



Standard Observation SOATM_103

Atmospheric deposition in precipitation

Version 0.6

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NOTE: THIS PROTOCOL IS STILL UNDER REVIEW.



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The present protocol is based on Part XIV of the ICP Forests Manual (Clarke et al. 2022).

To reference the methodology, the corresponding original document should be cited:

Clarke, N., D. Žlindra, E. Ulrich, R. Mosello, J. Derome, K. Derome, N. König, F. Geppert, G. Lövblad, G.P.J. Draaijers, K. Hansen, A. Thimonier, P. Waldner, and A. Verstraeten (2022): Part XIV: Sampling and Analysis of Deposition. In: *Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests*. Ed. by UNECE ICP Forests Programme Co-ordinating Centre. Version 2022-1. 34 p. + Annex. Eberswalde, Germany: Thünen Institute of Forest Ecosystems, 2022.

To reference the implementation of the requirements of the ICP Forest Manual at eLTER sites, the eLTER Standard Observation Protocol can be cited as:

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SO variable overview

Habitat:

Applies to all eLTER habitat groups

Variable(s):

- **Precipitation:** Reporting unit: mm
- **Ammonium (NH₄-N):** Reporting unit: mg N/L
- **Nitrate (NO₃-N):** Reporting unit: mg N/L
- **Nitrogen dioxide (NO₂-N):** Reporting unit: mg N/L
- **Total nitrogen (NTOT):** Reporting unit: mg N/L
- **Sulfate (SO₄-S):** Reporting unit: mg S/L
- **Phosphate (PO₄-P):** Reporting unit: mg P/L
- **Potassium (K):** Reporting unit: mg/L
- **pH:** Reporting unit: unitless
- **Total anion (ANION):** Reporting unit: meq/L
- **Total cation (CATION):** Reporting unit: meq/L
- **Dissolved organic carbon (DOC):** Reporting unit: mg/L
- **Alkalinity (ALK):** Reporting unit: µeq/L
- **Electrical conductivity (COND):** Reporting unit: µS/cm

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1 Introduction

NOTE: Source and provenance. The text of this Standard Observation protocol is largely reproduced from Part XIV of the ICP Forests Manual (Clarke et al. 2022) and the recommended citation is provided on the second title page. The variation from the ICP Forests protocol is in the minimum recommended frequency of sampling (here at least bi-weekly) and in greater flexibility in sampler design. The ICP Forests manual also includes details of throughflow and stemflow sampling. For forested sites where these are relevant, please refer directly to the ICP Forests Manual.

The deposition of pollutants to the ecosystems by precipitation is assumed to be a major factor affecting the natural processes in the environment. The main focus of the SO is the sampling and chemical analysis of precipitation with particular emphasis on the acidifying compounds and on nutrients.

For dry deposition, see SOATM_108. In forests, dry deposition is estimated from additional throughfall deposition measurements, which are described in SOATM_108 (PRIME method only).

2 Method

2.1 Scope and data product

SOATM_103 is a mandatory measurement for all eLTER habitat groups in both site categories, with no differences between the BASIC and PRIME methods.

Bulk deposition is sampled with a continuously open plastic funnel connected to a sample bottle. The funnel also collects parts of particulate and gaseous deposition during dry periods. Contributions from occult deposition are also included. This method can also be used to determine the fluxes of dissolved components from the atmosphere in rain, snow and hail in the open field. When bulk deposition is used in the estimation of total atmospheric deposition to the forests, estimation errors are introduced. This is because canopy exchange models need wet-only deposition as one of the input parameters. Wet deposition samples can also be collected using wet-only samplers, which use an electronic sensor for detecting rain and are only open for sampling during precipitation events. However, the choice of bulk measurements over wet-only measurements may be necessary because of financial constraints. The advantages compared with wet deposition monitoring are that it is cheap and simple, electrical power is not needed, and maintenance is low. However, in regions with calcareous soils, bulk deposition gives incorrect information on the pH and chemistry of atmospheric deposition and if a bulk sampler is used it is important to verify to which extent gases and particles are deposited to the bulk sampler, and to take measures to avoid/ reduce dry deposition to the sampler (Clarke et al. 2022, Annex 7). Where bulk deposition data are intended for use in canopy budget modelling (see SOATM_108, Dry deposition of N), the basis on which the dry contribution is accounted for should be documented.

2.2 Measurement design

2.2.1 Spatial design

Information on placing of precipitation collectors can be found in the EMEP (2001) and the manual for the GAW precipitation chemistry programme WMO (2004). The collectors should be set up on an open field site at the same altitude and exposure as any forest plot that may be present at the site and considering the prevailing wind directions. Level areas are preferable, although slopes of up to ± 15 percent are acceptable. Sudden changes of slope within 30 m of the collector should be avoided. There should be no obstacles (trees, topographical features etc.) above 30° from the rim of the precipitation collector. This means that the distance from the collector 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 collector. If fencing is used (e.g. to prevent damage from animals), it must be put up in accordance with these requirements. The height of surrounding vegetation should not be higher than half the height of the collector, measured from the ground to the sampling orifice (WMO 2004). In areas with high snow accumulations, a platform may be used to raise the collector. It is important that local sources of soil dust (gravel roads, farmyards or tilled agricultural fields) and ammonia (from farming) are avoided. Contamination from local residential heating with wood, peat or coal may also occur; potassium is an indicator of such contamination. Distances of 100 m to 2 km from local sources of contamination are recommended by EMEP (2001).

2.2.2 Equipment

For bulk sampling, all countries should use a type of collector, 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 collectors may be used. A minimum of three replicates is necessary. The design of this collector should as a minimum conform to the definition of the World Meteorological Organisation (WMO) minimum requirements for correct precipitation quantity measurements and 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.

2.2.3 Standard precipitation gauge according to WMO definition

"The commonly used precipitation gauge consists of a collector placed above a funnel leading into a container where the accumulated water and melted snow are stored between observation times" (WMO, 2008).

2.2.4 Collecting area

"The size of the orifice of the collector is not critical for liquid precipitation, but an area of at least 200 cm² is required if solid forms of precipitation are expected in significant quantity. An area of 200 to 500 cm² will probably be found most convenient" (WMO, 2008). The sampling area must be horizontal, as the collecting area will otherwise be reduced. The collecting surface should be known with a maximum margin of error of ± 2 percent. The collecting surface should be in the 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 because of aerodynamic blockage during high wind speed rain events will be greater with a larger collecting area (Bleeker et al. 2003). In areas where the precipitation is generally low and sampling frequency is high (due to eventual evaporation), a bigger funnel surface is recommended. The collecting surface must be verified at least once a year on all devices. The surface area of all collectors should meet the criteria of 2 percent variation coefficient. 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 collectors) but must be measured and documented. Because collectors may expand or shrink because of weather conditions, it is recommended to check the size of the collecting area at least once a year Bleeker et al. (2003) 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 percent of the time.

2.2.5 Rim

"The rim of the collector should have a sharp edge and should fall away vertically on the inside, and be steeply bevelled on the outside; the design of gauges used for measuring snow should be such that any narrowing of the orifice caused by accumulated wet snow about the rim is small" (WMO

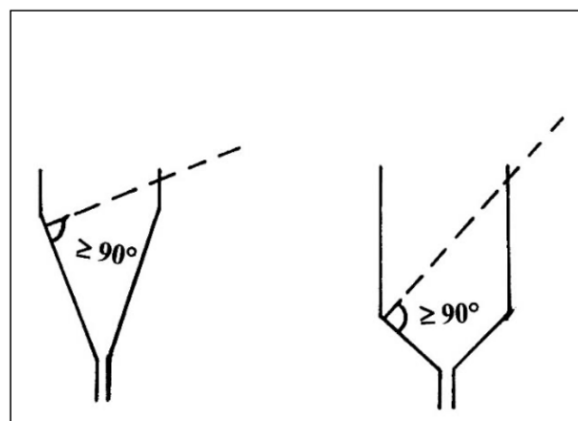


Figure 1: For satisfactory design of the precipitation sampler, the dashed line needs to cross the sampler wall for precipitation quantity sampling (reproduced from WMO, 1990).

2008). 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 (Bleeker et al. 2003).

2.2.6 Shape

WMO manuals recommend that the upper part of the collector should be very sharp and should go down vertically in the form of a cylinder. Collection vessels with sloping sides must 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 1 shows schematically the required design, i.e. a funnel.

2.2.7 Material

The upper part of the collector 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). 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.

2.2.8 Height above ground level

In order to avoid contamination of the samples, the rim of the collector should be 1.0-2.0 m above ground level. The sampling area must be horizontal; the collecting area will otherwise be reduced.

2.2.9 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, Bleeker et al. 2003) sieve or other inert sieves (aquaristic filter fleece) should be placed at the top of the neck of the collector. 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 (Bleeker et al. 2003). 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.

2.2.10 Bird wires

The upper exterior part of the collector 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 low bird density (e.g. in northern Fennoscandia). Bird rings could be necessary for both bulk and throughfall (throughfall deposition measurements see SOATM_108). 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.

2.2.11 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. 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. To slow down algal growth and nitrification in samples, the sample containers should be kept cold and in the dark. The best way of achieving cold and dark conditions are keeping the sampling container in a pit hole (Figure 2) or wrapping aluminium foil around the container (although this is considerably less effective than a pit hole). Another way to achieve this is to use PVC pipes (used for wastewater tubes), in which the bottles are placed (Figure 2). Ventilation holes in the pipes are necessary since these pipes can heat up inside. The collector has to be placed in the pipe in such a way that the upper part of the collector 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. When collectors and sample containers need to be connected black polyethylene tubes or other tubes excluding light and not interfering with the sample should be used. 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.

2.2.12 Bulk precipitation collectors for snow

The funnel-type bulk precipitation collectors are no longer appropriate when, according to meteorological statistics or prognoses, snow is common and important. 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. Special snow 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. 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. According to the experiences gained in countries with long periods of snowfall, the size of the collecting surface per collector 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 disposable heavy-gauge polyethylene

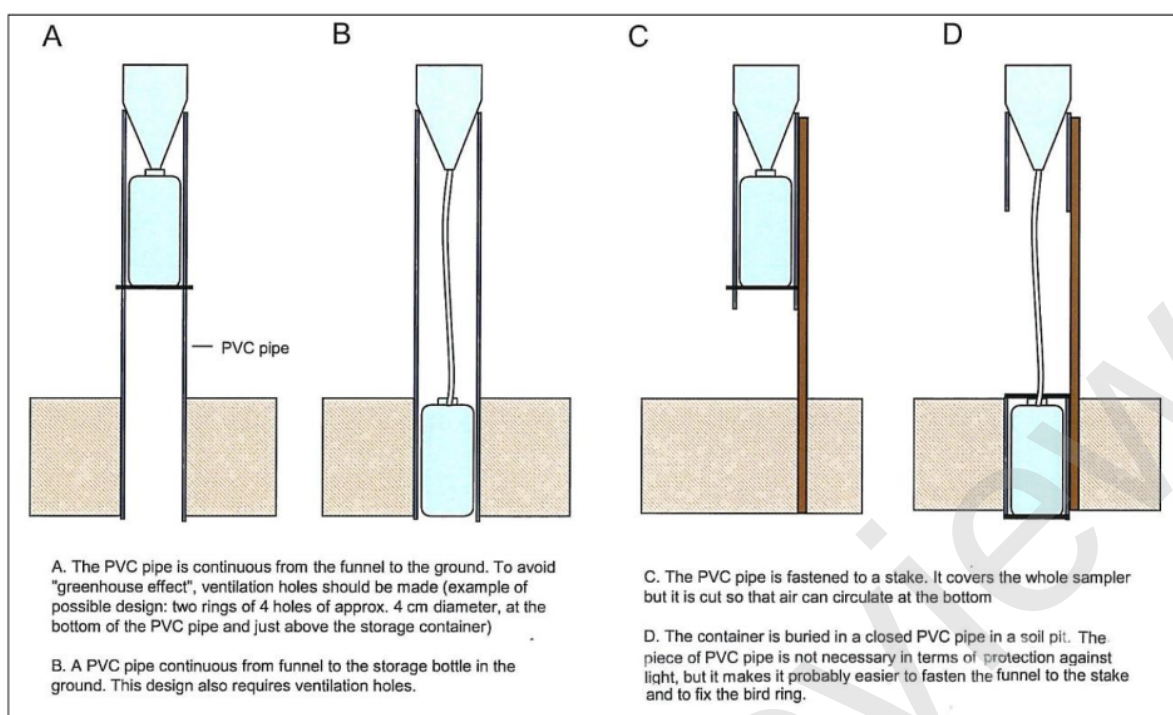


Figure 2: Possible measures to install the deposition sampler. Method D gives the best protection against light and heat. (reproduced from ICP Forests Manual Version 2022-1 (Clarke et al. 2022), Fig. 5)

plastic bag of sufficient thickness (100 μm) can be placed under the upper part of the collector (for example, suspended from a hoop attached to a support), which still has to fulfil the requirements defined. 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. In case of frequent changes between snow and rain, both types of collectors can be run in parallel. Depending on the proportion of snow or rain, the local operator will decide from which type of collector to collect the sample for analysis. Wet-only collectors 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). As is the case for rainfall collectors, all materials used should not interact with the sample solution. Examples of rain and snow collectors are shown in the manuals for Integrated Monitoring ICP Integrated Monitoring (1998) and EMEP (<https://projects.nilu.no//ccc/manual/index.html>).

2.2.13 Wet-only collectors

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 collectors should be run in parallel for at least one year at the same location. No internationally standardised design of wet-only collectors 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 collector, the way samples are stored inside the collector, heating or not of the collecting surface in winter etc. 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, for

some years. The WMO manual 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 collector must give comparable results to an official meteorological rain gauge. Comparability is defined by WMO as: “+0 to –20 percent for liquid equivalent depths of 0.5 to 2.5 mm of precipitation and +0 to –10 percent for liquid equivalent depths greater than 2.5 mm of precipitation”.

2.2.14 Temporal resolution

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 at least bi-weekly sampling. If it is temporarily not possible to analyse bi-weekly samples, pooling of samples to collective samples representing periods of up to one month is recommended. The frequency of emptying the containers should be the same for all deposition measurements (throughfall, stemflow and wet/bulk deposition, see also SOATM_108). If the same frequency is not possible then emptying of samplers should be done on the same day (e.g. if a weekly and bi-weekly frequency exist for two samplers, collecting both on the same day allows two weekly sample results to be averaged to match the bi-weekly sample).

2.3 Sample collection, transport and storage

Sampling, sample handling and cleaning should be carried out carefully. 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 field forms that accompany the samples to the laboratory and, if in use, the sampling logbook.

2.3.1 Before sampling

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

2.3.2 Prevention of algal growth and nitrification 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. If it is impossible to obtain low temperatures in sample bottles a possible precaution during the sunny and warm season, could be to add a preservative 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 collectors, 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.

Nitrification is a two-step process. Bacteria known as Nitrosomonas convert ammonium to nitrite. Next, bacteria called Nitrobacter finish the conversion of nitrite to nitrate. The reactions are generally coupled and proceed rapidly to the nitrate form. These bacteria known as “nitrifiers” are strict “aerobes,” meaning they must have free dissolved oxygen to perform their work. Nitrification occurs

Table 1: Temperature and nitrification

Temperature	Effect upon nitrification
> 45°C	Nitrification ceases
28-32°C	High risk of nitrification
16°C	Approx. 50% of nitrification rate at 30°C
10°C	Significant reduction in rate, approx. 20% of nitrification rate at 30°C
< 5°C	Nitrification ceases

only under aerobic conditions at dissolved oxygen levels of 1.0 mg/L or more. A sufficient population of nitrifying bacteria must be present in order to nitrify. These bacteria are attached growth organisms, meaning that they must attach themselves to the surface of an object. It is believed that nitrifiers may attach to the sides of the container, to particles in the sample and perhaps to algae particles. Nitrification stops at a pH below 6.0. Temperatures above 10-16 °C and below 45°C promote and increase nitrification (Table 1). As the temperature increases, the nitrification rate increases to a certain degree. If nitrification is lost, it will not resume until the temperature increases to well over 10°C.

To determine the potential nitrogen transformation, the following test can be made periodically. The standard collector, unpreserved and kept dark, is run in parallel with two extra collectors located close to the standard collector. One of the extra collectors 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.

2.3.3 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 cardboard covered in a polyethylene plastic bag 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.

2.4 Collecting the samples for analysis

After each sampling period, the volume of each individual 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. Volume can be determined by either weighing or using a measuring cylinder. 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 precipitation event (WMO 2004).

If the sample in the collector 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. The same procedure and the same precautions as mentioned above are applied. All samples must be clearly labelled with station code and name and dates of sampling period.

2.5 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 samples are weighted according to volume estimated using either a measuring cylinder or similar container, or from the weight. 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 collectors 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 (Bleeker et al. 2003). 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.

2.6 Storage and transport

2.6.1 Transportation to the laboratory

Each consignment of samples should be accompanied by a field form that informs the laboratory about the type and origin of the samples (e.g. plot number, collector number, 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. 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 also be used for this purpose.

2.6.2 Storage of samples prior to pre-treatment

2.7 Maintenance

The samples shall be kept in a refrigerator (0-4°C) prior to pre-treatment, as this will slow most chemical and biological sample degradation (sample temperature must be considered both in the field and in the laboratory prior to pre-treatment). 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. The maximum storage times for sub-samples for the individual analyses should be determined by the individual laboratories. The sub-samples should preferably not be frozen, as there is evidence in the literature to show that this can have an effect on the samples and analysis results (e.g. increased variance found by MacDonald and McLaughlin (1982)), although this has not always been found Dore et al. (1996) and Matilainen et al. (2002).

2.7.1 Pooling of samples from subsequent sampling periods

Weekly samples can be analysed as they are or, in order to save money, pooled 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.

3 Measurements

3.1 Measurements and reporting units

The parameters to be determined on the samples are listed in Table 2. 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 procedures should be used, preferably ISO or EN methods and/or those applied in the EMEP and ICP/Integrated Monitoring programmes. The list of ISO and EN methods is given in Annexes of Clarke et al. (2022). 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 EN standards and in the EMEP manual.

Table 2: Mandatory and optional parameters to be analysed in bulk deposition (DOC: dissolved organic carbon, N_{total} : total nitrogen, DON: dissolved organic nitrogen)

Sample type	Mandatory	Comments
Bulk deposition	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^+	
	Cl^- , NO_3^- , SO_4^{2-}	To check for contamination due to bird droppings either PO_4^{3-} or P_{total} can be measured. To calculate organic phosphorus both parameters have to be measured. NO_2^- may indicate pollen-driven NO_3^- reduction during spring.
	Alkalinity	Mandatory for individual samples if pH > 5
	DOC, N_{total} (N_{total} is not mandatory for bulk deposition, but is highly recommended)	HCO_3^- can either be obtained by calculation (from pH, total alkalinity, temperature and ionic strength) or by direct measurement

3.1.1 Reception at the laboratory, initial checks and temporary storage

Upon reception of the samples at the laboratory, the delivery should be checked and registered 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

Table 3: Analytical procedures recommended for the analysis of bulk precipitation samples

Parameter	Method/Instrument	Comments
pH	Potentiometry	Determined in the laboratory. Two-point calibration must be used.
Conductivity	Conductometry 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. Thorin 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 (azo dye after reduction to nitrite, CFA)	IC is the recommended method.
Nitrite	- Ion chromatography (IC) - Spectrophotometry (azo dye after reduction to nitrite, CFA)	IC is the recommended method.
Chloride	- Ion chromatography (IC) - Spectrophotometry	IC is the recommended method.
Phosphate	- Ion chromatography (IC) - Spectrophotometry	IC is the recommended method.
Ammonium	- Spectrophotometry (indophenol method, CFA or ammonia diffusion cell method, FIA) - Ion chromatography (IC)	IC: High Na concentrations can interfere and LOQ may be too high with some instruments. FIA: filtration and dialysis are needed, but automated FIA systems include this.
K, Na, Mg, Ca	- AAS - ICP/OES - Ion chromatography (IC)	Note: Results may differ between methods; IC determines ions, AAS and ICP total elements.
Total nitrogen (N-total)	- Spectrophotometry after oxidation to nitrate (persulphate in borate buffer or UV-digestion) - Total N analyser (chemiluminescence detection)	
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 optimal, use only if no TOC analyser is available.

- the bottles are properly closed, and no leakage has occurred
- possible damage to the box or bottles
- presence of visible contamination
- initial pH and conductivity check for indications of contamination
- sample registration and labelling with a unique sample number in the laboratory information system (or in the laboratory sample book)

The samples should be stored (protected from light at max. +4°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. Excessively long storage times should be avoided in order to prevent chemical changes caused by microbial activity in the samples.

It is recommended that all nitrogen compounds (nitrate, ammonium and total nitrogen) are analysed on the same day or within the same week in order to avoid nitrification and be able to trust the nitrogen budget. Also pH and conductivity measurements should be carried out as soon as possible, preferably on the day of arrival.

3.2 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. 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 sample should be filtered through a 0.45 μm membrane or syringe filter in order to remove any solid material and to stabilise the sample for the subsequent analyses. Filtration considerably decreases the possibility of microbially-induced changes (e.g. nitrogen transformations) in the samples as it removes all microorganisms (except viruses). Thus, the stability and lifetime of the samples are increased. The 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. Filter paper should not be used owing to possible contamination by NH^+ and carbon. Many types of membranes 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 (preferably) 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. Note that certain analysers may contain an internal filter to protect the device from damage by large particles, which could have a smaller pore size (e.g. 0.2 μm).

After filtration, sub-samples should be taken if needed for e.g. AAS or ICP techniques. These sub-samples should be acidified, e.g. with suprapure 65% HNO_3 to $pH < 2$ 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, e.g., ICP-MS, ICP-OES or AAS. Another subsample should be stored at +4°C and analysed as soon as possible for all other parameters. 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 chromatography columns), and possible interference in certain analyses.

3.3 Plausibility limits

Plausibility limits for deposition samples are given in Table 4. The values are the same as those used in the conformity tests for data submission. If the values lie outside those given below, a warning is given by the programme.

Table 4: Range tests for deposition samples

FIELD	UNIT	MIN	MAX	ERROR
alkalinity	µeq/L	-50	10000	w
Ca	mg/L	0.001	275	w
Ca	mg/L	0.0001	100000	e
Cl ⁻	mg/L	0.002	800	w
Cl ⁻	mg/L	0.0001	100000	e
conductivity	µS/cm	1	10000	w
DOC	mg/L	0.001	100	w
DOC	mg/L	0.0001	1000	e
K	mg/L	0.002	250	w
K	mg/L	0.001	10000	e
Mg	mg/L	0.0025	100	w
Mg	mg/L	0.0001	100000	e
Na	mg/L	0.003	500	w
Na	mg/L	0.0001	100000	e
N_NH ₄	mg N/L	0.002	175	w
N_NH ₄	mg N/L	0.001	100000	e
N_NO ₃	mg N/L	0.0001	100000	e
N_NO ₃	mg N/L	0.0001	100000	e
N_total	mg N/L	0.03	350	w
N_total	mg N/L	0.0001	100000	e
period		1	53	w
pH		2.5	9.4	w
pH		1	14	e
S_SO ₄	mg S/L	0.01	500	w
S_SO ₄	mg S/L	0.0001	100000	e
<i>Optional parameters</i>				
Al	mg/L	0.001	8	w
Al	mg/L	0	10	e
Cd	µg/L	0.008	100	w
Cd	µg/L	0.0001	10000	e
Co	µg/L	0.008	100	w
Co	µg/L	0.0001	10000	e
Cr	µg/L	0.008	100	w
Cr	µg/L	0.0001	10000	e
C_total	mg/L	0.03	500	w
C_total	mg/L	0.0001	10000	e
Cu	µg/L	0.06	850	w
Cu	µg/L	0.0001	10000	e

Continued on next page

Range tests for deposition samples (continued)

FIELD	UNIT	MIN	MAX	ERROR
DON	mg/L	0.001	100	w
DON	mg/L	0.0001	1000	e
Fe	mg/L	0	25	w
Fe	mg/L	0	100	e
HCO ₃ ⁻	mg/L	0	500	w
HCO ₃ ⁻	mg/L	0	10000	e
Hg	µg/L	0.02	100	w
Hg	µg/L	0.0000001	1000	e
Mn	mg/L	0	15.5	w
Mn	mg/L	0	100	e
N_NO ₂	mg N/L	0.002	175	w
N_NO ₂	mg N/L	0.0001	100000	e
Ni	µg/L	0.008	100	w
Ni	µg/L	0.0001	10000	e
Pb	µg/L	0.012	200	w
Pb	µg/L	0.0001	10000	e
P_PO ₄	mg P/L	0.0017	1000	w
P_PO ₄	mg P/L	0.0001	10000	e
P_total	mg/L	0.0017	1000	w
P_total	mg/L	0.0001	10000	e
S_total	mg/L	0.17	500	w
S_total	mg/L	0.0001	10000	e
Zn	µg/L	0.005	4500	w
Zn	µg/L	0.0001	10000	e

4 Data and metadata format

4.1 Data format

For all variables, raw data should be reported rather than e.g. weekly aggregates.

Data information can be provided as text format (e.g. csv or txt) in UTF-8 encoding.

In order to process the volume-averaged data in the best possible way, site-specific data needs to be provided at the highest available detail. All remaining variables that are necessary for the data processing will be derived centrally by the eLTER data service.

4.2 Reporting format

Reporting is conducted in accordance with the rules and conventions specified in Peterseil and Geiger (2020)¹ regarding file naming, file formats, and metadata scope.

5 Data validation

Data validation is used to determine whether the collected data have an acceptable completeness and reasonableness and to eliminate erroneous values. This step transforms raw data into validated data and is crucial to maintain high rates of data completeness during the monitoring program. There are many causes of erroneous data: damaged or malfunctioning samplers, data logger malfunctions,

¹Document is currently under revision.

Table 5: Metadata

Location data	Latitude, longitude (format? decimal degree?) (1 m resolution), altitude (1 m resolution), DEIMS link
Time stamp	format - UTC
Data structure	Data structure (e.g., header of comma separated values)
Auxiliary data	Detailed land use map, soil map, vegetation map, other site-specific features (1x1 km ²)
Contact person	name, email address

icing conditions among others. Therefore the data must be validated as soon as possible within a few days after transfer. It is very important to store the original raw data; the validation steps should be made on a copy of the original data set.

Data can be validated manually or automatically using computer software. The two main parts of data validation are data screening and data verification. Data screening may be performed using a series of validation routines or algorithms to screen all the data for questionable or erroneous values. It is recommended to print a data validation report which lists the suspect values. Data verification requires a case-by-case decision on what to do with the suspect values – retain them as valid, reject them as invalid or replace them with redundant valid values. A qualified person familiar with monitoring equipment and the local site should make this part of data validation.

Range tests are the simplest and most commonly used validation tests. The measured data are compared to allowable upper and lower limiting values. If the value meets a criterion then it is considered as valid. It is recommended to have several criteria checks because a single criterion is unlikely to detect all problems. Relational tests are based on expected physical relationships between various variables and ensure that physically improbable situations are not reported in the data without verification. Trend tests are based on the rate of change in a value over time.

Missing or invalid data (outcome of the plausibility checks) is flagged accordingly and as such reported.

6 PRIME method

6.1 Scope and data product

For this SO the prime method is the same as the basic method.

References

- [1] Bleeker, A., Draaijers, G. P. J., Veen, D. van der, Erisman, J. W., Möls, H., Fonteijn, P., and Geusebroek, M. "Field inter-comparison of throughfall, stemflow and precipitation measurements performed within the framework of the Pan European Intensive Monitoring program of EU/ICP Forest". In: *Environ. Pollut.* 125 (2003), pp. 123–138. DOI: [10.1016/s0269-7491\(03\)00142-8](https://doi.org/10.1016/s0269-7491(03)00142-8).
- [2] Clarke, N., Žlindra, D., Ulrich, E., Mosello, R., Derome, J., Derome, K., König, N., Geppert, F., Lövblad, G., Draaijers, G. P. J., Hansen, K., Thimonier, A., Waldner, P., and Verstraeten, A. "Part XIV: Sampling and Analysis of Deposition". In: *Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests*. Ed. by UNECE ICP Forests Programme Co-ordinating Centre. Version 2022-1. 34 p. + Annex. Eberswalde, Germany: Thünen Institute of Forest Ecosystems, 2022. ISBN: 978-3-86576-162-0. URL: <http://www.icp-forests.org/Manual.htm>.
- [3] Dore, J. E., Houlihan, T., Hebel, D. V., Tien, G., Tupas, L., and Karl, D. M. "Freezing as a method of sample preservation for the analysis of dissolved inorganic nutrients in seawater". In: *Mar. Chem.* 53 (1996), pp. 173–185. DOI: [10.1016/0304-4203\(96\)00004-7](https://doi.org/10.1016/0304-4203(96)00004-7).
- [4] EMEP. *Manual for Sampling and Chemical Analysis*. EMEP/CCC Report 1/95, Revision 2001. Norwegian Institute for Air Research. Kjeller, Lillestrøm, Norway, 2001.
- [5] ICP Integrated Monitoring. *Manual for Integrated Monitoring*. ICP IM Programme Centre, Finnish Environment Institute. Helsinki, Finland, 1998.
- [6] MacDonald, R. W. and McLaughlin, F. A. "The effect of storage by freezing on dissolved inorganic phosphate, nitrate and reactive silicate for samples from coastal and estuarine waters". In: *Water Res.* 16 (1982), pp. 95–104. DOI: [10.1016/0043-1354\(82\)90058-6](https://doi.org/10.1016/0043-1354(82)90058-6).
- [7] Matilainen, A., Lindqvist, N., Korhonen, S., and Tuhkanen, T. "Removal of NOM in the different stages of the water treatment process". In: *Environ. Internat.* 28 (2002), pp. 457–465. DOI: [10.1016/s0160-4120\(02\)00071-5](https://doi.org/10.1016/s0160-4120(02)00071-5).
- [8] Peterseil, J. and Geiger, S. *eLTER PLUS – Field Specification for data reporting (1.0)*. Zenodo [Technical note]. Version 1.0. 2020. DOI: [10.5281/zenodo.6373410](https://doi.org/10.5281/zenodo.6373410). URL: <https://zenodo.org/record/6373410>.
- [9] Sevruk, B., Hertig, J.-A., and Tettamanti, R. "The effect of orifice rim thickness on the wind speed above precipitation gauges". In: *Atmos. Environ.* 28 (1994), pp. 1939–1944. DOI: [10.1016/1352-2310\(94\)90334-4](https://doi.org/10.1016/1352-2310(94)90334-4).
- [10] WMO. *Manual for the GAW precipitation chemistry programme. Guidelines, data quality objectives and standard operating procedures*. Tech. rep. WMO TD No. 1251, GAW Report No. 160. World Meteorological Organization, 2004. URL: https://library.wmo.int/doc_num.php?explnum_id=92.