European Union / United Nations Economic Commission for Europe
International Co-operative Programme on Assessment and
Monitoring of Air Pollution Effects on Forests

Meeting of the Working Group on QA/QC
(subgroup of the Expert Panel Deposition)
together with experts in chemical analysis from other Expert Panels

Quality checks of results of atmospheric deposition and soil water analyses

Rosario Mosello & Tiziana Amoriello

CNR Institute Ecosystem Study, Verbania Pallanza
CRA Experimental Institute for Plant Nutrition, Rome

26-27 February 2007, DG Environment, Brussels, Belgium

Aspects to be considered to assure good analytical quality of results

Field — Sampling, transport and conservation of samples

Laboratory

- Skilled personnel
- Validated and written analytical methods
- Properly constructed, equipped and maintained laboratory facilities
- Use of high-quality glassware, reagents, de-ionised water and other testing material

Internal QC

- Calibration, adjustment, and maintenance of equipment
- Use of blanks, DL, QL
- Use of replicate samples
- Use of control samples and standard samples, with proper records (control charts)
- Validation and critique of results
- Archiving results

External QC

- Interlaboratory exercises
- Certified reference materials

From the ICP Forests manual, part VI

5. QUALITY ASSURANCE PROGRAMME IN THE LABORATORY

- 5.1. DEFINITIONS AND TERMINOLOGY
- 5.2. REFERENCE MATERIALS
- 5.3. WITHIN-LABORATORY QUALITY CONTROL
- 5.4. INTER-LABORATORY QUALITY CONTROL
- 5.5. CHECKING AND VALIDATING THE ANALYTICAL RESULTS

  5.5.1. Ionic balance
  5.5.2. Comparison between measured and calculated conductivity
  5.5.3. Sodium/chloride ratio
  5.5.4. Comparison between measured conductivity and ion concentrations
  5.5.5. Acceptance threshold values and use of a pre-defined calculation spreadsheet

Ionic balance

$$PD = 100 * \frac{(\Sigma \text{ cat} - \Sigma \text{ an})}{0.5\ (\Sigma \text{ cat} + \Sigma \text{ an})}$$

$$\Sigma_{\text{anions}} = \text{Alk} + [SO_4^{=}] + [NO_3^{-}] + [Cl^{-}] + [Org^{-}]$$

$$\Sigma_{\text{cations}} = [Ca^{++}] + [Mg^{++}] + [Na^{+}] + [K^{+}] + [H^{+}] + [NH_4^{+}]$$

Comparison between measured (CM) and calculated conductivity (CE)

$$CD = 100 * \frac{(CM-CE)}{CM}$$

for conductivity $\leq$ **100 µS cm^{-1}** $CE_{\infty} = \sum \lambda_i c_i$

for conductivity **>** **100 µS cm^{-1}** $CE = \sum \lambda_i f_i c_i$

λ_i ***equivalent ionic conductance***

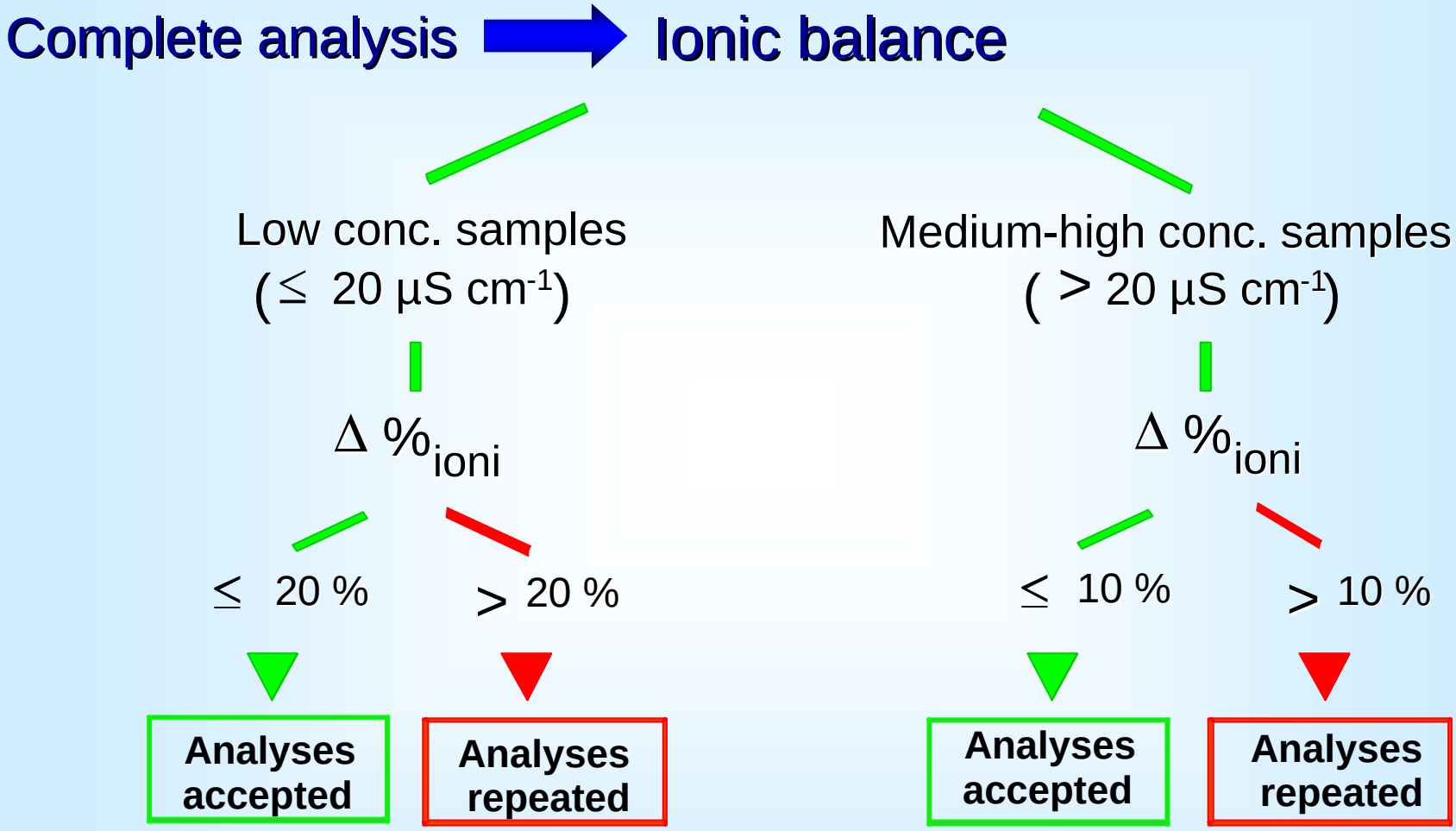
C_i ***Concentration of the ion i***

f_i *activity coefficient*

	Units	Factors to µeq L^{-1}	Equivalent conductance at 25°C kS cm^2 eq^{-1}
pH		10^6*10^{-pH}	0.3500
Ammonium	mg N-NH_4 L^{-1}	71.39	0.0735
Calcium	mg L^{-1}	49.90	0.0595
Magnesium	mg L^{-1}	82.29	0.0531
Sodium	mg L^{-1}	43.50	0.0501
Potassium	mg L^{-1}	25.58	0.0735
Alkalinity	meq L^{-1}	1000	0.0445
Sulphate	mg S L^{-1}	62.37	0.0800
Nitrate	mg N- NO_3 L^{-1}	71.39	0.0714
Chloride	mg L^{-1}	28.21	0.0764

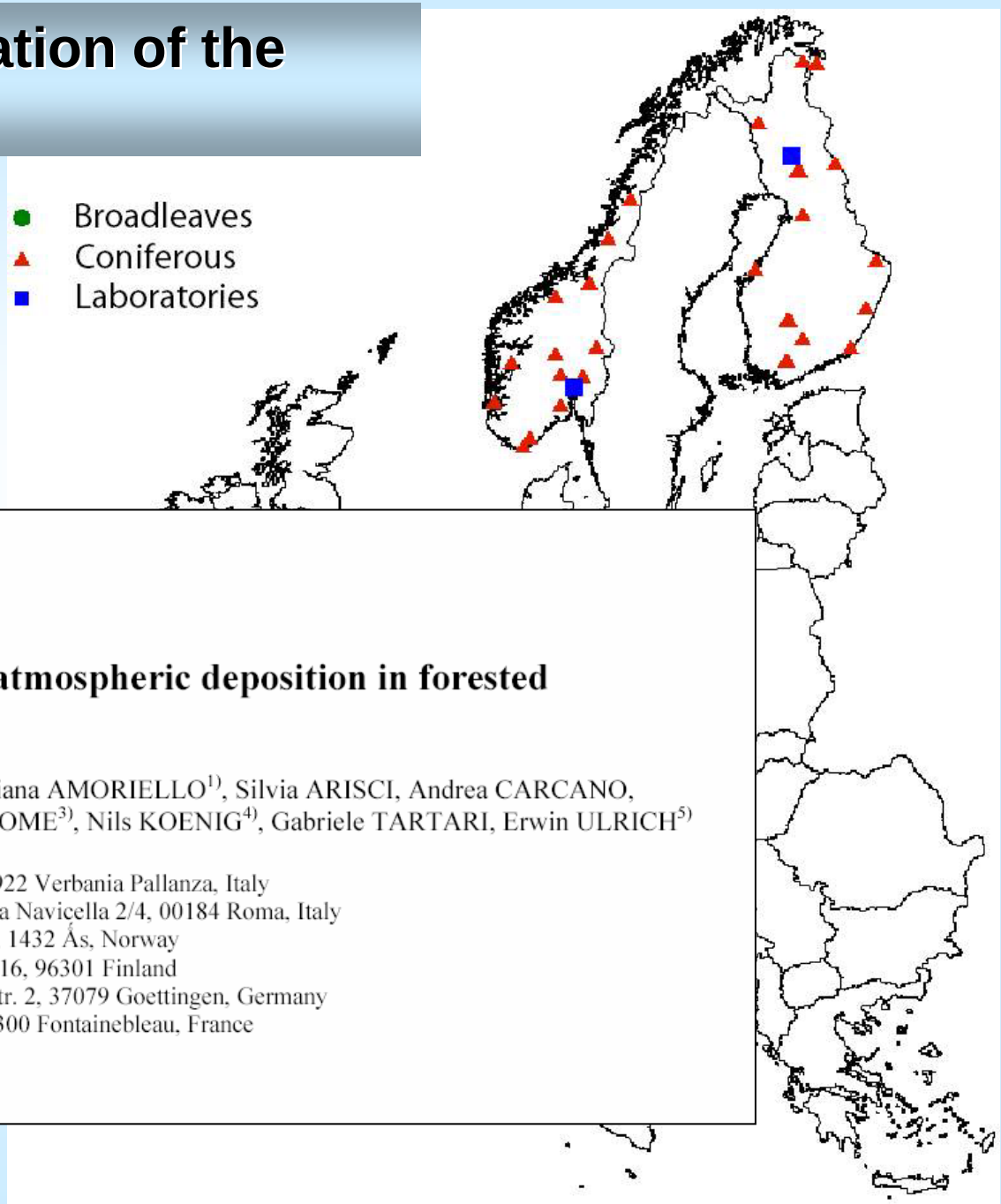
Acceptance threshold values in data validation based on the ionic balance and conductivity.

Conductivity of the sample 25 °C	Ionic balance	Conductivity
≤ 10 µS cm^{-1}	± 20%	±30%
< 20 µS cm^{-1}	± 20%	±20%
> 20 µS cm^{-1}	± 10%	±10%


Complete analysis
Ionic balance
Low conc. samples
(≤ 20 µS cm-1)
Medium-high conc. samples
(> 20 µS cm-1)
Δ %ioni
Δ %ioni
≤ 20 %
> 20 %
≤ 10 %
> 10 %
Analyses accepted
Analyses repeated
Analyses accepted
Analyses repeated

Examples of the application of the validation criteria

- **About 5000 analyses of deposition samples done from 7 different laboratories**



J. Limnol., 64(2): 93-102, 2005

Validation of chemical analyses of atmospheric deposition in forested European sites

Rosario MOSELLO*, Monica AMORIELLO[1)], Tiziana AMORIELLO[1)], Silvia ARISCI, Andrea CARCANO, Nicholas CLARKE[2)], John DEROME[3)], Kirsti DEROME[3)], Nils KOENIG[4)], Gabriele TARTARI, Erwin ULRICH[5)]

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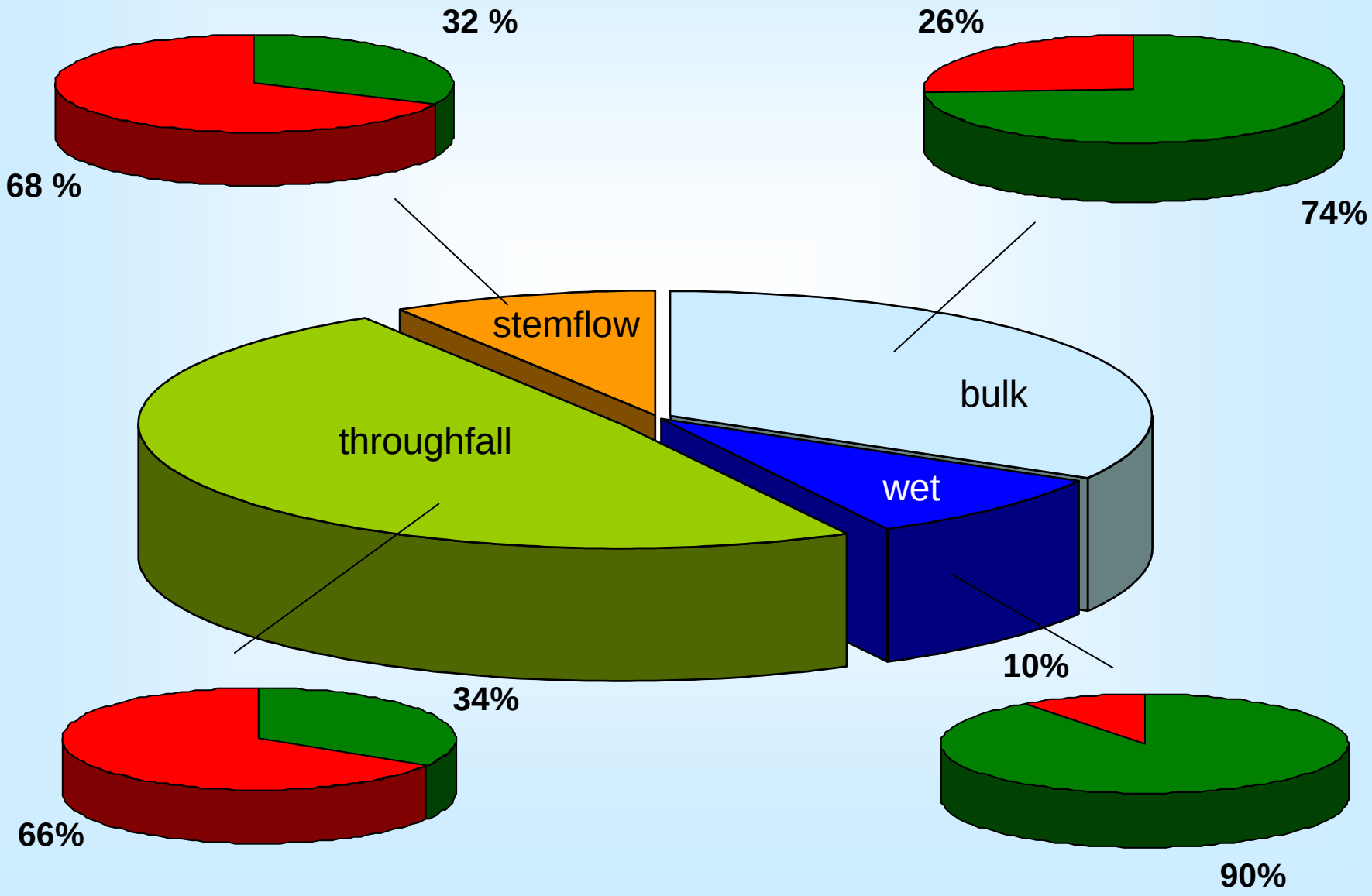
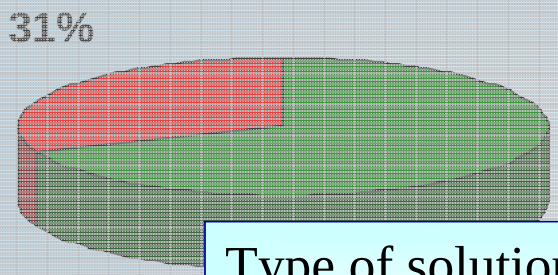
[1)]CRA Experimental Institute for Plant Nutrition, Via della Navicella 2/4, 00184 Roma, Italy
[2)]Norwegian Forest Research Institute, Hogskoleveien 12, 1432 Ås, Norway
[3)]Finnish Forest Research Institute, Rovaniemi, P.O. Box 16, 96301 Finland
[4)]Niedersaechsische Forstliche Versuchsanstalt, Graetzelstr. 2, 37079 Goettingen, Germany
[5)]Office National des Forêts, Boulevard de Constance, 77300 Fontainebleau, France
*e-mail corresponding author: r.mosello@ise.cnr.it

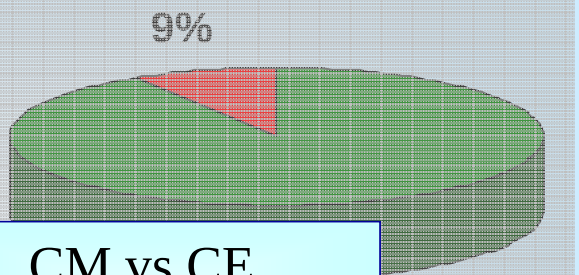
Δ Ion balance % accepted



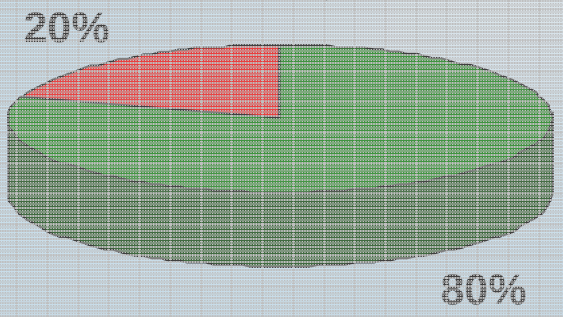
Measured vs calculated conductivity

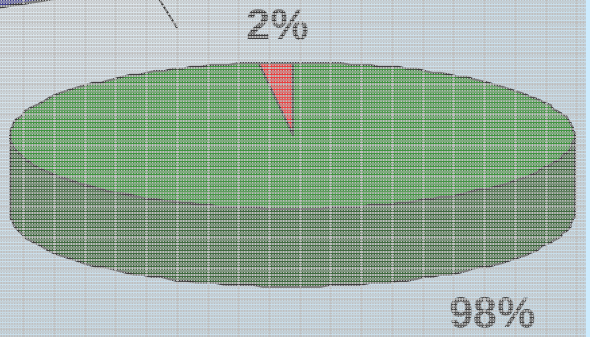
% valid



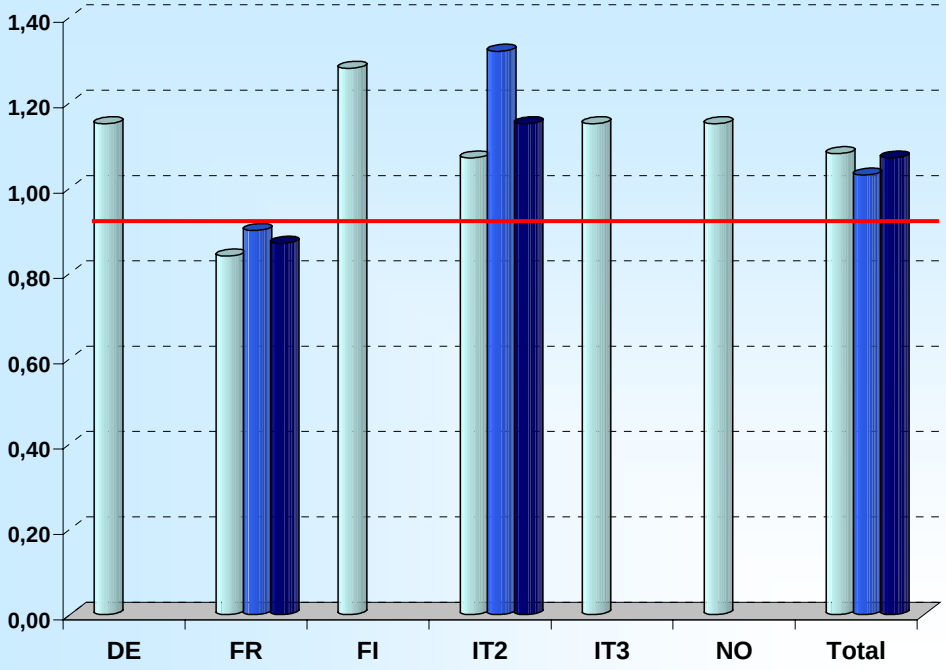


Type of solution	Ionic balance % valid	CM vs CE. % valid
BOF	**74**	**91**
WET	**90**	**98**
THR	**34**	**80**
ST	**32**	**69**





3. Na/Cl ratio validation test



– Marine Na/Cl ratio (0.86)

BOF

WET

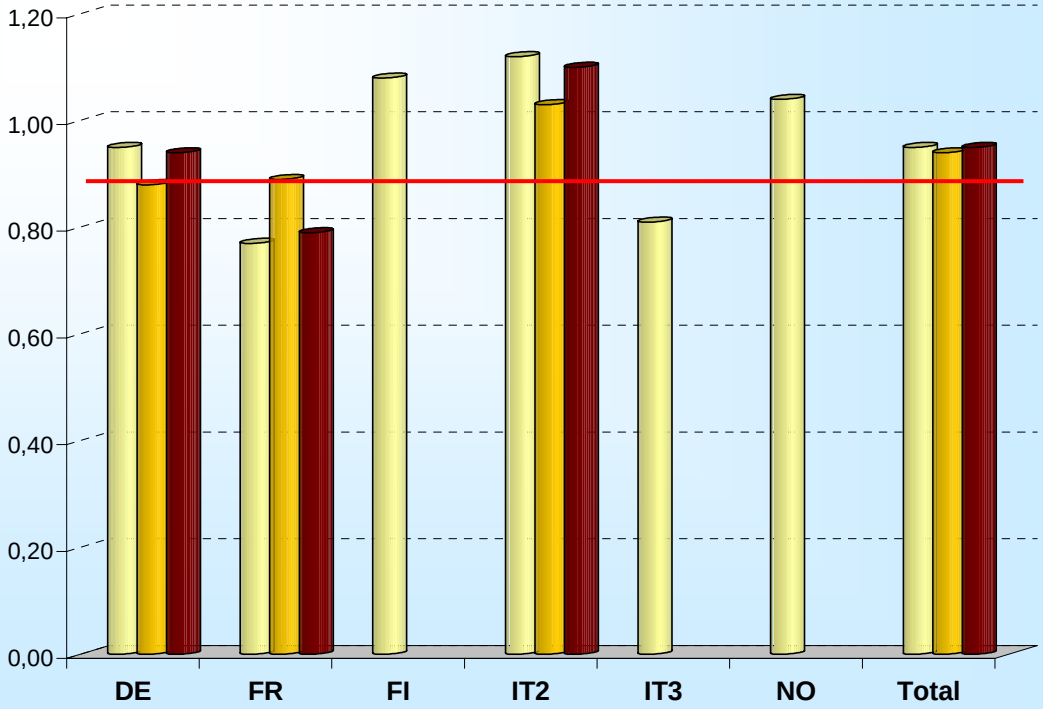
BOF + WET

– Marine Na/Cl ratio

THR

ST

THR + ST



4. Organic nitrogen validation test

$$TN = N\text{-}NO_3^- + N\text{-}NH_4^+ + (N\text{-}NO_2^-) + Org\_N$$

$$Org\_N = TN - N\text{-}NO_3^- - N\text{-}NH_4^+$$

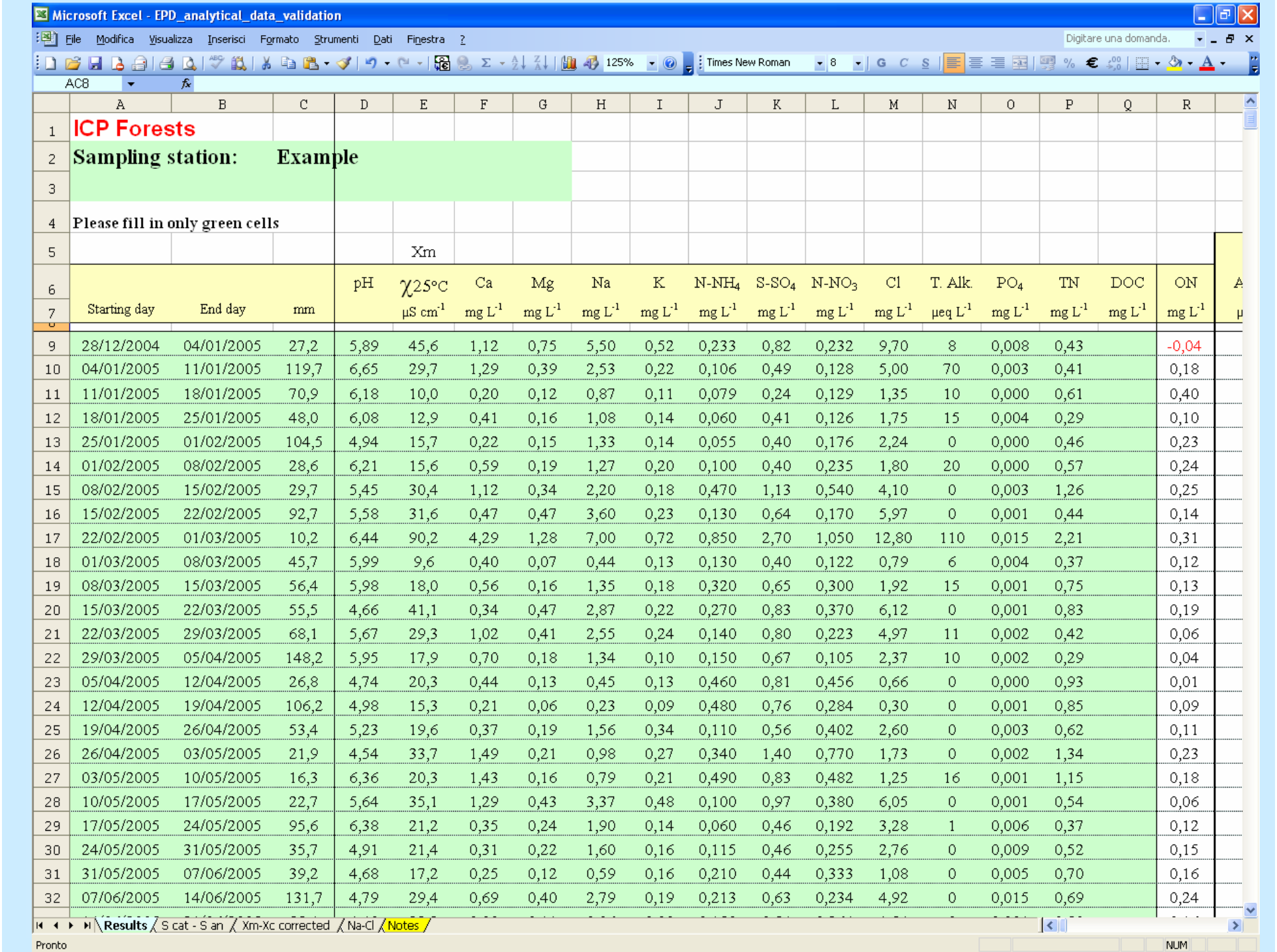
The concentration of organic nitrogen can not be negative!

$$TN - N\text{-}NO_3^- - N\text{-}NH_4^+ >= 0$$

Applicability of validation tests to different type of solutions

	ion balance	conductivity	Na/Cl	nitrogen
wet-only	yes	yes	yes	yes
bulk open field	yes	yes	yes	yes
throughfall	no	yes	yes	yes
stemflow	no	yes	yes	yes
runoff	?	yes	no	yes
soil water	no	yes	no	yes

? = applicable if TOC is lower than 5 mg C L^{-1}


Microsoft Excel - EPD_analytical_data_validation
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AC8
ICP Forests
Sampling station: Example
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Starting day | End day | mm | pH | χ25°C µS cm-1 | Ca mg L-1 | Mg mg L-1 | Na mg L-1 | K mg L-1 | N-NH4 mg L-1 | S-SO4 mg L-1 | N-NO3 mg L-1 | Cl mg L-1 | T. Alk. µeq L-1 | PO4 mg L-1 | TN mg L-1 | DOC mg L-1 | ON mg L-1
28/12/2004 04/01/2005 27,2 5,89 45,6 1,12 0,75 5,50 0,52 0,233 0,82 0,232 9,70 8 0,008 0,43 -0,04
04/01/2005 11/01/2005 119,7 6,65 29,7 1,29 0,39 2,53 0,22 0,106 0,49 0,128 5,00 70 0,003 0,41 0,18
11/01/2005 18/01/2005 70,9 6,18 10,0 0,20 0,12 0,87 0,11 0,079 0,24 0,129 1,35 10 0,000 0,61 0,40
18/01/2005 25/01/2005 48,0 6,08 12,9 0,41 0,16 1,08 0,14 0,060 0,41 0,126 1,75 15 0,004 0,29 0,10
25/01/2005 01/02/2005 104,5 4,94 15,7 0,22 0,15 1,33 0,14 0,055 0,40 0,176 2,24 0 0,000 0,46 0,23
01/02/2005 08/02/2005 28,6 6,21 15,6 0,59 0,19 1,27 0,20 0,100 0,40 0,235 1,80 20 0,000 0,57 0,24
08/02/2005 15/02/2005 29,7 5,45 30,4 1,12 0,34 2,20 0,18 0,470 1,13 0,540 4,10 0 0,003 1,26 0,25
15/02/2005 22/02/2005 92,7 5,58 31,6 0,47 0,47 3,60 0,23 0,130 0,64 0,170 5,97 0 0,001 0,44 0,14
22/02/2005 01/03/2005 10,2 6,44 90,2 4,29 1,28 7,00 0,72 0,850 2,70 1,050 12,80 110 0,015 2,21 0,31
01/03/2005 08/03/2005 45,7 5,99 9,6 0,40 0,07 0,44 0,13 0,130 0,40 0,122 0,79 6 0,004 0,37 0,12
08/03/2005 15/03/2005 56,4 5,98 18,0 0,56 0,16 1,35 0,18 0,320 0,65 0,300 1,92 15 0,001 0,75 0,13
15/03/2005 22/03/2005 55,5 4,66 41,1 0,34 0,47 2,87 0,22 0,270 0,83 0,370 6,12 0 0,001 0,83 0,19
22/03/2005 29/03/2005 68,1 5,67 29,3 1,02 0,41 2,55 0,24 0,140 0,80 0,223 4,97 11 0,002 0,42 0,06
29/03/2005 05/04/2005 148,2 5,95 17,9 0,70 0,18 1,34 0,10 0,150 0,67 0,105 2,37 10 0,002 0,29 0,04
05/04/2005 12/04/2005 26,8 4,74 20,3 0,44 0,13 0,45 0,13 0,460 0,81 0,456 0,66 0 0,000 0,93 0,01
12/04/2005 19/04/2005 106,2 4,98 15,3 0,21 0,06 0,23 0,09 0,480 0,76 0,284 0,30 0 0,001 0,85 0,09
19/04/2005 26/04/2005 53,4 5,23 19,6 0,37 0,19 1,56 0,34 0,110 0,56 0,402 2,60 0 0,003 0,62 0,11
26/04/2005 03/05/2005 21,9 4,54 33,7 1,49 0,21 0,98 0,27 0,340 1,40 0,770 1,73 0 0,002 1,34 0,23
03/05/2005 10/05/2005 16,3 6,36 20,3 1,43 0,16 0,79 0,21 0,490 0,83 0,482 1,25 16 0,001 1,15 0,18
10/05/2005 17/05/2005 22,7 5,64 35,1 1,29 0,43 3,37 0,48 0,100 0,97 0,380 6,05 0 0,001 0,54 0,06
17/05/2005 24/05/2005 95,6 6,38 21,2 0,35 0,24 1,90 0,14 0,060 0,46 0,192 3,28 1 0,006 0,37 0,12
24/05/2005 31/05/2005 35,7 4,91 21,4 0,31 0,22 1,60 0,16 0,115 0,46 0,255 2,76 0 0,009 0,52 0,15
31/05/2005 07/06/2005 39,2 4,68 17,2 0,25 0,12 0,59 0,16 0,210 0,44 0,333 1,08 0 0,005 0,70 0,16
07/06/2005 14/06/2005 131,7 4,79 29,4 0,69 0,40 2,79 0,19 0,213 0,63 0,234 4,92 0 0,015 0,69 0,24
Results S cat - S an Xm-Xc corrected Na-Cl Notes
Pronto
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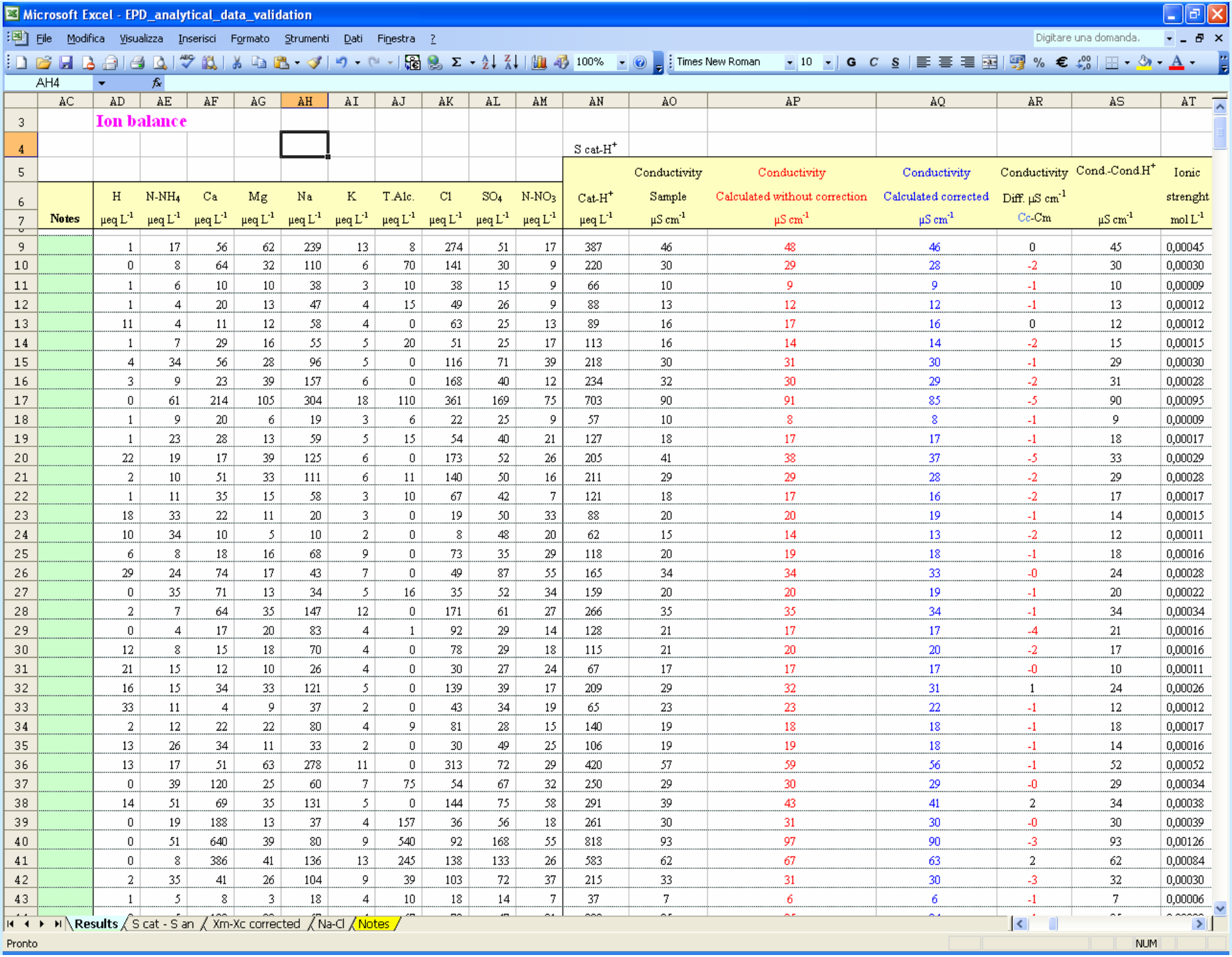
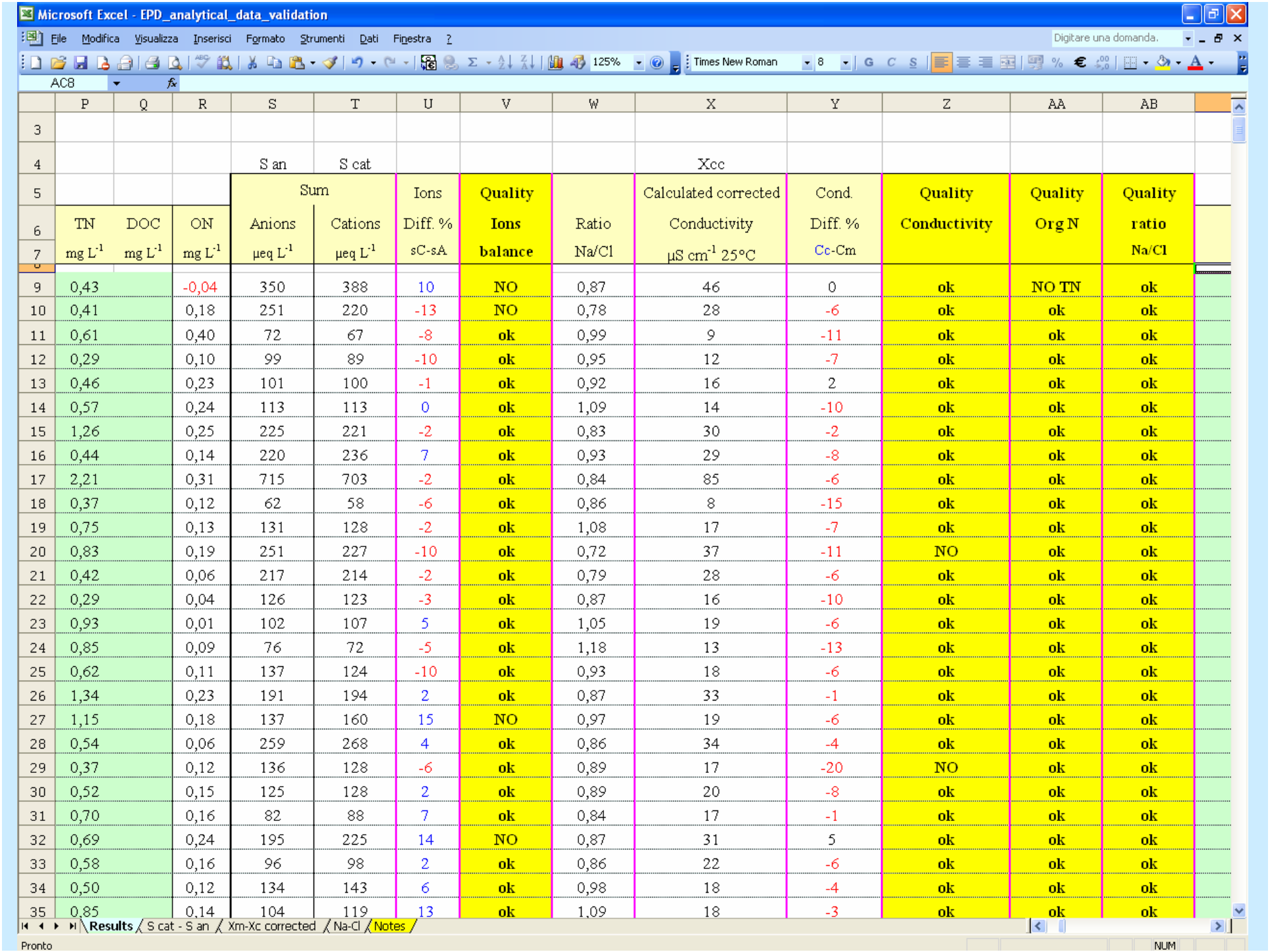


	AC	AD	AE	AF	AG	AH	AI	AJ	AK	AL	AM	AN	AO	AP	AQ	AR	AS	AT
3		**Ion balance**																
4												S cat-H^+						
5													Conductivity	Conductivity	Conductivity	Conductivity	Cond.-Cond.H^+	Ionic
6		H	$N\text{-}NH_4$	Ca	Mg	Na	K	T.Alc.	Cl	SO_4	$N\text{-}NO_3$	$Cat\text{-}H^+$	Sample	Calculated without correction	Calculated corrected	Diff. µS cm^{-1}		strenght
7	**Notes**	µeq L^{-1}	µeq L^{-1}	µeq L^{-1}	µeq L^{-1}	µeq L^{-1}	µeq L^{-1}	µeq L^{-1}	µeq L^{-1}	µeq L^{-1}	µeq L^{-1}	µeq L^{-1}	µS cm^{-1}	µS cm^{-1}	µS cm^{-1}	Cc-Cm	µS cm^{-1}	mol L^{-1}
9		1	17	56	62	239	13	8	274	51	17	387	46	48	46	0	45	0,00045
10		0	8	64	32	110	6	70	141	30	9	220	30	29	28	-2	30	0,00030
11		1	6	10	10	38	3	10	38	15	9	66	10	9	9	-1	10	0,00009
12		1	4	20	13	47	4	15	49	26	9	88	13	12	12	-1	13	0,00012
13		11	4	11	12	58	4	0	63	25	13	89	16	17	16	0	12	0,00012
14		1	7	29	16	55	5	20	51	25	17	113	16	14	14	-2	15	0,00015
15		4	34	56	28	96	5	0	116	71	39	218	30	31	30	-1	29	0,00030
16		3	9	23	39	157	6	0	168	40	12	234	32	30	29	-2	31	0,00028
17		0	61	214	105	304	18	110	361	169	75	703	90	91	85	-5	90	0,00095
18		1	9	20	6	19	3	6	22	25	9	57	10	8	8	-1	9	0,00009
19		1	23	28	13	59	5	15	54	40	21	127	18	17	17	-1	18	0,00017
20		22	19	17	39	125	6	0	173	52	26	205	41	38	37	-5	33	0,00029
21		2	10	51	33	111	6	11	140	50	16	211	29	29	28	-2	29	0,00028
22		1	11	35	15	58	3	10	67	42	7	121	18	17	16	-2	17	0,00017
23		18	33	22	11	20	3	0	19	50	33	88	20	20	19	-1	14	0,00015
24		10	34	10	5	10	2	0	8	48	20	62	15	14	13	-2	12	0,00011
25		6	8	18	16	68	9	0	73	35	29	118	20	19	18	-1	18	0,00016
26		29	24	74	17	43	7	0	49	87	55	165	34	34	33	-0	24	0,00028
27		0	35	71	13	34	5	16	35	52	34	159	20	20	19	-1	20	0,00022
28		2	7	64	35	147	12	0	171	61	27	266	35	35	34	-1	34	0,00034
29		0	4	17	20	83	4	1	92	29	14	128	21	17	17	-4	21	0,00016
30		12	8	15	18	70	4	0	78	29	18	115	21	20	20	-2	17	0,00016
31		21	15	12	10	26	4	0	30	27	24	67	17	17	17	-0	10	0,00011
32		16	15	34	33	121	5	0	139	39	17	209	29	32	31	1	24	0,00026
33		33	11	4	9	37	2	0	43	34	19	65	23	23	22	-1	12	0,00012
34		2	12	22	22	80	4	9	81	28	15	140	19	18	18	-1	18	0,00017
35		13	26	34	11	33	2	0	30	49	25	106	19	19	18	-1	14	0,00016
36		13	17	51	63	278	11	0	313	72	29	420	57	59	56	-1	52	0,00052
37		0	39	120	25	60	7	75	54	67	32	250	29	30	29	-0	29	0,00034
38		14	51	69	35	131	5	0	144	75	58	291	39	43	41	2	34	0,00038
39		0	19	188	13	37	4	157	36	56	18	261	30	31	30	-0	30	0,00039
40		0	51	640	39	80	9	540	92	168	55	818	93	97	90	-3	93	0,00126
41		0	8	386	41	136	13	245	138	133	26	583	62	67	63	2	62	0,00084
42		2	35	41	26	104	9	39	103	72	37	215	33	31	30	-3	32	0,00030
43		1	5	8	3	18	4	10	18	14	7	37	7	6	6	-1	7	0,00006



Microsoft Excel - EPD_analytical_data_validation

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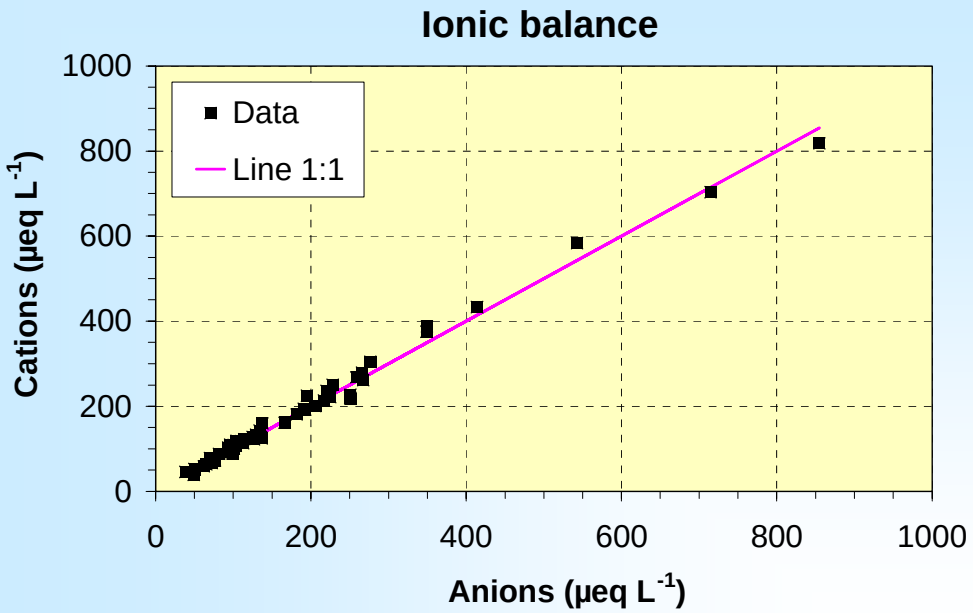
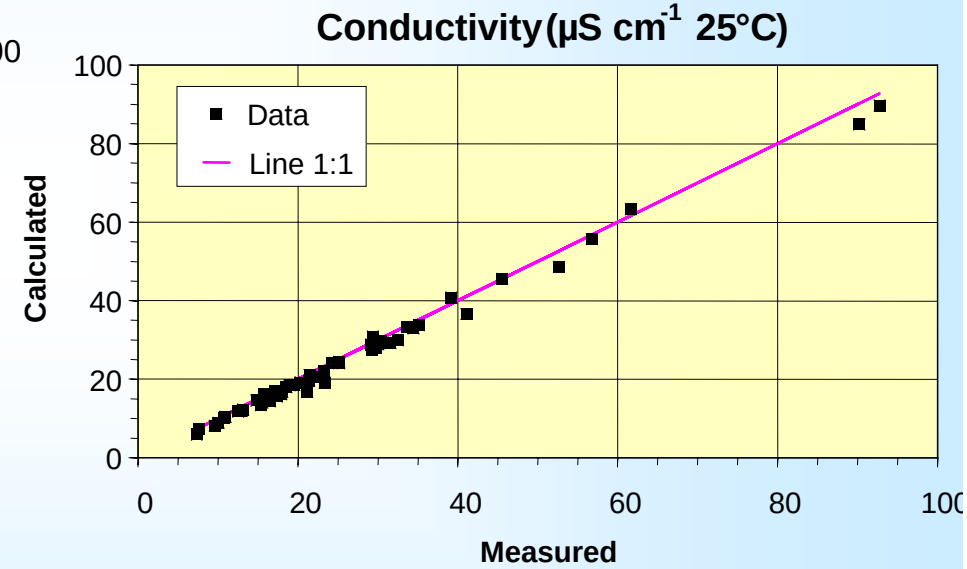
	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB
3													
4				S an	S cat				Xcc				
5				Sum		Ions	Quality		Calculated corrected	Cond.	Quality	Quality	Quality
6	TN	DOC	ON	Anions	Cations	Diff. %	Ions	Ratio	Conductivity	Diff. %	Conductivity	Org N	ratio
7	mg L^{-1}	mg L^{-1}	mg L^{-1}	µeq L^{-1}	µeq L^{-1}	sC-sA	balance	Na/Cl	µS cm^{-1} 25°C	Cc-Cm			Na/Cl
9	0,43		-0,04	350	388	10	NO	0,87	46	0	ok	NO TN	ok
10	0,41		0,18	251	220	-13	NO	0,78	28	-6	ok	ok	ok
11	0,61		0,40	72	67	-8	ok	0,99	9	-11	ok	ok	ok
12	0,29		0,10	99	89	-10	ok	0,95	12	-7	ok	ok	ok
13	0,46		0,23	101	100	-1	ok	0,92	16	2	ok	ok	ok
14	0,57		0,24	113	113	0	ok	1,09	14	-10	ok	ok	ok
15	1,26		0,25	225	221	-2	ok	0,83	30	-2	ok	ok	ok
16	0,44		0,14	220	236	7	ok	0,93	29	-8	ok	ok	ok
17	2,21		0,31	715	703	-2	ok	0,84	85	-6	ok	ok	ok
18	0,37		0,12	62	58	-6	ok	0,86	8	-15	ok	ok	ok
19	0,75		0,13	131	128	-2	ok	1,08	17	-7	ok	ok	ok
20	0,83		0,19	251	227	-10	ok	0,72	37	-11	NO	ok	ok
21	0,42		0,06	217	214	-2	ok	0,79	28	-6	ok	ok	ok
22	0,29		0,04	126	123	-3	ok	0,87	16	-10	ok	ok	ok
23	0,93		0,01	102	107	5	ok	1,05	19	-6	ok	ok	ok
24	0,85		0,09	76	72	-5	ok	1,18	13	-13	ok	ok	ok
25	0,62		0,11	137	124	-10	ok	0,93	18	-6	ok	ok	ok
26	1,34		0,23	191	194	2	ok	0,87	33	-1	ok	ok	ok
27	1,15		0,18	137	160	15	NO	0,97	19	-6	ok	ok	ok
28	0,54		0,06	259	268	4	ok	0,86	34	-4	ok	ok	ok
29	0,37		0,12	136	128	-6	ok	0,89	17	-20	NO	ok	ok
30	0,52		0,15	125	128	2	ok	0,89	20	-8	ok	ok	ok
31	0,70		0,16	82	88	7	ok	0,84	17	-1	ok	ok	ok
32	0,69		0,24	195	225	14	NO	0,87	31	5	ok	ok	ok
33	0,58		0,16	96	98	2	ok	0,86	22	-6	ok	ok	ok
34	0,50		0,12	134	143	6	ok	0,98	18	-4	ok	ok	ok
35	0,85		0,14	104	119	13	ok	1,09	18	-3	ok	ok	ok

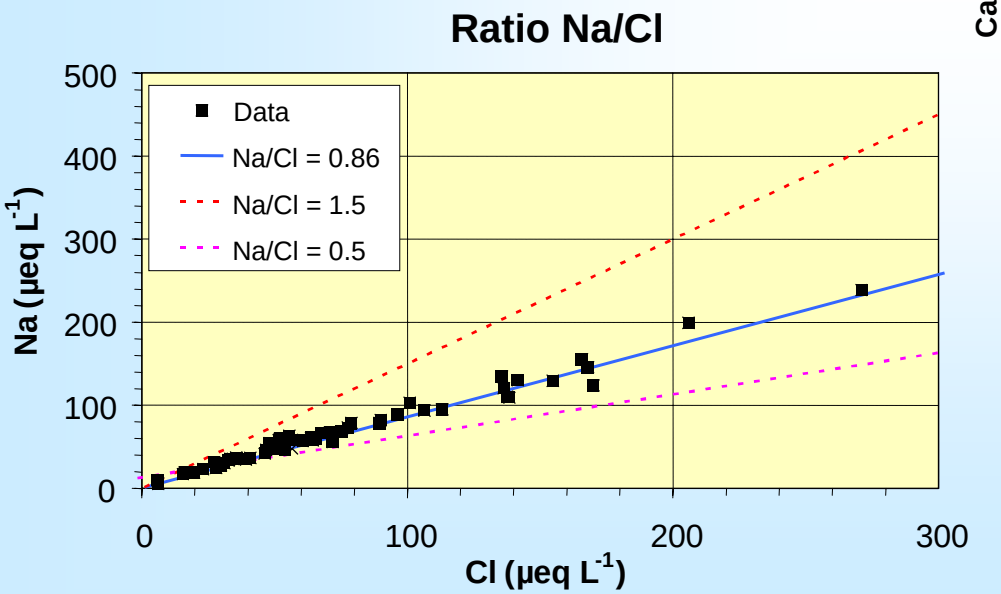
Results | S cat - S an | Xm-Xc corrected | Na-Cl | Notes

Pronto

NUM


Ionic balance
Data
Line 1:1
Cations (µeq L-1)
Anions (µeq L-1)
0
200
400
600
800
1000


Conductivity (µS cm-1 25°C)
Data
Line 1:1
Calculated
Measured
0
20
40
60
80
100


Ratio Na/Cl
Data
Na/Cl = 0.86
Na/Cl = 1.5
Na/Cl = 0.5
Na (µeq L-1)
Cl (µeq L-1)
0
100
200
300
400
500

Notes on Quality criteria

I **Quality criteria for the ion balance**:

PD=Ions % Diff. sC-sA =100x(S Cat - S An) / 0.5*(S Cat + S An)

if Cond ≤ 20 µS/cm, accepted if PD between +/- 20%.

if Cond > 20 µS/cm, accepted if PD between +/- 10%.

II **Quality criteria for conductivity**:

CD = % Diff. (CEc -CM) = 100 * (CEc -CM) / CM

if **Cond** ≤ 10 µS/cm, accepted if CD between +/- 30%;

if 10 µS/cm <**Cond** < 20 µS/cm, accepted if CD between +/- 20%;

if **Cond** > 20 µS/cm, accepted if CD between +/- 10%;

III **Organic nitrogen** (ON) is calculated from total nitrogen (TN) minus N-NO3 and N-NH4. ON must be a positive value or zero. If it is negative, something is wrong in the analyses.

VI Quality ratio **Na/Cl** OK for values between 0.5 and 1.5.

Notes on the interpretation of quality criteria for ion balance and conducti

a) Quality criteria for **conductivity** must always be satisfied (OK) for each type of samples (wet only, bulk open field, throughfall, stemflow, soil water and runoff).

b) Quality criteria for **ion balance** should be satisfied (OK) for open field samples (wet only and bulk) and runoff with low organic carbon concentrations. The ion balance criteria is not considered in the case of throughfall and stemflow samples because of the presence

c) Quality criteria for **ON** must always be satisfied (OK) for each type of samples (open field, throughfall, stemflow, soil water and runoff).

d) Quality criteria for **Na/Cl** ratio (marine ratio = 0.86, accepted range 0.5-1.5) should be satisfied for each type of samples, excluding soil water and runoff samples.

Notes on the use of graphs (S cat - S an; Xm-Xc corrected)

The sheets are not protected, you can change the scales of the axes.

Criteria proposed for the data validation are not rigid and mandatory, but should be used merely as guidelines for the person in charge of validation in each laboratory.

Analyses which do not fit with the validation criteria should be repeated and, if data are confirmed, they should be accepted and included in the database.

Further steps in the validation of results:

- Relationships between conductivity and ion (cation, anion) concentrations

It works nicely when hydrogen ion concentrations are low (pH>5.0);

When H^+ concentration is high, it contributes strongly to conductivity.

Ions	Equivalent conductance at 25°C kS cm^2 eq^{-1}
H^+	0.350
Ca^{++}, Mg^{++}, Na^+, K^+, NH_4^+, Cl^-, $SO_4^=$, NO_3^-	0.044-0.080

Criteria for the validation of the results of chemical analyses (atmospheric deposition, soil water)
Second step

Aims

Emphasise the use of data validation in the routine practice of analysis

Include DOC in the validation

Increase the number of laboratories involved in the exercise

Investigate on the meaning and relationships of DOC in atmospheric deposition and soil water

Laboratories at present involved in the study

Italy	C.N.R. Institute of Ecosystem Study, Pallanza
France	SGS Laboratories Wolff-Environment, Evry
Finland	Forest Research Institute, METLA, Rovaniemi
Norway	Norwegian Forest Research Institute, Ås
Germany	Niedersaechsische Forstliche Versuchsanstalt, Goettingen
Switzerland	WSL, Birmensdorf
Denmark	Forest & Landscape, Hørsholm
Flanders (Belgium)	Laboratorium Bodemkunde & IBW (pH and EC)
UK	Forest Research, Farhnam, Hampshire

Ionic balance

$$PD = 100 * \frac{(\Sigma \text{ cat} - \Sigma \text{ an})}{0.5\,(\Sigma \text{ cat} + \Sigma \text{ an})}$$

$$\Sigma_{\text{anions}} = \text{Alk} + [SO_4^{=}] + [NO_3^{-}] + [Cl^{-}] + [Org^{-}]$$

$$\Sigma_{\text{cations}} = [Ca^{++}] + [Mg^{++}] + [Na^{+}] + [K^{+}] + [H^{+}] + [NH_4^{+}]$$

[Org-] is measured as DOC (mg C L^{-1})

We indicate as DOC formal charge the apparent ionic charge of 1 mg/L of DOC assuming that:

- no errors are affecting the ion concentrations
- no other ions are present in solutions

Ionic balance

$$\Sigma_{anions} = Alk + [SO_4^{=}] + [NO_3^{-}] + [Cl^{-}] + [Org^{-}]$$

$$\Sigma_{anions} = Alk + [SO_4^{=}] + [NO_3^{-}] + [Cl^{-}] + f(DOC)$$

f (DOC) = slope * DOC + intercept

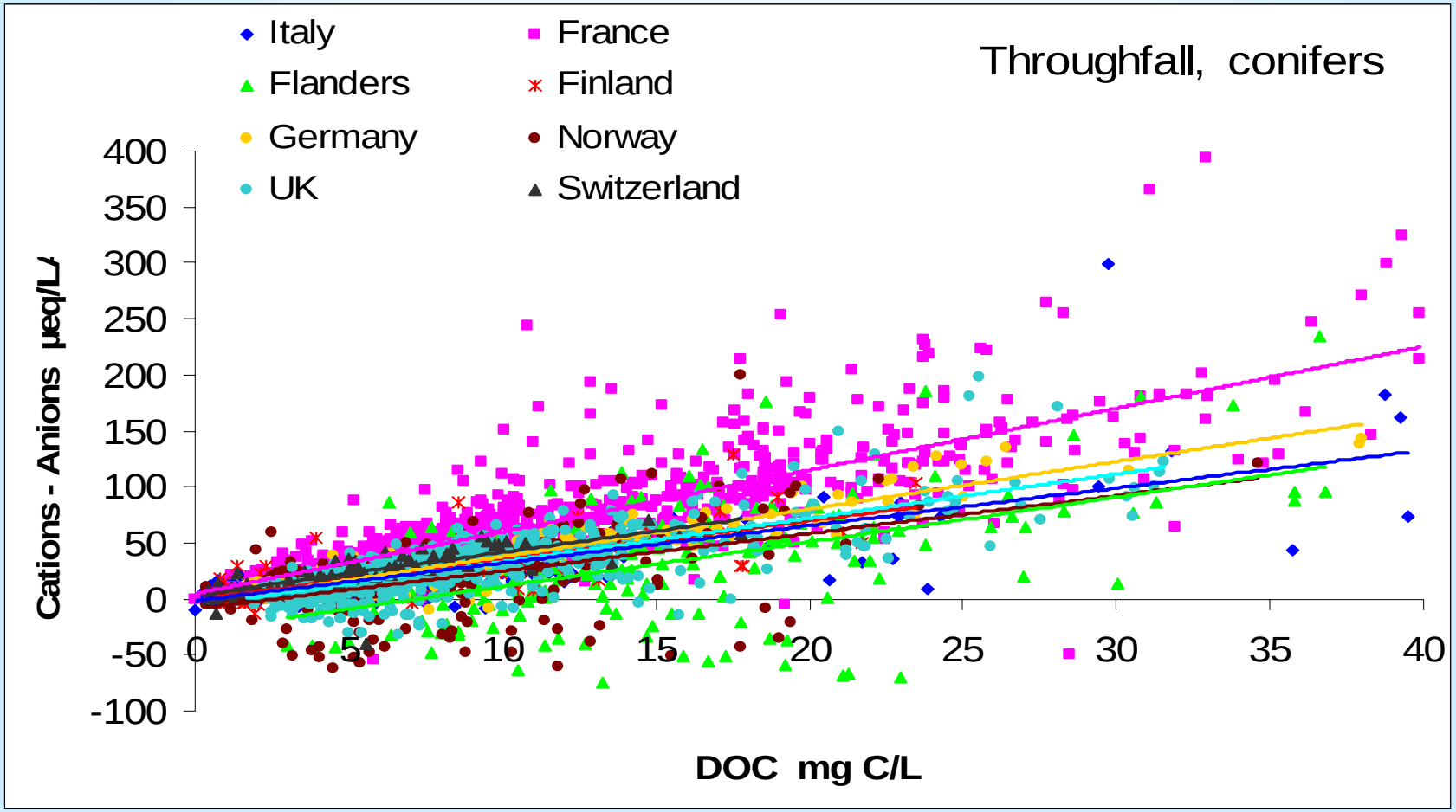
Number of data collected

Laboratory	BOF	THR Beech	THR Oak	THR other	THR Broadleaves	THR Pine	THR Spruce	THR other	THR Conifers
Italy	659	278	231	0	509	0	110	59	169
France	0	0	0	0	*1361*	0	0	0	0
Norway	181	0	0	0	0	0	216	51	267
Germany	268	99	33	0	132	66	198	0	264
Switzerland	307	132	88	0	220	45	42	28	115
Denmark	101	130	71	0	201	0	195	0	195
Flanders	402	208	0	105	313	108	0	0	108
UK	375	0	307	0	307	848	0	0	848

Laboratory	STF Broadleaves	STF Conifers	Soil water metals	
Italy	125	0	0	
France	*194*	0	1562	No data
Norway	0	0	267 ✶	T Al, Fe, Mn
Germany	0	0	1416 ✶	T Al, Al org, Fe, Mn
Switzerland	0	0	0	
Denmark	0	0	798 ✶	T Al, Fe, Mn
Flanders	105	0	475 ✶	T Al, Fe
UK	0	0	1287 ✶	T Al, Fe, Mn

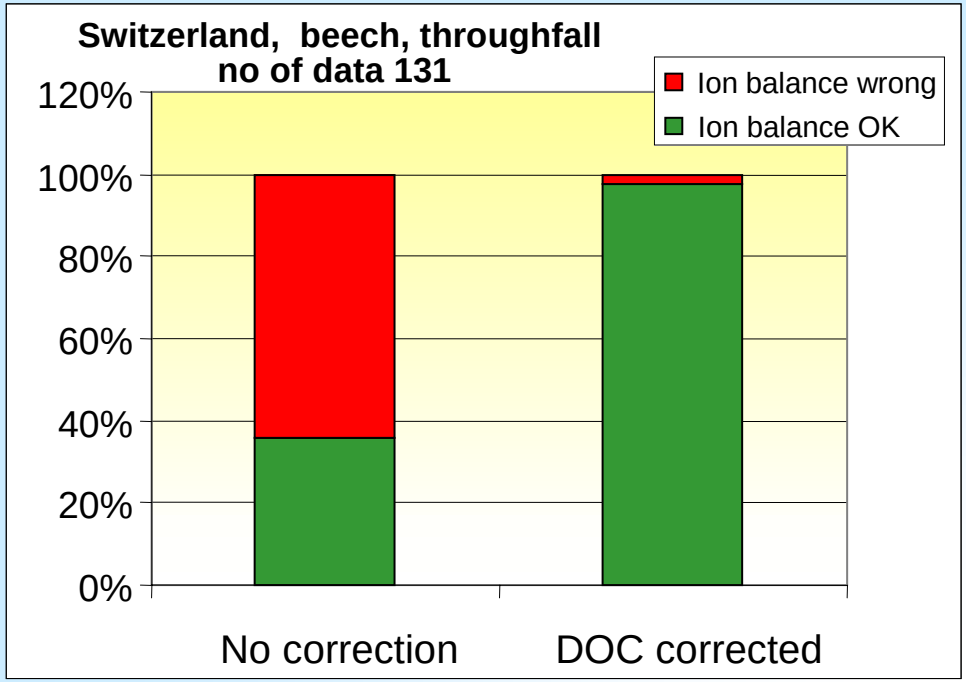
- Contribution of the organic carbon to the ion balance

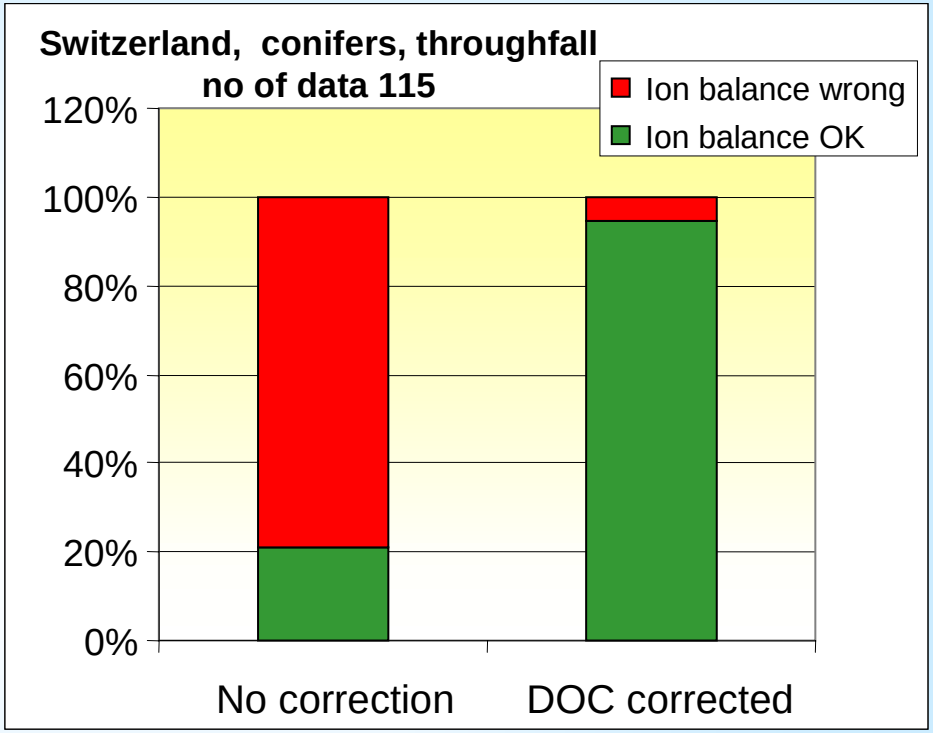
➢ The relationship between the difference ∑cations - ∑anions and the DOC concentration is tested. On this base a formal charge per mg/liter of organic carbon is assigned.

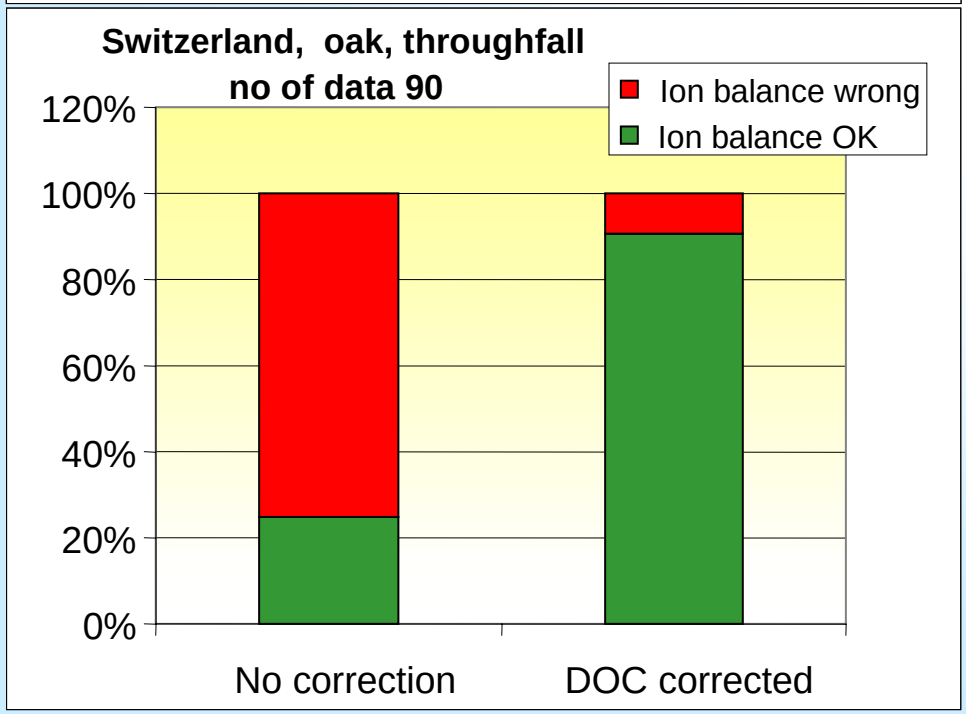


Country	slope	intercept	R^2
Italy	3,35	-1,53	0,57
France	5,52	4,62	0,65
Flanders	3,99	-28,79	0,29
Finland	3,51	-0,39	0,60
Germany	4,23	-4,43	0,85
Norway	3,37	-8,77	0,24
UK	3,91	-6,08	0,62
Switzerland	3,79	3,70	0,61

Switzerland, throughfall







Data treatment

- Data of each laboratory were validated using the standard excel file for the data validation, available in the web. Data of each laboratory were aggregated on the basis of (1) each single plot and (2) of the type of vegetation.
- Other graphs were added to those already present in the validation file. They are useful for a general exploration of data and include the relationship between **DOC** and **Σ cations – Σ anions.**
- The data used for the evaluation of DOC Formal Charge include those not fitting the validation criteria, but do not include the highest values (strong skewness).
- The evaluation of DOC FC using the slope of the linear regression must be considered as a preliminary approach.

General comments

✓ This approach requires high precision in the analyses, as the difference (∑cat - ∑anions) cumulate the systematic and random errors performed in the determination of each ion. In particular it is strongly dependent on systematic errors.

✓ Is it possible to find values of “formal charge” per mg/L of TOC for different types of solutions (bulk open field, throughfall, stemflow, soil water)?

✓ This can be reached with a statistical approach of data set obtained in different laboratories, identifying likely relevant variables:

Type of solution (bulk open field, throughfall, soil water, etc.)
Type of vegetation
Yearly amount of precipitation
Mean air temperature
??

Partial conclusions

Four different tests for the validation of chemical analyses were identified; they assist in the data screening, but they should be used with care, taking account of their limits.

An excel file makes the use of such criteria easier.

These criteria are exactly the same as are indicated in the ICP Forests manual, Part VI, Sampling and analysis of Deposition.

Both the manual and the excel file are easily downloadable from the ICP Forests web page
http://www.icp-forests.org/

Additional techniques for data validations are under evaluation

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