

## **ICP Waters**

20 year with monitoring effects of long-range transboundary air pollution on surface waters in Europe and North-America

International cooperative programme on assessment and monitoring of acidification of rivers and lakes

Convention on long-range transboundary air pollution



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ICP Waters

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### Foreword

The Convention on Long-range Transboundary Air Pollution has, since its adoption in 1979, based its political decision making upon sound science and the results of its scientific bodies. From the start, its Working Group of Effects has reported on the effects of sulphur compounds (acidification) on freshwaters and other parts of the environment.

The Convention's effects work was soon organized under International Cooperative Programmes (ICPs), and for rivers and lakes, ICP Waters provided "on a regional basis, the degree and geographic extent of acidification of surface waters." This work continues at increasing levels of sophistication whilst ICP Waters has also considered additional challenges such as the chemistry and effects of nitrogen deposition, persistent organic pollutants and heavy metals.

While the ICP was briefly led by Canada, Norway soon offered facilities for a Programme Centre and took over leadership in 1987. From the outset, ICP Waters has been a model of cooperation between UNECE countries, bringing scientists together from across the region to assess results and report to the Convention's Parties. It has been a vital driving force for protocols to cut emissions of sulphur and nitrogen.

In recent years the Programme has developed biological response relationships, critical loads estimates and dynamic models to provide greater insights into the effects of, and recovery from, pollution. However, monitoring has always been the basis of ICP Waters and the work has always been well supported by the Programme Centre at NIVA and the subcentre at the University of Bergen. ICP Waters data held by the Centre are now some of the most detailed, long-term measurements for freshwaters, being used for purposes never envisaged by those who developed the monitoring network. With emissions falling, ICP Waters is showing that there is environmental recovery in many areas. Improvements are slow and we still need further political action, but the positive signals are providing encouragement for this.

At this important stage in the development of the Convention there are still major challenges in our science. I congratulate ICP Waters on its many successes and its important contributions to the Convention's work and I encourage it to continue its efforts to support the Convention into the future.

#### Keith Bull

Secretary to the Convention on Long-range Transboundary Air Pollution UNECE

## 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 UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) in July 1985.

Since then, ICP Waters has been an important contributor documenting the effects of the implemented Protocols under the Convention. Numerous assessments, workshops, reports and publications – two of which appeared in Nature and Science – covering the effects of long-range transported air pollution have been published over the years.

The ICP Waters Programme Centre has found that success in running such a programme stems from a scientifically sound and active Task Force, focused aims, consistent programme management, frequent assessment of data, a detailed programme manual and frequent laboratory intercomparison exercises. But most of all, the Programme is dependant on high quality data from national monitoring programmes and active participation from national focal centres.

We are very grateful to all countries and all participating scientists that have contributed to the programme over the years, sharing their data and their knowledge. This cooperation is the basis for the work and the success of the Programme. ICP Waters is one of seven ICPs under the Working Group on Effects (WGE) under the LRTAP Convention. Close cooperation with other Programmes under the WGE and the continuous support from the Chairpersons of the WGE are greatly appreciated and has also been very valuable for the development of the programme. The Secretariat in Geneva has always been very supportive and important for running the programme as smoothly as possible.

Ms Berit Kvæven (Norwegian Pollution Control Authorities, SFT) has been Chairperson since the initiation of the Programme while the Programme Centre has been located at NIVA in Oslo, and the Programme subcentre at LFI, University of Bergen.

With more than 20 years of Programme activity, it is timely to take a look back and present an overview of its most important achievements and our view for ICP Waters in the future.

August 2008 Brit Lisa Skjelkvåle Programme Manager

## Abstract

Surface waters are much more responsive than either soils or terrestrial vegetation to changes in long-range transported acid deposition and are thus highly suitable for monitoring effects of measures to reduce emissions of air pollution.

The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters) was established under the Executive Body of the UNECE Convention on Longrange Transboundary Air Pollution (LRTAP) in July 1985. Since then, ICP Waters has been an important contributor documenting the effects of the implemented Protocols under the Convention. Numerous assessments, workshops, reports and publications covering the effects of long-range transported air pollution have been published over the years.

This report presents the major accomplishments of that work including acidification status of lakes and rivers in acid-sensitive areas in Europe and North America, biological recovery, long-term data on nitrate and dissolved organic carbon in surface waters, empirical support for critical loads of acid deposition, effects of climate change on acidification and recovery, heavy metals and persistent organic pollutants in freshwaters, predictions of future acidification status of surface waters using dynamic models, method harmonization and quality control.

Long-term monitoring data are the basis for all activity in ICP Waters. Monitoring data provide the ground truth upon which all modelling work such as modelling of critical loads relies. Continuation of the national programmes that monitor ecosystem effects is imperative in order to reliably document the effects of air pollution reduction measures.

The long-term comprehensive data sets from background sites in (semi-)natural ecosystems collected by ICP Waters are valuable also for assessing ecosystem impacts of climate and global change.

> **River Vedggio, Switzerland.** Photo: Sandra Steingruber, Switzerland





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## **Major achievements of ICP Waters**

## Lakes and rivers show strong signs of recovery in response to reduced acid deposition

Surface water quality in acid-sensitive areas has improved strongly in Europe and North America since the 1980s. The consistent pattern of chemical recovery (decreasing sulphate, and increasing pH and alkalinity) across a large number of sites is the strongest evidence that emission control programmes are having their intended effect. Monitoring data from the ICP Waters programme document that the reductions in acid deposition are mirrored in improved water quality in most regions. In many areas, water quality is now sufficient for the return of acid-sensitive species of fish, invertebrates and mussels.

## Biological recovery is slow and not widespread

Biological monitoring in the ICP Waters programme focuses on acid-sensitive invertebrate species. Improved chemical water quality has resulted in recovery of aquatic biota in the Nordic countries, in Canada, the UK and the Czech Republic. In the most acidified regions in Europe signs of biological recovery are more difficult to find. This may be because the water quality here has not recovered sufficiently to permit widespread biological recovery. The lack of documented examples of biological recovery is related to both the dynamic nature of biological responses, but also to a lack of appropriate long-term monitoring data.

## Distinct lack of chemical recovery in some regions

Despite reduced sulphate deposition, some regions show no reductions in sulphate concentrations in surface waters and no improved water quality. Clear examples are the Blue Ridge Mountains in Virginia (USA) and the Harz mountains in Germany. Here, deep soils with a large sulphate-adsorption capacity dominate and sulphate concentrations in surface water are controlled by desorption of S that was deposited in the past decades.

## Long-term trends in nitrate in surface waters are poorly understood

Nitrogen deposition does not show the widespread declines that we observe in S deposition. Most deposited N is retained in soils and vegetation and is not leached. Nitrate in surface waters exhibits positive, negative and neutral trends, unlike the decreasing trends in sulphate that show strong dependence on changing S deposition in most of Europe and North America. There is some evidence of reduced nitrate concentrations in regions where N deposition has declined. Elsewhere, trends in nitrate in surface waters are thought to be related to climate, forest growth and N saturation, or are simply not understood. Acid-sensitive ecosystems are continually enriched with nitrogen, which increases the probability of future acidification and eutrophication due to nitrate leaching.

## Increases in dissolved organic C are related to reduced S deposition

Trends in dissolved organic C (DOC) have been positive in almost all the ICP Waters sites in North America and Europe, beginning in the early 1990s, especially in areas where acid deposition has been considerable. This has led to a significant browning of surface waters. The extended database compiled by ICP Waters to assess DOC trends is the largest region-wide overview (>500 lakes and rivers in northern Europe and North America) that documents the trends in DOC. The DOC trends are related to declining atmospheric loads of sulphate. The browning of the waters is thus a sign of ecosystem recovery from acidification. In near coastal regions, seasalt deposition also affects DOC concentrations and trends.

## Modelled critical loads for surface waters are supported by ICP Waters data

Critical loads of acidifying components for surface waters have been modelled and reflect catchment sensitivity to acid deposition. Calculation of the difference between the *critical* load and *actual* load of S deposition results in the critical load *exceedance* – which is either positive

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(load of acid deposition is too high compared with the acid-tolerance of the water body) or negative (no exceedance). Measured lake chemistry in ICP Water sites indicates that the acid neutralizing capacities (ANC) of the lakes are consistent with the calculated critical load exceedances. In lakes with no exceedance, ANC was mostly above the critical lower limit. Conversely, in those lakes where critical loads were exceeded, ANC was mostly below the critical lower limit. The agreement between empirical lake chemistry and modelled critical loads indicates that critical load assessments for surface waters have a solid empirical foundation.



## Many sites in several regions of Europe will remain acidified after 2010.

Chemical recovery of many ICP Waters sites will not be sufficient to sustain biological recovery by 2010, according to predictions from dynamic acidification models given scenarios where S emissions are reduced according to the Gothenburg Protocol. Calculation of critical loads for acidifying components is a central activity in the LTRAP Convention work. Dynamic models provide an extension to steady-state critical load models by predicting the timescale of chemical recovery related to emission reductions. Dynamic models can also be used to determine deposition levels required to achieve a prescribed target chemistry in surface waters in a given timeframe, and are thus directly used to determine what further emission reductions will be necessary to protect aquatic ecosystems. ICP Waters will use the expertise within the ICP Waters network to support the modelling work under the Convention and assess the possibilities for using dynamic modelling for surface waters in Europe and North America.

## Climate change will affect acidification and recovery.

Future trends in recovery from acidification may be influenced by a number of factors that are independent of emissions of acidifying components. In particular, climate change-in the form of increasing drought frequency and higher precipitation extremes, more frequent storms (and consequently more sea salt deposition) and higher temperatures-may significantly influence the behaviour of both terrestrial and aquatic ecosystems. Long-term data series show sea-salt episodes setting back biological recovery several years. The extent of N retention in a warmer climate, and consequently the future influence of N on surface water acidification, represents a key uncertainty in recovery from acidification.

#### Heavy metals and persistent organic pollutants (POPs) are found in fish, sediments and waters in remote areas

In general, the concentrations of heavy metals in ICP Waters sites not influenced by local pollution sources are low. However, a number of ICP sites have concentrations of heavy metals above the critical limit, based on national (e.g., Swedish) guidelines on assumed effects on aquatic biota. The number of ICP Waters sites does not allow a geographically comprehensive evaluation of heavy metal levels in surface waters in Europe and North America.

The results from an assessment of POPs in the aquatic environment confirm previous studies indicating that global distillation processes (also called the grasshopper-effect) leads to elevated concentrations of contaminants in fish from arctic and alpine areas. There are very few sites with trend data, but they generally show decreasing levels of legacy POPs (i.e., all POPs covered by the Stockholm Convention and the LRTAP Convention). Levels of some newly studied substances, such as brominated flame retardants (PBDE) and PFOS, are probably rising.

## High quality database with long-term data from 200 surface water sites in 16 countries

Surface waters are much more responsive than either soils or terrestrial vegetation to changes in long-range transported acid deposition. Lakes and rivers also have the advantage that they integrate responses over the entire catchment area. The ICP site network is geographically extensive and includes long-term data series (10-20 years) for more than 200 sites. The network is thus well poised to document changes that result from implementation of the protocols. The long-term comprehensive data sets from background sites in (semi-) natural ecosystems collected by ICP Waters are valuable also for detecting impacts of climate and global change. The data are and will be used to develop acidification and recovery models for both chemistry and biology.

#### Harmonized methods and quality control

Each country contributes data from national monitoring programmes. Between-laboratory quality control is necessary to assure clear identification and control of the bias between analyses carried out by individual participants of the ICP Waters Programme. Such biases may arise from use of different analytical methods, errors in the laboratory calibration solutions, or through inadequate within-laboratory quality control. The number of participating laboratories in the chemical intercomparison has increased from 9 in 1987 to 72 laboratories in 28 countries in the 21st chemical intercomparison in 2007. The intercomparison confirms that the results are generally comparable between laboratories. The purpose of the annual biological intercalibration is to evaluate the quality of taxonomic identification. The 11th intercalibration was conducted in 2007. Twelve laboratories participate on a regular basis.

#### Monitoring = ground truth

Long-term monitoring data are the basis for all activity in ICP Waters. Monitoring data provide the ground truth upon which all modelling work such as modelling of critical loads relies. Continuation of the national programmes that monitor ecosystem effects is imperative in order to reliably document the effects of air pollution reduction measures.



## 1. Controlling acid rain: the LTRAP Convention

During the 1960s and 1970s, scientists demonstrated what almost a century before had been pointed out by Robert Angus Smith (see Text box 1) and described vividly by Henrik Ibsen in his theatre play 'Brand', i.e. interrelations between sulphur emissions in continental Europe and acidification and pollution of remote areas. Also North American data pointed increasingly towards a link between atmospheric emissions of pollutants, longrange transport and ecosystem damage far away from the source of the emissions. An understanding emerged that the solution to this environmental problem needed a multilateral approach.

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The Convention on Long-range Transboundary Air Pollution ("the Convention" or the "LTRAP Convention") was the first multilateral treaty aimed to protect the environment against the growing threat of acid precipitation. It was adopted in 1979 and entered into force in 1983. Eight protocols have been signed under the Convention, which specified further commitments by Governments to control air pollution (see Text boxes 2, 3 and 4).

The need for scientific underpinning of future decisions on air pollution was recognized. The Working Group on Effects (WGE), which addresses effects of air pollutants on human health and the environment, was established. International Cooperative Programmes (ICPs) were established under the WGE to carry out more detailed studies and to begin monitoring studies of endangered ecosystems and materials. The ICPs include ICP Waters, ICP Forests, ICP Modelling and Mapping, ICP Integrated Monitoring, ICP Materials and ICP Vegetation and a Joint Task Force on Health (see Text box 5).

Based on the work done in each ICP, the WGE provides information on the degree and geographic extent of the impacts of major air pollutants on human health and ecosystems. An important part of this work is long-term monitoring. The work is underpinned by scientific research on dose-response relationships, critical loads and levels and damage evaluation.

#### Text box 1: Discovery of the acid rain problem

Acid rain was first recognised as a problem as far back as the end of the 17th Century. In 1692, Robert Boyle published his book "A general history of the air". The term "acid rain" was first used in 1872 by the Manchester scientist, Robert Angus Smith (1817-1884), in his book "Air and Rain: The Beginnings of Chemical Climatology". It wasn't, however, until the 1960's that the large scale problem of acid rain was discovered. In 1967, Odén was the first to publish a complete theory of acid rain. His initial conclusions were that:

- acid precipitation was a large-scale regional phenomenon with well-defined source and sink regions;
- rain, lakes, and seawater were becoming increasingly acidic;
- air pollutants containing sulphur and nitrogen were being transported by winds over distances of 100 to 2,000 kilometers through several nations of Europe;
- the most likely cause of acid deposition in Scandinavia was airborne sulphur blown in from Great Britain and East and West Germany; and
- the probable ecological consequences would be changes in the chemistry of lakes, decreased fish populations, leaching of toxic metals from soils into lakes and streams, decreased forest growth, increased plant diseases, and accelerated damage to materials.

As a result of these scientific studies, political action was taken to try to reduce the problem of acid rain. See Text box 2.

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## Text box 2: Important milestones before the establishment of the Convention on Long-range Transboundary Air Pollution.

#### 1967

Writing in the country's leading daily, Dagens Nyheter, the Swedish scientist Svante Odén reported a gradual increase in the acidity of the precipitation over Europe since the 1950s, with consequent damage to soil and water ecosystems. The following November the Swedish minister of industry took up the matter at a meeting of the OECD, calling for greater attention to the danger of increasing airborne emissions of sulphur and other pollutants.

#### 1972

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At the first world environment conference of the United Nations, Sweden presents a report on acidification, in which it laid emphasis on the cross-border nature of the problem. Few countries were however willing to admit that their emissions could be causing environmental damage elsewhere.

#### 1977

Publication of the results of an OECD study that had been set up in 1972 confirmed that sulphur pollution was a cross-border problem. The OECD project later evolved into the Cooperative Programme for Monitoring and Evaluation of Long-Range Transmissions of Air Pollutants in Europe (better known as EMEP).

#### 1979

In November the Convention on Long-Range Transboundary Air Pollution (LRTAP) was signed by more than thirty countries as well as the EC.

This text is cited from



Special Anniversary Section No. 4, December 2007

#### Text box 3: The Convention on Long-range Transboundary Air Pollution

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International negotiations lead to the establishment of the Convention on Long-range Transboundary Air Pollution (CLRTAP or 'the Convention'). In 1979, the Member States of the UN Economic Commission for Europe (UNECE) adopted the Convention. It went into force in 1983 and was the first step towards enforcing international emission reduction measures, and aimed at controlling air pollutant emissions in Europe and North America. Eight Protocols have so far been negotiated under the Convention, see below.

#### year Name of the Protocol 1984 Protocol on Long-term Financing of the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) 1985 Protocol on the Reduction of Sulphur Emissions or their Transboundary Fluxes by at least 30 per cent 1988 Protocol concerning the Control of Nitrogen Oxides or their Transboundary Fluxes 1991 Protocol concerning the Control of Emissions of Volatile Organic Compounds or their Transboundary Fluxes 1994 Protocol on Further Reduction of Sulphur Emissions (the Oslo protocol) 1998 Protocol on Heavy Metals 1998 Protocol on Persistent Organic Pollutants (POPs) 1999 Protocol to Abate Acidification, Eutrophication

and Ground-level Ozone (Gothenburg Protocol)

#### Text box 4: The 1999 Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone

The Protocol sets emission ceilings for 2010 for four pollutants: sulphur, NOx, volatile organic compounds VOCs and ammonia. These ceilings were negotiated on the basis of scientific assessments of pollution effects and abatement options. Parties whose emissions have a more severe environmental or health impact and whose emissions are relatively cheap to reduce will have to make the biggest cuts. Once the Protocol is fully implemented, Europe's sulphur emissions should be reduced by at least 63%, its NOx emissions by 41%, its VOC emissions by 40% and its ammonia emissions by 17% compared to 1990.

The Protocol also sets tight limit values for specific emission sources (e.g., combustion plants, electricity production, dry cleaning, cars and lorries) and requires best available techniques to be used to keep emissions down. VOC emissions from such products as paints or aerosols will also have to be cut. Finally, farmers will have to take specific measures to control ammonia emissions. Guidance documents adopted together with the Protocol provide a wide range of abatement techniques and economic instruments for the reduction of emissions in the relevant sectors, including transport.

It has been estimated that once the Protocol is implemented, the area in Europe with excessive levels of acidification will shrink from 93 million hectares in 1990 to 15 million hectares. Areas with excessive levels of eutrophication will fall from 165 million hectares in 1990 to 108 million hectares. The number of days with excessive ozone levels will be halved. Consequently, it is estimated that life-years lost as a result of the chronic effects of ozone exposure will be about 2,300,000 lower in 2010 than in 1990, and there will be approximately 47,500 fewer premature deaths resulting from ozone and particulate matter in the air. The exposure of vegetation to excessive ozone levels will be down 44% compared to 1990.

#### Text box 5: The International Cooperative Programmes under the Working Group on Effects (WGE)

- 1. ICP Forests: ICP on Assessment and Monitoring of Air Pollution Effects on Forests
- 2. ICP Waters: ICP on Assessment and Monitoring of Acidification of Rivers and Lakes
- ICP Materials: ICP on Effects of Air Pollution on Materials, Including Historic and Cultural Monuments
- 4. ICP Vegetation: ICP on Effects of Air Pollution on Natural Vegetation and Crops
- ICP Integrated Monitoring: ICP on Integrated Monitoring of Air Pollution Effects on Ecosystems
- 6. ICP Modelling and Mapping: ICP on Modelling and Mapping of Critical Loads and Levels and Air Pollution Effects, Risks and Trends

Each programme is coordinated by a Task Force that meets annually and is responsible for the detailed planning of the Programme activities. Each programme also has a Programme Centre, which is responsible for collating data and information and for reporting results. A seventh Task Force was established in collaboration with the World Health Organization (WHO) under the Executive Body

7. Task Force on Health: Joint Task Force on the Health Aspects of Air Pollution.

#### Sulphur and nitrogen emissions in Europe and North America 1980- 2005

The Convention has been successful in reducing emissions of air pollutants. Sulphur emissions in Europe have declined by 60 per cent since 1980 (**Figure 1**) while in Canada and the United States the emissions have been almost halved (**Figure 2**).

In the case of nitrogen, emissions reduction measures have been less successful (**Figure 1**, Europe and **Figure 2**, North America).

The implementation of the Gothenburg Protocol calls for annual emissions of SO<sup>2</sup> and NO<sup>2</sup> in Europe to be a maximum of 16 Tg and 15 Tg in 2010, respectively. Regarding sulphur emissions, the Gothenburg Protocol has been fulfilled while nitrogen emissions are still too high. However, as will be illustrated in chapters to come, many rivers and lakes in Europe are still too acidified to allow for biological recovery.



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dioxide emission trend (upper panel) and nitrogen oxide emission trend (lower panel) in North America (US and Canada) 1980 - 2006 (Units: Tg SO2 and Tg NO2 ). Canadian SO2 and NOx emissions for 2003, 2004 and 2006 were estimated from the emissions measured for 2002 and 2005.

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**Source for sulphur graph:** Vestreng, V., Myhre, G., Fagerli, H. Reis, S., and Tarrasón, L.: Twenty-five years of continuous sulphur dioxide emission reduction in Europe. Atmos Chem. Phys., 7, 3663-3681, 2007

**Source for nitrogen graph:** Vestreng, V., Ntziachristos, L., Semb, A., Reis, S., Isaksen, I. S. A., and L. Tarrasón: Evolution of NOx emissions in Europe with focus on road transport control measures. Atmos. Chem. Phys. Discus., Submitted 2008

US Source: 1980-1984: EMISSIONS FROM 1900 to 1997, Emission Report-Criteria Air Pollutions, USEPA, U.S. EPA, Research Triangle Park, NC 27711, 1985-1995: National Emission Trends (NET) database, Emission Factor & Inventory Group, OAQPS, U.S. EPA, Research Triangle Park, NC 27711, 1996-2006: Tom McMullen, personal communication. National Emissions Inventory (NEI), Emissions Inventory & Analysis Group; Air Quality Assessment Division Office of Air Quality Planning and Standards, U.S. EPA, Research Triangle Park, NC 27711

Canadian Source: 1980-1984: MSC, Environment

Canada (EC) data, 1990, The 1990 Canadian Long-Range Transport of air Pollutants and Acid Deposition assessment Report Part 3: Atmospheric Sciences. P 3-18. **1985-2005:** David Niemi, personal communication. Criteria Air Contaminants Division, APP - Pollution Data Branch, Environment Canada,

## Spatial distribution of sulphur and nitrogen deposition in Europe and North America

Deposition rates of S and N are not spatially uniform. In Europe the highest deposition levels are found in Central Europe and lowest in Northern Norway and Sweden (**Figure 3** and **Figure 4**). In North America, the area of maximum deposition occurs in the eastern part of the continent (**Figure 5**).

The greatest deposition reductions have taken place in Central Europe. If the Gothenburg Protocol is 'fulfilled', S deposition in Europe will be lower than it has been for many decades. For N deposition, it is not likely that the Gothenburg requirements will be met in 2010.



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Nitrogen deposition, 1990



Nitrogen deposition, 2010

Nitrogen deposition, 2004

**Figure 4** N deposition (mg N m-2) in Europe 1990, 2004 and predicted for 2010. (Source: Transboundary acidification, eutrophication and ground level ozone in Europe since 1990 to 2004. EMEP report 1/2006.).

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**Figure 5** 5-year average (2000-2004) wet deposition of S (kg S ha/yr) and N (kg N/ha/yr) in North America. The monitoring stations (dots) north of 49°N latitude (western Canada-U.S. borders) are too few to justify extrapolation to the rest of Canada.( Source: U.S.- Canada Air Quality Agreement Progress Report 2006).

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#### **Further reading**

#### On the Convention on Long-range Transboundary Air Pollution:

- Convention on Long-range Transboundary Air Pollution CLRTAP, http://www.unece.org/env/ Irtap/welcome.html
- Clearing the Air 25 years of the Convention on Long-Range Transboundary Air Pollution. Sliggers J. and Kakebeeke, W. 2004. ISBN 92-1-116910-0. UN, Geneva Switzerland
- United Nations Economic Commission for Europe, UNECE, http://www.unece.org/Welcome.html
- EMEP Cooperativ programme for monitoring an evaluation of the long-range transmission of air pollutants in Europe http://www.emep.int/
- The Canada-United States Air Quality Agreement, http://www.ec.gc.ca/cleanair-airpur/Pollution\_Issues/Transboundary\_Air/Canada\_-\_United\_ States\_Air\_Quality\_Agreement-WS83930AC3-1\_ En.htm
- Review and assessment of air pollution effects and their recorded trends, Substantive report 2004. Convention on Long-range Transboundary Air Pollution, United Nations Economic Commission for Europe, Geneva.

#### On the Gothenburg Protocol

- Coordinated Effects Monitoring and Modelling for Developing and Supporting International Air Pollution Control Agreements. Bull, K.R. et al. 2001. *Water Air and Soil Pollution*. 130:119-130.
- Review of the Gothenburg Protocol by Task Force on Intergrated Assessment Modelling. CIAM report 1/2007 http://www.emep.int/publ/other/ TFIAM\_ReviewGothenburgProtocol.pdf

#### On the Working Group on Effects and all Integrated Cooperative Programs

- Working Group on Effects (WGE) http://www. unece.org/env/wge/welcome.html
- ICP Waters: ICP on Assessment and Monitoring of Acidification of Rivers and Lakes http://www. icp-waters.no/
- ICP Integrated Monitoring: ICP on Integrated Monitoring of Air Pollution Effects on Ecosystems http://www.environment.fi/
- ICP Forests: ICP on Assessment and Monitoring of Air Pollution Effects on Forests http://www. icp-forests.org/
- ICP Materials: ICP on Effects of Air Pollution on Materials, Including Historic and Cultural Monuments http://www.corr-institute.se/ICP-Materials/
- ICP Vegetation: ICP on Effects of Air Pollution on Natural Vegetation and Crops http://icpvegetation. ceh.ac.uk/
- ICP Modelling and Mapping: ICP on Modelling and Mapping of Critical Loads and Levels and Air Pollution Effects, Risks and Trends http://www. icpmapping.org/
- The Coordination Centre for Effects (CCE) http:// www.rivm.nl/cce/
- Task Force on Health: Joint Task Force on the Health Aspects of Long-range Transboundary Air Pollution http://www.euro.who.int/air/activities/20030528\_4

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## 2. ICP Waters – aims and structure

As is the case with all of the ICPs, ICP Waters plays an important role in supplying a sound scientific basis for evaluation of emission reduction measures. For the most recent protocols, the LRTAP Convention has chosen an effect-based approach: reductions of emissions are based on reducing and preventing adverse effects on ecosystems, and by taking into account that some ecosystems are more sensitive to air pollution than others.



ICP Waters excursion in the Vosges mountain, 2007. Photo: Anne Christine leGall, France

At present, about 20 countries participate in ICP Waters on a regular basis and supply data to the Programme's central database. Based on national monitoring programmes, each Focal Centre delivers data on the chemical and biological status of sensitive lakes and rivers. A Task Force meeting is organized annually in October and is hosted by one of the participating countries (see Figure 6). At the annual Task Force meetings, data analyses on the chemical and

biological status of lakes and rivers are presented, in addition to results of inter-laboratory comparisons of chemistry and biology. Also, specific topics relevant to the Convention such as POPs, heavy metals and the effect of climate change on chemical and biological recovery from acidification of surface waters are addressed. The results of the work of ICP Waters are presented annually at the WGE meetings, and published in reports and scientific papers.

ICP Waters was established in July 1985. The Programme Centre is located at the Norwegian Institute for Water Research (NIVA) in Oslo and the Programme chair is at the Norwegian Pollution Control Authority (SFT).

The main aim of the ICP Waters Programme is to assess, on a regional basis, the degree and geographical extent of the impact of atmospheric pollution, in particular acidification, on surface waters (**Text box 6**).

Results from the ICP Waters Programme are presented in reports and publications, but ICP Waters also contributes in international scientific arenas and participates in international conferences and workshops. ICP Waters also has close cooperation with ongoing EU-projects, related in particular to aspects of acidification of surface waters.

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#### Text box 6:

### Aims and objectives of the ICP Waters Programme Aims:

- Assess the degree and geographic extent of the impact of atmospheric pollution, in particular acidification, on surface waters;
- Collect information to evaluate dose/response relationships;
- Describe and evaluate long-term trends and variation in aquatic chemistry and biota attributable to atmospheric pollution.

#### **Objectives:**

- Maintain and develop an international network of surface water monitoring sites;
- Promote international harmonisation of monitoring practices by:

- maintaining and updating a manual for methods and operation;

- conducting inter-laboratory quality assurance tests;
- Compiling a centralised database with data quality control and assessment capabilities.
- Develop and/or recommend chemical and biological methods for monitoring purposes;
- Report on progress according to programme aims and short term objectives as defined in the annual work programme;
- Conduct workshops on topics of central interest to the Programme Task Force and the aquatic effects research community;
- Address water related questions in cooperation with other ICP's

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**Figure 6** Map showing the location of TF meetings throughout ICP Waters' history. Blue colour on the map indicate participation in the Programme at some stage during the programme history.

Overview of Task Force meetings and number of participating countries at each meeting

Task Force				
meeting				No. of
no.	Year	Place	Country	countries
1	1986	Grafenau	Germany	9
2	1986	Oslo	Norway	9
3	1987	Togliatti	Russia	12
4	1988	Korpilampi	Finland	11
5	1989	Freiburg	Germany	14
6	1990	Skøvde	Sweden	12
7	1991	Galway	Ireland	12
8	1992	Winnipeg	Canada	14
9	1993	Oisterwijk	Netherlands	15
10	1994	Budapest	Hungary	18
11	1995	Zelena Ruda	Czech Republic	15
12	1996	Silkeborg	Denmark	15
13	1997	Pitlochry	Scotland	16
14	1998	Zakopane	Poland	15
15	1999	Pallanza	Italy	17
16	2000	Riga	Latvia	14
17	2002	Lillehammer	Norway	16
18	2002	Moskva	Russia	16
19	2003	Lugano	Switzerland	16
20	2004	Falun	Sweden	16
21	2005	Tallinn	Estonia	20
22	2006	Bergen	Norway	19
23	2007	Nancy	France	19

#### Further reading:

#### **On ICP Waters**

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• www.icp-waters.no

#### On acidification status of surface waters in Europe and North America from the 1980s to present

- Trends in surface water chemistry and biota; The importance of confounding factors. De Wit H. Skjelkvåle B.L. (eds). 2007. NIVA-report SNO 5385-2007. ICP Waters report 87/2007.
- The 15-year report: Assessment and monitoring of surface waters in Europe and North America; acidification and recovery, dynamic modelling and heavy metals. Skjelkvåle, B.L. (ed). 2003. NIVA-report SNO 4716-2003. ICP Waters report 73/2003.
- The 12-year report; Acidification of surface water in Europe and North America; trends, biological recovery and heavy metals. Skjelkvåle, B.L. et al.

2000. Norwegian Institute for Water Research. NIVA-report SNO 4208/2000. **ICP Waters report 52/2000**.

- The Nine Year Report: Acidification of surface water in Europe and North America - Long-term Developments (1980s and 1990s). Lükewille, A. et al. 1997. Norwegian Institute for Water Research. NIVA-report SNO 3637-97. **ICP-Waters Report 41/1997**.
- The six year report: Acidification of surface water in Europe and North America. Dose/response relationships and long-term trends. Skjelkvåle, B.L. et al. 1994. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3041-94.
- The Three Year Report: Summary and Results 1987-1989. Wathne, B.M. 1991. Norwegian Institute for Water Research. ICP Waters report.

## 3. Key concepts in acidification of surface waters

#### Chemistry of surface waters

The chemical composition of surface waters is an important determinant of the aquatic organisms that can survive in any given lake or stream. Bedrock geology of the catchment, soils and surficial deposits, weathering rates, vegetation, hydrology and atmospheric deposition all play a role in determining the chemistry of lakes and rivers in areas that are little disturbed by direct human influences such as agriculture and silviculture.

Atmospheric deposition is influenced by long-range transported air pollutants, sea salts and soil dust (Figure 7). The chemical composition of precipitation depends on distance from the sea and anthropogenic pollution sources. It is modified by a number of processes when passing through a catchment. Such processes are biological (microbial activity, uptake by plants, release of ions through decomposition, etc.) and chemical (weathering, ion exchange, adsorption and desorption, redox processes, precipitation etc.). In general, soils derived from crystalline bedrock rich in silica have low weathering rates and yield waters with a low content of base cations and bicarbonate that consequently have little capacity to buffer acidification. On the other hand, soils derived from bedrock rich in base cations have higher weathering rates, release more base cations and bicarbonate, and yield surface waters with a higher buffering capacity.



**Figure 7**. Schematic diagram showing the different processes influencing surface water chemistry.

The total sum of ions from deposition and weathering together with all the various processes occurring within a catchment determine the chemistry of the runoff water. Additionally, in-lake processes can further modify the ionic composition of lake water.

#### **Biologically relevant chemistry**

The ultimate goal of emission control programmes is biological recovery, or the return of sensitive species that have been eliminated during the course of acidification. An assessment of trends in biologically relevant chemical parameters can only suggest that biological recovery is possible (or expected), not that it has occurred. When surface water trends are shown to be moving in the correct direction (e.g., increases in pH), they indicate improvement in the acid–base chemistry of lakes and streams. These improvements do not necessarily equate to a "recovered" ecosystem. The term "recovery" implies a change towards some pre-acidified status, such as pre-industrial levels of sulphate or alkalinity; trends indicate only that surface waters are moving toward this recovered status, not that they have reached it.

In the absence of good data on biological recovery, it is common to assume that biological recovery will eventually occur, after a sufficient time lag, when key chemical variables have recovered to their pre-acidification levels. These key chemical variables are those that have direct toxic effects on biota (primarily hydrogen ion and aluminium) and those that ameliorate some of the toxic effects (primarily base cations like calcium). For these reasons, evaluations of chemical recovery are often focused on acidity (pH and alkalinity), aluminium, and base cations (especially calcium).

#### Acidification and naturally acidified lakes

pH in a lake is affected by several natural processes within the catchment, such as the rate of geological weathering and production of bicarbonate, mobilization and leaching of organic acids derived from humic substances (organic anions, typically indicated by dissolved organic carbon/ total organic carbon levels), and input of sulphate from natural sulphide-bearing minerals. Low weathering rates, high input of organic anions, and high input of natural sulphate can depress pH in the lake or river. Inputs of anthropogenically derived sulphur and nitrogen that exceed the critical load for the catchment can also depress the pH to biologically harmful levels. It is not obvious, by measuring pH only, if a low pH value in a water body is due to anthropogenic or natural processes.

#### Alkalinity

Alkalinity is a measure of the waters ability to resist change in pH and to neutralize acid inputs. Alkalinity is a more integrative indicator of lake acidification than pH. The most important buffer systems in natural waters are the carbonate-system and organic acids. As increasing amounts of acid are added to a water body, the buffering capacity of the water is consumed, and the pH of the water decreases (acidification). At pH 5.5, most of the bicarbonate alkalinity is lost, and organic acids serve as the main natural buffer.

#### Acid neutralizing capacity (ANC)

Acid Neutralizing Capacity (ANC) is another measure of the acid-base status of surface waters similar to alkalinity. Where alkalinity is a *measured* entity, ANC is a *calculated* parameter that has been used successfully for dose/response relationships between (1) acid deposition and water chemistry and (2) between water chemistry and damage to the biological community. ANC is the parameter used as the critical chemical criterion for sensitive indicator organisms in surface waters within the international Critical Loads work. ANC with units of µeq/L is defined as the equivalent sum of base cations minus the equivalent sum of strong acid anions:

#### ANC = ( $[Ca^{2+}] + [Mg^{2+}] + [Na^{+}] + [K^{+}] + [NH_4^{+}]$ ) - ( $[Cl^{-}] + [SO_4^{2-}] + [NO_3^{-}]$ ).

#### Acid-sensitive sites

Surface water chemistry reflects the sensitivity of an area to acidification. Base cation and bicarbonate concentrations in surface waters are related to weathering rates in catchments and can thus be used to indicate acidsensitivity of the catchment. Low concentrations of base cations (<100  $\mu$ eq/L) indicate high sensitivity, intermediate concentrations (100 to 400  $\mu$ eq/L) indicate moderate sensitivity and high concentrations (>400 μeq/L) indicate general insensitivity to acid deposition.

A pristine, extremely acid-sensitive lake typically has an alkalinity of <20  $\mu$ eq/L, and a moderately sensitive lake has an alkalinity between 20 and 50  $\mu$ eq/L. Surface waters with an alkalinity over 200  $\mu$ eq/L are considered to be insensitive to acidification. The values are about the same for ANC.

#### Critical loads and critical loads exceedance

The critical load of sulphur and nitrogen acidity is the highest deposition of acidifying compounds that will not cause chemical changes leading to long-term harmful effects on ecosystem structure and function. It is a property of the lake and its catchment and is primarily controlled by weathering rates in the catchment.

To calculate a critical load, the target ecosystem must first be defined and in that ecosystem (e.g. a lake) a sensitive biological "element" must be identified (e.g., fish status). The next step is to link the status of that element to some chemical criteria (e.g., ANC or sometimes pH). Finally, a mathematical model needs to be created so that the deposition levels at which the chemical criteria reach the exact critical limit can be calculated. That deposition level is called the critical load and the difference between the current deposition level and the critical load is called exceedance. When the critical load is exceeded, the aquatic ecosystem is expected to become damaged. Thus, a positive value for a critical load exceedance means ecosystem damage, while a negative value (or zero) indicates either no damage or ongoing recovery.

#### Critical loads and biology

Exceedances of critical loads of acidity will lead to ecosystem damage, especially loss of sensitive aquatic organisms. In surface waters, critical limits of water chemistry for aquatic organisms have been studied extensively (see chapter 8) and relations between ANC (for example) and fish status are established. Agreement between exceedances of critical loads, water chemistry status and biological status gives support to the effect-based approach to control emissions of acidifying components under the LTRAP Convention.

## 4. Monitoring network and quality control

The ICP Waters monitoring programme is designed to assess, on a regional basis, the degree and geographical extent of acidification of surface waters. For that reason, ICP Waters sites are usually located in acid-sensitive areas receiving significant loads of acidic deposition. The ICP Waters Programme is based on voluntary contributions from existing national monitoring programmes in participating countries. National focal centres annually submit water chemical records and results from biological monitoring to the ICP Waters Programme Centre.

> Collected data provide information on relationships between doses of atmospheric acidic inputs and responses in surface water chemistry and biological status of lakes and streams.

> The ICP Waters sites need not be representative of all surface waters in a region, but rather represent the acid-sensitive surface waters. Most of the sites appear to be well suited to monitor changes in acidification in response to changes in acid deposition because they have low alkalinity and low critical loads of acidity.

> Occasional random surveys are used by some participating countries to indicate the frequency and geography of sensitive and acidified lakes and streams among their wider populations of surface waters.

> The ICP Waters sites cover most of the acid-sensitive areas in Europe that receive significant acid deposition although some potentially affected areas are poorly represented. There are insufficient data from many regions in eastern Europe to assess both the risk of acidification and the sensitivity of surface waters adequately. In North America, ICP sites cover several, but not all of the acidsensitive regions that receive significant acid deposition. At present, the Programme Centre holds data for about 200 monitoring sites in Europe and North America, many with time series more than 20 years long (**Figure 8**).

> The majority of the ICP Waters sites are acid sensitive. There is a good agreement between the measured ANC in the water and the calculated critical loads exceedance for the same site (Figure 9). A correlation between the calculated critical load exceedance versus present day (1990) ANC value at a number of ICP Waters sites showed that, where critical loads have been exceeded (thus, ecosystem damage can be expected), ANC was mostly below 20 µeq/L. Where critical loads



were not exceeded, ANC was mostly above 20  $\mu$ eq/L. In general, lakes with an ANC over 20  $\mu$ eq/L are more likely to have a healthy fish population.



**Figure 9** Exceedance of critical load of acidity and ANC in 1990 at ICP Waters sites in Europe. Sites in the lower right quadrant have positive critical loads exceedances and have ANC below ANClimit. Critical loads are not exceeded at sites in the upper left quadrant, and ANC is above ANClimit. Sites in both these quadrants are positioned as expected with respect to critical load, exceedance and response of water chemistry. Sites in the upper right quadrant show exceedances but have ANC above ANClimit. These sites may show delayed response to S deposition. Source: ICP Waters report 44/1998.

#### Quality control routines – chemistry and biology

Each country contributes data from its national monitoring programme and consequently, many laboratories are used for chemical analysis. Between-laboratory quality control is necessary to assure clear identification and control of the biases between analyses carried out by individual participants of the Programme. Such biases may arise by use of different analytical methods, errors in the laboratory calibration solutions, or through inadequate within-laboratory control.

An annual chemical intercomparison or between-laboratory control is conducted. Approximately 70 different laboratories from 26 different countries participate and analyse water samples containing major ions and heavy metals. The results are reported annually and confirm that the results are generally compatible between laboratories.

The quality of the biological monitoring of invertebrates is for a large part dependent on the correct identification of biological organisms. The purpose of the annual biological intercalibration is to evaluate the quality of the taxonomic work on the biological material delivered to the Programme Centre. The quality of the taxonomic identification affects the evaluation of the acidification index (see Text box 7), which is based on species and their acid tolerances. Each laboratory sends a sample of invertebrates from their own monitoring sites to the Programme Centre, where all species are identified and test samples, composed of the fauna from their own monitoring region, are made for each laboratory. Twelve laboratories participate on a regular basis. In general the results show very high quality and good taxonomic work amongst the participating laboratories.

#### Text box 7: Acidification Index for aquatic invertebrates

An acidification index has been developed for the assessment of damage to invertebrates in freshwater, based on knowledge of critical limits for different species. A score is given for the invertebrate assemblage using a range from 0 to 1.

Acidification index	Criteria
1	A score of 1 means that the locality contains one or more species with a low tolerance for acidic water (can tolerate a pH down to 5.5). If these species are found in a locality, there is little damage to invertebrate popula- tions.
0.5	A score of 0.5 indicates that none of the most sensitive species is present, but the locality contains species that are moderately sensitive to acidification (can tolerate a pH down to 5.0). Such a community could be considered moderately damaged if acidification has occurred.
0.25	A score of 0.25 implies the locality lacks all the sensitive species mentioned above, but contains species with a tolerance down to pH 4.7.
0	A score of 0 is given for localities containing only organisms with extremely high tolerance for acidic water [pH < 4.7].

**Source:** Fjellheim and Raddum, 1990. Acid precipitation: Biological monitoring of streams and lakes. Sci. Tot. Environ. 96:57-66.

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#### **Further reading**

On the Programme Manual of ICP Waters

 http://www.icp-waters.no/Manual/tabid/61/ Default.aspx

#### On the annual chemical intercomparisons

- Trends in intercomparisons 8701-9812: pH, K25, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K and aluminium - reactive and nonlabile, TOC, COD-Mn. Hovind, H. 2000. NIVA-Report SNO 4281-2000. ICP Waters Report 56/2000
- Intercomparison 0721: pH, Cond, HCO3, NO3--N, Cl, SO4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. Hovind, H. 2007. NIVA-report SNO 5486-2007. ICP Waters report 90/2007

#### On the annual biological intercalibration

 Biological intercalibration: Invertebrates 1107.
 Fjellheim, A. and Raddum, G. G. 2008. NIVAreport SNO 5551-2008. ICP Waters report 91/2008

#### On critical load and their exceedances

- Review of the Gothenburg Protocol: Chemical and biological responses in surface waters and soils. Wright, R.F. et al. 2007. NIVA-report SNO 5475-2007. ICP Waters report 89/2007.
- Critical loads and their exceedances for ICP-Waters sites. Henriksen, A. and Posch, M. 1998. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3821-98. ICP Waters Report 44/1998.



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# 5. Widespread chemical recovery of surface waters

The strongest evidence that emission control programmes are having their intended effect comes from a consistent pattern of recovery across a large number of sites. Decreasing emissions of sulphur dioxide result in decreasing sulphur deposition, which is expected to lead to lower sulphate  $(SO_4)$ concentrations in surface waters, subsequent increases in pH and alkalinity, and a recovery of biota.

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The strong link between sulphate deposition, sulphate in surface waters and acid-neutralizing capacity of the water is illustrated below for a Norwegian monitoring site (**Figure 10**).

Research programmes and national monitoring programmes were initiated in the 1970s and have produced long records of surface water chemistry in acid-sensitive catchments. Some data series even go back to the late 1960s but mostly they begin during the 1980s.

Sulphate concentrations from some of the ICP sites in Europe and North America are shown in **Figure 11**. The overall decreasing trend in sulphate is clear, but some sites show considerably more variations than others and some sites hardly show a declining trend. Also, the rate of decline is not constant with time. This illustrates the need for long-term records and sufficient numbers of monitoring stations for doing reliable trend assessments. Based on monitoring data from almost 200 sites across Europe and North America, ICP Waters has evaluated trends in key chemical variables in sites and in regions.

Trend assessments have been conducted several times during the Programme's history (see further reading at the end of the chapter for an overview). Results from the most recent trend analysis from the ICP Waters Programme covers the time period from 1994 to 2004 (**Figure 12**).

Results from the last assessment (1994-2004) for sulphate, nitrate, ANC and H<sup>+</sup> (pH) are shown in **Figure 13** to **Figure 16**. Each figure shows the trend slope for all sites used in the trend assessment, divided into regions as indicated in the map in **Figure 12**. If the numbers are less than 0 there is a decreasing trend, while numbers above 0 indicate an increasing trend. Trend slopes close to 0 indicate that there has been no change in the concentration level over the 10-year period of the analysis. These figures clearly show that, in general: (1) sulphate concentrations are decreasing in all regions; (2) nitrate shows no consistent pattern, either increasing or decreasing; (3) ANC is increasing in most regions; and (4) H<sup>+</sup> concentrations exhibit decreases in most regions (indicating that pH is increasing).

Results from the various trend assessments within ICP Waters over the years have shown that sulphate concentrations in surface waters have declined in all regions



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since 1980, with the exception of the Virginia Blue Ridge where decreases are not expected. In general, the decline was more gradual during the 1980s compared with the 1990s, except in Central Europe. Rates for sulphate decline are now slowly levelling off but are still steeper than during the 1980s. In Central Europe, reductions in sulphate were largest between 1980 and 1995 but have since levelled off. Many of the sites in Central Europe have deep soils with a considerable sulphate-adsorption capacity. Some of these sites show only slight declines in sulphate concentrations, because sulphate concentrations are more controlled by the release of adsorbed sulphate than by sulphate deposition. The decline in sulphate in the UK was less prominent than in the Nordic countries during the 1990s. We refer the reader to the individual trend assessments that more completely discuss variations in sulphate trends within each of the regions (see Further Reading at end of this chapter).

The most important findings of the trend assessments through the years are:

• There is an almost universal decrease in sulphate concentrations in lakes and streams throughout Europe and North America. In almost all cases

the decreases in the 1990s were larger than in the 1980s, while the trends since 2000 are beginning to level off or have already levelled off.

- Most sites show no significant trend in nitrate. In the last assessment (2004) roughly two thirds of all sites showed no trend in nitrate, whereas about one quarter of all sites showed a decreasing trend. Nitrate increased in less than 10% of the sites. The lack of a uniform trend in nitrate concentrations illustrates that nitrate leaching from catchments is affected by a variety of processes. This is in contrast to sulphate leaching from catchments, which is largely controlled by S deposition (see Chapter 6 about trends in N).
- The chemical recovery from surface water acidification we observe is closely associated with declining sulphate in deposition.
- Alkalinity and ANC showed significantly increasing trends at roughly one third of the sites, while very few sites showed decreases in these variables. This indicates that almost no sites are continuing to acidify, compared to 14% of the sites showing a decrease in alkalinity in 1990–2001. Of those few sites with decreasing ANC (Figure 15), many

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of them are located in Nova Scotia and Ontario, Canada. The cause of the continuing acidification was most likely due to the responses of other variables (e.g., declining base cations) that presently mitigate the recovery expected to accrue from decreasing sulphate.

 Dissolved organic carbon (DOC) has increased significantly between 1990 and 2004 in previously glaciated regions in northern Europe and North America (see Chapter 7 about trends in DOC).

#### Further reading:

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#### On trends in acidification and recovery

- Regional scale evidence for improvements in surface water chemistry 1990-2001. Skjelkvåle, B.L. *et al* 2005. *Environmental Pollution* 137: 165-176.
- Trends in surface waters acidification in Europe and North America (1989-1998). Skjelkvåle, B.L. *et al.* 2001. *Water Air Soil Poll.* 130:787-792.
- Regional trends in aquatic recovery from acidifica-



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tion in North America and Europe 1980-95. Stoddard, J. L., et al. 1999. *Nature* 401:575- 577.

 Acidification trends in surface waters in the International Programme on Acidification of Rivers and Lakes. Newell, A.D. and Skjelkvåle, B.L. 1996. *Water Air Soil Poll.* 93:27-57.

#### On trends in dissolved organic carbon

• Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Monteith, D.T. *et al.* 2007. *Nature* 450: 537-541.



**Figure 13** Values for "non-marine" sulphate are calculated by removing the trace amounts of sulphate from sea-salt spray that contribute to S deposition. Each box shows the range of slopes (25th to 75th percentiles, with line at the median), while lines (whiskers) show the range of the data that lay within the upper (lower) quartile plus 1.5 x the interquartile range (minus 1.5 x the interquartile range). The dots show outliers beyond this. (unit: µeq/L/ year). Source: ICP Waters report 87/2007.



**Figure 15** Box- and whisker plot showing the 1994 to 2004 trend slopes for ANC (unit:  $\mu$ eq/L/year) in the different regions of Europe and North America. Explanation and data source as in **Figure 13**.

On reports on acidification status of surface waters in Europe and North America from the 1980s to present

See recommended reports under further reading after Chapter 2



**Figure 14** Box- and whisker plot showing the 1994 to 2004 trend slopes for nitrate (unit:  $\mu$ eq/L/year) in the different regions of Europe and North America. Explanation and data source as in **Figure 13**.



**Figure 16** Box- and whisker plot showing the 1994 to 2004 trend slopes for H+ (unit:  $\mu$ eq/L/year) in the different regions of Europe and North America. Explanation and data source as in **Figure 13.** 

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## 6. Nitrogen leaching – an unsolved riddle

The global nitrogen (N) cycle has been severely altered by human activity, causing N enrichment of terrestrial and aquatic ecosystems. Atmospheric deposition of N has led to increased runoff of N from catchments in forests and mountainous regions, and contributes to acidification and nutrient enrichment of aquatic ecosystems. A large concern is N saturation, which is a gradual oversupply of N relative to other nutrients so that important ecosystem functions such as plant growth and biodiversity are negatively affected. The final stage of N saturation is viewed as massive leaching of N to surface and ground waters resulting in acidification of aquatic ecosystems.

In addition to N deposition, climate factors and forest management can lead to large inter-annual variations in nitrate concentrations and export in natural and semi-natural ecosystems. In fact, climate impacts may mask long-term trends in stream water nitrate driven by changes in N deposition, and can be a main driver itself of long-term trends in stream water nitrate. So far, there are no compelling data that show a widespread N saturation of catchments in high N deposition areas in North America and Europe, although relations between N deposition, soil N enrichment and N leaching have been found.

Nitrogen emissions to the atmosphere continue to be high, unlike sulphur emissions that have been reduced in Europe by more than 70% since the 1980s. Thus, it can be expected that N enrichment by atmospheric deposition will remain a scientific issue in the years to come. The lack of significant trends in nitrate for the majority of ICP Water monitoring sites (see Chapter 5) suggests that there is no imminent risk for wide-scale N saturation. However, a more elaborate analysis using N deposition data in addition to water chemistry for ICP Water sites in Europe yields interesting information on controls on N leaching (**Figure 17**). Nitrogen deposition at many sites in Europe has declined somewhat over the past 10 to 15 years, while corresponding data for water chemistry appear to show that dissolved inorganic N species (nitrate and ammonium) have been reduced in the same period of time.

While the general dependence of N leaching on N deposition has been illustrated by many previous analyses (i.e., high surface water concentrations of N never occur unless N deposition is also high), the results in **Figure 17** are a rare example showing that lower N deposition can lead to lower rates of N leaching.





The statistical analysis of nitrate trends in the previous chapter showed that there is no uniform regional trend in nitrate in surface water. However this empirical view of nitrate in 54 sites in Europe indicates that there is a tendency towards a relation between decrease of N in deposition and decrease of nitrate in surface waters.

Due to the decrease in sulphate concentrations in surface waters during the 1990s, nitrate has assumed greater importance as an acidifying anion at the ICP sites. While nitrate decline seems to be far more common than nitrate increase in surface waters, the majority of catchments show no significant trend. The data indicate no major change in N saturation at the ICP sites during the 1990s, indicating that progression to increased N saturation is a slow process with a time scale of decades.

Compared with sulphur, nitrogen is much more influenced by biological processes within ecosystems. Hence changes in N deposition may not always directly correlate with changes in inorganic N leaching in runoff. Besides N deposition, the overall N status of ecosystems, changes in climate or climate extremes and hydrology can strongly influence leaching of excess nitrate (and ammonium) from a catchment.



#### Further reading:

#### On nitrogen saturation

The stages of Nitrogen Saturation: Classification of catchments included in "ICP on Waters". Stoddard, J.L. and Traaen, T.S. 1994. In: M. Hornung, M.A. Stutton and R.B. Wilson (eds.) Mapping and Modelling of Critical Loads for Nitrogen: a Workshop Report. Proceedings of a workshop held in Grange-over-Sands (UK), 24-26 October 1994. pp. 69-76.

#### On trends and controls on nitrogen leaching

- Assessment of trends and leaching in Nitrogen at ICP Waters Sites (Europe and North America).
   Skjelkvåle, B.L. et al. 2001. NIVA-report SNO 4383-2001, ICP Waters report 54/2001.
- Assessment of Nitrogen leaching at ICP-Waters sites (Europe and North America). Stoddard et al., 2001. Water Air Soil Poll. 130:781-786
- An Assessment of Nitrogen Leaching from Watersheds included in ICP on Waters. Traaen, T.S. and Stoddard, J.L. 1995. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3201-95.



**Figure 17** Nitrogen  $(NO_3^- + NH_4^+)$  concentration in runoff and total inorganic N deposition for 54 European ICP Waters sites in 1990-93, 1996-99, and 2002-05 (deposition data for 2002-03 only). The dotted lines indicate the successive change in maximum total inorganic N deposition and inorganic N runoff  $(NO_3 + NH_4)$  with time. Source: ICP Waters report 87/2007.



# 7. Trends in DOC are a response to reduced acid deposition

Dissolved organic carbon (DOC) has increased since 1990 in formerly glaciated parts of Northern Europe and North America. DOC is of great interest in analysis of surface water recovery because it is an indicator of organic (natural) acidity, which may partly counteract the positive effect of declining sulphate. In addition, increase in DOC also contributes to increased mobilisation and transport of heavy metals and organic pollutants from soils to water. The brown colour of DOC-rich water is important for aquatic biota because it reduces light penetration. Additionally, drinking water treatment involves removing colour from surface waters. Along with the rise in DOC, costs for treating drinking water may increase.

> To strengthen a DOC trend assessment, ICP Waters in collaboration with National Focal Centres in Canada, US, UK, Norway, Sweden and Finland collected data from more than 500 acid sensitive sites in northern boreal, formerly glaciated areas of North America and northern Europe (Figure 18, Figure 19). The assessment showed that the increasing DOC trends identified in most regions for the period 1990 to 2004 could be explained by changes in the acid anion concentration of atmospheric deposition. DOC concentrations increased proportionally with the decline both in anthropogenic sulphur, and, in some regions, sea-salt deposition. The results suggest that DOC concentrations should stabilise as anthropogenic sulphur emissions decline to a stable level. They also reveal a potential weakness in the ability of current geochemically-based models to predict the impact of sulphur declines on the acidity of sensitive waters. So far, the mechanisms linking atmospheric deposition and surface water DOC remain poorly understood.

#### Further reading:

- Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Monteith, D.T. et al. 2007. Nature 450:537-540.
- Trends in surface water chemistry and biota; The importance of confounding factors. De Wit H.A. and Skjelkvåle B.L. (eds). 2007. NIVA-report SNO 5385-2007, ICP Waters report 87/2007.

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# 8. Dose/response relationships and the first signs of biological recovery

Evidence of a biological response to reduced surface water acidification is, so far, not uniform throughout the ICP Waters study area. The ICP Waters Programme has in recent years documented signs of recovery of invertebrates in the Scandinavian countries, UK and the Czech Republic, but improvements in water quality have not yet reached a level where widespread effects on biology can be detected in the most acidified central European sites.

#### Why is biological recovery so slow?

Biological data from some of the ICP waters monitoring sites show rising evidence of recovery in recent years. Our data indicate that recovery is most pronounced in regions with low buffering capacity. Recovery times vary among taxonomic groups - algae (0-1 year), some sensitive invertebrate species (1-10 years), some zooplankton species (3-7 years) and fish (2-20 years) all exhibit different responses during recovery, which may be roughly related to generation times. A return to preindustrial biological communities or to a fixed assemblage is highly unlikely due to the dynamic nature of biological communities.

## Several factors can delay biological recovery:

 Episodes of acid water connected with for example snowmelt and sea-salt deposition may prevent stable recovery and result in multiple recolonisations (an on/off situation for sensitive species)

- Bottlenecks arise due to problems of dispersal of sensitive species (arrival factors)
- Bottlenecks arise due to interactions and competition with other species (survival factors of the sensitive species)
- Dispersal mechanisms are affected by stream and lake characteristics such as size, morphology, distance from refuges, etc.
- Dispersal and recolonisation are dependent on life cycle and behaviour (resting eggs, flying insects, size etc.)

#### Evidence of biological recovery

The first signs of zooplankton recovery have recently been observed in some of the lakes in the Czech Republic (**Figure 20**). An example from zooplankton and fish in Southern Norway is presented in Text Box 8.

From the UK Acid Waters Monitoring Network, an assessment of a wide range of biological groups in acidified lakes and streams have provided clear indica-



**Figure 20** Abundance of zooplankton species, *Ceriodaphnia quadrangula* in the open water (average column densities) of the lake Černé in Czech Republic. In the years 1980–1996 no Ceriodaphnia were found. Note the logarithmic scale on the y-axis. Source: ICP Waters report 75/2004

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**Figure 21** The observed relationship between brown trout status and Acidification Index against surface water ANC at 827 sites and 140 in Norway, respectively. Source: Lien et al. 1996. A critical limit for acid neutralizing capacity in Norwegian surface waters, based on new analyses of fish and invertebrate responses. Science of the Total Environment 177:173-193.

tions of biological responses to improving water quality. The most obvious changes are found in benthic diatom (algal) species, with acid sensitive species becoming more abundant relative to acid tolerant species. The UK assessment has also documented that acid-sensitive macrophyte species, including *Myriophyllum alterniflorum* are detected for the first time only in the late 1990s in chemically recovering sites. Macroinvertebrate species composition was found to have changed in most sites where labile aluminium concentrations had declined, often reflecting gradual increases in acid-sensitive predatory stoneflies in streams and predatory web-spinning caddisflies in lakes.

## Critical limits of water quality for fish and invertebrates

Biological recovery can be expected only when chemical surface water quality has recovery sufficiently to sustain acid-sensitive populations. Large surveys of combined biological and water chemical data have shown that communities adapted to low alkalinity, pH and low calcium concentrations have a lower critical limit (i.e. a higher tolerance to acidity) than communities adapted to higher alkalinity.

There are good empirical relationships between water ANC and biological response. The most widely used is the observed population status for brown trout and the Acidification Index against ANC observed in Norwegian lakes (**Figure 21**). See also Text box 8.

Studies of the dose/response between water chemistry and invertebrates are conducted by ICP Waters. The results have showed strong relationship between water quality and fauna (**Figure 22**). The effect of acidification on invertebrates varied from region to region depending on the natural content of humic substances, calcium and ionic strength. In Norway and other areas close to the Atlantic ocean, the fauna had adapted to freshwater with low conductivity, pH > 5.8 and ANC > 10 µeq/l to survive. The presence of humic substances in this type of water increased the critical limit of ANC to about 20 µeq/l for sensitive species, and pH limits as low as 5.5. All sensitive species in regions with humic water become extinct at ANC < - 30 µeq/l and pH < 4.7.

On this basis different critical limits of acid-neutralizing capacity for invertebrates were suggested for different regions of Europe. In areas with originally high pH (6.0-8.0) and high calcium concentrations (e.g., southern Sweden, Germany and the Vosges Mountains of France) a critical ANC limit of 50 µeq/L was proposed. In areas where fauna had adapted to water with



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low conductivity, low pH (5.5 - 6.5) and low calcium concentrations (e.g., Ireland, UK and Norway), ANC limit of 20  $\mu$ eq/L were proposed, and in the high Alps and Pyrenees a limit of about ANC 30  $\mu$ eq/L was suggested.

#### Text box 8 Critical limit: links between S deposition, surface water chemistry, and fish in Lake Saudlandsvatn, southernmost Norway.

Saudlandsvatn, southernmost Norway, is an example of a lake that was acidified and had damage to the fish population and invertebrates in the 1980s, but has shown significant chemical and biological recovery in response to decreased S deposition since 1990. Since about 2000, S deposition has fallen below the critical limit of acidity (CLA) (upper panel) and water chemistry has improved, with ANC above ANClimit (second panel). Both fish populations (CPUE = catch per unit effort) and macroinvertebrate populations (Baetis rhodani, a very acid-sensitive mayfly) show improved recruitment and sensitive invertebrates have recolonized(lower panels).

**Source:** Norwegian institute for nature research (fish), Norwegian institute for water research (water chemistry), Norwegian institute for air research (deposition) University of Bergen (invertebrates)



#### Further reading:

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### On dose-response relationships between acidity and biota

- A critical limit for acid neutralizing capacity in Norwegian surface waters, based on new analyses of fish and invertebrate responses. Lien, L. et al. 1996. Science of the Total Environment 177:173-193.
- Fish status survey of nordic lakes: effects of acidification, eutrophication and stocking activity on present fish species composition. Tammi, J. et al. 2003. AMBIO, 32 (2) 98-105
- Critical Load of acidifying compounds to invertebrates in different ecoregions of Europe. Raddum, G.G. and Skjelkvåle B.L. 2001. Water Air Soil Poll. 130:825-830.
- Critical limits of acidification to invertebrates in different regions of Europe. Raddum, G.G., and Skjelkvåle, B.L. 1995.Water Air Soil Poll. 85: 475-480.
- The six year report: Acidification of surface water in Europe and North America. Dose/response relationships and long-term trends. Skjelkvåle, B.L. 1994. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3041-94.

#### On trends in biological recovery:

- Trends in surface water chemistry and biota; The importance of confounding factors. De Wit, H., and Skjelkvåle, B.L. (eds.) 2007. NIVA-report SNO 5385-2007. ICP Waters report 87/2007.
- Recovery from acidification of invertebrate fauna in ICP Water sites in Europe and North America. Raddum, G.G, et al. 2004. NIVA-report SNO 4864-2004. **ICP Waters report 75/2004.**
- Tracing recovery from acidification a multivariate approach. Halvorsen, G.A, Heergaard, E. and Raddum, G.G. 2002. NIVA-report SNO 4564-2002. ICP Waters report 69/2002.
- The 12-year report; Acidification of surface water in Europe and North America; trends, biological recovery and heavy metals. Skjelkvåle, B.L. et al.. 2000. Norwegian Institute for Water Research. NIVA-report SNO 4208/2000. ICP Waters report 52/2000.
- Workshop on biological assessment and monitoring; evaluation and models. Rosseland, B.O. et al. 1999. NIVA-Report SNO 4091-99. ICP Waters Report 50/1999.

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## 9. When to expect recovery?The use of dynamic models

The critical load of sulphur and nitrogen - the highest deposition of acidifying compounds that will not cause chemical changes leading to long-term harmful effects on the ecosystem structure and function – is a fixed ecosystem property and is primarily controlled by weathering rates in the catchment. Dynamic models provide an extension to critical loads by predicting the timescale of chemical recovery when emission reductions have been applied.

> Just as the damage to biota is delayed beyond the onset of acid deposition, so the recovery from acidification can also be delayed. The time sequence of acidification and chemical recovery has been described as occurring in 5 stages (see **Text box 9**); each stage may occur over a time span of years to centuries, depending on the variables that control it. Dynamic models give us the tools to explore how these time lags might vary under different deposition scenarios.

> ICP Waters reported on the possibilities and limitations in dynamic modelling of surface water chemistry in response to changes in acid deposition input. Four models were identified as being widely used, simple enough to be applied on a regional scale, and documented and tested with respect to the requirement of the Convention. Of these, the MAGIC model, focuses on surface water chemistry and is generally applied at the catchment scale.



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The modelling studies have shown that recovery of soil and water quality of the ecosystems is determined by both the magnitude, and the time of implementation, of emission reductions. According to the models, the timing of emission reductions determines the state of recovery over a short time scale (up to 30 years). The quicker the target level of reductions is achieved, the more rapidly the surface water and soil status recover. Model simulations also indicate that N emission controls can be very important for enabling maximum recovery in response to S emission reductions. Increased nitrogen leaching has the potential not only to offset the recovery predicted to occur in response to S emission reductions but also to promote substantial deterioration in the pH status of freshwaters and other N pollution problems in some areas of Europe.

In the EU-project RECOVER: 2010, the two widely used models MAGIC and SMART were applied to 12 acid sensitive surface water regions in Europe (Figure 23). The model results indicated that even after complete implementation of the Gothenburg Protocol and other current legislation, acidification with associated adverse biological effects will continue to be a significant problem in southern Norway, southern Sweden, the Tatra Mountains in Slovakia, the Italian Alps, and the Southern Pennines in the United Kingdom. More than 5% of the ecosystems in each of the regions evaluated would not meet the ANC criterion to protect sensitive aquatic organisms. Additional mitigation measures would be required in these regions to meet long-term European policy objectives. The model simulations also indicated that, as expected, the percent base saturation (%BS) of soils decreased during the long period of acidification of 1860-1980. Between 1980 and 2000, the large reduc-



1980

yellow: ANC 0-20  $\mu eq/l$  and sparse population of fish; blue: ANC > 20  $\mu eq/l$  and good population of fish.

1860

not give any information on when a recovery will occur. If the goal is to ensure recovery by a given year (and the time thereafter) one has to determine a so-called target load (for a specified target year). Target loads can only be determined by dynamic models, and meaningful target loads are always smaller than the critical load for the same ecosystem. In fact, a critical load can be viewed as the target load for target year 'infinity'.

tions in sulphur deposition appeared in most cases to be sufficient to stop the decrease in %BS but still insufficient to allow %BS to recover. The prognosis for the future indicated little or no recovery of base saturation in the soil, and in one of the modelled regions (the Tatra Mountains) the soil would continue to acidify.

Reducing deposition to (or below) critical loads ensures that an ecosystem recovers, but critical loads do

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#### Text box 9: The Posch model for delay times (Posch et al. 2003)

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The possible development of a chemical and biological variable in response to a 'typical' temporal deposition pattern can be summarised into five stages:

**Stage 1:** Deposition was and is below the critical load (CL) and the chemical and biological variables do not violate their respective criteria. As long as deposition stays below the CL, this is the 'ideal' situation.

**Stage 2:** Deposition is above the CL, but (chemical and) biological criteria are not violated because there is a time delay before this happens. No damage is likely to occur at this stage, therefore, despite exceedance of the CL. The time between the first exceedance of the CL and first violation of the biological criterion (the first occurrence of actual damage) is termed the Damage Delay Time (DDT=t3-t1).

**Stage 3:** The deposition is above the CL and both the chemical and biological criteria are violated. Measures (emission reduction) have to be taken to avoid a (further) deterioration of the ecosystem status.

**Stage 4:** Deposition is below the CL, but the (chemical and) biological criteria are still violated and thus recovery has not yet occurred. The time between the first non-exceedance of the CL and the subsequent non-violation of both criteria is termed the Recovery Delay Time (RDT=t6-t4).

**Stage 5:** Deposition is below the CL and both criteria are no longer violated. This stage is similar to Stage 1 and only at this stage can the ecosystem be considered to have recovered.

Stages 2 and 4 can each be further subdivided into two sub-stages: Chemical delay times (DDTc=t2-t1 and RDTc=t5--t4; dark grey in the figure and (additional) biological delay times (DDTb=t3-t2 and RDTb=t6-t5; light grey). Very often, due to the lack of operational biological response models, damage and recovery delay times mostly refer to chemical recovery alone and this is used as a surrogate for overall recovery.



#### Further reading:

#### On dynamic acidification modelling:

- Dynamic Modelling of Surface Waters: Impact of emission reduction - possibilities and limitations. Jenkins, A. et al. 2002. NIVA-report SNO 4598-2002. ICP Waters report 70/2002.
- Manual for Dynamic Modelling of Soil Response to Atmospheric Deposition. Posch, M. et al. (eds) 2003. Working Group on Effects of the Convention on Long-range Transboundary Air Pollution. RIVM Report 259101012, 71 pp.

#### On critical loads and target loads:

- Critical Loads, Target Load Functions and Dynamic Modelling for Surface Waters and ICP Waters Sites.
   Wright, R.F. et al. 2005. NIVA-report SNO 5166-2005. ICP Waters report 83/2006.
- Recovery of acidified European surface waters .
   Wright R.F et al. 2005 Env. Sci & Technology 39: 64-72



## 10. Modelling biological recovery

Biological recovery in response to improved water quality is mostly described in running waters in Scandinavia. Both moderate and highly sensitive species have recovered after improvements in water quality above critical limits. Conceptual models aiming to assess and predict biological recovery need to integrate the ecological dynamics of biological communities together with changes in water chemistry.

At present, only few biological models for recovery of aquatic fauna have been developed. ICP Waters has been involved in development of a dynamic model for recovery of invertebrates (MIRACLE) and a model for recovery of fish populations (FIB).

#### MIRACLE

The MIRACLE model (Modelling Invertebrate Recovery of ACidified Lotic/Lentic Ecosystems) by Raddum and Fjellheim (2002) assumes selected critical stages in recovery of sensitive invertebrates. The biological part of the model is coupled to the catchment model MAGIC that computes water chemistry. The model depicts four different, consecutive stages of biological recovery of invertebrates (see **Figure 24**):

#### Stage 1 – reaching the required water quality

Stage 1 is defined as the time necessary to reach the required water quality (critical limit) for the species. This corresponds to t5 in the Posch model in Text box 9. Based on expected deposition levels and catchment information, the chemical model (e.g., MAGIC) can be used to calculate the time to reach the desired chemical endpoint, related to the critical limit for the species concerned. The initial chemical conditions are important because they determine the faunal composition prior to the recovery process. Severely damaged ecosystems, which contain only very tolerant species, will recover more slowly than ecosystems where some sensitive species have survived.

#### Stage 2 – between reaching the required water quality and reappearance of species

Reappearance of a sensitive species depends on its ability to disperse, the distance to source populations, and dispersal between watersheds. Rapid dispersal occurs in species with winged adult stages (most insects), while invertebrates that spend their entire life cycle in water, like molluscs (snails) and oligochaetes (worms) disperse slowly. The lowest dispersal rate is probably among organisms fulfilling their life cycle in deep waters. Dispersal rate also depends on ecosystem type. In running waters, recovery can occur immediately through the drift of organisms from upstream refugia in the same river system. Dispersal from downstream areas is a regular aspect of the recolonization cycle for winged insects. This stage corresponds approximately to t6 in the Posch model in Text box 9.

### Stage 3 – between reappearance and establishment of species in the watershed

When the pioneer individuals have been established, intra-watershed dispersal may begin. Winged insects can spread out rapidly both downstream and upstream, while snails must migrate slowly, be transported in water, or sometimes be dispersed by birds through the air. The drift of invertebrates in running water helps a rapid dispersal downstream. Stage 3 is finished when all or most of the suitable habitats have been occupied by the species.

## Stage 4 – reaching ecological stability including natural fluctuations

The time needed for reaching the stage of natural fluctuations is difficult to predict and measure. An ecologically stable community is important for assessing the recovery process, but will mostly depend on biological interactions. For the most common and widespread species in running water, the time needed to achieve this stage appears to be close to that of stage 3. For



later the first observation of H. slitalai was made, and stage 2 -

expected year classes, typical for the given geographical and climatic zone, are represented. The occurrence of all expected year classes is the final goal of biological

recovery of fish populations.

In the severely acidified river Audna in southern Norway, a modelling study of recovery has shown that reaching the required chemical water quality that allows biological recovery (Stage 1) can take between 30 and 50 years. Stage 2 - reappearance of sensitive organisms - can take 2 - 10 years after chemical recovery above the chemical critical limit for the species. Stage 3 - the occupation of suitable habitat - can take 5 years.

other species, ecological stability is difficult to define,

especially for species with many generations per year

and species that are vulnerable to predation.

Thus, several decades are probably necessary for the recovery of sensitive species. The key factor for biological recovery is the rate and extent of chemical recovery of surface waters. The recovery of acid-sensitive invertebrate species in lakes is less predictable than recovery in streams due to a higher complexity of the in-lake processes.

#### The FIB and D-FIB model

The FIB-model ("Fish in Recovery") is a model that simulates for fish population recovery in response to changing water chemistry. Recently, this model has been modified to incorporate dynamic population size feed-back loops (D-FIB model). The FIB-models aim to estimate the expected time for a defined recovery, where the goal is to have a "healthy fish population". A healthy fish population is more than the presence of a sufficient number of fish. In the FIB-model, a "healthy fish population" is defined as a population where all

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In the D-FIB model, demographic processes (survival, recruitment and maturation) are modelled as functions of both population size and ANC. These functions have been established using statistical modelling based on long-term time-series data of brown trout (Salmo trutta) catch statistics from a lake in Southern Norway (Saudlandsvatnet). The various demographic functions are linked together in a dynamic population model that, from an initial population size and age structure, is driven by inputs of predicted ANC values retrieved from the model MAGIC.

The model explained 84% of the 1975 to 2005 temporal variation in brown trout population size in lake Saudlandsvatnet (Figure 25) and managed to reconstruct the age structure of the population with high precision.

The D-FIB model framework is a promising management tool to be used in evaluating the recovery potential of brown trout populations under different ANC scenarios, for instance evaluating the expected effect of cessation in lake liming.

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#### Further reading:

#### On the MIRACLE model and the FIB model:

 Dynamic biological response models – an overview. Raddum, G.G. and Rosseland. B.O. 2005. In: de Wit, H. and Skjelkvåle, B.L. (eds.) Proceedings of the 20th meeting of the ICP Waters Programme Task Force in Falun, Sweden, October 18-20, 2004. NIVA-report SNO 5018-2005, ICP Waters report 80/2005.

#### Other reports on biological modelling:

- Tracing recovery from acidification a multivariate approach. Halvorsen, G.A, Heergaard, E. and Raddum, G.G. 2002. NIVA-report SNO 4564-2002, ICP Waters report 69/2002.
- Tracing recovery from acidification in the Western Norwegian Nausta Watershed. Halvorsen, G.A., E. Heegaard, A. Fjellheim, and G.G. Raddum. 2003. Ambio, 32 (3): 234-239.
- Workshop on models for Biological Recovery from Acidification in a Changing Climate. 9-11 September 2002 in Grimstad, Norway. Wright, R.F. and Lie, M.C.(eds.) 2002. Workshop report. NIVAreport 4589-2002.
- Recovery from acidification of invertebrate fauna at ICP Water sites in Europe and North America. Raddum, G.G., et al., 2004. NIVA-report SNO 4864-2004. ICP Waters report 75/2004.



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# 11. Climate change effects on chemical and biological recovery from acidification

Recent episodes of extreme heat in the United States and Europe, long dry spells across western North America, and heavy episodes of rain and snow across much of North America and Eurasia hint at long-term changes in climate. Several of the world's most advanced climate models predict that much of the world will face an enhanced risk of heat waves, intense precipitation, and other weather extremes. Both changes in extremes and more gradual longterm climatic changes could affect the chemical and biological recovery of surface waters from acidification. The confounding effects of climate change on recovering water chemistry and biology will need to be considered as we look forward to continued recovery.

#### Sea-salt deposition

Episodic acidification of surface waters from sea-salt deposition may obscure long-term trends in recovery related to decreasing acid deposition. Recent climate forecasts predict greater frequency and intensity of sea-salt episodes and possibly higher loads of acidifying compounds may therefore be expected in coastal surface waters.

The "sea-salt effect" in surface waters is important in coastal areas in Norway, the U.K., Ireland, the U.S. and Canada. The sea-salt effect may temporarily increase the acidity of runoff water through ion-exchange of N<sup>a+</sup> from sea-salts with Al<sup>3+</sup> and H<sup>+</sup> in the catchment soil. Hence, sea-salt episodes can delay biological recovery. Monitoring data from the River Lygna in southern Norway demonstrate a clear relationship between a sea-salt event in 1993, which resulted in increased aluminium concentrations, and a reduced population of acid-sensitive mayfly species (**Figure 26**).

#### **Droughts**

A lower water table due to drought can lead to the occurrence of aerobic conditions in soils and sediments that are normally anaerobic. In aerobic conditions, previously-reduced sulphur species are oxidised to sulphate. When water tables rise again after a precipitation event, the resulting mobile sulphate can be exported and produce episodic acidification.

Drought has particularly influenced sulphate export from some lakes in Ontario, Canada, where reduction and storage of sulphate in wetlands, and subsequent

and storage of suip

re-oxidation and release, have been shown to have a major impact on runoff water quality and hence recovery trends. In the U.K., large flushes of sulphate were widely observed in streams following a drought in 1995 and in Norway following a summer drought in 1976.

Climate-regulated S retention and releases represent 'noise' within an overall recovery trend, but release of stored S will delay recovery where S pools are large.

#### **Climate warming**

Climate warming has led to reduced snow cover in areas where a stable snow pack used to be common. An unstable snow pack caused by frequent thaw periods provides less insulation than a thick, continuous snow pack. Thus, soils may become colder during winter despite an overall warmer climate, with potentially a large effect on temperature-sensitive processes that drive N leaching.

In the U.K. and the U.S., large pulses of nitrate have been observed in surface waters following severe winters with little snow cover, possibly as a result of soil freezing and the mobilization of N previously stored in soil biomass. Another effect of reduced snow cover was shown in Norway, where a downward trend in nitrate leaching correlated with less snow (see **Figure 27**). This was explained by less by-pass flow of atmospheric N that had accumulated in the snow due to more frequent thawing. Instead of a single snowmelt resulting in one episodic snowmelt event, multiple but smaller snowmelt events are more common.

Climate warming has increased the length of the grow-

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Figure 26 The effects on water chemistry and biology of a winter storm with high transport of seasalt in southern Norway, 1993. The upper panel shows chloride and inorganic aluminium in River Lygna from 1990 to 1996. The decrease in Al from 1990 to 1993 is due to chemical recovery in the river, while the peak in 1993 is due to the sea-salt episode. The lower panel shows the effect of the sea-salt episode on biota (number of Baetis rhodani) in the neighbouring river Audna. Source: ICP Waters report 87/2007.

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**Figure 27** Nitrate concentrations (µg N/L) and snow depth (cm) at Storgama in southeast Norway. Left panel shows years 1975-1982, right panel shows 1998-2003. Source: ICP Waters report 87/2007



#### Floods

ing season, and could lead to higher summer temperatures and warmer soils. Results from the CLIMEX project, where ambient air and soil temperatures were increased over three years, showed increased leaching of inorganic N, probably due to increased mineralization and nitrification rates in the soils.

Thus, climate warming may accelerate N leaching or reduce N leaching depending on season, climate zone and several other factors. Climate change is expected to lead to more intense precipitation events in some regions of the world. Water currents and water flow affect the structure of the riverbed, which are critical areas of macroinvertebrate (insects and snails) habitats. High flow maintains a coarser substrate, which is generally more favourable for benthic organisms, while decreased flow allows sedimentation of finer particles. Floods can lead to large disturbance of the bottom substrate in riverbeds with potentially very damaging effects on the faunal composition. Many benthic organisms use the river bottom as a refuge during high flow events; these refuges can be destroyed during catastrophic flow.

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#### **Further reading**

#### On climate change

• Intergovermental panel on climate change: http:// www.ipcc.ch/

#### On impacts of climate change on freshwaters

- EU-project Eurolimpacs Evaluating the Impacts of **global change** on European Freshwater Ecosystems http://www.eurolimpacs.ucl.ac.uk/
- Trends in surface water chemistry and biota; The importance of confounding factors. De Wit H. Skjelkvåle B.L. (eds). 2007. NIVA-report SNO 5385-2007, **ICP Waters report 87/2007**.
- Note on: Effect of year-to-year variations in climate on trends in acidification. Wright, R.F. 2001. NIVA-report SNO 4328-2001, ICP Waters report 57/2001.
- Workshop on models for Biological Recovery from Acidification in a Changing Climate. 9-11 September 2002 in Grimstad, Norway. Wright, R.F and Lie, M.C. (eds.) 2002. Workshop report. NIVAreport 4589-2002.
- Joint Workshop on Confounding Factors in Recovery from Acid Deposition in Surface Waters, 9-10 October 2006, Bergen, Norway; Summary and Abstracts. Skjelkvåle, B.L., et al. 2006. NIVA-report SNO 5310-2006. **ICP Waters report 88/2006.**

## 12. Heavy metals

Heavy metals have posed an environmental threat to human and animal health for centuries. Exposure to sufficiently high concentrations of heavy metals can lead to failure of organs and damage to nervous and reproductive systems. Emissions of heavy metals leading to longrange transport of these pollutants are mainly from industrial sources, combustion processes and waste incineration. Human exposure to heavy metals can be through drinking water, soil ingestion and by consuming plants and animals that have accumulated these pollutants.

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In 1998, the Executive Body of the Convention on Longrange Transboundary Air Pollution adopted the Protocol on Heavy Metals in Aarhus (Denmark) which focuses on regulating and reducing emissions of cadmium (Cd), lead (Pb) and mercury (Hg) (see **Text box 10**).

Text box 10: The Aarhus Protocol on Heavy Metals.

The Aarhus Protocol on Heavy Metals (UN/ECE 1998 (Aarhus, Denmark)) aims at regulation and reduction of emissions of heavy metals to the atmosphere.

The Protocol on Heavy Metals targets three particularly harmful metals: cadmium, lead and mercury. Parties will have to reduce their emissions for these three metals below emission levels in 1990 (or an alternative year between 1985 and 1995). The Protocol aims at cutting emissions from industrial sources (iron and steel industry, non-ferrous metal industry), from combustion processes (power generation, road transport) and from waste incineration. Stringent limit values for emissions from stationary sources are laid down and best available techniques (BAT) to reduce emissions are suggested, such as special filters or scrubbers for combustion sources and mercury-free processes.

Many factors influence the concentration level at which harmful effects of heavy metals can be expected. Usually, only the free or inorganically bound form of the metal is regarded as potentially toxic to aquatic biota while complexation with organic matter significantly reduces the concentration of the free metal ion and thus its toxicity. Organic matter is a strong complexing matter, higher concentrations of total metal can be tolerated without adverse effects on organisms. This complexation is particularly strong for Cu and Pb, and decreases in importance for Ni, Zn and Cd. However, high concentrations of organic matter also mean that potentially more pollutants are transported from soils to surface waters where they might become bioavailable through degradation of organic matter and other processes. Other factors such as pH and hardness also affect concentration of free metal ions and thus toxicity. There are at present no internationally agreed limits for toxic levels of heavy metals in surface waters.

agent in natural waters, and in the presence of organic

The ICP Waters Programme has made an assessment on heavy metals based on data delivered to the Programme from the national Focal Centres (Skjelkvåle et al., 1999). Additionally, a workshop on heavy metals was organised in 2002 in Lillehammer, Norway with a focus on monitoring and biological impacts.

Results from the Programme show that few sites have long time series on heavy metals. The analytical methods have changed and detection limits have generally improved (decreased) through the monitoring period for the sites with long-term trends.

Only sites with sufficiently long time-series and high quality data allow for evaluation of trends. A few sites like Cerne Lake (CZ01) in the Czech Republic have shown a decline in Pb and Cd over the last 10 years (**Figure 28**).

In general, the concentrations of heavy metals in ICP Waters sites not influenced by local pollution sources are relatively low. Based on existing guidelines (e.g., from Sweden), a number of the ICP sites exhibit



heavy metal concentrations above the critical limit(s). A more complete assessment of heavy metals in surface waters throughout Europe and North America would require additional heavy metal data for more sites with more complete geographical coverage.

The Nordic lakes survey in 1995 showed that direct and indirect influence of long-range transported air pollution is the most important factor explaining the distribution of Pb, Cd and Zn in lakes on a regional scale, while bedrock geology and overburden is the major controlling factor for Cu and Ni (with exception of areas around the smelters on the Kola Peninsula in Russia). The results further indicate that heavy metal pollution in lakes is a minor ecological problem on a regional scale in the Nordic countries. Hg was not included in this survey, and Hg is regarded as an environmental problem in Nordic lakes. Certain areas, particularly in southern Norway and Sweden, are affected by long-range transport leading to Pb, Cd and Zn concentrations in lakes above limits set by the national environmental authorities. There are indications that the ecological consequences of heavy metals may be larger for running waters than for lakes, especially in small streams where heavy metal concentrations may be higher. An example of the spatial distribution of Pb in surface waters in the autumn of 1995 is shown in (Figure 29)

Results from a Czech freshwater survey showed that

acid deposition mobilised Cd and Zn from overburden and bedrock. Direct atmospheric deposition was important for Pb concentrations in freshwaters.



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**Figure 29** Pb concentrations in Nordic lakes in the autumn of 1995. Missing data in Northern Sweden is due to lack of samples from this area. (Source: Skjelkvåle et al. 2001. Heavy metal surveys in Nordic lakes; concentrations, geographic patterns and relation to critical limits. AMBIO 30 (1) 2-10.)

The ICP Waters heavy metals workshop in 2002 covered critical limits, monitoring methods and dose/response relationships with modelling. The major conclusions were:

- Further review of existing data and information, including active cooperation with other bodies, EU research programmes and national research are recommended.
- The effect-based approach to the control of heavy metals in surface waters requires further development. Defining critical loads for individual heavy metals need not necessarily be the final step in the process. Additional methods may also prove to be advantageous.
- ICP Waters should 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.

#### Further reading:

#### On international policy on heavy metals

 The Aarhus protocol http://www.unece.org/env/ lrtap/hm\_h1.htm

#### On heavy metals in freshwaters

- The 12-year report; Acidification of surface water in Europe and North America; trends, biological recovery and heavy metals. Skjelkvåle, B.L., et al., 2000.Norwegian Institute for Water Research. NIVA-report SNO 4208/2000, ICP Waters report 52/2000.
- Proceedings from the Workshop on Heavy Metals (Pb, Cd and Hg) in Surface Waters; Monitoring and Biological Impact. March 18-20, 2002, Lillehammer, Norway. Skjelkvåle, B.L. and Ulstein, M. (eds). 2002. NIVA-report SNO-4563-2002, ICP Waters report 67/2002.
- The 15-year report: Assessment and monitoring of surface waters in Europe and North America; acidification and recovery, dynamic modelling and heavy metals. Skjelkvåle, B.L. (ed). 2003.NIVA-report SNO 4716-2003, ICP Waters report 73/2003.

#### On heavy metals in the Arctic

• Arctic Monitoring and Assessment Programme (AMAP): http://www.amap.no/



## 13. Persistent organic pollutants (POPs)

Of all pollutants released into the environment by human activity, persistent organic pollutants (POPs) are among the most dangerous. For many decades, these highly toxic chemicals have caused death and illnesses by damaging nervous, reproductive and immune systems. Cancer and birth defects are common effects of exposure to POPs.

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POPs are defined as man-made organic compounds that remain intact in the environment for long periods, that are widely distributed geographically and accumulate in the fatty tissue of living organisms, and that are toxic to humans and wildlife (see **Text box 11**).

Text box 11: According to the LRTAP Convention the following criteria should be met to in order to classify a substance as a long-range atmospheric transboundary POPs:

(i) possess toxic characteristics;

(ii) are persistent;

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(iii) bioaccumulate;

- (iv) are prone to long-range transboundary atmospheric transport and deposition; and
- (v) are likely to cause significant adverse human health or environmental effects near to and distant from their sources.

POPs have been distributed over the whole planet through a process known as the "grasshopper effect". Released POPs are transported through the atmosphere by repeated evaporation and deposition, and can thus end up in alpine and arctic areas far away from emission sources.

Several international agreements or treaties address the problem of dispersal of persistent organic pollutants in the environment. The most important are The Aarhus Protocol (under the LRTAP convention, see Text box 12) and the 2001 Stockholm Convention.

## Text box 12: The UNECE POPs Protocol (Aarhus Protocol)

The Executive Body adopted the Protocol on Persistent Organic Pollutants on 24 June 1998 in Aarhus (Denmark); the Protocol entered into force 23 October 2003. It focuses on a list of 16 substances (See **Table 1**) including 11 pesticides, 2 industrial chemicals and 3 by-products/contaminants. The ultimate objective of the Protocol is to eliminate any discharges, emissions and losses of POPs. The Protocol bans the production and use of some products outright (aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene) while others are scheduled for elimination at a later stage (DDT, heptachlor, hexaclorobenzene, PCBs). Finally, the Protocol severely restricts the use of DDT, HCH (including lindane) and PCBs.

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 Table 1
 The 16 persistent organic pollutants (POPs) with

 potential for long range atmospheric transport, included
 in the Aarhus Protocol on POPs. The first twelve constitute

tho	"Dirty Dozen"	which are	hazzarhhe	hy tha	Stockholm	Convention
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Substance	Posticido	Industrial	Unintended	Use or source/start of
Substance	restitue	compound	by-product	production
Aldrin	Х			insecticide/ 1940s
Endrin	Х			insecticide/1951
Dieldrin	Х			insecticide/ 1940s
Chlordane	Х			insecticide/ 1945
DDT	Х			insecticide/1945
Heptachlor	Х			insecticide/ 1950s
Mirex	Х			insecticide, flame retardant/1950s
Toxaphene	Х			insecticide/ 1949
Hexachlorobenzene	Х	Х	Х	fungicide, by-product/1945
PCB		Х		industrial products/1929
Dioxins and furans			Х	by-products of combustion
Polybrominated dephenyl ethers, PBDE		Х		flame retardants/ 1960s
Short chained paraffins, SCCP		Х		cutting oils, flame retardants
Polychlorinated naphtalenes, PCN		Х		coatings, lubricants
Polycyclic aromatic hydrocarbons, PAH			Х	incomplete combustion

The ICP Waters programme made an assessment on concentrations and levels of POPs from long-range transboundary air pollution in surface waters, freshwater fish and sediments. The report focused on 16 POPs that have been identified as particularly relevant for the LRTAP Convention. The report summarized recent levels of selected POPs, related to long-range transport, in freshwater fish and sediments in North America, Europe and circumpolar Arctic, based on data from central surveys.

Most surveys on POPs focus on concentrations in sediments and fish. There are fewer data on dissolved concentrations and trends in water. Analysis of water concentrations has been complicated by the presence of very low levels and analytical difficulties (detection limits).

The levels in fish are dependent on both the concentrations of the specific POPs in the surface waters and the degree of biomagnification (length of food webs). Sediments are often regarded as excellent tracers for trends in pollution. Dated sediment samples can document historical trends in flux of POPs to sediments (pollution history), and regional surveys of surface sediments can document the geographical deposition pattern (**Figure 30**).

The availability of data for POPs in fish shows a high variation. Legacy POPs (i.e. all POPs covered by

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the Stockholm Convention and the LRTAP Convention) like DDT and PCBs have been included in surveys while newer POPs (i.e. POPs not yet covered by any Convention or other international agreement) such as PBDE (brominated flame retardants) were not included until recently. There is a general lack of coordinated monitoring or regional surveys in freshwater environments that focus on POPs that originate dominantly from long-range atmospheric transport.

The results from the assessment confirm previous studies indicating that global distillation processes (the "grasshopper-effect") leads to elevated concentrations of contaminants in fish in arctic and alpine areas. There are very few sites with trend data, but they generally show decreasing levels of legacy POPs (**Figure 31**). Levels of some new substances, such as brominated flame retardants (PBDE) and PFAS, are probably rising.

There is an urgent need to establish systematic long-term monitoring of new POPs in areas without local pollution sources, so that the effects of long-range transported POPs can be documented. Coordinated international surveys, with harmonized methodology and reporting, would add additional important information on the geographic extent of problems.

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**Figure 30** Concentration of toxaphene in dated sediments from Lake Lochnagar, Scotland (left panel) and the historical production of toxaphene (right panel). This Figure shows how sediment cores can be used to document the historical record of the atmospheric deposition of a POP. Redrawn after Rose et al.,2001, An historical record of toxaphene and its congeners in a remote lake in Western Europe. Environmental Science & Technology, 35, 1312-1319.



**Figure 32** Time series of PCBs in pike muscle (µg/g lipid) from Lake Bolmen (southern Sweden) and Lake Storvindelen (northern Sweden). The trends show how the concentration of PCBs in fish decreases over time. Redrawn after Bignert, A. 2002: Comments concerning the national Swedish programme in fresh water biota 2001. Swedish Museum of Natural History, Contaminant Research Group. Report. 68 pp

#### **Further reading**

#### On international policy on POPs

- The Aarhus Protocol http://www.unece.org/env/ lrtap/pops\_h1.htm
- The Stockholm Convention: http://www.pops.int/

#### **On POPs in freshwaters**

• An assessment of POPs related to long-range air pollution in the aquatic environment. Fjeld, E. et al. 2005. NIVA-report SNO 5107-2005, ICP Waters report 79/2005.

#### On POPs in the Arctic

• Arctic Monitoring and Assessment Programme (AMAP): http://www.amap.no/



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## 14. ICP Waters in the future

For over two decades, ICP Waters has contributed solid empirical evidence and high quality research for the scientific underpinning of policy to reduce emissions of acidifying pollutants. The ICP Waters Programme has been active in reviews of several of the Protocols under the Convention, in particular the two S-protocols (1985 and 1994) and the Gothenburg Protocol (1999). The programme has also contributed to the review of the 1998 Heavy Metal Protocol. The future of ICP Waters is closely linked to the need for information to document the effects of implemented protocols and to develop new protocols, including the ongoing revision of the Gothenburg Protocol. This information falls into several classes.

#### Future acidification of surface waters

The Gothenburg Protocol is now fulfilled with regard to S, but there is still some way to go for N. This means that there at present are no expectations for further reductions of S-emissions in Europe. In North America emissions reductions will continue, but the magnitude of future decreases is likely to be smaller than in the past decades. Importantly, many lakes and rivers in southern Norway, southern Sweden, the Tatra Mountains in Slovakia, the Italian Alps, and the Southern Pennines in the United Kingdom and areas eastern part of U.S. and Canada still suffer from surface water acidification that is severe enough to inflict damage on biota. Dynamic acidification modelling suggests that these areas will continue to acidify in the future. Soil acidification continues, which jeopardizes the long-term recovery of lakes in these areas.

ICP Waters will continue to raise awareness in international forums about the continued problems of acidified waters and lacking biological recovery that occur in spite of reduced emissions, even in Europe where emission ceiling for sulphur has been attained.

The impacts of N-deposition will continue to be of concern. Current difficulties in predicting N-retention, and the multiple confounding factors (acidification, climate, natural variability) that affect the N cycle, mean that nitrogen will continue to be a key uncertainty in future recovery from surface water acidification. Much of the work that ICP Waters has done with nitrogen-based effects has focused on acidification. Because nitrogen is a nutrient, elevated N deposition can also disturb aquatic biological communities in oligotrophic (nutrient-poor) lakes. This is a problem ICP Waters will address in the near future.

#### **Biological response**

There is a major need for long term biological monitoring of acidified waters, often the first element to suffer under financial cuts, to continue to be supported and indeed enhanced. Recovery models predict significant time lags for biological recovery but at present only a few examples of recovery have been documented. The lack of such examples is related to the dynamic nature of biological responses but also to lacking monitoring data. Further biological monitoring is crucial for us to demonstrate the efficacy of international emissions control for acid sensitive ecosystems.

ICP Waters will continue to work on developing biological response models for use in assessing recovery from acidification. In this work, the continuation of biological and chemical monitoring at the same sites is essential.

#### Dynamic modelling and critical loads

Mapping critical loads for acidifying components is a key activity within the Convention work. Dynamic models provide an extension to critical loads by predicting the timescale of chemical recovery to emission reductions. Dynamic models can also be used to determine the deposition levels required to achieve a prescribed target chemistry within a given timescale, and so have direct input in the formulation of further emission reductions. ICP Waters can use the expertise within the ICP Waters network to support the modelling work under the Convention, and to assess the possibilities for using dynamic modelling for surface waters in Europe and North America. ICP Waters also holds much of the necessary data for calibration of such models.



#### Heavy metals and POPs

Heavy metals (in particular mercury, lead and cadmium) and POPs (persistent organic pollutants) from longrange transport have not received the same attention in monitoring programmes as acidifying components. In the future, ICP Waters plan to make recommendations for monitoring and the development of appropriate doseresponse relationships, and to participate in work on effect based approaches for POPs and heavy metals.

#### Effects of climate change and other "unknowns"

Future trends in recovery from acidification may be influenced by a number of confounding factors. Climate is widely believed to be undergoing long-term change, and the direction and degree of this change may significantly influence the behaviour of both terrestrial and aquatic ecosystems. Future monitoring, in particular in combination with the use of dynamic models, is important to understand the effects of climate change and other unknowns for acidification, as well as for heavy metals and POPs.

#### Contribution to other environmental policies

The work of ICP Waters, the ongoing monitoring of waters, and the long and extensive databases, provide participating countries with important environmental information that can be used in conjunction with other national and international environmental policies. For example, within the European Economic Region, policies such as the Water Framework Directive, the Convention on Biological Diversity and the Habitats Directive all can profit from ICP Waters. The databases can be used in assessments of climate change impacts relevant within the United Nations Framework Convention on Climate Change (Kyoto Protocol).

#### Success factors

The future success of ICP Waters is related to the factors that led to its success in the past: the combination of collecting and presenting high quality data from many countries; close contact with policy-makers and other ICP's; and good scientific collaboration within the Programme, with other international projects, and with other monitoring networks. The ICP Waters Programme Centre has experienced that the success in running our Programme is based on a scientifically sound and active Task Force, focused aims, consistent programme management, frequent assessment of data, a detailed programme manual, and frequent intercomparison exercises.

The crown jewels of ICP Waters are the data. Continuation of the national monitoring programmes that submit their data to ICP Waters, and the yearly chemical and biological intercalibration exercises are crucial and the most important activity in future work of the ICP Waters Programme.

All data are provided voluntarily by individual countries from national monitoring programmes. Many of these programmes are under severe budgets pressure. The value of all of these individual monitoring programmes is best realized through collection, analysis and interpretation in the integrated, multi-national studies for which ICP Waters is famous.





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