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MANUAL

on

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

Part X

Sampling and Analysis of Soil

Version 2020-1

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CONTENTS

1 Objectives

This Part of the Manual outlines the sampling, analysis and reporting procedures for the set of soil parameters measured in the ICP Forests programme. Investigating forest soils is important on both Level I and Level II plots of the monitoring scheme.

The purpose of the large-scale soil survey (Level I) is first of all the assessment of basic information on the chemical soil status and its changes over time, and secondly the assessment of soil properties which determine the forest soil's sensitivity to air pollution (e.g. acidification status). Besides providing soil data for the study of atmospheric deposition effects at the broader scale, the soil survey will serve other purposes, as supporting studies related to climate change (e.g. inventory of carbon storage) and sustainable forest management (e.g. nutrient and water balances studies).

A third major objective of the large-scale representative soil survey (Level I) is to allow the evaluation of the forest soil condition across Europe. For the sake of data comparability among countries, a prerequisite is that the same methods for soil sampling and analysis are used throughout the network. As such, analytical results obtained by national methods, different from those described in this manual, cannot directly be compared with analytical results obtained by the international reference methods of this manual. Notwithstanding, the participating countries are encouraged to make efforts (where necessary and possible) to allow the comparison of the data obtained in the first or second survey with those of future surveys.

The intensive soil studies are conducted on permanent plots (Level II) where other measurements and assessments for the analysis of the forest ecosystem are performed. Intensive soil measurements are essential in understanding the role of forest soils in cause-effect relationships and in ecosystem functions and services. The intensive soil study involves the soil characterisation, the evaluation of the soil condition and the study of the soil processes and dynamics on the long-term. Methods for the short-term soil dynamics are described in the Part XI on Soil Solution Collection and Analysis and partly in Part IX on Meteorological Measurements (soil temperature and soil water dynamics).

2 Scope and application

Soil analyses are relevant to many environmental applications such as studies on acidification, eutrophication, C stock assessment, nutrient fluxes, water balances, biodiversity assessments and impact of climate change. This Part presents all the soil related field and laboratory parameters that are required for these studies within the ICP Forests programme. Concerning the field observations and sampling, the aim is to provide a set of minimum requirements which need to be met to come to a harmonised approach. Related to the analyses in the laboratory, all laboratories have to use the reference methods, which mainly follow ISO standards.

The relevance of the key soil parameters is given in Table 1. Table 2 provides an overview on the mandatory and optional soil surveys. An overview on the mandatory and optional parameters and sampling depths is given in Table 11 for the set of soil physical and soil chemical parameters and in Table 7 and 9 for the soil moisture measurements.

Table 1: Relevance of the key soil parameters

Type of parameter	Key parameters	Layer	Relevance
Carbon and nitrogen	C_{tot}, $N_{tot,}$ (Carbonates)	Organic	Forest nutrition, atmospheric N deposition, climate change
		Mineral	Forest nutrition (0-20 cm), C- & N stocks (0-80 cm)
Nutrients	P, Ca, Mg, K, S, Mn	Organic	Atmospheric deposition of basic cations, stock of macronutrients
		Mineral	Weathering rates, critical loads of acidity, stock of macronutrients
Acidity, Exchange characteristics	pH, Carbonates, CEC, BS, Exchangeable cations, Exchangeable Acidity	Organic	Buffering acid input, acidification status
	pH, Carbonates, CEC, BS, Exchangeable cations, Exchangeable Acidity, Al_{ox}, Fe_{ox}	Mineral	
Heavy metals	Pb, Cu, Zn, Cd, Cr, Ni, Hg	Organic	Atmospheric metal deposition
		Mineral	Atmospheric metal deposition, calculation critical loads (0-20 cm), deficiency of oligo elements
Physical soil parameters	Particle size distribution and soil texture	Mineral	Profile description and soil classification, estimation of plant available water, nutrient exchange capacity
	Organic layer mass	Organic	Calculation of stocks
	Bulk density of the fine earth (BD_{fe}) and the coarse fragment content	Mineral	Calculation of stocks, nutrient supply to plants, index for compaction
	Soil Water Retention Characteristic (SWRC)	Organic Mineral	Water balance models, nutrient fluxes, estimation of soil porosity

Table 2: Overview of soil survey at the Level I, II and the Level II core plots

Soil survey	Level I	Level II	Level II core
Pedological characterisation	Mandatory (once at installation of plot)		
Soil sampling at fixed depths	Mandatory (every 10 - 20 years) *		
Soil sampling for bulk density at fixed depths	Mandatory		
Sampling for measurement of SWRC	Optional	Optional	Mandatory

* Pan-European synchronisation within a period of 3 years is essential

3 Objectives

This manual is designed to provide a consistent methodology to collect high quality, harmonised and comparable forest soil data across Europe. This will allow (i) the proper characterization and description of the soil condition; and (ii) to monitor changes in soil properties periodically (e.g. on a 10 years basis).

The soil survey comprises three main pillars (Table 2):

1 Pedological characterisation. At the plot installation a detailed soil profile pit description complemented by sampling according to genetic horizons should lead to a detailed soil

classification following the World Reference Base for Soil Resources (IUSS Working Group WRB, 2015).

2 Monitoring of the soil condition. Both the organic and the mineral soil layers are sampled and analysed in the laboratory at regular time intervals (e.g. every 10 years). For this purpose, composite samples are taken at fixed depth layers.

3 Determination of the soil water retention characteristic (SWRC). The assessment of the forest water budget is essential to study the nutrient fluxes in the forest ecosystem on the permanent monitoring plots. For the parameterisation of various water balance models meteorological data, stand characteristics and soil physical data are essential. For the validation of the models soil temperature, soil moisture and stand precipitation measurements are needed. To characterise the soil water retention, a series of undisturbed soil samples need to be taken and analysed in the laboratory. This survey is mandatory on all (core) plots where water budgets are assessed.

4 Location of measurements and sampling

4.1 Sampling design at plot level

Table 3 provides an overview of the sampling design on the Level I and Level II plots.

Table 3: Overview of sampling design on the Level I and Level II plots

Objective	Location of sampling regards the plot area	Sampling design	N° of sampling points	N° of soil layers per point	N° of soil samples per layer and point
Pedological characterization					
Level I	Representative for dominant soil type within the plot area	Judgemental	≥1	= N° of horizons	≥1
Level II	Buffer zone	Judgemental	≥1	= N° of horizons	≥1
Soil sampling at fixed depth					
Level I	Sampling sites should be located within the plot area.	Judgemental	≥ 5 (but on stony soils for optional depth layers ≥ 3)	3 to 8	1
Level II	Sampling sites should be located within the plot area or if not feasible, in the buffer zone of the plot.	Random design or systematic design with a random component.	≥24	5 to 8	1
Sampling at fixed depth for soil bulk density					
Level I	Not specified	Not specified	0 to 5	0 to 5	0 to 1
Level II	Not specified	Not specified	5	3 to 5	1
Sampling for soil water measurements					
Level II core	Within the plot	In vicinity of field soil moisture probes	3	3 to 7	≥1

4.1.1 Pedological characterization of the plot

4.1.1.1 Allocation of the soil sampling sites

The pedological characterization:

- Is mandatory for Level I and Level II plots but has to be carried out only once;
- Includes a detailed profile characterisation with information on soil parent material and at least one profile description with characterisation by horizons according to the Field Guidelines for Forest Soil Profile Description (see Annex 2) which are partly based on the 4th edition of the Guidelines for Soil Profile Description and Classification (FAO, 2006). The soils should then be classified according to the most recent official version of the World Reference Base of Soil Resources (WRB)-classification system. It is recommended to report all qualifiers. In addition, the correct reference needs to be made to the applied WRB reference system (IUSS Working Group WRB 2015). An overview of the mandatory and optional parameters for the pedological characterisation is given in Table 4.
- Includes the identification of the dominant humus form on the observation plot according to the adopted description and classification guidelines (Zanella *et al.,* 2009).
- The described soil profile(s) should be located at locations representative for the dominant soil type in the actual sampling area. For Level II this should be in the buffer zone of the plot. More detailed information on the location and orientation of the soil profile and on the required observations which need to be made while digging the profile are given in Annex 3.
- The parameter '**effective soil depth'** will be MANDATORY to report (it replace the previous parameters 'root' 'rock' and 'obstacle depth'. The 'effective soil depth' is defined as the depth to the 'continuous rock' (IUSS Working Group WRB, 2015). In case the 'continuous rock' is found at a depth of more than 1 meter, it is sufficient to report '>100 cm'. This will be an alpha-numerical field. Units are centimeters.

Continuous rock is consolidated material underlying the soil, exclusive of cemented or indurated pedogenetic horizons such as petrocalcic, petroduric, petrogypsic andpetroplinthic horizons.

Continuous rock is sufficiently consolidated to remain intact when an air-dried specimen, 25–30 mm on one side, is submerged in water for 1 hour.

The material is considered continuous only if cracks into which roots can enter are on average ≥ 10 cm apart and occupy < 20% (by volume) of the continuous rock, with no significant displacement of the rock having taken place (IUSS Working Group WRB, 2015).

- The depth to the mean highest and mean lowest groundwater table (HGWT, LGWT) is provided in PRF file according to 50 cm depth classes.

4.1.1.2 Sampling time

The pedological characterisation has to be carried out only once to make sure that all necessary information is available for soil classification according to WRB. See Annex 2: Guidelines for forest soil description.

Table 4: Overview of mandatory and optional parameters for the pedological characterisation of the plot on Level I and Level II

Parameter	Unit	Dec.	Mandatory / Optional	
Profile characterisation				
Coordinates of the profile pit (Lat/Long)	+/-DDMMSS	0	M	
Date of profile description	DDMMYY		M	
Elevation of profile pit	Metres asl	0	O	
WRB Reference Soil Group (see IUSS WG on WRB, 2015)	Code		M	
WRB qualifiers and specifiers (see IUSS WG on WRB, 2015)	Code		O	
Definition of diagnostic horizons, properties and materials (see IUSS WG on WRB, 2015)	Code		O	
Upper depth limit of diagnostic horizons, properties and materials	cm from mineral soil surface	0	O	
WRB reference publication	Code		M	
Parent material	Code		M	
Mean highest and mean lowest groundwater table depth	Code		O(1)	
Type of water table	Code		O(1)	
Effective soil depth	cm from mineral soil surface	0	M	
Horizon characterisation			***Org. Layer***	***Min. Layer***
Horizon number	Integer		M	M
Date laboratory analysis	DDMMYY		M	M
Horizon name (symbols for master horizon, subordinate symbol, indication of discontinuity, vertical subdivision)	Code		M(2)	M(2)
Upper and lower limit horizon	cm from mineral soil surface	0	M	M
Horizon distinctness and topography	Code		O	O
Structure	Code		O	M
Moist and dry colour of the soil matrix	Munsell colour code		O	M
Textural class	FAO (2006) code			M
Clay (0 – 2 micrometer fraction)	%	1		O
Silt (2 – 63 micrometer fraction)	%	1		O
Sand (63 – 2000 micrometer fraction)	%	1		O
Code coarse fragments	Code based on vol %		O	O
Coarse fragments	weight %	0	O	O
Total Organic Carbon content	g/kg	1	O	O
Total Nitrogen	g/kg	1	O	O
Total Calcium Carbonate	g/kg	0	O	O
Gypsum content	g/kg	0	O	O
pH		2	O	O
Electrical conductivity	$dS.m^{-1}$	0	O	O
Exchangeable Ca, Mg, K, Na	cmol(+)/kg	3	O	O
Cation Exchange Capacity	cmol(+)/kg	2	O	O
Code Porosity	Code		O	O
Measured or Estimated Bulk Density	kg/m^3	0	O	O
Method to determine Bulk Density	Text/code		O	O
Abundance classes of very fine, fine, medium and coarse roots	Code		O(3)	O(3)

[1] In hydromorphic soils, this parameter is mandatory; [2] Master symbol is always mandatory. Subordinate symbol, indication of discontinuity, vertical subdivision only when it is defined; [3] Mandatory on Level II core plots

4.1.1.3 Sampled layers

- Each pedological characterisation needs to be accompanied by sampling of the identified horizons.
- Note that for the mineral horizon designations, the FAO (2006) definitions are applied whereas for the organic horizons the European horizon symbols (OL, OF and OH, Hf, Hfs and Hs) which are in use in forestry for many years (see Annex 7).
- The analytical data required for soil classification should be reported in the PFH-file.

4.1.1.4 Number of samples

One sample for each identified horizon is sufficient. In case more than one sample for each horizon is analysed, the average value should be reported.

4.1.2 Soil sampling at fixed depths

4.1.2.1 Allocation of soil sampling sites

Sites that should be avoided are areas around tree stems (1m) and animal holes, disturbances like wind-thrown trees and trails. A record of the places sampled should be kept.

4.1.2.2 Sampling time

In order to reduce temporal variations, especially in the organic layer, sampling activities should be confined to periods with low biological activity, e.g. winter or dry season, based on expert judgement. However, the countries that participated in the first survey have to carry out the sampling activities in the same period (season) as for the first survey. The sampling dates have to be reported in the reduced plot file (*.PLS file).

4.1.2.3 Sampled layers

The organic layer at the soil surface is sampled separately from the underlying mineral soil. Buried organic layers are sampled in the same way as mineral layers.

Care should be taken to correctly separate the organic layer from the mineral soil material. Separation will be done in the field, but will be checked in the laboratory, following the internationally accepted criteria (FAO 2006, see Annex 7) to make a distinction between both layers. According to these criteria, organic carbon determination (which is mandatory for both Levels of the survey) has to be used to check whether the separation has been done correctly. If the separation was not done correctly, a new sample has to be taken.

Where possible, the organic and mineral soil should be sampled at exactly the same locations, i.e. sample the mineral soil where the organic layer has already been removed for sampling.

A distinction has to be made between an organic layer that is saturated (H) or not saturated (O) with water according to the FAO-definition (FAO, 2006). The organic layer in aerated conditions may consist of one or more of the following organic subhorizons (Zanella *et al*. 2009): litter (OL), fragmentation horizon (OF) and/or humus (OH). In water saturated organic layers a distinction has to be made between Hf, Hfs or Hs horizon. Detailed definition and descriptions can be consulted in Annex 7.

For the submission of data, these horizons are designated as OL, OF, OFH and OH for the aerated organic (O) layers and as Hf, Hs, Hfs for the saturated H-layers. The thickness of the different horizons has to be measured and reported.

If OL-horizon is sampled, it should be sampled separately. The OH-horizon has to be sampled separately only if it is thicker than 1 cm; otherwise, it may be sampled together with

the OF-horizon. Optionally, the individual horizons (OL, OF, OH) may be sampled and analysed separately.

In the mineral soil, sampling should be done by fixed depth. The top of the mineral soil corresponds with the zero reference level for depth measurements.

Mineral soil layers are designated as 'Mij', where i is the first number of the upper depth limit and j is the first number of the lower depth limit (e.g. M01 corresponds to the 0-10 cm layer). Table 5 shows the layers that should be sampled.

Table 5: Status of layers to be sampled in both levels

Level I (1)		**Level II** (1)	
Mandatory	**Optional**	**Mandatory**	**Optional**
OF+OH, H layer 0-10 cm 10-20 cm 20-40 cm	OL layer 0-5 cm 5-10 cm 40-80 cm (2)	OF+OH, H layer 0-10 cm 10-20 cm 20-40 cm 40-80 cm (3)	OL layer 0-5 cm 5-10 cm

[1] Note that the entire thickness of the predetermined depth should be sampled and not the central part of the layer only.
[2] Optional, but recommended if big changes between topsoil and subsoil are to be expected
[3] Only mandatory for a first assessment, not to be repeated (optional) for a second survey if all mandatory parameters were determined with the reference method, see also par. 5.2.1., key soil parameters

If the upper surface of an indurated horizon (e.g. parent rock) is above the lower limit of sampled soil (40 cm for Level I; 80 cm for Level II), the soil is to be sampled till the depth of the limiting horizon. For example, a M48 layer subsample taken at a location where the rock surface reaches up to 65 cm below the soil surface is composed of material from the mineral soil between 40 and 65 cm depth. The depth range of the upper limit of the indurated horizon is reported under 'Effective soil depth' in the PRF file.

Material discarded for the representative sample can be used to refill bore holes or pits.

Sampling of peatlands

The sampling design is based on the WRB definition of Histosols (= peat soils) which is based on the 40 cm boundary. As long as the peatlayer is less than 40 cm the existing sampling design for mineral forest soils shall be applied (separate sampling of the organic layers and mineral soil according to the fixed depth layers). From the moment the peat is ≥ 40 cm, the peatlayer shall be sampled according to the PEATLAND SAMPLING DESIGN.

This means that the peatlayer is sampled at fixed depths, mandatory 0 – 10 and 10 – 20 cm and optionally at 20 – 40 and 40 – 80 cm. In the reporting forms a separate name for the peatlayers shall be used, namely H01, H12, H24 and H48 in the records for the organic layers. The list of parameters (mandatory and optional) follow the rules for the OF, OH or OFH layer.

If the conditions allow (lower water table), the mineral soil below the peat soil (> 40 cm) can be further sampled till a depth of 80 cm (where the 0 cm reference is at the top of the peat layer). The standard sampling depths should be followed as much as possible.

4.1.2.4 Number of samples

Level I: For every layer, mandatory 5 subsamples have to be taken (a composite of 5 is allowed) (e.g. if taken with an auger >= 8 cm diameter), but more subsamples are required according to the variability of the site. Mandatory 1 composite sample has to be analysed and reported, more can be analysed optionally to determine the variability of the site. In case of very stony soils where sampling by auger is not possible, 1 composite of at least 3 subsamples can be accepted for the optional depth layers (M24 and M48) only.

Level II: For every layer, mandatory a MINIMUM of 24 subsamples has to be taken, to be combined in at least three composite samples (i.e. at least 3 composites of each 8 subsamples or 4 composite samples of each 6 subsamples). Each composite sample should be spatially clustered. Mandatory at least 3 values have to be reported (1 from each composite), to obtain information on the sampling variability among clusters (composites). The samples should be representative for the whole plot area. The distance between sampling clusters (composites) should be at least 5 meter in order to avoid autocorrelation.

The subsamples have to be of equal mass, except for situations with a variable lower depth limit. In such a case (e.g. an indurated horizon within the depth range of the sampled layer), the mass of each subsample is function of the thickness of the actually sampled layer. In the above example (section 4.1.2.3. last part), the mass of the subsample taken should be a proportion equal to (65-40)/(80-40) of the standard sample mass.

4.1.3 Sampling at fixed depth for soil bulk density

4.1.3.1 Allocation of the soil sampling sites

Not specified except when done in association with soil water measurements (see 4.1.4.1).

Determination of bulk density by measurement is mandatory for Level II, but if this measurement has been done according to the reference methods for the first survey, it has not to be repeated. For Level I, bulk density is a mandatory parameter too, but it can be estimated using pedo-transfer functions. If pedotransfer functions are used, regional calibration and validation are necessary. Information on how to determine the usefulness and predictive quality of bulk density PTFs for forest soils can be found in De Vos *et al*. (2005).

4.1.3.2 Sampling time

Not specified.

4.1.3.3 Sampled layers

The determination of the bulk density is mandatory on 3 depth layers (0-10 cm, 10-20 cm and 20-40 cm) on non-stony soils and optional on the 4th depth layer (40-80 cm).

4.1.3.4 Number of samples

Per plot, five samples with a minimal volume of 100 cm^3 have to be taken.

4.1.4 Sampling for soil water measurements

4.1.4.1 Allocation of the soil sampling sites

On each plot at least 3 profiles are sampled separately. The location of these profiles within the plot may be chosen freely, as long as their spatial design meets following requirements:

- The individual profiles are representative for the soil condition within the plot;
- The profiles are not located in one single profile pit (i.e. profiles are at least some meters apart);
- The profiles should be situated as close as possible to the location of the soil moisture measurement sensors;

The exact coordinates of each profile location should be determined and kept for internal record.

4.1.4.2 Sampling time

The samples should be taken when the soil is close to field capacity, which is often towards the end of the winter. Do not sample the soils when it is freezing. Ideally the undisturbed

cores are taken at the time of the installation of the soil moisture probes to assure 1) minimal soil disturbance and 2) that the cores are taken in the same layer and horizon as the soil moisture sensors.

4.1.4.3 Sampled layers and number of samples

At each location, adequate undisturbed soil sampling within the soil profile is done according to the sampling scheme in Table 7. At least one undisturbed core is taken within the fixed depth intervals 0 - 20, 20 - 40 and 40 - 80 cm, preferentially at the same depth as the soil moisture measurements. See also the submanual IX on Meteorological Measurements. The exact depth range of the soil core (top to bottom of core) is reported, along with the ring ID information.

When forest floor thickness (OF + OH layer) is > 5 cm, the OF+OH layer should be sampled also with a suitable cylinder or frame. Optionally, extra mineral soil layers or horizons could be sampled that are considered relevant for the hydrological regime of the soil profile.

Table 7: Sampling scheme for core samples to determine soil water retention characteristic

Matrix	Depth interval (cm)	Minimum number of replicates		Requirements for Level II core plots
		per profile	per plot	
Organic Layer	OF+OH > 5 cm thick OF+OH <= 5 cm thick	1 -	3 -	Mandatory Not required
Mineral layer	0 - 20 cm 20 - 40 cm 40 - 80 cm > 80 cm Extra (specific) layer	1* 1* 1* - -	3 3 3 - -	Mandatory Mandatory Mandatory Optional Optional

(*) if the mineral layer is difficult to sample (e.g. caused by higher gravel content) a higher number of samples are strongly recommended.

Concluding from Table 7, on each plot at least 9 undisturbed and representative samples should be taken if the forest floor is less than 5 cm thick and 12 samples if the forest floor is more than 5 cm thick.

For each undisturbed sample, the pedogenetic horizon according to the designations given in Annex 7, should be reported that contains the centre of the sampling cylinder. The pedogenetic horizon may be deduced from the soil profile description of the sampled plot.

Hence for each undisturbed core sample following information is reported:

- The exact depth range of the core cylinder in cm by reporting the depth of the upper and lower end of the cylinder (e.g. 10 -15 cm for a cylinder of 5 cm in height);
- Pedogenetic horizon containing the centre of the undisturbed sample (e.g. 12.5 cm is located in E horizon)

4.2 Sampling equipment

4.2.1 Pedological characterisation of the plot

A list of field equipment for profile description is provided in Annex 4.

4.2.2 Soil sampling at fixed depths

It is recommended to sample the **organic** layer with a frame of 25 by 25 cm, but alternatives with a minimum total surface of 500 cm^2 are acceptable; for mor humus, an auger with a diameter of 8 cm can be used. Sampling of the organic layer can be done by hand, supported by trowel, knife, spatula and/or brush.

For sampling of the **mineral** soil by auger, Annex 4 provides a list with recommended soil augers according to the soil texture type and moisture conditions.

Further following equipment is essential:

- Field forms, pencils and permanent marker
- Folding meter
- Knife
- Spade
- Impact free hammer
- Spatula
- Electronic field balance and spare batteries (only when subsamples are taken)
- Recipients for transporting the samples plus labels
- Sampling tray for mixing the subsamples of the composite samples

4.2.3 Sampling of undisturbed soil core cylinders

Undisturbed soil cores are taken in dedicated metal cylinders (sleeves) with a volume between 100 and 400 cm^3. Plastic cylinders are dissuaded. The same steel cylinders can be used for the soil water measurements (method SA14) as for determination of bulk density (method SA04). The sample ring dimensions should be representative of the natural soil variability and structure. The most frequently met dimensions (height x diameter in mm) of cylinders for forest soil sampling are: 50 x 53 (100 cm^3), 40.6 x 56 (100 cm^3) and 50 x 79.8 (250 cm^3). It is important to verify that the laboratory that will process the undisturbed samples is equipped for the type of sample rings used. The bottom of the sample ring should have a cutting edge. Plastic lids should perfectly fit to both ends of the steel cylinder.

In a soil profile pit, undisturbed samples can be taken directly using the sample ring, without extra material. When sampling is done in a bore-hole, a closed ring holder is recommended.

In conclusion, the sample material consists of:

- Steel cylinders (sample rings) with lids
- Open ring holder (optional)
- Closed ring holder (needed when sampling in boreholes)
- Spade and/or trowel for digging out the cylinder
- Impact absorbing hammer (for hard soil layers only)
- Small frame saw
- Spatula or knife
- Waterproof marker for labelling
- Plastic bags or foil for wrapping the rings

4.3 Sample collection

4.3.1 Pedological characterisation and profile pit sampling

By profile sampling, using a knife and a tray the soil is gently loosened from the respective horizon. By using the tray any material that accidentally is included in the sampled material can easily be removed before the material is brought into the bag.

As a general rule, and surely for taxonomic purposes, at least one sample per horizon should be taken. If a horizon is particular heterogeneous, e.g. due to strong mottling, it may be necessary to take several subsamples.

Samples for chemical analyses can be collected in various ways. The mode of sampling should be recorded, as for example on a sample list and by means of either a simple sketch or by special photos. The chosen sampling procedure should reflect the soil variability within the horizon and naturally the purpose of the prospection.

- The “composite” sample: several soil samples are collected throughout the horizon. These samples can be kept separate. If, as for example, from profile 12 the 4 subsamples a, b, c and d are collected in horizon 2, this can be labelled P12H2a, P12H2b, P12H2c, P12H2d, or they can be mixed together in one bag and labelled e.g. P12H2.
- The “massed average” sample: is a sample taken throughout the whole (vertical) thickness of the horizon.
- The “middle” sample: is a sample taken more or less in the middle of the horizon, there where the characteristics of the horizon are best developed. For classification purposes, the “middle” sampling strategy is recommended.

4.3.2 Sampling at fixed depths

4.3.2.1 Organic layer sampling

It is strongly recommended to make the description of the humus form simultaneously with the sampling of the organic layer.

Either all subsamples coming from the inside of the frame or from the auger are taken individually to the lab to determine the dry mass (kg/m^2), or the subsamples are first bulked in the field and subsequently a subsample is taken to the lab for further measurements. In the latter case, it is absolutely necessary that the fresh mass (kg/m^2) of each subsample and each organic subhorizon is measured in the field using an electronic field balance.

Record the total surface of each subhorizon (surface of the frame/auger * N° of subsamples) to allow stock calculations later on.

The frame is pushed carefully in the forest floor. Then the organic subhorizons are separately cut out along the frame using a sharp knife. Be careful not to include any mineral soil material in the OH sample. Living material (such as mosses, roots, etc.) and objects > 2 cm in diameter are removed from the sample but smaller twigs, fruits remain to determine the mass of the sample.

4.3.2.2 Mineral soil sampling

Augering is preferred but pits are allowed, especially in case of stony soils where augerings are difficult or impossible.

4.3.2.3 Size of samples

The minimum mass of each representative sample for chemical analysis should be large enough for all laboratory analyses (mandatory and optional parameters) and possible repetitions or reanalyses in time. It is also advisable to keep the sample in a storeroom. The absolute minimum mass of samples (field mass) with no or little gravel should be 500 grams but 1 kg is recommended for important (reference) samples.

4.3.3 Cores for bulk density and soil water retention measurements

The core method is applicable for stone-less and slightly stony soils. The samples are taken with core cylinders on horizontal sections.

The sampling procedure for undisturbed soil sampling (core sampling in steel rings) is as follows:

- Take soil cores carefully to ensure minimal compaction and disturbance to the soil structure:
- In a soil pit, undisturbed samples can be taken by hand pressure directly using the sampling ring.
- Alternatively, an open ring holder may be used. In such a holder, the ring is locked by means of a rubber or lever. Over the ring some space headroom is left allowing for taking an oversize sample. This prevents the sample for compaction during sampling.
- In hard soil layers, an impact absorbing hammer may be used for hammering the ring holder into the soil.
- When sampling in a bore hole, a closed ring holder is recommended. This type of ring holder holds the cylinder in a cutting shoe. The ring is clamped inside the cutting shoe and no water or soil can come into the ring from the top. Moreover, the sample ring is protected, the sample is oversized on both sides and there is no risk of losing or damaging the sample ring. In hard layers, an impact absorbing hammer may be used with care.
- The ring sample is taken vertically with its cutting edge downwards;
- Dig out the cylinder carefully with a trowel, if necessary adjust the sample within the cylinder before trimming flush, trim rough the two faces of the cylinder with a small frame saw. A spatula or knife may be used but care has to be taken to avoid smearing the surface (closing macro- and mesopores).
- Close both sides of the cylinders with suitable lids.
- Record sampling date, sample grid reference, horizon encompassing the centre of the core, and the exact sampling depths (depth of top and bottom of the cylinder with respect to the top of the mineral horizon).
- Label the cylinder on the lid clearly with the sample plot reference, the sampling date, the horizon code and the sample depth;
- Wrap the ring samples in plastic bags or a plastic or aluminium foil to prevent from drying.

4.3.4 Excavation method for sampling for bulk density

An alternative to core samples for bulk density, is sampling by the excavation method. Sampling of bulk density in stony soils is much more delicate, and surely much more time consuming than sampling in soils with none or little coarse fraction.

First a carefully levelled horizontal section is prepared. A soil volume is then excavated. The volume required depends on the general coarse fraction content. For example if the coarse fraction makes up about 30% of the soil volume, a sample of 20 dm^3 should be sufficient. While excavating the sample, compaction of the sides should be avoided. The sample is stored in a plastic bag, avoiding any compaction. Line the excavation hole with a thin but strong plastic film, fill the hole to excess with a known volume of sand. The hole is filled using a funnel kept 5 cm above the ground, level the surface and avoid compaction. Remove the excess sand into a graduated measuring cylinder, and read the volume. Calculate the total volume of sand filled into the excavation hole (see also Annex 1, SA04).

4.4 Sample storage and transport

The sample recipient should be properly labelled with a comprehensive code preferentially including location name, plot number, profile number, horizon number or layer name, depth of sample, and sampling date.

In the field all the samples either in bags, boxes, metal rings etc. should never be left exposed to the open air and sun. Otherwise water will evaporate from the sample and condense in the same bag or recipient, and there is a risk of ultra-desiccation. The warming up of the sample will also activate the biologic activity within the sample.

Samples for standard soil laboratory analyses are mostly kept either in plastic bags or boxes. If using plastic bags, the bags with a closing zipper and with a special label for writing the sample code are recommended. Also feasible is sampling and transporting the samples in plastic bags and then transferring them into plastic boxes for drying and laboratory treatments.

The undisturbed samples are transported in plastic boxes or aluminium cases. They protect the samples from heat, humidity or dust. If transported in vehicles over long distances, shocking of samples should be avoided by using shockproof materials. Prevent undisturbed soil samples from freezing. Store the samples at 1 to 2 °C to reduce water loss and to suppress biological activity until analysis. It is recommended to avoid weeks of storage of undisturbed soil samples. Ideally, undisturbed soil samples are analysed in the lab immediately after sampling.

The indoor preparation of the soil samples for further laboratory work is based on the ISO 11464 (1994) method (Soil quality – pretreatment of samples for physico-chemical analysis). Collected samples should be transported to the laboratory as soon as possible and air dried or dried at a temperature of 40 °C (ISO 11464, 1994). They can then be stored until analysis. To recalculate the analysis results on mass basis, the moisture content of the sample has to be determined by oven-drying the sample once at 105°C (ISO 11465, 1993).

Living macroscopic roots and all particles, mineral and organic, with a diameter larger than 2 mm, should be removed from the samples by dry sieving as a preparation for analysis. The particles not passing the 2-mm sieve are weighed separately for the determination of the coarse fragments content (required for bulk density). To guarantee a harmonised approach, samples should not be further milled or ground. For those analyses for which finely ground material is required [e.g. Carbonate content (SA07), Total Organic Carbon (SA08), Total Nitrogen (SA09),Total Elements (SA12),…] further milling or grounding is allowed.

4.5 Long-term storage of soil samples

The sample material for long-term storage should be kept without preservative under normal room conditions with minimal temperature and humidity fluctuations, shielded from incident light. When the humidity in the storage room cannot be controlled, the soil samples should be kept in air-tight containers. The samples should be stored at least till the next soil inventory.

5 Measurements

5.1 Physical characterization

5.1.1 Mass and thickness of organic layer

This is the determination of the mass (volume-dry mass, kg/m^2) and the thickness (cm) of the organic layer. For the method of soil moisture content, see Annex 1, SA02.

In the field, the total fresh mass of each layer (OL, OF and OH or Hf, Hsf, and Hs) has to be determined, together with the thickness of the concerning layer. Of each layer a subsample is collected for determination of moisture content (mass %) in the lab in order to calculate its total dry mass (kg/m^2). It is mandatory to report both, thickness and dry mass of all organic layers (OL, OF, OH).

5.1.2 Particle size distribution

The determination of the soil granulometry and classification according to the USDA-FAO textural classes (Figure 1) is mandatory for the mineral layers for Level II, only if not already determined during the first survey (no repetition required if this parameter was already measured). The particle size classes of the fine earth fraction (< 2 mm) are defined as follows (FAO, 2006):

Clay	< 2 μm
Silt	2 – 63 μm
Sand	63 – 2000 μm

For Level I, information on textural class for the mineral layers is mandatory too (though again only if not done in the first survey). However, for Level I an estimate based on the finger test in the field on 1 composite of each layer can be accepted for classifying the soil texture according to the USDA-FAO textural classes. In addition an estimate of the clay content is mandatory as well. Practical guidelines can be consulted in Annex 6. Repetition of the determination of the granulometry is not required. For Level I, extra time and costs are minimised if estimated by finger test (described in Annex 6).

Method

Level I: finger test for estimation of soil texture classified according to USDA-FAO texture triangle (FAO, 1990), and for estimation of the clay content (%). Optional: reference method as described for Level II.

Level II: reference method as described in Annex 1: SA03

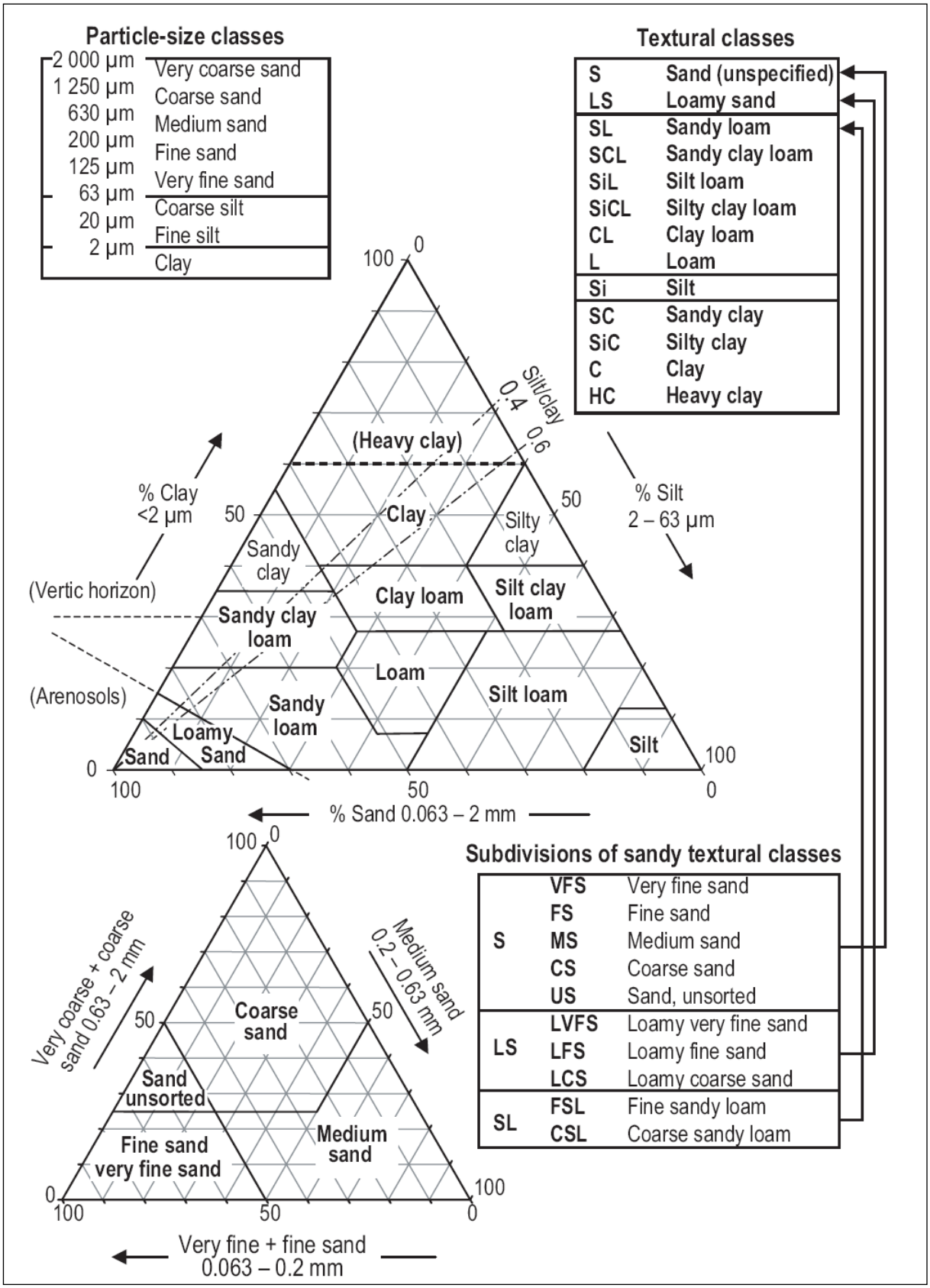

Figure 1: Relation of constituents of the fine earth by size defining textural classes and sand subclasses. Textural classes based on USDA (1951), adopted by FAO (1990) and refined by FAO (FAO, 2006)

5.1.3 Bulk density of the total mineral soil

Definition

Bulk density is defined as the mass of a unit volume of oven dry soil. The volume includes both solids and pores. In mineral soils without coarse fragments the bulk density of the total mineral soil is equal to the bulk density of the fine earth.

Optional and mandatory parameters

Three values of bulk density have to be reported mandatory for the mineral topsoil (0-10 cm, 10-20 cm and 20 – 40 cm) of non-stony soils. For Level I, these values may be obtained either by estimation, pedotransfer functions or measurement. For Level II, the bulk density has to be measured. Determination of the bulk density of the 40-80 cm layer is optional for both Levels. No re-measurement is required if this parameter was determined according to the reference method for the first survey.

Methodology

For measurement: five samples have to be taken with a minimal volume of 100 cm^3 per plot and per layer. In addition, the determination of bulk density requires estimation of coarse fragments according to the USDA-FAO classes (FAO, 1990). The latter can be measured or estimated in the soil profile. This estimation according to the fixed depths shall be done in addition to the normal profile description which follows the genetic layers.

5.1.4 Coarse fragments

Coarse fragments group all gravel, stones and boulders with a diameter larger than 2 mm. The size classes according to the greatest dimension of the individual gravels/stones are defined in Table 8.

Table 8: Size classes of the coarse fragments (FAO, 2006)

Size (cm)	Class name
0.2 – 0.6	Fine gravel
0.6 – 2.0	Medium gravel
2.0 – 6.0	Coarse gravel
6 – 20	Stones
20 – 60	Boulders
60 – 200	Large boulders

Report the amount of coarse fragments of the individual mineral layers in volume %. The abundance of coarse fragments can be measured in the laboratory, but is usually estimated during routine soil profile observations. In the case that very coarse materials are present (stones and boulders), the quantity of these materials has to be estimated in the field. Two methods are recommended: (i) the method established in Finland as described in Annex 1, SA05 or (ii) the method used in Germany (see Annex 1, SA04).

The determination of coarse fragments is mandatory for the 0-10, 10-20 and 20-40 cm mineral layer and optional for 40 - 80 cm mineral layers in both Level I and Level II. In case of re-assessment (if this parameter was already measured according to the reference method in first survey) the parameter is optional. For Level I the parameter may be estimated, for Level II it must be measured using the methods described in Annex 1: SA05.

5.1.5 Combined approach to estimate bulk density of the fine earth and the content of coarse fragments

Riek and Wolff (2006) have revealed that the soil physical parameters (in this case bulk density and fine earth stock) can only be recorded with field methods at specific locations in an inadequate or scarcely reproducible manner. This applies to soils with a high content of coarse gravel and/or the presence of stones and boulders. Because of their low volume, the

core samplers normally used in forest monitoring are unable to representatively collect stones or large portions of coarse fragments in the field. In these cases, the excavation method may produce good results but it may be too expensive, time-consuming and destructive in the framework of large-scale monitoring.

The combined approach can improve the determination of these parameters at locations with a high content of coarse gravel and/or the presence of stones and boulders and lead to a better approximation of the real coarse fragments content.

In the case of a high content of coarse gravel and/or the presence of stones and boulders, the quantity of bulk density of both fine earth and coarse fragments has to be estimated / sampled in the field. Methods should be selected according to the prevailing conditions (i.e. coarse fragment content and size) at each individual sampling site.

In the analysis each method or each combined method leads to the determination of (partially) different parameters which means that different calculation formulas are needed. A description of the different methods and/or combined methods, the related parameters and calculation methods are described in Annex SA04.

If the mineral soil contains no coarse fragments or the (estimated) coarse fragment portion is less than 5 % (**case 1**), then the bulk density of the fine earth (BD_{fe}) is approximately equivalent to the bulk density of the total mineral soil (BD_s) (see paragraph 5.1.3).

In case of mineral soils with a coarse fragment content of more than 5% which can be sampled with a core sampler or any other (representative) sampler for coarse fragments < 20 mm **(case 2)**, a representative volume sampling with core sampler, root auger, AMS core sampler with liner or hollow stem auger is done. When calculating the bulk density of the fine earth, the volume of the coarse fragment content is subtracted from the total volume of the sampler and the mass of the coarse fragments subtracted from the mass of the fine earth referring to this volume.

In case the mineral soil cannot be representatively sampled with a core sampler or any other samples (coarse fragments > 20 mm) **(case 3),** there are two possibilities of taking the coarse fragments into account. The amount of coarse fragments has to be estimated in the field or be determined by additional sampling with a shovel or a spade (representative volume sampling).

When representative volume sampling is not possible, sampling with mini-core samplers and estimation at the profile (coarse fragments > 60 mm) is required **(case 4).** The bulk density of the fine earth in the spaces between the coarse material [soil skeleton] is determined with a mini-core sampler. In addition, a disturbed spade /shovel sample is taken in order to determine factor f (correction factor for a possible coarse fragment portion in the mini-core sampler). Furthermore, the coarse fraction portion > 60 mm is estimated at the profile.

5.1.6 Determination of the soil water retention characteristic (SWRC)

In order to determine the SWRC, the volumetric water content (θ in volume fraction, $m^3\ m^{-3}$) is determined at predefined matric potentials (ψ, in kPa). As indicated in Table 9, six of these matric heads are mandatory to determine. Extra observations of the SWRC at pressures -10, -100 and -250 kPa are optional but they greatly improve fitting the SWRC.

Some matric heads immediately provide information on SWRC parameters: at 0 kPa the maximum water holding capacity (WHC) of the saturated soil sample is determined; depending on definitions and soil texture field capacity (FC) may be inferred from -10 till -100 kPa; permanent wilting point (PWP) is attained at a matric pressure of – 1500 kPa and dry bulk density (lowest pressure at about 10^{-6} kPa) derived in the oven at 105°C.

The standard instruments required for each determination are listed in Table 9. The reference methods for all physical parameters are listed in Table 10.

Table 9. Overview of matric heads to assess for the determination of the SWRC

Matric potential ψ			Recommended instrument	Estimator	Equivalent pore size diameter	M / O
cm H_2O	pF	kPa			Jurin's law, Hillel (1980)	
1	infinitely small	0	Pycnometer	≈θsat= water holding capacity = Total porosity	> 1 mm	M
10	1.0	-1	Sand suction table		300 µm	M
51	1.7	-5			60 µm	M
102	2.0	-10		Field capacity sand	30 µm	O
337	2.5	-33	Kaolin suction table	Field capacity siltloam	10 µm	M
1022	3.0	-100	Pressure plate extractor or pressure membrane cells	Field capacity clay	3 µm	O
2555	3.4	-250			1.2 µm	O
15330	4.2	-1500		Permanent wilting point	0.2 µm	M
10^7	7.0	-10^6	Oven	Dry BD	0.0003 µm	M

Where:
1) the pF is the logarithm of the absolute value of the matric potential expressed by the graduation of the water column (cm).
2) 1 kPa = 10.22 cm H_2O or 1 cm H2O column = 0.097885 kPa
3) 100 kPa = 1 bar

Table 10: Overview of the reference methods for physical parameters

Parameter	Reference Method	Unit
Particle size distribution (sand, silt, clay fractions)	Pipette method	%
	Finger test method (only allowed on Level I)	
Coarse fragments	Laboratory measurement	vol%
	Field estimate during soil profile description	
Soil water retention characteristic	0 kPa: Pycnometer measurement -1 till – 10 kPa: Sand suction table - 33 kPa: Kaolin suction table -100 till -1500 kPa Pressure plate extractor or pressure membrane cells	m^3/m^3
Bulk density	Oven drying at 105°C	kg/m^3
Volume dry mass of organic layer	Field measurement of total fresh mass Field measurement of the horizon thickness Determination of moisture content in the laboratory	kg/m^2 cm mass%

5.2 Chemical characterization of collected samples

5.2.1 Selected key soil parameters for the Level I and II Survey

An overview of the key parameters to be measured is presented in Table 11. Note that the minimum requirement for a number of the mandatory parameters, indicate that in the mineral layers below 20 cm the parameters should be measured once and not necessarily be re-measured a second time.

With regard to the nutrients, the amount extracted by aqua regia is mandatory for the OF+OH horizons and H layers of the organic layer and optional for the mineral topsoil. While from this extraction not the real total content is obtained, it is useful as an estimate of the nutrient stock. Extra costs and work are minimal as it can be measured from the same extraction to be made for the heavy metals (mandatory for both the OF+OH horizons, H-layers and the mineral topsoil). For the determination of the 'real' total amounts, more specialised material

and skill are required. As these 'real' total contents are important for the calculation of weathering rates and critical loads, they are optional for the mineral layers of Level II.

Note that the measurement of carbonates is required also for the correction of the organic carbon content if the pH($CaCl_2$) > 5.5 in the organic and > 6 in the mineral layer.

For the determination of the pH, measurement on a $CaCl_2$-extract is mandatory. pH(H_2O) has been made an optional parameter for reasons of comparability, as this is mostly used in literature.

Table 11: Chemical and physical key soil parameters on the samples taken at fixed depths[1]

Parameter	Unit	Deci-mals	Level I						Level II					
			Organic Layer		Mineral Layer				Organic Layer		Mineral Layer			
			OL	OF+OH, H- [2]	0-10 cm	10-20 cm	20-40 cm	40-80 cm	OL	OF+OH, H [2]	0-10 cm	10-20 cm	20-40 cm	40-80 cm
Physical soil parameter														
Organic layer mass	kg/m^2	2	O	M	-	-	-	-	O	M	-	-	-	
Coarse fragments	vol %	0	-	-	M [3], [4]	M [3] [4]	M [3] [4]	O [4]	-	-	M	M [3], [4]	M [3], [4]	O [4]
Bulk density of the fine earth	kg/m^3	0	-	-	M [3], [5], [6]	M [3], [5], [6]	M [3], [5], [6]	O	-	-	M [3], [5]	M [3], [5]	M [3], [5]	O
Particle size distribution (FAO, 1990)	-	-	-	-	M [3], [7]	M [3], [7]	O	O	-	-	M [3]	M [3]	M [3]	M [3]
Clay content	%	1	-	-	M [3], [7]	M [3], [7]	O	O	-	-	M [3]	M [3]	M [3]	M [3]
Silt Content	%	1	-	-	O	O	O	O	-	-	M [3]	M [3]	M [3]	M [3]
Sand Content	%	1	-	-	O	O	O	O	-	-	M [3]	M [3]	M [3]	M [3]
Chemical soil parameter														
pH($CaCl_2$)	-	2	-	M	M	M	O	O	-	M	M	M	M [3]	M [3]
pH(H_2O)	-	2	-	O	O	O	O	O	-	O	O	O	O	O
Total organic carbon	g/kg	1	-	M	M	M	M	M	-	M	M	M	M	M
Total nitrogen	g/kg	1	-	M	M	M	M	M	-	M	M	M	M	M
Carbonates	g/kg	0	-	M [8]	M [8]	M [8]	O	O	-	M [8]	M [8]	M [8]	O	O
Aqua Regia extracted P, Ca, K, Mg, Mn	mg/kg	1	O	M	O	O	O	O	O	M	O	O	O	O
Aqua Regia extracted Cu, Pb, Cd, Zn	mg/kg	1	O	M	M	-	-	-	O	M	M	-	-	-
Aqua Regia extracted Al, Fe, Cr, Ni, S, Hg, Na	mg/kg	1	O	O	O	-	-	-	O	O	O	-	-	-
Exchangeable Acidity, Free H^+, Exchangeable cations Al, Fe, Mn	$cmol_{(+)}$/kg	2	-	M [9]	M [9]	M [9]	O	O	-	M [9]	M 9]	M [9]	M [3], [9]	M [3], [9]
Exchangeable cations Ca, Mg, K, Na	$cmol_{(+)}$/kg	2	-	M [9]	M	M	O	O	-	M [9]	M	M	M [3]	M [3]
Total Elements: Ca, Mg, Na, K, Al, Fe, Mn	mg/kg	1	-	-	-	-	-	-	-	-	O	O	O	O
Oxalate extractable Fe, Al	mg/kg	1	-	O	O	O	O	O	-	O	M	M	M [3]	M [3]
Oxalate extractable P	mg/kg	1	-	O	O	O	O	O	-	O	O	O	O	O

[1] Abbreviations : M = mandatory parameter, O = optional parameter
[2] If the OH - horizon > 1 cm, the OF - and the OH - horizons should be analysed separately and each value has to be reported
[3] In case of a re-assessment (if the parameter was already measured according to the reference method for the first survey) , the measurement is optional
[4] May be obtained by estimation or measurement
[5] Mandatory only in non-stony soils
[6] May be obtained by estimation, pedo-transfer function or measurement
[7] May be obtained by finger test, consists of texture classified according to USDA-FAO texture triangle
[8] Only mandatory if pH($CaCl_2$) > 5.5 or in calcareous soils
[9] In calcareous soil, the measurement of this parameter is optional

5.2.2 Reference analytical methods

The full description of the reference methods is given in Annex 1.

Table 12 gives an overview of the reference methods for the chemical parameters. Note that the parameters are grouped according to the analytical method. As such it is obvious which elements can be measured in the same run, without additional costs and hardly extra work involved.

Table 12: Overview of reference methods for the chemical parameters

Parameter	Reference Analysis Method [1]					Unit [2]
	ISO	Extractant	Measurement method(s) [3]			
pH($CaCl_2$)	ISO 10390 (2005)	0.01 M $CaCl_2$	pH-electrode			
pH(H_2O)		H_2O	pH-electrode			
Total nitrogen	ISO 13878 (1998)	-	Dry Combustion			g/kg
	ISO 11261 (1995)	-	Modified Kjeldahl			
Total organic carbon[4]	ISO 10694 (1995)	-	Dry Combustion at ≥ 900 °C			
Carbonates	ISO 10693 (1994)	HCl	Calcimeter			
P	ISO 11466 (1995)	Aqua Regia by reflux digestion	ICP	Colorimetry		mg/kg
K, Ca, Mg, Mn				AAS		
Heavy metals: Cu, Cd, Pb, Zn						
Other: Al, Fe, Cr, Ni, Na						
Hg			ICP	Cold vapour AAS		
S			ICP			
		CNS - analyser				
Free Acidity (or sum of AC[5]) and free H^+	ISO 11254 (1994) modified	0.1 M $BaCl_2$	titration to pH 7.8 or 'German' method			$cmol_{(+)}$ /kg
Exchangeable Cations: Al, Fe, Mn	ISO 11260 (1994) modified	0.1 M $BaCl_2$	ICP	AAS	-	
Exchangeable Cations: K, Ca, Mg, Na					FES	
Reactive Fe and Al Oxalate extractable P	ISRIC (2002)	Acid ammonium oxalate	AAS	ICP		mg/kg
Total Elements: Ca, Mg, Na, K, Al, Fe, Mn	ISO 14869-1 (2001)	HF or $LiBO_2$	AAS	ICP		mg/kg

[1] Reference and full descriptions are given in Annex 1
[2] Results have to be expressed on an oven dry basis
[3] For the measurement of a number of parameters there are several alternatives for the equipment that can be used
[4] Note that for total organic carbon a correction has to be made for total inorganic carbon (carbonates)
[5] Alternative for the titration of the exchangeable acidity is the sum of the exchangeable Al, Fe, Mn and free H^+

5.3 Data quality requirements

The quality of the soil analytical data is controlled by the regular organisation of Interlaboratory Comparisons (ring tests) by the Forest Soil Co-ordinating Centre. Each soil laboratory participating in the ICP Forests programme should be qualified for the reported parameters. For qualification procedures, see Manual Part XVI on Quality Assurance and Control in Laboratories. Information on the performance of the concerning soil laboratory is reported to the data centre at each submission period.

5.3.1 Plausibility limits

See Manual Part XVI on Quality Assurance and Control in Laboratories, Table 3.3.2.1a "Plausible ranges for organic and mineral soil samples at the European level." Laboratories are invited to check the data that are outside these plausibility limits before reporting.

Plausibility limits for SWRC of mineral forest soils and organic layers will be developed in the future.

5.3.2 Data completeness

Tables 9 and 11 outline for all the physical and chemical soil parameters whether and under which conditions they are mandatory or optional to report. When a country/federal state decides to report optional parameters, they should also fulfil the data quality requirements.

Soil water retention data are considered complete if volumetric water content for all six mandatory matric heads (see Table 9) is determined. For scientific reasons analysing the optional matric heads also is strongly recommended. Interpolation of volumetric water content between matric pressures is not allowed.

5.3.3 Data quality objectives or tolerable limits

See Manual Part XVI on Quality Assurance and Control in Laboratories, Tables 3.4.1.2.2 for the tolerable limits of the measured parameters in the FSCC Interlaboratory Comparisons.

Tolerable limits for the determination of the SWRC for laboratory performance will be derived from the reproducibility data gained by performing interlaboratory physical soil ringtests.

All reported values should have been measured according to the methods described in Annex 1.

5.3.4 Data quality limits

The laboratory results are considered of sufficient quality when the laboratory received a qualification for the concerning parameter(s) after participation in the FSCC Interlaboratory Comparisons.

The soil chemical Interlaboratory Comparisons should include at least 5 soil samples (mineral and organic). When 50% of the samples in the ring test are within the tolerable limits, the laboratory is qualified to analyse the concerning parameter and the survey results can be reported to the central database.

6 Data handling

6.1 Data submission procedures and forms

Forms for data submission, dictionaries and explanatory items are found on the ICP Forests web page, at https://icp-forests.org/documentation/. The quality information on the labs has to be sent together with the PLS, PRF, PFH, SOM, SWC and SWA forms to the data centre..

The following rules apply:

- Data will be reported for the H- and O-horizons and for the mineral soil.
- For the organic layers reporting is done according to the OL-, OF-, OH-, OFH-, Hf, Hs, Hfs horizons or as described in Annex 7 of this Part of the Manual.
- For the mineral soil, reporting is done according to the defined mandatory depth layers.

- For the peat layers, reporting is done according to the defined depth layers (Mandatory: H01, H12 and Optional: H24 or H48) and following the parameter list for the OF, OH and H-layers of the organic horizons.

6.2 Data validation

Data checks should be done as soon as results from the analyses are available. Data validation and quality assurance should be applied in accordance with the guidelines for QA/QC procedures in the laboratory that are given in Manual Part III on QA/QC in laboratories (§ 3.3.2.2: Cross checks between soil variables).

6.3 Transmission to co-ordinating centres, with timetable and rules

All validated data should be sent to each national focal centre and to the European central data storage facility at the ICP Forests Programme Coordinating Centre. Detailed time scheduled is provided by the relevant bodies.

6.4 Data processing guidelines

6.4.1 Derived soil parameters

Chemical derived soil parameters such as cation exchange capacity (CEC), Base Saturation (BS), C:N ratio, C:P ratio are not reported, but are directly calculated from organic carbon, total nitrogen and phosphorus, exchangeable cations, acidity and Free H^+.

A typical example of derived soil physical parameters is the available water capacity (AWC), field capacity (FC), wilting point (WP) and total porosity which may be derived from the SWRC. Soil water retention curve models are fitted to the raw data. For forest soils, one of the best performing functions is the Van Genuchten equation defined by its empirical parameters θr, θs and empirical constants α, n and $m = 1-1/n$. The Van Genuchten model parameters should also be stored.

6.4.2 Data Classification

When presenting the forest soil condition data of Level I on a map, a selection of classes is required. The number of classes is best limited. The limits are then selected in function of the frequency distribution of the parameter results.

In case the results approximate a normal distribution, class limits are chosen more or less symmetrically around a central class. The difference between upper and lower class limits are kept constant, consequently more results are assigned to the middle class.

However, most parameters results are not normally distributed. Often the distributions are positively skewed, showing a tail towards larger values. In order to obtain a distribution of results among the classes similar to normally distributed parameters, the differences between upper and lower class limits are gradually increased.

For the classification of elevated heavy metal concentrations, use is made of available ‘toxic’ values found in literature and critical levels.

6.4.3 Clustering Soil Observation Plots

Soil chemical properties usually vary within a wide range. They are influenced by many external factors such as climate, soil parent material, age of the soil material and vegetation type. Evaluation of the soil condition based at a large number of observation sites involves the study of relationships among individual soil properties and among soil properties and external influencing factors. In order to investigate these relationships statistically, the need arises to compare groups of individual soils, having similar properties. Considering the site

factors that determine forest soil conditions and limitations associated with data availability, the following criteria for clustering each soil observation plot can be used: climatic region, atmospheric deposition load, soil type, parent material class, texture class, humus type, biogeographical region,…

6.4.4 Statistical methods

For each parameter, three statistical approaches can be applied:

1 Descriptive statistics (boxplots, histograms, frequency distributions, means, percentiles, etc)
2 Classical statistical data analysis and testing (parametric and non- parametric methods)
3 Geostatistical approach (including the spatial component)

The statically obtained information offers opportunities for further modelling.

6.5 Data reporting

Data should be accompanied by a “Data accompanying report” (DAR) and any other information requested by the European central data storage facility. The DAR should include all details on sampling and analytical procedures. In addition, irregularities in sampling and analytical procedure, missing data, estimated values and encountered errors in the validation, should be documented.

All details on how data are treated and how the calculations are made shall be documented and shall accompany the result to the data storage facility. If values are below the quantification limit (not the detection limit), a value of -1 should be reported. Definitions of the quantification and detection limits can be found in Section 3.2.3 of the Manual Part III on Quality Assurance and Quality Control in Laboratories.

7 References

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Annex I – Methods for Soil Analysis

Soil Analysis Method 1 (SA01) Pre-treatment of Samples

Pre-treatment of Samples	
Method sheet	SA01
Reference methods	ISO 11464
Method suitable for	Organic Layer; Mineral Layer

I Relevance in ICP Forests

All samples (organic and mineral) have to be prepared according to the standard methodology in order to maintain comparability among participating countries.

Priority	**Level I**	**Level II**
Organic Layer		
OL	*Optional*	*Optional*
OF+OH, H-layers	*Mandatory*	*Mandatory*
Mineral layer		
0- 10 cm [1]	*Mandatory*	*Mandatory*
10 – 20 cm	*Mandatory*	*Mandatory*
20 – 40 cm	*Mandatory*	*Mandatory*
40 – 80 cm	*Optional*	*Mandatory*

[1] Optionally this layer may be split in two layers: 0 – 5 cm AND 5 – 10 cm

II Principle

a. Organic layer

After removal of living material (such as mosses, roots, etc.) and objects > 2 cm, collected samples (preferably not less than 500 g fresh material) should be transported to the laboratory as soon as possible and should be air dried or dried at a temperature of 40 °C. They can then be stored until analysis. The sample is subsequently crushed or milled to size < 2 mm.

When the samples are bulked in the field and only a subsample is taken to the laboratory, the fresh mass (kg/m^2) of each organic sublayer should be measured in the field. Further it is strongly recommended to measure the thickness of each organic sublayer in each subsample in the field. Firstly, because the horizon thickness (in cm in terms of the upper and lower limit) is mandatory to report in the profile description file. Secondly it is useful as a cross check.

b. Mineral layer

After removal of living material (such as mosses, roots, etc.) and objects > 2 cm, collected samples (preferably not less than 500 g fresh soil) should be transported to the laboratory as soon as possible and should be air dried or dried at a temperature of 40 °C. They can then be stored until analysis.

Living macroscopic roots and all material, mineral and organic, with a diameter larger than 2 mm, should be removed from the samples by dry or wet sieving. The particles not passing the 2-mm sieve (after crushing), may be weighed separately for the determination of the coarse fragments content (SA05). The fraction smaller than 2 mm is used for the soil analysis. The mineral soil samples are crushed and sieved above a 2 mm sieve. Further grinding is allowed in accordance with ISO 11464 for the analysis of Carbonate content (SA07), Total Organic Carbon (SA08), total Nitrogen (SA09), Total Elements (SA12) and Aqua Regia Extractant Determinations (SA11).

Important Note: further grinding will change the test sample properties (e.g. specific surface area, sample homogeneity) compared to 2mm-sieved samples and will generally lead to higher reported concentrations of some aqua regia extractable elements depending on soil texture class and mineralogy. This may have implications for data analysis of time series.

In order to preserve methodological consistency of long-time data series, it is therefore required to conduct a comparative study when changing the extraction method (reflux vs. microwave) or milling procedure to determine the affected elements and magnitude of the effect on local soil samples. This study needs to be reported to the Expert Panel on Soil and Soil Solution.

The sample material for storage should be kept without preservative under normal room conditions with minimal temperature and humidity fluctuations, shielded from incident light.

III Apparatus

Drying oven.

Crusher, mill, mortar and pestle.

Plate sieve, mesh sieve

IV Reagents

No reagents.

V Procedure

Drying

Spread the material in a layer not thicker than 5 cm. If necessary, the sample is crushed while still damp and friable and again after drying. Dry the complete sample in a drying oven at a temperature of 40 °C, until the loss in mass of the sample is not greater than 5 % (m/m) per 24 h. Break down the size of larger clods (greater than 15 mm) to accelerate the drying process.

Removal of fraction < 2 mm

Remove stones and large objects by hand picking and sieving (< 2 mm). Minimise the amount of fine material adhered. Weigh separately the fraction not passing the 2 mm sieve for determination of coarse fragment content. Crush (not ground) the clods greater than 2 mm taking care that crushing of original particles is minimised. Homogenise the < 2 mm fraction.

Sieving and Milling

The organic sample is crushed or milled to size < 2 mm.

The mineral soil samples are crushed and sieved above a 2 mm sieve. Further grinding is allowed for the analysis of Carbonate content (SA07), Total Organic Carbon (SA08), Total Nitrogen (SA09), Total Elements (SA12) and aqua regia extractable elements (SA11).

Subsampling

For the preparation of an analysis subsample, split up (by hand, using a sample divider or by mechanical subsampling) the sample into representative portions until the required sample number and sample size is obtained.

VI Calculation

No calculations.

VII Report

The mineral fractions (> 2 mm) obtained after sieving with a 2 mm sieve may be used for determination of coarse fragments (SA05).

VIII Reference

ISO 11464. 2006. Soil Quality – Pretreatment of samples for physico-chemical analysis. International Organization for Standardization. Geneva, Switzerland. 9 p. [available at www.iso.ch].

Soil Analysis Method 2 (SA02): Determination of Soil Moisture Content

Soil Moisture Content	
Method sheet	SA02
Reference method	ISO 11465
Method suitable for	Organic Layer; Mineral Layer

I Relevance in ICP Forests

Recalculation of results obtained by lab analysis to “oven-dry mass”.

Priority	**Level I**	**Level II**
Organic Layer		
OL	*Optional*	*Optional*
OF+OH, H-layers	*Mandatory*	*Mandatory*
Mineral layer		
0- 10 cm [1]	*Mandatory*	*Mandatory*
10 – 20 cm	*Mandatory*	*Mandatory*
20 – 40 cm	*Mandatory*	*Mandatory*
40 – 80 cm	*Optional*	*Mandatory*

[1] Optionally this layer may be split in two layers: 0 – 5 cm AND 5 – 10 cm

II Principle

Calculation and reporting of the results of soil analysis is done on basis of "oven-dry" soil. The moisture content of air-dry soil is determined prior to soil analysis. To recalculate the analysis results on dry mass basis, the moisture content of the sample has to be determined by oven-drying a sample to constant mass. The difference in mass is used to calculate water content on a mass basis.

III Apparatus

Moisture tins or flasks (25 – 100 ml) with closely fitting lid

Drying oven

Analytical balance (accuracy 0.001 g)

Note: The use of an automated apparatus for measuring soil moisture content is allowed as long as it is based on the same principle.

IV Reagents

No reagents.

V Procedure

Mineral Layer: Transfer 5-15 g air-dried fine earth (fraction < 2 mm) to a dried, tared moisture tin and weigh. Dry at 105±5 °C (lid removed) until constant mass is reached.

Organic Layer : Transfer 5 – 10 g air dried organic layer material to a dried, tared moisture tin and weigh. Dry at 105 °C (lid removed) for 24 hours.

Remove tin from oven, close with lid, cool in desiccator and weigh.

VI Calculation

The moisture content in mass percentage is obtained by :

$$Moist\% = \frac{A - B}{B - tare\ tin} * 100$$

Where:

A : Mass of tared moisture tin and air-dried soil sample

B : Mass of tared moisture tin and oven-dried soil sample

The corresponding moisture correction factor for analytical results or for amount of sample to be weighed in for analysis is:

$$\text{moisture correction factor(MCF)} = \frac{100 + moist\%}{100}$$

Note: when reporting the results of Carbonate Content (SA07), Total Organic Carbon (SA08), Total Nitrogen (SA09), Exchangeable acidity, Free H^+, Exchangeable elements (SA10), Aqua Regia Extractable elements (SA11), Total elements (SA12), Acid Oxalate Extractable Fe and Al (SA13), the results on air-dry basis should be multiplied by the moisture correction factor (MCF) to obtain the result on oven-dry basis.

VII Report

Report moisture content (in %) with 1 decimal place.

VIII Reference

ISO 11465. 1993: Soil Quality – Determination of dry matter and water content on a mass basis – Gravimetric method. International Organization for Standardization. Geneva, Switzerland. 3 p. [available at www.iso.ch].

Soil Analysis Method 3 (SA03): Determination of Particle Size Distribution

Particle Size Distribution	
Method sheet	SA03
Reference methods	ISO 11277
Method suitable for	Mineral Layer
Method code	Sample preparation: MA02 Determination: DG02, DG03, DG04

I Relevance in ICP Forests

Particle Size Distribution : USDA-FAO texture Classification and Clay Percentage

Priority	Level I	Level II
Organic Layer	**-**	**-**
Mineral layer		
0 – 10 cm	*Mandatory[1, 2]*	*Mandatory[1]*
10 – 20 cm	*Mandatory[1, 2]*	*Mandatory[1]*
20 – 40 cm	*Optional*	*Mandatory[1]*
40 – 80 cm	*Optional*	*Mandatory[1]*

[1] if not determined in the first soil survey
[2] an estimation of clay content based on finger test is allowed

Particle Size Distribution : Silt and Sand Percentage

Priority	Level I	Level II
Organic Layer	**-**	**-**
Mineral layer		
0 – 10 cm	*Optional*	*Mandatory[1]*
10 – 20 cm	*Optional*	*Mandatory[1]*
20 – 40 cm	*Optional*	*Mandatory[1]*
40 – 80 cm	*Optional*	*Mandatory[1]*

[1] if not determined in the first soil survey

II Principle

Separation of the mineral part of the soil into various size fractions and determination of the proportion of these fractions. The analysis includes all soil material, i.e. including gravel and coarser material, but the procedure below is applied to the fine earth fraction (< 2 mm) only. Of paramount importance in this analysis is the pretreatment of the sample aimed at complete dispersion of the primary particles. Therefore, generally, cementing materials (usually of secondary origin) such as organic matter, salts, iron oxides and carbonates such as calcium carbonate are removed. After shaking with a dispersing agent, sand (63 µm-2 mm) is separated from clay and silt with a 63 µm sieve (wet sieving). The clay (< 2 µm) and silt (2-63 µm) fractions are determined by the pipette method (sedimentation).

III Apparatus

Sampling pipette (10 to 50 ml) with safety bulb and water reservoir, held in frame

Constant temperature room or thermoregulated bath (20 – 30 °C ± 0.5 °C)

Glass sedimentation cylinders (approx. diam. 50 mm, approx. length 350 mm) graduated 500 ml volume with rubber bungs or stirrer

Stirrer and rod

Glass weighing vessels (with masses known to 0.0001 g)

Mechanical shaker (30 – 60 revolutions/min)

Sieves (2 mm – 63 µm)

Balance (accuracy 0.0001 g)

Drying oven

Stopwatch (accuracy 1 s)

Glass filter funnel capable of holding the 63 µm sieve

Wash bottle

Desiccator

650 ml glass beaker with cover glass, 100 ml measuring cylinder, 25 ml pipette

Hot plate or bunsen burner

Electrical conductivity meter (accuracy 0.1 dS/m)

Optional: Centrifuge and 300 ml centrifuge bottle

IV Reagents

Hydrogen peroxide (H_2O_2), 30% volume fraction.

Dispersing agent: 3.3 % sodium hexametaphosphate and 0.7 % soda solution:

Dissolve 33 g sodium hexametaphosphate $(NaPO_3)_6$ and 7 g soda (Na_2CO_3) in water in a 1 l volumetric flask and make to volume. Both chemicals should be dried overnight at 105 °C prior to use. This solution is unstable and shall be replaced after one month.

Antifoaming agent (preferably octan-2-ol, alternatives are ethanol or methanol)

Calcium chloride solution ($CaCl_2$), conc. 1 mol/l

Hydrochloric acid (HCl), conc. 1 mol/l

V Procedure

Test sample

Depending on the soil type, weigh 10 (clay) to 30 g (sand) air-dried soil (fraction < 2 mm). Place the sample in the 650 ml glass beaker or 300 ml centrifuge bottle.

Destruction of organic matter

Add 30 ml water to the test sample (add if necessary a few drops of octan-2-ol to allow thoroughly wetting). Add 30 ml of the 30 % hydrogen peroxide solution and mix using the glass or plastic rod (add if necessary a few drops of octan-2-ol to control foaming). Cover and leave overnight. The next day, place the vessel on a hot plate or bunsen burner and warm. Control foaming with octan-2-ol and stir frequently. To avoid drying out, add water if necessary. Bring the suspension to a gentle boil until all signs of bubbling due to the decomposition of hydrogen peroxide have ceased. If undecomposed organic material is still present, cool the beaker and repeat the treatment with hydrogen peroxide.

If using a centrifuge bring the volume to 150 – 200 ml by addition of water. Centrifuge the bottle until obtaining a clear supernatant (recommended 15 min at a minimum relative centrifugal force (RCF) of 400 g) and remove this supernatant by decanting or by using a suction device.

If a centrifuge is not available the mineral residues may be flocculated by adding 25 ml of 1 mol/l calcium chloride solution, stirring and bringing to about 250 ml with water. Let stand until the supernatant is clear, then siphon or decant this from the residue. Add another 250 ml of water and repeat the washing procedure until the dark residues of the decomposed organic matter have gone (if using this method, take care to check the electrical conductivity (next step) before adding the salt).

Removal of soluble salts and gypsum

After destruction of organic matter add water until obtaining a soil:water ratio of 1:4 – 1:6 (v:v). Shake for 1 h using a shaking machine. Centrifuge to obtain a clear supernatant and measure electrical conductivity (E_c) on this supernatant. If E_c > 0.4 dS/m soluble salts and gypsum is present in considerable amounts and have to be removed. Remove the supernatant, add 250 ml water and shake for 1 h. Centrifuge and measure electrical conductivity again. Repeat this washing procedure until E_c < 0.4 dS/m.

Removal of carbonates

A distinction is made on basis of the presence or absence of calcium carbonate:

(1) Calcareous soils: pH(H_2O) > 6.8
(2) Non-calcareous soils: pH(H_2O) < 6.8

Where the carbonate content is greater than about 2 % mass fraction, add to the washed, centrifuged soil (above) 4 ml of 1 mol/l hydrochloric acid for each percent of carbonate, plus an excess of 25 ml of acid. Make up to about 250 ml with water, and place the suspension on the water bath at about 80 °C for 15 min, stirring the suspension from time to time. Leave the suspension to stand overnight. If the soil flocculates sufficiently to leave a perfectly clear supernatant, then this can be siphoned off or decanted, otherwise centrifugation and decantation will be necessary. Repeat the washing and decantation with water until the E_c of the supernatant is less than 0,4 dS/m.

If the carbonate content is less than about 2 % mass fraction, then only an initial 25 ml of 1 mol/l hydrochloric acid solution is required. It is recommended, therefore, that 20 ml of 1 mol/l calcium chloride solution is added at the same time as the acid. The rest of the procedure is identical as for a higher carbonate content.

Note: *if the carbonate content is that high that the results of the particle size distribution become unreliable, this should be mentioned in the Data Accompanying Report.*

Dispersion

Add sufficient water to the vessel so that the total volume is between 150 ml and 200 ml, shake the contents until all the soil is in suspension, and add 25 ml of dispersing agent from a pipette. Shake the bottle for 18 h on the end-over-end shaker.

Wet sieving at 63 µm

Place a 63 µm aperture sieve in the large glass funnel, and place the funnel in the stand so that the neck of the funnel is inside one of the 500 ml sedimentation tubes. Transfer the dispersed suspension from the centrifuge bottle quantitatively onto the sieve, and wash the soil using a jet of water from the wash-bottle until the water runs clear. The total volume of the washings should not exceed 500 ml.

Remove the sieve from the funnel and wash the residue on the sieve into an evaporating dish by means of a gentle spray from the wash-bottle. To alleviate sieve blockage, use the glass or plastic rod and rubber sleeve. Place this dish in an oven between 105 °C and 110 °C until the residue is dry. Record the mass to 0.0001 g (mf_s).

Wash any particles adhering to the inside of the funnel into the sedimentation tube. Make up the suspension in the sedimentation tube to 500 ml with water.

Calibration

Calibration sampling pipette

Clean and dry the pipette thoroughly and immerse the tip in water. Draw water into the pipette into the safety bulb. Drain off the water in the safety bulb through the outlet tube. Drain the pipette into a weighing bottle of known mass, and determine the internal volume of the pipette. Repeat this exercise three times and take the average of the three volumes as the internal volume of the pipette to the nearest 0.05 ml (V_c ml).

Calibration dispersing agent

Pipette 25 ml of dispersing agent solution into one of the glass sedimentation tubes, and fill the tube to the 500 ml mark with water. Mix the contents of the tube thoroughly. Place the tube in the constant temperature environment, and leave the tube for at least 1 h. Between any of the times at which samples may be taken from the sampling tube (Table SA03-1), take a sample (V_c ml) of the dispersing agent solution from the sedimentation tube using the sampling pipette. Drain the pipette into a weighing vessel of known mass, and dry the contents of the vessel between 105 °C and 110 °C. Allow the vessel to cool in the desiccator and determine the mass of the residue in the vessel to 0.0001 g (m_r).

Follow this procedure each time a new batch of dispersing agent is prepared.

Sedimentation

Place the sedimentation tube in the constant temperature environment. Agitate (at least 30 times/min for a minimum of 2 min) the contents of the sedimentation tube vigorously, either by means of the stirrer, or by inserting a bung in the tube, followed by end-over-end shaking. Replace the tube upright in the constant-temperature environment and start the timer.

About 15 s before a sample is to be taken (Table SA03-1), lower the pipette, with the tap of the safety bulb closed, vertically into the soil suspension, and centrally in the sedimentation tube, until the tip is the appropriate depth (± 1 mm) below the suspension surface (Table SA03-1). Take care to disturb the suspension as little as possible, and complete the

operation within about 10 s. Open the tap of the safety bulb and withdraw a sample of the suspension such that the pipette and a part of the safety bulb are full. This sampling operation shall take about 10 s. Withdraw the pipette from the suspension so that the tip of the pipette is clear of the top of the sedimentation tube. Run the surplus present in the safety bulb into a small beaker by the outlet tube. Wash with water from the water reservoir until no suspension remains in this part of the system.

Place a weighing vessel of known mass (to 0.0001 g) under the tip of the pipette and open the tap so that the contents of the pipette are delivered to the vessel. Wash any suspension left on the inner walls of the pipette into the vessel by allowing water from the water reservoir to run through the system. Place the weighing vessel and contents in the oven between 105 °C and 110 °C, and evaporate to dryness. Cool the vessel in the desiccator, weigh the vessel and its contents to the nearest 0.0001 g, and determine the mass of the residue the nearest 0.0001 g (ms_1). Clean the outside of the pipette of any adhering sediment, and take the other sample (fraction < 2 µm), in accordance with the times given in Table SA03-1, using the same pipetting procedure given above. Call the additional sample masse ms_2.

Table SA03-1: Pipette sampling times and fraction at different temperatures

Temperature (°C)	Time (after mixing) of starting sampling operation	
	Fraction : < 63 µm	**Fraction : < 2 µm**
	Sampling depth 200 mm ± 1 mm	**Sampling depth 100 mm ± 1 mm**
20	56 s	7 h 44 min 16 s
21	54 s	7 h 34 min 04 s
22	53 s	7 h 23 min 53 s
23	52 s	7 h 13 min 13 s
24	51 s	7 h 03 min 02 s
25	49 s	6 h 52 min 50 s
26	48 s	6 h 44 min 02 s
27	47 s	6 h 35 min 42 s
28	46 s	6 h 26 min 53 s
29	45 s	6 h 18 min 33 s
30	44 s	6 h 09 min 45 s

VI Calculation

Fractions < 63 µm

Calculate the mass of solids in suspension in 500 ml (mf_1 , mf_2) in grams, for each pipette sampling time from the equation:

$$\text{Mass} < 63\ \mu\text{m in 500 ml} : mf_1 = ms_1\ (500/V_c)$$
$$\text{Mass} < 2\ \mu\text{m in 500 ml} : mf_2 = ms_2\ (500/V_c)$$

where:

mf_x is the mass (g) of solid in suspension in 500 ml;
ms_x is the mass (g) of material from the xth pipette sampling;
V_c is the calibrated volume of the pipette.

Each fraction however, still contains a part of dispersing agent, which has to be corrected. The mass of solid material in 500 ml of dispersant solution, m_d, in grams, is given by:

$$\text{Mass dispersing agent in 500 ml: } m_d = m_r\ (500/V_c)$$

where:

m_r is the mass of residue, in grams;
V_c is the calibrated volume of the pipette, in millilitres.

This gives the final fraction masses:

Clay	Mass fraction < 2 µm	=	$mf_2 - m_d$
Silt	Mass fraction 2 – 63 µm	=	$mf_1 - mf_2$

Fraction 63 µm - 2 mm

Mass of the fraction 63 µm - 2 mm = mf_s

Proportion of fraction

The method of calculation assumes that the sample mass is the sum of the constituent fractions, and not the mass of the test sample. The mass of sample < 2 mm is thus the sum of the masses of the fractions obtained by wet sieving at 63 µm and the masses of the fractions obtained by calculation. Denote this total sample mass as m_t in grams.

Calculate the proportion in each fraction <2 mm as follows:

Proportions = mass of fraction/m_t

VII Report

It is an agreed convention that the percentage of each particle size grade is reported on the basis of oven-dry soil free of organic matter (1 decimal place).

Note: With this calculation, the clay, silt and sand fractions are obtained in percentage of the sum of the constituent fractions (after removal of carbonates and organic matter).

USDA-FAO texture classification is based on the USDA-FAO textural triangle (FAO, 1990) as shown in Figure 1.

VIII References

ISO 11277. 1998: Soil Quality – Determination of particle size distribution in mineral soil material – Method by sieving and sedimentation. International Organization for Standardization. Geneva, Switzerland. 30 p. [available at www.iso.ch].

FAO. 1990: Guidelines for soil description, 3rd (revised) edition.

Soil Analysis Method 4 (SA04): Determination of Bulk Density

Bulk Density	
Method sheet	SA04
Reference methods	ISO 11272
Method suitable for	Mineral Layer

I Relevance in ICP Forests

Priority	Level I	Level II
Organic Layer	**-**	**-**
Mineral layer		
0 – 10 cm	*Mandatory[1,2,3]*	*Mandatory[2,3]*
10 – 20 cm	*Mandatory[1,2,3]*	*Mandatory[2,3]*
20 – 40 cm	*Mandatory[1,2,3]*	*Mandatory[2,3]*
40 – 80 cm	*Optional*	*Optional*

[1] may also be obtained by using pedo-transfer functions

[2] only mandatory in non-stony soils

[3] in case of re-assessment (if the parameter was already measured according to the reference method in a previous survey, the measurement is optional

II Principle

The dry bulk density (BD) is the ratio between the mass of oven dry soil material and the volume of the undisturbed fresh sample. The ISO defines dry bulk density as the ratio of the oven-dry mass of the solids to the volume (the bulk volume includes the volume of the solids and of the pore space) of the soil.

Non-gravely soils (when coarse fragments content < 5%)

Several methods can be applied for the determination of bulk density, going from simple methods such as digging out holes of known volume to sophisticated gamma radiometry methods. The recommended method (core method) uses steel cylinders of known volume (100 cm^3, 400 cm^3) that are driven in the soil vertically or horizontally by percussion. Sampling large volumes results in smaller relative errors but requires heavy equipment. The method cannot be used if stones or large roots are present or when the soil is too dry or too hard.

Soils with high stone or root content or when the soil is too dry or too hard

In these conditions it is advised to use measuring methods based on the following principle (excavation method): a hole on a horizontal surface is dug and then filled with a material with a known density (e.g. sand which packs to a calibrated volume or water separated from the soil material by an elastic membrane). The obtained soil from the hole, is dried to remove the water and the dry mass is weighed. Methods measuring the volume of clods or aggregates should be avoided because they tend to underestimate macroporosity.

The volumetric percentage of the coarse fragments needs to be determined in order to calculate the bulk density of the fine earth.

Stony soils

Soils with a high content of gravel (0.2 – 6 cm) and/or the presence of stones (6 – 20 cm) and boulders (> 20 cm), have a low volume of fine earth. Core samplers normally used in forest monitoring are not able to representatively collect stones or large portions of coarse fragments in the field. In these cases, the above recommended excavation method will produce good results but may be considered very expensive, time-consuming and destructive. So, alternatively, a combined approach is described where the quantity of bulk density of both fine earth and coarse fragments (SA05) has to be estimated / sampled in the field.

Methods are according to the prevailing conditions (i.e. coarse fragment content and size) at each individual sampling site:

- In case of coarse fragment content of more than 5 %, the fine earth fraction must be sieved and weighed. Its volume must then be determined either directly or indirectly by establishing the coarse fragment volume. Furthermore, the density of the coarse fragments (specific weight) must be known or established.
- In case of content of coarse fragments > 20 mm, representative sampling is no longer possible with a core sampler. Then the coarse fragment content must be determined by additional sampling using a shovel or spade and/or estimations in the soil profile.
- In case of coarse fragments content of > 60 mm, representative volume sampling is not possible and sampling with mini-core samplers is combined with an estimation in the profile pit.

In the analysis each method or each combined method leads to the determination of (partially) different parameters which means that different calculation formulas are needed.

Note: The determination of the bulk density of the fine earth is incorrect when the sample contains significant portions of roots in addition to the coarse fragment portions. In these cases, this must be corrected.

III Apparatus

Core sample holders, thin-walled metal cylinders with a volume of 100 cm^3 to 400 cm^3, a steel cap for driving into the soil, and a driver (or root auger, hollow stem auger, AMS core sampler with liner or alike)

Oven (heated and ventilated, temperature 105 ± 2 °C)

Desiccator

Balance (accuracy 1/1000 of measured value).

Spade, shovel

Metal sieves (2 mm, 20 mm, 60 mm)

IV Reagents

No reagents.

V Procedure

Case 1: *Non-gravely soils (when coarse fragments content < 5%)*

Press or drive a core sample holder of known volume without deflection and compaction into either a vertical or horizontal soil surface far enough to fill the sampler. Carefully remove the sample holder and its contents to preserve the natural structure, and trim the soil extending beyond each end of the sample holder with a straight-edged knife or sharp spatula. The soil sample volume is thus equal to the volume of the sample holder. Take at least five core samples from each soil layer. Place the holders containing the samples in an oven at 105 °C until constant mass is reached (minimum 48 h). Remove the samples from the oven and allow them to cool in the desiccator. Weigh the samples on the balance immediately after removal from the desiccator (m_t). Control mass is reached when the differences in

successive weighings of the cooled sample, at intervals of 4 h, do not exceed 0,01% of the original mass of the sample.

Case 2: *Mineral soil with a coarse fragment content of more than 5% that can be sampled with a core sampler or any other representative sampler (coarse fragments < 20 mm)*

The mineral soil sample is collected in the field with core samplers from the undisturbed soil. In the laboratory the sample is then dried at a temperature of 105 °C for at least 48 hours to constant mass and weighed.

The sample is then passed through a 2 mm metal sieve and the sieve residue washed in order to break down clumpy fine earth material and to rinse off earth adhering to the stones. The washed sieve residue (= coarse fragment portion) is shaken into a beaker, dried at a temperature of 105°C in a drying oven and then weighed.

Case 3: *Mineral soil, which cannot be sampled with a core sampler or any other representative sampler (coarse fragments > 20 mm)*

Case 3.1.: *Combination of representative volume sampling with a core sampler and estimation of coarse fragments > 20 mm*

The mineral soil sample is collected in the field with core samplers from the undisturbed soil. In the laboratory the sample is dried at a temperature of 105 °C for at least 48 hours to constant mass and weighed.

The sample is passed through a 2 mm metal sieve and the sieve residue washed in order to break down clumpy fine earth material and to rinse off earth adhering to the stones. The washed sieve residue (= coarse fragment portion) is shaken into a beaker, dried at a temperature of 105 °C in a drying oven and then weighed. After that, the sieve residue is passed through a 20 mm sieve and the 2 – 20 mm sieve fraction (fine and medium gravel) weighed.

For the coarse fragment portion > 20 mm an estimation from the profile description must be available.

Case 3.2.: *Combination of representative volume sampling with a core sampler, disturbed sample and estimation of coarse fragments more than 60 mm at the profile*

The mineral soil sample is collected in the field with a core sampler from the undisturbed soil. In addition, a larger sample volume, which must be representative for the coarse fragment fraction 2 – 60 mm (gravel), is collected with a shovel or a spade. In the laboratory the two samples are then dried at a temperature of 105 °C for at least 48 hours to constant mass and weighed.

The core sample is then passed through a 2 mm metal sieve and the sieve residue is washed in order to break down clumpy fine earth material and wash off earth adhering to the stones. The washed sieve residue (= coarse fragment portion) is shaken into a beaker, dried in a drying oven at a temperature of 105 °C and then weighed.

The spade sample is also dried at a temperature of 105 °C to constant mass and then weighed. The spade sample is then passed through a 2 mm sieve and the sieve residue through a 60 mm sieve. The coarse fragment fraction 2 – 60 mm obtained in this way is weighed. For the coarse fragment content > 60 mm an estimation from the profile description must be available.

Case 4: *Representative volume sampling not possible, Sampling with mini-core samplers*

With core sampler caps or mini-core samplers (n ≥ 5) several samples are taken from the undisturbed soil. In addition, a larger sample volume, which must be representative for the coarse fragment fraction 2 – 60 mm, is collected with a shovel or a spade.

In the laboratory the core sampler caps together with their contents are dried at a temperature of 105 °C for at least 48 hours to constant mass and then weighed together. The empty mass of the core sampler caps is then deducted from the total mass.

The spade sample is dried at a temperature of 105 °C for at least 48 hours to constant mass and then weighed. The sample is then passed through a 2 mm sieve and the sieve residue through a 6 mm sieve. The sieve residue is then passed through a 60 mm sieve as well. The fractions obtained < 2 mm (fine earth), 2 – 6 mm (fine gravel) and 6 – 60 mm (medium and coarse gravel) are weighed.

Alternative to the combined approach of case 2 till case 4 in soils with high stone or root content or if the soil is too dry or too hard

In case of gravely or stony soils an alternative excavation method consist of excavating a quantity of soil, drying and weighing it, and determining the volume of the excavation by filling it with sand (cf. ISO 11272 – **excavation method**). Note that the excavation method measures the total dry bulk density.

VI Calculation

Case 1: *Non-gravely soils (when coarse fragments content < 5%)*

In case of measurements, the bulk density of the fine earth (BD_{fe}) is approximately equal to the bulk density of total soil. The bulk density (BD_s) the for *non-gravely soils* is calculated as follows:

$$BD_s = BD_{fe} = \frac{M_s}{V_s} \qquad \textit{(equation SA04.01)}$$

where:

BD_s = Bulk Density of the sample (kg/m^3)
BD_{fe} = Bulk Density of the fine earth (kg/m^3)
M_s = Dry Mass of the sample (kg)
V_s = Volume of the sample (m^3)

Case 2: *Mineral soil with a coarse fragment content of more than 5% that can be sampled with a core sampler or any other representative sampler (coarse fragments < 20 mm)*

In case of measurement with a core sampler, the bulk density of the fine earth of gravely soils (BD_{fe}) is calculated as follows:

$$BD_{fe} = \frac{M_{fe}}{V_{fe}} = \frac{M_s - M_{cf}}{V_s - V_{cf}} = \frac{M_s - M_{cf}}{V_s - \frac{M_{cf}}{\rho_{cf}}} \quad \textit{(equation SA04.02)}$$

where:

BD_{fe} = Bulk density of the fine earth (kg/m^3)
M_{fe} = Dry Mass of the fine earth taken with core sampler (kg)
V_{fe} = Volume of the undisturbed fine earth (m^3)

M_s = Dry Mass of the soil sample with gravel taken with core sampler (kg)
M_{cf} = Dry Mass of the coarse fragments taken with the core sampler (kg)
V_s = Volume of core sampler (m^3)
V_{cf} = Volume of the coarse fragments taken with the core sampler (kg)
ρ_{cf} = Density of the coarse fragments (approximated by 2650 kg/m^3)

The fine earth stock (FES) is the amount (kg) of fine earth in the soil layer under consideration expressed per ha. In stony soils, a correction for the volume of coarse fragments is required. It is calculated as follows:

$$FES = BD_{fe} \times d \times 10 \times \left(1 - \frac{V_{cf}}{V_s}\right) = BD_{fe} \times d \times 10 \times \left(1 - \frac{M_{cf}}{\rho_{cf} \times V_s}\right) \quad \textit{(equation SA04.03)}$$

where:
FES = Fine earth stock (t/ha)
BD_{fe} = Bulk density of fine earth (kg/m^3)
d = Thickness of the sampled layer (m)
Vs_{cf} = Volume of coarse fragment taken with core sampler (respectively core of root auger) (m^3)
M_{cf} = Dry Mass of coarse fragment taken with core sampler (respectively core of root auger) (kg)
ρ_{cf} = Density of the coarse fragments (approximated by 2650 kg/m^3)
V_s = Volume of core sampler (m^3)

Notes:

- If the core sampler sample cakes strongly as a consequence of drying, it might make sense to pulverise the sample with a crusher prior to sieving. The big stones should be removed beforehand. .
- In the case of non-cohesive soil (sand), there is no need to wash or dry the stones.

Case 3: *Mineral soil, which cannot be sampled with a core sampler or any other representative sampler (coarse fragments > 20 mm)*

Case 3.1. *Combination of representative volume sampling with a core sampler and estimation of coarse fragments > 20 mm*

The bulk density of the fine earth (BD_{fe}) is calculated using equation SA04.02.

The FES is calculated as follows:

$$FES = BD_{fe} \times d \times 10 \times \left(1 - \frac{V_{cf>20}}{100} - \frac{M_{cf(2-20)}}{\rho_{cf} \times V_s}\right) \quad \textit{(equation SA04.04)}$$

where:
FES = Fine earth stock (t/ha)
BD_{fe} = Bulk density of fine earth (kg/m^3)
d = Thickness of the sampled layer (m)
$M_{cf(2-20)}$ = Dry Mass of coarse fragment between 2 and 20 mm taken with core sampler (respectively core of root auger) (kg)
$V_{cf>20}$ = Percentage volume of coarse fragment of the fraction > 20 mm estimated at the profile (%)
ρ_{cf} = Density of the coarse fragments (approximated by 2650 kg/m^3)
V_s = Volume of core sampler (m^3)

Notes: see Case 2

Case 3.2. *Combination of representative volume sampling with a core sampler, disturbed sample and estimation of coarse fragments more than 60 mm at the profile*

The bulk density of the fine earth (BD_{fe}) is calculated using equation SA04.02.

The fine earth stock (FES) is calculated as follows:

$$FES = BD_{fe} \times d \times 10 \times \left(1 - \frac{V_{cf>60}}{100} - \frac{M_{ds(2-60)}}{BD_{cf}} \times \frac{BD_{fe}}{M_{ds} - M_{ds(2-60)} + BD_{fe} \times \frac{M_{ds(2-60)}}{\rho_{cf}}} \right)$$

(equation SA04.05)

where:

FES = Fine earth stock (t/ha)
BD_{fe} = Bulk density of fine earth (kg/m^3)
d = Thickness of the sampled layer (m)
$M_{ds(2-60)}$ = Dry Mass of coarse fragment between 2 and 60 mm of the disturbed sample (kg)
$V_{cf>60}$ = Percentage volume of coarse fragment > 60 mm estimated at the profile (%)
ρ_{cf} = Bulk density of the coarse fragments (approximated by 2650 kg/m^3)
M_{ds} = Total dry mass of the disturbed sample (kg)

Notes: see Case 2

Case 4: *Representative volume sampling not possible, Sampling with mini-core samplers*

From the mass of the sample < 6 mm and the mass of the coarse fragment fraction 2 mm – 6 mm, factor f, which is approximately the coarse fragment portion in the core sampler cap, is calculated as follows:

$$f = \frac{M_{ds(2-6)}}{M_{ds(<6)}} \quad \textit{(equation SA04.06)}$$

where:

$M_{ds(2-6)}$ = Mass of coarse fragment of the fraction 2 - 6 mm of the disturbed sample (kg)
$M_{ds(<6)}$ = Mass of the sample < 6 mm in the aliquot of the disturbed sample (kg)

For the coarse fragment content > 60 mm an estimation from the profile must be available.

The bulk density of the fine earth (BD_{fe}) is calculated using the following formula:

$$BD_{fe} = \frac{M_{TOT}MINI \times (1 - f)}{V_{TOT}MINI - \frac{M_{TOT}MINI \times f}{\rho_{cf}}} \quad \textit{(equation SA04.07)}$$

where:

M_{TOT}MINI = Mass of mini-core sampler (kg)
V_{TOT}MINI = Volume of mini-core sampler (m^3)
ρ_{cf} = Density of the coarse fragments (kg/m^3) (approximated by 2650 kg/m^3)

The fine earth stock (FES) is calculated using equation SA04.05.

VII Report

The dry bulk density (BD) is recorded in kg/m^3 with no decimal places.

In the case of stony or gravely soils the bulk density of the fine earth fraction (BD_{fe}) (< 2 mm) should be reported together with the coarse fragment content (vol %) (See also SA05).

Furthermore, the bulk density of the coarse fragments should be known, but this may be approximated as 2650 $kg.m^{-3}$. In the case that pedotransfer functions are used (Level I), the calculation procedure should be reported as well.

Note that the "excavation method" described in ISO11272, asks for the total dry bulk density of the soil, while in this programme the bulk density of the fine earth should be reported.

VIII Reference

ISO 11272. 1993. Soil Quality – Determination of dry bulk density. International Organization for Standardization. Geneva, Switzerland. 10 p. (available at www.iso.ch)

DIN ISO 11272, Normenausschuß Wasserwesen (NAW) in the Dt. Inst. für Normung e.V. [Eds.] (2001): Bodenbeschaffenheit - Bestimmung der Trockenrohdichte (Soil composition, Determination of bulk density)

Riek, W., Wolff, B., 2006: Evaluierung von Verfahren zur Erfassung des Grobbodenanteils von Waldböden – Erarbeitung von Empfehlungen für die Anwendung dieser Verfahren im Rahmen der Bodenzustandserhebung im Wald (BZE II)". Eberswalde (Evaluation of methods to determine the coarse fragment portion of forest soils – Drawing up recommendations for the use of these methods in forest soil surveys)

Soil Analysis Method 5 (SA05): Determination of Coarse Fragments

Coarse Fragments	
Method sheet	SA05
Reference methods	ISO 11464, ISO 11277
Method suitable for	Mineral horizons

I Relevance in ICP Forests

Priority	**Level I**	**Level II**
Organic Layer	**-**	**-**
Mineral layer		
0 – 10 cm	*Mandatory[1,2]*	*Mandatory*
10 – 20 cm	*Mandatory[1,2]*	*Mandatory[1,2]*
20 – 40 cm	*Mandatory[1,2]*	*Mandatory[1,2]*
40 – 80 cm	*Optional[1]*	*Optional[1]*

[1] may be obtained by estimation

[2] in case of re-assessment (if the parameter was already measured according to the reference method in a previous survey), the measurement is optional

II Principle

The abundance of coarse fragments can be measured in the laboratory, but is usually estimated during routine soil profile description (see Annex 2). When the estimation is based on such a visual observation, one should take into account the volume of the macropores (packing pores between the stones) which is often underestimated.

The most straightforward way to determine the volumes in the field of stones and boulders is by digging pits. This method, however, encounters practical problems such as hard manual work and destructive sampling. The 'Finnish method' or 'rod penetration method' is described here as an example of a non-destructive method. This method estimates the proportion (*volume %)* of coarse gravel (2 – 6 cm), stones (6 – 20 cm) and boulders (> 20 cm) in the 0 – 30 cm mineral layer by pushing a graduated metal rod down through the organic layer and as far as possible into the mineral soil.

Coarse fragments are separated from the fine earth fraction during the preparation of soil samples (SA01). The content of coarse fragments, *cf. (mass %),* is determined by weighing the residue left on a 2 mm sieve after washing and drying in the laboratory.

III Apparatus

Field estimation: *The 'Finnish method' or 'rod penetration method'*

graduated metal rod (diameter 10 mm, length 80 – 100 cm)

Laboratory measurement

No apparatus, using data obtained in preparation of soil sample (SA01).

IV Reagents

***Field estimation**: The 'Finnish method' or 'rod penetration method'*

No reagents.

Laboratory measurement

No reagents, using data obtained in preparation of soil sample (SA01).

V Procedure

***Field estimation**: The 'Finnish method' or 'rod penetration method'*

The volume of stones is estimated in the 0-30 cm mineral soil layer. A steel rod (d = 10 mm, length = 80…100 cm, with a tip of hard metal, gradation lines at 10 cm intervals, see Figure 1) is pushed down (through the organic layer) into the mineral soil with sufficient force that the rod will stop if it comes into contact with a stone of 2 cm or larger (moderate push). The measuring rod is pushed down into the mineral soil at e.g. 20 or 30 systematically located (using a tape measure or even paces) points. The depth of penetration is measured with respect to the surface of the ground. If there is an organic layer present, then its thickness has to be measured using the rod or by taking a sample of the organic layer and measuring its thickness, and then subtracted from the penetration depth. In Finland, penetration is measured and organic layer samples are taken at the same time. The average penetration value and stoniness of the 0-30 cm mineral soil layer is calculated as follows (only 5 points in this example):

Penetration depth (cm)	**Organic layer thickness (cm)**	**Penetration depth – organic layer thickness (cm)**	**Penetration in the ≤30 layer (cm)**
12	2	10	10
40	4	36	30
4	4	0	0
35	3	32	30
22	5	17	17
			Average = 17.4

The great advantage of the rod method is that a large number of measurements can be made easily and quickly over the whole plot. The inaccuracy and other drawbacks of the method outweigh the lack of representability involved in measuring (estimating) stoniness in a very restricted number of soil pits.

Figure 3: Tip of the penetration rod

Figure 2: Penetration rod

Laboratory measurement

No procedure, using data obtained in preparation of soil sample (SA01).

VI Calculation

Field estimation

0 – 30 cm layer

Volume of stones (%) = 83 - 2.75 * average penetration (cm) [Equation SA05.01]

The volume of stones in the example = 83 - 2.75 * 17.4 = 35 % in the 0-30 cm layer. According to equation SA05.01, the volume of stones is 0.5 % when the average penetration into the mineral soil is 30 cm, and volume of stones is 83 % when the average penetration is 0 cm.

It is possible to estimate the stoniness of thinner layers if the empirical relationship between penetration depth and volumetric stone percentage remains the same. The relevant equations are as follows:

0-10 cm layer

Volume of stones (%) = 83 - 8.25 * average penetration (cm) for the layer

0-20 cm layer

Volume of stones (%) = 83 - 4.125 * average penetration (cm) for the layer.

The constant maximum depth of each penetration should be set so that it reaches the target mineral soil depth, i.e. 30, 20 or 10 cm, through the thickest possible organic layer. On upland soils an extra 10 cm is commonly added to the target depth, i.e. there is a target depth of 40 cm if the studied layer is 0-30 cm, or to 30 cm if the layer is 0-20 cm.

Note: *Equation SA05.01 is based on a very specific material [Finnish till (morainic) soils] but has not been tested on other soils, and in some respects it is somewhat illogical (see Eriksson and Holmgren, 1996). It is therefore of utmost importance that the equation is calibrated locally before it can be applied on other soil types.*

Laboratory measurement

The content of coarse fragments, *cf (mass%),* is determined by weighing the residue left on a 2 mm sieve after washing and drying according to:

$$cf\,(mass\%) = \frac{mass\_of\_soil\_fraction > 2mm}{mass\_of\_the\_total\_oven\_dry\_soil} x100$$

In order to convert the content by mass to an expression by volume, the bulk density of both the coarse fragments and the fine earth should be determined.

$$cf\,(vol\%) = \frac{BDs}{BDcf} * cf\,(mass\%)$$

where:

BD_s	=	Bulk density of the total soil (kg/m^3)
BD_{cf}	=	Bulk density of the coarse fragments (approximated by 2650 kg/m^3)
cf(vol%)	=	Volumetric percentage of coarse fragments in the soil (%)
cf(mass%)	=	Mass percentage of coarse fragments in the soil (%)

VII Report

The amount of coarse fragments (stones and gravel with a diameter > 2 mm) has to be reported for the individual mineral layers in volume % without decimals.

Note*: The Rod penetration method only allows reporting for the 0 – 10 cm, 0 – 20 cm or 0-30 cm layer and for the coarse fragments > 2 cm*

VIII References

Eriksson, C.P., Holmgren, P. 1996. Estimating stone and boulder content in forest soils – evaluating the potential of surface penetration methods. Catena 28: 121 – 134.

ISO 11464. 1994. Soil Quality – Pretreatment of samples for physico-chemical analysis. International Organization for Standardization. Geneva, Switzerland. 9 p. [available at www.iso.ch].

ISO 11277. 1998. Soil Quality – Determination of particle size distribution in mineral soil material – Method by sieving and sedimentation. International Organization for Standardization. Geneva, Switzerland. 30 p. [available at www.iso.ch].

Mikkelsen, J. Cools, N., Langohr, R. 2006 Guidelines for Forest Soil Profile Description, adapted for optimal field observations within the framework of the EU Forest Focus Demonstration Project. BIOSOIL. Partly based on the 4th edition of the Guidelines for Soil Profile Description and Classification (FAO, 2006).

Tamminen, P. 1991. Kangasmaan ravinntunnusten ilmaiseminen ja viljavuuden alueellinen vaihtelu Etelä-Suomessa. Summary: Expression of soil nutrient status and regional variation in soil fertility of forested sites in Southern Finland. Folia Forestalia 777: 1-40.

Viro, P., 1947. Metsämaan raekoostumus ja viljavuus varsinkin maan kivisyyttä silmällä pitäen. Summary: The mechanical composition and fertility of forest soil taking into consideration especially the stoniness of the soil. Communicationes Instituti Forestalis Fenniae 35, 115.

- 1952. Kivisyyden määrittämisestä. Summary: On the determination of stoniness. Communicationes Instituti Forestalis Fenniae 40, 23.

- 1958. Suomen metsämaiden kivisyydestä. Summary: Stoniness of forest soil in Finland. Communicationes Instituti Forestalis Fenniae 49, 45

Soil Analysis Method 6 (SA06): Determination of Soil pH

pH	
Method sheet	SA06
Reference methods	ISO 10390
Method suitable for	Organic Layer; Mineral Layer
Method code	Sample preparation: MA02 Pretreatment: PA01 and PA02 Determination: DF01

I Relevance in ICP Forests

pH($CaCl_2$)

Priority	**Level I**	**Level II**
Organic Layer		
OL	*-*	*-*
OF+OH, H-layers	*Mandatory*	*Mandatory*
Mineral layer		
0 – 10 cm	*Mandatory*	*Mandatory*
10 – 20 cm	*Mandatory*	*Mandatory*
20 – 40 cm	*Optional*	*Mandatory*[2]
40 – 80 cm	*Optional*	*Mandatory*[2]

[2] in case of re-assessment (if the parameter was already measured according to the reference method in a previous survey), the measurement is optional

pH(H_2O)

Priority	**Level I**	**Level II**
Organic Layer	**Optional**	**Optional**
OL	*-*	*-*
OF+OH, H-layers	*Optional*	*Optional*
Mineral layer		
0 – 10 cm	*Optional*	*Optional*
10 – 20 cm	*Optional*	*Optional*
20 – 40 cm	*Optional*	*Optional*
40 – 80 cm	*Optional*	*Optional*

II Principle

The pH of the soil is potentiometrically measured in the supernatant suspension of 1:5 (volume fraction). This liquid is made up of a 0.01 mol/l solution of calcium chloride in water for pH($CaCl_2$) or deionised water for pH(H_2O).

III Apparatus

End-over-end shaking machine

pH meter with appropriate electrode

Thermometer (accuracy 1 °C)

Sample bottle (capacity at least 50 ml) with cap

Accurate measuring spoon

IV Reagents

Water (grade 2)

Calcium chloride ($CaCl_2$), conc. 0.01 mol/l

make a solution of 1.47 g $CaCl_2.2H_2O$/liter water

pH buffer solutions

V Procedure

Preparation of the suspension

Take a representative sample (at least a volume of 5 ml) of the air-dried soil (fraction < 2 mm) using the accurate measuring spoon. Place the test sample in the sample bottle and add five times its volume of calcium chloride solution (pH-$CaCl_2$) or deionised water (pH-H_2O). Shake or mix the suspension for 60 min +/- 10 min, using the mechanical shaker or mixer, and wait for at least for 1 hour before measuring but not longer than 3 hours. Ingres of air during standing after shaking should be avoided.

Calibration of pH meter

Calibrate the pH-meter as prescribed in the manufacturer' s manual, using the buffer solutions.

pH measurement

Measure the pH in the suspension at 20°C ± 2°C immediately after or whilst being stirred. The stirring should be at such a rate to achieve a reasonable homogeneous suspension of the soil particles, but entrainment of air should be avoided. Read the pH after stabilisation of the value is reached.

VI Calculations

No calculations.

VII Report

Note the recorded values to two decimal places.

VIII Reference

ISO 10390. 2005. Soil Quality – Determination of pH. International Organization for Standardization. Geneva, Switzerland. 5 p. [available at www.iso.ch].

Soil Analysis Method 7 (SA07): Determination of Carbonate Content

Carbonates	
Method sheet	SA07
Reference methods	ISO 10693, EN 15936
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA02, MA03, MA04, MA05 Determination: DA04, DA07, DA08

I Relevance in ICP Forests

Priority	**Level I**	**Level II**
Organic Layer		
OL	-	-
OF+OH, H-layers	*Mandatory*[1]	*Mandatory*[1]
Mineral layer		
0 – 10 cm	*Mandatory*[1]	*Mandatory*[1]
10 – 20 cm	*Mandatory*[1]	*Mandatory*[1]
20 – 40 cm	*Optional*	*Optional*
40 – 80 cm	*Optional*	*Optional*

[1] Only mandatory if pH($CaCl_2$) > 5.5 or in calcareous soils

II Principle

The soil sample is treated with a strong acid. The volume of the carbon dioxide produced is measured by using a calcimeter (Scheibler unit), and is compared with the volume of carbon dioxide produced by pure calcium carbonate.

Alternatively, when the laboratory is determining the total organic carbon by dry combustion, using the **indirect method** (see SA08 where TOC = TC - TIC), the measurement of the total inorganic carbon (TIC) according to EN 15936 (2012) can be used to report the carbonate content.

In case the **direct method** (see SA08) for TOC is used, the TIC content can be derived by analysing the sample twice. Once with acid treatment and once without acid treatment. The TIC content is derived indirectly by TIC = TC – TOC.

III Apparatus

Calcimeter (Scheibler unit)

Analytical balance (accuracy 0.0001 g)

Reaction vessels (capacity 150 ml)

Plastic cups (which can pass through the neck of the reaction vessel)

Tong

Watch glass

IV Reagents

Distilled water

Hydrochloric acid (HCl), conc. 4 mol/l

Dilute 340 ml of concentrated hydrochloric acid (ρ = 1.19 g/ml) to 1000 ml with water.

Calcium carbonate ($CaCO_3$), pure.

V Procedure

Preparation

The mass of the test portion is determined based on the carbonate content. For a preliminary test on carbonate content, add some hydrochloric acid to a portion of the soil on a watch glass. The carbonate content of the sample can be estimated on the basis of the intensity and duration of effervescence (Table SA07-1). Determine from Table SA07-1 the mass of test portion (air-dried soil fraction < 2 mm).

Table SA07-1: Mass of test portion for determination of carbonate content based on intensity of effervescence

Intensity of effervescence	Carbonate content (g/kg)	Mass of test sample (g)
None or only limited	< 20	10
Clear, but for a short time	20 – 80	5
Strong, for a long time	80 – 160	2.5
Very strong, for a long time	> 160	≤1[1]

[1] use sample that is crushed to a particle size of less than 250 µm

Measurement

Transfer the sample into the reaction vessels and add 20 ml of water. Fill the plastic cup with 7 ml of hydrochloric acid and place this, using tongs in the reaction vessel containing the test portion. Take care that there is no contact between the hydrochloric acid and the soil before the reaction vessel is connected to the calcimeter (Scheibler unit). Warm the reaction vessel by hand.

Connect the reaction vessel to the calcimeter. Carefully add the hydrochloric acid from the cup to the soil by tilting the reaction vessel at an angle. The gas produced will lower the water level in the tube on the right and at the same time will raise the water level in the tube on the left. Shake for 5 min and note the volume when it no longer varies. If it still varies, continue shaking until the volume is stable, but not longer than 1 h. At the end of the shaking period, bring the water level in both tubes to the same height and measure the volume of gas in the calibrated tube with an accuracy of 0.1 ml.

Calibration

Determinations of samples, blanks and the calcium carbonate used as standard material, shall be performed simultaneously in a room where temperature and pressure do not vary too much during the measurement.

Weigh the standards of 0.200 g and 0.400 g of calcium carbonate, transfer these amounts into the reaction vessels and add 20 ml of water. For the blank determinations, use reaction vessels containing 20 ml of water.

VI Calculations

$$w(CaCO_3) = 1000 \times \frac{m_2 (V_1 - V_3)}{m_1 (V_2 - V_3)}$$

$w(CaCO_3)$ = carbonate content of sample (g/kg) on basis of air dried soil
m_1 = mass (g) of test sample
m_2 = mean mass (g) of standards
V_1 = volume (ml) of CO_2 produced by test sample
V_2 = mean volume (ml) of CO_2 produced by standards
V_3 = volume change (ml) in blank determinations (can be negative)

In case the total inorganic carbon content was determined by dry combustion, following formula needs to be used to convert between TIC and $CaCO_3$, all expressed in g/kg:

TIC= $CaCO_3$ x 0.12
and $CaCO_3$ = TIC/0.12 = TIC x 8.33

VII Report

The results of the carbonate (g/kg) must be reported without decimals on the basis of oven-dried soil.

VIII Reference

ISO 10693. 1995. Reviewed and confirmed in 2016. Soil Quality – Determination of carbonate content - Volumetric method. International Organization for Standardization. Geneva, Switzerland. 7 p. [available at www.iso.ch].

ISO 10694. 1995. Reviewed and confirmed in 2016. Soil Quality – Determination of organic and total carbon after dry combustion (elementary analysis). International Organization for Standardization. Geneva, Switzerland. 7 p. [available at www.iso.ch

NBN EN 15936. 2012. Sludge, treated biowaste, soil and waste - Determination of total organic carbon (TOC) by dry combustion.

Soil Analysis Method 8 (SA08): Determination of Organic Carbon Content

Organic Carbon	
Method sheet	SA08
Reference methods	ISO 10694
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA02, MA03, MA04, MA05 Determination: DA01, DA02

I Relevance in ICP Forests

Priority	**Level I**	**Level II**
Organic Layer		
OL	-	-
OF+OH, H-layers	*Mandatory*	*Mandatory*
Mineral layer		
0 – 10 cm	*Mandatory*	*Mandatory*
10 – 20 cm	*Mandatory*	*Mandatory*
20 – 40 cm	*Mandatory*	*Mandatory*
40 – 80 cm	*Optional*	*Optional*

II Principle

The carbon present in the soil is oxidised to carbon dioxide (CO_2) by heating the soil to at least 900 °C in a flow of oxygen-containing gas that is free from carbon dioxide. The amount of carbon dioxide released is then measured by titrimetry, gravimetry, conductometry, gas chromatography or using an infrared detection method, depending on the apparatus used.

When the soil is heated to a temperature of at least 900 °C, any carbonates present are completely decomposed.

Total organic carbon can be determined directly or indirectly. Direct determination consists of previous removal of any carbonates present by treating the soil with hydrochloric acid. Indirect determination consists of a correction of the total carbon content for the carbonates present.

III Apparatus

Glassware

Analytical balance (accuracy 0.0001 or 0.00001 g)

Apparatus for determination of total carbon content (temperature at least 900 °C)

Crucibles proper for the apparatus

IV Reagents

Combustion gas - chemicals and catalysts proper to the apparatus

Calibration substances

Hydrochloric acid (HCl), conc. 4 mol/l

V Procedure

Laboratory sample

Use sample of air-dried soil (fraction < 2 mm) of known moisture and carbonate content.

Calibration of the apparatus

Calibrate the apparatus as described in the relevant manual using the calibration substances.

Direct determination of organic carbon content

Add an excess of hydrochloric acid (4 mol/l) to the crucible containing a weighed quantity of air-dried soil and mix. Wait 4 h and dry the crucible for 16 h at a temperature of 60 °C to 70 °C. The amount of test portion taken for analysis depends on the expected carbon content and on the apparatus used. Weigh out m_1 g of the air-dried sample in a crucible. Carry out the analyses in accordance with the manufacturer's manual for the apparatus.

Indirect determination of organic carbon content

The procedure is identical to the direct determination of organic carbon content, without adding hydrochloric acid. The measured total carbon content is calculated according to the amount of test portion taken for analysis which depends on the expected total carbon content and on the apparatus used. Weigh out m_1 g of the air-dried sample in a crucible. Carry out the analyses in accordance with the manufacturer's manual for the apparatus.

VI Calculation

Direct determination of organic carbon content

The organic carbon content (on basis of air-dried soil) is obtained by :

$$w_{C,o} = 1000 \times \frac{m_2}{m_1} \times 0.2727$$

where

$w_{C,o}$	=	Organic carbon content (g/kg) on basis of air-dried soil
m_1	=	Mass (g) of test portion
m_2	=	Mass (g) of released CO_2
0.2727	=	Conversion factor for CO_2 to C

Indirect determination of organic carbon content

The total carbon content (on basis of air-dried soil) is obtained by :

$$w_{C,t} = 1000 \times \frac{m_2}{m_1} \times 0.2727$$

where

$w_{C,t}$ = Total carbon content (g/kg) on basis of air-dried soil
m_1 = Mass (g) of test portion
m_2 = Mass (g) of released CO_2
0.2727 = Conversion factor for CO_2 to C

Calculate the organic carbon content of the sample using a correction for carbonates. The organic carbon content (on basis of air dried soil) is calculated by:

$$w_{C,o} = w_{C,t} - (0.12 \times w_{CaCO_3})$$

where

$w_{C,o}$ = Organic carbon content (g/kg) on basis of air-dried soil
$w_{C,t}$ = Total carbon content (g/kg) on basis of air-dried soil
0.12 = Conversion factor
w_{CaCO3} = Carbonate content (g/kg) on basis of air-dried soil

VII Report

Report organic carbon content (in g/kg) with 1 decimal place on the basis of oven-dried soil.

VIII Reference

ISO 10694. 1995. Reviewed and confirmed in 2016. Soil Quality – Determination of organic and total carbon after dry combustion (elementary analysis). International Organization for Standardization. Geneva, Switzerland. 7 p. [available at www.iso.ch].

Soil Analysis Method 9 (SA09): Determination of Total Nitrogen Content

Total Nitrogen	
Method sheet	SA09A
Reference methods	ISO 13878
Method suitable for	Organic Layer, Mineral Layer
Method code	Sieving/milling: MA02, MA03, MA04, MA05 Determination: DA01, DA02

I Relevance in ICP Forests

Priority	**Level I**	**Level II**
Organic Layer		
OL	*-*	*-*
OF+OH, H-layers	*Mandatory*	*Mandatory*
Mineral layer		
0 – 10 cm	*Mandatory*	*Mandatory*
10 – 20 cm	*Mandatory*	*Mandatory*
20 – 40 cm	*Optional*	*Optional*
40 – 80 cm	*Optional*	*Optional*

II Principle

The nitrogen content of a soil is determined by heating to a temperature of at least 900 °C in the presence of oxygen gas. Mineral and organic nitrogen compounds are oxidised and/or volatilised. The combustion products are oxides of nitrogen (NO_x) and molecular nitrogen (N_2). After transforming all nitrogen forms into N_2, the content of total nitrogen is measured using thermal conductivity.

III Apparatus

Laboratory glassware

Analytical balance (accuracy 0.0001 or 0.00001 mg)

Apparatus for determination of total nitrogen content (temperature at least 900 °C)

Crucibles proper for the apparatus

IV Reagents

Combustion gas - chemicals and catalysts proper to the apparatus

Calibration substances

V Procedure

Laboratory sample

Use fraction of air-dried soil (fraction < 2 mm) of known moisture content. If a soil mass of less than 2 g is required for nitrogen analysis, mill a representative subsample further, to pass a sieve of an aperture specified in the manufacturer's manual to ensure sufficient test reproducibility.

Calibration of the apparatus

Calibrate the apparatus as described in the relevant manual using the calibration substances.

Determination of total nitrogen content

The amount of test sample for analysis depends on the expected total nitrogen content and on the apparatus used. Weigh out m_1 g of the air-dried sample or subsample into a crucible. Carry out the analyses in accordance with the manufacturer's manual for the apparatus.

Normally the primary results are given as milligrams nitrogen (X_1) or a mass fraction of nitrogen (X_2), expressed as a percentage, referred to the mass of air-dry soil used (m_1).

VI Calculation

Calculate the total content of nitrogen (wN), in milligrams per gram, on the basis of the air-dried soil according to the following equations:

- For primary results given in milligrams of nitrogen:

$$w_N = \frac{X_1}{m_1}$$

- For primary results, given as percent mass fraction of nitrogen:

$$w_N = 10.X_2$$

where

w_N : total nitrogen content (g/kg) on basis of air-dried soil
m_1 : mass (g) of test portion
X_1 : primary result as milligrams N
X_2 : primary result as percentage N

VII Report

Report total nitrogen (in g/kg) with 2 decimals on the basis of oven-dried soil.

VIII Reference

ISO 13878. 1998. Soil Quality – Determination of total nitrogen content by dry combustion ("elemental analysis"). International Organization for Standardization. Geneva, Switzerland. 5 p. [available at www.iso.ch].

Total Nitrogen **Modified Kjeldahl method**	
Method sheet	SA09B
Reference methods	ISO 11261
Method suitable for	Organic Layer, Mineral Layer
Method code	Sieving/milling: MA02, MA03, MA04, MA05 Pretreatment: PB08 Determination: DF08

I Relevance in ICP Forests

Priority	**Level I**	**Level II**
Organic Layer		
OL	-	-
OF+OH, H-layers	*Mandatory*	*Mandatory*
Mineral layer		
0 – 10 cm	*Mandatory*	*Mandatory*
10 – 20 cm	*Mandatory*	*Mandatory*
20 – 40 cm	*Optional*	*Optional*
40 – 80 cm	*Optional*	*Optional*

II Principle

The modified Kjeldahl method determines the total nitrogen content (including ammonium-N, nitrate-N, nitrite-N and organic N) of a soil. The method is based on a Kjeldahl digestion, but instead of selenium (Kjeldahl method) titanium dioxide is used as the catalyst.

III Apparatus

Digestion flasks or tubes (50 ml)

Digestion stand

Distillation apparatus

Burette (intervals of 0.01ml or smaller)

IV Reagents

- Salicylic acid / Sulfuric acid: Dissolve 25g of salicylic acid in 1 litre of concentrated sulfuric acid (ρ = 1.84 g/cm^3)
- Potassium sulfate catalyst mixture: Grind and thoroughly mix the following substances;

  200 g of potassium sulfate

  6 g of copper (II) sulfate pentahydrate

  6 g of titanium dioxide with the crystal structure of anatase

- Sodium thiosulfate pentahydrate: Crush the crystals of Sodium thiosulfate pentahydrate until they form a powder that passes through a sieve with an aperture of 0.25mm
- Sodium hydroxide: c(NaOH) = 10 mol/l
- Boric acid solution: $\rho(H_3BO_3)$ = 20 g/l
- Mixed indicator: Dissolve 0.1 g of bromocresol green and 0.02 g of methyl red in 100 ml of ethanol
- Sulfuric acid: c (H^+) = 0.01 mol/l

V Procedure

Place a test portion from 0.2g (expected N-content 0.5%) to 1g (expected N-content of 0.1%) of the air-dried soil sample in the digestion flask.

Add 4 ml of salicylic/sulfuric acid and swirl the flask until the acid is thoroughly mixed with the soil. Let the mixture stand for at least several hours (or overnight).

Add 0.5 g of sodium thiosulfate trough a dry funnel with a long stem that reaches down into the bulb of the digestion flask. Heat the mixture cautiously on the digestion stand until frothing has ceased.

Cool the flask and add 1.1g of the catalyst mixture, heat until the digestion mixture becomes clear.

Boil the mixture gently for up to 5 h. (in most cases a boiling period of 2h. is sufficient) so that the sulfuric acid condenses about 1/3 of the way up to the neck of the flask. Make sure that the temperature of the solution does not exceed 400°C.

Allow the flask to cool down after the digestion and add about 20ml of water slowly while shaking. Then swirl the flask to bring any insoluble material into suspension and transfer then the contents to the distillation apparatus. Rinse tree time with water to complete the transfer.

Add 5 ml of boric acid to a 100 ml conical flask. Place the flask under the condenser of the distillation apparatus, make sure that the end of the condenser dips into the solution.

Add 20 ml of sodium hydroxide to the funnel of the apparatus and run the alkali slowly into the distillation chamber.

Distil about 40 ml of the condensate and rinse the end of the condenser.

Add a few drops of indicator to the distillate and titrate with sulfuric acid to a violet endpoint or use a potentiometric titration with endpoint pH=5.

Notes:

Carry out a blank test in which the same procedure is performed without soil.

A potentiometric titration is also possible (endpoint of titration should be pH = 5).

If steam distillation is used, a distillation rate up to about 25ml/min is applicable. Stop the distillation when about 100ml of distillate have been collected.

VI Calculation

The total nitrogen content is calculated by use of the following formula:

$$w_N = \frac{(V_1 - V_0) \times c(H^+) \times M_N}{m} \times \frac{100 + w_{H_2O}}{100}$$

Where

W_N	=	The total nitrogen content (mg/g = g/kg)
V_1	=	Volume of the sulfuric acid used in the titration of the sample (ml)
V_0	=	Volume of the sulfuric acid used in the titration of the blank sample (ml)
$c(H^+)$	=	Concentration of H+ in the sulfuric acid (moles/litre)
M_N	=	The molar mass of nitrogen (= 14 g/mol)
m	=	Mass of the air-dried soil sample (g)
w_{H2O}	=	Water content of the soil sample, based on oven-dried soil (% by mass)

VII Report

Report total nitrogen in g/kg with 2 decimals on the basis of oven-dried oil.

VIII Reference

ISO 11261. 1995. Soil Quality – Determination of total nitrogen – Modified Kjeldahl method. International Organization for Standardization. Geneva, Switzerland. 4 p. [available at www.iso.ch].

Soil Analysis Method 10 (SA10): Determination of Exchangeable Cations (Al, Ca, Fe, K, Mg, Mn, Na), Free H^+ and Exchangeable Acidity

Exchangeable acidity and exchangeable cations	
Method sheet	SA10
Reference Methods	ISO 11260 & ISO 14254
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA02 Pretreatment: PA03 Determination: DB**

I Relevance in ICP Forests

Basic exchangeable cations (Ca, Mg, K, Na)

Priority	**Level I**	**Level II**
Organic Layer		
OL	-	-
OF+OH, H-layers	*Mandatory[1]*	*Mandatory[1]*
Mineral layer		
0 - 10 cm	*Mandatory*	*Mandatory*
10 – 20 cm	*Mandatory*	*Mandatory*
20 – 40 cm	*Optional*	*Mandatory[2]*
40 – 80 cm	*Optional*	*Mandatory[2]*

[1] in calcareous soil ($CaCO_3$ > 20 g kg^{-1}), this parameter is optional
[2] in case of re-assessment (if the parameter was already measured according to the reference method in a previous survey), the measurement is optional

Acid exchangeable cations (Al, Fe, Mn), free H^+ acidity and Exchangeable acidity

Priority	**Level I**	**Level II**
Organic Layer		
OL	-	-
OF+OH, H-layers	*Mandatory[1]*	*Mandatory[1]*
Mineral layer		
0 - 10 cm	*Mandatory[1]*	*Mandatory[1]*
10 – 20 cm	*Mandatory[1]*	*Mandatory[1]*
20 – 40 cm	*Optional*	*Mandatory[1,2]*
40 – 60 cm	*Optional*	*Mandatory[1,2]*

[1] in calcareous soils ($CaCO_3$ > 20 g kg^{-1}), this parameter is optional
[2] in case of re-assessment (if the parameter was already measured according to the reference method in a previous survey), the measurement is optional

II Principle

The soil is first saturated with respect to barium by treating the soil one single time with a 0,1 mol/l barium chloride solution.

Concentrations of the exchangeable basic cations sodium, potassium, calcium and magnesium and the exchangeable acid cations iron, manganese, aluminium are determined in the 0.1 mol/l barium chloride extract of the soil using spectrometry.

To determine exchangeable acidity, the 0.1 mol/l extract is titrated with a 0.05 mol/l NaOH solution up to pH = 7.8. Determination of the free H^+ acidity is realised using a method in

which sodium fluoride is added to the soil extract before the titration (Aluminium ions are complexed and only the free H^+ acidity is detected during the titration process).

Note: *the reference method deviates from ISO 11260 & ISO 14254 in the sense that one single barium chloride extraction must be used instead of three extractions*

Alternatively the free H^+ acidity can be determined by the "German calculation method" based on the pH of the barium chloride solution before and after extraction (König *et al*. 2005). The exchangeable acidity is subsequently calculated based on the sum of the acid cations and the free H^+.

III Apparatus

Centrifuge + centrifuge tubes

Mechanical shaker

Laboratory glassware

Magnetic stirrer

Funnel (diam. approx. 110 mm)

Filter paper (diam. 150 mm)

PE-bottles

pH-meter

Burette

Atomic Absorption Spectrometer (AAS) / Flame Emission Spectrometer (FES) / Inductively Coupled Plasma Spectrometer (ICP)

IV Reagents

Barium chloride ($BaCl_2$) solution, conc. 0.1 mol/l

Sodium hydroxide (NaOH) solution, conc. 0.05 mol/l

Sodium fluoride (NaF) solution, conc. 1 mol/l

pH buffer solutions

Calibration substances

V Procedure

Laboratory sample

Use 2.5 g air-dried soil (particle size < 2 mm) of known moisture content.

Leaching procedure

Place the laboratory sample in a 50 ml centrifuge tube. Add 30 ml barium chloride solution and shake for 2 hours. Centrifuge at 3000 g for 10 min. Transfer the supernatant liquid through a filter into a PE-bottle. Retain the extract for analysis (Volume V).

If the filtered extract solution is not enough for the measurement of all cations and pH the extract solution can be diluted (for example 1:5) with barium chloride solution. This has to be considered when calculating the concentrations in the extract. Alternatively it is allowed to use higher volumes of barium chloride solution, but the ratio soil to solution must always be the same (e.g. 5.0 g soil and 60 ml barium chloride solution)!

Note: According to ISO 11260 & ISO 14254 three $BaCl_2$ extractions should be done and each time shaken for 1 hour in contrast to this analytical method (SA10).

Determination of exchangeable cations (Ca, Mg, K, Na, Al, Fe, Mn)

Measure the exchangeable cations in the extract using one of the spectrometric determination methods.

Determination of free H^+

Pipette 25 ml of the extract (Volume V_s). Add 1.25 ml of the sodium fluoride (1 mol/l) solution. Titrate with the sodium hydroxide (0.05 mol/l) solution to a pH value of 7.8. Titrate a blank in the same way.

Note: If 25 ml is not sufficient for the titration, new $BaCl_2$ extract, in accordance to ISO 11260, should be obtained and used.

Determination of exchangeable acidity

Pipette 25 ml of the extract into a container of sufficient capacity to also receive the electrodes of the pH-meter. Insert the electrodes and titrate with the sodium hydroxide (0.05 mol/l) solution until a pH value of 7.8 is reached and remains stable for 30 s. Repeat the procedure for a blank 0.1 mol/l $BaCl_2$ solution extract.

Note: If 25 ml is not sufficient for the titration, new $BaCl_2$ extract, in accordance to ISO 11260, should be obtained and used.

VI Calculation

Determination of exchangeable cations (Ca, Mg, K, Na, Al, Fe, Mn)

Calculation according to apparatus taking into account following equivalent mass in g/mol:

Na^+	= 22,99	Ca^{2+}	= 20,04	Fe^{3+}	= 18,62	Al^{3+}	= 8,99
K^+	= 39,10	Mg^{2+}	= 12,16	Mn^{2+}	= 27,47	H^+	= 1,01

Calculation of the ion equivalents per g soil:

$$IE = \frac{c * V}{m * EQ * 10}$$

where
IE ion equivalent in cmol/kg

c element concentration in the extract in mg/l
V volume of the added $BaCl_2$-solution in ml (30 ml)
m mass of the soil sample in g (2,5 g)
EQ equivalent mass of the element in g/mol

Determination of exchangeable acidity

The total exchangeable acidity on basis of air-dried soil is given by:

$$E_A = \frac{(V_a - V_B).c_{NaOH}.100.V}{V_s.m}$$

where

E_A total exchangeable acidity (cmol/kg) of the soil on basis of air-dried soil
V_A volume NaOH (ml) used for the test sample
V_B volume NaOH (ml) used for the blank
c_{NaOH} concentration of NaOH (mol/l)
V_S volume (ml) pipetted for analysis
m mass (g) of the laboratory sample
V final volume (ml) of the extract

Determination of free H^+

For free H^+ acidity use the same equation as for exchangeable acidity but use the volumes V_a and V_b for the volume NaOH used in the titration for free acidity.

Alternative method for the determination of free H^+ ("German" calculation method)

Calculation of the Proton equivalent per gram soil:

$$H^+(cmol/kg) = 10^{-1} * \frac{(10^{-pH_p} - 10^{-pH_0}) * V * 1000}{m * 0{,}88} - \frac{c(Al) * V}{m * M(Al) * \left(1 + \frac{10^{-pH_p}}{10^{-5{,}85}}\right)}$$

Or

$$H^+(cmol/kg) = 10^{-1} * \frac{(10^{-pH_p} - 10^{-pH_0}) * V * 1000}{m * 0{,}88} - \frac{c(Al) * V}{m * M(Al) * F}$$

Where

F = the Ulrich/Prenzel factor. Values of the F factor for different pH values can be read from Table SA10-1.

H^+ = Free H^+ in cmol/kg
10^{-1} = Conversion factor between units (µmol/g to cmol/kg)
pH_P = pH-value of the $BaCl_2$ extract after the leaching procedure
pH_0 = pH-value of the pure $BaCl_2$-extract
V = Final Volume of the extract in ml (30 ml)
m = Mass of the laboratory sample in g (2.5 g)
c(Al) = Concentration of the Aluminium in the $BaCl_2$ extract in mg/l
M(Al) = Molar mass of Aluminium in g/mol (26,98 g/mol)
F = Ulrich/Prenzel factor (cf. Table SA10-1)

Note:As alternative method, the exchangeable acidity can be calculated as the sum of the exchangeable acid cations (Al, Fe, Mn, free H^+).

Table SA10-1: The Ulrich/Prenzel factor (F) for a range of pH_p values (König and Fortmann, 1996)

pH	F	pH	F	pH	F	pH	F	pH	F	pH	F
		4.6	18.8	4.1	57.2	3.6	179	3.1	563	2.6	1774
		4.59	19.2	4.09	58.5	3.59	1 83	3.09	576	2.59	1816
		4.58	19.6	4.08	59.9	3.58	187	3.08	590	2.58	1858
		4.57	20.1	4.07	61.3	3.57	192	3.07	604	2.57	1900
		4.56	20.5	4.06	62.7	3.56	196	3.06	618	2.56	1943
		4.55	21	4.05	64.1	3.55	201	3.05	632	2.55	1993
		4.54	21.4	4.04	65.6	3.54	205	3.04	647	2.54	2035
		4.53	21.9	4.03	67.1	3.53	210	3.03	662	2.53	2084
		4.52	22.4	4.02	68.6	3.52	215	3.02	677	2.52	2134
		4.51	22.9	4.01	70.2	3.51	220	3.01	693	2.51	2183
		4.50	23.4	4	71.8	3.5	225	3	709	2.5	2233
		4.49	23.9	3.99	73.5	3.49	230	2.99	721	2.49	2289
		4.48	24.4	3.98	75.1	3.48	235	2.98	743	2.48	2341
		4.47	25	3.97	76.9	3.47	241	2.97	757	2.47	2401
		4.46	25.5	3.96	78.6	3.46	246	2.96	778	2.46	2451
		4.45	26.1	3.95	80.4	3.45	252	2.95	792	2.45	2511
		4.44	26.7	3.94	82.3	3.44	258	2.94	813	2.44	2571
		4.43	27.3	3.93	84.2	3.43	264	2.93	827	2.43	2631
		4.42	27.9	3.92	86.2	3.42	270	2.92	848	2.42	2691
		4.41	28.5	3.91	88.1	3.41	276	2.91	870	2.41	2751
		4.4	29.2	3.9	90.1	3.4	283	2.9	891	2.4	2821
		4.39	29.8	3.89	92.2	3.39	289	2.89	912	2.39	2881
		4.38	30.5	3.88	94.3	3.38	296	2.88	933	2.38	2961
		4.37	31.2	3.87	96.5	3.37	303	2.87	954	2.37	3021
		4.36	31.9	3.86	98.7	3.36	310	2.86	976	2.36	3091
		4.35	32.6	3.85	101	3.35	317	2.85	997	2.35	3161
		4.34	33.4	3.84	103	3.34	325	2.84	1024	2.34	3241
		4.33	34.1	3.83	106	3.33	332	2.83	1046	2.33	3311
		4.32	34.9	3.82	108	3.32	340	2.82	1067	2.32	3391
		4.31	35.7	3.81	111	3.31	348	2.81	1095	2.31	3471
		4 3	36.5	3.8	113	3.3	356	2.8	1117	2.30	3551
4.8	12.2	4.29	37.3	3.79	116	3.29	364	2.79	1145	2.29	3631
4.79		4.28	38.2	3.78	118	3.28	373	2.78	1173	2.28	3721
4.78		4.27	39	3.77	121	3.27	381	2.77	1202	2.27	3801
4.77	13	4.26	39.9	3.76	124	3.26	390	2.76	1230	2.26	3891
4.76	13.3	4.25	40.8	3.75	127	3.25	399	2.75	1258	2.25	3981
4.75	13.6	4.24	41.7	3.74	130	3.24	408	2.74	1286	2.24	4071
4.74	13.9	4.23	42.7	3.73	133	3.23	418	2.73	1315	2.23	4171
4.73	14.2	4.22	43.9	3.72	136	3.22	430	2.72	1350	2.22	4271
4.72	14.5	4.21	44.7	3.71	139	3.21	438	2.71	1378	2.21	4371
4.71	14.8	4.20	45.1	3.70	142	3.20	448	2.70	1413	2.20	4471
4.7	15.1	4.19	46.7	3.69	146	3.19	458	2.69	1442	2.19	4571
4.69	15.5	4.18	47.3	3.68	149	3.18	469	2.68	1477	2.18	4681
4.68	15.8	4.17	48.9	3.67	152	3.17	480	2.67	1512	2.17	4791
4.67	16.1	4.16	50	3.66	156	3.16	491	2.66	1548	2.16	4901
4.66	16.5	4.15	51.1	3.65	159	3.15	502	2.65	1583	2.15	5001
4.65	16.8	4.14	52.3	3.64	163	3.14	514	2.64	1618	2.14	5131
4.64	17.2	4.13	53.5	3.63	167	3.13	526	2.63	1654	2.13	5251
4.63	17.6	4.12	54.7	3.62	170	3.12	538	2.62	1695	2.12	5371
4.62	18	4.11	56	3.61	175	3.11	551	2.61	1731	2.11	5501
4.61	18.4	4.10	57.2	3.60	179	3.10	563	2.60	1774	2.10	5621
pH	**F**	**pH**	**F**	**pH**	**F**	**pH**	**F**	**pH**	**F**	**pH**	**F**

VII Report

Report (in $cmol_{(+)}/kg$) total exchangeable acidity, the exchangeable cations Al, Ca, K, Mg, Na, and free H^+ with 2 decimals; and Fe and Mn with 3 decimals on the basis of oven-dried soil.

VIII References

ISO 11260. 1994. Soil Quality – Determination of effective cation exchange capacity and base saturation level using barium chloride solution. International Organization for Standardization. Geneva, Switzerland. 10 p. [available at www.iso.ch].

ISO 14254. 1994. Soil Quality – Determination of exchangeable acidity in barium chloride extracts. International Organization for Standardization. Geneva, Switzerland. 5 p. [available at www.iso.ch].

König, N., Fortmann, H. 1996. Probenvorbereitungs-, Untersuchungs- und Element-bestimmungsmethoden des Umweltlabors der Niedersächsischen Forstlichen Versuchsanstalt und des Zentrallabors II des Forschungszentrums Waldökosysteme, Teil 4: Probenvorbereitungs- und Untersuchungsmethoden, Qualitätskontrolle und Datenverarbeitung; Berichte des Forschungszentrums Waldökosyst. B, Bd. 49, Untersuchungsmethode Boden AKEG1.1

Gutachterausschuss Forstliche Analytik 2005: Handbuch Forstliche Analytik. König, N., Bartens, H. (eds.): Loseblatt-Sammlung der Analysemethoden im Forstbereich, 433 pg. (Method A3.2.1.3)

Soil Analysis Method 11 (SA11): Aqua Regia Extractant Determinations P, Ca, K, Mg, Mn, Cu, Pb, Cd, Zn, Al, Fe, Cr, Ni, S, Hg, Na

Aqua Regia extractant determinations P, Ca, K, Mg, Mn, Cu, Pb, Cd, Zn, Al, Fe, Cr, Ni, S, Hg, Na	
Method sheet	SA11
Reference method	ISO 11466
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA02 Pretreatment: PB01 Determination: DB**

I Relevance in ICP Forests

Aqua Regia extractant determinations (P, Ca, K, Mg, Mn)

Priority	**Level I**	**Level II**
Organic Layer		
OL	*Optional*	*Optional*
OF+OH, H-layers	*Mandatory*	*Mandatory*
Mineral layer		
0 - 10 cm	*Optional*	*Optional*
10 – 20 cm	*Optional*	*Optional*
20 – 40 cm	*Optional*	*Optional*
40 – 80 cm	*Optional*	*Optional*

Aqua Regia extractant determinations (Cu, Pb, Cd, Zn)

Priority	**Level I**	**Level II**
Organic Layer		
OL	*Optional*	*Optional*
OF+OH, H-layers	*Mandatory*	*Mandatory*
Mineral layer		
0 - 10 cm	*Mandatory*	*Mandatory*
10 – 20 cm	*-*	*-*
20 – 40 cm	*-*	*-*
40 – 80 cm	*-*	*-*

Aqua Regia extractant determinations (Al, Fe, Cr, Ni, S, Hg, Na)

Priority	**Level I**	**Level II**
Organic Layer		
OL	*Optional*	*Optional*
OF+OH, H-layers	*Optional*	*Optional*
Mineral layer		
0 - 10 cm	*Optional*	*Optional*
10 – 20 cm	*-*	*-*
20 – 40 cm	*-*	*-*
40 – 80 cm	*-*	*-*

II Principle

According to the reference method (ISO 11466), the dried sample is extracted with a hydrochloric/nitric acid mixture by standing for 16 h at room temperature, followed by boiling under **reflux** for 2 h. The extract is then clarified and made up to volume with nitric acid.

Alternatively, the digestion of the sample under pressure in closed vessels (microwave digestion) is allowed (at 175°C +/- 5°C for 10 min +/- 1 min) followed by filtration according to ISO Standard 12914 (2012).

Elements are determined by spectrometry (atomic absorption or ICP/OES or ICP/MS).

III Apparatus

Analytical balance (accuracy 0.001 g)

Reference method (reflux):

Desiccator (2 l)

Reaction vessel (250 ml)

Reflux condenser

Absorption vessel, non return type, containing 15 ml of nitric acid (0.5 mol/l) (only necessary for determination of mercury)

Roughened glass beads or antibumping granules

Temperature-controlled heating apparatus

Funnel (diam. approx. 110 mm)

Volumetric flask (110 ml)

Filter paper (diam. 150 mm, pore size approx. 8 µm)

Microwave digestion (alternative)

Microwave apparatus (laboratory-grade microwave oven with temperature-feedback control mechanisms, temperature accuracy +/- 2.5°C) with rotating turntable (min. speed of 3 min^{-1})

Microwave extraction vessels with internal volumetric flasks, of capacity 50 ml or 100 ml

Filter papers, cellulose-based, 0.45 µm, hardened and resistant to aqua regia

Atomic Absorption Spectrometer (AAS) / Flame Emission Spectrometer (FES) / Inductively Coupled Plasma Spectrometer (ICP) / Colorimeter

IV Reagents

Water (grade 2)

Hydrochloric acid (HCl) concentration 12 mol/l, $\rho \approx 1.19$ g/ml

Nitric acid (HNO_3) concentration 15.8 mol/l, $\rho \approx 1.42$ g/ml

Nitric acid (HNO_3) concentration 0.5 mol/l

The aqua regia extractant is the mixture of the HCl:HNO_3 in a 3 to 1 ratio.

Anti-foaming agent

V Procedure

1) By reflux (reference method)

Laboratory sample

Weigh 3.000 g air-dried soil (particle size < 2 mm) of known moisture content in the 250 ml reaction vessel.

Moisten with about 0.5 ml to 1.0 ml of water and add, while mixing, 21 ml of hydrochloric acid followed by 7 ml of nitric acid (15.8 mol/l), drop by drop if necessary, to reduce foaming. Connect the condenser (and the absorption vessel) to the reaction vessel, and allow to stand for 16 h at room temperature to allow for slow oxidation of the organic matter in the soil.

The amount of aqua regia is sufficient only for oxidation of about 0.5 g of organic carbon. If there is more than 0.5 g of organic carbon in the 3 g subsample, proceed as follows. Allow the first reaction with the aqua regia to subside. Then add an extra 1 ml of nitric acid (15.8 mol/l) only to every 0.1 g of organic carbon above 0.5 g. Do not add more than 10 ml of nitric acid at any time, and allow any reaction to subside before proceeding further.

Raise the temperature of the reaction mixture slowly until reflux conditions are reached and maintain for 2 h, ensuring that the condensation zone is lower than 1/3 of the height of the condenser, then allow to cool.

Allow the reaction vessel to stand so that most of any insoluble residue settles out of suspension. (Add the contents of the absorption vessel to the reaction vessel, via the condenser, rinsing both the absorption vessel and condenser with a further 10 ml of nitric acid (0.5 mol/l)). Decant the relatively sediment-free supernatant carefully onto a filter paper, collecting the filtrate in a 100 ml volumetric flask. Allow all the initial filtrate to pass through the filter paper, then wash the insoluble residue onto the filter paper with a minimum of nitric acid (0.5 mol/l). Collect this filtrate with the first. before proceeding further. The extract thus prepared is ready for the determination of trace elements, by an appropriate method.

2) By microwave digestion

Weigh at least 0.5 g to max. 2.0 g +/- 0.1 g (based on dry mass) of the test sample (particle size < 250 μm), and transfer to the microwave extraction vessel.

Moisten the test portion with a few drops of water. Add separately 6 ml $\pm$ 0.1 ml of hydrochloric acid and then 2 ml $\pm$ 0.1 ml of nitric acid to the extraction vessel and mix well. If a vigorous reaction occurs, allow the reaction to subside before capping the vessel. If excessive foaming occurs, add a drop of anti-foaming agent.

The amount of nitric acid is sufficient for approximately 0.1 g of organic carbon in the sample. If the organic carbon percentage is higher, then add an extra 0.5 ml of nitric acid for every

0.05 g of organic carbon, up to a maximum of 4 ml of extra nitric acid for a sample with 0.5 g of organic carbon. Do not add >5 ml of nitric acid. Allow any reaction to subside before proceeding further.

Cap the extraction vessel and weigh it. Connect the extraction vessel to the microwave equipment or place it into the carrousel. Always fill all positions of the microwave equipment (usually 6, 12, 16 or 40 positions). If not all positions are occupied by test portions, fill the remaining extraction vessels with the same amount of aqua regia as in the sample vessels, to make sure that the energy is evenly absorbed.

Increase the temperature of the extraction mixture with a rate of approximately 10° C/min to a temperature of (175 ± 5)°C.

Maintain the extraction at 175 °C for 10 min ± 1 min. Then allow the extraction vessel to cool to room temperature following the manufacturer's manual. Weigh the extraction vessel again and record the mass. The mass loss can be considered consistent when it differs by less than 5 % of the mass loss of a well known reference material.

Uncap and vent the extraction vessel in a fume hood.

Transfer the extract quantitatively into a clean volumetric flask by rinsing the vessel with nitric acid and fill up with water to the mark. If appropriate, add releasing agents or internal standards solution necessary for the determination method before filling up to the mark.

Filtrate the extract using a filter paper before subsequent measurement. Alternatively, centrifugation at 2000 to 3000 rotations.min^{-1} for 10 min can be sufficient to clear the supernatant.

3) Determination of elements (P, Ca, K, Mg, Mn, Cu, Pb, Cd, Zn, Al, Fe, Cr, Ni, S, Na)

Measure the elements cations in the extract using one of the spectrometric determination methods.

*Notes**:***

1) *ISO 11047 can be used as a guideline for the determination of Cd, Cr, Cu, Pb, Mn, Ni and Zn.*

2) Particular attention needs to be paid to the cleaning of the laboratory equipment. It is recommended to thoroughly clean all laboratory equipment (e.g. vessels) and, as a minimum, leave the equipment standing overnight in 1 % to 5 % nitric acid.

VI Calculation

Determination of elements (P, Ca, K, Mg, Mn, Cu, Pb, Cd, Zn, Al, Fe, Cr, Ni, S, Hg, Na)

Calculation according to apparatus.

VII Report

Report aqua regia extract determinations (mg/kg) with 1 decimals and Cd with 2 decimals on the basis of oven-dried soil.

VIII References

ISO 11466. 1995. Soil Quality – Extraction of trace elements soluble in *aqua regia*. International Organization for Standardization. Geneva, Switzerland. 6 p. [available at www.iso.ch].

ISO 11047. 1998. Soil Quality – Determination of cadmium, chromium, cobalt, copper, lead, manganese nickel and zinc. Flame and electrothermal atomic absorption spectrometric methods. International Organization for Standardization. Geneva, Switzerland. 6 p. [available at www.iso.ch].ISO 12914. 2012. Soil quality − Microwave-assisted extraction of the aqua regia soluble fraction for the determination of elements. International Organization for Standardization. Geneva, Switzerland. 7 p. [available at www.iso.ch].

EN 16173. 2012 Sludge, treated biowaste and soil – Digestion of nitric acid and soluble fractions of elements.

Soil Analysis Method 12 (SA12): Determination of Total Elements Ca, Mg, Na, K, Al, Fe, Mn

Total Elements: Ca, Mg, Na, K, Al, Fe, Mn **Method 1 : Dissolution with hydrofluoric and perchloric acids**	
Method sheet	SA12A
Reference methods	ISO 14869
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA05 Pretreatment: PC03 Determination: DB**

I Relevance in ICP Forests

Priority	**Level I**	**Level II**
Organic Layer		
OL	-	-
OF+OH, H-layers	-	-
Mineral layer		
0 – 10 cm	-	*Optional*
10 – 20 cm	-	*Optional*
20 – 40 cm	-	*Optional*
40 – 80 cm	-	*Optional*

II Principle

This method specifies the complete dissolution, using hydrofluoric and perchloric acids, of the following elements in soils:

Al, Ba, Cd, **Ca**, Cs, Cr, Co, Cu, **Fe**, **K**, Li, **Mg**, **Mn**, **Na**, Ni, P, Pb, Sr, V, Zn.

This procedure may be appropriate for the subsequent determination of other elements provided their concentrations are high enough relative to the sensitivity of the measurement methods. The low acid concentration of the final solution allows the use of a large range of analytical devices and the volatilisation of silicon simplifies analytical procedures.

The dried and ground sample is pre-treated to destroy organic matter, and then digested with a mixture of hydrofluoric and perchloric acids. After evaporation to near dryness, the residue is dissolved in dilute hydrochloric or nitric acid. Hydrofluoric acid decomposes silicates by the reaction of F with Si to form volatile SiF_4. As it evaporates last, perchloric acid forms readily-soluble perchlorate salts.

To minimise the danger of acid ejection due to violent oxidation of organic matter by perchloric acid, two alternative procedures have been adopted to destroy organic matter prior to digestion:

- dry ashing at 450 °C;
- pretreatment with nitric acid.

III Apparatus

Mill

Drying oven and desiccator

Analytical balance (accuracy 0.0001 g)

Crucible of fused silica or platinum (10 - 30 ml)

Furnace (temperature 450 °C)

Evaporating dishes made of polytetrafluoroethylene (PTFE)

Hot plate (150 °C)

Fume hood

Volumetric flask of polypropylene (50 ml)

Atomic Absorption Spectrometer (AAS) / Flame Emission Spectrometer (FES) / Inductively Coupled Plasma Spectrometer (ICP)

IV Reagents

Water (grade 2)

Hydrofluoric acid (HF), conc. 27.8 mol/l, ρ = 1.16 g/ml

Perchloric acid ($HClO_4$), conc. 11.6 mol/l, ρ = 1.67 g/ml

Hydrochloric acid (HCl), conc. 12.1 mol/l, ρ = 1.19 g/ml

Nitric acid (HNO_3), conc. 15.2 mol/l, ρ = 1.41 g/ml

V Procedure

Attention!

Always use latex gloves while working with HF and keep the ointment against HF acid bites ready for eventual accidents!

Laboratory sample

Use air-dried soil milled as fine as possible. Weigh precisely 0.250 g of the milled sample.

Destruction organic matter

Dry ashing

Transfer soil sample to a crucible. Place the crucible in the furnace and allow the temperature to reach 450 °C, progressively over 1 h. Maintain this temperature for 3 h. Allow the furnace to cool to room temperature and transfer the ash quantitatively to a PTFE evaporating dish with a minimum amount of water. Using a platinum crucible of about 30 ml avoids ash being transferred to a PTFE dish and allows digestion to be performed in the same container as dry ashing.

Nitric acid pre-treatment

Transfer soil sample to an evaporating dish and add 5 ml of nitric acid. Place the dish on the hot plate at 150 °C and evaporate until approximately 1 ml of nitric acid remains. Note that several successive additions of nitric acid may be necessary until the emission of nitrous vapours ceases to remove all the organic matter. In such cases, remove the dish from the hot plate and cool to room temperature before adding the next portion of nitric acid. After the last addition of nitric acid, remove the dish from the hot plate and cool to room temperature.

Total digestion

Add 5 ml of hydrofluoric acid and 1.5 ml of perchloric acid to the pretreated test portion in the PTFE dish or the 30 ml platinum crucible. Heat this mixture on the hot plate until the dense fumes of perchloric acid and silicon tetrafluoride cease. Do not allow the mixture to evaporate to complete dryness. Remove the dish from the hot plate, allow to cool, add 1 ml of hydrochloric acid or 1 ml of nitric acid and approximately 5 ml of water to dissolve the residue. Warm the dish briefly on the hot plate to assist dissolution. Transfer this solution quantitatively to the 50 ml volumetric flask, fill to the mark and mix well.

A solid phase remaining in the resultant solution indicates incomplete dissolution. It may be of no importance with respect to the elements of interest, especially when pure silica constitutes the solid phase, but in that case, the procedure shall be completed by one of the following stages.

- The procedure is stopped at this point and failure of total dissolution with a possible effect on the determination of total contents is noted in the test report.
- The procedure is adjusted to improve the dissolution. One or a combination of the three following treatments is carried out.
- The procedure is started again with a new test portion but a further dose of 5 ml of hydrofluoric acid and 1.5 ml of perchloric acid is added after evaporation of the first one to near dryness. The second dose is also evaporated as above and the procedure is carried on as described above.
- The procedure is started again with a new test portion but after the addition of hydrofluoric and perchloric acids the mixture is left overnight at room temperature before being heated as described above.
- The whole procedure is not changed but the mass of the test portion is reduced.

If a solid phase remains in spite of these further treatments, then failure of total dissolution is mentioned in the test report.

Blank test

Use the same procedure, without the sample, to perform at least one blank test within each batch of digestions.

Determination of total elements (Ca, Mg, K, Na, Al, Fe, Mn)

Measure the total elements in the extract using one of the spectrometric determination methods.

VI Calculation

Determination of total elements (Ca, Mg, K, Na, Al, Fe, Mn)

Calculation according to apparatus.

VII Report

Report total elements (mg/kg) with one decimal place on the basis of oven-dried soil.

VIII References

ISO 14869-1. 2001. Soil Quality – Dissolution for the determination of total element content - Part 1: Dissolution with hydrofluoric and perchloric acids. International Organization for Standardization. Geneva, Switzerland. 5 p. [available at www.iso.ch].

Total Elements: Ca, Mg, Na, K, Al, Fe, Mn Method 2 : Total element analysis by fusion with lithium metaborate	
Method sheet	SA12B
Reference methods	ISO 14869
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA03 Pretreatment: PB10 Determination: DB**

I Relevance in ICP Forests

Priority	**Level I**	**Level II**
Organic Layer		
OL	-	-
OF+OH, H-layers	-	-
Mineral layer		
0 – 10 cm	-	*Optional*
10 – 20 cm	-	*Optional*
20 – 40 cm	-	*Optional*
40 – 80 cm	-	*Optional*

II Principle

This method specifies the fusion using lithium metaborate.

III Apparatus

Platinum crucibles

Muffle furnace

Magnetic stirring devices

Analytical balance (accuracy 0.0001 g)

Filter paper prewashed (with a 10% HNO_3 or HCl solution)

IV Reagents

Lithium metaborate ($LiBO_2$) on powder

Nitric acid (HNO_3), 4 %

V Procedure

Laboratory sample

Use air-dried soil (milled < 0.4 mm). Weigh 0.4 g of the milled sample.

Destruction organic matter

The sample is put to each platinum crucible and pre-ignited at 850°C for 30 min as to avoid damaging the platinum crucible when it would be mixed with lithium metaborate. The reason for this is that the soil organic matter can cause reduction of the platinum during the fusion.

Fusion

After the crucibles are cooled (usually it takes one night) the pre-ignited soil is mixed thoroughly (by means of a pipette tip) with 2 g of lithium metaborate powder in a platinum crucible and fused for 15 min at 950°C in a preheated muffle furnace. The crucible and flux that is formed are allowed to cool for one night. The reason for this is that if we try to remove them from the furnace immediately after heating by means of something metallic, there will be a reaction between the platinum and the metal.

The crucibles are immersed in a 100 ml beaker and covered with 70-80 ml of 4% nitric acid. A magnetic stirring bar is then placed inside the crucible and stirring can begin immediately. The flux is dissolved in 3 to 4 hr (occasionally it might take a little more) and the solution is made up to 100 ml, filtered through a prewashed (with a 10% HNO_3 or HCl solution) paper filter of 0.45 mm and stored for analysis.

Blank test

Use the same procedure, without the sample, to perform at least one blank test within each batch of digestions.

Determination of total elements (Ca, Mg, K, Na, Al, Fe, Mn)

Measure the total elements in the extract using one of the spectrometric determination methods.

VI Calculation

Determination of total elements (Ca, Mg, K, Na, Al, Fe, Mn)

Calculation according to apparatus.

VII Report

Report total elements (mg/kg) with one decimal place on the basis of oven-dried soil.

VIII References

Michopoulos, P. 1995. Studies on manganese cycling in forest soils. PhD Thesis. University of Aberdeen.

Potts, P.J. 1987. A handbook of silicate rock analysis. Blackie, New York.

Total Elements: Ca, Mg, Na, K, Al, Fe, Mn Method 3 : Total digestion with HNO_3 and HF	
Method sheet	SA12C
Reference methods	
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA05 Pretreatment: PC03, PD05 Determination: DB**

I Relevance in ICP Forests

Priority	**Level I**	**Level II**
Organic Layer		
OL	-	-
OF+OH, H-layers	-	-
Mineral layer		
0 – 10 cm	-	*Optional*
10 – 20 cm	-	*Optional*
20 – 40 cm	-	*Optional*
40 – 80 cm	-	*Optional*

II Principle

Nitric acid/hydrofluoric acid digestion is a dissolution in which the oxidising effect of nitric acid and the silica-dissolving property of hydrofluoric acid are combined. On the one hand, nitrate (with N^{V}) is converted to nitrous gases (NO_X, with N^{II-IV}) and the released oxygen causes the oxidation of the substances that are to be digested:

$$2\ HNO_3 \leftrightarrow 2\ HNO_2 + O_2$$

On the other hand, the hydrofluoric acid converts all silicates to fluorosilicic acid, which on fuming disintegrates into volatile silicontetrafluoride and hydrofluoric acid and thus removes the silicates from the system:

$$SiO_2 + 6\ HF \rightarrow H_2SiF_6 + 2\ H_2O$$

$$H_2SiF_6 \rightarrow SiF_4 + 2\ HF$$

Organic substances are dissolved completely in this digestion:

$$C_aH_bN_cO_dS_eP_fM_g + z\ O_2 \rightarrow a\ CO_2 + b/2\ H_2O + c\ NO_x + e\ SO_4^{2-} +$$

$$f\ PO_4^{3-} + g\ M^{+/2+/3+}$$

Mineral substances in the humus are also dissolved completely, with the exception of few special minerals (e.g. certain zircon compounds, topaz).

Digestion is carried out in a pressure vessel with teflon beakers, so that it is possible to carry out the digestion with highly volatile nitric acid and hydrofluoric acid at temperatures ranging from 170° to 190°C.

Disturbances

As the oxidising effect of the HF/HNO_3 mixture is not as strong as that of pure nitric acid, soil samples with high humus content may require pre-digestion with pure nitric acid in order to obtain complete digestion of the organic matter.

Under certain conditions some compounds are not completely digested, such as when they are chemically unstable or when the samples are insufficiently finely ground. In some cases, precipitation of phases of low solubility may occur during digestion. The following elements or precipitations can, for example, be subject to incomplete digestion: oxides of Al and Ti; fluorides of Al, Ca; sulphates of Ba, Pb and Sr.

The risk of contamination is high. Contamination can be effectively contained by rinsing the instruments used with diluted nitric acid.

Pressure vessels to be used are beakers of Teflon or related materials specially developed for this job. This minimizes the danger of memory effects.

III Apparatus and Instruments

- Digestion apparatus with Teflon pressure vessels

- Hot plate with temperature control; alternatively: drying cabinet with temperature control

- Balance (weighing precision +/- 0.1 mg)

- Volumetric flask 50 ml made of Duran-glas or PFA

- PFA bottles 50 ml

- Ceramic spatula

- Pipettes

- Dispenser

IV Reagents

Water, H_2O demin.

Nitric acid (HNO_3), 65% p.a. plus

Hydrofluoric acid (HF), 40% p.a.

Solutions

Rinsing acid 5% p.a. plus: 80 ml concentrated HNO_3 p.a. are measured in a graduation cylinder and topped up in a 1 l beaker with H_2O demin. and then transferred to a 2 l PE bottle with dispenser attachment.

Sample preparation

The samples have to be dried at 40 °C and milled as fine as possible.

V Procedure

Safety measures:

1 The work has to be carried out in a suitable fume cupboard!

2 The specific safety measures for the handling of hydrofluoric acid must be observed!

(a) Digestion

(1) Pre-digestion

(necessary only in the case of topsoil samples with high humus content or for a repeated digestion when a black precipitation is evident after total digestion).

200 mg sample material is weighed to a precision of 0.1 mg with a micro balance and filled into each Teflon beaker. Beneath the fume hood 4 ml conc. HNO_3 is added to the samples with a pipette, taking care that the liquid slowly flows down the beakers' inside wall. Rotate each Teflon beaker carefully by hand to allow the entire sample to be moistened by the acid. Cover beakers with a lid and allow to stand for one hour at room temperature until samples begin to react with the acid. Subsequently the numbered Teflon beakers are placed in the digestion block which is then screwed tight. After this the digestion block is placed into the drying oven or onto the hot-plate and heated slowly (within one hour) to 175°C. This temperature is to be maintained for at least 6 hours and the samples thus digested (possibly overnight).

On the morrow the digestion blocks are allowed to cool down before they are opened. Hold the crucible lids at a slight inclination when opening, while tapping the crucible lightly with the edge of the lid, so that any acid condensation adhering to the inside of the lid may drip back into the crucible. Crucible lids are rinsed with H_2O demin. and put aside for total digestion. Cover with a sheet of tissue to protect them from dust.

The teflon crucibles with the digestion solution are then placed into a fume cupboard and fumed at a maximum temperature of 120° C until nearly dry.

Remarks:

1 Use the spatula to place the sample material as deep down into the teflon beaker as possible in order to avoid electrostatic adherance of sample matrial to the beaker sides.

2 Because of the nitrous gases that are released, the hot-plate or drying-oven used for digestion should be placed beneath a fume hood.

3 In order to avoid or minimize contamination during fuming, the use of closed fume cupboards is strongly recommended (see Appendix 1).

(2) Total digestion

In case no pre-digestion was necessary, about 200 mg of sample material is weighed into each Teflon beaker with a micro balance. Otherwise total digestion is carried out with the nearly dry samples in the Teflon beakers. Underneath the hood, 4 ml conc. HNO_3 and 2 ml HF are added to humus samples and 2 ml conc. HNO_3 and 2 ml HF to soil samples using a pipette, taking care that the liquid slowly flows down the beakers' inside wall. Rotate each Teflon beaker carefully by hand so that the entire sample is moistened by the acid. Cover beakers with a lid and allow to stand for one hour at room temperature until samples start to react with the acid. If pre-digestion has been carried out, this step can be skipped.

Subsequently the numbered Teflon beakers are placed in the digestion block which is then screwed tight. The digestion block is placed into the drying-oven or onto the hot-plate and heated slowly (within one hour) to 175°C. This temperature is to be maintained for at least 6 hours and the samples thus digested (possibly overnight).

On the morrow the digestion blocks are allowed to cool down before they are opened. Hold the crucible lids at a slight inclination when opening while tapping the crucible lightly with the edge of the lid, so that any acid condensation adhering to the inside of the lid may drip back into the crucible. Crucible lids are rinsed with H_2O demin. and put aside for total digestion. Cover with a sheet of tissue to protect them from dust.

The Teflon crucibles with the digestion solution are then placed into a fume cupboard and fumed at a maximum temperature of 120° C until nearly dry.

Remarks:

1 Always wear latex gloves when handling HF and avail yourself of a specific cream against HF-cauterisation in case of an accident.

2 Use the spatula to place the sample material as deep down into the beaker as possible in order to avoid electrostatic adherance of sample material to the teflon beaker sides.

3 Because of the nitrous gases that are released, the hot-plate or drying-oven used for digestion should be placed beneath a fume hood.

4 In order to avoid or minimize contamination during fuming, the use of closed fume cupboards is strongly recommended.

(3) Ending digestion procedure

The residue left in the Teflon beaker after fuming is combined with 2 ml conc. HNO_3, then add 15 ml H_2O demin. reinst. with a dispenser.

Cover the beakers with lids and place the closed beakers in the digestion block which is then screwed tight. Place the digestion block into the drying-oven or onto the hot-plate and heat to 150° C. This temperature is held for at least one hour until the residue has dissolved.

The digestion block is then opened. The crucibles should now contain clear solutions. (If this is not the case, the digestion and pre-digestion must be repeated.)

In order to remove the digestion solution one beaker at a time is taken from the block and its lid carefully removed. Hold the crucible lids at a slight inclination when opening while tapping the crucible lightly with the edge of the lid, so that any acid condensation adhering to the inside of the lid may drip back into the crucible.

Subsequently the solution is poured directly into a 50 ml graduated flask. Rinse the beaker 3 x with 10 ml demin. each time from the dispenser and then add the rinsing solution to the contents of the graduated flask. The flask is then topped up with H_2O demin., closed and shaken. The digestion solution is finally poured into a 50 ml. PFA-bottle.

Remarks:

1 In case the residue has not completely dissolved, the concluding digestion procedure may be repeated after adding a small quantity of HCl.

2 The cleaning of used vessels and filters:

- Teflon beakers:

After each digestion as well as at the conclusion of the series, these are to be filled to the brim with 5% rinsing acid and closed with their lid. Any discolouration of the inner walls of the Teflon crucibles should be carefully wiped off with a sheet of tissue paper and H_2O demin. Leave to stand for one hour, then empty the beakers, rinse thoroughly with H_2O demin. and put to dry in a drying-cupboard. Cover with a piece of paper and do not allow the temperature to exceed 60°C.

- Graduated flasks:

Fill 50 ml graduated flask right to the top with rinsing acid and close with a bung. Just before re-using the flask, rinse thoroughly with H_2O demin.

- PFA bottles:

Pour 25 ml of rinsing acid into the 50 ml bottles, shake for one hour on the shaking machine, then rinse thoroughly with H_2O demin. Subsequently they are dried in the drying cupboard at 50° C, covered with a sheet of paper.

- Remaining instruments:

The pipettes used for the conc. HNO_3 and HF must be rinsed thoroughly with H_2O demin. at the end of each day in order to avoid corrosion. Pipette tips may be used for one series only.

(b) Element determination in the digestion solution

All elements can be measured in the digestion solution with ICP (main elements) or ICP with ultrasonic nebulizer or AAS with graphite furnace (heavy metals)

Remarks:

Take care that only matrix adapted acid solutions are used when preparing the standards and intermediate rinsing fluids with the ICP, AAS and with automatic dispensers.

VI Comparability with other methods

(a) Total digestion with HNO_3/HF using a microwave oven (method A3.3.2, Handbuch Forstliche Analytik): the results are fundamentally comparable.

(b) Total digestion with $HClO_4$/HNO_3/HF using a microwave oven (method A3.3.5, Handbuch Forstliche Analytik): the results are fundamentally comparable; however, the German advisory committee of silvicultural analysis has experienced deficiencies in the evaluation of chromium in $HClO_4$/HNO_3/HF digestion, especially where humus samples are concerned.

VIII References

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Soil Analysis Method 13 (SA13). Determination of Acid Oxalate Extractable Al, Fe and P

Acid Oxalate Extractable Fe and Al	
Method sheet	SA13
Reference methods	ISRIC, 2002
Method suitable for	Organic Layer, Mineral Layer
Method code	Sample preparation: MA02 Pretreatment: PA05 Determination: DB*¨*

I Relevance in ICP Forests

Priority	Level I	Level II
Organic Layer		
OL	-	-
OF+OH, H-layers	*Optional*	*Optional*
Mineral layer		
0 – 10 cm	*Optional*	*Mandatory (Optional for P)*
10 – 20 cm	*Optional*	*Mandatory (Optional for P)*
20 – 40 cm	*Optional*	*Mandatory[1] (Optional for P)*
40 – 80 cm	*Optional*	*Mandatory[1] (Optional for P)*

[1] In case of re-assessment (if the parameter was already measured according to the reference method in a previous survey), the measurement is optional

II Principle

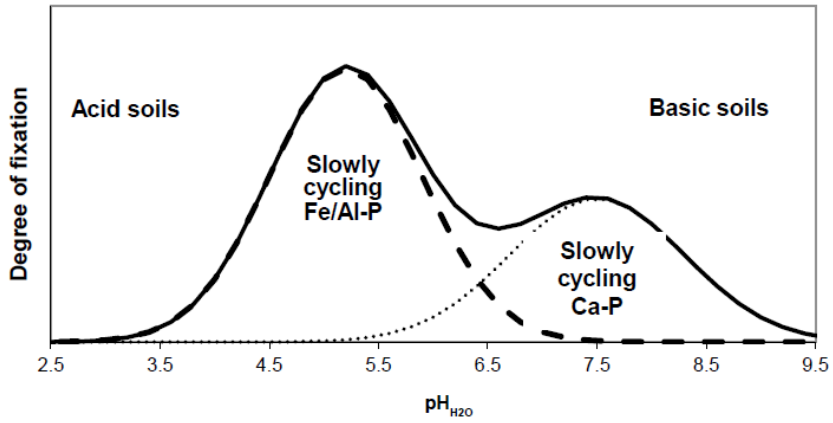

Figure 4: Degree of fixation of phosphorus in soil in relation to the soil acidity pH(H2O) (Stevenson and Cole 1999)

In the above figure Stevenson and Cole (1999) show that in acid soils with low soil pH, P is strongly absorbed to Fe and Al, while in soils with high pH value, P is absorbed to Ca. The maximum bioavailability of P lies around a pH of 6.

The principle of this analysis is to dissolve the “reactive” or “short range order” (≈ "amorphous") Al and Fe and a (variable) amount of organically complexed Fe and Al and the P in acid soils by shaking with a complexing acid ammonium oxalate solution. Subsequently the Al, Fe and P is determined in the extract by AAS or ICP-AES. The ammonium oxalate

buffer extraction is sensitive to light, especially UV light. The exclusion of light during the extraction reduces the dissolution effect of crystalline oxides.

Superfloc is added as a flocculent to the solution to remove the fine, suspended, solid particles, often made up of iron minerals (ferrihydrite). While conducting this analysis for classification purposes, no Superfloc should be added.

III Apparatus

Reciprocating shaking machine

Centrifuge

Atomic absorption spectrophotometer (with nitrous oxide/acetylene flame) or Inductive Coupled Plasma Atomic Emission Spectrofotometer (ICP-AES)

Polythene shaking bottles, wide mouth, 100 and/or 250 ml

IV Reagents

In this procedure *distilled* water is used since deionised water may contain Si.

Acid ammonium oxalate solution, 0.2 M in oxalate, pH 3:

- Dissolve 81 g $(COONH_4)_2.H_2O$ and 54 g $(COOH)_2.2H_2O$ in 4.5 l water and make to 5 l. Prepare 1 l of two separate 0.2 M solutions of NH_4-oxalate (28 g/l) and oxalic acid (25 g/l) and add some of either solution to the mixture until the pH is 3.

Potassium suppressant solution, 10,000 mg/l K:

- Dissolve 19 g KCl in 800 ml water and make up to 1 l.

"Superfloc" solution, 0.2%:

- Dissolve 0.1 g superfloc flocculent in 50 ml water. Stir overnight in the dark. (Note: store in the dark. This solution can be kept for about a week).
- Superfloc is a flocculent used in waste water treatment. E.g. Cyanamid Superfloc N-100 and Floerger Kemflock FA 20H

Diluent solution (5x):

- Make 2.38 g KCl and 25 ml conc. HCl to 1 l with water.

Diluent solution (20x):

- Make 2.01 g KCl, 158 ml acid ammonium oxalate solution and 21 ml conc. HCl to 1l with water.

Standard solutions Fe and Al, 250 mg/l:

- Dilute standard analytical concentrate ampoules (1g/l) according to instruction to make 1000 mg/l solutions. Dilute each to 250 mg/l by pipetting 50 ml into a 200 ml volumetric flask and making up to volume with water.

Mixed standard series of Fe and Al:

1 To each of five 250 ml volumetric flasks add 50 ml of the acid oxalate reagent, 25 ml of the KCl suppressant solution and 5 ml conc. HCl (or 10 ml 6 M HCl)

2 Of each 250 mg/l standard solution pipette 0-5-10-25-50 ml into the 250 ml volumetric flask (same volumes into same flasks respectively) and make to volume with water. The standard series are then: Fe, Al, 0-5-10-25-50 mg/l.

V Procedure

1 Weigh 1 g of fine earth (accuracy 0.01 g) into a 100 ml shaking bottle. Include two blanks and a control sample.

2 Add 50.0 ml oxalate reagent and close the bottle. (Note: for soils with relatively high contents of oxalate-extractable material (Al, Fe >2%) use 100.0 ml oxalate reagent and a 250 ml shaking bottle).

3 Shake for four hours **in the dark**.

4 Transfer about 35 ml to a 50 ml centrifuge tube

5 Add 3-4 drops of superfloc solution and swirl well (preferably on a Vortex mixer) and centrifuge.

6 Prepare 5x and 20x dilutions:

5x dilution

Pipette 1 ml of the clear supernatant and 4 ml of the diluent solution (5x) into a test tube and homogenise.

20x dilution

Pipette 1 ml of the clear supernatant solution and 19 ml (by varispencer or burette) of the diluent solution (20x) into a wide test tube and homogenise

7 Measure Fe by AAS at 248.3 nm using an air/acetylene flame and measure Al by AAS at 309.3 nm using a nitrous oxide/acetylene flame or measure by ICP-AES. Refer to the manufacturer's manual for operation.

Note: In case of over ranged (diluted) extracts, dilute these once more 1+1 with the zero standard solution. Therefore, of the latter an extra 250 or 500 ml should be prepared. Change the calculation accordingly.

VI Calculation

Calculate the oxalate extractable Fe, P and Al, on the basis of the air-dried soil according to the following equation:

$$Fe, Al, P\,(mg/kg) = \frac{(a-b)\times df}{s} \times mlox. \times 1000$$

where
a = mg/l Fe, Al, P in diluted sample extract
b = mg/l Fe, Al, P in diluted blank
df = dilution factor
ml ox. = ml of oxalate reagent used (50 or 100)

s = air dry sample weight in milligram
1000 = conversion factor to mg/kg basis

VII Report

Report oxalate extractable Fe, Al and P (mg/kg) with one decimal place on the basis of oven-dried soil.

VIII Reference

ISRIC, FAO. 2002. Procedures for soil analysis. Sixth ed. ISRIC Technical Paper 9. L.P. Van Reeuwijk (ed). Wageningen, The Netherlands.

USDA National Resources Conservation Service, 2004. Survey Laboratory Methods Manual. Soil Investigations report N°.42, Version 4.0, 312-317.

Stevenson, F.J. and Cole, M.A. 1999. Cycles of Soil (Carbon, Nitrogen Phosphorus Sulfur, Micronutrients). John Wiley and Sons Publishers, Hoboken, 427 p.

Soil Analysis Method 14 (SA14): Determination of the Soil Water Retention Characteristic

Soil water retention characteristic (pF analysis) (SWRC)	
Method sheet	SA14
Reference method	ISO 11274
Method suitable for	Mineral and organic soil horizons, undisturbed samples

I Relevance in ICP Forests

Priority	Level I and Level II	Level II core
Organic layer		
OL	*-*	*-*
OF-OH, H - layers	*Optional*	*Mandatory if > 5 cm*
Mineral layer		
0 – 20 cm	*Optional*	*Mandatory*
20 – 40 cm	*Optional*	*Mandatory*
40 – 80 cm	*Optional*	*Mandatory*
> 80 cm	*Optional*	*Optional*
Extra (specific) layer	*Optional*	*Optional*

The volumetric water content at matric heads 0, -1, -5, -33 and -1500 kPa plus the dry soil bulk density are mandatory to determine on Level II core plots. Extra observations of the SWRC at pressures -10, -100 and -250 kPa are optional but they greatly improve fitting the soil water retention characteristic (SWRC).

Some matric heads immediately provide information on SWRC parameters: at 0 kPa the maximum water holding capacity (WHC) of the saturated soil sample is determined; depending on definitions and soil texture field capacity (FC) may be inferred from -10 till -100 kPa; permanent wilting point (PWP) is attained at a matric pressure of –1500 kPa and dry bulk density (BD) (lowest pressure at about 10^{-6} kPa) derived in the oven at 105°C.

II Principle

This method sheet describes the determination of the soil water retention in the laboratory, extending from saturated soil (no pressure or suction; 0 kPa) to oven-dry soil (about -10^6 kPa) based on measurements of the drying or desorption curve. All methods described by ISO 11274 are allowed, except method B, using a porous plate and burette apparatus for matric pressures from 0 to -20 kPa.

In order to determine the SWRC, the volumetric water content (θ in volume fraction, $m^3\ m^{-3}$) is determined at predefined matric potentials (ψ, in kPa).

The volumetric soil water content at matric pressure 0 kPa is approximated by the total porosity of the soil.

The ISO 11274:1998 allows 4 methods to determine matric pressures within specific ranges:

- method using sand, kaolin or ceramic suction tables for determination of matric pressures from 0 kPa to - 50 kPa;
- method using a porous plate and burette apparatus for determination of matric pressures from 0 kPa to - 20 kPa; (single sample)

- method using a pressurized gas and a pressure plate extractor for determination of matric pressures from - 5 kPa to - 1500 kPa;
- method using a pressurized gas and pressure membrane cells for determination of matric pressures from - 33 kPa to - 1500 kPa.

Since method B allows only processing a single sample at the time, use of this method is not recommended. Laboratories are free to apply methods A, C and D according to the ISO 11274 standard. Guidelines for choosing the most appropriate method for specific soil types are given in ISO 11274, chapter 3.

Before applying methods A, C or D, general recommendations for sample preparation are:

- For measurements at pressures from 0 to -50 kPa, use a nylon mesh to retain the soil sample in the sleeve and secure it with an elastic band or tape;
- Ensure maximum contact between the soil core, mesh and the porous contact medium of the suction tables, plates or membranes; remove any small projecting stones if necessary;
- Avoid smearing the surface of (clayey) soils, especially when water saturated;
- Inspect the sample for bioturbation (worms, isopods) or germination of seeds during analysis; the use of a biocide is discouraged;
- Report the temperature at which the water-retention measurements are made;
- Ideally, measurements use field-moist samples [i.e. do not dry the undisturbed samples first (hysteresis effect)]. Prior to analysis, samples are saturated with water.
- Respect wetting times before starting measurements to obtain a saturated sample. General guidelines for wetting times according to ISO 11274 are:
  - sand 1 to 5 days
  - loam 5 to 10 days
  - clay 5 to 14 days or longer
  - peat 5 to 20 days.

Table SA14-1: Overview of matric heads to assess for the determination of the SWRC.

Matric potential ψ			**Recommended instrument / Method**	**Estimator**	**M/O**
cm H_2O	**pF**	**kPa**			
1	0.0	0	Pycnometer	≈θsat=WHC= Total porosity	M
10	1.0	-1	Sand suction table (method A)		M
51	1.7	-5			M
102	2.0	-10		FC sand	O
337	2.5	-33	Kaolin suction table (method A)	FC siltloam	M
1022	3.0	-100	Pressure plate extractor (method C) or Pressure membrane cells (method D)	FC clay	O
2555	3.4	-250			O
15330	4.2	-1500		PWP	M
10^7	7.0	-10^6	Oven	Dry BD	M

Where:

1) the pF is the logarithm of the absolute value of the matric potential expressed by the graduation of the water column (cm).
2) 1 kPa = 10.22 cm H_2O or 1 cm H_2O column = 0.097885 kPa
3) 100 kPa = 1 bar

III Apparatus

Method A: *Determination of the soil water characteristic using sand, kaolin and ceramic suction tables*

- Suction table (watertight, rigid container with outlet in base and close fitting cover)
- Drainage system for suction table, enabling to maintain suction at specific matric pressures
- Sand, silt or kaolin packing material, appropriate for use in suction tables (homogenous, sieved, graded and washed, free of organic material or salts). Material should achieve the required air entry values (see ISO 11274 for details)
- Drying oven capable of maintaining temperature of 105 ± 2 °C
- Balance (accuracy 0.1% of measured value)

Method C: *Determination of soil water characteristic by pressure plate extractor*

- Pressure plate extractor with porous ceramic plate
- Sample retaining rings/soil cores with discs and/or lids
- Air compressor (1700-2000 kPa), nitrogen cylinder or other pressurized gas)
- Pressure regulator and test gauge
- Drying oven capable of maintaining temperature of 105 ± 2 °C
- Balance (accuracy 0.1% of measured value)

Follow the manufacturer’s instruction to assemble and operate the apparatus.

Method D: *Determination of soil water characteristic using pressure membrane cells*

- Pressure cells with porous baseplates
- Cellulose acetate membrane
- Pressure regulator
- Air compressor (1700-2000 kPa, nitrogen cylinder or other pressurized gas)
- Drying oven capable of maintaining temperature of 105 ± 2 °C
- Balance (accuracy 0.1% of measured value)

Follow the manufacturer’s instruction to assemble and operate the apparatus.

IV Procedure

Method A: *Determination of the soil water characteristic using sand, kaolin and ceramic suction tables*

- Weigh the cores and then place them on a suction table at the desired matric pressure with table cover closed. The reference 0 cm height for setting the suction level is the middle of the core;
- Leave the cores for 7 days (minimum equilibration time). Equilibrium is reached if daily change in mass of the core is less than 0,02 %;
- If equilibrium is reached, weigh the cores, if not, replace cores firmly onto the suction table and wait until equilibrium is reached.

Method C: *Determination of soil water characteristic by pressure plate extractor*

- Take small subsamples from the undisturbed sample: soil cores of approximately 5 cm diameter and between 5 mm and 10 mm in height; smaller samples for lower pressures are used in order to avoid long equilibration times;
- It is acceptable to use disturbed samples at pressures lower than - 100 kPa, providing that the disturbance consists only in breaking off small pieces of soil and not in compressing or remoulding the soil.
- Use at least three replicate samples of each sample and place them on a presaturated plate;
- Wet the samples by immersing the plate and the samples until a thin film of water can be seen on the surface of the samples;
- Create a saturated atmosphere in the extractor;
- Apply the desired gas pressure and keep to a constant level, check for leaks;
- Record on a daily basis the evacuated water from the samples, when no change are observed (volume in a burette remains static) the samples have come to an equilibrium;
- At equilibrium status, soil samples are weighed, oven-dried and reweighed to determine the water content at the predetermined pressures

Method D: *Determination of soil water characteristic using pressure membrane cells*

- Soil subsamples are placed on a porous cellulose acetate membrane
- Equilibrium status is attained when water outflow from the pressure cell ceases and soil water content is determined by weighing, oven-drying and reweighing the sample.
- Gas pressure methods are only suited to determine matric pressures below - 33 kPa

V Calculation

V.1 Volumetric water content

ISO 11274 describes two procedures:

- Procedure for soils containing less than 20 % coarse material (diameter greater than 2 mm)
- Procedure for stony soils; conversion of results to a fine earth basis

1 For soils with less than 20% coarse material:

Calculate the water content mass ratio at matric pressure ψ_i using the formula:

$$WC\psi_i = (M\psi_i - M_{dry}) / M_{dry}$$

where
$WC\psi_i$ is the water content mass ratio at a matric pressure ψ_i, in grams;
$M\psi_i$ is the mass of the soil sample at matric pressure ψ_i, in grams;
M_{dry} is the mass of the oven-dried soil sample, in grams.

Calculate the volumetric water content at matric pressure ψ_i using the formula:

$$\theta\psi_i = [(M\psi_i - M_{dry}) / (V \times \rho_w)] \times 10^{-3}$$

alternatively

$$\theta\psi_i = WC\psi_i \times (\rho_b / \rho_w)$$

where
$\theta\psi_i$ is the water content volume fraction at matric pressure ψ_i, expressed in $m^3\ m^{-3}$ (volume of water per volume of soil);
$M\psi_i$ is the mass of the soil sample at matric pressure ψ_i, in grams;
M_{dry} is the mass of oven dried soil sample, in grams;
V is the volume of the soil sample in m^3
ρ_w is the density of water, in kg m^{-3}
ρ_b is the bulk density of oven dried soil at 105°C, in kg m^{-3}.

2 For soils with more than 20% coarse material, data needs conversion to a fine earth basis as follows:

The volumetric water content of the fine earth (θf) equals:

$$\theta f = \theta t / (1- \theta s)$$

where:
θf water content of the fine earth, expressed as a volume fraction ($m^3\ m^{-3}$);
θs volume of non-porous stones, expressed as a fraction of total core volume ($m^3\ m^{-3}$);
θt is the water content of the total earth, expressed as a fraction of total core volume ($m^3\ m^{-3}$);

For porous stones, a different correction should be applied as described in ISO 11274.

If volumetric water content is reported on fine earth basis, this should be clearly reported along with the volume of non-porous stones in the sample.

V.2 Calculation of the total porosity

A value for porosity can be calculated from the bulk density ρ_{bulk} and particle density $\rho_{particle}$:

$$\phi = 1 - \frac{\rho_{\mathrm{bulk}}}{\rho_{\mathrm{particle}}}$$

Often the particle density or true density of soil is approximated by 2650 $kg.m^{-3}$ (mineral density of quartz). But the direct measurement of the particle density is strongly recommended to be done by the means of a pycnometer.

V.3 Determination of dry bulk density

Determination of dry bulk density is done according to method SA04. The dry bulk density (BD) is recorded in kg m^{-3} with no decimal places.

In the case of stony or gravely soils the bulk density of the fine earth fraction (< 2 mm) should be reported. Furthermore, the bulk density of the coarse fragments should be known, but this may be approximated as 2650 $kg.m^{-3}$.

VI Report

Report for each undisturbed soil sample, the raw volumetric soil water content

(θ = VWC in m^3 m^{-3}) with four decimal places using the xx20xx.SWA data form. Report the dry bulk density (BD) in kg m^{-3} without decimal places using the xx20xx.SWC file.

Together with the laboratory results, following field data should be reported: plot ID, sampling data, pit ID, code depth layer, horizon number, sample ring depth (upper and lower side of the ring) in cm below the top of the mineral soil.

VII References

ISO 11274, 1998. Soil Quality – Determination of the water-retention characteristic – Laboratory methods. International Organization for Standardization. Geneva, Switzerland. 20 p. [available at www.iso.ch].

Annex II – VII

Please refer to additional document.

Annex VIII – Minor changes after 2020

Date	Minor change to latest published version in 2020	Affected sections of this document