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

PROGRAMME MANUAL

Complied by the Programme Centre,
(Norwegian Institute for Water Research)

Revised edition, Oslo, September 1996

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Contents

1. Introduction

1.1 Background

The International Cooperative Programme for Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters) was established in 1985 by the UN/ECE Executive Body (EB) for the Convention on Long-Range Transboundary Air Pollution. For the first phase, Canada was appointed the lead country, and during the implementation phase that followed, Norway assumed leadership and provided facilities for the Programme Centre. From the beginning, the ICP was designed to assess, on a regional basis, the degree and geographical extent of acidification of surface waters. As of 1995, the ICP includes participants from 20 countries who contribute technical information for assessment purposes, engage in annual Task Force meetings, and produce periodic reports evaluating the status of acidification effects on surface waters in the ECE Region.

This ICP is one of a collection of cooperative programmes established by EB (i.e. Forests, Crops, Materials and Integrated Monitoring) that seek to provide assessment information on the effects of acidic deposition and other airborne pollutants. In particular, some of the monitoring activities of Monitoring (ICP IM) overlap with ICP Waters, although the ICP IM tends to focus on terrestrial catchments and collects little information on lakes. Taken together, however, they cover a wide range of ecosystem components.

This ICP Waters operates from the middle of a monitoring hierarchy that is designed to evaluate the environmental effects of acidic deposition on surface waters, and predict future ecosystem changes occurring under different deposition scenarios. Lower in the hierarchy is a series of national networks that employ progressively less comprehensive and frequent sampling but greater spatial coverage, culminating in one-time regional surveys. Achieving the Programme objectives requires that both the temporally intensive and regionally extensive data are collected on a continuing basis.

In addition to the various national programs that voluntarily supply information (e.g. regional surveys) as a supplement to the ICP activities, some other international programs also provide complementary information, e.g. AL:PE/MOLAR (a research programme on high mountain lakes), ENCORE/DYNAMIC (a small catchment modelling programme), etc.

1.2 ICP Waters, its Aims and Objectives

The technical activities of ICP Waters focus on surface water monitoring and evaluation of the monitoring data. For purposes of this manual, the term "monitoring" will be defined as obtaining a series of periodic measurements of selected determinants, with the purpose of detecting temporal changes or trends in the determinants and in the ecosystems to which they relate. Thus, monitoring programmes describe the temporal variability of ecosystem components in contrast to surveys that establish spatial variance within a system at a given time. Logistical constraints often place an upper limit to the sampling frequency of extensive monitoring programmes. Thus it is expected that the primary effort of the ICP monitoring programme will be to define variations or trends having periods greater than one year.

Monitoring of the effects of acidification on the surface waters on an international scale cannot be achieved effectively without substantial costs. It is therefore imperative that clear aims and objectives be established so that the programme employs resources to the best advantage. In many cases, the resources and effort available for a monitoring programme are limited. The

ICP Water programme has to rely on national monitoring programmes and data being delivered to the Programme Centre for use under the convention.

The ICP objectives were established early in the Programme and they have guided its development and will continue to determine the ultimate use of the data produced. The ICP aims and objectives are summarised as follows:

Aims
- Assess the degree and geographic extent of acidification of surface waters;
- Collect information to evaluate dose/response relationships; and
- Define long-term trends and variations in aquatic chemistry and biota attributable to atmospheric pollution.

Objectives
- Establish an international network of surface water monitoring sites;
- Promote international harmonisation of monitoring practices by:
  - Specifying a manual on methods and operations,
  - Conducting interlaboratory quality assurance tests,
  - Compiling a centralised data base with data quality control and assessment capabilities;
- Develop and/or recommend chemical and biological methods for monitoring purposes;
- Report on programme aims and short-term objectives;
- Conduct workshops on topics of central interest to the Programme Task Force and the aquatic effects research community;
- Access water related questions in cooperation with other ICP's.

Short term objectives
The ICP Waters being established as a long term monitoring programme can also be used to answer short term objectives as addressed by the Working Group on Effects and imposed by the Programme Task Force. An example is the report in 1994 focusing on Nitrogen in particular, as a background report for the work on the Nitrogen Protocol under the convention. Such short term objectives are often joint activities between several of the ICP's and different issues will be addressed according to the needs of the convention.

1.3 Purpose of the manual

During the first Task Force meeting of the ICP (April, 1986), a "Manual for Chemical and Biological Monitoring" was formulated and later recommended to the ECE Working Group on Effects for implementation. The intent of that manual was to guide development of and harmonise the various national components that comprised the ICP monitoring programme by standardising sample collection and analytical methodologies. The manual is also an overall guide to activities and priorities of the work at the Programme Centre. An amendment to the manual was recommended by the seventh Task Force meeting (October, 1991). It added sections on assessment of regional monitoring and survey data, diatom monitoring, and fish population monitoring.

The tenth Task Force meeting (October, 1994) recommended that the manual be consolidated and updated (a) to reflect the technical advances that have occurred over the last decade and (b) to better express the accumulated experience now available for designing and operating an international programme to monitor the chemistry and biology of surface waters. In this regard, the experience gained from ICP quality assurance (QA) activities have been particularly important.

1.4 Status of the programme 1995

1.4.1 Hierarchy of the Monitoring Programme

The hierarchy of national monitoring programmes is reflected in the hierarchy of the ICP Waters programme to deal with:

- Data from small catchments, monthly or seasonal sampling (level I)
- Relatively large number of sites with minimum annual sampling frequency (level II)
- Regional surveys (level III). Sampling of many sites one time in several years.

ICP Waters focuses on level I, and deals with catchment data with sampling frequency from weeks to seasonal sampling. With the less frequent sampling the biological aspects become more important as they accumulate the effects of changing water quality in the previous period.

The level II and III data are important in particular to illustrate the regional picture of acidification situation and to evaluate the representativeness of the more intensively monitored catchments.

1.4.2 Water Chemistry

The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes has been designed to establish the degree and geographic extent of acidification of surface waters. Further, to collect information in order to evaluate dose/response relationships, and to define long-term trends and variations in aquatic chemistry and biota attributable to atmospheric pollution. The countries of Europe and North America have representatives in the Programme Task Force.

Long-term Monitoring
Investigation of water chemistry is carried out by each member country, and both lakes and rivers are sampled and studied. The sampling objective is to obtain a measurement that is representative of mean conditions of the lake or river for the period of sampling. As of 1995, the ICP database includes 30 chemical variables and information from 200 surface water stations for time records up to 20 years.

Approximately half of these have both biological and chemical data, the others have only chemical data. Sites included in the Programme are monitored by each country individually, although the monitoring methods used have been standardised across participants, and intercalibration studies are completed each year. The Programme Centre and the Programme database are located at the Norwegian Institute for Water Research (NIVA). A sub database for biological data is established at University of Bergen.

Trend analyses have been performed on the chemical data for sites with more than five years of monitoring. Results from trend analysis are compared to trends in deposition and climatic conditions, as well as to average physical characteristics at the monitoring sites. Short-term trends are expected to reflect the processes occurring at the sites, rather than predicting long-term change.

1.4.3 Biological Monitoring

Invertebrates
Analysis of invertebrate communities is a well established tool in many types of environmental investigations, including acidification studies. The most acid sensitive species (i.e. indicators) disappear very early in the acidifying process, while others are more tolerant. There is a gradient in the tolerance of invertebrate species/ groups in waters of varying acidity. For this ICP, qualitative samples of invertebrate fauna from streams or rivers are used. Absence or presence of indicator species reflect the water acidity. Short- and long-term trends may be detected from the resulting data.

As of 1995, the ICP database contains invertebrate information from 80 stations and 5 year records. The regional spread of available sites with biological data can, however, be improved.

Diatoms
In most lakes and streams diatoms occupy a variety of habitats and may be found on the surfaces of stones or macrophytes, attached to sand grains or living on the sediment surface as well as in the open water column. Most lakes support a diatom plankton fauna independent of pH. Within a single lake or stream, species distribution is strongly controlled by habitat, and within a single habitat species composition may vary, for example, between different macrophyte hosts, or along a sediment particle size gradient. Methods used by ICP Waters are designed to keep these sources of variation constant. Sediment samples are used to provide diatom samples integrated both spatially, (i.e. across all diatom source communities), and temporally (over a period of months for sediment traps, or years for surface sediments).

Fish population Monitoring
Monitoring the status of fish populations became part of the ICP from 1992. These investigations give information about the status of the population over time. Most fish species can live for many years and they usually have life stages with differing sensitivity to acidic water. Monitoring of fish employs methods that can detect changes in the different life stages of the population every year.

1.4.4 Regional Survey

Regional survey data are useful to the ICP Waters Programme because they allow us to answer important questions of the geographic extent of acidification, and permit the site-specific data collected from small catchments to be placed in a larger geographical context. This is important in establishing how typical or representative each ICP Waters catchment might be.

Currently, regional survey data are available from a limited number of countries. It is the aim of ICP Waters to maintain an accurate inventory of these datasets, rather than to maintain the data themselves. The data would then be available for special projects or data interpretations, as needed.

1.4.5 Data Quality Control

Data QA has been stressed as an important part of the programme. Annual laboratory intercalibration exercises have been established, involving for example, 26 laboratories from 17 countries in the chemical intercomparison test 9408. This has become a routine control of

normal laboratory practice in the participating laboratories. The Youden method (two samples approach) is used to assess laboratory performance. Annual reports show how target accuracies are met by the participating laboratories for most ions in natural waters. Further data base control covers continuity of data, inspection for outliers and ionic balance. Data are not excluded from the main ICP Waters database without approval by the originator. However, the Programme Centre plan to make a second dataset containing only data that fulfil certain criteria concerning regularity of sampling, parameters and data quality. The objective is to create a good quality database for efficient use in the near future as well as in the long run.

Quality control of biological parameters commenced in 1992. Participating laboratories receive unknown invertebrate samples of their own fauna. Parallel diatom samples from lakes in different countries have been distributed in the same way and examined by diatom experts. The identification of species is generally accurate.

1.4.6 Reporting

Reporting of ICP Waters activities occurs in several forms. First, results of inter-laboratory QA studies are reported annually by the Programme Centre. In addition, a data report encompassing all information submitted to the ICP Waters database within a given year is provided by the Programme Centre at the annual Task Force meeting so that participants may check the validity of their data and ensure that all data transfers have occurred successfully. Second, the annual Task Force meeting always conducts a "workshop" of technical presentations that may be either national or international in character. Either the host country or the Programme Centre produces and distributes a Workshop Proceedings. Finally, the most important reports produced by the ICP Waters are the so-called "Three Year Reports" that provide an overall synthesis and assessment of the accumulated information. As of 1995, the ICP Waters has produced the "Three Year Report" covering 1987-89, and the "Six Year Report" covering 1987-92. It is a continuing expectation that such synthesis reports will be produced every three years. Special reports on selected items and short term objectives will be performed in years in between according to priorities of Working Group on Effects and the Programme Task Force.

2. Site selection

2.1 General criteria

The site selection is the responsibility of the national focal centres. It is important to have a good regional coverage of sites, especially the regions with catchments that are sensitive to acid deposition. In regions with many potential sampling sites close to each other, the national focal centre should select one or a few sites that they consider the most appropriate one(s) to meet the objectives of the programme. It is more important to cover several regions than to have a lot of sites close to each other.

If possible, it is recommended to select sites from catchments receiving different levels of sulphur and nitrogen deposition.

Selection of sampling locations must depend upon the characteristics of the specific region or geographical area. In some regions lakes are the predominant aquatic ecosystem, while in others, rivers and streams are more important. The national programmes that will enter the international cooperative programme could be expected to consist of a number of stations believed to be sensitive to changes in acid deposition. The normal number would be 3 to 30 stations for chemical monitoring and biological sampling.

Where past records are available from previous survey programmes, statistical analyses can be applied to select representative monitoring sites and an optimum programme can be designed. In the absence of past records, it may be advisable to conduct a survey to provide a basis for the monitoring site selection.

2.2 Specific criteria

2.2.1 All sites

a) The ICP Waters programme is established to monitor Long-Range Transboundary air pollution and so the selected sites should not have a pronounced influence from local sources of pollution in the catchment that may lead to misinterpretation of chemical and biological data (e.g. domestic sewage, industrial waste water, agriculture etc.). ICP Waters should consist, as much as possible, of sites that don't have local impacts from other pollution sources.

b) In regions where surface waters are universally sensitive to acidification, sites, should be chosen to represent the diversity of the region (chemically, biologically and geographically). In regions where surface waters exhibit a wide range of acid-sensitivity, sites for ICP Waters should be chosen from among the most susceptible to acidification. The aim of the site selection should be to focus primarily on sites that are likely to change in response to acid deposition, and secondarily to represent the region as a whole (where possible).

c) Confidence in the future protection of the site from changes in local influences. Very valuable long-term records may be lost due to significant local changes. The loss of sample sites to liming mitigation programmes and changes in forestry practices must be avoided. Areas such as national parks and nature reserves are often well protected from changes and should be considered for sampling sites;

d) Sites should provide the opportunity for both chemical and biological monitoring;

e) Sufficient sites must be included to provide for statistical confidence in regional analysis of changes or trends. The number of sites should be balanced against the ability to support the monitoring on a sustainable, and long-term basis.

f) Reference or background sites should be included if possible to provide information by which the analyses can be compared with respect to climatic or other influences.

g) Sites with long time series of data are preferable if the other main criteria are met.

2.2.2 Lakes

Drainage lakes (i.e. with an outlet) are best suited for monitoring. Choose a deep site that is not directly influenced by any inlet stream, preferably in the outlet area. The lake outlet is an optional site selection. For long-term monitoring, epilimnion samples or surface samples (0.1-1m) are sufficient. Additional samples of the depth profile are optional.

Lakes with a moderate water renewal period, approximately 1 year or less are preferable. Lakes with very long residence times react slowly to changes in depositions of air pollutants and are not good candidates for detecting trends for decade timescales.

Lakes should preferably be selected in the headwater part of the catchment, without a larger lake upstream.

If a paleolimnological investigation of sediments is planned, the lake should be sufficiently deep to minimise resuspension.

2.2.3 Rivers

Running waters are usually well-mixed with homogeneous properties. The sampling sites should be chosen to avoid local gradients across the stream. Choose a site with turbulent water current, well below tributaries to ensure complete mixing. Representative samples can then be obtained by a surface grab sample away from streambank.

Usually a rather small river or brook is preferable. In general, small catchments react more rapidly than large ones to changes in deposition of airborne pollution.

To facilitate biological sampling the river bed should preferably be relatively stable with a variety of gravel and stones.

2.2.4 Regional surveys

The regional-scale assessment of the present and future status of surface water ecosystems depends on the continuing existence of all levels within the monitoring hierarchy. Regional-scale monitoring and survey data on surface water acidification is systematically collected in many countries participating in ICP Waters. The regional monitoring/survey sites have generally been selected to be representative of the areas considered sensitive to acidic deposition. In some countries (e.g. Canada, Finland, Sweden, U.S.A) statistical methods have

been used in the monitoring/survey site selection procedure, which is the most reliable way to assure the representativeness of these sites.

If a national regional network of sites is established a subset of data can be transferred to the Programme Centre. The selection criteria should be discussed in each case.

2.3 Catchment and site information

Interpretation of data obtained from the monitoring programme will require information concerning the characteristics of the monitoring sites. It is therefore of great importance to include documentation of each sampling site as an integral part of the monitoring programme. The experience from the former manual showed that when the list of catchment and site information is long and detailed, the forms will be incompleted and some information will be lacking from almost all sites. The list is therefore shortened to focus on the most important information and this should be available for most sites. A form for catchment and site data is shown in Appendix 1. An additional form for biological (benthos) sampling sites is shown in Appendix 2.

Required data for all sites:
Name and site code.
Latitude and longitude.
Catchment area upstream from the site, km^2.
Elevation of site, m.
Average precipitation, $mm.yr^{-1}$.
Average catchment runoff, $mm.yr^{-1}$ ($1\ l.s^{-1}.km^{-2} = 31.5\ mm.yr^{-1}$).
(Alternative to measured runoff: precipitation - estimated evapotranspiration).

Required additional data for lakes:
Hydrologic type (seepage or drainage lake).
Lake area, km^2.
Average depth, m.

Optional data:
Main type of bedrock.
Major catchment composition (lakes, vegetation types, farmland etc), % coverage.
Average soil depth.

***For biological (benthos) sampling sites only*:**
Characterisation of bottom substrate and site surroundings. Use form shown in Appendix 2.

Regional surveys
The site and sample documentation of the regional data sent to the Programme Centre should include the following characteristics:

- Name or identifying number.
- Longitude and latitude.
- Site type (lake or stream).
- Date of sampling (year only, if the sample is a calculated annual mean).
- Depth at which the sample was taken.
- Catchment area, km^2.
- Average catchment runoff, $mm.yr^{-1}$.

3. Water chemistry monitoring

3.1 Determinants

3.1.1 Chemical and physical parameters

The primary objective of the monitoring programme relates to the acidification of surface waters. Thus the essential determinants of the monitoring programme are those that define the degree of acidification or which are directly related to acidification of the waters. A secondary list of desirable determinants are those that may be useful in interpretation of the effects of acidification. The third list is considered the absolute minimum required for the ICP Waters data base.

Essential, desirable and minimum list of chemical parameters. with preferable units:

anions: alkalinity[1)] (mmol/l), sulphate (mg/l), nitrate (µgN/l), chloride (mg/l).

organic: dissolved carbon (mgC/l), or permanganate (mgO/l).

cations: pH, calcium (mg/l), magnesium (mg/l), sodium (mg/l), potassium (mg/l), ammonium[2)] (µgN/l) and inorganic (labile) aluminium[3)] (µg/l).

physical properties: specific conductance (mS/m at 25°C).

1) May be omitted at pH< 5.2 (alkalinity approximately zero if negative values are not measured by Gran titration). *Note that the preferable unit is changed from mg $CaCO_3$/l to mmol/l.*
*Conversion: Alkalinity (HCO_3^-) in mmol/l (equals meq/l) = $CaCO_3$ (mg/l) * 0.020.*
When mmol/l is used, please note that 1 mmol/l $CaCO_3$ equals 2 mmol/l HCO_3^-.
***Important**: if the titration is made to one single pH value (usually pH 4.5) it is necessary to state whether the given value is adjusted to be the endpoint value or represents the total acid consumption to pH 4.5.*
2) In areas where this component is important.
3) Difference between reactive (organic + inorganic) and non-labile (organic) aluminium. May be omitted at pH>5.5.

Desirable determinants with preferable units:

physical properties: water temperature (°C) and flow (m^3/s) at time of sampling.

nutrients: ammonium (µgN/l), total nitrogen (mgN/l), total phosphorus (µgP/l), soluble reactive phosphate (µgP/l), dissolved oxygen (mgO/l), silica ($mgSiO_2$/l).

metals: iron, manganese, cadmium, zinc, copper, nickel, lead (total, in µg/l)

other: fluoride (mg/l), colour (mg Pt/l), turbidity (FTU).

Minimum list of parameters:

If a complete primary analysis cannot be obtained, a determination of pH, calcium, magnesium, alkalinity, sulphate, chloride and nitrate may be accepted as a minimal monitoring report.

3.1.2 Fluxes of elements

The National Focal Points are called upon to report yearly input (preferably wet + dry) and output fluxes of S and N from catchments. Where local measurements of inputs are not available, the programme centre will provide EMEP data from the grid where the sites are situated (European sites only). Desirable parameters and units:

Yearly deposition of S (wet + dry, sea-salt corrected), $gS.m^{-2}.yr^{-1}$ or $kgS.ha^{-1}.yr^{-1}$.

Yearly deposition of N (wet + dry), $gN.m^{-2}.yr^{-1}$ or $kgN.ha^{-1}.yr^{-1}$.

Yearly runoff of S (sea-salt corrected), $gS.m^{-2}.yr^{-1}$ or $kgS.ha^{-1}.yr^{-1}$.

Yearly runoff of N, $gN.m^{-2}.yr^{-1}$ or $kgN.ha^{-1}.yr^{-1}$.

3.2 Methods

3.2.1 Sampling and handling

River water sampling

Flowing rivers are usually well-mixed with homogeneous properties. The sampling sites should be chosen to avoid local gradients across the stream. Representative samples can therefore be obtained by a surface grab sample away from streambank. When filling the bottle, keep the bottleneck against the current, well below the surface. Rinse the bottle and screwcap 3 times with sampling water prior to sampling. Avoid touching the inside of bottle and screwcap.

Lake water sampling

Water chemistry samples from the upper layer (0.1 - 1 m) or the lake outlet are sufficient for monitoring purposes. Discrete samples at the mid-point of the epilimnion or a mixed sample of the epilimnion are good alternatives.

If a water sampler is used, it should be tested for contaminants, especially if heavy metals are analysed.

Handling of water chemistry samples

A programme to measure and deal with waters of very low total ionic strength is needed to monitor the trends or changes in acidification of surface waters. Prevention of sample contamination or sample changes while in storage may be critical in obtaining accurate measurements. All containers used for either sample collection or storage must be free of any important quantity of the determinants in relation to the lowest concentration to be measured, and the containers must be of a material that will neither absorb nor release measurable quantities of the determinant. Extreme care must be exercised to avoid contamination and sample containers must be entirely full and tightly capped to minimise any interchange with entrapped air.

Samples intended for major ion and nutrient analysis should be collected, stored in the dark at about 4 °C and transferred to the laboratory for analysis as soon as possible.

Samples intended for metal analysis may be preserved by adding acid, usually using nitric acid. Preservation at pH 2 will in most cases retain the total and dissolved metals for several weeks. If the preservative is added in the field, extreme care must be observed to prevent contamination of the major ion sample with nitric acid. If determining the dissolved fraction it is necessary to filter the sample (0.45 µm) prior to preservation.

Sample identification and documentation of the sampling must be firmly and accurately maintained for every sample. This documentation is an integral part of the sample information and must be entered into the data base. Any lack or confusion of documentation may invalidate the resulting data. Sample documentation should include as a minimum:

- Sample site identification
- Date of sampling
- Sampling depth/location

3.2.2 Sampling frequency

Sample collection is an essential link in the monitoring programme and the accuracy and reliability of the final results depend upon the representativeness of the sample of the actual site characteristics that are to be monitored. If the sample is not representative, the data obtained and subsequent interpretation may be incorrect or misleading.

Whether the sampling is for chemical analysis or for biological assessment, the sampling procedure must consider local temporal and spatial variations and must yield a sample that is as representative of the local conditions as possible. Time scales that are intended for interpretation must be used as the determinants for collection methods and frequency but some general guidelines are given here.

Generally, monthly sampling (or more frequent) is recommended for all sites. If samples are taken less frequent than monthly, the samples must be taken at the same time of the year each year, preferably evenly spaced in time.

a) Lakes

Lakes exhibit a wide range of hydrologic characteristics, from very fast-flushing drainage lakes, to slow-flushing seepage lakes. Sampling of lakes should be carried out in such a way that each lake's annual variability is well-characterised. Monthly samples are recommended for most fast-flushing lakes; more frequent sampling may be required in lakes that undergo short-lived acidic episodes or nitrate peaks. Quarterly or seasonal sampling is likely to be adequate in lakes with long residence times. In remote areas where frequent sampling is impossible for practical and economical reasons, even one sample per year may be useful for long-term monitoring. Such samples must be taken at the same time of the year each year, preferably shortly after fall overturn. For yearly sampling it is recommended to select a group of lakes rather than a single lake.

b) Rivers

The temporal variability of water quality in rivers is related strongly to the river hydrograph. Periodic sampling is necessary, and samples should be collected at a minimum of monthly

intervals. For the basic sampling programme the samples should be equally spaced through the year. This practise would facilitate comparison of annual means for all sites.

Where flow data are available for calculations of yearly transport values of elements from catchments, increased sampling frequency in flood periods is recommended.

c) Regional surveys

The Programme Centre should maintain an inventory of regional data from participating countries. Databases from regional surveys should be maintained by the National Focal Centres. The Focal Centres are encouraged to make data (raw or processed) available for special ICP projects (workshops etc.).

3.2.3 Chemical methods

The use of adequate methods is the responsibility of the national focal centre. The majority of the participating countries have accepted the use of international standard methods such as prescribed by ISO/CEN in their national work. The EN (European standards) are legally prescribed for use by all EU nations. We therefore propose ICP Waters adopt ISO/CEN standard methods as a basis for the methods actually used. These methods usually have a high quality, are well verified and documented in a way accessible to the participants. Being aware that changing methods are often difficult, expensive and not necessarily desirable, it should at least be documented that the methods used have a quality equal to or better than the ISO/EN standard with respect to interferences and detection levels. A list containing a short description, detection limit, unit and reference to all reported parameters must be attached to the data delivered to the Programme Centre.

Recognising the above the following methods are recommended for the future work:

EN-ISO 7887:1994 Water quality- Examination of colour.

EN 25 813:1992 Water quality- Determination of dissolved oxygen- Iodometric method.

EN 25 814:1992 Water quality- Determination of dissolved oxygen- Electrochemical probe method.

EN 27 888:1993 Water quality- Determination of electrical conductivity.

ISO 9963-2:1994 Water quality- Determination of alkalinity. Part 2. Determination of carbonate alkalinity.

ISO 9964-1:1993 Water quality- Determination of sodium and potassium. Part 1. Determination of sodium by atomic absorption spectrometry.

ISO 9964-2:1993 Water quality- Determination of sodium and potassium. Part 2. Determination of potassium by atomic absorption spectrometry.

ISO 9964-3:1993 Water quality- Determination of sodium and potassium. Part 1. Determination of sodium and potassium by flame emission spectrometry.

ISO 10523-1:1994 Water quality- Determination of pH.

ISO 8245 Water quality- Guidelines for the determination of total organic carbon (TOC).

ISO 10566:1994 Water quality- Determination of aluminium -Spectrometric method using pyrocatechol violet.

For speciation of aluminium fractions, see e.g.: E.J.S. Røgeberg and A. Henriksen. An Automatic Method for Fractionation and Determination of Aluminium Species in Fresh-Waters. Vatten 1985, **41**(1), 48 - 53.

ISO 10304-1:1992 Water quality- Determination of dissolved fluoride, chloride, nitrite, orthophosphate, nitrate and sulphate- Part 1. Method for water with low contamination.

ISO 6878/1: 1986 Water quality- Determination of phosphorous - Part 1: Ammonium molybdate spectrometric method.

ISO/DIS 11732: Water quality- Determination of ammonium nitrogen by flow analysis and spectrometric detection.

ISO/DIS 13395: Water quality- Determination of nitrate and nitrite nitrogen and the sum of both by flow analysis.

ISO/DIS 11905-1: Water quality- Determination of nitrogen - Part 1: Method using oxidative digestion with peroxodisulfate.

Information of the ISO/CEN methods listed above can be obtained from :
1) The national standardisation agencies.
2) International Organisation for Standardisation, DIN, Burggrafenstrasse 6, 10787 Berlin, Germany.
3) ISO International Organisation for Standardisation, Case Postale 56, CH-1211 Genève, Switzerland.
4) CEN European Committee for Standardisation, rue de Stassart 36, B-1050 Brussels, Belgium.

3.3 Quality assurance

General

The general objective of a cooperative international programme to monitor the effects of acidic deposition requires that all data generated from the various participants be comparable on an objective basis. To achieve such comparability, the methods employed for chemical analysis must be thoroughly documented and a quality assurance programme must be carried out to demonstrate that results of adequate accuracy are being obtained. Only through such objective control can environmental variances or observed changes be assigned a degree of confidence.

Analytical methods of the participant laboratories may be employed if it can be demonstrated through the quality control programme that they produce results of the required accuracy.

In-laboratory quality control

All laboratories that participate in cooperative programmes should provide documented evidence that in-laboratory quality control is maintained to assure the accuracy and uniformity of routine laboratory analyses. Unless in-laboratory quality control is carried out as normal laboratory operating practice, there is little benefit of between-laboratory quality control programmes.

In-laboratory quality control should include:

(a) Complete and thorough documentation of the methods of control; (for example: standard deviation of a single sample, use of control samples and in particular control charts).

(b) Documented evidence of analytical performance, accuracy of in-house standards, within-run precision, between-run controls and accuracy of the methods employed;

(c) Evidence of sample specific data quality such as an adequate ionic balance or specific conductance determination for individual samples;

(d) Evidence of adequate performance by analysis of external audit materials, standard samples of adequate matrix, etc.

Between-laboratory quality control (Quality assessment)

Between-laboratory quality control is necessary in a multilaboratory programme to assure clear identification and control of the bias between the analyses carried out by individual participants of the programme. This quality assessment does not substitute for the routine in-laboratory control that assures consistency in day-to-day operations. Instead it is intended to assure that systematic biases do not exist between determinations of the different programme participants. Such biases may arise through the application of different methods, errors in laboratory standards or through inadequate in-laboratory control.

The between-laboratory quality control will be carried out by the Programme Centre so that an objective assessment is obtained. The procedures to be employed are based on the "round robin" concept and the procedure of Youden. Samples prepared by the control laboratory are targeted to test for biases in analyses of the principal determinants of the programme. Participating laboratories are assessed on their reported determinations in relation to the other participants.

A reasonable approach to interlaboratory control will be to circulate once a year a pair of synthetic or natural water samples with different concentrations of the particular ions in question.

Periodic assessment reports can provide evidence of analytical biases. These reports may be employed as guidelines for data quality assessment but are of primary use to initiate corrective actions that will eliminate the biases.

All between-laboratory quality assurance reports will be a part of the data archive of the cooperative programme. It is also important to start a between-laboratory quality control programme as soon as the monitoring programme starts. Laboratories are expected to participate in the control programme under full identification.

Application programs for data accuracy will for example include computation of the sum anions vs. cations and theoretical conductivity vs. measured conductivity.

The total error of individual analytical results should not exceed a value corresponding to the required detection limit (L), or a percentage of the result (P %), whichever is the greater. Laboratories using less sensitive methods should report deviations to the Programme Centre. Well-tested methods available for national or international use should be applied.

Suggested target accuracy's (P %) and detection limits (L) for the measurement of water quality determinants:

Determinant	**Detection limit (L)**	**P (%)**
Calcium	0.02 mg/l	10
Magnesium	0 01 "	10
Sodium	0.02 "	10
Potassium	0.02 "	10
Chloride	0.2 "	10
Sulphate, (as SO_4)	0.2 "	10
Nitrate (+ Nitrite)[1] , (as N)	10 µg/l	10
Reactive Aluminium	10 "	10
Non-labile (organic) Aluminium	10 "	10
Labile (inorganic) Aluminium	10 "	10
Dissolved Organic Carbon[2] ,(as C)	0.2 mg/l	10
pH	0.1 pH units	--
Conductivity	0.02 mS m^{-1}	5
Alkalinity	0.005 mmol/l	10
Total Phosphorus, (as P)	2 µg/l	10
Soluble Reactive Phosphate, (as P)	2 µg/l	10
Temperature	±0.2°C	

[1] Depending on the method if nitrite is included. In well aerated surface waters nitrite is usually close to zero.
[2] In samples with low particle content total organic carbon (TOC) may be used (no filtering).

Non-filtered samples are generally preferred, but filtering may be necessary in some cases.

The quality of the measurements should also be judged by the ion balance and by comparing calculated and measured conductivity. The target accuracy for the ion balance should be that *the difference between the sum of cations and sum of anions should not exceed 10% of the cations.* Organic anions can be approximated from TOC/DOC. The calculated conductivity will indicate if one or several analytical measurements are too low or too high. Details are described in Appendix 3.

4. Biological monitoring and assessment

Biological sampling must be carried out with respect to the species or organisms that are to be collected for monitoring using standard limnological methods.

For biological sampling methods refer to the IBP Handbook (Downing & Rigler 1984), or other standard methods (Hellawell 1978).

4.1 Biological indicator species

The monitoring of biological effects of acidification may be developed according to two categories selecting species or communities sensitive or tolerant of acid conditions, including a variety of chemical components. Because the regional extent of many species is restricted, universal indicators are not always available. Nevertheless species/acidity relationships are recognised and a limited degree of universality or identification of common indicators is possible (references below).

a) A number of species are known to be sensitive to acid conditions and their presence/absence will indicate both current and recent past water conditions. For example, molluscs are rarely found below pH 5.6, or gammarids below pH 6. For any water body to be sampled, these organisms should be sought and identified unequivocally to species level.

b) Species that are tolerant of acid conditions and favoured by the absence of predation in aquatic ecosystems should be monitored for relative abundance. For example, the abundance of Coleoptera, Corixids, Polycentropodidae, and the relative abundance of Ephemeroptera/-Plecoptera in running water will be indicative of the degree of acidity, see Raddum and Fjellheim (1994).

The quantitative use of identified biological species or communities as objective indicators of the acidity of surface waters can be developed in accordance with the influence of acidity on the various organisms. Numerical relationships relating pH of water and species response appear to be developed only for diatom assemblages, chrysophyte, chydorid and invertebrates communities where resolutions of 0.3 to 0.5 pH units are possible if calibrations to local conditions are developed.

Because universal indicators cannot be identified due to differences in geographical distribution, monitoring changes in community structure or population at selected key sites can provide indication of overall or regional change, and responses between regions can be compared.

Significant biological indicators of acidification include:

Macrophytes: Shifts to *Sphagnum* dominated beds have been noted to accompany acidification. At pH less than 5, benthic filamentous algae increase (mainly *Zygnema* spp., *Zygonium* spp. and *Mougeotia* spp. and/or *Juncus bulbosus*).

Phytoplankton: The diatoms may be one of the most sensitive groups. Regional calibration sets for the relationship between measured pH and living diatom communities should be established to improve pH-inferences. Sampling: either a vertical tow with plankton net (10 mesh size) or an integrated water column sample allowed to sediment out. Phytoplankton should be fixed with Lugol's solution. Refixation is then necessary either with lugol or formaldehyde.

Microphytobenthon: Diatom community structure of the benthos of lakes and rivers may be acid indicative as well. Sampling: Community structure can be studied by scrapings from stones, branches and rooted plants.

Zooplankton: Shifts in the community structure should be monitored as some species appear to decrease with acidification. Species of Cladocera are almost universally present, and Daphnids show low tolerance to clear acid water. Chydorids, too, exhibit markedly different tolerance towards acidity. The Cladoceran community will be highly valuable to monitor sensitive areas at species level. Sampling: 3 net hauls (60-90 μ mesh) from 20 m to surface, or bottom to surface (shallow lakes). Zooplankton should be transferred to 2-4% solution of formaldehyde.

Macro-invertebrates: Molluscs are highly acid sensitive. Snails are not generally found below pH 5.6. *Gammarus lacustris* is not generally found below pH 6.

Insects: Many species of mayflies (Ephemeropterans) appear to be sensitive indicators of acidic conditions, and are common, nearly universal taxa. Some species of Trichoptera and Plecoptera are not found below pH ≈ 5.

Fish: Most species of freshwater fish are sensitive to acid conditions. The North American and the European and Asian species show different responses to acidification, but the distribution of fish species and specific changes in fish populations indicate acidification.

Bearing in mind the loss of species from waters subject to acid episodes, the potential of communicating waters to supply organisms for recolonisation is important, and can be assessed by additional, but less intensive sampling in adjacent waters on a regular basis.

The quality of biological observations will be dependent on the sampling procedures and the accuracy of species attribution. For the latter, exchange of material between laboratories is advised. Biological index organisms should be archived for reference.

4.2 Invertebrates

It is understood that composite acidification scores developed according to the schema below will not provide indices of acidification which are fully comparable between the regions for which they are developed. Acidification scores are, however, already very useful regional indices for integrating the biological effects in space and time of the varying chemical water quality conditions. There is a clear need to continue identification of the acid tolerance in invertebrate species in order to improve the application of this methodology. Participants in the Program are recommended to start using acidification scores and report their results.

4.2.1 Determinants and explanation of the model indicator

The acid status of selected sites in different regions and countries can be estimated by use of a hierarchical system based on "acidification numbers", in order to compare regions with different faunas. Repeated measurements can be used to indicate trends in acidification at the monitored sites.

Indicator species with the same tolerance to acidity are assigned the same number or "acidification score". Four categories (A, B, C and D) are defined in the following:

A) Indicators extinct at pH 5.5-6.0, score 1
B) Indicators extinct at pH 5.0- 5.5, score 0.5
C) Indicators that tolerate acidity pH 4.7. score 0.25
D) Indicators that tolerate acidity to pH < 4.7, score 0

Based on studies of the fauna of surface waters in western Norway the following species can be used for illustration. The system can be adopted to surface waters elsewhere if similar hierarchical categories of species with known tolerance levels are identified.

Category	**Species/group**	**Acidification score**
A	Gammarus spp. Gastropods Baetis spp.	1
B	Daphnia spp. Apatania spp. Hydropsyche spp.	0.5
C	Small mussels Pisidium casertatum	0.25
D	Corixa spp. Odonata Coleopterans	0

The acidification score of **a site** is calculated as follows:

If a sample contains one or more species in category A, acidification score 1, the site is scored 1, independent of other species of different categories that may be present. At sites where category A species are absent, and if one or more species in category B are reported as common, the site is considered moderately acidified and the score is 0.5. At more pronounced levels of acidification, when category B species are absent, small mussels may still be found, indicating a pH around 5 with episodic values below 4.8. Acidification score is 0.25.

If category C species are absent, the locality is considered highly acidified and the score is 0.

Repeated sampling at the same site on the same occasion should give the maximum score even if all samples do not contain particular sensitive/tolerant species.

One locality can thus only obtain a value of 1, 0.5, 0.25 or 0 at any time but within a catchment or region a mean acidification score can be derived from a number of sites.
Example: The sum of the score of 15 sites in a watershed is 8.75. The acidification index of the watershed is then 8.75/15 = 0.58

A modification of the acidification score 1 can be done in running water by using the ratio between the number of half grown *Baetis sp.* and half grown tolerant stoneflies (B/S). In western Norway, rivers with pH > 6 this ratio is normally > 1. When pH fall from 6 to 5.5 the number of *Baetis sp.* decreases rapidly, while tolerant stoneflies seems unaffected. At pH 5.5 the ratio will be 0. By using this information in localities typical for both *Baetis* and stoneflies the acidification score 1 can be defined as 0.5 + B/S. In cases where the ratio B/S = 0.5 the

score should be set to 1. At ratio values < 0.5 the score will be a number between 0.5 and 1, indicating increasing acid stress when the value is 0.5.

4.2.2 Frequency

The sampling regularity from year to year is very important. Spring sampling is defined as the end of the spring flood (snowmelt). Summer sampling is restricted to July and August, while fall sampling should be carried out in the last half of September or in October. Each season can only be compared with itself. The variation in sampling date from year to year should be as constant as possible, ideally kept within two weeks.

In the longer term (e.g. 5 years) trends may become evident.

4.2.3 Methods

Benthic invertebrate samples from running water and lakes should be preserved in 70% ethanol.

a) *Benthic invertebrates* in streams; standard "kicksamples" to collect at least 200 individuals, similarly at lake margins.

b) *Benthic invertebrates* in lakes; Peterson, Ekman grabs or core samples, if this habitat is significant.

4.2.4 Quality assurance

Pending agreement on a standard manual of measurements, it is important that thorough documentation of methods employed be maintained as part of any biological records. Only through careful examination of such documentation can any confidence be ascribed beyond trends based on presence/absence.

4.3 Diatoms

4.3.1 Determinants

Introduction
Diatoms are microscopic unicellular algae (Class Bacillariophyceae). They are abundant in a wide range of freshwater, brackish, and marine environments and may be identified to a high degree of taxonomic precision. Their use in palaeolimnological studies of lake acidification is well established (e.g. Battarbee 1984; Charles & Whitehead 1986), as is their role in the biological monitoring of organic pollution (e.g. Descy 1973; Watanabe *et al.* 1988). This section/chapter outlines methods for the biomonitoring of acid waters using diatoms.

Habitats
In most lakes and streams diatoms occupy a variety of habitats, and may be found on the surfaces of stones (the epilithon) or macrophytes (the epiphyton), attached to sand grains (the epipsammon) or living on the sediment surface (the epipelon) (Round, 1981). Most lakes above *ca.* pH 5.5 also support a diatom plankton. Within a single lake or stream, species distribution is strongly controlled by habitat and within a single habitat species composition may vary, for example, between different macrophyte hosts, or along a sediment particle size gradient. In monitoring studies it is important to hold these sources of variation constant. Stone surfaces provide the most stable and easily comparable habitat, and the epilithon is

usually preferred for biomonitoring. When this habitat is absent the epiphyton may be sampled.

As an alternative to sampling the living assemblages directly, sediment traps or surface sediment samples may be used to provide diatom samples integrated both spatially, (i.e. across all diatom source communities), and temporally (over a period of months for sediment traps, or years for surface sediments). In shallow ponds an integrated sample can be obtained by hauling a plankton net (mesh size < 40 μm) through aquatic macrophytes and surface sediments (Dickman *et al.* 1987).

4.3.2 Frequency

Some benthic diatom taxa exhibit seasonality, although this may be limited in oligotrophic waters (Round 1990). Samples should be collected during the same season each year, and may be timed to coincide with particular events (e.g. spring samples to monitor the effects of depressed pH during snowmelt).

4.3.3 Methods

Sampling
In oligotrophic lakes and streams a single sample will usually be sufficient to characterise the epilithic association in terms of the dominant taxa, but will not be sufficient to record many of the rare taxa or to provide a quantitative estimate of the relative abundance of each taxon in the epilithon. Rather than count a large number of replicate samples, sub-samples may be collected and pooled to provide 2- 4 samples from each lake or stream. The following sampling procedure was developed for the United Kingdom Acid Waters Monitoring Network (UKAWMN) and provides a robust method of obtaining estimates of the relative abundances of dominant and rare forms in the epilithon (Juggins, unpublished data). The methods is described for the epilithon but is easily modified for the epiphyton.

At stream sites ten cobble size stones are selected from pools in three discrete locations over a 50 m reach. Stones should be collected from a depth below that of minimum flow. At lake sites ten cobble size stones are selected from a depth of 20 - 30 cm from 2-4 surveyed locations around the shore, avoiding stream inflows. Stones with attached macrophytes or those covered in sediment should be avoided.

Remove diatoms by brushing into a tray or funnel, and decant into plastic vials. The ten sub-samples from each location should be homogenised, and preserved with Lugols Iodine.

Preparation and counting
Sample may be prepared using the standard techniques described in Battarbee (1986) or Stevenson *et al.* (1987). Three hundred to five hundred valves should be counted from each sample and identified to species level where possible. Unidentified taxa should be photographed and described, and nomenclature should be stated. Duplicate diatom slides should be archived in a central repository.

Data storage
A species by samples table of diatom counts is a good example of a sparse matrix; there are many rare taxa present in only a few samples, and hence many zero entries in the table. Such data are best stored in a condensed form, i.e. where only non- zero values of the matrix are stored. Munro *et al.* (1990) gives details of how this form of storage may be implemented in a relational database. To facilitate manipulation and comparison of data from different sources the use of a standard set of species codes is recommended. Williams *et al.* (1988) give a

computer coded version of the Hartley (1986) checklist. An extended version of this list is used at University College London and includes most of the European acid water diatom flora.

Data presentation and summary
Diatom data for each site should be presented to the data centre in three forms:

1. A species list, giving relative abundance (percentage) of all taxa taxa greater than 1.0% of the total count. Where replicate samples are collected from the same lake or stream these may be amalgamated to give a single list for each site.

2. Summarised by pH preference groups; taxa are divided into a number of pH groups, and the percentage of the assemblage represented by each group is listed. The most frequently used classification scheme is that of Hustedt (1937-39). This system divides diatoms into 5 classes:

    (1) Alkalibiontic: occurring at pH values > 7
    (2) Alkaliphilous: occurring at pH about 7 with widest distribution at pH > 7
    (3) Indifferent: equal occurrence on both sides of pH 7
    (4) Acidophilous: occurring at pH about 7 with widest distribution at pH < 7
    (5) Acidobiontic: occurring at pH values < 7 with optimum distribution at pH 5.5 and under.

Battarbee (1984) gives a detailed discussion and examples of this scheme. Although many taxa were covered in Hustedt's original work a large number remain unclassified; for example, over thirty percent of taxa in the Surface Waters Acidification Programme (SWAP) surface sediment dataset were not included in Hustedt's scheme. New taxa may be assigned to a pH group. If assignments are unpublished they should be justified and clearly stated in a summary report. If many taxa are unclassified according to Hustedt, alternative schemes may be used. The UKAWMN uses a classification which groups diatoms according to their pH optimum derived by non- linear regression using the SWAP surface sediment dataset (Birks *et al.* 1990; Juggins *et al.* 1989). Four classes are identified:

    (1) pH optimum less than 6
    (2) pH optimum between 5 and 6
    (3) pH optimum greater than 6
    (4) Unknown

3. Diatom inferred pH. This may be calculated using the index B method of Renberg and Hellberg (1982) or by weighted averaging (ter Braak & van Dam 1989; Birks *et al.* 1990). For Index B the appropriate regression equation should be given. For weighted averaging inferences a reference should be given to the training data-set and pH optima.

An example of the required format is given in Appendix 4.

4.3.4 Quality assurance

Despite the availability of major diatom floras there may be considerable variation in taxonomic and nomenclatural usage in different laboratories. If results from several laboratories are to be compared it is essential that they follow agreed protocols for taxonomy and nomenclature, and participate in a program of quality control (e.g. Kingston 1986; Stevenson *et al.* 1991).

4.4 Fish

4.4.1. Introduction

The responses of fish community for monitoring the effects of acidification can be recommended for several reasons. First, there are fish species of different sensitivity to acidification both in lakes and rivers. Further, the sensitivity of fish depends on its life stage. From an ecological point of view, the predation of fish on other organisms like on zooplankton and zoobenthos affects the population and community dynamics of these invertebrates. Therefore, it is of importance to have at least a basic information of the fish community, when using zooplankton or zoobenthos as target groups in acidification monitoring.

The goal of the monitoring of fish populations is to provide such information about the fish community and fish populations that acidification-induced changes in the chosen parameters can be recorded in a statistically appropriate manner. Therefore, a sampling procedure is needed that results in site specific estimates of the variation for the parameters of interest. These variance estimates then allow the comparisons of parameters over time or between sites, and the statistical treatments needed for verification of the significance of recorded changes.

In the previous ICP Waters manual, a project manual using gillnet series in combinations of either single nets or multimesh size nets has been recommended (Rosseland 1991). This new manual recommends gill netting with multimesh nets for fish monitoring in lakes and electro-fishing in running waters. The precision of the monitoring can be set at different levels depending as well on the chosen parameters as the intensity of the monitoring. Because it is assumed that the number of lakes and rivers to be monitored in each country is relatively small (5-10) and that the monitoring will be of reasonable intensity, a quantitative approach is emphasized.

4.4.2. Test-fishing by multi-mesh gill nets in lakes

The aim of fish sampling with multimesh gill nets is to obtain a figure of the fish community and the relative abundance (number and biomass) of catchable fish species in a lake. For a single fish species, length frequency distribution, age distribution, back calculated growth and sex ratio can be determined.

As a standard gear for fish sampling in lakes, a multimesh bottom net, so called "Nordic surveynet" is recommended (Appelberg *et al.* 1995). This net is 1.5 x 30 m in size containing 12 panels, 2.5 m in length, of mesh sizes 5-55 mm (Table 4.1). In addition of using similar nets, it is essential to use them in a similar way. A stratified random sampling procedure is recommended. The stratification may be based on the depth zones of a lake by relating the effort of sampling to the areal proportion of each depth zone. Another possibility is to apply the net setting instuctions given in the Swedish manual for gill net sampling (Appelberg 1994). The number of unit efforts depends both of the area of the lakes and the morphometry of the basin. The direction of the gillnets to the shore is chosen after randomization. For details, see Degerman *et al.* (1988), Appelberg (1994).

Comparative studies carried out (Jensen & Hesthagen 1996 in press, Kurkilahti & Rask 1996 in press) support the better usefulness of multimesh nets in fish sampling compared to the gillnet series that were earlier commonly used in Norway (Rosseland *et al.* 1979) and Finland (Raitaniemi *et al.* 1988). Also the costs per unit effort are lower when using multimesh nets. This allows - at lower costs - the designing of a sampling programme suitable for statistical treatments. Further, with a smaller unit sample, the risk of changing the structure of entire fish

populations by sampling is smaller. For these reasons, the use of multimesh bottom nets in general, and the "Nordic surveyet" in special, has been recommended for use as a new standard within the ICP Waters (Rosseland 1996).

Table 4.1 The Nordic Surveynet is composed of 12 sections of 2.5 m long net panels with mesh sizes (m_i), twine diameters (Ø) and mesh ratios (Ratio, latter/former) given below. The net is 30 m long and 1.5 m high. The location of each mesh size was randomized during the planning of the net - since then, all the nets are similar.

m_i (mm)	Ø (mm)	Ratio
5.0	0.10	
6.25	0.10	1.25
8.0	0.10	1.28
10.0	0.127	1.25
12.5	0.127	1.25
15.5	0.147	1.28
19.5	0.147	1.22
24.0	0.147	1.23
29.0	0.202	1.21
35.0	0.202	1.21
43.0	0.202	1.23
55.0	0.234	1.28

4.4.3. Electro-fishing in running waters

Electro-fishing in running waters is carried out to build up a figure of the fish community structure, and to produce density estimates for species of interest in certain sites or in entire watersheds. The fish species composition and population density estimates can be then compared between watersheds or within a watershed over time. The samples describe the recruitment and the density of the youngest age-classes of the population. In addition to running waters, electro-fishing can be suitable also in lake littorals in order to complete the figure of fish communities obtained by gill netting.

The electro-fishing for monitoring purpose should be carried out in a fixed and marked site, and the area measured. The current velocity of a test fishing site should be < 1.5 m/s and the depth < 1 m. Recommended area is from 50 to 200 m^2, depending on fish density at the start of the monitoring. The number of test fishing sites in a watershed depends on the aim of precision as well as on the size of the watershed. If a density estimate for a fish species is to be produced, at least three successive fishing's in a site are to be performed in order to be able to assess the fish density on the basis of decreasing catches. For details, see Bohlin *et al.* (1989).

4.4.4. Quality assurance

Concerning the gill net sampling of fish in lakes as well as the electro-fishing in running waters it is essential that the persons doing the work are well experienced. To reach the goals of the monitoring, the test fishing's have to be planned correctly and carried out carefully. If age determinations or back calculations of growth are included in the monitoring, it is

important to use the same hard structures of a fish species in all participating countries of the programme. It has been shown that intercalibration studies in age determinations among different laboratories are necessary and can improve the quality of work and thereby the comparability of the results (Appelberg *et al.* 1995).

In electro-fishing it has to be taken into account that the electricity can damage the fish. This is avoided by using experienced persons and good equipment. In electrofishing the demands of working safety have to be taken seriously into account. Because of the lack of an international standard in electro-fishing equipment, it is at the moment impossible to intercalibrate the sampling method. However, we recommend the use of each countries "best ranked equipment".

Both gillnet and electro-fishing should be carried out at the end of the growing season but before the spawning migration. In northern countries the testfishing period for salmonid species has been generally between August 15 and October 15. In this period, it is possible to catch the young of the year, the different year-classes are most uniformly distributed prior to spawning, the nights are dark and the fish have high activity. In lakes inhabited by warm water species like cyprinids or percids, the test fishings should be performed earlier, mainly in August so that the cooling of water would not yet affect the activities of the fish.

4.4.5. Data presentation

As background information the date of sampling and the name and location (coordinates) of the sampling site must be provided. Lake characteristics like the surface area, maximum depth and mean depth are important and some main water quality parameters should be included (temperature, oxygen, pH, conductivity, colour). The fish data should include at least the list of existing fish species, tables showing species specific CPUE in numbers and biomass, length frequency distribution and sex composition. In a more advanced report, the age distributions and back calculated growth of the age groups may be presented. Data from different sites in a lake can be pooled together, while in the data from running waters, spawning grounds must be kept separately.

5. Data handling and delivery

5.1 Formats data exchange

The data should be in ASCII-code on 1.4 Mb high-density diskettes (3.5 inch) or 1.2 Mb high-density floppy disks (5.25 inch). If only magnetic tapes can be sent, they should be 9 tracks and 1600 bytes/inch.

5.2 Database management

The requirements within the activities of the Executive Body for definition of time changes or trends have, in common with many environmental programmes, been extensive. Past history of changes in acidity of the surface waters is needed to assess relationships to deposition values and biological responses to acidity changes are of even greater importance. Definition of changes that will occur in the future is vital for assessing the reaction of the system to possible changes in stress due to atmospheric deposition. Models that are presently under development for predicting responses or changes in the aquatic regime in reaction to changes in deposition levels can be validated only if accurate data can be provided for a period of several years.

The data base management portion of a cooperative programme represents the final link that leads to use of the information to achieve the programme objectives. The purpose of the management exercise is to assure accuracy of the data, to accumulate and archive the data, and to retrieve and summarise the data in response to user requirements. The data management may include facilities for extensive data manipulation for interpretative purposes and may also provide for a permanent historical depository.

Data base management systems are included in the water quality programmes of many countries. They may contain most of the elements that are required for a cooperative monitoring programme of the aquatic effects of acidification. However, it is to be expected that most of the existing data base systems are more suited to water chemistry information than to biological information, but nevertheless both kinds of data should be included in the data base at the Programme Centre.

The data base will contain 2 sets of monitoring data: 1) a complete dataset with all delivered data from all sites and 2) data from sites having a complete parameter list, quality controlled data and an adequate number of samples per year. For lake sites, only the upper (surface) sample will be included.

The adoption of an acidification "score" should help to reduce basic biological observations to a system compatible with other data records. Computer methods for biological data storage, and for interpretation and assessment of community and population structure are being developed, and their application to this programme will be kept under review.

5.3 Reporting

Reporting from National Focal Points to the Programme Centre
Data reported to the Programme Centre should be submitted before 1 May the year after the data had been collected. For new countries adding data to the programme on new catchments being incorporated, the data from previous years are accepted by the Programme Centre if quality standards have been met.

Each country participating in ICP Waters should, if possible, submit an *annual standardised summary report* containing an evaluation of the main results of all their montoring programmes and surveys on acidification of surface waters (Levels I-III), including also references to related scientific papers. These national summary reports are included (and summarised) in the annual report of the Programme. This procedure ensures that the expertise of the responsible national institutes is utilised and that no important information is lost in the evaluation process. Also national summary reports will fulfil this need. A draft outline of the content of such national summary reports are given in Appendix 5.

Reports from Programme Centre to Programme Task Force
The Programme Centre will perform an annual data report showing the development of the programme. The annual report serves us bases for quality control of deliverables from the National Focal Points. All data should be controlled according to the QA-system.

An extended report of ICP Waters, containing a more thorough assessment of the regional-scale acidification status of surface waters within the ECE, is published every third year. This *Three Year Report* is drafted in an international workshop by appointed experts and finalised by the Programme Centre. The report contains results of both detailed catchment studies (e.g. statistical trend analysis of Level I data and evaluation of dose-response relationships) as well as an assessment of regional-scale information (Levels II+III). The analysis of the regional-scale data is done cooperatively, thus ensuring that the local knowledge on, e.g., special catchment characteristics is fully utilised. For this workshop tables and figures based on available (aggregated) regional-scale data are prepared.

It is desirable that the national regional-scale data (Levels II+III) to be assessed, are made available to the Programme Centre. However, if this is not possible, the assessment of the regional acidification status is based on the annual summary reports only.

In order to allow comparison of results among the different countries, all regional-scale information should broadly meet criteria for sampling site selection as well as sample handling and analysis, described in the Programme manual.

The national presentations at Task Force meetings and workshops will also be made available by the Programme Centre in cooperation with the local organiser.

6. Literature

Appelberg, M. 1994. Metodik för provfiske i sjöar - preliminär version. Institute of Freshwater Research, Drottningholm. 13 p. (In Swedish).

Appelberg, M., Berger, H.M., Hesthagen, T., Kleiven, E., Kurkilahti, M., Raitaniemi, J. and Rask, M. 1995. Development and intercalibration of methods in nordic freshwater fish monitoring. *Water Air Soil Pollut.* **85**: 401-406.

Battarbee, R.W. 1984 Diatom analysis and the acidification of lakes. *Phil. Trans. R. Soc. Lond.* **B 305**, 451-477.

Battarbee, R.W. 1986 Diatom analysis. In, Berglund, B.E. (ed) *Handbook of Holocene Palaeoecology and Palaeohydrology*. 527-569. Wiley & Sons Ltd.

Birks, H.J.B., Line, J.M., Juggins, S., Stevenson, A.C. & ter Braak, C.J.F. 1990 Diatoms and pH reconstruction. *Phil. Trans. R. Soc. Lond.* **B 327**, 263-278.

Bohlin, T., Hamrin, S., Heggberget, T.G., Rasmussen, G. and Saltveit, S.J. 1989. Electrofishing - Theory and practice with special emphasis on salmonids. *Hydrobiologia* **173**: 9-43.

Charles, D.F. & Whitehead, D.R. 1986 The PIRLA project: Paleoecological investigations of recent lake acidification. *Hydrobiol.* **143**, 13-20.

Degerman, E., Nyberg, P. and Appelberg, M. 1988. Estimating the number of species and relative abundance of fish in oligotrophic Swedish lakes using multi-mesh gillnets. *Nordic J. Freshw. Res.* **64**: 91-100.

Downing, J.A.. and Rigler, F.H.(Eds.) 1984. A manual on methods for the assessment of secondary productivity in freshwaters. IBP Handbook no. 17 (2nd. edition) Blackwell Sci. Oxford.

Dickman, M.D., van Dam, H., van Geel, B., Klink, A.G. & van der Wijk, A. 1987 Acidification of a Dutch moorland pool - a palaeolimnological study. *Arch. Hydrobiol.* **109**, 377-408.

Hartley, B. 1986 A check-list of the freshwater, brackish and marine diatoms of the British Isles and adjoining coastal waters. *J. mar. biol. Ass. U.K.* **66**, 531-610.

Hellawell, J.M. 1978. Biological surveillance of rivers: a biological monitoring handbook. WRC, Special publication.

Hill, M.O. 1979. TWINSPAN - a Fortran programme for grouping multivariate data in an ordered two-way table by classification of the individuals and attributes. Cornell University, Ithaca, New York. (Thesis.)

Hustedt, F. 1937-39 Systematische und ökologische Untersuchungen über den Diatomeen-Flora von Java, Bali, Sumatra. *Arch. Hydrobiol.* (Suppl.) **15** and **16**.

Jensen, J.W. and Hesthagen, T. 1996. Direct estimates of the selectivity of a multimesh and a series of single gillnets for brown trout, Salmo trutta. *J. Fish Biol.* (in press).

Juggins, S., Watson, D., Waters, D., Patrick, S. & Jenkins, A. 1989 *The United Kingdom Acid Waters Monitoring Network. Introduction and Data Report for 1988-1989 (Year 1).* ENSIS Ltd.

Kingston, J.C. 1986 Diatom methods. In Charles, D.F. and Whitehead, D.R. (eds) *Paleoecological investigation of recent lake acidification methods and project description.* EPRI EA-4906, Electric Power Research Institute, Palo Alto, California.

Kurkilahti, M. and Rask, M. 1996. A comparative study of usefulness and catchability of multimesh gill nets and gill net series for sampling of perch (*Perca fluviatilis* L.) and roach (*Rutilus rutilus* L.). *Fisheries Research* (in press).

Munro, M.A.R., Kreiser, A.M., Battarbee, R.W., Juggins, S., Stevenson, A.C., Anderson, D.S., Anderson, N.J., Berge, F., Birks, H.J.B., Davis, R.B., Flower, R.J., Fritz, S.C., Haworth, E.Y., Jones, V.J., Kingston, J.C. & Renberg, I. 1990 Diatom quality control and data handling. *Phil. Trans. R. Soc. Lond.* **B 327**, 257-262.

Oliver, B.G., Thurman, E.M. and Malcolm, R.L. 1983. The contribution of humic substances to the acidity of colored natural waters. *Geochimica et Cosmochimica Acta*, **47**, 2031-2035.

Raddum, G.G. and. Fjellheim, A 1994. Invertebrate community changes caused by reduced acidification. In: Acidification of Freshwater Ecosystems: Implications for the Future (C.E.W. Steinberg, R.F.Wright, eds). John Wiley & Sons Ltd.

Raitaniemi, J., Rask, M. and Vuorinen, P.J. 1988. The growth of perch, *Perca fluviatilis* L., in small Finnish lakes at different stages of acidification. *Ann. Zool. Fennici* **25**: 209-219.

Renberg, I. & Hellberg, T. 1982 The pH history of lakes in southwestern Sweden, as calculated from the subfossil diatom flora of the sediments. *Ambio* **11**, 30-33.

Rosseland, B.O. 1991. Fish populations - Investigation programme. In (Alpe - acidification of mountain lakes: Paleolimnology and ecology), NIVA, Oslo 63 p.

Rosseland, B.O 1996. Biological monitoring. Fish population studies. In: Licskó, I. (ed.). Proceedings of the 10th Task Force Meeting of International Cooperative Programme on Assesment and Monitoring of Acidication of Rivers and Lakes, pp. 61 - 70, Budapest 1994, NIVA Report 95 pp.

Rosseland, B.O., Balstad, B., Mohn, E., Muniz, I.P., Sevaldrud, I. and Svalastog, D. 1979. Fish population studies, datafish-SNSF-77. Presentation of criteria for lake selection, data collection and use of data program in the SNSF-projects test fishing program in the period 1976-1979. SNSF-project TN 45/79. 63 pp. (In Norwegian).

Round, F.E. 1981 *The ecology of algae*. Cambridge University Press, Cambridge, 653pp.

Round, F.E. 1990 Diatom communities - their response to changes in acidity. *Phil. Trans. R. Soc. Lond.* **B 327**, 243-49.

Stevenson, A.C., Patrick, S.T., Kreiser, A.M. & Battarbee, R.W. 1987 *Palaeoecological evaluation of the recent acidification of susceptible lakes: methods utilised under DoE contract PECD 7/7/139 and the Royal Society SWAP project.* Palaeoecology Research Unit, University College London. Research Paper No 26, 36pp.

ter Braak, C.J.F. & van Dam, H. 1989 Infering pH from diatoms: a comparison of old and new calibration methods. *Hydrobiol.* **178**, 209-223.

Watanabe, T., Asai, K. & Houki, A. 1988 Numerical water quality monitoring of organic pollution using diatom assemblages. In Round, F.E. (ed) *Proceeding 9th International Diatom Symposium.* Biopress, Bristol. 123- 141.

Williams, D.M., Hartley, B., Ross, R., Munro, M.A.R., Juggins, S., & Battarbee, R.W. 1988 *A Coded Checklist of British Diatoms.* ENSIS Ltd. London, 74pp.

Wright, J.F. Ross, D. , Armitage, P.D. and Furse, M.T. (1984). A preliminary classification of running water sites in Great Britain based on macro-invertebrate species and the prediction of community type using environmental data. *Freshwater Biology* **14**: 221-256.

Appendix 1

Catchment data for all sites.

(For biological sampling sites: see also additional list for required site-specific information)

.

Country:	**District/County:**
Site code:	**Site name:**
Site longitude (E/W)[1]:	**Site latitude (N/S)[1]:**
River (R) / Lake (L) :	**Drainage (D) or Seepage (S) lake:**
Catchment data	
***Required data*:**	Elevation at site, m:
Catchment area, km^2:	Average runoff, $mm.yr^{-1}$:
Average precipitation, $mm.yr^{-1}$:	Average seepage[2], $mm.yr^{-1}$:
For lake sites: Lake area, km^2:	Average depth, m:
***Optional data*:**	
Main type of bedrock:	Average soil depth, cm:
Forest cover (total), %:	Deciduous, %: Coniferous, %:
Wetlands / Bogs, %:	Lakes, %: 8.9
Heather/tundra/grassland, %:	Rocks, %:
Farmland (fertilised), %:	Pasture (unfertilised), %:

[1] 1° = 60' and 1' = 60". Example: E0102429 means East 10°24'29"
N514604 means North 51°46'04"

[2] below the rooting zone

Historic, existing and anticipated land use in the catchment:

Land use disturbances in the catchment (forest fires, road construction, diversions, impoundments (sites having significant disturbances should be avoided):

Other comments:

Appendix 2

Site description for biological sampling sites.

Country:		**District/County:**	
Site code:		**Site name:**	
Terrestrial environment within 30 m from shoreline and 50 m upstream from sampling site:			
A. > 70% deciduous forest (X): ____		Comments:	
B. > 70% coniferous forest (X): ____			
C. 30-70%of A. and B. (X): ____			
D. < 30% forest cover	____ % grassland	____ % rocks	____ % heather
River (X)_____ or lake (X) _____ bottom:			
a. Sand & small stones (< 5 cm in diameter; X): _____		Comments:	
b. Stones (5 - 20 cm in diameter; X): _____			
c. Stones (> 20 cm in diameter; X): _____			
Cover of coarse/particulate organic material _____ %			
Cover of mosses on the bottom _____ %			
Cover of algae on the bottom _____ %			

A. - D. and a. - c. (X for dominating category): choose only **1** row, respectively.
For terrestrial category D also indicate % grassland, rocks and heather.

Comments:

Appendix 3

Ion balance calculations

Cations, µeq/l

Ca^{++}: mg/l * 49.9
Mg^{++}: mg/l * 82.26
Na^{+}: mg/l * 43.5
K^{+}: mg/l * 25.57
H^{+}: $10^{6} * 10^{-pH}$
NH_4^{+}: µgN/l * 0.0714
Al^{3+}: Al_{labile}, µg/l * 0.111

Anions, µeq/l

HCO_3^{-} (alkalinity)[1)]
$SO_4^{=}$: mg/l * 20.82
Cl^{-}: mg/l * 28.21
NO_3^{-}: µgN/l *0.0714
OA^{-}: see below

[1)] negative values: zero µeq/l

Organic anions (OA^{-}) for calculation of the ion balance can be estimated from DOC (or TOC if negligible amounts of particles). One widely used method is described by Oliver et al. 1983. For some waters the original Oliver method gives too high values for organic anions, so that the charge density may have to be adjusted to local conditions.

An alternative method is to use the following relationship found using data from the Norwegian 1000-lake survey in 1986 (Calculated from the anion deficit. Calibration range: 0-14 mg TOC/l):

$$CD = 4.7 - (6.87 * e^{-0.322*TOC})$$
$$OA^{-} = CD * TOC$$

where CD is charge density in µeq/mgTOC,
OA^{-} is organic anions in µeq/l, and
TOC is total organic carbon in mgC/l (if the water sample contains visible amounts of particles, preferably measure on filtered sample, e.g. DOC).

Calculation of theoretical specific conductivity.

Specific conductivity, mS/m at 25°C (ref.:Handbook of Chemistry and Physics, 52nd ed.(1971/72):

Ca^{++}: µeq/l * 0.00600
Mg^{++}: µeq/l * 0.00531
Na^{+}: µeq/l * 0.00509
K^{+}: µeq/l * 0.00745
H^{+}: µeq/l * 0.0350
HCO_3^{-}: µeq/l * 0.00433
$SO_4^{=}$: µeq/l * 0.00790
Cl^{-}: µeq/l * 0.00755
NO_3^{-}: µeq/l * 0.00706
NH_4^{+}: µeq/l * 0.00745

Since organic anions are not included in the list above, the sum of the theoretical conductivities in brown water is usually slightly lower than the measured conductivity. Samples with very high contents of dissolved salts may show a measured conductivity lower than the calculated one.

Appendix 4

An example for the required format for reporting of diatom data

Loch Coire nan Arr: diatom taxon list (1989)

Taxon	*Relative abundance (%)*
Achnanthes minutissima	9.4
Brachysira vitrea	20.6
Brachysira brebissonii	6.9
Cymbella microcephala	1.9
Cymbella lunata	1.6
Eunotia naegelii	1.4
Frustulia rhomboides var. saxonica	6.6
Peronia fibula	7.0
Synedra acus	3.2
Synedra minuscula	2.0
Tabellaria flocculosa	30.6

Loch Coire nan Arr: diatom pH preference groups and inferred pH (1989)

Preference groups	
Group 1	17.2
Group 2	42.3
Group 3	38.9
Unknown	1.6
Inferred pH	6.2

pH groups: 1 = optimum < 5.0, 2 = 5.0 - 6.0,
3 = > 6.0
Inferred pH derived using SWAP training set (Stevenson *et al.* 1991)

Appendix 5

Recommended structure of the National Summary Report

ANNUAL REPORT TO THE PROGRAMME CENTRE OF THE INTERNATIONAL COOPERATIVE PROGRAMME ON ASSESSMENT AND MONITORING OF ACIDIFICATION OF RIVERS AND LAKES

Country:
Year:
National Focal Centre (including contact person):
Collaborative institutes:

1. BACKGROUND INFORMATION

- Objectives of the national monitoring programme on surface water acidification
- Relationship of the surface water programme with other acidification monitoring programmes

2. MONITORING NETWORK DESIGN

2.1 Number of stations and sampling frequency

2.1.1 Lakes

2.1.2 Catchments

2.1.3 Rivers

- Map with different symbols for different networks (if changing from previous years)
- Starting year of monitoring
- Number of samples/year, season(s)

2.2 Determinants for analysis

- List of chemical variables
- List of biological species monitored (macro-invertebrates, fish, etc.)

3. DESIGN OF REGIONAL SURVEYS

- Reported once after each survey
- Short description only

4. RESULTS

4.1 Lakes

4.2 Catchments

4.3 Rivers

- Short summaries
- Results from regional surveys reported only once

5. CONCLUSIONS

- Acidification status
- Comparison with previous activities and results
- Trends
- Planned future activities

6. LITERATURE

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