Topic 2

1st Meeting of the Heads of the Laboratories
within ICP Forests
9.-10. June 2008 in Hamburg, Germany

Quality Assurance and Control in Laboratories

-a review of possible quality checks and other forms of assistance

ICP Forests Working Group on QA/QC in Laboratories
Authors: N. Clarke, N. Cools, J. Derome, K. Derome, B. De Vos,
A. Fuerst, N. Koenig, A. Kowalska, R. Mosello, G. A. Tartari, E. Ulrich

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

European Union/United Nations Economic Commission for Europe
International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests

Working Group on QA/QC in Laboratories

Quality Assurance and Control in Laboratories

A review of possible quality checks and other forms of assistance

ICP Forests Working Group on QA/QC in Laboratories
Authors: N. Clarke, N. Cools, J. Derome, K. Derome, B. De Vos, A. Fuerst, N. Koenig, A. Kowalska, R. Mosello, G. A. Tartari, E. Ulrich

(Version 1, May 2008)

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

5 different checks + excel worksheet for automatical quality check

12 different checks

practical solutions for contamination problems

Reference material + control charts (with excel sheet) + list of buyable certified reference materials

53 references

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

1. Use of reference material

reference material (RM):

a material or substance, one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials (ISO Guide 30, 1992).

Certified reference material (CRM):

Reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure, which establishes its traceability to an accurate realisation of the units in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence (ISO Guide 30, 1992).

Local reference material (CRM):

The Local Reference Materials are prepared by the laboratory itself for routine use and can be easily and cheaply prepared in large quantities. They can often also be prepared within the concentration ranges for the more important parameters. These LRMs are extremely important for QA/QC activities, mainly for use in control charts, if there is a need to maintain a constant (stable) quality over a longer time scale.

Topic 2	**1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany**

review of possible quality checks and other forms of assistance

CRMs are expensive and should be used only when really needed:

-**calibration**

-**method validation**

-**measurement verification**

-**evaluating measurement uncertainty** (Nordtest Report 537, 2003)

-**and for training purposes**.

LRMs are cheaper and should be used for daily routine control:

-**Contineous control of method/instrument**

-**Use for control charts**

-**To be measured with each batch of samples**

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

CRMs are buyable (list in annex 6.4 of the paper):

Reference material	Matrix	Type	Comments	Supplier
BCR-408	water	simulated rain water	low concentrations	European Commission, Directorate-General Joint Research Centre Institute for Reference Materials and Measurements Reference Materials Unit Retieseweg 111 B-2440 Geel Belgium E-Mail: jrc-irmm-rm-sales@ec.europa.eu Webpage: www.irmm.jrc.be Order by Fax: +32 (0)14 590 406
BCR-409	water	simulated rain water	high concentrations	see above
BCR-100	plant	beech leaves		see above
BCR-062	plant	Olea europea (olive leaves)		see above
BCR-129	plant	powdered hay		see above
BCR-141R	soil	calcareous loam soil		see above
BCR-142R	soil	light sandy soil		see above
BCR-143R	soil	sewage sludge	heavy metal	see above

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

LRMs can be prepared in the labs:

-**from standard solutions**

-**from soil or plant material**

-**mineral water can be used**

-**old ring test samples can be used**

Preparation of LRMs is described in the paper!

A short presentation will be given by Mireille Barbaste under topic 7!

Topic 2	**1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany**

review of possible quality checks and other forms of assistance

2. Control charts

Control charts are a useful tool for checking the quality and the variation in quality over a longer time scale.

The laboratory runs control samples (e.g. LRMs) together with the real samples in an analytical batch and, immediately after the run is completed, the control values are plotted on a control chart.

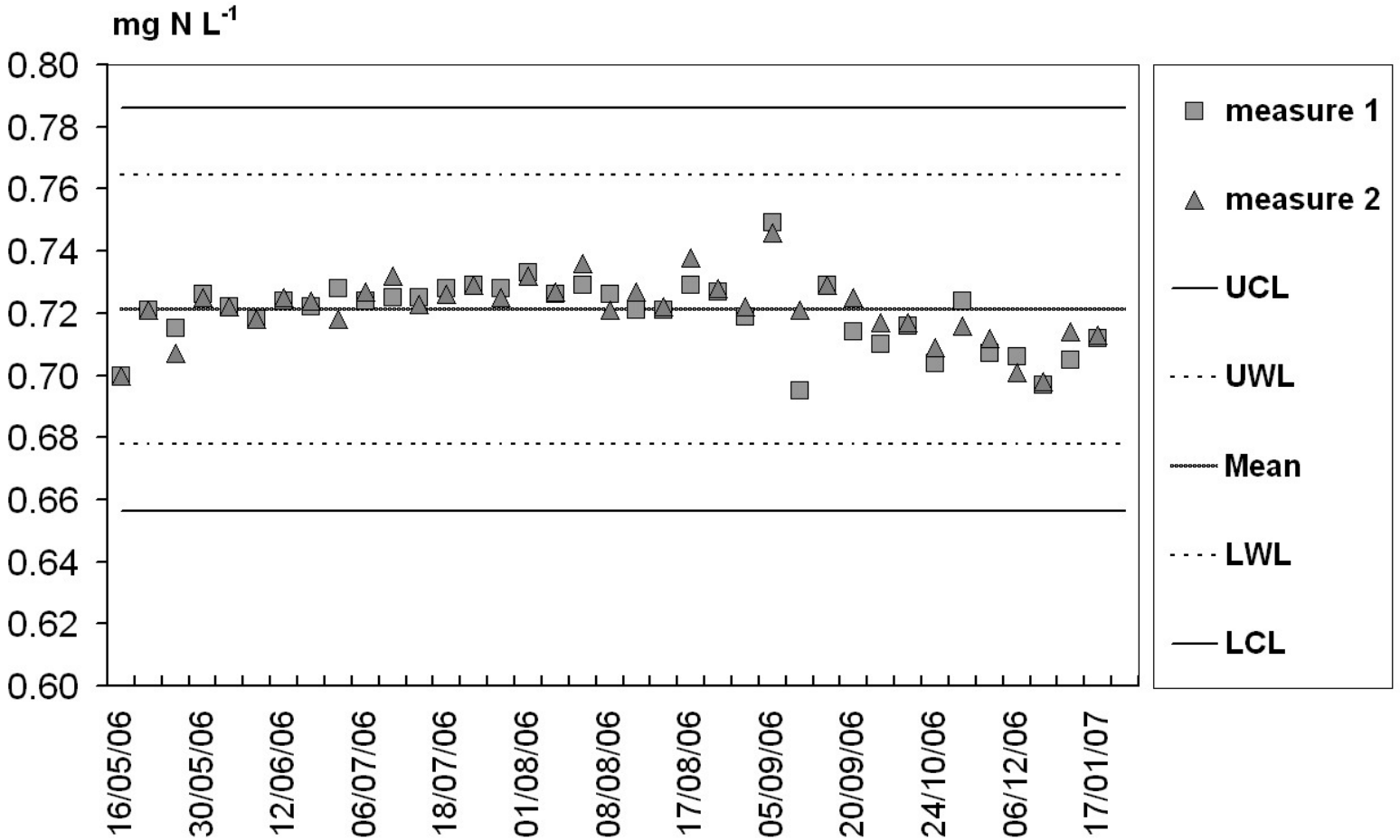
An excel file for control charts can be downloaded from the website!

A short introduction will be given by Kirsti Derome under topic 3!

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

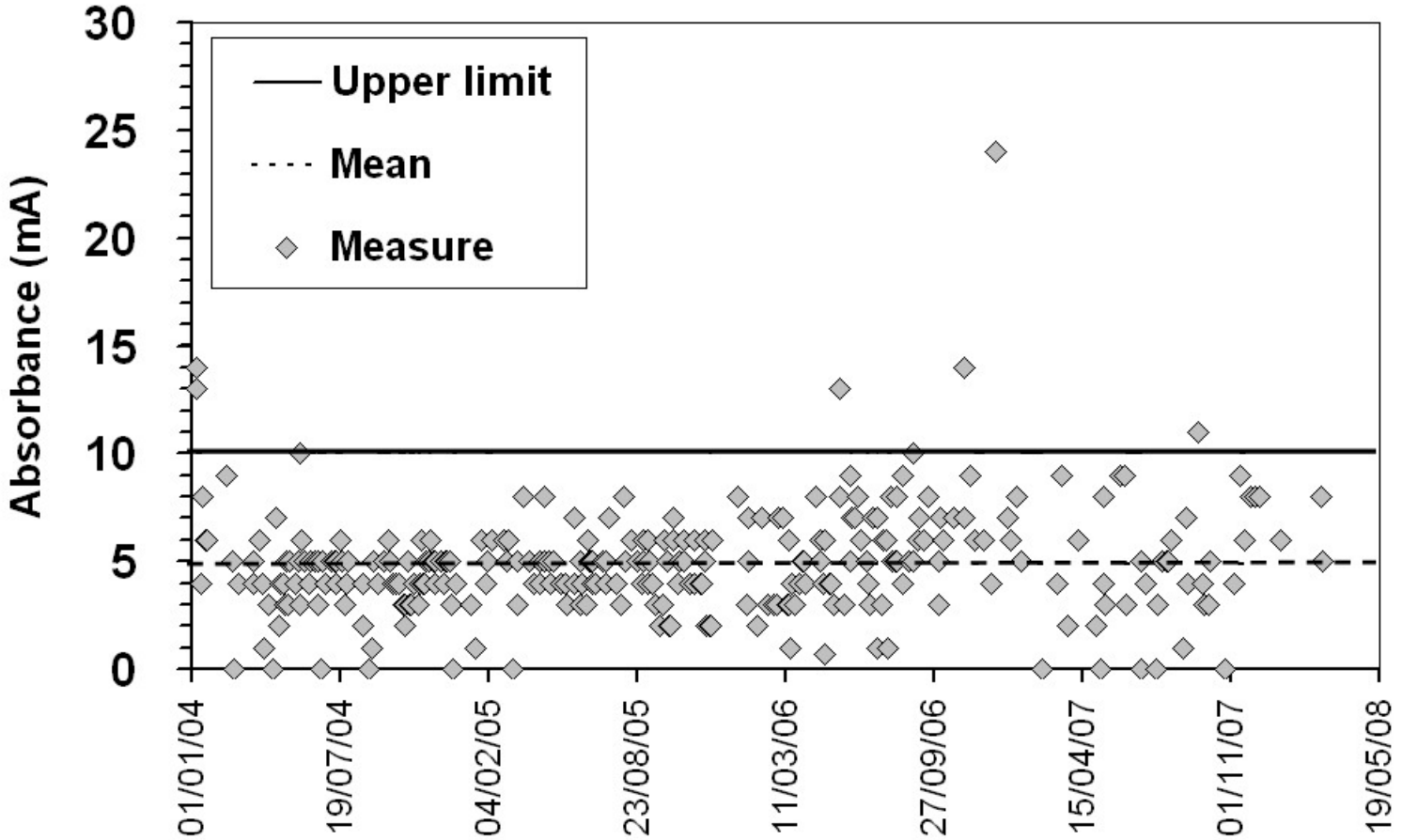
2. Control charts: a. mean chart



Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

2. Control charts: a. blank chart



3. Limit of Detection (LOD) and Limit of Quantification (LOQ)

The **limit of detection (LOD)** is the smallest measure, xL, that can be detected with reasonable certainty for a given analytical procedure.

The value of xL is given by the equation:
xL = xbi + Ksbi
where xbi is the mean of *n* blank measurements, sbi is the standard deviation of *n* blank measurements, and *K* is a numerical factor chosen according to the confidence level desired (IUPAC, 1997)

It is recommended that the number of blank measurements (*n*) is higher than 30, preferably determined under within-lab reproducibility conditions (e.g. different operators, different runs on different days).

The **limit of quantification (LOQ)** is generally agreed to begin at a concentration equal to 10 standard deviations of the blank (Kq = 10). Therefore, **LOQ is 3.3 times LOD**.

Topic 2	**1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany**

review of possible quality checks and other forms of assistance

3. Limit of Detection (LOD) and Limit of Quantification (LOQ)

The LOD is the concentration at which we can decide whether an element is present or not. It is the point where we can just distinguish a signal from the background.

The LOQ is the lowest concentration of an element which can be analysed with a given precision. Only above the LOQ quantitative analytical results can be indicated.

A distinction should be made between **instrument detection/quantification limits** and **method (or matrix) detection limits**. Generally, instrument detection limits (IDLs) are based on a clean matrix. Method/matrix detection limits (MDL) consider real-life matrices such as soil, organic matter and rainwater. Spectroscopists commonly accept that the MDL can be anywhere from about two to five times worse than the IDL.

Therefore, labs should clearly mention whether the reported limits are instrument or matrix detection limits. In the case of environmental research, MDLs provide more relevant information than IDLs.

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

3. Limit of Detection (LOD) and Limit of Quantification (LOQ)

Each laboratory has to determine the LOD/LOQ for each parameter and method!

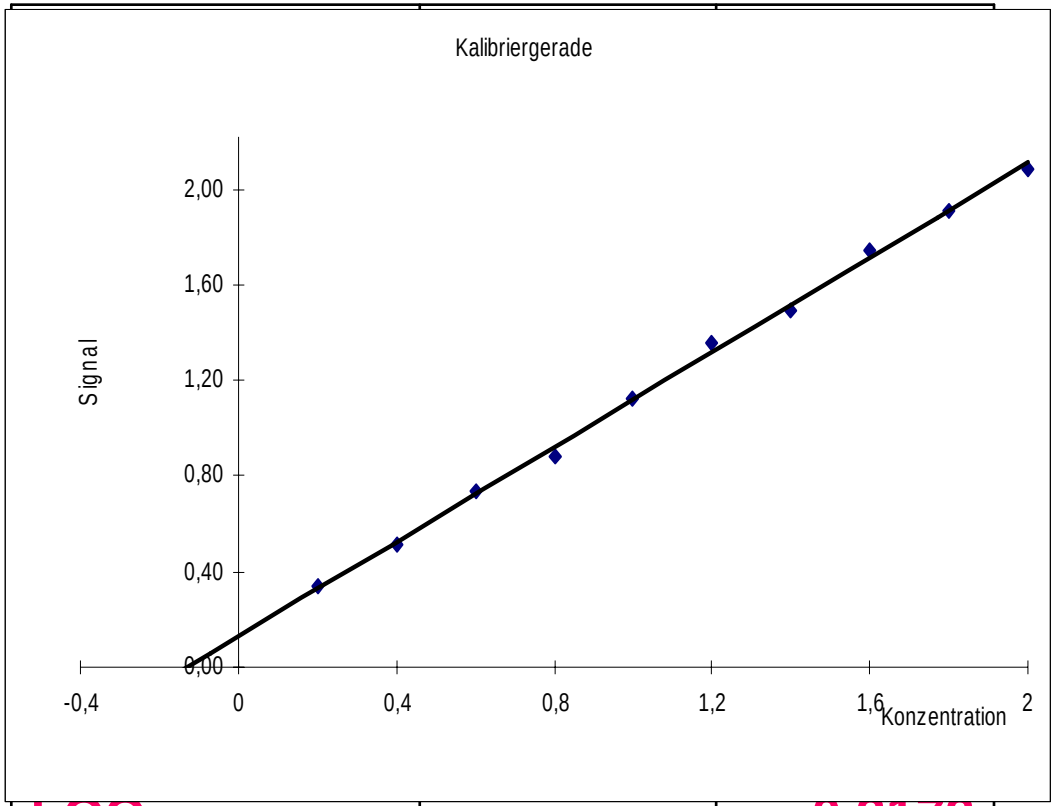
Results under the LOQ should not be reported!

review of possible quality checks and other forms of assistance

3. Limit of Detection (LOD) and Limit of Quantification (LOQ)

Element	Cd 2265	Aqua regia	1.1	iCAP6500i method ICP16.1	ICP-OES	21.02.2007

Eingabebereich:			
Nr.	Blindwerte	Kalibrierung	
		Signal	Konz. µg/l
1	0	0,3361	0,2
2	0	0,5149	0,4
3	0	0,7325	0,6
4	0	0,8793	0,8
5	0	1,126	1
6	0	1,362	1,2
7	0	1,497	1,4
8	0	1,748	1,6
9	0	1,91	1,8
10	0	2,089	2



LOQ 0,000 0,3172

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany
review of possible quality checks and other forms of assistance	

4. Check of analytical results

It is very important to check the analytical results directly after the analyses!

Only than you have the possibility to reanalyse the samples if the results of the first measurement are uncertain, wrong or inconsistent.

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

4a. Check of analytical results for water samples

4 different checks for water samples:

- **Ionic balance**
- **Comparison between measured and calculated conductivity**
- **Na/Cl ratio validation test**
- **Organic nitrogen validation test**

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

1. Ionic balance check

$$\Sigma_{anions} = [HCO_3^-] + [SO_4^{=}] + [NO_3^-] + [Cl^-] + [Org^-]$$

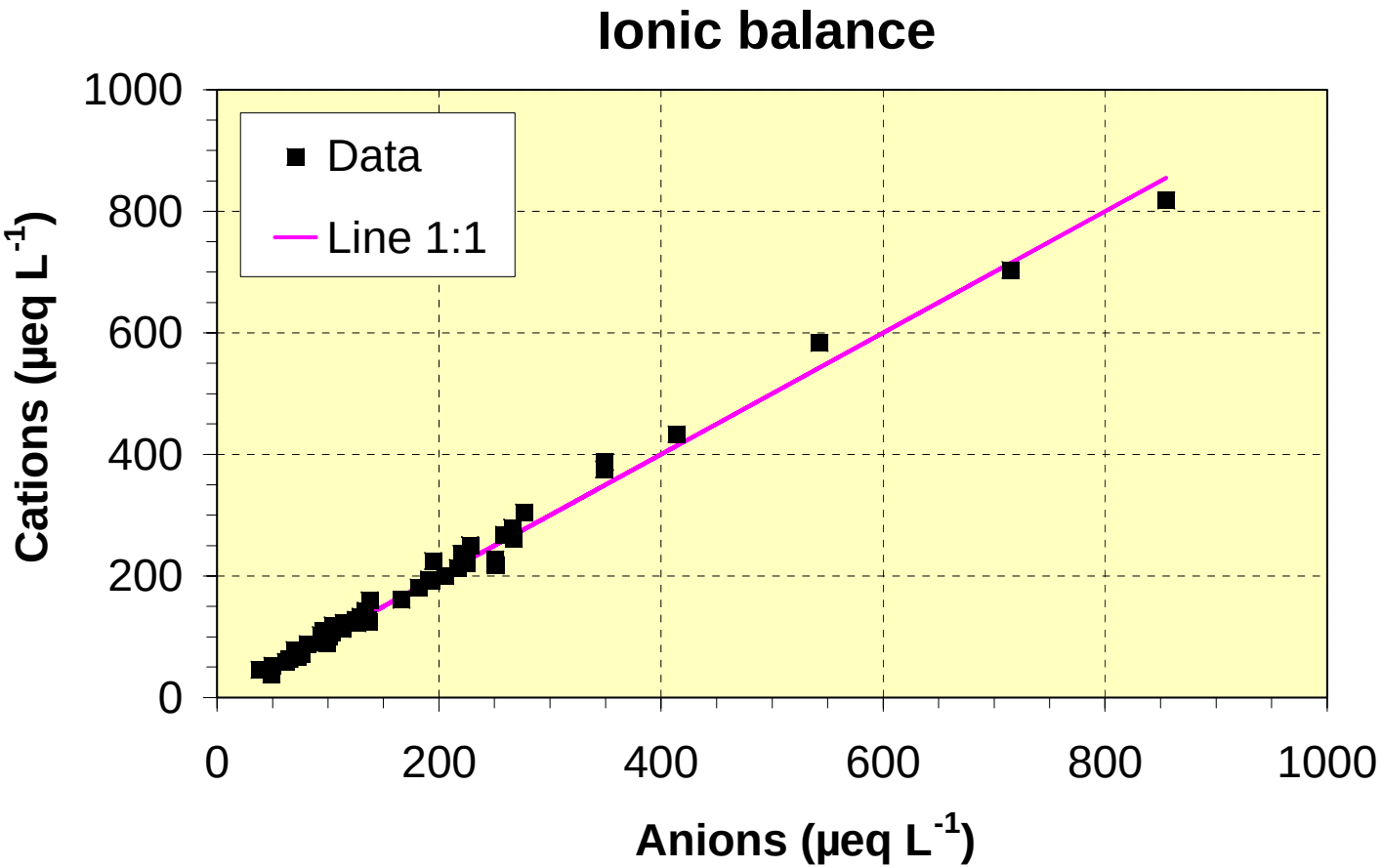
$$\Sigma_{cations} = [Ca^{++}] + [Mg^{++}] + [Na^+] + [K^+] + [H^+] + [NH_4^+] + [Met^{n+}]$$

$$PD = 100 * \frac{(\Sigma cat - \Sigma an)}{0.5 (\Sigma cat + \Sigma an)}$$

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

1. Ionic balance check



Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

2. Conductivity Check

Comparison between measured (CM) and calculated conductivity (CE)

for conductivity ≤ 100 µS cm^{-1} $CE_{\infty} = \sum \lambda_i C_i$

for conductivity > 100 µS cm^{-1} $CE = \sum \lambda_i f_i C_i$

λ_i *equivalent ionic conductance*

C_i *Concentration of the ion i*

f_i *activity coefficient*

$$CD = 100 * \frac{(CM-CE)}{CM}$$

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests
9.-10. June 2008 in Hamburg, Germany

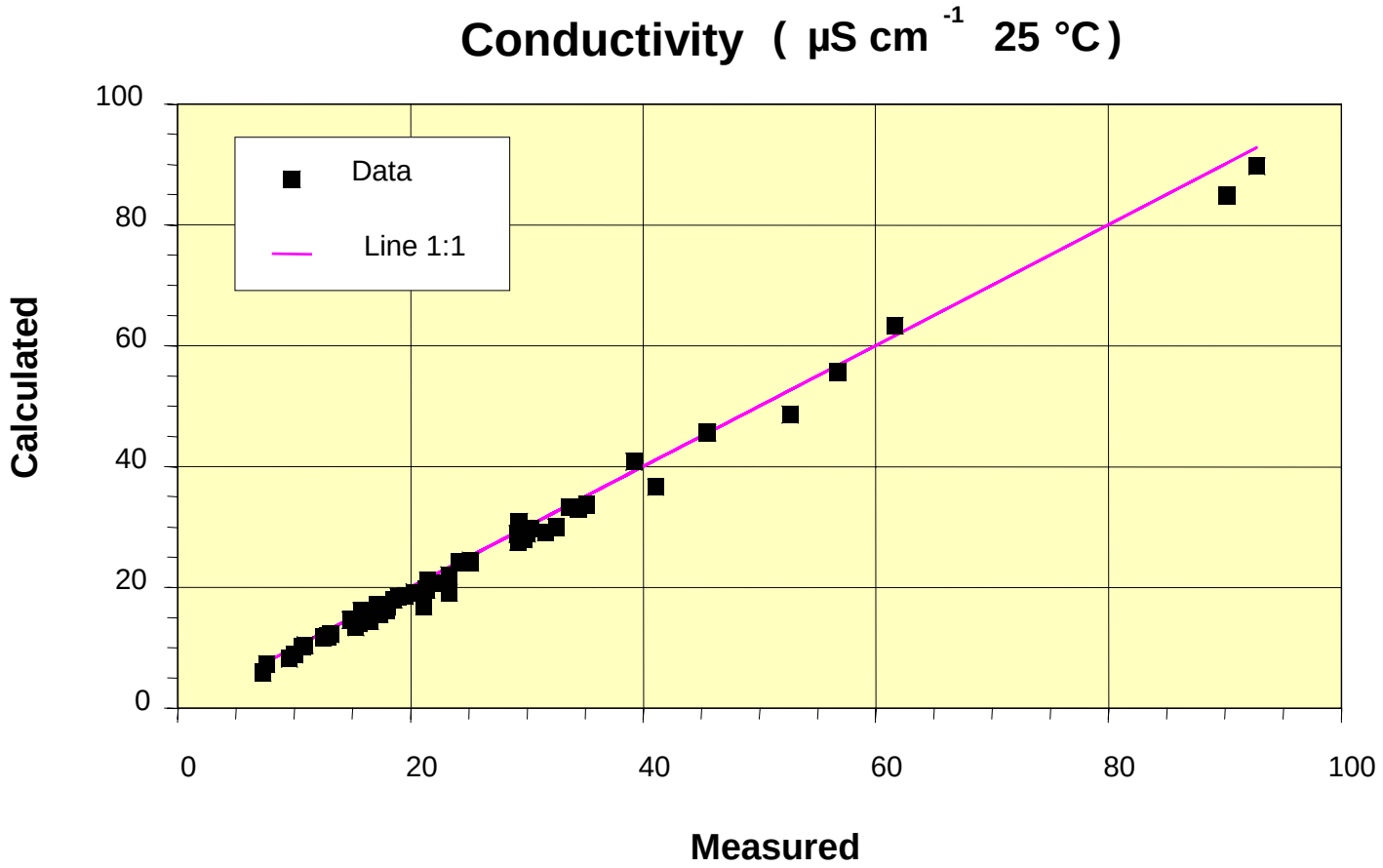
review of possible quality checks and other forms of assistance

	Units	Factors to µeq L^{-1}	Equivalent conductance at 25°C kS cm^2 eq^{-1}
pH		$10^6 * 10^{-pH}$	0.3500
Ammonium	mg N-NH_4 L^{-1}	71.39	0.0735
Calcium	mg L^{-1}	49.90	0.0595
Magnesium	mg L^{-1}	82.29	0.0531
Sodium	mg L^{-1}	43.50	0.0501
Potassium	mg L^{-1}	25.58	0.0735
Alkalinity	meq L^{-1}	1000	0.0445
Sulphate	mg S L^{-1}	62.37	0.0800
Nitrate	mg N- NO_3 L^{-1}	71.39	0.0714
Chloride	mg L^{-1}	28.21	0.0764

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

2. Conductivity Check



Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Acceptance threshold values in data validation based on the ionic balance and conductivity

Conductivity of the sample 25 °C	Ionic balance	Conductivity
≤ 10 µS cm^{-1}	± 20%	±30%
< 20 µS cm^{-1}	± 20%	±20%
> 20 µS cm^{-1}	± 10%	±10%

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Applicability of ion balance and conductivity tests to different type of solutions

	ion balance	conductivity	Na/Cl	nitrogen
wet-only	yes	yes	yes	yes
bulk open field	yes	yes	yes	yes
throughfall	no	yes	yes	yes
stemflow	no	yes	yes	yes
soil water	no	yes	no	yes
runoff	?	yes	no	yes

? = applicable if TOC is lower than 5 mg C L^{-1}

A presentation about DOC in ion balances will be given by Rosario Mosello under topic 4!

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

3. Na/Cl ratio check

In many parts of Europe sea salt is a major contributor of sodium and chloride ions in deposition and, as a result, the ratio between the two ions is similar to that of sea salt.

This is true even in parts of Europe situated far from the sea, as has been shown from a statistical study conducted on more than 6000 samples covering the area from Scandinavia to South Europe (Mosello et al., 2005).

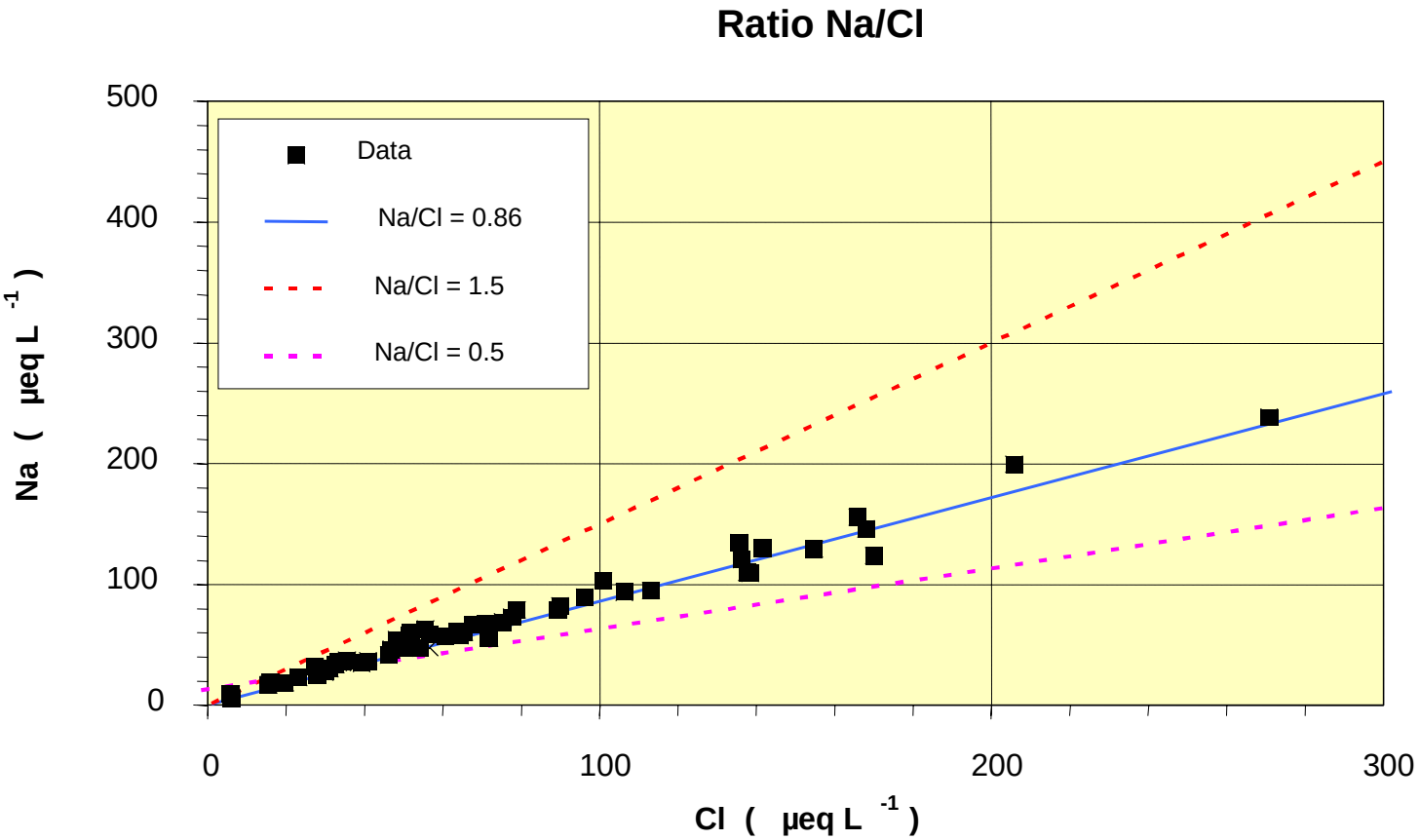
The ratio is calculated by expressing the concentrations on a molar (or equivalent) basis.

$$0.5 < (Na/Cl) < 1.5$$

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

3. Na/Cl ratio check

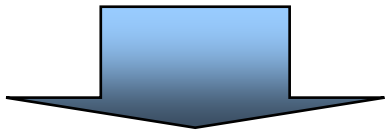


4. N Balance check

$$TN = N\text{-}NO_3^- + N\text{-}NH_4^+ + (N\text{-}NO_2^-) + Norg$$

$$Norg = TN - N\text{-}NO_3^- - N\text{-}NH_4^+$$

The concentration of organic nitrogen can not be negative!



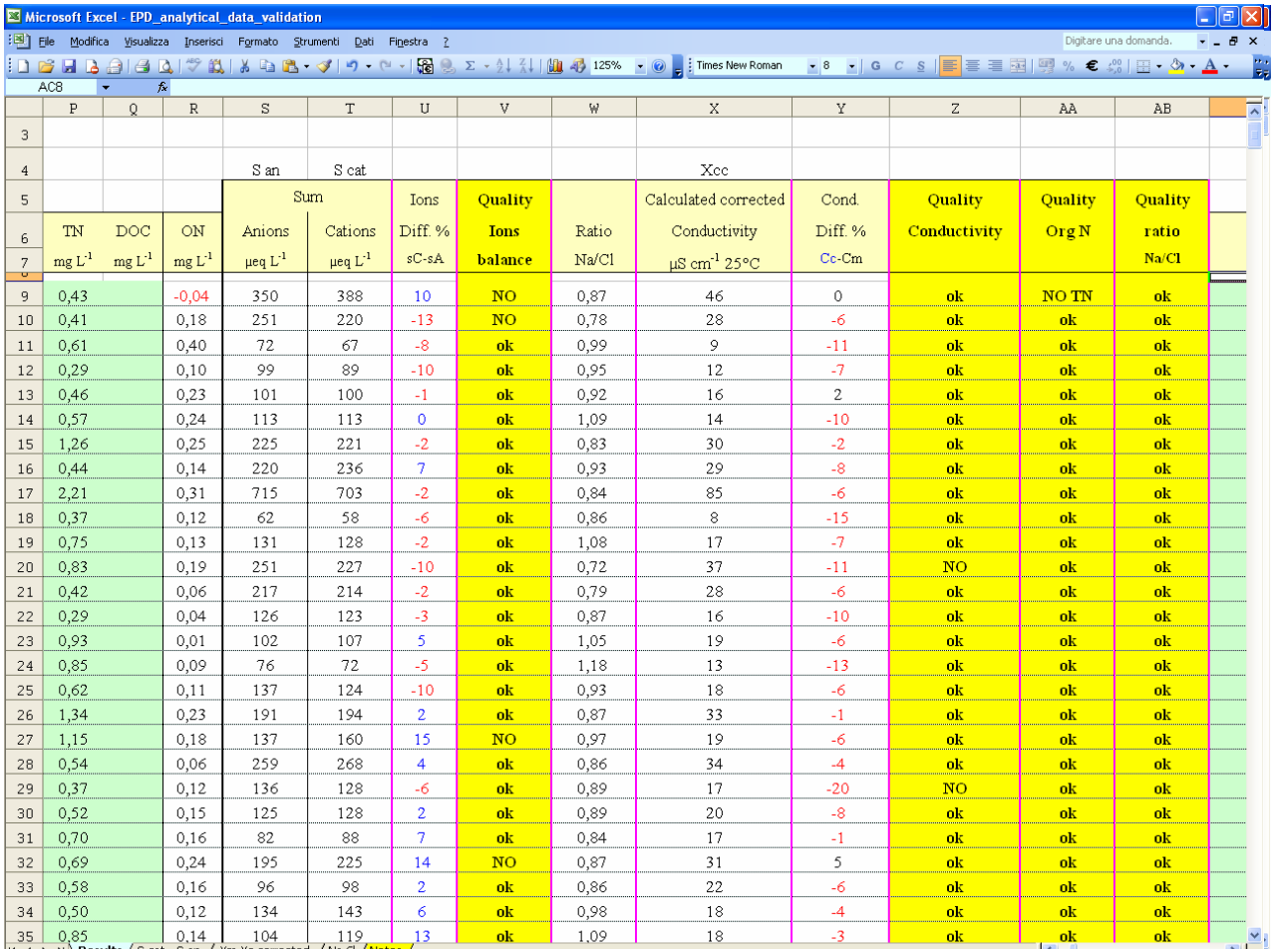
$$TN - N\text{-}NO_3^- - N\text{-}NH_4^+ >= 0$$

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Excel file for the automatic evaluation of the 4 presented quality checks:



	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB
3													
4				S an	S cat				Xcc				
5				Sum		Ions	Quality		Calculated corrected	Cond.	Quality	Quality	Quality
6	TN	DOC	ON	Anions	Cations	Diff. %	Ions	Ratio	Conductivity	Diff. %	Conductivity	Org N	ratio
7	mg L^{-1}	mg L^{-1}	mg L^{-1}	µeq L^{-1}	µeq L^{-1}	sC-sA	balance	Na/Cl	µS cm^{-1} 25°C	Cc-Cm			Na/Cl
9	0,43		-0,04	350	388	10	NO	0,87	46	0	ok	NO TN	ok
10	0,41		0,18	251	220	-13	NO	0,78	28	-6	ok	ok	ok
11	0,61		0,40	72	67	-8	ok	0,99	9	-11	ok	ok	ok
12	0,29		0,10	99	89	-10	ok	0,95	12	-7	ok	ok	ok
13	0,46		0,23	101	100	-1	ok	0,92	16	2	ok	ok	ok
14	0,57		0,24	113	113	0	ok	1,09	14	-10	ok	ok	ok
15	1,26		0,25	225	221	-2	ok	0,83	30	-2	ok	ok	ok
16	0,44		0,14	220	236	7	ok	0,93	29	-8	ok	ok	ok
17	2,21		0,31	715	703	-2	ok	0,84	85	-6	ok	ok	ok
18	0,37		0,12	62	58	-6	ok	0,86	8	-15	ok	ok	ok
19	0,75		0,13	131	128	-2	ok	1,08	17	-7	ok	ok	ok
20	0,83		0,19	251	227	-10	ok	0,72	37	-11	NO	ok	ok
21	0,42		0,06	217	214	-2	ok	0,79	28	-6	ok	ok	ok
22	0,29		0,04	126	123	-3	ok	0,87	16	-10	ok	ok	ok
23	0,93		0,01	102	107	5	ok	1,05	19	-6	ok	ok	ok
24	0,85		0,09	76	72	-5	ok	1,18	13	-13	ok	ok	ok
25	0,62		0,11	137	124	-10	ok	0,93	18	-6	ok	ok	ok
26	1,34		0,23	191	194	2	ok	0,87	33	-1	ok	ok	ok
27	1,15		0,18	137	160	15	NO	0,97	19	-6	ok	ok	ok
28	0,54		0,06	259	268	4	ok	0,86	34	-4	ok	ok	ok
29	0,37		0,12	136	128	-6	ok	0,89	17	-20	NO	ok	ok
30	0,52		0,15	125	128	2	ok	0,89	20	-8	ok	ok	ok
31	0,70		0,16	82	88	7	ok	0,84	17	-1	ok	ok	ok
32	0,69		0,24	195	225	14	NO	0,87	31	5	ok	ok	ok
33	0,58		0,16	96	98	2	ok	0,86	22	-6	ok	ok	ok
34	0,50		0,12	134	143	6	ok	0,98	18	-4	ok	ok	ok
35	0,85		0,14	104	119	13	ok	1,09	18	-3	ok	ok	ok

A presentation about the use of this ecxel file will be given by Rosario Mosello under topic 5!

5. Phosphorus concentration as a contamination check

If bird droppings pass into the precipitation/throughfall/stemflow sample, this will considerably alter the chemical composition of the sample. The concentrations of PO43-, K+, NH4+ and H+, for instance, will be affected.

A phosphate concentration of 0.25 mg l-1 has been suggested as the threshold value for sample contamination by bird droppings (Erisman et al., 2003).

Contamination by bird droppings is not always easily visible, so it may sometimes be detected only after the chemical analyses have been performed.

4b. Check of analytical results for organic and mineral soil samples

- **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**

4b-1. 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.

review of possible quality checks and other forms of assistance

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.

Topic 2	**1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany**

review of possible quality checks and other forms of assistance

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.

inbo

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

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.

inbo

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

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).**

inbo

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

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.

inbo

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

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**

inbo

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

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).

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests
9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

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

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests
9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

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

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests
9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

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

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests
9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

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

4b-2. 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.

Topic 2	**1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany**

review of possible quality checks and other forms of assistance

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 ?).

inbo

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**

inbo

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.

Topic 2	**1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany**

review of possible quality checks and other forms of assistance

9. Exchangeable element / aqua regia extractable 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:

$(K_{exch}$ x 391) ≤ Extracted K
$(Ca_{exch}$ x 200) ≤ Extracted Ca
$(Mg_{exch}$ x 122) ≤ Extracted Mg
$(Na_{exch}$ x 230) ≤ Extracted Na
$(Al_{exch}$ x 89) ≤ Extracted Al
$(Fe_{exch}$ x 186) ≤ Extracted Fe
$(Mn_{exch}$ x 274) ≤ 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:

Free H+ < EA

$EA \approx Al_{exch} + Fe_{exch} + Mn_{exch} + Free\ H+$

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.

Topic 2	**1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany**
review of possible quality checks and other forms of assistance	

4c. Check of analytical results for foliage and litterfall samples

4c-1. plausible range checks for foliage samples

For the plausible range check list the **Forest Foliar Coordinating Centre** removed 5% of the lowest and 5% of the highest results from the European Level I database. 90% of all the submitted Level I results fell within these limits. As the manual covers a large number of different tree species it was necessary, in order to obtain sufficient data for meaningful statistical analysis, to group them into the main tree genera.

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Code	Tree species	Count	Leaf type	Limit	N g/kg	S g/kg	P g/kg	Ca g/kg	Mg g/kg	K g/kg	C g/100g
20	Fagus sylvatica	611	0	low	20,41	1,26	0,89	3,44	0,65	4,81	*45*
			0	high	29,22	2,12	1,86	14,77	2,50	11,14	*55*
41	Quercus cerris	37	0	low	12,86	0,91	0,63	4,81	0,98	1,19	*45*
			0	high	30,79	3,24	2,29	16,49	3,24	15,64	*55*
46	Quercus ilex	141	0	low	11,95	0,81	0,69	4,00	0,76	3,42	*45*
			0	high	17,24	1,41	1,22	10,32	2,62	8,46	*55*
48	Quercus petraea	268	0	low	19,75	1,24	0,90	4,12	1,06	5,86	*45*
			0	high	29,84	2,01	1,85	10,46	2,26	11,16	*55*
50	Quercus pyrenaica (Q. toza)	27	0	low	17,85	1,18	1,48	4,60	1,40	3,52	*45*
			0	high	25,50	2,33	3,12	12,03	3,00	11,81	*55*

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Code	Tree species	Count	Leaf type	Zn µg/g	Mn µg/g	Fe µg/g	Cu µg/g	Pb µg/g	Cd ng/g	B µg/g
20	Fagus sylvatica	611	0	17,0	127	62	5,67	-	50	9,1
			0	54,2	2902	178	12,18	6,8	462	40,0
41	Quercus cerris	37	0	13,0	509	83	6,89	-	63	15,9
			0	-	-	-	-	-	-	-
46	Quercus ilex	141	0	12,7	278	73	4,00	-	-	21,7
			0	41,0	5385	717	*7,00*	-	-	-
48	Quercus petraea	268	0	11,0	905	60	5,39	-	24	5,5
			0	25,0	4209	149	11,64	-	-	-
50	Quercus pyrenaica (Q. toza)	27	0	18,0	434	81	8,07	-	-	-
			0	-	-	-	-	-	-	-

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Code	Tree species	Count	Leaf type	Limit	N g/kg	S g/kg	P g/kg	Ca g/kg	Mg g/kg	K g/kg	C g/100g
51	Quercus robur (Q. pedunculata)	313	0	low	20,31	1,36	0,97	3,33	1,09	5,80	*45*
			0	high	30,69	2,21	2,55	12,26	2,85	12,64	*55*
54	Quercus suber	39	0	low	11,39	0,85	0,47	4,29	1,22	4,37	*45*
			0	high	23,09	1,61	1,53	11,02	2,55	9,85	*55*
100	Abies alba	230	0	low	11,55	0,79	0,95	3,50	0,68	4,29	*47*
			0	high	16,16	1,69	2,23	11,71	1,90	8,48	*57*
			1	low	11,67	0,95	0,86	4,19	0,37	3,97	*47*
			1	high	16,46	1,79	2,21	16,39	1,70	7,57	*57*
118	Picea abies (P. excelsa)	1763	0	low	10,39	0,70	1,01	1,83	0,66	3,65	*47*
			0	high	16,68	1,31	2,10	7,01	1,56	8,36	*57*
			1	low	9,47	0,69	0,81	2,26	0,44	3,41	*47*
			1	high	15,97	1,34	1,82	9,77	1,51	7,05	*57*

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Code	Tree species	Count	Leaf type	Zn µg/g	Mn µg/g	Fe µg/g	Cu µg/g	Pb µg/g	Cd ng/g	B µg/g
51	Quercus robur (Q. pedunculata)	313	0	14,0	219	64	5,50	0,1	40	23,4
			0	50,0	2820	233	14,10	18,0	183	54,8
54	Quercus suber	39	0	17,0	291	62	6,11	-	-	17,5
			0	47,0	2887	621	*20,00*	-	-	-
100	Abies alba	230	0	22,0	185	21	2,31	-	48	15,5
			0	45,0	2510	85	5,89	-	-	-
			1	20,0	250	32	2,00	-	56	14,4
			1	47,5	5241	121	6,45	-	-	-
118	Picea abies (P. excelsa)	1763	0	16,0	165	22	1,41	-	-	7,2
			0	47,0	1739	91	5,94	2,9	226	29,4
			1	12,0	198	27	0,94	-	-	6,2
			1	51,8	2376	118	7,07	5,2	169	32,9

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Code	Tree species	Count	Leaf type	Limit	N g/kg	S g/kg	P g/kg	Ca g/kg	Mg g/kg	K g/kg	C g/100g
120	Picea sitchensis	108	0	low	12,67	0,98	1,04	1,21	0,78	5,56	*47*
			0	high	17,61	1,75	2,56	8,02	1,41	10,89	*57*
			1	low	11,87	0,92	0,84	1,41	0,50	4,62	*47*
			1	high	18,19	1,94	2,43	8,23	1,18	10,05	*57*
124	Pinus contorta	40	0	low	11,31	0,75	0,98	1,02	0,79	3,56	*47*
			0	high	21,51	1,66	1,73	2,70	1,31	6,06	*57*
			1	low	13,12	0,87	0,88	1,96	0,75	1,21	*47*
			1	high	20,22	*1,70*	1,55	4,41	1,50	6,02	*57*
125	Pinus halepensis	30	0	low	9,22	0,92	0,80	2,12	1,84	3,20	*47*
			0	high	14,28	1,68	1,79	8,04	2,89	8,67	*57*

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Code	Tree species	Count	Leaf type	Zn µg/g	Mn µg/g	Fe µg/g	Cu µg/g	Pb µg/g	Cd ng/g	B µg/g
120	Picea sitchensis	108	0	8,4	147	31	*0,70*	-	-	6,0
			0	33,8	1489	232	5,91	-	-	*42,0*
			1	9,5	160	33	*0,70*	-	-	5,0
			1	29,3	1734	133	4,67	-	-	*52,0*
124	Pinus contorta	40	0	-	-	-	-	-	-	-
			0	-	-	-	-	-	-	-
			1	-	-	-	-	-	-	-
			1	-	-	-	-	-	-	-
125	Pinus halepensis	30	0	23,0	32	230	-	-	-	-
			0	-	-	-	-	-	-	-

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Code	Tree species	Count	Leaf type	Limit	N g/kg	S g/kg	P g/kg	Ca g/kg	Mg g/kg	K g/kg	C g/100g
129	Pinus nigra	81	0	low	8,42	0,51	0,81	0,97	0,56	3,88	*47*
			0	high	21,18	1,44	1,57	4,42	2,08	8,30	*57*
			1	low	7,97	0,44	0,75	1,17	0,35	3,89	*47*
			1	high	23,49	1,93	1,71	6,90	2,06	7,34	*57*
130	Pinus pinaster	116	0	low	6,85	0,61	0,55	0,80	1,01	3,26	*47*
			0	high	13,71	1,29	1,24	3,80	2,47	7,14	*57*
			1	low	6,25	0,55	0,40	1,09	0,94	2,40	*47*
			1	high	13,27	1,44	1,38	6,02	2,88	6,86	*57*
131	Pinus pinea	24	0	low	7,51	0,65	0,58	1,53	1,80	3,25	*47*
			0	high	*11,30*	*1,65*	*1,20*	*4,40*	*3,00*	*6,70*	*57*

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Code	Tree species	Count	Leaf type	Zn µg/g	Mn µg/g	Fe µg/g	Cu µg/g	Pb µg/g	Cd ng/g	B µg/g
129	Pinus nigra	81	0	18,8	60	29	1,81	0,6	399	8,9
			0	67,7	1072	131	18,08	-	-	-
			1	19,0	109	69	1,80	0,9	380	8,7
			1	*70,0*	*1000*	-	-	-	-	-
130	Pinus pinaster	116	0	15,6	41	23	1,70	-	-	15,0
			0	39,0	825	579	5,03	-	-	-
			1	12,3	35	23	1,13	-	-	20,0
			1	36,8	794	111	4,68	-	-	-
131	Pinus pinea	24	0	6,0	89	44	4,30	-	-	28,5
			0	-	-	-	-	-	-	-

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Code	Tree species	Count	Leaf type	Limit	N g/kg	S g/kg	P g/kg	Ca g/kg	Mg g/kg	K g/kg	C g/100g
134	Pinus sylvestris	1859	0	low	11,40	0,75	1,11	1,61	0,64	3,77	*47*
			0	high	20,41	1,56	2,06	4,61	1,31	7,27	*57*
			1	low	10,94	0,77	1,00	2,57	0,50	3,51	*47*
			1	high	19,38	1,61	1,88	6,71	1,18	6,52	*57*
136	Pseudotsuga menziesii	137	0	low	13,54	1,00	1,00	1,98	1,02	5,17	*47*
			0	high	22,71	1,80	1,70	5,91	2,10	8,96	*57*
			1	low	13,55	0,99	0,71	3,09	1,14	2,97	*47*
			1	high	29,23	2,18	1,45	9,64	2,73	7,30	*57*

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Code	Tree species	Count	Leaf type	Zn µg/g	Mn µg/g	Fe µg/g	Cu µg/g	Pb µg/g	Cd ng/g	B µg/g
134	Pinus sylvestris	1859	0	32,0	172	18	2,28	-	50	9,2
			0	77,6	912	139	7,70	3,9	447	30,5
			1	31,5	222	28	1,96	0,1	60	7,4
			1	96,0	1332	171	6,88	5,6	507	33,9
136	Pseudotsuga menziesii	137	0	15,0	159	43	2,72	-	141	30,9
			0	45,3	1661	129	5,95	-	-	-
			1	14,0	444	58	2,91	-	-	-
			1	-	155	279	-	-	-	-

Topic 2	**1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany**
review of possible quality checks and other forms of assistance	

4c-2. plausible range checks for litterfall samples

To develop tolerable limits for litterfall is much more difficult than for foliage. Litterfall is sorted in different fractions – in minimum in two, foliar and non-foliar litter. Many countries sort it in three fractions – foliage, wood and fruit coins & seeds. Litterfall is analyzed then as a pooled sample or each fraction is analysed separately.

The plausible range of the results of the chemical analysis of litter must be much bigger than for foliage. An important fraction in the litter is the foliar fraction, and for this fraction plausible ranges for selected tree species, based on the expert experience, are given in the following tables. Plausible ranges for the non-foliar fraction in litterfall is a project for the future.

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Tree Species (Foliar litter)	Limit	C	S	N	P	K	Ca	Mg	Zn	Mn	Fe	Cu	B
		mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Betula pendula	low	*290*		*7.30*	*0.20*	*0.30*	*5.,00*	*1.00*	*105.00*	*600*	*45.0*	*6*	
	high	*330*		*21.00*	*1.20*	*1.40*	*12.50*	*2.00*	*170.00*	*3000*	*300.0*	*19*	*38*
Castanea sativa	low	*390*		*9.00*	*0.20*	*0.20*	*4.50*	*1.40*	*35.00*	*700*		*5*	
	high	*420*		*13.00*	*0.70*	*0.55*	*10.50*	*2.00*	*45.00*	*2500*	*90.0*	*13*	*100*
Fagus sylvatica	low	**460**	**1**	**9.00**	**0.50**	**2.00**	**4.00**	**0.80**	**25.00**	**650**	**70.0**	**4**	**2**
	high	**510**	**2.2**	**19.00**	**1.90**	**8.00**	**17.00**	**2.00**	**35.00**	**1600**	**140.0**	**7**	**40**
Fraxinus excelsior	low	*470*		*12.00*	*0.75*	*0.40*	*20.00*	*2.00*	*15.00*	*110*	*120.0*	*7*	
	high	*470*		*18.00*	*1.50*	*1.40*	*25.00*	*3.50*	*20.00*	*200*	*200.0*	*9*	*50*
Quercus frainetto	low		**1.1**	**8.00**	**1.10**	**4.50**	**14.00**	**1.20**					
(Q. conferta)	high		**1.1**	**11.70**	**1.30**	**5.20**	**18.30**	**1.40**					

review of possible quality checks and other forms of assistance

Quercus petraea	low	460		8.00	0.30	2.00	7.00	1.30	14.00	700	50.0	5	
	high	510		12.00	0.60	4.00	10.00	2.00	25.00	1700	200.0	8	35
Quercus robur	low	460	0.85	10.00	0.82	4.00	5.00	1.00	15.00	1000	90.0	6	7
(Q. pedunculata)	high	510	1.7	19.00	2.00	8,00	13.00	2.00	25.00	1200	150.0	7	35
Abies cephalonica	low			8.00		2.70	11.00	1.00					
	high			13.00		8.30	24.00	1.50					
Picea abies	low		1	6.50	0.60	1.00	2.50	0.70					
(P. excelsa)	high	520	1.5	12.60	1.20	4.20	16.00	2.20					
Picea sitchensis	low	440	1	6.00	0.60	1.50	4.00	0.60	15.00	250	40.0	2	
	high	530	1.1	13.00	1.10	3.00	11.00	1.00	35.00	1400	120.0	4	35
Pinus sylvestris	low	490	0.62	5.00	0.40	1.00	2.00	0.50	20.00	180	35.0	2	
	high	530	0.62	10.00	0.80	3.00	11.00	0.80	45.00	800	150.0	5	45

5. Analyses in duplicate

Performing duplicate analyses represents a very worthwhile quality check. The samples or digestion solutions/extracts are measured twice independently for the individual parameters, the results are compared, and their repeatability determined.

As this is a very time-consuming and expensive procedure when the number of samples is large, it may be sufficient to analyse only part (e.g. 5%) of the samples in duplicate. If this is adopted, 5% of the samples should be randomly selected and analysed again at the end of the batch.

Thus one can **check repeatability** on the one hand and **make sure that samples weren't mistakenly exchanged** (for example during bottling on a sampler) in the course of a series on the other. If a mistake was found all samples of this batch must be repeated twice.

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

5. Avoidance of contamination

a. Water samples

1. during the sampling period, e.g. as a result of bird droppings:
 - the laboratory should be informed about signs of any such contamination!

2. during the transfer of the water samples in the field from the sampling devices to the bottles used for transportation to the laboratory:
- the most important point during this step, as well as throughout the whole sample preparation procedure in the laboratory, is to avoid skin contact by using disposable gloves (non talc), and the use of clean equipment (e.g. glass- and plasticware)!

3. during filtering of the samples:
- at least separate plastic tubing (if used) or other filtering devices for different types of sample (bulk, throughfall, stem flow, soil solution) should be used.

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

- rinsing the filter capsule or funnel between the samples with the next sample, and not only with purified water, is recommended. If this is not possible, then an adequate amount of the next sample should be discarded after filtering before taking the sample for the analyses!
- contamination control samples (ultra pure water) should be used after every 20 to 30 samples depending on the type of filtering system.
- it is always recommendable to start working with cleaner samples (e.g. bulk first) and continue with the other types of sample.
- attention should also be paid to the different characteristics of the individual sample plots and their specific concentrations.
- the material of the filters should be suitable for the analyses to be carried out, e.g. paper filters can affect ammonium and DOC determinations through contamination and the release of paper fibres that of course contain C. In some cases, the opposite may occur: sample loss through adsorption on filters. For the filtration of samples on which DOC is to be determined, glass fibre filters are recommended.
- the filters and the amount of ultra pure water needed to rinse off possible contaminants should be tested and checked by using blank charts. The filters should be handled with clean forceps.

Topic 2	**1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany**

review of possible quality checks and other forms of assistance

4. during standard solution preparation:
- one highly recommendable procedure is to use a separate set of bottles for preparing the standard solutions for every single type of analysis.

5. other help:
- If the pH or conductivity value for a sample is exceptionally high, then it is recommendable to inform the persons carrying out the other analyses (which are usually performed later) about the “abnormal” sample.

There will be presentations from Carmen Iacoban about accidental contamination of water samples in the laboratory and from Daniel Zlindra about the measurement of total N in Water and problems with high blanks under topic 7!

Topic 2	**1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany**

review of possible quality checks and other forms of assistance

b. Soil samples

1. during the several preparatory steps prior to analysis:

- cleanliness of equipment, glass- and plastic-ware, is a prerequisite for avoiding contamination
- the milling equipment is one possible source of contamination. Metals, especially, may be released through abrasion of the inner compartments or sieves. The degree of contamination appeared to be a function of the hardness of the sample material (wood, bark) and the age of the sieve. The use of titanium rotors and sieves is therefore recommended, as well as periodical replacement of the sieves.
- the sieves should be clean, with no traces of oxidation on their metallic parts.
- attention should be paid to ensure that no residues from tools (crusher, pestle, brush, cleaning equipment) end up in the samples as a result of thorough cleaning by brushing or wiping.
- this also holds true for other equipment (sample divider, mixer, splitter, riffler).
- when pre-treating silty or clayey soil samples, appropriate methods (air extraction equipment) should be used to avoid contamination of other samples or equipment via the air.

Topic 2	**1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany**

review of possible quality checks and other forms of assistance

b. Soil samples

2. during extraction/digestion:

- if a separate container is used to weigh and transfer sub-samples to extraction vessels, then it should be carefully brushed clean between samples to avoid cross-contamination.
- all glass- and plastic-ware should be cleaned by rinsing with a dilute acid solution or appropriate cleaning agent. Rinsing twice with distilled or deionized water and drying before reuse is a common practice.
- ions adsorbed on the inner surfaces of extraction flasks or sample bottles coming into contact with extracts may be a source of contamination for subsequent analyses using the same containers.
- some types of filter paper used for filtration may contain contaminants. Many laboratories encounter problems with Na+ or other cations. Careful analysis of blanks and the filter material may indicate problematic elements that enhance the background noise.

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

c. foliage samples

Element	Possible contamination source
N	NH_3 from the laboratory air (only if the Kjeldahl method is used), reagents
S	Water (distilled or deionised), reagents
P	Dishwasher (detergent), water (distilled or deionised), reagents
Ca	Soil contamination from sampling, water (distilled or deionised), glassware, reagents
Mg	Soil contamination during sampling, water (distilled or deionised), glassware, reagents
K	Dishwasher (detergent), water (distilled or deionised), glassware, reagents
Zn	Soil contamination during sampling, Dishwasher (detergent), water (distilled or deionised), glassware, dust, reagents
Mn	Reagents
Fe	Soil contamination during sampling, water (distilled or deionised), glassware, dust, reagents
Cu	Water (distilled or deionised), glassware, reagents
Pb	Soil contamination during sampling, glassware, dust, reagents
Cd	Soil contamination during sampling, glassware, dust, reagents
B	Water (distilled or deionised), glassware, reagents
Cr, Ni	Instruments made of stainless steel used in sampling, pre-treatment etc.
C	Reagents

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany
review of possible quality checks and other forms of assistance	

6. Interlaboratory quality assurance

a. ring tests

b. exchange of knowledge and experiences with other laboratories

- assistance program
- exchange of samples
- exchange of know how by info sheets

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Info sheets:

Analytical Info Sheets

General introduction

Topic	Empty template	Finalized sheet
method comparisons	(EPDMC)	MC1: SO4 - Comparison of ICP-, IC- and spectrophotometric determination in colored soil solutions MC2: Comparison of pH measurements in soils according to ISO 10390 and DIN 19684-1 MC3: Comparison of HTCO CLD and PO UV-220 nm oxidation
new methods	(EPDNM)	.
material tests	(EPDMT)	MT1: Leaching of PE-bottles MT2: Comparison of two wet-only samplers: ANDERSEN and EIGENBRODT UNS 130
sample pretreatment and storage	(EPDSP)	SP1: Pair-wise comparison of filtered and not filtered precipitation samples SP2: Storage of soil water and depo samples under diferent conditions SP3: Influence of filtration on TOC content in different water samples
technical information	(EPDTI)	.

Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

Info sheets:

EPD	analytical Informations	TI(No)
method comparison	**Comparison of ICP-, IC- and spectrophotometric determination in colored soil solutions**	**SO_4**

1. compared methods:

a. Ion exchange chromatography without chemical suppression; eluent: phthalic acid with tris(hydroxymethyl)-aminomethan; column: shimpack IC-A1S, pre-column: shimpack IC-GA1; conductivity detector (König, Fortmann 1996 a)

b. S_{total}-determination with ICP, correction for organic sulfur: determination of DOC and subtraction of Corg [mg/l]/130 from total sulfur content; ICP with axial plasma (Polyscan 61E, Thermo Instruments); wavelength: 182,040 nm; cross-flow nebulizer; without internal standard; no interelement correction (König, Fortmann 1996 b)

c. CFA-spectrophotometric determination of SO_4 with Ba-methylthymol blue reaction after separation of interfering cations with a cation exchange column; elimination of the interference of humic acids by measuring the blind reaction with Ca-methylthymol blue on a second CFA-channel (König, Fortmann 1996 c)

2. procedure:

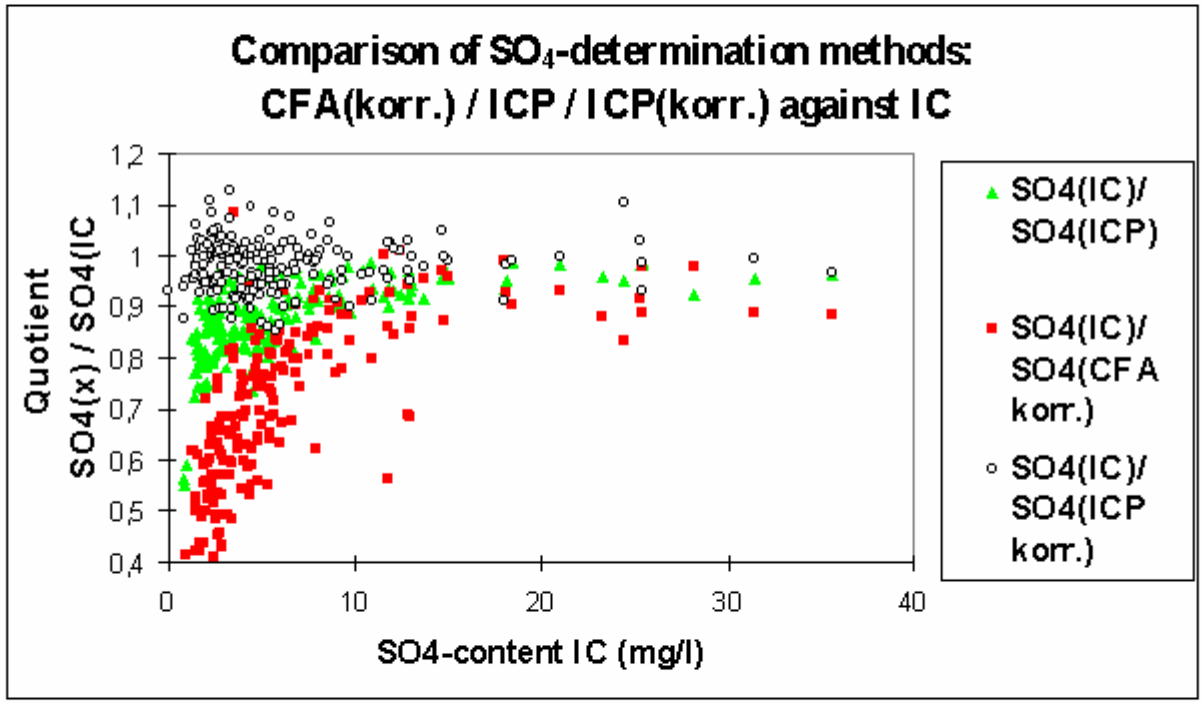
The soil solutions were filtrated with membran filters (0,45 µ). About 500 colored soil solutions were measured with the different SO_4 methods

Topic 2	1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

6. tables and graphs, appendix:

graph 1:



Topic 2

1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany

review of possible quality checks and other forms of assistance

EPD	analytical Informations	MT2

Material test	Comparison of two wet-only samplers: ANDERSEN and EIGENBRODT UNS 130	deposition samples

1. **Problem / question:** The old wet-only sampler (type ANDERSEN, right hand side of the picture below), used in the French level II network between 1993 and 2001 on 8 plots and in Luxemburg on one plot, had no more chance to be modernised, since the manufacturer had changed several times and this wet-only was electronically speaking no more up-to-date. We have therefore switched to a new generation of wet-onlys (type EIGENBRODT UNS 130, left hand side of the picture below) but had to be sure that there will not be a rupture in the results, due to the use of the new wet-only.

2. **Description of the test:**

7. References

5. References

Allan M.A. (ed). 2004. Manual for the GAW Precipitation Chemistry Programme. Guidelines, Data Quality Objectives and Standard Operating Procedures. WMO TD No. 1251: 170 pp.

Analytical Methods Committee. 1987. Recommendations for t… estimation and use of the detection limit. Analyst, 112: 19…

A.P.H.A., AWWA & WEF. 2005. Standard … water and wastewater. 21th ed. A… …iation, Washington.

Clarke, N., Danielsson… …speciation of aluminium and iron in a flo… …imica Acta, 306: 5-20.

Clarke, N.… …, L.T. 2007. Dissolved organic carbon concentratio… …spruce stands of different ages. Plant and Soil, 299: 275-285.

Cools, N., Verschelde, P., Quataert, P., Mikkelsen, J. and De Vos, B. 2006. Quality Assurance and Quality control in Forest Soil Analysis: 4th FSCC Interlaboratory Comparison. INBO.R.2006.6. Forest Soil Coordinating Centre,Research Institute for Nature and Forest, Geraardsbergen, Belgium. 66 pages + annexes (on CD-Rom).

Cools, N., Delanote, V., De Vos, B., Quataert, P., Roskams, P. and

53 references cited

Topic 2	**1st Meeting of the Heads of the Laboratories within ICP Forests 9.-10. June 2008 in Hamburg, Germany**
review of possible quality checks and other forms of assistance	

ICP Forests Working Group on QA/QC in Laboratories

Authors:
N. Clarke, N. Cools, J. Derome, K. Derome, B. De Vos, A. Fuerst, N. Koenig, A. Kowalska, R. Mosello, G. A. Tartari, E. Ulrich

Thanks to all authors!