Plausible range checks and crosschecks for forest soil analysis

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An important step in laboratory QA/QC is checking whether:

- the result of an analysis is within the "expected range" **=> plausible range checks**

- the general relationships between soil variables are valid **=> crosschecks**

plausible range checks

Definition:

For each soil variable, there is 95 % chance that the analytical result of an European forest soil sample will fall within a specific min-max interval. This interval is defined as the plausible range for that variable.

(remark: Foliar analysis uses 90 %)

Verifying if the analytical result is within the plausible range is called the plausible range check.

plausible range checks

Results outside that range may occur (1/20) and need special attention:

- checking equipment and method
- checking control samples/charts
- dilution factor applied
- reported unit
- sample characteristics
- evidence of pollution or admixtures

Re-analysis may be necessary when no obvious deviations were found in order to gain confidence on the trueness of the result.

plausible range checks

Specific plausible ranges were developed for:

- mineral soil samples
- organic material (forest floor, peat)

The number of decimals for each variable is in agreement with the reporting format described in the ICP forests manual IIIa on Sampling and Analysis of Soil.

The lower limit of the plausible range

- depends mostly on the limit of quantification (LOQ), which is determined by:
  - the method for calculating LOQ (to be discussed)
  - the applied instrument
  - the analysis method
  - the dilution factor

- instead of just mentioning 'LOQ', we listed the average LOQ reported by the soil laboratories that participated in the 4th FSCC Ringtest (Cools et al., 2006). This is more informative.

- Laboratories with lower LOQ than this average will be able to quantify lower concentrations reliably. However, each lab should always report concentrations lower than its LOQ as: "< *X.X*" with X.X the LOQ concentration using the required number of decimal places.

The upper limit of the plausible range

- The maximum of the plausible range is determined by the maxima (mostly 97.5 percentile values) found in the forest soil condition database of Europe (First ICP forest Level I Soil Survey).
- For variables not present in FSCDB, other databases were consulted (FSCC studies, ringtest data, Belgian forest soil databases)
- Information on methods and data evaluation may be found in the Forest soil condition report (EC, UN/ECE 1997).

The width of the plausible range

- By encompassing all European soil types, this range is rather broad.
- For some parameters, national plausible ranges will be more narrow due to a restricted set of soil and humus types and their local composition. It is worthwhile to develop regional plausible ranges specifically for soil samples originating from that region.
- When the analytical data of the BIOSOIL-soil programme will become available for elaboration, further fine-tuning of the plausible ranges will be possible at both a European and regional scale.

What to do when outside the plausible range ?

- **reported data should be marked with a flag for further investigation by the lab head and/or the responsible scientist**
- **the lab head should be able to make remarks in his report to explain the possible reasons for deviation**
- **if the sample is re-analysed, both the 'old' and 'new' result should be clearly reported and the reason for re-analysis and possible modifications to obtain the new result should be documented**

plausible range table (1/5)

Forest Soil samples		Organic sample Plausible range		Mineral soil sample Plausible range	
Variable	Unit	Min#	Max	Min#	Max
Moisture content (of air-dry sample)	%wt	< 0.1	10.0	< 0.1	10.0
pH(H_2O)	-	2.0	8.0	2.5	10.0
pH($CaCl_2$)	-	2.0	8.0	2.0	10.0
Organic carbon	g/kg	120.0	580.0	< 1.2	200.0
Total N	g/kg	< 0.5	25.0	< 0.1	20.0
$CaCO_3$	g/kg	< 3	850	< 3	850
Particle size: clay	%wt	--	--	< 0.6	80.0
Particle size: silt	%wt	--	--	< 0.4	100.0
Particle size: sand	%wt	--	--	< 0.6	100.0

 # Levels indicated in bold show the average limit of quantification (LOQ) reported by the laboratories (Cools et al, 2006). The syntax is 'less than' LOQ (< LOQ).

plausible range table (2/5)

Forest Soil samples		Organic sample Plausible range		Mineral soil sample Plausible range	
Parameter	**Unit**	**Min#**	**Max**	**Min#**	**Max**
Aqua regia extractable P	mg/kg	< 32.8	3000.0	< 35.2	10000.0
Aqua regia extractable K	mg/kg	< 74.2	10000.0	< 81.4	40000.0
Aqua regia extractable Ca	mg/kg	< 45.9	100000.0	< 50.0	250000.0
Aqua regia extractable Mg	mg/kg	< 33.3	80000.0	< 38.5	200000.0
Aqua regia extractable S	mg/kg	< 128.6	7500.0	< 134.6	3000.0
Aqua regia extractable Na	mg/kg	< 20.6	3000.0	< 21.1	1000.0
Aqua regia extractable Al	mg/kg	< 76.1	40000.0	< 77.1	50000.0
Aqua regia extractable Fe	mg/kg	< 75.5	50000.0	< 82.6	250000.0

plausible range table (3/5)

Forest Soil samples		Organic sample Plausible range		Mineral soil sample Plausible range	
Parameter	**Unit**	**Min#**	**Max**	**Min#**	**Max**
Aqua regia extractable Cu	mg/kg	< 1.9	300.0	< 2.0	100.0
Aqua regia extractable Pb	mg/kg	< 2.4	1000.0	< 2.4	500.0
Aqua regia extractable Ni	mg/kg	< 1.5	300.0	< 1.6	150.0
Aqua regia extractable Cr	mg/kg	< 3.3	600.0	< 3.3	150.0
Aqua regia extractable Zn	mg/kg	< 2.0	1000.0	< 2.1	500.0
Aqua regia extractable Cd	mg/kg	< 0.5	18.0	< 0.5	6.0
Aqua regia extractable Hg	mg/kg	< 0.3	4.0	< 0.3	2.0

plausible range table (4/5)

Forest Soil samples		Organic sample Plausible range		Mineral soil sample Plausible range	
Parameter	Unit	Min#	Max	Min#	Max
Exchangeable acidity	$cmol_+/kg$	< 0.23	10.00	< 0.21	8.00
Exchangeable K	$cmol_+/kg$	< 0.23	5.00	< 0.23	2.00
Exchangeable Ca	$cmol_+/kg$	< 0.25	60.00	< 0.22	40.00
Exchangeable Mg	$cmol_+/kg$	< 0.19	15.00	< 0.18	5.00
Exchangeable Na	$cmol_+/kg$	< 0.18	1.50	< 0.17	1.00
Exchangeable Al	$cmol_+/kg$	< 0.22	9.00	< 0.20	8.00
Exchangeable Fe	$cmol_+/kg$	< 0.05	0.70	< 0.04	2.00
Exchangeable Mn	$cmol_+/kg$	< 0.03	6.00	< 0.03	1.50
Free H+	$cmol_+/kg$	< 0.25	10.00	< 0.21	3.00

plausible range table (5/5)

Forest Soil samples		Organic sample Plausible range		Mineral soil sample Plausible range	
Parameter	**Unit**	**Min#**	**Max**	**Min#**	**Max**
Total K	mg/kg	< 50.0	10000.0	< 50.0	50000.0
Total Ca	mg/kg	< 20.0	100000.0	< 20.0	500000.0
Total Mg	mg/kg	< 5.0	80000.0	< 5.0	250000.0
Total Na	mg/kg	< 20.0	5000.0	< 20.0	12000.0
Total Al	mg/kg	< 40.0	50000.0	< 40.0	100000.0
Total Fe	mg/kg	< 3.5	60000.0	< 3.5	250000.0
Total Mn	mg/kg	< 0.5	35000.0	< 0.5	15000.0
Reactive Al	mg/kg	< 44.6	5000.00	< 44.6	7500.0
Reactive Fe	mg/kg	< 48.4	5000.00	< 48.4	7500.0

Crosschecks between soil variables

- Since different parameters are determined on the same soil sample and many soil variables are auto-correlated, crosschecking is a valuable tool to detect analytical aberrations.

Examples:

- soils high in organic matter => TOC ↑, N ↑
- Calcareous soils => pH↑, Ca_{exch}↑, Ca_{tot}↑, Exch Ac ↓

- Simple crosschecks were developed for easy verification and detection of erroneous results.

1. pH check

Check algorithm: $\mathbf{0 < [pH_{H2O} - pH_{CaCl2}] \leq 1.2}$

Note that for peat soils, differences between both pH measurements may be greater, up to 1.5 pH units (any studies ?).

2. Carbon check

In general, TOC is obtained by subtracting inorganic carbon (TIC) from total carbon (TC), both determined by the total analyser.
Inorganic carbon may be estimated from the carbonate measurement (ISO 10693) using the calcimeter

Check algorithm: $\mathbf{[C_{CaCO3}+TOC] \leq TC}$

with $\mathbf{C_{CaCO3} = CaCO_3 \times 0.12}$

and

Check algorithm: $\mathbf{C_{CaCO3} \approx TIC}$

The latter check cannot be performed if the carbonate content is below its limit of quantification (3 g kg-1 carbonate or 0.36 g kg-1 TIC).

3. pH-Carbonate check

Laboratories routinely analyse carbonates in soil samples with low pH levels. This is waste of resources. Based on a fast and cheap pH measurement it can be easily decided if carbonates are present and carbonate analysis is meaningful.

For an organic sample (> 200 g kg^{-1} TOC):

Check algorithm:

if pH_{CaCl2} < 6.0 then $CaCO_3$ < 3 g kg^{-1} (= below LOQ)

For a mineral sample:

Check algorithm:

if pH_{H2O} < 5 then $CaCO_3$ < 3 g kg^{-1} or

if pH_{CaCl2} < 5.5 then $CaCO_3$ < 3 g kg^{-1}

Conversely, if pHCaCl2 > 6, it is likely to detect quantifiable carbonates in the sample.

4. C/N ratio check

Most nitrogen in a solid forest soil sample is organically bound. Carbon and nitrogen are linked through the C/N ratio of organic matter which varies within a specific range.

For an organic sample (> 200 g kg-1 TOC):

Check algorithm: **5 < C/N ratio < 100**

For a mineral sample:

Check algorithm: **3 < C/N ratio < 75**

5. C/P ratio check

Similarly with C/N, a C/P ratio varies within expected ranges for organic and mineral samples.

For an organic sample (> 200 g kg-1 TOC):
Check algorithm: **100 < C/P ratio < 2500**

Note that for peat soils, C/P ratio may be greater than 2500. In the 5th FSCC soil ringtest, the C/P ratio of a peat sample amounted up to 4500.

For a mineral sample:
Check algorithm: **8 < C/P ratio < 750**

6. C/S ratio check

For organic samples only, the C/S ratio was found to vary between specific ranges.

For an organic sample (> 200 g kg-1 TOC):

Check algorithm: **20 < C/S ratio < 1000**

7. Extracted/total element check

In both organic and mineral samples the concentration of the aqua regia extractable elements K, Ca, Mg , Na, Al, Fe and Mn (pseudo-total extraction) should be less than their total concentrations after complete dissolution (total analysis).

Therefore:

Check algorithm: **Extracted element ≤ Total element**
for elements K, Ca, Mg ,Na, Al, Fe and Mn.

8. Reactive Fe and Al check

Acid oxalate extractable Fe and Al indicate the active (≈ "amorphous") compounds of Fe and Al in soils. Their concentration should be less than the total Fe and Al concentration.

Check algorithm: **Reactive Fe ≤ Total Fe**
Reactive Al ≤ Total Al

For mineral soils, reactive Fe is usually less than 25 % of the total Fe and reactive Al less than 10 % of total Al.

9. Exchangeable element/total element check

The elements bound to the CEC of the soil are easily extracted using Aqua regia. Therefore, the concentration of exchangeable cations should always be lower than their Aqua regia extractable concentration.

A conversion factor is needed to convert from cmol(+) kg-1 to mg kg-1.

Check algorithms:

$$(K_{exch} \times 391) \leq \text{Extracted K}$$
$$(Ca_{exch} \times 200) \leq \text{Extracted Ca}$$
$$(Mg_{exch} \times 122) \leq \text{Extracted Mg}$$
$$(Na_{exch} \times 230) \leq \text{Extracted Na}$$
$$(Al_{exch} \times 89) \leq \text{Extracted Al}$$
$$(Fe_{exch} \times 186) \leq \text{Extracted Fe}$$
$$(Mn_{exch} \times 274) \leq \text{Extracted Mn}$$

In general the ratio of an exchangeable element to an extracted element is higher in organic matrices than in mineral soil.

10. Free H+ and Exchangeable acidity check

Two checks may be applied to Free H+ and Exchangeable acidity (EA).

Check algorithms:

$$\textbf{Free H+} < \textbf{EA}$$

$$\textbf{EA} \approx \textbf{Al}_{\textbf{exch}} + \textbf{Fe}_{\textbf{exch}} + \textbf{Mn}_{\textbf{exch}} + \textbf{Free H+}$$

For mineral forest soils, Free H+ is usually < 60 % of the Exchangeable acidity.

11. Particle size fraction sumcheck

When correctly applying the Soil manual procedure (SA03) which is based on ISO 11277, including the correction for the dispersing agent, the sum of the three fractions should be 100 %. The mass of the three fractions should equal the mass of the fine earth (0-2 mm fraction), minus the mass of carbonate and organic matter which have been removed.

Check algorithm: **Σ [clay (%), silt (%), sand (%)] = 100 %**

Please check that the clay, silt and sand fraction are reported in the right field since mistakes occur regularly, even in ringtests.