DEVELOPMENT OF A CRITICAL LOAD METHODOLOGY FOR TOXIC METALS IN SOILS AND SURFACE WATERS: STAGE II

EPG 1/3/144: Final contract report; Part 1

Mike Ashmore[1], Anja Colgan[2], Margaret Farago[3], David Fowler[6], Jane Hall[2], Matt Hill[1], Crawford Jordan[7], Alan Lawlor[5], Stephen Lofts[5], Eiko Nemitz[6], Gang Pan[1,3], Graeme Paton[4], John Rieuwerts[3], Iain Thornton[3] & Ed Tipping [5]

1: Department of Environmental Science, University of Bradford, West Yorkshire BD7 1DP.
2: Centre for Ecology and Hydrology, Monks Wood, Abbots Ripton, Huntingdon, Cambridgeshire PE28 2LS.
3: T.H.Huxley School of Environment, Earth Sciences and Engineering, RSM Building, Prince Consort Road, London SW7 2BP.
4: Department of Plant and Soil Science, University of Aberdeen, Cruickshank Building , St. Machar Drive, Aberdeen AB24 3UU.
5: Centre for Ecology and Hydrology, Windermere, Far Sawrey, Ambleside, Cumbria LA22 0LP.
6: Centre for Ecology and Hydrology, Edinburgh, Bush Estate, Penicuik, Midlothian EH26 0QB.
7: Agricultural and Environmental Science Division, Department of Agriculture and Rural Development, Newforge Lane, Belfast BT9 5PX.

EXECUTIVE SUMMARY

- This report contributes to the development of critical loads methods for heavy metals in U.K. uplands based on bioavailable concentrations and describes the development of databases and methods to apply such an approach to national mapping within the U.K..

- The primary aims of this contract were to develop methods of mapping and modelling critical loads of metals in the U.K. and to contribute to the development of agreed European methods; to develop methods to model bioavailable concentrations of metals in upland soils and to assess the implications of basing critical loads on bioavailable rather than total soil concentrations; and to provide maps of critical loads of metals and their exceedance in upland areas of all parts of the U.K.. This built on earlier research on critical loads for metals under contract EPG 1/3/85. A national survey of metal concentrations in mosses was also undertaken, as described in the second part of this report. Furthermore, the research undertaken under this contract was closely integrated with research under the NERC Environmental Diagnostics programme, on deposition process and modelling, and on development and validation of dynamic models of metal pathways in upland catchments.

- Soil samples were collected from a depth of 0-5cm from 116 locations in five regions of upland Britain – the Lake District, Yorkshire Dales, Peak District, North Wales and Dartmoor.

- All samples were subject to a nitric/perchloric acid digest, a 0.43M HNO_3 extract, a 0.1M Na_2EDTA extract and a 0.01M $CaCl_2$ extract. Porewater was extracted from saturated soils in the laboratory using ‘Rhizon samplers’. In addition, a BCR 3-step sequential extraction was carried out on a sub-sample of 30 samples.

- The metal concentrations in porewater were determined using ICP-MS. These analyses were made at the NERC ICP/MS unit at Kingston University, as a result of a successful application to NERC for access to the facility. The metal concentrations in all the other extracts were analysed using ICP-AES.

- The pH of the porewater extract, dissolved organic content (DOC), and its base cation content were determined. Soil cation exchange capacity (CEC) was determined and organic content was estimated by loss-on-ignition (LOI) at 450^{o}C.
- The chemical form of the metal in porewater, and the partitioning between free ionic metal and that in organic complexes, was then simulated using the WHAM chemical speciation model. Empirical transfer functions were then derived between the modelled free-ion concentration in porewater and total soil solution and the total metal concentration in soil, using data on pH, base cation content and DOC.
- In all cases, metal concentrations were log-normally distributed, with a small number of soils with very high concentrations, reflecting a deliberate choice in the sampling strategy to include a small number of sites with very high historical contamination.

- The EDTA-extractable metal concentrations were assumed equivalent to the reactive soil component. Simple linear regressions between EDTA concentrations, total metal concentrations and LOI values provided transfer functions with high R^2 values to predict the reactive concentrations of each metal in soils throughout the U.K..

- The dependence of the partition coefficient (k_d) between total metal concentration and both measured porewater and modelled free-ion concentrations on soil properties was also determined using multiple regression. The derived transfer functions for free-ion concentrations had a high R^2 for pH alone for all four metals; in contrast, those for total porewater had lower R^2 values and involved DOC and LOI.

- The proportion of total porewater metal concentration existing as free-ions could be successfully modelled as a function of pH alone.
- The toxicity of porewater samples were determined using soil bacteria engineered to bioluminesce by insertion of *lux* genes. Luminescence measured after 15 minutes was assumed to be proportional to the vitality of the biosensor. The free-ion concentrations predicted by applying the WHAM model to the measured soil solution concentrations were strongly related to microbial toxicity.
- National GIS databases of soil characteristics were derived from regional datasets including pH, bulk density, porosity, organic carbon, dissolved organic carbon, average annual runoff and total soil metal concentrations.

- National maps of reactive soil concentrations, reactive soil pools, total porewater concentrations and porewater free-ion activities were produced using transfer functions derived from the dataset of analysed soil samples, and the derived national GIS databases.
- National maps of critical loads, critical reactive soil concentrations, and time to exceedance of critical load were similarly produced for cadmium and lead, using methods recently proposed within UN/ECE. The empirical transfer functions which we have developed allow us to apply a simple but effective approach to critical load assessments for metals in U.K. upland soils.

- An empirical methodology has been developed which can be used to apply the critical soil solution methods currently proposed within UN/ECE to national mapping of critical loads in the U.K..

- The GIS database on soil concentrations, land cover and soil characteristics provides a strong basis for analysis of metal dynamics and critical loads across the U.K..

- Critical limits of lead, but not those of cadmium, based on soil solution concentrations are exceeded over significant areas of the U.K.

- The degree of critical load exceedance for both lead and cadmium is lower than the area over which the critical soil solution concentration is currently exceeded. This almost certainly reflects the contribution of metal accumulation from historical deposition, which may have exceeded current levels of deposition.

- The simple static critical load approach currently proposed with UN/ECE does not give an accurate assessment of the potential risk of ecological effects of metals in soils in the U.K..

- The current rate of leaching of cadmium is estimated to exceed current deposition over almost all of the U.K., and a similar position is estimated to apply for lead over many parts of the U.K..

- The dynamics of metal accumulation to critical limit values in soil and soil solution is modelled to be about an order of magnitude faster for cadmium than for lead.

- The estimates of critical reactive soil pools and of the dynamics of metal accumulation are sensitive to small changes in pH in acid soils

- The order of magnitude uncertainty in current deposition rates of copper and zinc makes it impossible to assess critical load exceedance or the dynamics of these metals.

- Deposition rates to forested areas are significantly greater than those to non-forested areas, and this has significant effects on both the level of critical load exceedance for lead and the modelling of current balances and dynamics.

This project has made a major step forward in developing and applying critical load methodologies to the U.K. uplands, and provides a conceptual framework within which further research and development can take place. However, there remain many uncertainties both in the methodologies and in the correct parameterisation of many of the key terms and processes. Thus, further research is needed in many areas to provide a sounder scientific basis to future decisions on the control of atmospheric emissions of toxic metals.

DEVELOPMENT OF A CRITICAL LOAD METHODOLOGY FOR TOXIC METALS IN SOILS AND SURFACE WATERS: STAGE II

EPG 1/3/144: FINAL CONTRACT REPORT; PART 1

1. INTRODUCTION

Critical loads methods for toxic metals are currently being developed within UN/ECE, with a view to applying them in a revised protocol on the control of emissions in 2004/5. However, there is still considerable uncertainty, both as to the most appropriate methodological approach be used in applying critical loads, and as to detailed methods to calculate critical loads. A key issue in recent discussions has been the idea of basing critical loads for soils on bioavailable concentrations rather than the total soil concentrations, as these are more directly related to potential ecological effects. The main aims of this research contract were to contribute to the development of critical loads methods based on bioavailable concentrations and to develop databases and methods to apply such an approach to national mapping within the U.K..

This research contract formed part of a larger consortium project linked to the Natural Environment Research Council (NERC) Environmental Diagnostics programme, with other partners being funded through NERC and the Environment Agency (EA). The research supported by NERC and EA focussed on field measurements of dry deposition of metals to moorland, the development of models to estimate deposition of metals across the U.K., and on field validation of a dynamic model of metal flows through soils into freshwaters in upland areas of the U.K.. Copies of the final reports to NERC on the research carried out on these subjects have been appended to this report as Annexe 1 and Annexe 2, while the key links between this NERC-supported research and that supported by DETR are described in the relevant sections of this report. The research supported by DETR under this contract focussed on the development of models to predict bioavailable metal concentrations in soil solution, their application to spatial datasets of metal concentration and soil characteristics; and the development and testing of methods to map critical loads for metals in the U.K. This built on earlier research on critical loads for metals under contract EPG 1/3/85.

In April 2000, the contract was varied to include a new package of research which involved a survey of metal concentrations of mosses in the U.K.. Although this research had, as one of its objectives, the aim of improving our knowledge of the distribution of metal deposition across the U.K., in broad terms its objectives were quite distinct from those of the original contract. Furthermore, the report of this moss survey is directly relevant to the European survey of metal concentrations in mosses which has now been integrated into the work programme of ICP-Vegetation within the UN/ECE framework. For this reason, we have provided a separate report on this part of the work programme, which forms the second part of this final contract report. Where the results from the moss survey have provided information which has been used in critical load assessments, this is described in the relevant section of this report.

The report first summarises the main objectives. It then briefly considers the process of development of critical loads methods for metals within UN/ECE, which forms the main policy context of the research (Section 3). The results of the research are then described in two major sections – on soils (Section 4) and on critical loads methods and mapping (Section 5). Finally, the policy significance of the findings is briefly considered, and the main conclusions and recommendations are presented (Sections 6,7 & 8).

2. AIMS AND OBJECTIVES

The primary aims of this contract were:-

1. To develop methods of mapping and modelling critical loads of metals in the U.K. and to contribute to the development of agreed European methods

2. To develop methods to model bioavailable concentrations of metals in upland soils and to assess the implications of basing critical loads on bioavailable rather than total soil concentrations.

3. To provide maps of critical loads of metals and their exceedance in upland areas of all parts of the U.K.

The research described in this report has focussed on upland areas, because it was felt that the methods developed for application in lowland Europe (de Vries & Bakker, 1998) would need to be modified for application to such areas. Aerial deposition is the dominant input of metals to these areas, which are dominated by acid soils with a high organic content. Many areas of upland Britain have had high historic deposition through mining and smelting activities which are reflected in current soil concentrations. Nutrient cycling is a critical limiting factor to primary production in these ecosystems, and thus our effects assessment has focussed on microbial activity in surface soils. Finally, many of these upland areas have also been subjected to high levels of sulphur deposition, and it is important that the methods developed can also assess the impact of soil acidification on metal mobility.

It should be noted that complementary studies have been conducted on lowland agricultural systems in England & Wales, by a research consortium led by Prof. Brian Alloway (Reading University), with support from MAFF. We have sought collaboration with Prof. Alloway, and this has resulted in a comparison of U.K. deposition fields based on his measurements of bulk deposition with our estimates of U.K. deposition fields based on the moss survey, as described in the second part of this final contract report.

The research which has been conducted to meet these broad aims has focussed on two major areas: improved data and models for soils, and the development and application of critical load approaches using a GIS. The objectives within each of these two areas can be summarised as follows:-

(a). Soils

1. To compare different operational extractants used to define the reactive or bioavailable metal fraction in soils across a range of upland soils.

2. To develop methods to predict free-ion concentrations and total pore water concentrations in upland soils, from data on total soil concentrations and on soil characteristics, by combining empirical models with a chemical speciation model. These methods have been characterised as ‘transfer functions’ within the context of UN/ECE.

3. To compare relationships between microbial response in a standard toxicity test and total soil, porewater and free-ion metal concentrations.

(b). Critical Loads

1. To establish a national soils database for work on critical loads of metals, by combining data from Scotland and Northern Ireland with that which was already available for England & Wales.

2. To produce new maps of critical loads based on the bioavailable fraction of metals, using the empirical models developed in (a)2.

3. To model the dynamics of changes in soil pools of metals in response to changing atmospheric deposition

4. To assess methods of linking both the static and dynamic approaches to critical loads for metals to effects criteria for both soils and waters.

5. To model the effect of changes in soil pH on critical loads

6. To produce new maps of critical load exceedance based on new deposition fields developed from new data on moss concentrations and from a MAFF sponsored project.

All these objectives have been broadly met, although some changes to the work programme, and the emphasis placed on different objectives, have been made in consultation with the DETR Project Officer.

3. EUROPEAN DEVELOPMENT OF CRITICAL LOADS METHOD FOR METALS

Before describing the work carried out under this contract for the U.K., it is relevant to briefly consider the current position in terms of the development of critical loads for metals which might be applied under the Convention on Long-Range Transboundary Air Pollution (CLRTAP) within UN/ECE. In particular, since the start of this contract, there have been a number of important developments in the methodological approaches which are to be recommended for critical loads modelling and mapping. The research carried out under this contract has both contributed to this process, and provided an opportunity to assess the implications of the proposed methods for the U.K.. For this reason, the work programme has focussed more on the application of these new methods to soils, and less on the link to freshwaters, which is not currently an active area of discussion within UN/ECE, except for mercury. In this section, we briefly consider these developments in critical loads methods for metals; at the end of the report (Section 8), we review the results of our application of these methods in the U.K. in the context of current and future discussions within UN/ECE.

Two workshops on the development of critical loads methods for toxic metals were held over the course of this research project, the first in Schwerin in October 1999 (Gregor *et al.*, 1999) and the second in Bratislava in October 2000 (Curlik *et al.*, in press). At the second workshop, an agreement was made to produce a short summary of methods for the calculation of critical loads for metals. This document (Gregor *et al.*, 2000) provides a description of the simplest methods of mapping critical loads and emphasises the need to proceed with national mapping as soon as possible.

The recommendations of the Bratislava workshop also included a provisional timetable to complete the assembly of regional datasets and European critical loads maps for cadmium, lead and mercury by 2002-3, in preparation for a possible revision of the Protocol on heavy metals in 2004-2005. To meet this timeframe, the workshop also identified the need for a period of intensive research and collaboration on appropriate critical limits for different effects, and appropriate transfer functions between different metal pools in the soil, over the period 2000-2002. The programme described in this report will provide a useful contribution to this research need, although it should be emphasised that much further research is needed before critical loads methods are developed to a stage where they can confidently be applied either in U.K. or in pan-European assessments.

Gregor *et al*. (2000) also identify three basic approaches to assessing critical loads for metals, and the need to agree on one of these approaches as the basis for a pan-European approach. Here we summarise these three approaches and comment briefly on their relevance to this research programme. Further discussion of the appropriateness of each approach for the U.K., based on the results of this research programme, can be found in Section 8. The three identified approaches are (a) a stand-still approach (b) a critical load approach and (c) a simple dynamic approach. The stand still approach aims to avoid any accumulation of heavy metals in soils (Gregor *et al.*, 1999). However, this approach may not be adequate if current concentrations, due to historical deposition or geochemical features, already exceed critical limits for effects, whether based on total soil content or soil solution concentrations. Furthermore, a standstill in terms of soil content could be reached by high rates of leaching, with implications for metal concentrations in freshwaters. These issues are addressed further in terms of current metal contents across the U.K. in Section 5 of this report. However, at this point we note that the standstill approach appears to be inappropriate for application to upland areas of the U.K..

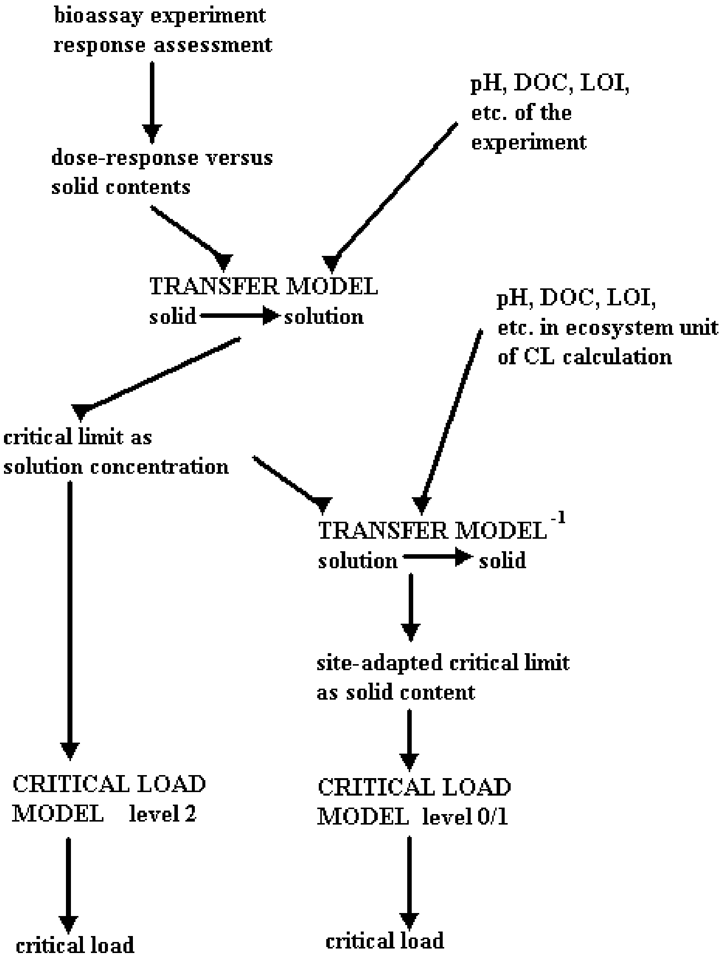
Many different approaches have been proposed for the calculation of critical loads, ranging from complex calculations, which are demanding in terms of data, to simple empirical approaches (de Vries & Bakker 1998; Gregor *et al* 2000). In the Schwerin workshop, it was agreed to move from an effects approach based on total soil concentrations to one based on bioavailable concentrations. At the Bratislava workshop, this objective was endorsed, and steps were taken to put this approach into effect, using effects criteria based on total soil solution concentrations. The work described in Section 4 of this report is a contribution to the development of this approach, as are the critical loads assessments presented in Section 5.

The application of transfer functions in the context of critical loads calculations based on soil solution criteria is illustrated in Fig. 3.1, taken from Curlik (2001). The transfer function may be applied to existing ecotoxicological data to estimate a critical limit expressed as a soil solution concentration. This could be compared directly with actual data on soil solution concentrations (Level 2 in Fig. 3.1), but in practice such data do not exist in spatial national inventories, which contain information on total or reactive soil concentrations. Hence transfer functions must be used either to estimate soil solution concentrations in equilibrium with current total soil concentrations, or to estimate the total or reactive soil concentration for given soil characteristics which corresponds to the critical limit in soil solution.

The interest in dynamic approaches reflects the fact that the timescales for soil or soil solution concentrations to reach critical limits for adverse effects when deposition exceeds critical loads for some metals may be of the order of hundreds or even thousands of years in certain soils (see e.g. Paces, 1998). While critical loads theoretically are applied with an unspecified timeframe, the timescales for metals in soils to reach critical concentrations are clearly potentially inconsistent with those over which the evaluation of measures to reduce pollutant emissions takes place. We therefore have consistently argued that critical loads for metals can only be considered alongside some form of analysis of system dynamics, in order to assess the likely timescales of response to changes in pollutant deposition.

Within the overall research consortium programme, we have adopted two approaches to assessing the dynamics of response of metal concentrations in the air/soil/water pathways. The first is a catchment based approach, using detailed modelling with extensive parameterisation; this approach was applied at three sites (in the Lake District and the northern Pennines). The model simulations within this programme used simulated deposition scenarios for both metals and acidity over the last 200 years. This research was supported by NERC and is described in Annexe 2. The second was a simpler approach, based on a modification of that suggested by Paces (1998). It was based on grid squares, rather than catchment boundaries, and assessed the timescale of response to fixed rates of deposition. This approach, which was supported under this DETR contract, was designed to be applied within a GIS across the U.K., and hence to allow comparisons to be made of the dynamics in different parts of the country. The results are described in detail in Section 5.5.

Figure 3.1 Flow diagram for transfer function use from solid soil limits to soil solution limits or *vice-versa* (source Curlik, in press)



4. SOILS

4.1. Sampling and Analytical Methods

Soil samples were collected from 116 locations in five regions of upland Britain – the Lake District, Yorkshire Dales, Derbyshire Peak District, North Wales and Dartmoor. The sampling strategy was designed to ensure that a wide range of soil series was included, and that sites with historical contamination from smelting activities were sampled. The samples in Dartmoor were primarily over granite, while those in the Yorkshire Dales were limestone. In the Lake District, there was a variety of parent materials, including igneous, sandstones, shales and limestones, while in north Wales, they were predominantly mudstones and shales. The sites with historical contamination were situated in Derbyshire. At each site, the sample was taken from a depth of 0-5cm.

The following extractions were carried on all samples:-

a) total metal concentrations (extracted using a nitric/perchloric acid digest)

b) reactive metal content. Two extractants were used, based on recommendations from the Schwerin workshop – 0.43M HNO_3, as used in the Netherlands, and 0.1M Na_2EDTA, as used in the U.K..

c) exchangeable metal content, using 0.01M $CaCl_2$, which allowed intercomparison with data obtained in North Wales in Phase 1 of this research programme.

d) porewater concentrations. Soil samples from the field were brought to field capacity in small boxes and then left to equilibrate for one week. Porewater was extracted from saturated soils in the laboratory using two 'Rhizon samplers' inserted diagonally into each box so that they sampled over the full depth of the box.

In addition, a BCR 3-step sequential extraction (Rauret *et al.*, 1999) was carried out on a sub-sample of 30 samples.

The metal concentrations in $CaCl_2$ and porewater were determined using ICP-MS. These analyses were made at the NERC ICP/MS unit at Kingston University, as a result of a successful application to NERC for access to the facility. The metal concentrations in all the other extracts were analysed using ICP-AES.

The pH of the porewater extract, its dissolved organic content (DOC), using a Dohrmann DC-190 TOC analyser, and its base cation content, using ICP-AES, were determined. Soil organic content was estimated by determining the loss-on-ignition (LOI) at 450^oC. The cation exchange capacity (CEC) of the soils was also determined.

The chemical form of the metal in porewater, and particularly the partitioning between free ionic metal and that in organic complexes, was then simulated using the WHAM chemical speciation model (Tipping, 1994). This model, which was evaluated further in the NERC-funded component of the research consortium (see Annexe 2) was then used to predict free-ion concentration in porewater from the total metal concentration in soils, using data on pH, base cation content and DOC.

4.2. Analytical Results

The metal concentrations in the different extracts are summarised in Table 4.2.1 for each of the four metals. In all cases, the metal concentrations were log-normally distributed, with a small number of soils with very high concentrations. This reflects a deliberate choice in the sampling strategy to include a small number of sites with very high historical contamination.

Table 4.2.1 Summary of metal concentrations in all extractants for whole dataset, in BCR for 30 samples and of pH, DOC, LOI & CEC for all samples. Tabulated values are median concentrations, with the range in brackets. All metal values are in units of ug g^{-1}, apart from porewater concentrations, which are expressed in units of ug l^{-1}, DOC in mg l^{-1}, LOI in % and CEC in meq 100g^{-1}

	Pb	Cd	Cu	Zn
Total	122 (32-33200)	1.0 (0.3-51.6)	20.5 (6-1790)	65.8 (19-5140)
0.43N HNO_3	80.3 (11-9660)	0.52 (0.08-44.9)	7.6 (2-144)	20.4 (2-2460)
EDTA	124 (7-13900)	0.55 (0.10-36.7)	6.6 (1-1500)	19.0 (0.7-2810)
$CaCl_2$	0.76 (0.01-122)	0.11 (0-3.2)	0.06 (0-50)	5.2 (0.01-122)
Porewater	12.8 (0.2 –13760)	0.53 (0.07-25.6)	7.1 (2.1-562)	60.4 (6-2182)
BCR step1	2.36 (0.2-6263)	0.31 (0.11-34.2)	0.69 (0.17-10.9)	9.68 (0.34-1711)
BCR step2	43.4 (15.6-16500)	0.30 (0.13-11.4)	2.33 (0.12-8.88)	5.13 (1.15-424)
BCR step3	5.8 (2.0-1570)	0.0 (0.0-0.53)	3.17 (0.72-66.1)	3.78 (0.64-215)

	Median	Minimum	Maximum
pH	4.38	3.35	8.28
LOI (%)	40.07	8.95	97.81
DOC (mg l^{-1})	52.62	5.29	705.01
CEC (meq 100g^{-1})	34.2	13.5	96.2

A comparison of the different extractants revealed some interesting differences between the metals in terms of the proportion of the total metal pool which is extracted. The two extractants used to characterise the reactive pool produced similar median concentrations, except in the case of Pb, for which the value in EDTA was higher. However, the reactive pool appeared, on the basis of the median concentrations, to be over two-thirds of the total pool for Pb, about half for Cd, and about one-third for Cu and Zn. The contrast was greater for the $CaCl_2$ extract, which was about 10% of the total pool for Cd and Zn, but less than 1% of the total pool for Cu and Pb. However, all these relationships are dependent on soil properties (see below).

BCR data reveals the proportions of each metal in each extract fraction to be different for different metals. Despite mean total concentrations almost twice that of zinc, lead has only one third the mean BCR step1 extract concentration of zinc. Zinc and cadmium have the majority (51%) of their mean concentration in the 'bioavailable' BCR step1 fraction. Copper has 11% in this fraction and lead 5%. These proportions are similar to the results of another study of potential metal mobility and toxicity (Davidson *et al*, 1998) where zinc had 42% of its extracted concentration in the BCR step1, cadmium 28%, copper19% and lead 3%.

4.2.1. Total and Reactive Soil Concentrations

The methodology adopted for critical loads approaches in soils clearly distinguishes between the total and reactive pools, and recommends that modelling of critical loads should be based on the reactive pool, as the one which is available for exchange with the soil solution. Reactive metal concentrations approximated by EDTA extracts do exist for England and Wales (McGrath & Loveland, 1992) and Northern Ireland (Jordan *et al*., 2000), but no data were available for Scotland. This necessitated the prediction of reactive soil metal concentrations from total metal concentrations.

Therefore, when the national metal inventory is based on the total metal concentration, transfer functions are needed to estimate the reactive soil concentration as a function of soil properties which are normally available in national soil databases. Two operational methods were used to estimate the reactive concentrations in the field samples – dilute nitric acid and EDTA. However, the available national soil concentration datasets used only EDTA extractants. Therefore, data analysis of the field sample data used the EDTA extracts as the operational definition of the reactive metal concentration.

The soil samples with DOC>200mgl^{-1} were removed from the set of 116 samples, then multiple regressions were run to establish equations of best fit to predict the reactive pool of copper, cadmium, lead and zinc from their measured total soil concentrations, pH and LOI. Table 4.2.2 summarises the results and R^2 values. Removal of samples with DOC>200mgl^{-1} reflected the range of values existing in U.K. upland soils, which never exceeded 200mgl^{-1}, according to figure 5.1.6. (although DOC was not directly measured nationally, but was derived from LOI as explained in section 5.1.5). If left within the dataset these extreme values may disproportionately affect the predictive equations which are derived.

Cadmium and zinc produce a different set of regression equations to copper and lead, whose reactive concentrations can be adequately estimated using total metal concentrations alone. The inclusion of LOI as a regression term significantly improves the prediction of reactive concentrations for cadmium and zinc, however. The inclusion of pH as a regression term produces little improvement in prediction of any metal reactive concentrations.

Table 4.2.2 Summary of metal concentrations (mg kg^{-1}) in EDTA extracts regressed against total metal concentrations (mg kg^{-1}), LOI (%) and pH (>200mgl^{-1} DOC samples removed). Transfer functions used in bold type, all logs are log$_{10}$.

Regression Equation	**R^2 (%)**
log(EDTACd) = -0.317482 + 0.998376*log(TotalCd)	64.71
log(EDTACd) = -0.656287+ 1.06545*log(TotalCd) + 0.00710635*LOI	**78.14**
log(EDTACd) = 0.0573196 - 0.0736321*pH + 1.10665*log(TotalCd)	68.17
log(EDTACd) = -0.787097 + 0.00774602*LOI + 0.0198145*pH + 1.04288*log(TotalCd)	78.08
log(EDTACu) = -0.801557 + 1.20424*log(TotalCu)	**90.26**
log(EDTACu) = -0.835098 + 0.00141085*LOI + 1.18037*log(TotalCu)	90.98
log(EDTACu) = -0.834266 + 0.00567306*pH + 1.20617*log(TotalCu)	90.10
log(EDTACu) = -1.06005 + 0.00255575*LOI + 0.0325197*pH + 1.181*log(TotalCu)	91.68
log(EDTAPb) = -0.243639 + 1.02857*log(TotalPb)	**83.00**
log(EDTAPb) = -0.357451 + 0.00367033*LOI + 1.00559*log(TotalPb)	84.15
log(EDTAPb) = -0.0987716 - 0.0239131*pH + 1.0209*log(TotalPb)	82.86
log(EDTAPb) = -0.547412 + 0.00459836*LOI + 0.0266137*pH + 1.00851*log(TotalPb)	84.15
log(EDTAZn) = -0.4464 + 0.91905*log(TotalZn)	42.84
log(EDTAZn) = -1.56308 + 0.0138722*LOI + 1.16272*log(TotalZn)	**79.07**
log(EDTAZn) = -0.0545823 - 0.160462*pH + 1.15395*log(TotalZn)	55.99
log(EDTAZn) = -1.48373 - 0.0159797*pH + 0.0133724*LOI + 1.17701*log(TotalZn)	78.93

4.2.2. Total and Soil Solution Concentrations

The partition coefficient (k_d) between total metal concentration and measured porewater is defined as the ratio of total soil metal to total porewater metal at equilibrium;

$$k_d(\text{total}) = \text{total soil concentration} / \text{total soil solution concentration}$$

and that between total metal concentration and modelled free-ion concentrations is defined as the ratio of total soil metal to porewater modelled free-ion concentrations at equilibrium;

$$k_d(\text{free-ion}) = \text{total soil concentration} / \text{modelled free-ion concentration}$$

The R^2 values obtained using modelled reactive soil concentrations to predict these k_d values were no better than using total soil concentrations. Since the use of reactive concentrations involves a further stage of modelling, it was decided to base predictions of porewater and free-ion concentrations on total soil concentrations. The dependence of the partition coefficient (k_d) between total metal concentration and both measured porewater and modelled free-ion concentrations on soil properties of pH, DOC and LOI was determined using multiple regression. These transfer functions from total metal concentrations to both porewater and free-ion concentrations are applied in critical loads assessments for U.K. upland soils, as described in Section 5.

Table 4.2.3 summarises the results of the regression analysis for the transfer functions, listing the terms and the R^2 values for the equations of best fit. It is noticeable that R^2 values for free-ion concentrations (Table 4.2.4) were consistently higher than for total porewater (Table 4.2.5); this effect was particularly marked for lead and copper.

As shown in Table 4.2.4, using pH alone provided R^2 values for the equations for modelled free-ion concentrations which were very similar to those for models including DOC and/or LOI in addition to pH. Thus, pH alone provided an adequate basis on which to predict the k_d between total soil and free-ion concentrations. However, in view of the significant association between pH and LOI in the dataset, it was felt that it was more robust to apply transfer functions incorporating both LOI and pH in the GIS analysis described in Section 5 (cf. Table 4.2.4).

Our results show that it is possible to develop simple transfer functions which can be used to estimate modelled free-ion concentrations from measurements of total metal concentrations. The same conclusion was reached by Sauvé *et al* (1998), who modelled the relationship for lead and copper between total soil concentrations and measured free-ion concentrations for soils with a wide range of pH values and organic contents. In our data, a transfer function based on pH alone was able to explain 64% of the variation in modelled free-ion concentration for lead, and 85% of the variation for copper. In contrast, the transfer function for total soil solution concentrations was weaker and also included DOC, which has to be estimated from other parameters within the national database (see Section 5.1.5).

Table 4.2.3 Summary of best fit multiple regressions of $\log_{10}$ k_d (ml/g) between total soil metal concentrations and total and free-ion porewater concentrations, used in GIS modelling.

Multiple regression equation	R^2
Pbtl = 2.97788 -0.00308307*DOC + 0.0060681*LOI + 0.18855*pH	49.1
Zntl = 1.02155 – 0.00197485*DOC + 0.012324*LOI + 0.210066*pH	51.8
Cdtl = 1.414 - 0.00167527*DOC + 0.010134*LOI + 0.235679*pH	51.0
Cutl = 2.50436 – 0.00203801*DOC + 0.00593759*LOI + 0.0558056*pH	23.9
(Mtl = log k_d of total porewater concentrations for metal M)	
Pbfl = 0.247082 + 0.0066581*LOI + 0.878097*pH	87.9
Znfl = 1.46078 + 0.000647016*LOI + 0.346293*pH	69.8
Cdfl = 1.60063 + 0.00309211*LOI + 0.334888*pH	65.9
Cufl = 0.473382 + 0.00666618*LOI + 0.729917*pH	83.9
(Mfl = log k_d of free-ion porewater concentrations for metal M)	

Table 4.2.4 Summary of multiple regressions of $\log_{10}$ k_d (ml/g) between total soil metal concentrations and free-ion porewater concentrations.

Multiple regression equation	R^2
Pbfl = 0.967599 + 0.796994*pH	86.9
Pbfl = 0.247082 + 0.878097*pH + 0.0066581*LOI	87.9
Pbfl = 1.18971 + 0.78349*pH - 0.00187976*DOC	87.8
Pbfl = 0.455029 + 0.866556*pH + 0.00685055*LOI - 0.00194017*DOC	89.1
Znfl = 1.52837 + 0.338942*pH	70.3
Znfl = 1.46078 + 0.346293*pH + 0.000647016*LOI	69.8
Znfl = 1.71468 + 0.326642*pH - 0.00154789*DOC	73.1
Znfl = 1.63372 + 0.335477*pH + 0.00078204*LOI - 0.00155408*DOC	72.9
Cdfl = 1.93493 + 0.296847*pH	65.1
Cdfl = 1.60063 + 0.334888*pH + 0.00309211*LOI	65.9
Cdfl = 2.00677 + 0.292581*pH - 0.000609521*DOC	65.1
Cdfl = 1.66478 + 0.331823*pH + 0.00321853*LOI - 0.000660145*DOC	66.4
Cufl = 1.15928 + 0.655742*pH	82.6
Cufl = 0.473382 + 0.729917*pH + 0.00666618*LOI	83.9
Cufl = 1.33683 + 0.643651*pH - 0.00145026*DOC	83.1
Cufl = 0.64278 + 0.719008*pH + 0.00681829*LOI - 0.00151152*DOC	84.8
(Mfl = log k_d of free-ion porewater concentrations for metal M)	

Table 4.2.5 Summary of multiple regressions of $\log_{10}$ k_d (ml/g) between total soil metal concentrations and total porewater concentrations.

Multiple regression equation	R^2
Pbtl = 3.49958 + 0.128425*pH	27.1
Pbtl = 3.44651 + 0.134421*pH + 0.000478808*LOI	27.2
Pbtl = 3.77804 + 0.126724*pH - 0.00413194*DOC	47.5
Pbtl = 2.97788 -0.00308307*DOC + 0.0060681*LOI + 0.18855*pH	49.1
Zntl = 2.08894 + 0.2046*pH	50.4
Zntl = 2.25033 + 0.186969*pH - 0.00150942*LOI	49.9
Zntl = 2.25883 + 0.201696*pH - 0.00243357*DOC	54.4
Zntl = 1.02155 – 0.00197485*DOC + 0.012324*LOI + 0.210066*pH	51.8
Cdtl = 2.45559 + 0.159018*pH	41.9
Cdtl = 2.34347 + 0.171818*pH + 0.00101403*LOI	50.1
Cdtl = 2.54824 + 0.15888*pH - 0.00140066*DOC	43.2
Cdtl = 1.414 - 0.00167527*DOC + 0.010134*LOI + 0.235679*pH	51.0
Cutl = 3.44803 - 0.00476277*pH	0.1
Cutl = 3.33611 + 0.0073973*pH + 0.00106312*LOI	0.0
Cutl = 3.6602 - 0.00901893*pH - 0.00301046*DOC	15.5
Cutl = 2.50436 – 0.0020380*DOC + 0.00593759*LOI + 0.0558056*pH	23.9
(Mtl = log k_d of total porewater concentrations for metal M)	

Table 4.2.5 demonstrates the relatively poor R^2 values produced in predicting the k_d between total soil and total porewater concentrations. DOC was consistently a significant contributor to equations of best fit for total porewater, but was less significant for free-ions. The value of the k_d for copper, in particular, was dominated by the effect of DOC, when total soil solution concentrations were considered. Since DOC estimates in national spatial datasets are very uncertain, this creates particular problems for the application of such empirical transfer functions to critical load modelling. This led to the choice of predicting the total porewater metal from the free-ion concentrations and pH measurements, as discussed in section 4.2.3.

4.2.3. Relationship between total porewater and modelled free-ion concentrations.

Once free-ion concentrations had been modelled, relationships between free-ion concentration and total porewater concentration were derived, using the measurements of total cadmium, copper, lead and zinc in porewater extracted from the 116 collected soil samples using the Rhizon samplers. In some cases, this approach might prove a more effective method of estimating total soil solution concentrations than a direct transfer function from total soil metal concentrations. Using regression analysis, pH was found to be the single independent variable with greatest predictive power for the proportion of free-ion of the total concentrations in porewater. Copper and lead were found to behave in a similar manner, but showed relationships with pH which were significantly different to cadmium and zinc (Figures 4.2.1-4.2.4).

Figure 4.2.1 Effect of pH on the proportion of total porewater free-ions (samples DOC>200mgl^{-1} removed)

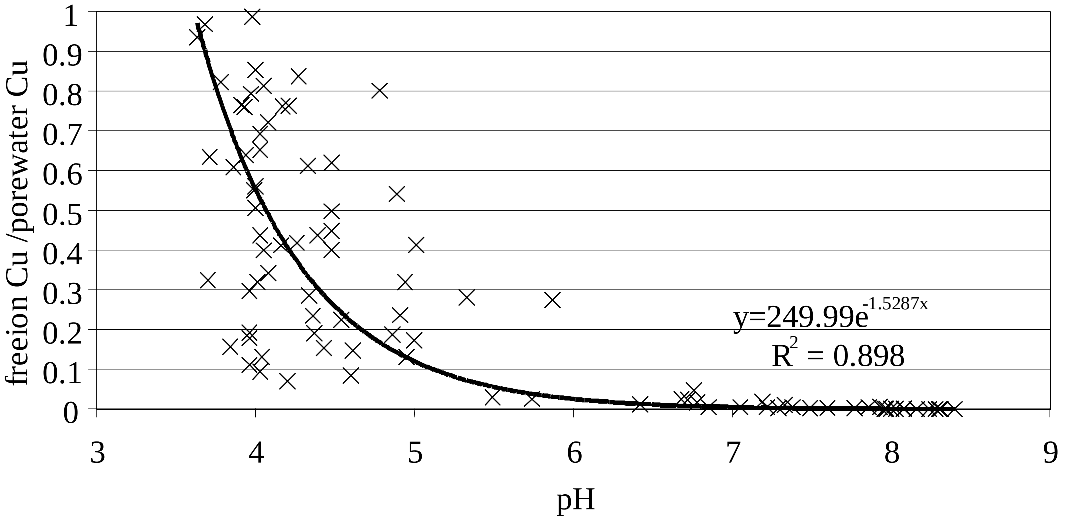
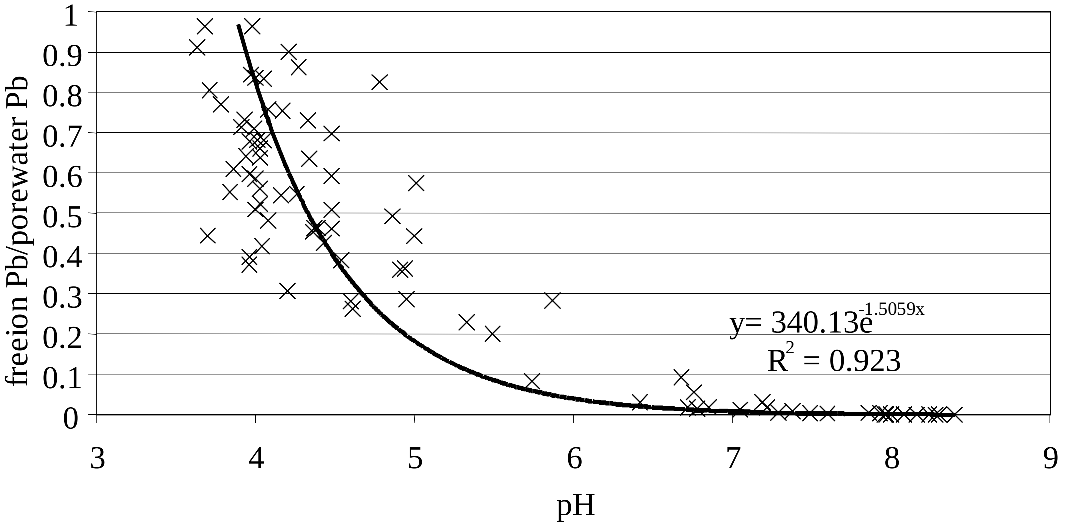


Figure 4.2.2 Effect of pH on the proportion of total porewater lead as free-ions (samples with DOC>200mgl^{-1} removed)



Sampled soils with DOC value greater than 200mgl^{-1} (8 samples) were removed from the regression as no database soils exhibited such high values. The exponential fit for copper and lead reflect the high proportion of those metals bound to organic material at high pHs, as exhibited in the low values for free-ion:total porewater concentration ratios at those pHs. Cadmium and zinc, however retain over 50% of their total porewater concentrations as free-ions at pH 7.

Figure 4.2.3 Effect of pH on the proportion of total porewater zinc as free-ions (samples with DOC>200mgl^{-1} removed)

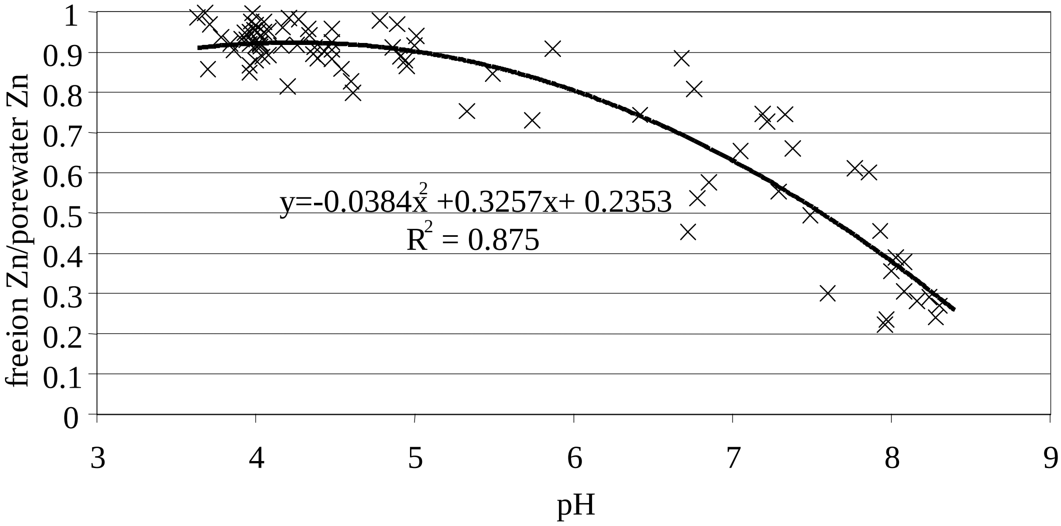
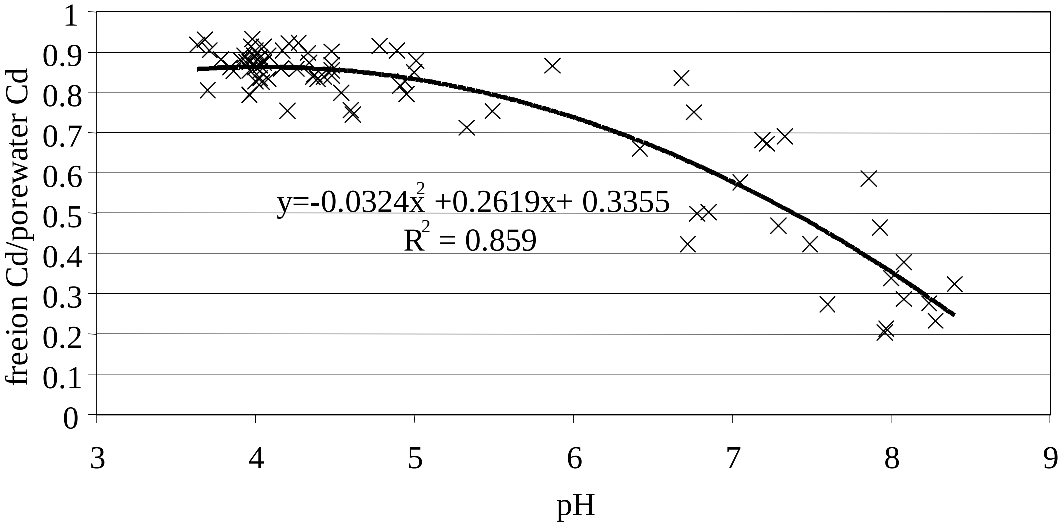


Figure 4.2.4 Effect of pH on the proportion of total porewater cadmium as free-ions (samples with DOC>200mgl^{-1} removed)



4.2.4. Soil Solution and Reactive Soil Concentrations

Dynamic modelling of changes in soil reactive metal concentrations using predictions of metal lost in runoff requires estimation of soil reactive concentrations in equilibrium with total porewater metal concentrations. The R^2 values for the reactive soil concentration/total porewater concentration k_ds are relatively low and similar to those for total soil concentration/total porewater concentration k_ds shown in Table 4.2.3. Therefore we sought better regressions by predicting reactive metal concentrations from total porewater concentrations, without estimating k_d , using soil parameters held in the national GIS.

Using total porewater metal concentrations rather than total soil metal concentrations produced lower R^2 values for every case in prediction of reactive metal concentrations (Table 4.2.2). However, the transfer functions in table 4.2.6have R2 values greater than 60% for Cd, Pb and Zn. The exception is Cu, for which the dominant effect is that of DOC.

Table 4.2.6 Summary of metal concentrations in EDTA (mg kg^{-1}) extracts regressed against total porewater metal concentrations (mg l^{-1}), LOI (%) and pH (>200mg l^{-1} DOC samples removed).

Multiple regression equation	**R^2(%)**
log(EDTACd) = -0.0480663 + 0.70867*log(porewaterCd)	39.1
log(EDTACd) = -0.178556 + 0.00269505*LOI + 0.676107*log(porewaterCd)	40.3
log(EDTACd) = -0.576732 + 0.104808*pH + 0.800091*log(porewaterCd)	47.6
log(EDTACd) = -1.64249 + 0.219224*pH + 0.0100082*LOI + 0.786113*log(porewaterCd)	65.0
log(EDTACu) = 0.295801 + 0.616832*log(porewaterCu)	14.7
log(EDTACu) = 0.138671 + 0.0035007*LOI + 0.614923*log(porewaterCu)	18.2
log(EDTACu) = 0.405958 - 0.0206521*pH + 0.615353*log(porewaterCu)	14.3
log(EDTACu) = -0.106135 + 0.0349283*pH + 0.00473268*LOI + 0.619302*log(porewaterCu)	18.2
log(EDTAPb) = 1.32509 + 0.785934*log(porewaterPb)	60.7
log(EDTAPb) = 1.34019 - 0.0000821409*LOI + 0.780199*log(porewaterPb)	59.7
log(EDTAPb) = 0.589505 + 0.117717*pH + 0.8891*log(porewaterPb)	64.4
log(EDTAPb) = 0.0494467 + 0.177525*pH + 0.00530409*LOI + 0.875534*log(porewaterPb)	65.7
log(EDTAZn) = -0.199296 + 0.876616*log(porewaterZn)	40.4
log(EDTAZn) = -0.272332 + 0.00522178*LOI + 0.782649*log(porewaterZn)	45.0
log(EDTAZn) = -0.776933 + 0.0757179*pH + 0.978289*log(porewaterZn)	43.0
log(EDTAZn) = -1.97667 + 0.210065*pH + 0.011885*LOI + 0.947909*log(porewaterZn)	60.5

4.3. Microbial Toxicity Tests

Nutrient cycling by soil microbes is a critical limiting factor to primary production in upland soil ecosystems, so our effects assessment has focussed on microbial activity in surface soils. Recent advances in the assessment of microbial activity have enabled the assessment of porewater toxicity using bioluminescent biosensors originally established for use in assessing the available fraction of a toxic element (e.g. McGrath *et al*., 1999; Chaudri *et al*., 2000). The toxicity of porewater samples were determined at Aberdeen University using soil bacteria engineered to bioluminesce by insertion of *lux* genes (Paton *et al*., 1995). For this study, strain HB 101 of *Escherichia coli* was used. Luminescence measured after 15 minutes was assumed to be proportional to the vitality of the biosensor.

Since the study is based on field samples, it is impossible to be certain which metal, or combination of metals, was responsible for the observed toxicity effects. Therefore the concentrations of different metals at the sample sites were first screened to assess whether they were present at potentially ecotoxic concentrations. On this basis, analysis of the microbial toxicity data focussed on copper and lead, as the two elements found in relatively high concentrations at the most polluted sites. Gompertz functions were fitted to the luminescence data and the total soil, total porewater, and modelled free-ion concentrations for both metals, and values of free-ion LD_{50} and LD_5 were estimated from the fitted curves.

Figures 4.3.1 and 4.3.2 show the response of the microbial test system to lead and to copper, expressed as total soil concentration, total porewater concentration, and modelled free-ion concentrations. It is important to note that the range of concentration on the x-axis is different for the three graphs. No clear relationship is seen between total soil concentrations of both metals and the measured luminescence, and only a weak relationship is discernible using the total porewater concentration. In contrast, the modelled free-ion concentrations provided a clearer distinction between a concentration range over which no measurable effect was detected and one over which the luminescence clearly declined.

The Gompertz function explained a significant amount of the variation in observed bioluminescence for the free-ion concentrations, with R^2 values of 0.88 for copper and 0.90 for lead. The values of LD_{50} and LD_5 based on free-ion concentrations estimated from the fitted Gompertz functions for lead were 9.3×10^{-8} M and 7.3×10^{-9} M, respectively. The equivalent values for copper were an LD_{50} concentration of 7.0×10^{-8} M and an LD_5 concentration of 5.5×10^{-9} M.

The approach of using *lux*-modified biosensors to assess which fraction of the soil metal burden is the best indicator of toxicity has been previously used in other studies, which have relied on direct measurement of free-ion activities, rather than the model-based approach which we have adopted. Chaudri *et al*. (2000) working with sewage sludge-amended soils, obtained similar results to ours with an R^2 value for zinc of 0.86 for free-ion activities. A clearer demonstration of the value of using free-ion activities is the work of McGrath *et al*. (1999), who applied sludge to arable and woodland soils, and found the relationships between bioluminescence and total zinc content was quite different on the two soils, whereas the relationship with measured free-ion concentrations was consistent on the two soils.

Sauvé *et al*. (1998) developed simple transfer functions between total soil concentrations and measured free-ion concentrations for lead and copper, based on pH alone. They then applied these transfer functions to soil toxicological data in the literature, concentrating on relatively long-term studies. In most, but not all, cases a better relationship with plant or microbial responses was found when the modelled free-ion concentration was used rather than the total metal content of the soil. By combining data from a number of studies, Sauvé *et al*. (1998) were able to estimate the mean concentration for a 50% reduction in the physiological response variable measured. These values were, for microbial processes, 7.9×10^{-9} M for lead, and 6.3×10^{-9} M for copper. These are approximately one order of magnitude lower than the LD_{50} values in our bioassay; however, they relate to long-term effects on growth or physiology rather than short-term effects on vitality, and hence such a difference is to be expected.

Figure 4.3.1. Response of the microbial test system response to total soil lead, total porewater lead and modelled free-ion lead activities.

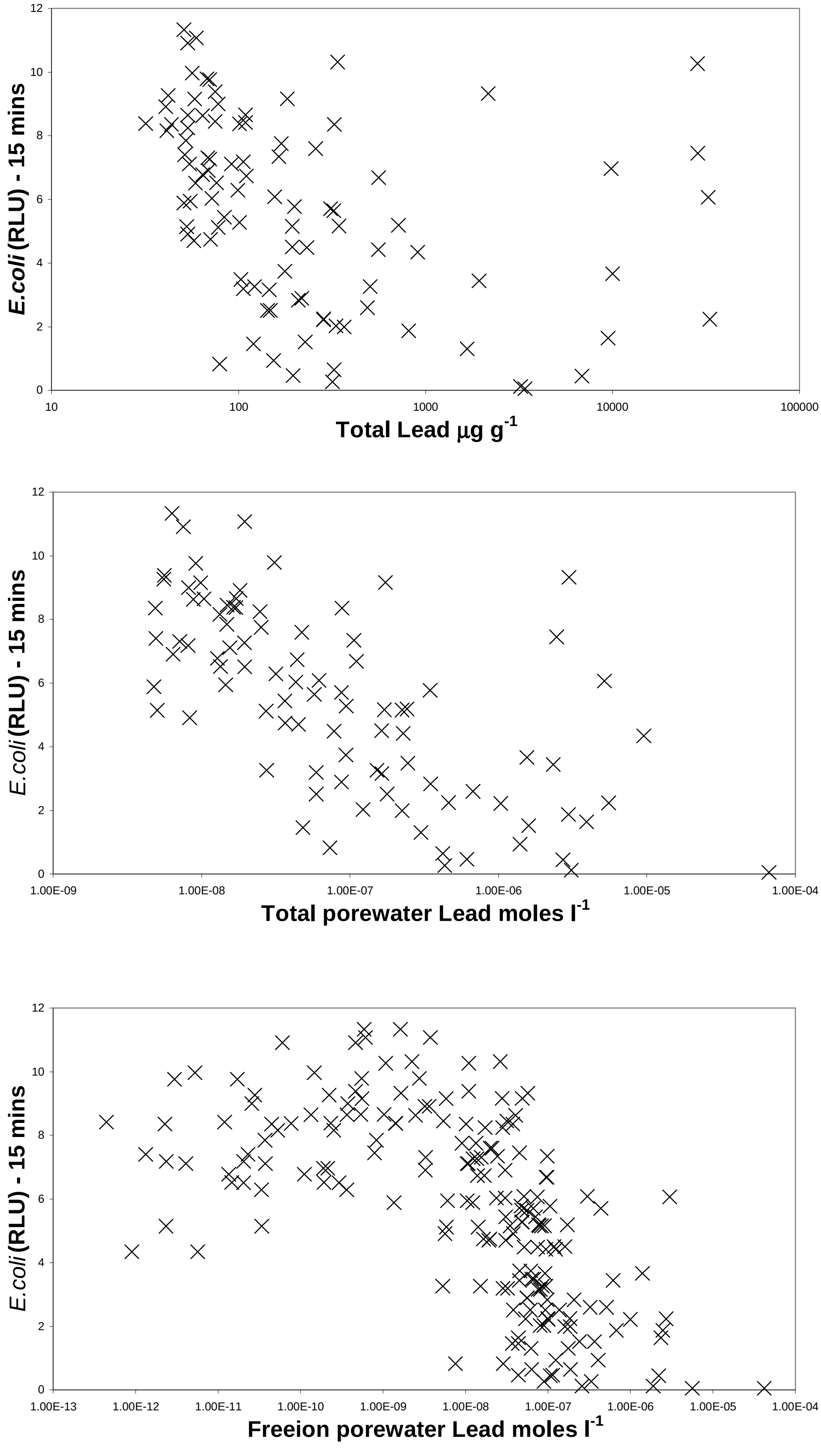
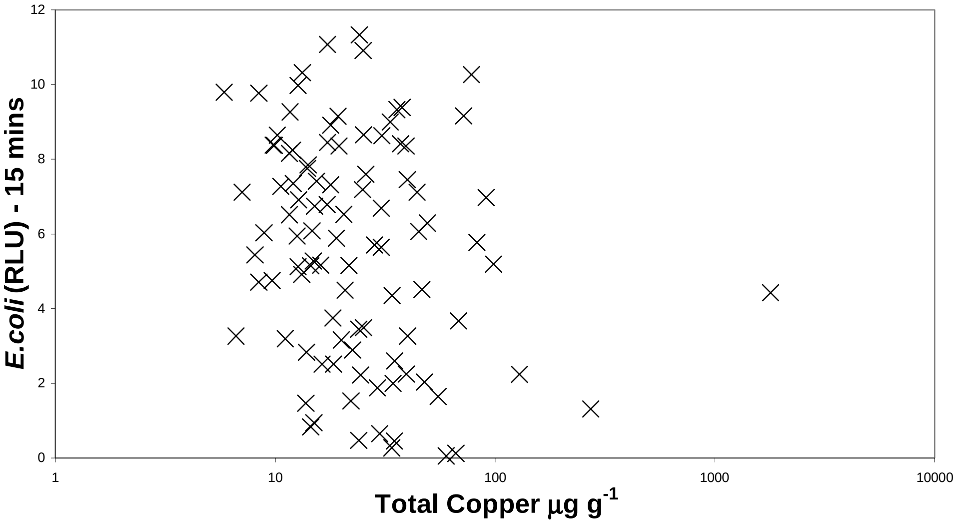
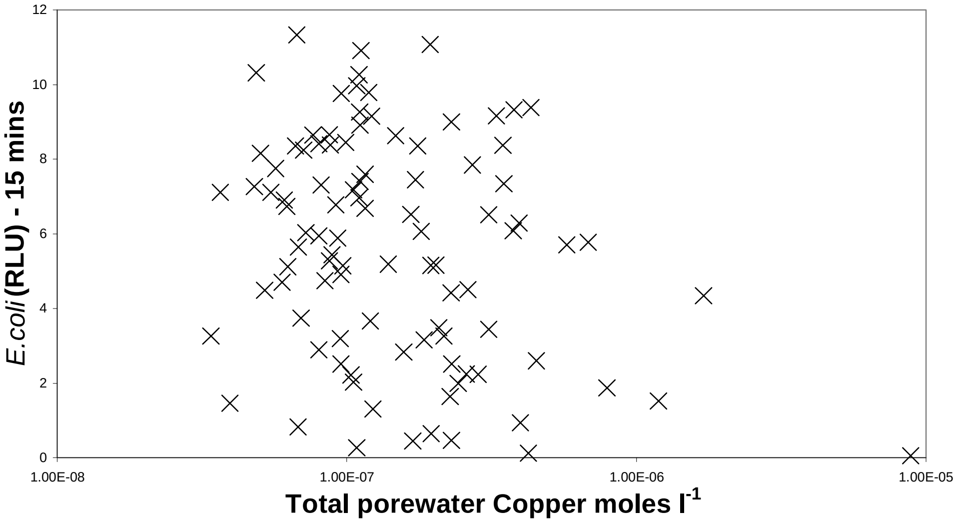
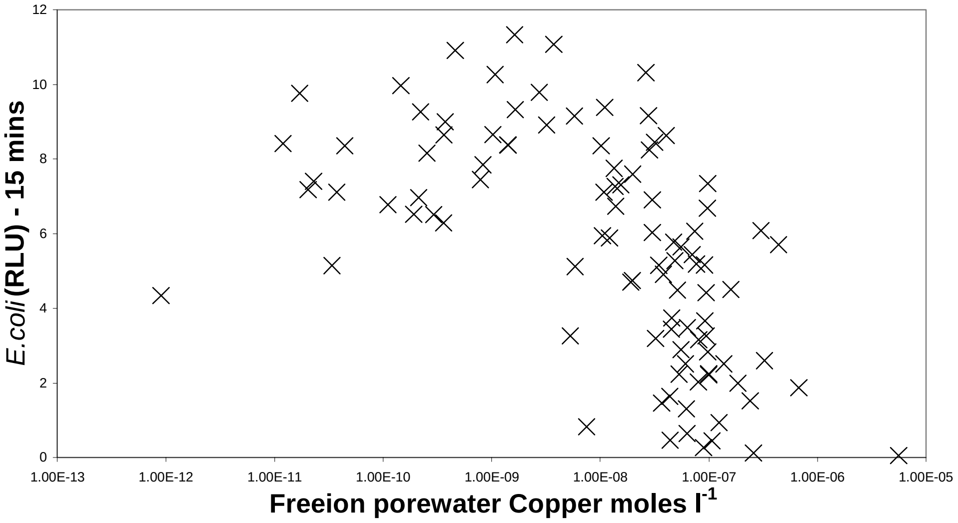


Figure 4.3.2. Response of the microbial test system response to total soil copper, total porewater copper and modelled free-ion copper activities.







5. CRITICAL LOADS

5.1. Development of Integrated National Dataset

The results in terms of critical loads which were presented in the Phase 1 contract were for England and Wales only. In this second phase, we have successfully created a national database, for upland areas, of metal concentrations and soil characteristics for use in critical load calculations and mapping. Here we briefly describe the methods used to incorporate the data from Scotland and Northern Ireland, consider any limitations of the process, and present the national datasets.

5.1.1. England & Wales

Geochemical data for England & Wales were obtained from Prof. Steve McGrath from the Institute of Arable Crop Research, Rothamstead (McGrath & Loveland, 1992). This data were available at 5km resolution and included total Cd, Cu, Pb, Zn concentrations [mg/kg], reactive Cd, Cu, Pb, Zn concentrations [mg/kg] using EDTA, pH and organic carbon [%].

Soil properties data were provided by the Soil Survey and Land Research Centre (SSLRC) at a 1km resolution. The dataset consisted of soil series, top horizon depth [m], organic carbon [%], bulk density [g/cm^3], cation exchange capacity (CEC) [meq/100g], soil texture class, sand [%], silt [%], clay [%] and pH. The soil properties are average values per soil series.

It is important to note that the geochemical data are based on a single point sample within each 5km square. The two datasets were spatially combined by using the 5km sample point coordinates to identify and extract the corresponding 1km data cells. These were then scaled up to be displayed at 5km resolution. This approach means that (a) the soil properties and soil chemistry data may not be well matched if there is significant heterogeneity within each 1km square and (b) the 5km values displayed in the maps in the rest of this section are based on data for one 1 km square within it, and may not be representative of the whole 5km square. These uncertainties, which apply in a similar fashion to the rest of the U.K., mean that it is not possible to interpret the data for specific squares within any confidence; instead it is the broad regional patterns which are of interest.

5.1.2. Scotland

Data for Scotland were leased from the Macaulay Land Use Research Institute (MLURI). The heavy metal dataset comprised topsoil concentration data of Pb [mg/kg], Cu [mg/kg] and Zn [mg/kg] and pH at a 10km resolution (i.e. one data point per 10km square). No data for EDTA extracts were available for Scotland. Unfortunately, topsoil concentrations of cadmium were also not available. The soil type dataset for topsoils included information on soil series, soil texture classes, organic carbon [%], CEC [meq/100g] and pH. It was provided at a 1km resolution, but for upland semi-natural and forest areas only. Note that the organic carbon, CEC and pH in this dataset, as for England and Wales, are average values per soil series. The two datasets were spatially combined in the following manner. Using the geographic coordinates of the heavy metals dataset (10km resolution) the corresponding 1km data cells of soils dataset were identified, extracted and scaled up to a 10km resolution. Thus, in the critical load calculations all data for Scotland are represented at the 10km resolution. Care must be taken in interpreting these values as they represent only one data point within a 10km square and not an average value for that square.

5.1.3. Northern Ireland

There was a lack of data for upland areas of Northern Ireland at the start of the project. Therefore new sites were sampled by the Department of Agriculture and Regional Development, Northern Ireland (DARDNI), at a density of approximately 5km. Metal concentrations were analysed by the Macaulay Land Use Research Institute, and therefore should be directly comparable with Scottish data. The results from this additional survey work have been incorporated into a new soil geochemical atlas of Northern Ireland which is shortly to be published (Jordan *et al.*, 2000).

DARDNI provided a 1km dataset for selected sites on soil series, pH, total Cd, Cu, Pb, Zn concentrations [mg/kg] and Cd, Cu, Pb, Zn concentrations in EDTA extracts [mg/kg] and a 5km dataset on soil series, horizon depth [cm], pH, CEC [meq/100g], OC [%], sand [%], silt [%], clay [%], bulk density [g/cm^3], total Cd, Cu Pb, Zn concentrations [mg/kg] and available Cd, Cu, Pb, Zn concentrations [mg/kg]. Because of the lack of soil properties information in the 1km dataset, only the 5km dataset was used in this study.

The data were provided with Irish National Grid coordinates. A simple shift to an approximate position in the Irish Sea was performed to display the data.

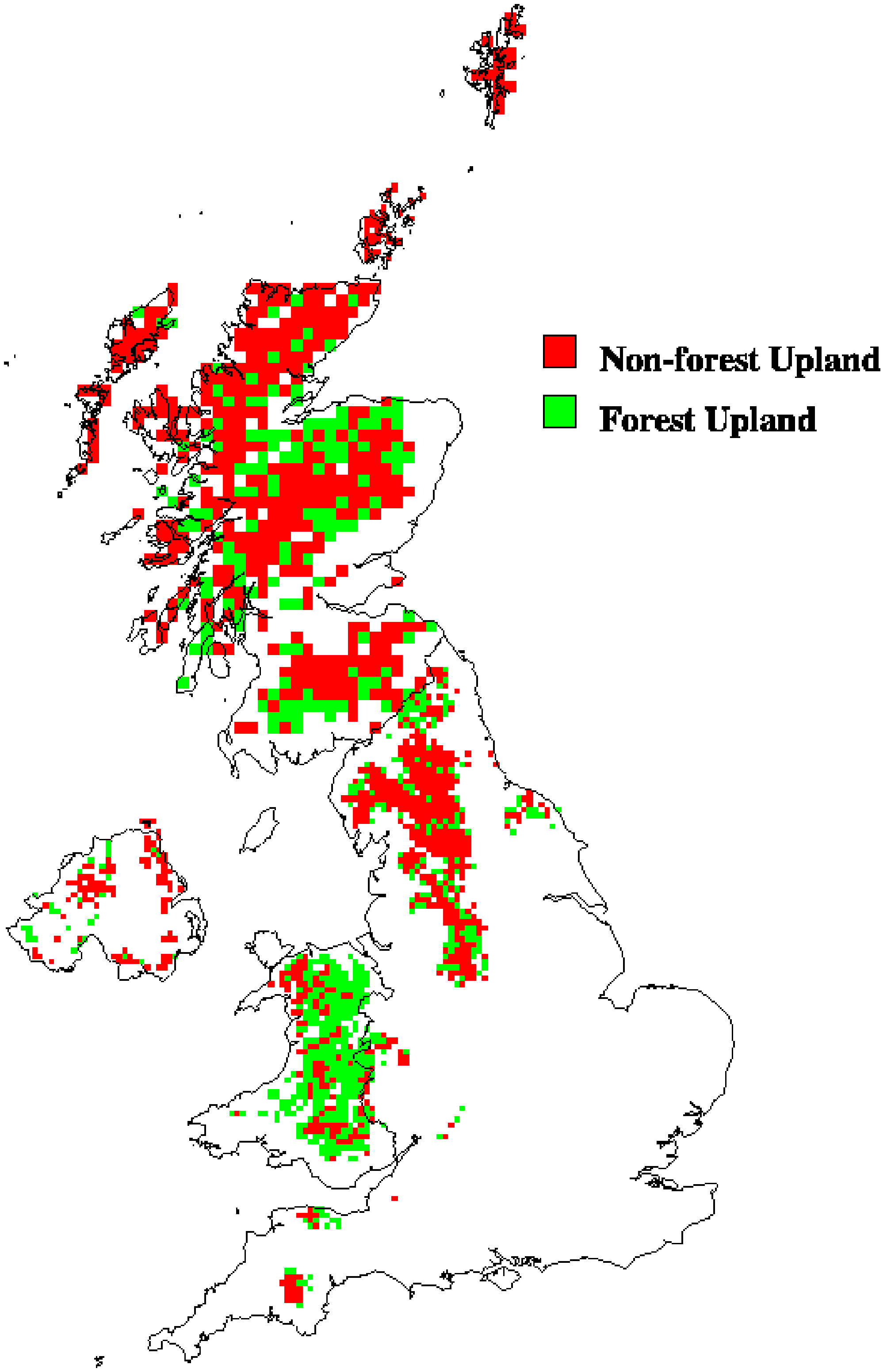
5.1.4. Creation of Upland Mask

The upland mask (Fig. 5.1.1) was derived using two different datasets. Upland areas of England, Wales and Scotland were based on the land classification of the Countryside Information System (CIS) (Bunce *et al.*, 1996). This dataset allocates one of 32 land classes to each 1km square in Great Britain. For this study, all land classes which are defined as upland or marginal upland by CIS were included in the upland mask. Unfortunately, this dataset does not extend to Northern Ireland.

Two methods were explored to define uplands of Northern Ireland. Firstly, we used the land cover classes of the CORINE dataset (Level 3). Although using a different dataset, this method draws on the same principles applied for the upland mask of England, Wales and Scotland. However, the results showed a very scattered pattern of upland areas. It was decided that this is unlikely to represent real uplands. The second method defined upland areas based on elevation. A DTM (Digital Terrain Model) of Northern Ireland was available to Crawford Jordan from the Department of Agriculture, Northern Ireland (data copyright OSNI). Using a spatial query he provided us with a map of all areas which exceed an altitude of 200m.

The critical load methodology currently uses a different approach for forests compared to other semi-natural ecosystems. A map of all forests (deciduous and coniferous) was produced using the ITE Land Cover Map (Fuller *et al.*, 1994). 1km squares were classed as ‘forested’ if more than 5% of the 25m squares in the ITE

Upland Mask for Great Britain



Critical Loads Mapping and Data Centre, CEH Monks Wood
January 2001

Fig. 5.1.1

Land Cover Map were deciduous or coniferous forest. Combining the forest map with the upland map resulted in an upland forest mask and an upland non-forest mask

5.1.5. National Maps of Soil Characteristics

The separate datasets were combined to present national maps by using GIS functions for merging spatially discrete maps. However, some parameters, such as bulk density, were only available for England & Wales and porosity was not available at all. These soil properties are necessary for the dynamic analysis presented in Section 5.5. The combined national datasets were derived as follows.

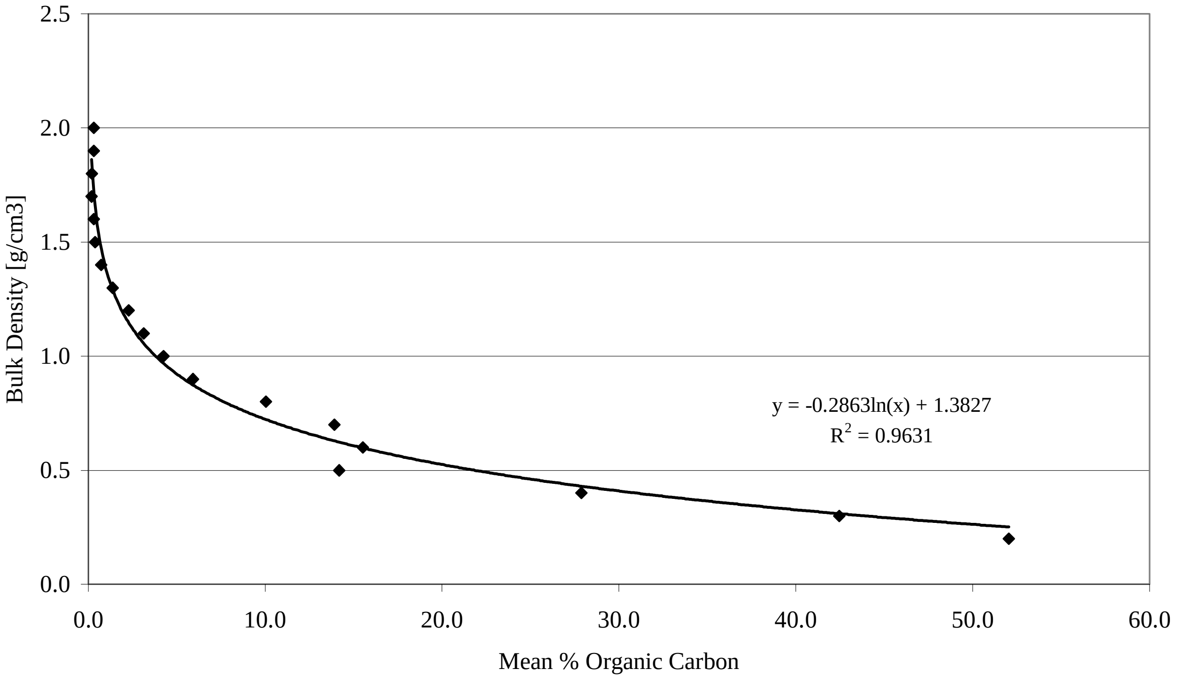
5.1.5.1 pH

pH values were merged from the available separate datasets to create a national dataset at 5km resolution for England, Wales and Northern Ireland and 10km resolution for Scotland. For mapping purposes Northern Ireland is displayed in an approximate position in the Irish Sea in all following maps. For Scotland the data obtained from MLURI described pH as average value per soil series, and thus may not represent the true spatial distribution. Data for Northern Ireland and England and Wales were derived from a measured sample within each 5km square.

5.1.5.2 Bulk density

The relationship between bulk density and organic carbon in the England & Wales data was established in order to interpolate bulk density for the rest of the country. Bulk density values ranged from 0.2 to 2.0 g/cm^3 and organic carbon ranged from 0.1 to 57.7%. The best fit was achieved when relating average organic carbon per bulk density value (0.2 – 2.0 in 0.1 increments) with the bulk density values (Figure 5.1.5.2)

Figure 5.1.5.2 Organic Carbon vs Bulk Density



$$\text{Bulk density} = -0.2863\text{Ln(OC)} + 1.3827 \qquad R^2 = 0.963$$

This relationship was used to estimate bulk density in Scotland and partially in Northern Ireland, where bulk density had not been measured at all sampling points.

5.1.5.3 Porosity

Broad porosity values were derived using a look-up table. The table, which originates from Ritjema (1970), relates soil texture classes to an approximate porosity value.

Table 5.1.1. Summary of porosity values for different soil textures

Soil Texture Class	Sub Classes used in Scotland	Porosity Value from Ritjema [%]
Sand (s)		36.1
Loamy sand (ls)	Humose loamy sand (hls)	29.6
Sandy silt loam (szl)	Humose sandy silt loam (hsz)	43.2
Sandy loam (sl)	Gravelly sandy loam (grs) Humose gravelly sandy loam (hgr) Humose sandy loam (hsl)	45.0
Fine sandy loam (fsl)	Humose fine sandy loam (fsl)	48.7
Silt loam (zl)		48.9
Sandy clay loam (scl)		37.2
Silty clay loam (zcl)		41.5
Clay loam (cl)		38.6
Silty clay (zc)		44.2
Clay (c)		42.1
Peat (p)	Organic (o)	76.5
Sandy clay (sc)		No data

The porosity values used are averages per soil texture class. However, soil texture classes are assigned to ranges of sand, silt and clay content and as the proportions vary within texture classes, porosity values are likely to vary.

5.1.5.4 Organic Carbon

Organic carbon data were merged from the available separate datasets to create a national dataset at 5km resolution (10km in Scotland). For Scotland the data obtained from MLURI described organic carbon as average value per soil series, and thus may not represent the true spatial distribution. Data for Northern Ireland and England and Wales were derived from a measured sample within each 5km square. Loss on Ignition values of organic matter were not directly available, but can be derived from organic carbon data. 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. In this application a mid-range value of 1.9 was chosen (LOI = 1.9 * organic C) and an upper limit of 99.9% was used where organic C content exceeded 50%. This conversion may not be suitable for organic soils.

5.1.5.5 Dissolved Organic Carbon

A national dataset of dissolved organic carbon (DOC) was not available for this study. Instead, a relationship from the report of the UN/ECE meeting at Bad Harzburg (1997) was used to derive DOC from organic carbon data.

$$\text{Log (DOC)} – 1.629 + 0.38 * \text{Log (\%LOI)}$$

The report stresses that this equation “is a very crude approximation (the percentage variance accounted for was only about 40% of the dissolved organic carbon concentration in Dutch forest soils)”.

5.1.5.6 Average Annual Runoff

This dataset, the 30-year mean annual data for 1941-70, was obtained from the Institute of Hydrology (now CEH), Wallingford at a 1km resolution. The locations of the sampling points of the metal datasets were used to select the corresponding 1km cell of the runoff dataset, which were then scaled up to be displayed at 5km for England, Wales and Northern Ireland or 10km for Scotland.

5.1.5.7 National maps

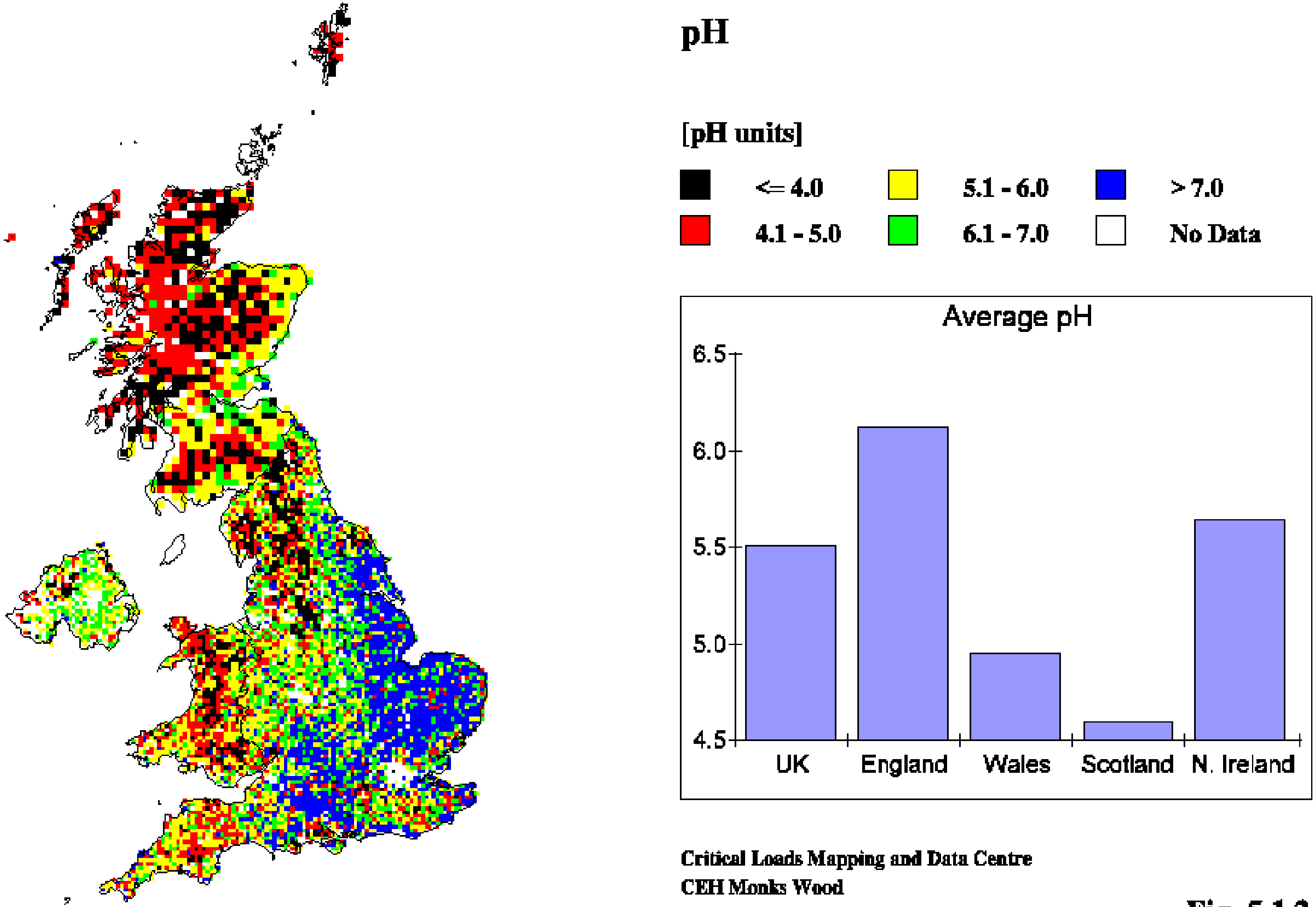
Figure 5.1.2 shows the maps for soil pH. Soil pH data, along with DOC & LOI, is needed to estimate metal concentrations in the reactive pool, the total porewater and free-ion fractions. The spatial pattern of pH is a general increase from less than pH 4 the north and west of Great Britain to greater than pH 7 in the south and east. Northern Ireland follows the same directional trend, although areas with more extreme pHs are relatively restricted. This overall trend is reflected in the average pHs for the different countries of the U.K..

Figure 5.1.3 shows the map of bulk density. Bulk density measurements are needed for dynamic modelling, and to relate measured soil concentrations per mass of soil to soil pools of metal per unit volume or area of the soil. Values of bulk density generally decease with increasing altitude, and values below 0.6 g cm^{-3} are usually found in uplands throughout the U.K..

Figure 5.1.4 shows the map of porosity. Soil porosity is used in dynamic modelling and in conversions between metal concentrations and pools. Soil porosity is almost the inverse of bulk density as mapped across the U.K., with high values at upland and organic soil sites, and low values in lowland mineral soils. As explained above, each soil texture class is assigned a distinct value of porosity. There are no values between 50 and 60%, in fact, the > 60 category comprises only the one value of 76.5%, and most values fall between 30 and 50% (cf. Table 5.1.1).

Figure 5.1.5 shows the maps of organic carbon. Soil organic carbon, along with DOC & pH, is used to estimate the reactive pool of metals from total soil metal concentrations, the total porewater and free-ion fractions. Soil organic carbon content follows a similar pattern to porosity values, increasing with altitude and highlighting lowland organic soils in Breckland and the Broads.

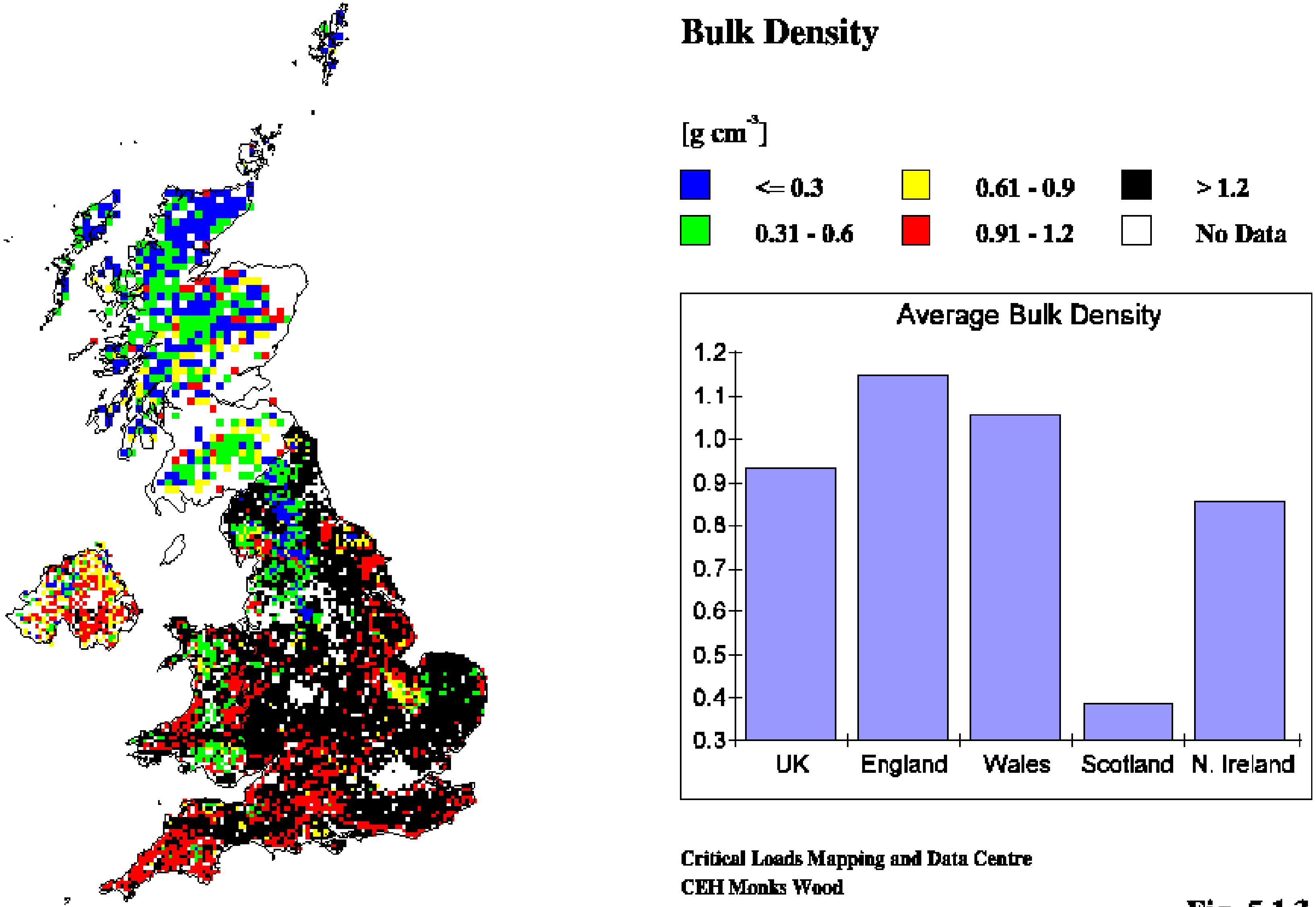
Figure 5.1.6 shows the derived map of Dissolved Organic Carbon (DOC). DOC follows the same patterns as porosity and soil organic carbon, with the highest



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

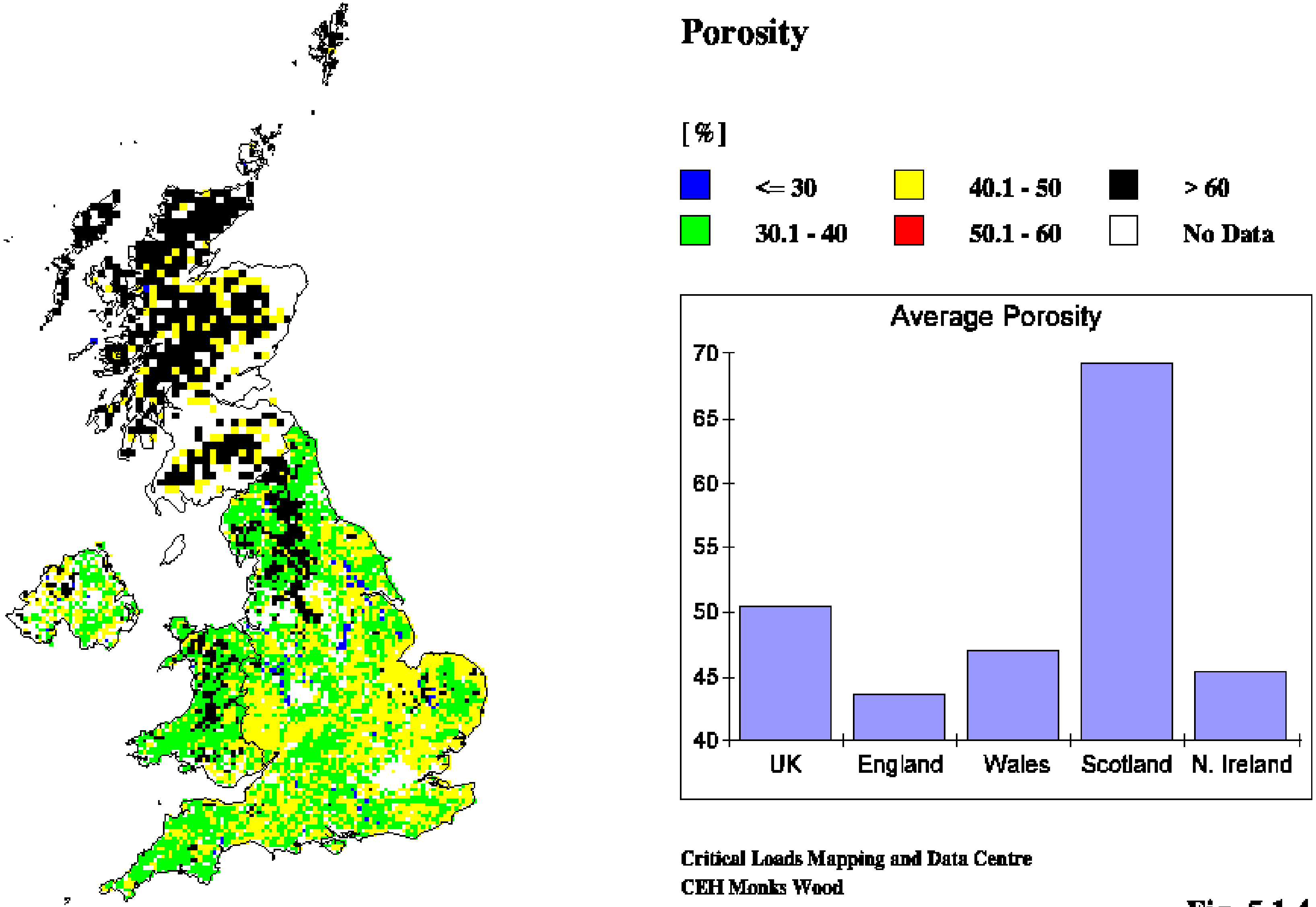
Fig. 5.1.2

Bulk Density



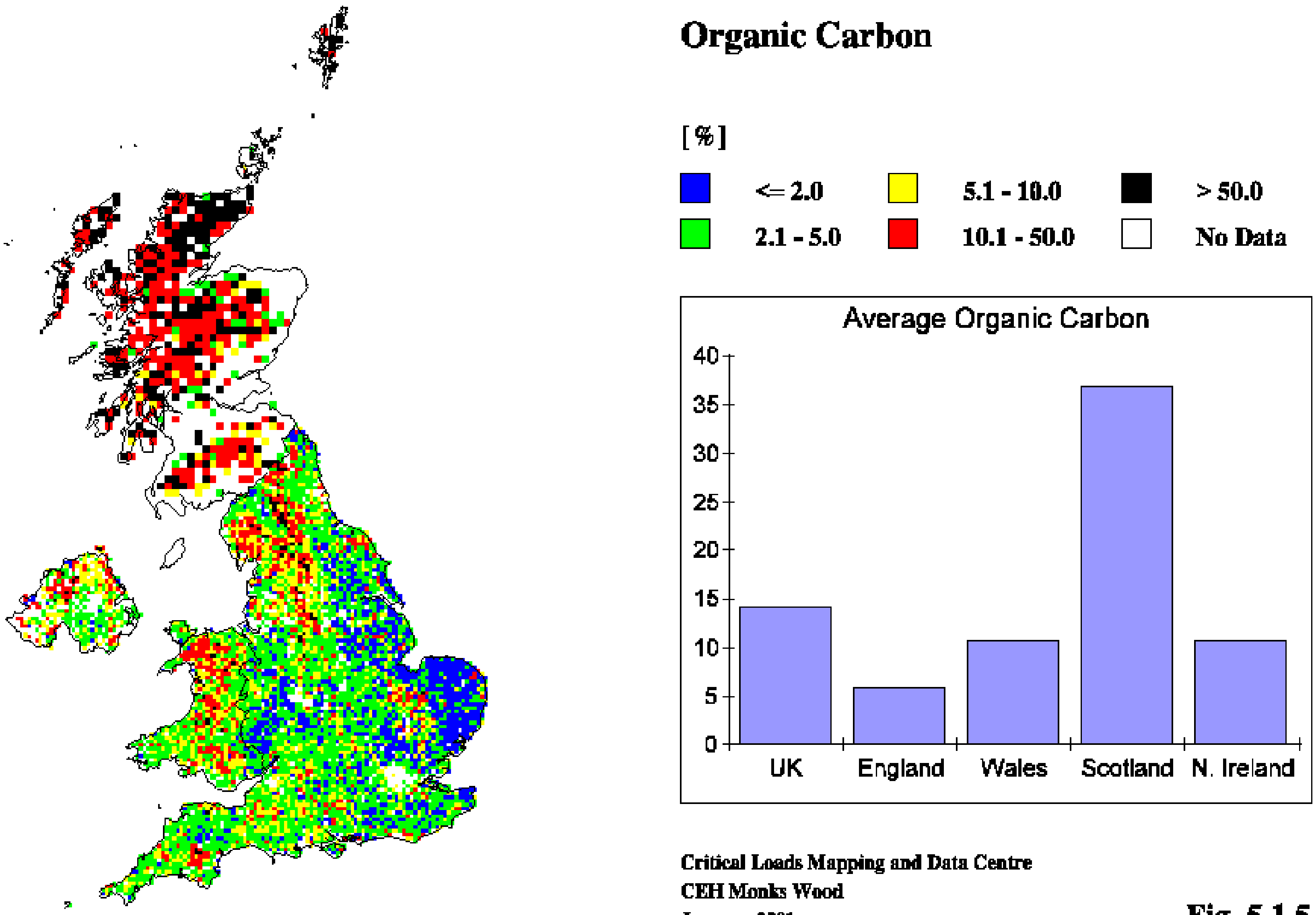
Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.1.3



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

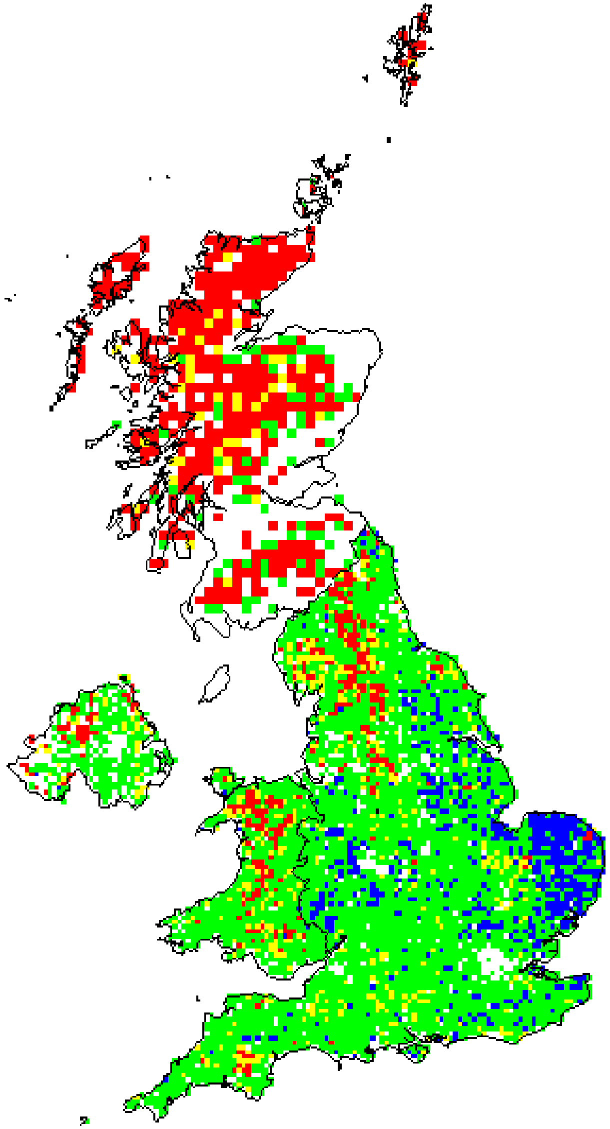
Fig. 5.1.4



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.1.5

Dissolved Organic Carbon



[mg l^{-1}]

🟦 <= 50

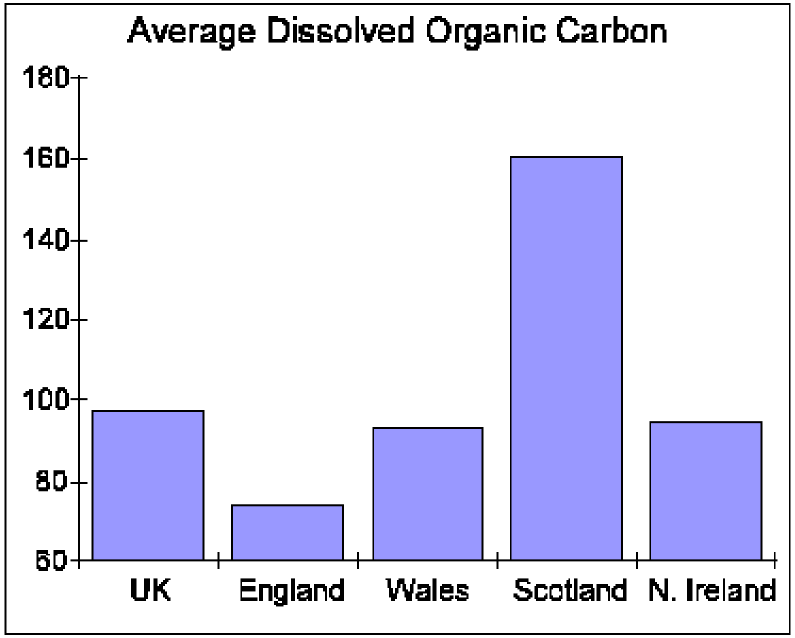
🟩 50.1 - 100

🟨 100.1 - 150

🟥 150.1- 200

⬛ > 200

⬜ No Data

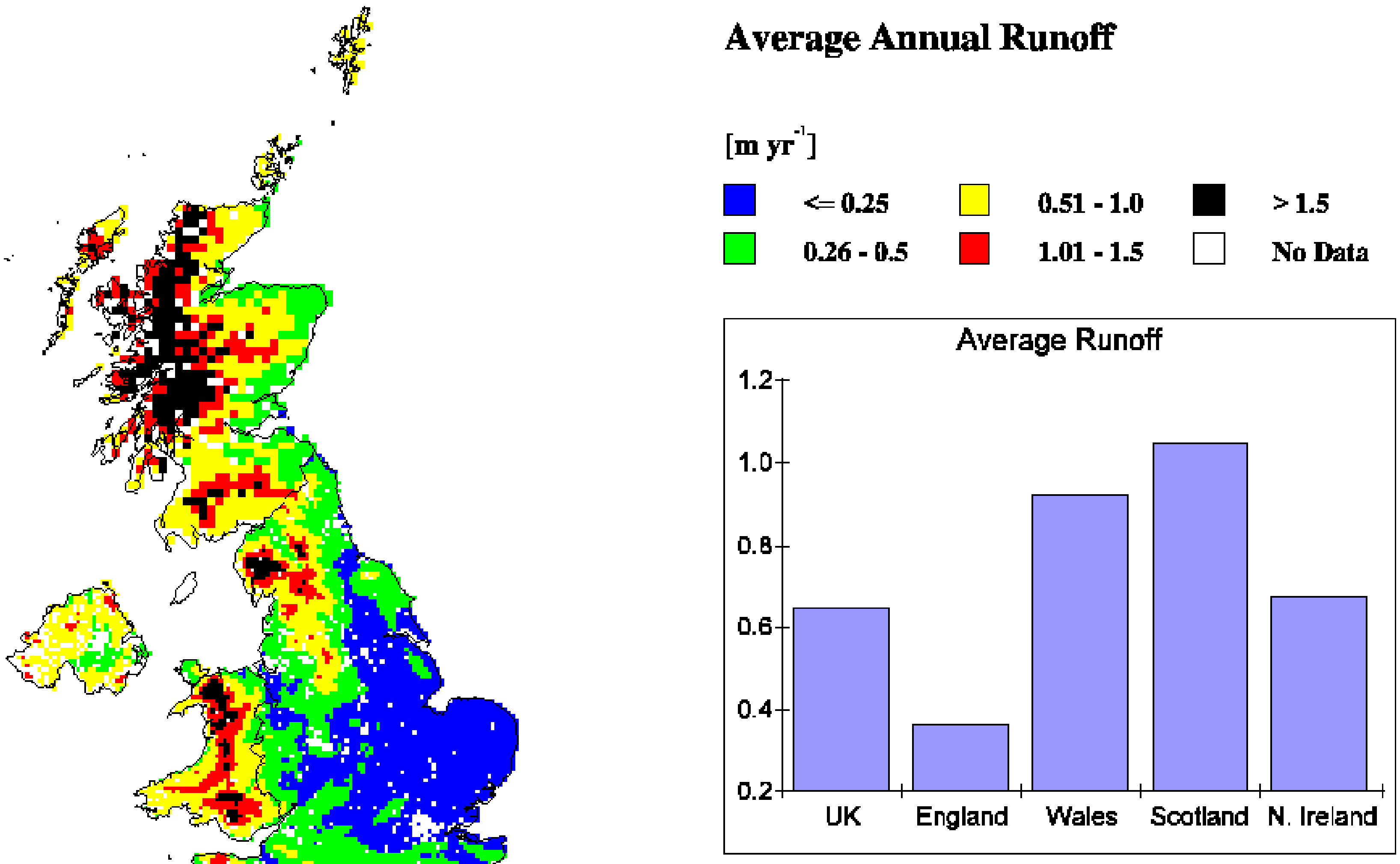


Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.1.6

average values in Scotland, the lowest for England, and Northern Ireland and Wales having the medium concentrations.

Figure 5.1.7 shows the maps of runoff. Average annual runoff is a key component of the calculation of critical loads, and is also used to calculate the amount of metal moving from upland terrestrial to aquatic ecosystems in dynamic modelling. The pattern follows rainfall, but is accentuated at higher latitudes and altitudes by the lower evapotranspiration fluxes throughout the year. Runoff is highest in the north and west of Great Britain, lowest in the east and south, with relatively uniform values equivalent to the Great Britain average in Northern Ireland.



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.1.7

5.2. Mapping of Soil and Soil Solution Concentrations

Before considering the application of critical limits and critical loads to the U.K., it is useful to assess the current position in terms of soil concentrations. As stated previously, many areas of the country have a long history of exposure to high levels of metal deposition, while elevated concentrations may be associated with the underlying geology in other areas. The transfer functions, whose derivation was described in Section 4, can be used along with the spatial datasets described in Section 5.1, to extend this analysis to an assessment of metal pools, expressed per unit land area rather than per unit soil mass, and to an assessment of the predicted soil solution and free-ion concentrations.

5.2.1. Total Soil Concentrations

Figures 5.2.1 to 5.2.4 show the ‘current’ total soil concentrations in topsoils across the U.K.. It is important to note that the data for England and Wales are from the early 1980s, when the Geochemical Atlas of England and Wales was completed. The data for Northern Ireland, in contrast were collected for this contract during 1999. The ‘no data’ areas represent urban areas, those covered by freshwater, and those where access is problematical. As explained earlier, the data for Scotland are based on a lower sampling density.

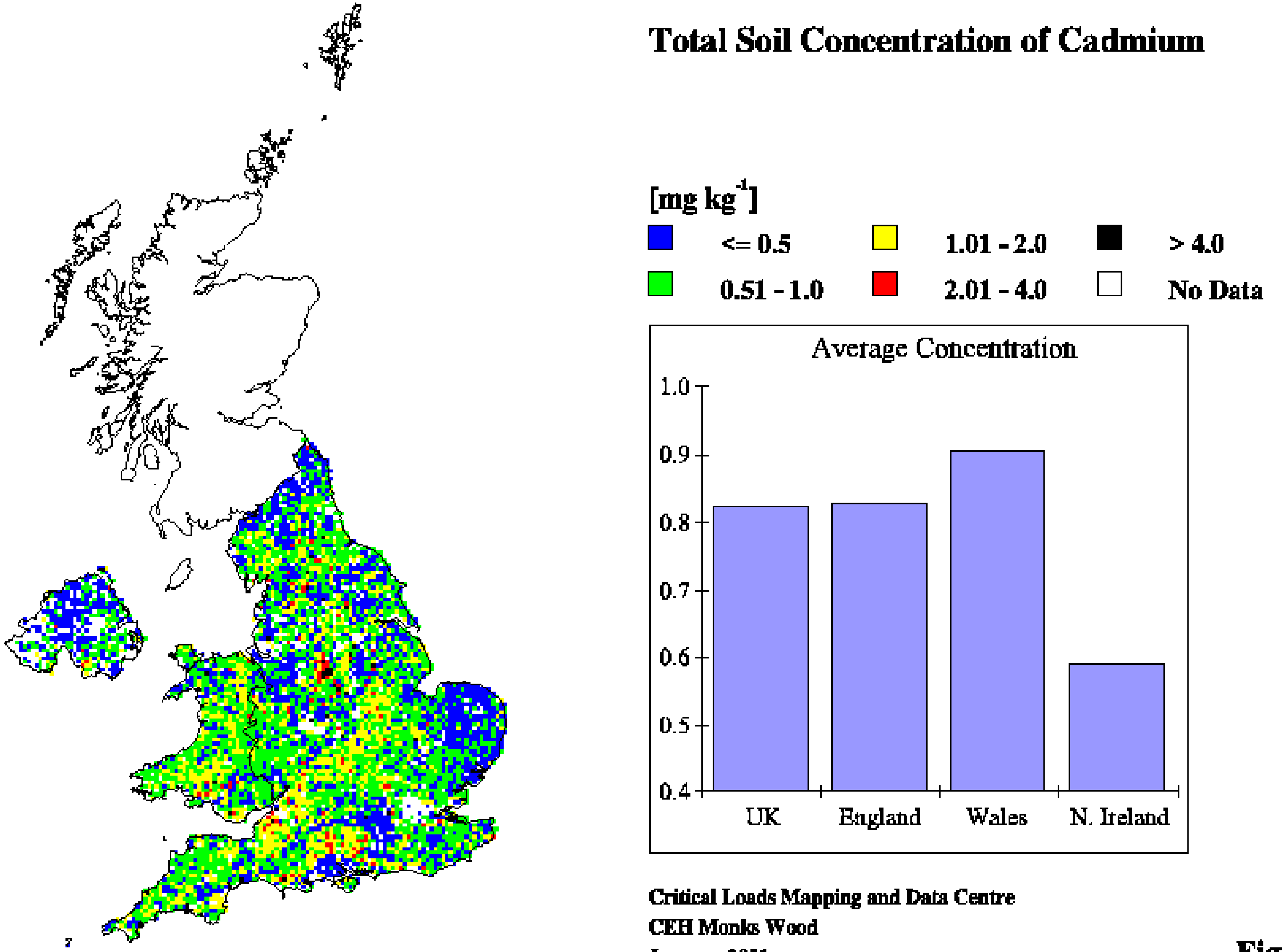
These maps were presented for England and Wales in the report of Phase I of this project (EPG 1/3/85). The data for Northern Ireland show lower concentrations of cadmium and lead than in England and Wales, possibly reflecting lower rates of deposition. However, concentrations of copper are significantly higher than those in England and Wales, with an area of particularly high concentrations in the basalt areas to the north of the province. Zinc concentrations are lower overall than in England and Wales, although there are, as for copper, higher concentrations in the north-east of the province.

No data are available for cadmium for Scotland. For lead, the data for the southern half of the country show a pattern which is similar to that for England and Wales, with the highest concentrations either in upland regions or close to urban areas. However, concentrations are consistently lower over the northern half of Scotland. Concentrations of copper and zinc in Scotland show a different pattern, with higher concentrations in the urban/industrial regions, and with concentrations in rural areas which are consistently lower than those in England and Wales.

5.2.2. Reactive Soil Concentrations

Figs 5.2.5-5.2.8 present the distributions of reactive soil concentrations, predicted using the transfer functions which were described in Table 4.2.2. Since these functions are based only on soils collected from upland areas, the upland mask has been applied in this and all subsequent maps throughout the country, as we cannot be sure that the transfer functions can be applied to lowland agricultural soils. There is no major difference in the spatial distributions of the measured total and modelled reactive soil concentrations, although the visual impression of the maps is quite different from the previous series, given the limited area which is considered.

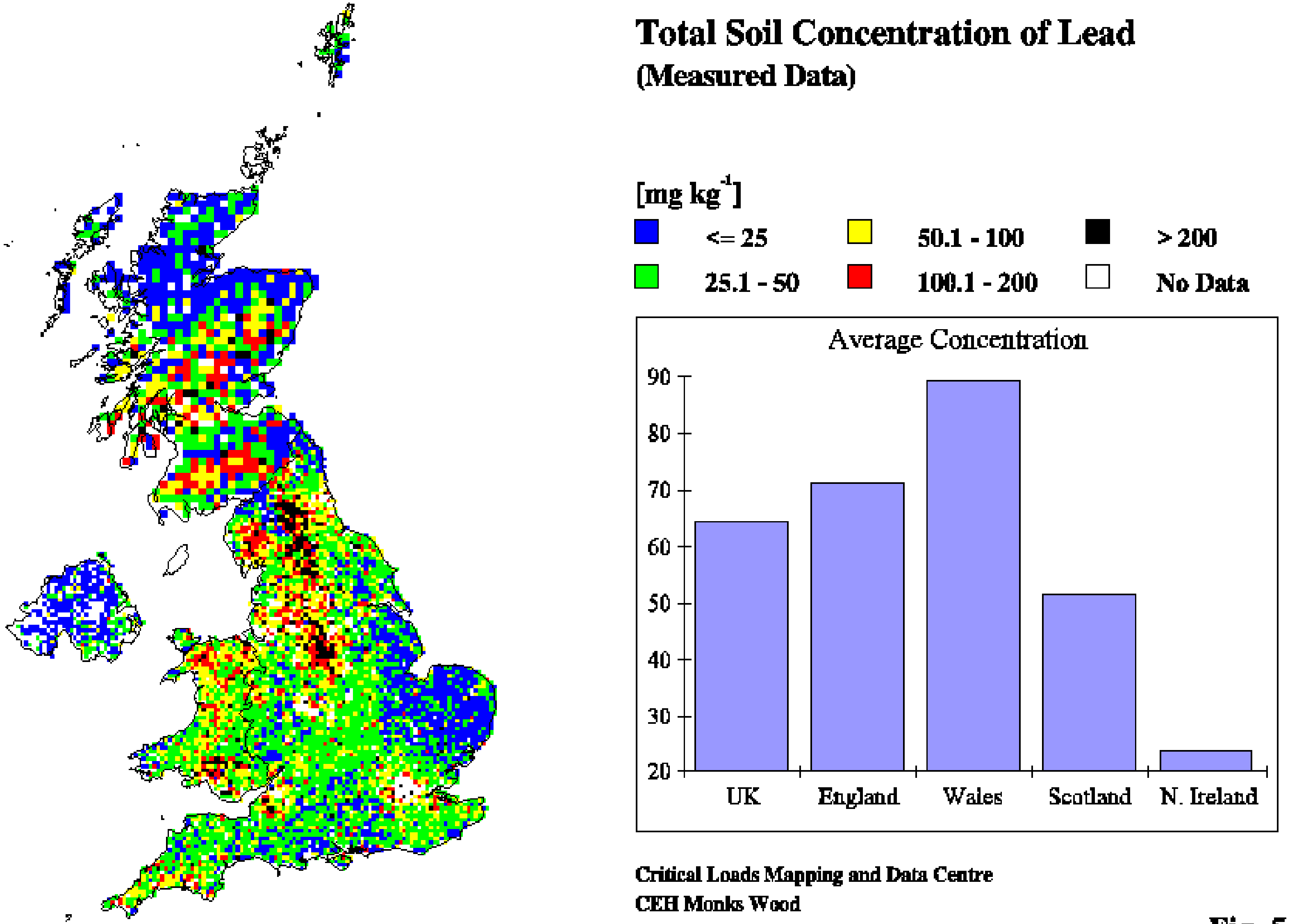
Total Soil Concentration of Cadmium



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

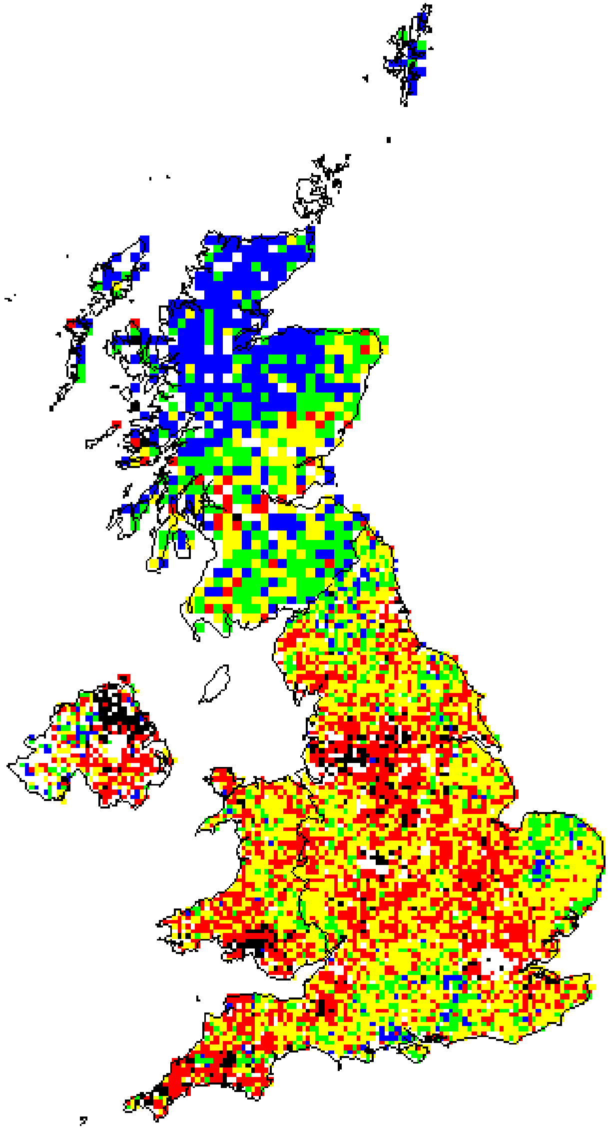
Fig. 5.2.1

Total Soil Concentration of Lead
(Measured Data)



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

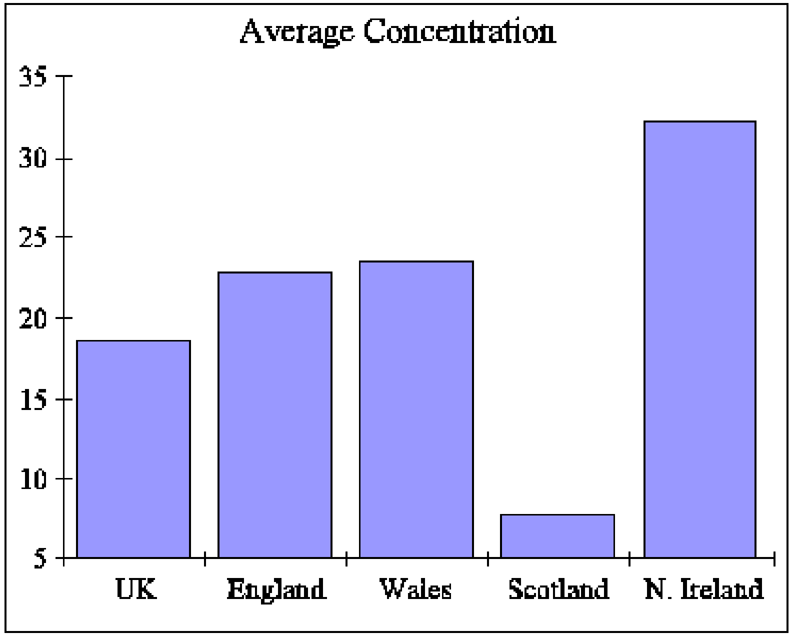
Fig. 5.2.2



Total Soil Concentration of Copper
(Measured Data)

[mg kg^{-1}]

🟦 <= 5 🟨 10.1 - 20 ⬛ > 50
🟩 5.1 - 10 🟥 20.1 - 50 ☐ No Data

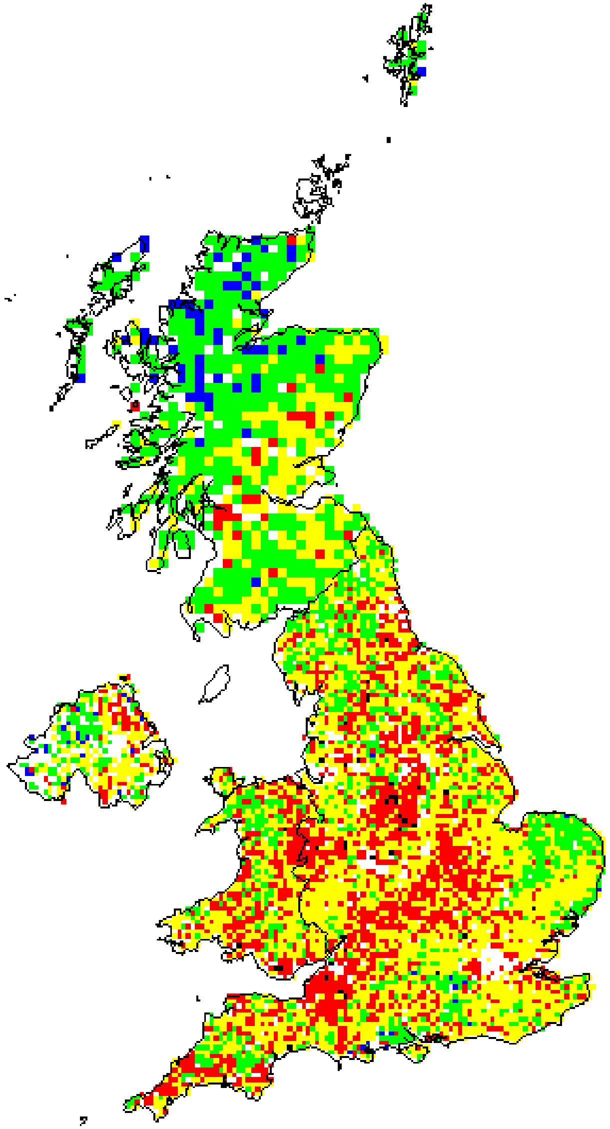


Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.3

Total Soil Concentration of Zinc

(Measured Data)



[mg kg^{-1}]

🟦 <= 10

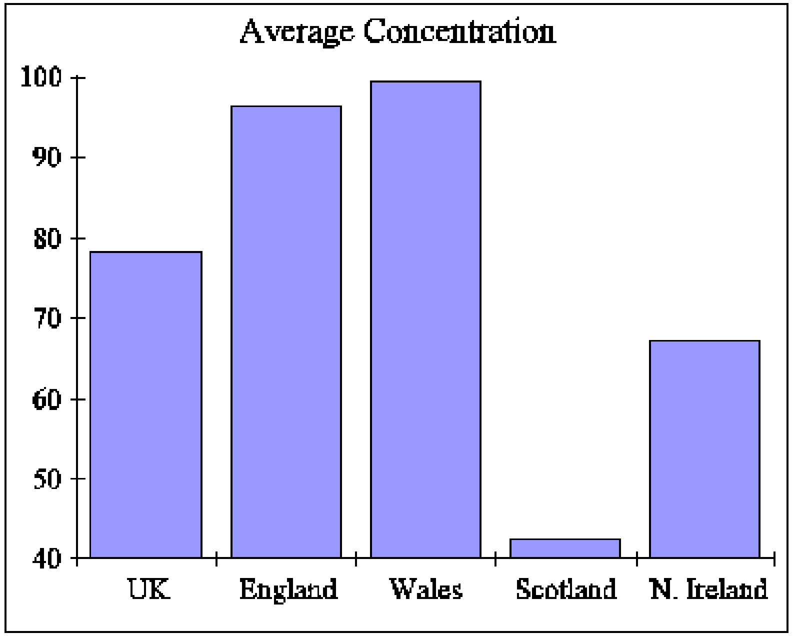
🟩 10.1 - 50

🟨 50.1 - 100

🟥 100.1 - 500

■ > 500

☐ No Data

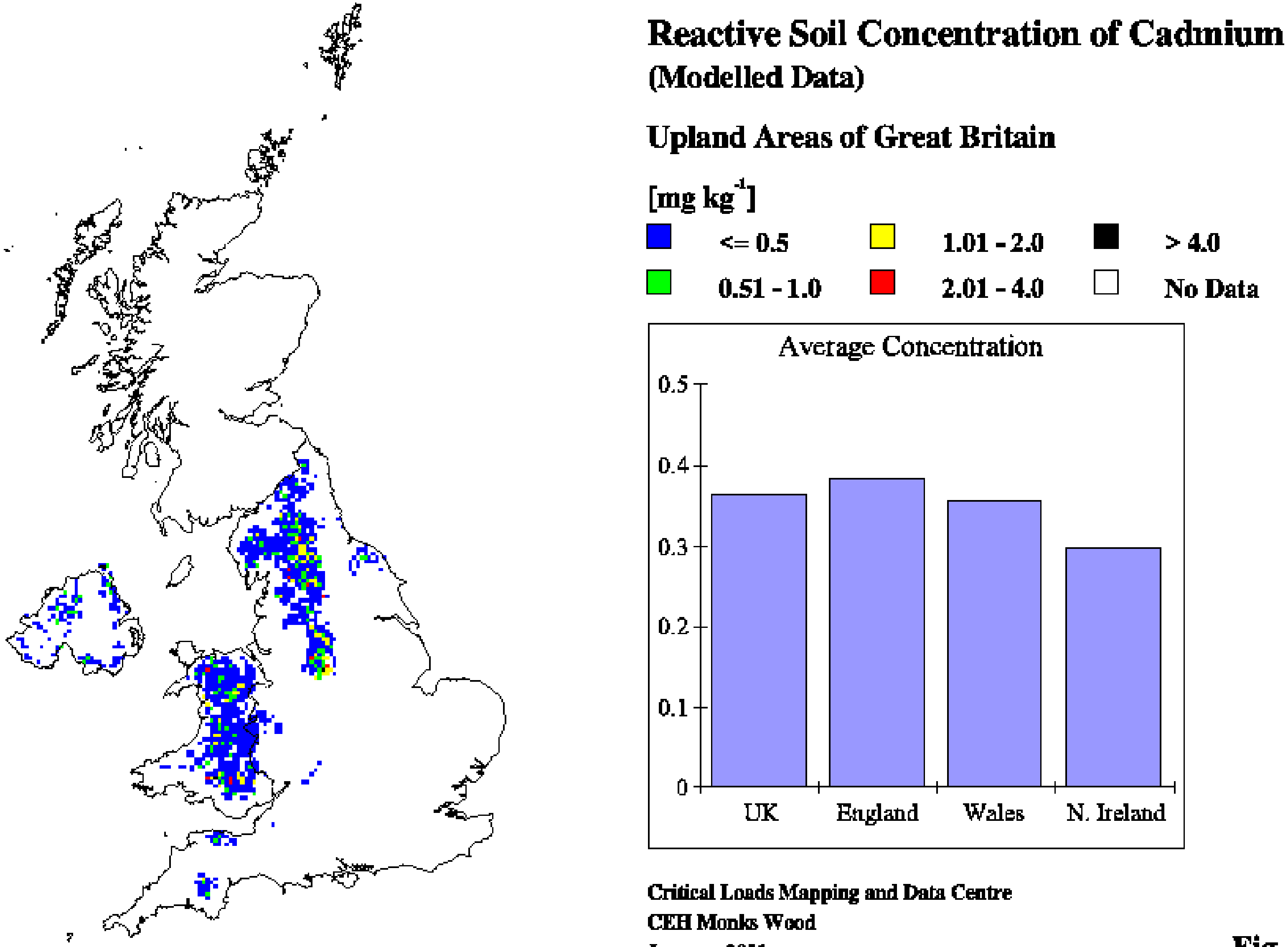


Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.4

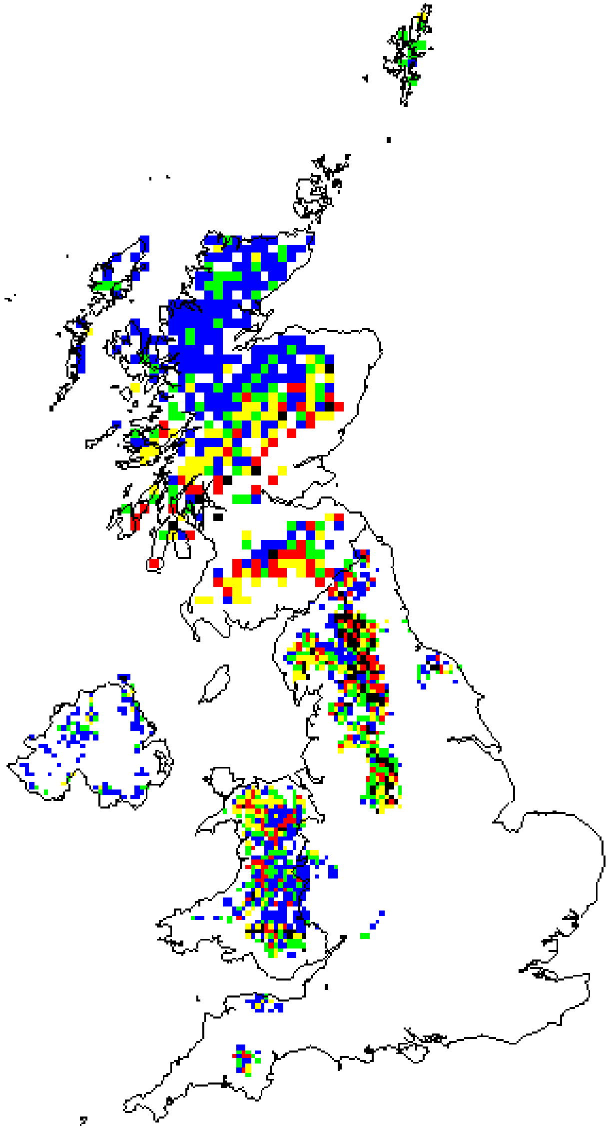
Reactive Soil Concentration of Cadmium
(Modelled Data)

Upland Areas of Great Britain



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.5

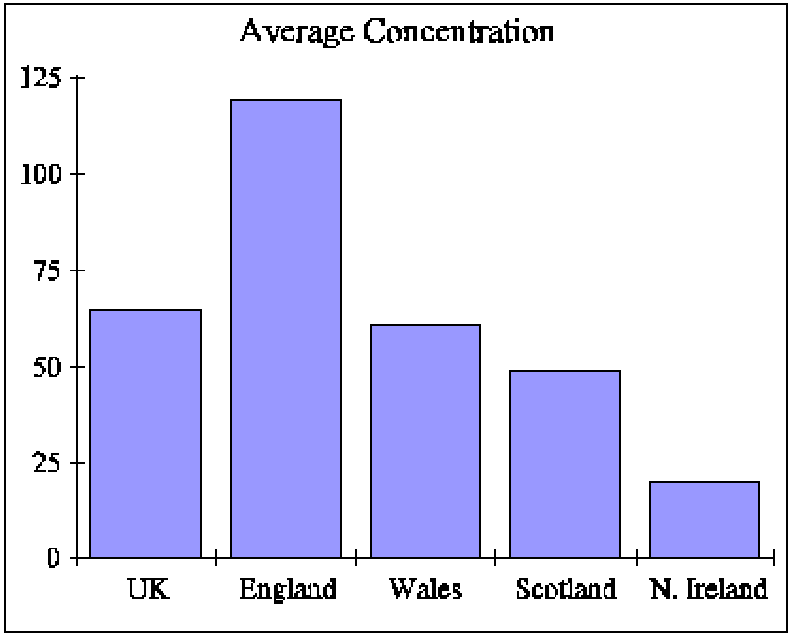


Reactive Soil Concentration of Lead
(Modelled Data)

Upland Areas of Great Britain

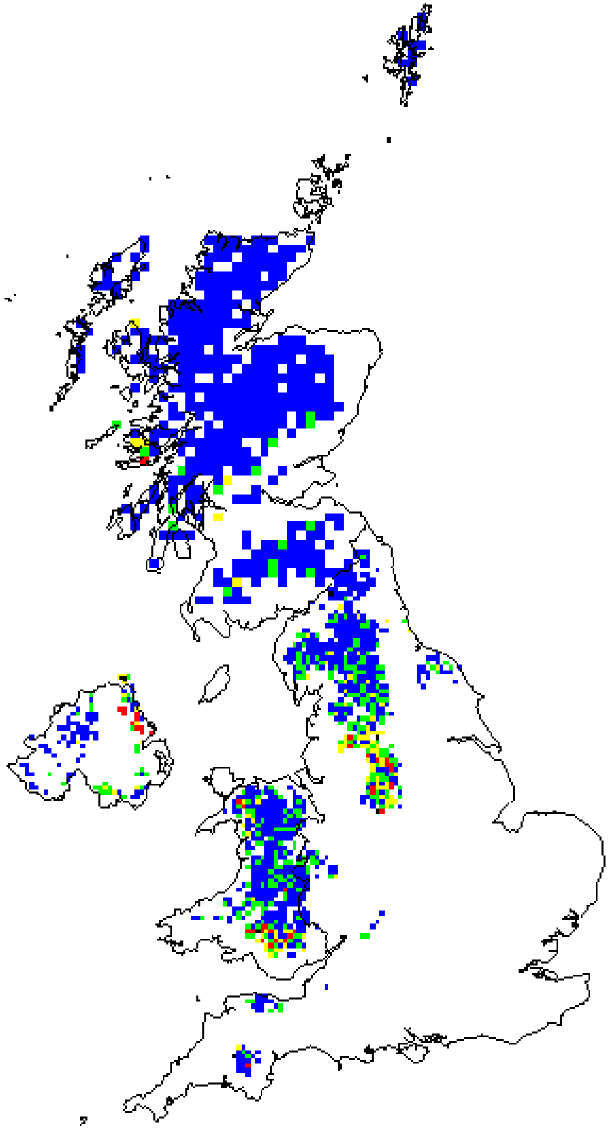
[mg kg^{-1}]

🟦	<= 25	🟨	50.1 - 100	⬛	> 200
🟩	25.1 - 50	🟥	100.1 - 200	☐	No Data



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.6



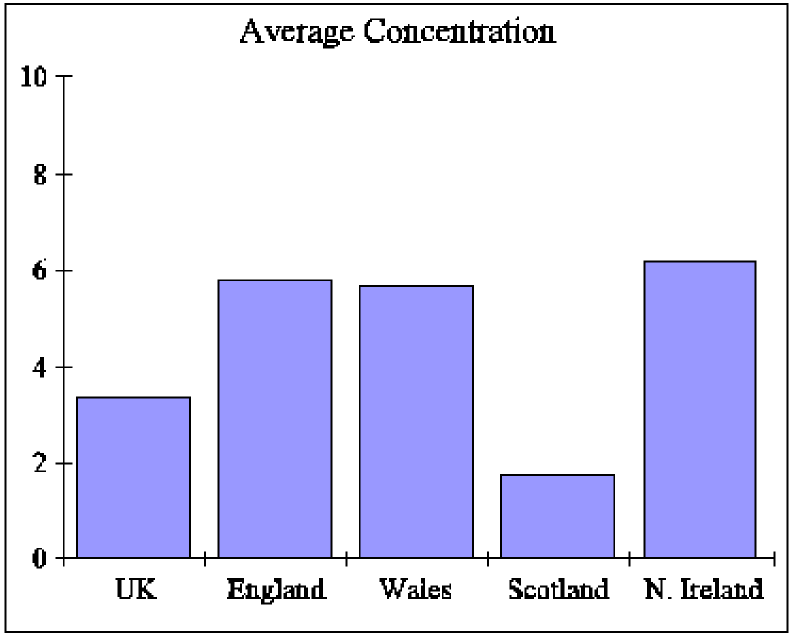
Reactive Soil Concentration of Copper

(Modelled Data)

Upland Areas of Great Britain

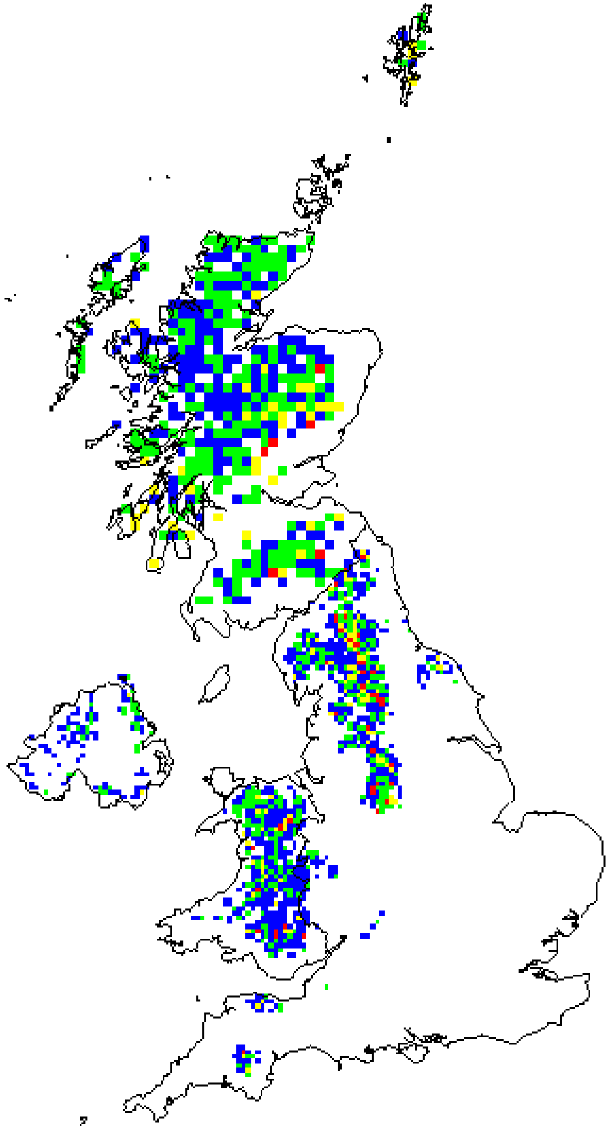
[mg kg^{-1}]

🟦	<= 5	🟨	10.1 - 20	■	> 50
🟩	5.1 - 10	🟥	20.1 - 50	□	No Data



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.7



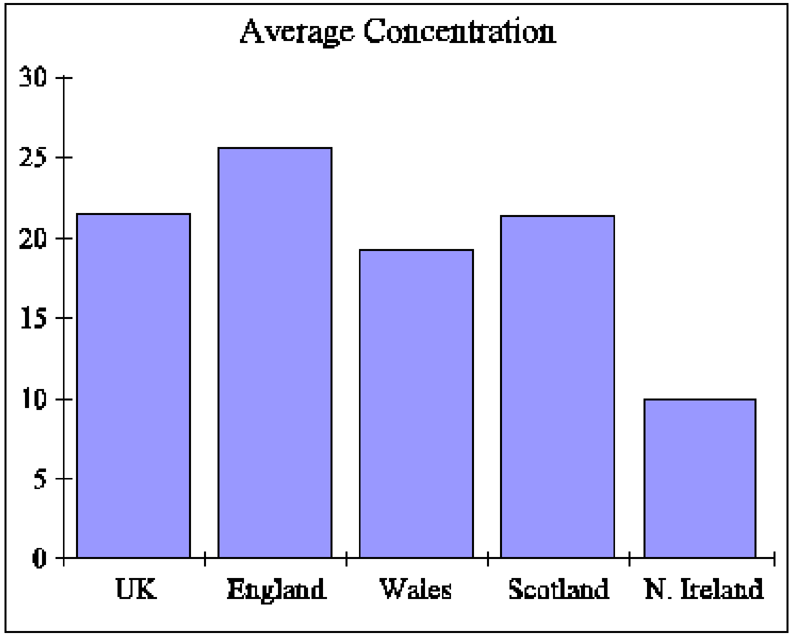
Reactive Soil Concentration of Zinc

(Modelled Data)

Upland Areas of Great Britain

[mg kg^{-1}]

🟦	<= 10	🟨	50.1 - 100	■	> 500
🟩	10.1 - 50	🟥	100.1 - 500	□	No Data



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.8

5.2.3. Reactive Soil Pools

The previous two series of maps presented the national or upland distributions of soil concentrations. However, when considering the dynamics of responses of soils to changes in metal deposition from the atmosphere, it is important to consider the pool of metal and not just the concentration. The conversion of metal concentration (in mg kg^{-1}) to metal pool (mg m^{-2}) depends on the bulk density and porosity of the soil, which, as shown in Figures 5.1.3 and 5.1.4, vary considerably across the U.K., and the assumed soil depth. The peat soils which dominate many U.K. upland areas have a low bulk density, and thus the metal concentrations in these areas may change more rapidly in response to a given metal deposition than would be the case in other soils. Values of the depth of the surface horizon were available for England & Wales and Northern Ireland, and an arbitrary depth of 15cm was used for data points where depth data were not available (primarily peats in Scotland and some points in England & Wales and Northern Ireland). The use of the surface horizon was based on the fact that this is where the majority of microbial activity takes place.

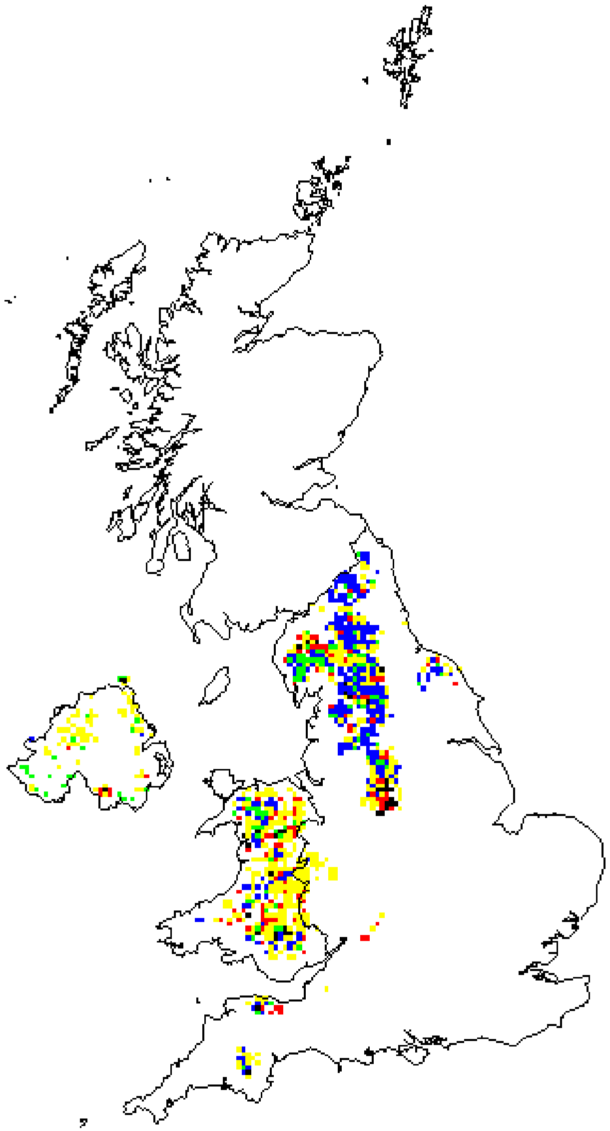
The dramatic effect of mapping soil pools rather than soil concentrations is clear from the map for cadmium, which in terms of concentrations showed elevated levels only in parts of the Pennines. Fig. 5.2.9 shows that the modelled reactive soil pool in parts of Wales and Northern Ireland is comparable to that in the more polluted parts of the Pennines.

Figs 5.2.10-5.2.12 show similarly, the reactive soil pools for lead, copper and zinc, which can be compared with the equivalent reactive pool concentrations in Figs. 5.2.6-5.2.8. In all cases, the lower bulk density in the northern Pennines and over much of Scotland compared to the rest of England, Wales and Northern Ireland, has a dramatic effect on the national distribution of metals. These maps probably provide a better picture of the relative impact of historical metal deposition than do those based on metal concentration.

5.2.4. Total Soil Solution and Free-Ion Concentrations

The transfer functions described in Section 4.2.2 have been used to model the soil solution and free ion concentrations which are in equilibrium with the total soil concentrations mapped in Figs 5.2.1-5.2.4. It is very important to note that in the field soil solution concentrations will show considerable temporal variation, and thus these modelled concentrations should only be considered as an approximate guide to the relative concentrations of these metals in soil solution in different parts of the country which are in equilibrium with the measured total soil concentrations.

Figs 5.2.13-5.2.16 show the modelled total soil solution concentrations for the four metals, using the relationships in Table 4.2.3 and in Figures 4.2.1-4.2.4. Total porewater concentrations can be predicted with most confidence from the modelled free-ion activities (using transfer functions in Table 4.2.3) and then the relationship between the proportion of soil solution metal as free-ions and pHs as shown in Figures 4.2.1-4.2.4. Where the derived total porewater concentration exceeds the modelled free-ion activity, however, uncertainties in the estimation of the proportion of metals as free-ions have a greater impact on predictions of total porewater concentrations. Therefore, when free-ion activity/total porewater concentration was

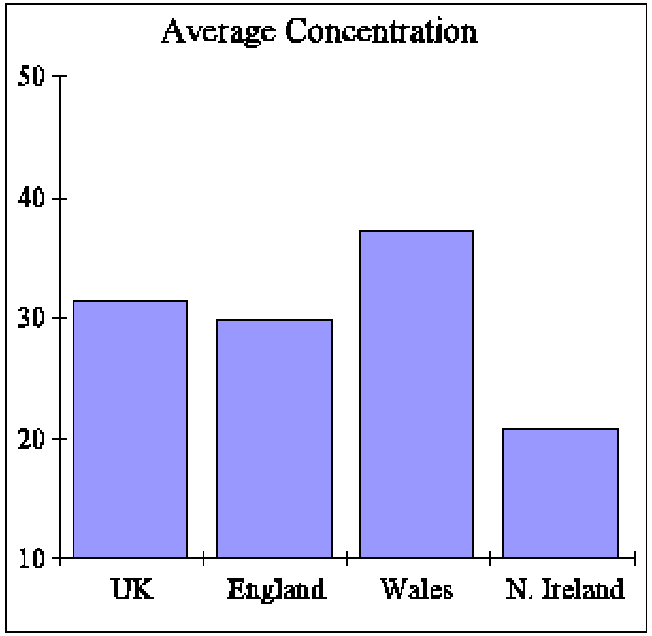


Reactive Soil Pool of Cadmium
(Modelled Data)

Upland Areas of Great Britain

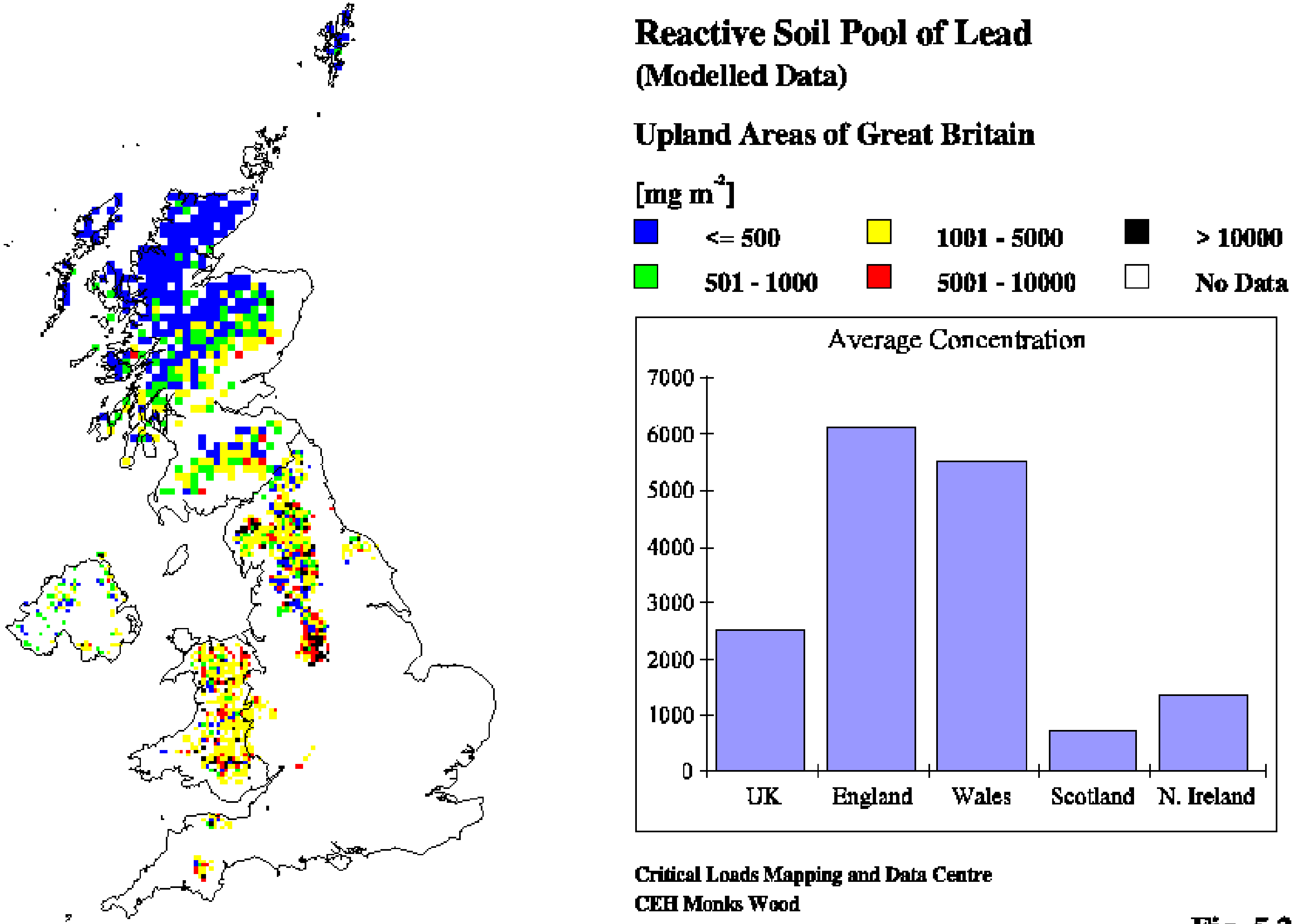
[mg m^{-2}]

🟦	<= 5	🟨	10.1 - 50	⬛	> 100
🟩	5.1 - 10	🟥	50.1 - 100	⬜	No Data



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.9



Reactive Soil Pool of Lead

(Modelled Data)

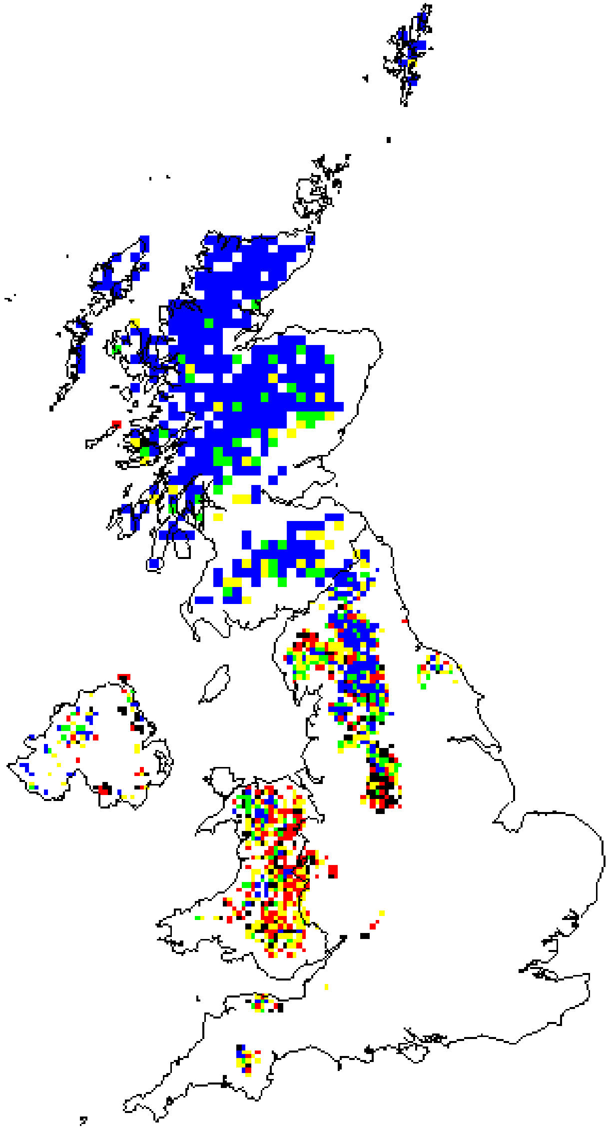
Upland Areas of Great Britain

[mg m^{-2}]

🟦 <= 500
🟩 501 - 1000
🟨 1001 - 5000
🟥 5001 - 10000
⬛ > 10000
☐ No Data

Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.10

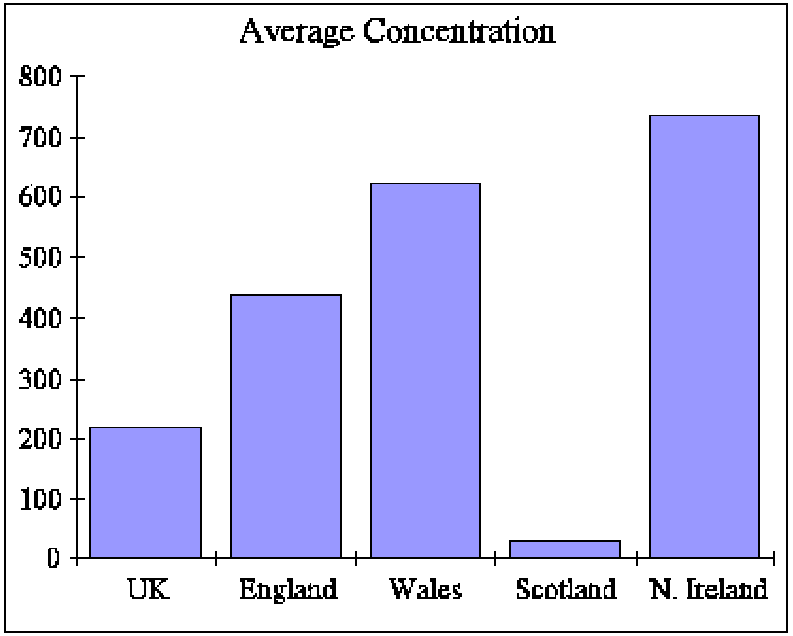


Reactive Soil Pool of Copper
(Modelled Data)

Upland Areas of Great Britain

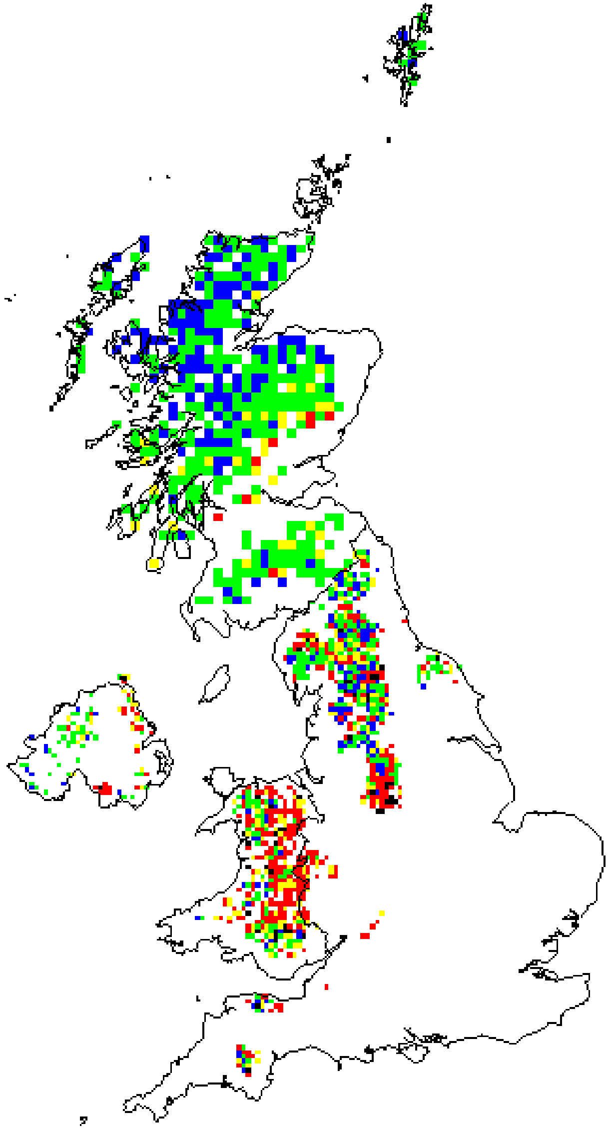
[mg m^{-2}]

🟦	<= 50	🟨	101 - 500	⬛	> 1000
🟩	51 - 100	🟥	501 - 1000	⬜	No Data



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.11



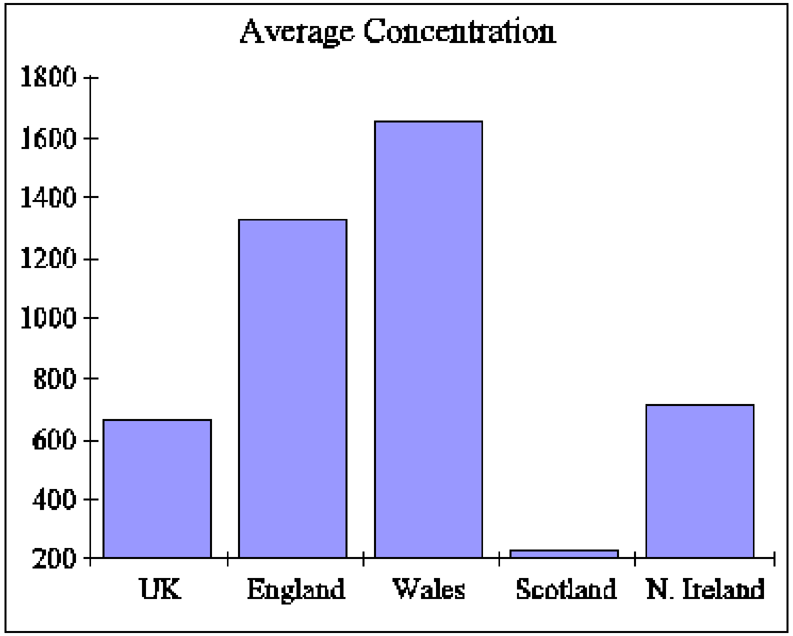
Reactive Soil Pool of Zinc

(Modelled Data)

Upland Areas of Great Britain

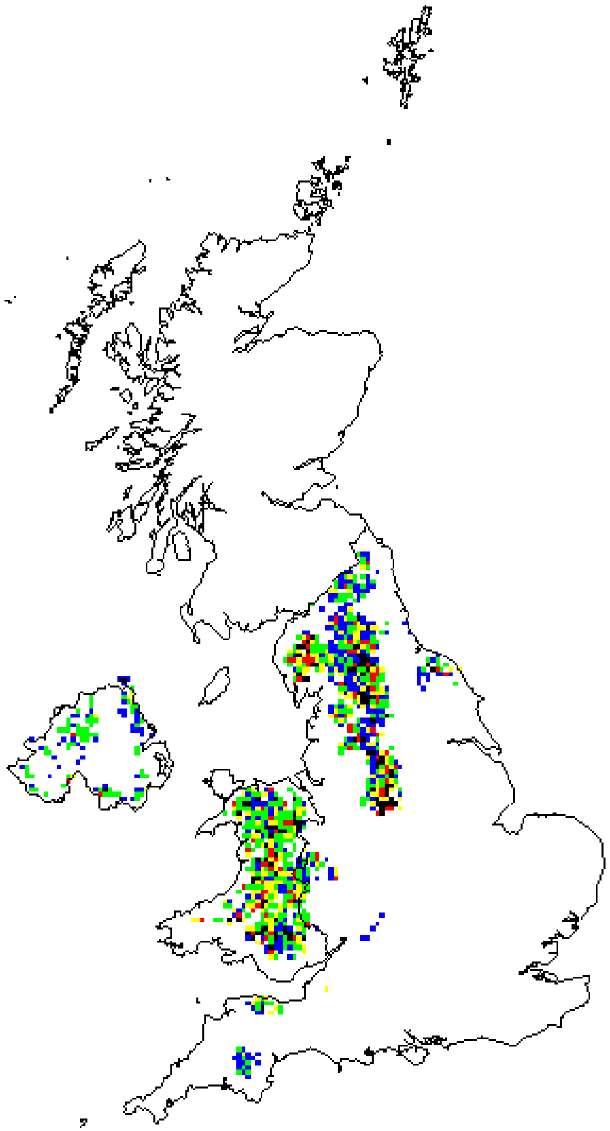
[mg m^{-2}]

🟦	<= 100	🟨	501 - 1000	■	> 5000
🟩	101 - 500	🟥	1001 - 5000	□	No Data



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.12



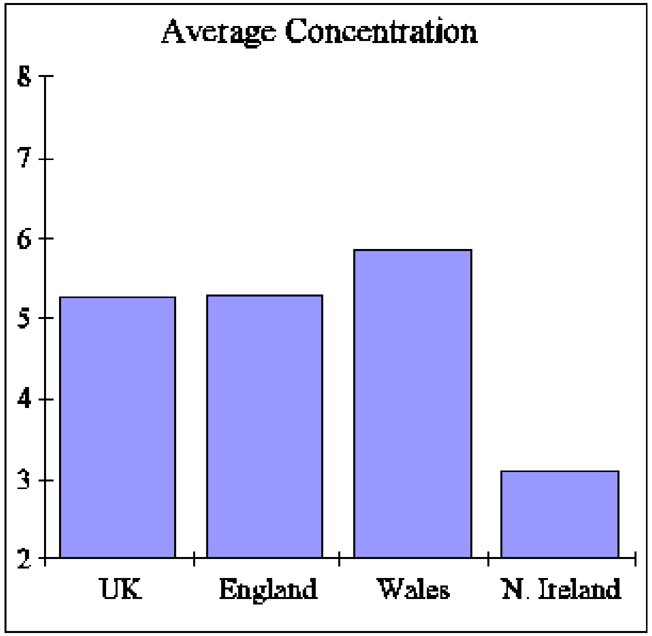
Total Soil Solution Concentration of Cadmium

(Modelled Data)

Upland Areas of Great Britain

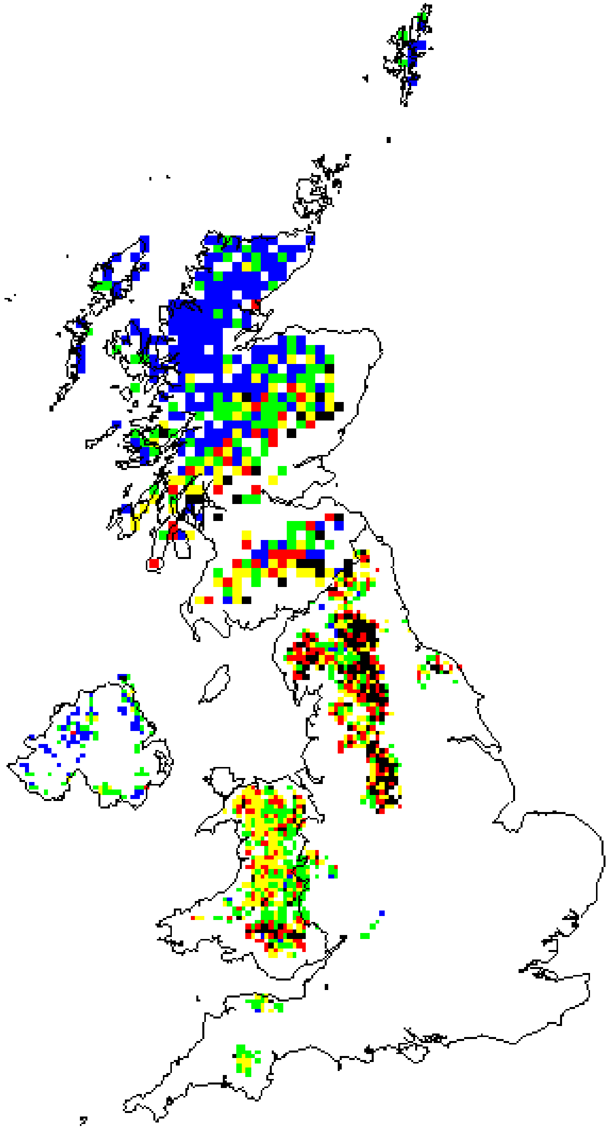
[10^{-9} mol l^{-1}]

🟦	<= 2.5	🟨	5.01 - 7.5	⬛	> 10.0
🟩	2.51 - 5.0	🟥	7.51 - 10.0	☐	No Data



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.13

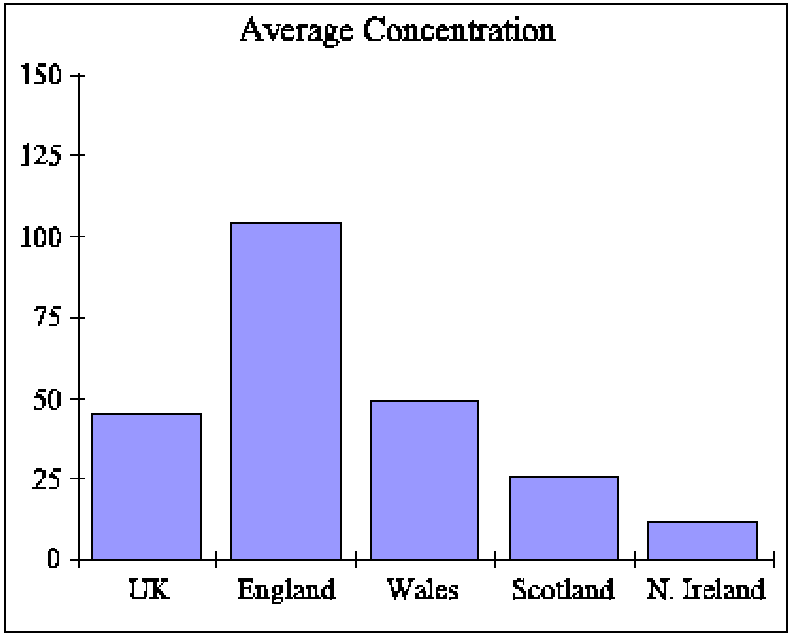


Total Soil Solution Concentration of Lead
(Modelled Data)

Upland Areas of Great Britain

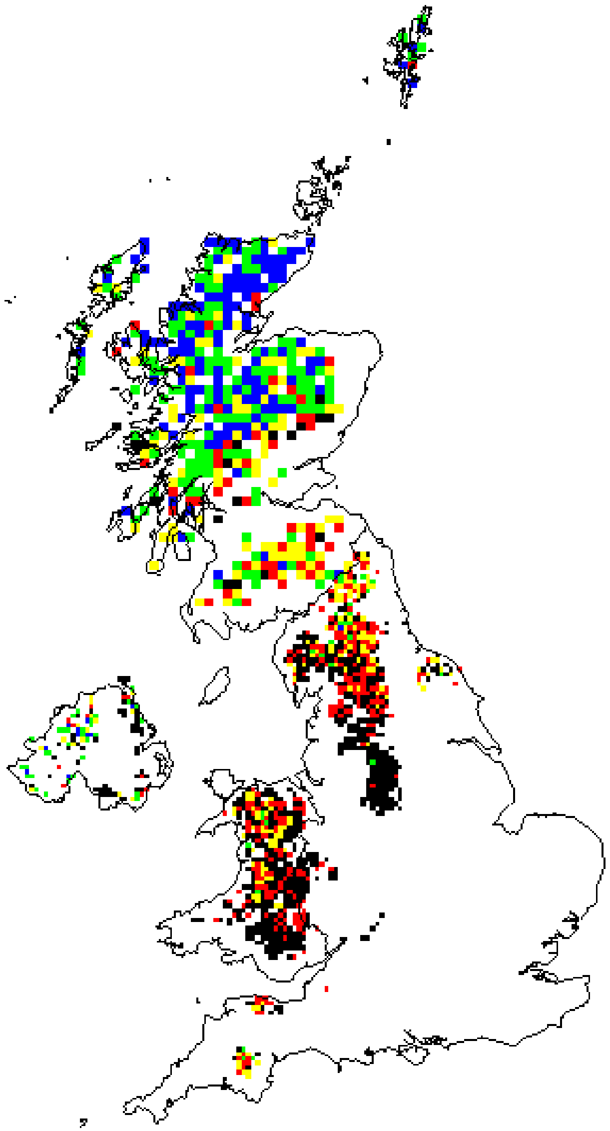
[10^{-9} mol l^{-1}]

🟦	<= 10	🟨	25.1 - 50	■	> 100
🟩	10.1 - 25	🟥	50.1 - 100		



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.14



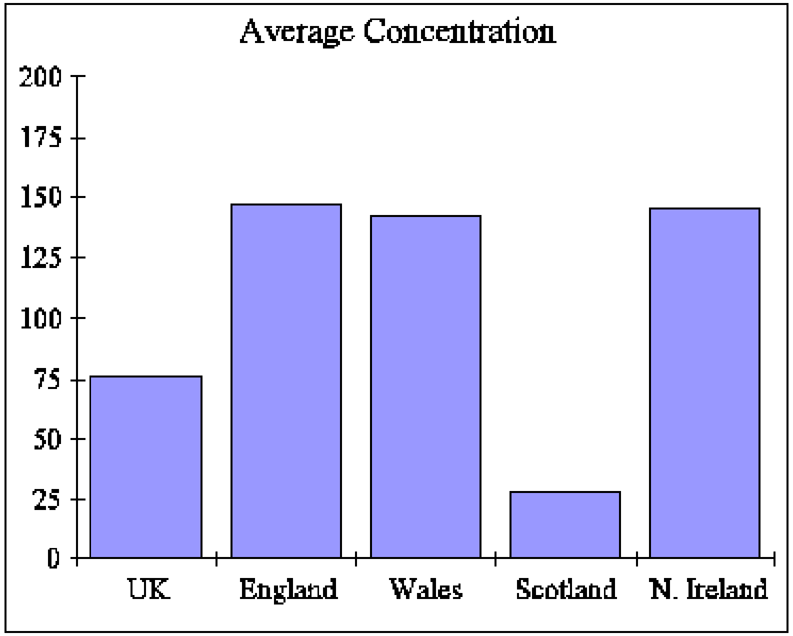
Total Soil Solution Concentration of Copper

(Modelled Data)

Upland Areas of Great Britain

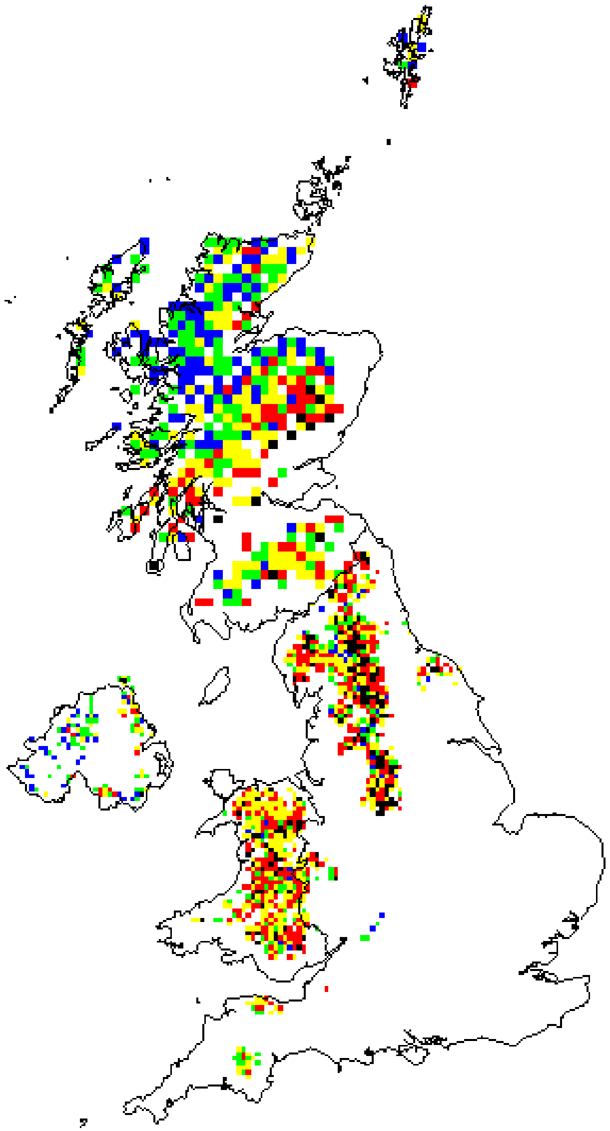
[10^{-9} mol l^{-1}]

- 🟦 <= 10
- 🟩 10.1 - 25
- 🟨 25.1 - 50
- 🟥 50.1 - 100
- ■ > 100



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.15



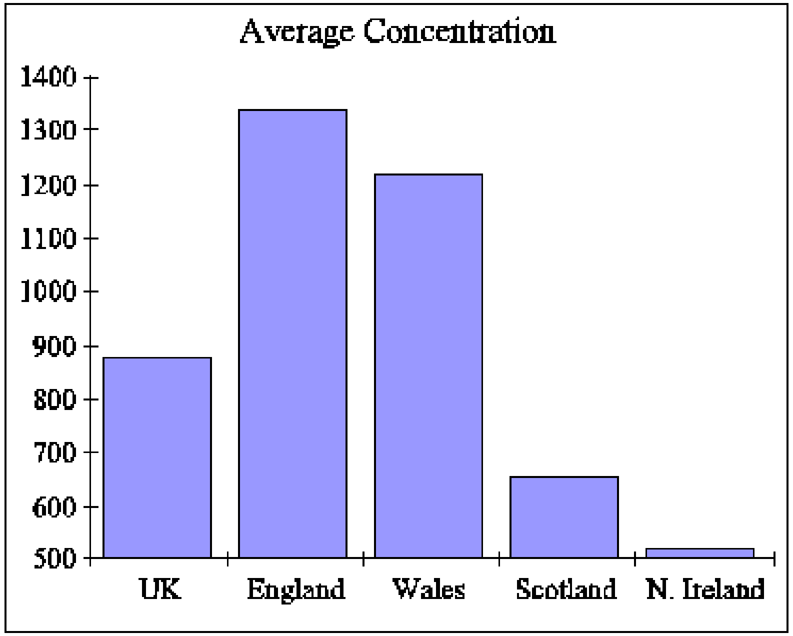
Total Soil Solution Concentration of Zinc

(Modelled Data)

Upland Areas of Great Britain

[10^{-9} mol l^{-1}]

🟦	<= 250	🟨	501 - 1000	⬛	> 2000
🟩	251 - 500	🟥	1001 - 2000	⬜	No Data



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.16

predicted to be less than 0.5, porewater concentration was then estimated using the k_d relationships for total porewater concentrations in Table 4.2.3. This empirical decision system is designed to minimise the effect of measurement and modelling uncertainties on predictions of total porewater concentrations.

Figs. 5.2.17-5.2.20 show the modelled free ion concentrations, derived using the relationships in Table 4.2.3. Given the high R^2 values, and the strong dependence on pH, there is less uncertainty in the transfer functions used to derive these maps than there is for the maps of total soil solution concentration. However, as for total soil solution concentration, these maps only give an indication of the broad regional patterns in free-ion concentration, given the strong spatial and temporal variability which is likely in the field. The maps of modelled free-ion and total soil solution concentration are interpreted together for each metal in the text below, including a comparison with the reactive soil concentrations shown in Figs. 5.2.5-5.2.8.

For cadmium, the spatial distribution of the modelled free-ion (Fig. 5.2.17) and total soil solution (Fig. 5.2.13) concentrations is very similar, reflecting the fact that our models suggest that most of this metal is in the form of free-ions at the ranges of pH in most upland soils. Whereas the map of reactive soil concentration (Fig. 5.2.5) shows only isolated areas of elevated concentrations, those of free-ion and total soil solution concentrations show elevated concentrations in many of the acidic soils of upland England and Wales, although the modelled concentrations in Northern Ireland are much lower.

In the case of lead, there is a stronger contrast between the modelled free-ion concentrations (Fig. 5.2.18) and the modelled total soil solution concentrations (Fig. 5.2.14). In particular, many areas of the Pennines have very high modelled concentrations of total soil solution lead, but rather low free-ion concentrations, reflecting the greater significance of organic complexes for lead than for cadmium. The relative spatial patterns of the modelled free-ion concentrations are broadly comparable to those of the reactive soil concentrations (Fig. 5.2.6).

There are major differences between all three distributions in the case of copper. The map of modelled reactive soil concentration (Fig. 5.2.7) shows only isolated areas of elevated concentration in South Wales, the southern Pennines and Northern Ireland. In contrast, the map of modelled total soil solution concentration (Fig. 5.2.15) shows elevated concentrations through much of the Pennines, Cumbria and Wales, and in parts of Northern Ireland, reflecting the effect of modelled DOC; the concentrations fall gradually when moving north across Scotland. The modelled free-ion concentrations (Fig. 5.2.19) shows a different pattern again; with concentrations being much lower than the modelled total soil solution concentrations, especially in Northern Ireland, and much of northern England and North Wales. As for lead, this reflects the significance of organic complexes in porewaters.

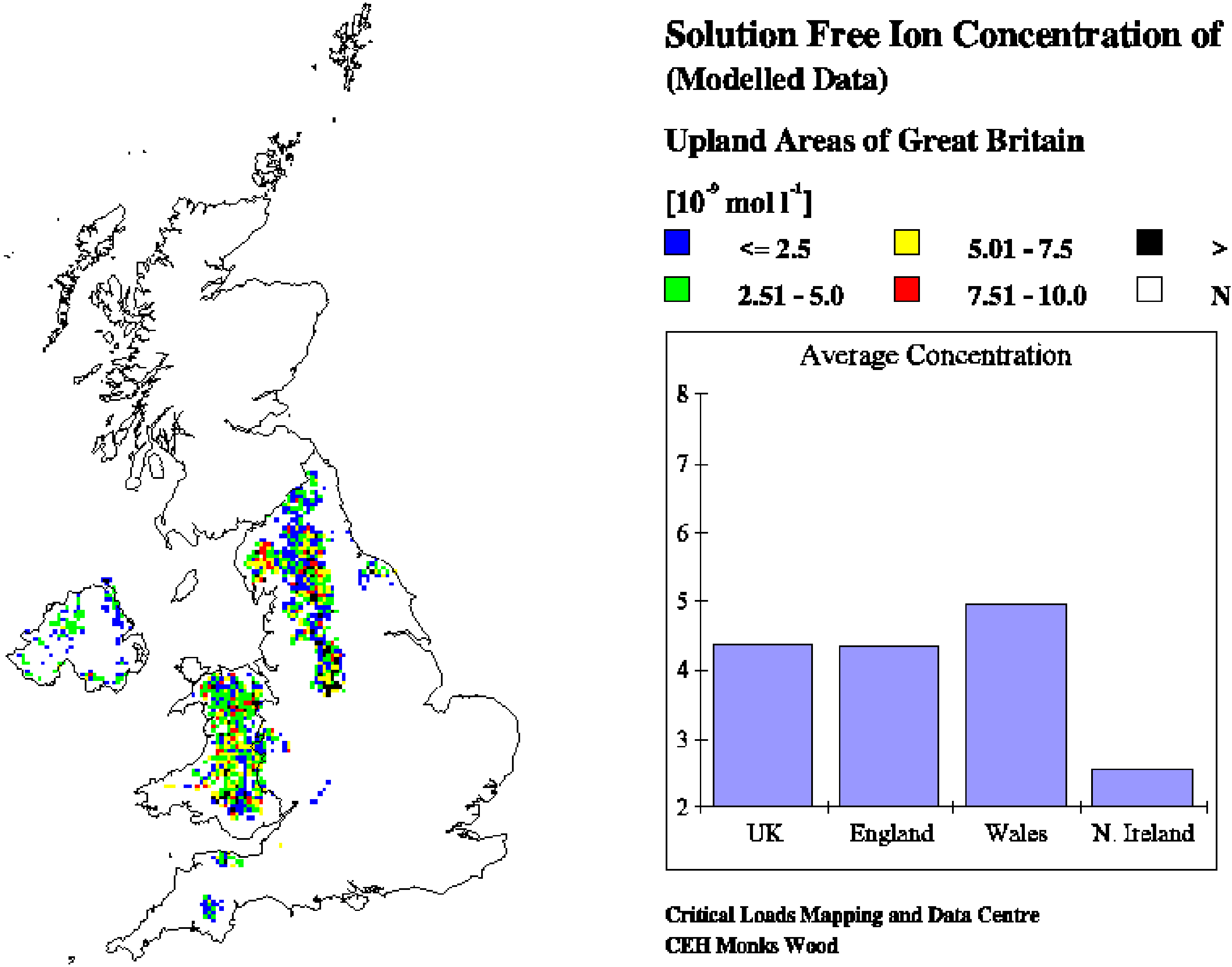
The pattern for zinc is comparable with that for cadmium. There is little difference between the absolute values of modelled total soil solution concentration (Fig. 5.2.16) and modelled free-ion concentration (Fig. 5.2.2), reflecting the predominance of uncomplexed ions over much of the upland pH range. There is a strong contrast between these maps and that for reactive soil concentration (Fig. 5.2.8), which shows little difference between the individual countries, with limited areas of elevated

Solution Free Ion Concentration of Cadmium
(Modelled Data)

Upland Areas of Great Britain

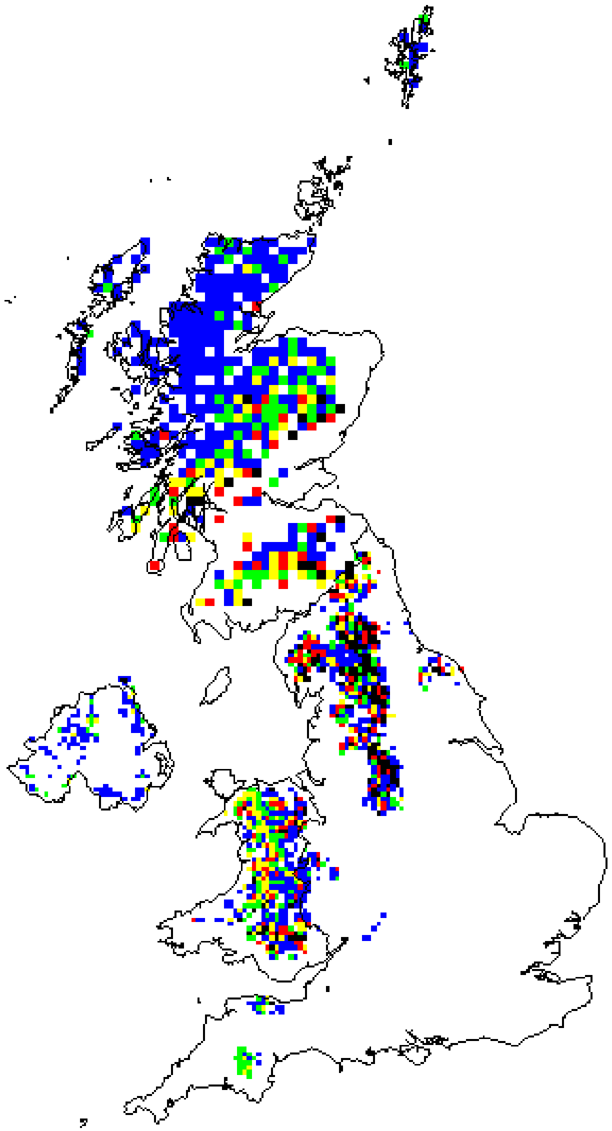
[10^{-9} mol l^{-1}]

🟦	<= 2.5	🟨	5.01 - 7.5	■	> 10.0
🟩	2.51 - 5.0	🟥	7.51 - 10.0	☐	No Data



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.17



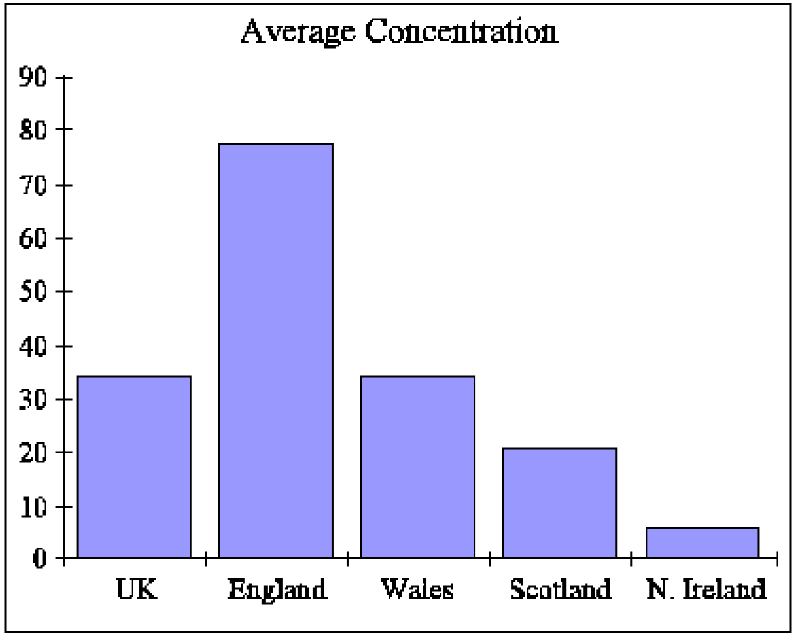
Solution Free Ion Concentration of Lead

(Modelled Data)

Upland Areas of Great Britain

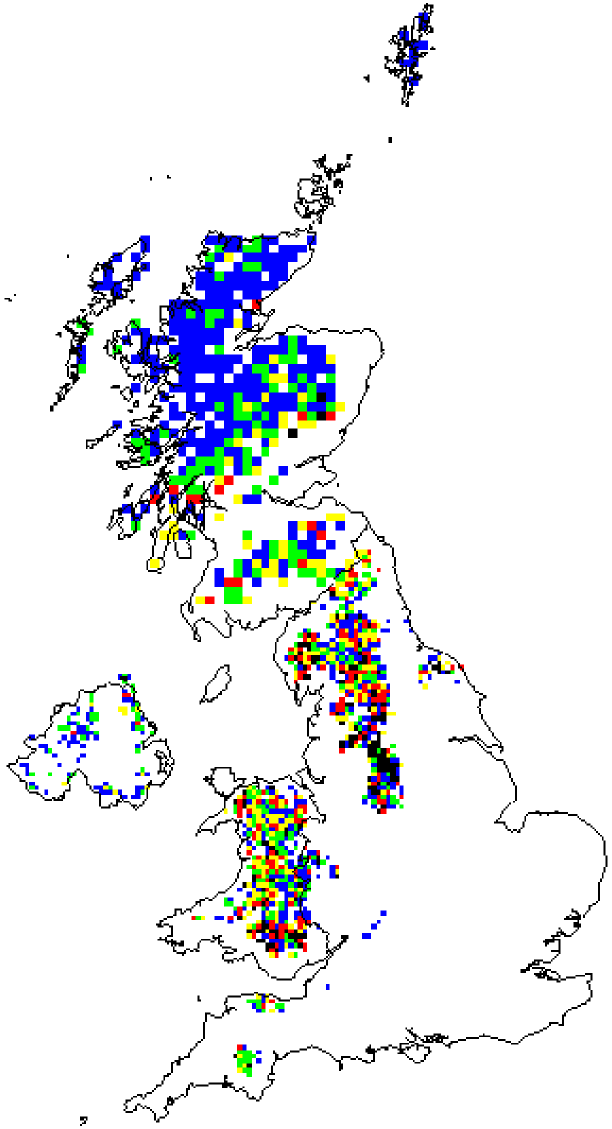
[10^{-9} mol l^{-1}]

🟦	<= 10	🟨	25.1 - 50	⬛	> 100
🟩	10.1 - 25	🟥	50.1 - 100		



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.18



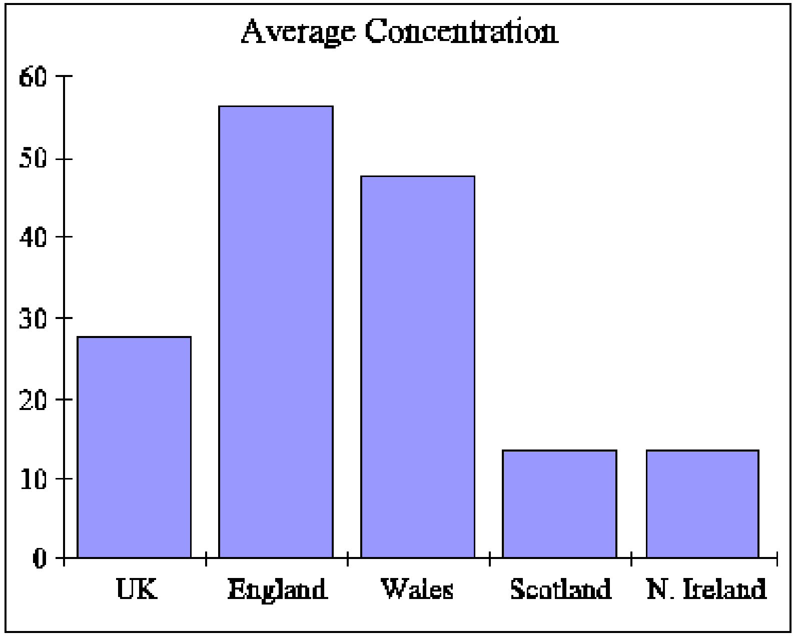
Solution Free Ion Concentration of Copper

(Modelled Data)

Upland Areas of Great Britain

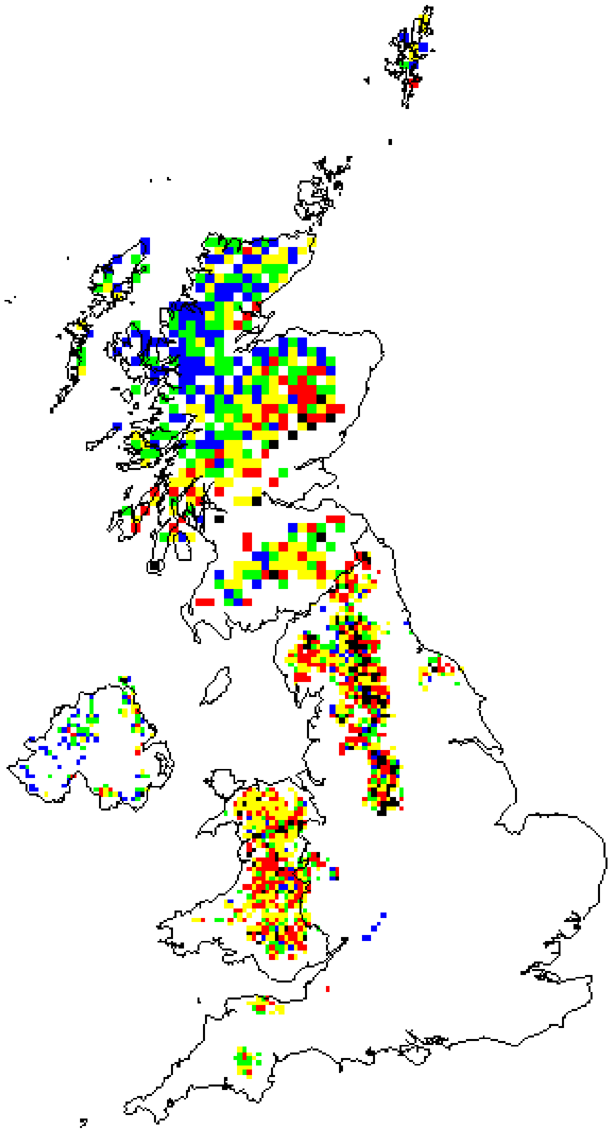
[10^{-9} mol l^{-1}]

🟦 <= 10
🟩 10.1 - 25
🟨 25.1 - 50
🟥 50.1 - 100
⬛ > 100



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.19



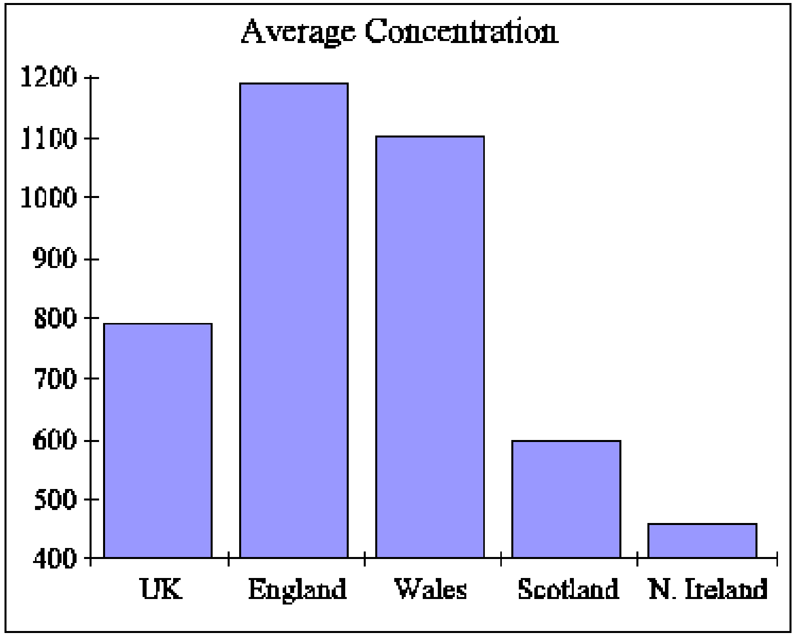
Solution Free Ion Concentration of Zinc
(Modelled Data)

Upland Areas of Great Britain

[10^{-9} mol l^{-1}]

🟦 <= 250 🟨 501 - 1000 ⬛ > 2000

🟩 251 - 500 🟥 1001 - 2000 ⬜ No Data



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.2.20

concentrations in each, whereas the modelled soil solution concentrations are much higher in England and Wales than in Scotland and Northern Ireland.

5.3. Critical Limit Values

5.3.1. Selection of Critical Limit Values

As explained in Section 1 of this report, there has been a decision within UN/ECE to move to a critical loads approach based on bioavailable concentrations. However, there is still considerable debate about appropriate critical limit values which should be used in such an approach. Most recently, the Ad-Hoc Expert group meeting in Bratislava, in October 2000, began the process of defining critical limits based on bioavailable rather than total soil concentration. Despite the evidence presented in Section 4, which clearly demonstrates that there are some operational as well as theoretical advantages to using free-ion concentrations rather than total soil solution concentrations, this concept was not accepted at the Bratislava meeting. Because the process of defining appropriate critical limit values for soil solution has only just begun, and because other critical limits are also relevant to the analysis presented in this report, we discuss here the basis of the critical limit values which have been adopted for our analysis.

The application of the critical load approach based on soil solution criteria requires critical limits to be defined as soil solution concentrations. The output of the Bratislava workshop provides proposed critical limits for lead and cadmium, based on two paradigms:- the precautionary approach and the maximum accepted damage approach. In simple terms, the former is based on estimating NOEC values from ecotoxicological data, i.e. it is set to be sure that there is no effect, while the latter is set so that the limit is the beginning of the effects zone, i.e. it is set so that it can be proved that there are effects above it. The latter paradigm is consistent with the approach which has been adopted in this project.

Table 5.3.1 summarises the proposed critical limits for lead and cadmium in the workshop recommendations, for total soil, reactive soil and total soil solution, with the sources of information. For comparison, we provide the values adopted in Phase 1 of this project for lead and cadmium based on total soil concentration, and in this report based on total soil solution concentration.

It is important to note that this workshop focussed only on lead, cadmium and mercury as these are judged to be the most important metals in terms of the possible need for policy interventions. Mercury is not considered in this contract, while copper and zinc are. However, in the absence of agreed critical limits based on soil solution concentrations for these elements, it is impossible to provide estimates of critical loads. Furthermore the NERC-funded work on the measurement and modelling of deposition of metals over the U.K., which is described in Annexe 1 of this report, found that there was great uncertainty in the current deposition fields of copper and zinc, which means that both dynamic modelling and critical loads exceedance assessment have little value for these metals at present. Further comment on these uncertainties in the deposition fields is provided in the second part of this report, on the moss survey.

Table 5.3.1: Critical limit values for soils proposed at the Bratislava workshop and used in this research project

ELEMENT	Cadmium		Lead	
	Bratislava	U.K.	Bratislava	U.K.
Total soil content (mg kg^{-1})	0.75 1.0	2.1 3.5	53 75	57 150
Reactive soil content (mg kg^{-1})	0.75		75	
Soil solution concentration (ug l^{-1})	30	3 1	5 200	8 2

Unfortunately, the process of proposing critical soil solution concentrations involved a collation of information provided by participants following the workshop. This did not allow a consistency between the criteria used to derive the critical limits for soil concentrations and for soil solution concentrations. Thus the values proposed for critical soil solution concentrations were based on effects on vegetation (30 µg l^{-1} for Cd and 200 µg l^{-1} for Pb) or on human health through the agricultural food chain (5µg l^{-1} for Pb). The latter is not appropriate for the U.K. uplands, while reviews of the literature undertaken in Phase 1 of this project clearly showed that effects on vegetation were likely to occur at higher concentrations than effects on soil invertebrates or on decomposition.

Another approach which was proposed for further development at the Bratislava workshop was to apply transfer functions to existing ecotoxicological data to estimate soil solution concentrations in tests with recorded values of total metal concentrations and appropriate soil characteristics (e.g. pH, organic matter content, clay content). This approach was applied by the German delegation to their datasets immediately after the workshop (Schütze & Throl, in press) and used to estimate the following critical soil solution concentrations, based on a NOEC analysis:-

1 µg l^{-1} for Cd
2 µg l^{-1} for Pb

In order to assess the relevance of the criteria for the total soil concentrations used in the earlier phase of this research programme, we have used the transfer functions derived in this project to estimate the corresponding soil solution concentrations. These concentrations were derived from the literature review of Tyler *et al* (1989) for the humic layer of forest soils. More recent data on microbial responses in such soils are provided by Bringmark & Bringmark (2000), who proposed that the critical concentration for effects of Pb should be lowered to 75 mg kg^{-1}. These values were obtained from soils with a pH of 4.4, an organic content of 45-50% and a DOC of 10-50 mg l^{-1}. These values are typical of many areas of the U.K. uplands (see Section 5.1). Applying the equations derived in Section 4 leads to critical limit values of:-

8 µg l^{-1} Pb, corresponding to the critical limit of 75 mg kg^{-1}; and
3 µg l^{-1} Cd, corresponding to a critical limit of 3.5 mg kg^{-1}

The critical limit values are much closer for the two metals when based on soil solution concentrations than total soil concentrations, reflecting the greater bioavailability of cadmium.

For the purposes of the mapping exercise, we have therefore employed two critical limit values for each metal in terms of soil solutions, representing the current uncertainty in the assessment process. The values can be summarised as follows:-

Based on a value above which adverse effects may be found in upland soils:-

8 µg l^{-1} for Pb
3 µg l^{-1} for Cd

Using the lowest critical limit values currently proposed within UN/ECE discussion which do not apply a safety factor – these are based on estimated NOECs from German ecotoxicological data:-

2 µg 1^{-1} for Pb
1 µg l^{-1} for Cd

In addition, it is useful to consider potential effects in freshwaters draining these soils. In this simple analysis, we employ the recommended critical limit value for effects on freshwaters, ignoring the effect of organic complexation in reducing bioavailability of metals in waters and the potential adsorption of metals by bedrock through which it passes before entering streams. Annexe 2 provides a description of the catchment based model, developed in the NERC component of the consortium project, which describes in more detail the movement of metals from the reactive soil pool to upland headwater streams and pools.

de Vries *et al*. (1998) present a table of statutory quality limits for metal concentrations in freshwaters for different countries and also an analysis of ecotoxicological data. For the U.K., there is a recommended limit of 10 µg l^{-1} for lead, which is broadly comparable to that derived from ecotoxicological data in the Netherlands, of 11 µg l^{-1}. Whichever value is selected, it is clear that the proposed critical limits for effects on freshwater organisms of lead are generally higher than those estimated for effects of soil solutions. Therefore, critical loads set to protect soil biodiversity and function should also serve to protect freshwater biodiversity.

The position is more complex for cadmium, for which there is no U.K. recommended value. Those for other countries, tabulated by de Vries *et al*. (1998), range from 0.09 ug l^{-1} in Sweden to 1 ug l^{-1} in Germany and 5 ug l^{-1} in Denmark. The recommendations of the critical limits group at the Schwerin workshop (Gregor *et al*,

1998) reflect this uncertainty, with recommended values being expressed as a range from 0.1-1.8 ug l^{-1}. Use of a value towards the lower end of this range is appropriate for streams with low pH which characterise much of the UK uplands. The ecotoxicological analysis provides a recommended value of 0.34 ug l^{-1}, as a NOEC value, which is consistent with a value estimated for food chain analysis of 0.35 ug l^{-1} (de Vries *et al*., 1998). For the analysis presented in this report, we have adopted a value of 0.35 ug l^{-1}, to assess the implications of applying a more stringent critical limit for freshwaters for cadmium on the assessment of critical loads in the U.K.

5.3.2 Comparisons of National Data with Critical Concentrations

These criteria can now be considered in terms of the maps of soil and soil solution concentrations which were presented in the previous sections.

Total and reactive soil concentrations

The critical limits based on reactive soil concentrations proposed by the Bratislava workshop for cadmium and lead can be compared with the modelled concentration data in Fig. 5.2.5. and 5.2.6 respectively. Although most areas, and all of Northern Ireland, have concentrations of cadmium below 1 mg kg^{-1} (slightly above the proposed critical limit of 0.75 mg kg^{-1}), concentrations above this are found in parts of Wales and in the Pennines. It should be noted that the lowest critical concentration used previously for cadmium in U.K. mapping has been 2.1 mg kg^{-1}, based on the analysis of ecotoxicological data presented by de Vries and Bakker (1998).

For lead, the situation is broadly comparable to cadmium, with areas above 100 mg kg^{-1} (critical limit 75 mg kg^{-1}) being found in parts of Wales and the Pennines, and parts of southern Scotland (an area not covered for Cd), but not in Northern Ireland. However, if the value of 57 mg kg^{-1} proposed by de Vries & Bakker were adopted, the area with concentrations above the critical limit would increase dramatically.

For copper and zinc, critical limits for multifunctionality used in Germany and the Netherlands, can be used to provide an approximate assessment of the position. These sources provide values of approximately 50 mg kg^{-1} for copper and 150 mg kg^{-1} for zinc (Tipping *et al*., 2000). Comparing the value for copper with that in Fig. 5.2.3, it appears that concentrations above this critical value are only found in isolated areas of northern England, SW England, south Wales and Northern Ireland. In many cases, this reflects the impact of historical mining activity and geological factors. In the case of zinc (Fig. 5.2.4) the areas in exceedance of 100 mg kg^{-1} are more widespread. For both copper and zinc, there is also a need to consider the issue of deficiency.

Total soil solution concentrations

Table 5.3.2 summarises the percentage of cells in the map for which the soil solution concentration exceeds the different critical limit values for Pb and Cd. The results are also broken down by country, although it should be remembered that no data are available for Scotland for Cd.

Table 5.3.2 Percentage of cells where critical limit for soil solution is exceeded in relation to number of available data cells.

Metal	Pb	Pb	Cd	Cd	Cd
Critical Limit	8 µg/l	2 µg/l	3 µg/l	1 µg/l	0.35 µg/l
U.K.	29.4	68.1	0.8	13.3	64.8
England	60.0	98.0	1.0	14.3	61.2
Wales	42.6	99.5	0.7	15.5	74.8
Scotland	17.0	50.6	-	-	-
N. Ireland	2.5	53.4	0.0	0.8	49.2

The results for lead show a considerable difference between the values for England and Wales and those for Northern Ireland and Scotland. Using the criterion of 8 ug l^{-1} for Pb, about 50 % of the area of England and Wales, but less than 20% of the land area of Scotland and Northern Ireland, is exceeded, giving a U.K. average of about 30%. When the critical soil solution concentration drops to the value of 2 ug l^{-1} proposed by the German analysis, then almost the whole of England and Wales is in exceedance, and about half of Scotland and Northern Ireland.

For cadmium, the area in exceedance of the soil solution criterion of 3 ug l^{-1} is trivial, and probably represents the effect of geochemical factors. With a value of 1 ug l^{-1}, then the area in exceedance in England and Wales increases to about 15%, although it remains less then 1% in Northern Ireland. For the lower value of 0.35 ug l^{-1}, the exceedance is much greater, reaching 60-70% in England and Wales. However, without a proper analysis of how far the modelled topsoil soil solution concentrations will be reduced before reaching freshwaters, it is impossible to interpret this result.

Free-ion concentrations

Criteria for comparison with the modelled free-ion concentrations are not available for cadmium or zinc, although it should be noted that at the acid pHs which dominate much of upland Britain, most of the metal in soil solution will be in the form of free ions. The long-term criteria derived by Sauvé *et al* (1998) for effects of lead on microbial activity was about 8 x 10^{-9}M (see Section 4.3). The modelled concentrations shown in Fig. 5.2.18 are above 10 x 10^{-9}M over more than 50% of the map cells in England and Wales, although concentrations below this are modelled for much of the northern half of Scotland and most of Northern Ireland.

Sauvé *et al*. (1998) provide a similar analysis of long-term effects criteria for microbial activity in soil for copper, producing a LD50 value of 6.3 x 10^{-9}M. Fig. 5.2.19 shows that, as for lead, this value is exceeded over much of England and Wales, but with a lower frequency in northern Scotland and Northern Ireland.

Although the amount of data available to assess the environmental implications of the free-ion concentrations is very limited, being confined to one major analysis of existing data, the results to date do indicate the potential concern over current levels of copper and lead in much of the U.K.. It is also important to note that these criteria are based on long-term studies, unlike those used for soil solution concentrations, which are mainly based on short-term ecotoxicological studies.

Freshwater concentrations

No sampling has been undertaken of concentrations of metals in freshwaters in the context of this contract. However, some comments on the possible significance of metal concentrations in freshwaters can be made on the basis of other information.

Rose *et al*. (1997) report the results of a survey of trace metal concentrations in a random sample of lakes in Scotland and Wales. For Pb, no sample showed a concentration above the detection limit of 1.1 ug l^{-1}, while only one sample or Cd exceeded a concentration of 0.35 ug l^{-1}, in an area of Wales with a history of mining activity. However, a substantial number of samples showed copper concentrations above 5 ug l^{-1} in both Wales and Scotland, while concentrations of zinc above 10 ug l^{1} were found at a number of sites in both countries. These data clearly suggest that current freshwater concentrations of lead and cadmium are too low compared with the proposed critical limits, further supporting the focus of our analysis on potential effects on soil processes.

5.4. Critical Loads

5.4.1. Critical Loads Methods

Critical loads methods proposed for metals in Europe were recently reviewed, in terms of effects criteria and methods for their application, at the workshop held in Bratislava in October 2000. This workshop agreed that critical loads for soils should be developed on the basis that critical limits were expressed in terms of the soil solution, rather than total soil content. In this section, we consider the implications of the Bratislava workshop in terms of the objectives of this contract and the research we have undertaken for the U.K.

As part of the contributions to the outcome of the Bratislava meeting, Gregor *et al* (2000) present a short guidance note on the calculation of critical loads using an effect based critical limit based on soil solution concentrations. This defines the critical load (CL(HM)) simply as:-

CL(HM) = HMu + HMle(crit) –HMw

Where Hmu is the uptake rate of the metal by vegetation
HMle(crit) is the leaching rate when the soil solution concentration reaches the critical limit
and HMw is the release of metal through weathering.

Throughout this project, we have assumed that the weathering rate in most upland areas is insignificant; this conclusion is supported by a sensitivity analysis carried out in the first part of the project. For non-forested areas of the uplands, we also assume that there is no significant removal of metal (Hmu) from the ecosystem; over the timescale required for the calculation of a critical load, the processes of uptake, litterfall and decomposition (i.e. internal cycling) are ignored. This means that the equations required for the calculation of the critical load are:

CL(HM) = HMle(crit) in non-forested areas; and
CL(HM) = Hmu + Hmle(crit) in forested areas

The term Hmle(crit) is simply defined as

Hmle(crit) = Q.c(crit)

Where Q is the runoff; and
C(crit) is the critical limit based on the soil solution

The same simple approach was used to provide critical load assessments in Phase I of this research programme, with the exception that the analysis used critical limits based on total soil concentrations. Modelled predictions of the value of the partition coefficient (k_d) were then used to estimate the equivalent soil solution concentration, and hence the rate of leaching. This effectively meant that lower critical loads were needed in areas in which the metal was tightly bound to the soil matrix, and hence leaching rates were lower. Application of a fixed soil solution concentration as a critical limit removes this anomaly.

5.4.2. Link to freshwater critical loads

Since the water leached from the soil will reach the headwaters of the streams draining these soils, it would also be possible to estimate a critical load for freshwaters in non-forested areas as:-

$$CL(HM) = Q.\ c(crit,fw)$$

Where c(crit,fw) is the critical limit for effects in freshwaters.

This approach contains a further series of assumptions about the relationship between metal concentrations in soil solution in the surface horizons and metal concentrations in catchment headwaters. However, it is clear that it does provide a simple method of linking an assessment of effects on soils and on freshwaters by simply writing:-

$$CL(HM) = Q.\ \min[c(crit),c(crit,fw)]$$

The relationship between metal deposition, soil pools and stream concentrations was investigated further in the NERC-funded component of the consortium project, as is summarised in Annexe 2.

5.4.3 Critical Load Maps

Fig 5.4.1 – 5.4.5 present maps of critical loads calculated using the method described in Section 5.4.1 and the critical limit values described in Section 5.3. These maps are presented for non-forest upland areas, i.e. areas where less than 5% of the landcover is forests. This approach underestimates the extent of non-forest area, but the broad regional patterns of the critical loads are clear. Critical loads for forests are considered further in section 5.7.

For cadmium, Figs. 5.4.1, 5.4.2 and 5.4.3 present critical loads calculated using the values of 3 ug l^{-1}, 1 ug l^{-1} and 0.35 ug l^{-1} respectively. In each of these maps, the key driving variable is the modelled runoff (cf. Fig 5.1.7), as the critical limit value is fixed. Therefore, in all these cases, there is a higher critical load estimated in the wetter parts of the country, with the mean critical load calculated for uplands of Wales being typically about 50% greater than that calculated for the uplands of England. The higher critical load in the wetter areas simply reflects the higher efflux of metals at the critical soil solution concentration, and hence the higher influx of deposited metal at steady state. As the critical limit used falls, so the modelled critical load values are likewise reduced.

The maps for lead (Figs. 5.4.4 and 5.4.5) reflect the same factors as for cadmium with lower values at lower critical limits and in areas with lower runoff.

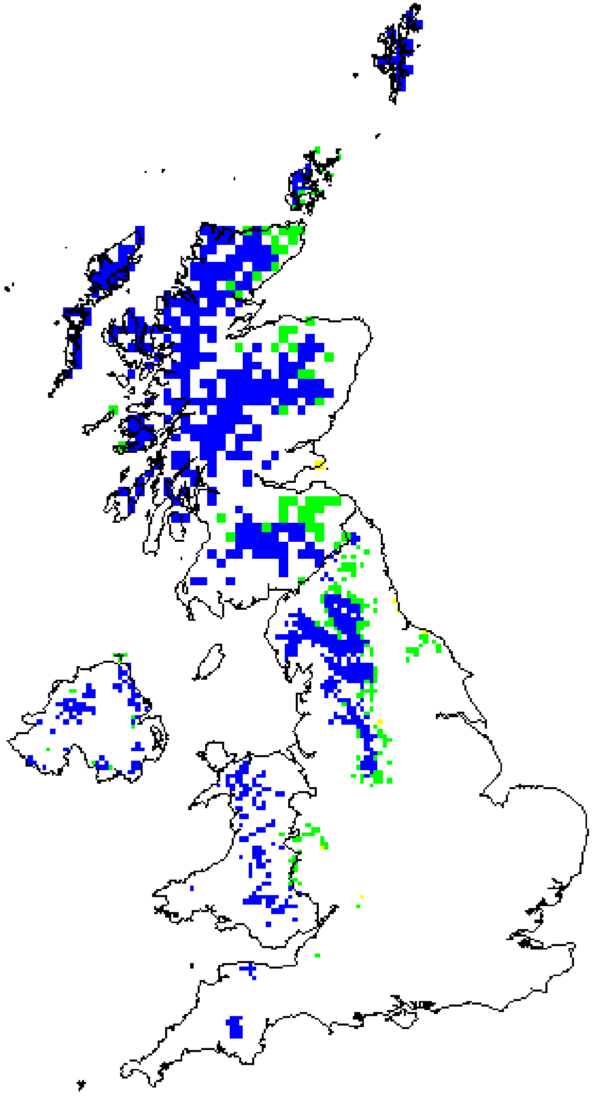
Critical Loads of Cadmium

(Modelled Data)

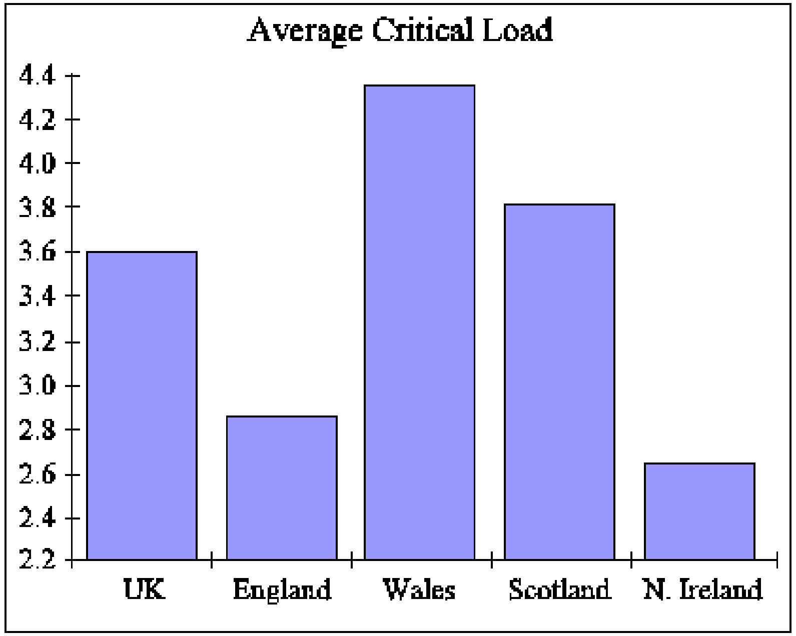
Non-forest Upland Areas of Great Britain

[mg m^{-2} yr^{-1}]

⬛	<= 0.25	🟨	0.51 - 1.0	🟦	> 2.0
🟥	0.26 - 0.5	🟩	1.01 - 2.0	⬜	No Data



Critical Limit = 3 ug l^{-1}



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.4.1

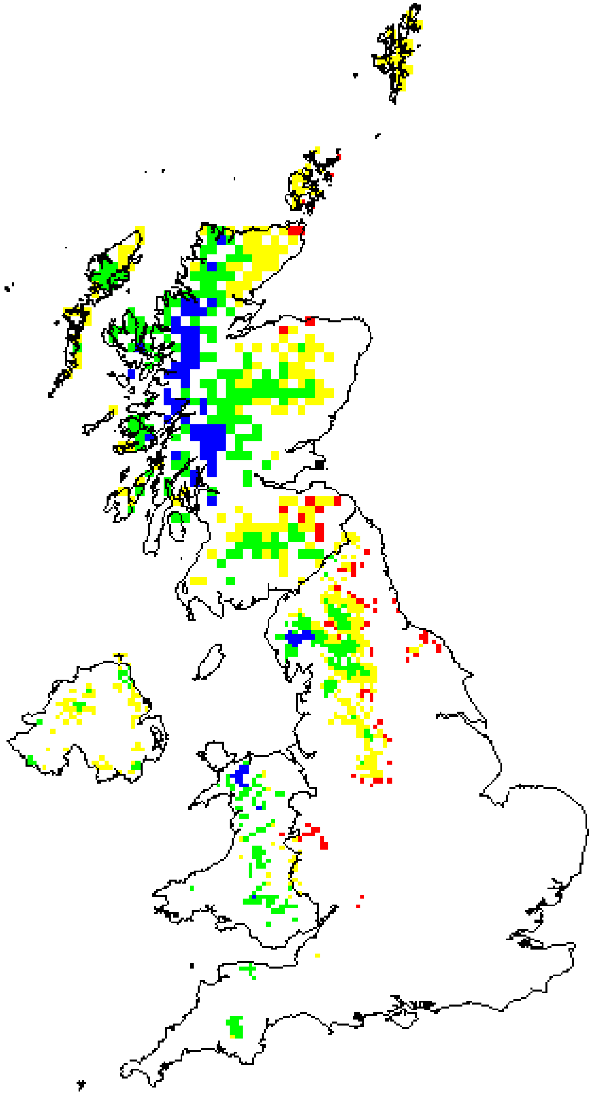
Critical Loads of Cadmium

(Modelled Data)

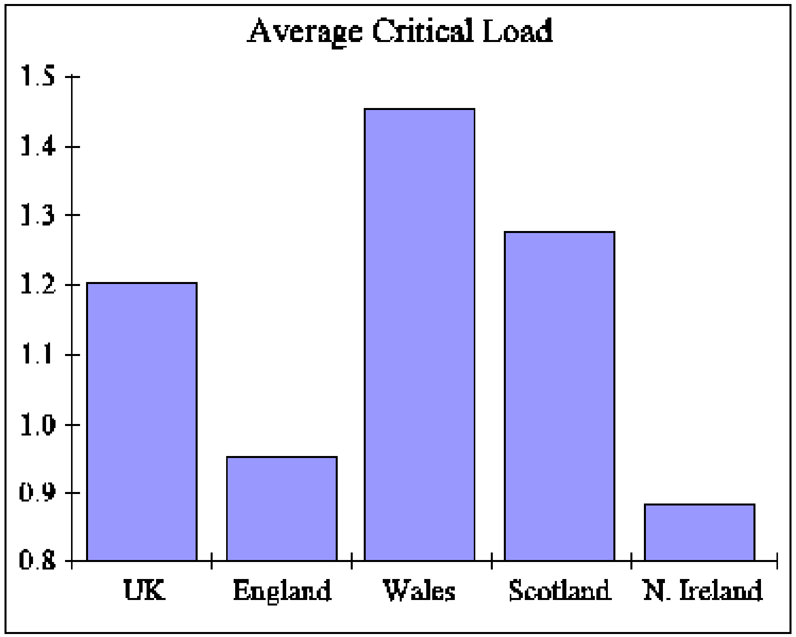
Non-forest Upland Areas of Great Britain

[mg m^{-2} yr^{-1}]

■	<= 0.25	🟨	0.51 - 1.0	🟦	> 2.0
🟥	0.26 - 0.5	🟩	1.01 - 2.0	☐	No Data



Critical Limit = 1 ug l^{-1}



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.4.2

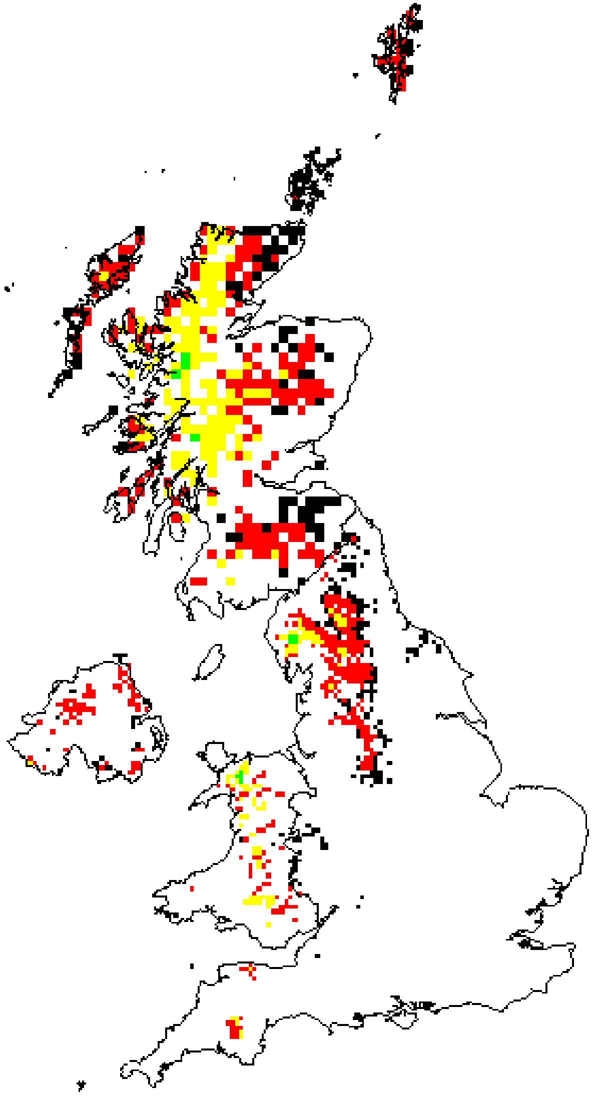
Critical Loads of Cadmium

(Modelled Data)

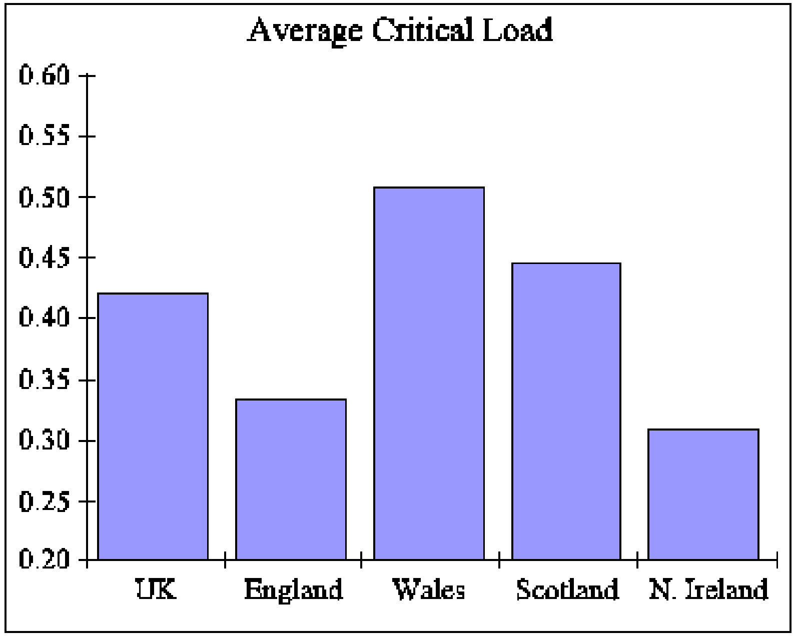
Non-forest Upland Areas of Great Britain

[mg m^{-2} yr^{-1}]

■	<= 0.25	🟨	0.51 - 1.0	🟦	> 2.0
🟥	0.26 - 0.5	🟩	1.01 - 2.0	□	No Data

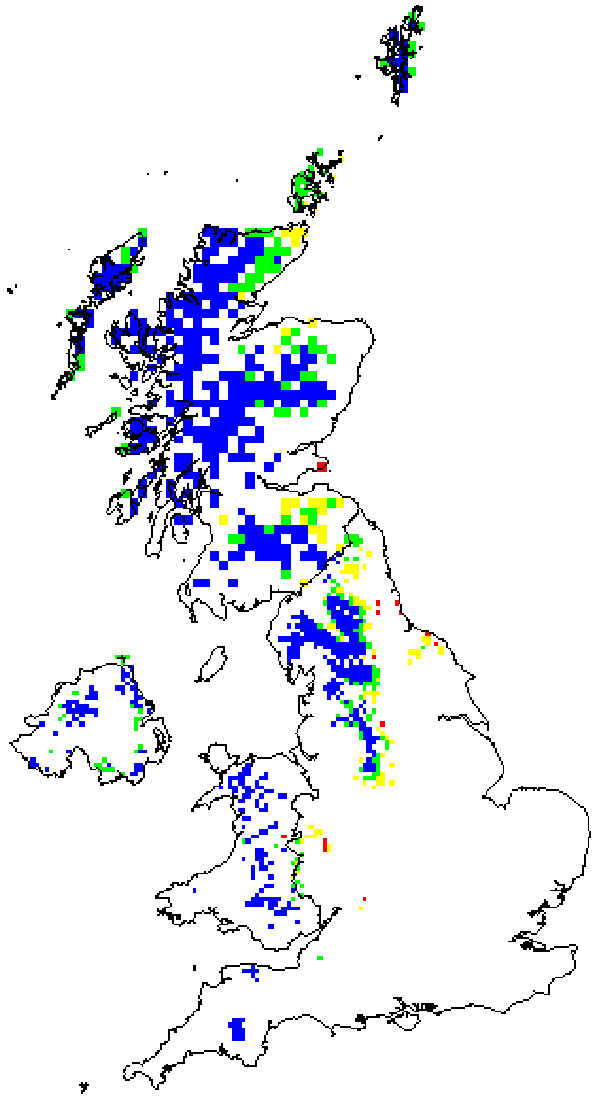


Critical Limit = 0.35 ug l^{-1}



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.4.3



Critical Limit = 8 ug l^{-1}

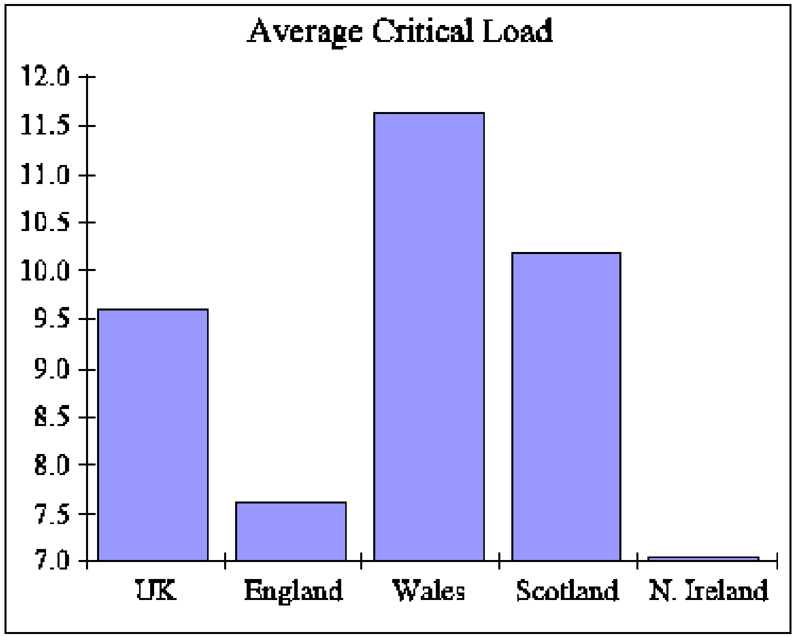
Critical Loads of Lead

(Modelled Data)

Non-forest Upland Areas of Great Britain

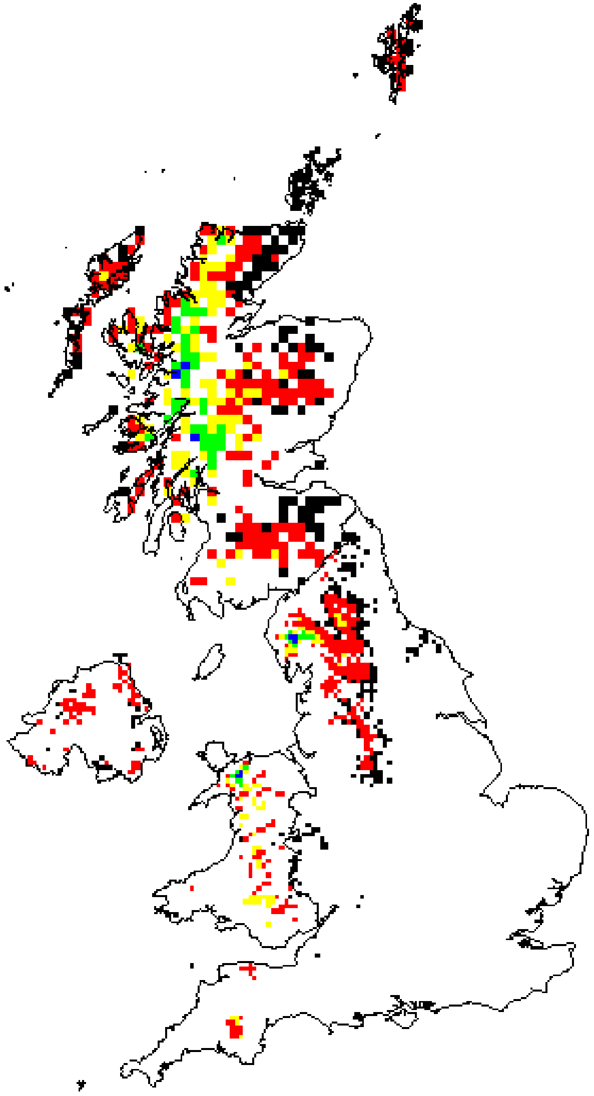
[mg m^{-2} yr^{-1}]

■	<= 1.5	🟨	3.01 - 4.5	🟦	> 6.0
🟥	1.51 - 3.0	🟩	4.51 - 6.0	□	No Data



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.4.4



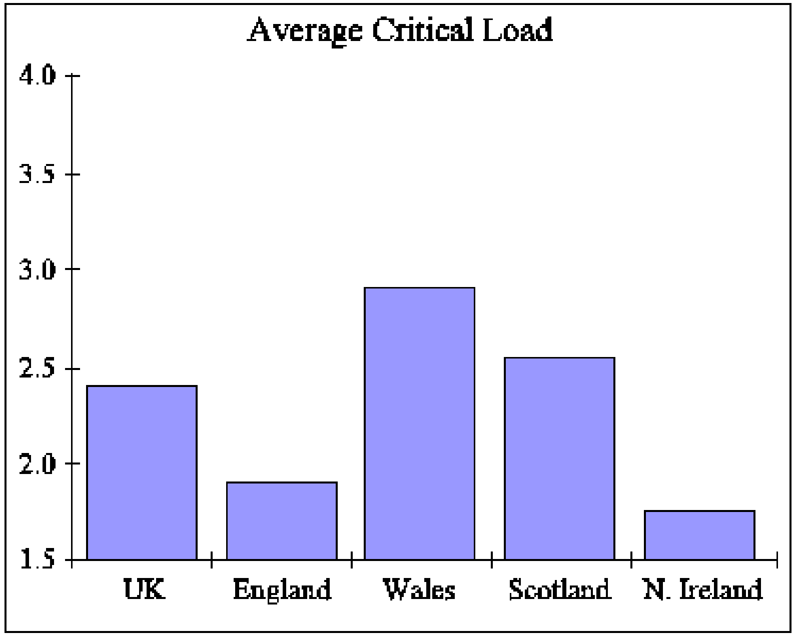
Critical Limit = 2 ug l^{-1}

Critical Loads of Lead
(Modelled Data)

Non-forest Upland Areas of Great Britain

[mg m^{-2} yr^{-1}]

■	<= 1.5	🟨	3.01 - 4.5	🟦	> 6.0
🟥	1.51 - 3.0	🟩	4.51 - 6.0	☐	No Data



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.4.5

5.5. Dynamic Modelling

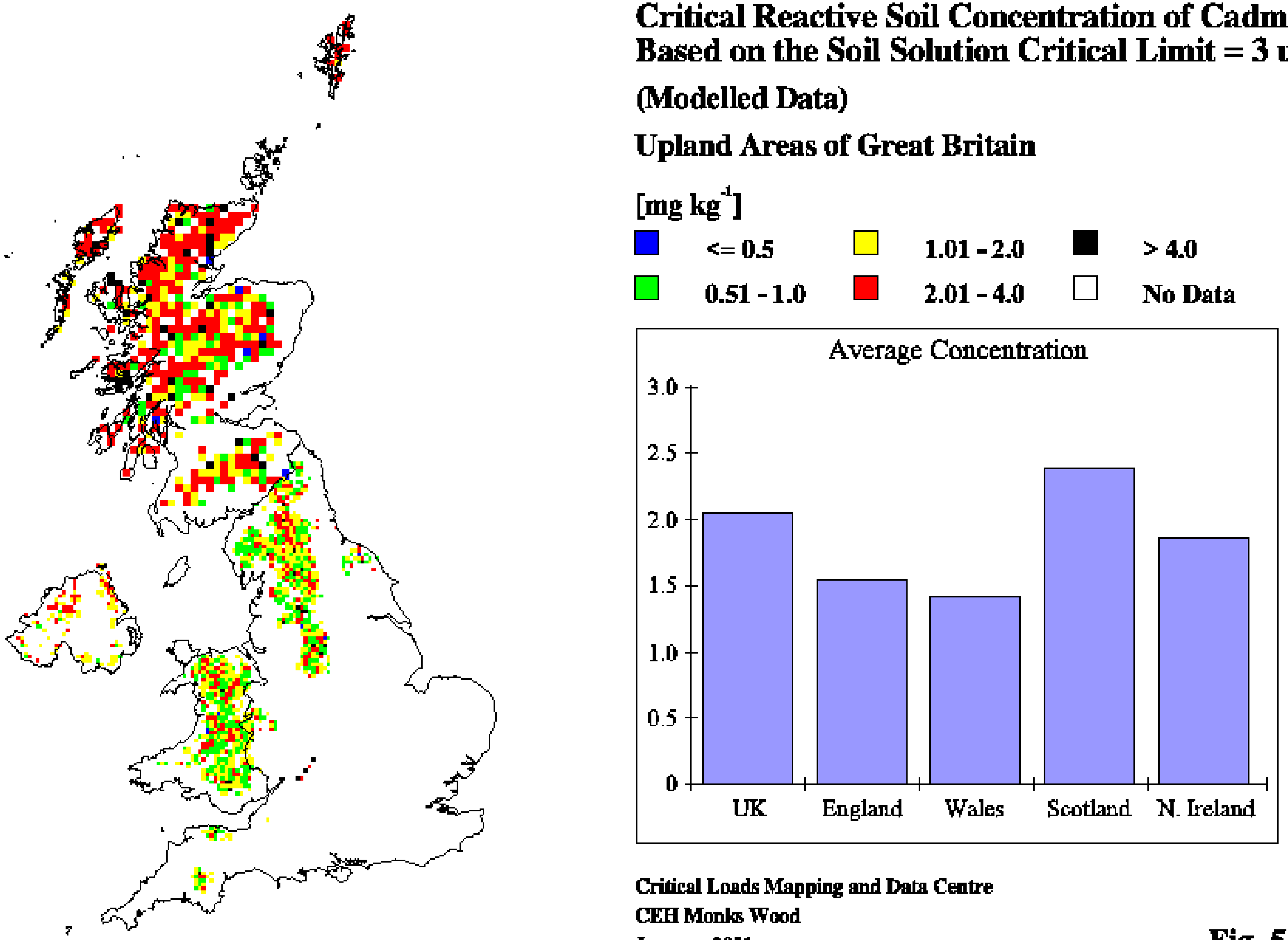
This simple critical load approach, however, ignores the dynamics of the response of soil/soil solution/freshwater systems to changes in metal deposition. The problem can most easily be explained by reference to the NERC-supported work on dynamic modelling carried out within this overall programme (cf. Annexe 2). Considering the dynamics in terms of annual timesteps, the model adds this year's deposition to the reactive metal soil pool, not the soil solution. This metal is then partitioned between the soil matrix and the soil solution (divided into free ion and complexed components) according to the WHAM model parameterised for the catchment. The metal accumulates in the reactive soil pool, not the soil solution, through time, until the point at which the soil solution concentration is in equilibrium with the reactive soil metal pool.

The practical consequences of this distinction between the steady-state and dynamic approaches are explored in more detail below. However, essentially in the simple steady-state method of Gregor *et al*. (2000), the critical load is only dependent on the runoff. However, if the partition coefficient is low (i.e. there is a higher soil solution concentration in equilibrium with the same reactive soil metal pool) then the critical soil solution will be reached at a lower value of the reactive soil metal pool, i.e. it will be reached in a much shorter time. Thus the areas identified as sensitive using the steady state method may differ greatly from those classified as sensitive if the calculation is made over a fixed timeframe.

The dynamic modelling approach which we have adopted for national mapping is a modification of the simple method described by Paces (1998), which was used in the initial assessment of metal dynamics presented in the Phase I contract report (EPG 1/3/85). The Paces method uses a single soil box, representing the reactive soil pool, and calculates the time taken for the reactive soil concentration to reach a critical value. To apply this dynamic approach to the new critical load methods, based on the critical soil solution concentration, it is therefore necessary first to calculate the critical reactive soil concentration which corresponds to the critical soil concentration, for given soil characteristics.

Figures 5.5.1 and 5.5.2 present maps of critical reactive soil concentration for the critical soil solution concentrations of 3 µg l^{-1} for cadmium and 8 µg l^{-1} for lead. These values were estimated using the transfer functions in Table 4.2.6. These transfer functions predict higher reactive soil concentrations in soils with higher pHs and with higher organic contents, and these factors are reflected in the two maps. For both metals, the modelled critical reactive metal concentrations vary by an order of magnitude across the country, and in some cases within small areas. The effect of pH is clear from the relatively high critical reactive soil concentrations in the Chilterns, while the relatively high critical reactive soil concentrations for cadmium in much of Scotland reflect the effect of high organic contents.

It is important to note that these maps present only the critical reactive soil concentration; in terms of dynamics, a further factor is the conversion of this concentration to a critical reactive soil pool. As was described in Section 5.1, the variation in bulk density and porosity across the country mean that the distribution of metal pools may be quite different from that of metal concentrations. Thus, in organic



Critical Reactive Soil Concentration of Cadmium Based on the Soil Solution Critical Limit = 3 ug/l

(Modelled Data)

Upland Areas of Great Britain

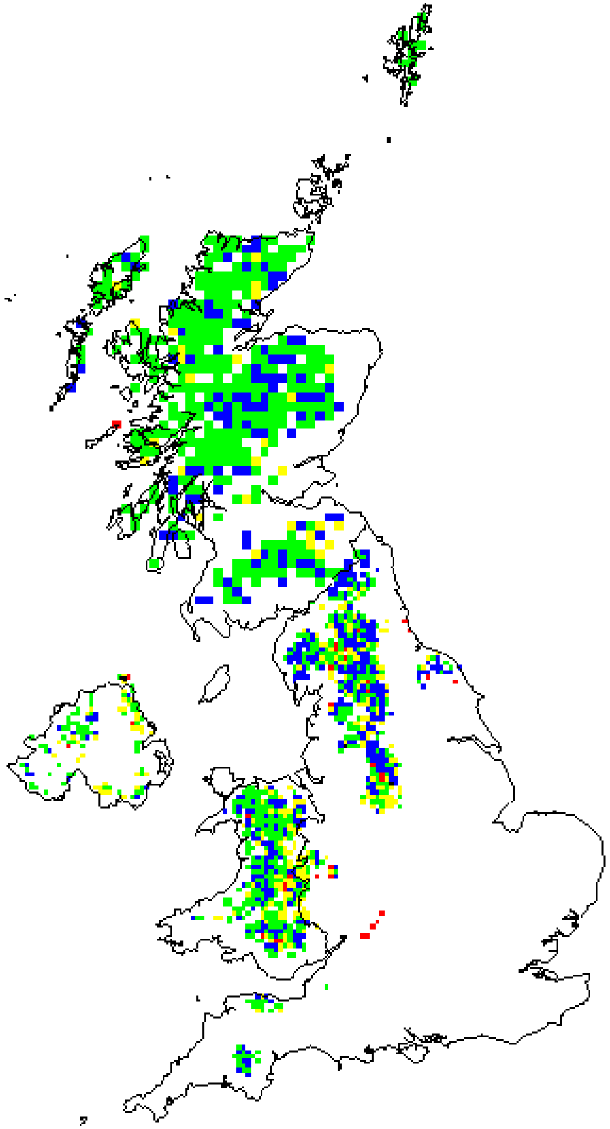
Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.5.1

Critical Reactive Soil Concentration of Lead Based on the Soil Solution Critical Limit = 8 ug/l

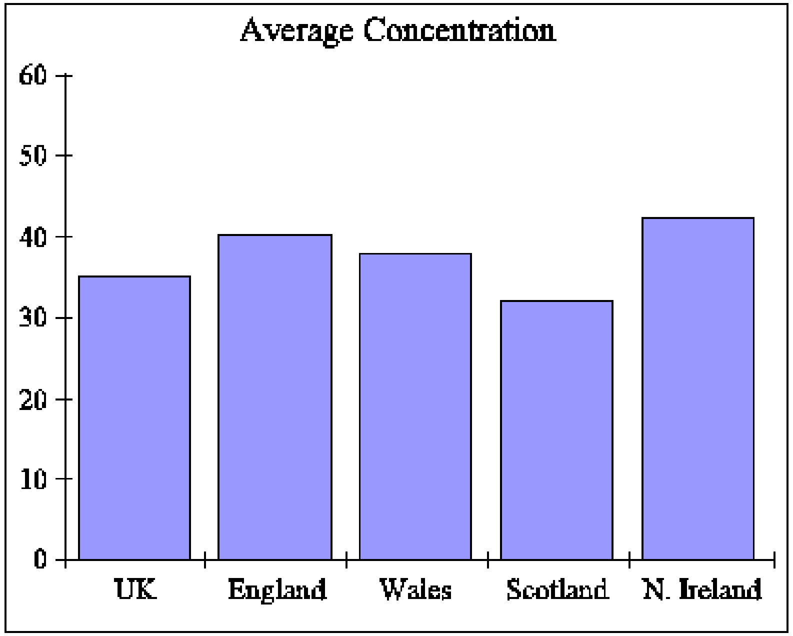
(Modelled Data)

Upland Areas of Great Britain



[mg kg^{-1}]

🟦	<= 25	🟨	50.1 - 100	⬛	> 200
🟩	25.1 - 50	🟥	100.1 - 200	☐	No Data



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.5.2

soils, the effect of LOI increasing the retention of the metal in the soil matrix may be more than offset by the low bulk density and the relatively low pool of metal for a given concentration.

5.5.1. Estimation of times to critical load exceedance

The effect of these different dynamics has been examined within the GIS in two different ways. Firstly, in order to focus simply on the effects of partitioning between soil solution and the soil reactive pool, the dynamics of metal accumulation in the reactive pool from a concentration of 0 to half the reactive critical pool (mg m^{-2}) have been modelled, assuming that the deposition rate in each grid square is equal to the critical load. This is a theoretical calculation, but allows the effects of different soil properties which influence the dynamics of metal accumulation to be assessed.

The time to a given reactive soil concentration or pool is given, following Paces (1998) by:

$$t_{crit} = -\frac{1}{k_{run}} \times \ln\left(\frac{F_{atm} - k_{run} \times \vartheta \times c_n}{F_{atm} - k_{run} \times \vartheta \times c_s}\right) \qquad [\mathrm{yr}]$$

where

$$k_{run} = \frac{Q}{\vartheta \times K_d}$$

with the terms and the predictive equations used being summarised in the table below.

Input Data	Description
k_d	partition coefficient between the reactive metal concentration and the soil solution concentration Pb: k_d = 2.88709 + 0.219352*pH + 0.00692691*LOI - 0.00441945*DOC Cd: k_d = 1.42589 + 0.235135*pH + 0.0104647*LOI - 0.00201747*DOC
Q	annual average runoff
ϑ	bulk density x thickness of top soil x (1 – porosity)
c_n	critical reactive concentration based on the critical limit in soil solution Pb: log(c_n) = 0.0494467 + 0.875534*log(8 µg/l) + 0.177525*pH + 0.0053041*LOI Cd: log(c_n) = -1.64249 + 0.786113*log(3 µg/l)+ 0.219224*pH + 0.0100082*LOI
ϑ x c_n / 2	half the critical reactive soil pool
c_s	initial reactive soil concentration (value = 0)
CL	critical load at the critical limit in soil solution

To calculate the time to reach half the critical reactive soil concentration the equation above becomes:

$$t_{crit} = -\frac{1}{k_{run}} \times \ln\left(\frac{CL - k_{run} \times \vartheta \times c_n \div 2}{CL - k_{run} \times \vartheta \times 0} \right) \quad \text{[yr]}$$

The second approach was to examine the timescale at current deposition loads for the current reactive soil pool to increase to the critical reactive soil pool. This gives an indication of how rapidly continued deposition at the current rate would lead to exceedances of the critical limit over wider areas of the country. The deposition values used are described in Section 5.8 below. It should be noted that the calculation of time to critical limit exceedance cannot be made (a) where the critical limit is already exceeded and (b) where the critical limit will never be reached (i.e. the critical load is not exceeded).

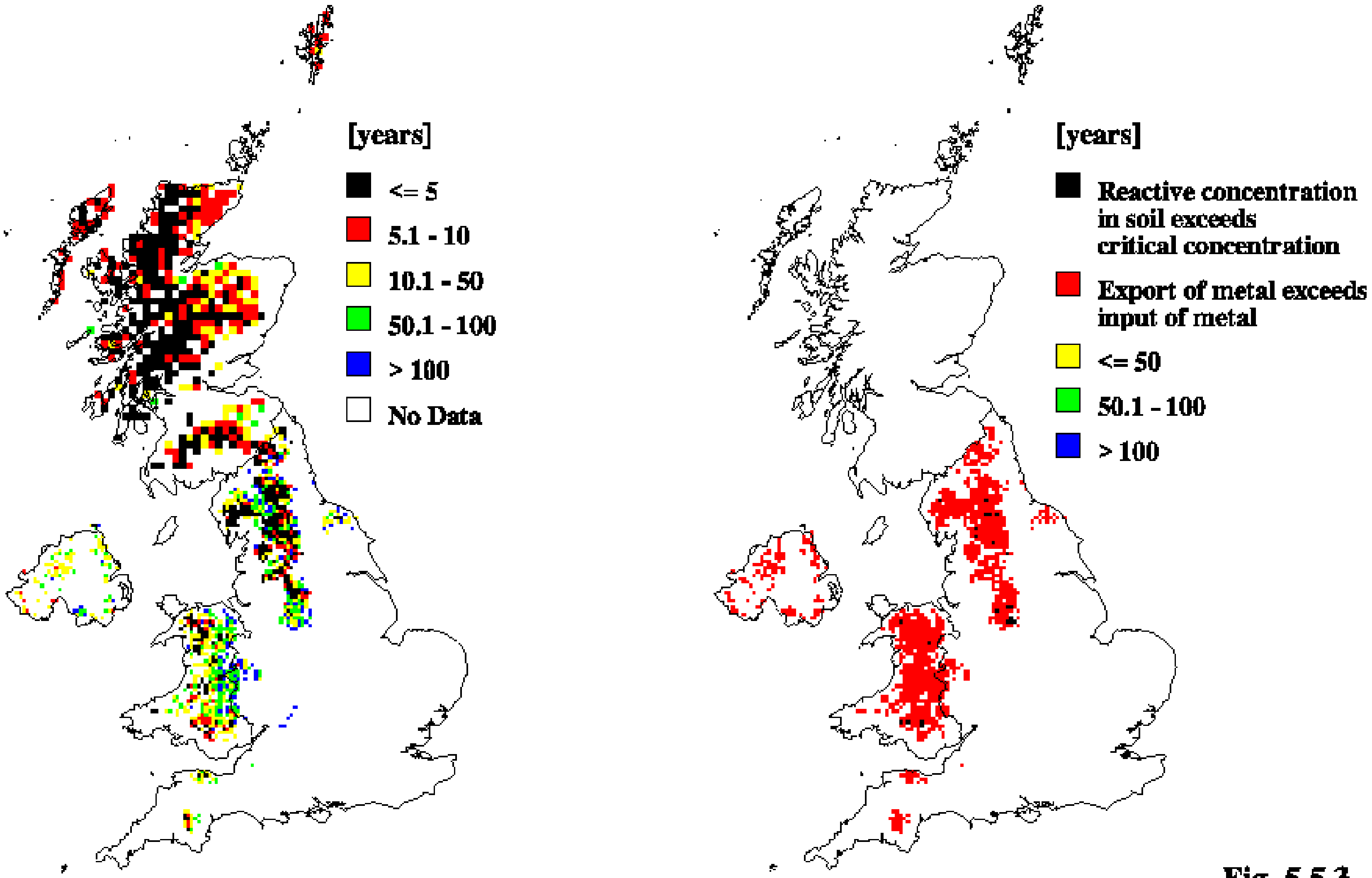
The equation then becomes:

$$t_{crit} = -\frac{1}{k_{run}} \times \ln\left(\frac{F_{atm} - k_{run} \times \vartheta \times c_n}{F_{atm} - k_{run} \times \vartheta \times c_s} \right) \qquad \text{[yr]}$$

with the input data as defined in the table below.

Input Data	**Description**
F_{atm}	current deposition data set based on moss survey 2000
ϑ	bulk density x thickness of top soil x (1 – porosity)
c_n	critical reactive soil concentration based on the critical limit in soil solution Pb: $\log(c_n)$ = 0.0494467 + 0.875534*log(8 ug/l) + 0.177525*pH + 0.0053041*LOI Cd: $\log(c_n)$ = -1.64249 + 0.786113*log(3 ug/l)+ 0.219224*pH + 0.0100082*LOI
ϑ *x* c_n	critical reactive soil pool
c_s	current reactive soil concentration Pb: $\log(c_s)$ = -0.547412 + 0.00459836*LOI + 0.0266137*pH + 1.00851*log(TotalPb) Cd: $\log(c_s)$ = -0.787097 + 0.00774602*LOI + 0.0198145*pH + 1.04288*log(TotalCd)
ϑ *x* c_s	current reactive soil pool

The results of both these calculations are presented in Fig. 5.5.3 and 5.5.4 for critical limits of 8 μg l^{-1} for lead, and 3 μg l^{-1} for Cd. The left-hand map in Fig. 5.5.3 shows the results of the first calculation for cadmium. Since this is theoretical calculation and does not consider current concentrations, it is possible to present data for Scotland. The maps show wide variations across the country, which reflect a combination of soil properties and variation in critical load values. In terms of the former, the low bulk density and high rainfall (and hence high critical loads) in many parts of Scotland and northern England lead to half-times which are less than 10



Modelled Time to Reach Half the Critical Reactive Metal Concentration of Cadmium

[years]

■	<= 5
🟥	5.1 - 10
🟨	10.1 - 50
🟩	50.1 - 100
🟦	> 100
□	No Data

Modelled Time to Reach the Critical Reactive Metal Concentration of Cadmium

[years]

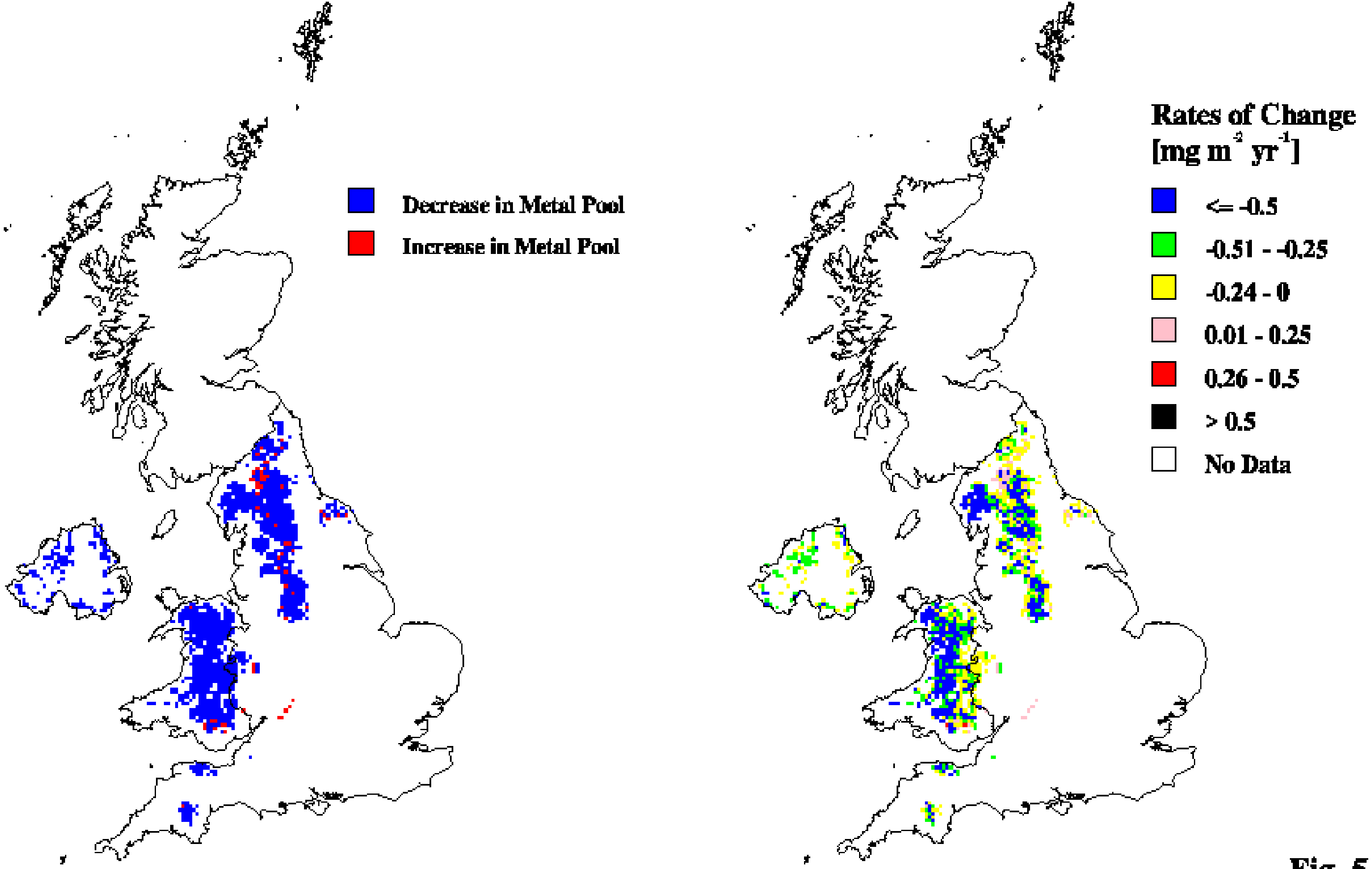
■	Reactive concentration in soil exceeds critical concentration
🟥	Export of metal exceeds input of metal
🟨	<= 50
🟩	50.1 - 100
🟦	> 100

Critical Loads Mapping and Data Centre, CEH Monks Wood January 2001

Fig. 5.5.3

Current Rates of Change in the Cadmium Pool

Upland Areas of Great Britain



Critical Loads Mapping and Data Centre, CEH Monks Wood   January 2001

Fig. 5.5.5

years. This would suggest that concerns about the long timescales to reach critical concentrations in the soil/soil solution are not of relevance to much of upland Britain. In contrast, in parts of the Pennines and in parts of Wales, the modelled timescales are much slower, of the order of 100 years.

However, these theoretical calculations should be considered alongside the right-hand map, which presents the current situation. The map is dominated by areas in which the model predicts that current efflux of metals from the soils exceeds current deposition. Hence, unless current rates of cadmium deposition were to increase significantly, there is no need, for the value of 3 ug l^{-1} Cd, to consider the timescales over which the critical limit might be reached. A similar conclusion was also reached for the critical limit value of 1 ug l^{-1}.

Fig 5.5.4 shows that the picture for lead is very different. In terms of the theoretical calculation at the critical load, the timescales over much of the Pennines and Wales exceed 500 years to reach a critical concentration. However, over much of Scotland and parts of upland England and Wales, the timescales are substantially lower, being less than 50 years.

There is also a very different picture in the right-hand map, representing the current position. It is important to note that this map does not fully reflect the balance between export and inputs, which are considered below. This is because the mapping procedure was for the areas where the reactive concentration currently exceeds the critical reactive concentration to take precedence. The main feature of the map is that over most of the country the simple model predicts either that critical concentrations are exceeded or that concentrations are currently falling. In those areas where this not the case (most notably in the eastern part of Wales), the modelled times to reach the critical reactive soil concentrations are high, generally in excess of 500 years.

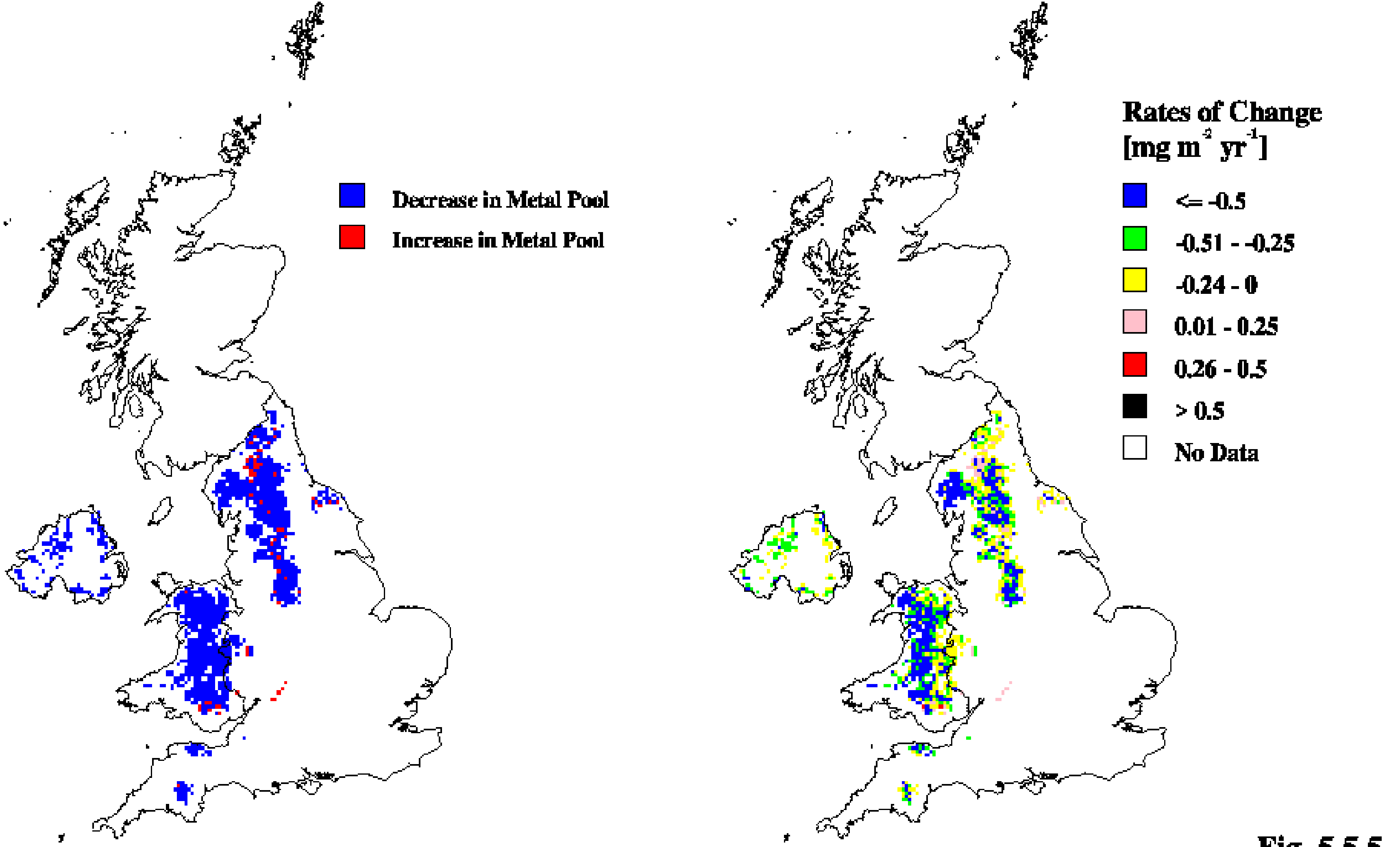
5.5.2 Current metal balance

The estimate presented in Figures 5.5.3 and 5.5.4 assumes that soil metal concentrations are currently increasing. However, if the historical deposition rate has been significantly higher than the current deposition rates, then it is possible that soil metal pools are now decreasing rather than increasing. Thus, the more detailed dynamic modelling carried out under the NERC-funded component of the project, suggests that in three upland catchments in Cumbria, soil concentrations of lead and copper may be increasing, but that those of cadmium and zinc are currently decreasing. To model the position nationally, we compared the current deposition rate with the modelled annual loss of metal, given by $Q.c_{ss}$.

The results for cadmium (Fig. 5.5.5), as was shown in Fig. 5.5.3, are that areas where current concentrations are decreasing dominate over England and Wales, with the highest net export in western Wales, parts of the Pennines and Cumbria. The areas where cadmium is modelled to be accumulating are limited to alkaline soils, for example in the Cotswolds and parts of the Pennines. Thus, our analysis suggest that environmental concerns over cadmium should be focussed on the effects of leaching of historical loads into freshwaters rather than on the further accumulation of high soil concentrations.

Current Rates of Change in the Cadmium Pool

Upland Areas of Great Britain



Critical Loads Mapping and Data Centre, CEH Monks Wood   January 2001

Fig. 5.5.5

The picture for lead (Fig. 5.5.6) is somewhat different than that for cadmium, although overall there are more areas where concentrations are predicted to be falling rather than rising. In parts of Wales and the Pennines in particular, there is strong spatial heterogeneity, with areas with high rates of net increase adjacent to areas with high rates of net efflux, presumably reflecting high spatial heterogeneity in soil characteristics.

These calculations were made for all upland areas, with the assumption that there is no removal from the system other than by leaching. For forests, as explained in the calculation of critical loads, the effect of the export of metals in the harvested wood needs to be considered. Therefore, the annual net export was included the calculation for forests, although this is clearly an artificial representation of the removal of wood every 50-100 years. For forests, it is also necessary to use the enhanced rates of metal deposition which are modelled (see Section 5.8 below).

Figs 5.5.7 and 5.5.8 show the results of the calculations of the current balance between input and export for forests, for cadmium and lead respectively. Comparing these maps with those in 5.5.5 and 5.5.6, it appears that there is little difference in the current balance for cadmium. In contrast, for lead, it is clear that the balance has shifted significantly towards a net accumulation of metal in the system. Hence the effect of the enhanced deposition of metal to forests compared to moorland and grassland outweighs the greater removal of metal from the system.

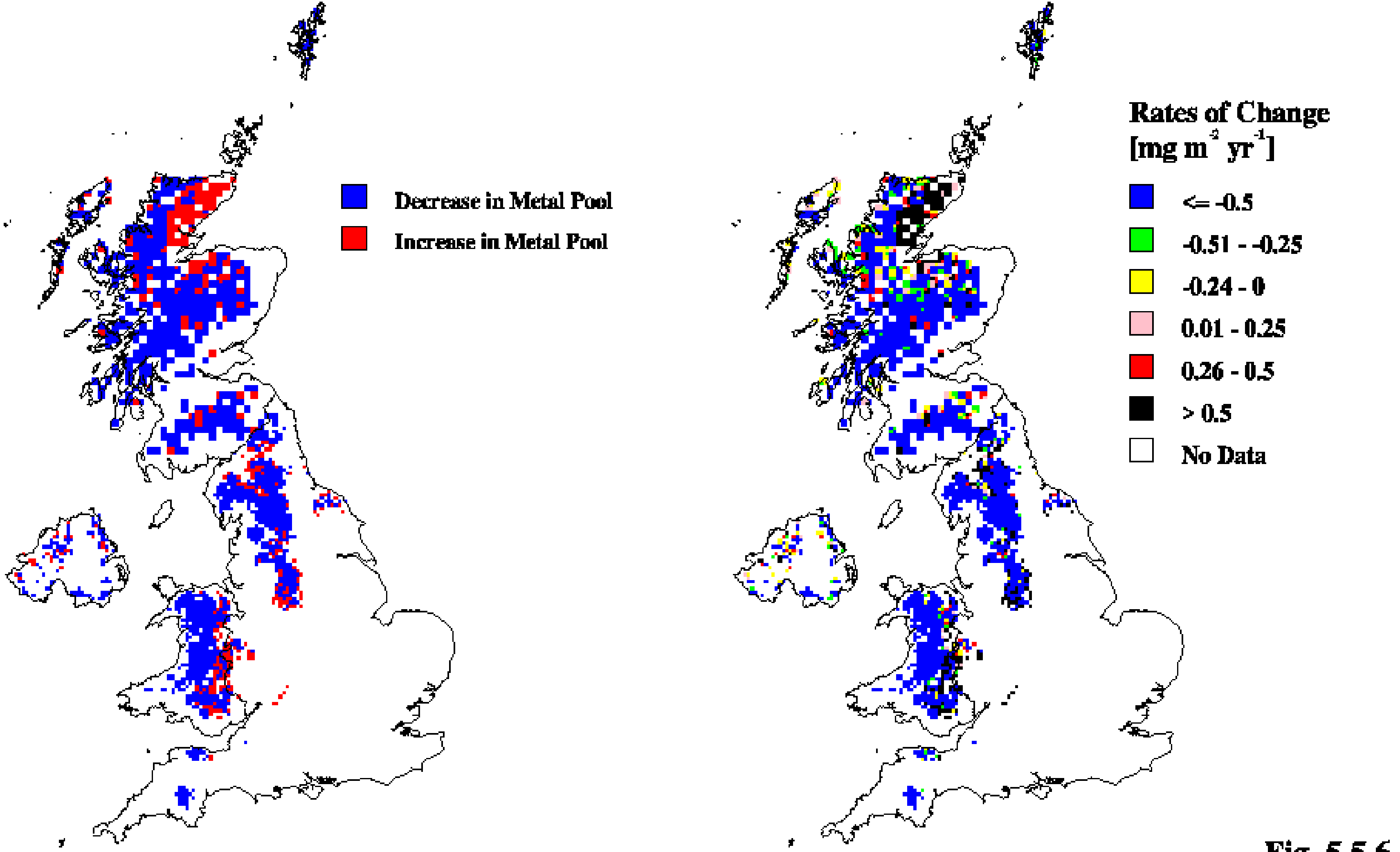
5.5.4. Catchment scale modelling

A more sophisticated model of metal dynamics in upland catchments was developed under the NERC-funded part of the consortium, as described in Annexe 2. The model has two boxes: soil and rock. Deposition is added to the total ‘available’ metal in the soil pool. The free-ion concentration and the total soil solution concentration are then calculated by equilibrating the whole available soil metal over the solids, DOC and free-ion using empirical transfer functions based on soil pH alone, or on soil pH and LOI, and the WHAM model (Tipping, 1994). The total porewater pool is then available for transfer to the rock pool. The output from rock box is stream flux and concentration.

This simple dynamic model has been run for three upland catchments in northern England, using assumed input acid and metal deposition scenarios for last 200 years. Comparisons of model predictions with current soil pools and current stream fluxes show reasonable agreement with observations. The results clearly show that metal pools have accumulated in these catchments over 100-200 years, but in the case of Cd and Zn are now declining as deposition has fallen. In contrast, the simulations for Pb and Cu show in these catchments that current inflows and effluxes and currently roughly balanced. The simulations also show a strong effect of incorporating acidification in these scenarios

Current Rates of Change in the Lead Pool

Upland Areas of Great Britain

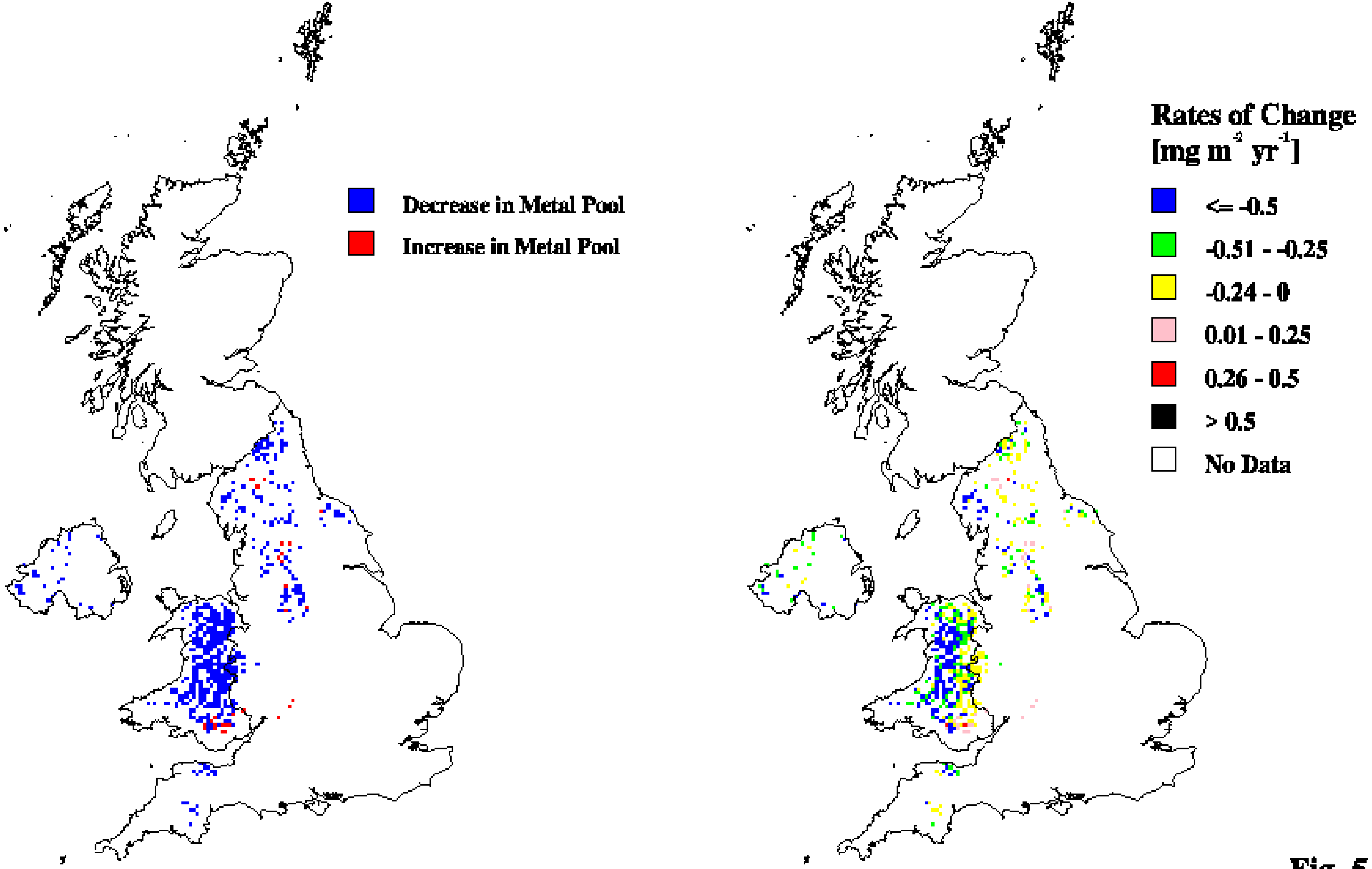


Critical Loads Mapping and Data Centre, CEH Monks Wood January 2001

Fig. 5.5.6

Current Rates of Change in the Cadmium Pool

Upland Forests of Great Britain

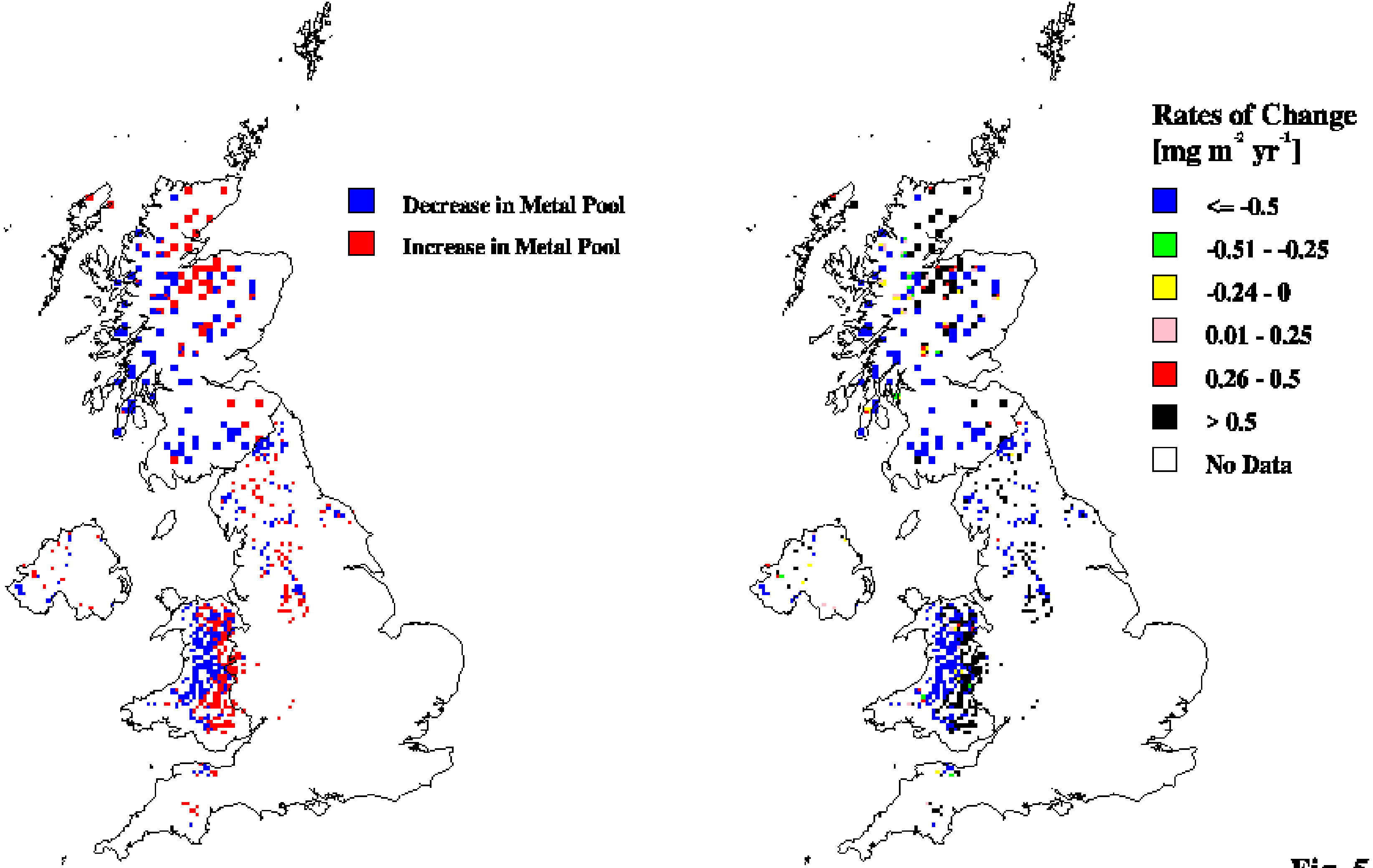


Critical Loads Mapping and Data Centre, CEH Monks Wood January 2001

Fig. 5.5.7

Current Rates of Change in the Lead Pool

Upland Forests of Great Britain



Critical Loads Mapping and Data Centre, CEH Monks Wood   January 2001

Fig. 5.5.8

5.6. Effect of Soil pH

pH is an important variable in determining the partitioning of metal between the reactive soil pool and soil solution, or free-ion, concentrations. The results from the site-specific dynamic modelling clearly demonstrate the importance of soil pH, and more specifically of accounting for the effects of soil acidification when simulating historical dynamics of metal behaviour (Annexe 2). It is not possible to apply this detailed catchment-based approach throughout the country. Therefore, a simpler approach has been used to assess the effect of pH across the country, in which the effect of a step change in pH of the soil in each grid square has been calculated. The assumed change in these calculations has been a fixed reduction, or increase, of 0.5 in pH.

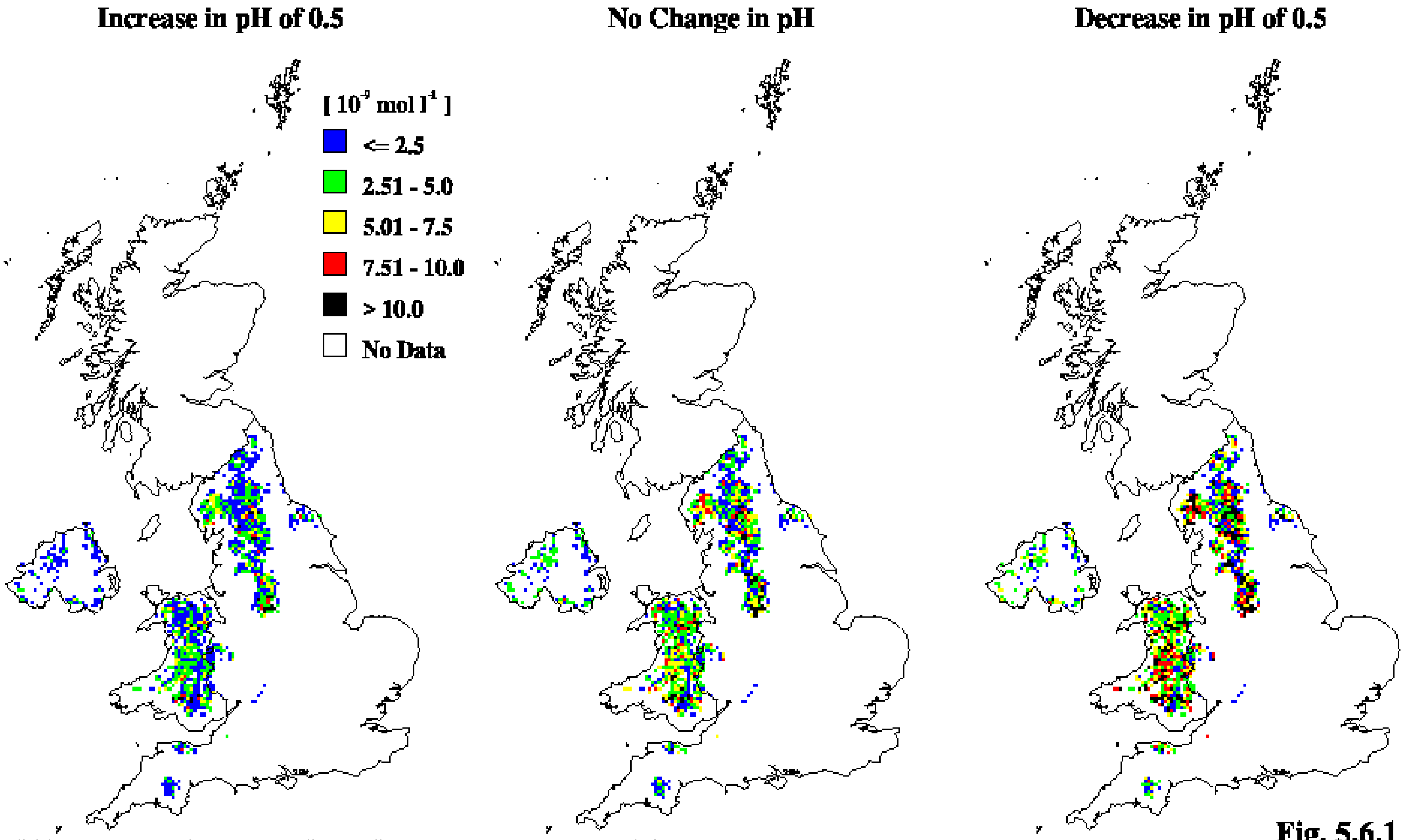
Under the current methodology proposed within UN/ECE, it is clear that the critical loads themselves are not affected by soil pH, as they depend only on the critical limit in soil solution and the annual runoff, in non-forested systems. However, a change in soil pH will have two effects:-

(a). It will influence the total soil solution concentration, or the free-ion activity, which is in equilibrium with current soil concentrations, i.e. it will alter the assessment of the risk of current concentrations.

Fig 5.6.1 and 5.6.2 demonstrate this effect for cadmium and lead respectively, in terms of free-ion concentration. The effect of the shift of 0.5 of a pH unit is insignificant in the areas with alkaline soils, such as in the Cotswolds. In contrast, on more acidic soils, the effect of this change in pH is considerable. Thus the area with modelled free-ion concentrations above 5 x 10^{-9} mol l^{-1} is substantially increased by a decrease in pH of 0.5, and substantially decreased by increase in pH. A very similar effect is observable in Fig. 5.6.2 for lead. The area with modelled free-ion concentrations above 50 x 10^{-9} mol l^{-1} is relatively small at pH values which are 0.5 above the current but is considerable at pH values which are 0.5 below the current pH values.

Figs. 5.6.3 and 5.6.4 present the same assessment for modelled soil solution concentrations for cadmium and lead respectively. The maps for cadmium show a strong effect of pH in increasing the modelled soil solution concentration of cadmium. With an increase of 0.5 of a pH unit, only small areas of Pennines and isolated squares in Wales show values above 10 x 10^{-9} mol l^{-1} (roughly equivalent to 1 ug l^{-1}). In contrast, with a decrease of 0.5 of a pH unit, a significant proportion of Wales, the Pennines and Cumbria, have modelled values above 10 x 10^{-9} mol l^{-1}. For lead, with an increase of 0.5 of a pH unit, modelled concentrations above 50 x 10^{-9} mol l^{-1} (equivalent to about 10 ug l^{-1}) cover a significant area in the Pennines and South Wales, but are limited to isolated squares in Scotland and elsewhere in Wales and are not exceeded in Northern Ireland. In contrast, with a decrease of 0.5 of a pH unit, areas above this threshold dominate the Pennines and Cumbria, cover a substantial part of Wales and southern Scotland, and are found in isolated squares in Northern Ireland.

The Effect of Change in pH in Modelling Free-ion Concentrations of Cadmium



Critical Loads Mapping and Data Centre, CEH Monks Wood   January 2001

Fig. 5.6.1

The Effect of Change in pH in Modelling Free-ion Concentrations of Lead

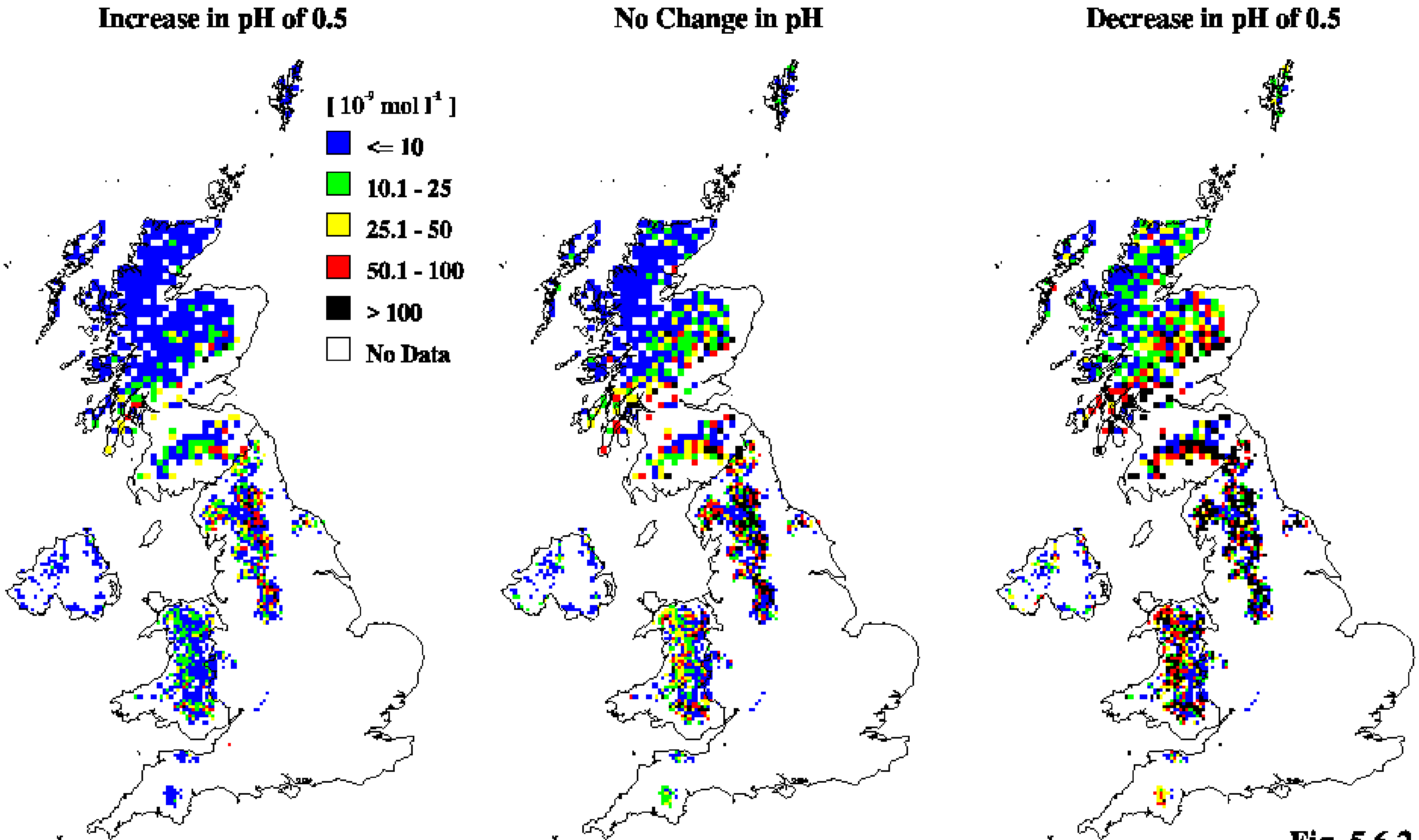
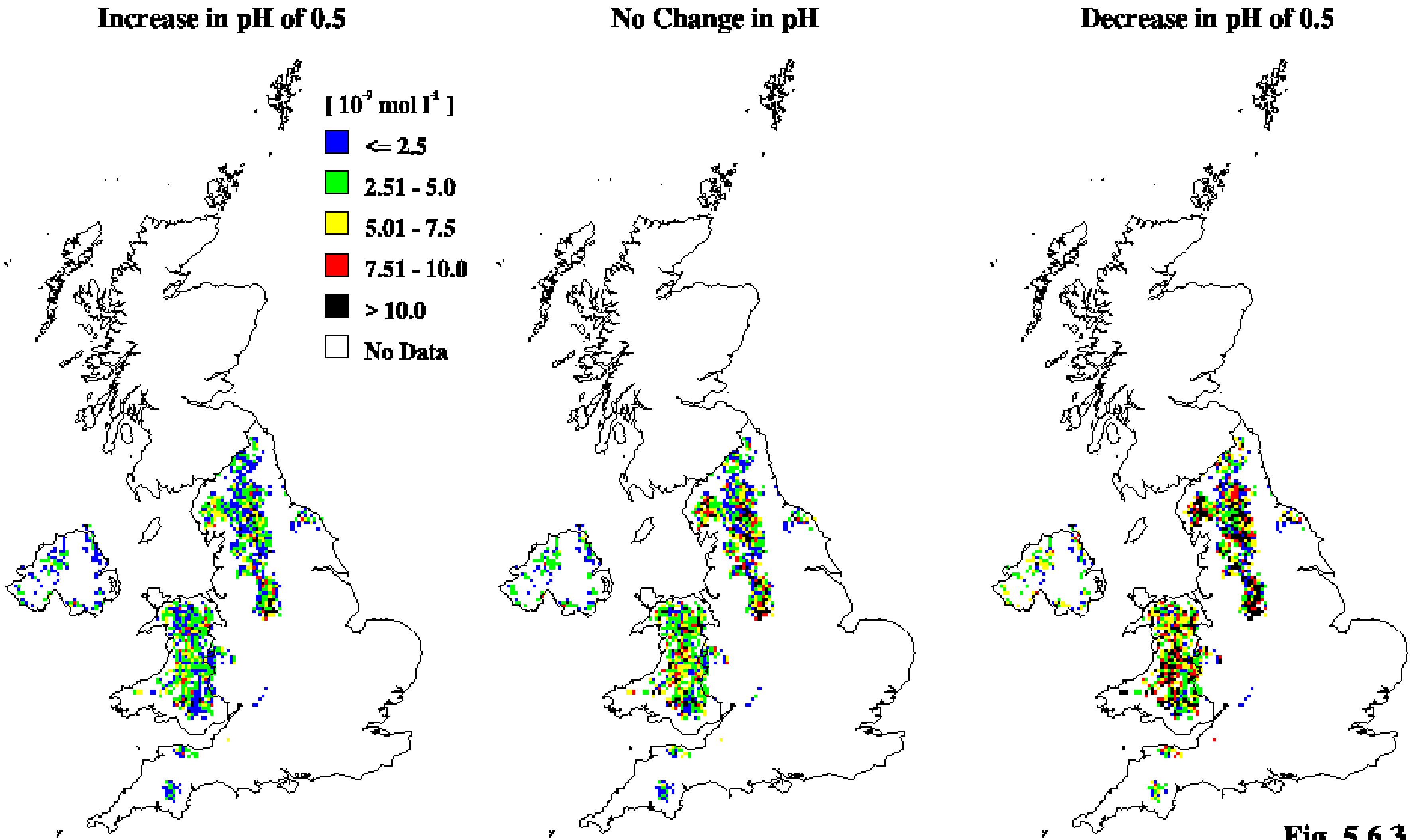


Fig. 5.6.2

Critical Loads Mapping and Data Centre, CEH Monks Wood January 2001

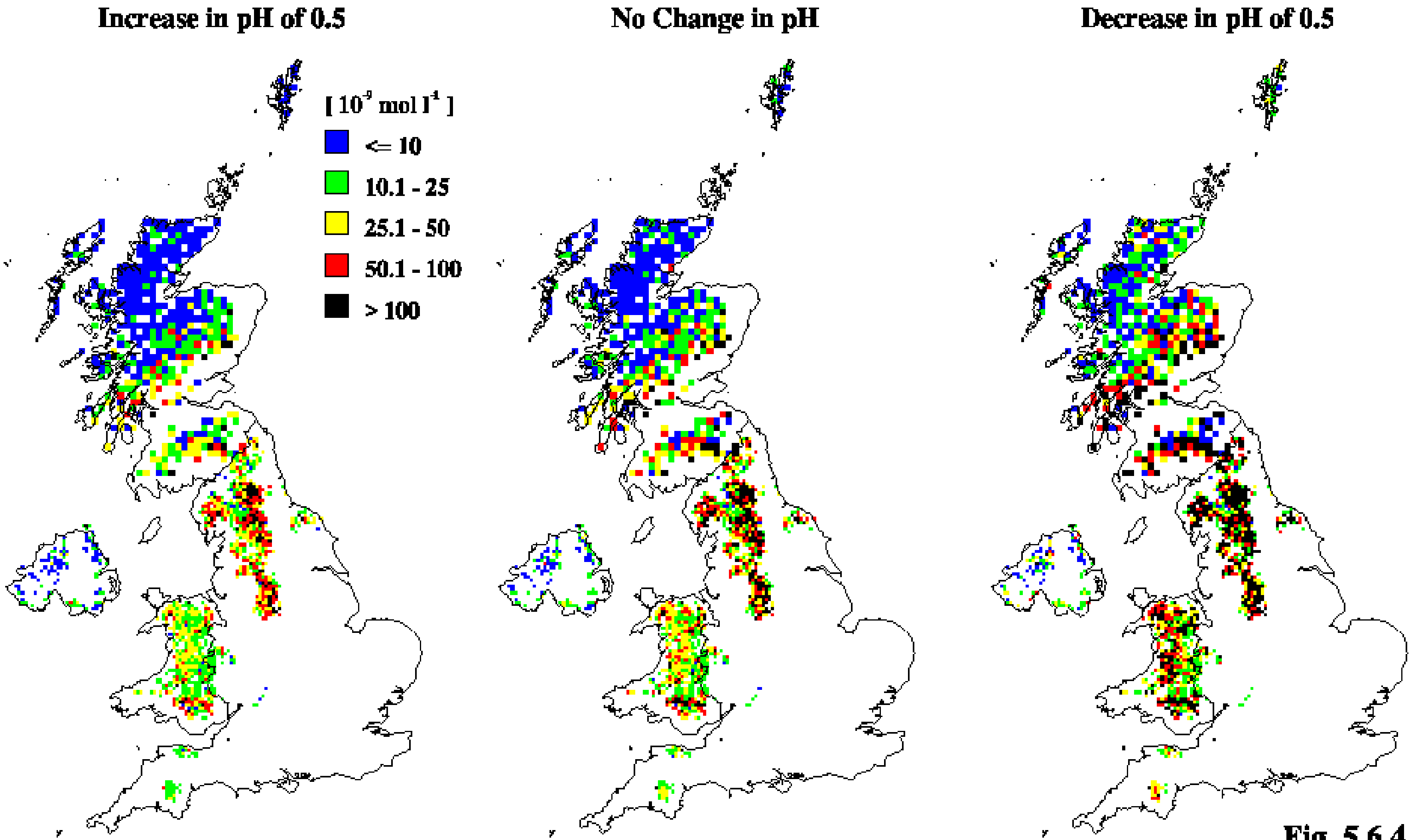
The Effect of Change in pH in Modelling Soil Solution Concentrations of Cadmium



Critical Loads Mapping and Data Centre, CEH Monks Wood January 2001

Fig. 5.6.3

The Effect of Change in pH in Modelling Soil Solution Concentrations of Lead



Increase in pH of 0.5

No Change in pH

Decrease in pH of 0.5

Critical Loads Mapping and Data Centre, CEH Monks Wood January 2001

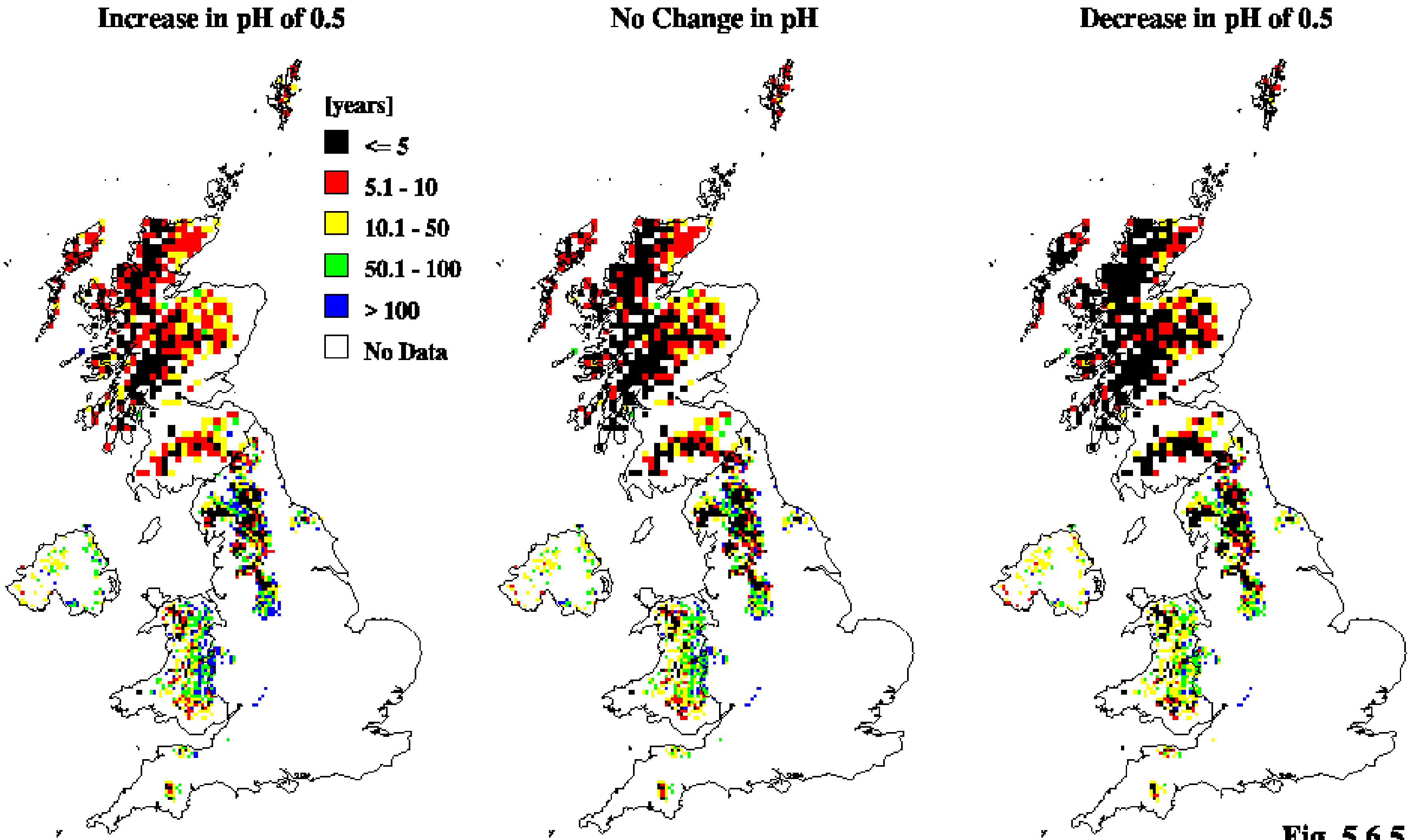
Fig. 5.6.4

(b). It will influence the dynamics of metal accumulation. As pH falls, so metal accumulation will be slower (loss in runoff will be greater), but the critical reactive soil pool will be smaller, so may be reached more quickly.

In order to illustrate this effect, Fig 5.6.5 and 5.6.6 show the effects of a change in pH on the time taken to increase from zero to half the critical reactive soil pool, for cadmium and lead respectively. The central map is equivalent to the left-hand map in Figs. 5.5.3 and 5.5.4 respectively. The results clearly show that the effect of reducing the critical reactive soil pool which is in equilibrium with the critical soil solution is the dominant one. While the effect of pH is not as strong as that on modelled soil solution and free-ion concentrations, probably because it reflects the action of two competing effects, the pattern is rather similar. That is, in areas with high pH and therefore long timescales to reach half the critical concentration, there is little effect of the modelled change of 0.5 of a pH unit. However, where soils are more acidic and timescales much shorter, the effect of falling pH in generally reducing the timescales is clearly visible.

Figures 5.6.7. and 5.6.8. present an equivalent analysis for cadmium and lead respectively, of the effect of changing pH on the time for the reactive soil pool to increase from the current level to the critical reactive soil pool at current rates of deposition. The central maps are equivalent to the right-hand maps in Figs. 5.5.3 and 5.5.4. For cadmium, there is only a small effect of pH on the numbers of squares where the reactive soil concentration currently exceeds the critical reactive soil concentration. Although the area where future exceedance of the critical reactive soil concentration is greater for lead (Fig. 5.6.8), there is only a marginal effect on the predicted timescales. Instead, the largest effect of pH is to increase the area where the critical reactive soil concentration is currently exceeded, in areas such as mid-Wales.

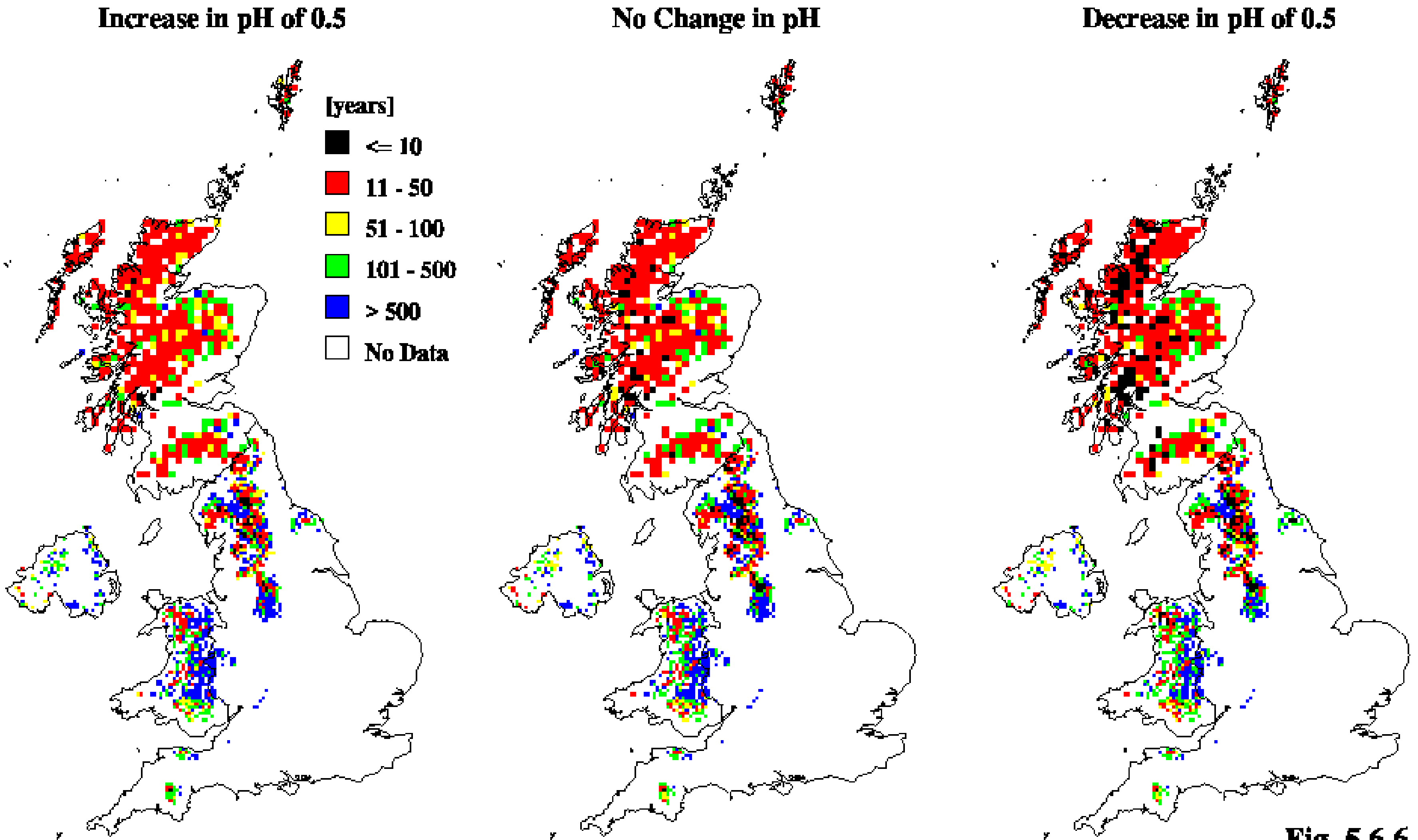
The Effect of Change in pH in Modelling Critical Reactive Half Times of Cadmium



Critical Loads Mapping and Data Centre, CEH Monks Wood   January 2001

Fig. 5.6.5

The Effect of Change in pH in Modelling Critical Reactive Half Times of Lead



Increase in pH of 0.5

No Change in pH

Decrease in pH of 0.5

Critical Loads Mapping and Data Centre, CEH Monks Wood January 2001

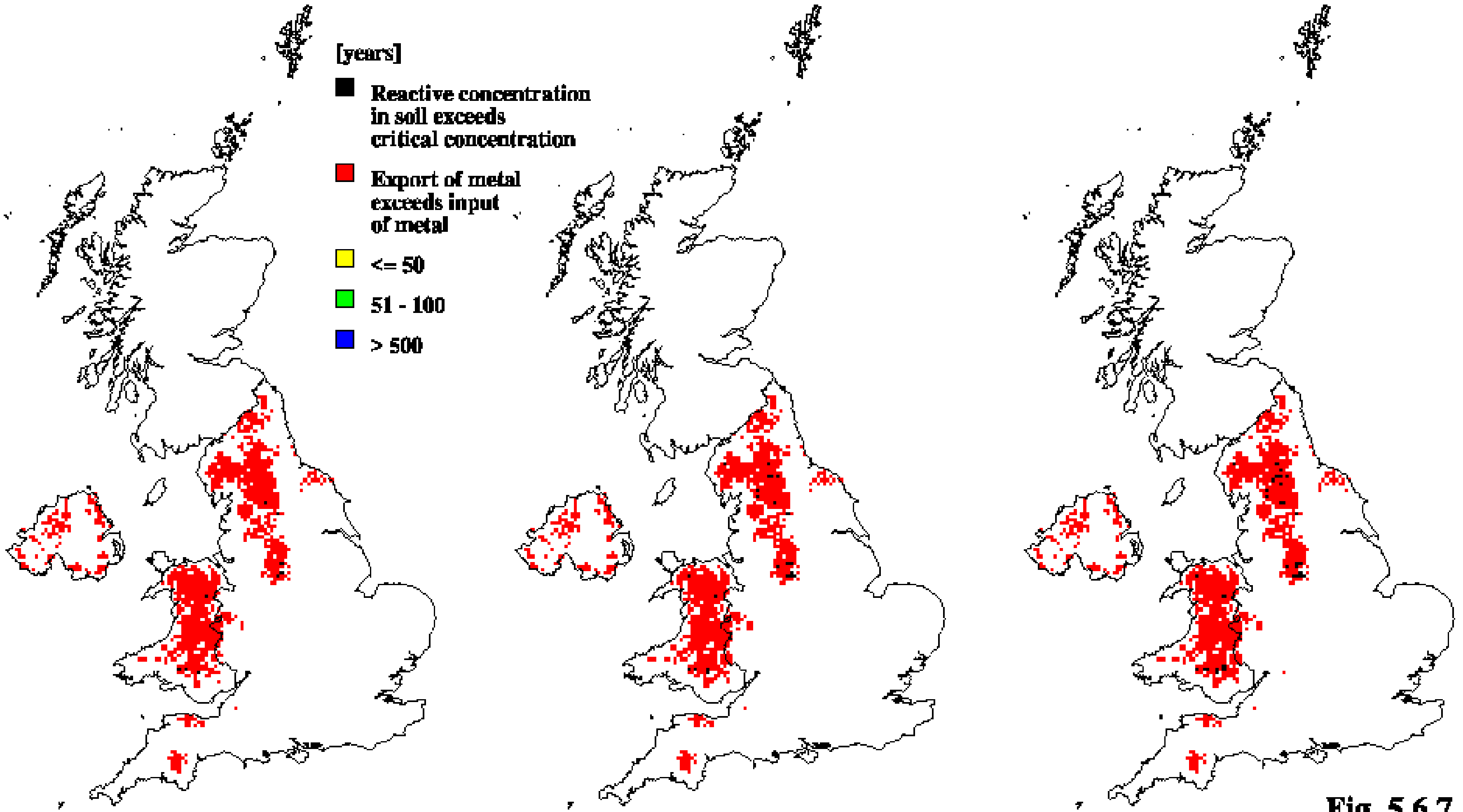
Fig. 5.6.6

The Effect of Change in pH in Modelling Critical Reactive Times of Cadmium

Increase in pH of 0.5

No Change in pH

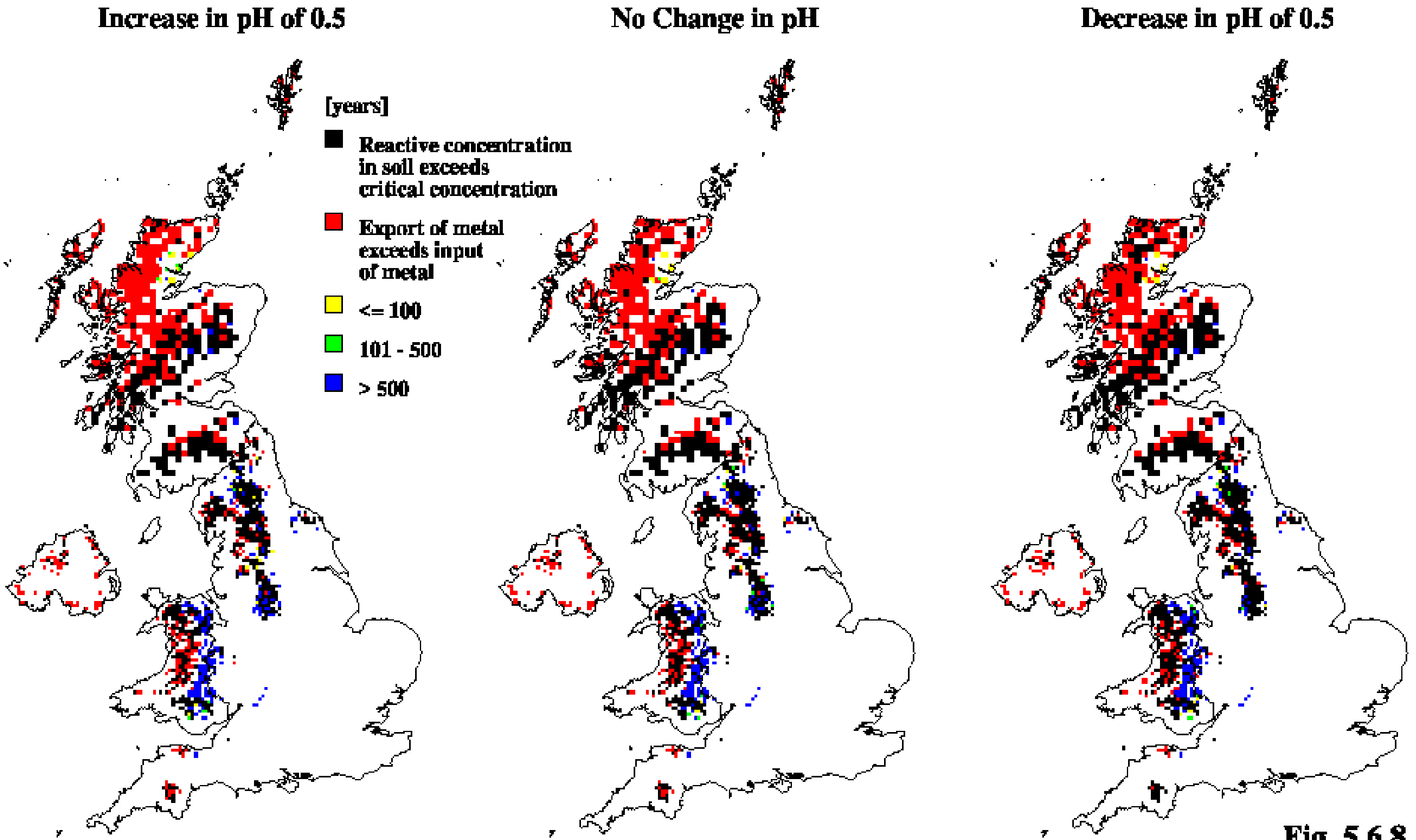
Decrease in pH of 0.5



Critical Loads Mapping and Data Centre, CEH Monks Wood January 2001

Fig. 5.6.7

The Effect of Change in pH in Modelling Critical Reactive Times of Lead



Critical Loads Mapping and Data Centre, CEH Monks Wood January 2001

Fig. 5.6.8

5.7. Critical Loads for Forestry

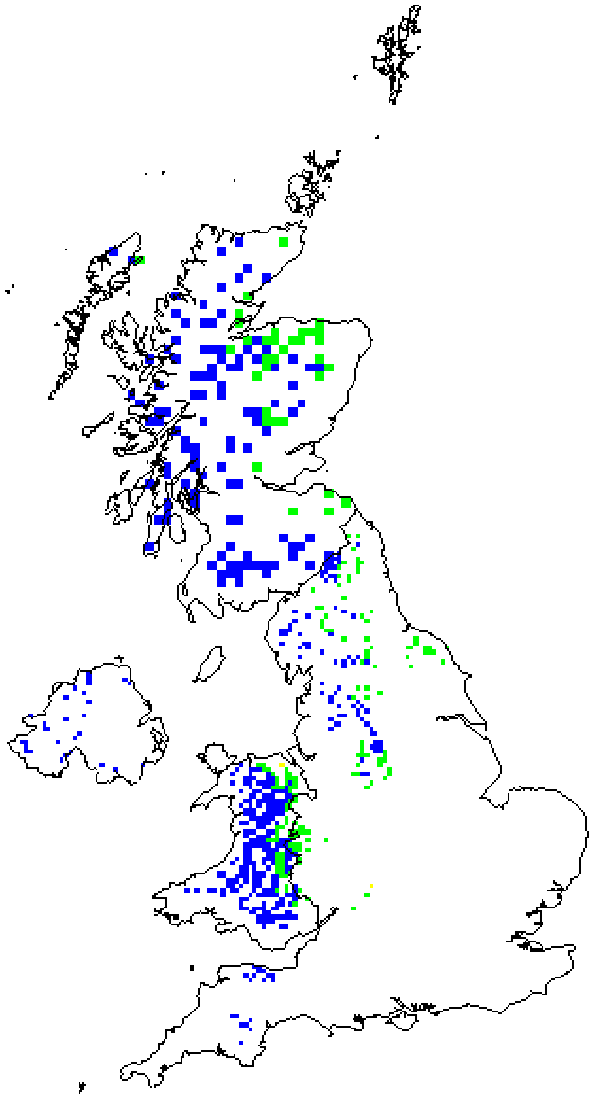
A key component of the simple method used to estimate critical loads, which is proposed by Gregor *et al*. (2000) and which has been adopted in our estimates for the U.K., is the rate of removal. For moorland and upland grassland, we assume that the removal in grazing animals is insignificant. However, for forested areas, the critical load needs to take account of the removal of metals in the harvested crop. In the U.K. forest removal of base cations has been estimated for mass balance calculations of critical loads of acidity, by multiplying the biomass removed by the mean base cation content. However, very few data exist for the metal content of harvested trees in the U.K.. Therefore, for these calculations we have used the information provided by the manual of de Vries & Bakker (1998).

This manual provides empirical relationships between metal deposition and growth uptake, thus taking into account the fact that metal content, and hence removal, may be greater at locations with higher rates of dry deposition. According to de Vries & Bakker (1998), deposition has a strong influence on the removal of copper and lead, but very little on that of cadmium and zinc, which have a greater availability in the soil solution, especially at low pHs. Furthermore, these equations only provide a good fit to the data when polluted sites with very high rates of metal deposition are included, and they may not be appropriate for use in national assessments for the U.K.

Therefore, for these calculations, mid-range values of wood metal content, provided by the manual of de Vries & Bakker (1998), were used. These suggest a value of 0.3 mg kg^{-1} for cadmium and 5.5 mg kg^{-1} for lead. It should be noted that these data are all from continental Europe and thus their application to U.K. calculations of critical loads introduces a significant uncertainty into the calculations. The critical loads calculated using these data are presented, in Fig. 5.7.1 and 5.7.2 respectively, for forested upland areas, i.e. those squares for which over 5% of the land area is forest. These maps can be compared with those presented in Figs. 5.4.1 and 5.4.4 for the non-forested uplands for the same soil solution concentrations of 3 ug l^{-1} Cd and 8 ug l^{-1} Pb. Since the squares mapped do not overlap in the two pairs of maps, only a broad picture can be gained of change in critical load introduced by including forest removal.

Comparison of Fig. 5.7.1 and 5.4.1 suggest that inclusion of harvested cadmium and lead in the calculation of critical loads for forests has an effect overall in slightly decreasing the critical load values which are calculated. This result does not reflect the effect of having an additional removal term, which should be to increase the critical load. Instead, it reflects the fact the runoff from the areas with higher forest cover is lower than from those with very little forest cover, and hence the reduction in the leaching term ($Q_{.ss}$) more than outweighs the additional removal through harvesting.

It should also be noted that forest cover will have additional effects, in particular in increasing deposition, as described in Section 5.8. Furthermore, forest cover will tend to have a net acidifying effect and to change the organic content of the topsoil, both of which will affect the estimation of critical reactive soil concentrations and the dynamics of metal response to changes in atmospheric deposition. Thus, although the rate of metal removal in forest harvest in the U.K. may be uncertain, it may have a relatively small effect on U.K. critical loads analysis compared with other factors.



Critical Limit = 3 ug l^{-1}

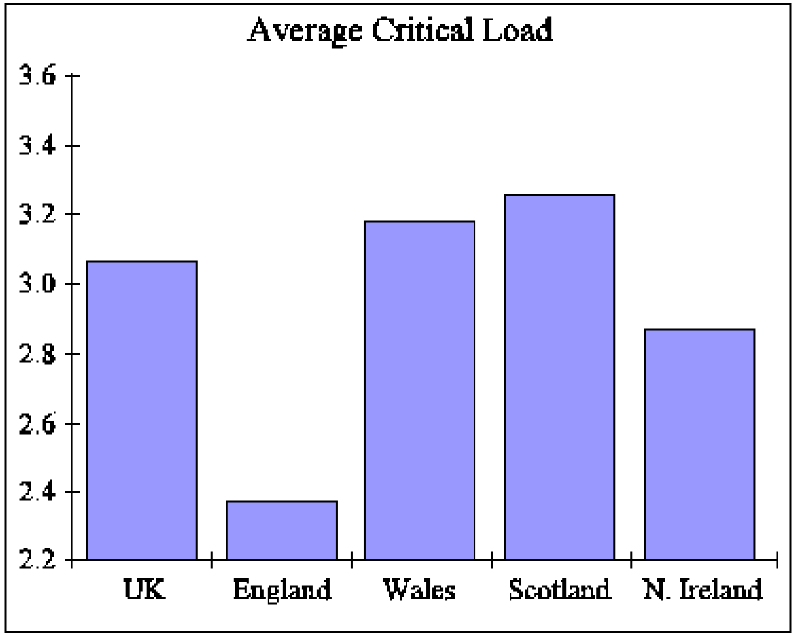
Critical Loads of Cadmium

(Modelled Data)

Forest Upland Areas of Great Britain

[mg m^{-2} yr^{-1}]

■	<= 0.25	🟨	0.51 - 1.0	🟦	> 2.0
🟥	0.26 - 0.5	🟩	1.01 - 2.0	☐	No Data



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

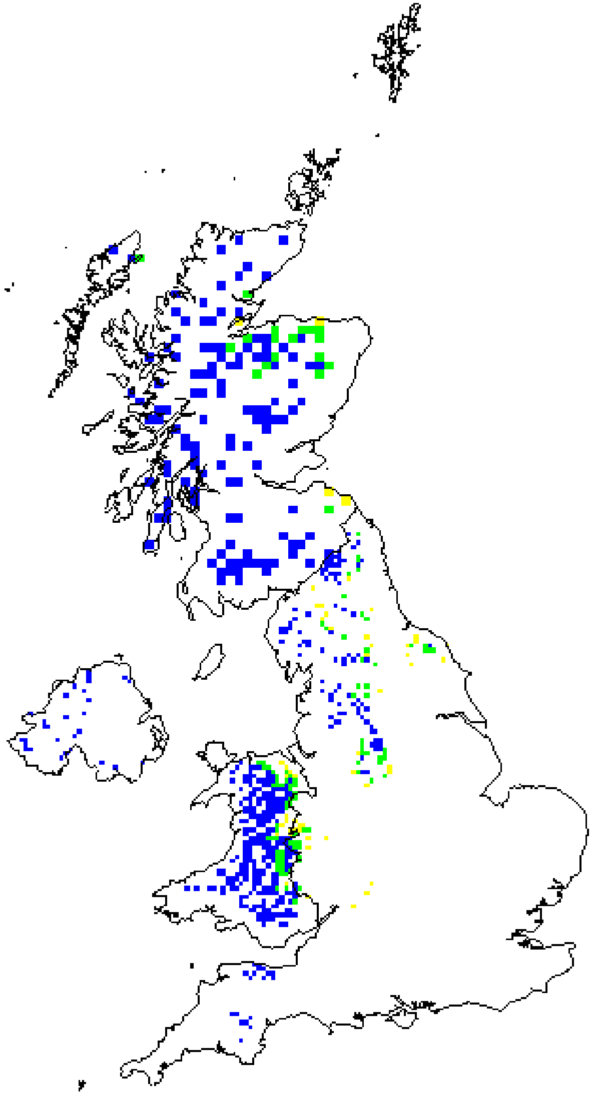
Fig. 5.7.1

Critical Loads of Lead
(Modelled Data)

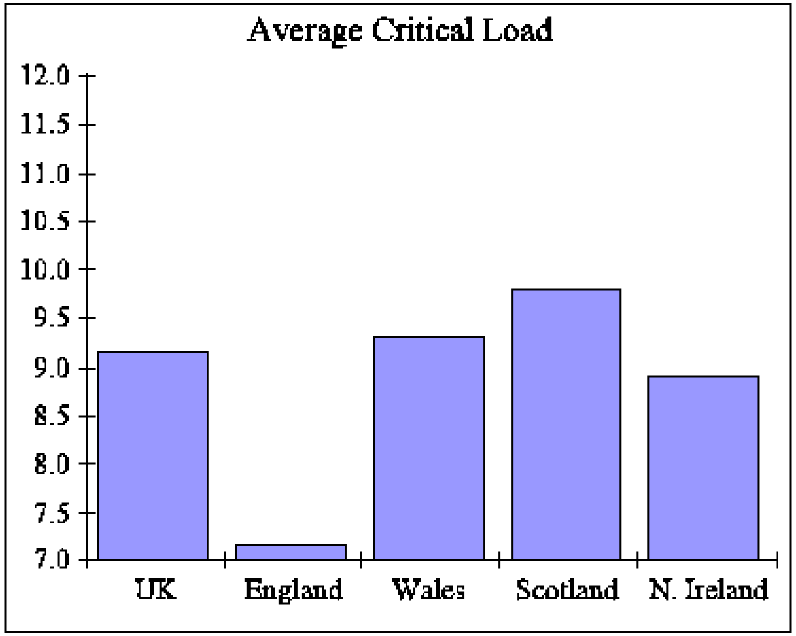
Forest Upland Areas of Great Britain

[mg m^{-2} yr^{-1}]

■	<= 1.5	🟨	3.01 - 4.5	🟦	> 6.0
🟥	1.51 - 3.0	🟩	4.51 - 6.0	☐	No Data



Critical Limit = 8 ug l^{-1}



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.7.2

5.8. Deposition

The problems of accurately defining both the absolute levels of deposition and the spatial variation across the U.K. have been covered in detail in the U.K. moss survey 2000, part II of this report. These issues are also summarised briefly in the final NERC report on deposition (cf. Annexe 1). For the purposes of this analysis of critical load exceedance, we have chosen to use the modelled deposition fields generated using the moss 2000 survey data; the methodology used to derive deposition fields from these data is described fully in Section 4 of the moss survey report. The limitations of this method are fully considered in that report, along with a comparison with other methods of assessing U.K. deposition fields. It is important to note that;

- There is an order of magnitude uncertainty in the estimates of copper and zinc deposition. This is the major reason why a critical load analysis has not been presented for these metals.

- There is a five-fold uncertainty in the estimates of cadmium deposition. However, this primarily reflects problems in the measurement of bulk deposition, and the moss survey estimates are in reasonable agreement with those derived from emission inventories.

- There is better agreement between the estimates of deposition for lead than for other metals, although the estimated total U.K. deposition still varies by about 50%. A specific problem relates to the fact that lead concentrations in mosses have fallen significantly between 1996 and 2000, but the evidence of a fall in bulk deposition rates is limited. The modelled deposition used in this analysis is based on correlations between moss concentrations in 2000 and deposition in the period 1996-98, and thus might be better seen as a representation of the deposition for 1996-98 rather than the present day. It is likely that falling emissions of lead from road traffic will have resulted in lower deposition by 2000, but this requires confirmation from bulk deposition data.

It is also important to note that some moss collection sites may be influenced by historical mining and smelting activity. This means that the derived maps of deposition may contain isolated ‘hot-spots’ which reflect local conditions around the moss collection site rather than regional deposition patterns.

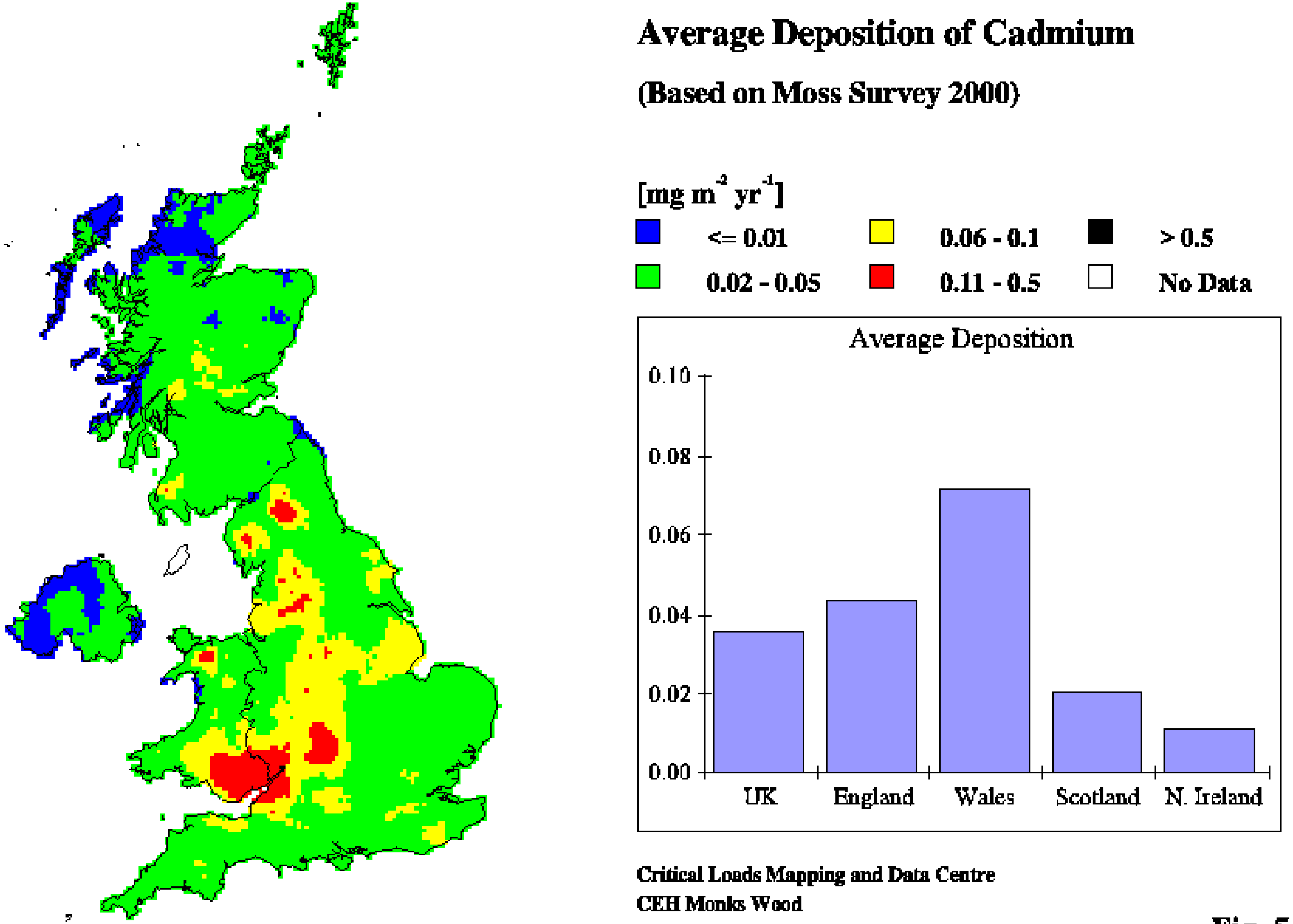
Figs 5.8.1-5.8.4 present the national deposition fields generated using these input data. The deposition fields are calculated separately for forests and for low vegetation (e.g. moorlands, grasslands, crops) because of the very different deposition velocities. Figs 5.8.1 and 5.8.2 present the overall average national deposition fields, in which the deposition to each 10km square is calculated as the weighted average of the modelled deposition to forest and non-forest vegetation, based on their relative land cover in the square. Figs. 5.8.3 and 5.8.4, in contrast, take no account of the land cover, but present the modelled deposition to forests as if every 10km. grid square was entirely covered by forests.

Fig 5.8.1. presents the modelled deposition field for cadmium. Deposition is markedly higher in England and Wales than in Scotland and Northern Ireland. The largest area of elevated deposition is found in South Wales and around Bristol, probably reflecting local industrial sources. Deposition is regionally elevated through the Midlands and NW England, but the high values in parts of North Wales and northern England may reflect only local site factors.

Fig. 5.8.2 presents the modelled deposition field for lead. The largest areas of elevated deposition are in South Wales and in the Midlands. The hotspots in northern Scotland, northern England and North Wales most probably reflect local site factors. It is important to note that no moss collections were made in urban areas, and that the maps do not reflect the elevated input of lead from motor vehicles in and around such areas.

Fig. 5.8.3 presents the deposition field for cadmium assuming total forest cover. The overall deposition levels are approximately double the average deposition rates shown in Fig. 5.8.1, reflecting the much greater deposition velocity to forests. The relative spatial pattern is broadly similar to that in Fig. 5.8.1.

Fig 5.8.4 presents the deposition field for lead assuming total forest cover. The overall deposition fields are nearly three times greater than the average deposition. The greater enhancement for lead than for cadmium is a reflection of the different particle size distributions of the two metals. It is noticeable that the enhancement is greater in England than in Wales, reflecting the lower forest cover in England, and hence the greater enhancement if it is assumed that all land cover is forests.

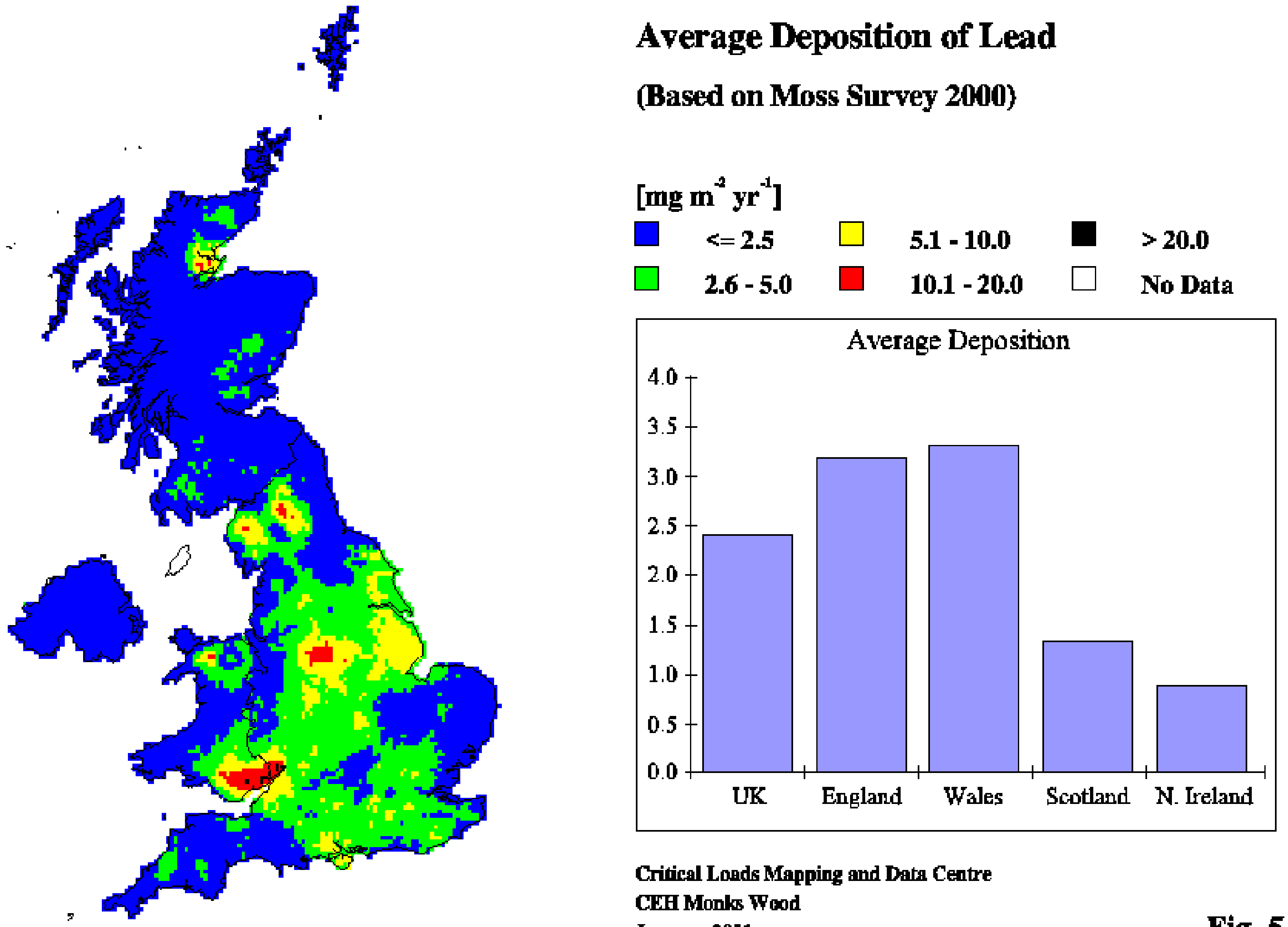


Average Deposition of Cadmium

(Based on Moss Survey 2000)

Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.8.1



Average Deposition of Lead

(Based on Moss Survey 2000)

[mg m^{-2} yr^{-1}]

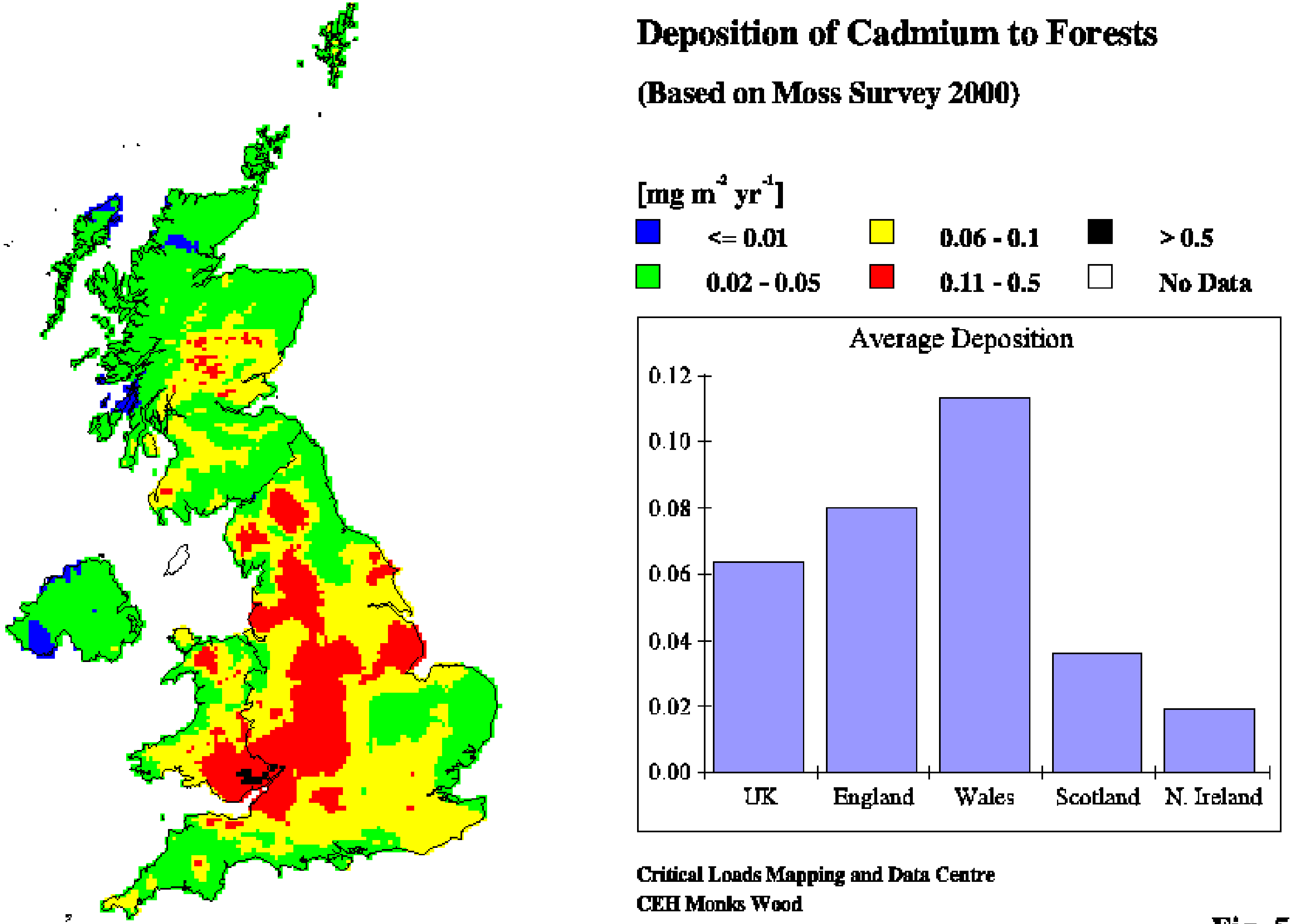
🟦	<= 2.5	🟨	5.1 - 10.0	■	> 20.0
🟩	2.6 - 5.0	🟥	10.1 - 20.0	□	No Data

Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.8.2

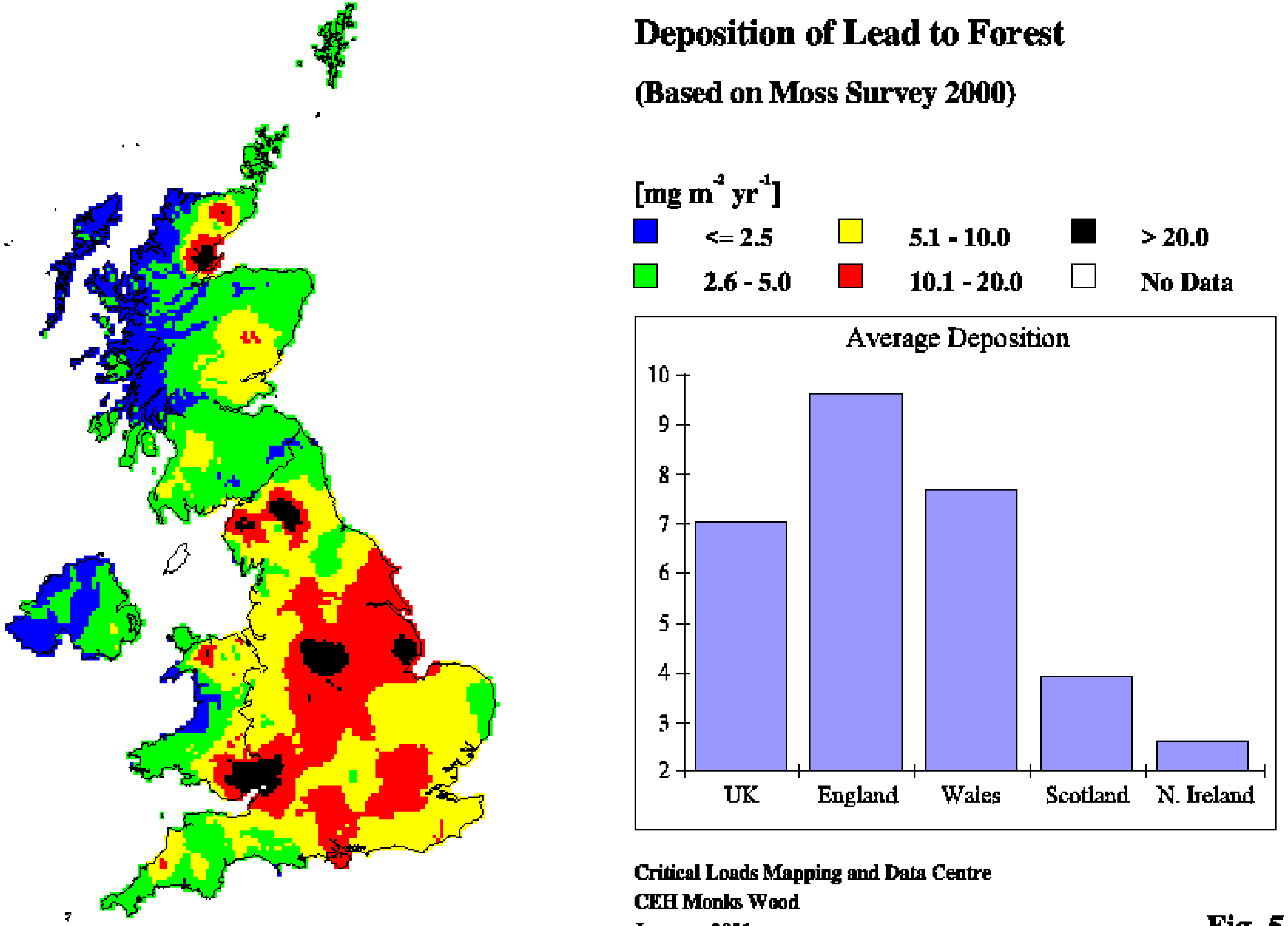
Deposition of Cadmium to Forests

(Based on Moss Survey 2000)



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.8.3



Critical Loads Mapping and Data Centre
CEH Monks Wood
January 2001

Fig. 5.8.4

5.9. Critical Load Exceedance

These deposition fields can then be combined with the critical load maps presented in Section 5.4 and 5.7 to estimate the areas of the U.K. uplands where critical loads are exceeded. In interpreting these maps it is important to be aware of the uncertainties in the deposition fields described above. To aid interpretation of this analysis of exceedance, the maps also identify areas where the modelled current soil solution concentration exceeds the relevant critical limit. Areas where the critical load is exceeded and the critical soil solution concentration is also exceeded are also identified separately.

The reason for providing this form of presentation is the effect of past metal deposition, which it is reasonable to assume was higher than current levels of deposition in most parts of the U.K. uplands. Thus, it is possible that the critical soil solution concentration can be exceeded because of the cumulative effect of historical deposition, even though the critical load is currently not exceeded. Conversely, it is possible that the critical load is currently exceeded, even though the modelled soil solution concentration is not exceeded, because of the long timescale in some areas for the reactive soil metal pool to accumulate to critical concentrations.

It should be noted that, for cadmium, the lack of current geochemical data for Scotland means that exceedance of the critical limit by the current modelled soil solution concentration cannot be assessed. The first series of maps (Figs. 5.9.1 – 5.9.5) present maps of all the U.K. uplands, but use deposition values and critical loads for non-forest ecosystems only. Figs. 5.9.6 and 5.9.7 present a comparison with forest deposition and forest critical loads, but only for those areas with a forest cover above 5%.

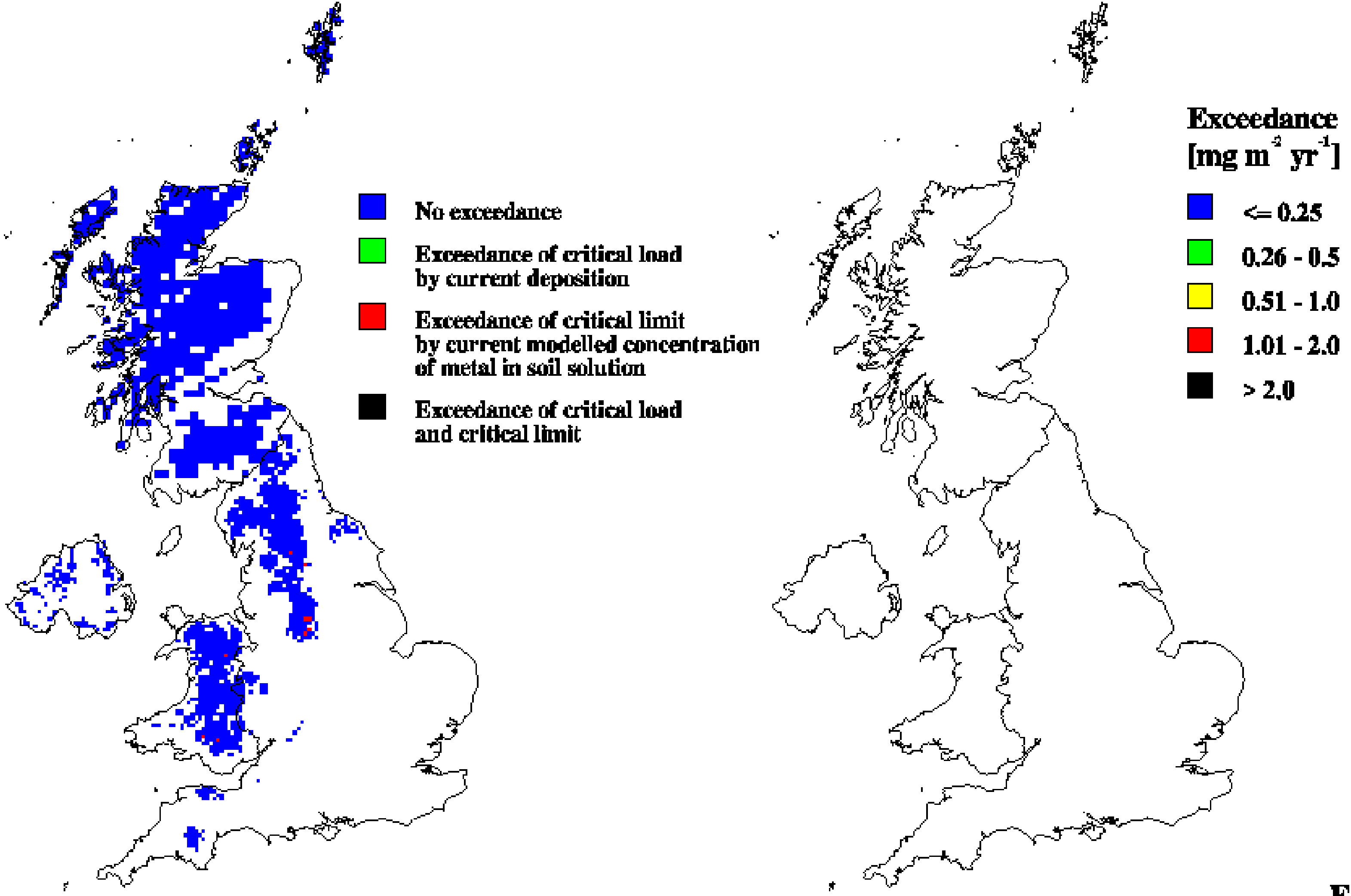
Fig. 5.9.1-5.9.3 present exceedance maps for cadmium, based on the critical limits of 3 ug l^{-1}, 1 ug l^{-1} and 0.35 ug l^{-1}, as described in Section 5.3. No exceedance of the critical load is shown in Figs. 5.9.1 and 5.9.2, even though there are areas of Wales, the Pennines and Cumbria where the critical limit is exceeded. This indicates that current deposition does not need to be reduced further to prevent an increase in the area where the critical limit is exceeded. However, there are areas where the critical limit is exceeded because of historical deposition, or because of geochemical anomalies.

The picture is rather different when the critical limit of 0.35 ug l^{-1}, based on effects in freshwaters is considered. In this case, a few isolated squares show exceedance of the critical load in south Wales and the Cotswolds, but more importantly the critical limit in soil solution is exceeded over the majority of England and Wales, and a considerable part of Northern Ireland. However, as discussed in Section 5.3, this map will significantly overestimate the real risk of ecological impacts of cadmium in freshwaters. Rather, this analysis indicates the need for further assessment of the ecological implications of leaching of cadmium into freshwaters.

Figs. 5.9.4 and 5.9.5 present the same analysis for lead for the critical limits of 8 and 2 ug l^{-1} respectively. For this metal, the full analysis can be made over the whole of the U.K., and the results offer a significant contrast with those for cadmium. Even for the higher critical limit of 8 ug l^{-1}, the critical load is exceeded in South Wales, and parts

Exceedance of Critical Loads of Cadmium in Upland Areas

Critical Limit = 3 ug/l

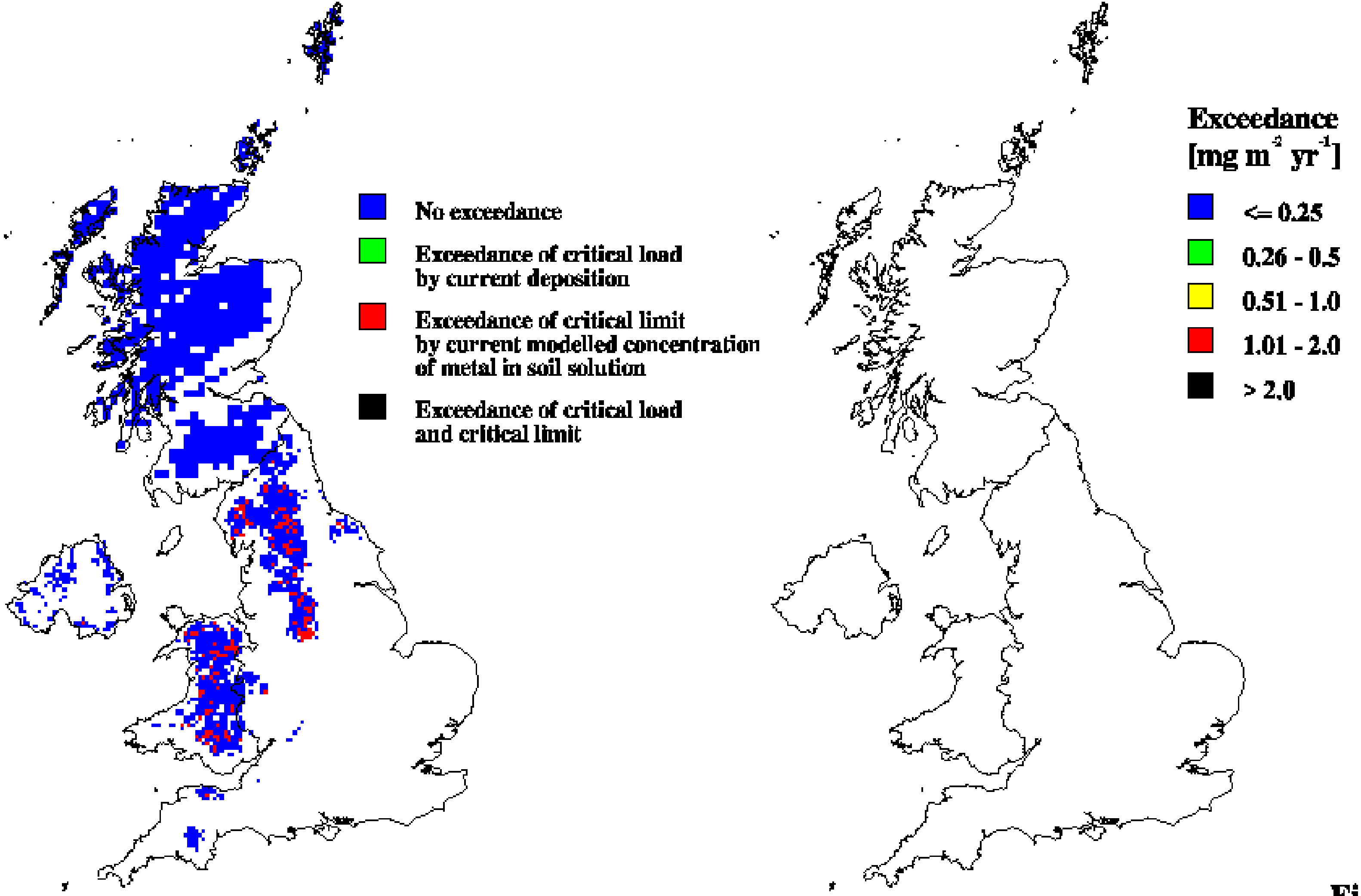


Critical Loads Mapping and Data Centre, CEH Monks Wood January 2001

Fig. 5.9.1

Exceedance of Critical Loads of Cadmium in Upland Areas

Critical Limit = 1 ug/l

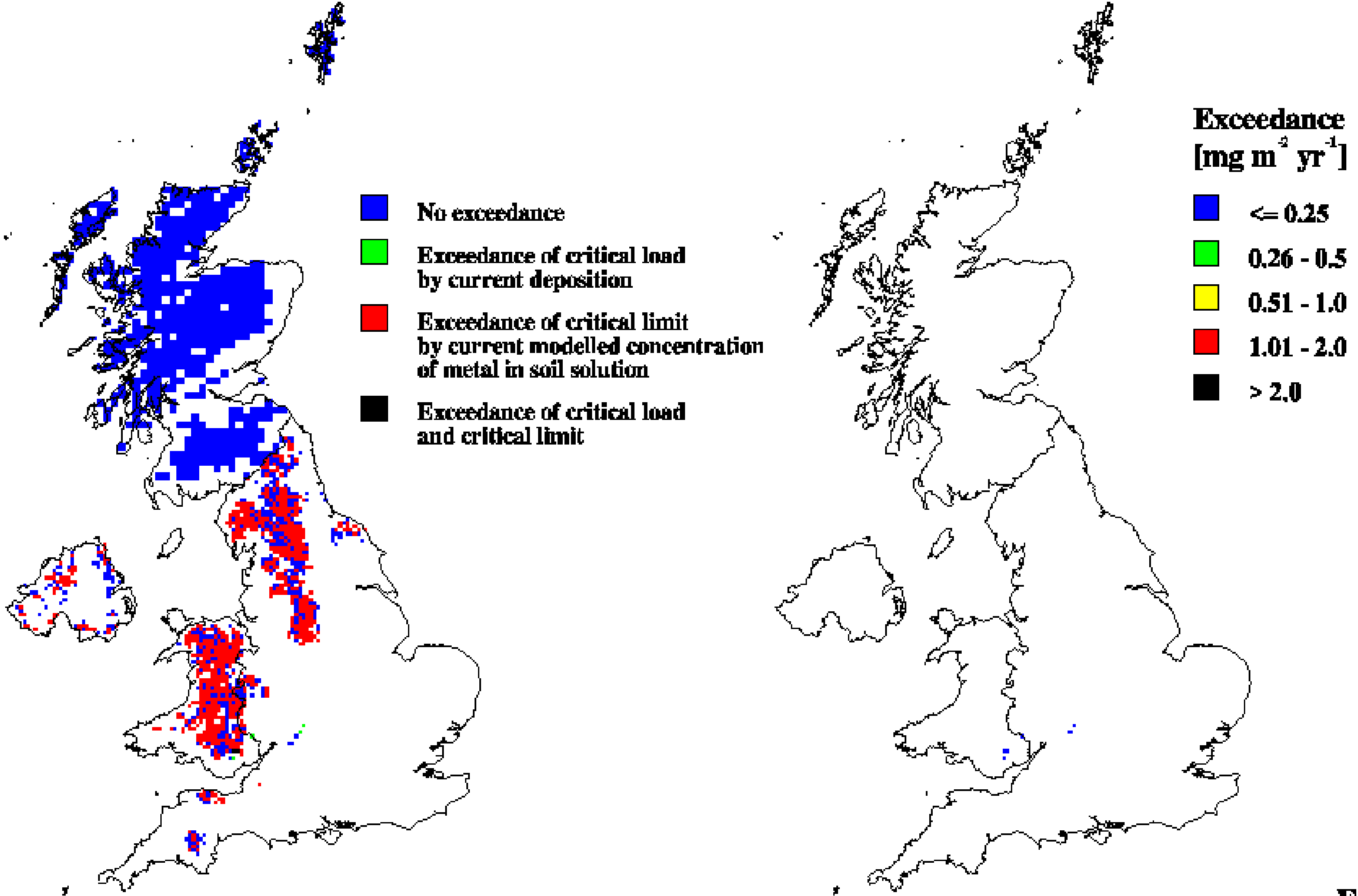


Critical Loads Mapping and Data Centre, CEH Monks Wood January 2001

Fig. 5.9.2

Exceedance of Critical Loads of Cadmium in Upland Areas

Critical Limit = 0.35 ug/l

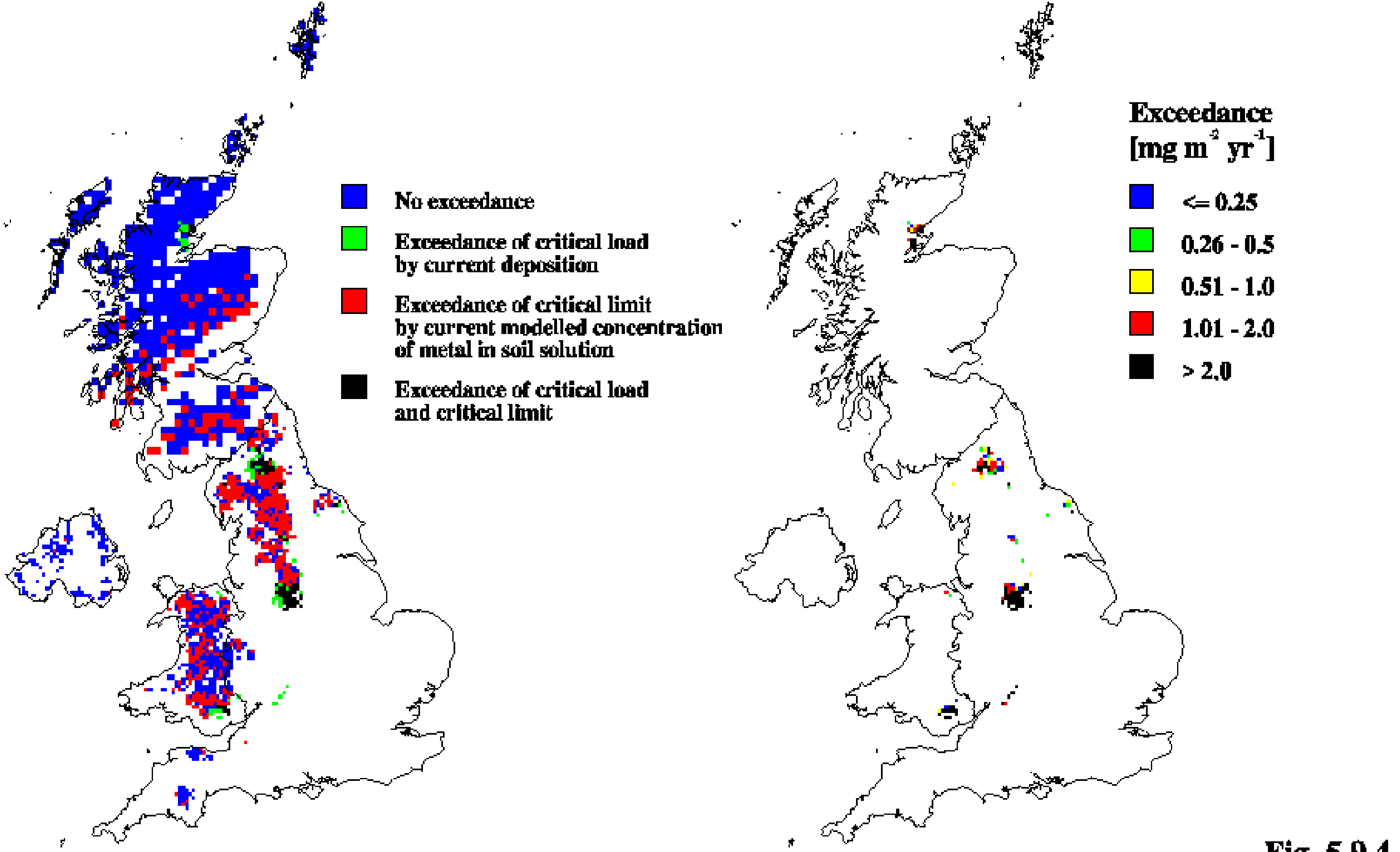


Critical Loads Mapping and Data Centre, CEH Monks Wood   January 2001

Fig. 5.9.3

Exceedance of Critical Loads of Lead in Upland Areas

Critical Limit = 8 ug/l

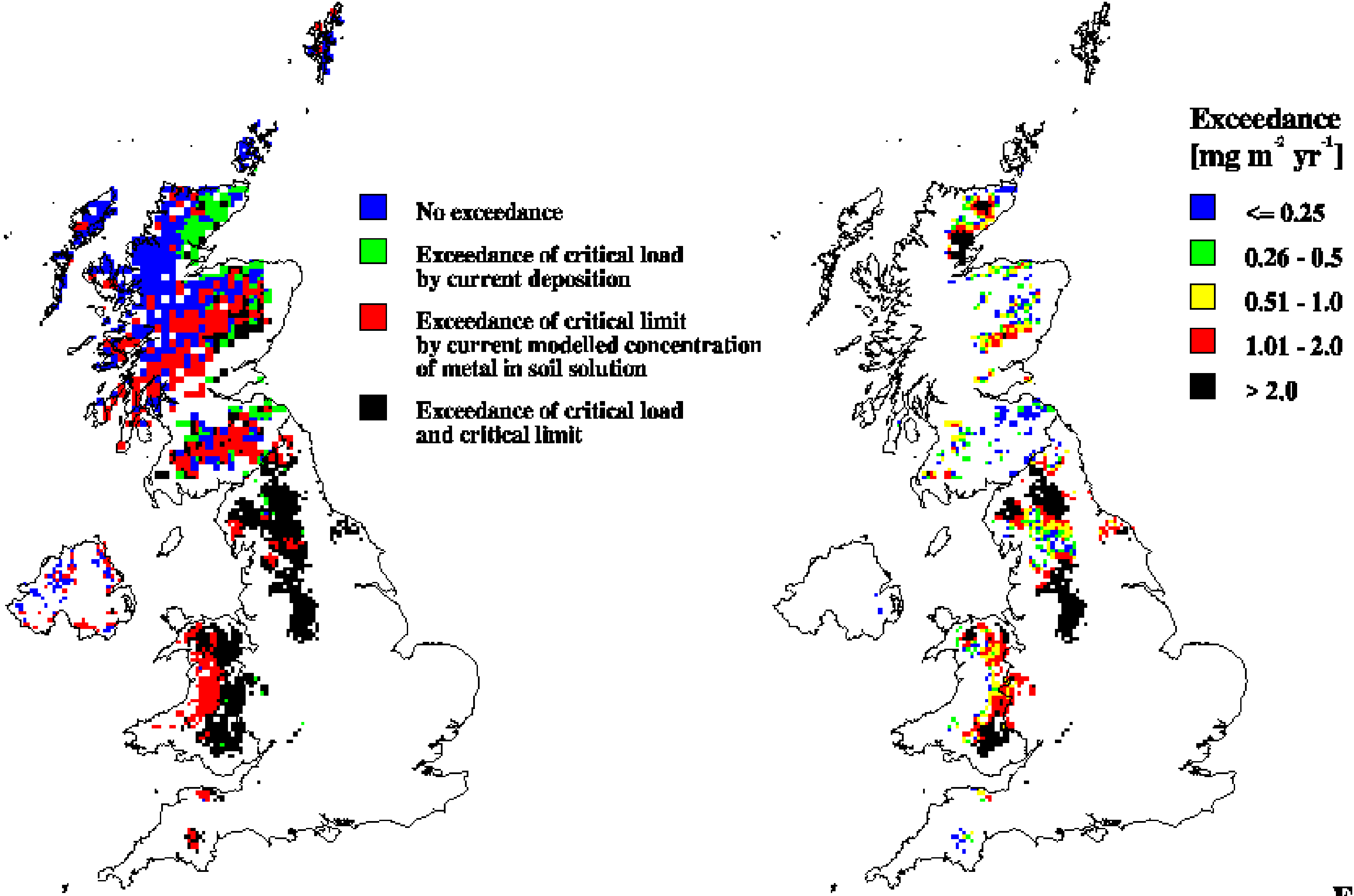


Critical Loads Mapping and Data Centre, CEH Monks Wood January 2001

Fig. 5.9.4

Exceedance of Critical Loads of Lead in Upland Areas

Critical Limit = 2 ug/l

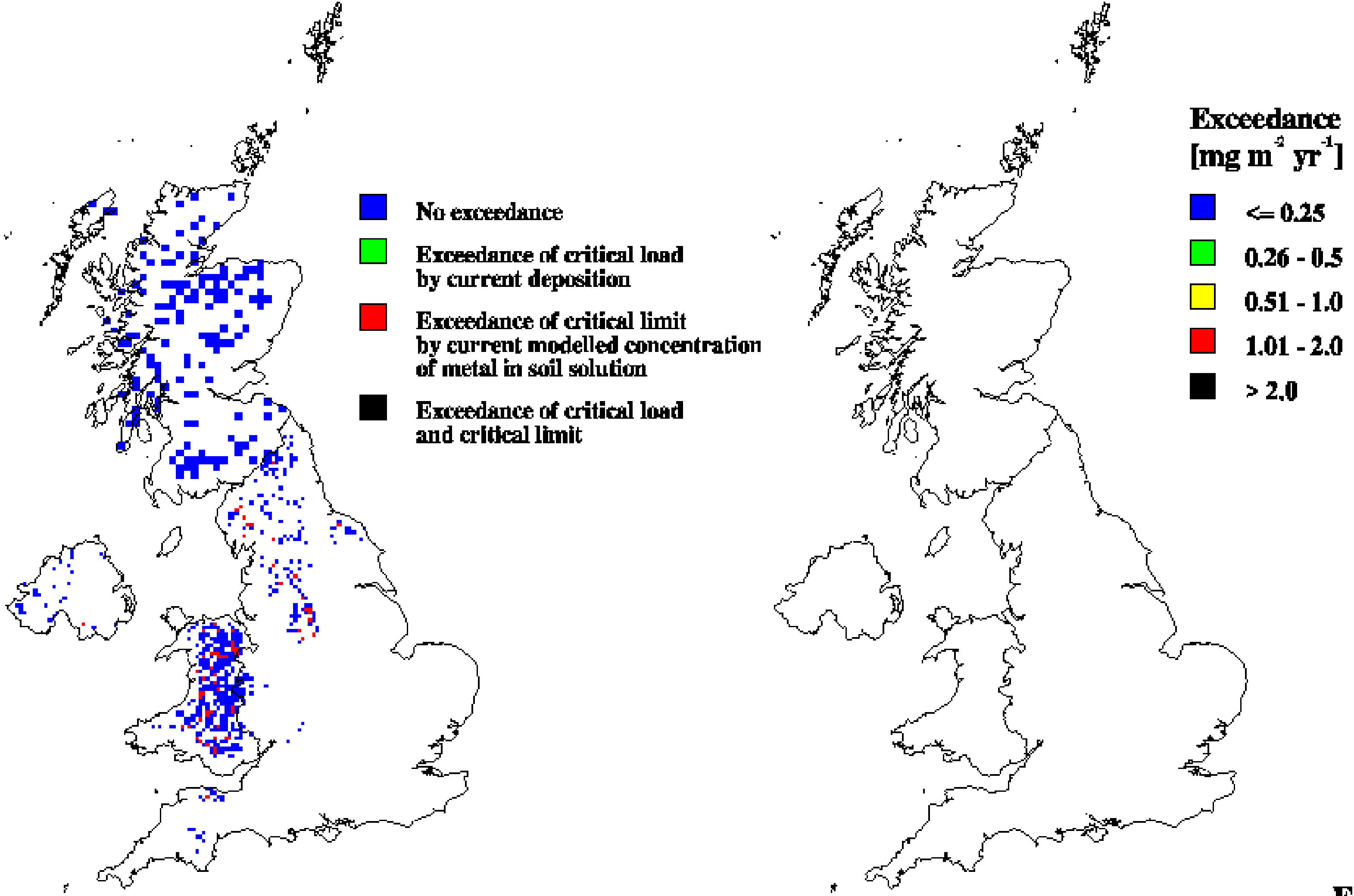


Critical Loads Mapping and Data Centre, CEH Monks Wood   January 2001

Fig. 5.9.5

Exceedance of Critical Loads of Cadmium in Forest Uplands

Critical Limit = 1 ug/l

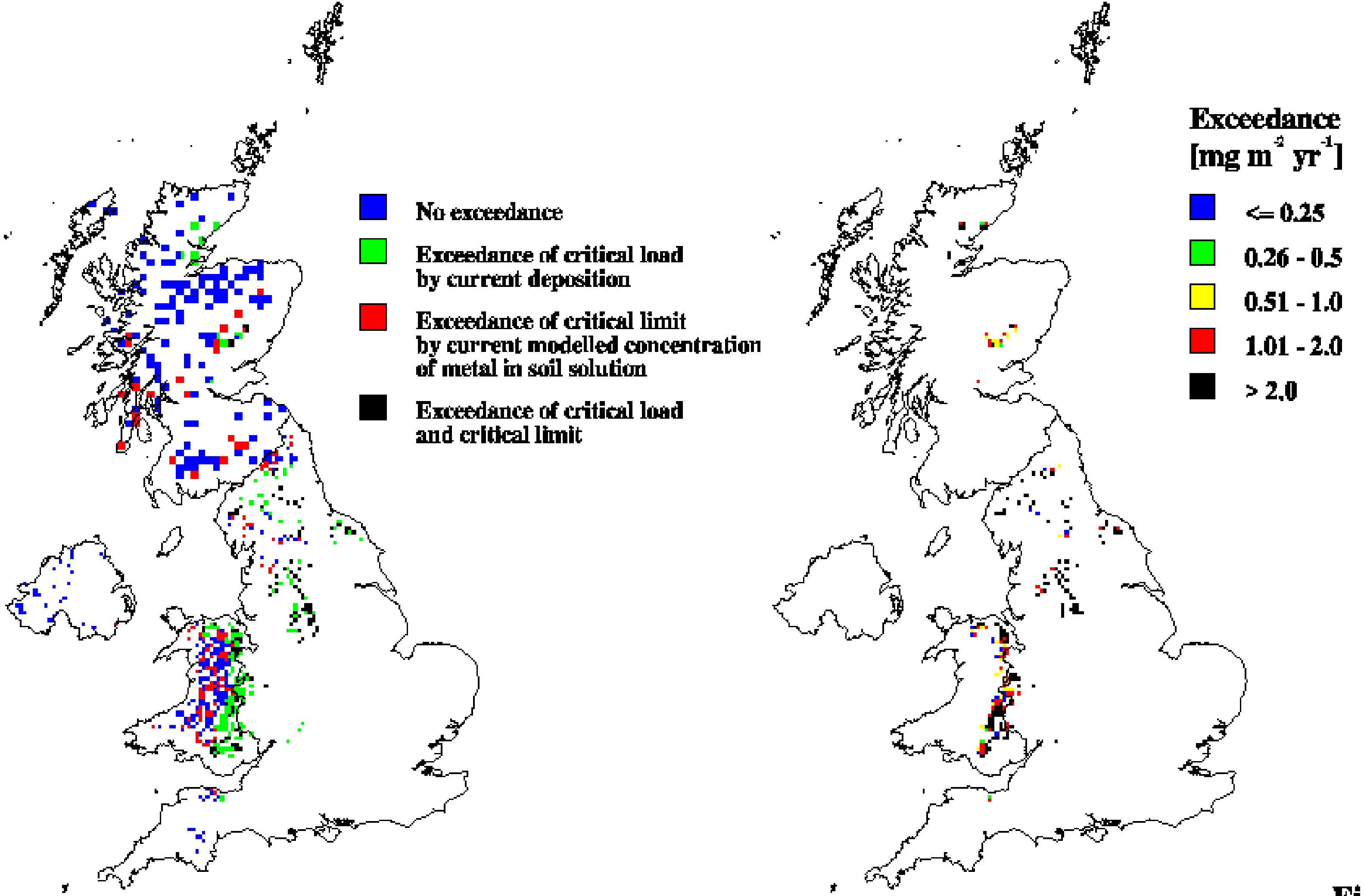


Critical Loads Mapping and Data Centre, CEH Monks Wood January 2001

Fig. 5.9.6

Exceedance of Critical Loads of Lead in Forest Uplands

Critical Limit = 8 ug/l



Critical Loads Mapping and Data Centre, CEH Monks Wood   January 2001

Fig. 5.9.7

of the southern and northern Pennines, and in a number of other squares. However, some of these areas (e.g. in northern Scotland) may reflect the impact of very local sources on the deposition field derived from the moss survey..

In some areas, such as the southern and northern Pennines, these areas of exceedance correspond with areas in which the critical limit is exceeded by the modelled soil solution concentration. However, unlike for cadmium, there are areas where the critical load is exceeded but the critical limit is not exceeded by the current concentration, such as the Cotswolds. This difference with cadmium most probably reflects the fact that lead is more tightly bound to the soil matrix. Hence, longer time is needed for metal deposited from the atmosphere to accumulate to levels in the reactive soil pool which are in equilibrium with concentrations above the critical limit in soils solution. It is of interest, therefore, that areas such as the Cotswolds are the ones for which our model predicts that current import is greater than current export (cf. Fig. 5.5.6), i.e. lead is still accumulating in the reactive soil pool.

Fig 5.9.5 shows the dramatic effect of using the lower value for soil solution concentrations proposed by the German analysis. The critical load is exceeded over most of England, and over most of eastern Wales and eastern Scotland, where runoff is lower. Most of these areas, except the northern half of Scotland, are ones where the critical limit is already exceeded by modelled soil solution concentrations. There are also significant areas of western Wales, southern Scotland and Northern Ireland where the modelled soil solution concentration exceeds the critical limit, but the critical load is not exceeded. As for cadmium, this reflects the effect of historical deposition, and these are all broadly areas where our model predicts that export is currently greater than import.

As explained in Section 5.8., the deposition to forests may be considerably greater than that for moorland and grassland. Therefore, Figs. 5.9.6 and 5.9.7 present the same analysis based on forest deposition of cadmium and lead, respectively, only for those squares where the forest cover exceeds 5%. Fig. 5.9.6 shows that using forest deposition alone has no effect in producing areas where the critical load is exceeded, and a similar conclusion was reached for the critical limit of 1 ug l^{-1} (data not shown).

The picture is somewhat different for lead, as shown in Fig. 5.9.7. A substantial new area in exceedance of the critical load based on 8 ug l^{-1} appears in the eastern half of Wales, and some additional squares in the Pennines and Cumbria show exceedance. In contrast to the upland map which used non-forest deposition and critical loads (Fig. 5.9.4), there are much larger areas where the critical load is exceeded but there is no current exceedance of the critical limit in soil solution. The reason for this is unclear. It may reflect the sampling strategy of the Soil Geochemical Atlas avoiding forested areas, or it may reflect the effect of changes in soil characteristics caused by afforestation which influence the partitioning between the soil matrix and soil solution, but which are not included in our models.

6. CONCLUSIONS

This research focussed on the development of methodological approaches. The research under this contract has succeeded in its aim in developing a conceptual methodological framework which can effectively be applied to national critical loads assessments and which has contributed to the ongoing process of international discussions of critical load methodologies for metals. This approach can also be used to link assessments in soils and freshwaters, to examine the significance of historical deposition, and to assess the impact of soil acidification, which may have significantly affected metal budgets in the U.K. uplands.

However, the uncertainties in this approach and in the parameterisation of the models which we have developed make it difficult to draw specific conclusions. While extensive spatial analysis has been presented, any specific conclusion, for instance about the degree of exceedance of a given critical load, must be made with a degree of caution which reflects the large degree of uncertainty in the input data and underlying models.

With these limitations in mind, the key conclusions from this study can be summarised as follows:-

- The free-ion concentrations predicted by applying the WHAM model to the measured soil solution concentrations were strongly related to microbial toxicity.

- Simple empirical relationships with high predictive power were derived to estimate free-ion concentrations from spatial data on pH and total metal concentrations.

- The empirical transfer functions which we have developed allow us to apply a simple but effective approach to critical load assessments for metals in U.K. upland soils.

- An empirical methodology has been developed which can be used to apply the critical soil solution methods currently proposed within UN/ECE to national mapping of critical loads in the U.K..

- The GIS database on soil concentrations, land cover and soil characteristics provides a strong basis for analysis of metal dynamics and critical loads across the U.K..

- Critical concentrations of lead, but not those of cadmium, based on soil solution concentrations are exceeded over significant areas of the U.K.

- The degree of critical load exceedance for both lead and cadmium is lower than the area over which the critical soil solution concentration is actually exceeded. This almost certainly reflects the contribution of metal accumulation from historical deposition, which may have greatly exceeded current levels of deposition.

- The simple static critical load approach currently proposed with UN/ECE does not give an accurate assessment of the potential risk of ecological effects of metals in soils in the U.K..

- Deposition rates to forested areas are significantly greater than those to non-forested areas, and this has significant effects on both the level of critical load exceedance for lead and the modelling of current balances and dynamics.

- The current rate of leaching of cadmium is estimated to exceed current deposition over almost all of the U.K., and a similar position is estimated to apply for lead over many parts of the U.K..

- The dynamics of metal accumulation to critical limit values in soil and soil solution is modelled to be about an order of magnitude faster for cadmium than for lead.

- The estimates of critical reactive soil pools, and of the dynamics of metal accumulation, are sensitive to small changes in pH in acid soils

- The order of magnitude uncertainty in current deposition rates of copper and zinc makes it impossible to assess critical load exceedance or the dynamics of these metals.

7. ACKNOWLEDGEMENTS

The table below summarises the data sources for all the maps presented in this report

Fig. 5.1.1	*Upland Mask of Great Britain* Data Acknowledgements: Countryside Information System, Department of Agriculture and Regional Development, Northern Ireland (DARDNI), Ordnance Survey Northern Ireland (OSNI), ITE Landcover Map
Fig. 5.1.2	*pH of the Topsoil* Soil Geo-chemical Atlas for England & Wales, Macaulay Land Use Research Institute (MLURI), DARDNI
Fig. 5.1.3	*Bulk Density of the Topsoil* Soil Survey & Land Research Centre (SSLRC), MLURI, DARDNI
Fig. 5.1.4	*Porosity of the Topsoil* SSLRC, MLURI, DARDNI, Ritjema (1970)
Fig. 5.1.5	*Organic Carbon of the Topsoil* Soil Geo-chemical Atlas for England & Wales, MLURI, DARDNI
Fig. 5.1.6	*Dissolved Organic Carbon of the Topsoil* derived from OC
Fig. 5.1.7	*Average Annual Runoff* Institute of Hydrology
Fig. 5.2.1	*Total Concentration of Cadmium* Soil Geo-chemical Atlas for England & Wales, MLURI, DARDNI
Fig. 5.2.2	*Total Concentration of Lead* Soil Geo-chemical Atlas for England & Wales, MLURI, DARDNI
Fig. 5.2.3	*Total Concentration of Copper* Soil Geo-chemical Atlas for England & Wales, MLURI, DARDNI
Fig. 5.2.4	*Total Concentration of Zinc* Soil Geo-chemical Atlas for England & Wales, MLURI, DARDNI
Fig. 5.2.5	*Reactive Soil Concentration of Cadmium* Modelled data
Fig. 5.2.6	*Reactive Soil Concentration of Lead* Modelled data
Fig. 5.2.7	*Reactive Soil Concentration of Copper* Modelled data
Fig. 5.2.8	*Reactive Soil Concentration of Zinc* Modelled data
Fig. 5.2.9	*Reactive Soil Pool of Cadmium* Modelled data
Fig. 5.2.10	*Reactive Soil Pool of Lead* Modelled data
Fig. 5.2.11	*Reactive Soil Pool of Copper* Modelled data
Fig. 5.2.12	*Reactive Soil Pool of Zinc* Modelled data
Fig. 5.2.13	*Total Soil Solution Concentration of Cadmium* Modelled data

Fig. 5.2.14	*Total Soil Solution Concentration of Lead* Modelled data
Fig. 5.2.15	*Total Soil Solution Concentration of Copper* Modelled data
Fig. 5.2.16	*Total Soil Solution Concentration of Zinc* Modelled data
Fig. 5.2.17	*Solution Free-ion Concentration of Cadmium* Modelled data
Fig. 5.2.18	*Solution Free-ion Concentration of Lead* Modelled data
Fig. 5.2.19	*Solution Free-ion Concentration of Copper* Modelled data
Fig. 5.2.20	*Solution Free-ion Concentration of Zinc* Modelled data
Fig. 5.4.1	*Critical Loads of Cadmium, Non-forest Uplands, CLimit = 3 ug/l* Modelled data
Fig. 5.4.2	*Critical Loads of Cadmium, Non-forest Uplands, CLimit = 1 ug/l* Modelled data
Fig. 5.4.3	*Critical Loads of Cadmium, Non-forest Uplands, CLimit = 0.35 ug/l* Modelled data
Fig. 5.4.4	*Critical Loads of Lead, Non-forest Uplands, CLimit = 8 ug/l* Modelled data
Fig. 5.4.5	*Critical Loads of Lead, Non-forest Uplands, CLimit = 2 ug/l* Modelled data
Fig. 5.5.1	*Critical Reactive Soil Concentration of Cd, based on CLimit = 3 ug/l* Modelled data
Fig. 5.5.2	*Critical Reactive Soil Concentration of Pb, based on CLimit = 8 ug/l* Modelled data
Fig. 5.5.3	*Modelled Critical Times for Cadmium, CLimit = 3 ug/l* Modelled data
Fig. 5.5.4	*Modelled Critical Times for Lead, CLimit = 8 ug/l* Modelled data
Fig. 5.5.5	*Current Rates of Change in Metal Pool, Cd, all uplands* Modelled data
Fig. 5.5.6	*Current Rates of Change in Metal Pool, Pb, all uplands* Modelled data
Fig. 5.5.7	*Current Rates of Change in Metal Pool, Cd, forest uplands* Modelled data
Fig. 5.5.8	*Current Rates of Change in Metal Pool, Pb, forest uplands* Modelled data
Fig. 5.6.1	*Effect of Change in pH on Free-ion Concentration of Cadmium* Modelled data
Fig. 5.6.2	*Effect of Change in pH on Free-ion Concentration of Lead* Modelled data

Fig. 5.6.3	*Effect of Change in pH on Soil Solution Concentration of Cadmium* Modelled data
Fig. 5.6.4	*Effect of Change in pH on Soil Solution Concentration of Lead* Modelled data
Fig. 5.6.5	*Effect of Change in pH on modelling critical reactive half times of Cadmium* Modelled data
Fig. 5.6.6	*Effect of Change in pH on modelling critical reactive half time of Lead* Modelled data
Fig. 5.6.7	*Effect of Change in pH on modelling critical reactive times of Cadmium* Modelled data
Fig. 5.6.8	*Effect of Change in pH on modelling critical reactive times of Lead* Modelled data
Fig 5.7.1	*Critical Loads of Cadmium, Forest Upland, CLimit = 3 ug/l* Modelled data
Fig 5.7.2	*Critical Loads of Lead, Forest Upland, CLimit = 8 ug/l* Modelled data
Fig 5.8.1	*Deposition of Cadmium, Average for all land uses* Moss Survey 2000, CEH Edinburgh
Fig 5.8.2	*Deposition of Lead, Average for all land uses* Moss Survey 2000, CEH Edinburgh
Fig 5.8.3	*Deposition of Cadmium to woodland* Moss Survey 2000, CEH Edinburgh
Fig 5.8.4	*Deposition of Lead to woodland* Moss Survey 2000, CEH Edinburgh
Fig 5.9.1	*Exceedance of Critical Loads of Cadmium, All upland* Modelled data
Fig 5.9.2	*Exceedance of Critical Loads of Cadmium, All upland* Modelled data
Fig 5.9.3	*Exceedance of Critical Loads of Cadmium, All upland* Modelled data
Fig 5.9.4	*Exceedance of Critical Loads of Lead, All upland* Modelled data
Fig 5.9.5	*Exceedance of Critical Loads of Lead, All upland* Modelled data
Fig 5.9.6	*Exceedance of Critical Loads of Cadmium, All upland* Modelled data
Fig 5.9.7	*Exceedance of Critical Loads of Lead, All upland* Modelled data

This work was also made possible by application ICP/156/1299 for use of the NERC ICP-MS facility at Kingston University.

8. PROJECT OUTPUTS

Verbal presentations:

Presentations of were made at:-

The 5th Symposium on the Geochemistry of the Earth's surface - Reykyavik, Iceland, August 1999.

Meeting of the UN/ECE Expert Group on Critical Limits, Bratislava, October 2000.

Annual meeting of ICP-Vegetation, Tervuren, January 2001.

Poster presentations

Posters presenting the work on this contract were presented at the following meetings:-

UN/ECE workshop on Effects-based Approaches to Heavy Metals, Schwerin, October 1999.

Third World Congress of Society of Environmental Toxicology and Chemistry, Brighton, May 2000, as part of a special session on NERC Environmental Diagnostics

Publications

Rieuwerts JS, Farago ME, Thornton I, Ashmore MR, Fowler D, Nemitz E, Hall JR, Kodz D, Lawlor A & Tipping E (1999). Critical loads in U.K. soils: an overview of current research. In Geochemistry of the Earth’s surface (H Armannsson, ed.), pp. 223-226. AA Balkema, Rotterdam.

Ashmore MR, Farago ME, Fowler D, Kodz D, Lawlor A, Nemitz E, Rieuwerts J, Thornton I, Tipping E & warr T (1999). Critical loads of metals for soils and freshwaters in the United Kingdom – an overview of current research. In: Proceedings of the Workshop on Effects-Based Approaches for Heavy Metals. Schwerin, Germany, pp. 109-110. Umweltbundesamt, Berlin.

Ashmore MR, Colgan A, Hill MTR, Gang Pan, Paton G, Rieuwerts J & Tipping E (2001). Modelling and microbial toxicity of pore-water free-ion concentrations of metals in upland soils. In: Proceedings of UN/ECE Ad-hoc International Expert Group on Effects-Based Critical Limits, Bratislava October 2000 (J Curlik, ed.) (in press).

Jordan C, Higgins AJ, Hamill KP & Cruickshank JG (2000). The Soil Geochemical Atlas of Northern Ireland. Agricultural and Environmental Science division, Department of Agricultural and Rural development, Newforge Lane, Belfast.

Future outputs

Several papers based on the research during this contract are in draft or planned for academic publications. In addition, further presentation of the findings of the project are planned during 2001. These include:-

A verbal presentation at the CCE workshop in the Netherlands in April 2001, on the application of the Bratislava recommendations to the U.K..

A verbal presentation at the meeting of ICP-Mapping and Modelling, in Bratislava in May 2001, on transfer functions and their applications in critical load assessment.

A verbal presentation at the annual meeting of the Society for Environmental Geochemistry and Health, in April 2001.

A verbal presentation on a final Environmental Diagnostics workshop on critical loads and environmental pathways, planned for May/June 2001.

A poster presentation at the end-of–programme conference of the NERC Environmental Diagnostics programme, to be held in London in September 2001.

9. REFERENCES

Bringmark L & Bringmark E (in press). Lowest effect levels of lead and mercury in mor layers of southern Swedish forest sites. Water Air & Soil Pollution

Broadbent, FE (1965). Organic Matter. In: Black CA (ed.). Methods of Soil Analysis Part 2: Chemical & Microbiological Properties. Madison,WI: American Society of Agronomy

Bunce, RGH, Barr, CJ, Gillespie, MK and Howard, DC (1996). The ITE Land Classification: Providing an environmental stratification of Great Britain. Environmental Monitoring and Assessment, 39, 39-46.

Chaudri AM, Lawlor K, Preston S, Paton GI, Killham K & McGrath SP (2000). Response of a *Rhizobium*-based luminescence biosensor to Zn and Cu in soil solutions from sewage sludge treated soils. Soil Biology and Biochemistry, 32, 383-388.

Curlik J (in press) Proceedings of the UN ECE/CLRTAP Meeting of the Ad-hoc International Expert group on critical Limits for Heavy metals, Bratislava, Slovak Republic, 11-13 October 2000

Davidson C.M., Duncan A.L., Littlejohn D., Ure A.M. & L.M. Garden (1998) A critical evaluation of the three-stage BCR sequential extraction procedure to asserss the potential mobility and toxicity of heavy metals in industrially-contaminated land, Analytica Chimica Acta, 363, 45-55.

de Vries W & Bakker DJ (1998). Manual for calculating critical loads of heavy metals for terrestrial ecosystems; guidelines for critical limits, calculation methods and input data. Report 165, DLO Winand Staring Centre, Wageningen, Netherlands.

de Vries W, Bakker DJ & HU Sverdrup (1998). Manual for calculating critical loads of heavy metals for aquatic ecosystems; guidelines for critical limits, calculation methods and input data. Report 166, DLO Winand Staring Centre, Wageningen, Netherlands.

EPG 1/3/85 Maggs R., Bell J.N.B., McNeill S., Shore R. & M.R. Ashmore (1997) An assessment of effects based literature for the setting of critical concentrations of heavy metals in U.K. upland ecosystems. contract report for the Department of the Environment; Centre for Environmental Technology, Imperial College of Science, Technology & Medicine.

Fuller R.M., Groom G.B. & Jones A.R. 1994. The land cover map of Great Britain: an automated classification of Landsat Thematic Mapper data. *Photogrammetric Engineering and Remote Sensing.* **60** 553-562

Gregor H-D, Mohaupt-Jahr B & Honerbach F (1999). Proceedings of the Workshop on Effects-based Approaches for Heavy Metals, Schwerin, Germany, 12-15 October 1999. Texte 87/99, Umweltbundesamt, Germany

Gregor H-D, Nagel H-D & Schutze G (2000). Short guidance for the calculation of critical loads for cadmium, lead and mercury from effect-based critical limits. ICP on Modelling and Mapping, to be published in Curlik *et al*. (in press)

Jordan C, Higgins AJ, Hamill KP & Cruickshank JG (2000). The Soil Geochemical Atlas of Northern Ireland. Agricultural and Environmental Science Division, Department of Agriculture and Rural development, Newforge Lane, Belfast.

McGrath, S.P. & Loveland, P.J. (1992). The soil geochemical atlas of England and Wales, Chapman & Hall.

McGrath SP, Knight B, Killham K, Preston S & Paton GI (1999). Assessment of the toxicity of metals in soils amended with sewage sludge using a chemical speciation technique and a lux-based biosensor. Environmental Toxicology and Chemistry, 18, 659-663.

Paces T (1998) Critical loads of trace metals in soils: a method of calculation. Water Air and Soil Pollution, 105, 451-458.

Paton GI, Campbell CD, Glover LA & Killham K (1995). Assessment of bioavailability of heavy metals using lux modified constructs of *Pseudomonas fluoresecens*. Letters in Applied Microbiology, 20, 52-56.

Proceedings of the Workshop on Critical Limits and Effect Based Approaches for Heavy Metals and Persistent Organic Pollutants. Bad Harzburg, Germany, 1997

Rauret G, Lopez-Sanchez JF, Sahuquillo A, Rubio R, Davidson C, Ure A & Quevauviller PH (1999) Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. Journal of Environmental Monitoring, 1, 57-61.

Ritjema, R.E. (1970) Soil Moisture Forecasting. Nota 513. Instituut voor Cultuurtechniek en Waterhuishouding, Wageningen

Rose NL, Bird D, Keohane R, Harriman R. & RW Battarbee (1997) The analysis of trace metals in surface waters from Scotland and Wales. University College London Environmental Change Research Centre research report no.39.

Sauvé S, Dumestre A, Mcbride M & Hendershot W (1998). Derivation of soil quality criteria using predicted chemical speciation of Pb^{2+} and Cu^{2+}. Environmental Toxicology and Chemistry, 17, 1481-1489.

Schütze G & Throl in Curlik J (in press) Proceedings of the UN ECE/CLRTAP Meeting of the Ad-hoc International Expert group on critical Limits for Heavy metals, Bratislava, Slovak Republic, 11-13 October 2000

Tipping E (1994). WHAM – a chemical equilibrium model and computer code for waters, sediments and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. Computers and Geosciences, 20, 973-1023.

Tipping E (1996). CHUM – a hydrochemical model for upland catchments. J Hydrology, 174, 305-330.

Tipping E, Smith EJ, Hughes S, Lawlor AJ, Lofts S, Simon BM, STevens PA, Stidson R & CD Vincent (2000) Metals in ombrotrophic peats across Scotland, CEH Windermere report to Scottish National Heritage.

Tyler G, Pahlsson A M B, Bengtsson G, Baath E & Tranvik L (1989) Heavy-metal ecology of terrestrial plants, microorganisms and invertebrates - a review. Water Air and Soil Pollution, 47:(3-4), 189-215

Annexe 1

Development of critical loads methodologies for toxic metals in soils and surface waters
- Estimation of the UK deposition fields of Cd, Pb, Cu and Zn -

Environmental Diagnostics GST/03/1709 – Final Report – December 2000

E. Nemitz[a], D. Fowler[a], A.G. McDonald[a], M.W. Gallagher[b], J. Dorsey[b], R.M. Harrison[c] and A.G. Allen[c]

a) Centre for Ecology and Hydrology, Edinburgh; b) Physics Department, UMIST, Manchester; c) Division of Environmental Health and Risk Management, University of Birmingham.

1. Objectives

The work described here addressed the overall objective number 1 of the Consortium Project, which was *to measure directly the deposition of metals at upland sites, to study the deposition processes and to develop models to estimate the pattern of deposition for the UK.*

Initially the detailed objectives were

1. to measure rates of dry deposition in the field of particles containing heavy metals.
2. to obtain from the measurements relationships between particle size and deposition velocity and explicitly to quantify the relationship between particle deposition velocity and friction velocity (u_*) for a range of particle size classes.
3. to measure the seasonal and diurnal cycles in concentrations of particulate material in the two size classes $PM_{2.5}$ and PM_{10}.
4. to obtain detailed size classifications of heavy metals across the entire range of atmospheric particle sizes, i.e. from below 50 nm to in excess of 10 μm diameter.
5. to measure the wet scavenging ratios of heavy metals to provide the basis for estimates of regional aerosol heavy metal concentrations throughout the UK.

A number of additional modelling objectives were added to these measurement objectives to provide deposition fields for the consortium for the assessment of critical loads exceedances. These included:

6. An operational inferential model linking annual mean deposition and air concentrations of heavy metals.
7. Deposition fields from moss surveys 1996/97 and 2000.
8. Deposition fields from the frisbee collector network run by the University of Reading.
9. Development of a fine resolution atmospheric transport and deposition model for heavy metals.

Objective 9 was added to the work programme when spatially disaggregated emission maps were compiled (i) by CEH through additional funding through National Power from the Joint Environment Programme and (ii) by NETCEN as part of the National Atmospheric Emissions Inventory (NAEI), providing additional benefits to the work programme.

2. Field measurements

Field measurements were specifically undertaken to provide the process understanding, required to develop parameterizations of the dry and wet deposition of heavy metals, which are representative for the UK.

2.1 Monitoring of air concentrations and wet deposition at Auchencorth Moss

Monthly averages of $PM_{2.5}$ and PM_{10} concentrations as well as wet-only deposition were obtained for the moorland site Auchencorth Moss, 20 km south of Edinburgh (NGR NT221562). These measurements commenced in 1995 under the EU LIFE programme and were continued until

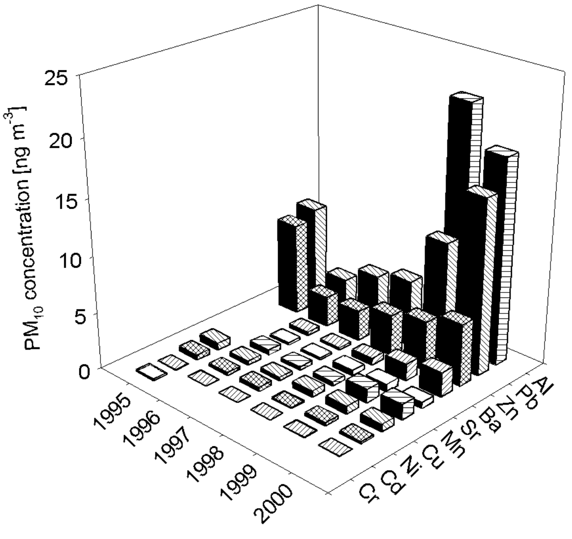


Figure 1. Yearly averages of metal concentrations in PM_{10} measured at Auchencorth Moss.

September 2000. In addition the site was used for 6-month intercomparisons between the frisbee-type deposition gauge used by the University of Reading and the bulk collector used by CEH Windermere in this project. Measurements of total suspended particulate matter (TSP) were added to estimate the contribution of locally resuspended particles to the frisbee measurements. The results were:

a. The air concentrations of metals in PM_{10} (Fig. 1) were in the range of concentrations measured at other rural sites in the UK. However, the expected downward trend of Pb was not observed. Instead Pb, Zn, Ba and Cu showed an increase from 1997 to 2000. Obviously, at Auchencorth the Pb reduction in petrol was more than offset either by an increase in the traffic volume in the area or by an increased activity of industrial sources.

b. Table 1 summarizes the measured wet deposition and the dry deposition estimated from the process measurements (see below), indicating that dry deposition constitutes 9 (Cd), 13 (Pb), 4 (Cu) and 3 % (Zn) of the total deposition at this site.

c. On average TSP exceeds PM_{10} concentrations by 8% for Cd and Pb, by 16 % for Zn and by 37 % for Cu. From these measurements it was concluded that depositon measurements with frisbee collectors may overestimate the depositon of Cu and Zn due to the collection of locally resuspended material.

Table 1. Yearly totals of wet and dry deposition [g ha yr^{-1}]; rainfall amount is given in parentheses.

		Cd	Pb
1995	wet	0.45	15.6
(824)	dry	0.12	5.6
	total	0.57	21.1
1996	wet	0.23	8.8
(828)	dry	0.02	2.0
	total	0.25	10.8
1997	wet	<0.2	29.1
(1016)	dry	0.01	2.6
	total	<0.21	31.6
1998	wet	1.61	66.9
(1366)	dry	0.01	2.8
	total	1.62	69.7
1999	wet	0.47	88.9
(940)	dry	0.03	4.9
	total	0.50	93.7
2000	wet	0.49	43.8
(982)	dry	0.05	6.6
	total	0.54	50.4

2.2 Micrometeorological measurements of size-dependent particle deposition velocities (V_d)

Size-dependent particle fluxes were measured at the moorland Auchencorth Moss during three periods in 1999 using the micrometeorological eddy-correlation technique with three different particle counters. These included a novel technique to measure total particle fluxes (down to a size of 11 nm). Fluxes were also measured above grassland near Braunschweig, Germany, and a major dataset of particle fluxes above heathland was re-analyzed, together with published fluxes above arable crop (Joutsenoja et al., 1992) and forest (Gallagher et al., 1997):

a. V_d ***for moorland / grassland was in the range of < 0.1 to 10 mm s-1, followed a diurnal cycle (Fig. 2) and increased with particle size.***

b. Values of V_d ***increased with particle size in a relationship that is consistent with theoretical model predictions (e.g. Slinn, 1982), if the parameters describing the morphology of the canopy are adjusted. This is in contrast to the relationship of*** $V_d(D_p)$ ***above forest, which can currently not be reproduced by any of the existing models.***

c. The measurements at the Dutch heath show a strong increase in the ratio V_d/u_*

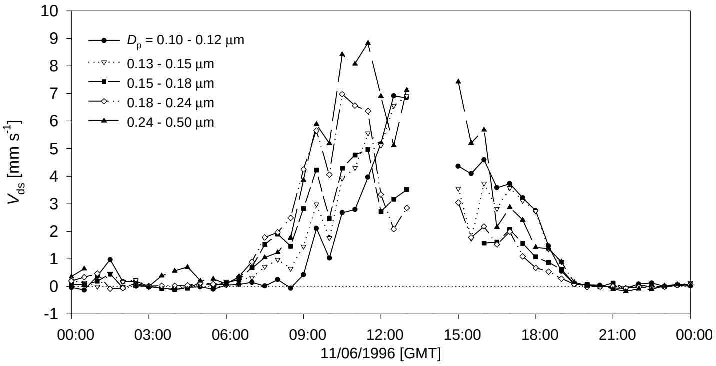


Figure 2. Example diurnal cycle of deposition velocities (V_d) for particles of different size-classes measured over a heathland.

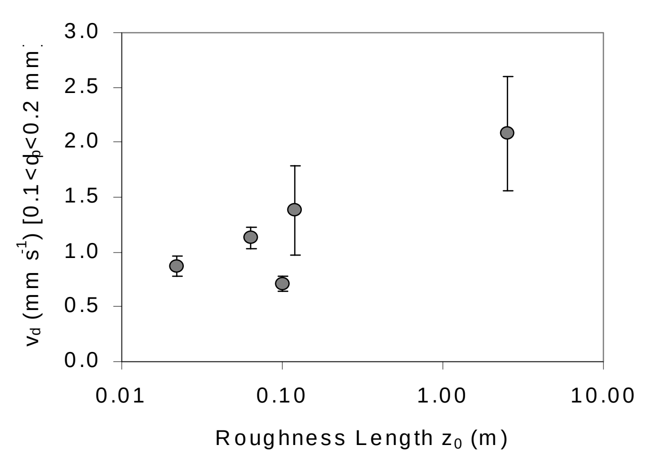


Figure 3. Dependence of the deposition velocity of small particles (0.1 < D_p < 0.2 µm) on the roughness length of the underlying surface, derived from various micrometeorological datasets.

for unstable conditions. This effect is, however, les
average, because of high windspeeds maintaining con

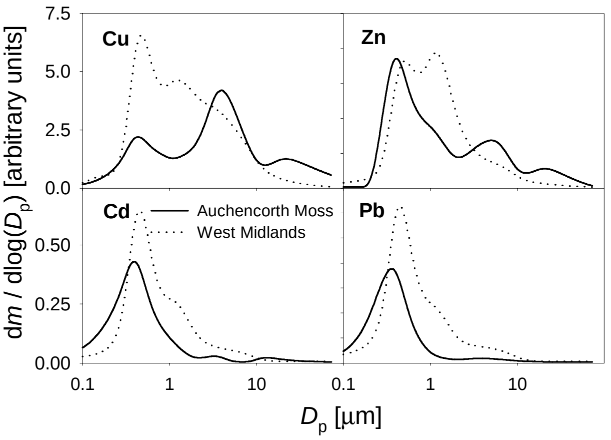


Figure 4. Averaged metal size distributions measured at Auchencorth Moss (Scotland) and two sites in the West Midlands.

d. ***V_d increases approximately logarithmically with roughness height (Figure 3).***
e. ***The first measurements of total particle number fluxes (D_p > 11 nm) above short vegetation indicate small deposition at V_d = 0.5 – 2 mm s^{-1}, an order of magnitude smaller than over forest (Buzorius* et al.*, 1998).***

2.3 Detailed measurements of the size-distributions of heavy metals in the UK

Typical size-distributions of heavy metals were measured at Auchencorth Moss (by CEH), using a standard impactor, and at two locations in the West Midlands (Univ. B'ham), contrasting two instruments. The isokinetic May impactor provides an improved capture efficiency for large particles (> 5 µm), while the 10-stage MOUDI impactor maximizes the resolution at the lower end of the size-spectrum. Size-distributions were similar between the sites, except for Cu, which at Auchencorth was more distinctly bi-modal. Conversely, Zn, Cd and Pb show a higher contribution of particles with a MMD of 1 µm, consistent with the closer proximity to source regions.

3. Modelling activities

3.1 Development of an inferential model to link deposition and air concentration

These data were used to derive parameterizations of the surface / atmosphere exchange applicable to the UK. Wet deposition was calculated using the wet scavenging ratio (w_m), the ratio of the concentration in rain and the concentration in air (both in µg kg^{-1}). Compared with literature values, UK measurements of w_m are at the lower end of the range for Pb and the higher end for Cu (Fig. 5). The values derived from the measurements at Auchencorth Moss compare well with other UK measurements. Slightly higher values for Zn may be explained by the contribution of insoluble Zn containing particles to the measurements at Auchencorth, while w_m for t

p
n
r
a
p

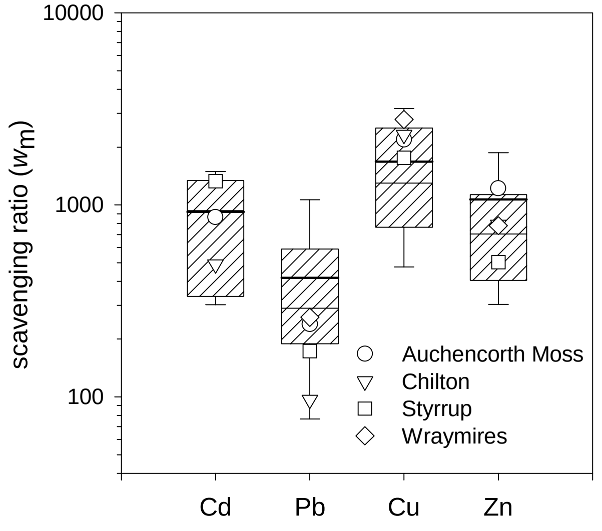


Figure 5. Ranges of mass-based scavenging ratios compared with UK measurements (English data from Baker *et al*., 1999), also indicating the average values used in this study.

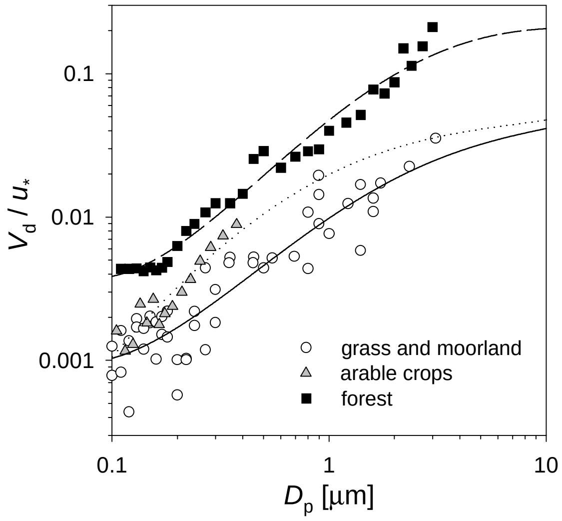


Figure 6. Parameterizations of the dry deposition velocity (V_d) as a function of particle diameter (D_p) for grass/moorland, arable crops and forest, derived from measurement data of Joutsenoja *et al*., (1992), Gallagher *et al*. (1997), and Nemitz *et al*., (2001a).

Table 2. Coefficients of proportionality (α) used to calculate the particle dry deposition velocity (V_d).

Land cover class	Cd	Pb	Cu	Zn
Grass / Moorland	0.0068	0.0065	0.017	0.012
Crops	0.012	0.012	0.025	0.020

For the calculation of occult deposition, cloud water enhancement factors (*E*) were derived from the literature.

3.2 Interpretation of data from the moss surveys 1996/97 and 2000

For the interpretation of the moss survey data, calibrations between metal concentrations and bulk deposition were derived from the few available UK bulk deposition data and compared with Scandinavian relationships (Berg and Steinnes, 1997). Rather than interpolating the deposition values directly and thereby ignoring the spatial patterns of precipitation, wind speed, cloud hours and land cover, the deposition map was derived from the concentration in moss in a four-step approach:

a. Deposition at the measurement sites was calculated using the available calibration data.
b. The air concentration at the measurement sites was derived from the deposition values using the inferential model in an inverse mode.
c. The air concentration field was then interpolated by bi-linear interpolation.
d. The inferential model was applied to this concentration field to derive the deposition field at a 5 km grid resolution.

3.3 Interpretation of the data from the frisbee collector network England&Wales

The deposition field was derived from the deposition values of the frisbee collector network in analogy to the moss survey interpretation, starting with step (b). The collection efficiency of the frisbee collectors for particles was assumed to equal that of arable crops, while the grassland / moorland values of V_d had been applied for the interpretation of the moss study.

3.4 Atmospheric transport and deposition modelling of heavy metal deposition to the UK

A stochastic multi-layer Lagrangian straight-line trajectory model (FRAME-HM) was developed from the existing Fine Resolution Ammonia Exchange (FRAME) model (Singles *et al*., 1998). The model is well suited to simulate the transport and deposition of heavy metals across the UK. Two emissions inventories were contrasted: the official UK National Emissions Inventory (NAEI; Goodwin *et al*., 2000) and an inventory compiled by CEH. Both inventories are based on the emissions data submitted by the operators of Part A industrial processes to the Environment Agencies and therefore are not entirely independent estimates. For Cd and Pb, EMEP provide modified model runs, in which UK emissions are omitted and these were added to the deposition field of the UK sources modelled here. For Cu and Zn, which are not treated by the CLRTAP, boundary concentrations for the UK model were generated by running the European straight-line trajectory model TERN (ApSimon *et al*., 1994) with the emission inventory by Berdowski *et al*. (1997), modified for changes between 1990 and 1998.

Numerical modelling is the only means by which the deposition caused by UK sources can be distinguished from the deposition due to non-UK sources. Table 3 provides a breakdown of the total UK budget due to the modelling by EMEP and CEH, demonstrating that (as with sulphur and nitrogen compounds), the UK is a net exporter of all metals. The deposition budget, however, is dominated by UK sources, with more than 70% of the UK deposition being deriving from national sources.

Table 3. Summary of the atmospheric budgets of heavy metals predicted by the EMEP model (Ilyin *et al*., 2000) and the CEH model (Nemitz *et al*., 2001a).

	United Kingdom			
	Cd	Pb	Cu	Zn
Emissions NAEI 1998	13. 0	1033	58.8	1047
Deposition EMEP 1998	7.9	478		
from UK sources	5.8	398		
non-UK sources	2.1	80		
net export	5.1	555		
Emissions CEH 1997	18.	1087	88.9	796
Deposition CEH 1997	8	567	59.3	435
from UK sources	11.	487	55.2	401
non-UK sources				

3.5 *Comparison of the budgets and deposition fields*

Table 4. Summary of the total emission and deposition for the UK as well as England and Wales only derived by the three methods. Also included are the EMEP model results for 1998 (Ilyin *et al.*, 2000).

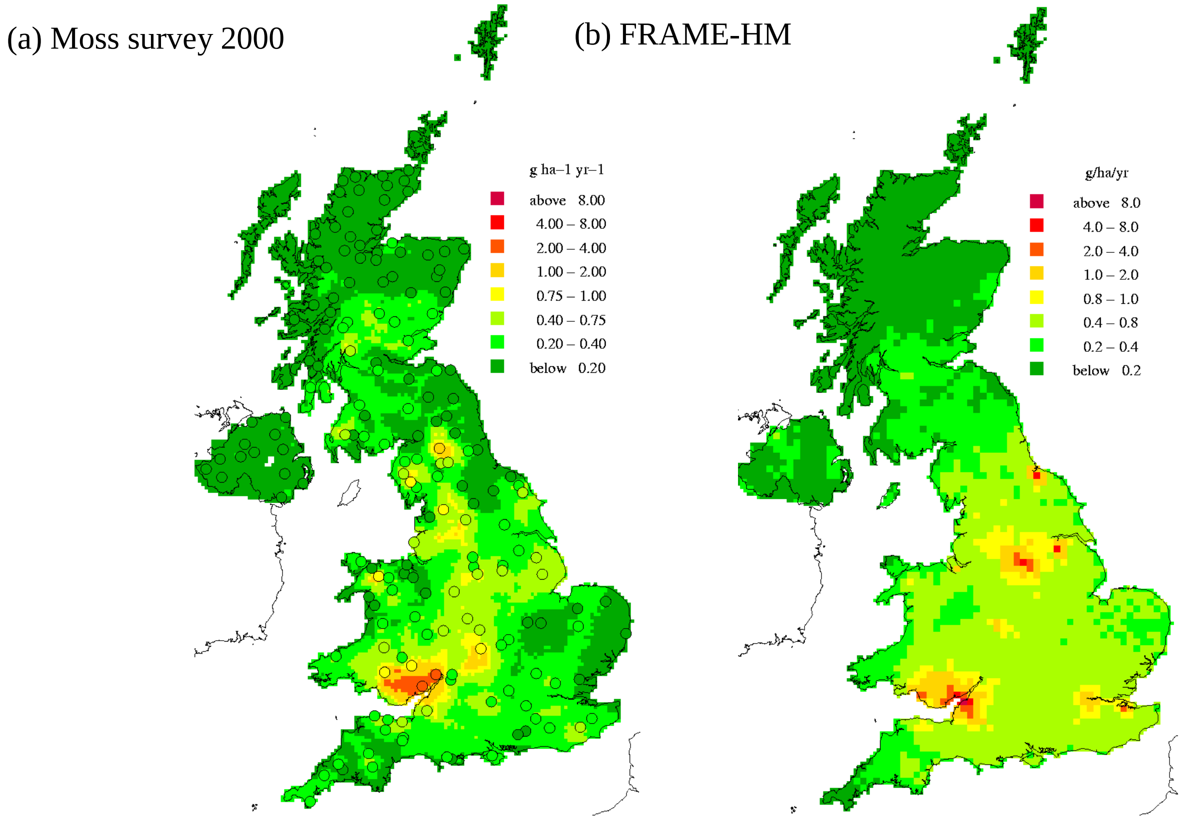
	United Kingdom				England & Wales			
	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn
Emissions								
NAEI 1995	15.7	1648	83.6	1207				
NAEI 1998	13.0	1033	58.8	1047				
CEH 1997	18.8	1087	88.9	796				
Deposition								
Moss 96/97	13.0	587	1574	6191	9.3	427	1098	4591
Moss 2000	8.0	659	783	3855	6.3	518	570	2985

The comparison of the deposition fields of Cd, Pb, Cu and Zn derived from the moss survey 2000 and with the FRAME-HM model are compared in Figs. 7 to 10. Due to space restrictions the deposition fields derived from the moss survey 1996/97 and the frisbee network are not shown, but they can be found in Nemitz *et al.* (2001e). Table 4 summarizes the deposition predicted by the four methods in comparison with EMEP modelling results for 1998. This results may be summarized as follows:

a. Deposition maps of Pb are broadly similar and the total deposition to the UK derived from the measurements is only slightly larger than that predicted on the basis of emission inventories.
b. The deposition budgets of Cd derived from the moss surveys and with FRAME-HM agree well, while much larger deposition fluxes are indicated by the frisbee deposition network.
c. For Cu and Zn the measurement derived deposition is a factor of 4 to 10 larger than can be explained with current emissions inventories. Although these large deposition values are on average consistent with bulk deposition measurements, these show large inconsistencies amongst themselves. In addition, much of the Cu and Zn accumulated in moss is soil derived, adding to the uncertainty in this estimate.
d. In general the frisbee network measured the largest deposition, while the modelling approach based on the emission estimates resulted in the smallest estimate. The frisbee collectors were designed to maximize the capture efficiency for large particles and capture some large locally resuspended (soil) particles, while current emission estimates are on the lower end of the range. Thus the frisbee collectors have introduced systematic errors overestimating the particle deposition. With further work it may be possible to quantify to quantify this effect.

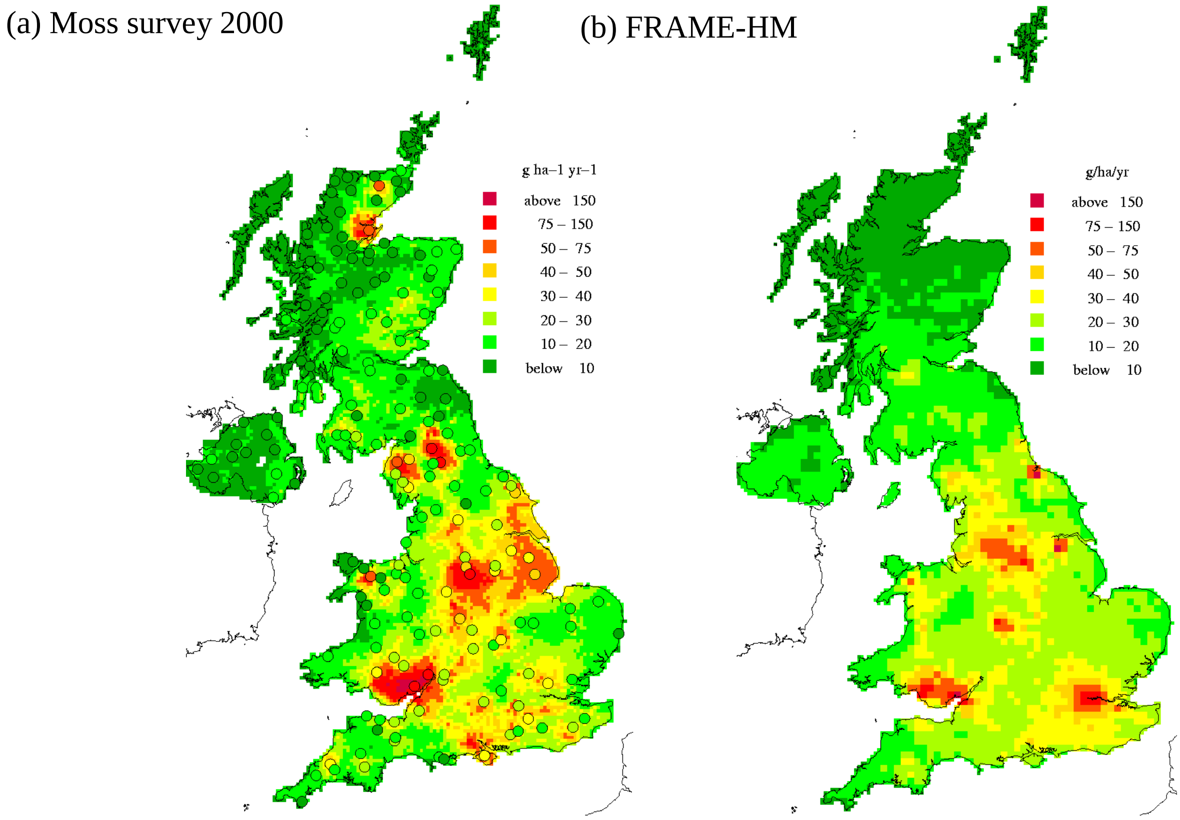
4. Summary and conclusions

The project has been successful in identifying and quantifying the parameters that govern the surface / atmosphere exchange of heavy metals with particular emphasis to UK conditions. In particular, we estimate that the parameterizations of V_d derived from micrometeorological measurements and measured size-spectra have reduced the uncertainty in this parameter from a factor of 5 to a factor of 2. Scavenging ratios were reviewed, new measurements were made, and values selected for UK conditions, and the parameterization of cloud deposition which was not investigated in detail is probably the least certain component in the inferential model.


(a) Moss survey 2000

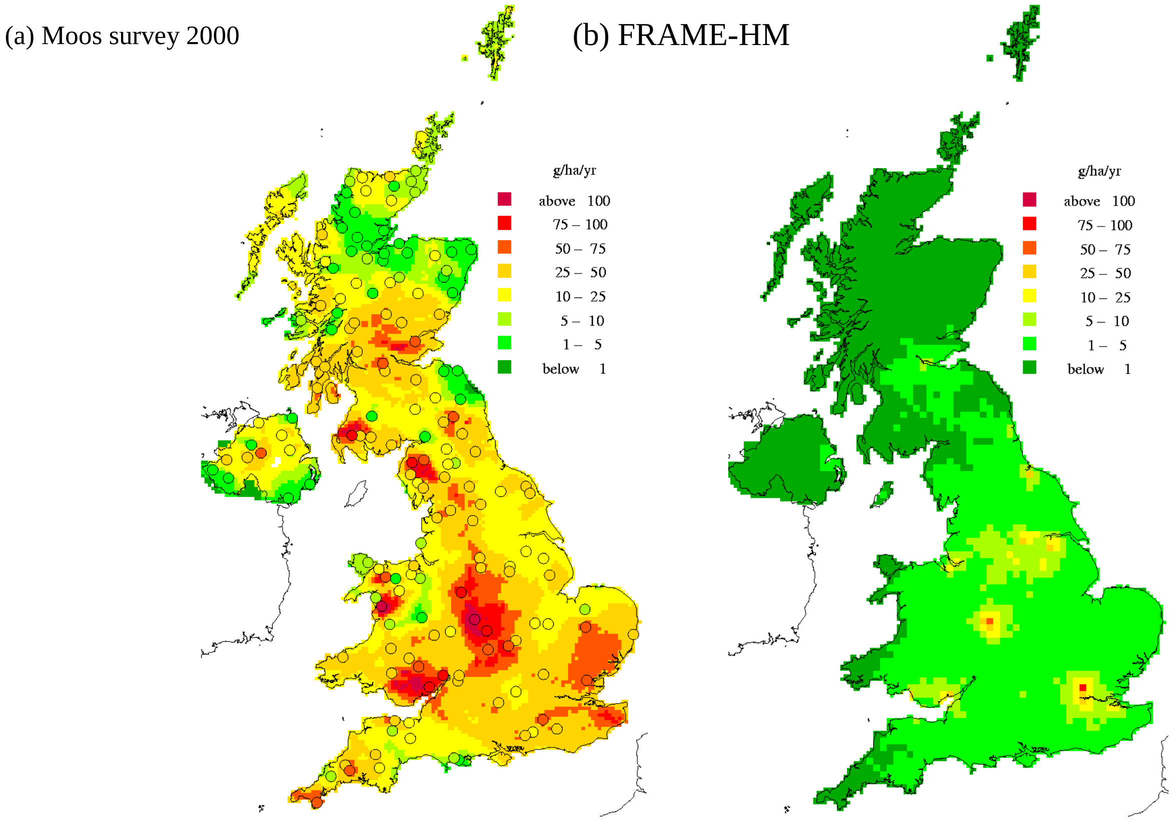
(b) FRAME-HM

Figure 7. Deposition fields of cadmium


(a) Moss survey 2000

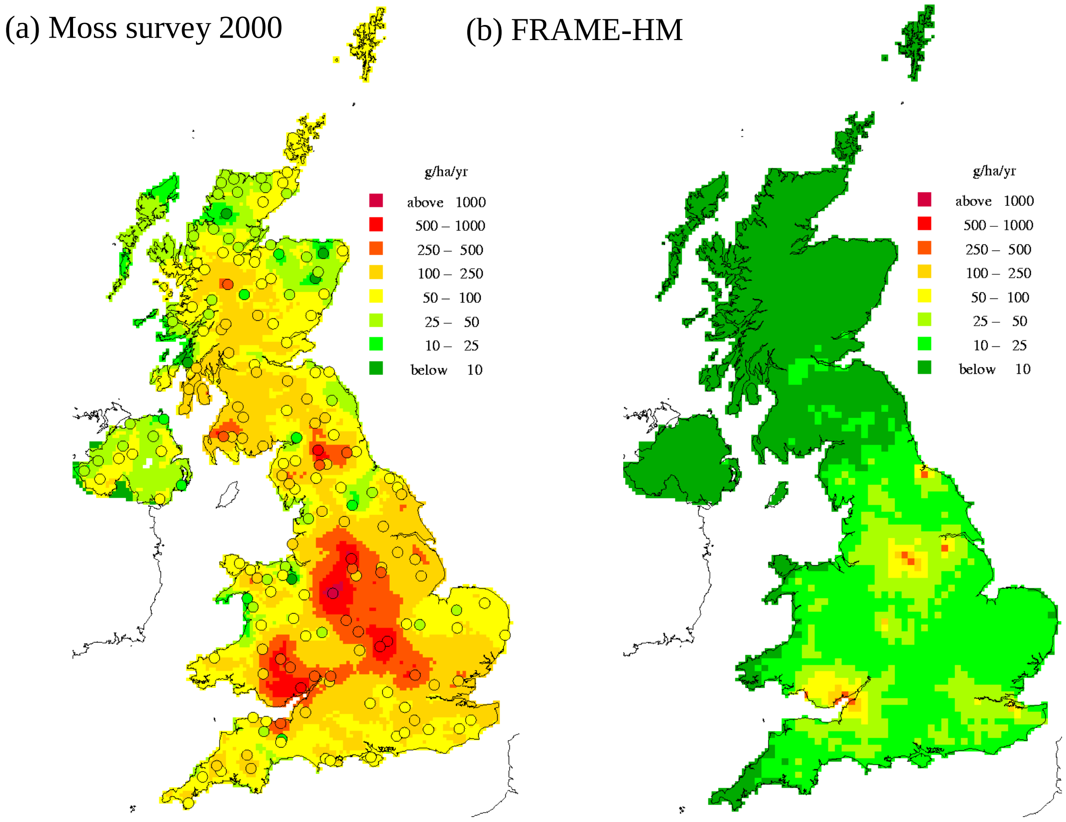
(b) FRAME-HM

Figure 8. Deposition fields of lead


(a) Moos survey 2000

(b) FRAME-HM

Figure 9. Deposition fields of copper


(a) Moss survey 2000

(b) FRAME-HM

Figure 10. Deposition fields of zinc

Fields of heavy metal deposition to the UK were derived by more methods than had been envisaged at the start of the project. The data from the frisbee network, the moss surveys and gridded emission inventories only became available during the study, some regrettably close to the end of the project. In particular, the development of an atmospheric transport and deposition model for heavy metals added additional value to the project.

With the exception of the Pb deposition field, there are marked differences between the modelled and measurement derived deposition fields of the metals, in particular for Cu and Zn, with the largest deposition derived from the frisbee network and the smallest deposition predicted on the basis of the emissions inventories. The large deposition values are on average consistent with the few bulk deposition measurements available for the UK. This indicates that either the national emission estimates are far too low or both UK bulk collectors and frisbee collectors derive values that are too large. These would then feed through to the moss calibration. Without a carefully quality-controlled bulk deposition network covering at least 20 remote sites the uncertainty in the deposition cannot be reduced.

Publications published to date

Ashmore M., Farago M., Fowler D., Hall J., Kodz D., Lawlor A., Nemitz E., Rieuwerts J., Thornton I., Tipping E. and Warr T. (1999): Critical loads of metals for soils and freshwaters in the United Kingdom – an overview of current research. in: Proceedings of the Workshop on Effects-Based Approaches for Heavy Metals, Schwerin, Germany 12-15 Oct. 1999. UN ECE Convention on Long-range Transboundary Air Pollution, Federal Environmental Agency, Postfach 330022, 14191 Berlin, Germany, pp 109-110.

Nemitz E., Fowler D., McDonald A., Dragosits U., Alloway B.J., Williams J.G. and Parry S.J. (1999): Development of an estimate of atmospheric heavy metal deposition to the UK. Abstracts of Poster Presentations. WMO/EMEP/UNEP Workshop on Modelling of Atmospheric Transport and Deposition of POPs and Heavy Metals. 16-19 November 1999, WMO, Geneva, CH.

Nemitz E., Sutton M.A., Choularton T.W., Gallagher M.W., Wyers G.P., Otjes R.P., Møls J.J., Mennen M.G., van Putton E.M. and van Hellemond J. (1997): Field investigations into the potential influence of ammonia and acidic gases on concentrations and surface - atmosphere exchange of aerosols. *J. Aerosol Science* **28**, suppl. 1: 337-338.

Nemitz E., Fowler D., Gallagher M.W., Milford C. and Flechard C.R. (1998): Deposition of heavy metals and ionic aerosol species at a Scottish moorland site. *J. Aerosol Sci.* **29**(Suppl. 1): S241-S242.

Publications submitted or in preparation (drafts of most of these are included in the Annex)

Nemitz $^{E.}$, McDonald A.G., Theobald M.R., Milford C. and Fowler D. (2001a): Concentrations and deposition of trace metals at a moorland site in Southern Scotland (in preparation for *Water Air Soil Poll.*)

Nemitz E., Sutton M.A., Wyers G.P., Otjes R.P., Mennen M.G., van Putten E.M., Hellemond J. and Gallagher M.W. (2001b): Gas-particle conversions above a Dutch heathland: II. Concentrations and surface exchange fluxes of atmospheric aerosol particles. (in prep. for *J. geophys. Res.*)

Nemitz E., Gallagher M.W. and Fowler D. (2001c): Micrometeorological measurements of particle deposition velocities to moorland vegetation. (in preparation for *Quart. J. Roy. Met. Soc.*)

Dorsey J.R., Flynn M., Gallagher M.W. and Nemitz E. (2001): Particle deposition velocities to cut and uncut grassland measured with a micrometeorological technique. (in preparation for *Quart. J. Roy. Met. Soc.*)

Allen A.G., Nemitz E., Shi J.P., Harrison R.M. and Greenwood J. (2001): Size-distributions of trace metals in atmospheric aerosols in the United Kingdom. (submitted to *Atmos. Environ.*)

Gallagher, M.W., Nemitz, E., Dorsey, J., Fowler, D.,Beswick, K.M., Williams, P.I., Sutton, M.,& Joutsenoja, T. (2001): Measurements, Model Comparisons and Parameterisations of Aerosol Deposition Velocities to Grassland, Arable Crops and Forest (in prep. for *Atmos. Environ.*)

Nemitz E., McDonald A.G., Dragosits U. and Fowler D. (2001d): Fine resolution modelling of heavy metal deposition in the United Kingdom. (in prepration for *Water Air Soil Poll.*)

Nemitz E., Fowler D., McDonald A.G., Alloway B.J., Reynolds B., Williams J.G., Parry S. and Ashmore M. (2001e): Comparison of three methods to derive deposition fields of Cd, Pb, Cu and Zn to the UK. (in preparation for *Environ. Poll.*)

References other than above

Baker S. J. (1999): Trace and Major Elements in the Atmosphere at Rural Locations: Summary of Data Obtained for the Period 1996 – 1998. (www.aeat.co.uk/netcen/airqual/reports/haps/ hapsexecsum.html

Berdowski J., Baas J., Bloos J.P.J., Visschedijk A.J.H. and Zandveld P.Y.J. (1997): The European Atmospheric Emission Inventory of Heavy Metals and Persistent Organic Pollutants. Umweltforschungsplan des Bundesministers für Umwelt, Naturschutz und Reaktorsicherheit - Luftreinhaltung. *Forschungsbericht* **104 02 672/03.** Umweltbundesamt, Berlin, D. 266 pp.

Berg T. and Steinnes E. (1997): Use of mosses (*Hylocomium splendens* and *Pleurozium schreberi*) as biomonitors of heavy metal deposition: from relative to absolute deposition values. *Environ. Pollut.* **98**(1): 61-71.

Buzorius G., Rannik Ü., Mäkelä J.M., Vesela T. and Kulmala M. (1998). Vertical aerosol particle fluxes measured by eddy covariance technique using condensation particle counter. *J. Aerosol Sci.* **29**(1/2): 157-171.

Gallagher M.W., Beswick K.M., Duyzer J., Westrate H., Choularton T.W. and Hummelshøj P. (1997): Measurements of aerosol fluxes to Speulder Forest using a micrometeorological technique. *Atmos. Environ.* **31**: 359-373.

Goodwin *et al.* (2000): UK Emissions of Air Pollutants 1970 to 1998. http://www.aeat.co.uk/netcen/airqual/naei/annreport/annrep98/naei98.html

Joutsenoja T. (1992) Measurements of aerosol deposition to a cereal crop. in: *Measurements and Modelling of Gases and Aerosols to Complex Terrain.* NERC Report 1992, GR3/7259 A.P.I. Choularton T.W., Appendix X1.2.

Singles R.J., Sutton M.A. and Weston K.J. (1998): A multi-layer model to describe the atmospheric transport and deposition of ammonia in Great Britain. *Atmos. Environ.* **32**(3): 393-399.

Slinn W.G.N. (1982): Prediction for particle deposition to vegetative canopies. *Atmos. Environ.* **16**(7): 1785-1794.

Appendix

Drafts of papers arising from the project GST/03/1709 (Submitted or in preparation)

1. **Gas-particle conversions above a Dutch heathland: II. Concentrations and surface exchange fluxes of atmospheric aerosol particles.** Nemitz E., Sutton M.A., Wyers G.P., Otjes R.P., Mennen M.G., van Putten E.M., Hellemond J. and Gallagher M.W. (in preparation for *J. geophys. Res.*)
2. **Micrometeorological measurements of particle deposition velocities to moorland vegetation.** Nemitz E., Gallagher M.W. and Fowler D. (in preparation for *Quart. J. Roy. Met. Soc.*)
3. **Size-distributions of trace metals in atmospheric aerosols in the United Kingdom.** Allen A.G., Nemitz E., Shi J.P., Harrison R.M. and Greenwood J. (submitted to *Atmos. Environ.*)
4. **Measurements, Model Comparisons and Parameterisations of Aerosol Deposition Velocities to Grassland, Arable Crops and Forest** Gallagher, M.W., Nemitz, E., Dorsey, J., Fowler, D.,Beswick, K.M., Williams, P.I., Sutton, M.,& Joutsenoja, T. (in preparation for *Quart. J. Roy. Met. Soc.*)
5. **Fine resolution modelling of heavy metal deposition in the United Kingdom.** Nemitz E., McDonald A.G., Dragosits U. and Fowler D. (in prepration for *Water Air Soil Poll.*)
6. **Comparison of three methods to derive deposition fields of Cd, Pb, Cu and Zn to the UK.** Nemitz E., Fowler D., McDonald A.G., Alloway B.J., Reynolds B., Williams J.G., Parry S. and Ashmore M. (in preparation for *Environ. Poll.*)

Annexe 2

Development of critical level methodologies for toxic metals in soils and surface waters – dynamic modelling

Environmental Diagnostics GST/04/1709 – Final Report – December 2000

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

Objectives

The Consortium Project had four overall objectives, the second of which covered all the work performed at CEH Windermere. This objective was:
To develop a dynamic model of the environmental pathways of metals (Ni, Cu, Zn, Cd, Pb) from the atmosphere through vegetation and soils and into freshwater systems, for upland ecosystems, and to make field measurements to validate the model. To review factors which influence these environmental pathways, especially bioavailability, mobility and impacts of metals in different soil types, and to develop methods to incorporate these factors in a national GIS.
The CEH Windermere contribution covered all of the first part, and some of the second. The following tasks were planned initially:

1) Field measurements to determine input and output fluxes of metals to several catchments in the uplands of northern England, and to estimate soil metal pools.
2) Use of the dynamic catchment model CHUM to simulate the retention and transport of metals, in order to test its ability to account for observed concentrations and fluxes of metals in surface water, and soil pools.
3) Development of a simpler dynamic model, suitable for implementation within a GIS, making use of national-scale data sets.

In addition, through an M.Sc. project, we carried out measurements of metal uptake by a bryophyte that occurred in several streams that were monitored for metal concentration and flux determination. We also collaborated with our Consortium partners in analysing metal partitioning data for upland soils.

Field measurements

Study sites Two locations were chosen for the field work. The first was the upper catchment of the River Duddon, in the south-west Lake District (NGR NY 250 020). This is a moorland area of high relief, with altitudes up to 850 m above sea level, the landscape having been shaped by glaciation. The annual rainfall is ca. 2-4 m, depending upon altitude and the annual temperature range (monthly averages) is *ca.* 4-15°C at an altitude of 100 m (Manley, 1989). Run-off is rapid and depends strongly upon antecedent rainfall. The catchment is underlain by metamorphosed igneous rocks, which display spatially heterogeneous weathering rates, therefore the sensitivity of stream waters to acid deposition varies widely. Peat rankers and stagnopodzols are the predominant soils (Jarvis et al., 1984). The deposition concentrations in rainfall of hydrogen ions and non-marine sulphate have shown significant decreases over the last 20-30 years, but there have been no significant changes in the concentrations of nitrogen species or non-marine base cations (Tipping et al., 1998). Chemical monitoring was carried out on five streams, ranging in average pH from ca. 5 to ca. 7. Their individual catchments are sufficiently close that they can be considered to receive rainfall with the same chemistry. The second study site was a moorland plateau area on the side of Great Dun Fell, Cumbria (NGR NY 700 300), where peat rankers and peat overlie sandstone. The area forms the catchment of a number of small pools, two of which were monitored. The annual rainfall is ca. 1.5 m. The pools differ in that one had a mean pH of 4.9 during the study, while that of the other was 6.8.
Sampling and analysis All apparatus used for sampling metals in rain and stream water was scrupulously acid cleaned, care was taken to avoid contamination during transport and handling, and laboratory procedures were carried out in a laminar flow hood. Clean room gloves were worn. Double sub-boiling point distilled HNO_3 was used in obtaining acid-recoverable metals. Frequent checks were made of instrument (ICP-MS) performance, and a strict quality control system was operated. Recoveries of metals from a certified rain water standard fell within the range 84 – 113 % (mean 99%). Detection limits ($\mu g\ L^{-1}$) were: Ni 0.19, Cu 0.18, Zn, 0.49, Cd 0.01, Pb 0.09. Major solutes were also determined in all rain and stream water samples. Rain samples were collected fortnightly, surface water samples weekly. Soil

samples were collected by digging small pits, and were analysed for bulk density and depth as well as metals, in order to estimate soil metal pools.

Results The following Table summarises the field monitoring results for metals recoverable with 0.1 M HNO$_3$ in 1998-99. Ranges and standard deviations are omitted to save space.

	Ni	Cu	Zn	Cd	Pb
Vol-wt mean concn. in bulk preciptn. (µg L^{-1})					
upper Duddon	0.39	0.40	2.35	0.019	0.77
Great Dun Fell	0.43	0.86	3.71	0.024	1.41
Loads in bulk deposition (g ha^{-1} a^{-1})[*]					
upper Duddon	12	12	72	0.6	24
Great Dun Fell	3	6	28	0.2	10
Mean stream and pool concentrations (µg L^{-1})	f / t[†]	f / t	f / t	f / t	f / t
upper Duddon D2 (mean pH 5.3)	0.30/0.32	0.31/0.33	5.2/5.3	0.08/0.08	0.25/0.29
D3 (mean pH 5.1)	0.19/0.26	0.24/0.33	3.9/4.2	0.07/0.09	0.42/0.44
D5 (mean pH 5.6)	0.24/0.29	0.25/0.26	4.7/5.0	0.08/0.09	0.23/0.24
D8 (mean pH 7.1)	0.39/0.42	0.24/0.25	1.6/2.1	0.02/0.03	0.07/0.10
D11 (mean pH 7.2)	0.31/0.42	0.50/0.67	0.9/1.1	0.05/0.06	0.05/0.15
Great Dun Fell Pool X (mean pH 4.9)	2.5/2.7	1.3/1.7	29/30	0.11/0.13	3.5/4.5
Pool Y (mean pH 6.8)	2.6/2.8	1.2/1.3	11/12	0.12/0.16	2.3/2.9
Mean stream and pool loads (g ha^{-1} a^{-1})[‡]	f / t[†]	f / t	f / t	f / t	f / t
upper Duddon D3	6 / 9	6 / 12	100 / 147	2 / 3	11 / 15
D5	7 / 10	6 / 9	130 / 175	2 / 3	6 / 8
D8	10 / 15	6 / 9	41 / 74	0.6 / 1	2 / 4
Great Dun Fell Pool X	19 / 20	10 / 13	210 / 230	0.9 / 1	26 / 34
Pool Y	9 / 21	9 / 10	79 / 89	0.9 / 1	17 / 22
Soil metal pools (g ha^{-1})					
upper Duddon D3	920	2000	4400	300	46000
D5	1000	6500	6100	200	45000
D8	1300	3600	5800	200	69000
Great Dun Fell	360	470	5300	100	23000

[*] True values may be somewhat higher (up to 20%), due to deposition of cloud water and dry deposition not captured by the bulk samplers.

[†] filtered / total. [‡] Calculated from modelled stream discharge (Duddon), and by assuming 500 mm evaporation (Great Dun Fell).

The main points to come out of these results, and from others that are not shown due to lack of space, are as follows. (TM = toxic metals, “acid-recoverable” = dissolved by 0.1 M HNO$_3$.)

(a) At both study sites [TM] in bulk precipitation lie towards the low end of ranges quoted by Barrie (1987) and Ross (1995) for rural areas.

(b) There are significant correlations ($r^2 = 0.18$ to 0.83) of the mean concentrations of [TM] in bulk precipitation with that of non-marine SO$_4$, indicating common pollution source areas.

(c) The depositional fluxes of TM at the Duddon are 1.3 – 3.9 times those at Great Dun Fell, mainly due to the differences in precipitation amount. The observed fluxes are similar to values reported for other similar locations (Berg et al., 1998, Wilkinson et al., 1997).

(d) Most (> 65%) of the acid-recoverable metal in bulk precipitation is in solution (0.45 µm filter).

(e) Input and output loads at the Duddon are generally similar except in the case of Cd, for which the output is ca. five times the input for streams D3 and D5, and for Pb in stream D8, where the output is 1/5 the input. At Great Dun Fell the output loads exceed the inputs by factors of two to eight.

(f) Metal concentrations in the Great Dun Fell pools are greater than those in the Duddon streams, despite the lower depositional inputs. Complexation by DOM in the pools is calculated (using WHAM / Model VI; Tipping, 1994,1998) to be significant for all five toxic metals.

(g) Average concentrations of Zn, Cd and Pb in Duddon stream waters vary with average pH, having their highest values in the lower pH streams. Nickel has its highest values in the higher pH streams, while Cu displays little stream-to-stream variation, possibly indicating varying weathering supplies from the catchment rocks, and/or different co-transport with dissolved organic matter (DOM).

(h) In the Duddon streams, concentrations of suspended particulate matter (SPM) are low (~ 1 mg L^{-1}), but in the higher-pH streams some metal is in particulate (non-filterable) forms (typically 10-20%, 70% for Pb in stream D11). At GDF ([SPM] = 6-10 mg L^{-1}) the particulate metal concentrations are rarely greater than 10% (max 20%) of the total, reflecting DOM complexation, holding metal in solution.

Modelling metal partitioning in upland soil samples

The partitioning of metals between the solid and solution phases of soils is a key process in controlling metal concentrations in soil and surface waters. In the mechanistic dynamic catchment model used in this work (CHUM – see below), the partitioning is assumed to be governed by equilibrium chemical reactions involving natural organic matter (humic and fulvic acids). These reactions are described by the speciation program WHAM (Tipping, 1994). WHAM is parameterised for ca. 30 metals, including those of interest here, on the basis of the results of laboratory experiments with isolated humic substances. Within the present project, we tested the model's ability to simulate metal partitioning in soils sampled from the study catchments.

Duddon and Great Dun Fell soils Batch titration experiments were conducted by taking soil samples and suspending them in dilute NaCl solutions, to which different amounts of HCl or NaOH had been added, to achieve pH ranges of ca 3-5 in the equilibrated suspensions. Measurements were made of pH, and concentrations of dissolved organic carbon (DOC), Al and toxic metals in the suspension supernatants, obtained by centrifugation. Soil Al and toxic metal contents were determined by extraction with acids of different concentrations. Base cation contents were determined by extraction with $BaCl_2$. Soil C content was determined with an elemental analyser. WHAM was applied by simulating the results of the batch titration experiments, for different assumed soil contents of humic substances and metals. The model was able to fit the data reasonably well, as illustrated by the plots in Fig. 1. The solution total metal concentrations – $[Al]_{aq}$ etc - pass through a minimum because of relatively weak binding at low pH and complexation by dissolved organic matter, which is increasingly released to solution as the pH is increased. The optimised soil metal contents agreed fairly well with contents determined by 0.1 M HNO_3 extraction (Fig. 2): optimised values for Ni, Cu and Zn were slightly greater than extracted ones, those for Cd were in close agreement, while optimised values for Pb were lower than extracted ones. In the case of Pb, this reflects a general finding of this work that Pb binds to the solid phases of organic-rich soils more strongly than anticipated from measurements on isolated humic substances. These are estimates of soil metals that are "active" in the sense of being able to exchange between the solid and solution phases. The average ratios of "active" metal to total metal determined by HF digestion, were 0.05 (Ni), 0.06 (Cu), 0.11 (Zn), 0.10 (Cd) and 0.28 (Pb), suggesting that much of the total soil metal is "inert" with respect to solid-solution exchange, and therefore transport and bioavailability; the possible slow release of metal from this "inert" pool deserves attention.

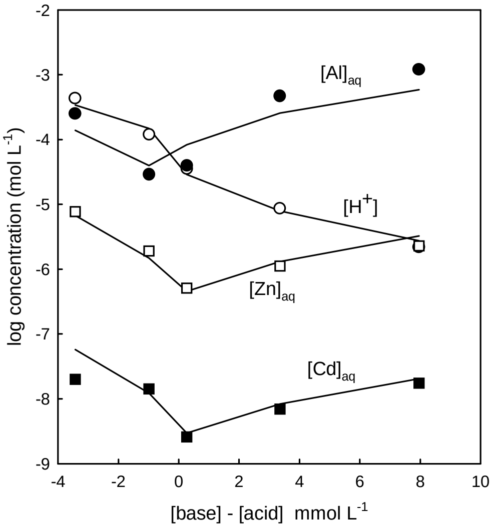


Fig.1 Observed (points) and fitted (lines) concentrations of H^+ and total dissolved metals in the supernatants of suspensions of a ranker soil from the Duddon catchment.

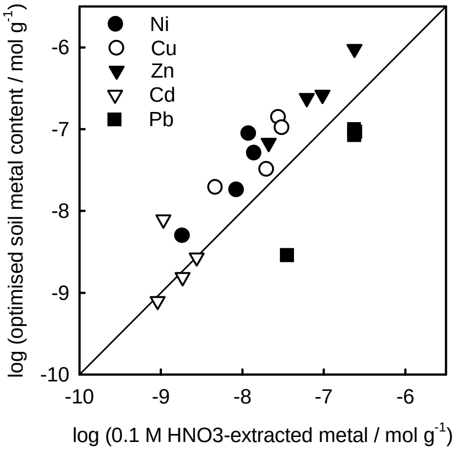


Fig. 2 Contents of "active" soil metals estimated by fitting with WHAM, plotted against contents estimated by extraction with 0.1 M HNO_3, for four soils. Similar relationships were obtained for metals extracted with 0.22 and 1 M HNO_3.

Soil survey data In work partly funded by the DETR, other Consortium members (J.Rieuwerts, M.Ashmore, M.Farago, M.Hill, G.Pan, I.Thornton) collected more than 100 soil samples from different upland locations (Derbyshire, North Wales, Lake District, Pennines). The soils were characterised by determining (among other variables) loss-on-ignition (LOI) and contents of extractable metals. They were incubated at high moisture content, the pore waters were sampled with “Rhizon” samplers, and analysed for metals, pH and DOC. The data covered wide ranges of LOI, soil metal contents and pH. One method of analysing the data was to use K_D values defined in terms of total dissolved metal concentrations, i.e. including any metal present as organic complexes. We used a different approach, using values of $K_{D,f}$, the ratio between adsorbed metal (mol g^{-1}) and the concentration of the free metal ion in solution (e.g. Cu^{2+} in the case of Cu). Adsorbed metal contents were taken to be the values obtained by extraction with 0.43 M HNO_3, but similar results were obtained using results from extractions with EDTA and *aqua regia*. The free metal ion concentrations were estimated by applying the WHAM speciation program to the soil solutions. The values of $K_{D,f}$ could be fitted to the equation:

$$\log K_{D,f} = \alpha \,\mathrm{pH} + \beta \,\mathrm{LOI} + \chi$$

with parameter values and r^2 values as shown on the right. Adsorption is found to increase with pH and soil organic content. The relationships provide useful descriptions of partitioning, which can be used in a simple dynamic model (see below).

	α	β	χ	r^2
Cu	0.70	0.0077	-2.86	0.79
Zn	0.28	0.0104	-2.14	0.20
Cd	0.28	0.0079	-1.44	0.46
Pb	0.84	0.0086	-2.36	0.86

The data were also analysed by applying the soils version of WHAM (i.e. predicting both solution speciation and solid-solution partitioning). It was assumed that 20% of all LOI was humic matter (a typical value found from using the model to fit data for major cations). First, values of $K_{D,f}$ were blind-predicted. This worked very well for Cu and Zn, but less well for Cd and Pb, for which relatively small adjustments to one of the model parameters (equilibrium constant for metal binding) were made.

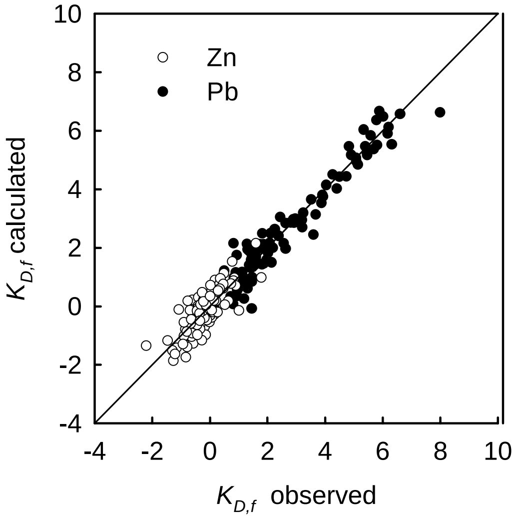


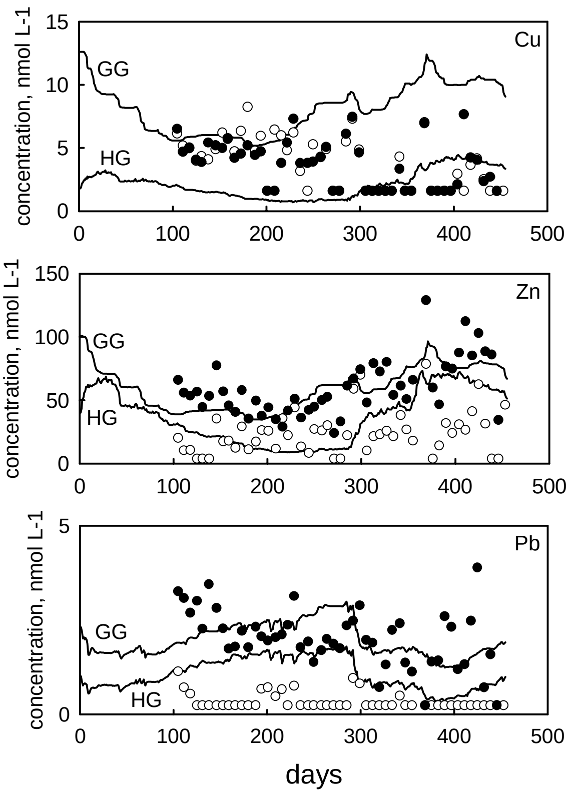
Fig. 3 Observed and WHAM-calculated $K_{D,f}$ (K_D based on free metal ion concentration) for upland soils. The WHAM results for Zn are predicted with default model parameters. For Pb, the equilibrium constant for binding by humic matter was optimised, the optimised value being four times the default.

The results of Fig. 3 show that the gross features of metal partitioning, across a number of locations, covering wide ranges of pH, LOI and DOC, can be rationalised very well, using a mechanistic model. This result demonstrates that metal-soil interactions can be described on the basis of fundamental chemical knowledge, i.e. from results obtained in laboratory studies of metal binding by humic substances. Thus, the use of basic chemistry to explain metal behaviour in the field is strongly supported.

The application of the dynamic hydrochemical model CHUM to the upper Duddon catchment

The CHemistry of the Uplands Model is designed to simulate the gains and losses of solutes as rainwater passes through the plants, soils and rocks of a catchment, and exits as surface water. The model can simulate both major solutes, as in applications to acidification, and minor solutes, as for the toxic metals considered in the present study. At the heart of CHUM is the WHAM chemical speciation model, which calculates the interactions of solutes with humic matter. WHAM deals with both adsorption by solid-phase organic matter and solution speciation. In the model, metal behaviour is also governed by adsorption in the zone underneath the organic-rich soil, where weathering (mineral dissolution) is taking place. Details of the model structure and sub-models are given by Tipping (1996).

CHUM was applied to two of the catchments in the upper Duddon, Gaitscale Gill (stream pH ~ 5) and Hardknott Gill (stream pH ~ 7). The model explains the stream pH differences by different weathering rates. The model was first configured to simulate variations in major solutes, then toxic metals were considered. During the course of the work, it became clear that changes over the past 200-300 years must be considered, because metal adsorption to the soil solids causes the build up of pools that are large relative to input and output loads. The overall aim of the CHUM simulations was to account for present-day observed metal pools, concentrations and loads, on the basis of known or assumed historical deposition scenarios of metals and acidifying pollutants (which are the same for both catchments). Of the acidifying pollutants, the dominant one in terms of long-term change is sulphur. Deposition of pollutant S over the period 1700-1850 was assumed to be zero, after which it was assumed to increase in parallel the emission scenario given by Bettelheim & Littler (1979), reaching a maximum at around 1970. Measured values for the Lake District are available from the mid-1970s to the present day. Metal deposition has declined over the past 30 years, as judged from measurements of metal concentrations in air at Wraymires, which is within 15 km of the study sites (Cawse et al., 1995). Deposition values for the study sites were estimated by ratio-ing measured deposition for 1998 with air concentrations, and then extrapolating back to 1970. From analysis of peat cores, Lee & Tallis (1973) deduced that Pb deposition in northern England increased markedly in the 18th and 19th centuries, reaching an apparent plateau by 1900. We assumed that this applied to the other metals also. Our scenario involves a linear increase, from zero, in metal deposition between 1850 and 1900, followed by constant deposition until 1970, and then a decline to present-day values. Weathering inputs of metal were ignored.



The diagrams on the left (Fig. 4) show observed and simulated concentrations of Cu, Zn and Pb in Gaitscale Gill (GG) and Hardknott Gill (HG) from January 1 1998 onwards. The closed symbols represent GG, the open ones HG. The simulations were obtained with just two parameter adjustments. The first was the constant within WHAM that characterises the binding of Pb by organic matter. This had to be increased by a factor of 4 in order to achieve reasonable soil pools and stream concentrations. The second adjustment was made to the strength of adsorption of metals to an assumed oxide-like phase in the weathering zone. It was assumed that the five metals were adsorbed with the same relative strengths as by model oxides, the relative values being taken from Lofts & Tipping (1998). Thus, if the binding constant of one metal was increased by 1 log unit, so were those of the others. Also, the same constants were applied to both catchments.

The simulated concentrations are of the correct magnitude, and in the case of Zn some of the temporal variability is reproduced, but this is not the case for the other metals. Fig. 5 shows that the model provides quite good estimates of present-day stream loads, and of the soil pools of Cu, Zn and Pb, while somewhat underestimating soil pools of Ni and Cd. It puts the metals in the correct order (e.g. Zn has the highest load, Pb the largest pool), which is due to the assumed depositional loads and the different adsorption strengths of the metals.

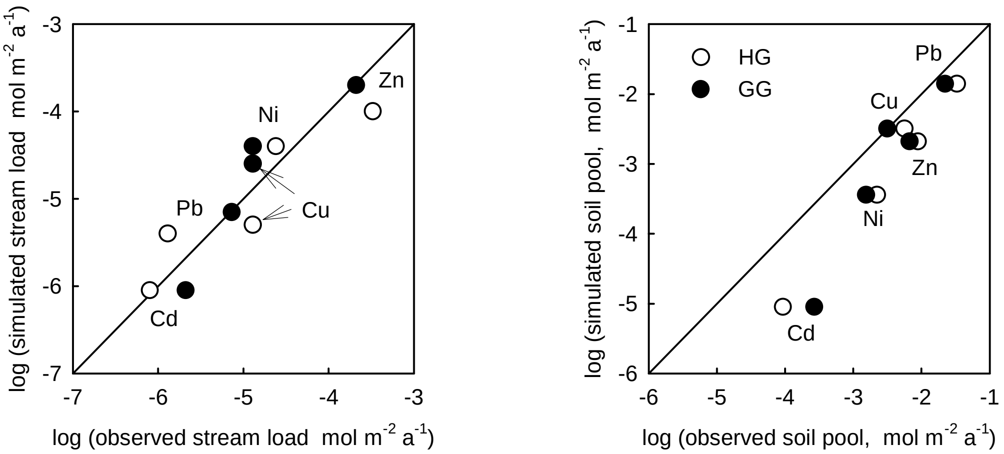


Fig. 5 Observed and CHUM-simulated present-day stream loads of dissolved metal and soil metal pools in the upper Duddon.

Fig. 6 shows simulations of soil pH and the soil metal pools of Zn and Pb, for the period 1800-2000. The pH decrease, due to atmospheric deposition of S, has a strong effect on Zn, because the adsorption of this is metal by soil solids is weak and therefore sensitive to changes in pH. Thus, between 1850 and 1900 the soil Zn pool increases, due to increased Zn deposition, but then, despite the deposition staying the same, it falls, due to the decreased soil pH. In contrast, the soil pool of Pb, which adsorbs strongly to the soil, continues to increase throughout the 200 year period, and is only now beginning to level off, as the depositional input declines. Ni and Cd behaved like Zn, Cu like Pb.

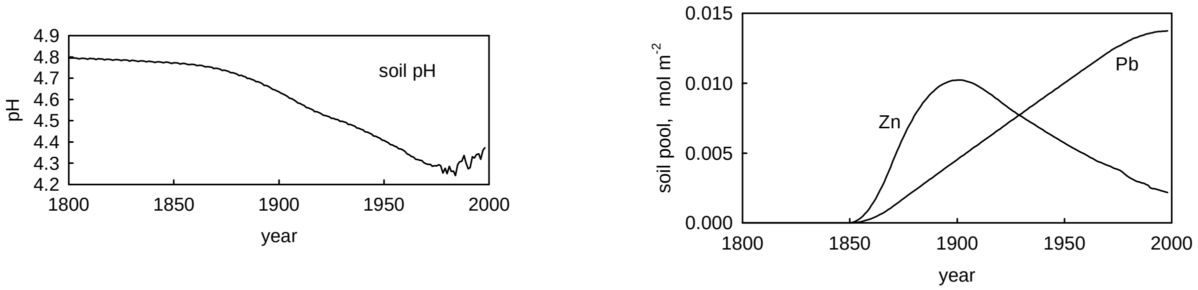


Fig. 6 Long-term simulations of soil pH and metal pools in the upper Duddon.

Thus, using plausible metal input scenarios, which were not adjusted to attempt to improve the agreement between observations and simulations, and with adjustment of only two parameters for metal binding, CHUM predicted present-day stream water metal concentrations and loads of the correct magnitude, and accounted reasonably well for present-day soil metal pools. The relative behaviours of the five metals were correctly simulated. The results support the underlying assumptions of the model, and suggest that metal behaviour in upland catchments can indeed be simulated realistically. The modelling exercise demonstrates the potential importance of changes in soil acid status in controlling metal behaviour, and also shows that metal dynamics in the uplands are operating on long time-scales (decades-to-centuries).

A simpler dynamic model of metals in upland catchments

The analyses with CHUM provide mechanistic insights into the behaviour of metals in upland catchments, but the model is too complex and data-hungry to be used in mapping of critical limits, and loads. Therefore a simpler dynamic model is desirable. However, the simpler model needs to distinguish processes occurring in the soil and in the weathering zone, and to be able to take account of the changing acid status of the soils. We developed such a model, making use of (a) the parameterised $K_{D,f}$ equations given above, (b) solution speciation calculated with WHAM (for waters), and (c) a simple model for adsorption of metals by oxide surfaces (for the weathering zone). The model is applied as follows:

1. A long-term scenario of annual loads is constructed for each metal.
2. A long-term scenario of soil pH, stream water pH and [DOC] is constructed.
3. The depth, bulk density and loss-on-ignition of the soil are specified (assumed constant).
4. Annual inputs of metals from weathering, and annual burial rates of metals are specified.
5. The model is run to output annual soil pools, stream loads, and free metal ion concentrations.

A novel feature of the model is to back-calculate pH conditions in the weathering zone, from observed stream water pH. This enables pH-dependent metal removal by adsorption to oxides to be estimated, without detailed knowledge of conditions in the weathering zone, for which data are not generally available. The model is simpler than CHUM, but still fairly complex, as it must be in order to differentiate among catchments and take long-term acidification into account. Nonetheless, most of the required input data is available, and so the model should prove useful in national-scale assessments. That it can provide useful results is shown by the plots in Fig. 7, summarising pools and loads at five of our study catchments.

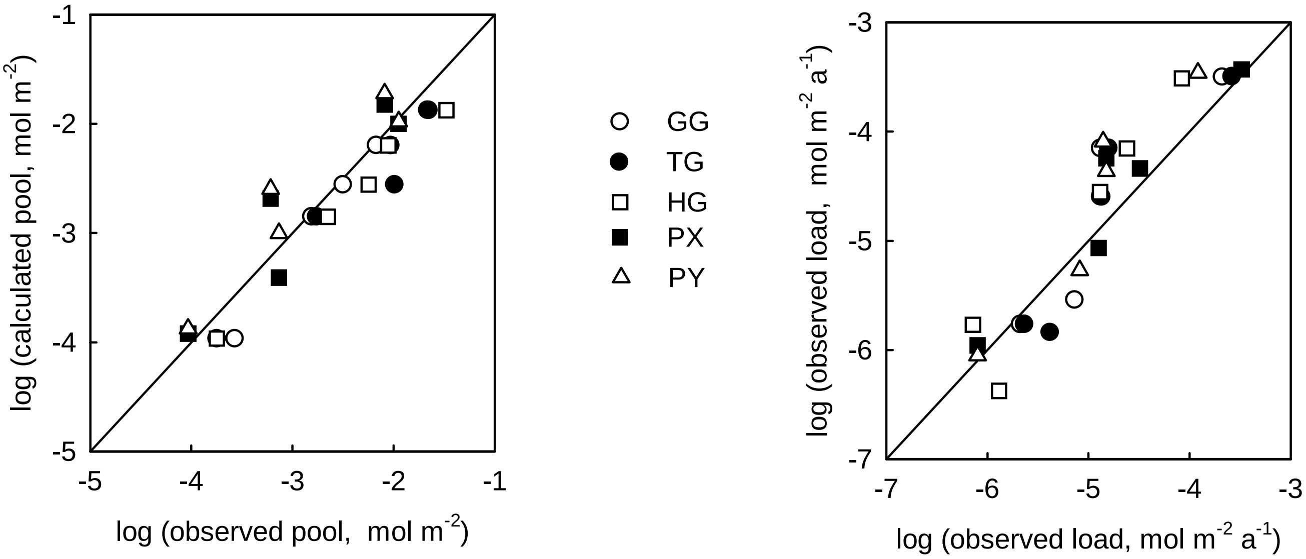


Fig. 7 Present-day soil metal pools and stream loads, observed and calculated with the simpler dynamic model using 200-year deposition scenarios. Key : GG Gaitscale Gill (D3), TG Troughton Gill (D5), HG Hardknott Gill (D8), PX pool X, PY pool Y.

Bioavailability and chemical speciation

Bryophyte studies Measurements were made of the contents of Al, Mn, Fe, Cu, Zn, Cd and Pb in *Scapania undulata* in streams D2, D5 and D11 (see Table above), which had average pH values of 5.35, 5.81 and 7.26 respectively. Extents of accumulation varied with stream pH and dissolved metal concentration. For Al, accumulation was greatest in streams D2 and D5. Mn accumulated most in D5 and Fe was without preference. Cu, Zn and Cd accumulated mostly in the plants in stream D11 and Pb accumulated more in D5 and D11. In terms of enrichment factors (amount of metal in the plants divided by stream water concentration) the sequence was Zn < Cd < Cu < Mn < Pb < Al < Fe. Laboratory experiments supported the findings of the field data, providing evidence that uptake increases with pH at constant total metal concentration. The results could be interpreted in terms of the chemical speciation of the metals in the stream water, and competition between metal ions and protons at the plant-water interface. It was concluded that Al, Cu, Zn, Cd and Pb behave according to chemical complexation, i.e. they obey the free-ion activity model, whereas redox processes and/or colloidal interactions may be significant for Mn and Fe. Bryophytes do not give direct information on metal concentrations in waters because of the competition, solution speciation and pH effects, but they are useful indicators of bioavailablity, defined in terms of total uptake by biota. This may prove useful in validating model predictions of metal bioavailability in surface waters, since the plants provide an integrated picture of metal uptake over a relatively long period.

Toxicity to bacteria Our colleagues in the Consortium (J.Rieuwerts, M.Ashmore, M.Hill, G.Pan, G.Paton) carried out toxicity tests with the soil waters obtained using "Rhizon" samplers, mentioned above. They used *E. Coli* modified by the insertion of *lux* genes as a bioluminescence-based biosensor. It was found that when the degree of toxicity (measured by the extent of light emission) was plotted against total soil metal, or against total dissolved metal concentration, there was no relationship between toxicity and metal concentration. However, when plots against free metal ion concentration (calculated with WHAM, Tipping, 1994;1998) were made, clear relationships were obtained, characterised by a change in toxic effect from ca. zero to ca. 100% over a ca. 10-fold change in free ion concentration (an S-shaped curve). Since these were experiments with soil waters, many metals were present. Interestingly, the characteristic S-shaped toxic response was shown for all the metals considered (Cu, Zn, Cd, Pb). This result contributes significantly to the setting of critical limits in terms of free metal ion concentrations.

Summary and conclusions

The majority of the originally planned work was completed, but there were some variations. CHUM was applied to fewer catchments than originally intended, and lowlands were not considered (Policy advice being more urgently required for the uplands). Forested catchments were not considered, although from the established principles and understanding obtained this would probably not be a large task. The work with the bryophytes, and the analyses of soil-solution partitioning and toxicity data obtained by our colleagues was not planned, but added significantly to the progress made. More progress than anticipated was made in developing a simpler dynamic model. The main outputs from the research are as follows:

1) Measurements of present-day depositional loads, soil metal pools, stream water concentrations and loads for two upland areas.
2) Modelling results for metal interactions with soil solids, which demonstrate that solid-solution partitioning can be explained to a large extent in terms of binding by natural organic matter.
3) Simulations of soil and stream chemistry (major solutes and toxic metals) for catchments of the upper Duddon, using a dynamic model (CHUM). The results demonstrate that metal behaviour can be understood in terms of processes represented in the model, that metal inputs and outputs occur over decade-to-century timescales, and highlight the importance of acidification status in metal behaviour.
4) A simpler dynamic model that shows promise for national-scale application.
5) The establishment of relationships between chemical speciation (specifically free metal ion activity) and bioavailablity, by application of the WHAM model to stream and soil waters.

The results described here, in combination with those obtained by our Consortium partners, have greatly improved our understanding of metals in UK uplands, and form a sound platform on which to derive integrated effects-based assessments of metal toxicity in soils and waters. However, more research will be needed before this goal can be achieved. For an account of the whole Consortium project, the reader is referred to the overview prepared by Professor M.Ashmore.

Publications to date

Rieuwerts, J.S., Farago, M.E., Thornton, I., Ashmore, M.R., Fowler, D., Nemitz, E., Hall, J., Kodz, D., Lawlor, A. & Tipping, E. (1999) Critical loads of metals in UK soils: an overview of current research. In Proc. 5th Internat. Symp. on Geochemistry of the Earth's Surface, H.Armannsson (ed) Balkema, Rotterdam, pp. 223-226.

Vincent, C.D., Lawlor, A.J., Tipping, E. (2001) Accumulation of Al, Mn, Fe, Cu, Zn, Cd and Pb by the bryophyte Scapania undulata in three upland waters of different pH. Environ. Pollut. In press.

Ashmore, M., Colgan, A., Hill, M., Pan, G., Paton, G., Rieuwerts, J., Tipping, E. (2000) Modelling and microbial toxicity of pore-water free ion concentrations of metals in upland soils. In Curlik, J. (ed.) Proc. NECEC/CLRTAP Meeting of the Ad-Hoc International Expert Group on Critical Limits for Heavy Metals, Bratislava, October 2000.

References

Berg, T. et al. (1998) Atmos. Env. 28, 3519. Bettelheim, J., Littler, A. (1979) CEGB Report PL-GS/E/1/79. Cawse, P.A. et al. (1995) AEA Technology Report AEA/CS/18358008/REMA-039. Jarvis, R.A. et al. (1984) *Soils and their Use in Northern England*. Soil Surv. England & Wales, Bulletin No. 10, Harpenden. Lee, J.A., Tallis, J.H. (1973) Nature 245, 216. Lofts, S., Tipping, E. (1998) Geochim. Cosmochim. Acta. 62, 2609. Manley, G. (1989) In Pearsall, W.H. & Pennington, W. *The Lake District*, Collins, London, p. 106. Ross, H.B., Vermette, S.J. (1995) In Salbu, B., Steinnes, E., eds. *Trace Element in Natural Waters*. CRC Press. Barrie et al. (1987) Atmos. Env. 21, 1133. Tipping, E. (1994) Computers & Geosciences 20, 973. Tipping, E. (1996) J. Hydrol. 174, 305. Tipping, E. (1998) Aquatic Geochem. 4, 3. Tipping, E. et al. (1998) Environ. Pollut. 103, 143. Wilkinson, J. et al. (1997) Hyd. Earth Syst. Sci. 1, 557.