Manual for Integrated Monitoring

CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION OF THE UNECE INTERNATIONAL COOPERATIVE PROGRAMME ON INTEGRATED MONITORING OF AIR POLLUTION EFFECTS ON ECOSYSTEMS

PUBLISHED BY THE ICP IM PROGRAMME CENTRE

Texts: Manual Revision group and Editorial group

Original version August 1998, updates in 2001, 2003 and 2004.
Changes in reporting of biological data (subprogrammes: VG, VS) in 2010.
Transferred to new webpages (SYKE) in 2013.
This PDF version is compiled from the content on SYKE website and is published by the ICP IM Programme Centre at the Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences (SLU) in 2022.

Please refer to the manual as shown below:

International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (2022). Manual for Integrated Monitoring. Edition 7. The Swedish University of Agricultural Sciences.

Please refer to individual chapters as shown below:

Name of chapter (Chapter 1). In: International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (2022). Manual for Integrated Monitoring. Edition 7. The Swedish University of Agricultural Sciences.

Note on additional files

All example files, code lists and other documents referred to in the text are linked to downloadable copies. Example files are also attached to this PDF document (Adobe Acrobat is required to access these).

SLU

wge Working Group on Effects of the Convention on Long-range Transboundary Air Pollution

Clean Air 40 YEARS

Contents

Preface

This manual replaces the 'Manual for Integrated Monitoring - Programme Phase 1993-1996' (Helsinki 1993), by which the UNECE ICP Integrated Monitoring was guided. At the Programme Task Force meeting in Vienna, Austria, 27-29 March 1996, it was decided to update the former manual and two working groups were established to update the relevant subprogrammes. The members of these groups: Elke Bieber (Germany), Sven Bråkenhielm (Sweden), Martin Forsius (Finland), Sergei Gromov (Russian Federation), Ramon Guardans (Spain), John Innes (Switzerland), Ales Pacl (Czech Republic), Michael Starr (Finland), Serguei Semenov (Russian Federation), Kjetil Tørseth (Norway) and Dick de Zwart (Netherlands), have carried the main responsibility for the revision work. The first version of the manual was been finalised by the IM Programme Centre with the assistance of the editorial group: Sven Bråkenhielm, John Innes and Michael Starr. Also a number of National Focal Points and individual scientists have contributed to the work.

The subprogrammes of this manual have as far as possible been harmonised with comparable activities of the other programmes under the UNECE LRTAP Convention (mainly ICP Forests, ICP Waters and EMEP). The manual also contains the first versions of a new (optional) subprogramme 'Toxicity Assessment (TA)', as well as an overview on the monitoring of persistent organic pollutants (POPs) and heavy metals. Moreover, it defines the different programme levels in a general framework of causes and effects.

This manual was accepted at the IM Task Force meeting in Tallinn, April 20-22, 1998, with minor changes incorporated by the editorial group and the IM Programme Centre. Some small corrections and updates have been included by the Programme Centre in 2001, 2003 and 2004. Changes in reporting of biological data (subprogrammes: VG, VS) were incorporated in 2010. The ICP Forests method of measuring epiphytic lichens (subprogramme: EP) was added to the manual in 2021

In 2013, a new edition was published on-line as web pages at syke.fi. In 2022, all webpages were compiled to the current pdf version, available at the IM web site at SLU.

1 Purpose of the Programme and Approaches to Monitoring

1.1 Aims of the programme

The overall aim of integrated monitoring was originally to determine and predict the state and change of terrestrial and freshwater ecosystems in a long-term perspective with respect to the impact of air pollutants, especially nitrogen and sulphur. This was to provide one basis for decisions on emission controls and assessment of the ecological impact of such controls within the UNECE Convention on Long-Range Transboundary Air Pollution. However, the full implementation of the Integrated Monitoring Programme will allow the ecological effects of tropospheric ozone, heavy metals, and persistent organic substances to be determined. Implementation of the Programme will

provide a major contribution to the international data requirements for examining the ecosystem impacts of climatic change, changes in biodiversity and depletion of stratospheric ozone. A primary concern is the provision of scientific and statistically reliable data that can be used in modelling and decision making. The main emphasis is to establish consistent time series for environmental variables rather than establishing representative surveys across the UNECE region.

The aims are fulfilled by:

- monitoring both biogeochemical trends and biological responses in small (10 - 1000 ha) hydrologically defined areas
- seeking to separate the noise of natural variation, including succession, from the signal of anthropogenic disturbance by monitoring natural or semi-natural ecosystems
- developing and applying tools, e.g. models, for regional assessment and prediction of long-term effects.

Implementation of the IM Programme by individual countries will fulfil many of the obligations of those countries to undertake impacts studies not only under the Convention on Long-Range Transboundary Air Pollution, but also under the Framework Convention on Climate Change, the Convention on Biological Diversity, and the EU National Emission Ceiling Directive.

1.2 The ecosystem monitoring concept

Integrated monitoring of ecosystems means physical, chemical, and biological measurements over time of different ecosystem compartments simultaneously at the same location. In practice, monitoring is divided into a number of compartmental subprogrammes which are linked by use of the same parameters (cross-media flux approach) and/or the same/close stations (cause-effect approach). The quantification of these fluxes and pools, and monitoring the speed of changes in them, are essential for the development of any effects based environmental policies (e.g. Johnson and Lindberg 1992, Moldan and Cerny 1994).

A small catchment (or other hydrologically well-defined area), such as an IM site, is large enough to encompass all the interacting components: atmosphere and vegetation, plants and soils, bedrock and groundwater, brook or lake, and surrounding land. A small catchment comprises a terrestrial ecosystem usually with a linked aquatic ecosystem of an adjacent brook. Some basins contain one or more ponds or lakes. A terrestrial ecosystem is conventionally viewed as an assemblage of living organisms interacting in a complex way with one another and with their environment, air, soil, and water (Moldan and Cerny 1994). A conceptual scheme of a small catchment ecosystem is given in Figure 1.1.

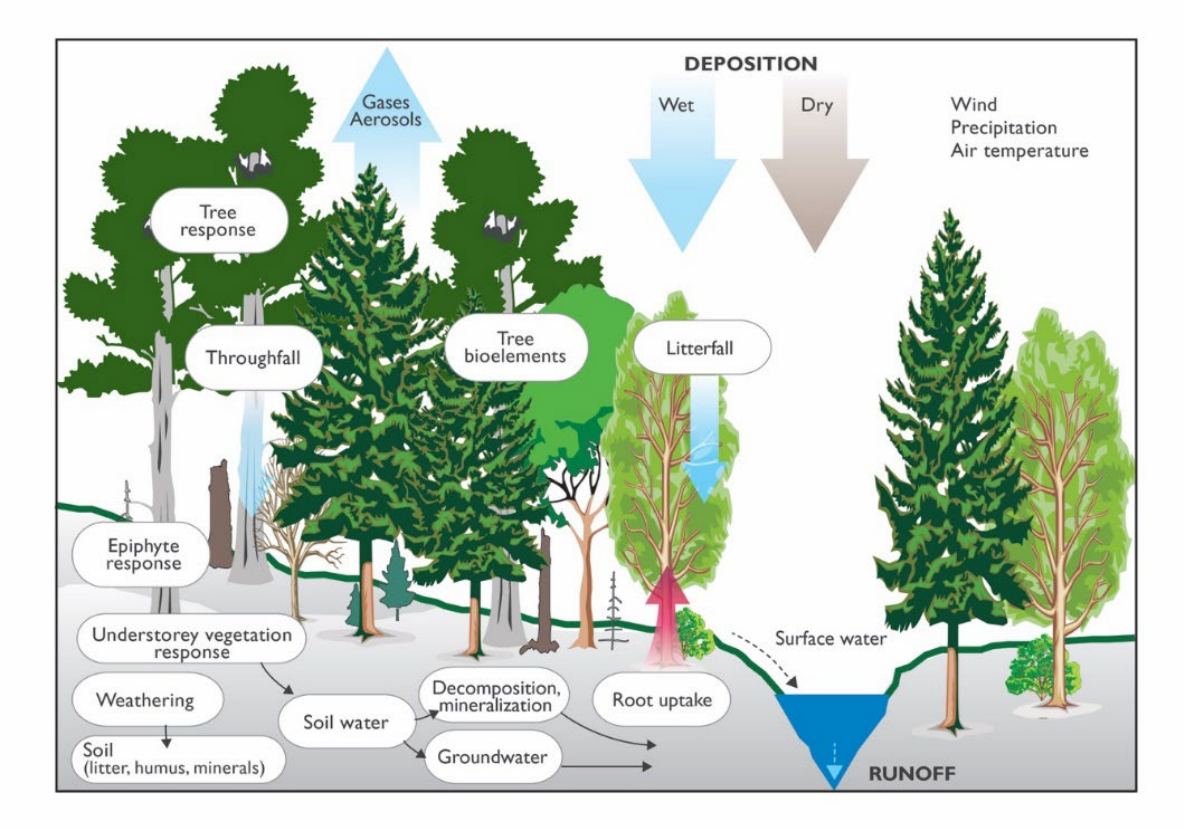


FIGURE 1.1 A CONCEPTUAL SCHEME OF A SMALL CATCHMENT ECOSYSTEM SHOWING MAIN COMPONENTS (POOLS) AND PROCESSES (FLUXES) WHICH ARE THE OBJECTS OF INTEGRATED MONITORING

Regional development of policy to regulate emission of anthropogenic pollutants (e.g. through development of critical loads) requires evaluation and assessment of environmental monitoring data (Figure 1.2). Assessment leading to policy definition is linked back to monitoring through the development and application of ecosystem models. The ICP IM falls within the monitoring component of this overall framework, and the following discussion will focus on its specific position and role.

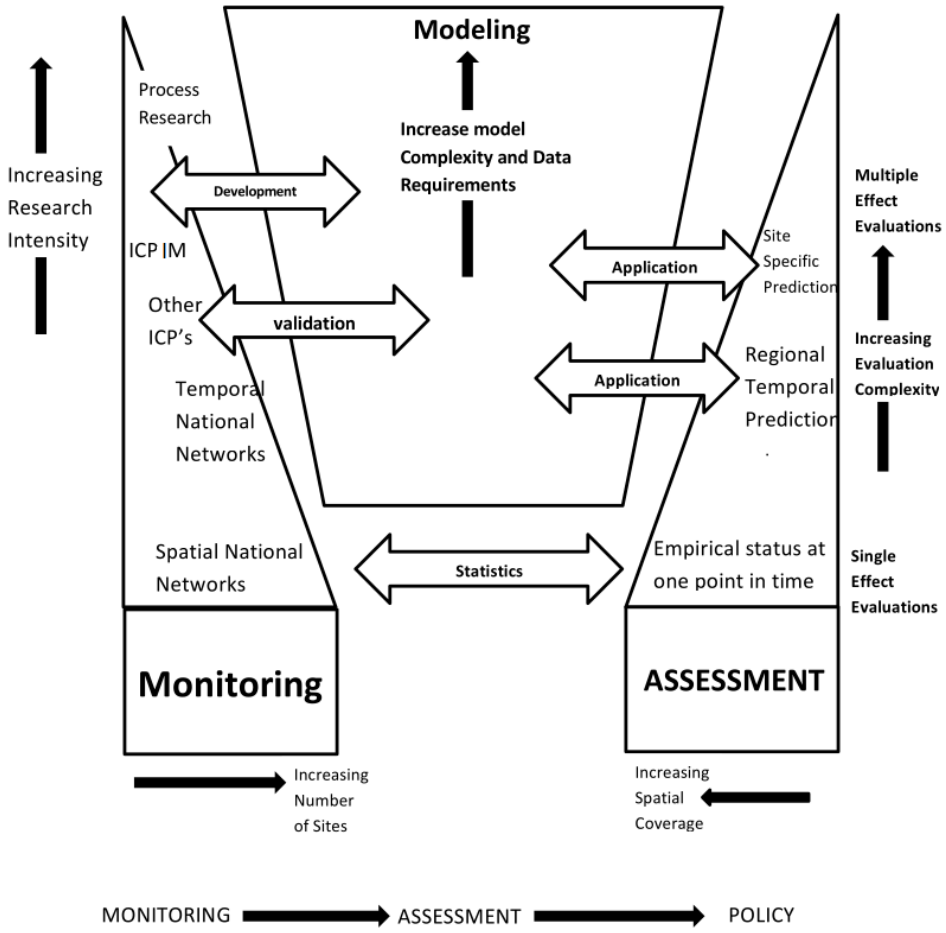


FIGURE 1.2 CONCEPTUAL MODEL OF THE MEANS BY WHICH RATIONAL ENVIRONMENTAL POLICY IS DEVELOPED THROUGH A SEQUENCE OF MONITORING AND ASSESSMENT. THE ICP IM PROGRAMME'S POSITION IN THE HIERARCHY OF MONITORING PROGRAMMES IS INDICATED.

A national or international monitoring programme to evaluate the environmental effects of any anthropogenic perturbation (e.g. acidic deposition, toxic contaminants, climate change etc.) is best organised in an integrated, hierarchical manner (represented by the left pyramid in Figure 1.2). At the apex of the pyramid is a small number of intensively monitored process research sites. Here sufficient information is collected so that time-dependent models may be developed to predict future changes in the state of the ecosystem. The changes may occur in response to increased or decreased pollutant inputs. Many ECE countries operate a small number (1-10) of such sites.

Beneath the apex regional monitoring networks are indicated which use progressively less frequent sampling at progressively more sites. The base of the monitoring pyramid is composed of national 'surveys' in which sampling may occur as infrequently as once or twice per decade. The number of hierarchical levels presented in Figure 1.2 is probably a minimum for effective ecosystem monitoring on an international scale.

Within the hierarchy, the ICP IM falls somewhat below the pyramid apex, and represents a source of information for comparison of complex and multiple effects across climatic gradients as well as geological, ecozone, and political boundaries. Much of the data reported to the international level

are time averaged (e.g. monthly volume-weighted runoff concentrations). They are very useful for validating models and testing 'universality'. Once confidence in model performance has been obtained, application to lower hierarchical levels produces regional assessment, involving either temporal or scenario-based production. Hence, multiple hierarchical levels of monitoring are necessary in order to supply the information needed for the model development - validation - application process. The IM presents the highest level having international co-operation and therefore, it is in an excellent position to respond to the needs of international policy makers. On its own, however, the ICP IM cannot supply policy related information (e.g. critical loads); for political decisions we also depend on the simultaneous existence of lower hierarchies indicating the regional variation.

Two other features of the monitoring hierarchy should be noted. First, there should be some overlap between hierarchies to ensure data and model transferability among levels. Some ECE countries maintain one or more monitoring sites that contribute not only to process research but also to the ICP IM and other ICP programmes. This is wise. Such sites are the primary source of 'ground truth' for validating and/or modifying ecosystem assessment models. Furthermore, it helps to maximise the scientific return obtained from the large resource expenditure required to operate such sites. Second, there is an inherent assumption of the continuing existence of all levels of the hierarchy. Piecemeal, intermittent, and short-term monitoring does not provide the information on temporal or spatial variations required to distinguish natural from anthropogenically induced effects. Arbitrary discontinuation of any given monitoring hierarchy may lead to collapse of the framework and an inability to effectively perform environmental assessment on either the national or international scales.

1.3 Mass balance performances

One of the central IM approaches is to monitor the mass balance of major chemical components within the site. Fundamental to this is the hydrological balance, which can be described as:

$P - E = R \pm \Delta S$

where, P = Precipitation, E = Evapotranspiration, R = Runoff and ΔS = Change in storage

The approach consists of an open-system analysis of external fluxes (Figure 1.3). The aim is to quantify fluxes and to monitor their rate over time. Simple mass balances can further be broken down into more complex ones for studying dose-response relationships (Figure 1.3).

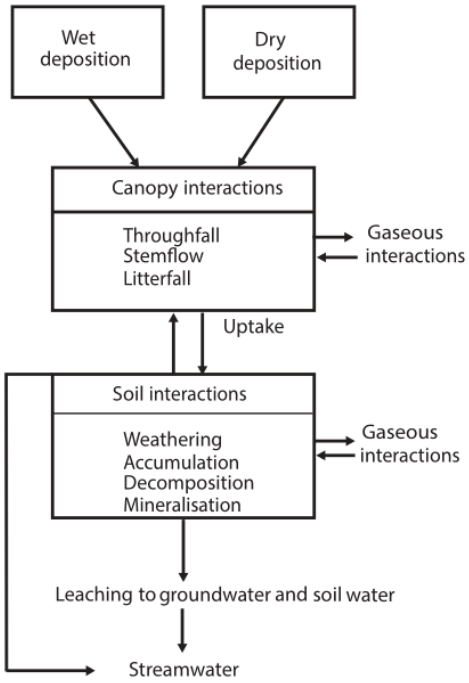


FIGURE 1. 3. FLOWS OF SUBSTANCES WITHIN A FOREST ECOSYSTEM. MODELS OF DIFFERENT COMPLEXITY CAN BE USED FOR DESCRIBING THE ECOSYSTEM MASS BALANCE.

1.4 Model applications

Prediction of the future response of ecosystems to changes in pollutant loading and environmental conditions is necessary from both a scientific and political viewpoint. These predictions provide the only basis for the formulation and quantification of remedial measures. In this respect, mathematical simulation models which are capable of predicting system response under future pollution deposition scenarios represent our best tools. These models must be capable of describing the physical, chemical, and biological relationships observed in ecosystems. The degree of damage to an ecosystem can then be estimated provided the models are based upon dose - response principles. Since the output from a model is only as good as the input data used to drive it, a comprehensive monitoring programme to identify the system function and provide adequate data for model calibration is essential.

Three well-known dynamic biogeochemical models (MAGIC, SAFE, SMART) have already been applied to selected IM sites (see: ICP IM Annual Report 1996, Forsius et al, 1998 a and b, Jenkins et al 2003). The advantage of applying the same model to many sites is that a consistent approach can be utilised, and sensible comparisons can be made. Once established, a model covering many sites can be used to evaluate emission control strategies, and long-term changes in policy, and used to investigate trends in the data. This is one of the most powerful ways of using ICP IM data for supporting work under the LRTAP Convention, and this topic should be given high priority also in the future. This requires a continuous effort to improve the data collection and reporting procedures in the IM Programme.

The widespread coverage of sites in the ICP IM is ideally designed for the application of models rather than model development. This is supported by the benefits of the central database allowing commonality of approach to data manipulation and aggregation for model calibration. Model development requires specific design of sampling and experimentation, and the task is better left to more process-oriented research programmes. The strength of the ICP IM modelling effort lies in scenario assessment through widespread site applications and the development of technologies for linking models for integrated assessment of environmental change utilising the integrated data sets available.

Currently available models generally focus on one aspect of an ecosystem, notably atmospheric deposition, soil/soil solution chemistry or biology. Biological models, on the other hand, require further development to achieve the mechanistic level of the hydrochemical and deposition models. Nevertheless, these models, when linked to predictions from hydrochemical models, provide useful prognoses of future behaviour of, e.g. long-term plant and vegetation response to changes in pollutant deposition.

There is some way to go in model development before ozone and heavy metals are incorporated as driving variables into ecosystem models, and even the role of nitrogen is not yet fully understood. These developments must take place outside the ICP IM. As new models are developed, however, they could be widely applied within the ICP IM framework, as could all suitable existing models. The ICP IM provides a unique database for validation and testing of such models, presuming complete data sets from the participating countries.

1.5 Bioindication

It is important to recognise biological indications of environmental stress because they are integrated responses to ecosystem change. Monitoring of biological variables makes it also possible to detect the cause-effect relationships within the ecosystem. One distinct advantage of the ICP IM is the possibility to integrate biological variables reliably to a wide selection of physico-chemical variables which are measured simultaneously. This is necessary if one tries to couple biological data in ecosystem modelling.

As the evaluation report (1992) of the pilot IM programme states, forest growth and nutritional status are the most important variables from the modelling point of view. In addition to these, a collection of a number of self-indicating biological variables is also recommended. Thus in the programme, a number of biological data are included which are not directly used in the models but can be used as indicators of changes.

There are also biological indices that may suit to the framework of the ICP IM, but which are not found in the variable list of the programme. The reason is that the suitability of a variable for long-term monitoring depends also on advancement of methodology, cost of equipment and materials, availability of trained personnel and potential sources of funding. Still underdeveloped methods are one of the main problems when applying biological parameters to a monitoring system and for this reason many good indices cannot be used.

Many aspects of bioindication will require national development because of the specific conditions within individual countries.

1.6 References

Evaluation of Integrated Monitoring in Terrestrial Reference Areas of Europe and North America. The Pilot Programme 1989-1991. Environment Data Centre, National Board of Waters and the Environment, Helsinki 1992.

Forsius, M., Guardans, R., Jenkins, A., Lundin, L. and Nielsen, K.E. (eds.) 1998. Integrated Monitoring: Environmental assessment through model and empirical analysis - Final results from an EU/LIFE-project. The Finnish Environment 218. Finnish Environment Institute, Helsinki. ISBN 952-11-0302-7.

Forsius, M., Alveteg, M., Jenkins, A., Johansson, M., Kleemola, S., Lükewille, A., Posch, M., Sverdrup, H., and Walse C. 1998. MAGIC, SAFE and SMART model applications at Integrated Monitoring sites: Effects of emission reduction scenarios. Water Air and Soil Pollution 105:21-30, 1998.

Jenkins, A., Larssen, T., Moldan, F., Hruška, J., Krám, P. and Kleemola, S. 2003. Dynamic modelling at Integrated Monitoring sites - Model testing against observations and uncertainty. The Finnish Environment 636. Finnish Environment Institute, Helsinki, Finland. ISBN 952-11-1440-1. 37 pp.

Johnson and Lindberg (eds), 1992. Atmospheric Deposition and Forest Nutrient Cycling. Ecological Studies 91. Springer-Verlag. New York 1992. ISBN 0-387-97632-9, ISBN 3-540-97632-9.

Kleemola S., Forsius M. (eds), 5th Annual Report 1996. UN ECE ICP Integrated Monitoring. The Finnish Environment 27. Finnish Environment Institute, Helsinki, Finland. ISBN 952-11-0045-1.

Moldan and Cerny (eds), 1994. Biogeochemistry of Small Catchments. A Tool for Environmental Research. Wiley. Chichester, England. ISBN 0-471-93723-1.

2 Cause/Effect Monitoring Requirements

The IM concept has been widely recognised as appropriate and timely means of monitoring ecosystem change, and efforts have been made in all participating countries to supply the relevant information. Because of the temporal and spatial variability in ecosystem dynamics a long-term commitment to Integrated Monitoring is required by each participating country. A long-term commitment means that integrated monitoring is carried out nationally for more than 10 years, implying an appropriate financial commitment. Due to its integrated nature, ICP IM is a costly programme to start and carry out, and reasonable ways to limit the costs have been sought. Accordingly different levels of monitoring intensity at the sites have been identified and the focus of the monitoring may vary according to national priorities and available financial resources. However, a common minimum level of the programme is required in order to allow evaluation of data at the international scale regarding the priority topics. The mandatory and optional subprogrammes are listed in Chapter 6.

The different programme levels can be defined in a general framework of causes and effects (Table 2.1). The priority topics are the cause/effect monitoring of nitrogen, sulphur, and ozone in ecosystems. The secondary topics are POPs, heavy metals, and climate change. For each of the six environmental/abiotic change factors the relevant IM subprogrammes, as well as general and specific indicators, are identified. Nitrogen, sulphur, and ozone are considered as priority subjects within the international policy context. The environmental impacts of heavy metals and persistent organic pollutants (POPs) are receiving increasing attention under the work of the UNECE LRTAP

Convention. Climate change is not a duty of the UNECE LRTAP Convention, but it is discussed here since ICP IM sites may be especially suited for detecting these kinds of effects. Internationally accepted methods for monitoring and assessing the ecosystem effects of all these problems, and in particular their impact on biodiversity, are therefore called for.

TABLE 2.1 GENERAL FRAMEWORK OF CAUSES/EFFECTS AND PROPOSED ICP IM SUBPROGRAMME COMBINATIONS

		Biological effect	
Environmental/abiotic cause	**Subprogramme**	**Specific indicator (+ subprogramme)**	**General indicator (+ subprogramme)**
NITROGEN (acidification, eutrophication)	PC, TF, SF, RW/SW, SC, AM, LC (if lake) (AC, LF, GW)	- Sensitivity index (VG) - Foliage chemistry (FC) - Aerial algae (AL)	- Biomass change (BI) - Species composition (VG, EP) - Forest damage (FD) - Aquatic species and biomass change (LB/RB) - (Fish) - Microbial decomposition (MB)
SULPHUR (acidification)	PC, TF, SF, RW/SW, SC, AM, LC (if lake) (AC, LF, GW)	- Sensitivity index (VG, EP) - Foliage chemistry (FC) - Diatoms (LB)	- Biomass change (BI) - Species composition (VG, EP) - Forest damage (FD) - (Fish) - Microbial decomposition (MB)
OZONE	AM, SW (incl. soil moisture availability) AC (or extrapolation from measurements/ models)	- Foliar damage (FD)	- Biomass change (BI) - Species composition (VG, BI) - Phenology (PH) for interpretation
POPs	PC, RW/SW, (GW), Bark chemistry, FC	-Bioaccumulation/ assay (lab) (TA)	- Biomass change (BI) - Species composition (VG, BI)

Heavy metals	MC, FC, PC, RW/SW, (GW)	-Bioaccumulation/ assay (lab) (TA) - Microbial decomposition (MB)	- Biomass change (BI) - Species composition (VG, BI)
Climate change	AM (incl. UVB and photosynthetic active radiation) AC (incl. CO_2)		- Biomass change (BI) - Biodiversity (VG, EP, BB, BI) - Microbial decomposition (MB)

3 Site Selection

Monitoring should preferably take place in hydrologically well-defined small catchments, where the interaction between all the subprogrammes can be used at the catchment scale. Where such catchments cannot be found other defined areas are acceptable provided input-output budgets can be made.

The following selection criteria should be met:

1. The site must allow for input-output measurements. Input measurements mean that deposition is measured at the site. Output measurements mean that the drainage water flux can be quantified, and its chemistry analysed.
2. The site should be hydrologically well definable and as geologically homogeneous as possible.
3. The site should not be less than a few tens of hectares and no more than a few square kilometres (range 10-1000 ha) and preferably buffered by a zone of similar land use.
4. The ideal site is one in which there are no ongoing management activities. Otherwise, land use within the area should be controllable. This normally means that the area is protected in some way. If management activities take place they must be well documented.
5. The site should be typical for the region.
6. It is desirable that other scientific research related to environmental assessment/modelling is carried out at or close to the site.
7. The closest significant point pollution source should be > 50 km away. Where the background level of pollutants is high, the distance to the pollution source can be less, but the distance should be greater when the background level is low.

4 Programme Administration

- 4.1 Division of tasks among organisational levels
- 4.2 Nomination of sites
- 4.3 Data submission
- 4.3.1 Data reporting formats
- 4.3.2 Use of flags

4.1 Division of tasks among organisational levels

- Expert institutes collect and report primary data to the National Focal Point (NFPs). They are responsible for data quality.
- The NFPs, with or without the help of expert institutes, treats the data according to the IM manual and reports data to the Programme Centre. Data should also take part in national and international data analysis and evaluation if required and feasible.
- The Programme Centre collects and stores data and, in contact with the NFPs, tests data quality. The Programme Centre should initiate a quality assurance programme in cooperation with all participating countries.
- The Programme Centre maintains an international database, including both current and available older time-series of monitoring data and provides access for researchers to data. The database should be particularly suitable for extracting information on environmental quality as a basis for policy.
- The Programme Centre is responsible for the cooperation among the ICPs.
- The Programme Centre is also responsible for the production of Annual Reports to the Task Force for ICP IM.
- The Task Force for ICP IM acts as the steering body of the programme, specifies the timetable for activities and reports progress to UNECE Working Group on Effects.

4.2 Nomination of sites

Choice of monitoring sites should be agreed upon between the Programme Centre and National Focal Points.

4.3 Data submission

The reporting period to the IM Programme Centre is on a calendar year (January-December) basis. Normally the deadline (set by the Task Force) for previous year's data is December. E.g. data from year 2011 (January-December) should be reported in December 2012 and results will be audited in April 2013. This will slow down the possibility to use fresh data but will compensate for better compatibility when data from all areas can be analysed simultaneously.

Data are sent to the IM Programme Centre as Excel (preferred) or ASCII files by e-mail.
Please name the files according to the rule area+subprogramme+datayear e.g., FI01_RW_2012.txt or FI01_RW_2012.xls

The contact address:
IM Programme Centre
SLU, Department of Aquatic Sciences and Assessment
P.O. Box 7050, SE-75007 Uppsala, Sweden

e-mail: im-database@slu.se

Please enclose a list of the files including the number of records per file.

4.3.1 Data reporting formats

Reporting formats are presented at the end of each of the subprogrammes as examples. All chemical subprogrammes have a common reporting format. Data from the biological subprogrammes:

Vegetation VG, Aerial green algae AL and Forest damage FD are reported using the B1 reporting format. Data from the rest of the biological subprogrammes: Trunk epiphytes EP, Tree bio elements and tree indication BI, Vegetation structure and species cover VS and Inventory of birds BB are reported using the B2 reporting format.

Generally, only aggregated data, normally monthly averages are reported to the Programme Centre.

Reporting format for the CHEMICAL SUBPROGRAMMES

column	data	
1-2	SUBPROG	subprogramme code, file identifier
3-6	AREA	country code area number
7-8	INST	2-letter code for institute
9-12	SCODE	4-digit code for station
13-20	MEDIUM	code for the sampled trees, soil etc, indicated in each subprogramme
21-22	LISTMED	medium code list (for NCC codes, soil codes and IM codes)
23-26	LEVEL	measurement level
27-32	YYYYMM	year month of the measurements
33-34	DAY	day, normally not given
35-37	SPOOL	spatial pool, number of devices/sampling points
38-45	SUBST	substance code
46-47	LISTSUB	list code for the parameter (DB or IM)
48-50	PRETRE	pre-treatment code (for DB codes)
51-53	DETER	determination code (for DB codes)
54-60	VALUE	value in suggested unit, maximum 3 decimals
61-68	UNIT	suggested units are given in each subprogramme, this is only verification
69-69	FLAGQUA	data quality flag (see use of flags)
70-71	FLAGSTA	status flag (2 letters reserved for the coding AM data) (see use of flags)
72-72	ADDIT	only for subprogramme FC (see subprogramme FC)

Reporting formats for the BIOLOGICAL SUBPROGRAMMES

B1-FORMAT (for subprogrammes VG, AL, FD)

column	data	
1-2	SUBPROG	subprogramme code, file identifier
3-6	AREA	country code area number
7-8	INST	2-letter code for institute
9-12	SCODE	4-digit code for station
13-20	MEDIUM	code for the sampled trees etc, indicated in each subprogramme
21-22	LISTMED	medium code list (for NCC codes)
23-26	TREE/	number of the sampled tree
	QUARTER	number of quarter on the intensive vegetation plot
27-32	YYYYMM	year month of the measurements
33-35	SPOOL	spatial pool, number of trees/sampling points
36-37	CLASS	diameter/height classes (only subprogramme VG)
38-45	PARAM	parameter code
46-47	PARLIST	parameter list code
48-54	VALUE	value in suggested unit, maximum 3 decimals
55-62	UNIT	suggested units are given in each subprogramme, this is only verification
63-64	FLAGSTA	status flag (2 letters reserved) (see use of flags)
65-100	DAMAGE	only subprogramme FD, cause of damage

B2-FORMAT (for subprogrammes EP, BI, VS and BB)

column	data	
1-2	SUBPROG	subprogramme code, file identifier
3-6	AREA	country code area number
7-8	INST	2-letter code for institute
9-12	SCODE	4-digit code for station
13-20	MEDIUM	code for the sampled trees etc, indicated in each subprogramme
21-22	LISTMED	medium code list (for NCC codes)
23-27	SIZE	size of the observed area (only subprogramme BI and BB)

28-33	YYYYMM	year month of the measurements
34-36	SPOOL	spatial pool, number of trees/sampling points
37-37	PFLAG	permanent/non-permanent trees (only in subprogramme EP)
38-45	SPECIES	code for the species
46-47	LISTSPE	species list code (NCC code lists)
48-49	CLASS	diameter/height /decomposition/vitality classes (only in BI)
50-57	PARAM	parameter code
58-59	PARLIST	parameter list code
60-66	VALUE	value in suggested unit, maximum 3 decimals
67-74	UNIT	suggested units are given in each subprogramme, this is only verification
75-75	FLAGQUA	quality flag (see use of flags)
76-77	FLAGSTA	status flag (2 letters reserved) (see use of flags)

4.3.2 Use of flags

Two types of flags are used in the data reporting when necessary: data quality flag and status flag. The possible codes for flags are (subprogrammes AM=Meteorology and TA=Toxicity assessment contain some additional codes indicated in these subprogrammes):

Data quality flag (FLAGQUA):

L = Less than detection limit (given as value)
E = Estimated from measured value
V = Species verified but no value given (in BB = Inventory of Birds)

For calculation of average values when values below detection limit are included (see Annex 7). Only if a primary value which is below detection limit is reported, the detection limit is given as the value and quality flag L is attached.

Status flag (FLAGSTA):

X = Arithmetic average, mean
W = Weighted mean
S = Sum
M = Mode

Primary values are reported without a status flag. When averages and other calculated values are reported a status flag is attached. For calculation of average values, please see Annex 7.

5 Field Structure and Design of IM Sites

Two different types of field work are undertaken at the IM sites: site description and monitoring. Site description refers to basic site characteristics, such as geographical situation, climate, land use history and distribution of soil types, plant communities and tree stands. The description may be supplemented with inventories over the whole site of for example soil types and plant species. Site information is essential for scaling results obtained in the monitoring subprogrammes to the site as a whole, and its importance should not be underestimated. The monitoring is carried out at permanent stations, the locations of which are carefully selected according to the subprogrammes described in Chapter 7. A central aim of integrated monitoring is to establish the relationships between chemical, physical and biological parameters. This is best achieved by carrying out the subprogrammes as close to each other as possible within the main habitat type(s) at the site.

5.1 IM site descriptions

- 5.1.1 Basic information requirements
- 5.1.2 Mapping
- 5.1.2.1 Base map
- 5.1.2.2 Bedrock
- 5.1.2.3 Soil material
- 5.1.2.4 Soil types
- 5.1.2.5 Plant communities
- 5.1.2.6 Tree stands
- 5.1.3 Inventories
- 5.1.3.1 Plant species inventory (optional)

5.1.1 Basic information requirements

Basic information of any IM site must be given when it is entered into the monitoring network of the programme. The mandatory information consists of:

- Country code (ISO alpha-2, see Annex 4)
- Number of the site (running per country)
- Name of the site
- Geographical coordinates (latitude, longitude, accuracy of minutes)
- Maximum elevation (m.a.s.l), highest point
- Minimum elevation (m.a.s.l), lowest point
- Political jurisdiction (state or province)
- County (smallest administrative region)
- Owner type (state, communal or private)
- Size of the site (ha)
- Water area (% of total)
- Dominant soil type
- Dominant vegetation (including tree stands)
- Long-term average precipitation (mm), last 30-year period
- Long-term average temperature (?C), last 30-year period
- Snow (%), percentage estimate of precipitation

- Length of the hydrological cycle (days/year), free water flow
- Length of the vegetation period (days/year), mean temperature > 5 ?C for 5 consecutive days
- Land-use history
- Earlier investigations
- Anthropogenic stresses to the site (e.g., siting of nearby industry or agriculture, recreation pressure, pasture of sheep etc.)

The above information can be given in free format or using the Site Description form (Annex 5).

Additional information is needed for the calibration of models. These data include detailed information on vegetation and physical as well as chemical characteristics of the soil. Some of the necessary values are not collected regularly but might exist from local model runs or special investigations carried out at the site. The models have quite different data requirements to the normal IM monitoring, and a variety of information may be needed. Such information will be sought directly by the modeller from the National Focal Points.

5.1.2 Mapping

The aim of mapping the monitoring site is to provide the basis for choosing the most representative locations for various types of sampling and to provide the basis for scaling the monitored information up to the site scale.

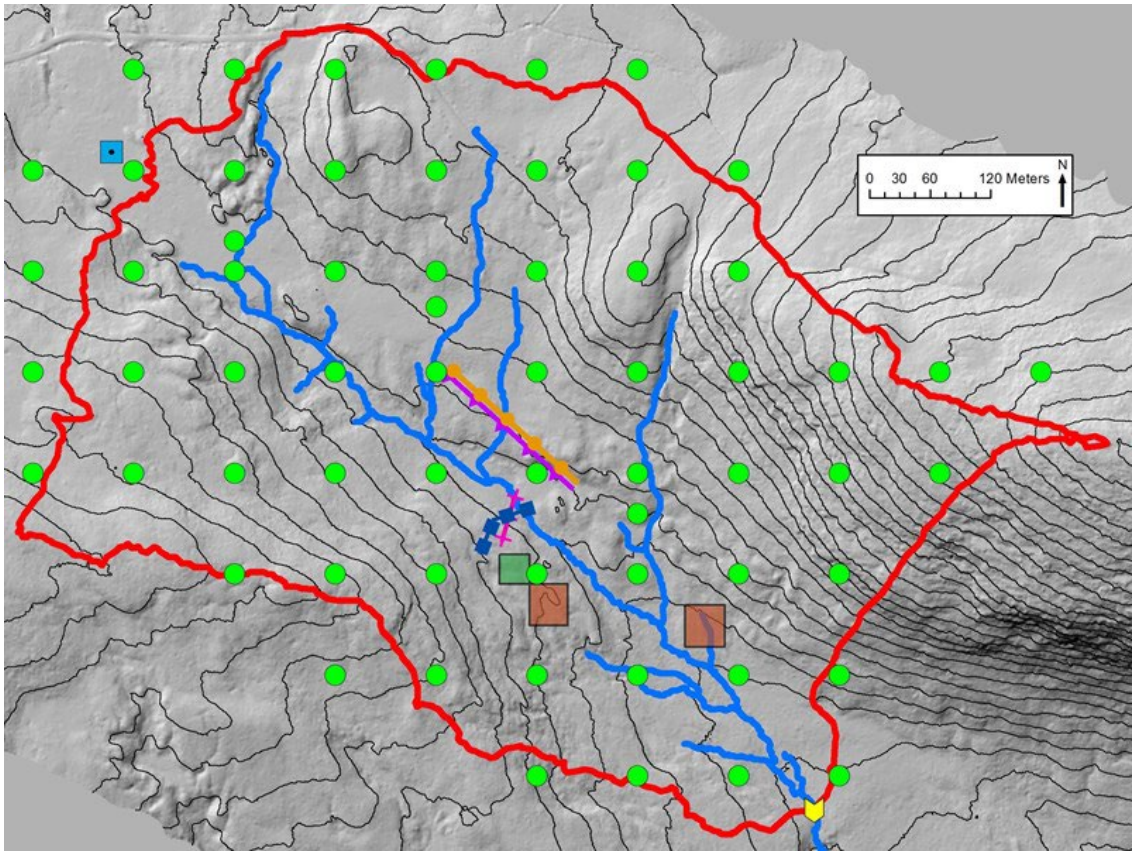


FIGURE 5.1 BASE MAP OF SITE SE16 GAMMTRATTEN SHOWING THE LOCATION OF PERMANENT PLOTS AND MEASUREMENT STATIONS

If no maps are available for the site, they should be prepared using standard mapping techniques. Site maps are a mandatory part of the IM programme. The maps produced should be sent to the Programme Centre. Digital maps can be sent via e-mail, preferably in an open GIS format. Good paper maps are also acceptable and should always be provided. Please enclose information about the coordinate systems used on the maps.

The Focal Points are responsible for ensuring that no copyright restrictions on maps are violated.

5.1.2.1 Base map

A base map of each IM site should be produced in scale 1:2 000-1:10 000, on which contours, streams and lakes are marked. The catchment/monitoring site should be outlined on the map and reference coordinates should be marked. If a digital elevation model of the IM site is available, this should also be sent to the Programme Centre.

All stations (permanent plots, observation sites, groups of trees used for measurements etc.) should be marked on the map (Figure 5.1). Stations are identified by station code, institute and subprogramme (see chapter 5.3.1). The same station code should be used for different subprogrammes when the measurements are carried out in the same plots or close to one another on the same habitat. Additional information concerning the stations should be available from NFPs upon request.

5.1.2.2 Bedrock

A geological map of the site should be provided, detailing at least the main rock types. This information is needed for estimating site weathering patterns.

5.1.2.3 Soil material

An overburden map of the site should provide information on at least the most important soil materials (e.g., peat, sand, loess), see Figure 5.3.

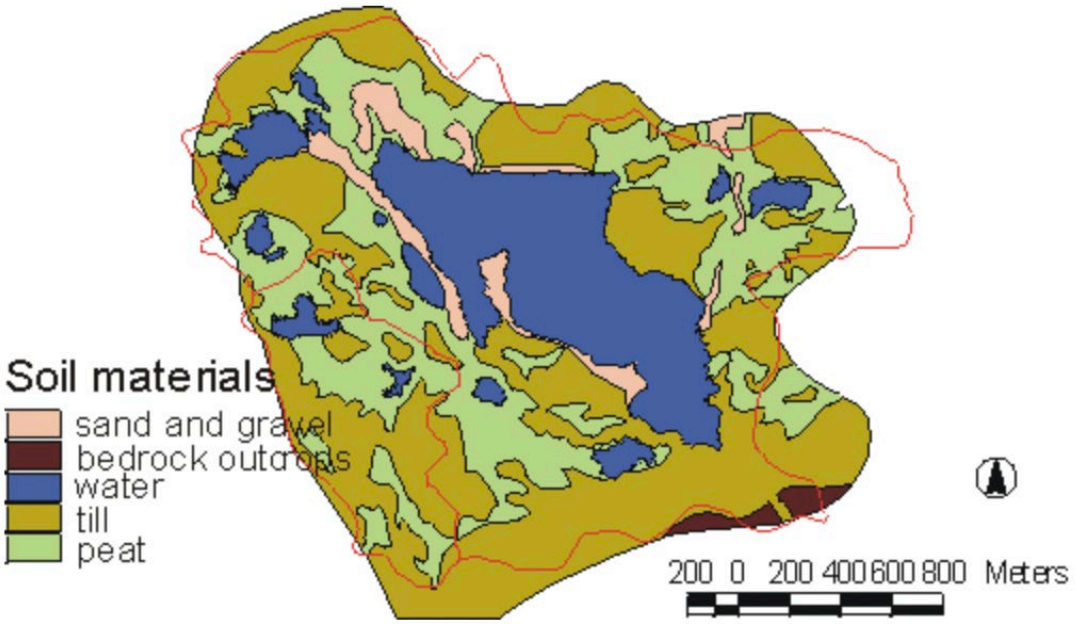


FIGURE 5.3 MAP OF SOIL MATERIAL FROM HIETAJÄRVI (FI03) IM SITE.

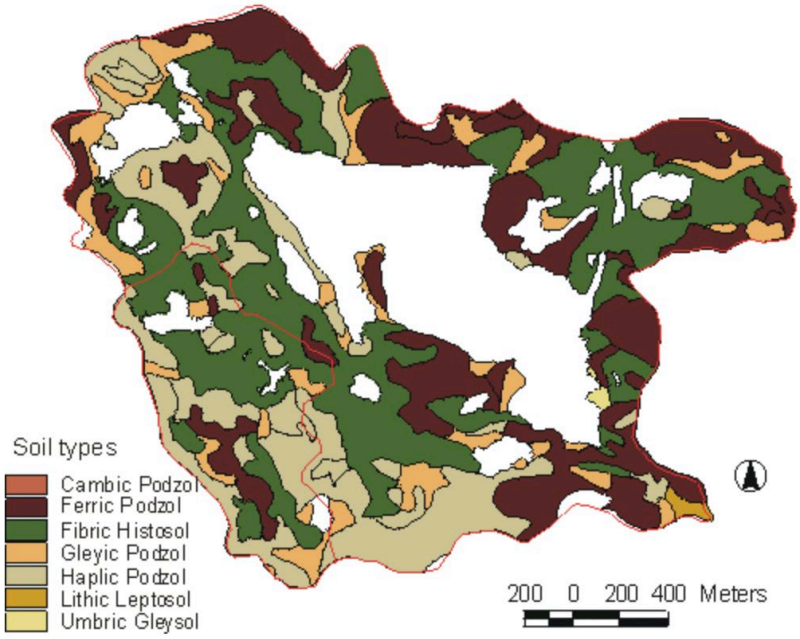


FIGURE 5.4 SOIL TYPE MAP OF HIETAJÄRVI (FI03) IM SITE.

5.1.2.4 Soil types

If no pedological map of the site exists, a pedological survey should be carried out. National pedogenic classifications should be annotated with the equivalent FAO soil units (Figure 5.4) (FAO UNESCO 1990. Soil map of the world. Revised legend, World Soil Resources Report 60. Rome 1990).

Each soil unit on the map should have the following information: humus form (mor, moder, mull) and thickness, soil texture (by hand, soil texture triangle), and soil depth (depth to bedrock) class (e.g., <1m, 1<>3m, >3m). Soil chemistry data (recommended: heavy metals, pH, TOC, CEC_E and BASA) is optional. This information, which can be obtained using systematic sampling or judgement sampling, is very useful for scaling-up results to the catchment and for catchment-scale modelling.

5.1.2.5 Plant communities

The plant communities, delimited at about the level of the Braun-Blanquet association or equivalent, are mapped (Figure 5.5) using standards relevant in the country. The mapping could preferably be performed using the permanent network of lines established for vegetation and soil surveys and monitoring of tree bioelements and tree population dynamics.

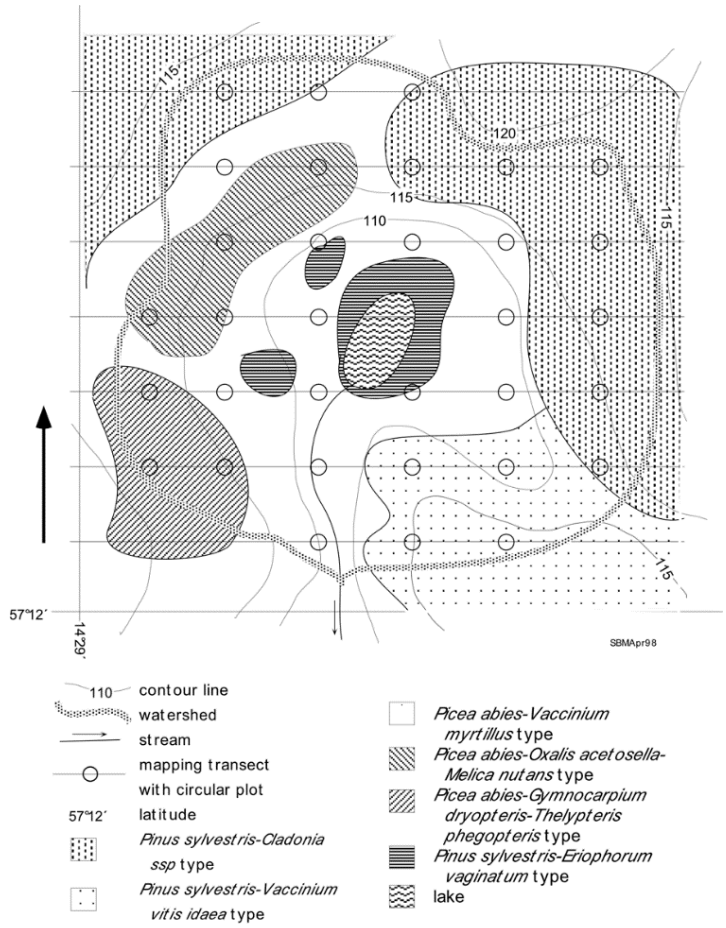


FIGURE 5.5 EXAMPLE OF A BASE MAP WITH DISTRIBUTION OF PLANT COMMUNITIES

5.1.2.6 Tree stands

Tree stands are mapped (Figure 5.6) according to relevant standards in the country. Preferably use the permanent lines as under Plant communities (Figure 5.5). Separate the stand types by visual inspection of dominant tree species, dominant height, layering, number of stems per unit area and development class.

Development classes:
0 = open area
1 = one age class; young, developing forest stand (trees <1.3 m)
2 = one age class; young, developing forest stand (trees >1.3 m)
3 = one age class; mature forest stand
4 = one age class; old, degenerating forest stand
5 = two age classes; young and mature or young and old forest stand (100 trees/ha of old generation)
6 = two age classes; mature and old forest stand (100 trees/ha of old generation)
7 = not possible to classify in classes 1-6

If required, the visual inspection may be supplemented with measured quantitative information such as basal area, tree heights, number of stems alive and dead, number of windthrown stems etc., preferably collected on sample plots (subprogramme BI).

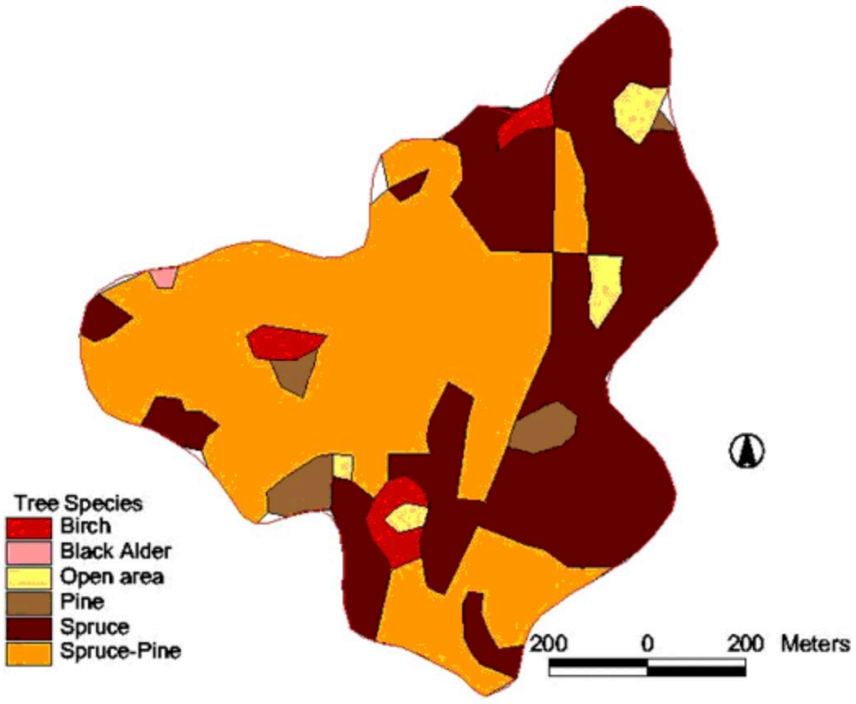


FIGURE 5.6 FOREST STAND MAP (DOMINATING TREE SPECIES) OF ZEMAITIJA (LT03) CATCHMENT.

5.1.3 Inventories

In connection with the assessment of biodiversity, inventories of plant and animal species at the site may be extremely useful. These should be maintained as species lists for each functional or taxonomic group (e.g., vascular plants, Lepidoptera etc.). Information on abundance will enhance the value of such lists. This information should be held at the National Focal Points. However, the IM Programme Centre should be informed about the availability of such data for particular sites. An example how to carry out the inventories are given in 5.1.3.1 Plant species inventory and in subprogramme VS, Vegetation structure and species cover.

Inventories of soil properties (e.g., field surveys of horizon thickness and texture) are important for modelling studies. Samples can be taken optionally for the analysis of soil chemical properties. Data should be held at National Focal Points and the IM Programme Centre informed of its availability.

5.1.3.1 Plant species inventory (optional)

The aim is to give the full plant species list with or without abundance of each species of the whole site irrespective of plots. The inventory could either include both soil-living plants and epiphytes or only the former. An inventory of plants on all substrates is especially valuable when biodiversity is in focus.

Method Species lists with or without abundance are prepared for soil-living plants per plant community and/or, for epiphytes, per type of substrate, e. g. mineral surfaces, tree trunks, branches, logs, dead wood, other understorey plants. Note that abundance in this case refers strictly to the number of individuals or shoots, not cover or dominance, and that each species is estimated independently from the others.

Abundance classes (Braun-Blanquet 1965):
1=very sparse
2=sparse
3=not numerous
4=numerous
5=very numerous

The survey is done initially and then repeated after major changes in the vegetation by, e. g. management measures, grazing, fire, windthrow and landslide. The season for the inventory of vascular plants should coincide with maximum development of vegetative and reproductive organs of most species in order to make the identification easy.

Parameters to be stored. Plant community names are recorded in extenso. They should refer to community types established and commonly used in the country, e. g. the Braun-Blanquet communities (Braun-Blanquet 1965) or the Nordic vegetation types (Påhlsson 1994), or communities used in the framework of EU Corine Land Cover (Cruickshank & Tomlinson 1996). Relevant substrate types are recorded with free names, but as far as possible the species names of tree substrates should be given.

PRESENCE/ABUNDANCE of soil-living species per community PRESENCE/ABUNDANCE of epiphytes per substrate

References

Braun-Blanquet, J., 1965: Plant Sociology; the study of plant communities (Transl. rev. and ed. by C.D. Fuller & H.S. Conard). Hafner, London.

Cruickshank, M.M. & Tomlinson, R.W., 1996: Application of CORINE land cover methodology to the U. K.: Some issues raised from Northern Ireland. -Global Ecology and Biogeography letters 5:235-248.

Påhlsson, L. (ed.), 1994: Vegetationstyper i Norden (Vegetation types in the Nordic countries). Tema Nord 1994:665. (In Swedish with introductions in Finnish, Icelandic and English.)

5.2 Monitoring stations

5.2.1 Layout and siting of stations

The type of permanent stations used for collecting monitoring data for different subprogrammes of the IM programme varies considerably (plots, groups of trees, sampling sites etc.). The location of stations depends on the heterogeneity of soil, forest stands and vegetation. The plots used for site representative monitoring are located throughout the monitoring site (see circular plots in Figures 5.5 and 5.7). The other stations are preferably located in the main habitat type or types of the monitoring site (Figure 5.7).

At least two stations for each subprogramme should be established so that the variation of parameters within the monitoring site can be assessed. The stations belonging to different subprogrammes should be grouped to form an intensive area to allow for comparability of monitoring data.

For some subprogrammes (e.g., throughfall and litterfall) the sampling could be done on two scales: 1) in association with the intensive monitoring area (target population = area), 2) transect across catchment (target population = catchment) to relate to catchment deposition. (Figure 5.7). Transect sampling has not been recommended by ICP Forests and depends on the available resources.

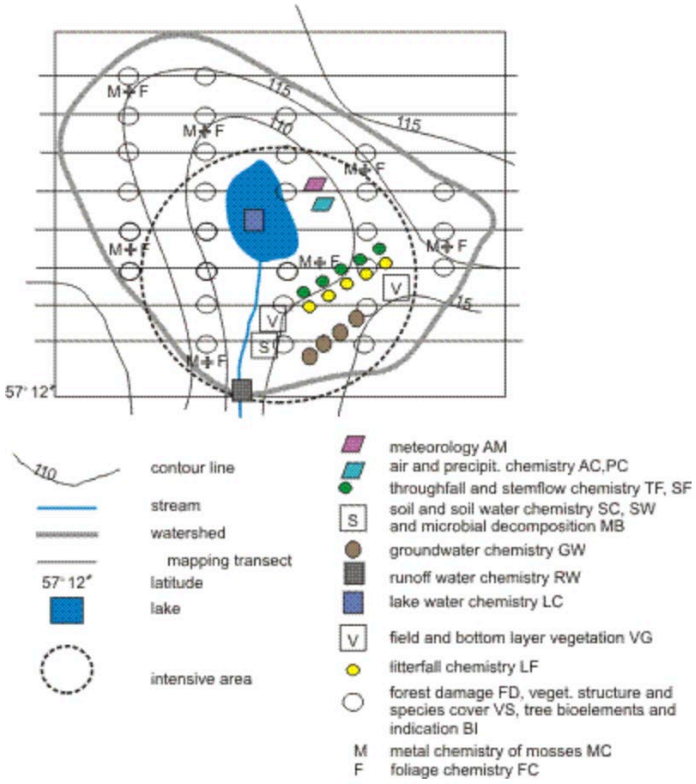


FIGURE 5.7 AN EXAMPLE OF THE ALLOCATION OF MONITORING STATIONS AT A SITE WITH ONE INTENSIVE AREA. BEDROCK/SOIL MATERIAL/SOIL TYPES/TREE STANDS AND PLANT COMMUNITIES, WHICH HAVE BEEN MAPPED, ARE ALSO INDICATED.

5.2.2 Intensive area

The most common or otherwise typical habitat type or types of the IM site, e.g., vegetation, soil type etc. is/are normally chosen for the stations. The places for different subprogrammes should be located close to one another to allow for wider ecosystem monitoring of a particular habitat. A group of these plots is called an intensive area and the station codes for each subprogramme belonging to the group should be the same (Figure 5.8). The size of an intensive area should not exceed two hectares.

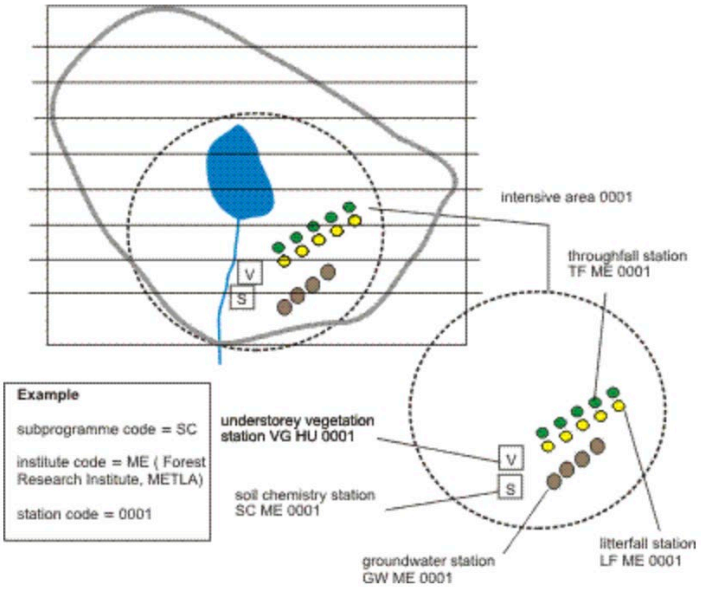


FIGURE 5.8 AN EXAMPLE OF INTENSIVE AREAS AND CODING OF A GROUP OF PLOTS. THE SAME 4-DIGIT STATION CODE IS USED FOR DIFFERENT SUBPROGRAMMES WHEN THE STATIONS ARE SITUATED ON THE SAME INTENSIVE AREA OR CLOSE TO ONE ANOTHER ON THE SAME HABITAT TYPE.

For maximum added-value and cost-efficiency, all subprogrammes which are not representing the whole site, e. g. meteorology, precipitation chemistry, throughfall, litterfall, field and bottom layer vegetation and soil water should be located in, or as near the intensive area/s as possible (Figure 5.7, 5.8).

5.2.3 Auxiliary stations

Auxiliary stations are stations which cannot for some reason be located within the IM site. Stations for subprogrammes meteorology and air chemistry are often located outside the monitoring site due to technical requirements and the cost of the equipment. Auxiliary stations should, however, be avoided because the data are not necessarily representative for the IM site.

5.3 Station descriptions

5.3.1 Coding of stations

National Focal Point (NFP) in each country is responsible for the coding of stations.

All sites belonging to the IM network are identified by: country area number, where:

- **country**: a 2-letter ISO code for country (see Annex 4)
- a**rea number**: a 2-digit running number per country

Stations within an IM site are identified by the following information: **station identification = subprogramme code office code station code**, where:

- **station code**: a 4-digit code for station
- **office code**: a 2-letter code for office/institute responsible for measurements (complete name also reported to the Programme Centre)
- **subprogramme**: a 2-letter code for subprogramme

Stations may represent plots, groups of trees, sampling sites etc. Stations belonging to one subprogramme can always be identified by the 2-letter subprogramme code (Figure 5.8). In order to allow for easier comparison of data each station should be coded so that the same 4-digit station code is used for different subprogrammes when the measurements are carried out on the same plots or when the stations are close to one another on the same habitat type.

A code belonging to an abandoned station should not be used again.

5.3.2 Basic information requirements for stations

The following information about stations should be delivered to the Programme Centre:

Station identification (see 5.3.1)

Establishment information:

- **Establishment month** (yyyymm)
- **Dismantling month** (yyyymm): Given when station is abandoned

Local coordinates:

Coordinates are given using local coordinates. The reference point (origo) is the left lower corner of the smallest rectangle enclosing the IM site. Origo is identified by latitude and longitude (degree, minute, second). The x-axis (S-N-axis) is drawn parallel to compass north and the y-axis is drawn perpendicular to the x-axis.

- **Local x coordinate**: Distance from the reference point in the S-N direction, 10 m accuracy.
- **Local y coordinate**: Distance from the reference point in the W-E direction, 10 m accuracy.
- **Elevation**: Altitude above sea level, 10 m accuracy.

Vegetation:

Information obtained from mapping of plant communities (chapter 5.1.2.5) and tree stands (5.1.2.6). The following information should be made available:

- **Vegetation type**: According to mapping of plant communities (see chapter 5.1.2.5)

The following information is given according to mapping of tree stands (see chapter 5.1.2.6):

- **Dominant tree species**
- **Basal area** (m^2/ha)
- **Development class**
- **Dominant tree height** (m)

Soil:

Information obtained from mapping of soil types (see chapter 5.1.2.4). The following information should be made available:

- **Soil type**
- **Pedotype**

Structure of the station:

- **Size of the station**: Size of the area (m^2) containing all collectors/sample plots/sample trees used for monitoring.
- **Number of sample plots/sample trees/collectors**: Number of sample plots refers to the individual smaller sampling plots used for sampling.
- **Size of individual sample plots**: E.g., in subprogramme VG size of smaller individual sample plots used for sampling (m^2).

Additional information:

This information should mandatorily be reported with the real data.

- Any information which might explain changes in the measured values of some parameters.
- Circumstances possibly affecting the measurements.
- Methods, if different from the recommended ones.
- The bases used for dividing vegetation into layers/levels.
- Upper and lower levels used in monitoring trunk epiphytes etc.

6 Types of Subprogrammes

6.1 Mandatory and optional subprogrammes

In addition to the mapping requirements presented in Chapter 5, the minimum level of the IM programme is presented in Table 6.1. This common minimum level of the programme is required in order to allow evaluation of data at the international scale regarding the priority topics of the IM programme. Table 6.1 also includes recommendations for sampling frequency. Depending on national priorities and available resources the subprogrammes which are marked optional may or may not be carried out. A table of parameters measured in individual subprogrammes is presented in Table 6.2.

Table 6.1 The minimum level of the IM programme

Chapter	Mandatory subprogrammes	Sampling frequency
7.1	Subprogramme AM: Meteorology	c/d
7.2	Subprogramme AC: Air Chemistry	c/d/w
7.3	Subprogramme PC: Precipitation chemistry	d/w/m
7.5	Subprogramme TF: Throughfall	w/m
7.7	Subprogramme SC: Soil chemistry	5y
7.8	Subprogramme SW: Soil water chemistry	w/2w
7.10	Subprogramme RW: Runoff water chemistry	d/w/m
7.12	Subprogramme FC: Foliage chemistry	y
7.13	Subprogramme LF: Litterfall chemistry	y
7.17	Subprogramme VG: Vegetation (intensive plot)	1-5y
7.20	Subprogramme EP: Trunk epiphytes	1-5y

Chapter	Optional subprogrammes	Sampling frequency
7.4	Subprogramme MC: Metal chemistry of mosses	5y
7.6	Subprogramme SF: Stemflow	w/m
7.9	Subprogramme GW: Groundwater chemistry	2m
7.11	Subprogramme LC: Lake water chemistry	2-6m
7.14	Subprogramme RB: Hydrobiology of streams	6m
7.15	Subprogramme LB: Hydrobiology of lakes	m/2m (in spring/autumn)
7.16	Subprogramme FD: Forest damage	y
7.18	Subprogramme BI: Tree bioelements and tree and tree indication	5y
7.19	Subprogramme VS: Vegetation structure and species cover	10-20y
7.21	Subprogramme AL: Aerial green algae	y
7.22	Subprogramme MB: Microbial decomposition	y
7.23	Subprogramme TA: Toxicity assessment	
7.24	Subprogramme BB: Inventory of birds	3-5y
7.25	Subprogramme PH: Phenology	d/w (in spring/autumn)

sampling intervals: c = continuous, d = daily, w = weekly, m = monthly, y = yearly

Table 6.2 List of mandatory and optional parameters

Mandatory and optional parameters (pdf)

7.1 Subprogramme AM: Meteorology

7.1.1 Introduction

Since meteorological parameters are the most driving variables that effect ecosystems, their magnitude and changes in time should be well known to differentiate between anthropogenic perturbations and natural phenomena. In this context the need for phenological observations is evident (subprogramme phenology PH is under development) since meteorological data have to be calibrated by plant reactions on each site separately.

The objectives are:

- description of climatic conditions of IM sites and changes in these conditions
- detection of periods of extreme weather conditions and events that stress tree vitality (freezing of soils, late frost, drought, storm)
- preparation of a data base which fulfils the requirements of deterministic computer models that are capable of predicting ecosystem responses under future input scenarios.

Data from neighbouring monitoring stations meeting the set criteria (e.g., national meteorological networks) may be used for ICP IM purposes, provided that they can be shown to be representative for the IM site. The representativity of meteorological data with respect to various landscape types within the monitoring area must be carefully evaluated by the data originator. However, some site-specific local data with relevance to hydrology, decomposition and soil classification are needed to interpret other measurements. Therefore at least soil and ground temperatures need to be measured at the IM site.

Traditional methods of data readings three times a day, carried out over decades, are useful for describing the climatic conditions of a given site. But for more sophisticated analysis of the weather dynamics the following variables should be measured on (quasi)continuously recording meteorological stations.

mandatory parameters	sampling height
precipitation	1.3 m*
temperature of the air	2 m
soil temperature	-5 cm, -10, -20 cm
relative humidity	2 m
wind velocity	10 m
wind direction	10 m
global radiation/net radiation	(2 m)
optional parameters	sampling height
photosynthetic active radiation	(2 m)
UVB-radiation	(2 m)

*For precipitation measurements some national standard heights exist. The resulting differences in precipitation amounts against the reference height should be tested and reported.

The height requirements are in accordance with WMO-Guidelines (1990) to ensure comparability with data from official weather stations and other monitoring sites.

Some compromise height specifications given for all radiation variables in brackets (..) should be considered as possible minima as far as the instrument is not shadowed by obstacles. At some sites radiation sensors have to be mounted near the top of the mast, which will complicate handling and maintenance of sensors.

7.1.2 Methods

7.1.2.1 Site requirements

Meteorological stations should be located in a clearing inside the IM site. Reflecting the large spatial variability especially of precipitation amounts and events the maximum distance to intensive monitoring plots should preferably not exceed 700-1000 m. According to WMO-Guidelines (1989) the minimum distance from the equipment to the next obstacle (tree) should be twice its hight, and the ground covered by short grass cut to lower than 10 cm.

Alternatively, towers that allow gradient measurements from above canopy to ground surface, are useful, but are also very expensive. Consequently, measurement towers normally are restricted to basic research stations.

Data from neighbouring meteorological stations may be used for ICP IM purpose, provided that they can be shown to be also representative for the IM site. However, some site-specific local data with relevance to hydrology, decomposition and soil classification are needed to interpret other measurements. Therefore at least soil and ground temperatures need to be measured at the IM site.

In this context the design of a field station is presented as an example. The station is running in remote forested areas, independently from mains. Its high reliability was successfully tested under various and rough climate conditions by the Bavarian State Institute of Forestry on its forest ecosystem monitoring network. Comparable instruments and sensors of any manufacturer may be used when fulfilling standard requirements.

7.1.2.2 Equipment

For mounting meteorological instruments at standardized heights, 10m masts are necessary (Annex X.1). Wind sensors are fixed at the top of the mast. Sensors at 2 m are clamped on arms (radiation to south, temperatures to north). Telescopic or some folding type masts facilitate installation, controlling and maintenance of instruments.

Data are recorded by means of a data logger, which is installed in a locker to prevent electronics from high humidity, preferably on or nearby the mast. The data logger should function reliably even at extremely low temperatures to minimize data losses. Note that storage on moving media (diskettes, tapes) is restricted to temperatures higher than -10°C, on memory cards (EPROMS) to temperatures below -20°C. The software programmes that are stored at EPROMS or downloaded from a notebook computer include, for each channel separately, sensor characteristics, reading and recording intervals, valid range and error setting, data conversion and compression as well as storage on memory cards. Procedures for on-site checks of sensors and the whole system are carried out with separate programme cards or by temporarily connected portable computers. The power supply can be ensured by batteries connected to solar and/or wind generators. It should be noticed that the efficiency of a fully charged battery may drop down to about 50% at very low temperatures over longer periods. Stoppage can be counteracted by additional batteries recharged on mains.

The whole equipment should be protected against lightning and all the cables should be shielded against electromagnetic fields. Also, the waterproofness of cable connections should be guaranteed by using high quality industrial standards. At some sites cables may be affected by mice.

7.1.2.2.1 INSTRUMENTS

7.1.2.2.1.1 PRECIPITATION

Besides the weekly or two-weekly precipitation amounts, which are measured in the framework of the precipitation chemistry subprogramme, precipitation intensity should be measured more frequently e.g., to estimate evapotranspiration processes and to get information about the interception process.

While floating and tipping type buckets are restricted to liquid precipitation, the weighing type is appropriate for measuring all kinds of precipitation (snow, hail, mixtures of snow and rain) without heating.

The model presented in Annex X.2 is a Hellmann type gauge with the standard collection area of 200 cm^2, working on battery. Precipitation is measured by an electronic weighing compartment with a resolution of 0.01 mm and high accuracy. The linearized output signals are stored directly on memory cards.

It is of great advantage that loss of water through evaporation or through emptying the container is compensated internally. There is no need to correct zero shifting on computers.

Mounting
The gauge is mounted on the upwind side of the mast with a horizontal distance of about 5-10 meters. The standard height is 1.3 m above ground which should be covered with short grass to prevent water from splashing in, and the collecting area is levelled plane.

Maintenance
The need for maintenance is reduced to emptying the container in time and to system and battery check, which can be done during the routine check of the whole station (see below).

7.1.2.2.1.2 TEMPERATURE

The most common method to measure temperature is the use of platinum wire whose resistance changes with temperature. The widely used Pt100-resistor-thermometer with a basic value of 100 Ohms at 0°C is very appropriate for long-term and long-range monitoring of air and soil temperatures (Annex X.3). It is used to transfer IPTS 1968 (International Practical Temperature Scale) between instrument locations.

Accuracy should be ±0.3 K (WMO 1990, German Industry Norm DIN 43760 Class B). When using Pt100 at different levels below and above ground, some elements should be calibrated simultaneously, and those exhibiting the most similar performance towards each other (zero-point deviation, slope) should be applied facilitating corrections by software and especially heat flow calculations.

For air temperature the platinum coil is encapsulated in hard glass, for soil temperature it is built in a waterproof stainless-steel tube.

Mounting
Sensors for air temperature are installed in weather and radiation shields (Annex X.1). The cover and the lamellae of these shields should be cleaned regularly and checked for scratches to ensure

appropriate reflection properties. Soil thermometers are to be placed in with good contact to the soil matrix.

Maintenance
Since characteristics of the Pt100 are very stable (artificially aged before use) over long time, maintenance is normally restricted to renewal upon damage. Once a year zero-point calibration in ice water may be carried out for air temperatures. Soil sensors normally should not be removed.

7.1.2.2.1.3 RELATIVE HUMIDITY

In battery supplied field stations two main types of passive humidity sensors with low power consumption are widely used, often combined with PT100 temperature sensors, namely: a) hair hygrometers and b) capacitive sensors. Accuracy should be within +/- 3%.

Mounting
Like thermometers humidity sensors are to be mounted inside a weather and radiation shield, prevented from precipitation, splashing water and direct solar radiation.

a) Hair hygrometers (Annex X.3)
The measuring element consists of a number of treated natural hairs or synthetic fibres that change in length when the relative humidity changes. This change is transmitted to a potentiometer creating an electrical output to a recorder/display. Natural treated hair elements are appropriate for most nemoral and boreal forest ecosystems, covering large temperature (-35°C-+70°C) and relative humidity ranges (10-100 % rel. humidity).

Maintenance
Hair elements dry out over longer periods with low air humidity resulting in too high values. This degeneration can be reversed by exposing the elements to warm saturated air. This can easily be done at the station by wrapping the case with a wetted cloth for about one hour. The humidity value then should be 97 %, otherwise, it has to be adjusted by the setting screw.

In forest ecosystems hair elements can be periodically exposed to pollen causing significant errors. If the weather shield is insufficiently protecting the hair, a protection device may be used which has to be checked and cleaned regularly.

Calibration
The above-mentioned procedure may also be used for a one-point calibration twice a year. Comparison with a portable standard aspiration hygrometer is useful to examine the lower part of the measuring range (40-50 % rel. humidity) and the long-term stability. New hair elements have to be calibrated in a humidity chamber. In foggy air it is self-calibrating.

b) Capacitive sensor (Annex X.3)
The capacity of a polymer film changes when absorbing water vapour. These capacity changes are detected by electrodes and converted to electric signals. Since they cover a temperature range from

-20°C to +80°C and a humidity range from 0-100 %, they might be more appropriate than hair hygrometers in warmer and dryer climates.

Maintenance
Stability of the endpoint can be checked by exposing the sensor to warm saturated air as described

above. The response time should be noted and compared with the user's manual to verify the permeability of the particle filter. Adherent dust affects the response time, and the filter has to be changed. Since the sensor housing can be sealed by ice layers during long cold periods, another sensor type may be selected under such winter conditions.

Calibration
Twice a year a two-point calibration procedure should be carried out using the manufacturer's calibration set with saturated salt solutions.

7.1.2.2.1.4 WIND SPEED AND DIRECTION

With a wind transmitter, both horizontal wind speed and direction can be measured by anemometer and wind vane. Commonly propeller and cup anemometers are used whose angular velocity is directly proportional to wind speed and is transmitted by signal generators of different types.

For example (Annex X.4), the ball bearings of the cup anemometer are coupled to a slotted drum, which is scanned opto-electronically which is insensitive to electromagnetic fields. The pulse frequency is proportional to wind speed. Quality criteria are a large measuring range (<1-50 m/s), a low starting speed (<0.3 m/s) and a distance constant of about 2-5 meters.

The ball-bearings of the wind vane are coupled to a code disk, from which the current code is detected opto-electronically. Since the response of a wind vane to sudden change in wind direction is characterized by overshooting and oscillation about its true position, the damping ratio should be in the range of 0.3-1.0. Satisfactory resolution and linearity in wind direction are 2°-5°.

Mounting
Through the first few (tens) of meters above the ground the wind speed varies considerably due to friction. For this reason, wind transmitter is to be mounted at the top of the mast at 10 m (at standard height). The case marking and the handle of the wind vane are aligned to compass north.

Where the standard exposure is impossible, the wind speed at 10 m may be derived from other heights by using the formula of Hellmann according to WMO-Guidelines.

Maintenance
The alignment of the wind transmitter should be checked regularly using a theodolite at a permanently marked fix point.

Unless heated, ice and snow can accumulate on cups leading to higher starting torque or cessation. This can be accepted in wintertime when the evapotranspiration is very small. Slots that can be clogged by dust should be regularly cleaned.

Depending on the instructions of the manufacturer, wind sensors are checked after several years of exposure in a laboratory on signs of wear of the ball bearings as well as after meteorological events (cup deformation by hail).

7.1.2.2.1.5 GLOBAL RADIATION

Direct solar radiation and diffuse sky radiation to a horizontal plane surface comprising the spectral range from 0.3 to 3.0 µm are referred to as global radiation. It is measured by pyranometers. Two measuring principles commonly used are:

a) black painted disks that absorb incoming short wave radiant energy, generate a heat flow through a thermal resistance to the pyranometer body. The temperature difference between disk and pyranometer body is converted into voltage.

b) differences in temperature between absorbing black and reflecting white areas are transformed with thermoelements into a proportional voltage.

Both sensors are shielded by glass domes that protect against wind, rain and energy losses but allow transmittance of the incoming short-wave radiation. Where the receiver is not completely sealed, it has to be protected by a desiccator against condensed moisture.

In this context a pyranometer of the a) type is recommended (technical details in Annex X.5). It fulfils the WMO requirements (ISO 9060) for a secondary standard and is calibrated by direct or indirect comparison with a primary standard. It defines geometry and temperature response characteristics as well as spectral sensitivity, stability, and linearity over time.

Mounting
Above the plane of the sensor the location should be as free as possible of any obstructions, which may shadow it at any time of the year. The elevation of any obstruction should not exceed 5° over the azimuth range between earliest sunrise and latest sunset to achieve correct measurements of direct solar radiation while diffuse radiation is much less affected.

Use of masts that allow frequent control and maintenance, causes conflict with the above-mentioned requirements, and should be minimized. In practice, the arm on which the sensor is mounted, should be oriented to the south (the mast itself to the north pole). As far as polar diagrams of directional radiation responses are available, the low error region of the sensor may be turned to the equator. The accurate horizontal levelling of the thermopile surface is done by levelling screws and a spirit level.

Maintenance
Pyranometers should be inspected daily as recommended by WMO. In large, forested sites intervals of one week should be sufficient at least outside periods of flowering and snowfall.

During inspections the glass dome of the instrument should be wiped clear and dry as gently as possible not to alter transmission characteristics. Frozen deposits are removed using a de-icing spray and the glass dome is cleaned (sa). The desiccator material (usually silica gel) should be renewed when discolouring.

Calibration
Apart from calibration procedures by standard pyrheliometers and pyranometers in qualified radiation centres, routine checks of calibration factors using the sun as radiation source, should be carried out at least once a year. A reference standard or a travelling working standard, preferably of the same type of instrument, is mounted side by side at the mast, allowing simultaneous recording over one or two days. The means over several time periods of both sensors are used to calculate a calibration factor of the sensor to be checked. Alternatively, the pyranometer may be exchanged by a similar calibrated one while recalibrating indoors.

7.1.2.2.1.6 UV-B RADIATION

The possible damaging effects of UV-B radiation, caused by thinning of the stratospheric ozone content, to biological systems has been discussed. Because the slope of energy flux in the wavelength band of 280-315 nm is very steep, accurate values can only be measured by scanning the spectrum with high resolution (1 nm). The necessary instrumentation is, however, costly and not appropriate for field stations.

Cheaper types of instruments are the broadband UV-B radiometers which cover a bandwidth of 20 to 40 nm or the whole UV-spectrum with varying peak wavelength and varying spectral response, depending on filter characteristics.

A solution considering costs, practicability and scientific value may be the use of narrowband sensors with defined peak wavelength and bandwidth. In Annex X.5 such a sensor is presented, the peak wavelength adjusted to 306 nm which is derived from human skin and solar spectra. To get a high accuracy the sensor is heated to 40°C. Consequently, there is high power demand that hardly can be satisfied at remote field stations.

Mounting and maintenance procedures are done according to 7.1.2.2.1.5. Calibration is based on standard lamps by special laboratories.

Since UV-B radiation energy at ground level is mostly determined by stratospheric processes, data from official weather or environmental network stations some tens of kilometres away can be used, taking into account the altitudinal dependency of radiation received.

Using non-scanning type sensors, peak wavelength and bandwidth have to by standardized to allow transboundary comparisons.

7.1.2.2.1.7 PHOTOSYNTHETIC ACTIVE RADIATION

The radiation spectrum of 400-700 nm that is used by plants for photosynthesis is referred to as photosynthetic active radiation, it amounts to about 50% of global radiation. So called quantum sensors (Annex X.6) count the number of photons in this spectrum falling per unit time and area through a spectral filter on a blue enhanced photocell, regardless of their energy. This is called the photon flux density in units of µEinstein or µmol photons(quanta)/m2/s.

The sensor should have a working range from 0 to 5mmol photons/m2/s. Quality criteria are high linearity (1%), long term stability (<±2%) and small temperature dependence (±0.15%).

Mounting is done according 7.1.2.2.1.5 and **maintenance** is reduced to cleaning the sensor surface and to checking the levelling. Although routine calibration should not be necessary the ageing of filter material and photocells under specific field conditions should be taken into account.

7.1.3 Technical quality assurance

When designing an automatic weather station, the site-specific weather conditions need to be kept in mind. The sensors and instruments need to be reliably running and give the reported accuracy even under extreme weather conditions. The performance of the instruments and sensors should be certificated, and the instruments should have clear instructions about calibration procedures and recalibration intervals both at field and laboratory. The lifetime of components should be known so

that the exchange of spares can be done in time. A modular construction of instruments enables easy replacement of spares and reduces data losses.

Once or twice a year an integral check of electronic components such as cables, connectors and analogue/digital converters should be carried out by simulating electronically the output signals of sensors according to their specifications. For example, given 100 and 88.22 Ohm to a Pt100 signal cable, 0°C and -30°C resp. should be seen on the screen. This procedure ensures that the sensor output is correctly transmitted to data logger input and converted to meteorological values.

At least weekly field checks should be carried out by well trained personnel, examining power supply and the correct operating of data logger and sensors. The specific maintenance needs are reported below. A formalized logbook, containing all details to be checked, facilitates the maintenance and the evaluation of data, too.

7.1.4 Data handling and quality control

Measuring and recording intervals
As pointed out earlier the weather station should work (quasi-)continuously to enable more in-depth analysis of for example plant-weather-relationships. This means, that measuring should be carried out at time steps of 1min. To detect also extremes of very dynamic variables like wind, where the speed of damaging gusts can reach a multiple of even a short time average, time resolution should be one second. For that reason, interval measurements in time steps of one hour for example are not sufficient regarding wind speed.

Data recording intervals may not exceed 60 minutes comprising averages and minimax of variables with the exception of wind direction, where frequency distributions are needed.

Data quality management
Downloading of records or exchange of memory cards is related to the capacity of storage media but should occur at regular intervals (4 weeks), preferably once a week during station service, to identify errors not detected by field workers. Therefore, data evaluation should also be carried out regularly (consequently at least monthly).

After transmission, data sets should be routinely examined on time consistency, missing values and error settings and edited if necessary. A subsequent plausibility routine should check on:

- working range exceedance of each sensor and sensor specific error data (e.g., zero offset of pyranometers at night-time by temperature gradients)
- internal consistency errors (for example: minimum temperature exceeds average)
- exceedance of absolute limits (e.g., wind direction), probable limits (absolute minima and maxima) and average frequency distributions which can be derived from long term records of the next official weather station, taken altitudinal gradients and specific orographic conditions into account.

Data that are formally invalid are to be flagged for particular inspection.

For the subsequent scientific analysis construction of diagrams on display is a very useful means: time sequences of each variable let detect erratic changes of normally conservative variables (temperature, humidity) or stability of normally dynamic variables (wind direction).

Comparisons with related variables facilitate the decision if there are technical problems or extraordinary weather events. Examples: the windvane may be fixed by icing while the anemometer is running; if there is a rapid decrease of air temperatures (20K) in wintertime during few hours then a change in predominant wind direction should have occurred.

All evident errors, missing and doubtful values, that are excluded from further calculations, as well as corrected (interpolated) values are flagged on the database.

In the sense of a final examination, preliminary calculations of averages, minimax and distributions on daily base should be carried out, allowing comparisons with corresponding data of neighbouring official weather stations. Significant non-explainable differences related to distribution, course, or range of different variables, should result in rechecking the data set. Principally the feedback time between field workers and scientist and vice versa should be as short as possible.

7.1.5 Data reporting

Meteorological variables are reported on monthly bases. Statistical status are mainly sums (precipitation), arithmetic averages as well as absolute and averaged extremes, that are flagged according to the table below.

Predominant wind direction is reported as mode. Individual recordings are classed for example to 12 sectors of the wind rose, each covering 30 compass point equivalents in degree, starting from NNE=30° (15°-45°) to N=360° (345°-15°). Calm (wind speed<0.2m/s) is reported as zero.

Even if only monthly values are to be reported to the IM programme centre, the original data are to be stored by the data originator and to be made available on request. Files containing validated hourly or at least daily values, should be deliverable upon request for sophisticated analysis.

Mandatory information

parameter	**medium**	**code**	**list**	**unit**	**values reported**
precipitation		PREC	DB	mm	sum, max daily sum
temperature of air	AIR	TEMP	DB	°C	avg/avg minimax/ minimax
temperature of soil	SOIL	TEMP	DB	°C	avg/avg minimax/ minimax
wind direction		WID	DB	degrees	predominant direction
wind velocity		WIV	DB	m/s	avg/avg maximum/ maximum
relative humidity		HH	DB	%	avg/minimax

global radiation		SOL_G	IM	W/m^2	avg/avg maximum/ maximum

Optional information

UV-B radiation	SOL_UVB	IM	W/m^2	avg/avg maximum/maximum
photosyn.act.radiation	SOL_PAR	IM	µmol/(m^2 s)	avg/avg maximum/maximum

Status information

status	**code**
monthly average	X
monthly minimum	A
monthly maximum	Z
average monthly minimum	XA
average monthly maximum	XZ
mode	M
sum	S
maximum daily sum	SZ

Example files (Excel format is preferred)

AM example Excel file
AM example ASCII file

- File identifier SUBPROG states the subprogramme.

- MEDIUM is given for temperature values as AIR or SOIL, for other parameters it is left blank.
- LEVEL is given as the absolute height/depth of the measuring equipment from the ground (cm).
- Spatial pool SPOOL refers to the number of individual recording devices used for each parameter.
- For each parameter several values are reported, averages, average maximums etc., the corresponding status flags needs to be included.
- Sampling year and month are given as YYYYMM, day field is left blank.

Additionally, the beginning and the length of ecologically important periods, that cannot be calculated from monthly data, should be reported. (Reporting of these values is done separately in free format).

For the beginning of the vegetation period the date is reported where mean air temperature exceeds the threshold value of 5°C for at least 5 consecutive days. The length of this period is then calculated by counting the number of days to that date on which mean temperature remain under 5°C.

Additional information	**format**	**unit**
beginning of the vegetation period	date	
length of the vegetation period	integer	days
beginning of the longest period without precipitation	date	
length of the longest period without precipitation	integer	days
beginning of snow cover period	date	
length of snow cover period	integer	days
ice days (max. air temperature <0°C)	integer	days
soil frost days (max. soil temperature <0°C)	integer	days
precipitation during vegetation period	real	mm

7.2 Subprogramme AC: Air chemistry

7.2.1 Introduction

Measurement of gases and aerosols carried out in the subprogramme AC gives information needed for assessing the input of air pollutants to the ecosystem due to long-range transport in the atmosphere. Gases and aerosols may interact with trees and vegetation via dry deposition either by direct interaction in the canopy or indirectly via interaction of the deposited pollutants in soils and surface waters.

Air pollution concentrations can be compared to critical levels of pollutants of noxious gases and aerosol particles in order to assess the risk of direct effects of these pollutants to the flora. In addition, from the air concentrations it may be possible to indirectly estimate the dry deposition. This is especially important for pollutants that are subject to up-take or leaching by the canopy, like nitrogen compounds, where throughfall measurements are subject to large uncertainties.

Data from neighbouring monitoring stations meeting the set criteria (e.g., EMEP sites) may be used for ICP IM purpose, provided that they can be proved by the data originator to be representative for the IM site.

Monitoring programme includes the following parameters:

Mandatory parameters
sulphur dioxide
nitrogen dioxide
ozone
particulate sulphate
the sum of nitrates in aerosols and gaseous nitric acid
$\sum(NO_3^-$ (part.) + HNO_3 (gas))

the sum of gaseous ammonia and ammonium in aerosols
$\sum(NH_3$ (gas) + NH_4^+ (part.))

Optional parameters
carbon dioxide

As an indicator of climate change and as an additional stress factor to the ecosystem, carbon dioxide should be included into the monitoring programme on a voluntary basis.

Measurements of heavy metals in aerosols are recommended to be performed in the IM programme on a voluntary basis.

EMEP programme has included recommendations for sampling of heavy metals in particles (EMEP, web-manual, Chapter 3.11) and sampling of mercury in precipitation and air (EMEP web-manual. Chapter 3.12).

It is strongly recommended that the participants of the ICP IM programme follow the recommended methods as described below. If methods other than recommended in this manual are used, their comparability to the recommended method should be proved by the data originators.

7.2.2 Methods

Siting of collectors
Besides the general siting criteria given in Chapter 5, the special siting criteria as described by EMEP, Chapter 2.2 should be followed. In order to monitor long-range transboundary air pollution, the AC site must be representative with respect to exposure to the air mass, i.e. deep valleys, mountain tops and passes should be avoided. The ideal is a freely exposed site in moderately undulating terrain. The air inlet should be 2 - 5 m above ground.

To avoid vegetation influencing the ambient air concentrations, the AC site should not be sheltered by vegetation, but located in a large open glade or a large clearing. If, in highly forested IM sites, no suitable location can be found, the AC station may also be located outside the proper IM site (preferably in the direct neighbourhood) or even on a platform above forest canopy. Data from neighbouring monitoring stations meeting the above-mentioned criteria (e.g., EMEP sites) may be used for ICP IM purposes, provided that they can be shown to be also representative for the IM site.

Sampling frequency
The requested measurement periods (frequencies) are 24 h (daily) up to 1 week (weekly) for all components besides ozone. Ozone is to be monitored continuously with 1 hour average values to be stored.

7.2.2.1 Sulphur dioxide

The most commonly used methods for sulphur dioxide measurements in EMEP today are the alkaline impregnated filter method and the hydrogen peroxide absorbing solution method (EMEP, Chapter 3.2.1). The recommended method for IM stations is the alkaline impregnated filter method, in combination with ion chromatography. At sites with annual average concentrations above 10 $\mu gS/m^3$, the absorbing solution method can still be accepted. The recommended method is described in the EMEP manual (see references below):

Principle: EMEP, Chapter 3.2.2
Interference: EMEP, Chapter 3.2.3
Sampling equipment / sample handling: EMEP, Chapter 3.2.4
Sample treatment: EMEP, Chapter 3.6

Chemical analysis: EMEP, Chapter 4.1
Calculation of results: EMEP, Chapter 3.2.4.4

7.2.2.2 Particulate sulphate

The recommended method for measurements of particulate sulphate at IM sites is the filter method in combination with ion chromatography (EMEP, Chapter 3.2.1). The aerosol filter can be mounted in front of the alkaline impregnated filter used for SO2 measurements in a filter pack. The recommended method is described in the EMEP manual (see references below):

Principle: EMEP, Chapter 3.2.2
Interference: EMEP, Chapter 3.2.3
Sampling equipment / sample handling: EMEP, Chapter 3.2.4
Sample treatment: EMEP, Chapter 3.6
Chemical analysis: EMEP, Chapter 4.1
Calculation of results: EMEP, Chapter 3.2.4.4

7.2.2.3 Nitrogen dioxide

The recommended method for measurements of nitrogen dioxide at IM sites is a manual method based on the absorption of NO_2 on a sodium iodide impregnated glass-sinter (EMEP, Chapter 3.3) followed by spectrophotometrical determination of the formed nitrite, either manually or automatically (flow injection analysis, continuous flow method). The recommended method is described in the EMEP manual (see references below):

Principle: EMEP, Chapter 3.3.1.2
Interference: EMEP, Chapter 3.3.1.3
Sampling equipment / sample handling: EMEP, Chapter 3.3.1.4
Sample treatment: EMEP, Chapter 3.3.1.7-3.3.1.9
Chemical analysis: EMEP, Chapter 4.11
Calculation of results: EMEP, Chapter 3.3.1.10

7.2.2.4 Sum of nitrates in aerosols and gaseous nitric acid

The recommended method for measurements of the sum of nitrates in aerosols and gaseous nitric acid $\sum(NO_3^-$ (part.) + HNO_3 (gas)) at IM sites is the *filter pack method*, a combination of an aerosol filter and an alkaline impregnated filter (EMEP, Chapter 3.4.2), followed by analysis with ion chromatography. The recommended method is described in the EMEP manual (see references below):

Principle: EMEP, Chapter 3.4.2.2
Interference: EMEP, Chapter 3.4.1
Sampling equipment / sample handling EMEP, Chapter 3.4.2.6
Sample treatment: EMEP, Chapter 3.4.2.6
Chemical analysis: EMEP, Chapter 4.1
Calculation of results: EMEP, Chapter 3.4.2.7

7.2.2.5 Sum of gaseous ammonia and ammonium in aerosols

The recommended method for measurements of the sum of gaseous ammonia and ammonium in aerosols $\sum(NH_3$ (gas) + NH_4^+ (part.)) at IM sites is the *filter pack method*, a combination of an aerosol filter and an acid-impregnated filter (EMEP, Chapter 3.4.3), followed by analysis with ion chromatography. The recommended method is described in the EMEP manual (see references below):

Principle: EMEP, Chapter 3.4.3.1
Interference: EMEP, Chapter 3.4.1
Sampling equipment / sample handling EMEP, Chapter 3.4.3.2
Sample treatment: EMEP, Chapter 3.4.3.5
Chemical analysis: EMEP, Chapter 4.1
Calculation of results: EMEP, Chapter 3.4.3.6

7.2.2.6 Ozone

The UV-absorption method using a continuous ambient air ozone analyser has been proven to be reliable and robust in field operation (EMEP, Chapter 3.9.1) and is therefore recommended for ozone measurements at IM sites. The recommended method is described in the EMEP manual (see references below):

Principle: EMEP, Chapter 3.9.3
Measuring equipment and handling: EMEP, Chapter 3.9.4. and 3.9.5 Calibration: EMEP, Chapter 3.9.5.2 and 3.9.5.3

Even though only monthly values (calculated from 1 hour average values) are to be reported to the IM programme centre, 1 hour average values are to be stored by the data originator and to be made available on request. In addition, the accumulated ozone exposure over a concentration of 40 ppb (AOT40) is to be calculated from the continuous measurements (ppbhours) and reported to the IM programme centre. The AOT40 values should be calculated for the day light hours (between 8 am and 8 pm) separately for each of the months April-September (using 1 hour average values).

The procedure for calculating AOT40 values is described in the manual of the UN/ECE-Mapping Programme (see reference below):

Calculation of results (AOT40): UN/ECE-Mapping Programme, Chapter3.2.4

7.2.2.7 Carbon dioxide

Measurements of carbon dioxide are not included in EMEP but are recommended to be performed in the IM programme on a voluntary basis. In the WMO programme GAW non-dispersive infra-red (NDIR) gas analysers have been widely used to measure CO_2 concentrations (WMO/TD-No.553). The NDIR method using a continuous ambient air CO_2 analyser is also recommended for CO_2 measurements at IM sites.

The recommended method is described in the WMO GAW guide (see references below):

Principle: WMO, Chapter 2.1.1
Measuring equipment and handling: WMO, Chapter 2.1.1
Calibration: WMO, Chapter 2.1.1

Alternative methods:
A simple method for the determination of SO_2, NO_2, NH_3 and O_3 is the so-called Passive flux sampling. The sampler consists of an impregnated filter where the absorption of the respective gases is a function of the ambient concentration. The method has proven to give comparable results with active sampling as described by the EMEP manual and may be beneficial at sites without electrical power supply. Passive flux sampling may also be applied to examine horizontal or vertical gradients e.g., in the study of representativity of neighbouring monitoring sites. For a detailed description of the method, it is referred to e.g. Ferm and Rohde, 1997.

7.2.3 Quality assurance / Quality control

It is very important to have a good quality of data, both being consistent in time (in order to assess trends) and space (for the comparisons between different sites and countries). The general procedures for quality assurance given by EMEP, Chapter 3.1.8 and in Chapter 8 of this manual should be followed. The QA/QC procedures should include all parts of the activities performed at the site, and in the laboratory.

Standard operation procedures should be followed for all activities. Necessary equipment, cleaning materials, sufficient supply of spare parts, etc. must be available. All operators should be well trained, sites and equipment must be inspected/controlled at least once a year by the quality assurance manager/data originator. The QA/QC routines in field also include field blanks and control samples, and sample transportation.

It is recommended that the chemical laboratory is accredited under one of the laboratory accreditation systems, or is performing close to these standards, e.g., EN 45001 and ISO/IEC guide 25. The laboratory must check on its performance, with respect to detection limits, precision, and repeatability, by repeated analysis of control solutions etc.

It is strongly recommended to participate annually in international intercomparisons for all analysed compounds. It is also recommended to participate in field intercomparisons. The IM programme centre will be able to give information about relevant intercalibrations. All data should be verified and validated following the instructions given by EMEP, Chapter 5 and 6.

7.2.4 Data reporting

Mandatory parameters	**list**		**unit**
SO2S	DB	sulphur dioxide as sulphur	µg/m^3
NDON	DB	nitrogen dioxide as nitrogen	µg/m^3

O3	DB	ozone	µg/m^3
AOT40	IM	Accumulated exposure Over a Threshold of 40 ppb	ppb*h
SO4S	DB	sulphate as sulphur (particulate, medium = PARTICLE)	µg/m^3
NO3N_T	IM	sum of nitrates in aerosols and gaseous nitric acid $\sum(NO_{3\ (part.)}^{-} + HNO_{3\ (gas)})$	µg/m^3
NH4N_T	IM	sum of gaseous ammonia and ammonium in aerosols $\sum(NH_{3\ (gas)} + NH_{4\ (part.)}^{+})$	µg/m^3
Optional parameters:	**list**		**unit**
CO2	DB	carbon dioxide	mg/m^3

Example files (Excel format is preferred)

AC example Excel file
AC example ASCII file

- File identifier SUBPROG states the subprogramme.
- MEDIUM refers to the analysed fraction, i.e., gaseous compound (GAS) or particulate compound (PARTICLE). Combined media are referred to as GASPART.
- LEVEL is given as the distance of the measuring equipment from the ground (cm).
- Spatial pool SPOOL gives the number of recording devices used for each parameter.
- For most parameters average monthly values are reported, status flag is X.
- General information on flags is given in Chapter 4.
- Sampling year and month are given as YYYYMM.

7.2.5 References

Berg, T., Hjellbrekke, A.G. and Skjelmoen, J.E., 1996. Heavy metals and POPs within the ECE region. EMEP/CCC-Report 8/96. Kjeller, Norwegian Institute for Air Research.

EMEP web-manual: EMEP manual for sampling and analysis
http://www.nilu.no/projects/ccc/manual/

EMEP manual for sampling and chemical analysis, EMEP/CCC-Report 1/95, NILU, Kjeller, Norway, March 1996.

Ferm, M. and Rohde, H., 1997. Measurements of air concentrations of SO2, NO2 and NH3 at rural and remote sites in Asia. J. Atmos. Chem. 27, 17-29.

UN/ECE-Mapping Programme. Manual on methodologies and criteria for mapping critical levels / loads. Umweltbundesamt Texte 71/96, Federal Environmental Agency, Berlin, Germany, September 1995.

WMO Global atmospheric watch guide, WMO / TD-NO. 553 World Meteorological Organization, 1993.

7.3 Subprogramme PC: Precipitation chemistry

7.3.1 Introduction

The purpose of the precipitation chemistry (PC) subprogramme is to quantify the input of precipitation and ions in precipitation (wet deposition) to the integrated monitoring area. The PC subprogramme shall also give information compatible with the throughfall (TF) subprogramme and further be comparable with other UNECE activities under the Convention on Long Range Transboundary Air Pollution (LRTAP). The deposition of pollutants to the ecosystems by precipitation is assumed to be a major factor affecting the natural processes in the environment. The main focus of the PC subprogramme is the sampling and chemical analysis of precipitation with particular emphasis on the acidifying compounds and on nutrients. By the simultaneous use of information from the subprogrammes on meteorology, air chemistry, throughfall, and stemflow, even total deposition to the site or parts of the site may be inferred for some compound.

At sites frequently influenced by fog and clouds, a significant fraction of the deposition input may deposit by fog (occult deposition). Since the usual precipitation sampler usually do not collect fog, other and more sophisticated methods are needed. At a workshop (Lövblad et al. 1993) current knowledge of cloud and fog deposition was evaluated. It should be noted, however, that the throughfall sampling will be influenced by fog deposition and may serve as an indicator of the amount of fog deposition.

It is strongly recommended that the participants of the ICP IM programme follow the recommended methods as described below. If methods other than those recommended in this manual are used, their comparability to the recommended method should be demonstrated by the data originators.

7.3.2 Sampling methods

7.3.2.1 Siting and number of collectors

Besides the general siting criteria given in Chapter 5.2, the specific siting criteria as described by EMEP, Chapter 2.2 should be followed.

The site should represent the deposition for the whole IM site. There should be no obstacles, such as trees, above 30° from the rim of the precipitation collector, and buildings, hedges, or topographical features which may give rise to updraughts or downdraughts should be avoided.

A detailed description of site requirements is given in the EMEP manual EMEP, Chapter 3.1.3. Data from neighbouring monitoring stations meeting the above-mentioned criteria (e.g. EMEP sites) may be used for ICP IM purposes, provided that they can be shown to be representative for the IM site.

It is recommended to control the measurements of precipitation with a standard rain gauge. It is also recommended to have at least two parallel collectors if weekly samples are taken.

7.3.2.2 Type of collector

Wet deposition may be determined using a bulk precipitation sampler (sampler open also in dry periods) or a wet only sampler. The advantage of the wet only sampler is the reduced deposition of gases and particulates compared to the bulk, which may be a problem at sites with local emission sources and particularly for the coarse particulates. On the other hand, the bulk sampler has several advantages, e.g. comparability to the throughfall measurements, no need for power supply, and the aerodynamical design may be better. In addition, the bulk sampler has several advantages over the wet only sampler during the winter period. If the bulk sampler is used, it is important to verify to which extent gases and particles are deposited to the bulk sampler, and to take measures to avoid/ reduce dry deposition to the sampler.

Due to the easy maintenance of the bulk precipitation sampler, it is recommended as the minimum mandatory equipment to be used at the IM sites.

The wet only sampling equipment is described in detail by EMEP, Chapter 3.1.4. including some general information about other types of collectors.

The construction principles for bulk deposition gauges are relatively simple. The sampler should not be too large or bulky, because this will obstruct the air flow around the sampler. On the other hand, the diameter of the collector must be large enough to provide samples large enough for chemical analysis. In practice, a diameter of 20 cm is sufficient for weekly sampling.

The sampling equipment normally consists of a funnel and a receiving vessel. If a funnel is used, there should be a vertical section of at least 5 cm height. An example of a bulk precipitation sampler is shown in figure 7.3.1. When precipitation is in the form of snow, it is advisable to use a special snow collector, an open cylinder of diameter 20 cm. The height of the cylinder should be at least twice the diameter to prevent "blow-out". The snow collector should be equipped with a tight-fitting lid, which is put on when the collector and sample is brought indoors for the sample to melt.

In order for the sample not to be contaminated from the ground during heavy rain, the rim of the funnel should be positioned 1.5-2 m above the ground level. Collectors should be designed to prevent contamination by bird droppings by e.g., a bird ring.

The material of the funnel and collection bottle should not in any way alter the chemical composition of the sample and give a reliable measure of the amount of precipitation. Both funnel and sampling bottle should be cleaned with deionized water when samples are taken (and at least weekly to avoid contribution from dry deposition) even if no precipitation events have occurred.

Evaporation changes can be particularly serious and may result in a significant enhancement of the concentration of the sample. Electrical heating of the precipitation collector in order to melt snow is therefore not recommended. Precipitation amount in the collector may by influenced by both low catch efficiency or blow off (particularly of snow) as well as evaporation. It is important the data originator verifies which of these processes have caused the deviation, and further reports the relevant amount for the determination of wet deposition (in case of evaporation, the observed amount should be reported whereas in case of lost sample, corrections should be made based on other available information). The simultaneous use of an automatic rain gauge and bulk deposition collectors is strongly recommended, as this will provide an indication of evaporative losses.

7.3.2.3 Sampling frequency

It is recommended that precipitation samples are taken so that correct monthly values can be derived. Due to quality assurance/quality control reasons individual sampling period should be as short as possible, weekly is recommended, daily if possible. If samples in addition are collected on the first of the month, monthly values can be determined. The sampling integration time should be harmonized with throughfall and stemflow and if practical with other relevant subprogrammes e.g., stream water.

Weekly sampling may to some extent cause biodegradation of the samples. By shielding the samplers using aluminium foil, this degradation will be strongly reduced. It is, however, not recommended to add preservatives. If samples are taken daily and kept cool, the decomposition, particularly of ammonium and nitrate, is strongly reduced.

Weekly samples can be analysed as they are or, in order to save expenses, mixed to monthly samples before analysis. If samples are mixed, they must be mixed in proportion to the total sample volume. Special care must be taken in the mixing procedure in order to avoid contamination and errors.

FIGURE 7.3.1. AN EXAMPLE OF A SUITABLE COLLECTOR FOR SAMPLING DEPOSITION

7.3.2.4 Collection and handling of precipitation samples

The sampling procedure is described in EMEP, Chapter 3.1.5. There are, however, special demands for the trace metal sampling. Recommendations on sampling of heavy metals in precipitation are included in the EMEP manual (see Chapter 3.10 in EMEP web-manual).

The general procedures for collection and handling of all water samples are described in Chapter 8.2.

7.3.3 Chemical analyses

The set of mandatory parameters for the PC subprogramme are: sulphate, nitrate, ammonium, chloride, sodium, potassium, calcium, magnesium, and alkalinity (depending on pH). However, it is also recommended for quality assurance reasons to determine the electrical conductivity.

The use of adequate methods is the responsibility of the national institutes. A list of available standards is given in section 8.5.

The recommended method for determination of the major ions is ion chromatography. Suitable alternative methods are, for example, atomic absorption spectrometry for Na, K, Ca, Mg, and spectrometric methods for ammonium. The recommended method is described in the EMEP manual, Chapter 4.1, alternative methods are described in EMEP, Chapters 4.2 - 4.6.

The recommended method for determination of pH, strong and weak acids is potentiometry, as described in the EMEP manual, Chapter 4.7. An alternative method for the determination of strong and weak acids is the coulometric titration method (modified Gran's titration). This method is described in the EMEP manual, Chapter 4.8.

The recommended method for determination of conductivity is conductometry. The method is described in detail in the EMEP manual, Chapter 4.9.

The EMEP has implemented heavy metals in its monitoring programme in 1999. Recommendations on sampling and chemical analysis of heavy metals are now included in the EMEP manual (see EMEP web-manual).

7.3.4 Quality assurance/Quality control

It is very important to have a good quality of data, both being consistent in time (in order to assess trends) and space (for the comparisons between different sites and countries). The general procedures for quality assurance given by EMEP, Chapter 3.1.8 as well as procedures in Chapter 8 of this manual should be followed. The QA/QC procedures should include all parts of the activities performed at the site, and in the laboratory.

Standard operation procedures should be followed for all activities. Necessary equipment, cleaning materials, sufficient supply of spare parts etc. must be available. All operators should be well trained, and sites and equipment must be inspected/controlled at least once a year by the quality assurance manager/data originator. The QA/QC routines in the field include addition of field blanks and control samples, and also requirements for sample transportation.

It is expected that the chemical laboratory is accredited under one of the laboratory accreditation systems, or is performing close to these standards, e.g., EN 45001 and ISO/IEC guide 25. The laboratory must check on its performance, with respect to detection limits, precision, and repeatability, by repeated analyses of control solutions etc.

It is strongly recommended to participate annually in international intercomparisons for all analysed compounds. It is also recommended to participate in field intercomparisons. The ICP IM Programme Centre will be able to give information about relevant intercalibrations. All data should be verified and validated following the instructions given by EMEP, Chapter 5 and 6.

7.3.5 Data reporting

Mandatory parameters	**list**		**unit**
PREC	DB	precipitation amount	mm
PH	DB	pH	
COND	DB	specific conductivity	mS/m
SO4S	DB	sulphate as sulphur	mg/l
NO3N	DB	nitrate as nitrogen	mg/l
NH4N	DB	ammonium as nitrogen	mg/l

CL	DB	chloride	mg/l
NA	DB	sodium	mg/l
K	DB	potassium	mg/l
CA	DB	calcium	mg/l
MG	DB	magnesium	mg/l
ALK	DB	alkalinity, GRAN plot (if annual mean pH>5)	µeq/l
Optional parameters:	**list**		**unit**
AL	DB	aluminium	µg/l
MN	DB	manganese	µg/l
FE	DB	iron	µg/l
AS	DB	arsenic	µg/l
CD	DB	cadmium	µg/l
CR	DB	chromium	µg/l
CU	DB	copper	µg/l
MO	DB	molybdenum	µg/l
NI	DB	nickel	µg/l
PB	DB	lead	µg/l
ZN	DB	zinc	µg/l

PO4P	DB	phosphate as phosphorous	µg/l
PTOT	DB	total phosphorous	mg/l
STOT	DB	total sulphur	mg/l
NTOT	DB	total nitrogen	mg/l

Example files (Excel format is preferred)

PC example Excel file
PC example ASCII file

- File identifier SUBPROG states the subprogramme.
- MEDIUM refers to either bulk deposition (BULK) or wet deposition (WET) sampler.
- LEVEL is given as the distance of collectors from the ground (cm).
- Spatial pool SPOOL refers to the number of individual samplers used for each parameter.
- Deposition values, except precipitation amount, are reported as monthly volume weighted means, status flag is W, monthly samples without status. Precipitation amount is reported as monthly sum, status flag is S. General information on flags is given in Chapter 4.
- Sampling year and month are given as YYYYMM, day field is left blank.
- No corrections for sea-salt derived sulphate should be made, rather it is emphasised that both sodium, magnesium and chloride should be reported. For calculation of volume weighted means, please see Annex 7.

7.3.6 References

EMEP web-manual: EMEP manual for sampling and analysis
http://www.nilu.no/projects/ccc/manual/

EMEP manual for sampling and chemical analysis, EMEP/CCC-Report 1/95, NILU, Kjeller, Norway, March 1996.

ICP Forests Manual, 2016
http://icp-forests.net/page/icp-forests-manual

ICP Forests manual, 1997. Manual on methods and criteria for harmonized sampling, assessment, monitoring, and analysis of the effects of air pollution on forests, 4th edition. Edited in 1997 by the Programme Coordination Centre Federal Research Centre for Forestry and Forest Products (BFH), Hamburg, Germany.

ICP Forests manual, 1994. Manual on methods and criteria for harmonized sampling, assessment, monitoring, and analysis of the effects of air pollution on forests, 1994 edition. Edited by the Programme Coordination Centres Hamburg and Prague.

Lövblad, G., Erisman, J.W. and Fowler, D. (Eds), 1993. Models and methods for the quantification of atmospheric input to ecosystems. Report from a workshop held in Gothenburg, Sweden, 3-6. November 1992. Copenhagen, Nordic Council of Ministers (Nordiske Seminar- og Arbeidsrapporter 1993:573).

7.4 Optional subprogramme MC: Metal chemistry of mosses

7.4.1 Introduction

Mosses are suitable for analysing heavy metal deposition and retention since they depend solely upon atmospheric water supply. However, in order to use the heavy metal content of moss as an indicator of atmospheric deposition, a relationship between the two has to be established. This relationship will be dependent on the moss species, geographical location, and will differ between the investigated chemical elements. In order to define this relationship, also measurements of atmospheric deposition have to be undertaken. The relationship is fairly good for the elements Pb, As (not in coastal areas), V, and Cd, relatively good for Cu and Ni, and relatively poor for Zn, Cr, and Fe (Cr and Fe are generally originating from soil dust in background areas).

MC as a bioaccumulator of heavy metal deposition can be used to relate deposition to the biological subprogrammes EP and VG (trunk epiphytes and field and bottom layer vegetation). Another advantage of the MC method is the possibility for detailed regional surveys. In this respect mosses have proven to be a cheap and efficient tool.

7.4.2 Methods

Sample mosses in open areas of forests or young plantations. The sampling place should be located at least 5 m from the nearest tree in order not to be exposed to direct throughfall or stemflow water. If such sampling places cannot be found, samples are taken from open heathland or peatland, where mosses often can be found (and should be sampled) in the neighbourhood of dwarf shrubs. Avoid a canopy of shrubs and large-leaved herbs. Do not sample on rocks.

Two moss species are preferred: *Pleurozium schreberi* and *Hylocomium splendens*. Where both are present priority is given to the former species. If these species do not exist other species can be used. A sample from an area should consist of only one of the two species - no mixture.

The sampling frequency for mosses is every 5 years.

Collect at least 3 composite moss samples. The most suitable collecting period is early summer, before the growing period of mosses. One composite sample should consist of five to ten subsamples spread around each sampling place. About 2 litres of moss material is needed (the final

dry weight of the cleaned material will be about 20 g). Use clean plastic gloves and do not smoke during sampling.

Place the subsamples side by side in large (5 dm^3) paper or plastic bags and carefully close the bags to prevent contamination during transport. Store the moss material in paper bags and dry at 40 °C as soon as possible. If stored in plastic bags (moist samples), the material should be moved to paper bags after air-drying or stored frozen until further treatment can take place.

Remove all dead material and attached litter from the samples so that only green (or brownish green) shoots from the three most recent years are included, i.e., three fully developed carpet segments of *Pleurozium schreberi* (or a corresponding portion of *Hylocomium splendens*), excluding the half-developed segment from the ongoing growing period if such exists. Broken individuals are discarded. Handle the mosses on clean laboratory paper, glass shields or clean polyethene and avoid contamination from smoke and laboratory tables.

Dry the samples at 40 °C to a constant weight, which is used as a reference in the calculations. Carefully close and store the dried material not used in the analyses in an environment specimen bank for later investigations.

Only wet ashes in closed systems are used during digestion of dried and homogenized mosses, since some metals (especially As) may escape when using dry ashing.

7.4.3 Chemical analyses

1 - 5 g of moss is boiled in conc. HNO_3 or in a 4:1 mixture of conc. HNO_3 and $HClO_4$. The solutions are filtered and kept in polyethylene bottles before analysis (AAS in flame and graphite furnace or ICP or neutron activation).

7.4.4 Quality assurance/Quality control

See data quality management in Chapter 8.

7.4.5 Data reporting

Parameters:

Parameters	**list**		**unit**
AS	DB	arsenic	mg/kg
CD	DB	cadmium	mg/kg
CR	DB	chromium	mg/kg
CU	DB	copper	mg/kg

FE	DB	iron	mg/kg
HG	DB	mercury	mg/kg
NI	DB	nickel	mg/kg
PB	DB	lead	mg/kg
ZN	DB	zinc	mg/kg

Example files (Excel format is preferred)

MC example Excel file
MC example ASCII file

- File identifier SUBPROG states the subprogramme.
- Station number SCODE is given as 9999 to represent the whole IM site.
- MEDIUM refers to the analysed moss species, i.e., *Pleurozium schreberi* (PLEU SCH) or *Hylocomium splendens* (HYLO SPL), medium code list is M2 (from NCC species codelists, see Annex 6).
- Spatial pool SPOOL refers to the number of sampling places from which the composite samples are taken (5 in the example).
- Sampling year and month are given as YYYYMM, day field is left blank.

7.4.6 References

Atmospheric heavy metal Deposition in the Northern Europe 1990. Nord 1992:12.

7.5 Subprogramme TF: Throughfall

7.5.1 Introduction

In forests part of the precipitation falls through gaps in the canopy without being intercepted and part is intercepted during its passage through the canopy. Together the parts are called (crown) throughfall. The part running down the tree trunk is called stemflow (see SF subprogramme). Together, throughfall and stemflow can be called total throughfall or stand precipitation. The main purpose of the TF subprogramme is to enable the total deposition input to the soil under the forest canopy and forest vegetation to be determined. Empirical methods have been used for the quantification of total deposition to forested ecosystems (Bredemeyer 1988). In forested areas, throughfall and bulk deposition from an open area (see subprogramme Precipitation chemistry, PC) are both needed to estimate the total deposition input to forested sites. This is done by comparing TF with PC, to assess canopy interception and the interaction and internal cycling of nutrients. For some types of forest stands, also stemflow (see Stemflow SF subprogramme) is needed.

7.5.2 Sampling methods

7.5.2.1 Siting and number of collectors

Besides the general siting criteria given in Chapter 5.2, those given in the ICP Forests manuals should be considered. Throughfall deposition measurements should be carried out in such a way that the other monitoring activities are not influenced significantly by the measurement procedure.

In order to take into account the large local variations in throughfall deposition, a sufficiently large number of collectors must be used. Less than 10 samplers are usually insufficient to cover the variability. Carry out a pre-study to assess the variability of the forest stand in relation to how many throughfall collectors are necessary to collect a sample representative for the forest in question.

The collectors can be sited randomly or systematically (recommended) around the vegetation or soil intensive monitoring plots or form their own station nearby. Disturbances to the TF collectors by large animals may be prevented by surrounding the TF collectors with a fence.

The throughfall collectors should be placed with the collection surface horizontal to the ground surface at a height of approximately 1 m to prevent contamination from the soil. It is important to shield the sample container from sunlight and warming. It is therefore recommended to store the sample containers in a cool and dark place e.g. in a pithole.

7.5.2.2 Type of collector

The TF collectors may be funnel or gutter types but must be constructed from a material which does not alter the chemical composition of the sample. The TF collectors should preferably be the same as used for the PC subprogramme. This is because the amount of precipitation collected, and evaporation losses vary with the type and design of collector. If the same collectors are used for both TF and PC, the collectors will have the same collection and evaporation efficiencies and that loss of water due to evaporation is compensated for by a corresponding increase in concentrations. For snow sampling special collectors are recommended. See also PC Chapter.

7.5.2.3 Sampling frequency

Sampling will be made monthly, weekly or at a time interval between the two, e.g. every two or three weeks, depending mainly on climate and method used. It is recommended that precipitation

samples are taken so that correct monthly values can be derived. Long sampling period may to some extent cause biodegradation of the samples. By shielding the samplers using aluminium foil, this degradation will be strongly reduced. It is, however, not recommended to add preservatives.

The sampling integration time should preferably be the same for all deposition measurements (i.e. throughfall, stemflow and bulk deposition).

After each sampling period, the volume of each individual throughfall sample must be determined. Throughfall samples from a number of collectors may be pooled to a composite sample representative for a certain stand. Weekly samples can be analysed or mixed to monthly samples before analyses. If samples are mixed, they must be mixed in proportion to the total sample volume. Special care must be taken in the mixing procedure in order to avoid contamination and errors.

7.5.2.4 Collection and handling of throughfall samples

The recommended methodology for sampling, sample handling and cleaning is described in detail by ICP Forests manual, part VI and by EMEP, Chapter 3.1.4 - 3.1.5. There are special demands for the trace metal sampling, recommendations on sampling of heavy metals are incorporated in the new EMP manual.

The general procedures for collection and handling of all water samples are described in Chapter 8.2.

7.5.3 Chemical analyses

The TF subprogramme consists of the following **mandatory parameters:**

sulphate, nitrate, ammonium, total N, chloride, sodium, potassium, calcium, magnesium, dissolved organic carbon and strong acid (by pH). It is also recommended to determine the electrical conductivity and to determine alkalinity in the samples if annual median pH>5. The determination of total S and heavy metals is optional.

The recommended method for determination of the major ions in precipitation samples is ion chromatography. Suitable alternative methods are for example atomic absorption spectrometry for Na, K, Ca, Mg and spectrometric methods for ammonium. The recommended method is described in the EMEP manual, Chapter 4.1, alternative methods are described in EMEP, Chapters 4.2 - 4.6. A list of available standards is given in Chapter 8.5.

Optional parameters:

The recommended method for the determination of total nitrogen is by oxidation to nitrate by peroxidisulphate following the standard ISO/DIS 11905-1 and analysis by the spectrophotometric Griess method (EMEP, Chapter 4.3). Alternatively, total nitrogen may be determined by the Kjeldahl method. A suitable method for the determination of total sulphur (optional) is inductively coupled plasma spectrometry (ICP) ISO - 11885.

The recommended method for determination of pH, strong and weak acids is potentiometry, as described in the EMEP manual, Chapter 4.7. An alternative method for the determination of strong and weak acids is the coulometric titration method (modified Grans titration). This method is described in the EMEP manual, Chapter 4.8.

It is recommended to determine alkalinity if annual median pH>5. The recommended method for determining alkalinity is described in the standard EN ISO 9963-1 or alternatively by colorimetric titration (see above).

The recommended method for determination of conductivity is conductometry. The method is described in detail in the EMEP manual, Chapter 4.9.

The EMEP has included recommendations on sampling and chemical analysis of heavy metals in the EMEP manual (see EMEP web-manual).

7.5.4 Quality assurance/Quality control

It is very important to have a good quality of data, both being consistent in time (in order to assess trends) and space (for the comparisons between different sites and countries). The general procedures for quality assurance given by EMEP, Chapter 3.1.8 as well as procedures in Chapter 8 of this manual should be followed. The QA/QC procedures should include all parts of the activities performed at the site, and in the laboratory.

Standard operation procedures should be followed for all activities. Necessary equipment, cleaning materials, sufficient supply of spare parts etc. must be available. All operators should be well trained, and sites and equipment must be inspected/controlled at least once a year by the quality assurance manager/data originator. The QA/QC routines in the field include addition of field blanks and control samples, and also requirements for sample transportation.

It is expected that the chemical laboratory is accredited under one of the laboratory accreditation systems, or is performing close to these standards, e.g. EN 45001 and ISO/IEC guide 25. The laboratory must check on its performance, with respect to detection limits, precision, and repeatability, by repeated analyses of control solutions etc.

It is strongly recommended to participate annually in international intercomparisons for all analysed compounds. It is also recommended to participate in field intercomparisons. The ICP IM Programme Centre will be able to give information about relevant intercalibrations. All data should be verified and validated following the instructions given by EMEP, Chapter 5 and 6.

The quality assurance programme described by ICP Forests manual, part VI should also be followed.

7.5.5 Data reporting

Mandatory parameters	**list**		**unit**
PREC	DB	throughfall amount	mm
PH	DB	pH	
COND	DB	specific conductivity	mS/m

SO4S	DB	sulphate as sulphur	mg/l
NO3N	DB	nitrate as nitrogen	mg/l
NH4N	DB	ammonium as nitrogen	mg/l
NTOT	DB	total nitrogen	mg/l
CL	DB	chloride	mg/l
NA	DB	sodium	mg/l
K	DB	potassium	mg/l
CA	DB	calcium	mg/l
MG	DB	magnesium	mg/l
ALK	DB	alkalinity, GRAN plot (if annual mean pH>5)	µeq/l
DOC	DB	dissolved organic carbon	mg/l
Optional parameters:	**list**		**unit**
AL	DB	aluminium	µg/l
MN	DB	manganese	µg/l
FE	DB	iron	µg/l
AS	DB	arsenic	µg/l
CD	DB	cadmium	µg/l
CR	DB	chromium	µg/l

CU	DB	copper	µg/l
MO	DB	molybdenum	µg/l
NI	DB	nickel	µg/l
PB	DB	lead	µg/l
ZN	DB	zinc	µg/l
PO4P	DB	phosphate as phosphorous	µg/l
PTOT	DB	total phosphorous	mg/l (corrected!)
STOT	DB	total sulphur	mg/l (corrected!)

Example files (Excel format is preferred)

TF example Excel file
TF example ASCII file

- File identifier SUBPROG states the subprogramme.
- MEDIUM refers to the dominating tree species (from NCC code list B4, see Annex 6) of the stand. If two species are equally dominant, the species reported as medium for throughfall is the one with the largest intercepting leaf area.
- LEVEL is given as the distance of sampling devices from the ground (cm).
- Spatial pool SPOOL refers to the number of individual samplers used for each parameter.
- Values from weekly measurements are reported as volume weighted monthly means, status flag is W. If the throughfall amount cannot be adequately measured, the concentrations for weekly measurements are reported as monthly means, status flag is X. Monthly measurements are reported without status. Throughfall amount is reported as monthly sum, status flag is S. For calculation of volume weighted means, please see Annex 7. General information on flags is given in Chapter 4.
- Sampling year and month are given as YYYYMM, day field is left blank

Codes for most common European tree species from NCC code list B4 (see Annex 6):

ABIE ALB, Abies alba
ABIE NOR, Abies nordmanniana
ACER CAM, Acer campestre
ACER PLA, Acer platanoides
ACER PSE, Acer pseudoplatanus

ALNU GLU, Alnus glutinosa
ALNU INC, Alnus incana
BETU PEN, Betula pendula
BETU PUB, Betula pubescens
BE PU.TO, Betula pubescens ssp.tortuosa
CARP BET, Carpinus betulus
FAGU SYL, Fagus sylvatica
LARI DEC, Larix decidua
LARI SIB, Larix sibirica
PICE ABI, Picea abies
PI AB.OB, Picea abies ssp. obovata
PICE GLA, Picea glauca
PICE OMO, Picea omorika
PINU SYL, Pinus sylvestris
POPU BAL, Populus balsamifera
POPU NIG, Populus nigra
POPU TRA, Populus tremula
PRUN PAD, Prunus padus
QUER PET, Quercus petraea
QUER ROB, Quercus robur
TILI COR, Tilia cordata
TILI PLA, Tilia platyphyllos
ULMU GLA, Ulmus glabra
ULMU LAE, Ulmus laevis

7.5.6 References

EMEP web-manual: EMEP manual for sampling and analysis
http://www.nilu.no/projects/ccc/manual/

ICP Forests Manual, 2016
http://icp-forests.net/page/icp-forests-manual

ICP Forests manual, 1997. Manual on methods and criteria for harmonized sampling, assessment, monitoring, and analysis of the effects of air pollution on forests, 4th edition. Edited in 1997 by the Programme Coordination Centre Federal Research Centre for Forestry and Forest Products (BFH), Hamburg, Germany.

ICP Forests manual, 1994. Manual on methods and criteria for harmonized sampling, assessment, monitoring, and analysis of the effects of air pollution on forests. 1994 edition. Edited by the Programme Coordination Centres Hamburg and Prague.

Bredemeier, M. 1988. Forest canopy transformation of atmospheric deposition. Water, Air, and Soil Pollution 40:121-138.

7.6 Optional subprogramme SF: Stemflow

7.6.1 Introduction

Stemflow measurements are made as part of the assessment of water and chemical fluxes within a forest stand (deposition). Precipitation reaches the ground directly, by dripping off foliage and branches and by trickling down the stem. It is the last category that is captured by stemflow measurements. In addition to providing information on fluxes, stemflow chemistry has an important influence on the corticolous lichens present on the stem (see subprogramme EP), and their associated microfaunas, and also has a significant impact on the soil properties at the base of the stem.

The amount of stemflow varies markedly between species and is strongly dependent on the branch structure. Trees with branches with upwards orientation (e.g. *Fagus sylvatica*) tend to have much greater amounts of stemflow (contributing 10-40% of total stand precipitation) than those with drooping branches (e.g. *Picea abies*) (contributing <1% of total stand precipitation). Consequently, stemflow need not be measured on all tree species.

7.6.2 Sampling methods

Ten trees each of the most important species (i.e. >20% of the basal area in the plot) should be monitored. Trees should be representative of the range of basal areas present in the study area.

Sampling will be made monthly, weekly or at a time interval between the two, e.g. every two or three weeks, depending mainly on climate or method used. It is recommended that samples are taken so that correct monthly values can be derived. The sampling integration time should preferably be the same for all deposition measurements (i.e. throughfall and precipitation chemistry).

A variety of different types of equipment exist for measuring stemflow. The majority are based on a spiral collector wrapped around the stem of the tree. When installing such collectors, a variety of points must be taken into consideration:

- Trees grow, and the design must allow for both the diurnal variations that occur in the circumference of a stem and the annual growth of a tree. Silicone is a good but expensive material for the purpose.
- Under no circumstances should the bark be damaged. Great care should be taken to ensure that the bark remains intact, otherwise sap may seep out, contaminating the stemflow. On species with rough bark (e.g. oak species), care should be taken to ensure that the flow is properly collected.

The collecting bottles must be of sufficient capacity to cope with large quantities of stemflow. For example, in beech, two 60 l containers may be necessary. Alternatively, sampling can be automated, and flow measured using a tipping-bucket mechanism.

- The collar should be fixed at of height of 0.5 to 1.5 m above the ground surface.

For the collection and handling of samples please refer to subprogramme Throughfall.

After each sampling period, the volume of each stemflow sample must be determined. If stemflow samples are pooled together, they can only be pooled for trees of the same species and similar size and dominance.

7.6.3 Chemical analyses

If the SF subprogramme is carried out, at least the following parameters should be determined: sulphate, nitrate, ammonium, total N, chloride, sodium, potassium, calcium, magnesium, and strong acid (by pH).

It is also recommended to determine the electrical conductivity and to determine alkalinity in the samples if annual median pH>5. The determination of total S and heavy metals is optional.

The same analytical methods as used for throughfall chemistry measurements should be adopted.

7.6.4 Quality assurance/Quality control

As for throughfall measurements.

7.6.5 Calculation of stemflow amount in mm from stemflow volumes

Stemflow amount is calculated **for each species separately** as:

Total stemflow volume in the plot for the species (in litres) =

[Total amount of SF collected from the species (l) x Stand basal area of the species (m^2/ha)] / [Basal area of the SF trees of that species (m^2/ha)]

The result is divided by the size of the plot (m^2) to get the stemflow amount for the species in mm.

7.6.6 Data reporting

Mandatory parameters	**list**		**unit**
PREC	DB	stemflow amount	mm
PH	DB	pH	

COND	DB	specific conductivity	mS/m
SO4S	DB	sulphate as sulphur	mg/l
NO3N	DB	nitrate as nitrogen	mg/l
NH4N	DB	ammonium as nitrogen	mg/l
NTOT	DB	total nitrogen	mg/l
CL	DB	chloride	mg/l
NA	DB	sodium	mg/l
K	DB	potassium	mg/l
CA	DB	calcium	mg/l
MG	DB	magnesium	mg/l
ALK	DB	alkalinity, GRAN plot (if annual mean pH>5)	µeq/l
DOC	DB	dissolved organic carbon	mg/l
Optional parameters:	**list**		**unit**
AL	DB	aluminium	µg/l
MN	DB	manganese	µg/l
FE	DB	iron	µg/l
AS	DB	arsenic	µg/l
CD	DB	cadmium	µg/l

CR	DB	chromium	µg/l
CU	DB	copper	µg/l
MO	DB	molybdenum	µg/l
NI	DB	nickel	µg/l
PB	DB	lead	µg/l
ZN	DB	zinc	µg/l
PO4P	DB	phosphate as phosphorous	µg/l
PTOT	DB	total phosphorous	mg/l
STOT	DB	total sulphur	mg/l

Example files (Excel format is preferred)

SF example Excel file
SF example ASCII file

- File identifier SUBPROG states the subprogramme.
- Stemflow measurements are reported for each species separately. MEDIUM refers to the tree species (from NCC code list B4, see Annex 6). For a list of most common tree species see subprogramme TF.
- LEVEL is given as the distance of sampling devices from the ground (cm).
- Spatial pool SPOOL refers to the number of individual samplers used for each parameter.
- Values from weekly measurements are reported as volume weighted monthly means, status flag is W. If the stemflow amount cannot be adequately measured, the concentrations for weekly measurements are reported as monthly means, status flag is X. Monthly measurements are reported without status. Stemflow amount is reported as monthly sum, status flag is S. For calculation of volume weighted means, please see Annex 7. General information on flags is given in Chapter 4.
- Sampling year and month are given as YYYYMM, day field is left blank.

7.6.7 References

ICP Forests Manual, 2016
http://icp-forests.net/page/icp-forests-manual

ICP Forests manual, 1997. Manual on methods and criteria for harmonized sampling, assessment, monitoring, and analysis of the effects of air pollution on forests, 4th edition. Edited in 1997 by the Programme Coordination Centre Federal Research Centre for Forestry and Forest Products (BFH), Hamburg, Germany.

7.7 Subprogramme SC: Soil chemistry

7.7.1. Introduction

Of the three environmental changes given the highest priority within the IM programme (see Chapter 2), only N and S deposition have implications for the soil chemistry subprogramme (the third, increasing atmospheric O_3 concentrations, can be expected to have little impact on soils, at least directly). Heavy metal pollution, which may be locally very important in terms of soil chemistry and ecotoxicological effects, has been given optional status only. *The minimum requirements of the SC subprogramme therefore reflects the acidification impacts of S and N deposition, and the eutrophication impact of N deposition.*

The parameters in the minimum SC subprogramme necessary for the relevant cause/effect relationships and for modelling (Table 7.7.1) include:

1. those properties describing the acid and N status of the soil, e.g. pH, CEC, BS, N, base cation concentrations. These represent the parameters for monitoring *soil quality per se,*

2. those background properties that largely determine soil acidity and nutrient status, i.e. organic matter content (OM) and particle size distribution (PSA). The soil quality parameters listed under i) above are strongly dependent on OM and PSA and therefore important in the interpretation of the soil quality parameters listed under point 1.

3. those parameters necessary for calculating soil chemistry pools/amounts, i.e. bulk density (BDEN) and stone content (SCONT). These parameters are required for making mass balance budgets of the soil quality parameters.

4. those soil properties/variables required by the various acidification and geochemical models that will be used within the IM programme, e.g. soil mineralogy (for weathering), parent material type, sulphate adsorption, nitrification rates, soil water retention characteristics.

It is important to distinguish between those soil parameters which are part of a routine monitoring programme describing soil quality (i.e. point 1. above) and those additional parameters which enable either interpretation or wider use of the soil quality data. The relationships between soil

quality parameters can be correlated with parameters from both within the SC subprogramme and from other subprogrammes. When the IM Programme Centre carries out modelling exercises, the NFPs will be contacted concerning the availability of data and parameters.

7.7.2. Methods

7.7.2.1. Field methods - Sampling

Principles

Because it is essential that the IM data is comparable in both time and space, it is better to sample the mineral soil by fixed depth soil layers rather than pedogenic horizons for monitoring purposes (but humus layer must be sampled separately). The arrangement of soil horizons varies spatially - not all the IM SC plots will have an E horizon, for example, and the thicknesses of the same horizon varies from site to site, making it difficult to compare soil nutrient pools. Since soil horizons and their mutual arrangement are the result of soil development processes, horizons have different properties. Therefore, the use of fixed depth layers may be criticised because a fixed depth layer may contain soil from more than one pedogenic horizon.

Nevertheless, as the SC plot should be as homogeneous as possible with respect to soil type and parent material, a fixed depth layer of the mineral soil would consist of the same soil material each time, and therefore be comparable between sampling occasions. Also, since all SC plots would have a 0-5 cm layer, for example, this layer can be compared directly between plots and IM sites (NB. 0=top of mineral soil). Finally, the amount of N in the 0-20 cm layer, for example, can be computed and compared directly among all SC plots and IM sites. For these reasons, it is recommended to use fixed depth layers in the minimum SC monitoring subprogramme.

However, a soil profile description should be made at the plot and samples taken by pedogenic horizon for classification and characterisation purposes. Also, the soil parameters required by relevant simulation models usually refer to soil horizons. This reflects the process orientation of such models. Such sampling need only be done once and from a single soil pit at each SC plot.

Permanent SC plot and sampling design

A permanent homogeneous SC plot of the order of 40 x 40 m, its size depending on the heterogeneity of the site, should be established (see Chapter 5.2). This SC plot should be located close to, but not coinciding with, the VG monitoring plot. The sampling procedure should abide by the following principles: it should be systematic, cover the whole soil plot each sampling occasion, and to include an adequate number of subsamples so as to give sufficient precision as to allow possible changes over time (decades) to be detected. A record of the places sampled should also be recorded, so that they will not be resampled at a later date.

An example of a SC plot and its sampling is shown in Figure 7.7.1. It is divided into 10 x 10 m subplots, which are further divided into 1 x 1 m subplots. A soil sample is taken from one of the 1 x 1 m subplots, which have not been used earlier or rejected because of logs, boulders, large roots etc., in each of the 10 x 10 m subplots so that the entire soil plot is covered. In the example, 16 10 x 10 m subplots are thus sampled.

Compositing

In order to reduce the number (and costs) of samples for analysis, soil samples are often composited. Compositing all the samples into a single sample for analysis, however, means that there is no information about the within-plot variability with which to test for significant differences

and calculate confidence limits. A number of compositing strategies can be used to obtain a limited number of samples for analysis while still retaining information about variability. For example, each of the samples can be analysed individually on at least one sampling occasion to determine a reference variability value and samples taken on subsequent sampling occasions bulked (Fig. 7.7.2 a); a limited number (3-4) of parallel samples can be taken at each sampling point, each of the parallel samples being composited over the entire plot (Fig. 7.7.2 b); individual samples taken at each sampling point can be composited on a random basis into 3-4 samples for the plot (Fig. 7.7.2 c).

Sampling timetable

Sampling should be carried out approximately every 5th year, each time at the end of the growing season in August-October. Sampling could be synchronised with other IM subprogrammes and EU European Programme for the Intensive Monitoring of Forest Ecosystems (Haussmann 1995) sampling timetable:1995, 2000, 2005.

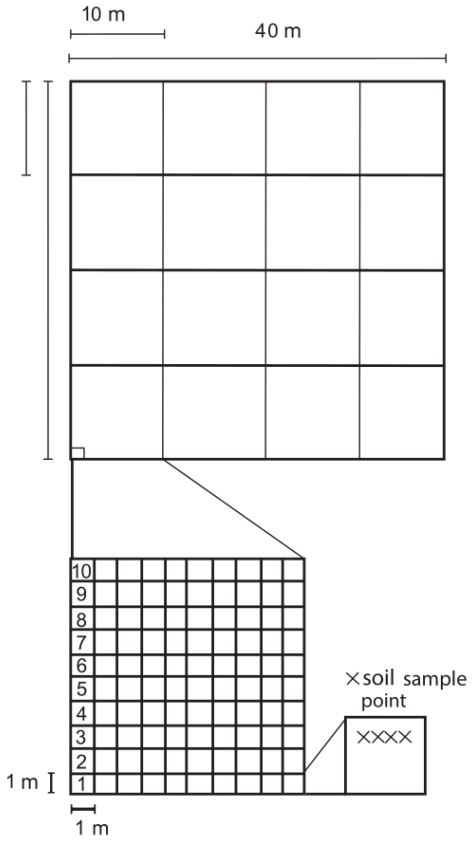


FIGURE 7.7.1 AN EXAMPLE OF A SC PLOT AND ITS SAMPLING.

Sampling procedure

The **humus layer** should be sampled separately with a cylinder (steel or some other such inert material) of known diameter. The sample should include only the Of+Oh organic layers, i.e. the green and litter (Ol) material should be excluded. Record thickness of each humus sample so that bulk density (BDEN) can be calculated. Humus form (mor, moder, mull) should also be recorded.

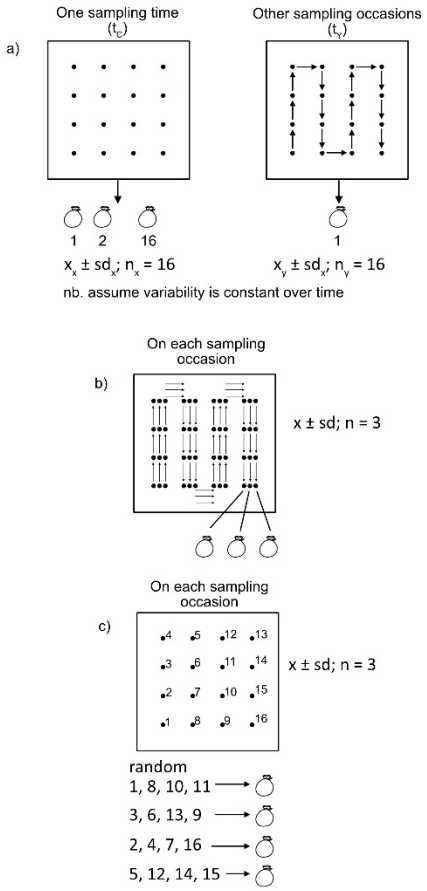


FIGURE 7.7.2 A-C. COMPOSITING STRATEGIES IN SC SAMPLING.

It is recommended that the following **mineral soil layers** are sampled: 0-5 cm, 5-10 cm, 10-20 cm, 20-40 cm, 40-80 cm. These layers are those advised in the ICP Forests Level II programme (ICP Forests 1994,1997) and are to be used within the EU European Programme for the Intensive Monitoring of Forest Ecosystems (Haussmann 1995). However, for those countries that have already started an IM SC subprogramme, it may be preferable to continue using the original SC recommended layers: 0-5 cm, 5-20, 20-40 and 60-80 cm or C horizon material (EDC 1993). In order to minimise disturbance, it is recommended to use a soil auger to take the samples. However, it may be difficult to take a sample from the deeper layers directly with an auger and some excavation may be necessary. Alternatively, only sample those layers that can be adequately sampled from the surface with an auger. If the thickness of a sample is less than a threshold thickness (e.g. 75% of the target thickness of a layer), it is rejected.

The volume of mineral soil samples taken with an auger are usually not accurate enough to allow bulk density to be calculated. Therefore, a set of undisturbed samples of the same layers should be taken for bulk density determination. These samples can be taken from a soil pit dug near to but outside the plot. Alternatively, transfer functions of the type described by Tamminen & Starr (1994) could be used. A sample of the deeper layers that were not possible to sample on the plot with the

auger could also be taken from this pit. It is also recommended that a profile description is made from this pit (Table 7.7.3) and a sample of each pedogenic horizon described taken.

Peat samples should be taken from the following depths: 0-5, 5-20 and 20-40 cm. It is relatively easy to take the peat samples volumetrically with a box-type sampler, e.g. 5 x 5 cm. A general description of the peat, including at least humification degree (von Post scale) and peat type (botanical composition), should be made from a profile at a representative point near the plot.

The soil samples should be kept in carefully labelled plastic bags in the dark and cold (+4ºC) until they can be pre-treated.

Sample pre-treatment
Dry the samples at approximately +40ºC to constant weight as soon as possible after collection. Sieve the samples through a 2 mm mesh (4 mm for organic samples or remove large material: cones, wood pieces etc, by hand). Retain the <2 mm material for analysis. The organic soil samples (humus layer and peat) should be milled into a fine powder. Keep the air-dried samples in dark, cool, and dry conditions to await analysis. (Note: If the samples cannot be analysed immediately following pre-treatment, it is better to store pre-treated samples than fresh samples).

7.7.2.2 Laboratory analyses

A list of parameters and codes for the minimum SC subprogramme are given in Table 7.7.1. The methods described in the previous manual (EDC 1993) are still recommended and should be referred to. The corresponding ISO method is also recommended where possible. Use of national method differing from those recommended is strongly advised against. However, if used, then a calibration regression model between the national method and one of the recommended methods is expected by the ICP IM Programme Centre, together with method description. In the original IM methods, 1 M NH_4Cl and 1M KCl were recommended as the extractants for the exchangeable chemistry. The use of 0.1 M $BaCl_2$ has a number of advantages however (Hendershot & Duquette 1986):

1) all the exchangeable chemistry can be done with one extractant instead of NH_4Cl and KCl,

2) the use of 0.1 M rather than 1M solutions results in less blocking of ICP and AAS burners. However, there is a health risk attached to the use of Ba.

A list of standards is available in Chapter 8.5

The laboratory should be made aware of possible problems with high reagent blanks due to impurities in reagents.

7.7.3 Quality assurance/Quality control

Each NFP is expected to ensure that good laboratory practice is followed and are responsible for the quality of data reported to ICP IM Programme Centre. The results of quality controls, laboratory intercalibrations etc. undertaken (either with IM samples in particular or of the laboratory in general) should be reported to the IM Programme Centre. The Programme Centre also encourages participation in international soil analysis intercalibration exercises. Any comparisons of national methods deviating from the recommended IM methods that have been made should also be reported.

See data quality management in Chapter 8.

7.7.4 Data handling

Derived SC parameters (see Table 7.7.1) can either be reported directly to the Programme Centre or the Programme Centre can calculate these parameters from the primary parameters.

7.7.5. Data reporting

See Tables 7.7.1 and 7.7.2 for a list of mandatory and optional parameters. An example of reporting mandatory and optional parameters. Profile descriptions will be reported separately.

Table 7.7.1 SC Mandatory (minimum) parameters

Parameter †	**Code (list)** **report also pre-treatment!**	**Reporting Units**	**Recommended methods and comments** ‡
Measured:			
pH (CaCl2)	PH (DB)	pH value	Original method (EDC 1993) or ISO/DIS 10390 (ISO-1:5 volume/volume and shaking time 5 min, let stand for 2-24 h before measurement, otherwise similar to original IM method).
S total	STOT (DB)	mg/kg	Original manual method (EDC 1993).
P total	PTOT (DB)	mg/kg	Original manual method (EDC 1993); no ISO method
N total	NTOT (DB)	mg/kg	Original manual method (EDC 1993), ISO 11261 Kjeldahl N or ISO 13878 dry combustion
Ca exchangeable	CA (DB)	meq/kg **	Original 1M NH_4Cl, 1M KCl or 0.1M $BaCl_2$ extraction (EDC 1993) (NB Health risk with Ba)

Mg exchangeable	MG (DB)	meq/kg	Original 1M NH_4Cl, 1M KCl or 0.1M $BaCl_2$ extraction (EDC 1993) (NB Health risk with Ba)
K exchangeable	K (DB)	meq/kg	Original 1M NH_4Cl, 1M KCl or 0.1M $BaCl_2$ extraction (EDC 1993) (NB Health risk with Ba)
Na exchangeable	NA (DB)	meq/kg	Original 1M NH_4Cl, 1M KCl or 0.1M $BaCl_2$ extraction (EDC 1993) (NB Health risk with Ba)
Al exchangeable	AL (DB)	meq/kg	Original 1M NH_4Cl, 1M KCl or 0.1M $BaCl_2$ extraction (EDC 1993) (NB Health risk with Ba)
TOC	TOC (DB)	mg/kg	Original IM method, LECO Carbon analyser (grinding of <2 mm fraction may be necessary first), ISO/DIS 10694. For non-calcareous soils, TOC can be approximated as Loss on Ignition (OM) × 0.58.
exchangeable titrable acidity (H+Al)	ACI_ET (IM)	meq/kg	Original 1M NH_4Cl, 1M KCl or 0.1M $BaCl_2$ extraction (EDC 1993) (NB 1. Health risk with Ba. 2. Not possible to do exchangeable titrable acidity due to Al only.)
Derived/calculated[§] :			
CEC	CEC_E (IM)	meq/kg	CEC_E is calculated as Ca+Mg+K+Na+ACI_ET (EDC 1993)
Base Saturation	BASA (DB)	%	BASA is calculated as((Ca+Mg+K+Na)×100) /CEC_E (EDC 1993)
Weathering	WEA (IM)	meq/m^2/yr **	Base cation $weathering_i = output_i - input_i +/- \Delta storage_i$,

Explaining:			where: $output_i$= stream discharge of element i, $input_i$ = total deposition of element i, $\Delta storage_i$ = vegetation and soil pools of element i. * i=Ca^{2+} + Mg^{2+}
Dry Bulk Density, <2mm	BDEN (IM)	kg/m^3	ISO/DIS 11272 - may need to correct for weight of >2mm fraction. Mineral soil values can be estimated from PSA and organic matter (e.g. Tamminen & Starr 1994). Values for humus layer can easily be determined
Stone content, >2mm	SCONT (IM)	m^3/m^3	Profile description, Viro's steel rod penetration method (Viro 1952); urgently in need of development
PSA, <2mm fraction	PSA_SAND (IM) PSA_SILT (IM) PSA_CLAY (IM)	% (sand) % (silt) % (clay)	Particle size analysis, ISO/DIS 11277. Sand=2000-63 µm, Silt=63-2 µm, Clay< 2 µm

†Analysis to be made on air-dried and <2 mm fraction (milled sample in case of peat and forest floor samples). Values to be reported on oven-dry (105ºC) basis (except pH). For pre-treatment of samples, see ISO/DIS 11464 Soil Quality — Pre-treatment of samples for physico-chemical analyses.

‡National methods should be calibrated against the reference IM methods on a representative set of samples and the calibration regression model reported to IM Programme Centre. For Draft ISO/DIS methods, see: ISO Standards Compendium.

Environment. Soil Quality. General aspects; chemical and physical methods of analysis; biological methods of analysis. First edition. 1994. ISBN 92-67-10203-6

§These do not have to be reported as can be calculated by ICP IM Programme Centre. Data already reported to the ICP IM Programme Centre may be used to develop transfer functions for non-reported parameters

* For stable ecosystems, change in storage can be assumed to be 0 (White A.F. & Blum A.E., 1995).

** meq/kg = mmol (+)/kg;= $meq/m^2/y$ = $mmol(+)/m^2/y$

Table 7.7.2 SC Optional parameters

Parameter[1]	**Code (list)** **report also pre-treatment code!**	**Reporting Units**	**Recommended methods and comments**[2]
pH (water)	PH (DB)	pH value	Original method (EDC 1993) or ISO/DIS 10390 (ISO-1:5 volume/volume and shaking time 5 min, let stand for 2-24 h before measurement, otherwise similar to original IM method.)
exchangeable Mn, Fe	MN, FE (DB)	meq/kg **	Original 1M NH_4Cl, 1M KCl or 0.1M $BaCl_2$ extraction (EDC 1993) (NB Health risk with Ba)
Trace elements (Pseudo total) Cd, Pb, Cu, Zn, Ni, As, Cr, Mo, Hg	CD, PB, (DB) CU, ZN etc.	mg/kg	Original 7M HNO3 & autoclave at 120ºC (EDC 1993). ISO/DIS 11466 Aqua Regia method - laborious, problems with soils with high OM content. For Hg, use vapour AAS.

[1]Analysis to be made on air-dried and <2 mm fraction (milled sample in case of peat and forest floor samples). Values to be reported on oven-dry (105ºC) basis (except pH). For pre-treatment of samples, see ISO/DIS 11464 Soil Quality -Pre-treatment of samples for physico-chemical analyses.

[2] National methods should be calibrated against the reference IM methods on a representative set of samples and the calibration regression model reported to IM Programme Centre. For Draft ISO/DIS methods, see: ISO Standards Compendium. Environment. Soil Quality. General aspects; chemical and physical methods of analysis; biological methods of analysis. First edition. 1994. ISBN 92-67-10203-6.

** meq/kg = mmol (+)/kg

Table 7.7.3 SC Soil profile description

Minimum soil profile description for the SC subprogramme (to be determined only once).

Parameter	Comments
FAO soil group and unit	FAO UNESCO 1990. Soil map of the world. Revised legend, World Soil Resources Report 60, Rome 1990, ISO 11259, or translate from national classification if necessary. OR FAO, 2015. World reference base for soil resources 2014 International soil classification system for naming soils and creating legends for soil maps. Update 2015. World Soil Resources Reports 106.
Parent material	FAO-ISRIC. 1990. Guidelines for Soil description. 3rd edition (revised) Soil Resources, Management and Conservation Service, Land and Water Development Division. Rome. pp.70.
Horizon designation	O, E, EA, A, Ah, B, Bw, Bt, Bs etc. Use FAO definitions - FAO UNESCO 1990. Soil map of the world. Revised legend, World Soil Resources Report 60, Rome 1990 for details.
Humus form	Mor, Moder, Mull, and any combinations/transitions, e.g. moder-like mor
Horizon lower boundary depth	The mean depth to lower boundary of each horizon identified in cm. Reference level (0 cm) from the surface of mineral soil. For humus layer, record mean thickness as negative value
Munsell colour code	Munsell colour code for each mineral soil horizon identified. Munsell Colour charts
Texture	Hand texture classification: e.g. sandy loam, silty loam, sand or from PSA
Stone content	Estimate of the stone (>2 mm fraction) content, m^3/m^3
Rooting depth	Estimate of the rooting depth m

Example files (Excel format is preferred)

SC example Excel file
SC example ASCII file

- File identifier SUBPROG states the subprogramme.
- MEDIUM refers to the soil type according to FAO classification.
- LEVEL is given as the lower limit of soil sample from the interface between humus and mineral soil. E.g. level for an 8 cm thick humus layer is - 8, for mineral soil sample between 0 - 5 cm from the ground level is 5, the mineral layer sample between 5 - 20 cm from the ground level is 20 etc.
- Spatial pool SPOOL refers to the number of individual samples taken for pooled analysis.
- Sampling year and month are given as YYYYMM, day field is left blank.

A list of soil type codes from the FAO classification
(updated from FAO World reference base for soil resources 2014, International soil classification system for naming soils and creating legends for soil maps. Update 2015. World Soil Resources Reports 106)

OH, Organic topsoil horizon/humus (not a FAO class!)
AC, Acrisols
AL, Alisols
AN, Andosols
AT, Anthrosols
AR, Arenosols
CL, Calcisols
CM, Cambisols
CH, Chernozems
CR, Cryosols
DU, Durisols
FR, Ferralsols
FL, Fluvisols
GL, Gleysols
GY, Gypsisols
HS, Histosols
KS, Kastanozems
LP, Leptosols
LX, Lixisols
LV, Luvisols
NT, Nitisols
PH, Phaeozems
PL, Planosols
PT, Plinthosols
PZ, Podzols
RG, Regosols
RT, Retisols
SC, Solonchaks
SN, Solonetz
ST, Stagnosols
TC, Technosols
UM, Umbrisols
VR, Vertisols

7.7.6. References

EDC, 1993. UN/ECE Environmental Report 5. Manual for Integrated Monitoring Programme Phase 1993-1996. EDC, Helsinki. ISBN 951-47-6750-0 ISSN 0788-3765. pp.114.

FAO, 2015. World reference base for soil resources 2014
International soil classification system for naming soils and creating legends for soil maps. Update 2015. World Soil Resources Reports 106.

FAO, 1990. FAO-ISRIC. Guidelines for Soil description. 3rd edition (revised) Soil Resources, Management and Conservation Service, Land and Water Development Division. Rome. pp.70.

Haussmann, T. 1995. Basic documents for the implementation of the European Programme of the Intensive Monitoring of Forest Ecosystems. European Commission - Directorate Agriculture (DG VI). VI/3908/95-EN. pp.97.

Hendershot, WH and Duquette, M. 1986. A simple barium chloride method for determining cation exchange and exchangeable cations. Soil Soc. Am. J. 50:605-608.

ISO STANDARDS COMPENDIUM. 1994. ENVIRONMENT. SOIL QUALITY. General aspects; chemical and physical methods of analysis; biological methods of analysis. 1st edition. ISBN 92-67-10203-6. pp.399.

ISO 11259. Soil Quality. Simplified soil description. ISO WG 190/1/1. 2nd CD 1995-06.

ICP Forests Manual, 2016
http://icp-forests.net/page/icp-forests-manual

ICP Forests manual, 1997. Manual on methods and criteria for harmonized sampling, assessment, monitoring, and analysis of the effects of air pollution on forests, 4th edition. Edited in 1997 by the Programme Coordination Centre Federal Research Centre for Forestry and Forest Products (BFH), Hamburg, Germany.

ICP Forests manual, 1994. Manual on methods and criteria for harmonized sampling, assessment, monitoring, and analysis of the effects of air pollution on forests. 1994 edition. Edited by the Programme Coordination Centres Hamburg and Prague.

Tamminen, P. & Starr, M. 1994. Bulk density of forested mineral soils. Silva Fennica 28(1):53-60.

Viro, PJ. 1952. Kivisyyden määrittämisestä (Summary: On the determination of stoniness). Communicationes Instituti Forestalis Fenniae 40(3): 1-23.

White A.F. & Blum A.E. 1995. Effects of climate on chemical weathering in watersheds. Geochimica et Cosmochimica Acta 59:1729-1747.

7.8 Subprogramme SW: Soil water chemistry

7.8.1 Introduction

Acidic water percolating through the soil dissolves and weathers minerals, releasing base cations for nutrient uptake by microbes and roots alike, for seepage to deeper layers and ground water, and ultimately for outflow to rivers and lakes. Soil water is intimately coupled with the chemical and biological processes in the upper soil layers and is sensitive to both acidification and nitrogen pollution. The SW subprogramme is therefore one of the most essential subprogrammes for understanding geohydrochemical interaction with biological/microbiological effects at both plot and catchment scales.

It is therefore unfortunate that soil water sampling should be so fraught with difficulties. The installation of soil water collectors, whether traditional zero-tension lysimeters or suction samplers, results in disturbance that affects the integrity of the soil water being sampled. As installation affects diminish with time, those associated with the plugging of the collector can be expected to increase. Separating the soil water phase from the soil matrix, with which it is continually attempting reach an equilibrium, can be expected to alter its chemistry. Similarly, the degassing of CO_2 from soil water brought to equilibrium with the atmosphere can be expected to alter its chemistry. The spatial variability in soil water chemistry and flow is known to be considerable resulting unrealistic numbers of samplers being required to meet true mean 95% confidence levels. It is not possible to measure the soil water flux with suction samplers since the soil volume from where the water is drawn is not known and varies with soil moisture content. Flux values based on zero-tension lysimeters are also probably suspect because of altered hydrological conditions resulting from the design and installation of the lysimeter. Tension samplers collects a different fraction of the soil water than zero-tension lysimeters, and both do not collect the soil water in which plant roots and microbes are in intimate contact. Nevertheless, soil water sampling provides important information about the status of the soil, indicating nutrient and toxicological conditions for plant roots and microbes, and—when coupled with water fluxes—nutrient, acidity, and pollutant leaching.

7.8.2 Methods

7.8.2.1 Field methods and sampling

Principles

Soil water can be sampled for monitoring purposes by using either zero-tension lysimeters, which collects percolate (gravitational) water, or with suction samplers (porous plates, cups), which collect percolate and water held by the soil up to the tension applied and that can reach the sampler during the time the suction is on. For a comparison of zero-tension lysimeters and suction samplers see e.g. Barbee & Brown (1986) and Haines et al. (1982). Furthermore, the suction (tension or negative

pressure) applied to the suction sampler can be constant or a falling (see Nordic Council of Ministers 1989). Soil water can also be sampled by centrifugation (e.g. Reynolds 1984, Elkhatib et al. 1987), but this method involves removing a soil sample to the laboratory each time, and therefore unsuited for monitoring.

Choice of sampler

It is recommended to use suction cup samplers. Cups are made in a variety of materials, all of which may affect the sample to some extent (e.g. Nagpal 1982, Debyle et al. 1988, Raulund-Rasmussen 1989, Hughes & Reynolds 1990, Grossmann & Udluft 1991). It is therefore not possible to recommend one type of cup above another; only that they should be made of reasonably inert material and not weather easily. The IM Programme Centre will collect a list of samplers and suppliers that have been used to date within ICP IM.

Cup samplers come in a variety of forms (see Nordic Council of Ministers 1989 for illustrations). Usually it consists of a small cup made of porous material, the open end of which is attached to non-porous tubing through which the vacuum is applied, and the sample retrieved. If the cup is attached to a non-porous tube of the same diameter as the cup, the sample can be collected within the body of the sampler itself (e.g. Soilmoisture Equipment Corporation soil water samplers, model 1900). Often, however, the buried cup is attached to a capillary tube which extends up through the soil surface and connects to a vessel in which both the sample is collected, and the vacuum applied.

Sampling design and installation

The samplers should be located in upland (non-organic) SC plot(s) only; and at least in the SC plot considered the most important for the IM site. A randomized or systematic pattern may be used for the allocation of the samplers, although local factors (stones, low water yield) may make a more subjective allocation necessary. To avoid unnecessary walking on the plot, the samplers are best located around the edges of the plot so that they can be serviced from outside the plot, or in a separate area nearby.

Soil water chemistry and hydrology is extremely variable, both spatially and temporally. To be within the 95% confidence limit of the plot's true mean soil water solute concentrations would almost certainly require an unrealistic number of samplers. Therefore, rather than trying to determine true plot mean solute concentrations, emphasis should be on whether there is change in soil water chemistry collected at the same limited number of locations within the plot over time. The ratios of solutes, e.g. Ca/Al, NO_3N/NH_4N, probably show less spatial variability than the individual parameters.

Towards this aim, at least 3-6 samplers per depth should be installed. The depth to install the samplers should be within the 10-20 cm layer and the 30-50 cm layer, i.e. within and below the main rooting zone (0=mineral soil surface). If possible, record the horizon in which the cup is located. Suction samplers do not work well in humus layers because of difficulties in maintaining good soil contact. Therefore, if possible, it is recommended to install small zero-tension lysimeters immediately under the humus layer. A nest of samplers (one at each depth) can be installed at locations along the edge of the plot (see SC Chapter Fig. 7.7.2).

The installations should be made in such a way that disturbances are minimised, e.g. by using a soil auger. Ensure good contact with the cup and the soil by pouring a slurry made of local soil material, having first removed any stones and gravel, and water into the hole. It is also good practice to attach a piece of nylon string to the cup so that it can be relocated if the capillary tubing is severed below

ground by animals. In addition, it is good to have the capillary tubing inside another tubing to protect it from burrowing animal damage.

Replace/reinstall a sampler if it persists in not collecting a sample. Rather than continuing on from abandoned samplers, new samplers start a new time series. This because of the high degree of spatial variability, even over short distances (m). The risk of increased weathering of ceramic cups and progressive plugging of samplers in general may also be a reason for replacement after some years.

Sampling
Apply a suction of 0.3–0.6 bars to the sampler. Depending on the type of sampler, soil type and soil moisture conditions, the vacuum should be placed on the sampler for a period of 18 hours to two weeks. The samplers can be connected to large vacuum vessels (2 litres) which are able to maintain such a suction without the need for repeated pumping. Either a falling or a constant vacuum system may be used. Maintenance of the vacuum depends on whether the pores of the cup dry-out, letting air pass in. Therefore, pore size is important–the smaller the pores, the more difficult it is for the cup to dry out.

Attempt to take at least 1 sample per month. Record the volume of sample collected so that volume weighted monthly mean concentrations can be calculated (NB. the sample volume cannot be used to calculate a water flux since the area from where the sample came is unknown). In sites with snow accumulation, samples are usually not collected during the snow period.

Samples of small volume (<25-50 ml) may be rejected because such samples often have extremely variable chemistries and are atypical of the bulk soil water chemistry (Starr 1985). Because of the large spatial variability likely to be encountered, it is recommended that the samples are not composited but analysed individually. If this is not possible all the time, then bulk samples only from the same depth.

Use acid-washed collection vessels. These should be periodically replaced throughout the season. The samples should be transferred to acid-washed polyethylene bottles for transport to the laboratory (preferably in cold boxes) as soon as possible.

For details on handling water chemistry samples, see Chapter 8.2.

7.8.2.2 Laboratory analyses

The transport and storage period should be kept to a minimum. The set of parameters to determine are given in data reporting part 7.8.5. Total N has been added and enables organic N to be calculated.

The analytical techniques described in the previous manual (EDC 1993) are still valid. Priority in the analysis schedule should be given to the non-metal determinations: pH, N compounds, DOC etc. Acid should be added to ensure desorption of metals from the walls of the storage bottle (e.g. 0.5 ml conc. HNO3 suprapur quality per 100 ml sample). During analysis, the samples should be kept in a dark and cold store (+4°C).

Because the porous cup itself acts as a filter, filtering of the sample for analysis is probably unnecessary. Tests in Sweden have found little effect on the concentrations of DOC and total Al

collected with P80 cups (from Hoechst). Indeed filtering may actually contaminate the samples (REF). Further testing is advised before using expensive membrane filters. However, filtering for some analytical procedures may be necessary, e.g. with ion chromatography to preserve the exchange columns for longer. It is also important to note the limits of some techniques, e.g. the detection limits for metals determined by ICP, at least emission spectrometer models, are relatively high. It may be necessary to analyse a subset of samples by AAS/graphite furnace in order to get more exact concentrations.

7.8.3 Quality assurance/Quality control

Each NFP is expected to ensure that good laboratory practice is followed and are responsible for the quality of data reported to ICP IM Programme Centre. For methods on checking data, QC and precision and accuracy, see American Public Health Association. 1985. The results of quality controls, laboratory intercalibrations etc. undertaken (either with IM samples in particular or of the laboratory in general) should be reported to the IM Programme Centre. The Programme Centre also encourages participation in international intercalibration exercises.

A simple check can be made to see if the sum of cations is balanced by the sum of anions. If there is a difference that cannot be explained by any missing ions, then this should be brought to the attention of the laboratory. Other simple checks include looking at scatter plots between the parameters, e.g. SO4S - Total S concentrations and strongly correlated, PO4P - Total P concentrations and strongly correlated, NO3N + NH4N - total N concentrations, and Total inorganic N (NO3N + NH4N) strongly correlated to DOC. Careful screening for outliers can substantially reduce the variability of the data. If any of the metal concentrations determined with an ICP in simultaneous mode are outliers, then there is reason to check the chemistry of the whole sample.

See data quality management in Chapter 8.

7.8.4 Data handling

In order to calculate solute leaching, soil water flow estimates are required. Although methods to measure soil water fluxes exist (e.g. tensiometry, TDR), they are not widespread or routine (Cassel & Nielsen 1986). There are a number of models which can compute runoff (drainage to ground water in this case) and since they rely on the laws of physics, they can be rather reliable (e.g. SOIL, Jansson 1991). However, such models require data that is difficult to obtain and considerable training in order to run them. Water balance/soil water deficit models probably offer the simplest approach (Nordic Council of Ministers 1989, Dingman 1994). The problem of obtaining soil water flux values for IM sites clearly needs to be further looked into. Any developments should be brought to the attention of the IM Programme Centre.

7.8.5 Data reporting

Mandatory and optional parameters

Parameter	**Code + list**	**Units**	**Recommended methods* and comments**
Mandatory:			**Report also pre-treatment codes!**
pH	PH DB		
Electrical conductivity	COND DB	mS/m	
Alkalinity, Gran plot	ALK DB	µeq/l**	Only if pH>4.5
N total	NTOT DB	mg/l	
N ammonium	NH4N DB	mg/l	
N nitrate	NO3N DB	mg/l	
P total	PTOT DB	µg/l	
Ca	CA DB	mg/l	
Mg	MG DB	mg/l	
K	K DB	mg/l	
Na	NA DB	mg/l	
Aluminium total	AL DB	µg/l	
Aluminium labile	ALL DB	µg/l	Only if pH<4.5, modelled value acceptable
Sulphate as sulphur	SO4S DB	mg/l	

Chloride	CL DB	mg/l	
Dissolved organic carbon	DOC DB	mg/l	
Optional:			
Manganese	MN DB	µg/l	
Iron	FE DB	µg/l	
Silica	SIO2 DB	mg/l	
Phosphate as phosphorous	PO4P DB	µg/l	
S total	STOT DB	µg/l	
Trace elements	AS,... DB	µg/l	As, Cd, Cr, Cu, Mo, Ni, Pb, Zn, Hg
Soil water flow	FLOW DB	l/(s x km^2)	
Derived/calculated:			
Cation Anion balance		meq/l	Quality control purposes
Organic N		mg/l	Total N-(NH4N+NO3N)

Example files (Excel format is preferred)

SW example Excel file
SW example ASCII file

- File identifier SUBPROG states the subprogramme.
- MEDIUM refers to the type of soil coded according to the FAO soil classification (see SC subprogramme).
- LEVEL refers to the depth of the base of the sampler from the mineral soil surface (cm).
- Spatial pool SPOOL refers to the number of individual lysimeters used for discrete soil levels.
- If the sample volume is recorded and the sampling is done more than once a month, concatenations values should be given as volume weighted means (see Annex 7) and flagged

with W. Single monthly values are reported without status. Soil water flow, if available, is reported as a monthly mean. General information on flags is available in Chapter 4. For values below detection limit see Annex 7.

- Sampling year and month are given as YYYYMM, day field is left blank.

7.8.6 References

American Public Health Association. 1985. Standard methods for the examination of water and wastewater. 16th edition. ISBN 0-87553-131-8. xlix + 1268 pp.

Barbee, GC & Brown, KW , 1986. Comparison between suction and free-drainage soil solution samplers. Soil Sci. 141(2), 149-154.

Cassel, DK & Nielsen, DR, 1986. Field capacity and available water capacity. Chap. 36. In: Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods-Agronomy Monograph no. 9. 2nd ed. (Ed: Klute, Arnold) American Society of Agronomy-Soil Science Society of America, Madison, USA, 901-926.

Debyle, NV; Hennes, RW & Hart, GE, 1988. Evaluation of ceramic cups for determining soil solution chemistry. Soil Sci.146, No. 1, 30-36.

Dingman, SL, 1994. Physical Hydrology. Macmillan Publishing Company. ISBN 0-02-329745-x, XIV, 575 pp.

Elkhatib, EA; Hern, JL & Staley, TE, 1987. A rapid centrifugation method for obtaining soil solution. Soil Sci. Soc. Am. J. 51, 578-583.

Grossmann, J & Udluft, P, 1991. The extraction of soil water by the suction-cup method: A review. Journal of Soil Science 42, 83-93.

Haines, BL; Waide, JB & Todd, RL, 1982. Soil solution nutrient concentrations sampled with tension and zero-tension lysimeters: report of discrepancies. Soil Sci. Soc. Am. J. 46, 658-661.

Hughes, S & Reynolds, B, 1990. Evaluation of porous ceramic cups for monitoring soil-water aluminium in acid soils: comment on a paper by Raulund-Rasmussen (1989). Journal of Soil Science 41, 325-328.

Jansson, P-E. 1991. Simulation model for soil water and heat conditions. Description of the SOIL model. Swedish University of Agricultural Sciences, Dept. of soil Science, Uppsala. Report 165.72 pp.

Nagpal, NK, 1982. Comparison among and evaluation of ceramic porous cup soil water samplers for nutrient transport studies. Can. J. Soil Sci. 62, 685-694.

Nordic Council of Ministers, 1989. Methods for Integrated Monitoring in the Nordic countries. Miljørapport 1989:89. 280 pp.

Raulund-Rasmussen, K, 1989. Aluminium contamination and other changes of acid soil solution isolated by means of porcelain suction-cups. Journal of Soil Science 40, 95-101.

Reynolds, B, 1984. A simple method for the extraction of soil solution by high-speed centrifugation. Plant and Soil 78, 437-440.

Starr, MR, 1985. Variation in the quality of tension lysimeter soil water samples from a Finnish forest soil. Soil Sci. 140(6), 453-461.

7.9 Optional subprogramme GW: Groundwater chemistry

7.9.1 Introduction

Groundwater is defined as subsurface water, which occurs in the water saturated zone of ground. It may lie near surface or deep in the bedrock. Groundwater is present everywhere and is, hence, one of the output media for elements in the terrestrial ecosystem. The monitoring of groundwater chemistry is dependent on the definition of the hydrological area. Usually it is monitored in open wells and observation tubes penetrating the loose overburden covering the bedrock. Monitoring may also take place in springs.

7.9.2 Methods

7.9.2.1 Sampling frequency

The frequency of water sampling should be adapted to the overall chemical composition of the groundwater in the particular sampling point. With high sampling frequency the annual variation will be well covered. On the other hand, it will increase the costs. So, a compromise will be necessary. Due to low temperature during the winter period it is often impossible to carry out sampling. Ground water should be sampled not less than 6 times a year, preferably more frequently in spring during the snowmelt period.

7.9.2.2 Allocation of groundwater tubes

Concentrate groundwater sampling to the discharge area of the catchment (Figure 7.9.1) where there is natural groundwater seeping belts or springs. Note that groundwater catchment usually differs from that of surface water. For ideal monitoring an additional line of groundwater tubes should be established covering both the recharge and discharge areas. The well line should run perpendicularly to slope contours (Figures 7.9.1 and 7.9.2). Placing of groundwater tubes in recharge areas should be planned in association with soil water samplers. In the ideal case monitored groundwater is found in a surficial aquifer composed of glaciofluvial material (sand and gravel) with

relatively high hydraulic conductivity. In till deposits groundwater flow is often very slow and retention time is in the order of months or years. This hinders an appropriate temporal monitoring.

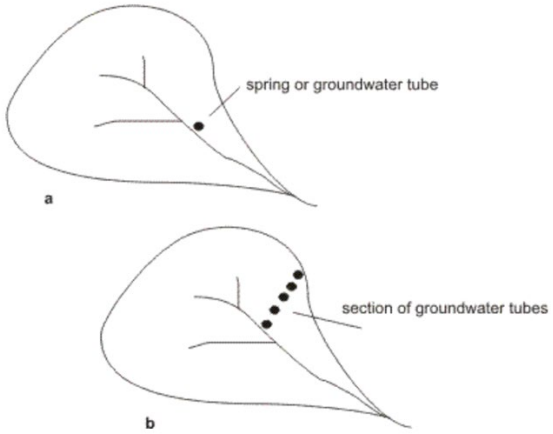


FIGURE 7.9.1 SITING PROPOSAL FOR GROUNDWATER MONITORING WITHIN A CATCHMENT.

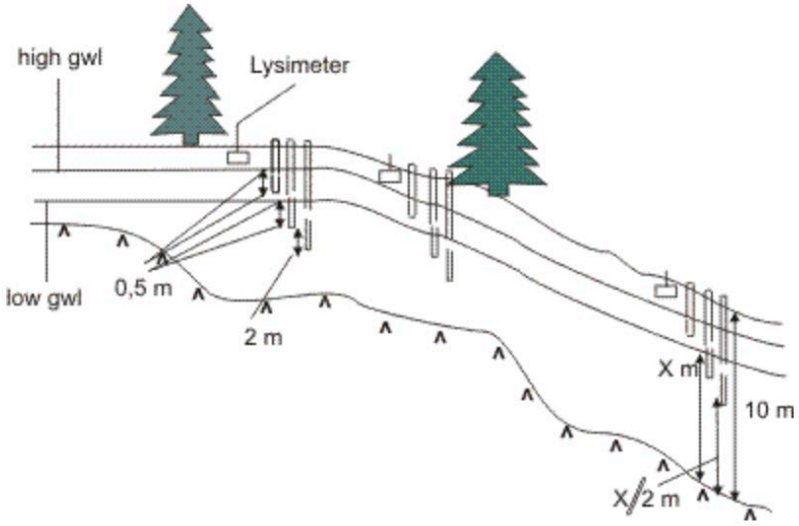


FIGURE 7.9.2 ILLUSTRATION OF A SLOPE WITH POSITIONS FOR SAMPLING TUBES AND LYSIMETERS.

7.9.2.3 Groundwater sampling

Groundwater tubes installed in the terrain must be simultaneously strong and made of such material, that absolutely no contamination occurs (e.g. polyamide). All materials used in sampling should be analytically verified to eliminate contamination risks. For practical reasons, minimum inner diameter of the tube is ca. 30 mm. The top of the tube must be capped to avoid external dirt while allowing proper air circulation. Always use disposable gloves when handling instruments used in sampling. Smoking is forbidden and no petrol driven engine (e.g. snowmobile) is let to run in the vicinity of sampling site.

Sampling equipment
As an example of simple, manually operated, sampling equipment, used for soaking up groundwater through an observation tube from a maximum depth of 5-6 metres is shown in Figure 7.9.3. The

equipment is adapted for use in areas where no electricity is available and where the sampling sites are far from roads. A hollow, cylindrical body, made of polyamide or other inert material is designed to be lowered into the sampling tube below the groundwater table. It is equipped with a weight embedded in the bottom part of the body. Water can pass through holes in the cylinder walls. An uncoloured silicon tube is connected to the top of the cylinder. These parts are kept during transportation in a protection tube manufactured of grey PVC. The protection tube is filled with deionized water, which is exchanged between the sampling occasions. The silicon tube is connected to a longer plastic tube, which is connected to 2-3 litre Pyrex or glass bottle, equipped with a polyethene or polyamide plug. The plug has two outlets, one for the tube from groundwater to the sampler and one for the air vacuum pump. When vacuum is created by the hand pump groundwater is sucked into the sampler bottle. When the bottle plug is not in use store it in an extra polyethene bag or similar clean place.

If groundwater is on such a deep level that it is impossible to suck up, submersible pumps should be used. Note that all the metal parts of the pump may create a definite risk of contamination. A weakness of the described sampling equipment is the unavoidable CO_2 -escape.

Water pumped up from a groundwater tube often contains suspended clay mineral particles. Groundwater samples for heavy metals analysis should always be filtered through 0.45 µm membrane before acid conservation. If there are still clay particles left in the sample when the acid is added, metals in clay are released or metals in the groundwater may adsorb to negatively charged clay particles.

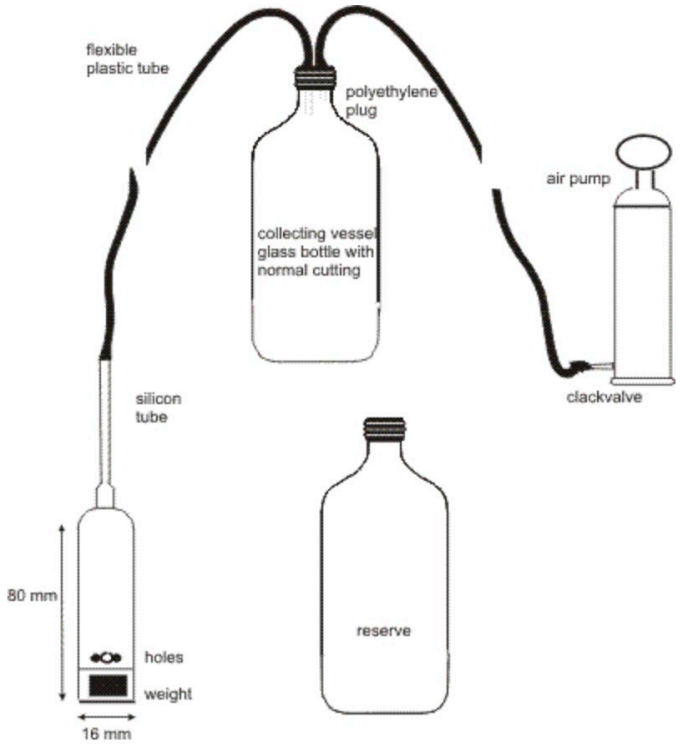


FIGURE 7.9.3 SIMPLE EQUIPMENT FOR GROUNDWATER SAMPLING.

Sampling from wells and springs

If the sampling site is a well, water is percolating in a natural way and no flushing pumping is

necessary. Be sure that water has not stayed unchanged for a long time (see observation tubes below). It is, however, desirable for the interpretation of the analysis results if the results can be correlated to either the well flow or to the groundwater level in some upstream observation tube. Water for the analysis of physical properties and primary constituents is sampled by filling the sample bottle directly from the well. The bottle can also be filled using a syringe (without filter). For metal and trace-element analysis filtering and preservation with acid is necessary.

Sampling from observation tubes
Establish the groundwater level by plumbing. Use plumbs made of inert material. Turnover pumping is necessary to avoid "stagnant" water, which has been in contact with both the atmosphere and the tube walls, and therefore differs chemically from the groundwater in the aquifer. If the sample should represent the groundwater closest to the screen of the sampling tube, the volume of water contained in the tube is pumped 1.5 - 2 times. If the sample should represent a larger part of the aquifer, the water is turned several times more.

When "fresh" water has reappeared, the actual sampling can begin. Put on disposable plastic gloves. Pump some water into the collection vessel and rinse it. Avoid touching the bottom with the flexible suction tube, since the water may become clouded. Fill the collecting vessel with pumped water. Lift the plastic plug and put in on the extra collecting vessel to ensure that it is not contaminated.

Rinse the 250-500 ml plastic bottle, intended for anion analyses, with water from the collecting vessel. Fill the bottle to the brim and screw on the lid to ensure that as few air bubbles as possible are left in the bottle. Samples for heavy metal determinations must be filtered and preserved by adding 0.5 ml of suprapur quality conc. HNO_3 per 100 ml of sampling water. If possible use automatic dosing pipette with a disposable nose.

For details on collection and handling of water samples, please see Chapter 8.2.

7.9.3 Analyses

7.9.3.1 Field analyses

If field analyses are carried out these should be done immediately after the water has been pumped to minimize changes in quality. Pour water from the collecting vessel into a beaker for field analysis and measurements of certain parameters (e.g. pH, conductivity, dissolved oxygen). Never make measurements directly in the collecting vessel, except temperature.

7.9.3.2 Laboratory analyses

For a list of available standards, see Chapter 8.5

7.9.4 Quality assurance/Quality control

See data quality management in Chapter 8.

7.9.5 Data reporting

Mandatory parameters	**list**		**unit**
SO4S	DB	sulphate as sulphur	mg/l
NO3N	DB	nitrate as nitrogen	mg/l
NH4N	DB	ammonium as nitrogen	mg/l
NTOT	DB	total nitrogen	mg/l
CA	DB	calcium	mg/l
NA	DB	sodium	mg/l
K	DB	potassium	mg/l
MG	DB	magnesium	mg/l
CL	DB	chloride	mg/l
DOC	DB	dissolved organic carbon	mg/l
AL	DB	total aluminium	µg/l
ALL	DB	labile aluminium	µg/l
PH	DB	pH	
COND	DB	specific conductivity at 25 °C	mS/m
ALK[1)]	DB	alkalinity, GRAN plot	mmol/l
FLOW	DB	groundwater flow	l/(s x km^2)

WL	DB	groundwater level	cm from surface
Optional parameters:	**list**		**unit**
TEMP	DB	temperature	^{o}C
STOT	DB	total sulphur	mg/l
PO4P	DB	phosphate as phosphorous	µg/l
PTOT	DB	total phosphorous	µg/l
SIO2	DB	silica (as silica)	mg/l
MN	DB	manganese	µg/l
FE	DB	iron	µg/l
AS	DB	arsenic	µg/l
CD	DB	cadmium	µg/l
CR	DB	chromium	µg/l
CU	DB	copper	µg/l
MO	DB	molybdenum	µg/l
NI	DB	nickel	µg/l
PB	DB	lead	µg/l
ZN	DB	zinc	µg/l

1) Please note the change of unit.

Example files (Excel format is preferred)

GW example Excel file
GW example ASCII file

- File identifier SUBPROG states the subprogramme.
- MEDIUM refers to either tube sampling (TUBE) or spring sampling (SPRING).
- LEVEL is given as sampling depth (cm) from the ground (or spring water surface).
- Spatial pool SPOOL refers to the number of individual sampling points.
- If groundwater flow can be calculated and the sampling is done more than once a month, the chemical component values should be given as flow weighted means, status flag is W. Monthly values are reported without status. Groundwater flow is reported as a monthly mean. For calculation of flow weighted means, please see Annex 7. General information on flags is available in Chapter 4.
- Sampling year and month are given as YYYYMM, day field is left blank.

7.10 Subprogramme RW: Runoff water chemistry

7.10.1. Introduction

Runoff is the main output of solutes from a catchment area. The amount of element loss can be calculated by measuring the runoff and analysing the concentrations of runoff water.

The parameters included on the mandatory list are, with few exceptions, those also mandatory in the ICP Waters programme and mainly related to acidification. The optional determinants are also mostly those listed optional in the ICP Waters programme.

Mandatory parameters:

anions: alkalinity, sulphate, nitrate, chloride
organic: dissolved organic carbon
cations: pH, calcium, magnesium, sodium, potassium, inorganic (labile) aluminium [1)]
nutrients: total nitrogen, ammonium
physical properties: stream runoff, specific conductivity

[1)] Difference between reactive (organic + inorganic) and non-labile (organic) aluminium. May be omitted at pH>5.5.

Optional parameters:

physical properties: water temperature
nutrients: total phosphorus, soluble reactive phosphate, total sulphur, silica
metals: iron, manganese, cadmium, zinc, copper, nickel, lead, arsenic, chromium, molybdenum, total aluminium
other: fluoride, colour

7.10.2 Methods

7.10.2.1 Discharge measurements

The discharge must be determined in order to calculate catchment budgets. The best approach is to establish permanent weirs with continuous recording stage height recorders (see e.g. Nord 1989:11). At least daily values of runoff should be recorded. During periods of high flow- snow melting, heavy rains, storms - discharge measurements should be carried out more frequently. Discharge should also be measured always when water chemistry samples are taken.

7.10.2.2 Water chemistry sampling

Locate the runoff chemistry sampling close to the runoff recording device. If a weir is present, sampling is done at some distance up-stream from the weir because of the risk of chemical contamination from the weir material. If no weir is present, sample in a deep flowing part of the stream at a depth sufficient to avoid sediment and surface contamination. Samples are taken with a water sampler from 10-50 cm depth. In shallow streams, where this is not possible, samples are taken in such a way that contamination and sampling of surface films is avoided. When filling the bottle, keep the bottleneck against the current, well below the surface. Rinse the bottle and screwcap 3 times with sampling water prior to sampling. Avoid touching the inside of bottle and screwcap.

If some form of automatic water sampler is used, it should be tested for contaminants, especially if heavy metals are analysed.

The aim of the sampling should be to obtain spatially and temporally representative samples. Spatial representativeness in this context refers to the pattern of variation in water chemistry across the stream cross-section. This is a function of the turbulence within the stream: the water in small streams with rocky beds and steep gradients is better mixed than water in larger, slower-moving rivers. Temporal representativeness may be particularly difficult to achieve, especially for small streams fed primarily by precipitation (as opposed to groundwater-fed streams). Consequently, samples should be collected at such intervals that no important cycle of change in concentration could pass unnoticed between sampling times.

Runoff water samples are taken at least once a month. However, for establishing catchment budgets a flow weighed sampling is recommended. Discharge should also be measured always when water chemistry samples are taken. The sampling integration time should if practical be harmonized with other relevant subprogrammes e.g. deposition and throughfall measurements.

7.10.2.3 Handling of water chemistry samples

Please see Chapter 8.2 for details.

7.10.3 Analytical techniques

For a list of available standards, see Chapter 8.5.

7.10.4 Quality assurance/Quality control

See data quality management in Chapter 8.

7.10.5 Data reporting

Mandatory parameters	**list**		**unit**
Q	DB	stream runoff	l/(s x km^2)
PH	DB	pH	
COND	DB	specific conductivity at 25 °C	mS/m
NA	DB	sodium	mg/l
K	DB	potassium	mg/l
CA	DB	calcium	mg/l
MG	DB	magnesium	mg/l
ALL	DB	inorganic labile aluminium	µg/l
NO3N	DB	nitrate as nitrogen	µg/l
NH4N	DB	ammonium as nitrogen	µg/l
NTOT	DB	total nitrogen	µg/l
ALK [1)]	DB	alkalinity, GRAN plot	mmol/l
CL	DB	chloride	mg/l

SO4S	DB	sulphate as sulphur	mg/l
DOC	DB	dissolved organic carbon	mg/l
Optional parameters:	**list**		**unit**
PO4P	DB	phosphate as phosphorous	µg/l
PTOT	DB	total phosphorous	µg/l
STOT	DB	total sulphur	µg/l
SIO2	DB	silica (as silica)	mg/l
CNR	DB	colour number	Pt mg/l
TEMP	DB	temperature	^{o}C
F	DB	fluoride	mg/l
FE	DB	iron	µg/l
MN	DB	manganese	µg/l
AL	DB	total aluminium	µg/l
AS	DB	arsenic	µg/l
CD	DB	cadmium	µg/l
CR	DB	chromium	µg/l
CU	DB	copper	µg/l
MO	DB	molybdenum	µg/l

NI	DB	nickel	µg/l
PB	DB	lead	µg/l
ZN	DB	zinc	µg/l

1) Please note the change of unit.

Important: if the titration is made to one single pH value (usually pH 4.5) it is necessary to indicate (using the correct determination code in DB list) whether the given value is adjusted to be the endpoint value or represents the total acid consumption to pH 4.5.

Example files (Excel format is preferred)

RW example Excel file
RW example ASCII file

- File identifier SUBPROG states the subprogramme.
- MEDIUM is left blank.
- LEVEL is given as sampling depth from the surface (cm).
- Spatial pool SPOOL refers to the number of sampling points.
- If sampling is carried out more than once a month, the values should always be given as flow weighted means, status flag is W, except for temperature, colour number and conductivity, which are reported as arithmetic averages for several sampling dates/month. Monthly values are reported without status. Stream runoff is reported as a monthly mean. For calculation of flow weighted means, please see Annex 7. General information on flags is given in Chapter 4.
- Sampling year and month are given as YYYYMM, day field is left blank.

7.10.6 References

ICP Waters Programme manual. Compiled by the Programme Centre, Norwegian Institute for Water Research. Revised edition, Oslo.

Methods for Integrated Monitoring in the Nordic Countries. Miljøraport 1989:11 section 5. Nordic Council of Ministers, Copenhagen 1989.

7.11 Optional subprogramme LC: Lake water chemistry

7.11.1. Introduction

Lakes intercept the flow (and fluxes) in an area. The chemistry of lake water thus gives an integrated picture of the fluxes from atmospheric and terrestrial environments. Processes occurring in lakes, like net sedimentation, turnover and freeze-over in the northern latitudes, may change the concentrations in the water. Thus the retention of fluxes in lakes might affect the values in the output to some degree. Lakes as intermediate pools of element fluxes are important bodies for compound changes, which in turn might cause reactions in their hydrobiological nature. If a lake exists within an IM area the lake water chemistry should be monitored for the understanding of the effect of internal fluxes.

The parameters included on the mandatory list are those also mandatory in the ICP Waters programme and mainly related to acidification. The optional determinants are those also listed optional in the ICP Waters programme.

Mandatory parameters:

anions: alkalinity, sulphate, nitrate, chloride
organic: dissolved organic carbon
cations: pH, calcium, magnesium, sodium, potassium, inorganic (labile) aluminium [1)]
nutrients: total nitrogen, ammonium
physical properties: specific conductivity

[1)] Difference between reactive (organic + inorganic) and non-labile (organic) aluminium. May be omitted at pH>5.5.

Optional parameters:

physical properties: water temperature
nutrients: total phosphorus, soluble reactive phosphate, total sulphur, silica, dissolved oxygen
metals: iron, manganese, cadmium, zinc, copper, nickel, lead, arsenic, chromium, molybdenum, total aluminium
other: fluoride, colour

7.11.2 Methods

7.11.2.1 Water chemistry samples

Establish a permanent lake water chemistry sampling site at the deepest point of the lake away from littoral influences. A bathymetric survey of the lake will help the allocation of sampling site. Lakes are sampled at depths of 0.5 m (or 1 m), 3 m, 5 m, halfway to the bottom and 1 m above the bottom. At the deepest point of the lake, a water profile should be established which should be followed up annually.

Lake water samples should be taken 2 - 6 times per year.

Use water samplers of the cylindrical open-top (e.g. Limnos) type, made of materials like Teflon, polypropene and polyethylene. The sampler is hoisted up and down with a rope. A polyethylene sampler must be equipped with a plastic-embedded weight and a Teflon sampler must have a sufficiently thick bottom in order to make it sink.

7.11.2.2 Handling of water chemistry samples

Please see Chapter 8.2 for details.

7.11.3 Analytical techniques

For a list of available standards, see Chapter 8.5.

7.11.4 Quality assurance/Quality control

See data quality management in Chapter 8.

7.11.5 Data reporting

Mandatory parameters	**list**		**unit**
PH	DB	pH	
COND	DB	specific conductivity at 25 °C	mS/m
NA	DB	sodium	mg/l
K	DB	potassium	mg/l
CA	DB	calcium	mg/l
MG	DB	magnesium	mg/l

ALL	DB	inorganic labile aluminium	µg/l
NO3N	DB	nitrate as nitrogen	µg/l
NH4N	DB	ammonium as nitrogen	µg/l
NTOT	DB	total nitrogen	µg/l
ALK [1)]	DB	alkalinity, GRAN plot	mmol/l
CL	DB	chloride	mg/l
SO4S	DB	sulphate as sulphur	mg/l
DOC	DB	dissolved organic carbon	mg/l
Optional parameters:	**list**		**unit**
O2D	DB	dissolved oxygen	mg/l
PO4P	DB	phosphate as phosphorous	µg/l
PTOT	DB	total phosphorous	µg/l
STOT	DB	total sulphur	µg/l
SIO2	DB	silica (as silica)	mg/l
CNR	DB	colour number	Pt mg/l
TEMP	DB	temperature	^{o}C
F	DB	fluoride	mg/l

FE	DB	iron	µg/l
MN	DB	manganese	µg/l
AL	DB	total aluminium	µg/l
AS	DB	arsenic	µg/l
CD	DB	cadmium	µg/l
CR	DB	chromium	µg/l
CU	DB	copper	µg/l
MO	DB	molybdenum	µg/l
NI	DB	nickel	µg/l
PB	DB	lead	µg/l
ZN	DB	zinc	µg/l

1) Please note the change of unit.

Important: if the titration is made to one single pH value (usually pH 4.5) it is necessary to indicate (using the correct determination code in DB list) whether the given value is adjusted to be the endpoint value or represents the total acid consumption to pH 4.5.

Example files (Excel format is preferred)

LC example Excel file
LC example ASCII file

- File identifier SUBPROG states the subprogramme.
- MEDIUM is left blank.
- LEVEL is given as sampling depth from the lake surface (cm).
- Spatial pool SPOOL refers to the number of sampling points.
- Monthly values are reported without status. Values for several sampling dates per month are reported as arithmetic averages with status flag X. For calculation of weighted means, please see Annex 7. General information on flags is given in Chapter 4.
- Sampling year and month are given as YYYYMM, day field is left blank.

ICP Waters Programme manual. Compiled by the Programme Centre, Norwegian Institute for Water Research. Revised edition, Oslo.

7.12 Subprogramme FC: Foliage chemistry

7.12.1 Introduction

Foliage analysis provides several types of information. Most importantly, it provides information on the nutritional status of trees. However, the chemical analysis of materials on and in the foliage may under some circumstances provide information on the relative loading of different types of pollutants.

Foliage sampling needs to be undertaken regularly and at the same phenological stage. For example, deciduous species must be sampled in summer, with late summer (after the completion of growth but before the onset of senescence) being best. Evergreen species are best sampled in the dormant season. The chemical composition of foliage needs to be sampled annually if the dynamic nature of the composition is to be fully interpreted.

Elements to be determined: Ca, K, Mg, Na, N, P, S, Cu, Fe, Mn, Zn and TOC
Optional: Al, As, B, Cd, Cl, Cr, F, Mo, Ni and Pb

7.12.2 Methods

7.12.2.1 Field methods

Number of trees
At least 8 trees of each main species (>10% of stems in plot) should be sampled annually. A composite sample for each species should be prepared by mixing equal quantities of foliage from each individual sample. Every five years, the sample trees should be analysed individually in order to determine the variability of the total element concentrations in the plot.

Selection of sample trees
The number of trees needed for the sampling should be selected in such a way that:

- the trees are spread over the total plot area, or around the plot if the stand is homogeneous over a larger area
- the trees belong to the predominant and dominant crown classes (forest with closed canopy) or are within ± 20% of the average height of the forest canopy
- the trees are in the vicinity of the locations where soil samples were taken for analysis. Care must be taken to ensure that the main roots of the sample trees have not been damaged by the soil sampling
- the trees are different from those used for the crown assessment, so as to avoid that successive sampling induces a loss of foliage. If stand and site conditions are homogeneous over an area larger than the plot where crown condition has been assessed, it is advisable to choose the sample trees outside the plot
- the trees are representative of the mean defoliation level of the plot (± 5% of the mean foliage loss).

The same trees should be sampled each year; the trees must therefore be numbered. For species with small crowns and few needles (or leaves) in any given year, it is possible (but not recommended) to alternate between two sets of 8 trees, when necessary, to avoid excessive damage to the sample trees. Each set of trees should respond to the above conditions.

Selection of leaves and needles to be sampled
No trees should be felled for foliar sampling.

The sampled leaves or needles should have developed in full light. Usually, the current year needles or leaves of evergreen species are the most suitable for judging the nutrition level but, for a number of elements, comparing element concentrations in older needles with that in the current year may provide more useful results.

The foliage should be sampled from the upper third of the crown, but not from the uppermost (1-4) whorls in conifers. In stands where the different whorls can be clearly identified, it is advisable to sample between the 7th and 15th whorls.

The current year leaves of broad-leaved trees should be sampled.

For evergreen species, the current year, second year and (if present) third year foliage should be sampled.

For all species, only mature leaves should be sampled. Care is therefore required when sampling species with several flushes during the year or with indeterminate growth.

For *Larix* spp. and *Cedrus* spp., samples should be taken from the short twigs of the previous year.

Orientation
Sampling should be carried out in such a way that all orientations are represented in the set of sample trees. If necessary, it is possible to sample different orientations on each tree of the sample set. In special sites with evident influence of one orientation (e.g. on steep slopes or with a dominant wind direction), only one orientation should be sampled, and this should always be the same. This should be documented.

Quantity of material to be sampled
The recommended quantities are:

- 20 grams of fresh needles or leaves for each sampled age class, if only major elements and Fe, Mn, Zn and Cu are being analysed
- 50 grams of fresh needles or leaves if other elements (e.g. F, Cl, Cd, Pb, Al and B) are being analysed.

Larger samples should be taken if samples are being archived.

Sampling methods
Any method of sampling is possible, but some basic precautions should be taken to reduce the possibility of sample contamination.

Pre-treatment of samples prior to despatch for analysis
For foliage from broadleaves, it is advisable to detach the leaves from the twigs (and even, in certain species, the small leaves from the axis) but this is not necessary for conifer needles. The shoots of the current year and those of the second year are separated and preserved in separate bags. The use of high-density polyethylene bags is recommended. If possible, samples should be dried in a clean room and stored in a cool, dark place in perforated polyethylene bags.

7.12.2.2 Chemical analyses

Only the total element concentration should be determined. More detailed information is available if separate fractions are analysed, and these can be of considerable value. However, such studies lie outside the scope of the standard IM work.

Treatment before analysis
The mass of 100 leaves or 1,000 needles, should be determined.

It is not necessary to cut the petioles off the leaves but in the case of compound leaves, the small leaves should be detached from the axis if this has not been done in the forest. Avoid contamination, use plastic gloves.

It is not necessary to systematically wash the samples, but it may be advisable in regions with a high level of air pollution or near the sea. The samples should be washed in water without any additions. Once a decision to wash or not to wash has been taken, this should be adhered to in subsequent years.

Oven drying should be done at 80ºC for 24 hours. The needles should be removed from the twigs using the same precautions as for detaching small leaves from their axis.

Dry samples should be ground in order to obtain a fine powder, as homogeneous as possible. There will always remain some fibres, depending on the tree species, this is not a major inconvenience if they are small and if the powder is mixed carefully before taking samples for analysis. When determining Mn, Fe, Cu, Cd, Al and Pb, check that the grinder does not contaminate the samples. The grinder can be tested by grinding dried fibrous cellulose and analysing it for these elements before and after the grinding.

7.12.2.2.1 DIGESTION AND ANALYSIS

There is no single way in which analyses should be taken. Rather, the best way is to use the standard procedures for the laboratory and calibrate the results through the use of ring tests. As an indication, the four main groups of methods for wet digestion or dry ashing are given below.

Wet digestion in acid and/or oxidizing conditions
For instance:

1. Kjeldahl method for N Organic N is digested in concentrated H_2SO_4, in the presence of catalysts and converted into NH_4^+. N eventually present in NO_3^- or NO_2^- form is not transformed into NH_4^+ and therefore not determined by methods specific for NH_4^+.

2. Digestion by oxidants and hot acids at atmospheric pressure.

- $H_2SO_4 + H_2O_2$ (for N and P analysis);
- $H_2SO_4 + HNO_3$;
- HNO_3;
- $H_2O_2 + HNO_3$
- HNO_3 or H_2O_2 followed by $HClO_4$. Perchloric acid is very efficient but dangerous (risk of explosion on contact with organic material or drying and heating perchlorates). The storage and manipulation must be done very cautiously. $HClO_4$ digestion must be preceded by cold attack of the sample powder by H_2O_2 110 V or concentrated HNO_3 during 24 hours in order to digest most of the organic tissues before adding $HClO_4$.
- HNO_3 + HF, Teflon vessels; after digestion the HF should be dispersed with HNO_3. These methods may be used for N ($H_2SO_4 + H_2O_2$), P, S, Ca, Mg, K, Na, Mn, Zn and Cu.

3. Digestion with $H_2O_2 + HNO_3$ in a microwave oven.

4. Pressurized digestion with HNO_3, or $HNO_3 + H_2O_2$ in Teflon bombs at 180. 200 mg vegetal powder + 3 ml concentrated HNO_3. This method may be used for the same elements as for A2 methods except N: S, P, Ca, Mg, K, Na, Mn, Zn, Cu and for Al, Cd, Pb, Cl and B.

5. Digestion in HNO_3 under a backward column. This method is used for Ca and Pb determination, but may be used for other elements with the exception of N.

Dry ashing

The sample powder is heated at 450-600ºC for 4 hours and ashes are dissolved in water or dilute acids (HCl, HNO_3, $HClO_4$).

1. Dry ashing at atmospheric pressure in a furnace at 450-600ºC, according to the element, in platinum, porcelain, quartz or Ni crucibles. Ash dissolution may be made with acids, such as HNO_3, HCl, or $HClO_4$.

This method is convenient for P, K, Na, Ca, Mg, Fe, Mn, and Zn. For P, the analysis should be delayed for 24 hours in order to ensure complete oxidation of P in to PO_4^-.

There may be Si and Al precipitates which are insoluble in HCl, and which may absorb a small quantity of elements; but the associated error is usually very small. It can be avoided by filtration of

the ash in a HCl solution, calcination of the filter in a platinum crucible, dissolution of the filter ashes in HF, dry evaporation, dissolution of the residue in HCl, and addition of this solution to the first filtrate.

The latter procedure is necessary for Al analysis, the solubilization of which is not complete without using HF, and for elements present in very small quantities in the plant tissue (Cu). A platinum crucible is necessary when using HF, although Teflon and carbon are viable alternatives.

For several elements (Cl, S, Pb, Cd), dry ashing at atmospheric pressure causes loss by volatilization. In order to prevent this, stabilizers should be added: $Mg(NO_3)_2$ (for S), NH_4NO_3 (for Cd and Pb), Na_2CO_3(for Cl), CaO for (B, F) and NaOH (for F).

2. Low temperature (50-60ºC) ashing in O_2 atmosphere excited by a radiofrequency magnetic field over 8 hr can be used for F analysis.

3. Combustion in a Schöniger flask, a closed flask in which plant powder is burnt in O_2 atmosphere and directly dissolved in acidic or alkalic solution. This method is used for many elements, including S, P, and Cl, but is very time-consuming because only one sample can be ashed and digested at a time.

Integrated oxidation and detection

More and more frequently, special apparatus are being used, performing automatically, in a closed circuit, detection and quantification of gases released during oxidation. Several firms sell this CHN or NS equipment.

Analysis of N and S by these methods is likely to become increasingly frequent. Unlike the Kjeldahl method, these methods give total N concentration, including NO_2^- and NO_3^- forms. When reporting results for N, it is therefore important to state which method was used.

X-ray fluorescence

All metals and non-metals down to F can be determined with X-ray fluorescence, without digesting or ashing, in compacted vegetal powder.

7.12.2.2.2 DETERMINATION

Many ways for the determination of the various elements are possible.

Titration

- NH after digestion by the Kjeldahl method and distillation of NH_3 in HBO_3;
- Cl: by $AgNO_3$ in the presence of CrO (the end of precipitation of AgCl is detected by the red colour of Ag_2CrO_4;
- Cl: by micro-titration with $AgNO_3$ in acetonic solution and potentiometric indication.
- SO_4 by titration with $BaCl_2$ and thorine as an indicator.

Colorimetry

- NH_4: indophenol blue; or FIA method (diffusion of NH_3 through a Teflon membrane, and colorimetry in a solution of phenol + ethanol + NaCl + NaOH).
- P: phosphovanadomolybdate (yellow) or molybdene blue.
- Cl: colorimetry of $Fe(SCN)_3$ after reaction of $Hg(SCN)_2$;
- S: metorine (8); DMSA III and other colour indications.
- B: 1-1'dianthrimide.

Turbidimetry

- S: turbidimetry of a suspension of insoluble $BaSO_4$ with a tensioactive agent (Tween 80).

Ionic chromatography for P, S, Cl, F.

Specific ion electrodes for F, Cl.

Capillary electrophoresis for Cl, S, P and N as NO_3 or NH_4.

Flame emission spectrometry for K, Na.

Atomic absorption spectrometry

1. Flame AAS: Na, K, Ca, Mg, Fe, Mn, Zn, Al, and Cu.

2. Graphite furnace AAS: Pb, Cd and Cu.

ICP (Inductively coupled plasma) after atomic emission spectrometry

1. Without ultrasonic nebulisation: Na, K, Ca, Mg, Fe, Mn, Zn, Al, Cu, P, S, Cl and B.

2. With ultrasonic nebulisation: Pb, Cd and Cu.

Processes (ashing with direct determination, in CHN or NS apparatus) and (direct determination by X-ray fluorescence) can be combined.

7.12.2.2.3 THE MOST FREQUENTLY USED METHODS FOR SPECIFIC ELEMENTS

Nitrogen

a) N organic + NH_4:

Digestion
Kjeldahl method: concentrated H_2SO_4 with K_2SO_4 and Se as catalysts Methods derived from the Kjeldahl method: catalysts other than Se, which is toxic in the environment, such as Ti or Cu; H_2SO_4 + H_2O_2 without a catalyst.

Determination
NH_4^+ colorimetry (indophenol blue or FIA method)
NH_3 distillation and titration.

Total N: CHNS apparatus.

Sulphur

a) Digestion or ashing.

- Wet acidic and oxidizing digestion: HNO_3; $H_2O_2 + HNO_3$; $H_2O_2 + HClO_4$; $HNO_3 + HClO_4$
- HNO_3 in Teflon bombs
- dry ashing with addition of Mg $(NO_3)_2$ and MgO; ash dissolution in HCl or water
- Schöniger flask

b) Determination

- Turbidimetry by $BaSO_4$ (preferably with dissolution by HCl and filtration before $BaSO_4$precipitation)
- ICP
- Ionic chromatography (after ash dissolution in water)
- Colorimetry

c) Direct determination in CNS apparatus.

d) Direct determination by X-ray fluorescence.

Phosphorus

a) Digestion and ashing

- wet acidic and oxidizing digestion: $H_2SO_4 + H_2O_2$; $H_2SO_4 + HNO_3$; HNO_3; $HNO_3 + H_2O_2$; H_2O_2+ $HClO_4$; $HNO_3 + HClO_4$
- HNO_3, or $HNO_3 + H_2O_2$, in Teflon bombs
- dry ashing at 450-500ºC at atmospheric pressure (wait for 24 h after ash dissolution in HCl or $HClO_4$ before determining PO_4^{2-})
- Schöniger flask

b) Determination

- Colorimetry: phosphovanadomolybdate or molybdene blue
- ICP-AES
- Ionic chromatography
- X-ray fluorescence (direct determination)

Calcium, Magnesium, Iron, Manganese, Zinc

a) Digestion or ashing

- Wet acid and oxidizing digestion at atmospheric pressure (HNO_3, $H_2SO_4 + HNO_3$, $HNO_3 + H_2O_2$; $H_2O_2 + HClO_4$, $HNO_3 + HClO_4$)
- HNO_3 or $HNO_3 + H_2O_2$, in Teflon bombs
- Dry ashing at atmospheric pressure, ash dissolution in HCl or $HClO_4$

- Schöniger flask

b) Determination

- Atomic absorption spectrometry
- ICP-AES
- X-ray fluorescence (direct determination in ash)

Potassium, Sodium

a) Digestion or ashing

b) Determination

- Flame emission spectrometry
- Atomic absorption spectrometry
- ICP-AES
- X-ray fluorescence (direct determination in ash)

Chloride

a) Digestion or ashing

- HNO_3 or $HNO_3 + H_2O_2$, in Teflon bomb
- Dry ashing at 450-550ºC after addition of Na_2CO_3 and ash dissolution in hot water
- Schöniger flask

b) Determination

- Titrimetry with $AG(NO_3)_2$
- Colorimetry of $Fe(SCN)_3$ after reaction with $Hg(SCN)_2$
- Ionic chromatography
- Capillary electrophoresis
- Specific electrode
- ICP
- X-ray fluorescence

Boron

a) Digestion or ashing

- HNO_3 or $HNO_3 + H_2O_2$, in Teflon bomb
- Dry ashing at 450-500ºC after addition of CaO, and ash dissolution in 25% acetic acid
- Schöniger flask

b) Determination

- Colorimetry by 1-1'dianthrimide
- Direct determination by X-ray fluorescence

- ICP

Fluoride

a) Dry ashing

- At 600ºC for 16 hours (after progressive temperature increase) with addition of CaO (1 g sample + 0.2 g CaO); ash dissolution in 4N $HClO_4$
- At 450ºC for 16 hours in Ni crucible, with addition of NaOH; ash dissolution by pH 5.7 buffered acid (Buffer HCl) acetic or HCl/citric acid). The muffle must be covered with Ni.
- Low temperature ashing in O_2 atmosphere
- Schöniger flask

b) Determination

- Specific electrode (eventually after micro-diffusion procedure of trimethylfluorosilane (TMFS) in 0.1 M NaOH, after ash dissolution in $HClO_4$
- Ionic chromatography

Aluminium

a) Digestion or dry ashing

- Dry ashing at 450-500ºC in platinum crucible, ash dissolution by HCl, filtration, collection of the filtrate, calcination of the filter, digestion of ash by HF, dry evaporation, dissolution of the residue in HCl and addition to the first filtrate
- Dry ashing at 450-500ºC in platinum or Ni crucible, followed by alkaline fusion of the ashes in lithium borate $LiBO_2$, and uptake in diluted HNO_3
- HNO_3, or HNO_3 + H_2O_2, in Teflon bomb

b) Determination

- Flame atomic absorption spectrometry
- ICP
- X-ray fluorescence

Copper

a) Digestion or ashing

- Wet acid digestion (HNO_3, HNO_3 + H_2O_2, HNO_3 + $HClO_4$, H_2O_2 + $HClO_4$)
- HNO_3, or HNO_3 + H_2O_2, in Teflon bomb
- Dry ashing and ash dissolution in HCl or $HClO_4$
- Dry ashing, dissolution in HCl, filtration, calcination of the filter, HF, dry evaporation, dissolution in HCl (as for Al determination)

b) Determination

- Flame atomic absorption spectrometry

- ICP
- ICP with ultrasonic nebulisation
- Lead and Cadmium (5g sample)

a) Digestion or ashing

- HNO_3 or HNO_3 + H_2O_2, in Teflon bomb
- Acid extraction by HNO_3 in a flask with a backward column
- Dry ashing at 450-550ºC after addition of NH_4NO_3, ash dissolution in HCl (for determination by ICP) or HNO_3 (for determination by atomic absorption)

b) Determination

- Electrothermic atomic absorption spectrometry (after ash dissolution in HNO_3)
- ICP with ultrasonic nebulisation (after ash dissolution in HCl)
- Flame atomic absorption spectrometry

7.12.2.2.4 DATA EXPRESSION UNITS

The total concentration in needles and leaves should be given by reference at 105ºC dried material. The residual water content after drying at 60-80ºC must be determined by drying at 105ºC and weighing, and the results given by the analysis performed on 65-80ºC dried powder must be corrected. Samples should be dried at 65-80ºC immediately before weighing them for analysis.

Major elements (N, P, S, K, Mg, Ca, and TOC) must be expressed in mg/g dry powder.

Trace elements (Fe, Mn, Na, Zn, Cu, Al, As, B, Cd, Cl, Cr, F, Mo, Ni and Pb) must be expressed in µg/g dry powder.

7.12.3. Validation of the analytical results

The total element concentrations obtained by the laboratories' standard methods need to be checked in order to determine the accuracy of these methods. Two steps of quality assurance are recommended:

Comparison of the results of the national methods with the concentrations of reference standard samples. These reference standard samples, with certified total element concentrations supplied e.g. by the Central Bureau of References of the EC or by ISO (International Standard Organization), or by the US group of foliar analysis, will be sent to participating laboratories for analysis. The certified concentrations will be supplied to individual laboratories once a sufficient amount of laboratories have submitted their results.

In order to permanently check the accuracy of the analyses, it is also recommended that each laboratory provides several of its own standard samples for analysis in each batch of samples. The data should only be accepted if the analyses of the known samples match the reference results.

See also Chapter 8 for data quality management.

7.12.4. Data reporting

Values are reported on oven dry basis (105ºC).

Mandatory parameters	**list**		**unit**
RE_T	IM	oven-dry sample weight of 1000 needles/100 leaves	g
STOT	DB	total sulphur	mg/g
NTOT	DB	total nitrogen	mg/g
PTOT	DB	total phosphorus	mg/g
CA	DB	calcium	mg/g
MG	DB	magnesium	mg/g
K	DB	potassium	mg/g
NA	DB	sodium	µg/g
MN	DB	manganese	µg/g
FE	DB	iron	µg/g
CU	DB	copper	µg/g
ZN	DB	zinc	µg/g
TOC	DB	total organic carbon	mg/g
Optional parameters:	**list**		
AL	DB	aluminium	µg/g

AS	DB	arsenic	µg/g
B	DB	boron	µg/g
CD	DB	cadmium	µg/g
CL	DB	chloride	µg/g
CR	DB	chromium	µg/g
F	DB	fluoride	µg/g
MO	DB	molybdenum	µg/g
NI	DB	nickel	µg/g
PB	DB	lead	µg/g

Example files (Excel format is preferred)

FC example Excel file
FC example ASCII file

- File identifier SUBPROG states the subprogramme.
- MEDIUM refers to the dominant tree species of the stand. (from NCC code list B4 (=LISTMED), see Annex 6 and TF Chapter for a list of common tree species).
- LEVEL is given as the sampling height from the ground (cm).
- Spatial pool SPOOL refers to the number of individual samples taken for pooled analysis.
- Please NOTE! the pre-treatment codes and determination codes in use are listed in Code list DB.
- C in the last field NEEDLES indicates results from current year needles, P= previous year's needles. General information on flags is given in Chapter 4.
- Sampling year and month are given as YYYYMM, day field is left blank.

7.12.5 References

ICP Forests Manual
http://icp-forests.net/page/icp-forests-manual
(2010, 2016)

ICP Forests manual, 1997. Manual on methods and criteria for harmonized sampling, assessment, monitoring, and analysis of the effects of air pollution on forests, 4th edition. Edited in 1997 by the

Programme Coordination Centre Federal Research Centre for Forestry and Forest Products (BFH), Hamburg, Germany.

The most up-to-date methods of analysis are available from Official Methods of Analysis of AOAC International, link to publication

7.13 Subprogramme LF: Litterfall chemistry

- 7.13.1 Introduction
- 7.13.2. Field methods
- 7.13.3 Chemical analyses
- 7.13.4 Data reporting

7.13.1 Introduction

Foliar analyses are an effective means of recognizing pollutant-related stress in forest trees. Foliar analyses provide the means for assessing changes in the content of nutrients and contaminants in needles and leaves. Analyses of both live material (foliage chemistry) and dead material (shed foliage = litter chemistry) are important for assessing nutrient fluxes and nutritional status of forest trees.

Elements to be determined: Ca, K, Mg, Na, N, P, S, Cu, Fe, Mn, Zn and TOC
Optional: Al, As, B, Cd, Cl, Cr, F, Mo, Ni and Pb

7.13.2. Field methods

Undertake litterfall sampling systematically or randomly, not just under the dominant tree species. Litterfall collectors should be placed in connection with throughfall collectors, with the purpose of assessing litterfall for the catchment as a whole. Connection with permanent soil plots is less important. Six to 12 collecting sacks are used.

Litterfall is collected with litter sacks. Litter sacks should be made of inert material and be 0.5 m deep to prevent litter from blowing away. Attach the sack to a wooden frame of known area (0.25 - 0.5 m^2). The frame should be horizontal and applied to poles, one in every corner, driven into the ground. The sack should not touch the ground as moisture entering the sack will accelerate the decomposition process.

All shed brown needles/leaves should be sorted out from the rest of the fine litter and analysed for chemistry. Comparisons with foliage concentrations provide information about translocation and nutrient status.

Sampling should be undertaken at least monthly, but samples can be pooled to periodic samples. Transfer the litter to large paper/plastic bags using gloves and transport them to the laboratory.

Make pooled samples of litterfall for chemical analysis. Avoid all contamination from smoke or laboratory tables. Handle the samples on clean laboratory paper, glass shields or clean polyethene.

Dry the samples at 40ºC to a constant weight. Alternatively, samples can be cooled lower than 5ºC until drying can be performed.

7.13.3 Chemical analyses

For chemical analyses see chapter FC Foliage chemistry.

7.13.4 Data reporting

Values are reported on oven dry basis (105ºC). Parameters and units are the same as in Foliage chemistry.

Mandatory parameters	**list**		**unit**
LDEP	IM	litterfall amount (oven dry weight)	g/m^2
STOT	DB	total sulphur	mg/g
NTOT	DB	total nitrogen	mg/g
PTOT	DB	total phosphorus	mg/g
CA	DB	calcium	mg/g
MG	DB	magnesium	mg/g
K	DB	potassium	mg/g
NA	DB	sodium	µg/g
MN	DB	manganese	µg/g
FE	DB	iron	µg/g
CU	DB	copper	µg/g
ZN	DB	zinc	µg/g
TOC	DB	total organic carbon	mg/g

Optional parameters:	**list**		
AL	DB	aluminium	µg/g
AS	DB	arsenic	µg/g
B	DB	boron	µg/g
CD	DB	cadmium	µg/g
CL	DB	chloride	µg/g
CR	DB	chromium	µg/g
F	DB	fluoride	µg/g
MO	DB	molybdenum	µg/g
NI	DB	nickel	µg/g
PB	DB	lead	µg/g

Example files (Excel format is preferred)

LF example Excel file
LF example ASCII file

- File identifier SUBPROG states the subprogramme.
- MEDIUM refers to the dominant tree species of the stand where litterfall is collected (NCC code list B4, see Annex 6 and TF chapter for a list of common tree species).
- LEVEL is given as sampling height from the ground (cm), optional here.
- Spatial pool SPOOL refers to the number of individual samples taken for pooled analysis.
- Litterfall amount is given as a sum for the period, status flag is S. General information on flags is given in Chapter 4.
- Sampling year and month are given as YYYYMM, in the example as 201100 when the pooled sampling is assumed to have covered a period of several months. Day field is left blank.

7.14 Optional subprogramme RB: Hydrobiology of streams

7.14.1 Introduction

The biotic composition and biomass of streams react differently to acidification due to different species tolerance (sc. acidification scores). Macroinvertebrates are considered good indicators of acidification and the frequency of acid shocks to streamwater, however universal indicators cannot be identified due to differences in geographical distribution.

7.14.2 Methods

Local circumstances, like depth and bottom consistency, should be taken into consideration when choosing sampling sites. Macrozoobenthos samples are preferably taken from hard bottoms with rapidly running water. An adequate sampling site often covers a stream length of ca. 10 times the width of the stream.

Macrozoobenthos samples are collected twice a year, preferably in spring and autumn. Sampling in spring is done immediately after snow melt, and sampling in autumn should coincide with periods of low flow.

Sample with the kick-sampling method which is suitable for the majority of species living on coarse-grained bottoms and submersed vegetation as well as in fine material between and under stones (sessile species may be underrepresented). Kick-sampling can be performed in waters with velocities of 0.1 - 1 m/s and down to 1 m depth.

Use a sampling net with triangular or square opening (sides 25 cm) and a mesh size of 0.5 mm (Figure 7.14.1). The net and its handle can be cm-graded for recording depth of water. The net should be sterilized between use at different locations to avoid the spreading of possible diseases. This is done by soaking it in formaldehyde or ethanol.

Place the net on the bottom facing streamflow. Turn stones and kick the bottom sediment within an area of 25 x 40 cm^2 for 60 seconds. The loose material should pass the net. Take 3 - 6 replicate kick-samples at each site.

Thoroughly rinse every sample and transfer the net residue to a plastic vessel by turning and brushing the net. Pick attached specimens with soft pincers. Transfer the sample to 1 litre jars containing 96 % ethanol.

Transfer the sample in small portions to Petri dishes and sort them under magnification (e.g. 10 x). Handle the animals with soft pincers. If the determination of species is done afterwards, store the animals according to taxonomic groups and keep the material in air-tight glass capsules in 70 % ethanol. Count the specimens during determination; for fragmented material only identifiable parts are counted. Taxonomic identification should be as accurate as possible (species/genus level).

References how to identify to family level are given in references.

Measure the biomass as conserved wet weight after the animals have been placed in clean water for 10 minutes. When measuring wet weight of preserved material wait for ca. 1 month.

See also Chapter 4 in ICP Waters manual.

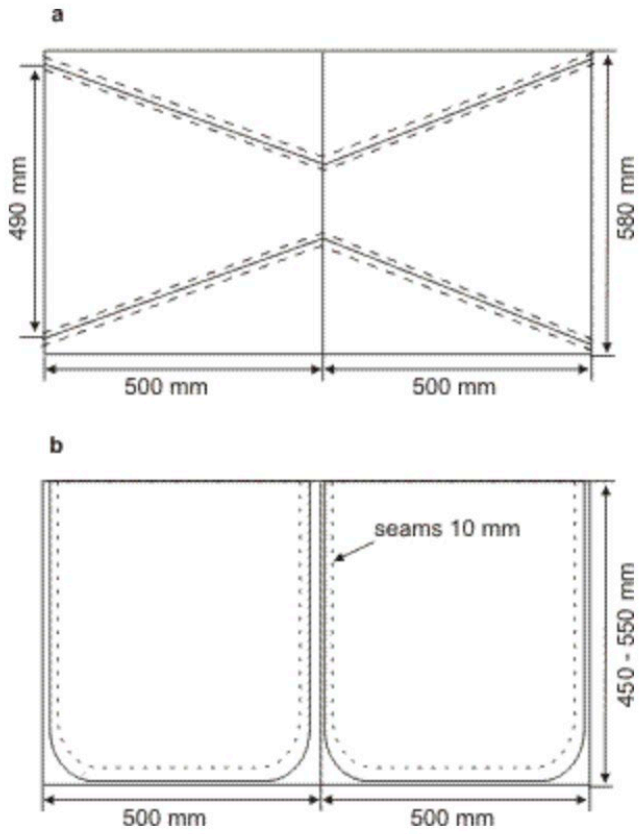


FIGURE 7.14.1 SUGGESTED PATTERNS FOR NETS.

7.14.3 Data reporting

Due to the specific nature of the Macrozoobenthos data, these data are recommended to be stored at the National Focal Points, this is partly due to problems in coding the species and the local expertise needed in evaluation of the data. The assessment of these data will be carried out periodically and a special request will be made for the NFPs prior to the assessment.

The data should cover the characteristics of the sampling site and sampling information, species names with specimen density (ind/m^2) and biomass (g/m^2), and also the Shannon-Wiener diversity index (for calculation, see Annex 7).

7.14.4 References

ICP Waters Programme manual. Compiled by the Programme Centre, Norwegian Institute for Water Research. Revised edition, Oslo.

ISO 7828 - 1985

References how to identify the species to family level:

1. A KEY TO THE BRITISH SPECIES OF FRESHWATER CLADOCERA, WITH NOTES ON THEIR ECOLOGY.
D.J. Scourfield & J.P. Harding, Third edition, 1966. (Reprinted 1994)

2. A KEY TO THE BRITISH FRESH- AND BRACKISH-WATER GASTROPODS, WITH NOTES ON THEIR ECOLOGY
T.T. Macan, Fourth edition, 1977. (Reprinted 1994)

3. A KEY TO THE ADULTS AND NYMPHS OF THE BRITISH STONEFLIES (PLECOPTERA), WITH NOTES ON THEIR ECOLOGY AND DISTRIBUTION
H.B.N. Hynes, Third edition, 1977. (Reprinted 1993)

4. A KEY TO THE BRITISH FRESHWATER CYCLOPID AND CALANOID COPEPODS, WITH ECOLOGICAL NOTES
J.P. Harding & W.A. Smith, Second edition, 1974

5. A KEY TO THE BRITISH SPECIES OF FRESHWATER TRICLADS (TURBELLARIA, PALUDICOLA)
T.B. Reynoldson, Second edition, 1978

6. A KEY TO THE LARVAE, PUPAE AND ADULTS OF THE BRITISH DIXIDAE (DIPTERA), THE MENISCUS MIDGES.
R.H.L. Disney. 1975

7. AN ILLUSTRATED KEY TO FRESHWATER AND SOIL AMOEBAE, WITH NOTES ON CULTIVATION AND ECOLOGY.
F.C. Page. 1976

8. A NEW KEY TO FRESHWATER AND SOIL GYMNAMOEBAE, WITH INSTRUCTIONS FOR CULTURE
F.C. Page. 1988

9. A KEY TO THE LARVAE AND ADULTS OF BRITISH FRESHWATER MEGALOPTERA AND NEUROPTERA, WITH NOTES ON THEIR LIFE CYCLES AND ECOLOGY
J.M. Elliott. 1977

10. A KEY TO THE FRESHWATER PLANKTONIC AND SEMI-PLANKTONIC ROTIFERA OF THE BRITISH ISLES.
R.M. Pontin. 1978

11. A KEY TO THE BRITISH AND EUROPEAN FRESHWATER BRYOZOANS.
S.P. Mundy. 1980

12. A KEY TO THE LARVAE OF THE BRITISH ORTHOCLADIINAE (CHIRONOMIDAE).
P.S. Cranston. 1982

13. THE PARASITIC COPEPODA AND BRANCHIURA OF BRITISH FRESHWATER FISHES: A HANDBOOK AND KEY
G. Fryer. 1982

14. EPHEMEROPTERA, WITH NOTES ON THEIR ECOLOGY
J.M. Elliott & U.H. Humpesch. 1983

15. KEYS TO THE ADULTS, MALE HYPOPYGIA, FOURTH-INSTAR LARVAE AND PUPAE OF THE BRITISH MOSQUITOES (CULICIDAE), WITH NOTES ON THEIR ECOLOGY AND MEDICAL IMPORTANCE
P.S. Cranston, C.D. Ramsdale, K.R. Snow & G.B. White. 1987

16. LARVAE OF THE BRITISH EPHEMEROPTERA: A KEY WITH ECOLOGICAL NOTES
J.M. Elliott, U.H. Humpesch & T.T. Macan. 1988

17. ADULTS OF THE BRITISH AQUATIC HEMIPTERA HETEROPTERA: A KEY WITH ECOLOGICAL NOTES
A.A. Savage. 1989

18. A KEY TO THE CASE-BEARING CADDIS LARVAE OF BRITAIN AND IRELAND
I.D. Wallace, B. Wallace & G.N. Philipson. 1990

19. BRITISH FRESHWATER CRUSTACEA MALACOSTRACA: A KEY WITH ECOLOGICAL NOTES
T. Gledhill, D.W. Sutcliffe & W.D. Williams. 1993

20. A REVISED KEY TO THE CASELESS CADDIS LARVAE OF THE BRITISH ISLES, WITH NOTES ON THEIR ECOLOGY
J.M. Edington & A.G. Hildrew. 1995

7.15 Optional subprogramme LB: Hydrobiology of lakes

7.15.1 Introduction

Studies concerning diversity and abundance of hydrobiological groups and environments often indicate changes of the water quality. Very often, all groups must be monitored to understand the changes, but even single groups may indicate certain trends of its environment. Interpretation of the changes requires knowledge of species tolerance and biology.

7.15.2 Methods

A more detailed description is found in Keskitalo and Salonen, 1994. See also ICP Waters manual.

7.15.2.1 Macrozoobenthos

Local circumstances, like depth and bottom consistency, should be taken into consideration when choosing sampling sites. Macrozoobenthos samples are preferably taken from vegetation free soft bottoms of accumulation type. These are often found in the deepest parts of the lake. Distribution of

individual sampling may be random or systematic. Chosen sites should be marked to ensure revisits (e.g. buoys).

For sampling macrozoobenthos on soft bottoms a bottom-sampler (of the Ekman type or of similar design) is needed. Apply a weight and a rope to the sampler. Collecting vessels of size 10 - 15 litres with lids and a sieve with 0.5 mm mesh size as well as preservation jars of size 0.5 litre with lids and preservative (96 % ethanol) and other equipment.

Zoobenthos samples are taken at least four times a year to receive a better documentation of time series. First samples in spring are taken shortly after ice breakup in areas with lake freeze-over, not later than end of May. Last samples are taken in September-November. Sampling during extreme cold is not recommended. Also times with strong winds should be avoided.

Lower the grab-sampler vertically, slowly, but steadily to ensure good bottom contact. Lock the sampler and retrieve at a steady pace. Move the sampler over the collection vessel. Take care that the sampler does not leak. Turbid water during retrieval of sampler may indicate leakage.

Record the texture, odour etc. for the sediment if sedimentological research otherwise is omitted. Pour the sample on the sieve carefully in order not to miss any material. Normally the sample is sieved at once.

Sieve with alternating vertical and horizontal movements just beneath the water surface of the vessel. One to three minutes is normally sufficient. Avoid using pressurized water. In tight sediments clumps of clay may remain in the sieved sample.

Move the sieving rest to a preservation container (e.g. a 0.5 l plastic jar) using a spraying bottle containing 96 % ethanol. Remove large animal rests with soft pincers. Wash the sieve before reuse.

7.15.2.2 Chlorophyll α (alpha)

Chlorophyll alpha is determined twice a month in summer, including sampling also in autumn and spring when the production maximum often occurs. Samples are taken with a tube sampler each covering water layers 0 - 1 m, 1 - 2 m, etc. In deep waters thicker layers may be appropriate.

Chlorophyll samples must be filtered on the sampling day. (An absolute limit is the morning of the following day, assuming that the samples have been stored at +4 ºC). The samples (normally 0.1-2 litres) are filtered through glass fibre filters (e.g.Whatman GF/F) with a vacuum < 20 kPa. The filters are dried in darkness and stored in dark and frozen (at least -20 ºC) if the determination cannot take place immediately. Maximum storage time is one month.

Chlorophyll is extracted from the algae by immersing the filter in 94% ethanol. The volume of the extractant (5 - 25 ml) must be known precisely. The extraction is carried out in glass or plastic tubes with air-tight stoppers. The sample tubes are to be placed for five minutes in a 75 ºC water bath so that the sample is completely submerged. The tubes are allowed to cool down to room temperature. If the determination cannot continue immediately, the samples can be kept overnight at +4 ºC protected from light. The absorbance of the centrifuged or filtered extract (glass fibre filters) is measured spectrophoto-metrically at 665 and 750 nm. The blanks are measured with 94% ethanol.

Calculation and expression of the results:

The chlorophyll concentration of the sample is calculated with the formula:

$C_{hl} = (A_{665} - A_{750}) \times (V_1 \times 10^3) / (V_2 \times L \times 83.4)$

where:
C_{hl} = chlorophyll alpha concentration of the sample (mg/m^3)
V_1 = ethanol volume (ml)
A_{665} = sample absorbance at 665 nm (absorption maximum of chlorophyll α)
A_{750} = sample absorbance at 750 nm (turbidity) 83.4 = constant; absorption coefficient of chlorophyll α in 94% ethanol
V_2 = sample volume filtered (l)
L = cuvette length (cm)

The results are expressed as (CP) mg/m^3 (for each depth zone).

7.15.2.3 Planktic activity

Phytoplankton primary production is determined by the acidification and bubbling modification of the radiocarbon method. The sampling frequency should be at least twice a month in summer. Samples are collected into glass bottles with a nontoxic PFTE coated or plastic sampler. Samples are taken from five depths covering illuminated epilimnion as a geometric series, so that the sample density is highest near to the surface.

Radiocarbon solution is injected into the light and dark bottles which are then incubated at the depths of sampling. Two control samples killed in 1 % formaldehyde are incubated near to the surface and at the greatest depth. After 24 h the bottles are taken away and biological activity is stopped by adding 40 % unbuffered formaldehyde to 1 % final concentration in each bottle. Particular care should be taken to minimise the exposure of dark bottles to the light.

Determination of dissolved inorganic carbon is necessary for the calculation of the primary production results. It should be determined with a carbon analyser on the sampling day.

In the laboratory appropriate subsamples in liquid scintillation vials are acidified with phosphoric acid and put into a vacuum hood for 2 days to exchange inorganic radiocarbon with carbon dioxide in the air. Formaldehyde poisoned control samples are treated similarly. The radioactivity is measured with liquid scintillation counter, using appropriate scintillation liquid/sample water ratio. In the calculation of primary production dark results are subtracted from the light ones.

Respiration of plankton is determined by measuring either oxygen consumption or carbon dioxide accumulation in dark bottles. The choice between the methods depends on the methods available and carbon dioxide concentration. Select the method yielding the best sensitivity. Samples are taken as described above, but particular care should be taken to ascertain that the determinations of initial and final concentrations, from which the respiration is calculated as a difference, are made of the same water. This is done by letting water flow from the sampler tube into the bottles through a Y-shaped divider.

Carbon calculations:

- **Assimilated inorganic carbon** at each sample depth is calculated using the formula:

$C = (1.05 \times C_1) \times (R_v - R_p) / (R_t - R_k)$

where:
C = concentration of assimilated inorganic carbon (mg/m^3)
1.05 = rejection coefficient for radiocarbon
C_1 = concentration of inorganic carbon in the sample (mg/m^3) Rv = radioactivity of the light sample (average of two determinations, dpm or Bq) R_p = activity of the dark sample (dpm or Bq) R_t = radioactivity added to the sample (dpm or Bq) (average of two determinations, calculated to the same volume as R_v, R_p and R_k)
R_k = mean activity of the two control samples (surface, deepest sample) (dpm or Bq)

The results are expressed as assimilated carbon (CINOA) mg C/m^3/d (for each analysed depth).

- **Carbon dark fixation** at each sample depth is calculated using the formula:

$C_p = (1.05 \times C_1) \times (R_p - R_k) / (R_t - R_k)$

where:
C_p = carbon dark fixation (mg C/m^3)
1.05 = rejection coefficient for radiocarbon
C_1 = inorganic carbon concentration of the sample (mg/m^3)
R_p = radioactivity of the darkened sample (dpm or Bq)
R_k = mean activity of the two control samples (at surface and lowermost depth) (dpm or Bq)
R_t = radioactivity added to the sample (dpm or Bq) (average of two determinations, calculated to the same sample volume as R_p and R_k)

The results are expressed as (CINOD) mg C/m^3/d (for each analysed depth).

7.15.3 Data reporting

Chlorophyll α and planktic activity parameters can be reported using the common format for chemical subprogrammes, see Chapter 4, for an example see e.g. subprogramme Lake chemistry, LC.

Parameters	**list**		**unit**
CP	DB	chlorophyll alpha	mg /m^3
CINOA	IM	inorganic assimilated carbon	mg C/m^3/d

CINOD	IM	carbon dark fixation	mg $C/m^3/d$
O2R	IM	respiration	mg $O_2/m^3/d$

Profundal benthos

Due to the specific nature of the Macrozoobenthos data, these data are recommended to be stored at the National Focal Points, this is partly due to problems in coding the species and the local expertise needed in evaluation of the data. The assessment of these data will be carried out periodically and a special request will be made for the NFPs prior to the assessment.

The data should cover the characteristics of the sampling site and sampling information, species names with specimen density (ind/m^2) and biomass (g/m^2), and also the Shannon-Wiener diversity index (for calculation, see Annex 7).

7.15.4 References

Keskitalo, J., Salonen, K. Manual for Integrated Monitoring Subprogramme Hydrobiology of Lakes. Publications of the National Board of Waters and the Environment. Series B. Finland, 1994.

ICP Waters Programme manual. Compiled by the Programme Centre, Norwegian Institute for Water Research. Revised edition, Oslo.

ISO standards: ISO 9391: 1993 (E), ISO 7828-1985 (E)

7.16 Optional subprogramme FD: Forest damage

7.16.1 Introduction

The aim of assessing tree defoliation and discolouration annually is to obtain early quantitative indications of changes in the most important photosynthetically active parts of the trees.

7.16.2 Methods

7.16.2.1 Selection of sample trees

Several sampling designs are acceptable. These can range from a large number of small plots to a small number of large plots. However, in all cases, the trees should be chosen objectively. The total number of trees assessed in any given year at an IM site should exceed 100.

The trees may be marked for easier re-location, but this is not essential. If a marked tree has died since the last inventory, then it should be replaced. The replacement should have an identification number that has not been used previously. Plot locations should not be moved between inventories unless the sample size is very large, as such moves will create a large amount of variability in the data.

For a given sample size, the year-to-year variation in a sample of marked trees will be lower than that of a sample of unmarked trees. However, if the same objective system of tree selection is used each year and the plot centres remain the same, the samples of unmarked trees will consist of approximately the same individuals each year.

On regularly distributed plots
If a network of regularly distributed forest plots has been established over the site, sample trees should be selected on these plots.

On special plots
If sample plots have not and will not be established over the area the following procedure is followed. Select one to three forest stands representing the typical stand type(s) of the site. Determine the dominant tree species of the stand. Choose 20 or more trees of this species from an area not larger than 1 hectare, e.g. a circular plot with radius ca. 50 m.

7.16.2.2 Recommended observation method

Sample trees should meet the following criteria:

- alive
- predominant, dominant, or codominant social class
- <50% mechanical damage
- crown at least partly visible (1-4) (see part 4 in Annual Procedure, below)

Only that part of the crown that is exposed to light and not shaded by neighbouring trees - the assessable crown - should be considered. This means that on free-standing trees the whole crown should be included, while in forest stands it is usually only the upper part of the crown. Epicormic shoots on the stem below the crown are excluded from the estimate.

The following types of damage should not be considered as defoliation:

- those parts of the crown directly thinned by competition or other interactions with neighbours, e.g. whipping
- old, dead branches which have lost their twigs

Annual procedure

1) Determine the social class of the tree to make sure that it is predominant, dominant, or codominant.

- Pre-dominant (including free standing) = trees with upper crown standing above the general level of the canopy.
- Dominant = trees with crowns forming the general level of canopy.

- Co-dominant = trees extending into the canopy and receiving some light from above, but shorter than the first two.

2) Decide which part of the crown will be included in the assessment.

3) Decide what should be excluded as defoliation.

4) Decide on and note the visibility of the crown (important for evaluation of results):

- 1= whole crown visible
- 2= crown partially visible (parts clearly visible)
- 3= crown poorly visible (no parts clearly visible)
- 4= crown only visible with backlight (in outline)

5) Estimate and note defoliation in 5% steps (definition: needle/leaf loss in the assessable crown as compared to an imaginary, fully needled/leafed tree of the same type, regardless of the cause of loss).

6) Estimate and note discolouration (definition: a deviation from the usual colour of the living foliage for that species; dead needles/leaves are excluded) as proportion of needles/leaves affected in 5% classes.

7) Record any cause of damage that could have significantly influenced the defoliation of the tree, e.g. insects, stem rot, deer, wind, frost, drought, fire, snow, neighbouring windthrow.

The observations should be done by two trained observers using binoculars in full daylight and changing points of observation. Both observers must reach a common score. Suitable time periods are July-August for broadleaves and July-September for conifers, depending on the latitude and altitude of the site.

A photo-guide will help to maintain the assessment standards through time. Use of a photo-guide implies that absolute reference trees are being used. These represent the most suitable standard for long-term assessments of tree condition. Absolute reference trees are the best possible trees of a genotype or species, regardless of site conditions or tree age. The use of absolute reference trees in Integrated Monitoring is strongly recommended over the use of local reference trees.

Other assessments

Record stem diameter at breast height, tree height, crown length and crown width of each tree. These measurements should be repeated at least every 5 years. Details of assessment techniques are given in the Increment Sub-Manual of ICP Forests.

7.16.3 Quality assurance/Quality control

As customary in national forest inventories, a proportion (e.g. 5-10%) of the sample plots measured by each survey crew, must be remeasured by an independent check survey crew. This control inventory covers all measurements and assessments made by the field crews. In case of significant discrepancies, adjustments of instruments of clarification of instructions and their application must be arranged immediately to avoid serious systematic errors.

See also an overview data quality management in Chapter 8.

7.16.4 Data reporting

Annually reported parameters:

Parameters	**list**		**unit**
VISIB	IM	visibility of the crown	code (1 - 4)
DEFO	IM	defoliation	%
DISC	IM	discoloration	%
DAMAGE	IM	damage, cause of damage reported in col 65-100, e.g.: "Elatobium abietinum", "Browsing damage", "Lightning".	

Other parameters:

Parameters	**list**		**unit**
DBH	IM	diameter of stem (at breast height)	cm
HEIG	IM	height of trees	m
HCROW	IM	crown length	m
WCROW	IM	crown width	m

Variables are reported by plot and tree (number 1, 2, 3, ...).

Example files (Excel format is preferred)

FD example Excel file
FD example ASCII file

- File identifier SUBPROG states the subprogramme.
- Species code for the tree is reported as MEDIUM using NCC species codes (see Annex 6 and subprogramme TF for a list of common species).
- The number of the tree is given as TREE.
- Spatial pool (SPOOL) is here always 1.
- General information on flags is given in Chapter 4.
- Sampling year and month are given as YYYYMM, day field is left blank.

7.16.5 References

ICP Forests Manual, 2016 (including older parts)
http://icp-forests.net/page/icp-forests-manual

ICP Forests manual, 1997. Manual on methods and criteria for harmonized sampling, assessment, monitoring, and analysis of the effects of air pollution on forests, 4th edition. Edited in 1997 by the Programme Coordination Centre Federal Research Centre for Forestry and Forest Products (BFH), Hamburg, Germany.

Photoguides for crown defoliation:

Ferretti, M. (ed.). 1994. Mediterranean Forest Trees. A guide for crown assessment. CEC, Brussels. Available from: Commission of the European Communities, DG VI, 200 Rue de la Loi (L120-10/197 A), B-1049 Brussels, Belgium, or from PCCW. No charge. (Separate editions in English, French, German, Greek, Italian, Portuguese, and Spanish are available).

Innes, J.L. 1990. Assessment of tree condition. Forestry Commission Field Book 12. HMSO, London. Available from Technical Publications Office, Forestry Commission, Forest Research Station, Alice Holt Lodge, Wrecclesham, Farnham, Surrey GU10 4LH, England. Cost £15 + p. & p. (In English, with German, French and Russian summaries)

Müller, E. and Stierlin, H.R. 1990. Sanasilva Kronenbilder, mit Nadel- und Blattverlustprozenten. Swiss Federal Institute for Forest, Snow and Landscape Research, Birmensdorf. Available from: F. Flück-Wirth, Internationales Buchhandlung fur Botanik und Naturwissenschaften, CH-9053, Teufen, Switzerland. (Multilingual: in German, English, French, Italian). Cost: SFr. 24 + p. & p.

7.17 Subprogramme VG: Vegetation (intensive plot)

Revised in 2010

7.17.1 Introduction

The main aim of the VG subprogramme is to obtain sensitive bioindication of changes in pollutant deposition or other atmospheric factors, e. g. warming, on a representative plant community and its species. Another aim is to obtain data on the dynamics of tree biomass and canopy structure representative at least for the intensive area where a number of subprogrammes are also being conducted. This is especially important where the BI subprogramme (Tree bioelements and tree indication) is lacking. Data on dead trees, logs and stumps are useful for following the decay process and the dead wood as habitat for fungi, mosses, and insects. Also detailed monitoring of soil-living plants as part of the biological diversity of the site is achieved.

The understorey vegetation includes soil-growing vascular plants, bryophytes, and lichens, not fungi or algae.

For the interpretation of data it is especially important to have access to data from subprogrammes Precipitation chemistry (PC), Throughfall (TF) and Soil chemistry (SC).

7.17.2 Methods

7.17.2.1 Selection and establishment of the plot

Establish one or two permanent intensive plots about 40x40 m (preferably between 20x20 and 50x50 m) (Fig. 7.17.1) in a homogeneous part of one or two plant communities representative of the monitoring site and preferably also widespread in the region. Establish the plot when most plants are fully developed. It is practical to orientate the plots in north-south/east-west directions. Mark permanently the corners of the plot.

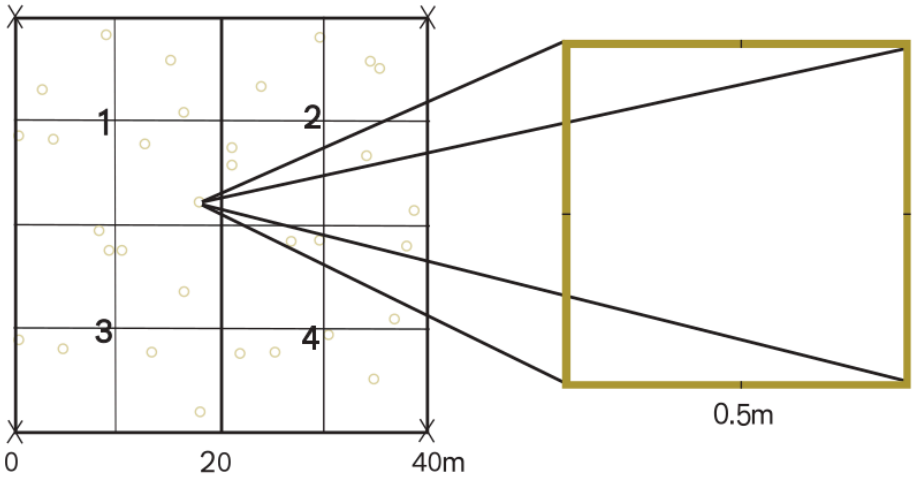


FIGURE 7.17.1. AN EXAMPLE OF AN INTENSIVE PLOT (40X40 M). SAMPLE PLOTS (SP, 50X50 CM) FOR UNDERSTOREY VEGETATION ARE DISTRIBUTED IN A STRATIFIED RANDOM FASHION - EACH 10X10 M SUBSQUARE (SS) IS SAMPLED BY, FOR EXAMPLE, TWO RANDOM PLOTS. THE INTENSIVE PLOT CAN BE SUBDIVIDED INTO FOUR QUARTERS (Q, 1-4), BUT THIS IS NOT OBLIGATORY BECAUSE MORE SUBSQUARES, EACH WITH TWO SAMPLE PLOTS, WERE CHOSEN IN SOME IM SITES.

Distribute randomly or by stratified random sampling a sufficient number of sample plots, e. g. 50x50 cm, on the intensive plot and mark them permanently (Fig. 7.17.1). In order to counteract unwanted activity from animals on the sample plot the marking should be insignificant. 20-40 plots should be sufficient, depending on the variability of the understorey vegetation and the size chosen of the sample plots. Exclude plots where unwanted substrates, e.g. stone or log occupy more than a certain part. Make sure that disturbing influence, e.g. trampling, especially on the small sample plots, from various monitoring activities are excluded.

7.17.2.2 Observations

According to its stratification and functional groups the vegetation of the intensive plot should be separated into layers. No specific height limits of trees and shrubs can be given, but here is an example:

- **tree layer:** trees > 5 m
- **shrub layer:** trees 1-5 m, morphological shrubs >1 m
- **field layer:** trees and shrubs <1 m, other vascular plants irrespective of height
- **bottom layer:** bryophytes and lichens

According to this classification a tree species can be present in both tree, shrub, and field layers. If desirable the tree layer could be separated into an upper and a lower stratum.

Tree layer and dead wood

Observe living and dead trees that belong to the tree layer according to definition and, if feasible, also logs and stumps over the whole intensive plot!

- Note the species of all trees and other objects mapped and measured!
- Map the trunk bases of living and dead trees, preferably by coordinates using an origo, e. g. the SW corner of the intensive plot.
- Note dbh (=diameter at breast height, i. e. 1.3 m above ground) (cm) of all trees mapped, crown diameter (m) and crown limit (m) only of living trees. Where the tree crown is very eccentric a diameter value is estimated which gives an approximation of the real cover.
- Measure the heights (m) of trees. Where trees are numerous and tops difficult to see heights could be measured only on a selection of representative individuals of different dbh-classes. Then the heights of the others are estimated using the regression between dbh and height.
- Logs and stumps (clearly not connected with logs) above a minimum size, e.g. 5 or 10 cm diameter, should also be mapped and measured. The position and length of a log can be inferred from co-ordinates for its top and base ends. Dbh should be measured 1.3 m from the base to be comparable with that of standing trees. On tall stumps (1.3 m) dbh is measured, on low ones the diameter of the upper surface.

Take care to avoid trampling on the small sample plots when mapping and measuring the trees and shrubs!

Shrub layer

Map living and dead trees and shrubs in the shrub layer, according to definition, in the same way as trees of the tree layer. Where a shrub has several trunks the thickest is chosen for position and dbh measurement. Thickets of shrubs may be mapped directly by drawing the outline on a map of the intensive plot.

Field and bottom layers

The main parameter observed is quantity, expressed as percentage cover for all individual species. In order to keep external conditions as uniform as possible, only plants living on relatively homogeneous soil should be included. This excludes plants growing on other substrates, e.g. stones and logs.

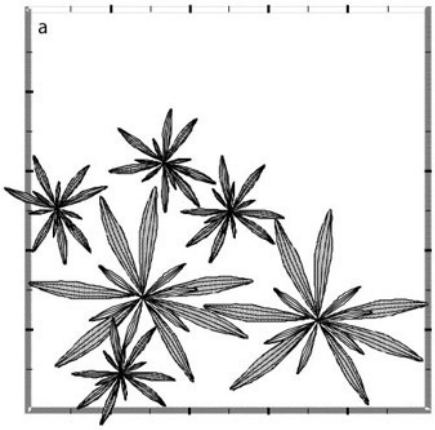
Estimate the **cover** of the field and bottom layers and their species. Cover percentage (%) of the sample plot is the area that above-ground living parts of a plant occupy when projected vertically on to the ground (shade when sun in zenith) (Figure 7.17.2). A mesh, made of a frame and strings, with 10x10cm mesh size can be put on sample plots in order to help estimating cover. Do not remove specimens from the sample plots. If identification requires samples for determination they must be sought outside the plots.

In the 1998 version of the manual vigour expressed as flowering value was also used. The monitoring of this parameter can be continued but its value for bioindication is of minor importance. Subsequently spatial distribution, expressed as plot frequency, is calculated if reporting is done according to the old manual.

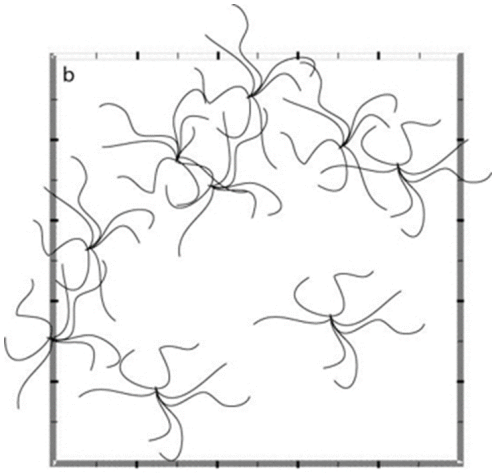
Optional: Vigour

Estimate presence of flowering organs (bud, flower, fruit, fruit rest of the current year) of species in the field layer using the fertility codes:

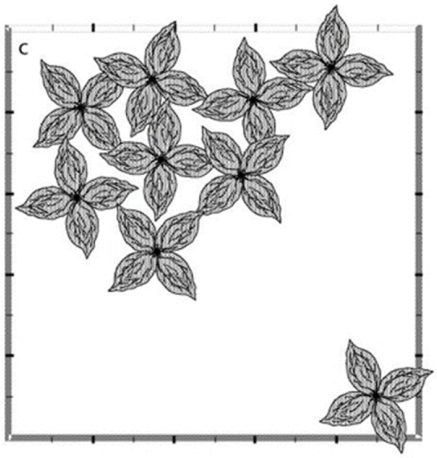
- 0 = species sterile
- 1 = <10 % of all shoots/individuals with flowering organs
- 2 = >10 % of all shoots/individuals with flowering organs



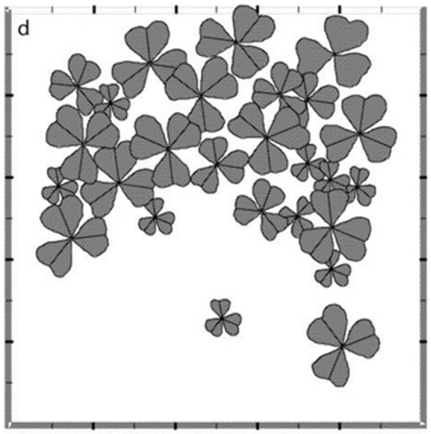
a: Scorzonera humilis



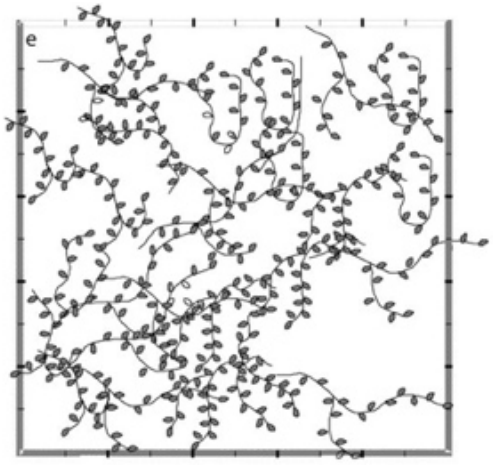
b: Deschampsia flexuosa



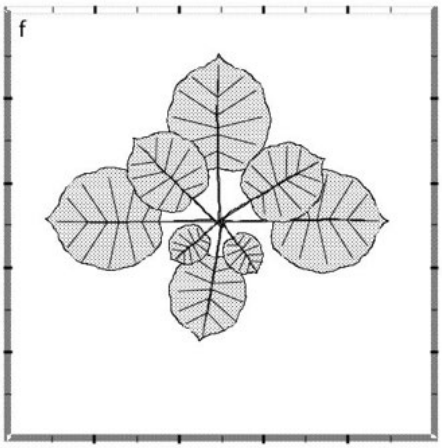
c: Paris quadrifolia



d: Oxalis acetosella



e: Vaccinium oxycoccos



f: Alnus incana

FIGURE 7.17.2. SIX CASES OF PLANT COVER. TEST YOUR ACCURACY OF COVER ESTIMATE! (TRUE VALUES IN % AFTER PARAGRAPH 7.17.4.)

7.17.2.3 Frequency of observations

Tree and shrub layers should be observed every five years.

Depending on the stability and vulnerability of the vegetation, the intervals between observations of the field and bottom layers could be 1 - 5 years. In order for a time-series to be established as soon as possible annual observations are recommended. Make observations when the majority of species are fully developed. In deciduous forest there may be two peaks of development, one before leafing and one later.

7.17.3 Quality assurance/Quality control

As far as possible the same person should do all estimates - as separate from measurements - at one site. A new observer should calibrate him-/herself against the former. In order to get an estimate of the observer error it is recommended to repeat the estimate of at least 10 sample plots and report the variation. The accuracy of the estimate regarding the true cover may be enhanced by training on computer-made pictures with known exact cover (an example is given in Figure 7.17.2) and/or measuring the cover of at least dominant species on photographs of a selection of sample plots with frame visible on the photo.

Statistical power analysis is a useful tool to calculate the number of plots required to detect a certain change in a variable and, conversely, to calculate which change can be detected with a given number of plots. In both cases the analysis must be based on the known variation of the vegetation on the plots.

7.17.4 Data pre-treatment

Trees

Estimate the height of those trees whose heights were not measured in the field by using the regression between dbh and height of those trees which were measured.

At sites where the BI subprogramme is not performed it is recommended to estimate the biomass of the tree stand of the intensive area using the data from the intensive plot. Thereby the procedure and reporting format of the BI subprogramme should be applied.

Cover (COVE)

In the 1998 version of the manual aggregated mean values of percent cover of species per quarter were reported. The problem with this reporting schema is twofold: 1) many IM sites did not set up their intensive plots according to the proposed design so that sample plots cannot be aggregated to quarters; 2) statistical power is lowered when using aggregated values. Thus, with the new 2010 version of the manual only raw data, i.e. percent species cover per sample plot, is reported.

Net cover (excluding overlap between individuals) of the tree and shrub layers and their species is given as percentage (%) of the whole intensive plot. Cover of shrub thickets, mapped directly in the field, could be measured on the map. Cover of the field and bottom layers and their species is reported for each sample plot (Fig.7.17.1). The sample plots are the basic units of observation, and

each must be labelled in the field QUARTER! Each sample plot within an intensive plot must have a unique label. The labelling format describes the design of the intensive plot.

In the new the new 2010 coding system QUARTER describes the design of the intensive plot. If the described design with quarters is used, then e.g. sample plot 2 in subsquare 3 of the first quarter is coded as 132 (Q, SS, SP) in QUARTER. If other designs are used, reporting is done for each sampling plot without including information on the inner design of the intensive plot. In such cases QUARTER is used to number each sampling plot of the intensive plot.

Flowering (FERT)

Flowering value for each field layer species is calculated for all sample plots using the formula:

flowering value (%) = $100 \times [\sum(n_i * F_i)] / 2N$

where
$F_i = 1, 2$
n_i = number of plots with fertility Fi
N = total number of plots with species occurrence

Example: A species is found on 8 sample plots. On 2 plots it is sterile, on 3 plots it has fertility 1 and on 3 plots fertility 2. Then the calculation will be like a). If it has fertility 2 on all plots, i. e. maximal value, it will be like b):

a) $100 \times [(3 \times 1) + (3 \times 2)] / 2 \times 8 = 56\%$ b) $100 \times [(0 \times 1) + (8 \times 2)] / 2 \times 8 = 100\%$

Flowering index (FERT_I) for the whole field layer of all sample plots is calculated as the mean of the flowering values of all species.

Plot frequency (FREQ)

Calculate per cent (%) plot frequency of the whole intensive plot for each species in the field and bottom layers by dividing the number of sample plots where the species is present by the total number of plots and multiplying by 100. When reporting is done according to the new format (sample plot wise) than it is not necessary to calculate and report frequencies.

In the 1998 version of the manual so called “sensitivity indices” were reported. We rename these indices to “Ellenberg indices” to better reflect what they really are. These parameters are optional and only applicable if the proposed design shown in Fig. 7.17.1 is used. In general, indicator analyses using Ellenberg indices will primarily be done centrally by using sample plot data and harmonised Ellenberg values.

Optional: Ellenberg indices (R and N)

Original indicator values of species (on a 1-9 ordinal scale) (Ellenberg 1991) or regionally modified ones for soil pH (R) and nutrient (N) preferences are used as a basis for calculation of environmental conditions of a plot. If possible, the indicator values should be modified to fit the region if other than central Europe where Ellenberg's values were established.

Ellenberg indices should be calculated for each quarter of an intensive plot using the formulas:

R-index = $\sum P_i * R_i$
N-index = $\sum P_i * N_i$

where Pi = relative cover of the i th species Ri or Ni = indicator value R or N of the i th species

Proceed thus:

Calculate relative cover of all field and bottom layer species, i. e. the cover of each species divided by the sum of the covers of all species which have an indicator value; the sum of all relative cover values will be 1.

Multiply the relative cover value for each species by its R or N indicator value.

Sum the products. The sum gives the Ellenberg index.

Values for the Figure 7.17.2, per cent (%) cover:
a: Scorzonera humilis 20
b: Deschampsia flexuosa 1.3
c: Paris quadrifolia 27
d: Oxalis acetosella 32
e: Vaccinium oxycoccos 19
f: Alnus incana 22

7.17.5 Data reporting

Mandatory parameters

Parameters	list	
COVE_T	IM	mean cover of layer/species (%) in tree layer for the whole intensive plot or COVE_T1 and COVE_T2 if the tree layer is divided into two layers
COVE_S	IM	mean cover of layer/species (%) in shrub layer for the whole intensive plot
COVE_F	IM	cover of layer/species (%) in field layer per sample plot
COVE_B	IM	cover of layer/species (%) in bottom layer per sample plot
NUM_LD	IM	number of living trees per 5 or 10 cm dbh class per species and total CLASS: 0=0-4 cm 5=5-9 cm, 10=10-14 cm, 15=15-19 cm etc.), for the whole intensive plot
NUM_DD	IM	number of dead trees per 5 or 10 cm dbh class per species and total; (classes as NUM_LD), for the whole intensive plot
NUM_FD	IM	number of fallen trees (logs) per 5 or 10 cm dbh class per species and total (classes as NUM_LD), for the whole intensive plot
NUM_LH	IM	number of living trees per 1 or 5 m height class per species and total (CLASS: 1=1.3-4m, 5=5-9 m, 10=10-14 m, 15=15-19 m etc.), for the whole intensive plot
NUM_LCL	IM	number of living trees per 1 m crown-limit class per species and total (CLASS: 0=0-0.9 m, 1=1.0-1.9 m, 2=2.0-2.9 m, 3=3.0-3.9 m etc.), for the whole intensive plot
NUM_LCW	IM	number of living trees per 1 m crown-width class per species and total (CLASS: 0=0-0.9 m, 1=1.0-1.9 m, 2=2.0-2.9 m, 3=3.0-3.9 m etc.), for the whole intensive plot

Optional parameters

Parameters	list	
FERT	IM	flowering value per field layer species (%) for the whole intensive plot
FERT_I	IM	flowering index of all field layer species (%) together
FREQ	IM	plot frequency per field/bottom layer species (%) for the whole intensive plot
SENS_R	IM	Ellenberg soil acidity index (R) of the community, i. e. all species in field and bottom layers per quarter (1-4) (2 decimals), report QUARTER!
SENS_N	IM	Ellenberg nutrient index (N) of the community, i. e. all species in field and bottom layers per quarter (1-4) (2 decimals), report QUARTER!

Example files (Excel format is preferred)

VG example Excel file
VG example ASCIII file

- File identifier states the subprogramme.
- Species are reported as MEDIUM using codes of the Nordic Code Centre (see Annex 6). Single species not found in the code lists may be reported using preliminary codes (see Annex 6), the full scientific name (including taxonomic authors) with the preliminary code needs to be given separately.
- QUARTER is used to specify each sample plot by either giving a consecutive number or by giving quarter (1-4), subsquare (1-4) and sample plot (1, 2, ..., n) as a 3 (or 4)-digit number. For variables reported for the whole intensive plot, QUARTER is left empty. (*In the old 1998 reporting format and where required, the quarters of the intensive plot were indicated in a separate column, e.g. QUARTER= 4 means quarter number 4 and was reported with cover values and Ellenberg indices for the field and bottom layer.)*
- Sampling year and month are given as YYYYMM.
- Spatial pool (SPOOL) is the number of sample plots or trees/shrubs from where the mean value is derived.
- Report dbh, height and crown-limit classes as CLASS.
- Report which environmental optimum values that are applied, whether Ellenberg´s original values or others!
- Report the definitions of the layers, especially the minimum sizes of trees and shrubs observed!
- Tree and shrub layer data are derived from the whole intensive plot without subdivisions.
- Attach the layer codes T, S, F, B to the parameter values for the tree, shrub, field, and bottom layers respectively!
- If two tree layers are reported, use layer codes T1 and T2!
- Values are reported as mean or sum, i. e. status flags X and S respectively. General information on flags is given in Chapter 4.

7.17.6 References

Bråkenhielm, S. & Liu, Q. 1995. Comparison of Field Methods in Vegetation Monitoring. Water, Air and Soil Pollution 79:75-87.

Ellenberg, H., Weber, H. E., D., R. Wirth, V., Werner, W. & Paulissen, D. 1991. Zeigerwerte von Pflanzen in Mitteleuropa. -Scripta Geobotanica 18.

7.18 Optional subprogramme BI: Tree bioelements and tree indication

7.18.1 Introduction

The chief purpose of the BI subprogramme is to estimate the state and change in amount of chemical elements that is contained in the tree biomass, including roots, and the dead wood of a catchment. In the forest ecosystem this is one of the most important pools of elements and is sometimes more substantial than the soil pool.

Other aims are:

- to keep record of the trees as influencing deposition (subprogramme Throughfall (TF)), overall transport, internal circulation (subprogrammes Foliage chemistry (FC) and Litterfall (LF)) and ion balance of elements in the catchment
- to monitor tree populations as biological indicators of pollution and other atmospheric changes.

This subprogramme is complemented with the vegetation structure monitoring of subprogramme VS, Vegetation structure and species cover.

The BI subprogramme cannot be applied meaningfully where forest stands are missing or so sparse as not to contribute significantly to the biomass of the site. Its full application is impaired where functions for biomass calculation and values of element concentrations are missing. However, in such cases it is acceptable to use simpler functions or functions established in other regions, if not too dissimilar to the actual one.

Tree biomass estimate should be complemented with a biomass estimate of the field and bottom layers after suitable methods have been developed.

7.18.2 Methods

7.18.2.1 Selection of plots

Data are collected by a combination of tree stand mapping and sampling of tree characteristics on plots representing each stand in the catchment.

Measurements are performed on plots, preferably circular of 10 m radius, on or near those established for subprogramme VS, i. e. in a quadratic network (BI Annex Figure 1). After mapping the stands it is decided how many plots in each stand type are needed. It is recommended that the largest stand (up to 1 km^2) should have no more than 20 sample plots and the smallest stand (minimum 0.25 ha) should have at least two plots.

Reject plots where more than one stand is represented! If this rule leads to too great a loss of plots for meaningful monitoring, accept plots with two stand types and measure only those trees which clearly belong to the dominant one. Plots with more than two different stand types are rejected in any case. Plots that are regarded as "impossible" with respect to topography, heterogeneity etc. are also excluded.

7.18.2.2 Observations

Measurements of trees, logs, and stumps (clearly not connected with logs) may be performed at two levels of ambition. The higher level includes measuring the position of each individual tree on the plot while at the lower level this is not done. In the former case the biomass change through time is better estimated and the population dynamics can be followed more in detail.

Defoliation, discolouration, and damage according to the subprogramme Forest damage (FD) preferably should be observed on the BI plots.

Living trees

- Measure the diameter at breast height (dbh; at 1.3 m above ground) of all living trees on the plot above a minimum dbh and determine the species. Which minimum size to choose depends on the character of the tree stands at the site. 5 or 10 cm are recommended for tall forest. If small trees make up a substantial part of the stands a smaller dbh should be chosen.
- Measure the heights of living sample trees objectively selected from each diameter class. For example, take the first tree in each 5 or 10 cm dbh class of each species encountered when moving clockwise round the plot starting from the north (Figure 7.18.1). This procedure ensures that all diameter classes are represented.
- Measure the height to the lower crown limit and the crown diameter of the sample tree (the two latter if necessary for biomass functions or for calculation of canopy cover and crown volume).
- Classify the vitality of all trees as follows:
  1 - healthy,
  2 - generally weak,
  3 - dying
- At the higher level of ambition measure the position of each tree-base centre (core) as to direction and distance from the plot centre.

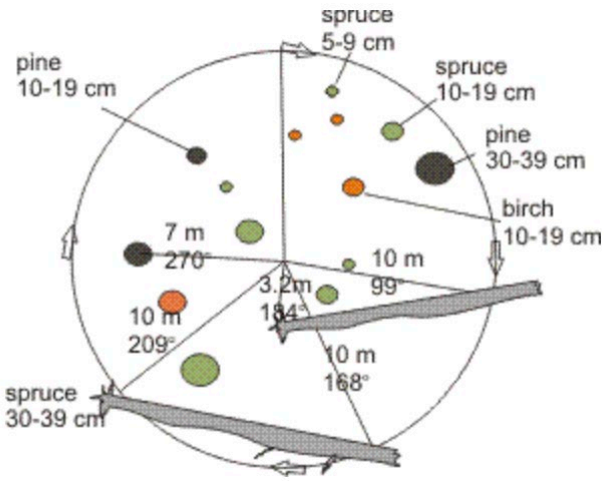


FIGURE 7.18.1 SUGGESTED PROCEDURES FOR MEASURING POSITIONS AND TRUNK DBH AND SELECTING SAMPLE TREES ON A CIRCULAR PLOT. START FROM NORTH AND GO CLOCKWISE SELECTING TREES OF ALL DBH CLASSES PRESENT OF EACH SPECIES. THE CALLIPERS ARE ORIENTED WITH THE HANDLE POINTING TO THE CENTER OF THE PLOT.

Dead trees, logs, and stumps

- Measure dbh of dead standing trees and diameter at 1.3 m from the base on logs (windthrows). On tall stumps dbh is measured, on low ones the diameter of the upper surface. Apply the same minimum diameter as for living trees.
- Stage of decomposition of wood may be classified as follows (use a sharp knife to test the penetrability of the wood):
  0 - fresh, bark left,
  1 - bark gone, all wood hard,
  2 - <10% by volume of wood soft (=penetrable),
  3 - 10-50% of wood soft,
  4 - 50-75% of wood soft,
  when >75% of wood is soft the windthrow is not observed
- At the higher ambition level measure the position of each object as to direction and distance from the plot centre. The position and length of a log can be inferred from coordinates for its base and top ends on those parts of the log that are within the plot circumference.

Stand areas

- Measure the area of the whole site and of each stand on the map.

7.18.3 Frequency of observations

Observations are repeated every five years.

7.18.4 Quality assurance/Quality control

Train the field crew for accuracy in measurements! Check the field data for "impossible" figures both when collecting them and before and after storing into computer! The chance of storing correct data

is increased if an electronic field data storer is used. There is a great risk to make mistakes and get faulty data in the many operations of biomass and bioelement calculations unless ready-made and controlled programmes are used.

7.18.5 Data pre-treatment

Estimate height, crown diameter and crown limit of all trees from the regression between dbh/height, dbh/crown diameter, and dbh/crown limit on the sample trees, thus ensuring an acceptably accurate estimate of the biomass with little extra input of time in the field.

It is recommended that each country makes its own calculations of bioelements since the functions and parameters are more or less locally limited. An example of functions and parameters based on Scandinavian measurements are presented in the BI Annex. Some of them are based on small samples, especially as regards deciduous trees. There is a full account of the steps needed for calculation included in the BI Annex.

If functions for biomass estimate and data on element concentrations are missing only the number of trees and their sizes per stand type are reported. As a complement either a stand map or data on the area of each stand should be reported.

7.18.6 Data reporting

Parameters	**list**	**description + unit**
NUM_LD	IM	number of living trees per 5 or 10 cm diameter class per species, per stand type (e.g.: 5 cm-classes:0=0-4 cm, 5=5-9 cm, 10=10-14 cm, 15=15-19 cm etc.) (UNIT=trees)
NUM_LH	IM	number of living trees per 5 m height class per species, per stand type (e.g. 5 m classes 1=1.3-4 m, 5=5-9 m,10=10-14 m,15=15-19 m etc.) calculated by regression from sample trees (UNIT=trees)
NUM_LCL	IM	number of living trees per 1 m crown-limit class per species per stand type (e.g. classes: 0=0-0.9 m, 1=1.0-1.9 m, 2=2.0-2.9 m, 3=3.0-3.9 m etc.) (UNIT=trees)
NUM_LCW	IM	number of living trees per 1 m crown-width class per species per stand type (e.g. classes: 0=0-0.9 m, 1=1.0-1.9 m, 2=2.0-2.9 m, 3=3.0-3.9 m etc.) (UNIT=trees)
VITA	IM	vitality (3 classes, CLASS=1,2,3) of living trees, number of trees per class total and per species, per stand type (UNIT=trees)
NUM_DD	IM	number of dead standing trees per 5 or 10 cm diameter class per species, per stand type (see NUM_LD) (UNIT=trees)

NUM_FD	IM	number of fallen trees (logs) per 5 or 10 cm diameter class per species, per stand type (see NUM_LD) (UNIT=trees)
NUM_SD	IM	number of stumps per 5 or 10 cm diameter class per species, per stand type (see NUM_LD) (UNIT=trees)
DECO	IM	decomposition degree (5 classes, CLASS=0,1,2,3,4) of dead fallen trees (windthrows) and stumps, number of trees per class total and per species, per stand type (UNIT=trees)
BIOM	IM	biomass (tons) total for the catchment
Bioelements		per element total (kg or g) for the catchment
NTOT	DB	total nitrogen (kg)
STOT	DB	total sulphur (kg)
PTOT	DB	total phosphorus (kg)
NA	DB	sodium (kg)
K	DB	potassium (kg)
CA	DB	calcium (kg)
MG	DB	magnesium (kg)
FE	DB	iron (kg)
MN	DB	manganese (g or kg)
ZN	DB	zinc (g or kg)
CU	DB	copper (g or kg)

B	DB	boron (g or kg)

Example files (Excel format is preferred)

BI example Excel file
BI example ASCII file

- File identifier SUBPROG states the subprogramme.
- Station number SCODE is given as 9999 to represent the whole IM site (or use a SCODE of your choice).
- Report stand type code as MEDIUM. Enclose a separate list of those (full) stand type names and codes that are used. The country code is given as the list name (LISTSPE), e.g. SE for a Swedish code list. (List codes will be unified by the Programme Centre).
- Report which minimum dbh classes is applied in the measurements.
- Report area of stand type, necessary for calculation of biomass etc. as SIZE.
- Spatial pool (SPOOL) gives the number of plots representing the stand.
- Tree species is reported as SPECIES, using NCC codes (list code B4, see Annex 6, for the most common species see throughfall subprogramme, TF).
- Report dbh, height, vitality, and decomposition classes as CLASS.
- Sampling year and month are given as YYYYMM.
- General information on flags is given in Chapter 4.

7.18.7 References

van Ek, R. & Draaijers, G.P.J., 1991. Atmospheric Deposition in Relation to Forest Stand Structure. Inst. of Geographical Research, Dept of Physical Geography, Univ. of Utrecht.

Annex to BI subprogramme- Procedure for calculating biomass and bioelements

1 Equations and functions needed

1. Regression equation for calculating tree height from DBH, per tree species.
2. Biomass (dry weight) functions for compartments, per tree species (Annex 6).
3. Parameters of element concentrations in compartments of a tree, per tree species (Annex 6).

2 Procedures

Step 1. Height of all trees

1. Select all living trees!
2. Select sample trees!
3. Construct the regression equation of height - DBH, i. e. Height = a + b * Log (DBH) for each species!
4. Calculate height for all tree individuals by the regression equation!

Step 2. Biomass of tree compartments

Calculate biomass of tree compartments per tree individual according to species specific functions! The compartments are usually *stem wood, stem bark, living branches, leaves/needles, dead branches, stump* and *roots.* With functions where the crown limit is included the estimate is more precise.

Step 3. Stand types

1. Classify stand types based on tree species composition, dominance and stand structure! Assign to each plot its stand type! Note that not all plots are representatives of the stand in which they are placed on the map!
2. Calculate the total forested area!
3. Calculate the area of each stand type!

Step 4. Biomass

Calculate and store data on the biomass of the whole area via (1) tree compartments, (2) species and (3) stand types!

Step 5. Bioelements

1. Calculate element amount by multiplying biomass per tree compartment by element concentration!
2. Sum the element content of all the compartments per element and species and lastly for each stand type.
3. Multiply the data by the total area of each stand type obtained from mapping. The result is an estimate of the total biomass and the total bioelements for the whole catchment.

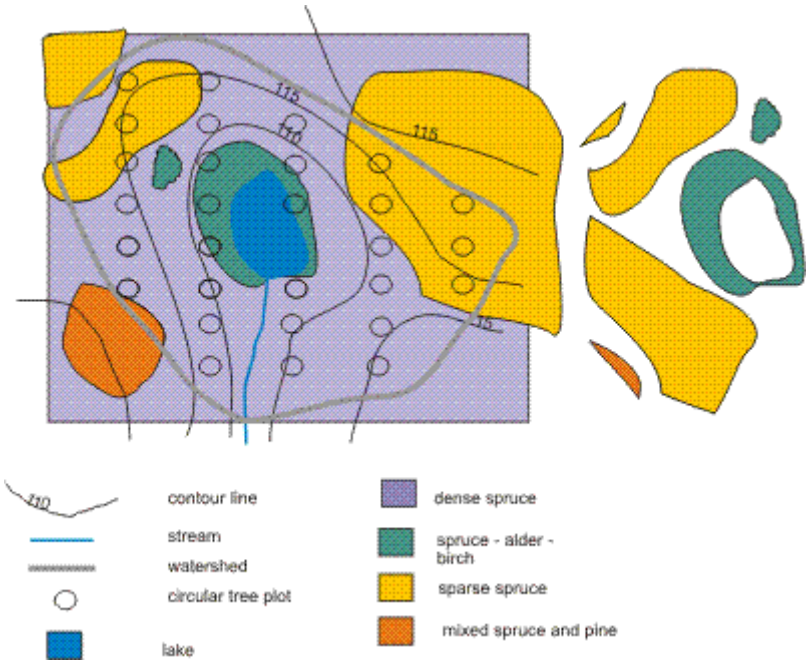


Figure 1. Tree stand map of a catchment (left) and the map fragmented for area determination.

Table 1. Examples of functions for the calculation of biomass of tree compartments in Scots pine (*Pinus sylvestris*) mainly based on Swedish conditions.

Pinus sylvestris		**(Marklund 1988)**
Stem + bark	T1	Ln(SW+BA)= -2.3388+11.3264*d/(d+13)
	T2	Ln(SW+BA)= -2.6768+7.5939*d/(d+13)+0.015*h+0.8799*Ln(h)
Stem	T5	Ln(SW)= -2.2184+11.4219*d/(d+14)
	T6	Ln(SW)= -2.6864+7.6066*d/(d+14)+0.02*h+0.8658*Ln(h)
Bark	T9	Ln(BA)= -2.9748+8.8489*d/(d+16)
	T10	Ln(BA)= -3.2765+7.2482*d/(d+16)+0.4487*Ln(h)
Branch + needles	T13	Ln(LB+NE)= -2.8604+9.1015*d/(d+10)
	T14	Ln(LB+NE)= -2.5413+13.3955*d/(d+10)-1.1955*Ln(h)
Needles	T17	Ln(NE)= -3.7983+7.7681*d/(d+7)
	T18	Ln(NE)= -3.4781+12.1059*d/(d+7)+0.0413*h-1.5650*Ln(h)
Dead branch	T21	Ln(DB)= -5.3338+9.5938*d/(d+10)
	T22	Ln(DB)= -5.8926+7.1210*d/(d+10)-0.0465*h+1.1060*Ln(h)
Stump + root	T25	Ln(ST+RO)= -3.3913+11.1106*d/(d+12)
	T26	Ln(ST+RO)= -1.5530+11.2246*d/(d+12)-0.0314*SI-0.0019*NKO
Stump	T28	Ln(ST)= -3.9657+11.0481*d/(d+15)
	T29	Ln(ST)= -2.1762+9.5137*d/(d+15)+0.3105*Ln(t)-0.0326*NKO
Root ≥ 5cm	T31	Ln(RO≥5)= -6.3413+13.2902*d/(d+9)
	T32	Ln(RO≥5)= -3.5882+13.6524*d/(d+9)-0.0467*SI-0.0306*NKO
Root ≤ 5cm	T34	Ln(RO≤5)= -3.8375+8.8795*d/(d+10)
	T35	Ln(RO≤5)= -3.5912+8.9776*d/(d+9)-0.0162*SI

BA= bark (on stem)
CT= current twig
DB= dead branch
LB= living branch
LE= leaves
NE= needles
RO= roots
ST= stump
SW= stemwood
T1 etc= number of function in literature source
Ln= natural logarithm
d= diameter at breast height, cm
h= height, m
NKO= latitude coordinate (Marklund 1988)
SI= site quality index (Marklund 1988)
M, L, D = various habitat qualities

Table 2. Example of bioelement concentrations (g/kg dry weight) in Norway spruce (*Picea abies*), Scots pine (*Pinus sylvestris*) and birch (*Betula pendula* and *B. pubescens*). Data are means of several published values from Scandinavia (Andersson 1970, Bringmark 1977, Finér 1989, Finér & Brække 1991, Mälkönen 1977, Mälkönen 1977, Mälkönen & Saarsalmi 1982).

Species	**Compartment**	**N**	**P**	**K**	**Ca**	**Mg**	**Fe**	**Mn**	**Na**	**S**	**Zn**	**Cu**	**B**
Spruce	Stem wood	0.72	0.05	0.26	0.73	0.11	0.0032	0.124	-	-	0.010	0.0077	0.000
Pine	Stem wood	0.59	0.03	0.24	0.48	0.15	0.0025	0.047	0.05	0.45	0.005	0.0010	0.000
Birch	Stem wood	1.04	0.06	0.27	0.54	0.15	0.0040	0.068	-	-	0.010	0.0010	0.000

Spruce	Stem bark	4.09	0.47	1.92	9.60	0.74	0.4530	0.784	-	-	0.100	0.0030	0.020
Pine	Stem bark	3.83	0.40	1.19	3.46	0.50	0.1605	0.099	0.02	0.07	0.020	0.0040	0.010
Birch	Stem bark	5.13	0.29	0.93	4.33	0.38	0.0220	0.386	-	-	0.120	0.0050	0.020
Spruce	Needles	12.95	1.36	4.78	4.63	1.02	0.0603	0.838	-	-	0.050	0.0078	0.010
Pine	Needles	13.67	3.91	4.04	3.02	0.90	0.0537	0.417	0.01	0.08	0.030	0.0045	0.010
Birch	Leaves	22.90	1.21	6.45	8.02	2.75	0.0840	1.033	-	-	0.060	0.0100	0.020
Spruce	Live branches	5.80	0.63	2.28	4.39	0.62	0.5400	1.344	-	-	0.050	0.0063	0.010
Pine	Live branches	5.12	0.56	2.33	2.50	0.60	0.0600	0.883	0.01	0.13	0.020	0.0045	0.010
Birch	Live branches	4.98	0.39	0.99	3.61	0.57	0.0290	0.23	-	-	0.690	0.0070	0.010
Spruce	Dead branches	3.28	0.18	0.27	4.71	0.12	0.1300	0.108	-	-	0.040	0.0047	0.010
Pine	Dead branches	3.51	0.18	0.26	2.06	0.14	0.8415	0.05	-	-	0.020	0.0035	0.000
Birch	Dead branches	4.52	0.21	0.39	3.20	0.33	0.0130	0.18	-	-	0.060	0.0080	0.010
Spruce	Branches+leaves	9.38	1.00	3.53	4.51	0.82	0.3002	1.091	-	-	0.050	0.0071	0.010
Pine	Branches+leaves	9.40	2.24	3.19	2.76	0.75	0.0569	0.65	0.01	0.11	0.025	0.0045	0.010
Birch	Branches+leaves	13.94	0.80	3.72	5.82	1.66	0.0565	0.6315	-	-	0.375	0.0085	0.015
Spruce	Stump+root	1.49	0.12	0.88	1.44	0.16	0.0625	0.15	-	-	0.010	0.0020	-
Pine	Stump+root	0.74	0.09	0.65	0.39	0.12	-	-	0.01	0.13	-	-	-
Birch	Stump+ big root	3.52	0.15	0.58	1.83	0.31	0.2250	0.083	-	-	0.020	0.0030	0.000
Spruce	Root	6.70	0.51	1.60	3.30	0.45	0.4000	1.05	-	-	0.040	0.0060	-
Pine	Root (1-5 cm)	1.21	0.21	1.14	0.66	0.24	-	-	0.01	0.06	-	-	-

References

Andersson, F. 1970. Ecological studies in a Scanian woodland and meadow area, southern Sweden. II. Plant biomass, primary production and turnover of organic matter. Botaniska notiser 123: 8-51.

Bringmark, L. 1977. A bioelement budget of an old Scots pine forest in central Sweden. Silva Fennica 11: 201-209.

Finér, L. 1989. Biomass and nutrient cycle in fertilized and unfertilized pine, mixed birch and pine and spruce stands on a drained mire. Acta Forestalia Fennica 208: 33.

Finér, L., Braekke. F.H. 1991. Understorey Vegetation on Three Ombrotrophic Pine Bogs and the Effects of NPK and PK Fertilization. Scandinavian Journal of Forest Research 6: 113-128.

Marklund, L.G. 1988. Biomassafunktioner för tall, gran och björk i Sverige [Biomass functions for pine, spruce and birch in Sweden]. Umeå, Sveriges lantbruksuniversitet, Institutionen för skogstaxering.

Mälkönen, E. 1978. Annual primary production and nutrient cycle in a birch stand. Communicationes Instituti Forestalis Fenniae 91: 1-35.

Mälkönen, E., Saarsalmi, A. 1982. Biomass production and nutrient removal in whole tree harvesting of birch stands. Folia Forestalia, Institutum Forestale Fenniae 534: 17.

Nihlgård, B., Lindgren, L. 1977. Plant biomass, primary production and bioelements of three mature beech forests in South Sweden. Oikos 28: 95-104.

7.19 Optional subprogramme VS: Vegetation structure and species cover

Revised in 2010

7.19.1 Introduction

The main aim of the VS subprogramme is to follow any major changes in the structure and species composition of whole plant communities of the monitoring site. The data also serves the needs of plant diversity monitoring of trees, shrubs and field and bottom layer species of the entire catchment.

Methods for the estimate of biomass and its chemical elements of the understorey vegetation should be developed to complement the estimate of elements in the tree stands (subprogramme BI).

7.19.2 Methods

7.19.2.1 Selection of plots

Observations are carried out on permanent plots, preferably circular. An area of 100 m2 (radius 5.64 m) makes cover estimates easy (1 m2=1%). The plots could preferably be distributed along transect mapping lines (Figure 5.7) on or near the plots of the BI (Tree bioelements and tree indication) subprogramme, i.e. in a quadratic network, using the same station codes. Soil data may be available for the BI plots, and they can be used as explaining variables in the VS subprogramme. Location outside the BI plots is recommended for sensitive vegetation in order to avoid influence by trampling. The centre of the plot is marked permanently for revisits.

If a plot is "impossible" with regard to topography, heterogeneity etc. or if the dominant plant community does not cover 50% or more, it is rejected.

Whatever design that is used, the observed parameters should be representative for the entire catchment. In the new 2010 reporting format, reporting is made at the level of plots and not at the level of plant communities (as in the 1998 format).

The original sampling design focused on plant communities in order to achieve a representative sample of the entire catchment. As several different designs are used, the reporting at the level of

plant communities resulted to very heterogeneous data: After mapping the communities, preferably Braun-Blanquet communities, Nordic vegetation types or CORINE land cover types, the number of plots per community should be decided upon. (The plant community could be defined thus: an assemblage of plants of different species forming a more or less distinctive unit.) It is recommended that the largest community (in an area of maximum 1 km2) should have no more than 20 sample plots and the smallest community (not smaller than 0.25 ha) should have at least two plots.

7.19.2.2 Observations

Divide the vegetation into tree, shrub, field, and bottom layers according to its stratification and life forms. No specific height limits of trees and shrubs can be given, but here is an example:

- **tree layer:** trees > 5 m
- **shrub layer:** trees 1-5 m, morphological shrubs >1 m
- **field layer:** trees and shrubs <1 m, other vascular plants irrespective of height
- **bottom layer:** bryophytes and lichens

According to this classification a tree species can be present in both tree, shrub, and field layers. If desirable the tree layer could be separated into an upper (T1) and a lower (T2) stratum.

Estimate the total cover of each vegetation layer and the cover of each species in each layer for each sample plot. Cover is defined as the area that above-ground living parts of a plant occupy when projected vertically on to the ground (shade when sun is in zenith) (Figure 7.17.2). Normally percentage cover-classes are used. In practice one per cent classes can be applied at the ends of the scale, while in the middle, i. e. round 50%, such fine estimates are practically impossible. However, all values are reported as per cent.

Note that plants growing on divergent surfaces e. g. on rocks and wind thrown objects should not be observed.

7.19.3 Frequency of observation

The survey is repeated after 10-20 years or after major changes, such as heavy management measures, increased grazing, fire, extensive storm felling, avalanche, and landslide. The season for the inventory should coincide with maximum development of vegetative and reproductive organs of plants.

7.19.4 Quality assurance/Quality control

The estimate of cover on a 100 m2 large plot is crucial and data do not permit any fine changes to be detected. However, even rough cover figures of separate layers tell much about the vertical stratification and dominance in a community. The observer is advised not to spend too much time trying to find the "true cover" but concentrate on finding and identifying the species. Regarding insignificant species, such as some small hepatics, the observer is, however, warned against perfectionism.

7.19.5 Data reporting

Mandatory parameters

Parameter	list	description + unit
COVE_T	IM	cover of layer/species (%) in tree layer per sample plot
COVE_S	IM	cover of layer/species (%) in shrub layer per sample plot
COVE_F	IM	cover of layer/species (%) in field layer per sample plot
COVE_B	IM	cover of layer/species (%) in bottom layer per sample plot

Example files (Excel format is preferred)

VS example Excel file
VS example ASCII file

- File identifier SUBPROG states the subprogramme.
- Station number SCODE identifies the sample plot
- The plant community the sample plot belongs to is reported as MEDIUM. Enclose a separate list of those (full) community names and codes that are used. Note which sociological system has been applied or whether local names and codes have been established. The country code is given as the list name (LISTMED), e.g. SE for a Swedish code list. (List codes will be unified by the Programme Centre and already established Codelists for countries can be obtained from the Programme Centre). (*In the old 1998 reporting format MEDIUM was mandatory since a number of sample plots were aggregated to describe the plant communities. The spatial pool (SPOOL) was the number of circular plots in one plant community that constitutes the sample. In the new 2010 version, reporting is done at the level of sample plots.)*
- In the new 2010 reporting format spatial pool (SPOOL) it is always 1.
- Plant species are reported as SPECIES, using NCC codes (see Annex 6).
- Layers (T=tree, S=shrub, F=field, B=bottom) are indicated by the parameter codes (PARAM).
- Sampling year and month are given as YYYYMM.
- General information on flags is given in Chapter 4.

7.19.6 References

Cruickshank, M. M. & Tomlinson, R. W., 1996. Application of CORINE land cover methodology to the UK. Some issues raised from Northern Ireland. -Global Ecology and Biogeography Letters 5: 235-248.

van Ek, R. & Draaijers, G.P.J., 1991. Atmospheric Deposition in Relation to Forest Stand Structure. Inst. of Geographical Research, Dept of Physical Geography, Univ. of Utrecht.

Påhlsson, L. (ed.), 1994. Vegetationstyper i Norden (Vegetation types in the Nordic countries). Tema Nord 1994:665. Nordic Council of Ministers. (In Swedish, with introduction and type names in English.)

7.20 Subprogramme EP: Trunk epiphytes

7.20.1 Introduction

The aim is to obtain sensitive bioindication in epiphytic lichens of changes in, primarily, acidifying deposition. Lichens are directly exposed to atmospheric gases and dissolved pollutants, and they possess different sensitivities to these factors. By calculating an index for the whole lichen community based on all species present a tool for estimating the environmental impact on biota is available. A similar index, based on the same principle, is the one for understorey vegetation (subprogrammes Vegetation (VG), Vegetation structure and species cover (VS)).

7.20.2 Methods

The method is based on lichens on the bark of living trees. If possible a combination of permanent and temporary trees should be used. The former ensure minimum spatial variation through time, the latter minimize effects from tree growth and enhance representativity of the site.

7.20.2.1 Selection of plots and trees

Select groups of trees preferably distributed evenly over the site. Each group constitutes a sample plot, representing one or more major tree species of the site. In an area of 50 ha five to ten plots with permanent trees and/or the same number with temporary trees will be sufficient. The number depends on how many tree species are involved and the variation in the lichen community. In each group (=plot) there should be 5-10 neighbouring trees. The genera *Pinus, Picea, Quercus, Fagus, Populus, Fraxinus* and *Betula* should preferably be represented.

Criteria for selection of the plot and the individual tree respectively:

- ecological conditions of the plot and the individual tree should be mesic; i. e. avoid extremes, such as sheltered depressions, wind exposed heights, steep topography, very wet or very dry soil, forest edges, very dense or open tree stand
- tree trunk close to vertical
- mature trees
- neither crown nor bark with severe visible damage
- as stable bark as possible
- lichen community not deviating much from surrounding trees of the same species

Permanent trees are substituted when they have undergone disqualifying changes, e.g. grown too thick, become injured or died. Temporary trees are resampled each time taking into account the state of the lichen community.

7.20.2.2 Observations

Observe either all lichen species or, if this is not possible, at least most fruticose, and foliose plus a few crustose species which can be easily identified and have indicator values (e. g. Hultengren et al. 1992, Insarova et al. 1992). The observations are made on tree trunks between 50 and 200 cm above ground, either by the line cover (A), the point frequency (B) or the species list (C) method, each of them including observations on lichen health (D). A fifth option is to follow ICP Forests' manual for monitoring of epiphytic lichens (E) (Stofer et al. 2016). In addition photographing is recommended if feasible. Line cover and point frequency are particularly suitable on permanent trees.

Method A: Line cover
Note lichens along a measuring tape fastened round the trunk of the sample tree at one or more of the levels 60, 90, 120, 150 cm above ground of which the 120 cm level is mandatory. Note the beginning and end (mm) of each thallus that is crossed by the upper edge of the tape when watched horizontally. Take sample of species unidentifiable in the field.

It is recommended to make a list of all species on the trunk at 50-200 cm above the ground (method C) as a complement to the line cover observation.

Method B: Point frequency
The method is based on a quadrat with a number of points, where species hits are counted. With permanent trees first select randomly on which side of the tree the quadrat should be placed. Use e. g. eight compass directions (N, NE, E, SE, S, SW, W, NW). With temporary trees the position of the quadrat on the tree should always be the same, e.g. facing the north.

Fasten the corners of a transparent plastic sheet (30x40 or 40x40 cm in size) on to the trunk of the sample tree. The sheet should have 100 400 points in a regular grid. The centre of the sheet should be about 120 cm above the ground. Mark the position of the quadrat on the trunk of permanent trees. The marking could be a small plastic screw or nail which will negligibly damage the tree.

Count the number of points that hit each species.

It is recommended to make a list of all species on the trunk at 50-200 cm above the ground (method C) as a complement to the point frequency observation.

Method C: Species list
Establish a species list of lichens occurring between 50 and 200 cm above ground on each tree on the plot.

Method D: Lichen health
The following additional parameters should be observed on lichens occurring between 50 and 200 cm above ground on all sample trees irrespective of which of the methods above was used:

- **Length of thallus:** Measure or estimate on each tree and for each pendulous lichen species the length of the tallest thallus.

- **Vitality:** Estimate the overall vitality of a common foliose lichen, e. g. *Hypogymnia physodes* or *Parmelia sulcata*, on each one of the sample trees, applying the scale:
  1=normal
  2=slight damage
  3=distinct damage
  4=severe damage
  5=dead

Method E: ICP Forests (added in 2021)
In accordance with the ICP Forests manual for monitoring of epiphytic lichens (Stofer et al. 2016), all five sub quadrates of the grid frame are examined for lichen species. The occurrence of each species within each sub quadrate is recorded, and the frequency of each species in the whole grid frame is calculated (by summing up the sub quadrates in which the species is found, ranging from 0 to 5) and documented.

Photographing
In addition to methods A, B, C and E, it is recommended on permanent trees to photograph permanently marked quadrats on the trunks of one or several trees using a rigid photo frame. The quadrat should be marked, e. g. by boring a plastic screw into the wood. In method B and E the place is the same as that of the quadrat, in methods A or C the recommended height (centre of quadrat) is 120 cm above ground. Preferably high-resolution digital photography is used. The identification of species on the photo is enhanced by noting in the field which species are present inside the photo frame. Using the photo method any change of a lichen thallus between two observations can be easily seen and quantified, though some species will not be identifiable. The method makes retrospective studies of long-term changes possible.

7.20.3 Frequency and conditions for observation

The observation is repeated every one to five years, preferably under dry conditions any time of the year.

7.20.4 Quality assurance/Quality control

One important source of error in lichen monitoring is the determination of species. When all species present are to be determined usually a lichen expert is needed. Another source of error is the sample size. A considerably larger sample is required if monitoring is based on temporary, each year newly selected trees, than on permanent ones, provided the same precision of change estimate is required.

7.20.5 Data pre-treatment

Mandatory: Cover, Point frequency and Species list

Method A: The line cover (%) is defined as the total length of intersections of a lichen species along the measuring tape in per cent of the tree circumference at the same level. Calculate the mean cover of each lichen species for each tree species per plot. If there is only one value from a plot it is treated as a mean.

Method B: The mean point frequency (%) is defined as the percentage of points where the species was noted out of the total number of points in the grid. Calculate mean frequency of each lichen species for each tree species per plot. If there is only one value from a plot it is treated as a mean.

Method C: Calculate the frequency of a lichen species as the number of trees of the same species where it is present on a plot.

Method D: Calculate the mean maximum thallus length of all trees on each plot, including also value 0 from trees where pendulous lichens are missing. If these lichens are missing on all trees no values are reported. Find the mode of the vitality values for each species on all trees on the plot. In both cases tree species is disregarded.

Method E: Calculate mean sub quadrat frequency of each lichen species for each tree species per plot. If there is only one value from a plot it is treated as a mean.

Optional: Sensitivity index (S)

Sensitivity values of species (classes 1-9 or 1-10) (Hultengren et al. 1991, Insarova et al. 1992) or regionally modified ones, if available, are used as a basis for calculation of sensitivity indices of the site. The values of Hultengren (1991) are derived from observations in Sweden, the ones from Insarova (1992) from various parts of the world and thus more widely applicable.

The sensitivity index, ranging between 1 and 9 of each sample plot and all trees irrespective of species, is calculated using the formula

$S = \sum P_i * S_i$

where P_i = relative cover/point frequency/tree frequency of the i:th species and S_i = sensitivity value S (1-9) of the i:th species

Proceed thus:

- Calculate relative cover etc. of each species. i. e. its cover divided by the sum of the covers of all species which have sensitivity values; the sum of all relative cover values will be 1.
- Multiply the relative cover etc. value for each species by its sensitivity value.
- Sum the products. This gives the sensitivity index of each sample plot.

7.20.6 Data reporting

Mandatory parameters

Parameter	**list**	**description + unit**
Method A:		
ACOVE	IM	cover (%), mean per lichen and tree species per plot

OR Method B:		
BPOFR	IM	point frequency (%), mean per lichen and tree species per plot
OR Method C:		
CFREQ	IM	frequency (number of trees with presence), per lichen and tree species per plot
OR Method E:		
EFREQ	IM	Sub quadrat frequency (count), mean per lichen and tree species per plot
AND Method D:		
LENG	IM	mean of all max. thallus lengths (cm) per plot, irrespective of tree species
VITA	IM	mode of lichen thallus vitality per plot (vitality class code), irrespective of tree species

Optional parameters

Parameter	**list**	**description + unit**
SENS_S	IM	sensitivity index per sample plot, including all trees irrespective of species

Sensitivity values of lichens present, if available, are reported in a separate list.

Example files (Excel format is preferred)

EP example Excel file
EP example ASCII file

- File identifier SUBPROG states the subprogramme.

- Station code SCODE is a group of trees (=sample plot).
- Report host tree species as MEDIUM, using NCC codes for trees (list code B4, see Annex 6 and for the most common tree species subprogramme Throughfall, TF).
- Spatial pool SPOOL refers to the number of sample trees of the same species on one sample plot.
- Flag PFLAG indicates whether the tree is permanent (P) or temporary (T).
- Epiphyte species reported as SPECIES (see Annex 6).
- Values are reported as means or modes, status flags X and M respectively, see above. General information on flags is given in Chapter 4.
- Sampling year and month are given as YYYYMM.

7.20.7 References

Huckaby, L.S. (ed.), 1993. Lichens as Bioindicators of Air Quality. USDA Forest Service. General Technical Report RM-224.

Hultengren, S., Martinsson, P.-O. & Stenström, J., 1991. Lichens and air pollution. Classification of sensitivity and calculation of indices in epiphytic lichens. Swedish Environment Protection Agency. Report 3967. (In Swedish with English summary.)

Insarova, I.D., Insarov, G.E., Bråkenhielm, S., Hultengren, S., Martinson, P.-O. & Semenov, S., 1992. Lichen sensitivity and air pollution. Swedish Environment Protection Agency. Report 4007.

Kovács, M., 1992. Lichens. In: Kovács, M. (ed.). Biological Indicators in Environmental Protection. Ellis Horwood. London.

Stofer S, Calatayud V, Giordani P, Neville P, 2016. Part VII.2: Assessment of Epiphytic Lichen diversity. In: UNECE ICP Forests Programme Co-ordinating Centre (ed.): Manual on methods and criteria for harmonized sampling, assessment, monitoring, and analysis of the effects of air pollution on forests. Thünen Institute of Forest Ecosystems, Eberswalde, Germany, 13 p. + Annex [http://www.icp-forests.org/manual.htm].

7.21 Optional subprogramme AL: Aerial green algae

7.21.1 Introduction

The aim is to obtain sensitive bioindication of changes in deposition of eutrophicating substances, mainly nitrogen, in green algae on needles, mainly *Pleurococcus vulgaris* (syn. *Protococcus viridis*). The present experience shows that the more nitrogen fallout, the thicker the algal cover and the

more rapid their colonization. However, also other environmental factors may act as strongly. Therefore some caution in the conclusions is recommended. For the interpretation of data it is especially important to have access to data from subprogrammes Precipitation chemistry (PC) and Throughfall (TF).

This subprogramme can only be applied at sites where Norway spruce is present.

7.21.2 Methods

7.21.2.1 Selection of plots and trees

Select 15-20 small (5-10 m tall) spruces near each other in a fairly open coniferous stand, if feasible near an intensive plot. The spruces should, if possible, stand free from other trees. They must not stand under deciduous trees. They should preferably stand on well-drained soil, have normal crown density and needle size and neither be stunted nor very fast-growing. The branches at eye-height must be so old as to be free from needles on the oldest annual shoot near the trunk. Preferably the same trees should be observed through the years until they are disqualified and must be substituted.

7.21.2.2 Observations

On the needles of three opposing branches at eye-height (ca 160 cm) the following is noted on the main branch axis, using a weak magnifying glass (2-5x):

First note whether algae are missing altogether on the whole branch!

If algae are present note on any twig (axis) of the same branch:

- thickness of algal cover where it is the thickest (Fig. 7.21.1), according to the scale
  1 = sparse, patchy or thin
  2 = intermediate
  3 = very thick, rough structure and easily seen bare spots where coat has disappeared
- youngest shoot where algae can be found; note the age of the shoot
- number of annual shoots which have more than 5 and 50 % needles left respectively

7.21.3 Frequency and conditions for observation

The algae should be observed annually in July-September under good light conditions when the needles are dry.

7.21.4 Quality assurance/Quality control

The main cause of uncertainty for the observer is how to estimate the thickness, since it is practically impossible to give an absolute standard. However, since classes 1 and 3 are relatively distinct care should be taken to pinpoint them. It is recommended not to spend too much time looking for small spots of algae when searching for the youngest shoot with algae.

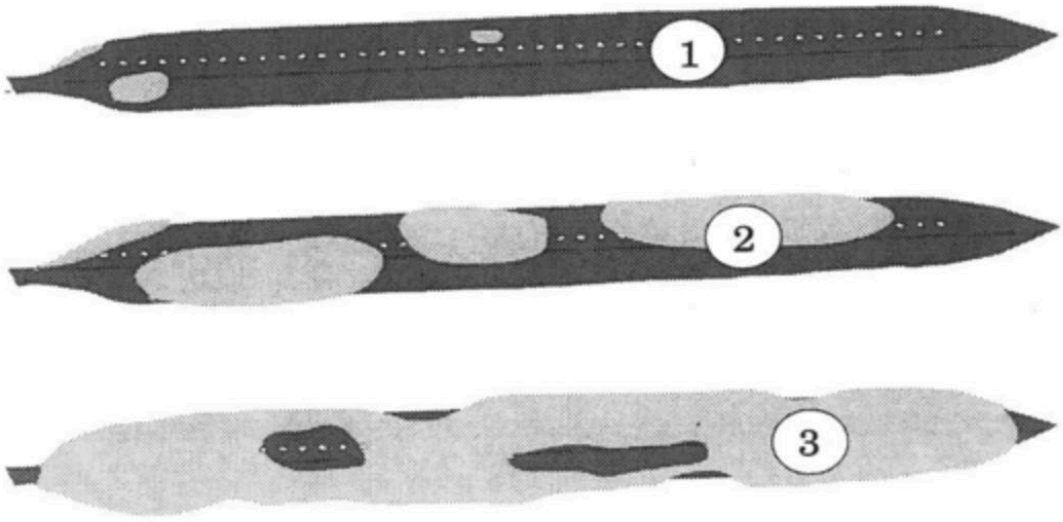


FIGURE 7.21.1. ALGAL COVER CLASSES ON SPRUCE NEEDLES

7.21.5 Data reporting

Parameter	list	description + unit
ABS	IM	number of branches (max. 3) on the current tree where algae are missing
YALG	IM	youngest shoot with algae (age in years), mean per tree
COAT	IM	thickest coating of algae (code), mean of the values from the three branches per tree
NMED	IM	number of annual shoots with >50 % needles left, mean per tree
NMAX	IM	number of annual shoots with >5% needles left, mean per tree

Example files (Excel format is preferred)

AL example Excel file
AL example ASCII file

- Data for each individual tree is reported, which makes it possible to calculate, with variation, whether a change is significant or not.
- File identifier SUBPROG states the subprogramme.

- The host tree species is *Picea abies*. MEDIUM always PICE ABI, list code B4 (Annex 6).
- Report tree number (1- 20) in column TREE.
- Sampling year and month are given as YYYYMM.
- Spatial pool SPOOL refers to the number of trees, here always 1.
- Values are reported as means, status flag is X. General information on flags is given in Chapter 4.

7.21.6 References

Bråkenhielm, S. and Liu, Q., 1995. Spatial and temporal variability of algal and lichen epiphytes on trees in relation to pollutant deposition in Sweden. Water, Air and Soil Pollution 79: 61-74.

Göransson, A. ,1988. Luftalger och lavar indikerar luftföroreningar. SNV Rapport 3562. (In Swedish.)

Peveling, E., Burg, H. and Tenberge, K.B., 1992. Epiphytic Algae and Fungi on Spruce needles. Symbiosis, 12: 173-187.

Söchting, U., Jensen, B., Unger, L., 1992. Epifylfloraen på Rödgran. En undersögelse af belægninger på grannåle. Miljöministeriet, Skov- og Naturstyrelsen og Köbenhavns Universitet, Institut for Sporeplaner. (In Danish with summary in English).

Thomsen, M. G., 1992. Epifyttisk belegg på barnåler i Norge i relasjon til nitrogendeposisjon og klima. Rapp. Skogforsk. 23/92:1-11. (In Norwegian with summary in English

7.22 Optional subprogramme MB: Microbial decomposition

7.22.1 Introduction

Microbiological activity determines the net-mineralisation of nutrients in the ecosystem; thus any disturbance in ordinary activity will result in a change of decomposition and change in nutrient uptake. The cause might be pollutants accumulated in the soil. Lowered decomposition leads to reduced nutrient uptake and to build-up of organic material. When the organic material has increased to a new steady state, the nutrient delivery will again be equal to nutrient flow in litter input to soil.

7.22.2 Methods

Field incubation of well identifiable pieces of organic material are used for monitoring of annual decomposition under the weather conditions of the field site.

7.22.2.1 a. Decomposition of standard litter

Collect needles from one selected stand of young coniferous trees. Other litter types could be selected if they are relatively resistant to decomposition. Brown needles are collected from the trees each year, at the time of formation of brown needles but before they are shed. Weigh about 1 g of needles and place them in a bag of inert material (e.g. terylene or nylon) with mesh size 1 mm, a so-called litter bag. Determine the water content of the litter material for use in calculations of initial dry weight. The exact weight in mg and the year is written on a tape and placed in the mesh bag, which is closed with stitches or staples of inert material. Place 3 litter bags per 10 x 10 m^2 subplots (see Soil chemistry, SC subprogramme, an example of a SC plot) in September - October on the moss/ litter layer in the permanent soil plot in sections not used for soil sampling. The bags are reserved for collection after 1, 2 and 3 years. After collection the litter bags are immediately air-dried to halt the decomposition process. Rinse using tweezers until only needle remnants remain, dry and weigh. Calculate the loss of weight (%).

7.22.2.1 b. Decomposition of cellulose material

Decomposition may be determined using a standard material such as bleached alfa cellulose sheets (1 mm thick, 30 mm wide and 50 mm long). Each individual sheet is dried at 105 ºC, stabilized for two hours in room temperature and weighed. Four cellulose sheets are placed one after another in a bag of inert material (e.g. terylene or nylon) with mesh size 1 mm.

For litter layer studies 3 bags per 10 x 10 m^2 subplots (see SC subprogramme, an example of a SC plot) are placed horizontally on the surface of moss/litter and covered with natural litter. To study cellulose decomposition in 0 - 5 cm layers 3 bags per 10 x 10 m^2 subplots (see SC subprogramme, an example of a SC plot) are installed in soil at a 15º angle.

Bags are installed in September-October in the permanent soil plot in sections not used for soil sampling. The bags are reserved for collection after 1, 2 and 3 years. Ingrown roots and mosses are cleaned off and the bags are gently washed. The cellulose sheets are dried in 105ºC, stabilized for two hours in room temperature, and weighed. The loss of weight (%) is calculated.

7.22.2.2. Microbiological activity

Potential microbial activity is determined under standard laboratory conditions (with respect to temperature and moisture) on samples taken from the organic surface horizons in the permanent soil plot every fifth year. 20-36 spatially independent samples are measured. Some chemical pollution related parameters are also determined on these samples, e g pH, C/N-ratio, Cd, Hg, Pb. Evaluation of correlations with these parameters are more important than comparisons of mean values of biological activity between years.

Soil respiration:
Take 20-36 samples in the soil plot in a grid design, preferably at >8 m distances for spatial independence. The upper half of the organic horizon (fermentation or F-layer) is taken by a soil auger of about 8 cm diameter. Depth of sample should not exceed 5 cm. Bring samples to the laboratory as quickly as possible, without exposure to extreme temperatures. Sieve with 4 mm mesh sieve. Adjust moisture to about 60% WHC using distilled water.

20 g of moistened organic soil material is placed in small plastic cup to rest for 12 days at 20.0 ºC with additions of distilled water to original weight.

Measurement is made by incubation of sample in its cup in one-litre air-tight vessel. A beaker with 5 ml 0.2M NaOH is also placed in the vessel. After about 18 hours (exact time recorded to the minute) BaCl2 is added to the beaker with NaOH. Excess NaOH is immediately titrated with 0.050M HCl to the endpoint of phenolphthalein. The soil sample in its cup is dried and weighed. Loss on ignition or carbon content is later determined on the same sample.

Six blanks without soil samples are incubated with NaOH and titrated. A good blank value is essential for the calculations.

There are also several other alternatives e.g. using IR-gas analyser or gas chromatography. Respiration rate could also be monitored in automatic respiration machine with time resolution of 30 minutes, Then base respiration could be directly observed after shorter resting time (5 days) and additional parameters in the respiration response after glucose additions could be determined (substrate induced respiration, lag time). These latter parameters are often more sensitive to pollution, particularly heavy metals, than base respiration.

Acid phosphatase activity:
Use the same samples as for soil respiration. Sieve the fresh samples, preferably within a few days after sampling with a 4 mm mesh (2 mm for mineral soils). Store about 150 ml of the sieved sample in a refrigerator for two months in order to stabilize the enzyme activity. The samples should be kept moist, but not anaerobic, e.g. in plastic pots with perforated lids.

Paranitrophenylphosphate (PNP-P) is used as substrate for the enzymatic reaction. Put 1.0 g of moistened organic soil in small bottle, add water until total water content of 2 ml is reached, add 8 ml acetate buffer (pH 5.00) and 2 ml 0.115M PNP-P. Incubate exactly 2 hours in water bath at 25.0ºC, then add 2 ml 0.5M $CaCl_2$ and 8 ml 0.5M NaOH to stop the enzyme process. Mix. filtrate. Dilute filtrate 50 times with 0.01M NaOH. After 1 hour measure light absorbance at 400 nm and compare with standard solutions of PNP (in the range 0-0.04 mM, with $CaCl_2$ and NaOH as in samples).

Make a second set of blind incubations for each soil sample to subtract humus colour. PNP-P is not added at these incubations until the enzyme process has been stopped.

Moisture content for dry weight estimate is measured on separate soil samples.

Net mineralization of nitrogen:
Soil samples sieved and moistened for respiration are also used for nitrogen mineralization.

Place four 10.0 g portions of moistened material in vessels suitable for subsequent extractions. One portion is immediately extracted, the others are stored for 3, 5 and 7 weeks at 20.0ºC with additions of distilled water. Original moisture content and loss on ignition are determined on a separate subsample.

At extraction, 150 ml 0.1M KCl is added to soil sample and shaken for 1 hour. The extract is filtered and diluted to 250 ml. Can be frozen. NH_4N, NO_2N and NO_3N in extract are determined. Make certain that the blanks have a low content of measured ions.

7.22.3 Data pre-treatment

Decomposition of standard litter:

$L = ((f \times W_0 - W_n) / (f \times W_0)) \times 100$

where L is weight loss (%), f is dry/most ratio of original litter material, W_0 is original moist weight (mg), W_n (where n=1,2 or 3) is final dry weight after 1, 2 or 3 years.

Respiration rate:

$R= 1.1 \times D \times t^{-1} \times W^{-1}$

where R is respiration rate (mg CO_2/(g · h)), D is difference in HCl consumption compared to blank (ml), t is incubation time (hours) and W is dry weight or organic weight (g).

Acid phosphatase activity:

Calculate concentrations of PNP in filtrate from standard curve and subtract humus colour obtained in blind incubations. Then

$P = 22 \times C \times d \times t^{-1} \times W^{-1}$

where P is phosphatase activity (µmol / (g · h)), C concentration of PNP in filtrate (mM), d is dilution factor, t is incubation time (hours) and W is dry weight or organic weight (g).

Nitrogen mineralization:

Inorganic N is calculated for each soil sample by summation of NH_4N, NO_2N and NO_3N (µg N/g, dry weight or organic weight). N-mineralization (µg N/g) or N-mineralization rate (µg N/(g x day)) is calculated by difference to inorganic N content at time zero.

7.22.4 Data reporting

Parameters	**list**		**unit**
(L/S)DEC_1	IM	weight loss of litter bag/cellulose sheet due to decomposition after 1 year	%
(L/S)DEC_2	IM	weight loss of litter bag/cellulose sheet due to decomposition after 2 years	%
(L/S)DEC_3	IM	weight loss of litter bag/cellulose sheet due to decomposition after 3 years	%
PNP	DB	phosphatase activity of soil	µmol/(g · h)

CO2R	IM	soil respiration	µg CO_2/(g · h)
N_MIN	IM	N-mineralization	µg N/g

Example files (Excel format is preferred)

MB example Excel file
MB example ASCII file

- File identifier SUBPROG states the subprogramme.
- MEDIUM refers to either the dominating tree species of the stand, where standard litter bags/cellulose sheets have been implanted for decomposition studies, or the type of pedology for soil microbial activity measurements. NCC codelist B4 (see Annex 6) and FAO soil classification are used for reporting the medium. For the most common tree species see TF chapter and for FAO classification see subprogramme SC.
- LEVEL refers to the sampling depth for microbiological activity determinations (cm).
- Spatial pool SPOOL refers to the number of individual implanted bags/implanted sheets/ samples used for microbial activity determinations.
- Observation year and month are given as YYYYMM (in the example 200100), day field is left blank.

7.22.5 References

Torstensson, L. (Ed.). 1993. Swedish Environmental Protection Agency, Report 4262.

Nordgren, A. 1988. Soil Biol. Biochem. 20:955-958.

ISO 10381-6. Sampling. Aerobic microbial processes.

ISO 14238. Soil Quality. Biological Methods. Determination of nitrogen mineralization and nitrification in soils and the influence of chemicals on these processes.

7.23 Optional subprogramme TA: Toxicity assessment

7.23.1 Introduction

Toxification of the environment is related to the introduction and dispersion of chemicals to such an extent that adverse effects may be invoked in plants, animals, or man. The number of chemicals introduced into the environment has grown exponentially over the past century. Of the approximately 10-million substances known at the present day, about 100 000 have toxic properties which make them a potential subject of environmental policy and control. Due to toxicant diversity it is virtually impossible to monitor all toxic compounds and their effects individually. The groups of toxicants currently most important for the assessment of large-scale air pollution are the heavy metals (HM) and the persistent organic pollutants (POPs).

The intrinsic toxicity of heavy metals (zinc, cadmium, copper, mercury, lead, chromium, nickel, and arsenic) is documented in the international literature. However, the bioavailability, or the actual exposure concentration experienced by biota is very much related to the local situation with respect to masking by complexation. This in turn is related to e.g. acidification, redox-potential and soil type (CEC and organic contents). For heavy metals, the organisms in chronically exposed populations generally possess adapted excretion mechanisms, leading to reduced exposure levels and thus reduced effects.

The situation is much more complex regarding the toxicity of the organic compounds. Due to the high structural diversity, the intrinsic toxicity of many organic contaminants is unknown. However, the level of volatility and persistence required for organic contaminants to be airborne for a longer period of time, puts a limit on the types of compounds of interest. The most important groups of airborne organics are the chlorinated organic substances (PCBs, pesticides, dioxines, etc.) and the polycyclic aromates (PCA), which have well documented toxicities.

The ecological effects possibly occurring as a consequence of the excessive presence of toxicants are very diverse. This is because the effects can be exerted along different major pathways. Some effects are directly related to the uptake of toxicants, which then can interfere with physiological processes according to their mode of action. The uptake of toxicants can either be direct from the environment or through the food chain.

- Direct uptake from the environment is mainly producing effects in primary producers and small animals living in close contact with water. Water soluble toxicants are directly taken up from surface, rain, or soil water, while gaseous compounds are absorbed by the leaves of plants. The resulting toxicant concentration inside the exposed organism, depends on the uptake rate and the rate of excretion, the rate of toxicant conversion (degradation) or the

rate of dilution by growth. Given adequate time with constant exposure, the toxicant concentration in the organism will reach an equilibrium, where the internal concentration of the toxicant is generally considerably higher than the environmental concentration. This process is called bioconcentration. For organic substances the bioconcentration factor is mainly governed by the lipophilic properties of the toxicant and the fat content of the exposed organism. Bioconcentration of heavy metals may be controlled by the ability of the exposed organism to reduce inherent metal toxicity by forming comparatively harmless complexes (e.g. with metallothioneine). The resulting internal equilibrium concentration may be below or above the threshold concentration for effects.

- Exposure through the food chain is of increasing importance for terrestrial herbivores, detrivores and carnivores, respectively. Due to a low (approx. 10%) metabolic conversion factor, these animals need to ingest relatively large portions of food to fulfil their energy requirements. This food may have comparatively high concentrations of bioconcentrated toxicants, which may lead to a high rate of toxicant uptake. In general, the excretion or elimination rate of toxicants is observed to be lower in terrestrial air breathing animals than in aquatic organisms with respiratory gas exchange with the water (skin/gill respiration). The resulting higher body burden of toxicants in terrestrial animals makes them more vulnerable to toxicants which are passed on through the food chain. For truly aquatic species, the comparatively high excretion rate causes the difference in body burden between direct uptake and food chain transfer to be less pronounced. The process resulting in a higher body burden of toxicants through the food chain is called biomagnification. The overall effect of a higher toxicant concentration in the tissues of exposed organisms then in their environment, irrespective of the exposure pathway, is called bioaccumulation.
- Excluding the effects related to the uptake of toxicants, organisms can also suffer indirect effects originating from toxicity related changes in community structure. For a particular species, these effects can be negative in case of reduced availability of food organisms, and positive in case of reduction in the abundance of competitive species.

From the first part of this introduction on toxicity assessment, it will be clear that an identification of options for toxicity monitoring requires the chain of causes and effects to be studied in detail as depicted in figure 7.23.1.

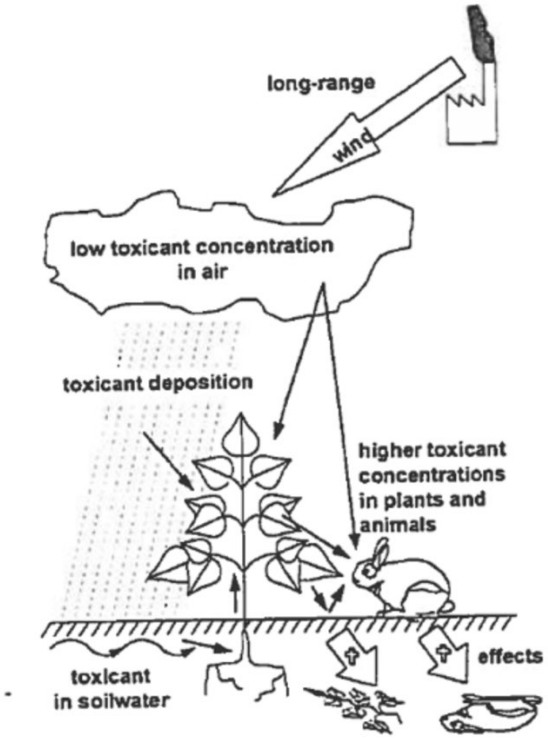


FIGURE 7.23.1. SIMPLIFIED CAUSE-EFFECT CHAIN.

For proper evaluation of toxicity, it is essential that the determination of concentrations and loads of a wide variety of toxicants in air, deposition, soil, soilwater, ground water and surface water is covered under the appropriate subprogrammes. However, for some of the contaminants to be expected, the concentrations in these media may be well below the chemical analytical detection limit. It is therefore indispensable to assess ecotoxicological effects occurring in the local biological community as the consequence of prime concern, together with the toxicant concentration inside exposed organisms as the immediate causative factor.

In the chain of causality for ecotoxicity, the effects on biological systems are primarily decisive as to the seriousness of the impact. Especially the occurrence of indirect effects makes it very difficult to conclude toxicological effects by analysing the results of inventories on community structure. In other words: toxicological effects may be there but cannot be distinguished from effects on community structure resulting from other disturbing factors. Analysing shifts in community composition in concert with observed body toxicant burden in target organisms may reveal toxicity induced community responses. A regular estimate on community composition of plants and birds is covered by the separate subprogrammes VG and BB.

Ecotoxicity can also be estimated by controlled experimental exposure of test organisms to serial dilutions of environmental samples. Two types of laboratory bioassays can be distinguished:

- The easiest, cheapest, and least sensitive methods are targeted towards the determination of the external concentration at which acute effects are invoked in the exposed test organisms. Acute effects are generally defined as mortality occurring within 1 to 4 days of exposure. However, in aquatic ecotoxicology there is a tendency for the development of short-term tests solely relying on subtle physiological or cytological changes, which may

even occur in-vitro (biomarkers; cell cultures, isolated enzymes, etc.). Several validated acute test systems exist for exposure through the aquatic and soil environment. Ecotoxicological tests for air exposure have not (yet) been developed. Especially in terrestrial organisms, the short exposure duration may prevent the partitioning process to reach equilibrium with the internal toxicant concentration experienced by the test organisms. Furthermore, these tests deliberately exclude effects that may occur through the food chain process of biomagnification. For the ICP IM monitoring programme, mainly executed at sites which are relatively undisturbed by local sources of pollution, it is therefore very unlikely that acute toxicity testing will demonstrate any effects, even when the environmental sample is tested without dilution.

- Prolonged exposure experiments are capable of detecting sub-lethal effects (retarded growth, reduced reproduction, etc.) and will include effects linked with accumulation and food chain magnification. These types of toxicity tests are generally much more sensitive and may be able to detect the toxicity associated with long-range dispersion of heavy metals and POPs as air pollutants. For the aquatic environment, some standardised and validated semi-chronic tests are available, with a test duration of 4 to approximately 30 days, depending on the type of test organism (algae, daphnia, fish). A limited number of prolonged tests on soil or soil water ecotoxicology are still in the process of being standardised and validated, while tests for air exposure are non-existent. However, the execution of all prolonged exposure tests is extremely costly, requiring specialised facilities and highly trained personnel, which renders widespread application in a monitoring network virtually impossible.

When, due to natural variability, the relationship between community responses observed in the field and ecotoxicity can only be assessed with great difficulty and uncertainty and the execution of environmental bioassays for the detection of contamination introduced by long-range air pollution is considered to be unfeasible, the only solution to the problem of toxicity assessment is to analyse for bioaccumulation of selected toxicants in target organisms. Because the observed internal concentrations of toxicants only reflect toxicity in a relative manner - as long as models for predicting community or population effects from bioaccumulated toxicant concentration are not yet fully developed - the target species should be common organisms with a widespread occurrence. Furthermore, the target species should be relatively insensitive towards the bioaccumulated toxicant level, in order to produce a wide range indication of potential toxicity The determination of bioaccumulated toxicants has the additional advantage over the determination of toxicant levels in air, soil or water, that the target species will integrate the contamination over time, so that monitoring frequency can be comparatively low.

In the subprogrammes on foliage (FC) and litterfall chemistry (LF) as well as in the subprogramme on metal chemistry of mosses (MC), some determinations are made on the internal concentrations of mainly heavy metals. Chemical analysis of a larger variety of toxicants in a larger variety of species or specific parts of species will greatly enhance possibilities for ecotoxicological risk assessment. Many additional target species with established bioaccumulative capacity for specific groups of contaminants are described in literature:

- Duck weed (*Lemna* sp.) is known for its accumulation of heavy metals over a wide concentration range (e.g. Jenner et al., 1993)
- Many species of lichens are used for analysis on the accumulation of heavy metals, polycyclic aromates and organo-chlorines (Calamari et al., 1991)

- The concentration of volatile organochlorine compounds in bark, leaves and needles of selected tree species is widely used for assessing the level of air contamination (Simonich et al, 1995ab; Thompson et al., 1995)
- Fish species with a high fat content (e.g. Eel; *Anguilla* sp.) are good indicators for the bioaccumulation of persistent organics (RIZA, 1996)
- The tissue of both fresh water and marine mussels (e.g. *Dreissena* sp. and *Mytilus* sp.) is globally used to assess the level of mercury pollution (Musselwatch Programme; NAS, 1980), cadmium pollution and PCB pollution (e.g. Mersch et al., 1992)
- Lower soil organisms like the earthworms (*Lumbriculidae*) and the more commonly occurring species of the threadworms (*Enchytraeidae*) as well as wood lice (*Isopoda*) are capable of accumulating heavy metals (Martin and Coughtrey, 1982; Hopkin, 1989) and organic pollutants (Callahan et al., 1991)

In general it can be stated that the accumulation of toxicants by biota is subject to much variability. Between remote populations of a single species, the variation is mainly introduced by adaptation differences in the efficiency of excretion and metabolic degradation. Within a local population the differences in accumulation are mainly governed by the age of individuals and their nutritional status. It is therefore essential to analyse composite samples of a relatively large number of randomly picked individuals of approximately the same age. For heavy metals the determinants should be normalised to unit dry weight, while the accumulation of organic pollutants is best expressed per unit lipid content.

7.23.2 Methods

In analysing and reporting bioaccumulated contaminants, there is a lot of freedom in procedures which can be executed to obtain correct and interpretable results. This chapter only gives a very simplified outline of possible procedures for both heavy metal and organic contaminants All procedures consist of the following steps required:

- Composite sampling
- Sorting
- Cleaning
- Composite Sub-sampling for replicates
- Transport storage
- Prolonged storage
- Sample pre-treatment
- Sample clean-up
- Analysis
- Data preparation
- Data reporting

7.23.2.1 Field methods

Adequate numbers of the required material are collected in the field. Immediately after collection, the sampled animals or parts of plants are hand-sorted to uniform age and composture. If necessary, the material is rinsed clean of debris with distilled water. Triplicate composite samples containing sufficient material (10-20 grams) are composed to be analysed independently. The unpreserved composite samples are immediately stored in PE containers or suitable plastic bags, which should be

kept cool (+4°C) and in the dark for a short period of time until they can be transferred to a freezer (-20°C) in the laboratory.

7.23.2.2 Laboratory methods

If samples require pre-treatment, as for instance the removal of shells from mussels, or the dissection of target organs from larger animals, this has to be performed prior to freezing. The samples can be stored under refrigeration for a prolonged period of time. Upon analysis, the samples are freeze-dried and subsequently ground with an agate mortar to obtain a dry powder.

Trace metal analysis

Arsenic, cadmium, chromium, copper, lead, nickel, zinc
An adequate and metered amount of the dry powdered sample is mineralised by a suitable wet acidic-oxidative destruction procedure. The resulting liquid sample is topped to known volume with distilled water and filtered. The filtrate can be kept in PE bottles prior to AAS or ICP analysis.

Mercury
Mercury requires leaching of samples with acid inclosed vessels followed by cold vapour AAS.

Analysis of organic residues

A known weight of dry powdered sample is subject to extraction of the lipophilic fraction. The first extraction is performed by prolonged (16 hrs) shaking with a hexane/acetone mixture (3: 1). The extraction is repeated three times with decreasing extraction periods and decreasing solvent volume. In order to determine the lipid contents, the solvents are evaporated to dryness and the residue is weighed. The extract is then dissolved in a small amount (ml)of hexane and purified by addition of some 95% sulphuric acid. After mixing and separation of the two resulting phases by centrifugation, the cleaned-up hexane solution is analysed by appropriate LC, GC, or GC-MS methods.

7.23.3 Quality assurance/Quality control

With all types of analysis standard addition techniques are used to account for matrix interactions. Procedural blanks are run to assess contamination possibly occurring during the different stages of sample preparation. Various chemical-analytical supply houses offer a variety of certified standards containing biological tissues with known amounts of organic and inorganic environmental pollutants. This type of standards can and should be used to validate sample pre-treatment and analysis.

7.23.4 Data pre-treatment

The data should be normalised to unit dry weight for the heavy metal content of organisms, and to unit lipid content for organics. The arithmetic average, geometric average, standard deviation, and number of replicate analytical results for the same date-place-species-compound combination should be calculated and reported separately.

7.23.5 Data reporting

Variables
All measured individual toxicants or summary variables (e.g. AOX) should be reported.

COL	CONTENTS	EXPLANATION	EXAMPLE	ABBREVIATION OF
1-2	Subprogramme	Obvious	TA	Toxicity Assessment
3-6	Area	Obvious	NL01	Netherlands 01
7-8	Institute	Obvious	RV	RIVM
36137	Station	Obvious	6	Fen Kliplo
36179	Medium	Analysed species	ANGU ANG	Anguilla
21-22	Medium list	Obvious	F1	Fish
23-26	Level	Not Applicable		
27-32	Year+month	YYYYMM	199711	November 1997
33-34	day	DD	5	day of the year and month above
35-37	Spatial pool	Number of replicates	3	3 replicates
38-45	Substance	Chemical agent	PCB123	PCB 123
46-47	Substance list	Obvious	DB	DB
48-50	Pretreatment	Code for pretreatment method		
51-53	Determination	Code for determination		

54-60	Value	Obvious	1.25	1.25
61-68	Units	Obvious	mg/kglc	mg per kg lipid content
69-69	Quality flag	Not Applicable		
70-71	Status flag	Way of calculation	G	Geometric average
	or		D	Standard deviation
	or		X	Arithmetic average
72-72	Additional field	Not Applicable		

Additional status flags D (standard deviation) and G (geometric average) used here.

7.23.6 References

Calamari D, E Bacci, S Pocardi, M Morosini and M Vighi. M. Environ. Sci. Technol., 1991, 35: 1489-1495.

Callahan CA, CA Menzie, DE Burmaster, DC Wilborn and T Ernst. Environm. Contam. and Toxicol., 1991, 10: 817-826.

Jenner HA and JPM Janssen-Mommen. Arch. Environ. Contam. Toxicol., 1993, 25: 3-11.

Martin MH and PJ Coughtrey. Biological monitoring of heavy metal pollution. Applied Science Publication, London, New York, 1982.

Mersch J, A Jeanjean, H Spor and J-C Pihan. In: Limnologie Aktuell (Neumann/Jenner eds.), The Zebra Mussel Dreissena polymorpha, Gustav Fisher Verlag, 1992, p. 227-244.

NAS (National Academy of Sciences, The International Mussel Watch, Washington DC, 1980, pp. 148.

RIZA (Netherlands Ministry of Transport and Public works. Biologische monitoring zoete rijkswateren (in Dutch), Notanummer 96.009, 1996.

Simonich SL and RA Hites. Science, 1995a, 269: 1851-1854.

Simonich SL and RA Hites. Environm. Sci. and Technol., 1995b, 29: 2905-2914.

Thompson TS and RG Treble. Chemosphere, 1995, 31: 4387-4392.

7.24 Optional subprogramme BB: Inventory of birds

7.24.1 Introduction

Several groups of animals have been used in environmental monitoring. For a small catchment area, animals with migratory habits or with wide ranges are less suitable. Emphasis should be laid on animals that breed within the area. Suitable group is therefore breeding birds. Inventory is repeated every 3-5 years.

7.24.2 Methods

The area for bird census should be allocated in a representative core of the catchment area and should be sufficiently large to incorporate a statistically satisfactory sample. It can therefore slightly extend beyond the IM area proper. Natural habitats should be represented in the inventory area in the same proportion as within the whole IM area. For observations the inventory area is divided into a grid with 50 x 50 m^2 meshes (so-called territory mapping method), each used as an inventory point.

The observation area is visited thoroughly 10 times during the breeding season, April-June, and all bird observations (species, sex, number, and behaviour) are marked on a map.

The data are analysed by species and the number of pairs are calculated by the occurrence of territorial clusters and nests on a grid map. Since analysing species cluster maps requires expertise, it is advantageous if the same person makes the interpretations from time to time.

Observe, that if a lake occurs within the observation area, also species associated with the lake must be recorded.

7.24.3 Data reporting

Parameters

Parameter	**list**	**unit**
SPECDEN	IM	number of pairs/ha

Example files (Excel format is preferred)

BB example Excel file
BB example ASCII file

- File identifier SUBPROG states the subprogramme.
- Station number SCODE is given as 9999 to represent the whole IM site (or use a SCODE of your choice).
- Size of the area used for the inventory is given (60 ha in the example) as SIZE.
- Spatial pool SPOOL here always one.
- The observed species are given as SPECIES using NCC codes (see Annex 6), species list for birds is A1.
- Values correspond to the number of pairs/ha observed during the year. In the case, that a species has been observed, but not assessed to have formed breeding pairs in the area, no value is given but the quality flag V (= species verified but value not given). General information on flags is given in Chapter 4.
- Inventory year with no specific month (200100 in the example) is given as YYYYMM.

7.24.4 References

Koskimies, P., Väisänen R. A., 1991. Monitoring Bird Populations. Zoological Museum, Finnish Museum of Natural History.

7.25 Optional subprogramme PH: Phenological observations

This subprogramme has not been incorporated into the ICP IM manual.
Please see ICP Forests Manual, part VI, Phenological Observations, 2010.

8 Data Quality Assurance and Management

- 8.1 Overview of data quality management in the IM programme
- 8.1.1 General
- 8.1.2 Definitions
- 8.1.3 Quality assurance steps in the IM Programme
- 8.2 Quality assurance routines in the field and in sampling
- 8.2.1 Collection and handling of water chemistry samples
- 8.3 Laboratory practices
- 8.3.1 In-laboratory quality control
- 8.3.2 Between-laboratory quality control
- 8.3.3 Quality of measurements
- 8.3.4 Specific data quality control procedures
- 8.3.5 Water analysis
- 8.3.5.1 Determination of accuracy and precision
- 8.3.6 Soil analysis
- 8.3.7 Plant materials
- 8.4 Audits
- 8.5 Analytical techniques
- 8.6 References and further reading

8.1 Overview of data quality management in the IM programme

8.1.1 General

Many environmental monitoring programmes have failed to achieve their aims because of inadequate data quality management. It is often forgotten that the quality of the data determines the nature of the analyses that can be undertaken, and the quality of the results. Given the subtle nature of many of the changes in ecosystem processes associated with the atmospheric deposition of pollutants, the required data quality is very high.

The general objective of a cooperative international programme to monitor the effects of air pollution on ecosystems requires that all data generated by the various participants should be comparable on an objective basis. It is very important to have a good quality of data, both being consistent in time (in order to assess trends) and space (for the comparisons between different sites and countries). To achieve such comparability, the methods employed to collect materials and to undertake chemical analyses of these must be thoroughly documented. 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. The Quality Assurance and Quality Control procedures should include all parts of the activities performed at the site, and in the laboratory.

8.1.2 Definitions

Quality Assurance (QA) is defined as "those operations and procedures which are undertaken to provide measurement data of stated quality with a stated probability of being right" (Taylor 1987).

Quality Control (QC) relates to the laboratory procedures used to reduce random errors and systematic errors or maintain them within certain specified tolerable limits.

QA samples are used to assess data quality (as defined above) and for monitoring the internal QC procedures. QA samples are submitted blind to laboratories, i.e., their identity in the batch and their composition are unknown to the analyst. They are usually included in duplicate and randomly placed among the routine samples. QC samples are known to (created by) the laboratory and used to evaluate calibration and standardisation on instruments, problems of contamination or analytical interference.

Each NFP is required to submit a report on the QA/QC procedures followed by the laboratories involved. This should include the detection limits (DL) of the equipment used to analyse each substance. In the case of the Soil chemistry subprogramme, the DLs refer to the concentration of the substance in the extract/digestion.

Data Verification are procedures performed on the raw data that allow transcription errors to be identified and removed, and the checking of the completeness, precision, and consistency of the data. Once the raw data has been verified, it can then be **validated**. Validation procedures include the identification of outlying data points and their assessment for inclusion or omission based on assigned levels of confidence. **Internal consistency checks** (ICC) are useful in identifying outliers and errors. ICCs are checks made on the routine sample results and consist of standard relationships, e.g., total S ≥ SO4-S, total N and organic C should show a strong positive correlation, etc..

8.1.3 Quality assurance steps in the IM Programme

A major problem with data derived from international monitoring programmes is their consistency through time and between countries. Most countries have preferred techniques which they use for the assessment of environmental parameters. These techniques often produce results that are not directly comparable, creating major problems for assessments of data derived from more than one country. In some cases, differences between methodologies invalidate the combination of data into international datasets. These problems have been identified by ICP Waters, who in 1996 undertook a major evaluation of the data held in their database, resulting in many data being discounted from future analyses.

In order to avoid these problems, the ICP Integrated Monitoring has implemented the following steps. These are based on ensuring the scientific quality of the results, even at the expense of rejecting some of the data submitted by National Focal Points.

1. In certain critical cases, field methods have been clearly specified for specific parameters, and data obtained for these parameters using other field methods are unacceptable.
2. Laboratories involved in chemical analyses of materials derived from IM sites should be certified under one of the laboratory accreditation systems, e.g., EN 45001 and ISO/IEC guide 25. Data from uncertified laboratories will be subject to more detailed scrutiny prior to acceptance.
3. When a laboratory's practices deviate from the recommended analytical method, the laboratory is obliged to demonstrate that the methods produce values that are similar (± 10%) to the recommended method.
4. All chemical parameters are the subject of ring tests.
5. All laboratories are obliged to take part in ring tests under full identification. If a particular parameter lies outside an acceptable (± 10%) deviation, no data related to that parameter are included in the database. Only data from laboratories that have participated in ring tests are acceptable.
6. ICP IM recognises the major difficulties with the assessment and/or interpretation of some biological response parameters, and in particular with the parameters associated with the Forest damage subprogramme. Consequently, where such uncertainties exist, it has reduced the emphasis given to these parameters in favour of more reliable indicators of biological response.
7. Each NFP is expected to ensure that good laboratory practice is followed and is responsible for the quality of data reported to ICP IM Programme Centre.
8. The results of quality controls, laboratory intercalibrations etc. undertaken (either with IM samples in particular or of the laboratory in general) should be reported to the IM Programme Centre. The Programme Centre also encourages participation in international intercalibration exercises.

8.2 Quality assurance routines in the field and in sampling

Traditionally, the greatest amount of attention in QA programmes is given to laboratory procedures. For the analysis of materials collected in the natural environment, such an emphasis is misplaced as the greatest sources of error are related to field sampling, transportation back to the laboratory, and sample preparation stages (Summers 1972). In the IM Programme, particular attention must be given to these stages.

Materials collected in the IM programme include water samples (from precipitation, throughfall and stemflow, soil water, groundwater, running water and lake water), plant materials, organic and inorganic soil materials, and entire organisms (e.g., benthic animals). Each of these requires separate methods and consequently separate QA protocols.

All methods used within a country should be documented and change in methods over time noted. Standard operational procedures should be followed for all activities. Necessary equipment, cleaning materials, sufficient supply of spare parts etc. must be available. All operators should be well-trained, and sites and equipment must be inspected/controlled at least once a year by the quality assurance manager/data originator. The QA/QC routines in the field include addition of field blanks and control samples, and also requirements for sample transportation and storage.

8.2.1 Collection and handling of water chemistry samples

Prevention of sample contamination or sample changes during collection or while in storage may be critical in obtaining accurate measurements. All containers used for either sample collection or storage must be free of any important quantity of the determinants in relation to the lowest concentration to be measured, and the containers must be of a material that will neither absorb nor release measurable quantities of the determinant.

Materials
All materials which come in contact with the sample must be chemically inert. Polyethylene, tetrafluoroethylene and tetrafluoroethylene-fluorinated ethyl-propylene copolymer are generally recommended because of their excellent chemical properties. The mechanical properties of these materials must be taken into account in the construction of samplers. Polyethylene may become brittle when exposed to sunlight and should be replaced after 1 year of use involving exposure to sunlight. Borosilicate glass should be properly acid-washed and rinsed in deionized water prior to use, but the use of glass is not generally recommended. Soft glass will contaminate the sample with alkali and alkaline earth cations. Metals, and artificial materials with unknown chemical properties or composition should be avoided. If such materials have to be used in joints or in other constructional details of the sampling equipment, boil a sample of the material in deionized water and analyse the water afterwards as a water sample.

Cleaning
Rinse all bottles before use carefully with deionized water. All other sampling equipment must be leached in diluted acid for two to three days before being used and stored in plastic bags. When analysing trace metals, samples must be collected and stored in acid-washed bottles. Extreme care must be exercised to avoid contamination and whenever possible sample containers must be full and tightly capped to minimise any interchange with entrapped air. Glass bottles are recommended for samples for carbon and mercury determinations. New glass containers should be initially washed in hot chromic acid solution. Later cleaning can be done using a mild detergent followed by rinsing in tap water and then finally in distilled or deionised water. Plastic bottles should be washed with concentrated hydrochloric acid or 50% nitric acid, or with a commercial decontaminant such as Decon (Cryer and Trudgill 1990).

Sample quantities
A general principle is that the larger the sample is, the lower will be effects of contamination from the sample bottle. For lake and river water samples, a sample size of 1 litre is normally collected. Precipitation and soil water samples are normally variable, being determined by availability.

Storage conditions between collections
It is important that bottles are kept away from light and kept cool during and after sampling. If the sample cannot be stored in a pithole, it should be covered, for example using aluminium foil.

Transportation to the laboratory
All laboratory bottles shall be clearly marked with plot number, collector number, sample type (e.g. throughfall, stemflow) and sampling period. 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. Sample documentation should include as a minimum:

- Sample site identification
- Date of sampling
- Sampling depth
- Additional notes (e.g. of suspected contamination)

Laboratory bottles should be transported to the laboratory as soon as possible, under warm weather conditions preferably in cold boxes.

Sample storage
Samples intended for major ion and nutrient analysis should be collected, stored in the dark at about 4°C and transferred to the laboratory for analysis as soon as possible. The transport and storage period between sampling and analysis should be kept at the minimum. Samples stored in polyethylene bottles for even a few hours are likely to lose some of their solutes (particularly phosphorus) as a result of adsorption onto the bottle walls.

Surface water samples (Runoff water, lake chemistry) intended for metal analysis may be preserved by adding acid, usually using nitric acid. Preservation at pH 2 will in most cases retain the total and dissolved metals for several weeks. If the preservative is added in the field, extreme care must be taken to prevent contamination of the major ion sample with nitric acid. If determining the dissolved fraction, it is necessary to filter the sample prior to preservation. Filters, when used, should have a 0.40 - 0.45 µm membrane (Whatman 42 or GFC) and be rinsed with deionized water prior to use. In general filtration is not necessary and if samples are filtered, this should be indicated when reporting the results.

Field blanks for water samples
In order to check on possible contamination on the site, field blank tests should be carried out a least once every month. For this purpose, 50-100 ml deionized water samples should be poured into the sample collector (where appropriate) after it has been washed/rinsed or re-installed in the field. The samples should be subjected to the same procedure as an ordinary water sample.

8.3 Laboratory practices

8.3.1 In-laboratory quality control

All laboratories that participate in co-operative programmes should provide documented evidence that in-laboratory quality control is maintained to assure the accuracy and uniformity of routine laboratory analyses. Such documentation is routine for a certified laboratory. 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:

1. 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).
2. Documented evidence of analytical performance, accuracy of in-house standards, within-run precision, between-run controls, and accuracy of the methods employed.
3. Evidence of sample specific data quality such as an adequate ionic balance or specific conductance determination for individual samples.
4. Evidence of adequate performance by analysis of external audit materials, standard samples of adequate matrix, etc.

8.3.2 Between-laboratory quality control

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.

It is strongly recommended to participate annually in international inter-comparisons for all analysed compounds. It is also recommended to participate in field inter-comparisons. The IM Programme Centre will be able to give information about relevant inter-calibrations. All data should be verified and validated.

Between-laboratory quality control on water samples will be carried out by the ICP Waters programme. Quality control for plant and soil materials will be organised by the Forest Foliar Co-ordinating Centre (Vienna) and the Forest Soil Co-ordinating Centre (Gent), respectively.

8.3.3 Quality of measurements

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 used also by ICP Waters programme is: *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.

8.3.4 Specific data quality control procedures

In some subprogrammes (e.g. Meteorology, Soil chemistry), data quality procedures are specific and have been described within the appropriate chapter. However, many quality control procedures are more general and are described here.

8.3.5 Water analysis

The laboratory must check on its performance, with respect to detection limits, precision, and repeatability, by repeated analysis of control solutions etc. All data should be verified and validated.

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. Data Quality Objectives for EMEP are:

- 10% accuracy or better for oxidized sulphur and oxidized nitrogen in single analysis in the laboratory
- 15% accuracy or better for other components in the laboratory
- 0.5 units for pH
- 15-25% uncertainty for the combined sampling and chemical analysis
- 90% data completeness of the daily values.

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

Determinant	**Detection limit (L)**	**P(%)**
Calcium	0.02 mg/l	10
Magnesium	0.01 mg/l	10
Sodium	0.02 mg/l	10
Potassium	0.02 mg/l	10
Chloride	0.2 mg/l	10
Sulphate (as SO_4)	0.2 mg/l	10
Nitrate (+ Nitrite)[1], (as N)	10 µg/l	10
Reactive aluminium	10 µg/l	10
Non-labile (organic) aluminium	10 µg/l	10
Labile (inorganic) aluminium	10 µg/l	10

Dissolved organic carbon[2], as C	0.2 mg/l	10
pH	0.1 pH units	-
Conductivity	0.2 mS/m	5
Alkalinity	0.005 mmol/l	10
Total phosphorus, as P	2 µg/l	10
Soluble reactive phosphate, (as P)	2 µg/l	10
Temperature	±0.2 ºC	-

1) Depending on the method if nitrite is included. In well-aerated surface waters nitrite is usually close to zero

2) In samples with low particle content total organic carbon (TOC) may be used (no filtering).

The quality of the water chemistry data is strongly linked to the performance of the chemical laboratory. Control samples should be prepared, and analysed regularly as ordinary water samples, in order to keep an independent check on the chemical analyses performed. Standard rainwater samples are available from NIST and BCR, and it is advised to use such samples as an external reference solution analysed only 2-4 times during the year, and in-laboratory prepared control samples for daily control work. The control samples should approximate the expected mean concentration in the water samples, and may be prepared using the following compounds:

- $(NH_4)2SO_4$
- Nitric acid
- $CaSO_4 \cdot 2H_2O$
- $MgSO_4 \cdot 7H_2O$
- NaCl
- KCl

8.3.5.1 Determination of accuracy and precision

In order to quantify the precision and accuracy and detection limit in the laboratory:

- 5% of the samples should be split and the results used to quantify the analytical precision
- 5% of the samples should have known, and realistic, concentrations and should be run between the normal samples to control the performance of the analytical system
- 5% of the samples should be blank samples used to quantify the analytical detection limit.

The methods used to determine accuracy, precision and the detection limits from these data are provided in the EMEP Manual (Sections 5.6 and 5.7).

8.3.6 Soil analysis

The greatest degree of variation in the results obtained for the element contents in soils are likely to arise from the nature of the extractants used for the analyses. In this respect, it is important to note that the total content of a particular element may bear little relation to the content available to plants. There is no general agreement over the most suitable extractant for each element, and conscientious laboratories will undertake repeat analyses using different extractants.

Data Plausibility
Detailed information on methods on checking data, QC and precision and accuracy, is regularly published by the American Public Health Association.

A simple plausibility check can be made to see if the sum of cations is balanced by the sum of anions. If there is a difference that cannot be explained by any missing ions, then this should be brought to the attention of the laboratory. Other simple checks include looking at scatter plots between the parameters, e.g. SO_4S - Total S concentrations and strongly correlated, PO_4P - Total P concentrations and strongly correlated, $NO_3N + NH_4N$ - total N concentrations, and Total inorganic N ($NO_3N + NH_4N$) strongly correlated to DOC. Careful screening for outliers can substantially reduce the variability of the data. If any of the metal concentrations determined with an ICP in simultaneous mode are outliers, then there is reason to check the chemistry of the whole sample.

QA Samples
QA samples should include: 1) field replicates (see sampling procedures), 2) preparation duplicates, i.e. after preparation of the routine samples for analysis (drying and sieving), duplicate subsamples are taken for chemical analysis and placed randomly within the batch, and 3) Natural audit samples, i.e. large amounts of typical soils that have been collected to be used as reference samples. These samples will be supplied by the ICP IM in cooperation with the Forest Soils Co-ordination Centre in Gent. The audit samples, randomly placed in the batch of routine samples to be analysed, can be used to evaluate within-batch precision and analytical differences among laboratories (accuracy). Usually these natural audit samples are submitted blind to the laboratory (accuracy can then be objectively assessed by the ICP IM) but it is recommended that some natural audit samples should not be blind to the laboratory and used in every batch. If the analytical results for these non-blind quality control audit samples are outside designated intervals, the batch must be reanalysed in order to bring the audit samples within tolerance specifications. This will ensure that each laboratory meets a rigid standard for each batch of samples analysed. Batch error and laboratory difference would thereby be reduced.

Besides calibration blanks (to check instrument drift), matrix spikes (to check on recovery), and analytical duplicates (subsamples of the extraction/digestion of a routine soil sample to check on within-batch precision and identifying instrumental drift), QC samples should include reagent blanks (sometimes referred to as a process blank) for those methods involving sample preparation, e.g., soil extraction. The reagent blank should be composed of all the reagents used and in the same quantities used in preparing the soil sample for analysis. The reagent blank should undergo the same digestion and extraction procedures as a routine sample and should be used to identify contamination by reagents. The ICP IM will supply extraction audit samples, and the results will be used to differentiate between systematic bias resulting from extraction and instrument sources of

error. If these liquid audit samples are known to the laboratory, then the laboratory can check on these sources of error.

Verification of data

- Blank concentrations should be less than DL
- Relative standard deviation (RSD) of the audit pairs, field replicates, preparation duplicates, and analytical duplicates should be less than 10% (or other stated percentage) of the DL. (RSD is calculated by dividing the standard deviation of each pair by the mean, and then multiplying this value by 100)
- Spike recovery should be within 15% (or other stated percentage) of the original spike concentration
- Internal consistency checks (proposed standard analyte relationships):
- sand+clay+silt=100
  organic soils/samples ≥ 12% organic carbon
  pH water>pHsalt and correlation of ≥ 0.95
  PCEC>ECEC and correlation of ≥ 0.80
  ACI_ET , AL_ET correlation of ≥ 0.80
  ACI_ETB>ACI_ET
  ACI_ETB, C_TOT correlation ≥ 0.90
  Exchangeable Ca>Mg>K>Na (units: meq/L)
  total concentrations extractable concentrations
  N_TOT, C_TOT correlation ≥ 0.95
  S_TOT, N_TOT correlation ≥ 0.75 (mineral soil samples only)
- Identification of outliers: highest and lowest 1% of values, values >±3 Studentized residuals

8.3.7 Plant materials

The total element concentrations obtained by the laboratories' standard methods need to be checked in order to determine the accuracy of these methods. Two steps of quality assurance are recommended:

Comparison of the results of the national methods with the concentrations of reference standard samples. These reference standard samples, with certified total element concentrations supplied e.g. by the Central Bureau of References of the EC or by ISO (International Standard Organization), or by the US group of foliar analysis, will be sent to participating laboratories for analysis. The certified concentrations will be supplied to individual laboratories once a sufficient number of laboratories have submitted their results.

In order to permanently check the accuracy of the analyses, it is also recommended that each laboratory provides several of its own standard samples for analysis in each batch of samples. The data should only be accepted if the analyses of the known samples match the reference results.

8.4 Audits

Performance audits should be carried out by representatives of the technical staff from the institution operating the site once each year to see that the field operations work as intended.

System audits should be carried out by the IM QA Manager in cooperation with the designated National Focal Point QA Managers at regular intervals.

A detailed checklist to be filled in during these inspections should be worked out, and the WMO GAW checklist (WMO 1994) may be used during audits of the wet deposition part of the measurements. The filled-in forms should be assessed by a scientist to ensure that all aspects of the field programme operate as intended. The auditors should bring with them copies of the filled-in forms from the last visit when performing a site inspection. Corrective action should be taken immediately when necessary.

The system audits should include:

- Check the quality system in general
- Inspect the sample locations and the site surroundings, and any changes since the last visit should be noted
- Follow the staff during their routines, and correct bad handling of equipment
- Check and calibrate the equipment and instruments
- Inspect the field journals
- Evaluate the need for improvements

An audit plan and guidelines for the audit should be worked out for this purpose.

8.5 Analytical techniques

The use of adequate methods is the responsibility of the national institutes. The majority of the participating countries have accepted the use of international standard methods such as prescribed by ISO/CEN in their national work. The EN (European standards) are legally prescribed for use by all EU nations. ICP IM should also adopt ISO/CEN standard methods as a basis for the methods actually used, as has been done in the ICP Waters programme. The ISO/CEN 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. The main pre-treatment method and determination codes (available in DB codelist) should be included in the data delivered to the Programme Centre.

Information of the ISO/CEN methods listed in available standards can be obtained from:

1. The national standardisation agencies.
2. International Organisation for Standardisation, DIN, Burggrafenstrasse 6, 10787 Berlin, Germany.
3. ISO International Organisation for Standardisation, Case Postale 56, CH-1211 Genève, Switzerland.
4. CEN European Committee for Standardisation, rue de Stassart 36, B-1050 Brussels, Belgium.

8.6 References and further reading

Allen, S.E. (1974) Chemical analysis of ecological materials. Blackwell Scientific, Oxford.

Cryer, R. And Trudgill, S.T. 1990. Solutes. In Goudie, A., Anderson, M., Burt, T., Lewin, J., Richards, K., Whalley, B. And Worsley, P. (eds) Geomorphological Techniques. Unwin Hyman, London, pp. 260-279.

EMEP. EMEP manual for sampling and chemical analysis, EMEP/CCC-Report 1/95, NILU, Kjeller, Norway, March 1996.

Hem, J.D. 1970. Study and interpretation of the chemical characteristics of natural water. U.S. Geological Survey Water Supply Paper N. 1473, 2nd edition.

ICP Waters. ICP Waters Programme manual. Compiled by the Programme Centre, Norwegian Institute for Water Research. Revised edition, Oslo, September 1996.

Jones, J.B. 1988. Comments on the accuracy of analytical data in the published scientific literature. Soil Science Society of America Journal 52, 1203-1204.

Kalra, Y.P. and Maynard, D.G. 1991. Methods manual for forest soil and plant analysis. Information Report NOR-X-319. Forestry Canada, Northwest Region, Northern Forestry Centre, Edmonton. 116 pp.

Lindberg, S.E., Turner, R.R., Ferguson, N.M. and Matt, D. 1977. Walker Branch watershed element cycling studies: collection and analysis of wetfall for trace elements and sulphate. In: Correll, D.L. (ed.) Watershed research in eastern North America. Volume 1. Smithsonian Institute, Edgewater, 125-150.

Reynolds, B. 1981. Methods for the collection and analysis of water samples for a geochemical cycling study. Institute of Terrestrial Ecology, Bangor, Occasional Paper No. 5.

Summers, W.K. 1972. Factors affecting the validity of chemical analyses of natural waters. Groundwater 10, 12-17.

Taylor JK.1987. Quality Assurance of Chemical Measurements. Lewis Publishers, Chelsea Michigan, 328 pp.

US-EPA 1988. Direct/Delayed Response Project: Quality Assurance Report for Physical and Chemical Analyses of Soils from the Southern Blue Ridge Province of the United States. EPA/600/PS8-86/100. September 1988.

WMO (1994) Report of the workshop on precipitation chemistry laboratory techniques. Hradec Kralove, Czech Republic, 18-21 October 1994. Edited by V. Mohnen, J. Santroch, and R. Vet. Geneva (WMO/GAW No. 102).

Annexes to ICP IM Manual

Annex 1: Measuring heavy metals and POPs at ICP IM sites

Annex 2: Code List DB

Annex 3: removed

Annex 4: Country codes

Annex 5: Site description formula

Annex 6: Coding of biological taxa

Annex 7: Data calculations

Annex 1: Measuring heavy metals and POPs at ICP IM sites

1 Introduction

An overview by Ramon Guardans (original text, not updated). The growing interest in international fora(1) that have carried out advanced research on the potential impacts on health and ecosystems of the long range transport of air pollution has promoted several international co-operative efforts to establish with as much detail and accuracy as possible the main magnitudes characterising the processes of emission, transport, deposition and potential damage to human health and the environment resulting from an increased exposure to heavy metals and persistent organic pollutants.

Table 1 Simplified layout of the main elements that participate in the process of assessing and responding to potential risks to the environment and health. [2] The items of principal interest for ICP IM are in bold type and refer to ecosystems.

Research	Risk assessment	Integrated Assessment
Lab.&field data on effects	Hazard identification	
Extrapolation Characterization/abatement from high to low doses	Dose-response	Risk
Field measurement of exposure and characterization of populations	**Exposure assessment**	

The regional and global nature of the processes make international efforts to generate comparable measurements the only basis on which further knowledge on the pools and fluxes can rest. A recent UNECE workshop (3) concluded that while the number of measurements of HM was large the intercomparability was low and that only a few POPs had been measured at a few sites.

To achieve a better quantitative understanding of the relative impact of ongoing, past, and natural emissions of heavy metals it is important to improve the coverage and resolution of the assessment of the current pools and fluxes of these substances in the environment.

For persistent organic pollutants and some metals the reversibility of deposition processes and the consequent re-emission make soils and vegetation relevant sinks and sources as well as receptors at risk and therefore the assessment of existing concentrations in different media is an important step to develop effective control measures based on an improved understanding the current status of the relevant pathways and potential effects of the different substances under consideration in different environments.

The objective of the cooperative effort in ICP IM is to compile and review physicochemical properties and environmental measurements of POPs and HMs and assemble these data in a form suitable for input to CLRTAP and global scale modelling used to identify long term and large scale trends in concentration in the environment of the different pollutants and assess the occurring and potential effects on ecosystems of the long range atmospheric transport heavy metals and persistent organic pollutants. This is a difficult task given the very large number of substances of potential interest.

The contribution of ICP IM in the forthcoming years could be very significant if comparable and simultaneous measurements of atmospheric concentrations, wet, bulk, and dry deposition, concentration in soils, sediments, water, and vegetation (lichens, mosses, needles, leaves, bark) could be obtained for a range of different ecosystems in different regions such as the ICP IM network.

Such information would be of very great value to a) enhance the precision of vegetation samples as indicators, b) improve the estimates of local pools and fluxes and of uncertain, substance and site-specific parameters on which exposure estimates can be developed and c) by reporting these

information's to the modelling community improve the accuracy of extensive regional modelling of long-range atmospheric transport of HM and POPs.

Another line of work, that at that stage should be of a lower priority but in the long term is a key element to assess the potential impacts on ecosystems and health, is the measurement of concentrations in the nodes of the trophic web, the quantitative assessment of pathways by which pollutants bioaccumulate and ultimately accumulate in sensitive tissues of individuals in human and animal populations.

2 List of priority elements and substances.

Concerning heavy metals the priority elements identified by the Preparatory Working Group for an initial protocol are Pb, Cd and Hg.

Future developments might include Cu, Zn, As, Cr and Ni.

Among the priorities that have been identified (Pacyna 1993, De Leeuw 1996) are the evaluation of Hg re-emission from aquatic and terrestrial environments, and the natural emissions of Hg. As well as the chemical forms in which metals are found in the environment.

Concerning Persistent Organic Pollutants, there are two kinds of lists to be considered on the one hand the list arrived at in the UN/ECE/Preparatory Working Group by applying a series of screening criteria and aimed at focusing policy action on the abatement of transboundary fluxes of these substances and on the other hand there is the list of compounds that existing networks and laboratories have been measuring and that from a practical and analytical point of view are recommended for an initial phase of a measuring effort.

The Executive Body of LRTAP at its 14th session (Nov 1996) indicates the following 16 substances to be considered in the negotiations, starting in January 1997, for a UNECE/LRTAP binding protocol:

aldrin, chlordane, chlordecone, DDT, dieldrin, dioxins and furans, endrin, heptachlor, hexabromobiphenyl , hexaclorobenzene, mirex, PAHs(*), PCBs, pentachlorophenol, toxaphene, lindane and short chain chlorinated paraffins.

The workshop (EMEP 1996) recommended for an initial phase of measurements

- PAHs (Benzo(a)pyrene)
- Polychlorinated biphenyls PCB IUPAC-28 52, 101, 118, 153, 138, 180.
- Hexachlorobenzene HCB
- gamma and alpha Chlordane
- Lindane
- a-Hexachlorocyclohexane HCH
- DDT/DDE

It is understood that the main focus of this manual is to inform interested laboratories on how to prioritize and plan the sampling strategy and carry out the field work, the analytical work will only be considered by reference inasmuch as it is assumed that users of the manual will in most cases rely on experienced laboratories to do the measurements on the samples.

Several kinds of measurements are of great relevance, in the first place to obtain direct, comparable and simultaneous measurements in different media (air/water/soil/biota) is necessary to establish seasonal variation, and temporal and spatial trends on a regional and global basis, second to interpret those measurements and to improve the precision of models (Pacyna 1996, De Leeuw 1996) there is urgent need for field information on the chemical forms and characteristic coefficients (i.e. Vapour-particle partitioning, Octanol air partition coefficient, Octanol water partition coefficient, Water solubility, Henry's law constant) for different substances in different environmental conditions (Bidleman 1988, Mackay et al 1995 Sánchez-Camazano 1993a, b, Sánchez Martin 1993, Mackay 1981, Suntio 1988, Murray 1996)

3 Methods, guidance on how to measure them in the field.

3.1 Air

These aspects are also covered in other sections of the manual dealing with other subprogrammes but repeating some of it here helps to have the wide picture.

HM Air sampling (AMAP 93, NILU and IVL 1993)

Cd and Pb: Most frequently used method is by particle filtration on an appropriately low background filter.

Hg (gas-phase): Recommended (with pre-concentration) two sequential collectors using gold-amalgamation technique.

Hg (particulate): Air filtration using quartz fibre filter or quartz-wool plugs.

Sampling frequency: 24 hour measurements during 3-4 weeks campaigns.

The detection limit of Pb/Cd will determine if it is possible to measure on a daily basis at a specific site.

Analysis (Maenhaut 89)

Extraction from filter

Inductively Coupled Plasma -Mass Spectrometry (ICP-MS) is recommended (Iverfeldt 1996) as reference method for Pb, Cd, Cu, Zn, As, Cr and Ni in air.

Hg (both phases): recommended cold-vapour atomic fluorescence spectrometry (CVAFS)

POPs Air sampling

Recommended (AMAP 1993) high volume sampler (20-25 m3h-1 and a volume of 1000-2000 m3 per sample are common values) with glass or quartz filter and solid absorbent trap (polyurethane foam) for both the gas and particle phases of: three chlorine and higher PCBs, DDTs, Chlordanes, Dieldrin, Toxaphene, three ring and higher PAHs, Dioxins, Dibenzofurans and Mirex.

HCB, HCH: Recommended use of amberlite XAD-4 and XAD-8 macroporous resins instead of polyurethane (polyurethane foam is acceptable for HCB only in winter Arctic conditions)

Analysis

Extraction from filter and trap: Soxhlet apparatus with solvents

PCB and pesticides: GC-ECD

Dioxin, Toxaphene, Dibenzofurans: GC-MS

PAHs: GC-MS or HPLC with fluorescence detection.

3.2 Deposition

Dry deposition estimates come from measurements of the gaseous and particulates in air monitoring with the high-volume samplers coupled to a deposition velocity (obtained from other experiments or theory). Wet depositions are more direct. For both organics and trace metals in precipitation, collection of rain and snow is done with large aperture wet-only collectors. Since the volume of water required to make an accurate determination of organics in water is on the order of litters, the aperture of the organics collectors are bigger than for inorganics or trace metals in precipitation.

HM Deposition sampling
Sampling for trace metals in precipitation is not an easy measurement to make as there are a number of problems that can distort the real concentration in rain. Two major problems are that many elements have affinity for the collection bucket or bag, and the very real possibility of contamination from the many metal surfaces in the vicinity. Obtaining Bulk collector technique is preferred, compared to the wet only collector, as the reference method for deposition sampling for trace metals. The same type of bulk collector should be used at all stations. (Barrie 1989, IAND 1994. Iverfeldt 1996).

Analysis
Pb, Cd: ICP-MS
Hg: CVAFS

POPs Deposition sampling
The National Waters Research Institute, Canada in the Integrated Atmospheric Deposition Network, uses MIC organic precipitation collector that consist of a coated metal funnel of 0.2 m2 area which drains to a wetted column of XAD-2 resin. The column removes the organics from the precipitation passing through it by gravity flow. The column is kept wet by use of a U-Tube at the column outlet. The collection columns are kept in place for 14-day periods. The columns are removed, placed in Teflon bags, stored in a cooler and shipped to the laboratory with the comment sheets. (Burniston 1994, Kawamura 1986, Farmer 1986, Mazurek 1987, McVeety 1988, Murray 1992, Leister 1994, Brorström-Lundén. 1996,)

Analysis
Extraction from filter and trap: Soxhlet apparatus with solvents
PCB and pesticides: GC-ECD
Dioxin, Toxaphene, Dibenzofurans: GC-MS
PAHs: GC-MS or HPLC with fluorescence detection.

As a good and complete illustration and as base to (dis) agree on recommended methods we quote from (Iwata 1994):

"Polyurethane foam plugs (31 mm, length 50 mm) were used as adsorbents for air sampling. (...) Six precleaned plugs were packed in a glass column (27 mm, 390 mm) with polyethylene caps at both ends and sealed in polyethylene bags until sampling. Air sampling was carried out using the prepared glass column connected with a low volume air pump. About 26-115 m3 of air (flow rate 35-38 litters/min) was collected for from several hours to two days. The flow rate was monitored at the beginning and the end of the sample.

"For water sampling, precleaned Amberlite XAD-2 (styrenedivinylbenzene copolymer macroreticular) resin packed in a glass column (i.d. 18 mm, length 50 mm) was used as adsorbent. Five to 75 litters of river and estuarine water were collected in polyethylene containers, which were washed previously with acetone, and immediately passed through the XAD-2 resin column by siphonage at a flow rate of less than 0.3 litres/min. After adsorption of organochlorines in the column, several ml of formalin were added to the column to avoid biological degradation of these compounds.

"Surface sediment samples (0 - 5 cm) were collected using a stainless-steel grab sampler. Sediments were well mixed in a precleaned aluminium plate and preserved in a polyethylene bag with several ml of formalin.

"The air, water, and sediment samples were transported to the laboratory and stored at -20ºC until analysis.

The methods to extract the substances from the samples and to analyse them are also well described in the literature (Murray 1996, Leister 1994, Brorström-Lundén. 1996, Iwata 1993) and are beyond the scope of this chapter now.

3.3 Soil

There is no general agreement on a reference method for sampling and measurement specifically for HM or POPs a frequent reference is (NCM 1988). The section in this manual for soil water and soil matrix sampling is a starting point but the corresponding provisions to avoid contamination of the samples should be implemented. The following laboratory methods for HM are cited by (AMAP 1993): ISO/CD 11466, ISO/TC 190/SC 3/WG 1 N 24.

There is much work to be done to generate comparable quantitative information on the influence of soil properties and environmental conditions on HM and POPs mobility and bioavailability in soils (i.e. Sánchez-Camazano 1993a, b, Sánchez Martin 1993, Mackay 1981, Suntio 1988, Torstenson, 1992, Schinner 1993)

3.4 Plant material

Many efforts have been carried out over the last decades to interpret measurements of HM from plant material, the relative scarcity of comparable and simultaneous air, deposition and plant measurements over extended periods has hindered the accuracy of these methods, however several large-scale surveys (NCM 1992) have been carried out successfully.

HM

Humus

NCM 1988, Field Manual Nat. Board of Waters and Env., Finland 1989, ICP Forests Manual.

Lichens

ISO/CD 11466, ISO/TC 190/SC 3/WG 1 N 24.

Mosses

NCM 1992

Mushrooms

NCM 1988

ISO/CD 11466, ISO/TC 190/SC 3/WG 1 N 24.

Leaf/needle
ICP Forests
POPs
A review (Simonich 1995a) and several papers (Simonich 1994, Calamari 1991, Simonich 1995b) present the great potential and the limitations of vegetation samples to carry out regional surveys. The following processes are listed in a simplified uptake model (Simonich 1995a)

- Vapour-particle partitioning
- Octanol air partition coefficient
- Octanol water partition coefficient
- Water solubility
- Henry's law constant
- Organic content of the soil
- Plant species
- Plant surface area
- Plant lipid concentration

Most of these coefficients are substance specific and will vary with environmental conditions and have been identified as important sources of uncertainty in models (Wania 1995, Murray 1996, De Leeuw 1996). It must be stressed that the interpretation of measurements obtained from plant material are still subject to many sources of uncertainty, the work in this program could help significantly in reducing some of them and consequently improving the accuracy of the assessments of pools and fluxes from a local to a regional and global scale.

It is also important to underline that the information on the atmosphere-water-soil-vegetation exchange of Persistent Organic Pollutants is relevant to understand the potential impact climate change in the long-range transport of POPs.

3.5 Animal tissues

Many sampling programs and reference methods have been developed to sample animal tissues and small marine and freshwater organisms. We refer the reader at that stage to good summaries such as (Muir 1988, Murray 1994 and 96, SEPA).

3.6 Paleoenvironments

Many interesting attempts have been made (Valette-Silver 1992) at using sediments and peat bog cores to establish the long-term record of deposition for heavy metals and persistent organic pollutants, historic samples in museum collections have also been to establish deposition levels in the recent past (Jones 1992). Sampling and analytical methods are similar to what has been described, the interpretation of these data present many problems that configure a worthy challenge for future research.

4 QA/QC

The complexity of the sampling and analytical procedures, the low concentrations that are measured and the large risk of artefact and contamination make a careful and tight QA/QC set of procedures absolutely necessary to achieve any kind of meaningful results on a regional basis. Recent work in

existing networks (EMEP 1993, Ebinghaus 1996, Cuisson 1994) provides ample base to develop appropriate QA/QC guidance in a later phase (of the drafting process).

5 Data pre-treatment

There are several distinct phases from the field to the laboratory in the obtention of measurements of environmental concentrations of HM and POPs and the later use of them to assess physico chemical parameters and effective exposures rate coefficient. The pretreatment and QA/QC will have to be designed in a way to ensure the best use of available information and resources. (i.e. Blackwood 1992, Brown 1978, Crump 1979) and to enable advanced statistical treatment and accurate estimates. (AMAP 1993, Burniston 1994) provide a complete description of the data flow provisions in existing large-scale networks.

6 Reporting

AMAP 1993, Burniston 1994 provide extensive examples.

7 List of variables + suggested units

Site
Date (in out)
Sampler/analytical method
Substance
Air concentration
Deposition
Wet
Bulk
Dry
Soil and surface water
Sediment
Vegetation lipid fraction
Animal tissue lipid fraction

8 References

AMAP, Arctic Monitoring and Assessment Programme, http://www.amap.no/

AMAP 1993. The Monitoring Programme for the Arctic Monitoring and Assessment Programme.

AMAP Report 93.3 AMAP, P.O Box 8100, 0032 Oslo.

Barrie, L. A. and R. S. Schemenauer 1989. Wet deposition of Heavy Metals, pp 203-231 in Control and Fate of Atmospheric Trace Metals, Kluwer Academic, Dordrecht.

Bidleman, T. F. 1988. Atmospheric processes, Wet and dry deposition of organic compounds are controlled by their vapour / particle partitioning. Environ. Sci. Technol., 22 361-367.

Blackwood, L. G. 1992. The lognormal distribution, environmental data, and radiological monitoring. Environmental Monitoring and Assessment 21: 193-210.

Brorström-Lundén, E. 1996. Atmospheric Deposition of Persistent Organic Compounds to the Sea Surface. Journal of Sea Research 35,81-90.

Brown, C. 1978. Statistical aspects of extrapolation of dichotomous dose-response data. J.Natl. Cancer Inst, 60, 101-108.

Burniston, D. A. 1994. Integrated Atmospheric Deposition Network, Standard Operating Procedures Rev.2. Lakes Research Branch, NWRI, Burlington, Ontario.

Calamari, D. E. Bacci, S. Focardi, C. Gaggi, M. Morosini and M. Vighi 1991. Role of Plant Biomass in the Global Environmental Partitioning of Chlorinated Hydrocarbons. Environ. Sci Technol. 25, 1489-1495.

Crump, K. S. and D. Masterman, 1979. Review and evaluation of methods of determining risk for chronic low-level carcinogenic insult. In Environmental Contaminants in Food. Office of technology Assessment, U.S. Congress, Washington D.C.

Cuisson, S 1994. Integrated Atmospheric Deposition Network, Quality Assurance Program Plan. Environment Canada, US EPA, Ontario Ministry of Environment and Energy. IADN. Canada/US Great Lakes Water Quality Agreement.

De Leeuw,F.A.A.M. 1996. Proceedings of the EMEP workshop on European Monitoring Modelling and Assessment of Heavy Metals and Persitent Organic Pollutants. RIVM report 722401013.

Ebinghaus, R. et al 1996. International field intercomparison of measurements of atmospheric mercury species at Mace Head, Ireland. 5Th International Conference on Mercury as a Global pollutant, Hamburg August 5-8, 1996. GKSS Research Center, Geesthacht, Germany.

EMEP Manual http://www.nilu.no/projects/ccc/manual/

EMEP 1993. Long term plans, Annex 1: Measurement programme For Heavy Metals (Toxic Trace Elements) EMEP/CCC-note 2/93. NILU.

EMEP-MSCE Workshop on Assessment of EMEP Activites Concerning Heavy Metals and Persistent Organic Pollutants and their Further Development, Moscow 24-26 Sept. 1996., (proceedings in progress).

FAO 1993 Codex alimentarius vol 2: pesticide residues in food. second edition FAO, Rome pp 475.

FAO 1993 Codex alimentarius vol 13: methods of analysis and sampling. second edition FAO, Rome pp 134.

Farmer, W. T. and Wade, T. 1986. Relationship of Ambient Atmospheric Hydrocarbon (C12-C32) Concentrations to Deposition, Water Air and Soil Pollution, 29, 439-452.

Foreman, W. T. and Bidleman, T. F. 1990. Semivolatile Organic Compounds in the Ambient air of Denver, Colorado. Atmos. Environ 24 A, 2405-2416.

Hart, K., I. Loran and J. Pankow 1992. High-Volume Air Sampler for Particle and Gas Sampling Performance. Environ. Sci. Technol.. 26, 1048-1052.

Hoff, R. M., W. M. Strachan, C. W. Sweet, C. H. Chan, M. Shackleton, T. F. Bidleman, K. A Brice, D. A. Burniston, S. Cussion, D. F. Gatz, K. Harlin and W. H. Schroeder 1996. Atmospheric deposition of toxic chemicals to the Great Lakes: a review of data through 1994. Atmospheric Environment 30, 3505-3527.

IAND 1994. Standard Operation Procedures. AES SPM Rev2.

Iverfeld, A., E. Brorström-Lundén, J. Schaug and T. Berg 1996. Measurement program for Heavy Metals and Persistent Organic Pollutants in Air and Deposition in Europe. Background document for the workshop on Assessment of EMEP Activities Concerning Heavy Metals and Persistent Organic Pollutants and their Further Development, Moscow 24-26 Sept. 1996.

Iwata, H., S. Tanabe, N. Sakai and R. Tatsukawa 1993. Distribution of Persistent Organochlorines in the Oceanic Air and Surface Seawater and the Role of the Ocean on Their Global Transport and Fate. Environ. Sci. Technol. 27, 1080-1098.

Iwata, H., S. Tanabe, N. Sakai, A. Nishimura and R. Tatsukawa. 1994. Geographical distribution of persistent organochlorines in air, water and sediments from Asia and Oceania and their implications for global redistribution from lower latitudes. Environmental Pollution 85 15-33.

Jones, K. C., G. Sanders, S. R. Wild, V. Brunett, A. E. Johnston 1992. Nature 356, 137-139.

Kawamura, K. and I. R. Kaplan 1986. Biogenic and Anthropogenic Organic Compounds in Rain and Snow Samples Collected in Southern California. Atmos. Environ. 20, 115-124.

Leister, D and J. Baker 1994. Atmospheric deposition of Organic Contaminants to the Chespeake Bay. Atmos. Environ. 28,1499-1520.

Maenhaut, W. 1989.Analytical Techniques for Atmospheric Trace Elements. pp 259-301 in Control and Fate of Atmospheric Trace Metals, Kluwer Academic Publishers. Dordrecht.

Mackay, D and W. Y. Shiu 1981. A critical review of Henry's law constant for chemicals of environmental interest. J. Phys. Chem. Ref. data 10,1175-1199.

Mackay, D. and F. Wania 1995. Transport of contaminants to the Arctic: partitioning processes and models. The Sci. of Total Environ. 160/161 25-38.

Mazurek, M., B. R. T. Simoneit, L. Standley, D. Firedman and C. Beeman 1987. Design and Use of a Collector for In Situ Isolation of Particulate Trace Organic Species in Precipitation. Water Air and Soil Pollution 36,193-206.

McVeety, B. and R. Hites 1988. Atmospheric Deposition of Polycyclic Aromatic Hydrocarbons to Water Surfaces: a Mass Balance Approach. Atmos. Environ.22,511-536.

Moore, G. L. 1989. Introduction to inductively coupled plasma atomic emission spectrometry, Analytical Spectroscopy Library Vol 3. Elsevier, Amsterdam.

Muir, D., R. J. Norstrom and M. Simon 1988. Organochlorine contamination in arctic marine food chains: accumulation for specific polychlorinated biphenyls and chlordane- related compounds. Environ. Sci. Technol. 22.1071-1079.

Murray, J. L., R. G. Shearer, 1994. Synopsis of Research Conducted Under the 1993/94 Northern Contaminants Program. Environment Studies No 72. ISBN 0-662-22692-5.

Murray, J. L., R. G. Shearer, S. L. Han 1996. Synopsis of Research Conducted Under the 1994/ 95 Northern Contaminants Program. Environment Studies No 73. ISBN 0-662-24414-1.

Murray, M. and A. Andren 1992. Precipitation Scavenging of Polychlorinated Biphenyl Congeners in the Great Lakes Region. Atmos. Environ.26 A, 883-897.

NILU and IVL 1993. EMEP Long term plans, Annex 1: Measurement programme For Heavy Metals (Toxic Trace Elements) EMEP/CCC-note 2/93.NILU.

NCM, 1988 Nordic Council of Ministers. Env. Rep.1 Nord 1988:26, pp 28-30.

NCM, 1992 Atmospheric Heavy Metal deposition in Northern Europe 1990. Nord 1992:12.

Oheme, M. and Stray, H. 1982.Quantitative Determination of Ultra-traces of chlorinated Compounds in High-Volume Air Samples for the Arctic using Polyurethane Foam as Collection Medium. Z. Anal. Chem.311, 665-673.

Pacyna, J. M., E. Voldner, G. J. Keeler and G. Evans 1993. Proceedings of the first workshop on Emissions and Modelling of Atmospheric Transport of Persistent Organic Pollutants and Heavy Metals. EMEP/CCC - rep 7/93, NILU.

Pacyna, J. M, E. Brorstöm Lunden, J. Paasivirta, E. Runge and F. Wania 1996. Emissions and behaviour of selected persistent organic pollutants in the northern environment. Part I: Development of the cycling model and emission and environmental data bases. NILU OR 17/96 ISBN 82-425-0754-6.

Sánchez Camazano, M., J. M. González-Pozuelo and J. M. Sánchez-Martin 1993a. Influence of soil properties on ethofumesate mobility. J. Environ. Sci. Health B28(4), 459-471.

Sánchez Camazano, M., J. M. Sánchez-Martin 1993b. Mobility of cadmium as influenced by soil properties studied by soil thin-layer chromatography. Journal of Chromatography, 643 ,357-362.

Sánchez Martin, M. J., J. M. Gonzalez-Pozuelo, M. Sánchez Camazo, 1993. Adsorption of thofumesate by agricultural and natural soils. Water Research 33, 479-486.

SEPA, Swedish Env. Prot. Agency. PMK kodlista MK. Huvudprogr. Miljögifter. Pogr. HTER BIN HM1084201.

Simonich, S. L. and R. A. Hites 1994. Importance of vegetation in removing polycyclic aromatic hydrocarbons from the atmosphere Nature 370, 49-51.

Simonich, S. L. and R. A. Hites 1995a. Organic Pollutant Accumulation in Vegetation. Environ. Sci Technol. 29, 2905-2914.

Simonich, S. L. and R. A. Hites 1995b. Global Distribution of Persistent Organochlorine Compounds. Science 269, 1851-1854.

Schinner, F. et al (ed) 1993: Bodenbiologische Arbeitsmethoden, Springer.

Suntio, L. R., W. Y. Shiu, D. Mackay, J. N. Seiber and D. Glotfelty 198. Critical review of Henry's law constants for pesticides Rev. Environ. Contam. 103, 1-59.

Torstensson, L (ad) 1992. Guidelines. Soil variables in environmental hazard assessment EPA-Report 4262.

Valette-Silver, Nathalie 1992. Historical Reconstruction of Contamination Using Sediment Cores: A Review. NOAA Technical Memorandum NOS/ORCA 65.

Wania, F. and D. Mackay, 1995. A global distribution model for persistent organic chemicals. Sci Total Envir. 160/161 211-232.

Comments:

[1]Oslo and Paris Commission (OSPARCOM) that has assessed the situation for the North Sea and the Atlantic the Helsinki Commission (HELCOM) that has assessed the situation in the Baltic, the IGAC (International Global Air Chemistry) programme form IGBP and the Arctic Monitoring and Assessment Programme (AMAP) among others.

[2] Based on Nat.Acad. Sci 1983, Risk assessment in the federal government: Managing the process. Nat.Acad. Press, Washington.

[3] Oslo and Paris Commission (OSPARCOM) that has assessed the situation for the North Sea and the Atlantic the Helsinki Commission (HELCOM) that has assessed the situation in the Baltic, the IGAC (International Global Air Chemistry) programme form IGBP and the Arctic Monitoring and Assessment Programme (AMAP) among others.

Annex 2: Code List DB

CODE LIST FOR CHEMICAL, PHYSICAL, BIOLOGICAL AND MICROBIOLOGICAL DETERMINANTS MEASURED IN ENVIRONMENTAL RESEARCH

1 Preface

The Finnish Environment Institute, the Swedish Environmental Protection Agency and the Institute of Applied Environmental Research of the Stockholm University have developed this code list from a list originally created by the Nordic Code Centre. Abbreviation 'Determinants, Code List DB' is used then referring to this list.

2 Structure

Code List DB consists of three different sub-codes: substance, pre-treatment, and determination.

Substance code list is divided into five sub-groups:

- Inorganic substances
- Organic substances
- Physical parameters
- Biological parameters
- Microbiological parameters

The main purpose of this code list is to simplify data handling of physico-chemical determinants and they carry sufficient peripheral information about data quality for data users. They are not unambiguous if the main interest is analytical method. Codes in the Code List DB are not specific for units. These should be documented separately in the data bases.

3 Maintenance

Maintenance of the code list is continuous. New codes are added into the code list on the basis of the requests made by the users. Proposals for the new codes should be sent using the code request form. A new code can be taken in use, with the list designator DB, only after it has been accepted by the maintainer (Finnish Environment Institute, SYKE) of this code list.

The basic idea in the maintenance of the code list DB is that changes which could change the basic meaning of the code will not be made. Codes with the list designator DB are stable and unique.

Code requests will be automatically sent to the SYKE. Decisions on these requests will be made in co-operation with the SYKE and the Swedish Environmental Agency.

4 Code examples

4.1 Substance codes

Examples of substance codes

Inorganic substances:

ACI	Acidity	
AG	Silver	
AL	Aluminium	
ALK	Alkalinity	
BASA	Base saturation	
BOD	Biochemical oxygen demand	Essential to state incubation time see pre-treatment list: Incubation
CS134	Cesium 134	

Organic substances:

ACA	Acetic acid
ACAL	Acetic aldehyde
ACD	Alpha-chlordane
ACL	Allylchloride

4.2 Pre-treatment codes

Examples of pre-treatment codes:

D	DIGESTION
D1	Digestion in HNO3
D2	Digestion in HNO3-H2O2
D3	Digestion in HNO3-H2SO4
D4	Digestion in HNO3-HClO4
D5	Digestion in H2SO4

F	FILTRATION
F1	Filtration, membrane 0.45 µm
F2	Filtration, membrane 0.40 µm
F3	Filtration, glass fibre 50g/m^2-100g/m^2

4.3 Determination codes

Examples of determination codes:

AA	ATOMIC ABSORPTION SPECTROMETRY
AAC	Atomic absorption spectrometry, cold vapour
AAF	Atomic absorption spectrometry, flame
AAG	Atomic absorption spectrometry, graphite furnace
AAH	Atomic absorption spectrometry, hydride generation
AE	ATOMIC EMISSION SPECTROMETRY

GC	GAS CHROMATOGRAPHY
GCA	Gas chromatography, atomic emission spectrometry
GCE	Gas chromatography, electron capture
GCF	Gas chromatography, flame ionization

4.4. Code combinations

Examples how sub-codes are combined.

The accuracy of the codes can be selected freely depending on needs. Pre-treatment and/or determination codes can be missing. If several pre-treatment codes are included in the code combination, the order of these codes is the same as the order of the different pre-treatments during analyse.

Description of the code combination is composed by means of the names of the codes included in the combination (see examples below).

Substance	Pretreatment	Determination	Description
AL			Aluminium
AL	D		Aluminium, digestion
AL	D1		Aluminium, digestion in HNO3
AL		AA	Aluminium, atomic absorption spectrometry
AL		AAF	Aluminium, atomic absorption spectrometry, flame

5 Download codes

Code lists updated 30 September 2020. **Please note that only DB codes are included** in substance list, additional IM codes are also used in the ICP IM programme included in separate file 'Parameter codes on IM list'. Also a list including all Parameter codes (DB and IM) used for individual Subprogrammes is added 'Parameters for each Subprogramme'.

substance.xlsx
pretreatment.xlsx
determination.xlsx (17 June 2021)
Parameter codes on IM list.xlsx
Parameters for each Subprogramme.xlsx

Annex 3 : Removed

ANNEX 4: ISO Area codes

A list of ISO alpha-2 codes used in coding of the areas:

AT Austria
BY Belarus
BE Belgium
BA Bosnia and Herzegovina
BG Bulgaria

CA Canada
HR Croatia
CZ Czech Republic
DK Denmark
EE Estonia
FI Finland
FR France
GE Georgia
DE Germany
GR Greece
HU Hungary
IS Iceland
IE Ireland
IT Italy
KZ Kazakhstan
LV Latvia
LI Liechtenstein
LT Lithuania
LU Luxembourg
MK Macedonia
ME Montenegro
NL Netherlands
NO Norway
PL Poland
PT Portugal
RO Romania
RU Russia
RS Serbia
SK Slovakia
SI Slovenia
ES Spain
SE Sweden
CH Switzerland
TR Turkey
UA Ukraine
GB United Kingdom
US United States

Annex 5: Site description formula

SUBMITTED BY:	
COUNTRY:	AREA CODE:
AREA NAME:	
GEOGRAPHICAL COORDINATES (lat, long):	
MAX ELEVATION (m.a.s.l):	MIN ELEVATION (m.a.s.l):
POLITICAL JURISDICTION (state or province):	
COUNTY (smallest administrative region):	
OWNER TYPE (state, communal, private):	
SIZE OF THE SITE (ha):	WATER AREA (% of total):
DOMINANT SOIL:	
DOMINANT VEGETATION:	
LONG TERM AVERAGE PRECIPITATION (mm, last 30 years):	
LONG TERM AVERAGE TEMPERATURE (°C, last 30 years):	
SNOW (% of precipitation):	
LENGTH OF THE HYDROLOGICAL CYCLE (days/year, free water flow):	
LENGTH OF THE VEGETATION PERIOD (days/year, mean temp. >5 °C for 5 consecutive days):	
LAND USE HISTORY:	
EARLIER INVESTIGATIONS:	

ANTHROPOGENIC STRESSES TO THE SITE:

Annex 6: Coding of biological taxa

Codes for biological taxa are widely used in the IM programme, in particular in subprogrammes Vegetation VG, Trunk epiphytes EP, and in optional subprogrammes Vegetation structure and species cover VS, Hydrobiology of streams RB, Hydrobiology of lakes LB, and Inventory of birds BB. The 'Nordic Code centre' (NCC) has created a number of codelists, which are used in the ICP IM programme. The original zip files can be downloaded from: https://figshare.com/articles/dataset/Example_files_linked_to_from_ICP_IM_Manual/19181891

File name	List abbreviation and name, geographic range
Algae	PX ALGAE: PHYTOPLANKTON and MARINE BENTHIC SPECIES, Northern Europe
Amphibia	H0 AMPHIBIA, Global
Aves	A1 AVES, Global
Balt_inv	Ö1 BALTIC INVERTEBRATES, the Baltic Sea and Kattegatt
Bryophy	M2 BRYOPHYTA - hepatic and musci, Europe and the Azores
Coleopte	C2 COLEOPTERA, the Nordic countries, including Karelia, and the Baltic countries
Crustace	K1 CRUSTACEA, the Nordic countries
Cyanophy	CY CYANOPHYCOTA, the Nordic countries
Dermapte	DE DERMAPTERA, the Nordic countries
Dinophyc	DN DINOPHYCEAE, Northern Europe and adjacent waters
Ephemero	W2 EPHEMEROPTERA, Europe including Asia minor and Northern Africa
Euglenop	EU EUGLENOPHYCOTA, Fennoscandia and Denmark plus adjacent waters
Fish	F0 FISH, the Northern Hemisphere

Fungi	16 FUNGI - Macromycetes, the Nordic countries
Hemipter	HE HEMIPTERA, Finland, Sweden, Norway and Denmark
Lepidopt	L1 LEPIDOPTERA,the Nordic countries
Lichenes	12 LICHENES (codelist is called L2 in the IM programme), Europe
Mammalia	D1 MAMMALIA, Global
Mollusca	M3 MOLLUSCA, the Nordic countries
Nematoda	NX NEMATODA, the Baltic Sea and Kattegatt
Odonata	W1 ODONATA, Europe, Northern Africa and Asia minor
Orthopte	RX ORTHOPTERA, the Nordic countries
Pauropod	J1 PAUROPODA, Global
Plecopte	W3 PLECOPTERA, Europe, Northern Africa and Asia Minor
Reptilia	XX REPTILIA, Europe
Rhodophy	RH RHODOPHYCOTA, Fennoscandia and Denmark plus adjacent waters
Rotifera	RF ROTIFERA, the Nordic countries
Tracheop	B4 VASCULAR PLANTS, the Nordic countries
Trichopt	W4 TRICHOPTERA, Europe and adjacent territories of North Africa and Asia Minor (i.e. the Western Palearctic)
Zoobenth	ZB NORTH SEA ZOOBENTHOS, North Sea oil platforms

Codes are normally formed from the scientific names according to the following rules:

Species
4 digits of genus name, a blank, 3 first digits of species epithet; e.g. PICE ABI = Picea abies

Genus
7 first digits of genus name followed by Z; e.g. EQUISETZ = Equisetum sp; PICEA Z = Picea sp

Family
7 first digits of family name followed by X; e.g. CERATIIX = Ceratiidae

These codes should be used whenever possible. Unfortunately there are no lists available for plant communities, tree stands and all the invertebrate groups, neither is the geographic coverage large enough, which makes own coding necessary. If new codes are added the code, full scientific name with authority, taxonomic class and order must be reported with the data. The additional codes should also be identified with specific codelist abbreviations (see below).

Preliminary list abbreviation and name:

AX	PRELIMINARY ANNELIDA
CX	PRELIMINARY COLEOPTERA
KX	PRELIMINARY CRUSTACEA
DZ	PRELIMINARY DIPTERA
HX	PRELIMINARY HEMIPTERA
LX	PRELIMINARY LICHENS
MZ	PRELIMINARY MOLLUSCA
MX	PRELIMINARY MOSSES
WX	PRELIMINARY ODONATA
OX	PRELIMINARY ORDINES MINORES

PX	PRELIMINARY PLANKTON
BX	PRELIMINARY VASCULAR PLANTS

Annex 7: Data calculations

1. Conversion from ions to elements
2. Calculation with L-flags in data series
3. Calculation of mean of pH
4. Calculation of weighted means
5. Calculation of sea-salt corrected values
6. Biodiversity indices

1 Conversion from ions to elements

Calculate the results to be reported in S, N and P using the formula

concentration of element = factor x concentration of ion

eg.
conc SO2S = 0.5005 x (conc SO2)
conc SO4S = 0.3338 x (conc SO4)
conc NO2N = 0.3045 x (conc NO2)
conc NO3N = 0.2259 x (conc NO3)
conc NH4N = 0.7765 x (conc NH4)
conc PO4P = 0.3261 x (conc PO4)

2 Calculation with L-flags in data series

If the primary data-series contains values below the detection limit (quality flag L), these values are compensated by 0.5 x the detection limit value prior to statistical mean calculations and no quality flag is reported with the mean values. Additional information on flags in Chapter 4 (4.3.3).

3 Calculation of mean of pH

The original pH values must be converted to conc H^+ before calculations - the mean concentration H^+ is then reconverted to a pH-value

$$\bar{H}^+ = 1/n \sum_{i=1}^{n} 10^{-pH_i}$$

where:

$\bar{H}^+$ = mean proton activity,
pH_i = pH - values of samples,
n = number of samples.

$$\overline{pH} = -\log_{10} (\overline{H^+})$$

where:

$\overline{pH}$ = mean pH - value.

4 Calculation of weighted means

Volume weighted means for precipitation (precipitation, throughfall and stemflow) chemistry are calculated using the formula:

$$\overline{X} = \frac{\sum_i c_i m_i}{\sum_i m_i}$$

where:

c = measured concentration during a period
m = precipitation during the period

Flow weighted means for runoff, soil water and groundwater chemistry are calculated using the formula:

$$\langle c \rangle = \frac{\sum_{i=1}^{n} c_i Q_i}{\sum_{i=1}^{n} Q_i}$$

where:

$\langle c \rangle$ = mean concentration weighted with respect to discharge
Q_i = discharge at sampling time
c_i = concentration at sampling time
n = number of samples

5 Calculation of sea-salt corrected values

In the IM programme sulphate values are reported as uncorrected sulphur - not sea-salt corrected anthropogenic sulphur. A method for sea-salt correction is given here. Sea-salt corrected values are marked with an asterisk (*) and calculated as:

[Ca*] = [Ca] - 0.037 [Cl]
[Mg*] = [Mg] - 0.198 [Cl]
[Na*] = [Na] - 0.858 [Cl]
[K*] = [K] - 0.018 [Cl]
[SO4*] = [SO4] - 0.103 [Cl]

where [ ] is concentration expressed in µeq/l.

6 Biodiversity indices

Shannon-Wiener index of species diversity

$$DIX\_SW = -\sum_{i=1}^{s} (p_i)(\log_2 p_i)$$

where:

s = number of species
p_i = proportion of total sample belonging to i^{th} species