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

Future work on QC/QA in laboratories: evaluation of data from monitoring programs under the aspect of QC/QA

Nils König & Rosario Mosello

Niedersaechsische Forstliche Versuchsanstalt, Goettingen
CNR Institute Ecosystem Study, Verbania Pallanza

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

- Continuing the assessment of the validation criteria, using interlaboratory studies (going on: ion balance and DOC in atmospheric deposition and soil water), involving different laboratories than those already participating in the WG.
- Pushing to get more laboratories performing all the chemical determination and using a QA/QC approach in their activity;
- Continuation on a regular basis (suggested yearly frequency) of the WRT for the analysis of leaves, soil, water.
- Working Ring Tests: is it possible to include common aspects to the three analytical fields (leaves, soil, water)?
- Creation of a space (regular meetings?) where persons working in analytics may have discussion.

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

Further steps in the validation of results:

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*

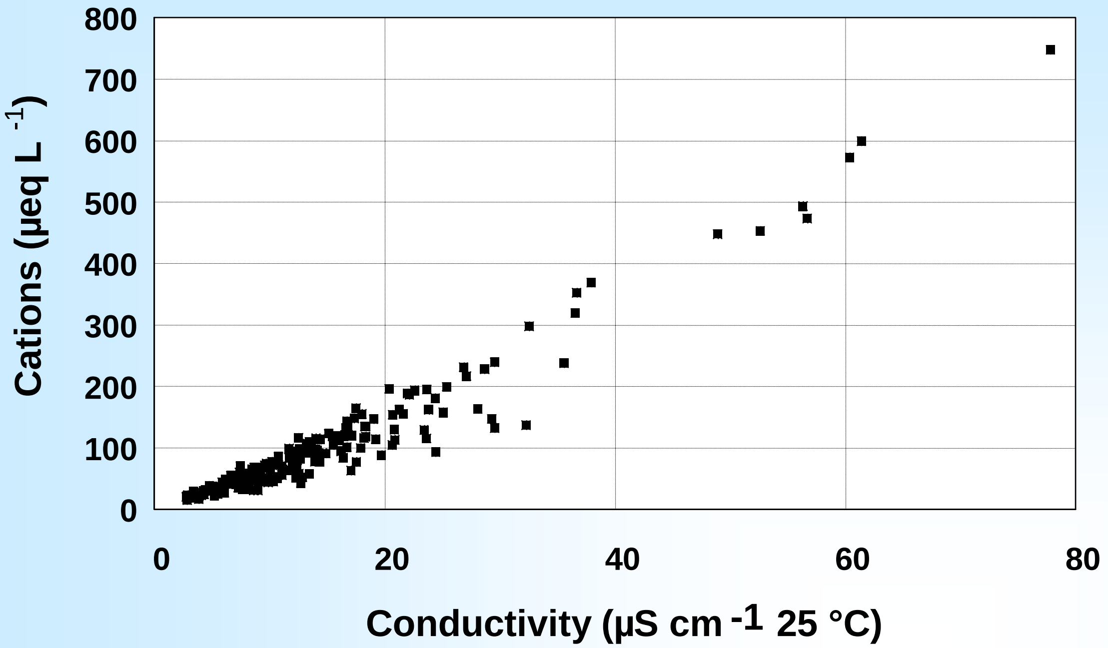
Further steps in the validation of results:

- <u>Relationships between conductivity and ion (cation, anion) concentrations</u>

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



800
700
600
500
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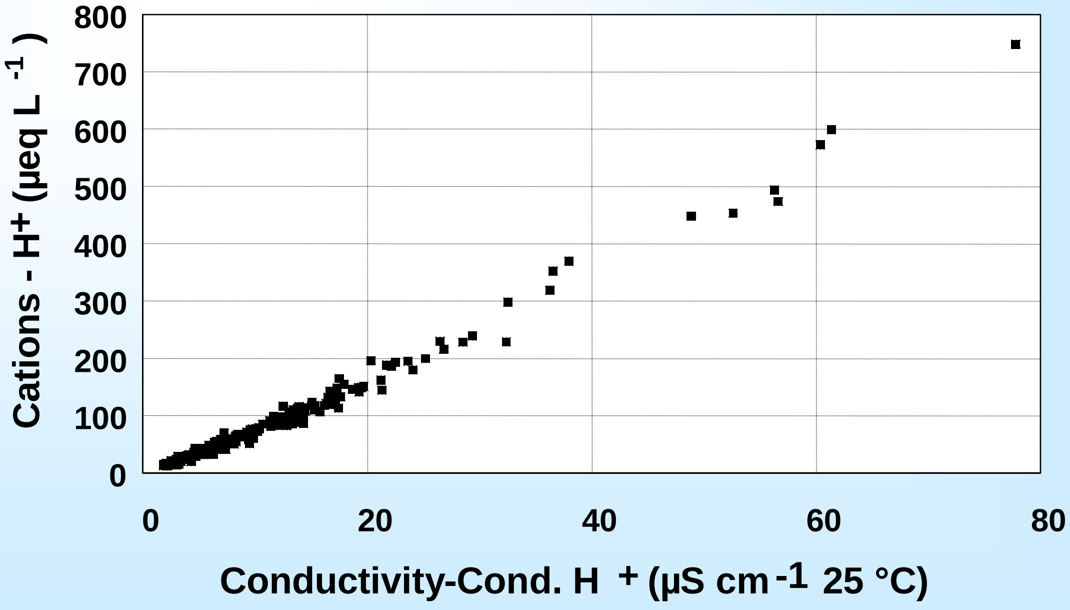
200
100
0
Cations (µeq L -1)
0
20
40
60
80
Conductivity (µS cm -1 25 °C)



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Cations - H+ (µeq L -1)
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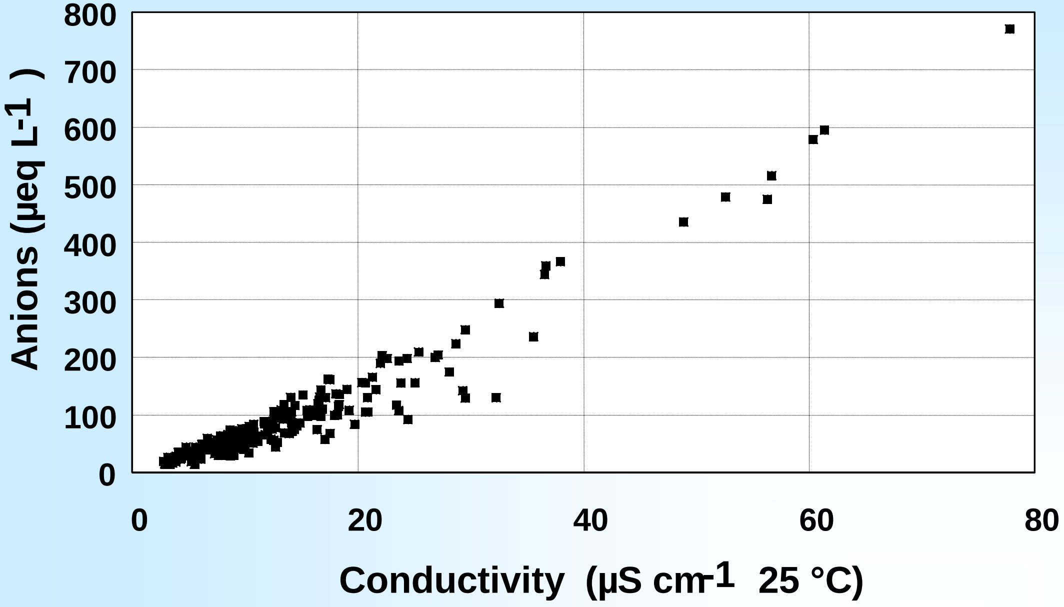
Conductivity-Cond. H + (µS cm -1 25 °C)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Anions (µeq L-1)
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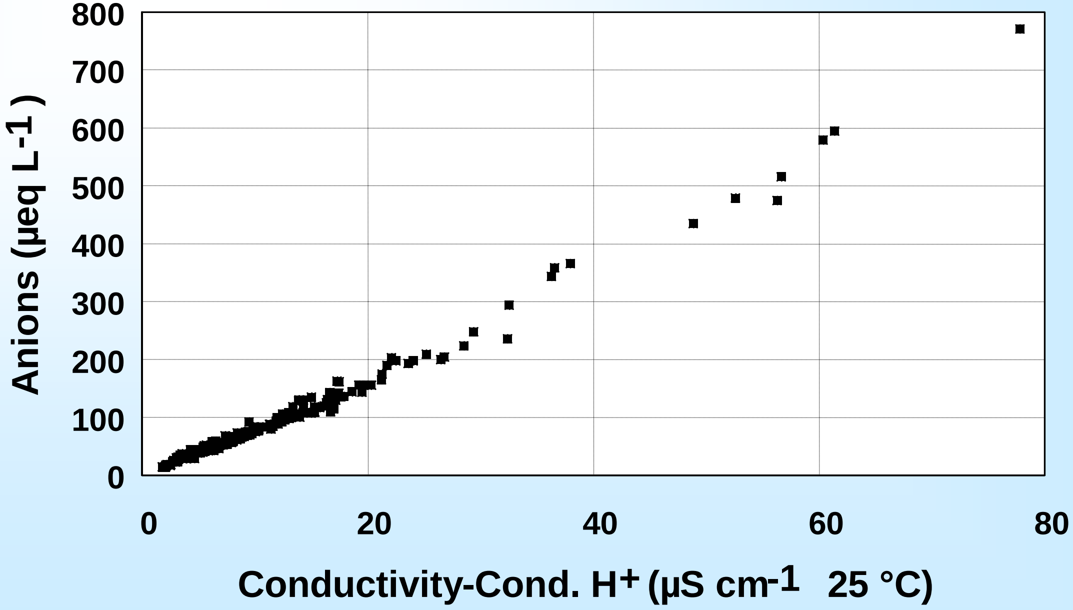
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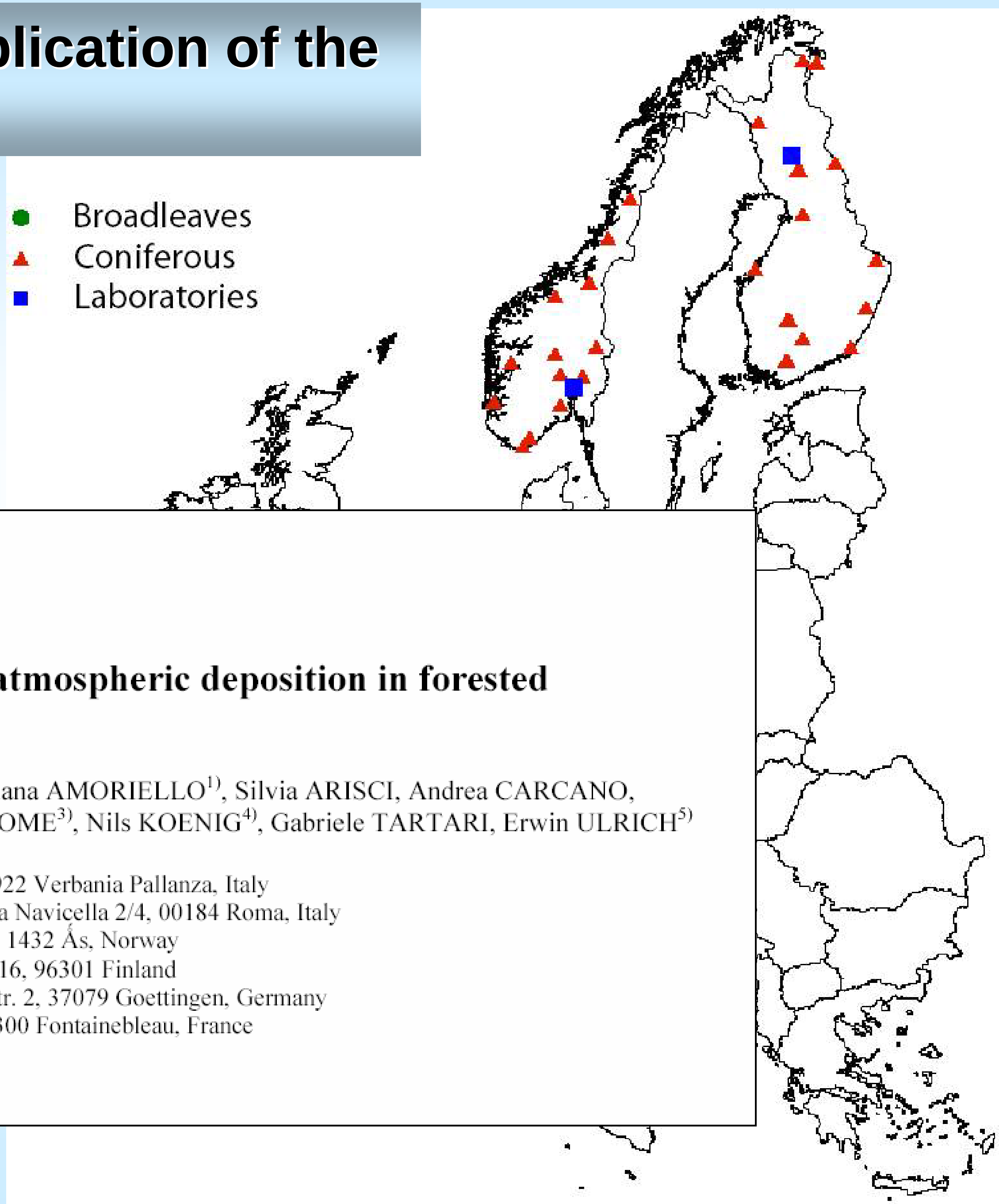
0
Anions (µeq L-1)
0
20
40
60
80
Conductivity-Cond. H+ (µS cm-1 25 °C)

Further steps in 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

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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
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

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

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

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

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

We indicate as DOC formal charge 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

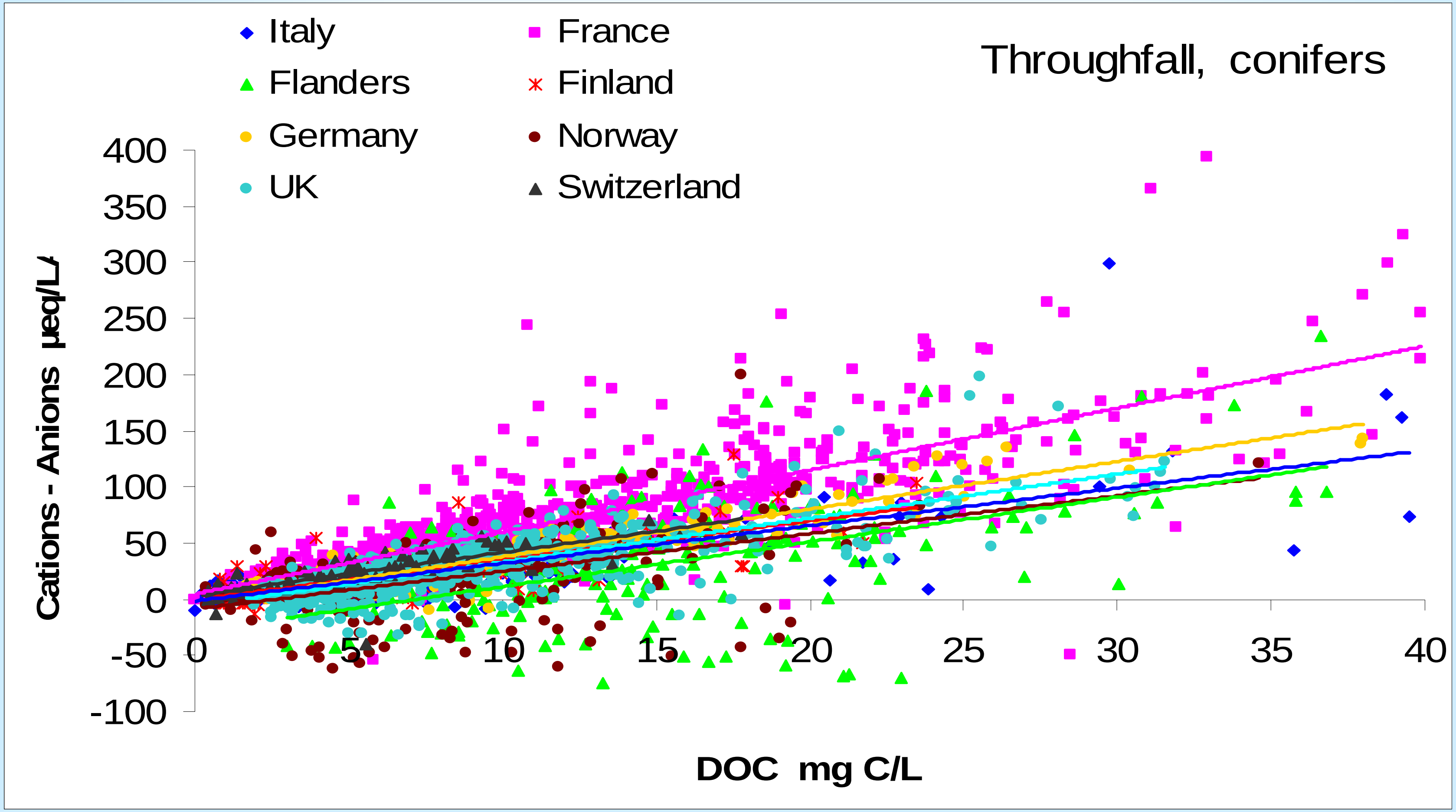
Number of data collected

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.



The slope of the regression DOC (mg L^{-1}) vs Cat-An (μeq L^{-1}) is an evaluation of the DOC Formal Charge

Slope = Δ y / Δ x = μ eq L^{-1} / mg C L^{-1} = μeq / mg C

Relationship between (∑cat - ∑an) and DOC

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

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
  ??

Soil water

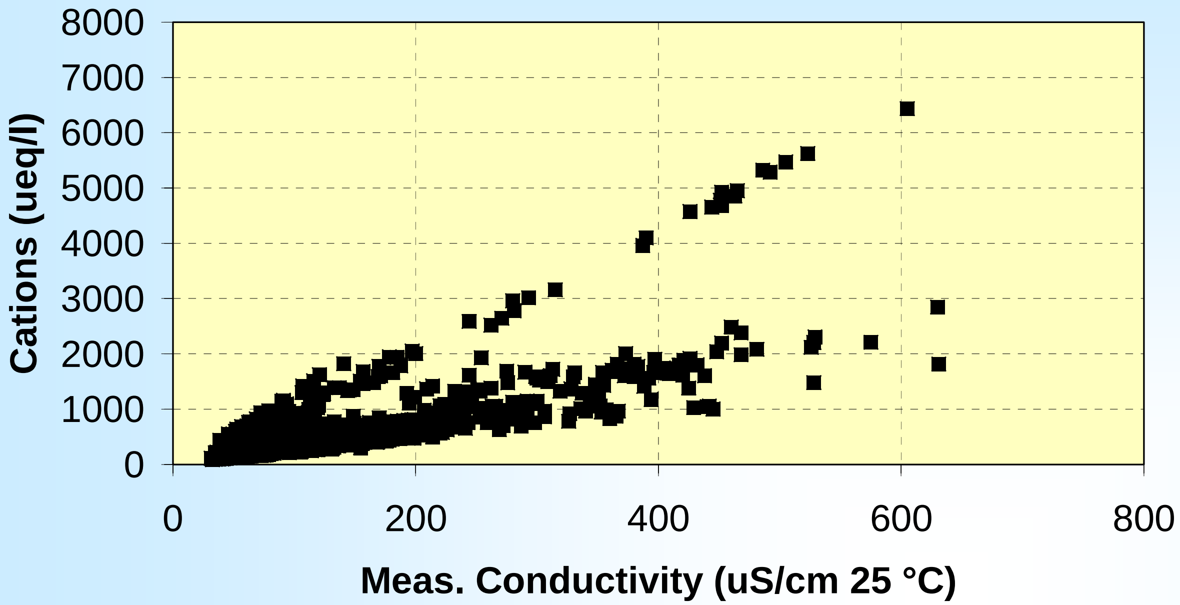
In the case of soil water both organic carbon and trace metals are important in the ion balance.

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).

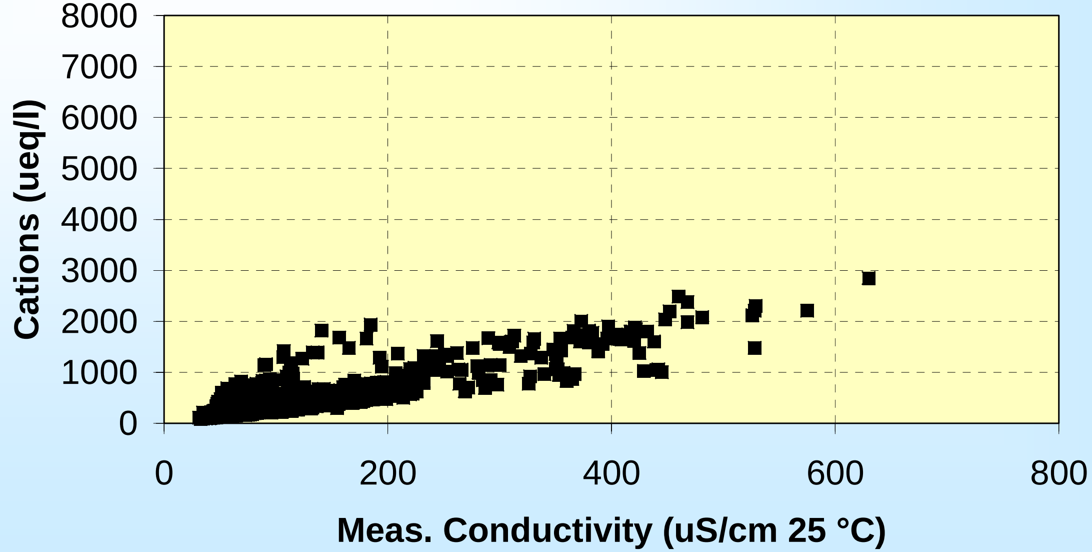
These aspects do not exclude the possibility to check for correlations among variables, assuming a full dissociation of trace metals

Germany, soil water

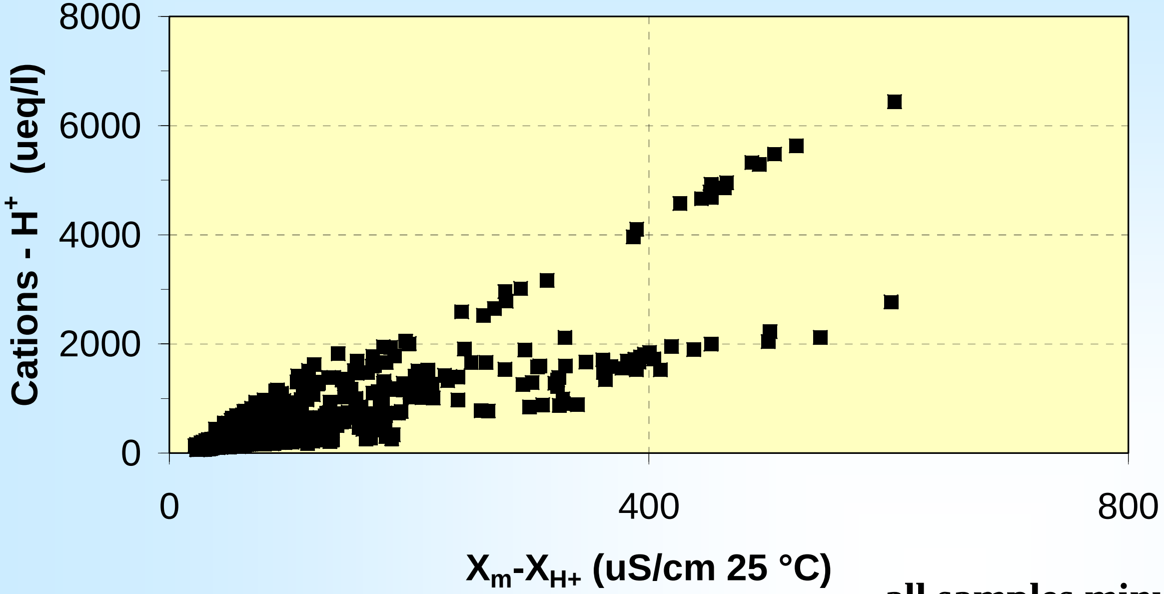
all samples



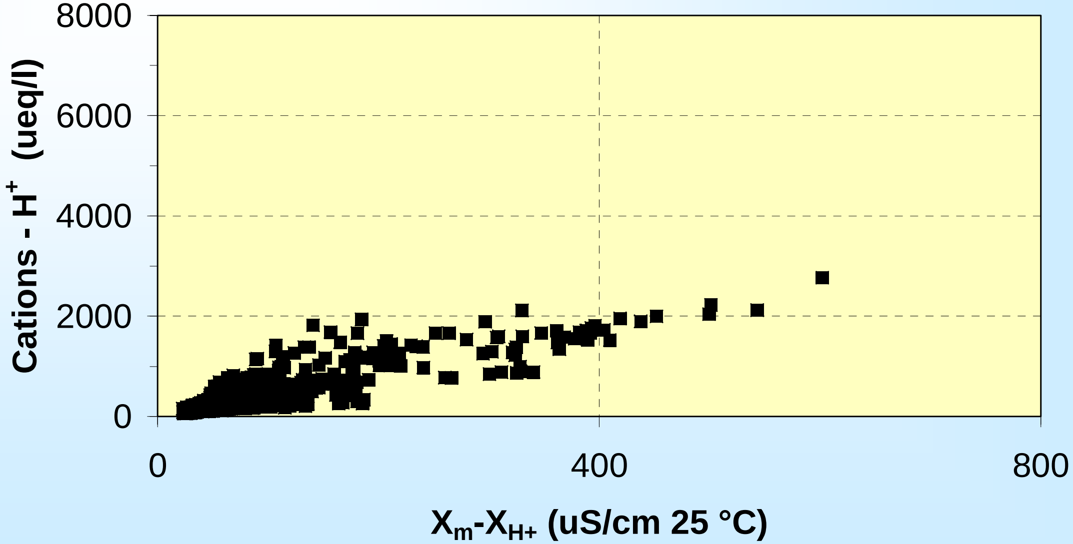
all samples minus samples without Al (Al>1 mg/l)



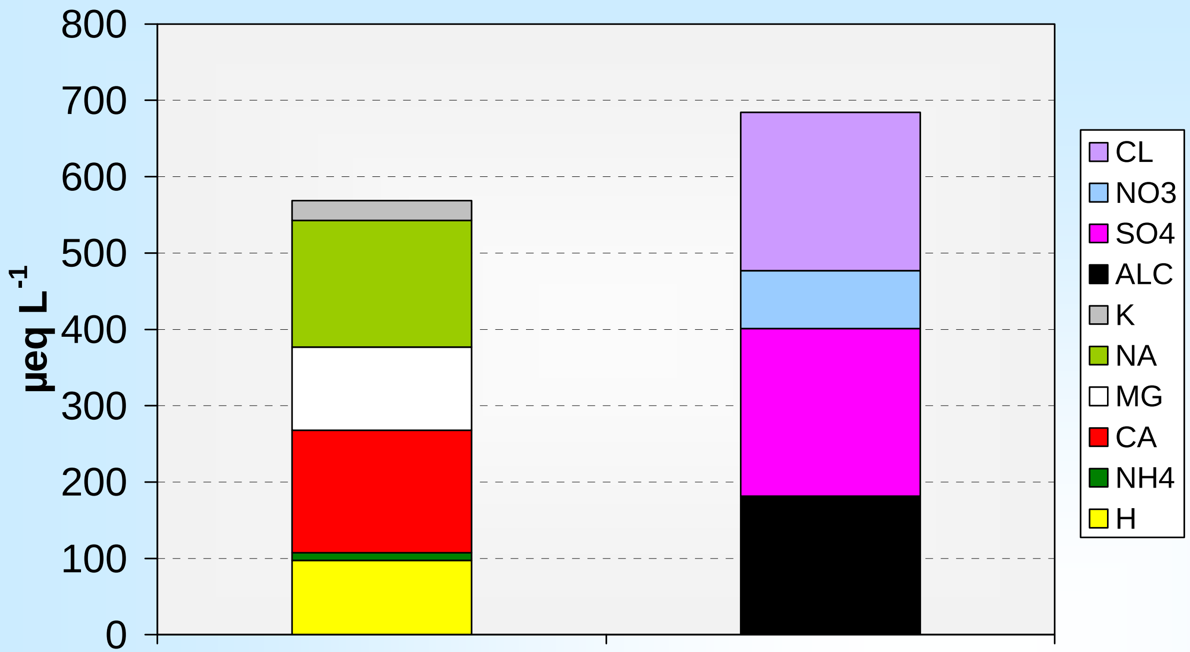
all samples

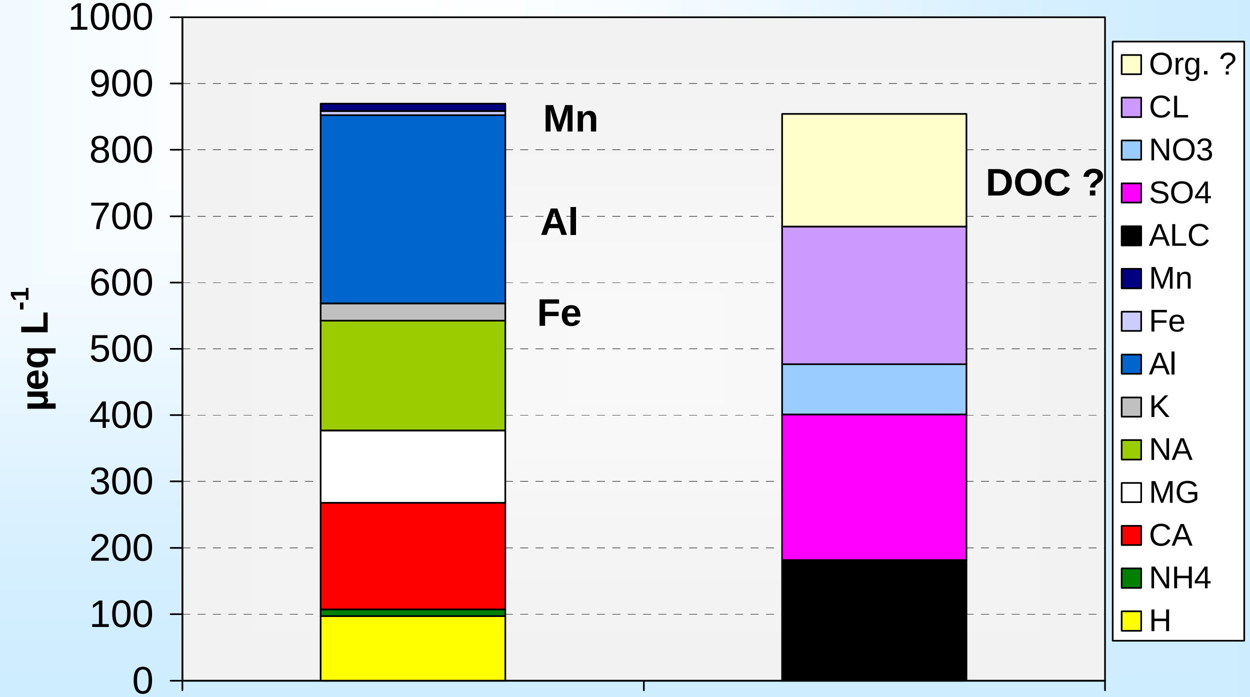


all samples minus samples without Al (> 1 mg/l)



Germany, soil water





Partial conclusions

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

An excel file makes easier the use of such criteria.

These criteria are exactly the same 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 the data validations are under evaluation.

Interlaboratory studies are useful tools to increase awareness of the need of a QA/QC approach to analytical activity.