Final Report on Defra Contract CPEA 24

DEVELOPMENT OF AN EFFECTS-BASED APPROACH FOR TOXIC METALS

M Ashmore, L. van den Berg, A. Terry
University of York

E.Tipping, A.J.Lawlor, S.Lofts, S.A.Thacker, C.D.Vincent
Centre for Ecology and Hydrology Lancaster

J. Hall, S O'Hanlon
Centre for Ecology and Hydrology Monks Wood

L. Shotbolt
Queen Mary, University of London

H. Harmens, A. Lloyd, D. Norris
Centre for Ecology and Hydrology, Bangor

E. Nemitz
Centre for Ecology and Hydrology, Bush Estate

K. Jarvis
NERC ICP-MS Facility, Kingston University

C. Jordan
Agri-Food and Biosciences Institute, Belfast

EXECUTIVE SUMMARY

Background and Objectives

1. The cumulative long-term deposition of metals from the atmosphere can have direct adverse impacts on soil and freshwater biota, the long-term sustainability of soils, and indirect effects on human health through the food chain.

2. To minimise the risk of these adverse effects, there are ongoing discussions, both nationally and within the UN/ECE Convention on Long-range Transboundary Air Pollution (CLRTAP), of the need for, and benefit of, further measures to reduce emissions of potentially toxic metals to the atmosphere. Assessment of the impacts of metal deposition within CLRTAP uses the concept of the critical load, ie,, the rate of deposition of metal from the atmosphere which, at steady state, leads to the metal concentration in soils or waters reaching a threshold for adverse effects (a critical limit).

3. However, there are important uncertainties in the use of this approach for metals that significantly constrain the ability of the UK government to assess the ecological and health impacts of atmospheric metal deposition and to assess the benefits of future emissions reductions. This research project aimed to reduce these uncertainties. It had the following specific objectives:-

- To develop improved national maps of critical loads and critical limits of lead, cadmium, copper zinc and nickel, and their exceedance
- To map the geographical distribution of metals in mosses throughout the UK, and to compare the results with those in previous surveys.
- To provide model predictions of changes in concentrations of metals in soils and freshwaters in responses to future changes both in metal deposition and in deposition of sulphur and acidity.
- To contribute to the implementation and further development of critical loads methods for lead and cadmium CLRTAP.

4. The methods, findings and conclusions for each of these objectives are described in turn below.

Mapping of critical limits and critical loads

5. New data on the effects of metals published since 2004 was collated and used to assess if the critical limit functions first derived under the previous contract needed to be updated. The critical limit functions for lead, cadmium and copper were largely unchanged, but those for zinc and nickel were modified.

6. An extensive field survey was carried out to determine concentrations of dissolved organic carbon (DOC) in soil, because metal bound to DOC is a major route by which metals are lost from upland soils in the UK. DOC concentrations were highest in bogs, followed by heathlands, forests and grasslands. The only soil parameter which showed a

strong relationship with annual mean DOC concentration was the carbon to nitrogen ratio of the soil.

7. These new findings were used to recalculate critical loads of metals. The recalculated critical loads were compared with deposition data for metals which were provided by the Defra funded UK Heavy Metals Monitoring Network. The measurements of metal concentrations in rainfall and in atmospheric particles were interpolated to generate deposition fields on a 5x5 km grid of the UK. By comparing the calculated critical load and the interpolated deposition to different types of habitat we were able to calculate the area of that habitat for which the critical load for that metal is exceeded.

8. The results showed no areas of exceedance of the critical load for nickel and almost none for cadmium. There was very little exceedance of copper, lead and zinc critical loads for the bog and heathland habitats, and areas exceeded were also relatively small for grassland and managed coniferous woodland However, over 50% of the areas of managed broadleaved woodland and unmanaged (coniferous and broadleaved) woodland were exceeded for copper, lead and zinc. The most widespread exceedance of critical loads was across central, eastern and southern England, where critical loads are generally lower.

9. We compared these exceedance results with earlier calculations in 2004, which used less reliable data. The calculated areas of critical load exceedance are smaller for all metals and habitats in 2007 compared to 2004. The reduction in exceedance is relatively small for copper, but is more substantial for both lead and zinc.

10. We also compared calculated critical limits, which are expressed as free-ion concentrations with current soil metal concentrations obtained from national soil surveys which are expressed as total soil metal concentrations. Transfer functions are used to convert the free-ion concentrations to total concentrations to enable this comparison.

11. Despite the exceedance of critical loads for lead, there was virtually no exceedance of the critical limit for Pb for any habitat. Conversely, although there is virtually no exceedance of critical loads of cadmium, there are small areas of critical limit exceedance for all habitats, with the highest exceedances in the Peak District area.

12. Exceedances of the critical limit for copper extend across England and Wales, with significant areas of exceedance for broadleaf and unmanaged woodland. The areas of critical limit exceedance for all habitats are highest for zinc.

13. We consider that the main reason for the different patterns of critical limit and critical load exceedance for the four metals is the different rates of change in soil metal pools in relation to changes in metal deposition.

Metal Concentrations in Mosses

14. Mosses are an ideal sampling medium for metals deposited from the atmosphere to vegetation. We conducted a survey of metal concentrations in mosses in 2005, with a

focus on detecting temporal trends of metal concentrations in mosses in the UK since 1995.

15.Mosses were sampled from 170 sites according to a standard protocol for sampling and analysis. The metal concentrations in different moss species were standardised to a single species by applying calibration equations determined by sampling different mosses at the same locations.

16. Since 1995, the median concentrations have declined for all metals, e.g. for cadmium by 49%, for copper by 30%, for nickel by 50%, for lead by 68%, and for zinc by 35%.

17. The decline of heavy metal concentrations in mosses reflects the decline in emission and atmospheric deposition of these metals across Europe in recent decades. However, some regions do show an increase in concentration of some metals, such as copper, since 2000; especially in areas with high traffic densities.

Dynamic modelling

18. Assessment of the impacts of metals, and the performance of dynamic models, requires knowledge about the inputs of metals from natural weathering of rocks to soil-water systems. Surprisingly, there has been little study of the processes by which heavy metals are transferred from minerals into soil, and these weathering inputs are poorly known.

19. We are therefore conducting long-term laboratory measurements, in which the release of elements from a number of representative mineral specimens is monitored. The rates of decline in the ratios are similar for the different mineral samples, and for the five heavy metals.

20. Field studies were carried out in two areas with medium to high historic acid and metal deposition to test the ability of the dynamic models which we have developed to explain current metal levels in soils, waters, and sediment records. Although the model simulations did not precisely match the observed soil, water and sediment data, neither of the case studies revealed systematic errors in either the process basis of the model, or our assumed patterns and magnitudes of historic atmospheric metal deposition.

21. The model was then applied to assess the effect of thirteen future scenarios on the time course of metal concentrations in soils and waters in five contrasting UK catchments.

22. With respect to policy, the results of this scenario analysis suggest that further reductions in the deposition inputs of zinc and cadmium would have widespread beneficial effects during the 21st Century. The responses for these metals are similar in different catchments.

23. In contrast, beneficial effects cannot be expected for Cu and Pb, except over much longer timescales. Some catchments will respond more quickly than others, and for Cu and Pb the responses of different catchments may not even be in the same direction under the same scenario.

24. The differences between the two sets of metals reflect the stronger sorption of Cu and Pb to soil solids. The long timescales of recovery for these two metals result from the legacy of high past deposition and slow loss rates. It is also important to ensure that metal deposition does not rise, and that soil organic matter is protected.

Contribution to policy development within CLRTAP

25. The most important contribution to the work of CLRTAP was the organisation of an open meeting in Windermere on critical loads of heavy metals, at the end of this contract. This contributed significantly to the dissemination of key results from this work within CLRTAP. Members of this research group contributed three oral and two poster presentations. The report of this workshop will be considered in more detail by expert groups within CLRTAP during 2008.

26. This workshop recommended that execeedance of steady-state critical loads should be not be considered in isolation in evaluations of the need for policies to reduce deposition of metals due to long-range transport, but should be evaluated alongside information on exceedance of critical limits and the results of simple dynamic models.

27. Within CLRTAP, active discussions have now begun on revision of the Heavy Metal Protocol on control of emissions for three priority metals. Proposals for a revision of this Protocol rely on an assessment of the costs and benefits of measures to further reduce emissions of these metals.

28. However, these additional measures also need to be justified on the basis of their environmental and health benefits. The assessment considered to date within CLRTAP only considers benefits in terms of critical load exceedance.

29. This approach has important limitations in terms of assessing benefits which are highlighted by the results of this project. These limitations mean that the current critical load exceedance analysis may provide an inadequate basis on which to assess policies that may have significant economic implications in the UK and more widely in Europe.

30. In summary, there is strong evidence that deposition of metals from the atmosphere in the UK has decreased over the past 3 decades, including that from the moss surveys reported here. However, the results of our analysis and modelling suggest that the full environmental benefits of these reductions in emissions and deposition may only be felt at some point in the future.

31. Furthermore, the benefits of any additional measures to reduce emissions may be very limited for metals with long residence times such as lead, although benefits within 20-30 years may be experienced for metals with shorter residence times such as cadmium.

Future work

32. Within the context of future policy assessment within CLRTAP, we have identified two major limitations to the work reported here.

33. Firstly, the Heavy Metals Protocol considers three priority metals – lead, cadmium, and mercury. This work provides an extensive analysis for lead and cadmium but there is an urgent need to extend it to mercury, especially as this metal shows a greater exceedance of critical loads across Europe.

34. Secondly, the dynamic models have to date only been applied in the UK. To provide a basis for policy assessment within CLRTAP, they need to be applied to a wider range of locations across Europe, with different histories of metal deposition, different climates and different vegetation and soils.

1. Introduction

The cumulative long-term deposition of metals from the atmosphere can have direct adverse impacts on soil and freshwater biota, and the long-term sustainability of soils, and indirect effects on human health through the food chain. Although UK emissions of metals such as lead, cadmium, copper and zinc have decreased significantly over the past two decades, concentrations of these and other metals still exceed critical limits in some parts of the country, while in others current rates of deposition of metals such as lead still exceed critical loads. To minimise the risk of these adverse effects, there are ongoing discussions, both nationally and within the UN/ECE Convention on Long-range Transboundary Air Pollution (CLRTAP), of the need for, and benefit of, further measures to reduce emissions of potentially toxic metals to the atmosphere. Within CLRTAP, agreement has been reached on new critical load methods to assess the long-term impacts of atmospheric deposition of toxic metals, in particular lead, cadmium and mercury.

Nevertheless, at the start of this research project, there were important limitations to the development of effects-based approaches for metals that significantly constrained the ability of the UK government to assess the extent of current ecological and health impacts of atmospheric deposition of toxic metals, to assess the benefits of future emissions reductions, and to respond to policy proposals within both the EU and CLRTAP. The most important of these were:-

- there are many significant uncertainties in the parameterisation of models used to map critical limits and critical loads of lead, cadmium, zinc and copper, which lead to uncertainties in the assessment of the degree of exceedance of critical limits and critical loads;

- the methods of critical load calculation adopted for use within UN/ECE are based on steady-state methods, despite the very long-timescales (decades or centuries) to steady-state for some metals, although any appraisal of the benefits of emission control must consider the dynamics of the system;

- high levels of historical deposition of metals in many parts of the U.K. has led to high soil concentrations, which mean that the rate of recovery in response to decreasing rates of metal deposition is of major interest:

- although future emissions and deposition of S, N and acidity may significantly affect the future mobility and toxicity of metals, there has to date been no attempt to develop integrated risk assessments for these different emissions.

This research described in this report aimed at address these key gaps in knowledge. It built on work undertaken by members of this consortium under previous research contracts with Defra. The links between the work carried out under this contract and under previous contracts is summarised at appropriate points in the report.

The major aims of the work were as follows:-

- To develop improved national maps of critical loads and critical limits of lead, cadmium, copper zinc and nickel, and their exceedance, which reduce the level of uncertainty in the modelled values and incorporate new data and new methods of calculation.

- To provide improved predictions of changes in concentrations of metals in soils and freshwaters in responses to future changes both in metal deposition and in deposition of sulphur and acidity.

- To map the geographical distribution of metals in mosses throughout the UK, and to compare the results with those in previous surveys.

- To contribute to the implementation and further development of critical loads methods for lead and cadmium within the UN/ECE Convention on Long-Range Transboundary Air Pollution (CLRTAP).

This report summarises the key findings of the research project. Further details on technical aspects of the work are available in the technical reports and papers which are appended to this report. The bulk of the report is divided into two major sections. The first of these is on the further development of steady-state critical loads for the UK, while the second describes the development, testing and application of dynamic models in the UK. Finally, the report describes the contribution of team members, and this work in particular, to critical loads activities within the CLRTAP and the policy implications of the work.

2. Steady-state critical load mapping

2.1. Introduction and overview of methods

The methods used to calculate steady-state critical loads for ecological effects in soils were developed for application in the UK primarily under the previous contract (EPG/3/188) and have been adopted for use within CLRTAP for lead and cadmium (mm ref). A paper summarising the methods and their previous application to the UK (Hall et al., 2006) is included in the annexe to this report. The work undertaken in this contract has primarily served to update and improve key aspects of these methods, and to compare the calculated critical loads with new estimates of UK deposition fields from Defra contract EPG 1/3/204. Overall, these developments lead to significant revisions in the extent of exceedance of critical limits and critical loads in the UK; therefore, in presenting the results from this work, we have paid particular attention to comparison with previous calculations for the UK.

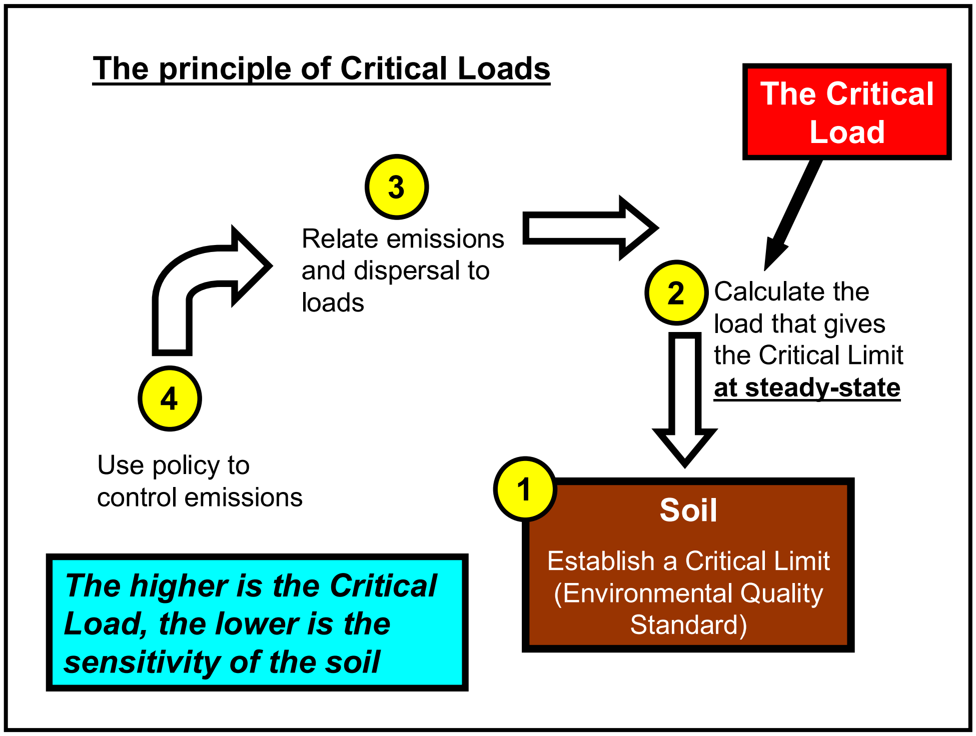
Figure 2.1 outlines the process of calculating critical loads in soils. Working backwards, we first need to calculate a critical limit at which significant adverse ecological effects occur for the metal of interest. The method employed bases this on a pH-dependent free ion function; in this contract, we have revised these critical limit functions, as described in Section 2.2.2. This critical limit can be compared with measured total concentrations of metals in soils, based on national surveys; converting the free-ion based critical limit to an equivalent soil concentration requires the use of a transfer function which depends on soil properties. The national patterns of exceedance of critical limits can then be mapped. Since we have modified both the critical limit free-ion function and the values of DOC, which influence the relationship between free ion and total soil and soil solution concentrations (see Section 2.2.3 below), the patterns of exceedance of critical limits have changed.

The next stage is to calculate the critical load at steady-state, i.e. when the rates of input and output of metal balance at the critical limit. Since DOC concentrations influence the rate of leaching of metal at a given soil concentration, the critical loads calculated based on this new research will also change.

Finally, the steady-state critical load is compared with the current rate of deposition to determine areas of critical load exceedance; measures to reduce emission control may target the reduction of such areas of exceedance. Estimates of deposition of toxic metals in the UK have improved significantly since the original assessments of critical load exceedance in 2004, primarily due to the establishment of a national deposition network under Defra contract EPG 1/3/204. These changes are briefly described in Section 2.3.1 below.

.

Figure 2.1. The principles of the Critical Load approach, for metals in soils. The arrows indicate the direction of transport of the metals. The numbers show the sequence in which the method is developed.



2.2. Modifications to Methods

Critical loads, based on pH dependent free-ion critical limits have been calculated for five metals: cadmium copper, lead, nickel and zinc. The following changes have been made to the calculations since the 2004 report:

- The models are now applied to 6 habitat classes: managed conifer, managed broadleaf, unmanaged wood, grassland (acid & calcareous), dwarf shrub heath, bog. (see section 2.2.1)
- Updated critical limit functions are used for each metal (see section 2.2.2)
- Updated DOC values are used for four habitat categories (see section 2.2.3).
- Updated model (WHAM VI) is used for calculating critical loads based on pH-dependent free-ion critical limits
- Updated model (SDM) used for calculating the number of years to reach within 10% of the critical limit values.
- Updated deposition data are used based on the new national deposition network.

Parameterisation of the models with respect to soil properties (pH, LOI) and average annual runoff remains unchanged from 2004 and is not repeated here. Updates to the models are described elsewhere; this section describes the updates to the mapping data and presents the updated maps of deposition, critical loads, critical load exceedance, critical limit exceedance and timescales to reach critical limits.

2.2.1 Updates to the habitat maps

The individual habitat distribution maps remain unchanged from 2004. However, the habitats to which the models are applied partly depends on the habitat-specific data available. For example, in 2004 DOC values were only available for three habitat types: grassland, heath/bog and woodland (applied to all managed and unmanaged woodland). In 2007, separate DOC values were derived for heath and bog (Section 2.2.3) and so critical limits and loads were calculated separately for these habitats. The habitat categories used in 2004 and 2007 are shown in Table 2.1 below.

Table 2.1 Habitat categories for critical loads mapping

2004 habitat categories used for:		**2007 habitat categories used for:**		
Models	**Maps in report'**	**Models**	**Critical load maps in report**	**Exceedance maps in report**
Grassland (acid & calcareous) & montane	Semi-natural unforested vegetation	Grassland (acid & calcareous)	Minimum critical load of all habitats	Mapped
Dwarf shrub heath & bog		Dwarf shrub heath		Not mapped
		Bog		
Managed coniferous woodland	Managed woodland	Managed coniferous woodland		Mapped
Managed broadleaved woodland		Managed broadleaved woodland		Mapped
Unmanaged woodland	Unmanaged woodland	Unmanaged woodland		Mapped

[1] In 2004 critical load maps were based on the minimum value of the habitats shown and the maximum value for critical load exceedances.

2.2.1. Ecotoxicity data

The objective of this work was to update the critical limit functions first derived under the previous contract, by adding new literature ecotoxicity data published since then and recalculating the critical limit functions including these new data. New ecotoxicity data were gathered by thoroughly reviewing the literature and toxic endpoints were selected using the criteria laid out in the published work describing the critical limit function derivation (Lofts et al. 2004). The new data are summarised in Table 2.2.

Table 2.2. Summary of new studies used in the recalculation of critical limits

Metal	Species/Process	Endpoints	Reference
Ni	*Hordeum vulgare*	16	Rooney et al. 2007
Ni	*Lycopersicon esculentum*	16	Rooney et al. 2007
Cu	*Hordeum vulgare*	2	Ali et al. 2004
Cu	*Lycopersicon esculentum*	17	Rooney et al. 2006
Cu	*Hordeum vulgare*	18	Rooney et al. 2006
Cu	*Lactuca sativa*	2	Gharbi et al. 2005
Cu	*Spinacia oleracea*	1	Gharbi et al. 2005
Cu	*Enchytraeus albidus*	1	De Barros Amorim et al. 2005
Cu	*Enchytraeus luxuriosus*	4	De Barros Amorim et al. 2005
Cu	*Folsomia candida*	6	De Barros Amorim et al. 2005
Cu	*Lumbricus rubellus*	1	Spurgeon et al. 2004
Cu	*Lumbricus rubellus*	1	Galay Burgos et al. 2005
Cu	Nitrification	1	Wilke et al. 2005
Cu	Respiration	1	Wilke et al. 2005
Cu	Nitrification	2	Fait et al. 2006
Zn	Nitrification	1	Mertens et al. 2006
Zn	Nitrification	5	Smolders et al. 2004
Zn	Respiration	1	Smolders et al. 2004
Cd	*Lumbricus rubellus*	1	Spurgeon et al. 2004
Cd	*Paronychiurus kimi*	1	Son et al. 2007
Cd	*Lumbricus rubellus*	1	Galay Burgos et al. 2005
Cd	*Folsomia candida*	1	Menta et al. 2006
Cd	*Sinella coeca*	1	Menta et al. 2006
Cd	*Folsomia candida*	7	van Gestel & Koolhaas
Pb	*Paronychiurus kimi*	1	Son et al. 2007
Pb	*Folsomia candida*	1	Menta et al. 2006

Updated critical limit functions were calculated using the same methodology as the previous contract. Ecotoxicity data and the corresponding critical limit functions are presented in Fig. 2.2.

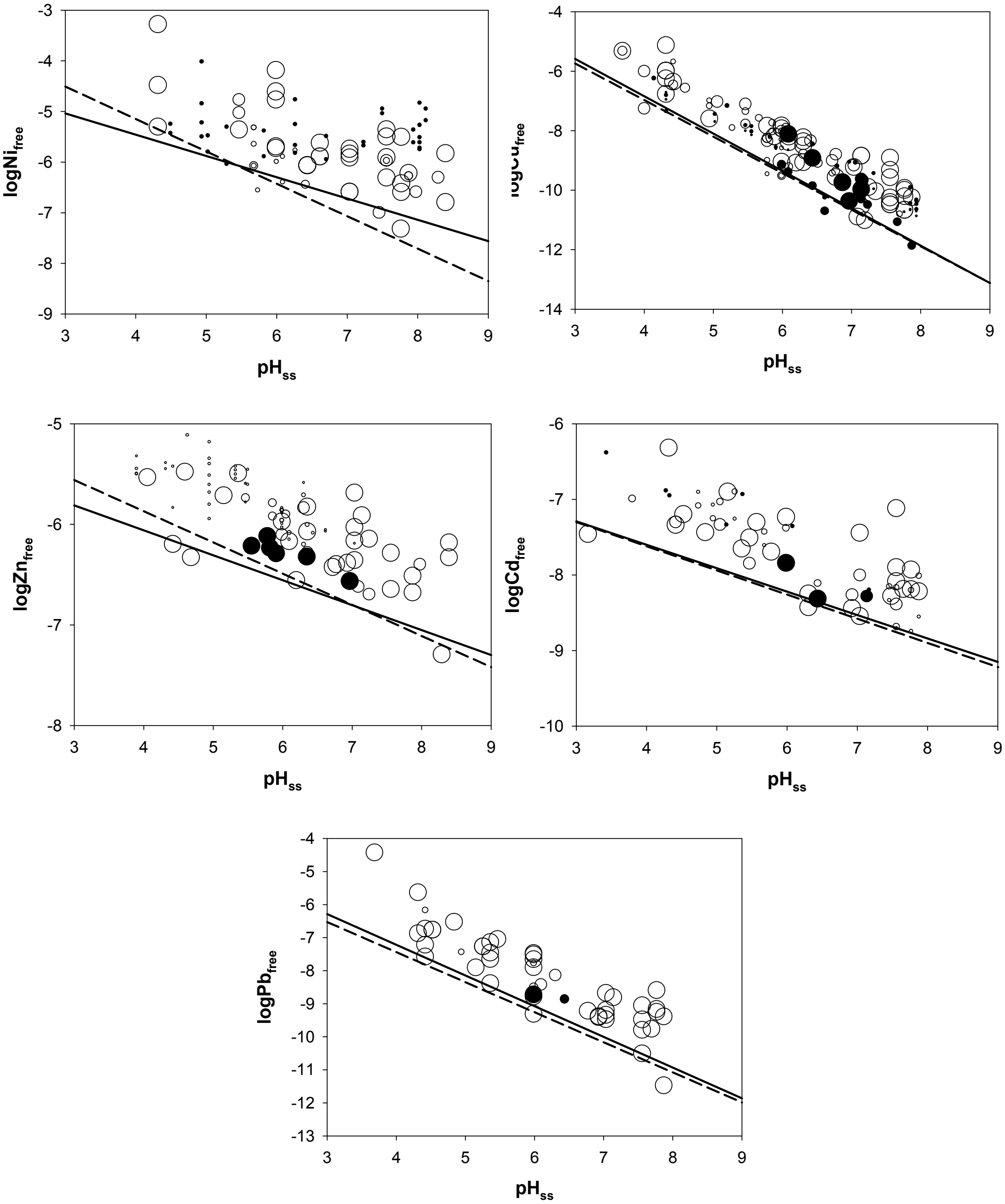


Fig 2.2. Toxicity test endpoints (symbols) and critical limit functions (lines). Open symbols represents previously used toxicity data, closed symbols are new data. Symbol size relates to the weighting given to the data point. Solid lines are the recalculated functions, dashed lines are the old functions.

Additional data points for Cd and Pb are small in number and the recalculated critical limit functions are little changed. The recalculated function for Cu is also little changed, despite the addition of data from 13 new studies. The slope of the Zn function is lowered somewhat, from -0.31 to -0.25; this results in lower predicted critical Zn below approximately pH 7.0, although the difference is not great (from example, critical Zn at pH 6.0 is 83% of the value calculated with the old function). The slope of the new function for Ni is lowered from -0.64 to -0.42; this results in a new function that gives lower critical limits below approximately pH 5.5 and higher critical limits above this pH. Thus the new limit predicts that soils below pH 5.5 will be more sensitive to Ni than previously calculated, and soils above pH 5.5 will be less sensitive. For example, at pH 4.5 (i.e. an acidic soil) the new Ni critical limit is 1.6 times lower than the old limit, while at pH 7.5 (i.e. a neutral soil) the new limit is 2.9 times higher than the old.

2.2.2. Dissolved Organic Carbon (DOC)

Background

Dissolved organic carbon (DOC), the fraction of the soil organic carbon pool that is mobile in the soil porewater, and which is formed primarily by the microbial degradation of soil organic matter, desorption of organic substances from soil solids and leaching of organic substances from fresh litter. Under laboratory conditions, DOC leaching has been shown to be affected by a range of variables including temperature, soil moisture, ionic strength, sulphate concentration, C/N ratio, leaching frequency, metal saturation and pH, but results are sometimes contradictory and concentrations measured in laboratories are often very high and bear little relationship to values in the field. However, field studies have largely concentrated on forest soils and even within this habitat DOC concentrations have been found to vary widely between different studies (typically by an order of magnitude). DOC is a major area of uncertainty in critical loads calculations for lead and cadmium, as was demonstrated by the uncertainty analysis conducted under Defra contract EPG 1/3/188. DOC is important in the assessment of critical loads for two reasons:-

- our critical limit model assumes that only metal present in soil solution as free ions is ecotoxic; metal bound to DOC is unlikely to have adverse effects. Hence, high concentrations of DOC are likely to reduce the toxicity of the same total concentration of metals in soil solution
- metal bound to DOC is mobile and may be leached from the topsoil; hence higher concentrations of DOC may be associated with higher rates of leaching loss and higher values of critical loads

Methods

We identified a minimum of eight sites from the six major semi-natural land use classes as determined by Land Cover Map (2000): bogs, heathlands, deciduous woodlands, coniferous woodlands, acid to neutral grasslands and calcareous grasslands. Data from ongoing sampling and analysis as part of other unrelated inventory work was also included to increase the number of sites and the geographical range of sampling. These sites include data from CEH Lancaster and long-term environmental monitoring programmes from the environmental change network (ECN) and forest ecosystems from the Level II programme of the UK research agency of the forestry commission. Data from a total of 53 sites were actually used for analysis. Sampling was done at either monthly or 3 weekly intervals, depending on the source of the data.

At each site, a minimum of 5 suction samplers were installed in the A horizon; if there was no clear differentiation between horizons, a depth of 10 cm was used. For ECN and Level II sites, suction samplers are used, while for the samples collected by CEH and York University, rhizon suction samplers (Eijkelkamp Agrisearch Equipment, the Netherlands) were used. Each sampler produced one sub-sample for every sampling date. The volume of sample per sampler was noted before sub-samples were pooled to produce one sample for the site. Samples were transported cool to the laboratory and conductivity and pH was measured immediately on the unfiltered samples before storage at 4^{o}C. Prior to analysis, samples are filtered using Whatman 0.45 micron filters.

All suction samplers operate in a similar way, by applying suction tension to the soil porewater. All suction samplers were made from PTFE and quartz in order to overcome problems which have been reported with the use of ceramic suction samplers. DOC analysis was done at the University of York using a LiquiTOC (Elementar, Germany). For quality control, we analysed and compared the DOC concentrations of 61 samples measured in York and at CEH Lancaster (TOCVCPN/CPN analyzer, Shimadzu, Kyoto, Japan). We found no significant differences between the two analysis ($t=-0.869$; $p=0.388$) and a highly significant correlation ($r=0.963$, $p=0.000$). The effect of storage on the DOC concentrations was analysed by comparing the DOC values of 6 different samples before and after 11 months of storage at 4^{o}C. No significant storage effects were found on DOC concentrations ($t= 1.090$; $p=0.325$) and samples were highly correlated ($r =0.968$, $p=0.002$).

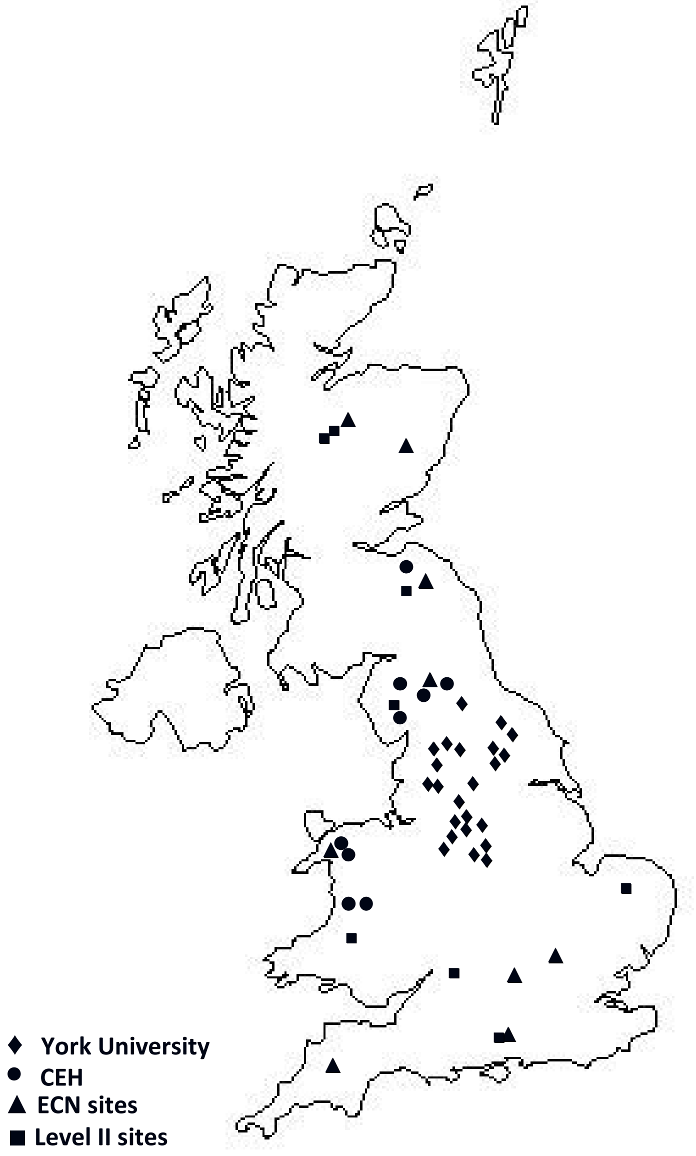


Fig. 2.3. Location of DOC sampling sites

Suction samplers collect the soil porewater by means of an applied tension over a sampling period. In dry periods there is less porewater available and the tension samplers have an increased risk to lose their tension. Both these factors result in marked differences in sample volume between sites and in time. The lack of samples in the calcareous grassland sites during the late summer is caused by this for example. Moist vegetation classes such as bogs and heaths never lacked samples. Tests to see if a lower sampling volume correlated with highly concentrated samples and thus higher DOC concentrations, revealed no significant relations between volume and DOC concentration in any of the vegetation classes indicating that DOC was not significantly diluted in moist periods nor diluted in dry periods.

Results

DOC values differed significantly between vegetation types and in time. In general, DOC values increased during the summer and early autumn and decreased during the winter (Figure 2.4). DOC values were averaged over the year and compared between vegetation classes (Figure 2.5). The DOC concentrations of bogs (average DOC = 60.3 mg l^{-1}) was significantly greater than that of all other vegetation classes . Coniferous woodlands (average DOC 24.5 mg l^{-1}) did not significantly differ from heaths (average DOC 31.4 mg l^{-1}) and deciduous woodlands (average DOC 24.1 mg l^{-1}) but the latter significantly differed from heaths. Both calcareous and acid to neutral grasslands had significantly lower DOC values than heaths and bogs, but did not differ from each other (average DOC 18.4 mg l^{-1} and 16.6 mg l^{-1} respectively).

Since there were no significant differences between the grasslands, we pooled the concentrations to give a new annual average grassland DOC value of 17.5 mg l^{-1} for use in critical load modelling. This was also done for the two forest vegetation classes which resulted in a new woodland DOC concentration of 24.3 mg l^{-1}. The average DOC year concentrations which are listed in Table 2.3 were rounded for the purpose of calculating critical load and critical limit values.

Identification of factors associated with variation in DOC concentrations is important to improve prediction of this parameter. Although strong seasonal effects were shown in DOC concentrations for all vegetation classes, a preliminary analysis with rainfall data did not reveal any significant relationships. Further research on evaporation and fluxes are needed to unravel the dynamics of DOC concentrations within these vegetation types and would help in predicting more accurately the seasonal variation in DOC concentrations.

Soil characteristics and soil parameters were available for almost all sites apart from the ECN data. We found no significant relationship between soil porewater pH and DOC concentrations ($R^2 = 0.18$). In addition we did not find a significant relationship between the organic content of the soil, measured here as Loss On Ignition, (LOI, $R^2 = 0.16$). However a strong relationship was found between C:N ratio of the top soil and DOC concentration ($R^2 = 0.49$; Figure 2.6). Such strong relationships are reported elsewhere for surface waters and could possibly be used for predictions of DOC concentrations at sites from which only C to N ratios are known.

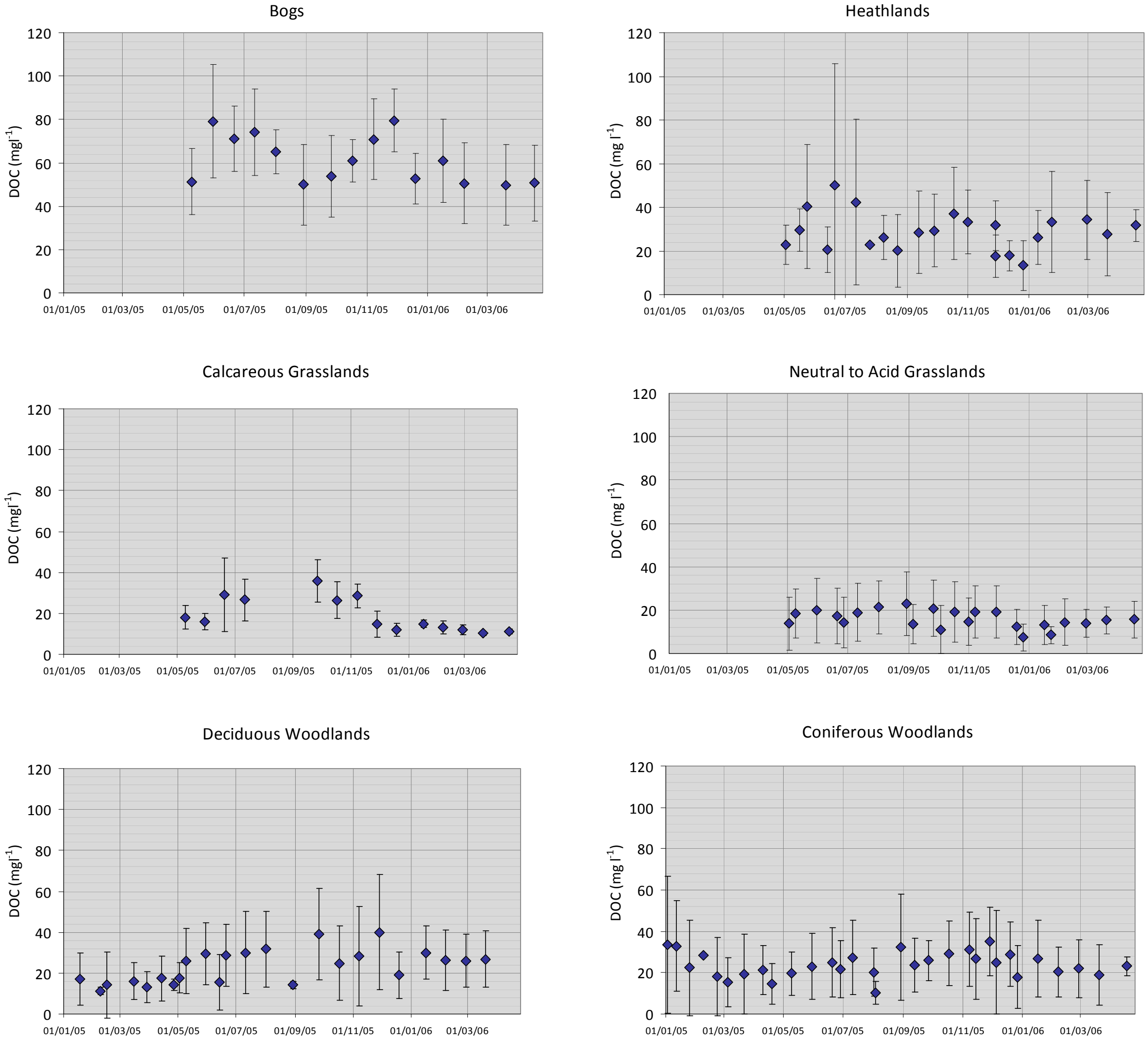


Figure 2.3 Average DOC concentrations (in mg l^{-1} +/- SD) for each vegetation class over a 1 year period.

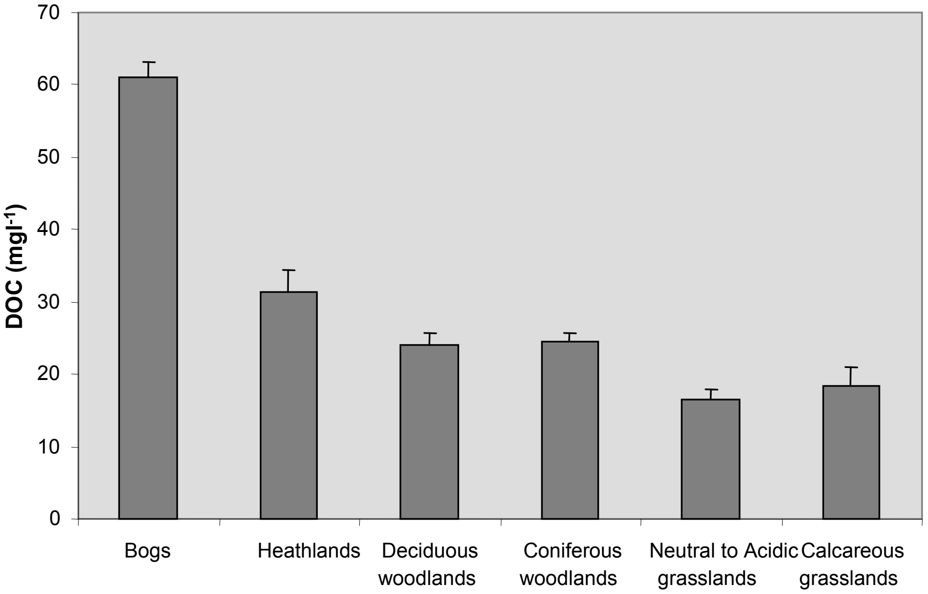


Figure 2.5. Average yearly DOC concentrations (in mg l^{-1} +/- SEM) for each land cover category.

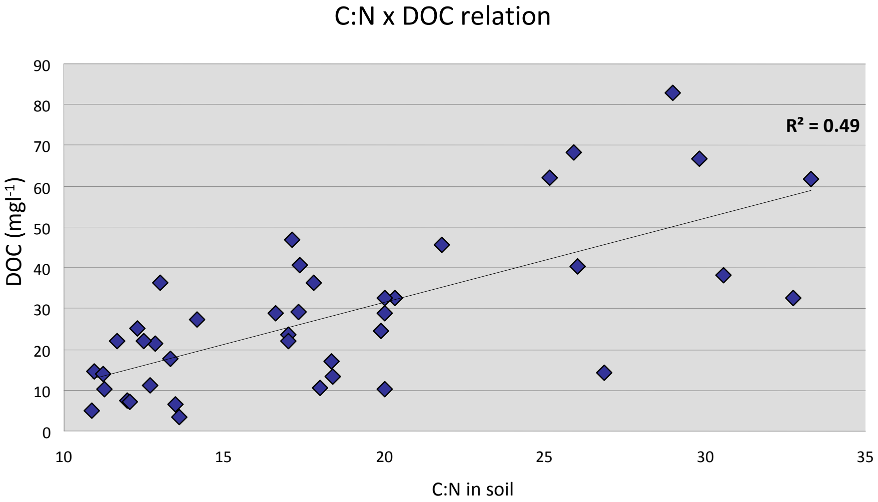


Figure 2.6 Relationship between C:N ratio in the soil and DOC concentration in mg l^{-1}

Table 2.3. DOC concentrations by habitat class

Habitat	**DOC mg l^{-1}**	**Rounded DOC values (mg l^{-1})**
Grassland	17.48	20
Heathland	31.39	30
Bog	60.95	60
Woodland	24.27	25

2.3 Heavy metal deposition data

Deposition data used for critical load exceedance calculations were provided by the Defra funded UK Heavy Metals Monitoring Network (Fowler et al., 2006). The measurements of bulk deposition and heavy metal concentrations in PM_{10} were interpolated by CEH Edinburgh to generate deposition fields on a 5x5 km grid of the UK. The calculation of wet deposition includes treatment of the seeder-feeder effect to account for enhanced rainfall at higher altitudes. For dry deposition, the dry deposition velocity (V_d) is calculated from the land use maps and local wind data for each 5x5 km square. In addition to average deposition to each grid cell, land cover specific deposition loads were provided for (a) grassland/moorland and (b) woodland. Exceedance calculations using the woodland deposition values are used for the three woodland habitats and the grassland deposition values for all other semi-natural non-forested habitats.

At the time of the 2004 report, only provisional deposition data for 2004 were available. More recently an updated (final) data set for 2004 (using improved rainfall data) as well as data for 2005 have become available (Fowler et al., 2006) and have been used in the recent analyses. The table below (Table 2.4) compares the mean deposition values for each of these data sets.

Table 2.4. Summary of mean deposition values

		Mean deposition values (g ha^{-1} yr^{-1}) for the UK		
		Provisional 2004 data (used in 2004 report)	**2004 final deposition data**	**2005 deposition data**
Cd	Woodland	0.88	0.69	0.69
	Grassland	0.45	0.31	0.29
Cu	Woodland	26.2	21.4	22.5
	Grassland	10.3	9.92	9.39
Ni	Woodland	10.7	7.48	10.9
	Grassland	3.69	3.28	4.52
Pb	Woodland	36.9	35.1	28.0
	Grassland	12.6	14.7	10.9
Zn	Woodland	237	127	114
	Grassland	85.4	74.7	69.4

The final 2004 data set shows lower mean values for all metals with the exception of Pb, where the mean value for grassland is slightly higher than the provisional data set. This is due to the elimination of contaminated samples and outliers from the measurement data set from which the maps were derived. Comparing the 2005 data with the final 2004 data, mean values for Cd and Cu are similar for both years, mean values are slightly larger for Ni, and mean values for Pb and Zn are somewhat smaller.

The maps of deposition (2005) to grassland and woodland for the five metals are shown in Figures 2.7 and 2.8 In general, the maps show higher deposition in the north west of Scotland, Wales, central and parts of southern England, often in areas where rainfall, and hence, wet deposition will be higher. The maps for forest also show areas of higher deposition across south and eastern England.

2.4.Critical loads

The principles of the critical load calculations remain unchanged from 2004, but include the updated inputs as described above. The minimum, maximum and mean critical load values for each habitat across the UK are given in Table 2.5, together with the values for 2004 for comparison. These results show that the mean critical loads are similar in both data sets for Cd, have increased by more than 50% for Cu and for Pb, and decreased by around 20-50% for Ni and Zn. The changes for Ni and Zn are broadly consistent with changes to the calculations of the free-ion critical limits (Section 2.2.2), The increased values for Cu and Pb are mostly likely related to the use of improved values of DOC, as these metals are strongly bound to organic matter.

The critical load maps shown in Figures 2.9 and 2.10 re based on the minimum of the critical load values present for different habitats (up to six) in each 1x1 km square. In general the lowest critical loads are found in the south and east of the UK, and the higher values in the north and west. This reflects the national pattern of the critical leaching flux of metal from the soil, which is higher in areas with higher rainfall and runoff. In the south and east where the leaching flux is lower metal is likely to be retained in the soil for longer and hence the critical load is lower than in the north and west. This is in contrast to the acidity critical load maps where the more sensitive regions are in the north and west of Britain.

Table 2.5. Minimum, maximum and mean critical load values for 2007, with the results for 2004 in parentheses.

Metal	Habitat	**Critical loads (g ha^{-1} yr^{-1})** **Values for 2004 in parentheses**		
		Min	**Max**	**Mean**
Cd	Managed coniferous woodland	2 (2)	145 (138)	20 (18)
	Managed broadleaf woodland	1 (1)	116 (106)	10 (8)
	Unmanaged woodland	1 (1)	131 (120)	12 (11)
	Grassland (acid & calcareous)[*]	1 (1)	181 (171)	22 (21)
	Heathland[**]	1 (1)	184 (174)	36 (33)
	Bog	1	184	39
Cu	Managed coniferous woodland	14 (15)	5244 (3523)	172 (105)
	Managed broadleaf woodland	9 (10)	1655 (1064)	70 (46)
	Unmanaged woodland	5 (1)	1588 (1021)	88 (53)
	Grassland (acid & calcareous)	3 (6)	6241 (4188)	176 (104)
	Heathland	7 (8)	6205 (4266)	358 (224)
	Bog	8	6350	441
Ni	Managed coniferous woodland	42 (21)	11718 (33641)	1176 (2209)
	Managed broadleaf woodland	38 (17)	9014 (24761)	454 (658)
	Unmanaged woodland	37 (16)	9512 (23833)	631 (1014)
	Grassland (acid & calcareous)	30 (13)	14655 (40243)	1398 (2931)
	Heathland	41 (18)	14876 (40884)	2381 (4953)
	Bog	47	14888	2819
Pb	Managed coniferous woodland	9 (7)	2941 (1660)	153 (83)
	Managed broadleaf woodland	6 (5)	1504 (821)	61 (34)
	Unmanaged woodland	4 (3)	1445 (789)	80 (43)
	Grassland (acid & calcareous)	5 (4)	3503 (1974)	176 (97)
	Heathland	7 (5)	3483 (2012)	319 (177)
	Bog	12	3564	407
Zn	Managed coniferous woodland	72 (74)	2583 (4332)	428 (582)
	Managed broadleaf woodland	35 (38)	2164 (3369)	209 (255)
	Unmanaged woodland	27 (29)	2448 (3812)	250 (324)
	Grassland (acid & calcareous)	21 (24)	3173 (5362)	427 (645)
	Heathland	31 (34)	3228 (5461)	691 (1039)
	Bog	37	3231	733

[*] In 2004 the grassland habitat additionally included montane areas (excluded in 2007)

[**] In 2004 the heathland and bog areas were treated as a single habitat.

2.5 Critical load exceedances

Critical load exceedances have been calculated using the above critical loads and the 2005 deposition data. The results show no exceedance for any habitat for Ni and virtually no exceedance for Cd, with the exception of 3 ha of managed coniferous woodland. There was very little exceedance of Cu, Pb and Zn critical loads for the bog and heathland habitats, and areas exceeded were also relatively small for grassland and managed coniferous woodland (Table 2.6). However, over 50% of the areas of managed broadleaved woodland and unmanaged (coniferous and broadleaved) woodland were exceeded for Cu, Pb and Zn.

Table 2.6. Crtical load exceedance by habitat type

Habitat	**Percentage area critical load exceedance for:**		
	Cu	**Pb**	**Zn**
Grassland	8	3	9
Heathland	<0.01	0.1	0.1
Bog	<0.01	0	0.1
Managed conifer	6	11	6
Managed broadleaf	50	62	58
Unmanaged woodland	50	58	54

Exceedance maps for Cu, Pb, Zn for the woodland and grassland habitats (Figures 2.11 to 2.16) show the most widespread exceedance of critical loads across central, eastern and southern England, where critical loads are also lower. For Cu, the highest exceedances are around Kent (Figures 2.11 and 2.12). Large areas of woodland across these regions of England have high exceedances for Pb (Figures 2.13 and 2.14), with smaller and less extensive exceedances for grassland habitats. For Zn there are high exceedances for unmanaged woodland across eastern England, but the higher exceedances for the managed woodlands tend to be in the midlands of England (Figure 2.15 and 2.16).

To compare the current exceedance results (based on 2007 critical loads and 2005 deposition) with those from the 2004 report, Table 2.7 shows the percentage areas of critical load exceedance for three aggregated habitat categories (managed woodland, unmanaged woodland and semi-natural).

Table 2.7 Percentage areas of habitat where critical loads for Cu, Pb and Zn are exceeded for the 2004 and 2007 data sets.

Habitat	**Percentage habitat area exceeded for 2007 with 2004 results in parentheses**		
	Cu	**Pb**	**Zn**
Managed woodland	27 (32)	35 (61)	30 (48)
Unmanaged woodland	50 (57)	58 (79)	54 (69)
Semi-natural	3 (5)	1 (8)	4 (5)

This shows that the areas of critical load exceedance are smaller for all metals and habitats in 2007 compared to 2004. The results are similar for the two data sets for Cu, and decreases in the area exceeded for both Pb and Zn. This is consistent with the increase in the mean Pb critical loads and the lower mean Pb deposition values. For Zn although mean critical loads have decreased, the mean deposition values are also smaller resulting in smaller areas of habitat exceedance.

2.6 Critical limit exceedance

The free-ion critical limits used in the calculation of critical loads, have been compared with the current soil metal concentrations. The latter are obtained from the national soil surveys (NSRI, Macaulay, DardNI) and expressed as total soil metal concentrations. Transfer functions are used to convert the free-ion concentrations to total concentrations to enable this comparison. However, soil concentration data are not available for Ni for the UK, or for Cd for Scotland; hence Ni is not included in this analysis, and the Cd results are for England, Wales and Northern Ireland only.

Results for individual habitats are given in Table 2.8 which shows virtually no exceedance of the critical limit for Pb for any habitat. There are small areas of exceedance for all habitats for Cd, with the highest exceedances in the Peak District area (Figures 2.17 and 2.18). Exceedances of the critical limit for copper extend across England and Wales, with significant areas of exceedance for broadleaf and unmanaged woodland (Figures 2.19 and 2.20). The areas of critical limit exceedance for all habitats are highest for Zn (Table 2.8); the maps (Figures 2.21, 2.22 and 2.23) do not show any real spatial pattern of exceedance, though higher values appear to be associated with upland areas where peat soil may dominate).

Table 2.8 Percentage area of free-ion critical limit exceedance by habitat

Habitat	**Percentage area critical limit exceedance for:**			
	Cd	**Cu**	**Pb**	**Zn**
Grassland	8	18	1	44
Heathland	5	2	1	26
Bog	1	1	0.5	26
Managed conifer	6	8	0.2	36
Managed broadleaf	9	50	1	56
Unmanaged woodland	10	42	1	53

To compare with the 2004 report results, the 2007 results have been aggregated to the three broader habitat categories (Table 2.9). The results show small decreases in the area where the critical limits are exceeded in the 2007 data set for Cd and Cu, and increases of around 10% where the Zn critical limit is exceeded.

Table 2.9. Percentage area of critical limit exceedance for the 2007 and 2004 data sets

Habitat	**Percentage habitat area exceeded for 2007 with 2004 results in parentheses**			
	Cd	**Cu**	**Pb**	**Zn**
Managed woodland	8 (10)	28 (33)	0.4 (1)	46 (34)
Unmanaged woodland	10 (12)	42 (49)	1 (1)	53 (44)
Semi-natural	7 (8)	8 (10)	1 (1)	33 (20)

These changes in areas of critical limit exceedance are a consequence of the changes to the free-ion critical limit calculations (Section 2.2.2); the total soil concentration data and the transfer functions are unchanged from 2004. Table 2.10 summarises the impact of the change in critical limits on the exceedance results.

Table 2.10. The effect of changes in the free-ion critical limit calculations on the area of exceedance of critical limits.

Metal	**Effect on critical limit exceedance**
Cd	Not much change
Cu	Exceedance smaller in areas of low soil pH
Ni	Exceedance greater in areas of low soil pH Exceedance smaller in areas of high soil pH
Pb	Exceedance smaller in areas of low soil pH
Zn	Exceedance greater in areas of low soil pH

2.7 Critical limit and critical load exceedances

Critical limit exceedance occurs where the total soil metal concentration is greater than the critical limit concentration and provides an indication of the current soil condition. Critical load exceedance occurs where current atmospheric deposition exceeds the steady-state critical load and provides an indication of areas potentially at risk when steady-state is reached. Hence both provide different, but useful information. It is possible, as for Pb above, for the critical load to be exceeded but not the critical limit, however, if deposition continues at current levels exceedance of the critical limit may happen at some point in the future. It is therefore important to look at exceedance of both critical loads and critical limits. In addition, dynamic models can provide information on the timescales involved for these processes, as described in Section 3.

The exceedance data have been used to examine the results by four exceedance categories:

- No exceedance of critical load or critical limit
- Exceedance of critical load (critical limit not exceeded)
- Exceedance of critical limit (critical load not exceeded)
- Exceedance of critical load and critical limit

Table 2.11 shows the area of each habitat class in each exceedance category. It has not been possible to include Ni in this analysis due to the lack of soil concentration data.

For Cd there is no critical load exceedance so data only fall into two of the exceedance categories (no exceedance or critical limit exceedance); small areas of habitats (1-6%) are in areas where the critical limits are exceeded.

The copper results show very little exceedance of critical loads and critical limits for heathland. Exceeded areas in each category are also relatively small for grassland and managed coniferous woodland. The results for managed broadleaved woodland and unmanaged woodland are similar with around 20% of the habitat with critical load exceedance and about 30% of the habitat where both critical loads and critical limits are exceeded. Areas where the critical load or critical load and limit are exceeded are largely in south-east England (Figure 2.24a), with areas of critical limit exceedance only scattered across other parts of England, Wales and Northern Ireland.

There are few areas with critical limit exceedance for Pb for any habitat, and no areas of heath or bog with both critical limit and critical load exceedance. Very small areas of the woodland and grassland habitats show both critical limit and critical load exceedance; for unmanaged woodland this occurs around the Peak District (central England). There are significant areas of woodland with critical load exceedance (11-62%), mainly across south and eastern England and the Welsh borders.

Zinc shows larger areas of critical limit than critical load exceedance for grassland, heathland, bog and managed coniferous woodland, where there is little exceedance of the critical loads. Managed broadleaved woodland and unmanaged woodland show a more equal distribution across the exceedance categories, with 20-30% where either the critical load, critical limit, or both are exceeded. The areas where both critical limits and loads are exceeded are across south and eastern England, with areas of critical limit exceedance only across Wales, south west and northern England and the southern half of Scotland (Figure 2.24b).

Table 2.11. Areas (km^2) and percentages of habitats occurring in the four exceedance categories.

Metal	**Exceedance category**	**Managed conifer**		**Managed broadleaf**		**Unmanaged woodland**		**Grassland**	
		Area (km^2)	**%**	**Area (km^2)**	**%**	**Area (km^2)**	**%**	**Area (km^2)**	**%**
Cd	**No Exceedance**	2199	94	4908	91	2300	90	7304	92
	Load Exceeded	0	0	0	0	0	0	0	0
	Limit Exceeded	129	6	502	9	257	10	667	8
	Load & Limit Exceeded	0	0	0	0	0	0	0	0
Cu	**No Exceedance**	5845	88	1702	29	1247	38	11256	80
	Load Exceeded	238	4	1223	21	657	20	357	3
	Limit Exceeded	374	6	1206	21	378	12	1860	13
	Load & Limit Exceeded	159	2	1700	29	980	30	671	5
Pb	**No Exceedance**	5870	89	2153	37	1351	41	13581	96
	Load Exceeded	731	11	3641	62	1892	58	442	3
	Limit Exceeded	12	0.2	13	0.2	7	0.2	117	1
	Load & Limit Exceeded	3	<0.1	25	0.4	11	0.3	4	<0.1
Zn	**No Exceedance**	3969	60	915	16	757	23	7182	51
	Load Exceeded	256	4	1621	28	771	24	643	5
	Limit Exceeded	2263	34	1534	26	751	23	5695	40
	Load & Limit Exceeded	128	2	1761	30	982	30	624	4

To compare the results with those from the 2004 report, once again the 2007 results have been aggregated to the three broader habitat categories. The results are shown in Table 2.12. for Cd and Cu are similar for both data sets; the results for Pb and Zn show the decrease in the area of critical load exceedance and for Zn the increase in the area of critical limit exceedance.

Table 2.12. Comparison of the areas in the four exceedance categories using the current data and the results from the 2004 report.

Metal	**Exceedance category**	**Percentage area of habitat in each exceedance category for 2007 (2004 results in parentheses)**		
		Managed woodland	**Unmanaged woodland**	**Semi-natural**
Cd	**No exceedance**	92 (90)	90 (88)	93 (92)
	Load exceedance	<0.01 (0)	0 (0.05)	0 (0)
	Limit exceedance	8 (10)	10 (12)	7 (8)
	Load & Limit exceedance	0 (0)	0 (0)	0 (0)
Cu	**No exceedance**	61 (54)	38 (31)	91 (89)
	Load exceedance	12 (13)	20 (20)	1 (2)
	Limit exceedance	13 (14)	12 (12)	6 (7)
	Load & Limit exceedance	15 (19)	30 (37)	2 (3)
Pb	**No exceedance**	64 (40)	41 (20)	98 (91)
	Load exceedance	35 (60)	58 (78)	1 (8)
	Limit exceedance	0.2 (0.2)	0.2 (0.3)	1 (1)
	Load & Limit exceedance	0.2 (1)	0.3 (1)	0.01 (0.2)
Zn	**No exceedance**	39 (40)	23 (23)	65 (77)
	Load exceedance	15 (26)	24 (33)	2 (3)
	Limit exceedance	31 (12)	23 (8)	31 (18)
	Load & Limit exceedance	15 (22)	30 (36)	2 (2)

2.8. Dynamic modelling: maps

The complex dynamic models described in Section 3 are designed for catchment-specific application. The Simple Dynamic Model (SDM) is designed for broader scale application and can be used to predict the timescales to reach a particular condition. These results should be interpreted as indicating the broad timescale for response, with the more complex models described in Section 3 provided more reliable, site-specific estimates. For this purpose, we have used the SDM to calculate the number of years for the soil metal concentration to reach within 10% of the critical limit value. These calculations assume deposition is at the critical load. It is important to emphasises, therefore, that these are not predictions based on current deposition; rather they indicate the relative timescale for change at a fixed deposition rate. Because, the deposition rate is set at the critical load, the timescale estimated may be much longer than in a situation in which the deposition rate is much greater than the critical load.

Figures 2.25 and 2.26 show the results for Cu, Zn and Pb for managed broadleaved woodland, and are mapped in four classes:

- Current deposition below critical loads (ie, critical loads not exceeded)
- Current soil metal concentration above the critical limit (ie, critical limit exceeded)
- Two time classes, showing the number of years for the soil metal concentration to reach within 10% of the critical limit. This calculation is only made for cases where the critical limit is not exceeded but the critical load is exceeded.

For Cu (Figure 2.25a) the critical load is not exceeded in Scotland and parts of northern and south-western England, and Wales. However, the current soil metal concentration already exceeds the critical limit across many parts of England and Wales (Section 2.6). Where the critical limit is not currently exceeded, it is predicted that at deposition rates equal to the critical load it could take over 1000 years for the soil metal concentration to reach within 10% of the critical limit value. These areas are primarily in southern England and parts of central and eastern England.

The map for Zn (Figure 2.25b) shows a similar spatial pattern, although there are some scattered areas in Scotland, and larger areas across Wales where the critical limit is currently exceeded. Timescales to reach within 10% of the critical limit are again likely to be greater than 1000 years, particularly in southern and eastern England.

The picture for Pb is quite different as the critical limit is only exceeded in a few small areas within the Peak District, Wales and East Anglia (Figure 2.26). For most of northern and south-western England, Wales and Scotland the current deposition is below the critical load. Where the critical load is exceeded, but the critical limit is not yet exceeded, it is predicted that for most areas of England it will take up to 1000 years to reach within 10% of the critical limit with deposition at the critical load.

For Cd there is virtually no exceedance of the critical load (Section 2.5) and only 9% of the managed broadleaf habitat has exceedance of the critical limit (Section 2.6). Within these areas it is possible to calculate the time taken for the current soil metal concentration to **decline** to within 10% of the critical limit value, again assuming deposition at the critical load. Figure 2.27 shows these areas scattered across England and Wales; there does not appear to be any obvious spatial pattern for the different timescale classes.

3. Dynamic Modelling

3.1. Mineral weathering studies

Assessment of the impacts of potentially-toxic heavy metals, and the performance of dynamic modelling require knowledge, or assumptions, about the natural weathering inputs of metals to soil-water systems. Surprisingly, there has been little study of the processes by which heavy metals are transferred from primary minerals into soil, and weathering inputs are poorly known.

One approach to their estimation is to scale them to inputs of base cations, i.e. Mg, Ca etc, (de Vries & Bakker, 1998), by multiplying the ratio of the trace metal to base cation in the parent minerals by the base cation weathering rate. This may be appropriate in systems where the base cations and trace metals have a common source, but such a situation does not pertain in most of the catchments that we are studying in this project. In most of our catchments, base cations are derived from small amounts of carbonates, whereas we assume that the heavy metals are coming from the silicate minerals. Therefore in our dynamic modelling work to date (Tipping et al., 2005, 2007), we have taken ratios of metals to Si in parent weathering materials, making the assumptions (a) that Si fluxes in streams are in approximate steady-state and that there is no significant continuing removal of Si into secondary minerals, and (b) the minerals are dissolving congruently, i.e. at steady state the element release rates are proportional to their contents in the mineral.

3.1.1. Element release from multi-component mineral matter

Consider a rock comprising two silicate minerals. At steady state, their release (dissolution) rates of Si are $D_{Si,1}$ and $D_{Si,2}$ moles g^{-1} s^{-1}, so the total rate of release of Si at steady state is

$$D_{Si} = X_1 D_{Si,1} + X_2 D_{Si,2} \tag{3.1}$$

where X_i is the fraction of mineral i in the rock. If the molar ratios of a second element (E) to Si in the two minerals are R_1 and R_2 then for congruent dissolution at steady state the total rate of release of E, D_E, is given by

$$D_E = X_1 D_{Si,1} R_1 + X_2 D_{Si,2} R_2 \tag{3.2}$$

and the overall ratio of release rates, D_E/D_{Si}, by

$$D_E/D_{Si} = \frac{X_1 D_{Si,1} R_1 + X_2 D_{Si,2} R_2}{X_1 D_{Si,1} + X_2 D_{Si,2}} \tag{3.3}$$

The element ratio in the rock is given by

$$R_{rock} = X_1 R_1 + X_2 R_2 \tag{3.4}$$

Therefore the ratio of release rates, D_E/D_{Si} does not generally equal R_{rock}, which means that our current means of estimating weathering inputs of metals may be in error. In other words, the "ratio of ratios" i.e. $(D_E/D_{Si}) / R_{rock}$ may deviate from unity, which is the expected value for congruent dissolution of the whole rock.

Deviations of $(D_E/D_{Si}) / R_{rock}$ from unity are most likely when R_1 and R_2 differ greatly, but also when $D_{Si,1}$ and $D_{Si,2}$ differ greatly. Consider the following cases, in which $R_2 = 0$, i.e. only component 1 contains dissolving metal.

A. If $D_{Si,1} = D_{Si,2}$ then $(D_E/D_{Si}) / R_{rock} = 1$ for any values of X_1 and X_2.

B. If $D_{Si,1}$ = 100×$D_{Si,2}$, and X_1 =X_2 then (D_E/D_{Si}) / R_{rock} = 1.98. But if X_1 = 0.01×X_2 then (D_E/D_{Si}) / R_{rock} = 50. This would occur if the rock contained a small amount of one mineral that was responsible for essentially all the supply of both metal and Si.

C. If $D_{Si,1}$ = 0.01×$D_{Si,2}$, and X_1 =X_2 then (D_E/D_{Si}) / R_{rock} = 0.0198. But if X_1 = 0.01×X_2 then (D_E/D_{Si}) / R_{rock} = 0.01. This would occur if the rock contained a small amount of one mineral that was responsible for all the supply of metal, but with the second mineral providing almost all the Si.

It is indeed known that different silicate minerals dissolve at rates covering several orders of magnitude (Wolff-Boenisch et al., 2006), and that they differ in their heavy metal contents (Loring, 1991). Therefore it is difficult to predict heavy metal weathering inputs with any certainty and the “fully congruent” assumption, although practical, may under- or over-estimate the true inputs of metals.

To attempt to determine steady-state heavy metal/Si release rates for our study catchments we are conducting long-term laboratory dissolution measurements, in which the release of elements from a number of representative mineral specimens is monitored.

3.1.2. Methods

Samples of rocks and pebbles were collected from the field sites to which dynamic modelling with CHUM was applied. The samples were split into approximately cubic fragments of side 1 cm. Ten fragments with all fresh surfaces were selected from each sample. They were washed for 15 minutes by sonication in deionised water, the process being repeated 10 times, with three deionised water rinses between each sonication. After a final rinse with deionised water the samples were allowed to dry in air.

Experiments were performed in 500 cm^3 Teflon bottles, that were acid washed and pre-weighed before use. The washed mineral samples were placed in the acid-washed bottles, which were then reweighed and sample weight calculated. Approximately 250 cm^3 Milli-Q deionised water were added, and the bottles re-weighed to determine the total liquid volume. The pH was adjusted to 3.0 by the addition of 0.156 M HNO_3. The bottles were incubated at 10°C with gentle orbital shaking.

At each sampling time, samples were taken for the determination of pH (5 cm^3), silicon (5 cm^3), major cations (10 cm^3) and trace metals (10 cm^3). The samples for trace metals (ICPMS) were acidified prior to analysis, whereas those for major cations (ICPOES) were not. The remainder of the solution was discarded, and fresh HNO_3 (pH 3.0) was added.

In all, 18 samples of silicate minerals were subjected to the leaching procedure. Of these, ten were selected for detailed characterisation, carried out by the BGS laboratories. Elemental contents were determined by XRF, and mineral constituents were identified with XRD.

3.1.3. Results

The compositional data on the ten selected silicate samples are shown in Table 3.1. Although the samples cover a range of rock types, they cannot be claimed to represent all of the UK, not even just the UK uplands.

Table 3.1 Mineral samples used in weathering experiments.

Sample	Site	A	C	E	G	K	M	Mi	KF	Q
		Mineral content in %*								
W1	R. Etherow					not analysed				
W2	R. Etherow	-	-	-	-	1	-	2	7	90
W3	R. Etherow	12	-	-	-	3	-	2	-	83
W4	Old Lodge	-	-	-	11	2	-	3	3	81
W5	Old Lodge					not analysed				
W6	Old Lodge					not analysed				
W7	Great Dun Fell	-	-	-	-	3	-	-	-	97
W8	Great Dun Fell	-	-	-	-	-	-	5	-	96
W9	Great Dun Fell					not analysed				
W10	Lochnagar	25	-	-	-	-	-	2	35	39
W11	Lochnagar					not analysed				
W12	Lochnagar	25	-	-	-	-	-	2	37	37
W13	Hardknott Gill									
W14	Gaitscale Gill	29	13	8	-	-	4	4	26	16
W15	Gaitscale Gill					not analysed				
W16	Gaitscale Gill	45	15	5	-	-	5	-	10	20
W17	Castle How Gill	27	13	13	-	-	1	2	27	18
W18	Castle How Gill					not analysed				

* A albite, C chlorite, E episode, G goethite, K kaolin, M magnesiohornblende, M mica, KF K-feldspar, Q quartz

3.1.4. Analysis of leaching data

Concentrations of Si and Zn in 1 mM HNO_3 leachates from sample W2 are shown in Figure 3.1. The hypothesis is that after sufficient time, the rates of release of both elements will become constant, and their ratio will become equal to that in the parent sample. The final ratio is then given by the mineral composition in Table 3.2 and is 7.9×10^{-6} mol mol^{-1}. As shown by the points in Figure 3.2, the ratio after 954 days is 1.67×10^{-3} mol mol^{-1}, having fallen from a value of 0.035 mol mol^{-1} during the early days of the experiment. The line in Figure 3.2 is plotted according to the assumption of an exponential trajectory to the steady state value. At the final steady state, the ratio of the rates of release of an element and Si is equal to the ratio of their contents in the dissolving mineral matter, R_C. At the start of the experiment, the ratio is higher. Therefore, the ratio at any given time t can be written;

$$R_t = R_C + (R_0 - R_C)\, e^{-kt} \tag{3.5}$$

Values of R_C are obtained from analysis of the mineral specimen, and k is obtained by fitting the data using least-squares with Excel Solver.

Table 3.2 Elemental compositions of selected silicate samples, determined by X-ray fluorescence at the British Geological Survey analytical laboratory.

		W2	W3	W4	W7	W8	W10	W12	W14	W16	W17
SiO2	%	93.2	89.7	74.7	97.6	94.9	75.7	76.1	55.3	56.9	56.9
TiO2	%	0.1	0.1	0.4	0.1	0.2	0.3	0.2	1.1	1.2	1.1
Al2O3	%	2.8	4.9	3.2	0.8	1.2	12.4	12.7	17.1	15.2	17.2
Fe2O3t	%	1.0	1.7	16.5	0.3	1.6	1.3	1.0	8.0	9.0	7.6
Mn3O4	%	<0.01	<0.01	0.1	<0.01	<0.01	0.0	0.0	0.2	0.2	0.2
MgO	%	0.1	0.1	0.1	<0.05	0.1	0.3	0.3	3.5	5.2	3.6
CaO	%	0.0	0.0	0.0	0.0	0.0	0.4	0.5	4.9	3.5	4.9
Na2O	%	0.1	1.4	<0.05	<0.05	<0.05	3.1	3.2	2.9	4.2	3.0
K2O	%	1.0	0.2	0.3	0.1	0.2	4.9	5.3	3.1	1.3	3.0
Cd	ppm	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Ba	ppm	205	25	91	9	82	268	292	736	453	750
Cr	ppm	32	46	137	87	154	48	39	85	170	92
Co	ppm	<1	2	24	<1	<1	2	1	24	31	19
Ni	ppm	2	4	18	2	4	3	3	18	47	22
Cu	ppm	3	3	15	3	4	4	3	14	3	5
Zn	ppm	8	3	107	<1	9	25	25	55	53	46
Sr	ppm	44	36	17	15	6	95	84	254	229	269
Pb	ppm	5	7	18	2	2	32	34	15	11	14

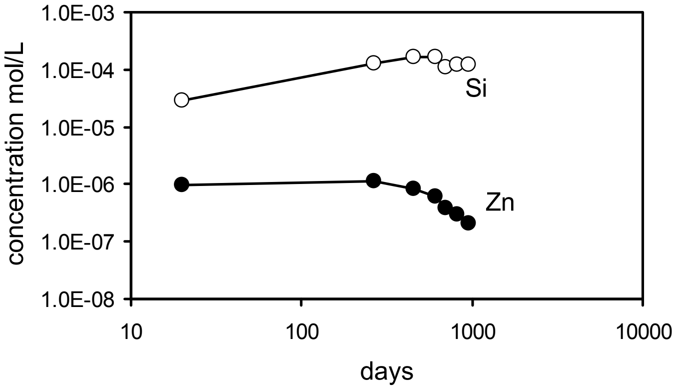


Figure 3.1 Concentrations of Si and Zn in leaching solutions from sample W2.

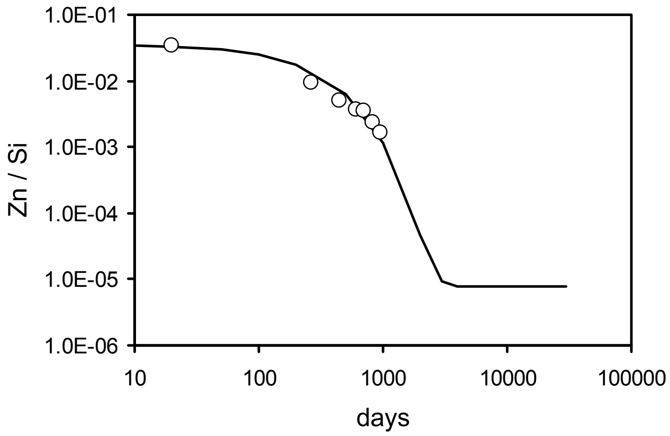


Figure 3.2 The Zn:Si ratio of sample W2 as a function of time, fitted with equation (3.5).

It is evident from Figure 3.2 that even though the experiment has been proceeding for about 1000 days, the desired steady-state condition has not been reached. If the data continue to follow the model, approximately 3000 days will be required in total, i.e. about 5 more years from the present.

The rate constant *k* for the data of Figure 3.2 is 0.0034 day^{-1}. Values derived to date for all five of the heavy metals of interest for all 10 of the mineral specimens are shown in Table 3.3. Of course, these values may change as more data are gathered, and the model may cease to apply. In the majority of cases the model provides a reasonable or good fit of the data. The values do not vary greatly among the samples, nor among the metals. We cannot yet conclude that element release from these mineral samples can reach steady-state, with congruent dissolution. On the other hand, the results obtained so far are broadly consistent with that hypothesis, and so there is no need for it to be rejected. We must collect several more years' data before a firm conclusion can be reached.

Table 3.3 Rate constants (day^{-1} × 1000) from equation (3.5).

	Ni	Cu	Zn	Cd	Pb	mean
W2	3.2	2.6	3.4	3.5	2.3	3.0
W3	5.2	3.5	5.2	7.0	3.0	4.8
W4	0.6	0.5	2.4	2.6	0.6	1.3
W7	5.1	-	4.4	4.6	1.9	4.0
W8	2.7	1.0	3.7	5.3	1.4	2.8
W10	3.7	3.7	5.3	6.7	3.8	4.6
W12	2.1	2.3	2.9	2.2	2.9	2.5
W14	2.1	0.3	2.1	4.4	-	2.2
W16	1.2	1.9	1.9	2.0	-	1.8
W17	2.5	1.9	3.0	3.3	3.9	2.9
mean	2.8	2.0	3.4	4.2	2.5	3.0

3.1.5 Summary of weathering studies

The results do not yet disprove the simplifying assumption that heavy metal release rates can be related to the composition of the dissolving rock material. However, continued monitoring is clearly necessary in order to establish true steady-state conditions. Therefore it is reasonable to continue to employ the congruent-dissolution assumption in the dynamic modelling. But it should be noted that should the metal release rates in the experiments not continue to fall, then the results will imply that greater proportions of the metals in soil and water come from non-anthropogenic (i.e. weathering) sources, and therefore that the environmental enrichments in heavy metals would be lower than shown in Tables 3.5 and 3.13.

3.2 Dynamic modelling of Scoat Tarn and Howden Reservoir

The objectives of this part of the project were to understand and quantify the contribution of historic heavy metal deposition to current metal burdens in soils, waters and sediments. If this could be done, confidence in the predictions of dynamic models would be increased.

The research focused on two field sites, the catchments of Scoat Tarn and Howden Reservoir (Table 3.4). Scoat Tarn is a natural corrie lake in the western Lake District. Howden Reservoir was constructed in 1914 in the valley of the River Derwent, Derbyshire. In each case, the sediments of the standing water body provide a record of metal accumulation. Dynamic modelling with CHUM-AM (CHemistry of the Uplands Model – Annual, Metals) was carried out in order to attempt to account simultaneously for observations of (a) metal pools in the catchment soil, (b) metal concentrations in the lake or reservoir, and (c) sediment metal contents as a function of depth (time). The methodology was similar to that already used for Lochnagar (Tipping et al., 2007).

Table 3.4 Characteristics of the two study catchments

	Scoat Tarn	Howden Reservoir
Locality	Lake District Cumbria	Peak District Derbyshire
Position	54°29′ N 3°18′ W	53°26′ N 1°44′ W
Altitude (m)	598	275
Catchment area (ha)	95	3550
Surface area (ha)	5.2	66
Mean depth (m)	8.1	11.1
Soils	Organic rankers, podzols, peat	Peat, podzols
Vegetation	Acid grassland	Heather moorland, forest (7%)
Geology	Borrowdale Volcanic Series	Millstone Grit series
Annual rainfall (m)	3.1	1.3
Annual temperature °C	5	8

3.2.1. Soil and water modelling

3.2.1.1. Field measurements and data

Details of the methods are given by Tipping et al. (2006 a,b, 2007) and Ashmore et al. (2004). The following is a brief description. Catchment soils were sampled over different depth intervals (one, two or three) depending upon the nature of the soil. Each sample was analysed for stone content, bulk density, C, N, heavy metals, and pH. The data were combined to create for each catchment an average idealised soil comprising two layers, for the purposes of modelling. Stream and lake waters were sampled fortnightly and analysed for total and filterable heavy metals. For the streams, and for Howden Reservoir, measurements were also made of pH, major solutes, and DOC; for Scoat Tarn itself, these data were taken from the long-term records of the Defra-funded Acid Waters Monitoring Network. Additional data on the chemistry of Howden Reservoir, including heavy metal concentrations, were obtained from Severn Trent Water.

CHUM-AM (see below) is driven by annual data on rainfall volume and composition, together with dry deposition of N and S, and total deposition of reactive heavy metals. For Scoat Tarn, rainfall inputs were based on measurements at Ambleside (20 km east of the study site), corrected for altitude (Tipping et al., 2006a), major-solute rainwater chemistry was taken from the monitoring records of CEH Lancaster for Cockley Beck (10 km south-east of the study site), and dry deposition was estimated as described in Tipping et al. (2006a). Heavy metal inputs were reported by Tipping et al. (2006b). Past scenarios for all atmospherically-deposited chemical components were constructed as described by Tipping et al. (2006a, b), using data on emissions, measured metal deposition at other sites from the 1970s to the present (Baker, 2001; Fowler et al., 2006), and lakewater sediment records for the longer term (Ochsenbein et al., 1983; Hamilton-Taylor, 1979). This is described more fully in Section 3.3.1.2. For Howden Reservoir, we used the same historical scenarios as in previous work with the catchment of the River Etherow (which is just to the north-west of the Howden catchment), except that a road salt component used for R. Etherow was omitted. The heavy metal deposition histories assumed for the two sites are shown in Figure 3.10; the history for Gaitscale Gill / Hardknott Gill was applied to Scoat Tarn, that for R. Etherow to Howden Reservoir.

3.2.1.2. CHUM-AM

CHUM-AM (Tipping et al., 2005a,b, 2007) represents an upland catchment in terms of an average soil, comprising two horizons, and underlain by a permeable zone of weathering mineral matter. Figure 3.3 shows the components of the model, as applied to catchments in the Duddon Valley, Cumbria. The same arrangement of horizons, fluxes and reactions is used for other catchments, but each has to be calibrated separately for the major (non-heavy metal) components.

CHUM-AM simulates the behaviour of heavy metals (Ni, Cu, Zn, Cd, Pb) in soil over periods of decades and centuries. The metals enter as atmospheric deposition or weathering. They react with the soil solids and with components of the soil solution, and leave the soil either in solution, where they may be complexed to dissolved organic matter (DOM), or in particulate form, adsorbed to suspended particulate matter (SPM). The model keeps an account of the inputs and outputs, and of the soil metal content, and calculates the solution speciation, to provide the concentrations of the key reactive species, the free metal ion (e.g. Ni^{2+}, Pb^{2+}), in soil and water.

In previous Defra-funded work, measured soil properties (depth, bulk density, %C) were used to configure the model, which was driven by annual rainfall (varying between years when data were available) and evaporation, deposition of major wet and dry components, and the production of dissolved organic matter. It was spun up to steady state for the year 1400, using “pristine” inputs. Then adjustments were made of parameters governing soil N and S accumulation and release, and weathering rates, in order to reproduce currently-observed soil pH and N and S contents, together with major stream chemical variables (pH, concentrations of major ions). The optimised model was then used to predict heavy metal behaviour, on the basis of estimated past deposition, and by assuming that weathering inputs of metals arise from congruent dissolution of mineral matter, so that they can be taken to be proportional to the observed Si flux. Comparison of contemporary modelled and observed soil metal pools and streamwater metal concentrations showed reasonable agreement without parameter adjustment for Ni, Cu, Zn and Cd. However in the case of Pb, the soils of most catchments appear to bind the metal more strongly than was predicted, and to rectify this, a parameter in the WHAM chemical speciation was modified (Tipping et al., 2005b).

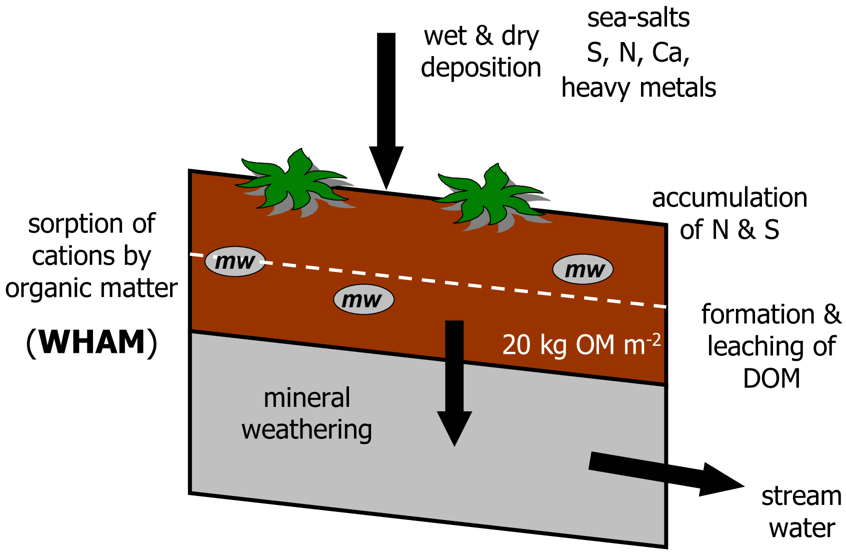


Figure 3.3 Diagram of the soil-water-rock dynamic model, CHUM-AM

For each model run, CHUM-AM forces the soil to steady state with respect to weathering and deposition inputs under pristine conditions. Then the deposition history unfolds, from about 1500 to the present, thereby simulating the soil and water chemical composition. The model was calibrated for the two catchments to simulate major solutes as described by Tipping et al. (2006a) by adjusting parameters for N and S cycling, together with the weathering rate constants of Na, Mg, Al, K, Ca, and Si, to match both soil pH and surface water chemistry. In both cases the calibration was reasonably successful. Soil pH was reproduced to within 0.1 units, the observed and simulated values for Scoat Tarn being 4.3 and 4.4 respectively, and those for Howden Reservoir 3.8 and 3.8. Heavy metal weathering rates were estimated by ratio-ing to the Si flux, as described in Section 3.1.

Plots of observed and simulated surface water chemical variables against time for the period 1980 – 2010 are shown in Figures 3.4 and 3.5. Figure 3.6 compares soil metal pools and water concentrations for the two sites. Bearing in mind the simple and restricted calibration possibilities, the simulations are acceptable. In the case of Scoat Tarn, the simulated lakewater metal concentrations are all too high by a factor of about two, which may indicate that metal deposition is overestimated, although of the soil pools only those of Ni and Cu are overestimated. There is less bias for Howden Reservoir, with some concentrations being somewhat higher than the observed values and others somewhat lower. The results show comparable agreement to those for other catchments to which CHUM-AM has been applied (see also Section 3.3).

Comparison of the simulated soil metal pools and surface water concentrations for the present day with those for past "pristine" conditions provides a measure of the enrichments of the catchments with heavy metals, due to anthropogenic inputs (Table 3.5). The enrichments are generally larger for Zn, Cd and Pb. In the case of Pb at Howden Reservoir, very large enrichments are estimated, because the local rock samples that we have analysed are poor in this metal, and so under pristine conditions a very low weathering rate is calculated. The calculated enrichments are strongly dependent upon the assumptions about weathering rates, and these are not yet fully quantified (see Section 3.1).

With the model configured to describe the soil and water of the two catchments, the next step is to attempt to account for metal accumulation in the sediments of the two water bodies.

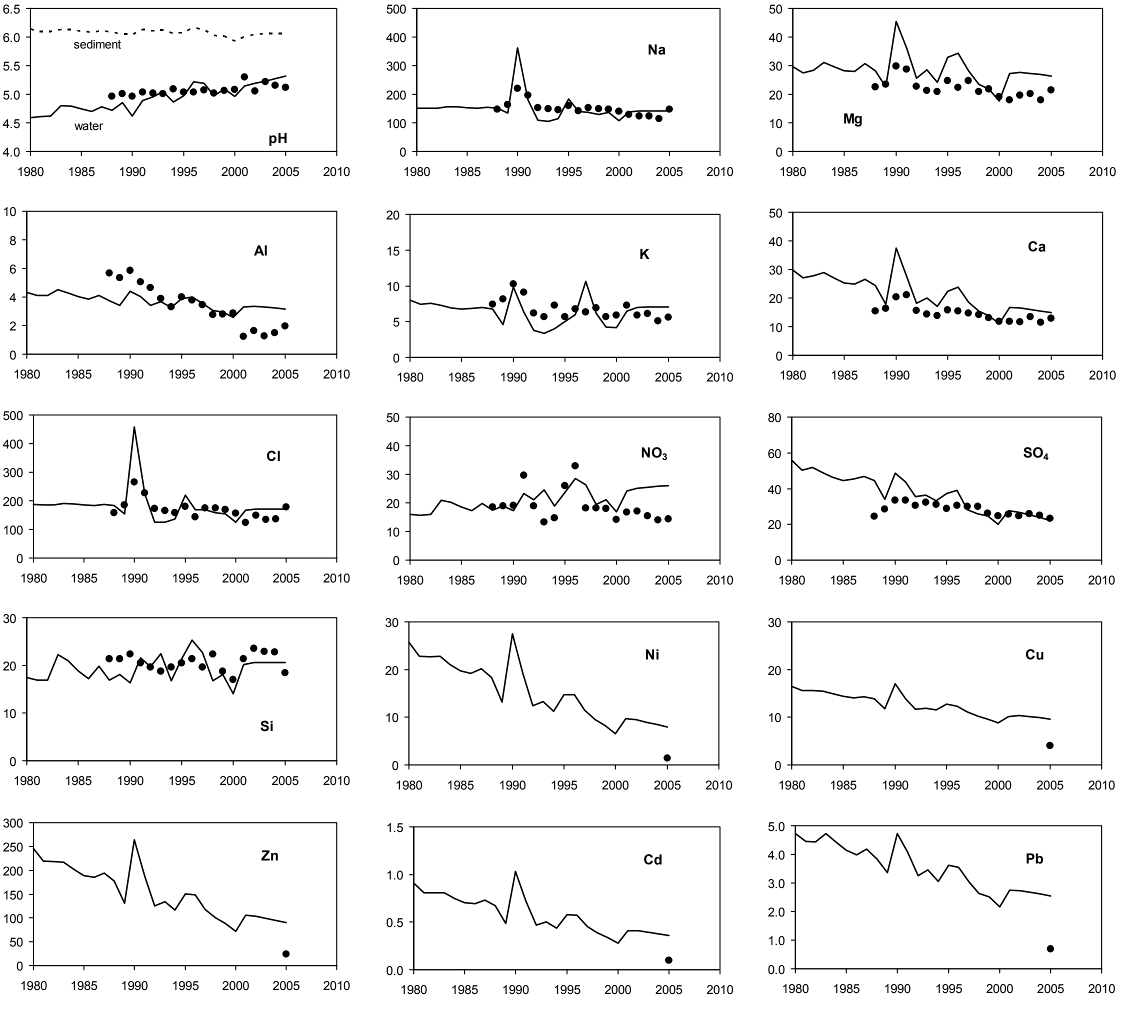


Figure 3.4 Scoat Tarn surface water chemistry, observed (points) and simulated (lines). All concentrations are in μmol l^{-1}.

Table 3.5 Ratios of simulated current metal soil pools and surface water concentrations to those under pristine conditions, i.e. heavy metal enrichment factors.

	Ni	Cu	Zn	Cd	Pb
Scoat Tarn					
soil	4.3	8.7	36	17	12
surface water	4.5	9.0	38	31	15
Howden Reservoir*					
soil	1.7	12	19	13	230
surface water	4.0	6.6	45	47	470

* Note that Howden Reservoir did not exist under pristine conditions, and so the calculated ratios refer to a hypothetical surface water.

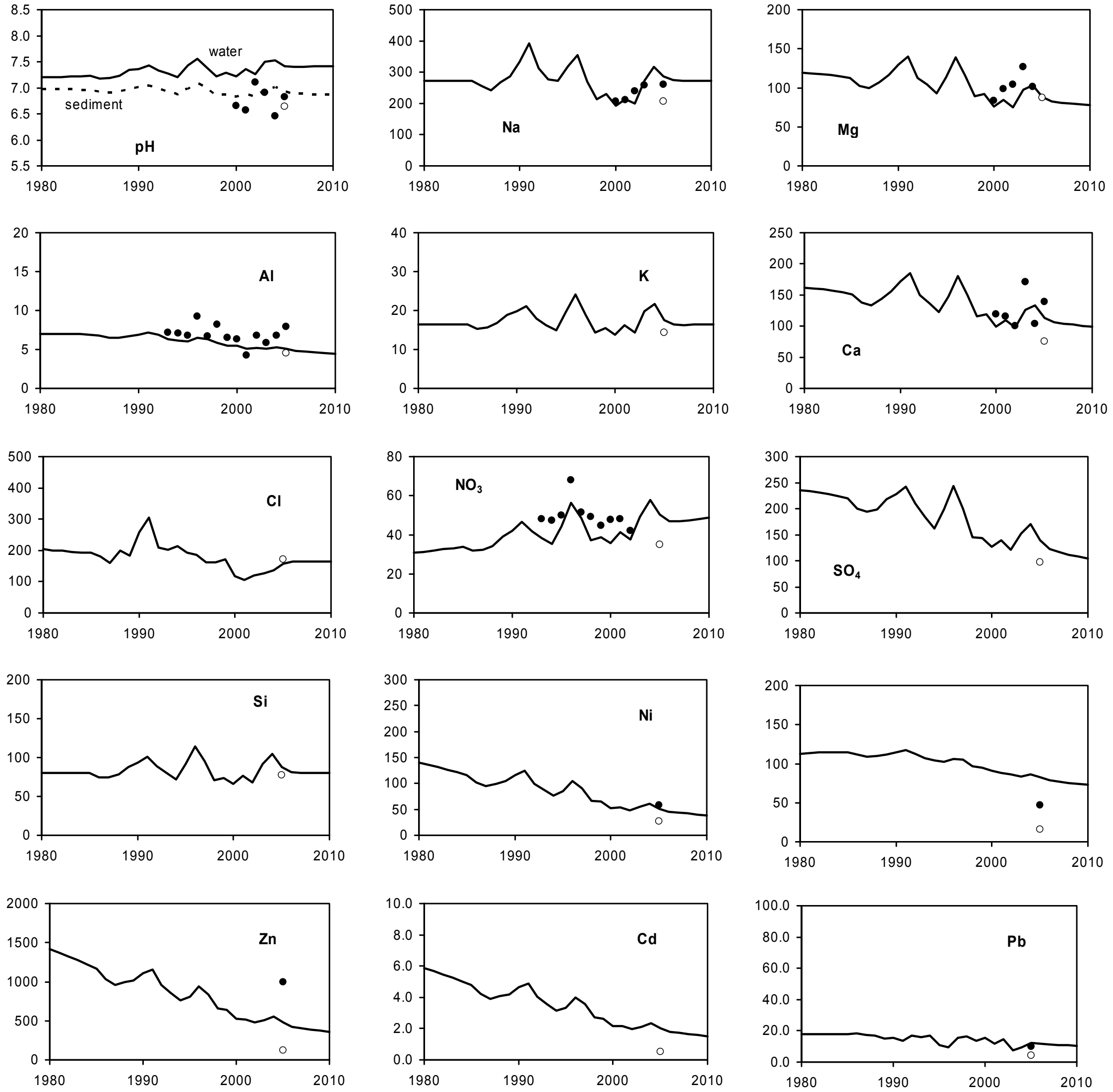


Figure 3.5 Observed (points) and simulated (lines) surface water chemistry for Howden Reservoir. All concentrations are in µmol l^{-1}.

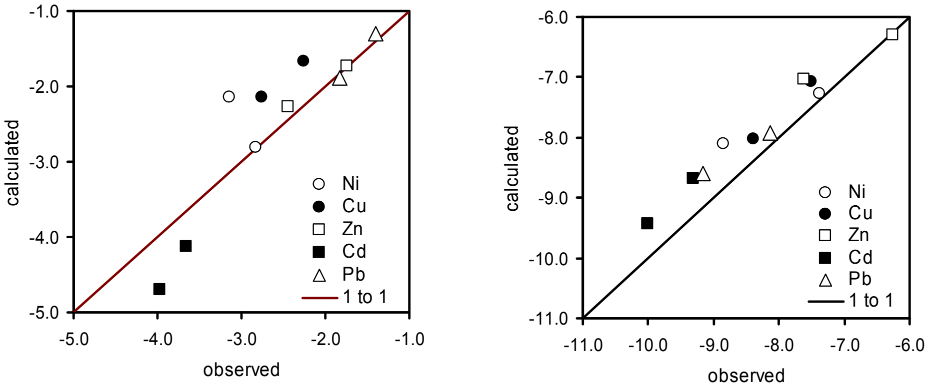


Figure 3.6 Calculated vs. observed soil metal pools in log mol m^{-2} (left) and surface water concentrations in log mol l^{-1} (right) for Scoat Tarn and Howden Reservoir.

3.2.2. Determination of sediment metal budgets

3.2.2.1. Scoat Tarn

Six cores were collected in 2005 using a gravity corer, at different water depths. Cores were extruded and then sliced at 1 to 4 cm intervals and dried at 40^{o}C prior to determination of sediment weight. Samples were analysed for total and extractable metal content. Total metals were determined by digestion using a concentrated nitric acid digest in sealed vessels in a CEM X microwave followed by analysis using a Varian pro-axial ICP-OES. Extractable ("reactive") metals were determined by shaking with a 0.1 M HNO_3 solution followed by analysis using a Varian pro-axial ICP-OES.

It was not possible to determine sediment depth as cores did not reach the bottom of deposits. Around 20 to 30 cm of sediment was retrieved whereas 80 cm cores have previously been retrieved (Haworth & Lishman, 1991; Tallantire, 1997). Little sedimentation appeared to be occurring only in water < 8 m deep: attempting to core at shallower depths led to the core tube hitting rocks and breaking. Total sediment load, therefore, cannot accurately be determined. However, sediment metal loads during the period of atmospheric metal deposition can be estimated (see below).

We planned to estimate dates corresponding to depths within the cores by comparison of magnetic properties with those for two cores from Scoat Tarn that had been collected by others (Haworth & Lishman, 1991; AWMN, 1992) and dated with ^{210}Pb. Comparison of trends in magnetic susceptibility, ARM (anhysteretic remnant magnetization) and SIRM (saturation isothermal magnetization), were made, but unfortunately the profiles did not show significant similarity. The heavy metal profiles were broadly similar, with Cu, Zn and Pb each showing both a subsurface peak, and a clear increase above levels deeper in the core.

Sediment pools and sediment metal pools were estimated for each of four zones within the lake. Zone 1 covered depths from 14 to 17 m (Cores 1, 2 and 3); Zone 2, 11-14 m (Cores 4 and 5); Zone 3, 8-11 m (Core 6); Zone 4, 0-8 m. As already noted, little sedimentation appeared to be occurring in Zone 4. Sediment stores of Zones 1 to

3 were calculated from the average bulk density and depth of cores collected within each zone (to the base of the industrially impacted zone). Metal inventories for each sedimentary zone were determined by multiplying the sediment load by average metal concentrations in cores taken within them.

3.2.2.2. Howden Reservoir

Metal storage in the sediments of the Howden reservoir was calculated by (a) detailed mapping of the reservoir basin and identification of sedimentary zones, (b) coring all sedimentary zones and determining a sediment storage and a metal inventory for each, and (c) summing the sediment and metal inventories for each sedimentary zone.

A bathymetric map of the reservoir providing detailed information on the morphology of the reservoir basin was obtained from Severn Trent Water Plc. Alongside field observations during the dry summer of 2003, when the reservoir water level was low, the map was used to identify low gradient zones where sedimentation is taking place within the reservoir. The bathymetric map was digitised using ESRI ArcMap 9 and several sedimentary zones were defined by their location with respect to the inflow and the slope of the reservoir basin. The bathymetric map was then geo-registered within ESRI ArcMap 9 using control points from 1:10,000 scale Ordnance Survey mapping. A total of eight sedimentary zones (Zones 1 – 8) were identified, and their enclosed area was calculated through digitisation of geo-referenced polygons within the GIS.

Twenty-one cores were collected between 1998 and 2005 using a 1 m long Mackereth mini-corer (Mackereth, 1969). In most cores a clear interface between lacustrine deposits and the underlying valley floor material was apparent and sediment depth was easily determined. However, sediment depth was more difficult to determine in some marginal cores, and sediment may have been deeper than the core tube (1 m) leading to possible underestimation of sediment storage in some marginal locations. We were unable to collect cores from Zone 8 as sediments were not retained by the Mackereth mini-corer, either because they were too coarse, or due to lack of sedimentation in this zone.

Each core was extruded and then sliced at intervals of 1 cm (central cores) and 4 cm (marginal cores) and dried at 40 ^{o}C for determination of bulk density. All cores were subjected to a pseudo-total, strong acid digestion. Cores collected in 1998 and 2000 were cold digested overnight in a 90% HNO_3, 10% HCl acid mixture, before refluxing for at least 8 hours until the oxidisation process was complete (Shotbolt, 2002). Metal analysis was carried out using a F-AAS (Unicam 939). Recovery of Pb from Buffalo River Sediment Certified Reference NBS SRM 2704 was 90.2% ± 3.88 (95% CL). Cores collected in 2005 were digested using a concentrated HNO_3 digest in sealed vessels in a CEM X microwave (Shotbolt et al., 2007). Pb analysis was undertaken using a pro-axial ICP-OES (Varian). Recovery of BCR sewage sludge amended soil CRM 143R was 92.9% ± 3.84 (95% CL). Although two digestion procedures were used, both are very efficient and comparable recoveries were obtained. The 2005 cores were also analysed for geochemically-active ("reactive") metals by extraction from the soils by shaking overnight in a 0.1 M HNO_3 solution prior to centrifugation at (16000 rpm, JA-17 rotor) and filtration (0.45 μm Whatman PP filter) and using a pro-axial ICP-OES (Varian).

Sediment stores in Zones 1 – 7 were calculated from the average bulk density and depth of cores collected within each zone. Metal inventories for each sedimentary zone were determined by multiplying the sediment load by average metal concentrations in cores taken within them (there was little downcore variation in metal concentration). Sedimentation in the channels and less steep marginal areas (Zone 8) was estimated from different plausible sedimentation scenarios.

A detailed temporal record of metal concentrations in the Howden Reservoir sediment was obtained by analysis of a central, undisturbed sediment core at 1 cm intervals. Dates estimated with ^{210}Pb from a previously collected core from approximately the same location were applied to this core by matching magnetic susceptibility and metal profiles. This provided 13 dated horizons. Dates for the remaining sections were derived through interpolation. Although we recognise that this does involve some reduction in the precision of the temporal record, sedimentation rates as derived from ^{210}Pb dating were relatively consistent throughout the core except for during an inwash of sediment in 1959.

3.2.2.3. Results

The metal contents of the sediments of the two water bodies are shown in Table 3.6. The total amounts (in kg) in Howden Reservoir exceed those in Scoat Tarn by between 90-fold (Pb) and 420-fold (Ni). This is partly because Howden Reservoir is larger, and partly because the sediment metal contents are greater. Thus the metal pool expressed in mol m^{-2} are also greater for Howden Reservoir, by between 7-fold (Pb) and 30-fold (Ni), and this reflects a higher rate of delivery of both particulate matter and metals from the catchment, i.e. the erosion of metal-contaminated soil. Temporal variations in sediment metals are considered in the next Section.

Table 3.6 Sediment metal pools.

		Ni	Cu	Zn	Cd	Pb
Scoat Tarn	kg	4.3	6.6	40	0.52	78
(from ~1850)	mmol m^{-2}	3.9	5.5	32	0.24	20
Howden Reservoir	kg	1800	1500	7300	69	7100
(from 1914)	mmol m^{-2}	120	91	420	2.3	130

3.2.3. Sediment metal modelling

3.2.3.1. Scoat Tarn

The lakewater is treated as a constant volume, completely-mixed compartment. Its chemical composition is determined by atmospheric deposition to the water surface, streamwater input, lakewater output, particle sedimentation, and sediment-water exchange of solutes. The sediment model focuses on the top layer of sediment, which is considered to be in steady state with respect to particulates. Thus, the input sedimentation flux is equal to the effective downward transfer of material, as sediment accumulates. Solutes enter the sediment adsorbed to settling particles, or by exchange with the sediment pore water. Within the sediment layer, complete reduction of Fe(III), nitrate, and sulphate take place; this assumption follows the field observations of Alfaro-De La Torre & Tessier (2002) on an acid oligotrophic lake in Canada. The WHAM model is used to compute chemical speciation within the sediment layer, including binding to solid-phase humic acid, which is assumed to represent the active particulate adsorbent. Once material has moved downwards from the active surface layer, its composition is considered to be fixed. Based on the results of Alfaro-De La Torre & Tessier (2002), a sediment active depth of 2.0 cm, and a solute exchange coefficient of 1.5 mm day^{-1}, were assumed, and a pCO_2 of 10 times the atmospheric value was employed. The sediment was assigned a constant bulk density of 0.1 g cm^{-3}. From observations made during coring, it was assumed that sediment accumulated over 36 % of the lake area. Annual sedimentation rate was set to 132 g m^{-2} a^{-1} based on the budget calculations (Section 3.2.2.1), and this required an average net input concentration of suspended particulate matter of 1.05 mg l^{-1}.

CHUM-AM simulates only reactive heavy metal, i.e. that part of each metal that can enter into partitioning reactions with the soil, or with suspended solids in surface water, and reversible reactions in solution. The sediments however also contain other "inert" forms of the metal, and the standard analytical methods for determining sediment metal contents are highly likely to extract essentially all sediment heavy metal, and so will include this inert fraction. One form of inert metal is in aerosol particulates deposited directly to the surface of the lake. This is presumed to join the sediment almost immediately. Hamilton-Taylor et al. (1993) measured the release to solution of metals from aerosols collected in NW England. They found that 47 ± 11 % of Cu was rapidly released, 74 ± 8 % of Zn, and 41 ± 15 % of Pb. Therefore an appreciable fraction of the directly-deposited metal (26 – 59 %) may not pass into solution, and so can be rapidly incorporated into the sediment without entering into chemical reaction with solutes or other suspended particles. We used the values reported by Hamilton-Taylor et al. (1993) to estimate this contribution to sediment metal for Cu, Zn and Pb. For Ni and Cd we used the average of the values for the three investigated metals, i.e. 54 %.

A second "inert" input is due to heavy metals contained in physically-eroded mineral matter from the catchment. We estimated sedimentary metal from this source on the basis of the mineral content of the sediment (c. 25% by mass), and the measured heavy metal contents of samples taken for weathering experiments (Section 3.1). Then the total metal in the sediment was matched to the observed values (Table 3.6) by adjusting the contribution of inert metal deposited directly to the lake surface. The calculated contributions of the different sources of metal to the sediment are shown in Table 3.7.

Table 3.7 Modelled metal inputs to Scoat Tarn sediments

Metal	Sediment pool mmol m^{-2}		Fractional modelled contributions to sediment metal		
	calc	obs	Direct deposition	Physical erosion	Reactive
Ni	12	3.9	0.83	0.15	0.02
Cu	15	5.5	0.87	0.03	0.10
Zn	28	32	0.84	0.10	0.07
Cd	0.25	0.24	0.97	0.01	0.03
Pb	22	20	0.95	0.01	0.04

The calculated sediment metal pools are of similar magnitude to the measured values, with close agreement for Zn, Cd and Pb. The calculations suggest that nearly all ($\geq$ 90 %) of the sediment metal is due to the "inert" forms, and mostly due to direct deposition from the atmosphere to the surface of the lake.

The sediment analyses included estimates of geochemically-active (or "reactive") metal (Section 3.2.2.1) and these accounted for 13 % (Ni), 23 % (Cu), 57 % (Zn), 63 % (Cd) and 51 % (Pb) of the totals. The model estimates are much lower. This apparent discrepancy probably arises because much of the "inert" atmospherically deposited metal is "reactive" in the sense that it can be released by dilute acid, but unreactive under the conditions of the lakewater. Therefore it is quite possible for metal that might dissolve slowly, under acid soil conditions for example, to be transferred and locked in the sediment, while remaining "reactive" to dilute acid.

The simulated and observed patterns of the sediment contents of Cu, Zn and Pb over time (Figure 3.7) are in reasonable agreement. This does not reflect successful modelling of reactive metal in soil and water, but rather results from the relatively simple process of metal accumulation, due almost entirely to metal directly deposited to the lake surface and then transferred to the sediment. However it does confirm that the timing of metal deposition assumed in the catchment modelling is approximately correct.

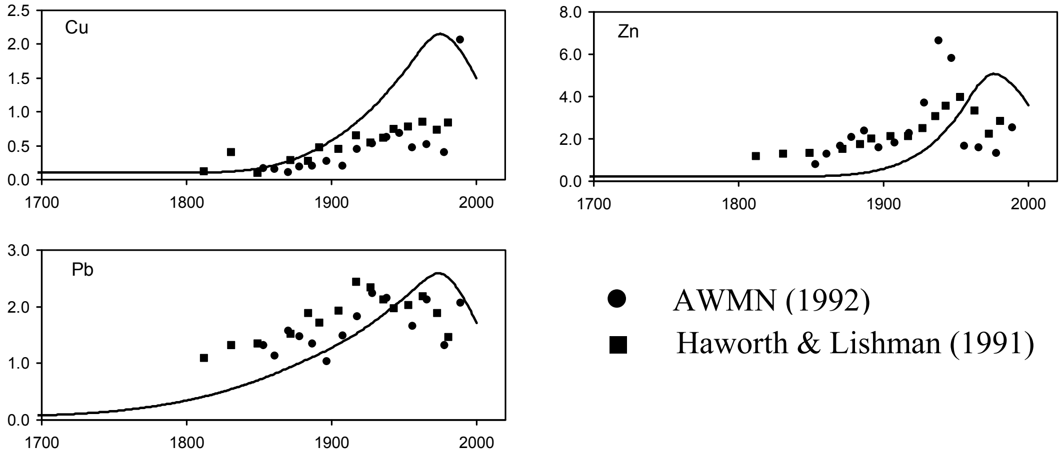


Figure 3.7 Observed and simulated sediment metal concentrations for Scoat Tarn. The y-axis has units of µmol g^{-1} in each case.

3.2.3.2. Howden Reservoir

Sediment metal accumulation in Howden Reservoir was modelled in the same way as for Scoat Tarn. The reservoir has a much greater sediment accumulation rate, averaging 1800 g m^{-2} a^{-1}, about 14 times that for Scoat Tarn. This accords with the much higher stormflow suspended particulate concentrations in the area of Howden Reservoir (Rothwell et al., 2007). The reservoir sediment differs from that of the tarn, in having a greater mineral content and higher bulk density (0.4 g cm^{-3}). The third major difference is that the reservoir has only existed since 1914, and so sediment accumulation covers less than 100 years.

Metal contents of the Howden Reservoir sediment were calculated by summing the contributions of (a) "inert" metal directly deposited from the atmosphere to the reservoir surface and transferred to the sediment, using the same fractions dissolved as for Scoat Tarn, (b) "inert" metal entering in physically eroded mineral matter, estimated from the compositions of local rock samples (Table 3.2), and (c) reactive metal, calculated by the model to be transported sorbed to particulates or captured from the water column.

Table 3.8 Modelled metal inputs to Howden Reservoir sediments

Metal	Sediment pool mmol m^{-2}		Fractional modelled contributions to sediment metal		
	calc	obs	Direct deposition	Physical erosion	Reactive
Ni	31	120	0.33	0.16	0.51
Cu	77	91	0.31	0.06	0.62
Zn	780	420	0.05	0.01	0.94
Cd	2.8	2.3	0.14	0.02	0.84
Pb	110	130	0.29	0.03	0.69

The calculated sediment metal pools are of similar magnitude to the measured values, with reasonable agreements for Cu, Cd and Pb, but underestimation by a factor of four for Ni and overestimation by nearly a factor two for Zn The calculated fractions of the three sources of metal differ appreciably from those for Scoat Tarn, since now the reactive metal is dominant in all cases.

Measurements of reactive metal in Howden Reservoir sediments (Section 3.2.2.2) indicate this fraction comprises 17 % (Ni), 55 % (Cu), 43 % (Zn), 90 % (Cd) and 68 % (Pb) of the total metal. Except for Ni, these are much higher than the values for Scoat Tarn, and this difference is also found in the calculated values, with reasonably good agreements for Cu, Cd and Pb, but overestimation of the reactive fraction of Zn.

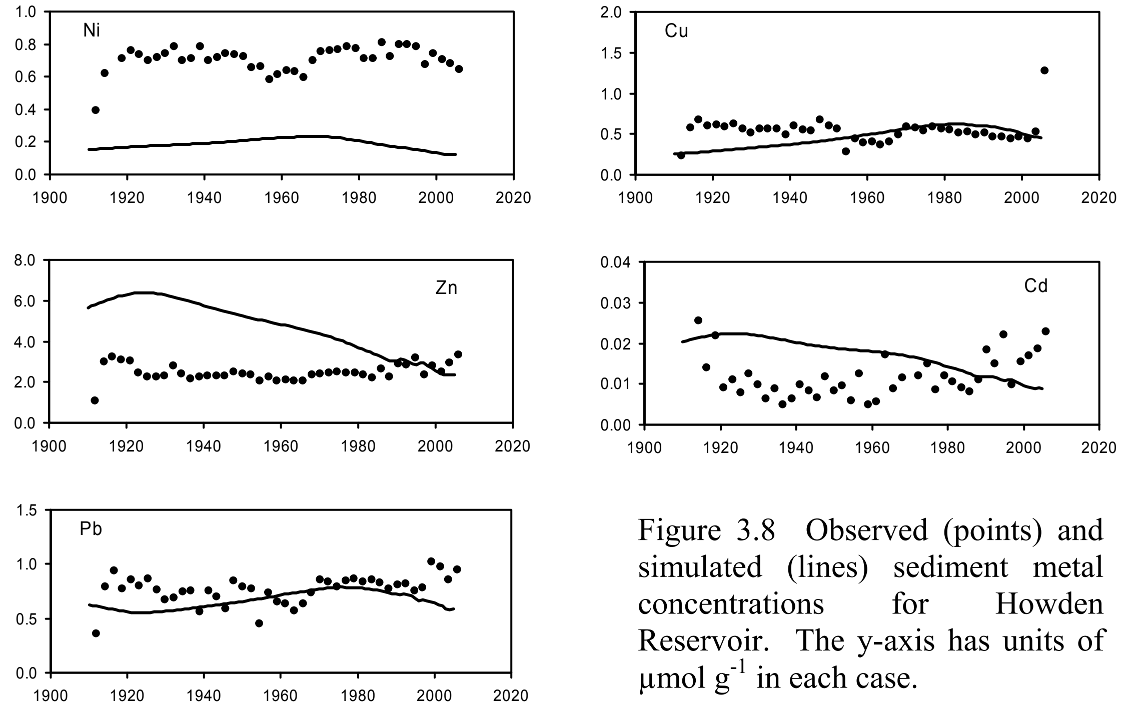


Figure 3.8 Observed (points) and simulated (lines) sediment metal concentrations for Howden Reservoir. The y-axis has units of µmol g^{-1} in each case.

Observed metal sediment profiles for Howden Reservoir (Figure 3.8) differ markedly from those for Scoat Tarn (Figure 3.7) in that none of the metals shows a pronounced subsurface sediment metal peak. The simulations show more variation with time than the observations, but they are less pronounced than those calculated for Scoat Tarn, in agreement with the observations.

The simulations for Howden Reservoir indicate that most the sedimentary metal is derived from the catchment, with less than 35% coming from direct deposition to the reservoir surface. This agrees with Shotbolt et al. (2007), who concluded that most of the Pb in the sediment was anthropogenically-derived, "initially deposited onto drainage basin soils and subsequently entering the reservoir via erosion and leaching processes".

3.2.4. Summary and conclusions

The two water bodies differ considerably in the way that their sediments have accumulated metals. Scoat Tarn has received most of the metals from direct atmospheric deposition to the water surface, whereas the metals in the Howden Reservoir sediments have largely originated from the catchment, due to transfer of soil that was contaminated with metals in the past.

In the case of Scoat Tarn, the results provide general support for our estimates of the timing and magnitude of metal inputs in the past. The results from deep in the sediment suggest higher background inputs than the model currently assumes. This may mean that atmospheric deposition rates were higher in the past, or that inputs from physical erosion are underestimated.

The metal contents and variation (or lack of variation) with depth for Howden Reservoir sediments fit the picture of high deposition to the soils, deduced to have occurred in the 19th Century (see Figure 3.10 below). On this basis, the model produces sediment metal contents of the right magnitude for four of the heavy metals, while underestimating that of Ni.

Neither of these case studies has produced data that can truly test the geochemical process basis of CHUM-AM to a greater degree than has been possible before, but there has been no major challenge to the model's assumptions. It is perhaps too much to ask the model faithfully to reproduce the sediment records, given that several processes combine to determine metal accumulation, and that each of them is inevitably only approximated by the model. However, the plots in Figures 3.7 and 3.8 show that the magnitudes of sediment metal contents can be accounted for (except for Ni at Howden Reservoir). Also, the approximate dates of peak metal accumulation in the Scoat Tarn sediments are fairly well estimated.

Consideration of Tables 3.7 and 3.8 shows that the simulated total sediment metal contents are acceptably close to the observed values for Cd and Pb. The Ni content is overestimated for Scoat Tarn, but underestimated for Howden Reservoir. Copper is overestimated at Scoat Tarn, but correct for Howden Reservoir, whereas the opposite applies to Zn. Overall, therefore, the present results to not call into question the assumed patterns and magnitudes of atmospheric metal deposition that we are using in our dynamic modelling studies.

3.3. Scenario analysis with CHUM-AM

The objective of this part of the project was to model heavy metal behaviour in soils and waters in a selection of UK upland catchments, in order to provide information and understanding about the magnitude and timing of future heavy metal responses to changes in (a) the atmospheric deposition of metals, (b) soil and water acidity, and (c) the carbon status of soils and waters. This was done using the process-based catchment model CHUM-AM (see Section 3.2.1).

3.3.1. Study catchments

As a result of this previous modelling, and some further refinements applied in the present project, versions of CHUM-AM were available for 11 upland UK catchments. Of these, five contrasting catchments were chosen for scenario analysis (Table 3.9). It should be noted that the catchments were not chosen on the basis of their heavy metal levels, but in order to explore and quantify the soil and water processes that control heavy metals, for representative cases. Thus the five catchments considered here are not especially impacted by heavy metals.

Table 3.9 Catchments chosen for scenario analysis

Catchment	Rain mm	Vegetation	Soils	Weathering	Soil pH*	Stream pH*
Cote Gill Pennines	1210	Calcareous grassland	Brown earths	Carbonate	5.3	8.3
R Etherow Pennines	1210	Heather moorland	Blanket peat	Silicate	3.7	6.1
Gaitscale Gill Lake District	3060	Acid grassland	Rankers, podzols	Silicate, carbonate	4.5	5.3
Hardknott Gill Lake District	3060	Acid grassland	Rankers, podzols	Silicate, carbonate	5.4	6.7
Old Lodge Ashdown Forest	830	Heathland	Podzols	Silicate	4.4	4.9

* in 2000

3.3.1.1. Major component histories

The major components determine the acidification status etc of the soil and water, against which the metals operate. Past observed and simulated pH, nitrate and sulphate concentrations, for the soils and streamwaters of the study catchments are shown in Figure 3.9. The observations are from CEH work (Tipping et al., 1998, 2000) and from the AWMN (Monteith, 2005; Shilland et al., 2006) for R. Etherow and Old Lodge. The major change over the past 200 years has been the increase then decline in sulphate concentrations, due to atmospheric deposition. However in the two Lake District catchments (Gaitscale Gill and Hardknott Gill) there are now signs of an increase in nitrate concentration. The increase is not fully clear from the results in Figure 3.9, but other Defra-funded work shows a clear increase in nitrate concentrations over the past 50 years in Lake District lakes, attributable to atmospheric deposition (Tipping et al., 2007).

The five catchments differ with respect to their streamwater DOC concentrations, the average values of which (in mg l^{-1}) vary from 1.0 in Gaitscale Gill and Hardknott Gill to 2.2 in Cote Gill, 4.0 in the Old Lodge stream, and 6.9 in the R. Etherow. This export of organic matter from the catchment soils plays an important role in the transport of metals, especially Cu and Pb, because of strong metal-organic interactions. Taking account of these interactions is an important part of the modelling.

3.3.1.2 Metal deposition histories

To run the model, heavy metal deposition histories were constructed. These comprised (a) a "background" deposition pattern assumed to apply to all UK catchments. Tipping et al. (2005b) derived the following equation to describe the contribution of anthropogenic activities to this pattern, up to 1960;

$$D_A = D_{A,\max} \times (y - y_0 / 1960 - y_0)^n \tag{3.6}$$

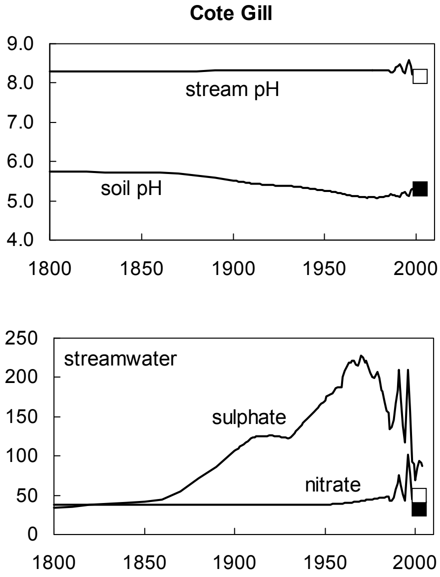
Here, D_A is the anthropogenic deposition in a given year (y). The year in which anthropogenic deposition began is y_0, and n is a parameter that describes the rate at which deposition increased, to the maximum at 1960. Deposition was assumed constant from 1960 to 1970, with a subsequent linear decrease (fitted to the data reported by Baker, 2001) to the 2000 value. Background deposition (D_B) was calculated from the estimates by Nriagu (1989) of global natural sources of atmospheric trace metals, deposition being assumed to equal emission, and to be evenly spread over the Earth's surface. The value of $D_{A,\max}$ was obtained by subtracting D_B from the observed total for 1970. Then, given D_B, $D_{A,\max}$ and n, deposition from 1400 to 1960 could be calculated. The parameter values are shown in Table 3.10.

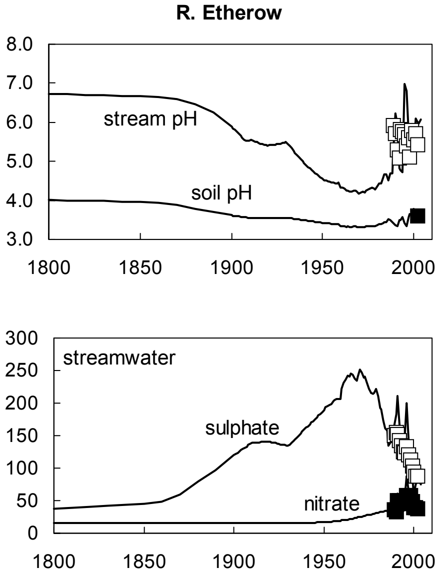
Table 3.10 Heavy metal parameters for background deposition; see equation (3.6). Deposition (D_B, $D_{A,max}$) is in μmoles m^{-2} a^{-1}.

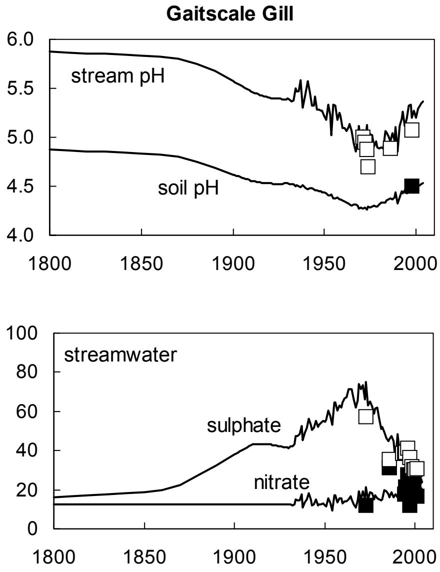
	D_B	y_0	n	$D_{A,max}$			
				CG	Eth	GG & HG	OL
Ni	1.0	1800	1.5	67	81	67	66
Cu	0.9	1800	2.5	127	150	81	78
Zn	1.4	1800	4.5	710	850	650	630
Cd	0.02	1800	3.5	2.9	3.5	2.4	2.4
Pb	0.11	1600	3.5	120	140	79	77

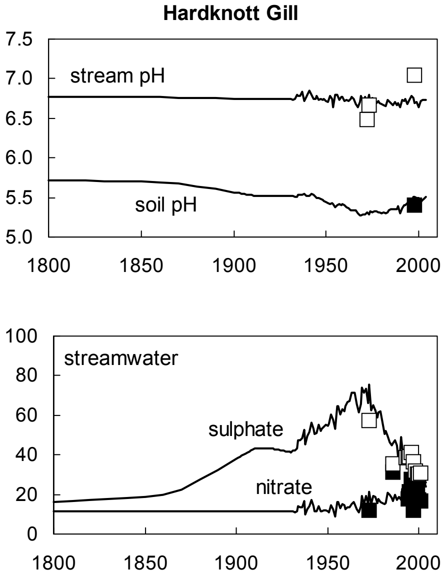
For two of the sites considered in the present study, additional heavy metal deposition took place in the 19th Century, due to nearby intensive mining and smelting (Ashmore et al., 2004). Therefore, a second deposition pattern, estimated from mining records, was added to the background pattern.

Figure 3.10 shows the deposition histories assumed for each metal at the five study sites. The proximity of the Gaitscale Gill and Hardknott catchments means that identical deposition histories could be used for this pair of sites. To put the histories into context, values for the years 1965 and 2000 are compared with measured values for recent years, and with Critical Loads, in Table 3.11. Deposition rates fell markedly during the last decades of the 20th Century, but there has been little systematic change over the last 7 years.









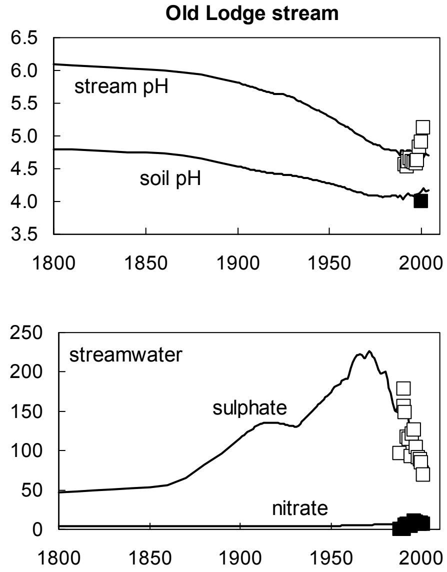


Figure 3.9 Evolution of soil and streamwater major component concentrations, 1800-2000. The points are observations (yearly averages), the lines are CHUM simulations.

Table 3.11 Metal deposition rates (µmoles m^{-2} a^{-1}); modelled for 1965 and 2000, measured at the study sites for 2002-3, and interpolated for 2004&5 from Fowler et al. (2006). Critical Loads* are also shown, in italics.

metal	years	Cote Gill	River Etherow	Gaitscale Gill	Hardknott Gill	Old Lodge
Nickel	1965	68	82	68	68	67
	2000	9.0	11	11	11	8.8
	2002-3	15	12	13	13	7.9
	2004&5	10	15	14	14	7.2
	[CL]	*900*	*12000*	*13000*	*4900*	*1300*
Copper	1965	130	150	82	82	79
	2000	23	28	18	18	15
	2002-3	16	20	13	13	15
	2004&5	25	48	23	23	24
	[CL]	*9.7*	*440*	*160*	*52*	*19*
Zinc	1965	710	850	650	650	630
	2000	180	220	200	200	160
	2002-3	140	140	130	130	110
	2004&5	170	270	200	200	130
	[CL]	*420*	*1500*	*3300*	*2100*	*280*
Cadmium	1965	2.9	3.5	2.4	2.4	2.4
	2000	0.91	1.1	0.90	0.90	0.73
	2002-3	1.1	0.68	0.52	0.52	0.46
	2004&5	0.44	0.76	0.51	0.51	0.41
	[CL]	*7.5*	*28*	*60*	*37*	*5.1*
Lead	1965	120	140	79	79	77
	2000	26	31	21	21	17
	2002-3	11	17	11	11	8.2
	2004&5	12	22	14	14	11
	[CL]	*2.6*	*100*	*60*	*17*	*6.6*

* Calculated using catchment-specific data, and averaged for the years 1965 and 2000.

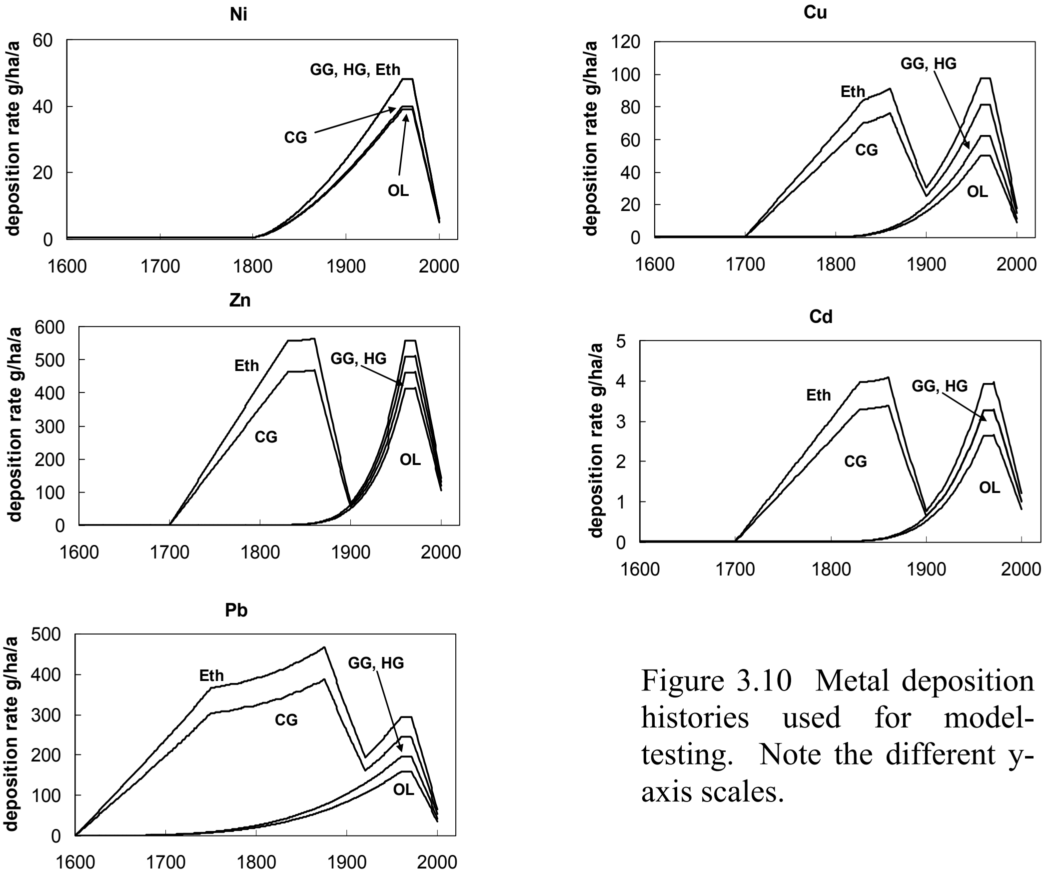


Figure 3.10 Metal deposition histories used for model-testing. Note the different y-axis scales.

3.3.1.3. Weathering inputs

Weathering inputs of heavy metals to the catchments of the River Etherow, Gaitscale Gill, Hardknott Gill, and Old Lodge were estimated by assuming congruent dissolution of catchment silicate minerals, and that the observed Si fluxes in the streams were in steady state. Then metal input fluxes to the soil-water system were obtained by multiplying the element/Si ratios in the mineral matter by the Si fluxes. Experimental work to investigate whether this approach is justified is described in Section 3.1. Inputs to Cote Gill were estimated from limestone metal contents (Bárány-Kevei et al., 2001), with ratio-ing to the Ca flux instead of the Si flux. The weathering inputs to the five study catchments are shown in Table 3.12. The values can be compared with inputs from deposition; they generally fall between those estimated for deposition under "pristine" conditions (Tables 3.10) and present-day deposition (Table 3.11).

Table 3.12 Heavy metal weathering inputs (µmoles m^{-2} a^{-1}) estimated assuming congruent dissolution of minerals (see Section 3.1). The upper values are the inputs to the soil layer only, the lower values the total weathering input.

metal	Cote Gill	River Etherow	Gaitscale Gill	Hardknott Gill	Old Lodge
Nickel	3.6	7.7	2.2	3.7	1.3
	23	12	7.8	7.6	1.9
Copper	1.3	5.3	1.2	2.1	0.88
	8.0	7.9	4.4	4.2	1.3
Zinc	5.3	6.5	2.9	4.9	1.1
	34	9.7	10	10	1.6
Cadmium	0.013	0.011	0.0058	0.0097	0.0018
	0.083	0.016	0.021	0.020	0.0027
Lead	0.44	0.38	0.22	0.37	0.063
	2.8	0.57	0.79	0.77	0.095

3.3.1.4. Simulation of contemporary conditions

Model runs were conducted using the histories described above, to simulate present-day heavy metal soil pools and streamwater concentrations. Figure 3.11 shows observed and simulated contemporary soil pools and streamwater concentrations for the five study catchments, and also for Lochnagar, which was analysed as part of the previous Defra-funded contract, the results of which are published (Tipping et al., 2007) in a book covering all aspects of the lake (Rose, 2007).

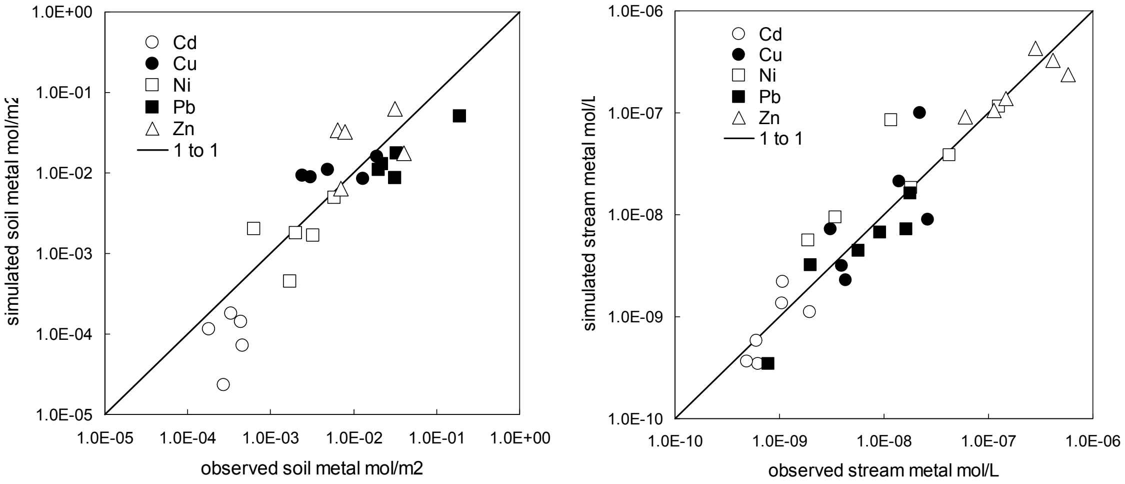


Figure 3.11 Observed and simulated soil metal pools and streamwater concentrations (mean annual values). Data for Cote Gill are omitted from the left panel, because the acid extraction method used to determine geochemically-active soil metal would have dissolved residual limestone, to give erroneously high values.

Bearing in mind that the results are predictions, apart from those for Pb (see above), and that there are inevitable uncertainties in both the input data (metal deposition rates) and the estimates of geochemically-active metals, the agreement is reasonable, mostly to within a factor of three. The ability of the model to achieve this level of agreement is the justification for performing scenario analyses to forecast possible future behaviours of the heavy metals in the five study catchments. However, the modelling provides only a first approximation, and has not been fully tested, for example with time-series data.

The calculations provide estimates of the extents of enrichment of the soils and waters with pollutant heavy metals. This can be done by comparing the current metal soil pools and streamwater concentrations with those calculated for the "pristine" steady state conditions that are assumed to have pertained before the onset of anthropogenic inputs to the atmosphere. The results depend strongly on the pristine conditions, which are quite crudely estimated from assumed metal weathering inputs and background atmospheric deposition. Therefore the current / pristine ratios of Table 3.13 are our best available estimates, but must be treated with due caution. The ratios display considerable variation among metals, among catchments, and between soil and water.

Table 3.13 Ratios of simulated metal variables in 2000 to those under past "pristine" conditions.

	Cote Gill	River Etherow	Gaitscale Gill	Hardknott Gill	Old Lodge
Soil metal pools					
Ni	2.8	2.0	3.6	5.0	3.5
Cu	3.4	10	5.6	4.8	3.0
Zn	17	22	30	34	15
Cd	11	20	14	22	7.3
Pb	13	135	14	3.6	22
Streamwater concentrations					
Ni	1.6	2.4	3.4	6.8	11
Cu	1.1	11	4.3	1.9	1.9
Zn	3.1	24	24	38	47
Cd	5.2	30	24	41	33
Pb	1.2	54	11	1.3	22

For soils, the enrichments due to human activities are generally greatest for Zn, Cd and Pb, the ratios for these three metals averaging 25, compared to the average of 4.4 for Ni and Cu. The differences reflect both the higher relative deposition of Zn, Cd and Pb (Table 3.10) and their lower relative weathering inputs (Table 3.12). This is especially true for the R. Etherow catchment. The Hardknott Gill soil is relatively un-enriched in Pb because its higher pH and moderately high weathering input mean that under pristine conditions the soil Pb content was fairly high.

Streamwaters tend to follow the same pattern of greater enrichments in Zn, Cd and Pb, but neither Cote Gill nor Hardknott Gill is much enriched in either Cu or Pb, because strong sorption by the soil effectively traps atmospherically deposited metal.

The Critical Loads approach deals with steady-state, but none of the catchments considered here are near to this condition with respect to heavy metals. Soil pools of the three metals, Ni, Zn and Cd, that bind relatively weakly to the soil solids are calculated to have varied substantially over the last 100-200 years, due to increased inputs and changing acidity status. Copper and lead are less affected by acidification, but their strong sorption properties mean that their steady-state pools would be large, and the time period of metal capture has been too short for them to approach steady state, even with respect to the reduced current metal deposition.

3.3.2. Future scenarios

CHUM-AM was run with different future scenarios to explore the extent and timing of heavy metal behaviour. In constructing the scenarios, we planned to examine variations in the following:

- Deposition of heavy metals
- Deposition of pollutant sulphur
- Deposition of pollutant reduced nitrogen
- Deposition of pollutant oxidised nitrogen
- The flux of dissolved organic matter within and from soils
- The soil content of organic matter

However it is impractical to investigate all combinations of the above. If, for example, three separate scenarios were decided for each of the six variables, and all combinations of scenarios were run, the total number of runs for each study site would be 3^6, i.e. 729, or a total of 3645 runs for all five sites together. This would produce an unmanageable amount of output. Therefore, we focused on a limited number of possibilities, choosing the most realistic scenarios, but also examining some more extreme cases in order to establish the range of conceivable outcomes.

Because we know that at some sites, and for some metals (notably Cu and Pb), rates of change in metal pools is likely to be slow, we have to take both a short-term and a long-term perspective. The scenarios were therefore constructed to cover the period 2000-3000, but the outputs were scaled to provide progressive forecasts, for the years 2030, 2060, 2100, 2300 and 3000.

3.3.2.1 Scenarios for heavy metals

There are currently no reliable forecasts for future heavy metal deposition, as there are for S and N (see below). It is known that deposition rates fell substantially between the 1970s and the present. Thus, for the 10 sites to which CHUM has so far been applied, the Critical Load (deposition) was exceeded in 2000 in only four cases; for Cu and Pb at Cote Gill (Pennines), and for Pb at Hardknott Gill (Lake District) and Old Lodge (Ashdown Forest). Comparison of data from the 1998-2002 with the most recent data from the Heavy Metals Monitoring Network (Fowler et al., 2006), suggests that metal deposition is possibly continuing to fall for Ni, Zn, Cd and Pb, but that Cu deposition may have risen at some sites. However, we cannot be sure that this will continue to be the case, and changes in economic activity, and long range transport, may give rise to future increases. Therefore, the following four scenarios were employed.

M1	Metal deposition rates stay constant at 2000 values.
M2	Deposition rates fall linearly to background levels (i.e. estimated past conditions with metals only deposited from natural sources) between 2000 and 2050, then stay constant.
M3	Rates increase linearly to 1990 values between 2000 and 2050, then stay constant.
M4	Deposition falls to 50% of the 2000 value by 2020, then stays constant.

Scenario M3 is unlikely, but provides a yardstick against which to judge the two low-deposition scenarios, and to show the rate of change of soil and water metal concentrations. Scenario M4 is similar to forecasts from the ESPREME EU project (http://espreme.ier.uni-stuttgart.de).

3.3.2.2. Scenarios for sulphur deposition

Sulphur deposition has been decreasing for some time, and according to forecasts based on the Gothenburg Protocol (GP), it will fall further. However, there is evidence that emissions are increasing due to shipping, associated with the rise of the Chinese economy. Therefore, we adopted a second scenario in which there is no further change in S deposition from 2000.

S1	Use forecasts from the GP of the relative decrease in S deposition from 1990 to 2010, scale these to the measured or estimated values for the individual field site. After 2010, keep the deposition rate constant.
S2	S deposition held constant at the 2000 value.

3.3.2.3. Scenarios for nitrogen deposition

For the sites under study, the form (oxidised or reduced) of deposited N is not important, because the model treats all input N as equivalent, and the leached form is predominantly nitrate at all the study sites. Therefore we can use deposition scenarios just of total N, and simplify the analysis. On the basis of the Gothenburg Protocol, the deposition of nitrogen is forecast to fall between 1998-2000 and 2010. For comparative purposes, it is proposed to compare the forecast based on the Gothenburg Protocol with a scenario in which N deposition stays constant. Furthermore, scenario N3 was included, because it avoided the re-acidification of the GG site in particular, which may even occur under scenario N1 (this depends upon N “breakthrough” due to soil overload, which is yet to be fully understood; see Tipping et al., 2007).

N1	Use forecasts from the GP of the relative decrease in N deposition from 1990 to 2010, scale these to the measured or estimated values for the individual field site. After 2010, keep the deposition rate constant.
N2	N deposition held constant at the 2000 value.
N3	N deposition falls to 50% of 2000 value by 2020, then stays constant

3.3.2.4. Scenarios for DOM (dissolved organic matter) concentration

A key process in metal behaviour is co-transport with dissolved organic matter (DOM), which is especially important for Cu and Pb. Concentrations of DOM -

[DOM] - have been increasing in upland UK waters for several decades (Worrall et al., 2004) and this has implications for metal transport. It is not yet known with any certainty what is causing the increases, but the best-argued case is currently in favour of a reversal of acidification (Evans et al., 2005). This operates through the pH-dependence of DOM solubility, and therefore the current increase can be considered the recovery phase, i.e. there was presumably a decrease in [DOM] during the development of acidification. Dynamic metal modelling to date has assumed constant [DOM]. Therefore it is of interest to compare forecasts that include changes in [DOM] with those that consider it constant. The model currently assumes that the soil water flux of DOM is the same as that in the streamwater. The scenarios used were as follows.

DOM1	[DOM] remains constant at average values over the recent record.
DOM2	[DOM] increases by a factor of two between 2000 and 2050, after which it is constant.

3.3.2.5. Scenarios for SOM (soil organic matter) content

Changes in temperature and soil moisture, fertilisation by increases in atmospheric CO_2 and by N deposition, and other drivers, may affect soil organic matter (SOM) pools, and this could have consequences for heavy metal behaviour because components of SOM are mainly responsible for metal adsorption by soil. To date, we have assumed that SOM pools are in steady state.

Changes in SOM pools are difficult to forecast on the basis of present knowledge. It is possible that SOM pools could either decrease, due to increased rates of decomposition (e.g. due to warming and drying), or increase, due to the greater availability of C, or nutrient N. Bellamy et al. (2005) claimed that SOM in organic-rich soils (which dominate our study sites) has declined substantially over the last 25 years, and from their results changes in SOM pools of about one-third can be calculated. However, these results are controversial and remain to be confirmed. Therefore the SOM scenarios involve both increases and decreases, as follows.

SOM1	SOM pools remain constant.
SOM2	SOM pool increases by 25% between 2000 and 2100, and then stays constant.
SOM3	SOM pool decreases by 25% between 2000 and 2100, and then stays constant.

A point to bear in mind in relation to changes in soil SOM is that the model was modified by changing the SOM pool expressed in g m^{-2}, but the volume of soil was not changed. Therefore the concentration of SOM also changed in proportion. For highly organic soils this would imply a change in bulk density, which seems unrealistic – thinning or thickening of the active layer would be more likely. Nonetheless, the calculations should provide some insight into the effects of changes in SOM on metal behaviour.

3.3.2.6. Combinations of scenarios

The individuals scenarios were combined into 13 combinations, named SC1 to SC13 as follows. Table 3.14 presents the scenarios in words, and provides brief descriptor phrases.

	M1	M2	M3	M4	S1	S2	N1	N2	N3	DOM1	DOM2	SOM1	SOM2	SOM3
SC1	●				●		●			●		●		
SC2		●			●		●			●		●		
SC3			●		●		●			●		●		
SC4	●					●		●		●		●		
SC5			●			●		●		●		●		
SC6	●				●		●				●	●		
SC7			●		●		●				●	●		
SC8	●				●		●			●			●	
SC9			●		●		●			●			●	
SC10	●				●		●			●				●
SC11			●		●		●			●				●
SC12	●				●				●	●		●		
SC13				●	●		●			●		●		

Table 3.14 The 13 scenarios.

	Description	Descriptor phrase
SC1	Baseline metals, N, S, DOM, SOM	*baseline*
SC2	Baseline N, S, DOM, SOM - metal inputs fall to background by 2050	*background metals*
SC3	Baseline N, S, DOM, SOM - metal inputs increase to 1990 values by 2050	*higher metals*
SC4	Baseline metals, DOM, SOM - N and S inputs remain at 2000 levels	*high N & S*
SC5	Baseline DOM, SOM - metal inputs increase to 1990 values by 2050, and N and S inputs remain at 2000 levels	*higher metals,* *higher N & S*
SC6	Baseline metals, N, S, SOM - [DOM] doubles by 2050	*higher DOM*
SC7	Baseline N, S, SOM - metal inputs increase to 1990 values by 2050, [DOM] doubles by 2050	*higher metals,* *higher DOM*
SC8	Baseline metals, N, S, DOM - SOM increases by 25% by 2100	*higher SOM*
SC9	Baseline N, S, DOM - metal inputs increase to 1990 values by 2050, SOM increases by 25% by 2100	*higher metals,* *higher SOM*
SC10	Baseline metals, N, S, DOM - SOM decreases by 25% by 2100	*lower SOM*
SC11	Baseline N, S, DOM - metal inputs increase to 1990 values by 2050, SOM decreases by 25% by 2100	*higher metals,* *lower SOM*
SC12	Baseline metals, S, DOM, SOM - N inputs fall by 50% by 2020	*lower N inputs*
SC13	Baseline N, S, DOM, SOM - metal inputs fall to 50% of 2000 levels by 2020	*lower metals*

3.3.3. Scenario analysis results

3.3.3.1. Acidification status

Before considering the results for the heavy metals, it is worth considering the effects of the scenario choices on soil and water pH, since these respond non-linearly to changes in N and S deposition. The scenarios to consider first are those in which N and S inputs differ, with other factors remaining the same, i.e. SC1 (*baseline*, involving scenarios N1 and S1), SC4 (*high N and S*, S2 and N2) and SC12 (*lower N inputs*, S1 and N3). Predicted soil and stream pH values are plotted for these three scenarios for Gaitscale Gill and R. Etherow in Figure 3.12.

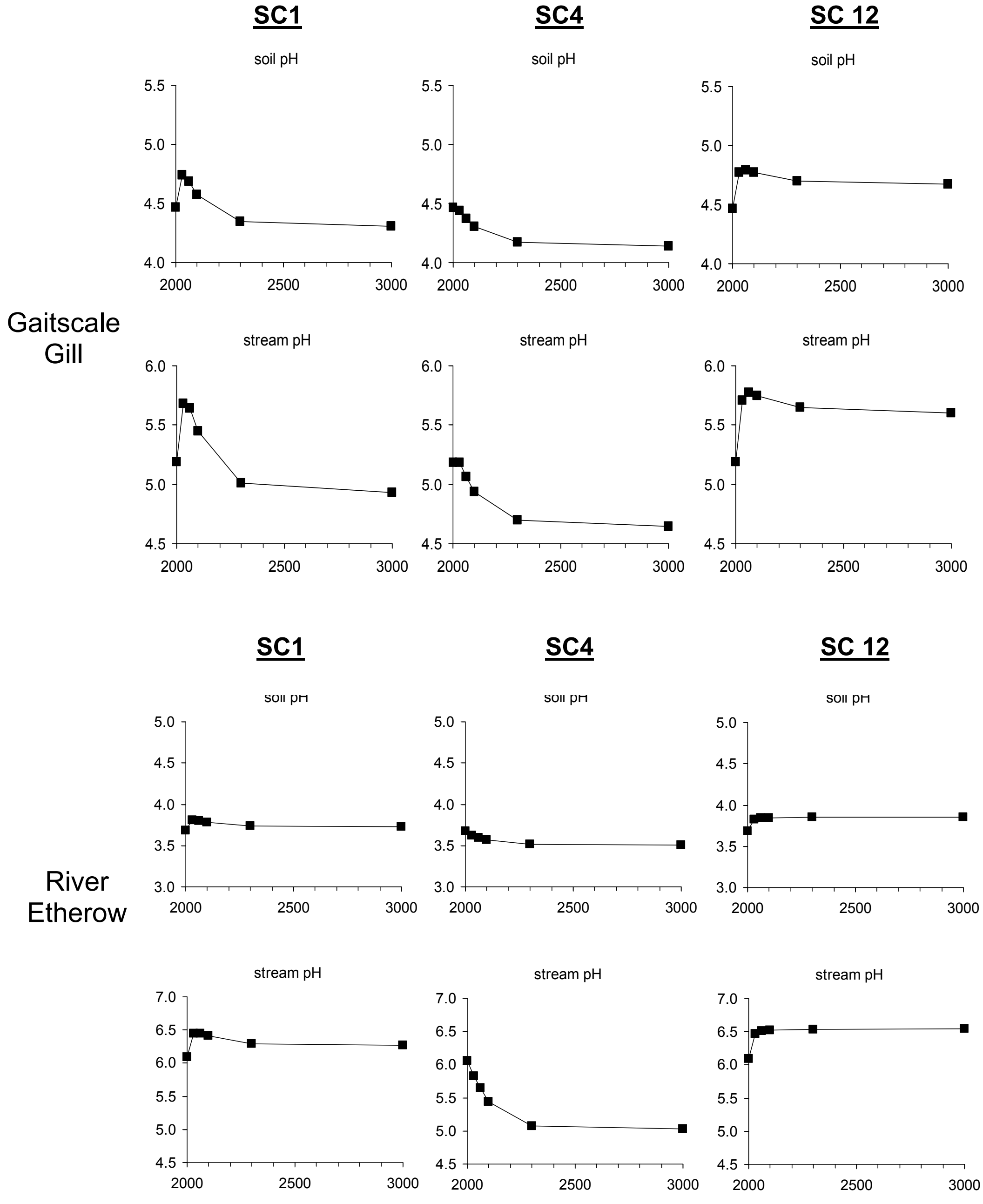


Figure 3.12 Soil and stream pH for Gaitscale Gill and R. Etherow, under scenarios SC1, SC4 and SC12

For Gaitscale Gill, SC1 predicts soil and stream acidification, due to the saturation of the system with N, and consequent breakthrough of nitrate, which follow from the model's way of describing the N cycle (see Tipping et al. 2005a). The effect is more severe under scenario SC4, but the reduction of N inputs under SC12 approximately stabilises the degree of acidification. The same trends are apparent at R. Etherow, but here the soil is able to absorb more N, and so nitrate breakthrough is manifest only in SC4. The forecasts for Old Lodge are approximately intermediate between Gaitscale Gill and R. Etherow, while Hardknott Gill and Cote Gill are sufficiently well buffered to resist the effects of nitrate breakthrough.

Changes in organic matter have small effects on acidification for the study catchments. Increasing DOM slightly acidifies the streams at Etherow and Old Lodge. Increasing SOM casues slight acidification during build up to new steady state, while decreasing it has the reverse effect.

3.3.3.2. Metal variables

For each metal, there are four variables to consider –

$\mathbf{M_{soil}}$	the total soil metal pool, expressed in mol m^{-2}, which provides a measure of the accumulation and release of atmospherically-deposited metals
$\mathbf{[M]_{stream}}$	the streamwater metal concentration, a measure of transfer and leaching loss
$\mathbf{RFI_{soil}}$	the ratio of the soil free metal ion concentration to the critical limit value, a measure of metal toxicity in soil
$\mathbf{RFI_{stream}}$	the ratio of the streamwater free metal ion concentration to the critical limit value, a measure of metal toxicity in surface water. (Note that for this exercise we assumed the surface water Critical Limit Functions to be the same as those for the soil.)

Even though the number of scenarios was minimized (see above), there are still many possibilities to consider. If we take these four metal variables, for each of the five metals, for the 13 scenarios, and five catchments, and for five different times, we have a total of 6500 data points. To reduce this number, we treat the metals individually, and confine the analysis to variables averaged over the five catchments, so that 52 data points must be considered for each metal.

We identify only those cases for which the change in the metal variable, compared to the starting value in 2001, is a factor of two or more. This means logarithmic values that are less than -0.3, or more than +0.3. A negative value means that the variable has decreased by at least twofold, a positive value means that has at least doubled.

Generally, a decrease in a variable (negative logarithm) means an improvement in the soil or water conditions, but care must be taken in the interpretation because we are dealing with transient situations.. If M_{soil} decreases, the system is losing metal and therefore becoming less contaminated. However, this loss from the soil could be associated with an increase in the stream concentration, $[M]_{stream}$. More directly significant are RFI_{soil} and RFI_{stream} since these are measures of toxicity.

The changes are summarised in Tables 3.15 to 3.19. These are now discussed for each individual metal, firstly with outputs averaged over all five catchments in order to obtain a representative view of the overall response, then by catchment for SC13.

3.3.3.3. Nickel (Table 3.15, Figure 3.13)

[Ni.1] In 2001, none of the study catchments has Critical Limit exceedances, i.e. all the values of log RFI are negative, and by at least 0.93, i.e. the free-ion concentrations in the soils and waters of all 5 sites are at least 9 times lower than the critical concentration.

[Ni.2] None of the metal variables is predicted to change by a factor of two or more during the next 60 years.

[Ni.3] By 2100, changes (decreases) in three of the four metal variables occur under SC2, as the Ni contents of the catchment decrease due to lowered metal inputs.

[Ni.4] By 2300, 11 changes of a factor of two or more occur, and all are negative, i.e. metal pools, stream metal concentrations, or toxicities decline. Eight of these are accounted for by SC2 and SC13, i.e. those in which metal inputs decrease. Acidification (SC4) causes decreases in the soil Ni pool and in RFI_{stream}. Under SC10 (decrease in SOM), the soil Ni pool decreases, due to soil acidification.

[Ni.5] By 3000, 13 changes of a factor of two or more occur, again all negative. All four metal variables decrease under SC2 and SC13. Three variables decrease under SC4 (*high N & S*), and one each under SC1 and SC10.

[Ni.6] The largest number of changes in the Ni variables result from decreases in Ni inputs (SC2 and SC13). The next most important effect is acidification (SC1, SC4). Under SC10 (*lower SOM*) two changes occur.

[Ni.7] Under several scenarios, no significant changes are predicted, even over 1000 years. In these cases, the decreases described above due to acidification or DOM increases are countered by increased metal inputs (SC3, SC5, SC6, SC7, SC8, SC9, SC11, SC12).

[Ni.8] The largest changes occur under SC2, and are in RFI_{soil} up to 2100 and in M_{soil} thereafter.

[Ni.9] Figure 3.13 compares the changes in Ni variables for the five individual catchments, under scenario SC13. In this scenario, the metal inputs decline by a factor of two between 2000 and 2020, and then remain constant. The soil and water of all five catchments also undergo some acidification under SC13, the changes being most pronounced for Gaitscale Gill and Old Lodge.

The five catchments show similar qualitative responses in all four metal variables. The main quantitative differences among the catchments are in the magnitudes of the changes, and the longer response times, lasting for at least 1000 years, for Cote Gill and Old Lodge. For the other three sites a rapid initial decline, to 2100, is followed by relatively little change over the next 900 years.

The key conclusions for Ni are as follows.

- **(a) Decreases in depositional inputs of Ni during the first part of the 21st Century would significantly reduce the concentrations and toxicity of the metal over 100 years.**
- **(b) Acidification would also reduce Ni levels and toxicity.**
- **(c) Increases in Ni inputs at the levels assumed for the scenarios are unlikely to worsen the concentrations or toxicity of the metal, because of the compensating effects of acidification and/or DOM increase.**
- **(d) The similar qualitative responses of the five catchments mean that the averaged results are probably representative of most upland areas of the UK.**

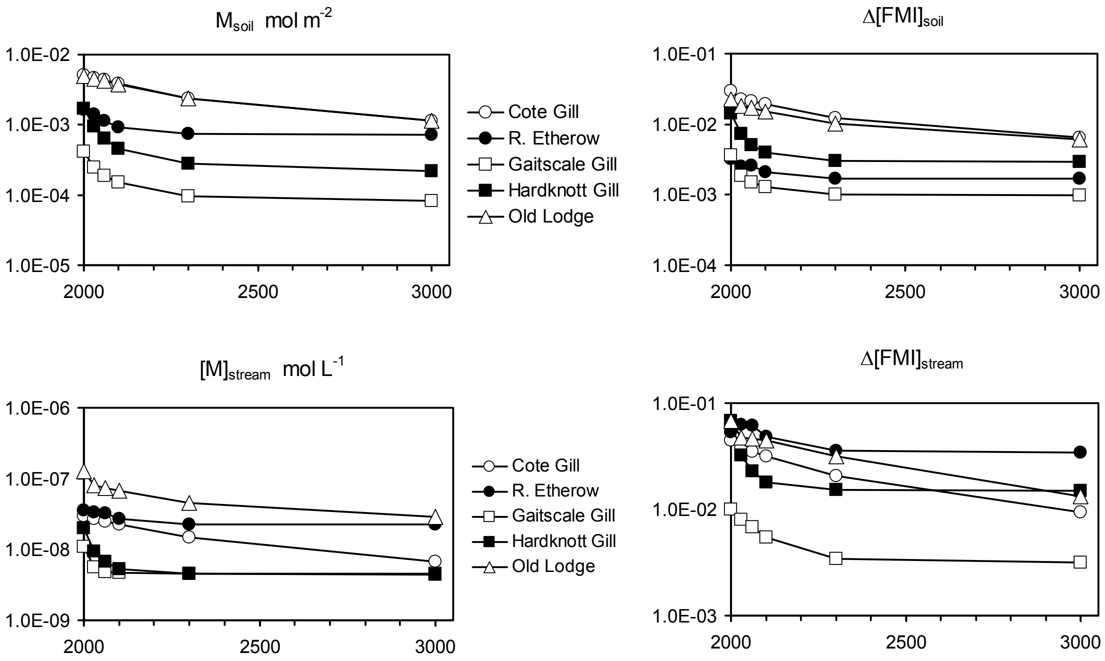


Figure 3.13 Changes in nickel variables in scenario SC13. Note that for the free-metal-ion (FMI) variables, a ratio of 1.0E+00 means that the concentration of Ni^{2+} is equal to that at the critical limit.

Table 3.15 Scenario results for Ni, averaged over five catchments

Exceedances of free-ion Critical Limits in 2001; values of log RFI

	Cote Gill	R. Etherow	Gaitscale Gill	Hardknott Gill	Old Lodge
Soil	-1.53	-2.49	-2.44	-1.84	-1.65
Stream	-0.93	-1.27	-2.00	-1.17	-1.17

Number of scenarios with changes greater than a factor of two

year	M_{soil}	$[M]_{stream}$	RFI_{soil}	RFI_{stream}	Total
2030	0	0	0	0	0
2060	0	0	0	0	0
2100	1	1	1	0	3
2300	4	2	2	3	11
3000	5	2	3	3	13
total	10	5	6	6	27
% of maximum	15	8	9	9	10

Total changes per scenario

		No. of changes	Inc / Dec
SC2	*background metals*	11	Dec
SC13	*lower metals*	8	Dec
SC4	*high N & S*	5	Dec
SC10	*lower SOM*	2	Dec
SC1	*Baseline*	1	Dec
SC3	*higher metals*	0	-
SC5	*higher metals, higher N & S*	0	-
SC6	*higher DOM*	0	-
SC7	*higher metals, higher DOM*	0	-
SC8	*higher SOM*	0	-
SC9	*higher metals, higher SOM*	0	-
SC11	*higher metals, lower SOM*	0	-
SC12	*lower N inputs*	0	-

Largest changes

Year	Scenario	Variable	Log change	Factor
2030				
2060				
2100	SC2	RFI_{soil}	-0.45	0.35
2300	SC2	M_{soil}	-0.65	0.22
3000	SC2	M_{soil}	-0.81	0.15

3.3.3.4. Copper (Table 3.16, Figure 3.14)

[Cu.1] In 2001, none of the soils in the study catchments has a Critical Limit exceedance, i.e. all the values of log RFI_{soil} are negative. Two of the streamwaters have positive values of log RFI and one has log RFI = 0, indicating that copper is likely to be exerting toxic effects. Only for Old Lodge is log RFI_{stream} comfortably less than zero.

[Cu.2] No changes of a factor of two or more are forecast by 2060. By 2100, an increase in RFI_{soil} occurs under SC11 (*higher metals, lower SOM*), and RFI_{stream} increases under both SC10 (*lower SOM*) and SC11.

[Cu.3] Further changes occur by 2300. Under SC11, there are increases in $[Cu]_{stream}$, RFI_{soil} and RFI_{stream}, but there are now no changes under SC10, due to an opposing trend at R. Etherow. Scenario SC5 (*higher DOM, higher N & S*) gives higher $[Cu]_{stream}$ and RFI_{stream}, while SC3 (*higher metals*) just gives higher RFI_{stream} and SC7 (*higher metals, higher DOM*) just higher $[Cu]_{stream}$. One scenario, SC2 (*background metals*), gives decreases, in M_{soil} and RFI_{soil}.

[Cu.4] Of the 19 changes occurring by 3000, 8 are negative, occurring under SC2 (all four variables), SC4 (M_{soil}), SC6 (RFI_{soil}) and SC13 (M_{soil} and RFI_{soil}. Positive changes occur under SC3 ($[M]_{stream}$, RFI_{soil} and RFI_{stream}), SC5 ($[M]_{stream}$ and RFI_{stream}), SC7 ($[M]_{stream}$), SC9 ($[M]_{stream}$ and RFI_{stream}) and SC11 ($[M]_{stream}$, RFI_{soil} and RFI_{stream}).

[Cu.5] Ten of the scenarios causes changes in the Cu variables, six of which worsen the situation and four improve it, most notably SC2 (*background metals*). The coupling of higher metal inputs and a decrease in SOM (SC11) is the most damaging.

[Cu.6] Over the first 300 years of the scenarios, the largest changes (increases) occur under SC11 (*higher metals, lower SOM*). Only after 1000 years do the effects of reducing Cu inputs to background levels result in SC2 being the most scenario causing the largest change.

[Cu.7] Figure 3.14 compares the changes in Cu variables for the five catchments, under scenario SC13. In this scenario, the metal inputs decline by a factor of two between 2000 and 2020, and then remain constant. The soil and water of all five catchments also undergo some acidification, the changes being most pronounced for Gaitscale Gill and Old Lodge.

The catchments differ in the way that the Cu variables change over time. In two cases, R. Etherow and Gaitscale Gill, there are decreases in M_{soil}, and at R. Etherow also a decrease in $[M]_{stream}$. These changes reflect the fact that the soils of both catchments are acid, with Gaitscale Gill soil becoming more acid, so that the metal is not held as strongly as in the other soils, and can be leached. Although Old Lodge soil is also acid, the low runoff at that catchment means a low leaching rate. At Cote Gill, the soil continues to accumulate Cu, despite the reduced input. For the same reasons, the toxicity indicators RFI_{soil} and RFI_{stream} decrease over time at R. Etherow and Gaitscale Gill, while they change relatively little at the other three catchments. However the changes at the two responsive catchments are slow, requiring hundreds of years to take place.

The key conclusions for Cu are as follows.

(a) **Decreases in depositional inputs during the first part of the 21st Century would not reduce the concentrations and toxicity of the metal within 100 years. Significant improvements would require large reductions and take hundreds of years, even in responsive catchments.**

(b) **If depositional inputs remain at current levels, there will be no average change in conditions; some catchments will improve, others worsen.**

(c) **The worst scenario combines higher Cu inputs with a decrease in soil organic matter.**

(d) **Copper is relatively insensitive either to changes in acidification status or increases in DOM production and transport.**

(e) **Copper responses are complex, and differ qualitatively between catchments. Predictions of average behaviour do not therefore fully characterise metal response.**

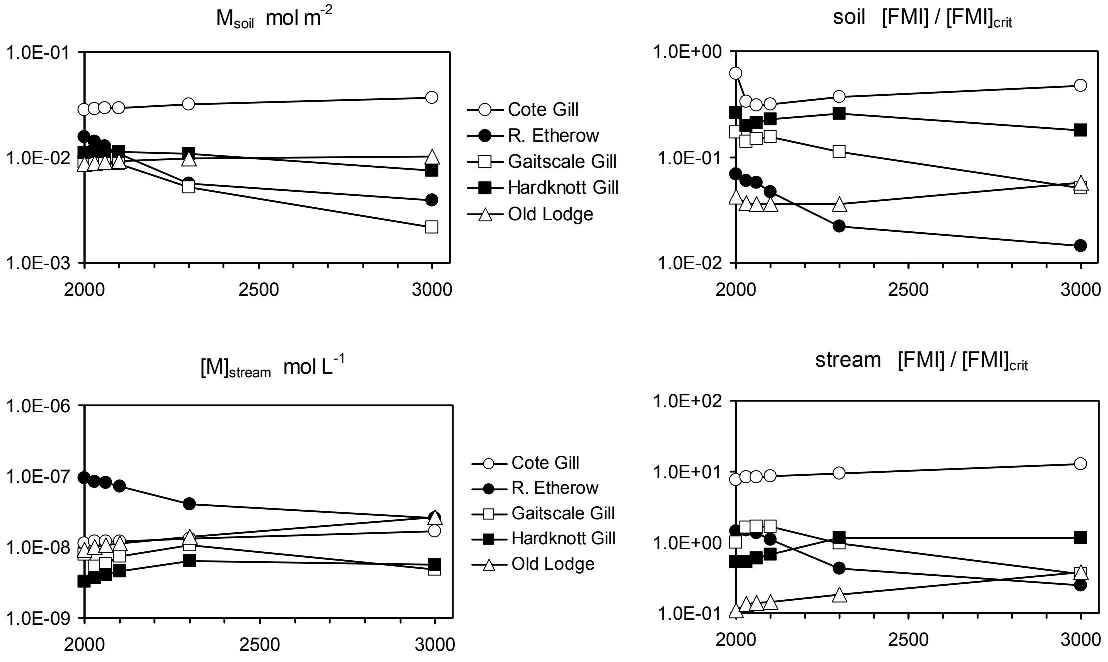


Figure 3.14 Changes in copper variables in scenario SC13. Note that for the free-metal-ion (FMI) variables, a ratio of 1.0E+00 means that the concentration of Cu^{2+} is equal to that at the critical limit.

Table 3.16 Scenario results for Cu, averaged over five catchments

Exceedances of free-ion Critical Limits in 2001; values of log RFI

	Cote Gill	R. Etherow	Gaitscale Gill	Hardknott Gill	Old Lodge
Soil	-1.22	-1.16	-0.77	-0.58	-1.38
Stream	1.16	0.16	0.00	-0.28	-0.98

Number of scenarios with changes greater than a factor of two

year	M_{soil}	$[M]_{stream}$	RFI_{soil}	RFI_{stream}	Total
2030	0	0	0	0	0
2060	0	0	0	0	0
2100	0	0	1	2	3
2300	1	3	2	3	9
3000	3	6	5	5	19
total	4	9	8	10	31
% of maximum	6	14	12	15	12

Total changes per scenario

		No. of changes	Inc / Dec
SC11	*higher metals, lower SOM*	8	Inc
SC2	*background metals*	6	Dec
SC3	*higher metals*	4	Inc
SC5	*higher metals, higher N & S*	4	Inc
SC7	*higher metals, higher DOM*	2	Inc
SC9	*higher metals, higher SOM*	2	Inc
SC13	*lower metals*	2	Dec
SC4	*high N & S*	1	Dec
SC6	*higher DOM*	1	Dec
SC10	*lower SOM*	1	Inc
SC1	*baseline*	0	-
SC8	*higher SOM*	0	-
SC12	*lower N inputs*	0	-

Largest changes

Year	Scenario	Variable	Log change	Factor
2030				
2060				
2100	SC11	RFI_{stream}	+0.43	2.7
2300	SC11	RFI_{stream}	+0.47	3.0
3000	SC2	RFI_{soil}	-0.85	0.14

3.3.3.5. Zinc (Table 3.17, Figure 3.15)

[Zn.1] In 2001, none of the soils in the study catchments has a Critical Limit exceedance, i.e. all the values of log RFI are negative. However, all the values lie between -1.0 and zero, and the ratios of free [Zn^{2+}] to the critical value are between 0.15 and 0.80. The streamwater [Zn^{2+}] at Cote Gill exceeds the critical value by a factor of 2, and the values for the other streams are not greatly lower than the critical limits.

[Zn.2] None of the metal variables is predicted to change by a factor of two or more during the next 60 years. After 100 years, all four variables will decrease under SC2, i.e. if metal inputs fall to background levels, but no changes are seen under the other scenarios..

[Zn.3] By 2300 the response under SC2 continues Under SC11 (*higher metals, lower SOM*), RFI_{soil} increases.

[Zn.4] By 3000, the responses of all four variables continue under SC2, while M_{soil} and RFI_{soil} decrease under SC13 and M_{soil} decreases under SC4 (*high N & S*) due to acidification. Increases in RFI_{soil} and RFI_{stream} take place under SC11, and increases in RFI_{soil} under SC3 (*higher metals*) and SC5 (*higher metals, higher N & S*).

[Zn.5] Under seven of the scenarios there are no predicted changes of twofold or more over the 1000 years of simulation.

[Zn.6] The largest changes come under SC2, in RFI_{soil}.

[Zn.7] Figure 3.15 compares the changes in Zn variables for the five individual catchments, under scenario SC13. In this scenario, the metal inputs decline by a factor of two between 2000 and 2020, and then remain constant. The soil and water of all five catchments also undergo some acidification under SC13, the changes being most pronounced for Gaitscale Gill and Old Lodge.

The five catchments show similar qualitative responses in all four metal variables, and most of the changes largely occur by 2300.

The key conclusions for Zn are as follows.

- **(a) Decreases in depositional inputs of Zn during the first part of the 21st Century would reduce the concentrations and toxicity of the metal within 100 years.**
- **(b) Acidification would also reduce Zn levels and toxicity.**
- **(c) Increases in Zn inputs at the levels assumed for the scenarios could increase the toxicity of the metal in the long term.**
- **(d) The similar qualitative responses of the five catchments mean that the averaged results are probably representative of most upland areas of the UK.**

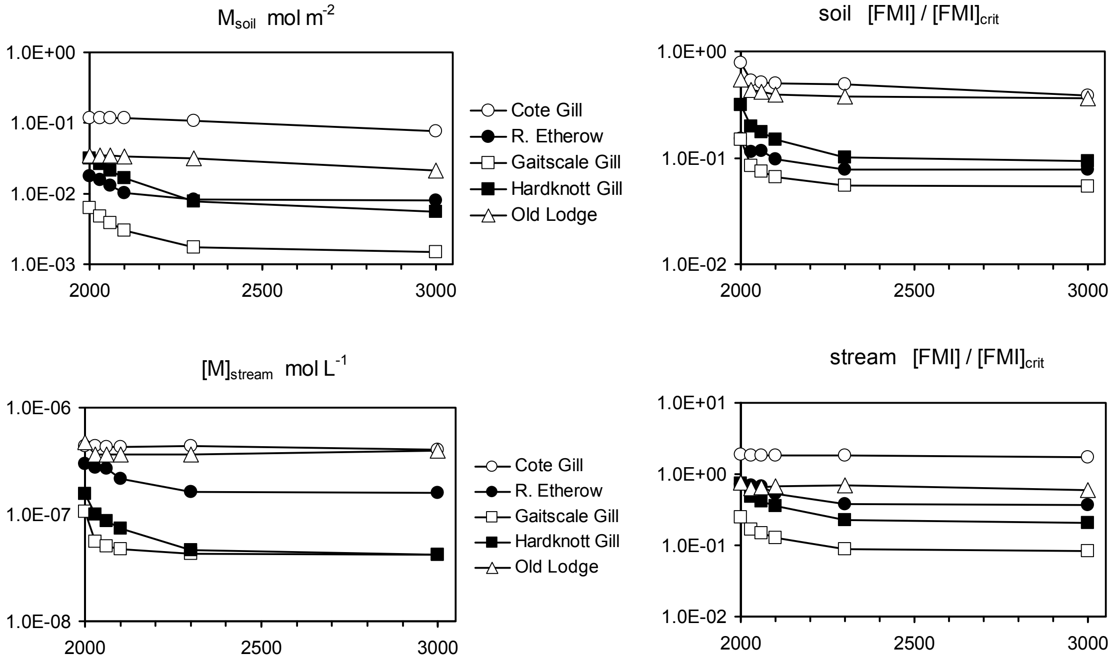


Figure 3.15 Changes in zinc variables in scenario SC13. Note that for the free-metal-ion (FMI) variables, a ratio of 1.0E+00 means that the concentration of Zn^{2+} is equal to that at the critical limit.

Table 3.17 Scenario results for Zn, averaged over five catchments

Exceedances of free-ion Critical Limits in 2001; values of log RFI

	Cote Gill	R. Etherow	Gaitscale Gill	Hardknott Gill	Old Lodge
Soil	-0.21	-0.82	-0.83	-0.50	-0.26
Stream	-0.02	-0.15	-0.61	-0.13	-0.12

Number of scenarios with changes greater than a factor of two

year	M_{soil}	$[M]_{stream}$	RFI_{soil}	RFI_{stream}	Total
2030	0	0	0	0	0
2060	0	0	0	0	0
2100	1	1	1	1	4
2300	1	1	2	1	5
3000	3	1	5	2	19
total	5	3	8	4	20
% of maximum	8	5	12	6	8

Total changes per scenario

		No. of changes	Inc / Dec
SC2	*background metals*	12	Dec
SC11	*higher metals, lower SOM*	3	Inc
SC13	*lower metals*	2	Dec
SC3	*higher metals*	1	Inc
SC4	*high N & S*	1	Dec
SC5	*higher metals, higher N & S*	1	Inc
SC1	*baseline*	0	-
SC6	*higher DOM*	0	-
SC7	*higher metals, higher DOM*	0	-
SC8	*higher SOM*	0	-
SC9	*higher metals, higher SOM*	0	-
SC10	*lower SOM*	0	-
SC12	*lower N inputs*	0	-

Largest changes

Year	Scenario	Variable	Log change	Factor
2030				
2060				
2100	SC2	RFI_{soil}	-0.59	0.26
2300	SC2	RFI_{soil}	-1.21	0.062
3000	SC2	RFI_{soil}	-1.49	0.032

3.3.3.6. Cadmium (Table 3.18, Figure 3.16)

[Cd.1] In 2001, none of the soils in the study catchments has a Critical Limit exceedance, i.e. all the values of log RFI are negative, and four are less than -1.0, i.e. [Cd^{2+}] is an order of magnitude below the Critical Limit. The streamwater [Cd^{2+}] at Cote Gill is close to the critical limit, while the values for the other streams are all well below the limits.

[Cd.2] None of the metal variables is predicted to change by a factor of two or more during the next 60 years. After 100 years, all four variables will decrease under SC2, i.e. if metal inputs fall to background levels.

[Cd.3] By 2300 the response under SC2 continues, but there are no changes under the other scenarios.

[Cd.4] By 3000, the responses under SC2 continue, M_{soil} and RFI_{soil} decrease under SC13, and M_{soil} decreases under SC4 (*high N & S*) due to acidification.

[Cd.5] Under 10 of the 13 scenarios there are no predicted changes of twofold or more over the 1000 years of simulation.

[Cd.6] The largest changes come under SC2, in RFI_{soil} up to 2300 and in M_{soil} thereafter.

[Cd.7] Figure 3.16 compares the changes in Cd variables for the five individual catchments, under scenario SC13. In this scenario, the metal inputs decline by a factor of two between 2000 and 2020, and then remain constant. The soil and water of all five catchments also undergo some acidification under SC13, the changes being most pronounced for Gaitscale Gill and Old Lodge.

The five catchments show similar qualitative responses in all four metal variables, and most of the changes largely occur by 2300.

The key conclusions for Cd are as follows.

(a) **Decreases in depositional inputs of Cd during the first part of the 21st Century would reduce the concentrations and toxicity of the metal within 100 years.**

(b) **Acidification would also reduce Cd levels and toxicity.**

(c) **Increases in Cd inputs at the levels assumed for the scenarios are unlikely to worsen the concentrations or toxicity of the metal, because of the compensating effects of acidification.**

(d) **The similar qualitative responses of the five catchments mean that the averaged results are probably representative of most upland areas of the UK.**

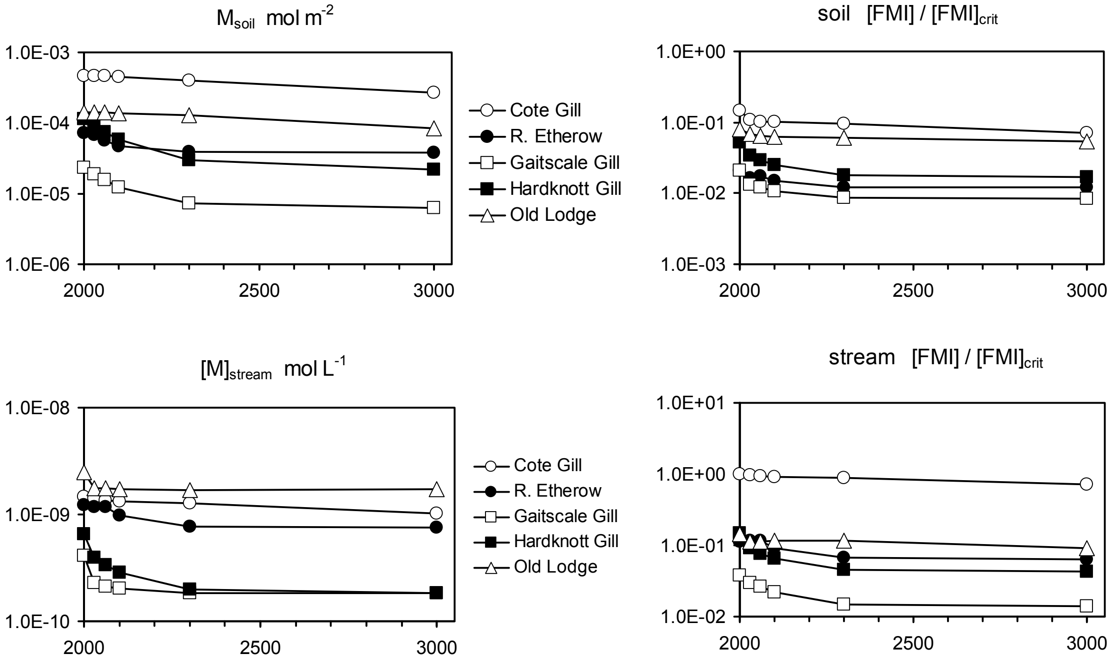


Figure 3.16 Changes in cadmium variables in scenario SC13. Note that for the free-metal-ion (FMI) variables, a ratio of 1.0E+00 means that the concentration of Cd^{2+} is equal to that at the critical limit.

Table 3.18 Scenario results for Cd, averaged over five catchments

Exceedances of free-ion Critical Limits in 2001; values of log RFI

	Cote Gill	R. Etherow	Gaitscale Gill	Hardknott Gill	Old Lodge
Soil	-0.91	-1.68	-1.67	-1.28	-1.09
Stream	-0.15	-0.94	-1.43	-0.82	-0.85

Number of scenarios with changes greater than a factor of two

year	M_{soil}	$[M]_{stream}$	RFI_{soil}	RFI_{stream}	Total
2030	0	0	0	0	0
2060	0	0	0	0	0
2100	1	1	1	1	4
2300	1	1	1	1	4
3000	3	1	2	1	7
total	5	3	4	3	15
% of maximum	8	5	6	5	6

Total changes per scenario

		No. of changes	Inc / Dec
SC2	*background metals*	12	Dec
SC13	*lower metals*	2	Dec
SC4	*high N & S*	1	Dec
SC1	*baseline*	0	-
SC3	*higher metals*	0	-
SC5	*higher metals, higher N & S*	0	-
SC6	*higher DOM*	0	-
SC7	*higher metals, higher DOM*	0	-
SC8	*higher SOM*	0	-
SC9	*higher metals, higher SOM*	0	-
SC10	*lower SOM*	0	-
SC11	*higher metals, lower SOM*	0	-
SC12	*lower N inputs*	0	-

Largest changes

Year	Scenario	Variable	Log change	Factor
2030				
2060				
2100	SC2	RFI_{soil}	-0.58	0.26
2300	SC2	RFI_{soil}	-1.14	0.072
3000	SC2	M_{soil}	-1.43	0.037

3.3.3.7. Lead (Table 3.19, Figure 3.17)

[Pb.1] In 2001, the Cote Gill soil Critical Limit is exceeded. For the other four soils, values of log RFI are negative, but in three cases the ratio of [Pb^{2+}] to the critical value is greater than 0.1, and at Old Lodge it is 0.45. Two of the values of log RFI_{stream} are greater than zero, and three are lower, but overall, the surface waters are close to the Pb Critical Limits.

[Pb.2] The scenario calculations forecast no changes of a factor of two or more for any of the lead variables, averaged over all five catchments, by 2060. When 2100 is reached, increases in $[M]_{stream}$ occur under SC4 (*high N & S*) and SC5 (*higher metals, higher N & S*). Under SC10 (*lower SOM*) RFI_{soil} increases, while both RFI_{soil} and RFI_{stream} increase under SC11 (*higher metals, lower SOM*).

[Pb.3] Further changes, all increases, occur by 2300. These are in $[M]_{stream}$ under SC3, SC4, SC5, SC6, SC7, SC10 and SC11, in RFI_{soil} under SC5 and SC11, and in RFI_{stream} under SC3, SC4, SC5, SC10 and SC11.

[Pb.4] By 3000, $[M]_{stream}$ and RFI_{stream} are higher under 10 of the scenarios, and RFI_{soil} under four. The only decreases forecast for Pb are in M_{soil} and RFI_{soil} under SC2 at 3000 years.

[Pb.5] Of the total of 48 changes forecast for Pb, only two are decreases. However, the changes are, on average, fairly small. The largest increase, even after 1000 years is by a factor of 7.4.

[Pb.6] Figure 3.17 compares the changes in Pb variables for the five catchments, under scenario SC13. In this scenario, the metal inputs decline by a factor of two between 2000 and 2020, and then remain constant. The soil and water of all five catchments also undergo some acidification, the changes being most pronounced for Gaitscale Gill and Old Lodge.

At R. Etherow and Gaitscale Gill, M_{soil} decreases over time, while it stays approximately constant at the other three catchments. At both Hardknott Gill and Old Lodge, $[M]_{stream}$ increases appreciably, due to soil acidification and the consequent increased mobility of Pb. Although this mechanism also operates at R. Etherow and Gaitscale Gill it is countered by the diminishing supply from the soil pool. At Hardknott Gill, mobilisation of Pb increases its toxicity in both the soil and stream, whereas the opposite applies to R. Etherow and Gaitscale Gill, and only stream toxicity changes (increases) at Old Lodge. The Pb status of Cote Gill is nearly constant.

The results for Pb are more similar to those for Cu than Ni, Zn and Cd, reflecting the stronger interactions of Pb and Cu with soil solids. Both these metals display complex behaviour. However, Pb is less prone to change, and only under one quite extreme scenario (SC2, *background metals*) are improvements predicted. But as with Cu, the variable behaviour of Pb among catchments means that in some there can be improvements, in some there is little change, and in others the situation may worsen.

The key conclusions for Pb are as follows.

(a) **Decreases in depositional inputs during the first part of the 21st Century would not reduce the concentrations and toxicity of the metal within 100 years. Significant improvements would require large reductions and take hundreds of years, even in responsive catchments.**

(b) **If depositional inputs remain at current levels, or increase, the average situation will worsen, although not greatly.**

(c) **The worst scenario combines higher Pb inputs with a decrease in soil organic matter.**

(d) **Lead pools and concentrations are not especially sensitive to acidification, but in some soils, acidification increases metal mobility sufficiently to increase its toxicity.**

(e) **Lead is relatively insensitive to increases in DOM production and transport.**

(f) **Lead responses are complex, and differ qualitatively between catchments. Predictions of average behaviour do not therefore fully characterise metal response.**

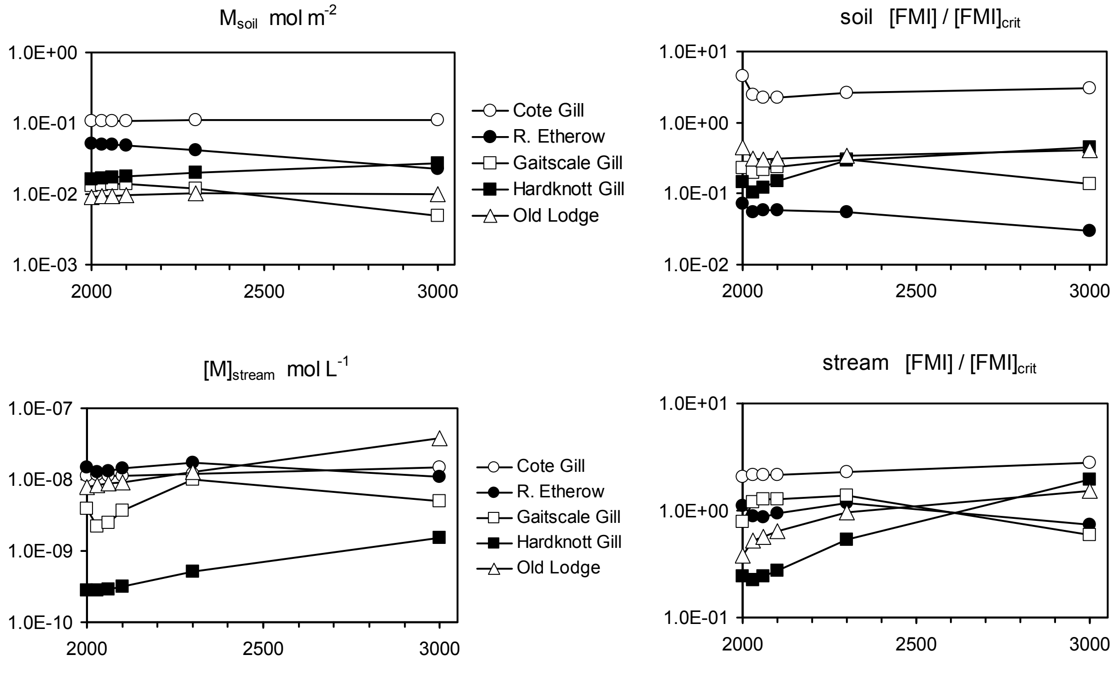


Figure 3.17 Changes in lead variables in scenario SC13. Note that for the free-metal-ion (FMI) variables, a ratio of 1.0E+00 means that the concentration of Pb^{2+} is equal to that at the critical limit.

Table 3.19 Scenario results for Pb, averaged over five catchments

Exceedances of free-ion Critical Limits in 2001; values of log RFI

	Cote Gill	R. Etherow	Gaitscale Gill	Hardknott Gill	Old Lodge
Soil	0.14	-1.14	-0.63	-0.84	-0.36
Stream	0.07	0.04	-0.13	-0.49	-0.49

Number of scenarios with changes greater than a factor of two

year	M_{soil}	$[M]_{stream}$	RFI_{soil}	RFI_{stream}	Total
2030	0	0	0	0	0
2060	0	0	0	0	0
2100	0	2	1	2	5
2300	0	7	2	5	14
3000	4	10	5	10	30
total	4	19	8	17	48
% of maximum	6	29	12	26	18

Total changes per scenario

		No. of changes	Inc / Dec
SC11	*higher metals, lower SOM*	8	Inc
SC5	*higher metals, higher N & S*	7	Inc
SC3	*higher metals*	6	Inc
SC10	*lower SOM*	5	Inc
SC4	*high N & S*	5	Inc
SC7	*higher metals, higher DOM*	4	Inc
SC9	*higher metals, higher SOM*	4	Inc
SC1	*Baseline*	2	Inc
SC2	*background metals*	2	Dec
SC6	*higher DOM*	2	Inc
SC8	*higher SOM*	2	Inc
SC12	*lower N inputs*	1	Inc
SC13	*lower metals*	0	-

Largest changes

Year	Scenario	Variable	Log change	Factor
2030				
2060				
2100	SC11	RFI_{stream}	+0.44	2.8
2300	SC5	$[M]_{stream}$	+0.67	4.7
3000	SC5	$[M]_{stream}$	+0.87	7.4

3.3.3.8. Simplified analysis over 100 years

From the results presented for the individual metals in the preceding Sections, three scenarios can be identified that represent, overall, the most likely future conditions (SC13), the best-case scenario (SC2) and the worst-case scenario (SC11). Given that the Critical Loads approach is based on effects, expressed through Critical Limits, and that soils have been the focus to date, the most important metal variable is RFI_{soil}, i.e. the measure of soil metal toxicity.

Therefore by considering changes in RFI_{soil} over the next 100 years, we can straightforwardly obtain an overall picture of the ranges of responses of heavy metals in the short-to-medium term. Figure 3.18 shows, for each metal, the range of RFI_{soil} over the five catchments.

Nickel, zinc and cadmium exhibit similar behaviour. For each metal, RFI_{soil} in the most sensitive catchment decreases (improves) by about a factor of 10, while the value for the least sensitive catchment hardly changes. For the most sensitive catchment, the change under SC2 is appreciably greater than that under SC13. Under SC11, RFI_{soil} increases by about a factor of three in the most sensitive catchment.

The responses of Cu and Pb are different, with relatively small improvements (decreases in RFI_{soil}) over the next 100 years, even under SC2. However, increased depositional inputs of these two metals (SC11) are predicted to increase their toxicity in soil.

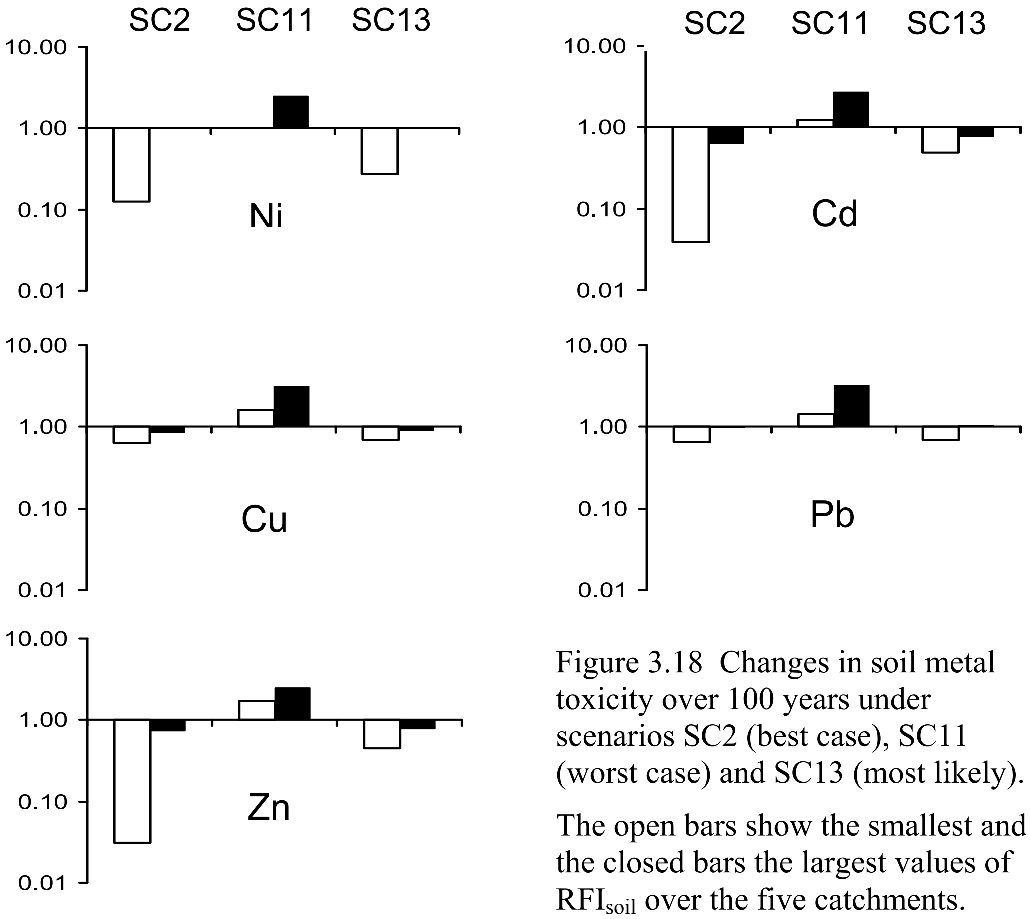


Figure 3.18 Changes in soil metal toxicity over 100 years under scenarios SC2 (best case), SC11 (worst case) and SC13 (most likely).

The open bars show the smallest and the closed bars the largest values of RFI_{soil} over the five catchments.

3.3.4. Scenario analysis: conclusions

The scenario analyses described above have been thorough in considering many permutations of possible future environmental conditions. Moreover, heavy metal behaviour in soil-water systems is complex and differs among metals, and metal toxicity depends upon pH. These factors make it difficult fully to comprehend all the model outputs. However, some definite conclusions can be drawn, presented below.

Before listing the conclusions and commenting on them, it is worth emphasising that the analysis deals only in relative changes. Although the modelling can account approximately for current metal pools and concentrations (Section 3.3.1.4), there remain appreciable discrepancies, typically of a factor of three between observed and simulated values (Figure 3.11). Thus, we cannot expect to predict precisely the metal contents of soils and waters, nor their absolute toxic effects. But we can provide defensible estimates of the directions and relative magnitudes of changes in the four key variables M_{soil}, $[M]_{stream}$, RFI_{soil}, and RFI_{stream} (Section 3.3.3.2).

Another point to bear in mind is that the scenario analyses refer mainly to upland UK sites, with semi-natural moorland vegetation, and mostly with high rainfall. Extrapolation to other types of catchment at the same level of detail is not justifiable.

1. Substantial changes in metal variables may occur.

Considering the scenario outputs averaged over the five catchments, the largest factor of change in a metal variable over the next 100 years is 3.9, shown by a decrease in RFI_{soil} for Zn. This variable also shows the largest change over the next 1000 years, a decrease of 30-fold. At the level of individual catchments, after 100 years a decrease in Zn of 30-fold could occur at Gaitscale Gill, and after 1000 years a decrease of more than 100-fold.

Although Zn is the most responsive metal, only slightly smaller changes are forecast for Ni and Cd. Changes for Cu and Pb are generally smaller. For example, the largest change in Pb over the next 100 years is a six-fold increase in RFI_{stream} at Gaitscale Gill under SC11. Over 1000 years, a 40-fold increase in RFI_{stream} at Hardknott Gill is forecast under SC5.

2. There are appreciable differences among scenarios.

The results show that heavy metals are indeed sensitive to future conditions, i.e. their pools, concentrations and toxic effects will change. The ranges of possibilities can be gauged by comparing predictions for the most likely scenario, SC13, with the best-case (SC2) and the worst-case (SC11). For example, Figure 3.18 shows that over 100 years under SC11 soil metal toxicity will increase for all five metals. But under SC13 it will decrease, while under SC2 the decrease will be greater.

3. There are appreciable differences among catchments.

Figures 3.13 - 3.17 show that some catchments respond more quickly than others, and that for Cu and Pb the responses of different catchments may not even be in the same direction.. Thus, while it is useful to consider average responses in order to judge the effects of different scenarios (Tables 3.15 - 3.19) it must be borne in mind that the averaging hides quite divergent behaviour.

4. Metal deposition, acidification and soil organic matter content are significant.

Considering all the results presented in Sections 3.3.3.3 - 3.3.3.7, the single biggest effect, in terms of both the number and the magnitude of the responses is the reduction of metal deposition to background levels, under SC2. However, this is an extreme case, employed to determine the range of possible responses. If we consider all single-factor scenarios except SC2, SC13 (50% reduction in metal inputs) emerges as the one producing the greatest number of changes (14). But the next most influential factor with 13 changes is acidification (SC4), followed by SC3 (higher metals) with 11 changes and SC10 (decrease in soil organic matter) with 7 changes. Acidification and organic matter changes are especially important for Pb and Ni. The other changes considered, higher dissolved organic matter (SC6) and higher soil organic matter (SC8) had little effect on metal variables.

Therefore, although metal depositional inputs are the single biggest factor in determining future effects of heavy metals, these other two factors (acidification and loss of soil organic matter) should also be taken into account.

5. Timescales for improvement differ among metals.

The plots in Figures 3.13, 3.15 and 3.16 show that under the most likely scenario (SC13) the pools, concentrations and toxic effects of Ni, Zn and Cd will decrease over the next 100 years. These changes can be attributed to the expected decrease by a factor of two in metal deposition. The results for SC2 in Figure 3.18 show that if deposition were reduced further, then greater decreases would occur, by as much as a factor of ten in sensitive catchments.

Improvements in Cu and Pb will take much longer. Figures 3.14 and 3.17 show that only for two of the catchments (R. Etherow, Gaitscale Gill) are decreases in metal variables expected under SC13, and these will take several hundred years. Figure 3.18 shows that over 100 years, the decreases under SC2 are hardly greater than those under SC13, which means that there is little short-term response to changes in metal deposition.

The differences between the two sets of metals reflect the stronger sorption of Cu and Pb to soil solids. The long timescales of recovery for these two metals result from the legacy of high past deposition and slow loss rates.

6. Increased metal inputs combined with soil organic matter loss are a danger.

If heavy metal atmospheric deposition were to return to the rates of 1990 (which were already substantially below the maximum past values), increases in the key metal variables would occur, and the effects would be exacerbated by loss of soil organic matter. For example RFI_{soil} would increase by about a factor of two for all metals, averaged over the five catchments, by 2100. In the longer term, RFI_{soil} would increase by as much as a factor of 10, in the case of Pb.

With respect to policy, the results of this analysis suggest that

- Further reductions in the depositional inputs of Ni, Zn and Cd would have widespread beneficial effects during the 21st Century.
- Beneficial effects cannot be expected for Cu and Pb, except over much longer timescales.
- It is important to ensure that metal deposition does not rise, and that soil organic matter is protected.

3.4. Intermediate Dynamic Model for Metals (IDMM)

The work described above with CHUM-AM was performed to provide the best-available descriptions of metal behaviour, taking into account acidification in particular, and also soil organic matter effects. Furthermore, CHUM-AM includes variations in soil depth, weathering contributions of mineral matter underlying the soil, and simulates streamwater chemistry and lake sediment accumulation of metals. It thus provides a comprehensive picture of catchment metal behaviour. In our opinion, it was necessary to work at this level of detail in order to test our understanding of heavy metal geochemistry, and thereby provide the currently best possible assessment of the key processes, pool sizes, concentrations, and toxic effects.

However, CHUM-AM is too complex and data-demanding to run for the large number of sites that would be required to assess, by dynamic modelling, heavy metal impacts, and the benefits of emission reductions, at the national scale. Therefore we have developed two simpler models. One of these, the Simple Dynamic Model for Metals (SDMM) was described in a previous report (Ashmore et al., 2004), and has been used in the present work (see Section 2). The SDMM essentially calculates the time taken to reach steady state starting from present conditions.

Here we present the IDMM, which falls between the SDM and CHUM-AM. The IDMM is based on the same principles as CHUM-AM, but the model uses empirical transfer functions instead of the WHAM speciation model to calculate solid-solution partitioning, and requires soil pH values over time to be provided as input data, rather than calculating these within the model. The model only applies to a single layer of soil. The output data from the model are loaded into the Excel workbook within which the calculated outputs can be compared with Critical Limits for Ni, Cu, Zn, Cd and Pb.

3.4.1. Model description and operation

The IDMM simulates the behaviour of heavy metals (Ni, Cu, Zn, Cd, Pb) in soil over periods of decades and centuries. The metals enter as atmospheric deposition or weathering. They react with the soil solids and with components of the soil solution, and leave the soil either in solution, where they may be complexed to dissolved organic matter (DOM), in particulate form, adsorbed to suspended particulate matter (SPM). The model keeps an account of the inputs and outputs, and of the soil metal content, and calculates the solution speciation, to provide the concentration of the key reactive species, the free metal ion (e.g. Ni^{2+}, Pb^{2+}).

3.4.1.1. Input data

The user needs to supply data to describe the soil and the input of metals. Values are required of soil bulk density and depth, the volume due to stones, average moisture content, pCO2, weathering input rates of the heavy metals (mol m^{-2} a^{-1}), annual runoff (which must exceed zero), and the proportion of the catchment area that is bare rock.

The following time-dependent variables must also be provided; soil pH, soil organic matter content, soil solution DOC concentration, concentration of SPM, deposition rates of the heavy metals.

Parameters describing the chemical reactions, and metal toxicity, are provided as part of the software. These are derived from studies of metal solid-solution partitioning

(Tipping et al., 2003), a review of soil Al chemistry (Tipping, 2005), and analysis of soil toxicity data (Lofts et al., 2004).

3.4.1.2. *Chemical calculations*

The model performs the following chemical calculations.

- From the pH, the concentrations of Al^{3+} and Fe^{3+} are computed, either using solubility products, or in the case of Al at low pH, empirical functions.
- From the pH, $[Al^{3+}]$, $[Fe^{3+}]$, pCO2, [DOC], [SPM], total solution concentrations of the heavy metals, an assumed fixed concentration of NaCl (1 mM), and initial guesses of the concentrations of Ca, NO_3, and SO_4, the solution speciation is calculated using WHAM6. During this process, the total concentration of Ca (higher pH) or of NO_3 plus SO_4 (acid pH) are adjusted to achieve a charge balance.
- The previous calculation involves the calculation of SPM-bound metal from the pH, metal free ion concentrations, and organic matter content, using the Freundlich isotherm;

  $$M_{ads} = K_F\,[M^{2+}]^n \tag{3.7}$$

  where K_F is given by

  $$\log_{10} K_F = a + b\,\mathrm{pH} + c\,\log_{10}\%\mathrm{OM} \tag{3.8}$$

  The values of *a*, *b* and *c* come from analysis of data for metal partitioning in soils. SPM is assumed to have the same sorption properties as the bulk soil. The results of this calculation also provide the amounts of metal bound to the bulk soil.

An initial steady state is calculated, based on the fact that the total metal amount leaving the soil in solution (including SPM) must equal the inputs from weathering and atmospheric deposition. This also gives the initial amount of each metal sorbed to the soil. From this starting-point, the evolution of metal retention and transport can be calculated.

3.4.1.3. *Metal dynamics*

- For each year, the amount of each metal leaving in drainage is calculated from the solution concentration and the runoff.
- The new supply of metal from weathering and deposition is computed from the input data. The metal deposition is assumed to change linearly between the years for which input data are supplied.
- The new total metal in the soil is obtained from the initial total, the loss and the gain.
- The soil speciation is calculated, and the new total dissolved metal found.
- The process is repeated for the next year. Outputs of soil metal content, dissolved metal, free metal ion concentration, and soil metal concentration ($\mu g\ g^{-1}$) are reported to the output file every 10 years.

3.4.1.4. *Critical Limits*

The output data from the model are loaded into the Excel workbook "DYSIM_plots_NN.XLS" (where NN is the name of the site in question). Within this workbook, time-series plots are made of soil metal concentrations (µg g^{-1}) and also free metal ion concentrations, and the values are compared with Critical Limits.

3.4.2 Preliminary testing

The model has been used to predict soil metal pools for five of the catchments that have been analysed with CHUM-AM (Section 3.3). Comparisons with observed values are presented in Figure 3.19.

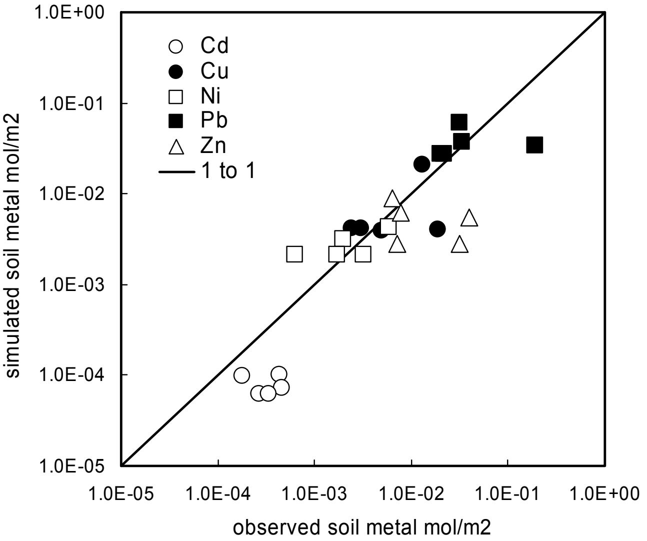


Figure 3.19 Current soil metal pools predicted by the IDMM plotted against measured values, for R. Etherow, Gaitscale Gill, Hardnott Gill, Lochnagar and Old Lodge.

The agreements are not quite as good as those achieved with CHUM-AM (Figure 3.11), but they are reasonable. Therefore it is certainly worth continuing to evaluate and improve the IDMM.

3.4.3 Possible developments and applications

Applications of the model to other soils are clearly desirable. Its ease of application means that it can be tested for many sites, using generic histories of metal deposition and acidification, but taking into account local variations where known. Thus, in principle the IDMM can be applied to sufficient representative soils to permit national assessments of the effects of heavy metals, and possible future changes.

A useful development would be to use soil data to calibrate the model directly, by optimising the pedotransfer coefficients (equations 3.7 and 3.8) instead of relying on values determined from soil experiments. This could provide tighter relationships between prediction and observation, and thereby more precise predictions. Another possible improvement would be to add a second soil box, so that the slow downward movement of metals through soil could be represented. The need for this could be evaluated by comparison with CHUM-AM simulations.

The IDMM provides a suitable framework within which to test the influence of processes not currently considered in heavy metal dynamic models. For example, it could be used to assess the influence of metal storage and cycling in biomass, and the effects of "ageing" processes whereby metal added to soil is rendered unreactive by quasi-permanent incorporation into mineral matter. (These possibilities were identified during an International Workshop on Critical Loads of Heavy Metals, under LRTAP and UNECE, towards the end of the present project.).

4. Survey of Heavy Metals in Mosses

4.1 Introduction

Carpet-forming moss species obtain most elements directly from wet and dry deposition and have a high capacity to retain heavy metals. Lack of an elaborate rooting system means that uptake from the substrate is normally insignificant. Therefore, mosses are an ideal sampling medium for metals deposited from the atmosphere to vegetation. The moss technique provides a time-integrated measure of the spatial patterns of heavy metal deposition and was first developed and tested in the Nordic countries. The moss biomonitoring network gradually extended to the Balkan countries and from 1990 onwards included many European countries. Since 1990, the U.K. has contributed data to the European moss survey at five-yearly intervals. In 2005, the total nitrogen concentration was also determined to establish whether mosses can be used as biomonitors of nitrogen pollution. A pilot study in the Nordic Countries showed that the nitrogen concentration in mosses was linearly related to the deposition rates of nitrogen (Harmens *et al.*, 2005b). Here we report on the results of the moss survey conducted in 2005, with a focus on the metals Cd, Cu, Ni, Pb and Zn, and on the temporal trends of heavy metal concentrations in mosses in the U.K. since 1990. The 2005 U.K. moss data were submitted to the ICP Vegetation (Defra contract AQ0810) for incorporation in the European moss survey 2005/6.

4.2 Sampling and analytical procedures

A repeat of the 2000 survey was carried out between May and September 2005. All the 2000 sites were re-visited and mosses were sampled from 170 sites according to the moss monitoring manual (Harmens *et al.*, 2005a). The following moss species were sampled: *Pleurozium schreberi* (65 sites), *Hylocomium splendens* (45 sites), *Rhytidiadelphus squarrosus* (34 sites), *Hypnum cupressiforme* (24 sites), and *Pseudoscleropodium purum* (2 sites); for details on where each species was sampled, see Fig 4.4. Fresh samples were dried at room temperature, sorted for the last three year's growth and analysed for heavy metals at the NERC ICP-MS facility at Kingston University according to the procedure applied in 2000 (Ashmore *et al.*, 2002). Analytical precision was typically between 2-8% where concentrations were not close to the limits of detection. For most of the metals the recovery in moss reference material M2 and M3 (Steinnes *et al.*, 1997) was between 79% and 107%. Only the recovery for V (57-62%) was consistently low for both the reference samples, which was similar to the average recovery for V in 2000. The total N concentration in homogenised moss samples (dried at 40 ^{o}C) was determined by CHN 2000 combustion analysis. The recovery of the total N concentration in a certified apple standard was 96%.

Data processing and mapping

The metal concentrations in mosses were standardised to *Pleurozium schreberi* (Ps) applying the interspecies calibration equations determined in the 2000 UK moss survey (Ashmore *et al.*, 2002). The Ps-standardised heavy metal concentrations were subsequently mapped using ArcGIS (version 9). The 2005:2000 ratio of the metal concentrations was determined and mapped across the U.K. to compare changes in heavy metal concentrations in mosses between 2000 and 2005 for individual sites.

The temporal trends in heavy metal concentrations in mosses were also determined for the period 1990 – 2005.

4.3 Concentrations in mosses

A brief description of the maps for 2005 and a comparison with the results for 2000 for each metal is provided below (see Ashmore *et al.* (2002) for a more detailed description).

Cadmium (Cd)
In the 2005 European moss survey, the levels of Cd in pristine areas such as Northern Scandinavia were less than 0.1 mg kg^{-1}. Similar concentrations were found in northern and eastern parts of Scotland and Northern Ireland (Fig. 4.1). For the majority of sites in the UK, the Cd concentrations were below 0.15 mg kg^{-1}. Values above 0.25 mg kg^{-1} were predominantly found in central parts of northern England. The Ps-standardised mean value was reduced significantly between 2000 and 2005 (Table 4.1), as the Cd concentration had declined at about 65% of the sites. The highest declines were observed in Cumbria and southern Wales.

Copper (Cu)
As Cu has an essential micronutrient function, the background concentration in mosses in the U.K. appears to be around 3 mg kg^{-1}. At the majority of sites in the U.K. the Cu concentration in mosses was below 5 mg kg^{-1} (Fig. 4.1; Table 4.1) and the lowest concentrations (< 2.5 mg kg^{-1}) were mainly found in North-West Scotland. The highest values are predominantly found in areas with intensive road transportation (currently the main source of Cu emission) and the same areas show generally an increase in the Cu concentration between 2000 and 2005, reflecting the increase in the volume of road transportation. Nevertheless, the Ps-standardised mean value was reduced significantly between 2000 and 2005 (Table 4.1).

Lead (Pb)
In the 2005 European moss survey, the levels of Pb in pristine areas such as Northern Scandinavia were typically less than 2 mg kg^{-1}. Similar concentrations were found predominantly in northern Scotland and Northern Ireland (Fig. 4.2). For the majority of sites in the UK, the Pb concentrations were below 3 mg kg^{-1} and higher Pb concentrations were found mainly in central areas across England. The Ps-standardized mean value was reduced significantly between 2000 and 2005 (Table 4.1) and the Pb concentration had declined at about 60% of the sites. However, the Pb concentration in mosses had not changed dramatically between 2000 and 2005.

Nickel (Ni)
In recent European moss surveys, the levels of Ni in northern Scandinavia were typically less than 1 mg kg^{-1}. The majority of sites in the UK fall within this category with higher levels observed at sites likely to be influenced by local pollution sources (Fig. 4.2). The highest levels of Ni were found in build-up areas and areas with industrial emissions, such as South Wales, the Midlands and parts of northern England. The Ps-standardised mean value did not change between 2000 and 2005 (Table 4.1); considerable increases in Ni concentrations in mosses were observed in western Scotland, most likely due to the presence of petrol refining industry (Fig. 4.2).

Zinc (Zn)

The median value for 2005 (20.3 mg kg^{-1}) is lower than those in the Nordic countries (ca. 30 mg kg^{-1}). In coastal areas, especially in Scotland, large concentrations of sea salt ions may reduce the uptake of Zn by mosses. Like Cu, Zn is an essential micronutrient and background concentration in mosses in the U.K. appears to be ca. 20 mg kg^{-1}. Sites exceeding 50 mg kg^{-1} appear to be mainly located in areas with intensive road transportation, with some sites probably affected by local industries (Fig. 4.3). The Ps-standardised mean value was reduced significantly between 2000 and 2005 (Table 4.1) and the Zn concentration had declined at 64% of the sites.

Nitrogen (N)

N is an essential macronutrient and recycled in mosses from old to new growing tissue. Therefore, a background concentration of ca. 0.5% is present in mosses (Harmens *et al.*, 2005). The median N concentration in mosses in the U.K. was 0.79%, with low concentrations generally found in Scotland, Northern Ireland and parts of northern and southern England and Wales (Fig. 4.4). The highest concentrations were found in mid and east England. The fact that different moss species were sampled across the U.K. might confound the interpretation of the results as different moss species potentially accumulate N at different rates. Currently, no interspecies calibration data are available for the four main moss species sampled. The N data will be compared in detail with N deposition and critical loads data under Defra contract AQ0810.

Temporal trends 1990 - 2005

Since 1995, the median Ps-standardised concentrations had declined for all metals, i.e. As - 65%, Cd - 49%, Cr - 38%, Cu - 30%, Ni - 50%, Pb - 68%, V - 53% and Zn - 35% (Table 4.1). Comparison of these temporal trends with 1990 is confounded by the use of different analytical techniques. The decline of heavy metal concentrations in mosses reflects the decline in emission and atmospheric deposition of heavy metals across Europe in recent decades (see Harmens *et al.*, 2007a,b).

Table 4.1. Summary of *Pleurozium schreberi*–standardised heavy metal concentrations in mosses between 1990 and 2005. Note: the analytical technique in 1990 (atomic absorption spectroscopy: AAS) was different from that in later years (inductively coupled plasma mass spectrometry: ICP-MS).

Year	**Parameter**	**As** (mg/kg)	**Cd** (mg/kg)	**Cr** (mg/kg)	**Cu** (mg/kg)	**Ni** (mg/kg)	**Pb** (mg/kg)	**V** (mg/kg)	**Zn** (mg/kg)
1990	Number	-	164	192	200	199	174	188	200
	Min	-	0.040	0.05	2.60	0.18	0.30	0.10	11.6
	Max	-	6.500	3.25	14.20	13.19	213.23	12.70	164.0
	Median	-	0.139	0.63	5.13	1.41	5.07	1.20	26.0
	Mean	-	0.235	0.77	5.57	1.81	7.50	1.41	30.5
	Stdev	-	0.601	0.47	1.68	1.44	16.48	1.16	17.9
1995	Number	101	108	108	108	99	108	108	107
	Min	0.110	0.065	0.15	2.22	0.17	1.25	0.33	17.3
	Max	8.100	1.120	9.96	18.54	9.41	36.43	8.98	110.6
	Median	0.393	0.190	1.42	5.17	1.54	8.27	1.53	31.4
	Mean	0.741	0.228	1.83	5.91	1.96	9.67	1.97	37.1
	Stdev	1.099	0.152	1.37	2.96	1.66	6.44	1.52	18.6
2000	Number	170	170	164	170	144	170	170	170

	Min	0.008	0.025	0.21	1.78	-0.08	0.82	0.34	7.6
	Max	4.493	1.197	3.84	10.03	3.96	34.48	5.72	209.1
	Median	0.167	0.113	1.44	4.23	0.80	2.97	1.00	22.6
	Mean	0.309	0.146	1.45	4.34	0.99	4.59	1.23	30.2
	Stdev	0.571	0.148	0.61	1.40	0.68	5.07	0.77	24.9
2005	Number	168	168	168	168	168	168	168	168
	Min	0.021	0.028	0.18	1.59	0.18	0.54	0.15	0.8
	Max	2.992	0.545	7.79	34.31	9.53	34.37	4.82	170.3
	Median	0.139	0.096	0.87	3.60	0.77	2.62	0.72	20.3
	Mean	0.222	0.111	0.98	4.15	0.99	3.50	0.85	25.8
	Stdev	0.397	0.069	0.72	2.95	0.93	3.69	0.58	20.4

Conclusion

In 2005, the median metal concentration in mosses was generally similar (As, Cu) to or even lower (Cd, Ni, V, Zn) than those found in (some of) the Nordic countries. Only for Cr and Pb the median concentrations were higher in the U.K. than in some of the Nordic Countries. Between 2000 and 2005, the Ps-standardised concentrations had declined significantly for Cd, Cr, Cu, Pb, V and Zn. However, comparison at the individual species level showed that only the decrease for Cr and V was significant for all four species. Since 1995, the median Ps-standardised concentrations had declined for all metals; comparison with 1990 is confounded by the use different analytical techniques. The decline of heavy metal concentrations in mosses reflects the decline in emission and atmospheric deposition of heavy metals across Europe in recent decades (see Harmens *et al.*, 2007a,b).

4.4. UK heavy metal deposition maps based on the moss survey 2005

4.4.1 Calculations

The deposition was mapped according to the procedure described by Ashmore *et al.* (2002), using the moss calibration (relationship between bulk deposition and concentration in moss), derived by collocated sampling of mosses at the monitoring sites of the Heavy Metal Deposition Network (HMDN) in 2004/5 (Fowler *et al.*, 2006; Defra Project EPG 1/3/204). These relationships were significant at P = 0.01 for Pb, just failed to be significant at P = 0.05 for As, Cd, Ni, Se, V and Zn, but were too weak for Cr and Cu for relationships to be established. Using these calibrations bulk deposition was estimated for the sampling sites of the moss survey 2005, from the Ps-standardised concentrations. The scavenging ratios (Fowler *et al.*, 2006) were then used to derive the air concentration at the sampling sites, which was then interpolated to calculate the air concentration map for the whole of the UK. Based on this air concentration map, total deposition was calculated for each grid cell. Dry and occult deposition was calculated, consistent with the mapping procedures of the HMDN data, while wet deposition was calculated from the scavenging ratios, using the rain field for 2004, taken into account topographic enhancement of precipitation (seeder-feeder effect).

4.4.2 Deposition fields

The deposition fields of Cd, Ni, Pb, and Zn derived from the 2005 moss survey are shown in Fig. 4.5 to 4.8, where they are compared with the maps from the 2000 moss survey (using the same calibration of Fowler *et al.* (2006)) and the latest available maps from the UK Heavy Metal Deposition Network for 2004 (Fowler *et al*., 2006). It should be noted that there is not always perfect agreement between the average of the grid cell and the sample for two reasons: firstly, the local map values are also affected by the surrounding measurement points, due to the interpolation routine used. Secondly, the grid cell reflects the weighted average to the different land-cover forms, while deposition to moss represents deposition to short vegetation only. Since the moss deposition fields are referenced to the HMDN, the deposition estimates are not fully independent, although the spatial patterns are.

Cadmium
Both total and spatial patterns are similar between the different deposition estimates of Cd. As with some of the other trace elements (see Zn), the HMDN derives higher deposition estimates for the West Highlands, which is due to a combination of the elevated background levels observed at Inverpolly, high precipitation amounts and seeder-feeder effects in this area.

Lead
Deposition estimates based on the UK moss calibration derive values which are very similar to the HMDN values, although the HMDN suggests somewhat lower background deposition values. While hotspots are similar in the HMDN and 2000 moss survey, the latest moss survey places hotspots near Birmingham rather than Manchester and suggests reduced deposition in South Wales.

Nickel
For nickel the moss surveys derive nearly twice the deposition estimated by the HMDN. The spatial patterns differ greatly between the two approaches, indicating that Ni concentrations in moss may be more affected by local pollution sources. Alternatively, the HMDN network sites in South-East England fail to capture the European input, which would elevate concentrations in the South-East.

Zinc
Moss survey estimates of Zn show fairly little structure and this is due to the relatively weak correlation between concentration in moss and deposition, with a high intercept. The moss derived estimates are only half of the HMDN value. The spatial structure between the two moss surveys is similar, reflecting mainly the effect of the precipitation patterns. As with Cd, the deposition of Zn in the Western Highlands of Scotland is likely to be overestimated in the HMDN.

4.4.3 Conclusion

Moss derived metal deposition fields are similar to those derived from the HMDN for Cd and Pb, but derives a higher estimate for Ni and a lower estimate for Zn. HMDN derives higher deposition estimates for the West Highlands of Scotland for Cd and Zn and the spatial patterns differ greatly for Ni and Zn for both methods. The HMDN approach has the advantage of being a more direct measurement of the deposition, but it is more likely to miss out localised hotspots, due to the smaller number of sites. In addition, elevated measurement values at a HMDN measurement station affects a large area as seen by the high estimates of deposition predicted for the West Highlands of Scotland.

5. Contributions to CLRTAP

The contributions to the work of the CLRTAP which were originally planned fell into two main categories which we consider in turn.

5.1. Calls for National Data

The first main aim was to respond to calls by the Co-ordinating Centre for Effects (CCE) for national data. This was done in the autumn of 2004, using values of critical loads calculated under contract EPG 1/3/188. Values were submitted for ecotoxicological effects of lead and cadmium in soils. Seventeen countries submitted critical loads data; the results of the call are published by Slootweg et al. (2005).

We anticipated that a further call for national data would be made in the period 2005-2007, with priority given to a response to a probable call for data on the time scales to reach critical limits that was expected in 2006. However, due to changed priorities within CLRTAP, no further call for national data were received, and staff time was instead devoted to improved estimates of national critical loads using the new data available from research in this contract. This work means that the UK is well-placed to respond to new calls for data in 2008 or 2009 with updated critical load values for lead and cadmium effects in soils. It is important to note that, due to the lack of any further calls for data, European wide assessments of critical load exceedance are based on UK data which are now out of date

5.2 Contribution to work of Expert Panel on Heavy Metals

The work of the CLRTAP joint Expert Group on Dynamic Modelling has been very heavily focussed over this period on dynamic modelling of nitrogen. They have therefore shown little interest in discussion of the work on dynamic models of heavy metals, although the importance of nitrate leaching on heavy metal mobility highlights the need for better integration of these areas of work in the future. Therefore, the input of the research consortium has remained to provide significant inputs to the work of the Expert Panel on critical loads for heavy metals within the ICP on Mapping and Modelling. Prof. Ashmore, Prof. Tipping and Dr Lofts have all been actively involved in the work of this Expert Panel.

The most important contribution to the work of CLRTAP, which was not planned in the original contract, was the organisation of an open meeting on critical loads of heavy metals, designed to time with the end of this contract, and hence to contribute significantly to the dissemination of key results from this work within CLRTAP. This meeting was held in Windemere in November 2007, and was made possible by complementary funding from CEH. Members of this research group contributed three oral and two poster presentations, and the work on heavy metal deposition measurement in the UK was also presented. The report of this workshop, which is currently being drafted, will be considered in more detail by the Expert Panel, and will also be considered by the Working Group on Effects in September 2008. The implications of some of the key recommendations from this workshop in terms of their wider policy relevance are considered below.

6. Policy implications

Within the Convention on Long-range Transboundary Air Pollution (CLRTAP), active discussions have now begun in the Task Force on Heavy Metals (TFHM) on revision of the Aarhus Protocol for three metals – lead, cadmium, and mercury. Proposals for a revision of this Protocol rely on an assessment by the TFHM of the costs and benefits of measures to further reduce emissions of these heavy metals, which are listed under Annexe 1 of the existing Protocol. The TFHM has produced detailed technical assessments of a number of options for further emission control, assessing their advantages, disadvantages and cost-effectiveness.

However, additional measures also need to be justified on the basis of their environmental and health benefits. The assessment considered by the TFHM was primarily based on a detailed analysis of the costs and practicality of a range of emissions control options that was undertaken by TNO. However, it could be argued that the work undertaken by TNO does not properly 'assess the quantitative and, where this was not possible, qualitative information on health and ecosystem benefits of further measures to reduce emissions of heavy metals' as was required by the work plan of the Task Force on Heavy Metals. Rather it provides an assessment in terms of critical load exceedance. This approach has a number of important limitations in terms of assessing benefits which are highlighted by the work undertaken in this project.

The first, and important, limitation of an assessment based on critical load exceedance is that this is a steady state approach which does not consider the dynamics of responses of environmental concentrations of these metals, and hence their impacts, to increases or decreases in emissions. While critical load exceedance is important in indicating the potential for adverse environmental or health effects of atmospheric deposition of metals, it has significant limitations. In particular, the work undertaken in this contract has demonstrated that exceedance patterns for critical loads can be quite different that those of critical limits, which show where thresholds for adverse effects are currently exceeded. It has also shown, for the UK, that the dynamics of changes in heavy metal concentrations in soils and waters in upland catchments in response to changes in deposition is of the order of decades to centuries or, for lead in particular, longer. This has a number of profound implications for the assessment of benefits using an approach such as critical loads that is based on steady-state assumptions:-

1. Firstly, and most obviously, the benefits of measures taken now may only be experienced a long time into the future, with obvious implications for cost-benefit assessments. Unless this factor is taken into account, the benefits of emission control will be greatly over-estimated by using exceedance of a steady-state critical load as the criterion.

2. Secondly, and slightly less obviously, because of these long timescales, and the fact that rates of metal deposition have changed significantly in the last 30 years, it is likely that there is almost nowhere in the UK in which the steady-state assumptions underlying a critical load based analysis are currently valid. This means that patterns of exceedance of critical limits for effects of metals in soils and waters now may be quite different from those of exceedance of critical loads at steady state. For example,

in the UK we predict using the calculation methods set out in the Mapping Manual that exceedance of critical loads is much greater for lead than cadmium, but that only a small area of the country has soil concentrations of lead due to atmospheric deposition which are above the critical limit. In such a case, use of reductions in exceedance of critical loads over-estimates the benefits of emission control because adverse effects are not expected where critical limits are not exceeded.

3. Finally, the very long timescale of response to changes in emissions of metals to the atmosphere may mean that other environmental factors and hence other policy measures may have a greater impact on metal exposure and effects over this century than reductions in metal emission. For example, results from UK dynamic modelling suggest that effects of nitrogen deposition leading to increased nitrate leaching could significantly influence the mobility of metals and the rates of change of concentrations in soils and waters. Hence other policies not specifically focussed on metal emissions could in principle have a greater cost-benefit in terms of reducing environmental exposures to metals or could negate any benefits of measures to reduce metal emissions. Where there is a high metal burden in soils due to historical deposition, it is even possible that increases in stream concentration of Pb and Cu can occur as rates of deposition of these metals decrease.

These major limitations of the use of critical loads to evaluate the benefits of different policy measures mean that the current analysis used by THFM may provide an inadequate basis on which to assess policies that may have significant economic implications in the UK and more widely in Europe. This was recently recognised at the Windermere workshop. This workshop recommended that execeedance of steady-state critical loads should be not be considered in isolation in evaluations of the need for policies to reduce deposition of metals due to long-range transport, but should be evaluated alongside information on exceedance of critical limits and the results of simple dynamic models.

In summary, there is strong evidence that deposition of metals from the atmosphere in the UK has decreased over the past 3 decades, including that from the moss surveys reported here. However, the results of our analysis and modelling suggest that the full environmental benefits of these reductions in emissions and deposition may only be felt at some point in the future, and may partly depend on future scenarios for organic matter and acidification in upland catchments. Furthermore, the benefits of any additional measures to reduce emissions may be very limited for metals with long residence times such as lead, although benefits within 20-30 years may be experienced for metals with shorter residence times such as cadmium.

7. Future Work

There are two major priorities that we would identify for future research focussed on key issues in resolving whether the costs of any further control of the three priority metals (lead, cadmium and mercury) under the Heavy Metals Protocol are justified by the environmental benefits.

Firstly, the research we have carried out to date has only focussed on lead and cadmium. The third metal involved in the Aarhus Protocol is mercury, and at a European scale this metal shows greater areas of critical load exceedance than either lead or cadmium, with an estimated 78% of the area of Europe (and 30% of the area of the UK) showing exceedance of critical loads, based on 2000 deposition data. However, development of critical loads methods for mercury has largely been based on Scandinavian research. Because of concerns over the validity of these methods, and their transferabilty to the UK, data on critical loads for mercury have not been submitted by the UK.

Within CLRTAP, active discussions have now begun in the Task Force on Heavy Metals on revision of the Aarhus Protocol for these three metals, including assessment of the use of critical loads in identifying the needs for further reductions in emissions to the atmosphere. In the case of mercury, discussion has identified a number of policies to reduce emissions to the atmosphere from industrial and other sources. These policies may have significant economic implications in certain sectors in the UK, but at present there is no capacity to assess the environmental benefits of these measures in the UK.

Given the degree of exceedance of current critical loads for mercury, there is likely to be considerable pressure for further measures to reduce emissions of mercury to the atmosphere. However, the methods used to calculate critical loads for mercury are based on a limited body of data and are not consistent with the free ion toxicity model which is now applied for cadmium and lead. Furthermore, experience with lead and cadmium suggests that the dynamics of response of soil and water concentrations to changes in atmospheric deposition is very slow and hence the benefits of emissions reductions may only become real well into the future. There is a lack of appropriate dynamic models to assess the significance of these effects for mercury.

A considerable amount of new research and field work would be needed to fully develop and apply ecotoxicologically based critical load methods for mercury in the UK. However, an initial assessment of the extent of the current risk of adverse effects of mercury in the UK and the timescale for recovery after emissions reductions, would be very valuable, and the results would provide a scientific basis for assessing the benefits of emissions control. Such an assessment would also provide a basis for prioritising further new field and experimental research to reduce the level of uncertainty in the initial assessment that will be possible using existing data.

Secondly, our scenario analysis using the suite of dynamic models that we have developed has only been carried out for upland catchments of the UK. This analysis was carried out with one of these models, CHUM-AM, which was used to assess the changes in lead and cadmium soil pools, stream concentrations and toxicity at different locations in the UK in response to different future scenarios. However, if a more dynamic approach is to be applied to assess the benefits of additional control measures under the Aarhus Protocol, then this type of analysis would need to be undertaken more widely across Europe.

For this application to be effective, the dynamic model needs to have a sufficiently strong mechanistic basis for application to different types of climate, soils waters and metal deposition histories, but not to be too demanding in terms of input data. CHUM-AM would be too complex and data-demanding for this purpose. However, it would be possible to use the “Intermediate Dynamic Model for Metals” (IDMM), which has been developed under this contract. The IDMM is based on the same principles as CHUM-AM, but the model uses empirical transfer functions instead of the WHAM speciation model to calculate solid-solution partitioning, and requires soil pH values over time to be provided as input data, rather than calculating these within the model. Another simplification is that the model only applies to a single layer of soil. The IDMM has been shown to provide estimates of current soil metal pools that are in reasonable agreement with measured values, and with CUM-AM outputs. The IDMM has a potential advantage over CHUM-AM in that it can be calibrated to current soil data, thereby increasing precision.

The IDMM and CHUM-AM allowed us to assess for five different catchments in the UK the effects not only of metal deposition, but also sulphur and deposition and climate change (through effects on soil organic matter). This is an important element which has been omitted from the analysis undertaken by TFHM to date, as only synergies with particulate emission control have been considered. Under some UK conditions and scenarios, the impacts of control of acid and nitrogen deposition could be as important as direct control of metal emissions in terms of metal toxicity. Hence application of the IDMM will allow an assessment to be made of the conditions under which control of acidity and nitrogen could be more effective than direct control of metal emissions, or might negate the benefits of measures to control metal emissions. This would provide valuable additional information for the work of the CLRTAP.

Since it is not practicable to apply the IDMM in every 50km grid square throughout Europe, this work would need to proceed by identifying key regions to be selected for parameterisation and application of the model, in order to provide for an appropriate combination of metal deposition history, current metal deposition, climate, soils and acid deposition. In theory the results of such an analysis could also be used to provide an economic analysis of the benefits different control measures if appropriate valuation approaches could be identified.

7. Summary of Outputs

(a) Peer-reviewed papers

Hall, J., Ashmore, M., Fawehinmi, J., Jordan, C., Lofts, S., Shotbolt, L., Spurgeon, S., Svendsen, C. & Tipping, E. 2006. Developing a critical load approach for national risk assessments of atmospheric metal deposition. Environmental Toxicology and Chemistry, 25, 883-890.

Harmens, H., Norris, D.A., Koerber, G.R., Buse, A., Steinnes, E., Rühling, Å. (2007a). Temporal trends in the concentration of arsenic, chromium, copper, iron, nickel, vanadium and zinc in mosses across Europe between 1990 and 2000. Atmospheric Environment 41: 6673-6687.

Harmens, H., Norris, D.A., Koerber, G.R., Buse, A., Steinnes, E., Rühling, Å. (2007b). Temporal trends (1990 – 2000) in the concentration of cadmium, lead and mercury in mosses across Europe. Environmental Pollution. In press.

Tipping, E. (2005) Modelling Al competition for heavy metal binding by dissolved organic matter in soil and surface waters of acid and neutral pH. Geoderma 127, 293-304.

Tipping, E., Lawlor, A.J. & Lofts, S. (2005a) Simulating the long-term chemistry of an upland UK catchment; major solutes and acidification. Environ. Poll. 141, 151-166.

Tipping, E., Lawlor, A.J., Lofts, S. & Shotbolt, L. (2005b) Simulating the long-term chemistry of an upland UK catchment; heavy metals. Environ. Poll. 141, 139-150.

Tipping, E., Thacker, S.A., Wilson, D. & Hall, J.R. (2007) Long-term nitrate increases in two oligotrophic lakes, due to the leaching of atmospherically-deposited N from moorland ranker soils. Environ. Poll. In press.

(b) Book chapters and reports

Harmens, H. and the participants of the European moss survey (2005a). Heavy metals in European mosses: 2005/2006 survey. Monitoring manual. ICP Vegetation Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK. http://icpvegetation.ceh.ac.uk

Harmens, H., Mills, G., Hayes, F., Williams, P., De Temmerman, L. and the participants of ICP Vegetation (2005b). Air pollution and vegetation. ICP Vegetation Annual Report 2004/2005. UNECE ICP Vegetation Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK. http://icpvegetation.ceh.ac.uk

Tipping, E., Yang, H., Lawlor, A.J., Rose, N.L. & Shotbolt, L. (2007) Trace metals in the catchment, loch and sediments of Lochnagar: measurements and modelling. In Rose, N.L. (Ed.) Lochnagar: The Natural History of a Mountain Lake. Springer, Dordrecht, pp. 345-373.

Acknowledgements

British Geological Survey for analysis of mineral samples
Severn Trent Water plc for provision of data about Howden Reservoir*
Staff of the UK Acid Waters Monitoring Network (D.T.Monteith, M.Bonjean) for provision of surface water chemistry data.
B. Tebay for the provision of rainfall and temperature data for the Ambleside station.
E.Y.Haworth (Freshwater Biological Association) for helpful discussions, and for the provision of data on Scoat Tarn*
S.Buckingham (CEH Lancaster & Lancaster University) for help with sampling
C.D.Evans (CEH Bangor) for advice on the Gothenburg protocol forecasts, and provision of data
The National Trust for permission to sample soils in the catchments of Scoat Tarn and Howden Reservoir
The Rangers of the Peak District National Park for assistance with access to the upper parts of the Howden Reservoir catchment.
J.J.Rothwell (Manchester Metropolitan University) for helpful discussions about the Howden Reservoir catchment.
The person who did the magnetics on the sediments

* You may want to check with Laura about this wording
We would like to thank the following persons for sampling the mosses:
Laurence Jones and Simon Grant (CEH Bangor), Louise Ross and Laura Flegg (CEH Banchory), Ian Leith and Netty van Dijk (CEH Edinburgh), David Benham, Lisa Norten and Michelle Taylor (CEH Lancaster), Sarah Hulmes, Kevin Walker and Peter Nuttall (CEH Monks Wood), Caroline Boffey (CEH Dorset), Ben Haworth (University of York) and Alex Higgins (AFBI, Northern Ireland).

References

Alfaro-De La Torre, M.C. & Tessier, A. (2002) Cadmium deposition and mobility in the sediments of an acidic oligotrophic lake. Geochim. Cosmochim. Acta 66, 3549-3562.

Ali, N. A., Ater, M., Sunahara, G. I., and Robidoux, P. Y. 2004. Phytotoxicity and bioaccumulation of copper and chromium using barley (*Hordeum vulgare* L.) in spiked artificial and natural forest soils. Ecotoxicology and Environmental Safety, 57, 363-374.

Amorim, M. J. D., Rombke, J., Schallnass, H. J., Mortagua, A., and Soares, V. M. 2005. Effect of soil properties and aging on the toxicity of copper for Enchytraeus albidus, Enchytraeus luxuriosus, and Folsomia candida. Environmental Toxicology and Chemistry, 24, 1875-1885.

Ashmore, M., Bell, S., Fowler, D., Hill, M., Jordan, C., Nemitz, E., Parry, S., Pugh, B., Reynolds, B., Williams, J. (2002). Survey of the UK metal content of mosses 2000. Part II of EPG 1/3/144 final contract report: development of a critical load

Ashmore, M., Shotbolt, L., Hill, M., Hall, J, Spurgeon, D., Svendsen, C., Fawehinmi, J., Heywood, E., Tipping, E. Lofts, S., Lawlor, A & Jordan, C. (2004) Further Development of an Effects (Critical Loads) Based Approach for Cadmium, Copper, Lead and Zinc. Report to the Department of the Environment, Transport and the Regions, the Scottish Executive, the National Assembly for Wales and the Department of the Environment in Northern Ireland. Contract EPG 1/3/188. University of York.

AWMN (1992) UK Acid Waters Monitoring Network. Summary of data for year 3 (1990-1991). Report to the Department of the Environment Contract PECD 7/12/02. ENSIS Ltd.

Baker, S.J. (2001) Trace and Major Elements in the Atmosphere at Rural Locations in the UK: Summary of Data for 1999. Report AEAT/R/ENV/0264 to the Department of the Environment, Transport and the Regions, the Scottish Executive, the National Assembly for Wales and the Department of the Environment in Northern Ireland. AEA Technology, Abingdon.

Bárány-Kevei, I., Goldie, H., Hoyk, E. & Zseni, A. (2001) Heavy metal content of some Humgarian and Englsh karst soils. Acta Climat. Chorol. 34-35, 81-92.

Bellamy, P.H., Loveland, P.J., Bradley, R.I., Lark, R.M. & Kirk, G.J.D. (2005) Carbon losses from all soils across England and Wales 1978–2003. Nature 437, 245-248.

Burgos, M. G., Winters, C., Sturzenbaum, S. R., Randerson, P. F., Kille, P., and Morgan, A. J. 2005. Cu and Cd effects on the earthworm *Lumbricus rubellus* in the laboratory: Multivariate statistical analysis of relationships between exposure, biomarkers, and ecologically relevant parameters. Environmental Science & Technology, 39, 1757-1763.

Evans CD, Monteith DT & Cooper DM (2005) Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. Environ. Poll. 137, 55-71.

Fowler D., McDonald A.G., Crossley A., Nemitz, E., Leaver, D., Cape, J.N., Smith R.I., Anderson D., Rowland P., Ainsworth G., Lawlor, A.J., Guyatt, H. & Harmens H. (2006) UK Heavy Metal Monitoring Network Project Number EPG 1/3/204 Report to Defra.

Fait, G., Broos, K., Zrna, S., Lombi, E., and Hamon, R. 2006. Tolerance of nitrifying bacteria to copper and nickel. Environmental Toxicology and Chemistry, 25, 2000-2005.

Gharbi, F., Rejeb, S., Ghorbal, M. H., and Morel, J. L. 2005. Plant response to copper toxicity as affected by plant species and soil type. Journal of Plant Nutrition, 28, 379-392.

Hall, J., Ashmore, M., Fawehinmi, J., Jordan, C., Lofts, S., Shotbolt, L., Spurgeon, S., Svendsen, C. & Tipping, E. 2006. Developing a critical load approach for national risk assessments of atmospheric metal deposition. Environmental Toxicology and Chemistry, 25, 883-890.

Hamilton-Taylor, J. (1979) Enrichments of zinc, lead, and copper in recent sediments of Windermere, England. Environ. Sci. Technol. 13, 693-697.

Hamilton-Taylor, J., Yang, Y.-L., Arewgoda, C.M., Hewitt, C.N. & Davison, W. (1993) the trace metal dissolution kinetics of three rural atmospheric aerosols in a range of natural fresh water types. Water Res. 27, 243-254.

Harmens, H. and the participants of the European moss survey (2005a). Heavy metals in European mosses: 2005/2006 survey. Monitoring manual. ICP Vegetation Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK. http://icpvegetation.ceh.ac.uk

Harmens, H., Mills, G., Hayes, F., Williams, P., De Temmerman, L. and the participants of ICP Vegetation (2005b). Air pollution and vegetation. ICP Vegetation Annual Report 2004/2005. UNECE ICP Vegetation Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK. http://icpvegetation.ceh.ac.uk

Harmens, H., Norris, D.A., Koerber, G.R., Buse, A., Steinnes, E., Rühling, Å. (2007a). Temporal trends in the concentration of arsenic, chromium, copper, iron, nickel, vanadium and zinc in mosses across Europe between 1990 and 2000. Atmospheric Environment 41: 6673-6687.

Harmens, H., Norris, D.A., Koerber, G.R., Buse, A., Steinnes, E., Rühling, Å. (2007b). Temporal trends (1990 – 2000) in the concentration of cadmium, lead and mercury in mosses across Europe. Environmental Pollution. In press.

Haworth, E.Y. & Lishman J.P. (1991) Recent changes to upland tarns in the English Lake District. Hydrobiologia 214, 181-186.

Lofts, S., Spurgeon, D. J., Svendsen, C., and Tipping, E. 2004. Deriving Soil Critical Limits for Cu, Zn, Cd, and Pb: A Method Based on Free Ion Concentrations. Environmental Science & Technology, 38, 3623-3631.

Loring, D.H. (1991) Normailization of heavy-metal data from estuarine and coastal sediments. J. Mar. Sci. 48, 101-115.

Mackereth F.J.H. 1969. A short core sampler for sub-aqueous deposits. Limnol. Oceanogr. 14: 145–151.

Menta, C., Maggiani, A., and Vattuone, Z. 2006. Effects of Cd and Pb on the survival and juvenile production of *Sinella coeca* and *Folsomia candida*. European Journal of Soil Biology, 42, 181-189.

Mertens, J., Degryse, F., Springael, D., and Smolders, E. 2007. Zinc Toxicity to Nitrification in Soil and Soilless Culture Can Be Predicted with the Same Biotic Ligand Model. Environ. Sci. Technol., 41, 2992-2997.

Monteith, D.T. (Ed.) (2005) United Kingdom Acid Waters Monitoring Network 15 Year Report. Analysis and Interpretation of Results, April 1988 - March 2003. ENSIS Publishing, London.

Nriagu, J.O., 1989. A global assessment of natural sources of atmospheric trace metals. Nature, 338, 47-49.

Ochsenbein, U., Davison, W., Hilton, J., Haworth, E.Y. (1983) The geochemical record of major cations and trace metals in a productive lake. Arch. Hydrobiol. 98, 463-488.

Rooney, C. P., Zhao, F.-J., and McGrath, S. P. 2006. Soil factors controlling the expression of copper toxicity to plants in a wide range of European soils. Environmental Toxicology and Chemistry, 25, 726-732.

Rooney, C. P., Zhao, F. J., And McGrath, S. P. 2007. Phytotoxicity of nickel in a range of European soils: Influence of soil properties, Ni solubility and speciation. Environmental Pollution, 145, 596-605.

Rose, N.L. (Ed.) (2007) Lochnagar: The Natural History of a Mountain Lake. Springer, Dordrecht.

Rothwell, J.J., Evans, M.G. & Allott, T.E.H. (2007) Lead contamination of fluvial sediments in an eroding blanket peat catchment. Appl. Geochem. 22, 446-459.

Shilland, E.M., Monteith, D.T., Bonjean, M. & Beaumont W.R.C. (Eds.) (2006) UKAWMN Summary of Data for Year 18 (2005-2006) Report to the Department for Environment, Food and Rural Affairs (Contract EPG 1/3/160).

Shotbolt, L. (2002) The use of southern Pennine reservoir sediments as records of atmospheric heavy metal deposition. Unpublished Ph.D. thesis. University of Salford, 374 pp.

Shotbolt, L., Hutchinson, S.M. & Thomas, A.D. (2007) Sediment stratigraphy and heavy metal fluxes to reservoirs in the southern Pennine uplands, UK. Journal of Paleolimnology 35: 305–322.

Slootweg, J., Hettelingh, J.-P., Posch, M. (eds), Dutchak, S., Ilyin, I. 2005. Critical loads of cadmium, lead and mercury in Europe. Report 259101015/2005. Collaborative report by ICP M&M Coordination Centre for Effects and EMEP Meteorological Synthesizing Centre – East. Netherlands Environmental Assessment Agency, Bilthoven, Netherlands.

Smolders, E., Buekers, J., Oliver, I., and Mclaughlin, M. J. 2004. Soil properties affecting toxicity of zinc to soil microbial properties in laboratory-spiked and field-contaminated soil. Environmental Toxicology and Chemistry, 23, 2633-2640.

Son, J., Ryoo, M. I., Jung, J., and Cho, K. 2007. Effects of cadmium, mercury and lead on the survival and instantaneous rate of increase of *Paronychiurus kimi* (Lee) (Collembola). Applied Soil Ecology, 35, 404-411.

Spurgeon, D. J., Sturzenbaum, S. R., Svendsen, C., Hankard, P. K., Morgan, A. J., Weeks, J. M., and Kille, P. 2004. Toxicological, cellular and gene expression responses in earthworms exposed to copper and cadmium. Comparative Biochemistry and Physiology C-Toxicology & Pharmacology, 138, 11-21.

Steinnes, E., Rühling, Å., Lippo, H., Mäkinen, A. (1997). Reference material for large-scale metal deposition surveys. Accreditation and Quality Assurance 2, 243-249.

Tallantire, P.A. (1997) Plant Macrofossils form the Historiacl Period from Scoat Tarn (Wasdale), English Lake District, in relation to environmental and climatic change. Bot. J. Scotl. 49 (1) 1-17.

Tipping, E. (2005) Modelling Al competition for heavy metal binding by dissolved organic matter in soil and surface waters of acid and neutral pH. Geoderma 127, 293-304.

Tipping, E., Lawlor, A.J. & Lofts, S. (2005a) Simulating the long-term chemistry of an upland UK catchment; major solutes and acidification. Environ. Poll. 141, 151-166.

Tipping, E., Lawlor, A.J., Lofts, S. & Shotbolt, L. (2005b) Simulating the long-term chemistry of an upland UK catchment; heavy metals. Environ. Poll. 141, 139-150.

Tipping, E., Rieuwerts, J., Pan, G., Ashmore, M.R., Lofts, S., Hill, M.T.R., Farago, M.E. & Thornton, I. (2003) The solid-solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales. Environ. Pollut. 125, 213-225.

Tipping, E., Thacker, S.A., Wilson, D. & Hall, J.R. (2007) Long-term nitrate increases in two oligotrophic lakes, due to the leaching of atmospherically-deposited N from moorland ranker soils. Environ. Poll. In press.

Tipping, E., Yang, H., Lawlor, A.J., Rose, N.L. & Shotbolt, L. (2007) Trace metals in the catchment, loch and sediments of Lochnagar: measurements and modelling. In Rose, N.L. (Ed.) Lochnagar: The Natural History of a Mountain Lake. Springer, Dordrecht, pp. 345-373.

Van Gestel, C. A. M., and Koolhaas, J. E. 2004. Water-extractability, free ion activity, and pH explain cadmium sorption and toxicity to *Folsomia candida* (Collembola) in seven soil-pH combinations. Environmental Toxicology and Chemistry, 23, 1822-1833.

de Vries, W. & Bakker, D.J. (1998) manual for calculating critical loads of heavy metals for terrestrial ecosystems. Report 166 DLO & TNO, Netherlands.

Wilke, B. M., Mai, M., Gattinger, A., Schloter, M., and Gong, P. 2005. Effects of fresh and aged copper contaminations on soil microorganisms. Journal of Plant Nutrition and Soil Science-Zeitschrift Für Pflanzenernahrung und Bodenkunde, 168, 668-675.

Wolff-Boenisch, D., Gislason, S.R. & Oelkers, E.H. (2006) the effect of crystallinity on dissolution rates and CO_2 consumption capacity of silicates. Geochim. Cosmochim. Acta 70, 858-870.

Worrall F, Harriman R, Evans CD, Watts CD, Adamson JK, Neal C, Tipping E, Burt T, Grieve IC, Montieth D, Naden PS, Nisbet T, Reynolds B & Stevens P. (2004) Trends in dissolved organic carbon in UK rivers and lakes. Biogeochem. 70: 369-402.

Yang, H. (2000) Trace metal storage in lake systems and its relationship with atmospheric deposition with particular reference to Lochnagar, Scotland. Unpublished PhD thesis. University of London. 340pp.

Yang, H., Rose, N.L., Battarbee, R.W. & Boyle, J.F. (2002a) Mercury and lead budgets for Lochnagar, a Scottish mountain lake and its catchment. Environ. Sci. Technol. 36, 1383-1388.