11th Needle Leaf Interlaboratory Comparison Test

Results & Re-Qualifikation

Alfred Fürst

Forest Foliar Co-ordinating Centre

2nd Labhead Meeting

Warsaw/Poland

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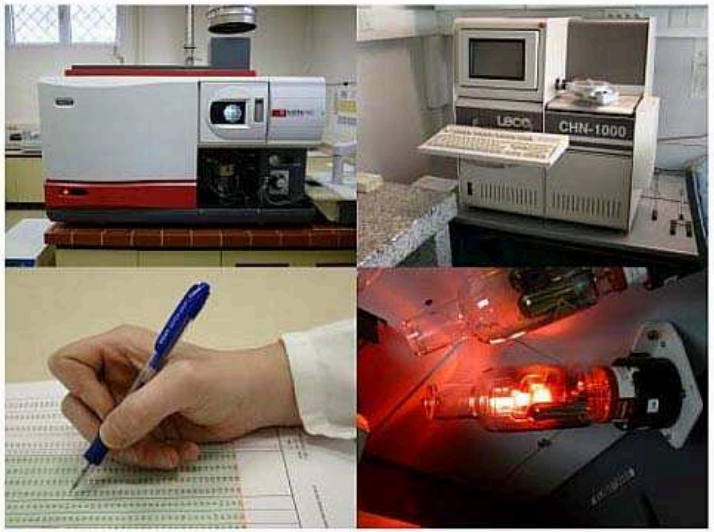
CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION
INTERNATIONAL CO-OPERATIVE PROGRAMME ON ASSESSMENT AND
MONITORING OF AIR POLLUTION EFFECTS ON FORESTS

United Nations
Economic Commission
for Europe

LIFE + / QA-RFoliar 09

11th Needle/Leaf Interlaboratory Comparison Test 2008/2009



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11th Ringtest - Timetable

- Information of the participants (April 2008)
- Deadline registration (2008-07-04)
- Submission of the test samples (July 2008)
- Deadline of data submission (2009-01-04)
- First results (2009-01-19)
- Qualification Reports (Febuary/March 2009)
- Final Report / QA-Rfoliar09 (February/March 2009)
- *Re-qualification started (decided in Hamburg in January 2009)*
- *Re-qualification finished (Deadline **2009-10-01**)*

Sample material

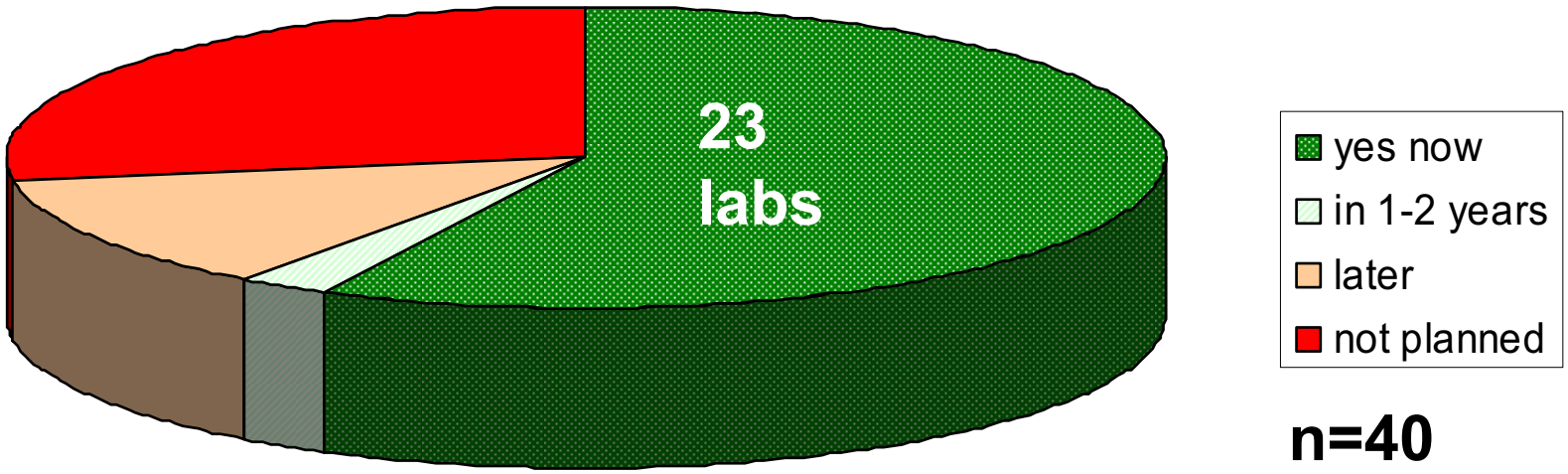
- Pine branches - Finland
- Pine needles (Pinus brutia) - Turkey
- Maple leaves - Austria
- Spruce needles – Finland (= Sample 1 from 3rd Test)

Special thank to John Derome (Finland) and Mehmet Sayman (Turkey) and their employees for sampling and preparing samples for this ringtest!

Countries/Laboratories

Interlaboratory Comparison Test	Number of countries	Number of laboratories
1st	21	24
2nd	25	39
3rd	29	51
4th	29	52
5th	29	53
6th	26	46
7th	23	43
8th	30	52
9th	28	53
10th	29	54
11th	28	56

Accreditation status (EN 17025)



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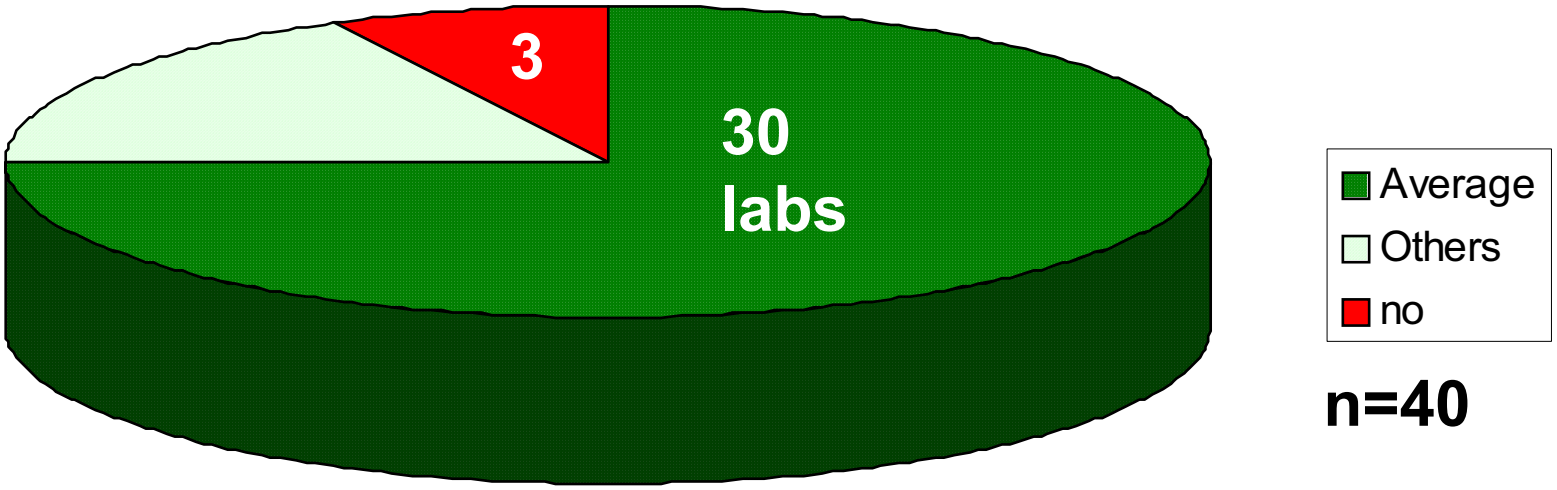
Usage of contol chats



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Comparison between 3rd and 11th Interlaboratory Comparison Test

Element (Unit)	3rd Interlaboratory Comparison Test 1997/98 (Sample 1) Mean	*Number of Labs*	11th Interlaboratory Comparison Test 2008/09 (Sample 4) Mean	*Number of Labs*
Nitrogen (mg/g)	11,74	*45*	11,73	*48*
Sulphur (mg/g)	0,91	*46*	0,91	*47*
Phosphorus (mg/g)	1,56	*50*	1,59	*51*
Calcium (mg/g)	3,55	*49*	3,48	*51*
Magnesium (mg/g)	1,33	*49*	1,33	*51*
Potassium (mg/g)	5,18	*50*	5,23	*50*

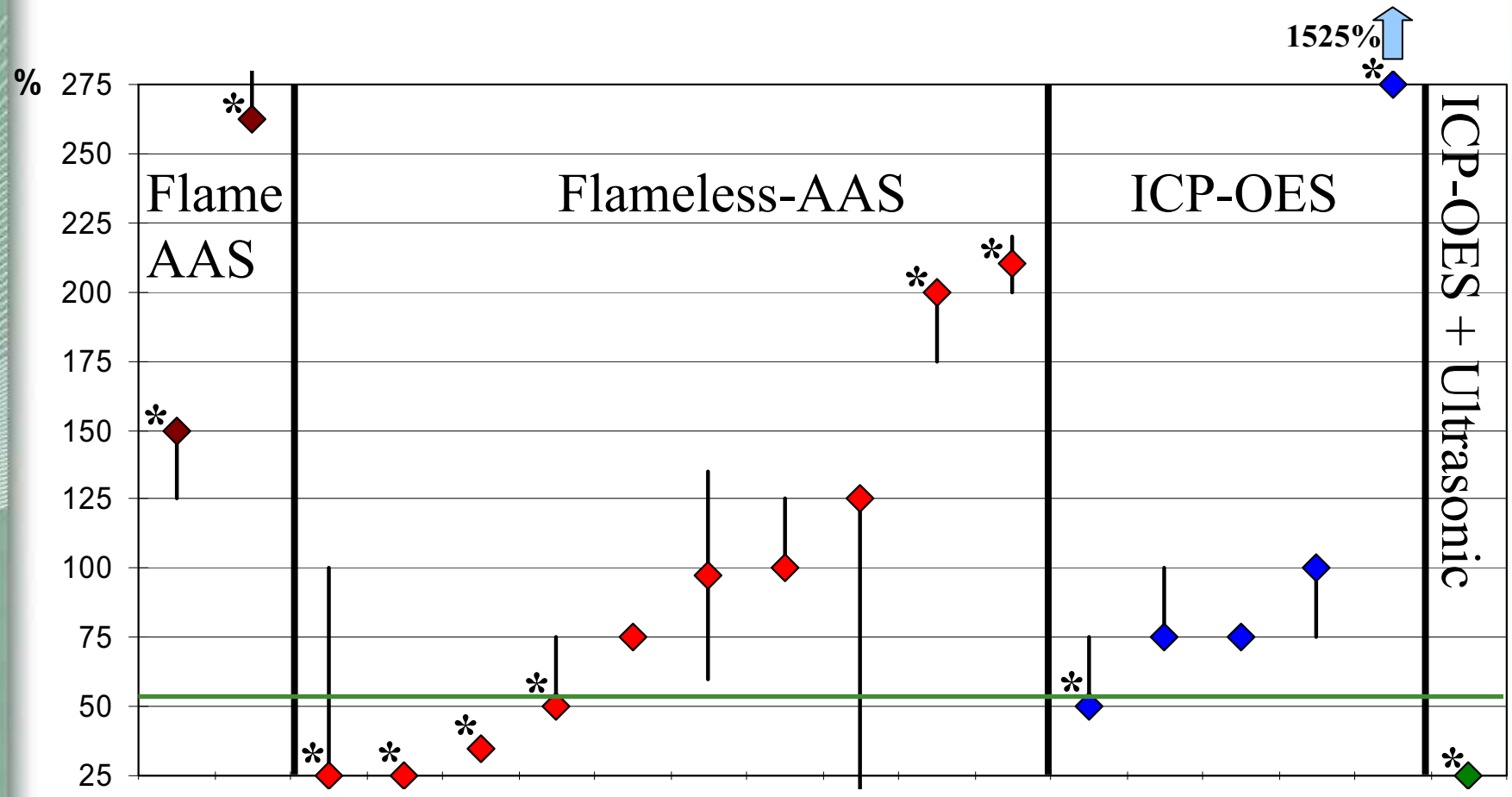
Comparison between 3rd and 11th Interlaboratory Comparison Test

Element (Unit)	3rd Interlaboratory Comparison Test 1997/98 (Sample 1) Mean	*Number of Labs*	11th Interlaboratory Comparison Test 2008/09 (Sample 4) Mean	*Number of Labs*
Zinc (µg/g)	24,75	*45*	25,09	*41*
Manganese (µg/g)	338,2	*46*	334,9	*42*
Iron (µg/g)	45,45	*45*	44,56	*40*
Copper (µg/g)	2,65	*38*	2,52	*41*
Lead (µg/g)	0,40	*18*	0,21	*12*
Cadmium (ng/g)	36,60	*13*	20,49	*16*
Boron (µg/g)	8,58	*23*	7,91	*21*
Carbon (g/100g)	50,96	*17*	51,38	*37*

Comparison between 3rd and 11th Interlaboratory Comparison Test

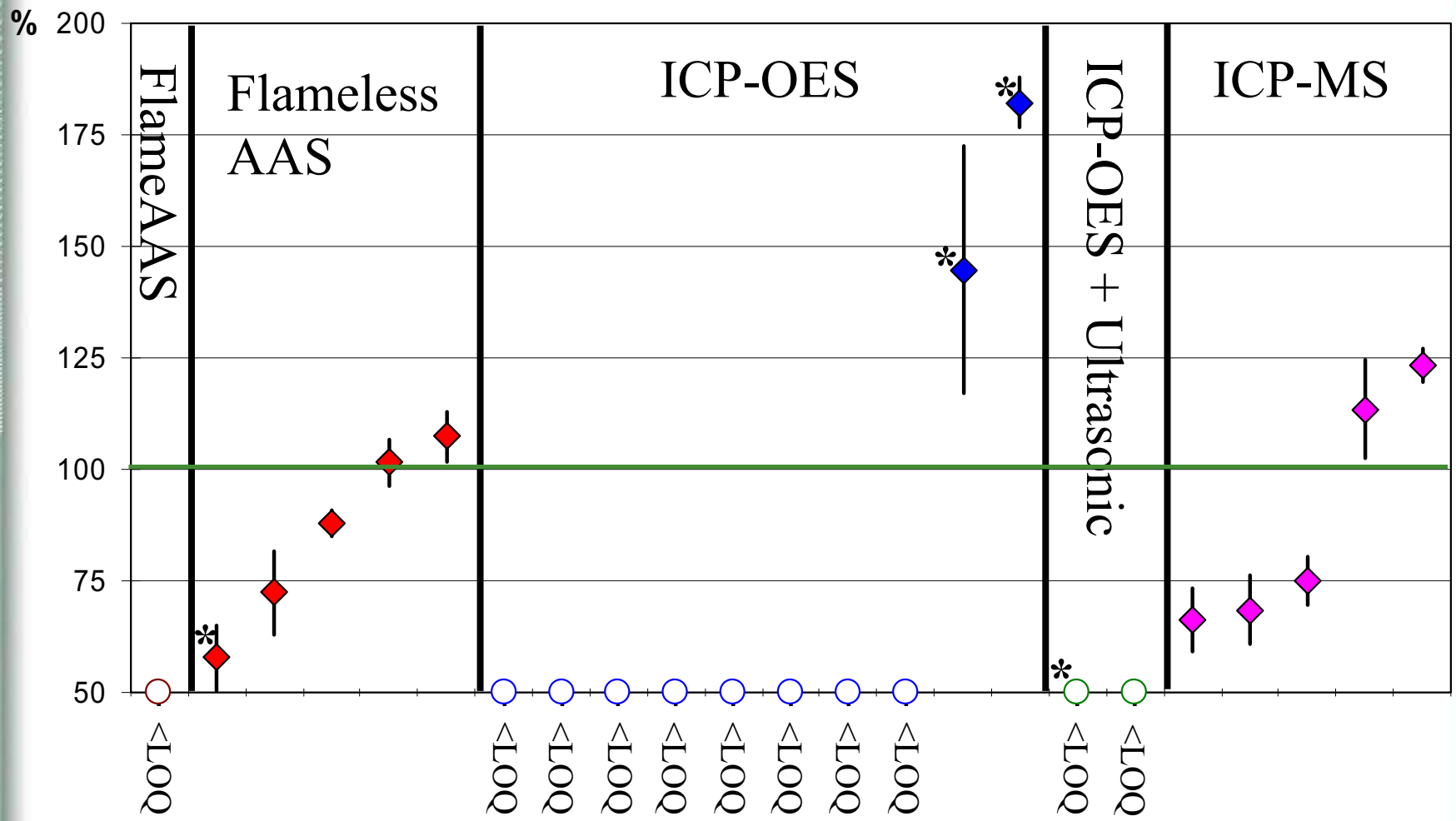
- Most of the results are very good comparable
- Only the Cd and Pb results show small differences (lowerer results in 2008/2009)
  - Low concentration
  - Progress in analytical chemistry (1997 to 2008) (instrumentation and knowledge)
  - Avoid open digestion method, use of GF-AAS and ICP-MS

3rd Test - 1997/1998 („0.40 Pb mg/kg“)



* Outside of the tolerable limits

11th Test - 2008/2009 („0.21 Pb mg/kg“)



Tolerable limits

Element	Tolerable deviation from mean in %	for concentrations above
N	**90-110**	**5mg/g**
S	**85-115**	**0.5mg/g**
P	**90-110**	**0.5mg/g**
Ca	**90-110**	**3mg/g**
Mg	**90-110**	**0.5mg/g**
K	**90-110**	**1mg/kg**
Mn, Zn	**85-115**	**20 μ g/g**
Cu	**80-120**	**-**
Fe	**80-120**	**20 μ g/g**
Pb	**70-130**	**0.5 μ g/g**
B	**80-120**	**5 μ g/g**
Cd	**70-130**	**-**
C	**95-105**	**-**

Tolerable limits for low concentrations

Element	Tolerable deviation from mean in %	for concentrations below
N	85-115	5mg/g
S	80-120	0.5mg/g
P	85-115	0.5mg/g
Ca	85-115	3mg/g
Mg	85-115	0.5mg/g
K	85-115	1mg/kg
Zn	80-120	20 μ g/g
Mn	80-120	20 μ g/g
Fe	70-130	20 μ g/g
Pb	60-140	0.5 μ g/g
B	70-130	5 μ g/g

Element	Tolerable limits (± %)	10th Labtest 2007/2008		11th Labtest 2008/2009	
		Non tolerable (%)	Number of mean values	Non tolerable (%)	Number of mean values
N	10	**2,6**	*196*	**10,4**	*192*
S	15	**15,4**	*188*	**14,4**	*188*
P	10	**13,2**	*204*	**14,2**	*204*
Ca	10	**17,2**	*204*	**19,1**	*204*
Mg	10	**10,8**	*204*	**18,6**	*204*
K	10	**16,8**	*208*	**17,5**	*200*
Zn	15	**10,2**	*176*	**6,7**	*164*
Mn	15	**2,8**	*180*	**6,5**	*168*
Fe	20	**5,7**	*176*	**13,1**	*160*
Cu	20	**4,9**	*164*	**17,1**	*164*
Pb	30	**13,0**	*100*	**9,8**	*92*
B	20	**13,5**	*96*	**12,5**	*88*
Cd	30	**17,0**	*100*	**7,7**	*104*
C	5	**3,2**	*156*	**16,9**	*148*

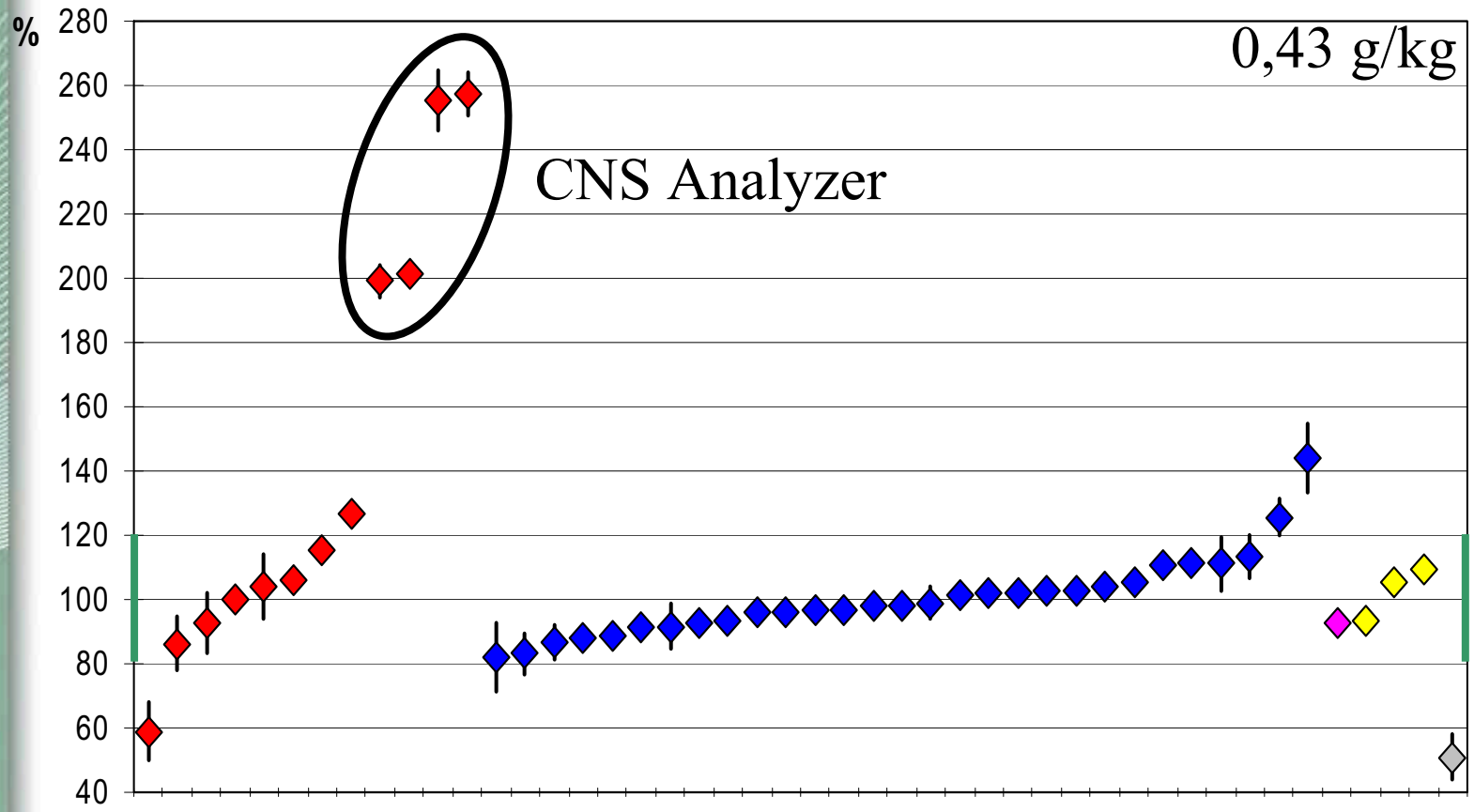
Mean element concentrations and percentage of non-tolerable results

Parameter	Unit	Sample 1 Pine branches	Sample 2 Pine needles- *Pinus brutia*	Sample 3 Maple leaves	Sample 4 Spruce needles
N	mg/g	3,23	12,6	21,15	11,73
	%	22,92	**8,33**	**6,25**	**6,25**
S	mg/g	0,43	1,81	2,63	0,91
	%	21,28	**12,77**	**12,77**	**10,64**
P	mg/g	0,14	1,46	1,37	1,59
	%	23,53	**11,76**	**11,76**	**9,80**
Ca	mg/g	2,67	6,15	22,12	3,48
	%	**19,61**	**23,53**	**15,69**	**17,65**
Mg	mg/g	0,23	1,85	3,05	1,33
	%	29,41	**17,64**	**13,73**	**13,73**
K	mg/g	0,38	4,27	9,18	5,23
	%	28,00	**14,00**	16,00	**12,00**

Mean element concentrations and percentage of non-tolerable results

Element	Unit	Sample 1 Pine branches	Sample 2 Pine needles- *Pinus brutia*	Sample 3 Maple leaves	Sample 4 Spruce needles
Zn	µg/g	28,73	30,64	34,14	25,09
	%	7,32	4,88	4,88	9,76
Mn	µg/g	104,4	52,37	97,51	334,9
	%	7,14	4,76	4,76	9,52
Fe	µg/g	240,2	243	108,6	44,56
	%	32,50	2,5	5,00	12,5
Cu	µg/g	2,96	2,88	7,39	2,52
	%	24,39	17,07	4,88	21,95
Pb	µg/g	6,93	5,41	0,49	0,21
	%	8,70	4,35	8,70	17,39
Cd	ng/g	246,2	161,8	62,89	20,49
	%	3,85	3,85	3,85	15,38
B	µg/g	3,43	19,35	60,72	7,91
	%	22,73	9,09	0,00	18,18
C	g/100g	52,01	51,67	48,3	51,38
	%	18,92	16,22	16,22	16,22

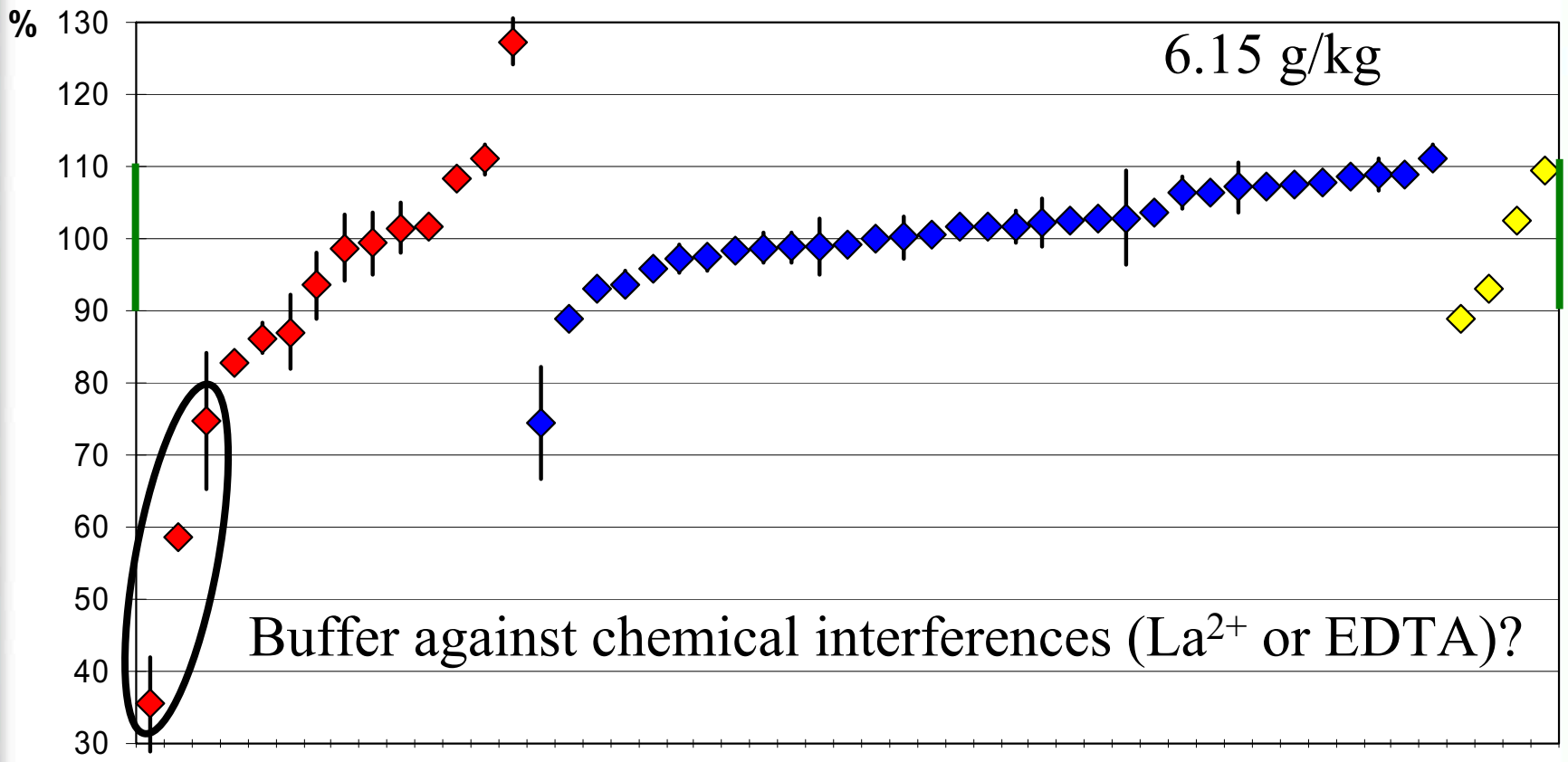
Sulphur - Determination (Sample 1)



Pine branches

- Element-analyzer
- ICP-OES
- ICP-MS
- X-Ray
- Turbidimetry

Calcium - Determination (Sample 2)

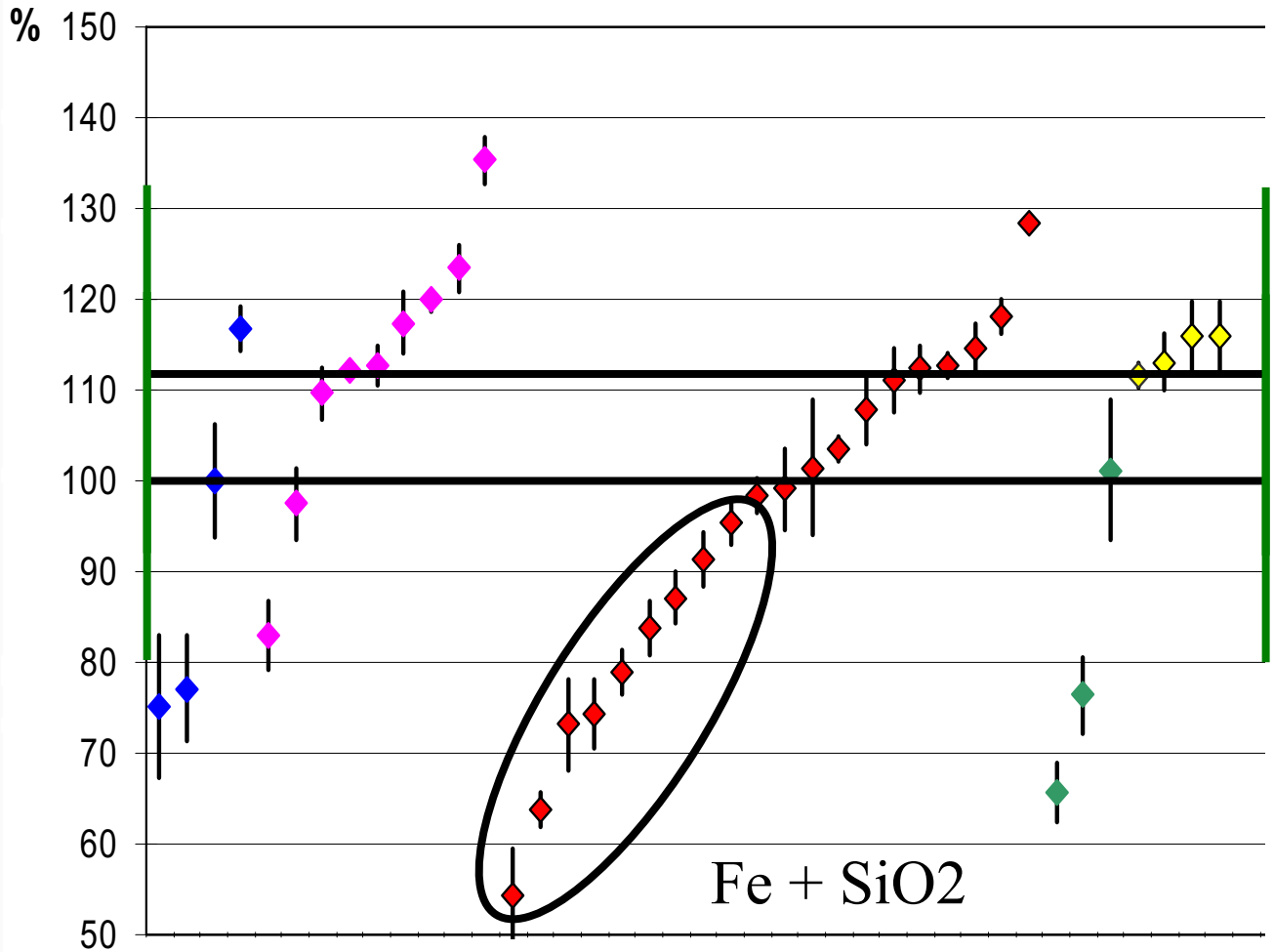


Pine needles (pinus brutia)

Iron – Pretreatment methods (*pine branches*)

Method	mg/kg Mean	Std.dev.
Dry ashing (3)	195	39
Open digestion (4)	222	44
Microwave (20)	229	46
Pressure digestion (9)	270	35
Pellets and X-Ray (3)	273	9

Iron - Digestion method (Sample 1)

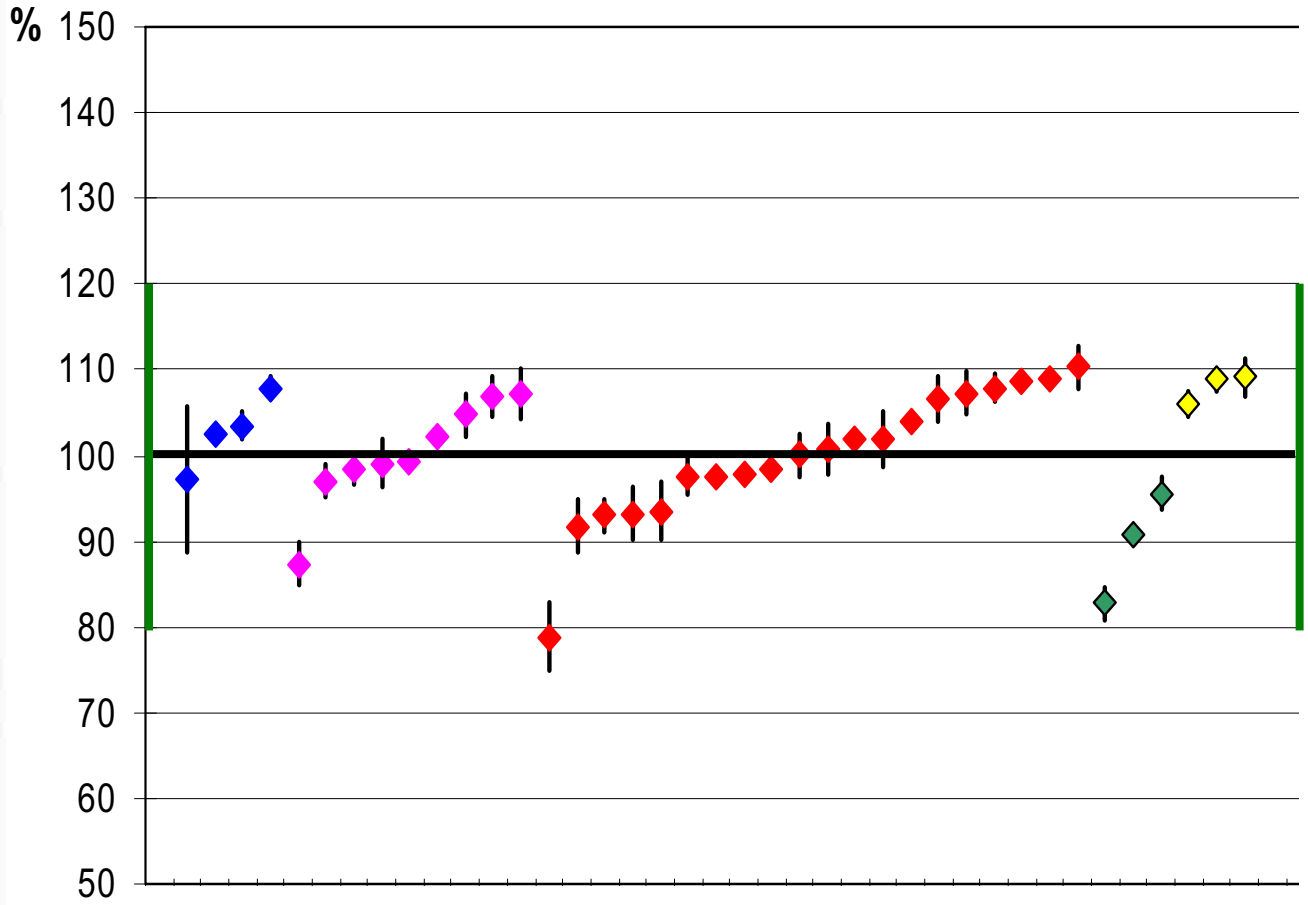


240,2 mg/kg

Pine branches

- Open digestion
- Pressure digestion
- Microwave
- Dry ashing
- Pellets (X-Ray)

Iron - Digestion method (Sample 2)

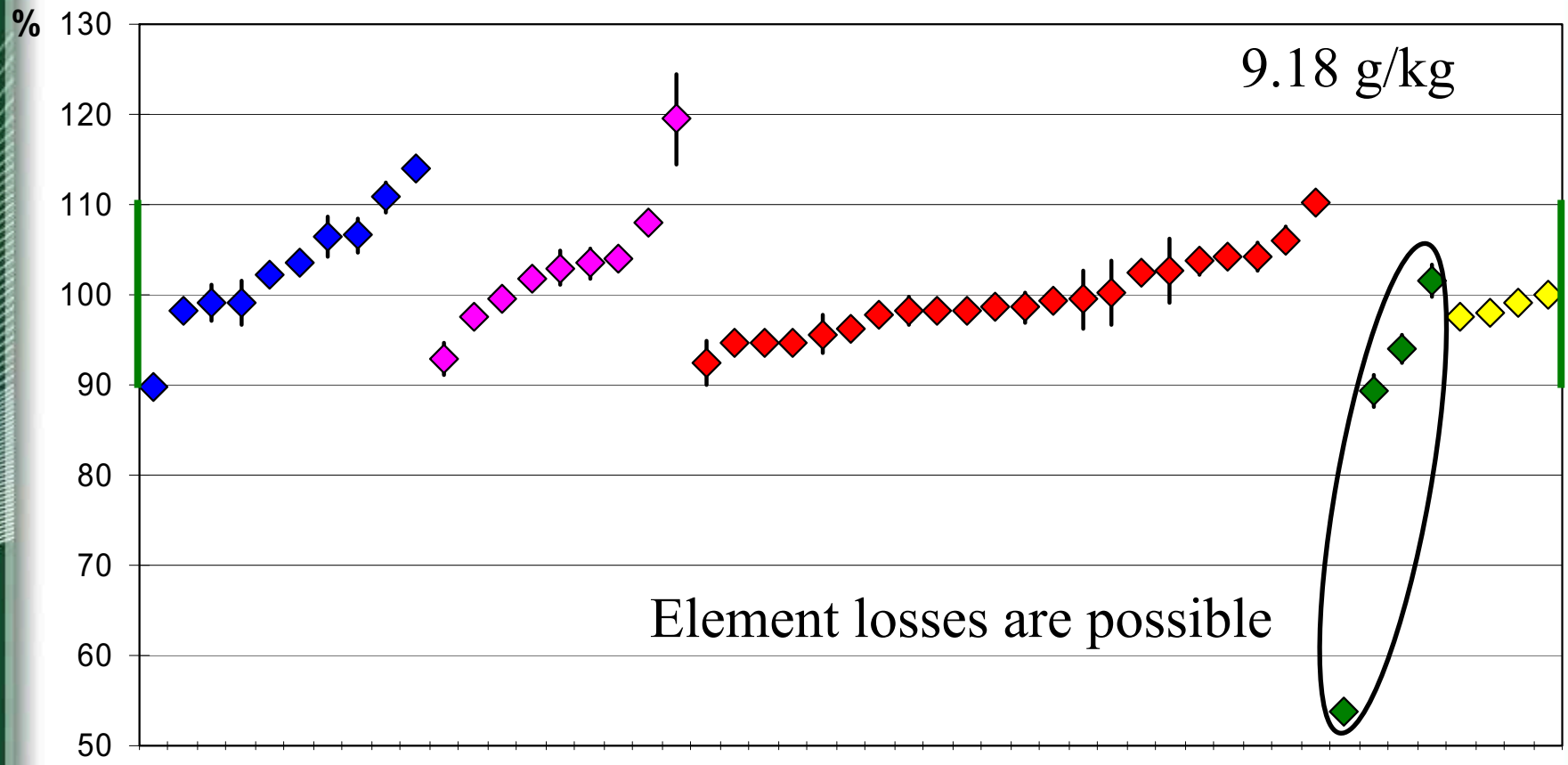


243,0 mg/kg

Pine needles (pinus brutia)

- Open digestion
- Pressure digestion
- Microwave
- Dry ashing
- Pellets (X-Ray)

Potassium - Digestion (Sample 3)



Open digestion
Pressure digestion
Microwave
Dry ashing
Pellets (X-Ray)

Maple leaves

Decrease of non-tolerable Results

- **Zn** **(6.7% non tolerable)**
  - avoid of contamination
  - avoid of open digestion methods
- **Pb** **(9.8% non tolerable)**
  - avoid of contamination
  - avoid of open digestion methods
  - LOQ fixed and used from more laboratories (ICP-OES not sensitive enough!)
- **Cd** **(7.7% non tolerable)**
  - avoid of contamination
  - avoid of open digestion methods
  - LOQ fixed and used from more laboratories

Feedback from the laboratories - Reasons for wrong results

- New instrument / methodic problem (4 labs)
- Too small sample weight for element-analyzer → „wrong“ instrumentation (2 labs)
- Old instrumentation (2 labs)
- Wrong calibration (4 labs)
- No reason found (3 labs)
- Wrong blanks / contamination (3 labs)
- Submit results in wrong units (5 labs)
- Wrong/no moisture correction (5 labs)

„Common“ Instrumentation

- **N, C and (S)**: Element-analyzers
- **S, P, Ca, Mg, K, Mn, Zn, Fe, Cu, B**: Pressure or Microwave digestion & ICP-OES
- **Pb and Cd**: Pressure or Microwave digestion & ICP-MS, Flameless-AAS

Instrumentation

- Buy „good & common“ well known instruments which is used from other laboratories too
- Use Google group QA/QC to inform yourself about different instruments
- Laboratory assistance programme
- 40 laboratories submit their instrumentation information for the needle/leaf Interlaboratory test – each participant get detailed information about the instrumentation (type & companies)
- **For a new instrument a training course is needed!**

Wrong Units

Nitrogen [mg/g] - approximate range: 5.00 - 40.00 mg/g

	Replicate 1	Replicate 2	Replicate 3	Replicate 4
Sample 1 (*Spruce needles*)				
Sample 2 (*Oak leaves*)				
Sample 3 (*Bears garlic*)				
Sample 4 ()				

Pretreatment: 0 - No information

Determination: 0 - No information

Level II/FutMon (Foliage or Litter): ☐

STORE RESULTS | RESET FORM | BACK

Moisture Correction

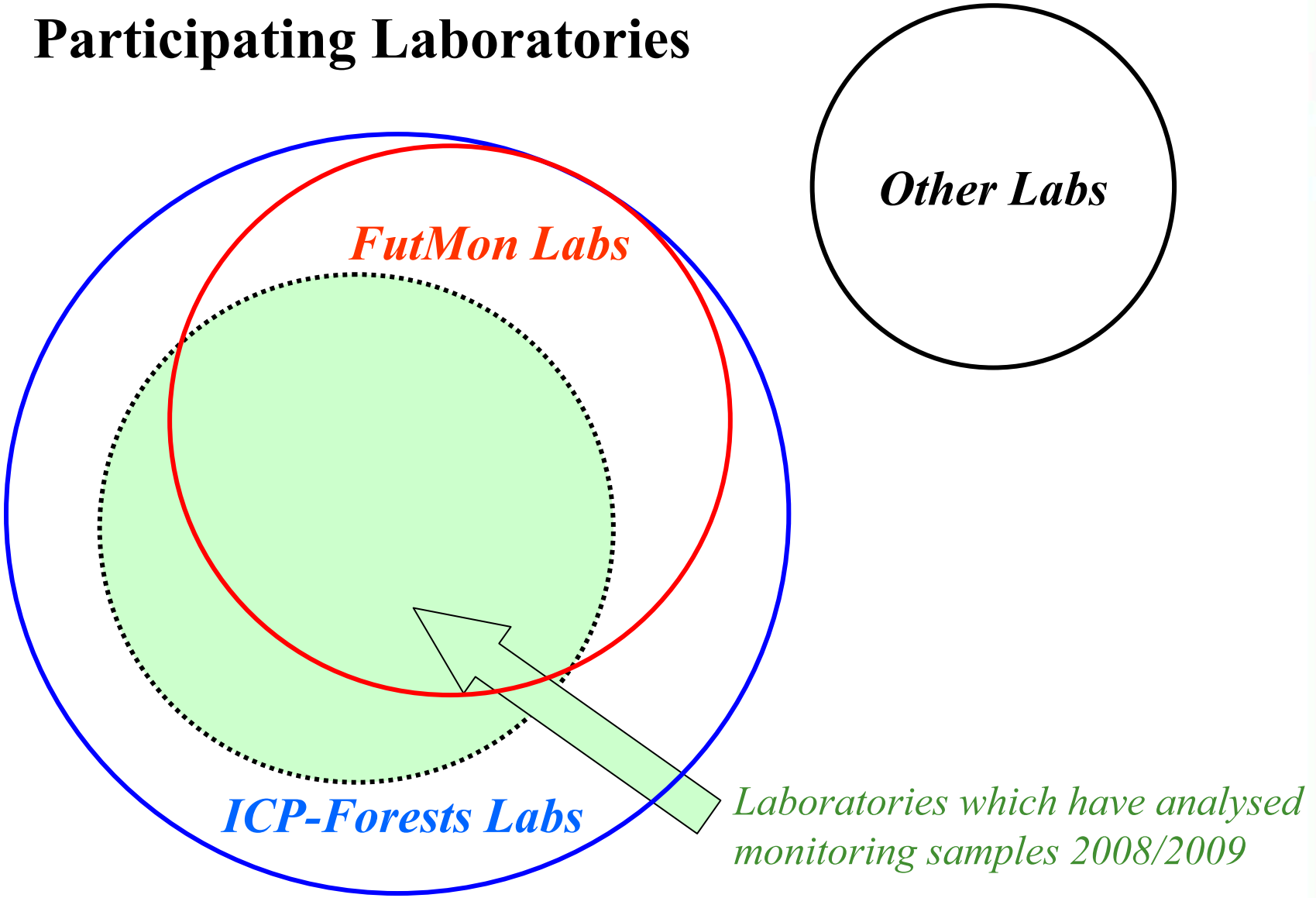
- All results should be reported on **dry matter 105° C**

- Moisture correction factor must be always **greater than 1**!

Factor = wet weight / dry weight

Re-Qualification Process

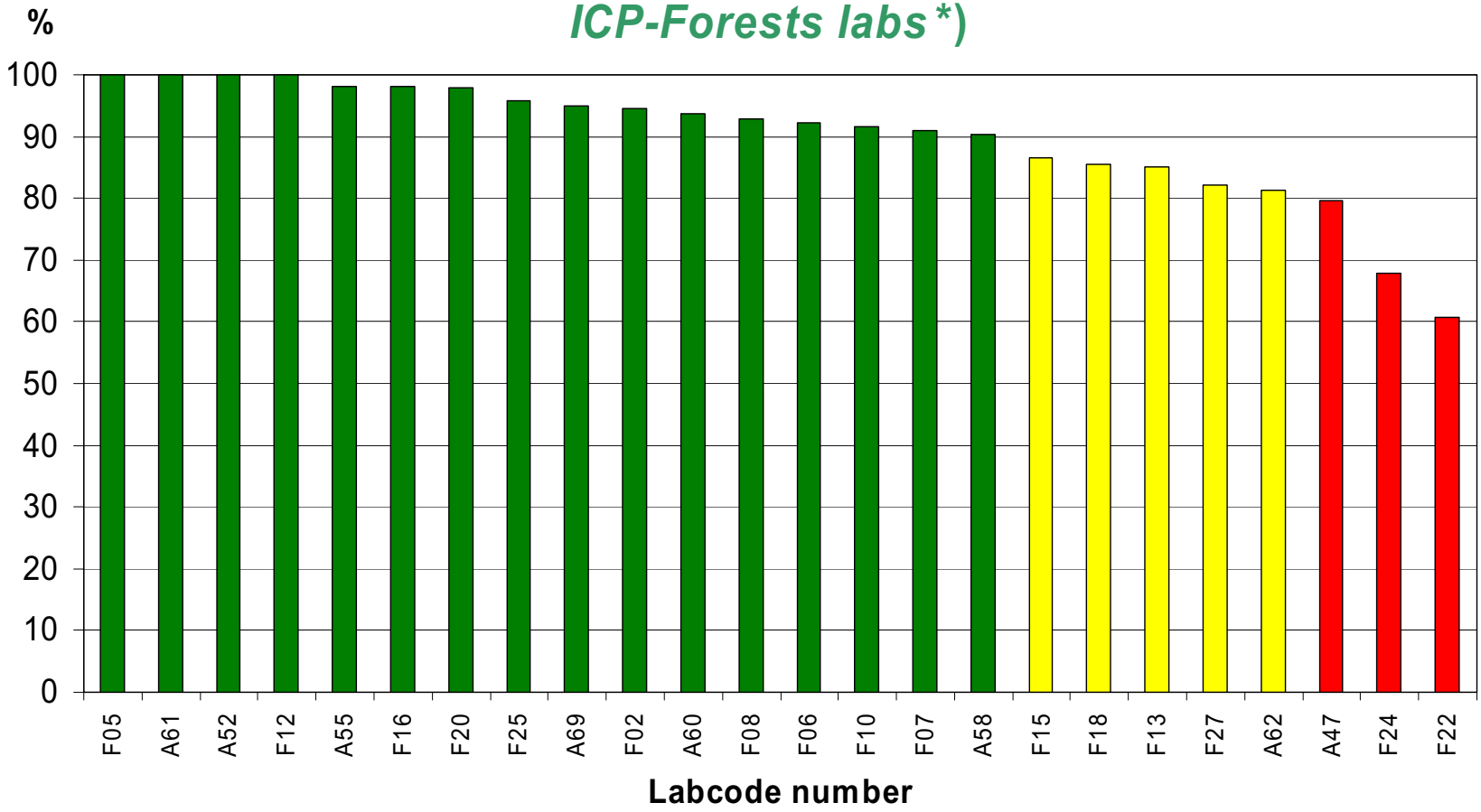
Participating Laboratories



Results per Laboratory

11th Ringtest / Percentage of correct results

ICP-Forests labs)*



*) Laboratories which have analysed 2008/2009 monitoring samples for ICP-Forests

Laboratories with „problems“

failed with	all labs	„*ICP-Forests*“ labs *)
1 element	15	6
2-3 elements	6	1

*) Laboratories which have analysed 2008/2009 monitoring samples for ICP-Forests

*ICP-Forests**) Laboratories with problems

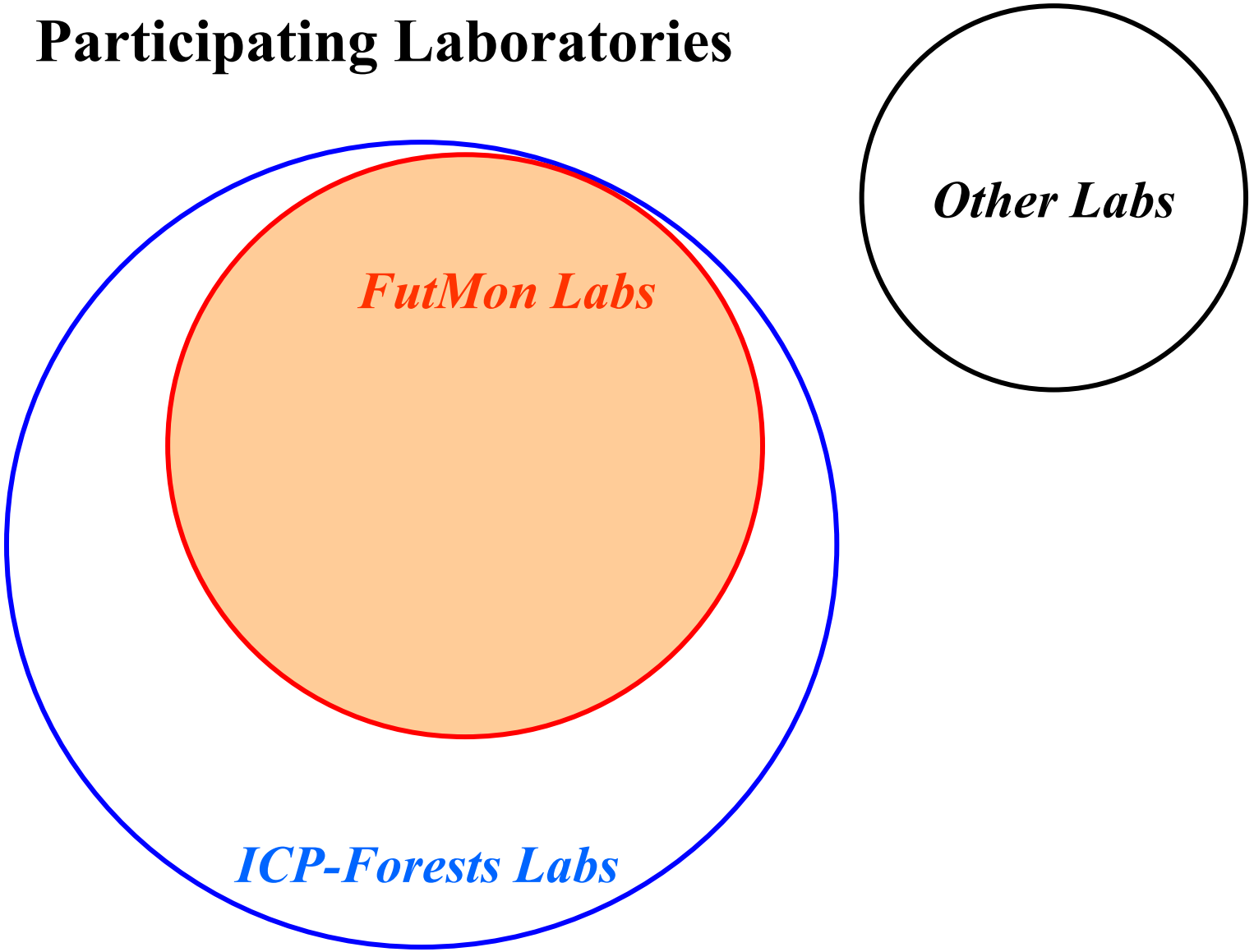
New Code	Country	failed with	Madatory param. not analyzed
F22	Italy	**P, K, Ca**	
F24	Latvia	**S**	
A47	Begium/Wallonia	**C**	
F18	Estonia	**C**	
F15	Germany	**C**	
F08	Germany	Cu	
A60	Denmark	Cu	N
A62	Croatia		Ca, Mg, K

*) Laboratories which have analysed 2008/2009 monitoring samples for ICP-Forests

Re-Qualification Process

FutMon labs

Participating Laboratories



Re-qualification

- The laboratory **must participate** for all **mandatory parameters** (N, S, P, Ca, Mg, K, C)
- It has been decided to **qualify** the results of **each parameter separately**
- If **50% or more** of the results for this parameter for all the samples of the ringtest are within the tolerable limits, the laboratory is **qualified**.
- **Re-qualification is mandatory for laboratories of the FutMon partners and recommended for ICP-Forests laboratories**

Re-qualification

- The report should be sent to FFCC (add the laboratory code number on your report!). A form for the re-qualification report can be downloaded from www.ffcc.at
- In case there is not enough sample material left – FFCC will send additional ringtest sample material.
- The ringtest samples should be **re-analyzed** and **all printouts, sample weights, dilution factors** and **calibration factors** should be submitted too.
- If the reason for the wrong results is a decimal error in the data submission or some other miscalculation, a short statement is enough.
- FFCC will send an updated qualification report to the laboratory and inform PCC.

Labs of the FutMon Beneficiaries

- 33 laboratories
- 19 are qualified and 14 laboratories failed (not tolerable results or no participation)
- 10 of the 14 laboratories has passed the re-qualification
- What is with the rest (4 laboratories)???

Status 1st of October 2009

FutMon Beneficiaries - Problems with Mandatory Parameters

FutMon Beneficiary	Labcode new	N	S	P	Ca	Mg	K
		mandatory parameters					
003	F03						>>>
008	A60	n.a.	>				<
012	A43		n.a.	<<	>>>>	<<<	>>>
013	F21	>>>	n.a.	<<	>>>	>	<
020	F26	>>>>	>>>>	>>>>	<<<	<<<>	<<>>
020	F01	>	n.a.		<<>>	<	<<<<
021	F28		<<>				>
023	F17	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
038	F24	>	<<<<		<	<	<
040	F22	<	>	<<<	<<<	<<<	

n.a. = not analyzed

FutMon Beneficiaries - Problems with Optional Parameters

FutMon Beneficiary	Lab-code new	Zn	Mn	Fe	Cu	Pb	B	Cd	C
		optional parameters							
008	A60				<<<		n.a.		n.a.
009	F18			<	<<	n.a.			<<<<
012	A43	>>>>	<<<	n.a.		n.a.	n.a.	n.a.	n.a.
013	F21	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	>>>>
021	F28			>>	>>>>	n.a.	<<	n.a.	
028	F15						n.a.		<<<<
031	F08				>>>				
034	F11			<<<	<>>		n.a.	>	

n.a. = not analyzed

Not qualified *FutMon* labs

- Denmark (A60): Cu
- Greece (A43): **S**, **Ca**, **Mg**, **K**, Zn, Mn
- Hungary (F21): **S**
- Romania (F01): **S**

Status 1st of October 2009

12th Needle Leaf Interlaboratory Comparison Test

Alfred Fürst

Forest Foliar Co-ordinating Centre

2nd Labhead Meeting

Warsaw/Poland

2009-10-12

12th Ringtest -Timetable

- Information of the participants (March/April 2009)
- Deadline registration (2009-07-06)
- Submission of the test samples (July 2009)
- Deadline of data submission (Deadline 2010-01-03)
- First results (January 2010)
- Qualification Reports (Febuary/March 2010)
- Final Report / QA-Rfoliar09 (February/March 2010)
- Requalification finished (2010-10-01)

Sample material

1. Spruce needles
2. Oak leaves
3. Bears garlic
4. Spruce needles

Special thank to John Derome (Finland), Mireille Barbaste (France), Peter Waldner (Switzerland) and their employees for collecting and prepairing samples for this ringtest.

Good ~~luck~~ for your 12th ringtest participation!

Your good results in the 12th ringtest will be based on:

- Your better **kowledge**,
- Your good **instrumentation** and
- **QA/QC** in daily routine

Thank you for your attention!

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