

**9° Meeting of the Expert Panel on Deposition
(28-29 September 2006, Ski, Norway)**

**Activities of the Working Group on QA/QC
in Laboratories**

Rosario Mosello

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

Plan of the presentation

Short introduction on the activities of the WG on QA/QC

Validation of results – The ion balance and the charge of DOC in atmospheric deposition and soil water.

First results, next steps

Plans for the 3^o Working Ring Test

Report on help given to laboratories

Future activities of the WG on QA/QC

Aims of the WG on QA/QC

- The WG on QA/QC will promote actions, discussions and meetings to achieve a general improvement of the QA/QC in the analytical activities performed within the ICP Forests;
- Regularly conduct working ring tests (WRT), analyse the results, present them at the EPD-meeting or at other occasions and publish the results;
- Identify each year a maximum of 2-3 laboratories to be actively helped; fix targets with these labs and follow their progress according to mutually agreed targets;
- Advise and assist all laboratories which seek help or which have been identified as having analytical difficulties in progressing with their own QA/QC;

Aims of the WG on QA/QC

- Update the ICP Forest manual when necessary, taking into account the evolution of analytical techniques and instrumentation and the specific problems of the ICPF analytical team;
- Develop and follow annually a 5-7 main analytical QA/QC indicators designed to show objectively the evolution/progress in QA/QC made by all participating countries;
- Collaborate with the institution appointed to store and elaborate the data (JRC and BFH) relating to the QA/QC of the laboratories, and to perform data validation and elaboration;
- Cooperate with the QA/QC executives from the soil expert panel to check the possibility of a combined working group.

WG on QA/QC, present composition

Rosario Mosello, Gabriele Tartari, Verbania Pallanza, Italy

John and Kirsti Derome, Rovaniemi, Finland

Erwin Ulrich, Fontainebleau, France

Nils König, Goettingen, Germany

Nicholas Clarke, Ås, Norway

Anna Kowalska, Warsaw, Poland

Polona Kalan, Ljubljana, Slovenia

WG on QA/QC - Activities done and going on

- Collection of information on the analytical methods going on in the laboratories involved in the deposition/soil water analyses.
- Web page for information and exchange of documents (www.icp-forests.org). It becomes in one year the central tool for the circulation of information within the WG and all laboratories. NFCs and any data user are invited to regularly get connected to this site.
- Technical notes as an easy tool for information among laboratories about studies done within a laboratory but for which no publication was made.
- Pointing out criteria for the validation of chemical analyses;

WG on QA/QC - Activities done and going on

Criteria for the validation of chemical analyses

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

Ionic balance

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

$$\Sigma_{\text{anions}} = \text{Alk} + [\text{SO}_4^-] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{Org}^-]$$

$$\Sigma_{\text{cations}} = [\text{Ca}^{++}] + [\text{Mg}^{++}] + [\text{Na}^+] + [\text{K}^+] + [\text{H}^+] + [\text{NH}_4^+]$$

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

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

for conductivity $\leq 100 \mu\text{S cm}^{-1}$ $CE_{\infty} = \sum \lambda_i c_i$

for conductivity $> 100 \mu\text{S cm}^{-1}$ $CE = \sum \lambda_i f_i c_i$

λ_i *equivalent ionic conductance*

C_i *Concentration of the ion i*

f_i *activity coefficient*

	Units	Factors to $\mu\text{eq L}^{-1}$	Equivalent conductance at 25°C $\text{kS cm}^2 \text{eq}^{-1}$
pH		$10^6 \cdot 10^{-\text{pH}}$	0.3500
Ammonium	$\text{mg N-NH}_4 \text{ L}^{-1}$	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	$\text{mg N- NO}_3 \text{ L}^{-1}$	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
$\leq 10 \mu\text{S cm}^{-1}$	$\pm 20\%$	$\pm 30\%$
$< 20 \mu\text{S cm}^{-1}$	$\pm 20\%$	$\pm 20\%$
$> 20 \mu\text{S cm}^{-1}$	$\pm 10\%$	$\pm 10\%$

Complete analysis  Ionic balance

Low conc. samples
($\leq 20 \mu\text{S cm}^{-1}$)

$\Delta \%_{\text{ions}}$

≤ 20

> 20

Analyses
accepted

Analyses
repeated

Medium-high conc. samples
($> 20 \mu\text{S cm}^{-1}$)

$\Delta \%_{\text{ions}}$

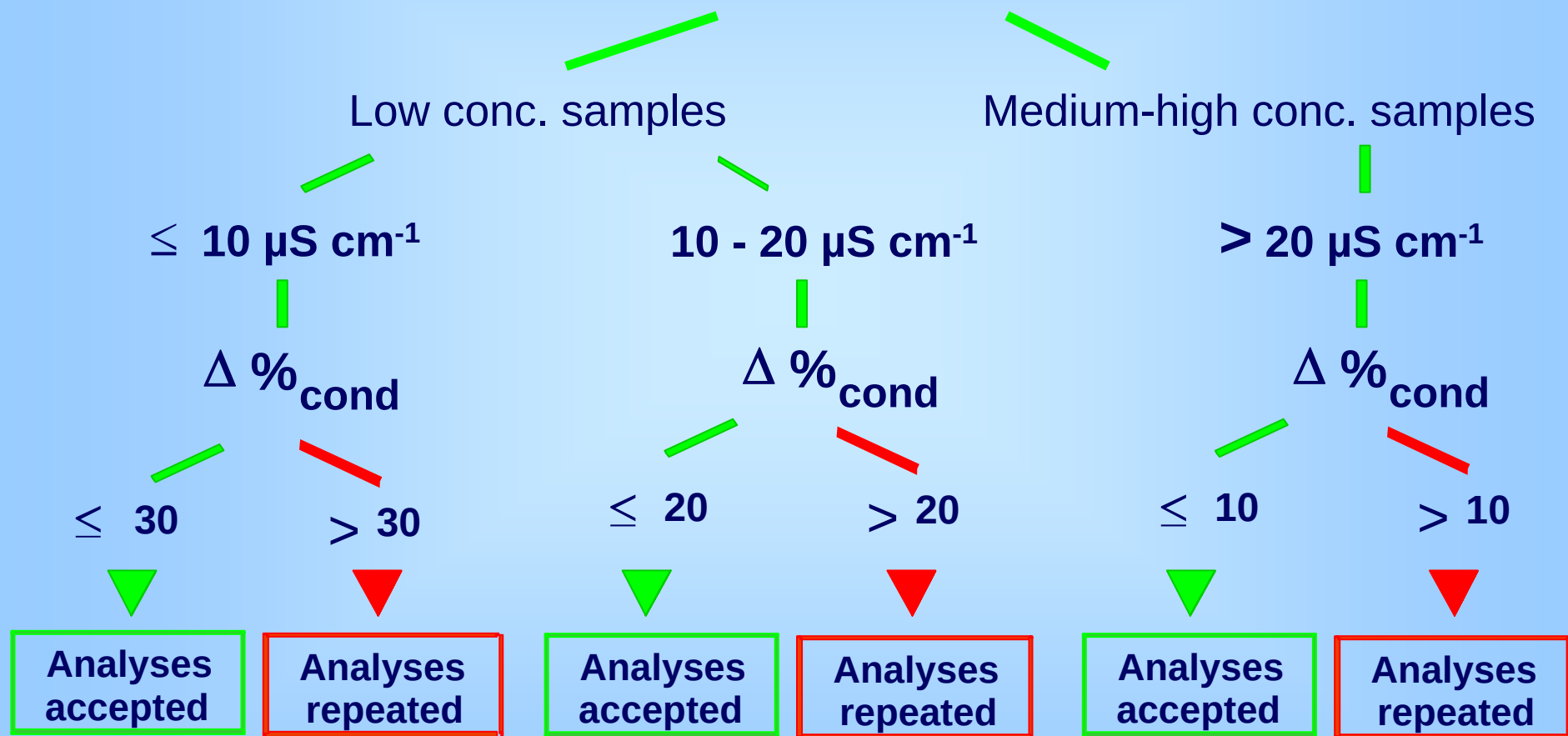
≤ 10

> 10

Analyses
accepted

Analyses
repeated

Complete analysis → Conductivity comparison



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
runoff	?	yes	no	yes
soil water	no	yes	no	yes

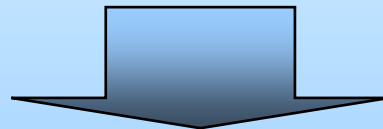
? = applicable if TOC is lower than 5 mg C L⁻¹

Organic nitrogen validation test

$$\text{TN} = \text{N-NO}_3^- + \text{N-NH}_4^+ + (\text{N-NO}_2^-) + \text{Org_N}$$

$$\text{Org_N} = \text{TN} - \text{N-NO}_3^- - \text{N-NH}_4^+$$

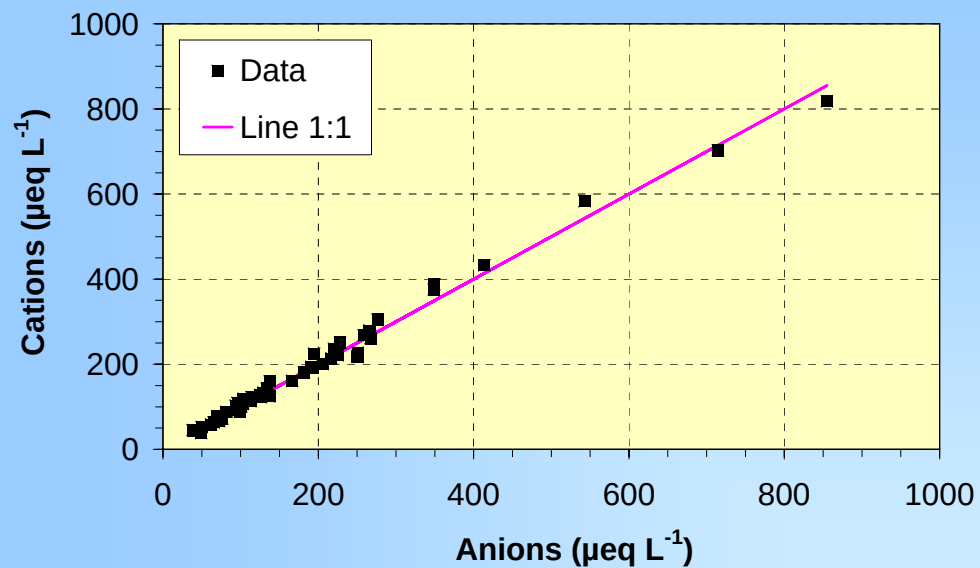
The concentration of organic nitrogen
can not be negative!



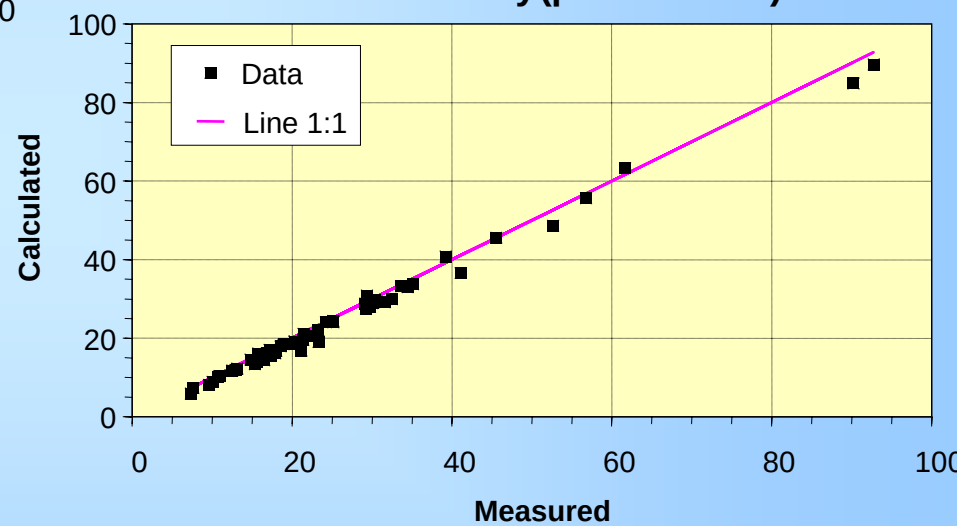
$$\text{TN} - \text{N-NO}_3^- - \text{N-NH}_4^+ \geq 0$$

Microsoft Excel - EPD_analytical_data_validation														
Digitare una domanda.														
AC8														
	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	

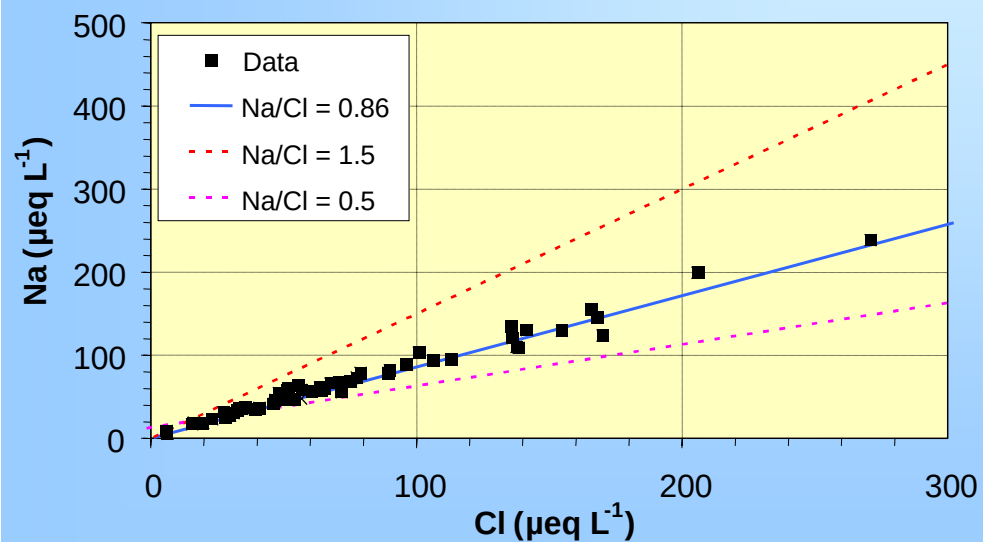
Ionic balance



Conductivity ($\mu\text{S cm}^{-1}$ 25°C)



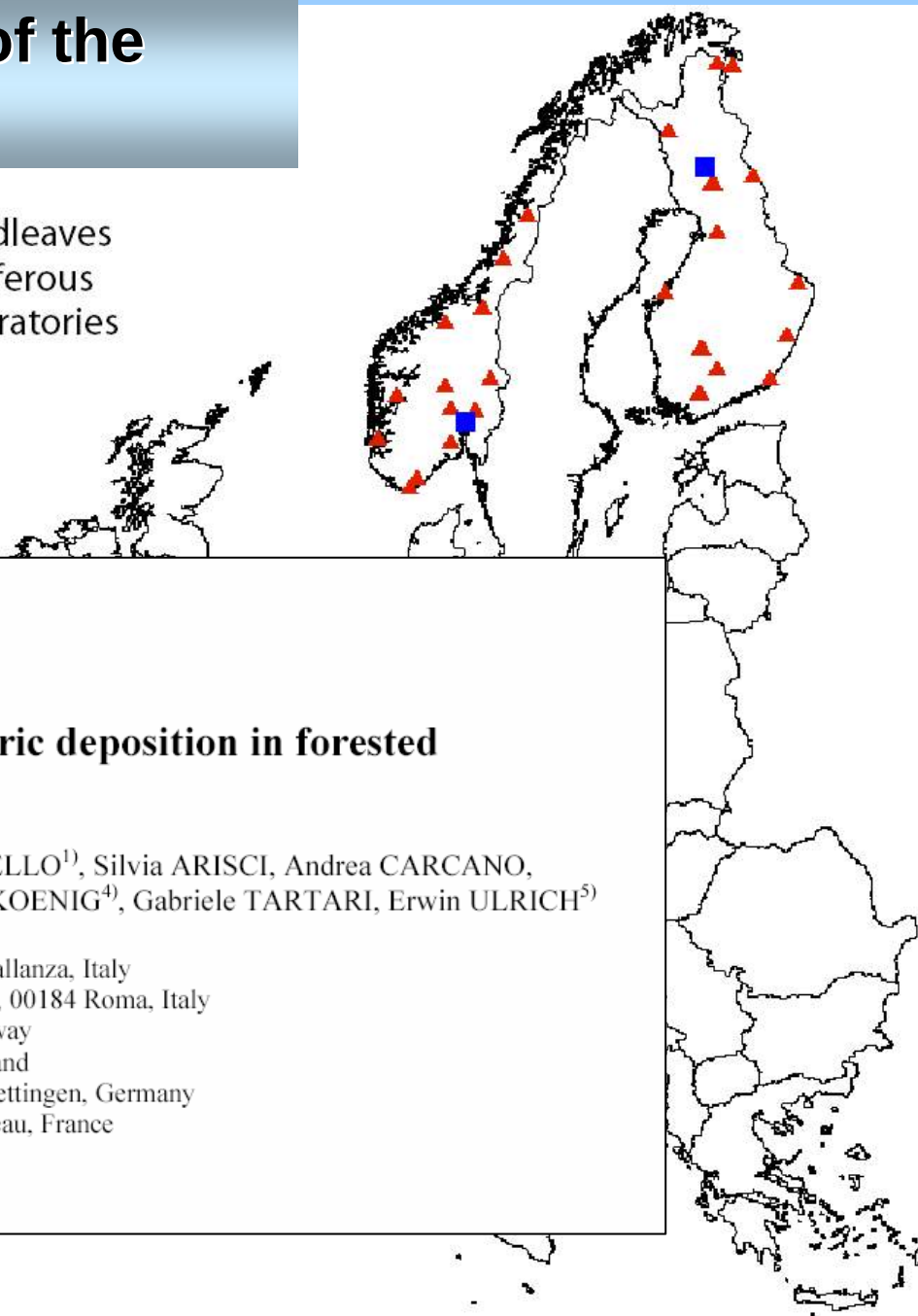
Ratio Na/Cl



Examples of the application of the validation criteria

➤ About 5000 analyses of deposition samples done from 7 different laboratories

● Broadleaves
▲ Coniferous
■ Laboratories



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

Validation of chemical analyses of atmospheric deposition in forested European sites

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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.

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, Farham, Hampshire

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	<u>1361</u>	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	<u>194</u>	0	1562
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

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.

Ionic balance

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

$$\Sigma_{\text{anions}} = \text{Alk} + [\text{SO}_4^-] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{Org}^-]$$

$$\Sigma_{\text{cations}} = [\text{Ca}^{++}] + [\text{Mg}^{++}] + [\text{Na}^+] + [\text{K}^+] + [\text{H}^+] + [\text{NH}_4^+]$$

[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:

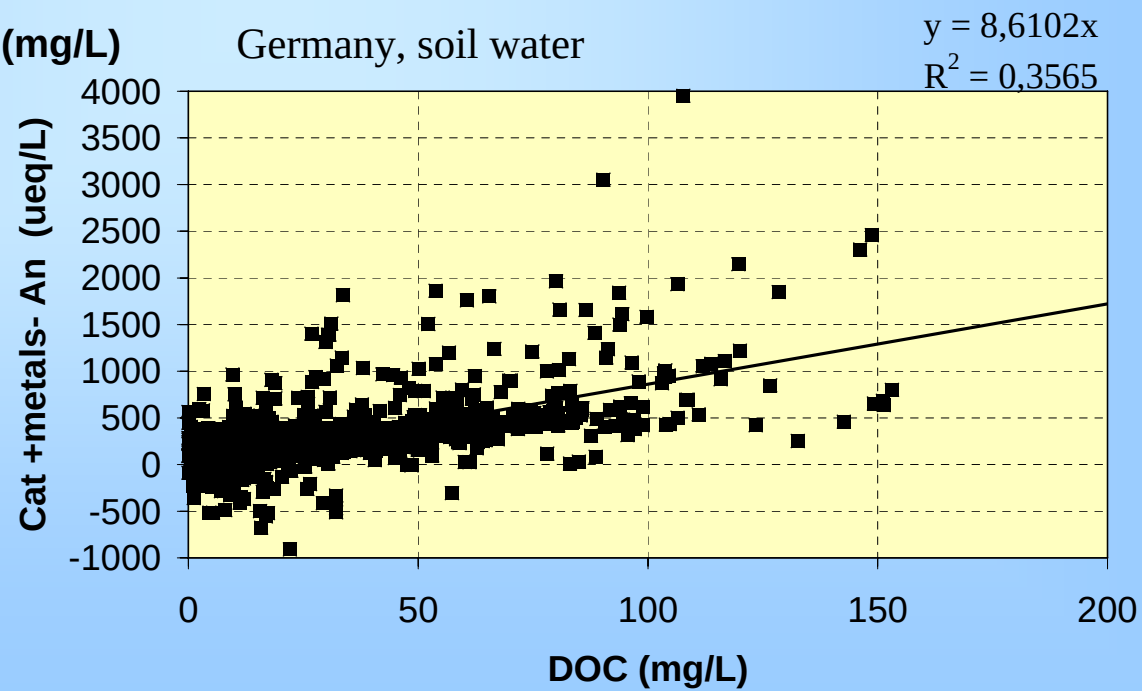
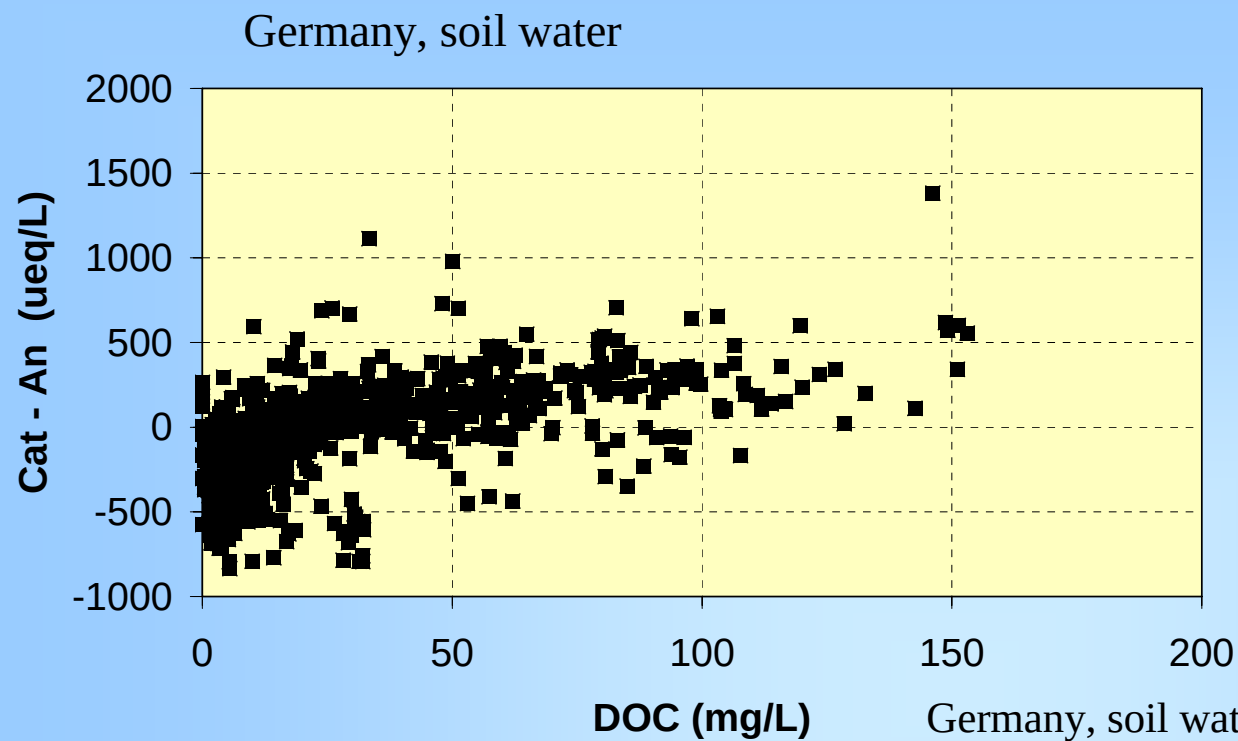
- no errors are affecting the ion concentrations
- no other ions are present in solutions

Ionic balance

$$\Sigma_{\text{anions}} = \text{Alk} + [\text{SO}_4^=] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{Org}^-]$$

$$\Sigma_{\text{anions}} = \text{Alk} + [\text{SO}_4^=] + [\text{NO}_3^-] + [\text{Cl}^-] + f(\text{DOC})$$

$$f(\text{DOC}) = \text{slope} * \text{DOC} + \text{intercept}$$



Number of data collected

Laboratory

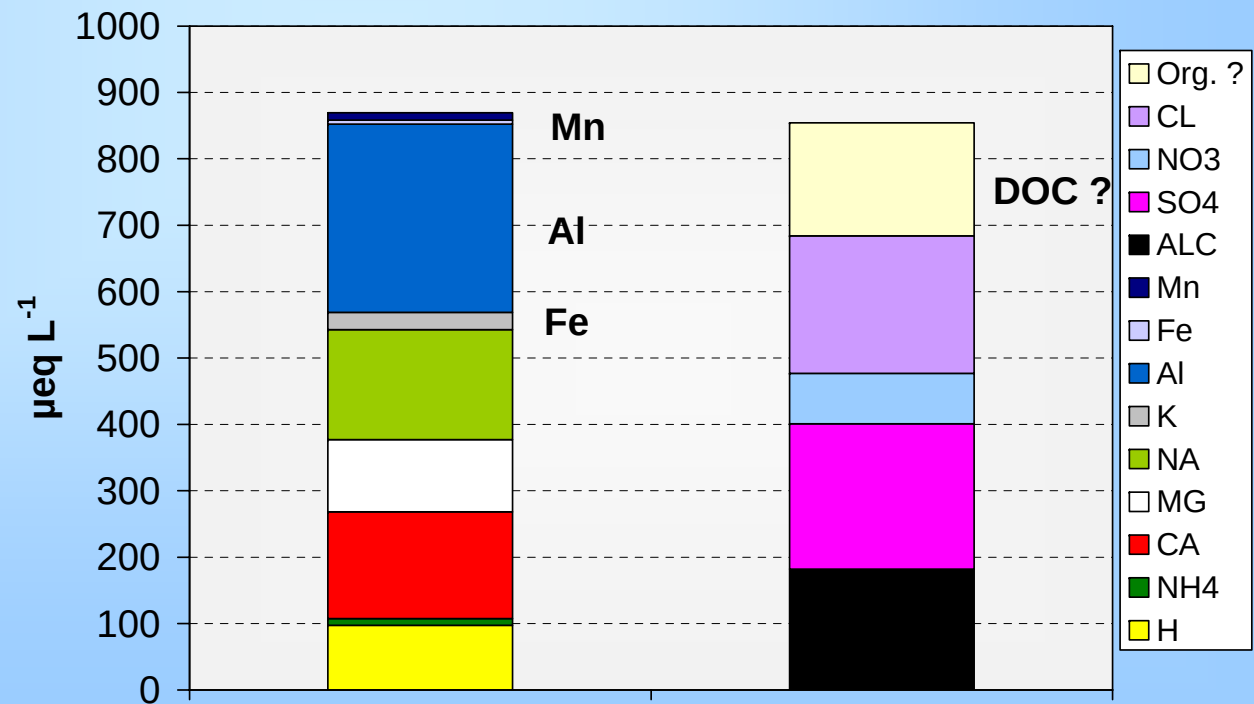
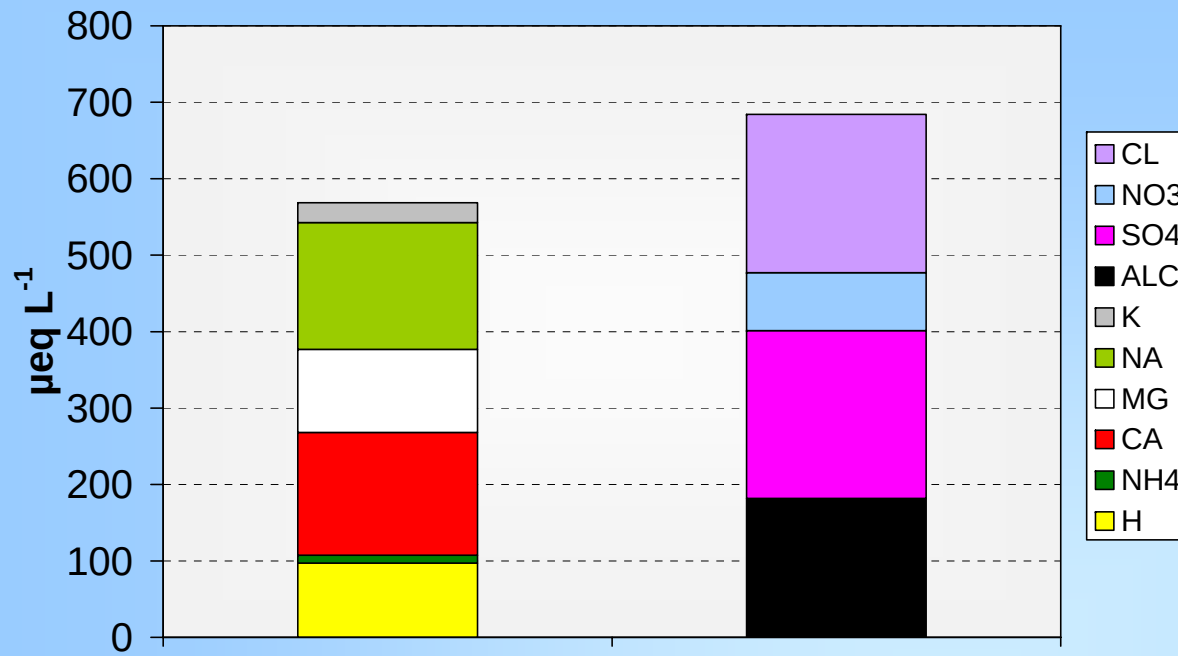
Italy
France
Norway
Germany
Switzerland
Denmark
Flanders
UK

Soil water

metals

0	
1562	no data
267 *	T Al, Fe, Mn
1416 *	T Al, Al org, Fe, Mn
0	
798 *	T Al, Fe, Mn
475 *	T Al, Fe
1287 *	T Al, Fe, Mn

Germany, soil water



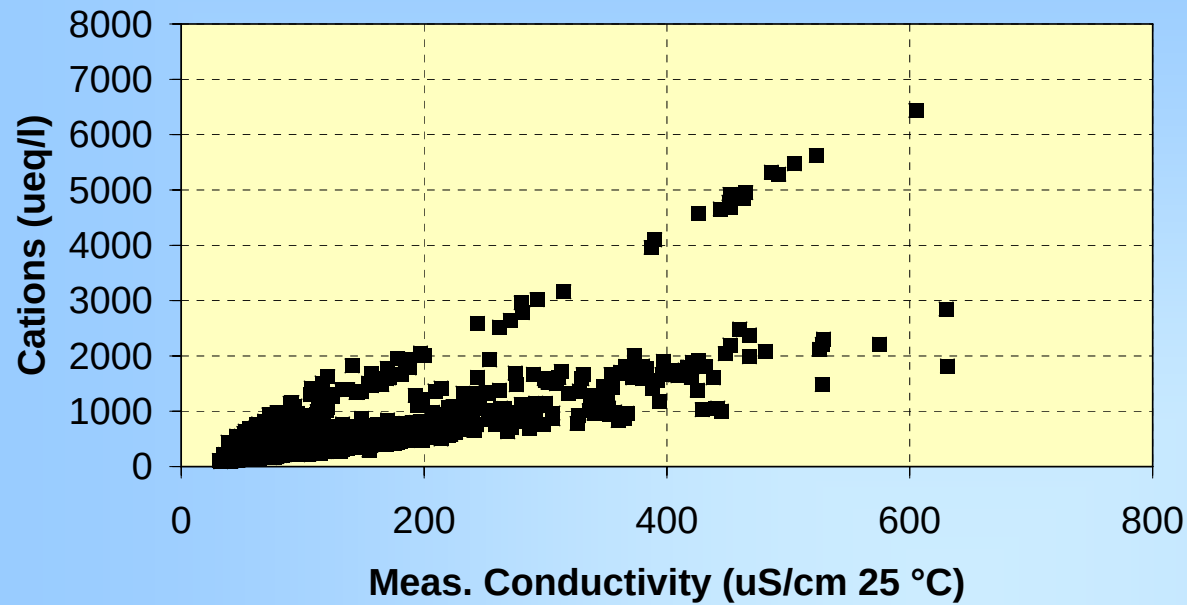
Soil water

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).

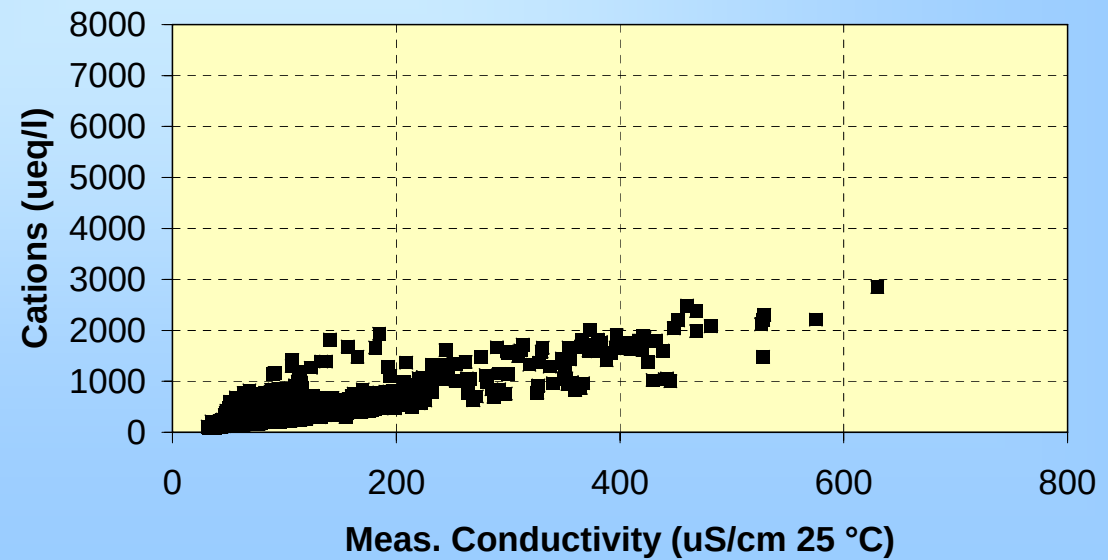
These aspects do not exclude the possibility to check for correlations among variables, assuming a full dissociation of trace metals

all samples

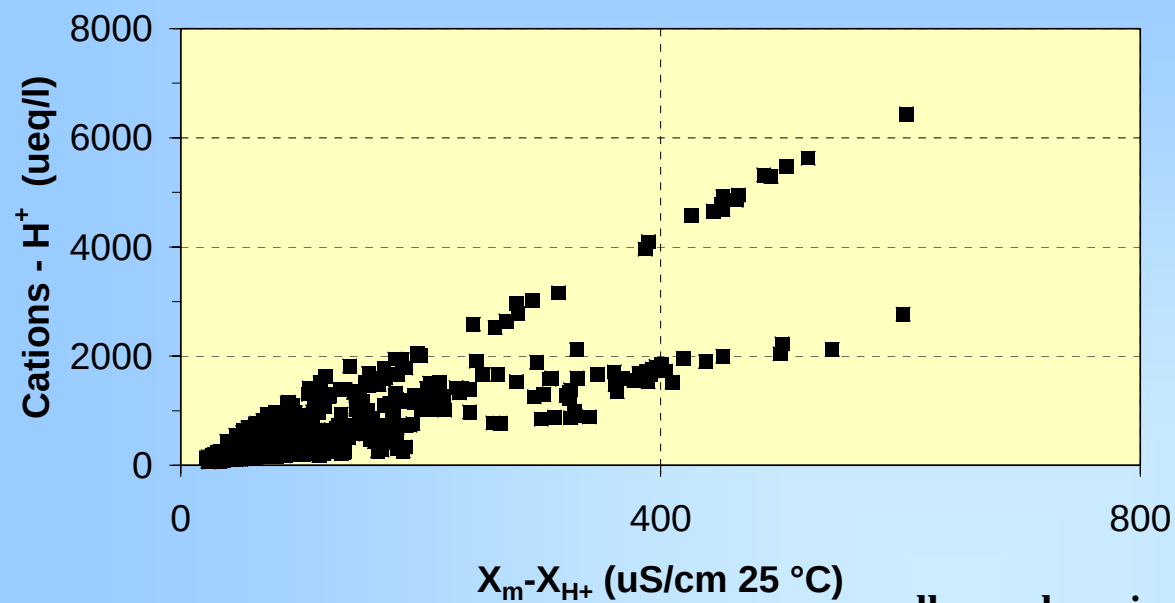


Germany, soil water

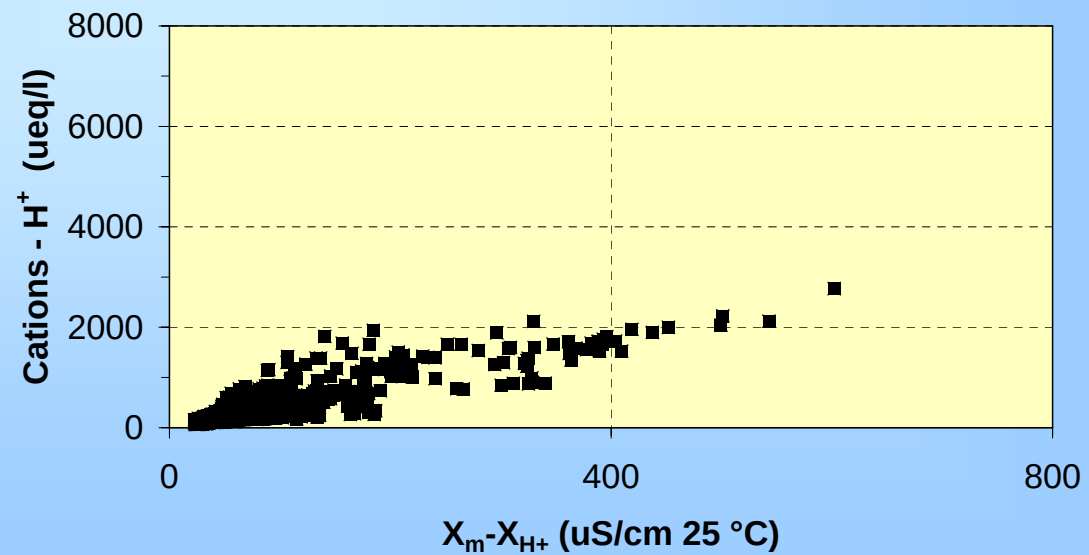
all samples minus samples without Al (Al > 1 mg/l)



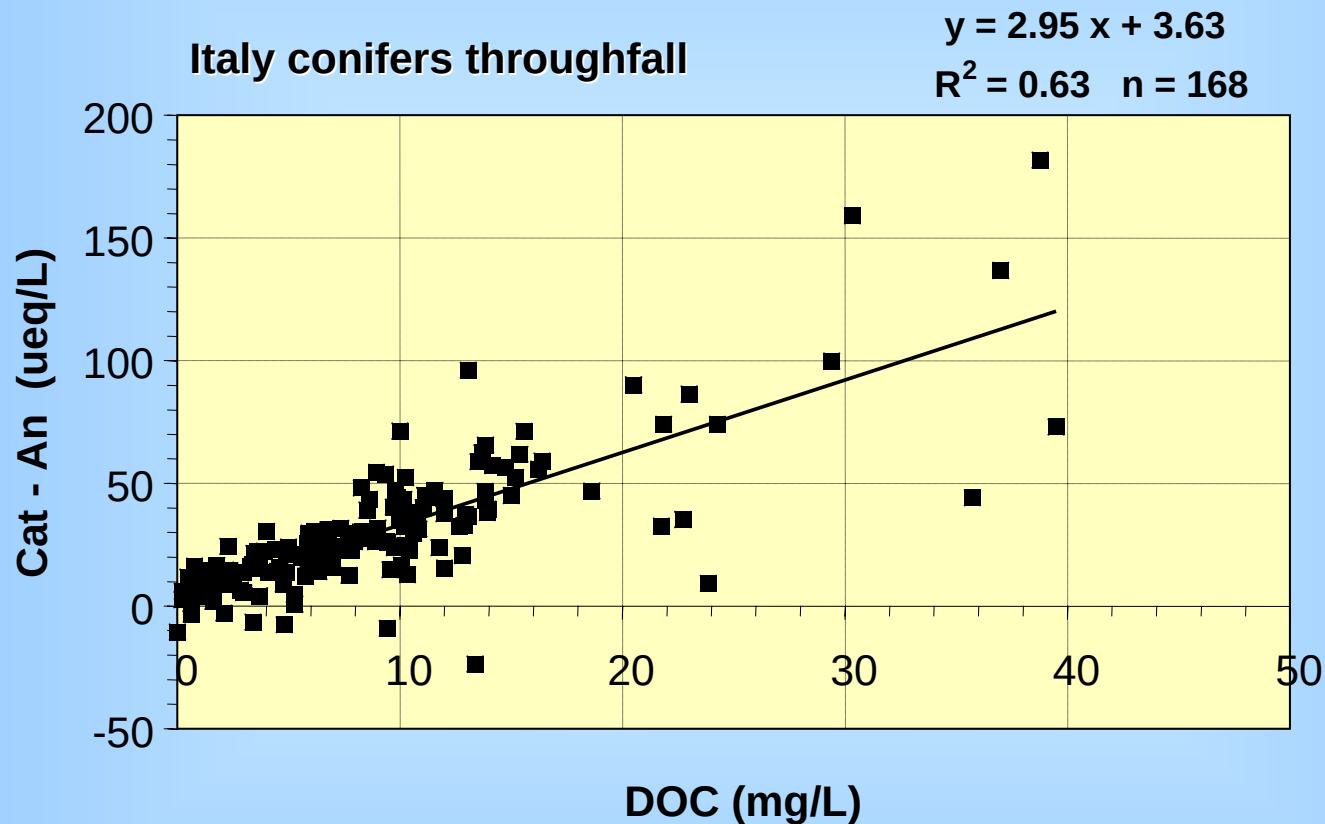
all samples



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

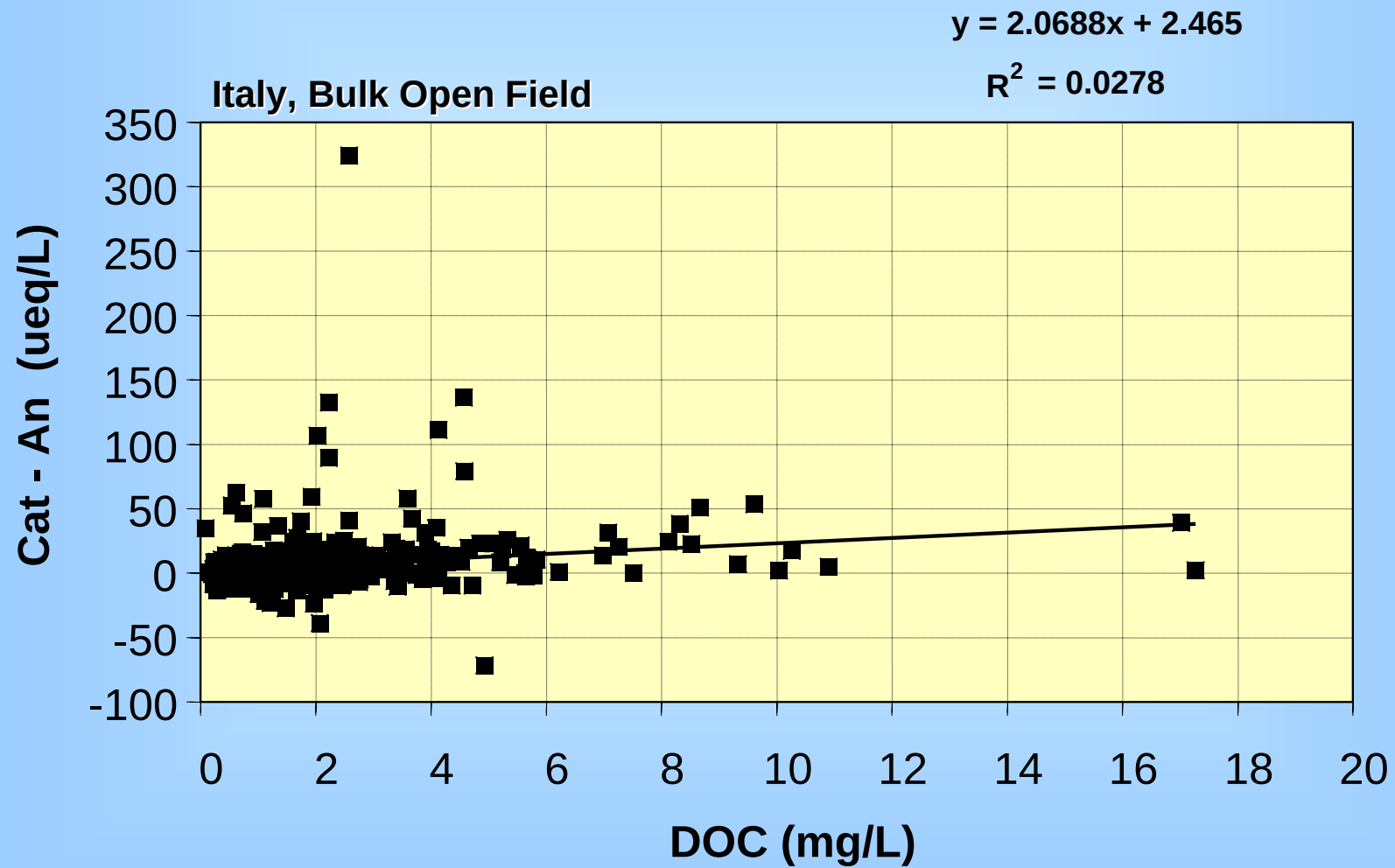


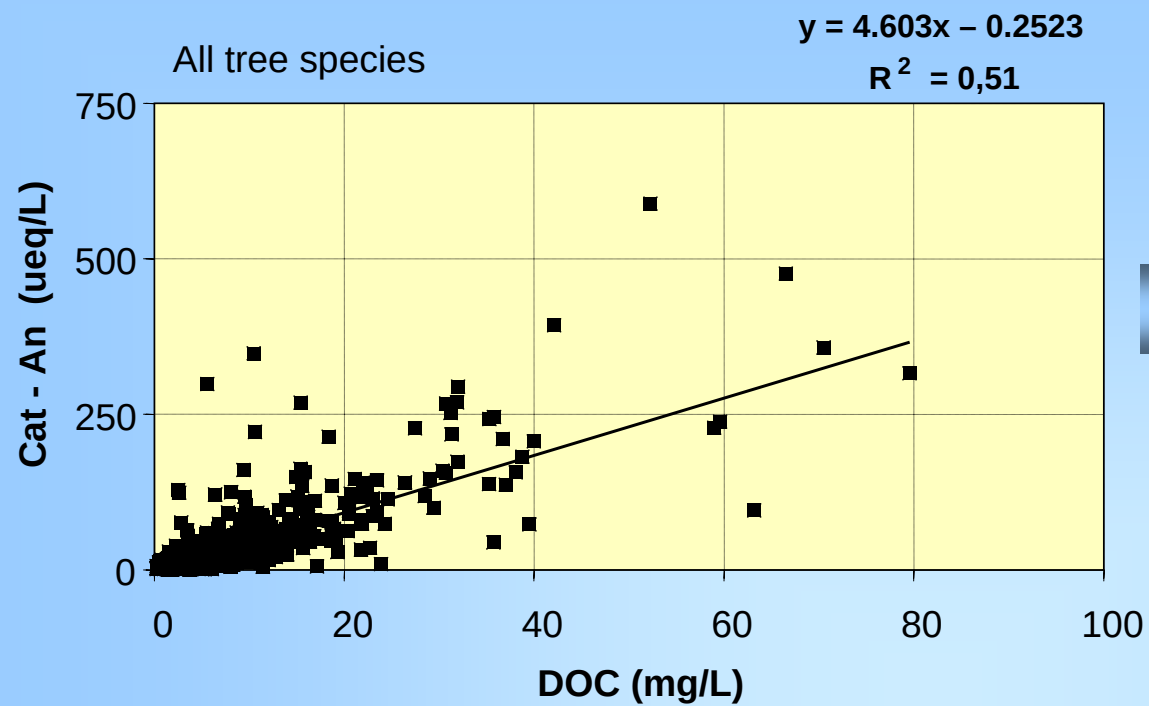
The slope of the regression DOC (mg L⁻¹) vs Cat-An (μeq L⁻¹)
is an evaluation of the DOC Formal Charge



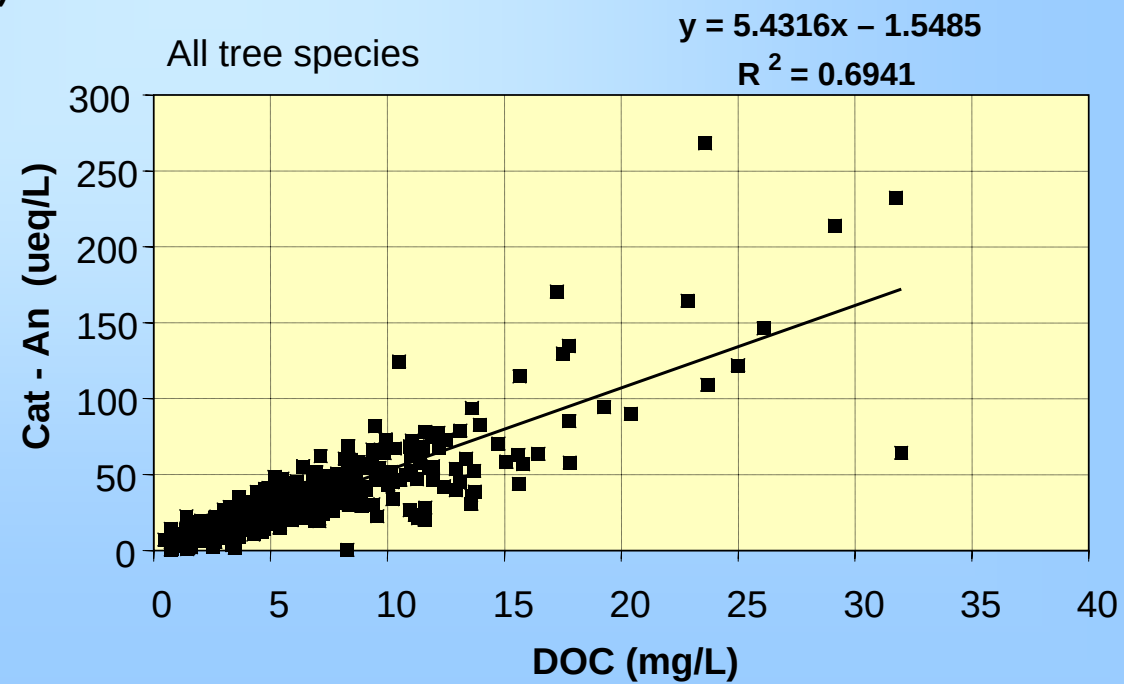
$$\text{Slope} = \Delta y / \Delta x = \mu \text{ eq L}^{-1} / \text{mg C L}^{-1} = \mu \text{ eq} / \text{mg C}$$

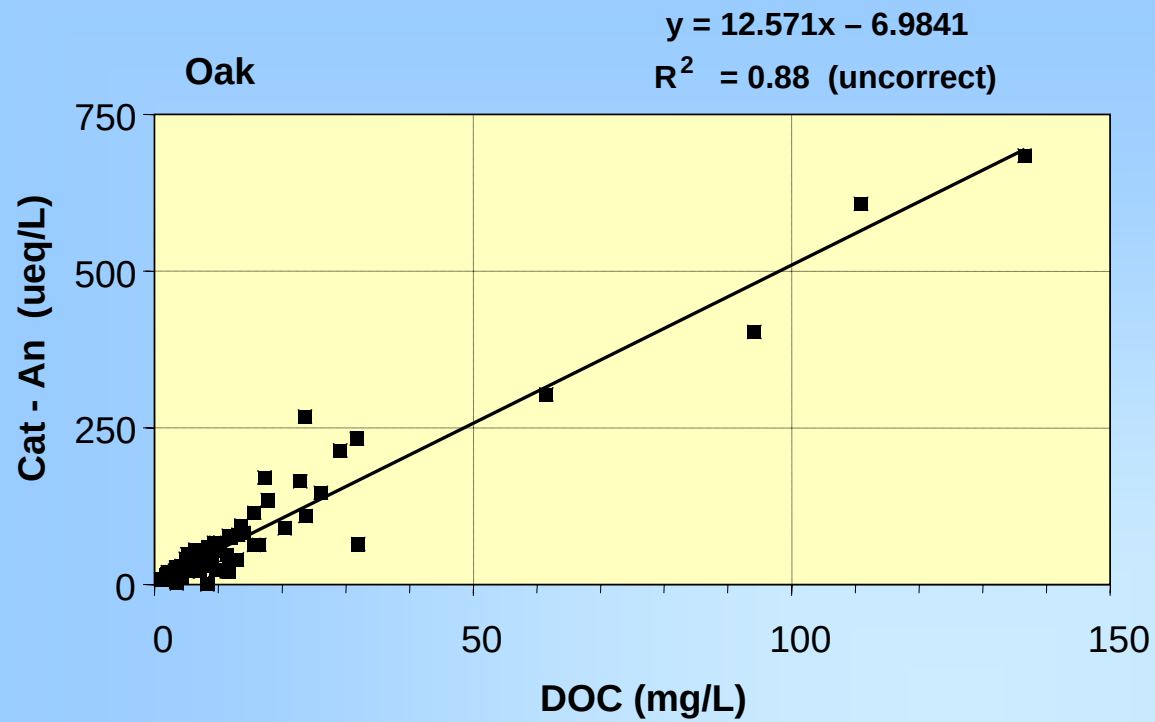
Atmospheric deposition, bulk open field



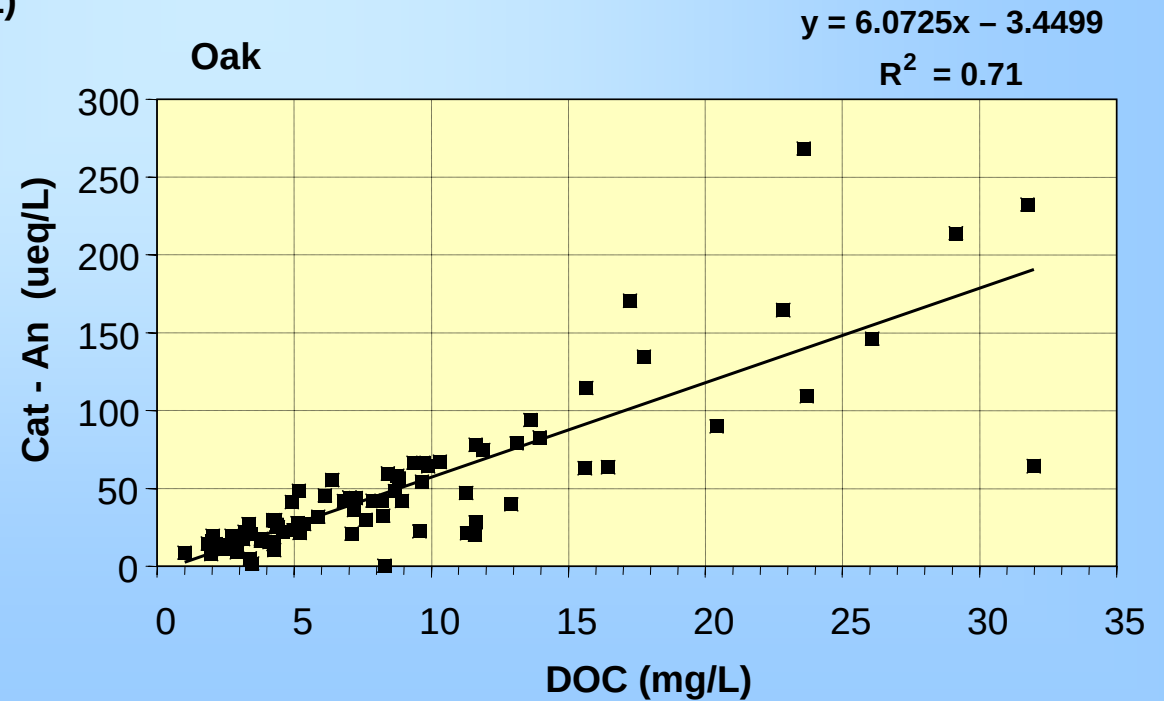


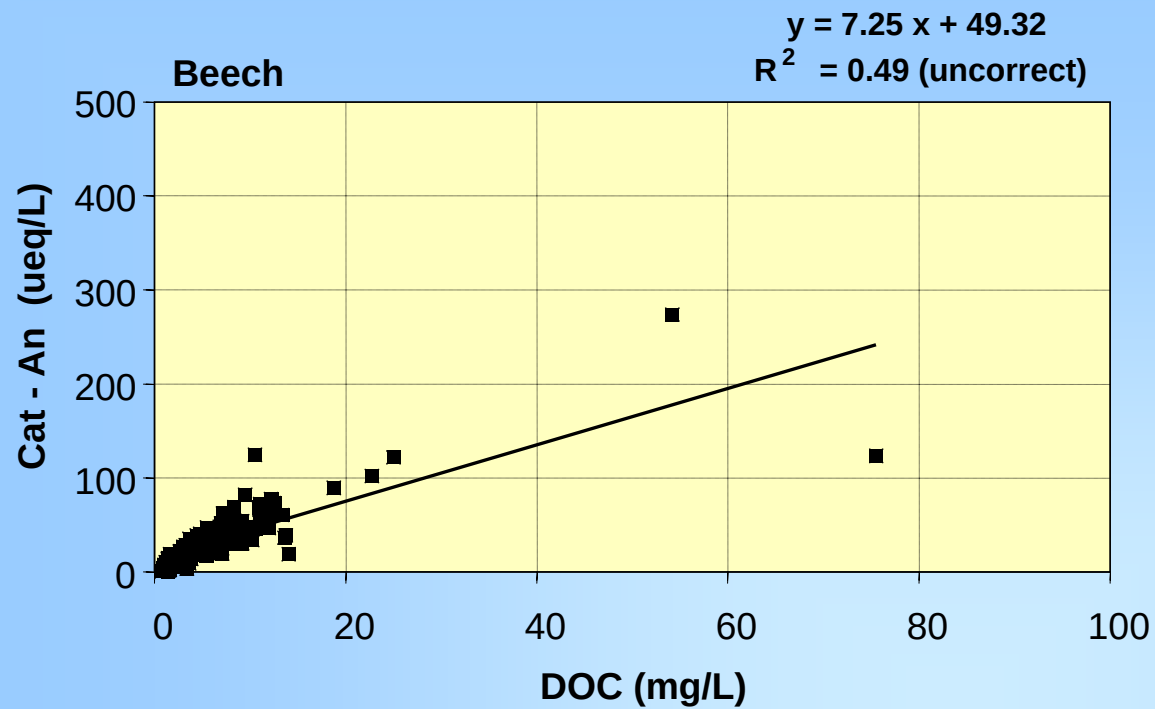
Switzerland, throughfall



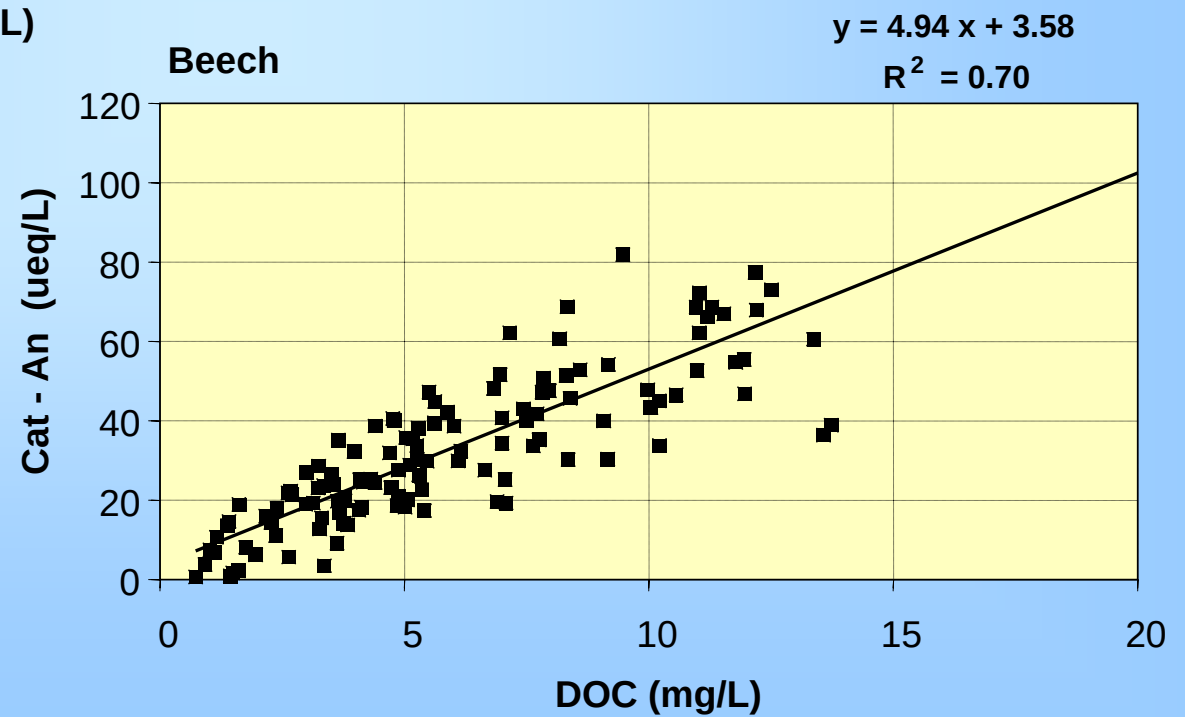


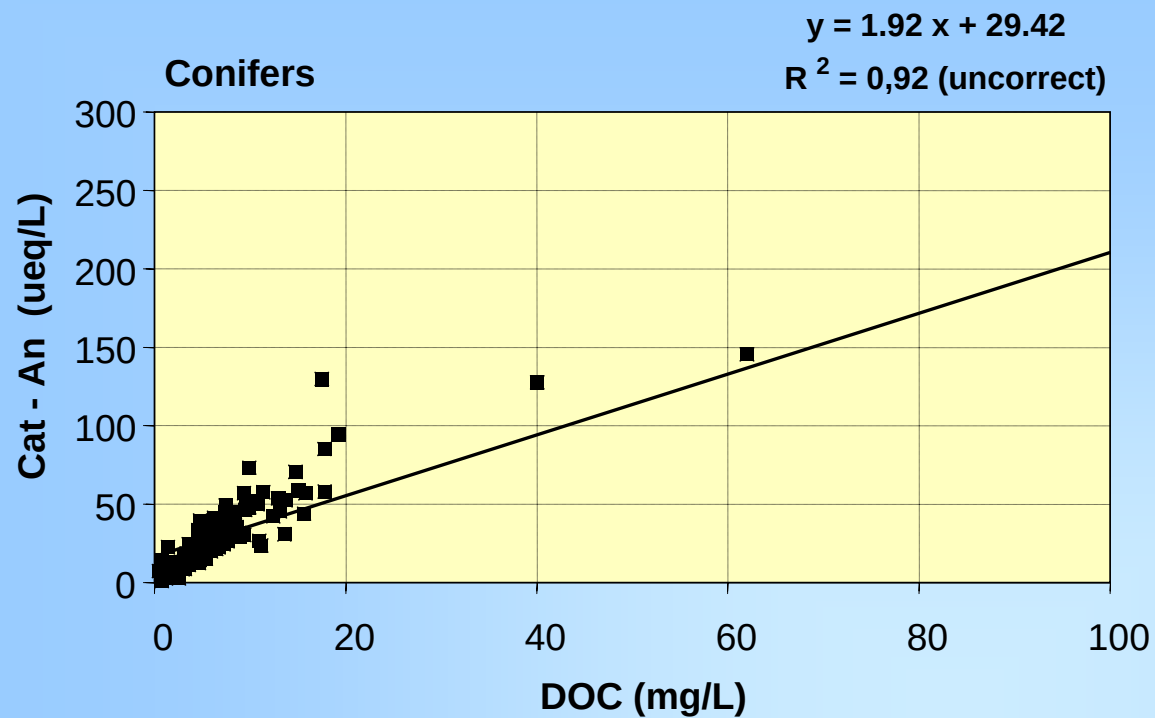
Switzerland, throughfall



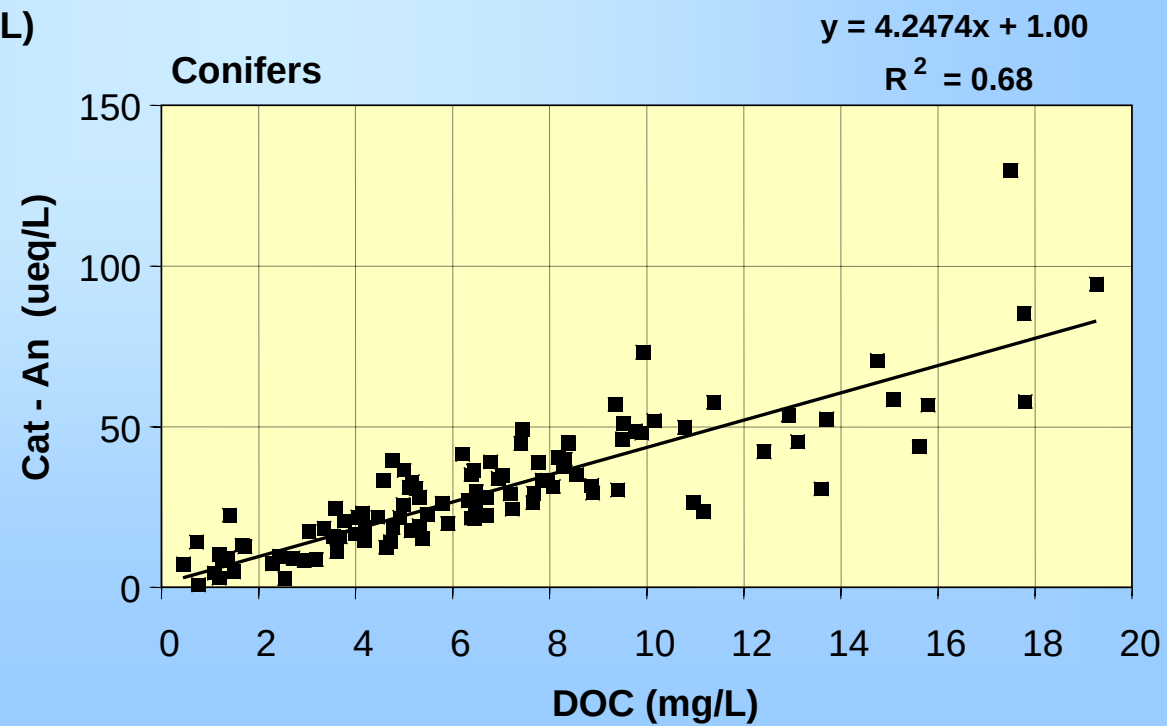


Switzerland, throughfall





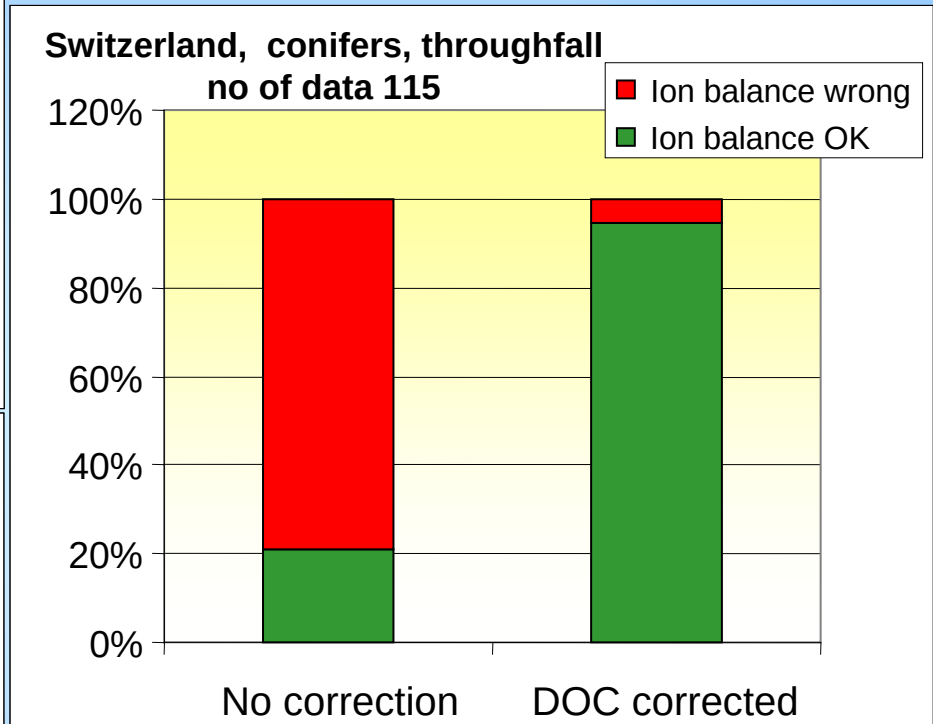
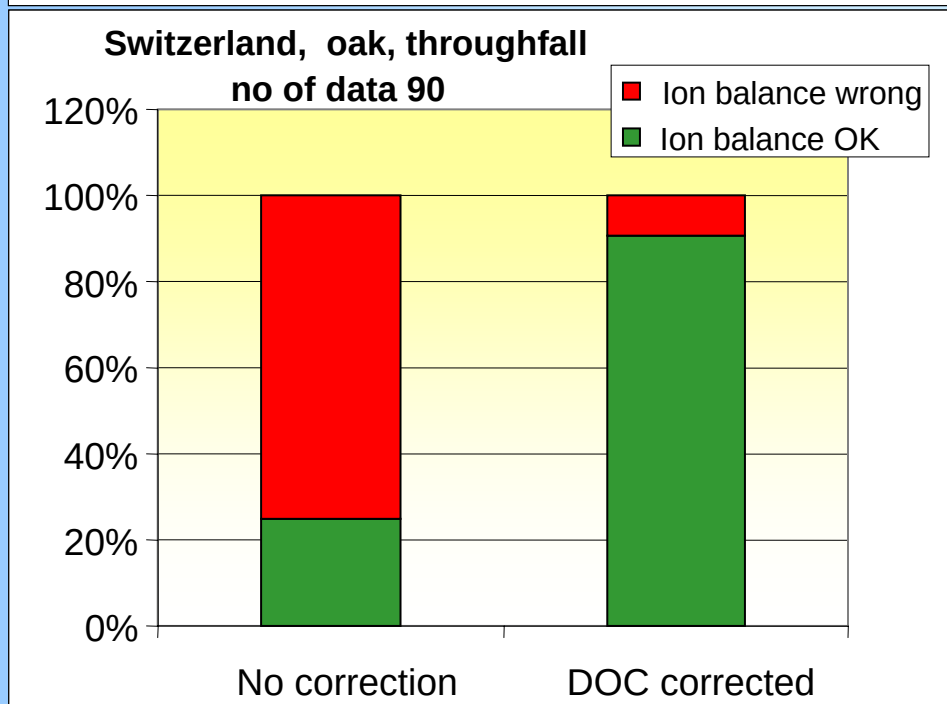
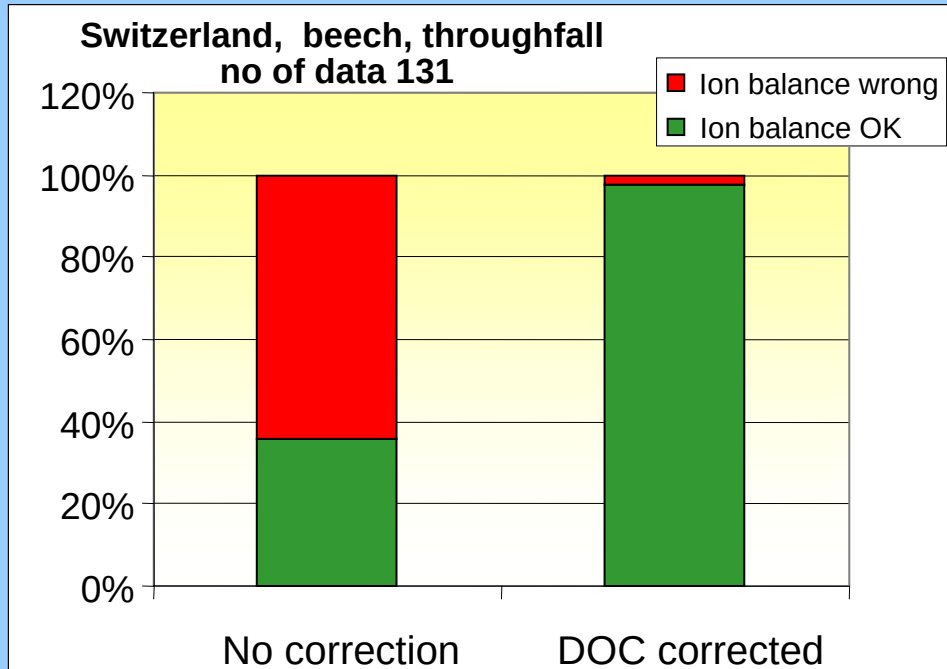
Switzerland, throughfall



Regression DOC (mg L⁻¹) vs Cat-An (μeq L⁻¹) Switzerland

	slope	intercept	n	r ²
Beech	4.94	3.58	134	0.70
Oak	6.07	-3.45	88	0.71
Conifers	4.25	1.00	118	0.68
All tree species	5.43	-1.55	340	0.69

Switzerland, throughfall



**Regression DOC (mg L⁻¹) vs Cat-An (μeq L⁻¹)
values of the slope (μeq/mg C L⁻¹)**

	Switzerland	Italy
Beech	4.9	3.5
Oak	6.1	5.4
Conifers	4.3	3.0
All tree species	5.4	4.6

Partial conclusions

A DOC Formal Charge can be evaluated and used in the ion balance evaluation in the case of throughfall and stemflow deposition, but not in the case of bulk deposition.

Better results are obtained considering separately the different tree species.

Further data elaboration is needed to evaluate the role of systematic errors in affecting the value of the DOC Formal Charge.

Further elaboration of data

Questions:

Data elaboration should be done after the elimination of results not fitting with the validation criteria?

How much systematic errors and/or missing variables may affect the evaluation of DOC Formal Charge?

Which variables affects mostly the values of DOC Formal Charge?

Proposed evaluation (1)

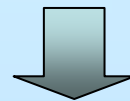
For each laboratory and type of solution:

- ❖ Does the organic carbon formal charge (OCFC) exist as a function of DOC?

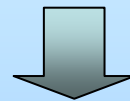
If yes, does the OCFC depend on **type of vegetation** (broad leaves/conifers)?

Use the Analysis of Covariance (ANCOVA) to test: $(\text{Cat-An}) = f(\text{DOC}, \text{veg})$.

If there are differences between solutions from broadleaves/conifers plot,



$(\text{Cat-An}) = f(\text{DOC}), R^2, \text{intercept, slope, number of data } n$



Comparison among the regressions from all laboratories through test F.

- ❖ Does the OCFC depend on **sampling station** (code)?

Use the Analysis of Covariance (ANCOVA) to test: $(\text{Cat-An}) = f(\text{DOC}, \text{code})$.

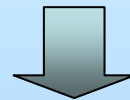
Proposed evaluation (2)

For all laboratories and for each type of solution:

- ❖ Does the OCFC depend on **type of vegetation** (broad leaves/conifers)?

Use the Analysis of Covariance (ANCOVA) to test: $(\text{Cat-An}) = f(\text{DOC}, \text{veg})$.

If there are differences between solutions from broadleaves/conifers plot,



$(\text{Cat-An}) = f(\text{DOC}), R^2, \text{intercept, slope}$

Proposed evaluation (3)

For all laboratories and for each type of solution and vegetation:

- ❖ Does the OCFC depend on the **geographic variables** (altitude, latitude, longitude) and the **climatic variables** (mean annual temperature AT, annual amount of precipitation PR)?

Use the Analysis of Covariance (ANCOVA) to test:

$$(\text{Cat-An}) = f(\text{DOC}, \text{alt}, \text{lat}, \text{lon}, \text{AT}, \text{PR})$$

For all laboratories and vegetation and for each type of solution:

- ❖ Does the OCFC depend on the **geographic variables** (altitude, latitude, longitude) and the **climatic variables** (mean annual temperature AT, annual amount of precipitation PR)?

Use the Analysis of Covariance (ANCOVA) to test:

$$(\text{Cat-An}) = f(\text{DOC}, \text{alt}, \text{lat}, \text{lon}, \text{AT}, \text{PR})$$

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

Second step

- To make successfully this analysis it is needed the strict collaboration of the persons in charge of the chemical results of each laboratory aimed at:
- excluding unreliable results.
- verifying that no errors were done during the data manipulation.
- analysing and commenting results of the statistical analysis.

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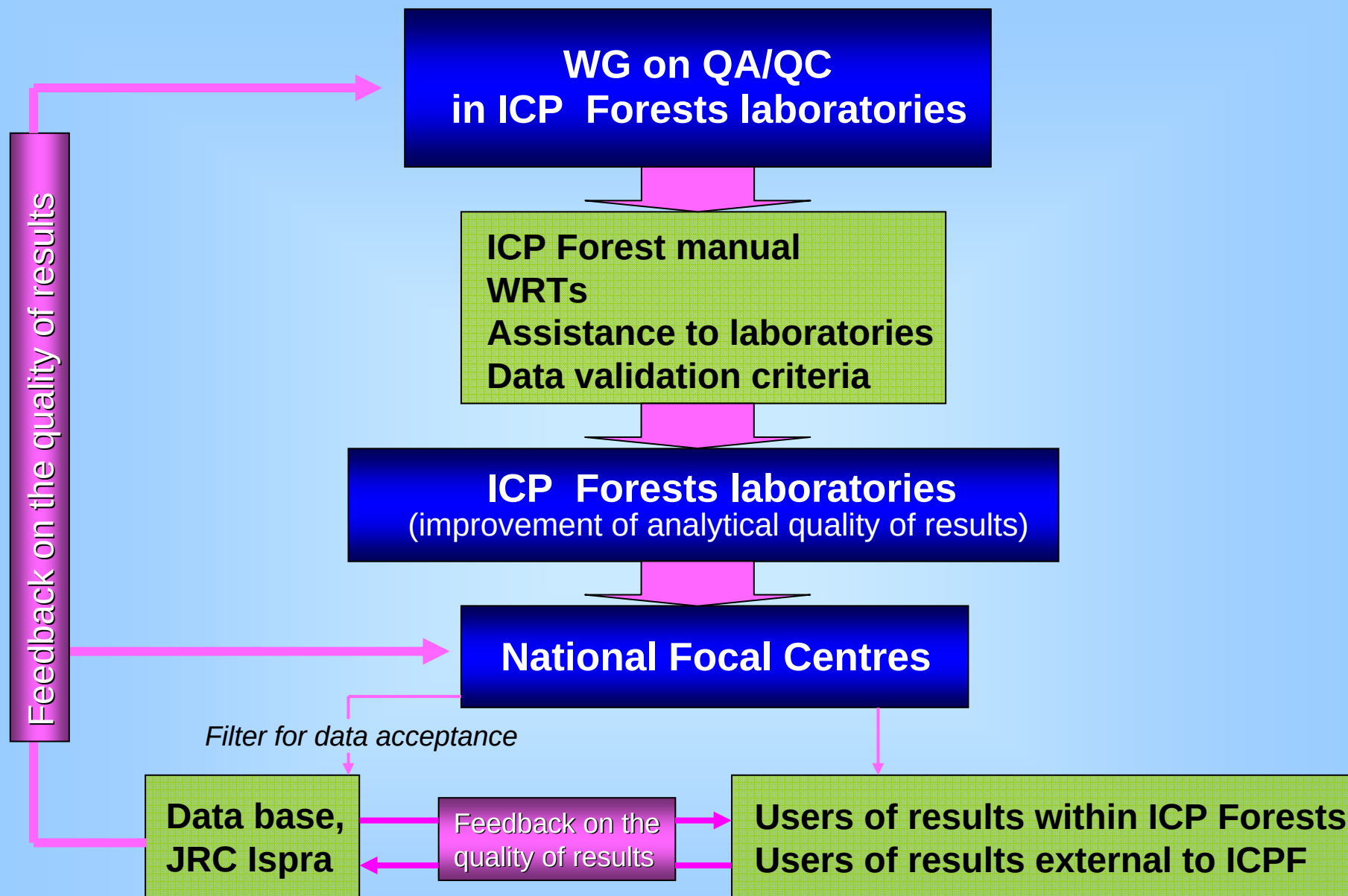
**Tamara Jakovljevic, Maria Cristina Brizzio,
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Tiziana Amoriello

Thanks for your attention:

Discussion is open!



WG on QA/QC Activities done and going on

1. Update of the Part VI (Sampling and analysis of atmospheric deposition) of the ICP Forests manual, dealing with QA/QC in chemical analyses and data validation

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

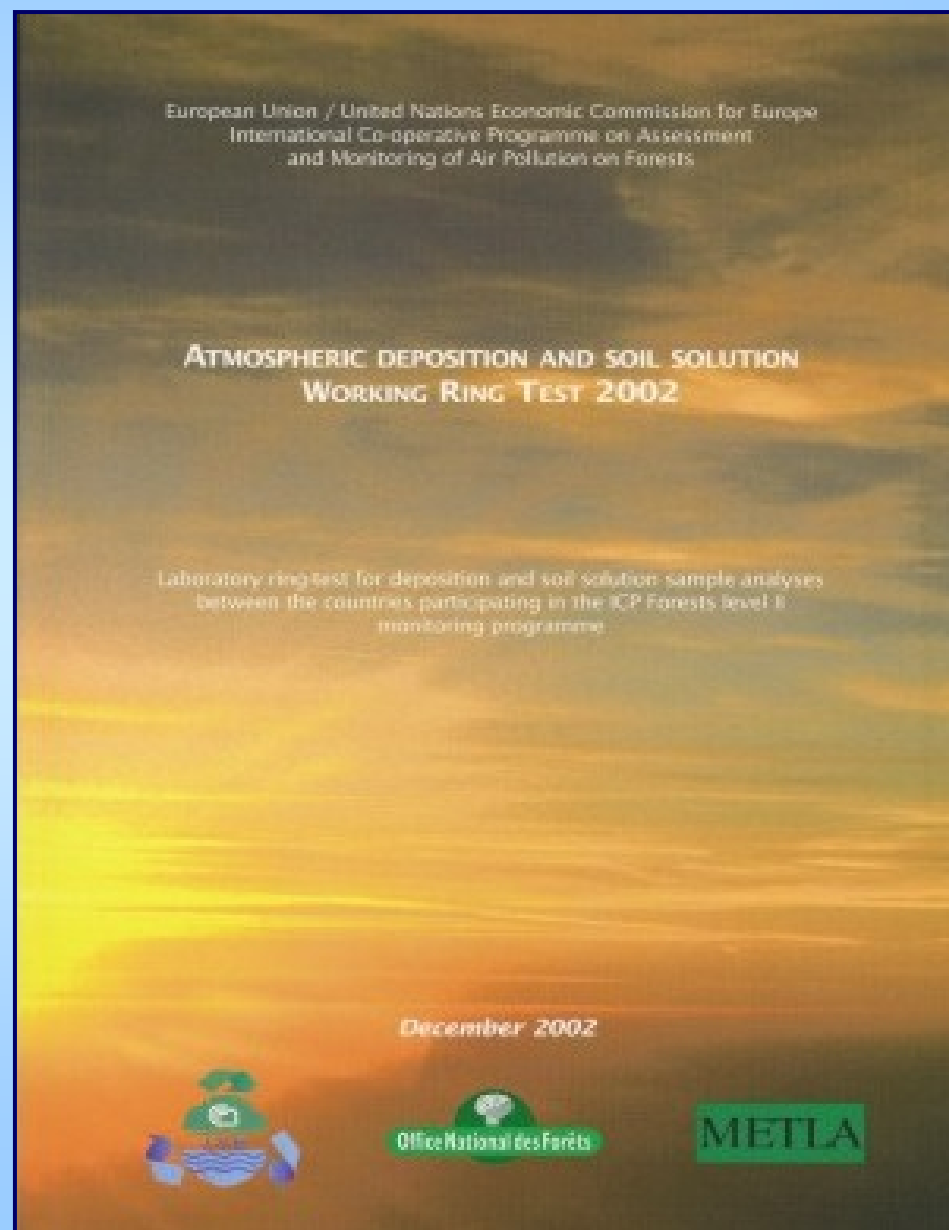
Part VI

Sampling and Analysis of Deposition

updated: 06/2004

WG on QA/QC Activities done and going on

2. Working Ring Test 1 (2002)



WG on QA/QC Activities done and going on

3. Working Ring Test (2005)

