QAQC: 5th FSCC Interlaboratory Comparison 2007

Results and comparison with previous ring tests

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http://fscc.inbo.be

Registration and data submission

- Web interface developed by

  Programming: Alfred Fürst, Forest Foliar Co-ordinating Centre

  Database & Web-Servermanager: Hans HAUER

  Plant Analysis Unit

  Federal Research and Training Centre for Forests, Natural Hazards and Landscape (BFW)

  Vienna, Austria

- Registration (01/05/'07) and data submission (01/09/'07) on-line:
  - Analytical results in triplicate
  - Information on the lab methods by drop-down lists for each method and each sample
- No additional questionnaire

Registration and Data Submission

Country	Registered	Results	Country	Registered	Results
1. Austria	**1**	**1**	**16. Latvia**	**1**	**1**
2. Belgium	**2**	**2**	**17. Lithuania**	**1**	**1**
3. Bulgaria	**1**	**1**	**18. Poland**	**1**	**1**
4. Croatia	**1**	**1**	**19. Portugal (incl.Azores)**	**2**	**2**
5. Cyprus	**1**	**1**	**20. Romania**	**1**	**1**
6. Czech Rep.	**1**	**1**	**21. Russia**	**3**	**2**
7. Denmark	**1**	**1**	**22. Serbia**	**1**	**1**
8. Estonia	**2**	**2**	**23. Slovak Republic**	**1**	**1**
9. Finland	**2**	**2**	**24. Slovenia**	**1**	**1**
10. France	**1**	**1**	**25. Spain**	**2**	**2**
11. Germany	**14**	**13**	**26. Sweden**	**1**	**1**
12. Greece	**1**	**0**	**27. Switzerland**	**1**	**1**
13. Hungary	**2**	**2**	**28. Turkey**	**2**	**2**
14. Ireland	**1**	**1**	**29. United Kingdom**	**1**	**1**
15. Italy	**1**	**1**	Total	51	48

Samples

Sample	Min/Org	Country	Soil type	Depth
A	Min	Norway	Loamy sand, Cambic Arenosol	Iron B hor
B	Min	Belgium	Loam	20 – 40 cm
C	Min	Spain	$CaCO_3$ rich	C hor: 7 – 29 cm
D	Min	Germany	Colluvial brown earth	40 – 80 cm
E	Org	Sweden	Peat	

Sample preparation and homogeneity

Parameter	Sample	N° sub-samples	Gen. mean	St.dev. within sub-samples	St.dev. between sub-samples	General St.dev.	CV	% variation between sub-samples	% variation within sub-samples	
W&B	***A***	***8***	***1.19***	***0.04***	***0.05***	***0.06***	***5.11***	***62***	***38***	***>***
W&B	C	8	4.61	0.30	0.00	0.30	6.59	0	100	OK
W&B	D	8	0.62	0.02	0.00	0.02	3.06	1	99	OK
LOI	E	7	99.03	0.02	0.00	0.02	0.02	8	92	OK
As	A	8	4.70	0.34	0.00	0.34	7.25	0	100	OK
As	C	7	13.03	1.85	0.00	1.85	14.18	0	100	OK
As	D	8	11.94	1.17	0.48	1.26	10.56	14	86	OK
Ca	A	8	2426.27	562.40	429.52	707.66	29.17	37	63	OK
Ca	C	7	74438.48	3967.47	0.00	3967.47	5.33	0	100	OK
Ca	D	7	108.29	38.33	8.15	39.19	36.19	4	96	OK
Ca	E	8	1038.16	31.61	20.94	37.92	3.65	31	69	OK
K	A	8	2382.54	558.59	418.69	698.09	29.30	36	64	OK
K	C	7	8146.37	1296.75	0.00	1296.75	15.92	0	100	OK
K	D	7	5868.12	1388.12	1048.97	1739.89	29.65	36	64	OK
K	E	8	135.83	8.27	4.66	9.49	6.99	24	76	OK
Mg	A	8	3131.85	191.41	126.07	229.20	7.32	30	70	OK
Mg	C	7	2882.77	204.70	42.46	209.05	7.25	4	96	OK
Mg	D	7	4159.14	221.50	37.15	224.59	5.40	3	97	OK
Mg	E	8	468.58	11.84	7.45	13.99	2.99	28	72	OK
Mn	A	8	548.25	272.76	0.00	272.76	49.75	0	100	OK
Mn	C	7	396.00	53.28	0.00	53.28	13.45	0	100	OK
Mn	***D***	***8***	***980.85***	***143.68***	***200.75***	***246.87***	***25.17***	***66***	***34***	***>***
Mn	E	8	20.28	0.71	0.11	0.72	3.55	2	98	OK
Na	***A***	***8***	***78.47***	***16.05***	***17.03***	***23.41***	***29.83***	***53***	***47***	***>***
Na	C	7	197.61	50.10	22.91	55.09	27.88	17	83	OK
Na	***D***	***7***	***268.87***	***60.92***	***82.13***	***102.26***	***38.03***	***65***	***35***	***>***
Na	***E***	***8***	***87.79***	***5.35***	***6.83***	***8.68***	***9.89***	***62***	***38***	***>***
P	A	8	706.77	39.54	0.00	39.54	5.59	0	100	OK
P	C	7	446.67	40.69	8.06	41.48	9.29	4	96	OK
P	D	8	283.67	13.56	7.42	15.46	5.45	23	77	OK
P	E	8	200.05	5.76	1.59	5.98	2.99	7	93	OK
S	A	8	106.15	9.29	0.00	9.29	8.75	0	100	OK
S	C	7	498.39	51.07	23.05	56.03	11.24	17	83	OK
S	***D***	***8***	***181.20***	***10.73***	***27.80***	***29.80***	***16.44***	***87***	***13***	***>***
S	E	8	1294.23	38.42	25.41	46.07	3.56	30	70	OK

Analytical methods

Analysis	Reference Method	Decription
Particle Size Distribution	ISO 11277	Pipette method
Soil pH	ISO 10390	Potentiometric pH (volumetric)
Carbonate Content	ISO 10693	Calcimeter
Organic Carbon Content	ISO 10694	Total Organic Carbon by dry combustion
Total Nitrogen Content	ISO 13878 ISO 11261	Elemental analysis by dry combustion Modified Kjeldahl method
Exchangeable Acidity and Free H^+ Acidity Exchangeable Cations	ISO 14254 ISO 11260	Titration or German method Extraction by 0.1 M $BaCl_2$, , single extraction
Aqua Regia Extractant Determinations	ISO 11466	Extraction by Aqua Regia
Reactive Fe and Al	ISRIC 1992	Extraction by Acid Oxalate
Total Elements	ISO 14869 ISO 14869	Dissolution with hydrofluoric and perchloric acids Total element analysis by fusion with lithium metaborate

New coding system for the analytical methods

Problems:

1. Sieving and Milling
   - Samples were sieved at 2 mm by FSCC
   - This code referred to further processing by the individual labs if necessary (e.g. for certain total analyses)
   - Confusion by putting 'reference method' in the drop down list
2. Removal of Compounds
   - Difficult to answer when treatment is different for organic and mineral samples; $CaCO_3$ rich samples
   - Difficult to answer when multiple removals were done. New selection items in drop-down list necessary.
3. Pretreatment
4. Determination
   - 'No information' was used by several labs...

Statistical data analysis

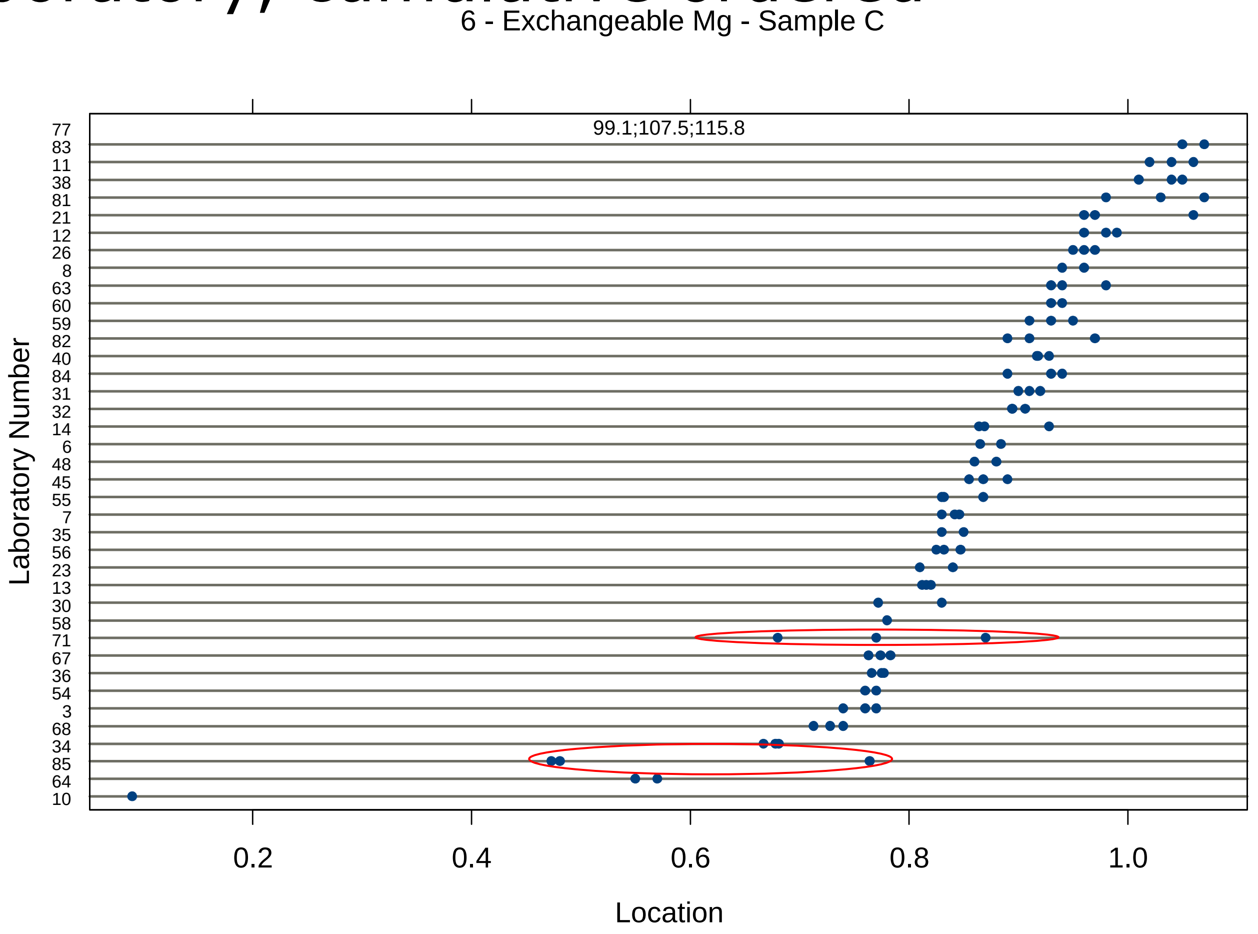
- Annex 5, for 42 parameters and 5 samples:
  1. Dotplot of all reported values
  2. Histogram of the mean
  3. Boxplot of the mean
  4. Mandel's h plot
  5. Histogram of the standard deviations
  6. Boxplot of the standard deviations
  7. Mandel's k plot

Variation between labs (items 1–4)

Variation within labs (items 5–7)

Exploratory data analysis

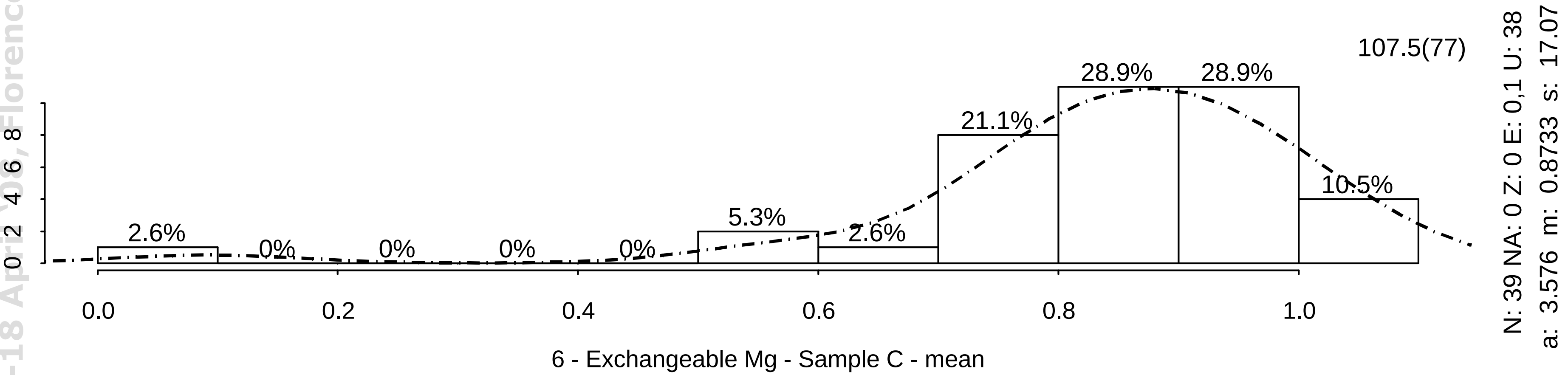
1. Dotplot of the reported values of each laboratory, cumulative ordered



14th FSEPM, 16-18 April '08, Florence Italy

Exploratory data analysis

2. Histogram of the mean



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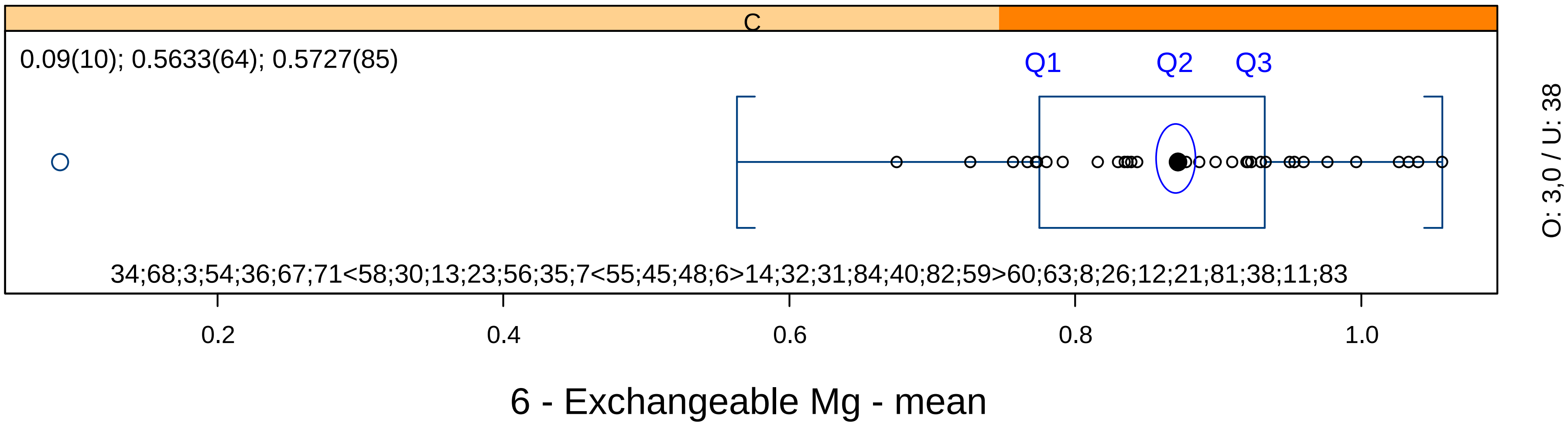
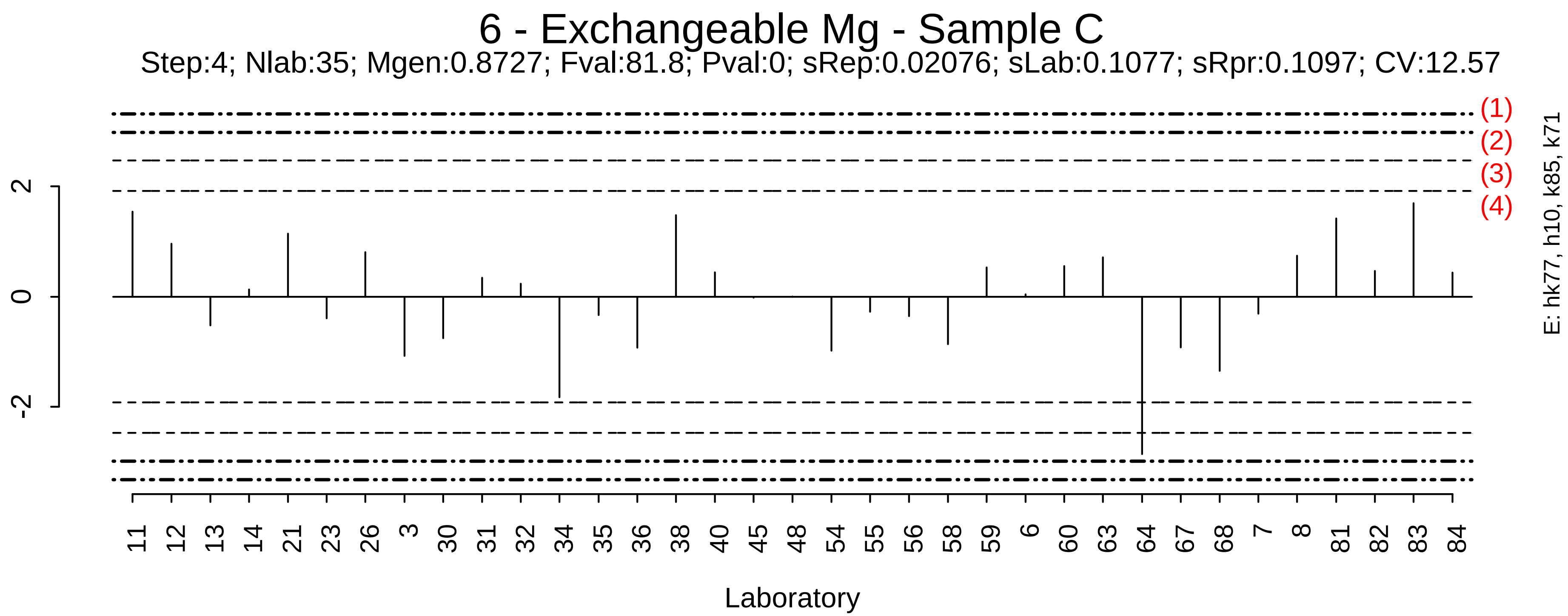
Exploratory data analysis

3. Box-plot of the mean



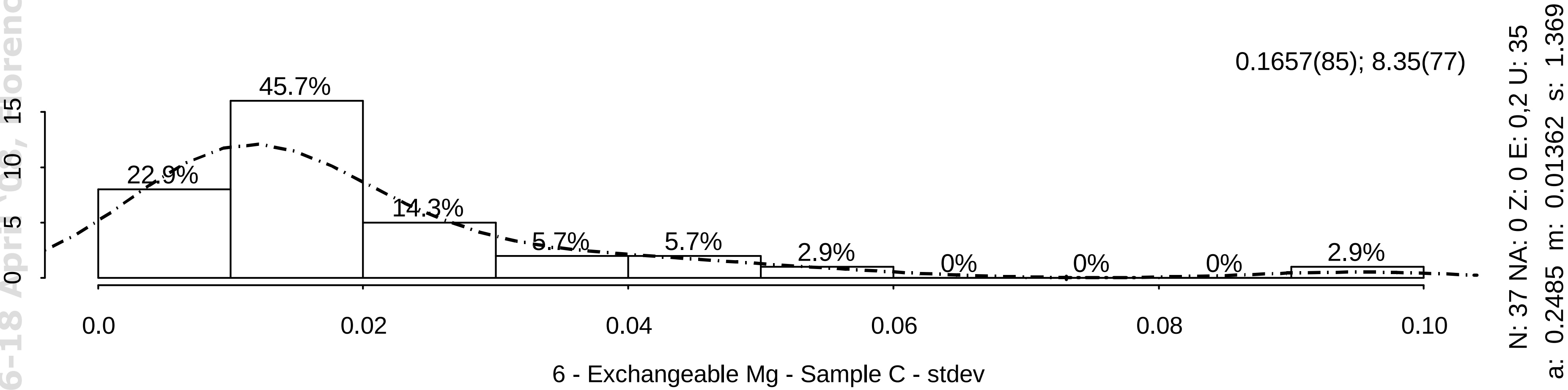
4. Mandel's h plot



14th FSEPM, 10 April '08, Florence Italy

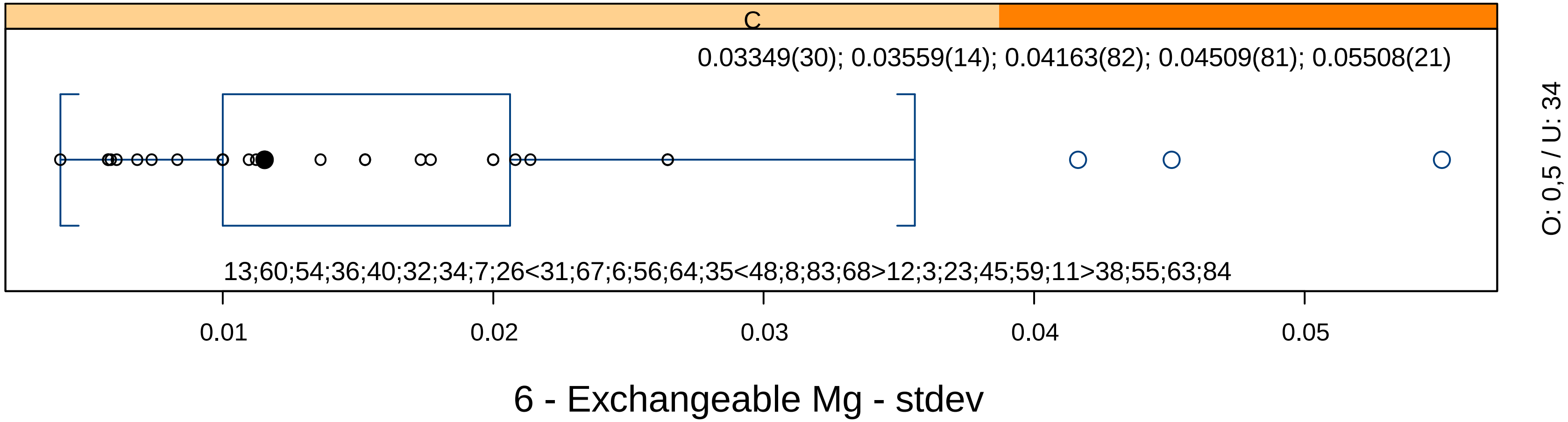
14th FSEPM, 16-18 April '08, Florence Italy

5. Histogram of the standard deviation



Exploratory data analysis

6. Boxplot of the standard deviation



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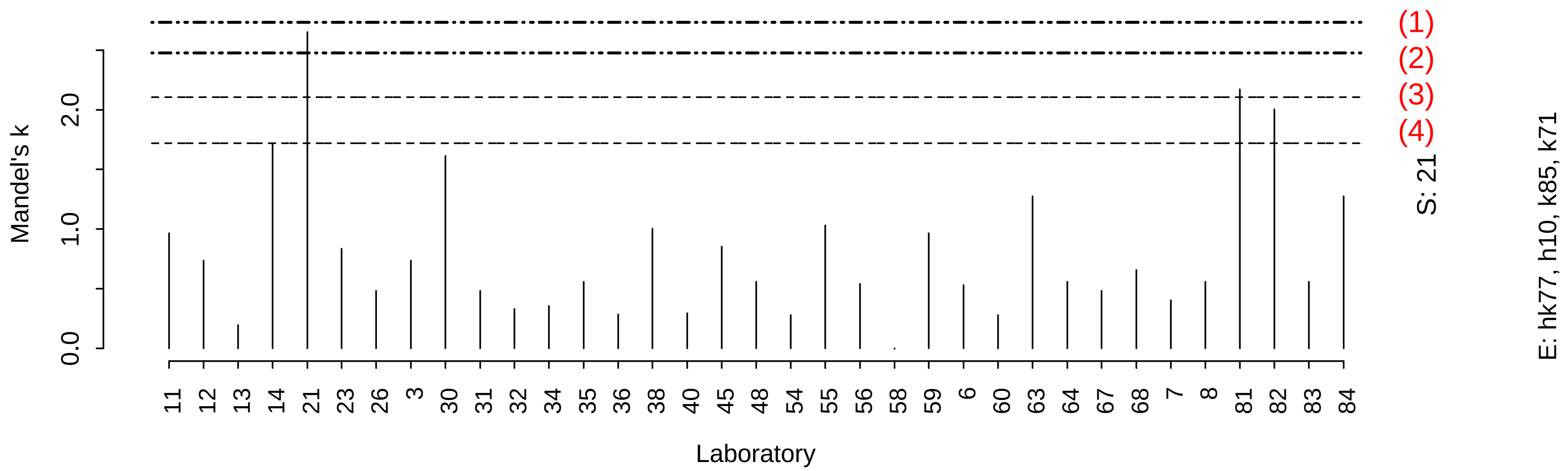
7. Mandel's k plot

Laboratory



When the critical level is exceeded, the H-null hypothesis "no difference between the mean values" will be rejected:

1. Critical value: H_0 rejected at probability level of 95%
2. Critical value: H_0 rejected at probability level of 99%
3. Critical value: H_0 rejected at probability level of 95% after application of the Bonferroni rule for n laboratories
4. Critical value: H_0 rejected at probability level of 99% after application of the Bonferroni rule for n laboratories

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Laboratory performance based on the number of outliers

- Table 5 on pg. 28 and 29 in the RT report
- Each laboratory has been given a score for **every analysed parameter**, based on the frequency that a laboratory has been excluded for the Mandel's h and/or k statistics
- Given its Lab N°, a lab can see how well they performed for each parameter
- Empty cells = not analysed or values below the LOQ

+++	No outlier has been defined for the reported samples, neither for inter - nor intralaboratory variability
++	≤ 20% outliers
+	20 % < outliers ≤ 40%
-	40 % < outliers ≤ 60%
--	60 % < outliers ≤ 80%
---	80 % < outliers ≤ 100%

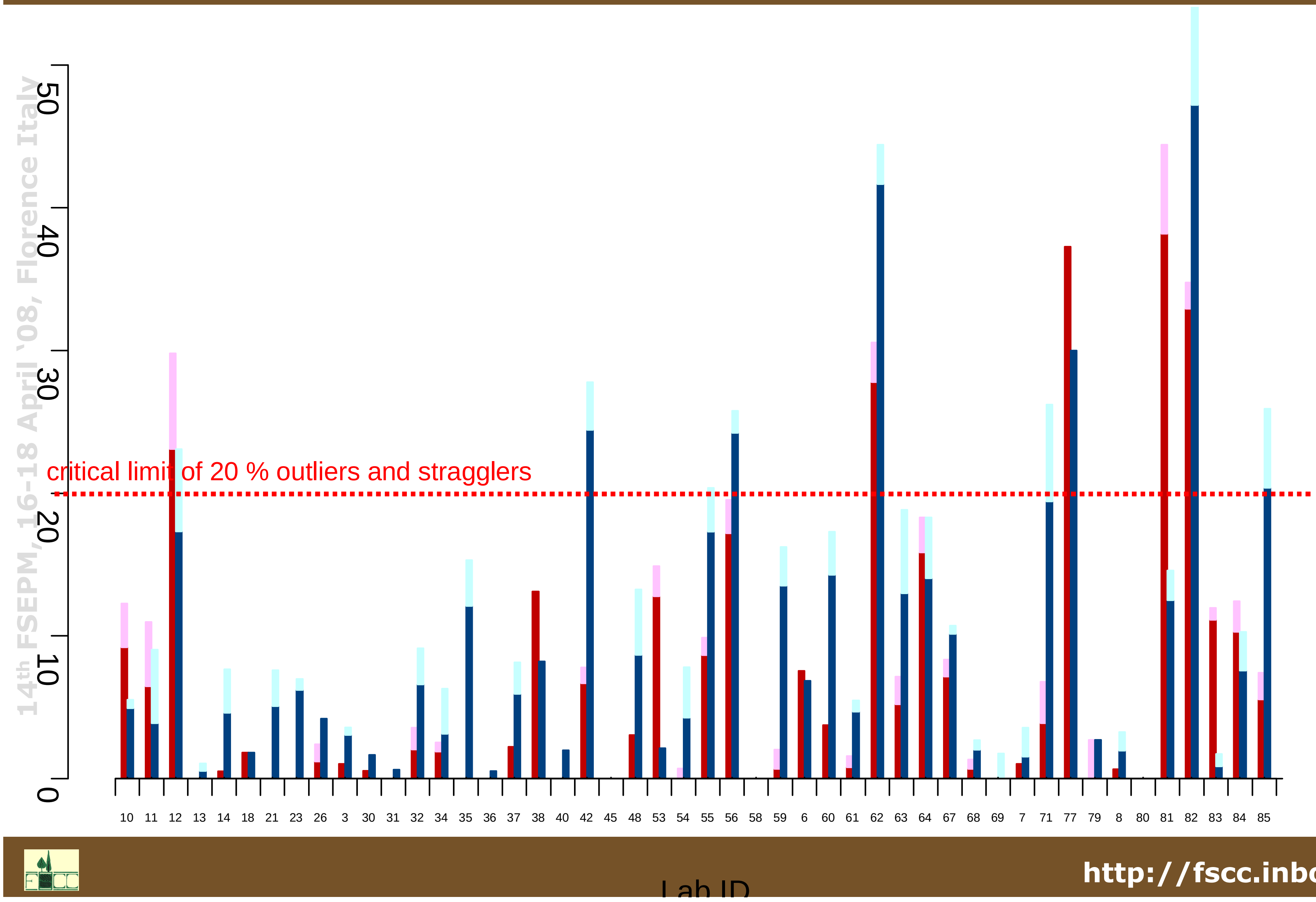
Example: Lab N° 37

Lab ID	37	Lab ID	37	Lab ID	37
Particle size clay	++	Free H	+++	Extractable Zn	+++
Particle size sand	+++	Extractable Al	+	Reactive Al	+++
Particle size silt	+++	Extractable Ca	++	Reactive Fe	+++
pHCaCl2	+++	Extractable Cd	+++	Total Al	
pHH2O	+++	Extractable Cr	+++	Total Ca	
CaCO3	+++	Extractable Cu	+++	Total Fe	
OC	+++	Extractable Fe	+++	Total K	
Total N	+++	Extractable Hg		Total Mg	
Exchangeable Acidity	+++	Extractable K	+	Total Mn	
Exchangeable Al	+++	Extractable Mg	+++	Total Na	
Exchangeable Ca	+++	Extractable Mn	+++		
Exchangeable Fe	+++	Extractable Na	++		
Exchangeable K	+++	Extractable Ni	+++		
Exchangeable Mg		Extractable P	+++		
Exchangeable Mn	+++	Extractable Pb	+++		
Exchangeable Na		Extractable S	+++		

Recommended reading of Annex

1. Identify problem parameters based on Table 5
   Eg. **Extractable Al**
2. Go to Annex 4, Group 7 (Al, Fe, Cr, Ni, S, Hg, Na)
3. Study the dot plots A till E to have an overall idea of the submitted data :
   Sample A, B, C, D Lab 37 reported (nearly) highest values
   Sample E reported average values
4. Study the histogram of the mean
   No outliers in the histogram and so not excluded from the boxplots
5. Study the boxplots of the mean
   Sample B, C and D: outliers in the boxplots
6. Study the histogram of the standard deviation
   No outliers in the histogram and so not excluded from the boxplots
7. Study the boxplots of the standard deviation
   Sample A, C and D: outliers in the boxplot
8. Study the Mandel's h and k plots
   Mandel's h outlier for sample D and Mandel's k outliers for samples A, C and D

% o1 (outliers) and o5 (stragglers) for variation between and within the labs



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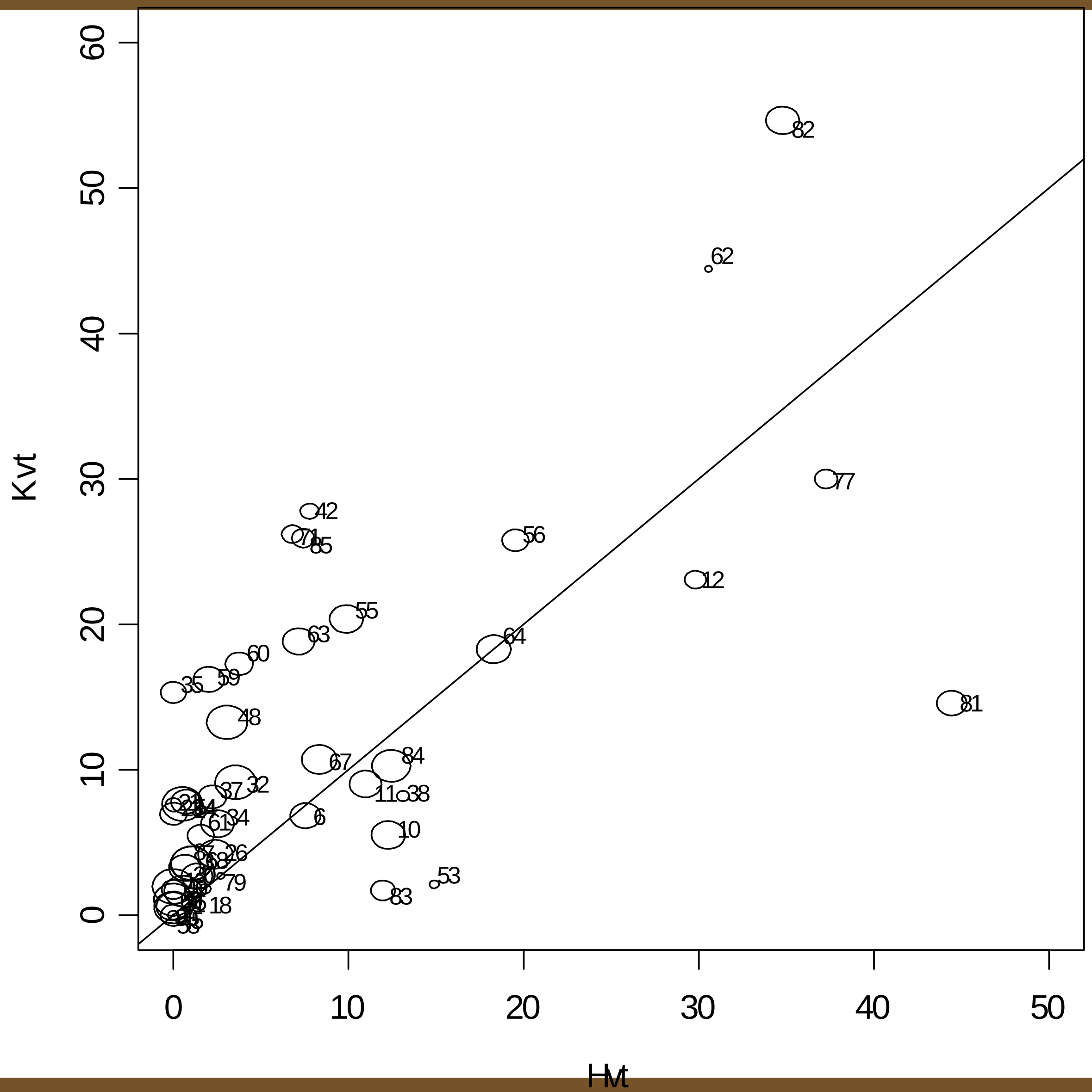
Bubble plot showing the h and k strategists



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Percentage of outlying labs per element and per sample

	sample				
Element	**A**	**B**	**C**	**D**	**E**
Particle size clay	3	9	9	6	
Particle size sand	9	6	0	9	
Particle size silt	0	3	9	12	
pH($CaCl_2$)	4	13	9	6	***21***
pH(H_2O)	7	4	2	2	2
$CaCO_3$			0		
OC	10	2	2	***22***	7
Total N	9	0	14	0	2
Exchangeable Acidity	3	12	***33***	3	16
Exchangeable Al	3	8	7	3	6
Exchangeable Ca	***28***	***26***	15	***30***	8
Exchangeable Fe	***21***	13	16	18	8
Exchangeable K	16	18	20	13	11
Exchangeable Mg	18	***23***	10	13	***21***
Exchangeable Mn	8	5	17	8	8
Exchangeable Na	***37***	***29***	***31***	***30***	***26***
Free H	***41***	4	***38***	***23***	7

Percentage of outlying labs

	sample				
Element	**A**	**B**	**C**	**D**	**E**
Extractable Al	14	11	20	***23***	3
Extractable Ca	18	8	13	11	14
Extractable Cd	19	***35***	***25***	***36***	***24***
Extractable Cr	0	3	3	11	8
Extractable Cu	10	10	17	15	14
Extractable Fe	14	14	11	11	11
Extractable Hg	20	18	***35***	***25***	***33***
Extractable K	14	8	8	8	11
Extractable Mg	***21***	18	5	5	5
Extractable Mn	3	5	5	13	5
Extractable Na	12	15	6	15	6
Extractable Ni	13	18	10	13	15
Extractable P	11	13	11	5	5
Extractable Pb	7	7	15	12	15
Extractable S	4	11	7	7	7
Extractable Zn	12	5	5	7	20

Percentage of outlying labs

	sample				
Element	**A**	**B**	**C**	**D**	**E**
Total Al	9	***27***	9	9	10
Total Ca	18	***27***	9	18	***40***
Total Fe	9	9	9	9	20
Total K	9	9	9	9	***22***
Total Mg	9	***27***	9	18	10
Total Mn	9	18	9	***27***	10
Total Na	18	9	***36***	***27***	0
Reactive Al	11	11	7	11	0
Reactive Fe	7	7	7	11	4

Coefficients of variation

Sample						All samples	Group
Element	**A**	**B**	**C**	**D**	**E**		
Moisture	20.3	22.6	17.1	16.4	41.0	23.5	
Particle size clay	34.2	20.3	28.5	14.2		24.3	
Particle size sand	4.9	30.8	19.6	16.5		18.0	**23**
Particle size silt	37.9	28.6	23.1	13.4		25.8	
pHCaCl2	2.5	2.4	2.7	2.0	2.3	2.4	**3.2**
pHH2O	3.4	3.4	3.4	3.9	5.8	4.0	
CaCO3			45.3			45.3	**45**
OC	14.6	17.3	28.7	9.6	7.5	15.5	**16**
Total N	21.9	27.0	4.7	21.8	10.2	17.1	**17**
Exchangeable Acidity	39.7	16.1	81.1	30.0	42.9	42.0	
Exchangeable Al	35.0	26.7	90.8	29.2	37.2	43.8	
Exchangeable Ca	62.6	38.5	18.2	39.4	35.4	38.8	
Exchangeable Fe	64.3	29.5	89.3	103.1	47.1	66.7	**49**
Exchangeable K	48.7	33.3	29.2	31.5	34.7	35.5	
Exchangeable Mg	58.4	34.0	12.6	31.8	30.4	33.5	
Exchangeable Mn	29.2	27.6	85.2	25.7	36.6	40.8	
Exchangeable Na	88.7	53.3	93.2	65.9	38.3	67.9	
Free H	84.2	91.1	61.7	67.3	54.5	71.8	

Coefficients of variation (continued)

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Sample						All samples	Group
Element	**A**	**B**	**C**	**D**	**E**		
Extractable Al	14.9	13.6	17.7	14.9	25.8	17.4	
Extractable Ca	40.0	44.9	8.4	48.2	12.3	30.7	
Extractable Cd	48.7	57.1	35.8	44.6	24.9	42.2	
Extractable Cr	23.3	18.8	24.9	27.2	62.9	31.4	
Extractable Cu	9.9	14.1	11.4	14.4	48.2	19.6	
Extractable Fe	13.2	8.3	14.7	33.2	21.0	18.1	**26**
Extractable Hg	30.4	22.7	40.1	16.0	17.0	25.2	
Extractable K	43.3	22.0	36.4	45.0	22.9	33.9	
Extractable Mg	10.4	7.1	14.1	31.0	12.1	15.0	
Extractable Mn	22.4	12.6	19.0	9.4	25.5	17.8	
Extractable Na	52.3	50.4	47.6	54.0	58.9	52.6	
Extractable Ni	9.8	13.1	11.6	9.7	49.1	18.7	
Extractable P	6.7	17.3	11.1	29.7	28.4	18.7	
Extractable Pb	31.1	23.1	17.9	26.7	15.1	22.8	
Extractable S	35.9	33.0	54.2	29.5	26.1	35.7	
Extractable Zn	11.9	14.3	15.7	14.6	13.5	14.0	

Coefficients of variation (continued)

Sample						All samples	Group
Element	**A**	**B**	**C**	**D**	**E**		
Total Al	4.3	3.3	5.1	11.8	20.8	9.1	**9.0**
Total Ca	11.0	4.0	4.7	12.5	4.9	7.4	
Total Fe	8.9	4.3	4.7	4.0	19.4	8.2	
Total K	4.0	3.3	3.0	3.3	19.7	6.7	
Total Mg	6.7	2.5	6.0	2.7	8.5	5.3	
Total Mn	11.3	7.6	9.4	3.4	11.0	8.6	
Total Na	4.4	3.3	4.9	6.7	69.8	17.8	
Reactive Al	7.7	9.6	21.1	33.0	39.0	22.1	**20**
Reactive Fe	10.0	8.1	17.9	20.2	32.5	17.7	
Average per sample	**27.6**	**22.6**	**28.1**	**25.4**	**28.2**	**26.7**	

Comparison with previous RTs

	2nd FSCC RT	3rd FSCC RT	4th FSCC RT	5th FSCC RT
Group 1: Particle size distribution	NA	53	37	23
Group 2: pH	3.25	3.5	3.1	3.2
Group 3: Carbonate content	NA	206	129	45
Group 4: Organic carbon	41.5	18	13	16
Group 5: Total N	25	17	*27*	17
Group 6: Exchangeable cations	52	71	54	49
Group 7: Aqua regia extractable elements	35	47	33	26
Group 8: Total elements		21		9
Group 9: Acid oxalate extractable Fe & Al	NA	44	12	20

Data integrity expert rules or "cross checks between soil variables"

with the samples FSCC sent a list of updated data integrity expert rules:

	Organic Sample	Mineral sample
Parameter	**Rule**	**Rule**
pH($CaCl_2$)	0 < [pH(H_2O) - pH($CaCl_2$)] <= 1.2	0 < [pH(H_2O) - pH($CaCl_2$)] <= 1.2
pH(H_2O)	0 < [pH(H_2O) - pH($CaCl_2$)] <= 1.2	0 < [pH(H_2O) - pH($CaCl_2$)] <= 1.2
Organic carbon	($CaCO_3$-C)+TOC<=TC with C($CaCO_3$) = $CaCO_3$ x 0.12	($CaCO_3$-C)+TOC<=TC with C($CaCO_3$) = $CaCO_3$ x 0.12
Total N	5 < C/N ratio < 100	3 < C/N ratio < 75
$CaCO_3$	if pH($CaCl_2$) < 6.0, $CaCO_3$ = 0	if pH(H_2O) < 5, $CaCO_3$ = 0 or: if pH($CaCl_2$)<5.5, $CaCO_3$ = 0
Particle size: clay		100-clay%-silt%-sand% = 0
Particle size: silt		100-clay%-silt%-sand% = 0
Particle size: sand		100-clay%-silt%-sand% = 0
Extracted P	100 < C/P ratio < 2500	10 < C/P ratio < 750
Extracted Ca		Extracted Ca <= Total Ca
Extracted K		Extracted K <= Total K
Extracted Mg		Extracted Mg <= Total Mg
Extracted Mn		Extracted Mn <= Total Mn
Extracted Al		Extracted Al <= Total Al
Extracted Fe		Extracted Fe <= Total Fe
Extracted S	20 < C/S ratio < 1000	

Data integrity expert rules or “cross checks between soil variables”

	Organic Sample	Mineral sample
Parameter	**Rule**	**Rule**
Exchangeable acidity		EA = Al-exch+Fe-exch+Mn-exch+Free H^+
Exchangeable Ca		(Ca-exch * 200) <= Extracted Ca <= Total Ca
Exchangeable Mg		(Mg-exch*122) <= Extracted Mg <= Total Mg
Exchangeable K		(K-exch*391) <= Extracted K <= Total K
Exchangeable Na		(Na-exch *230) <= Extracted Na <= Total Na
Exchangeable Al		(Al-exch*89) <= Extracted Al <= Total Al
Exchangeable Fe		(Fe-exch*186) <= Extracted Fe <= Total Fe
Exchangeable Mn		(Mn-exch*274) <= Extracted Mn <= Total Mn
Total Al		Total Al >= Extracted Al
Total Ca		Total Ca >= Extracted Ca
Total Fe		Total Fe >= Extracted Fe
Total K		Total K >= Extracted K
Total Mg		Total Mg >= Extracted Mg
Total Mn		Total Mn >= Extracted Mn
Total Na		Total Na >= Extracted Na
Free H+		Free H^+ < Exchangeable Acidity
Reactive Fe		Reactive Fe <= Total Fe
Reactive Al		Reactive Al <= Total Al

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.

Crosschecks (1/5)

1. pH check

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

RT5:

- Lab N° 85
- Peat soils: differences between both pH measurements for 59% of the labs were greater, up to 1.5 pH units (any studies ?)

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

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

and

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

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.

RT5: pH values of samples A, B, D and E should have been below 5.0 but 3 labs did report $CaCO_3$

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**

RT5: one Lab too low (low OC) and one Lab too high (high OC)

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**

RT5: 18/35 Labs had for peat soils, C/P ratio greater than 2500

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

RT5: 9/35 labs C/P ratio was lower, one lab too high (low P)

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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.

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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.

crosschecks

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:

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

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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 %**

RT5:

rounded to one digit: 13/35 labs: OK

for most other labs: differences smaller than 1%

Lab N°55: sum of sand and silt = 100% and additionally clay

Follow up 4th FSCC Interlaboratory Comparison

See minutes 13th FSEPM:

1. Poor performing laboratories: a follow-up questionnaire
2. *FSCC indicates 1 well performing lab per region*
3. *FSCC will bring the laboratories in contact with each other*
4. If the results of the 14 German labs are much better that whole set of laboratories => German approach might be interesting
5. Poorly performing laboratory receive again material from the 4th FSCC ring test
6. Laboratories should make better use of control charts
7. FSCC will distribute FSCC reference material
8. The moisture content should always be reported together with the analytical results (to be included with the data integrity expert rules)
9. FSCC will try to have an internet platform organised to post questions, organise discussion for a, and improve the exchange of information

Follow up 4th FSCC Interlaboratory Comparison

- 9 poorly performing laboratories received the questionnaire (Labs N° 12, 18, 20, 42, 64, 71, 73, 74, 75); NFC in cc
- 8 completed the questionnaire (Lab N° 18 not)
- The NFCs of the Lab N° 18, 73, 74 and 75 decided not to have future analyses done by the concerning labs
- Lab N° 71 reanalysed the samples and FSCC re-assessed their results:
  - Between-laboratory variability: the reanalysed results were good; one outlier (Exchangeable K for sample D)
  - But no improvement on within-laboratory variability
  - After participation in 5th FSCC RT: results remain similar
- Lab N° 20 and 64 could usually identify their problems
- lab N° 12 and 42 could often not trace back the problem and had not enough experience with certain methods

Follow up 4th FSCC Interlaboratory Comparison

N° labs	Particle size	pH	CaCO3	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

Conclusions

- 48 laboratories reported their results (of 51 registrations)
- 9 laboratories reported outliers and stragglers for more than 20 % of the total:
  - 5 based on the between-laboratory variability
  - 8 based on the within-laboratory variability
- High N° of outliers:
  - (1) Exchangeable elements, especially Na, Ca, free H^+, Mg, Acidity and Fe
  - (2) Heavy metals Hg and Cd extracted by Aqua Regia, Extractable Al and Mg
  - (3) Carbon content in sample D with low organic carbon content
  - (4) pH($CaCl_2$) determination in the peat sample
- In general: more problems when the concentrations are low
- Compared to the 4th FSCC interlaboratory comparison:
  - CV have improved or remained at a similar level
  - Sample B (same sample in both RTs): CV improved by 20% (Aqua Regia extractable elements)
- Data integrity expert rules: often violations
  - The rules might need further refinement: e.g. pH in organic layer

Recommendations and follow-up

- Data integrity expert rules should be better applied
- Plausibility ranges should be respected
  - problems with reporting units will be identified!
  - FSCC recommend to set up plausibility ranges per region/ soil type
- Laboratory meetings of the heads is shown to be worthwhile
  - Meeting of the heads of the labs 9 – 10 June, Hamburg