

**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

**Report of the QC/QA work and the previous ring tests  
within the Expert Panel on Deposition**

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

# **Working Group on QA/QC**

## **atmospheric deposition and soil water**

**Nils König**, Goettingen, Germany

**Rosario Mosello, Gabriele Tartari**, Verbania Pallanza, Italy

**John and Kirsti Derome**, Rovaniemi, Finland

**Erwin Ulrich**, Fontainebleau, France

**Nicholas Clarke**, Ås, Norway

**Anna Kowalska**, Warsaw, Poland

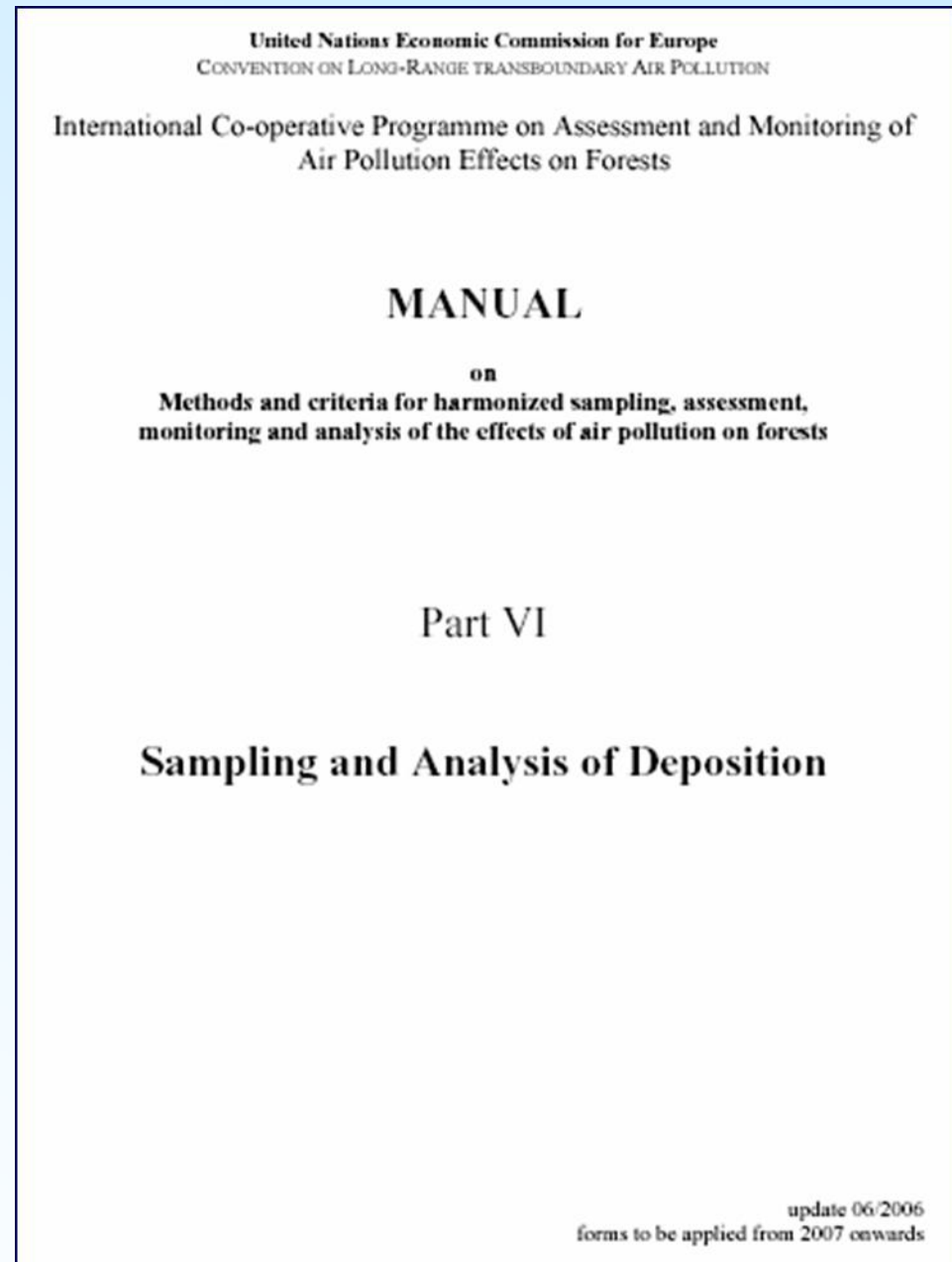
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## **Aims of the WG on QA/QC**

**The WG on QA/QC promotes actions, discussions and meetings to achieve a general improvement of the QA/QC in the analytical activities performed within the ICP Forests.**

## Activities done and going on:

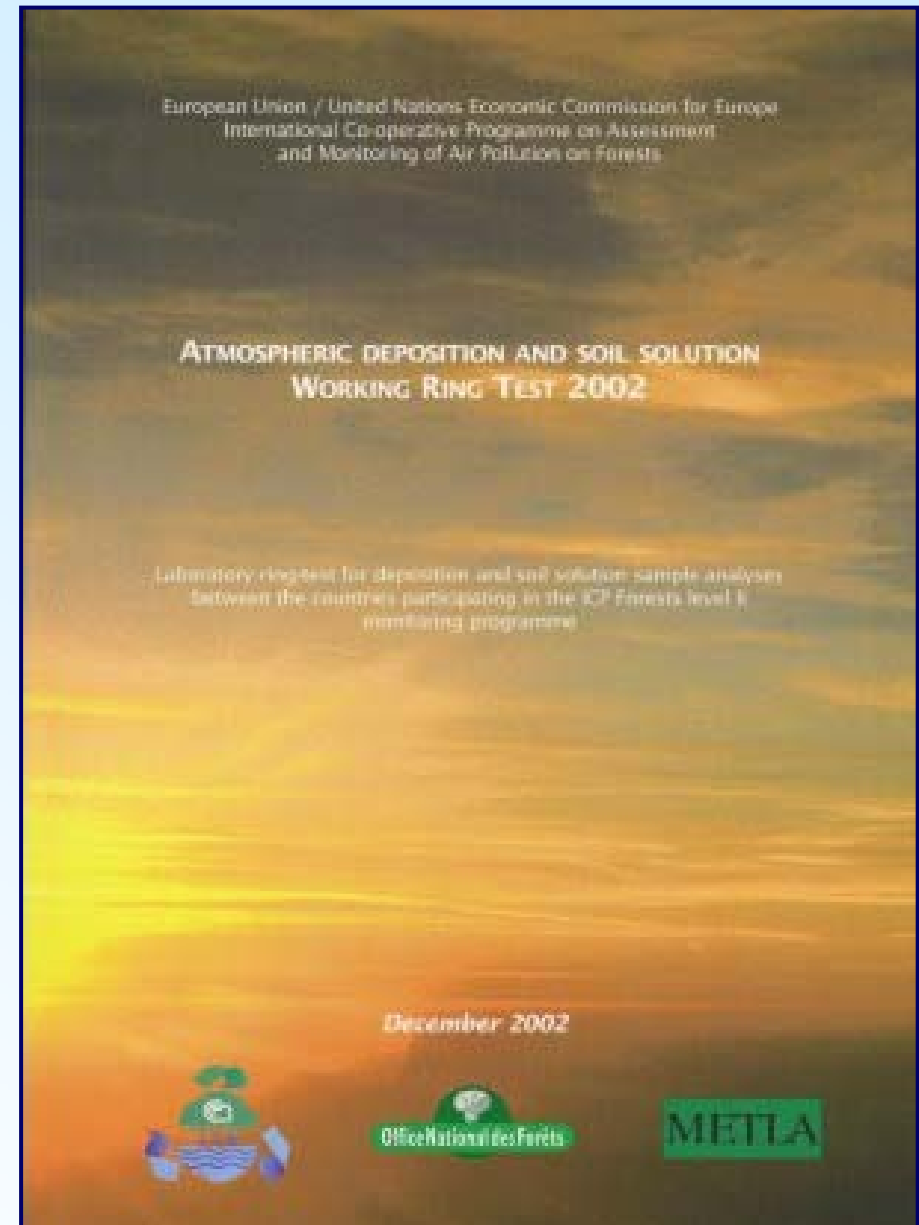
1. Update of the Part VI (Sampling and analysis of atmospheric deposition) of the ICP Forests manual, dealing with QA/QC in chemical analyses and data validation



# Working Ring Tests

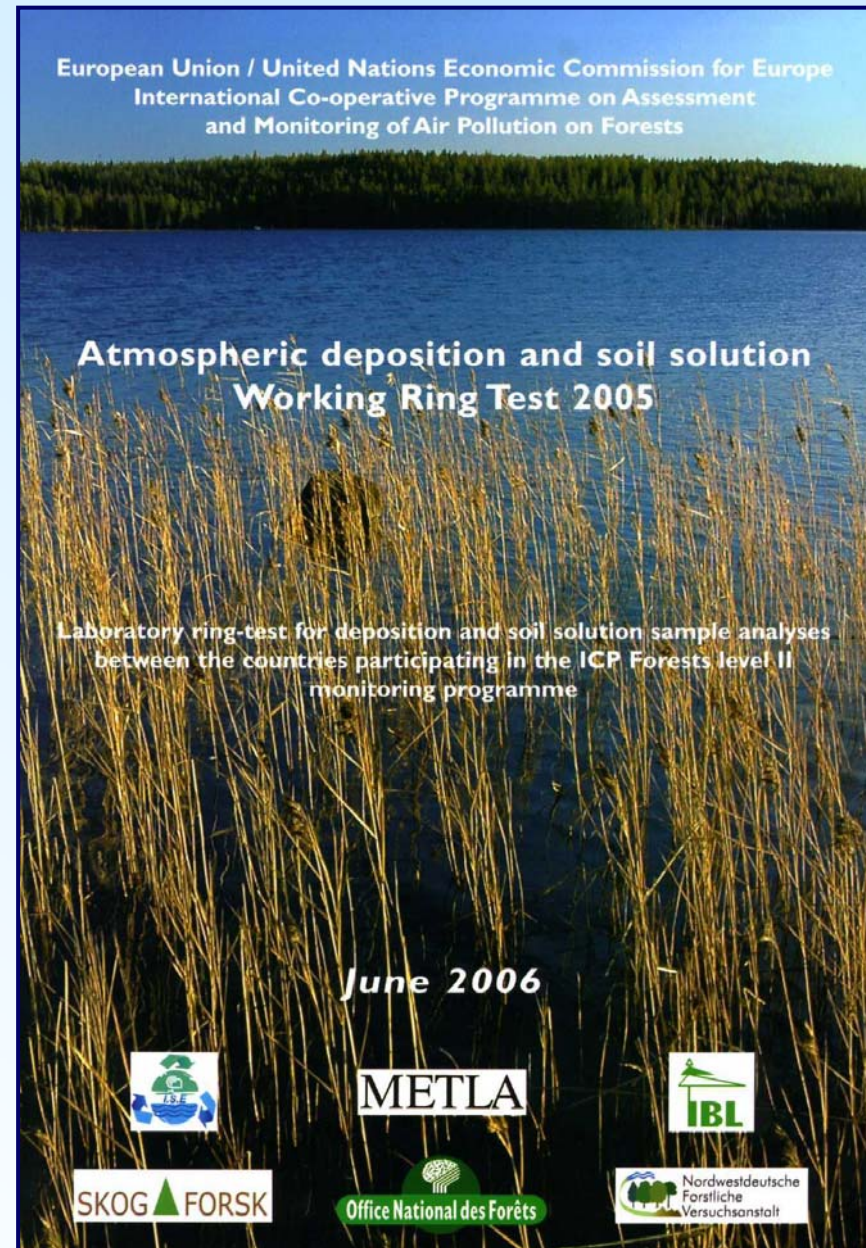
## 2. Organisation of Working Ring Tests (WRT) for the analyses of atmospheric deposition and soil water.

### Working Ring Test 1 (2002)



# Working Ring Tests

## Working Ring Test 2 (2005)



# Working Ring Tests

## 3. Criteria for the validation of chemical analyses:

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

**Table 5.5.2:** Acceptance threshold values in data validation based on the ionic balance and conductivity. PD and CD are defined in chapters 5.5.1 and 5.5.2 respectively.

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 $\mu\text{S cm}^{-1}$	$\pm 10\%$	$\pm 10\%$

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

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

CM= measured conductivity

CE= conductivity calculated

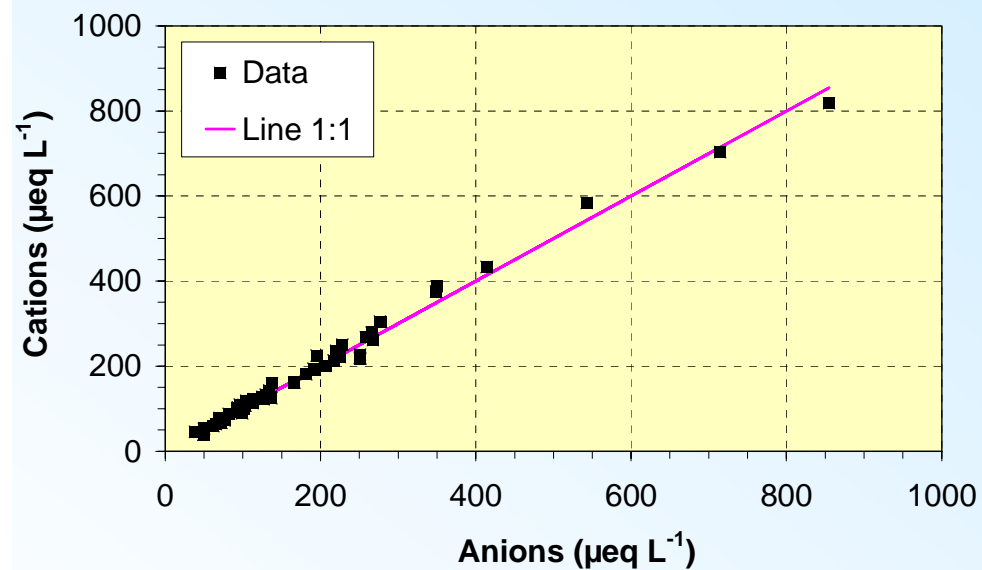
From the MANUAL on “*Methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests*”,  
Part VI Sampling and Analysis of Deposition, updated June 2004.



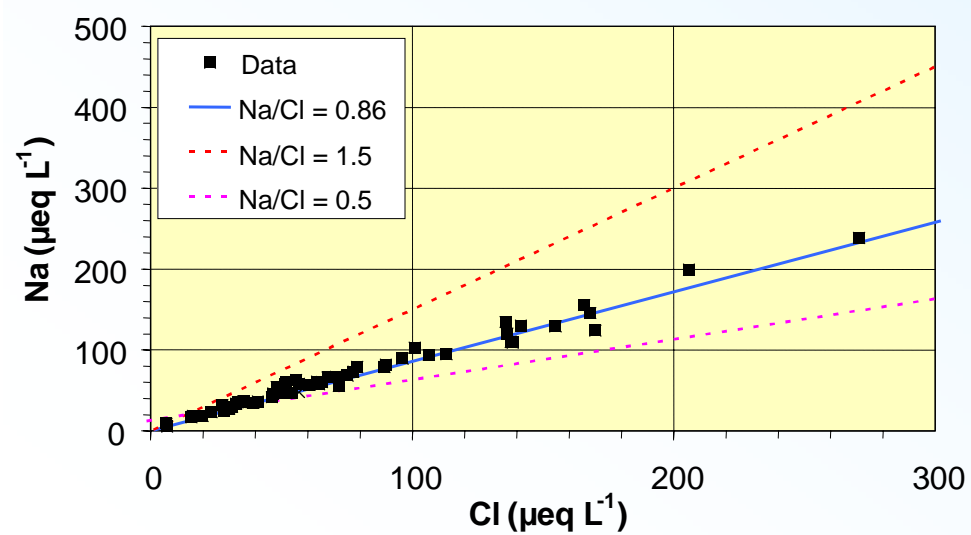


Microsoft Excel - EPD_analytical_data_validation													
ACB													
	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB
3													
4				S an	S cat				Xcc				
5				Sum		Ions	Quality		Calculated corrected	Cond.	Quality	Quality	Quality
6	TN	DOC	ON	Anions	Cations	Diff. %	Ions	Ratio	Conductivity	Diff. %	Conductivity	Org N	ratio
7	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	µeq L <sup>-1</sup>	µeq L <sup>-1</sup>	sC-sA	balance	Na/Cl	µS cm <sup>-1</sup> 25°C	Cc-Cm			Na/Cl
8													
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

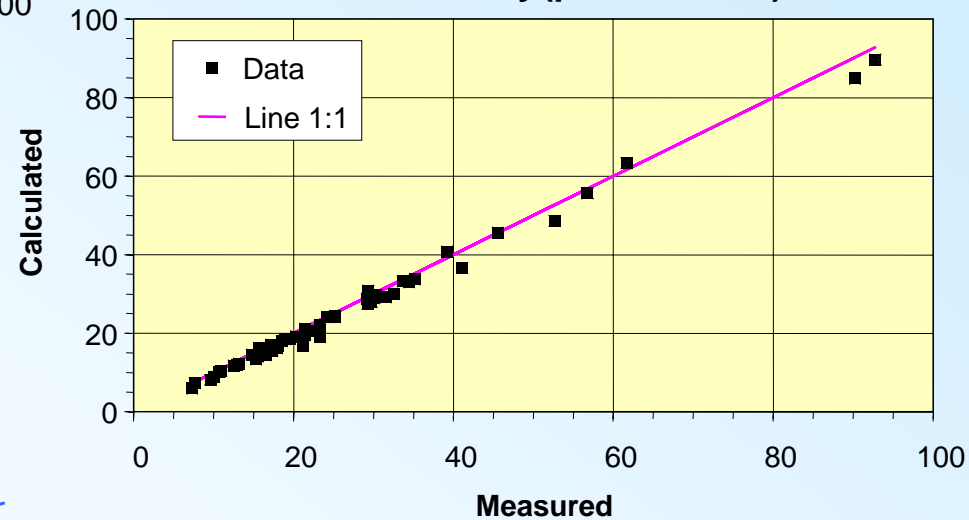
### Ionic balance



### Ratio Na/Cl



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



## **Working Ring Tests**

**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.**

**4. Advise and assist all laboratories which seek help or which have been identified as having analytical difficulties in progressing with their own QA/QC.**

**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.**

## Exchange of researchers/technicians within the active help to laboratories

Name	Organisation	Raison of travel	Overall costs paid by ONF (Grant agreement)
Polona Kalan	Slovenian Forestry Institute	Göttingen meeting April 2005	yes
Anna Kowalska	Polish Forest Research Institute	Göttingen meeting April 2005	yes
Nicholas Clarke	Norwegian Forest Reserach Institute	Göttingen meeting April 2005	yes
Anna Kowalska	Polish Forest Research Institute	Pallanza meeting Sept. 2005	yes
Nicholas Clarke	Norwegian Forest Reserach Institute	Pallanza meeting Sept. 2005	yes
Irina Smirnova	Soil Science Faculty, Moscow State Unive	Lab. visit to Warszawa	yes
Olga Plyaskina	Soil Science Faculty, Moscow State Unive	Lab. visit to Warszawa	yes
Zhanna Lytkina	Institute of Biology, Komi Scientific Cent	Lab. visit to Warszawa	yes
Tatyana Sytar	Institute of Biology, Komi Scientific Cent	Lab. visit to Warszawa	yes
Anita Stansikova	National Forest Service, Slovakia	Lab. visit to Göttingen	yes
Jana Durkovicova	National Forest Service, Slovakia	Lab. visit to Göttingen	yes
T. Jakovljevic + M. Hle	Croatian Forest Research Institute	Lab. visit to Pallanza	yes
R. Mosello, G. Tartari	CNR-ISE	Lab. visit in Sárvár (Hungary)	no
J. Sitkey + M. Józsefné	Hungarian Forest Research Institute	Lab. visit to Pallanza	no
T. Jakovljevic	Croatian Forest Research Institute	Lab. visit to Pallanza	no

**5. 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.**

Number of participants at the WRTs and to the discussion meeting of the WRT results.

Number of countries helped on how many parameters by the working group on QA/QC in labs.

Number of solved problems from the participants received by the working group on QA/QC.

Number of labs getting better/worse in WRTs.

Number of labs with a reproducibility on sulphate, nitrate and ammonia of less than 10% for a concentration of ...(to be defined).

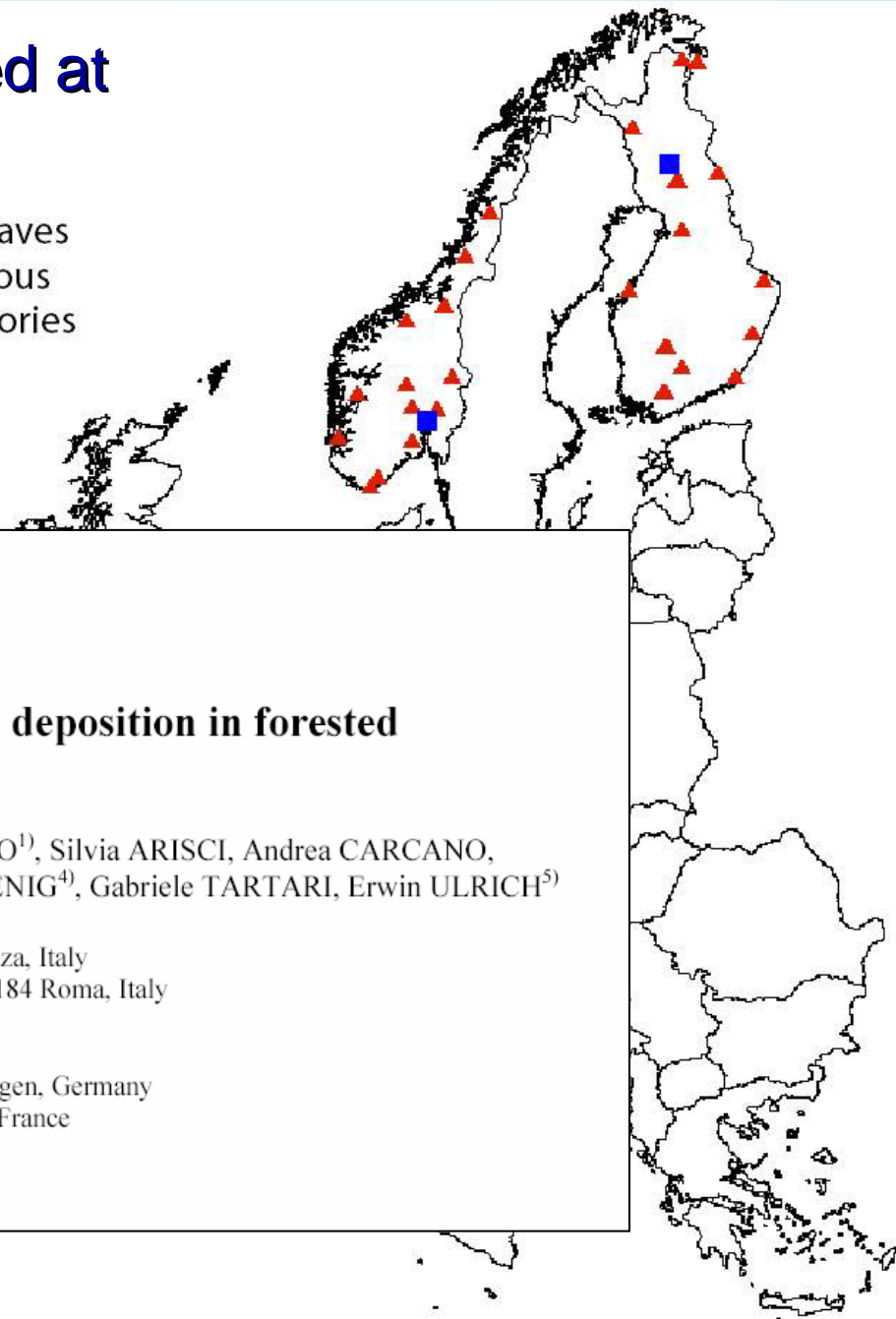
WRTs results: % of laboratories which perform all the measurements, % of outlier results.



## 6. Inter-laboratory studies aimed at testing validation checks

➤ 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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<sup>3)</sup>Finnish Forest Research Institute, Rovaniemi, P.O. Box 16, 96301 Finland

<sup>4)</sup>Niedersächsische Forstliche Versuchsanstalt, Graetzelstr. 2, 37079 Goettingen, Germany

<sup>5)</sup>Office National des Forêts, Boulevard de Constance, 77300 Fontainebleau, France

\*e-mail corresponding author: r.mosello@ise.cnr.it



## **7. EPD-Info-sheets**

### **Why EPD-Info-sheets:**

- **In all good laboratories many experiences are gained during daily work. Different materials are tested, analytical methods are compared, new methods are tested.**
- **With the EPD-info-sheets we try to make these experiences available for all members of the expert panel on deposition and the authorized laboratories of the member countries.**

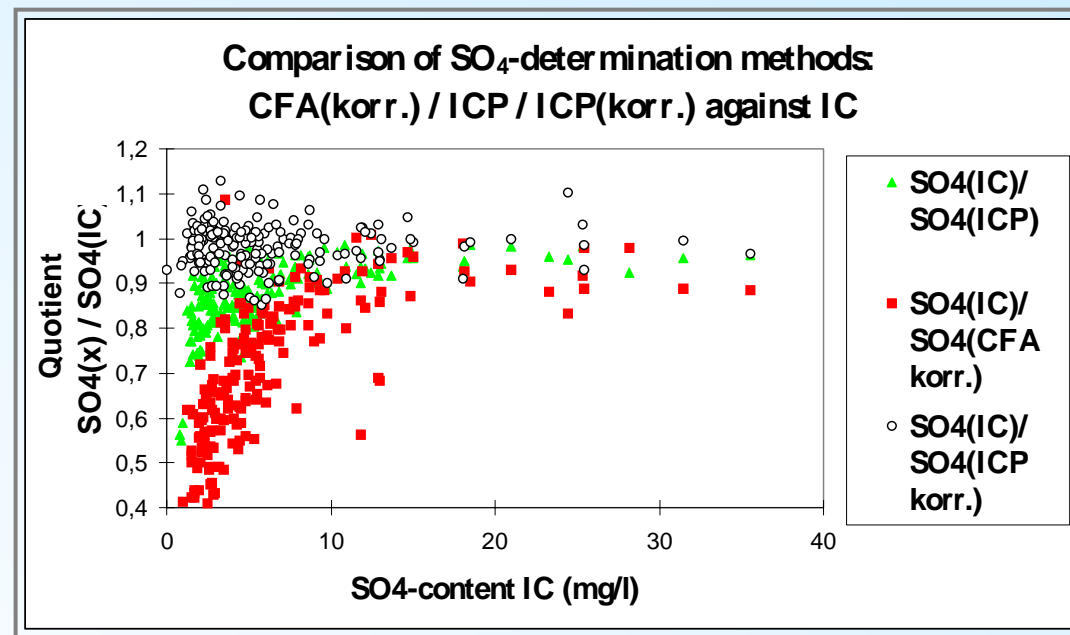
<b>EPD</b>	<b>Analytical informations</b>	<b>TI (No)</b>
method comparison	Comparison of ICP-, IC- and spectrophotometric determination in colored soil solutions	<b>SO<sub>4</sub></b>

## 1. Compared methods:

Ion exchange chromatography without chemical suppression; eluent: phthalic acid with .....(König, Fortmann 1996 a)

Total S determination with ICP, correction for organic sulfur: determination of DOC and subtraction of Corg [mg/l]/130 from total sulfur content; ..... (König, Fortmann 1996 b)

CFA-spectrophotometric determination of SO<sub>4</sub> with Ba-methylthymol blue reaction after separation of interfering ..... (König, Fortmann 1996 c)



2. procedure

3. results

4. literature

5. executive laboratory:

Niedersächsische Forstliche Versuchsanstalt

Nils König, Göttingen, [nils.koenig@nfv.gwdg.de](mailto:nils.koenig@nfv.gwdg.de)

Programme Structure - ICP Forests, Hamburg - Microsoft Internet Explorer

File Modifica Visualizza Preferiti Strumenti ?

Indietro Cerca Preferiti Val Collegamenti

Indirizzo http://www.icp-forests.org/WGqual\_lab.htm

# ICP Forests

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

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## Working Group on quality assurance and quality control in laboratories

### Chairman

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### Members

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[John Derome](#), Finland  
[Erwin Ulrich](#), France  
[Nils König](#), Germany  
[Nicholas Clarke](#), Norway  
[Mrs. Polona Kalan](#), Slovenia  
[Mrs. Anna Kowalska](#), Poland

### Documents / Presentations

- [Aims and work of the group](#)
- [Deposition and soil solution working ringtest 2002](#) (pdf 1 MB)
- [K. Derome](#): Use of control charts as QA/QC tool (Rovaniemi 05)
- [N. Koenig](#): Determination of total N (Rovaniemi 05)

[Excel file for analytical data validation](#)  
[Excel file for definition of QA/QC methods within single laboratories](#)  
[Excel file with instruction and example of control chart use](#)

### Expert Panel Deposition Info sheets

[General information](#)

Operazione completata Internet

- 9. Collaboration 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.**