7th WRT 2015 for deposition and soil solution

WG QA/QC, 17-18th September, 2015
Vienna

Kirsti Derome
Natural Resources Institute Finland (Luke), Oulu

- General
- Samples
- Results
- Requalification
- Conclusions

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Participants …

- 39 laboratories from 25 countries (40/ 22 in 6th WRT)

  2 new labs/ 1 new country registered too late (sent results only for requalification)

- Number of participants has stayed quite stabile during ten years time of WRT's, slightly decreasing (2002, 2005, 2009, 2010, 2011, 2013, 2015)

- Would be good to know/ follow what laboratories are analysing samples for the programme, and the changes happening in the countries

WRT participants 2009 -2015

Country	2009	2010	2011	2013	2015	Notes!	
Austria				A83			
Austria	D02	D02	D02				
Austria				F02	F02		
Austria			S01	S01	S01		
Belgium - Wallonia	A47		A47	A47	A47		
Belgium/Flanders	F03	F03	F03	F03	F03		
Bulgaria	D05	D05	D05	D05	D05		
Bulgaria	D06	D06	D06	D06	D06		
Canada				D69	samples from Ireland		
Croatia	A62						
Cyprus	F04	F04	F04	F04	F04		
Czech Republic	F05	F05	F05	F05	F05		
Denmark	A60	A60	A60	A60	A60		
Estonia	F18	F18	F18	F18	F18		
Finland	S03	S03	S03	S03	S03		
France	D12		D12				
France					D70	new lab	
Germany	A52	F32	F32	F32	F32		
Germany	A55			A55		F12	
Germany	D24	D24	D24	D27	D27		
Germany	D26/ S25	S25	S25	S25	S25		
Germany	F06	F06	F06	F06	F06		
Germany	F07	F07	F07	F07	F07		
Germany	F08	F08	F08	F08	F08		
Germany	F10	F10	F10			F12	
Germany	F12	F12	F12	F12	F12		
Germany	F14	F14	F14	F14	F14		
Germany	F15	F15	F15	F15	F15		
Germany	F16	F16	F16	F16	F16		
Greece	A43	A43	A43		A43		
Hungary	F21	F21	F21	F21	F21		
Ireland	A69	A69					
Ireland					D71		
Italy	D32	D32	D32	D32			
Italy	D33	D33	D33	D33			
Italy	D34	D34	D34	D34	D34		
Italy	D35	D35	D35	D35	D35		
Latvia	F24	F24	F24		F24		
Lithuania	F23	F23	F23	F23	F23		
Netherlands	F30	F30					
Norway	D39	D39	D39	D39	D39		
Norway			D59				
Poland	F25	F25	F25	F25			
Romania	F01	F01	F01	F01	F01		
Russia	A39	A39	A39	A39	A39		
Russia	A40	A40					
Russia	A71	A71	A71				
Russia				D68	commercial Shimadzu lab!		
Slovakia	F28	F28	F28	F28	F28		
Slovenija	F27	F27	F27	F27	F27		
Spain			D63		D63		
Spain	F17	F17	F17				
Sweden	D47	D47		D47			
Sweden	D48	D48					
Sweden				D60	D60		
Switzerland	A49	A49	A49	A49	A49		
Turkey					A85	new lab	
UK	A61	A61	A61	A61	A61		
	48	43	43	41	39		

In some countries labs are changing

- Difficult to know if there's same lab with a new name/ contact person (D48/ D60)
- Changes in German labs was well informed
- Problems when contacting labs for the next ring test
- Problems with trend analysis

Labs not participating to every ring test

- Information about the reason why not participate

Better information to expert panel members/ NFC's

Samples

- Natural samples

Sample 1. Deposition from Denmark

Sample 2. Deposition from UK

Sample 3. Deposition from Finland

Sample 4. Soil solution from Belgium

Sample 5. Soil solution from Finland

- Synthetic sample

SYN 6. For measuring alkalinity only

Stability of the samples

- The samples were analysed once in a month from December 2014 to May 2015 to check their stability

- Problems only in sample 1 (DOC median in ring test 2,92mg/l, $mean_{stability}$ 2,36 mg/l for whole period; $mean_{stability}$ (from Dec to March) 2,80 mg/l)
  - May have influence to requalification measurements done in April and May (Lab D70 analysed 18th May, not passed)

- Keep samples in refrigerator, no freezing!
- Acidify samples for ICP or AAS measurement at once after delivery

Problems with samples 1

Sample 1:

high pH, decreased by acid to 5,8 for stability reason, pH > 6 again from January on (stability measurements ok), Nitrite-N > Nitrate-N, DOC and DN decreased during January to April

Phosphate-P excluded because of low concentration

Sample 3:

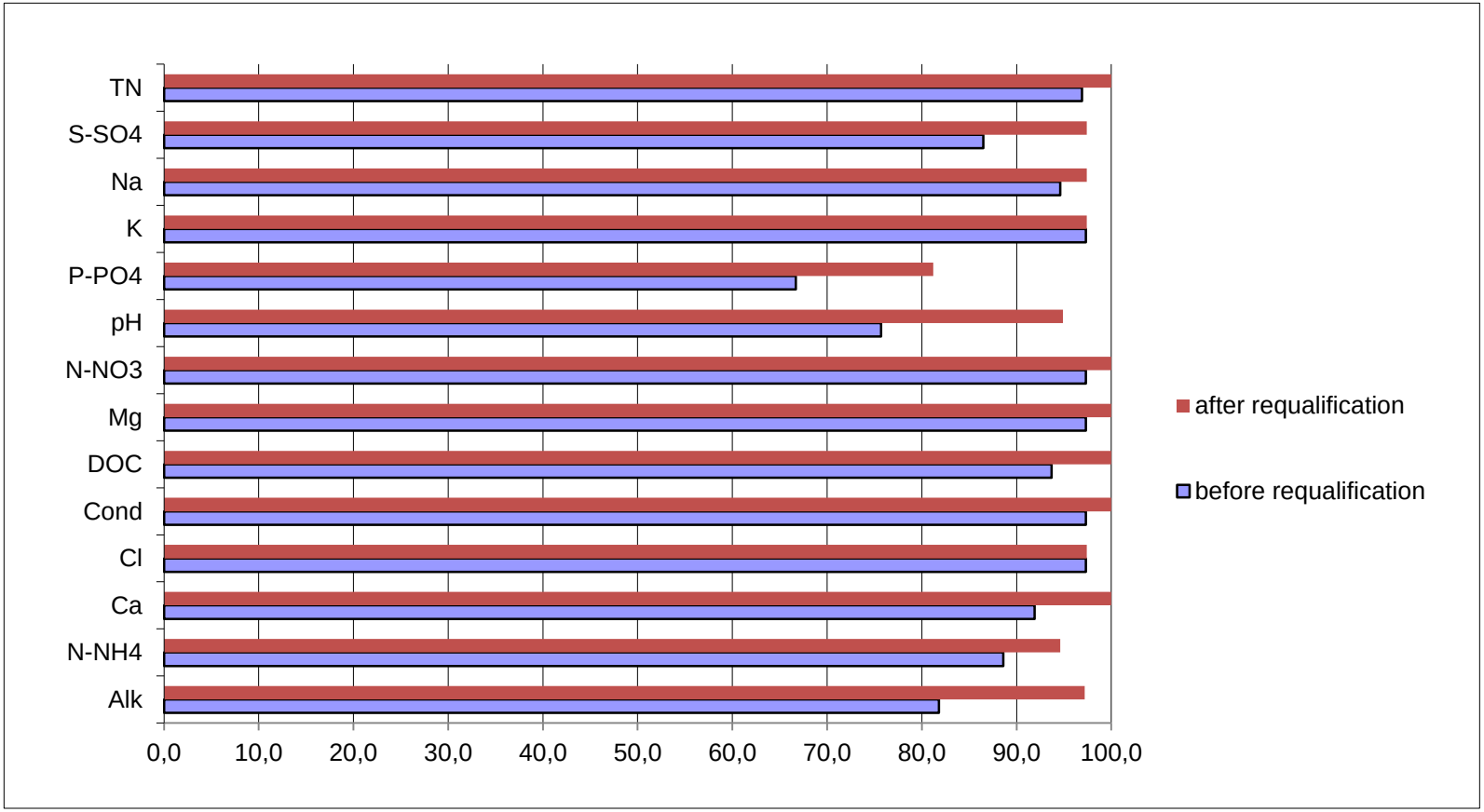
Ammonium-N, Nitrate-N, Phosphate-P and total Nitrogen excluded because of low concentrations

Sample 2, 3 and 4:

Alkalinity excluded (Samples 2 and 4 pH<5, Sample 3 pH 5,3)

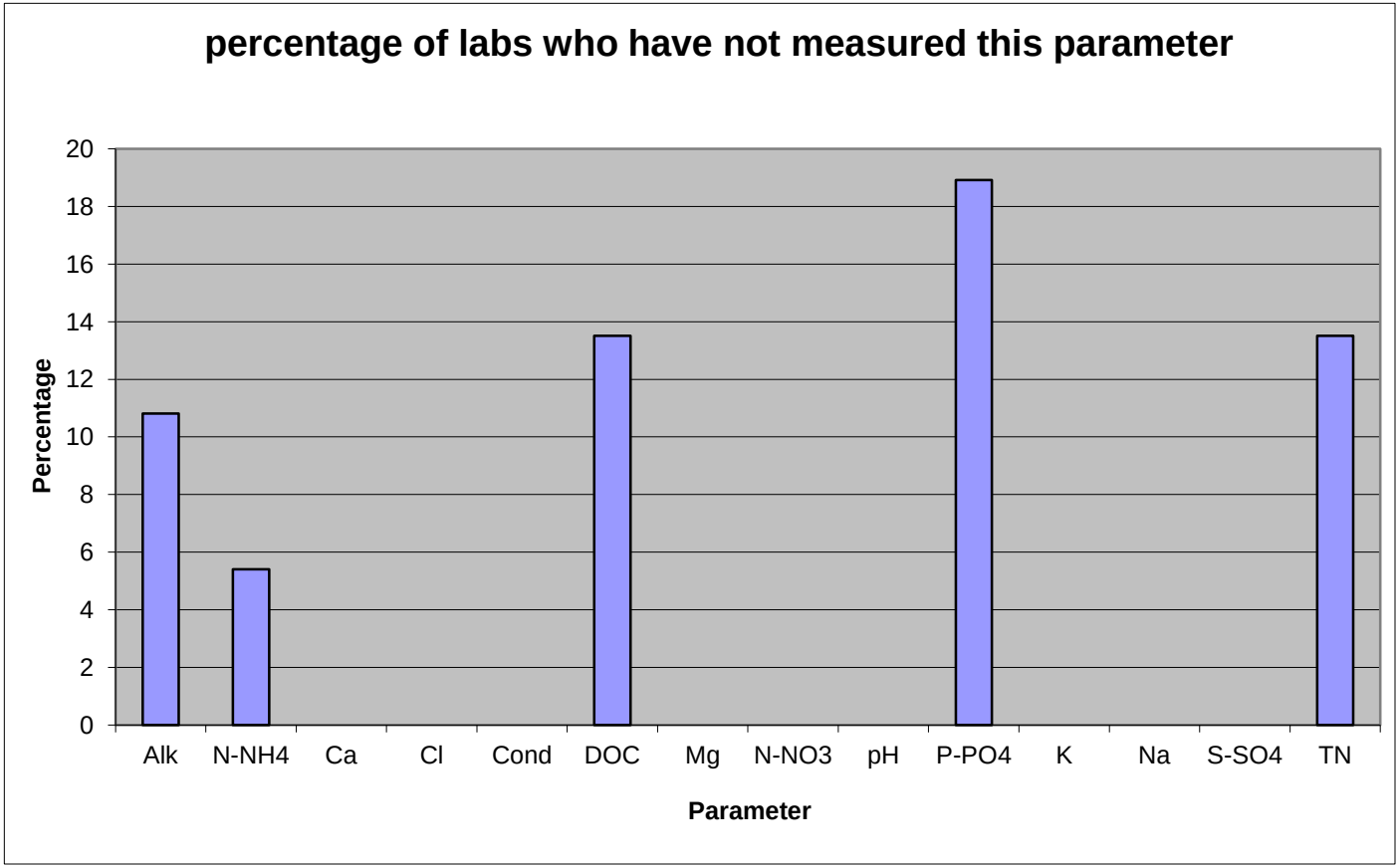
Low concentration means that 33% or more of results are < LOQ

Percentage of accepted results for each parameter
(only labs who have measured the parameter)



Problems with parameters 1

mandatory parameters except PO4-P



Problems with parameters 2

too high LOQ's

PARAMETER_NAME	LABORCODE	LOQ
ALKALINITY	A39	<100
ALKALINITY	D06	<78
ALKALINITY	D71	<48
AMMONIUM	A39	<0,3
AMMONIUM	F21	<0,1
CALCIUM	F24	<0,6
CALCIUM	D06	<0,5
MAGNESIUM	D06	<0,5
MAGNESIUM	F24	<0,4
NITRATE	F23	<0,12
NITRATE	F32	<0,1
NITRATE	F21	<0,1
PHOSPHATE	F21	<0,16
PHOSPHATE	S03	<0,13
TOTAL NITROGEN	S25	<1
TOTAL NITROGEN	A47	<1

max LOQ's

Parameter	Unit	max. LOQ
Alkalinity	µeq L^{-1}	10
Ammonium-N	mg L^{-1}	0,08
Ca	mg L^{-1}	0,2
Cl	mg L^{-1}	0,2
Conductivity	µS cm^{-1}	5
DOC	mg L^{-1}	1
Mg	mg L^{-1}	0,1
K	mg L^{-1}	0,4
Nitrate-N	mg L^{-1}	0,08
Phosphate-P	mg L^{-1}	0,1
K	mg L^{-1}	0,4
Na	mg L^{-1}	0,1
Sulphate-S	mg L^{-1}	0,1
Total N	mg L^{-1}	0,5

Requalification

- Requalification process
  - dead line May 9th (7 weeks time for analyses)
  - 20 labs (from 39)
  - 148 measured results should be reanalysed or send other explanations
  - 1 to 5 parameters/ lab
  - 3 to 32 measurements/ parameter
  - 2 labs never sent their requalification results
- Big variation in requalification reports
  - No explanations, no measuring or calibration tables etc.
  - Some reports excellent
  - Not always the measuring date involved
- Some reports arrived late, or too late!

Problems with parameters 3

- pH/ 9 labs/ 32 meas (presentation by Frank Symossek)
  - Calibration and condition of the electrode has to be checked by a natural water control sample
  - old electrode or equipment

- Alkalinity/ 6 labs/ 14 meas (presentation by Aldo Marchetto)
  - Must be measured if pH >5
  - If ”real” pH <5, but lab has result pH>5, they measure alkalinity , that’s OK. In this case, if the lab have a result for alkalinity >LOQ, that’s not OK.
  - Now we exclude all those results
  - Many labs have too low LOQ <0,01µeq/l the lowest, <100 µeq/l the highest

  - Method validation needed! Checking of units important!

Problems with parameters 4

- Nitrate-N/ 1 lab/ 4 meas (presentation by Aldo Marchetto):
  - Good overall results
  - Some labs (A39, D60, D71, F06, F08, F14, F23 maybe) actually measured Nitrate+Nitrite-N
  - Sample 1 bad results, Sample 5 partly, Samples 2 and 4 OK

  Be aware what you're measuring!

- Phosphate-P/ 10 labs/ 16 meas:
  - LOQ problems: LOQ < 0,001 mg/l lowest, < 0,16 mg/l highest
  - Some labs have results 0,001 or 0,002 mg/l

  Method validation needed!

- Sulphate-S/ 5 labs/ 17 meas
  - old columns mostly

Results of the 7th WRT (requalification not done)

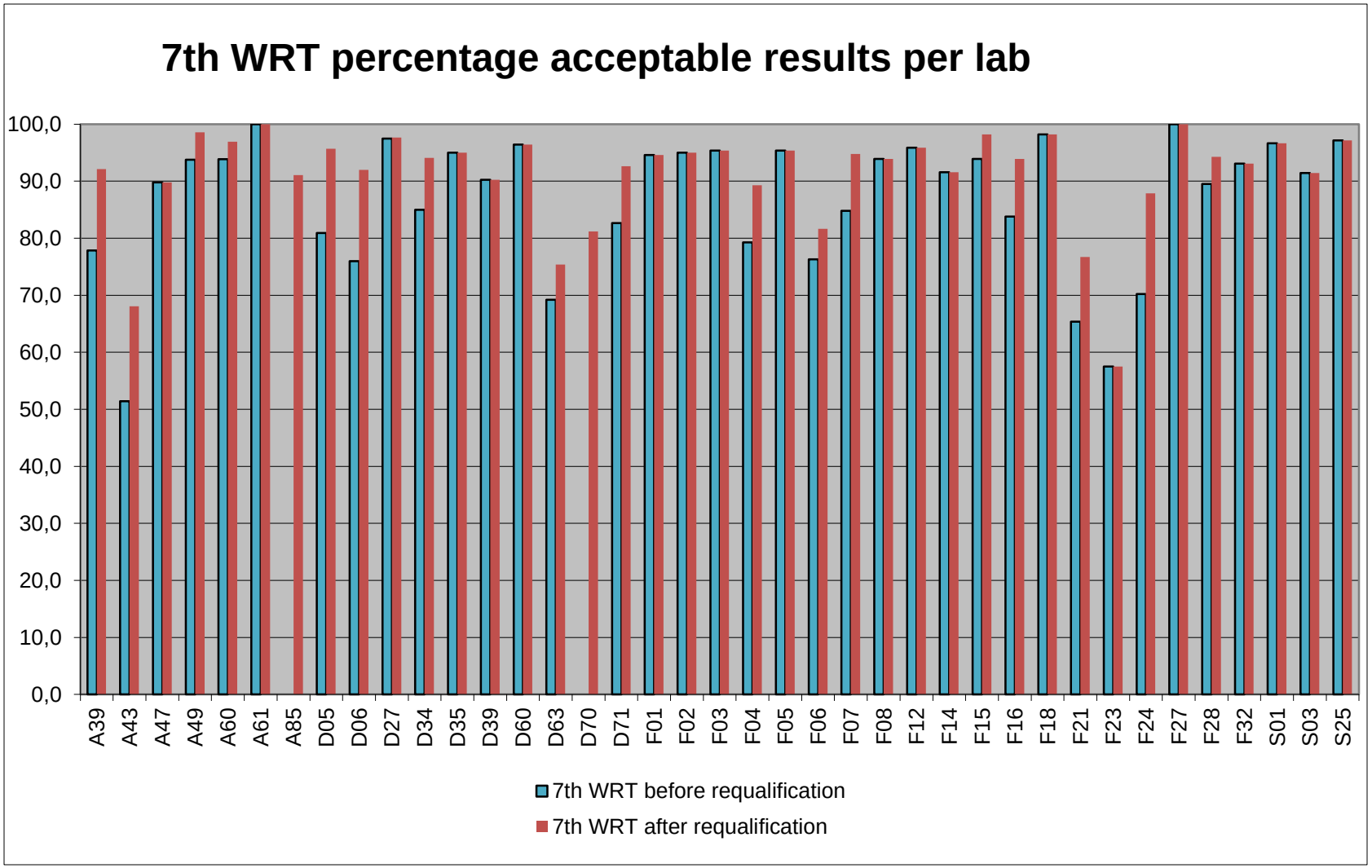
Labcode	Alk	N-NH4	Ca	Cl	Cond	DOC	Mg	N-NO3	pH	P-PO4	K	Na	S-SO4	TN
A39	**0**	**0**	100	100	60	100	100	50	100	100	100	100	80	100
A43	67	**0**	**0**	100	60	n.a.	80	50	**20**	n.a.	60	80	**0**	100
A47	100	100	80	80	100	100	100	100	100	67	100	100	80	50
A49	100	100	100	100	100	100	100	100	80	**33**	100	100	100	100
A60	100	100	80	100	100	100	80	100	**40**	n.a.	100	100	100	100
A61	100	100	100	100	100	100	100	100	100	100	100	100	100	100
A85	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	n.a.	**0**	**0**	**0**	**0**
D05	**33**	100	60	100	100	**40**	80	100	100	100	100	100	**20**	100
D06	**0**	n.a.	**40**	100	100	n.a.	**40**	100	80	n.a.	100	100	100	n.a.
D27	n.a.	100	100	100	100	100	100	100	100	67	100	100	100	100
D34	n.a.	75	80	100	100	100	80	100	**40**	n.a.	100	100	100	n.a.
D35	100	75	100	100	100	80	100	100	100	100	100	100	100	75
D39	**33**	75	100	100	100	n.a.	100	100	100	n.a.	100	100	100	75
D60	100	100	100	100	100	100	100	50	100	100	100	100	100	100
D63	67	**0**	80	100	**0**	60	100	100	60	**33**	100	100	100	n.a.
D71	100	75	100	100	100	80	100	75	**40**	67	100	100	**20**	100
F01	100	75	60	100	100	n.a.	100	100	100	n.a.	100	100	100	100
F02	100	100	80	80	80	n.a.	100	100	100	100	100	100	100	n.a.
F03	100	75	100	100	100	80	100	100	80	100	100	100	100	100
F04	100	75	80	100	100	60	80	75	**40**	100	100	80	**20**	100
F05	100	75	100	100	100	80	100	100	80	100	100	100	100	100
F06	100	100	100	100	80	100	100	**0**	**20**	**33**	100	100	60	75
F07	67	100	100	100	100	80	100	100	**40**	**0**	100	100	100	100
F08	100	100	100	100	100	80	100	75	60	100	100	100	100	100
F12	100	75	100	100	100	100	100	100	100	67	100	100	100	100
F14	67	100	100	80	100	80	100	75	100	100	100	80	100	100
F15	100	75	100	100	100	**40**	100	100	100	100	100	100	100	100
F16	100	75	100	100	100	80	100	100	60	**33**	100	100	100	**25**
F18	100	75	100	100	100	100	100	100	100	100	100	100	100	100
F21	**0**	75	60	80	100	100	100	75	100	**0**	60	**0**	100	n.a.
F23	100	100	100	**0**	100	80	100	75	**0**	100	**0**	**0**	**0**	50
F24	**33**	75	**0**	100	100	80	60	75	**20**	100	80	60	100	100
F27	100	100	100	100	100	100	100	100	100	n.a.	100	100	100	100
F28	100	100	100	100	100	80	100	100	60	**33**	100	100	80	100
F32	n.a.	100	100	100	100	80	100	75	80	100	100	100	100	75
S01	n.a.	n.a.	100	100	100	80	100	100	100	100	100	80	100	100
S03	100	100	100	100	80	100	100	100	100	**0**	100	100	100	100
S25	100	100	100	100	100	100	100	100	100	100	100	100	60	100

red cells = laboratory failed the ringtest
green cells = laboratory passed the ringtest
yellow cells = laboratory failed the ringtest (result of the re-qualification in green or red letters, old results are shown when mouse is over the cell)
n.a. = not analyzed

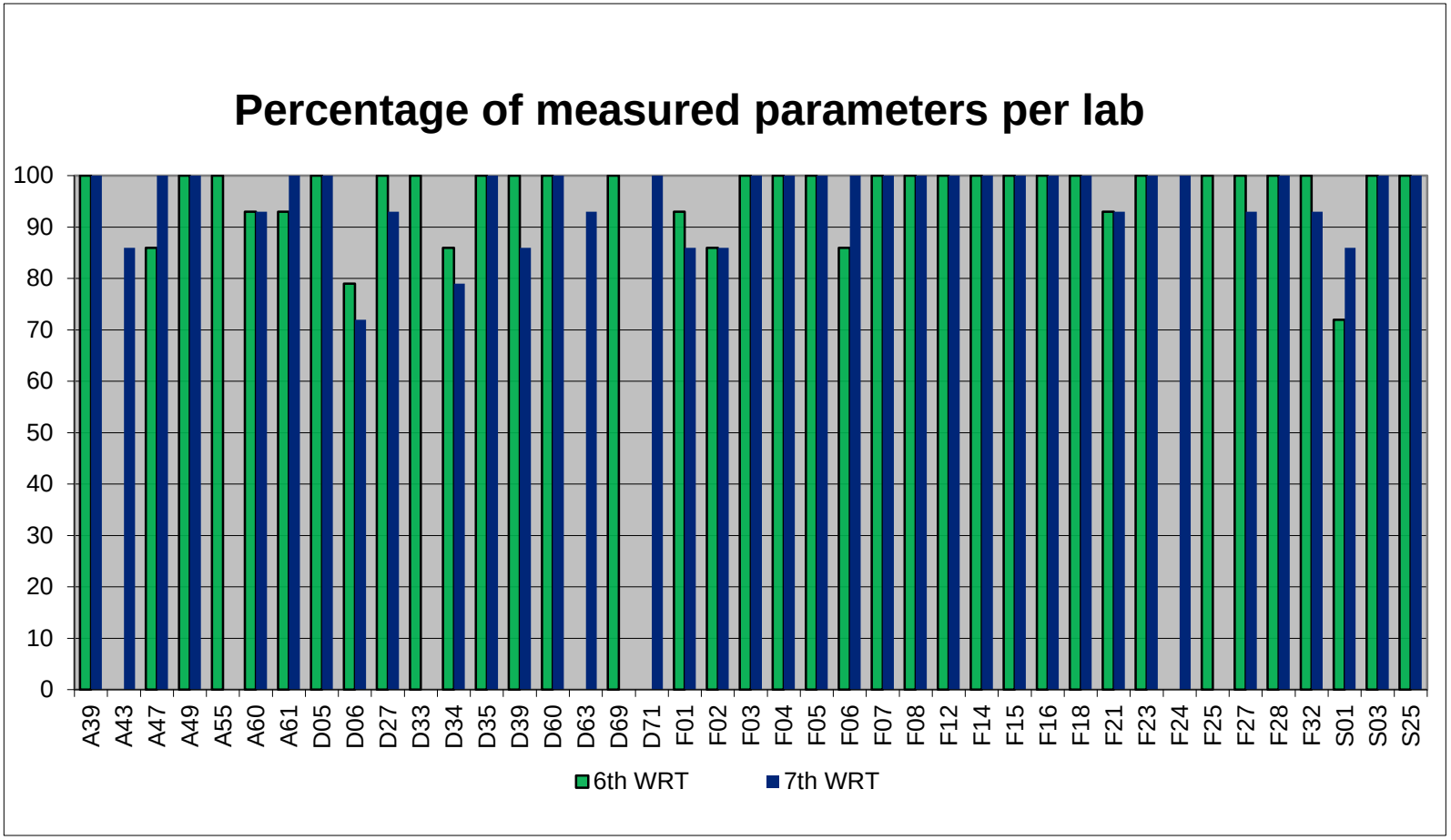
Results of the 7th WRT (after requalification)

red cells = laboratory failed the ringtest , green cells = laboratory passed the ringtest
yellow cells = laboratory failed the ringtest (result of the re-qualification in green or red letters, old results are shown when mouse is over the cell) , n.a. = not analyzed

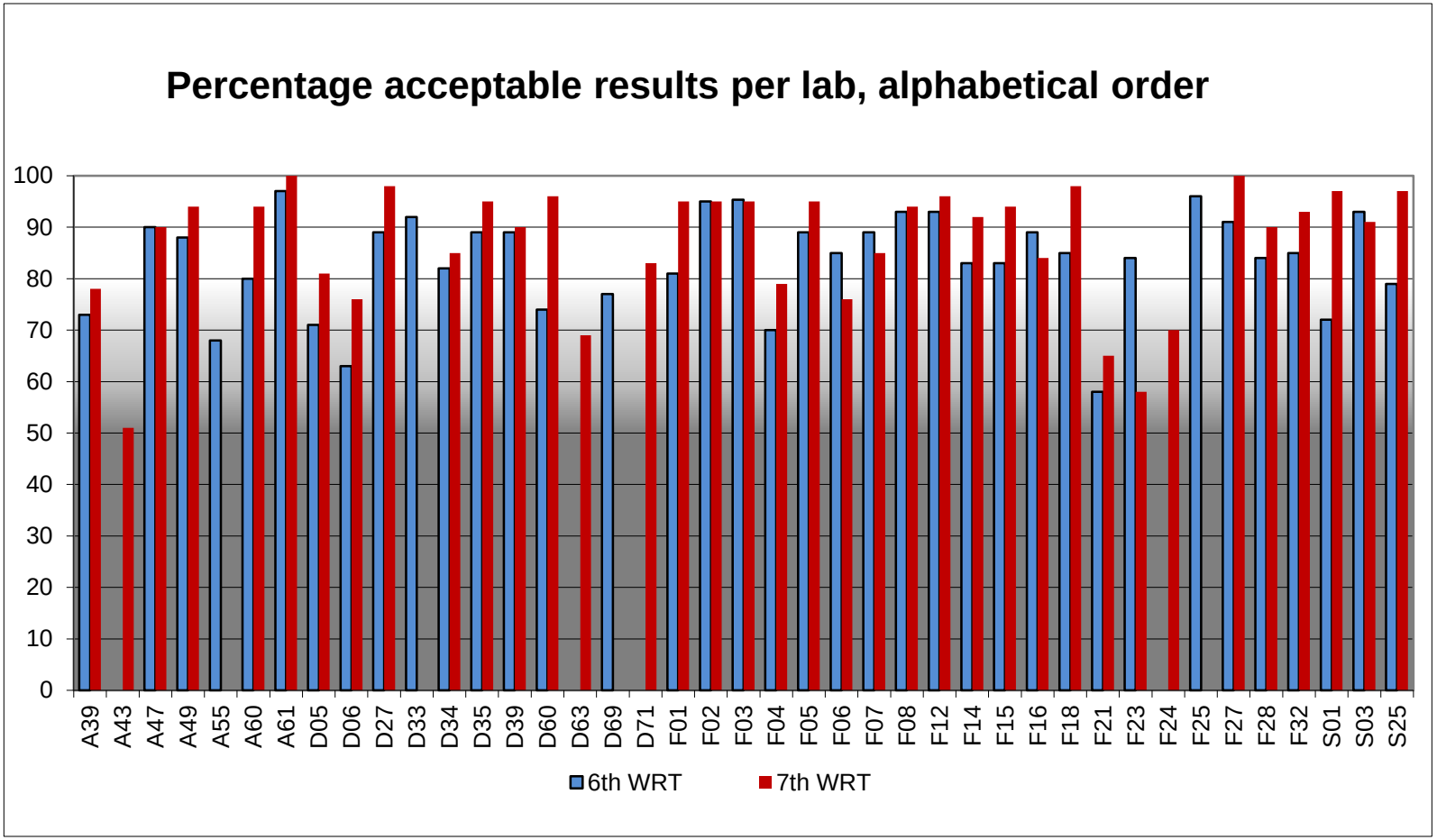
Labcode	Alk	N-NH4	Ca	Cl	Cond	DOC	Mg	N-NO3	pH	P-PO4	K	Na	S-SO4	TN
A39	100	100	100	100	60	100	100	50	100	100	100	100	80	100
A43	67	0	80	100	60	n.a.	80	50	80	n.a.	60	80	60	100
A47	100	100	80	80	100	100	100	100	100	67	100	100	80	50
A49	100	100	100	100	100	100	100	100	80	100	100	100	100	100
A60	100	100	80	100	100	100	80	100	100	n.a.	100	100	100	100
A61	100	100	100	100	100	100	100	100	100	100	100	100	100	100
A85	100	75	100	100	100	100	100	100	100	0	100	100	100	100
D05	100	100	60	100	100	100	80	100	100	100	100	100	100	100
D06	100	n.a.	80	100	100	n.a.	60	100	80	n.a.	100	100	100	n.a.
D27	100	100	100	100	100	100	100	100	100	67	100	100	100	100
D34	n.a.	75	80	100	100	100	80	100	100	n.a.	100	100	100	n.a.
D35	100	75	100	100	100	80	100	100	100	100	100	100	100	75
D39	33	75	100	100	100	n.a.	100	100	100	n.a.	100	100	100	75
D60	100	100	100	100	100	100	100	50	100	100	100	100	100	100
D63	67	0	80	100	80	60	100	100	60	33	100	100	100	n.a.
D70	67	50	100	100	100	60	100	100	60	0	100	100	100	100
D71	100	75	100	100	100	80	100	75	100	67	100	100	100	100
F01	100	75	60	100	100	n.a.	100	100	100	n.a.	100	100	100	100
F02	100	100	80	80	80	n.a.	100	100	100	100	100	100	100	n.a.
F03	100	75	100	100	100	80	100	100	80	100	100	100	100	100
F04	100	75	80	100	100	60	80	75	100	100	100	80	100	100
F05	100	75	100	100	100	80	100	100	80	100	100	100	100	100
F06	100	100	100	100	80	100	100	75	20	33	100	100	60	75
F07	67	100	100	100	100	80	100	100	80	100	100	100	100	100
F08	100	100	100	100	100	80	100	75	60	100	100	100	100	100
F12	100	75	100	100	100	100	100	100	100	67	100	100	100	100
F14	67	100	100	80	100	80	100	75	100	100	100	80	100	100
F15	100	75	100	100	100	100	100	100	100	100	100	100	100	100
F16	100	75	100	100	100	80	100	100	60	100	100	100	100	100
F18	100	75	100	100	100	100	100	100	100	100	100	100	100	100
F21	67	75	60	80	100	100	100	75	100	0	60	80	100	n.a.
F23	100	100	100	0	100	80	100	75	0	100	0	0	0	50
F24	100	75	100	100	100	80	60	75	100	100	80	60	100	100
F27	100	100	100	100	100	100	100	100	100	n.a.	100	100	100	100
F28	100	100	100	100	100	80	100	100	60	100	100	100	80	100
F32	n.a.	100	100	100	100	80	100	75	80	100	100	100	100	75
S01	n.a.	n.a.	100	100	100	80	100	100	100	100	100	80	100	100
S03	100	100	100	100	80	100	100	100	100	0	100	100	100	100
S25	100	100	100	100	100	100	100	100	100	100	100	100	60	100



Comparison of the 6th and 7th WRT's



Comparison of the 6th and 7th WRT's



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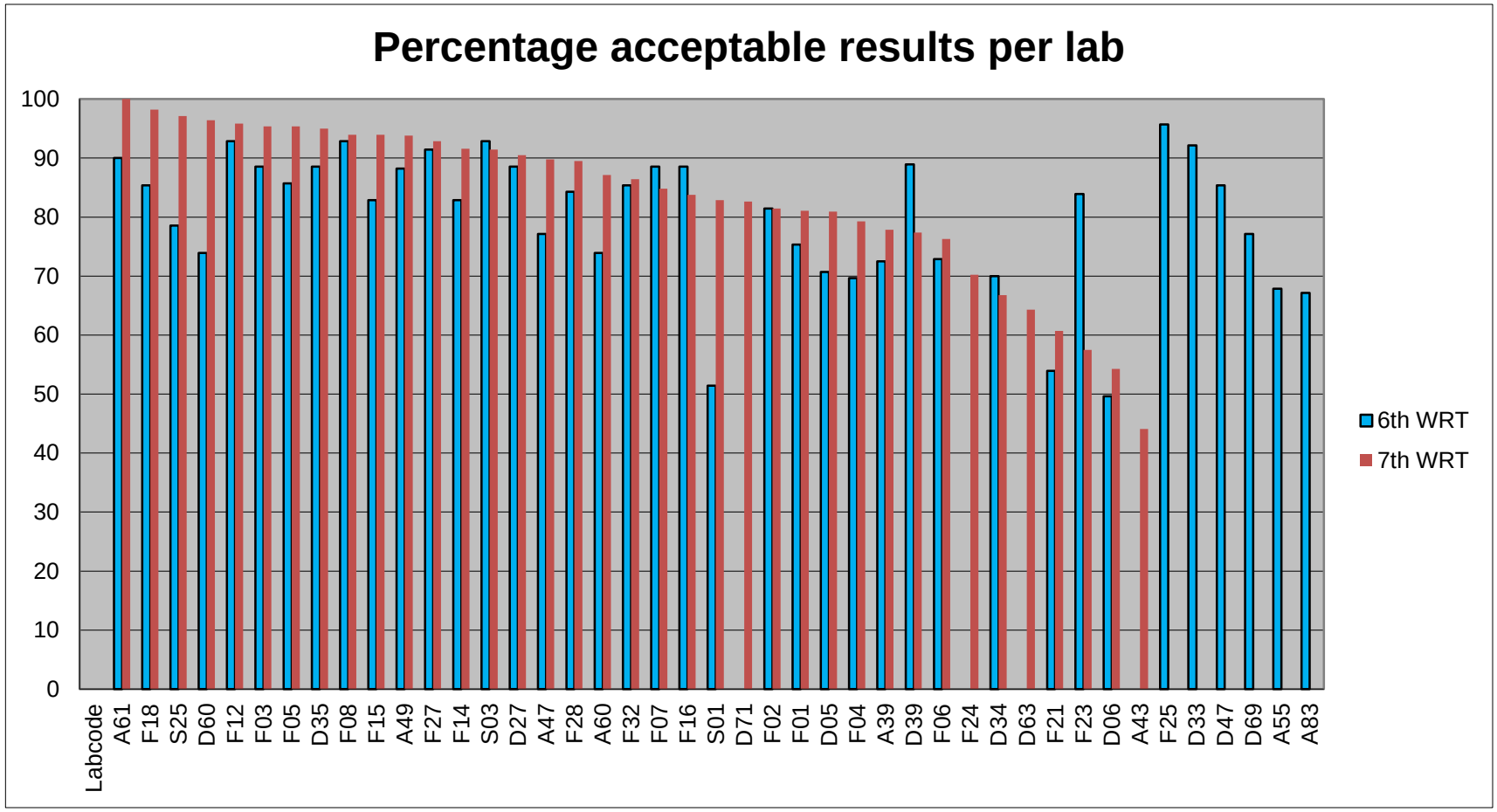
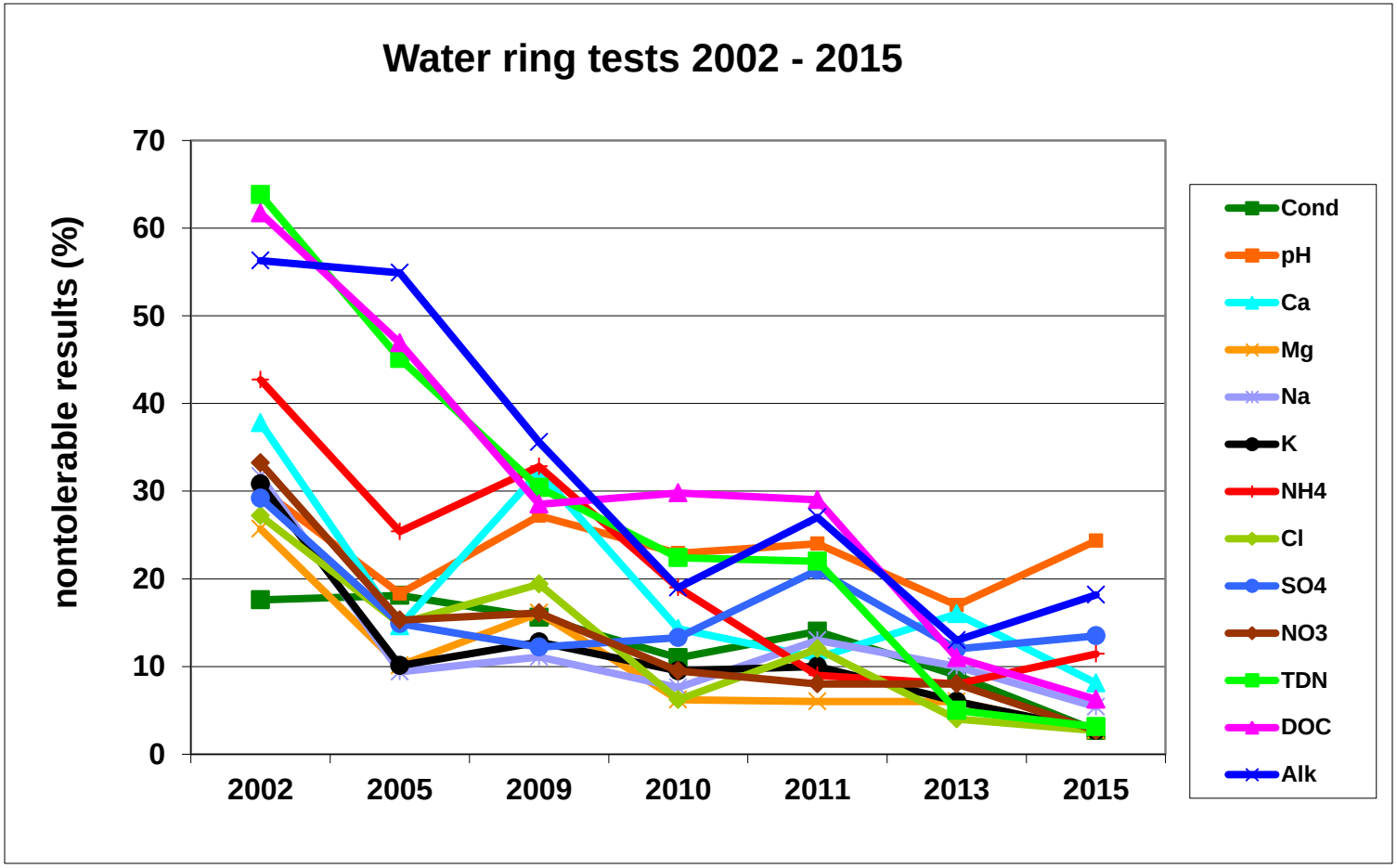
Comparison of the 6th and 7th WRT's



Trends in 2002 – 2015

2013 and 2015 low concentration samples rejected



Conclusions 1, future ring tests

- All mandatory parameters are not involved in ring test
  - Quality in the results database

- Connection between LQA forms and ring test report

  LQA forms countrywise/ Ring test report labwise

  Ring tests 2002 and 2005 not easy to link with monitoring results

- Feedback for the next ring test is valuable:
  - Type of samples
  - Samples collected by participants
  - Concentrations of parameters
  - Time table of the ring test
  - Organizer of the ring test

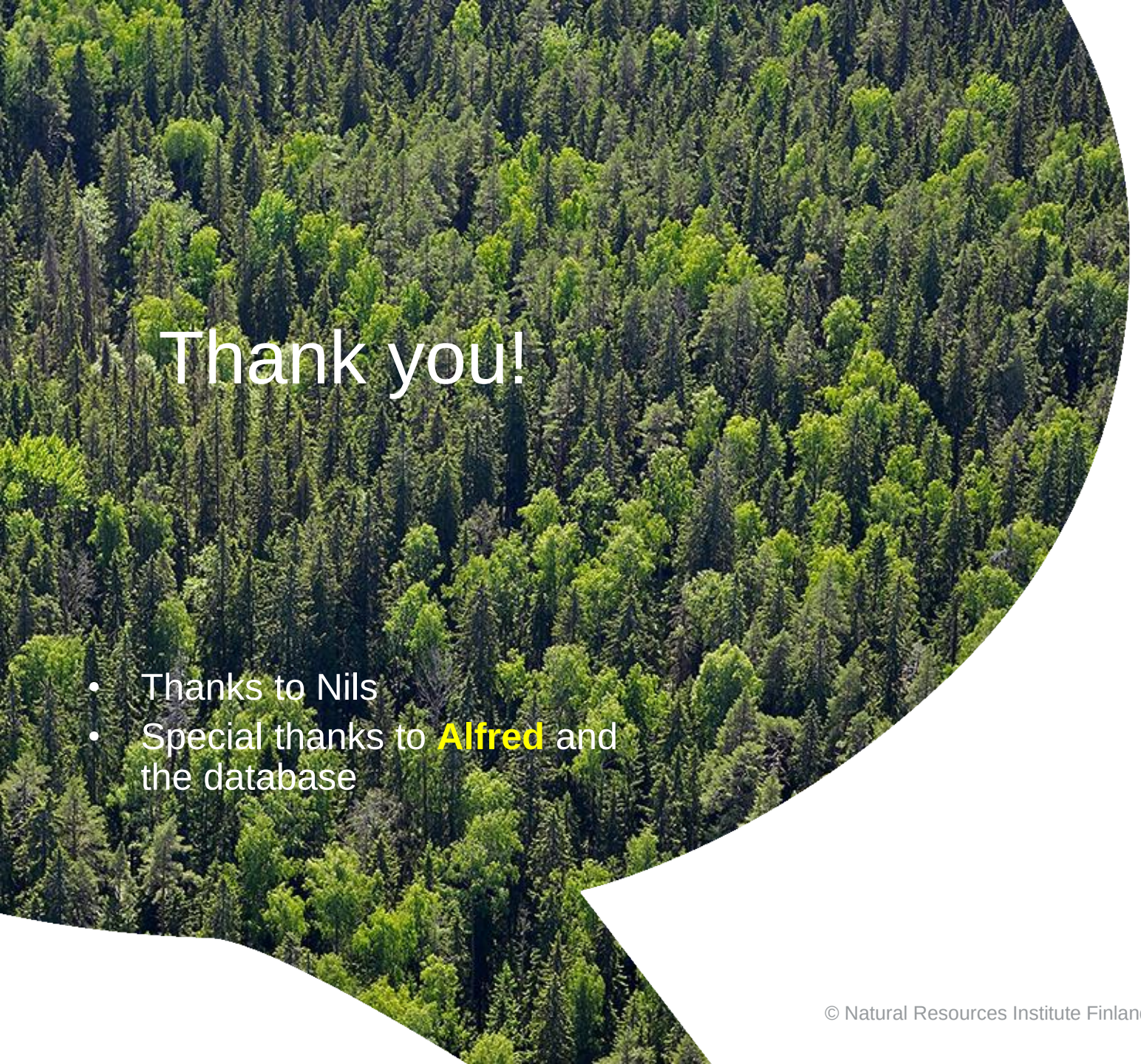
Conclusions, 2

- Good quality level reached during the time of ring tests
- Most parameters 15 % or less non tolerable results
- pH, alkalinity and NH_4-N could be better

- Updated database is very helpful with registering and invoicing
- Take care that all information (contact person, addresses etc.) will be updated between the ring tests also

- Don’t register before you’re sure about participation

- Use always lab code in correspondence (in mail subject, file name etc.)



Thank you!

- Thanks to Nils
- Special thanks to **Alfred** and the database

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