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Working Group on Effects

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Item 4 of the provisional agenda

RECENT RESULTS AND UPDATING OF SCIENTIFIC AND TECHNICAL KNOWLEDGE

WORKSHOP ON CRITICAL LOADS FOR HEAVY METALS

Report by the workshop organizers[1]

INTRODUCTION

1. The workshop on critical loads for heavy metals was held from 21 to 22 November 2007 in Windermere, United Kingdom, as agreed by the Working Group on Effects (ECE/EB.AIR/WG.1/2006/2, para. 52) and endorsed by the Executive Body at its twenty-fourth session, and reported here in accordance with item 3.1 of the workplan approved by the Executive Body at its twenty-fifth session (ECE/EB.AIR/91/Add.2). It was organized by the

[1] By tradition, the Convention has used the term "organizers" to indicate the nationally appointed rapporteurs who report workshop results.

Centre for Ecology and Hydrology (CEH). The Swedish Environmental Protection Agency and the German Federal Environmental Agency supported the meeting.

2. Thirty-eight experts attended the workshop. The following Parties to the Convention were represented: Belgium, Bulgaria, Canada, France, Germany, Italy, Latvia, the Netherlands, Norway, the Russian Federation, Spain, Sweden, Switzerland, Ukraine and the United Kingdom of Great Britain and Northern Ireland. A representative from the International Council on Mining and Metals (ICMM) attended the meeting. Also present were representatives of the International Cooperative Programme (ICP) on Waters, ICP Vegetation, and ICP Modelling and Mapping and its Coordination Centre for Effects (CCE). A member of the Convention secretariat also attended.

3. Mr. E. Tipping (United Kingdom), Mr. M. Ashmore (United Kingdom) and Mr. B. Groenenberg (Netherlands) chaired the meeting.

I. AIMS OF THE WORKSHOP

4. The purpose of the workshop was to discuss and review the methodologies, as described in the *Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads and Levels and Air Pollution Effects, Risks and Trends* (hereinafter *Modelling and Mapping Manual* (hereinafter *Modelling and Mapping Manual*), for calculation of heavy metal critical loads, in particular with reference to:

(a) Dynamic modelling of heavy metal transfer and effects through the terrestrial and freshwater environments;

(b) Methods for setting toxic thresholds (critical limits) for different effects, including methods for metals not currently considered (e.g. arsenic (As), selenium), critical limits for waters, methods for considering metal mixtures;

(c) The methodology for calculating critical loads, including significant processes and fluxes, and the relevance across the whole UNECE geographic area;

(d) Identifying, and where possible, quantifying, uncertainties in critical load methods.

5. In addition, a further aim of the workshop was to make recommendations for further development and refinement of these methodologies. These would be subsequently considered by ICP Modelling and Mapping, and possibly used to revise and update the *Modelling and Mapping Manual* for calculating critical loads of heavy metals.

6. Mr. Tipping welcomed the participants on behalf of CEH.

II. CONCLUSIONS AND RECOMMENDATIONS

A. Recent major research results

1. Topical reviews

7. Ms. G. Schultz (Germany) presented the work on heavy metals under ICP Modelling and Mapping and the contribution to the recent sufficiency and effectiveness review of the Protocol on Heavy Metals. New scientific knowledge and data should be used to update the methodologies described in the *Modelling and Mapping Manual.* A method enabling the application of dynamic models at the national focal centres would need to be agreed upon.

8. Ms. I. Schoeters (ICMM) presented the need of knowing, in relation to heavy metals, the properties of substances so that they could be produced and used safely. These requirements, which should be linked with existing national and international legislation, also supported the aims of sustainable development and product stewardship. The need to have harmonized data at the regional scale was emphasized, as was the potential versatility of dynamic models as compared to critical loads.

9. Mr. E. Steinnes (Norway) summarized the use of mosses as indicators of atmospheric metal deposition in Norway, which showed a substantial decrease in the last 30 years but still indicated transboundary influence. The nationwide surveys of natural surface soils showed that southernmost Norway had already been strongly affected by transboundary transport 150 years ago, but deposition of heavy metals had decreased significantly since the 1970s. Soils had become contaminated by the long-range transport of some metals (e.g. lead (Pb), cadmium (Cd), zinc (Zn) and As) as well as lake waters, sediments, plants and wildlife.

2. Processes in selected environmental compartments

10. Mr. D. Fowler (United Kingdom) presented wet and dry deposition monitoring networks of major metals in the rural United Kingdom that provided regional patterns of deposition. Modelled deposition level based on national emissions underestimated measured deposition for many metals (especially copper (Cu), Zn, Pb and As) by a factor of three to five. Atmospheric models did not reproduce measured Europe-wide deposition due to underestimates of emissions throughout Europe and due to resuspension of metal containing aerosols by wind and mechanical wear.

11. Ms. F. Degryse (Belgium) presented the ageing of metals in soils, which decreased the fraction of metals in equilibrium with the solution phase and depended on element, time and soil properties. Ageing decreased solution concentrations and bioavailability.

12. Mr. Ashmore presented the new data to revise values of dissolved organic compounds (DOC) for different ecosystems in the United Kingdom. The variation in annual mean DOC

values within a vegetation type could be used to assess uncertainty in critical loads. Soil carbon-to-nitrogen ratio (C/N) might be a useful predictor of DOC concentrations.

3. Metal toxicity in soils and waters

13. Mr. S. Lofts (United Kingdom) presented critical limits for effects in the terrestrial environment. Free ion critical limit functions for direct toxicity of Pb, Cd, nickel (Ni), Cu and Zn to soil organisms were reviewed. Key assumptions have been tested with new data for copper, allowing a proposed refinement to be made for the method of improving the validity of the functions by accounting for the ageing process. The free ion approach had not yet been applied to mercury (Hg) or aquatic ecosystems.

14. Mr. L. Bringmark (Sweden) presented Hg toxicity with a focus on forest soil humus layers. Hg accumulation in forest humus layers was directly influenced by recent deposition levels and has placed soil microbiota at risk. No decrease of Hg in humus in Sweden was observed during the period 1983–2005, while Pb and Cd had decreased. He suggested that effects-based critical limit criteria might be characteristic for specific humus layers.

15. Mr. B.O. Rosseland (Norway) presented metal toxicity in water. A critical level for a single metal should include a range of data on biotic and abiotic factors and should consider the interaction between several different stressors. The most sensitive target organism in actual eco-regions and catchments should be identified, and critical levels based on their most sensitive life history stage established.

4. Dynamic modelling

16. Mr. M. Posch (CCE, the Netherlands) presented very simple dynamic modelling of heavy metals, as a minimal extension of simple mass balance critical loads. Suitable scaling of variables allowed for the investigation of the qualitative behaviour of metal concentrations, time horizons and target loads, independent of site conditions.

17. Mr. Tipping presented the dynamic modelling of soils and catchments. The simple dynamic model indicated that the time to reach steady-state depends on soil amount (layer depth, bulk density, active exchange sites), runoff and metal partitioning strength. Models could be constructed of increasing complexity and degree of integration based on the objective. Temporal responses of Ni, Zn and Cd were relatively fast and simple while responses of Cu, Pb and probably Hg were slower and more complex.

18. Mr. M. Meili (Sweden) presented the dynamic modelling of mercury in terrestrial forested and aquatic freshwater ecosystems in Sweden. Biogeochemical cycling of Hg is to large extent controlled by biological processes. Hg levels have not changed significantly during past 30 years. The further reductions of the emissions below 2000 levels would be needed to prevent further increase in fish Hg concentrations.

B. Steady-state critical load methods

1. Emission and deposition of metals

19. The workshop noted there were uncertainties in emission and deposition scenarios for use in effects assessment. It recommended:

(a) Improving the emission inventories needed to model deposition;

(b) Enhancing dialogue between emissions inventory and deposition modeller communities;

(c) Noting that the spatial resolution of the EMEP model in 50 km × 50 km grid could underestimate local deposition, and considering possibilities to incorporate an improved atmospheric dispersion model;

(d) Harmonizing methodologies of deposition measurements.

20. The workshop discussed the need to include speciation in deposition and recommended to:

(a) Including speciation once the metal (Cd, Pb, Hg) was deposited in the soil;

(b) Dividing the deposited metal between fractions that were extractable in concentrated and dilute acid, as a complete speciation was not deemed practical.

21. The workshop noted the need to have more measurements of reactive mercury (Hg(II)) to estimate deposition load.

22. The workshop recommended adding a section on heavy metal deposition in the *Modelling and Mapping Manual* to provide detailed information for the national focal centres.

2. Metal partitioning and transfer functions

23. The workshop noted the need for more measurements of Hg in soils other than podzols to validate the relationship between solid and solution phase. A detailed report will be made available separately.

24. Concerning the methyl Hg, the workshop recommended:

(a) Improving databases relating fish Hg levels to water chemistry and other environmental variables, in order to validate the empirical relationships for aquatic systems outside the Nordic area or conditions;

(b) Assessing ecotoxicological effects (e.g. on fish-eating birds and mammals) in addition to impacts on human health.

3. Interpretation of critical load and exceedance maps

25. Critical load exceedance maps have been produced based on simple mass balance methods. These proved useful in giving an indication of potential risk. For enhanced policy evaluation, information on current exceedance of critical limits and dynamics was also needed. For example, it was possible that maps showed large areas of critical load exceedance, whilst there was almost no area with exceedance of critical limits by current soil concentrations. It was therefore important to calculate current exceedance of critical limits and to apply dynamic methods as soon as possible.

26. The workshop recommended applying, in addition to critical load exceedance, dynamic models and current exceedance of critical limits for further policy evaluation.

27. Based on information from critical load mapping, the direction of the trends could also be mapped ("category maps"). These would show whether the receptors were safe or not, at present and in future.

28. The workshop noted the problems of applying steady-state methods in Mediterranean areas where runoff was very low. ICP Modelling and Mapping was to be informed on the experiences of applying steady-state methods in different regions.

C. Methods for critical limits

1. Human health

29. Current methods for critical limits related to crop uptake of metals did not account for bioavailability effects on uptake. Data and models existed on the uptake of cadmium by ryegrass and wheat, including bioavailability considerations. The workshop recommended that biouptake mechanisms be more explicitly considered in deriving critical limits for metal contents in crops, where possible.

30. Direct deposition of metal to plant surfaces should be considered as a process determining food concentrations. This could be the dominant uptake mechanism for Pb. The workshop recommended considering in models the direct deposition from the atmosphere on Pb and Hg to crops, including the resuspension of soil particles.

31. Cattle and sheep ingest soil, but the degree of transfer of ingested metals to flesh and milk is unclear. Specific organs, e.g. the liver, might accumulate relatively high concentrations of metals. Information available was deemed rather scarce. The workshop recommended:

(a) Reviewing information on the accumulation of metals in farmed animal tissues (included specific organs) and milk, available in the recent report of Convention's Joint Task

Force on the Health Effects of Air Pollution (Task Force on Health) and reports on risk assessment of the European Union (EU);

(b) Considering the relative risks of metal ingestion by humans in food, in addition to risks due to other exposure pathways.

32. The workshop noted that the current model of Hg accumulation in fish was calibrated with data from Nordic countries. The workshop recommended:

(a) Testing the model for Hg accumulation in fish outside its current geographical range, with possible recalibration to expand its range of applicability;

(b) Considering the report of Task Force on Health on Hg exposure pathways.

2. Ecotoxicology

33. The EU risk assessment reports for Cd and Pb indicated high concentrations of metals in higher animals (e.g. mammals and birds), indicating potential effects. This might be more important than direct effects to plants, invertebrates and biota. The workshop recommended:

(a) Reviewing knowledge on secondary poisoning of higher animals;

(b) Considering whether methods for calculating critical limits for this endpoint could be proposed.

34. The workshop noted the possibility that risks due to metal mixtures were not being considered using the existing approach. A method for assessing mixture risks for ecological effects had been proposed using current data. There should be an emphasis on mixture effects at metal concentrations close to thresholds for individual metal effects. The workshop recommended:

(a) Continuing assessing mixture effects in ecologically relevant laboratory tests;

(b) Reviewing interactive effects of metals at concentrations around their effects thresholds (critical limits and concentrations of no observed effects);

(c) Assessing whether effects might significantly increase risks due to mixture exposure.

35. The workshop recommended that, where possible, variations be considered in the sensitivity of the natural environment in setting critical limits. In addition to bioavailability, the organisms in sensitive environments (e.g. very soft waters) might be physiologically adapted in ways that influenced their sensitivity to metal stress. The workshop recommended that data on responses of relevant organisms in sensitive environments be used, where available, to derive the critical limits relevant to such environments.

3. Critical limit function

36. Critical limits for soils and waters (ecological effects) were currently derived by different methods. Specifically no or incomplete account was taken of bioavailability in the aquatic critical limits. The use of common critical limits for Cd and Pb in soils and waters had been previously proposed, but was not currently used.

37. Organisms in waters might also be exposed to metals via their diet. Little information was currently available on the significance of this exposure pathway.

38. The workshop noted that no account was currently taken of exposure of sedimentary organisms to metals. Under steady state, concentrations of sediment metals might exceed current limits given in EU risk assessment reports.

39. The workshop recommended:

(a) Reviewing the relative sensitivities of soil and aquatic species to metals, and reconsidering the 2004 proposal to use common critical limit functions for Cd and Pb;
(b) Monitoring scientific literature for ecologically relevant studies on dietary exposure of aquatic organisms;
(c) Considering whether models can be developed to account for dietary exposure;
(d) Calculating concentrations of metals in lake sediments under steady-state conditions at the aquatic critical limit, and comparing these with current sediment limit values given in EU risk assessment reports.

40. There were a small numbers of technical issues on current critical limit functions. A new data set on copper had allowed some of these assumptions to be tested. The workshop recommended that:

(a) Effects of aging in toxicity tests be considered where possible, in estimating free ion from added metal;
(b) Protective effects of ions, in addition to protons (H^+), be evaluated when relevant data becomes available, and the model should be updated if necessary;
(c) Transfer functions to relate geochemically active metal to free ion be based on as high levels of metal concentrations as possible;
(d) Current transfer functions be tested against data on spiked soils, if data were available, and updated if necessary;
(e) Side-effects of high ionic strength on organisms in toxicity tests be considered for Pb.

D. Dynamic modelling

1. Important processes

41. The workshop considered that a systematic evaluation was needed to examine the influence of a changing environment on metal fluxes, biouptake and toxicity, including changes in:

(a) Heavy metal deposition (load and speciation);
(b) Other atmospheric pollutants (deposition of sulphur and nitrogen) and resulting changes in pH, plant growth and other relevant factors;
(c) Climate (runoff and temperature) and resulting changes in quantity and quality of solid and dissolved organic matter in soils, partial pressure of carbon dioxide (pCO2), pH and other parameters;
(d) Land use (biouptake and harvesting) and resulting changes in quantity and quality of solid and dissolved organic matter in soils, pH and other parameters.

42. The workshop recommended further systematic evaluation of key processes and factors on metal fluxes and biouptake/toxicity, including:

(a) Metal partitioning and its short-term kinetics in soils, in particular ageing (immobilization) in comparison with weathering (mobilization), influence of solution speciation and added as opposed to natural fractions of metals;
(b) Long-term ageing (sequestration as a potentially infinite sink) as opposed to weathering (natural input), both of which were connected to soil formation;
(c) Speciation of metal input in the deposition, divided to reactive and weatherable fractions, and the speciation of metal output through leaching with only a reactive fraction;
(d) Biotic turnover rates and retention times of metals.

2. Model complexity and geographical scale

43. The workshop recommended that the simple dynamic models be used for mapping at the national and European scales. Intermediately complex models were deemed fit for scenario analyses. Complex models were recommended for validation of process studies at the catchment scale.

3. Outputs of dynamic models

44. The workshop recommended preparing maps showing the time to reach a certain state, in particular near the steady state, approaching from either below or above the critical limits. The maps should also include grid percentile information.

45. The workshop noted that tentative target loads could also be computed and mapped.

46. The workshop recommended preparing maps for various deposition scenarios. These should include the depositions based on current load (“best estimate”) and the critical load.

47. The operational definition for a “steady state” (i.e. the tolerated deviation from a mathematical value) was agreed to tentatively be 10%. Comparisons should be made with alternative tolerances, derived from sensitivity analyses, and/or related to the uncertainty of critical limits.

48. The workshop recommended starting systematic mapping of the present state of contamination. It further recommended compiling and harmonizing national databases on ecosystem contamination into an international database for mapping current spatial patterns and for model validation.
