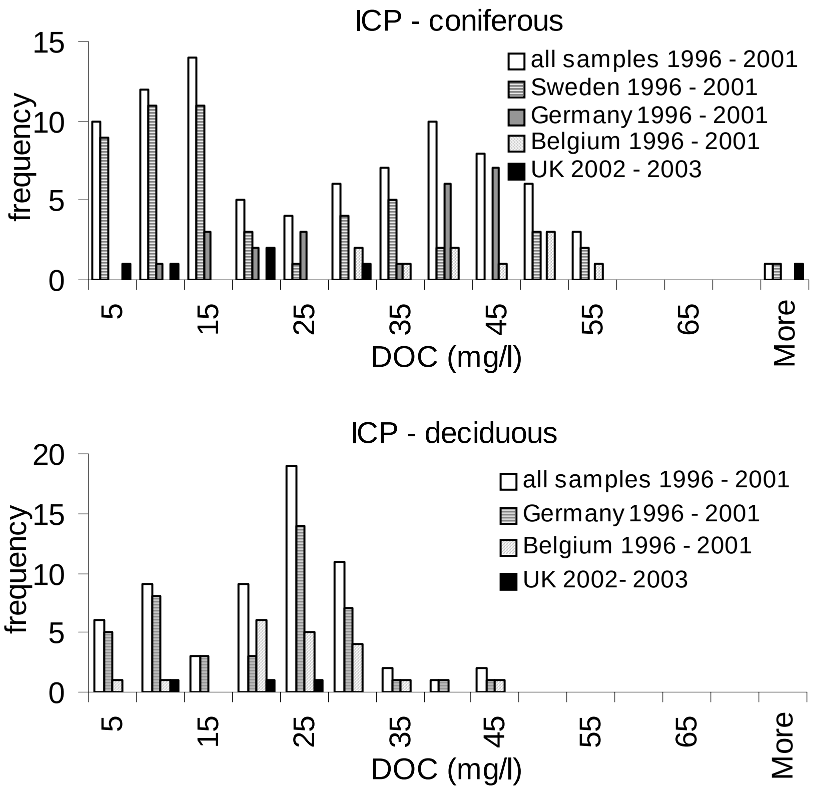


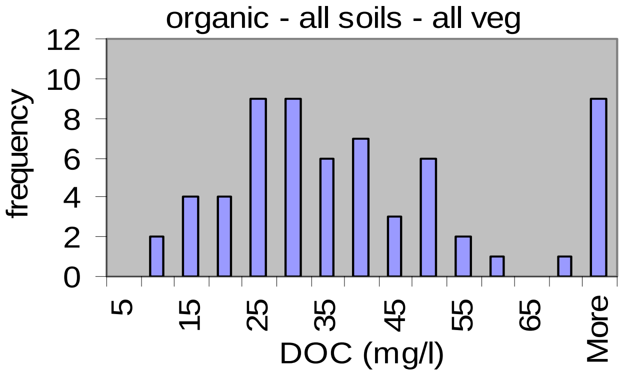
Figure 2. Histograms of DOC concentration in the upper 10 cm of soil at ICP Forest sites.

DOC measured at UK sites tends to be at the lower end of the European distribution, although this is uncertain as the number of sites is small, and very high DOC is measured at Thetford Forest (Suffolk, on calcareous sands) (Figure 2). The ICP Forest data appear to demonstrate differences in DOC distributions for individual countries, although the low number of sites (23) limits the interpretation of these trends (Figure 2).

3. DOC measured in unpublished UK studies

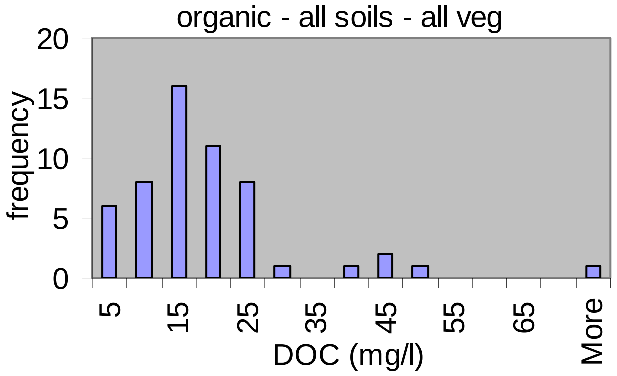
DOC concentration

Researchers at CEH Bangor have produced a database of DOC concentrations in UK soils (predominantly unpublished research at CEH, collated by Chris Evans). Analysis of this dataset further indicates that DOC concentrations in UK soils are low in comparison to global averages, but still highly variable (Figures 3 and 4).



Global
Median = 32.50
Mean = 40.95
5% = 12.6
95% = 101.64
n = 63

Figure 3. Histogram of DOC concentrations in upper (O & A) horizons of soils worldwide (Evans, pers. Comm.)



UK
Median = 14.52
Mean = 17.14
5% = 3.84
95% = 42.71
n = 55

Figure 4. Histogram of DOC concentrations in upper (O & A) horizons of UK soils (Evans, pers. Comm.)

We also found a relationship between DOC concentration and habitat, with heathland having the highest average DOC concentrations and acid grassland the lowest (Table 3). However the number of sites is low.

Table 3. Summary statistics for DOC concentrations measured under different habitats in the UK.

Soil type	Horizon	Conifers				Deciduous			
		n	5%	median	95%	n	5%	median	95%
	Upper (O, A)	17	4.9	15.0	46.3	9	7.7	17.2	21.1
	Lower (B)	14	3.1	5.1	23.4	27	3.6	7.7	16.1
		Acid Grassland				**Heathland**			
		n	5%	median	95%	n	5%	median	95%
	Upper (O, A)	19	3.6	10.7	16.7	11	11.4	23.3	44.5
	Lower (B)	12	1.7	4.1	8.5	4	3.3	9.2	20.3

DOC flux

DOC flux for the UK sites was determined by estimating the annual runoff (based on UK wide precipitation and evaporation data) for each site in the dataset and multiplying this by the DOC concentration. Analysis of the DOC flux data found a relationship between DOC flux, runoff and habitat type (Figure 5). Although the variability and low number of data points means the relationships are weak, there does appear to be a non-linear increase in DOC with runoff, tending towards a maximum flux. This empirical relationship may tentatively be said to have a process-based explanation: DOC concentration in soils may be envisaged as a function of both the generation and accumulation of DOC in soil, and the removal by runoff. Therefore higher DOC flux relative to runoff is found in soils with low runoff but higher total flux where runoff is high.

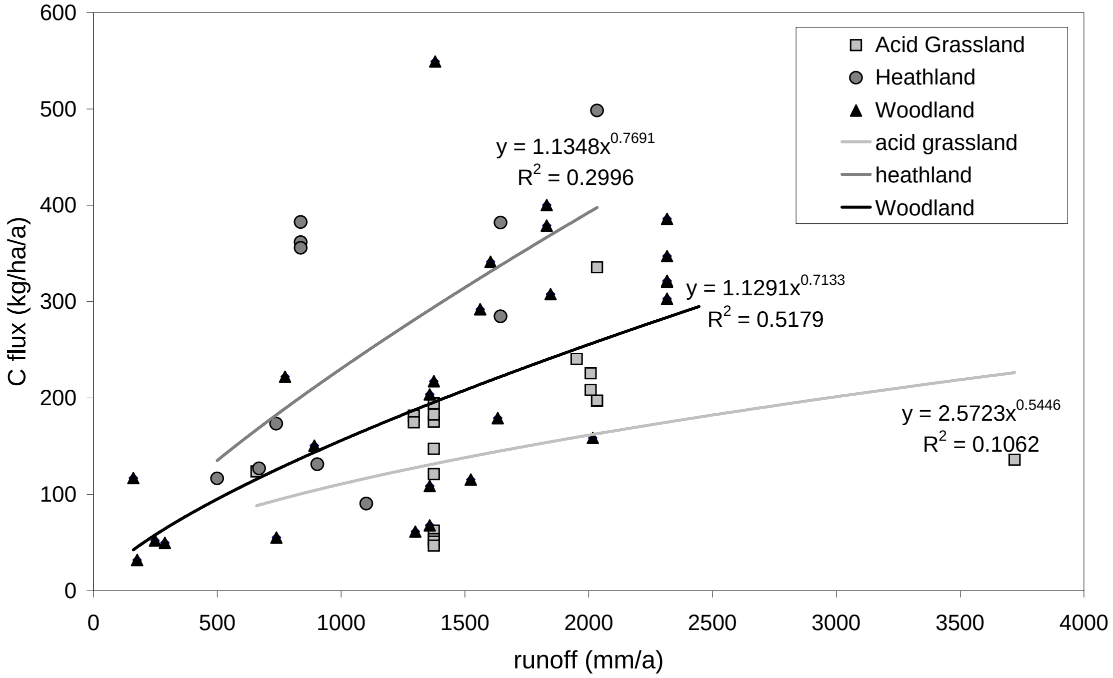


Figure 5. Relationship between DOC flux and runoff in UK soils.

DOC concentrations were derived for different habitats based on runoff using the following equations (a rearrangement to determine concentration from the regression equations shown in Figure 5):

DOC Acid Grassland (mg l^{-1}) = 257.23*runoff (mm $yr^{-1})^{-0.4554}$ (Eq. 1)

DOC Heathland (mg l^{-1}) = 113.48*runoff (mm $yr^{-1})^{-0.2309}$ (Eq. 2)
DOC Woodland (mg l^{-1}) = 112.91*runoff (mm $yr^{-1})^{-0.2867}$ (Eq. 3)

4. Conclusions

Data on DOC concentrations are scarce. A thorough evaluation of the available data suggests that DOC concentrations in the UK tend to be low in comparison to global averages. It is thought that this is a result of the combination of relatively high runoff and lower temperatures in the UK which limit the generation and build up of DOC. For critical loads calculations we have used the relationship between DOC flux and runoff to determine DOC concentration for calculation of critical loads. Although the relationships between DOC concentration and runoff are not strong and may introduce significant uncertainty, we feel that the trends shown are plausible and provide a more realistic estimation of DOC than accepting the default value of 20 mg l^{-1} recommended in the UNECE Mapping Manual, which is high in comparison to the UK median and does not account for the influence of runoff.

DOC is a major area of uncertainty in critical loads calculations. Critical loads calculations for metals would benefit considerably from further experimental work to improve estimation of both concentrations and fluxes of DOC through UK soils.

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