

Submanual on Soil Solution Collection and Analysis

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1. Objectives

The purpose of this submanual is to harmonize the procedures of collection and chemical analysis of soil solution samples on the Level II plots in the European network in order to ensure comparability of the chemical soil solution data.

The general aims of this part of the programme are:

- 1) to determine and monitor long-term trends in soil solution chemistry in response to stress factors (e.g. acidifying deposition, climate change),
- 2) to gain an insight into the relationships between forest condition and environmental stress, specifically air pollution and acidifying deposition, and
- 3) to determine input-output budgets of ions from forest ecosystems in relation to deposition and forestry practices.

In addition to the direct effects of stress factors on the forest canopy, forest condition is also influenced by indirect, soil-mediated effects via the root systems of the tree stand. Determination of the chemical composition of the soil solution provides information about the nutrient availability and possible inhibition of nutrient uptake caused by the potentially toxic effects of aluminium and other stress factors on plant roots and mycorrhizas. The continuous monitoring of soil solution quality also contributes to the prediction of future trends in soil condition.

2. Soil solution sampling techniques

Soil solution sampling is being used to an ever-increasing extent for monitoring the effects of air pollution and other stress factors on soil properties. Soil solution can be collected by non-destructive and destructive methods. Non-destructive methods involve the installation of a soil solution collector (a lysimeter) that samples soil solution at the same point. Destructive methods involve soil sampling and subsequent extraction of soil solution in the laboratory. Four sampling techniques are recommended for monitoring soil solution:

- Tension lysimetry
- Zero-tension lysimetry
- Centrifugation of soil samples (centrifuge drainage)
- Saturation extraction

The four procedures differ considerably with respect to the soil solution fraction sampled, the effects of sampling on the site, as well as the extent to which they provide information about temporal and spatial variation in the properties of soil solution. The different soil solution fractions sampled by the four techniques are shown in Fig. 1.

Of the four methods, zero-tension lysimetry is the only one which samples a clearly definable fraction of the soil solution, i.e. free-flowing water that percolates down through the soil when the field capacity is exceeded. Even so, there are drawbacks to this method because zero-tension lysimeters do not necessarily collect, for technical reasons, all of the free-flowing water at the sampling point, and the volume of water collected/surface area of the collector is therefore not always equal to the water flux at the sampling point. Tension lysimetry samples a relatively broad fraction of the soil solution. Soil solution samples are obtained by this technique only when the magnitude of the negative pressure (vacuum) applied exceeds that of the hydraulic forces holding the water in the soil. Tension lysimetry obviously also samples free-flowing water when it is present.

There are important differences between the chemical composition of soil solution obtained by the different techniques. The percolation water obtained using zero-tension lysimeters is the soil solution fraction that is primarily involved in soil formation processes, e.g. the transport of ions down the soil profile, from one horizon to another in the podzolisation process. On the other hand, the chemical composition of soil solution obtained using tension lysimeters usually represents the end result of e.g. buffering and neutralization processes in the different soil horizons.

Tension lysimetry is the technique most widely used for soil solution sampling. The tension lysimeters are mainly based on three types of material: ceramic (e.g. P80 and Aluoxide), plastic (e.g. Prenart) and glass (Fig. 2).

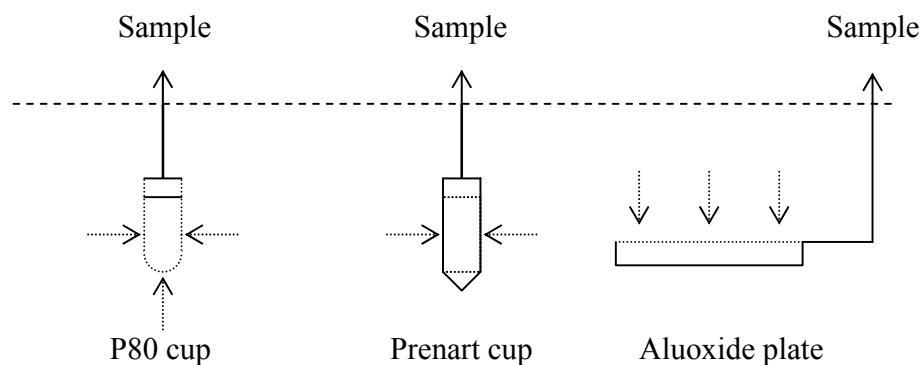


Fig. 2. Examples of the construction of different types of tension lysimeter.

Tension lysimetry utilises vacuum pumps to draw soil solution, via capillary connections, into the lysimeter. The vacuum is also used to lift the soil solution samples up into collections vessels located at or close to the ground surface. Although it is recommended to use a continuous vacuum system, discontinuous systems are much cheaper. The vacuum can be kept constant throughout the sampling period by means of a hanging water column system or by using a pump that constantly maintains the vacuum at the desired level. In a variable tension lysimeter system, the vacuum is continuously regulated to a level that is slightly above the soil water tension. Normally 300 - 600 hPa vacuum are used for soil solution sampling (Beier et al. 1989). In theory, tension lysimeters can be installed

at almost any depth. However, their use in the organic layer is restricted because they are relatively long (6 – 8 cm) and it is also usually difficult to maintain capillary contact with the humus material during dry periods. Plate lysimeters can usually only be installed close to the soil surface because insertion at greater depths results in considerable disturbance to the soil profile.

Zero-tension lysimeters are mainly of two types: plate and funnel lysimeters (Fig. 3).

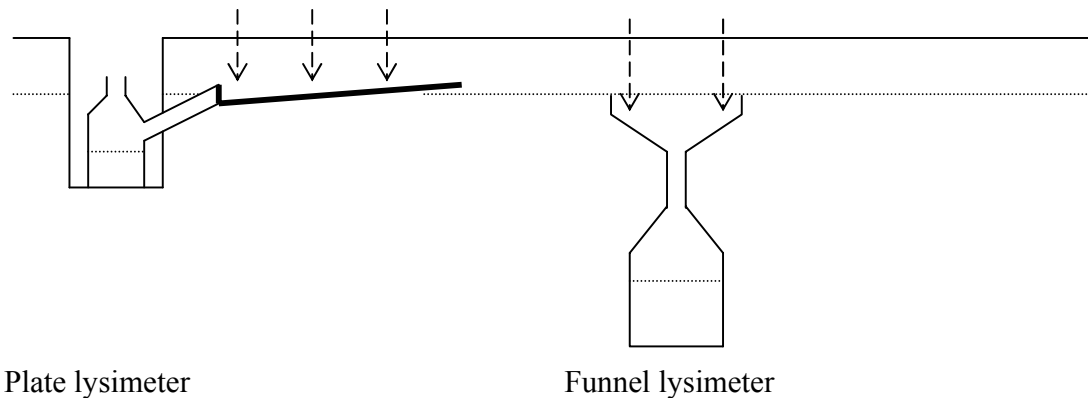


Fig. 3. Examples of different types of zero-tension lysimeter.

The installation of zero-tension lysimeters in stony soils can be difficult. Plate lysimeters can be easily installed under the organic layer on any type of soil, but successful installation in e.g. till soils can be problematic and cause considerable changes in the overlying soil (e.g. aeration and hydrological changes caused by trench excavation). Funnel lysimeters have been successfully installed using special large-diameter soil augers on relatively stony soils down to depths of 40 cm even.

The centrifuge drainage method can also be used, but it has certain restrictions compared to lysimeter techniques. In this method, fresh soil samples (intact cores or mixed composite samples) are centrifuged at high speed in two-piece cups. The soil solution from the soil sample in the upper cup is carried, as a result of centrifugal forces, down into the lower cup. In sandy soils the speed and duration of centrifugation has little effect on the volume of soil solution obtained, but in loamy soils they may have a considerable effect. Therefore, standardization, for instance, at a mean centrifugal force of 10,000 x g for 30 minutes, is advised. Materials such as polyethylene or poly-oxymethylene (deldrin) can be used for the centrifuge cups. The centrifuge cup (250 - 500 ml) consists of an upper cup (holding about 100 – 250 ml of soil) with a perforated base attached to a lower cup to collect the soil solution (Fig. 4). This method is an intermediate form between traditional soil sampling and lysimetry, and its use is restricted by the same limitations associated with soil sampling, e.g. it is a destructive method, the information obtained is relevant only to the sampling instant, and the determination of temporal variation requires successive samplings.

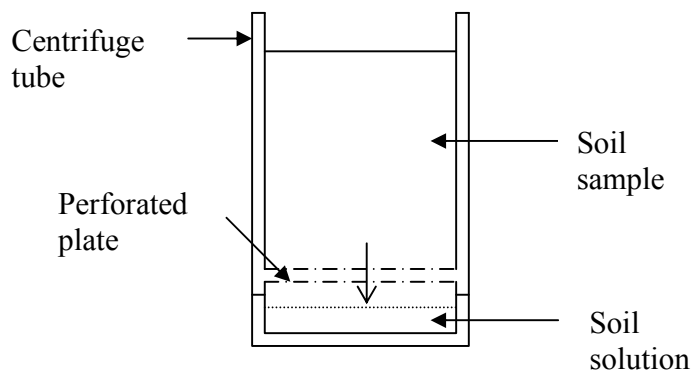


Fig. 4. Cross-section of the 2-piece centrifuge tube used for extracting soil solution from soil samples by the centrifuge drainage method.

Another destructive technique, the saturation extract method (Roades 1982), is appropriate for stony and (heavy) clay soils, and also in soils where other methods will not be successful (e.g. soils in a very dry or cold climate). As with centrifugation, a composite sample can be used. The saturation extract method has the disadvantage of destroying the soil structure and of diluting the soil solution as a result of adding water to saturate the sample. For conservative anions such as chloride and nitrate, the original concentrations can be recalculated if the water content of the soil sample and the amount of water added is known.

A number of reviews and comparison studies have been carried out on the different techniques used to obtain samples of soil solution (Raulund-Rasmussen 1989, Zabowski & Ugolini 1990, de Vries et al. 1995, Giesler et al. 1996, Lawrence & David 1996, Titus & Mahendrappa 1996, Ludwig et al. 1999, Nissinen et al. 1999).

As the type of soil solution sampling technique employed depends on the aim of soil solution monitoring, the following recommendations can be made:

- Repeated soil sampling results in considerable disturbance to the site. Therefore, to produce a time series with short sampling intervals, a non-destructive method is the most appropriate. For continuous monitoring of soil solution chemistry on the Level II plots, tension lysimetry is thus the reference method.
- For monitoring with large time intervals, repeated soil sampling followed by centrifugation (or a saturation extract when centrifugation is impossible) is also appropriate, especially as this approach reduces spatial variation.

3. Preparation and installation of soil solution collectors

Materials suitable for use in lysimeter systems

A summary of the materials used in lysimeter systems is given in Annex 1. The materials considered to be sufficiently free of contaminants are as follows: ceramic material, aluminium oxide, glass sinter, polyamide, polytetrafluoroethylene (PTFE; e.g. Teflon), silica flour, stainless steel powder, polyvinylidene fluoride (PVDF) and polypropylene (PP). If sampling is performed using glass bottles these should be made of clear borosilicate glass, and preferably of laboratory grade.

When sampling for heavy metals, plastic materials are more appropriate than ceramic or aluminium oxide. However, a recent study indicates that Prenart cups absorb heavy metals at low concentrations (Andersen et al. 2002). Ceramic and aluminium oxide lysimeters have also been reported to adsorb significant amounts of heavy metals (except Pb) from soil solutions with a pH > 4.0 (Grossmann et al. 1990). The cation exchange capacity of these materials also affects the soil solution sample. Teflon is hydrophobic, which would make it difficult to obtain soil solution after dry periods. However, the hydrophobic property of teflon has been overcome with the PRENART cups by giving them a special coating.

A number of plastic materials are available for the tubing used in lysimeter systems. However, nylon (PA, polyamide) tubing should be avoided because the softener (benzene sulphonamide) added to certain grades of nylon tubing is water soluble and will result in elevated DOC, N_{tot} and S_{tot} concentrations in the soil solution samples. This problem cannot be eliminated by washing such tubing prior to use, because the softener is an integral part of the plastic and not merely applied to the surface of the tubing. All the materials used in lysimeter systems should be tested for possible contamination problems before use.

The bottles used in collecting water samples from tension lysimeters are invariably made of glass owing to the relatively high negative pressures applied. There is a considerable range of bottles on the market, and contamination from or adsorption by the glass material can pose a considerable problem because the samples remain standing in the bottles for periods of two to four weeks before they are taken to the laboratory or emptied. The bottles selected should be tested in the laboratory.

All parts of the lysimeter system that will be in contact with the soil solution sample should be acid washed (1 N HCl), followed by rinsing with deionized water (see Beier et al. 1989), prior to installation in the field. Care should be taken during installation of the lysimeters in order to minimize disturbance to the soil profile.

Tension lysimeters

A hole is drilled with an auger having a diameter slightly larger than that of the cup. The hole can be made vertically or at an angle (e.g. 45°) to the ground surface, or from the wall of a soil pit. If the soil is very loose it is difficult to install a cup without contaminating the hole with material from the overlying horizons. Horizontal installation from a pit will minimize this problem. However, horizontal installation is not always successful as there may be problems in sucking the soil solution sample from the lysimeter into the collection bottle.

It is vital to achieve good hydraulic contact between the suction cup and the soil. This is achieved by installing the cup in a slurry of the material taken by the auger from the bottom of the hole. If this material is not very fine-textured, hydraulic contact can be improved by sieving soil taken at a corresponding depth in a pit dug outside the subplot/plot. The fine material passing through the sieve is used to prepare the slurry. If acid-washed, quartz powder has to be used, then great care should be taken to ensure that all traces of elements (especially Ca) have been removed by prolonged washing. Bentonite may not be used as this can release ions that affect the soil solution chemistry. If the cup does not have a rigid supporting tube, the hole should be backfilled with material from the corresponding horizons. Soil from the auger is an obvious source of backfill material, but additional material is usually required from a nearby source.

Water should be prevented from seeping down the tube running from the ground surface down to the lysimeter. This can be avoided by completely burying the lysimeter tube in the soil, or by attaching a collar of a flexible inert material around the top of the tube. If the lysimeters are connected with thin tubing, this problem can be avoided by running the tubing horizontally through the humus layer towards the collection bottle. Installing the lysimeter at an angle has the advantage that the soil layer lying above the lysimeter is not disturbed. Replacement of the part of the tubing that runs above ground can be facilitated by inserting a connector at the point where the tubing passes down into the ground. This also reduces the likelihood of losing a lysimeter because, if the above-ground tubing is pulled up (or gnawed by animals), the part of the tubing leading down to the lysimeter remains intact.

Zero-tension lysimeters

There are two types of zero-tension lysimeter currently in use in the ICP Forests Programme – plate lysimeters and funnel lysimeters.

To install zero-tension plate lysimeters, a pit has to be dug and the lysimeter installed into the wall. This should be done immediately next to the selected location of the lysimeter so that it can be installed with as little disturbance to the overlying soil as possible. Plate lysimeters can also be installed immediately below the humus layer by cutting out a square of humus larger than the plate, and then carefully lifting off the intact humus “mat”. Part of the underlying mineral soil is then removed so that the lysimeter plate slopes towards the collector tube on the side of the plate. The humus mat is then carefully replaced. The main disadvantage to this technique is that the roots of the trees and ground vegetation have to be cut, and it may take a considerable time before the installation site

returns to normal. This problem can be partly avoided by inserting the plate through a single cut through the humus layer. However, although it is relatively easy to insert the plate, it is difficult to ensure that the plate is sloping in the right direction (i.e. towards the collector tube).

One type of funnel lysimeter consists of a plastic funnel containing acid-washed, fine quartz fitted to the top of a plastic collector bottle. The lysimeters are installed by first removing an intact soil core (larger than the diameter of the funnel) down to the required depth using a special auger, and the lysimeters are then placed in a shaft sunk below the removed soil core. The soil core is then carefully replaced. Soil solution is removed from the lysimeters by means of a plastic tube leading down into the collection bottle (for details of the construction, see Derome et al. 1991). One problem with funnel lysimeters is that the roots leading into the overlying soil profile are always cut during installation. This means that soil solution chemistry will not necessarily reflect the normal situation until the roots have grown back into the soil core. For instance, there is frequently a flush of DOC and macronutrients in the soil solution following installation owing to the cessation of nutrient uptake by the roots and an increase in nutrient mineralization.

Caution should be taken when interpreting soil solution data from recently installed lysimeters as chemical reactions with the porous cup or disturbance of the soil due to installation may affect the results. The samples from the first 2 or 3 sampling events after installation should therefore be discarded. In the case of funnel lysimeters, a period of one year for the roots to grow back is required. In long-term monitoring, however, this is not a problem.

4. Sampling criteria

4.1. Location of the samplers

The soil solution samplers (lysimeters) should be installed near to the plot where the crown vitality assessment is conducted. The lysimeters should also be located as close as possible to the plot used for throughfall sampling. If a subplot has been established for throughfall sampling this can be used for soil solution sampling. A separate representative subplot can also be used. The lysimeters should be randomly or systematically located over the whole soil solution subplot, although this may be limited by the presence of stones or tree stems (no minimum distance to a tree is specified). It is recommended that wooden walkways be used to access the sampling points in order to minimise soil compaction and damage to the surrounding ground vegetation. Because of disturbance to the soil during installation, zero-tension lysimeters should not be installed in the immediate vicinity of the plot where tree parameters are monitored. Lysimeters that have already been installed can be maintained, but new lysimeters should be installed in accordance with the above.

4.2. Sampling depths

It is recommended to install the lysimeters at fixed depths, but installation by horizon is also acceptable.

Soil solution collectors

It is strongly advised to install lysimeters at two depths at least, i.e. within the rooting zone (suggested depth 10 - 20 cm) in order to be able to monitor the concentrations of nutrients and toxic elements near the fine roots, and below the rooting zone (suggested depth 40 - 80 cm) in order to be able to estimate the output of elements. The depth of the lysimeters is measured from the interface between humus and mineral soil. It is also advised to install lysimeters immediately below the humus layer.

Soil samples

If soil solution is to be obtained using the centrifugation or saturation extract methods, the same soil layers as those specified in the soil manual are to be sampled: humus layer, and the 0 - 10, 10 - 20, 20 - 40 and 40 - 80 cm mineral soil layers. A selection or combination of these layers can be sampled.

4.3. Number of replicates

The extremely high spatial variation in both soil solution chemistry and percolation water fluxes, caused by e.g. variation in tree cover, ground vegetation, microtopography and soil properties, means that a large number of samples (replicates) is needed to obtain a sufficient representative estimate of soil solution chemistry on a plot scale. However, it should be recognised that there is a clear difference between sampling to obtain a representative estimate of soil solution chemistry on the whole subplot/plot (goal 1), and sampling to obtain an empirical estimate of the volume of water percolating down through the whole subplot/plot (goal 2). The number of replicate samplers required to achieve goal 1 is much lower than that for goal 2 and, in addition, goal 2 presupposes the use of zero-tension lysimeters or similar equipment.

The number of samples at the same sampling depth required to obtain a plot mean that is within $\pm 20\%$ of the population mean, with a confidence level of 95 %, is at least 10 to 12 (Grossmann and Moss 1994, de Vries and Leeters 1994, Manderscheid and Matzner 1995). However, the number of samples also varies according to the ion or element in question. According to Bille-Hansen (2002), the number of replicate lysimeters at a depth of 80 cm required to obtain a reliable estimate of Ca and K using tension lysimeters was 5, for Na, Cl, SO₄ and NO₃ ca. 9, and for DOC and Al > 10.

Considering the limited budget available, an increase in the number of replicates at each depth would result in a decrease in the number of plots that could be monitored. Consequently, at least 3 replicates are considered mandatory at each soil depth. It is also strongly advised that two extra lysimeters are installed at each depth in order to ensure that at least 3 samples are obtained at each sampling. It should be noted that 3 replicate

samples provide information on the trends in soil solution chemistry at specific points in the stand, rather than a fully representative estimate of the site. If soil solution monitoring is being used in budget studies, then it is strongly advised to install at least 10 replicates.

Soil solution samples collected with lysimeters at the same depth may also be pooled to reduce the number of samples to be analysed. However, there are considerable disadvantages to this procedure. Pooling means that spatial variation cannot be estimated, and missing values can result in incorrect means if the spatial variation between the individual lysimeters is high. For example, if soil solution from the sampler with the highest or the lowest concentration is missing during a sampling period, this will cause considerable bias in the mean value. This problem can be avoided to some extent if the spatial variation between the lysimeters has been earlier quantified. The values of missing samples can then be generated using regression equations and volume-weighted values. The use of values derived from pooled samples rather than mean values of individual samples also considerably restricts the possibilities of investigating the relationships between e.g. soil solution quality and foliar chemistry at the plot level.

Missing subsamples do not cause any problems in the case of soil sampling for centrifugation or the extraction of soil solution because a large number of subsamples (e.g. 25) can be pooled to give reliable mean values of soil solution chemistry.

4.4. Sampling frequency

On plots with other intensive monitoring activities, e.g. deposition and meteorological measurements, soil solution sampling should be carried out at the same time as deposition sampling. Monthly, or preferably biweekly, sampling is required when calculating the input-output budgets for all elements on the more intensive 10% of the Level II plots. On the other Level II plots, soil solution should be collected once, but preferably four times a year (twice during the growing period and twice during the dormant period unless the ground is frozen) in order to obtain a periodic estimate of nutrient availability and the concentrations of toxic elements in the rooting zone. In the case of soil sampling for the extraction of the soil solution, four samplings is the maximum permissible number because of the destructive sampling procedure. Sampling should be carried out in the same month in consecutive years.

4.5. Sampling procedures

The volume of the soil solution samples should be determined in the field using a volumetric cylinder or portable balance (weight). Individual volume measurements are required when calculating mean ion or element concentrations if the analyses are carried out on individual samples. Furthermore, there is frequently an inverse relationship between sample volume and ion concentrations, especially when sampling during relatively dry conditions. If soil solution samples are to be pooled in the field, then all the samples from the same sampling depth should be mixed in a suitable plastic container.

4.6. Perched water and groundwater

At many forested sites in northern and central Europe the surface soil is periodically subjected to a rise in the groundwater table or perched water level. In addition, short-term water-logging of the surface soil can also following snowmelt in the spring when the ground is still partly frozen. Only water that is present in the unsaturated soil layers above the perched water and groundwater levels should be sampled. However, this is not always easy to comply with in practice. The position of the groundwater table or perched water level can be followed by means of observation pipes installed at suitable points on the plots, as well as estimated if soil moisture measurements are carried out on the plot as part of the meteorological monitoring work.

5. Protection of the samples in the field and during transportation to the laboratory

5.1. Soil solution

Protecting the samples in the field from spoilage caused by microbial activity is one of the most important aspects of soil solution sampling. The location of the samples (i.e. belowground with zero-tension lysimeters or aboveground with tension lysimeters) and the length of time that the samples remain in the collection vessel varies depending on the type of lysimeter used and on the length of the sampling period (i.e. continuous or discontinuous sampling). There are a number of ways of ensuring that the samples remain pristine.

Keeping the soil solution in a cool ($< +4^{\circ}\text{C}$), dark location within the lysimeter system is the recommended means of minimising biological activity.

In the case of zero-tension lysimeters this is not usually a problem because the soil solution flows freely into a collection vessel located below the depth of the lysimeter. However, if the temperature of the soil at the sampling depth rises substantially, then sampling must be carried out at shorter intervals. These sub-samples can then be bulked in the laboratory to give the required sampling period.

The collection bottles used in tension lysimetry are usually located close to the ground surface. Keeping the bottles dark in boxes or holes, or covering them with aluminium foil if they have to be located on the ground surface, is usually sufficient except during the warmest parts of the year. However, dark bottles should not be used for this purpose because they can contaminate the samples. If the temperature of the air or the surface soil rises substantially, then sampling must be carried out at shorter intervals. These sub-samples can then be bulked in the laboratory to give the required sampling period. The use of organic or inorganic preservatives is permitted, but should be avoided as far

as possible because it may interfere with the chemical analyses. According to the literature, the sampling interval used in lysimeter studies can vary from two days to one month (Alberts et al. 1977; Beier et al. 1992, Haines et al. 1982; Hendershot and Courchesne, 1991).

It is preferable not to replace the collecting bottle after each sampling period since it is soil solution from the same lysimeter that is collected each time. This will help to minimise the risk of contamination through human error. However, if there are signs of algal and fungal growth in the bottle, then it should be immediately replaced with a clean, acid-washed bottle. All the bottles should be removed and acid-washed in the laboratory at suitable intervals.

Any lysimeter tubing that is lying on the ground surface should be protected against sunlight. It is recommended that this tubing be replaced each year.

Transportation to the laboratory should be carried out as quickly as possible using closed boxes containing cold packs. If the transportation distance is long, it is recommended to use express post or a courier service that can guarantee delivery within 24 hours (preferably to arrive at the laboratory the following morning). Special boxes should be used for this purpose.

5.2. Soil samples for centrifugation or extraction

Soil samples collected in the field should be kept cool in plastic or polyethylene bags and transported and stored at $< +4^{\circ}\text{C}$ until centrifugation or the preparation of the saturation extract. Changes occur relatively rapidly in the samples due to excision of the roots and exposure to an oxygen-rich atmosphere. According to Giesler (1996), centrifugation should be carried out within one day (18 - 30 hours) after soil sampling. This problem can be minimised by standardising the time elapsed between sampling and centrifuging or extracting the samples.

6. Chemical analysis

A list of the chemical and physical parameters to be determined is given in Table 7. Although the list includes both mandatory and optional parameters, in practice all the cations and anions that are present in significant amounts in the samples are required for calculating ion balances (see Section 8), as well as Na for calculating acid-base budgets. The list of parameters measured in the individual countries will therefore depend on the prevailing conditions. Similarly, it is advisable to measure NH_4 in areas with high NH_4 deposition (e.g. above 20 kg $\text{NH}_4\text{-N/ha/a}$). The concentrations of Zn and Cu are also important for nutrient cycling studies because they are important micronutrients.

Table 7. The chemical and physical parameters (mandatory and optional) to be determined on soil solution samples.

Parameter	unit	mandatory/optional
Electrical conductivity	$\mu\text{S cm}^{-1}$ 25 °C	mandatory
pH		mandatory
Alkalinity	$\mu\text{molc/l}$	optional (if pH > 5)
DOC	mg/l	mandatory
Na	mg/l	optional
K, Mg, Ca,	mg/l	mandatory
Al _{total}	mg/l	mandatory (if pH < 5)
Al _{labile}	mg/l	optional
Fe, Mn,	mg/l	optional
P _{total}	mg/l	optional
NO ₃ -N, SO ₄ -S	mg/l	mandatory
NH ₄ -N	mg/l	optional
Cl	mg/l	optional
Zn, Cu	$\mu\text{g/l}$	optional
Cr, Ni, Pb, Cd	$\mu\text{g/l}$	optional
Si	mg/l	optional

Immediately on arrival in the laboratory (or after extraction in the laboratory), the soil solution samples should be transferred to a cold (+4°C), dark storage space (e.g. refrigerator) up until analysis. Electrical conductivity and pH should be determined as soon as possible on a separate aliquot of the unfiltered sample. Many types of pH electrode release K⁺ into the sample and therefore a separate aliquot of the sample should be used to avoid contamination. Similarly, if electrical conductivity is measured on the same aliquot of sample, then this should be done before pH measurement.

The remaining sample should then be filtered (0.45 μm membrane filter). Although this procedure is not necessarily required for samples obtained by tension lysimetry, it does increase the stability and lifetime of the samples. Many analytical techniques also require this procedure (e.g. ion chromatography). The make/type of membrane filter used should be tested beforehand in order to ensure that there is no release of soluble or particulate, carbon-containing material/compounds from the membrane. Many types of membrane release small amounts of particulate material (containing carbon) when first used, and this will affect the DOC determination. However, this problem can be avoided by “rinsing” the membrane in the membrane holder with a known volume of pure water or sample prior to filtration of the sample proper. Each laboratory should determine the minimum amount of rinsing water required. Tests on a number of membrane types have shown that ca. 50 ml is sufficient.

pH measurement can also be repeated at this stage if it is required for determining the ion balance of the sample (see Section 8). After filtration, a subsample should be stored at +4 °C and analysed as soon as possible for alkalinity, dissolved organic carbon (DOC), labile

Al (Al^{3+}), $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ and, if applicable, for other cation and anions. Excessively long storage times should be avoided in order to prevent chemical changes caused by microbial activity in the samples. However, as the samples have been filtered through a $0.45\ \mu\text{m}$ filter, they should be relatively sterile. This problem can also be avoided by freezing the samples, since there are reports that freezing does not have a detrimental effect on the results of analysis of $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, N_{total} , and other cation and anions. However, the freezing of samples with relatively high DOC values can result in the precipitation of part of the DOC after thawing. Alkalinity and labile Al should not be determined on frozen samples.

Labile Al can be determined by a number of different techniques (Wickstrøm et al. 2000), but the simplest and cheapest way is to remove this fraction by passing the sample through a cation exchange column. The difference between the Al concentration before and after passage through the column is equal to the labile Al concentration. The Al concentration before and after passage can be determined by AAS or ICP, or by e.g. FIA. The work load on the laboratory can be considerable if labile Al has to be determined on a large number of samples as soon as possible after they arrive at the laboratory. This problem can be reduced by carrying out the determination in two stages: 1) immediate fractionation of Al_{total} using a cation exchange column, and 2) preservation of the two solutions to be analysed for Al with suprapure 65% HNO_3 , and subsequent determination up to 2-3 weeks after fractionation (Derome et al. 1998).

Another subsample should be acidified (e.g. with suprapure 65% HNO_3 to $\text{pH} < 2$) in order to avoid the absorption of metal cations on the inside surface of plastic bottles (if used), as well as possible changes caused by microbial activity. The preserved samples can be stored for several weeks prior to analysis by AAS, ICP etc.

7. Quality assurance programme and data verification

7.1. Quality assurance programme

Quality assurance and control in the field and in the laboratory are dealt with in detail in the Submanual on the Measurement of Deposition, and not repeated here.

7.2. Data verification

It is extremely important to check the results of all chemical analyses for errors. Two procedures are appropriate for checking the validity of analyses carried out on soil solution samples: 1) ion balances, and 2) comparison of measured and calculated electrical conductivity values.

7.2.1. Ion balances

In order to make the results of ion balance calculations meaningful, they should include all the major ions present in the solution. It is therefore recommended that all the major cations and anions be determined on the samples, irrespective of whether they are mandatory or optional (see Section 7). In a solution, the sum of negative and positive charges must be equal. The so-called percentage difference (PD) is used to check the ion balance of a solution:

$$PD = 100 \times (\sum \text{cations} - \sum \text{anions}) / (0.5 \times (\sum \text{cations} + \sum \text{anions})),$$

where the concentration of each cation and anion is expressed as $\mu\text{eq/l}$.

The use of ion balances for verifying soil solution data is associated with a number of analytical and practical problems:

- 1) All analytical methods include a certain amount of error, and the individual ions in an ion balance calculation each have their own error component. A typical ion balance may include 7 major cations (e.g. H^+ , Al^{3+} , Ca^{2+} , Mg^{2+} , Ca^{2+} , Na^+ , NH_4^+) and 5 anions (e.g. SO_4^{2-} , NO_3^- , Cl^- , ALK^- , OA^-). OA refers to organic anions, which are weak acids, and ALK to alkalinity (primarily HCO_3^-). As this error factor is cumulative, it is clear that the total analytical error can be considerable and, in practice, it is not usual to achieve a perfect balance between the number of negative and positive charges. The acceptable difference between cations and anions for solutions of different ranges of ion concentration has been set by WMO-GAW as:

Anions and cations	Acceptable ion difference
≤ 50 ($\mu\text{eq/l}$)	$\leq \pm 60\%$
$> 50 \leq 100$ ($\mu\text{eq/l}$)	$\leq \pm 30\%$
$> 100 < 500$ ($\mu\text{eq/l}$)	$\leq \pm 15\%$
> 500 ($\mu\text{eq/l}$)	$\leq \pm 10\%$

- 2) The H^+ ions in a soil solution sample are calculated from the pH value. However, because the pH is measured prior to filtration but the other ions are determined after filtration, there will be an error introduced into the ion balance calculation if filtration changes the pH of the solution. This is very often the case if the sample contains fine particles of organic matter or if the DOC concentration is relatively large. It is therefore recommended that the pH of samples which are likely to have a relatively high DOC concentration should also be measured after filtration, and this pH value be used in calculating the ion balance of the sample.
- 3) The charge on the dissolved organic matter in a soil solution sample can be determined by titration, but this is rather demanding and time-consuming, and not

- necessarily a very precise procedure. The charge on dissolved organic matter in the soil solution can be calculated from the DOC concentration using an equation (e.g. Oliver et al. 1983). However, as this equation was originally developed for surface waters, there is reason to assume that the dissolved organic matter in soil solution samples varies according to the sampling depth and to the type of tree cover on the monitoring plot. The participating countries should derive equations for their individual monitoring plots (and possible different sampling depths) using the soil solution data collected so far from these plots.
- 4) The concentrations of metals used in calculating ion balances may not in all cases be the same as the concentrations of the corresponding metal ions. This is true for Al, and also to some extent for Ca and Mg and possibly other metals, in samples with high DOC concentrations. In podzolic soils, for instance, a relatively high proportion of the Al determined by AAS or ICP is in fact complexed with organic matter, and the concentration of the ionic form of Al (i.e. labile Al, Al³⁺) is low. This will cause considerable errors in the ion balance calculation. Similarly, the concentrations of Ca and Mg determined by ion chromatography are frequently much lower than the concentrations obtained by AAS or ICP.
 - 5) Alkalinity measurement is not very satisfactory for HCO₃⁻ determination because other substances (e.g. organic anions and Al) may be titrated as well. HCO₃⁻ can also be determined as inorganic carbon with a carbon analyser, but the detection limit is not always good. Bicarbonate can also be estimated from the pH using equilibrium calculations.

7.2.2. Comparison of measured and calculated electrical conductivity values

A relatively reliable and easy way to check the validity of the data is to compare the electrical conductivity of a sample, calculated from the concentrations of the individual ions, with the measured electrical conductivity value (MEC). The calculated electrical conductivity (CEC) is obtained using the formula:

$$CEC = \sum \lambda_i C_i$$

The values of λ for the individual ions at 20° and 25°C are given in the Submanual on the Measurement of Deposition. The calculation procedure is also described in detail in the same submanual.

The acceptable difference between the measured and calculated electrical conductivity values for solutions with different electrical conductivity ranges has been set by WMO-GAW as:

Measured electrical conductivity	Acceptable conductivity difference
≤ 5 ($\mu\text{S}/\text{cm}$)	$\leq \pm 50\%$
$> 5 \leq 30$ ($\mu\text{S}/\text{cm}$)	$\leq \pm 30\%$
> 30 ($\mu\text{S}/\text{cm}$)	$\leq \pm 20\%$

8. Assessment of soil water fluxes

Soil water fluxes are required for determining input-output budgets of ions in the monitoring plots. Since soil water fluxes usually cannot be measured directly, they have to be estimated indirectly using models (Kutilek & Nielsen 1994).

Four types of method are recommended for the estimation of soil water fluxes on the level II plots:

- Climatic water balance
- Storage models
- Richards' models
- Chloride balance

These models are of varying complexity and require a number of parameters, and initial and boundary conditions (Table 8.1). The temporal resolution of the models varies between several minutes and one year. The input/output time step also differs with respect to the spatial resolution.

Table 8.1. The parameters, and initial and boundary conditions required by the different methods for estimating soil water fluxes.

Parameter	Climatic water balance	Storage model	WATBAL model	Richards' models	Chloride balance
Precipitation	X	X	X	X	X
Evapotranspiration	X	X	(X) ⁵	X	
Soil water retention curve ($\Theta - \Psi$)		X ²	(X) ⁶	X	
Hydraulic conductivity ($k - \Psi$)		X ³		X	
Vertical distribution of water uptake	X ¹	X ¹		X	
Water content (Θ)	X ¹	X ¹	(X) ⁶	X ⁴	
Soil water potential (Ψ)			(X) ⁶	X ⁴	
Cl ⁻ concentration in stand throughfall and soil solution					X

¹ is required for estimating the water flux within the rooting zone, ² for determination of the storage capacity (e.g. field capacity), ³ in some storage models, ⁴ is used as a control value in calibrating the model, ⁵ is calculated by WATBAL using latitude, precipitation, temperature and cloudiness input data, and ⁶ WATBAL requires the soil-available, water holding capacity, which can be calculated from these parameters..

All the methods require the amount of precipitation as input. The amount of precipitation within the stand has to be used for the chloride balance method. Evapotranspiration is another important boundary condition for all the methods except for the chloride balance method. Evapotranspiration is the sum of interception, evaporation, and transpiration. Potential evapotranspiration is regulated only by the meteorological conditions and stand characteristics, whereas the actual evapotranspiration may be lower due to limited water availability.

Like the soil water flux, potential evapotranspiration has to be estimated indirectly by means of empirical or physically based models. Relatively simple empirical models include the formulae of Haude 1958, Turc 1954, and Makkink 1957. The semi-empirical models of the Penman-Monteith type are most frequently used, but they require more input parameters (Monteith 1965). Frequently used models are discussed by Brutsaert 1982, Crago & Brutsaert 1992, and Wallace 1993.

Actual evapotranspiration can be estimated from the potential evapotranspiration by means of a reduction factor, which is dependent on the soil water content or soil water potential and atmosphere demand (e.g. Feddes et al. 1978). Interception can be estimated from open field and stand precipitation measurements, or by means of an interception

model (e.g. Rutter et al. 1971, Gash 1979). Potential soil evaporation can be estimated from the potential evapotranspiration using soil coverage (e.g. leaf area index) as a reduction factor (Ritchie 1972, Belmans et al. 1983). Actual soil evaporation can be calculated by taking into account the length of the dry period (Black et al. 1969).

The choice of an appropriate method for estimating the soil water flux depends on the overall soil water regime of the plot. All four types of model are suitable for soils with one-dimensional, vertical water flow, and no upward flow of water from the groundwater to the rooting zone. Richards' model covers the widest range of flow regimes because of its physically based structure.

8.1. Climatic water balance

For the water balance of soils the continuity equation takes the form:

$$Q_v = P - (I - E - T) - Q_s \pm \Delta\Theta \quad (1)$$

where Q_v = soil water flux, P = precipitation, $(I - E - T)$ = evapotranspiration, i.e. (Interception + Evaporation + Transpiration), Q_s = surface runoff, $\Delta\Theta$ = change of soil water content.

In forest ecosystems in southern and central Europe, surface runoff is usually negligible. For longer periods, the change in the soil water content also becomes negligible; thus the difference between precipitation and evapotranspiration equals the soil water flux. In temperate regions the soil water content at the beginning of the growing season is assumed to be at field capacity. Hence, the annual soil water flux can easily be calculated if precipitation and actual evapotranspiration are available. However, care should be taken, because an extremely dry or wet period at the beginning of the growing season may cause a strong deviation of the soil water content from field capacity.

For periods shorter than one year, the climatic water balance equation can only be applied if the soil water content is known. If information on the vertical distribution of water uptake by plant roots is available, flux rates can be computed for different soil layers. The outflow from the upper layer is the inflow for the underlying layer.

8.2. Storage models

Storage or field capacity models are an extension of the climatic water balance. In storage models, the flow in the soil is routed through one or more storages, which are usually represented by soil layers. The storage capacity is usually defined by the field capacity. In its simplest form, the storage is increased by precipitation or by inflow from an upper soil layer (storage) and decreased by evapotranspiration and outflow from the storage. It is assumed that outflow only occurs above the maximum storage capacity (2a). Below the

maximum storage capacity, the soil water content can only be reduced by evapotranspiration (2b).

$$\frac{\partial \Theta}{\partial t} = \frac{\partial (J(\Theta))}{\partial z} - S(\Theta) + P \quad (\Theta > \Theta_{fc}) \quad (2a)$$

$$(\Theta < \Theta_{fc}) \quad (2b)$$

where Θ = the actual soil water content, Θ_{fc} = the soil water content at field capacity, and S = a sink term.

More complex models of this type restrict the vertical water flux in accordance with the soil water content or hydraulic conductivity. An upward soil water flux can also be included in these models (Wesselink et al. 1995).

The WATBAL model

WATBAL (Starr 1999, Barnette & Starr 2000) is a monthly water balance model for forested stands/plots, i.e. it calculates the components of the water balance equation:

$$P = ET + R \pm \Delta SM,$$

where: P = precipitation, ET = evapotranspiration, R = runoff (the soil water flux), and $\pm \Delta SM$ = changes in soil moisture storage. All units are in mm of water, and the time interval is monthly. It uses relatively simple and readily available climate variables (e.g. precipitation, air temperature and cloudiness) and the available water capacity (AWC) of the soil, which can be derived using transfer functions based on soil texture, bulk density, organic matter content (i.e. data collected on level II plots) or from the soil moisture curve. It handles sloping sites if the appropriate slope factors are given and snowmelt. Evapotranspiration is calculated using an estimation of global radiation using a reference crop equation adjusted by a crop (forest stand) coefficient to take into account the greater evapotranspiration from forests. Besides giving soil water flux values, all the components of the water balance are determined: potential and actual evapotranspiration, soil moisture, snowpack store and snowmelt, as well as global (direct and diffuse) radiation. Drought stress to the stand can be calculated as either the difference between PET and AET or AWC and SM. WATBAL is freely available at: http://www.metla.fi/hanke/3098/ewat_bal.htm.

8.3. Richards' models

This class of models is physically based. It is the most detailed one, and usually requires the most input parameters. A combination of the Darcy equation and the continuity equation yields the Richards' equation, which can be formulated in a one-, two-, or three-dimensional form. For the one-dimensional type:

$$\frac{\partial \Theta}{\partial t} = \frac{\partial}{\partial z} [K(\psi) \cdot (\frac{\partial \psi}{\partial z} + 1)] - S(\psi) \quad (3)$$

where $S(\psi)$ = a sink or source term.

For practical purposes, the Richards' equation is usually solved numerically. Analytical solutions are restricted to special boundary conditions. The essential input parameters are the soil water retention curve and the hydraulic conductivity as a function of soil water potential. Richards' models usually have to be calibrated, and they are limited to situations in which the Darcy equation holds. Macropore flow usually cannot be simulated with Richards' models, but there are some hybrid models that deal with both matrix flow and macropore flow. Richards' models are also not very suitable for the estimation of water fluxes in organic layers.

8.4. Chloride balance

This method is ideally suited for use with soil solution data obtained using zero-tension lysimeters because these lysimeters only sample soil solution (i.e. percolation water) flowing down from overlying soil layers. The inherent problem with tension lysimeters is that they sample soil solution from soil layers of varying thickness both above and below the lysimeter, depending on the vacuum applied and the moisture content of the soil during the sampling period.

The chloride balance method is based upon the assumption of a balanced Cl^- input/output budget of the soil:

$$Q_i \cdot c_i = Q_v \cdot c_v \quad (4a)$$

solving for Q_v

$$Q_v = Q_i \cdot \frac{c_i}{c_v} \quad (4b)$$

where Q_i = the input water flux, Q_v = the output water flux, c_i = the input Cl⁻ concentration, and c_v = the output Cl⁻ concentration.

This method only requires data on chloride concentrations in the soil solution and in stand throughfall, and can be applied for all soil layers where soil solution sampling is conducted. Because the input signal is not constant and some chloride is retained in the ecosystem, this method cannot be applied for periods of less than a couple of years. The water flux within one time step should be more than the water content at field capacity for the respective soil volume.

8.5. Recommendations

The major objective of the determination of soil water fluxes is the estimation of element (ion) fluxes below the rooting zone on an annual basis. Temporal trends of element fluxes over periods lasting for several years are also required. The climatic water balance method is the recommended method for these purposes. It is recommended that the climatic water balance method be mandatory on plots for which deposition and meteorological measurements are available. It is also recommended that the Makkink formula be used for the estimation of evapotranspiration. The use of the Makkink formula requires the measurement of global radiation and air temperature. However, the Makkink formula contains an empirical factor that is valid for a limited region only, and for other regions this factor has to be derived through inverse calibration (e.g. Choisnel et al. 1990). The application of storage models or Richards' models is recommended if detailed information on the water content or soil water potential are available, and if water fluxes within the rooting zone or for short time steps have to be determined. The chloride balance may be used only if information on the accumulation or loss of elements in/from the soil is needed.

Potential evapotranspiration (Makkink 1957):

$$Etp_{Mak} = \frac{s}{s + \gamma} (C_1 \cdot R_G + C_2)$$

R_G = global radiation (W/m²)

s = derivative of the saturated water vapour curve (hPa/K)

γ = psychrometer constant (0.65 hPa/K)

L = specific heat of evaporation (J/g)

c_1, c_2 = constants

Makkink (1957), The Netherlands: $c_1 = 0.61, c_2 = 0.12$

de Bruin (1987), The Netherlands: $c_1 = 0.65, c_2 = 0$

Choisnel et al. (1990), Europe (EU): $c_1 = 0.75, c_2 = 0$

References

Alberts, E.E., Burwell, R.E. & Schuman, G.E. 1977. Soil nitrate-nitrogen determined by coring and solution extraction techniques. *Soil Sci. Soc. Am. J.* 41:90-92.

Andersen, M.K., Raulund-Rasmussen, K., Strobel, B.W. & Hansen, H.C.B. 2002. Adsorption of cadmium, copper, nickel and zinc to a poly(tetrafluorethene) porous soil solution sampler. *Journal of Environmental Quality* 31:168-175.

Barnette, M. & Starr, M. 2000. Soil Water flux modelling with WATBAL. In: Kleemola, S. and Forsius, M. (Eds), 9th Annual Report 2000. UN ECE ICP Integrated Monitoring. Finnish Environment Institute, Helsinki, Finland. *The Finnish Environment* 427: 36-38.

Beier, C., Butts, M., v. Freiesleben, N.E., Jensen, K.H. & Rasmussen, L. 1989. Monitoring of chemical conditions and ion fluxes in soils. In: *Methods for integrated monitoring in the Nordic countries*. The Steering Body for Environmental Monitoring. The Nordic Council of Ministers. *Miljorapport* 1989, 11:63-138.

Beier, C., Hansen, K., Gunderson, P. & Andersen, B.R. 1992. Long term field comparison of ceramic and poly(tetrafluoroethene) porous cup soil water samplers. *Environ. Sci. Technol.* 26:2005-2011.

Belmans, C., Wesseling, J.G., & Feddes, R.A. 1983. Simulation model of the water balance of a cropped soil: SWATRE. *J. Hydrol.* 63:271-286.

Bille-Hansen, J. 2002. In: Derome, J, Bille-Hansen, J. & Lindroos, A-L. Review of the lysimeter techniques employed in monitoring soil-solution quality in the European level II intensive plot network, and assessment of the intercompatibility of the soil solution data. BMVEL, Germany, 41 pp.

Black, T.A., Gardner, W.R. & Thurtell, G.W. 1969. The prediction of evaporation, drainage and soil water storage for a bare soil. *Soil Sci. Soc. Am Proc.* 33:655-660.

Brutsaert, W. 1982. *Evaporation into the atmosphere: Theory, History and Applications*. Boston, Reidel, 299 pp.

Choisnel, E., de Villele, O. & Lacroze, F.. 1990. Une approche uniformisee du calcul de l'evapotranspiration potentielle pour l'ensemble des pays de la Communaute Europeenne. Rapport final, Direction de la Meteorologie Nationale Paris, 69 pp.

Crago, R.D. and Brutsaert, W. 1992. A comparison of several evaporation equations. *Water Resour. Res.* 28:951-954.

Derome, J., Niska, K., Lindroos, A-J. & Välikangas, P. 1991. Ion-balance monitoring plots and bulk deposition in Lapland during July 1989 - June 1990. In: Tikkanen, E. & Varmola, M. (eds.), *Research into forest damage connected with air pollution in Finnish*

Lapland and the Kola Peninsula of the U.S.S.R., The Finnish Forest Research Institute, Research Papers, 373:49-76.

Derome, K., Derome, J. & Lindroos, A-J. 1998. Techniques for preserving and determining aluminium fractions in soil solution from podzolic forest soils. *Chemosphere*, 1143-1148.

de Vries, W. & Leeters, E.E.J.M. 1994. Effects of acid deposition on 150 forest stands in the Netherlands. Chemical composition of the humus layer, mineral soil and soil solution. DLO Winand Staring Centre for Integrated Land, Soil and Water Research. Rep. 69.1, Wageningen, The Netherlands, 84 p.

de Vries, W. van Grinsven, J.J.M., van Breemen, N., Leeters, E.E.J.M. & Jansen, P.C. 1995. Impacts of acid deposition on concentrations and fluxes of solutes in acid sandy forest soils in the Netherlands. *Geoderma*, 67:17-43.

Feddes, R.A., P.J. Kowalik & Zaradny, H.. 1978. Simulation of field water use and crop yield. Simulation Monograph. PUDOC, Wageningen, 189 pp.

Gash, J.H.C. 1979. An analytical model of rainfall interception by forests. *Q. J. R. Meteorol. Soc.* 105:43-55.

Giesler, R. Lundström, U.S. & Grip, H. 1996. Comparison of soil solution chemistry assessment using zero-tension lysimeters or centrifugation. *European Journal of Soil Science*, 47:395-405.

Grossmann, J. & Moss, R.. 1994. Variability of water quality in a spruce stand. *Zeitschr. Pflanzenernahr. Bodenk.* 157:47-51.

Haines, B.L., Waide, J.B. & Todd, R.L. 1982. Soil solution nutrient concentrations sampled with tension and zero-tension lysimeters: Report of discrepancies. *Soil Sci. Soc. Am. J.* 46:658-661.

Haude, W. 1958. Ober die Verwendung verschiedener Klimafaktoren zur Berechnung der potentiellen Evaporation and Evapotranspiration. *Meteorologische Rundschau* 11:96-99.

Hendershot, W.H. & Courchesne, F. 1991. Comparison of soil solution chemistry in zero tension and ceramiccup tension lysimeters. *J. Soil Sci.* 42:577-583.

Kutilek, M. & Nielsen, D.R. 1994. Soil hydrology. Cremlingen-Destedt, Catena, 370 pp.

Lawrence, G.B. & David, M.B. 1996. Chemical evaluation of soil-solution in acid forest soils. *Soil Science*, 161:298-313.

Ludwig, B., Meiwes, K.J., Khanna, P., Gehlen, R., Fortmann, H. & Hildebrand, E.E. 1999. Comparison of different laboratory methods with lysimetry for soil solution

- composition – experimental and model results. *Journal of Plant Nutrition and Soil Science*, 162:343-351.
- Makkink, G.F. 1957. Testing the Penman formula by means of lysimeters. *J. Inst. Water Eng.* 11:277-288.
- Manderscheid, B. & Matzner E.. 1995. Spatial and temporal variation of soil solution chemistry and ion fluxes through the soil in a mature Norway spruce (*Picea abies* (L.) Karst.) stand. *Biogeochemistry* 30:99-114.
- Monteith, J.L. 1965. Evaporation and environment. *Symp. Soc. Exp. Biology* 19:205-234.
- Nissinen, A., Kareinen, T., Tanskanen, N. & Ilvesniemi, H. 1999. Apparent cation-exchange equilibria and aluminium solubility in solutions obtained from two acidic forest soils by centrifuge drainage method and suction lysimeters. *Water, Air and Soil Pollution*, 00:1-21.
- Oliver, B.G., Thurman, E.M. & Malcom, R.L. 1983. The contribution of humic substances to the acidity of natural waters. *Geochim. Cosmochim. Acta*, 47:2031-2035.
- Raulund-Rasmussen, K. 1989. Aluminium contamination and other changes of acid soil solution isolated by means of porcelain suction cups. *J. Soil Sci.* 40:95-101.
- Ritchie, J.T. 1972. A model for predicting evaporation from a row crop with incomplete cover. *Water Resour. Res.* 8:1204-1213.
- Roades, J.D. 1982. Soluble salts. In: Page, A.L., Miller, R.H. & Keeney, D.R. (eds.) *Methods of soil analysis, Part 2. Chemical and microbiological properties. Agronomy Monograph No. 9 (2nd edition):*167-178.
- Rutter, A.J., Kershaw, K.A., Robins, P.C. & Morton, A.J.. 1971. A predictive model of rainfall interception in forests, 1. Derivation of the model from observations in a plantation of Corsican pine. *Agric. Meteorol.* 9:367-384.
- Starr, M. 1999. WATBAL: A model for estimating monthly water balance components, including soil water fluxes. In: Kleemola, S. & Forsius, M. (eds). 8th Annual Report 1999, International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems. The Finnish Environment Institute, 325:31-35.
- Titus, B.D. & Mahendrappa. 1996. Lysimeter systems designs used in soil research, a review. Newfoundland and Labrador Region, Information Report N-X 301:1-103.
- Turc, L. 1954. Calcul du bilan de l'eau: Evaluation en fonction des precipitations et des temperatures. *IAHS Publ.* 38:188-200.

Wallace, J.S. 1993. Recent developments in evaporation modelling. A. Becker, B. Sevruc, M. Lapin (eds.): *Evaporation, Water Balance and Deposition, Proc. Symp. on Precipitation and Evaporation*, Vol. 3, 20-24. Sept. 1993, Bratislava (Slovakia), 43-54.

Wesselink, L.G. & Mulder, J.. 1995. Modelling AI-solubility controls in an acid forest soil, Solling, Gemany. *Ecol. Modelling* 83:109-117.

Wickstrøm, T., Clarke, N., Derome, K., Derome, J. & Røgeberg, E. 2000. Comparison study of five analytical methods for the fractionation and subsequent determination of aluminium in natural fresh water samples. *Journal of Environmental Monitoring*, 2:171-181.

Zabowski, D. & Ugolini, F.C. 1990. Lysimeter and centrifuge soil solution: Seasonal differences between methods. *Soil Science Society of America Journal*, 54:1130-1135.

Annexes

Annex 1

Materials used for the construction of tension soil water samplers.

Material	Type	Special properties	Disadvantages
Ceramic	P 80 Czeratzki Alundum Soil moisture	cheap, widely used, well known	retains P, may weather/ release ions (e.g. Al, Si), relatively fragile, high exchange capacity
Teflon	Morrison Prenart	chemically inert, easy to install, robust, adjustable to pore size according to soil type	expensive, may release low Ca, may absorb heavy metals
Glass	Fritted Sintered	cheap	fragile, adsorption/ desorption may release Na, Si
Nylon	Filter	low ion exchange capacity	relatively fragile, may release N, C and S compounds, expensive
Polyvinylidene fluoride	Filter	low ion exchange capacity	relatively fragile, expensive, some material eaten by animals
Plastic	Filter Porous Supralene	no adsorption/desorption	some retain Al

Annex 2.

Procedures for the chemical analysis of soil solution samples.

Parameter	Method / Instrument
Electrical conductivity	conductivity measurement
pH	potentiometry
Alkalinity	potentiometric titration, determination of inorganic C and calculation of inorganic C species
DOC	catalytic oxidation, persulphate oxidation
Na, K, Mg, Ca Fe, Mn, Al(t),	atomic absorption spectrometry (AAS), ICP emission spectrometry
Al (labile)	cation exchange, kinetic discrimination
NH ₄ -N	spectrophotometry e.g. indophenol method, ion chromatography, ion sensitive electrode
NO ₃ -N	ion chromatography, spectrophotometry, ion sensitive electrode
N (total)	elementary analysis, Kjeldahl digestion and ammonium analysis
SO ₄ -S	ion chromatography, potentiometric determination
Cl	ion chromatography, spectrophotometry (Hg-thiocyanate iron method), titration with AgNO ₃
Cr, Ni, Zn, Cu, Pb	atomic absorption spectrometry (AAS) graphite furnace, ICP - MS

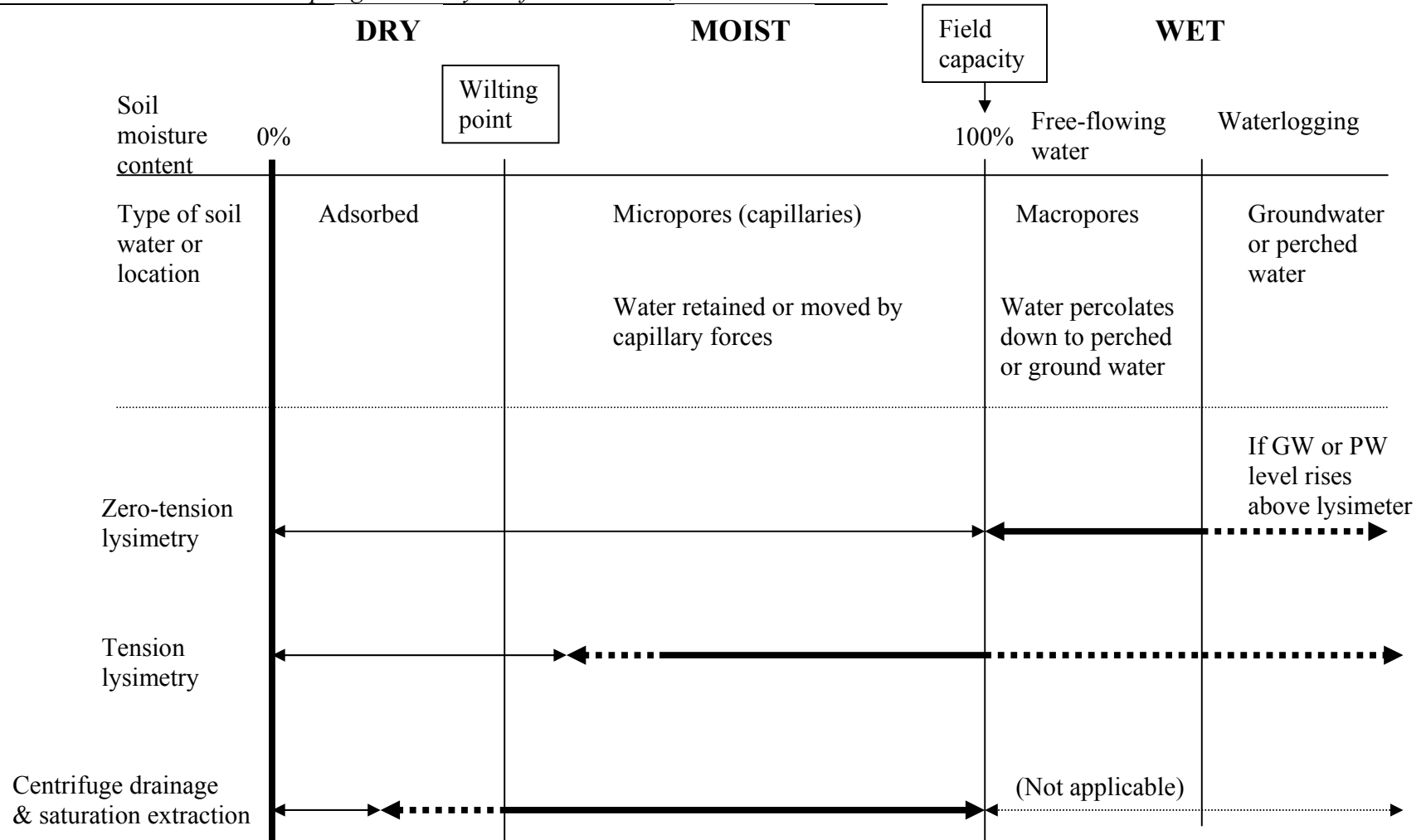


Fig. 1. The soil water fractions sampled by zero-tension lysimetry, tension lysimetry and centrifuge drainage (thick lines). The thin lines indicate the fractions that cannot be sampled. The actual fractions sampled by tension lysimetry can vary depending on the size of the vacuum applied and the moisture content of the soil during sampling (dotted lines). Similarly the amount of adsorbed water sampled by centrifuge drainage depends on the centrifugation speed

Annex 5

Abbreviations

AAS	Atomic Absorption Spectrometer
BD	Bulk Density
BS	Base Saturation
CEC	Cation Exchange Capacity
E _c	Electrical conductivity
F	Fermentation horizon
FAO	Food and Agriculture Organization
FES	Flame Emission Spectrometer
H	Humus horizon
ICP	Inductivity Coupled Plasma Spectrometer
IRM	International Reference Material
ISO	International Organization for Standardization
JRC	Joint Research Centre, Ispra, European Commission
L	Litter horizon
LRM	Local Reference Material
M	Mandatory parameter
MBD	Mineral Bulk Density
NFC	National Focal Centre of the Intensive Monitoring Programme
NRM	National Reference Material
O	Optional parameter
OM	Organic Matter
QA/QC	Quality Assurance and Quality Control
SA	Soil Analysis method
SAG	Scientific Advisory Group of the Intensive Monitoring Programme
SD	Standard Deviation
SFC	Standing Forestry Committee
WRB	World Reference Base for Soil Resources