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Problems with conductivity checks

- Meeting of the Heads of the Laboratories
- 7.-8.9.2017 in Pallanza

Problem 1

In 2015 soil solution conformity report we've found warnings for almost half of the results for conductivity (45%)

- Checking the results by analytical data validation ion balance excel sheet
- Comparison of "cond not fit" against "cond no", Table 1.

Note!

- Calculated conductivity was in most cases more or less the same in both conformity report and excel sheet
- Same data taken from database, not original laboratory results
 - -1 reversed to LOQ/2 in excel sheet

Table 1. Comparing conformity report vs analytical data validation Soil solution 2015

Plot	Samples	Conformity report		Analytical data validation		Same sample not fit and cond no	
		conductivity not fit		cond ok	cond no		
1	11	1		7	4	1	
3	15	3		13	2	0	
5	18	10		9	9	7	
6	18	9		6	11	7	
10	32	17		27	4	4	
11	33	18		20	12	7	
12	34	7		23	9	1	
13	34	14		22	7	4	
16	27	21		14	13	11	
17	17	6		11	5	2	
19	8	0		5	2	0	
20	15	11		3	11	9	
Total	262	117	45 %	160	89	34 %	53

Problem 1, cont.

- The same inspection with 2015 deposition data, Table 2.

Note!

- Calculated conductivity was in most cases more or less the same in both conformity report and excel sheet
- Same data from database, not original laboratory results
 - -1 reversed to LOQ/2 in excel sheet

Table 2. Comparing conformity report vs analytical data validation Deposition 2015

Plot	Samples	Conformity report		Analytical data validation		In same sample not fid and cond no	
		conductivity not fit		cond ok	cond no		
1	26	2		16	10	1	
3	26	0		15	11	0	
5	26	0		15	11	0	
6	26	0		14	12	0	
10	26	3		20	6	3	
11	26	1		22	4	0	
12	26	9		9	17	8	
13	26	2		16	10	1	
16	26	1		16	10	1	
17	26	5		10	16	5	
19	26	2		16	10	2	
20	26	3		17	9	3	
Total	312	28	9 %	186	126	40 %	24

Problem 1. Causes, explanations

- Different interpretation of the difference between measured and calculated conductivity
- Interpretation of $< \text{LOQ}$ values
- Impact of DOC under estimated in excel sheet, esp. in soil solution
- Phosphate-P is not involved in calculations in excel sheet, how in conformity calculations?

Problem 2.

Increasing trend of "not fit" in conformity reports in soil solution

Year		Soil solution	Deposition
2015	%	45	9
2014	%	35	6
2013	%	13	16
2012	%	18	11
2011	%	8	4

Problem 2. Possible causes, explanations

- Methods changed = lower LOQ
 - Nitrate-N from IC to FIA (soil solution 2014 -)
 - 0,041 mg/l to 0,002 mg/l
 - Ammonium-N from FIA to spectrophotometric measurement (soil solution 2014 -, deposition 2015 -)
 - 0,030 mg/l to 0,005 mg/l
- Sample pooling = less "no results"
 - Soil solution, started in 2012

Thank you!

