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ICP Waters Programme Manual 2010

International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes

Convention on Long-Range Transboundary Air Pollution

Norwegian Institute for Water Research
– an institute in the Environmental Research Alliance of Norway

REPORT

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Abstract

The ICP Waters Programme Manual is a handbook for sampling and analyzing surface waters, lake sediments and aquatic biota. Sampling and the performance of the analytical work of water, sediments and biota is structured in such way that it should reflect the effects or changes in chemistry or aquatic biota attributable to long range transported air pollution; acid rain (sulphur and nitrogen), trace metals and persistent organic pollutants (POPs). The first ICP Water manual was published in 1987, and was later revised in 1996. This version of the manual (2010) is a revised and updated version of the 1996 Manual but it also includes new parts describing methods for sampling and analysis of trace metals and persistent organic pollutants (POPs) in surface waters, sediments and fish. The revision of the manual is a process that started at the 23rd ICP Waters Task Force meeting in 2007 and ended at the 26th TF meeting in 2010, where the revised Manual was adopted.

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CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON ASSESSMENT AND MONITORING EFFECTS OF AIR POLLUTION ON RIVERS AND LAKES

ICP Waters Programme Manual

2010

Prepared at the ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, November 2010

Preface

The international cooperative programme on assessment and monitoring of effects of air pollution on rivers and lakes (ICP Waters) was established under the Executive Body of the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) in July 1985. Since then ICP Waters has been an important contributor to document the effects of implementing the Protocols under the Convention. Numerous assessments, workshops, reports and publications covering the effects of long-range transported air pollution has been published over the years.

The ICP Waters Programme Centre is hosted by the Norwegian Institute for Water Research (NIVA), while the Norwegian Climate and Pollution Agency (Klif) leads the programme. The Programme Centre's work is supported financially by Klif.

The main aim of the ICP Waters Programme is to assess, on a regional basis, the degree and geographical extent of the impact of atmospheric pollution, in particular acidification, on surface waters. More than 20 countries in Europe and North America participate in the programme on a regular basis.

ICP Waters is based on existing surface water monitoring programmes in the participating countries, implemented by voluntary contributions. The ICP site network is geographically extensive and includes long-term data series (more than 20 years) for many sites. The programme conducts yearly chemical and biological intercalibrations.

The basis for an international monitoring programme is a manual describing how to design the monitoring programmes, how to perform sampling and analyses. The first ICP Water manual was published in 1987, and was later revised in 1996. This version of the manual (2010) is a revised and updated version of the 1996 Manual but it also includes new parts describing methods for sampling and analysis of trace metals and persistent organic pollutants (POPs) in surface waters, sediments and fish.

The revision of the manual is a process that started at the 23rd ICP Waters Task Force meeting in 2007 and ended at the 26th TF meeting in 2010, where the revised Manual was adopted. The reference group for the revisions have been: Dean Jeffries, John L. Stoddard, Jens Fölster, Anders Wilander, Aldo Marchetto, Jussi Vouremaa, Arne Fjellheim, Lars Eriksson, Bjørn Olav Rosseland, Jochen Schaumburg, Lluis Camarero, Jaakko Mannio, and Anne Christine Le Gall.

The revision work has been led by the Programme Centre under the lead of Bente M. Wathne, with strong support from Sissel B. Ranneklev, Bjørn Olav Rosseland, Hans Fredrik Veiteberg Braaten, and Arne Fjellheim.

We are very grateful to all Task Force members for all good discussions at Task Force meetings and all fruitful comments and suggestions to the Manual.

Brit Lisa Skjelkvåle
ICP Waters Programme Centre

Oslo, November 2010

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1. Introduction and general information

1.1 The role of ICP Waters

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

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

The programme aims and objectives (reviewed at the ICP Waters 15th Task Force meeting in Verbania Pallanza, Italy October, 1999) are:

Aims:

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

Objectives:

- Maintain and develop an international network of surface water monitoring sites;
- Promote international harmonisation of monitoring practices by:
  - maintaining and updating a manual for methods and operation;
  - conducting interlaboratory quality assurance tests;
  - compiling a centralised database with data quality control and assessment capabilities.
- Develop and/or recommend chemical and biological methods for monitoring purposes;
- Report on progress according to programme aims and short term objectives as defined in the annual work programme;
- Conduct workshops on topics of central interest to the Programme Task Force and the aquatic effects research community;
- Address water related questions in cooperation with other ICP's

1.2 Purpose of the manual

The purpose of the manual is to give guidance and recommend methods for surface waters monitoring. The aim is to harmonize methodology to secure possibilities for comparison and common evaluation of data between all participating countries. This will lead to a greater reliability of the data assessments and a higher probability to detect impacts of atmospheric pollution on surface waters.

The term "monitoring" is defined here 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. Monitoring programmes describe the temporal variability of

ecosystem components in contrast to surveys that establish spatial variance within a system at a given time.

1.3 Manual development

During the first Task Force meeting of the ICP (April, 1986), a "Manual for Chemical and Biological Monitoring" (1987) was accepted. 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 was also an overall guide to activities and priorities of the work at the Programme Centre. An amendment to the manual (1991) 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 10th Task Force meeting (October, 1994) recommended that the manual should be consolidated and updated (a) to reflect the technical advances that had 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 was particularly important. This resulted in the first revised version of the ICP Waters Programme Manual (1996).

At the 23rd Task Force meeting in October 2007, it was again decided to update the Manual in line with the Programme development during the last decade.

1.4 Design of the ICP Waters Monitoring Programme

ICP Waters operates from the middle of a monitoring hierarchy that is designed to evaluate the environmental effects of air pollutants on surface waters chemistry and biology, 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 continually basis.

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

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

ICP Waters focuses on Level I, and deals with water chemical data from catchments with a sampling frequency from weekly to seasonal. With the less frequent sampling, the biological aspects become more important as they accumulate the effects of changing water quality in the previous period. Also monitoring of sediments will provide possibilities for a coherent and comprehensive picture of the impact of long-range transboundary air pollution on the freshwater ecosystems.

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.

In addition to the various national programmes that voluntarily supply information (e.g. regional surveys) as a supplement to the ICP Waters activities, some other international programmes also have provided complementary information, e.g. EU projects AL:PE/MOLAR/EMERGE (research

programmes on high mountain lakes, http://www.mountain-lakes.org/), and ENCORE/DYNAMIC (a small catchment modelling programme), etc.

All activities agreed to under the ICP Waters Programme will also take into consideration the EU Water Framework Directive and its guidance given for monitoring and surveillance (Guidance document No 7. Monitoring under the Framework Directive). Rules and regulations emerging under this directive will be followed closely.

1.5 Monitoring effects of long-range transboundary air pollution on freshwater ecosystems

1.5.1 Chemical monitoring

Monitoring water chemistry components is a basic activity within a programme where the aims are to assess effects of long-range transboundary air pollution on fresh water systems, and collect information to link chemical dose with biological response. From the beginning, ICP Waters was designed to assess, on a regional basis, the degree and geographical extent of acidification of surface waters, and concentrated on monitoring components essential for assessing the acidification status. Today the Programme is extended and includes a wider range of long range transboundary air pollutants, including trace metals and persitant organic micropollutants (POPs).

Acidification
Long-range transported air pollution contains nitrogen and sulphur compounds contributing to acidification of soils and freshwaters. Acidification of acid sensitive freshwater systems provided some of the earliest evidence of the damage caused by sulphur and nitrogen emissions. The sensitivity of these systems suggested that they were ideal for studying the effects and response to changes in pollution deposition.

Trace metals and POPs
The Executive Body adopted the Protocols on Heavy Metals and Persistent Organic Pollutants (POPs) on 24 June 1998 in Aarhus (Denmark), which entered into force on 23 October 2003 (www.unece.org).

The Heavy Metals Protocol targets three particularly harmful metals: cadmium, lead and mercury. The Protocol aims to cut emissions from industrial sources, combustion processes, and waste incineration. For the POPs Protocol a list comprised of 11 pesticides, 2 industrial chemicals, and 3 by-products have been selected, and the ultimate aim is to eliminate discharges, emissions, and looses of these substances.

The general concentrations of trace metals and POPs in environmental water samples are low, and as a result chemical analysis applied to detect and quantify the presence of these components in water is challenging. To overcome this challenge, scientists have developed unconventional sampling techniques in order to preconcentrate/up-concentrate the components prior to the analysis. Another solution, when the goal is to assess the degree and impact of atmospheric pollution in the aquatic environment, is to sample lake or river sediments and analyse for the different long-range transported components.

For the nearest future we foresee an increasing focus and interest for trace metals and organic micropollutants. Due to preparations for a revision of the POPs and heavy metals protocols under CLRTAP, these components will be followed closely within ICP Waters.

In an ICP Waters report (Fjeld et al. 2005) it is shown that there is a general lack of coordinated monitoring or regional surveys that focus on POPs in the freshwater environments for which LRTAP is a major source. Methodology regarding sampling, analytical methods and reporting makes comparison between results from the different projects very difficult. An important recommendation from the report is that there is an urgent need to establish systematic long-term monitoring of new POPs in background areas, and coordinated international surveys with harmonized methodology and reporting.

1.5.2 Biological monitoring

Acidification

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, and because the sensitivity of different life history stages of a species varies according to the chemical environment, 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.

- *Sensitive species*. 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 any water body to be sampled, these organisms should be sought and identified unequivocally to species level.
- *Tolerant species*. 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, Corixidae, 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 acidification level of surface waters can be quantified by identified invertebrate species or communities. Objective indicators can be developed in accordance with the acidity influence on the various organisms. Numerical relationships between pH of water and species response are developed for 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 relationship between measured pH and living diatom communities should be established to improve pH-inferences. Sampling is done either by 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 of 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 is done by 3 net hauls (60-90 µ mesh) from 20 m to surface, or bottom to surface (shallow lakes). Zooplankton should be treated with alkaline Lugols solution (Utermöhl 1958), and 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 caddisflies (Trichoptera) and stoneflies (Plecoptera) and leeches (Hirudinea) 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 identification. For the latter, exchange of material between laboratories through intercalibration exercises is currently performed yearly in the ICP Waters programme. Biological index organisms should be archived for reference.

Trace metals and POPs

For some of the trace metals/heavy metals and Persistent Organic Pollutants (POPs), chemical analyses of water will not be able to track the compounds, while the bio-concentration, -accumulation and -magnification in biota enable us to identify these compounds. Many fish species are relatively long lived, which means they will bio-accumulate environmental pollution like trace metals and POPs to a much higher degree than i.a. the rather short-lived invertebrates, and are thus selected for assessing the long-range transport and pollution levels of trace metals/heavy metals and POPs.

For fish, pollution level in different organs will always be linked to age, as well as size (length and weight). Proper ageing of fish is therefore imperative. However, the same fish species (same age, and size) can in two lakes with the same background pollution level of mercury (Hg), have different levels of Hg in their muscle. The difference is due to the biomagnification properties of Hg, with the piscivorous (fish eating) fish having the highest concentration, and linking individual fish to its trophic level is imperative to achieve a full understanding of food chain related pollution of Hg.

An assessment report from ICP Waters (Fjeld et al. 2005) concludes that previous studies are confirmed, indicating that the global distillation processes (grasshopper-effect) leads to elevated concentrations of contaminants in fish from arctic and alpine areas and that levels are increased in background areas not affected by local pollution.. This shows that the issue has an important relevance for ICP Waters.

1.6 Organisation of the manual

The manual gives recommendations on monitoring design and methods for:

- Monitoring effects of LRTAP of S and N deposition on water chemistry and presences/ absence of aquatic biota.
- Monitoring effects of LRTAP of deposition of trace metals (in particular Hg, Pb and Cd) on surface water chemistry, lake sediments and concentrations in aquatic biota.
- Monitoring effects of LRTAP of POPs deposition on surface water chemistry, lake sediments and concentrations in aquatic biota.

The manual gives also recommendations on analytical methods and quality control.

1.7 References

EC 2003. Common Implementation Strategy for the Water Framework Directive (2000/60/EC), Guidance Document No. 7. Monitoring under the Framework Directive. http://www.wrrl-info.de/docs/Guidance_doc_7_monitoring_klein.pdf

Fjeld, E., Le Gall, A.-C., & Skjelkvåle, B.L. 2005. Concentrations and levels of POPs from long-range transboundary air pollution in freshwater fish and sediments. *NIVA-report SNO 5107-2005, ICP Waters report 79/2005.*, 68.

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.

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2. Site selection

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 effects of air pollution (acidification, heavy metals and POPs). 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 air pollution, in particular 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 ICP Waters could be expected to consist of a number of stations believed to be sensitive to changes in air pollution. 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.

2.1 Specific criteria for site selection

a) The ICP Waters monitoring network should consist, as much as possible, of sites that do not have impacts from local pollution sources (e.g. domestic sewage, industrial waste water, agriculture etc.). ICP Waters is established to monitor effects of long-range transboundary air pollution on surface waters, and a pronounced influence from local sources of pollution in the catchment may lead to misinterpretation of chemical and biological data. Sites should be chosen that represent the diversity of the region (chemically, biologically and geographically);

b) In regions where surface waters exhibit a wide range of acid-sensitivity, the sites should be chosen among the most susceptible to air pollution and with no strong lithological contribution. The aim of the site selection should be to focus primarily on sites that are likely to change in response to air pollution, 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. 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) A larger number of sites increases the possibilities to make trend tests at a regional scale, but a high sampling frequency should be prioritised to the number of sites. The number of sites should also be balanced against the ability to support the monitoring on a sustainable and long-term basis.

f) As reference sites, sensitive sites in low deposition areas can be used. In high deposition regions, reference sites for acidifications can be selected from sites with moderate buffering capacity, where biological impact from acidification is not found. Sites with long time series of data are preferable if the other main criteria are met.

g) When forestry is performed in the catchment area, the size of the catchment should be large enough in relation to the scale of the forestry activities so that single measures such as clear-cuts will have no major impact on the water quality.

2.1.1 Lakes

Drainage lakes (i.e. with an outlet) are best suited for monitoring. Lakes with a moderate water renewal period, approximately one 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 or sediment sampling are planned, the lake should be sufficiently deep to minimise resuspension.

2.1.2 Rivers

A small river or brook is preferable. In general, small catchments react more rapidly than large ones to changes in deposition of airborne pollution. However, the site should be large enough to sustain a permanent flow throughout the year. The presence of upstream lakes should be minimal.

In regions with a large number of lakes, two types of river stations can be identified. One type with a large influence of lakes within the catchment which are representative for the region, and one type with a minimum of lake influence which better shows the response of deposition and climate on stream ecology.

2.1.3 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 air pollution. 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. An example is the cyclic survey in the Swedish national monitoring, where 1/6 of a set of randomly selected lakes are monitored each year in a six year cycle related to the Water Frame Directive. This gives a description of the distribution of lake chemistry not biased by the weather a particular year, which is the case for synoptic surveys.

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.

2.2 Catchments 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.

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 temperature, °C
- 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)

Average period for these calculations is defined as the official normal period 1971-2000 (WMO) if it is available, or the recent 10 years. If there are not site-specific hydrological/meteorological measurements in the ICP Waters site, statistics from the nearest meteorological/runoff stations (or modelled information) have to be used.

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

Regional surveys: The site and sample documentation of the regional data Programme Centre should include the following characteristics:
- Name or identifying number
- Longitude and latitude
- Site type (lake or stream)
- Date of sampling
- Depth at which the sample was taken
- Catchment area, km^2
- Average catchment runoff, $mm.yr^{-1}$

2.3 Data reporting

Data and information regarding the catchments and monitoring sites, as described above, shall be delivered to the Programme Centre once for each monitoring site. Registration forms for all sites and a special registration form for biological sampling sites are here:

http://www.icp-waters.no/

2.4 References

EC 2003. Common Implementation Strategy for the Water Framework Directive (2000/60/EC), Guidance Document No. 7. Monitoring under the Framework Directive. http://www.wrrl-info.de/docs/Guidance_doc_7_monitoring_klein.pdf

ISO 2006. ISO Standard 5667-1:2006. Water quality – Sampling – Part 1: Guidance on the design of sampling programmes and sampling techniques.

Utermöhl, H. 1958. Zur Vervollkommung der quantitativen phytoplankton-methodik. Mitt Int. Ver. Limnol. 9: 38.

Figure 1. Example of forms for reporting catchment data

Catchment data - water chemistry sites

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, %:
Heather/tundra/grassland, %:	Rocks, %:
Farmland (fertilised), %:	Pasture (unfertilised), %:

[1] 1^o = 60' and 1' = 60". Example: E0102429 means East 10^o24'29"
N514604 means North 51^o46'04"

[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:

Catchment data – sites with biological observations

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:

3. Acidification - water chemistry

3.1 Determinants

A list of mandatory determinants related to S and N-deposition (acidification) consists of those that define the degree of acidification or which are directly related to acidification of the waters (*Table 1*). A secondary list include desirable or optional determinants that may be useful for the interpretation effects of acidification (*Table 2*). The third list is considered the absolute minimum required for the ICP data base (*Table 3*).

Table 1. *Mandatory list of chemical parameters with preferable units*

Parameters	Name	Units
Alkalinity[1]	ALK	µeq/L
Sulphate	SULF	mg SO4/L
Nitrogen as nitrate	NO3-N	µg N/L
Chloride	Cl	mg/L
Dissolved carbon, total organic carbon or permanganate	DOC /TOC PERM	mg C/L mg O/L
pH		pH
Calcium	Ca	mg/L
Magnesium	Mg	mg/L
Sodium	Na	mg/L
Potassium	K	mg/L
Ammonium as nitrogen[2]	NH_4-N	µg N/L
Inorganic (labile) aluminium[3]	LAL	µg/L
Specific conductivity at 25°C	K25	mS/m
Total phosphorus	TOTP	µg P/L

1. May be omitted at pH< 5.2 (alkalinity approximately zero if negative values are not measured by Gran titration) or the end point of the titration method. If pH is below the endpoint of the alkalinity method, determination of acidity, as a titration with hydroxide to the same endpoint is suggested. In this way there is a fixed pH-value for the determination. Use of Gran evaluation of a titration curve gives the equivalence point as end-point for the determination. This pH-value varies depending on the protolytes in the water.
2. In areas where this component is important.
3. Difference between reactive (organic + inorganic) and non-labile (organic) aluminium.

***Table 2**.Optional parameters with preferable units*

Parameters	Name	Units
Water temperature	TEMP	°C
Flow at time of sampling	RUNOFF	m3/s
Total nitrogen	TOTN	µg N/L
Soluble reactive phosphate	ORTP	µg P/L
Dissolved oxygen	OKS	mg O/L
Silica	SIO2	mg SiO2/L
Fluoride	F	mg/V
Colour[4]	COLOUR	mg Pt/V
Turbidity	TURB	FTU
Total aluminium	TAL	µg/L

4. Filtered absorbance at 420 or 436 nm could be used as alternative to colour. The results from the traditional method for colour have shown to be highly person-related.

Table 3. Minimum list of parameters

Parameters	Name	Units
Alkalinity[5]	ALK	µeq/L
Sulphate	SULF	mg SO4/L
Nitrogen as nitrate	NO3-N	µg N/L
Chloride	Cl	mg/L
pH		pH
Calcium	Ca	mg/L
Magnesium	Mg	mg/L
Sodium	Na	mg/L
Potassium	K	mg/L

5. May be omitted at pH< 5.2 (alkalinity approximately zero if negative values are not measured by Gran titration) or the end point of the titration method. If pH is below the endpoint of the alkalinity method, determination of acidity, as a titration with hydroxide to the same endpoint is suggested. In this way there is a fixed pH-value for the determination. Use of Gran evaluation of a titration curve gives the equivalence point as end-point for the determination. This pH-value varies depending on the protolytes in the water.

3.2 Sampling

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. Choose a site with turbulent water current, well below tributaries, to ensure complete mixing. Representative samples can therefore be obtained by a surface grab sample away from stream bank. When filling the bottle, keep the bottleneck against the current, well below the surface. Rinse the bottle and screw cap 3 times with sampling water prior to sampling. Avoid touching the inside of bottle and screw cap. In the larger streams with a depth > 1 m, a water sampler can also be used for sampling. In the river sampling, turbulation of sediment and surface water film contamination should be avoided.

Lake water sampling

Choose a deep site that is not directly influenced by any inlet stream, preferably in the "middle" of the lake or at a cape or at a pier outside the influence of any aquatic vegetation. A good solution is normally also to sample in the outlet area, but a sample in the outlet may not always be representative for the lake. During the stratified season, seiches can give hypolimnion water in the outlet, and at low flow, the contribution of groundwater discharging into the stream can be significant, even at a short distance downstream the lake threshold. 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.

Water sampling of trace metals and persistent organic pollutants (POPs) require more specific equipment and techniques and are described in more detailed in chapter 7 and 9.

If a water sampler is used, it should be tested for contaminants, especially if also 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 polypropene or any other 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 4ºC 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, and if the preservative is added in the field, extreme care must be observed to prevent contamination of the major ion sample with nitric acid. Water sampling for analysis of trace metals or POPs (persistent organic pollutants) is described in separate chapters (see chapters 6 and 8).

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

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 (seasonal sampling), 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.).

3.3 Analysis

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) is legally prescribed for use by all EU nations. We therefore propose ICP-Waters to 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. Different methods for alkalinity are at present used between the member countries, and to fully understand possible differences both during intercomparison and between analytical reports, a comment attached to the data should indicate the method used. 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 listed in Table 4 are recommended for the work:

Table 4. List of ISO and CEN methods to be used for analysis and QA/QC procedures in the laboratory.

Parameters	ISO or CEN No	Name of standard
alkalinity	ISO 9963-2:1994	Water quality- Determination of alkalinity. Part 2: Determination of carbonate alkalinity.
Sulphate	ISO 10304-1: 2007	Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate.
Nitrogen as nitrate	ISO 10304-1: 2007	Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate.
Nitrogen as nitrate II	EN ISO 13395: 1996	Water quality – Determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection.
Chloride	ISO 10304-1: 2007	Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate.
Dissolved carbon and total organic carbon	ISO 8245 1999	Water quality- Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC).
Permanganate	ISO 8467:1995	Water quality – Determination of permanganate index
pH	ISO 10523-1:1994	Water quality- Determination of pH.
Calcium	EN ISO 14911:1998	Water quality – Determination of dissolved Li+, Na+, NH4+, K+, Mn2+, Ca2+, Mg2+, Sr2+ and Ba2+ using ion chromatography. Method for water and waste water.
Magnesium	EN ISO 14911:1998	Water quality – Determination of dissolved Li+, Na+, NH4+, K+, Mn2+, Ca2+, Mg2+, Sr2+ and Ba2+ using ion chromatography. Method for water and waste water.
Sodium	EN ISO 14911:1998	Water quality – Determination of dissolved Li+, Na+, NH4+, K+, Mn2+, Ca2+, Mg2+, Sr2+ and Ba2+ using ion chromatography. Method for water and waste water.
Potassium	EN ISO 14911:1998	Water quality – Determination of dissolved Li+, Na+, NH4+, K+, Mn2+, Ca2+, Mg2+, Sr2+ and Ba2+ using ion chromatography. Method for water and waste water.
Ammonium as nitrogen	ISO 11732: 2005	Water quality – Determination of ammonium nitrogen – Method by flow analysis (CFA and FIA) and spectrometric detection.
Ammonium as nitrogen II	EN ISO 14911:1998	Water quality – Determination of dissolved Li+, Na+, NH4+, K+, Mn2+, Ca2+, Mg2+, Sr2+ and Ba2+ using ion chromatography. Method for water and waste water.
Inorganic (labile) aluminium		No standard
specific conductivity at 25°C	EN 27 888:1993	Water quality- Determination of electrical conductivity.
Total nitrogen	ISO 11905:1997	Water quality – Determination of nitrogen – Part 1: Method using oxidative digestion with peroxodisulfate
Total phosphorus	ISO 6878: 2004	Water quality – Determination of phosphorus – Ammonium molybdate spectrometric method.
Soluble reactive phosphate	ISO 10304-1: 2007	Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate.

Parameters	ISO or CEN No	Name of standard
Dissolved oxygen	EN 25 814:1992	Water quality- Determination of dissolved oxygen- Electrochemical probe method.
Dissolved oxygen	EN 25 813:1992	Water quality- Determination of dissolved oxygen- Iodometric method.
Silica	ISO 16264:2002	Water quality – Determination of soluble silicates by flow analysis (FIA and CFA) and photometric detection
fluoride	ISO 10304-1: 2007	Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate.
Colour	EN-ISO 7887:1994	Water quality- Examination of colour.
Turbidity	EN-ISO 7027:2000	Water quality – Determination of turbidity
Total aluminium	ISO 11885:2007	Water quality -- Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)

Information of the ISO/CEN methods listed above can be obtained from:

- The national standardisation agencies.
- ISO International Organisation for Standardisation, Case Postale 56, CH-1211 Genève, Switzerland. http://www.iso.org
- CEN European Committee for Standardisation, Rue de Stassart 36, B-1050 Brussels, Belgium. http://www.cen.eu

3.4 Quality assurance and quality control

Quality assurance and quality control are the responsibility of the National Focal Points. In the following chapter 3.6 on Data Reporting, a description of the possibilities for quality assurance and quality control by use of the Reporting form for ICP Waters is given. The Programme Centre will, however, to ensure data quality and correct technical transfer of data, do data quality control according to the following:

1. looking for outliers
2. looking for continuity in time series
3. ionic balance

Comparison of measured and theoretically calculated specific conductivity is another method for quality control of measured data. Explanation and details for these calculations are given in 3.5, and the formulas for automatic calculation and control is also included in the form for reporting monitoring data as described under 1.5.

Also in manuals for ICP Forests (UNECE ICP Forests, 1999) and ICP on Modelling and Mapping (UNECE ICP Modelling and Mapping 2004), methods with quality assurance and quality control are described.

Ion balance

In particular the ionic balance is done by a data programme made in two versions, the first including all major ions, the second also including Al, NH4 and TOC. The first set of equations is the following:

Table 5. I Major ions for calculations of ionic balance for quality control

Description	Acronym	Equation
Sum anions	SAN	$[Cl^-] + [NO_3^-] + [SO_4^{2-}] + [ALK]$
Sum cations	SCAT	$[Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+] + [H^+]$
Difference cations/anions	DIFF	SCAT - SAN
Difference in percent	D-PRO	DIFF in % of SCAT (DIFF*100/SCAT)

For samples where analysis of Al, NH4 and TOC are present, the second set of equations is used:

Table 6. II. Major ions including LAl, NH_4^+ and TOC for calculations of ionic balance for quality control

Description	Acronym	Equation
Sum anions	SAN2	SAN + OAN-]
Sum cations	SCAT2	SCAT + $[LAl^{(*)}]$ + $[NH_4^+]$
Difference cations/anions	DIFF2	SCAT2 – SAN2
Difference in percent	D-PRO2	DIFF2 in % of SCAT2 (DIFF2*100/SCAT2)

Where LAl = Σ (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$) and
$OAN^- = 4.7 - 6.87 * \exp^{(-0.322 * TOC)}$*TOC (see chapter 3.5)

In order to check the ion balance, all of the necessary variables for calculating the sums of cations and anions must be analysed. For good analytical results, the difference in % between sum cations and anions should be <= 10%.

A further check of the ion balance is made by comparing the measured conductivity to the conductivity calculated from the measured ions. Also a check of non marine Na (Na*) may indicate possible problems in Cl – analysis in many areas.

All analyses with D-PRO or D-PRO2 >10 % are checked and should be reanalysed if necessary. For analyses with DIFF eller DIFF2 < 10 µeq/l, but D-PRO or D-PRO2 > 10% the analysis is accepted.

3.5 Calculations

Calculation of non-seasalt fraction of ions

At sites where seasalt may constitute noticeable amounts of air transported components, sesalt corrections of the measured values might be necessary to estimate correctly the long-range transported air pollution.

Of the strong acid anions Cl is the most mobile one and follows normally the water through the catchment, which means that $Cl_{in} = Cl_{out}$. The main chloride source is seasalts carried to the cathment through wet and dry deposition. By using the relationship between chloride and the other seawater ions, you may therefore calculate the contribution from non-marine sources in the run-off. This is done by the following equations (Lyman and Fleming, 1940 cited in Sverdrup, 1946 :

$$[Ca^{2+}]^* = [Ca^{2+}] - 0.037*[Cl^-]$$
$$[Mg^{2+}]^* = [Mg^{2+}] - 0.196*[Cl^-]$$
$$[Na^+]^* = [Na^+] - 0.859*[Cl^-]$$
$$[K^+]^* = [K^+] - 0.018*[Cl^-]$$
$$[SO_4^{2-}]^* = [SO_4^{2-}] - 0.103*[Cl^-]$$

In the tables are seasalt corrected values for SO_4 (non-marin sulfate SO_4*), included. Seasalt corrected values are always marked with an asterix *.

Calculations of ANC

For assessing effects of air pollution, the ANC (Acid Neutralizing Capacity) is a useful parameter. ANC is defined as the potential of a solution to neutralise additions of strong acids to a given level. ANC is defined by Reuss and Johnson 1986:

$$\mathbf{ANC = [HCO_3^-] + [A^-] - [H^+] - [Al^{n+}]}$$

For lakes with negligible content of organic matter we may assume that $[A^-]$ and $[Al^{n+}] \approx 0$ resulting in:

$$\mathbf{ANC = [HCO_3^-] - [H^+]}$$

Ion balance in water is given by:

$$\mathbf{\Sigma \text{ charge of cations [µeq/l]} = \Sigma \text{ charge of anions [µeq/l]}}$$

$$\mathbf{\Sigma [H^+]+ [Al^{n+}] + [Ca^+]+ [Mg^{2+}] + [Na^+] + [K^+] + [NH_4^+] = \Sigma [Cl^-] + [SO_4^{2-}]+ [NO_3^-]+ [HCO_3^-]+ [A^-]}$$

This will give:

$$\mathbf{ANC = ([Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+]+ [NH4^+]) - ([Cl^-] + [SO4^{2-}] + [NO3^-])}$$

$$\mathbf{ANC = \Sigma \text{ base cations} - \Sigma \text{ strong acid anions}}$$

ANC calculated as the difference between base cations and acid anions, is widely used as a measure of freshwater acid status, and an indicator of biological conditions. Unlike pH and alkalinity, ANC is conservative with respect to CO_2 degassing and reactions with aluminium or organic species. However, since ANC is calculated as the residual of a large number of individual ion determinations, it is potentially sensitive even to relatively small analytical errors. It is suggested that a more stable measurement of ANC may be obtainable based on titration alkalinity, DOC and aluminium concentrations (Evans et al.2001).

Calculation of charge of organic complexes for ionic balance calculations

Organic anions (OAN^-) 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 (Henriksen et al. 1988) (Calculated from the anion deficit. Calibration range: 0-14 mg TOC/l):

$$\mathbf{OAN^- = CD * TOC}$$

where CD is charge density in µeq/mg TOC.

TOC is total organic carbon in mg C/l (if the water sample contains visible amounts of particles, preferably measure on filtered sample, e.g. DOC).

Other methods for calculations of organic matter are described and documented in the scientific literature and might be useful (Hruška *et al.* 2003, Kortelainen 1992, 1996, Driscoll, *et al.* 1994 and Tipping, 1994).

Calculation of theoretical specific conductivity.

Specific conductivity, mS/m, at 20°C and 25°C (ref.: Handbook of Chemistry and Physics, 52nd ed.(1971/72) is given in *Table 7*.

Table 7. Specific conductivity in mS/m at 20 °C and 25 °C.

Component in µeq/L	Specific conductivity at 20°C mS/m	Specific conductivity at 25°C mS/m
Ca2+	0.0543	0.006
Mg2+	0.0486	0.00531
Na+	0.0459	0.00509
K+	0.0670	0.00745
H+	0.3151	0.035
HCO3-	0.0394	0.00433
SO42-	0.0712	0.0079
Cl-	0.0680	0.00755
NO3-	0.0636	0.00706
NH4+	0.0670	0.745

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.

3.6 Data Reporting

The water chemistry results are reported to the Programme Centre and stored in the ICP Waters database. The water chemistry results should be reported in a special form prepared as an excel-file. The form with an example included (Data from Italy 2007 and Switzerland 2007) is attached to this document. Central parts of the form and file are shown in *Figure 2*.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X
1	ICP FORM for data validation and transmission																						Please fill only in green cells. Within the white cells are equations for	
2	Test for Italy 2007																							
3	Code	Nat	Date	pH	Cond.	Cond.	K25/Cond.	NH_4	Ca	Mg	Na	K	Alk	SO_4	SO_4^*	NO_3	Cl	F	TOTN	TOTP	ORTP	OKS	Si	DOC
4					µS/cm 20°C	µS/cm 25°C	mS/m 25°C	µgN/l	mg/l	mg/l	mg/l	mg/l	µeq/l	mg/l	mg/l	µgN/l	mg/l	mg/l	µgN/l	µgP/l	µg P/l	mgO/l	mg Si/l	mg C/l
5																								
6	IT06		08.01.07	7,03	51,0	56,6	5,66	21	4,08	0,94	4,22	0,63	161	4,6	4,32	1757	2,8		1760	21	15		15,1	0,6
7	IT06		19.02.07	7,14	53,8	59,7	5,97	33	4,30	1,00	4,59	0,63	186	2,8	2,30	1795	5,0		1810	29	22		15,3	0,6
8	IT06		19.03.07	7,15	54,4	60,4	6,04	25	4,56	1,03	4,74	0,64	190	3,1	2,61	1807	4,9		1840	33	23		14,7	1,0
9	IT06		16.04.07	7,28	56,1	62,3	6,23	17	4,59	1,07	5,03	0,74	221	3,1	2,60	1646	5,0		1780	43	29		15,8	0,9
10	IT06		14.05.07	7,31	53,7	59,6	5,96	15	4,41	0,99	4,82	0,74	216	3,0	2,52	1554	4,8		1760	54	39		16,5	1,1
11	IT06		11.06.07	7,25	51,1	56,7	5,67	15	4,00	0,95	4,24	0,60	182	3,4	2,98	1701	4,2		1820	28	19		13,8	1,1
12	IT06		09.07.07	7,23	50,1	55,6	5,56	14	4,08	0,91	4,16	0,93	188	3,0	2,58	1478	4,2		1740	27	16		14,8	1,8
13	IT06		07.08.07	7,34	56,5	62,7	6,27	7	4,32	0,98	5,13	0,73	214	3,0	2,43	1440	5,7		1520	49	40		16,4	1,0
14	IT06		03.09.07	7,22	55,5	61,6	6,16	8	4,24	1,02	4,85	0,76	219	2,9	2,39	1401	5,1		1510	41	32		15,8	1,0
15	IT06		01.10.07	7,17	56,8	63,0	6,30	7	4,65	1,05	4,97	0,88	219	3,1	2,60	1578	5,0		1670	29	22		17,0	1,3
16	IT06		05.11.07	7,23	59,8	66,4	6,64	2	4,81	1,14	5,07	0,73	245	3,1	2,54	1546	5,7		1650	40	26		17,7	1,0
17	IT06		19.11.07	7,14	58,7	65,2	6,52	11	4,75	1,15	5,03	0,74	226	3,0	2,47	1640	5,3		1770	33	27		17,8	1,0

H^+	NH_4	Ca	Mg	Na	K	Alk	SO_4	NO_3	Cl	F	S Cat.	S An.	% Diff.	Quality	S Ions	Cond. Measured	Cond. Calculated	Cond. Diff. %	Quality Cond.
µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l	µeq/l		Ions balance	µeq/l	µS/cm 20 °C	20°C		
0,1	1	204	77	183	16	161	96	125	78		482	460	2	ok	942	51,0	50,9	-0	ok
0,1	2	215	82	200	16	186	58	128	142		515	515	0	ok	1030	53,8	55,4	3	ok
0,1	2	228	85	206	16	190	65	129	137		537	521	1	ok	1057	54,4	56,8	4	ok
0,1	1	229	88	219	19	221	65	118	141		556	544	1	ok	1100	56,1	58,5	4	ok
0,0	1	220	81	210	19	216	62	111	134		531	524	1	ok	1055	53,7	56,0	4	ok
0,1	1	200	78	184	15	182	71	121	118		479	493	-1	ok	971	51,1	52,2	2	ok
0,1	1	204	75	181	24	188	62	106	119		484	475	1	ok	959	50,1	51,3	3	ok
0,0	0	216	81	223	19	214	62	103	160		538	539	0	ok	1078	56,5	57,5	2	ok
0,1	1	212	84	211	19	219	60	100	145		526	524	0	ok	1051	55,5	55,8	0	ok
0,1	0	232	86	216	23	219	65	113	142		558	538	2	ok	1096	56,8	58,3	3	ok
0,1	0	240	94	220	19	245	65	110	159		573	579	-1	ok	1152	59,8	61,1	2	ok
0,1	1	237	95	219	19	226	62	117	150		570	555	1	ok	1125	58,7	59,8	2	ok

Figure 2. Central parts of the ICP Waters data reporting form with data from Italy 2007.

When you fill in the green cells in the form, you can automatically have your results converted to charged values, in µeq/l, and validation and check routines are available. Included in the forms are possibilities for control of ion balance and comparison of measured conductivity against calculated theoretical specific conductivity, and you will have the results both in the table and presented in graphs as shown below in *Figure 3* and *Figure 4*.

The reporting forms are available at the ICP Waters homepage (http://www.icp-waters.no/)

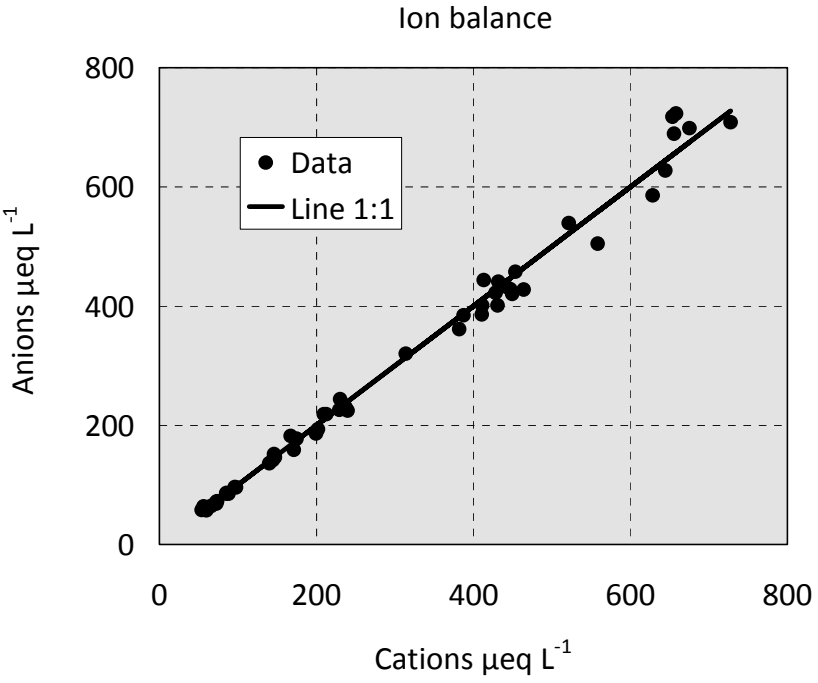

Figure 3. Control of ion balance. Excel worksheet from the ICP Waters data report and validation file. Data from Switzerland 2007.

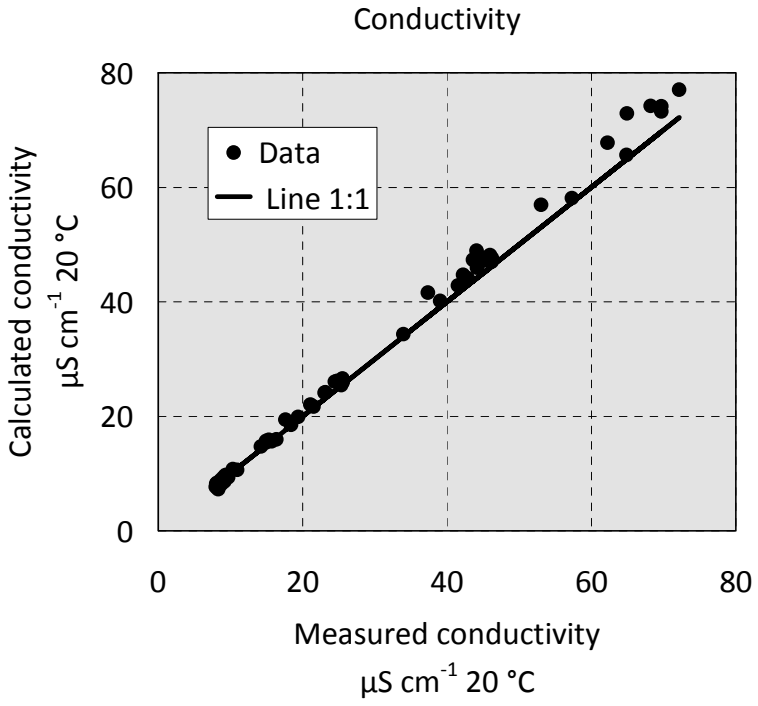

Figure 4. Control of measured and calculated conductivity. Excel worksheet from the ICP Waters data report and validation file. Data from Switzerland 2007.

3.7 References

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4. Acidification - invertebrates

4.1 Determinants

The agreed mandatory and optional determinants for ICP Waters are listed in *Table 8*.

Table 8. Mandatory and optional invertebrate determinands for ICP Waters

Mandatory components	Optional components
Ephemeroptera	Odonata
Plecoptera	Diptera
Trichoptera	Coleoptera
Turbellaria	
Mollusca	
Hirudinea	
Daphnia	
Malacostraca	

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 detect regional differences of acid-tolerance and to improve the application of this methodology. Participants in the Programme are recommended to use acidification scores and report their results.

4.2 Sampling

Sampling methods

Sampling of invertebrates must be carried out with respect to the species or organisms that are to be collected for monitoring using standard limnological methods. An overview of European methods of sampling benthic invertebrates is given by Friberg et al. (2006).

Methods for biological sampling and data handling refer to the listed ones in the *Table 9*.

Table 9. Standard sampling methods and data handling for benthic macro invertebrates.

ISO No	Name of standard
ISO 7828:1985	Water quality - Methods of biological sampling - Guidance on hand net sampling of aquatic benthic macro invertebrates
ISO 8265:1988	Water quality - Design and use of quantitative samplers for benthic macro-invertebrates on stony substrata in shallow freshwaters
ISO 8689-1:2000	Water quality - Biological classification of rivers - Part 1: Guidance on the interpretation of biological quality data from surveys of benthic macro-invertebrates
ISO 8689-2:2000	Water quality - Biological classification of rivers - Part 2: Guidance on the presentation of biological quality data from surveys of benthic macro-invertebrates

A lot of work aiming to harmonise sampling procedures is currently being done in connection with the Water Framework Directive (WFD). We recommend sampling procedures in accordance with this.

Benthic invertebrate samples from running water and lakes should be preserved in ethanol with a final concentration of, after adding ethanol to the sample, 70-80%.

A. *Benthic invertebrates in streams;* standard "kick samples", similarly at lake margins.
B. *Benthic invertebrates in lakes;* Littoral kick samples or profundal grab or core samples (Peterson, Ekman), if this habitat is significant.

Sampling 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.

4.3 Analysis

Benthic invertebrate samples should be sorted using a stereo-microscope. Further identification should be performed using necessary optics and relevant taxonomic literature.

4.4 Quality assurance and quality control

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.

To evaluate the quality of the taxonomic work on biological material delivered to the Programme centre, annual biological intercalibrations are carried out as described under chapter 11.2 Between-laboratory quality control (Quality assessment).

4.5 Acidification scores - calculations

There are several indicators developed for monitoring invertebrates in both running waters and lentic waters. Examples are the Medin Acidification index (Henrikson and Medin 1986), the Raddum indexes (Fjellheim and Raddum 1990, Raddum, 1999), the Acid Water Indicator community (Davy-Bowker et al. 2005) and The multimetric index for lake acidification (MILA, Johnson and Goedkoop, 2007)

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

As an example, The Raddum index I assign species with the same tolerance to acidity with 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 (See *Table 10*). The system can be adapted to surface waters elsewhere if similar hierarchical categories of species with known tolerance levels are identified. The acidification scores obtained in Norway can, however, not be applied to other regions without testing the critical limits of the actual species.

Table 10. Standard sampling methods and data handling for benthic macroinvertebrates.

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 spp.	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 *Baetis sp*. and 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.

4.6 Data reporting

Results shall be reported to the ICP Waters Programme Subcentre (Laboratory of Freshwater Ecology and Inland Fisheries University of Bergen) with a copy to the Programme Centre. The reporting forms are available at the ICP Waters homepage (http://www.icp-waters.no/)

4.7 References

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5. Acidification – diatoms

5.1 Determinants

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 and 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 fauna. 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).

5.2 Sampling

Sampling methods

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

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.

A lot of work aiming to harmonise sampling procedures is currently being done in connection with the Water Framework Directive (WFD). We recommend sampling procedures in accordance with this.

Sampling 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).

5.3 Analysis

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 none 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.

5.4 Quality assurance and quality control

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).

5.5 Data reporting

Diatom data for each site should be presented to the data centre in three forms:

A. A species list, giving relative abundance (percentage) of all 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.

B. 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:

Table 11. Classification scheme of Hustedt (1937-39) where taxa are divided into 5 pH groups.

Class	Description	pH window
1	Alkalibiontic	pH values > 7
2	Alkaliphilous	pH about 7 with widest distribution at pH > 7
3	Indifferent	equal occurrence on both sides of pH 7
4	Acidophilous	pH about 7 with widest distribution at pH < 7
5	Acidobiontic	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:

Table 12. UKAWMN Classification of diatoms according to their pH optimum, derived by non linear regression using the SWAP surface sediment dataset.

Class	pH optimum
1	pH values < 5.0
2	pH values 5.0 – 6.0
3	pH values > 6.0
4	Unknown

C. Diatom inferred pH. This may be calculated using the index B method of Renberg and Hellberg (1982) or by weighted averaging (ter Braak and 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 for the required format for reporting of diatom data is given here:

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)

The reporting forms are available at the ICP Waters homepage (http://www.icp-waters.no/)

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6. Acidification - fish

6.1 Indicator species

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 history stage, where the smolt stage of Atlantic salmon (*Salmo salar*) is the most sensitive (Rosseland and Skogheim 1984, Kroglund *et al.* 2007, 2008). 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 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, gillnet series in combinations of either single nets or multimesh size nets has been recommended (Rosseland 1991). We now recommends the Nordic Gillnet series (Appelberg *et al*. 1995) with multimesh nets for fish monitoring in lakes and electro-fishing in running waters. Sampling of live fish from lakes by traps or rod fishing, gives an added value to the monitoring of environmental pollution as blood analyses, organ histology or gill-metal concentration give valuable information on early warning biomarkers for mixed or multiple stressor effects (Rosseland et al. 2007). 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.

6.2 Sampling

6.2.1 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, sex ratio and maturation stage 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 of 2.5 m in length, and with mesh sizes between 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, Kurkilahti & Rask 1996) 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 13. The Nordic Survey net is composed of 12 sections of 2.5 m long net panels with mesh sizes (mi), 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.

mi (mm)	Ø (mm)	Ratio
5	0.1	
6.25	0.1	1.25
8	0.1	1.28
10	0.127	1.25
12.5	0.127	1.25
15.5	0.147	1.28
19.5	0.147	1.22
24	0.147	1.23
29	0.202	1.21
35	0.202	1.21
43	0.202	1.23
55	0.234	1.28

6.2.2 Electro-fishing in running waters

Electro-fishing in running waters is carried out to document 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 then be 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. This method, however, should be looked upon as a supplement, and never as an alternative to gillnet fishing.

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 m2, 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 fishings 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). The normal procedure of electrofishing is to release the fish after species determination and measuring of individual length and weight.

6.2.3 Sampling of fish for further analysis

A sampling procedure for live or dead fish sampled by either rod, traps or gillnets are given in Chapter 11 Trace metals and Persistent Organic Pollutants – Fish. The manual is a modification of the EMERGE Manual (Rosseland et al. 2001) and the base for a certification system for students and scientist (national and international) working with environmental pollution and fish, given by the Norwegian University of Life Sciences (Rosseland 2008).

When live fish are captured, they should be kept in keep nets until sampling. Time at catch (for gillnets the time the nets have been in the lake) and the time kept in the keep nets until individual sampling must be noted, in order to evaluate i.e. blood sample analyses related to sampling stress. Also any signs of skin and mucus damage should be noted, as such damage will interfere with osmoregulation and result in loss of plasma ions independent of the water quality. When sampling organs, it is of vital importance to follow the dissection (and time) procedure as the different organs will start to decade at different time after the fish has been killed.

6.3 Sampling timing

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.

6.4 Quality assurance and quality control

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. In the EMERGE project (http://www.mountain-lakes.org/emerge/), each national responsible person for the fish sampling programme had to be "certified" by going through a training workshop for sampling of organs. To reach the goals of the monitoring, the test fishing has 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 (mainly otholiths) 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 Raitaniemi *et al*, 1998).

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 country's "best ranked equipment".

6.5 Data reporting

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, TOC, calcium, aluminium (species)). 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 as well as data on pollution load in different organs linked to age, size (length and weight) and the link to the trophic level (analyses of stable isotope ratios of nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) to establish individual fish and species in the food chain), se Rognerud *et al.* 2002 and Rosseland *et al*. 2007. To be able to compare food chain related pollution between lakes, the $\delta^{15}N$ of the primary producers of the lakes has to be analysed. Data from different sites in a lake can be pooled together, while in the data from running waters, spawning grounds must be kept separately.

6.6 References

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7. Trace metals – surface waters

7.1 Determinants

Lake water samples are collected for primary trace metals (heavy metals) regarded as mandatory and optional trace metals as listed below in *Table 14*.

Table 14. Mandatory trace metals (heavy metals) sampled and analysed within ICP Waters

Trace metal	Name	Units
Lead	Pb	µg/L
Cadmium	Cd	µg/L
Mercury	Hg	ng/L

Table 15. Optional trace metals sampled and analysed within ICP Waters

Trace metal	Name	Units
Iron	Fe	µg/L
Manganese	Mn	µg/L
Copper	Cu	µg/L
Zinc	Zn	µg/L
Chromium	Cr	µg/L
Nickel	Ni	µg/L

Metal concentrations in remote lakes are expected to be low, so clean procedures should be followed to prevent sample contamination with metals from sampling gear or hands. For mercury special samples are collected as described in the following chapters.

7.2 Sampling for trace metals (except Hg)

Sampling of trace metals at natural concentrations in soft waters, need special care to avoid contamination. When samples are taken from a pier, metal constructions and impregnated wood is a potential source for contamination. This can be avoided if the sample bottles are mounted on a stick so that the sample is taken a bit away from the pier. When samples are taken from a helicopter, the exhausts are a potential contaminator. By using a sampler of Ruttner type this risk is minimised. Leaded gasoline should be avoided. To control for contamination it is recommended that several samples are taken from the same site at one occasion. If there is a variability in any concentration, that is an indication of contamination.

Equipment and supplies needed for sample collection and processing:

- Glass or PE bottles (100-500 mL)
- Ziplock/plastic bags for storage of sampling bottles (one per bottle)
- Disposable gloves
- Ultra pure/deionised water for potential rinsing of equipment
- Concentrated HNO3 (/HCl) for conservation of the water samples
- pH meter if knowledge of pH is desired (the meter must be calibrated at least the same day as sampling)
- Conductivity meter and temperature meter if desired
- Permanent marker (labelling tape) to mark the bottles
- Form and pen to note field descriptions, sample IDs, pH, conductivity, temperature, etc

Pre-cleaning of equipment

The PE/glass bottles should have been thoroughly cleaned with nitric acid solution prior to sampling. Bottles should be filled to the top with the nitric acid solution (pro analysi, approximately 5% v/v) and left filled for at least 24 hours. The bottles may be soaked in acid solution so that the outside is cleaned as well (important for new bottles and bottles used for potential metal contaminated water).

During sampling, each bottle should be kept in separate plastic bags. The bagged bottles are kept together in one larger shared plastic bag. The sampling bottles should only be touched by clean, plastic gloves, and the plastic bags should not be opened more than necessary.

While sampling, the sampling bottle is to be opened and filled partially with water, shaken with the cap on, emptied and the procedure repeated twice. The final filling should fill the bottle completely, and the cap should be replaced under water. (NB! If the bottles are planned to be frozen during storage, approximately two centimetres in the glass bottle neck should not be filled due to expansion!) Be careful not to sample the surface layer of the water.

If the sample is to be analysed for dissolved metal, it is filtered in accordance with the procedure described below:

Set up the filtration by using the shortest piece of pump tubing as is feasible. The top of the liquid holder should be covered by plastic bag through the whole procedure. The equipment must have been cleaned with dilute nitric acid prior to sampling and between each sample. If the sampling follows a "low to high concentration" strategy, washing with ultra pure water is enough between the samples.

In addition to the cleaning with ultra pure water, the sampled water should be run through the pump three times before collection of filtered water. The filter may also be analysed; put the filter in a separate plastic bag (after it has been folded in two).

Conservation and storage

All the water samples must be added concentrated HNO_3 (Suprapur® or similar quality) for conservation (acidify to pH < 1-2). In the case of hydride analysis (an option for some metals/metalloids), HCl should be used for acidification. 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. The samples should be analysed within one month after sampling.

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

7.3 Passive samplers for determination trace metals in water

The technique of diffusive gradients in thin films (DGT) is a useful tool for in situ measurement of labile metal ions in water. The DGT method may be used for several elements including Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Zn, and Pb. A performance study of diffusive gradients in thin films for 55 elements is described by Garmo et al (2003), and a full description of the sampling method is given in a technical documentation from DGT Research Ltd (http://www.dgtresearch.com/TechnicalInfo.aspx).

7.4 Sampling for mercury (Hg)

Equipment and supplies needed for sample collection and processing:

- Glass or FPE (Fluorinated Polyethylene) bottles (100-250 mL)
- Ziplock/plastic bags for storing of sampling bottles (two per bottle)
- Disposable gloves
- Filtration equipment if the water is to be analysed for dissolved Hg
- Ultra pure water for the filtration procedure
- Concentrated HCl for conservation of the water samples
- pH meter if knowledge of pH is desired (the meter must be calibrated at least the same day as sampling)
- Conductivity meter and temperature meter if desired
- Form and pen to note field descriptions, sample IDs, pH, conductivity, temperature, etc

Pre-cleaning of equipment

The glass or FPE bottles should have been thoroughly cleaned with nitric acid solution prior to sampling. Bottles should be filled to the top with the nitric acid solution (pro analysi, approximately 5% v/v) and left filled for some days – a week (minimum 24 hours). The bottles may be soaked in acid solution so that the outside is cleaned as well (important for new bottles and bottles already used for potential metal contaminated water).

Sampling

- During sampling, the bottles should be kept inside two plastic bags. The plastic bags should not be opened more than necessary. When touching the sample bottle, clean plastic gloves must be put on.
- While sampling, the glass or FPE bottle should be opened under water, partly filled, shaken with the lid/cap on, and the bottle emptied downstream. Repeat twice. When filling the bottle the final time, put on the lid/cap under water when the bottle is FULL. (NB! If the bottles are planned to be frozen during storage, approximately two centimetres in the glass or FPE bottle neck should not be filled due to expansion!). Do not sample the upper layer of the water.
- Put the bottle into the plastic bags as quickly as possible.
- If the sample is to be analysed for dissolved Hg, it is filtered in accordance with the procedure described below:
    - Set up the filtration by using the shortest piece of pump tubing as is feasible. The top of the liquid holder should be covered by plastic bag through the whole procedure. The equipment must have been cleaned with dilute nitric acid prior to sampling and between each sample. If the sampling follows a "low to high concentration" strategy, washing with ultra pure water is enough between the samples.
    - In addition to the cleaning with ultra pure water, the sampled water should be run through the pump three times before collection of filtered water. The filter may also be analysed; put the filter in a separate plastic bag (after it has been folded in two).

Conservation and storage

- NIVA procedure: Concentrated HCl (Suprapur® or similar quality) has to be added to all water samples when daily sampling is accomplished. The volume that should be added is approximately 0.4% of the volume of sample. A blank sample (ultra pure water) should also be added HCl (same amount) to determine potential Hg in the acid (if the quality is not met or the Hg concentration of the acid is not known).
- Samples where only total Hg should be determined (and not methylmercury) are preserved by adding BrCl (2 mL to 250 mL bottle) (EPA Method 1631).

- ISO 5667-3 procedure: Concentrated HNO_3 (Suprapur® or similar quality) added to pH<1-2, and also addition of an oxidant, typically $K_2Cr_2O_7$ (0.05% [m/m] of final concentration). Beware the Hg concentration of the oxidant added!

Do not expose samples to light or heat. The samples should be analysed within one month after sampling.

7.5 Analysis

Chemical analysis of the samples should be done according to international standards such as prescribed by ISO/CEN. The EN (European standards) is legally prescribed for use by all EU nations. We therefore have proposed that ICP-Waters adopt ISO/CEN standard methods as a basis for the methods actually used for all chemical analysis. 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 listed in *Table 16* are recommended for the work:

Table 16. List of ISO and CEN methods to be used for analysis and QA/QC procedures in the laboratory.

Trace metal	ISO or CEN No	Name of standard
Fe: iron Mn: manganese Cd: cadmium Zn: zinc Cu: copper Ni: nickel Pb: lead Cr: chromium Hg: mercury	EN-ISO 15586:2003	Water quality - Determination of trace elements with graphite furnace atomic absorption spectrometry
	EN-ISO 11885:1998	Water quality - Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy
	EN-ISO 17294-2:2004	Water quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements

Information of the ISO/CEN methods listed above can be obtained from:

- The national standardisation agencies.
- ISO International Organisation for Standardisation, Case Postale 56, CH-1211 Genève, Switzerland. http://www.iso.org
- CEN European Committee for Standardisation, Rue de Stassart 36, B-1050 Brussels, Belgium. http://www.cen.eu

USEPA (United States Environmental Protection Agency) Method 1631 describes the procedure for determination of mercury in water by oxidation, purge and trap, and cold vapour atomic fluorescence spectrometry (USEPA, 2002).

7.6 Quality assurance and quality control

Quality control of sampling and filtering procedures

A sample of distilled (or pure) water may be divided into two (A+B), where one part (A) is kept in the lab (at least not brought in the field) and the other part (B) is transported in the field where it again is divided into two (b_1 and b_2) if any of the samples taken in the field are to be analysed for dissolved

Hg. One of these water parts (b_1) is filtrated following previously described procedure, while the other (b_2) is not. The filtrated sample (b_1) will identify errors from contamination during filtration when compared to b_2, while the other (b_2) identifies errors from contamination due to transportation when compared to A.

Quality assurance and quality control of analytical results

Quality assurance and quality control are the responsibility of the National Focal Points. The Programme Centre will, however, to ensure data quality and correct technical transfer of data, do data quality control according to the following:

1. looking for outliers
2. looking for continuity in time series

7.7 Data Reporting

The water chemistry results, including trace metals, are reported to the Programme Centre and stored in the ICP Waters database as described under this manuals part 3.1 Acidification – Water chemistry. An example of the reporting form showing central parts of the form and file (excel-file) is shown in *Figure 5*. (Data from Italy 2007).

ICP FORM for ion registered in the green celles.

Test for Italy 2007

Code	Nau	Date	Fe	Mn	Cd	Zn	Cu	Ni	Pb	Cr	As	Hg
			µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	ng/l
IT06		08.01.07	4	0,1	0,0	3,6	0,0	0,7				
IT06		19.02.07	2	0,1	0,0	6,7	0,5	0,3				
IT06		19.03.07	3	0,2	0,0	2,5	0,7	0,4				
IT06		16.04.07	11	0,5	0,0	8,7	1,3	1,2				
IT06		14.05.07	9	0,4	0,0	5,3	2,6	0,5				
IT06		11.06.07	10	0,3	0,0	4,0	1,0	0,5				
IT06		09.07.07	19	0,5	0,0	13,8	2,5	0,8				

Figure 5. Parts of the form (EXCEL-file) for water chemistry, with trace metals included, for reporting results to the ICP Waters Programme Centre. (Data from Italy 2007.)

The reporting forms are available at the ICP Waters homepage (http://www.icp-waters.no)

7.8 References

EC 2003. Common Implementation Strategy for the Water Framework Directive (2000/60/EC), Guidance Document No. 7. Monitoring under the Framework Directive. http://www.wrrl-info.de/docs/Guidance_doc_7_monitoring_klein.pdf

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Garmo Ø. A, Davison W., Zhang H. 2008. Effects of Binding of Metals to the Hydrogel and Filter Membrane on the Accuracy of the Diffusive Gradients in Thin Films technique**.** *Analytical Chemistry* 2008 *80* (23), 9220-9225

Garmo, Ø. A,. Røyset, O., Steinnes, E. Flaten T. P. 2003. Performance study of diffusive gradients in thin films (DGT) for 55 elements. *Anal. Chem.*, 2003, *75* (14), pp 3573–3580.

Røyset, O., Garmo, Ø. A. Steinnes, E. Flaten T. P. 2002. Performance study of diffusive gradients in thin films (DGT) for 55 elements. NIVA Report 4604-2002.

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8. Trace metal – sediments

As the general concentration of trace metals in water is low, making chemical analysis to detect and quantify their presence a challenge, chemical analysis of sediments might be a solution to assess the degree and impact of atmospheric pollution in the aquatic environment.

8.1 Determinants

Sediments samples are collected for primary trace metals (heavy metals) regarded as mandatory and optional trace metals as listed below in *Table 17* and *Table 18*.

Table 17. Mandatory trace metals (heavy metals) sampled and analysed within ICP Waters

Trace metal	Name	Units
Lead	Pb	µg/L
Cadmium	Cd	µg/L
Mercury	Hg	ng/L

Table 18. Optional trace metals sampled and analysed within ICP Waters

Trace metal	Name	Units
Iron	Fe	µg/L
Manganese	Mn	µg/L
Copper	Cu	µg/L
Zinc	Zn	µg/L
Chromium	Cr	µg/L
Nickel	Ni	µg/L

Metal concentrations in remote lakes are expected to be low, so clean procedures should be followed to prevent sample contamination with metals from sampling gear or hands. For mercury special samples are collected as described in the following chapters.

8.2 Sampling

Sampling equipment and techniques
The techniques are applicable to sample sediments in inland lakes, rivers, and streams. Sampling point must be chosen on the basis of where the sediments are least disturbed; often the deepest area of the lake.

There is a variety of sampling equipment to be considered, but core samplers are often the best alternative when it is preferred to keep the layers intact. A gravity corer, such as a Kajak corer, is easy to use (*Figure 6*) although the sediment core will be somewhat compressed. (The smaller the diameter of the corer, the more the core is compressed.)

Another option is a piston corer. These collectors are more difficult to handle, but will not compress the sediment cores (as it has a piston to create a low pressure inside the corer). Additionally, longer cores are obtainable. If the sediment layers are not of concern, grab samplers are an option. (*Figure 7*). The condition of the sediments is also of importance when choosing sampling equipment. A preliminary investigation may be necessary in order to avoid certain equipment problems during sampling.

Figure 6. A gravity corer for layered sediment samples

Figure 7. A grab sampler.

Samplers for different sediment types:

- **Gravel:** Grab systems
- **Sand:** Both grab and corer systems may be applied
- **Clay:** Corer samplers may be necessary as grabs can experience problems with penetrating easily
- **Peat:** Hard to sample. A special peat borer may be needed
- **Consolidated bottom sediment:** Both grab and corer systems
- **Unconsolidated bottom sediment:** Corer systems better than grab systems, but care is essential as the sampler may sink through the sediments

These are only recommendations, as the sampler type versus the sediment type should be determined by experimentation. Additionally, there are different grab samplers made for specific sediment types.

The corer material may be chosen dependant on the analyte. Steel can generally be used for metal samples. If this is not desirable, plastic materials may be used for sampling of metal samples.

Sample containers
Sample containers must be chosen on the basis of the specific analyte. Sediments for mercury (Hg) should always be sampled in glass or PTFE containers.

Other equipment:

- Disposable gloves
- Labelling tape and permanent marker
- Aluminium foil
- Distilled/deionised water or acetone/methanol for rinsing the equipment between samples
- Bucket(s) for the handling of unsatisfactory grab/core samples
- Safety vests

The containers must be thoroughly cleaned with nitric acid solution prior to sampling. Containers should be filled to the top with the nitric acid solution (pro analysi, approximately 5% v/v) and left filled for at least 24 hours (preferably more when Hg is to be determined). The containers may be

soaked in acid solution so that the outside is cleaned as well (important for new containers and containers used for potential metal contaminated material). Rinsing is necessary; deionised/distilled water is appropriate. Potential sampling tools must also be properly cleaned prior to use.

Sampling procedure

- In rivers and streams, it is advisable to sample during low flow and low water levels if possible.
- Remember to properly tie the sediment sampler to a suitable object before it is released into the water!
- If a grab sampler does not close completely, the sample must be discarded. Do not throw the sample in the water body before a satisfying sample has been collected! (Empty the grab into a bucket.)
- When the sediment core has been collected, it can be put in suitable containers and labelled. This is only relevant if the core can not be kept in the corer until arrival at the laboratory (or other "base" location). Be careful not to ruin the layering of the core during processing if this is of importance. Do not touch the sediments with bare hands; use disposable gloves.
- Grab samples may also be put in suitable containers dependant on the specific analyte to be determined.
- At least five samples should be sampled from each sampling site to get representative results.
- The sample containers should be filled entirely (save approximately one cm on top if the samples are to be frozen to allow for expansion).
- If there is unease in relation to potential contamination of the sediment samples/cores, sample material may be collected from the inner part of the cores (not in contact with the sampler material).

Conservation and storage
During transportation, sediment cores are recommended to be kept in a cooler and placed in up right position. The sediment samples should be stored in a cool (1-4°C) and dark place prior to analyses. Details for different analytes follow.

- **Metals and trace elements:** Air dried soil samples may be stored in room temperature in dust tight containers (glass or PE bags) for six months (dark). Wet samples (stored in 1-4°C, dark) must be analysed within one month after sampling, while frozen samples may be stored for six months (dark). Experience show that samples may be stored considerably longer without losing analytes if frozen.
- **Mercury***:* The loss of elemental Hg or volatile Hg compounds may occur. Wet soil samples (stored in 1-4°C, dark) should be analysed within eight days after sampling. Frozen samples (< -20°C) may be stored for one month (dark).Experience show that samples may be stored considerably longer without losing tot-Hg if frozen.
- **Chromium VI***:* Refrigerated samples must be analysed within two days from sampling (stored in 1-4°C, dark).

8.3 Analysis

Chemical analysis of the samples should be done according to international standards such as prescribed by ISO/CEN. The EN (European standards) is legally prescribed for use by all EU nations. We therefore have proposed that ICP-Waters adopt ISO/CEN standard methods as a basis for the methods actually used for all chemical analysis. 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 listed in *Table 19* are recommended for the work:

Table 19. ISO and CEN methods to be used for analysis and QA/QC procedures in the laboratory.

Trace metal	ISO or CEN No	Name of standard
Fe: iron Mn: manganese Cd: cadmium Zn: zinc Cu: copper Ni: nickel Pb: lead Cr: chromium Hg: mercury	EN-ISO 15587-2: 2002	Water quality - Digestion for the determination of selected elements in water - Part 2: Nitric acid digestion

Information of the ISO/CEN methods listed above can be obtained from:

- The national standardisation agencies.
- ISO International Organisation for Standardisation, Case Postale 56, CH-1211 Genève, Switzerland. http://www.iso.org
- CEN European Committee for Standardisation, Rue de Stassart 36, B-1050 Brussels, Belgium. http://www.cen.eu

8.4 Quality assurance and quality control

Quality assurance and quality control are the responsibility of the National Focal Points. The Programme Centre will, however, to ensure data quality and correct technical transfer of data, do data quality control according to the following:

1. looking for outliers
2. looking for continuity in time series

Use of blanks, standards, (certified) reference materials and/or regular participation in laboratory intercomparison are strongly recommended.

8.5 Data Reporting

The analytical results are reported to the Programme Centre and stored in the ICP Waters database. The results should be reported in a special form prepared as an excel-file. The form with an example included is attached to this document.

The reporting forms are available at the ICP Waters homepage (http://www.icp-waters.no/)

8.6 References

EC 2008. Directive 2008/105/EC of the European Parliament and of the Council on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council.

EC 2010. Common Implementation Strategy for Water the Framework Directive (2000/60/EC): Guidance Document No. 25 on Chemical Monitoring of Sediment and Biota under the Water Framework Directive.

ISO 1995. ISO Standard 5667-12:1995. Water quality - Sampling - Part 12. Guidance on sampling of bottom sediments.

ISO 1999. ISO Standard 5667-15. Water quality - Sampling - Part 15. Guidance on preservation and handling of sludge and sediment samples.

ISO 2007. ISO Standard 18512:2007. Soil quality – Guidance on long and short term storage of soil samples.

9. Persistent Organic Pollutants – water

There is a general lack of coordinated monitoring or regional surveys that focus on POPs in the freshwater environments for which LRTAP is a major source. Methodology regarding sampling, analytical methods and reporting makes comparison between results from the different projects very difficult. It is recommended to coordinate international surveys with harmonized methodology and reporting (Fjeld et al. 2005).

In *Table 20* the list of the POPs regulated by the Aarhus protocol is given.

Table 20. Substances regulated by the POPs protocol under the LRTAP Convention.

Aldrin
Chlordane
Chlordecone
DDT
Dieldrin
Dioxine/Furane
Endrin
HCH (incl Lindane)
Heptachlor
Hexabromobiphenyl
Hexaclorobenzene (HCB)
Mirex
PAH
PCBs
Toxaphene

9.1 Determinants

Lake water samples are collected for primary persistent organic pollutants regarded as mandatory and optional persistent organic pollutants as listed below in *Table 21* and *Table 22*

Table 21. Mandatory persistent organic pollutants sampled and analysed within ICP Waters

Group	Component	Comment
PAH	Acenaphthene	PAH-16
PAH	Acenaphthalene	PAH-16
PAH	Anthracene	PAH-16
PAH	Benzo(a)anthracene	PAH-16
PAH	Benzo(a)pyrene	PAH-16
PAH	Benzo(b)fluoranthene	PAH-16
PAH	Benzo(ghi)perylene	PAH-16
PAH	Benzo(j+k)fluoranthene	PAH-16
PAH	Chrysene	PAH-16
PAH	Dibenz(a,c+a,h)anthracene	PAH-16
PAH	Phenanthrene	PAH-16

Group	Component	Comment
PAH	Fluoranthene	PAH-16
PAH	Fluorene	PAH-16
PAH	Indeno(1,2,3-cd)anthracene	PAH-16
PAH	Naphthalene	PAH-16
PAH	Pyrene	PAH-16
PCB	PCB 28	7-dutch
PCB	PCB 52	7-dutch
PCB	PCB 101	7-dutch
PCB	PCB 118	7-dutch
PCB	PCB 138	7-dutch
PCB	PCB 153	7-dutch
PCB	PCB 180	7-dutch
PCB	PCB 209	7-dutch
Halogenated compounds	-hexachlorocyclohexane (-HCH)	Lindane
Halogenated compounds	-hexachlorocyclohexane (-HCH)	
Halogenated compounds	hexachlorobenzene (HCB)	
Halogenated compounds	pentachlorobenzene (PeCB)	
Halogenated compounds	octachlorostyrene (OCS)	
Halogenated compounds	DDD	
Halogenated compounds	DDE	
Halogenated compounds	DDT	

Table 22. Optional persistent organic pollutants sampled and analysed within ICP Waters

Group	Component	Comment
Brominated compounds	BDE 47	
Brominated compounds	BDE 99	
Brominated compounds	BDE 138	
Brominated compounds	BDE 153	
Brominated compounds	BDE 154	
Brominated compounds	BDE 183	
Brominated compounds	BDE 209	

9.2 Sampling methods

The general concentration of POPs in environmental water samples is low and as a result chemical analysis applied to detect and quantify the presence of POPs in water is challenging. Considerable effort is done in laboratories with methodology to improve the limit of detection (LOD) in order to comply with the trace levels found in environmental water samples (Rodil et al., 2007; Wang et al., 2007; Prieto et al., 2008). Unfortunately, at present LODs are often higher than the concentration of

various POPs in the water phase. Most conventional laboratories offer analyses where the detection levels are at μg/L, while POPs-concentrations found in the environment are often at ng/L or less.

By adding a pre-concentration step in field prior to analysis in laboratory, improved detection may be achieved. Most POPs in water are sampled by use of conventional bottle sampling technique (a bottle is simply filled with water sample), and consequently, concentrations of many POPs in the aquatic environment are unknown or often reported as less than the LOD. This is well illustrated in the RID-monitoring programme (Riverine input and direct discharges into Norwegian costal waters/Joint Monitoring Programme under the OSPAR convention), where 93 and 100% of the river samples analysed for lindane and PCBs were under the detection limits, respectively. As a result, this uncertainty makes it difficult to get a picture of fluxes of the POPs in a watershed, determine their mobility through the ecosystems, track sources (point or diffuse), monitor the spatial and temporal variation, and perform risk assessment in relation to biota.

To overcome this challenge, scientists have developed unconventional sampling techniques in order to preconcentrate/up-concentrate the POPs prior to the analysis, and this field is today under development (Allan et al., 2009).

A brief overview of the most frequent alternative sampling techniques for POPs in water is given below.

9.3 Sampling POPs associated to suspended particulate matter

Many POPs are characterised by low water solubility, high lipid solubility, semi-volatile nature, and relatively high molecular masses. Due to the low water solubility and high lipid solubility, POPs are often associated to suspended particulate matter (SPM) in the water column. Based on the chemical and physical characteristic in the watershed, fractions of this POPs-suspended material will be present in the water column, while other parts will settle as bottom sediments. Several techniques have been developed to up-concentrate this SPM-fraction of the POPs; i) sediment traps, ii) time-integrative SPM samplers, iii) large volume sampling, and iv) continuous-flow centrifuge.

Sediment traps: This is the traditional way to sample suspended particulate matters in a water column. Sediment traps, consisting of containers which are positioned at pre-determined depth in the water column collect settling SPM. After a certain length of time the traps are retrieved, and material collected in the traps is analysed. Sediment traps works well in lakes, but in rivers where strong current prevents sedimentation, sediment traps may be inefficient for sampling of SPM. When deployment time is long, preservation has to be added to reduce the microbial activity. Collection of enough SPM to achieve the LODs is a challenge, as well as he POPs subjected to aging.

Time-integrative SPM samplers: Here, SPM is collected in advanced sedimentation boxes/devices, where substantial volumes of water are directed to flow through inlet openings. Mechanism inside the box reduces the water velocity in order to permit sedimentation of the SPM, which is collect in a sedimentation basin. The boxes may be checked and emptied monthly. Samples may be subjected to ageing during collection and at high velocity collection capability decreases.

Large volume sampling: Basically, large volume of water is pumped through a filtration system. This is an operationally defined procedure since the size of the filter pores determine the fractions which is retained on the filter or passed through (filtrate). In order to collect enough material to meet the LOD requirements, a substantial amount of water has to be filtered when the SPM-concentration is low. At high SPM-concentrations lower volume water has to be filtered, but the risk of clogging the filter is high. Quantification is either done by knowing the volume of water filtered and/or by weighing the amount retained on the filter. Sampling of POPs in the filtrate may be done by use of resins, but

retention efficiency is difficult to control. Sampling may be considered as time consuming, and care should be taken in order to collect a representative sample.

Continuous-flow centrifuge: Samples of SPM in the water column are obtained by centrifuging a large amount of water. Water is pumped from the source into the running centrifuge. Based on the particle size and density difference between the liquid and solid phases, SPM particles are settled out in the centrifuge drum, while the remaining water is discharged. SPM settled on the drum is collected for analysis. Sampling may be conducted over hours to days, but care should be taken to provide a representative samples. Considerable litres of water may be processed, which may provide enough SPM material to handle the LOD. In addition, standardisations of water flow in/out, rotation velocity, and others parameters that may affect the sedimentation of the SPM is required. Mobile and stationary centrifuges are available. POPs associated with the dissolved fraction (supernatant) can be collected by use of resins.

For all sampling devices there is a possibility of contamination of the POPs associated with SPM. Strictly clean handling during sampling and analysis is required, and care should be taken to avoid sorption of POPs on the walls of equipment used. In addition, measured should be taken to secure that the laboratories performing the analyses are experienced in handling of complex matrixes like SPM-associated POPs.

9.4 Passive samplers for determination of dissolved POPs in water

Although that a considerable fraction of POPs in the aquatic phase is associated to SPM, a minor but important fraction of the POPs is found in the dissolved water phase. Depending on physical and chemical parameters in the water, a partition of the POPs between the SPM and the dissolved phase will take place. This dissolved fraction, not separated from the total concentration measured by use of conventional bottle sampling, is considered as bioavailable. An approach to yield information about this biologically relevant fraction is by use of passive samplers instead of biomonitoring. Results have shown that passive samplers are comparable to biomonitoring of a wide range of POPs, and many of the challenges when using biota is avoided. By use of passive samplers, the target POP is collected and pre-concentrated in situ and a time-averaged concentration is provided, depending on the time the sampler was exposed. A considerable numbers of passive samplers are available for several POPs, and for a comprehensive review the paper by Vrana et al., 2005 is recommended.

A basic introduction to the use of the Semi Permeable Membrane Devices (SPMDs), which is frequently used passive sampler to monitor organic pollutant, is given below. One specific SPMD is used as an example in the following description.

Semi Permeable Membrane Devices (SPMDs) are designed to sample chemical pollution. They are extremely sensitive to contamination so this must be minimized when handling the samplers. Samplers exposed to air may concentrate significant amounts of air pollutants. The SPMD is extremely sensitive to fumes from engines, oils, tars, gasoline, diesel, paints, solvents, cigarette smoke, etc.

Prior to use, the samplers should remain in the clean, sealed metal can. Whether you intend it or not: the moment the container is opened, sampling begins. Prior to opening the container, or during retrieval, make sure that:

- you are as close as possible to the sampling location. Minimize the time between the opening of the metal can and submersion of the deployment device. Likewise, during retrieval, the individual samplers should quickly be protected from airborne pollution.
- you are in an area free of chemical fumes, smoke, etc.
- your exposed skin or gloves are clean and free of lotions, insect repellents,
- etc. (a normal amount of oil from your skin is OK).
- the surface of the water is not coated with floating oils, solvents, etc.

Once the deployment device is retrieved, immediately place the samplers in the provided metal can and seal with the metal lid. Make sure the lid is sealed all the way around to prevent air leaking into the can.

All samplers (including Field Blanks) are to be kept frozen before and after the deployment. Blanks should also be kept frozen during the period between the deployment and retrieval trips. The samplers and travel/field blanks should be transported frozen or on ice packs in a cooler.

Cans containing Field Blanks are to be opened (the samplers are not to be removed) during deployment and retrieval. The blanks will monitor for any contamination not due to the deployment in the water.

Field personnel should submit a Field Data Sheet which indicates changes in field sample names, dates of deployment and retrieval, and any other relevant information.

Sampler deployment:
Relevant equipment:

- Field/transport blanks, new samplers in tins that are to be marked with the date they were set out
- Plastic strips, gloves, thermometer, rope
- Cool box with freeze element
- Potential oceanographic equipment
- Cleaned and solvent rinsed SPMD holders and cages

1. Carry out any eventual oceanographic work, profiling, water samples etc. first
2. Turn off any boat engine if possible
3. Make sure that all equipment is in place before starting, felt blind, fresh gloves, new samplers, etc
4. Securely attach the steel cage (without the lid) to the rope rig
5. Open the correct felt blind tin BUT DO NOT REMOVE THE SAMPLER and place it in a safe place nearby
6. Put on fresh gloves
7. Take a new SPMD sampler out from its tin and attach it to the holder. This is most easily done by starting at the steel pin at the opposite end from the spring. This is the one without a steel wheel around it but not the one in the centre. Place the loop of the sampler over this pin and then wind the sampler around the all the other pins in a zigzag (see diagram).Place the clip through the loop at the other end and attach this to the spring.
8. Check that the sampler sits correctly and evenly on the holder (*Figure 9*), adjust by turning the wheels of the pins
9. Place the holder in the steel cage and screw on the lid
10. Secure the lid to the cage using plastic strips
11. Put the rope/anchor/float/cage set up back into the water and immediately close both steel tins and place them into the cool box. (Mark the tins if not already done so)
12. Complete the relevant sampling sheet provided and report abnormalities
13. On return to the laboratory SPMD felt blinds should be frozen (-20^{o}C)

Sampler retrieval
Collect all the relevant equipment before starting:

- Field/transport blanks, appropriate empty sampler tins
- Plastic strips, gloves, thermometer
- Cool box with freeze element.
- Potential oceanographic equipment/sample bottles

Figure 8. A SPMD ready for deployment

Figure 9. SPMD sampler correctly mounted on the holder

1. Carry out any eventual oceanographic work, profiling etc. first
2. Turn off any boat engine if possible
3. Make sure that all equipment is in place before starting, felt blind (sjø), fresh gloves, knife and the empty steel box for the relevant sampler
4. Pull up the equipment and remove the rope attached to the steel cage
5. Open the correct felt blind tin BUT DO NOT REMOVE THE SAMPLER and place it in a safe place nearby, this should ideally be done just before the cage reaches the water surface during 4) above, but just after is ok
6. Cut the plastic strip and unscrew the top of the cage
7. Put on fresh gloves
8. Take out the holder the sampler is fixed to
9. Remove the sampler from the holder. This is most easily done by holding the spring and the clip and pushing them together, the clip can then be pulled out from the loop of the sampler and kept safe. Now carefully unwind the sampler and fold it neatly into the correct tin. The sampler must not come into contact with anything other than the gloved hand.
10. Seal tin immediately. A good way to do this is to turn it upside down and press firmly against something hard
11. Remove gloves
12. Seal the felt blind tin immediately taking care not to drop water into the tin
13. Place both tins into the cool box
14. Complete the relevant sampling sheet provided and report abnormalities

On returning to the laboratory, SPMDs should be frozen (-20^{o}C) and SPMD equipment cleaned ready for the next sampling.

Eventual shipping should be carried out cold.

9.5 General sampling of water for the determination of POPs

Equipment and supplies needed for sample collection and processing:

- Glass bottles with PTFE cap liner
- Ziplock/plastic bags for storing of sampling bottles
- Disposable gloves
- pH meter if knowledge of pH is desired (the meter must be calibrated at least the same day as sampling)
- Form and pen to note field descriptions, sample IDs, pH, conductivity, temperature, etc
- Acetone for rinsing

No plastic containers must be used for this sampling, as the plastic most likely will interfere with the determination of various POPs.

Pre-cleaning of equipment:
Glass containers (preferably brown) should be cleaned with inorganic, alkaline soap in distilled water, rinsed with tap water, distilled water, MilliQ water and the extraction agent used during the analyses (or acetone/methanol). Then the glass containers (and aluminium foil) should undergo glowing/burning at approximately 500°C for two hours to remove organic constituents. Containers for reuse must be extracted for 12 hours by acetone, rinsed by hexane and oven dried as previously described.

Sampling:
The sample bottle must not be pre-rinsed by the sample water prior to filling, nor must it be filled completely. Do not sample the upper layer of the water.

Conservation and storage:
The preservation in a cold environment (1-5°C) is normally sufficient. If the samples are to be frozen, this should be done immediately after sampling (by keeping a freezer box nearby). For POPs determination, freezing is actually not recommended during storage, as samples often precipitate on thawing (PCBs, pesticides). The samples should be analysed within five to seven days after sampling. Bottles should be kept in the dark.

9.6 Analysis

Chemical analysis of the prepared samples should be done according to international standards such as prescribed by ISO/CEN. The EN (European standards) is legally prescribed for use by all EU nations. We therefore have proposed that ICP-Waters adopt ISO/CEN standard methods as a basis for the methods actually used for all chemical analysis. 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 listed in *Table 23* are recommended for the work.

Table 23. List of ISO and CEN methods to be used for analysis and QA/QC procedures in the laboratory.

Component	ISO or CEN No	Name of standard
PAH	ISO 28540: 2009	Water quality - Determination of 16 polycyclic aromatic hydrocarbons (PAH) in water - Method using gas chromatography with mass spectrometric detection (GC-MS)
PAH	ISO 17993:2002	Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction
PCB	ISO 17858:2007	Water quality -- Determination of dioxin-like polychlorinated biphenyls -- Method using gas chromatography/mass spectrometry
Chlorobenzenes and PCB	ISO 6468:1996	Water quality -- Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes -- Gas chromatographic method after liquid-liquid extraction

Information of the ISO/CEN methods listed above can be obtained from:

- The national standardisation agencies.
- ISO International Organisation for Standardisation, Case Postale 56, CH-1211 Genève, Switzerland. http://www.iso.org
- CEN European Committee for Standardisation, Rue de Stassart 36, B-1050 Brussels, Belgium. http://www.cen.eu/CEN

9.7 Quality assurance and quality control

Quality assurance and quality control are the responsibility of the National Focal Points. The Programme Centre will, however, to ensure data quality and correct technical transfer of data, do data quality control according to the following:

1. looking for outliers
2. looking for continuity in time series

Use of blanks, standards, (certified) reference materials and/or regular participation in laboratory intercomparison are strongly recommended.

9.8 Data Reporting

The analytical results are reported to the Programme Centre and stored in the ICP Waters database. The results should be reported in a special form prepared as an excel-file. The reporting forms are available at the ICP Waters homepage (http://www.icp-waters.no/)

9.9 References

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10. Persistent Organic Pollutants - sediments

Sediment samples are collected for Persistent Organic Pollutants (POPs) analyses. POPs concentrations in remote lakes and their sediments are expected to be low, so clean procedures should be followed to prevent sample contamination from sampling gear or hands.

10.1 Sampling

The techniques are applicable to sample sediments in inland lakes, rivers, and streams.
Sampling point must be chosen on the basis of where the sediments are least disturbed; often the deepest area of the lake.

There is a variety of sampling equipment to be considered, but core samplers are often the best alternative when it is preferred to keep the layers intact. A gravity corer, such as a Kajak corer, is easy to use *(Figure 10.)* although the sediment core will be somewhat compressed. (The smaller the diameter of the corer, the more the core is compressed.)

Figure 11. A gravity corer for layered sediment samples

Figure 12. A grab sampler.

Another option is a piston corer. These collectors are more difficult to handle, but will not compress the sediment cores (as it has a piston to create a low pressure inside the corer). Additionally, longer cores are obtainable. If the sediment layers are not of concern, grab samplers are an option. *Figure 13.*

The condition of the sediments is also of importance when choosing sampling equipment. A preliminary investigation may be necessary in order to avoid certain equipment problems during sampling.

Samplers for different sediment types:

- **Gravel:** Grab systems
- **Sand:** Both grab and corer systems may be applied

- **Clay:** Corer samplers may be necessary as grabs can experience problems with penetrating easily
- **Peat:** Hard to sample. A special peat borer may be needed
- **Consolidated bottom sediment:** Both grab and corer systems
- **Unconsolidated bottom sediment:** Corer systems better than grab systems, but care is essential as the sampler may sink through the sediments

These are only recommendations, as the sampler type versus the sediment type should be determined by experimentation. Additionally, there are different grab samplers made for specific sediment types.

The corer material may be chosen dependant on the analyte. Steel can generally be used for both for POPs and metal samples.

Sample containers must be chosen on the basis of the specific analyte.

Other equipment:
- Disposable gloves
- Labelling tape and permanent marker
- Aluminium foil
- Distilled/deionised water or acetone/methanol for rinsing the equipment between samples
- Bucket(s) for the handling of unsatisfactory grab/core samples
- Safety vests

Glass containers (preferably brown) should be cleaned with inorganic, alkaline soap in distilled water, rinsed with tap water, distilled water, MilliQ water and the extraction agent used during the analyses (or acetone/methanol). Then the glass containers (and aluminium foil) should undergo glowing/burning at approximately 500°C for two hours to remove organic constituents. Containers for reuse must be extracted for 12 hours by acetone, rinsed by hexane and oven dried as previously described.

Sampling procedure

- In rivers and streams, it is advisable to sample during low flow and low water levels if possible.
- Remember to properly tie the sediment sampler to a suitable object before it is released into the water!
- If a grab sampler does not close completely, the sample must be discarded. Do not throw the sample in the water body before a satisfying sample has been collected! (Empty the grab into a bucket.)
- When the sediment core has been collected, it can be put in suitable containers and labelled. This is only relevant if the core can not be kept in the corer until arrival at the laboratory (or other "base" location). Be careful not to ruin the layering of the core during processing if this is of importance. Do not touch the sediments with bare hands; use disposable gloves.
- Grab samples may also be put in suitable containers dependant on the specific analyte to be determined.
- At least five samples should be sampled from each sampling site to get representative results.
- The sample containers should be filled entirely (save approximately one cm on top if the samples are to be frozen to allow for expansion).
- If there is unease in relation to potential contamination of the sediment samples/cores, sample material may be collected from the inner part of the cores (not in contact with the sampler material).

10.2 Analysis

Chemical analysis of the prepared samples should be done according to international standards such as prescribed by ISO/CEN. The EN (European standards) is legally prescribed for use by all EU nations. We therefore have proposed that ICP-Waters adopt ISO/CEN standard methods as a basis for the methods actually used for all chemical analysis. 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 method listed in *Table 24* is recommended for the work:

Table 24. List of ISO and CEN methods to be used for analysis and QA/QC procedures in the laboratory.

Component	ISO or CEN No	Name of standard
PAH	ISO 18287: 2006	Soil quality - Determination of polycyclic aromatic hydrocarbons (PAH) - Gas chromatographic method with mass spectrometric detection (GC-MS)
PCB	ISO 17858:2007	Water quality -- Determination of dioxin-like polychlorinated biphenyls -- Method using gas chromatography/mass spectrometry
Chlorobenzenes and PCB	ISO 6468:1996	Water quality -- Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes -- Gas chromatographic method after liquid-liquid extraction
Organochlorine pesticides and PCB	ISO 10382:2002	Soil quality -- Determination of organochlorine pesticides and polychlorinated biphenyls -- Gas-chromatographic method with electron capture detection

Information of the ISO/CEN methods listed above can be obtained from:

- The national standardisation agencies.
- ISO International Organisation for Standardisation, Case Postale 56, CH-1211 Genève, Switzerland. http://www.iso.org
- CEN European Committee for Standardisation, Rue de Stassart 36, B-1050 Brussels, Belgium. http://www.cen.eu

10.3 Quality assurance and quality control

Quality assurance and quality control are the responsibility of the National Focal Points. The Programme Centre will, however, to ensure data quality and correct technical transfer of data, do data quality control according to the following:

1. looking for outliers
2. looking for continuity in time series

Use of blanks, standards, (certified) reference materials and/or regular participation in laboratory intercomparison are strongly recommended.

10.4 Data Reporting

The analytical results are reported to the Programme Centre and stored in the ICP Waters database. The results should be reported in a special form prepared as an excel-file. The reporting forms are available at the ICP Waters homepage (http://www.icp-waters.no/)

10.5 References

EC 2008. Directive 2008/105/EC of the European Parliament and of the Council on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council.

EC 2010. Common Implementation Strategy for Water the Framework Directive (2000/60/EC): Guidance Document No. 25 on Chemical Monitoring of Sediment and Biota under the Water Framework Directive.

Fjeld, E., Le Gall, A.-C., & Skjelkvåle, B.L. 2005. Concentrations and levels of POPs from long-range transboundary air pollution in freshwater fish and sediments. *NIVA-report SNO 5107-2005, ICP Waters report 79/2005.*, 68.

Green, N.W., Dahl, I., Kringstad, A., og Schlabach, (2008). Joint Assessment and Monitoring Programme (JAMP). Overview of analytical methods 1981-2007. Norwegian Pollution Control Authority, Monitoring report no.1016/2008 TA no. 2370/2007. NIVA-rapport 5563-2008, 93 pp. ISBN number 978-82-577-5298-9.

OSPAR, 2002, JAMP [Joint Assessment and Monitoring Programme] Guidelines for Monitoring Contaminants in Sediments. OSPAR Commission, ref.no.2002-16. 48 pp.

11. Trace metals and persistent organic pollutants in fish

Many fish species are relatively long lived, which means they will bio-accumulate environmental pollution like trace metals and Persistent Organic Pollutants (POPs) to a much higher degree than e.g. the rather short-lived invertebrates. For some of the POPs, chemical analyses of water will not be able to track the compounds, while the bio-concentration, -accumulation and -magnification in biota enable us to identify these compounds. Proper ageing of fish is imperative, and only well trained experienced experts should be used. Pollution level in different organs will always be linked to age, as well as size (length and weight). However, the same fish species (same age, and size) can in two lakes with the same background pollution level of mercury (Hg), have different levels of Hg in their muscle. The difference is due to the biomagnification properties of Hg, with the piscivorous (fish eating) fish having the highest concentration. Only by linking individual fish to its trophic level by analyses of stable isotope ratios of nitrogen ($\delta^{15}N$) and carbon ($\delta\ ^{13}C$), can we determine whether it is a biotic or abiotic (physico, chemical pollution load) reason for the level of Hg, see Rognerud *et al.* 2002 and Rosseland *et al*. 2007. To be able to compare food chain related pollution between lakes, the $\delta^{15}N$ of the primary producers of the lakes has to be analysed for establishing the comparable baseline.

11.1 Determinants and species

11.1.1 Selection of fish species

The fish species are chosen on the basis of their bio-accumulative and bio-magnification properties, as those species which are known to accumulate high concentrations of contaminants are preferred. Ideally, one piscivorous (p) fish and one bottom-feeder (bf) should be sampled in rivers and lakes. Local adaptations should be considered, but some recommended target species for inland freshwaters in different animal geographic regions are shown in the table below:

Table 25.List of recommended target species in inland freshwaters in different animal geographic regions.

Northern Europe, incl. Russia, Nordic and Baltic countries	**Europe except Northern part**	**North America**
European Perch, (p) and (bf)	European Perch, (p) and (bf)	White bass, (p) and (bf)
Walleye, (p)	Common carp (bf)	Largemouth bass/Smallmouth bass/Black crappie/White crappie, (p) and (bf)
Pike, (p)	Common bream	Walleye, (p)
Perch, (p)	European catfish, Roach	Yellow perch, (p) and (bf)
Brown trout/Arctic charr/Rainbow trout (p) and (bf)	Brown trout/Arctic charr/Rainbow trout (p) and (bf)	Pike, (p)
		Pikeperch, (p)
		White sucker, (bf)
		Channel catfish/Flathead catfish, (p) and (bf)
		Lake trout/Rainbow trout (p) and (bf)

11.1.2 Trace metals

The agreed mandatory determinants for analysis of trace metals in biota/fish are the most important heavy metals expected with long-range transported air pollution:

Table 26. List of agreed mandatory determinants for analysis of trace metals in biota/fish

Organ	Determinand
Muscel	Mercury (Hg)
Kidney (or liver)	Lead (Pb) cadmium (Cd)

while optional determinants useful for interpretation of effects of long-range transported air pollution are:

Table 27. List of optional determinants useful for interpretation of effects of long-range transported air pollution

Organ	Determinand
Muscle	Stable isotopes of nitrogen (N) and carbon (C) ($^{15}N/^{14}N = \delta YN$ & $^{13}C/^{12}C = \delta\ ^{13}C$)
Gill tissue:	aluminium (Al) iron (Fe) copper (Cu) zink (Zn) cadmium (Cd) ead (Pb) chromium (Cr) nickel (Ni) manganese (Mn) selenium (Se)
Kidney	arsenic (As) and selenium (Se) in

11.1.3 Persistent Organic Pollutants (POPs)

The agreed mandatory determinants for analysis of POPs in biota/fish are:

Table 28. List of agreed *mandatory determinants for analysis of POPs in biota/fish*

Sum Polychlorinated biphenyls (PCBs)
Dichlorodiphenyltrichloroethans (DDTs)
Hexachlorobenzene (HCB),
Hexachlorocyclohexanes (HCHs)

while optional determinants are:

Table 29. List of optional determinants for analysis of POPs in biota/fish

PCB congeners
Polycyclic Aromatic Hydrocarbons (PAH) in bile
Brominated flame retardents (PBDE)
Heptachlor epoxide (HCE) in liver or muscle.

11.2 Sampling techniques

Fish for analysis of trace metals and POPs should be sampled by either rod, traps or gillnets. A detailed description of fishing by multi-mesh gill nets in lakes and electro-fishing in running waters is given in part 3.4 of the ICP Waters Manual (Acidification – Monitoring and assessment of Fish), mainly following the EMERGE –Manual (Rosseland et al. 2001).

Personnel must wear clean gloves when the samples are taken from the gill net. The samples should be transferred to the laboratory as quickly as possible and rinsed with clean freshwater to remove any material adhering to the surface. If this is not possible, the fish must be frozen immediately after sampling.

For a satisfactory statistical significance of the results, at least 25 fish of different lengths should be collected.

11.3 Sampling timing

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.

11.4 Organ containers

The organs for POPs determination must not be stored in plastic containers, but in glass containers with aluminium sealing under the cap. Organs for metal determination may be stored in both plastic and glass containers.

Aluminium foil may be used to pack the organ sample into; the package can be put in plastic bags. The aluminium foil must be pre-cleaned (this implies burning in the case of organs for POPs determination).

Pre-cleaning:

The glass/PTFE containers (preferably brown) for organs meant for POPs determination should be cleaned with inorganic, alkaline soap in distilled water, rinsed with tap water, distilled water, MilliQ water and the extraction agent used during the analyses (or acetone/methanol). Then the glass containers and aluminium foil should be incinerated at approximately 500°C for two hours for removal of potential organic material.

The containers for organs meant for metal determination should have been thoroughly cleaned with nitric acid solution. Containers should be filled to the top with the nitric acid solution (pro analysi, approximately 5% v/v) and left filled for minimum 24 hours. The containers may additionally be soaked in acid solution so that the outside is cleaned (important for new containers and containers already used for potential metal contaminated material).

11.5 Preparation of fish samples for analysis

Before dissection, label all sample containers with a unique code for the fish and name the organ which will be placed inside. The dissection procedure is based on NIVA procedure and modified procedure by Rosseland et al. 2001.

The samples (fish) are to be sampled alive and frozen (-20°C) if not analysed immediately (do not cut the throat if stored). Analyses should be performed as fast as practically feasible. (Only fish in good condition should be sampled).

Procedure for the dissection of fish:

The procedure applies fresh fish. Frozen fish must partly defrost prior to dissection. Disposable gloves must be worn throughout the procedure. Do not let the fish touch any other material than mentioned below (as well as the clean table top).

Before starting the dissection procedure, the participant has prepared clean dissection instruments, a work bench with Al-foil protection (glossy side up), pre-marked vials for the different organs, and schemes and "scale envelope" for notification of specimen and analysis data. **Never touch by hand any organ to be sampled! Use tweezers! All samples must be marked carefully with a specific code identifying fish number, lake, sample type, date etc. Each "lake" and individual fish is given their unique code. The marking must be performed with dedicated pens etc. to provide permanent marks (i.e. "Cryo-pens" for liquid N_2 etc.).**

1. **Blood sampling.** After the kill of a fish by a blow on the head, place fish on its right side, head towards left, and sample blood from the ventral aspect of the tail (caudal vein) with a heparinised syringe (when using I-Stat, heparin is not necessary, *Figure 14*). Point needle to hit straight under the vertebra before sucking (*Figure 15*). Analyse the blood by **I-Stat** (by ABBOT) for plasma ions, blood gasses and acid/base parameters.

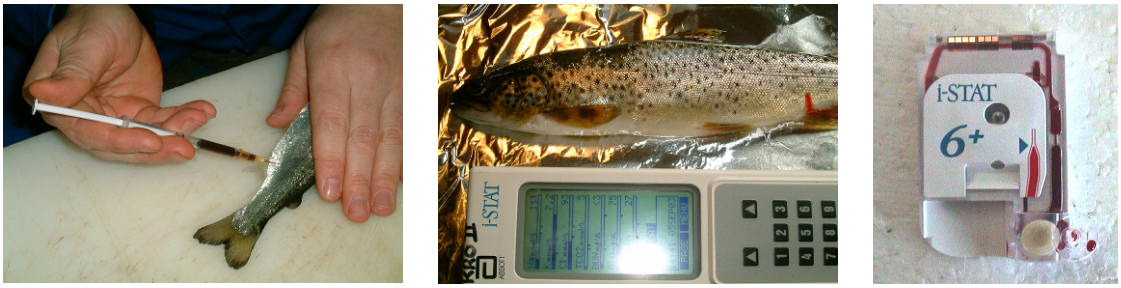


Figure 14. Blood sampling from caudal vein (left). I-STAT used for blood analyses (middle and right).

Figure 15. The needle is inserted half way between the anal fin and the sideline, and pointed to hit the blood vessels directly under the spine.

2. **Measure weight and length** (from the nose to the end of the tail), and sample **scales** from the area above the lateral line, between the dorsal and adipose fin (*Figure 16*). Note data on both scheme and envelope. Store scales in the envelope.

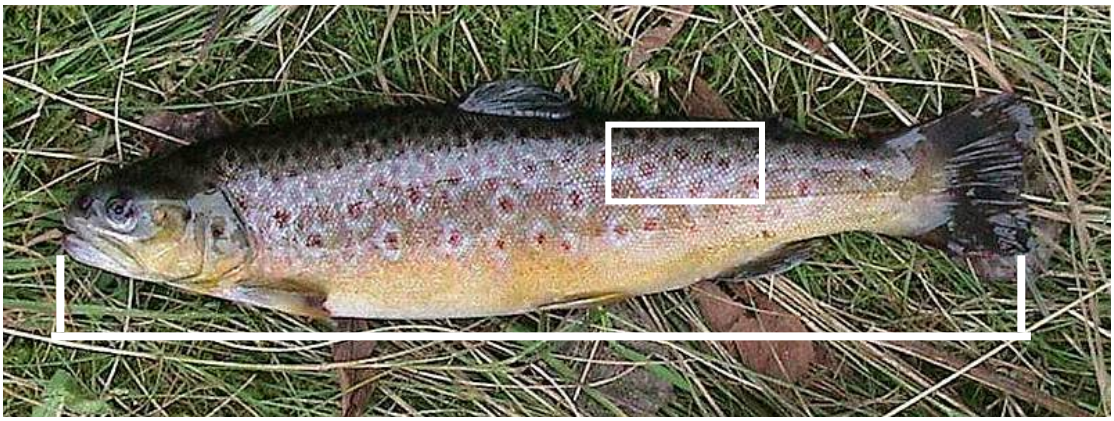


Figure 16. Length measurements and area for scale sampling.

3. **Metal analyses of gills** by excise the 2rd gill arch on the right side of the fish (*Figure 17*) and put it in a small plastic vial (pre-numbered for weight calibration) for metal analysis. Use tweezers.

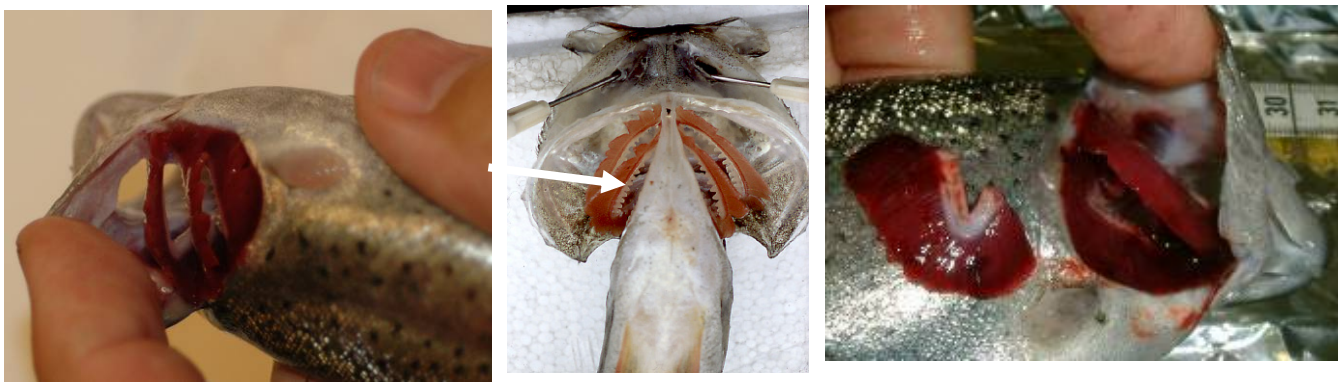


Figure 17. Gill arches seen from the bucal side (left and centre). 2nd gill arch on the right side is indicated.

4. **Open the abdomen**: Cut the abdominal wall to open for dissection of inner organs (Fig. 5 left), and lay the fish on its right side with head to left. Lay the abdominal wall tissue with scales down, and use as storage protection of other organs (*Figure 18* right and *Figure 22*). **N**ote the flesh colour (red, pink, white), sex, maturation stage (I-VII, see *Figure 19*and *Figure 20*) and stomach filling (0-5, 0= empty, 1 = only food remains in the end of the intestine, 5 = full)

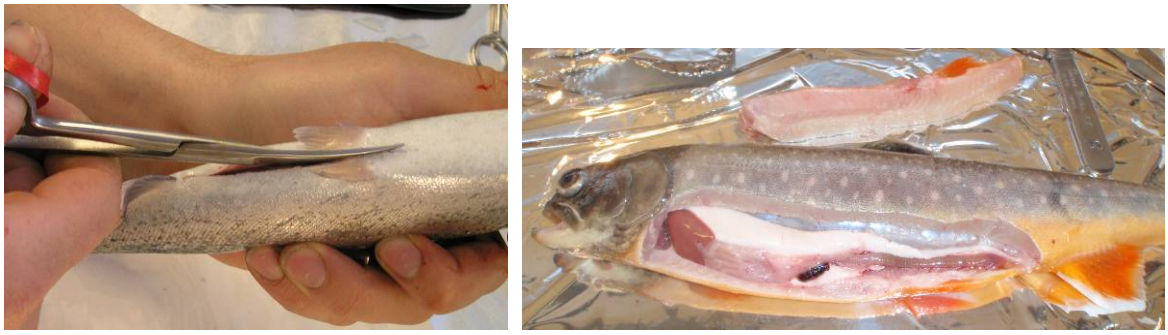
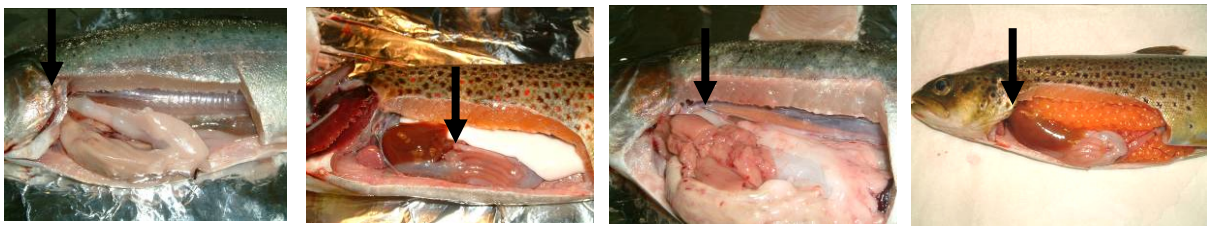


Figure 18. Opening of the abdomen.



Male I | Male IV-V | Female I-II | Female IV-V

Figure 19. Opened abdomen, showing males stage I and IV-V, and female stage I and IV-V.

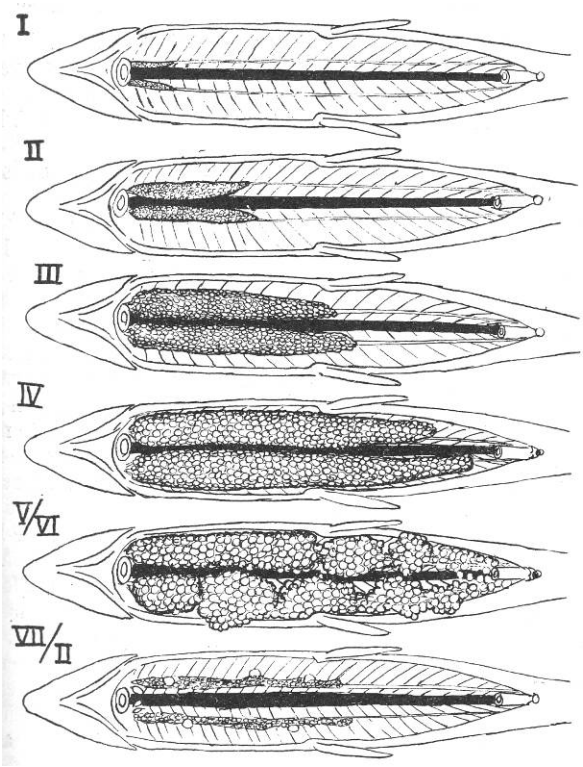


Figure 20. Gonadal development in female salmonidae. After: Sømme, J. (1941). Ørretboka, page 223.

5. **Bile bladder.** Dissect the bile bladder from the liver (*Figure 21*) and transfer the whole bladder to proper vial. Alternatively, use a syringe with a needle to suck out the bile and transfer to vial.

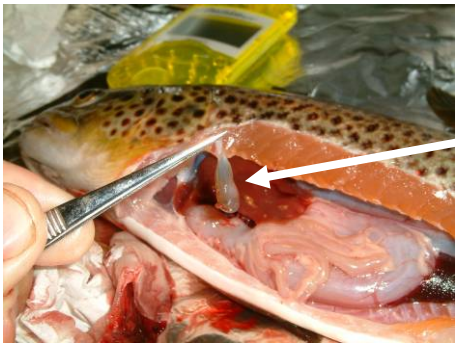


Figure 21. Dissection of bile bladder.

6. **Liver.** Cut 3 pieces of about 100 mg from the distal lobe (see square in *Figure 22* left); one for histology (vial with formalin), and two for oxidative stress parameters and enzyme activity studies (vials for freezing in liquid N_2). **NB! Make a small hole in the cap before placing vial in liquid nitrogen (*Figure 22* down right)!**
   - Free the whole liver and put it onto the abdominal wall (*Figure 22* right). Divide in two, and wrap the pieces thoroughly in Al-foil:
     - one piece for heavy metal (for freezing).
     - one piece (need to be more than 0.5 g) for POP and PAH analysis
   - Place Al-foil wrapped samples in plastic zip bags, and mark the bags (*Figure 23*).

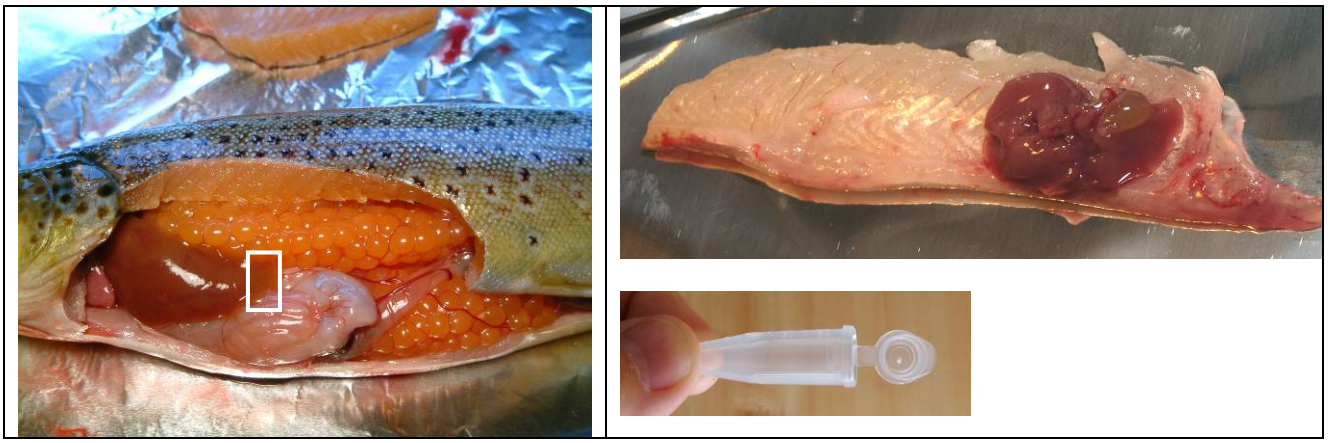


Figure 22. Small pieces of the liver are cut from the distal part of the liver, see square on Figure (left). Place the liver after dissection onto the stomach wall (Figure right). Make a hole in the cap of vial before placing in liquid nitrogen.

Figure 23. Tissue samples (muscle for POPs, Isotopes and Hg, kidney and liver) wrapped in Al-foil and placed in plastic zip bags. Both Al-foil and plastic bag must be marked with Fish code and type of sample.

7. **Stomach.** Remove the stomach of the fish and keep it at a cool place for further dissection (continues as stage 12).

8. **Kidney.** Remove the swim bladder, and with the scalpel, cut along the edges of the kidney and free tissue from lining (*Figure 24*). The whole kidney is then removed from the fish an wrapped in Al-foil and placed in plastic zip bag (*Figure 23*) and frozen.

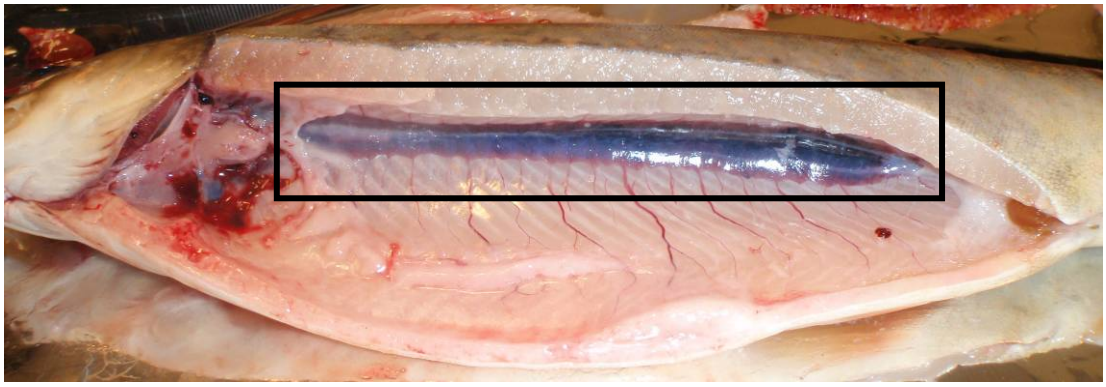


Figure 24. Kidney

9. **Muscle sample.** After cutting to expose axial muscle from the area above the lateral line and between the dorsal and adipose fin (*Figure 25*), tear off the dorsal skin on left side of the fish. Remove the "red muscle" (a bit darker superficial muscle layer) along the lateral line by scraping with a scalpel. If the fish is small, use muscle on both sides, but assure that the same "areas are used for metals and POPs (*Figure 25*).
   - Take about 5 g of muscle (*Figure 25* marked a) and wrap into Al-foil for mercury (mark: "Hg").
   - Take about 1 g of muscle (*Figure 25*marked b) for stable isotope analyses, and wrap into Al-foil and mark: "Isotopes"
   - Collect about 15-20g of muscle (*Figure 25* marked c), and wrap in Al-foil and mark: "POPs".

All tissue samples are then placed individually into plastic zip bags and frozen (see *Figure 23*).

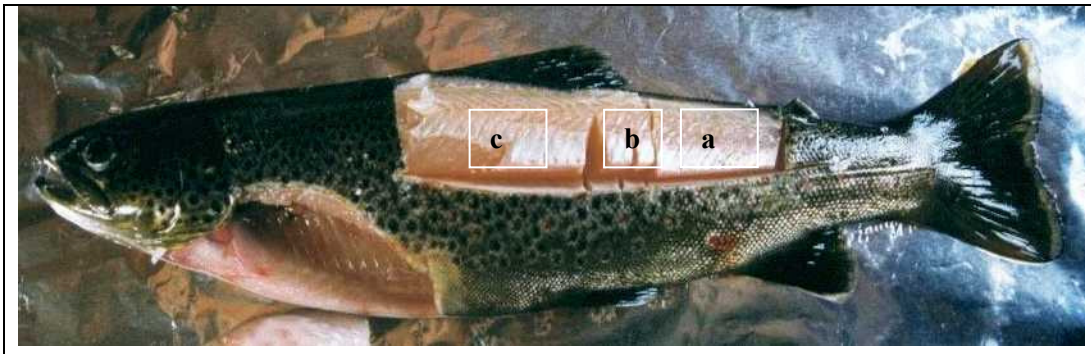
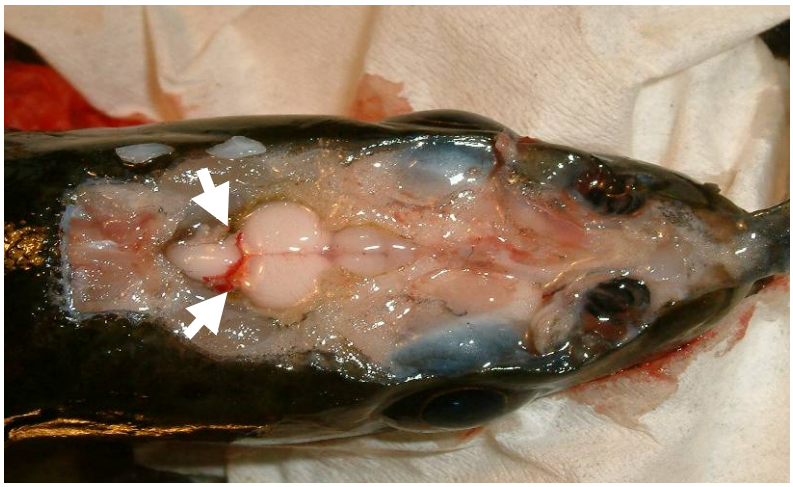


Figure 25. Muscle samples for mercury (a), stable isotopes of N and C (b), and POPs (c).

10. Eye. For analyses of UV-effects or cataract, take out the lens of the eye (*Figure 26*). Wrap in Al-foil and freeze in N_2.

Figure 26. Dissection of eye to remove lens.

11. Otoliths: Open the roof of the head in order to see the brain (*Figure 27*). Collect the two otoliths and put them into the paper envelop together with the scales.



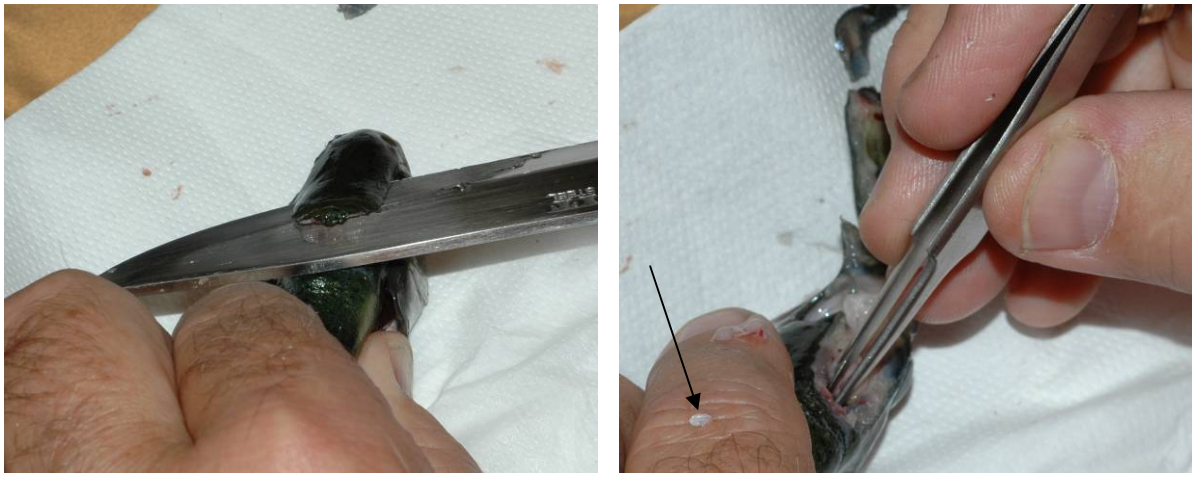


Figure 27. Sampling otoliths. Use tweezers directed vertical at arrow points.

12. **Continue with the fish stomach:** Open the stomach and collect the food items which are not yet digested. If needed, divide the stomach content into 3 parts (*Figure 28*):
    - Put the first 1/3 of the stomach content into a white scintilation tube wit screw cap and freeze for metals and isotope analysis (baseline data).
    - Put the 2nd part for species analyses, into a glass container filled with 70% alcohol and put a piece of paper with the fish number **written with pencil**.
    - The 3rd part goes into a glass container for organic analyses.

If no chemical analyses of the stomach content are planned for the investigation, follow the 2nd stage and place the whole stomach content in a vial with alcohol.

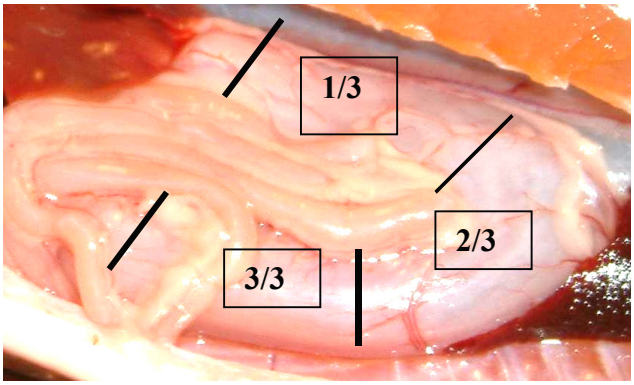


Figure 28. Fish stomach, with suggestion for dividing into three parts to separate content for different analytical purposes (see text).

13. **One fish is finished:**
    - store well marked samples
    - clean dissection instruments,
    - change scalpel blade
    - mark new vials
    - start over again using the next fish

11.6 Conservation and storage:

Biological samples must be frozen if stored (< -20^{o}C, dark).

11.7 Analysis

Chemical analysis of the prepared samples should be done according to international standards such as prescribed by ISO/CEN. The EN (European standards) is legally prescribed for use by all EU nations. We therefore have proposed that ICPWaters adopt ISO/CEN standard methods as a basis for the methods used for all chemical analysis. These methods usually have 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 methods listed in *Table 30* are recommended for the work:

Table 30. List of ISO and CEN methods to be used for analysis and QA/QC procedures in the laboratory.

Component	ISO or CEN No	Name of standard
PAH	ISO 18287: 2006	Soil quality - Determination of polycyclic aromatic hydrocarbons (PAH) - Gas chromatographic method with mass spectrometric detection (GC-MS)
PCB	ISO 17858:2007	Water quality -- Determination of dioxin-like polychlorinated biphenyls -- Method using gas chromatography/mass spectrometry
Chlorobenzenes and PCB	ISO 6468:1996	Water quality -- Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes -- Gas chromatographic method after liquid-liquid extraction
Organochlorine pesticides and PCB	ISO 10382:2002	Soil quality -- Determination of organochlorine pesticides and polychlorinated biphenyls -- Gas-chromatographic method with electron capture detection

Information of the ISO/CEN methods listed above can be obtained from:

- The national standardisation agencies.
- ISO International Organisation for Standardisation, Case Postale 56, CH-1211 Genève, Switzerland. http://www.iso.org
- CEN European Committee for Standardisation, Rue de Stassart 36, B-1050 Brussels, Belgium. http://www.cen.eu

11.8 Quality assurance and quality control

Concerning the gill net sampling as well as the electro-fishing and sampling of organs, it is essential that the persons doing the work are well experienced. In the EMERGE project (http://www.mountain-lakes.org/emerge/), each national person responsible for the fish sampling programme had to be "certified" by going through a training workshop for sampling of organs. To reach the goals of the monitoring, the test fishings 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 Raitaniemi *et al*, 1998).

For quality assurance and quality control throughout the chemical analysis, use of blanks, standards, (certified) reference materials and/or regular participation in laboratory intercomparison are strongly recommended.

11.9 Data Reporting

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, TOC, calcium, aluminium (species)). The fish data should include the list of existing fish species, tables showing species specific catch per unit effort (CPUE) in numbers and biomass, length frequency distribution and sex composition combined with the age distributions and back calculated growth of the age groups as well as data on pollution load in different organs linked to age, size (length and weight) and the link to the trophic level (place in the food chain), se Rognerud *et al.* 2002 and Rosseland *et al*. 2007. Data from different sites in a lake can be pooled together, while in the data from running waters, spawning grounds must be kept separately.

Reporting forms are available at the ICP Waters homepage (http://www.icp-waters.no/)

11.10 References

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12. Quality assurance

The general objective of a cooperative international programme to monitor the effects of deposition of long-range transported air pollutants 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.

12.1 Water chemistry

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:

- 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).
- Documented evidence of analytical performance, accuracy of in-house standards, within-run precision, between-run controls and accuracy of the methods employed;
- Evidence of sample specific data quality such as an adequate ionic balance or specific conductance determination for individual samples;
- 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 multi-laboratory 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 (i.e. total error) 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 inter-laboratory 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.

Data Reporting – Water chemistry
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 co-operative 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 programmes for data accuracy will for example include computation of the sum anions vs. cations and theoretical conductivity vs. measured conductivity. (See also chapter 3. 6 and the reporting form for these calculations of data accuracy.)

Suggested target accuracy's (P %) and detection limits (L) for the measurement of water quality determinants are shown in *Table 31*. The targeted accuracy should be given for a coverage factor of 2 (i.e. the combined standard measurement uncertainty is multiplied with 2 to obtain an expanded measurement uncertainty). This corresponds to a confidence level of 95%, and is given in table 27.

Table 31. Suggested target accuracy's (P %) and detection limits (L) for the measurement of water quality determinant

Determinant	Detection limit (L)	P (%)
Calcium	0.02 mg/l	20
Magnesium	0.01 mg/l	20
Sodium	0.02 mg/l	20
Potassium	0.02 mg/l	20
Chloride	0.2 mg/l	20
Sulphate, (as SO4)	0.2 mg/l	20
Nitrate (+ Nitrite)1), (as N)	10 µg/l	20
Reactive Aluminium	10 µg/l	20
Non-labile (organic) Aluminium	10 µg/l	20
Labile (inorganic) Aluminium	10 µg/l	20
Dissolved Organic Carbon2) ,(as C)	0.2 mg/l	20
Conductivity	0.02 mS/m	10
Alkalinity	0.005 mmol/l	20
Total Phosphorus, (as P)	2 µg/l	20
Soluble Reactive Phosphate, (as P)	2 µg/l	20
pH		0.2 pH units
Temperature		±0.2°C

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

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.

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 chapter 3.5 and 3.6.

12.2 Invertebrates

Between-laboratory quality control (Quality assessment)
To evaluate the quality of the taxonomic work on biological material delivered to the Programme centre, annual biological intercalibrations are carried out. The quality can influence on the evaluation of the samples, which is based on the species and their tolerance (Raddum *et al.* 1988, Fjellheim and Raddum 1990, Raddum 1999). Control is therefore important for evaluation of the significance of trends in biotic indexes both for a specific site/watershed, as well as for comparisons of trends between different regions and countries. The material may also be used for multivariate statistical analysis (Larsen *et al.* 1996, Skjelkvåle *et al.* 2000, Halvorsen *et al.* 2002).

The results of this type of data treatment are especially sensitive to the quality of the species identification. The biological intercalibration focuses on the taxonomic skills of the participants, and is a tool for improving the quality of work at the different laboratories as well as harmonisation of the biological database.

The methods for intercalibration of biological material were outlined in 1991 at the 7th ICP Waters Task Force meeting in Galway, Ireland. The different countries/laboratories have to know, first of all, their home fauna. Since the fauna in different geographical regions vary, it is necessary to prepare specific samples for each participating laboratory, based on their home fauna. It is a problem for the exercise of the intercalibration that it is not possible to use standardised samples for all participants. To solve this problem each laboratory sends samples of invertebrates from their own monitoring sites to the Programme centre. The Programme centre may additionally add species known to be present in the region of the specific laboratory. Based on this, each laboratory receives individual test samples composed of species representing their own monitoring region.

Data Reporting - Invertebrates
The Programme centre, as responsible for the intercalibration, calculates a quality assurance index for the participants, see Raddum (2005). This index evaluates the skill of identifying the species as well as the genus. It also takes into account the effort of identifying all specimens in the sample. The results are described in separate reports.

12.3 References

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13. Data handling and delivery

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.

13.1 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 monitoring 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 is given at the ICP Waters homepage (http://www.icp-waters.no/.)

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 co-operatively, 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.

Reports and publications from the ICP-Waters Programme

All reports from the ICP Waters programme from 1987 up to present are listed below. All reports are available from the Programme Centre. Reports and recent publications are also accessible through the ICP-Waters website; http://www.icp-waters.no/

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