THE 2002 AND 2005 ATMOSPHERIC DEPOSITION AND SOIL SOLUTION WORKING RING TESTS

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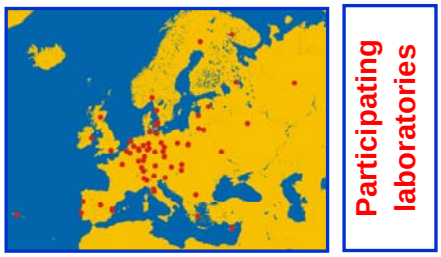
Rationale

One of the aims of forest monitoring is to determine trends in forest ecosystems, and to relate these trends to changes in the driving forces, such as air pollutants and climate change. However, in order to obtain comparable, long-term time series it is necessary to define precise protocols for the field sampling, and the chemical analysis and quality assurance and control (QA/QC) of the samples.
In order to obtain coherent results from the more than 50 laboratories analysing deposition and soil solution samples, it is necessary to devise structured, continuously updated harmonization procedures for each measurement technique. Regular contacts among the laboratories can also help in resolving analytical problems and ensuring high quality results.
Procedures for quantifying analytical quality, such as the Working Ring Tests (WRTs) presented here, are very important for detecting analytical deficiencies and problems, thus helping to improve the analytical quality of the individual laboratories and the overall comparability of the results.
Data of poor analytical quality are of no use to either the scientific community or to the policy makers. Harmonisation and QA/QC procedures in the laboratories are essential to ensure data quality and comparability and, in the long run, they are both of prime importance for ensuring the robustness of the monitoring activities.
The activities and resources devoted to QA/QC procedures should be seen as a sound investment for ensuring fully comparable results from the monitoring programmes.

Aims

Two Working Ring Tests (WRT) were organised in 2002 and 2005 within the framework of the EU Regulation (EC) No 2152/2003 ("Forest Focus") and the UN/ECE ICP Forests Programme in order to evaluate the overall performance of the laboratories monitoring atmospheric deposition and soil solution in Europe, and to verify improvements in analytical quality resulting from the QA/QC work carried out in the laboratories.



Participating laboratories and ring test samples

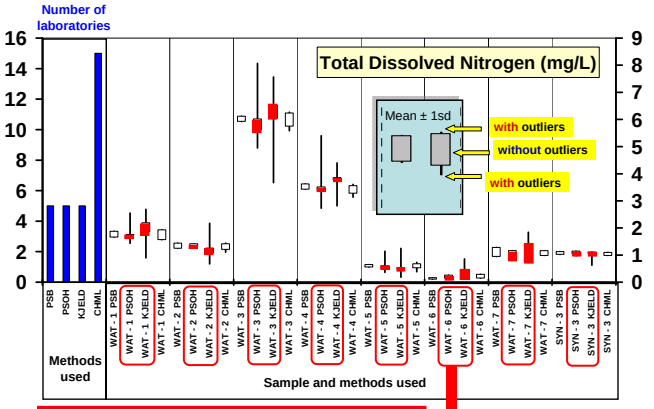
59 laboratories participated in the 2002 WRT and analyzed 9 natural deposition and soil solution samples and 6 synthetic solutions, and 52 laboratories in the 2005 WRT which comprised 9 natural and 6 synthetic samples. 44 of the laboratories participated in both exercises.
Each laboratory analyzed all the samples using the methods routinely employed in their monitoring activities.

WRT 2005 median values, after outlier rejection.
Dark grey = below the cutoff value
Light grey = not to be measured

Working Ring Test 2005 - Samples concentrations

Variable	Unit	WAT-1	WAT-2	WAT-3	WAT-4	WAT-5	WAT-6	WAT-7	SYN-1a & 2a	SYN-1b & 2b	SYN-3 & 4
pH		4.19	5.14	3.91	5.23	5.49	4.94	4.17	6.96	6.11	4.85
Conductivity at 25°C	µS cm^{-1}	50.3	24.5	111.9	67.3	17.0	27.6	58.5	30.3	74.0	34.0
Calcium	mg L^{-1}	0.73	0.25	0.66	0.92	0.40	0.91	2.32			0.46
Magnesium	mg L^{-1}	0.19	0.21	0.39	0.57	0.19	0.40	0.67			0.19
Sodium	mg L^{-1}	0.90	1.67	2.91	5.15	0.73	2.02	1.16			0.62
Potassium	mg L^{-1}	1.56	0.20	3.12	2.68	1.72	0.17	0.82			3.61
Ammonium	mg N L^{-1}	0.34	0.69	2.20	1.82	0.20		0.13			0.76
Sulphate	mg S L^{-1}	1.36	0.56	2.15	1.19	0.50	2.18	2.59			0.69
Nitrate	mg N L^{-1}	1.34	0.36	3.53	1.29	0.11					0.33
Chloride	mg L^{-1}	1.45	2.95	5.37	9.08	1.03	1.47	1.34			2.65
Alkalinity	µeq L^{-1}				24	18			149	35	
Phosphate	mg L^{-1}	0.021	0.097	0.528	0.031	0.237		0.066			
Total Dissolved Nitrogen	mg N L^{-1}	1.8	1.3	6.0	3.5	0.6	0.2	1.1			1.1
Dissolved Organic Carbon	mg C L^{-1}	3.0	1.0	8.1	19.6	11.7	4.1	37.8			7.2
Alluminium	µg L^{-1}	12	13	53	65	38	183	1304			734
Cobalt	µg L^{-1}							6			
Copper	µg L^{-1}	3		2	2	5		4			85
Iron	µg L^{-1}	10		13	21	16	13	333			180
Mercury	µg L^{-1}	0.10					0.12	0.06			0.02
Manganese	µg L^{-1}	146	5	31	60	60	17	166			100
Nichel	µg L^{-1}							6			
Lead	µg L^{-1}				32						
Zinc	µg L^{-1}	19	125	17	43	21	10	42			87
Total Phosphorus	mg P L^{-1}			0.180		0.091		0.051			0.891
Total Sulphur	mg S L^{-1}	1.37	0.58	2.27	1.33	0.57	2.29	2.90			1.99
Silicon	mg Si L^{-1}						0.12	1.06			0.15

Detection of unreliable methods



Parameter	Analytical methods that gave unsatisfactory results
Alkalinity	Acidimetric titration with colorimetric detection of the end-point and single fixed end-point without correction
Sulphate	Turbidimetry, $BaSO_4$ excess and methyl thymol, continuous flow analysis with $BaSO_4$
Nitrate	Spectrophotometry with UV detection at 220 nm
Chloride	Argentometric titration
Ca, Mg	EDTA titration
Ammonium	Nessler spectrophotometric method, ion selective electrode
DTN	Kjeldahl digestion, alkaline persulphate digestion (PSOH)
Total Sulphur	ICP MS
DOC	Spectrophotometry with detection at 320 nm

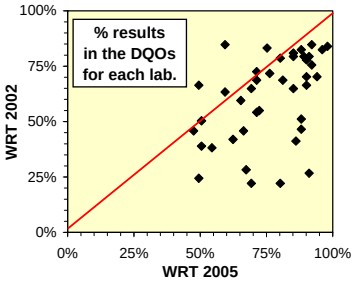
Some analytical methods were found to be unsuitable for the samples used in this WRT, and thus also for deposition samples collected in European forests. They also included outdated and environmentally hazardous methods.

Increase in laboratory performance

Data Quality Objectives (DQOs) identified for the WRTs, compared with the Global Atmosphere Watch Precipitation Chemistry Programme (GAW), and with the DQOs used in the EMEP network 2004 inter-comparison exercise.

Measured parameter	Data Quality Objectives (DQOs) Gaw laboratory inter network bias	EMEP radii for Youden plot	ICP Forests WRT 2005 proposed
pH	± 0.07 units	± 0.1 units	**± 0.1 units**
Conductivity	± 7%	± 10%	**± 10%**
Calcium	± 15%	± 15%	**± 15%**
Magnesium	± 10%	± 15%	**± 15%**
Sodium	± 10%	± 15%	**± 15%**
Potassium	± 20%	± 15%	**± 15%**
Ammonium	± 7%	± 15%	**± 15%**
Sulphate	± 7%	± 10%	**± 10%**
Nitrate	± 7%	± 15%	**± 15%**
Chloride	± 10%	± 15%	**± 15%**
Aluminium	-	± 15%	**± 15%**
Alkalinity	± 25%	± 25%	**± 25%**
Total Dissolved Nitrogen (TDN)	-	± 20%	**± 20%**
Dissolved Organic Carbon (DOC)	-	± 20%	**± 20%**
Other	-	± 20%	**± 20%**

Comparison between the results of the 2005 and 2002 WRTs clearly indicated that there has been an improvement in the analytical performance of the laboratories participating in both exercises. This was attributed to the successful adoption of QA/QC procedures.



Conclusions

The Working Ring Tests have shown considerable potential for improving QA/QC in the laboratories participating in the EU Forest Focus and ICP Forests monitoring programmes, and should be carried out on a regular basis in order to maintain QA/QC at a high level and to ensure full comparability between the laboratories.

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Activity carried out in the framework of the EU Regulation (EC) No 2152/2003 ("Forest Focus")

pdf files available on
http://www.icp-forests.org/WGqual_lab.htm