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CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests

Proposed update of the
MANUAL

on
Methods and criteria for harmonized sampling, assessment,
monitoring and analysis of the effects of air pollution on forests

Part VI

Sampling and Analysis of Deposition

updated 2009

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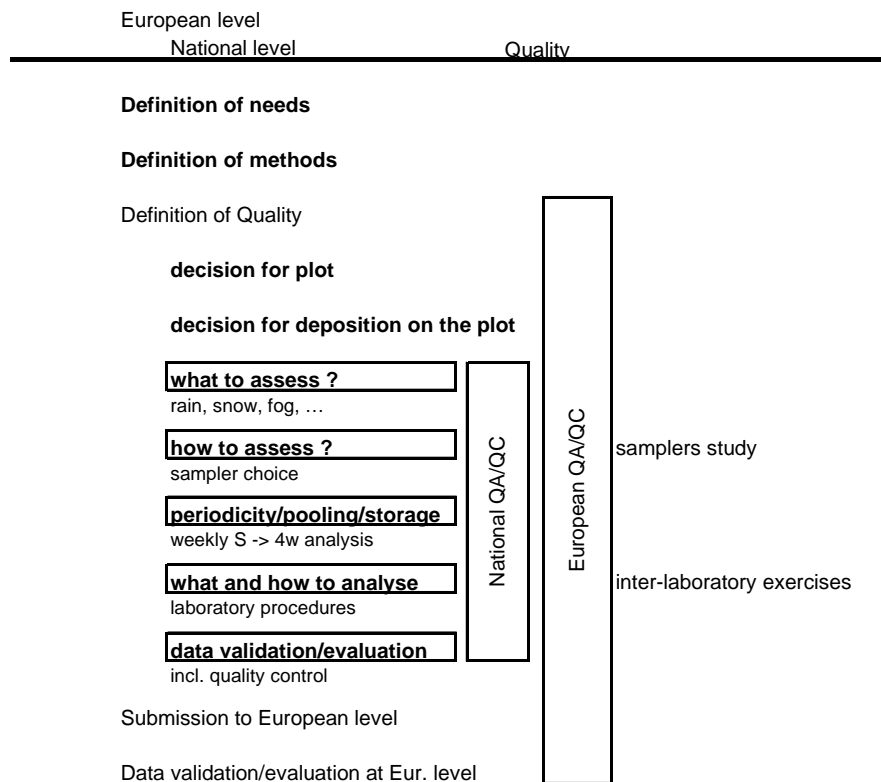
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1. Introduction

In 1994, the implementation of the Pan-European Programme for the Intensive Monitoring of Forest Ecosystems started. Within this programme deposition is one of the key factors in the causal chain between emission of air pollutants and effects in forest ecosystems. It is therefore necessary to quantify atmospheric deposition at the Intensive Monitoring sites (Level II). Here you will find a manual describing the methods used and the QA/QC procedures necessary to quantify site-specific deposition. The objective of deposition monitoring on the Level II plots is to estimate atmospheric deposition (concentrations, amount of deposition, fluxes) and soil loads at the sites, on which intensive monitoring is performed and to contribute to the understanding and quantification of deposition processes to forest ecosystems of Europe. The objective of this sub-manual on deposition is to provide procedures for throughfall, stemflow, bulk and wet deposition measurements in order to harmonise the deposition estimates within ICP Forests and to create comparability with other deposition measurements within ECE programmes. In order to fulfil the objectives it is necessary to determine atmospheric deposition with a total accuracy of ±30% as a first step. Later on, ±20 or ±10% might be the aim. For example, EMEP has defined a data quality objective of 15-25%. The laboratory quality is for example very well defined by the World Meteorological Organisation in its guidelines (WMO, 2004, http://www.wmo.ch/web/arep/reports/gaw160.pdf). How can we measure, determine the real value and the precision or accuracy in the field? In the long run, the deposition measurements on the Level II plots will improve the input for the UN-ECE mapping of critical loads and their exceedances, and further improve the abatement strategies over Europe.

This manual consists of a main text and several technical annexes. The main text first gives some background information on deposition processes (Chapter 2). An overview of deposition monitoring activities is given in Chapter 3. The main activities in the field up to the analysis of samples in the laboratory are described in Chapter 4. Chapter 5 gives brief information on methods and QA/QC requirements for analysis of the samples, while data handling and reporting is outlined in Chapter 6.

2. Deposition monitoring process

A very general approach of deposition monitoring, including both European and National level activities, is given in Figure 1. It shows that the definition of needs, methods and quality assurance at the European level should directly influence National activities, starting with the choice of the plot and ending with data validation and evaluation.

Deposition monitoring can be divided into 12 major activities. All these activities are linked to specific QA/QC procedures. All the QA/QC procedures aim, with their feedback, to improve the quality of the whole monitoring process and therefore also the quality of the published data. The flowchart of the deposition monitoring process is defined in more detail in Figure 2. In the following chapters the different activities are defined.

European level
  National level   Quality

Definition of needs

Definition of methods

Definition of Quality

  decision for plot

  decision for deposition on the plot

  what to assess ?
  rain, snow, fog, …

  how to assess ?
  sampler choice

  periodicity/pooling/storage
  weekly S -> 4w analysis

  what and how to analyse
  laboratory procedures

  data validation/evaluation
  incl. quality control

National QA/QC

European QA/QC

samplers study

inter-laboratory exercises

Submission to European level

Data validation/evaluation at Eur. level

Figure 1: General approach of the deposition monitoring activities on the European and national level and of the associated quality assurance/quality control programme.

Proposals for objectives:
- Quantification of annual deposition of acidity, all forms of nitrogen and precipitation by the throughfall method with a precision of +-30% (95% significance level)
- Detection of a temporal trend of the deposition on a plot. Detect a change of +-30% (3% per year) within 10 years (95% significance level)

2.1. Definition of the different deposition types

Wet-only deposition (of ions): flux of dissolved components from the atmosphere in open field with rain, snow, hail. The samplers open automatically at the onset of precipitation and close at the end, thus avoiding the collection of dust during dry periods.

Advantages:	It gives valuable information on the chemistry of atmospheric deposition; Gives information on rather long range transport of air masses
Disadvantages:	It needs electric power and maintenance; It does not work correctly in case of heavy snow.

Bulk deposition: flux of dissolved components from the atmosphere in open field with rain, snow, hail. It is sampled with a continuously open plastic funnel and bottle, which also collects parts of particulate and gaseous deposition during dry periods. Contributions from occult deposition are also included.

Advantages:	It does not need electric power, it is cheap and simple, low maintenance.
Disadvantages:	It is very sensitive to dust from the neighbouring areas; in regions with calcareous soils bulk deposition gives incorrect information on pH and chemistry of atmospheric deposition.

Dry deposition: flux of gases and particles from the atmosphere during dry periods, due to gravity (sedimentation), impaction, and interception. Dry deposition concerns mostly the forest canopy, but also at a minor level bulk deposition in open field. The values are strongly influenced by:

- type of surfaces (leaves, needles, rocks, water. etc);
- humidity of surfaces;
- macro- and micrometeorology (stomata closure).

The measurement of dry deposition is very difficult and very expensive; there are several techniques, but all have their limits. Some models, e.g. the EMEP or EDACS models or some national models, evaluate dry deposition over Europe.

Occult deposition: deposition coming from fog, rime, mist and cloud water.

Stand throughfall deposition: sampled beneath the forest canopy and containing bulk + leached + dry deposition-absorbed ions. Contributions from occult deposition are included.

Stemflow deposition: sampled on stems and contains precipitation, occult deposition and leachates from the bark and leaves

Total atmospheric deposition on the forest: wet-only + dry deposition to the canopy excluding internal ion exchange process. Only for sodium and sulphur throughfall + stemflow is considered to be equal to total deposition, in some cases also for nitrate.

3. Overview of the main activities

The aim is to determine total atmospheric deposition under forest cover as one of the major external driving forces of ecosystem development. To do so, we have to distinguish between internal and external fluxes of elements, as the canopy may strongly interact with gases, particles or water passing through. This effect is known as canopy exchange and accounted for by using so-called canopy budget models. These allow estimation of whether the leaves and twigs act as a source or a sink for the element under consideration. In order to apply such models for deposition the feasible and cost-efficient way is to measure bulk deposition in the open field (reference value without influence of plant surfaces) and beneath the canopy as throughfall, stemflow (for beech only) and litterfall (especially for heavy metals). These measurements include rain, snow, fog, rime, mist, cloud water, dry deposition of gases and leaching from leaves and needles.
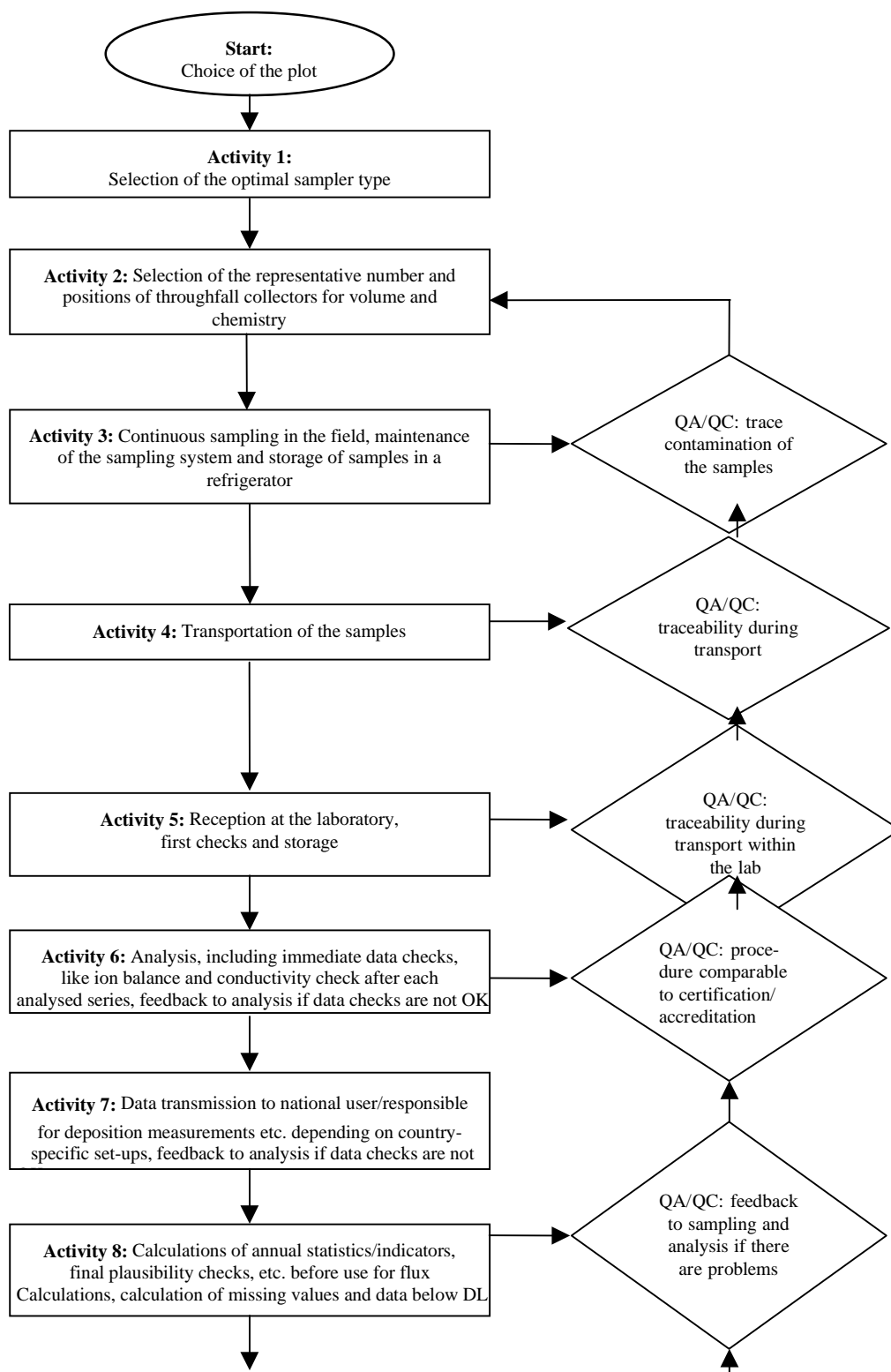
Figure 2a: Flowchart of deposition monitoring process in a country/part of a country. The next steps are shown on the following page. The different activities are described more in detail in the text. DL = detection limit.
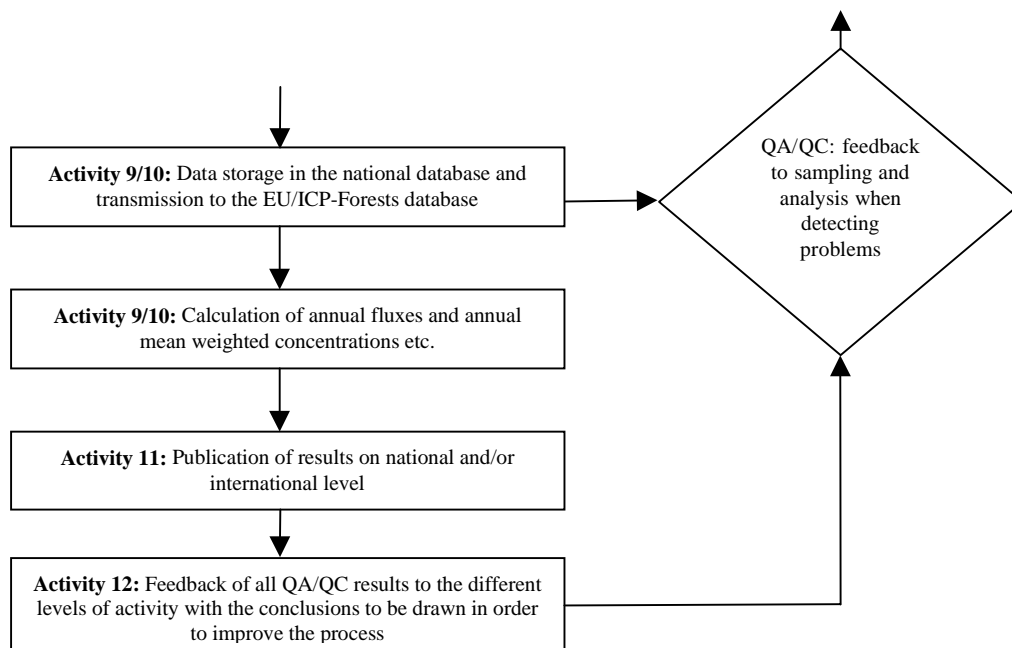
Figure 2b: Flowchart of deposition monitoring process in a country/part of a country. The different activities are described more in detail in the text.

Using bulk deposition induces estimation errors in total atmospheric deposition to the forest, because canopy exchange models need wet-only deposition as one of the input parameters. The choice of bulk measurements is justified because of financial constraints.

4. Sampling

Deposition monitoring must be representative for the site and it is recommended that measurements should be made, as far as possible, on <u>all</u> Level II sites. If deposition is only measured on a selection of plots, it is recommended to choose them in such a way that they are spatially well distributed over the country; preference should be given to the following points:

(i)   Choose the plots in such a way that they are spatially well distributed over the country so that different deposition ranges can be observed according to the geo-climatic and emission situations,

(ii)   Each plot should correspond to the main species or main mixture of species, the mean climatic conditions and ecosystem type within the concerned forested area,

(iii)   Homogenous stands, representative for regional environmental climate, far from local sources (industry, farms, traffic, etc.),

(iv)   Prefer those plots on which other important monitoring activities take place.

The plots on which deposition is measured must be described in detail. Some of the information is already included in the descriptions of the forest monitoring plots (longitude, latitude, altitude, exposure, tree species, etc.) Other information needs to be documented with special consideration to the deposition situation (exposure to any smaller local or regional emission sources and local land use location in relation to forest edges etc.) For interpretation and understanding of the deposition processes, information on factors such as canopy roughness, height of the stand, structure, leaf area index, evolution of the stand (density), vitality, biotic stresses (insect plagues) and several meteorological parameters etc. is valuable (see monitoring programmes on crown condition, increment assessment).

Preliminary studies should be carried out to determine the number of samplers required in order to obtain a representative sample of the deposition parameter being measured, the need for stemflow measurements, and the type of precipitation collectors used. Statistical analysis of the measurements should be made for each plot in order to ensure that the sampling procedure meets the fixed criteria. If monitoring sites or procedures are changed, parallel stations or parallel equipment should be run for a sufficient long period (3-12 months depending on the type of change) in order to ensure the consistency of the time series.

4.1. Choice of method

Several methods can be used to measure or estimate deposition to forests. However, only one of them, the throughfall method, meets the requirements of being relatively simple and economically feasible for most countries. Throughfall can also be used in complex terrain, such as forested areas on exposed heights and slopes. Another advantage is that contributions from occult deposition are included in the throughfall deposition. In addition to throughfall, wet deposition (deposition via precipitation) or bulk deposition in the open field should be measured and, for some types of forest stands, also stemflow.

The main drawback of the throughfall method is the interaction between the canopy and the throughfall water for nitrogen, potassium, calcium, magnesium, manganese and protons. However, the results from throughfall monitoring can still be used as a valuable indicator for the nitrogen and base cation deposition to the forest. Throughfall deposition can give information on the lower limit of the true deposition of nitrogen and the upper limit of true deposition of base cations other than sodium. For sodium and sulphur the canopy uptake and leaching is considered to be negligible and consequently the throughfall flux is used to estimate the total deposition.

To estimate the dry deposition of nitrogen and canopy uptake of nitrogen compounds, dry deposition can be estimated using air concentrations of nitrogen compounds and meteorology as input data, or canopy budget models can be applied. To determine deposition of base cations, canopy budget models have to be applied to differentiate the contributions from leaching and dry deposition in the net throughfall (throughfall plus stemflow minus wet deposition).

Rain and snow are collected in the open field close to the forest stand. The samplers may be open all the time (bulk collector) or open only during periods of precipitation (wet-only collector). The bulk collector will sample not only the wet deposition but to some extent also dry deposition (from gases and particles) and occult deposition. The dry deposition contribution varies geographically. In polluted areas and in areas subject to impact from Saharan dust, dust from anthropogenic sources or sea salt, the contribution of dry deposition may be significant; in other areas it may be small. As for throughfall, the precipitation amount in the bulk samplers is determined by measuring the sample volume. In addition to that, in the open field the use of a standard meteorological (manual) rain gauge is recommended in order to obtain an independent control of the precipitation amount at the sampling site.

Throughfall deposition measurements should necessarily be made on the plot itself (it might be in the subplot or buffer zone). Wet or bulk deposition should be measured in the open field close to the plot. The measurements should in no way interfere with other measurements of soil and vegetation. Caution must be taken not to cause any damage to the forest plot. Air pollution measurements should also be site specific, but could for practical reasons, or for reasons of co-ordination with other projects, be made at some distance. The maximum acceptable distance depends on the emission situation in the vicinity of the forest and on the orientation in hilly or mountainous terrain. There must, however, be no influence from local point emission sources. The

measurement site must not be influenced by climatic conditions other than those, which are found on the forest plot.

4.2. Techniques for bulk and wet deposition monitoring

4.2.1. Bulk precipitation samplers for rain

For bulk sampling, all countries should use a type of sampler, which is comparable among countries concerning some minimum requirements, developed below. For the liquid (e.g. rain) and the solid phase (e.g. snow) different types of samplers may be used. A minimum of three replicates is necessary.

The design of this sampler should as a minimum conform to:

- the definition of the World Meteorological Organisation (WMO) minimum requirements for correct precipitation quantity measurements,
- the needs for the stability of the sample for chemical analysis (no contamination, no absorption of compounds, no excessive heating or light)

These minimum requirements are defined below.

Sampler design according to WMO definition of a standard precipitation gauge

Collecting area
According to the WMO definition of a standard precipitation gauge, the sampling surface should be at least 200 cm² and at maximum 500 cm². The collecting surface should be known with a maximum margin of error of ±2%. The collecting surface should be in form of a circle (200 cm² = diameter of 16 cm; 500 cm² = diameter of 25.2 cm). In areas with high wind, a larger number of collectors with a smaller surface area are preferable, because under-catch as a result of aerodynamic blockage during high wind speed rain events will be greater with a larger collecting area (Draaijers et al. 2001). In areas where the precipitation is generally low and sampling frequency is high (due to eventual evaporation), a bigger funnel surface is recommended. When the collecting surface is not equal to 200 cm², the measurements must be matched against a WMO device fitting empirically the function $P=KP_{wmo}$. The collecting surface has to be verified at least once a year on all devices. The surface area of all collectors should meet the criteria of 2% variation coefficient. To estimate the true collecting area, half of the rim area should be included, as droplets falling on the rim are assumed to splash into the container 50% of the time.

Rim
The rim must be of hard material to minimise changes in the collecting area. Both the shape and the width of the collector rim will influence the extent of aerodynamic blockage. Sharp rims induce more turbulence than flat rims, while thick rims lead to greater undercatch than thinner rims (Sevruk et al. 1994).

Shape
WMO manuals recommend that the upper part of the sampler should be very sharp and should go down vertically in the form of a cylinder. Collection vessels with sloping sides have to be avoided in order to prevent any loss of precipitation due to splashing especially during precipitation events, during which rain droplets impact with high kinetic energy. The vertical part of the collector should be deep enough to avoid any ejection or loss by wind of the incoming precipitation. Figure 3 shows schematically the required design.
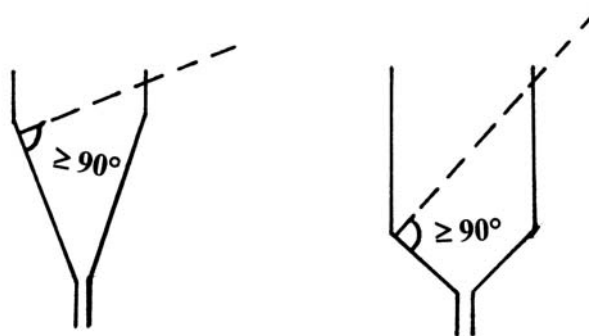
Figure 3: The only satisfactory design for precipitation quantity sampling (after WMO, 1990).

Capacity of the sampling container
The volume of the sampling bottle/container, linked to the sampler, should be big enough to collect all liquids in one sampling interval (99%), occurring between two sampling dates. Thus it is possible to avoid an underestimation of most of the real precipitation quantity, which is one of the most important variables for the flux calculations.

Material
The upper part of the sampler should have smooth surfaces, with no breaks or ridges in the connections in order to limit evaporation losses and ensure rapid water flow. The material, of which the collector and its containers, tubes, glue, bird wires etc. is made, must not interact with the sample solution. Polyethylene is a suitable material recommended for the studies of macro-ions. A test for the release of solutes has to be done for all new material before use in the field and laboratory (e.g. filtration). For sampling heavy metals, separate polyethylene equipment, which is acid washed at the laboratory before use, must be used. Polyethylene can become brittle when exposed to sunlight and may need to be replaced annually (EMEP 2001). Tetrafluoroethylene and tetrafluoroethylene-fluorinated ethylpropylene copolymer are other materials that are recommended by EMEP (2001). Metals or materials with unknown chemical properties should not be used.

Height above ground level
In order to avoid contamination of the samples, the rim of the sampler should be 1.0-1.5 m above ground level. The sampling area must be horizontal; the collecting area will otherwise be reduced.

Sieves and filters
In order to avoid larger objects (insects, parts of leaves or needles, etc.) from falling into the bottle and contaminating the sample, for instance a polyethylene net (mesh width 1 mm has been recommended, Draaijers et al. 2001) sieve or other inert sieves (aquaristic filter fleece) should be placed at the top of the neck of the sampler. The design of the sieve should be such that eventual debris is not concentrated in the neck of the collector forcing all rain to pass through the accumulating debris. The sieve must not impede the water flow: sieves that are not fixed in position are therefore recommended (Draaijers et al. 2001). It is possible to use a filter afterwards, with a pore size small enough to exclude small particles and microorganisms. The distance between the sieve and the filter would have to be large enough to allow the water to pass through both easily.

Bird wires
The upper exterior part of the sampler could be surrounded by a so-called "bird wire" or "bird ring" in order to prevent droppings from birds sitting on the top of the collector entering the sample. Exceptions are plots situated in areas with a very low bird density (e.g. in northern Scandinavia). Bird rings could be necessary for both bulk and throughfall. In regions with bird dropping problems, either a bird sitting ring or a bird rejection device can be used. They should be

sufficiently slim, so that they neither represent an aerodynamic blockage, nor attract birds to sit on them.

Storage containers and tubing
The collection bottle shall be large enough to contain the largest amount of precipitation expected during the sampling period at the sampling location. In many cases 2 - 5 litre bottles are used.

To slow down microbial or chemical degradation of the sample, the sample containers should be kept cool and in the dark e.g. in a pithole. One way to achieve this is to use PVC pipes (used for wastewater tubes), in which the bottles are placed. The sampler has to be placed in the pipe in such a way that the upper part of the sampler extends by several cm (5-10 cm) above the upper part of the pipe. All parts of the sample have to be kept far from possible contamination by soil splashing from the ground.

Other ways of achieving cool and dark conditions are keeping the sampling container in a pithole or wrapping aluminium foil around the container (although this is considerably less effective than a pithole).

Collectors and sample containers should be connected with black polyethylene tubes or other tubes excluding light and not interfering with the sample. The length and angle of the tubes should allow rapid throughflow in order to minimise evaporation loss. On no account should there be dips in the tubes.

4.2.2. Bulk precipitation samplers for snow
Rain collectors are changed to snow collectors when, according to meteorological statistics or prognoses, there is great risk for snow. The time period for this differs of course between regions and even within regions (e.g. with altitude or distance to the coast).

Snow collection in the open field is more difficult than rain collection and more difficult in the open field compared to within the forest. For snow sampling, special collectors should be used. A minimum of three replicates is necessary. So far, however, there are no scientific studies upon which recommendations for equipment could be based. According to the experiences gained in countries with long periods of snowfall, the size of the collecting surface per sampler should be much larger (≥ 500 cm²) in areas with heavy snowfall and in the form of a circle. In order to be able to store the snow, a polyethylene plastic bag of sufficient thickness (≥ 100 µm) can be placed under the upper part of the collector, which still has to fulfil the requirements defined in Section 5.3.1. In case of frequent changes between snow and rain, both types of samplers can be run in parallel. Depending on the proportion of snow or rain, the local operator will decide from which type of sampler to collect the sample for analysis.

Wet-only samplers are not recommended for collection of snow because the aerodynamic design is not suitable and because heating of the funnel to melt the snow may cause serious evaporation losses (EMEP 2001).

Examples of rain and snow collectors are shown in the manuals for Integrated Monitoring (ICP Integrated Monitoring, 1998) and EMEP (EMEP 2001).

4.2.3. Wet-only samplers

Information on the contribution of dry deposition and on the differences observed between wet-only and bulk collectors can, in many cases, be obtained by the EMEP monitoring experiences in each

country. Alternatively, in a pre-study, the two types of samplers should be run in parallel for at least one year at the same site.

No internationally standardised design of wet-only samplers exists. Some examples are given in the EMEP manual. There might be substantial differences from one collector to another, even with the same general design. This is a result of air turbulence, the detection of precipitation (type of resistance, heating or not, optical detector, etc.), the time delay in opening or closing the sampler, the way samples are stored inside the collector, heating or not of the collecting surface in winter etc. For these reasons it is difficult to consider wet-only deposition monitoring results between different countries as being really comparable. Each country should compare its wet-only collector for at least a year with an official rain gauge, in order to know its collecting efficiency. However, the comparison between bulk and wet-only measurements should be done more systematically in each country, and not for the length of some months, but for some years.

The WMO manual (WMO 2004,
 http://www.wmo.ch/pages/prog/arep/gaw/documents/gaw160_000.pdf) presents a list of criteria for a well performing wet-only collector. One crucial point is the sensitivity of the sensor. It is stated that the wet-only sampler must give comparable results to an official meteo rain gauge. Comparability is defined by WMO as: "+0% to –20% for liquid equivalent depths of 0.5 to 2.5 mm of precipitation and +0% to –10% for liquid equivalent depths >2.5 mm of precipitation".

4.2.4. Siting criteria for bulk and wet-only samplers

Information on siting of precipitation samplers can be found in the EMEP manual (EMEP 2001) and the manual for the GAW precipitation chemistry programme (WMO 2004).The samplers should be set up on an open field site at the same altitude and exposure as the forest plot (ICP Integrated Monitoring 1998), and with consideration of the prevailing wind directions. Level areas are preferable, although slopes of up to ±15% are acceptable. Sudden changes of slope within 30 m of the sampler should be avoided.

There should be no obstacles (trees, topographical features etc.) above 30º from the rim of the precipitation collector. This means that the distance from the sampler to the obstacle should be twice the height of the obstacle. Topographical features, buildings or hedges giving rise to updraughts or downdraughts should be avoided. Any object over 1 m high that can deflect wind should not be located within 5 m of the sampler. If fencing is used (e.g. to prevent damage from animals), it must be put up in accordance with these requirements.

It is important that local sources of soil dust (gravel roads, farmyards or tilled agricultural fields) and ammonia (from farming) be avoided. Contamination from local residential heating with wood, peat or coal may also occur: potassium is an indicator of such contamination. If heavy metals are to be determined, local metal sources (e.g. metal surfaces, building materials, paint) must also be avoided. Distances of 100 m to 2 km from local sources of contamination are recommended by EMEP (2001).

The height of surrounding vegetation should not be higher than half the height of the sampler, measured from the ground to the sampling orifice (WMO 2004). In areas with very high snow accumulations, a platform may be used to raise the sampler.

4.3. Techniques for throughfall monitoring

Throughfall measurements should be made in such a way that the results are representative for the plot area and should provide information on the coefficient of spatial variation by parameter. This means that a sufficiently large number of samplers should be used and the samplers should be placed in such a way that the variation is covered. This section only applies to precipitation in the form of rain.

4.3.1. Number of samplers to be used
Number of throughfall samplers
A throughfall collector samples only the small area where it is placed. In order to take into account the large local variations in throughfall deposition in a forest stand, a sufficiently large number of collectors must be used. Table 1 presents the minimum number of samplers (funnels of 100-600 cm²) to be used on sample areas up to 2500 m² (minimum 500 m²). These numbers guarantee, according to the currently available knowledge in international literature (see Annex 1), measurements with at least 20% error of the mean with a 90% confidence interval for most of the measured ions and for precipitation quantity. The number of samplers is dependent on the forest type and increases with increasing heterogeneity (due to e.g. species mixture, stand density, nearness to forest edges, precipitation types etc.) If gutters are used, the number and length of gutters must be sufficient to cover the variability of the stand deposition. Far fewer scientific studies exist for gutters and therefore no guidelines can be given here, which hints at the necessity of local studies. Guidance on the number, of how many and how large samplers are needed should be obtained in a study. It is necessary to carry out studies of the variations within the plot and repeat them following major structural changes (e.g. thinning, storm damage, fire). In such studies a large number of collectors should be used. Critical parameters should be measured during these studies such as total nitrogen, ammonium, nitrate and conductivity. The study should concentrate on throughfall deposition and not on volume or concentration only. The criterion for deciding the number of samplers is that deposition for all major ions on the plot should be estimated within ±20% of the mean. *Only if such studies cannot be made, e.g. for financial reasons, should Table 1 be used as a guideline for the minimum requirements.*

Table 1: Recommended number of throughfall samplers (funnels of 100-600 cm²), depending on forest type. The numbers are from different publications (see Annex 1, www.icp-forests.org/DocsDepo/Rovan05_Publicat_samplers.doc).

Forest type	Minimum number of samplers needed in order to reach 20% error and a 90% confidence interval in most cases for plot areas of up to 2500 m²
Very homogenous single species **conifer** forest (systematically planted, no openings)	20
Very homogenous single species **broad-leaved** forest (systematically planted, no openings)	25
Heterogeneous single species (e.g. uneven aged) and **mixed forest** of 2 or more tree species, whether they are conifers or not, **with small openings**	35-40
Heterogeneous single species (e.g. uneven aged) and **mixed forest** of 2 or more tree species, whether they are conifers or not, with **big gaps**	> 40

4.3.2. Spatial arrangement of the samplers in the plot
Method to approach a statistically representative spatial distribution

The samplers should be spatially representative of the area of the whole (and not only the sub-plot) level II plot.

Neither a systematic nor a random approach can be considered as the only solution: both are valid. A systematic distribution is one that is ordered and regular (see below for an example). A random distribution is not the same as subjective: if a random design is chosen, it has to be random in a statistical sense, i.e. every part of the plot has an equal chance of being selected. However, it is necessary to approach the spatial distribution of the samplers in connection with the number of samplers to be used on a given study area.

The spatial representativity of throughfall deposition (and <u>not</u> concentration) has to be checked for each plot for a minimum of one year (depending on the period covered by rainfall) with a high number of samplers (e.g. 30-40). Distribution of samplers should avoid systematic errors, e.g. siting of samplers equidistant to the stems of neighbouring trees. On plots on which precipitation in the form of snow contributes to more than 20% of the annual throughfall, the spatial arrangement study should be done for both snow and rain, i.e. during the vegetation and winter periods. Snow type and quality is quite different during the winter and the frequency of the different snow types depends on latitude and longitude. Very few scientific studies on the variability of snow under the forest cover exist, which hints to this necessity of local studies.

Systematic or random distribution can be used, or even better a combination of both (Figure 4). A combination of systematic and random distributions has the big advantage of covering the whole plot used for deposition monitoring. Thus, the plot area is divided in quadrates of equal sizes (length to be adapted to the size of the study area). Within each quadrate, the sample points are chosen randomly on a grid. This couples the advantages of random and systematic sampling. Like the random sampling, it does not violate the assumption of independence between sampling units. At the same time, like the systematic sampling, it takes into account the spatial dependency of the data, enabling an even distribution of the collectors on the plot area (Ferretti and Mosello 2002). Further examples of studies are given in the reference list at the end of this document (see Annex 1).

If possible, repetition of the given design is recommended to allow statistical treatment.
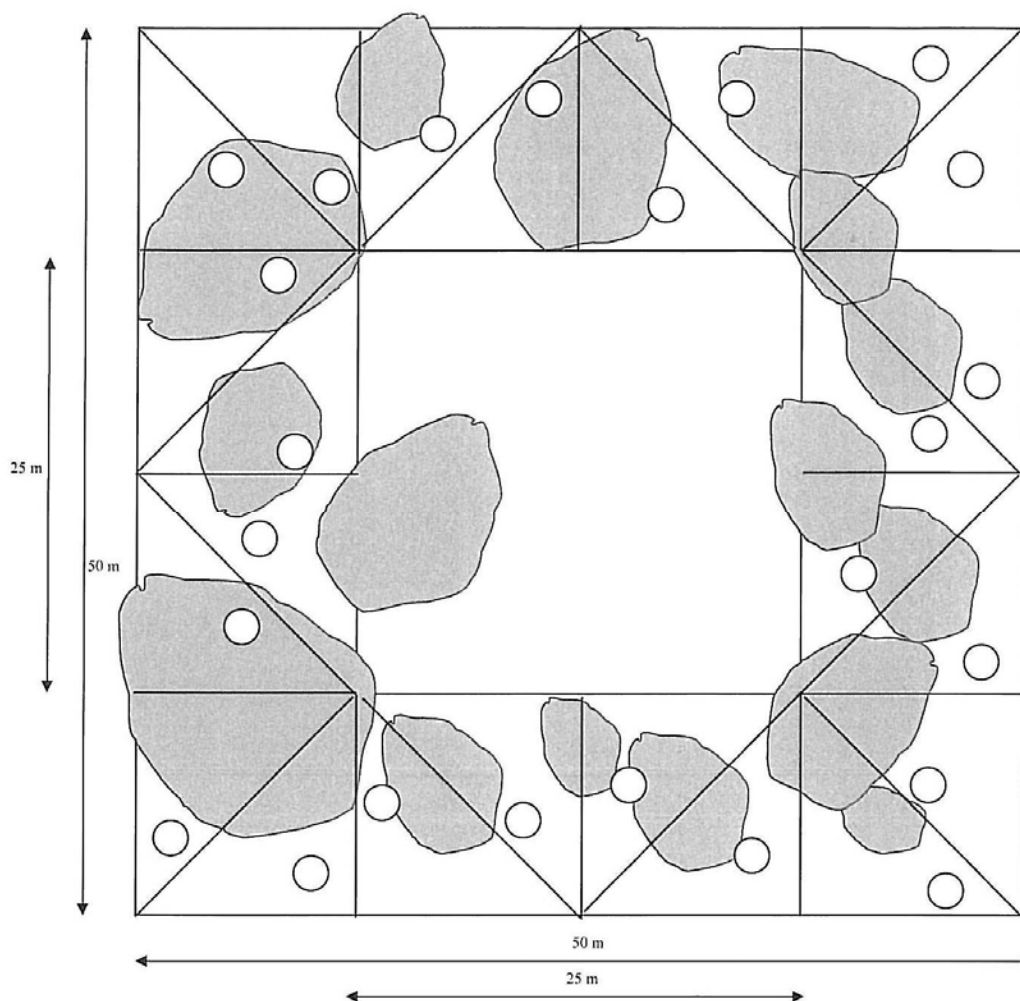
Figure 4: Combination of systematic and random sampling on the same plot or random selection of sites within previously selected equally-sized parts of the plots. Sampling is carried out in the buffer zone of the plot.

The decision on the number of sampling points necessary can also be made using principal component analysis (e.g. Houston et al. 2002) or by optimising the coefficient of variation (maximum 20%) and 90% confidence interval. This check can even be done after several years of monitoring, but it is essential to be able to define the error induced in the deposition estimates by the chosen field approach.

4.3.3. Throughfall samplers for precipitation other than snow

Comparability on both a national and an international scale is essential, allowing deposition data to be of multiple use. Throughfall samplers may be either funnels or gutters. It is preferable to use the same type of collector for throughfall and for open field sampling. Gutters integrate over a larger canopy gradient than funnels (*in* Thimonier 1998).

Among sampler characteristics that can affect sample volume and/or solute concentrations are the collecting area, the shape of the collector, the material of which it is made, the height of the orifice above ground level, and the height of the vertical side wall and the width of the rim.

Collecting area

For funnels, the collecting area shall be wide enough to collect sufficiently large samples for analysis of all ions/elements of interest. In most cases a diameter of between 16 and 25 cm is suitable (giving a surface area between 200 and 500 cm^2), similar to bulk precipitation samplers. In areas where the precipitation is generally low and sampling frequency is high, a larger funnel diameter is recommended. Collecting area will also affect the amount of dry deposition included in the sample: Starr et al. (2007) observed an increase in throughfall solute loads with decreased funnel size, which was interpreted as being due to increased efficiency in trapping dry deposition.

The true collecting area cannot be assumed to be identical to the theoretical value (e.g. as given by the manufacturer or assumed in the case of home-made samplers), but must be measured and documented. Because collectors may expand or shrink as a result of weather conditions, it is recommended to check the size of the collecting area at least once a year (Draaijers et al. (2001) recommend twice a year). To estimate the true collecting area, half of the rim area should be included, as droplets falling on the rim are assumed to splash into the container 50% of the time.

Rim

The rim must be of hard material to minimise changes in the collecting area. Both the shape and the width of the collector rim will influence the extent of aerodynamic blockage. Sharp rims induce more turbulence than flat rims, while thick rims lead to greater undercatch than thinner rims (Sevruk et al. 1994). A round rim probably induces less turbulence than a flat rim (Draaijers et al. 2001).

Shape of collectors

Throughfall collectors often have the same shape as collectors of bulk precipitation (Section 4.2.1). This has the advantage of achieving compliance of canopy interaction models. Collection vessels with sloping sides must be avoided in order to prevent any loss of precipitation due to splashing (see section 4.2.1), especially during precipitation events when rain droplets impact with high energy. The upper part of the sampler should be vertical and deep enough to avoid any ejection or loss by wind of the incoming precipitation. A vertical upper part to the funnel may result in significantly greater throughfall deposition loads, even though volumes are unaffected: this has been attributed to increased retention of dry deposition and litterfall (Starr et al. 2007).

In the case of gutters, several short gutters are preferable to one long gutter as wetting and evaporation losses are lower (*in* Thimonier 1998).

Material

For information about material, refer to Section 4.2.1.

Height above ground level

The throughfall collectors should be placed with the sampling area at a height of approximately 1 m above the ground level. It is important to avoid contamination by soil splash or blown soil. The sampling area must be horizontal; the collecting area will otherwise be reduced. Gutters, of course, must be placed at an angle to ensure good water flow and minimise evaporation; however, the effect this has on the collecting area has to be taken into account.

Sieves

For information about sieves, refer to Section 4.2.1.

Bird wires

For information about bird wires, refer to Section 4.2.1.

Storage containers and tubing
For information about storage containers and tubing, refer to Section 4.2.1.

4.3.4. Throughfall snow samplers

For snow sampling special collectors are recommended. In the EMEP manual (2001), it is advised to use an open polyethylene cylinder with a diameter of 20 cm. The height of the cylinder should be at least twice the diameter in order to prevent blow-out. The snow collector should be equipped with a tight-fitting polyethylene lid, which is put on when the collector is brought indoors for the sample to melt.

An alternative type of snow sampler consists of a disposable heavy-gauge plastic bag suspended from a hoop attached to a support. Bags may be easier to transport than solid containers, but special care has to be taken to avoid breakage. It is important that the plastic is thick in order to minimise the risk for this.

As is the case for throughfall in the form of rain, all materials used should not interact with the sample solution.

4.4. Techniques for stemflow monitoring

Stemflow measurements are considered mandatory in beech stands and optional in all other stands. Stemflow may however give important contributions for other deciduous stands and for young spruce stands. Where it is not clear whether stemflow should be measured or not, it is recommended to verify its importance to the total deposition at each plot for a period of at least one year. As for throughfall, stemflow measurements should be made in such a way that the results are representative for the plot area and should provide information on the coefficient of spatial variation by parameter. Thus, a sufficiently large number of samplers should be used and the samplers should be placed in such a way that the variation is properly covered.

4.4.1. Stemflow sampler design

Stemflow collectors, attached directly to the tree stems, may be either spirals or collars. The collector must be firmly attached to the bark to prevent stemflow from flowing behind it. However, it is important that the bark is not damaged as sap may then run out, contaminating the sample. The collectors should be placed at a height of between 0.5 and 1.5 m. The slope of the collecting surface should be more than 25° to prevent obstruction of the water flow (Draaijers et al. 2001). The width of the collecting surface is also important – if it is too wide, the risk of contamination by litter and throughfall is increased, while if the sampler leans towards the bark, the water may run over. It is important that the cross-sectional area (width x depth) is large enough to prevent water overflow even during heavy storms. The collector surface should be smooth and without obstructions in order to ensure rapid flow and limit losses due to evaporation. A filter should be used to minimise sample contamination by litter, dead insects etc. However, it is important that water is able to penetrate the filter effectively in order to prevent wetting loss. Loose filters are therefore recommended. Tubes from the stemflow collector to the storage container should allow water to flow rapidly in order to minimise wetting loss. There must not be dips in the tubes. Storage containers should be large enough to prevent overflow in cases of large precipitation amounts. It is also important that the containers are kept cool and dark to minimise microbiological or chemical changes in the sample. As is the case for throughfall, the material of which the collector and its containers, tubes, glue etc. is made should not interact with the sample solution. However, trees grow and there is diurnal

variation in the stem circumference, and these factors must be taken into consideration when choosing the material. Silicone has been recommended (ICP Integrated Monitoring 1998).

4.4.2. Spatial distribution of stemflow collectors

The spatial distribution of the stemflow collectors will rather be influenced by the presence of trees representative of the diameter class distribution of the species in the plot. Stemflow collectors shall be attached to trees growing on or adjacent to the plot. If the tree size is very different, stemflow shall be sampled on trees of different basal area or canopy size classes, proportionally to their frequency distribution. The stemflow collectors shall be placed around the stem of the trees between 0.5 and 1.5 meter above ground level. Sample containers should be kept cool and in the dark. As for throughfall sampling, care should be taken not to interfere with other monitoring activities on the plot and not to damage the trees.

4.4.3. Number of collectors for stemflow sampling

Variations in stemflow are larger than for throughfall, depending on the variation in tree species and tree size at the plot. To cover this variability, a minimum of 20 to 60 stemflow samplers would be necessary, but in many cases this is not feasible in practice. Therefore, given the fact that in most cases stemflow on beech represents "only" up to 15-30% of the total stand precipitation and even less for deposition of different ions, the compromise is to recommend 5 to 10 stemflow collectors. The recommended study can also identify whether stemflow measurements are important in the final sampling programme and if so, how many and which types of trees shall be sampled. It is also possible to connect a number of trees to one sampler. When tipping buckets are used to record water amounts, a greater number of trees can be included in the sample.

Guidelines for calculating quantities from stemflow volumes are given in Annex 2.

4.5. Recommendations for a harmonised sampler

Based on the above paragraphs, it is possible to make recommendations for a harmonised sampler for throughfall and bulk deposition. The sampling equipment should consist of a funnel and a receiving vessel. The material used for the collector should be high density polyethylene. The diameter of the collecting surface should be 16 cm, the sampling area horizontal and the upper part of the sampler vertical, following the design shown in Fig. 3. The surface of the collector must be smooth. The height of the sampling surface should be 1 m above ground level. An inert sieve with a mesh size of 1 mm should be placed loosely at the top of the neck of the sampler. A bird ring is recommended. Sample containers should be kept cool and in the dark, preferably in pitholes if this is possible.

4.6. Sampling frequency

Ideally, the sampling period should be short, in order to minimise artefacts due to evaporation or algal growth in the sample containers. The risk of data loss due to contamination should also be considered. It is worse to lose one of relatively few long-term samples than to lose one of many short-term samples. It is recommended to use weekly sampling. If it is not possible to analyse weekly samples, for example for financial reasons, pooling of weekly samples to collective samples representing periods of up to one month is recommended. If weekly sampling is not practical, sampling may be carried out monthly or a time interval of every two or three weeks, depending

mainly on climate, access to the plot and method used. The frequency of emptying the containers should be the same for all deposition measurements (throughfall, stemflow and wet/bulk deposition).

4.7. Sampling, sample handling and cleaning

General procedure
Sampling, sample handling and cleaning should be carried out in the same manner for bulk/wet deposition, throughfall and stemflow monitoring. During sampling all possible contamination of samples and equipment must be avoided. It is a general precaution never to touch the surface of the equipment that comes into direct contact with the sample solution. Disposable talc-free polyethylene gloves may be used as an additional precaution. All incidents, special procedures and observations during sampling and sample handling should be recorded in the forms that accompany the samples to the laboratory and, if in use, the sampling logbook.

Before sampling
A clean collection gauge is used to collect the sample solution. The equipment should be rinsed with deionised water before sampling. Alternative methods include placing a new strong polyethylene plastic bag in the sample container for each sampling period or to replace the entire collector.

Storage conditions during sampling
For information about storage conditions during sampling, refer to section 4.2.1.

Prevention of algal growth during sampling
Cool and dark storage will to a considerable extent prevent growth of algae and chemical reactions. In many cases and especially during the darker and colder season, keeping the bottle dark is sufficient. As an additional precaution during the sunny and warm season, a preservative can be added to the sample container before sampling. A variety of chemicals can be used for this purpose. The main criterion is to use an effective, non-volatile preservative, which does not interfere with the analysis of any ion of interest (this should be checked with the laboratory and its use validated first). If interferences cannot be avoided, it may be necessary to use two parallel samplers, one with preservative and one without. Persistent chemicals such as mercury should be avoided for environmental reasons. Any use of preservatives shall be recorded in the logbook.

To determine the potential nitrogen transformation, the following test can be made periodically. The standard sampler, unpreserved and kept dark, is run in parallel with two extra samplers located close to the standard sampler. One of the extra samplers is run with preservative, while the other is unpreserved and exposed to light. All samples are analysed for nitrogen compounds, nitrate, ammonium and organic nitrogen. The difference in nitrogen concentration will indicate the degree of nitrogen transformation.

Snow samples
A special problem with snow sampling is that a frozen cap of ice/rime/snow can form on top of the collector, and it is then difficult to accurately estimate how much of this cap should be included in the sample. One solution is to place a sheet of clean cardboard on top of the cap and then push sharply downwards. Thus, snow that should have fallen into the collector will be included in the sample.

Collecting the samples for analysis

After each sampling period, the volume of each individual throughfall and stemflow sample must be determined. If only an aliquot of the sample is sent to the laboratory, the volume of each sample must be determined in the field. If the whole sample is sent to the laboratory, the volume may be determined in the laboratory. If identifiable contamination has occurred so that it is necessary to discard a sample, the volume and reason for discarding should be recorded. The sample is decanted by means of a clean funnel into a clean measuring cylinder, taking great care to avoid spillage or contamination, or alternatively is determined gravimetrically. Each sample can then be analysed separately or be pooled together to separate collective samples (to reduce risk of contamination, each sample should be kept in two separate parts). A suitable aliquot of each sample, or of the collective sample, is transferred to a clean laboratory bottle. The funnel, measuring cylinder and laboratory bottle used should be made of chemically inert material. Polyethylene, tetrafluoroethylene or tetrafluoroethylene-fluorinated ethylpropylene polymer are recommended by EMEP (2001). Borosilicate glass may be used if properly cleaned, but some glass may contaminate the sample with alkali and alkali earth cations (EMEP 2001). Metals or materials with unknown chemical properties should be avoided. Precautions shall be taken to avoid contamination.

Extreme care should be taken if samples are collected during precipitation events, as there is then a higher likelihood for contamination of the sample during handling. If possible, sampling should be carried out during a pause in the event (WMO 2004).

If the sample in the throughfall sampler is frozen or in the form of snow, the collection gauge is removed, replaced with a new collector, and the frozen collector closed with a tight cover and taken indoors to melt the snow. Then the same procedure and the same precautions as mentioned above are applied.

Pooling of samples from the same sampling period

Pooling of samples can be carried out in either the field or the laboratory. If only part of the total sample is transported to the laboratory, this must be a representative part. All sub-samples (i.e. all samples from individual containers) must therefore be thoroughly mixed in the field before taking an aliquot. If complete sub-samples cannot be pooled (for example, due to too large sub-sample volumes), portions of the sub-samples may be pooled instead as long as these portions are mixed in proportion to their volumes. Bulk deposition and throughfall samples are weighted according to volume estimated using either a measuring cylinder or similar container, or from the weight. Stemflow samples may be weighted either by basal area or collected volume. If stemflow samples are pooled together, they can only be pooled for trees of the same species and of similar size and dominance. Throughfall and stemflow samples must be kept separate. All details of the pooling procedure shall be recorded in the logbook.

If samples are pooled to collective samples, sub-samples that are suspected of being contaminated (e.g. because of odour or colour in the field) must not be included in the collective samples but should be analysed separately. Only if chemical analysis shows no contamination to be present in these sub-samples should the data from them be included with the data from the other sub-samples.

In the case of missing sub-samples (for example, due to contamination of one of the samplers by bird droppings), a correction can be performed for both volume and concentration of the missing sub-sample, based on correlations derived from other sampling periods (Draaijers et al. 2001). However, this may not be necessary if a large number of collectors are used and only one sub-sample is missing, as the remaining sub-samples are then likely to provide a satisfactory estimate.

4.8. Quality assurance in the field

Before any choice of deposition field samplers and distribution over the plot, a detailed approach of spatial variability, optimal sampling of <u>all</u> types of precipitation and thus choice of sampling methods, representative for the plot, should be made, in using the below guidelines.

A national reference manual or standard operating procedures should be prepared, in which each step in the monitoring procedure is strictly defined and given to the personnel in connection with training in the field. Every step of the work, including special precautions needed to avoid contamination during sampling and cleaning procedures, should be well documented. A system of field blank samples and spiked samples should be employed at regular intervals in order to check the cleaning of samplers and possible sample contamination or degradation in the field and during transportation. This would be optimal, even though in practice it is very difficult to do it on a routine basis.

A plentiful supply of spare parts should be kept in store so that broken, stolen or vandalised parts of the sampling equipment can be rapidly (within one week) replaced.

Communication between the field personnel and central project manager should be regular. All the operations and specific incidents or observations at the plot should be noted in the sampling logbook. Regular visits should be made to the sampling plots and the sampling procedures checked by the project manager at least once a year.

One of the most important sources of error in deposition sampling is the procedure of snow sampling, leading to a systematic underestimation of precipitation. Unfortunately there are no specific hints to improve the sampling of snow: efforts should be made in this field.

4.9. Storage and transport

Transportation to the laboratory
Each consignment of samples should be accompanied by a field form that informs the lab about the type and origin of the samples (e.g. plot number, collector number, sample type (throughfall, stemflow), and sampling period), specific observations that may be relevant for performing the analyses, such as suspected contamination or alteration of sampling volume etc. The measured total volume of the samples should also be noted on these forms. In some countries the total sample is transported to the laboratory in order to maintain accuracy. The volume is therefore noted on the analytical record.

The samples should be transported in special insulated boxes in order to protect the samples from light and heat and to avoid breakage of the sample containers. The use of freezer packs ("blue ice") and of a maximum/minimum thermometer in the boxes, to permit stricter control of possible degradation, is recommended.

Storage of samples prior to pre-treatment
The samples shall be kept in a cool (0-4°C) and dark store prior to pre-treatment, as this will slow most chemical and biological sample degradation. The storage period should be kept as short as possible. This is especially important for parameters known to change upon storage, such as organic carbon.

Pooling of samples from subsequent sampling periods
Weekly samples can be analysed as they are or, in order to save money, mixed to samples representing longer time periods (e.g. two weeks to one month) before analysis. If samples are mixed, they must be mixed in proportion to their volumes. However, special care must be taken in the mixing procedure. Every additional step in the sample preparation involves additional risks of contamination and errors.

5. Analysis

The volume of work necessary in order to reach an acceptable level of analytical quality according to ISO and EN norms is quite important, especially during the first 1-3 years. The volume of work depends especially on the current quality level of each laboratory. The chapters below try to guide as well as possible the ICP Forests laboratories in their work in concentrating on the most essential information taken from a variety of ISO and EN/CEN guidelines.

In a period in which the general demand for higher quality assurance is growing, it is of high importance that within the deposition expert panel the participating laboratories maintain a definable and acceptable level. This level should allow the production of data on a European level with known analytical errors and ranges, as this will also be the case for field methods. Thus the data can be transmitted to any user with error ranges allowing a more optimal use for all types of calculations on European level.

5.1. Reception at the laboratory, initial checks and temporary storage

Upon reception of the samples at the laboratory, the delivery should be checked immediately, and discrepancies noted, for the following:

- the accompanying forms are included in the delivery
- the number of sample bottles corresponds to that stated on the accompanying forms
- the bottles are properly closed and no leakage has occurred
- damage to the box or bottles
- presence of visible contamination
- initial pH and conductivity check for indications of contamination
- registration in the laboratory sample book

The samples (wet-only and bulk deposition, throughfall or stemflow) should be stored (protected from light at max. $+4^{o}C$) in such a manner that there will be no changes in the chemical parameters to be determined before the samples are analysed (any changes in concentration should be smaller than the precision of the analyses). If sub-samples are taken for pH and conductivity measurements prior to pre-treatment, then these sub-samples should be stored in the same way.

The samples should be pre-treated and analysed as soon as possible.

5.2. Pre-treatment of the samples

A separate sub-sample should be taken, prior to filtration, for the determination of pH and conductivity (as stated in ISO 10523 and ISO 7888). However, this is done only if the volume of the sample is sufficient for the other chemical analyses. This sub-sample should not be used for any of the other analyses.

The sample should be filtered through a 0.45 µm membrane filter in order to remove any solid material and to stabilise the sample for the subsequent analyses. Filtration considerable decreases the possibility of microbial-induced changes (e.g. nitrogen transformations) in the samples as it removes all micro-organisms (except viruses). Filter paper should not be used owing to possible contamination by NH_4 and carbon.

The samples should be divided into sub-samples for the individual analyses of the different analytes. The sub-samples to be used for the determination of metals by e.g. AAS or ICP techniques should be acidified by the addition of a suitable aliquot of reagent-grade nitric acid. One of the purposes of acid addition is to prevent the metals to be analysed from being adsorbed on the surface of the plastic bottles.

The analyses should be performed as soon as possible. The maximum storage times for sub-samples for the individual analyses should be determined by the individual laboratories. The sub-samples should not be frozen, where there is evidence in the literature to show that this has an effect on the samples and analysis results.

The use of preservatives in the laboratory (chloroform, formaldehyde, mercury compounds, iodine etc.) is not recommended owing to occupational health hazards, the danger of damaging laboratory equipment (e.g. ion chromatograph columns), and possible interference in certain analyses.

5.3. *Chemical determinations and analytical methods*

The parameters to be determined on the samples are listed in Table 2 according to whether their determination is mandatory or optional. Mandatory parameters are those that are considered essential for the activities of the ICP Forests Deposition Monitoring Programme, and should therefore be determined on a regular basis in all European countries. Optional parameters are those that are determined in order to meet regional or national requirements. In practice, most countries will have to determine both mandatory and optional parameters because all the cations and anions that are present in significant amounts in the samples are required for data validation purposes, e.g. for calculating ion balances.

Participating countries and laboratories are free in their selection of analytical methods as long as the analytical work is performed in accordance with the guidelines. Standardised analytical methods and procedure should be used, preferably ISO or CEN methods and/or those applied in the EMEP and ICP/Integrated Monitoring programmes. Methods suitable for the analysis of bulk precipitation, throughfall, stemflow and fog are given in Table 3: detailed descriptions are given in Annex 3. Methods that are **not** recommended, since they tend to give poor results in laboratory inter-comparisons, are given at the end of Annex 3. The list of ISO and CEN methods is given in Annex 4. The lists of possible methods are not complete, and only include the most frequently used methods. The tables also give some information about any additional pre-treatment necessary for specific analytical methods. More details can be found in the ISO and CEN standards and in the EMEP manual.

Table 2: Mandatory and optional parameters to be analysed in bulk deposition, throughfall, stemflow and fog samples. DOC = dissolved organic carbon, and N_{total} = total nitrogen.

Sample type	Mandatory	Optional	Comments
Bulk deposition, throughfall, stemflow	Amount of precipitation		This variable is essential for the determination of fluxes. It must be measured as accurately as possible.
	pH and conductivity at 25°C		
	Na, K, Mg, Ca, NH_4	Al, Mn, Fe, and other heavy metals, e.g. Cu, Zn, Hg, Pb, Cd, Co, Mo, Ni	
	Cl, NO_3 SO_4	P_{total}, PO_4^{3-}	Phosphate indicates contamination due to bird droppings. However P_{total} is a more stable parameter to measure for this purpose.
	Total alkalinity		Mandatory for individual samples if pH > 5
	DOC, N_{total} (N_{total} is not mandatory for bulk deposition, but is highly recommended)	S_{total}, HCO_3, N_{org}, C_{total}	HCO_3 can either be obtained by calculation (from pH, total alkalinity, temperature and ionic strength) or by direct measurement
Fog, frozen fog (rime)		PH, conductivity	
		Na, K, Mg, Ca, NH_4	
		Cl, NO_3, SO_4, P_{total}	
		Alkalinity	
		Al, Mn, Fe, and other heavy metals, e.g. Cu, Zn, Hg, Pb, Cd, Co, Mo, Ni	

Table 3: Analytical procedures recommended for the analysis of bulk precipitation, throughfall, stemflow and fog samples. For further details, see Annex 3.

Parameter	Method/Instrument	Additional pre-treatment required	Comments
PH	• Potentiometry		Determined in the laboratory. Two-point calibration must be used.
Conductivity	• Conductimetry at 25°C		Conductivity measurements made in the field can help to give a rough estimate of the quality of the sample and to reject contaminated samples.
Total alkalinity	• Titrimetric determination (Gran, two end-point, titration to pH 4.5 with correction for extra acid)		Mandatory for all samples with pH > 5. One end-point titration without correction should **not** be used

Sulphate	• Ion chromatography (IC) • Spectrophotometry, e. g. the Thorin method or Methyl-thymol-blue method (CFA) • Potentiometric determination • ICP/OES (S_{total} for bulk deposition)		IC is the recommended method. The use of ICP for stemflow and throughfall samples requires correction for organic S at high DOC concentrations. Spectrophotometric methods should not be used for coloured samples without correction.
Nitrate	• Ion chromatography (IC) • Spectrophotometry, e.g. azo dye after reduction to nitrite (CFA)		IC is the recommended method.
Chloride	• Ion chromatography (IC) • Potentiometric detection (CFA, FIA) • Spectrophotometry, e.g. Hg-thiocyanate method (CFA)		IC is the recommended method.
Total phosphorus (P_{total})	• Spectrophotometry, molybdenum blue method • ICP/OES		Ion chromatography is not recommended due to the high limit of quantification. Spectrophotometry: P_{total} is determined as PO_4 after digestion with strong oxidising agents.
Ammonium	• Spectrophotometry e. g. indophenol method (CFA) or ammonia diffusion cell method (FIA) • Ion chromatography (IC)		IC : high Na concentrations may interfere with the analysis; the limit of quantification is also often too high FIA : filtration and dialysis of the samples is necessary: however, automated FIA systems include this.
Na, K, Mg, Ca	• AAS Flame • AES Flame (only for Na and K) • ICP/OES • Ion chromatography (IC)		Note! Differing results are possible depending on the methods used: IC determines ions, AAS and ICP total elements
Al and heavy metals (e.g. Co, Cr, Cu, Cd, Pb, Ni, Zn) (not Hg)	• AAS Graphite furnace • ICP/MS • ICP/OES • ICP/OES with ultrasonic nebulizer	The samples are preserved with nitric acid. Pre-concentration of samples may be necessary	Instruments with low quantification limits are necessary due to the low concentrations, Control of blanks and avoidance of contamination is important.
Hg	• Cold vapour fluorescence • Cold vapour AAS	The sample collectors have to be pre-acidified	

Total nitrogen (N_{total})	• Elementary analysis • Spectrophotometry after oxidation to nitrate using persulphate in borate buffer solution or UV-digestion • total N analyser with chemiluminescence detection		
Organic nitrogen	• N_{total} analysis, and nitrate and ammonium analysis		Organic N = N_{total} – (NO_3-N + NH_4-N + NO_2-N (if present))
Dissolved org. carbon (DOC)	• Infrared spectroscopy after oxidation to CO_2 • Flame ionisation after reduction to CH_4 • UV absorbance (254 nm)	Use glass fibre membrane filters (not cellulose acetate/nitrate)	UV absorbance is not the optimal method and should only be used by laboratories without TOC analyser

5.4. Quality assurance programme in the laboratory

Quality Assurance and Quality Control (QA/QC) are national issues. The National Focal Centre (NFC) is responsible for adequate QA/QC programs and for the final quality of the results. Each national institute should draw up a quality assurance programme for the measurements to be carried out. One important step in the programme is to document all the actions, including deviations and other observations, during sampling, sample handling and analysis (see ISO 9000). The laboratory (or laboratories) in each country should use well-defined and documented procedures for sample handling and analytical methods in accordance with national or European standards for good laboratory practices. The NFC is responsible for the full comparability of data produced in the country and for their full comparability with those produced in the other countries participating in the programme. Laboratories certified in their own country and working according to their own national standards, which are very often relatively close to or even direct translations of the ISO standards, can use their own standards. It is recommended that all samples (or at least the same parameter on all samples) are analysed at the same laboratory in each country. This laboratory should preferably be accredited and working in accordance with EN ISO/IEC 17025:2000. Although laboratories use different equipment and methods, their proper use and application should lead to correct and comparable results. To achieve comparability of results within and between laboratories, it is essential to link the individual measurement results to a common, stable reference or measurement standard. The results can be compared through their relationship to the reference standard. This strategy of linking results to a reference is termed "traceability".

Regular inter-comparisons between the organisations responsible for sampler collection in the individual countries are necessary in order to determine whether there are significant differences in collection efficiency and sampling procedure. Inter-laboratory exercises and technical meetings for the discussion of the results are essential for improving the analytical competence. Laboratory inter-comparisons are necessary tools for studying discrepancies in the analytical procedure. All the countries should regularly take part in laboratory and field inter-comparisons.

Guidelines for QA/QC procedures in the laboratory are given in the Sub-manual on laboratory QA/QC (http://www.icp-forests.org/DocsQualLab/QualCheckMay2008.pdf), and a list of relevant ISO and CEN methods is given in Annex 4. Documentary proof of the QA/QC adopted in each laboratory should be submitted, together with the annual results, to the European-level data centre.

6. Data handling and reports

Simple guidelines for calculations are given in Annex 2. All concentrations means should be volume weighed. To calculate the deposition at the site, the precipitation amount obtained by the sampling collector is to be used. It is recommended to compare with the results from the meteorological standard gauge. If the difference is significant, the selection of sampler must be reconsidered. Guidelines for interpretation of throughfall data are given in Annex 5.

It is recommended that all countries carry out canopy budget modelling (see Annex 6) and other methods of deposition estimates and report via submitted reports on national data evaluation. In this way, countries are responsible for delivering atmospheric deposition estimates and not only throughfall, stemflow and precipitation fluxes, which can be regarded as input data to the deposition estimate. Moreover, canopy budgets will give insight in the quality of results. Only high-quality measurements give reliable estimates.

6.1. Forms for data submission

Forms for data submission and explanatory items are found on the ICP Forests web page, at http://www.icp-forests.org/Manual.htm. The quality information from the labs has to be sent together with the PLD, DEM and, in the case of optional data, DEO forms to the data centre using the submission form "XX2008DP.LQA". The form and related explanatory items are available at the ICP Forests webpage.

6.1.1 Submission of data from pooled sampling periods and periods without any sample quantity

For data submission of pooled sampling periods the quantity of each single period must be submitted. The ion concentrations have to be submitted for all periods of the pooled analysed sample with the same concentrations. Only if a parameter was not analysed a blank space has to be used for submission of its concentration.

A "0" (zero) has to be submitted only for sample quantity, if no sample could be taken due to no precipitation in the sampling period.

Example for mandatory deposition data submission with DEM (samples from 060109 to 020209 were pooled, no precipitation in period# 1 and 4; Potassium (K) was below quantification limit in period 6):

Seq.	Plot	Start date	End date	period#	sampler	quantity	pH	cond.	K
….									
31	21	301208	050109	1	2	0			
32	21	060109	120109	2	2	10	4.7	148	2.1
33	21	130109	190109	3	2	34	4.7	148	2.1
34	21	200109	260109	4	2	0			
35	21	270109	020209	5	2	27	4.7	148	2.1
36	21	030209	090209	6	2	53	5.1	110	-1
….									

6.2. Data validation

Data checks should be done as soon as results from the analyses are available. Data validation and quality assurance should be applied in accordance with the guidelines for QA/QC procedures in the laboratory that are given in the Sub-manual on laboratory QA/QC (http://www.icp-forests.org/DocsQualLab/QualCheckMay2008.pdf). The countries should use these methods to check data before submitting it. For the validation, data should be scrutinised with regard to ion balances, conductivity, presence of extreme values, and any discrepancies in the covariation between parameters and between stations. All discrepancies noted and corrected must be documented and must accompany the results to the data storage. Excel files for analytical data validation, definition of a laboratory's methods including QA/QC procedures, and a control chart can be downloaded from the ICP Forests web page (http://www.icp-forests.org/WGqual_lab.htm).

6.3. Transmission to co-ordinating centres

All validated data should be sent yearly to each national focal centre and to the European central data storage.

6.4. Guidelines for the treatment of missing values

In the validated data set, gaps due to missing values have to be filled in order to estimate the yearly mean concentration and yearly deposition. To calculate a sufficiently reliable yearly mean <u>concentration</u>, not more than 4 weekly or one monthly value per year should be missing.

If data are missing ($\leq$ 4 weekly values and one monthly value), calculate the yearly mean concentration in the sample solution based on the available data. The yearly deposition is estimated by multiplying the yearly mean concentration with the annual sample volume. A separate measurement of precipitation amount is valuable when wet deposition, throughfall or stemflow samples are missing. Some conclusions may be drawn as regards the missing volume for one period in relation to the total annual volume. If there are large seasonal variations in pollution concentrations, a more "true" annual mean may be obtained if the weekly or monthly value missing is extrapolated with consideration to season. In this extrapolation, the seasonal variation of results from a near-by plot and its normal covariation with the plot of interest is used. In case that gaps are filled by extrapolating or interpolating data, this information needs to be provided in the Laboratory QA data submission form.

6.5. Data reporting

Data should be accompanied by a "Data accompanying report – questionnaire" (DAR-Q) and any other information requested by the European central data storage facility. The DAR-Q should include all details on sampling and analytical procedures. In addition, irregularities in sampling and analytical procedure, missing data, estimated yearly deposition and encountered errors in the validation, should be documented. The preparation of a national annual report on data during the year is recommended. A comparison with other national results as regards deposition to forests is recommended as a further step in the validation of the results. The document shall contain the results obtained and the interpretation of results.

All details on how data are treated and how the calculations are made shall be documented and shall accompagny the result to the data storage. If values are below the *quantification* limit (not the detection limit), a value of -1 should be reported. Definitions of the quantification and detection limits can be found in Section 2.3 of the manual on laboratory QA/QC.

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8 Annexes

Annex 1.   Publications linked to sampler design, sampling design and number of samplers for bulk, wet-only, throughfall and stemflow measurements

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Annex 2. Simple guidelines for calculations

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

Where:

$$factor = \frac{atomic\ weight\ of\ element}{formula\ weight\ of\ ion}$$

e.g.

conc SO_2S	=	0.5005 (conc SO_2)
conc SO_4S	=	0.3338 (conc SO_4)
conc NO_2N	=	0.3045 (conc NO_2)
conc NO_3N	=	0.2259 (conc NO_3)
conc NH_4N	=	0.7765 (conc NH_4)
conc PO_4P	=	0.3261 (conc PO_4)

Calculation of mean pH

The original pH values must be converted to conc H^+
before calculation - the mean conc H^+ is then
reconverted to a pH-value:

$$\overline{H}^+ = 1 / n \sum_{i=1}^{n} 10^{-pH_i}$$

where:

$\overline{H}^+$ = mean proton activity

pH_i = pH-values of samples

n = number of samples

$$\overline{pH} = \log_{10}(\overline{H}^+)$$

Calculation of volume weighted means

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

Guidelines to calculate quantities in mm from stemflow volumes

The volumes of the stemflow are measured in litres per tree per period. In order to calculate the
total deposition per hectare it is necessary to recalculate these volumes into volumes per period.
The volumes are to be reported in mm per period.

As only a limited number of trees (e.g. 5) are measured for stemflow, an estimate has to be calcu-
lated for the total stemflow for all trees in the plot.
It is recommended to use the following method to calculate the total stemflow per hectare per year.
It is based on the total basal area of the trees used for the stemflow measurements and the total
basal area of all the trees in the plot (of 0.25 ha). Guidelines for calculating the basal area are given
in the sub-manual on growth (www.icp-forests.org/manual).

The formula used is:

$$\text{Total volume in the plot}_n = (\text{Total stemflow of n trees}) * \frac{\text{Total basal area of all trees in the plot}}{\text{Total basal area of the n trees}}$$

where:

- *n* is the number of trees used for the stemflow measurements (e.g. 5)
- the *Total stemflow of n trees* is stated in litres
- the *Total basal area of all trees in the plot* is stated in m^2
- the *Total basal area of the n trees* is stated in m^2

The result (in litres) is then divided by the plot area (in hectares) to calculate the total volume per hectare. Division with 10 000 results in the quantity in mm.
This should be reported per measuring period.

Annex 3. Procedures for ensuring high quality analytical results

The following suggestions and recommendations concerning measurements and analytical methods are based on the results and workshops of the first and second Working Ring Tests on Atmospheric Deposition and Soil Solution carried out in 2002 and 2005 within the framework of the ICP Forests Expert Panel on Deposition (Mosello et al. 2002, Marchetto et al. 2006). They do not necessarily refer directly to the analytical methods or procedures actually used in each laboratory, but are intended as suggestions and general guidelines for the correct application of the methods.

A3.1. pH

Calibration:
- This must be carried out with two buffer solutions, the pH values of which cover the range of pH values expected in the samples.
- The temperature and stirring (or not stirring) conditions must be the same for the buffer solutions and for the samples.
- Calibration can be done at weekly intervals if the pH meter is not turned off after each batch of measurements, and if other conditions (e.g. temperature, voltage) are kept constant. However the accuracy of this must be checked and validated by the laboratory.
- Read and follow carefully the instructions given for calibration in the pH meter manual.

Measurement:
- Measurement is performed on <u>unfiltered</u> samples (as stated in ISO 10523).
- The electrodes must be rinsed with pure water and then with the next sample to be measured in order to prevent contamination from the previous sample.
- Initial agitation of the sample for at least one minute is recommended; the measurement may be made on the stirred or quiescent sample as described in point 7.3.1. of ISO 10523).
- Stabilisation of the reading should be achieved within 5-10 minutes. A longer stabilisation time indicates either problems with the electrode, or that the sample or standard has not become stabilised with the laboratory atmosphere.
- The use of either low flow (GLF) or high flow (GHF) glass electrodes seems, in most cases, to be unimportant. Good quality and maintenance of the pH electrode are more relevant.
- Separate equipment (electrodes) must be used for "clean" and "dirty" samples. Avoid the use of pH electrodes designed for meat or cheese.

Maintenance:
- The electrode must be stored as indicated by the manufacturer, normally in 3M KCl. Do not use de-ionised water or buffer solutions.
- Follow carefully the instructions for the maintenance of the solution inside the electrode.

General:
- Do not measure conductivity or carry out chemical analyses on the same solution on which pH has been measured. The same sample can be used provided that conductivity is measured first.
- Several textbooks and papers are available on pH measurement, and guidelines for correct measurement are given in most analysis handbooks (e.g. A.P.H.A., A.W.W.A., W.E.F., (1998); Westcott, (1978).

A3.2. Total alkalinity

A3.2.1. Definition of total alkalinity

The alkalinity of a solution is its capacity to neutralise acids, defined as the amount of acid needed to neutralise the bases present in the solution itself. Alkalinity is then the sum of all the bases in the sample, and is determined by means of an acidimetric titration. In freshwater or precipitation, these bases are primarily bicarbonate, as well as hydroxyl ions at pH values above 8.0, sulphide and non-ionic compounds such as calcite or certain organic compounds.

Figure 5 shows the evolution of pH, its first derivative and the concentration of hydrogen ions during an acidimetric titration. The critical point in the titration is the determination of the equivalent point, where it can be assumed that all the bases have been neutralised. If we assume that the main base in solution is bicarbonate, then the equivalent point is the inflection point of the titration curve between bicarbonate and carbonic acid + carbon dioxide (Stumm & Morgan 1981). This value depends on the CO_2 concentration in solution at this point, which is a function of the total concentration of the carbonate system. Consequently, the equivalence point of the alkalinity titration depends on the alkalinity to be determined (Kramer et al. 1986), and it ranges between pH 5.0 and 5.6.

To detect the inflection point, it is possible to monitor the pH and to plot the titration curve and its first derivative during the titration. This technique is difficult and often not precise at very low alkalinity for the difficulties related to the choice of suitable added volumes and for the slow response of pH electrodes.

For this reason some techniques were developed to estimate the equivalence point indirectly. The most used are the Gran method (Gran 1952) and the titration with two fixed end-points, spaced 0.3 pH units, which are described in this chapter.
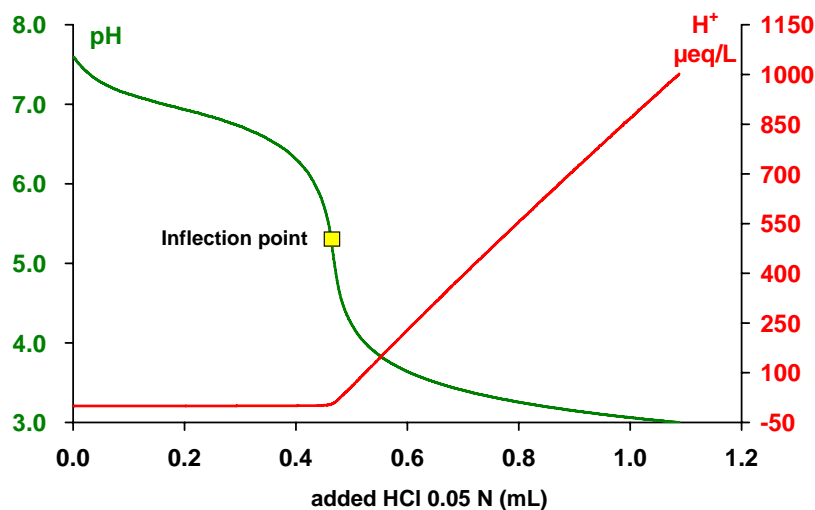
**Figure A3.1:** Plot of pH and hydrogen ion concentration during an acidimetric titration.

A3.2.2. Two end points titration

This technique requires the continuous reading of pH during titration. Acid (with normality N_{Ac}) is added after the equivalence point, leading the pH of the solution to decrease down to 4.5 (or less), where the titration is stopped (first end point) and the first volume (V_1, in mL) noted (Figure 6). Then acid is added again until the pH decreases of exactly 0.3 units. This is the second end point, and the total volume added (V_2, in mL) is noted again.

A decrease in pH of 0.3 units means a doubling of the hydrogen ion concentration, and simplifies the calculation of alkalinity at the equivalence point, which simply results

$$\text{Total alkalinity (meq L}^{-1}) = \frac{(2V_1 - V_2) \times N_{Ac} \times 1000}{\text{Sample volume (ml)}}$$
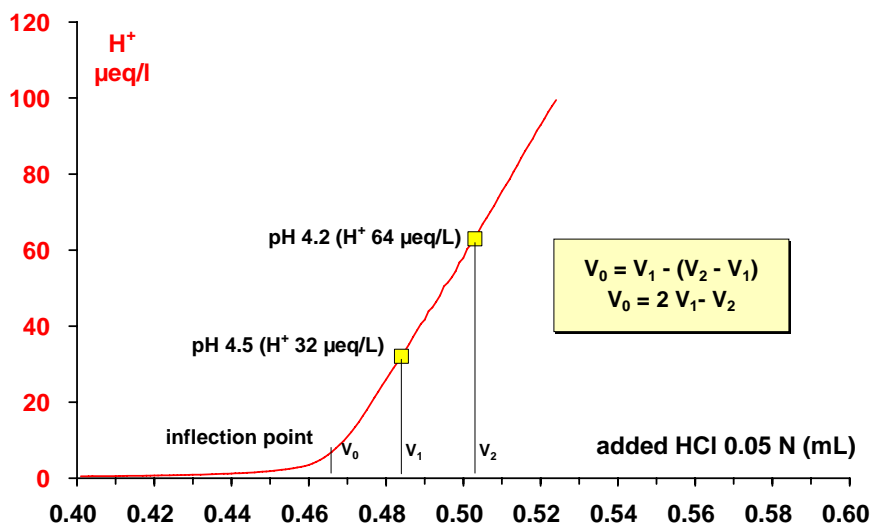
Figure A3.2: Plot of the concentration of hydrogen ions during the final part of an acidimetric titration, showing the extrapolation to the equivalence point, i.e. the intercept on the x-axis of the line straight line passing through the two end points.

A.3.2.3. The Gran method

This is the most precise technique to measure alkalinity and is very much recommended for low values (Gran 1952).

After adding enough acid to drive the pH down to 4 units or less, a number of acid additions (10-30 µL) are performed and pH is measured. At each point, the following function is calculated:

$$\text{Gran's } F_1 = (\text{sample volume} + \text{added volume}) \bullet 10^{-pH}$$

A regression line between Gran F_1 and added volume is then calculated, with an intercept point to the x-axis at the equivalence point V_0 (Figure 7).

Total alkalinity is then calculated as follows:

$$\text{Total alkalinity (meq L}^{-1}) = \frac{V_0 \times N_{Ac} \times 1000}{\text{sample volume (ml)}}$$
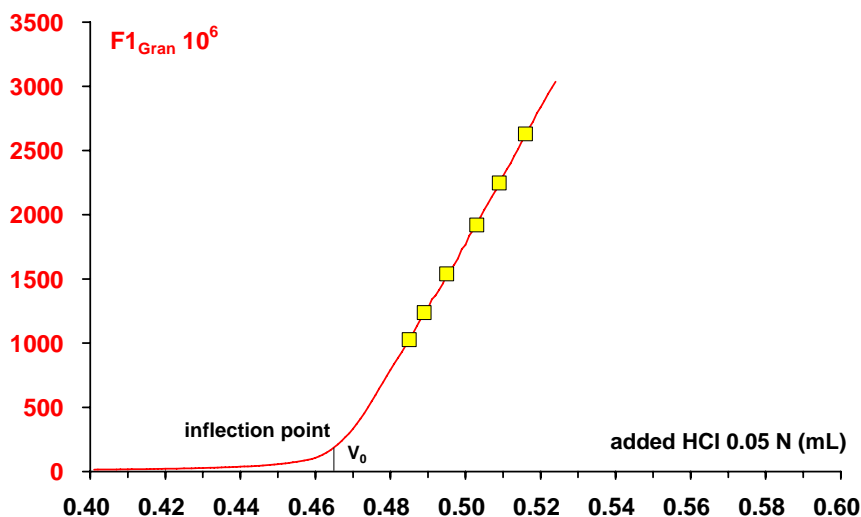
Figure A3.3: Plot of Gran titration.

A3.2.4. Suggestions for a correct titration

- Within the alkalinity range 0-5 meq L^{-1}, if the sample volume is around 30-75 ml it is possible to use an acid solution 0.05 N.
- Refrigerated samples, and calibration buffers, should be let to warm to 18-24°C before titration. The pH meter has to be calibrated before titration, at least weekly.
- It is important to take care of electrode rinsing, both with de-ionized water and with the sample or the calibration buffer, before starting reading.
- Any air bubble in the acid should be eliminated by adequate purging.
- The concentration of the acid should be verified before the first titration, and then at least every six months, measuring samples with known alkalinity.

A3.3. Conductivity

- Conductivity is a master variable for the quality control of chemical analyses (see Chapter 7.3). It is a rapid measurement that gives valuable information on the nature of the water sample, primarily the concentration of solutes.
- The type of errors made in the measurement of conductivity are typically systematic, due to poor calibration of the equipment; random errors may be due to a lack of care in rinsing the electrodes.
- Conductivity is strongly dependent on the temperature of the sample. The reference temperature is +25°C. Many instruments are equipped with temperature compensation. Such instruments should be calibrated strictly in accordance with the manufacturer's instructions. If the instrument does not have automatic compensation for temperature, correction factors must be used. Correction tables are available in most water analysis standards and manuals (see below).
- A small systematic error is introduced when either automatic or manual corrections are used, as the correction factors apply to water samples with the chemical characteristics of surface water, where the ranking of concentrations of individual cations and anions is usually $Ca > Mg > Na > K$, and $HCO_3 > SO_4 > Cl > NO_3$. The chemical characteristics of bulk deposition, throughfall and stemflow are usually different.
- The calibration of the equipment should be regularly checked every six months using KCl solutions, as indicated in the main water analysis references (e.g. ISO 7888-1985; A.P.H.A,

A.W.W.A. & W.E.F. 1998). Of course a higher calibration frequency is needed if the same instrument measures very polluted samples (e.g. sewage), but this should be avoided, as far as possible.

A3.4. ICP and AAS-flame determinations

A3.4.1. ICP/OES

Calibration/blank:
- Generally the calibration curve is linear over 5-6 decades. It is usually sufficient to carry out a 2-point calibration if the linearity has been checked. The calibration must be verified with an independent control sample.
- It is important to check the purity of the blank (Note! The use of glassware may release sodium).
- Depending on the measuring time, a control sample should be measured every 10 to 20 samples in order to maintain drift and carry-over control.

Automatic sampler/carry-over:
- The use of automatic samplers can cause contamination of samples and standards because the containers in the sampler are open for a considerable period of time. Carry-over from preceding samples into blanks may also occur. These problems can be minimized by covering the sampler, and by frequent replacement of the blank solution.
- The rinse time (with rinsing solution) has to be sufficient to avoid carry-over between samples. The aspiration time of the sample has to be sufficiently long to reach equilibrium in the mixing chamber and in the plasma.

Matrix/addition of acid:
- The standards should be adjusted to correspond to the matrix of the samples. This is especially important for standards containing only one element in trace amounts.
- All samples and standards have to be acidified in a consistent manner (0.5 - 3 ml of conc. HNO_3/100 ml sample).

Background correction:
- Background correction is normally necessary. To set the points for the background correction, all possible interfering elements have to be taken into account and tested.

Inter-element correction (IEC):
- Inter element-correction interferences, caused by line overlay, can be minimised by numerical methods. Exact determination of the correction factors for the type of line overlay is necessary.

Internal standard:
- The use of internal standards is normally helpful. Problems caused by oscillations of the plasma and the physical influence of the sample matrix can be compensated to a large extent. The different behaviour of atom lines and ion lines has to be taken into account.
- The sample may not contain the element used for the internal standard. The same amount of internal standard solution has to be added to all the samples and standard solutions. This can normally be automated.

Radial or axial plasma:
- The sensitivity can be increased ten times by using axial plasma.
- Because of ionisation effects, the measurement of alkaline elements is very problematic. These interferences can be reduced by adding an ionisation buffer.

Ultrasonic nebulizer (USN):
- The use of an USN can increase the sensitivity 2-5 times.
- The USN is highly sensitive to matrix influences. Matrix homogenisation by the addition of e.g. CsCl gives clearly better results.

Table A3.1: Selection of wavelength in ICP/OES determinations.

Element	Wavelength proposed by DIN EN ISO11885	Remarks
Ca	317.933 315.887 393.366	Sensitive, ionisation buffer important with axial plasma (Fe interference at 317.933)
Mg	285.213 279.079 279.553	Interference only with a high matrix concentration
Na	589.592 588.995 330,237	Not very sensitive and very difficult to analyse by axial plasma; ionisation buffer important
K	766.490 769,900	Not very sensitive and very difficult to analyse by axial plasma; ionisation buffer important
Al	396.152 167.08 308.215	Contamination problems at low concentrations (OH interference at 308.215)
Mn	257.610 293,306	Acid addition important at low concentrations in order to minimise memory effects
Fe	259.940 238.20	Acid addition important at low concentrations in order to minimise memory effects
Cu	327.396 324.754	Problems with USN; matrix and acid concentration have an effect; important to add an alkali or earth alkali element (e.g. Cs or Ca) (Fe interference at 324.754) (OH interference at 324.754; can be minimised by using USN)
Zn	206.191 213.856	Contamination problems (Fe interference at 213.856)
P	178.287 213.618 214,914	Not very sensitive
S	182.036 180.669	Problems with USN; influence of matrix (Ca interference at 180.669)

A3.4.2. AAS

Calibration/blank:
- Normally the calibration curve is linear over 2-3 decades. Calibration has to be verified using an independent control sample.
- It is important to check the purity of the blank (Note! The use of glassware may release sodium).
- In order to control the drift of the measurement a control sample should be measured every 15-30 samples (depending on the element and burner type).

Automatic sampler/carry over:
- The use of an automatic sampler can cause carry over from samples into the blank solutions. This problem can be minimised by frequent replacement of the blank solution.

Matrix/additives:
- The standards should be adjusted to correspond to the matrix of the samples.
- Additives are necessary for the determination of some elements in order to avoid ionisation interference and oxide formation. A mixture of La and Cs can be used to remove all interferences for Na, K, Ca and Mg (0.2 % La and 0.02 % CsCl).

Background correction:
- Measuring the background is not normally necessary for water samples.

Burner/gas:
- An air/acetylene flame or a N_2O/acetylene flame and a corresponding burner are used for a number of elements (see Table 7).

Table A3.2: Selection of wavelength in AAS determinations.

Element	Wavelength	Remarks
Ca	422.7	Small slit (interference NO); Flame: N_2O/acetylene, Cs additive important (if using a reducing air/acetylene flame, then La addition is needed)
Mg	285.2 (202.5)	Very sensitive at 285.2; crosswise burner possible at 285.2; Flame: air/acetylene; La additive is needed (if using a N_2O/acetylene flame, then Cs addition is needed)
Na	589.0 (589.6)	Contamination problems; Cs addition important (can also be measured by AES-Flame)
K	766.4 (769.9)	No problems; Cs addition important (can also be measured by AES-Flame)
Al	309.3	Not very sensitive; Flame: N_2O/acetylene (the correct stoichiometry of the flame is important); Adjustment of the burner important; Cs addition important
Mn	279.5	No problems
Fe	248.3	No problems with water samples; Small slit needed (many interferences)
Cu	324.7	No problems
Zn	213.8	No problems
P	---	No direct method available
S	---	No direct method available

## A3.5. Dissolved organic carbon (DOC)

In natural waters, total organic carbon (TOC) is the sum of particulate and dissolved organic carbon. Dissolved organic carbon (DOC) is operationally defined, usually as organic carbon that passes through a 0.45 µm membrane filter. Cellulose acetate or nitrate filters should not be used for this purpose due to contamination or adsorption problems. Filter paper may contaminate the sample with NH_4 and organic carbon. Glass fibre filters are preferable. The possible release of organic fibres from the membrane used should be tested, and suitable pre-rinsing procedures developed if required.

Although the discussion below concerns DOC, much of it applies to TOC as well. Organic carbon is most often determined after oxidation to CO_2 using combustion, an oxidant such as persulphate, UV or other high-energy radiation, or a combination of some of these. If only UV radiation with oxygen as oxidant is used, underestimates of the DOC concentration may be obtained in the presence of humic substances. A variety of methods are used for detection, including infrared spectrometry, titration and flame ionisation detection after reduction to methane. Always follow the instrument manufacturer's instructions.

For the determination of DOC, dissolved inorganic carbon (DIC) must be either removed by purging the acidified (for example with phosphoric acid) sample with a gas that is free from CO_2 and organic compounds, or determined and subtracted from the total dissolved carbon. If acidification followed by purging is used, care should be taken, as volatile organic compounds may also be lost. After acidification, the CO_2 is removed by blowing a stream of pure carbon-free inert gas through the system for at least 5 minutes.

For calibration, standard solutions are most often potassium hydrogen phthalate for total dissolved carbon and sodium bicarbonate/sodium carbonate for dissolved inorganic carbon. The DOC concentration should be within the working range of the calibration. If necessary the sample can be diluted.

DOC may also be determined by UV absorbance. A typical absorbance spectrum for DOC is shown in Figure 8. At higher wavelengths absorbance is lower, so care should be taken when measuring in this region.
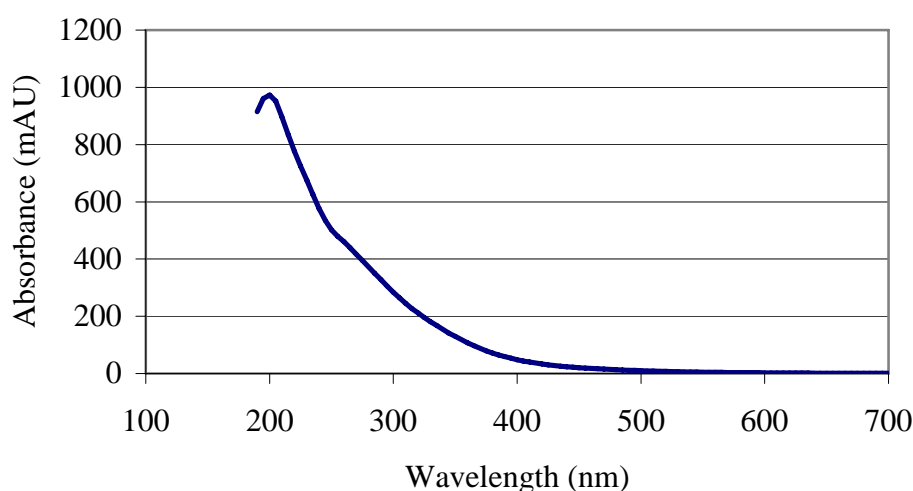
Figure A3.4:   Absorbance spectrum of DOC.

DOC may be determined by absorbance at 254 nm (Brandstetter et al. 1996). This is not the optimal method, but may be used if a carbon analyser is not available. Regression equations are given by Brandstetter et al. for estimation of DOC from the absorbance measurements:

DOC (mg/l) = 0.44 A_{254} (m^{-1}) + 0.9 for throughfall

DOC (mg/l) = 0.86 A_{254} (m^{-1}) - 11.7 for stemflow

where A_{254} = absorbance at 254 nm.

For wet deposition, an equation is given by Bartels (1988):

DOC (mg/l) = 0.46 A_{254} (m^{-1}) - 0.10

Carbon is ubiquitous in nature, so reagents, water, and glassware cannot be completely cleaned of it. Method interferences (positive bias) may be caused by contaminants in the carrier gas, dilution water, reagents, glassware, or other sample processing hardware (for example a homogenisation device). All of these materials must be routinely demonstrated to be free from interference under the conditions of analysis by running reagent blanks.

Plastic bottles can bleed carbon into water samples, especially when they are new or starting to degrade, or when they are used for low-level samples (less than 200 ppb C). Any new bottles (especially plastic) should ideally be filled with clean water for a period of several days or boiled in water for a few hours before use. Glass or high-density polyethylene bottles are recommended. The use of high purity or purified reagents and gases helps to minimise interference problems. It is very important to use ultra-pure water with a carbon filter or boiled distilled water just before preparing stock and standard solutions, in order to remove dissolved CO_2. The stock solution should not be kept too long (about one week). For most DOC instruments a correction for DOC (due to dissolved CO_2) in the dilution water used for calibration standards is necessary, especially for standards below 10 ppm C. The carbon in the blank should only be subtracted from standards and not from samples.

Sample DOC concentrations below about 50 ppb C can be affected by atmospheric exposure. In these cases, sampling bottles should be kept closed whenever possible, and autosampler vials should be equipped with septa for needle piercing by the autosampler.

A3.6. Spectrophotometric determination and flow systems

General remarks

Samples to be analysed by spectrophotometric methods should not be turbid or of a colour that interferes with the determination. Turbidity should not normally be a problem because all samples are filtered through a 0.45 µm membrane filter prior to analysis. However, turbidity may subsequently develop by the time the samples are to be analysed. The problems associated with turbid or coloured samples can be eliminated in a number of ways:

- Make sure that all the samples are free from particles by refiltration (0.45 µm membrane) prior to the analysis,
- The colour can be removed from solutions by means of sorptive materials (e.g. C18) or dialysis. Dialysis can be performed statically in dialysis tubes or dynamically by means of a dialysis membrane in a flow cell with an upper and top stream (usually a component of CFA Systems)

- Colour compensation can also be employed; this is most common in manually performed spectrophotometric measurements. The zero point of the photometer is adjusted with a sample containing all the components of the colorimetric method but without the colour reagent. Repeated measurement of the same sample including the colour reagent results gives an absorption measurement that is not affected by the colour of the sample.

The linearity of the working range for spectrophotometric methods is typically given over 1 decade of concentration. Absorption intensity is influenced by the length of the optical path, the concentration ratio between sample and colour reagent, the temperature of the measured solution, and the reaction time between the addition of the colour reagent to the sample solution and the start of the absorption measurement.

The measurements can be performed in manual mode or in flow systems (SCFA or FIA).

The advantages of a flow system are:
- The measurements can be made in an automated system with high sample throughput.
- All conditions (volume dosage, temperature and colour development time) are well reproducible because they are controlled by the system conditions.
- Sample preparation procedures (dialysis, thermal, UV and peroxide dissolution, reduction reaction prior to colour development) are fully integratable.
- Detection can be performed as absorption measurement (increasing or decreasing) or based on potentiometry (ISE).

The selectivity and sensitivity of photometric and flow system methods are rather high. In some cases, however, there can be problems.

Reagents
All reagents should be of "analytical grade". Check solution stability with respect to the solubility of salts (non-saturated solutions). Store the reagent solutions in a cool dark place, and degas the reagent solutions prior to analysis by stirring, helium-degassing, membrane filtration (under pressure) or ultra-sonic treatment of the reagent bottles.

Calibration
Calibration prior to the start of daily analysis should be performed using at least five calibration standards per working range; this should be verified by means of an independent control sample. Check the precision and stability of photometers and flow systems by replicate measurement of calibration or verification standards every 15th to 20th sample. Some instruments can perform automatic drift correction by replicated measurements of standards after a predefined number of samples.

Table A3.3: Information about photometric and flow methods.

Parameter	Method	Remarks
Sulphate	Ba/Ca Methyl-Thymol blue	2-channel method: absolute simultaneous flow of the Ba and Ca channel is required. The signal is obtained as the absorption difference between the two channels. As no dialysis pre-treatment is possible, there is no membrane available for good SO_4 diffusion. High concentrations of cations cause problems.
Nitrate	Sulphanilamide Cd or hydrazinium reduction	High concentrations of Fe, Cu and other metals cause problems in analysis; add EDTA to the buffer solution to prevent problems. When a Cd-reduction column is used, ensure that the column is completely degassed and avoid drying out of the Cd granules.
Chloride	Hg-Fe-SCN	Bromide and iodide cause interference at concentrations exceeding 30 mg/l.

	potentiometry	Sulphide ions also cause interference. Ensure that Hg-containing waste solution are collected and recycled in accordance with environmental regulations.
Ammonium	Indophenol blue Gas Diffusion	High amino acid concentrations increase the measured ammonium concentration. High Mg concentrations cause precipitation of $Mg(OH)_2$; add sodium citrate to avoid the problem.
N_{total}	Sulphanilamide Cd or hydrazi-nium reduction	After oxidation, detection of N_{total} as nitrate. High concentrations of Fe, Cu and other metals cause problems in analysis; add EDTA to the buffer solution to avoid this problem. Use calibration standards containing NH_4 and NO_3 components.
Phosphate	Molybdenum blue	Reducing components can interfere. Silicates cause problems; the same molybdenum-blue complex is formed.

A3.7. Ion chromatography

Advantages
- This technique can be used for the measurement of both anions and cations; in such cases, the use of two separate instruments is recommended.
- Small sample volumes required, which means that small amounts of precipitation can be analysed successfully.

Methods
- Use a known standard (e.g. CEN, ISO …)
- Follow the recommendations of the supplier and consult with other users concerning specific problems and techniques.
- Analytical columns are expensive and easily damaged or destroyed: always use a pre-column.

Calibration
- For Cl^-, NO_3^-, SO_4^{2-} (eluent CO_3^{2-}/HCO_3^-) and NH_4^+, we recommend quadratic calibrations in the range of two orders of magnitude, obtained using at least five standards, two of which should be at the limits of the measurement interval.
- For Cl^-, NO_3^-, SO_4^{2-} (eluent CO_3^{2-}/HCO_3^-) and NH_4^+, linear calibrations should only be in the range of one order of magnitude, using at least three standards corresponding to the limits and the centre of the measurement interval.
- The use of KOH as eluent improves the linearity for Cl^-, NO_3^- and SO_4^{2-}.
- For Na^+, K^+, Mg^{2+} and Ca^{2+}, linear calibrations (with at least three standards) up to two orders of magnitude may be used.
- The standards used in calibration must cover the values of the samples analysed.

Measurement
- Calibrate and analyse the samples only when the instrument is stable (after one hour's operating time at least).
- After the initial calibration, a new calibration or a control standard measurement should be performed every 20-30 samples; more frequent calibrations do not appear to be necessary.
- End the batch of analysed samples with a complete calibration - compare it with the previous one in order to check for drift.
- Analyse every day at least one sample of ultrapure water (blank) and at least one control chart sample.

General

- Take care to avoid contamination during preparation of the samples: perspiration on one's fingers contains appreciable amounts of NaCl. This is a common and well known problem, but often forgotten.
- We advise using the autosampler to optimise the analysis time and to programme the analysis of batches of samples including calibration, blank, control chart, 20-30 samples, calibration or control standard, 20-30 samples etc. The use of manual injections does not seem to affect the quality of the analyses.
- Two injections per sample or standard are not essential. However, the main causes of errors are to be found in incorrect calibration, contamination during the handling of samples and standards etc.
- When analysing samples with a low ionic content, it is advisable to use injection loops of 100 µl or more.
- Careful quality control must be designed specifically for ion chromatography analysis, even when using external quality controls (certified reference materials) to limit the occurrence of systematic errors.

Practical experience

- Separation of the Na^+ and NH^+_4 peaks needs to be improved. Because NH^+_4 elutes after the Na^+ peak, some columns reduce the tailing.

- An increase in the inlet pressure is usually due to the clogging of the inlet frit. Never try to clean it, but discard it and replace with a new one.

- The connecting tubes and sampling loop of some equipment can adsorb and release Ca^{2+} ions; this is often indicated by unusually high Ca controls. If the problem is not due to the quality of the eluent, replace the injection loop and, if the problem persists, the tubing inlet to the detector.

- Care should be taken when analysing anions and cations on the same system, as the individual eluents are usually incompatible. The system should be carefully rinsed and tested.

A3.8. Methods that give a high dispersion of results

Some methods give a high dispersion of results, and are thus not recommended for use in the monitoring programme. These methods are summarised in Table A3.4. See also Mosello et al. (2002) and Marchetto et al. (2006).

Table A3.4: Analytical methods that frequently give high dispersion of results.

Analyte	Methods
Alkalinity (low values)	Acidimetric titration with colorimetric detection of the end-point Acidimetric titration with single fixed end point without correction
Sulphate	Turbidimetry Spectrophotometry with $BaSO_4$ excess and methyl thymol Continuous flow analysis with $BaSO_4$ excess and methyl thymol
Nitrate (in samples with high DOC)	Spectrophotometry with UV detection at 220 nm
Chloride	$AgNO_3$ titration with K_2CrO_4 indicator

Ca and Mg	EDTA titration
Ammonium	Nessler spectrophotometric method Ion selective electrode
Total Nitrogen	Kjeldahl digestion Alkaline persulphate digestion ($K_2S_2O_8$ and NaOH, PSOH)
Total Sulphur	ICP MS
Aluminium	AAS Flame
DOC	Spectrophotometry with detection at 320 nm

Annex 4. List of ISO and CEN methods to be used for the analysis and QA/QC laboratory procedures. See also Eurochem/CITAC (2000).

CEN or ISO n°	Name of standard
ISO 7150/1	Water quality – determination of ammonium – part 1: manual spectrometric method (recommended to be used for soil solution only)
ISO 7150/2	Water quality – determination of ammonium – part 2: automated spectrometric method
ISO 7888	Water quality – determination of electrical conductivity
ISO 8245	Water quality – guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)
ISO 8258	Shewhart control charts
ISO 9963-1	Water quality – determination of alkalinity – part 1: determination of total and composite alkalinity
ISO 9963-2	Water quality – determination of alkalinity – part 2: determination of carbonate alkalinity
ISO 10523	Water quality – determination of pH
ISO 11732	Water quality – determination of ammonium nitrogen by flow analyses (CFA and FIA) and spectrometric detection
ISO 11885	Water quality – determination of selected elements by inductively coupled plasma atomic emission spectroscopy
ISO 10304-1	Water quality – determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulphate ions, using liquid chromatography of ions – part 1: method for water with low contamination
ISO 10304-4	Water quality – determination of dissolved anions by liquid chromatography of ions – part 4: determination of chlorate, chloride and chlorite in water with low contamination
ISO/TR 13530	Water quality – guide to analytical quality control for water analysis
ISO 14911	Water quality – determination of dissolved Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} using ion chromatography – method for water and waste water
ISO 9964-1:1993	Water quality -- Determination of sodium and potassium -- Part 1: Determination of sodium by atomic absorption spectrometry
ISO 7980:1986	Water quality -- Determination of calcium and magnesium -- Atomic absorption spectrometric method
ISO 9964-2:1993	Water quality -- Determination of sodium and potassium -- Part 2: Determination of potassium by atomic absorption spectrometry
ISO 15682	Water quality : chloride determination with CFA or FIA with photometric or potentiometric determination
ISO 12020:1997	Water quality -- Determination of aluminium -- Atomic absorption spectrometric methods
ISO 9174:1998	Water quality -- Determination of chromium -- Atomic absorption spectrometric methods
ISO 15586	Water quality -- Determination of trace elements using atomic absorption spectrometry with graphite furnace
ISO 5961: 1994	Water quality -- Determination of cadmium by atomic absorption spectrometry
ISO 8288:1986	Water quality -- Determination of cobalt, nickel, copper, zinc, cadmium and lead -- Flame atomic absorption spectrometric methods
ISO/IEC 17025:2005	General requirements for the competence of testing and calibration laboratories

Annex 5. Interpretation of the throughfall data

Some details on data evaluation of throughfall and precipitation results are given below. Further details are given in Draaijers et al., 1998.

Sulphur: Throughfall (plus stemflow) are in most areas of Europe representative for the total deposition to the forest. Some questions remain about throughfall data in very low-polluted areas.

Dry deposition (including contributions from fog/cloud water deposition, can be calculated as the difference between throughfall and wet deposition. This difference is also called net throughfall. For this purpose, wet deposition should ideally be measured using wet-only collectors.

However in areas where very low dry deposition contributions are obtained to the bulk collector, also bulk deposition data are possible to use. In areas with a high fog frequency, fog and cloud water deposition can be measured optionally and be separated from the dry deposition part of the net throughfall.

Nitrogen: Oxidised, reduced and organic nitrogen is analysed separately in throughfall and stemflow. The sum of these compounds is the total nitrogen in the throughfall plus stemflow flux.

Total nitrogen in throughfall and stemflow can be compared to the total nitrogen (mainly nitrate and ammonium) in wet deposition. In areas with a low nitrogen load, the throughfall plus stemflow nitrogen flux is often lower than the wet deposition due to high canopy up-take. This means that nitrogen fluxes in throughfall plus stemflow systematically underestimate deposition fluxes. In areas with high throughfall deposition, evidence of high nitrogen load to the soil is also indicated by e.g. leaching of nitrate to soil water.

The total nitrogen deposition from the atmosphere to the forest includes also the amount of gaseous nitrogen compounds taken up by vegetation via stomata and the amount of nitrogen deposited to the tree surface, and taken up by the tree or by lichens, algae and other organisms. Today there are no generally validated procedures to estimate the amount taken up by the tree.

A recommended procedure to make a rough estimate of nitrogen deposition is given in Annex 6.

Optionally total nitrogen deposition with fog and cloud water can be determined by separate measurements.

Base cations   The main source of sodium is atmospheric deposition of sea salt. The sodium in throughfall is considered to be a good measure of the total sodium deposition.

Magnesium, calcium and potassium can be derived from both leaching and atmospheric deposition. This means that base cation deposition is smaller than the measured throughfall plus stemflow fluxes. There are several approaches used today to separate the contributions from the two processes. However, these so called canopy budget models need accurate monitoring data. A good knowledge of the nutrient status etc. of the forest stand is valuable for the interpretation of results. Canopy budget approaches used in Europe and the USA are presented in Annex 6.

Annex 6.   *Canopy Budget Models Applicable for Use within the Intensive Monitoring Program (Geert P.J. Draaijers).* To be updated.

Introduction

The major aim of the Intensive Monitoring Program is to gain a better insight in the impacts of air pollution (specifically the elevated deposition levels of SO_x, NO_y and NH_x) on forest ecosystems. To achieve this aim among others, relationships have to be derived between deposition amounts and effect parameters. For optimal assessment and interpretation of these relationships, deposition estimates should be as accurate as possible. Within the Intensive Monitoring Program, atmospheric deposition is estimated from results of throughfall, stemflow and precipitation measurements in combination with canopy budget models to estimate canopy exchange. In this way atmospheric deposition of sulphur, sodium, and chloride can be estimated reasonably well. Unfortunately, up to now relatively large uncertainties are involved with the estimation of canopy leaching of potassium, calcium and magnesium and canopy uptake of oxidised and reduced nitrogen using canopy budget models. Considering the major aim of the Intensive Monitoring Program, the Expert Panel on Deposition recommended to perform additional research to improve these estimates (Lövblad, 1996).

In this paper first the theory of canopy exchange is given (A6.1) followed by an overview of available models to estimate canopy exchange and evaluation of the models with respect to applicability for use within the Intensive Monitoring Program (A6.2). A6.3 presents recommendations for future activities to improve canopy exchange estimates within the Intensive Monitoring Program.

A6.1.   Canopy exchange processes

Throughfall fluxes are found to be influenced by passive diffusion and ion exchange between the surface water and the underlying apoplast of canopy tissues. Passive diffusion is found to be the major cause of elevated anionic concentrations in throughfall while both diffusion and ion exchange contribute to cationic concentrations in throughfall (Schaefer & Reiners, 1990). The rate of canopy exchange depends on tree species and ecological setting. For example, during the growing season deciduous tree species tend to lose more nutrients from the crown foliage through leaching than coniferous tree species. Conifers, however, stay green all the year round and continue to lose nutrients throughout the dormant season (Smith, 1981). The age distribution of leaves and soil nutrient status also affects the magnitude of leaching to a large extent. Young immature leaves/needles tend to lose much more nutrients compared to older ones (except when they are hydrophobic; Parker, 1990), and fertilization is found to enhance canopy leaching considerably (Matzner et al., 1983). Biotic stresses like insect plagues may initiate large canopy leaching. Bobbink et al. (1990) monitored throughfall in heather vegetation and observed a marked increase of canopy losses occurring simultaneously with an outbreak of a heather-beetle plague. Furthermore, abiotic stresses like drought and temperature extremes are found to enhance canopy leaching (Tukey & Morgan, 1963). The presence of certain pollutants may also be of importance. Large concentrations of ozone, for example, were found to enhance the permeability of cell membranes in canopy foliage, thereby increasing ion leakage (Evans & Ting, 1973). Moreover, the amount and timing of precipitation is found to be relevant with respect to canopy leaching. Relatively long residence times during drizzle account for relatively high leaching rates compared to short rain periods with large rainfall intensities. Large rain amounts may deplete leachable pools within the canopy, thereby inhibiting ion leaching (Lovett & Lindberg, 1984). Losses from leachable pools within the canopy are believed to be replenished within 3-4 days after a large storm by increased root uptake or translocation from other parts of the tree (Parker, 1983).

Sulphur compounds

SO_2 may be taken up by the stomata. If a significant part of the SO_2 is retained in the foliage and translocated from the canopy to the roots, this would result in an underestimate of sulphur deposition by measuring throughfall. Gay & Murphy (1989) found that up to 70% of the SO_2 absorbed by foliage during short-term experimental exposures could not subsequently be removed by washing. However, Schaefer & Reiners (1990) and Granat & Hällgren (1992) conclude that essentially all of the dry deposited sulphur dioxide is eventually extracted out of the apoplast pools (i.e. aqueous layer on the outside of cell membranes) by rain and appears in throughfall.

Fowler & Cape (1983) and Cape et al. (1987) compared net throughfall measurements in a Scots pine stand with estimates of SO_2 dry deposition using eddy correlation techniques. For a 71-day spring period, SO_2 dry deposition appeared to be equal to the net throughfall flux of sulphate. For an 84-day autumn period, SO_2 deposition only accounted for 8% of the sulphur flux in net throughfall. The latter observation led Fowler & Cape (1983) to the conclusion that canopy leaching is a major component of the net enrichment in throughfall. According to Ivens (1990), this large difference between both estimates in the autumn period can also be explained by the omission of dry particulate sulphur deposition which can make up 30 % of the total sulphur deposition (Lindberg et al., 1986), and by sulphur leaching from senescent leaves, which also has been observed by Meiwes & Khanna (1981). Based on a comparison of throughfall data with deposition measurements of SO_2 and particulate sulphate on a large number of sites throughout the Unites States (Integrated Forest Study, IFS), Lindberg et al. (1990) and Johnson & Lindberg (1992) conclude that foliar leaching of $SO_4{}^{2-}$ contributed maximally 15% to the net throughfall flux of sulphate.

Several radioactive $^{35}SO_4{}^{2-}$ studies have been conducted to evaluate the applicability of the throughfall method to estimate sulphur deposition (Garten et al., 1988; Lindberg & Garten, 1989; Cape et al., 1992; Wyers et al., 1994). Garten et al. (1988) added radiolabelled $SO_4{}^{2-}$ through single-stem well injection into the internal nutrient store of two Red Maple and two Yellow Poplar trees and analysed the amount of radiolabelled $SO_4{}^{2-}$ and total sulphate present in throughfall. During a 104-day period in the growing season, less than 10% of the net throughfall flux of sulphate could be accounted for by foliar leaching. Similar experiments with several individuals of Loblolly pine trees led to the same conclusion (Lindberg & Garten, 1989). Because the experiments conducted by Garten et al. (1988) and Lindberg & Garten (1989) were performed on isolated trees or trees situated at forest edges, the contribution of canopy leaching to net throughfall fluxes measured by these experiments may be larger in forest interiors (Fowler et al., 1992).

Cape et al. (1992) applied radioactive sulphate to the soil below a closed Scots pine forest canopy during a four month period in summer. Results suggest (assuming rapid equilibrium of $^{35}SO_4{}^{2-}$ with sulphate in the soil) that root-derived sulphate contributed approximately 3% of sulphate in net throughfall and that dry deposition of SO_2 and sulphate particles contributed 97% to the total net throughfall flux of sulphate. However, there were some indications that equilibrium could not be safely assumed. For this reason, the possibility of a significant contribution of soil-derived sulphate to sulphate deposition in net throughfall could not be ruled out on the basis of this experiment (Cape et al., 1992).

At catchments at Lake Gardsjön on the Swedish west coast forested with Norway spruce, the deposition and watershed output has been studied during a period of 10 years by means of throughfall, precipitation and runoff measurements (Hultberg, 1985; Hultberg & Grennfelt, 1992). Runoff and throughfall sulphate fluxes were found to be very similar, suggesting uptake of sulphur by tree roots and transport to the tree canopy being of minor importance. Moreover, sulphate fertilization in several catchments did not enhance sulphate throughfall fluxes significantly, supporting the hypothesis that sulphate throughfall provides a reasonable good measure for sulphur ($SO_2 + SO_4{}^{2-}$ aerosol) deposition (Hultberg & Grennfelt, 1992). Similar conclusions were drawn by Likens et al. (1990) for catchments covered with deciduous forest at Hubbard Brook (USA).

Nitrogen compounds

Present knowledge on canopy exchange of nitrogen compounds is limited due to the complexity of the exchange processes involved. Up to now, leaching of inorganic nitrogen from forest canopies has not been reported in the literature. On the contrary, numerous reports indicate that inorganic nitrogen may be taken up by canopy foliage, stems, epiphytic lichens or other microflora. Canopy foliage has been demonstrated experimentally to be capable of absorbing and incorporating gaseous NO_2, HNO_3 and NH_3 as well as NO_3^- and NH_4^+ in solution (Reiners & Olson, 1984; Bowden et al., 1989). In laboratory experiments, NH_4^+ in solution was found to be exchanged with base cations present in leaf tissues (Roelofs et al., 1985). Epiphytic lichens were also shown to be active absorbers of NO_3^- and NH_4^+ in solution (Lang et al., 1976; Reiners & Olson, 1984).

Based on information available in the literature, Ivens (1990) suggested the above ground uptake of total inorganic nitrogen by forests to be between 150 and 350 eq.ha^{-1}.yr^{-1}, not clearly related to tree species. Within the Integrated Forest Study, Johnson & Lindberg (1992) measured throughfall and stemflow fluxes of NO_3^- and NH_4^+ in several forest stands scattered over the United States. Simultaneously, dry deposition amounts of NO_2, NO, HNO_3, HNO_2, NO_3^-, and NH_3 and NH_4^+, respectively, were estimated. Moreover, wet and cloud water deposition fluxes of nitrate and ammonium were determined. Canopy retention of inorganic nitrogen was estimated by total deposition (dry + wet + cloud water) minus soil flux (throughfall + stemflow). It was concluded that, on average, 40% of all inorganic nitrogen input to forests was retained by the vegetation, whereas 60% was found back in the throughfall as NO_3^- and NH_4^+. (Johnson & Lindberg, 1992). Total inorganic nitrogen uptake amounted up to 850 eq.ha^{-1}.yr^{-1}, with a strong positive relationship between deposition and uptake for spruce and spruce-fir stands. Other tree species showed a rather constant inorganic nitrogen uptake (200-300 eq.ha^{-1}.yr^{-1}), with only little response to deposition amount (Johnson & Lindberg, 1992).

In the same study, part of the inorganic nitrogen retained by the canopy was supposed to be converted into organic substances and subsequently leached. Total nitrogen (organic + inorganic) in throughfall and stemflow was about 84% of the total inorganic nitrogen deposition (Johnson & Lindberg, 1992). Microbes were assumed to play an important role in the conversion of inorganic to organic N, if it occurs. However, it was recognised that organic N in throughfall also arises from internal pools and surfaces of plants and lichens, and from microparticulate detritus and pollen (Johnson & Lindberg, 1992). Atmospheric deposition of organic nitrogen compounds is estimated to be small, i.e. < 100 eq.ha^{-1}.yr^{-1} (Beringen et al., 1992). Carlisle et al. (1966) reported for a *Quercus petraea* stand an organic nitrogen throughfall flux of ± 350 eq.ha^{-1}.yr^{-1}. Similar or somewhat larger throughfall fluxes of organic nitrogen were measured by Alenäs & Skärby (1988) in Picea abies forest stands.

More insight has been gained on nitrogen uptake by tree canopies by performing experiments with radio-labelled [15]N. Bowden et al. (1989), for example, simulated cloud water deposition by fumigating *Pinus rubens* seedlings with a fine water spray. Essentially, they conclude that the total uptake of NH_4^+ and NO_3^- ions from cloud water is small compared to the amount of nitrogen required to create new growth. Foliar retention of [15]NH_4^+ appeared to be larger compared to uptake of [15]NO_3^-. Garten & Hanson (1990) applied radiolabelled NH_4^+ and NO_3^- to *Acer rubrum* and *Quercus alba* through simulated rain. They concluded that [15]NO_3^- deposited to deciduous tree leaves is easily removed by washing with water, while [15]NH_4^+ is retained and presumably assimilated into the leaf. Experiments with radiolabelled ^{15}N made by Vose et al. (1989) show that foliar uptake of dry deposited HNO_3 is small. In the Netherlands the fate of nitrogen within the forest canopy is also being studied by the means of spraying labeled nitrogen (Slanina et al., 1990). However, no results have been published so far.

Sodium and chloride
Although Fassbender (1977) reported some sodium uptake by young spruce trees during his laboratory experiments, sodium and chloride are normally considered to be more or less conservative elements showing only minor canopy exchange (Parker, 1983). In Germany, Bredemeier (1988) found a clear downwards gradient with increasing distance from the North Sea in sodium

and chloride in bulk precipitation as well throughfall, indicating a major contribution of sea-salt particles to these fluxes. Ivens (1990) found a strong correlation between sodium and chloride in both bulk precipitation and throughfall samples, respectively, compiled from all over Europe. Sodium and chloride were found to occur in the same molar ratio as in sea water, i.e. 0.86. Moreover, sodium in throughfall was linearly related to sodium in bulk precipitation with an intercept of the regression line not significantly different from zero, suggesting nil canopy exchange (Ivens, 1990). Based on a comparison of throughfall data with deposition measurements on a large number of sites in the United States, Johnson & Lindberg (1992) also conclude that Na^+ in throughfall may be considered as solely derived from atmospheric deposition. All these studies show the inertness of Na in the canopy.

Magnesium, calcium, potassium and phosphate
A substantial part of magnesium, calcium and potassium in throughfall is normally caused by canopy leaching (Parker, 1983). These ions are leached in association with foliar excretion of weak organic acid anions (Tukey, 1980; Hoffman et al., 1980) or through exchange with H^+ and NH_4^+ in leaf tissues (Roelofs et al., 1985). K^+ is found to be relatively more susceptible to canopy leaching compared to Mg^{2+} and Ca^{2+} because it is not so tightly bound in structural tissues or enzyme complexes (Wood & Bormann, 1975). A literature compilation made by Parker (1990) indicates that it is not clear to which degree these base cations present in throughfall originate from atmospheric deposition and foliar leaching, respectively. Canopy leaching contributed between 10% and 80% to the total flux of these base cations reaching the forest floor. At coastal forest sites, magnesium in throughfall was predominantly caused by atmospheric deposition of sea-salts (Parker, 1983). Johnson & Lindberg (1992) suggest that calcium in throughfall may be enhanced at sites located in areas with calcareous soils or near calcium fertilized arable land. Observations done by White & Turner (1970), Abrahamson et al. (1976) and Alcock & Morton (1981) suggest that magnesium and calcium may also be irreversibly retained within the canopy. Ivens (1990) hypothesizes that canopy uptake may occur if tree canopies suffer from base cation deficiencies due to limited cation supplies from the soil.

    Negligible amounts of phosphorus in ambient air suggest that canopy leachates contribute more than 90% to throughfall phosphate (Parker, 1983). Minor amounts of phosphate in throughfall may originate from soil dust, especially in forests situated near fertilized arable land. Furthermore, bird droppings may contribute to phosphate in throughfall (Van der Maas et al., 1990; Ivens, 1990).

Hydrogen
Deciduous stands in regions remote from acid precipitation are usually found to have a higher throughfall pH in comparison to incident precipitation indicating canopy retention of protons (Parker, 1983). There are, however, a number of exceptions to this rule, especially at high acid deposition rates (e.g. Künstle et al., 1981; Skeffington, 1983). For coniferous stands, reports of higher throughfall pH (e.g. Abrahamsen et al., 1976; Miller, 1984) are as common as reports of lower pH (Parker, 1983).

    In polluted areas remote from ammonia emission sources, throughfall is generally more acid than bulk precipitation (Georgii et al., 1986; Bredemeier, 1988). In the Netherlands, the proton flux under the forest canopy is found to be smaller than in the open field (Van Breemen et al., 1982; Houdijk, 1990; Ivens, 1990). This is attributed to canopy uptake of protons through exchange with cations like magnesium, calcium and potassium, and to the neutralising effect of dry deposition of ammonia onto the water layers present on the tree surface (Ivens, 1990).

Bicarbonate and organic compounds
Bicarbonate in throughfall is usually found in regions away from acidified precipitation where it originates from atmospheric CO_2 (Cronan, 1978). In such regions, bicarbonate may even be the

dominant anion because leachate cations commonly transfer as bicarbonate salts (Tukey, 1970). Partly, bicarbonate in throughfall may originate from canopy leaching of carbon or bird droppings (Parker, 1983).

A variety of organic compounds including sugars, amino acids, organic acids, hormones, vitamins, pectic and phenolic substances are probably leached from the canopy but difficult to measure due to their low stability in throughfall water and their high volatility (Parker, 1990).

A6.2.   An overview of models and methods available to estimate canopy exchange
Several models have been developed to estimate canopy exchange. In many of these models canopy exchange is calculated solely on the basis of throughfall, stemflow and precipitation measurements. This is the case with *i)* the regression model of Lovett and Lindberg (1984), *ii)* the canopy budget model of Ulrich (1983) which was further developed by Bredemeier (1988) and Van der Maas and Pape (1991) using the 'filtering approach', *iii)* the model of Beier et al. (1992) using the 'forest edge approach', *iv)* models developed by Mayer and Ulrich (1974) and Miller et al. (1976) and the empirical model of Johnson and Lindberg (1992). Besides other models and methods have been used to estimate canopy exchange e.g. *i)* the stomatal uptake model of Bouten and Bosveld (1992) and *ii)* the inferential deposition model EDACS described by e.g. Erisman et al. (1994) and Erisman and Draaijers (1995). All mentioned models and methods are discussed below, focussing on the applicability for use within the Intensive Monitoring Program.

Model of Lovett and Lindberg (1984)
Monitoring throughfall and precipitation fluxes on an event basis allows the application of the regression model developed by Lovett and Lindberg (1984). This empirical model is based on the calculation of a multiple regression using event net throughfall (NTF) as the dependent variable and the duration of the antecedent dry period (DDP) and precipitation amount (P) as independent variables: $NTF=b_1*DDP+b_2*P$. The regression coefficients (b_1 and b_2) represent the mean dry deposition and canopy exchange rate, respectively. If information on the total duration of dry periods and the annual rainfall amount is available, these coefficients can be used to calculate yearly mean dry deposition and canopy exchange amounts. The model has proven very valuable for estimating canopy exchange and atmospheric deposition in forests situated in areas with convective storms and extended dry weather periods (e.g. Lovett and Lindberg, 1984; Puckett, 1990), but was found less useful in areas characterized by frequent low-intensity rainfall and relatively short dry periods (Lindberg et al., 1990; Ivens, 1990; Draaijers et al., 1994b). The model can only be used in case throughfall and precipitation are measured on an event-basis, which limits its application in the Intensive Monitoring Program.

Model of Ulrich (1983) and Van der Maas and Pape (1991)
An alternative to regression modeling is application of the canopy budget model developed by Ulrich (1983), which was extended by Bredemeier (1988) and Van der Maas and Pape (1991). This model allows discrimination between canopy exchange and atmospheric deposition using long-term throughfall and precipitation fluxes, as is the case in the Intensive Monitoring Program. Dry deposition and canopy leaching of Ca^{2+}, Mg^{2+} and K^+ is computed by means of the so-called 'filtering approach', assuming a fixed relationship between wet and dry deposition of particles and taking Na^+ as a tracer (Ulrich, 1983). The total canopy uptake of H^+ and NH_4^+ is taken equal to the total canopy leaching of Ca^{2+}, Mg^{2+} and K^+ taking place via ion exchange. Based on experiments in the laboratory (Van der Maas et al., 1991), it is assumed that H+ has per mol an exchange capacity six times larger than NH_4^+. Canopy exchange of SO_4^{2-} and NO_3^- is assumed to be negligible. A more detailed description of the model is presented by Draaijers et al. (1994b) and Draaijers and Erisman (1995) as well as in Appendix 1 of this paper. For the Speulder forest and other Dutch forests, the combination of throughfall measurements and application of the model resulted in deposition estimates, which were similar to deposition estimates derived from micrometeorological measurements and inferential modelling, deposition of NO_y being the only

exception. The discrepancy found for NO_y could in part be explained by the (probably wrong) assumption that canopy uptake of oxidized nitrogen compounds is negligible. Up to now, several basic assumptions in the model (e.g. the ratio in exchange capacity between H^+ and NH_4^+) are not properly evaluated for different environmental conditions (tree species, ecological setting, pollution climate), which limits its application (Draaijers et al., 1994b; Draaijers & Erisman, 1995). Up to now the model has only been validated in relatively polluted areas as the Netherlands and Denmark.

Model of Beier et al. (1992)
A major weakness of the 'filtering approach' is the assumed relation between wet and dry deposition of particles. To overcome this weakness a new approach was formulated by Beier et al. (1992), using Na^+ to base cation ratios in fractions originating from the same process, i.e. dry deposition. Their approach can be used if throughfall and stemflow measurements are made both inside and near the edge of the forest stand ('forest edge approach'), which means that this approach can in general not be used within the framework of the Intensive Monitoring Program. The fraction of dry deposition to leaching inside the stand is estimated based on the assumptions that only <10% of the throughfall flux of Ca^{2+} and Mg^{2+} under the edge trees and >95% of K^+ inside the stand are caused by leaching. The calculations of Beier et al. (1992) show that, especially for Ca^{2+} and Mg^{2+}, the influence of this choice is relatively small. However, process-oriented studies are necessary to obtain more precise knowledge on these properties for different environmental conditions.

Models of Mayer and Ulrich (1974) and Miller et al. (1976)
Mayer and Ulrich (1974) took throughfall to precipitation flux ratios in winter to estimate dry deposition in summer, assuming canopy exchange only takes place in the summer period and trees have the same dry deposition catching efficiency in summer and winter. Miller et al. (1976) and Lakhani and Miller (1980) proposed to calculate canopy leaching from the intercept of the regression of bulk precipitation versus throughfall, assuming a functional relationship between wet deposition and dry deposition, and furthermore canopy exchange to be independent of wet and dry deposition. Considering present knowledge on canopy exchange and deposition processes, the assumptions underlying the approaches of Mayer and Ulrich (1974) and Miller et al. (1976) may be regarded questionable (Spranger, 1992; Erisman and Draaijers, 1995). For distinguishing canopy exchange and atmospheric deposition on the basis of throughfall and precipitation measurements, the 'multiple regression approach', 'filtering approach' and 'forest edge approach' can be considered much more reliable.

Model of Johnson and Lindberg (1992)
An estimate for canopy uptake of oxidised and reduced nitrogen can also be obtained by using empirical results of the Integrated Forest Study (IFS) reported by Johnson and Lindberg (1992). Johnson and Lindberg (1992) found for 12 sites in the USA the above ground uptake of inorganic nitrogen, $[CU_N]$, significantly related to the total deposition of inorganic nitrogen, $[TD_N]$, according to:

$$[CU_N] = 0.41*[TD_N] + 54.2 \qquad (r^2 = 0.66) \qquad [1]$$

For the same sites, the throughfall + stemflow flux of inorganic nitrogen, $[TF_N+SF_N]$, was significantly related to $[TD_N]$, according to:

$$[TF_N+SF_N] = 0.59*[TD_N] - 54.2 \qquad (r^2 = 0.80) \qquad [2]$$

Combining equation [1] and [2] provides the relationship between the canopy uptake and the throughfall + stemflow flux of inorganic nitrogen (in eq ha^{-1} yr^{-1}):

$$[CU_N] = 0.69*[TF_N+SF_N] + 91.9 \qquad\qquad [3]$$

Johnson and Lindberg (1992) made their measurements at sites situated in areas with relatively low air concentrations of N compounds in comparison to those found in certain areas in Europe. Throughfall + stemflow fluxes of inorganic nitrogen in the IFS ranged between 100 and 1000 eq.ha$^-$^{1} yr$^-$^{1}. Equation [3] therefore may only be applied for this range of inorganic nitrogen fluxes. It is not clear if uptake rates will increase linearly at higher throughfall + stemflow fluxes because nitrogen saturation in the canopy might be expected. Another restriction for using equation [3] is made by Johnson and Lindberg (1992) themselves. In their study the relationship between uptake and deposition appeared to be quit strong for spruce and spruce-fir forests but was found much less pronounced for other tree species. Canopy uptake of nitrogen will not only be governed by deposition amount but also by numerous other factors as was already explained in chapter 2.1. Process-oriented research on canopy uptake of nitrogen in relation to these factors is therefore recommended. While $[TF_N+SF_N]$ gives a minimum estimate for nitrogen deposition, $[TF_N+SF_N]$-$[CU_N]$, with $[CU_N]$ estimated according to equation [3], provides a more realistic estimate for nitrogen deposition to forests.

Model of Bouten and Bosveld (1992)
For estimating stomatal uptake of gaseous nitrogen compounds (NO_2, NO, HNO_3, HNO_2 and NH_3) a model developed by Bouten and Bosveld (1992) can be applied. This model uses air concentrations and meteorology as input data. Stomatal conductance is described as a product of response functions for water vapor deficit, global radiation, temperature, soil moisture status and leaf area index. To obtain realistic values for stomatal uptake of nitrogen compounds from the model of Bouten and Bosveld (1992), results from air concentration measurements made at or near the forest site under consideration need to be used. Diffuse samplers may be useful for measuring air concentrations due to the low costs involved and no need for electricity. Air concentration data representative for the large scale pollution climate (as collected e.g. within the framework of the EMEP Program) are of limited value for use at specific sites. Especially concentrations of oxidised and reduced nitrogen compounds have been found subject to considerable small scale variability as they are strongly influenced by local sources and climatic conditions. Meteorological measurements should ideally be performed at the site as well, but meteorological data can also be obtained from nearby sites part of a routine network. Due to the data necessary this model does not seem applicable for current use within the framework of the Intensive Monitoring Program.

Model of Erisman et al. (1994)
Another estimate of nitrogen canopy uptake and base cation leaching can be obtained by comparing throughfall + stemflow fluxes with deposition estimates derived from inferential deposition models. Inferential deposition models like DEADM (Erisman, 1992) and EDACS (e.g. Erisman et al., 1994; Erisman and Draaijers, 1995) which are generally used to estimate atmospheric deposition on regional scales, also provide the possibility to estimate dry deposition to specific forest sites. In inferential models, dry deposition is calculated by multiplying air concentrations with dry deposition velocities. Dry deposition velocities are calculated from land-use and meteorological information using detailed parameterizations of the dry deposition process. To estimate dry deposition of nitrogen to specific forest sites, information is necessary on *i)* site characteristics (location, main tree species and tree height, *ii)* air concentrations (NO_2, NO, HNO_3, HNO_2, NO_3, NH_3 and NH_4) and *iii)* meteorology (wind speed, temperature, dew point temperature or relative humidity, cloud cover and precipitation amount). Dry deposition estimates will improve if also information on canopy coverage, leaf area, tree density and/or distance to forest edges is available. Erisman (1992) used the DEADM model for estimating dry deposition to specific forest sites in the Netherlands. More recently, the EDACS model has been successfully applied to estimate dry deposition to forest sites in Germany (Van Leeuwen et al., 1996) and Europe (Draaijers et al., 1996). The EDACS model could be used to calculate nitrogen and base cation dry deposition for

the level II plots. Site characteristics can be obtained though PCC, air concentrations from EMEP (N compounds) or derived from precipitation concentrations in combination with scavenging ratios (base cations), and meteorological data from ECMWF.

A6.3.   Major uncertainties and suggested activities for the future
From the overview in chapter 2 it can be concluded that within the framework of the Intensive Monitoring Program the following models are applicable for estimating canopy exchange: *i)* the canopy budget model of Ulrich (1983) and Van der Maas and Pape (1991), *ii)* the empirical model of Johnson and Lindberg (1992) and *iii)* the inferential model EDACS of Erisman and Draaijers (1995).

The canopy budget model of Ulrich (1983) and Van der Maas and Pape (1991) has proven very useful to estimate canopy exchange of the different components in relatively nitrogen polluted areas such as the Netherlands and Denmark but was up to now not validated under other pollution climates. Major uncertainties associated with this model are the wrong assumption of nil canopy uptake of oxidised nitrogen and the fixed uptake efficiency ratio between H^+ and NH_4^+ of 6, which in reality will vary according to the ecological setting of the forest.

The empirical model of Johnson and Lindberg (1992) can only be applied in areas with relatively low nitrogen pollution (< 1000 eq ha^{-1} yr^{-1}). It is not clear if uptake rates will increase linearly at higher throughfall + stemflow fluxes because nitrogen saturation in the canopy might be expected. The relationship between uptake and deposition appeared to be quit strong for spruce and spruce-fir forests but was found much less pronounced for other tree species. Canopy uptake of nitrogen will not only be governed by deposition amount but also by numerous other factors as explained in Chapter 1. Process-oriented research on canopy uptake of nitrogen in relation to these factors is therefore recommended.

The inferential model EDACS of Erisman et al. (1994) can also be used to estimate of nitrogen canopy uptake and base cation leaching by comparing site-specific deposition estimates derived from the model with throughfall + stemflow fluxes. Deposition estimates from the EDACS model may be improved by using site-specific data on air concentrations and meteorology and by improving parameterisations to calculate dry deposition velocities. The latter are often derived from measurement made at one or only few sites and may not be representative for other ecological conditions and pollution climates.

In view of the above-mentioned uncertainties the following activities may be considered necessary to improve the canopy exchange estimates made within the framework of the Intensive Monitoring Program:

The uptake efficiency between NH_4^+ and H^+ should be investigated in relation tree species and ecological setting. This is possible by means of a relatively simple combined field and laboratory experiment. In summer, six first-order branches need to be collected from different trees using a branch cutter. The branches need to be transported to the laboratory in plastic bags immediately after cutting. The first order branches are subsequently cut into pieces through which several sub-samples are obtained. The different year classes of needles need to be represented in proportion to the amount present in the forest. The wounds resulting from cutting need to be connected to parafilm to prevent leakage of plant sap. About 80 g fresh plant material is put in plastic 1l bottles with a wide opening. The material is shaken for one hour with 900 ml distilled water to remove dry deposition from the branches. Subsequently the branches are shaken for 24 hours (with a speed of about 60 rpm) with 900 ml 100 µM and 1000 µM NaCl, HCl and NH$_4$Cl solution (in total six different solutions). For each solution at least 4 replicates need to be performed. Moreover, for each treatment two blanks are taken along, i.e. the same procedure is followed as described above but than without branches/plant material. The solution is analysed for pH, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^- and SO_4^{2-}. The ratio of H^+ and NH_4^+ uptake for each site can be derived from the differences in exchange activity for the different

concentration levels of the solutions (after Van der Maas et al., 1991). Ratios can be analysed in relation to tree species and ecological parameters also measured at plot. For one or several level II plots also the seasonal variability in the ratio should be investigated by performing described combined field and laboratory experiment on a monthly basis. Mentioned experiment should be performed at every level II plot or e.g. only at plots with strongly deviating pollution climates and ecological setting through which relationships between uptake efficiency ratios and parameters representing the pollution climate or the ecological setting can be derived. These relationships can be incorporated into the canopy budget model of Ulrich (1983) and Van der Maas and Pape (1991). For one or several level II plots also the seasonal variability in the ratio should be investigated by performing described combined field and laboratory experiment on a monthly basis.

Process-oriented research on canopy exchange of oxidised and reduced nitrogen and base cations is necessary to derive relationships between canopy exchange and site parameters also measured within the Intensive Monitoring Program. An estimate of nitrogen uptake and base cation leaching for all Level II plots in Europe can be obtained by *i)* using the canopy budget model of Ulrich and Van der Maas and Pape (1991), *ii)* using the empirical relationship between uptake and deposition of Johnson and Lindberg (1992) and *iii)* comparing throughfall + stemflow fluxes with deposition estimates derived from the EDACS inferential deposition model. Site parameters for which relationships with canopy uptake need to be investigated include tree species, stand age, altitude, soil type, crown condition, foliar nutrient content, soil nutrient status and deposition amount. These relationships may e.g. be used to add a special module in the canopy budget model of Ulrich and Van der Maas and Pape (1991) on canopy uptake of oxidised nitrogen and to evaluate the empirical relationships between nitrogen canopy uptake and deposition derived by Johnson and Lindberg (1991), especially in relation to tree species and nitrogen deposition amounts larger than 1000 eq ha^{-1} yr^{-1}.

Appendix A6.1.   The filtering approach

Model assumptions and a short overview of the calculation scheme for the filtering approach are presented here. The following abbreviations are used: TF = throughfall flux, SF = stemflow flux, DD = dry deposition flux, BP = bulk precipitation flux, CL = canopy leaching, CU = canopy uptake, wa = weak acids, cat = total cations, an = total anions, bc = sum of base cations Ca^{2+}, Mg^{2+} and K^+. DDF = dry deposition factor and EF = excretion factor. An appropriate time step for running the model is 0.5-1 year but, in principle, monthly data can be used as well. In the model, Na^+ in throughfall is assumed not to be influenced by canopy exchange. Furthermore, particles containing Ca^{2+}, Mg^{2+}, K^+, Cl^- and PO_4^{3-} are assumed to have the same mass median diameter as Na^+ containing particles. Dry deposition of Ca^{2+}, Mg^{2+}, K^+, Cl^- and PO_4^{3-} can subsequently be calculated according to (Ulrich, 1983):

$$DD = DDF * BP$$

The dry deposition factor equals:

$$DDF = (TF_{Na}+SF_{Na}-BP_{Na})/BP_{Na}$$

Canopy leaching of these ions is calculated according to:

$$CL = TF+SF-BP-DD.$$

Canopy leaching computed for Cl^- is regarded as deposition of HCl (gas) as Cl^- leaching is generally assumed negligible (Draaijers, 1993). The total canopy uptake of H^+ and NH_4^+ is assumed to equal the total canopy leaching of Ca^{2+}, Mg^{2+} and K^+ minus canopy leaching of Ca^{2+}, Mg^{2+} and K^+ associated with foliar excretion of weak acids (canopy uptake should always balance canopy leaching). To calculate the latter, Van der Maas and Pape (1991) define an excretion factor equal to:

$$EF = CL_{wa}/(CL_{Mg}+CL_{Ca}+CL_{K})$$

where CL_{wa} is computed according to:

$$CL_{wa} = TF_{wa}+SF_{wa}-BP_{wa}-DD_{wa}.$$

It is assumed that all organic acids are leached in a neutral salt form. For the calculation of the excretion factor it is very important that all ions significantly contributing to the cation-anion balance are measured, and also with the highest possible accuracy (Van der Maas and Pape, 1991; Draaijers, 1993). TF_{wa} is assumed equal to TF_{cat}-TF_{an}, SF_{wa} equal to SF_{cat}-SF_{an} and BP_{wa} to BP_{cat}-BP_{an} (e.g. Guiang *et al.*, 1984). Dry deposition of weak acids is assumed equal to bulk precipitation of weak acids (Van Locht and Van Aalst, 1988). The canopy leaching of base cations through exchange with H^+ and NH_4^+ is computed according to:

$$CL_{bc} = (CL_{Mg}+CL_{Ca}+CL_{K}) * (1-EF)$$

Canopy uptake of H^+ and NH_4^+ is subsequently calculated from the sum of exchanged ions of Ca^{2+}, Mg^{2+} and K^+ where it is assumed that, based on experiments in the laboratory (Van der Maas *et al.*, 1991), H^+ has an exchange efficiency (= exchange activity) six times larger than NH_4^+:

$$CU_H = CL_{bc} / (1+ (1 / [6*(TF_H/TF_{NH4})))$$
$$CU_{NH4} = CL_{bc} - CU_H$$

Knowing their canopy uptake, the dry deposition flux of H^+ (from H_2SO_4, $(NH_4)HSO_4$, HNO_3 and HCl) and NH_4^+ (NH_3 and NH_4^+ aerosol) can be computed from TF+SF+CU-BP. Finally, it is assumed that canopy leaching of SO_4^{2-} and NO_3^- is zero allowing the calculation of dry deposition of SO_4^{2-} (SO_2 and SO_4^{2-} aerosol) and NO_3^- (NO, NO_2, HNO_2, HNO_3 and NO_3^- aerosol) according to TF+SF-BP (Van der Maas and Pape, 1991).