General enquiries on this form should be made to:
Defra, Science Directorate, Management Support and Finance Team,
Telephone No. 020 7238 1612
E-mail: research.competitions@defra.gsi.gov.uk

defra
Department for Environment Food and Rural Affairs

SID 4

Annual/Interim Project Report for Period Nov2005-Nov 2006

- **ACCESS TO INFORMATION**
  The information collected on this form will be stored electronically and will be required mainly for research monitoring purposes. However, the contents may be used for the purpose of notifying other bodies or the general public of progress on the project. Defra may also disclose the information to any outside organisation acting as an agent authorised by Defra to process research reports on its behalf.
  Defra may be required to release information, including personal data and commercial information, on request under the Environmental Information Regulations or the Freedom of Information Act 2000. However, Defra will not permit any unwarranted breach of confidentiality or act in contravention of its obligations under the Data Protection Act 1998. Defra or its appointed agents may use the name, address or other details on your form to contact you in connection with occasional customer research aimed at improving the processes through which Defra works with its contractors.
- This form is in Word format and boxes may be expanded or reduced, as appropriate.

Project details

1. Defra Project code: CPEA24
2. Project title: Development of an effects-based approach for toxic metals
3. Defra Project Manager: Dr. Soheila Amin-Hanjani
4. Name and address of contractor:
   Environment Department
   University of York
   Heslington
   York
   Postcode YO10 5DD
5. Contractor's Project Manager: Prof Mike Ashmore
6. Project: start date .... November 2004
   end date .... November 2007

Scientific objectives

7. Please list the scientific objectives as set out in the contract. If necessary these can be expressed in an abbreviated form. Indicate where amendments have been agreed with the Defra Project Manager, giving the date of amendment.

To contribute to the implementation and further development of critical loads methods for lead and cadmium within the UN/ECE Convention on Transboundary Air Pollution To maintain and develop a national capacity to map critical limits and critical loads for the UK for lead, cadmium, copper, zinc and nickel To undertake fieldwork and further data analysis to reduce the uncertainty of key input parameters, in particular dissolved organic carbon To modify calculations and mapping of critical loads and limits, and their exceedance, to take account of new field data and critical load model parameterisation To carry out field studies in areas with medium to high historic acid and metal deposition to test dynamic models To further develop existing dynamic models to allow integrated assessment of the impacts of changes in deposition of metals, sulphur, nitrogen and acidity To map concentrations of metals and nitrogen in four moss species across the UK To estimate the metal deposition field in the UK using moss data, and compare the values with estimated critical load values To provide a comparison of metal concentrations in mosses since 1990.

Summary of Progress

8. Please summarise, in layperson’s terms, scientific progress since the last report/start of the project and how this relates to the objectives. Please provide information on actual results where possible rather than merely a description of activities.

Work Package 1

Members of the consortium attended the 2nd Meeting of the Expert Panel on Critical Loads of Heavy Metals in Berlin in January 2006, and contributed to further discussion of the status of calculations of critical loads of metals within CLRTAP. The importance of UK work in demonstrating extension of critical loads to metals other than Pb, Cd and Hg, and in dynamic modelling of responses to changes in metal deposition for scenario analysis, was recognised. Members of the consortium also contributed to relevant sections of the report on Sufficiency and Effectiveness (S&E) of the Heavy Metals Protocol which was produced in April 2006, and which summarised information on the current status and uncertainties in the application of critical load approaches. Ad-hoc advice has continued to be provided to Defra, in response to requests from the project officer.

It should be noted that no further formal calls for data are expected from the CCE during the period of this contract.

Work Package 2

Literature searching and data collation for ecotoxicity data have continued. Analysis of these data will be undertaken, as planned, in the final year of the contract.

National database

The national databases required for critical loads and dynamic modelling have been reviewed and checked in preparation for running the updated models in 2007. Deposition data (Cd, Cu, Pb, Zn) for the year 2004 have been received from CEH Edinburgh (contract ref) and we expect the data for 2005 early next year; these will be used to calculate critical load exceedances for the updated critical loads.

DOC Measurements

For DOC measurements, 28 sites covering 6 key landuse types (deciduous forest, coniferous forest, calcareous grasslands, acid grassland, bogs and heathland) and 6 soil types (brown earths, stagnogleys, podzols, rendzinas, peats and argillic brown earths) were sampled over the course of a year. At each site, soil water samplers were installed and sampled every 3 weeks. In addition, data from other sites sampled by ECN and others has been gathered, resulting in data from 54 sites in total. In a separate PhD project at CEH Lancaster, measurements of DOC concentrations and fluxes in topsoils have been performed at 7 sites in Cumbria, with contrasting soil types, and these will also be included. DOC concentrationss, pH, conductivity and absorbance at 340 nm were analysed in York. This work will be completed during November 2006. Tests were performed to validate methods and instruments: DOC concentration measurements were calibrated against standard solutions and also against other analysers (CEH Lancaster) to calibrate the results from York. Other tests showed that storage of samples at the facilities in York for almost 1 year did not affect DOC concentrations significantly.

The data show great variations in DOC concentrations both in time (a seasonal effect with a high peak in DOC in the late summer) and between sites within the same vegetation type. In addition DOC values differed markedly between vegetation types; bogs for example had high DOC concentrations of on average 70 mg/l whereas calcareous grasslands had much lower concentrations of 19 mg/l (Fig. 1), close to the default value currently used for all vegetation types in the UNECE mapping manual.

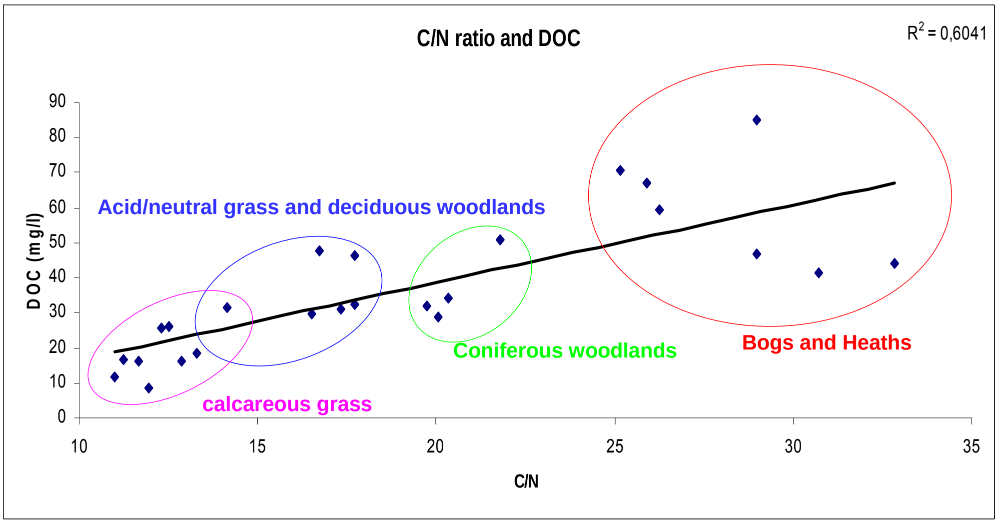

Figure 1: Relationship between DOC concentration (mg l^{-1}) and C/N ratio at 26 sites

Data on rainfall, air temperature and evaporation data have been obtained to estimate monthly runoff at each site and hence to calculate DOC flux. For all sites other relevant site data, on vegetation (using NVC classification), soil type, slope and aspect were gathered. For two sampling dates, soil loss-on-ignition (LOI), ratios of total soil carbon to total soil nitrogen (C:N), cation exchange capacity (CEC) and soil water pH were analysed, one in the late-summer period (high DOC) and one in the winter period (low DOC). An early analysis shows that DOC concentrations are related to prevailing C/N ratios in the soil across habitat types (Fig. 1).

Work Package 3

Field work and analysis

Sampling of soils and waters at Scoat Tarn and Howden Reservoir is complete. Analytical work on water samples is complete. The surface water chemistry data appear to be as expected on the basis of previous work. The soils have been analysed for bulk density, carbon and nitrogen contents, loss-on-ignition, and pH. The last determinants are the heavy metals, analysis of which should be completed before the end of 2006. There have been delays to these analyses because of the illness of a key member of the Environmental Analysis Group at CEH Lancaster.

We have determined metal inputs to the sediment over the lifespan of the reservoir and lake through the analysis of bulk metal concentration in all zones of the reservoir (marginal and central areas). The lake sediments collected from Scoat Tarn and Howden Reservoir have been digested to determine total and potentially available fractions. Determinations of Pb, Cd, As, Cu, Zn and Ni, and of LOI and C/N ratios, have been completed. The cores will be dated in November using VSM and magnetic susceptibility techniques.

An initial analysis shows that cumulative total Pb loads are substantial in Howden reservoir (Table 1) are strongly dependent on the assumptions made for sedimentation.

Table 1. Pb load in Howden reservoir.

	Assumptions made in calculating sediment and Pb loads	Sediment load (t)	Pb load (kg)
Deposition as calculated above for zones 1 to 7 plus:			
1	No deposition in either channels or margins (i.e. only sedimentation in zones 1 to 7).	47025.4	5700.2
2	Deposition in channels to a depth of half the average for the reservoir (26.4 cm), mean bulk density (0.40 g cm3) and mean Pb (121.9 ug g)	53285.1	6463.2
3	Deposition in both channels and margins to a depth of 26.4 cm, mean bulk density and Pb.	65769.4	7984.6
4	Deposition in channels to the average for the reservoir (52.8 cm) and to a depth of 26.4 cm in the margins, mean bulk density and Pb.	72029.1	8747.6

Weathering studies

The long-term (several years) dissolution of mineral samples from the study catchments is continuing. Although we have reached the end of the planned monitoring period, the experiments are being continued in order establish steady-state conditions more definitely. Metal concentrations in the leachates are declining to what seem “reasonable” near-steady-state values. This suggests that our current assumptions about background weathering inputs within study catchments are approximately correct, i.e. that reasonable estimates of weathering inputs can be made by assuming congruent dissolution of minerals, and ratio-ing heavy metal fluxes to those of silicate, or in the case of carbonate-dominated systems, calcium. This approach may be a good way to estimate “background” levels of heavy metals in soils and waters more generally, e.g. in connection with the Water Framework Directive.

Dynamic modelling

The CHUM-AM model has been calibrated for Scoat Tarn and Howden Reservoir, in terms of major solutes. For Scoat Tarn, use was made of AWMN data covering 15 years. The model will be run for heavy metals within the next few months, and the predictions compared with field observations of stream metal concentrations and soil metal contents.

CHUM-AM has been prepared for scenario analyses, to forecast how heavy metals would respond to changes in soil and water acidity caused by pollutant N and S, and to changes in soil carbon cycling. Proposed future scenarios will be circulated to other members of the Project Team, and to Dr. Amin-Hanjani (Defra) for comment before the scenario runs are conducted.

Formulation and testing of The Intermediate Dynamic Model (IDM) has been completed. This model enables long-term metal behaviour to be simulated, with user-defined variations in metal inputs and soil pH. The model will be tested against CHUM-AM during the course of the scenario analyses.

The Simple Dynamic Model has been improved, and is now ready to be used in mapping times to the Critical Limit condition, under constant metal inputs at the Critical Load.

Additional support was obtained for use of the NERC ICP-MS Facility for further analysis of herbarium moss samples collected under the previous contract for different Pb isotopes. On the basis of an initial set of samples, analysis of the full set of samples has been approved. This should provide additional information for the development of historic Pb deposition scenarios for dynamic modelling.

Work Package 4

The main focus in the second year of the programme has been the determination of metal concentrations in mosses collected in the previous year from 173 sites across the UK. The following metals were analysed at the NERC ICP-MS facility in London: aluminium (Al), antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), titanium (Ti), vanadium (V) and zinc (Zn). Table 2 shows the provisional results for the median values of the metal concentrations in mosses for 2005 and a comparison with the results from previous surveys. The general trend of a decline in the metal concentration in mosses during the last decade of the 20th century has continued in the first five years of the 21st century, although at a slower rate. Further data processing, interpretation and mapping will be conducted in the final year of the contract, as will be the determination and mapping of the nitrogen concentration in mosses.

Table 2. Median concentration of metals in mosses across the UK between 1990 and 2005.

	Median ($\mu g\ g^{-1}$)			
Metal	1990	1995	2000	2005*
As	-	0.37	0.16	0.12
Cd	0.16	0.19	0.11	0.09
Cr	0.60	1.40	1.47	0.83
Cu	6.10	5.43	4.32	3.60
Fe	145	347	-	-
Ni	1.60	1.52	0.83	0.81
Pb	6.40	8.27	2.92	2.60
V	1.40	1.55	0.99	0.68
Zn	29.2	34.2	22.7	20.2
Al	-	-	-	98.1
Sb	-	-	-	0.11
Ti	-	-	-	10.2

* provisional data

Amendments to project

9. Are the current scientific objectives appropriate for the remainder of the project? .... **YES** ☒ **NO** ☐
If **NO**, explain the reasons for any change giving the financial, staff and time implications.
Contractors cannot alter scientific objectives without the agreement of the Defra Project Manager.

Progress in relation to targets

10. (a) List the agreed milestones for the year/period under report as set out in the contract or any agreed contract variation.

It is the responsibility of the contractor to **check fully that all milestones have been met** and to provide a detailed explanation when they have not been achieved.

Milestone		Target date	Milestones met	
Number	Title		In full	On time
2.2	Completion of field sampling for DOC	April 2006	Yes	No
2.3	Completion of analysis and interpretation of field data for DOC	October 2006	No	No
3.3	Completion of lake sampling and weathering studies	October 2006	No	No
4.	Completion of analysis of heavy metals in mosses	October 2006	Yes	Yes

(b) Do the remaining milestones look realistic?..**YES** ☒ **NO** ☐

If you have answered **NO**, please provide an explanation.

Milestones for the catchment and lake sediment study, and the DOC field study, have not been met on schedule because of delays in the chemical analysis of field samples, caused by a combination of staff illness and malfunction of analytical equipment. Almost all analysis is complete, and data analysis is already in progress, so that the delay in meeting the milestones should be no more than two months. This delay will not have any significant impact on the completion of the GIS and dynamic modelling components of the work, and hence fulfilment of all remaining milestones in the contract.

With respect to Milestone 3.3, in terms of the weathering studies, these have been completed within the terms of the contract, but we are continuing them in order to improve the data set further.

Publications and other outputs

11. (a) Please give details of any outputs, e.g. published papers/presentations, meetings attended during this reporting period.

Papers

Spurgeon, D.J., Lofts, S., Hankard, P.K., Toal, M., McLellan, D., Fishwick, S., Svendsen, C. Effect of pH on metal speciation and resulting metal uptake and toxicity for earthworms. Environmental Toxicology & Chemistry, 25(3), 788–796 (2006).

Two papers from the last report (on mercury-organic matter interactions, and on heavy metals at Lochnagar) are still in press.

A paper on the use of herbarium mosses in reconstructing deposition histories, based on work in the previous contract, has been accepted for Environmental Pollution, and is in press.

A feature article on the outcome of the Critical Loads Workshop in Baltimore, USA in November 2005 has been submitted, with Lofts as first author.

Presentations at conferences/workshops:

S. Lofts. Critical loads of trace elements to terrestrial systems: an introduction, key concepts and scientific issues. Presentation to Special Symposium on critical loads of trace elements to terrestrial systems, Society for Environmental Toxicology and Chemistry Europe Annual Meeting, The Hague, 7-11 May 2006.

D. Spurgeon, J. Hall, S. Lofts. Can a simple speciation model unify soil and freshwater ecotoxicological data? Presentation to Special Symposium on critical loads of trace elements to terrestrial systems, Society for Environmental Toxicology and Chemistry Europe Annual Meeting, The Hague, 7-11 May 2006.

S. Lofts. Speciation modelling in soil and soil solution. Presentation to Workshop on Critical Loads to Soils due to Emissions from Products of Metals and other Trace Elements, Wye Woods, Baltimore, USA, 12-13 November 2005.

Tipping presented the Simple and Intermediate Dynamic Models (SDM & IDM) to the UNECE Expert panel at the meeting in Berlin in January, and they were well-received. Other research groups are using the SDM already.

Tipping and Lofts attended the Critical Loads Workshop held during SETAC in the Hague in May. Lofts was a co-convenor of the meeting. We both gave invited talks, as did Spurgeon (CEH Monks Wood). There was a lot of interest in Critical Loads, and the European contribution, including the UK Defra-funded work, was well-recognised.

Tipping gave a research seminars on Heavy Metal Critical Loads to the University of Liverpool Geography Department (February) and at ETH Zürich in October. Work from the project was also presented at the AquaNet Conference on Environmental Colloids (Plymouth, September).

Van den Berg gave a summary of the analysis of DOC concentrations in soil solution to date at the annual meeting of the Committee on Air Pollution Effects Research at Edinburgh in April.

Other meetings attended

19^{th} Task Force Meeting ICP Vegetation, Caernarfon, UK, 30 Jan – 2 Feb 2006 (Ashmore, Harmens).

4th BioMAP (Biomonitoring Atmospheric Pollution) workshop, Crete, Greece, 17-21 September 2006 (Harmens)

CCE Workshop & ICP Mapping & Modelling Task Force meeting in April, which included sessions on heavy metal critical loads (Hall).

(b) Have opportunities for exploiting Intellectual Property arising out of this work been identified? .... **YES** ☐ **NO** ☒

If **YES**, please give details.

(c) Has any other action been taken to initiate Knowledge Transfer?.................................. **YES** ☐ **NO** ☒

If **YES**, please give details.

Future work

12. Please comment briefly on any new scientific opportunities which may arise from the project.

The research within this contract has focussed on a limited number of metals – lead, cadmium, copper, zinc and nickel. The prime focus within the contract is on lead and cadmium, as these are priority metals within the Convention on Long-Range Transboundary Air Pollution (CLRTAP). However, within CLRTAP, methods of mapping and modelling critical loads of mercury have also been developed and accepted for application in policy evaluation. Although the potential for full-scale national mapping of exceedance of critical loads and critical limits for mercury is constrained by the availability of data in the UK, the methods which have been developed and applied within this contract could now be extended to include mercury, on the basis of some additional work, to provide an initial assessment for this important metal. This would provide valuable additional information for assessment of policy based on critical loads for mercury in the UK and within CLRTAP.

Declaration

13. I declare that the information I have given is correct to the best of my knowledge and belief.

Name

Date

Position held