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

1st Meeting of the Heads of the Laboratories

(9.-10. June 2008, Hamburg, Germany)

DOC in ion balance of atmospheric deposition solutions

Validation criteria of water chemical analyses (atmospheric deposition, runoff, soil water)

Rosario Mosello and Gabriele Tartari

CNR Institute of Ecosystem Study, Verbania Pallanza, Italy
WG on QA/QC in laboratories within ICP Forests

Plan of the presentation

✓ **DOC in ion balance of atmospheric deposition solutions**

- Validation criteria for chemical analyses: the ICP Forests manual
- The first collective study on validation criteria for atmospheric deposition
- The second collective study: role of DOC in ion balance, results and discussion

✓ **Presentation of an excel sheet for the validation of chemical analysis**

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, deionised 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

Validation criteria for chemical analyses: the ICPF manual

- Ionic balance;
- Comparison between measured and calculated conductivity;
- Na/Cl ratio validation test;
- Organic nitrogen validation test.

Validation criteria

Part VI of the
ICP Forests Manual

Download from web page ICP Forests
http://www.icp-forests.org/Manual.htm

United Nations Economic Commission for Europe
CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests

MANUAL

on

Methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests

Part VI

Sampling and Analysis of Deposition

updated: 06/2004

Ionic balance

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

$$\Sigma_{anions} = [HCO_3^-] + [SO_4^=] + [NO_3^-] + [Cl^-] + [Org^-]$$

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

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*

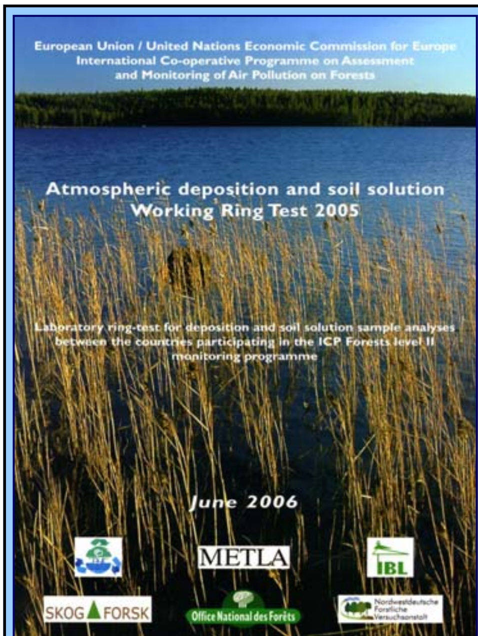
C_i *Concentration of the ion i*

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

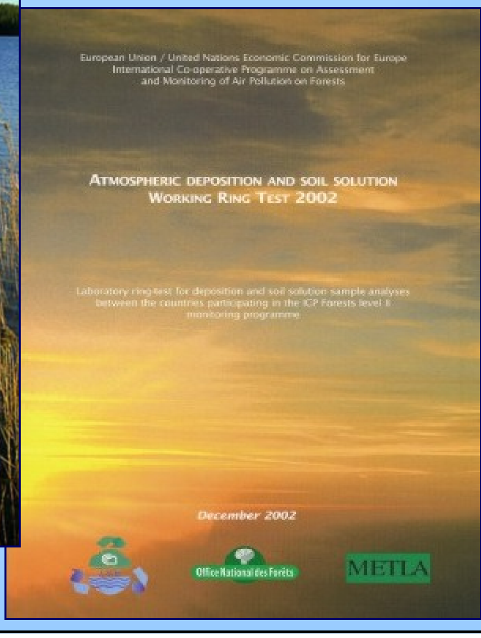
Acceptance threshold values in data validation based on the ionic balance and conductivity

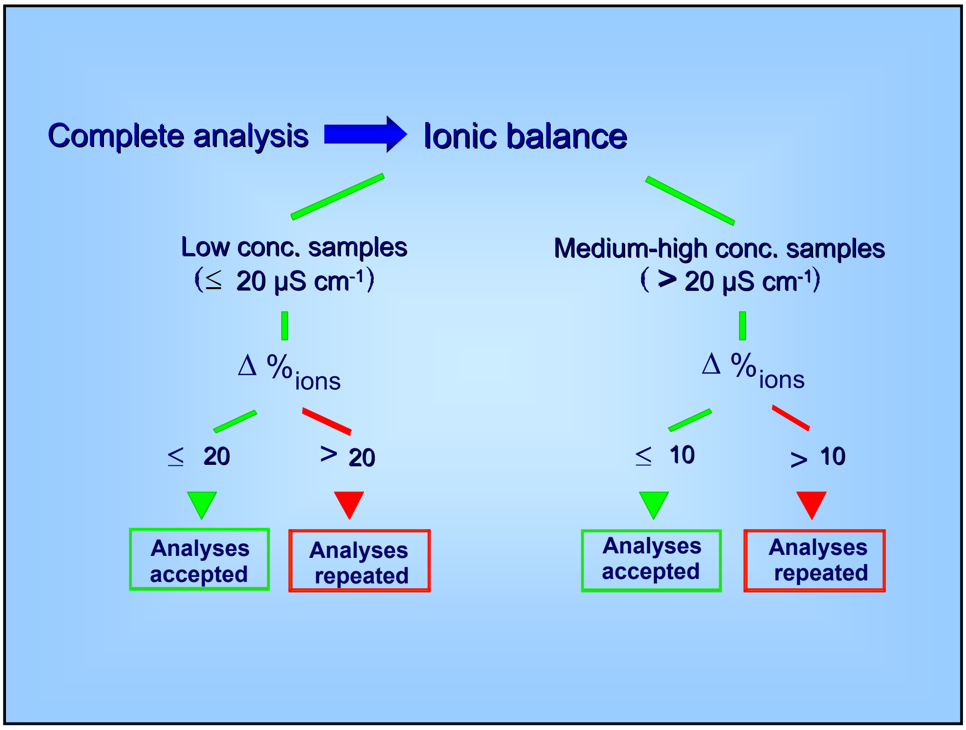
Conductivity of the sample 25 °C	Ionic balance	Conductivity
$\leq$ 10 µS cm^{-1}	± 20%	±30%
< 20 µS cm^{-1}	± 20%	±20%
> 20 µS cm^{-1}	± 10%	±10%

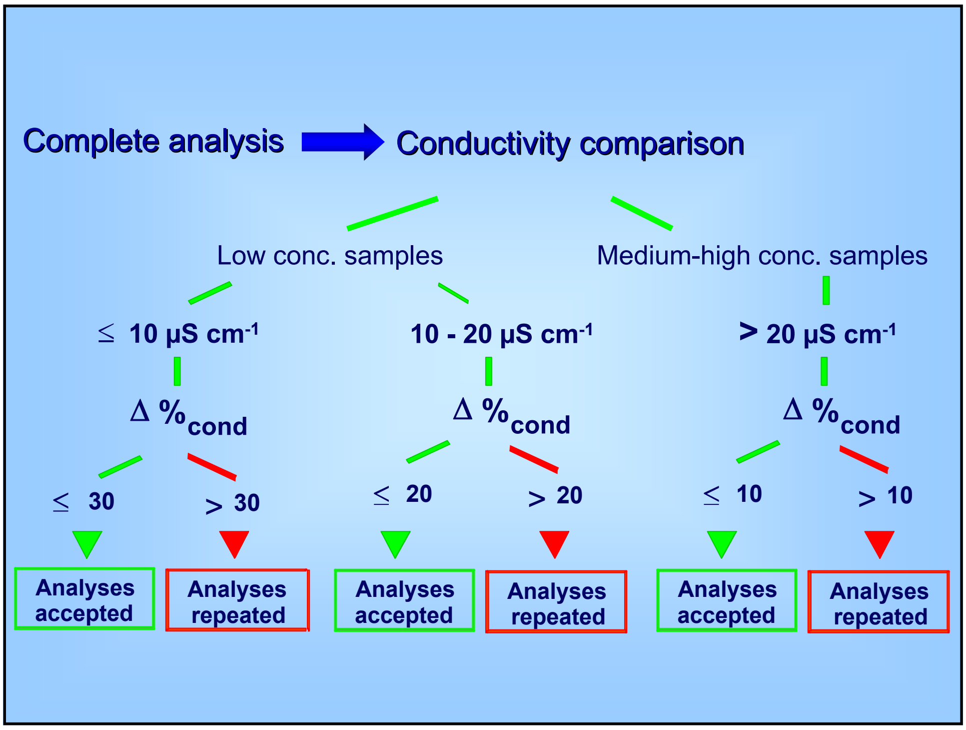


Working Ring Test 2 (2005)

Working Ring Test 1 (2002)




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


Complete analysis
Conductivity comparison
Low conc. samples
Medium-high conc. samples
≤ 10 µS cm-1
10 - 20 µS cm-1
> 20 µS cm-1
Δ %cond
Δ %cond
Δ %cond
≤ 30
> 30
≤ 20
> 20
≤ 10
> 10
Analyses accepted
Analyses repeated
Analyses accepted
Analyses repeated
Analyses accepted
Analyses repeated

Na/Cl ratio validation test

Hypothesis:

Na^+ and Cl^- in atmospheric deposition originate manly from sea spray, so that the ratio Na/Cl is close to those in sea water (0.86, molar or equivalent concentrations).

Consequences:

other ions, such as Mg^{++}, SO^{--}_4, should in part derive from sea water.

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!

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

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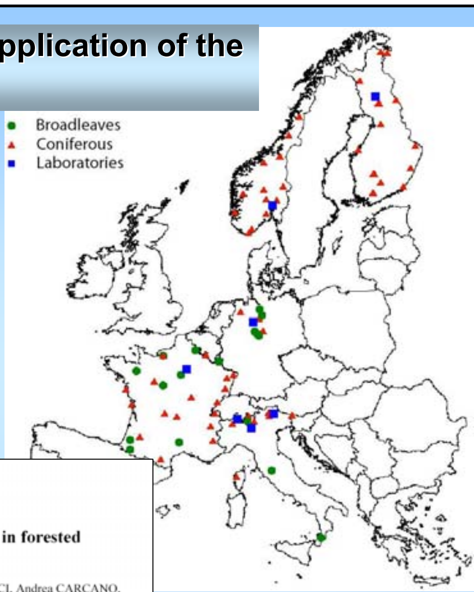
First collective study on the application of the validation criteria

- **About 5000 analyses of deposition samples done from 7 different laboratories**
- **Samples were representative of different geographic and climatic situations**



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]

CNR Institute Ecosystem Study, Largo V. Tonolli 50, 28922 Verbania Pallanza, Italy
[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

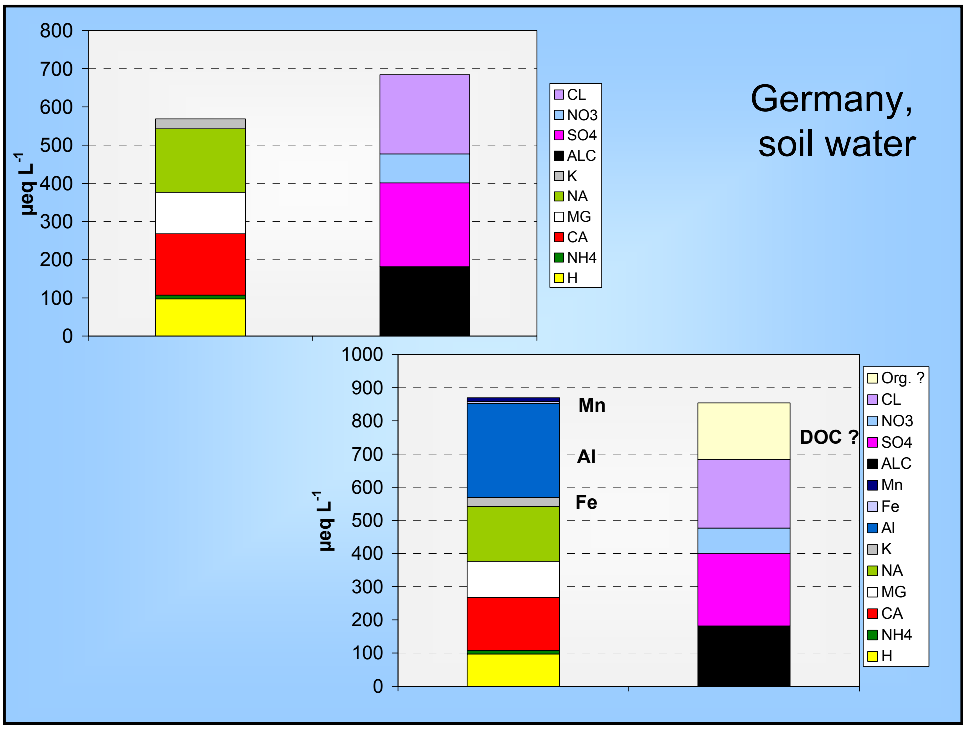
Applicability of ion balance and conductivity tests to different type of solutions

	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
soil water	no	?	no	yes
runoff	?	yes	no	yes

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

? Questions ?

- **Why organic anions contribute to ion balance and do not contribute to conductivity?**
- **Why soil water is different from atmospheric deposition and runoff?**

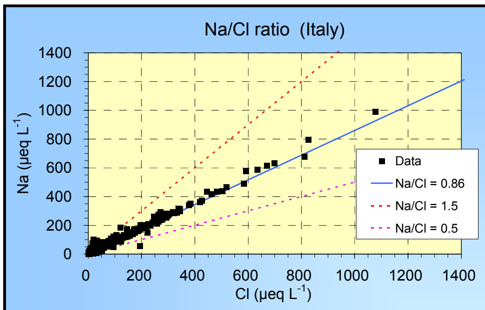


Soil water

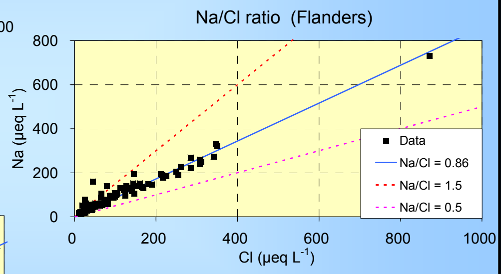
In the case of soil water both organic carbon and trace metals are important in the ion balance.

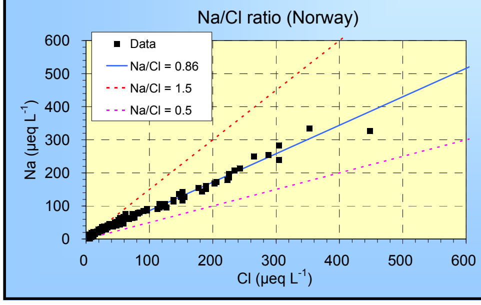
However there are problems in evaluating the ionic contribution of trace metals to the ion balance, because of the dependence of the metal speciation from pH and the possibility of complexation with organic substance (DOC).

These aspects do not exclude the possibility to check for correlations among variables, assuming a full dissociation of trace metals



Is Na/Cl ratio close to 0.86, the value in sea water?





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.

Plan of the presentation

- ✓ **DOC in ion balance of atmospheric deposition solutions**
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- ✓ **Presentation of an excel sheet for the validation of chemical analysis**

Criteria for the Validation of the Results of Chemical Analyses (atmospheric deposition, run off)
Second Step

Aims

- **Emphasise the use of data validation in the analyses routine practice**
- **Include DOC in the ion balance 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 Involved in the Study

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

Second collective study on the application of the validation criteria

- **About 6000 analyses of deposition samples done from 8 different laboratories**
- **Emphasis given to the role of DOC and organic anions**

J. Limnol., 67(1): ??-??, 2008

Validation of chemical analyses of atmospheric deposition on forested sites in Europe: 2. DOC concentration as an estimator of the organic ion charge

Rosario MOSELLO*, Tiziana AMORIELLO[1], Sue BENHAM[2], Nicholas Clarke[3], John DEROME[4], Kirsti DEROME[4], Gerrit GENOUW[5], Nils KOENIG[6], Arianna ORRÙ, Gabriele TARTARI, Anne THIMONIER[7], Erwin ULRICH[8] and Antti-Jussi LINDROOS[4]

CNR Institute of Ecosystem Study, L.go Tonolli 50, 28922 Verbania, Italy
[1]CRA Experimental Institute for Plant Nutrition, Via della Navicella 2/4, 00184 Roma, Italy
[2]Forest Research Laboratory, Farnham Surrey, UK
[3]Norwegian Forest and Landscape Institute, Hogskolevein 12, 1432 Ås, Norway
[4]Finnish Forest Research Institute, P.O. Box 16, 96301 Rovaniemi, Finland
[5]Research Institute for Nature and Forest, Geraardsbergen, Belgium
[6]Nordwestdeutsche Forstliche Versuchsanstalt, Graetzelstr. 2, 37079 Goettingen, Germany
[7]WSL, Birmensdorf, Switzerland
[8]Office National des Forests, Boulevard de Constance, 77300 Fontainebleau, France
* e-mail corresponding author: r.mosello@ise.cnr.it

R. Mosello et al.

Fig. 1. Location of the sampling plots: dots broadleaves, triangles conifers.

Data used in the study

Number of samples used for the statistical analysis of each type of solution (in brackets: number of samples used for testing the regressions).

Tree	Solution	BE	CH	DE	FIN	FR	IT	NO	UK	Total
Conifers	BOF	144	106	92	162		214	167	79	964
Conifers	THR	186	70	243 (443)	121	306 (513)	214 (80)	216 (236)	301 (397)	1657 (1699)
Broad leaves	BOF	199	136	88			604		78	1105
Broad leaves	STF	275				143	179			597
Broad leaves	THR	253	126	121 (210)		372	299 (300)		283	1454 (510)
Total		**1057**	**438**	**544 (653)**	**283**	**821 (513)**	**1510 (380)**	**383 (236)**	**741 (397)**	**5777 (2179)**

Data Handling

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

Ionic balance

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

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

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

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

We indicate as DOC formal charge (β1) the apparent ionic charge of 1 mg/L of DOC assuming that:

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

Ionic Balance

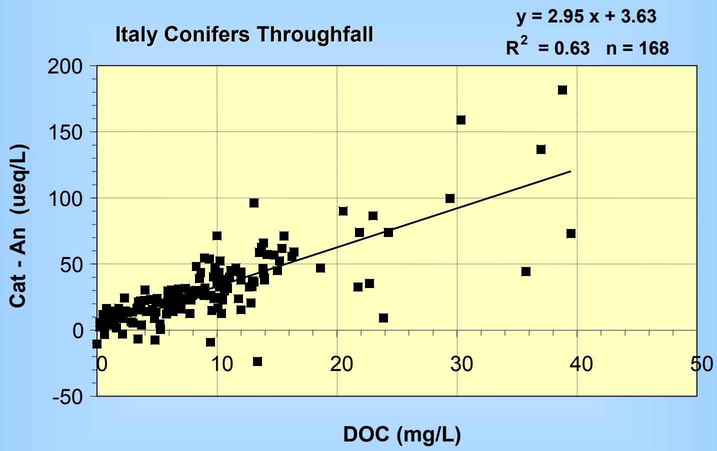
$$\Sigma_{anions} = [HCO3-] + [SO_4^{=}] + [NO_3^{-}] + [Cl^{-}] + [Org^{-}]$$

$$\Sigma_{anions} = [HCO3-] + [SO_4^{=}] + [NO_3^{-}] + [Cl^{-}] + f(DOC)$$

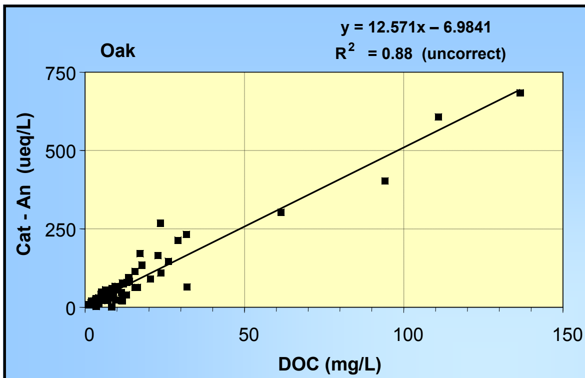
f (DOC) = slope * DOC + intercept

$$f(DOC) = \beta_1 * DOC + \beta_0$$

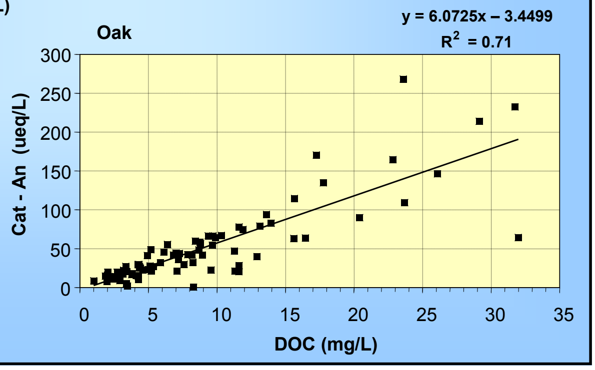
Evaluation of the DOC Formal Charge Using the Regression Slope of DOC (mg C L^{-1}) vs Cat-An (μeq L^{-1})



Slope = $\beta_1 = \Delta y / \Delta x$ = μ eq L^{-1} / mg C L^{-1} = μeq / mg C



Switzerland Throughfall



Role of DOC (mg C L^{-1}) in the Ion Balance

Hypotheses tested on the data set from different laboratories and type of solutions (1-4), and on the regression coefficients β1 (formal charge) of the significant regression Δ vs DOC.

1) Do differences in the data set from different laboratories exist?
2) Are there differences between data set from different type of solutions?
3) Are there differences between data set from solutions deriving from broadleaves or conifer plots?
4) Are there differences between data set of deposition with high or low marine salt content?

5) Are there differences between the coefficients (β1) from different types of solutions?
6) Are there differences between coefficients from different plots?
7) Are there differences between coefficients related to geographic/climatic conditions of the plots?

Role of DOC (mg C L^{-1}) in the Ion Balance

1) Do differences in the data set from different laboratories exist?

Yes, the statistical analysis shows highly significant differences between the data set with a 30% of the variability explained by the variable "laboratory".

2) Are there differences between data set from different type of solutions?

The comparison between the data set of THR and STF solutions was possible only in the case of BE, FR and IT; in all these cases the differences resulted significant with a relative contribution to the total variance of 19, 4 and 2% respectively.

3) Are there differences between data set from solutions deriving from broadleaves or conifer plots?

The comparison was possible in the case of six countries (BE, DE, FR, IT, UK, CH) and resulted in all cases being highly significant, although the contribution to the total variance of the model was very low (0.5 %).

4) Are there differences between data set of deposition with high or low marine salt content?

Yes, this variable explains 3% and 9% of the total variability of the model for THR (8 labs) and STF solutions (3 labs), respectively.

Role of DOC (mg C L^{-1}) in the Ion Balance

Hypotheses tested on the data set from different laboratories and type of solutions (1-4), and on the regression coefficients β1 (formal charge) of the significant regression Δ vs DOC.

1) Do differences in the data set from different laboratories exist?
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5) Are there differences between the coefficients (β1) from different types of solutions?
6) Are there differences between coefficients from different plots?
7) Are there differences between coefficients related to geographic/climatic conditions of the plots?

Role of DOC (mg C L^{-1}) in the Ion Balance

5) Are there differences between the coefficients (β1) from different types of solutions?

The slopes β1 of the regressions do not show significant differences for the solutions STF and THR; this is limited to the solutions of BL plots from IT, BE, FR, for which both THR and STF data are available.

6) Are there differences between coefficients from different plots?

7) Are there differences between coefficients related to geographic/climatic conditions of the plots?

Role of DOC (mg C L^{-1}) in the Ion Balance

6) Are there differences between coefficients from different plots?

Tab. 8 - Range, mean values and standard deviations of β1 and β0 in different plots and types of solutions

	Througfall conifers	Throughfall broad leaves	Stemflow broad leaves
n. of plots	46	32	11
$\beta_1 \pm \sigma$	**4.73 ± 1.58**	**5.91 ± 1.99**	**4.95 ± 1.60**
range β_1	2.33, 9.08	2.22, 10.65	2.98, 8.34
$\beta_0 \pm \sigma$	**-3.06 ± 15.87**	**-4.46 ± 14.81**	**-4.97 ±13.08**
range β_0	-48.47, 34.85	-43.46, 27.21	-22.61, 14.42

Role of DOC (mg C L^{-1}) in the Ion Balance

7) Are there differences between coefficients related to geographic/climatic conditions of the plots?

Geographic variables: latitude, longitude, altitude

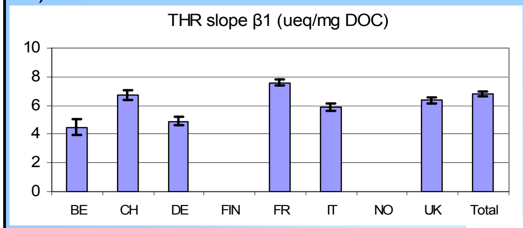
Climatological variables: mean annual temperature and amount of precipitation

The statistical analyses did not give any significant indication on regular variations of β_1 using these variables.

It is not possible to verify how much weight the broad approach in the definition of the tree types (broad leaves and conifers) and the associated errors to the chemical data have on this result.

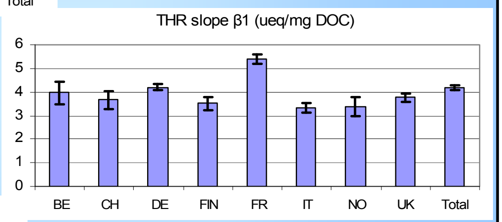
Role of DOC (mg C L^{-1}) in the Ion Balance

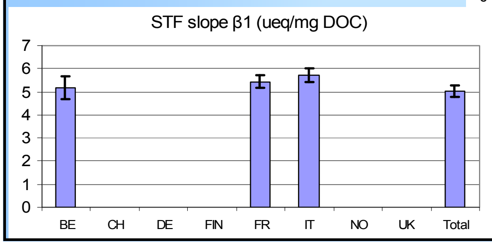
5) Are there differences between the coefficients (β1) from different types of solutions?



Broad leaves, throughfall

Conifers, throughfall

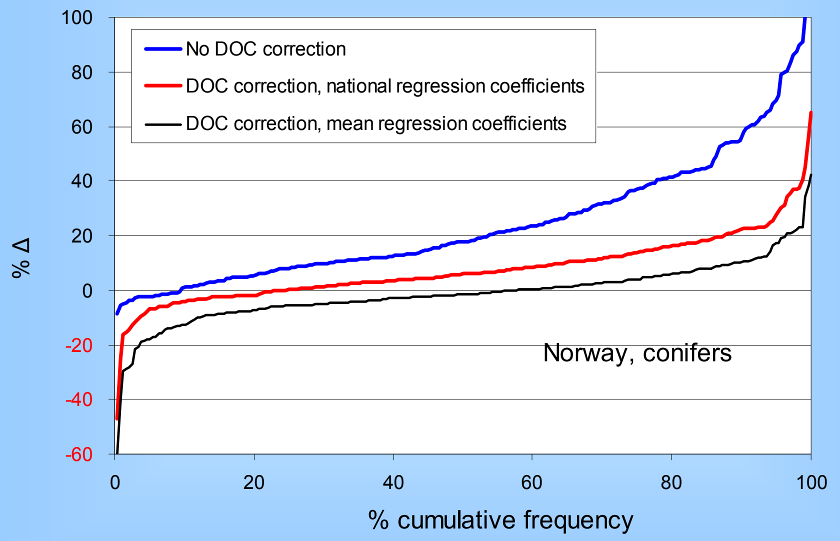




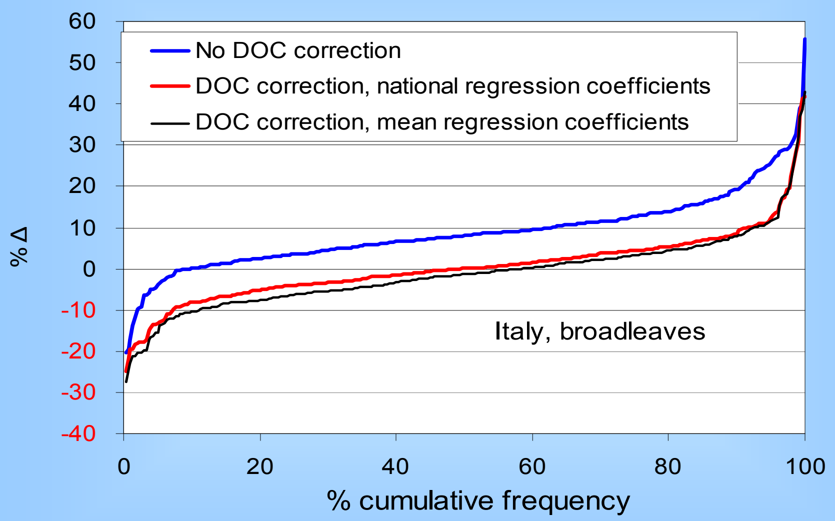
Broad leaves, stemflow

		Broad Leaves		Conifers
	units	THR	STF	THR
N	-	1454	597	1657
pH range	u	4.0 - 7.9	3.8 - 8.1	4.1 – 7.0
pH mean± σ	u	5.8±0.6	5.6±0.6	5.3±0.5
DOC range	mg C L^{-1}	0-37	14246	0-40
DOC mean± σ	mg C L^{-1}	8±6	11±7	10±7
∑ cat range	μeq L^{-1}	37-2736	30-5287	13-2601
∑ cat mean± σ	μeq L^{-1}	418±321	593±539	316±278
∑ an range	μeq L^{-1}	29-2606	22-5303	250102
∑ an mean± σ	μeq L^{-1}	377±304	545±523	279±265
∑ ca t- ∑ an range	μeq L^{-1}	258	263	225
∑ cat - ∑ an mean± σ	μeq L^{-1}	41±59	48±58	37±41
Slope β1	μeq (mg $C)^{-1}$	**6,80±0,16**	**5.04±0.25**	**4.17±0.11**
Intercept β0	μeq L^{-1}	**-12,32±1,63**	**-6.67±3.29**	**-5.01±1.32**
P-value		<0,0001	<0.0001	<0,0001
R^2		0.56	0.4	0.47

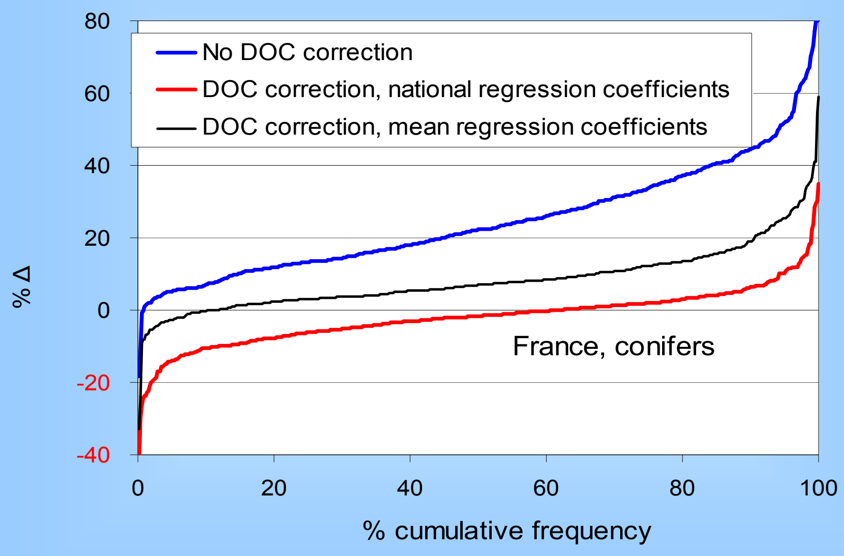
Use of DOC Formal Charge in the evaluation of the ion balance



Use of DOC Formal Charge in the Evaluation of the Ion Balance



Use of DOC Formal Charge in the Evaluation of the Ion Balance



Percent of analyses validated based on conductivity and ion balance tests

1) no correction 2) regression calculated for each country
3) regression calculated from the mean of all countries

		n. samples	Conductivity test %	Ion balance test % (1)	(2)	(3)
Belgium	BL STF	120	81	60	92	93
	BL THR	91	82	70	77	87
	CON	60	90	73	92	73
Switzerland	BL	148	58	27	93	89
	CON	111	56	20	87	78
Germany	BL	210	91	67	93	93
	CON	443	92	52	89	95
Finland	BL	-	-	-	-	-
	CON	104	51	26	60	53
France	BL	-	-	-	-	-
	CON	514	100	17	88	72
Italy	BL	300	100	61	84	81
	CON	82	91	26	70	73
Norway	BL	-	-	-	-	-
	CON	236	87	36	78	84
UK	BL	-	-	-	-	-
	CON	396	100	58	67	66

Conclusions

The investigations done on about 6000 data from 8 laboratories indicates DOC concentrations can helpfully be used to evaluate the formal charge of DOC in the ion balance to check the results of THR and STF samples analyses.

Statistical analyses indicate that the main cause of variability is linked to “laboratory”, i.e. to systematic (and random) errors associated to chemical analyses.

The comparison between formal charges associated to DOC/TOC in atmospheric deposition and freshwater does not indicate relevant differences.

The large range of geographic and climatic conditions of the plots used in the study indicates that as a first approach the mean values of β_1, β_0 evaluated in this paper can be considered for general use, but…

Specific studies carried out in each laboratory, aimed at testing the regression between Δ and DOC, are strongly recommended as part of the validation of the analytical results.

Future Work

A complete set of analyses was available only for 8 labs out of 52-59 laboratories participating in the WRT1 and WRT2. The number of laboratories performing all the analyses indicated from the ICP Forests manual should increase.

Differences between the results obtained in laboratories was the most important cause of variability, explaining about 30% of the total variance. The comparability of data produced in different laboratories must be improved.

To reach this goal it is essential an improvement in QA/QC both in and between laboratories. Working Ring Tests and collaborative studies such as the present one, and the following discussions, can greatly help in improving the quality of analytical data.

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Norway	Nicholas Clarke
Germany	Nils Konig
Switzerland	Anne Pelletier, Maria Dittrich, Daniele Pezzotta
Denmark	Karin Hansen
Flanders (Belgium)	Nicole Vindevogel, Gerrit Genouw
UK	Sue Benham
Slovenia	Tamara Jakovljevic