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**HEAVY METAL AND NITROGEN STUDIES  
AT ICP INTEGRATED MONITORING SITES**

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

1. Estimating fluxes, pools and critical thresholds of both heavy metals and nitrogen compounds has been a priority within the ICP Integrated Monitoring. The integrated monitoring approach, where samples are taken in different ecosystem compartments, gives a good basis for such work, which is carried out both in international projects and by combining and assessing information from detailed national studies.

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## I. HEAVY METALS

2. Metals have accumulated in soils over long time periods and unnaturally high levels exist at many sites. The elevated metal concentrations might have a direct influence on the local soil but could also be transported to other locations and eventually be leached to surface waters. Existing conditions and ongoing processes need to be followed. In such investigations, the catchment approach, such as in the ICP Integrated Monitoring programme, is most suitable. The detailed monitoring of compartments in the element budgets provides complete coverage. The budget compartments include atmospheric input by wet and dry deposition, accumulation and transport in the soil from surface organic layers to deeper mineral soils and groundwater along the pathways from upslope recharge to downslope discharge areas and surface water formation. Monitoring all these compartments and flows makes it possible to identify crucial processes. Priority is given to the three heavy metals cadmium (Cd), mercury (Hg) and lead (Pb), currently covered by the 1999 Protocol on Heavy Metals.

3. During 2003/04 work on methods for critical loads of Pb, Cd and Hg has been completed by ICP Modelling and Mapping with participation from ICP Integrated Monitoring. This is a major task for monitoring and assessment under the Convention. ICP Integrated Monitoring could contribute to the credibility of mass balance models by applying them to selected ICP Integrated Monitoring sites. Some results from Swedish studies, on which methods have been tested, are presented below. The aim is to extend such work to a larger number of ICP Integrated Monitoring sites during 2004.

### A. Mass balances for lead, cadmium and mercury at Swedish ICP Integrated Monitoring sites

4. Mass balance calculations from ICP Integrated Monitoring sites have previously been reported in several studies (Aastrup et al., 1995; Munthe et al., 1998; Ukonmaanaho et al., 2001). In the ICP Integrated Monitoring studies, the sum of litterfall (LF) and throughfall (TF) is taken as an approximate measure of total deposition to forest stands. The particulate dry deposition effectively caught in tree canopies is added to throughfall and to litterfall. Internal circulation is neglected, an assumption that could be disputed. Input of Pb analysed from three Swedish ICP Integrated Monitoring catchments clearly exceeds output flux in run-off water (RW) (see  $RW / (LF + TF)$  ratios in table 1). Even throughfall alone exceeds run-off transport for Pb. A comparison of output with the fairly mobile store that has been accumulating in the humus layer (O) (see  $RW / O$  ratio in table 1) shows that recovery is a matter of centuries on the catchment scale, even if a portion of the store is natural background. Humus layers would improve faster than catchments and negative mass balances of those layers are now observed in some investigations.

5. Also cadmium, considered more mobile than Pb, shows retention in most catchments. An almost balanced output/input ratio is evident for the Kindla site (table 2). However, Cd stores are also large compared to Cd output. Hg is effectively retained in most catchment sites to an even higher degree than Pb (table 3). Preliminary critical load calculations for Pb are presented in table 4.

**Table 1.** Stores, annual input and output of Pb at three Swedish ICP Integrated Monitoring sites during the 1990s and early 2000s (mg/m<sup>2</sup>)

	Aneboda	Kindla	Gammtratten
<u>Annual transport</u>			
Bulk deposition (BD)			
Throughfall (TF)	1.43	1.33	0.71
Litterfall (LF)	1.41	1.06	0.39
Run-off (RW)	0.27	0.26	0.13
<u>Stores</u>			
Humus layer (O)	680	680	15.5
Mineral soil 0 - 40 cm (M)	3480	2230	1890
<u>Ratios</u>			
RW / O	0.0004	0.0004	0.008
RW / (LF+TF)	0.095	0.11	0.13

**Table 2.** Stores, annual input and output of Cd at three Swedish ICP Integrated Monitoring sites during the late 1990s and early 2000s (mg/m<sup>2</sup>)

	Aneboda	Kindla	Gammtratten
<u>Annual transport</u>			
Throughfall (TF)	0.053	0.038	0.031
Litterfall (LF)	0.065	0.027	0.026
Run-off (RW)	0.012	0.054	0.010
<u>Stores</u>			
Humus layer (O)	3.8	4.6	1.8
Mineral soil 0 - 40 cm (M)		17	21
<u>Ratios</u>			
RW / O	0.003	0.012	0.006
RW / (LF+TF)	0.10	0.83	0.18

**Table 3.** Stores, annual input and output of Hg at four Swedish Integrated Monitoring sites during the later part of the 1990s and early 2000s (mg/m<sup>2</sup>)

	Gårdsjön	Aneboda	Kindla	Gammtratten
<u>Annual transport</u>				
Throughfall (TF)	0.020	0.017	0.012	0.007
Litterfall (LF)	0.026	0.023	0.013	0.005
Run-off (RW)	0.0034	0.0022	0.0010	0.002
<u>Stores</u>				
Humus layer (O)	2.2	2.3	2.1	0.7
Mineral soil 0 - 40 cm (M)	20	15	11	7.3
<u>Ratios</u>				
RW / O	0.0015	0.0010	0.0005	0.003
RW / (LF+TF)	0.074	0.055	0.040	0.19

**Table 4.** Critical Pb concentrations in mor layers of Swedish ICP Integrated Monitoring sites calculated according to the preliminary manual for critical loads. Comparison with present metal levels at the sites

Integrated Monitoring site	Pb solution	Pb total soil	Pb total soil
	(µg/l)	(µg/g)	(µg/g)
	critical	critical	present
Aneboda	4.7	25	81
Gårdsjön	3.3	30	35
Kindla	4.0	27	62
Gammtratten	2.6	34	44

## B. Conclusions from the heavy metal calculations

6. In spite of decreasing loads, accumulation is still going on and requires continued monitoring. For this important environmental work, the ICP Integrated Monitoring sites provide the possibility for complete ecosystem surveillance. Not only the chemical compounds but also the biological effects need to be monitored. Heavy metal terrestrial translocations should be investigated as well as leaching to surface water outflow. In the surface waters, further observations are needed to follow the biological consequences, including those influencing human health. Detailed mass balance calculations, such as those of ICP Integrated Monitoring, are also needed to develop and test the critical load concepts for heavy metals.

## II. NITROGEN PROCESSES AND C/N INTERACTIONS

7. In recent years, ICP Integrated Monitoring data have been used in several studies to quantify various aspects related to effects and critical thresholds of nitrogen (N). A critical

deposition threshold of about 8-10 kg N ha<sup>-1</sup> year<sup>-1</sup>, indicated by several previous assessments, was confirmed by the input-output calculations with the ICP Integrated Monitoring data (Forsius et al. 2001). Soil organic horizon C/N-ratios seem to give a reasonable estimate of the annual export flux of N for European forested sites receiving throughfall deposition of N up to about 30 kg N ha<sup>-1</sup> year<sup>-1</sup>. When stratifying data based on C/N ratios less than or equal to 25 and greater than 25, highly significant relationships were observed between N input and nitrate leached (Dise et al. 1998, MacDonald et al. 2002). Such statistical relationships from intensively studied sites can be efficiently used in conjunction with regional monitoring/survey data (e.g. ICP Forests data) for risk assessment purposes. The plan is also to update available trend calculations (Forsius et al. 2001) regarding deposition and leaching data from ICP Integrated Monitoring sites during 2004-2005.

8. Data of both ICP Integrated Monitoring and the ICP Forests level II (intensive monitoring programme) are currently used in the European Union project "Carbon and Nitrogen Interactions in Forest Ecosystems" (CNTER, web site [www.flec.kvl.dk/cnter/](http://www.flec.kvl.dk/cnter/)). ICP Modelling and Mapping is providing deposition estimates and scenarios for the project. The work started in May 2001 and the project is ending in 2004. Work is currently ongoing to make a special scientific publication with papers covering the following main themes:

- (a) Approaches to estimate C sequestration in forests soil on the regional and continental scale;
- (b) Effect of N deposition interaction on C sequestration;
- (c) N retention in European forests;
- (d) Effects of forest management on C and N pools and fluxes;
- (e) Results from <sup>15</sup>N experiments and site-specific modelling.

9. The aim is to make a joint report of the three ICPs involved to the Working Group on Effects in 2005 summarizing the main findings of the project.

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