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

I. INTRODUCTION

1. The fifteen-year report, prepared within the framework of the International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters), presents programme activities during the three-year period from 1999 to 2001. Twenty-three countries participated in one or more activities during this period. The report reviews and summarizes the work done and the main results achieved on: (i) trends in surface water chemistry 1990-2001; (ii) the biological recovery from acidification; (iii) dynamic modelling of surface waters; (iv) heavy metals in surface waters; and (v) future work.
II. TRENDS IN SURFACE WATER CHEMISTRY 1990-2001

2. A major goal of the work of ICP Waters is to evaluate the changes in surface water chemistry in relation to emission reductions in deposition. The strongest evidence that emissions control programme are having their intended effect would result from a consistent pattern of recovery (decreasing sulphate and increasing pH and alkalinity) across a large number of sites. For this reason, ICP Waters is reporting trends for aggregations of ICP sites. The geographic regions used in the report were formed according to a number of objectives. Most importantly, an attempt was made to group together sites with similar acid-sensitivity (e.g. similar geology, soil characteristics and rates of deposition). In some cases, in order to reach sufficient sample sizes (i.e. number of sites) sites grouped into regions were more heterogeneous than would be ideal. The list of regions is therefore based on both scientific and pragmatic decisions resulting from the availability of data.

3. The most significant finding in the regional trend analysis, as in others conducted on earlier data (Stoddard et al. 1999, Skjelkvåle et al. 2001), is the almost universal decrease in sulphate concentrations in lakes and streams throughout Europe and North America. Only one region in this analysis failed to show a significant sulphate decrease, and this is a region (the Virginia Blue Ridge) where soil characteristics make a sulphate decrease unlikely.

4. Fewer than half the ICP Waters regions exhibited a significant regional trend in nitrate, and only the Alps region showed a significant increase. Regional declines in nitrate since ca. 1990 have been noted elsewhere (Stoddard et al. 1999, Skjelkvåle et al. 2001), and need to be interpreted cautiously. The time period of data analysed in the current programme’s report, and in previous reports, is in the order of a decade. Long-term catchment responses to N deposition may occur on the time scale of centuries, rather than decades. In the 1990s (actually, 1900-2001), ICP Waters sites have shown decreasing nitrate concentrations in the Adirondack Mountains, Appalachian Mountains and the Virginia Blue Ridge (all in North America), and increasing nitrate in the Alps. In all other regions, individual sites show either decreasing or increasing nitrate, with no clear regional pattern.

5. One of the expected responses of catchments to decreasing sulphate is a decrease in base cation (CaMg) concentrations. All of the evaluated regions show some tendency toward decreasing CaMg. One of the key findings of earlier regional assessments (Stoddard et al. 1999, Skjelkvåle et al. 2001) is the larger-than-expected decreases in CaMg in some regions, particularly in North America. When rates of CaMg decline are equal, or nearly equal, to rates of sulphate and nitrate decline, then recovery (increasing alkalinity and pH) is prevented. In the European regions, rates of CaMg decrease are moderate (often insignificant), and always smaller than those for sulphate. Rates of CaMg decline in North America tend to be larger than in Europe, and in some cases are in the same range as sulphate declines.

6. The decrease in sulphate and the slight increase or decrease in nitrate combined with more moderate declines in base cations, produce an expectation of recovery in alkalinity (measured) or acid neutralizing capacity (ANC) (calculated) and pH. In Europe there are two regions showing significant improvement in alkalinity and ANC (Southern Nordic, East-Central Europe). One region (West-Central Europe) shows no regional increase in alkalinity despite substantial
decreases in sulphate, but, curiously, ANC suggests a strong recovery in this region. Two regions (United Kingdom and Ireland, Northern Nordic) show an upward tendency for both variables although not a significant one. In the Alps, no significant recovery is discernable in the data. In North America there are four regions showing significant improvement in alkalinity (Vermont/Quebec, Adirondacks, Appalachians and Upper Midwest), one region with no change (Virginia Blue Ridge), and the only ICP Waters region in the current analysis exhibiting significant further acidification (Maine/Atlantic Canada). Recovery in the Adirondack and Appalachian mountains, and in the Upper Midwest, is an important finding because none of these regions showed significant improvement in previous regional analyses (e.g. Stoddard et al. 1999, Skjelkvåle et al. 2001). The region of Maine and Atlantic Canada is the only ICP Waters region where significant acidification has been taking place during the 1990s and early 2000s. It is occurring despite significant (but small) decreases in surface water sulphate. Many of the programme sites in this region are exhibiting larger decreases in base cations than their sulphate declines.

7. Only two of the regions exhibit a significant pH increase (Southern Nordic and Adirondack regions) and both are among the top three regions in terms of alkalinity improvement. While more significant improvements in pH might be expected, it is important to recognize that pH is among the most difficult variables to measure accurately in the laboratory. Variability in measurements makes it more difficult to detect incipient trends, but many of the regions exhibit trends that are very close to being significant.

8. Dissolved organic carbon (DOC) is of great interest in any analysis of surface water recovery, because it is an indicator of organic (natural) acidity. The previous ICP Waters trends report (Skjelkvåle et al. 2000) was one of the first to note the widespread increases in DOC now being observed throughout Europe and North America. All but one of the regions analysed in the current report exhibit positive slopes for DOC, and nearly all of the regional increases were significant. Increasing DOC at ICP Waters sites indicates that concentrations of organic acids are almost certainly rising as concentrations of inorganic acids are declining. The increase in DOC could offset roughly a half to a quarter of the declines in sulphate observed in ICP Waters region.

III. BIOLOGICAL RECOVERY FROM ACIDIFICATION

9. During the past decades a significant reduction in sulphur emission has taken place in both Northern Europe and North America. Large-scale recovery from acidification has been documented for surface waters. Documentation of biological response to reduced surface water acidification has so far been more scattered. ICP Waters has evaluated the reason for this seeming lack of biological recovery. It has focused on the most important factors determining biological recovery in different regions and what could have been expected in relation to the recovered chemical status. Some important issues are:

(a) Improvements in water chemistry have not yet reached the level necessary for acid-sensitive species to recover (biological recovery cannot start before water quality is suitable);
(b) Episodes of acid water connected with snowmelt, sea-salt deposition, etc. will prevent sustainable recovery and result in multiple recolonizations (an on/off situation of sensitive species);
(c) Bottlenecks due to dispersal of sensitive species (arrival factors);
(d) Bottlenecks due to interactions/competitions with other species (survival factors of the sensitive species);
(e) Dispersal mechanisms affected by stream/lake characteristics such as size, morphology, distance from refuge, etc.;
(f) Dispersal and recolonization dependent on life cycle and behaviour (resting eggs, flying insects, size, etc.);
(g) What is biological recovery? Is it the reversal of acidification to a pre-acidic species assemblage, or the development of a community reflecting the current chemical and physical environment? The recovery pathways will be affected by global warming, sea-salt episodes, droughts, changing hydrology, etc. and these must be evaluated to understand the recovery.

10. Water chemistry data consist of measured chemical concentrations, i.e. exact numbers, where the detection limits determine the significance level of the analyses. Biological data are less accurate and do not have the same possibilities for tracing small changes.

11. Results from ICP Waters have shown that many regions had early signs of recovery in water chemistry during the 1980s, and that the rate of recovery accelerated during the 1990s. The extent of chemical recovery from acidification varied over time, between regions and between sites within regions. Important factors are the magnitude of deposition change, catchment characteristics, land management, and the role of so-called confounding factors. In general there is clear evidence that reduced deposition of Sulphur has led, or will ultimately lead, to significant improvements in the chemical status of acidified surface waters throughout Europe.

12. Lakes and rivers situated in Scandinavia and in high mountain areas with thin soils show rapid acidification as well as rapid chemical recovery. The lakes and rivers monitored in Norway are typical. Improvements in water chemistry should be quick and biological recovery should have an early start. This is what is found in these areas (Raddum et al. 2001).

13. In regions with deep and old soils, acidification of surface waters is slower due to the high retention of sulphur and cation exchange. Acidified lakes and streams in such areas recover more slowly (Central Europe, parts of the United Kingdom, parts of Sweden). The scattered and often poor biological recovery is mostly associated with these regions. The sensitive biology has responded in accordance with the critical limits of the species and the changes in water quality, which in most cases are low. Recovery of sensitive species is stepwise and not smooth as with water chemistry. The changes in chemistry must therefore be sizeable before biological recovery can be measured. So limited biological recovery in such areas can be expected.

14. The reappearance of extinct sensitive species in a chemically recovered locality will vary depending on the type of organism. Zooplankton can develop from resting eggs in the sediment. Winged insect can easily be transported through air, but distance to source localities, flying ability, longevity and dispersal behaviour will be important. In running water, downstream drift will be an additional important dispersal mechanism from a source locality.
15. Biotic recovery in lakes takes longer and is less predictable than recovery in rivers (Yan et al. 2003 (in prep)). Competition and predation effects, especially on zooplankton in lakes from fish and invertebrate predators, make it difficult to evaluate recovery. In running water, fish predation on invertebrates is relatively low and can seldom be measured. Arrival and dispersal have been studied in the river Audna in southern Norway, where the water quality becomes acceptable for most acid-sensitive species immediately after liming (Raddum and Fjellheim 2003). The reappearance/arrival of sensitive species took from 2 to 10 years. After arrival, the different sensitive species dispersed to the whole limed stretch within 5 years.

16. Liming provides an idea of the expected invertebrate recovery following fully recovered water chemistry. The chemical differences between the limed and unlimed parts of the river Audna illustrate the status of the chemical recovery in unlimed parts of the river. Sensitive species in this part are about one third of those in the limed part after 15 years of liming. This further demonstrates that recovery in water chemistry has not yet been sufficient for recovery of the most sensitive invertebrates.

17. Biological recovery will occur when the water quality is good enough for sensitive fauna to recover. Since all biological communities are dynamic, there is a need to understand the sequence of steps in the ecological recovery process. This implies that an ecological system is unlikely to return to an earlier stage, but will always reflect the current physical, chemical and biological environment.

IV. DYNAMIC MODELLING OF SURFACE WATERS

18. Dynamic models provide an extension to critical loads by predicting the timescale of chemical recovery due to emission reductions. They can also be used to determine the deposition levels required to achieve a prescribed target chemistry within a given timescale and so have a direct use in the formulation of future emission reductions. Dynamic models can contribute to the Convention in two important areas; firstly, they can provide an estimate of the expected surface water chemistry at any time in the future in response to the implementation of the Gothenburg Protocol (assessment of the impact of emission reductions), and secondly, they can be used to assist in the calculation (optimization) of further emission reductions (input to the process of integrated assessment modelling).

19. Just as the damage to biota was delayed beyond the onset of acid deposition, so the recovery from acidification will also be delayed. In the chain of events from the deposition of strong acids to the damage of key indicator organisms there are two major factors that can give rise to time delays. Biogeochemical processes can delay the chemical response in the catchment soils and, consequently, surface waters and biological processes can further delay the response of indicator organisms, such as damage to fish. The models used to determine critical loads consider only the steady-state condition, in which the chemical and biological response to a change in deposition is complete. Dynamic models, on the other hand, attempt to estimate the time required for a new (steady) state to be achieved. ICP Waters has assessed the possibilities and limitations of using dynamic models to better define the limits and timescales of the recovery processes.

20. Four widely used biogeochemical models which are simple enough to be applied on a
Regional scale have been documented and tested with respect to the requirements of the Convention (Posch et al. 2003). Of these, the MAGIC model (Model of Acidification of Groundwater In Catchments) (Cosby et al. 1985a) focuses on surface water chemistry and is generally applied at catchment scale. MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on soils and surface water chemistry. The model simulates soil solution chemistry and surface water chemistry to predict the annual average concentrations of the major ions in lakes and streams. MAGIC has been modified and extended several times from the original version of 1984 and been extensively applied and tested at many sites and in many regions around the world (Cosby et al. 2001). Model testing included comparison with observed long-term data, comparison with results from large-scale manipulation experiments, and comparison with historical reconstructions using paleolimnological data (diatoms). Overall, the model has proven to be robust, reliable and useful in a variety of scientific and environmental management activities.

21. Regional assessment of surface water response to the implementation of the Gothenburg Protocol has been conducted under the European Union’s RECOVER:2010 project (Ferrier et al. 2001). Regional modelling produces a time-series output for each of the sites under consideration and that can be summarized to provide regional responses through time.

22. Dynamic models are currently capable of assessing the implications of achieving the emission reductions agreed under the Gothenburg Protocol. They can also address the question of whether the current agreements promote an appropriate response in surface water chemistry within a given time frame and help to identify regions where further reductions might be required to achieve a specified target chemistry at some specified time. If it is determined that further emission reductions are desirable, the models can also determine the level of deposition that must be met within a certain time to reach the specified target chemistry within a specified time. This capability provides a clear advantage over the concept of critical loads, which can only estimate the deposition required to reach the specified target chemistry at some unspecified time in the future, when the aquatic system has reached an equilibrium with the deposition chemistry. This is likely to take several decades or even hundreds of years.

23. There are uncertainties in the application of all mathematical models. Technical uncertainties in the dynamic modelling of surface waters are related to the estimation of model inputs and parameters from observed data, and these are due mainly to measurement errors and variability in both time and space. Methodological uncertainties such as nitrogen dynamics, the role of organic matter and climate impacts including sea-salt events are more difficult to assess (Ferrier et al. 2001). The lack of scientific understanding is an important factor for this group of uncertainties, in particular the current lack of understanding of the controls on N leakage from terrestrial to aquatic systems have been intensively studied, but remain a major source of uncertainty in model predictions.

24. Future work should include dynamic biological responses in the recovery process. The widespread improvement in surface water quality during the past 15-20 years should give rise to biological recovery. Thus far, however, there are relatively few documented examples of biological recovery. The reason might be lags in biological response but also a lack of appropriate long-term monitoring data.
25. The application of MAGIC to those areas of Europe where surface waters are considered to be acid-sensitive depends primarily on the availability of soil and surface water chemistry data with which to parameterize and calibrate the model. The role of the ICPs (Forests, Mapping and Modelling, Waters and Integrated Monitoring) is crucial in providing this information. The MAGIC model is currently capable of wide application across acid-sensitive areas of Europe in support of the objectives of the Convention. However, there is still a need to further develop the model, with respect to both its application and its interpretation. These developments are required in the near future if the full potential of dynamic models are to be realized in time for the forthcoming review of the Gothenburg Protocol.

V. HEAVY METALS IN SURFACE WATERS

26. In 1999 (within its 12-year report) ICP Waters assessed heavy metals in surface waters based on the data in the programme’s database (Skjelkvåle et al. 2000). The results showed that the ICP Waters database contained a number of sites with heavy metal data, but these sites were located in relatively few countries. In addition, data on heavy metals are reported from fewer sites in each of these countries than major solutes. To be able to give a good picture of the general level of heavy metals in surface waters throughout Europe and North America, heavy metal data for more sites with a larger geographical coverage are needed.

27. Few sites have long time series for heavy metals. Analytical methods have changed and the detection limits have generally decreased throughout the monitoring period for the sites with long-term measurements. Both the changes in method and the changes in detection limit make it difficult to identify time trends in heavy metals for many sites.

28. Heavy metal data in the ICP Waters database have been analysed with different analytical methods and analytical precision. In recent years the inductively-coupled plasma – mass spectrometry (ICP-MS) method has increasingly become the standard and has resulted in major improvements in detection limits for many metals. Regular intercalibration of analyses of heavy metals is of great importance for improving the quality of results and ensuring the comparability of data within the programme. All laboratories reporting data to ICP Waters participate in national and international intercalibrations.

29. Heavy metals in freshwater are much more frequently influenced by local pollution sources and human activities in the catchments than the acidification components (sulphate, nitrate, pH). Hence, the selection of sites for monitoring the effects of heavy metals resulting from air-transported pollution must be made with great care.

30. The results of the ICP Waters assessment of heavy metals in surface waters for the years 1999-2001 presented in the 15-year report confirm the results of the 12-year report. However, due to the low number of sites with heavy metals data and because of shortcomings in the data available (short series, changes in analytical methods), it is still not possible to carry out an analyse long-term trends in heavy metals on a regional scale, as has been done for acidification. The assessment of regional surface water contamination and time trends of heavy metals would require more sites with high-quality data.
31. An important task is to harmonize the water quality criteria for heavy metals used by different countries. At present critical limits for many heavy metals differ by more than an order of magnitude between countries.

VI. FUTURE WORK

32. The results from ICP Waters clearly show that surface waters respond to changes in atmospheric deposition. 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 reflect an effects response that is integrated over the entire catchment area. The ICP Waters site network is geographically extensive and its database includes long-term data series (> 15 years) for many sites. The network is thus well placed to document changes that result from implementation of the protocols.

33. 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. If this is the case it may have a major influence on the future acidification status of surface waters. Continuation of the national monitoring programmes that submit their data to ICP Waters and the yearly chemical and biological intercalibration exercises remain the most important activities in the future work of ICP Waters.

34. Mapping critical loads for acidifying components is a key activity under the Convention. ICP Waters will use the expertise and data available within its 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.

35. Future work should also include dynamic biological responses in the recovery process. The widespread improvement in surface water quality during the past 15-20 years should give rise to biological recovery. Yet there are relatively few documented examples of biological recovery. The explanation may be found in the dynamic nature of biological response but also in a lack of appropriate long-term monitoring data. ICP Waters will explore the possibilities of developing biological response models for assessing recovery from acidification.

36. Heavy metals (in particular lead, cadmium and mercury) and persistent organic pollutants (POPs) from long-range transport have not yet received the same attention in monitoring programmes as acidifying components. In the future ICP Waters plans to undertake an assessment of existing data for POPs (both chemical and biological) and prepare recommendations for monitoring and for deriving appropriate dose-response relationships. It will thus actively participate in the further development of effect-based approaches for POPs and heavy metals.

VII. REFERENCES


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