Organisation and evaluation of future ring tests for Soil

a. Short report on the organisation and evaluation of the previous ring tests of the Expert Panel on Soil

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Overview Previous ring tests

	Aim	Year	by	
1st	Comparison of national and reference method	1992	Flemish soil expert group	Brussels
2nd	• Comparison between labs • Comparison between reference methods and national methods	1997	FSCC	UGent
3rd	• Test for quality of lab soil analyses • Test of the revised manual (new ref methods) • Link performance labs with background information	2002 - 2003	FSCC	INBO
4th	Follow-up quality of soil analyses	2005	FSCC	INBO

3rd FSCC Interlaboratory Comparison

- **Organisation**
  - **3 samples (A, B: mineral) and C (organic)**
  - **52 laboratories**
  - **Including all mandatory and optional parameters (Manual 2003)**
  - **Accompanying questionnaire**
- **Evaluation**
  - **Phase 1: Procedure following ISO 5725-2**
    - <u>(Graphical) consistency measures</u>

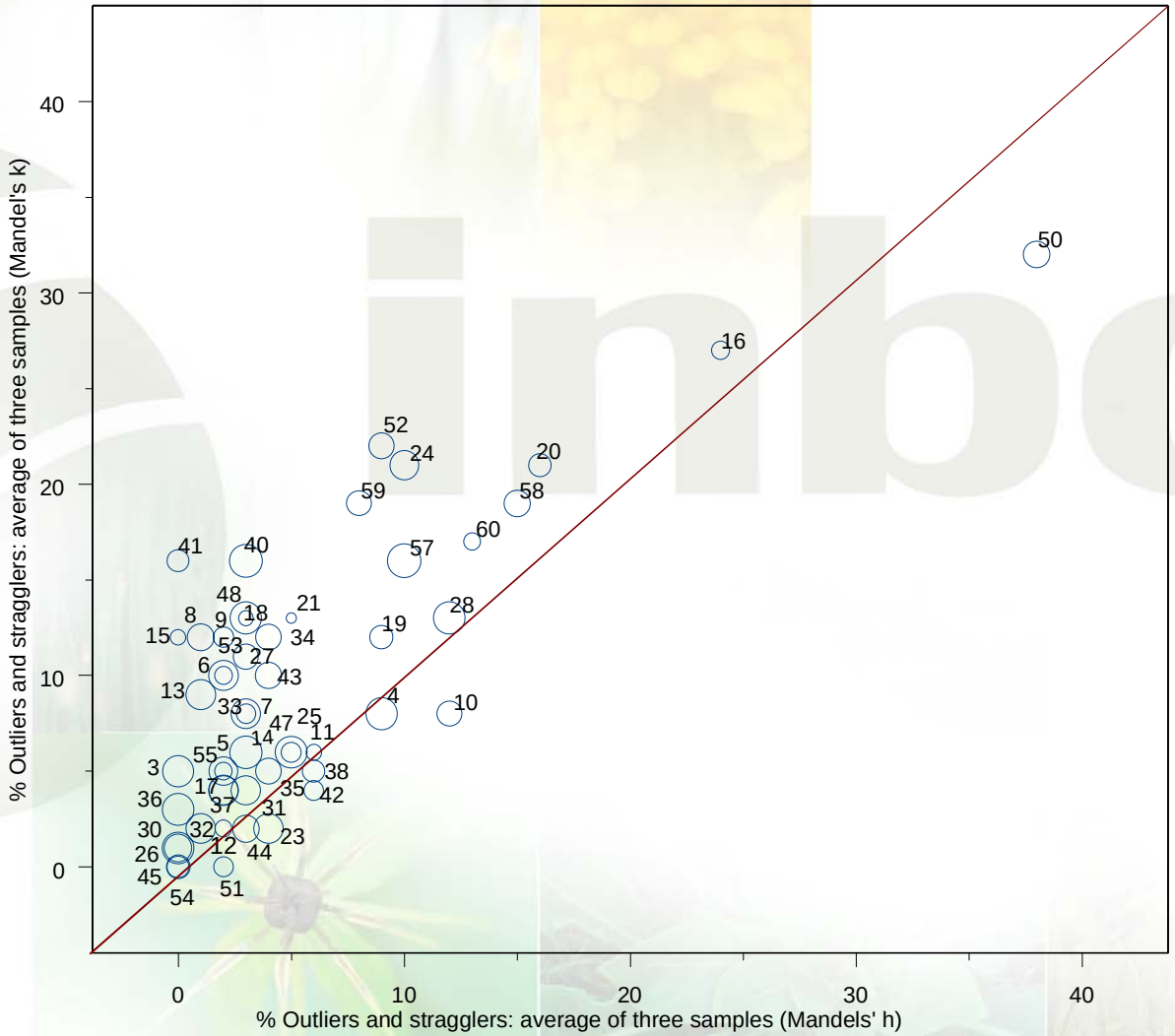
    Between-laboratory consistency statistics (Mandel's h)

    Within-laboratory consistency statistics (Mandel's k)
    - <u>Numerical outliers techniques</u>

    If test statistic > 1% critical value = outlier

    If test statistic > 5 % critical value = straggler
    - Step-by-step procedure where outliers are rejected
    - Bonferroni rule = correction to minimise false outliers when performing p tests (the threshold α = 0.01/p and 0.05/p)

3rd FSCC RT: % of outliers per lab



3rd FSCC Interlaboratory Comparison

- **Phase 2: Integration of information from the questionnaire:**

  Can performance of laboratories (Mandel's h and k statistics) be linked to background information?

  - Use of ref. method (yes, no)
  - Level of experience (little, high)
  - Training of the personnel (yes, no)
  - Accreditation (yes, no)
  - Statute of laboratory (university, state, private, other)
  - Type of laboratory (soil, plant, general)
  - Forest specialisation (yes, no)
  - Region in Europe (north, east, south, west)

Between-laboratory variability

Factor	Sample	RefmC	ExpLevC	Trained	Accr	Statute	Type	For est	Region
Group									
Particle Size									
pH Soil									
Carbonates									
OC						**S < U**			**S < E**
Total Nitrogen									
Exchangeable						**S < U**			**W < E**
Extractable			**0 < 1**			**P,S<U**	**G<P<B**		**W < S,E** **N < S**
Total elements				**1 < 0**	**1 < 0**	**U,S < P**			**W < S,E**
Reactive Fe and Al		**1 < 0**			**1 < 0**	**S<U<P** **O<U,P**			

Legend: 1: use of reference method, or has trained personnel, or has received accreditation
When indicated as smaller, Hv is smaller so between-laboratory variability is significantly smaller
S= State, U = University, P = Private, O = Other
W = West Europe, S = South, E = East

Between-laboratory variability

- No significant effect for particle size distribution, pH, carbonates, total N
- Government laboratories better than university for OC, Exch., Extr., Fe&Al
- Not expected for Extr. el: exp Level and type of laboratory
- Differences between region
- For Tot el and Fe&Al: Accreditation helps
- Training level significant for Total el
- Use of ref method significant for Fe&Al

Within-laboratory variability

Factor	Sample	RefmC	ExpLevC	Trained	Accr	Statute	Type	Forest	Region
Group									
Particle Size							**G<B,P**		
pH Soil				**1 < 0**					
Carbonates									
Organic Carbon									
Total Nitrogen	**A<C**								
Exchangeable elements	**B<A<C**	**0 < 1**				**O<S<P** **U<P**			
Extractable elements	**A<B,C**					**O<S<P** **O<U<P**			
Total elements			**1 < 0**					**1 < 0**	
Reactive Fe and Al						**U<S**	**P,G<B**	**0 < 1**	

Legend: A,B and C = Sample names
1: use of reference method, or has experience, has trained personnel or is a specialised forest laboratory
S= State, U = University, P = Private, O = Other
When indicated as smaller, Kv is smaller so between-laboratory variability is significantly smaller.

Within-laboratory variability

- No significant effects for carbonates, OC
- Sample C (organic) largest internal variability
- Poorer performance of private laboratories
- Region not significant

Conclusions

- Design unbalanced
- Contradictory results univariate and multivariate statistics

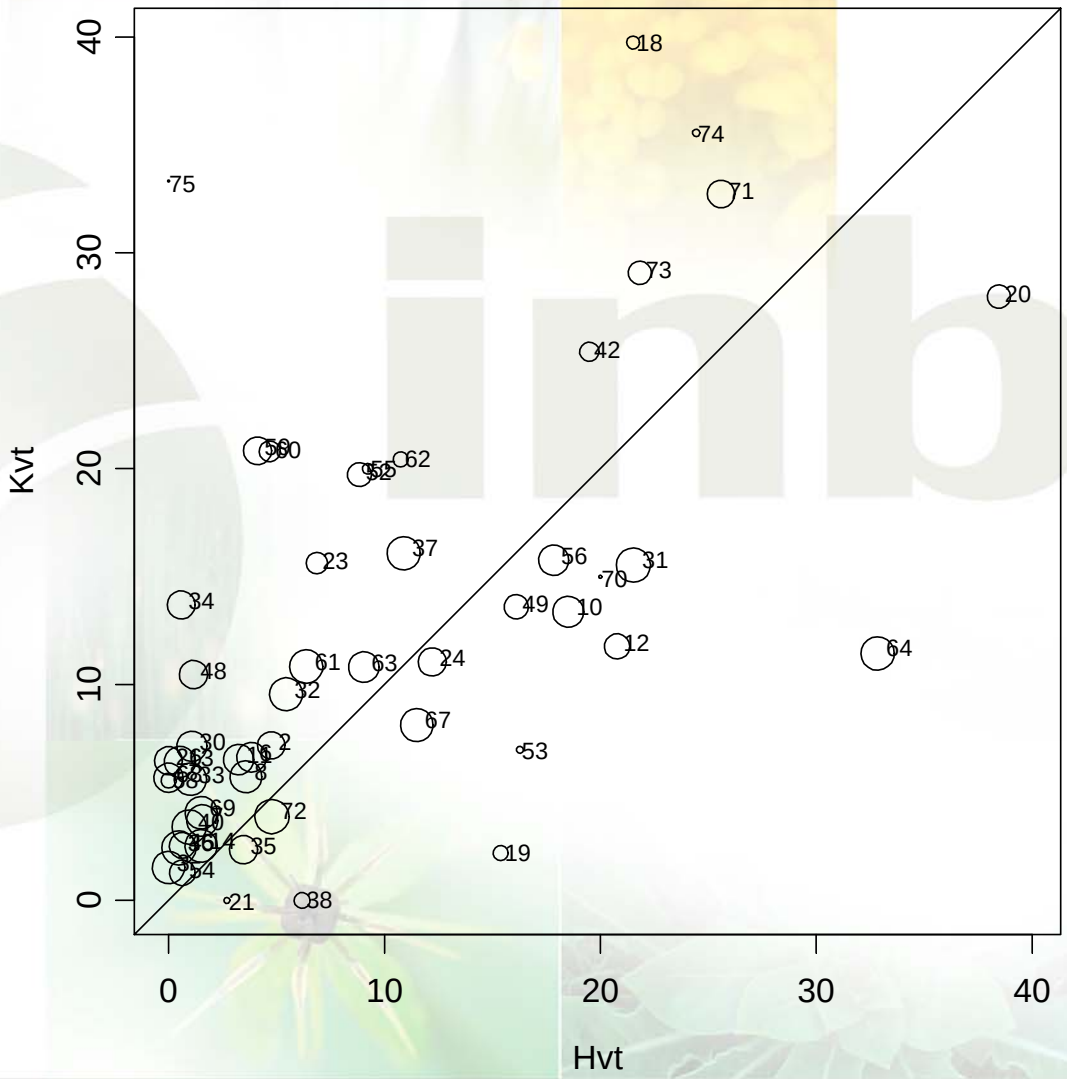
=> care with interpretation of results

- No consistent trends
- No prove that ref method is better
- Nor reported experience

4th FSCC Interlaboratory Comparison

- **Organisation**
  - **7 samples**
    4 mineral (A, B, C, D)
    1 organic (E)
    2 aqua regia extracted samples (F, G)
    B and F from the same sample
  - **52 laboratories**
  - **Including all mandatory and optional parameters (Manual 2003)** except Total analysis
  - **Questionnaire:** list of question per group of parameters (9 groups)
- **Evaluation**
  - **Phase 1: Procedure following ISO 5725-2**
  - **Questionnaire info: descriptive statistics, no Phase 2**

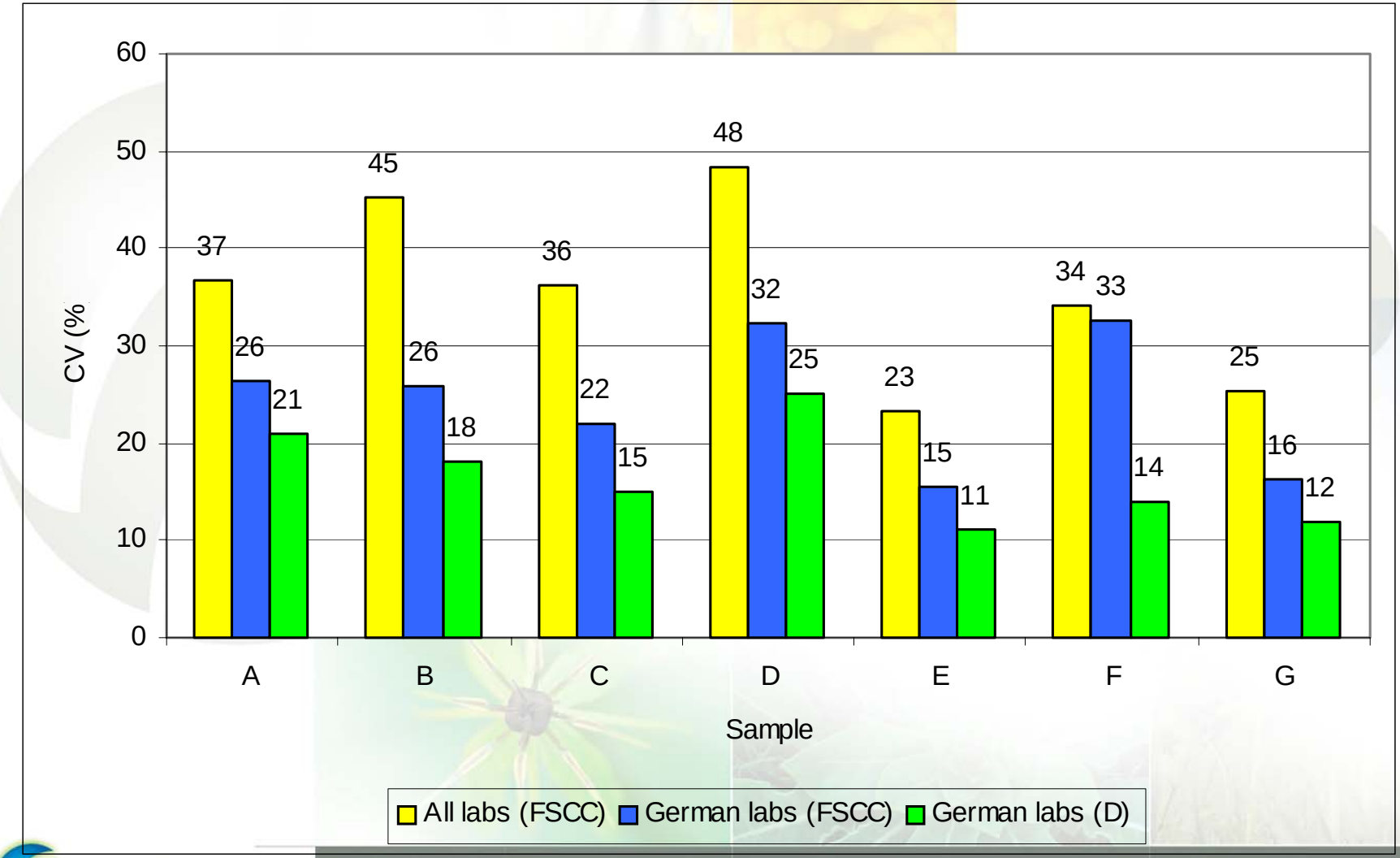
4th FSCC RT: % of outliers per lab



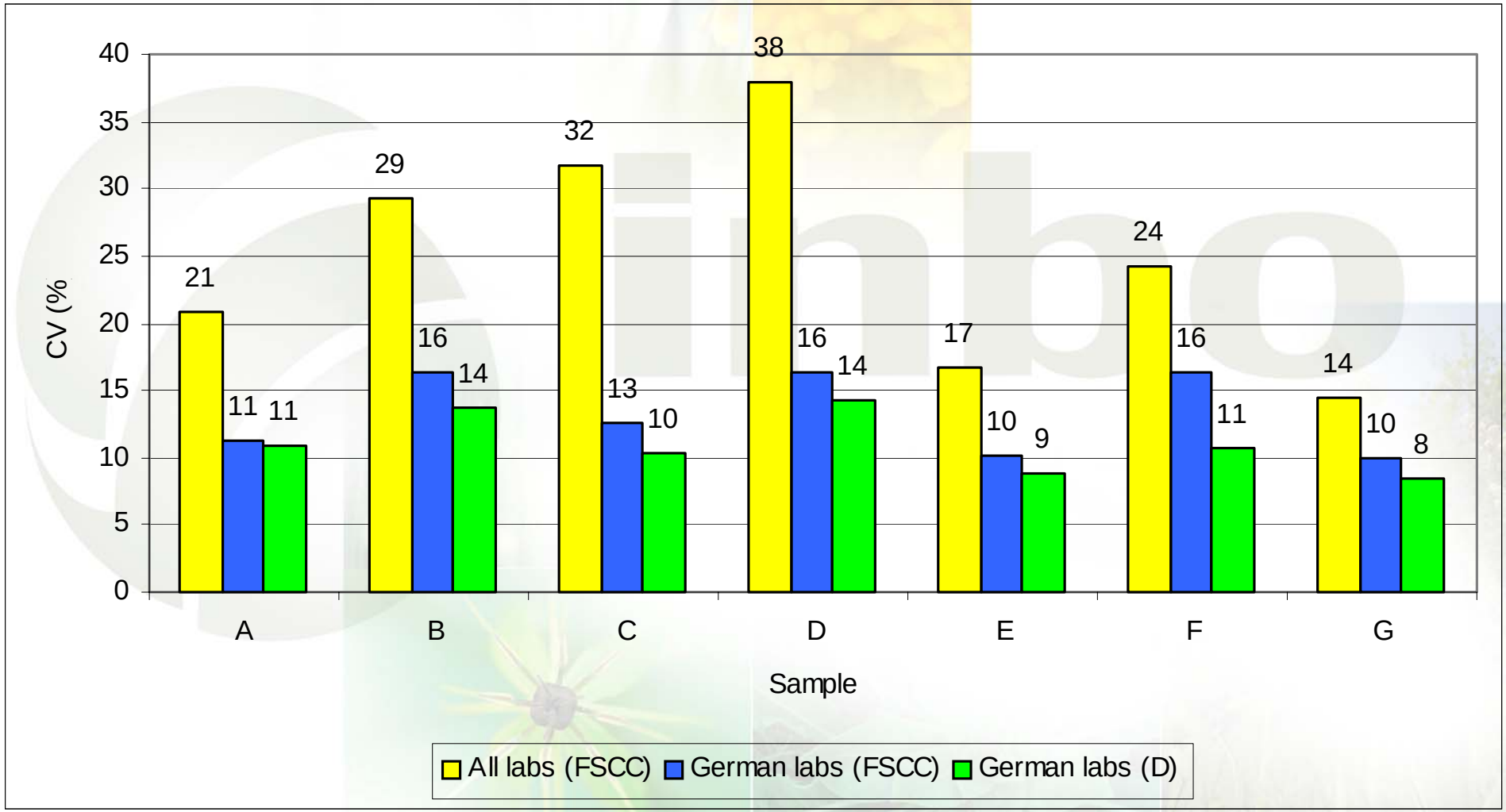
Overall Coefficients of variation
(after elimination of outliers)

	2nd FSCC RT	3rd FSCC RT	4th FSCC RT
Group 1: Particle size distribution	**NA**	**53**	**37**
Group 2: pH	**3.25**	**3.5**	**3.1**
Group 3: Carbonate content	**NA**	**206**	***129***
Group 4: Organic carbon	**41.5**	**18**	**13**
Group 5: Total N	**25**	**17**	***27***
Group 6: Exchangeable cations	**52**	**71**	**54**
Group 7: Aqua regia extractable elements	**35**	**47**	**33**
Group 9: Acid oxalate extractable Fe and Al	**NA**	**44**	**12**

4th RT: Mean CV per sample



4th RT: Median CV per sample



3rd and 4th RT by FSCC/INBO

Questionnaire	3rd FSCC RT (2002 - 2003)	4th FSCC RT (2005 - 2006)
Use of reference method	**65 %**	**82 %**
Experience with reference methods	**30 % (high)** **45 % (normal)** **24 % (low)**	**47 % (high)** **43 % (normal)** **8 % (low)** **2 % (no answer)**
Use of reference material	**77 %**	**86 %**
Use of control charts	**50 %**	**65 %**
Accreditation for the reference method	**13 %**	**11 %**
Use of calibration standards	**73 %**	**63 %**

4th RT: Problem parameters (≥ 20 % outliers)

- **Aqua regia extractable elements**
  - **Heavy metals: Cd, Cr, Cu, Hg, Ni, Pb, Zn**
  - **S**
- **$BaCl_2$ Exchangeable elements**
  - **All elements for at least one sample ≥ 20% outliers**
  - **Exception: exchangeable acidity**
- **Organic carbon content of Sample D**
  - **Mean = 1.7 g/kg (close to LOQ)**
- **Carbonate content of Sample A**
  - **Since pH($CaCl_2$) < 6.0 => no use of measuring $CaCO_3$**

4th RT: % of o1 (outliers) and o5 (straggler) as a measure of laboratory performance

- **Between laboratory variability**
  - **7 laboratories** reported outliers and stragglers for **more than 20%** of the total number of reported parameters.
- **Within-laboratory variability**
  - **6 laboratories** reported outliers and stragglers for **more than 20 %** of the reported parameters

=> 9 problem **laboratories**

Follow - up of poorly performing labs

N° labs (Total N° = 9)	Particle size	pH	$CaCO_3$	TOC	Tot N	Exch. El.	Aqua Regia	Ac.Ox. Fe & Al
Reported	6	6	2	6	6	8	7	2
Failed	5	4	0	3	2	6	7	1
in %	83	67	0	50	33	75	100	50

Follow-up questionnaire:

1. Definition of the method
   Using coding system (see next item)
2. Definition of the problem
   Questions per group of failed elements

Problem definition

What was/were the reason(s) for the wrong results (please mark the check-box)?

Variation:	A	B	C
1. no reason found	✓		
A. SAMPLE PREPARATION			
A1. wrong size of particle size (< 2 mm fraction, reference method: no further grinding allowed!)			
A2. wrong sample weight			
A3. mixing-up of samples			
A4. dilution error			
A5. no use of reference method (which is the reflux method)			
A6. contamination			
A7. losses			
A8. other problem with sample preparation (please specify):....			

Variation	A	B	C
B. DETERMINATION			
B1. calibration problem			
B2. wrong units			
B3. instrument error			
B4. contamination			
B5. losses			
B6. error in recalculation on oven-dry basis			
B7. results close to detection limit			
C. LABORATORY CONDITIONS			
C1. new (or poorly educated) staff			
C2. no experiences with a new instrument			
C3. no experiences with the method			
OTHER PROBLEMS (PLEASE SPECIFY):			

Results of problem questionnaire

Group	No reason found	A1	A2	A3	A4	A5	A6	A7	A8	B1	B2	B3	B4	B5	B6	B7	C1	C2	C3	C4
Aqua Regia Extractant Determinations												x	x							
Aqua Regia Extractant Determinations									x				x			x				
Aqua Regia Extractant Determinations																x				
Aqua Regia Extractant Determinations									x			x				x			x	
Aqua Regia Extractant Determinations																				
Aqua Regia Extractant Determinations																				
Exch.Ac - Exch. Cations-Free H+	x			x	x							x								
Exch.Ac - Exch. Cations-Free H+	x			x	x							x				x				
Exch.Ac - Exch. Cations-Free H+											x									
Exch.Ac - Exch. Cations-Free H+											x								x	
Exch.Ac - Exch. Cations-Free H+									x	x	x	x				x			x	
Exch.Ac - Exch. Cations-Free H+																				
Exch.Ac - Exch. Cations-Free H+												x	x			x				
Exch.Ac - Exch. Cations-Free H+					x		x					x				x				
Extractable Fe & Al												x								
Organic Carbon																				
Organic Carbon																x				
Particle Size	x																		x	
Particle Size	x																			
Particle Size	x																		x	
Particle Size	x																		x	
Particle Size																			x	
Particle Size																			x	
Soil pH												x								
Soil pH	x																			
Total Nitrogen		x		x						x										
Total Nitrogen																		x		

Follow-up of poor performing labs

- Lab N° 71 reported new results after re-analysis of new batch of samples
  - Interlaboratory comparison improved
  - Within-laboratory variability did not improve
- 3 labs were planning to do so but:
  - Lab 64 and 42: Problem in request for new RT sample material
  - Lab 73: No results received so far

Organisation and evaluation of future ring tests for Soil

b. Organisation and costs of the future ring tests

c. Evaluation of future ring tests

5th FSCC Interlaboratory Comparison (2007)

- Aim:
  - Ring test simultaneous to analyses within BioSoil project
  - Quality of ring test could be linked to quality of the BioSoil survey
  - Test between-lab variability and within-lab variability (repeatability conditions)
- Timing
  - End of April: distribution of samples
  - End of Aug – beginning Sept: reporting of results to FSCC
  - End Oct – beginning Nov : draft report online
- 5 samples:
  - 4 mineral: German, Belgian, Norwegian, Spain
  - 1 peat sample: Sweden *(?)*
- Special attention to laboratories participating in BioSoil
  - Will be evaluated separately as a subset
- Data Integrity Expert Rules before data submission

FSCC soil reference material

- Loamy, acid forest soil (Flanders)
- Distributed Feb ’07 to 23 labs
- Reporting dates to FSCC: 01/06/’07, 01/09/’07, 01/12/’07, 01/03/’08 and 01/06/’08
- FSCC reports: 15/07/’07, 15/10/’07, 15/01/’08, 15/04/’08, 15/07/’08
- Aims:
  - Stimulate laboratories to construct control charts
  - Assess reproducibility capacity of the individual laboratories (while 5th interlaboratory comparison tests repeatability)