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FURTHER DEVELOPMENT OF AN EFFECTS (CRITICAL LOADS) BASED APPROACH FOR CADMIUM, COPPER, LEAD AND ZINC

Final Report for Defra

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EXECUTIVE SUMMARY

- Critical loads methods for toxic metals are being developed for application within the United Nations Economic Commission for Europe (UN/ECE) Convention on Long-range Transboundary Air Pollution (CLRTAP). However, at the start of this project, there were still major uncertainties over the best methodological approach, and whether a critical load approach was the best method for risk assessment of atmospheric deposition of metals.

- This report summarises the outcome of a collaborative research project aimed at further development of a critical loads approach for metals that is appropriate for application in the U.K. and at contributing to improved risk assessment methods within CLRTAP.

- The work focussed on lead and cadmium, as the metals of greatest concern within CLRTAP, but also considered copper, zinc and nickel. An initial assessment was also made of the feasibility of applying the critical load approach to mercury and arsenic.

- There were three major areas of work:- (i) development of improved ecosystem effects criteria (critical limits); (ii) development and testing of dynamic models to assess long-term effects of metal deposition on concentrations in soils and freshwaters; and (iii) development and application of improved procedures for modelling and mapping critical loads and critical limits, and their exceedence, in the U.K.

- This executive summary considers the main outcomes of the work under each of these themes before considering the policy implications of the work and drawing brief general conclusions.

(i) Ecosystem Effects Criteria

- Prior to this project, critical limits for metals for use within CLRTAP had been defined as total soil, total freshwater or total soil solution concentrations, although there is considerable evidence that effects are more closely related to free ion activity.

- Literature from ecotoxicological studies for each metal was collated, carefully screened for key quality criteria, and those studies with sufficient chemical information to model free ion activity were identified.

- The database developed within this project was harmonised with information collected by European collaborators, and from EU Risk Assessment evaluations, to create a larger body of data.

- Species sensitivity distributions were constructed and critical limits were set to protect 95% of species.

- It was found for soils data that the toxicity of the modelled free-ion activity was dependent on soil pH, with the same free-ion activity having a greater effect at higher values of pH.

- Based on this important new finding, the concept of a fixed critical limit was replaced by the concept of a critical limit function, expressing the critical limit as a function of pH.

- Although chronic aquatic toxicity data were less extensive than the soils database, the critical limit functions derived from soil toxicity data were consistent with the aquatic data.

(ii) Dynamic modelling

- Field measurements of soil and water chemistry were completed successfully in four catchments, and the results were combined with previous values to obtain data for a total of ten catchments that were suitable for the calibration and/or testing of the dynamic model CHUM-AM.

- After calibrating the model to simulate catchment behaviour for major chemical components, it was used, together with estimated historical deposition scenarios of heavy metals, to simulate current soil pools and mean streamwater concentrations of metals.
- Historical deposition scenarios were constructed based on a review of literature on historical emissions and sediment and peat core records.

- The deposition scenarios were based on defining a general national time trend, which can be scaled for local application based on peak deposition rates in the 1960s/1970s. Superimposed on this were deposition histories from local mining activity, based either on an analysis of local records or, as a default, a national mining-related scenario.

- Herbarium samples from 1850 to the present day were collected within 40km. of the study catchments and analysed for their metal content. Although there was considerable scatter in the data, the time series were broadly consistent with the historical deposition scenarios developed from literature evaluation. The exception was the Lake District, probably because of local variation in mining activities.

- The results of the CHUM-AM simulations were in general agreement with measurements for the nine catchments with acid soils. This finding supports the basic assumptions of the model, and provides some confidence in predictions of future metal behaviour. However, the lack of time series data means that we cannot be certain about simulations of the temporal variations in metal levels.

- The assumption that background metal deposition was 20% of the present day values permitted the model to reproduce observed metal levels. However, there is uncertainty about long-term weathering inputs. For Pb, Cu and Ni, estimated weathering rates were comparable to the assumed background deposition, implying either that true background levels should be lower or that the model predictions are in error. However, the estimate of weathering rate is based on untested assumptions, and further work is required to resolve this issue.

- Streamwater concentrations in the one catchment with limestone soils were comparable to those for catchments with acid soils, despite the stronger binding of metals to soil solids that would be expected. The contribution of geochemically inactive metals derived from dissolution of carbonates is uncertain, and makes validation of the CHUM-AM model for this catchment uncertain.

- Simulated sediment records for Lochnagar agree with observed values in that they show increases in metal levels, from the end of the 19th Century. The simulated sediment Cu levels are about 50% of the observed values, while those of Zn are similar to the observed values. However, metal deposition inputs at Lochnagar are low, and the modelling approach could be usefully applied to more polluted catchments.

- Future metal behaviour was predicted for two acid catchments under three deposition scenarios. At the more acid catchment, with higher [DOM], the soil Cd pool is calculated to take several hundred years to reach a steady state, while that of Pb will require almost 1000 years. At the currently less-acid catchment, with low [DOM], the timescales are longer still. However, at this catchment, nitrate leaching is predicted to cause a severe acidification, which will increase the rates of change of metal concentrations.

- Concentrations of free metal ions in soil solutions, simulated using the CHUM-AM model, were compared to critical limit values, for 1970 and 2000. For Zn, in only one case (Old Lodge in 1970) did the free ion concentration approach to the critical limit. However, the free ion concentration of Pb was close or equal to the critical limit in six of the eight catchments in 1970 and in four catchments (all in the Lake District) in 2000. There were no exceedences for Ni, Cu or Cd.

- A simple dynamic model was constructed to calculate times for soil metal pools to reach critical limits. The model was shown to be in broad agreement with CHUM-AM, with both models showing that the rate of change of soil Cd pools is about an order of magnitude greater than that of soil Pb pools.

- In summary, the dynamic modelling suggests that the timescales of change of soil metal pools are of the order of decades to centuries. Future metal behaviour will depend on the historical interactions between acidification and metal deposition, both of which have passed through maxima in recent decades, and future changes in acidification status, linked to nitrogen saturation.

(iii) Critical Loads Modelling and Mapping

- Pedotransfer functions between free ion concentrations in soil solution and total, or reactive, metal concentrations are essential to application of critical limits and critical loads

- Soil samples were taken from five land-use types to test whether transfer functions developed in a previous phase of the work from acid grassland sites were applicable over a wider range of sites. Satisfactory agreement was obtained for Pb and Cu, but systematic errors were found for Zn and Cd, There was also poorer agreement for Zn and Cd with transfer functions derived from Dutch data.

- Therefore, all the UK data were combined to produce transfer functions for national application, based on Freundlich partitioning coefficients. These provide good fits to data and could be applied across a wide range of UK soils and land covers.

- Algorithms were written to calculate critical loads and critical limits for soils based on the pH dependent free ion function using a national GIS database. The calculations were performed separately for four habitats – semi-natural vegetation, unmanaged forest, managed deciduous forest and managed coniferous forest.

- Dissolved organic carbon (DOC) is an important term in the calculation of critical loads that is not held in the GIS. A literature review was conducted, and a compilation of UK measurements was made, to improve modelling of DOC. As a result, instead of the constant value recommended by the Mapping Manual, functions were developed to predict DOC as a function of land cover and runoff.

- New data were collected on wood metal concentrations from Forest Level II plots, and uptake rates were calculated based on growth rates over appropriate harvest cycles for five species.

- Calculated metal uptake rates were comparable to, or exceeded, current rates of deposition at some sites for all metals apart from lead, for which uptake never exceeded 30% of deposition. This indicates the significance of metal uptake rates in critical load assessments.

- Critical limits for cadmium were exceeded over 11.2% of the country, excluding Scotland, Critical limits for lead were only exceeded over 1.2% of the U.K. Compared with the previous method of using a single reactive soil concentration as a critical limit, the use of the pH dependent free ion critical limit function reduced the area of exceedence for lead and increased the area of exceedence for cadmium.

- Critical limits for copper and zinc were exceeded over 39.5% and 38.4% of the UK respectively, primarily across lowland England.

- Critical loads of all metals varied by two to three orders of magnitude across the country. Critical loads showed a bimodal distribution, with the lowest critical loads being found in lowland areas of England and Wales, reflecting an association with low runoff, low DOC and high pH.

- Mapped values of metal deposition rates to forests and to semi-natural vegetation were provided by CEH Edinburgh and were used to map exceedence of critical loads.

- Critical loads of cadmium were not exceeded except for a very small area of unmanaged forest. However, critical loads of lead were exceeded over most of central, southern and eastern England for semi-natural vegetation. For forests, the area of exceedence extended to parts of Wales, northern England, Scotland and Northern Ireland, because of the higher modelled rates of deposition, especially for lead.

- Critical loads of copper and zinc were exceeded over most of central, eastern and southern England, with zinc also exceeded in parts of Wales and South West England

- A simple dynamic model was used to assess probable timescales to exceedence of critical loads at current rates of deposition. As cadmium deposition is predominantly below critical loads, only an insignificant area (<0.001% of managed forests) is likely to reach critical limits, and this is predicted to take more than 500 years. Hence, the areas of current exceedence of cadmium critical levels reflect the impact of historical deposition, weathering or other soil inputs.

- For lead, current efflux was modelled to exceed net input for most of Scotland and Northern Ireland for forests. These areas are therefore unlikely to ever reach exceedence for the critical limit. This area extended to much of northern England and Wales for semi-natural vegetation,. The difference is due to the greater deposition to forests which significantly exceeds the greater uptake in managed forests. For the rest of the country, the modelled times to reach critical limit exceedence were 100-500 years.

- For copper and zinc, current efflux was modelled to exceed net input for most of Scotland, Northern Ireland and Wales. This area extended to Northern England and South West England for copper and semi-natural vegetation only for zinc. For zinc and copper the net input to forests (deposition minus uptake) is higher than that for semi-natural vegetation, thus current deposition is below critical loads for a smaller area. For the rest of the country, critical limits are already exceeded, or the modelled times to reach critical limits were greater than 500 years.

- The results for critical limit and critical load exceedence of cadmium and lead are consistent with the more rapid dynamics of cadmium compared to lead, as indicated in the dynamic modelling. Soil concentrations of cadmium may have increased more rapidly in the past to exceed the critical limit, but are now declining, whereas soil concentrations of lead have not exceeded the critical limit yet, but may do so over the next century if current rates of deposition continue.

- The results for critical limits and loads exceedence for copper and zinc indicate that those most areas exceeding critical limits are not recovering (i.e. they still have deposition rates that exceed critical loads). Despite reductions in deposition, Cu and Zn are still accumulating in these areas although the rate of increase is probably now relatively slow.

- Critical loads were calculated for the 22 catchments of the Acid Waters Monitoring Network (AWMN), based on a combination of water chemistry data extracted from the AWMN database and soil and catchment data extracted from the national database. Critical loads were compared with modelled deposition for the catchments

- Critical loads for cadmium, zinc and nickel were not exceeded at any of the 22 sites. However, critical loads were exceeded at three sites for copper and four sites for lead.

- The most sensitive catchments, and those at which the critical loads were exceeded, tended to be in England and Wales

- The sites within the AWMN are not ideally positioned for monitoring of the impacts of changing metal deposition on sensitive catchments, and more catchments in lowland England and Wales need to be considered.

- Sensitivity and uncertainty analyses were conducted for calculations of critical loads for soils for one forested grid square, in which critical limits are exceeded for copper and critical loads are exceeded for copper, lead and zinc.

- The values of critical loads and critical limits, and their exceedence, were all found to be extremely sensitive to the value of the terms in the critical limit function, while these were also the dominant uncertainty. This reflects the limited database available for derivation of the critical limit function.

- In terms of other parameters, critical load exceedences were most sensitive to variation in the values of deposition, runoff, pH and DOC, while critical limit exceedences were most sensitive to values of transfer function coefficients, soil concentration, pH, and soil organic content.

- The results of an uncertainty analysis for a fixed critical limit showed that coefficients of variation for critical loads varied between 40% and 60% for the different metals.

- The uncertainty analysis allowed exceedence of critical load to be evaluated in a probabilistic manner rather than as a deterministic value, which might provide a stronger basis for future policy evaluation.

(iv) Critical Loads Methods for Mercury and Arsenic

- The possibility of applying critical loads methods for national risk assessment of the effects of deposition of arsenic (As) and mercury (Hg) in the UK was assessed. Since critical limits and critical loads methods for Hg have already been defined and adopted for application within CLRTAP, but this is not the case for As, the focus was on Hg.

- Critical limits currently adopted for use in the Mapping Manual for ecotoxicological effects in soils are based on a study in Scandinavian forests, do not consider direct effects of organic and methyl mercury, and are expressed as total soil solution concentrations. All these factors are considered to make them inappropriate for application in the UK.

- There are a sufficient number of ecotoxicological studies of effects of both Hg and As to provide a basis to set more objective critical limits for direct effects, based on all the available literature.

- The current critical limit of Hg for freshwaters is linked to fish concentrations, and is based on health effects linked to Scandinavian patterns of local fish consumption, which differ from those in the U.K. Ecotoxicological criteria might be more appropriate for the U.K.

- Concentrations of Hg and As have been measured in a range of environmental media in the UK over the past thirty years. These include soils, stream and lake sediments, mosses, water, fish, and predators. It is also possible that some archived samples could be analysed for these elements.

- Analysis of environmental samples for trace amounts of Hg and As is difficult, with high blank values due to laboratory and instrumental contamination, and loss of volatile Hg during storage. Hence interpretation of older datasets is problematic unless good QA/QC information is available. This is particular problem for waters.

- Much of this data relates to specific sites or small networks, such as the Environmental Change Network and the Acid Waters Monitoring Network. There is a national database of soil concentrations of Hg and As that covers England and Wales, but no national coverage of water concentrations.

- There is national data on stream sediment concentrations for As, that could be used if appropriate critical limits and critical loads methods were defined for sediments.

- Deposition data from the current metals deposition network provide adequate information for comparisons with critical loads. However, older network data for air concentrations and deposition of Hg are likely to be unreliable.

- The interactions of Hg with organic matter are likely to be of great importance in evaluating ecotoxicological data and developing critical loads methods. An initial investigation with the WHAM model, which has been used for critical loads of lead and cadmium, showed reasonable predictions for the binding of Hg with natural organic matter.

- The methods of mapping critical loads for mercury that are proposed in the Mapping Manual are based on dubious assumptions, uncertain critical limits, and unreliable parameterisations, and hence cannot be recommended for application in the UK

- Development of a risk assessment approach for the UK for mercury, and possibly arsenic, should be based in the first instance on improved values of critical limits that could then be compared with available data on concentrations in relevant environmental media.

- Policy assessment of the effects of emissions reductions might then best be approached by the development of dynamic models, rather than by the development of steady-state critical load methods.

(v) Contributions to Policy Development

- Throughout the course of this research project, there has been active engagement in ongoing discussions within UN/ECE CLRTAP of appropriate critical loads methods for toxic metals. Four members of the research consortium have acted as members of the Expert Panel that advised on the development of new methods and their incorporation within the Mapping Manual of the ICP Mapping and Modelling.

- The pH dependent free-ion function has now been accepted within the UN/ECE CLRTAP Mapping Manual as the best approach to setting critical limits of lead and cadmium for ecotoxicological effects in soils. Furthermore, the methods developed within this project to model and map critical loads based on this approach have been broadly incorporated into the Mapping Manual. However, the pH dependent free-ion function has not been accepted for modelling of critical loads for ecotoxicological effects in freshwaters.

- The methods for health-based critical loads and for critical loads of mercury within the draft Mapping Manual are not recommended for application in the U.K.

- The importance of dynamic modelling for policy evaluation has been emphasised by members of the research consortium in discussions within CLRTAP. While methods for dynamic modelling of metals have not been evaluated within CLRTAP to date, it has been accepted that this issue will receive greater attention in the future.

(vi) Overall Conclusions and UK Policy Implications

- New critical limit and critical load methods have been developed and applied in the U.K. These provide a sounder mechanistic basis for assessment of the environmental risks of metal deposition from the atmosphere. There is a potential to extend these methods to mercury. However, the uncertainty analysis conducted within this project indicated that the conclusions in terms of critical limit and critical load exceedence need to be interpreted with caution.

- It is clear that understanding the dynamics of response to soil and freshwater metal concentrations to deposition is crucial to interpreting maps of critical load and critical limit exceedence, and their policy implications. Furthermore, future effects of changing deposition of acidity and nitrogen, and changing DOC fluxes, may be as significant as changing rates of metal deposition.

- Given these major constraints and uncertainties, the following broad conclusions can be drawn:-

- There is no evidence of any exceedence of critical limits and critical loads for nickel

- For lead, critical loads for soils are exceeded over much of lowland Britain, but critical limits in this area are not exceeded. Soil concentrations may continue to increase at current deposition rates, and critical limits may then be reached over the next 100 years or more. Critical loads of lead were also exceeded for freshwaters in some catchments in this region, which raises concerns about the continued accumulation of lead within them.

- For cadmium, critical loads are not exceeded, and it is to be expected that soil concentrations will fall over the coming century, reducing the extent of critical limits exceedence.

- Critical limits for copper are exceeded over significant areas of England and Wales. Critical loads are also exceeded, though predominantly across southern, midland and Eastern England. In this area, soils are either already exceeding critical limits or are predicted to, although not for at least 500 years. Current reductions in deposition are not leading to a reduction in soil copper levels across much of England.

- Critical limits for zinc are also exceeded over much of England and Wales. Critical loads are also exceeded extensively across England and parts of Wales. Again, current reductions in deposition are not resulting in major reductions in soil zinc levels across lowland England.

- However, the level of uncertainty in these broad conclusions is such that substantial further research is needed to provide more definitive judgements on the policy implications of the impacts of past and future atmospheric deposition of metals.

1 INTRODUCTION

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

The major objectives of the research were:

- To establish critical threshold concentrations of bio-available metals for effects on a range of taxonomic groups in soils and freshwaters;

- To develop improved models for predicting and mapping current bio-available concentrations of metals in soils and freshwaters;

- To develop and test improved dynamic models to assess the long-term effects of changing patterns of atmospheric deposition on metal concentrations in soils and freshwaters; and

- To develop improved models and mapping procedures for critical limits and critical loads in the UK, and to contribute to the development of internationally agreed methods with UN/ECE.

This report summarises work carried out, and the major outcomes and policy implications, covering each of the three Work Packages in turn. Further details of the work, and key publications and reports arising from it, are presented in the Annexe that accompanies this report.

2 WORK PACKAGE 1: ECOSYSTEM EFFECTS CRITERIA

2.1 Introduction

The overall objective of Work Package 1 was to establish critical threshold concentrations of bioavailable metals (Cu, Zn, Cd, Pb) for effects on a range of taxonomic groups in soils and freshwaters. The main tasks may be summarised as:

- Collection of literature data on toxic effects of metals to organisms (microbes, plants, animals) in soils and freshwaters, based on set minimum data requirements.

- Calculation of threshold concentrations for effects, expressed as the free metal ion concentration (soils and freshwaters) and the total soil solution concentration (soils only).

- Derivation of critical limits using a species sensitivity distribution approach

For soils, the work focused on both total soil concentrations and free metal ion concentrations, because the former approach was recommended at the UN/ECE Bratislava workshop in 2000, and was originally also by recommended for use within CLRTAP. However, critical limits based on the concentration of free-ions present in soil solution were shown by research carried out under the previous contract (EPG 1/3/144) to be more effective in critical load assessment than those based on total soil solution concentrations, and hence the emphasis of the work has been on developing the free-ion approach.

A paper describing the results has been published in the journal Environmental Science and Technology (Annexe 1). New critical limits have been proposed, based on a model of pH-dependent free-ion toxicity. A brief summary of the principle of the new method is provided below, but the detail is provided in Annexe 1. Subsequent to publication of the paper, the parameters of the pH-dependent free-ion toxicity functions have been changed to reflect new data and revised assessments of data quality, as described below.

Extension of the work to nickel (under Option 5 of the original tender) has also been done. Soil toxicity data for nickel have been analysed and critical limits calculated using the new model.

2.2 Analysis of toxicity data

Chronic toxicity data for soils have been collated and critically screened. Toxic endpoints, expressed as lowest observed effect concentrations (LOECs), no observed effect concentrations (NOECs) and EC_{10} values, were related to soil pH and organic matter content. Through the use of transfer functions, relating free metal ion concentrations (Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}) to soil pH, organic matter content and metal content, the toxic end-points were expressed in terms of free-ion concentrations and pH. Species sensitivity has also been taken into account, and critical limit functions have been derived that protect 95% of species. The critical limit functions take the form:

$$\log M_{\mathrm{free,crit}} = \alpha_{EC}\,\mathrm{pH} + \gamma_{EC} \qquad \text{(Eq. 1)}$$

where $M_{\mathrm{free,crit}}$ is the critical limit expressed as the concentration of metal free-ion, and α_{EC} and γ_{EC} are constants.

Expression of the critical limits in this way establishes a direct link between chemical speciation and toxicity, and simplifies the calculation of the critical load. The same calculation methodology also provides critical limit functions expressed in terms of total soil metal, and taking into account variations in pH and organic matter content. Annexe 1 comprises a manuscript describing the derivation of the critical limit functions, and the necessary coefficients. Following the publication of this manuscript the decision was taken to harmonise the soil toxicological databases as far as possible with those being used under EU Risk Assessment processes. Revised values of the parameters α_{EC} and γ_{EC} for Cu, Zn, Cd and Pb, and new parameters for Ni, are given in Table 1.

Table 1 Critical limit function parameters for Ni, Cu, Zn, Cd and Pb

	Ni	Cu	Zn	Cd	Pb
α_{EC}	-0.64	-1.23	-0.31	-0.32	-0.91
γ_{EC}	-2.59	-2.05	-4.63	-6.34	-3.80

The transfer functions used in our work were derived from literature data, including data obtained and analysed in previous Defra-funded work (Tipping *et al.*, 2003a). We have also collaborated with Dutch colleagues in the derivation of improved transfer functions for Cd and Pb. These improved transfer functions will eventually be used in the derivation of critical limit functions recommended for use within Europe.

Chronic aquatic toxicity data have also been analysed. These are less extensive than the soils data, and the direct derivation of critical limit functions is therefore not possible at present. However, values of $M_{\mathrm{free,tox}}$ – i.e. free-ion concentrations corresponding to LOEC, NOEC and EC_{10} values – appear to be similar to the values for soils. Therefore, it seems reasonable to assume that the same critical limit functions could be used for both surface waters and soil solutions. This point is discussed further in the UK Background Document presented at the UN/ECE Expert Panel Meeting in Paris on April 9-10 2003 (Annexe 2). Aquatic toxicity data for Ni were not analysed; however, on the basis of the evidence for the similarity of toxic endpoint for the other metals, it is reasonable to assume that the critical limit function for Ni may be applied to both soils and waters. Fig. 1 shows the toxicity data for soils and waters, and the associated critical limit functions.

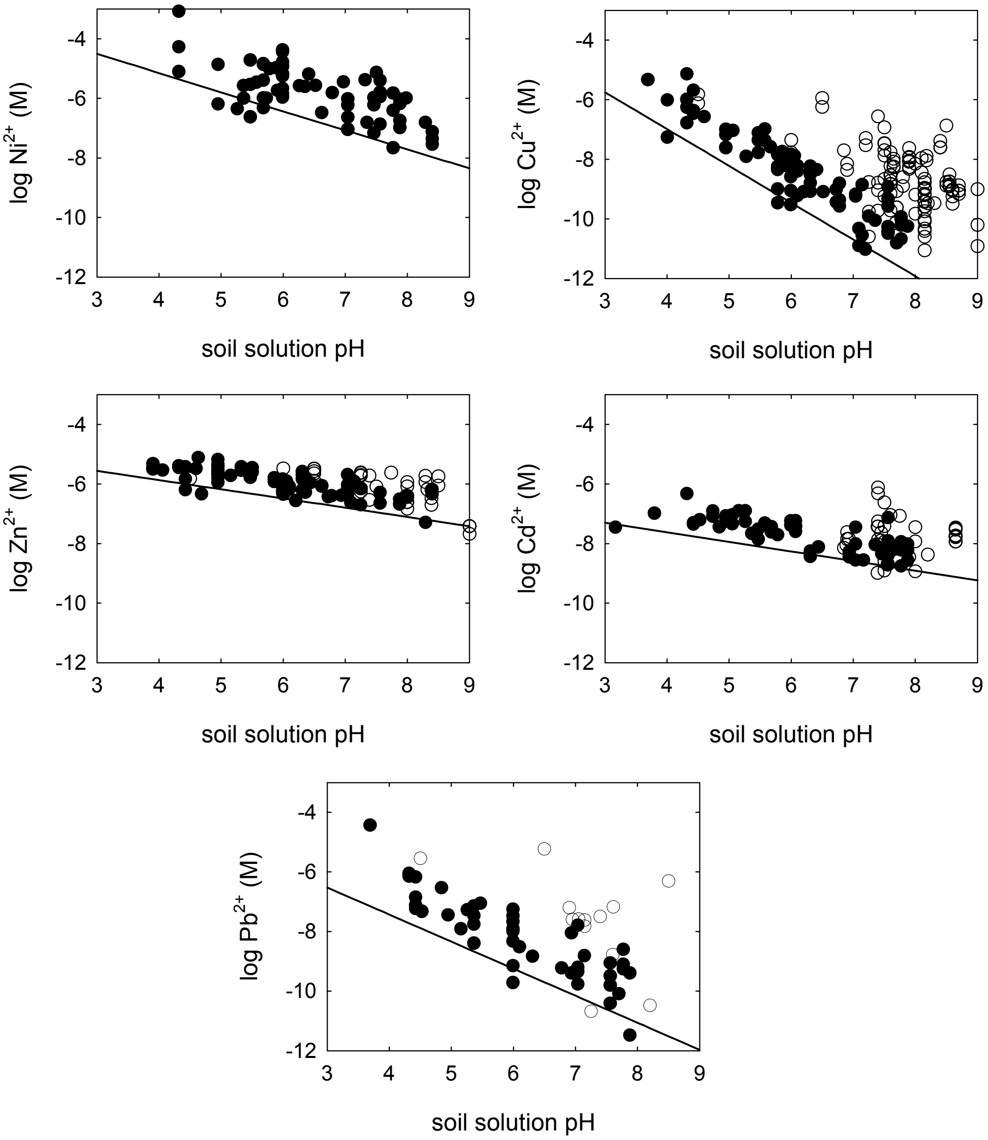


Figure 1. Distributions of toxic endpoint data, and critical limit functions, for Ni, Cu, Zn, Cd and Pb. Toxicity data are presented as free metal ion plotted against soil solution pH. Closed symbols refer to soil toxicity data, used to derive the critical limit functions (shown as lines). The open symbols refer to aquatic toxicity data; note that there are no aquatic data for Ni.

2.3 Application in calculating critical loads

The methodology for calculating metal critical loads from the free-ion critical limit functions was presented to the UN/ECE ICP Modelling and Mapping Expert Group in the UK Background Document to the Paris Meeting, April 9-10 2003 (Tipping *et al.*, 2003; Annexe 2). On this basis, a computer program was written to calculate steady state critical loads using UK databases, and this has been used in the creation of maps for the UK (see Section 4.4 on critical loads mapping and modelling).

The program is based on the WHAM6 chemical speciation model (Tipping, 1994, 1998), and takes into account competition by Al and Fe for the binding of heavy metals by dissolved organic matter. For this application, empirical equations were developed to predict dissolved Al and Fe concentrations in different soils. These equations have been reported in a manuscript which is now in press (Tipping, 2004; Annexe 3).

2.4 Limitations of and suggestions for further work on critical limits

The free ion approach for deriving critical limit functions has been developed with the express aim of allowing more scientifically realistic critical limits for metals to be derived, while using existing ecotoxicology data. The approach has been successfully applied to all the metals considered. At the same time, some limitations of the approach have become apparent, which centre on the use of literature data. The two most significant limitations are:

1. The need to convert toxicity data expressed as the reactive soil metal concentration, to the free ion concentration. The use of transfer functions to relate these two metal pools is highly convenient; however, the resulting uncertainties in the calculated free ion concentrations gives rise to uncertainties in the critical limit function parameters, and hence to uncertainties in both critical limits and critical loads. The implications of this is explored in Section 5.

2. The approach assumes that the variation with pH in the toxic response of organisms to the free metal ion is the same for all organisms. There is no reason to assume that this is necessarily so, but the limitations of the current toxicity data do not allow this to be examined in more detail.

3. The majority of the soils in which literature toxicity tests have been carried out are low in organic matter content (mainly less than 20%). For national scale application in the UK, a greater proportion of tests in soils more closely representative of the range of organic matter content found in UK soils would be appropriate.

Given these limitations, the development of new toxicity datasets for the metals in question would be of most benefit in advancing the development of the critical limit functions. Ideally, new toxicity datasets would comprise a set of standard tests on a set of specific organisms, each carried out on a set of soils whose chemical properties (pH and organic matter content) were broadly representative of UK soils. It would also be highly beneficial to make direct measurements of free metal ion concentrations in such tests. However, methods for measuring the free ion remain for the most part technically complex, time consuming and expensive, and so are not necessarily feasible in practical terms. There is current work being undertaken at the European level to generate new systematic toxicity datasets for copper and zinc (Ilse Schoeters, Lidia Regoli, *pers. comm.*), and the work on copper does include measurement of the free ion in the tests. For these metals, therefore, the potential exists to re–calculate critical limits based on such data if it becomes available. To our knowledge, however, so such systematic toxicity work is current being done for nickel, lead or cadmium.

3 WORK PACKAGE 2: DYNAMIC MODELLING

The dynamic modelling work involved the mathematical description of heavy metal accumulation and transport within soil, transfer to surface waters, and, for one study catchment, accumulation in lake sediments. It was recognised that the processes controlling the responses of soil and water metals to changes in atmospheric deposition take place over long timescales. Therefore we needed to take into account long-term changes in metal deposition rates, and also in soil and water properties, notably acidification status. In previous work under the NERC Environmental Diagnostics programme, the hydrochemical model CHUM was applied to catchments in the Lake District and at Great Dun Fell, both in Cumbria. In the present study, a new version of CHUM, CHUM-AM, was developed, more suitable for the necessary long-term applications.

CHUM-AM was applied to the Lake District and Great Dun Fell sites, using existing data. Data were also obtained for four additional catchments, providing a wider range of conditions for model application. Furthermore, CHUM-AM was applied to Lochnagar, using data obtained in Defra-funded work performed by scientists at University College, London.

The aims of the dynamic modelling work were:

- to measure and account for present day pools, concentrations and fluxes of heavy metals, on the basis of likely past scenarios of metal deposition and acidification;
- to use the calibrated model to explore the consequences of future changes in the atmospheric deposition of metals and acidifying pollutants;
- to produce a simple dynamic model for use within the mapping programme.

3.1 Field sampling and chemical analysis

The locations of field sites are shown in Fig. 2. The field programme within the present project focused on the first four catchments shown in Table 2. Sites studied previously, or by other workers, are also shown. At each site, measurements were made of atmospheric metal deposition, soil metal contents, stream water metal concentrations, and metal weathering. Measurements were also made of soil depth, bulk density and pH. Methods are described in Annexe 4. Tables 3 to 6 summarize the results obtained. Data are also presented for sites studied in previous work, funded by Defra and the NERC Environmental Diagnostics Programme. Data for Lochnagar, collected by Drs N. Rose and H. Yang, and colleagues, of University College London, in work partly funded by Defra, are also shown.

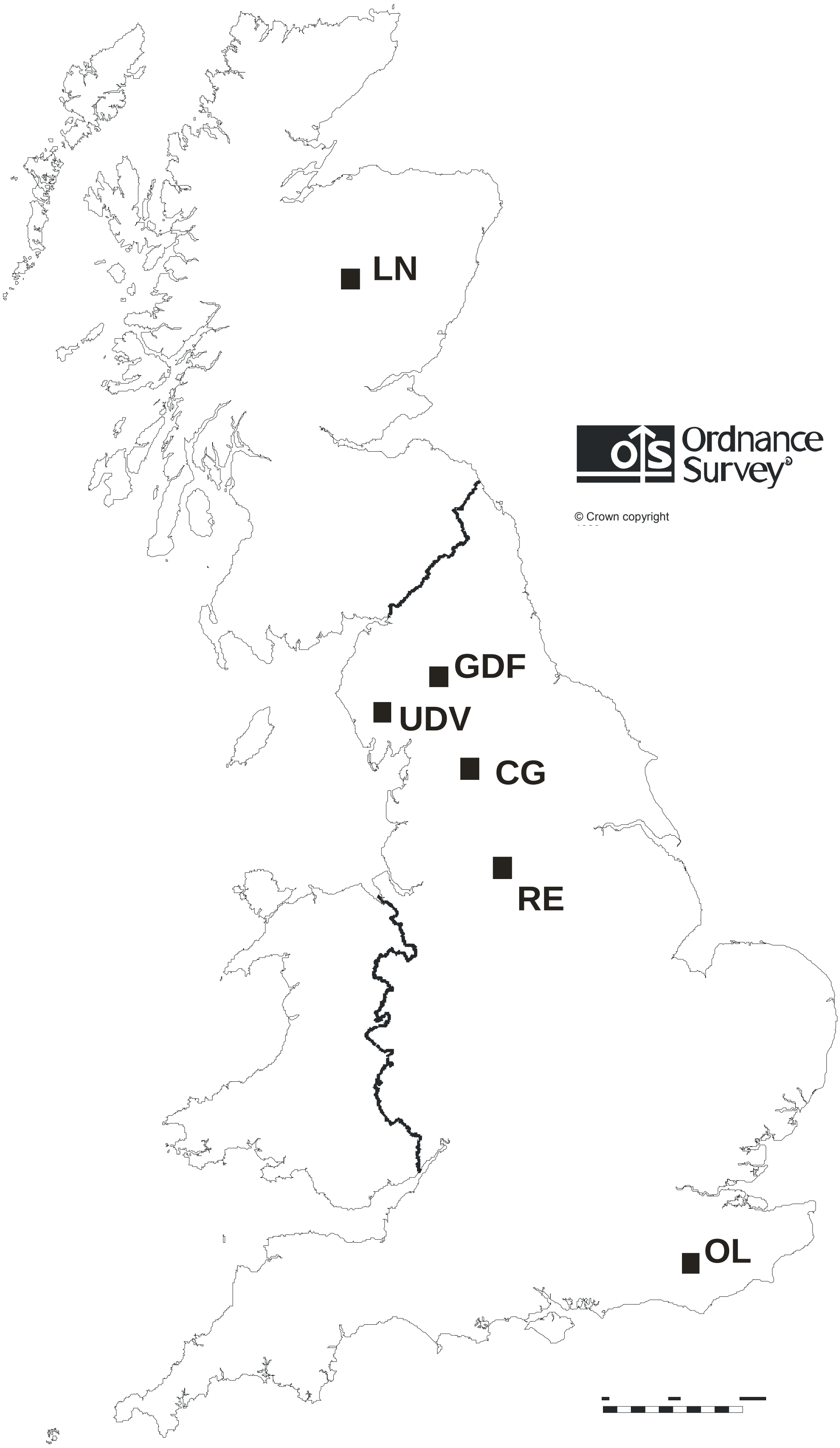


Figure 2 Locations of field sites used in dynamic modelling. Full site names are given in Table 2.

Table 2 Study catchments used in the present work.

Sites sampled in the present work	
Castle How Beck Upper Duddon valley (UDV), Cumbria	The catchment is partly forested. The data and modelling permit the effects of forestry to be examined, by comparison with previous results for moorland sites in the upper Duddon valley.
River Etherow (RE) Southern Pennines	The catchment is part of the Acid Waters Monitoring Network. The river drains peat moorland that has received high inputs of atmospherically deposited pollutants.
Old Lodge (OL) Ashdown Forest, Surrey	The catchment is part of the Acid Waters Monitoring Network, and provides insight into metal behaviour in the southern U.K.
Cote Gill (CG), Littondale, Yorkshire Dales	This is a limestone catchment, providing comparisons with the other acid catchments.
Sites studied in previous or other work	
Gaitscale Gill Troughton Gill Hard Knott Gill Upper Duddon valley (UDV), Cumbria	Moorland sites with the same atmospheric deposition, but different base cation weathering rates, and consequently different stream pH.
Pool X Pool Y Great Dun Fell (GDF), Cumbria	Peat drainage water.
Lochnagar (LN) Cairngorms, Scotland	Remote loch, part of the Acid Waters Monitoring Network, and a focus of study by University College London in several EU projects.

3.1.1 Atmospheric deposition of metals

Currently, bulk metal deposition loads are fairly similar at all the rural sites. No one site in Table 3 has the highest load of all metals. The upper Duddon valley and River Etherow sites have somewhat higher loads than the others, presumably due in the first case to the high rainfall, and in the second case to the proximity of pollution sources.

Table 3 Bulk deposition of heavy metals (g ha^{-1} a^{-1}).

Site	**dates**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**
Upper Duddon valley	1998-1999	12	12	72	0.6	24
Upper Duddon valley	2002-2003	6	7	70	0.5	20
Great Dun Fell	1998-1999	3	6	28	0.2	10
Old Lodge	2002-2003	2	4	34	0.3	8
River Etherow	2002-2003	6	11	76	0.6	30
Cote Gill	2002-2003	7	8	76	0.5	19
Lochnagar[1]	1999-2003	2	3	47	0.3	10

[1] data of Yang and Rose.

3.1.2 Soil properties

Soil bulk properties are shown in Table 4, as configured for CHUM-AM modelling (see section 3.2 and Annexe 4). Soil pools of "geochemically active" metals (i.e. extractable with 0.1 M HNO_3) are shown in Table 5. The catchment of the River Etherow has the highest soil level of Pb, attributable to high historic loadings from industrial and urban sources. The Cote Gill soils have apparently high metal levels, but these may not truly reflect available metal for soil-solution partitioning, since the extraction method is likely to have dissolved calcium carbonate, causing the release of heavy metals locked within its matrix. The soils of the partially-forested Castle How Beck catchment are not noticeably richer in metals than those of the other, moorland, catchments of the upper Duddon valley, which suggests that the greater scavenging of metals by trees has not resulted in the transfer of much additional metal to the soil-water system.

Additional work was carried out to assist the modelling of Lochnagar (see below). Soil samples studied by Dr. Handong Yang (UCL) were analysed for heavy metals using a somewhat milder extraction technique than he used. Only modest differences have been found; our method gives slightly lower soil contents (50-70% of the Yang values) for Ni, Cu and Zn, and slightly higher ones (110-120%) for Cd and Pb. Soil pH, Al, Fe and heavy metals have also been measured on new samples taken from the Lochnagar catchment.

Table 4 Average soil bulk properties, used in CHUM-AM modelling.

Catchment	**L1**			**L2**			**pH**
	d	BD	% C	*d*	BD	% C	
Gaitscale Gill	12	0.26	26	14	0.32	17	4.5
Troughton Gill	11	0.23	30	21	0.31	5	4.7
Hardknott Gill	8	0.20	30	8	0.20	30	5.5
Castle How Beck	9	0.18	35	12	0.30	24	4.8
Great Dun Fell X	10	0.10	50	10	0.10	50	3.9
Great Dun Fell Y	10	0.10	50	10	0.10	50	3.9
R.Etherow	7	0.15	50	7	0.15	50	3.6
Old Lodge	6	0.60	10	24	1.00	14	4.1
Cote Gill	11	0.77	5	11	0.77	5	6.4
Lochnagar	14	0.30	38	14	0.30	38	4.6

d = thickness of layer (cm) BD = bulk density (g cm^{-3}) %c = percentage carbon

Table 5 Geochemically-active soil metal pools (g m^{-2}).

Site		**Ni**	**Cu**	**Zn**	**Cd**	**Pb**
Upper Duddon valley	Castle How Beck	0.1	0.5	0.9	0.02	8.3
	Gaitscale Gill	0.1	0.2	0.5	0.03	4.6
	Hardknott Gill	0.1	0.4	0.6	0.02	6.1
	Troughton Gill	0.1	0.7	0.6	0.02	4.5
Great Dun Fell X		0.02	0.02	0.4	0.007	1.5
Great Dun Fell Y		0.02	0.02	0.4	0.007	1.5
Old Lodge		0.1	0.3	1.2	0.01	2.1
River Etherow		0.2	1.2	2.6	0.05	40
Cote Gill		1.8	1.8	31	2.1	22
Lochnagar[1]		-	0.1	1.1	0.03	3.0

[1] Data of Yang (2000), corrected for differences in analytical methodology.

3.1.3 Surface water metal concentrations

Stream metal concentrations in the upper Duddon valley are fairly similar for all four sites (Table 6). Concentrations are substantially higher at GDF, due to the high DOC concentrations, which promote the formation of organic complexes (Lawlor & Tipping, 2003). Metal concentrations in the Old Lodge stream are fairly high, especially that of Ni. Despite the high soil contents of Cu and Pb at the River Etherow catchment, stream water concentrations are not especially high. Cote Gill has high concentrations of Zn, Cd and Pb.

Table 6 Average surface water total metal concentrations (µg l^{-1}); dissolved concentrations were very similar.

Site		Ni	Cu	Zn	Cd	Pb
Upper Duddon valley	Castle How Beck	0.2	0.3	3.9	0.03	0.2
	Gaitscale Gill	0.2	0.2	3.9	0.07	0.4
	Hardknott Gill	0.4	0.2	1.6	0.02	0.07
	Troughton Gill	0.2	0.2	4.7	0.08	0.2
Great Dun Fell X		2.7	1.7	30	0.13	4.5
Great Dun Fell Y		2.8	1.3	12	0.16	2.9
Old Lodge		10	1.7	18	0.1	1.9
River Etherow		1.2	0.8	13	0.1	1.7
Cote Gill		0.7	0.9	38	0.2	3.3
Lochnagar[1]		0.08	0.1	4.8	0.03	0.6

[1] Data of Yang and Rose.

3.1.4 Weathering inputs of heavy metals

Samples of rock and stones were collected from the study catchments, broken up if necessary, and subjected to leaching with 1 mM HNO_3 over a period of 20 days. The solution phases were analysed for pH, Si, Ca and heavy metals, and the results were used to evaluate the contribution of mineral weathering to soil and stream heavy metals. Details of the experiments are given in Annexe 4.

3.2 Development of CHUM-AM

The original CHUM model (Tipping, 1996) was modified to suit the needs of the dynamic modelling of heavy metals. As the long timescales in metal accumulation and release from soils became clear, the main requirement was to develop a version capable of simulating soil and surface water chemistry over ca. 1000 years. The model was therefore adapted to run on an annual time step, and this version is called CHUM-AM. The model is described in detail in Annexe 5. Its principal features are:

- two soil layers and one rock / till layer;
- an annual time step, with a constant rate of water percolation;
- the description of solute interactions with solid-phase and dissolved organic matter, using the WHAM / Model VI chemical speciation model (Tipping, 1994, 1998);
- simple sub-models for soil N and S cycling;
- weathering inputs of major elements (Na, Mg, Al, K, Ca, Si, Fe) and heavy metals;

- specification, in an input file, of the concentrations of dissolved organic matter (DOC) and suspended particulate matter (SPM) in percolating and drainage water.

A version of the model including a lake and its sediment was also formulated, for analysis of the data from Lochnagar.

The model is configured on the basis of catchment soil properties (Table 4). The key functional component of the soils, according to the modelling approach used here, is the organic matter, in particular humic substances (HS), since these determine the ability of the soil to interact with protons and metals. Soil contents of HS in organic-rich surface horizons were estimated using the average value of 0.17 g per g organic matter determined by Tipping *et al.* (2003) for 98 surface soil samples from the uplands of England and Wales. Values for mineral horizons were estimated from the value of 0.5 g per g organic matter reported by Tipping *et al.* (1995). The ratio of humic acid (HA) to fulvic acid (FA) in the rankers and O horizons was taken to be 84:16, that for the mineral horizons 50:50 (Tipping *et al.*, 1995).

3.2.1 Deposition scenarios used with CHUM-AM

The model is driven by data for annual rainfall and evaporation, and the deposition of major solutes and heavy metals. Table 7 summarises the sources of measured data that were used. For the period before measurements were started, deposition scenarios were constructed for major components by scaling all pollutant inputs except N to past sulphur emissions and by using the long-term variation in N deposition estimated by Pitcairn *et al.* (1995). Details of the method are given in Annexe 5.

For heavy metal deposition at the Lake District sites, the sediment record of a local lake, Blelham Tarn, published by Ochsenbein *et al.* (1983), was used to derive relative changes in deposition of the different metals, and these were scaled to the measured values, assuming maximum deposition to have occurred in 1960-1970. Details of this procedure are given in Annexe 5. The Lake District deposition pattern (Fig. 3) was assumed to be common to all the sites, i.e. to represent diffuse metal inputs; absolute deposition amounts were then estimated by scaling to measured present-day values. In the case of the two sites in the Pennines (R.Etherow and Cote Gill), additional deposition, taking place in the late 19th Century, was also assumed, based on the analysis reported in Section 3.10; this meant that the Pennine sites received high levels of deposition from ca. 1850 to 1980, with a minimum early in the 20th Century. For moorland, dry and occult deposition of metals was assumed to contribute a further 20% to the measured (or modelled) bulk deposition. The heavy metal deposition scenario for Lochnagar was developed by comparison of model output with the metal sediment record (see below).

In the case of Castle How Beck, the catchment in the upper Duddon valley which has forest on about half of its area, account was taken of the increases in dry and occult (cloudwater) deposition of major components and trace metals due to the trees, which were planted in around 1950. The work of Reynolds *et al.* (1997) was used to estimate the additional deposition of major components. Heavy metal uptake due to dry deposition by forest can be 2-10 times that of grassland (D.Fowler, E.Nemitz, pers. comm), therefore the deposition scenario for heavy metals to the trees was modified accordingly. For the period when trees were present, deposition to the catchment as a whole (50% forest) was set to 1.25 times the amount for the moorland catchments in the upper Duddon valley.

Table 7 Data sources for deposition (measured values)

Data	**Source**
Rainfall amounts, Lake District	B Tebay *pers. comm.*
Rainfall amounts, other sites	BADC, ADMN
Evaporation	BADC (MORECS)
Major solutes in Lake District rainfall, 1983-2001	CEH
Major solutes in rainfall Lochnagar, 1999-2002	N Rose (UCL) *pers. comm.*.
Major solutes in rainfall at other sites, 1986-2002	ADMN
Dry deposition of N and S	UKRGAR (1997)
Heavy metal deposition at Wraymires, Chilton, Oxfordshire and Styrrup, Nottinghamshire,1972-2000	Baker (2001)
Heavy metal deposition, Lake District, 1978	Hamilton-Taylor & Willis (1990)
Heavy metal deposition at Lochnagar, 1999-2002	N Rose (UCL) *pers. comm.*
Heavy metal deposition at study sites, 1998	Lawlor & Tipping (2002)
Heavy metal deposition at study sites, 2002-4	This study

ADMN	Acid Deposition Monitoring Network
BADC	British Atmospheric Data Centre
UKRGAR	United Kingdom Review Group on Acid Rain

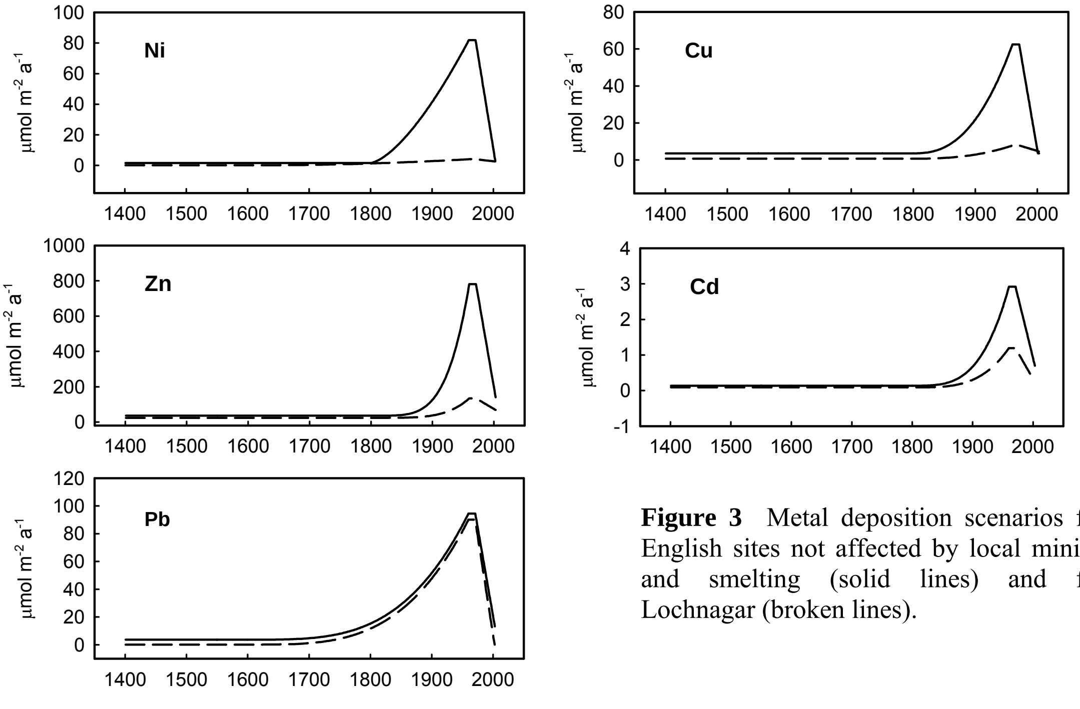


Figure 3 Metal deposition scenarios for English sites not affected by local mining and smelting (solid lines) and for Lochnagar (broken lines).

3.3 Applications of CHUM-AM to stream catchments with acid soils

Stream catchments were chosen for most of the model applications, because they provide relationships between soil chemistry and surface water chemistry that are simpler than those in catchments containing lakes.

The first step in applying CHUM-AM to a catchment was to calibrate the model to describe the chemistry of the major components. This involved adjusting parameters that describe N and S cycling and weathering rates, in order to match as closely as possible the currently-observed soil pH and pools of N and S, together with the observed streamwater chemistry. Data for streamwater chemistry were available that covered at least 10 years; they came from CEH Windermere / Lancaster monitoring programmes (Lake District, Great Dun Fell), or from the Acid Waters Monitoring Network (R.Etherow, Old Lodge). Fig. 4 shows that there was broad agreement between values of observed and simulated streamwater pH for the 8 streams that were modelled.

The second step in the model application was to run the model to simulate heavy metal behaviour over time. The period that was simulated started in 1400 and ended in 2003. However, the available data for heavy metals are restricted to very recent determinations, i.e. those carried out in the present study. Therefore, model performance cannot be gauged by comparison of simulated and observed time-series data, and the only way to test whether the model is providing a satisfactory description of metal behaviour is to compare its simultaneous simulation of both soil metal pools and streamwater metal concentrations.

Initially, the metal simulations were performed using default values of the WHAM / Model VI parameters that characterise metal binding by soil organic matter, the main process governing metal behaviour. Furthermore, it was assumed that weathering inputs of the heavy metals were negligible. Soil pool and stream water concentrations simulated on the basis of these assumptions are shown in Fig. 5, for Ni, Cu, Zn and Cd. Considering that no adjustments of parameters characterising metal binding to soils were made, the model can be said to perform convincingly for these four metals, predicting the pools and concentrations to within 0.5 log units (i.e. a factor of three). The one consistent discrepancy is the underestimation of soil Cd. In comparing the observed and simulated results, it should be borne in mind that the measurement of "geochemically active" metal (see above) relies on a simple extraction, and is only an approximation to the true value.

The predictive modelling was less successful for lead. In some cases the model underestimated the soil pool and overestimated the streamwater concentration. The results could be improved by adjusting the WHAM / Model VI equilibrium constant (LKMA) for Pb binding to organic matter, and this method was used to optimise the Pb simulations. The values of LKMA for the different catchments are shown in Table 8. For Lochnagar, the default constant is adequate, but in the other cases an increase is required. This finding that WHAM / Model VI requires an increase of, on average, 0.4 in the LKMA value agrees with results obtained from laboratory work on a range of soil samples (Tipping *et al.*, 2003). The points for Pb in Fig. 5 were obtained with the individual LKMA values (Table 8), either for each catchment, or group of

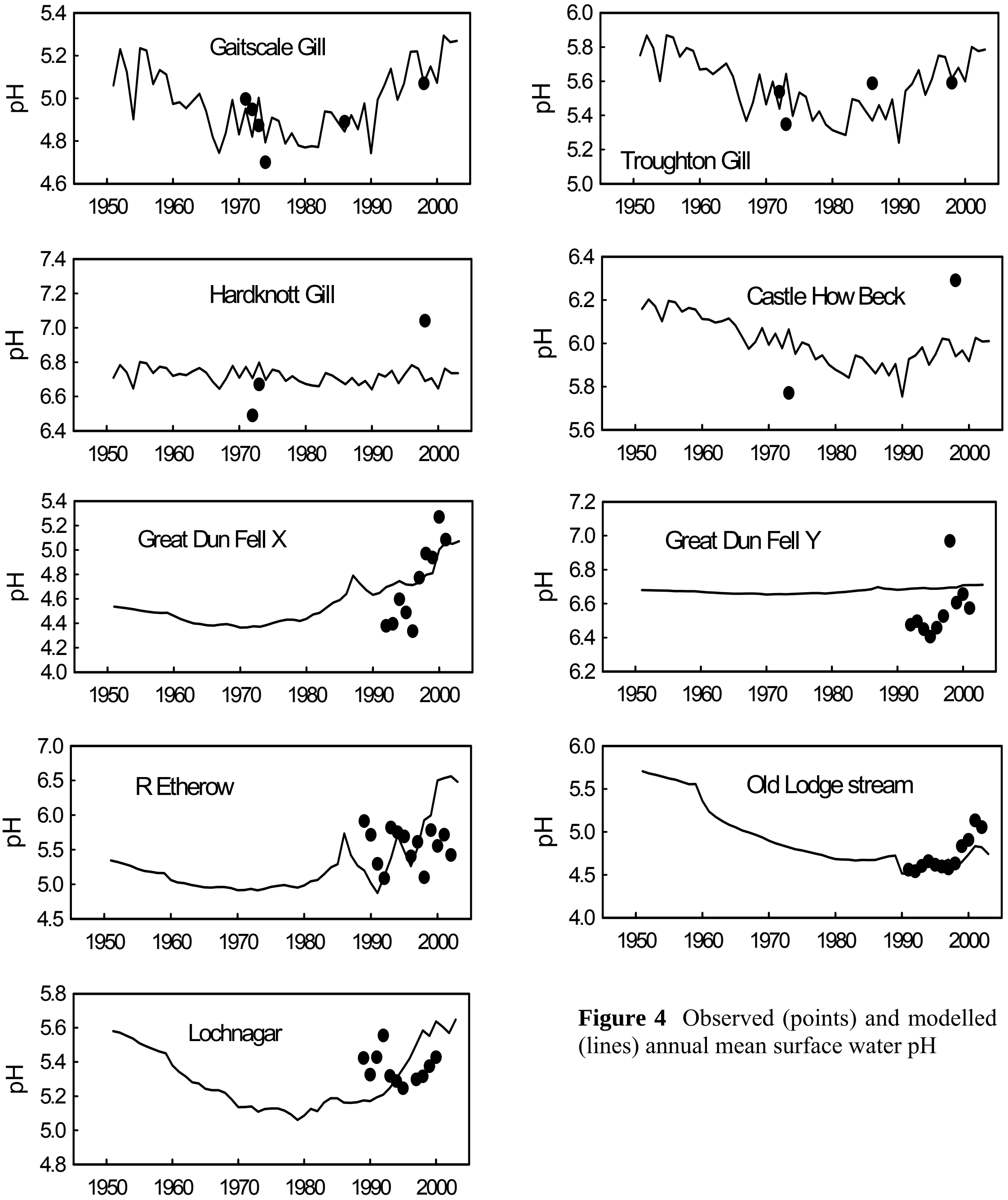


Figure 4 Observed (points) and modelled (lines) annual mean surface water pH

Table 8 Optimised LKMA values for Pb (see text).

Catchment	LKMA
Upper Duddon valley (4 sites)	2.6
Two Great Dun Fell (2 sites)	2.3
Old Lodge	2.5
R.Etherow	2.4
Lochnagar	2.1

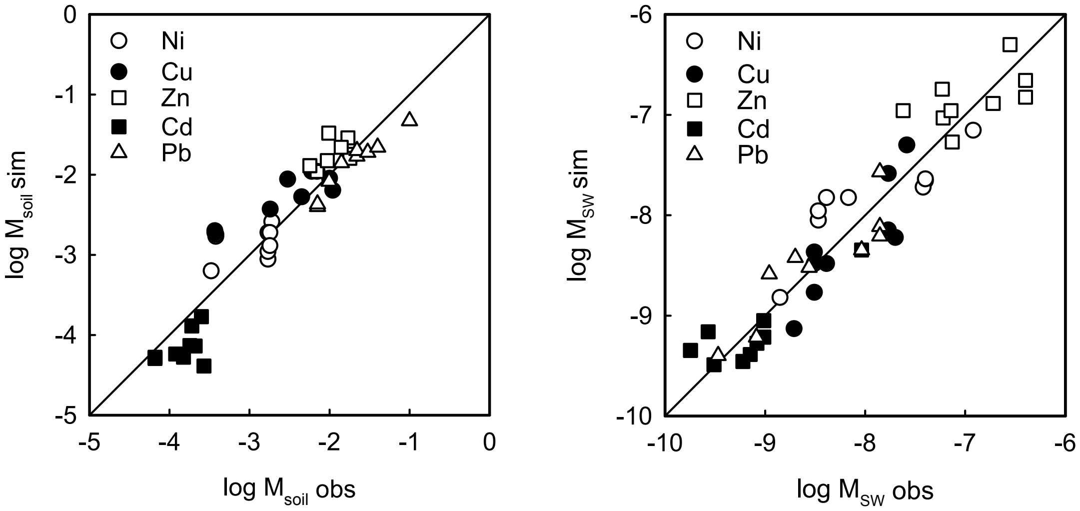


Fig. 5 Observed and simulated soil metal pools (left panel) and mean surface water concentrations (right panel) of heavy metals for all the catchments of Table 2.1 except Cote Gill. The simulated values for Ni, Cu, Zn and Cd were obtained with default values of the model parameter LKMA; those for Pb were obtained with optimised values of LKMA (see text). The standard deviations of the observed values were typically ±50% corresponding to a logarithmic range of ±0.3.

3.3.3 Castle How Beck

This catchment in the upper Duddon valley was chosen for monitoring and modelling in order to examine the possible effects of trees on heavy metal accumulation and leaching. The catchment was 50% afforested until 2002, the conifer forest having been established in around 1950. The CHUM-AM model was calibrated for major components taking into account increased deposition due to trees. It was then run to predict heavy metal behaviour in three ways;

(a) assuming no change in atmospheric deposition of metals, nor any uptake of metals by trees; this is equivalent to a moorland-only version of the catchment, i.e. with no increased forest scavenging of heavy metals;
(b) assuming an increased deposition of heavy metals due to trees (see above);
(c) assuming an increased deposition of heavy metals due to trees, and also uptake of heavy metals by the trees.

According to the model simulations, the greater scavenging of metals but without metal retention by the trees (case (b)) would lead to increased soil metal pools compared to case (a); the pools in 2000 would be greater by 21% (Ni), 7% (Cu), 20% (Zn), 12% (Cd) and 11% (Pb). To explore the effects of plant uptake, it was assumed that the trees absorb 90% of the deposited metals, and release 1% of the total plant metal pool per annum (see Annexe 5). With this assumption, the soil metal pools in 2000 were very close to those in case (a), i.e. the calculated tree uptake was about equal to the deposition increase due to scavenging. The rates of metal accumulation by the trees were calculated to be 0.7, 1.6, 14, 0.09 and 11 mg g^{-1} a^{-1} for Ni, Cu, Zn, Cd and Pb respectively. The values for Cu, Zn and Cd are close to the measured values, while that for Pb is about 7 times too high (see section 4.3.4 and annexe 11); no measured data are available for Ni.

Although forest uptake of metals has a significant effect on the build up of soil pools in the short term (i.e. 1950 to the present), this would not apply under steady-state conditions, in which the return of metals to the soil-water system would equal the uptake rate. However, continued harvesting of the trees could operate as a continuing sink for the atmospherically-deposited heavy metals.

3.3.4 Weathering inputs of heavy metals

The applications of CHUM-AM in which the only inputs of heavy metals are from atmospheric deposition led to reasonable simulations of soil pools and streamwater concentrations. However, heavy metals will also enter the soil-rock-water system by mineral weathering. A simple way to estimate weathering inputs is to assume that the sources of metals are minerals dissolving congruently (i.e. stoichiometrically, not forming a mineral residue of different composition). If this is the case, then the heavy metal:Si ratios in the minerals can be multiplied by the flux of Si in stream water to estimate the weathering input, assuming the streamwater flux of Si to be due only to weathering (i.e. that there is negligible atmospheric input). Weathering fluxes were estimated in this way using present-day silicon fluxes in streamwater combined with geochemical data on element compositions of the global crust and of granitic rocks (Mason, 1966). It is not clear which of these is more generally appropriate for the present study, except that the rocks at Lochnagar are certainly granitic. The calculated weathering fluxes are compared with modelled background and maximum atmospheric inputs of heavy metals in Table 9.

The first point about the values in Table 9 is that for none of the metals, in none of the catchments, does the estimated weathering input come close to the maximum anthropogenic input to the catchment. The highest weathering inputs, relative to anthropogenic inputs, are for Ni and Cu at the R. Etherow, if the global crust data are used for the weathering estimates, and in these cases the weathering inputs are ca. 30% and 20% respectively of the anthropogenic inputs. This means that for all the catchments studied the geochemically-active soil metal contents can be attributed primarily to anthropogenic inputs.

The weathering inputs based on granitic rock are generally lower than, or of the same order as, the assumed background inputs estimated as 20% of current deposition. For Zn and Cd, the weathering values are far lower, but for the other metals they are comparable. With respect to the dynamic modelling, if the assumed background depositional inputs were reduced, and granite-based weathering inputs introduced, the model would give essentially the same results. But this is not a major issue, since the key point of the dynamic modelling work was to explore the long-term behaviour of anthropogenic metals.

Weathering rates estimated from the global crustal composition are mostly greater than the granitic values, and for Ni and Cu the weathering inputs exceed the assumed background values. Therefore, it is possible that background inputs of these two metals are greater than has been assumed, using 20% of atmospheric deposition as the background input. In that case the model would predict higher soil Ni and Cu pools, and higher streamwater concentrations, than in the present evaluation. It is therefore possible that the modelling results for Ni and Cu are incorrect. The uncertainty could be resolved by making site-specific measurements of mineral weathering inputs, and we attempted such measurements in the present project. However, the method employed involved only short-term dissolution experiments, and the metal:Si ratios were substantially greater (by about a factor of ten) than the ratios for global crust or the granitic rocks. We consider that longer-term experiments are required to resolve this issue, and we do not think it correct to use our present results to make weathering estimates.

Table 9 Estimated weathering inputs of heavy metals (μmol m^{-2} a^{-1}), compared with assumed background and maximum deposition inputs. GC: weathering inputs based on global crustal averages; Gr: weathering inputs based on granite averages; d_{BG}: background deposition used in modelling; d_{max}: maximum deposition used in modelling.

	Ni				**Cu**			
Catchment	**GC**	**Gr**	**d_{BG}**	**d_{max}**	**GC**	**Gr**	**d_{BG}**	**d_{max}**
Lake District	10	0.2	2	80	7	1	4	60
Great Dun Fell	2	0.0	0.7	30	1	0.2	1	30
Old Lodge	3	0.1	0.8	40	2	0.4	2	30
R Etherow	20	0.3	0.7	70	10	2	1	50
Lochnagar	3	0.1	0.05	4	2	0.4	0.7	8

	Zn				**Cd**			
Catchment	**GC**	**Gr**	**d_{BG}**	**d_{max}**	**GC**	**Gr**	**d_{BG}**	**d_{max}**
Lake District	8	4	40	800	0.01	0.0	0.1	3
Great Dun Fell	1	0.7	10	30	0.00	0.0	0.06	1
Old Lodge	2	1	20	400	0.00	0.0	0.07	2
R Etherow	10	6	10	600	0.02	0.0	0.06	2
Lochnagar	3	1	20	100	0.00	0.0	0.09	1

	Pb			
Catchment	**GC**	**Gr**	**d_{BG}**	**d_{max}**
Lake District	0.5	2	4	100
Great Dun Fell	0.1	0.2	2	40
Old Lodge	0.1	0.4	2	50
R Etherow	0.7	2	2	70
Lochnagar	0.2	0.5	0.1	90

3.4 Application of CHUM-AM to Cote Gill

The Cote Gill catchment was selected for investigation because its soils are developed on limestone and the streamwater has high pH (c. 8.0) and high alkalinity (ca. 3 meq l^{-1}). Given the strong tendency for metal sorption to soil solids to grow stronger with pH, it would be expected that streamwater metal concentrations, and free metal ion concentrations, would be low in this catchment. However, the observed streamwater metal concentrations are no different from those for the more acid streams (Table 6). Measurements made by CEH workers on three streamwaters from limestone-dominated catchments in the Eden valley (Simon *et al.*, 2004) provide heavy metal data that can be compared with the Cote Gill values (Table 10). In the case of Ni and Cu, the concentrations are very similar in all four streams, but Cote Gill has higher concentrations of Zn, Cd and Pb.

As noted above, the measured soil metal pools (Table 5) are greater than for the other soils, and this is attributed not to greater deposition, but to the release of geochemically-inactive metals from soil solids, due to dissolution of carbonates. Complete dissolution of mineral samples from the Cote Gill catchment, performed as part of the weathering studies (see above), confirmed the high levels of heavy metals in the calcium carbonate. Therefore we could not use these data to test the model, and had to rely on the streamwater metal concentrations.

In an initial application of CHUM to Cote Gill, the soil organic matter (ca. 10% by weight) was assumed to consist only of humic substances, and the soil pH in the field was assumed to be the measured average value of 6.4. The model was run with an atmospheric deposition scenario for heavy metals that included maxima in both the 19th and 20th centuries, to take account of local mining activities (see above). Simulated retention of atmospherically-deposited metals by the soil was high, but soil metal pools were lower than observed, as expected because of likely carbonate dissolution. Heavy metal concentrations in soil water, and therefore stream water, were low; the streamwater concentrations were 1-2 orders of magnitude lower than the observed values.

In a second application, the measured soil pH was assumed to be greater than the *in situ* value, on the grounds that degassing of CO_2 following soil collection, and on making the soil suspension for pH measurement, would lead to an increase in pH. Configuring CHUM-AM to give an ambient soil pH of 5.5 then gave streamwater heavy metal concentrations fairly close to the observed values (Table 10). With this picture of the catchment soils, the relatively high concentrations of heavy metals in the Cote Gill streamwater, compared to the other streams of Table 10, could be attributed to greater atmospheric deposition.

Although the model can be made to give reasonable simulations of present-day streamwater metal concentrations in Cote Gill, due entirely to atmospheric deposition, another possibility is that the soils have actually retained high proportions of the atmospherically-deposited metals, and that the streamwater metal concentrations are controlled by weathering of the local limestone. From the complete dissolution of limestone samples in acid, the following ratios of Ni, Zn, Cd and Pb to Ca were obtained; 0.005, 0.04, 0.002, 0.0003. The Cu content of the limestone was below detection limit. If an equivalent dissolution process were to occur in the field, then, without a major, permanent, removal process for heavy metals in the weathering zone (L3 in CHUM-AM), streamwaters would have heavy metal concentrations several orders of magnitude greater than those that are observed. This raises further questions about the process of mineral dissolution in the field, and its contribution to streamwater metal concentrations, to be added to the uncertainties arising from analysis of the acid catchments, discussed above.

Table 10 Chemistry of streams with catchments containing limestone. The last three streams are in the Eden Valley (Cumbria).

Stream	pH	Alk	Ni	Cu	Zn	Cd	Pb
		meq l^{-1}	µg l^{-1}	µg l^{-1}	µg l^{-1}	µg l^{-1}	µg l^{-1}
Cote Gill	8.1	3.0	0.7	0.9	38	0.2	3.3
Cote Gill simulated	*8.1*	*3.0*	*3.2*	*0.3*	*21*	*0.2*	*5.4*[1]
Artlegarth Bridge	7.6	2.9	1.0	0.7	1.4	0.04	0.3
Upper Scandal Beck	8.3	2.9	1.2	0.8	1.8	0.04	0.5
Coal Pit Syke	8.3	4.0	1.1	0.5	1.4	0.1	0.2

[1] Using the default value of LKMA (cf. Table 8).

3.5 Application of CHUM-AM to Lochnagar

The Lochnagar system is more complex than the other acid catchments because it includes a lake and its sediments. We adapted CHUM-AM to include transfer of water, solutes and suspended particulate matter from the catchment to the lake water, and to include the accumulation of particulate matter and metals in the lake sediment. In characterising the chemistry of the lake sediment, we made use of the work of Alfaro-De La Torre & Tessier (2002) who carried out detailed measurements on a lake of similar chemical characteristics in Canada. An especially significant point is the higher pH of the lake sediment (by about 0.5 pH units, due to sulphate reduction) compared to the lake water; this increases the extent of binding of metals to sedimentary organic matter. It was also found helpful to take into account the transfer of metals associated with eroded mineral matter from the catchment to the sediment; this contribution ranged from 6% (Cd) to 90% (Ni) of the background sediment level.

The model was calibrated against the extensive data set on Lochnagar and its catchment that has been obtained by Drs N Rose and H Yang of University College London. The data include deposition compositions of both major components and heavy metals, soil metal pools, lakewater metal concentrations, and sediment profiles. Much of the information is in the thesis of H Yang (2000); additional unpublished data were also made available to us.

To calibrate the model, parameters were first optimised for the major component chemistry, to fit soil pH, lakewater solute concentrations and lakewater pH. Then, in optimising the model for heavy metals the aim was to match as closely as possible observed and simulated soil metal pools, lakewater metal concentrations, and sediment metal concentrations as a function of sediment depth. To do this, the deposition scenario for each metal was adjusted, in order to minimise an objective function that combined soil, lakewater and sediment metal contents. This was done using the deposition model described in Annexe 6, with adjustment of the values of D_B (background deposition) and $D_{A,\max}$ (maximum anthropogenic deposition).

Values of observed and simulated soil metal pools and lakewater metal concentrations are included in Fig. 5, and these fell reasonably close to the 1:1 line. Fig. 6 shows plots of observed and simulated sediment profiles of Cu, Zn, Cd and Pb. In the case of Cu, the shapes of the observed and simulated profiles agree well, having their maximum values at around 1980. However, the observed sediment content of Cu is higher than the model predicts; the model cannot be made to predict a higher sediment content, without causing a significant overestimation of soil and lakewater Cu. In the case of Zn, the sediment contents are in good agreement, but the profile shapes differ, the simulated maximum being appreciably later than the observed one; this may possibly reflect post-sedimentation mobility of Zn, which the model does not take into account. Similar remarks apply to Cd. The simulation of the sediment content of Pb is quite close to the observations. The modelling results indicate that the amounts of atmospherically deposited metal reaching the sediment via direct deposition onto the lake surface are similar to those reaching the sediments through the catchment.

The deposition scenarios derived for Lochnagar are compared with those for the Lake District in Fig. 3. The results suggest that, as metal atomic weight increases, the ratio of deposition at Lochnagar to that in the Lake District also increases, so that for Ni, the deposition at Lochnagar is very low, while for Pb the scenarios are very similar.

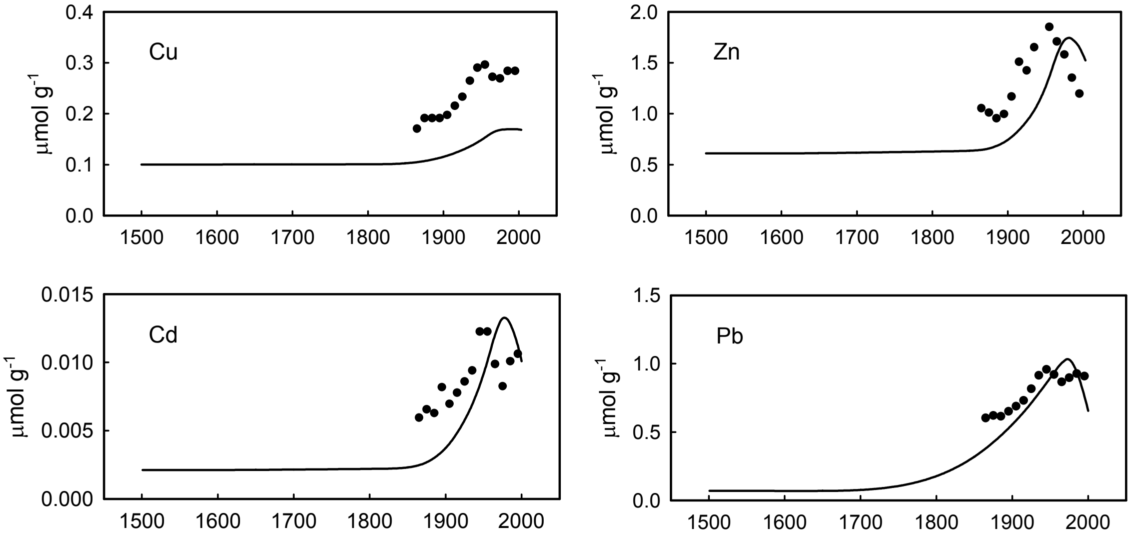


Figure 6 Observed (points) and simulated (lines) concentrations of metals in the sediments of Lochnagar, expressed in terms of dates derived from sediment cores.

3.6 CHUM-AM simulations of future metal behaviour

Future metal behaviour was simulated using the following three scenarios, which were run until 2500:

A. No change in deposition from 2000 onwards.
B. 50% decrease in S and N deposition from 2000 to 2020, then constant.
C. 50% decrease in S, N and metals deposition from 2000 to 2020, then constant.

Two contrasting acid catchments were selected for detailed examination. The catchment of Great Dun Fell X in the northern Pennines has blanket peat and ranker soils, receives ca. 1500 mm of annual rainfall, and its surface water is acid and high in DOC (ca. 15 mg l^{-1}). The catchment of Gaitscale Gill in the upper Duddon valley (Lake District) has thin ranker soils, high in aluminium, receives ca. 3000 mm of rain per annum, and its surface water is acid and low in DOC. For each catchment, the long-term behaviours of Cd and Pb are described; these are two of the three metals (the other is Hg) of primary concern within UNECE / CLRTAP, and they represent, respectively, metals that bind relatively weakly and strongly to natural organic matter.

The soil pH at GDF-X is predicted to stabilise quite soon in the future (Fig. 7), under all three scenarios. It will be slightly higher under B and C, due to the reductions in N and S deposition. However, the future pH differences will not affect metal behaviour very much, as shown by the near-coincidence of the soil pools of Cd and Pb in Scenarios A and B. Therefore in this catchment, the decrease in the soil pool depends primarily on the desorption and leaching of metal that accumulated in the past, which will not be replenished by future deposition. The pool of the weaker-binding metal, Cd, will approach steady state in about 300 years, whereas that of Pb will only be half-way to the steady-state value by 2500. Note that most of the loss of Pb is as complexes with DOM, and this is more effective than at Gaitscale Gill (see below and Fig. 8) because of the higher DOC concentration in drainage water at GDF (ca. 15 mg l^{-1} compared to 1 mg l^{-1} at GG).

The trends in surface water concentrations of Cd and Pb at GDF-X generally follow those in the soil pools (Fig. 7). The shapes of the surface water curves differ somewhat from the those of the soil pools because the metals have to be translocated within the soil (from the upper soil to the lower) before they are released into drainage water, and this delaying effect tends to flatten the surface water response. Otherwise, the timescales of change in the surface water are similar to those for the soils.

The Gaitscale Gill (GG) catchment gives more complex responses to the three scenarios (Fig. 8). Firstly, soil and water pH do not reach constant values as quickly as at GDF. In Scenario A, the continued accumulation of soil N, and its ultimate leaching as nitrate, leads to a serious acidification over the next several hundred years, and decreasing soil and stream pH. In Scenarios B and C the acidification is checked, and soil and stream pH approximately stabilise after about 50 years. Soil acidification (Scenario A) leads to a decline in soil Cd, and a steady state is reached after about 300 years. Again, under Scenario B a steady state is reached, but the pool is about twice the size of that under Scenario A because the soil binds the metal more strongly, due to the higher pH. Surface water Cd concentrations reach steady value rather rapidly;

initially they are not in true steady state, but the pH-dependent adsorption to soil compensates for variations in the size of the Cd soil pool.

The soil pool of Pb at Gaitscale Gill declines very slightly under Scenario A, due to increasing acidification. With more constant soil pH the pool continues to rise over the next 500 years; this increase reflects the fact that, despite high atmospheric deposition and efficient retention of Pb in the past, the soil pool was not at all near to the steady-state value that is associated with deposition at the current (relatively low) rate of deposition. Reduction in atmospheric deposition and stable soil pH lead to a steady soil Pb pool from 2000 onwards, although this is not a true steady-state as can be seen from the gradually increasing surface water Pb concentrations under Scenario C. The greater increase in surface water Pb concentration under Scenario A is due to acidification, promoting the desorption of the metal from the soil, although the absolute loss rate from the soil is low relative to the size of the soil Pb pool.

Fig. 9 shows predicted variations in the soil pools of Cd and Pb in a further three catchments. These assume no change in the deposition of either major components or heavy metals in the future, i.e. they can be compared with the results for Scenario A in Figs. 7 and 8. In each case, the model predicts the build-up of N in the soil, and acidification due to nitrate leaching, although not to the same extent as at Gaitscale Gill (Fig. 8). At each catchment, the soil pool of Cd is predicted to decrease, but whereas at the R. Etherow and Old Lodge the pool quite quickly becomes steady, the change at Lochnagar is much slower; this reflects the relatively high pH of the Lochnagar soil, and its consequently stronger binding of Cd. Slow declines in soil Pb are predicted for the R. Etherow and Lochnagar, but at Old Lodge the pool increases, because the period of the highest Pb deposition at Old Lodge led only to a modest increase in the soil pool, and the current deposition is sufficient to cause continued accumulation.

It is difficult to generalise about metal behaviour, because it is governed by a number of interacting factors. In the CHUM-AM model used in the present work, the leaching rate of metals from soil is positively related to run-off, DOC concentration, and soil Al levels, and negatively related to soil pH, organic matter content and base cation weathering inputs. In addition, future metal behaviour depends on the historical interactions between acidification and metal deposition, both of which have passed through maxima during the last few decades. One general conclusion that can be made is that soil metal pools will change on timescales that are long compared to, for example, recent changes in acidification by pollutant sulphur; thus we may have to wait for centuries or millennia for soil metal pools to come close to steady state with respect to deposition. However, it is important to note that dissolved metal concentrations in both soil solution and surface waters, that are more directly related to effects, can respond more quickly.

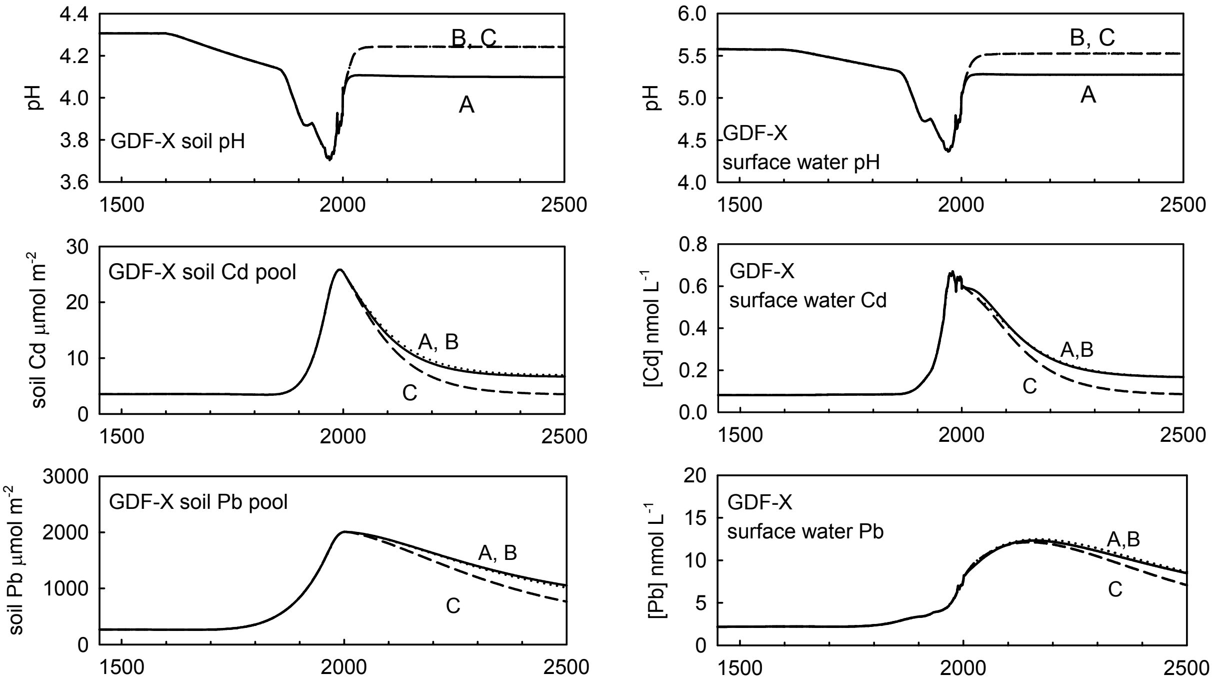


Figure 7 Simulated soil pH, soil pools of Cd and Hg, stream pH, and stream concentrations of Cd and Pb at Great Dun Fell X, for Scenarios A, B and C (see text).

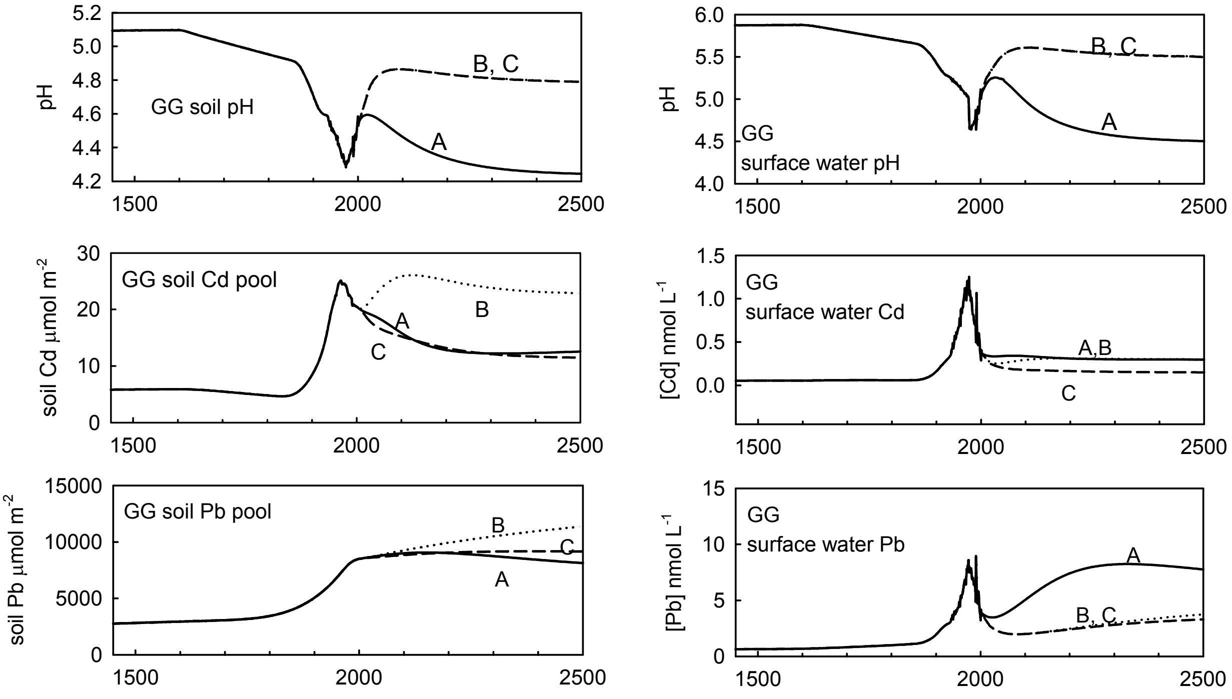


Figure 8 Simulated soil pH, soil pools of Cd and Hg, stream pH, and stream concentrations of Cd and Pb at Gaitscale Gill, for Scenarios A, B and C (see text).

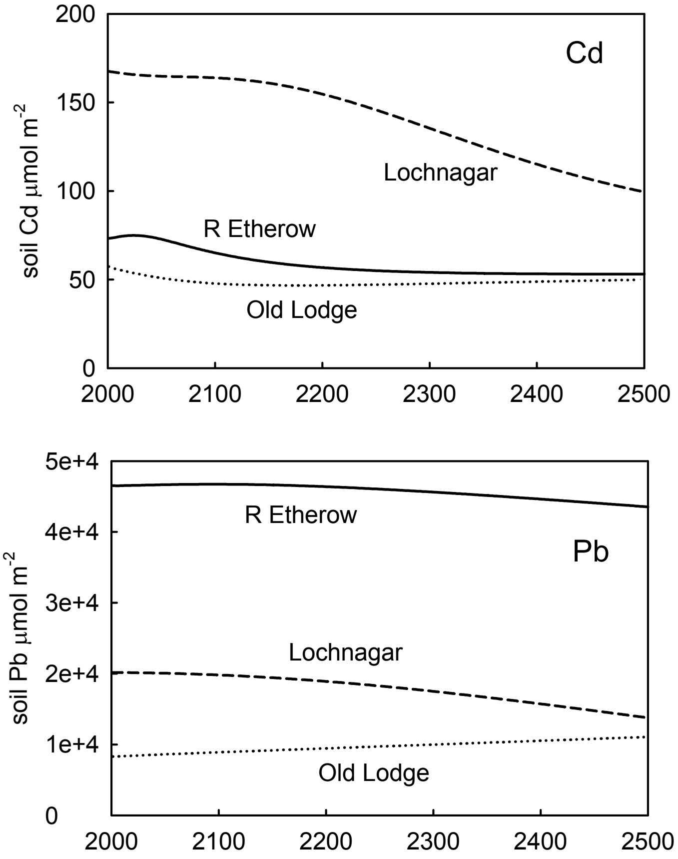


Figure 9. Simulated changes in soil pools of Cd and Pb at three catchments, based on the assumption that current deposition of major components and heavy metals remains constant.

3.7 Simulated free metal ion concentrations and critical limits

The sites chosen for the dynamic modelling work were originally selected to provide contrasting catchment conditions, but not necessarily to include cases where adverse ecological effects might occur. Only one site, the River Etherow, was chosen with pollution effects in mind. Therefore, it is not to be expected that critical limits will generally be exceeded. Nonetheless, it is of interest to compare computed free metal ion concentrations for soils with critical limit values, calculated from the critical limit functions on the basis of pH (see section 2). Such comparisons are made, in terms of logarithmic values, in Table 11, for 1970 and 2000. Cases where the calculated free-ion concentration was half the critical limit or greater are highlighted.

The results in Table 11 show that, in the catchments considered, the soil free-ion concentrations of Ni, Cu and Cd are calculated to be appreciably lower (log values more negative) than the critical limit values. In the case of Zn, in only one case (Old Lodge in 1970) did the free-ion concentration come close to the critical limit. However, for Pb, the free-ion concentration was close or equal to the critical limit in six of the eight catchments in 1970 and in four catchments (all in the Lake District) in 2000. The Old Lodge and R. Etherow soils had considerably lower free-ion concentration of Pb in 2000 than in 1970, sufficient to counter the decrease in critical limit caused by the increase in soil pH between 1970 and 2000 at the two sites.

Comparisons of this kind, and more extensive simulation modelling, provide insight into how the metal concentrations in soils and waters will vary, in relation to the critical limits, which themselves vary, being pH-dependent. However, although CHUM-AM accounts in general terms for soil metal pools and dissolved metal concentrations in a range of catchments (Fig. 5), it cannot yet provide precise simulations of metal concentrations. Consequently, prediction of future metal toxic effects will be subject to considerable uncertainty.

The fact that the simulated free-ion concentrations have altered in many cases by an order of magnitude over the period 1970 to 2000 (cf. Table 11) emphasises the fact that soil porewater concentrations can vary much more rapidly than the total soil metal pools that are shown in Figs. 7 to 9.

Table 11 Simulated (sim) concentrations (log mol l^{-1}) of free metal ions in soil solution, compared with critical limit concentrations (CL). Log concentrations greater than the log critical limits minus 0.3 are highlighted; this shows absolute concentrations half the critical limit or greater.

	Ni				**Cu**			
	1970		**2000**		**1970**		**2000**	
	sim	**CL**	**sim**	**CL**	**sim**	**CL**	**sim**	**CL**
Castle How Beck	-7.5	-5.4	-8.9	-5.4	-8.0	-7.5	-8.2	-7.5
Gaitscale Gill	-7.5	-5.3	-8.9	-5.4	-7.8	-7.2	-8.4	-7.5
Hardknott Gill	-7.5	-5.7	-8.9	-5.9	-8.7	-8.1	-9.1	-8.4
Troughton Gill	-7.5	-5.3	-8.9	-5.5	-7.9	-7.3	-8.5	-7.6
Great Dun Fell X	-7.9	-5.0	-10.1	-5.3	-9.1	-6.6	-10.3	-7.2
Great Dun Fell Y	-7.8	-5.0	-9.6	-5.2	-9.0	-6.6	-9.9	-7.1
Old Lodge	-6.9	-5.0	-8.5	-5.2	-7.2	-6.6	-8.8	-7.2
River Etherow	-7.1	-4.7	-8.4	-5.0	-7.4	-6.2	-8.3	-6.7

	Zn				**Cd**			
	1970		**2000**		**1970**		**2000**	
	sim	**CL**	**sim**	**CL**	**sim**	**CL**	**Sim**	**CL**
Castle How Beck	-6.5	-6.0	-7.7	-6.0	-8.9	-7.8	-10.2	-7.8
Gaitscale Gill	-6.5	-5.9	-7.7	-6.0	-9.0	-7.7	-10.2	-7.7
Hardknott Gill	-6.5	-6.1	-7.7	-6.2	-8.9	-7.9	-10.1	-8.0
Troughton Gill	-6.5	-6.0	-7.7	-6.0	-9.0	-7.7	-10.2	-7.8
Great Dun Fell X	-7.1	-5.8	-9.1	-5.9	-9.5	-7.5	-11.5	-7.7
Great Dun Fell Y	-6.9	-5.8	-8.6	-5.9	-9.3	-7.5	-11.0	-7.7
Old Lodge	**-6.0**	**-5.8**	-7.4	-5.9	-8.4	-7.5	-9.8	-7.7
River Etherow	-6.1	-5.7	-7.4	-5.8	-8.5	-7.4	-9.8	-7.5

	Pb			
	1970		**2000**	
	sim	**CL**	**sim**	**CL**
Castle How Beck	**-7.8**	**-7.8**	**-7.9**	**-7.8**
Gaitscale Gill	**-7.6**	**-7.6**	**-8.0**	**-7.8**
Hardknott Gill	**-8.5**	**-8.3**	**-8.7**	**-8.5**
Troughton Gill	**-7.7**	**-7.7**	**-8.1**	**-7.9**
Great Dun Fell X	-8.5	-7.2	-9.7	-7.6
Great Dun Fell Y	-8.4	-7.2	-9.3	-7.5
Old Lodge	**-7.3**	**-7.2**	-8.5	-7.6
River Etherow	**-6.9**	**-6.9**	-7.8	-7.2

3.8 Simple dynamic model for mapping

The aim was to compute times for soil metal pools to reach values close to those that correspond to steady-state critical limits, expressed as free metal ion concentrations in soil solution. This could happen in two ways;

(a) If the free-ion concentration is currently lower than the critical limit value, the soil, if subjected to continuous metal deposition corresponding to the steady-state critical load, will accumulate metal over time. In this case, the model calculates the time required for the soil metal pool to increase to 90% of the value corresponding to the critical limit.

(b) If the free-ion concentration is currently higher than the critical limit value, the soil, if subjected to continuous metal deposition corresponding to the steady-state critical load, will release metal over time. In this case, the model calculates the time required for the soil metal pool to decrease to 110% of the value corresponding to the critical limit.

The W6SDM model was formulated to perform these calculations. It is run in conjunction with W6SCL, the model used to compute steady-state critical loads, based on free metal ion critical limits, and current soil metal exceedences. Both models are further explained in sections 4.3.5 and 4.4.4.

Table 12 shows times-to-steady-state, calculated for the acid catchments studied in the present work. In nearly all of the cases examined, the current soil metal level is below the critical limit, and the times refer to the build-up of soil metal pools, under deposition at the critical load. Generally they agree with the CHUM-AM modelling. For example, both modelling approaches predict that the rate of change of Cd pools is about an order of magnitude greater than that of Pb pools. Furthermore, both predict change in the upper Duddon valley catchments to be slower than at Great Dun Fell. In interpreting the absolute values for this assessment, it is important to note that the timescales will be significantly faster when deposition is substantially above the critical load, rather than equal to it, as was assumed for the calculations summarised in Table 12.

In one case (Pb at the R. Etherow), the current metal level is calculated to exceed the critical limit, and the time for it to fall to the critical level is given. In another case (Cu at the R. Etherow), the current soil metal pool is calculated to be at the critical limit. This finding is not consistent with the CHUM-AM model, which calculates the R. Etherow Cu pool to be lower than the critical limit (cf. Table 11). The difference is due firstly to the underestimation by CHUM-AM of the Cu pool, which could arise because the Cu deposition to the catchment is underestimated. Secondly, CHUM-AM calculates stronger binding of Cu to the R. Etherow soil than does the pedotransfer function (see section 4.2.1) used in the simple dynamic model; this arises because CHUM-AM takes account of the lack of Al competition for Cu binding, whereas the transfer function yields a binding strength averaged over a range of soils.

Table 12 Outputs from the simple dynamic model (W6SDM). The data are times in years for the soil pools to come to within 10% of the value of corresponding free-ion critical limit, with metal deposition at the critical load. Positive values indicate that the soil pool increases towards the steady-state value; negative values indicate that metal must be lost to move downwards towards the steady-state value.

	Ni	Cu	Zn	Cd	Pb
Castle How Beck	210	2400	100	720	7200
Gaitscale Gill	150	1400	70	450	4200
Hardknott Gill	290	3400	180	1400	16000
Troughton Gill	210	2400	100	700	8000
Great Dun Fell X	290	540	120	670	2600
Great Dun Fell Y	290	600	120	680	2700
River Etherow	150	0	10	290	-1300
Lochnagar	520	4000	240	1600	10000
Old Lodge	600	1900	180	1500	10000

3.9 Conclusions from dynamic modelling

1. The modelling approach, based in particular on the key role of natural organic matter, integrates processes governing both major chemical components (acidity, base cations, aluminium etc) and heavy metals. CHUM-AM simulated reasonably successfully heavy metal soil pools and streamwater concentrations in ten contrasting upland and heathland catchments in England and Scotland, using the same parameter values for four heavy metals (Ni, Cu, Zn and Cd); only in the case of Pb was catchment-specific calibration required to match the observations. The model is a useful tool to predict future changes, the interactions between acidification and heavy metal pollution, and free metal ion concentrations that can be compared with critical limit values.

2. The dynamic modelling used historical scenarios for the deposition of heavy metals, derived from direct measurements, and from records from a lake sediment in Cumbria and peat cores from the Pennines. A common pattern of deposition, associated with diffuse sources, was assumed to apply to all the study sites. At Pennine sites close to areas of historic mining activity, an additional peak in the 19th century was included. In combination with CHUM-AM, these scenarios gave consistent simulations of soil pools and streamwater concentrations. A further test was made in the application of the model to Lochnagar. The model could reproduce reasonably well the variations in sediment metals with depth, while simultaneously providing reasonable matches to the soil metal pools and lakewater metal concentrations.

3. An assumption that background metal deposition was 20% of the present day values seems reasonable, in that it permits the model to reproduce observed metal levels. However, there is uncertainty about weathering inputs from silicate minerals, and if these are significant compared to the assumed background levels, then the true deposition background levels should be lower. Weathering inputs estimated simply from rock compositions (both silicates and carbonates), assuming congruent dissolution, may be overestimates.

4. The dynamic modelling suggests that timescales of change in soil metal pools are of the order of centuries (Ni, Zn, Cd) to millennia (Cu, Pb). Future metal behaviour will depend on the historical interactions between acidification and metal deposition, both of which have passed through maxima during the last few decades, and also future changes in acidification status, especially in catchments susceptible to nitrogen saturation and nitrate leaching. Metal behaviour depends upon a number of interacting factors, notably metal deposition pattern, run-off, soil organic matter content, soil pH, soil Al, weathering inputs of base cations, and DOC concentration. The relative importance of these factors varies among catchments, making it difficult to generalise about future changes in metal pools and concentrations.

5. Results for a catchment that was afforested in c. 1950 suggest that the increased scavenging of metals by trees was compensated by the internalisation of metals within the plants.

6. A simple dynamic model (W6SDM) was developed for mapping purposes. The model provides estimates of times required to reach steady-state metal levels under deposition at the critical load, and gives rates of change in metal pools that are broadly consistent with the CHUM-AM findings.

3.10 Past heavy metal deposition scenarios.

Historical deposition scenarios used in dynamic modelling have been described in section 3.2.1. This has been strongly influenced by the preliminary findings of a review of the literature on past heavy metal deposition and an analysis of metals in moss samples stored in herbarium collections. It has not been possible to fully incorporate the findings of the literature review and moss sample analysis in the dynamic modelling although a scaled ‘general’ deposition scenario, based on the Lake District lake sediment records, has been used which is very similar to deposition histories presented in Figs. 13 and 15. Furthermore, the deposition histories presented in Fig. 13 have been used for modelling at Cote Gill and The Etherow. For future dynamic modelling applications a more systematic application of the reconstructed deposition scenarios will be used.

3.10.1 Review of the literature on past heavy metal deposition

The key findings of the literature review into environmental and historical records of past heavy metal deposition are outlined below.

For the purposes of reconstructing past heavy metal deposition, emission sources in the UK can be divided into

- *‘General’ sources,* such as vehicular emissions, energy production and manufacturing that occur across the UK.
- *Isolated sources,* most importantly mining and smelting on orefields, occurring (or rather that historically occurred) in a few specific areas of the UK.

Reconstructing trends in heavy metal deposition at specific sites must take into account both categories of emitters. An assumption has been made that the 'general' sources have resulted in a UK wide deposition pattern for each metal that can be described by a single trend. Trends in mining-related emissions are, however, likely to be more site specific. A mining-related deposition trend for Cote Gill, Castle How Beck and the Etherow (as catchments close to major mining areas) must also be considered. In effect, two deposition trends must be reconstructed and amalgamated for each region; one reconstructing local mining and smelting related inputs and one reconstructing a national deposition trend.

'General' deposition trends.

Fig. 10 shows trends in non-mining related heavy metal deposition. These trends are based on a number of different sources of data. From 1970 to present trends are based on emissions estimates (Goodwin *et al.*, 2002). They also strongly reflect trends measured since 1972 at three UK sites (Baker *et al.*, 1999). Prior to 1972 trends are based on:

- metal profiles in lake sediments remote from mining areas (e.g. Sugden, 1993; Eades *et al.*, 2002; Yang *et al.*, 2002; Rippey, 1990, Rose and Rippey, 2002; Weiss *et al.*, 2002)
- spheroidal carbonaceous particle profiles from UK lake sediments (Rose *et al.*, 1995). SCP are particles only emitted by high temperature fossil fuel production, therefore are unambiguous indicator of trends in industrial deposition
- trends in lead emission from petrol (Wu and Boyle, 1997)
- global emissions estimates (Nriagu, 1979, 1996).

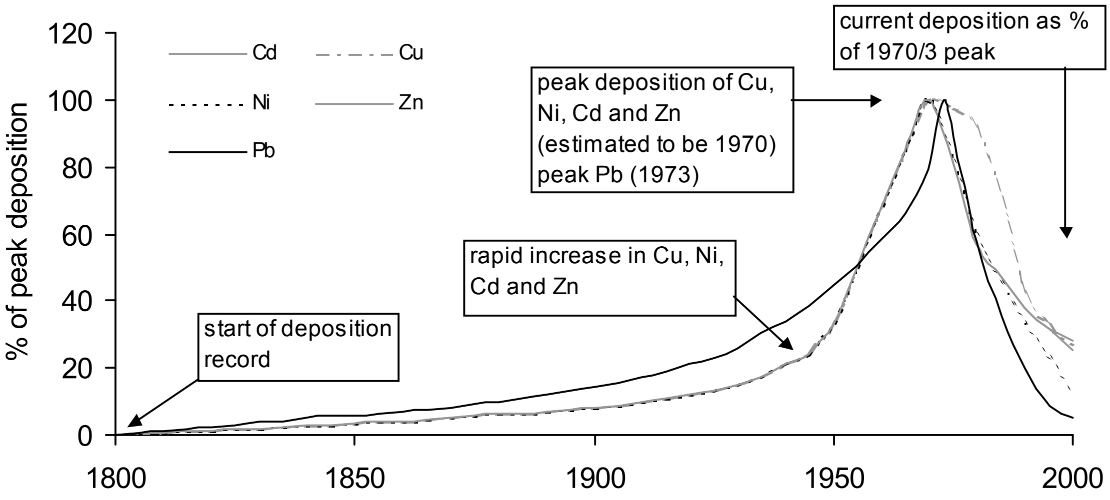


Figure 10. trends in heavy metal deposition from 'general' sources: energy production, manufacturing, vehicle emissions and waste incineration.

General metal deposition trends for Cd, Cu, Ni and Zn across the UK can be considered in three stages: a start date of around 1800, a more rapid increase from around 1950 and a decline to present from a peak around 1970. Pb deposition trends vary slightly from this; palaeo-records and emission inventories indicate an earlier increase with a sharp peak in 1973.

Local mining-related deposition histories.

Mining of Pb, Cu and Zn has been an important industry in the UK, particularly in the 19th century (Schmitz, 1979; Ford and Rieuwerts, 1983; Willies and Parker, 1999). A history of ore extraction has been collated by Schmitz (1979) (Fig. 11). Of the five catchments investigated, Cote Gill, Castle How Beck and the Etherow are in areas close to historical mining and most likely to be impacted, although Castle How Beck is separated from mining areas by mountainous terrain.

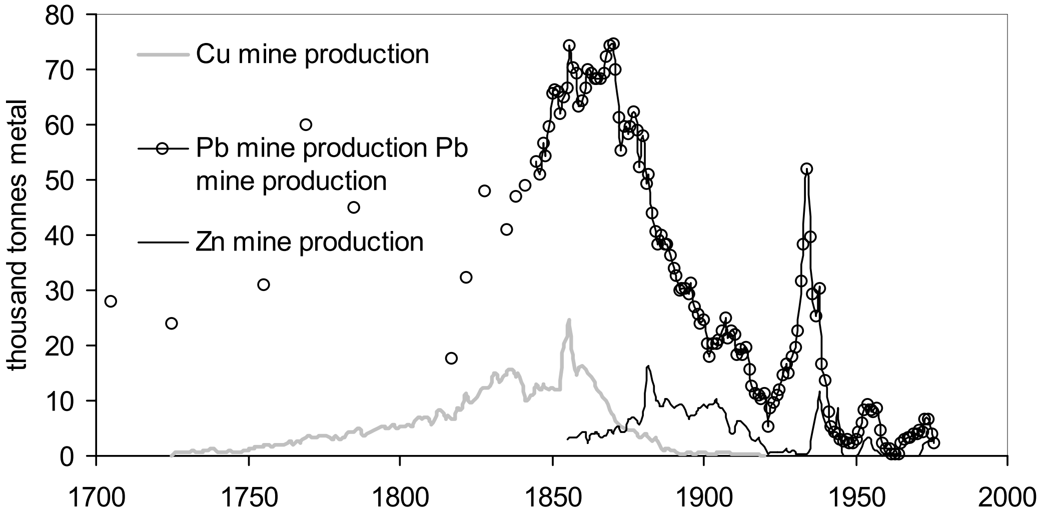


Figure 11. Records of ore output (Schmitz, 1979) based on government sources and publications of international organisations.

The localised nature of the mining industry suggests the UK production record (Fig. 11) will be insufficient for reconstructing deposition trends at individual locations. An alternative source of information may be found in environmental archives - peat and lake sediment records from close to the study catchments. Despite an extensive literature review, few good records were found to exist in the UK. Nevertheless, peat core records were found from close to the Cote Gill and Etherow catchments and a lake sediment core has been collected from Blelham Tarn close to the Castle How beck catchment (Lee and Tallis, 1973; Livett *et al.*, 1979; Livett *et al.*, 1988; Ochsenbein *et al.*, 1983). These provide an alternative record of heavy metal deposition. Fig. 12 illustrates Pb concentrations in peat and lake cores close to the Etherow, Cote Gill and Castle How Beck catchment.

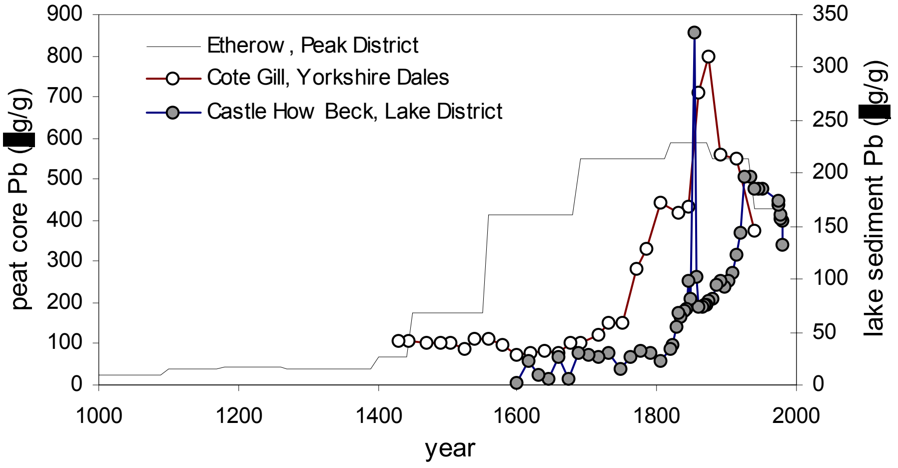


Figure 12. Peat core records of Pb deposition from Grassington Moor close to the Cote Gill catchment (Livett *et al.*, 1979); Featherbed Moss close to the Etherow (Lee and Tallis, 1973), and a lake sediment core from Blelham Tarn close to Castle How Beck (Ochsenbein *et al.*, 1983).

These records indicate a large historical deposition of Pb to the Cote Gill and Etherow catchments, with less to Castle How Beck as expected from the location of the sites in relation to mining areas. There are, however, some significant difficulties with interpreting the peat and lake sediment records. Records can only be considered reliable for Pb and Cu (Zn is likely to be subject to dissolution in acid soils). In addition peat accumulates very slowly (a few cm per century) providing only a low resolution record. Furthermore, lake records only partly reflect changing deposition due to the flux of sediment and metals from the catchment. Most problematically, the existence of just one environmental record from each region means there is no way of verifying the temporal trends indicated.

Deposition scenarios for the five catchments.

To determine site-specific trends in deposition from these records, the general and mining-related deposition profiles have been combined (Fig. 13). To establish absolute rates of deposition from these relative records, deposition at points on the trend profiles must be quantified. Heavy metal deposition monitoring carried out in each catchment between 2002 and 2003 has allowed the magnitude of deposition to be reconstructed from the trends. The mining-related peak can be determined from the flux to the local peat cores and the flux to Blelham Tarn relative to the flux in 1970 (as the actual flux to the lake will be higher than deposition due to inputs from the catchment).

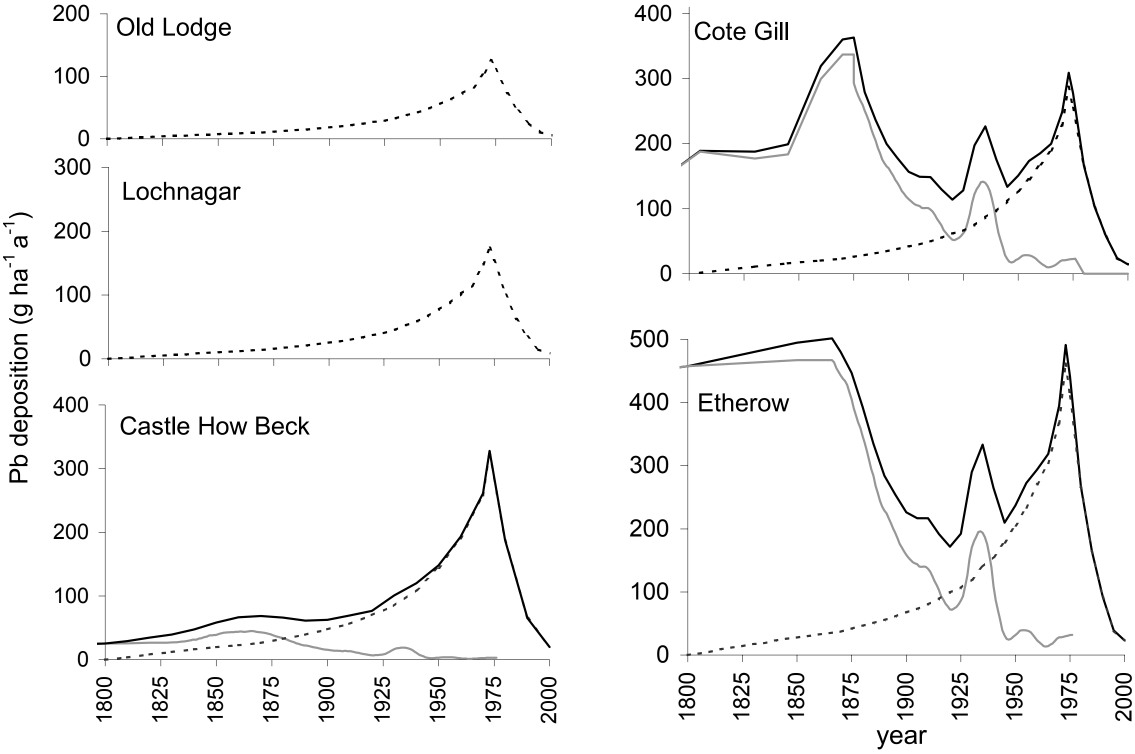


Figure 13. Pb deposition estimates from environmental and historical records. Dotted lines are 'general' deposition estimates, grey lines are mining-related deposition estimates, solid lines are total deposition estimates (the sum of general and mining-related deposition).

Most data is available for Pb, and therefore most confidence can be had in the resulting deposition histories for this metal. Fig. 13 shows Pb deposition histories for the 5 catchments. Deposition histories for the other metals are included in Annexe 7.

Although we are reasonably confident about recent (late 20th century) estimates of deposition, we are much less certain about early deposition, particularly the impact of mining on the Northern England catchments. Much of this uncertainty is due to the lack of historical or environmental records available for heavy metal pollution of these regions. To test the historical deposition scenario and to provide an additional source of information on historical deposition trends, we have investigated the potential for herbarium moss samples to provide an alternative record of past heavy metal deposition.

3.10.2 Herbarium moss sample records of past heavy metal deposition

Samples of four carpet forming moss species, *Hylocomium splendens*, *Hypnum cupressiforme*, *Pleurozium schreberi* and *Rhytidiadelphus squarrosus*, were collected from UK herbaria. A total of 143 moss samples were collected, from between 1850 and 2000, from sites close to the five study catchments (at the most 30 miles, dependent on source rock and landscape units but generally much less). Contributing herbaria were the Manchester Museum, the Natural History Museum, London (including the former herbarium of Kew Gardens), he National Museum of Wales, Cardiff and the Royal Botanical Gardens Edinburgh.

0.1 g of moss was washed thoroughly with double distilled water. Samples and washings were digested for 30 minutes in a CEM-MDS 2000 microwave before ICP-MS analysis. The analytical methodology is close to that used in the national moss surveys using the same acids at the same concentrations. The methodology diverges through the inclusion of a washing step, designed to ensure any contamination by soil particles or from storage in the herbarium was detected. Where no soil or other contamination was found, sample and washing concentrations were combined to give a total moss metal concentration.

Moss samples were analysed for Ni, Cu, Zn, Cd, Pb and As. Results of the analysis of Pb in mosses will be shown to illustrate the methods applied and provide a comparison to the Pb deposition profiles of Fig. 13. Concentrations of Pb in all the mosses analysed are shown in Fig. 14.

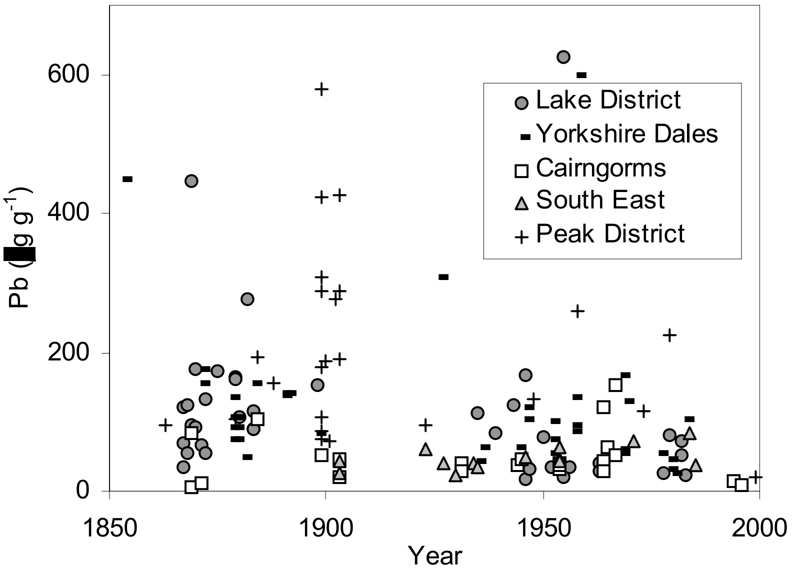


Figure 14. Concentration of Pb in herbaria moss samples.

Relationships to deposition

Strong linear relationships have been found between Pb deposition and Pb concentration in *Pleurozium schreberi* and *Hylocomium splendens* at sites in Norway (Berg and Steinnes, 1997). Relationships to deposition were also strong for Cd and As but weak for Cu, Zn and Ni (Annexe 8). These relationships can be used to relate herbaria moss Pb concentration to rates of deposition (Equations 2 and 3).

Pb deposition (g ha a^{-1}) = -0.773 + 1.758 Pb_{PS}($\mu g\ g^{-1}$) [r2 = 0.980] (Eq. 2)
Pb deposition (g ha a^{-1}) = -1.112 + 1.675 Pb_{HS} ($\mu g\ g^{-1}$) [r2 = 0.984] (Eq. 3)

There are no data available on the relationship between *Hypnum cupressiforme* or *Rhytidiadelphus squarrosus* and Pb deposition. However, an assessment of the differences in metal accumulation between species was made as part of the UK moss survey 2000 (Ashmore *et al.*, 2002a). This study found linear relationships between Pb concentrations in moss species, from which a *Pleurozium schreberi* standardised concentration was determined. This allowed deposition to also be calculated from Pb concentrations in *Hypnum cupressiforme* and *Rhytidiadelphus squarrosus* (Equations 4 and 5). Similar relationships were found for the remaining metals in *Hypnum cupressiforme* and *Rhytidiadelphus squarrosus*, allowing a *Pleurozium schreberi* standardised concentration to be determined. However, there was no significant relationship between Cu and As uptake in *Hypnum cupressiforme* and PS and therefore these moss metal concentrations could not be standardized (Annexe 8).

$$\mathrm{Pb_{PS}}\ (\mu\mathrm{g\ g^{-1}}) = 1.323 + 0.506\ \mathrm{Pb_{HC}}\ (\mu\mathrm{g\ g^{-1}}) \qquad [r^2 = 0.764] \qquad \text{(Eq. 4)}$$

$$\mathrm{Pb_{PS}}\ (\mu\mathrm{g\ g^{-1}}) = 0.933 + 0.577\ \mathrm{Pb_{RS}}\ (\mu\mathrm{g\ g^{-1}}) \qquad [r^2 = 0.885] \qquad \text{(Eq. 5)}$$

Pb deposition estimates from herbaria mosses and a comparison to the deposition histories estimated from literature are shown in Fig. 15.

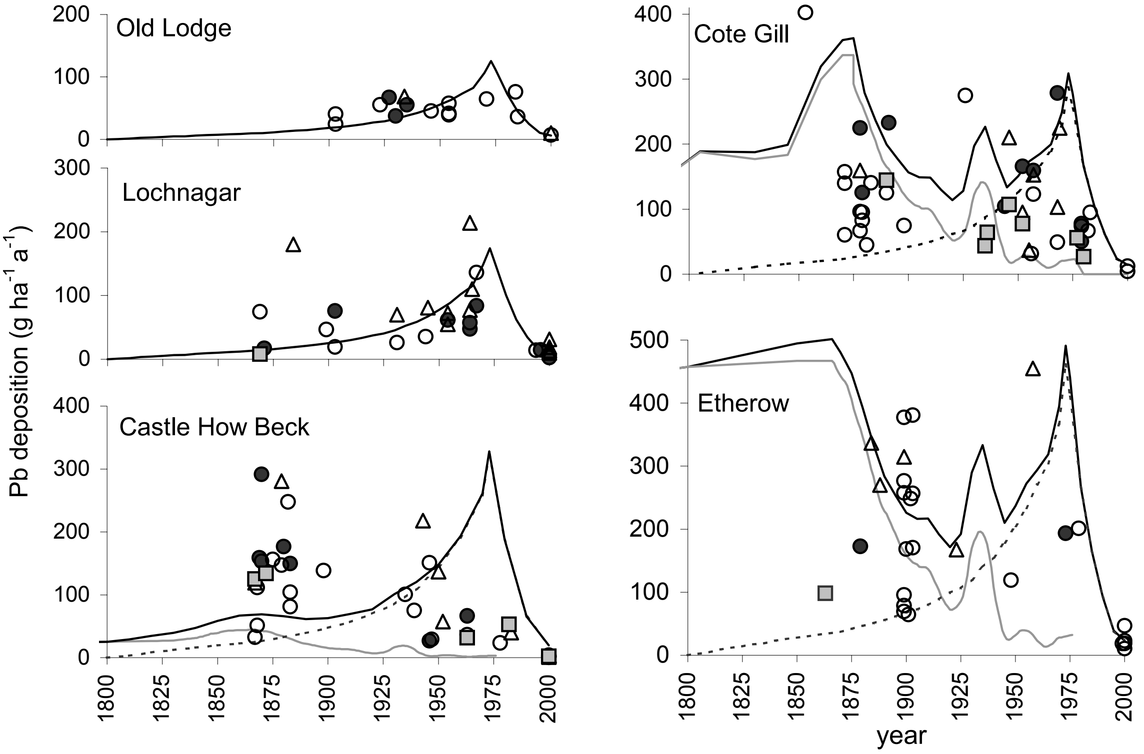


Figure 15. Pb deposition estimates from herbarium mosses and environmental and historical records: a) South East; b) Cairngorms; c) Lake District; d) Yorkshire Dales; e) Peak District.

3.10.3 Comparison of literature review and herbarium moss sample estimates of deposition

There are some difficulties in making a comparison between deposition estimated from mosses and deposition estimated from other sources in the literature. Mosses are collected from a region, whereas the deposition scenarios are directed towards particular catchments. The regional distribution of mosses is partly the source of the wide scatter in moss deposition estimates and is particularly important earlier in the record, where there are more localised sources of pollution. Another source of variability is the result of, by necessity, analysing very small quantities of material. Thus trends in deposition are difficult to quantify from the mosses.

Nevertheless, for Pb, for which we have most confidence in both the literature review based records and moss sample records, there is broad agreement shown in Fig 15, in both the magnitude of deposition and general trends over time. In particular, the moss deposition record confirms that deposition at Lochnagar and Old Lodge is low in comparison to the Northern England catchments. Mosses from the Cairngorms show no indication of any mining-related input. Unfortunately the lack of early moss samples in the South East means that we cannot confirm the lack of mining-related deposition to Old Lodge.

Data from the moss samples indicate high historical deposition at the Cote Gill and Etherow catchments. Moss records also, however, suggest high 19th century deposition in the Lake District, which is not found in the Blelham Tarn sediment record. This is thought to be because mosses are predominantly from the north of the region where most historical mining has been carried out. In contrast, the Castle How Beck catchment and literature review scenario are from the south.

4 WORK PACKAGE 3: CRITICAL LOADS MAPPING AND MODELLING

4.1 Introduction

The national databases compiled within a GIS under the previous contract (EPG 1/3/144) provided the basis for developing maps of critical limits, critical loads and their exceedence. However, these maps were limited to upland areas of the UK. Under this contract, the UK mapping capability was extended to the lowlands, and new methods were developed to apply the new critical limits developed under Work Package 1. The method development in the UK was closely linked to on-going discussions within CLRTAP, to ensure that the methods proposed for pan-European mapping were relevant and applicable to the UK. Policy development in relation to critical loads for metals is discussed in section 8 of this report.

The main aims of the critical loads work were:

- To develop improved methods to map critical limits, critical loads and their exceedence within the UK

- To extend the transfer functions used for the uplands to forests and lowland non-agricultural areas

- To develop methods of applying simple dynamic models at a catchment level within the national GIS

- To contribute to the development of critical loads methods within CLRTAP, and to submit data on critical limits and critical loads to CLRTAP as requested

This section first describes the results of new fieldwork to derive transfer functions suitable for application across the UK (4.2). It then describes methods used to calculate critical limits and exceedence based on pH dependent free-ion toxicity, critical loads and their exceedence, and compares the free-ion based critical loads maps to those derived under contract EPG 1/3/144 that used methods based on reactive soil content (4.3). This section also describes the parameterisation of the latest methods. Finally, maps of critical loads, assessment of exceedence of metal critical limits and loads, and an analysis of the time taken to exceed critical limits are then presented in section 4.4.

4.2 Transfer functions

Transfer functions used in the previous mapping of critical loads were based on extensive sampling of non-forested upland soils. To extend critical load mapping onto lowland soils and forested uplands, the applicability of these transfer functions had been tested. 56 soil samples of 5 land-use types (acid grassland, heathland, upland and lowland coniferous forest and deciduous woodland) were collected from ‘background’ sites (largely from National Nature Reserves and Forestry Commission sites, at least 100 m from roads). These were analysed for a range of soil and soil solution variables.

Methods used on the upland soil samples under DETR contract EPG 1/3/144 have been replicated in order to provide a comparable dataset. Variables measured were soil and soil water pH, loss-on-ignition, cation exchange capacity, % clay, porewater Ni, Cu, Zn, Cd, Pb, base cations and major anions, edta extractable and pseudo-total Ni, Cu, Zn, Cd and Pb. Free-ion metal activities were determined using WHAM (Tipping 1994; 1998).

A small additional exercise has also been completed by a MSc project at Bradford University, in which soil samples from sites in the Northern Pennines were analysed using the same methods. This dataset includes sites significantly contaminated by historical mining and smelting. Total metal concentrations of up to 40,000 µg Pb g^{-1}, 7170 µg Zn g^{-1}, 340 µg Cu g^{-1} and 15 µg Cd g^{-1} have been measured at the contaminated sites.

The ability of transfer functions determined from regression analysis of the upland soils dataset under EPG 1/3/144 to predict soil metal pools in the 56 ‘mixed landuse’ samples and the 16 ‘historically mined’ soils was tested. Transfer functions were recalculated as Freundlich partitioning coefficients (K_f) (Table 13). This type of transfer function is preferred as it enables us to use the same partitioning equation to calculate either free-ion or reactive soil metal (Römkens *et al.*, 2004). Furthermore, the non-linear Freudlich model allows us to take into account, if necessary, the tendency of binding strength to decrease as the amount of metal sorbed increases. In fact, only Cd prediction was found to be improved by using the Freundlich model. Partitioning of the remaining metals is best explained by a linear relationship with soil parameters (n = 1, Table 13). K_f is related to soil properties such that:

$$\log K_f = a + b\,\text{pH} + c\log \text{LOI} \qquad [\text{where } K_f = Q_{\text{reactive}} / Q_{\text{free}}^{n}] \qquad (\text{Eq. 6})$$

Table 13. Regression coefficients for determining partitioning between reactive (edta) soil metal concentration and free-ion activity. Derived from the upland non-forested dataset.

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

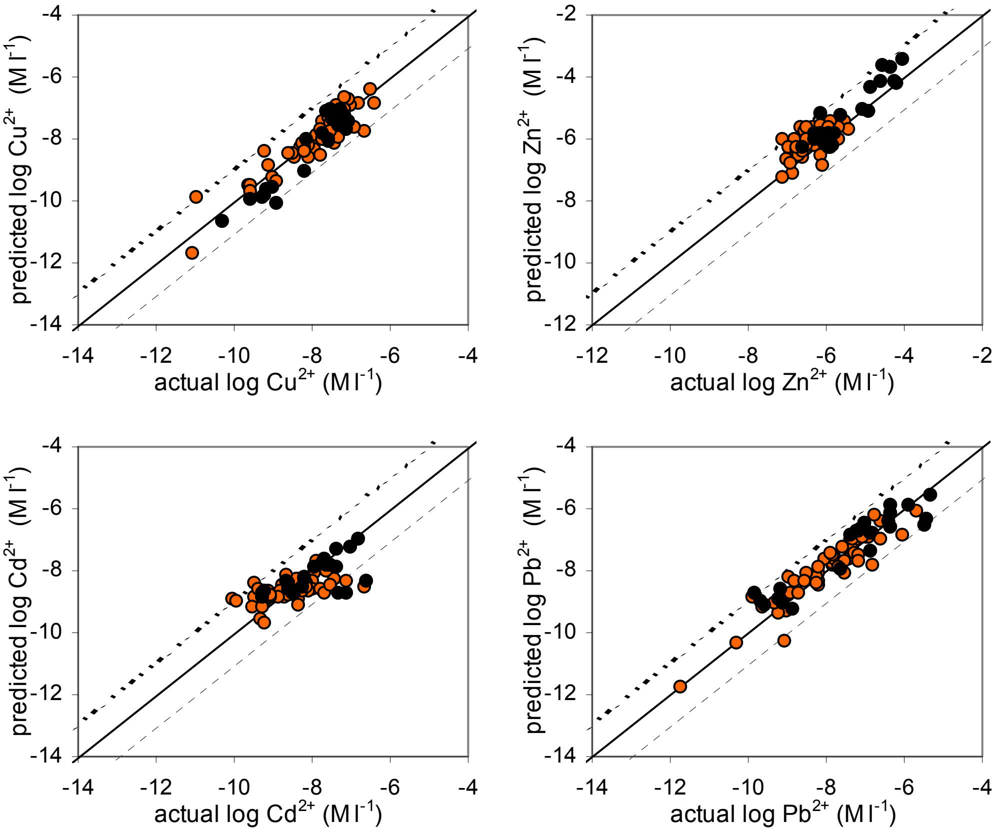


Figure 16. Predicted free-ion activity (M l^{-1}) from upland transfer functions. Red circles are the mixed landuse samples, black circles are historically mined sites.

Fig. 16 illustrates the capacity of the upland transfer functions to predict free-ion metal activity on a wider range of soils and habitats. Transfer functions perform satisfactorily for Pb and Cu, however Zn free-ion activity is slightly overpredicted and Cd is imprecisely predicted at the ends of the distribution.

The performance of other transfer functions was tested on the mixed land use and historically mined soils (Sauve *et al.*, 1998, 2000; Römkens *et al.*, 2004). In general these performed less well (Annexe 9). This probably results from methodological differences in the extraction of porewater and metals and the determination of pH. Less likely, but also plausible is that these functions developed in different countries may not be applicable to the particular soil, vegetation and environmental conditions in the UK.

4.2.1 New UK transfer functions

Europe wide transfer functions will be required for critical loads methods within CLRTAP. However, for UK critical loads calculations, a greater level of accuracy can be achieved through using UK-based transfer functions (given the difficulty in applying transfer functions developed outside the UK). We have combined all UK data to produce a set of transfer functions suitable for all landuse and soil types across the UK (Fig. 17, Table 14).

These transfer functions are based on the relationship between total soil metals and free-ion metals. This modification of the methods used previously (which used a two step transfer function, free-ion to reactive to total metal concentrations) simplifies and reduces uncertainty associated with the critical loads calculations.

Table 14. Regression coefficients for determining partitioning (K_f) between total soil metal concentration and free-ion activity. Derived from all UK soils data

	a	*b*	*c*	n	r^2	s.e.
log K_f Cu	-4.289	1.116	0.603	1	0.922	0.452
log K_f Zn	-2.573	0.323	0.121	0.83	0.588	0.381
log K_f Cd	-5.712	0.399	0.727	0.63	0.665	0.372
log K_f Pb	-4.191	1.175	0.762	1	0.919	0.483

$\log K_f = a + b\,\text{pH} + c \log \text{LOI}$ [where $K_f = Q_{total} / Q_{free}^{n}$] (Eq. 7)

This simplification has not been possible for Ni. Free-ion Ni activity was not determined under EPG/1/144 and the range in Ni concentrations in the new UK data is not great enough to derive total to free-ion transfer functions. The relationship between free-ion ion activity and reactive Ni concentrations has, however, been determined on the mixed land use data and found to be similar to relationships in data from Russia (Pampura *pers. comm.*) and Holland (Weng *et al.*, 2002). These data have been combined to produce free-ion to reactive Ni transfer functions (Annexe 9). The relationship between total and reactive Ni has been determined from the upland and mixed land use data. Here a direct transfer function (Q_c) had to be derived because a partitioning function did not provide a useful relationship. Thus Ni transfer functions must be performed in two stages (Tables 15 and 15).

Table 15. Regression coefficients for determining partitioning (K_f) between reactive (edta) Ni concentration and free-ion Ni activity. Derived from the mixed landuse dataset, Pampura *et al.*, *pers. comm.* and Weng *et al.*, 2002.

	a	*b*	*c*	n	r^2	s.e.
Log K_f Ni	-4.85	0.353	0.952	0.73	0.708	0.339

$\log K_f = a + b\,\text{pH} + c \log \text{LOI}$ (where $K_f = Q_{reactive} / Q_{free}^{n}$) (Eq. 8)

Table 16. Regression coefficients for determining partitioning (K_f) between reactive (edta) Ni concentration and free-ion Ni activity. Derived from mixed landuse and upland grassland data

	a	*b*	*c*	d	r^2	s.e.
log $Ni_{reactive}$	-4.351		0.663	0.628	0.558	0.249
log Ni_{total}	-1.580	0.007	-0.484	0.626	0.534	0.252

$\log Q_{reactive} = a + b\,\text{pH} + c \log \text{LOI} + dQ_{free}$ (Eq. 9)
$\log Q_{total} = a + b\,\text{pH} + c \log \text{LOI} + dQ_{reactive}$ (Eq. 10)

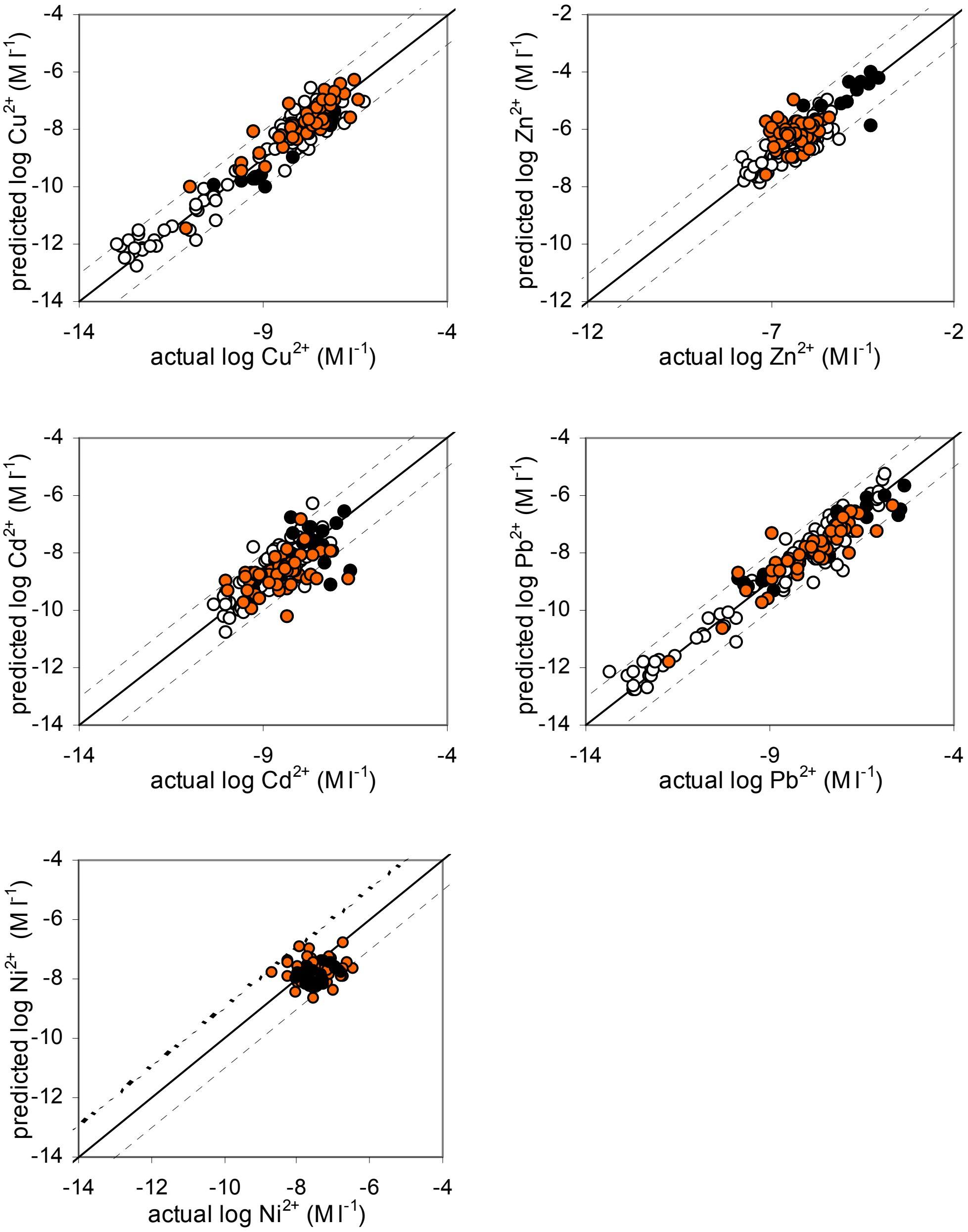


Figure 17. Predicted free-ion activity (M l^{-1}) from transfer functions based on all UK data (and for Ni some additional data from Pampura *et al.*, pers. com and Weng *et al.*, 2002). Red circles are the mixed landuse samples, black circles are historically mined sites, open circles are the upland non-forested samples.

Fig. 17 illustrates the capacity of the new transfer functions to predict free-ion metal activity on all UK soils. For each metal a small amount of precision has been lost from the original upland transfer functions (r^2 values are slightly lower for Cu, Zn, Cd and Pb). This is an expected outcome due to the extension of the transfer functions to use across a wider range of soils and habitats. The accuracy of predictions is, however, increased with no over or under-prediction, nor bias at the ends of the distributions (residuals are independent of metal concentrations).

The differences between predicted and actual free-ion activity are up to around an order of magnitude for Pb and Cu although this is across samples with free-ion metal activity varying by 7 orders of magnitude. Errors are slightly higher for Cd and Zn. Ni, despite the relatively low range in the data, the need for two transfer functions and the use of non-UK data to derive the transfer functions, seems to be predicted well.

It is, therefore, possible to describe metal partitioning in soils across the UK with one set of transfer functions. Nevertheless, the prediction of free-ion metal activity from soil parameters remains one of the larger sources of uncertainty in critical loads calculations (Section 5).

4.3 Critical Loads Methods and Models

4.3.1 Introduction

Due to developments in the modelling of heavy metal (HM) Critical Loads, six major changes have been made to the calculation and mapping of critical loads since the last call for data by the CCE in March 2002 (Hettelingh *et al.*, 2002).

- Critical loads have been calculated for five metals – lead, cadmium, zinc, nickel and copper.
- Habitat masks have been extended to include lowland and upland areas covering: managed conifers, managed broadleaf, unmanaged woodland and semi-natural areas.
- 1km national data sets for soil properties were derived from values assigned to soil series for England and Wales, Northern Ireland and Scotland.
- The WHAM model (Tipping, *et al.*, 2003) version six has been loosely coupled with the GIS to calculate critical loads based on pH dependant free-ion critical limit values for the UK (Annexe 1). In previous reports, the critical loads were calculated via a mass balance approach, based on fixed critical limit values.
- Dynamic maps with estimates of the number of years taken to reach critical limits have been produced based on current soil metal pool and other soil characteristics derived from CHUM.
- The latest UK heavy metal deposition data (McDonald *pers. comm*) has been applied to calculate exceedence of critical loads.

Results will be presented for all metals, however, national datasets for soil nickel concentrations were not available to the project, so critical limits exceedence and time to reach critical limit in the future could not be modelled for this metal.

4.3.2 Updates to the habitat maps

In the previous report, critical loads were presented for two habitats: forested uplands and non-forested semi-natural uplands. Updates have been made to include semi-natural lowland areas resulting in four habitats (Figs. 18 and 19) to which the critical load models have been applied nationally:

- unmanaged woodland
- semi-natural unforested habitats
- managed broadleaved woodland
- managed coniferous woodland.

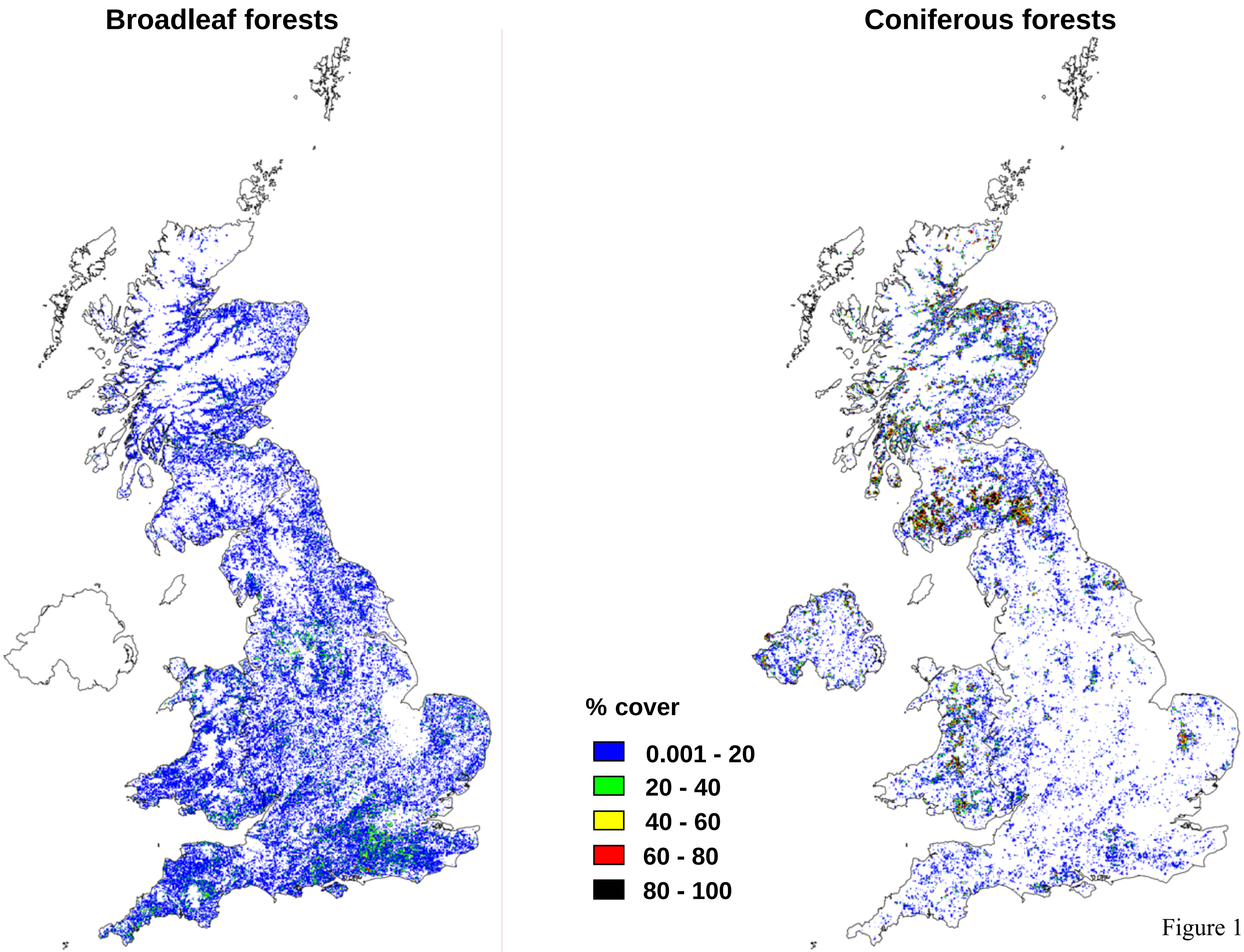
Figs. 18 and 19 show the total percentage cover of each habitat type within each 1km square. These maps have been derived at 1km resolution from data sets produced under Defra contract EPG 1/3/185.

For mapping heavy metal critical loads, the managed coniferous and broadleaved woodland habitats were grouped together as managed woodland, assumed to be primarily managed as productive forest, where harvesting and removal of trees takes place. The unmanaged woodland consists of ancient and semi-natural woodland, which includes yew and Scots pine, and are woodlands "managed" for biodiversity or amenity, but not timber production. The semi-natural class combines areas of acid grassland, calcareous grassland, dwarf shrub heath, montane and bog. Full details on the data and methods used to derive all habitats maps are given in Hall *et al.* (2003).

4.3.3 Updates to the soil properties maps

In previous reports, 5 km resolution maps of soil properties and critical loads were presented. These were based on the nationally available spatial soils data, and represented a single point sample within each square. For Scotland some of the data were only available at 10 km resolution but were mapped at 5 km resolution for consistency with the rest of the UK. However, the nature of these data meant that only a small number of 1 km data points were actually represented on the maps. Now, due to the current developments in the methods, the heavy metal soil concentrations are no longer required to calculate critical loads at steady state. Without the need to use these data it has been possible to generate 1 km resolution maps of soil properties by using information provided by the national soil surveys. These data give soil properties by soil series and have been generated into a spatial data set by linking them with the dominant soil series in each 1 km square.

Woodland habitat distributions

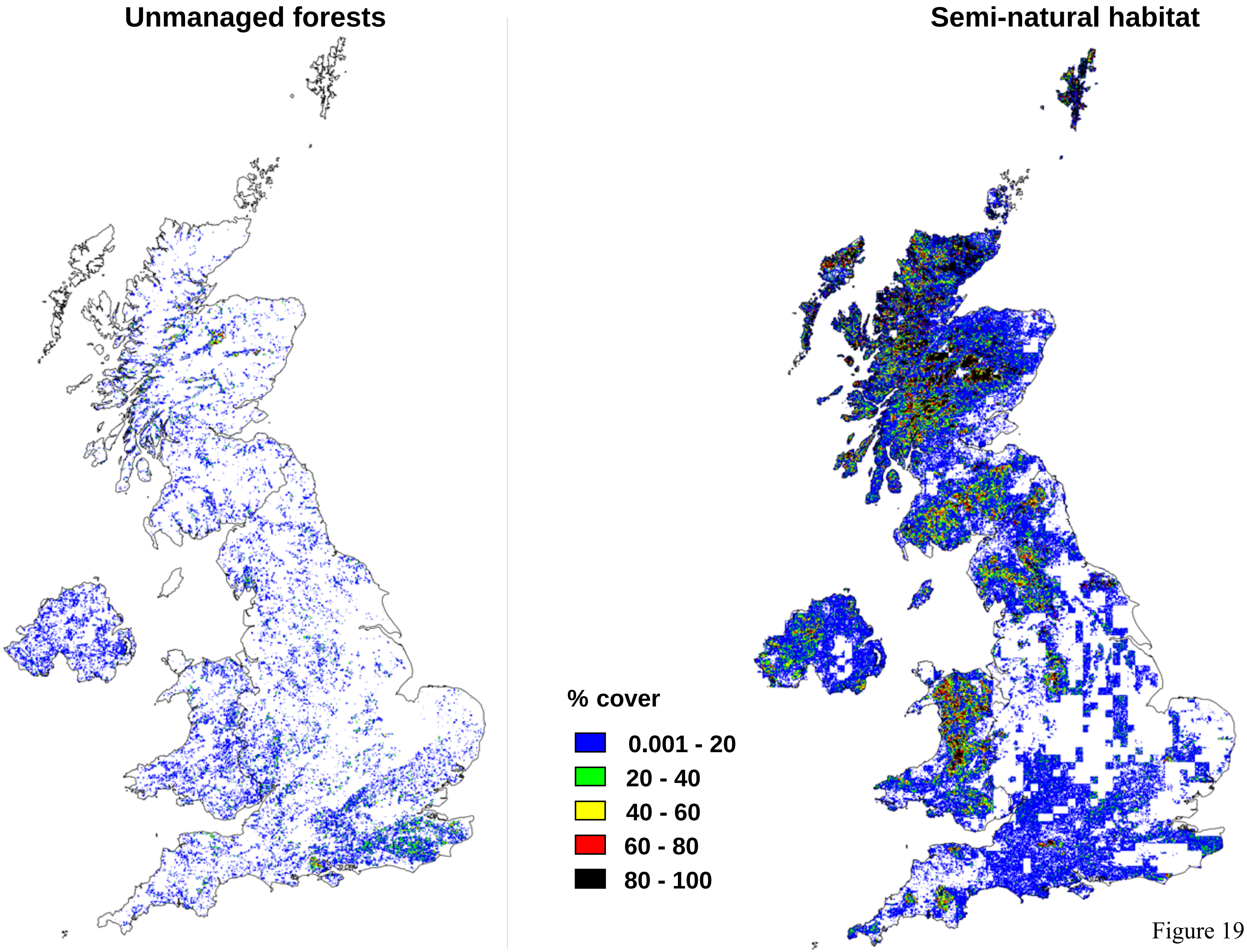


Broadleaf forests

Coniferous forests

Figure 18

Unmanaged and semi-natural habitats



Unmanaged forests

Semi-natural habitat

Figure 19

4.3.4 Parameterisation of critical limits and loads models in GIS

National maps of soil properties were produced by combining the datasets for England and Wales, Scotland and Northern Ireland. Detailed description of the data and how they have been derived can be obtained from final contract report (EPG 1/3/144). Changes that have been applied to the national datasets are summarised below.

pH

pH values were merged from the available separate datasets sets to create a 1km resolution data set for the UK. These data sets are derived from measurements in a soil water extract and are described as average values per soil series. Equation 11 is used to convert these pH values to the soil pH used in deriving transfer functions (i.e. extraction with Rhizon samplers) and the mapping manual definition of soil pH (UNECE mapping manual).

$$pH = 1.0462 * pH - 0.2847 \qquad \text{(Eq. 11)}$$

pH values for the UK dataset, ranged from 2.8 to 8.1 with a mean of 5.8, while the mapping manual pH values ranged from 2.6 to 8.2 and a mean of 5.8.

Loss-on-ignition (LOI)

LOI values for the UK were not directly available, but were derived from Organic Carbon (OC) data based on a relationship suggested by Broadbent (1965). LOI was derived using the formula LOI = 1.9 * OC with a maximum value of 99.9%.

Average Annual Runoff

The original data set obtained from CEH Wallingford at 1km resolution based on a 30 year (1941-1970) mean rainfall data, with measurement units in m year^{-1} was converted to mm year^{-1} to fit in with the requirements of WHAM. It should be noted that a recent study by Holmes *et al.* (2002) suggests that runoff values for areas with lower rainfall (East Anglia) might be over-estimated by the current model used to derive this data set.

issolved organic carbon (DOC)

A national dataset of DOC concentrations was not available for this project. An extensive review of available literature on DOC values from lysimeter-based studies indicated that DOC concentrations in the UK were generally lower than global averages but still highly variable (Annexe 10, table 17).

Table 17. Summary statistics for DOC concentrations measured in studies in i) the UK and ii) Europe and North America (Annexe 10).

Soil type	Horizon	DOC mg/l											
		Conifers				Deciduous				Non-forest			
		n	5%	median	95%	n	5%	median	95%	n	5%	median	95%
UK	Upper (O, A)	17	4.9	**15.0**	46.3	9	7.7	**17.2**	21.1	30	3.7	**13.4**	42.9
	Lower (B)	14	3.1	**5.1**	23.4	27	3.6	**7.7**	16.1				
Europe	Upper (O, A)	26	16.2	**39.1**	85.1	23	12.6	**32.4**	109.0	14	13.4	**24.0**	90.4
and North America	Lower (B)	22	2.7	**10.9**	42.4	17	2.9	**7.0**	26.8				

Some relationship was found between DOC flux, runoff and habitat type (Fig. 20). Although the variability and low number of data points means the relationships are weak, there does appear to be some increase in DOC with runoff tending towards a maximum flux. This empirical relationship may tentatively be said to have a process-based explanation: DOC concentration in soils may be envisaged as a function of both the generation and accumulation of DOC in soil, and the removal by runoff. Therefore higher DOC flux relative to runoff is found in soils with low runoff but higher total flux where runoff is high.

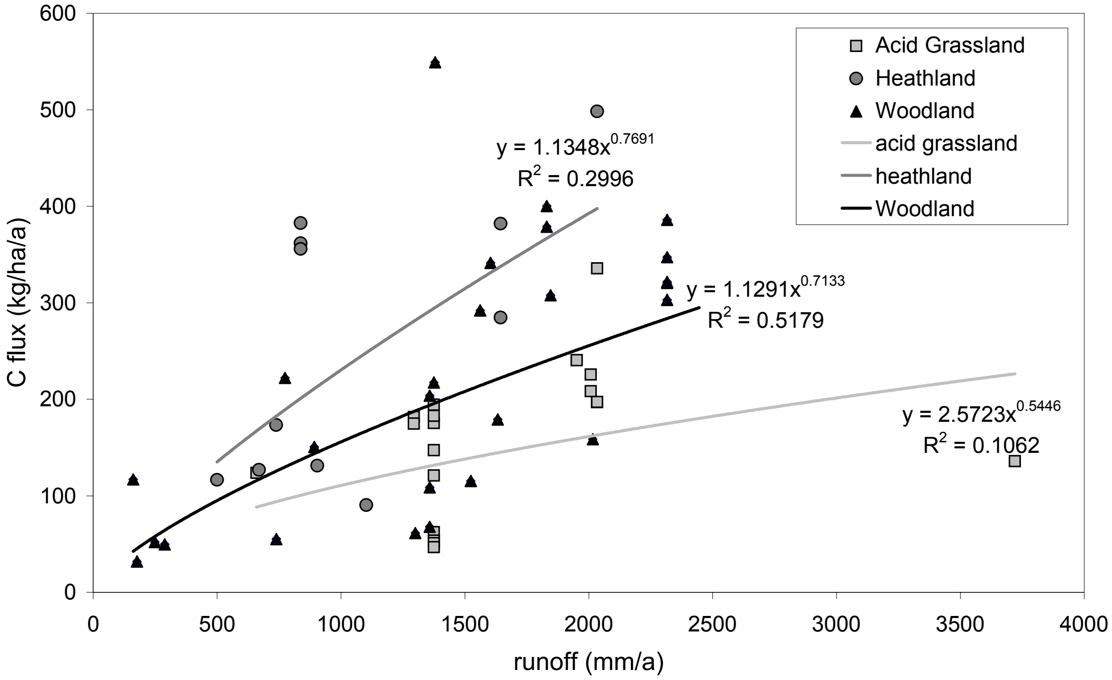


Figure 20. Relationship between carbon flux and runoff in UK soils.

DOC concentrations were derived for different habitats based on runoff using the following equations (a rearrangement to determine concentration from the regression equations shown in Fig. 20):

DOC Acid Grassland $(\text{mg l}^{-1}) = 257.23 * \text{runoff } (\text{mm yr}^{-1})^{-0.4554}$ (Eq. 12)

DOC Heathland $(\text{mg l}^{-1}) = 113.48 * \text{runoff } (\text{mm yr}^{-1})^{-0.2309}$ (Eq. 13)
DOC Woodland $(\text{mg l}^{-1}) = 112.91 * \text{runoff } (\text{mm yr}^{-1})^{-0.2867}$ (Eq. 14)

The relationships between DOC concentration and runoff are not strong and may introduce significant uncertainty. Nevertheless, they provide a more realistic estimation of DOC than accepting the default value of 20 mg l^{-1} recommended in the UNECE Mapping Manual, which is high in comparison to the UK median and does not account for the influence of runoff.

pCO_2 and SPM

National data sets for pCO_2 and SPM were not available and could not be derived with any measure of confidence. For the critical load calculations, pCO_2 was set to 30 times atmosphere and SPM was set to 5 mg l^{-1}, both based on expert advice.

Soil metal concentrations

Soil metal concentration datasets used in previous calculations for this project were based on a 5km sampling resolution for most parts of the UK for Cd, Zn, Pb and Cu. To calculate exceedence of critical limits for each of the 1km squares, the 5km dataset was resampled to higher resolution. This process, executed within the GIS, applied the value for the sampling point within each 5km square to all the enclosed 1km squares. This process does not create any new data or change any value within the existing dataset.

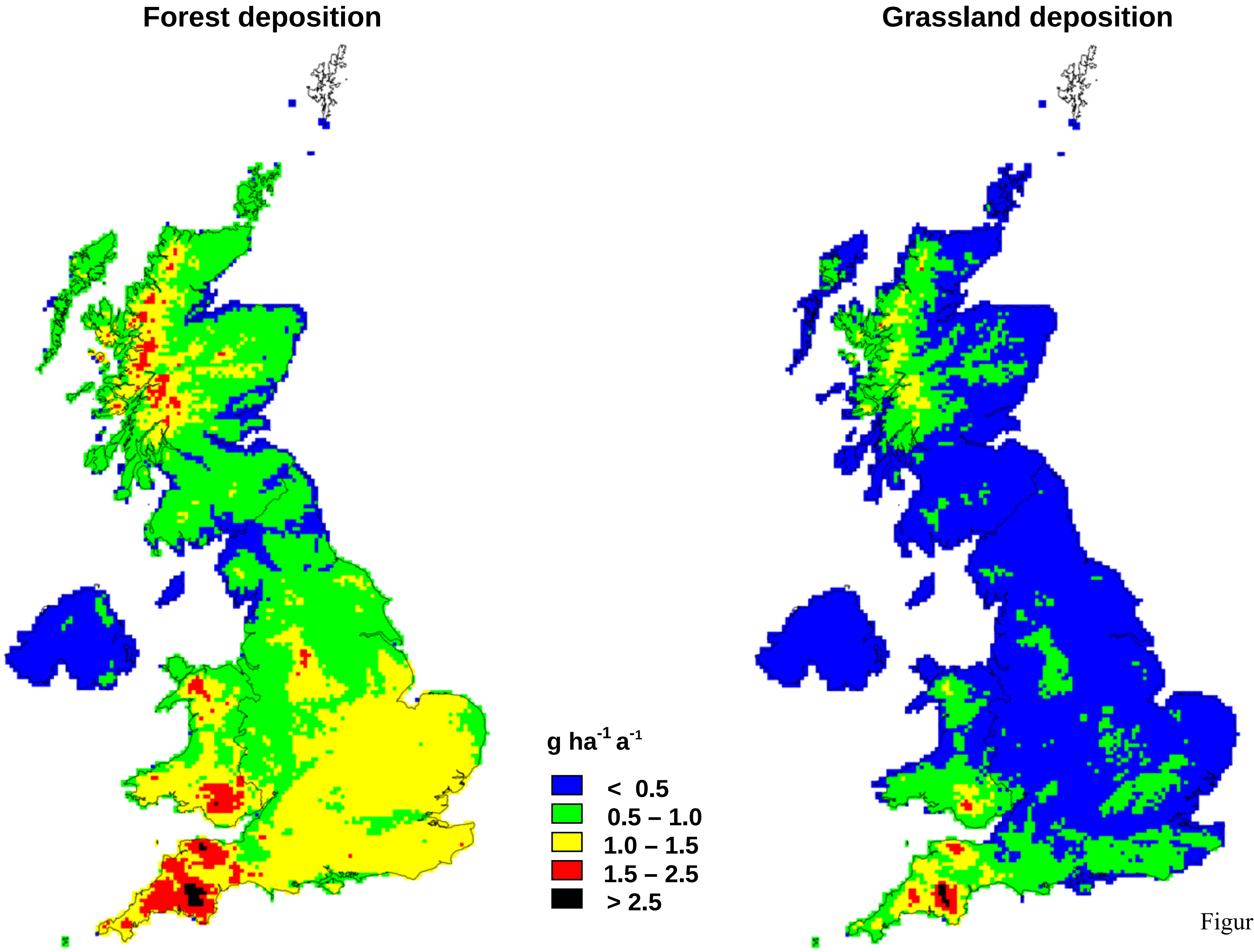
Heavy metal deposition data

Deposition data used in critical load calculations are from the Defra funded Heavy Metals Monitoring Network. The heavy metals network consists of 15 sites located around the UK. Of these, 10 of the sites sample for metals contained in PM_{10} particles in rain, whilst a further 3 sites sample for metal content in rain only. The remaining 2 sites are at high altitude and are focussed on sampling for metals in rain and cloud droplets.

The data are interpolated by CEH Edinburgh using ArcView GIS and a fixed radius of 300km, to create a $5km^2$ grid based on the OS grid. To calculate wet deposition, the seeder-feeder effect is then applied to the metal concentrations to account for enhanced rainfall at higher altitudes. To calculate dry deposition, the dry deposition velocity (V_d) is calculated from the land-use maps and local wind data for each $5km^2$ grid square. The annual dry deposition is then calculated.

Figs. 21 & 22 present the cadmium and lead deposition maps for the UK. These maps represent the national total average deposition to grassland and to forests, in each case assuming all 5km grid squares are entirely covered by the habitat type. Cadmium deposition (Fig. 21) is highest in southwest England, Wales and the Scottish Highlands. This distribution suggests annual rainfall is a significant factor in determining total Cd deposition, although the high deposition in the south west of England is not entirely explicable. Lead deposition is highest across much of southern England , Wales and the Scottish highlands. The distribution suggests annual rainfall is a factor, but that proximity to sources of Pb is also important.

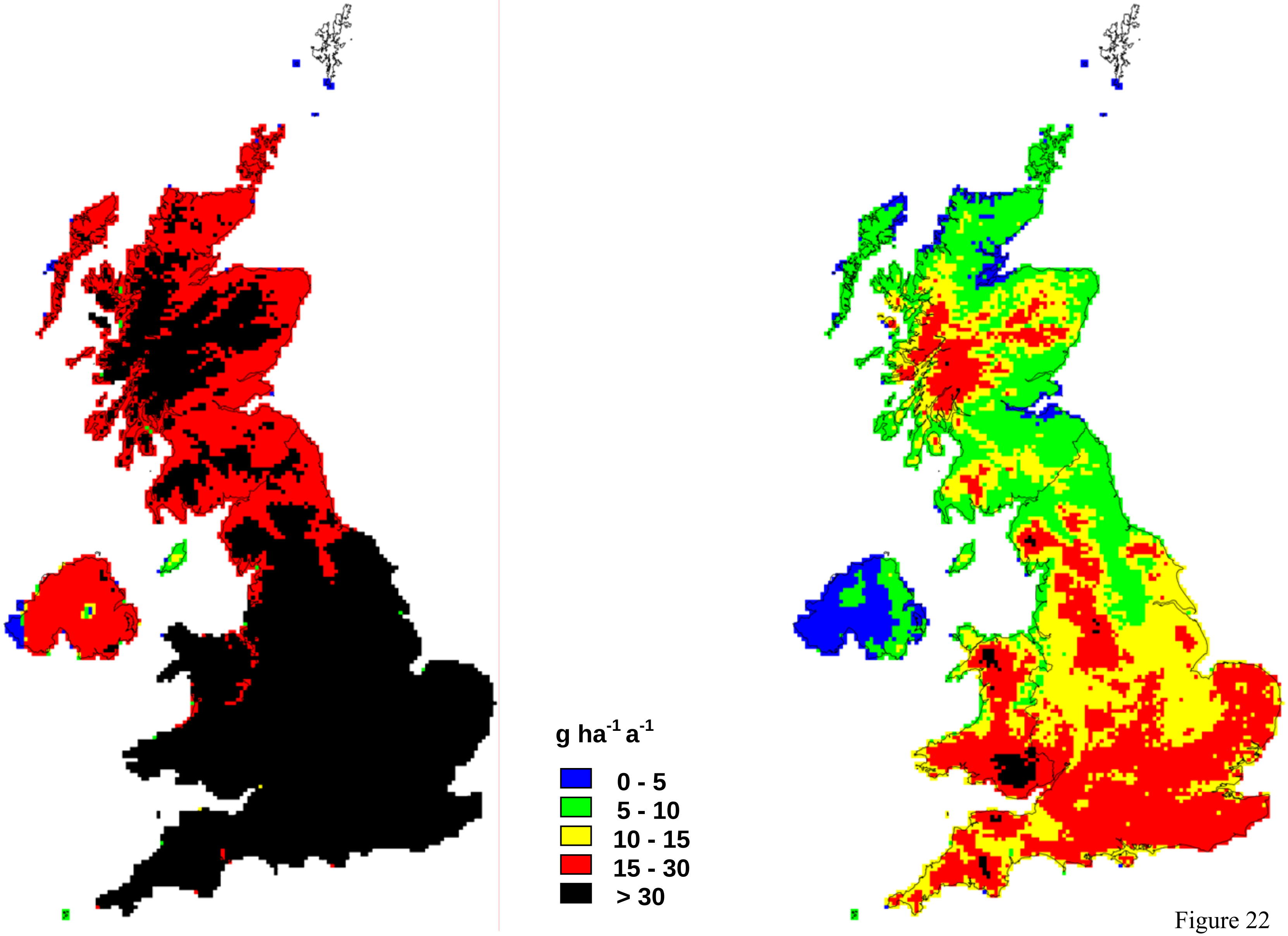
Cadmium deposition (g ha^{-1} a^{-1}) for the UK


Forest deposition

Grassland deposition

Figure 21

Lead deposition (g ha^{-1} a^{-1}) for the UK



Forest deposition

Grassland deposition

Figure 22

Metal uptake

An important component of the calculation of the critical load for soils is the uptake term, which expresses the removal of metals from the ecosystem through harvesting. Since the project does not deal explicitly with agricultural systems, the emphasis for this work, which was carried out through a variation in the original contract, was on forestry. Since forests generally receive higher rates of deposition, they may appear to have greater exceedence of critical loads, but they also have greater rates of removal of metals through harvesting. Hence improved quantification of the harvesting rate for forests is important.

The work was carried out by Forest Research, based on data from the Forest Survey Level II plots. The work is described in detail in Annexe 11. Wood cores were taken from all these plots, which comprised four oak stands, six beech stands, four Scots pine stands, two Norway spruce stands and four Sitka spruce stands. The analysis used other data from these plots to derive the requisite information.

The metal analyses included inner wood, outer wood, and bark, which allowed some assessment to be made of the importance of surface deposition as opposed to uptake. For lead and zinc, in particular, bark concentrations were much higher than wood concentrations, and also higher in rough-barked species (e.g. oak) than smooth-barked species (e.g. beech), suggesting a dominant role for surface deposition.

To calculate uptake rates, concentrations of metals in wood measured at the different sites were combined with estimated biomass increments over the course of the rotation at the different sites. Table 18 summarises the mean values and the range for the different sites.

Table 18. Summary of calculated metal uptake rates (g ha^{-1} yr^{-1}) at the 20 UK Level II sites, expressed as a mean and range

	Mean (g ha^{-1} yr^{-1})	Min. (g ha^{-1} yr^{-1})	Max. (g ha^{-1} yr^{-1})
Copper	10.3	2.2	29.5
Zinc	46.4	3.7	226.0
Cadmium	0.61	0.07	1.68
Lead	3.69	0.51	12.3
Nickel	4.6	1.0	32.2

For all five metals, there was a variation in uptake rates between the twenty sites of an order of magnitude or more. In two cases (zinc and nickel) one site gave very high values, possibly reflecting a local source, or local soil contamination. Part of the variability reflected differences between species, with conifers having a higher mean uptake rate than broadleaves.

At ten sites, it was possible to compare the estimated uptake rate with measured rates of deposition. In the case of cadmium, uptake accounts for the majority (>60%) of deposition at most sites, and exceeds deposition at three sites. In contrast, for lead, the uptake term was low relative to deposition, with the maximum being 30% of deposition. Copper and zinc were intermediate in values between those for lead and cadmium, with a wide range in the uptake/deposition ratios between the ten sites. A general conclusion from the these comparisons, and from the range of uptake values between sites (Table 18) is that uptake is a significant term in critical load calculations for forests, and that spatial variation, and differences between species, in uptake rates could have a significant effect on the spatial variation in critical loads and their exceedence for all metals except lead.

For national mapping of critical loads, two sets of values were used, based on the mean uptake rates for broadleaves and conifers, excluding the two outliers for zinc and for nickel. Given the range of values at different sites, and the significance of uptake rates compared with deposition, it would be valuable in future to develop a predictive model which linked uptake rate to soil concentrations and/or deposition rates. However, this was out of scope of the present project and would require more detailed soil analysis at the Level II plots.

4.3.5 Critical limits and loads calculations

Critical limits and exceedence calculations

Transfer functions as derived in section 4.2.1 were used to convert the critical limit values from free-ion activity to total concentrations. To estimate exceedence of critical limits, these values were compared with national data on soil metals, which are expressed as total soil metal concentrations.

Critical loads calculations

Critical loads are calculated via a mass balance equation:

$$CL(M) = M_u + M_{we} + M_{le(crit)}$$

Where:

$CL(M)$ = critical load of a heavy metal M (g ha^{-1} year^{-1})
M_u = net uptake of metal in harvestable parts of plants under critical load conditions (g ha^{-1} year^{-1})
M_{we} = weathering rate of the metal (g ha^{-1} year^{-1})
$M_{le(crit)}$ = critical leaching flux of heavy metal M from the considered soil layer (g ha^{-1} year^{-1})

The weathering rate is set to zero and the uptake rate is calculated for managed forests only. The critical leaching flux is calculated as:

$$M_{le(crit)} = Q_{le} * [M]_{crit}$$

Where:

Q_{le} = flux of drainage water leaching from the soil, ie, runoff (m year^{-1})
$[M]_{crit}$ = total concentration of metal in the soil drainage water at the critical limit, comprising total dissolved metal, together with metal bound to suspended particulate matter (SPM).

The total dissolved metal concentration is calculated from the critical free-ion concentrations using the WHAM speciation model (below), and the SPM-associated metal is calculated from the critical free-ion concentration using the appropriate transfer function (section 4.2.1), assuming that the SPM has the same metal-binding properties as the soil.

Critical loads for Cd and Pb were calculated separately for different habitats: grassland (acid, calcareous) and montane, dwarf shrub heath and bog, managed coniferous woodland, managed broadleaved woodland and unmanaged coniferous and broadleaved woodland. In order to present the results as single maps for each metal, the minimum critical load value occurring in each 1km grid square was mapped.

Critical load exceedence was calculated as current deposition minus critical load for each 1 km^2.

The WHAM chemical speciation model
The chemical speciation of metals in solution was calculated using WHAM / Model VI (Tipping, 1994; 1998). Model VI describes the competitive interactions of protons and metal ions with dissolved organic matter (DOM), using parameters derived from laboratory experimental data with isolated humic substances (Tipping, 2002). In WHAM, Model VI is combined with an inorganic speciation model, the species list and constants for which were given by Tipping (1994).

4.4 Mapping and modelling

4.4.1 Maps of critical limits and exceedence

Figs. 23 and 24 present exceedence of critical limits for Cd and Pb respectively. For display purposes, the unmanaged and managed forest habitats have been combined. The cadmium map excludes Scotland due to lack of current total Cd concentration data. For Cd a total of 11.2% of the 1km grid squares mapped show critical limit exceedence. Exceedences are mainly around the Peak District, south and western England and across Wales, with more scattered areas of exceedence across lowland England. For Pb only 1.2% of the 1km squares mapped exceed critical limits. The main areas where the limits are exceeded occur in central England (White Peak area of the Peak District), the Northern Pennines (Yorkshire Dales and Northern Pennines) and south Wales, with smaller areas also in other parts of Wales, England (including Cumbria) and across Scotland.

Fig. 25 presents exceedence of critical limits for Cu and Zn. All habitats have been combined and, where exceedence varies across the different habitats, the greatest exceedence is presented. For Cu, 39.5% of the 1km grid squares mapped show critical limit exceedence, for Zn, 38.4% of the 1km grid squares show exceedence. For both Cu and Zn, exceedence is widespread across the lowlands of England and Wales, although Zn critical limits are also exceeded in numerous upland areas. The highest levels of Cu exceedence occur in the White Peak, South Wales, Northern Ireland, parts of South West England and just south of Birmingham. Zn exceedence is greatest across large areas of Wales, Shropshire, the White Peak, Somerset and Gloucestershire, the South-West, Pennines and Lake District. No maps of critical limit exceedence have been produced for Ni due to the unavailability of soil Ni data.

Interpreting critical limits exceedence.
Critical limit exceedence occurs where current soil metal levels (or actually soil metal levels at the end of the last century) are higher than levels set to protect 95% of species. These 'current' soil levels will be the result of both past and present inputs of metals. Although the areas mapped are semi-natural landuse or commercial forest and therefore we expect the primary input of anthropogenically derived metals to be atmospheric, it is also important to consider that some areas may receive metal inputs from geological sources or from agricultural application, particularly across lowland grassland areas. .

We must also consider that the critical limits set are precautionary because:

1. Toxicity tests carried out in freshly metal spiked soils (such as those used to determine critical limits) give toxicity statistics that are usually lower than is the case in a field soil that received metal input over time. This "aging effect," the cause of which is uncertain but may result from metals becoming progressively bound into less available forms through time, is well documented and is currently being written into the EU metals risk assessment policy by including a lab-field extrapolation factor of three on calculated limit values (Lock and Janssen, 2003a & b; Spurgeon and Hopkin, 1995). Thus the critical limits used in this study may be considered conservative.

2. No allowance has been made for natural variability in metal concentrations in soils. In certain areas, high soil metal levels occur naturally as a result of bedrock inputs, and although sensitive species may be inhibited from colonising these soils, the communities that are present are likely to be adapted (either through genetic changes in the populations or pollution induced community tolerance). This should mean that soil process and primary production are not inhibited at these locations even though soil metal concentrations are above the critical limit. Thus, critical limits are arguably too low in areas with naturally high metal concentrations.

3. Where more than one level of exceedence is calculated per grid square, only the maximum exceedence is presented.

Exceedence of Cd in these, largely rural areas may be due to local geological inputs, particularly in parts of the Peak District underlain by black shales and Somerset. Agricultural sources, e.g. fertiliser and sewage sludge applications, may also be important inputs in other areas but past industrial deposition will certainly have been a factor in some areas.

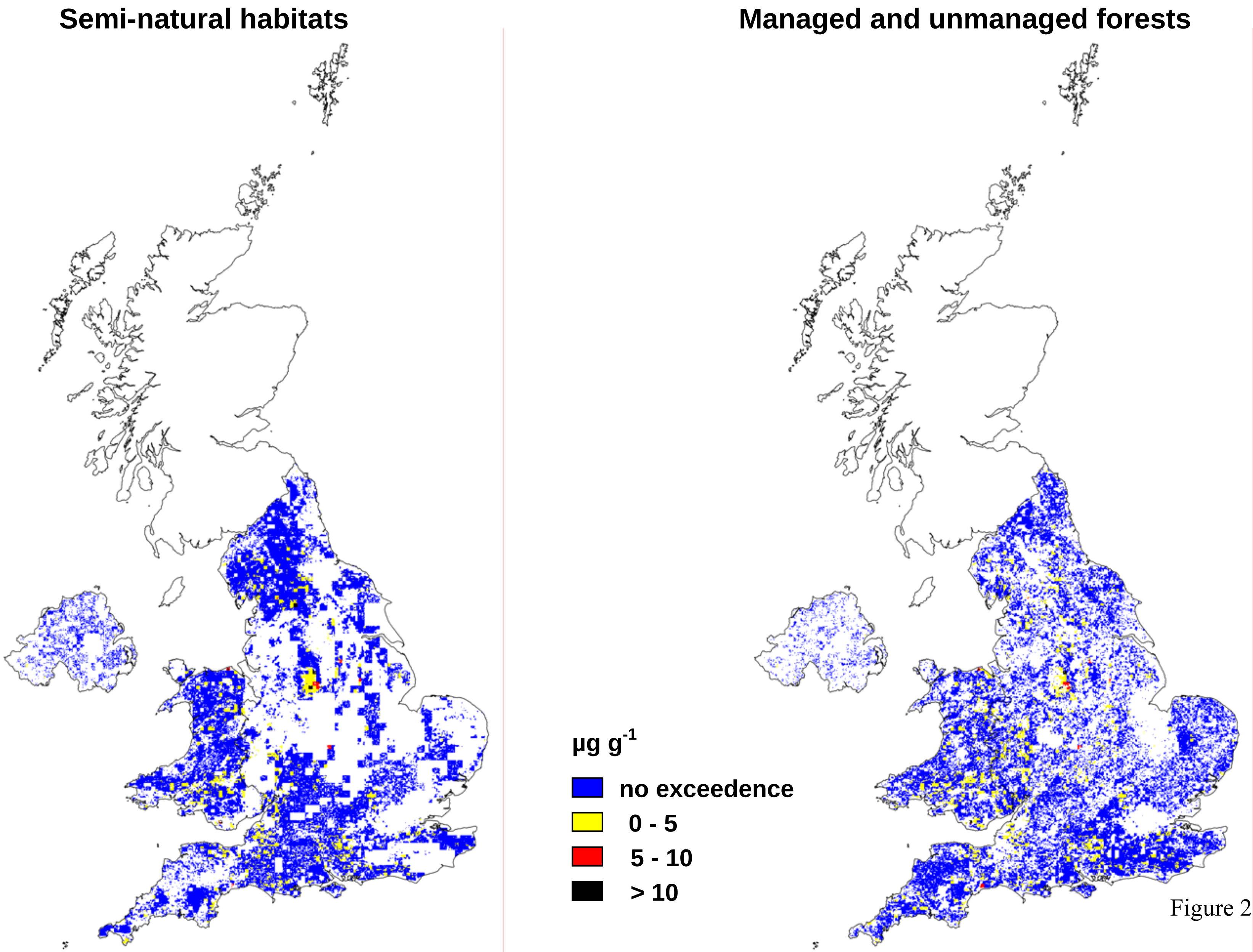
Exceedence of Pb appears to strongly reflect geology and perhaps historical pollution with the main areas of exceedence around areas of historical Pb mining. Exceedence is very limited despite the long history of Pb deposition in the UK.

Exceedence of Cu, however, is widespread. The basalt rocks of County Antrim have produced the high Cu exceedences in Northern Ireland. In South West England, Cu rich bedrock and particularly the exploitation of Cu ores will have resulted in locally high concentrations of Cu. This may also be the reason for Cu exceedence in the White Peak, with small amounts of Cu extracted associated with Pb and Zn ores.

Exceedence of Cu critical limits is, however, too widespread to be explained by geological inputs alone. Exceedence is most widespread over lowland England and Wales and thus may represent the impact of Cu deposition from industrial emissions. As will be demonstrated in section 4.4.3, Cu deposition, despite recent reductions, is still in exceedence of critical loads over much of lowland England indicating that these soils have a large potential to accumulate Cu. Historical deposition of Cu from nearby industrialised towns and cities, may have been a significant contributor to elevated soil concentrations in many parts of lowland Britain. Cu accumulation in soils across lowland England and Wales may, however, also have occurred from agricultural inputs, in particular as a result of additions from phosphorus fertilisers or sewage sludge to improved pasture.

Exceedence of Zn is equally widespread, however, the distribution is slightly different. Zn exceedence appears to be significantly influenced by geology resulting in exceedences in upland areas such as the Pennines, Lake District and Peak District, as well as Somerset and Cornwall. Away from areas of high background Zn, exceedence may, like Cu, be the result of atmospheric deposition, agricultural practice or both.

Exceedence of Free-ion Critical Limit of Cadmium ($\mu g\ g^{-1}$)

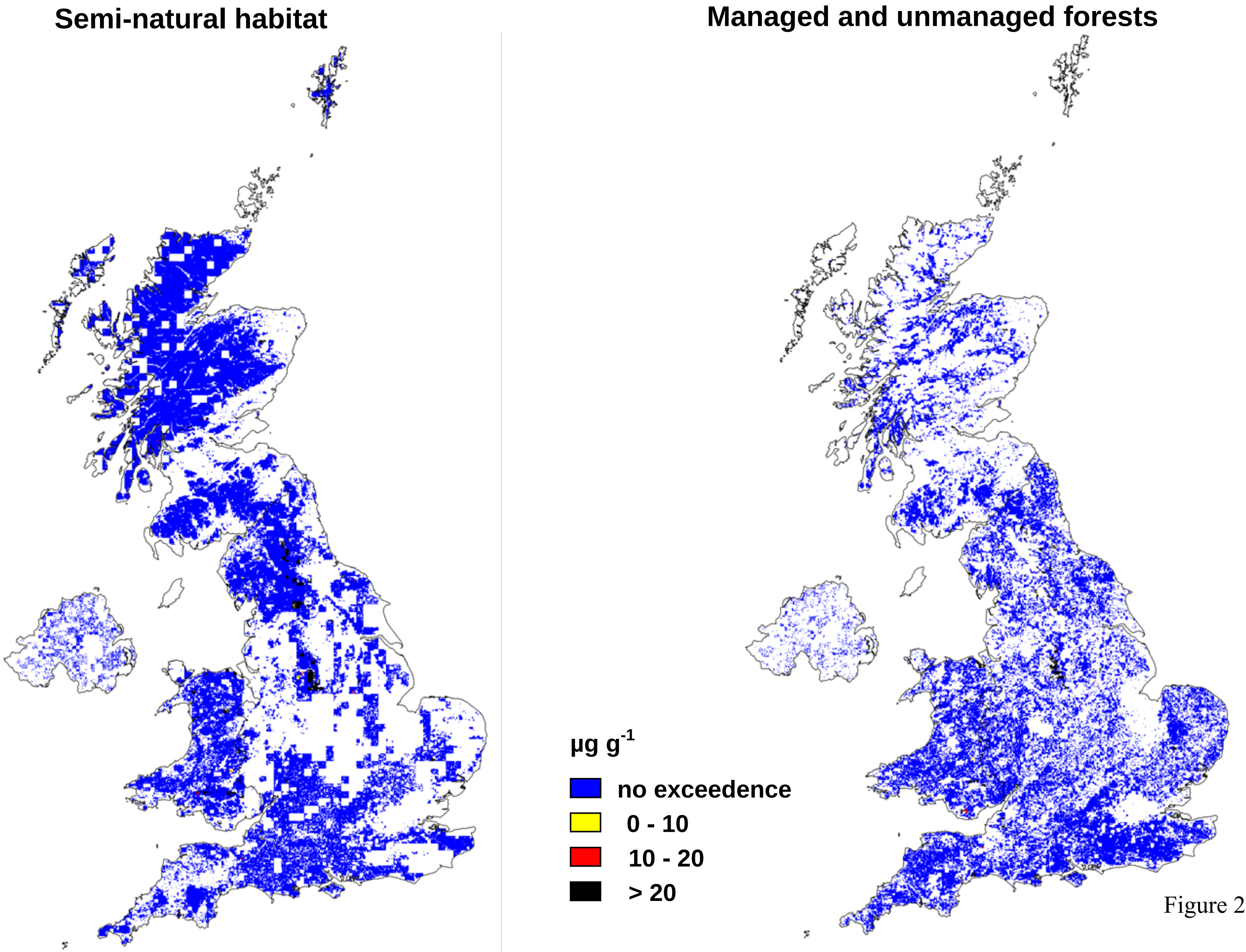


Semi-natural habitats

Managed and unmanaged forests

Figure 23

Exceedence of Free-ion Critical Limit of Lead (µg g^{-1})

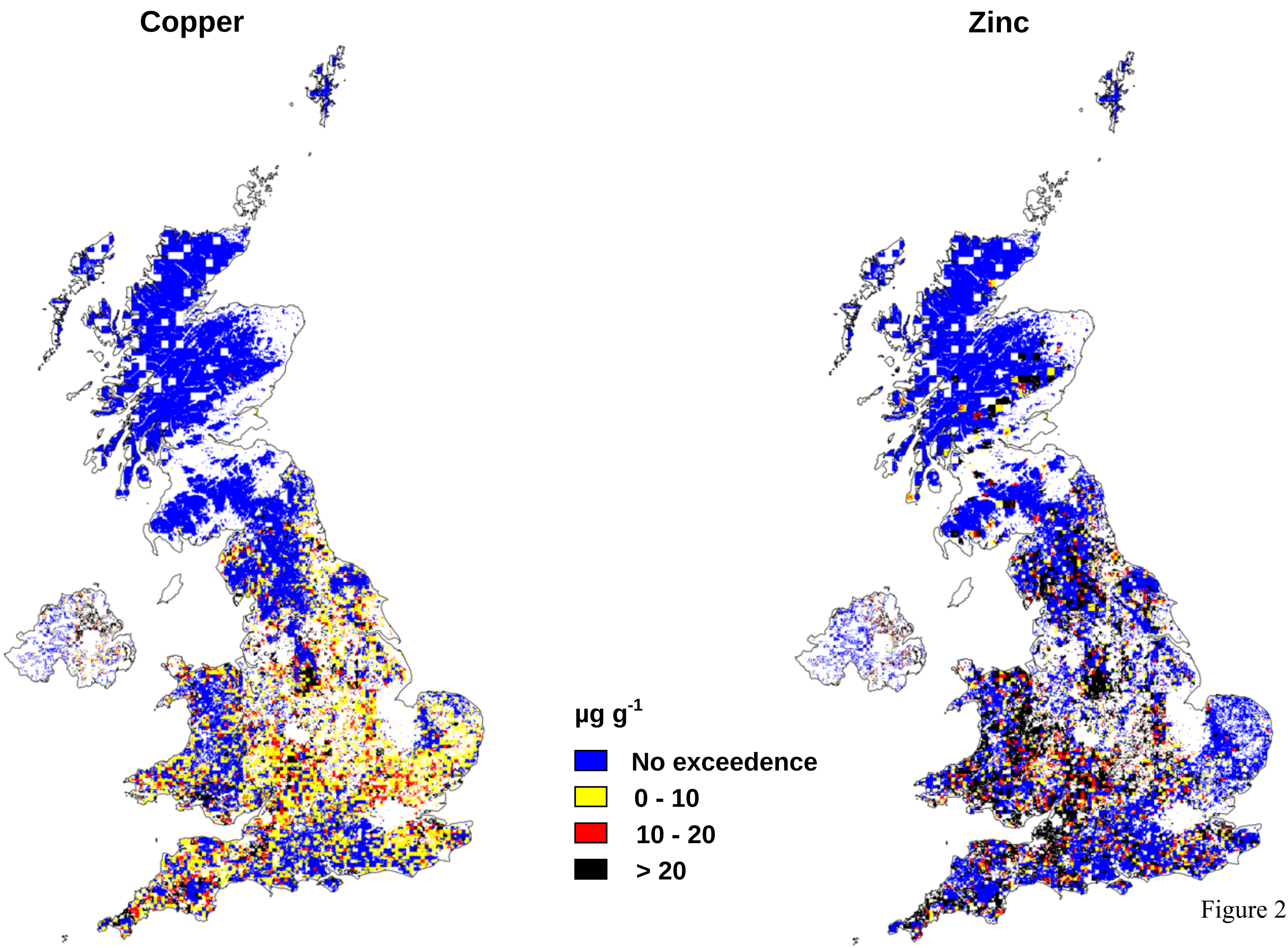


Semi-natural habitat

Managed and unmanaged forests

Figure 24

Exceedence of Free-ion Critical Limits for Copper and Zinc (μg g^{-1})



Copper

Zinc

Figure 25

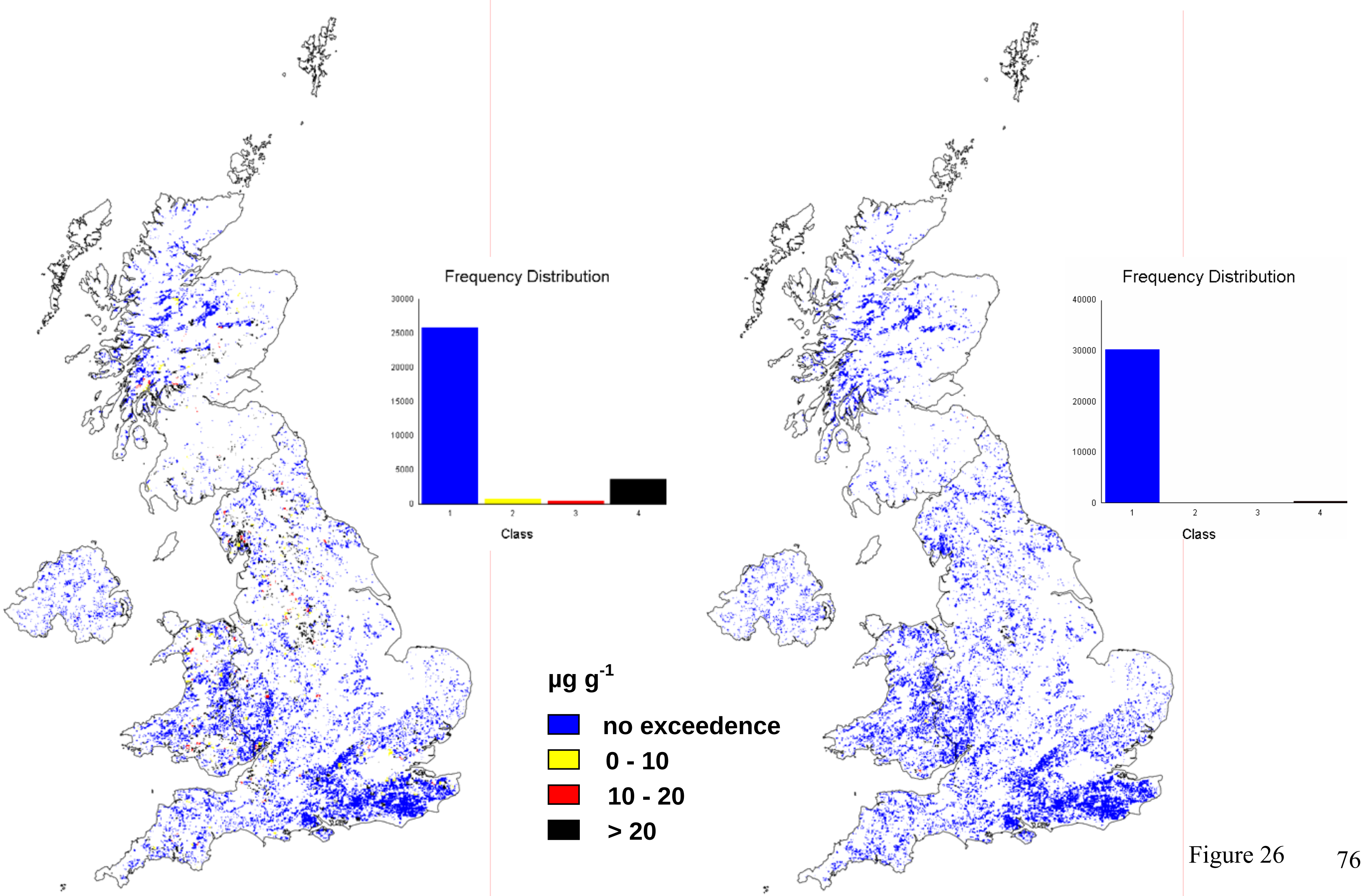
Comparison to fixed critical limits

Figs. 26 and 27 compare Pb and Cd free-ion based critical limits exceedence maps with maps produced based on fixed critical limits as reactive soil concentrations (8 and 3 μg g^{-1} respectively) under contract EPG 1/3/144. Exceedences calculated using free-ion Cd critical limits are more widespread than exceedences calculated using the fixed critical limits. Both methods show Cd critical limit exceedence in the southern Pennines and a few locations in the south east of England. Free-ion critical limits are also exceeded in parts of southern Wales and the Welsh borders.

The reverse is true for Pb, where the fixed critical limit of 8 μg g^{-1} was exceeded in a relatively large number of grid squares across the Pennines, Lake District, North and South Wales, the Scottish highlands and South East England. Free-ion critical limits are only exceeded in a few locations on the Pennine hill chain (and largely in the Peak District) where Pb ore extraction has taken place.

This comparison highlights how the choice of both the limit values and the methods used to derive them can have a significant impact on the outcome of risk assessments and subsequent policy decisions that may result from their use. One possible factor of relevance, that was highlighted in Section 2, is the systematic difference between the test soils that are used in the ecotoxicological studies from which the critical limits were derived, and those found in semi-natural and forest systems across the U.K. The ecotoxicological test soils, with relatively low organic content, are likely to have a higher availability of metals such as lead, that are strongly bound to organic matter, than is the case in the more organic soils found in the field; hence the critical limits based on reactive soil concentrations for lead are likely to be low relative to those based on free-ion activity, and hence show more exceedence. In contrast, for metals such as cadmium, with weak binding to organic matter, the relatively high pH in ecotoxicological tests relative to field values will lead lower availability and hence to critical limits based on reactive soil concentrations that are likely to be high relative to those based on free-ion activity. Therefore less exceedence is to be expected for critical limits based on reactive soil concentrations than for those based on free ion activity in the case of cadmium.

Exceedence of Critical Limit of Lead, Unmanaged Forests (μg g^{-1})



Fixed critical limits

pH dependent free-ion critical limits

Figure 26

Exceedence of Critical Limit of Cadmium, Unmanaged Forests (μg g^{-1})

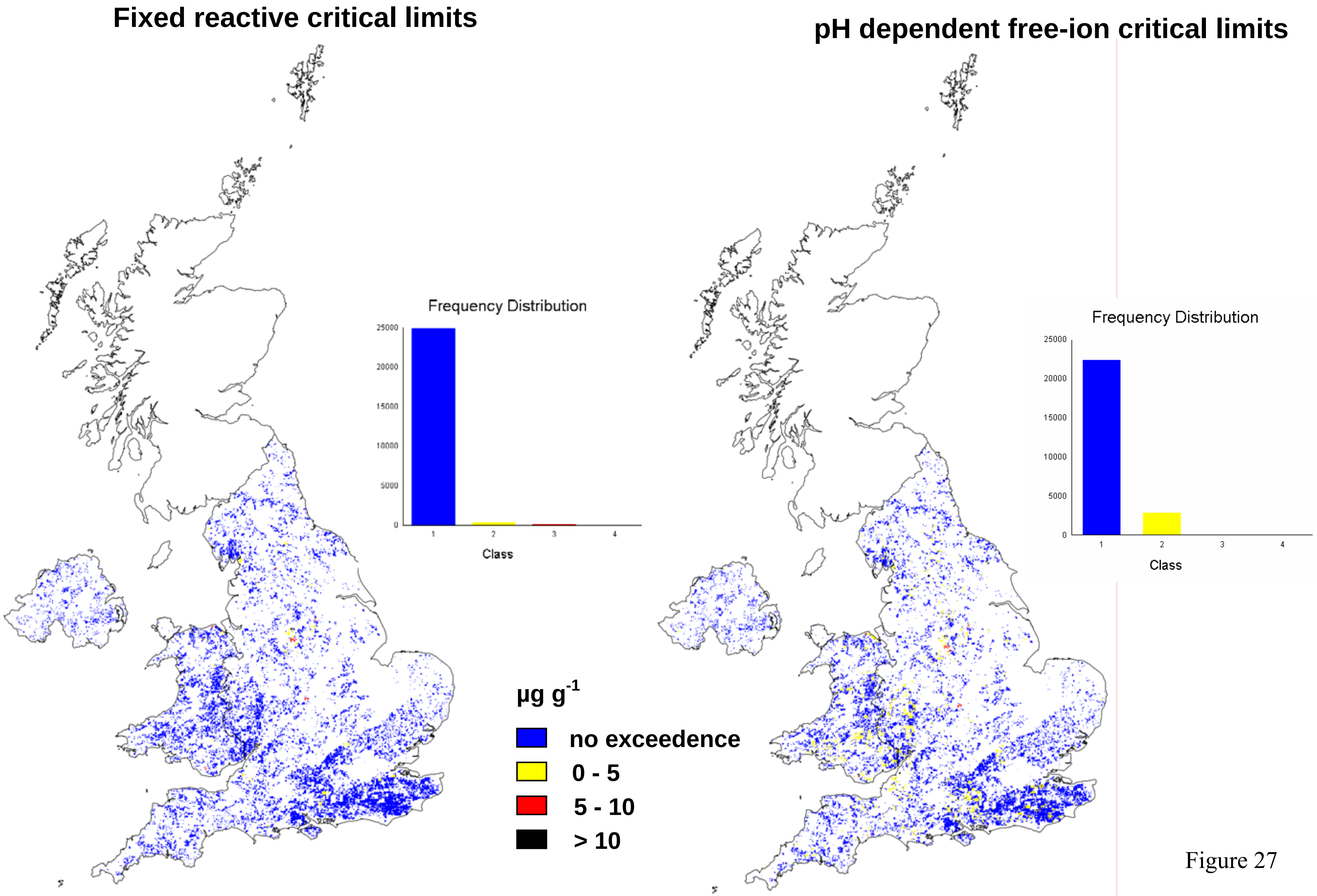


Figure 27

4.4.2 Maps of critical loads

Figs. 28 to 30 present maps of critical loads. For presentation purposes, the semi-natural habitat and unmanaged woodland habitat of Cd and Pb (and all habitats for Ni, Cu and Zn) have been combined, by mapping the minimum critical load value in each grid square, where more than one habitat occurs.

The critical loads for Cd (Fig. 28) range from 0.87 g ha^{-1} $year^{-1}$ to 171 g ha^{-1} $year^{-1}$, with a mean value of 17.7 g ha^{-1} $year^{-1}$. The values for Pb are higher (Fig. 29), with a minimum of 3.08 g ha^{-1} $year^{-1}$, a maximum of 2011 g ha^{-1} $year^{-1}$ and a mean of 84.7 g ha^{-1} $year^{-1}$. Critical loads for Cu (Fig. 30) range from 5.6 to 4266 g ha^{-1} $year^{-1}$ with a mean value of 94.9 g ha^{-1} $year^{-1}$. Ni range from 13.1 to 40730 g ha^{-1} $year^{-1}$ with a mean of 2423 g ha^{-1} $year^{-1}$. Finally, critical loads for Zn vary between 23.9 to 5367 g ha^{-1} $year^{-1}$ with a mean of 553 g ha^{-1} $year^{-1}$.

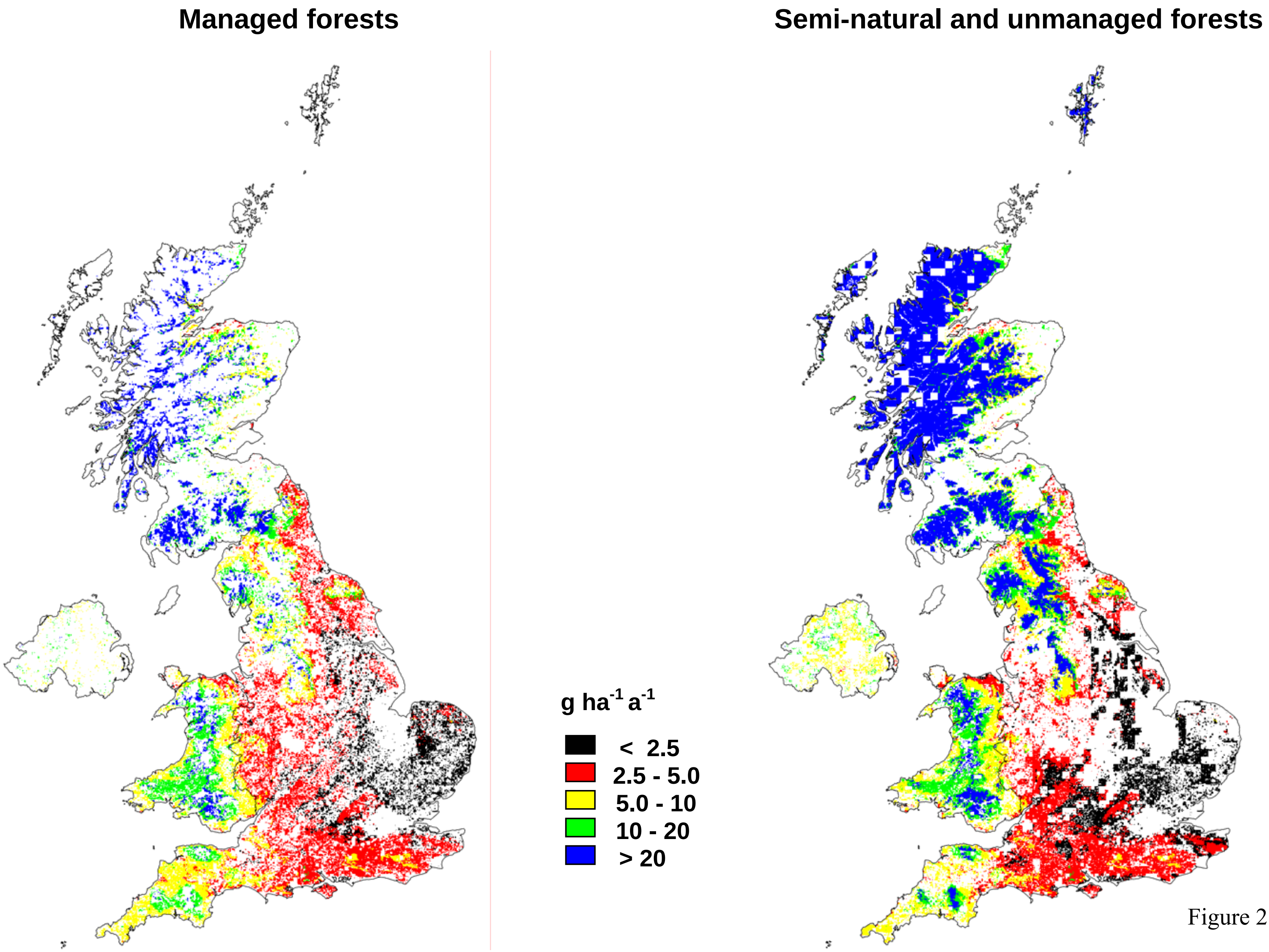
Although the range of values differs for the metals, all display the same general trends across the country, with generally the lowest critical loads across lowland areas of England and the highest critical loads in upland areas of Wales, northern England and Scotland.

Interpretation of critical loads.

Critical loads represent acceptable levels of deposition that, under steady state conditions would result in soil metal concentrations at the critical limit. As a result, the range in critical loads varies between metals in response to differences in the critical limit and metal speciation within the soil system.

For each metal, the critical loads vary by a factor of at least two orders of magnitude between grid squares. This large degree of variation demonstrates the large effect that variation in factors such as soil organic matter, pH, land cover and runoff can have on critical limits and critical loads. One reason for the large degree of variation is the bimodal distribution shown when the frequency distribution of critical loads is plotted (Figs. 31 and 32). This reflects a high spatial co-variance of a set of factors, i.e. low pH, high soil organic matter, and high runoff, that are all associated with high values of critical loads.

Cadmium Critical Loads (g ha^{-1} a^{-1}) for the UK


Managed forests

Semi-natural and unmanaged forests

Figure 28

Lead Critical Loads (g ha^{-1} a^{-1}) for the UK

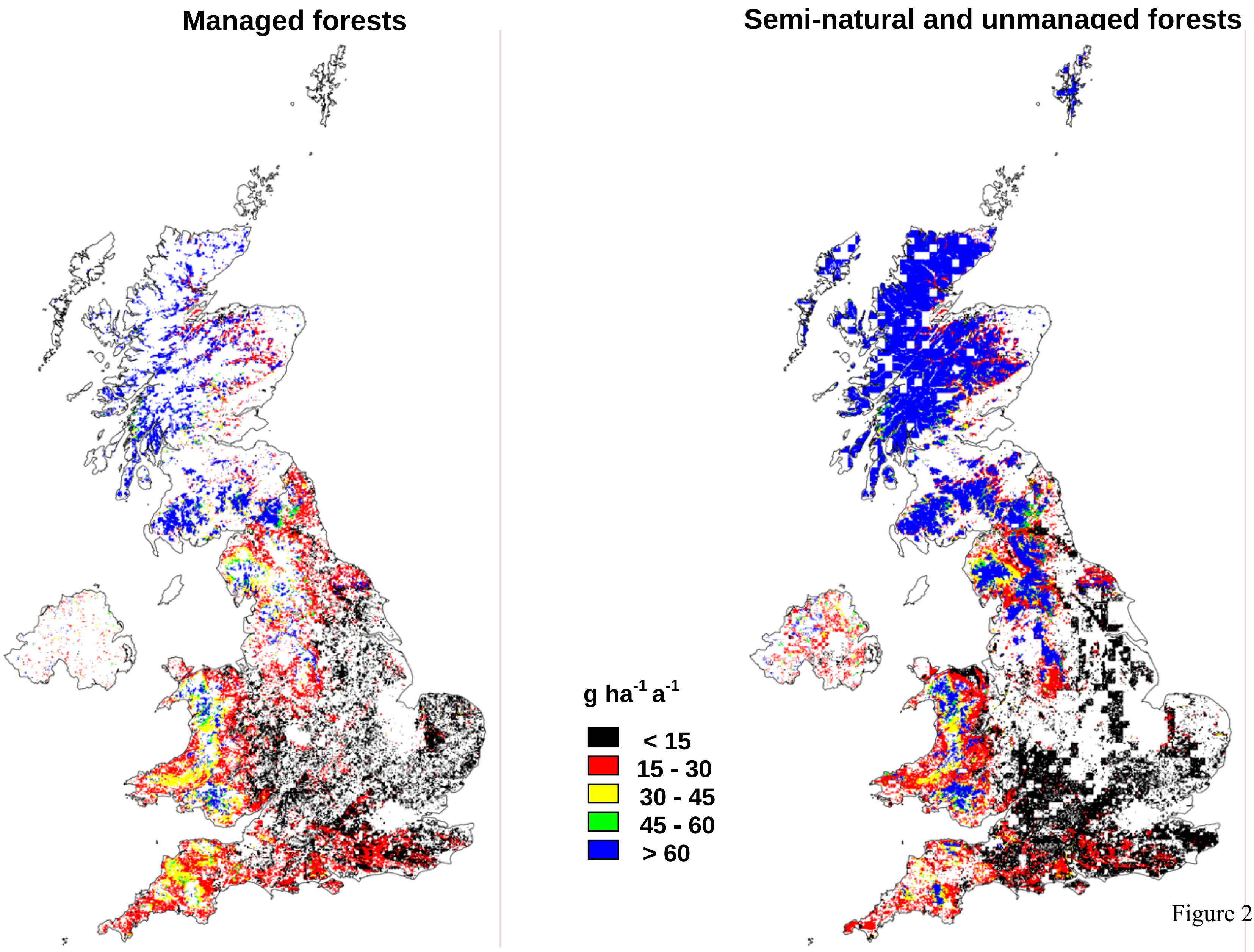


Figure 29

Copper, Nickel and Zinc Critical Loads (g ha^{-1} a^{-1}) for the UK

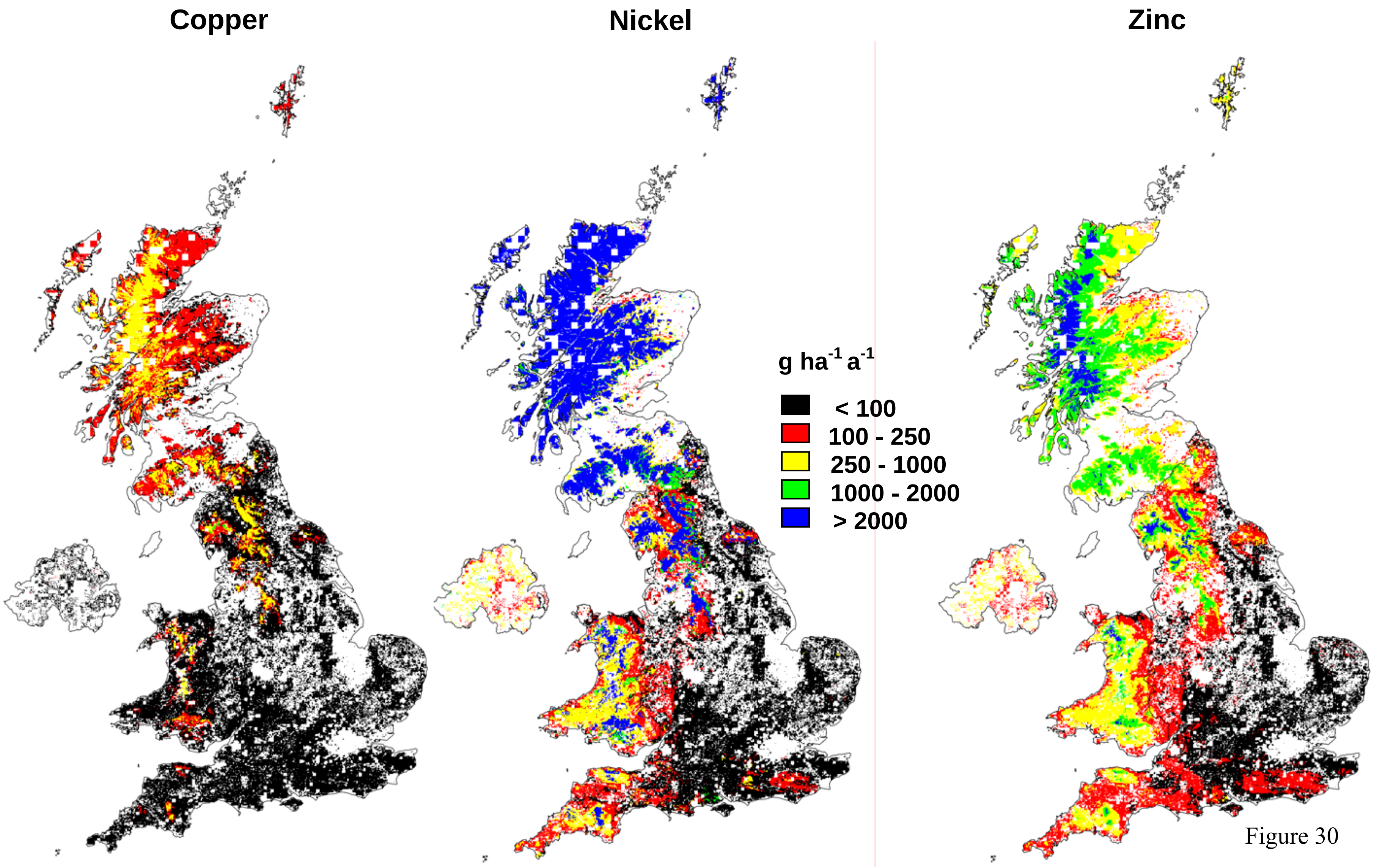


Figure 30

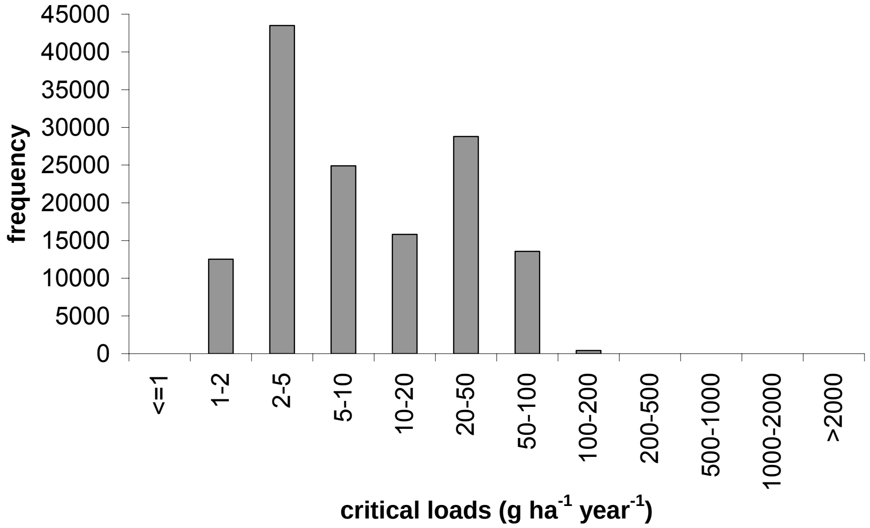


Figure 31. Frequency distribution of cadmium critical loads

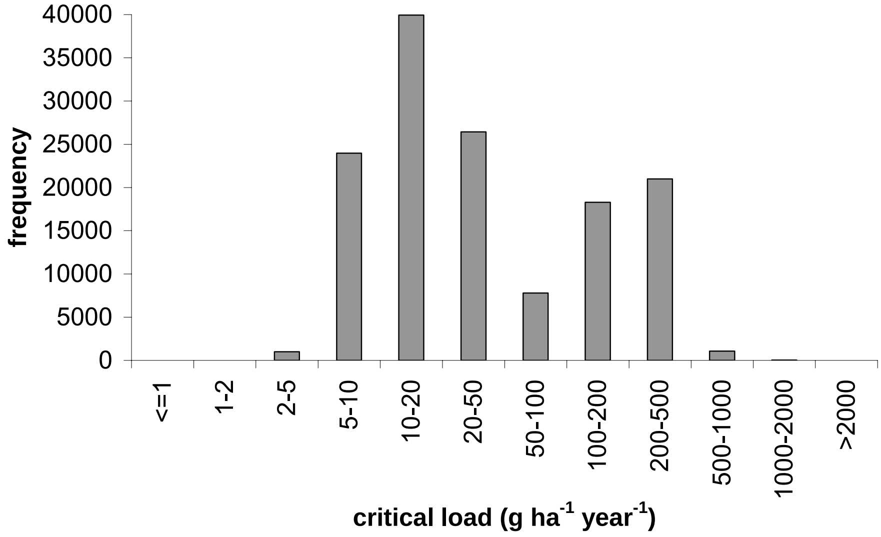
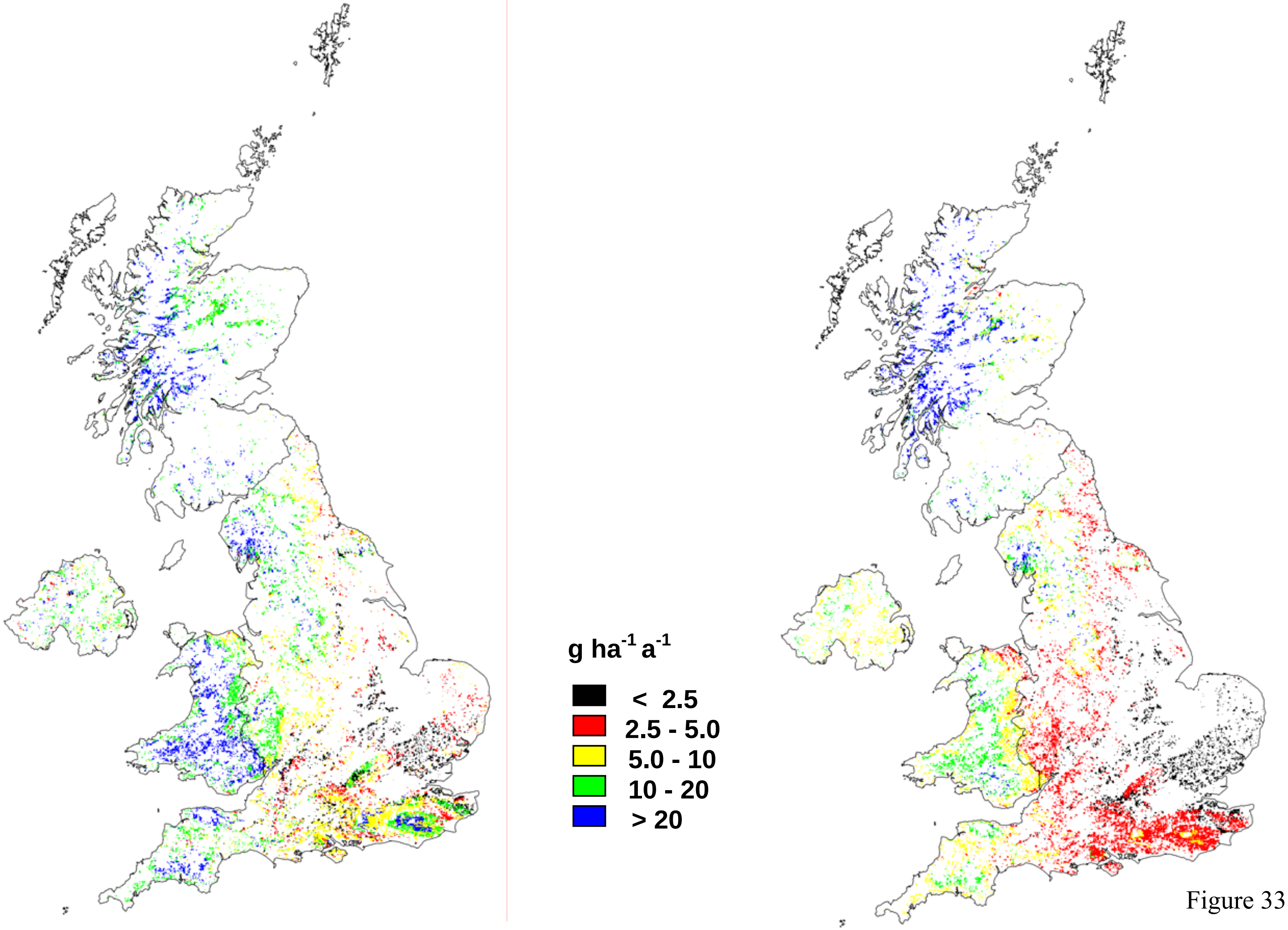


Figure 32. Frequency distribution of lead critical loads

The spatial pattern of the critical loads values also reflects spatial variation in these key variables, with high runoff, high DOC and low pH, which are all associated with high critical loads, in the upland areas of north and west Britain. These maps tend to show the opposite pattern to that of critical load maps for acidification, for which the soils with the lowest critical loads, that also have low pH and high runoff, which occur in the north and west of Britain, are derived largely from base poor rocks offering little buffering from acid deposition (Hornung *et al.,* 1995). Comparison to critical loads calculations based on fixed critical limits

Figs. 33 and 34 compare new Cd and Pb critical loads maps for unmanaged forests with those calculated under contract EPG 1/3/144 using fixed critical limit values based on reactive soil concentrations. The updated critical loads methods result in some significant differences. The critical loads for cadmium are consistently lower than previously suggested with mean value decreasing from 15.36 g ha^{-1} yr^{-1} for the fixed critical limit method, to 10.58 g $ha^{-1}yr^{-1}$ for the free-ion based critical loads. Conversely Pb critical loads have risen from a mean of 7.16 g ha^{-1} yr^{-1} using the fixed critical limit based method to a mean of 43.09 g $ha^{-1}yr^{-1}$ based on the free-ion. These trends reflect the differences in critical limit exceedences that were discussed above, and, as for those maps, are likely to reflect discrepancies between the characteristics of soils used for ecotoxicological testing and those found in semi-natural ecosystems and forests in the UK; these discrepancies have difference effects for lead and cadmium because of the difference in their strength of binding to organic matter. Although the range of values differs for the two methods, and the two metals, both display the same general trends across the country, with the lowest critical loads across lowland areas of England (and Wales for Pb) and the highest critical loads in upland areas of Wales, Northern Ireland, northern England and Scotland.

Critical Loads of Cadmium, Unmanaged Forests (g ha^{-1} a^{-1})

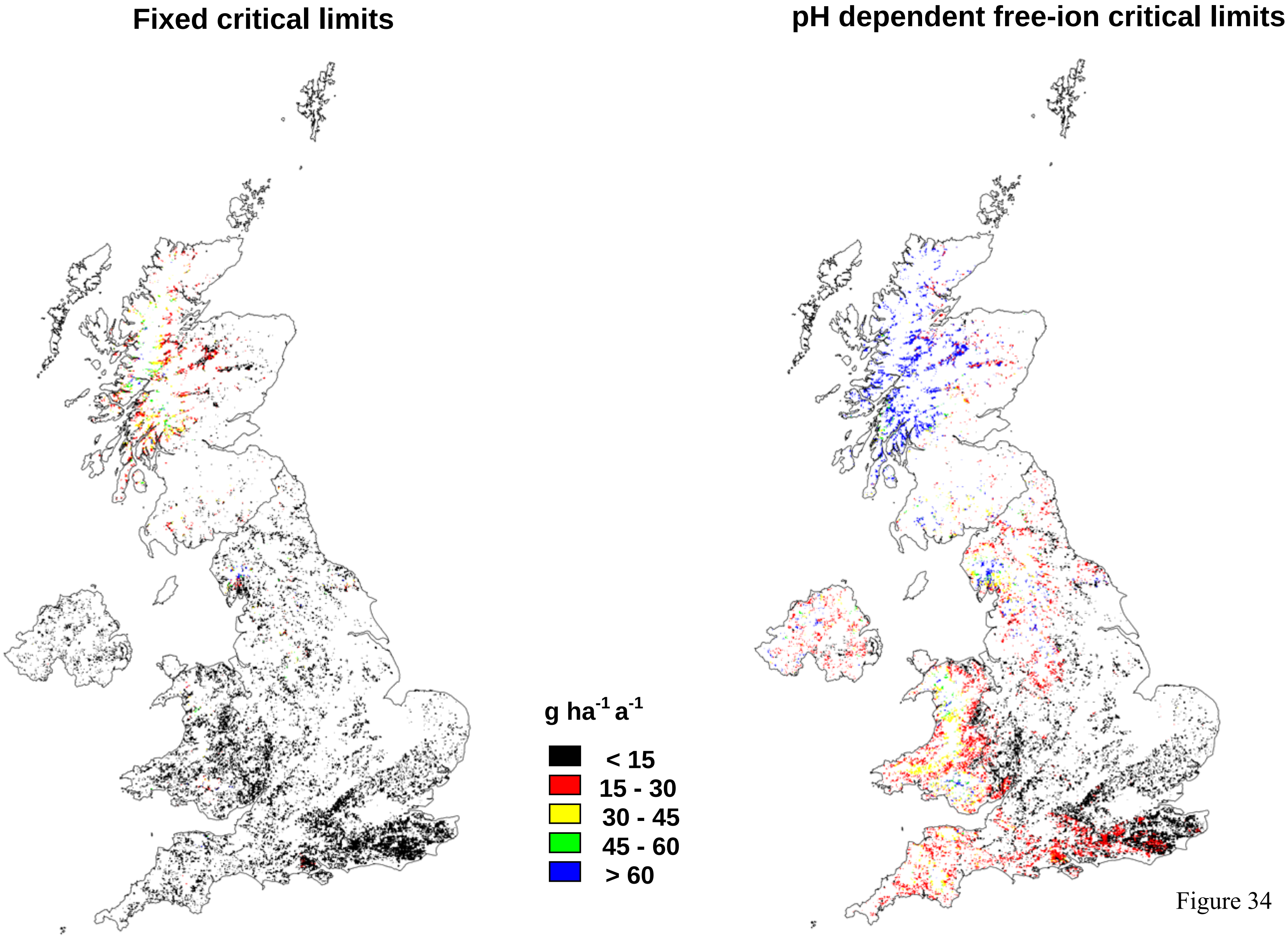


Fixed reactive critical limits

pH dependent free-ion critical limits

Figure 33

Critical Loads of Lead, Unmanaged Forests (g ha^{-1} a^{-1})



Fixed critical limits

pH dependent free-ion critical limits

Figure 34

4.4.3 Exceedence of critical loads

The latest heavy metal deposition data for the UK, from the Defra funded Heavy Metals Monitoring Network have been provided for calculating critical load exceedences for this project.

Fig. 35 presents the critical loads exceedence maps for cadmium for each of the three habitat types: unmanaged forests, managed forests and semi-natural vegetation. No areas are exceeded for managed forests or semi-natural habitats and less than 0.01% of the unmanaged woodland areas are exceeded in northern England (based on the proportion of 1 km grid squares demonstrating exceedence).

Fig. 36 presents the exceedence of critical load maps for lead across the three habitats. These maps identify more areas of exceedence across the UK than for cadmium. They also demonstrate the influence of vegetation type with forests showing greater exceedence. While the inclusion of the uptake term due to harvesting will tend to reduce the critical load, this appears to be more than compensated for by the greater deposition to forests (Figs. 21 and 22).

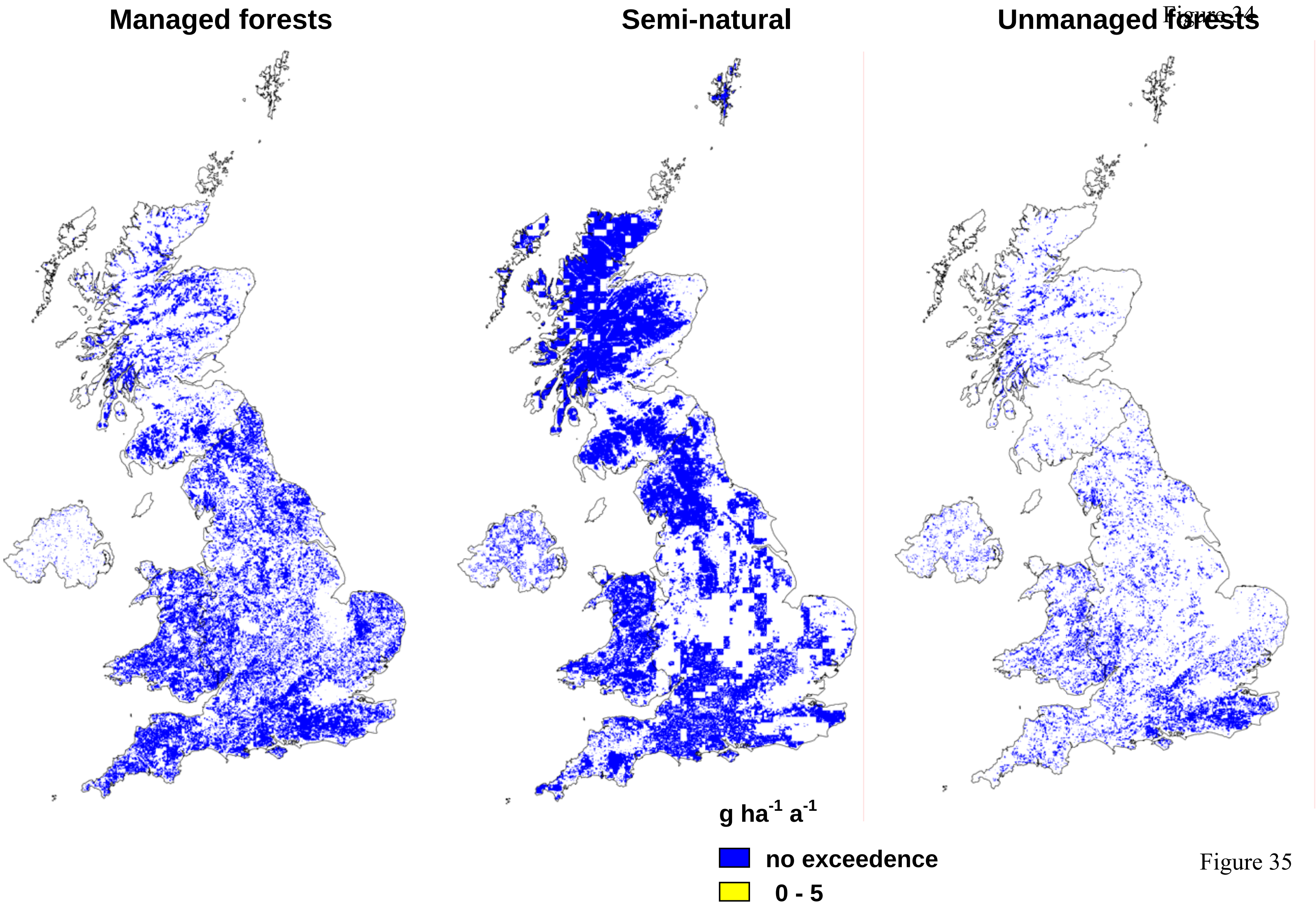
Fig. 37 presents critical loads exceedence for Cu and Zn. Habitats have been combined and highest exceedences are shown. Although not shown, the current levels of Ni deposition are consistently below critical loads and there is, therefore, no exceedence.

For all metals, areas in south and south east of England have the highest exceedences and this trend is observed across the three habitats, though with the highest exceedences observed in the forest habitats. For Pb, the exceedence of critical loads across southern England is in marked contrast to exceedence of critical limits. This is primarily because exceedence of critical limits of Pb is largely restricted to historically mined areas (i.e. areas with naturally high soil Pb concentrations enhanced by mining and smelting activity). Critical loads only relate to atmospheric deposition and do not consider the time-scale over which steady-state may be reached, which may be decades or centuries. For lead, in particular, the slow response of soil pools to changes in metal deposition was highlighted by the dynamic modelling (cf. Section 3). Hence, one interpretation of the maps of critical load and critical level exceedence is that, despite two centuries of elevated atmospheric deposition of lead, at rates above the critical load, the soil concentrations have not yet increased to the point that the critical limit is exceeded across large areas of the country.

In the case of cadmium, the reverse is true as for lead – i.e. the critical limit is exceeded over a larger area of the country than the critical load. This may, as for lead, reflect the contribution of sources other than atmospheric deposition to soil concentrations and critical limit exceedence. However, since the response of soil cadmium pools was demonstrated by dynamic modelling to be much faster than that of soil lead pools, another possible explanation is that deposition of cadmium historically lead to accumulation of soil concentrations to a level in some parts of the U.K. that exceeded the critical limit, but that deposition has now fallen to a level at which the critical load is no longer exceeded.

For Cu and Zn, exceedence of critical limits and critical loads correspond much better, although exceedence of critical limits extends further west and north than loads. The finding that critical loads for Cu and Zn are exceeded, despite the reductions in deposition, in approximately the same areas as critical limits exceedence does suggest that atmospheric deposition could be the key factor causing the high concentrations of Cu and Zn in these soils assuming that spatial patterns of current and historic deposition across the U.K. are correlated.

Exceedence of Critical Loads of Cadmium (g ha^{-1} a^{-1})



Managed forests

Semi-natural

Unmanaged forests

Figure 34

Figure 35

Exceedence of Critical Loads of Lead (g ha^{-1} a^{-1})

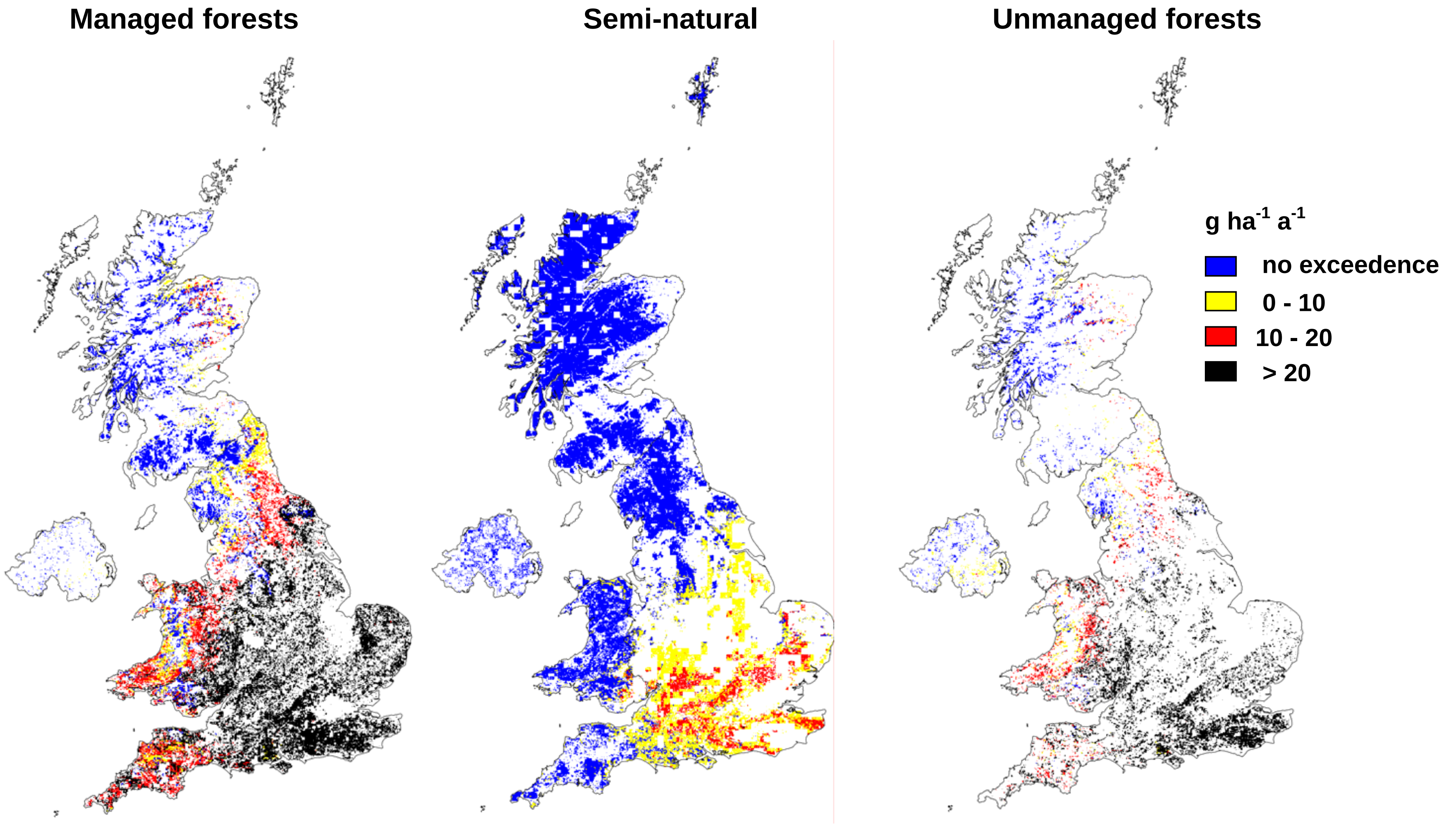


Figure 36

Exceedence of Critical Loads for Copper and Zinc (g ha^{-1} a^{-1})

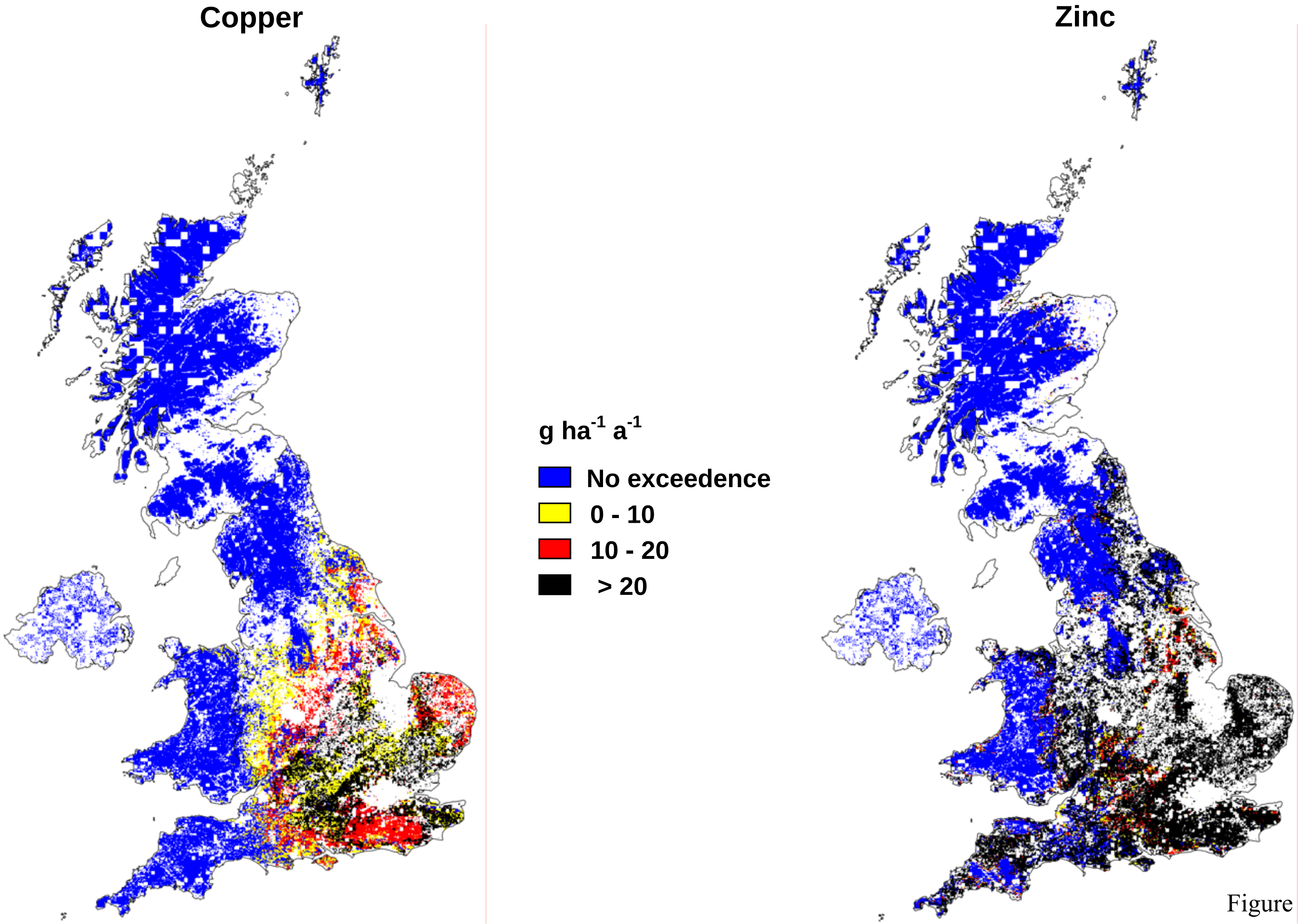


Figure 37

4.4.4 Modelling time to reach critical limits - application of the simple dynamic model (W6SDM)

The WW6SDM model (also see section 3.8) assumes from the starting date for each of the runs that the following remain constant: metal deposition (at the steady-state critical load), soil pH, the ratio of total aqueous-phase metal concentration to free metal ion concentration and runoff.

Output units are years and represent the number of years for the metals at each site to come to within 10% of the critical limit, either by increasing or decreasing. The model has only been run to determine time to critical limit under one scenario, i.e. that soil metals are currently below critical limit, although areas above critical limit are highlighted. The W6SDM model is based on the pH dependant free-ion critical limits functions and requires the current soil properties and scenarios for metal deposition and soil pH variations into the future

Figs. 38 and 39 show modelled time to reach critical limit for unmanaged forests for cadmium, and semi-natural, unmanaged and managed woodland habitats for lead. Figs. 40 and 41 show time to reach critical limit for Cu and Zn. All habitats are combined and the minimum time to critical limit is shown where this varies. The outputs of the model are combined with the exceedence of critical load maps to also show areas where the rate of reduction of soil metal concentrations through leaching and uptake exceeds the total deposition rate, and hence where soil concentrations will never reach the critical limit. In addition, the maps also show areas where the critical limits are already exceeded for the metals. Ni is not shown because nickel deposition is consistently below critical loads across all habitats.

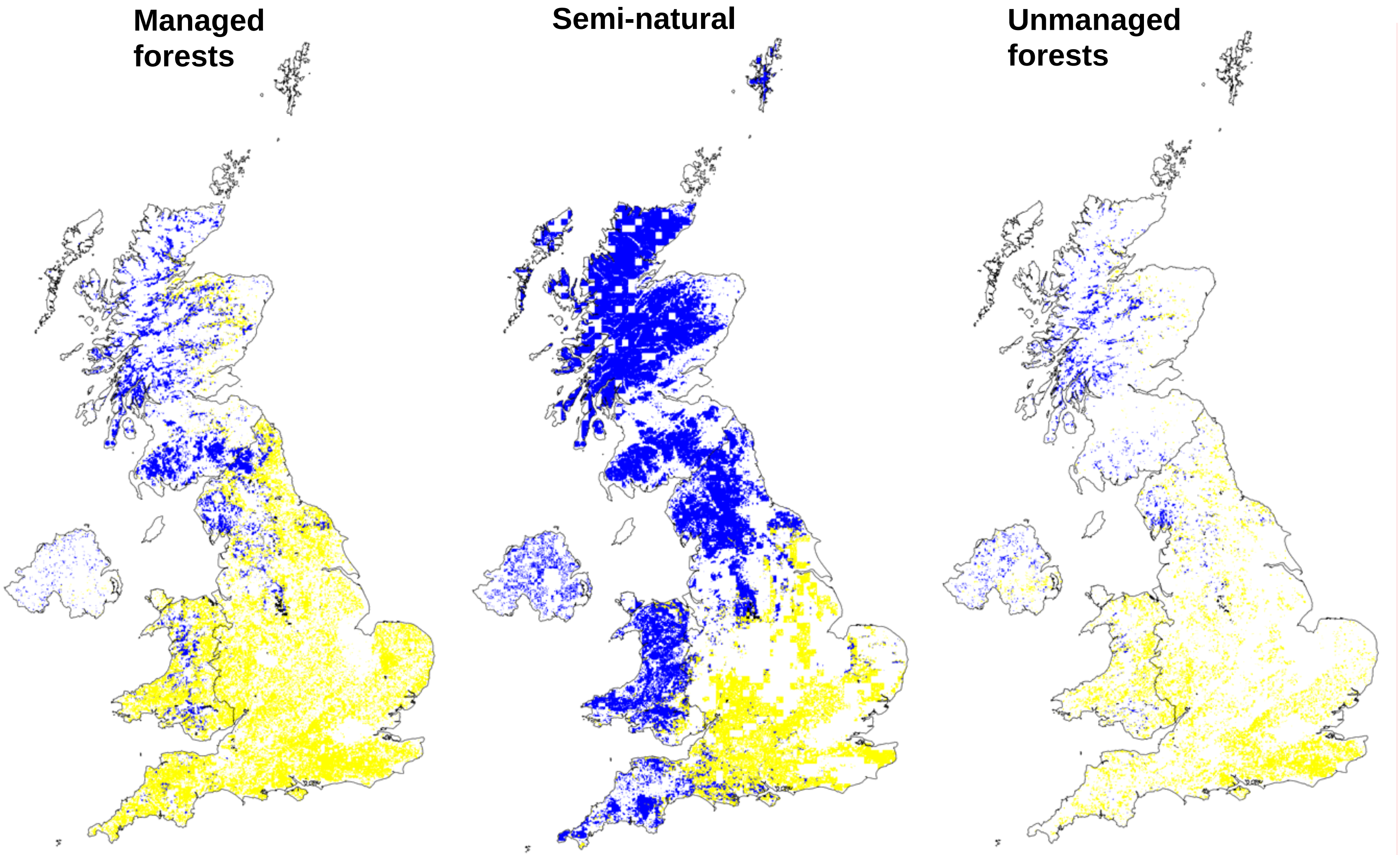
For Cd, time to critical load maps are only shown for one habitat type (unmanaged forest) (Fig. 39). This is because current cadmium deposition is consistently below the critical loads for managed and semi-natural habitats and so for these two habitats, cadmium will probably never reach the critical limit. Less than 0.001% of UK managed forests would reach Cd critical limits after 500 years (in south east England).

The lead maps (Fig. 38) show that deposition across large areas of the UK is below critical loads (largely Scotland, Northern England and Northern Ireland for all habitats and Wales for managed forests) and therefore soil Pb concentrations will never reach the critical limit. The rest of the UK, apart from the small area that is already above critical limits, is predicted to reach critical limits within 100 to 500 years. Forests habitats are more vulnerable to Pb deposition, and are more likely to reach critical limits more quickly than are semi-natural habitats.

Copper and zinc levels (Figs. 40 and 41) show a similar pattern, with deposition over most of Scotland, Northern England, Northern Ireland and Wales (and the South West for copper) below critical loads and therefore no expectation of soils in these areas reaching critical limits. The area where deposition is currently below critical loads extends further into England for semi-natural vegetation (across much of the Midlands). The rest of the UK is either already above critical limits, or predicted to reach critical limits, but not for at least 500 years. As with Pb, forest habitats appear more vulnerable due to the greater levels of deposition.

In general, the south and east of England is most vulnerable to further increases in soil metal pools of Cu, Zn and Pb. The majority of Scotland does not appear vulnerable to current or future critical limits exceedence, while Wales, Northern and South West England are predicted to experience some future exceedence of Pb and Zn. While exceedence of Cu and Zn is currently widespread, in the next 100 to 500 years, Pb critical limit exceedence is predicted to be more extensive than the area where Cu and Zn are exceeded. Therefore, measures to further reduce current rates of Pb deposition appear to be of greater priority than measures to reduce Cd, Cu or Zn deposition.

Modelled time to reach critical limit based on current soil lead concentration



■ Soil metal concentration exceeds critical limit

🟦 Current deposition is below critical loads

🟨 100 – 500years

🟩 > 500 years

Figure 38

Modelled time to reach critical limit based on current soil cadmium concentration

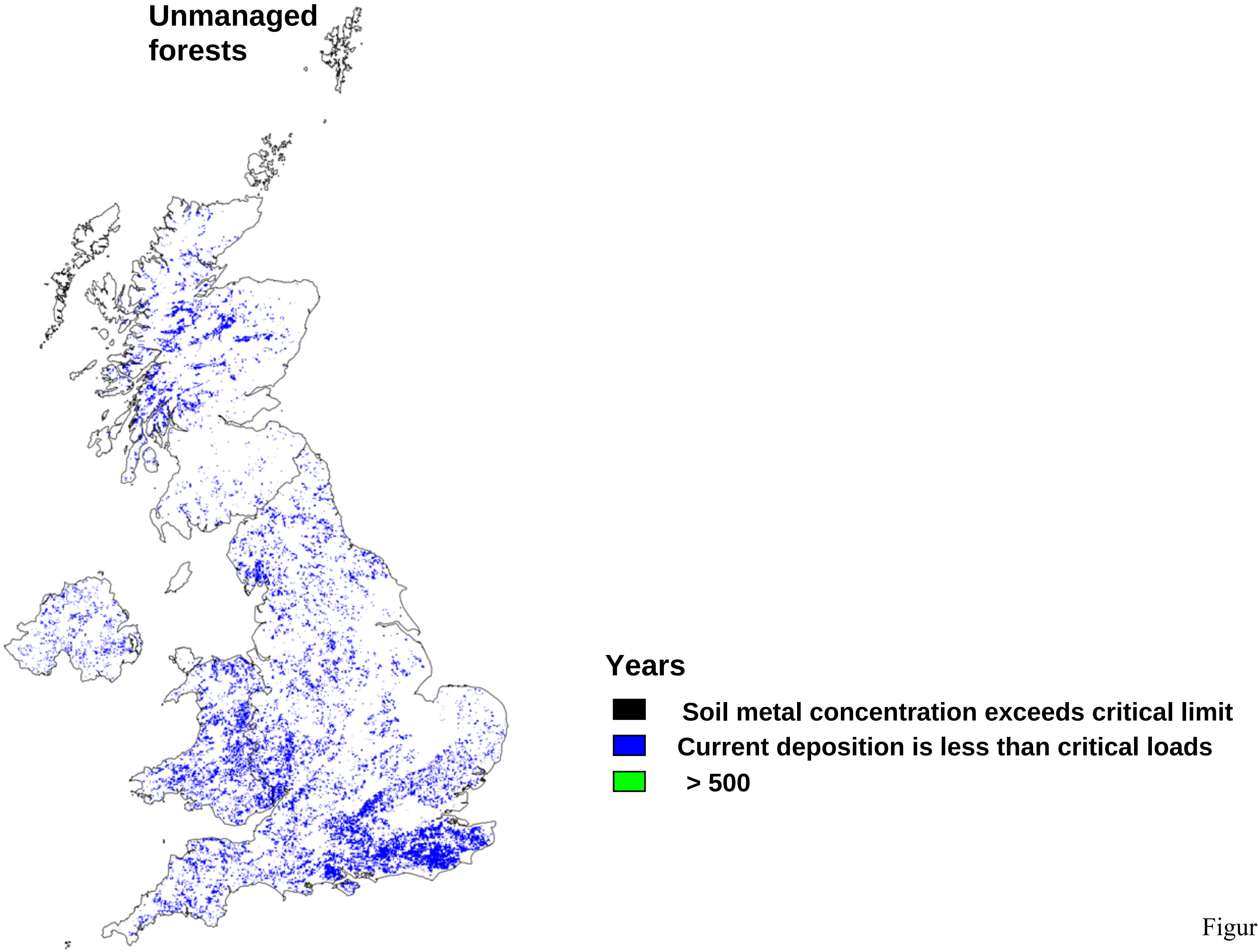


Figure 39

Modelled time to reach 10% of the critical limit based on current soil copper concentration

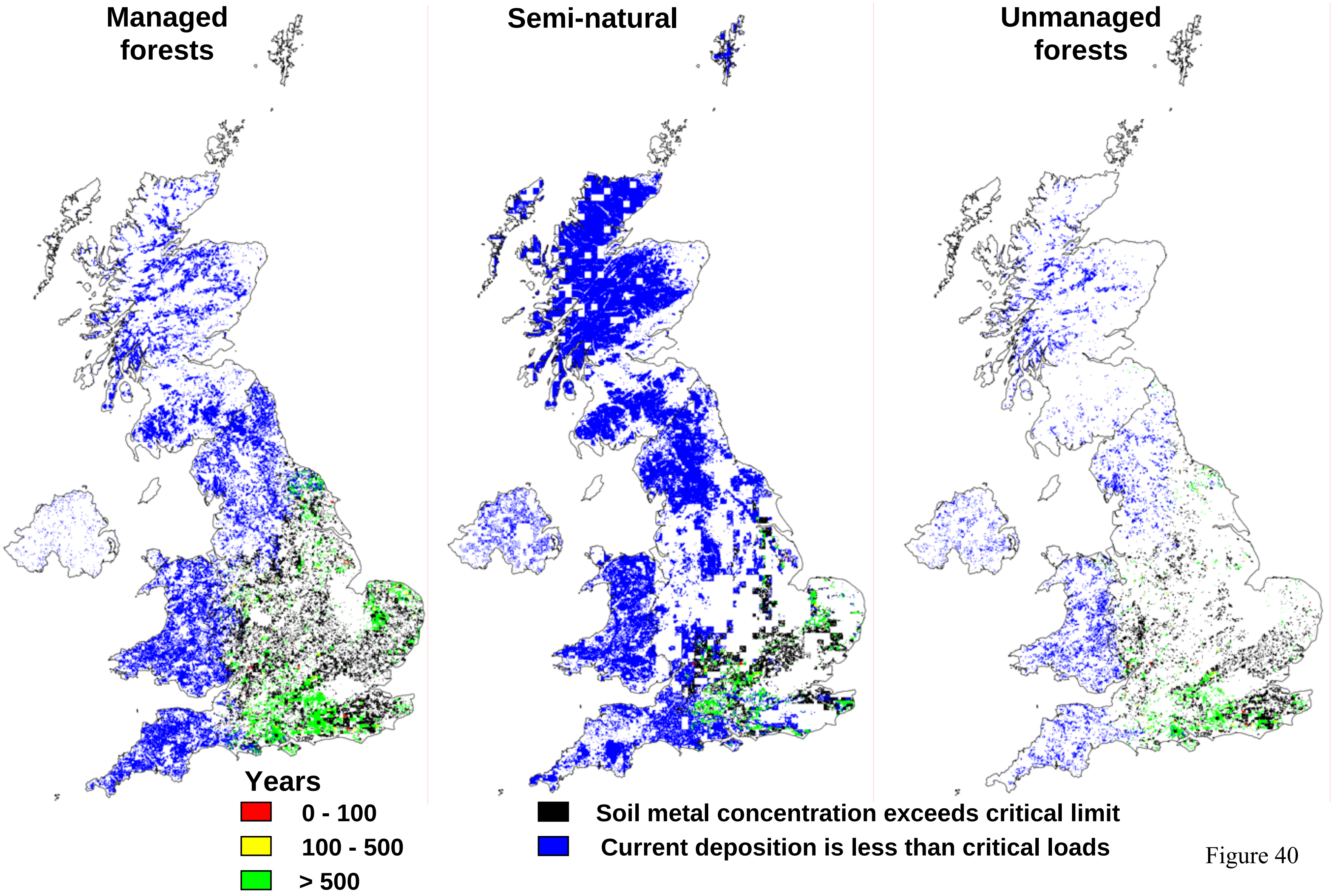


Figure 40

Modelled time to reach 10% of the critical limit based on current soil zinc concentration

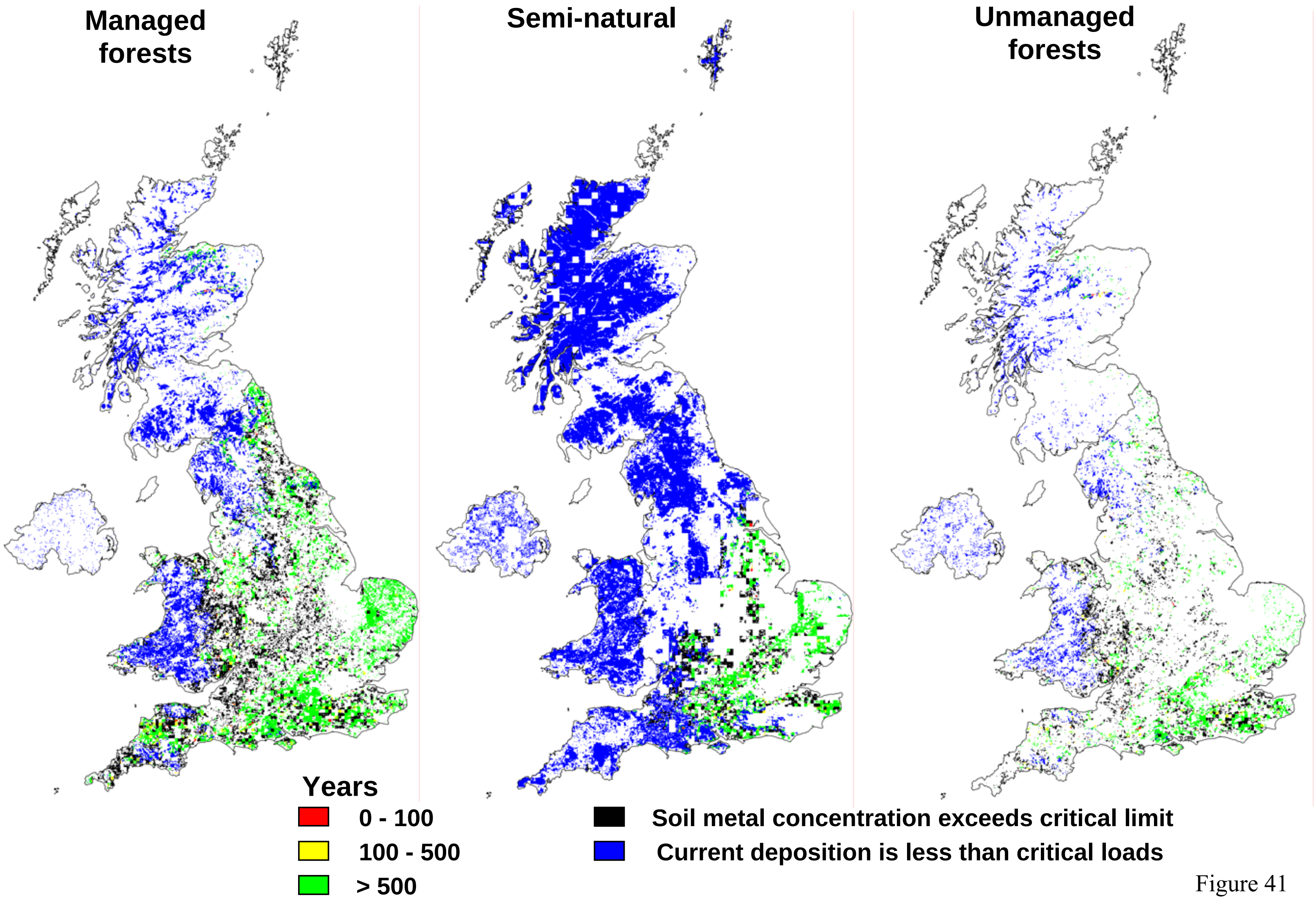


Figure 41

4.4.5 Conclusions.

There are significant sources of uncertainty in the underlying databases and model parameterisation that mean that the details of the maps derived in this analysis must be interpreted with caution, especially at a local scale. As for all soil quality criteria, comparisons of spatial data with critical limits need to take account of spatial heterogeneity and uncertainty in soil concentrations, and ideally be based on a probabilistic approach especially for values close to the critical limit. Furthermore, there is still debate about the appropriate values of critical limits or critical limit functions to use to either compare with current concentrations or to calculate critical loads.

Nevertheless, the results do indicate a potential threat to soil function and biodiversity in both upland and lowland areas of the UK. Critical limits for Cu and Zn are exceeded over large areas of lowland England. Despite recent decreases in deposition, critical loads of Cu, Zn and Pb are still exceeded across much of England and parts of Wales (and Eastern Scotland for Pb) with concentrations of Pb across much of England and lowland Wales potentially reaching critical limits over the next 100-500 years, if no measures are taken to reduce current levels of deposition further.

5 WORK PACKAGE 3: SENSITIVITY AND UNCERTAINTY ANALYSIS

5.1 Introduction

A formal analysis of the uncertainties in heavy metal critical loads and their exceedences and critical limit exceedences has been carried out. Work has focused on a detailed assessment of sources of uncertainty at Alice Holt, a deciduous forested site.

The main aims of the uncertainty analysis are:

- to identify the key parameters driving the critical load and critical load exceedence and critical limit exceedence calculations.
- to derive the uncertainties in the input parameters to the critical load, critical load exceedence and critical limit exceedence calculations.
- to estimate the uncertainty in critical loads for a given critical limit and set of transfer functions for four metals.
- to give cumulative function distribution for critical load exceedence for a given critical limit and set of transfer functions for four metals.
- to give the uncertainty in estimating critical limit exceedence (varying all input parameters) for five metals.

5.2 Site

A deciduous forested site at Alice Holt in S. England (479500, 140500) was chosen as the example location. The site was used for experiments on pollutant effects on trees (Broadmeadow, 2004). The critical limit is exceeded at the site for copper only and the critical load is exceeded for copper, zinc and lead according to the UK critical load database. The soil is clay.

5.3 Sensitivity analysis

This section summarises the results of the sensitivity analyses carried out on the inputs to the calculations of critical loads, critical load exceedence and critical limit exceedence. Sensitivity analyses look at the sensitivity of the output variable, in this case to changes in one input variable, with the others held constant. These analyses therefore provide an objective basis for ranking the parameters of the equations according to their effects on the output. The sensitivity analysis has been carried out by perturbing the Alice Holt soils input values. It should be noted that this analysis assumes no interaction between the input parameters. Deposition only affects the critical load exceedence calculation and soil concentration only affects the critical limit exceedence calculation.

Sensitivity analyses have been carried out for each heavy metal although the results for copper only have been presented. Where there are significant differences in sensitivity between the metals this has been noted in the text.

5.3.1 Critical load results

For the copper critical load for Alice Holt (Table 19) the Cu critical limit parameters has the largest effect on the critical load (α_{EC} then γ_{EC}), followed by run-off , DOC and pH. The sensitivity to acidity was calculated in two ways. One was to vary the raw pH value by $\pm 20\%$ and the other was to vary the hydrogen ion concentration by the same amount. The resulting change in critical load was significant for variation in pH but not for variation in hydrogen ion concentration. Because of the formulation of the critical load equations changing the value of some parameters increases the critical loads while others decrease the critical loads for the same perturbation.

Table 19. The effect of perturbing input values to the copper critical load equation for Alice Holt

Parameter	Percentage effect on critical load	
	-20%	+20%
Runoff (Q)	-16.5%	+16.5%
Percentage organic matter (PCOM)	- 0.1%	+0.1%
[1]pH	-12.8%	-31.6%
[2]H+ ions (pH)	+ 0.4%	-0.4%
Partial pressure carbon (pC02)	+ 1.7%	-1.5%
Soil Particulate Matter (SPM)	- 0.2%	+0.2%
Dissolved organic carbon (DOC)	-16.0%	+16%
Uptake (Cu_u)	- 3.5%	+ 3.5%
[3]Critical limit parameter α_{EC}	-79.1%	+683.5%
[3]Critical limit parameter γ_{EC}	-45.2%	+83.8%
Transfer coefficient cQ1	+11.3%	-0.7%
Transfer coefficient cQ2	-0.6%	+2.8%
Transfer coefficient cQ3	-0.1%	+0.1%
Transfer coefficient cQ4	+5.0%	-0.7%

[1] Decreasing the pH decreases the critical load exceedence slightly but further decreases cause an increase in critical load exceedence.

[2] $\left[H^+\right] = 10^{pH}$, 20% of a log scale (pH) is the same in the analysis

[3] $\log M_{\mathrm{free,crit}} = \alpha_{EC}\, \mathrm{pH} + \gamma_{EC}$

These analyses highlight the parameters that have the most influence on the critical load values and the importance of these inputs being based on the best available data. The sensitivity results are linear for all parameters except the metals data i.e. critical limit parameters and transfer function coefficients.

All other metals also showed the largest response to critical limit parameters. Run-off showed approximately the same response for all metals but although DOC was the next most significant input parameters for all metals the other metals were not as sensitive to DOC as copper. All other metals were more sensitive to hydrogen ion concentration than copper.

5.3.2 Critical load exceedence results

A sensitivity analysis to examine the impacts of perturbing the inputs to critical load exceedence calculations has also been carried out. For copper, the exceedence is calculated using total copper deposition. Table 20 shows the results of perturbing total copper deposition on copper critical load exceedence.

Table 20. The effect of perturbing the input values to the calculation of copper critical load exceedence calculation.

Parameter	Percentage effect on critical load	
	-20%	+20%
Runoff (Q)	+23.5%	-23.5%
Percentage organic matter (PCOM)	+ 0.1%	-0.1%
[1]pH	+18.3%	+45.2%
[2]H+ ions (pH)	- 0.6%	+0.6%
Partial pressure carbon (pC02)	- 2.4%	+2.1%
Soil Particulate Matter (SPM)	+ 0.2%	-0.2%
Dissolved organic carbon (DOC)	+22.9%	-22.9%
Uptake (Cu_u)	+ 5.1%	+ 5.1%
[3]Critical limit parameter α_{EC}	+113.0%	-976.7%
[3]Critical limit parameter γ_{EC}	+64.6%	-119.8%
Transfer coefficient cQ1	-16.1%	+1.1%
Transfer coefficient cQ2	+0.9%	-4.0%
Transfer coefficient cQ3	+0.1%	-0.2%
Transfer coefficient cQ4	-7.2%	+1.0%
Copper deposition	-48.6	+48.6

[1] Decreasing the pH decreases the critical load exceedence slightly but further decreases cause an increase in critical load exceedence.

[2] $\left[H^{+}\right] = 10^{pH}$, 20% of a log scale (pH) is the same in the analysis

[3] $\log M_{\mathrm{free,crit}} = \alpha_{EC}\,\mathrm{pH} + \gamma_{EC}$

Increasing or decreasing the inputs leads to approximately linear increases and decreases in the critical load exceedence values (apart from the critical limit and transfer coefficient input parameters). Overall, perturbing the critical limit parameters has the largest effect on the exceedence values. Changing deposition input also has a large effect on the resulting exceedence values. As expected, increasing deposition increases the exceedence values. After deposition run-off, DOC and pH were important input parameters.

All the other metals were also most sensitive to the critical limit parameters. However they were all less sensitive to deposition than copper. One of the reasons for this is that the sensitivity to deposition will be greater for a large deposition value than a small one.

5.3.3 Critical limit exceedence

To estimate the exceedence of the critical limits, the values were compared with the estimate of total soil copper concentration at Alice Holt. Table 21 shows the results of perturbing the input values on copper critical limit exceedence.

Table 21. The effect of perturbing the input values to the calculation of copper critical limit exceedences.

Parameter	Percentage effect on critical load	
	-20%	+20%
Percentage organic matter (PCOM)	+ 27.8%	-24.5%
H+ ions (pH)	- 1.7%	+1.4%
pH	-23.2%	+16.2%
Partial pressure carbon (pC02)	- 2.4%	+2.1%
Soil Particulate Matter (SPM)	+ 0.0%	-0.0%
Dissolved organic carbon (DOC)	+ 0.0%	- 0.0%
Critical limit parameter (α_{EC})	+277.8%	-1337.4%
Critical limit parameter (γ_{EC})	-180.5%	+119.2%
Transfer coefficient cQ1	+327.4%	-4956.0%
Transfer coefficient cQ2	+273.2%	-1236.6%
Transfer coefficient cQ3	+41.6%	-47.2%
Transfer coefficient cQ4	-2206.5%	+302.5%
Copper concentration	-90.1%	+90.1%

Increasing or decreasing the inputs leads to approximately linear increases and decreases in the critical load exceedence values (apart from the critical limit and transfer function input parameters). Perturbing the critical limit and the transfer function coefficients has the largest effect on the critical limit exceedence values. Changing the soil concentration also has a large effect on the resulting exceedence values. As expected, increasing the soil concentration increases the exceedence values.

All metals were most sensitive to the transfer coefficients and critical limit input parameters. Copper was the most sensitive metal to soil concentration. The other metals showed a smaller response.

5.4 Monte Carlo Analysis

Monte Carlo analysis is a well-established method for assessing the effects of uncertainty in model parameters on model outputs. Parameter values are sampled from known or assumed distributions, and the model is run repeatedly to generate a distribution of output values. The model needs to be run many times to generate a stable output distribution: in this application we ran the model 500 times. Critical loads for the Alice Holt site were calculated by repeated application of the WHAM6 chemical speciation model (Tipping, 1994, 1998).

The results of the Monte Carlo analysis depend critically on the means, ranges and distribution types chosen for each parameter. Attempts were made to produce the best possible estimates and the methodology is described below.

5.4.1 Heavy metal Deposition

The heavy metal deposition data is from 2003/2004. A full uncertainty estimate is not available at this point. However expert judgement assumes that we could explore the effect of a factor of 2 for the time being. It should be noted that the uncertainty increases with distance from the nearest monitoring station and in vicinity of source areas. The deposition estimates are all strongly correlated with one another so a correlation coefficient of 0.95 was used between all parameters. A 95% confidence band around the deposition estimate for a critical load exceedence calculation of ±100% was chosen to represent the factor of 2.

5.4.2 Heavy metal Uptake

Heavy metal uptake uncertainty for deciduous woodland was calculated from the uptake value for the ten deciduous UK Level II sites. Four of the heavy metals fitted a normal distribution and lead fitted a log-normal distribution. The CVs were 40%, 54%, 53%, 50% and 92% for Cu, Zn, Cd, Ni and Pb respectively.

The uptake parameters are clearly correlated, however due to the small sample size the only significant correlations were between Cu and Cd and Cu and Ni for which a value of 0.562 and 0.705 was employed respectively.

5.4.3 Runoff

The value of Q, the long-term mean runoff or effective rainfall, is considered to be known with a CV of 23% for UK catchments Arnell *et al.* (1990). A normal distribution is assumed.

5.4.4 pH and LOI

There are two sources of uncertainty attached to our estimate of these parameters. One is that they are both calculated as an average value per soil series, and hence subject to error. Also the pH and OC for soils is based on the dominant soil in each 1km grid square according to the national soil databases. For Alice Holt the pH and OC values for all soil types were examined and this showed that:

- The most dominant soil type had a pH of 6.3 and OC of 2.9
- The soil with the lowest pH (and highest OC) present in the square was Lawford with an average pH of 6.0 and an average OC of 3.5.

- The soil with the highest pH present in the square was Evesham with an average pH of 7.5.
- The soil with the lowest OC present in the square was Wickham with an average OC of 2.8.

Hence uncertainty has been estimated using triangular functions, with the pH and OC value of the dominant soil type as the maxima of the distribution, and the minimum and maximum pH and OC values representing the tails of the distributions. Additionally, the pH and OC ranges have been extended to incorporate the additional element of uncertainty of these values being an average over the soil series.

However LOI is actually calculated as:

LOI = 1.9 * organic matter concentration with a max value of 99.9%

Broadbent (1965) suggest that although the ratio of organic matter to organic C is variable, it usually falls in the range from 1.8 to 2.0 for surface horizons of mineral soils. Hence this was used as the range to convert from OC to LOI (a uniform distribution was used).

Since pH is correlated with LOI it would be misleading to allow these parameters to vary independently in the Monte Carlo analysis. The correlation coefficient used in the Monte Carlo analysis was -0.715 (calculated from the national dataset).

5.4.5 DOC

The raw DOC data for all forests fitted a log-normal distribution and had a coefficient of variation of 74%.

5.4.6 pC02 and SPM

Expert judgment suggests that pCO2 might vary from 5 times atmospheric to 50 times atmospheric. SPM could vary from 0 to 50 mg/L. A uniform distribution was chosen for the analysis although a triangular distribution could also have been used.

5.4.7 Critical limit parameters

The uncertainty in critical limit parameters was not considered by classical statistics, but by bootstrapping. 10,000 pairs of estimates for α_{EC} and γ_{EC} were generated from which 95% confidence intervals were generated for the limit function for each metal. Table 22 gives the 5th, 95th and default values for each metal.

Table 22. Critical limit parameters and their 5th and 95th percentiles

Metal	α_{EC}			γ_{EC}		
	5th percentile	**Default**	**95th percentile**	**5th percentile**	**Default**	**95th percentile**
Ni	-0.62	-0.64	-0.65	-1.18	-2.59	-4.08
Cu	-1.22	-1.23	-1.23	-0.47	-2.05	-3.67
Zn	-0.32	-0.31	-0.29	-3.14	-4.63	-6.32
Cd	-0.34	-0.32	-0.31	-4.85	-6.34	-7.84
Pb	-0.93	-0.91	-0.88	-2.36	-3.80	-5.33

5.4.8 Transfer function coefficients

The total metal predicted using cQ direct transfer functions coefficients were derived from regression analyses. The default and 5th and 95th percentiles for all coefficients are presented in Table 23 for all metals apart from Ni. This was because Ni was derived differently and the percentile data is not available.

Table 23. Default transfer function coefficients and their 5th and 95th percentiles

Metal	**Q1**			**Q2**			**Q3**			**Q4**		
	5th %ile	**Default**	**95th %ile**	**5th %ile**	**Default**	**95th %ile**	**5th %ile**	**Default**	**95th %ile**	**5th %ile**	**Default**	**95th %ile**
Cu	-6.33	-5.90	-5.47	0.42	0.52	0.62	0.21	0.37	0.53	0.35	0.44	0.53
Zn	-4.09	-3.54	-2.98	0.23	0.28	0.32	-0.13	0.04	0.21	0.54	0.62	0.21
Cd	-7.83	-7.18	-6.53	0.30	0.34	0.39	0.49	0.65	0.82	0.33	0.41	0.49
Pb	-5.44	-4.94	-4.44	0.80	0.90	0.99	0.50	0.70	0.90	0.67	0.74	0.81

5.5 Uncertainty analysis

5.5.1 Varying critical limits

The sensitivity analysis suggested that the uncertainty in critical limit parameters will dominate all other sources of uncertainty in the critical load and critical load exceedence calculations and have a very significant effect on the critical limit exceedence calculations. However we must bear in mind that they are multipliers of the log free-ion and so in linear terms will give changes of greater than +/-20% in the critical limit when they're altered. Therefore in order to estimate realistic best and worst case estimates of the critical load and critical limit exceedence (due to uncertainty in critical limit parameters), the 5th and 95th percentiles of α_{EC} and γ_{EC} were used in the calculations (Table 24). This simple bounding calculation allowed us to determine the size of the effect we may expect when varying the critical limit parameters between realistic bounds.

Table 24. The effect of perturbing the critical limit values between realistic bounds on the calculation of critical loads, critical load exceedence and critical limit exceedences.

Metal	**Critical load**		**Critical load exceedence**		**Critical limit exceedence**	
	5th %ile	95th %ile	5th %ile	95th %ile	5th %ile	95th %ile
N_i	4.58	2340.8	6.8	-2329.5	-0.948	-90.0
C_u	5.11	219.8	37.4	-177	15.11	-50.9
Z_n	13.2	2376.4	269.5	-2093	52.6	-683.9
C_d	0.32	86.5	0.907	-85.27	0.30	-3.7
P_b	2.6	190.8	54.61	-133.6	6.9	-3012.3

Varying critical limit coefficients between realistic bounds gave a considerable, non-linear relationship between the critical limit parameters and the critical load and critical limit exceedence for all heavy metals. The results showed that the critical load for copper varied from +880% to -80% of the deterministic value. Critical load exceedence varied to such an extent it was impossible to tell whether the critical load was exceeded or not for any heavy metal. Critical limit exceedence varied within wider limits between +383% and -1389%.

5.5.2 Varying transfer coefficients

The critical load response to variation in transfer coefficients was also non-linear so a bounding calculation was again carried out using the 5th and 95th percentiles for cQ_1, cQ_2, cQ_3 and cQ_4 (Table 25).

Table 25 The effect of using 5th and 95th percentiles of the transfer coefficients on the calculation of critical loads, critical load exceedence and critical limit exceedences. The variation in Ni was not calculated.

Metal	Critical load		Critical load exceedence		Critical limit exceedence	
Using:	5th %ile	95th %ile	5th %ile	95th %ile	5th %ile	95th %ile
C_u	25.19	24.90	17.21	17.5	3.95	3.95
Z_n	120.4	117.8	161.6	164.9	-152.8	29.58
C_d	4.10	4.06	-2.9	-2.8	-2.5	0.0
P_b	25.5	10.1	31.71	47.11	-1109	-39.7

Table 25 shows that varying the transfer coefficients between realistic uncertainty bounds has very little effect on the critical loads, apart from lead. However transfer coefficients do have a significant effect on critical limit exceedence.

5.5.3 Critical loads results

Due to software issues it was problematic to vary critical limit parameters and transfer function coefficients for the critical load and critical load exceedence uncertainty analysis so it was decided to attach zero uncertainty to these parameters, i.e. the Monte Carlo uncertainty analysis will be of the uncertainty in estimating critical loads and critical load exceedence for a given critical limit and set of transfer functions. The results in Table 23 show that including the uncertainty in the critical limit values dominates all other sources of uncertainty so it may well be more informative to keep these constant. The results in Table 23 show that not varying transfer function coefficients would make very little difference to the critical load and critical load exceedence results apart from lead. Hence lead was not included in the critical load uncertainty analysis.

These results for critical loads for Alice Holt (Table 26) show:

- The 95th percentile of predicted Ni is 3 times the mean: the mean is 2.14 times the 5th percentile. The probability distribution is approximately log-normal.
- The 95th percentile of predicted Cu is 2 times the mean: the mean is 2.5 times the 5th percentile. The probability distribution is approximately log-normal.
- The 95th percentile of predicted Zn is 1.2 times the mean: the mean is 1.26 times the 5th percentile. The probability distribution did not fit a normal or log-normal distribution but was positively skewed.
- The 95th percentile of predicted Cd is 1.4 times the mean: the mean is 1.83 times the 5th percentile. The probability distribution is approximately normal.

Table 26. The deterministic, median, 5th and 95th percentile values and coefficient of variation for Ni, Cu, Zn, Cd. These results do not include uncertainty for critical limits or transfer function coefficients.

Critical load	Critical load values (g ha^{-1} $year^{-1}$)					Coefficient of variation (%)
	Deterministic	Mean	5th percentile	95th percentile	Standard deviation	
Ni	85	60	28	108	26	42
Cu	24	20	8	40	12	60
Zn	118	105	49	168	41	39
Cd	4.07	3.4	1.7	5.7	1.4	41

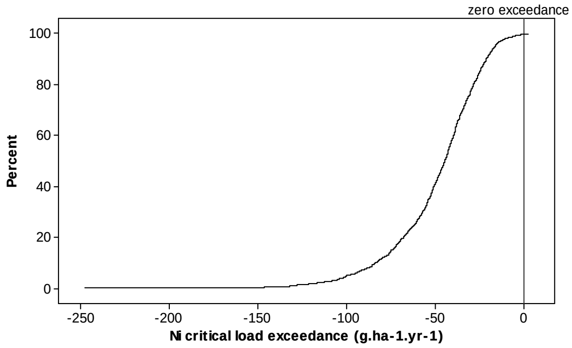
The means are less than the deterministic values ie, the value normally calculated, probably due to the use of a log-normal distribution for the DOC uncertainty to which the critical load calculation is sensitive (see Table 19). The largest variation is in copper. This is because copper is the metal most sensitive to DOC and DOC has a very large uncertainty associated with it (74%). If DOC is not varied in the uncertainty analysis copper has the smallest coefficient of variation.

5.5.4 Critical load exceedence results

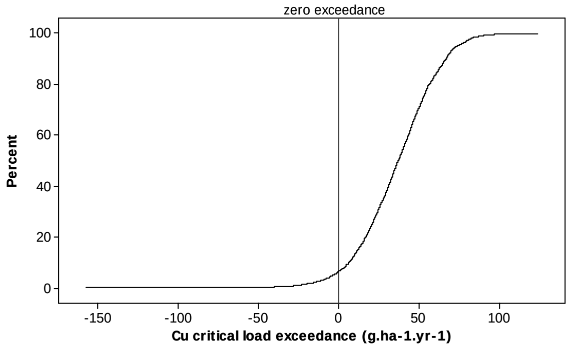
The critical load exceedence results demonstrate the wide range of values that we might expect. Cumulative distribution functions (CDF) for exceedence have been generated. Figure 1 shows the CDFs of the predicted exceedence at the Alice Holt site using the 2003/2004 emissions inventory for nickel, copper, zinc and cadmium respectively. Table 27 shows the standard deviation, probability of exceedence and deterministic exceedence for each of the heavy metals (coefficient of variation is not a meaningful statistic of exceedence). The figures and table indicate that for nickel we have a high degree of confidence that the Alice Holt site is **not** exceeded. For zinc it is quite likely that the site is exceeded. We are less certain whether cadmium and zinc are exceeded or not and further study should be recommended on those parameters that dominate the overall uncertainty.

Table 27 Standard Deviation and Probability of Exceedence of the Critical Load for Ni, Cu, Zn, Cd. These results do not include uncertainty for critical limits or transfer function coefficients.

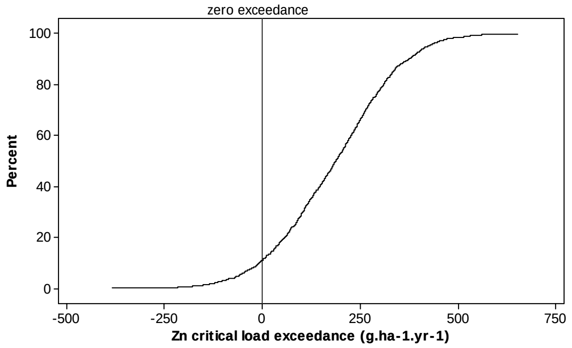
Heavy Metal	Deterministic	Standard Deviation ($g.ha^{-1}yr^{-1}$)	Probability of Exceedence (%)
Ni	-74.4	26	<0.01
Cu	+17.5	26	84
Zn	+164.0	148	89
Cd	-2.8	1.5	3.4



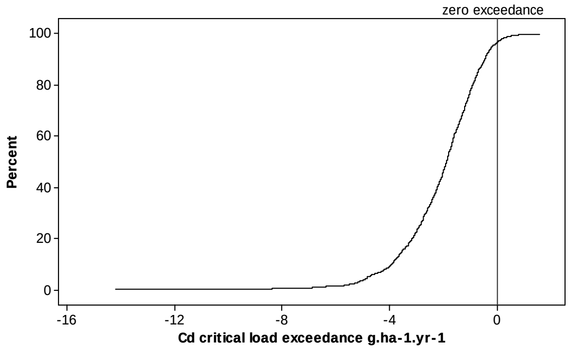
5th percentile = -100 g.ha-1.yr-1; 95th percentile = -16 g.ha-1.yr-1



5th percentile = -18 g.ha-1.yr-1; 95th percentile = 64 g.ha-1 yr-1



5th percentile = -61 g.ha-1.yr-1; 95th percetile = 422 g.ha-1yr-1



5th percentile = -4.8 g.ha-1.yr-1; 95th percentile = 0 g.ha-1.yr-1

Figure 42. Cumulative probability distribution of Ni, Cu, Zn and Cd critical load exceedence for Alice Holt. These results do not include uncertainty for critical limits or transfer function coefficients.

5.6 Critical limit and critical limit exceedence results

Uncertainty in the critical limits for Cu, Zn, Cd and Pb was found by considering the uncertainties in the critical limit parameters α_{EC} and γ_{EC} and in the transfer function parameters cQ_1, cQ_2, cQ_3 and cQ_4. Cumulative distribution functions of critical limits, as the total soil metal (mg/kg), are shown in Fig. 43, for consideration of all uncertainties, uncertainty in the critcal limit parameters only, and uncertainty in the transfer function parameters only.

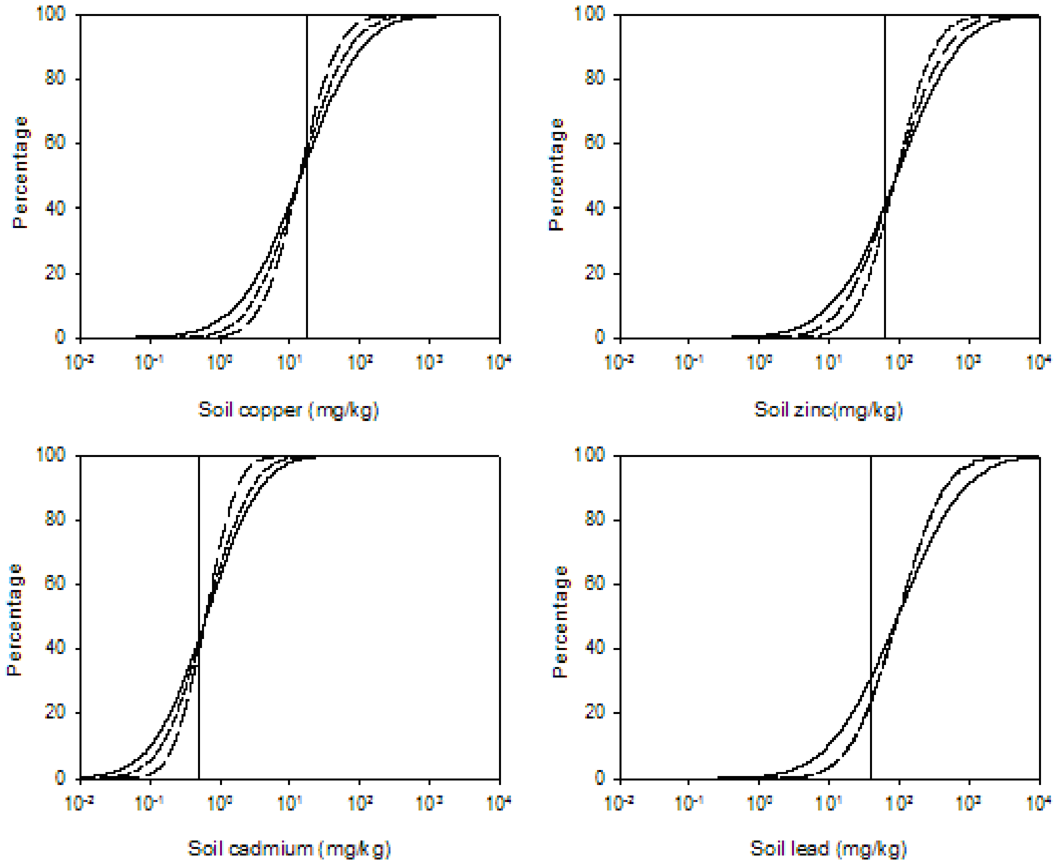


Figure 43. Cumulative distribution functions of critical limits for Cu, Zn, Cd, and Pb, expressed as the total soil metal (mg/kg), for the Alice Holt site. Solid lines: considering all uncertainties; long dashed lines: considering uncertainity in the critical limit parameter only; short dashed lines: considering uncertainty in the transfer function parameters only. The solid vertical lines represent the measured soil metal concentrations.

The uncertainties appear to be approximately lognormally distributed. The 5- and 95-%iles of the limit CDFs span approximately two orders of magnitude (Table 28). The probabilities of exceeeding the critical limit show that Cu is expected to exceed the limit while the other metals are not; however, all the probabilities are close to 50% and therefore we cannot say with certainty whether or not the critical limits are exceeded.

The uncertainty in the critical limits results from the need to transform current ecotoxicity data (expressed as metal added to the test soil) to the free metal ion. If ecotoxicity data could be expressed directly as the free-ion (i.e. by measurement in toxicity tests), then the uncertainty in the critical limit would be greatly reduced. Measurement of the free-ion in toxicity tests is currently being done for some metals (e.g. Cd; van Gestel & Koolhaas, 2004)

Table 28. The deterministic, 5%ile, and 95%ile critical limits for Ni, Cu, Zn, Cd and Pb for the Alice Holt site, also for all except Ni the probability that the critical limit is exceeded.

Heavy Metal	Deterministic critical limit (mg/kg)	5%ile of critical limit (mg/kg)	95%ile of critical limit (mg/kg)	Probability of Exceedence (%)
Ni	3746	581	23941	--
Cu	14.3	0.9	187	55
Zn	90.4	5.3	1275	41
Cd	0.6	0.06	6.1	43
Pb	94.4	5.2	1627	31

5.7 Conclusions from the assessment of uncertainties

The sections below summarise the key findings from the formal assessment of uncertainties in critical loads and their exceedences.

5.7.1 Sensitivity analyses

The sensitivity analysis of the critical load equation led to the following conclusions:

- The critical load equation used for a deciduous woodland ecosystem, Alice Holt, was most sensitive to the critical limit values, run-off and DOC.
- The most influential parameter on the calculation of critical load exceedence was the critical limit parameters for all metals. Deposition was the next most important input for copper, zinc and lead but not so important for nickel and cadmium because the deposition was small for these heavy metals.
- Critical limit exceedence was most sensitive to critical limit parameters and transfer function coefficients for all heavy metals.

5.7.2 Uncertainty ranges

Plausible ranges of input parameters and their uncertainties have been identified based on a literature survey, collected data, and interviews with experts on the parameter of interest. The parameter ranges and distributions used for copper are shown in Table 29.

Table 29. Parameter Ranges used in the Monte Carlo Analysis for copper

Parameter	Units	Type of Distribution	Default	Minimum	Maximum	SD
Cu_{dep}	g ha^{-1} yr^{-1}	Normal	42.5	0	-	21.2
Cu_u	g ha^{-1} yr^{-1}	Log-normal	4.42	0	-	1.8
Q	mm yr^{-1}	Normal	288	0	-	66.3
pH	-	Triangular	6.306	6.0	8.0	-
OC	%	Triangular	2.9	2.7	3.6	-
OM:OC	-	Rectangular	1.9	1.8	2.0	-
DOC	mg l^{-1}	Lognormal	22.265	0	-	16.5
Cu concentration	ug g^{-1}	Lognormal	17.8	0	-	5.874
pC02	times air	Rectangular	30	5	50	-
SPM	mg l^{-1}	Rectangular	5	0	50	-

5.7.3 Uncertainty in the calculations of critical loads

The critical limit parameters were varied between their 5th and 95th percentiles and found to have an enormous effect on critical load and critical load exceedence. Hence the uncertainty analysis estimated critical loads and critical load exceedence uncertainty for a given critical limit.

The uncertainties in Ni, Cu, Zn and Cd critical loads were investigated for the Alice Holt site. Statistics calculated showed:

- The 95th percentiles of the predicted critical loads (Ni, Cu, Zn and Cd) varied between 1.3 to 3 times greater than the mean value.
- The 5th percentiles of the predicted critical loads (Ni, Cu, Zn and Cd) varied from 1.3 to 2.5 of the mean value.
- Coefficients of variation varied between 39 and 60%.
- The probability distributions of the critical loads approximated to normal and log-normal distributions.

5.7.4 Effects of uncertainties in critical loads and deposition data on critical load exceedences

Monte Carlo analysis showed:

- For nickel, the Alice Holt 1km grid square had a very low (<0.01%) probability of exceedence.
- For copper, the Alice Holt 1km grid square had a relatively high (84%) probability of exceedence.
- For zinc, the Alice Holt 1km grid square had a high (89%) probability of exceedence.
- For cadmium, the Alice Holt 1km grid square had a low (<5%) probability of exceedence.

5.7.5 Effects of uncertainties on critical limit and critical limit exceedence

There is quite a large degree of uncertainty in the critical limit (5%, 95%iles span approximately one order of magnitude). This results from the current need to transform toxicity data from soil metal to free-ion. Direct measurement of the free-ion in future toxicity experiments would greatly reduce this uncertainty.

6 WORK PACKAGE 3: CATCHMENT CRITICAL LOADS FOR FRESHWATERS

6.1 Introduction

After consultation with the Defra nominated officer, it was agreed to focus this analysis on the 22 catchments of the Acid Waters Monitoring Network (AWMN), with the additional objective being to identify those sites for which metal impacts might be most significant and hence there might be greatest value in including monitoring of metal concentrations in AWMN protocols. The location of these sites is indicated in Fig. 44.

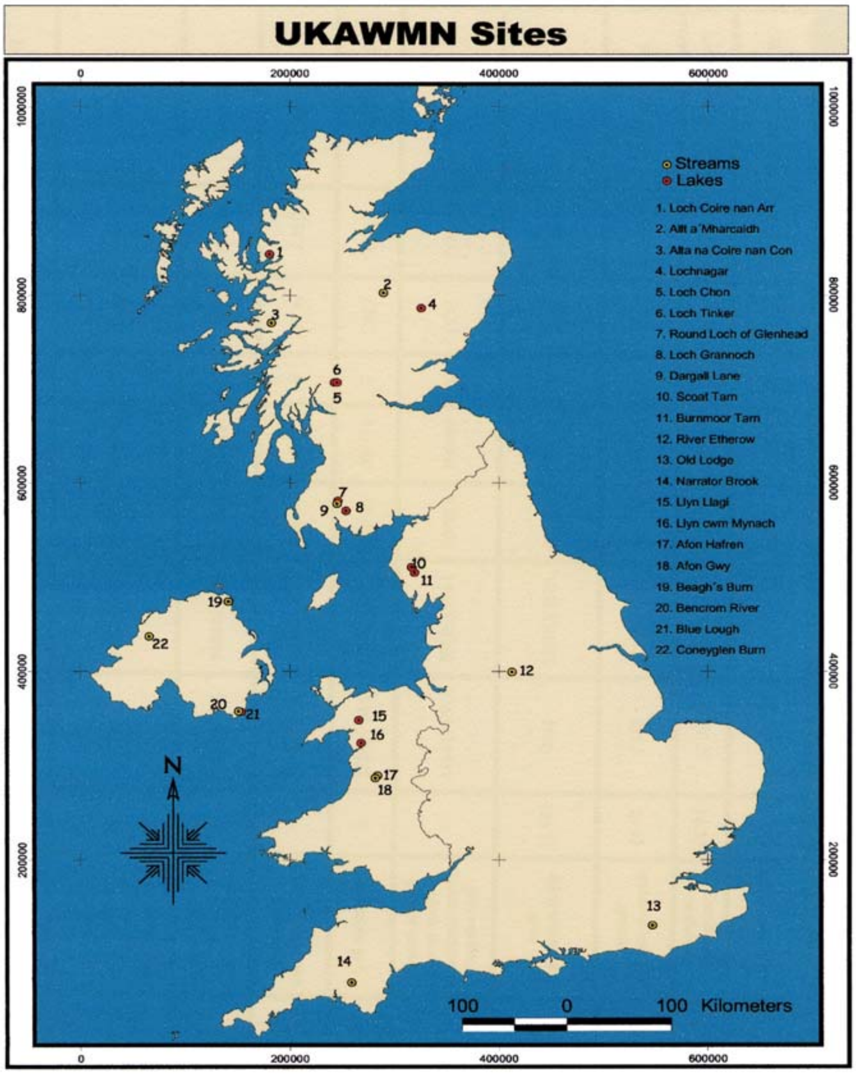


Figure 44. Acid Waters Monitoring Network sites.

The key results for the critical loads at the 22 sites based on the pH dependent free-ion toxicity model are summarised here. This research has been carried out as part of an M.Sc. thesis at the University of Bradford and further methodological details, including comparison of critical loads based on the free-ion toxicity model used for soils and critical loads based on total water concentrations can be found in this thesis (Gaona, 2004).

6.2 Critical loads and critical load exceedence

The critical loads calculated on the basis of the pH dependent free-ion toxicity model were compared with deposition rates provided by CEH Edinburgh. For three metals (cadmium, nickel and zinc), there were no exceedences of the calculated critical loads at any of the sites. However, exceedence of the critical load was found for lead and copper. Table 30 summarises the critical loads for these two metals calculated for the 22 sites, highlighting the three sites for copper and the four sites for lead for which the critical load was exceeded.

Table 30. Summary of Critical Loads (g ha-1 yr-1) for sites in the AWMN. Sites are ranked by their overall sensitivity.

Site	Abbrev.	Copper	Lead
Old Lodge	Lodg	12.9	11.9
Narrator Brook	Nart	9.6	12.5
Allt a'Mharcaidh	Mhar	13.3	57.8
Burnmmoor Tarn	Burnmt	21.1	30.0
Lochnagar	Naga	10.4	48.6
Bencrom River	Benc	28.6	21.1
River Etherow	Ethr	30.0	46.2
Afon Gwy	Gwy	22.3	22.2
Dargall Lane	Darg	16.6	60.6
Afon Hafren	Hafr	25.0	23.4
Llyn cwm Mynach	Myn	29.0	26.0
Blue Lough	Blu	29.0	31.3
Loch Chon	Chn	34.4	45.9
Beaghs Burn	Beah	60.1	33.0
Coneyglen Burn	Cony	46.2	90.2
Allt Coire nan Arr	Ancc	44.3	67.9
Glenhead	Rlgh	34.2	66.6
Loch Tinker	Tink	44.1	104.5
Scoatt Tarn	Scoatt	22.7	68.2
Llyn Llagi	Lag	37.9	66.8
Loch Coire nan Arr	Arr	39.0	142.0
Loch Grannoch	Lgr	64.3	90.6

The sites in Table 30 are ranked according to their sensitivity to metal deposition, based data for all five metals. Fig. 45 shows this ranking of sites, based on calculating for each metal the critical load for each site as a percentage of the mean for that metal and then averaging the values for the five metals. This normalisation process was conducted to ensure that no metal had a greater weight than the others on the ranking. The values ranged from 40% to 200%, i.e. there was five-fold difference on average between the sites.

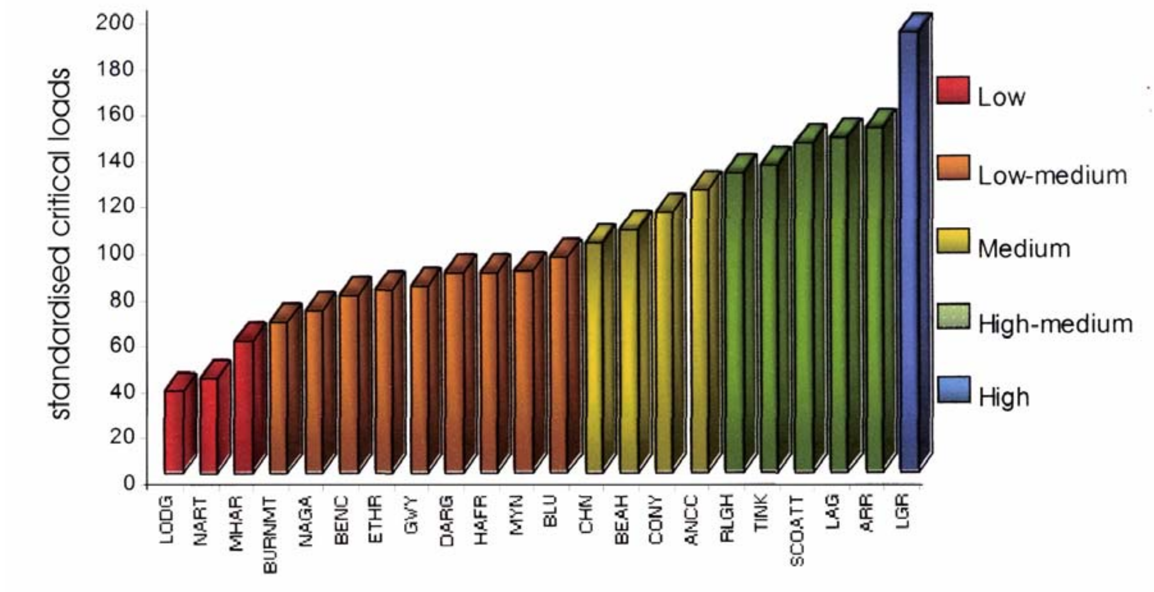


Figure 45. Critical loads for each site (based on all metals) ranked according to sensitivity (i.e. Old Lodge being the most sensitive).

Four of the five sites that showed critical load exceedence for copper or lead were either in southern England (Old Lodge and Narrator Brook) or Wales. The one exception was Lochnagar, which showed exceedence of the critical load for copper. Three factors were identified as significant in determining the value of the critical load were runoff, as for critical loads for soils, pH and DOC. Table 31 summarises the correlations between critical loads for lead, cadmium, copper and zinc and water DOC and pH. For cadmium and zinc, which are less strongly bound to organic matter, there was a strong negative correlation with pH; this reflects the underlying free-ion toxicity model. However, for copper, there is a strong positive correlation with DOC, and no correlation with pH, reflecting the stronger influence of organic matter. For lead, the critical load was significantly correlated with either pH or DOC.

Table 31. Correlation between calculated critical loads for four metals and water DOC and pH

	DOC	pH
Lead	-0.05 ns	0.325 ns
Copper	0.682 ***	-0.01 ns
Cadmium	-0.189 ns	-0.471 *
Zinc	-0.284 ns	-0.501 *

Critical loads and their exceedence were also calculated for soils in each of the catchments. However, unlike the critical loads for waters, these were not obtained from catchment specific data, but were based on data extracted from the national database. No exceedences of critical loads were found for nickel, zinc and cadmium, as for waters, and also for copper. Two sites (Old Lodge and Narrator Brook) showed critical load exceedence for soils for lead.

6.3 Critical limits and critical limit exceedence

Critical limits could not be compared with current metal concentrations, as these were not available at the AWMN sites. However, a limited comparison between the calculated critical limits and the concentrations measured in the catchments used for dynamic modelling was possible. For two metals (cadmium and nickel), there was no overlap (i.e. the range of critical limit values was higher than the range of measured concentrations). For copper, zinc and lead, there was an overlap, suggesting a possibility of critical limit exceedence. Table 32 presents a comparison for these three metals of critical limits and measured concentrations for the three AWMN sites that were used, highlighting the cases of exceedence.

Table 32. Comparison of critical limits based on the pH dependent free-ion toxicity model with measured concentrations at three AWMN sites

Site	Value (μg l^{-1})	Lead	Copper	Zinc
River	Critical limit	1.06	2.54	37.0
Etherow	Measured conc.	1.7	0.8	13.0
Old Lodge	Critical limit	2.72	3.06	60.9
	Measured conc.	1.9	1.7	18.0
Lochnagar	Critical limit	0.64	0.67	36.0
	Measured conc.	0.6	0.1	4.8

Only at one site (Etherow) was a critical limit exceeded, for lead, although at Lochnagar, the measured concentration for copper was essentially the same as the critical limit. Despite the long history of deposition to the Etherow catchment, the measured concentration was no higher than that at Old Lodge.

6.4 Conclusions on aquatic critical loads modelling

The analysis conducted for the 22 catchments suggest that atmospheric deposition of cadmium and nickel does not appear to be a major concern. For zinc, there may be sites with critical limit exceedence (critical limit range 21-64 μg l^{-1}; measured concentrations 2-38 μg l^{-1}). For copper and lead, however, exceedence of critical loads was found, and current exceedence of critical limits could also be demonstrated. For these metals, further assessment of critical loads and limits for waters, and the potential benefits of emission control measures, would be valuable.

In terms of the AWMN, the location of sites, which was designed to focus on catchments that are sensitive to acid deposition, is not ideal in terms of assessment of the impacts of metal deposition. All three English sites showed exceedence of either the critical load or the critical limit for lead, and two of the four Welsh sites also showed exceedence of critical loads for either copper or lead. Within the AWMN, these sites should be prioritised in terms of metal monitoring, but there may also be a need to identify other sites in lowland England, in particular, for more detailed assessment.

7 EXTENSION OF METHODS TO MERCURY AND ARSENIC

7.1 Introduction

A brief review was undertaken of the feasibility of extending critical load assessment in the U.K. to include mercury and arsenic. The review considered the derivation of appropriate critical limits, the availability of national data on deposition, soil, water and sediment concentrations, the potential for modelling binding of mercury to organic matter using the WHAM model, and the appropriateness of the critical loads methods recommended by UN/ECE. Since critical limits and critical loads methods for Hg have already been defined and adopted for application within CLRTAP through the methods described in the Mapping Manual, but this is not the case for As, it was agreed with Defra that the major focus of the review should be on Hg. The full review is presented in Annexe 12, while this section summarises the main conclusions.

7.2 Critical limits

The critical limits currently adopted for use in the Mapping Manual for ecotoxicological effects in terrestrial ecosystems are based on studies in Scandinavian forests, and do not consider direct effects of organic and methyl mercury. The lack of peer review of parts of these studies, and the fact that the critical limit is based only a group of studies conducted outside the UK, raises serious concerns about their application. It would be preferable to consider critical limits based on a rigorous analysis of all quality assured, peer-reviewed studies, as has been done for cadmium and lead. The fact that a different approach has been adopted in the Mapping Manual for mercury is of concern and raises doubts about the use of the recommended value of 0.5 mg kg^{-1} organic matter widely across Europe.

Moreover, for consistency with cadmium and lead, critical limits of Hg are now re-defined in the Mapping Manual as soil solution concentrations. Based on the strong binding of Hg with organic matter, a transfer function has been proposed to predict total mercury in soil solution as a function of the product of soil Hg concentration, expressed as mg per kg of organic matter, and the concentration of dissolved organic matter (DOM). Assuming a concentration of 20 mg l^{-1} DOM (or 10 mg l^{-1} DOC), the critical soil solution concentration of mercury is calculated to be 10 ng l^{-1}. However, since, unlike for lead and cadmium, there is no evidence that Hg toxicity is related to free-ion activity, which is extremely low, it is not obvious that there is any advantage to expressing the critical limit of Hg as a soil solution concentration rather than a total soil metal concentration. Furthermore, modelling of DOC, or DOM, is a major uncertainty in application of critical limits of lead and cadmium based on free-ion activity in soil solution, and this uncertainty would also dominate any assessment of exceedence of critical limits of mercury. This approach therefore introduces significant additional uncertainty in mapping critical limit exceedence in the UK

A survey of available literature indicated that there is likely to be a sufficient number of ecotoxicological studies of effects of both Hg and As to provide a basis to set more objective critical limits for direct effects, based on all the available literature. Effects through bioaccumulation in the food chain have not been considered to date in a critical loads context, although they may be important. This approach is recommended as a more objective basis than that currently recommended for Hg in the Mapping Manual.

7.3 Availability of UK data

Concentrations of Hg and As have been measured in a range of environmental media in the UK over the past thirty years. These include soils, stream and lake sediments, mosses, water, fish, and predators. It is also possible that some archived samples could be analysed for these elements. However, analysis of environmental samples for trace amounts of Hg and As is difficult, with high blank values due to laboratory and instrumental contamination, and loss of volatile Hg during storage. Hence interpretation of older datasets is problematic unless good QA/QC information is available. This is particular problem for waters.

Much of the available data relates to specific sites or small networks, such as the Environmental Change Network and the Acid Waters Monitoring Network. There is a national database of soil concentrations of Hg and As that covers England and Wales, but there is no national coverage of freshwater concentrations. However, there are national data on stream sediment concentrations for As, that could be used if appropriate critical limits and critical loads methods were defined for sediments. Hence, the present position is that it would only be possible to conduct a partial national assessment of exceedence of the critical limit proposed for effects of mercury in soils, by combining available data on Hg concentrations and on organic content. This assessment would only cover England and Wales. The position would be similar for As, should critical limits be set.

Deposition data from the current metals deposition network should provide adequate information for comparisons with critical loads of mercury. However, older network data for air concentrations and deposition of Hg are likely to be unreliable.

7.4 Binding with organic matter

The interactions of Hg with organic matter are likely to be of great importance in evaluating ecotoxicological data and developing critical loads methods. An initial investigation with the WHAM model, which has been used for critical loads of lead and cadmium, showed that it is able from chemical first principles to give reasonable predictions for the binding of Hg with natural organic matter. Hence it could potentially be used to improve the modelling of partitioning of Hg between soil and soil solution in critical loads methods.

7.5 Critical loads methods

The methods proposed in the Mapping Manual for mercury relate to the following effects:-

- Human health effects based on metal concentrations below the rooting zone, to protect ground water.

- Human health effects from the consumption of freshwater fish

- Effects on ecosystem functioning in forests, based on effects on soil microbial function and soil invertebrates

- Effects on ecosystem functioning in freshwaters, based on effects on algae, crustacea, worms, fish and top predators

However, within the UK, critical loads mapping for other metals, such as lead and cadmium, has only focussed on effects on ecosystem functioning. This is because a spatial analysis is considered inappropriate for health effects, for which it would be more appropriate to assess the contributions of atmospheric deposition to metal concentrations in a range of foodstuffs, and then compare these with acceptable daily intake values (ADIs), as applied by the Food Standards Agency. Furthermore, the current critical limit of Hg in fish is based on health effects linked to Scandinavian patterns of local fish consumption, which differ substantially from those in the U.K.

Mapping of critical loads for mercury for soils would follow similar principles as for lead and cadmium, with the output at the critical limit balancing deposition at steady state. The major issues, as identified above, relate to the choice of critical limit, and modelling of the efflux of mercury with DOC. The methods proposed for freshwaters are more complex and need more detailed consideration. They are based on critical Hg concentrations within standard fish species, which can be adjusted based on body weight distributions. These critical concentrations could be related to both human health and ecotoxicological endpoints. Having defined the critical concentration, it is then proposed to use site-specific transfer functions to relate the critical fish concentration to a critical mercury concentration in precipitation. Derivation of these transfer functions is described based on relationships derived between measured runoff and measured fish concentrations, with the transfer functions being predicted from key catchment properties, such as total organic carbon and total phosphorus levels in lake waters. By selecting such parameters, which are widely monitored in freshwaters, mapping of critical loads is in principle possible.

However, derivation of these transfer functions is almost entirely based on studies in Scandinavia, and it is not clear that they would be applicable in the UK, or indeed that the major determinants of the empirical transfer functions would be the same. A major programme of field measurement would be needed either to validate the Scandinavian transfer functions or develop new empirical functions for the UK. Furthermore, the whole method makes a major assumption, which is that the catchments that are studied are at steady state. If soil, lake sediment and fish concentrations reflect the cumulative effect of decades or centuries of deposition, as they do for cadmium and lead, then this assumption is highly likely to be false. As concentrations in deposition have fallen over recent decades, this will cause a significant underestimate to be made of the critical load, since current deposition is lower than that at equilibrium with current soil or fish concentrations.

7.6 Conclusions

The current methods of mapping critical loads for mercury are based on dubious assumptions, uncertain critical limits, and unreliable parameterisations, and hence could not be recommended for application in the UK. In theory, these methods could be improved, but this would require a very substantial research effort for freshwaters because of the empirical approach that has been recommended. Development of methods for soils could build on the work for cadmium and lead and hence is more practicable. However, a wider question arises from the fact that deposited mercury is re-volatilised, and hence source-receptor matrices, that are used for policy assessments based on the critical load approach, are no longer applicable. Hence, it is arguable that development of a risk assessment approach for the UK for mercury, and by association arsenic, should be based in the first instance on evaluation of current concentrations against improved values of critical limits. This can best be supported in policy terms, not by the development of critical load methods, but by the development of dynamic models that would allow the effects of changing rates of deposition to be assessed.

8 CONTRIBUTION TO POLICY DEVELOPMENT

Over the three years of this research project, members of the consortium have contributed significantly to the development of new methods of critical load calculation and mapping within the Expert Panel on Critical Loads for Heavy Metals, of which Prof. Ashmore, Dr. Lofts, Dr. Spurgeon and Prof. Tipping are members. This Expert Panel has worked within the UN/ECE ICP on Modelling and Mapping, and has played a major road in the production of a draft Mapping Manual for use within ICP Modelling and Mapping for mapping of critical loads of Pb, Cd and Hg. This work has become an important priority within the Convention on Long-Range Transboundary Air Pollution, since the Protocol on Heavy Metals has now been ratified by sufficient countries to bring it into force.

An important specific contribution has been a document fully describing the proposed methodology for determining critical loads of cadmium and lead using the pH-dependent free-ion model for critical limits (Tipping *et al.*, 2003b; Annexe 2). This document was circulated to the Expert Panel in June 2003, following initial presentation and discussion of the approach, which has been developed within this research programme, at a meeting of members of the Panel in Paris in April 2003. Subsequently, the information in this document was used by the chairperson of the Expert Panel, Gudrun Schutze, to produce a first draft of a chapter of the ICP Mapping Manual for metal critical loads. This draft was modified following comments from UK and other members of the Expert Panel, and then discussed in detail at a meeting in Straussberg, Germany in October 2003, which was attended by Prof. Ashmore, Dr Lofts and Prof. Tipping.

Following this meeting, a draft chapter of the Mapping Manual on critical loads for metals was produced. National Focal Centres were asked to evaluate the draft Mapping Manual chapter, and to produce critical load maps using it, to test the clarity and practical application of the draft chapter. UK maps for Pb and Cd for soils of forests and semi-natural ecosystems were submitted to this call, as part of this research programme. A formal open workshop on critical loads of heavy metals was then held in Potsdam in March 2004, to formally approve the draft Mapping Manual chapter and to review the experience of National Focal Centres in using it. Members of the research consortium were active in giving plenary presentations and chairing working groups at this workshop. A final version of the Mapping Manual chapter was then presented for approval to the annual meeting of the ICP Mapping and Modelling, and has now been formally incorporated into the Mapping Manual.

Hence, the research consortium has played a very active role in discussion of new critical loads for heavy metals within UN/ECE over the course of the whole research programme. The methods which have now been formally adopted for modelling and mapping of critical loads of lead and cadmium for ecological impacts in soils are based almost entirely on the methods that have been developed in the course of this research programme. However, the application of the free-ion critical limit function for ecological effects in freshwaters for lead and cadmium was not accepted due to the paucity of data, and the methods in the Mapping Manual continue to rely on the use of fixed total freshwater concentrations.

Moreover, there are three important issues on which the views of the members of the research consortium are not in agreement with the methods now proposed for risk assessment within CLRTAP:

1. The draft Mapping Manual chapter contains recommended methods for calculation of critical loads based on effects on human health through crops (for cadmium) and fish (for mercury). However, these methods assume a spatial co-location of the consumed product and the consumer that is not consistent with risk assessment methods for food in the U.K., and in other countries. Hence, it is not recommended that the U.K. submit values of health-based critical loads.

2. The draft Mapping Manual chapter contains recommended methods for calculation of critical loads for mercury. However, as noted in section 7, these methods are based very largely on Scandinavian data and experience, and it is not clear that they are appropriate for application in the U.K.. Hence it is not recommended that the U.K. submit values of critical loads for mercury.

3. The draft Mapping Manual makes no reference to the dynamics of response to decreasing emissions and deposition of metals, despite the fact that the long time-scale of these responses, as demonstrated in this research programme, mean that this is a very important consideration for policy evaluation. This issue has begun to be recognised through inclusion of metals within the work programme of the CRTAP Expert Group on Dynamic Modelling and through a proposal to prepare for submission of data on the dynamics of metal critical load exceedence in 2006.

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- Mark Broadmeadow for data on rates of metal uptake in coniferous and deciduous forest
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- G.Hayman for providing data from the Acid Deposition Monitoring Network.
- The staff of the CEH Windermere, Merlewood and Lancaster analytical laboratories for chemical analyses and help with field work.

10 OUTPUTS

The following written and oral outputs were produced over the course of the contract. Those marked * are incorporated into the Annexe to this report.

A website describing the work on this project has been established at University of Bradford, with appropriate links to Defra and the National Focal Centre for critical loads modelling and mapping, at: www.brad.ac.uk/acad/envsci/hmcritloads

Papers and documents

Hall, J., Ashmore, M.R., Fawehinimi, J., Lofts, S., Shotbolt, L., Spurgeon, D., Svendsen, C. & Tipping, E. (submitted) Developing a critical load approach for national risk assessments of atmospheric metal deposition. Environmental Toxicology and Chemistry.

E. Tipping (2004) Modelling Al competition for heavy metal binding by dissolved organic matter in soil and surface waters of acid and neutral pH. Geoderma in press*

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

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

E. Tipping, S.Lofts, E.J.Smith, L.Shotbolt, M.R.Ashmore, D.J.Spurgeon & C.Svendsen (2003) Information and proposed methodology for determining critical loads of cadmium and lead; a UK contribution. Background Document contributed to the UNECE ICP Modelling and Mapping Meeting, Paris April 9-10 2003.*

Ashmore, M., Fawehinmi, J., Hall, J., Lawlor, A., Shotbolt, L. & Tipping, E. (2003) Further developments of an effects-based approach for determining metal critical loads in the UK. Proceedings of the Expert Meeting on Critical Limits for Heavy Metals and Methods for their Application. Berlin December 2002, 184-188.

Hall, J., Fawehinmi, J., Ashmore, M., Hill, M. & Tipping, E. 2002. UK National Focal Centre report. In: Preliminary modelling and mapping of critical loads for cadmium and lead in Europe (eds. J.-P. Hettelingh, J. Slootweg, M. Posch, S. Dutchak, I. Ilyin). RIVM Report No. 259101011/2002. RIVM, Bilthoven, Netherlands. pp 113-117.

Papers in preparation

Several papers are planned on the results of this research. including:

Lofts S., Spurgeon D., Svendsen C and Tipping, E. Fractions affected and probabilistic risk assessment of Cu, Zn, Cd and Pb in soils, using a free-ion approach. In preparation for Environmental Toxicology and Chemistry.

Shotbolt, L. Ashmore, M.R., Büeker, P. and Tipping, E. The history of lead deposition onto five contrasting regions of the UK In preparation for Environmental Science and Technology

Shotbolt, L., Bueker, P. and Ashmore, M.R. The use of herbarium moss sample archives for reconstructing past heavy metal deposition. In preparation for Environmental Pollution

ICP Meetings

UNECE ICP Modelling and Mapping Expert Meeting on Critical Limits for Heavy Metals and Methods for their Application, Berlin, December 2-4, 2002. Attended by A.Irving, D.J.Spurgeon, L.Shotbolt, E.Tipping. Papers presented by D. Spurgeon and E. Tipping.

UNECE ICP Modelling and Mapping, Expert Group Meeting, Paris April 9-10 2003. Paper presented by E.Tipping.

UNECE ICP Modelling and Mapping, Expert Group Meeting, Strausberg, Germany, October 23-24 2003. Attended by M.R.Ashmore, S. Lofts, E.Tipping.

UNECE ICP Modelling and Mapping. Expert Meeting on Critical Limits for Heavy Metals and Methods for their Application. Potsdam,Germany.March 2004. Attended by M.Ashmore, S.Lofts, L.Shotbolt, E.Tipping. Papers presented by E.Tipping, S.Lofts & L. Shotbolt.

Papers presented at other national and international meetings

E. Tipping. Invited participation. SETAC-sponsored Workshop on Hazard Identification Approach for Metals and Metal Substances, Pensacola Beach, Florida, May 3-8, 2003.

E. Tipping. Al competition for heavy metal binding by dissolved organic matter in soil and surface waters of acid and neutral pH. Ninth International Humic Substances Society Meeting, Nordic Chapter, Sundsvall, Sweden, May 19-21, 2003.

E. Tipping. Invited presentation. The significance of Al(III) and Fe(III) interactions with humic matter in waters and soils. Seventh International Conference on the Biogeochemistry of Trace Elements, Uppsala, Sweden, June 15-19, 2003.

S. Lofts, D.J.Spurgeon, C.Svendsen & E.Tipping. Incorporating chemical influences into soil quality criteria for cadmium and lead. British Society of Soil Science / SETAC Joint Meeting, Aberdeen September 8-10, 2003.

E. Tipping. Invited Presentation. Heavy metals in British upland waters. Evidence of change in upland waters – effects on aquatic ecosystems. The Future of Britain's Upland Waters meeting. University College London. April 2004

L. Shotbolt. Heavy metal pollution of UK soils and freshwaters: developing effects-based critical load methodologies. British Society of Soil Science. University of Nottingham April 2004

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