Meeting of the Working Group QA/QC in Laboratories
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Proposal for tolerable limits in atmospheric deposition/soil water chemical analyses

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WG on QA/QC in laboratories within ICP Forests

Data Quality Objectives for the measurement of chemistry of atmospheric deposition/soil solution within ICP Forests

- Single laboratories have (or should have) estimations of the precision of the different analytical methods at different level of concentrations.

- In the case of a group of laboratories working together for common aims, which thresholds of error can we accept?

Data Quality Objectives for Precipitation Chemistry Measurements from GAW

(Global Atmosphere Watch 11/2004)

Table 1.1: Data Quality Objectives (DQOs) for GAW Precipitation Chemistry Measurements .

Measurement Parameter	Detection Limits	Precision Overall	Precision Laboratory	Inter-Network Bias Overall	Inter-Network Bias Laboratory	Calibration Levels	Completeness
pH (pH units)	*	± 0.1 pH unit at pH > 5 ± 0.03 pH unit at pH < 5	± 0.04 pH unit at pH > 5 ± 0.02 pH unit at pH < 5	±0.24 pH unit at pH > 5 ±0.12 pH unit at pH < 5	± 0.07 pH unit	4.0 & 7.0 low ionic strength reference solutions	90 %PCL(1) 70 %TP(2)
Conductivity ($\mu S\ cm^{-1}$)	± 2	*	*	*	± 7%	In a range between the 2nd & 98th percentile concentrations	90 %PCL(1) 70 %TP(2)
Acidity/ Alkalinity ($\mu mole\ L^{-1}$)	*	*	*	*	± 25%	In a range between the 2nd & 98th percentile concentrations	90 %PCL(1) 70 %TP(2)
SO_4^{2-} ($mg\ L^{-1}$)	0.06	0.06	0.03	± 0.42	± 7%	In a range between the 2nd & 98th percentile concentrations	90 %PCL(1) 70 %TP(2)
NO_3^- ($mg\ L^{-1}$)	0.09	0.06	0.03	± 0.36	± 7%	In a range between the 2nd & 98th percentile concentrations	90 %PCL(1) 70 %TP(2)
Cl^- ($mg\ L^{-1}$)	0.04	0.02	0.02	± 0.05	± 10%	In a range between the 2nd & 98th percentile concentrations	90 %PCL(1) 70 %TP(2)
NH_4^+ ($mg\ L^{-1}$)	0.02	0.02	0.01	± 0.08	± 7%	In a range between the 2nd & 98th percentile concentrations	90 %PCL(1) 70 %TP(2)
Ca^{++} ($mg\ L^{-1}$)	0.02	0.02	0.01	± 0.05	± 15%	In a range between the 2nd & 98th percentile concentrations	90 %PCL(1) 70 %TP(2)
Mg^{++} ($mg\ L^{-1}$)	0.01	0.01	0.01	± 0.02	± 10%	In a range between the 2nd & 98th percentile concentrations	90 %PCL(1) 70 %TP(2)
Na^+ ($mg\ L^{-1}$)	0.02	0.01	0.01	± 0.03	± 10%	In a range between the 2nd & 98th percentile concentrations	90 %PCL(1) 70 %TP(2)
K^+ ($mg\ L^{-1}$)	0.02	0.01	0.01	± 0.02	± 20%	In a range between the 2nd & 98th percentile concentrations	90 %PCL(1) 70 %TP(2)
Formate ($mg\ L^{-1}$)	*	*	*	*	*	In a range between the 2nd & 98th percentile concentrations	90 %PCL(1) 70 %TP(2)
Acetate ($mg\ L^{-1}$)	*	*	*	*	*	In a range between the 2nd & 98th percentile concentrations	90 %PCL(1) 70 %TP(2)
Standard Gauge Precipitation Depth (mm)	0.2	0.1 daily 0.3 weekly	n/a n/a	± 5% for rain ± 15% for snow ± 10% rain+snow	n/a n/a	In a range between the 2nd & 98th percentile depth values	95 %PCL - annual 90 %PCL - quarterly
Sample Depth (mm)	0.2	0.1 daily 0.3 weekly	n/a n/a	± 5% for rain ± 15% for snow ± 10% rain+snow	n/a n/a	In a range between the 2nd & 98th percentile depth values	90 %PCL(1) 70 %TP(2)

* -- Not Available n/a -- Not Applicable

1) %PCL is Percent Precipitation Coverage Length (see Sections 6.10.3 and A.7 for detailed explanation).

2) %TP is the Percent Total Precipitation (see Section 6.10.3 and A.7 for detailed explanation).

Data Quality Objectives for Precipitation Chemistry Measurements from EMEP

(XXIII Intercomparison 6/2004).

In Figures 18–33 the reported data are presented in Youden plots.

Table 1: Youden plot parameters.

Radii	**Components**
10%	SO_2 in abs.sol, NO_2 in abs.sol.
20%	SO_2, HNO_3 and NH_3 in impregnated filter
Radii = DQO	**Components**
10% accuracy or better	SO_4^{2-}-S , NO_3^--N
15% accuracy or better	NH_4^+, Cl^-, Ca^{2+}, K^+, Mg^{2+}, Na^+ , cond
0.1 units	pH
Criteria	**Colour**
Within 0.5*DQO	Blue
Within DQO	Green
Within 2*DQO	Orange
> 2*DQO	Red

Data Quality Objectives for Precipitation Chemistry Measurements from GAW (11/2004), EMEP (XXIII Intercomparison 6/2004) and proposed for ICP Forests WRT 2005.

Measurement Parameter	Unit	GAW Laboratory Inter-Network Bias	EMEP radii for Youden plot	ICP Forests WRT 2005 proposed
pH		± 0.07 u. pH	± 0.1 u. pH	**± 0.1 u. pH**
Conductivity	µS cm^{-1}	± 7 %	± 15 %	**± 10 %**
Calcium	mg L^{-1}	± 15 %	± 15 %	**± 15 %**
Magnesium	mg L^{-1}	± 10 %	± 15 %	**± 15 %**
Sodium	mg L^{-1}	± 10 %	± 15 %	**± 15 %**
Potassium	mg L^{-1}	± 20 %	± 15 %	**± 15 %**
Ammonium	mg N L^{-1}	± 7 %	± 15 %	**± 15 %**
Sulphate	mg S L	± 7 %	± 10 %	**± 10 %**
Nitrate	mg N L^{-1}	± 7 %	± 10 %	**± 15 %**
Chloride	mg L	± 10 %	± 15 %	**± 15 %**
Alkalinity	µeq L^{-1}	± 25 %	-	**± 25 %**
Total Nitrogen	mg L^{-1}	-	-	**± 20 %**
DOC	mg L^{-1}	-	-	**± 20 %**
Other				**± 20 %**

Participating laboratories

EPD Working Ring Test 2005

	WRT2
Germany	14
Russia	5
Italy	4
Spain, Belgium, Denmark, Netherlands, Portugal	2
Austria, Bulgaria, Cyprus, Czech Rep., Estonia, Finland, France, Great Britain, Greece, Hungary, Ireland, Latvia, Lithuania, Norway, Poland, Slovakia, Slovenia, Sweden, Switzerland	1
Total	**52**

Laboratories participating to WRT1: 59

Laboratories participating both to WRT1 and WRT2: 41

Number of laboratories measuring the different variables

pH	52
CONDUCTIVITY	52
ALKALINITY	39
SULPHATE	51
NITRATE	51
CHLORIDE	52
CALCIUM	52
MAGNESIUM	52
SODIUM	51
POTASSIUM	51
AMMONIUM	50
TOTAL NITROGEN	32
PHOSPHATE	38
DOC	37

Discussion of the results

Analytical methods that frequently give high dispersion of the results

Parameter	Method
Alkalinity	Colorimetric detection of the end-point, one end-point without correction
Sulphate	Turbidimetry, nephelometry , Ba sulphate excess, methyl thymol
Nitrate	Ion selective electrode, spectroph. UV 220 nm
Ammonium	Nessler's reagent in spectrophotometry ion selective electrode
TN	Kjeldahl analysis and ammonium analysis
Chloride	Argentometric titration, ion selective electrode
Ca, Mg	EDTA
Na, K	Ion selective electrode
DOC	Spectrophotometry UV detection 320 nm

Data Quality Objectives for Precipitation Chemistry Measurements proposed for ICP Forests compared with the WRT 2005 results

Measurement parameter	ICP Forests objectives proposed	95 % results (2 sd) after outliers removal WRT 2005		
		Min.	Max.	No. outliers
pH	± 0.1 u. pH	0.12 u	0.31 u	15
Conductivity	± 10 %	12 %	15 %	7
Calcium	± 15 %	13 %	32 %	15
Magnesium	± 15 %	12 %	22 %	20
Sodium	± 15 %	9 %	17 %	27
Potassium	± 15 %	9 %	36 %	20
Ammonium	± 15 %	12 %	49 %	34
Sulphate	± 10 %	9 %	18 %	29
Nitrate	± 15 %	10 %	57 %	16
Chloride	± 15 %	8 %	25 %	35
Alkalinity	± 25 %	65 %	190 %	5
Total Nitrogen	± 20 %	8 %	80 %	25
DOC	± 20 %	14 %	97 %	14
Other	± 20 %			

Data Quality Objectives for Precipitation Chemistry Measurements proposed for ICP Forests compared with the WRT 2005 results

Measurement parameter	ICP Forests objectives proposed	95 % results (2 sd) after outliers removal WRT 2005		
		Min.	Max.	No. outliers
Alluminium	± 20 %	10 %	131 %	5
Cadmium	± 20 %			
Cobalt	± 20 %			
Copper	± 20 %	17 %	73 %	2
Iron	± 20 %	16 %	85 %	4
Mercury	± 20 %	86 %	256 %	1
Manganese	± 20 %	11 %	37 %	6
Molybdenum	± 20 %			
Nichel	± 20 %			
Lead	± 20 %			
Zinc	± 20 %	17 %	30 %	5
Total Phosphorus	± 20 %	10 %	48 %	4
Total Sulphur	± 20 %	18 %	56 %	0
Silicon	± 20 %	33 %	98 %	2

Below cut off limit

Below cut off limit

Below cut off limit

Below cut off limit

Below cut off limit

First proposal: less restrictive DQOs for samples with low conductivity

	Mean of samples Cond>20			Sample Cond<20		
	Objective	2 s.d.	No. outliers	Objective	2 s.d.	No. outliers
pH	± 0.1 u.	0.21	1.5	± 0.2 u.	0.31	1
Cond	± 10%	13%	0.7	± 20%	13%	1
Ca	± 15%	19%	2.0	± 25%	32%	1
Mg	± 15%	16%	2.1	± 25%	22%	5
Na	± 15%	12%	3.0	± 25%	13%	6
K	± 15%	16%	2.6	± 25%	14%	2
NH4	± 15%	21%	4.3	± 25%	37%	4
SO4	± 10%	13%	3.6	± 20%	17%	4
NO3	± 15%	22%	1.7	± 25%	31%	4
Cl	± 15%	16%	4.6	± 25%	24%	3
Alk	± 25%	122%	1.0	± 40%	180%	2
Total N	± 20%	90%	3.4	± 30%	22%	1
DOC	± 20%	24%	1.7	± 30%	18%	2
other	± 20%			± 30%		

During discussion it was noted that samples with low conductivity may have different concentrations, depending also on the sample typology (deposition, throughfall, soil water).

Specific thresholds for each variable based on its values were then preferred.

Second proposal: less restrictive DQOs for values lower than specific tresholds (higher in the case of pH)

	Threshold	Mean of samples > threshold			Mean of samples < threshold		
	mg/L	Objective	2 s.d.	No. outliers	Objective	2 s.d.	No. outliers
pH	5.0	± 0.2 u.	0.27	2.0	± 0.1 u.	0.17	1.6
Cond	10 µs/cm	± 10%	13%	0.7	± 20%	n/a	n/a
Ca	0.25	± 15%	18%	1.7	± 20%	31%	2.5
Mg	0.25	± 15%	14%	1.5	± 25%	20%	3.5
Na	0.5	± 15%	12%	3.4	± 25%	n/a	n/a
K	0.5	± 15%	11%	2.3	± 25%	30%	3.0
$N\text{-}NH_4$	0.25	± 15%	16%	4.3	± 25%	42%	4.0
$S\text{-}SO_4$	1	± 10%	7%	3.8	± 20%	11%	3.3
$N\text{-}NO_3$	0.5	± 15%	10%	1.8	± 25%	38%	2.3
Cl	1.5	± 15%	11%	5.3	± 25%	22%	3.5
Alk	100 µeq/L	± 25%	66%	0.0	± 40%	161%	1.3
Total N	0.5	± 20%	15%	3.3	± 40%	51%	2.5
DOC	1	± 20%	20%	1.75	± 30%	98%	2.0

The threshold value is compared to the expected value (mean or median) of the samples considered in the intercomparison.