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**ECONOMIC COMMISSION FOR EUROPE**

**EXECUTIVE BODY FOR THE CONVENTION ON  
LONG-RANGE TRANSBOUNDARY AIR POLLUTION**

Working Group on Effects  
(Twenty-second session, Geneva, 3-5 September 2003)  
Item 4 (f) of the provisional agenda

**DEVELOPING, MODELLING AND MAPPING OF CRITICAL LOADS**  
Addendum

**PROGRESS IN THE DEVELOPMENT OF  
HEAVY METALS CRITICAL LOADS METHODOLOGY <sup>1/</sup>**

**I. INTRODUCTION**

1. Pursuant to the conclusions and recommendations of the ad hoc meeting of an international expert group on effect-based critical limits for heavy metals, held on 11–13 October 2000 in Bratislava, and in line with the decisions of the Working Group on Effects, taken at its twentieth session, to further develop relevant methodologies, a follow-up expert meeting was organized in 2002.
2. The meeting took place from 2 to 4 December 2002 in Berlin. It was hosted by the German Federal Environment Agency and sponsored by the German Ministry of the Environment,

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<sup>1/</sup> Progress report summarizing the results of the expert meeting on critical limits for heavy metals and methodologies for their application (December 2002, Berlin) and the subsequent meeting of the editorial group for the proceedings of the expert meeting (April 2003, Paris), prepared by the organizers.

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Nature Conservation and Nuclear Safety. It was attended by 39 experts from the following Parties to the Convention: Austria, Belgium, Czech Republic, Finland, France, Germany, Italy, Netherlands, Poland, Russian Federation, Slovakia, Spain, Sweden, Switzerland, Ukraine, and the United Kingdom. The Bureau of the Working Group on Effects, the International Cooperative Programmes (ICPs) on Forests, Modelling and Mapping, on Vegetation and Waters, the Task Force on the Health Aspects of Air Pollution, and the Coordination Center for Effects (CCE) were represented.

3. The meeting was chaired by Ms. Gudrun Schuetze (Germany), the organizer of the meetings of the expert groups on critical limits for heavy metals under ICP Modelling and Mapping.

4. Taking into account the medium-term work-plan of the Working Group on Effects (EB.AIR/WG.1/2002/4), the main objectives of the meeting were to agree on operational approaches and to provide the scientific basis for a future review and possibly effect-based revision of the 1998 Protocol on Heavy Metals. Therefore, experts in biology or toxicology as well as experts in chemistry and/or modelling, but also were invited and attended the meeting.

## II. AIMS AND ORGANIZATION OF THE WORKSHOP

5. The results of the first, preliminary European mapping exercise on critical loads for cadmium and lead (EB.AIR/WG.1/2002/13) had been discussed indepth at the twelfth CCE workshop, held back to back with the eighteenth meeting of the Task Force of ICP Modelling and Mapping (April 2002, Sorrento, Italy), and a list of conclusions and recommendations for further work was agreed. This list served as the guideline for the work on critical limits and transfer functions for heavy metals until the expert meeting in December 2002, which was structured to address the most important tasks:

- (a) Review of the harmonized set of critical limits for heavy metals for soils and waters, with the inclusion of limits for Hg and of human health effects being the most important;
- (b) Further development of transfer functions of Pb, Cd and Hg for soils and sediments, with an emphasis on their applicability to the broad spectrum of European soils;
- (c) General methodological aspects, including:
  - Choice of approaches (critical loads model versus stand-still model) according to the "decision tree", proposed in Sorrento (2002);
  - Identification and Europe-wide mapping of present heavy metal pollution of soils (Pb, Cd, Hg) and its sources;
  - Methods to consider heavy metal inputs to soils and surface waters other than atmospheric pollution;
  - Specific features and applicability of an effect-based approach for Hg.

6. The meeting was organized in three plenary sessions and working group discussions. The three main tasks mentioned in paragraph 5 above were also the themes of draft background documents which outlined the scope of the three working groups and were circulated before the meeting.

7. The working groups were chaired by the first authors of the background papers:
- (a) De Vries et al. (2002): Critical limits for cadmium (Cd), lead (Pb) and mercury (Hg) related to ecotoxicological effects on soil organisms, aquatic organisms, plants, animals and humans;
  - (b) Groenenberg et al. (2002): Transfer functions for the calculation of critical loads of Pb, Cd and Hg;
  - (c) Farret et al. (2002): Background paper on general methodology.
8. For each of these items a list of the most relevant questions was prepared. In addition, several background papers concerning critical limits and effects-based methods for Hg, presented at different levels of complexity, were provided.

### III. CONCLUSIONS AND RECOMMENDATIONS

9. Some general conclusions related to questions given to all discussion groups were drawn:
- (a) The methods were designed to be scientifically sound, while producing a result which could be used in integrated assessment modelling (IAM);
  - (b) The critical loads mass balance equations for Pb and Cd, as well as the scheme of the decision tree, were ready for inclusion into a revised Mapping Manual;
  - (c) A complete model for human exposure pathways was not needed in the critical load methodology, since using food quality criteria was a good alternative. Specific tasks concerning this aspect could be undertaken within the further work of the ad hoc expert group on critical limits.

#### Critical limits

10. There were clear, targeted suggestions to improve critical limits related to direct ecotoxicological effects.
11. For soils it was assumed that most or nearly all eco-toxicological data were related to soil solution effects. Critical limits for free and total metal (Cd, Pb and Hg) concentrations in soil solution have to be derived as a function of pH and dissolved organic carbon (DOC). This implies applying transfer functions on 'no observed effect concentration' (NOEC) soil data.
12. For surface waters it was questionable whether (total) concentrations could be related to effects on aquatic organisms without accounting for environmental chemistry. An applicable approach could be to look for pH, alkalinity and DOC to improve the relationships.
13. For Hg in surface waters the end point was human health, with content in fish as an indicator. Functions to relate levels in water to levels in fish were available for Sweden. They should be tested in other countries.

14. Hg in soils Crops were not so important for Hg intake by humans. In forest soils the end points were microbial processes. Preliminary transfer functions for Hg in forest soil relating solution concentration to soil concentration and dissolved organic matter (DOM) were available. Further elaboration may be needed.

15. Information would be provided to show how exposure limits relate to food quality criteria, including scientific background material (European Union data). In this context information would be given on the most recent exposure limits from the Task Force on the Health Aspects of Air Pollution. Food quality criteria could be back-calculated to critical limits in soils from Cd content in crops, and in waters from Hg in fish. Such a procedure was, however, not possible for Pb and Hg in soils (therefore possibilities for quantifying the direct uptake from the atmosphere should be checked). The pathway of Cd via wheat was the most important for human health. World Health Organization (WHO) drinking water limits, i.e.  $3 \mu\text{g l}^{-1}$  for Cd,  $10 \mu\text{g l}^{-1}$  for Pb and  $1 \mu\text{g l}^{-1}$  for Hg, could be considered in addition to lowering the critical concentrations in soil solution as far as necessary.

16. Indirect effects on soil-eating animals were possible for Cd, Pb, Hg but gave much higher results than critical limits for direct effects. Critical limits for Cd in soil were very low in view of the impacts on worm-eating birds, but considered too uncertain to apply in the critical load calculation.

17. Methods to consider the original (natural) concentrations of heavy metals in soils were independent from the setting of critical limits. It might be very difficult to derive those pedo-geogenic contents, in particular pedo-geogenic concentrations in soil solution.

#### Transfer functions

18. For Cd and Pb three data sets were recently used to derive transfer functions (Germany, Netherlands, United Kingdom). A more complete overview of the transfer functions proposed till now has to be finalized.

19. Differences in the extraction techniques used had to be considered. There was a recommendation to continue with both  $\text{NH}_4\text{NO}_3$  /  $\text{HNO}_3$  methods, but to put forward a scheme explaining which extraction method was the most appropriate for which purpose. Further work was necessary on transfer functions for humus layers and calcareous soils.

20. When considering the type of transfer function to use, it was recommended to relate adsorption constants to soil properties which could be used to calculate soluble metal concentrations from solid metal concentrations or vice versa. Transfer functions that took into account solution speciation were preferred.

21. There are no Hg transfer functions at present in Europe, but potential data sets could be derived from German, Slovak and Swedish data. Transfer functions for Hg analogous to those for other metals will be derived from the data from Sweden.

22. One possible way of decreasing uncertainty would be to derive transfer functions for groups of soils, rather than forcing one transfer function through the whole data set.
23. It was possible to take account of future changes in soil properties in determining steady state critical loads (such as increasing pH). Either the present value or a future expected value (at steady state) should be used.

#### General methodological aspects

24. Policy may ultimately require knowledge of the time scales involved. Currently, science was being improved to enable the assessment of critical loads on a European scale. Maps of critical loads could be used in a future stage as a basis for assessing exceedances, i.e. quantifying damage and recovery time delays using dynamic modelling.
25. A decision tree, which was provided in annex III to the minutes of the meeting indicated the different tasks, which were to be undertaken in a continuum:  
National Focal Centre (NFC) → CCE → IAM.  
The determination of critical limits as well as the computation and mapping of critical loads, including the consideration of dominant natural input, were fully within the scope of this expert group and ICP Modelling and Mapping.
26. The decision tree provided information on how to deal with the differentiation between the pedo-geogenic and anthropogenic shares of the heavy metal content in soils. Historical inputs affected future damage and recovery time delays. These helped to explain the origin of the problem in particular to the public, industry and policy analysts. They were also important as input to dynamic modelling.
27. The current work-plan focused on the assessment of critical loads for possible use in IAM. Stand-still loads, which were not a branch in the decision tree, could become part of a future stage involving dynamic modelling.
28. A critical load for human health was feasible (relevant to agricultural ecosystems as well as aquatic ecosystems). Separate critical load calculations would be done for each receptor (ecosystems, human health). Integrated assessment modellers should be able to differentiate between human health and environmental end points for policy support.
29. The end points to assess Hg impacts were human health, top predators in (water-) ecosystem, and decomposers in forest top-soils. The Simple Mass Balance method could be applied. Also models with an increasing level of complexity could be explored.
30. The critical loads methodology should take into account humus layers/humic soils, but more work was needed.
31. To calculate exceedances of critical loads by actual loads in agricultural ecosystems, methods to quantify non-atmospheric inputs (at least fertilizers) were required. Geological releases

(natural inputs) were already considered in the critical loads.

#### Reporting the outcome of the meeting

32. More detailed information on the scientific contributions to the expert meeting (December 2002, Berlin) concerning critical limits, transfer functions and their use in critical loads models for Pb, Cd and Hg, as well as the conclusions and recommendations, were provided in the minutes of the meeting and in the proceedings. These documents can be found on the web page of ICP Modelling and Mapping (<http://www.icpmapping.org>).

#### IV. FUTURE WORK, BASED ON THE RECOMMENDATIONS OF THE EXPERT MEETING IN BERLIN AND UPDATED BY THE RESULTS OF THE EDITORIAL MEETING IN PARIS

33. It was not possible to reflect all the new information addressing critical limits and transfer functions in the revised background papers of the expert meeting in Berlin. The experts would make full use of the new knowledge in their further activities.

34. Five data sets on effects were available, which were intended to be lumped together and used to calculate critical limits related to free ion activities. If this approach worked then, in the future, the use of transfer functions would be limited mainly to deriving critical limits. Therefore, the need to consider the full range of European soil types was no longer so important. The methodology for Hg had to be discussed more in depth in 2003 to come up with some proposals for the relevant chapter in the Mapping Manual before spring 2004. Uncertainties of critical loads for Pb, Cd and Hg should be estimated. The recommended minor changes in wording within the decision tree should be made.

35. The Task Force on ICP Modelling and Mapping at its nineteenth meeting (22 – 23 May 2003, Tartu, Estonia) confirmed the definition of critical loads of heavy metals to be related to total anthropogenic inputs (Guidance 2001), and requested the Working Group on Effects to consider, keeping in mind the implications of this definition, how fertilizer inputs might be addressed.

36. The activities of the experts on critical limits and transfer functions should be united to only one expert panel on critical loads of heavy metals under ICP Modelling and Mapping and Modelling, which would also address general methodological aspects.

37. The draft chapter on critical loads for heavy metals of the revised Mapping Manual should be produced only when the development of new methods according to the recommendations of the meeting in Berlin was finished. It was recommended: (i) to inform NFCs on the status of the methods and the developments at the nineteen meeting of the Task Force of ICP Modelling and Mapping; and (ii) to distribute to them by October 2003 a detailed draft chapter of the Manual to enable them to test the revised methods.

38. A follow-up workshop to the expert meeting in Berlin on critical loads for heavy metals

was scheduled for early spring 2004. The goal would be to reach agreement on methods to be recommended to the Task Force on ICP Modelling and Mapping at its twentieth meeting, and, with its approval, to the Working Group on Effects. The results of test calculations based on the revised methods (work in kind) including documentation on methods and databases used, should be circulated among NFCs and made widely available in 2004 (preferably before the workshop).

39. Summarizing time-table:

May 2003	Publish the proceedings of the expert meeting in Berlin in 2002, report to the Task Force of ICP Modelling and Mapping at its nineteenth meeting, 22–23 May 2003, Tartu, Estonia;
Summer 2003	Further develop of critical limits and transfer functions of Pb, Cd and Hg, according to the results of the expert meeting in Berlin;
September-October 2003	Draft peer-reviewed scientific articles, distribute draft manual chapter to NFCs based on the revised methodology;
November 2003-January 2004	Test the revised methodology by the expert group and by interested NFCs, circulation of results;
Spring 2004	Workshop (planned) to agree on the revised methodologies for Pb, Cd (and perhaps also Hg), recommendation for adoption by the Task Force of ICP Modelling and Mapping;
Autumn 2004	Call by CCE for data on critical loads for Cd and Pb (perhaps Hg);
Spring 2005	Potentially applicable products for the work under the Convention, in the form of maps of critical loads of heavy metals.