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CATCHMENT BUDGETS AND CRITICAL LOADS OF HEAVY METALS AT ICP INTEGRATED MONITORING SITES

Report prepared by the International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP Integrated Monitoring)

INTRODUCTION

1. Heavy metal loads exceeding critical values can be hazardous to ecosystems. Impacts may occur in terrestrial and freshwater systems exposed to leaching. In the soil, microorganisms and soil fauna (e.g. nematodes and earthworms) can be influenced by heavy metals. Present levels of heavy metals were estimated to be high enough to cause damage at 5–25% of European sites (Rademacher 2001). Effects can also occur on vegetation (root damage being one example). Heavy metals can be leached to surface waters, where freshwater organisms, in particular fish, may reach elevated content levels. Secondary effects on human health can arise, especially via consumption of fish with high mercury content.

2. Metals have accumulated in soils and catchments over long time periods. The accumulation has resulted in unnaturally high concentration levels at many sites. At such sites, the elevated concentrations could exert negative influences. This would eventually lead to deterioration of the biological system and of conditions for surface waters and limnic life.

3. Studies on heavy metals in ecosystems (including work within ICP Integrated Monitoring) have increased the understanding of relevant processes and provided data for modelling and calculating critical levels and loads. Cadmium (Cd), lead (Pb) and mercury (Hg) were identified as being of priority concern in the 1998 Protocol on Heavy Metals. Currently no extensive and long-term monitoring exists for Hg.

4. Studies on effects require the availability of data on pollutant loads. Deposition calculations made by EMEP indicated relative changes for the period 1980–2000 (EMEP 2004), when emissions of Cd, Pb and Hg decreased substantially. The reductions in deposition were 80% for Pb and 70% for Cd but only 30% for Hg. Site-specific values for the sites in this study were calculated from measured bulk deposition, throughfall and litterfall.

5. The integrated monitoring approach comprises identifying concentrations in several ecosystem compartments, fluxes between the compartments, pools, budgets and critical load calculations. Comparisons between the last two items can confirm the mass balance models for critical loads, although all sites deviated from the steady-state conditions postulated for critical load, due to the ongoing accumulation. This report studied total deposition of Cd, Hg and Pb to forests and input/output balances for catchments. Deposition was compared with calculated critical loads for some sites (Bringmark et al. 2006).

I. METHODS

6. The catchment-wide approach, with controlled input and output, was considered most suitable for studying heavy metal pools, fluxes and critical loads. Input was derived from direct atmospheric deposition (bulk deposition, BD), throughfall (TF) and litterfall (LF). In some cases litterfall included internally circulated elements.

7. ICP Integrated Monitoring provided data for fifteen sites for selected years between 1996 and 2003. The sites were located in eight countries: Austria (1 site), Czech Republic (2), Finland (2), Germany (1), Latvia (2), Lithuania (2), Sweden (4) and United Kingdom (1). Forests dominated the land cover to varying extents. One site (GB 01) was mainly covered by shrubs and grass (table 1).

Table 1. Description of ICP Integrated Monitoring sites included in this study. Country codes are AT: Austria, CZ: Czech Republic, DE: Germany, FI: Finland, GB: United Kingdom, LT: Lithuania, LV: Latvia and SE: Sweden. Land cover denotes the simplified forest type, T the long-term annual mean temperature and P the long-term annual mean precipitation.

Site	Land cover	Area (km^2)	Altitude (m)	T (^oC)	P (mm)
AT01	Mixed mountain forest, beech dominated	0.90	550–950	+7	1 650
CZ01	Forest 91%, coniferous dominated	2.68	464–633	+7	621
CZ02	Spruce: 70% over 20 years, 30% younger	0.27	829–949	+5	953
DE01	Mixed mountain forest 65%	0.69	787–1250	+5	1 300
FI01	Forest 66%, spruce dominated	0.30	150–190	+3	618
FI03	Forest, pine dominated	4.64	165–214	+2	592
GB01	Heather and fescue grassland	9.98	225–1111	+6	1 000
LV01	Mixed forest (pine, birch, spruce)	6.65	6–16	+6	772
LV02	Mixed mesic coniferous forest	0.27	184–192	+5	727
LT01	Coniferous forest (pine, spruce)	1.02	159–189	+6	682
LT03	Coniferous forest (pine, spruce)	1.47	147–180	+6	788
SE04	Mixed mesic coniferous forest	0.04	114–140	+7	1 143
SE14	Mixed mesic coniferous forest	0.20	210–240	+6	712
SE15	Mesic coniferous forest, spruce dominated	0.20	312–415	+4	900
SE16	Spruce and pine forests	0.45	410–545	+1	750

8. Site conditions were varied: sorted sediments on sedimentary bedrock, morainic landscapes on igneous bedrock, peatland and lakes. Mineral soils dominated in general, but in Finland and the United Kingdom there were mainly peaty soils. The underlying bedrock was mainly granite. Especially in Austria, the dolomite and limestone furnished karstic conditions with complicated water flows. Appropriate water runoff was calculated with observed hydrological balances from a catchment area extending beyond the original site.

II. RESULTS AND DISCUSSION

A. Metal deposition to forests

9. Heavy metals stored in soils are related to high pollutant loads of previous decades. The deposition of Pb in 2000 as estimated by EMEP was 0.5–1 mg m^{-2} in large parts of Europe, with peaks of 5 mg m^{-2} in some parts of Central Europe (EMEP 2004). This corresponded to the bulk deposition measured at the sites.

10. The general range of deposition in 2000 was 0.01–0.025 mg m^{-2} for Cd and 0.02–0.03 for Hg, as estimated by EMEP. In some regions both depositions peaked at 0.15 mg m^{-2}. Bulk deposition measured at the sites in the last decade, at least for Cd, was comparable with the

highest regional levels estimated by EMEP. Only a few case studies were available for Hg (figure 1).

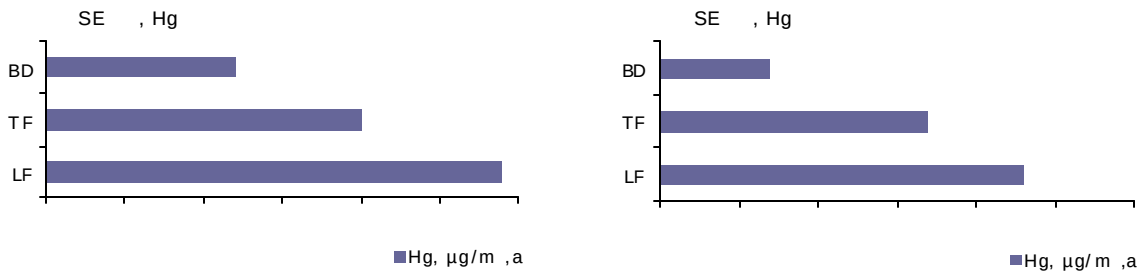

Figure 1. Input of mercury (Hg) at two Swedish sites (SE04 and SE14) by bulk deposition (BD), throughfall (TF) and litterfall (LF)

11. A large part of metal TF in forests was in the form of particles scavenged by tree canopies, with subsequent deposition to the forest floor. The downward transfer was water-borne in the throughfall and associated with organic material in LF. Hg was to a large degree associated with litterfall. The LF-TF ratio was 1.4 at the southern site (SE14) and 1.1 at the northern site (SE16) in Sweden. The amount of litterfall was low in the sparse tree stand of the northern site (figure 5), which affects the amount of the metal flux. Hg input by both LF and TF was substantially larger than BD, demonstrating the impact of canopy interception.

12. Deposition of Cd and Pb under the canopy (TF) was not always increased compared to BD. But, when available, adding LF to TF gave estimated flows beneath canopies that were always larger than BD. Litterfall was a substantial component of the flows. The LF-TF ratio was 0.6–1.0 for Pb and 0.8–1.2 for Cd. Cd is often considered to be more associated with the solution phase than Pb, but this was not shown for deposition in the stands. Cd is often considered to be more associated with the throughfall solution phase than Pb, and Pb is more combined to litterfall than Cd. However, these were not always shown by the LF-TF ratios in the site stands.

13. Forest density directly influenced litterfall. The tree species affected the amount of interception. Deciduous trees with autumn shedding of leaves yielded much lower annual total deposition to the soil than evergreen coniferous trees. This was observed for TF of beech and spruce at the Austrian site (AT01).

14. The dry deposition intercepted by forests can be assessed in various ways. At least for increased pollutant loads, TF+LF can be used as a rough estimate of total deposition. This assumes that tree uptake from the soil is negligible and no internal circulation occurs. However, this can leave to an overestimation. In this study TF+LF was used as a measure of total deposition, resulting in levels several times higher than BD, in the case of Hg up to five times (figure 1). Total deposition loads lead to the build-up of stores in the soil and possible soil

microbial effects, and thus are relevant for critical load estimates. LF could only be reported for a few sites, therefore, in most cases TF or BD was used as a measure of input.

B. Catchment output – metals in streamflow

15. Element runoffs are highly dependent on discharge amounts. Annual catchment discharges can vary widely. Mountain sites subject to high precipitation and low evapotranspiration had discharges of 800–1,200 mm (AT01, DE01 and GB01). Low-altitude sites in Eastern Europe with rather low precipitation and fairly high evapotranspiration had streamwater discharges of only 50–200 mm. All Swedish sites and the Czech highland site (CZ02) had annual waterflows of 280–520 mm.

16. The general range of streamwater flows for Pb was 0.04–0.3 mg m^{-2}. High values were encountered in Scandinavia, where soils are shallow. Two exceptional sites (CZ02 and DE01) had much higher flows. In continental Europe very low stream transports of Pb were found for different sites irrespective of whether water discharge was low or high. For example, AT01 had alkaline soils with a discharge of about 1,200 mm, and CZ01 had a discharge of only 56 mm, but both had low Pb runoff. Alkaline soils were especially effective in immobilizing metals, and organic matter could act in a similar way. Pb retention remained at 1–17% of TF during the study period, although deposition loads were substantially decreased.

17. The two sites with high outflows of Pb (CZ02 and DE01) were both located in the highlands at the Czech-German border. Stream transports of Pb were higher than or equal to TF. The sum of LF and TF was larger than output even at the German site (DE01) (figure 2). The metal pollution had been intense at high altitudes of the two highland sites. Pb outflows at Swedish and Finnish sites were considerably lower than calculated input as TF or TF+LF (figure 3).

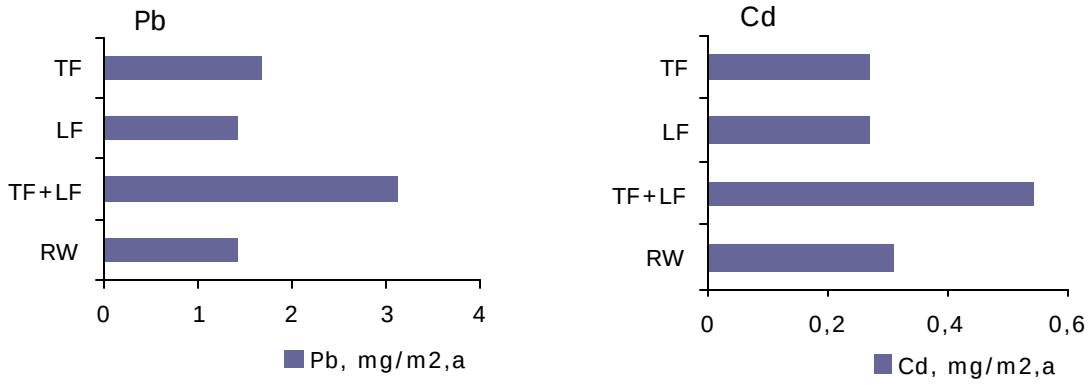

Figure 2. Lead (Pb) and cadmium (Cd) input and output for the German site (DE01), including throughfall (TF), litterfall (LF) and runoff (RW)

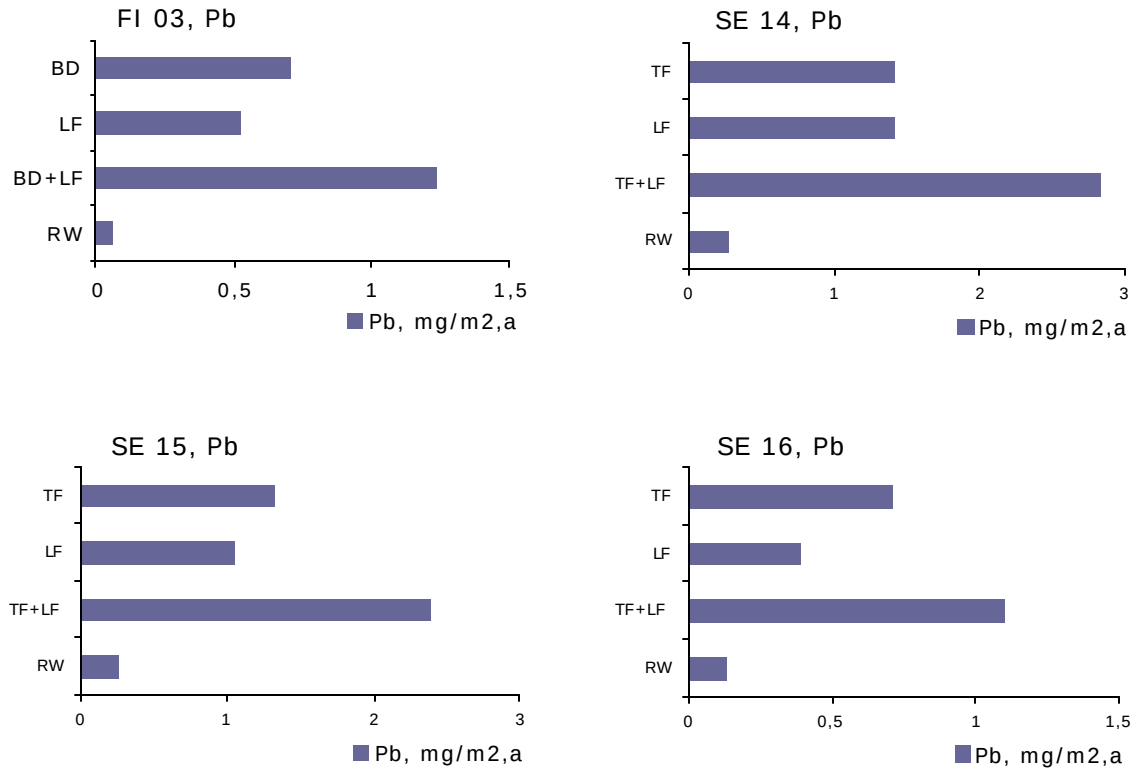

Figure 3. Lead (Pb) input and output for one Finnish site (FI03) (note BD instead of TF) and for three Swedish sites (SE14, SE15 and SE16), including throughfall (TF), litterfall (LF) and runoff (RW)

18. Cd is considered more mobile than Pb in soils. Cd is occurring more in the soil solution phase than Pb and is influenced by cation exchange. Pb is mainly incorporated in organic molecules and is not easily transported The range of Cd flows at eight sites was 0.005–0.02 mg m^{-2} $year^{-1}$, irrespective of large differences in water discharge. From three Swedish sites the outflow of Cd was 5–30% of input by TF (figure 4). Events of large water discharges were probably decisive for Cd outflows. This was also relevant for mountain sites, such as CZ02 and AT01. One Swedish site (SE15) had large Cd discharge at low organic content of the solution (figure 4).

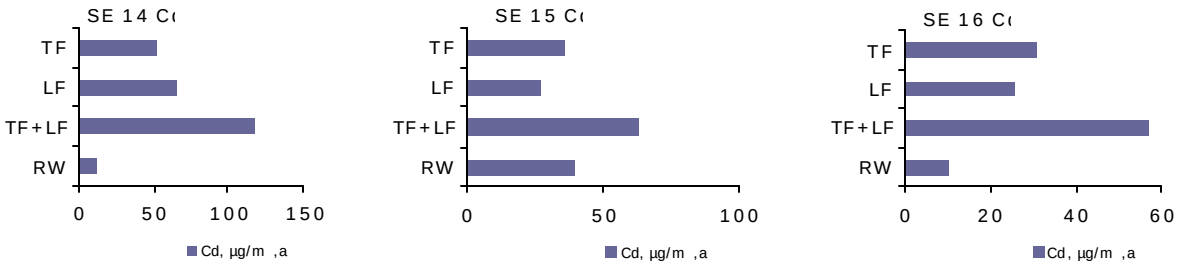

Figure 4. Cadmium (Cd) input and output for three Swedish sites (SE14, SE15 and SE16), including throughfall (TF), litterfall (LF) and runoff (RW)

19. Hg was considered to be strongly bound to organic material in soils, and its transport was controlled by movement of organic material. Transport in the Swedish streams studied was in the range of 0.001–0.003 mg m^{-2} $year^{-1}$ and retention was 4–19% of total input (figure 5). Hg deposition was still elevated and possibly led to further accumulation.

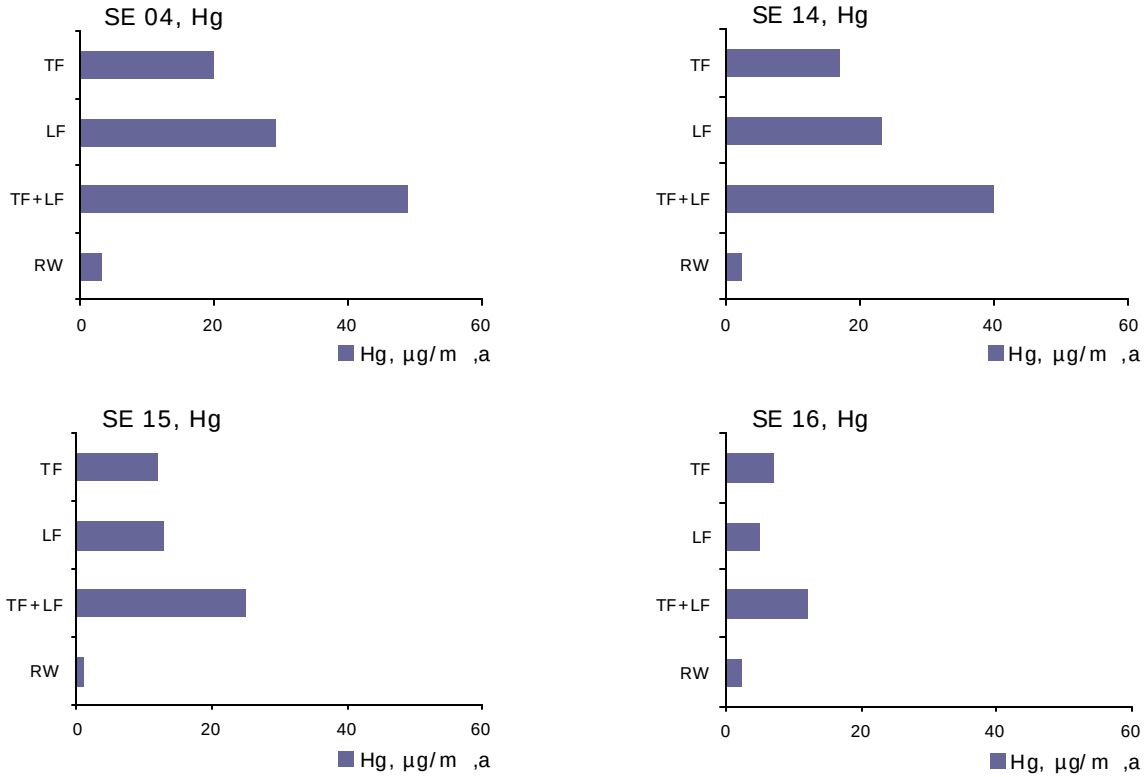

Figure 5. Mercury (Hg) input and output for four Swedish catchments (SE04, SE14, SE15 and SE16), including throughfall (TF), litterfall (LF) and runoff (RW)

C. Calculation of critical loads

20. The critical load is a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur, according to present knowledge. A methodology for deriving critical loads of Pb, Cd and Hg has been developed within the Convention. The method is described in the Convention's *Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads and Levels and Air Pollution Effects, Risks and Trends* and has been used for Europe-wide mapping (Slootweg et al. 2005).

21. The calculations of critical loads for Cd and Pb with a soil biological endpoint for harmful effects required data on content of soil organic matter, pH, dissolved organic carbon (DOC) and annual waterflow. Some other parameters needed for the calculations were given general values valid for all sites. Critical loads of Hg required data only on DOC and waterflow.

22. Total deposition (TF+LF) at four Swedish sites exceeded calculated critical loads for Hg (figure 5 and table 2). For Pb the E-horizon was at risk, while the organic layer appeared safe. Cd deposition was below the critical load.

Table 2. Critical loads for two soil layers at three Swedish sites

Site, layer	Cd mg m^{-2} $year^{-1}$	Pb mg m^{-2} $year^{-1}$	Hg mg m^{-2} $year^{-1}$
SE14 humus layer	0.8	5	0.016
SE14 E-horizon	0.6	1.6	
SE15 humus layer	1.0	4	0.006
SE15 E-horizon	0.9	2.0	
SE16 humus layer	1.4	8	0.013
SE16 E-horizon	1.0	1.0	

III. CONCLUSIONS

23. Positive balances between input and output flows showed that accumulation of heavy metals was still ongoing in spite of decreasing deposition loads, indicating the necessity for continued monitoring. The observed depositions at sites were higher than those estimated by EMEP; thus the accumulation may in general be higher than that estimated earlier. Site-specific input included dry deposition, captured by combined litterfall and throughfall measurements, which gave different values than the EMEP model.

24. ICP Integrated Monitoring provides data for a comprehensive ecosystem assessment. Not only chemical compounds but also biological effects need to be considered in future evaluations. Heavy metal translocations within the terrestrial system should be investigated, as should leaching to surface water outflow. In the surface waters, further observations should follow the biological consequences, including effects on human health. Critical load concepts for heavy metals should be tested by biological assessments.

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