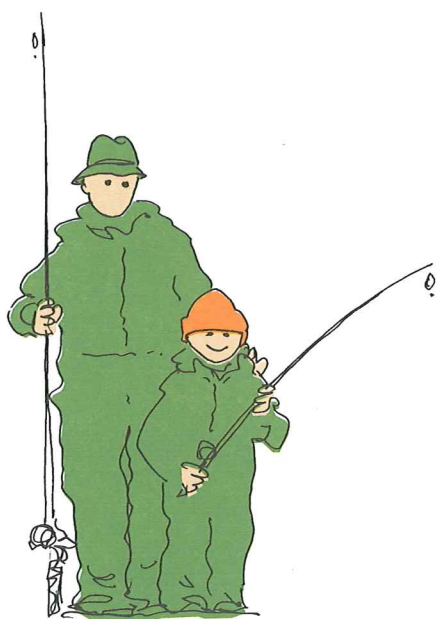


Convention on Long-range Transboundary Air Pollution

International Cooperative Programme on Assessment and
Monitoring of Acidification of Rivers and Lakes

ICP-WATERS REPORT



Norwegian Institute for Water Research

67/2002

**Proceedings from the
Workshop on Heavy
Metals (Pb, Cd and
Hg) in Surface Waters;**

Monitoring and Biological Impact.
March 18-20, 2002, Lillehammer,
Norway.

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Abstract This report contains the proceedings from the Workshop on Heavy Metals (Pb, Cd and Hg) in Surface Waters; Monitoring and Biological Impact. March 18-20, 2002, Lillehammer, Norway.

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CONVENTION ON LONG-RANGE TRANSBOUNDARY
AIR POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON
ASSESSMENT AND MONITORING OF ACIDIFICATION
OF RIVERS AND LAKES

**Proceedings from the Workshop on Heavy Metals (Pb, Cd
and Hg) in Surface Waters; Monitoring and Biological
Impact. March 18-20, 2002, Lillehammer, Norway.**

Prepared by the ICP Waters Programme Centre,
Norwegian Institute for Water Research
Oslo, June 2002

Preface

The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters) was established under the Executive Body of the Convention on Long-Range Transboundary Air Pollution at its third session in Helsinki in July 1985. The Executive Body has also accepted Norway's offer to provide facilities for the Programme Centre, which has been established at the Norwegian Institute for Water Research, NIVA. A Programme subcentre is established at the Laboratory of Freshwater Ecology and Inland Fisheries at University of Bergen. The ICP Waters Programme has been lead by Berit Kvæven, Norwegian Pollution Control Authority.

The Programme objective is to establish an international network of surface water monitoring sites and promote international harmonization of monitoring practices. One of the tools in this work is to conduct workshops on topics of central interest to the Programme Task Force and the aquatic effects research community.

We here report the results from the workshop “Heavy Metals (Pb, Cd and Hg) in Surface Waters; Monitoring and Biological Impact.” March 18-20, 2002, Lillehammer, Norway.

We thank the Norwegian Pollution Control Authority (SFT) and Nordic Working Group on Monitoring and Data (NMD) under Nordic Council of Ministers (NMR) for financial support.

We thank all participants, key-note speakers, chairman, rapporteurs and our financial supporters for a very interesting and fruitful meeting!

ICP Waters Programme Centre
Oslo, June 2002

Brit Lisa Skjelkvåle and Merete Ulstein

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1. Introduction

The workshop on Heavy Metals (Pb, Cd and Hg) in Surface Waters; Monitoring and Biological Impact.” March 18-20, 2002, Lillehammer, Norway is a contribution from ICP Waters to the ongoing work under 1998 Århus Protocol on Heavy Metals (UN/ECE, 1998) under the UN/ECE Convention on Long-Range Transboundary Air Pollution.

The 1998 Århus protocol on Heavy Metals targets three particularly harmful metals: Cd, Pb and Hg. According to one of the basic obligations, Parties will have to reduce their emissions for these three metals below their levels in 1990 (or an alternative year between 1985 and 1995). In the protocol there is also a request for looking into the possibilities for an effect based approach for setting reduction targets for the purpose of formulating future optimized control strategies which also take into account economic and technological factors;

The effects based approach, including critical limits and calculation of critical loads has been a subject on a series of workshop arranged by ICP Modelling and Mapping. Looking at the major conclusions and recommendations from these workshops we see that there has been a development in the understanding Pb, Cd and Hg in aquatic ecosystems

Bad Harzburg 1997 (Umweltbundesamt, 1998)

- Hg should define the critical limits in terms of the concentration in fish.
- Cd should define the critical limits in terms of total dissolved concentrations
- For Pb it was recommended that the present water quality criteria should be refined
- Calculations of Critical Loads for Cd and Pb appears feasible
- Steady-state modelling of Cd and Pb has potential problems, because certain key-processes will never reach steady-state
- Methods for calculating Critical Loads for Hg are not available at present, but possible ways to proceed has been identified

Schwerin 1998 (Umweltbundesamt, 1999)

- Available Critical Limits vary widely, with most of them not based on biological effects and expressed as total concentrations
- Existing Critical Limits were found not adequate for Critical Loads calculations (in particular for soils)
- There is a need to map Critical Loads for waters
- Modelling Hg is now possible
- Candidate models for Pb and Cd are now ready for testing

Bratislava 2000 (Ćurlík *et al.* 2000)

Ad-hoc International expert group Meeting on Effect-based Critical limits for Heavy metals Recommending critical limits for metals in soils, and also suggesting limits for waters.

In tight cooperation with the work in the workshops, several manuals for calculating critical loads for aquatic ecosystems are made (de Vries *et al.* 1998, de Vries *et al.* 2001).

In 2002 the first call for data on Critical Loads on heavy metals for soils and surface waters has been emitted. This submission of data is voluntary. The first report on modelling and

mapping of critical loads and levels for cadmium and lead in Europe is published in 2002. (Hettelingh *et. al* 2002).

ICP Waters Report on Heavy Metals

In 1999 ICP Waters made an assessment of heavy metals in surface waters based on data we hold in the Programme database (Skjelkvåle *et al.* 1999). The results showed that the ICP Waters database contains a number of sites with heavy metal data, and that these sites are located in relatively few countries. In addition data on heavy metals are reported from fewer sites in each of these countries than major solutes. To be able to give a good picture of the general level of heavy metals in surface waters throughout Europe and North America, heavy metal data for more sites with a larger geographical cover are needed. Some Focal Centres reported that there exist data on heavy metals from additional rivers. These sites are not likely to be suitable for monitoring the effects of air-transported heavy metals to surface waters due to input from local sources in the catchment and not long-range air pollution in particular.

The report concluded that heavy metals is much more influenced by local pollution sources and human activities in the catchments, than the acidification components (sulphate, nitrate, pH) and that selection of sites for monitoring the effects on HM from air-transported pollution must therefore be very careful.

Few sites have long time series on heavy metals. The analytical methods have changed and the detection limit has generally decreased through the monitoring period for the sites with long-term trends. Both the change in method and the change in detection limit make it difficult to identify time trends in heavy metals for many sites.

Heavy metal data in the ICP Waters database has been analysed with different analytical methods and analytical precision. All the laboratories reporting data to ICP Waters participate in national and international intercalibrations. To be able to compare the data within the programme it is of great importance to conduct intercalibration of analysis of heavy metals for improvements of results.

Based on the results from this report the ICP Waters programme decided to arrange a workshop on heavy metals in aquatic ecosystems to look more closely into the possibilities and problems related to heavy metals in surface waters from long-range transported air pollution.

The major aim of the Heavy Metal Workshop at Lillehammer was to:

- Agree on monitoring and analytical methods
- Contribute and participate in the ongoing discussions on Critical Limits and Critical Loads for heavy metals in surface waters

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2. Overall conclusions from the Workshop

The opening presentations at the workshop showed that numerous national and international activities and research programmes, monitoring, regional and national surveys, intensive studies and experiments, have substantially increased present knowledge over the last years on the effect of long-range transport of heavy metals on aquatic ecosystems, including concentration levels, spatial variability, trends in time, effects on the biota (bioavailability, biomagnification, bioaccumulation) and modelling.

The workshop reviewed the present knowledge and understanding in three areas,

- (i) Critical limits;
- (ii) Monitoring methods;
- (iii) Dose/response, resp. its modelling.

The results of in-depth discussions were presented to the plenary by rapporteurs for further consideration. After some additions/amendments the three sets of conclusions and recommendations were approved by the Workshop.

The Programme Centre was requested to prepare a short summary report of the Workshop, with the three reports from the working groups annexed in full, circulate it to all participants, and attach it to the minutes of the 17th meeting of the Task Force on ICP Waters.

The organizers will publish proceedings of the workshop and make it available to the 18th meeting of the Task Force on ICP Waters.

The workshop encouraged further review of existing data and information, including active cooperation with other bodies, EU research programmes and national research. ICP Water has to make full use of information in other programmes and visa versa. The report should be made accessible to a larger audience and possibly be put on the home page. It should also be presented as conference-room report to the Working Group Meeting in August this year (2002).

Effect based approach to the control of heavy metals in surface waters requires further development. It was felt that defining critical loads for individual heavy metals need not necessarily be a final step in the process. Additional methods may also prove to be advantageous.

ICP Waters was encouraged to act as a facilitator in providing data and information for development of critical limits for heavy metals in aquatic ecosystems. This implies activity from national focal points.

ICP Waters should revise and update the Programme manual and continue intercomparisons on heavy metals.

3. Report from the working groups

3.1 Monitoring methods for heavy metals in surface water

Chair: Anders Wilander

Rapporteur: Jaakko Mannio

Participants: Alberto Barbieri, Gunnar Stein Jonsson, Gennady Kalabin, Istvan Licsko, Iraida Lyulko, Stephen Norton, Stephano Pozzi, Sigurd Rognerud, Neil Rose, Eiliv Steinnes, Reet Talkop, Josef Vesely, Merete ulstein, Brit Lisa Skjelkvåle (part time)

The group discussed monitoring programmes and analytical methods, in order to recommend suitable guidelines for further elaboration of a manual amendment for heavy metal monitoring in aquatic environment within WGE (ICP Waters and ICP IM) Two main lines were followed:

To answer questions *why, what, where, when, how* and, *time scales* for response in the aquatic system and sampling frequencies.

Monitoring is required to support the 1998 Protocol on Heavy Metals. The priority elements are Hg, Cd, and Pb. The selected methods should be applicable and comparable to cover wide geographical areas and natural conditions, and not requiring too advanced techniques.

The suggested programme of sampling, analysis and assessment should cover, as in the case of acidification, both the spatial (*where, how many lakes?*) aspect and the more intensive, process-oriented (*why, when?*) aspect.

The programme core is based mainly on previously selected sites within ICP Waters programme. Therefore, site selection criteria were not discussed thoroughly. The existing Programme Manual (1996) is focused on monitoring of acidification and gives guidelines to site selection, catchment information, sampling techniques and frequency, chemical methods and QA/QA. Most of these principles can be regarded as relevant for heavy metal survey and monitoring practices as well.

Heavy metal monitoring of the proposed media need both detailed guidelines and additional information from the surrounding environment to be fully and effectively interpreted. Only a small part of that information was possible to discuss. A more detailed guideline for monitoring these media suggested here could be prepared from existing protocols/manuals in related international monitoring and research programmes (ICP IM, AMAP, MOLAR / EMERGE). This will enhance the compatibility between programmes and will improve future global assessments.

The group agreed to recommend the following matrices: water, lake sediment cores, surface lake sediments and fish. All these matrices may not be relevant for all sites, and the spatial and temporal sampling frequency have to be adjusted to local conditions and information needs.

Other matrices discussed (lake sediment traps, lower biota) were considered, but not judged as primary due to special requirements, limitations in applicability, or lack of experience within our group.

Sediment loading

Sediment cores were considered important in the initial phase of study to reveal the history of metal sedimentation, both anthropogenic and natural background. Sediment surface sampling is used to survey larger regional patterns of metal contamination. With this method also a reference depth may be sampled to elucidate the geochemical background concentration (usually >ca. 30 cm). Sedimentation traps may be useful monitoring tools for the monitoring of yearly changes in metal fluxes to sediments.

Lake and river water

Water monitoring will produce data directly reflecting the status and trends in effects of deposition. But of course processes within the drainage area and the lake itself modify the information about deposition. The seasonal variation in concentration was recognised, and could necessitate a relatively high sampling frequency. However, sampling within a selected, relatively stable period diminishes that variation thus allowing as few as one sample per year for relevant information.

Monitoring of running water requires a high sampling frequency, at least six times per year, preferably 12 or 24 times. In this context episodic high concentrations were discussed. It was noted that levels for acute toxicity seldom will be reached even during these events, but actual knowledge on this matter is scarce.

As a rule, sampling should take place in the middle of the lake and of surface water (0,5 m). Outlet sampling can be chosen when it has been proven that the water is representative for the lake.

Filtration (0.45µm) is normally not used in lake monitoring. Even in running waters an attempt to filtrate particles is questionable (contamination, adsorption), because these types of headwaters are not turbid.

The knowledge about the dissolved part of metals was considered important, due to its obvious link to bioavailability and dose-response. New fractionation methods such as DGT membranes for separating the dissolved part are promising, but are still in the stage of development, not ready for monitoring purposes. Ultrafiltration is also an option, but would require electricity in field conditions.

The challenge for water monitoring is still the actual concentration level vs. detection (determination) limit. Another weakness is the small number of laboratories with capability to determine Hg. Mercury determinations in water are, however, reliable at the ng l⁻¹ level in clean laboratories.

Biota

Fish tissues have been traditionally monitored for heavy metal accumulation in aquatic environments. For Hg studies, (predatory) fish muscle is the most common biological matrix. The accumulation is often age-dependent, therefore fish studies must include at least length and weight information, but age determination is strongly recommended. The specific species to be sampled were not discussed. Stable nitrogen isotopes are used to estimate the trophic level of the species. For metals other than mercury muscle is not appropriate, and liver may be a more appropriate organ. Kidney was suggested as a possible option instead of liver tissue, in which seasonal variation in concentration may represent a problem. Fish population studies are already included in the Programme Manual for ICP Waters (1996), which may have contributed contaminant information already from selected sites.

None of the other biotic groups (aquatic mosses, snails, other invertebrates, zooplankton) received broader support in the discussion. Aquatic mosses, usually *Fontinalis* have been used mainly for monitoring purposes in locally polluted sites (for Pb and Hg). However, the suitability for LRTAP application was questioned. Acidic conditions restrict the use of mosses for Cd monitoring, and snails may not be present at such sites. Invertebrates (bottom fauna) may be suitable in cases, but the concentrations vary according to their feeding habits, thus making inter-lake comparisons difficult. Carnivorous invertebrates are an option for monitoring in very acidic fishless lakes, already monitored in ICP waters Programme. Zooplankton for Hg measurements was brought up in the discussion, but the method has been used only in research projects.

Analytical methods and quality assurance

Cleanliness during sampling is crucial. Whenever possible water samples should be collected directly in the sample bottle. If a sampler is used, it must be tested for contaminating materials. There is a wide range of materials used for sample bottles (Teflon, HDPE). Bottles and cleaning procedures should be tested before use. The valuable work by NIVA, undertaking interlaboratory calibrations, now including trace metals, was gratefully recognised. It was agreed that regular use of certified reference material should be promoted.

Integration with other site specific information

As a basis for interpretations, several additional information sources are needed. Deposition data of heavy metals is essential. Sampling in the vicinity of an EMEP-level deposition station is beneficial. In integrated monitoring sites, throughfall and litter fall monitoring will enable better interpretations. For more regional purposes, terrestrial moss surveys can integrate deposition over several years. This technique has been used for a long time in the Nordic countries. A survey on the European scale was conducted in 2000, and ICP Vegetation Programme will be coordinating this activity in the future. Concentration in the soil humus layer can elucidate the historical burden of metals. In order to interpret correctly the atmospheric contribution of metals to the humus layer some knowledge about the background concentrations in the mineral soil is required. This may be obtained e.g. by analysis of samples from the C-horizon taken at the same site as the humus sample.

Table 1. Overview of recommended monitoring methods for heavy metals in surface waters.

Media	recommendation	Spatial /Temporal	time scale	Sampling frequency	N of samples	Target elements	Target information	Key additional information needed	Reference programmes
sediment cores	+	T	<10-100> yr	10-30 yr	10-30/core 2-5 cores	all	geochemical signal, trends, and pollution history	bathymetry, dating (isotopes), org. matter	AMAP, EMERGE
sediment surface & reference depth	+	S	>10->100 yr	10 yr	2-5 /core	all	regional information and geochemical signals	bathymetry, org. matter	NIVA
fish muscle	+	S,T	5-15 yr	1-5 yr	5-20 fish	Hg	bioaccumulation, critical limit for food	fish age, N- isotopes	EMERGE, AMAP
fish liver /kidney	(+)	S,T	5-15 yr	1-5 yr		Cd, Pb	bioaccumulation	- " -	EMERGE
sedimentation traps	(+)	T	<1 yr	<1 yr		all	metal sink, budgets	org. matter	EMERGE
invertebrates	?	S,T	<1-2 yr	<1 yr		Hg	bioaccumulation		
zooplankton	?	S,T	<1 yr	<1 yr		Hg	bioaccumulation		
aquatic mosses	--	S,T	<1 yr	<1 yr		Pb, Hg	temporal variation (sorption)		NIVA
lake water	+	S,T	months	1-12 /yr	1 (+QC)	all	spatial and/or temporal variation in concentration	general water chemistry	ICP Waters & ICP IM
river water	+	S,T	weeks	12- 26> /yr	1 (+QC)	all	spatial and/or temporal variation in conc., fluxes	general water chemistry, runoff	ICP Waters & ICP IM

The table is incomplete in places, where relevant information may exist, but not discussed in the workshop

+ recommended, selection site specific

(+) recommended in special cases

? too little experience for recommendation

■ problematic, but possible

3.2 Report from the working group on: How should critical limits (Cd, Pb, Hg) for surface waters be derived?

Chair: Espen Lydersen

Rapporteur: Gudrun Schuetze

Participants: Stefan Loefgren, Tor Traaen, Alberto Barbieri, Kjell Johansson, Gunnar G. Raddum, Tatiana Moiseenko, Arne Henriksen, Anne Christine Le Gall, Bjørn O. Rosseland, Erle Grieg Astrup

Critical limits for heavy metals in surface waters are defined in accordance to the "Manual for calculateing critical loads of heavy metals for aquatic ecosystems (deVries et al 1998, point 3.2)

Cadmium and lead

Conclusions

- the availability of Cd/Pb is influenced by several parameters of the aquatic system like pH, BC concentration, TOC
- therefore the total concentration of the metal in water is not appropriate to describe a critical limit
- we should be aware of the bioavailability of the metals by doing studies on toxicity in relation e.g. to curves of BC concentrations in the water at the same level of pollution
- despite of this the existing critical limits for surface waters have a sound scientific background and we should use them at this point
- evaluation of effects from sediment concentrations is not possible at current stage of knowledge
- evaluating the toxicity:
 - o several trophic levels should be included
 - o gill breathing organisms are good indicators,
 - o we should also consider the life cycle stage of organisms
- only headwater lakes are appropriate to study effects of atmospheric depositon of metals in these ecosystems
- we need new surveys on metal concentrations in the surface waters to obtain time trends
- we need information on background values (natural pollution) to be considered in comparison with critical limits.
- episodic concentrations (peaks) may be relevant in some cases and should therefore considered
- we need more intercomparisons of measurement methods and harmonisation
- also for background concentrations we should judge the bioavailability with similar methods as for critical limits, the methods should be simple and should be well discribed in the studies/publications)
- we are aware of new and upcoming analytical methods (DGT)

Recommendations:

- a literature study should be done aiming at a classification of surface water ecosystems or at deriving pH/BC concentration functions, the feasibility of a classification by TOC should be tested
- the range of existing critical limits could then be splittet in a set of limits, of which each value is related to specific conditions of the ecosystem (“quasi free ion activities”)
- recommended range for Cd (total concentrations):
0.1 – 1.0 ug/l
- range for Pb (total concentration):
1 – 10 ug/l
- for the future we should do efforts to use free ion activities as critical limits for surface waters

Mercury**Conclusions:**

- there is poor relationship between concentration in water and concentration in fish
- the accumulation in the predatory fish depends on methylation and the number of levels of the aquatic food chain
- background concentrations are between 0.1 – 0.2 mg/kg
- current deposition has delayed influence on the concentration in fish, if the pools in the surrounding environment are very high as a result of historical LRT of Hg.
- climate change can influence methylation processes
- there are studies showing that liming can lead to increasing methylation rates
- there are first results on effects of Hg on behaviour of fish, reproduction and other functions, even at low levels of concentration
- because there is no clear dose-response relationship, we are not able at the moment to recommend a critical limit (Hg) protecting the functioning of the aquatic system
- the problem with Hg in fish is linked to boreal aquatic ecosystems with high TOC levels (concentrations and fluxes) and with long food chains. High Hg-levels in fish (as observed in some high mountain lake) may occur even in lower TOC-waters, hosting piscivorous fish.
- It should be focused on the role of redoxpotential-gradients as a driving Hg-methylation force.

Recommendations:

- we should use the guidelines for Hg contents in fish as critical limits of Hg: 0.3 mg/kg (EPA) or 0.5 mg/kg (WHO),
- we should calculate the critical loads for soils aiming at no further accumulation. However, there are already those studies showing that this means to reduce the total deposition by 80 % (= zero anthropogenic emission of Hg)
- we should investigate effects of climate change on Hg circles in more detail
- we should study the influence of liming

3.3 Report from the working group on: Dose-Response Relationships for Heavy Metals in Surface Waters (Steady-state and Dynamic Models)

Chair: Alan Jenkins

Rapporteur: Max Posch

Participants: Alberto Barbieri, Radovan Chrast, Eirik Fjeld (part-time), Martin Forsius (part-time), Tore Høgåsen, Berit Kvaeven, Thorjörn Larssen, Markus Meili, Bjørn O. Rosseland (part-time), Dorota Rzychon, Brit Lisa Skjelkvåle (part-time), Ed Tipping, Matti Verta, Adam Worsztynowicz, Staffan Åkerblom

First, the group discussed and agreed that in the given context a dose-response relationship means a relationship describing the change (reduction) in concentration of a heavy metal (Cd, Pb, Hg) in a surface water (or biota) as a consequence of a change (reduction) in deposition of the heavy metal. Despite a (strong) decline in emissions of especially Pb in (western) Europe and North America, clear evidence of a (concurrent) decline in concentrations can be only found in lake sediments in Scandinavia, whereas such trends are much less pronounced in runoff water. (However, it was recognised that the group did not include enough expertise to make a comprehensive statement on this matter). An explanation could be the potentially very long (average) residence times of heavy metals in soils, caused by the large pools in comparison to the annual fluxes. As a consequence, it may take very long for a system (catchment) to come into equilibrium with heavy metal inputs, i.e. to reach a desired steady state when changing emissions to critical loads. Thus dynamic models are needed to investigate dose-response relationships for heavy metals.

For the effects-work under the LRTAP Convention, not the heavy metal concentration in the surface water is of interest, i.e. the endpoint, but its damage of biological species and impact on (human) health. Thus the endpoints were defined as gill-breathing animals (for Cd and Pb) and the consumer of fish (pike; for Hg). In order to estimate the impacts of heavy metals on these endpoints, the following (biogeochemical) data are needed:

- (a) Bio-available metal concentrations, together with
- (b) related parameters, such as organic matter, pH, [Ca], temperature
- (c) during sensitive development stages of the organism

In the ensuing discussion, it was noted that

- (a) the speciation of metals needs to be modelled, together with other parameters. If, however, only total concentrations are available, they should be reported together with, e.g., turbidity data to enable estimating the particulate fraction.
- (b) episodes (sub-annual time steps) are difficult to model deterministically, especially in the context of the large regional scales. But maybe statistical measures relating the intensity and duration of episodes to long-term averages could be explored.

It was also questioned, however, whether the (variation in) toxicity increases during episodes, i.e. do free ion activities (bio-available concentrations) increase during episodes? Episodes might mostly increase non-bio-available concentrations and/or are accompanied by, e.g., higher concentrations of Ca ions, which compete for sites at biotic ligands. To answer this

question it was recommended that the toxicity variability over time (especially during episodes) should be studied.

Next, the Group embarked on discussing existing critical load (steady-state) and dynamic models for heavy metals. There was agreement that Hg should be treated separately from other metals (Cd, Pb).

Steady-state Models (for critical load calculations):

Cd, Pb:

- Model(s): exist and are well-documented (Manual)
- (So far) little experience with application to surface waters
- Endpoint: gill-breathing animals

Hg:

- CLAP model (Meili et al.) : in preparation for Sweden; semi-empirical, based on Swedish data
- Endpoint: pike (consumer)

Dynamic Models:

Cd, Pb:

- Model(s): CHUM (Tipping et al.): also simplified version exists which uses partitioning functions instead of full chemistry
- Output: free metal ions (speciation), [H], [Ca], ..., i.e. all inputs needed for biological response models
- Problems: Initialisation, i.e. initial metal amounts in catchment soils. Such data could come from sediments/peat/soils or historic emission inventories (the latter also requiring atmospheric dispersion modelling!)

Hg:

- Model(s): Metal Cycling Model (MCM; EPRI/US-EPA) (various versions)
- Lake model only, i.e. output from catchment soils is input to the model
- Very data intensive
- Endpoint: Me-Hg in fish (fish modelled in MCM!)

It was also noted that other heavy metal models are under development, but their emphasis is on soils. Mention was also made of Biotic Ligand Models (BLMs), which could/should be linked to the biogeochemical models to simulate the (acute) impact on indicator organisms. The dearth of biologists in the Group prevented an in-depth discussion of this subject.

At the end of the day, the Group agreed on the following *recommendations* with regards to:

Data:

- Further collect new and analyse (new and existing) data. But be aware of changes in analytical techniques over time.

Critical loads:

- Critical load models should be tested where data are available; however,
- Critical loads may not be the ultimate tool for assessing emission reductions due to a lack of understanding in defining dose-response relationships; and other methods should be considered and developed.

Dynamic models:

- Dynamic models should be developed and tested (further) to improve the:
 - (a) understanding of (key) processes
 - (b) substantiation of (recovery) time scales (rates of change)
 - (c) setting of target loads

4. Invited key-note presentations

4.1 Ecosystem functioning: Biological impacts of pollution of heavy metal in aquatic ecosystems; examples from ongoing projects.

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Pristine areas, especially in high mountain areas in Europe, are important sources of water supplies as well as recreational destinations for large populations. Fishing is a popular activity in these areas, not only by tourist, but also by the locals who exploit and cultivate their fishing resources in a sustainable way. Contamination of heavy metals and organic pollutants, especially mercury (Hg) and persistent organochlorine pollutants (POPs), has been of major concern especially for people living in northern areas where fish can be important dietary sources. These contaminants have certain properties which make the especial vulnerable to organisms:

- They are *bioavailable* (a compound that exist on a form being reactive to an organism by binding or absorption, leading to an effect on the organism),
- They *bioaccumulate* (a component accumulating to a higher concentration in an organism than in the water, with accumulation depending on concentration and time of exposure, and where levels depend on different biotic and abiotic factors),
- and finally they *biomagnify* (a component increases in concentration in an organism depending on the throphic level of the organism, which means food chain effect).

The properties and importance of heavy metals differs. Some heavy metals are essential to the organism, like Cu, Zn, while Cd, Pb and Hg are non-essential. Their source in nature differs, but all metals except of Cu has a long range transportation profile. Their bioavailability are influenced by other physico-chemical factors like pH, organics, temperature etc. In most cases, increased TOC decreases bioavailability of Cu, Zn, Cd and Pb. Mercury differs, as the bioavailability of Hg depends on the MeHg which have the highest concentration in humic lakes because of a reduced photo-degradation of MeHg.

Once inside an organism, the strategy for detoxification can be one of exclusion, or inactivation by binding to low molecular compounds called metallothioneins (MT) having specific binding sites for metals. MTs are mainly found in gills, liver, kidney, muscle.

The ecotoxicological effects of metals differ. Some have an acute effect by being gill reactive (Cu, Cd, Zn, Mn), which can result in direct binding to gill surfaces resulting in hypoxia and loss of blood plasma ions and mortality. As a general effects, heavy metals reduces enzyme-activity, increases deformities (development of eye is Hg sensitive), cause failure in heart development, reduced hatching (reduced embryo activity) and yolk sac absorption, affect

behaviour and metabolism (reduced growth). Problems for a proper management is the fact that in literature, we find great variations in concentrations affecting behaviour, depending on species, life history stage, experimental design (cover/non-cover) etc.

Concentrations of Hg and POP in fish are to a certain degree influenced by the contamination level of lake water and sediment. However, it is the food web structure and biological factors, such as longevity and growth, that are of most importance. Fish are opportunistic feeders whose diets change as they grow. The diet can vary significantly among individuals of the same species. Generally, there is a significant enrichment of the heavy isotope of nitrogen (^{15}N) relative to light isotope (^{14}N) through the food web. Hence, the ratio ($\delta^{15}\text{N}$) provide a time-integrated and continuous measure of the relative trophic position of consumers. The fractionation of ^{13}C in the food chain is much less, and the $\delta^{13}\text{C}$ is more indicative of the carbon sources of the assimilated diet than trophic position. Thus, a dual isotope approach can indicate structures of the food web essential for explaining concentrations of contaminants in fish.

Until recently there were few data concerning contamination levels of these pollutants in fish from alpine lakes in central- and southern Europe. Through the EU projects AL:PE 2, MOLAR and the ongoing EMERGE, new data from precipitation to sediments, water column and fish have demonstrated that many POPs and Hg are pollutants of intermediate volatility with a widespread distribution in the atmosphere on the northern hemisphere. Sediment studies in European alpine lakes indicate an increase of anthropogenic atmospheric deposition of POPs and Hg especially since the 1950's. The systematic transfer of these compounds from warmer to colder areas (referred to as "cold condensation") and a slow degradation of POPs in cold environments, are factors which may cause stronger enrichment of pollutants in alpine and arctic lakes than elsewhere. In fact, the higher congeners of PCB have been found to accumulate to the larger degree in sediments and fish in the highest elevations in Europe's mountain areas.

Documentation of very high Hg levels in "large" cannibalistic Brown trout and Arctic charr populations in Norway in 200-2001, found a shift in Hg level which correspond to an increased $\delta^{15}\text{N}$ signal. To understand the Hg levels in a fish population, we therefore need information of the trophic level of the individual fish.

Conclusions

Effects of heavy metal on biota depends on a series of abiotic and biotic factors. General water chemistry can affect speciation and bioavailability of metals. Long range transport of heavy metals have resulted in high concentrations of Pb, Cd, Zn and Hg in some areas. The Long range transport of Pb has been reduced, and is reflected in lake water chemistry. No change in Hg are seen. In Norway, there are few problems outside local pollution sources related to changes in biodiversity by Pb, Cd and Zn, but the main problem for human health concerns Hg. Great concern are focusing on the increased TOC and increased MeHg in lakes. To separate effects of bioaccumulation and biomagnification, we need $\delta^{15}\text{N}$ and food web studies to interpret the background for the Hg load to the lake biota. New studies of "large grown" brown trout and Arctic charr have documented high levels and led to consumption

regulations in many lakes. Trade level of 0,5 ppm Hg/kg means 1 monthly meal after the new recommendations

We have extremely few toxicity and effect data from both fish and invertebrate species related to heavy metals and POPs. At least in Norway, we have 2000-3000 animal species in freshwater, including 30-40 species of fish, but have only data from < 70 species of invertebrates and no or few data on whole life cycles. We find great variations in given toxicity levels within and between species, and important data on speciation of heavy metals (L- og HMW) and bioavailability under chronic and episodic conditions, are lacking.

ICP Waters should include fish and micropollutants in their studies.

4.2 Monitoring Heavy Metals (Cd, Hg, and Pb) Through Time

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Very limited reliable data are available for atmospheric deposition of Cd and Pb prior to about 1980 and of Hg prior to 1990. Thus both spatial and temporal understanding of air pollution by these metals is restricted to the last 20 years and for only a few countries. Understanding modern conditions in surface waters and target organisms, and extrapolation to the future require that we have an understanding of trends in past atmospheric deposition. Natural archives of atmospheric deposition exist that permit us to develop this historic perspective and to help understand the natural processing of these metals in watersheds. Long-term archives with resolution typically on the order of 5 to 10 years include ice cores, lake and peat sediment, forest soils, and overbank sediment. Intermediate-term archives have a resolution of less than 5 years and include forest litter and vegetation, and terrestrial moss. Short-term variation in deposition is recorded by precipitation collection and analysis (at virtually any desired frequency), stream chemistry, and lake chemistry. Stream chemistry and lake chemistry both result from an integrated response from the entire watershed - reflecting past deposition, modern watershed processes, and contemporary deposition. Lakes integrate and average highly variable stream chemistry plus in-lake processes.

Very modest atmospheric pollution for at least Hg and Pb, representing long range transport, is detectable in archives starting about 5,000 years before present (2002). Roman time, centering on 0 A.D., was marked by substantial deposition of Hg and Pb, detectable in all long-term archives. By the early 1800s in Europe and late 1800s in North America, substantial regional air pollution started. The maximum atmospheric deposition for the three metals was reached in 1970-1980 in North America, perhaps slightly later for Hg in Europe. Since that peak, deposition of Cd and Hg has decreased more than 50% in North America and probably comparable percentages in Europe. Pb deposition has decreased more than 90%. The rapid response of seepage lake chemistry to these decreases contrasts with the relative lack of response of drainage lakes, indicating a major role for watersheds as secondary sources of pollution to surface waters, well after the atmospheric pollution has decreased.

Numerous factors obscure the direct linkage of atmospheric deposition and surface water quality. They include:

1. Changing amounts and proportions of wet and dry atmospheric deposition
2. Atmosphere-canopy interactions
3. Variations in watershed retention of metals
4. Changing pH of water draining the watershed, affecting particularly Cd and Hg
5. Changing dissolved organic carbon in draining waters, affecting particularly Hg and Pb
6. Variations in particulate matter
7. Seasonality of watershed processes
8. Variations in the state of acidification, affecting particularly Cd

Based on what has been learned from the various archives, the following recommendations seem appropriate:

1. The spatial and temporal patterns of air pollution by metals are now reasonably well established. Only new hypothesis-driven sediment core work needs to be continued. But, surface sediment, forest litter, vegetation, and terrestrial moss spatial studies should be repeated periodically, perhaps every 5 years.
2. Process-related research linking soil archives of stored metals with streams need to be understood better. Relating dissolved metals in streams and lakes to atmospheric deposition and watershed-stored metals can be accomplished best by using isotopic characterization of the metals with ICP-MS methods. Isotopic studies should be carried out in a sub-set of ICP watersheds.
3. The ultimate goal of metals monitoring is to develop the capability of predicting the response of ICP waters to changes in atmospheric deposition and watershed processes. Protocols for emission reductions and target/critical loads anticipate a quantitative understanding of linkages between the atmosphere and surface waters. Consequently, comprehensive hypothesis-driven studies should be developed to understand sources, storage, and mobilization processes in a subset of ICP waters.
4. Streams integrate up-stream processes but are nonetheless highly variable. Metal budgets and dynamics for first-order ICP streams can not be documented with fewer than 20-25 water samples per year.
5. Regional surveys of ICP lakes should be repeated with a sampling frequency of 2 to 4 samples per year, and at least on a yearly basis.
6. All data gathered should be of the highest quality obtainable with modern instrumentation so that future trend analysis is meaningful.

4.3 Dose/response relationships for Hg in surface waters

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Atmospheric Hg deposition is considered a threat to lake fish consumers and to the soil microflora in the boreal forest zone. Hg deposition has increased 2- to >20-fold over the last centuries due to anthropogenic emissions and subsequent dispersal on different scales. Based on recent atmospheric modelling (e.g. EMEP), the deposition of Hg from local, regional, and global sources can now be quantified regionally. Atmospheric levels or fluxes of Hg can then be related to environmental levels of Hg in terrestrial and aquatic ecosystems.

In Sweden, Hg levels in fish exceed health advisory guidelines in tens of thousands of lakes. Furthermore, there are indications of toxic effects on forest ecosystems at Hg levels near those observed in south Sweden. The current Swedish policy is (1) to avoid further increase of Hg in soils and (2) to keep future Hg levels in predatory fish below 0.5 mg per kg fresh weight in most lakes. Current Hg levels in forest soils are highest in south Sweden where they reach about 0.5 mg per kg organic matter. The critical level of atmospheric pollution (CLAP) to comply with these goals is estimated to be similar to the pre-industrial level, since the Hg loss from soils is very slow (centuries to millennia), and since fish Hg levels are naturally high in many boreal lakes (e.g. Meili et al. 1999 and in prep.).

The Hg issue is accentuated by the fact that present Hg levels in most soils and lakes are still far from equilibrium with atmospheric Hg pollution. This is evident not only from mass balance calculations, but also from the delayed response of surface waters to the Hg pollution pulse of the past decades. Hg concentrations in fish are thus likely to increase further during several centuries and to reach levels much higher than the current ones, if Hg emissions are continued. The increase will be particularly pronounced in humic lakes, which already today show the highest Hg concentrations in fish, and to which most Hg is supplied by soil runoff in highly bioavailable form but substantially delayed (Meili et al. 1999 and in prep.).

In many humic lakes, even the natural levels of Hg in predatory fish are estimated to touch the widely used limit of 0.5 mg/kg fresh weight. In clearwater lakes on the other hand, which respond to environmental changes more rapidly (years or decades) and which today show a similar degree of contamination as the humic lakes, natural Hg levels are estimated to be often less than 0.1 mg/kg. Thus, the frequently assumed background of 0.1-0.2 mg/kg fresh weight in predatory fish does not account for the natural variation among lakes and is exceeded by far in humic lakes. This can be attributed to the bioavailability of Hg, which is highly variable and largely dependent on the degree of net methylation (balance between methylation and demethylation), which in turn is controlled by the abundance and hydrological proximity of anoxic zones rich in organic matter (e.g. wetlands). Hg levels in fish are further controlled by the biomagnification of Hg along food chains, i.e. the number of trophic levels and the Hg enrichment per trophic level. However, neither the Hg enrichment nor the basic trophic structure in boreal lakes is known to differ regionally. Regional differences in fish Hg levels

may thus be linked predominantly to watershed biogeochemistry and climatic factors, whereas aquatic food web structures may contribute to the local variation among lakes (e.g. Meili 1997).

Current efforts to assess the variability of lake susceptibility to Hg pollution show substantial regional differences in Sweden (Figure 4.3.1). The spatial patterns also suggest that high Hg levels in fish previously attributed to local Hg emissions may instead represent an issue of regional susceptibility to global Hg emissions. In the regions with the highest fish Hg levels, also soil Hg levels are elevated, potentially reflecting a historical local pollution, which has been largely eliminated already two decades ago. However, fish Hg levels in these regions show much larger deviations from other regions than expected from a secondary Hg pollution via soil runoff, and the current atmospheric Hg input is low. This is illustrated by corresponding concentration ratios (Figure 4.3.1), which are related to corresponding response/dose ratios, and which reflect the environmental susceptibility to atmospheric Hg

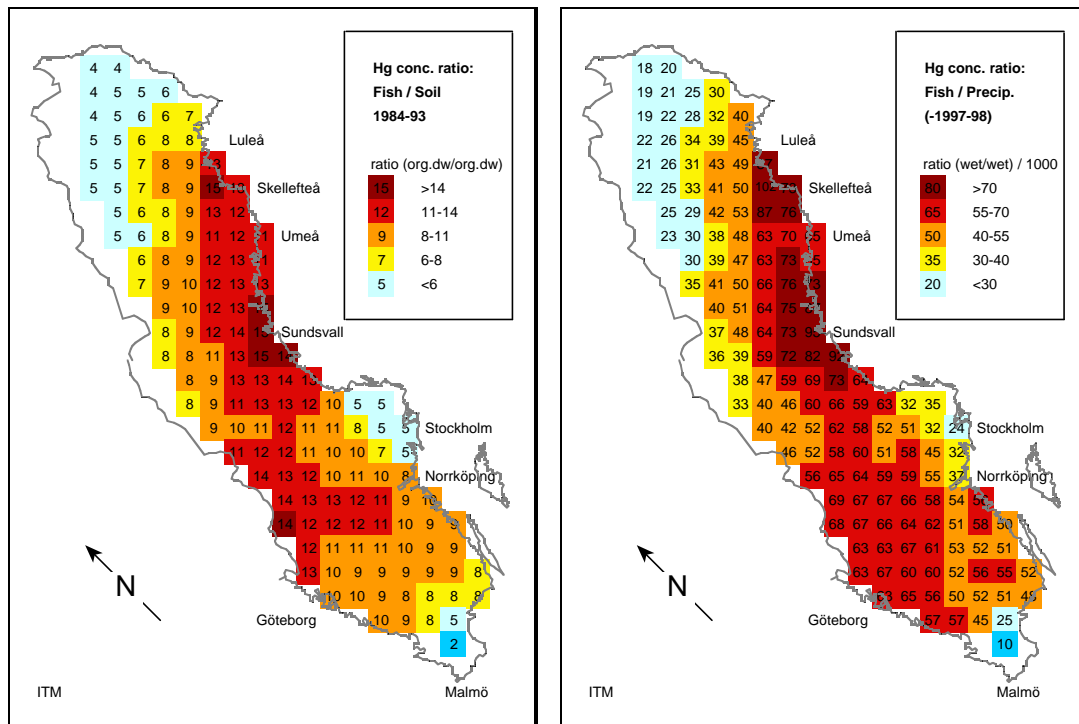


Figure 4.3.1. Mercury concentration ratios between freshwater fish and forest soil (left) and between freshwater fish and precipitation (right). Fish data: standardised concentrations in muscle tissue of 1-kg pike (*Esox lucius*); regional interpolation based on over 5000 individual pike data from over 1000 lakes. Soil data: Mercury in the mor layer of forest soils; standardised concentrations expressed per unit of organic matter; regional interpolation based on data from 356 standardised sampling points. Precipitation data: Based on EMEP model calculations calibrated with data from long-term national monitoring. Preliminary maps, from Meili (2001).

input: Concentration ratios in north-east Sweden are up to tenfold higher than in southernmost Sweden where the Hg deposition is highest, and up to fivefold higher than in northern regions with similar Hg deposition at present.

It is important to note that the current concentration ratios may not reflect a steady state, but are more likely to gradually increase, since the response of environmental Hg levels to changes in atmospheric Hg pollution (in either direction) is very slow and non-linear. This implies among other that emission reductions cannot be expected to result in proportional changes of environmental Hg levels within a few years. This also implies that such reductions are necessary for a long-term sustainability.

Further work should aim at (1) quantifying the relationships between the environmental susceptibility to atmospheric Hg pollution and commonly available environmental data, and (2) quantifying the response dynamics of environmental Hg levels to changes in atmospheric Hg emissions.

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4.4 Heavy metal concentrations in the Nordic lakes in relation to presently used Critical Limits - a state of the art review

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The goal of this work was to make a risk assessment of the chemical and biological effects of metals in reacidified, limed water bodies in Norway and Sweden. The risk assessment is based on a literature review and evaluations of water chemical data from the 1995 Nordic Lake Survey. Compared to the preliming period, it is unlikely that enhanced remobilization of inorganic aluminium or other toxic metals (metal bomb hypothesis) from the catchment, the lake sediment and/or the streambed will occur when limed waters reacidify. Rather, the concentrations in surface waters are expected to be lower than before liming started, because of reduced atmospheric inputs of both strong acids and metals as Cd, Pb, Hg and Zn during the last 10-20 years. The concentrations in lakes relative to the biological effect levels, as well as the chemical properties of the different metals suggest that the potential biological risks associated to reacidification of limed lakes decrease in the order Al >> Cd > Pb (Table 1). The risks associated with Fe, Mn, Zn, Cu, Cr and Ni are very low and do not have to be considered except in waters with known concentrations larger than the lowest biological risk level. However, such waters are most certainly very rare (<2%, Table 1). Aluminium is the metal, which should set the limit for judging the risk of biological damage due to reacidification of limed surface waters.

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Table 1. Percentage of non-limed lakes in Norway (n = 985), Sweden (n = 820, n = 1124 for As) and Finland (n = 462), and limed Swedish lakes (n = 261) below the lowest biological risk levels (LBRL) according to Swedish criteria (Alm et al., 1998). The concentration for Al is labile aluminium (LAL), the toxic fraction of Al. No LBRL-values for LAL are established in Norway or Sweden. Thus, the tentative LBRL-values are for Atlantic salmon/roach (20 µg Al L⁻¹) and brown trout/perch (80 µg Al L⁻¹).

Metal	LBRL µg L ⁻¹	Share of lakes with conc. <LBRL (%)			
		Norway No lime	Sweden No lime	Sweden Limed	Finland No lime
Zink	20	99.3	99.3	98.9	99.4
Cadmium	0.1	96.6	95.5	97.7	99.4
Copper	3.0	99.3	98.4	99.6	99.1
Lead	1.0	91.5	93.0	93.5	98.3
Nickel	15	100	99.8	100	99.4
Chromium	5	99.9	99.6	100	100
Arsenic	5	99.8	99.8	100	100
<i>Aluminium</i>					
<i>Salmon/Roach</i>	<i>20</i>	<i>76.9</i>	<i>80.7</i>	<i>86.0</i>	<i>n.d.</i>
<i>Trout/Perch</i>	<i>80</i>	<i>95.5</i>	<i>91.4</i>	<i>92.4</i>	<i>n.d.</i>

4.5 Dose / response relationships for Pb and Cd in surface waters

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Introduction

The relationships of the title refer to the **dose** of atmospheric deposition and two kinds of **response**, namely the biogeochemical processing of metals by the soil, rock and water of the catchment and the possible toxicity of the metals towards aquatic biota. This account is based on work carried out in the United Kingdom with the aim of assessing the feasibility of setting critical loads for heavy metals in soils and waters. A brief review is presented of the processes that control metals, input and output metal fluxes to soils, and soil metal pools, metal speciation in surface waters, and toxicity modelling.

Catchment processes

Entry of metals into soil or water The first process to consider is whether deposited Pb and Cd are in biogeochemically active forms. Put simply, deposited metal may be either relatively quickly converted into ionic forms, or it may remain inert. For bulk deposition in northern England, we have found that, of the Pb and Cd that can be determined following treatment with dilute HNO₃, at least 65% is in filterable forms. Other workers have shown that metals in aerosols collected at rural sites rapidly dissolve on immersion of the particulate matter in aqueous solution. Thus, it appears that most of the deposited metal is indeed biogeochemically active, and its behaviour can be considered and analysed in terms of the properties of ionic metals. For Pb this means Pb²⁺ and its reaction products, for Cd it is Cd²⁺ and its reaction products.

Soil processes The two most important processes that control Pb and Cd in soil are (a) solid-solution partitioning, dependent upon competition by H⁺ and other cations, and (b) transport in the soil solution, including transport of metal bound by DOC. In addition, metals may be added by weathering, or by management practices, notably fertilisation. Metals may be lost from the biogeochemically active pool by harvesting of vegetation, by burial during peat formation, by incorporation into inert forms in precipitated minerals, for example oxide concretions, and by physical erosion.

Processes associated with rock weathering Soil drainage water may pass through a weathering zone, in which dissolution of mineral matter adds major and minor solutes, including trace metals. As in the topsoil, solid-solution partitioning may take place, also conversion to inert forms, and the loss of metal in eroding particulate matter. Often, this zone

will have a higher pH than the topsoil, favouring metal retention. The weathering zone may be by-passed at high water flows.

Steady states and their attainment

In the simplest case, the only input of metal to a catchment is via atmospheric deposition, and the only output is via surface water. The situation may be modified by the other soil processes discussed above. At steady state, the input metal load (e.g. in $\text{g ha}^{-1} \text{a}^{-1}$) equals the output load, although the chemical forms of the metal are generally not the same; for example exported Pb may be mainly in organic complexes with DOC.

Steady state descriptions provide a useful framework for considering the dominant system processes. However, the time taken to reach steady state needs to be considered also. For example, if a steady state methodology for setting and enforcing critical loads were to be developed, it would be useful to know the timescale over which the system might respond to changes (both increases and decreases) in metal deposition.

Soil pools and fluxes

Some insight into timescales can be obtained by comparing observed input and output loads, together with soil metal pools. Table 1 shows some present-day results for sites in northern England. It is obvious that the loads are small relative to the pools. For example the pool of Cd in the Lake District soil would take ca. 400 years to accumulate at present loads, while the Pennine pool of Pb would take ca. 900 years to be leached at the present output rate, even if the input were stopped completely. Note however, that the soil pools were developed under much higher input loads than are presently observed. Therefore the very large pool of Pb in the Lake District soil did not take 2000 years to build up; most if it probably accumulated during the last 200 years.

This simple analysis suggests that times to steady state at these sites would be very long, compared to a human lifetime, the development of a new technology, or the period between elections! It is clearly important to perform such assessments for other locations. Pačes (1998) estimated long response times for Czech soils.

Table 1 Input and output loads of Cd and Pb to catchments in the Lake District and the Pennines (N. England).

		input	output	pool
		$\text{g ha}^{-1} \text{a}^{-1}$	$\text{g ha}^{-1} \text{a}^{-1}$	g ha^{-1}
		1	1	
Lake District	Cd	0.6	2	230
	Pb	24	9	50,000
Pennines	Cd	0.2	1	100
	Pb	10	28	23,000

Use of a simple dynamic model of metal accumulation in soil

A dynamic model was formulated using empirical expressions for solid-solution partitioning of Cd and Pb, that allowed the effect of pH to be taken into account. Speciation of the metals in the solution phase was calculated with WHAM (Tipping, 1994). The model was applied to Lake District soil, by using historical deposition functions of the kind shown for Pb in Fig. 1. Fig. 2 shows the assumed variation in soil pH, simplified from separate modelling with CHUM (Tipping, 1996). The calculated soil metal pools are shown in Fig. 3.

In the case of Pb, the calculations suggest that 99% of the deposited metal has been retained in the soil. Only now is the pool reaching its maximum value, as deposition decreases. For Cd, only 42% of the deposited metal has been retained, because its affinity for the soil solids is relatively weak. The decrease in the rate of accumulation, evident at the early part of the 20th Century, reflects soil acidification, and a weakening of Cd binding affinity. The calculated present-day soil metal pools are about half of the observed values, which is most likely explained by underestimation of the historical input loads.

Streamwater chemistry

Concentrations of Cd and Pb in surface waters (Table 2) reflect the soil and weathering interactions. The results for the Lake District streams show how metals tend to be retained at higher pH, brought about by faster weathering rates. The same effect is seen for Pb in the Pennine pools. The high concentrations of DOC in the Pennine pools are responsible for the higher concentrations of dissolved Pb than seen in the Lake District, because Pb has a relatively high affinity for organic matter.

The equilibrium speciation model WHAM / Model VI (Tipping, 1994, 1998) was used to calculate the chemical forms of dissolved Cd and Pb in the surface waters. The model takes into account complexation by DOC and inorganic ligands, pH effects, and competition by other metals, notably the abundant alkaline earth cations Mg²⁺ and Ca²⁺ and species of Al and Fe. As shown in Table 3, Cd is complexed rather little by DOC at low pH, but more so in the neutral waters, and most in the neutral water high in [DOC]. Pb is appreciably complexed in all the waters, but most in Pool Y. The free metal ion concentrations (Table 3) are the best guide to metal bioavailability, by exposure to the solution, i.e. not including uptake in particulate matter.

Table 2 Mean concentrations of dissolved Cd and Pb in streams from the Lake District (D3 – D8) and Pennine pools (X and Y).

	D3	D5	D8	Pool X	Pool Y
Stream pH	5.1	5.6	7.1	4.9	6.8
DOC mg L ⁻¹	1	1	1	22	15
dissolved Cd nM	0.6	0.7	0.2	1.0	1.1
dissolved Pb nM	2.0	1.1	0.3	17	11

Table 3 Computed metal speciation. [DOC] is in mg L⁻¹. Metal concentrations in mol L⁻¹.

	pH	[DOC]	% Cdorg	% Pborg	log [Cd ²⁺]	log [Pb ²⁺]	log [Al ³⁺]
D3	5.1	1	3	15	-9.2	-8.7	-5.6
D5	5.6	1	15	40	-9.2	-9.0	-5.8
D8	7.1	1	37	84	-10.0	-10.7	-10.3
Pool X	4.9	22	44	62	-9.6	-8.8	-6.9
Pool Y	6.8	15	64	94	-9.7	-10.0	-9.6

Toxic levels of Cd and Pb

Table 4 shows some literature data from toxicity testing involving Cd, Pb and Al, with toxic levels expressed in terms of free metal ion concentrations. Comparison of the results for Cd and Pb with the concentrations of Cd²⁺ and Pb²⁺ of Table 3 suggests that the surface water metal concentrations are appreciably lower than levels required to bring about 50% lethality in acute tests. Also, the concentration of Pb²⁺ required to exert a detectable sub-lethal toxic effect at pH 7, is one-to-two orders of magnitude greater than the observed values for the neutral pH waters (i.e. stream D8 and Pool Y). However, the concentration of Al³⁺ required to cause 50% lethality at pH 5 is very similar to the values estimated for streams D3 and D5.

These results suggest that in some cases Al may pose a greater toxic threat to freshwater fish than do Cd and Pb. However, the data presented are only illustrative, and a full review of metal toxicity data is required before firm conclusions can be drawn. Furthermore, the threat of Al may diminish as a result of acidification reversal. It is important to bear all potential toxicants in mind when assessing environmental effects.

Table 4 Some toxicity data for fish in soft waters. LOEC = lowest observed effect concentration. Concentrations in mol l⁻¹.

Cd	Pb	Al
pH 5 log (LC ₅₀) = -6.6	pH 7 log (LC ₅₀) ~ -6.2	pH 5 log (LC ₅₀) = -5.7
pH 7 log (LC ₅₀) < -8.4	pH 7 log(LOEC) ~ -8.3	
Cusimano et al. 1986	Mance 1987	Roy & Campbell 1997

Describing metal toxicity with the “biotic ligand” concept

It will be noted from the data for Cd in Table 4 that metal toxicity is not uniquely described by the concentration of the free metal ion; the LC₅₀ at pH 7 is lower than that at pH 5. Toxicity at a given concentration of Cd²⁺ can also depend upon concentrations of other metals, such as Mg and Ca. Further, metal toxicity can be relieved by the addition of DOC or bicarbonate, while keeping the pH and total dissolved metal concentration constant. To take these effects into account, the concept of the “biotic ligand” can be used (Morel 1983; Campbell, 1995; Paquin et al, 2000). The basic idea is that the metal exerts its toxic effect by interacting with a receptor possessed by the organism – i.e. the biotic ligand. The greater is

the occupancy of this ligand by the metal, the greater is the toxicity. The biotic ligand has equilibrium constants that characterise its binding of the toxic metals and other cations (H^+ , metals), and these can be combined with the equilibrium reactions in the solution phase to calculate the extent to which toxic metals occupy the receptor sites. Thus, the description of toxicity is essentially reduced to a chemical speciation calculation.

The biotic ligand approach might provide a straightforward way of connecting metal concentrations in surface waters to toxic effect, without having to specify different critical limits, dependent upon, for example pH, [DOC] and water hardness. The critical limit would be defined in terms of the loading of the biotic ligand. This approach merits careful evaluation by toxicologists and biogeochemists.

Acknowledgements

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5. Posters and other oral presentations

5.1 Recent and future activities of ICP Modelling and Mapping related to heavy metals

*Gudrun Schütze, German Federal Environmental Agency,
on behalf of Hans-Dieter Nagel, acting chairman of ICP Modelling and Mapping*

Currently two Protocols of the Convention on Long-range Transboundary Air Pollution are in the main focus of the ICP Modelling and Mapping. These are the Multipollutant Protocol (Gothenburg 1999) and the Protocol on Heavy Metals (Århus 1998), which will probably be revised in 2004 or 2005, respectively.

Article 6 (g) of the Protocol on Heavy Metals sets the task to derive an effects-based approach for emission reductions of these persistent pollutants, especially for lead, cadmium and mercury as first priority metals. In the past years methods to calculate steady-state critical loads for heavy metals in terrestrial and aquatic ecosystems have been elaborated.

Two international working groups have been established according to recommendations of the 17th Task Force Meeting (May 2001, in Bratislava, Slovak Republic). A common report of both groups, reflecting the work in 2001 (DeVries et al. 2002)¹, is available. This work will continue until 2003 and will include mercury.

According to the medium term workplan of the Working Group on Effects (WGE) ICP Modelling and Mapping, in particular the CCE, started a first official call for data on critical loads for cadmium and lead in terrestrial and aquatic ecosystems in December 2001. The main goal was to get experience in the work with these pollutants, to compare mapping results and to find conclusions and recommendations for the further work. Results of the international working groups on critical limits and transfer functions have been applied in a Guidance (DeVries et al 2001)² for the response to this call for data. An evaluation of the national responses will be presented at the 12th CCE Workshop and the 18th Task Force Meeting of ICP Modelling and Mapping (back to back, 15 – 19 April 2002, in Sorrento, Italy). Those mapping exercises will continue in 2003. A progress report on preliminary mapping results of critical loads and exceedances for heavy metals (in collaboration with EMEP/MS-CHE) will be provided to WGE in May 2002. ICP Modelling and Mapping plans to be prepared for the upcoming revision of the Protocol on Heavy Metals in 2005.

More details on the work of ICP Modelling and Mapping, including the report on the two international working groups on Critical Limits and the medium-term workplan of the programme can be found on the web site www.icpmapping.org.

¹ De Vries, W., G. Schütze, R. Farret, M. Ashmore, B. J. Groenenberg and P. Römkens (2002) Proposed harmonised critical limits and transfer functions for the calculation of critical loads for lead and cadmium, UN/ECE ICP Modelling and Mapping, international working groups on harmonisation of Critical Limits and transfer functions of heavy metals, final report of working phase 1 (June to Nov 2001)

² De Vries, W., G. Schütze, P. Römkens and J.-P. Hettelingh (with contributions by R. Farret, M. Ashmore and B.-J. Groenenberg) (2001): Guidance for the Calculation of Critical Loads for Cadmium and Lead in Terrestrial and Aquatic Ecosystems, provided in preparation of the Call for Voluntary Submission of Critical Loads of Lead and Cadmium by CCE Bilthoven in Dec. 2001

5.2 Trace metal monitoring in the Lochnagar ecosystem.

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Introduction

Over the last 20 years Lochnagar has become an important part of both national and international monitoring networks and research programmes. The loch lies to the south-east of the Cairngorm Mountains in Scotland and experiences some of the harshest conditions in the UK. Its altitude and underlying geology also make it particularly sensitive to atmospherically deposited pollutants. Further, prevailing south-westerly winds carry pollutants to the site from the main industrial centres of the UK.

The monitoring of trace metals started in 1996, when sampling for the EU MOLAR project and a linked PhD study (Yang, 2000) began. The combined aims of these studies was to try and link depositional fluxes of metals at Lochnagar to the lake sediment record in such a way that historical deposition could more accurately and quantitatively be determined. Since then, monitoring has continued with support from the Department of the Environment, Food and Rural Affairs (DEFRA).

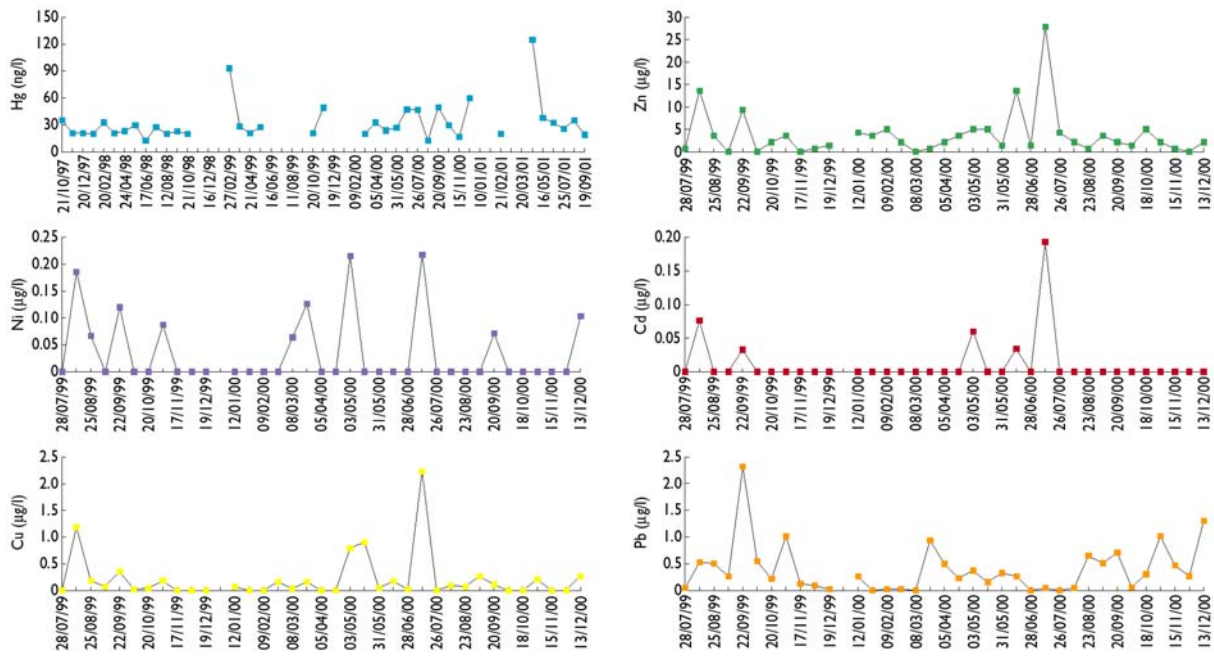
Examples of the trace metals data obtained from the main ecological compartments are shown on this poster. However, multi-core sampling of the lake sediment basin and catchment soils have also been undertaken to ascertain storage of historically deposited metals. More recently, size-fractionated zooplankton (63 – 200 µm and >200 µm and macro-invertebrate sampling have also been included. More details of the sampling and analytical procedures can be found in Curtis (2002)

Bulk deposition

NILU-type bulk deposition collectors are deployed at the site and emptied fortnightly. Samples are acidified to 1% Aristar HNO₃ and analysed for a suite of trace elements by inductively coupled plasma – mass spectrometry (ICP-MS). A separate IVL-type collector has been installed for Hg deposition. Samples are collected monthly and sent to the Norwegian Institute of Air Research (NILU) for analysis by cold vapour – atomic fluorescence spectroscopy (CV-AFS). Recently samples have additionally been sent to IVL in Sweden for methyl Hg analysis.

Essential information on meteorological parameters are monitored automatically at Lochnagar. These include air temperature, air pressure, wind speed and direction, relative humidity and rainfall. Net radiation and solarimeter sensors were added in August 2000. These measurements are ongoing.

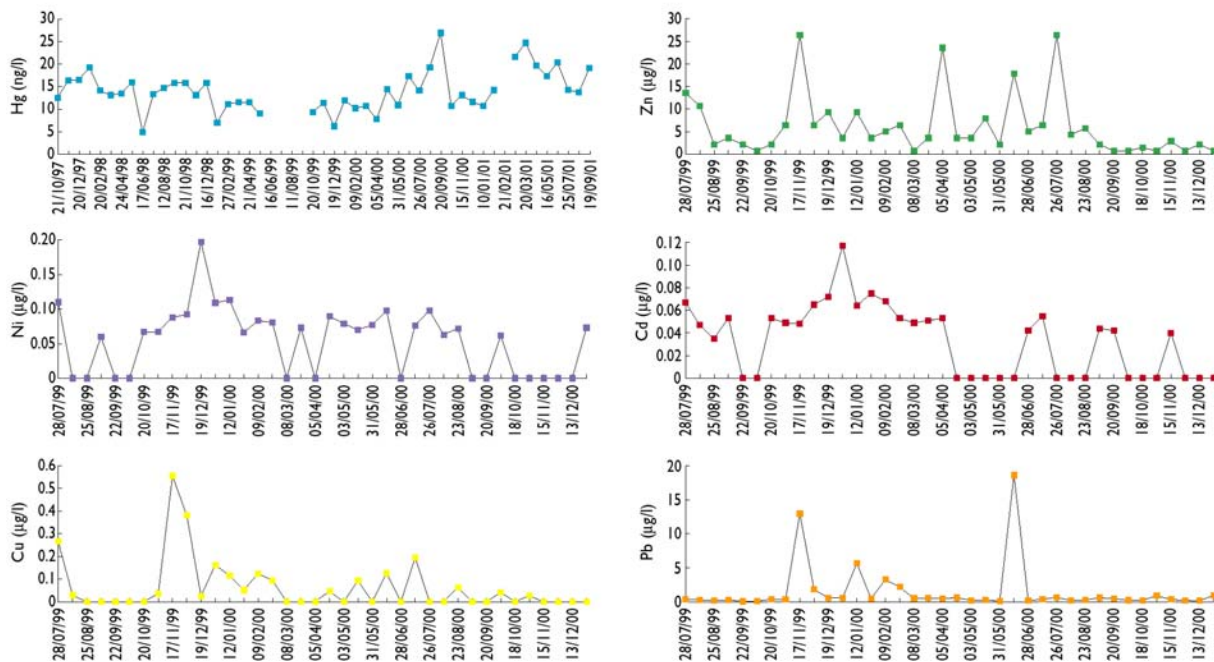
Bulk deposition



Lake water

Lake water samples are collected by submerging a rigorously acid leached 250 ml Teflon bottle approximately 20 cm beneath the surface of the water near the outflow where the lake water is well mixed. Samples are taken fortnightly for trace metal analyses and monthly for Hg. Water column temperature is measured using a chain of nine thermistors recording every hour. Further, an automated pressure sensor located in the outflow and recording every 15 minutes allows an accurate assessment of loss of metals to the system.

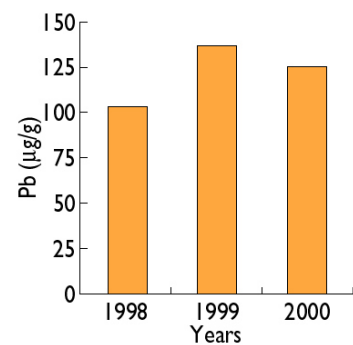
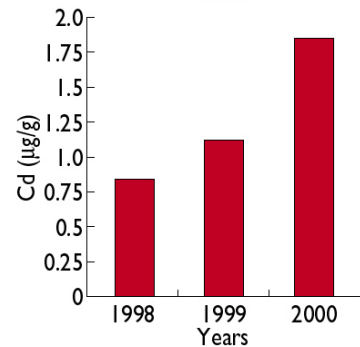
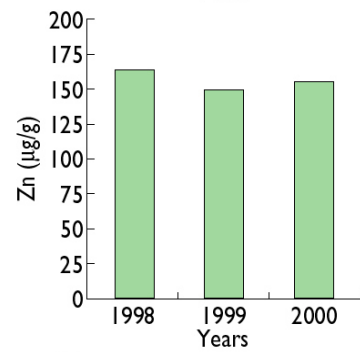
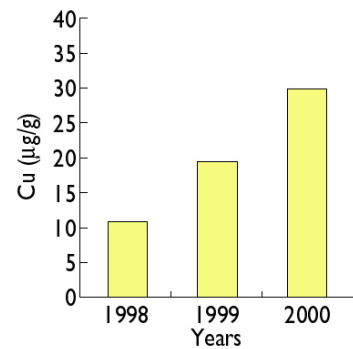
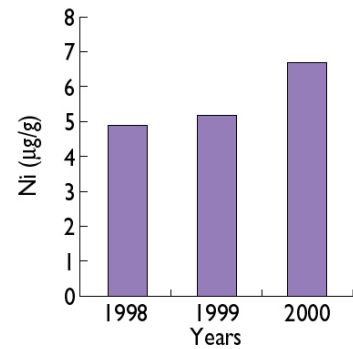
Lake water



Sediment trapping

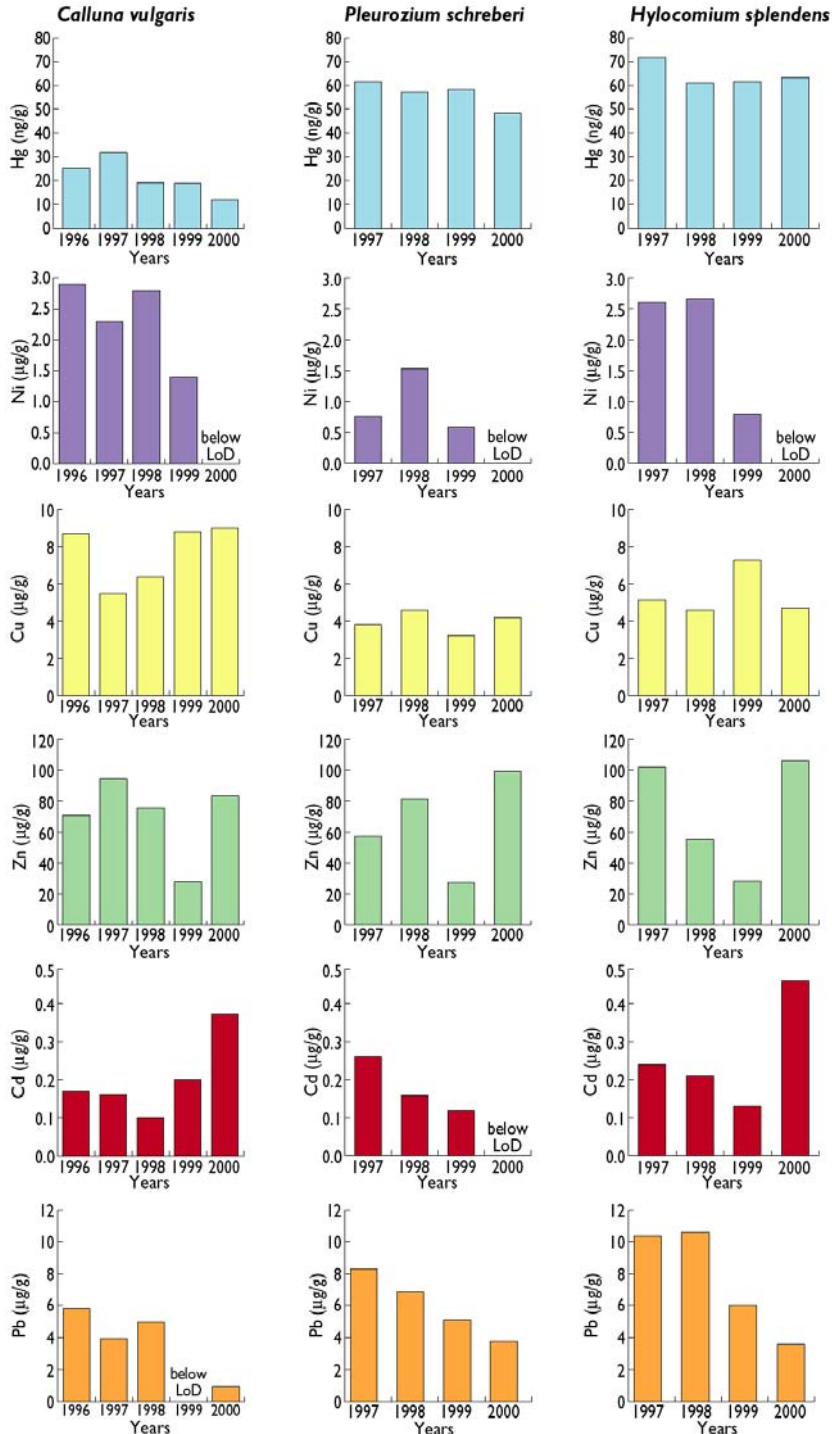
Sediment trapping at Lochnagar began in 1991 as part of the UK Acid Waters Monitoring Network. The sediment traps, deployed c.1m above the sediment-water interface, are a simple tube design with a diameter of 5 cm and an aspect ratio (length to diameter) of 7:1. From 1998, an additional array of three traps was deployed at c. 2m below the water surface. However, samples prior to 1998 were preserved for diatom analysis making them unsuitable for metal measurements. Samples are now collected untreated and freeze-dried making them suitable for analysis of trace metals including Hg.

Deepwater sediment traps



Catchment plants

Samples of the main terrestrial plant species are collected annually in late summer. These include mosses, *Pleurozium schreberi* and *Hylocomium splendens*; grasses and rushes, *Nardus stricta* and *Juncus sp.*; and ericaceous species *Calluna vulgaris*, *Vaccinium myrtillus* and *Vaccinium vitis-idaea*. Leaf and shoot samples for each species are collected at various locations around the catchment and then combined to form a single sample. The sampled vegetation is rinsed with deionised water and stored cool until freeze-dried prior to analysis.



Aquatic macrophytes

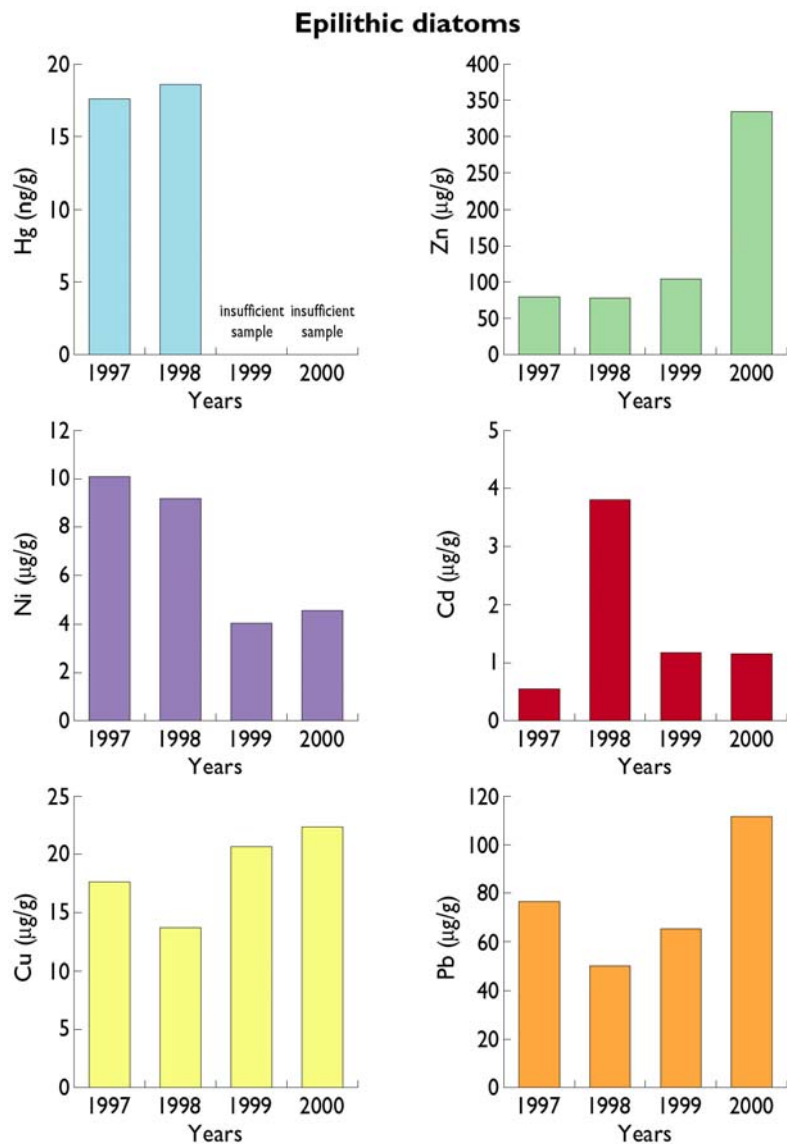
Aquatic plants are collected using an Ekman grab operated from an inflatable boat, again during late summer. This grab sampling technique cannot guarantee collection of species especially as many do not grow extensively within the loch. For this reason sampling of all selected species is not always possible in each year. However, the main species collected are: liverworts, *Nardia compressa* and *Scapania undulata*; aquatic mosses, *Fontinalis antipyretica* and *Sphagnum auriculatum*, and the aquatic macrophyte, *Isoetes lacustris*. Once sampled by the Ekman grab, the entire aquatic growth (whole plant excluding root) is collected, washed, freeze-dried prior to analysis.

Epilithic diatoms

Artificial substrates are deployed in the littoral areas of the loch in the spring of each year and retrieved in late summer. Diatom growth is removed and stored cool until freeze-drying. The amount of diatom growth on the substrates is never very extensive in Lochnagar and the amount collected, when freeze-dried, represents only a very small mass of material. On occasion, this does not permit the full suite of analyses to be undertaken.

Zooplankton

Zooplankton samples are collected annually in late summer by using horizontal and vertical hauls of a 200 µm mesh net from an inflatable boat in the deep-water area of the loch. The zooplankton are stored in a polyethylene bottle and then filtered and washed prior to freeze-drying.



Conclusions

- Hg data suggest that atmospheric deposition has increased over the last three years. A longer dataset is needed to follow, and confirm, this trend
- Hg deposition concentrations are greater than their equivalent lake water concentrations. This suggests that Hg is bound and stored in catchment soils. This is supported by other studies and implies that there is a massive store of Hg and other trace metals in the catchment soils which could be released as a result of, for example, future climate change.
- Other metals show a decline in deposition, and all except Pb show a decline in lake water concentrations.
- V and Cu, like Hg, show deposition concentrations greater than lake water concentrations most of the time. However, all metals have higher concentrations in lake water than deposition during the winter period November 1999 – February 2000. The reason for this is currently, unclear, but maybe due to wind directions from a more northerly (less polluted) direction during the winter.
- Most terrestrial plant species followed similar decreasing trends to those of atmospheric deposition, suggesting possibilities as a monitoring tool. *Hylocomium splendens* and *Pleurozium schreberi*, widely and inter-changeably used in monitoring programmes, generally showed good agreement with atmospheric trends and with each other.
- Reeds and grasses (*Nardus stricta* and *Juncus sp.*) showed poor agreement with atmospheric deposition trends.
- Aquatic plants showed less agreement with depositional trends and generally showed no trend or an increase over the period. This may be due to increased inputs from the catchment.
- Epilithic diatoms on artificial substrates showed limited usefulness primarily due to the low amounts of material produced. They may be more useful at more productive sites.
- Sediment traps show very good potential for monitoring lake metal trends and suggest catchment inputs may be very important.
- Longer periods of monitoring are required to identify any trends. Monitoring needs to be undertaken at other upland sites to confirm Lochnagar results. In particular extended spatial monitoring is particularly important for Hg, as there are so few UK data.

Acknowledgements

We thank Jo Porter and members of the ECRC for sampling at Lochnagar, Spiros Pergantis (University College London), John Boyle (University of Liverpool) and Torunn Berg (NILU) for help with metals analyses and the EU and DEFRA for funding.

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5.3 Heavy metals in the Polish Tatra Mountains

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Mountain lakes situated far from pollution sources, hardly accessible and with little human activity in their catchment areas, might be loaded by airborne pollutants even from distance sources. Due to poor buffering capacities of soil and rocks and sparse vegetation cover in the watersheds, high mountain lakes are very sensitive to acidification. Since 1992 the chemistry of wet deposition and water of two lakes: Długi Staw and Zielony Staw situated in the Polish Tatra Mts (1783 and 1632 m e.s.l.) have been studied. Lake water samples have been taken fortnightly at the outflow from the lakes. Weekly precipitation has been collected in vicinity of the studied lakes. A dominant role of precipitation quality on chemical composition of the lake has been shown. Seasonal variability in lake water chemical composition is caused mainly by seasonal changes in meteorological conditions.

Heavy metals in lake water and precipitation have been determined since November 2000. Heavy metal concentrations in the precipitation from the Tatra Mts has been four time lower than in the precipitation from the highly urbanized Silesia Region. However, high precipitation volume (average 1600 m³/year) result in the fact that the Tatra catchment areas are loaded with a relatively high deposition of Cd, Pb, Zn, and Cu (respectively about 0.5, 4, 130 and 12 mg/m² year) from the air. The up-to-date results prove a distinct effect of precipitation on metal content in lake waters. The highest concentrations of heavy metals were noted during melting periods and after intensive rain. Higher metal concentrations were recorded in the more acidified water of Długi Staw. Both lake basins turned out to better absorb Zn and Cu of atmospheric origin than Cd and Pb.

The level of heavy metal concentrations in the Tatra Mountain lakes is significantly higher than in Scandinavian lakes, however it is similar to the concentration levels noted in the Czech waters. Samples from the Tatra lakes taken sporadically in the past indicated much higher heavy metal concentrations. Also analyses of sediment cores from both lakes made in the framework of AL:PE Program in 1993 showed elevated contents of heavy metals in comparison to sediments of other European mountain lakes. A systematic drop in emission of heavy metals in Poland and in Europe results in reduction of their deposition from the atmosphere. Nevertheless, further monitoring studies are needed to assess the effect of deposition changes on the catchment areas of the Tatra Mountain lakes.

5.4 Heavy Metals In Alpine Streams. Comparison between GFAAS and Voltammetry (Southern Central Alps, Switzerland)

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Heavy metals in high mountain streams and lakes are present in very low concentrations, often lower than the quantification limits of a common analytical method, Graphite Furnace Atomic Absorption (GFAAS). The highest performance for trace metals determination is achieved with ICP-MS, but this method is very expensive. The study described in this paper was designed to test the performance of a less well known but cheaper method: voltammetry.

A collaboration between the Ufficio Protezione e Depurazione Acque (UPDA-SPAAS) in Lugano (CH) and the Metrohm AG in Herisau (CH) was started to compare GFAAS with the voltammetry method, for the analysis of metals in waters characterised by low ions and organic carbon concentrations (<1500 µeq l⁻¹ and 1.5 mg l⁻¹, respectively).

The UPDA-SPAAS is involved in the International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP waters) and the Convention on Long-Range Transboundary Air Pollution, and since 2000, with the support of the Federal Office for Environment, Forests and Landscape, it has been monitoring 4 alpine streams and 20 alpine lakes located on the southern side of the Swiss Central Alps.

12 samples were analysed to compare GFAAS and voltammetry. 8 were taken in December 2001 and January 2002 in the 4 mountain streams, 2 were synthetic samples and 2 comprised the NIVA ring test 2001 [RT-E, RT-F, Håvind, 2001]. The metals determined were Zn, Cd, Pb, Cu and Ni. Co was also measured by voltammetry.

The voltammetry analyses were performed following the Metrohm Application Bulletin 231. Stream samples could be analysed without sample preparation, whereas ring test samples were analysed in HCl 0.17 M after UV digestion to overcome matrix problems. The two synthetic samples were analysed with and without UV digestion. The quantification limit is 50 ng l⁻¹ for all the heavy metals determined. In this working range it was possible to determine Zn, Pb, Cu, and Ni for all the samples, with the exception of Zn in the digested solution, due to the smaller working range produced by the interference of high H⁺ concentrations. Cd was determined only in the ring tests and in the synthetic samples because concentrations were above the LOQ. However, the LOQ of Cd can be lowered by using a specific electrode that allows longer deposition time.

GFAAS analyses were performed following the Varian manual [Rothery, 1988]. All samples were analysed at least three times; no sample preparation was necessary. The quantification limits are 0.5 µg l⁻¹ for Zn, 0.15 µg l⁻¹ for Cd, 1.5 µg l⁻¹ for Cu and 3 µg l⁻¹ for both Ni and Pb.

In this working range all the metals could be determined only in the ring test and the synthetic samples; in the stream samples only Zn was determined.

A comparison between GFAAS and voltammetry analyses can be made in the stream samples only for zinc, because the concentrations of the other metals in the majority of the samples are below their GFAAS LOQ. The results obtained with these two analytical methods are quite similar, even though those obtained by voltammetry are slightly higher than those produced by GFAAS.

A further, complete comparison between the two analytical techniques was possible for the two synthetic and the two ring test samples because of their higher metal concentrations. Certified and median values are also available for these samples. Both analytical methods produced reliable results (Figure 1).

Both methods gave good results in the analysis of metal concentrations higher than LOQ values. However, voltammetry made it possible to quantify Pb, Ni and Cu concentrations lower than GFAAS LOQ, allowing these metals to be determined in alpine stream samples. Since one of the main objectives of the Swiss ICPw project is the long-term monitoring of alpine streams and lakes, the high performance of voltammetry at low concentrations could make it a valuable analytical tool.

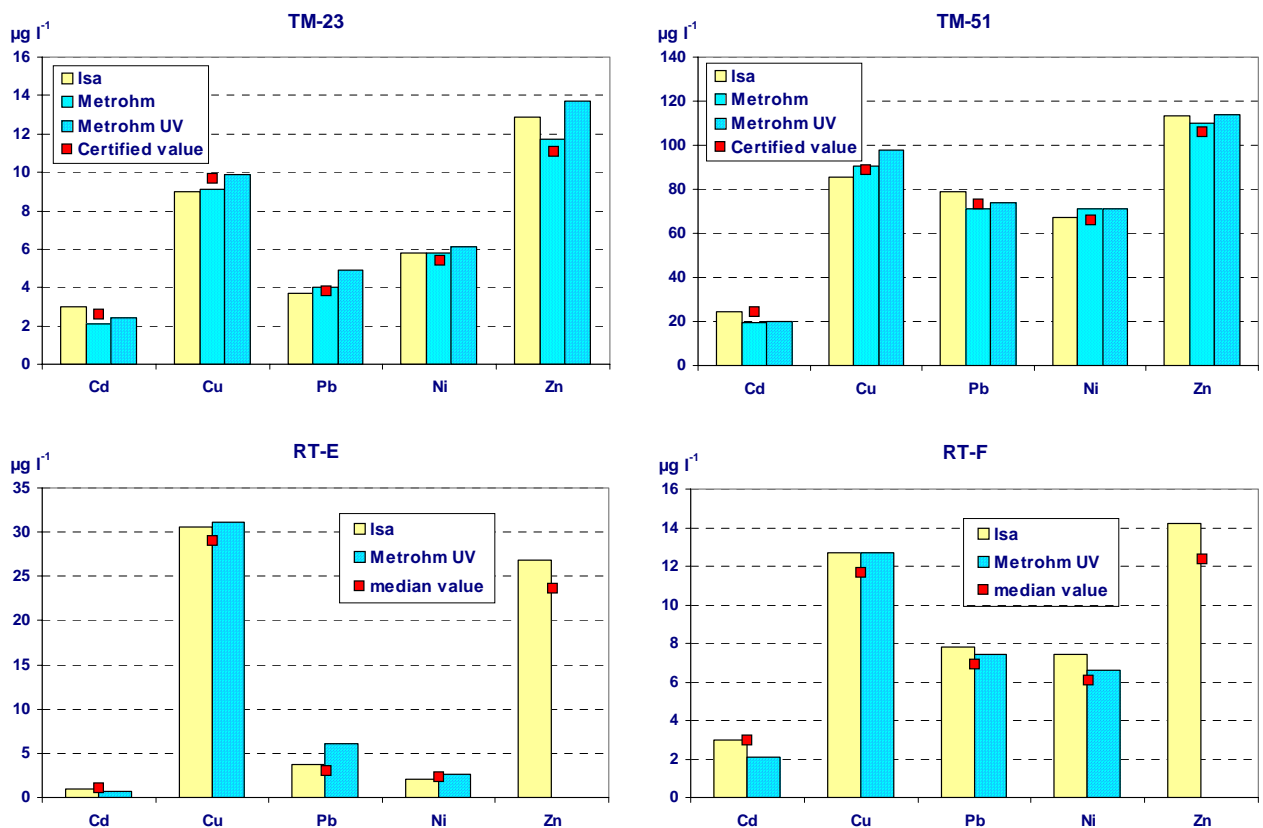


Figure 1. Comparison between voltammetry and GFAAS results for synthetic (TM-23 and TM-51) and ring test samples (RT-E and RT-F)

References

Håvind, H.: 2001. Intercomparaison 0115. pH, K25, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, reactive and non-labile aluminium, total organic carbon, chemical oxygen demand, Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-Report SNO 4416-2001, ICP-Waters Report 64/2001, ISBN 82-577-4059-4, 81 pp.

Rothery E., 1988: Analytical Methods for Graphite Tube Atomizers, Publication No. 85-100848, Varian Techtron pty. Limited, Mulgrave, Victoria, Australia

Appendix A. Workshop program

Monday, 18 March 2002

Opening session - Chair: Merete Ulstein, NIVA

- 13:00 Welcome – Harald Dovland, Chairman of the Executive Body of the LRTAP
- 13:20 Introduction, background and objectives – Brit Lisa Skjelkvåle, NIVA
- 13:35 Presentations from representatives from WGE and other ICPs; current status of work related to heavy metals.

Afternoon session – Chair: Tatjana Moiseenko, Russian Academy of Sciences

- 14:00 Ecosystem functioning: Biological impacts of pollution of heavy metal in aquatic ecosystems; examples from ongoing projects.
Bjørn Olav Rosseland, NIVA, Norway
- 14:45 Monitoring methods of heavy metals in surface waters
Steve Norton, University of Maine, USA
- 15:30 Critical limits for heavy metals in surface waters - a state of the art review
Stefan Løfgren, SLU, Sweden
- 16:00 Dose/response relationships for Hg in surface waters
Markus Meili, ITM, Sweden
- 16:30 Dose/response relationships for Pb and Cd in surface waters
Ed Tipping, Centre for Ecology and Hydrology, UK

17:00 - 18:00 Poster presentations, Chair: Brit Lisa Skjelkvåle, NIVA

Tuesday 19 March

09:00 – 12:00 Working groups

- 12:00 - 13:00 Lunch
- 13:00 - 15:00 Excursion in Lillehammer/Maihaugen - alternativ skiing
- 15:00 - 17:30 Working groups

Wednesday, 20 March

Chair: Merete Ulstein

- 08:30 Presentations of the results from the working groups
- 10:30 Coffee break
- 10:45 Discussions - future work - conclusions
- 12:00 Close

Questions to the working groups

Critical limits for heavy metals in surface waters

Chair: Espen Lydersen, NIVA, Norway

Rapporteur: Gudrun Schuetze, Økodata, Germany

What is a Critical limit?

Problems

Limitations

Etc....

Expected outcome:

Recommended critical limits for Cd, Pb and Hg in surface waters, or suggested functions (including hardness, TOC etc)

What more work is needed to establish acceptable limits for use in the Critical loads work?

Monitoring methods for heavy metals in surface water

Chair: Anders Wilander, SLU, Sweden

Rapporteur: Jaakko Mannio, FEI, Finland

Why should we monitor heavy metals in surface waters?

Which monitoring methods should we use? (aquatic mosses, sediments, lake water, running water, aquatic biota)

What are their possibilities and limitations?

What is the relation between effort and results?

What basic information do we need to make a dedicated monitoring programme? (regional surveys of lake water and running water, etc.)

Which analytical methods should be recommended?

Expected outcome:

Which monitoring methods and analytical methods will the workshop recommend as adequate for monitoring effects of long-range transport of heavy metals on surface water quality and biota? The output should be used as a draft outline for a manual.

Dose/response relationships for heavy metals in surface waters

Chair: Alan Jenkins, CEH, UK

Rapporteur: Max Posch, RIVM, The Netherlands

What is the current status of steady-state and dynamic models for heavy metals in surface water?

How to proceed in the future - which models to focus on?

...for Pb?

...for Cd?

...for Hg?

Expected outcome:

Exchange of knowledge on how to model impact of heavy metal deposition for surface waters. Agreement on how to proceed with future work.

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Appendix C. Reports and publications from the ICP-Waters Programme

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