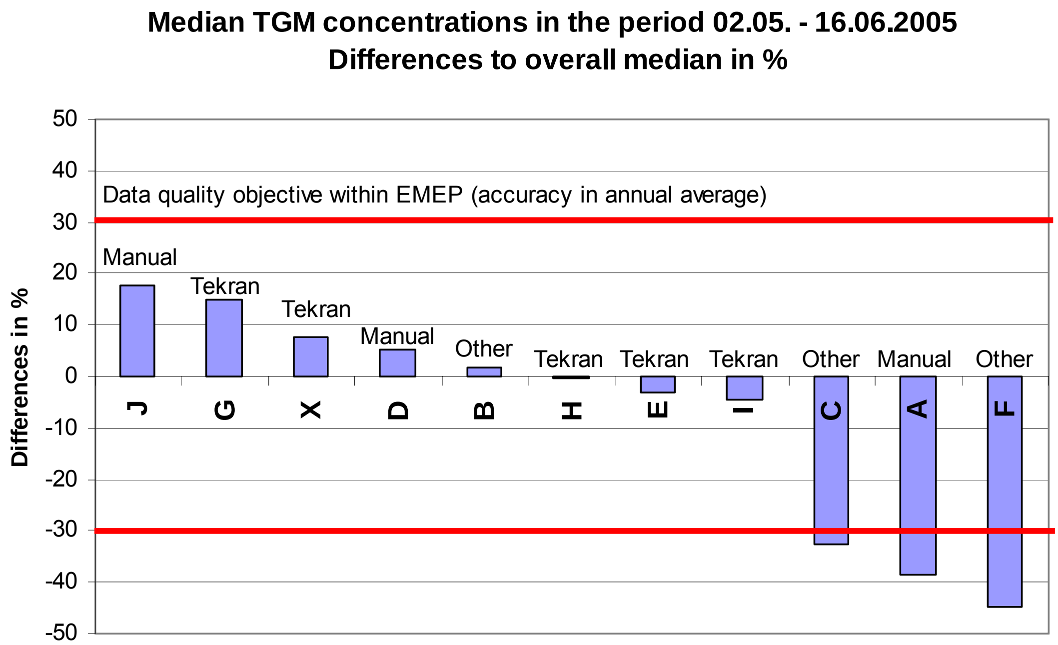
EMEP/CCC-Report 4/2006

EMEP Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe

Data quality 2004, quality assurance, and field comparisons

Wenche Aas (ed.)



Norwegian Institute for Air Research
PO Box 100, NO-2027 Kjeller, Norway
Chemical Co-ordinating Centre of EMEP (CCC)

NILU : EMEP/CCC-Report 4/2006
REFERENCE : O-95024
DATE : AUGUST 2006

EMEP Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe

Data quality 2004, quality assurance, and field comparisons

Wenche Aas (ed.)

Chapter 5: Christian Temme[1], Ralf Ebinghaus[1], Hans Herbert Kock[1], Andreas Schwerin[2] and Elke Bieber[2]

[1] *GKSS Research Centre Geesthacht, Institute for Coastal Research, Geesthacht, Germany*
[2] *German Federal Environment Agency (UBA), Langen, Germany*

Norwegian Institute for Air Research
P.O. Box 100, N-2027 Kjeller, Norway

Contents

Summary

This report is mainly concerned with the quality of the 2004 data and new results from field and laboratory comparisons. A special chapter is devoted to a field intercomparison of mercury measurements in ambient air and precipitation that carried out at the German EMEP Station DE02 Waldhof in order to investigate the quality and comparability of mercury measurements within EMEP. For Total Gaseous Mercury (TGM) it can be concluded in general, that the concentration data reported by the individual laboratories give comparable results. For total mercury in precipitation it can be concluded that a fairly good agreement of the individual laboratory results with the assigned value could be achieved. However, if a constant reproducibility standard deviation is set to 25% as default, some of the laboratories are not capable to match with the designated quality threshold value.

The requirement with respect to data completeness for the main components in precipitation and air, i.e. 90 per cent, is generally met. For heavy metals, VOC and POPs the data capture is lower, especially for air samples mainly due to less sampling frequencies, i.e. once or twice a week.

To obtain a reliable estimate of the concentration level it is generally stated that 75% of the measurements should be above the detection limit. Heavy metals and POP measurements have generally more problems to meet this requirement than the main components, but also for these measurements there are labs that need to look into whether their methods are suited for low background concentration levels.

The ion balance for many countries was within ± 20 per cent, which indicate valid data when pH is less than 5.5. For higher pH values there is often a systematic difference that is not yet fully understood. However, it should be emphasized that the ion balance does not give an exact assessment of the quality, but some labs have very scattered ion balance plot indicating that their QA/QC routines needs to be improved.

Laboratory comparison of the main components in precipitation and air is carried out annually. The main message is that the laboratory performances in general are satisfactory, but that there nevertheless is room for improvements for some components like chloride, calcium, and potassium. Laboratory comparison of heavy metals is also performed annually. The measurements of high concentration samples give hardly any problem, but at many EMEP sites these are not very representative. Several countries have problems measuring low concentration samples of Cr, Ni, As and Cd.

The main components in air and precipitation has been assigned a DQ flag based on results in the laboratory and field intercomparison.

Annex 5 contains detection limits and estimates of precision, both for the complete measurement methods applied, and for the chemical method in the laboratories. This Annex is based on the information and data the participants themselves have forwarded to the CCC.

Data quality 2004, quality assurance, and field comparisons

1. Introduction

The aim of quality assurance is to provide data with sufficiently good and known quality, and this series of reports is intended to document the EMEP data quality and the progress made. The present report is relevant for the 2004 data. All data included in the EMEP program is covered by this data quality report, most of the information available on the data quality is, however, on acidifying and eutrophying components. In addition we have a special chapter devoted to mercury measurements.

Much of the information given here are collected from the participating laboratories, this being data on detection limits and precision, and results from parallel sampling. CCC organizes annually different types of comparisons, and the EMEP Laboratory intercomparison and results from field comparisons with reference instrumentation provide important information of the data quality. Information of both these types of comparisons is used in a new flagging system of data quality.

Calculations of ion balances in precipitation samples are important supplementary information to evaluate the data quality; however, the ion balance (IB) check is mainly a control of the analytical procedure, and contamination or other field problems are not detected by this control. In addition, at high pH and/or at low ion strength the IB test is more uncertain. A flagging system has been developed to fully get use of the information from the ion balance test, however the flags are not implemented to the database yet.

2. Measurement programme and data completeness

EMEP's measurement programme in 2004 is given in Table 1. Details on the sampling program and measurement frequency at the different sites are found in the different data reports (Fjæraa, 2006a and b; Yttri and Aas, 2006; Aas and Breivik, 2006; Solberg, 2006).

Many Parties do not fulfil the measurement program. There is in general a big lack of measurements of particles, VOC, POPs and heavy metals. The monitoring strategy being developed for 2004–2009 (EB.AIR/GE.1/2004/5) aims to improve this situation and a better spatial coverage is expected in the future. In addition few Parties measure all the inorganic species in air. Very few countries report base cations, and several labs that use the filterpack method report sum of nitrogen species in air and aerosols, even though these should be reported separately.

According to the Data Quality Objectives (DQO) of EMEP (Annex 1), the data completeness should be at least 90 per cent for main ions and heavy metals. In Annex 2 there is a summary of the data capture for all the EMEP data for 2004.

For the precipitation components most participants broadly met the DQO, but the data completeness for the air components is less satisfactory.

Table 1: EMEP's measurement programme 2004.

	Components	Measurement period	Measurement frequency
Gas	SO_2, NO_2	24 hours	Daily
	O_3	Hourly means stored	Continuously
	Light hydrocarbons C_2-C_7	10-15 mins	Twice weekly
	Ketones and aldehydes (VOC)	8 hours	Twice weekly
	Hg	24 hours	Weekly
Particles	SO_4^{2-}, NH_4^+, NO_3^-, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-	24 hours	Daily
	Cd, Pb (first priority), Cu, Zn, As, Cr, Ni (second priority)	Weekly	Weekly
	PM_{10} mass	24 hours	Daily
Gas + particles	HNO_3(g)+NO_3^-(p), NH_3(g)+NH_4^-(p)	24 hours	Daily
	POPs (PAH, PCB, HCB, chlordane, lindane, α-HCH, DDT/DDE)	Daily/weekly	Once weekly
Precipitation	Amount, SO_4^{2-}, NO_3^-, Cl^-, pH, NH_4^+, Na^+, Mg^{2+}, Ca^{2+}, K^+, conductivity	24 hours/weekly	Daily/weekly
	Hg, Cd, Pb (first priority), Cu, Zn, As, Cr, Ni (second priority)	Weekly	Weekly
	POPs (PAH, PCB, HCB, chlordane, lindane, α-HCH, DDT/DDE)	Weekly	Weekly

For heavy metals, VOC and POPs the data capture is lower than for the main components, especially for air samples. The reason is that several countries analyse e.g. one or two air samples weekly. This will give poor data completeness, but the seasonal distribution is anyhow satisfactory, and the annual average will probably give a reasonable estimate even though there are no measurements on the majority of the days.

Even though percentage of measurements above detection limit is not defined in the DQO it is important that most of the data is measurable, otherwise the uncertainty in the average will become quite high. The exact level of what is acceptable depend somewhat on the concentration level and the component in question. In Annex 3 it is given a summary of the number of samples below the detection limit for main components and heavy metals. Limits of 75%, 50% and 25% are given. Heavy metal and POP (not shown) measurements have more problems than the main components, but there are also some things to point out for these, i.e. the SO_2 measurements in France.

3. Ion balances

The ion balance is a good test on consistency and errors in the analytical results, but will not necessarily reveal a contamination of the sample. This will depend on whether or not the contamination occurred before the analysis started. The ion balance will also fail to discover errors related to the precipitation sampling.

The ion balances for all precipitation samples from 2004 are presented in Annex 4, as a function of pH. Ion balances for samples with pH < 5 were, for many countries, better than 15–20%, indicating fairly good accuracy in the determination of the individual ions. Some results give very scattered plot of the ion balance, i.e. in CZ, EE, RU, BY and CS. This may indicate that the quality assurance routines need to be improved. In IT0001 the ion balance show a large excess of anions, indication that there might be an error in the reported concentration, e.g. reported SO_4^{2-} instead of SO_4-S. This will be further investigated after this report has been printed.

At some sites there were many samples with pH > 5. This is particularly the case in Mediterranean countries due to alkaline dust as clearly seen from the Portuguese and Spanish results, as well as at other continental sites and in the far north of Europe. It is an experience made that ion balances become markedly poorer with increasing pH above 5–6. Some countries seem to have systematic deficit of anions, i.e. in contrast to the large spread in the ion balances seen in the Mediterranean. This is seen at many sites, e.g. in Croatia, Switzerland and Norway. In other countries, e.g. in Denmark and Ireland, the systematic anion deficit does not occur.

The reason for the poor ion balances at pH values above 5–6 is not yet fully understood. One contributing factor is certainly due to unmeasured ion species present in the sample, i.e. organic acids and bicarbonate. Biological degradation of some precipitation components may also contribute. The systematic deficit of anions at pH above 5–6 is a general problem, which also occurs in other networks in other parts of the world. The current situation with the very poor ion balances for samples with pH above 5 is highly unsatisfactory since we will only have limited information about the consistency of these results. Countries having weakly acidic samples as a larger fraction of their precipitation could supplement their current pH measurements with titration for determining weak acid concentrations, preferably as described in the Manual (EMEP/CCC, 1996). This is hardly done at any sites today.

4. Accuracy, detection limits and precision

A request for quality assurance data for the main components was made earlier this year: measurement and laboratory lower detection limit and precision results from control samples, and detection limits and precision for monitors. The information collected on detection limits and precision is given in Annex 5.

There are various ways of defining the measurement and laboratory precision and detection limit. The methods for calculating these data are defined in the EMEP Manual (EMEP/CCC, 1996). To quantify the precision in the measurements, parallel sampling is necessary and the precision should be given as M.MAD and CoV, relative standard deviation (RSD) is also an informative parameter. M.MAD expresses the spread of the data and equals the standard deviation if the population has a normal distribution. CoV expresses the relative spread of the data, and, similar to the M.MAD, approaches the relative standard deviation for a normal distributed population. Both parameters are non-parametric statistics, which make them particularly useful for measurements with spikes in the data. The definitions of M.MAD and CoV are (Sirois and Vet, 1994):

$$M.MAD = \frac{1}{0.6754}\, median\left(\left|e_i - median\left(e_i\right)\right|\right)$$

where e_i is the error in the two measurements

$$CoV \; \frac{M.MAD}{median\left(\overline{C}\right)} * 100\%$$

where $\overline{C}$ is the average of the two corresponding results. If a reference method is used to evaluate the national/local measurements, the median of the reference measurements is used.

The detection limit is calculated using three times the standard deviation of the field blanks and given in the same unit as the measurement data. By using split samples and laboratory blank samples, laboratory precisions and detection limits can be assessed in a similar way.

5. Field intercomparison of mercury measurements within EMEP

5.1 Introduction

After signing the UN/ECE Heavy Metals Protocol (Aarhus, 1998), measurements of mercury in air and precipitation became part of the EMEP monitoring programme. Important elements in the quality assurance concept for EMEP measurements are reference operating procedures and regular method intercomparisons. For this reason an international field intercomparison on measurements of mercury in ambient air and precipitation was carried out at the German EMEP Station DE02 Waldhof in order to investigate the quality and comparability of mercury measurements within EMEP. The project was funded by the German Federal Environment Agency (Umweltbundesamt, UBA).

The main goals of this field intercomparison were to harmonize and assure the quality of mercury measurements within EMEP and to derive recommendations for reproducible and comparable mercury measurements at EMEP sites. In order to compare the results with a robust statistics, which is well established in other fields, procedures for the statistical evaluation of round robin tests in drinking water, sludge or sediment analysis were used.

A joint evaluation workshop was held from June 12–14, 2006 at GKSS Research Centre Geesthacht (near Hamburg), Germany. During this workshop the results were discussed and evaluated in consideration of (i) the involved Standard Operation Procedures (SOPs) of the participating laboratories and (ii) their relevance for comparability under field conditions within EMEP.

This executive summary gives an overview of the major results of the field intercomparison study and is an extract of the detailed final report (Umweltbundesamt, 2006). Major conclusions and recommendations derived during the joint workshop have been considered for the preparation of the executive summary.

5.2 Organisation, preparation, and realisation of the field inter-comparison of mercury measurements in ambient air and precipitation within EMEP

5.2.1 General information

The German Federal Environment Agency (Umweltbundesamt, UBA) acted as host institution and organized the field intercomparison with the support of GKSS Research Centre (as a contractor to UBA) in close co-operation with the EMEP CCC.

The field intercomparison covered measurements of mercury in air and precipitation:

– total gaseous mercury (TGM) in ambient air:
  28 daily measurements within 6 weeks, starting in May 2005

– total mercury in precipitation ($Hg_{[prec]}$) :
  6 month (weekly sampling), i.e. 20 weekly samples with sufficient amount of precipitation
  for the analysis of mercury (May–November 2005)

Sampling periods and frequencies were based on the requirements of the EMEP monitoring strategy.

The field intercomparison was carried out at the German EMEP station Waldhof, a measurement site of the German Federal Environment Agency Waldhof and a typical Northern German low land site. Waldhof is located in the eastern "Lueneburger Heide" in a flat terrain, 100 km south-east of Hamburg or 100 km north-east of Hanover, in a clearing. The nearest vicinity is mostly agriculturally used area. The next village is Langenbrügge, approximately 3 km west, with 300 inhabitants. No industrial facilities are located in the surrounding area.

All participants provided their own measurement and/or sampling equipment (if possible sampling equipment in duplicate). GKSS/UBA provided technical support in setting up and disassembling the instruments and samplers in the field. During the entire field intercomparison GKSS/UBA provided technical support (operation and maintenance of the instruments, changing of samples, field blanks, shipping of the samples etc.) according to guidelines of each participant.

Shipping of samples and data was carried out according to the participants' requests. The chemical analysis of the samples, except for the continuous methods, was carried out in the laboratories of the participants. The individual results were reported by the participants on a predetermined schedule. The final statistical evaluation, a critical assessment of the results, including cause analysis and the derived method recommendations, was prepared by GKSS in close cooperation with UBA.

The field intercomparison was open for all EMEP laboratories performing mercury analysis in air and/or precipitation for EMEP. Also, a cooperation with the CEN working group on Mercury measurements in ambient air and deposition" (CEN/TC 264/WG 25) was intended.

A detailed technical description of all applied measurement methods for TGM and $Hg_{[prec]}$ can be found in the comprehensive final report (Umweltbundesamt, 2006).

5.2.2 Participants

11 laboratories from 8 European countries take part in the field intercomparison:

Belgium

Vlaamse Milieumaatschappij (VMM)
Dr. Edward Roekens
E-mail: e.roekens@vmm.be

Centrum voor onderzoek in diergeneeskunde en agrochemie
Dr. Ludwig De Temmerman
E-mail: ludet@var.fgov.be

Germany

Umweltbundesamt (UBA)
Dr. Elke Bieber
E-mail: elke.bieber@uba.de

UMEG
Dr. Ralf Lumpp
E-mail: lumpp@umeg.de

GKSS Research Centre Geesthacht GmbH
Prof. Dr. Ralf Ebinghaus
E-mail: ralf.ebinghaus@gkss.de

Lithuania

Atmospheric Pollution Research Lab., Institute of Physics
Dr. Andrius Urba
E-mail: urba@ktl.mii.lt

The Netherlands
Laboratory of Environmental Monitoring (LVM)
Arien Stolk, jr.
E-mail: arienstolk@rivm.nl

Norway
Norwegian Institute for Air Research (NILU)
Dr. Torunn Berg
E-mail: torunn.berg@nilu.no

Poland
Institute of Environmental Protection
Anna Degorska
E-mail: anna.degorska@ios.edu.pl

Spain
Instituto de Salud Carlos III; Centro Nacional de Sanidad Ambiental;
Area de Contaminacion Atmosferica
Maria del Carmen Ramos Diaz
E-mail: mcramos@isciii.es

Sweden
Swedish Environmental Research Institute (IVL)
Dr. Ingvar Wängberg
E-mail: ingvar.wangberg@ivl.se

6 of 11 laboratories measure both parameters. CODA/Belgium, as a contractor of VMM, Lithuania and Spain measure total gaseous mercury in ambient air only. UMEG/Germany, as a contractor of the German Federal Environment Agency and the Netherlands measure total mercury in precipitation only.

Participating laboratories can be identified by their lab codes which were provided before the start of the intercomparison and which were used throughout the following report:

TGM

Name	Country	Code
IOS	Poland	A
GARDIS	Lithuania	B
VMM 1	Belgium	C
IVL	Sweden	D
UBA	Germany	E
VMM 2	Belgium	F
NILU	Norway	G
GKSS	Germany	H
ISCIII	Spain	I
CODA	Belgium	J
UBA STATION	Germany	X

$Hg_{[prec]}$ and $Hg_{[dep]}$

Name	Country	Code	Comments
IVL	Sweden	1	
VMM	Belgium	2	
UBA	Germany	3	
IOS	Poland	4	
LVM	The Netherlands	5	
NILU	Norway	7	
GKSS	Germany	8	
UMEG	Germany	9	
GKSS	Germany	GKSS_F	filtered before BrCl
UMEG	Germany	Bergerh.	Bergerhoff sampler
UMEG	Germany	Wet+Dry	wet+dry sampler

5.3 Statistical analysis and critical evaluation of the results of the field intercomparison

Procedures for the statistical evaluation of round robin tests in drinking water, sludge or sediment analysis are widely used but an implementation for intercomparison experiments of air and deposition measurements has not been intended. We have decided to use a German DIN procedure on these field intercomparison data in order to compare the results with a robust statistics, which is well established in other fields. DIN is the German standardization system and the national correspondent to CEN or ISO. Therefore, the results for total gaseous mercury in ambient air and total mercury in precipitation are converted into a Z_u-score according to DIN 38402-45 (Deutsches Institut für Normung, 2003).

Generally the Z-score contains the following interpretations: assuming that the test results have a normal distribution, the probability of the absolute amount of Z not exceeding value 2 is approximately 95%. Given a reproducibility standard deviation s, a Z-score may be written Z = (x-m)/s, where m is the total mean value of all the laboratories and x is the test result of each single laboratory. In this case the assigned value m is estimated by a robust estimator (*Hampel*-Estimator) on the basis of the test results. Furthermore the robust *Q*-Estimator is used for the reproducibility standard deviation, since this estimator is highly efficient and is able to handle a large number of outliers. Both estimators are robust against outliers. Z_u-scores were used here because the reproducibility standard deviation is estimated on the basis of a few laboratories. The normal Z-score would be too sensitive on variations of the reproducibility standard deviation. Especially with larger relative standard deviations (> 25%) as expected in the case of $Hg_{[prec]}$, the Z_u-scores allow far greater fairness in fixing the tolerance limit than the normal Z-scores, since no preference is given to laboratories whose recovery rates are too low. Besides, the Z_u-scores can be expected to come closer to the normal distribution than the distribution of the normal Z-scores.

The tolerance limit is set to g = 2. That means that the conditions are complied with an absolute value of Z_u less than ± 2.

This way of data evaluation has the advantage that each participating laboratory can easily identify for the own results if systematic deviations from the assigned value are appearing and if one direction (too high – too low) is prevailing. Additionally it can be directly seen, if the reported data are within the data quality objectives or not.

As an example the following Figure 1 is used to demonstrate how the individual laboratory results have been presented in the comprehensive summary report in order to combine the relevant information of all samples taken for one particular measurement parameter.

The applied colour codes mean:
white: no data available, blue: within limit Z_u = ± 2,
yellow: Z_u exceeded ±2, red: Z_u exceeded ± 3 (concrete value included in figure)

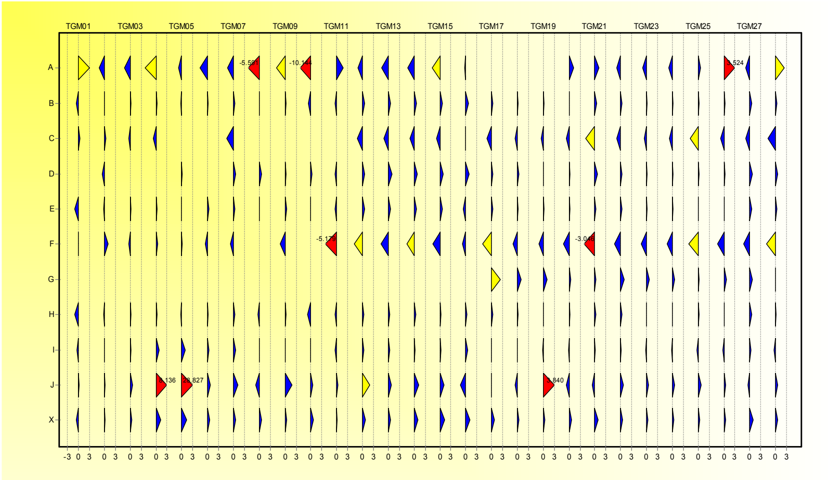


Figure 1: Exemplary illustration of Z_u-scores for all labs (A-X) and all 28 TGM samples, calculated with the rel. reprod. s.d. of each sample.

5.3.1 Total gaseous mercury (TGM)

Samples and participating laboratories

A sampling interval of 24 hours was defined. TGM was sampled on 28 days within six weeks, starting on May 2nd 2005. Start and end time for each sample was 9:00 GMT. Participants using manual systems were requested to submit their results for each sample (sampling day). Participants with automatic systems and higher time resolution were requested to submit 24-hours mean values (9:01 GMT – 9:00 GMT next day). Concentrations are given in ng/m³.

For the following statistical analysis each sampling day is treated as an individual sample and samples were numbered serially from TGM01 to TGM28. For the purpose of comparison, the TGM concentrations from the EMEP station Waldhof (operated by the German Federal Environment Agency [UBA]) were included in the data analysis as an additionally participating laboratory. One participant used two independent analysers from the same manufacturer. All together 11 datasets were submitted by the participants. In order to avoid any weighting or influence of the assigned value or the reproducibility standard deviation by the number of instruments from the same manufacturer, only TGM results from up to three instruments from the same manufacturer were used to calculate the assigned value and the reproducibility standard deviation. For example the TGM results from the *Tekran* analysers operated by UBA at Waldhof station and by GKSS in the container were disregarded to achieve the assigned value and the reproducibility standard deviation.

Based on all 28 individual samples and the corresponding Z_u-scores (see Figure 1), the overall relative reproducibility standard deviation as the mean of all relative reproducibility s.d. of all individual TGM samples is estimated to be 26 ± 11%.

For further evaluation of the data designations on median and quartiles have been applied, in order to assess the variance of the individual laboratory results relatively to the overall average of all reported data.

Figure 2 shows median, lower and upper quartile, arithmetic mean and the overall median and quartiles for TGM for each participating laboratory. The statistical evaluation was carried out with the complete set of officially reported laboratory measurement results, covering the entire measurement period.

The bar diagram is ordered by descending median and additionally contains information on the applied measurement methodology (*Tekran* analyser, *Manual* system or *Other* automatic system).

Supplementary to Figure 2 information on the individual laboratory deviance from the overall median is given in percent in Figure 3. This Figure also shows that the overall median TGM concentrations for the individual labs are mostly within EMEP manual data quality objective of 30% accuracy in annual average. Three labs reveal higher variations and lower concentrations.

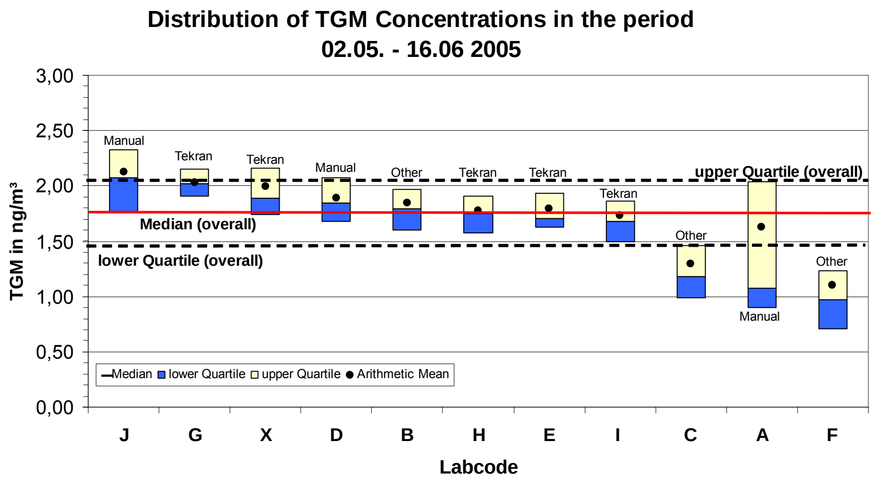


Figure 2: Distribution of TGM concentrations in the period 02.05.–16.06.05.

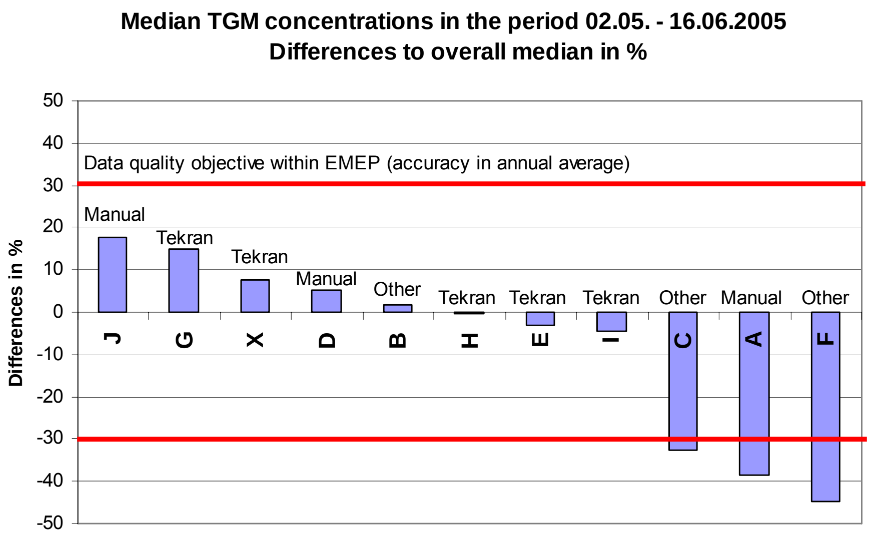


Figure 3: Median TGM concentrations in the period 02.05.–16.06.05; differences to overall median in %. The limits at 30 % represent the data quality objective within EMEP.

5.3.2 Total mercury in precipitation ($Hg_{[prec]}$)

A weekly sampling interval was defined. $Hg_{[prec]}$ was sampled for 27 weeks, starting on May 4th 2005 and ending on November 9th 2005. The week before the official start was meant for testing the equipment (week number 0). Only weekly samples with sufficient amount of precipitation for the analysis of mercury (> 5 mm) were considered for the intercomparison report. Therefore, only 20 samples (including one funnel blank) were taken into account for further analysis. Start and end time for each sample was 10:00 GMT each Wednesday. Concentrations are given in ng/L.

For the following statistical analysis each sampling week is treated as an individual sample for $Hg_{[prec]}$. Samples were numbered according to their sampling week from HGP01 to HGP27.

No precipitation occurred during week 16. On behalf of all participants a funnel rinse was organized by GKSS field personnel at the end of this sampling week.

For that purpose, 20 L of a rinsing solution containing *MilliQ* water and HCl *Suprapur* (*Merck*) to a concentration of 0.2 % was prepared. A documented volume of this solution was poured through each funnel on August 24th. The resulting samples were clearly labelled and treated like normal samples.

Moreover 250 ml of the rinsing solution were provided in clean glass bottles for each laboratory and were shipped together with the funnel blank solution.

Schedule, weekly precipitation, temperature and sample numbers

Week number	0	1	2	3	4	5	6	7	8	9	10	11	12	13
Start date 2005	27.04.	04.05.	11.05.	18.05.	25.05.	01.06.	08.06.	15.06.	22.06.	29.06.	06.07.	13.07.	20.07.	27.07.
End date 2005	04.05.	11.05.	18.05.	25.05.	01.06.	08.06.	15.06.	22.06.	29.06.	06.07.	13.07.	20.07.	27.07.	03.08.
Weekly prec. in mm (from UBA)	12,1	38,8	19,5	5,1	17,3	6,6	8,1	4,4	1,6	15	43,3	13,4	37,8	9,1
Weekly av. temp. in °C (from UBA)	15,0	8,6	9,2	13,8	18,4	13,2	12,2	19,3	18,5	18,4	17,9	19,2	15,9	18,5
Sample number	Test	**HGP01**	**HGP02**	**HGP03**	**HGP04**	**HGP05**	**HGP06**	< 5mm	< 5mm	**HGP09**	**HGP10**	**HGP11**	**HGP12**	**HGP13**

Week number	14	15	16	17	18	19	20	21	22	23	24	25	26	27
Start date 2005	03.08.	10.08.	17.08.	24.08.	31.08.	07.09.	14.09.	21.09.	28.09.	05.10.	12.10.	19.10.	26.10.	02.11.
End date 2005	10.08.	17.08.	24.08.	31.08.	07.09.	14.09.	21.09.	28.09.	05.10.	12.10.	19.10.	26.10.	02.11.	09.11.
Weekly prec. in mm (from UBA)	16	5,3	0	2,4	9,6	3,3	26,5	8,7	15,7	0	0	24,8	2,4	6,6
Weekly av. temp. in °C (from UBA)	14,1	15,3	19,0	15,7	18,7	18,2	11,1	13,5	10,7	13,0	8,1	10,3	11,9	9,6
Sample number	**HGP14**	**HGP15**	**HGP16 (FB)**	< 5mm	**HGP18**	< 5mm	**HGP20**	**HGP21**	**HGP22**	< 5mm	< 5mm	**HGP25**	< 5mm	**HGP27**

FB = Funnel Blank

Figure 4 shows for each laboratory the median, upper and lower quartile, the precipitation weighted mean and the overall median and quartiles for $Hg_{[prec]}$. The corresponding sampling methods are shown on top of the boxes (*bulk* = bulk sampler, *w-o* = wet only sampling technique). The statistical evaluation was carried out with the complete set of officially reported laboratory measurement results, covering the entire measurement period.

Figure 4 shows that the $Hg_{[prec]}$ concentrations of most laboratories during this 27 weeks intercomparison are well comparable regarding median concentrations and variability. This is independent from the applied procedure (wet-only or bulk sampler).

Supplementary to Figure 4 information on the overall precipitation weighted means for all participating labs is given in detail in Figure 5, including the corresponding sampling methods. The left bar represents the reproducibility standard deviation for the weighted means which is ± 5.8 ng/L (rel.S_R = 40.7%). Figure 5 shows that the weighted mean concentrations for the individual labs mostly exceed the EMEP manual data quality objective of 30% accuracy in annual average.

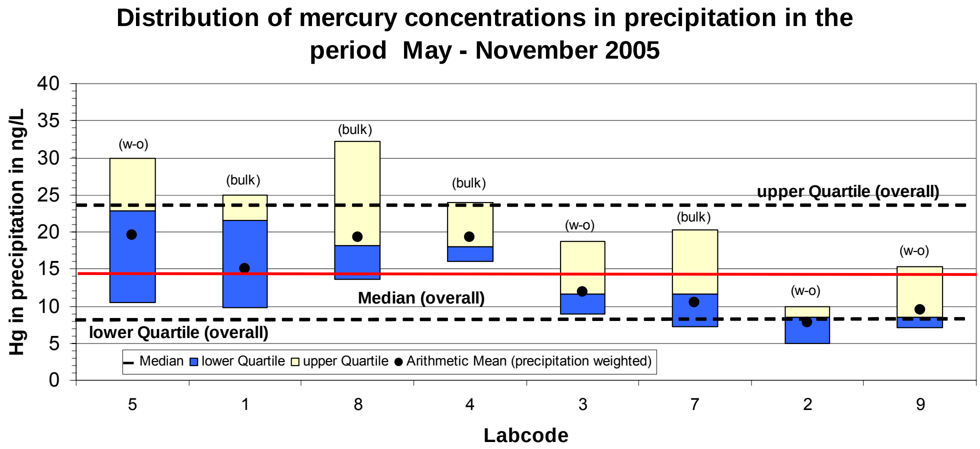


Figure 4: Distribution of mercury concentrations in precipitation in the period May–November 2005.

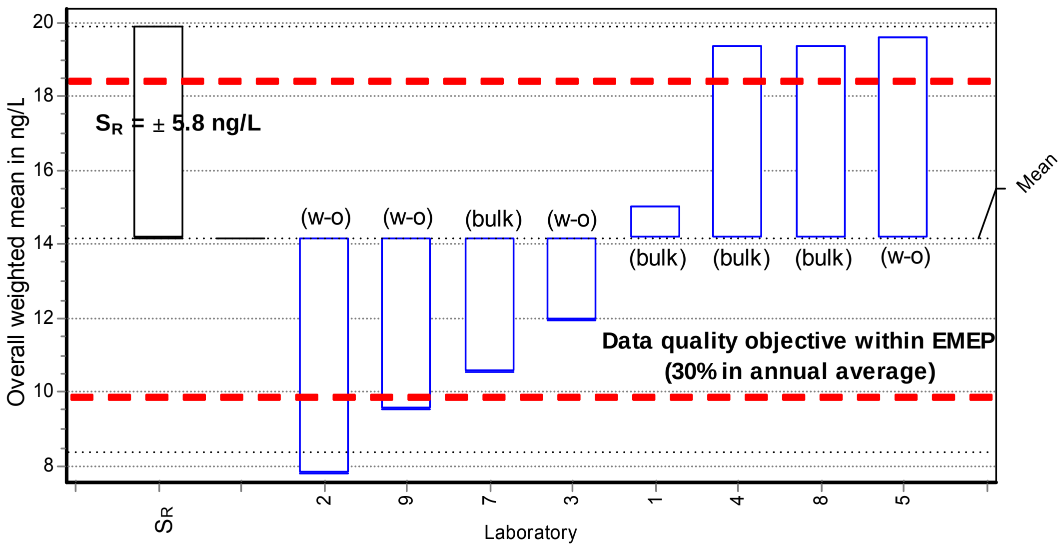


Figure 5: Reproducibility standard deviation (= 5.8 ng/L) and assigned value (= 14.1 ng/L) for the precipitation weighted means for all participating labs. The red dashed lines represent the data quality objective within EMEP (30 % in annual average).

5.3.3 Deposition rates ($Hg_{[dep]}$)

All calculated deposition rates are based on weekly precipitation measurements ($Hg_{[prec]}$) but expressed as daily deposition rates. $Hg_{[dep]}$ rates are given in ng/(m^2 d). Weekly precipitation amounts were measured by the individual labs, if not the official Waldhof station data were applied. The funnel blank was not considered for calculating $Hg_{[dep]}$ rates. For the purpose of comparison, Hg deposition data from three additional groups/devices were included in the data analysis as an additionally participating laboratory.

1. Weekly deposition rates calculated from filtered aliquots (PTFE, 0,45 µm) from GKSS bulk samplers (**GKSS_F**). Samples were filtered prior to oxidation with BrCl.
2. Monthly average deposition rates from four UMEG *Bergerhoff* bulk samplers (**Bergerh.**). Most samples were 4-weekly samples, which normally covered the individual calendar month.
3. Monthly wet+dry deposition rates from UMEG prototype *Eigenbrodt* system, adding measured monthly dry deposition rates to an average monthly wet deposition rate from weekly sampling (**Wet+Dry**). Most "dry-only" samples were 4-weekly samples, which normally covered the individual calendar month.

All together 11 datasets for $Hg_{[dep]}$ were used for further analysis.

Figure 6 shows for each laboratory the median, upper and lower quartile, the arithmetic mean and the overall median and quartiles for daily total mercury deposition rates $Hg_{[dep]}$. The corresponding sampling methods are shown on top of the boxes (*bulk* = bulk sampler, *w-o* = wet only sampling technique). Results from the three additional groups/devices are included but treated separately in the right part of the plot and were not included for the calculation of the overall median and quartiles. The statistical evaluation was carried out with the complete set of officially reported laboratory measurement results, covering the entire measurement period.

Supplementary to Figure 6 information on the individual laboratory deviance from the overall median is given in percent in Figure 7.

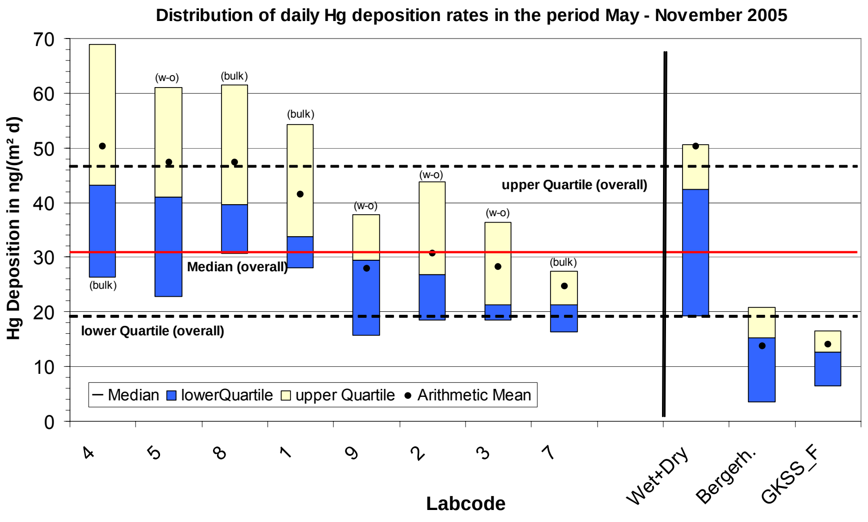


Figure 6: Distribution of daily Hg deposition rates in the period May–November 2005.

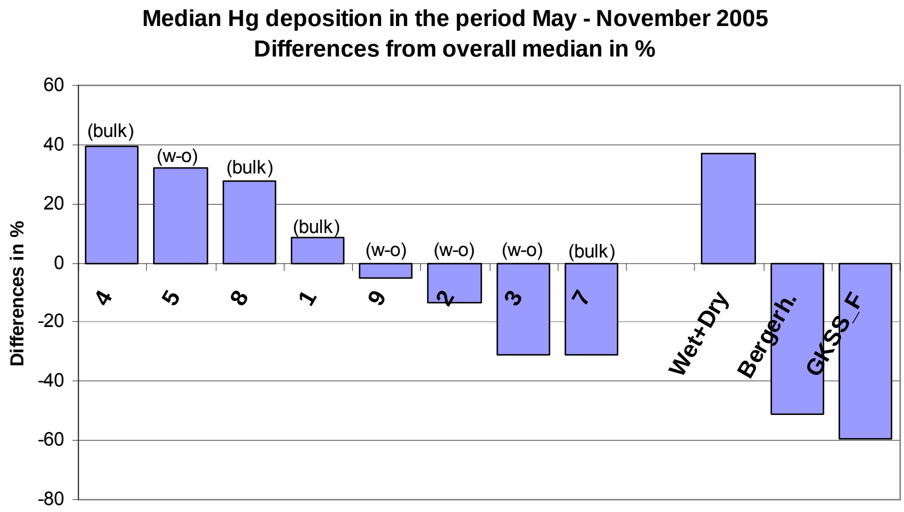


Figure 7: Individual laboratory deviance for median total mercury deposition rates in the period May–November 2005 from the overall median in percent.

Both figures show that calculated total mercury deposition rates of most laboratories during this 27 weeks intercomparison are comparable regarding median concentrations and variability. This is independent from the applied procedure (wet-only or bulk sampler). Bergerhoff bulk samplers (Bergerh.) and weekly filtered aliquots (GKSS_F) however, entail significantly lower deposition rates compared with other laboratories and methods.

Mercury associated to particles (dry deposition) and the evaporation of mercury and rainwater during the sampling process seems to play an important role for quality and performance in the determination of total mercury in precipitation and the corresponding deposition rates.

Figure 8 shows the total Hg deposition estimates for the complete time period calculated as the product of the total precipitation amount measured (from UBA rain gauge and/or individual labs) and the precipitation weighted mean of the $Hg_{[prec]}$ concentration, and the sum of the weekly/monthly Hg deposition. Calculated total depositions range from less than 2 µg/m^2 to almost 8 µg/m^2, depending on the procedure for $Hg_{[prec]}$ and the source for the precipitation amount.

The rel. reproducibility s.d. for total Hg deposition estimates remains 40.7% as for the precipitation weighted mean, if the same precipitation amount is used for all labs (from UBA rain gauge). If the variations in the precipitation amount measured by each individual lab are taken into account to calculate an overall uncertainty by error propagation, the final uncertainty for the total Hg deposition estimates slightly increases to 42.2%. It demonstrates that the error from the precipitation amount measurements is of minor importance.

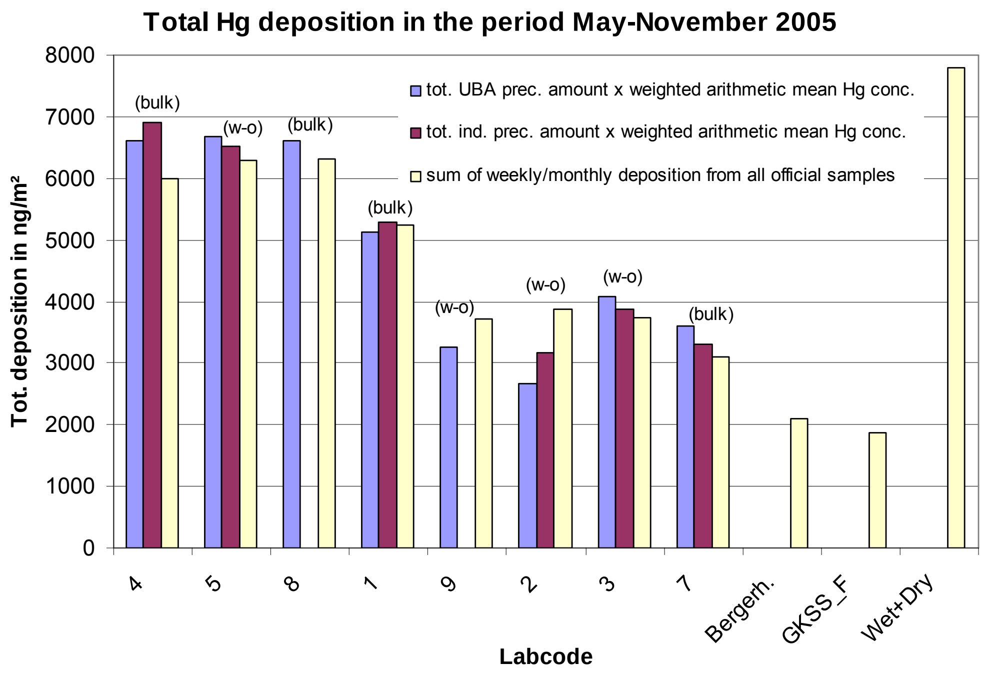


Figure 8: Total Hg deposition for the complete time period calculated as the product of the total precipitation amount measured (from UBA rain gauge and individual lab) and the weighted mean of the Hg conc. in precipitation and the sum of the weekly/monthly Hg deposition.

5.4 Summary and conclusions

Quality and comparability of chemical measurements in air and precipitation in every participating country are key issues of EMEP, and consequently reference operating procedures and regular method intercomparisons are important elements involved.

For this reason an international field intercomparison on measurements of mercury in ambient air and precipitation was carried out at Waldhof in order to investigate the quality and comparability of mercury measurements within EMEP. The project was funded by the German Federal Environment Agency (Umweltbundesamt, UBA).

The field intercomparison exercise was scheduled to start on May 01st 2005 and covered 28 daily measurements of total gaseous mercury in ambient air within 6 weeks and 20 weekly samples for total mercury in precipitation. 11 laboratories from 8 European countries participated in the field intercomparison.

For the interpretation of the results achieved during this exercise DIN 38402-45 (Deutsches Institut für Normung, 2003) was chosen for evaluation with a mature and robust statistical method, which has shown to be suitable for classical round robin test, e.g. in the field of water, soils or sediments.

For Total Gaseous Mercury (TGM) it can be concluded in general, that the concentration data reported by the individual laboratories give comparable results. Reported daily average values of the individual laboratories were mainly in the range of < ± 50% of the reproducibility standard deviation, for several samples even better, i.e. < ± 25%. This finding is independent of the applied methodology, i.e. manual or automated sampling and quantification. Based on the median for the complete intercomparison period it could be shown that almost all labs (i.e. 75%) are within the ± 30% range of the overall median, i.e. meet the EMEP data quality objective. As a result, conclusions concerning annual average concentration at different EMEP stations can be derived with high credibleness within an acceptable measurement uncertainty. However, the shorter the considered time scales are the harder it is to distinguish significantly between true concentrations differences and methodological variations within a measurement uncertainty of up to 25-50% for individual applied procedures.

For total mercury in precipitation it can be concluded that a fairly good agreement of the individual laboratory results with the assigned value could be achieved. However, if a constant reproducibility standard deviation is set to 25% as default, some of the laboratories are not capable to match with the designated quality threshold value. In addition the precipitation weighted means are within ± 40.7% of the assigned value for the complete period and exceed the EMEP quality objective of 30% for most laboratories.

Calculated total depositions range from less than 2 $\mu g/m^2$ to almost 8 $\mu g/m^2$, depending on the procedure for $Hg_{[prec]}$ and the source for the precipitation amount. The reproducibility for total Hg deposition estimates is 42.2%. It is comparable to the result for the precipitation weighted means for total Hg in precipitation as the error contribution from the precipitation amount measurements is of minor importance.

Taking into account that measurement uncertainties related to the determination of mercury concentrations in precipitation and especially wet deposition rates are more manifold and complex than those involved in the measurement of TGM, this finding is not surprising but also not yet satisfactory.

Results, summary and conclusions presented here have been intensively discussed and finally agreed on by all participants during the joint evaluation workshop, held from June 12–14, 2006 at GKSS Research Centre Geesthacht. Major recommendations from the evaluation workshop comprise methodical aspects including sample treatment for precipitation measurements, data processing and reporting of results to EMEP and address to future intercomparison exercises such as the one in preparation by CEN/TC 264/WG 25: "Mercury measurements in ambient air and deposition".

6. Results from laboratory comparisons

6.1 Main components

The twenty-second intercomparison (Hjellbrekke et al., 2005) of main components in air and precipitation is relevant for the data reported for 2004. The results of the systematic and random errors are shown in Table 2 and Table 3, respectively. The details on how these calculations are done are presented in Aas et al. (2003). Some labs submit data to EMEP but do not participate in the laboratory intercalibration, these latter are marked in grey in Table 2.

The results are mostly good. Except for a few labs, i.e. PT, RU, HR, EE and PL05 that have difficulties with some of the elements that. This is not necessarily the general performance for the laboratory an outlier may cause the problems, one should look at the performance for several years if one needs a general picture. However, large deviations are signs of QA/QC problems in the lab, and the lab routines need to be checked extra carefully. Another point is than some of the results are not representative for the data reported. I.e., Spain makes it quite poor for SO_2 and NO_2, but the data reported to EMEP is by monitors and therefore not affected by the performance in the lab.

Table 2: Random errors (2RSD%) in the 22nd laboratory intercomparison for precipitation and air.

	Precipitation										Air and aerosols			
lab Country	SO_4^{2-}-S	NO_3-N	NH_4-N	pH	Mg	Na	Cl	Ca	K	Cond	SO_2	NO_2	NH_3-N	HNO_3
1 AT	0.1	0.6	2.1	11.1	4.4	0.9	2.3	2.3	0.5	2.7				
21 CH	0.7	0.6	0.4	3.5	0.4	1.8	1.4	1.6	1.5	3.3		0.8		
3 CZ	1.1	0.6	2.1	4.1	2.2	5.0	0.5	2.3	3.8	1.5	0.4		1.6	
7 DE	2.5	0.3	1.2	15.3	2.2	0.6	0.7	2.1	1.5	8.4	1.5	3.3	7.2	3.0
8 DE Leipz	0.1	0.2	1.1	2.6	0.4	0.9	0.4	1.6	0.5	1.9				
4 DK	0.2	0.8	0.6	3.2	1.8	1.5	3.7	2.8	4.2	1.8	0.7	1.3	2.5	1.8
38 EE	2.1	1.3	1.7	37.2	0.4	0.7	2.6	11.1	1.1	11.1	4.4	6.3		
19 ES	7.4	4.3	1.4	4.3	0.4	1.1		3.6	1.3	2.6	11.2	48.0	3.9	
5 FI	0.8	0.2	0.7	3.7	1.1	0.3	2.2	0.2	2.5	3.2		1.1	3.0	2.0
6 FR	0.6	1.1	2.1	3.8	1.8	1.6	2.3	2.0	1.5	1.0		50.5		
23 GB	0.3	1.3	3.4	5.4	4.0	2.8	3.8	7.0	2.5	2.4	1.1	2.5		
35 HR	2.5	0.4	1.5	3.2	5.5	13.1	1.8	40.8	4.6	3.4	3.3			
10 HU	6.3	0.9	0.1	7.5	0.7	2.4	23.9	2.8	2.9	3.1	1.8		14.8	
12 IE	0.4	0.5	2.3	6.8	1.5	0.8	1.8	1.5	2.4	4.8	1.1			
11 IS	1.4	0.9		1.7	1.5	1.1	2.0	1.5		2.9				
13 IT	0.3	4.7	5.6	2.7	0.4	4.3	4.3	1.8	2.4	2.7			12.5	
30 IT	4.0	4.1	25.7	9.9	5.6	13.9	9.7	13.1	31.5	1.9				
32 LT	2.8	2.4	1.1	5.2		2.4	3.4	12.0	2.7	1.7	2.9	5.5	8.6	2.3
33 LV	0.8	0.3	0.7	5.4	1.5	2.1	1.8	2.1	1.6	2.6	1.1	3.4	9.3	8.7
40 MK		5.1	23.5	5.5	9.9	8.3	6.3	25.9	2.7	5.9				
14 NL	0.6	1.3	0.6	2.8	1.5	3.0	4.4	1.0	8.0	5.1				
15 NO	1.2	1.7	2.1	3.5	2.6	2.1	2.1	0.8	1.6	2.3	1.8	7.6	2.1	9.5
16 PL	1.6	1.5	3.3	5.7	2.2	0.3	4.0	1.3	1.5	2.3	4.4	3.7	28.6	2.7
39 PL05	3.3	2.0	5.0	3.0	0.6	2.0	4.8	6.6	0.9		1.5	2.3	6.1	2.3
17 PT	0.3	1.7	4.4	22.1	2.9	3.6	17.9	2.8	1.6	0.3		48.1		
22 RU	44.5	2.0	2.8	10.5	0.7	7.9	16.9	3.8	15.5	2.7	1.8	1.7		7.9
20 SE	1.4	1.2	3.3	1.5	4.0	3.4	1.1	5.6	4.0	3.4	5.4	5.9	4.9	5.6
36 SI	1.6	0.2	0.8	2.1	2.2	0.9	3.1	1.5	2.4	2.8	1.8	15.2	2.0	6.3
31 SK	2.4	2.2	10.5	4.1	5.1	5.7	3.9	4.4	8.2	3.1	2.2	0.8		2.3
34 TR	0.6	0.6	4.1	3.4	0.4	12.9	1.8	1.8	4.0	1.7	2.5	1.9	5.4	1.0
24 YU	2.9	2.8	1.7	1.9	8.4	1.6	7.2	2.5						

1-2 DQO   > 2 DQO   not participated

Table 3: Systematic errors (RB%) in the 22nd laboratory intercomparison for precipitation and air.

	Precipitation											Air and aerosols			
	SO_4^{2}-S	NO_3-N	NH_4-N	pH	H	Mg	Na	Cl	Ca	K	Cond	SO_2-S	NH_3-N	NO_2-N	HNO_3-N
1 AT	0	-2 A	-7 A	0	-14 A	-5	0	-7 A	1	-1 A	-5 A				
21 CH	2 A	-2 A	0	-11 A		0	-2	1	1	-3 A	-2	1 A			
3 CZ	1	-1 A	10 A	-14 A		-1	1	-4 A	5	-1	-3 A		-4 A	0	
8 DE	1 A	1 A	-3 A	-16 A		0	-3 A	0	0	-2 A	-8 A	1	11	1	1
7 DE Lepz	4 A	1 A	-3 A	-7		-5 A	-1 A	-1	-6 A	-4 A	-12				
4 DK	3 A	-5 A	-1	-10 A	-8 A	0	10 A	-7 A	0	-2	-5 A	1	2 A	-3 A	-2 A
38 EE	-6 A	-2 A	1	128 A		-12 A	-2 A	-6 A	-3	-22 A	-13	-2		9 A	
19 ES	-5	8 A	-2 A	-40 A		0	-1		9 A	4 A	-5 A	-98 A	-10 A	51 A	
5 FI	1 A	2 A	-1 A	-10 A		-1	1 A	-5 A	2 A	1	-1	6 A	0		2
6 FR	-3 A	-2 A	-5 A	-5 A		-6 A	0	-5 A	1	-4 A	-10 A	-3			
23 GB	-2 A	4 A	5 A	-12 A		-5	-11 A	-2	-5	-3	-6 A	8 A		2	
35 HR	5 A	-4 A	4 A	-19 A		-42 A	9	-1	13	-18 A	-6 A			3	
10 HU	8 A	0	-5 A	0		-1	-8 A	26 A	1	5 A	-3		-16 A	5 A	
12 IE	2 A	-1	1	-4		2	-1 A	2	-6 A	0	1			5 A	
11 IS	-2	-1 A		-16 A		-6 A	-6 A	-5 A	-9 A		-5 A				
13 IT	5 A	4	-3	-13 A		0	-7	-7 A	-1	-3 A	-7 A		13 A		
30 IT	10 A	4 A	21	-16 A		15	9	-3	14	2	-6 A				
32 LT	-5	1	4 A	-5			8 A	-7 A	-17 A	-4 A	-8 A	4	-1	4	7 A
33 LV	4 A	-3 A	0	-8 A		-5 A	-1	-2	-8 A	-5 A	-5 A	7 A	5 A	-1	12 A
40 MK		26 A	186 A	-58 A		-22 A	-4	6 A	-5	-2	-41 A				
14 NL	4 A	-7 A	-2 A	-19 A	-13 A	-3 A	9 A	-21 A	1	13 A	-4				
15 NO	-1	2	-4 A	-13 A		0	5 A	2	1 A	-1	-3 A	-4	3 A	-6 A	-9
16 PL	-3 A	-2 A	3	-12 A		-6 A	-2 A	-8 A	1 A	-7 A	-9 A	6 A	4	-17 A	-2
39 PL05	4 A	3 A	2	-11 A		-4 A	-5 A	13 A	58 A	-3 A		3 A	0	1	6 A
17 PT	0	0	15 A	21		5 A	-18 A	63 A	-30 A	-57 A	-8 A	-98 A			
22 RU	113 A	-3	16 A	-18 A		-13 A	-12 A	3	-32 A	-17	-5 A	-2		4 A	-15 A
20 SE	-2 A	0	-1	-17 A		-14 A	-6 A	-6 A	-15 A	-3 A	-3	4	-3	8	-1
36 SI	-3 A	-2 A	4 A	-17 A		0	2	-4 A	5 A	-7 A	-7 A	15 A	3	0	0
31 SK	-10 A	5 A	9 A	-15 A	-10 A	-1	-1	-11 A	14 A	0	-3 A	6 A		1	-3 A
34 TR	0	-4 A	-3	-18 A	-18 A	0	2	-3 A	7 A	-1	-6 A	6 A	-7 A	4	8 A
24 YU	2	-2	-1	-12 A		-2	-8 A	7 A	-5 A						

systematic bias | more than 20 % or less than -20% bias | between 10 and 20 % or between -10 and -20 % bias

6.2 Heavy metals

The data quality objectives (DQO) in EMEP states that the accuracy in the laboratory should be better than 15% and 25% for high and low concentrations of heavy metals, respectively (Annex 1). One important measure to check the data quality is the laboratory ring test. There is a marked improvement in the laboratory performance for both lead and cadmium since the beginning of the laboratory comparison in 1995. The intercomparison completed last year is relevant for the 2004 data (Uggerud et al., 2005). In Table 4, there is a summary of the results from this laboratory intercomparison. Sweden and Iceland were not participating because these measurements were analyzed in Norway. The measurements of high concentration samples are generally quite OK, however, at many EMEP sites these high concentrations are not very representative. For the priority compounds Pb and Cd, Denmark has some problems with both of these, while CZ, SI and EE needs to check their Cd measurements. In addition, there are some countries reporting measurements data without participation in the laboratory intercomparison: Belgium, Ireland, Portugal, and Spain. Data from these countries are of unknown quality; and it is therefore strongly recommended that they take part in the annual laboratory intercomparison.

Table 4: Average per cent error (absolute) in low and high concentration samples, results from heavy metal laboratory intercomparison in 2004.

	Cr		Ni		Cu		Zn		As		Cd		Pb	
	low	high	low	high	low	high	low	high	low	high	low	high	low	high
AT	1	3	1	2	8	5	7	0	3	1	5	8	6	4
BE	20	1	10	10	5	1	78	8	5	7	3	1	2	4
CS	3	5	6	4	2	5	6	2	4	4	3	4	6	2
DK	0	3	15	8					31	33	860	829	46	3
FI	3	4	2	1	2	0	3	1	1	1	5	1	2	4
FR	14	2	400	12	164	8	259	3	48	46	471	35	9	12
DE	0	0		6	3	2	1	2		5	0	0	5	0
NL	21	4	15	3	11	1	0	2	3	1	12	2	4	4
NO	3	5	4	5	12	10	6	2	2	3	8	2	2	5
PL	0	0	0	2	0	2	3	2			22	61	37	78
GB	13	5	15	2	10	1	20	0	8	6	18	10	0	1
SK	19	12	26	10	25	8			18	12	13	9	9	6
LT	13	18	0	8	12	12	21	24	13	11	25	17	3	4
SI	7	5	0	3	3	5	30	12	0	2	7	4	7	4
EE		10		8	21	5	69	8		27		11	22	23

1/2 - 1 DQO 1 - 2 DQO > 2 DQO

7. QA flags for 2004

The data quality (DQ) flag is divided in two two-digit numbers, the leftmost two digits describing the performance in field comparisons and the two rightmost being based on the laboratory comparisons, the definitions are found in Annex 6. The two-digit flags are furthermore defined by letting the first digit represent an estimate of the systematic error and the second digit the random error. Most of the SO_2 and NO_2 in air and SO_4 in aerosols data have been given a four-digit DQ flag. The rest of the air data have not been assigned any flag due to few field- and laboratory comparisons for these components. For precipitation data there has been very few field comparisons and therefore only two flags representing the performance in the laboratory comparisons are given. Details on how these flags are defined are found in Aas et al. (2003).

It should be noted that the field comparisons have been far less both in number and in length with respect to different meteorological situations than desirable, and that the DQ flag cannot be expected to give a precise estimate of the quality. The flags will give a data user a quick overview of the expected errors in a data set and hopefully also give the user reasonable estimates of systematic deviations from a reference and of random errors in the data.

One may also group the different flags in a simpler classification, i.e. A, B, and C or as shown in Table A6.1 and Table A6.2 in three colour codes. The data series flagged with any of the red flags (C) will be classified as invalid data. The rest of the data are classified as valid data although those marked with a green colour (A) is considered by CCC as the most accurate data in the EMEP database. The data user may create other criteria or quality groups depending on the use of the data.

Several countries have never participated in field comparisons, and some countries have changed their measurement method since they took part. The comparisons carried out so far are therefore far from sufficient to express the comparability of all measurements. There are probably many comparisons performed outside EMEP, and if this information is made available, further updates of the flags will be done.

The results obtained in one comparison are used to flag data for all the years this method has been in use at the site. A poor performance in a field comparison can therefore influence the flagging for many years of data. If the data quality is determined to a large extent by the sampling method then this seems to be an acceptable approach. If on the other hand the sampling is fairly simple and the laboratory work determines most of the overall measurement quality, then the performance in the annual laboratory comparisons will more important than the results from a field comparison. Details on the flags for SO_2 and SO_4 in air and CCC's recommendations on whether the field or laboratory flag should be prioritised is shown in Annex 5 in Aas et al. (2004).

In Table 5 and Table 6 the flags relevant for 2004 are listed. The field flags are based on last results in the latest field intercomparison that the country has participated in, while the laboratory flag is based on the results in the 22nd laboratory intercomparison (Hjellbrekke et al., 2005). For SO_4 in air, only field flags are shown since this component is taken out from the laboratory intercomparison. SO_4 in precipitation should be representative for the laboratory performance also for SO_4 on filters.

As seen there are very few measurements that should be considered invalid (marked in red); however, the B category is rather big for especially SO_2 and NO_2 measurements. It is up to the data user to select which data to be used based on the quality flags depending on the accuracy needed.

Table 5: QA flag and category for main components in precipitation.

Code	pH		SO_4		NH_4		NO_3		Na		Mg		Cl		Ca		K		cond	
AT	00	A	00	A	20	A	00	A	00	A	00	A	20	A	00	A	00	A	00	A
CH	40	B	00	A	00	A	00	A	00	A	00	A	00	A	00	A	00	A	00	A
HR	40	B	00	A	30	B	00	A	00	A	00	A	00	A	00	A	00	A	00	A
DE0003	21	B	00	A	00	A	00	A	00	A	00	A	00	A	20	A	00	A	40	B
DE	40	B	00	A	00	A	00	A	00	A	00	A	00	A	00	A	00	A	20	A
DK	20	A	00	A	00	A	00	A	30	B	00	A	20	A	00	A	00	A	20	A
EE	72	C	20	A	00	A	00	A	00	A	40	B	20	A	00	A	60	B	40	B
ES	60	B	20	A	00	A	10	A	00	A	00	A			10	A	00	A	20	A
FI	40	B	00	A	00	A	00	A	00	A	00	A	00	A	00	A	00	A	00	A
FR	20	A	00	A	20	A	00	A	00	A	20	A	00	A	00	A	00	A	20	A
GB	40	B	00	A	00	A	00	A	40	B	00	A	00	A	20	A	00	A	20	A
HR	40	B	00	A	00	A	00	A	10	A	80	C	0	A	32	B	40	B	20	A
HU	00	A	10	A	00	A	00	A	20	A	00	A	51	B	00	A	00	A	00	A
IE	00	A	00	A	00	A	00	A	00	A	00	A	00	A	20	A	00	A	00	A
IS	40	B	00	A			00	A	20	A	20	A	20	A	20	A			20	A
IT	40	B	10	A	00	A	00	A	20	A	00	A	20	A	00	A	0	A	20	A
IT	40	B	10	A	51	B	00	A	10	A	31	B	00	A	30	B	2	B	20	A
LT	0	A	20	A	00	A	00	A	10	A			20	A	40	B	00	A	20	A
LV	20	A	00	A	00	A	00	A	0	A	00	A	00	A	20	A	00	A	00	A
NL	40	B	00	A	00	A	20	A	10	A	00	A	60	B	00	A	30	B	00	A
NO	40	B	00	A	00	A	00	A	0	A	00	A	00	A	00	A	00	A	00	A
PL	40	B	00	A	00	A	00	A	0	A	20	A	20	A	00	A	20	A	20	A
PL05	40	B	00	A	00	A	00	A	0	A	00	A	30	B	70	C	00	A		
PT	51	B	00	A	30	B	00	A	40	B	10	A	71	C	60	B	80	C	20	A
RU	40	B	73	C	30	B	00	A	40	B	40	B	01	A	60	B	41	B	00	A
SE	40	B	00	A	00	A	00	A	20	A	40	B	20	A	40	B	00	A	00	A
SI	40	B	00	A	00	A	00	A	00	A	00	A	00	A	10	A	20	A	20	A
SK	40	B	40	B	00	A	10	A	00	A	00	A	40	B	30	B	00	A	00	A
TR	40	B	00	A	00	A	00	A	00	A	00	A	00	A	10	A	00	A	20	A
YU	40	B	00	A	00	A	00	A	20	A	00	A	10	A	00	A				

Table 6: QA flag and category for main components in air.

	SO_2			NO_2			SO_4		SNO_3			SNH_4		
	qa flagg	field	lab	qa flagg	field	lab	qa flagg	field	qa flagg	field	lab	qa flagg	field	lab
AT	22--	B	-	-	-	-	-	-	-	-	-	-	-	-
CH	3200	B	A	33--	B	-	-	-	-	-	-	-	-	-
CZ	12--	B	-	0300	-	A	-	-	00	-	A	--00	-	A
DE	0100	A	A	--00	-	A	00--	A	--00	-	A	--30	-	B
DK	0000	A	A	--00	-	A	00--	A	--00	-	A	--00	-	A
EE	1200	B	A	6210	B	A	-	-	-	-	-	-	-	-
ES	32--	B	--	30--	B	--	00--	A	-	-	-	--20	-	A
FI	1010	A	A	-	-	-	00--	A	--00	-	A	--00	-	A
FR	2003	B	C	-	-		20--	B						
GB	1010	B	A	5300	B	A	00--	A	-	-		-	-	
HU	-	-	-	1310	B	A	-	-	-	-		--40	-	B
IE	00--	A	-	5000	B	A	-	-	-	-		-	-	
LT	1000	B	A	3200	B	A	10--	B	1010	B	A	--00		A
LV	5010	B	A	0200	B	A	22--	B	1030	B	B	0210	A	A
NL	11--	B	-	03--	-	-	00--	A	-	-		-	-	
NO	0000	A	A	0020	A	A	00--	A	--20	-	A	--00	-	A
PL	0010	A	A	4340	B	B	01--	A	--00	-	A	--01	-	A
PL05	2000	B	A	5200	B	A	32--	B	--10	-	A	--00	-	A
SE	0000	A	A	1010	B	A	00--	A	--00	-	A	--00	-	A
SI	0031	A	B	--00	-	A	20--	B	--00	-	A	--00	-	A
SK	--10	-	A	5300	B	A	-	-	--00	-	A	-	-	-
TR	0010	A	A	--00	-	A	-	-	--10	-	A	--20	-	A
YU	-	-	-	53--	B	-	-	-	-	-		-	-	

8. Audits

Audit is not being done regularly from CCC, but will be done when needed. It is recommended regular audits at all EMEP sites, at least as an internal control every year, but also with visitors from e.g. neighbouring countries. Forms to be used for auditing main components in air and precipitation, and ozone can be downloaded from EMEP's homepage, http://www.nilu.no/projects/ccc/qa/index.htm. It is recommended that all the external auditing is reported to CCC.

9. References

Aas, W. and Breivik, K. (2006) Heavy metals and POP measurements, 2004. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 7/2006).

Aas, W., Hjellbrekke, A.-G., Manø, S., Schaug, J. and Uggerud, H.T. (2004) Data quality 2002, quality assurance, and field comparisons. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 4/2004).

Aas, W., Hjellbrekke, A.-G. and Schaug, J. (2003) Data quality 2001, quality assurance, and field comparisons. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 6/2003).

Deutsches Institut für Normung (2003) Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung - Allgemeine Angaben (Gruppe A) - Teil 45: Ringversuche zur externen Qualitätskontrolle von Laboratorien (A 45). Berlin, Beuth Verlag (DIN-Norm 38402-45).

EMEP/CCC (1996) Manual for sampling and chemical analysis. Revised November 2001. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 1/95). URL: http://www.nilu.no/projects/ccc/manual/index.html.

Fjæraa, A.M. (2006a) Data report 2004. Acidifying and eutrophying compounds. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 1/2006).

Fjæraa, A.M. (2006b) Ozone measurements 2004. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 2/2006).

Hjellbrekke, A.-G., Uggerud, H.T., Hanssen, J. E. and Schaug, J. (2005) The twenty-second intercomparison of analytical methods within EMEP. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 8/2005).

Sirois, A. and Vet, R.J. (1994) Estimation of the precision of precipitation chemistry measurements in the Canadian air and precipitation monitoring network (CAPMoN). In: *EMEP Workshop on the Accuracy of Measurements. Passau, 1993*, ed. by T. Berg and J. Schaug. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 2/94). pp. 67-85.

Solberg, S. (2006) VOC measurements 2004. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 8/2006).

Uggerud, H.T. and Hjellbrekke, A.-G. (2005) Analytical intercomparison of heavy metals in precipitation, 2003 and 2004. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 7/2005).

Umweltbundesamt (2006) Field Intercomparison of Mercury Measurements within EMEP. Final report. Langen, German Federal Environment Agency, 2006 (available October 2006).

WMO (2004) Manual for the GAW precipitation chemistry programme – Guidelines, data quality objectives and standard operating procedures. Ed. by M.A. Allan. Geneva, WMO (Global Atmosphere Watch No. 160).

Yttri, K.E. and Aas, W. (eds.) (2006) Measurements of particulate matter, 2004. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 3/2006).

10. List of participating institutions and the national quality assurance managers (NQAM)

Country	Institute	NQAM
Austria	Umweltbundesamt	Christian Schuetz
Croatia	Meteorological and Hydrological Service of Croatia	Sonja Vidic
The Czech Republic	Czech Hydrometerological Institute	Nadezda Melichova
Denmark	National Environmental Research Institute	Lone Grundahl
Estonia	Estonian Environmental Research Lab. Ltd	Toivo Truuts
Finland	Finnish Meteorological Institute	Veijo Pohjola
France	l'Ecole des Mines de Douai Laboratories Wolff	Patrice Coddeville
Germany	Umweltbundesamt	Markus Wallasch
Greece	Ministry of Environment Physical Planning and Public works Environmental Chemical Processes Laboratory, University of Crete	Vasiliki Smirnioudi GR02: Nikos Mihalopoulos
Hungary	Hungarian Meteorological Service, Institute for Atmospheric Physics	Laszlo Haszpra
Island	The Icelandic Meteorological office	Johanna Thorlacius
Ireland	Environmental Protection Agency	Concannon Colman
Italy	CNR Instituto Inquinamento Atmosferico	Cinzia Perrino
EU at Ispra, IT04	Joint Research Center (JRC)	Jean-Philippe Putaud
Latvia	Latvian Hydrometeorological Institute	Iraida Lyulko
Lithuania	Institute of Physics	Dalia Sopauskiene and Vidmantas Ulevicius (HM and POP)
The Netherlands	National Institute for public Helath and Environmental Protection (RIVM)	Arien Stolk
Norway	Norwegian Institute for Air Research (NILU)	Jan Erik Hanssen
Poland	Institute of Meteorology and Water Management and Institute of Environmental Protection	Barbara Obminska and for PL05: Anna Degorska
Portugal	Instituto de Meteorologia	Amelia Lopes
Russia	Institute of Global Climate and Ecology	Alexey Ryaboshapko
Serbia	Republic Hydrometeorological Service of Serbia	Liljana Novakovic
Slovenia	Environment Agency - Slovenia	Brigita Jesenovec
Slovak Republic	Slovak Hydrometeorological Institute	Marta Mitosinkova
Spain	Subdirección General de Calidad Ambiental	Alberto González Ortiz
Sweden	Swedish Environmental Research Institute (IVL)	Karin Sjöberg
Switzerland	Swiss Federal Laboratory of testing Materials and Research (EMPA)	Robert Gehrig/ Claudia Zellweger
Turkey	The Ministry of Health of the Republic of Turkey	Lütfü Kýlýçla
United Kingdom	AEA Technology	Keith Vincent

Annex 1

Data quality objectives

DQO for the acidifying and eutrophying compounds

- 10% accuracy or better for oxidised sulphur and oxidised nitrogen in single analysis in the laboratory,
- 15 % accuracy or better for other components in the laboratory,
- 0.1 units for pH,
- 15–25% uncertainty for the combined sampling and chemical analysis (components to be specified later),
- 90 % data completeness of the daily values.
- The targets, with respect to precision and detection limit follow the DQO of the WMO/GAW precipitation programme (WMO, 2004):

Measurement parameter	Detection limits	Precision	
		Overall	Laboratory
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
SO_4^{2-} (mg S L^{-1})	0.02	0.02	0.01
NO_3^- (mg N L^{-1})	0.02	0.01	0.01
Cl^- (mg L^{-1})	0.04	0.02	0.02
NH_4^+ (mg N L^{-1})	0.02	0.02	0.01
Ca^{++} (mg L^{-1})	0.02	0.02	0.01
Mg^{++} (mg L^{-1})	0.01	0.01	0.01
Na^+ (mg L^{-1})	0.02	0.01	0.01
K^+ (mg L^{-1})	0.02	0.01	0.01
Standard Gauge Precipitation Depth (mm)	0.02	0.2 daily 0.3 weekly	n/a n/a
Sample Depth (mm)	0.2	0.1 daily 0.3 weekly	n/a n/a

n/a Not applicable

The targets for the wet analysis of components extracted from air filters are the same as for precipitation. For SO_2 the limit above for sulphate is valid for the medium volume method with impregnated filter. For NO_2 determined as NO_2^- in solution the accuracy for the lowest concentrations is 0.01 mg N/l.

DQO for heavy metals

- 90% completeness
- 30% accuracy in annual average
- Accuracy in laboratory (c= concentration):

Pb:	15%	if c > 1 µg Pb/l
	25%	if c < 1 µg Pb/l
Cd:	15%	if c > 0.5 µg Cd/l
	25%	if c < 0.5 µg Cd/l
Cr:	15%	if c > 1 µg Cr/l
	25%	if c < 1 µg Cr/l
Ni:	15%	if c > 1 µg Ni/l
	25%	if c < 1 µg Ni/l
Cu:	15%	if c > 2 µg Cu/l
	25%	if c < 2 µg Cu/l
Zn:	15%	if c > 10 µg Zn/l
	25%	if c < 10 µg Zn/l
As:	15%	if c > 1 µg As/l
	25%	if c < 1 µg As/l
Hg:	15%	if c > 0.01 µg Hg/l
	25%	if c < 0.01 µg Hg/l

Annex 2

Data capture

Table A2.1: Data capture for main components in precipitation in 2004, in per cent.

Code	mm	mm off	pH	SO_4	XSO_4	NH_4	NO_3	Na	Mg	Cl	Ca	K	cond
AT0002R	100	-	100	100	100	100	100	100	100	100	100	98	100
AT0004R	19	-	100	100	100	100	100	100	100	100	100	100	100
AT0005R	100	-	100	100	100	100	100	100	100	100	100	99	100
AT0048R	69	-	100	100	100	100	100	100	100	99	100	97	100
BY0004R	99	-	99	86	73	97	86	68	68	59	68	68	81
CH0002R	100	-	100	98	98	98	98	98	98	98	98	98	100
CH0004R	100	-	100	100	100	100	100	100	100	100	100	100	100
CH0005R	99	-	98	98	98	98	98	98	97	98	98	98	98
CZ0001R	100	-	97	92	90	100	92	94	95	92	-	94	98
CZ0003R	100	-	96	96	96	96	96	96	96	96	96	96	96
DE0001R	100	-	100	100	100	100	100	100	100	100	100	100	100
DE0002R	100	-	100	100	100	100	100	100	100	100	100	100	100
DE0003R	100	-	95	95	95	95	95	95	95	95	95	95	95
DE0004R	16	-	99	99	99	99	99	99	99	99	99	99	99
DE0005R	45	-	100	100	100	100	100	100	100	100	100	100	100
DE0007R	89	-	99	99	99	99	99	99	99	99	99	99	99
DE0008R	100	-	99	99	99	99	99	99	99	99	99	99	99
DE0009R	100	-	99	99	99	99	99	99	99	99	99	99	99
DK0005R	100	-	100	100	100	98	100	98	100	100	100	100	90
DK0008R	100	-	100	100	100	100	100	100	100	100	100	100	91
DK0022R	100	-	100	100	100	100	100	100	100	100	100	100	91
EE0009R	99	-	100	99	99	99	99	99	99	99	99	99	100
EE0011R	99	-	100	100	100	100	100	100	100	100	100	100	100
ES0007R	100	-	94	93	93	92	93	92	92	93	92	92	94
ES0008R	100	-	95	95	95	95	95	94	94	95	94	94	90
ES0009R	100	-	96	-	-	94	94	92	92	94	92	92	95
FI0004R	100	-	100	100	100	100	100	100	100	100	100	100	100
FI0009R	99	100	98	98	98	98	98	98	98	98	98	98	98
FI0017R	99	-	89	89	89	89	89	89	89	89	89	89	89
FI0022R	99	-	100	100	100	100	100	100	100	100	100	100	100
FR0008R	100	-	99	99	99	99	99	99	99	99	99	99	99
FR0009R	100	-	98	98	98	98	98	98	98	98	98	98	98
FR0010R	100	-	97	97	97	97	97	97	97	97	97	97	97
FR0012R	100	-	90	89	89	89	89	89	89	89	89	89	90
FR0013R	100	-	97	96	96	96	96	96	96	96	96	96	97
FR0014R	100	-	97	97	97	97	97	97	97	97	97	97	97
FR0015R	100	-	91	91	91	91	91	91	91	91	91	91	91
FR0016R	100	-	81	81	81	81	81	81	81	81	81	81	81
FR0017R	100	-	91	91	91	91	91	91	91	91	91	91	91
GB0002R	100	-	100	100	100	100	100	100	100	100	100	100	100
GB0006R	14	-	100	100	-	100	100	100	100	100	100	100	100
GB0013R	88	-	81	100	100	81	100	100	100	100	100	81	100
GB0014R	99	-	100	100	100	100	100	100	100	100	100	100	100
GB0015R	100	-	100	100	100	100	100	100	100	100	100	100	100
HR0002R	-	44	90	91	-	87	91	89	88	89	88	89	91
HR0004R	-	40	100	98	-	97	98	96	95	100	97	96	100
HU0002R	100	100	92	100	100	92	100	100	100	100	100	92	100
IE0001R	100	100	99	99	99	99	99	99	99	99	99	99	99
IS0002R	100	-	100	100	-	-	-	100	-	-	-	-	-
IS0090R	100	100	100	100	-	100	100	100	100	100	100	100	100
IS0091R	100	100	100	100	100	100	100	100	100	100	100	100	100
IT0001R	17	-	100	100	100	100	100	100	100	100	100	100	99
IT0004R	100	-	100	99	99	99	99	99	99	99	99	85	100
LT0015R	100	-	100	100	-	100	100	100	-	100	100	100	99

Table 2.1, cont.

Code	mm	mm off	pH	SO_4	XSO_4	NH_4	NO_3	Na	Mg	Cl	Ca	K	cond
LV0010R	100	-	95	93	93	94	93	93	93	93	93	93	95
LV0016R	100	-	53	90	90	95	90	94	94	90	94	92	97
NO0001R	100	-	98	100	100	100	100	100	100	100	99	100	99
NO0008R	98	-	98	98	98	98	98	98	98	98	98	98	97
NO0015R	100	-	94	99	99	99	99	99	99	99	96	99	97
NO0039R	100	-	97	99	99	98	99	99	99	99	98	98	99
NO0055R	100	-	88	97	97	95	97	97	97	97	97	95	91
PL0002R	100	-	99	99	99	99	99	99	99	99	99	99	99
PL0003R	100	-	99	99	99	99	99	99	99	99	99	99	99
PL0004R	100	-	98	98	98	98	98	98	98	98	98	98	98
PL0005R	100	100	100	99	99	99	99	99	99	99	99	99	92
PT0001R	-	100	74	74	74	74	74	74	74	74	74	74	74
PT0003R	-	100	94	94	94	94	94	94	94	94	94	94	94
PT0004R	-	100	89	89	89	60	89	89	89	89	87	89	89
RU0001R	100	-	100	100	100	100	100	100	100	100	100	100	100
RU0013R	100	-	100	100	100	100	100	100	100	100	100	100	100
RU0016R	100	-	100	100	100	100	100	100	100	100	100	100	100
RU0017R	100	-	98	100	100	100	100	100	100	100	100	100	100
SE0005R	100	-	99	99	99	99	99	99	99	99	99	99	99
SE0011R	100	-	100	100	100	100	100	100	100	100	100	100	100
SE0014R	100	-	100	100	100	99	100	99	100	100	100	100	99
SI0008R	100	100	96	98	98	98	98	98	98	98	98	98	96
SK0002R	100	-	75	92	92	90	93	90	91	92	91	90	75
SK0004R	100	-	84	96	96	95	96	95	96	95	94	96	84
SK0005R	83	-	99	99	87	98	99	98	92	99	92	99	99
SK0006R	100	-	87	95	-	96	95	95	96	95	96	95	87
SK0007R	81	-	94	99	99	99	99	93	99	99	99	93	94
TR0001R	76	-	99	100	100	99	100	99	99	100	99	99	99
YU0005R	100	-	70	70	-	70	70	70	70	70	70	70	70

Table A2.2: Data capture for main components in air in 2004, in per cent.

Code	SO_2	NO_2	SO_4	XSO_4	SNO_3	NO_3	HNO_3	SNH_4	NH_4	NH_3	Na	Mg	Cl	Ca	K
AT0002R	94	70	97	-	-	97	93	-	97	97	97	97	-	97	97
AT0004R	95	19	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0005R	89	32	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0048R	94	99	-	-	-	-	-	-	-	-	-	-	-	-	-
BE0001R	-	85	-	-	-	-	-	-	-	-	-	-	-	-	-
BE0032R	-	90	-	-	-	-	-	-	-	-	-	-	-	-	-
BE0035R	-	29	-	-	-	-	-	-	-	-	-	-	-	-	-
CH0001G	95	85	98	-	-	-	-	-	-	-	-	-	-	-	-
CH0002R	99	99	99	-	90	-	-	90	-	-	-	-	-	-	-
CH0003R	-	100	-	-	-	-	-	-	-	-	-	-	-	-	-
CH0004R	100	100	-	-	-	-	-	-	-	-	-	-	-	-	-
CH0005R	99	87	100	-	98	-	-	99	-	-	-	-	-	-	-
CZ0001R	100	100	100	-	100	-	-	100	-	-	-	-	-	-	-
CZ0003R	100	100	100	-	100	-	-	99	-	-	-	-	-	-	-
DE0001R	97	83	98	-	100	-	-	30	-	-	-	-	-	-	-
DE0002R	100	91	-	-	-	-	-	-	-	-	-	-	-	-	-
DE0003R	86	87	90	-	88	-	-	33	-	-	-	-	-	-	-
DE0004R	56	48	58	-	57	-	-	24	-	-	-	-	-	-	-
DE0005R	58	38	-	-	-	-	-	-	-	-	-	-	-	-	-
DE0007R	94	90	99	-	92	-	-	39	-	-	-	-	-	-	-
DE0008R	91	89	-	-	-	-	-	-	-	-	-	-	-	-	-
DE0009R	98	90	99	-	98	-	-	39	-	-	-	-	-	-	-
DE0041R	97	90	98	-	97	-	-	30	-	-	-	-	-	-	-
DK0003R	100	-	99	-	99	-	-	99	-	-	100	-	-	-	-
DK0005R	-	87	-	-	-	-	-	-	-	-	99	-	-	-	-
DK0008R	99	93	100	-	99	-	-	99	-	-	-	-	-	-	-
EE0009R	96	99	-	-	-	-	-	-	-	-	-	-	-	-	-
EE0011R	99	98	-	-	-	-	-	-	-	-	-	-	-	-	-
ES0007R	99	96	96	-	96	96	-	97	-	-	-	-	-	-	-
ES0008R	98	97	59	-	95	59	-	92	-	42	-	-	-	-	-
ES0009R	95	94	89	-	98	89	-	95	-	36	-	-	-	-	-
ES0010R	96	94	90	-	91	90	-	91	-	-	-	-	-	-	-
ES0011R	95	94	94	-	94	94	-	98	-	-	-	-	-	-	-
ES0012R	95	94	97	-	98	97	-	99	-	-	-	-	-	-	-
ES0013R	98	98	95	-	99	95	-	99	-	-	-	-	-	-	-
ES0014R	98	98	93	-	98	93	-	95	-	-	-	-	-	-	-
ES0015R	97	97	91	-	96	91	-	93	-	-	-	-	-	-	-
ES0016R	98	96	92	-	96	92	-	96	-	-	-	-	-	-	-
FI0009R	96	91	96	-	96	-	-	95	-	-	-	-	-	-	-
FI0017R	97	99	99	-	99	-	-	99	-	-	-	-	-	-	-
FI0022R	96	91	98	-	98	-	-	98	-	-	-	-	-	-	-
FI0037R	97	98	99	-	99	-	-	99	-	-	-	-	-	-	-
FR0008R	97	-	96	-	-	-	-	-	-	-	-	-	-	-	-
FR0009R	99	-	99	-	-	-	-	-	-	-	-	-	-	-	-
FR0010R	98	-	98	-	-	-	-	-	-	-	-	-	-	-	-
FR0012R	95	-	93	-	-	-	-	-	-	-	-	-	-	-	-
FR0013R	94	98	94	-	-	-	-	-	-	-	-	-	-	-	-
FR0014R	95	-	94	-	-	-	-	-	-	-	-	-	-	-	-
FR0015R	100	76	99	-	-	-	-	-	-	-	-	-	-	-	-
FR0016R	91	-	92	-	-	-	-	-	-	-	-	-	-	-	-
FR0017R	95	-	96	-	-	-	-	-	-	-	-	-	-	-	-
GB0002R	99	-	99	-	-	-	-	-	-	-	-	-	-	-	-
GB0006R	92	100	97	-	-	100	100	-	100	100	-	-	-	-	-
GB0007R	-	-	98	-	-	-	-	-	-	-	-	-	-	-	-
GB0013R	84	-	95	-	-	-	-	-	-	-	-	-	-	-	-
GB0014R	99	-	100	-	-	-	-	-	-	-	-	-	-	-	-
GB0015R	100	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0036R	-	96	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 2.2, cont.

Code	SO_2	NO_2	SO_4	XSO_4	SNO_3	NO_3	HNO_3	SNH_4	NH_4	NH_3	Na	Mg	Cl	Ca	K
GB0037R	-	90	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0038R	-	93	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0045R	-	73	-	-	-	-	-	-	-	-	-	-	-	-	-
HU0002R	93	99	93	-	-	93	93	-	93	93	-	-	-	-	-
IE0001R	99	100	99	-	100	-	-	100	-	-	100	100	-	100	100
IS0002R	-	-	99	-	-	-	-	-	-	-	-	-	-	-	-
IS0091R	-	-	100	-	-	100	-	-	-	-	-	100	-	-	-
IT0001R	93	98	93	-	-	93	93	-	93	93	-	-	-	-	-
IT0004R	64	89	92	-	-	92	-	-	92	-	-	-	-	-	-
LT0015R	97	96	97	-	97	-	-	97	-	-	-	-	-	-	-
LV0010R	98	98	98	-	98	98	-	97	97	-	-	-	-	-	-
LV0016R	100	100	100	-	100	100	-	100	100	-	-	-	-	-	-
NL0009R	-	99	-	-	-	-	-	-	95	-	-	-	-	-	-
NO0001R	99	100	99	99	94	94	99	93	93	99	98	98	98	98	98
NO0008R	94	100	94	94	84	84	84	84	84	84	94	94	93	94	94
NO0015R	100	100	99	99	72	72	73	73	73	73	100	100	100	100	100
NO0039R	99	100	100	100	82	82	85	83	83	84	100	100	99	100	100
NO0042G	96	-	96	96	79	79	82	82	82	82	96	96	96	96	96
NO0055R	93	100	92	92	71	71	76	71	73	-	93	93	93	93	93
PL0002R	98	97	98	-	98	98	-	97	97	-	-	-	-	-	-
PL0003R	100	100	100	-	100	100	-	100	100	-	-	-	-	-	-
PL0004R	100	99	100	-	99	99	-	98	100	-	-	-	-	-	-
PL0005R	99	98	99	-	99	-	-	99	-	-	-	-	-	-	-
RU0001R	91	-	92	-	-	92	-	-	94	-	-	-	-	-	-
RU0016R	55	-	56	-	-	56	-	-	56	-	-	-	-	-	-
RU0017R	84	-	80	-	-	80	-	-	80	-	-	-	-	-	-
SE0005R	100	99	100	-	99	-	-	99	-	-	-	-	-	-	-
SE0008R	100	93	100	-	-	-	-	-	-	-	-	-	-	-	-
SE0011R	100	99	100	-	100	-	-	100	-	-	-	-	-	-	-
SE0014R	80	99	95	-	80	-	-	94	-	-	-	-	-	-	-
SI0008R	98	49	98	98	98	-	-	98	-	-	98	98	98	98	66
SK0002R	97	97	97	-	-	-	-	-	-	-	-	-	-	-	-
SK0005R	99	98	99	-	-	99	99	-	-	-	-	-	-	-	-
SK0006R	97	97	96	-	-	96	97	-	-	-	-	-	-	-	-
SK0007R	91	100	91	-	-	91	91	-	-	-	-	-	-	-	-
TR0001R	92	91	92	-	92	92	92	90	88	92	-	-	-	-	-
YU0005R	96	95	-	-	-	-	-	-	-	-	-	-	-	-	-

Table A2.3: Data capture for particulate matter in air in 2003, in per cent.

Code	PM_{10}	$PM_{2.5}$	PM_1	SPM
AT0002R	98	94	98	-
AT0004R	22	-	-	-
AT0005R	93	-	-	-
AT0048R	95	93	-	-
CH0001G	-	-	-	94
CH0002R	98	99	-	-
CH0003R	100	-	-	-
CH0004R	100	98	99	-
CH0005R	100	-	-	-
CY0002R	98	-	-	-
DE0001R	96	-	-	-
DE0002R	100	98	99	-
DE0003R	96	96	-	-
DE0004R	42	42	-	-
DE0005R	42	-	-	-
DE0007R	100	-	-	-
DE0008R	100	-	-	-
DE0009R	100	-	-	-
DE0041R	96	-	-	-
DK0005R	68	-	-	-
ES0007R	96	94	-	-
ES0008R	59	62	-	-
ES0009R	89	83	-	-
ES0010R	89	87	-	-
ES0011R	94	94	-	-
ES0012R	96	97	-	-
ES0013R	95	93	-	-
ES0014R	93	92	-	-
ES0015R	89	89	-	-
ES0016R	91	84	-	-
GR0002R	27	-	-	-
IT0001R	96	-	-	-
IT0004R	96	92	-	-
LT0015R	-	-	-	100
NO0001R	98	98	-	-
SE0005R	-	-	-	100
SE0008R	-	-	-	94
SE0011R	61	57	-	99
SE0012R	98	84	-	-
SE0014R	-	-	-	99
SE0035R	94	19	-	-
SI0008R	16	32	-	-
SK0002R	-	-	-	100
SK0004R	90	-	-	-
SK0005R	99	-	-	-
SK0006R	98	-	-	-
SK0007R	-	-	-	101

Table A2.4: Data capture for heavy metals in precipitation in 2004, in per cent.

Code	Pb	Cd	Zn	Hg	Ni	As	Cu	Co	Cr	Mn	V	Fe	mm
BE0004R	-	-	-	100	-	-	-	-	-	-	-	-	94
CZ0001R	100	100	-	-	100	-	-	-	-	100	-	-	100
CZ0003R	98	98	-	-	98	-	-	-	-	98	-	-	100
DE0001R	99	99	97	100	99	99	97	99	96	99	99	99	100
DE0002R	98	98	98	100	98	98	98	98	98	98	98	98	100
DE0003R	91	91	91	-	91	91	86	91	91	91	91	91	100
DE0007R	76	75	76	74	76	76	76	76	76	75	76	76	100
DE0008R	100	100	100	-	100	100	100	97	100	100	100	100	100
DE0009R	100	100	99	100	100	100	99	100	100	100	100	100	100
DK0008R	100	100	100	-	100	100	100	-	100	-	-	-	92
DK0020R	100	100	100	-	100	100	100	-	100	-	-	-	92
DK0022R	100	100	100	-	100	100	100	-	100	-	-	-	100
DK0031R	100	100	100	-	100	100	100	-	100	-	-	-	100
EE0009R	100	100	100	-	-	100	100	-	-	-	-	-	100
EE0011R	100	100	100	-	-	100	100	-	-	-	-	-	100
ES0008R	100	100	100	-	100	100	100	-	100	-	-	-	99
ES0009R	40	16	-	-	64	6	100	-	96	-	-	-	96
FI0008R	100	100	-	-	100	100	100	-	100	100	-	100	100
FI0017R	100	100	100	-	100	100	100	-	100	100	100	100	100
FI0022R	100	100	100	-	100	100	100	-	100	100	100	100	100
FI0036R	100	100	100	-	100	100	100	-	100	100	100	100	100
FI0053R	100	100	-	-	100	100	100	-	100	100	-	100	100
FI0092R	100	100	100	-	100	100	100	-	100	100	100	100	100
FI0093R	100	100	100	-	100	100	100	-	100	100	100	100	100
FI0096G	-	-	-	100	-	-	-	-	-	-	-	-	97
FR0090R	100	100	100	-	100	100	100	-	100	-	-	-	100
GB0006R	100	100	100	-	100	100	100	-	100	-	-	-	100
GB0013R	100	99	100	-	100	100	100	-	100	-	-	-	95
GB0017R	100	100	100	-	100	100	100	-	100	-	-	-	88
GB0091R	96	96	96	-	95	-	94	-	96	-	-	-	87
IE0001R	100	100	100	100	100	100	100	-	100	100	100	-	100
IS0090R	98	98	98	-	98	98	98	-	98	98	98	98	100
IS0091R	100	100	100	-	100	-	100	-	100	100	-	100	100
LT0015R	100	100	100	-	-	-	100	-	-	-	-	-	100
LV0010R	95	96	96	-	96	96	96	-	-	96	-	-	102
LV0016R	99	98	99	-	99	99	99	-	-	99	-	-	100
NL0009R	84	84	84	-	84	68	84	-	84	-	-	-	89
NL0091R	100	100	100	91	100	100	100	-	100	-	-	-	90
NO0001R	100	100	100	100	100	100	100	100	100	-	100	-	84
NO0039R	100	100	100	-	-	-	-	-	-	-	-	-	100
NO0047R	99	99	100	-	99	99	99	99	99	-	-	-	99
NO0055R	99	99	99	-	-	-	-	-	-	-	-	-	100
NO0056R	100	100	100	-	-	-	-	-	-	-	-	-	100
PL0004R	100	100	77	-	100	-	100	-	100	-	-	-	100
PL0005R	99	99	99	77	99	99	99	-	99	-	-	-	99
PT0001R	74	74	74	-	74	-	74	-	-	74	-	-	-
PT0003R	94	94	94	-	94	-	94	-	-	94	-	-	-
PT0004R	89	89	89	-	89	-	89	-	-	89	-	-	-
PT0010R	58	58	58	-	58	-	58	-	-	58	-	-	-
SE0014R	-	-	-	100	-	-	-	-	-	-	-	-	97
SE0051R	100	100	100	-	100	100	100	-	100	99	100	-	100
SE0097R	100	100	100	-	100	100	100	100	100	100	100	-	97
SK0002R	100	97	56	-	100	100	87	-	100	-	-	-	99
SK0004R	100	100	69	-	100	100	100	-	100	-	-	-	99
SK0005R	100	100	68	-	100	100	100	-	100	-	-	-	99
SK0006R	100	100	33	-	89	100	100	-	100	-	-	-	99
SK0007R	100	100	73	-	100	100	100	-	89	-	-	-	99

Table A2.5: Data capture for heavy metals in air in 2004, in per cent.

Code	Pb	Cd	Zn	Hg	Ni	As	Cu	Co	Cr	Mn	V	Fe
AT0002R	16	16	-	-	4	4	-	-	-	-	-	-
AT0005R	16	16	-	-	-	-	-	-	-	-	-	-
AT0048R	16	16	-	-	-	-	-	-	-	-	-	-
CZ0001R	46	46	-	-	-	-	-	-	-	-	-	-
CZ0003R	49	49	-	-	-	-	-	-	-	-	-	-
DE0001R	98	98	50	-	92	50	98	-	-	98	98	98
DE0002R	98	98	98	-	98	98	98	-	-	98	98	98
DE0003R	98	98	50	-	98	50	98	-	-	98	98	98
DE0007R	99	99	99	-	99	99	99	-	-	99	99	99
DE0008R	98	-	50	-	98	50	98	-	-	98	98	98
DE0009R	98	98	48	-	96	50	98	-	-	96	98	98
DK0003R	99	99	99	-	99	99	99	-	99	99	-	99
DK0008R	100	100	100	-	100	100	100	-	100	100	-	100
DK0011G	83	-	83	74	83	83	83	-	83	83	-	83
DK0031R	85	85	85	-	85	85	85	-	85	85	-	85
ES0008R	10	10	-	-	-	-	10	-	-	-	-	-
ES0009R	13	13	-	-	-	-	13	-	-	-	-	-
FI0036R	100	100	100	-	100	100	100	-	100	100	100	100
FI0096G	-	-	-	69	-	-	-	-	-	-	-	-
GB0013R	100	100	100	-	100	100	100	-	100	-	-	-
GB0017R	28	28	28	49	28	28	28	-	28	-	-	-
GB0091R	66	66	66	28	66	66	66	-	66	-	-	-
IS0091R	92	92	96	99	99	96	96	-	100	96	96	99
LT0015R	99	99	99	-	-	-	99	-	-	-	-	-
LV0010R	100	98	98	-	100	-	100	-	-	98	-	-
LV0016R	100	100	100	-	96	100	100	-	-	100	-	-
NL0009R	50	50	50	-	50	50	-	-	-	-	-	-
NO0001R	96	96	96	96	96	96	96	96	0 95.90	-	96	-
NO0042G	28	28	28	85	28	28	28	28	1 28.41	28	28	-
NO0090R	-	-	-	67	-	-	-	-	-	-	-	-
PL0005R	-	-	-	13	-	-	-	-	-	-	-	-
SE0014R	97	97	-	26	97	97	-	-	-	-	-	-
SI0008R	17	17	-	-	17	17	17	-	17	-	-	-
SK0002R	96	90	98	-	96	100	100	-	90	96	-	-
SK0004R	86	86	84	-	80	84	84	-	78	84	-	-
SK0005R	95	97	97	-	95	99	97	-	99	93	-	-
SK0006R	87	89	90	-	99	90	97	-	99	95	-	-
SK0007R	97	92	97	-	97	97	97	-	94	97	-	-

Table A2.6: Data capture for ozone in 2004, in per cent.

Code	O_3	Code	O_3	Code	O_3	Code	O_3	Code	O_3
AT0002R	90	CY0002R	91	ES0011R	94	GB0031R	89	NO0052R	99
AT0004R	22	CZ0001R	98	ES0012R	94	GB0032R	99	NO0055R	99
AT0005R	95	CZ0003R	96	ES0013R	98	GB0033R	98	NO0056R	100
AT0030R	91	DE0001R	96	ES0014R	97	GB0034R	96	PL0002R	100
AT0032R	96	DE0002R	89	ES0015R	96	GB0035R	99	PL0003R	100
AT0033R	92	DE0003R	95	ES0016R	97	GB0036R	90	PL0004R	100
AT0034G	92	DE0004R	56	FI0009R	90	GB0037R	85	PL0005R	98
AT0037R	96	DE0005R	56	FI0017R	98	GB0038R	96	PT0004R	62
AT0038R	96	DE0007R	91	FI0022R	92	GB0039R	96	SE0005R	58
AT0040R	95	DE0009R	96	FI0037R	99	GB0044R	96	SE0011R	99
AT0041R	93	DE0012R	86	FR0008R	97	GB0045R	93	SE0012R	95
AT0042R	91	DE0026R	96	FR0008R	97	GR0001R	100	SE0013R	100
AT0043R	91	DE0035R	91	FR0008R	98	GR0002R	76	SE0014R	100
AT0044R	90	DE0039R	91	FR0008R	98	HU0002R	89	SE0032R	99
AT0045R	70	DE0042R	87	FR0009R	97	IE0001R	73	SE0035R	100
AT0046R	95	DE0045R	89	FR0010R	96	IE0031R	98	SE0039R	98
AT0047R	90	DE0046R	70	FR0012R	85	IT0001R	98	SI0008R	94
AT0048R	95	DE0047R	93	FR0013R	96	IT0004R	81	SI0031R	95
BE0001R	90	DK0005R	83	FR0014R	93	IT0004R	86	SI0032R	99
BE0032R	86	DK0031R	87	FR0015R	99	LT0015R	95	SI0033R	87
BE0035R	88	DK0041R	97	FR0016R	98	LV0010R	92	SK0002R	90
BG0053R	99	EE0009R	99	FR0017R	98	MT0001R	89	SK0004R	99
BG0053R	98	EE0011R	98	GB0002R	91	NO0001R	98	SK0006R	83
CH0002R	94	ES0007R	98	GB0006R	75	NO0015R	99	SK0007R	98
CH0003R	95	ES0008R	97	GB0013R	97	NO0039R	100		
CH0004R	95	ES0009R	95	GB0014R	99	NO0042G	99		
CH0005R	94	ES0010R	94	GB0015R	84	NO0043R	100		

Table A2.7: The number of samples of hydrocarbons (HC) and carbonyls (Carb) in 2003.

Station	Number of samples	
	HC	Carb
Pallas	93	-
Utö	100	91
Zingst	-	95
Waldhof	-	95
Schmücke	-	97
Brotjacklriegel	-	42
Hohenpeissenberg[1)]	340	-
Košetice	91	98
Starina	86	-
Rigi[1)]	301	-
Donon	103	51
Peyrusse Vieille	80	48
La Tardiere	84	52
Campisábalos	99	102

Table A2.8: Data capture for POPs in 2004, in per cent.

	precip	precip + dry dep	air	sampl frequenzy
BE0004R	94			
CZ0003R	91		14	1 day a week
DE0001R	94			
DE0009R	100			
ES0008R			2	14 -20 Dec, daily
FI0096R		23	23	1 week a month
GB0014R			99	Biweekly sampling, 3 monthly analysis
IS0091R	100		100	Biweekly
LV0010R			100	Monthly
LV0016R			100	Monthly
NL0091R	100			
NO0042G			29	2 days a week
NO0001R	100		13	1 day a week
SE0012R		32	21	1 week a month
SE0014R		91	91	Biweekly

Annex 3

Below detection limit

Table A3.1: Number of samples below the detection limit for main components in precipitation in 2004, in per cent.

Code	pH	SO_4	XSO_4	NH_4	NO_3	Na	Mg	Cl	Ca	K	cond
AT0002R	0	0	0	0	0	4	1	1	0	15	0
AT0004R	0	0	0	0	0	0	9	0	0	11	0
AT0005R	0	0	0	2	0	16	4	9	1	27	0
AT0048R	0	0	0	0	0	9	3	11	0	22	0
BY0004R	0	0	0	0	0	0	0	0	0	0	0
CH0002R	0	0	0	0	0	8	2	0	19	14	0
CH0004R	0	0	0	0	0	2	0	0	17	13	0
CH0005R	0	0	0	0	0	13	3	0	20	11	0
CZ0001R	0	2	2	4	4	0	0	2		6	0
CZ0003R	0	1	1	1	1	1	0	0	4	3	0
DE0001R	0	0	0	4	0	0	0	0	0	8	0
DE0002R	0	0	0	0	0	2	1	0	0	2	1
DE0003R	0	0	0	0	0	9	27	0	9	51	0
DE0004R	0	0	0	0	0	4	15	0	12	65	0
DE0005R	0	0	0	0	0	9	9	9	0	30	0
DE0007R	0	0	0	0	0	3	8	0	0	26	0
DE0008R	0	0	0	0	0	9	21	2	4	47	0
DE0009R	0	0	0	4	2	0	0	0	0	32	0
DK0005R	0	0	0	0	0	0	0	0	0	0	0
DK0008R	0	0	0	0	0	0	0	0	0	0	0
DK0022R	0	0	0	0	0	0	0	0	0	0	0
EE0009R	0	0	0	7	11	0	0	0	9	4	0
EE0011R	0	0	0	0	17	0	0	0	0	0	0
ES0007R	0	0	0	35	2	0	0	15	0	0	1
ES0008R	0	0	0	7	1	0	0	0	0	0	0
ES0009R	0	0	0	20	5	6	0	19	0	5	4
FI0004R	0	0	0	0	0	0	0	0	0	0	0
FI0009R	0	0	0	0	0	0	0	0	0	0	0
FI0017R	0	0	0	0	0	0	0	0	0	0	0
FI0022R	0	0	0	0	0	0	0	0	0	0	0
FR0008R	0	1	1	2	0	8	44	5	3	24	0
FR0009R	0	0	0	0	0	5	27	2	1	15	0
FR0010R	0	0	0	1	0	3	23	1	1	9	0
FR0012R	0	0	0	5	1	5	20	4	1	22	0
FR0013R	0	0	0	2	0	3	24	2	1	14	0
FR0014R	0	0	0	1	1	12	40	6	1	26	0
FR0015R	0	0	0	0	1	0	2	0	0	9	0
FR0016R	0	0	0	12	0	26	37	15	2	28	0
FR0017R	0	0	0	1	0	6	22	5	4	23	0
GB0002R	0	0	0	6	1	2	5	2	4	7	25
GB0006R				2							
GB0013R	0	0	0	5	0	0	0	0	0	0	5
GB0014R	0	0	0	0	0	0	0	0	0	0	0
GB0015R	0	0	0	41	11	4	0	0	0	4	7
HR0002R	0	0	0	0	0	0	0	0	0	0	0
HR0004R	0	0	0	0	0	0	0	0	0	0	0
HU0002R	0	0	0	25	5	0	0	0	0	2	0
IE0001R	0	0	0	22	2	0	1	0	1	1	0
IS0002R	0	1				0					
IS0090R	0	0		0	0	0	0	0	0	0	0
IS0091R	0	0	0	43	5	0	0	0	0	2	0
IT0001R	0	0	0	0	0	0	0	0	0	0	0
IT0004R	0	0	0	0	0	0	0	0	0	0	0
LT0015R	0	0	0	0	0	0		0	0	0	0
LV0010R	0	0	0	0	0	0	1	0	0	5	0
LV0016R	0	0	0	0	0	2	2	3	1	4	0
NO0001R	0	1	1	4	2	0	1	0	0	7	0
NO0008R	0	0	0	2	1	0	4	0	0	1	0
NO0015R	0	1	1	1	6	0	6	0	0	1	0
NO0039R	0	1	1	12	23	0	3	0	0	1	0
NO0055R	0	2	2	2	2	0	3	2	0	0	0
PL0002R	0	0	0	0	0	0	0	0	0	0	0
PL0003R	0	0	0	0	0	0	0	0	0	0	0

Table A3.1, cont.

Code	pH	SO_4	XSO_4	NH_4	NO_3	Na	Mg	Cl	Ca	K	cond
PL0004R	0	0	0	0	0	0	0	0	0	0	0
PL0005R	0	0	0	2	0	0	0	1	0	0	0
PT0001R	0	5	5	10	33	24	33	0	0	33	0
PT0003R	0	2	2	30	32	0	5	0	3	16	0
PT0004R	0	0	0	38	14	0	0	0	0	10	0
RU0001R	0	0	0	0	0	0	0	0	0	0	0
RU0013R	0	0	0	0	0	0	0	0	0	0	0
RU0016R	0	0	0	0	0	0	0	0	0	0	0
RU0017R	0	0	0	0	0	0	0	0	0	0	0
SE0005R	0	0	0	0	0	40	36	10	33	50	0
SE0011R	0	0	0	0	0	10	6	0	12	43	0
SE0014R	0	0	0	1	0	1	2	0	5	27	0
SI0008R	0	0	0	2	0	9	12	1	4	20	0
SK0002R	0	0	0	0	0	2	11	1	1	5	0
SK0004R	0	0	0	0	0	1	11	0	1	2	0
SK0005R	0	0	0	0	0	0	0	0	0	0	0
SK0006R	0	0	0	0	0	2	7	1	0	1	0
SK0007R	0	0	0	0	0	0	0	0	0	3	0
TR0001R	0	0	0	0	0	0	0	0	0	0	0
YU0005R	0	0	0	0	0	0	0	0	0	0	0

between25 and 50% below the detection limit
between 50 and 75% below the detection limit
more than 75% below the detection limit

Table A3.2: Number of samples below the detection limit for main components in air in 2004, in per cent.

Code	SO_2	NO_2	SO_4	XSO_4	SNO_3	NO_3	HNO_3	SNH_4	NH_4	NH_3	Na	Mg	Cl	Ca	K
AT0002R	0	0	0			0	0		0	0	0	5		0	0
AT0004R	0	0													
AT0005R	0	0													
AT0048R	0	0													
BE0001R		0													
BE0032R		0													
BE0035R		0													
CH0001G	5	0	11												
CH0002R	0	0	0		0			0							
CH0003R		0													
CH0004R	0	0													
CH0005R	0	0	0		0			0							
CZ0001R	0	19	0		0			0							
CZ0003R	0	7	0		0			0							
DE0001R	0	0	0		8			7							
DE0002R	1	0													
DE0003R	0	0	0		15			46							
DE0004R	0	0	0		2			2							
DE0005R	1	0													
DE0007R	0	0	0		4			10							
DE0008R	12	0													
DE0009R	0	0	0		2			14							
DE0041R	0	0	0		8			7							
DK0003R	0		0		0			0			1				
DK0005R		12									0				
DK0008R	1	3	0		0			0							
EE0009R	0	0													
EE0011R	0	0													
ES0007R	0	0	0		1	0		1							
ES0008R	0	0	0		0	0		1		0					
ES0009R	0	0	0		0	0		0		17					
ES0010R	0	0	0		1	0		1							
ES0011R	0	0	0		1	0		1							
ES0012R	0	0	0		0	0		0							
ES0013R	0	0	0		2	0		0							
ES0014R	0	0	0		0	0		0							
ES0015R	0	0	0		1	0		1							
ES0016R	0	0	0		2	0		0							
FI0009R	0	0	0		0			0							
FI0017R	1	0	0		0			0							
FI0022R	0	0	0		0			0							
FI0037R	0	0	0		0			0							
FR0008R	58	0	1												
FR0009R	44		0												
FR0010R	75		2												
FR0012R	59		3												
FR0013R	44	0	0												
FR0014R	73		1												
FR0015R	52	0	0												
FR0016R	90		3												
FR0017R	73		1												
GB0002R	0		0												
GB0006R	0	7	0			0	0		0	0					
GB0007R			0												
GB0013R	0		0												
GB0014R	0		0												
GB0015R	0														
GB0036R		0													
GB0037R		0													
GB0038R		0													
GB0045R		0													
HU0002R	1	0	0			1	1		3	5					
IE0001R	10	7	0		4			1			4	20		17	28
IS0002R			1												
IS0091R			0			0							0		

Table A3.2, cont.

0□4□□□□□□□ NL0009R□□0□□□□□□□0□□□□□□□ NO0001R□2□0□0□0□0□3□32□0□18□4□1□22□34□24□16□ NO0008R□5□1□1□1□0□4□51□0□28□0□0

(yellow)	between25 and 50% below the detection limit
(orange)	between 50 and 75% below the detection limit
(red)	more than 75% below the detection limit

Table A3.3: Number of samples below the detection limit for heavy metals in precipitation in 2004, in per cent.

Code	Pb	Cd	Zn	Hg	Ni	As	Cu	Co	Cr	Mn	V	Fe
CZ0001R	47	8			61					6		
CZ0003R	21	0			62					6		
DE0001R	0	0	0	0	0	0	0	0	0	0	0	0
DE0002R	0	0	0	0	0	0	0	0	0	0	0	0
DE0003R	0	0	0		0	0	0	0	0	0	0	0
DE0007R	0	0	0	0	0	0	0	0	0	0	0	0
DE0008R	0	0	0		0	0	0	0	0	0	0	0
DE0009R	0	0	0	0	0	0	0	0	0	0	0	0
DK0008R	0	0	0		0	0	0		0			
DK0020R	0	0			0	0	0		0			
DK0022R	0	0	0		0	0	0		0			
EE0009R	83	33	92			58	0					
EE0011R	75	17	33			67	0					
ES0008R	0	0	0		0		0		0			
ES0009R	0	0			0		0		3			
FI0008R	0	0			0	0	0		0	0		0
FI0017R	0	0	0		0	0	0		0	0	0	0
FI0022R	0	0	0		0	0	0		17	0	0	0
FI0036R	0	0	0		0	0	0		25	0	0	8
FI0053R	0	0			0	0	0		0	0		0
FI0092R	0	0	0		0	0	0		17	0	0	0
FI0093R	0	0	0		0	0	0		0	0	0	0
FI0096G				0								
GB0006R	8	8	8		0	0	0		17			
IE0001R	58	92	0	100	83	100	0		92	8	100	
IS0090R	0	65	0		2	17	0		31	0	0	6
IS0091R	0	52	0		17		0		24	0		2
LT0015R	0	0	0				0					
LV0010R	7	5	37		41	84	14			77		
LV0016R	13	19	57		49	95	16			87		
NO0001R	0	91	0	0	91	49	60	98	98		45	
NO0039R	27	98	6									
NO0047R	0	61	0		0	9	0	11	36			
NO0055R	0	27	0									
NO0056R	0	88	0									
PL0004R	0	0	0		0		0		0			
PL0005R	0	0	0	55	0	0	0		0			
PT0001R	62	100	0		95		33			57		
PT0003R	68	98	0		94		32			70		
PT0004R	67	100	0		90		71			76		
SE0014R				0								
SE0051R	0	8	0		0	15	0		62	0	0	
SE0097R	0	0	0		0	50	0	17	33	0	0	
SK0002R	0	0	0		8	0	0		0			
SK0004R	0	0	0		25	8	0		8			
SK0005R	0	0	0		8	8	0		8			
SK0006R	0	0	0		36	0	0		8			
SK0007R	0	0	0		42	8	0		9			

between25 and 50% below the detection limit

between 50 and 75% below the detection limit

more than 75% below the detection limit

Table A3.4: Number of samples below the detection limit for heavy metals in air in 2004, in per cent.

Code	Pb	Cd	Zn	Hg	Ni	As	Cu	Co	Cr	Mn	V	Fe
AT0002R	0	7			20	40						
AT0005R	11	63										
AT0048R	9	74										
CZ0001R	0	0										
CZ0003R	0	0										
DE0001R	0	0	0		0	0	0			0	0	0
DE0002R	0	0	0		0	0	0			0	0	0
DE0003R	0	0	0		0	0	0			0	0	0
DE0007R	0	0	0		0	0	0			0	0	0
DE0008R	0		0		0	0	0			0	0	0
DE0009R	0	0	0		0	0	0			0	0	0
DK0003R	0	83	3		5	7	8		61	1		0
DK0008R	3	89	8		2	11	17		67	9		0
ES0008R	8	16	7	50	29	43	0		93			
ES0009R	30	13					2					
FI0036R	0	0	0		0	2	0		19	0	0	0
FI0096G				0								
IS0091R	0	4	0	0	0	0	0		0	0	0	0
LT0015R	0	0	0				0					
LV0010R	2	4	6		4		2			2		
LV0016R	0	2	0		10	4	0			2		
NO0001R	23	22	16		31	41	46	60	98		24	
NO0042G	2	38	49	0	30	49	24	8	78	0	30	
NO0090R				0								
PL0005R				6								
SE0014R	0	0		0	0	0						
SI0008R	0	0			0	0	0		0			
SK0002R	0	0	23		4	23	28		21	0		
SK0004R	0	0	2		0	2	0		2	0		
SK0005R	0	0	0		0	0	0		9	0		
SK0006R	0	0	0		2	0	0		2	0		
SK0007R	0	0	4		0	0	2		0	0		

between25 and 50% below the detection limit
between 50 and 75% below the detection limit
more than 75% below the detection limit

Table A3.5: Number of samples below the detection limit for particulate matter in 2004, in per cent.

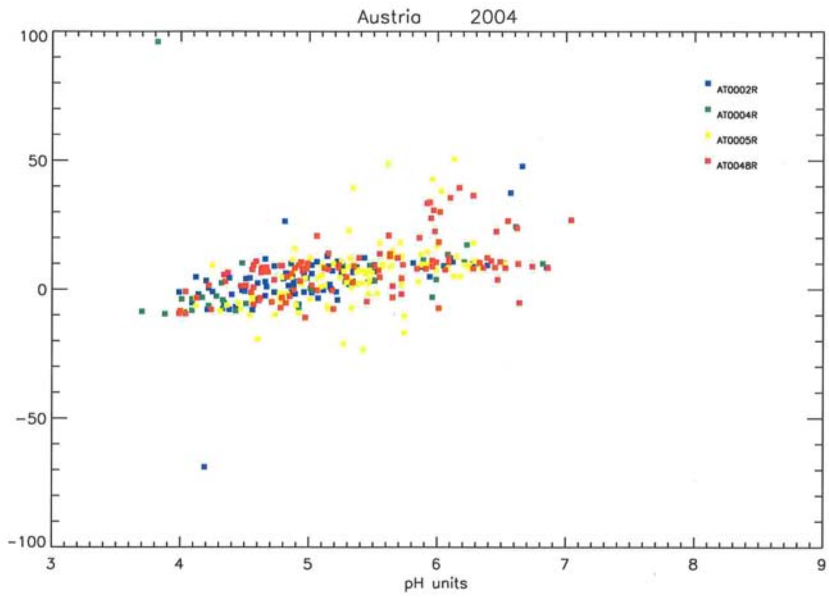
Code	PM10	PM2.5	PM1	SPM
AT0004R	0			
AT0005R	0			
AT0048R	0	0		
CH0001G				26
CH0002R	0	0		
CH0003R	0			
CH0004R	0	0	0	
CH0005R	0			
CY0002R	0			
DE0001R	0			
DE0002R	0	0	0	
DE0003R	2	1		
DE0004R	0	0		
DE0005R	0			
DE0007R	0			
DE0008R	0			
DE0009R	0			
DE0041R	0			
DK0005R	1			
ES0007R	0	0		
ES0008R	0	0		
ES0009R	0	0		
ES0010R	0	0		
ES0011R	0	0		
ES0012R	0	0		
ES0013R	0	0		
ES0014R	0	0		
ES0015R	0	0		
ES0016R	0	0		
GR0002R	0			
IT0001R	0			
IT0004R	0	0		
LT0015R				0
NO0001R	2	0		
SE0005R				97
SE0008R				71
SE0011R	5	11		70
SE0012R	4	19		
SE0014R				82
SE0035R	12	32		
SI0008R	0	0		
SK0002R				2
SK0004R	0			
SK0005R	0			
SK0006R	0			
SK0007R				0

between25 and 50% below the detection limit
between 50 and 75% below the detection limit
more than 75% below the detection limit

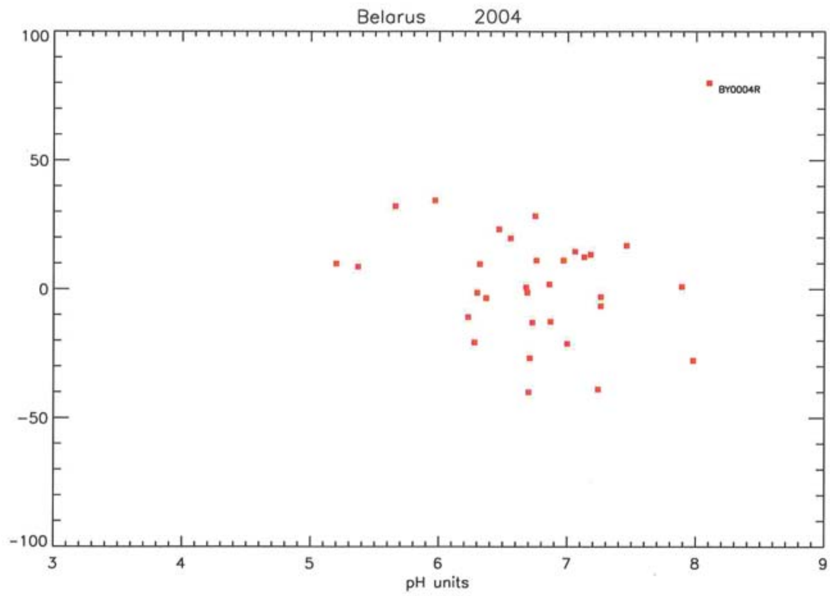
Annex 4

Ion balances in precipitation samples 2004

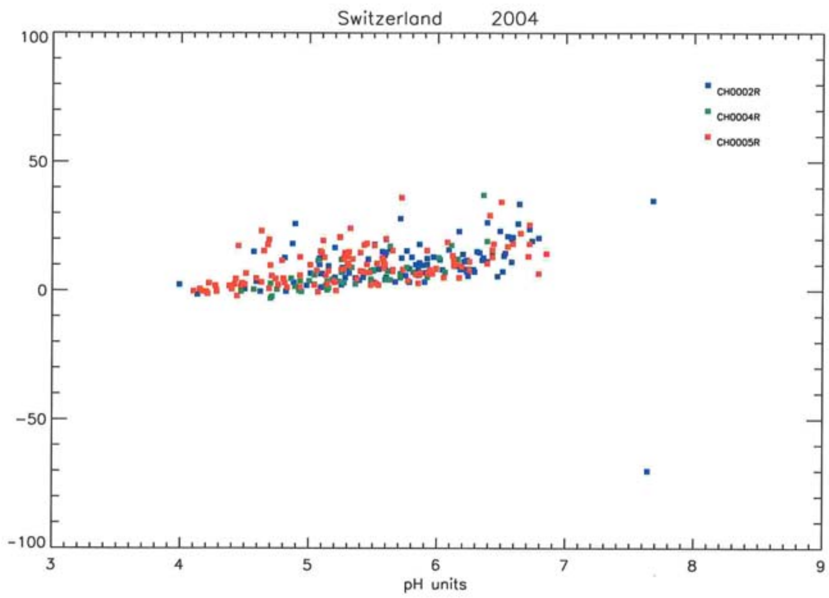
Units: Ion balance (per cent)



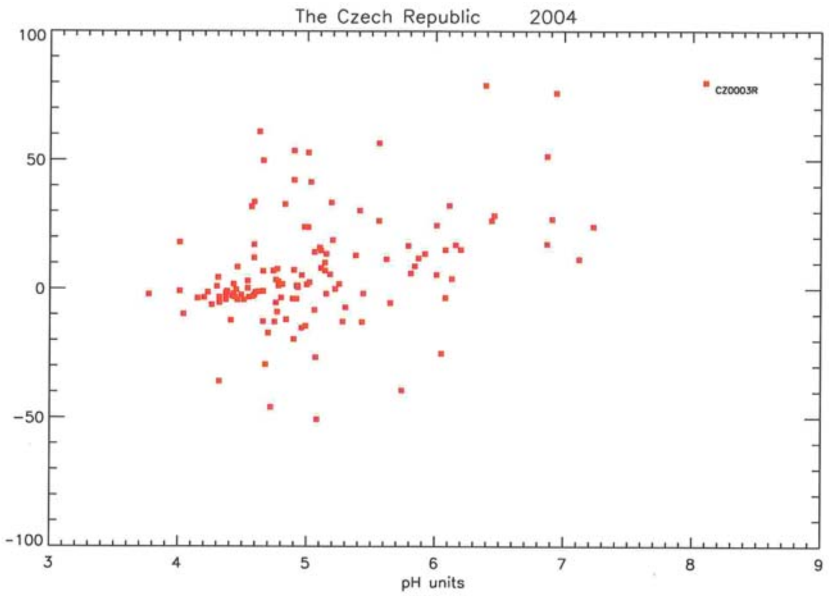
Austria 2004
AT0002R
AT0004R
AT0005R
AT0048R
pH units

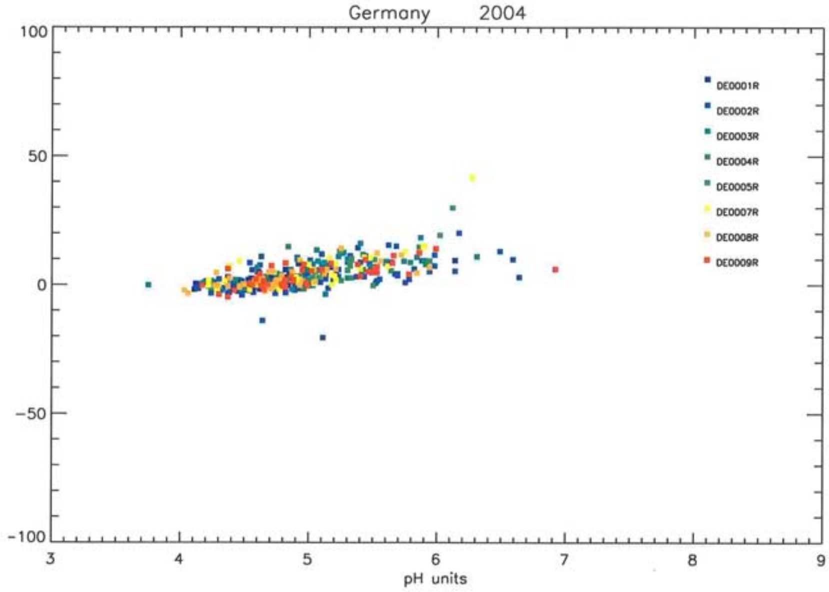


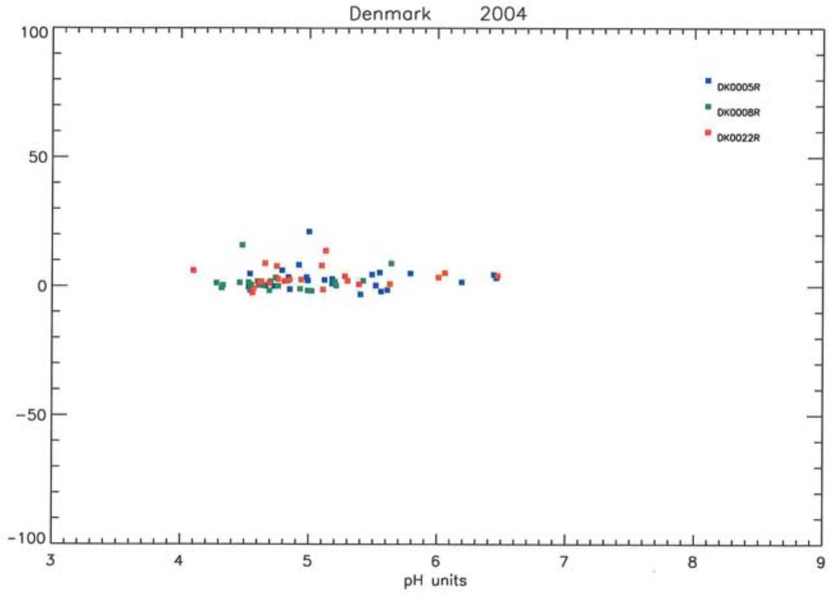
Belarus 2004
BY0004R
pH units

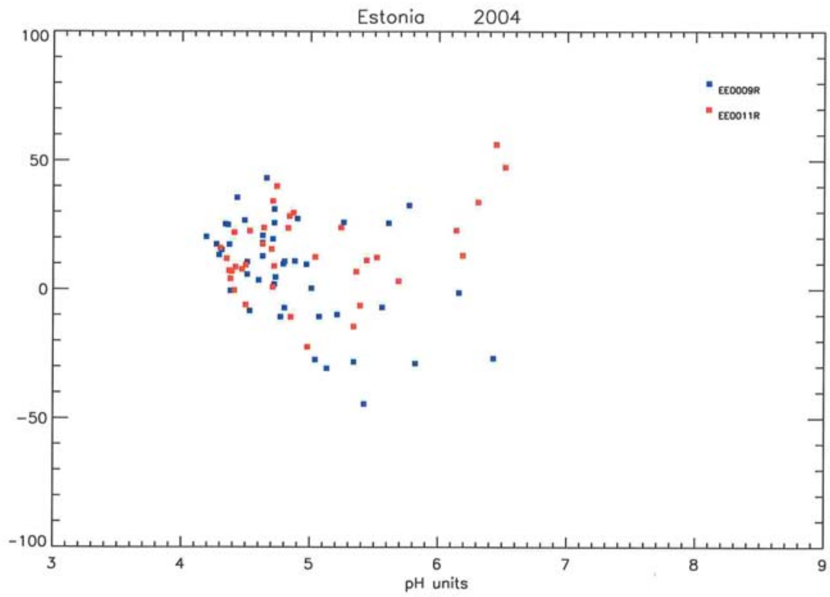


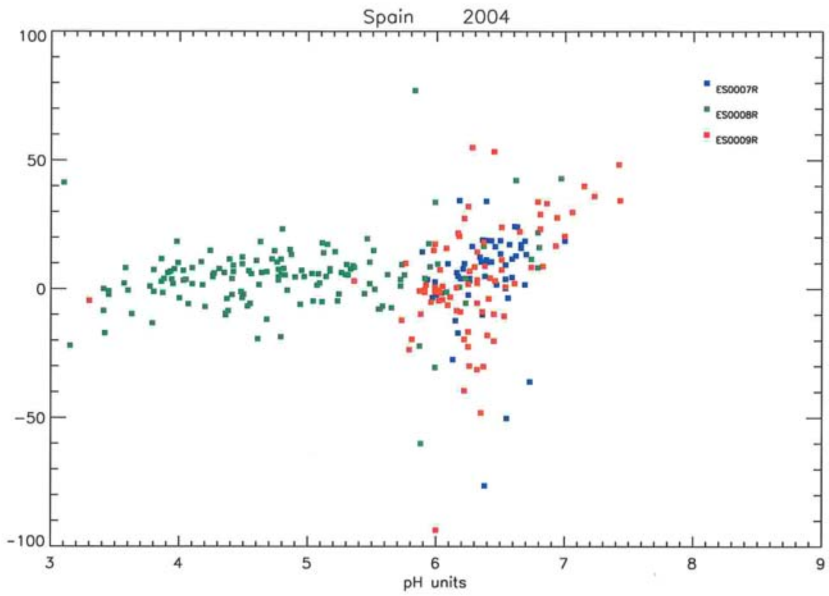
Switzerland 2004
CH0002R
CH0004R
CH0005R
pH units

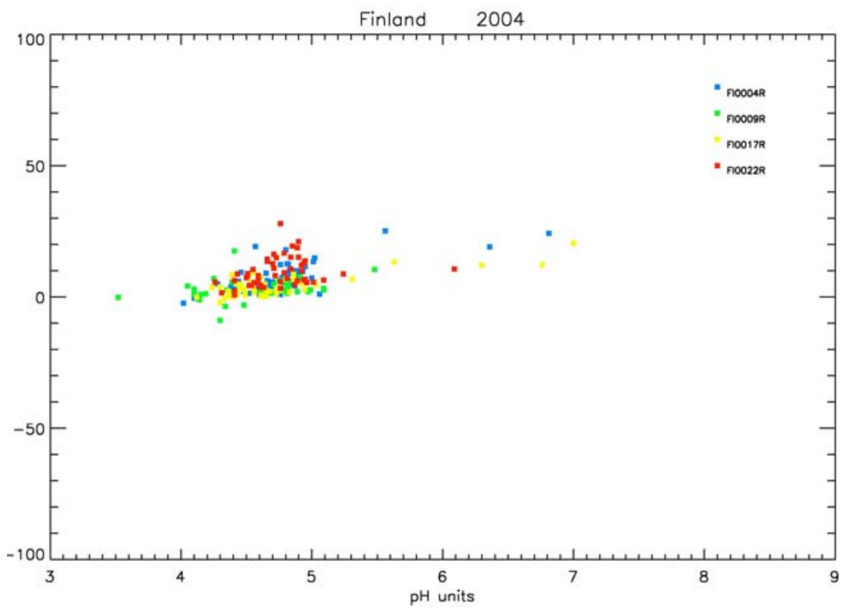

The Czech Republic 2004
CZ0003R
pH units

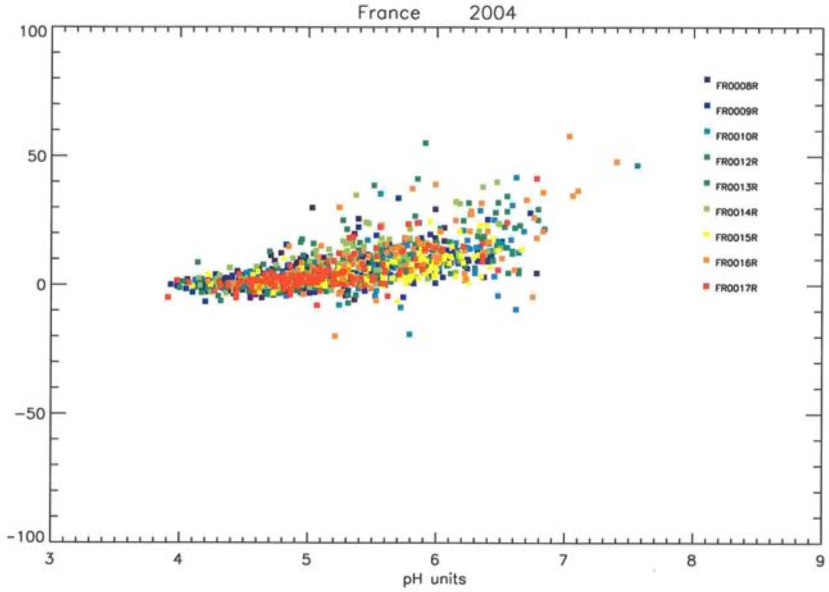

Germany 2004
DE0001R
DE0002R
DE0003R
DE0004R
DE0005R
DE0007R
DE0008R
DE0009R
pH units

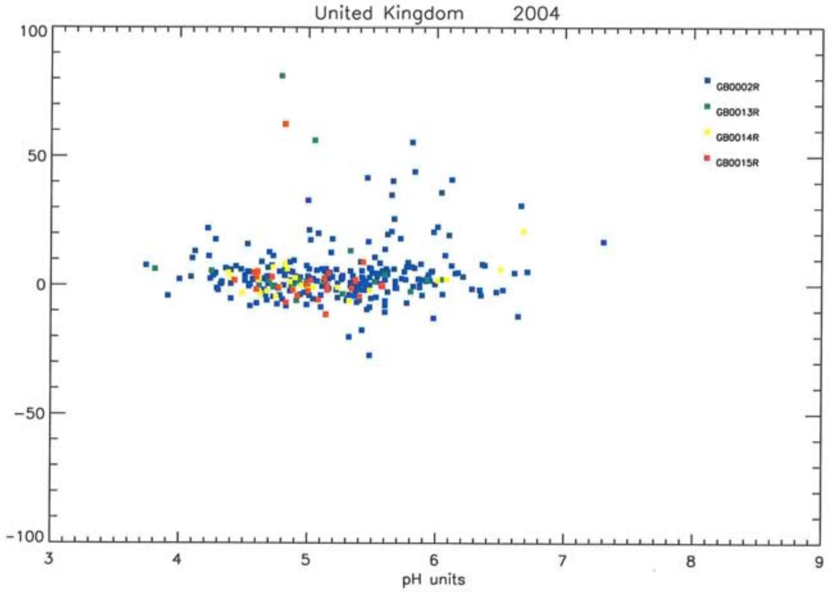

Denmark 2004
DK0005R
DK0008R
DK0022R
pH units

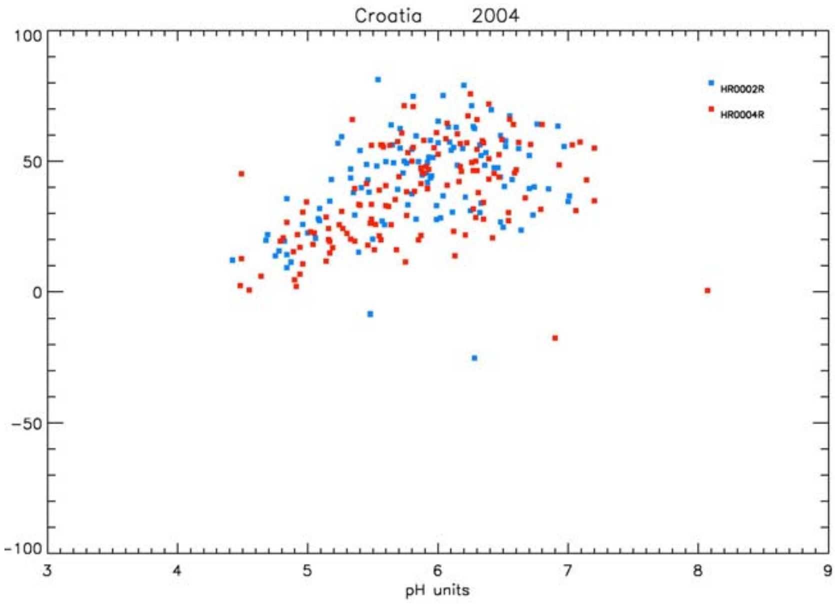

Estonia 2004
EE0009R
EE0011R
pH units

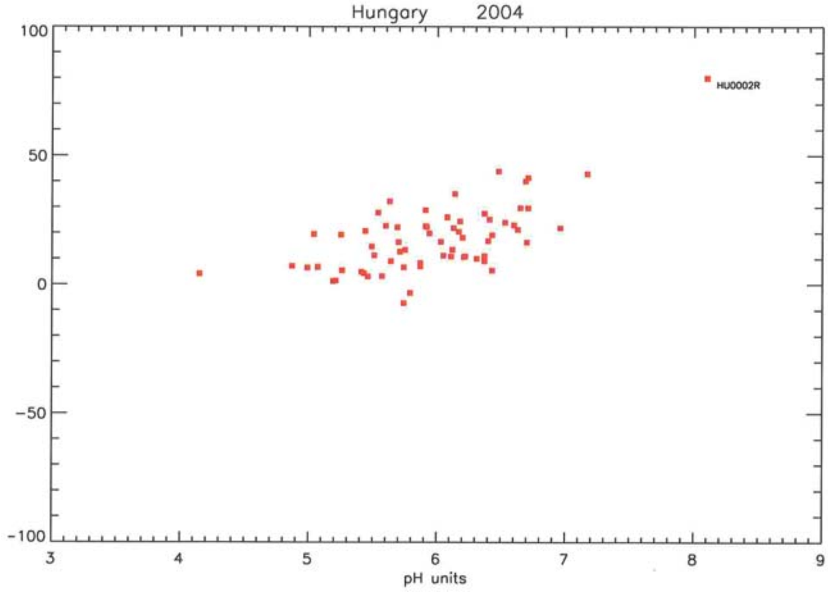

Spain 2004
ES0007R
ES0008R
ES0009R
pH units

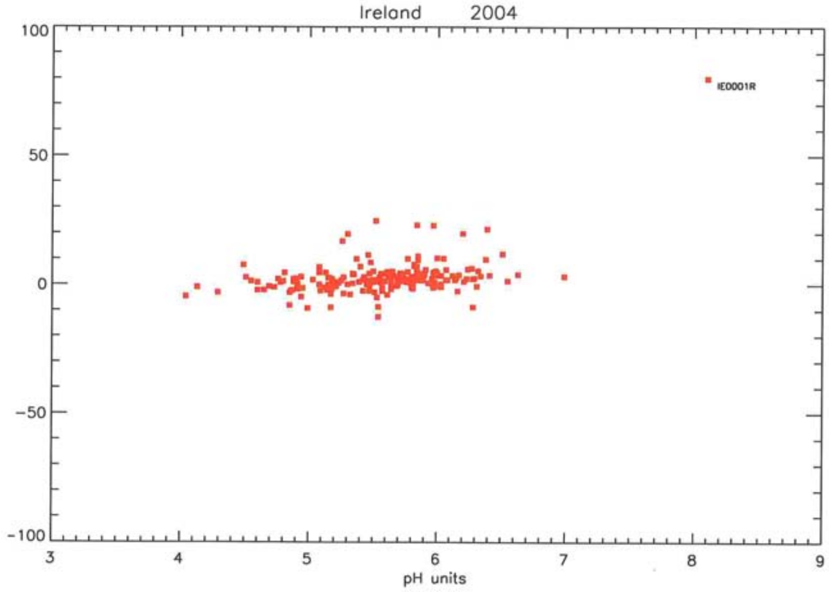

Finland 2004
FI0004R
FI0009R
FI0017R
FI0022R
pH units

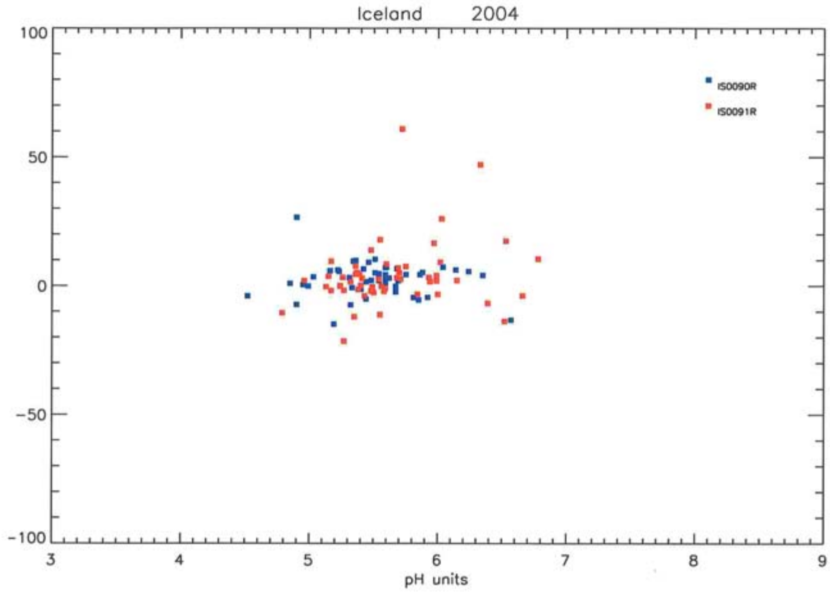

France 2004
FR0008R
FR0009R
FR0010R
FR0012R
FR0013R
FR0014R
FR0015R
FR0016R
FR0017R
pH units

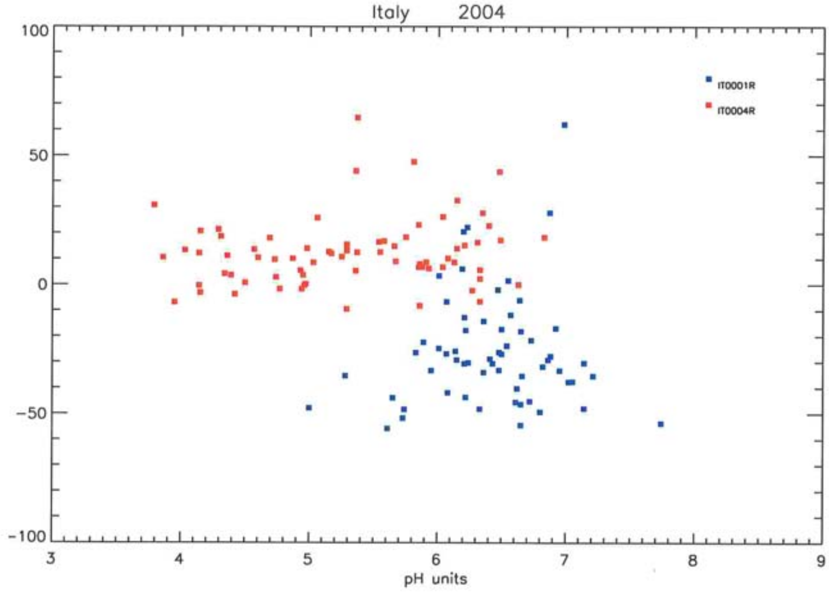

United Kingdom 2004
GB0002R
GB0013R
GB0014R
GB0015R
pH units

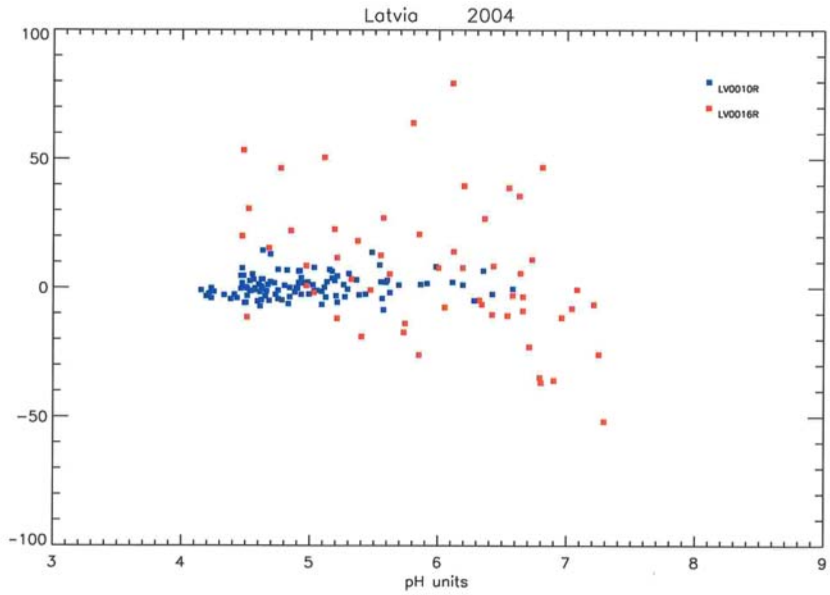

Croatia 2004
HR0002R
HR0004R
pH units

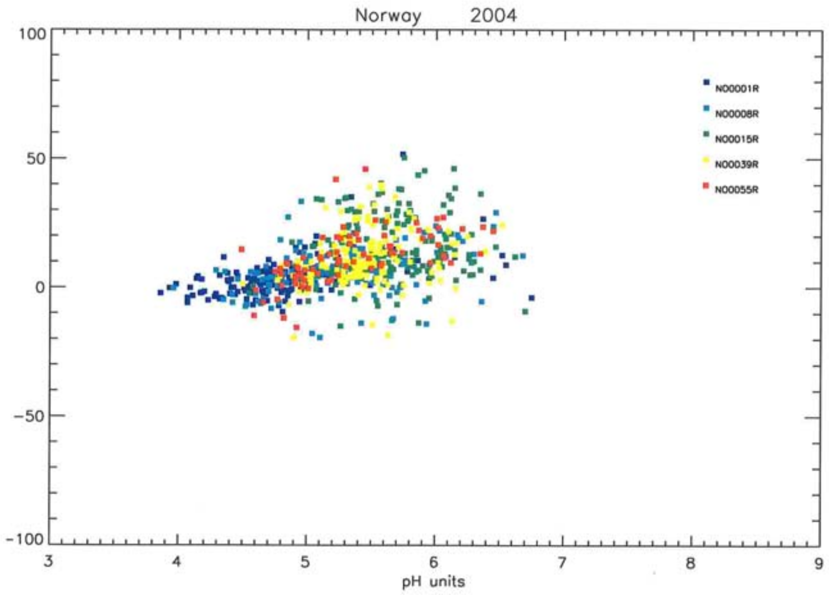

Hungary 2004
HU0002R
pH units

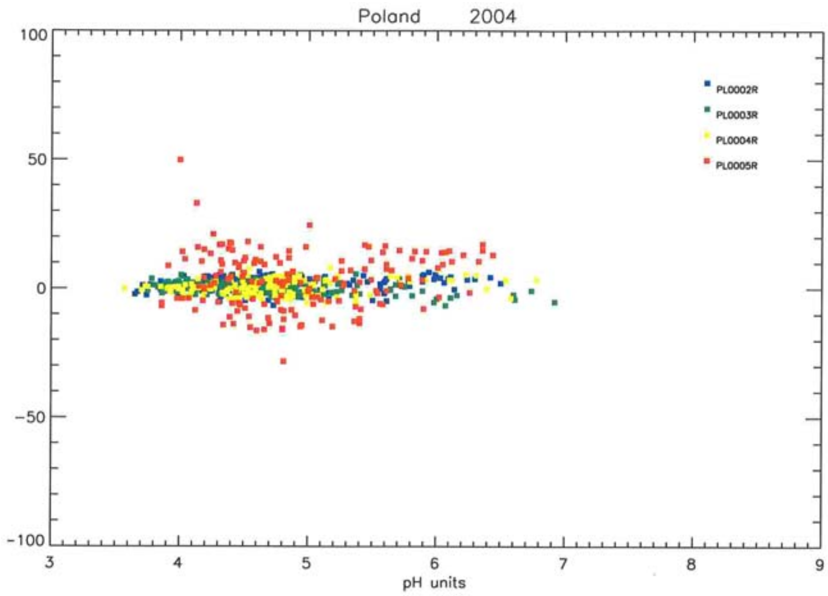

Ireland 2004
IE0001R
pH units

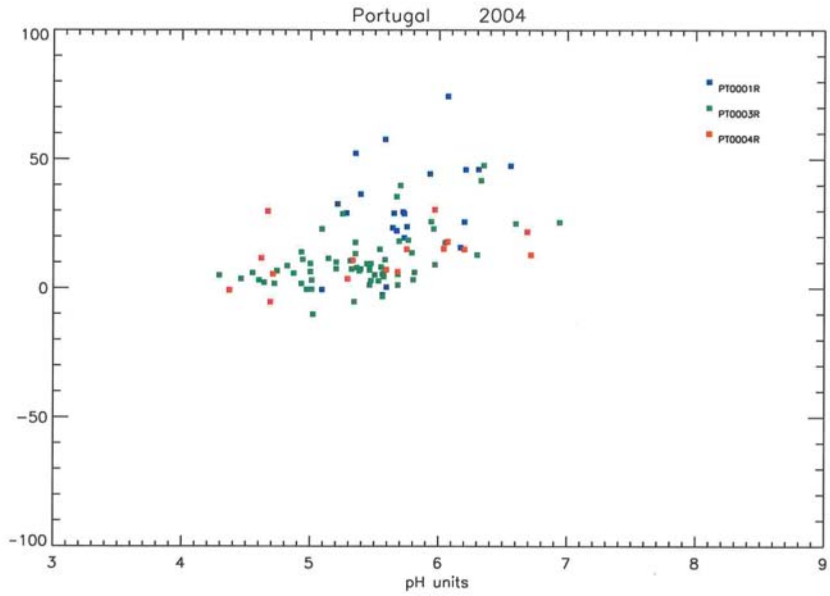

Iceland 2004
IS0090R
IS0091R
pH units

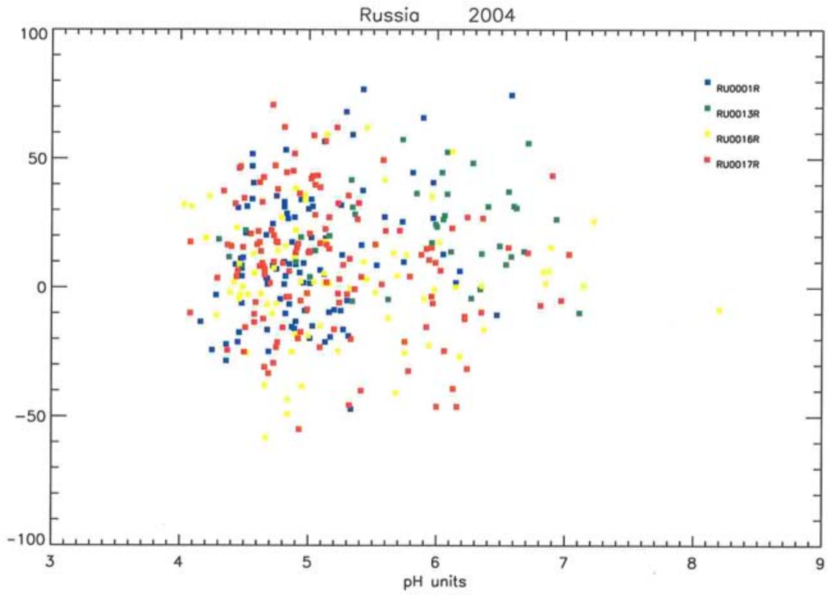

Italy 2004
IT0001R
IT0004R
100
50
0
-50
-100
3
4
5
6
7
8
9
pH units

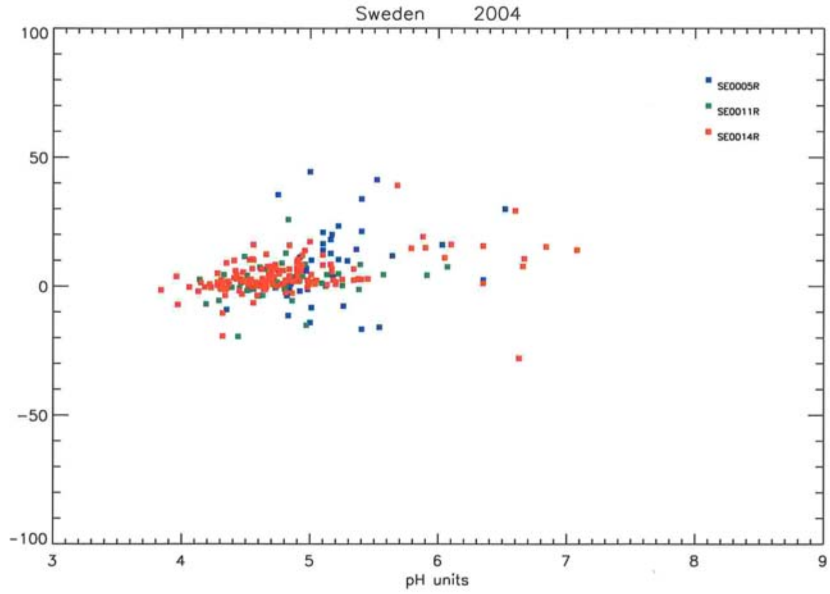

Latvia 2004
LV0010R
LV0016R
100
50
0
-50
-100
3
4
5
6
7
8
9
pH units

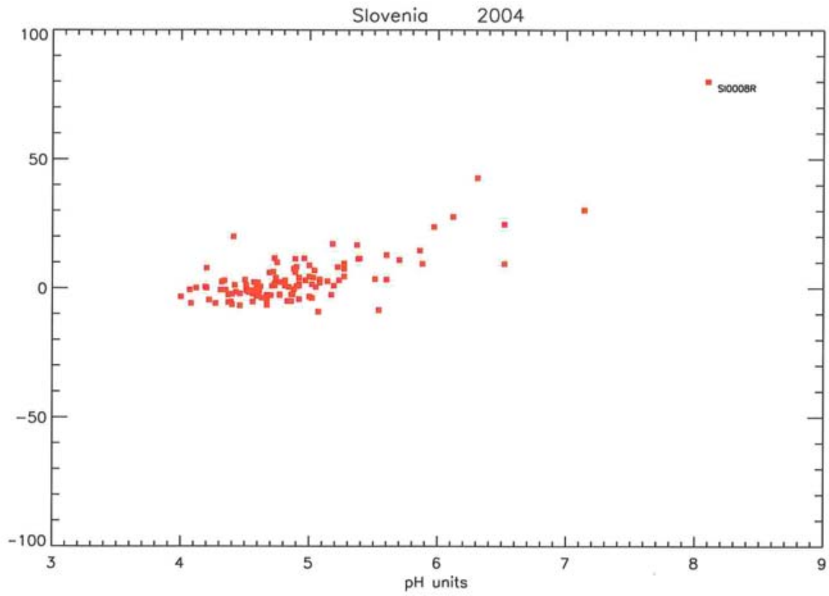

Norway 2004
NO0001R
NO0008R
NO0015R
NO0039R
NO0055R
100
50
0
-50
-100
3
4
5
6
7
8
9
pH units

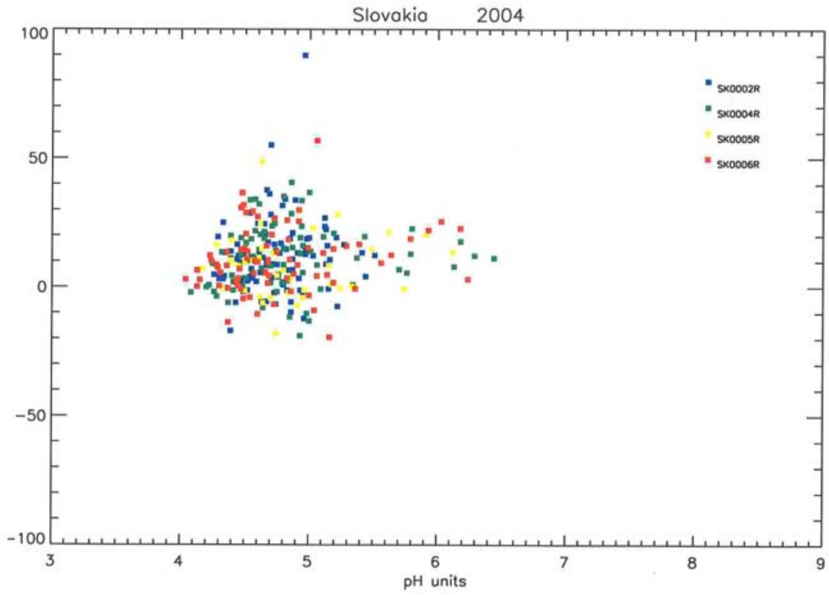

Poland 2004
PL0002R
PL0003R
PL0004R
PL0005R
pH units

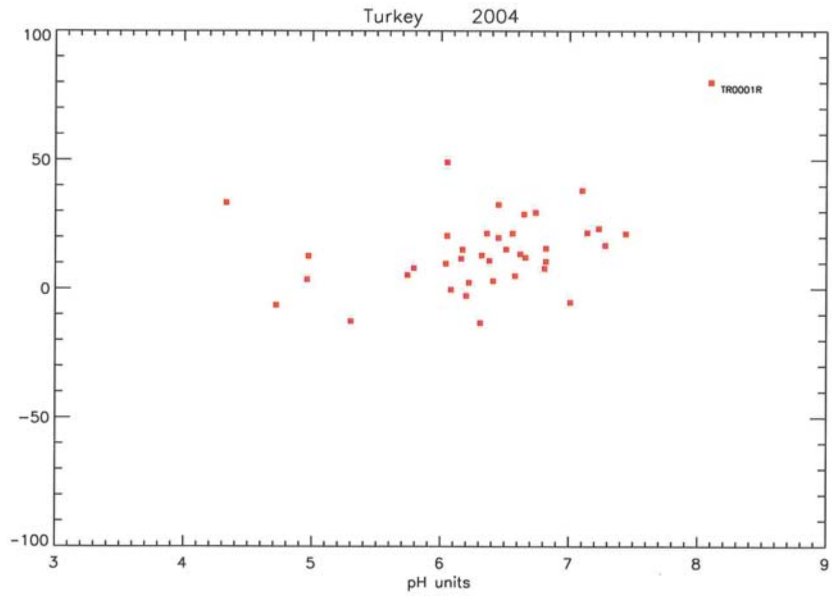

Portugal 2004
PT0001R
PT0003R
PT0004R
pH units

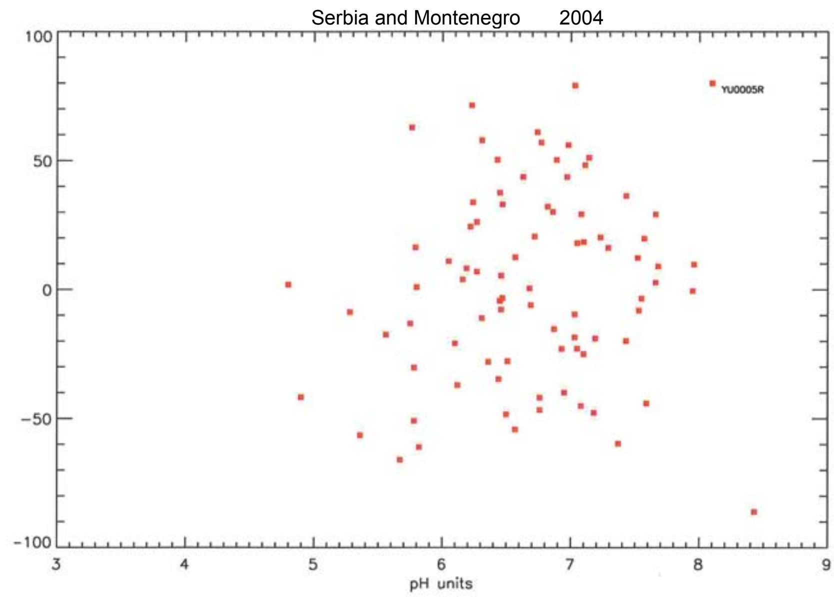

Russia 2004
RU0001R
RU0013R
RU0016R
RU0017R
pH units


Sweden 2004
SE0005R
SE0011R
SE0014R
pH units


Slovenia 2004
SI0008R
pH units


Slovakia 2004
SK0002R
SK0004R
SK0005R
SK0006R
pH units


Turkey 2004
TR0001R
pH units


Serbia and Montenegro 2004
YU0005R
pH units

Annex 5

Detection limits and precision

Table A5.1: Detection limits and precision of ozone.

Country	Precision	Detection limit	Instrument
Austria* AT02,04 AT05	1 ppb	0.4 ppb 0.5 ppb	Horiba APOA 350E Horiba APOA 360
Belgium*	1 ppb	1 ppb 0.5 ppb	O341M Ozone Analyzer Monitor Labs, ML 9812
Czech Republic	RSD: 10%	2 µg/m^3	Thermo Electron Series 49
Denmark		1 ppb	API Model 400 and 400A
Estonia*		2 µg/m^3	Thermo Environmental Instruments TEI 49 C
Finland FI04 FI09 FI17 FI22	2 µg/m^3	2 µg/m^3	TEI 49 C Dasibi 1008 PC, from 09.10.2003 Horiba APOA 360 TEI 49 C Dasibi 1008 PC
France FR08,09,10, 12,13,14,15,16	2 µg/m^3	2 µg/m^3	Environnement SA, O341M
Germany		2.0 µg/m^3	
Hungary			Thermo Environmental Instrument, Model 49
Ireland (IE01)			API Model400
Italy* (IT01)	2 µg/m^3	1 µg/m^3	API Model400
Italy, EU* (IT04)	2 ppb	2 ppb	Thermo Environmental Instrument, Model 49
Latvia	1%	1 ppb	O341M Ozone Analyzer
Netherlands*	1%	4 µg/m^3	Thermo Environmental Instruments TEI 49 W
Norway	2 µg/m^3	2 µg/m^3	API Model 400
Poland PL05	2 µg or 1%, whichever is greater RSD 1.8%	2 µg/m^3 1 ppb	Monitor Labs Inc. ML-9810 Monitor Labs Inc. ML-9810
Portugal PT04	1 ppb	1 ppb	Dasibi Environmental corp. 1008 PC
Russia	2 µg/m^3	2 µg/m^3	Dasibi Environmental corp., DAS 1008 PC
Slovakia	2 µg/m^3	2 µg/m^3	TEI M49 (SK06, 07); API M400 (SK02); Horiba APOA 360 (SK04)
Slovenia, SI08,32 SI31,33	1 ppb RSD: 0.5%	1 ppb 1 µg/m^3	Thermo Environmental Model 49 C API Model 400A
Spain	2% 2 µg/m^3	1 ppb 2 µg/m^3	MCV, S.A. Model 48 AUV MCV, S.A. Model 0341 M
Sweden, SE11,12,14 SE32 SE13,35,39	1 ppb 1 ppb 1 ppb	1 ppb 1 ppb 1 ppb	Monitor Labs, ML 9810 (ML 9810 B at SE 12) Thermo Environmental Instrument, Model 49C Monitor Labs, ML 8810
Switzerland, CH02,03,04,05	uncertainty (95% conf. int.): 3%	2 µg/m^3	Thermo Environmental Instruments TEI 49C
UK*, all sites except: GB32 GB43 GB44	2 ppb		Monitor Labs, ML 8810 TECO, TE49 Ambirack API Model 400

*Data from AT, BE, EE, IT, NL and UK are taken from earlier years

Table A5.2: Detection limits and precision of sulphur dioxide.

Country	Measurements		Laboratory	
	Precision	**Detection limit; $\mu g\ S/m^3$**	**Precision**	**Detection limit**
Austria* [1]	0.7 ppb	0.1 ppb		
Czech Republic	CoV: 12.62% M.MAD : 0.194 $\mu g\ SO_2/m^3$	0.02	RSD : 3%	0.02 mg S/l
Denmark	M.MAD: 0.02; CoV: 5 %	DK03: 0.01 DK05: 0.02 DK08: 0.02	M.MAD: 0.01 $\mu g\ S/m^3$; CoV: 1.3%	0.01 $\mu g\ S/m^3$
Estonia*		0.48		
Finland		0.04	M.MAD: 0.003 $\mu g\ S/m^3$ CoV: 1.0%	0.01 $\mu g\ S/m^3$
France Abs. sol.			at 0.01<c<0.1 mg S/l: RSD = 8-12% at 0.1<c<0.5 mg S/l: RSD = 1-3%	0.1 mg S/L
France Filterpack	M.MAD 0.19 CoV: 5.4%	0.01		0.02 mg S/l
Germany	M.MAD: < 0.02			0.01 $\mu g/m^3$
Hungary		3.62	M.MAD: 0.157 $\mu g\ S/m^3$ CoV: 3.08%	8.60 $\mu g\ S/m^3$
Iceland		0.01	RSD: 4% at 1 mg S/l	0.02 mg S/l
Ireland				0.05 $\mu gS/m^3$
Italy* (IT01)	RSD: 7.0% at 2.0 $\mu g\ S/m^3$	0.1		0.002 mg S/l
Italy, EU* (IT04) [2]	0.5 ppb	1 ppb		
Latvia		0.06	RSD: 1.5%	0.014 mg S/l
Lithuania	0.021	0.021 $\mu g\ S/m^3$	at c<0.7 $\mu g\ S/m^3$: 2.4% RSD; at c>0.7 µgS/m3: 0.5-1.0 % RSD	0.017 mg S/l
Netherlands* [4]	1%	1.5		
Norway	M.MAD 0.04; CoV: 12%	0.03		0.01 µg S/m3
Poland		0.2		0.04 mg S/l
Poland PL05	M.MAD = 0.13; CoV= 11.2%	0.1	RSD: 0.73%	0.09 mg S/l
Serbia and Montenegro				2.50 $\mu g\ S/m^3$
Slovakia			CoV: 9.36%	0.15 µg S/filter
Slovenia		0.02	RSD: 1.6% (at 0.334 mg S/l)	0.02 mg S/l
Spain	1% or 0.2 ppb	0.08 ppb		
Sweden	uncertainty (95% conf. int): 13%	0.02	R: 2%	0.01 $\mu g\ S/m^3$
Switzerland CH01	RSD: 4%	0.02		
Switzerland [3]CH02, CH04, CH05	uncertainty (95% conf. int.): 9%	0.3		
Turkey		0.07	M.MAD: 0.011; CoV: 2.03%	0.044 mg S/l
UK*				0.01 mg S/l

[1] AT, Monitor, (TEI 43BS to 15th December, after that TEI 43 C trace level)
[2] IT04. Monitor Environment SA, AF 21M
[3] CH02, CH04, CH05: TEI 43C TL
[4] NL: TEI 43W

*Data from AT, EE, IT, NL and UK are taken from earlier years

Table A5.3: Detection limits and precision of nitrogen dioxide.

Country	Measurements		Laboratory	
	Precision	Detection limit, µg N/m³	Precision	Detection limit
Austria* [1]	1 ppb	0.5 ppb		
Belgium* (BE01) (BE02)	0.6 µg N/m³ 1%	0.3 0.5 ppb		
Czech Republic	RSD: 12%	0.23	RSD: 3.4%	0.06 mg NO_2/l
Denmark		DK08: 0.07	M.MAD: 0.01 µg N/m³; CoV: 3.45%	0.07 µg N/m³
Estonia*		0.07		
Finland**	0.3 µg N/m³	0.3		
France		0.7 ppb		
Hungary		0.06	M.MAD: 0.006 µg N/m³; CoV: 4.98%	
Ireland				0.1 µg N/m³
Italy* (IT01)	0.6 µg N/m³	0.3		
Italy, EU* (IT04)[2]	0.5 ppb	0.5 ppb		
Latvia		0.11	RSD: 2.8%	0.005 mg N/l
Lithuania		0.08	RSD 3.75-6.9% at c<2.0 µg N/m³	0.03 mg N/l
Netherlands* [4]	1%	0.3		
Norway	M.MAD: 0.13; CoV: 5%	0.03	RSD: 7.0% at c=0.03 mgN/l RSD: 4.6% at c=0.17 mgN/l RSD: 4.2% at c=0.08 mgN/l	0.0045 mg N/l
Poland		0.2	RSD: 1.0% at 0.304 mgN/l RSD: 5.9 % at 0.015 mgN/l	0.008 mg N/l
PL05	M.MAD: 0.37; CoV: 24.5%	0.02	RSD: 3.17%	0.02 mg N/l
Serbia and Montenegro				0.3 µg N/m³
Slovakia			CoV: 3.73%	0.01 mg N/l
Slovenia		0.09		0.01 mg N/l
Spain	0.05 ppb	0.03 ppb		
Sweden	uncertainty (95% conf.int.): 6%	0.3	R: 2%	0.02 mg N/l
Switzerland[3] CH04, CH05	uncertainty (95% conf. int.): 10%	0.06		
CH02, CH03	uncertainty (95% conf. int.): 7%	0.3		
CH01	uncertainty (95% conf. int.): 10%	0.02		
Turkey	M.MAD: 0.080; CoV: 9.13%	0.11	M.MAD: 0.118; CoV: 16.87%	0.015 mg N/l
UK*	3.5 ppb			

[1]AT: Monitor, HORIBA APNA 360
[2]IT04: Monitor, Thermo Environment 42C
[3]CH04 and CH05: Monitor Labs 9841A; CH02 and CH03: APNA 360; CH01: Eco Physics CLD 770AL ppt + PLC 760
[4] NL: TEI 43W

*Data from AT, BE, EE, IT, NL and UK are taken from earlier years
** FI: Monitor, Thermo Environment 42TCL

Table A5.4: Detection limits and precision of sulphate in air.

Country	Measurements		Laboratory	
	Precision	**Detection limit, µg S/m^3**	**Precision**	**Detection limit**
Austria*		0.05 µg/m^3	RSD: 2.3%	0.0028 µg/m^3
Czech Republic	M.MAD: 0.225 µg/m^3, CoV: 8.6%	0.02	RSD: 3%	0.02 mg/l
Denmark	M.MAD: 0.05 µg S/m^3 CoV: 6.5%	DK03: 0.01 DK05: 0.02 DK08: 0.01	M.MAD: 0.01 µg S/m^3, CoV: 1.25%	0.02 µg S/m^3
Estonia*		0.53		
Finland		0.04	M.MAD: 0.02 µg S/m^3; CoV: 1.26%	0.01 µg S/m^3
France Prefil. air			at 0.01<c<0.1 mg S/l: RSD = 8-12% at 0.1<c<0.5 mg S/l: RSD = 1-3%	0.2 µg S/filter
France Filterpack	M.MAD 0.058 CoV: 6.1%	0.01		0.02 mg S/l
Germany	M.MAD < 0.02 µg/m^3			0.01 µg/m^3
Hungary		0.10	M.MAD: 0.008 µg S/m^3; CoV: 1.84%	0.038 µg S/m^3
Iceland		0.01	RSD: 4% at 1 mg S/l	0.05 mg S/l
Ireland				0.02 µg/m^3
Italy* (IT01)	RSD: 1.3% at 1 µg S/m^3	0.01		0.002 mg S/l
Italy, EU* (IT04)		0.009 ppm	CoV: 1.3%	0.004 mg S/l
Latvia		0.06	RSD: 2.4%	0.02 mg S/l
Lithuania		0.024	RSD: 7.2% at c<1.0 µgS/m^3 RSD: 1.0% at c>1.0 µgS/m^3	0.024 mg S/l
Netherlands*			SD: 0.3 µg/m^3	1.2 µg/m^3
Norway	M.MAD 0.009 µg S/m^3 at c<2.4 µg S/m^3	0.01		
Poland		0.18		0.04 mg S/l
PL05	M.MAD: 0.08; CoV=10.4%	0.1	RSD: 4%	0.09 mg S/l
Russia	RU16: M.MAD 0.02; CoV=2.15%		CoV: 1.75 µg/m^3	0.02 mg/l
Slovakia			CoV: 6.15%	0.33 µg S/filter
Slovenia		0.005	RSD: 1.6% (at 0.334 mg S/l)	0.02 ml S/l
Spain (in PM_{10})				0.02 µg S/m^3
Sweden	uncertainty (95% conf. int.): 13%	0.005 µg SO_4-S/m^3	R: 2%	0.005 mg S/l
Switzerland	RSD: 10%	0.04		
Turkey		0.04	M.MAD: 0.010; CoV: 2.20%	0.040 mg S/l
UK*			RSD: 2%	0.01 mg S/l

*Data from AT, EE, IT, NL and UK are taken from earlier years

Table A5.5: Detection limits and precision of nitrate and nitric acid in air.

Country	Measurements		Laboratory	
	Precision	**Detection limit, µg N/m3**	**Precision**	**Detection limit**
Austria*		HNO_3: 0.020 µg/m^3 NO_3: 0.011 µg/m^3	HNO_3: RSD: 1.7%	HNO_3: 0.0006 µg/m^3 NO_3: 0.0009 µg/m^3
Czech Republic	aNO_3: M.MAD: 0.252 µg/m^3, CoV: 7.49%	0.02	RSD: 2%	0.02 mg N/l
Denmark	M.MAD: 0.04 µg N/m^3, CoV: 7,3%	DK03: 0.04 DK05: 0.06 DK08: 0.03	NO_3; M.MAD: 0,01 µg N/m^3, CoV: 1.2%	NO_3: 0.01 µg N/m^3
Finland		0.02	M.MAD: 0.001 µg N/m^3 CoV: HNO_3 = 5.0% and NO_3 = 0.9%	0.005 µg N/m^3
Germany	< 0.02 µg/m^3 M.MAD			0.01 µg/m^3
Hungary		HNO_3: 0.04; NO_3: 0.04	HNO_3: M.MAD: 0.021; CoV: 4.98% NO_3: M.MAD: 0.012; CoV: 6.08%	HNO_3: 0.033; NO_3: 0.014
Ireland				0.02 ng N/m^3
Italy* (IT01)	HNO_3: RSD: 6.2% at 0.25 µg N/m^3 NO_3: RSD: 1.5% at 1 µg N/m^3	HNO_3: 0.01 NO_3: 0.01		0.002 mg N/l
Italy, EU* (IT04)		0.024	CoV: 1.2%	0.011 mg N/l
Latvia		HNO_3, NO_3: 0.01	RSD: HNO_3 1.2%, NO_3 2.9%	HNO_3: 0.006 mg N/l NO_3: 0.015 mg N/l
Lithuania		0.014	RSD 0.5-1.2% at c=0.3-1.0 µg N/m^3	0.013 mg N/l
Norway	M.MAD 0.012 at <1.6 µg N/m^3	0.02		
Poland		0.02		0.01 mg N/l
PL05	M.MAD: 0.11; CoV: 16.9%	0.2	RSD: 2%	0.05 mg N/l
Russia	NO_3: M.MAD 0.01			0.01 mg/l
Slovakia			HNO_3: CoV 6.93%; NO_3: CoV 4.66%	HNO_3: 0.1 µg N/filter; NO_3: 0.4 µg N/filter
Slovenia		NO_3^-: 0.018 HNO_3: 0.005l	RSD: 2.2% (at 0.113 mg N/l)	0.007 mg N/l
Spain				0.06 µg N/m^3
Sweden	uncertainty (95% conf. int.): 12%	NO_3-N: 0.005; HNO_3-N: 0.01	R: 2%	NO_3-N: 0.005; HNO_3-N: 0.01 mg N/l
Switzerland	RSD: 8%	0.04		
Turkey		NO_3: 0.04 HNO_3: 0.075	NO_3: M.MAD: 0.006; CoV: 4.03% HNO_3: M.MAD: 0.006; CoV: 18.49%	NO_3: 0.04 mg N/l HNO_3: 0.05 mg N/l

*Data from AT and IT are taken from earlier years

Table A5.6: Detection limits and precision of ammonia and ammonium in air.

Country	Measurements: Precision	Measurements: Detection limit, µg N/m^3	Laboratory: Precision	Laboratory: Detection limit
Austria*		NH_3: 0.10 µg/m^3 NH_4: 0.013 µg/m^3	NH_4: M.MAD: 0.03 µg N/m^3, CoV: 4.1% NH_3: M.MAD: 0.01 µg N/m^3, CoV: 1.4%	NH_4^+: 0.01 µg N/m^3 NH_3: 0.01 µg N/m^3
Czech Republic	aNH_4: M.MAD: 0.315 µg/m^3 CoV: 12.10%	0.016	RSD: 2%	0.016 mg N/l
Denmark	M.MAD: 0.13 µg N/m^3 CoV: 6.6%	DK03: 0.05 DK05: 0.06 DK08: 0.03	NH_4: M.MAD: 0.01 µg N/m^3; CoV: 1.3% NH_3: M.MAD: 0.01 µg N/m^3; CoV: 1.0%	NH_4^+: 0.02 µg N/m^3 NH_3: 0.02 µg N/m^3
Finland		0.04	M.MAD: 0.004 µg N/m^3; CoV: 1.5%	0.01 µg/m^3
France	M.MAD 0.385 µg N/m^3 CoV: 14.5%	0.1		0.02 mg N/l
Germany	M.MAD < 0.02 µg/m^3			0.01 µg/m^3
Hungary		NH_4: 0.03; NH_3: 0.34	NH_4: M.MAD: 0.005 µg N/m^3; CoV: 0.832% NH_3: M.MAD: 0.031 µg N/m^3; CoV: 3.46%	NH_4^+: 0.015 µg N/m^3 NH_3: 0.367 µg N/m^3
Ireland				0.08 µg N/m^3
Italy* (IT01)	NH_3: RSD: 3.9% at 1 µg N/m^3 NH_4: RSD: 4.2% at 2 µg N/m^3	0.1		0.001 mg N/l
Italy, EU* (IT04)		0.17	CoV: 2.4%	0.074 mg N/l
Latvia		NH_3: 0.09 NH_4: 0.08	RSD: NH_4: 4%; NH_3: 2%	NH_4; 0.03 mg N/l NH_3: 0.02 mg N/l
Lithuania		0.027	RSD: 4.0% at c<1.0 µg N/m^3 RSD 0.6-1.8% at c>1.0 µg N/m^3	0.04 mg N/l
Netherlands*	NH_3: RSD: <2%	NH_3: 0.1	NH_4, SD: 0.05 µg/m^3	NH_4: 0.2 µg/m^3
Norway		0.05-0.1		
Poland		0.06		0.03 mg N/l
PL05	M.MAD: 0.24; CoV: 20.8%	0.03	RSD: 1.64%	0.01 mg N/l
Russia	NH_4: RU01: M.MAD 0.05; CoV=5.37% NH_4: RU16: M.MAD 0.03; CoV=5.13% NH_4: RU18: M.MAD 0.01; CoV=0.84%		NH_4: M.MAD: 0.01 µg/m^3 CoV: 3.39 µg/m^3	NH_4: 0.02 mg/l
Slovenia		NH_4^+: 0.02 NH_3: 0.05		NH_4-N: 0.048 mg N/l NH_3-N: 0.030 mg N/l
Spain		0.03	2.68 %	0.03 µg N/m^3
Sweden	uncertainty (95% conf. int.): 13%	NH_3-N: 0.03; NH_4-N: 0.02	R: 3%	0.02 mg N/l
Switzerland	RSD: 7%	0.1		
Turkey		NH_4: 0.09 µg N/m^3 NH_3: 0.07 µg N/m^3	NH_4: M.MAD: 0.014; CoV: 3.79% NH_3: M.MAD: 0.022; CoV: 6.42%	NH_4: 0.034 mg N/l NH_3: 0.044 mg N/l

*Data from AT, IT and NL are taken from earlier years

Table A5.7: Detection limits and precision of sulphate in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, mg S/l	Precision	Detection limit, mg S/l
Austria*		0.012	RSD: 0.92%	0.002
Belarus*				0.100
Czech Republic	CoV: 5.5% M.MAD: 0.153 mg/l	0.013	RSD: 1.4%	0.013
Denmark			M.MAD: 0.01 mg S/l; CoV: 2.5%	0.03
Estonia*		0.347		0.221
Finland			M.MAD: 0.006 mg S/l; CoV: 2.0%	0.02
France			at c<0.2 mg S/l: RSD = 5-10% at 0.2<c<0.5 mg S/l: RSD = 3-5% at 0.5<c<5 mg S/l: RSD = 1-3%	0.02
Germany				0.01
Hungary	CoV: 5.76% M.MAD: 0.149 mg/l		M.MAD=0.187; CoV=6.17%	
Iceland		0.1	RSD: 4% at 1 mg S/l	0.05
Ireland				0.02
Italy* (IT01)	RSD: 1.1% at 1 mg S/l	0.01	RSD: 0.8% at 0.5 mg S/l RSD: 1.6% at 0.05 mg S/l	0.002
Italy, EU* (IT04)			CoV: 1.3%	0.004
Latvia		0.06	CoV: 3.9%	0.012
Lithuania			RSD: 3.4% at c<0.5 mg S/l RSD: 1.0% at c>0.5 mg S/l	0.02
Netherlands*			SD: 0.2	0.07
Norway	M.MAD: 0.03, CoV: 7%		SD: 0.041 at c=2.23 mgS/l SD: 0.019 at c=0.85 mgS/l	0.01
Poland			RSD: 1% at 6.7 mg S/l RSD: 1.8% at 0.67 mg S/l RSD: 2% at 0.33 mgS/l	0.03
PL05	M.MAD: 0.03; CoV: 2.7%	0.1	M.MAD: 0.01; CoV: 2.1%	0.09
Portugal			0.75%	0.04
Russia	RU01: M.MAD: 0.02; CoV: 4.6% RU16: M.MAD: 0.02; CoV: 0.05% RU18: M.MAD: 0.01; CoV: 0.75%		CoV: 0.78%	0.02
Serbia and Montenegro				0.02
Slovakia			CoV: 3.18%	0.017
Slovenia		0.07	RSD: 1.6% (at 0.334 mg S/l)	0.02
Spain			CoV: 1.4 %	0.07
Sweden	uncertainty (95% conf. int.): 5% (0.004-1 mg/l) uncertainty (95% conf. int.): 1% (1-28 mg/l)	0.005	R: 2%	0.005
Switzerland	M.MAD: 0.01 mg S/l			0.01
Turkey			M.MAD: 0.017; CoV: 1.54%	0.036
UK*			1%	0.01

*Data from AT, BY, EE, IT, NL and UK are taken from earlier years

Table A5.8: Detection limits and precision of nitrate in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit mg N/l	Precision	Detection limit mg N/l
Austria*		0.013	RSD: 0.7%	0.001
Belarus*				0.100
Czech Republic	CoV: 5.4% M.MAD: 0.155 mg/l	0.009	RSD: 0.9%	0.009
Denmark			M.MAD: 0.01 mg N/l; CoV: 2.7%	0.02
Estonia*		0.302		0.167
Finland			M.MAD: 0.003 mg N/l; CoV: 1.5%	0.01
France			at c<0.2 mg N/l: RSD = 5-10% at 0.2<c<0.5 mg N/l: RSD = 3-5% at 0.5<c<5 mg N/l: RSD = 1-3%	0.02
Germany				0.01
Hungary	CoV: 8.21% M.MAD: 0.189 mg/l		M.MAD=0.133; CoV=7.65%	
Iceland		0.1	RSD: 7% at 1 mg N/l	0.01
Ireland				0.01
Italy* (IT01)	RSD: 1.4% at 1 mg N/l	0.01	RSD: 0.7% at 0.5 mg N/l RSD: 1.5% at 0.05 mg N/l	0.002
Italy, EU* (IT04)			CoV: 1.2%	0.011
Latvia		0.04	CoV: 1.9%	0.0052
Lithuania			RSD: 5.1% at c<0.5 mg N/l RSD: 1.8% at c>0.5 mg N/l	0.013
Netherlands*			SD: 0.01	0.06
Norway	M.MAD: 0.03, CoV: 8%		SD: 0.023 at c=0.86 mg N/ml SD: 0.016 at c=0.39 mg N/ml	0.01
Poland			RSD: 1.7% at 4.5 mg N/l RSD: 1.9% at 0.45 mg N/l RSD: 2.0% at 0.23 mg N/l	0.015
PL05	M.MAD: 0.02; CoV: 4.3%	0.09	M.MAD: 0.00; CoV: 0%	0.09
Portugal			0.25%	0.02
Russia	RU16: M.MAD: 0.01			0.01
Serbia and Montenegro				0.02
Slovakia			CoV: 3.73%	0.01
Slovenia		0.07	RSD: 2.2% (at 0.113 mg N/l)	0.007
Spain			CoV: 1.2%	0.08
Sweden	uncertainty (95% conf. int.): 5% (0.006-1 mg/l) uncertainty (95% conf. int.): 1% (1-6 mg/l)	0.006	R: 2%	0.006
Switzerland	M.MAD: 0.01 mg N/l			0.01
Turkey			M.MAD: 0.007; CoV: 1.53%	0.034
UK*			1%	0.01

*Data from AT, BY, EE, IT, NL and UK are taken from earlier years

Table A5.9: Detection limits and precision of ammonium in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, mg N/l	Precision	Detection limit, mg N/l
Austria*		0.02	RSD 2.98%	0.007
Belarus*				0.050
Czech Republic	CoV: 11.4% M.MAD: 0.169 mg/l	0.016	RSD: 2%	0.016
Denmark			M.MAD: 0.01 mg N/l; CoV: 3.1%	0.02
Estonia*		0.064		0.077
Finland			M.MAD: 0.001 mg N/l; CoV: 0.5%	0.002
France			at c<0.2 mg N/l: RSD = 5-10% at 0.2<c<0.5 mg N/l: RSD = 3-5% at 0.5<c<5 mg N/l: RSD = 1-3%	0.03
Germany				0.01
Hungary	CoV: 9.06% M.MAD: 0.048 mg/l		M.MAD=0.001; CoV=0.32%	
Ireland				0.04
Italy* (IT01)	RSD: 0.8% at 0.5 mg N/l	0.005	RSD: 0.5% at 0.5 mg N/l RSD: 1.8% at 0.05 mg N/l	0.001
Italy, EU* (IT04)			CoV: 2.4%	0.014
Latvia		0.06	CoV: 3.7%	0.015
Lithuania			RSD: 3.3% at c<1.0 mg N/l RSD: 1.0% at c>1.0 mg N/l	0.04
Netherlands*			SD: 0.01	0.03
Norway	M.MAD: 0.06, CoV: 20%		SD: 0.016 at c=0.64 mg/l SD: 0.013 at c=0.32 mgN/l	0.01
Poland			RSD: 2.7% at 1 mg/l RSD: 4.6% at 0.1 mg/l	0.03
PL05	M.MAD: 0.04; CoV: 10.9%	0.01	M.MAD: 0.00; CoV: 0.5%	0.01
Portugal			0.79%	0.03
Russia	RU18: M.MAD: 0.01; CoV: 0.85%		CoV: 2.24%; M.MAD: 0.02	0.02
Serbia and Montenegro				0.02
Slovakia			CoV: 2.87%	0.01
Slovenia		0.09	RSD: 1.6% (at 0.298 mg N/l)	0.02
Spain			CoV: 2.7%	0.08
Sweden	uncertainty (95% conf. int.): 5% (0.01-1 mg/l) uncertainty (95% conf. int.): 2% (1-10 mg/l)	0.01	R: 3%	0.02
Switzerland	M.MAD: 0.02 mg N/l			0.02
Turkey			M.MAD: 0.017; CoV: 3.81%	0.034
UK*			1%	0.01

*Data from AT, BY, EE, IT, NL and UK are taken from earlier years

Table A5.10: Detection limits and precision of calcium in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, mg/l	Precision	Detection limit, mg/l
Austria*		0.34	RSD: 2.02%	0.003
Belarus*				0.001
Czech Republic	CoV: 13.5% M.MAD: 0.107 mg/l	0.033	RSD:5.0%	0.033
Denmark			M.MAD: 0.01 mg/l; CoV: 4.5%	0.13
Estonia*		0.407		0.382
Finland			M.MAD: 0.001 mg/l; CoV: 2.2%	0.005
France			at c<0.2 mg/l: RSD = 10-20% at 0.2<c<0.5 mg/l: RSD = 5-10% at 0.5<c<5 mg/l: RSD = 1-5%	0.02
Germany				0.01
Hungary	CoV: 4.26% M.MAD: 0.065 mg/l		M.MAD: 0.007; CoV: 2.65%	
Iceland		0.1	RSD: 1-3% at 1<c<6 mg Ca/l	0.02
Ireland				0.05
Italy* (IT01)	RSD: 1.8% at 1 mg Ca/l	0.01	RSD: 1.2% at 0.5 mg Ca/l RSD: 3.6% at 0.05 mg Ca/l	0.002
Italy, EU* (IT04)			CoV: 16%	0.014
Latvia		0.05	CoV: 4.5%	0.02
Lithuania			RSD: 5.5% at c<0.2 mg Ca/l RSD: 1.5% at c>0.2 mg Ca/l	0.02
Netherlands*			SD: 0.01	0.06
Norway	M.MAD: 0.03; CoV: 59%		SD: 0.010 at c=0.27 mg/l SD: 0.006 at c=0.15 mg/l	0.01
Poland			RSD: 0.9% at 2 mg/l RSD: 1.8% at 0.8 mg/l RSD: 2.1% at 0.4 mg/l	0.03
PL05	M.MAD: 0.03; CoV: 8%	0.001	M.MAD: 0.004; CoV: 2.4%	0.001
Portugal			1.31%	0.06
Russia	RU01: M.MAD: 0.04; CoV: 13.5% RU13: M.MAD: 0.04; CoV: 5.2% RU16: M.MAD: 0.02; CoV: 1.18% RU18: M.MAD: 0.05; CoV: 7.01%		CoV: 5.88%; M.MAD: 0.03	0.04
Serbia and Montenegro			81%	0.02
Slovakia			CoV: 2.29%	0.03
Slovenia		0.09	RSD: 2.4% (at 0.300 mg/l)	0.02
Spain			CoV: 7.4%	0.04
Sweden	uncertainty (95% conf. int.): 10% (0.05-1 mg/l)	0.05	R: 5%	0.04
Switzerland	M.MAD: 0.02 mg/l			0.02
Turkey			M.MAD: 0.007; CoV: 0.60%	0.04
UK*			1%	0.02

*Data from AT, BY, EE, IT, NL and UK are taken from earlier years

Table A5.11: Detection limits and precision of potassium in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, mg/l	Precision	Detection limit, mg/l
Austria*		0.014	RSD: 2.85%	0.005
Belarus*				0.050
Czech Republic	CoV: 10.4% M.MAD: 0.015 mg/l	0.007	RSD: 6%	0.007
Denmark			M.MAD: 0.01 mg/l; CoV: 7.8%	0.05
Estonia*		0.095		0.1
Finland			M.MAD: 0.002 mg/l; CoV: 3.5%	0.006
France			at c<0.2 mg/l: RSD = 10-20% at 0.2<c<0.5 mg/l: RSD = 5-10% at 0.5<c<5 mg/l: RSD = 1-5%	0.02
Germany				0.01
Hungary	CoV: 11.04% M.MAD: 0.031 mg/l		M.MAD: 0.005; CoV: 2.85%	
Iceland		0.1	RSD: 5-10% at 1<c<6 mg K/l	0.4
Ireland				0.05
Italy* (IT01)	RSD: 1.4% at 1 mg K/l	0.01	RSD: 1.5% at 0.5 mg K/l RSD: 3.0% at 0.05 mg K/l	0.03
Italy, EU* (IT04)			CoV: 3.7%	0.005
Latvia		0.03	CoV: 2.3%	0.03
Lithuania			RSD: 8.1% at c<0.5 mg K/l	0.02
Netherlands*			SD: 0.01	0.04
Norway	M.MAD: 0.03; CoV: 59%		SD: 0.027; c=0.61 mg/l SD: 0.015; c=0.20 mg/l	0.01
Poland			RSD: 1.0% at 0.5 mg/l RSD: 2.9% at 0.1 mg/l RSD: 2.4% at 0.05 mg/l	0.02
PL05	M.MAD: 0.026; CoV: 22.5%	0.003	M.MAD: 0.004; CoV: 5.4%	0.003
Portugal			1.69%	0.077
Russia	RU01: M.MAD: 0.01; CoV: 2.41% RU13: M.MAD: 0.03; CoV: 4.15% RU16: M.MAD: 0.04; CoV: 5.01% RU18: M.MAD: 0.04; CoV: 5.1%		CoV: 5.20%; M.MAD: 0.02	0.03
Serbia and Montenegro			98%	0.02
Slovakia			CoV: 2.80%	0.03
Slovenia			RSD: 6.6% (at 0.100 mg/l)	0.02
Spain			CoV: 18%	0.05
Sweden	uncertainty (95% conf. int.): 10% (0.08-1 mg/l) 6% (1-15 mg/l)	0.08	R: 8%	0.05
Switzerland	M.MAD: 0.01 mg/l			0.01
Turkey			M.MAD: 0.006; CoV: 2.4%	0.015
UK*			1%	0.02

*Data from AT, BY, EE, IT, NL and UK are taken from earlier years

Table A5.12: Detection limits and precision of chloride in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, mg/l	Precision	Detection limit, mg/l
Austria*		0.034	RSD: 2.65%	0.009
Belarus*				0.050
Czech Republic	CoV: 14.5% M.MAD: 0.072 mg/l	0.018	RSD: 1.4%	0.018
Denmark			M.MAD: 0.08 mg/l; CoV: 3.4%	0.08
Estonia*		0.463		0.155
Finland			M.MAD: 0.003 mg/l; CoV: 1.4%	0.01
France			at c<0.2 mg/l: RSD = 10-20% at 0.2<c<0.5 mg/l: RSD = 5-10% at 0.5<c<5 mg/l: RSD = 1-5%	0.05
Germany				0.01
Hungary	CoV: 8.37% M.MAD: 0.053 mg/l		M.MAD: 0.070; CoV: 11.51%	
Iceland		0.1	RSD: 4% at 1 mg Cl/l	0.1
Ireland				0.05
Italy* (IT01)	RSD: 0.7% at 0.5 mg Cl/l	0.005	RSD: 0.6% at 0.5 mg Cl/l RSD: 1.1% at 0.05 mg Cl/l	0.001
Italy, EU* (IT04)			CoV: 2.1%	0.009
Latvia		0.07	CoV: 4.4%	0.07
Lithuania			RSD: 4.7% at c<0.5 mg Cl/l RSD: 2.3% at c>0.5 mg Cl/l	0.01
Netherlands*			SD: 0.04	0.18
Norway	M.MAD: 0.16, CoV: 22%		SD: 0.028 at c=1.16 mg/l SD: 0.02 at c=0.46 mg/l	0.01
Poland			RSD: 1.9% at 10 mg/l RSD: 2% at 1 mg/l RSD: 2.6% at 0.5 mg/l	0.02
PL05	M.MAD: 0.12; CoV: 24.5%	0.06	M.MAD: 0.02; CoV: 4.5%	0.06
Portugal			0.53%	0.03
Russia	RU01: M.MAD: 030; CoV: 2.70% RU13: M.MAD: 0.04; CoV: 2.15% RU16: M.MAD: 0.05; CoV: 3.12% RU18: M.MAD: 0.04; CoV: 4.10%			0.03
Serbia and Montenegro				0.04
Slovakia			CoV: 3.75%	0.04
Slovenia		0.06	RSD: 2.7% (at 0.500 mg/l)	0.04
Spain			CoV: 4.9%	0.31
Sweden	uncertainty (95% conf. int.): 8% (0.05-1 mg/l) uncertainty (95% conf. int.): 3% (1-32 mg/l)	0.05	R: 2%	0.05
Switzerland	M.MAD: 0.02 mg/l			0.02
Turkey			M.MAD: 0.069; CoV: 7.9%	0.043
UK*			1%	0.02

*Data from AT, BY, EE, IT, NL and UK are taken from earlier years

Table A5.13: Detection limits and precision of magnesium in precipitation.

Country	Measurements		Laboratory	
	Precision	**Detection limit, mg/l**	**Precision**	**Detection limit, mg/l**
Austria*		0.023	RSD: 1.34%	0.002
Belarus*				0.001
Czech Republic	CoV: 10.6% M.MAD: 0.015 mg/l	0.001	RSD: 3%	0.001
Denmark			M.MAD: 0.02 mg/l; CoV: 3.9%	0.05
Estonia*		0.077		0.089
Finland			M.MAD: 0.001 mg/l; CoV: 2.1%	0.003
France			at c<0.2 mg/l: RSD = 10-20% at 0.2<c<0.5 mg/l: RSD = 5-10% at 0.5<c<5 mg/l: RSD = 1-5%	0.02
Germany				0.01
Hungary	CoV: 2.19% M.MAD: 0.010 mg/l		M.MAD: 0.002; CoV: 1.24%	
Iceland		0.1	RSD: 1-3% at 1<c<6 mg Mg/l	0.005
Ireland				0.05
Italy* (IT01)	RSD: 1.1% at 0.5 mg Mg/l	0.005	RSD: 0.8% at 0.5 mg Mg/l RSD: 3.2% at 0.05 mg Mg/l	0.001
Italy, EU* (IT04)			CoV: 2.2%	0.002
Latvia		0.05	CoV: 4.1%	0.020
Netherlands*			SD: 0.01	0.02
Norway	M.MAD: 0.01, CoV: 30%		SD: 0.012 at c=0.31 mg/l SD: 0.007; c=0.19 mg/l	0.01
Poland			RSD: 1.0% at 0.25mg/l RSD: 1.0% at 0.1 mg/l RSD: 2.4% at 0.025 mg/l	0.007
PL05	M.MAD: 0.004; CoV: 13.4%	0.001	M.MAD: 0.001; CoV: 2.3%	0.0005
Portugal			0.60%	0.03
Russia	RU01: M.MAD: 0.01 RU13: CoV: 1.84% RU18: M.MAD: 0.03; CoV: 0.64%		CoV: 8.17%; M.MAD: 0.09	0.001
Serbia and Montenegro			99.5%	0.01
Slovakia			CoV: 2.01%	0.01
Slovenia		0.017	RSD: 2.3% (at 0.100 mg/l)	0.04
Spain			CoV: 7.2%	0.02
Sweden	uncertainty (95% conf. int.): 20% (0.02-1 mg/l) uncertainty (95% conf. int.): 5% (1-15 mg/l)	0.02	R: 5%	0.01
Switzerland	M.MAD: 0.01 mg/l			0.001
Turkey			M.MAD: 0.002; CoV: 1.03%	0.005
UK*			1%	0.01

*Data from AT, BY, EE, IT, NL and UK are taken from earlier years

Table A5.14: Detection limits and precision of sodium in precipitation.

Country	Measurements		Laboratory	
	Precision	**Detection limit, mg/l**	**Precision**	**Detection limit, mg/l**
Austria*		0.030	RSD: 1.8%	0.003
Belarus*				0.050
Czech Republic	CoV: 15.5% M.MAD: 0.019 mg/l	0.004	RSD: 3%	0.004
Denmark		DK03: 0.09 $\mu g/m^3$ DK05: 0.14 $\mu g/m^3$ DK08: 0.09 $\mu g/m^3$	M.MAD: 0.10 mg/l; CoV: 1.8%	0.05 $\mu g/m^3$
Estonia*		0.095		0.1
Finland			M.MAD: 0.001 mg/l; CoV: 0.9%	0.002
France			at c<0.2 mg/l: RSD = 10-20% at 0.2<c<0.5 mg/l: RSD = 5-10% at 0.5<c<5 mg/l: RSD = 1-5%	0.02
Germany				0.01
Hungary	CoV: 3.11% M.MAD: 0.051 mg/l		M.MAD: 0.008 mg/l; CoV: 1.07%	
Iceland		0.1	RSD: 1-3% at 1<c<6 mg Na/l	0.01
Ireland				0.05
Italy* (IT01)	RSD: 0.9% at 0.5 mg Na/l	0.005	RSD: 1.3% at 0.5 mg Na/l RSD: 2.0% at 0.05 mg Na/l	0.001
Italy, EU* (IT04)			CoV: 2.1%	0.011
Latvia		0.05	CoV: 3.6%	0.03
Lithuania			RSD: 2.4-5.7%	0.02
Netherlands*			SD: 0.01	0.05
Norway	M.MAD: 0.09, CoV: 22%		SD: 0.025 at c=0.75 mg/l SD: 0.011 at c=0.30 mg/l	0.01
Poland			RSD: 0.8% at 1 mg/l RSD: 1.4% at 0.4 mg/l RSD: 2.3% at 0.2 mg/l	0.02
PL05	M.MAD: 0.023; CoV: 14.6%	0.002	M.MAD: 0.003; CoV: 5.4%	0.002
Portugal			0.54%	0.025
Russia	RU01: M.MAD: 0.02; CoV: 3.71% RU13: M.MAD: 0.03; CoV: 2.10% RU16: M.MAD: 0.02; CoV: 0.75% RU18: M.MAD: 0.03; CoV: 3.12%		CoV: 0.45%	0.01
Serbia and Montenegro			98.25%	0.02
Slovakia			CoV: 2.11%	0.04
Slovenia		0.06	RSD: 2.7% (at 0.200 mg/l)	0.02
Spain			CoV: 14%	0.1
Sweden	uncertainty (95% conf. int.): 6% (0.12-1 mg/l) uncertainty (95% conf. int.): 2% (1-15 mg/l)	0.12	R: 4%	0.05
Switzerland	M.MAD: 0.02 mg/l			0.02
Turkey			M.MAD: 0.013; CoV: 1.79%	0.064
UK*			1%	0.01

*Data from AT, BY, EE, IT, NL and UK are taken from earlier years

Table A5.15: Detection limits and precision of arsenic in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, µg/l	Precision	Detection limit, µg/l
Estonia		0.2		
Finland			M.MAD: 0.008 µg/l; CoV: 10.5%	0.006
Germany				0.004
Iceland				0.1
Latvia			CoV: 5.5%	1.3
Lithuania			SD: 0.02	0.05
Netherlands			SD: 0.02	0.06
Norway				0.05
Poland PL05			7.5%	0.05
Slovakia			CoV: 2.06%	0.04
Spain				1.50
UK				0.04 mg/l

Table A5.16: Detection limits and precision of cadmium in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, µg/l	Precision	Detection limit, µg/l
Czech Republic	CoV: 2.32% M.MAD: 0.021 µg/l	0.01	RSD: 7%	0.01
Estonia		0.01		
Finland			M.MAD: 0.002 µg/l CoV: 3.0%	0.002
Germany				0.003
Iceland				0.005
Latvia			CoV: 5.7%	0.04
Lithuania			SD: 0.002	0.006
Netherlands			SD: 0.002	0.01
Norway				0.002
Poland PL05			8.2%	0.002
Slovakia			CoV: 3.18%	0.03
Spain				0.15
UK				0.04 mg/l

Table A5.17: Detection limits and precision of chromium in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, µg/l	Precision	Detection limit, µg/l
Finland			M.MAD: 0.04 µg/l; CoV: 21.8%	0.02
Germany				0.01
Iceland				0.2
Lithuania			SD: 0.05	0.2
Netherlands			SD: 0.08	0.3
Norway				0.1
Poland PL05				0.02
Slovakia			CoV: 2.26%	0.04
Spain				1.15
UK				0.008 mg/l

Table A5.18: Detection limits and precision of copper in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, µg/l	Precision	Detection limit, µg/l
Estonia		26		
Finland			M.MAD: 0.057 µg/l; CoV: 4.7%	0.05
Germany				0.01
Iceland				0.1
Latvia			CoV: 4.6%	0.4
Lithuania			SD: 0.1	0.3
Netherlands			SD: 0.05	0.2
Norway				0.5
Poland PL05				0.01
Slovakia			CoV: 2.81%	0.2
Spain				0.42
UK				0.003 mg/l

Table A5.19: Detection limits and precision of iron in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, µg/l	Precision	Detection limit, µg/l
Czech Republic	CoV: 1.02%, M.MAD : 0.012mg/l	6	RSD: 7%	6
Finland			M.MAD: 3.21 µg/l CoV: 9.6%	1.5
Germany				0.5
Netherlands			SD: 3	13

Table A5.20: Detection limits and precision of manganese in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, µg/l	Precision	Detection limit, µg/l
Czech Republic	CoV: 10.75% M.MAD: 0.839 µg/l	0.4	RSD: 6%	0.4
Finland			M.MAD: 0.073 µg/l CoV: 3.4%	0.005
Latvia			CoV: 8.8%	10
Slovakia			3.5%	0.05

Table A5.21: Detection limits and precision of nickel in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, µg/l	Precision	Detection limit, µg/l
Czech Republic	CoV: 9.12% M.MAD: 0.210 µg/l	0.6	RSD: 8%	0.6
Finland			M.MAD: 0.04 µg/l CoV: 15.5%	0.02
Germany				0.2
Iceland				0.2
Latvia			CoV: 6.0%	0.9
Lithuania			SD: 0.1	0.3
Netherlands			SD: 0.05	0.06
Norway				0.1
Poland PL05				0.02
Slovakia			CoV: 1.75%	0.1
Spain				3.57
UK				0.009 mg/l

Table A5.22: Detection limits and precision of lead in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, µg/l	Precision	Detection limit, µg/l
Czech Republic	CoV: 10.73% M.MAD: 0.325 µg/l	0.5	RSD: 8%	0.5
Estonia		0.6		
Finland			M.MAD: 0.049 µg/l CoV: 3.7%	0.03
Germany				0.002
Iceland				0.01
Latvia			CoV: 4.0%	0.4
Lithuania			SD: 0.03	0.09
Netherlands			SD: 0.02	0.06
Norway				0.01
Poland PL05				0.01
Slovakia			CoV: 2.5%	0.2
Spain				2.07
UK				0.002 mg/l

Table A5.23: Detection limits and precision of zinc precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, µg/l	Precision	Detection limit, µg/l
Czech Republic	CoV: 8.92% M.MAD: 0.002 mg/l	3	RSD: 6%	3
Finland			M.MAD: 0.183 µg/l CoV: 3.1%	0.03
Germany				0.2
Iceland				0.1
Latvia			CoV: 6.0%	10
Lithuania			SD: 0.3	1.0
Netherlands			SD: 0.5	1.9
Norway				0.1
Poland PL05	M.MAD: 2.0 µg Zn/l; CoV: 24%	0.2	M.MAD: 0.2; CoV 2%	0.3
Slovakia			CoV: 7.35%	1.7
Spain				0.16
UK				0.1 mg/l

Table A5.24: Detection limits and precision of arsenic in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Czech Republic	CoV: 8.56% M.MAD: 0.052 ng/m^3	0.02	RSD: 10%	0.107 µg/l
Germany				0.004 µg/l
Iceland		0.0004		
Latvia		0.05	CoV: 5.0%	1.2 µg/l
Lithuania			SD: 0.3	1 ng/m^3
Netherlands			0.04	0.2 ng/m^3
Norway, NO42				0.04 ng/m^3
Slovakia			CoV: 1.49%	4.7 ng/filter
Slovenia				0.162 ng/m^3

Table A5.25: Detection limits and precision of cadmium in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Czech Republic	CoV: 15.1% M.MAD: 0.021 ng/m^3	0.005	RSD: 5%	0.025 µg/l
Germany				0.003 µg/l
Iceland		0.0002		
Lativia		0.01	CoV: 3.5%	0.20 µg/l
Lithuania			SD: 0.01	0.03 ng/m^3
Netherlands			0.01	0.04 ng/m^3
Norway, NO42				0.004 ng/m^3
Slovakia			CoV: 1.95%	1.0 ng/filter
Slovenia				0.081 ng/m^3
Spain				0.01 ng/m^3

Table A5.26: Detection limits and precision of chromium in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Iceland		0.02		
Norway				1 ng/m^3
Slovakia			CoV: 2.61%	8 ng/filter
Slovenia				0.3 ng/m^3

Table A5.27: Detection limits and precision of copper in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Germany				0.01 µg/l
Iceland		0.0004		
Latvia		0.12	CoV: 2.5%	3.0 µg/l
Lithuania			SD: 0.01	0.5 ng/m^3
Norway				0.2 ng/m^3
Slovakia			CoV: 1.90%	4 ng/filter
Slovenia				0.3 ng/m^3
Spain				0.18 ng/m^3

Table A5.28: Detection limits and precision of manganese in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Germany				0.002 µg/l
Iceland		0.0008		
Latvia		0.25	CoV: 2.5%	7.0 µg/l
Norway				0.01 ng/m^3

Table A5.29: Detection limits and precision of nickel in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Germany				0.01 μg/l
Iceland		0.0001		
Latvia		0.20	CoV: 4.3%	3.3 μg/l
Lithuania			SD: 0.2	0.8 ng/m^3
Norway				0.09 ng/m^3
Slovakia			CoV: 2.01%	10 ng/filter
Slovenia				0.3 ng/m^3

Table A5.30: Detection limits and precision of lead in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Czech Republic	CoV: 9.01% M.MAD: 0.734 ng/m^3	0.01	RSD: 3%	0.05 μg/l
Germany				0.002 μg/l
Iceland		0.00004		
Latvia		0.05	CoV: 2.0%	2.0 μg/l
Lithuania			SD: 0.1	0.5 ng/m^3
Netherlands			0.06	0.2 ng/m^3
Norway				0.1 ng/m^3
Slovakia			CoV: 2.34%	3 ng/filter
Slovenia				3.2 ng/m^3
Spain				0.4 ng/m^3

Table A5.31: Detection limits and precision of zinc in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Iceland		0.0004		
Latvia		0.42	CoV: 3.6%	14 μg/l
Lithuania			SD: 0.6	2 ng/m^3
Netherlands			3.6	15 ng/m^3
Norway				0.2 ng/m^3
Slovakia			CoV: 2.22%	70 ng/filter

Table A5.32: Detection limits and precision of measurements of particulate matter.

Country	Precision	Detection limit
Germany (PM_{10})		1 μg/m^3
Italy IT01 (PM_{10})	2.00%	2 μg/m^3
Lithuania ($PM_{2.5}$)	1 μg/^{m3}	3 μg/m^3
Netherlands		10 μg/m^3
Norway (PM_{10})	RSD: 5%	0.2 μg/m^3
Slovakia (TSP)	CoV: 1.80%	0.06 mg/filter
Slovenia		1 μg/m^3
Spain (PM_{10} and $PM_{2.5}$)	2.00%	1 μg/m^3
Sweden (PM_{10}, hr mean)	2.2 μg/m^3	3 μg/m^3
Switzerland (PM_{10}/$PM_{2.5}$/PM_1)	Uncertainty- (95% conf. int.): 10%	1 μg/m^3
UK	4 μg m^{-3}	

Table A5.33: Detection limits and precision of volatile organic carbons, VOC.

	Laboratory detection limit. [ppb]					
Compound	**Czech Republic**	**France**	**Germany**	**Finland**	**Spain**	**UK**
VOC (general)		0.01	0.01		0.01	0.01
Ethane	0.055			0.006		
Ethene	0.020			0.008		
Ethyne	0.041			0.020		
Propane	0.008			0.007		
Propene	0.011			0.010		
Propyne	0.003			0.013		
N-butane	0.003			0.007		
2-methyl propane (i-butane)	0.005			0.008		
2-methyl propene (i-butene)	0.006			0.008		
1-butene	0.009			0.008		
Trans-2-butene	0.004			0.009		
Cis-2-butene	0.008			0.007		
1,3-butadiene	0.009			0.009		
N-pentane	0.003			0.007		
2-methyl butane (i-pentane)	0.008			0.007		
1-pentene						
Trans-2-pentene	0.012			0.011		
Cis-2-pentene	0.009			0.010		
2-methyl pentane	0.003			0.008		
3-methyl pentane	0.012			0.006		
Isoprene	0.006			0.010		
N-hexane	0.011			0.006		
Hexene						
Cyclohexane	0.003			0.006		
N-heptane	0.023			0.005		
Benzene	0.012			0.004		
Methyl benzene (toluene)	0.021					
Ethyl benzene	0.019					
1,3-dimethyl benzene (m-xylene)	0.058					
1,2-dimethyl benzene (o-xylene)	0.013					
1,3,5-trimethyl benzene	0.013					
1,2,4-trimethyl benzene	0.007					
2 and 3-methyl pentane (combined areas)	5.8					
OC in general					0.05 ng/l	
		in ug/m^3				
methanal		0.03				
ethanal		0.025				
propanone		0.03				
propenal		0.03				
propanal		0.03				
MVK		0.025				
butanal+isobutanal		0.04				
benzaldéhyde		0.03				
pentanal+tolualdehyde		0.04				
hexanal		0.03				
glyoxal		0.025				
methylglyoxal		0.03				
methylpropenal		0.025				
ethylmethylketone		0.03				

Table A5.34: Detection limits and precision of persistent organic pollutants (POP).

Compound	Laboratory detection limit, pg/m³				
	Czech Republic	Norway	UK	Iceland	Latvia
PCB 28	1	0.7		1.0 – 8.0	
PCB 31	1	0.5		0.7 – 7.6	
PCB 52	1	0.2		0.2 – 2.2	
PCB 101	1	0.06		0.2 – 0.3	
PCB 105	1	0.01		0.2 – 0.3	
PCB 118	1	0.05		0.3	
PCB 138	1	0.05		0.2 – 0.3	
PCB 153	1	0.05		0.2 – 0.3	
PCB 153	1	0.05		0.2 – 0.3	
PCB 180	1	0.02		0.2 – 0.3	
alfa-HCH	1	0.1		0.2 – 0.5	
beta-HCH	1			0.3 – 0.7	
gamma-HCH	1	0.3		0.3 – 0.5	
delta-HCH	1				
HCB	1	0.05		0.2 – 1.0	
p,p'-DDE	1	0.05		0.3	
p,p'-DDD	1	0.05		0.3	
p,p'-DDT	1	0.05		0.3 – 1.0	
Hexachlorbenzene	1	0.05			
Pentachlorbenzene	1				
tr-chlordane		0.06		0.2	
cis-chlordane		0.08		0.2	
tr-nonachlor		0.04		0.2	
cis-nonachlor		0.02			
Dieldrin				0.3	
Toxaphene				0.2 – 0.3	
PAH (general)		1			
Naphtalene	5				
Acenaphthylene	5				
Acenaphthene	5				
Fluorene	5				
Phenanthrene	5				
Anthracene	5				
Fluoranthene	5				
Pyrene	5				
Benz[a]antracene	5				
Chrysene	5				
Benzo[b]fluorantene	5				
Benzo[k]fluorantene	5				
Benzo[a]pyrene	5		< 10		< 50
Indeno[123cd]pyrene	5				
Dibenz[ah]anthracene	5				
Benzo[ghi]perylene	5				

Annex 6

Classification of the QA flags

Table A6.1: Criteria used for classification of data quality based on field comparison results.

M.MAD / CoV		≤ 0.25 µg S/m³	[0, 25 %]	≤ 0.50 µg S or N/m³	< 25%, 50 %]	> 0.50 µg S or N/m³ and < 50%, → >
Regression slope (a) Ref = a*Lab	[1.50, → >	80	81	82	83	84
	[1.30, 1.50]	60	61	62	63	64
	[1.20, 1.30]	40	41	42	43	44
	[1.10, 1.20]	20	21	22	23	24
	[0.90, 1.10]	00	01	02	03	04
	[0.80, 0.90]	10	11	12	13	14
	[0.70, 0.80]	30	31	32	33	34
	[0.50, 0.70]	50	51	52	53	54
	< ←, 0.50]	70	71	72	73	84

Table A6.2: Criteria used for classification of data quality based on laboratory comparison results.

2RSD %		<0, 1*DQO]	<1*DQO - 2*DQO]	<2*DQO - 4*DQO]	<4*DQO, → >
RB %	< ←, -40 >	80	81	82	83
	[-40, -20 >	60	61	62	63
	[-20, -10 >	40	41	42	43
	[-10, - 5 >	20	21	22	23
	[-5, +5]	00	01	02	03
	< 5, 10]	10	11	12	13
	< 10, 20]	30	31	32	33
	< 20, 40]	50	51	52	53
	< 40, → >	70	71	72	73