

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

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ABSTRACT

A Working Group on Quality Assurance/Quality Control of analyses in laboratories active in the chemical analysis of atmospheric deposition and soil water has been created within the framework of the Integrated Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (UN-ECE/ICP Forests) and the EU/Forest Focus Programme (Regulation 2152/2003). This paper is a follow up to an earlier paper dealing with the validation of chemical analyses, in which validation techniques (ion balance, comparison between measured and calculated conductivity, Na/Cl ratio and relationship between different forms of N) were tested on a set of real analysis data obtained from different laboratories. This paper focuses on the validation of chemical analysis of samples containing high dissolved organic carbon (DOC) concentrations ($> 5 \text{ mg C L}^{-1}$), where the ion balance criterion fails because of the presence of weak organic acids. About 6000 chemical analyses of bulk open field, throughfall and stemflow samples, which contained complete sets of all ion concentrations, conductivity and DOC, produced in 8 different laboratories, were used to calculate empirical relationships between DOC and the difference between the sum of cations and the sum of anions, with the aim to evaluate a formal charge per mg of organic C. Regression coefficients were obtained for data from each laboratory, as well as for all the data combined. The coefficients were further tested using an independent set of data from each country. The differences between the individual laboratory and the overall regression coefficients are discussed. The results are also considered in the light of formal charge values for DOC/TOC obtained in studies on freshwater. The formal DOC charge proved to be useful for estimating the contribution of organic acids in the ion balance test, thus considerably improving the applicability of the ion balance as a validation criterion for samples with high DOC values.

Key words: atmospheric deposition chemistry, chemical analysis, validation criteria, European network, DOC

1. INTRODUCTION

The Working Group on Quality Assurance/Quality Control for laboratories participating in ICP Forests and EU Forest Focus was created to assist laboratories responsible for the analysis of atmospheric deposition, soil and soil solution, and leaves/needles, within the programmes. The validation of chemical analyses of atmospheric deposition collected on the monitoring plots was considered to be an important task of the working group, these questions being covered to some extent already in the manual of the ICP Forests programme (Ulrich *et al.* 2006). In a previous paper (Mosello *et al.* 2005), four validation criteria were proposed and tested on a set of 5000 analyses carried out in seven laboratories in five different countries. The results clearly demonstrated that

the comparison between measured and calculated conductivity was the most widely applicable criterion for the validation of water samples, as it was equally applicable to open field (bulk and wet only), throughfall and stemflow deposition. On the other hand, although the ion balance of the most common cations (H^+ , NH_4^+ , Ca^{++} , Mg^{++} , Na^+ , K^+) and anions (HCO_3^- , SO_4^- , NO_3^- , Cl^-) is reliable in the case of bulk open field and wet-only samples (in the following referred to as BOF and WET), it is not applicable in the case of throughfall and stemflow (THR and STF) samples owing to the presence of significant amount of organic anions, collectively measured as dissolved organic carbon (DOC).

The other two validation criteria (the Na/Cl ratio and a consistency test of the concentrations of different forms of nitrogen) are applicable to the four types of

deposition, but their descriptive properties are definitely lower than those of the tests based on conductivity and ion balance.

The present paper aims to investigate the DOC concentration of different types of precipitation, and to evaluate the possibility of using the DOC concentrations to evaluate the ionic contribution of the organic anions in solution. The difference between the sum of cations and the sum of anions is therefore compared with the DOC concentration in order to evaluate whether DOC can be used to evaluate the existing ionic differences.

As systematic errors are a possible source of bias in the cation and anion determinations, the data analyses were performed on a set of data provided by 8 different laboratories; it is very unlikely that the same systematic errors occur in all of the laboratories. In the second step, the regression coefficients between ($\Sigma_{\text{cat}} - \Sigma_{\text{an}}$) and DOC for the different laboratories, and for different types of solution, are discussed in relation to the analytical methods used and the geographic and climatic characteristics of the sample plots. Finally, the results are discussed in relation to other attempts to quantify the relative contribution of organic anions in the ion balance of atmospheric deposition and freshwater.

2. METHODS

2.1. Sources of data, type of solutions used and analytical methods

Names and acronyms of the laboratories involved in the study are given in table 1, and the distribution of the sample plots in figure 1.

The type of solutions (BOF, THR, STF) and the number of samples of each type, after exclusion of samples that did not pass the validation criteria, are listed in table 2. The results were validated at the national level by the National Focal Centres of the ICP Forests and Forest Focus programmes, and submitted as official results for the years 2002–2003. In addition, the samples analysed by the individual laboratories were further stratified according to the type of tree cover on the plot (broadleaves BL, conifers CON), and the relative importance of salts of marine origin using a Cl^- concentration of $50 \mu\text{eq L}^{-1}$ as the threshold to distinguish between

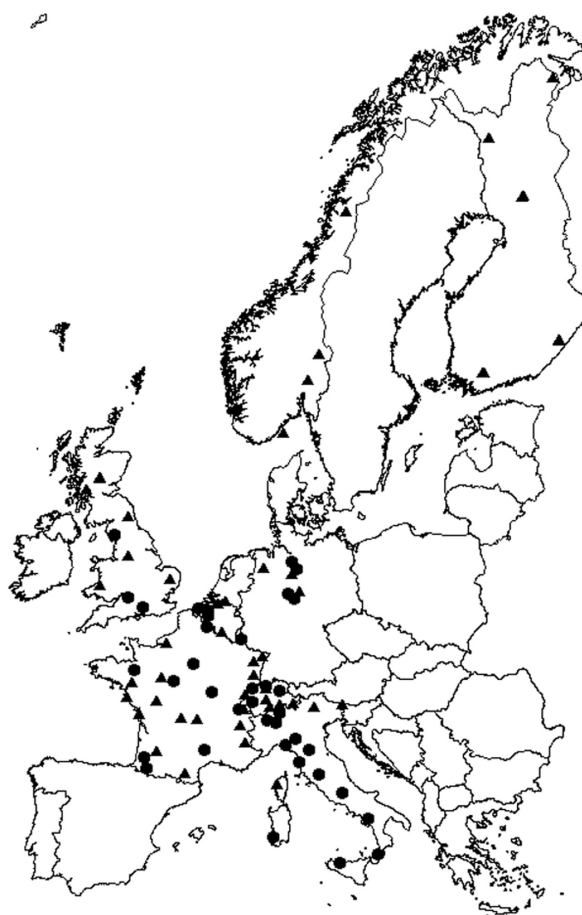


Fig. 1. Location of the sampling plots: dots broadleaves, triangles conifers.

samples with strong or weak marine influence. Table 2 also shows the number of samples forming a subset of independent analyses used to validate the effects of the DOC correction on the results of the ion balance calculations. The analytical methods used in each laboratory are listed in table 3. All the laboratories follow a QA/QC program, and participated in the two intercomparison exercises performed within the framework of the programmes (Mosello *et al.* 2002; Marchetto *et al.* 2006).

Tab. 1. Laboratories participating in the study.

BE	Laboratory of Soil Science, Ghent (main ions and DOC)
BE	Research Institute for Nature and Forest, Geraardsbergen (pH and conductivity)
CH	WSL, Birmensdorf, Switzerland
DE	Nordwestdeutsche Forstliche Versuchsanstalt, Göttingen, Germany
FI	Finnish Forest Research Institute, Rovaniemi, Finland
FR	SGS Laboratories Wolff-Environment, Evry, France
IT	C.N.R. Institute of Ecosystem Study, Verbania Pallanza, Italy
NO	Norwegian Forest Research Institute, Ås, Norway
UK	Forest Research Institute, Alice Holt Lodge, Farnham Surrey, Great Britain

Tab. 2. Number of analysis sets supplied by the individual countries used for the statistical analysis on each type of solution (number of analysis sets used for testing the regressions in parentheses). BOF = bulk open field, THR = throughfall, STF = stemflow.

Tree cover	Type solution	BE	CH	DE	FI	FR	IT	NO	UK	Total
Conifer	BOF	144	106	92	162		214	167	79	964
Conifer	THR	186 (60)	70 (111)	243 (443)	121 (104)	306 (514)	214 (82)	216 (236)	301 (396)	1657 (1946)
Broadleaf	BOF	199	136	88			604		78	1105
Broadleaf	STF	275 (120)				143	179			597 (120)
Broadleaf	THR	253 (91)	126 (148)	121 (210)		372	299 (300)		283	1454 (749)
Total		1057 (271)	438 (259)	544 (653)	283 (104)	821 (514)	1510 (382)	383 (236)	741 (396)	5777 (2815)

Tab. 3. Main analytical methods used by the laboratories.

Lab.	pH	Conductivity	Alkalinity	NH ₄ ⁺	Ca ⁺⁺ , Mg ⁺⁺ , Na ⁺ , K ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻	DOC
BE	POT GEN	CORR	POT 2EP	IC	AAS	IC	IC	IC	THIR
CH	POT LIS	CORR	POT Gran	CF GD	ICP OES	IC	IC	IC	THIR
DE	POT LIS	CORR	POT Gran	CF Phe	ICP OES	CF AgCl	CF Cd	ICP OES	THIR
FI	POT LIS	25 °C	POT 2EP	CF GD	IC	IC	IC	IC	THIR
FR	POT GEN	CORR	POT 2EP	IC	IC	IC	IC	IC	THIR
IT	POT LIS	CORR	POT Gran	SPEC Phe	IC	IC	IC	IC	THIR
NO	POT GEN	25 °C	POT 4.5	CF GD	ICP OES	IC	IC	IC	THIR
UK	POT LIS	25 °C	POT 2EP	CF Phe	ICP OES	IC	IC	IC	THIR

Legend

Acronym	Method description
POT GEN	pH - potentiometric with unspecified electrode
POT LIS	pH - potentiometric with low ionic strength electrode
25 °C	Conductivity - measurement performed at 25 °C
CORR	Conductivity - measurement performed at different temperature and corrected to 25 °C
POT	Gran Alkalinity - potentiometric titration with Gran method for extrapolation of the equivalent point
POT 2EP	Alkalinity - potentiometric titration with two end point extrapolation of the equivalent point
POT 4.5	Alkalinity - potentiometric titration with one end point extrapolation of the equivalent point, results corrected for acid addition
SPEC Phe	Ammonium - spectrophotometry indophenol blue method
CF Phe	Ammonium - continuous flow analysis with indophenol blue method
CF GD	Ammonium - continuous flow analysis with gas diffusion
IC	Ion chromatography with chemical or electrochemical eluent suppression
ICP OES	Inductively coupled plasma optical emission spectrometry
CF AgCl	Chloride - continuous flow analysis with Ag/AgCl electrode
CF Cd	Nitrate - continuous flow analysis with Cd reduction
AAS	Atomic absorption spectrophotometry
THIR	Thermal combustion and IR detection

2.2. Validation checks outlined in the ICP Forests manual

As prescribed in the ICP Forests manual (Ulrich *et al.* 2006), each laboratory is to perform a check of the ion

balance (only BOF and WET) and a comparison between the measured (CM) and calculated (CE) conductivity (on all types of samples) in order to validate the analysis results. A third check is performed to confirm that the Na/Cl ratio is between 0.5 and 1.5. According to the

instructions given in the manual, if the thresholds of these checks are exceeded then the analyses must be repeated; if the result is confirmed and the thresholds are still exceeded, the results must be accepted. The relationships used in the validation are the concentration of anions vs the concentration of cations (\sum_{cat} vs \sum_{an}), and the measured conductivity vs the calculated conductivity (CM vs CE):

$$\begin{aligned}\sum_{\text{cat}} &= [\text{Ca}^{++}] + [\text{Mg}^{++}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] + [\text{H}^+] \\ \sum_{\text{an}} &= [\text{HCO}_3^-] + [\text{SO}_4^{--}] + [\text{NO}_3^-] + [\text{Cl}^-] \\ \text{CE} &= \sum \lambda_i \text{ Ci}\end{aligned}$$

$i = \text{H}^+, \text{Ca}^{++}, \text{Mg}^{++}, \text{Na}^+, \text{K}^+, \text{NH}_4^+, \text{HCO}_3^-, \text{SO}_4^{--}, \text{NO}_3^-, \text{Cl}^-$; λ_i = equivalent conductance at infinite dilution of the ion i (Tab. 4). As the concentrations are expressed in $\mu\text{eq L}^{-1}$, λ_i is given as $\text{kS cm}^2 \text{eq}^{-1}$ in order to obtain the conductivity in $\mu\text{S cm}^{-1}$.

Bicarbonate is calculated from total alkalinity (Gran's alkalinity) in relation to the pH, assuming that it is determined only by inorganic carbon species, proton and hydroxide:

$$\text{TA} = -[\text{H}^+] + [\text{OH}^-] + [\text{HCO}_3^-] + [\text{CO}_3^{--}]$$

This definition is not completely correct in the case of high DOC values ($> 5 \text{ mg C L}^{-1}$) (see discussion in Section 4.2).

The ion balance check is based on the test of the electroneutrality of the water samples: the total number of negative and positive charges must be equal. The constants required to transform the units used in the ICP Forests Deposition Programme into $\mu\text{eq L}^{-1}$ are given in table 4. Using \sum_{cat} and \sum_{an} to indicate the concentrations

($\mu\text{eq L}^{-1}$) of cations and anions, respectively, the percentage difference (PD) is:

$$\text{PD} = 100 \times (\sum_{\text{cat}} - \sum_{\text{an}}) / (0.5 \times \sum_{\text{cat}} + \sum_{\text{an}})$$

High concentrations of dissolved organic matter, if present, must, be taken into account. Organic matter in deposition samples acts as an organic anion, producing a systematic bias in which the concentrations of cations are higher than those of inorganic anions. Corrections based on DOC concentration developed e.g. by Oliver *et al.* (1983) cannot be directly applied to throughfall and stemflow samples because they were primarily based on stream, lake, bog and ground water. Corrections for the presence of dissolved organic matter, specific for each site and each type of sample (bulk deposition, throughfall etc.), can be developed on the basis of earlier analyses on deposition samples.

The percentage difference between the measured and calculated conductivity is given by the ratio:

$$\text{CD} = 100 \times (\text{CE} - \text{CM}) / \text{CM}$$

In deposition samples with low ionic strength (below 0.1 meq L^{-1}), the CD value between the measured and calculated conductivity should be no more than 2% (Miles & Yost 1982). For an ionic strength higher than 0.1 meq L^{-1} and lower than 0.5 meq L^{-1} , the Davies correction of the activity of each ion can be used, as proposed e.g. by A.P.H.A., A.W.W.A., W.E.F. (2005). The acceptance threshold values of PD and CD adopted in the ICP Forests manual vary according to the ion concentrations, as shown in table 5.

Tab. 4. Concentration units used, factors for transforming concentration into $\mu\text{eq L}^{-1}$, and equivalent conductance at infinite dilution of the individual ions.

	Unit	Factor to $\mu\text{eq L}^{-1}$	Equivalent conductance at 25°C $\text{kS cm}^2 \text{eq}^{-1}$
pH		$10^{(6-\text{pH})}$	0.3500
Ammonium	mg N L^{-1}	71.39	0.0735
Calcium	mg L^{-1}	49.9	0.0595
Magnesium	mg L^{-1}	82.24	0.0531
Sodium	mg L^{-1}	43.48	0.0501
Potassium	mg L^{-1}	25.28	0.0735
Alkalinity	$\mu\text{eq L}^{-1}$	1	0.0445
Sulphate	mg S L^{-1}	62.37	0.0800
Nitrate	mg N L^{-1}	71.39	0.0714
Chloride	mg L^{-1}	28.2	0.0764

Tab. 5. Acceptance threshold values in data validation based on the ion balance and conductivity.

Conductivity (25°C)	PD	CD
$<10 \mu\text{S cm}^{-1}$	$\pm 20\%$	$\pm 30\%$
$<20 \mu\text{S cm}^{-1}$	$\pm 20\%$	$\pm 20\%$
$>20 \mu\text{S cm}^{-1}$	$\pm 10\%$	$\pm 10\%$

The third relationship tested is the ratio between Na^+ and Cl^- ; assuming that most of these ions are derived from sea spray; a ratio relatively close to the marine value (0.86) should be expected (Keene *et al.* 1986). If other sources of these ions are involved, then the range of "acceptable" values is widened from 0.5 to 1.5 (Ulrich *et al.* 2006).

2.3. Hypothesis tested and statistical methods

The goal of the data elaboration is to verify whether a relationship exists between $\sum_{\text{cat}} - \sum_{\text{an}}$ (hereafter indicated as Δ) and the DOC concentration, and whether the regression coefficients are affected by the analysis methods used in the laboratories, the type of solution, the type of tree cover and the concentration of marine-derived NaCl. The overall aim of this study is to select the best estimate of the coefficients for general use in evaluation of the ion balance. The hypotheses listed in table 6 were tested.

Analysis of covariance (ANCOVA) was used to test the statistical significance of the differences among the laboratories, between the types of sample, between the samples from broadleaf/conifer plots, and between "marine" and "non-marine" samples (Hypotheses 1-5). This modelling technique represents an integration of the analysis of variance and regression analysis, and it is appropriate when there are both quantitative and qualitative (grouping) factors. The basic advantage of this is a reduction in the bias caused by the differences between the groups. The ANCOVA model treats both between-group and regression variance as systematic components. The statistical model is:

$$\Delta_{ij} = \delta_0 + \tau_i + \delta_1 \sum (x_{ij} - x_i) + \epsilon_{ij}$$

where:

Δ_{ij} = dependent variable score ($\sum_{\text{cat}} - \sum_{\text{an}}$) of the j^{th} unit in the i^{th} treatment

δ_0 = population mean (of dependent variable) common to all observations

τ_i = effect of treatment:

- laboratory i (a constant associated with all units in laboratory i)

- solutions from broadleaf/conifer plots
- "marine" and "non marine" solutions
- type i of solutions (THR, ST)

δ_1 = linear regression coefficient of y on x

x_i = mean of all units on covariate DOC

x_{ij} = covariate score for the j^{th} unit in the i^{th} treatment

ϵ_{ij} = error component associated with the j^{th} unit in the i^{th} treatment.

Multi-linear regressions were used to construct a statistical model for analyzing the linear relationship between the regressions ($\text{Org} = b \times \text{DOC} + a$) and the geographical and climatic information (Hypothesis 7). The statistical model is:

$$Y_{1,2}^k = \alpha_0 + \alpha_1 X_{1k} + \alpha_2 X_{2k} + \alpha_3 X_{3k} + \alpha_4 X_{4k} + \alpha_5 X_{5k} + \epsilon_k$$

where:

$Y_{1,2}^k$ = dependent variable (1 = slope, 2 = intercept)

α_0 = general mean effect (intercept)

X_{1k} = latitude

X_{2k} = longitude

X_{3k} = altitude

X_{4k} = precipitation

X_{5k} = mean air temperature

α_i = linear regression coefficient of Y on X_i
($i = 1, \dots, 5$)

ϵ_k = random error.

Both ANCOVA and regression analysis are analysed using the general linear models (GLM) procedure. This procedure uses the method of least squares to fit the general linear model and handles the models relating one or several continuous dependent variables to one or several independent variables. The independent variables may be either classification variables, which divide the observation into discrete groups, or continuous variables.

3. RESULTS

3.1. Validation of the results of the chemical analyses

The data submitted by each country had already been validated by the National Focal Centres, although not necessarily using the criteria proposed in the ICP Forests

Tab. 6. Hypotheses tested on the data set comprising analyses made by different laboratories and on different types of solutions (1-4), and on the regression coefficients β_1 (formal charge) of the significant regression Δ vs DOC.

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- 1) Are there differences in the data sets produced in different laboratories?
 - 2) Are there differences between the data sets for different types of solution?
 - 3) Are there differences between the data sets for solutions sampled on broadleaf or conifer plots?
 - 4) Are there differences between the data sets for deposition with a high or a low marine salt content?
 - 5) Are there differences between the coefficients (β_1) obtained for different types of solution?
 - 6) Are there differences between the coefficients for different plots?
 - 7) Are there differences between the coefficients related to the geographic/climatic conditions of the plots?
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manual (UN ECE 2004; Ulrich *et al.* 2006) as they are not mandatory. For the purpose of this paper, the data sets were “cleaned” to remove (1) incomplete analysis sets, and (2) results that did not pass the test of conductivity (see Section 2.2). Samples with excessively high Σ_{cat} , Σ_{an} or DOC values were also removed in order to eliminate skewness in the data distribution and to obtain normal (Gaussian) distributions. This, of course, will have to be taken into account when the regression coefficients are adopted, and only used for samples falling within the range of values given in tables 7a and 7b. These procedures resulted in the elimination of about 15% of the submitted data. The number of analysis sets used in the statistical analysis of each type of solution and laboratory/country are reported in table 2. The number of analysis sets used in generating the regression coefficients and the number used in testing them are given separately.

3.2. Description and statistics of the data

The main statistical indicators of the set of data for each country are given separately for BL and CON in tables 7a and 7b. The deposition samples with higher solute concentrations in all three types of solution (BOF, THR, STF) are from those plots in Italy, UK, Norway and Belgium that are influenced by marine spray, while the lowest ion concentrations are from Finland and Switzerland. The solute concentrations increased in the order BOF, THR, STF. The DOC concentration also increased regularly in the order BOF, THR and STF (mean \pm s.d. 2 ± 1 , 8 ± 6 , 11 ± 7 mg C L⁻¹, respectively), with the highest values occurring in the samples from Italy and Belgium.

The statistical analysis for the THR data sets indicated highly significant differences between the data sets (Hypothesis 1 in Tab. 6), with 30% of the variability explained by the variable “laboratory”. Contrast analysis showed four pairs of countries with no differences: DE and FI; DE and IT; FI and IT; FI and UK. These differences reflect, at least partially, the analytical (systematic and/or random) errors within each laboratory. On the other hand, there were no statistical differences between the three data sets (DE, FR, IT) in the case of the STF solutions.

Comparison between the THR and STF data sets was possible only in the case of the countries BE, FR and IT, and in all three cases the differences were significant (Hypothesis 2 in Tab. 6), with a relative contribution to the total variance of 19, 4 and 2%, respectively.

Comparison between the THR data sets collected on broadleaf and conifer plots was possible for six countries (BE, DE, FR, IT, UK, CH) and the differences were highly significant in all cases (Hypothesis 3 in Tab. 6), although the contribution to the total variance of the model was very small (0.5%).

In the case of marine and non-marine solutions

(Hypothesis 4 in Tab. 6), the contribution was 3% and 9% of the total variance in the model for THR (8 labs) and STF solutions (3 labs), respectively.

3.3. Significance and regression coefficients of the relationships Δ vs DOC

The regressions between Δ vs DOC were not significant for the deposition samples collected in the open field (BOF) in any of the individual laboratory's data-sets, so no further statistical analyses were carried out on the BOF data sets. On the other hand, the regressions were significant for BL and CON in all the laboratories for both throughfall and stemflow samples (Tab. 7a, b). The values of the slope (THR) ranged between 4.48 and 7.60 $\mu\text{eq (mg DOC)}^{-1}$ for broadleaves, while they were systematically lower for conifers (range 3.33 – 5.41 $\mu\text{eq (mg DOC)}^{-1}$ (Fig. 2). This suggests that there were differences in the composition of the organic acids in throughfall collected under the two types of tree cover. The values for the stemflow solutions, which were available only from BL and for 3 laboratories, ranged between 5.19 and 5.72 $\mu\text{eq (mg DOC)}^{-1}$. The mean THR values for all the set of data were 6.80 and 4.17 $\mu\text{eq (mg DOC)}^{-1}$ for BL and CON, respectively.

There were no significant differences between the slope β_1 of the regressions Δ vs DOC for the STF and THR solutions; this comparison is limited to the solutions from BL plots in BE, FR, and IT for which both THR and STF data were available (Hypothesis 5 in Tab. 6).

As it was not originally intended to compare the β_1 values obtained at the individual plot level, in some cases there was not enough data to obtain significant values for the regression coefficient. For this reason, only those plots with more than 16 analysis sets were investigated. The values of the regression slopes and intercepts for throughfall on broadleaf and conifer plots and stemflow on broadleaf plots are presented in table 8.

Overall the mean values of the slope β_1 (the physical significance of which is the formal charge in $\mu\text{eq per mg of DOC}$) values ranged between 4.7 ± 1.6 and 5.9 ± 2.0 $\mu\text{eq (mg DOC)}^{-1}$, without any statistically significant differences between them (Hypothesis 6 in Tab. 6).

The final aim of this work was to look for differences between the coefficients related to geographic (latitude, longitude, altitude) and climatic (mean annual temperature and annual precipitation) variables (Hypothesis 7 in Tab. 6). The statistical analyses did not indicate any significant relationships between the formal charge and these variables. It is not possible to verify the possible negative effect of the broad approach taken in defining the type of tree cover (broadleaves and conifers) and/or the associated errors in the chemical data.

Tab. 7a. Broad-leaves - Statistical values (number of data, range, mean \pm 1 standard deviation), slopes, intercepts (β_1 , β_0 , \pm 1 standard error) and significance of the regressions for the different laboratories. No broadleaves plots for Finland (FIN) and Norway (NO).

Type of solution	BROAD LEAVES	Units	BE	CH	DE	FI	FR	IT	NO	UK	Total
BOF	N	-	199	136	88			604		78	1105
BOF	pH range	u	4.2-7.1	4.3-6.8	4.6-6.0			4.2-7.4		4.7-7.0	4.2-7.4
BOF	pH mean \pm σ	u	5.6 \pm 0.5	5.5 \pm 0.7	5.1 \pm 0.3			5.7 \pm 0.7		5.7 \pm 0.6	5.6 \pm 0.7
BOF	DOC range	mg C L ⁻¹	0-8	0-3	1-6			0-17		0-6	0-17
BOF	DOC mean \pm σ	mg C L ⁻¹	2 \pm 2	1 \pm 1	2 \pm 1			2 \pm 1		2 \pm 1	2 \pm 1
BOF	Σ_{cat} range	μ eq L ⁻¹	70-685	26-326	66-363			24-737		75-437	24-737
BOF	Σ_{cat} mean \pm σ	μ eq L ⁻¹	239 \pm 114	85 \pm 48	139 \pm 63			182 \pm 141		171 \pm 80	176 \pm 127
BOF	Σ_{an} range	μ eq L ⁻¹	83-665	20-290	56-354			20-696		72-419	20-696
BOF	Σ_{an} mean \pm σ	μ eq L ⁻¹	255 \pm 114	77 \pm 45	131 \pm 65			180 \pm 139		169 \pm 81	176 \pm 128
BOF	$\Sigma_{cat}-\Sigma_{an}$ range	μ eq L ⁻¹	-123 \pm 45	-6 \pm 36	-12 \pm 30			-50 \pm 90		-36 \pm 28	-123 \pm 90
BOF	$\Sigma_{cat}-\Sigma_{an}$ mean \pm σ	μ eq L ⁻¹	-16 \pm 27	8 \pm 7	9 \pm 7			2 \pm 12		2 \pm 12	0 \pm 17
BOF	Slope β_1	μ eq (mg C) ⁻¹	0.15 \pm 1.19	3.71 \pm 1.03	3.66 \pm 0.8			1.49 \pm 0.38		4.19 \pm 1.26	0.14 \pm 0.39
BOF	Intercept β_0	μ eq L ⁻¹	-16.01 \pm 3.21	3.61 \pm 1.36	3.41 \pm 1.38			-0.34 \pm 0.74		-4.7 \pm 2.39	-0.1 \pm 0.82
BOF	P-value		0.8996	0.0005	<0.0001			<0.0001		0.0013	0.7119
BOF	R ²		0.00008	0.09	0.2			0.03		0.13	0.0001
STF	N	-	275				143	179			597
STF	pH range	u	3.8-6.7				4.1-6.9	4.1-8.1			3.8-8.1
STF	pH mean \pm σ	u	5.5 \pm 0.6				5.6 \pm 0.5	5.9 \pm 0.5			5.6 \pm 0.6
STF	DOC range	mg C L ⁻¹	2-39				1-31	1-39			1-39
STF	DOC mean \pm σ	mg C L ⁻¹	13 \pm 7				8 \pm 7	10 \pm 7			11 \pm 7
STF	Σ_{cat} range	μ eq L ⁻¹	166-5287				30-1231	52-2064			30-5287
STF	Σ_{cat} mean \pm σ	μ eq L ⁻¹	871 \pm 621				336 \pm 273	370 \pm 314			593 \pm 539
STF	Σ_{an} range	μ eq L ⁻¹	180-5303				22-1229	34-1801			22-5303
STF	Σ_{an} mean \pm σ	μ eq L ⁻¹	823 \pm 604				284 \pm 251	326 \pm 284			545 \pm 523
STF	$\Sigma_{cat}-\Sigma_{an}$ range	μ eq L ⁻¹	-95 \pm 358				-5 \pm 202	-20 \pm 273			-95 \pm 368
STF	$\Sigma_{cat}-\Sigma_{an}$ mean \pm σ	μ eq L ⁻¹	49 \pm 68				52 \pm 43	43 \pm 49			48 \pm 58
STF	Slope β_1	μ eq (mg C) ⁻¹	5.19 \pm 0.49				5.44 \pm 0.28	5.72 \pm 0.29			5.04 \pm 0.25
STF	Intercept β_0	μ eq L ⁻¹	-16.58 \pm 7.10				8.47 \pm 2.91	-16.17 \pm 3.65			-6.67 \pm 3.29
STF	P-value		<0.0001				<0.0001	<0.0001			<0.0001
STF	R ²		0.29				0.73	0.69			0.4
THR	N	-	253	126	121		372	299		283	1454
THR	pH range	u	4.0-7.0	4.0-7.3	4.6-6.6		4.3-7.5	4.3-7.9		4.4-7.3	4.0-7.9
THR	pH mean \pm σ	u	5.8 \pm 0.5	6.2 \pm 0.7	6 \pm 0.6		5.8 \pm 0.5	5.9 \pm 0.6		5.6 \pm 0.5	5.8 \pm 0.6
THR	DOC range	mg C L ⁻¹	0-34	1-26	1-11		0-37	1-36		1-37	0-37
THR	DOC mean \pm σ	mg C L ⁻¹	6 \pm 6	6 \pm 4	5 \pm 3		10 \pm 8	8 \pm 7		8 \pm 6	8 \pm 6
THR	Σ_{cat} range	μ eq L ⁻¹	126-2596	56-922	111-523		73-1696	37-2736		96-1351	37-2736
THR	Σ_{cat} mean \pm σ	μ eq L ⁻¹	636 \pm 386	205 \pm 131	265 \pm 75		368 \pm 236	494 \pm 236		370 \pm 184	418 \pm 321
THR	Σ_{an} range	μ eq L ⁻¹	131-2522	45-654	92-493		56-1405	29-2606		90-1160	29-2606
THR	Σ_{an} mean \pm σ	μ eq L ⁻¹	629 \pm 361	168 \pm 104	239 \pm 75		288 \pm 189	455 \pm 404		338 \pm 173	377 \pm 304
THR	$\Sigma_{cat}-\Sigma_{an}$ range	μ eq L ⁻¹	-137 \pm 238	2 \pm 268	1 \pm 79		-9 \pm 380	-62 \pm 294		-32 \pm 395	-137 \pm 395
THR	$\Sigma_{cat}-\Sigma_{an}$ mean \pm σ	μ eq L ⁻¹	8 \pm 59	37 \pm 33	26 \pm 16		81 \pm 68	39 \pm 52		31 \pm 45	41 \pm 59
THR	Slope β_1	μ eq (mg C) ⁻¹	4.48 \pm 0.57	6.72 \pm 0.34	4.91 \pm 0.31		7.6 \pm 0.23	5.9 \pm 0.27		6.35 \pm 0.24	6.8 \pm 0.16
THR	Intercept β_0	μ eq L ⁻¹	-21.22 \pm 4.97	-5.1 \pm 2.57	0.09 \pm 1.86		7.87 \pm 2.88	-11.32 \pm 2.98		-20.69 \pm 2.48	-12.32 \pm 1.63
THR	P-value		<0.0001	<0.0001	<0.0001		<0.0001	<0.0001		<0.0001	<0.0001
THR	R ²		0.2	0.76	0.67		0.74	0.61		0.71	0.56

Tab. 7b. Conifers - Statistical values (number of data, range, mean \pm 1 standard deviation), slopes, intercepts (β_1 , β_0 , \pm 1 standard error) and significance of the regressions for the different laboratories.

Type of solution	CONIFERS	Units	BE	CH	DE	FI	FR	IT	NO	UK	Total
BOF	N	-	144	106	92	162		214	167	79	964
BOF	pH range		4.4-7.0	4.3-6.7	4.6-6.3	4.3-6.7		4.2-6.4	4.2-6.4	4.3-7.2	4.0-7.2
BOF	pH mean \pm σ	u	5.6 \pm 0.5	5.4 \pm 0.7	5.2 \pm 0.5	4.8 \pm 0.3		5.6 \pm 0.3	4.9 \pm 0.3	5.5 \pm 0.6	5.3 \pm 0.6
BOF	DOC range	mg C L ⁻¹	0-11	0-5	39600	0-7		0-11	0-8	0-8	0-11
BOF	DOC mean \pm σ	mg C L ⁻¹	2 \pm 2	1 \pm 1	1 \pm 1	2 \pm 1		2 \pm 2	2 \pm 1	2 \pm 1	2 \pm 1
BOF	Σ_{cat} range	μ eq L ⁻¹	82-599	22-242	66-285	20-181		9-517	16-398	45-484	9-599
BOF	Σ_{cat} mean \pm σ	μ eq L ⁻¹	262 \pm 110	73 \pm 40	140 \pm 58	59 \pm 31		81 \pm 69	106 \pm 74	168 \pm 90	120 \pm 98
BOF	Σ_{an} range	μ eq L ⁻¹	101-638	14-237	57-280	11-176		10-502	17-372	36-476	10-638
BOF	Σ_{an} mean \pm σ	μ eq L ⁻¹	280 \pm 114	66 \pm 38	134 \pm 60	48 \pm 31		78 \pm 70	108 \pm 77	164 \pm 87	119 \pm 104
BOF	$\Sigma_{cat}-\Sigma_{an}$ range	μ eq L ⁻¹	-101+56	-29+44	-17+19	-10+59		-72+22	-75+65	-32+55	-101+65
BOF	$\Sigma_{cat}-\Sigma_{an}$ mean \pm σ	μ eq L ⁻¹	-18 \pm 26	7 \pm 8	6 \pm 6	11 \pm 10		2 \pm 9	-2 \pm 20	4 \pm 14	1 \pm 18
BOF	Slope β_1	μ eq (mg C) ⁻¹	-0.04 \pm 1.18	4.96 \pm 1.11	1.36 \pm 0.81	-0.12 \pm 0.61		0.22 \pm 0.38	1.01 \pm 1.12	3.31 \pm 1.14	-0.49 \pm 0.40
BOF	Intercept β_0	μ eq L ⁻¹	-18.08 \pm 3.63	1.23 \pm 1.51	4.37 \pm 1.34	11.61 \pm 1.36		1.81 \pm 0.91	-3.79 \pm 2.32	-2.37 \pm 2.70	1.90 \pm 0.90
BOF	P-value		0.9737	<0.0001	0.0959	0.8387		0.5561	0.369	0.005	0.2171
BOF	R ²		0.000008	0.16	0.03	0.0003		0.002	0.005	0.1	0.002
THR	N	-	186	70	243	121	306	214	216	301	1657
THR	pH range		4.1-6.4	4.2-6.5	4.3-6.4	4.2-5.7	4.1-7.0	4.1-6.7	4.3-6.2	4.5-6.7	4.1-7.0
THR	pH mean \pm σ	u	5.3 \pm 0.5	5.3 \pm 0.5	5.1 \pm 0.4	4.7 \pm 0.3	5.5 \pm 0.6	5.6 \pm 0.5	5.0 \pm 0.3	5.5 \pm 0.5	5.3 \pm 0.5
THR	DOC range	mg C L ⁻¹	3-37	0-18	2-38	1-23	0-40	0-40	0-35	2-30	0-40
THR	DOC mean \pm σ	mg C L ⁻¹	15 \pm 7	6 \pm 4	10 \pm 6	7 \pm 5	12 \pm 8	9 \pm 7	8 \pm 5	9 \pm 5	10 \pm 7
THR	Σ_{cat} range	μ eq L ⁻¹	133-1601	28-685	87-1075	14-324	44-2601	13-1311	21-1264	63-1132	13-2601
THR	Σ_{cat} mean \pm σ	μ eq L ⁻¹	614 \pm 240	113 \pm 93	296 \pm 160	88 \pm 50	426 \pm 389	144 \pm 151	250 \pm 234	43 \pm 186	316 \pm 278
THR	Σ_{an} range	μ eq L ⁻¹	134-1570	15-654	51-969	14-295	35-2584	10-1266	17-1313	48-1087	250102
THR	Σ_{an} mean \pm σ	μ eq L ⁻¹	583 \pm 223	88 \pm 86	259 \pm 147	64 \pm 48	352 \pm 371	116 \pm 136	231 \pm 228	365 \pm 185	279 \pm 265
THR	$\Sigma_{cat}-\Sigma_{an}$ range	μ eq L ⁻¹	-74 \pm 234	-41 \pm 71	-10 \pm 143	-13 \pm 129	-5 \pm 271	-11 \pm 299	-62 \pm 200	-33 \pm 181	-74 \pm 299
THR	$\Sigma_{cat}-\Sigma_{an}$ mean \pm σ	μ eq L ⁻¹	31 \pm 52	28 \pm 18	37 \pm 28	24 \pm 24	74 \pm 51	28 \pm 31	19 \pm 37	28 \pm 26	37 \pm 41
THR	Slope β_1	μ eq (mg C) ⁻¹	3.96 \pm 0.46	3.67 \pm 0.37	4.2 \pm 0.12	3.51 \pm 0.26	5.41 \pm 0.21	3.33 \pm 0.20	3.38 \pm 0.40	3.76 \pm 0.19	4.17 \pm 0.11
THR	Intercept β_0	μ eq L ⁻¹	-28.66 \pm 7.65	4.59 \pm 2.58	-4.09 \pm 1.36	-0.44 \pm 2.33	7.38 \pm 3.10	-1.39 \pm 2.24	-9.08 \pm 4.00	-5.01 \pm 1.97	-5.01 \pm 1.32
THR	P-value		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
THR	R ²		0.29	0.59	0.84	0.6	0.68	0.57	0.25	0.56	0.47

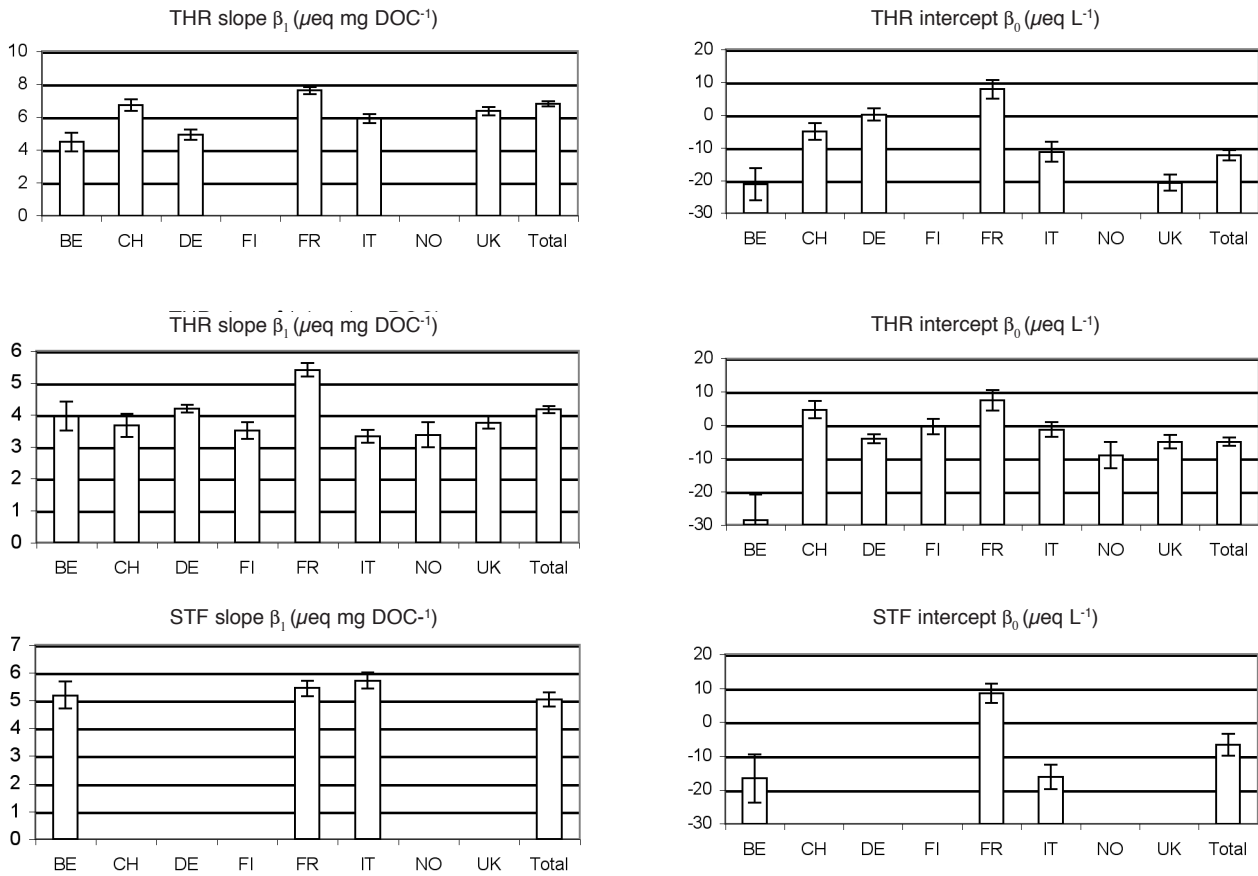


Fig. 2. Coefficient of regressions between Δ and DOC, stratified on laboratories, type of solution and type of vegetation. Legend: CON conifers, BL broadleaves, THR throughfall, STF stemflow.

Tab. 8. Range, an values and standard deviations of β_1 and β_0 for the different types of solution on the two types of plot.

	Throughfall conifer	Throughfall broadleaf	Stemflow broadleaf
number 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

4. DISCUSSION

4.1. Testing the regression coefficients

In order to test the improvement in the validity of the ion balance after correction for the contribution of the DOC formal charge, an independent data set was used to test the procedure on the analyses carried out in some of the countries (IT, UK, FR, DE, NO) and for the two types of tree cover (BL and CON). Evaluation of the ionic charge associated with DOC $[\text{Org}^-]$ was done for

each country using both regression coefficients (slope and intercept) calculated from the data of the same country, and the mean values of the regression coefficients obtained from the pooled data, separately for BL and CON (Tab. 7a, b):

$$[\text{Org}^-] = \beta_1 \times \text{DOC} + \beta_0$$

where $[\text{Org}^-]$ and β_0 units are $\mu\text{eq L}^{-1}$, DOC and β_1 units are mg C L^{-1} and $\mu\text{eq (mg C)}^{-1}$.

The effects of the two corrections were evaluated on the basis of the ion balance test (Tab. 5). The DOC correction substantially increased the number of acceptable analyses (Tab. 9), producing a percentage of validated analyses close to that validated using the conductivity test. The percentage of validated analyses obtained from the country regression coefficients and from the mean of all the data were comparable, with the highest differences in the case of FR and IT (conifers). This result, together with the high representativity of the deposition sample, indicated that the pooled regression coefficients are, in fact, widely applicable. The effects of the two different DOC corrections on the frequency distribution of the differences between the sum of cations and the corrected sum of anions are shown in figure 3. In this case, the positive effect of the DOC correction is also clear.

4.2. Comparison with the formal charge of DOC obtained in other studies

Several studies have investigated the ion charge contribution of total and dissolved organic carbon (TOC and DOC) in freshwater, but no studies are available for atmospheric deposition. The freshwater studies have mainly concentrated on evaluating the contribution of TOC/DOC to alkalinity, and the relative importance of weak and strong acidity in freshwater acidification.

Two main approaches have been used: the relationship between $\sum_{\text{cat}} - \sum_{\text{an}}$ and TOC (e.g., Köhler *et al.* 2000), and depiction of the acidity of organic anions in terms of dissociation constants, using both the monoprotic and triprotic approaches (e.g., Oliver 1983;

Schecher & Driscoll 1987; Kopáček *et al.* 2000). A third approach estimates the dissociation of organic acid [Org] using total alkalinity and DOC (Köhler *et al.* 2000).

Two conclusions presented in the above studies are relevant for the aims of the present paper:

1) Total alkalinity values are affected by the contribution from TOC/DOC due to the protonation of weak acids [Org], in addition to the contribution of dissolved inorganic carbon species and of other proton acceptors A^- (e.g. Al^{n+} , phosphate, borate, etc).

$$TAlk = -[H^+] + [OH^-] + [HCO_3^-] + [CO_3^{2-}] + [Org^-] + [A^-]$$

where the units are in $\mu\text{eq L}^{-1}$.

It is difficult to quantify the contributions of weak acids and other proton acceptors by ordinary analytical techniques, as they consist of a mixture of chemical compounds, which may vary in relation to the type of water (freshwater/atmospheric deposition) and several other factors (seasonality, hydrology, type of deposition, etc.). The first quantification of the contribution of [Org] as $4.6 \mu\text{eq (mg DOC)}^{-1}$ was proposed by Oliver *et al.* (1983) for freshwater, on the basis of empirical data. This value has been widely applied in subsequent papers, mainly based on empirical data sets.

2) The DOC formal charge is pH-dependent, and increases with increasing pH (Munsen & Gherini 1993; Köhler *et al.* 2000).

The values of the formal charge, β_1 , calculated by different authors for TOC/DOC in freshwater are summarised in table 10. Values of β_1 range from 3.1 to $12.9 \mu\text{eq (mg TOC)}^{-1}$, with a very clear relationship with pH.

Tab 9. Percent of analyses validated on the base of the conductivity test and ion balance (1) **not** using DOC correction, (2) using [Org] charge calculated from the regression of each country and (3) using [Org] charge calculated from the mean values from all the countries. n= number of validated analyses.

		N. samples	Conductivity test %	Ion balance test (1) %	Ion balance test (2) %	Ion balance test (3) %
BE	BL STF	120	81	60	92	93
BE	BL THR	91	82	70	77	87
BE	CON	60	90	73	92	73
CH	BL	148	58	27	93	89
CH	CON	111	56	20	87	78
DE	BL	210	91	67	93	93
DE	CON	443	92	52	89	95
FI	BL	-	-	-	-	-
FI	CON	104	51	16	60	53
FR	BL	-	-	-	-	-
FR	CON	514	100	17	88	72
IT	BL	300	100	61	84	81
IT	CON	82	91	26	70	73
NO	BL	-	-	-	-	-
NO	CON	236	87	36	78	84
UK	BL	-	-	-	-	-
UK	CON	396	100	58	67	66

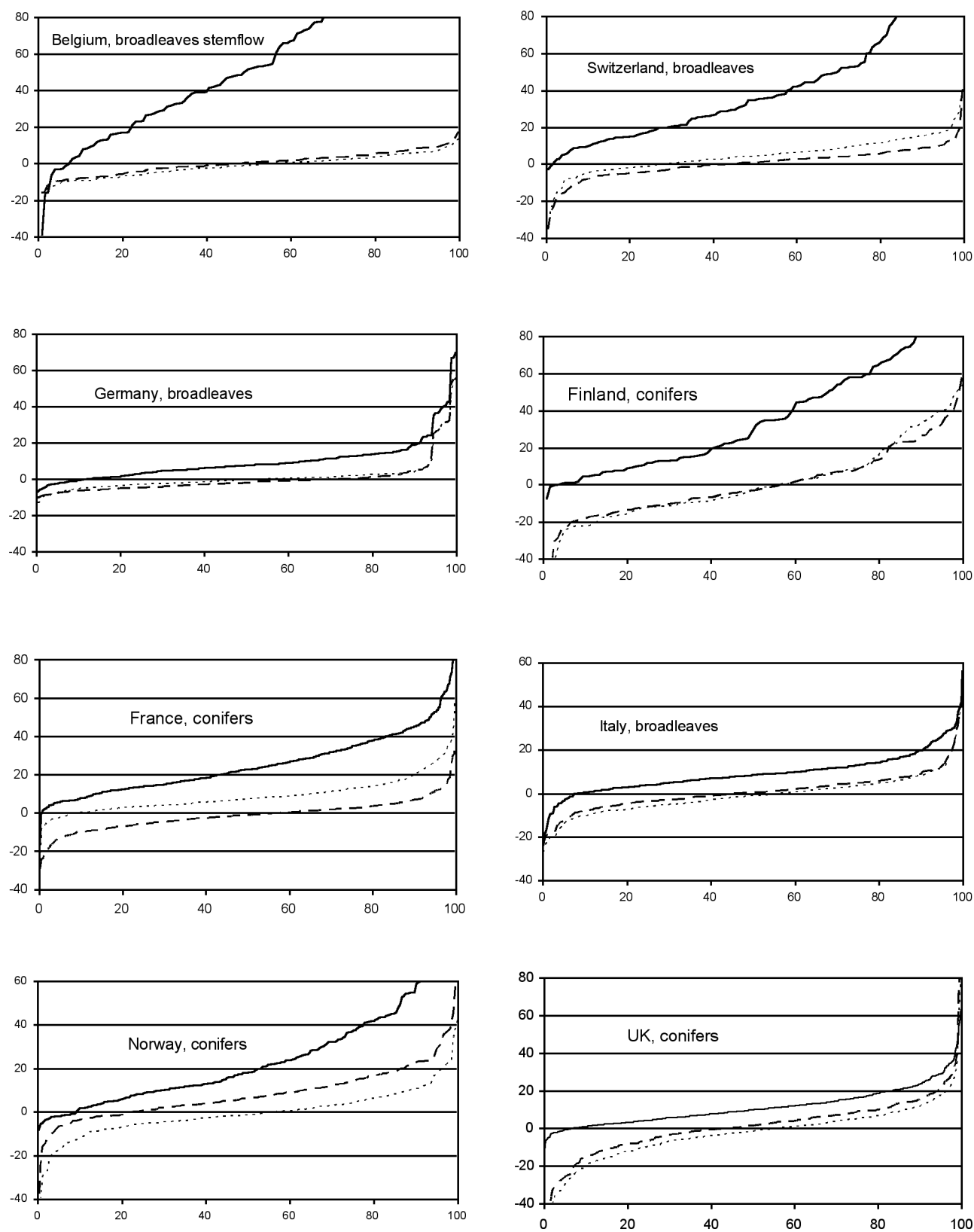
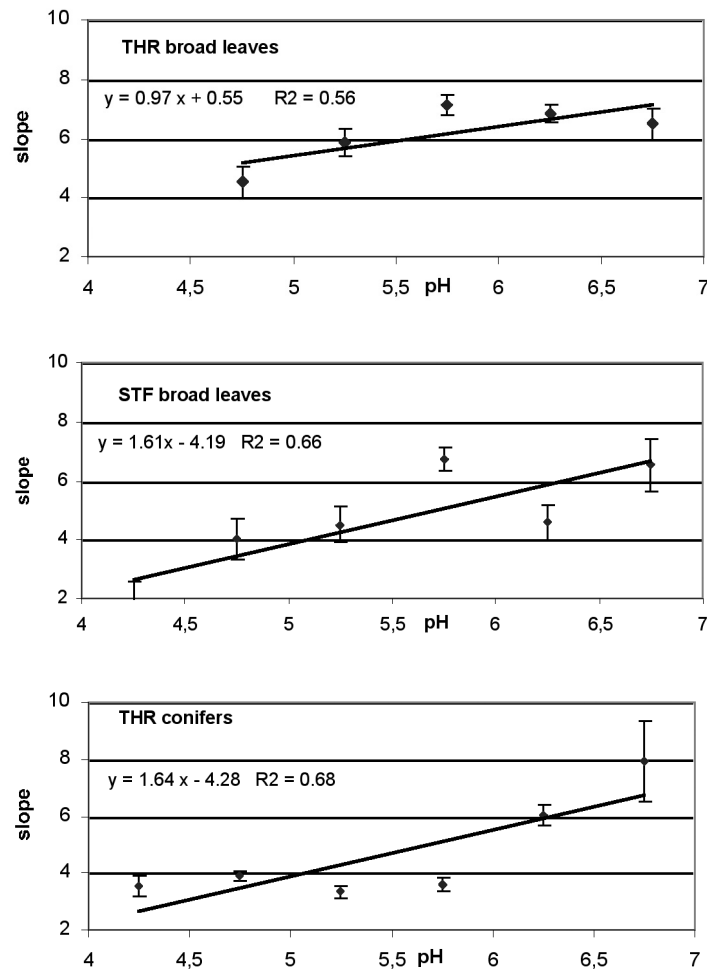


Fig. 3. Examples of cumulated frequency curves for Δ without and with the DOC correction (line: original data; dotted line: DOC correction using coefficients calculated from the regression of each country; dashed line: DOC correction using coefficients calculated from the mean values from all the countries).

Tab. 10. Comparison between formal charge values (mean values $\pm 1 \sigma$) of TOC calculated in different studies.

Formal charge mep (mg TOC) ⁻¹	pH range	Type of waters	Reference
4.4 \pm 0.1	4.0-4.5	Swedish surface waters	Köhler <i>et al.</i> 2000
5.8 \pm 0.5	5.0-5.5		
8.4 \pm 1.5	6.0-6.5		
12.9 \pm 2.4	7.0-7.5		
3.1	4.0-4.5	Adirondack, NY	Driscoll <i>et al.</i> 1994
4.6	5.0-5.5		
11.7	6.0-6.5		
5.2	4.0-4.5	Finnish waters	Kortelainen 1992
6.4	5.0-5.5		
8.1	6.0-6.5		
10.3	7.0-7.5		
6.2 \pm 0.8	3.8-6,3 (median 4.32)	Bohemian forest streams	Kopáček <i>et al.</i> 2000
8.6 \pm 0.8	4.2-5,5	Streams, Northern Sweden	Hruška <i>et al.</i> 2001

**Fig. 4.** Variation in the values of β_1 (formal charge, $\mu\text{eq (mg DOC)}^{-1} \pm 1$ standard error vs pH.

The range for atmospheric deposition obtained in our study at the individual plot level was between 2.2 and 10.6 $\mu\text{eq (mg DOC)}^{-1}$ (Tab. 8).

4.3. Testing the dependence of the DOC formal charge (β_1) on pH

In order to investigate the dependence of the β_1 values on pH, the set of data from each laboratory, separately for THR BL, STF BL and THR CON, were pooled and grouped within successive pH ranges of 0.5 units; the value of β_1 and the relative standard error was calculated for each range and plotted against the mean value of pH of each range (Fig. 4). The increases in β_1 per unit pH ranged between 0.97 and 1.64 $\mu\text{eq (mg DOC)}^{-1}$. These values are in the lower range of those calculated from the literature data for freshwater (1.16, 2.43, 3.44 $\mu\text{eq (mg DOC)}^{-1}$ respectively Kortelainen 1992; Driscoll *et al.* 1994; Köhler *et al.* 1999). As in the case of freshwater, the increase in the formal charge with pH for atmospheric deposition is undoubtedly due to greater dissociation of the weak acids which constitute part of DOC, creating sites which may be protonated.

5. CONCLUSIONS

Validating the results of individual analyses is strongly recommended in the ICP Forests manual as a part of the routine laboratory activities (Ulrich *et al.* 2006). Validation should be performed as soon as possible after the chemical analyses have been completed when part of the sample is still available, so that, if needed, some of the determinations can be repeated. Validation is important for detecting both analytical random errors and transcription errors, the latter not being uncommon in the laboratory. If unexpected (abnormal) results are confirmed on the basis of the second set of analyses, these must be accepted and stored in the database.

The analysis of about 6000 data set allows us to conclude that, in addition to the validation techniques already described (Mosello *et al.* 2005; Ulrich *et al.* 2006), the DOC concentration can be successfully used in the ion balance to check the analysis of THR and STF samples. The simplest linear model was chosen to describe the relationship between the DOC concentration and the difference between cations and anions owing to the strong influence of analytical errors, which do not allow more sophisticated approaches. This was clearly demonstrated in our study by the strong influence on the total variance of the variable “laboratory” (one central laboratory for each country was included), which contributed 30% to the total variance. However, the statistics did not allow estimation of the extent to which the differences between the regression coefficients of each laboratory reflect systematic errors or real differences due, for instance, to the type of tree cover or the amount of precipitation. The type of deposition (THR or STF)

and the relative importance of the marine salt contribution were of less relevance in the total variance; the factor “type of vegetation” proved to be less important, although significant, in determining the total variance (0.5%), although the distinction between “conifers” and “broadleaves” is of course only a very general approach. In addition, the failure to quantify the contribution of other factors, such as the geographic location and climatic conditions on the plots (mean annual temperature and amount of precipitation), may be related to the large variance attributable to analytical errors.

The regression coefficients, β_1 , obtained from the pooled data of the different laboratories gave DOC corrections that were close to the specific country coefficients. This suggests that the pooled β_1 values can be successfully used in evaluating the contribution of DOC to the ion balance in laboratories that did not participate in this study. The DOC correction, which was tested on an independent set of analysis results, considerably improved the applicability of the ion balance test for THR and STF solutions. The ion balance procedure should, together with the conductivity test, remain the primary reference method for validating the analyses.

However, it is strongly recommended to carry out specific studies in each laboratory, i.e. to test the regression between Δ and DOC as a part of the validation of the analytical results. These regression coefficients, after a comparison with those obtained in this study, will strongly increase the possibility of validating THR and STF results by the ion balance test, combined with the conductivity test.

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