EMEP/CCC-Report 4/2004

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

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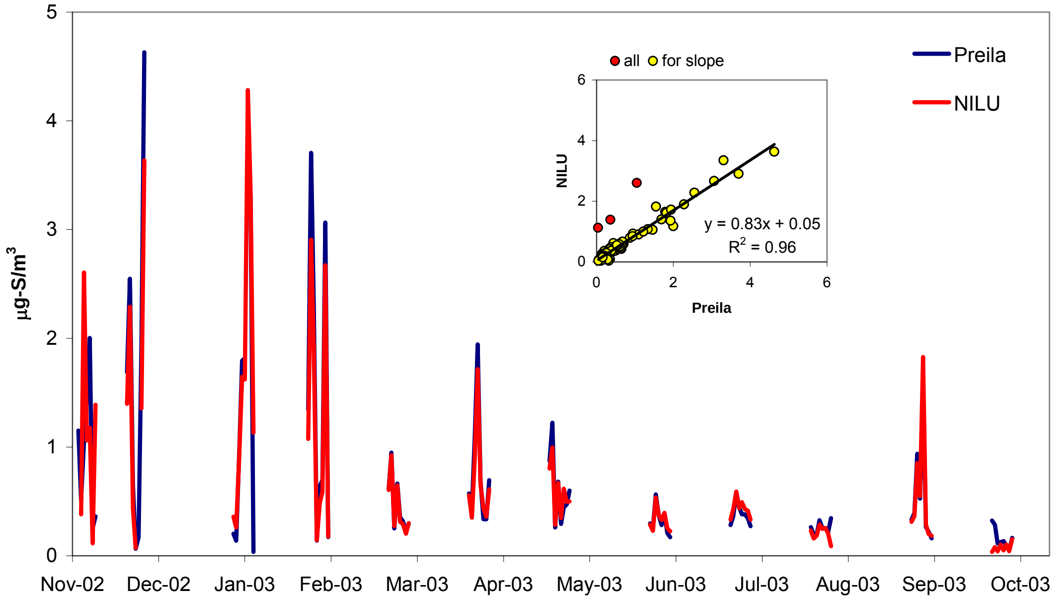
Jan Schaug and Hilde Th. Uggerud**



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# Summary

This report is mainly concerned with the quality of the 2002 data and new results from field and laboratory comparisons.

The requirement with respect to data completeness for the main components in precipitation, i.e. 90 per cent, is generally met, and only two participants have less than a complete precipitation measurement programme. The situation is less favourable for air components with respect to data completeness. There is a strong need for more sites for nitrogen components in air, and only two countries perform accurate measurements of nitric acid and particulate nitrate, and ammonia and ammonium in particles separately by use of denuder systems.

The ion balance for many countries was within ± 20 per cent, which indicate valid data when pH is less than 5.5 (Annex 2). 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. A flagging system has been developed to fully utilize the information from the ion balance test.

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, magnesium, 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 results from the POP laboratory intercomparison, round 2 was in general satisfactory and the average deviation from the median are mostly within 50%.

Results from the field comparisons in Estonia, Latvia and Lithuania are presented in this report. The results from Preila (LT15) are very satisfactory, except for $NO_2$. The average difference is less than 10% and the spread is very small, especially for $SO_2$ and $SO_4^{2-}$. $NO_2$ is overestimated at LT15 and the spread is large. The comparison in Rucava (LV10) indicates some problems with the $SO_2$ measurements, which are systematically overestimated. The $SO_4^{2-}$ measurements are quite satisfactory although they underestimate the concentration somewhat. The measurements of both the sum of nitrate and nitric acid, and the sum of ammonia and ammonium are very good. The $NO_2$ measurements are also very good, the precision is not so very high but the correlation is perfect. The results from the Lahemaa intercomparison are not satisfactory. For $SO_2$ it is OK, both the manual method and the monitor show nice correlation with the reference, however, both methods systematically underestimate the concentration, the monitor more than the manual method. The $NO_2$ measurements are more uncertain. The manual method is almost half of the reference concentration and the precision is also quite low. For $SO_4^{2-}$ there are unresolved problems. There is no correlation between the measurements and these data should not be used. It is

highly recommended that Estonia change their methodology, i.e. using a filterpack with higher flow.

National organized field comparisons of heavy metals in precipitation have been performed in Germany and Belgium comparing wet only and bulk collector. In the German comparison there are large deviations for some elements, especially cadmium indicating influence of dry deposition of coarse particles in the bulk collector. The Belgium data shows no correlation between the samples and it is apparent that Belgium needs to evaluate their QA/QC routines for the heavy metal measurements.

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

Annex 3 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 2002, 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 2002 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.

Parts of the information given here are collected from the participating laboratories, this being data on detection limits and precision. CCC organizes annually different types of comparisons, and the EMEP Laboratory inter-comparison 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 based on statistical criteria.

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.

## 2. Measurement programme and data completeness

EMEP's measurement programme in 2002 is given in Table 1. Details on the sampling program and measurement frequency at the different sites are found in the different data reports (Hjellbrekke, 2004a and 2004b; Aas, 2004; Solberg, 2004).

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 new monitoring strategy being developed for 2004 -2009 aims to improve this situation and a better spatial coverage is expected.

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 2002.

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 2002.*

| | 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),<br>Cu, Zn, As, Cr, Ni (second priority) | weekly | weekly |
| | $PM_{10}$ mass | 24 hours | daily |
| Gas + particles | $HNO_3$(g)+$NO_3^-$(p),<br>$NH_3$(g)+$NH_4^-$(p) | 24 hours | daily |
| | POPs (PAH, PCB, HCB, chlordane, lindane, $\alpha$-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),<br>Cu, Zn, As, Cr, Ni (second priority) | weekly | weekly |
| | POPs (PAH, PCB, HCB, chlordane, lindane, $\alpha$-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.

## 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 2002 are presented in Annex 3, 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.

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 Austria, Latvia and Norway. In other countries, e.g. in Denmark and Germany, 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, 1996). Only one site does this today, Kollumerwaard, Netherlands (NL09).

## 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 4.

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, 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. Results from field comparisons

## 5.1 Main components in air

### *5.1.1 Introduction*

Many Parties have applied measurement methods different from the recommended ones, and this has contributed to systematic concentration differences and a comparability problem in EMEP. Laboratory comparisons and field studies are organized in order to quantify systematic differences and errors and, as far as possible, to assess the measurement accuracies. Field comparisons have been carried out, and so far completed in United Kingdom, Ireland, Portugal, France, Germany, Poland, the Czech Republic, Croatia, Spain, Netherlands, Slovenia and Switzerland (e.g. Aas et al., 2003). Results from the field intercomparison in Estonia, Latvia and Lithuania are presented in this report.

The comparisons are carried out at an EMEP site using a set of reference instruments that corresponds to the specifications in the EMEP Manual. An inherent advantage of the reference methods is that the samples are stable and may be mailed from one country to another without any deterioration or change of concentrations. In order to make the comparison valid for a representative period, it was decided to distribute the comparison measurements over a whole year and for the air components about 100 measurements were considered necessary. The reference sampler is usually sampled one week every month. The measurements are assigned a QA flag in accordance to the definitions described in Chapter 7.

### *5.1.2 Reference instrumentation*

The EMEP manual recommends a filterpack method with an aerosol filter for collection of sulphate, and subsequent absorption of sulphur dioxide on a cellulose filter impregnated with KOH. This filterpack is also suitable for determining the sum of nitrate aerosol and gaseous nitric acid. Evaporation of ammonium nitrate collected on the aerosol filter during the sampling period will lead to nitric acid that is collected on the impregnated filter. The quantity of nitrate accumulated on the impregnated filter will therefore usually represent an overestimate of the airborne gaseous nitric acid.

For nitrogen dioxide, the recommended sampling method is conversion to nitrite, using sodium iodide as reducing agent, which is added to a glass sinter frit in a glass bulb. The methods are described in more detail in the EMEP Manual for Sampling and Chemical Analysis (EMEP, 1996).

### *5.1.3 Comparison at Preila (LT15), Lithuania*

At Preila they use the reference methods for measuring the main ions and gases in air. Sum of nitric acid and nitrate and sum of ammonia and ammonium are sampled using a one stage filterpack with KOH and oxalic acid impregnated Whatman 40 filter respectively, the flow is 16-17 m$^3$/day. $SO_2$ and $SO_4$ are sampled using a two-stage filterpack; the aerosol filter is a Whatman 40, and then a KOH impregnated Whatman 40 filter for $SO_2$, the flow is 24 m$^3$/day. For $NO_2$ KI impregnated glass sinters are used. The analytical methods used in the laboratory at Institute of Physics are also in accordance to the recommendations in the EMEP Manual, using IC for sulphate and nitrate and spectrophotometry for $NO_2$ and ammonium. The difference between the co-located NILU samplers is the location of the filters; the filters from the local sampler are placed inside a box with openings, similar box as for finding standard meteorological parameters. The NILU sampler has the filters outside covered with a plastic cap to prevent rain on the filterpack. Preila is located very close to the Baltic Sea and a proper cover is necessary to prevent too much sea spray on the filters.

The results from this comparison are found in Figure 1–Figure 5 and Table 2.

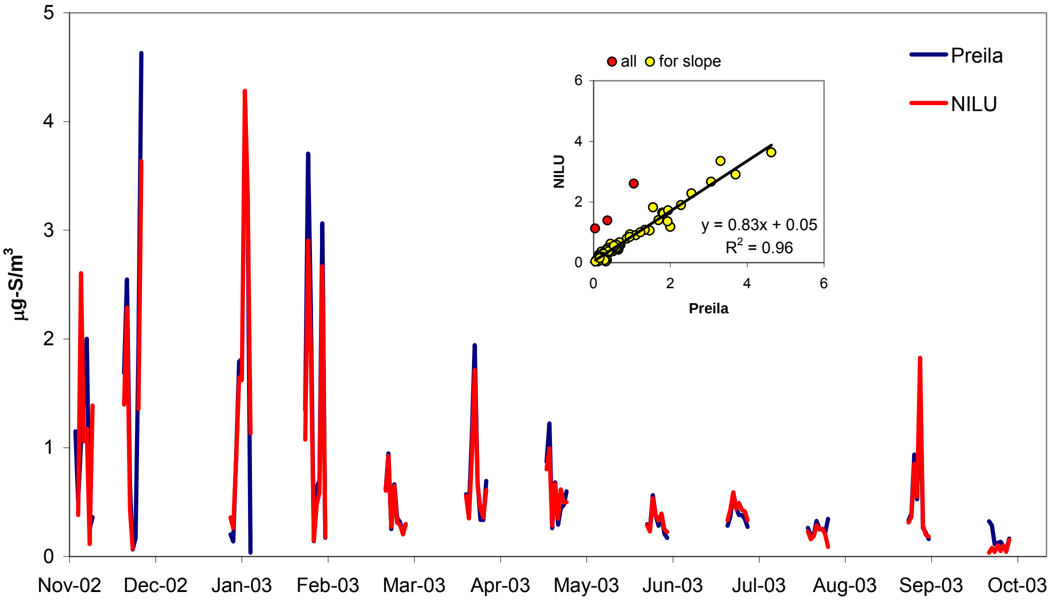


*Figure 1: Comparison of the co-located measurements of $SO_2$ at Preila. Outliers (red dots in xy plot) are not included to estimate the slope.*

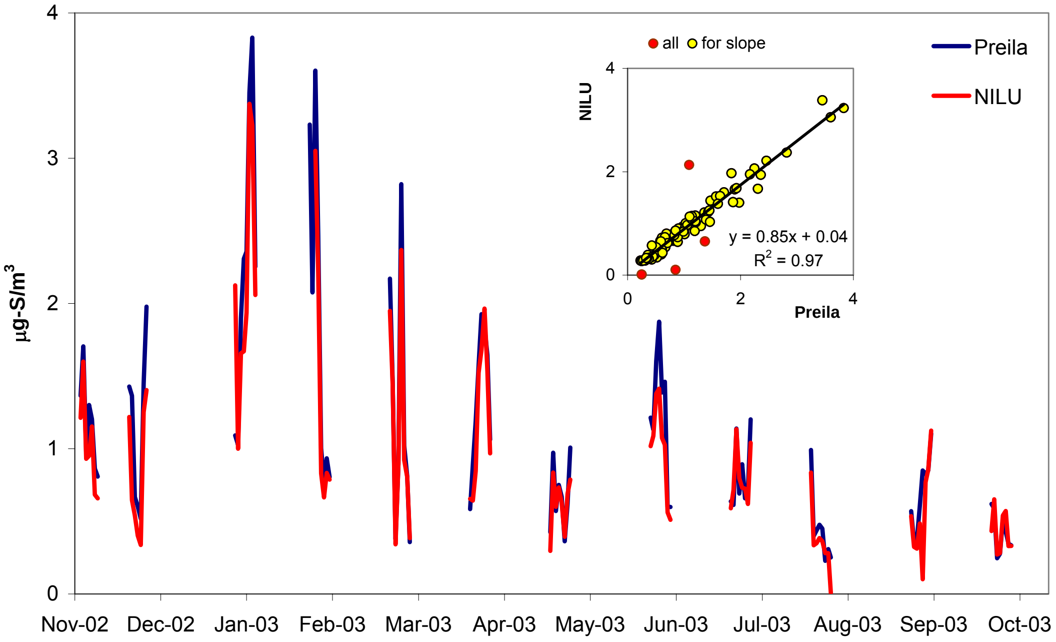


*Figure 2: Comparison of the co-located measurements of $SO_4^{2-}$ at Preila. Outliers (red dots in xy plot) are not included to estimate the slope.*

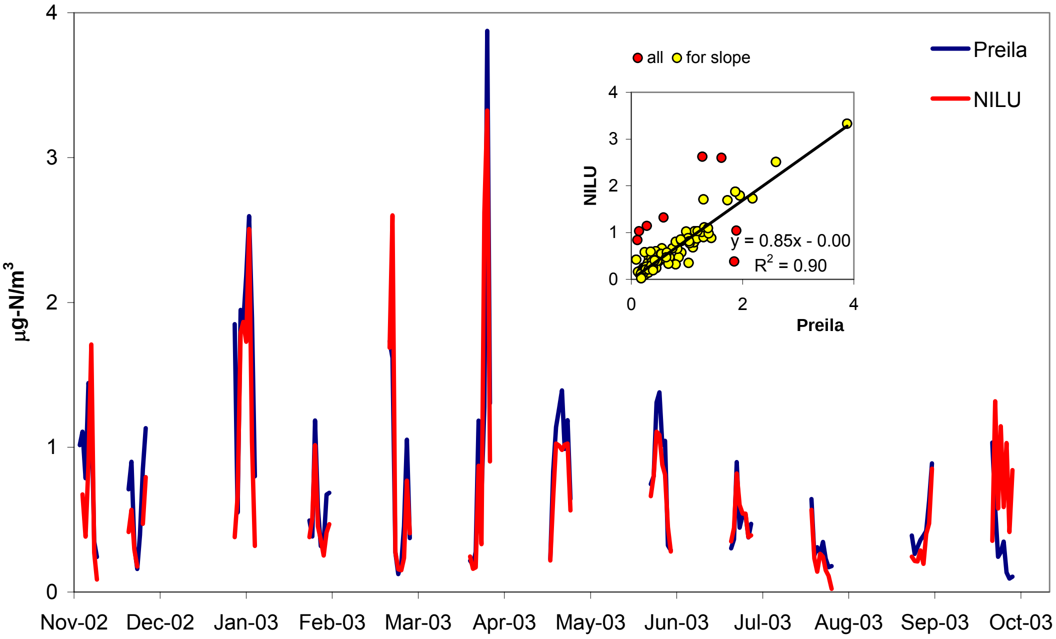


*Figure 3: Comparison of the co-located measurements of sum($HNO_3$ + $NO_3^-$) at Preila. Outliers (red dots in xy plot) are not included to estimate the slope.*

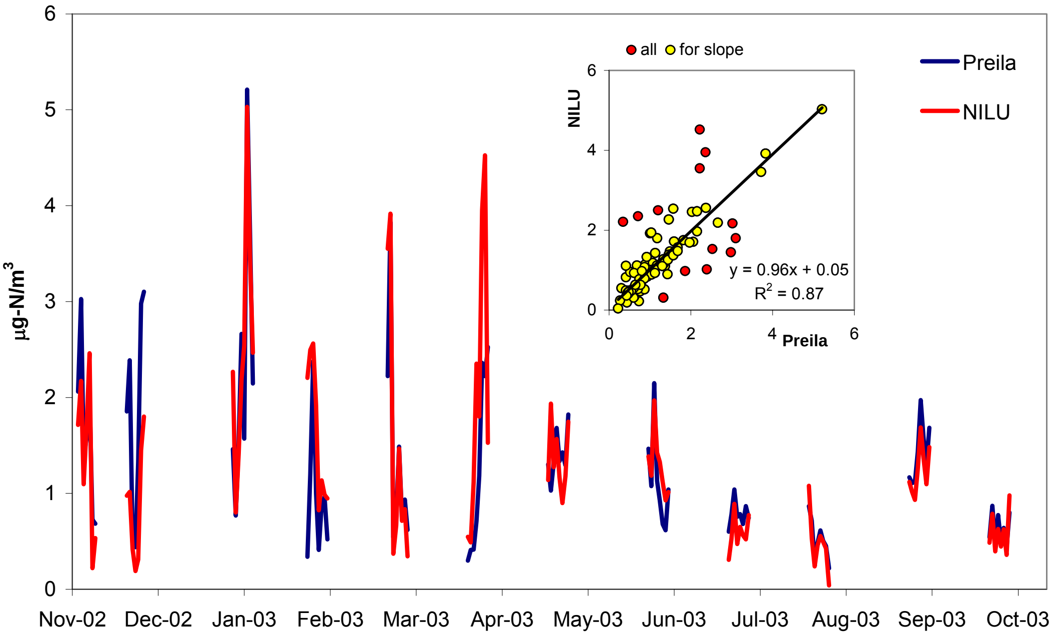


*Figure 4: Comparison of the co-located sum($NH_4^+$ + $NH_3$) measurements at Preila. Outliers (red dots in xy plot) are not included to estimate the slope.*

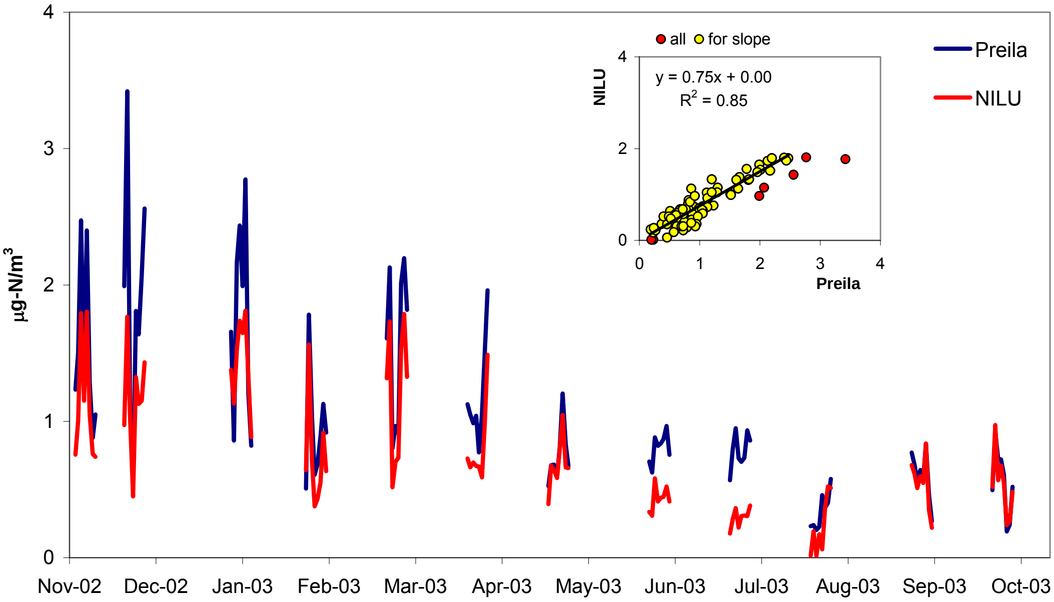


*Figure 5: Comparison of the co-located $NO_2$ measurements at Preila. Outliers (red dots in xy plot) are not included to estimate the slope.*

*Table 2: Summary of results of co-located measurements at Preila, in $\mu g/m^3$.*

| | $SO_4$ | $SO_2$ | $NO_2$ | sum$NH_4$ | sum$NO_3$ |
|---|---|---|---|---|---|
| Mean ref: | 0.95 | 0.68 | 0.77 | 1.30 | 0.69 |
| Mean: | 1.07 | 0.72 | 1.06 | 1.27 | 0.76 |
| Median ref: | 0.79 | 0.40 | 0.66 | 1.09 | 0.47 |
| Median: | 0.88 | 0.36 | 0.86 | 1.03 | 0.56 |
| Num pairs: | 92 | 91 | 96 | 94 | 92 |
| Average of diff: | -0.12 | -0.04 | -0.29 | 0.03 | -0.07 |
| Median of diff: | -0.09 | -0.01 | -0.28 | -0.07 | -0.08 |
| M.MAD: | 0.13 | 0.09 | 0.28 | 0.25 | 0.16 |
| CoV: | 17% | 22% | 43% | 23% | 35% |
| slope | 0.85 | 0.83 | 0.75 | 0.96 | 0.85 |
| QA flag | 10 | 10 | 32 | 00 | 10 |
| QA category | B | B | B | A | B |

The results from this comparison are very satisfactory, except for $NO_2$. The average difference is less than 10% and the spread is very small especially for $SO_2$ and $SO_4^{2-}$. The reason for not defining all the filterpack measurements within the QA category A is because the slopes are below 0.90 for all except sum$NH_4$ indicating a systematic overestimation; however this is rather small. For $NO_2$ the overestimation is larger; in addition the spread is quite large with a CoV of 43%. One reason might be that the $NO_2$ intake at Preila is rather close to the floor. Another reason can be a problem with field blanks. One can see in Figure 5 that in some months the difference between the co-located measurements are rather big (i.e. June and July), but the measurements are clearly correlated indicating that the field blanks used to correct the data is biased.

### *5.1.4 Comparison at Rucava (LV10), Latvia*

At Rucava they use 2 filterpacks with Whatman 41 filters and a flow of 13-18 $m^3$/day to measure $SO_2$, $SO_4$ and sum of nitrate and sum of ammonium. The Latvian Hydrometeorological Agency (LMA) analyse $SO_2$, $SO_4$ and sum of nitrate using ion chromatography (IC) while ammonium is analysed using spectrophotometry (Indophenol method). $NO_2$ is sampled using absorbing tubes with glass granules and KI solution. The flow is 0.3-0.5 $m^3$/day. $NO_2$ is analysed spectrophotometrically using the Griess method. In addition, in two of the months (2 x 2 weeks) an extra set of filters were installed at Rucava, filter 3-packs identical to the reference method. These filters were analysed at LMA while the original filters from Rucava were sent to NILU for analysis. This was done to better understand the origin of the differences in field or laboratory.

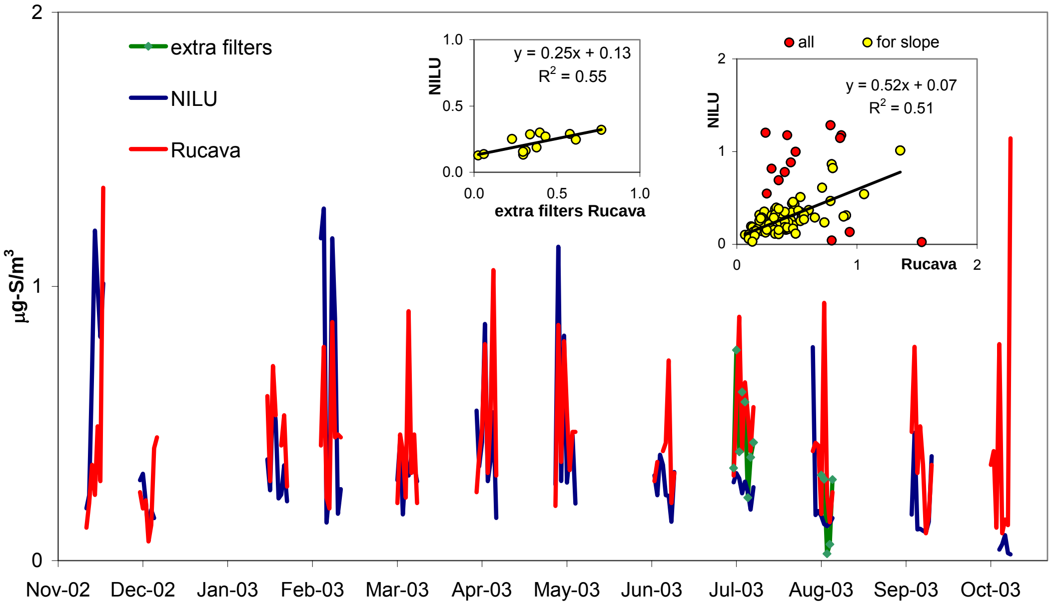


*Figure 6: Comparison of the co-located measurements of $SO_2$ at Rucava. Outliers (red dots in xy plot) are not included to estimate the slope.*

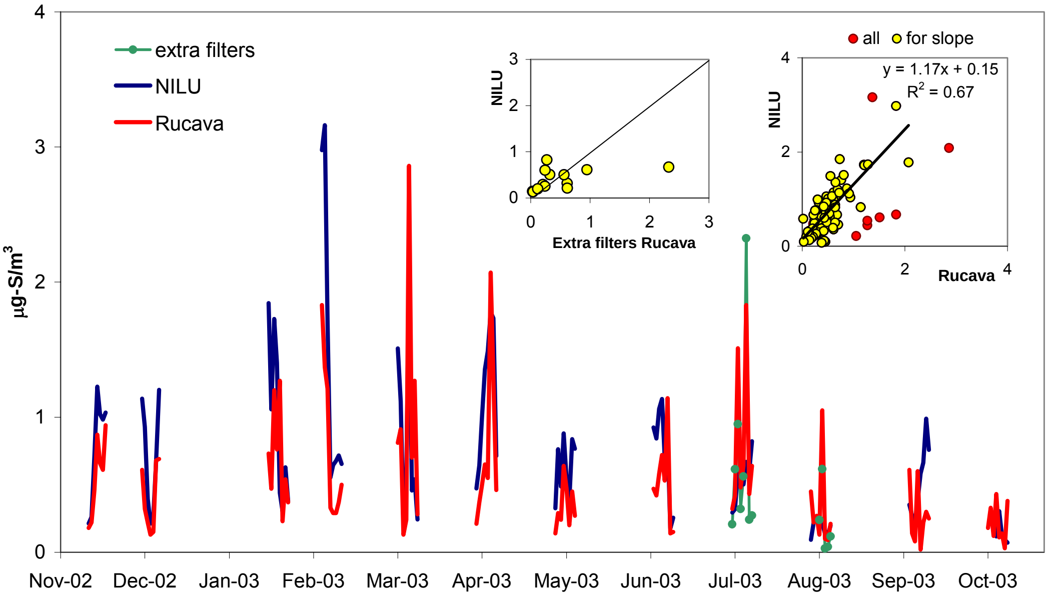


*Figure 7: Comparison of the co-located measurements of $SO_4^{2-}$ at Rucava. Outliers (red dots in xy plot) are not included to estimate the slope.*

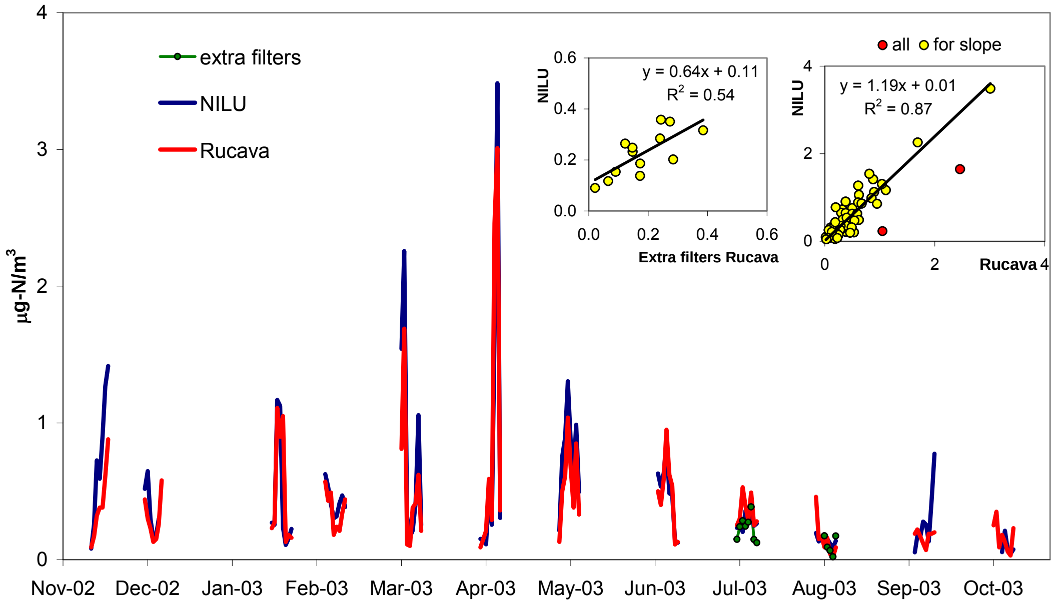


*Figure 8:* *Comparison of the co-located measurements of sum($HNO_3 + NO_3^-$) at Rucava. Outliers (red dots in xy plot) are not included to estimate the slope.*

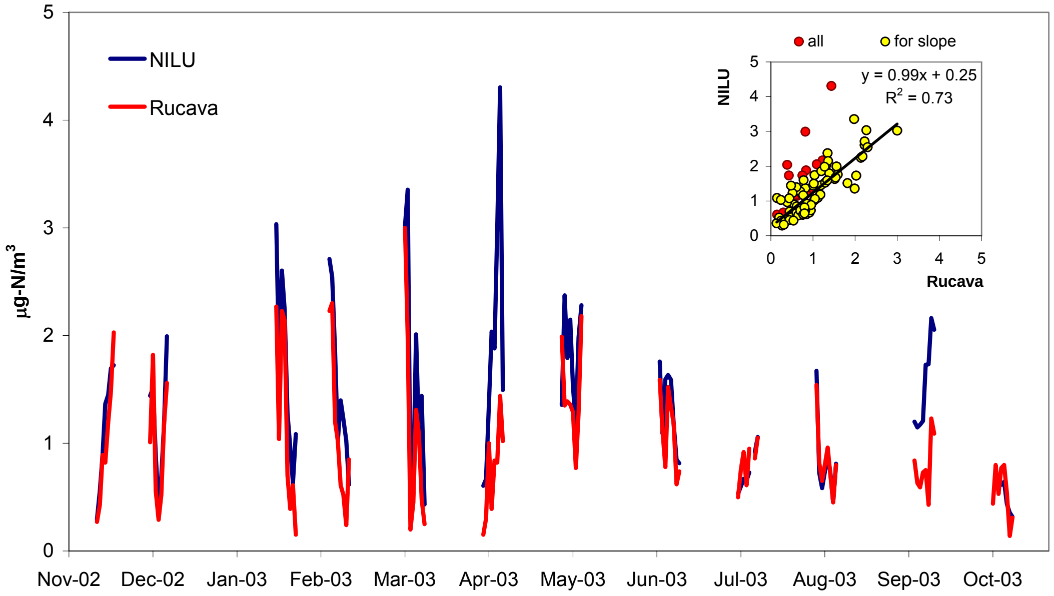


*Figure 9:* *Comparison of the co-located sum($NH_4^+ + NH_3$) measurements at Rucava. Outliers (red dots in xy plot) are not included to estimate the slope.*

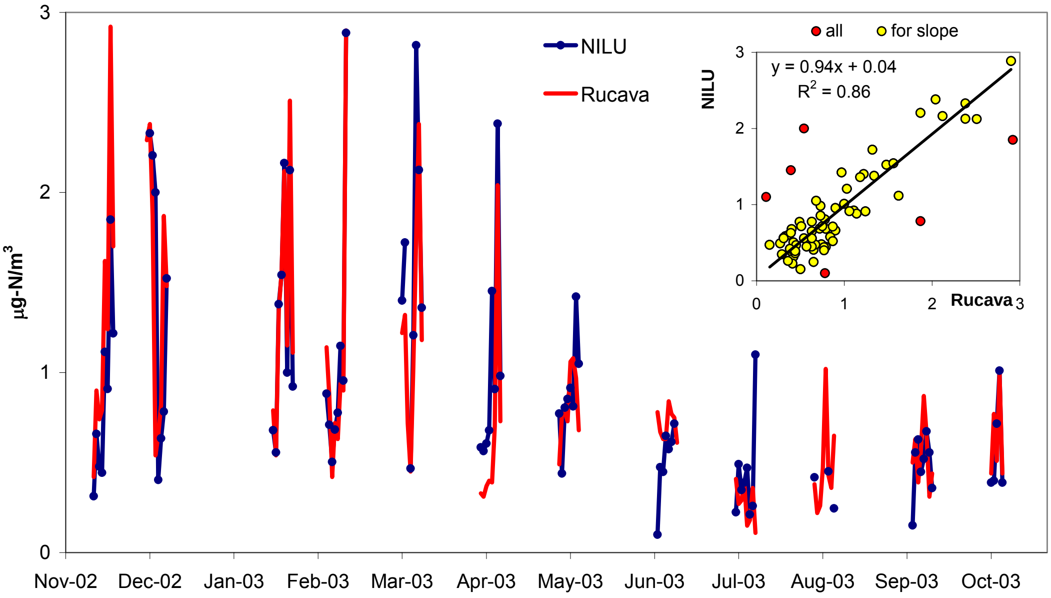


*Figure 10: Comparison of the co-located $NO_2$ measurements at Rucava. Outliers (red dots in xy plot) are not included to estimate the slope.*

*Table 3: Summary of results of co-located measurements at Rucava, in µg/m$^3$.*

|  | $SO_2$-S | $SO_4$-S | Sum$NO_3$-N | Sum$NH_4$-N | $NO_2$-N |
|---|---|---|---|---|---|
| Mean ref: | 0.36 | 0.73 | 0.48 | 1.35 | 0.90 |
| Mean: | 0.44 | 0.55 | 0.41 | 0.98 | 0.90 |
| Median ref: | 0.29 | 0.62 | 0.30 | 1.18 | 0.68 |
| Median: | 0.40 | 0.44 | 0.27 | 0.84 | 0.73 |
| Num pairs: | 89 | 92 | 91 | 91 | 74 |
| Average of diff: | -0.08 | 0.17 | 0.07 | 0.37 | 0.00 |
| Median of diff: | -0.05 | 0.18 | 0.04 | 0.24 | 0.00 |
| M.MAD: | 0.19 | 0.28 | 0.13 | 0.36 | 0.30 |
| CoV: | 66% | 45% | 44% | 30% | 44% |
| slope | 0.52 | 1.17 | 1.19 | 0.99 | 0.94 |
| QA flag | 50 | 22 | 10 | 02 | 02 |
| QA category | B | B | B | B | B |

The comparison indicates some problems with the $SO_2$ measurements; nevertheless the results are within the limit of what is acceptable, and falls in QA category B. The correlation is good but the local measurement is systematically overestimating the $SO_2$ concentration. The comparison with the extra filters does not give an obvious answer to the problem, as these results are pretty uncertain because of very high field blanks. But even when subtracting with these very high field blanks the local measurements are overestimating the $SO_2$ concentration. The only difference between the reference measurements and the extra filter is that extra filters are prepared and installed by the local lab; the analysis of both filters is done at NILU. It is therefore presumable that the large deviations are due to the preparation of the filters, e.g. contamination of the impregnation solution, or

$SO_2$ in the laboratory atmosphere. However, the preparation of the filters are done in a special sampling division outside the chemical laboratory, no sources of $SO_2$ are found here.

The $SO_4^{2-}$ measurements are on the other hand somewhat underestimated, but the difference is not critical and the precisions is OK so the measurements are quite satisfactory. The sum of nitrate and nitric acid measurement is very good. There is a small underestimation, but it can just as well be some overestimation for the reference since NILU have experienced some $NH_4NO_3$ contamination problems lately. This is then also true for the sum of ammonia and ammonium which show excellent correlation if one exclude the measurements in April and September. The $NO_2$ measurements are also very good, the precision is not so very high but the correlation is perfect.

### 5.1.5 *Comparing the measurements at Rucava and Preila*

These two sites are very close to each other and one would expect correlated results for long range transported air pollution. The comparisons were therefore done at the same days so it would add an extra dimension to this comparison.

There is a strong correlation between the $SO_4$ measurements at the two sites. The same is seen for sum of nitrate, sum of ammonia and nitrogen dioxide. The correlation between the two reference samplers are better than comparing the local measurements. This is natural since the difference is then mainly due to difference in air quality and not influenced by laboratory and field methods. For $SO_2$ there is hardly any correlation, except for some months were there is a correspondence between the two reference methods. This indicates that the $SO_2$ concentration is influenced by local sources or contaminants.

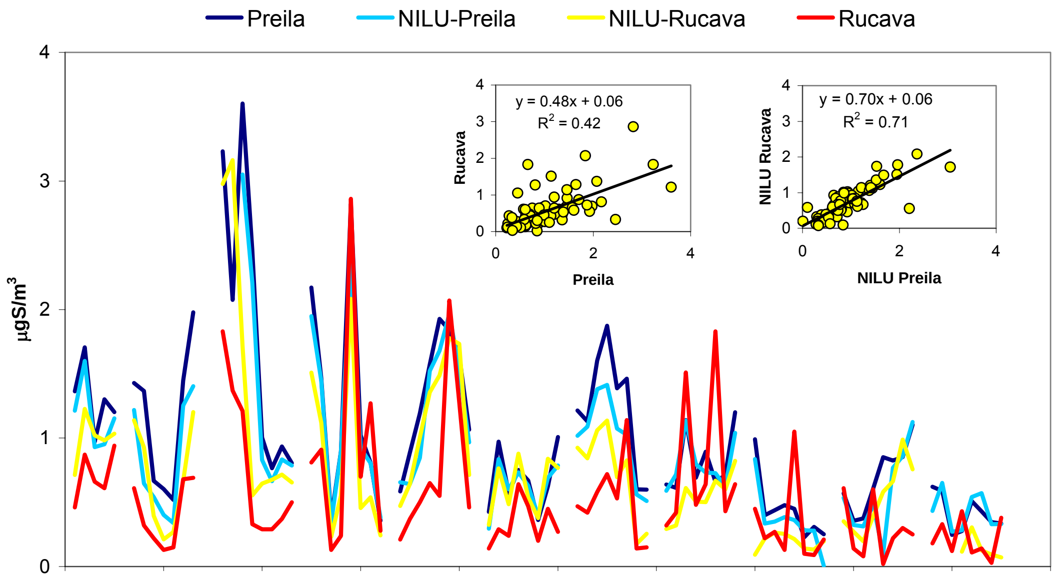


*Figure 11: Comparison of the co-located $SO_4^{2-}$ measurements at Rucava and Preila.*

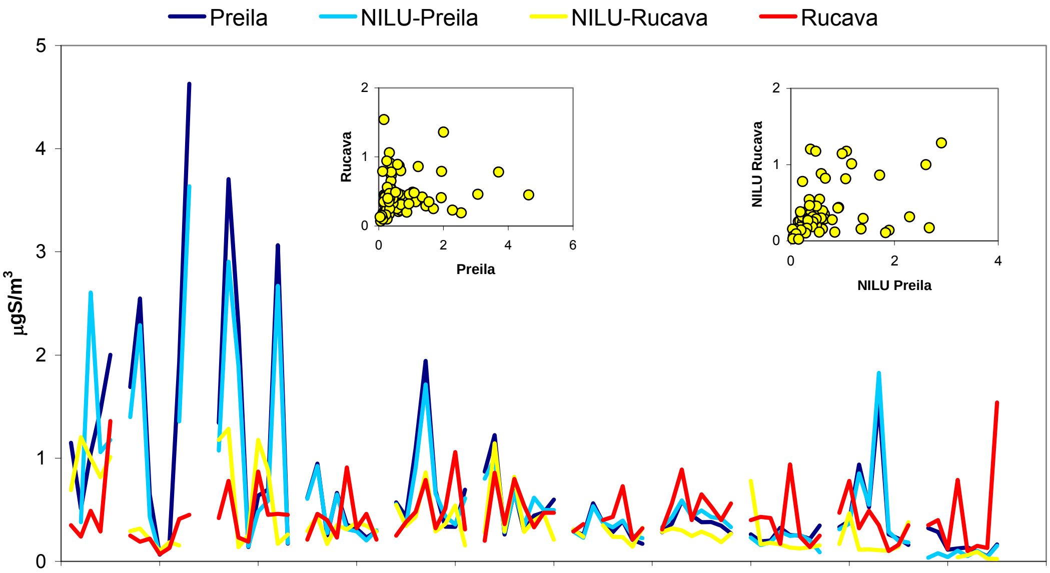


*Figure 12: Comparison of the co-located $SO_2$ measurements at Rucava and Preila.*

### 5.1.6 *Comparison at Lahemaa, Estonia*

At Lahemaa there is both manual and automatic measurements of $SO_2$ and $NO_2$. The manual $SO_2$ and $SO_4^{2-}$ measurements are done using a filter 2-pack with an aerosol filter (Whatman 40) and a NaOH-impregnated Whatman 40 filter; the flow is 4-5 $m^3$/day. The manual $NO_2$ method is absorbing tubes with a KI solution; the flow is 0.3 $m^3$/day. The Chemiluminescence and UV-fluorescence monitors are from Horiba. The national parallel measurements of $SO_2$ and $NO_2$ are performed for two full years, 2002 and 2003.

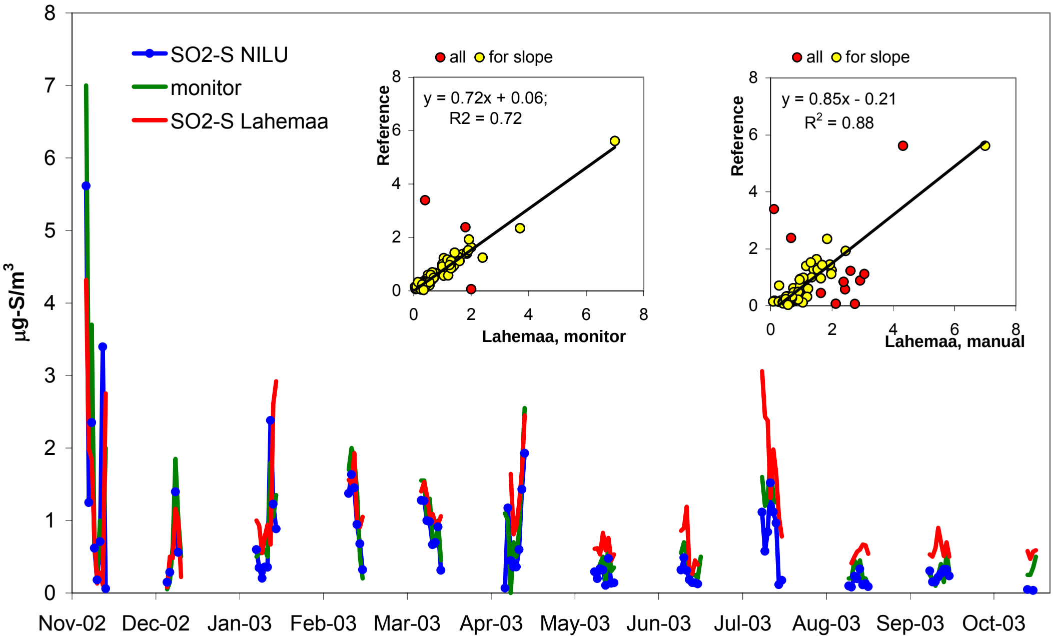


*Figure 13: Comparison of the co-located $SO_2$ measurements at Lahemaa. Outliers (red dots in xy plot) are not included to estimate the slope.*

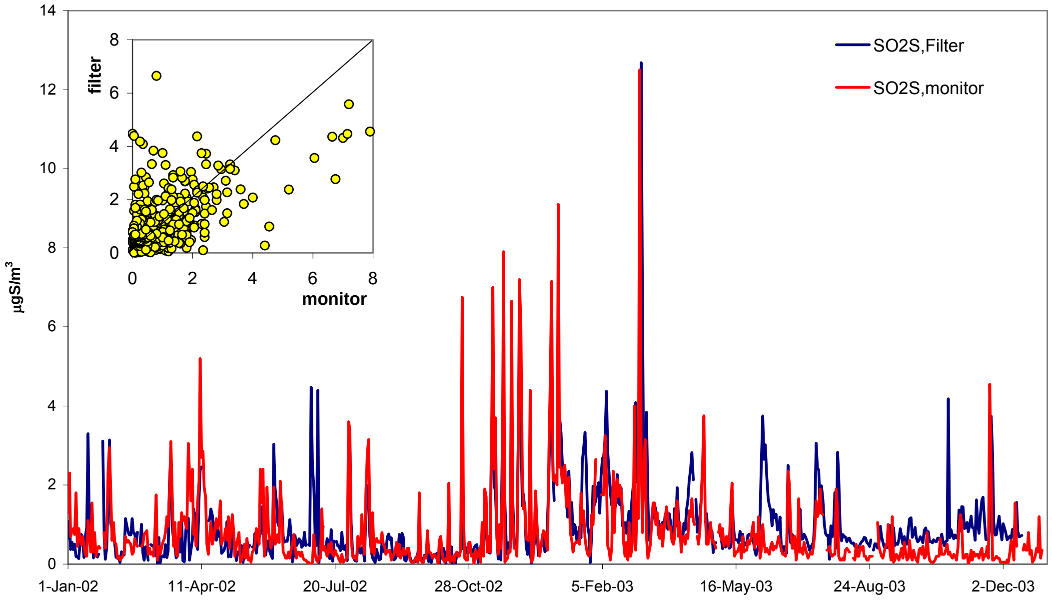


*Figure 14: Comparison of the national* $SO_2$ *measurements at Lahemaa, 2002 and 2003.*

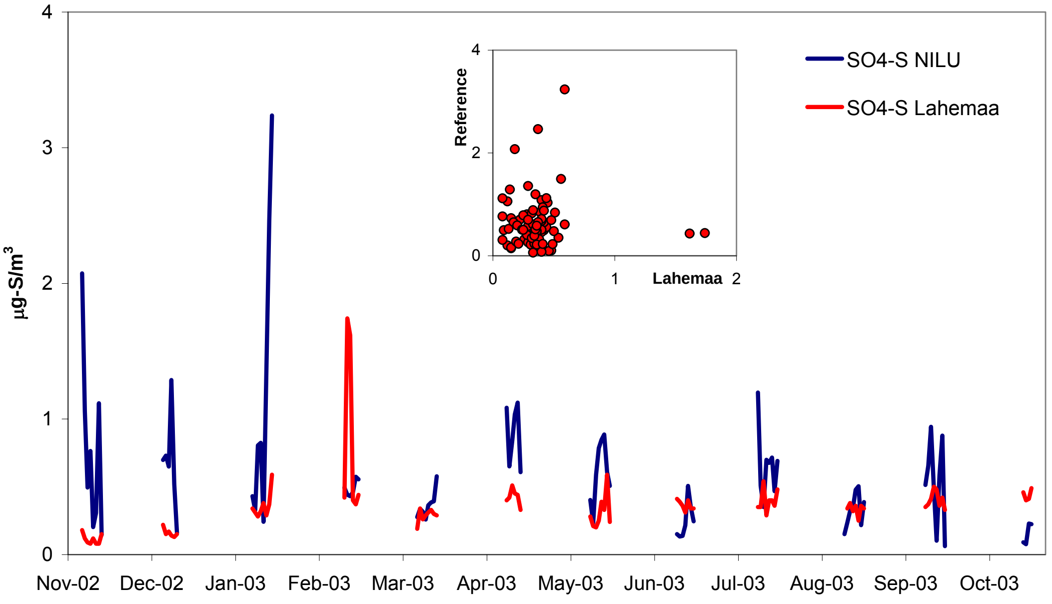


*Figure 15: Comparison of the co-located* $SO_4^{2-}$ *measurements at Lahemaa.*

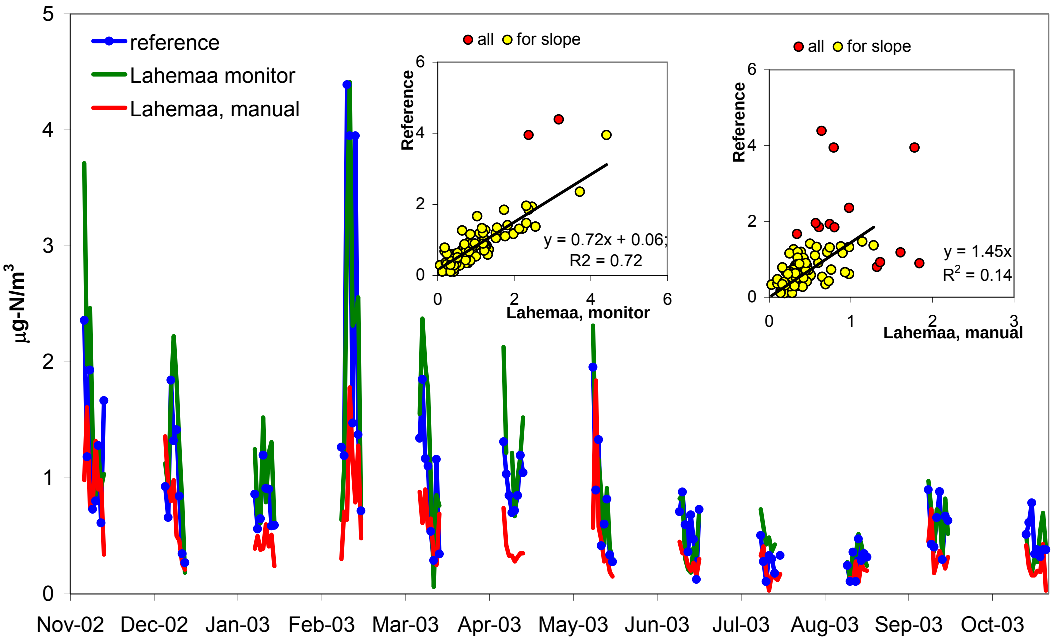


*Figure 16: Comparison of the co-located $NO_2$ measurements at Lahemaa. Outliers (red dots in xy plot) are not included to estimate the slope.*

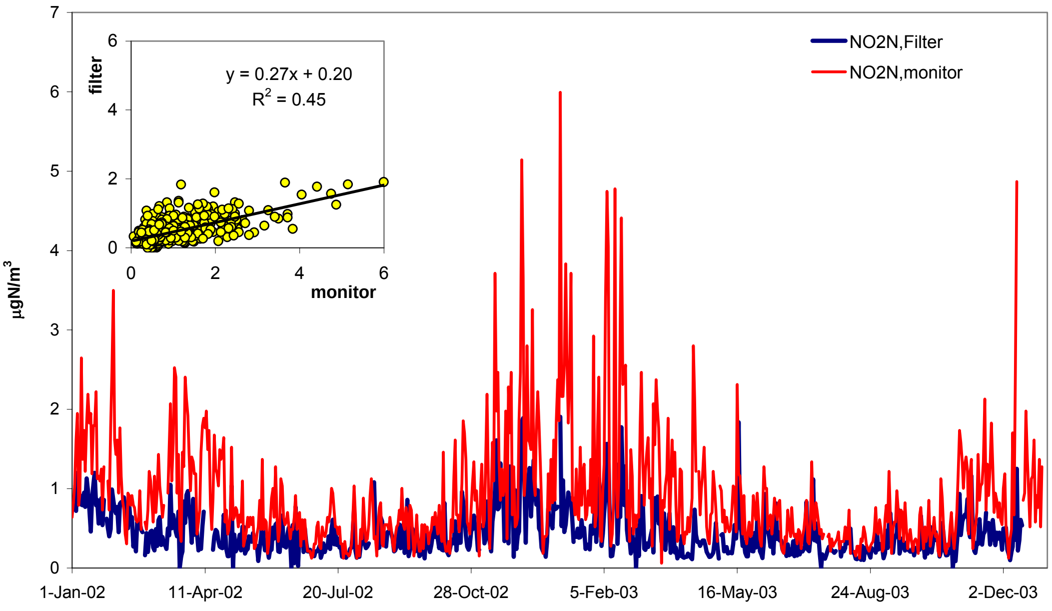


*Figure 17: Comparison of the national $NO_2$ measurements at Lahemaa, 2002 and 2003.*

*Table 4: Summary of results of co-located measurements at Lahemaa, in μg/m*$^3$*.*

| | $SO_4^{2-}$ | $SO_2$ manual | $SO_2$ monitor | $NO_2$ manual | $NO_2$ monitor |
|---|---|---|---|---|---|
| Mean ref: | 0.61 | 0.68 | 0.70 | 0.87 | 0.88 |
| Mean: | 0.36 | 1.08 | 0.86 | 0.49 | 1.01 |
| Median ref: | 0.50 | 0.35 | 0.36 | 0.69 | 0.69 |
| Median: | 0.34 | 0.86 | 0.50 | 0.35 | 0.79 |
| Num pairs: | 83 | 79 | 79 | 94 | 92 |
| Average of diff: | 0.25 | -0.4 | -0.17 | 0.39 | -0.13 |
| Median of diff: | 0.12 | -0.39 | -0.13 | 0.31 | -0.10 |
| M.MAD: | 0.33 | 0.27 | 0.19 | 0.32 | 0.30 |
| CoV: | 65% | 76% | 54% | 46% | 43% |
| Slope | - | 0.85 | 0.72 | 1.45 | 0.72 |
| QA Flag | 82 | 12 | 30 | 62 | 32 |
| QA Category | C | B | B | B | B |

*Table 5: Summary of results of national co-located measurements at Lahemaa, in μg/m*$^3$*.*

| | SO2-S | NO2-N |
|---|---|---|
| Mean manual: | 0.94 | 0.44 |
| Mean monitor: | 0.80 | 0.90 |
| Median manual: | 0.67 | 0.36 |
| Median monitor: | 0.45 | 0.67 |
| Num pairs: | 669 | 674 |
| Average of diff: | 0.15 | -0.46 |
| Median of diff: | 0.15 | -0.31 |
| M.MAD: | 0.47 | 0.36 |
| CoV: | 71% | 99% |

The results from the Lahemaa intercomparison are not satisfactory. For $SO_2$ it is OK, both the manual and the monitor show nice correlation with the reference method both methods systematically underestimate the concentration, the monitor more than the manual method. This is also true when comparing the national measurements for two full years, Table 5. The $NO_2$ measurements are more uncertain. The manual method is almost half of the reference concentration and the precision is also quite low. The $NO_2$ monitor shows better correlation with the reference method. When comparing the national measurements for two years it is quite clear that the manual method totally underestimate the $NO_2$ concentration. It is recommended that the $NO_2$ method at Lahemaa is changed to the reference method or that the monitor data are reported to EMEP. For $SO_4$ there are problems. There is no correlation between the measurements and these data should not be used. Estonia has reported that the detection limit for sulphate in air is 0.5 μg-S/m$^3$. This is much too high for a background site. The reason is probably that the flow is too low for this method and it is highly recommended that Estonia change their methodology, i.e. using a filterpack with higher flow.

## 5.2 Heavy metals in precipitation

One site in Belgium (BE04) and one in Germany (DE03) have parallel wet only and bulk sampler for measurements of heavy metal in precipitation. In the EMEP Manual (1996) it is recommended to use a wet only for weekly precipitation sampling of heavy metals, however, if the bulk sampler shows equivalent results this may also be used.

### *5.2.1 Parallel sampling of wet-only and bulk at Langenbrügge (DE02)*

At Langenbrügge there was in 2002 one wet only collector that was sampled weekly and one bulk collector that was sampled every day both reported to EMEP. The monthly and annual mean were compared, Table 6. If the differences are within 10% one may say that the methods are equivalent. The results for the different elements are varying somewhat; in general there is a slightly larger heavy metal concentration in the bulk collector compared with the wet only. There are a few exceptions were the wet only shows a higher level, this can be due to contamination. Cadmium shows much higher concentration in the bulk collector compared with the wet only in all months, but the concentration level is quite low so the absolute difference is not that high. Nevertheless this comparison shows clearly that dry deposition of particles with heavy metals has an influence of the concentration in the bulk precipitation.

### *5.2.2 Parallel sampling of wet-only and bulk at Knokke (BE04)*

At Knokke they have had parallel sampling of wet only and bulk collectors for several years. They report monthly concentrations to the CAMP program, however it is unclear whether this is the real sampling time or not. Is not recommended to have longer sampling time than one week for heavy metals in precipitation to minimize the problems with contamination. In Figure 18 a scatter diagram shows the volume weighted annual average concentrations of the heavy metals in the two collectors. There are obvious problems with measuring heavy metals in precipitation. Hardly any correlation is seen between the two collectors and the concentrations are in general higher in the wet only collector. Some of the difference can be explained by differences in the precipitation amount, which is more than 20% higher in the bulk collector, but the main reason must be the method used, many of the measurements are e.g. under the detection limit. It is highly recommended that Belgium evaluate their methods; today these measurements are not very useful.

*Table 6: Monthly and annual average concentration of heavy metals at DE02 in precipitation, 2002, in µg/l and per cent difference.*

🟪 < -50 🟦 <-50,-10> 🟩 <-10,10> 🟨 <10,50> 🟥 >50

| | | Jan | Feb | Mar | Apr | May | June | July | Aug | Sept | Oct | Nov | Dec | 2002 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **As** | bulk | 0.09 | 0.09 | 0.18 | 0.22 | 0.27 | 0.25 | 0.09 | 0.14 | 0.11 | 0.09 | 0.23 | 0.18 | 0.15 |
| | wet only | 0.06 | 0.10 | 0.12 | 0.23 | 0.22 | 0.15 | 0.08 | 0.12 | 0.08 | 0.09 | 0.20 | 0.16 | 0.13 |
| Difference | | 36% | -6% | 54% | -3% | 20% | 65% | 18% | 21% | 35% | -7% | 11% | 13% | 15% |
| **Cd** | bulk | 0.09 | 0.12 | 0.11 | 0.17 | 0.24 | 0.17 | 0.12 | 0.14 | 0.12 | 0.07 | 0.10 | 0.07 | 0.13 |
| | wet only | 0.02 | 0.03 | 0.06 | 0.07 | 0.07 | 0.05 | 0.03 | 0.05 | 0.03 | 0.03 | 0.03 | 0.03 | 0.04 |
| Difference | | 370% | 310% | 98% | 156% | 257% | 254% | 343% | 196% | 303% | 103% | 197% | 115% | 218% |
| **Cr** | bulk | 0.20 | 0.21 | 0.17 | 0.26 | 0.41 | 0.31 | 0.23 | 0.18 | 0.16 | 0.12 | 0.12 | 0.12 | 0.20 |
| | wet only | 0.19 | 0.10 | 0.14 | 0.17 | 0.27 | 0.32 | 0.21 | 0.18 | 0.23 | 0.24 | 0.20 | 0.49 | 0.22 |
| Difference | | 3% | 110% | 24% | 55% | 53% | -3% | 9% | 1% | -32% | -52% | -41% | -75% | -6% |
| **Co** | bulk | 0.02 | 0.02 | 0.05 | 0.04 | 0.08 | 0.06 | 0.03 | 0.03 | 0.03 | 0.02 | 0.04 | 0.05 | 0.04 |
| | wet only | 0.01 | 0.02 | 0.03 | 0.04 | 0.06 | 0.04 | 0.03 | 0.02 | 0.02 | 0.02 | 0.04 | 0.02 | 0.03 |
| Difference | | 75% | 11% | 64% | 11% | 27% | 48% | 36% | 39% | 63% | 41% | -9% | 153% | 29% |
| **Cu** | bulk | 3.47 | 1.68 | 3.45 | 2.11 | 2.35 | 2.04 | 3.11 | 4.08 | 1.43 | 1.12 | 0.89 | 0.69 | 2.49 |
| | wet only | 0.73 | 1.44 | 1.67 | 1.62 | 2.02 | 1.82 | 0.99 | 1.34 | 2.25 | 1.32 | 0.92 | 1.98 | 1.36 |
| Difference | | 377% | 17% | 107% | 30% | 16% | 12% | 213% | 204% | -36% | -15% | -3% | -65% | 83% |
| **Fe** | bulk | 37 | 45 | 42 | 46 | 85 | 68 | 39 | 41 | 44 | 27 | 34 | 18 | 42 |
| | wet only | 13 | 22 | 34 | 35 | 58 | 39 | 27 | 36 | 17 | 16 | 37 | 9 | 30 |
| Difference | | 176% | 107% | 21% | 31% | 48% | 75% | 45% | 14% | 162% | 69% | -9% | 99% | 43% |
| **Pb** | bulk | 0.93 | 1.23 | 2.03 | 1.93 | 2.26 | 2.17 | 1.09 | 1.58 | 0.72 | 1.00 | 1.59 | 1.15 | 1.43 |
| | wet only | 0.88 | 1.35 | 1.42 | 2.07 | 2.10 | 1.72 | 0.99 | 1.82 | 0.48 | 0.94 | 1.30 | 1.32 | 1.39 |
| Difference | | 5% | -9% | 43% | -7% | 7% | 26% | 10% | -13% | 51% | 6% | 23% | -13% | 3% |
| **Mn** | bulk | 1.84 | 4.40 | 3.68 | 3.68 | 6.79 | 6.20 | 2.85 | 3.06 | 4.28 | 3.10 | 2.56 | 1.18 | 3.42 |
| | wet only | 1.03 | 1.93 | 2.82 | 2.31 | 5.22 | 3.27 | 2.21 | 2.34 | 1.59 | 1.55 | 2.35 | 1.08 | 2.31 |
| Difference | | 79% | 128% | 30% | 59% | 30% | 90% | 29% | 31% | 170% | 100% | 9% | 10% | 48% |
| **Ni** | bulk | 0.49 | 0.73 | 0.58 | 0.55 | 0.85 | 0.72 | 0.76 | 0.42 | 0.48 | 0.32 | 0.26 | 0.35 | 0.56 |
| | wet only | 0.29 | 0.25 | 0.16 | 0.59 | 0.51 | 0.59 | 0.46 | 0.39 | 0.45 | 0.33 | 0.33 | 0.33 | 0.40 |
| Difference | | 69% | 191% | 261% | -7% | 66% | 23% | 65% | 8% | 7% | -3% | -20% | 7% | 38% |
| **V** | bulk | 0.38 | 0.54 | 0.90 | 0.60 | 0.83 | 0.49 | 0.39 | 0.25 | 0.67 | 0.37 | 0.35 | 0.28 | 0.44 |
| | wet only | 0.31 | 0.74 | 0.55 | 0.55 | 0.64 | 0.39 | 0.29 | 0.21 | 0.45 | 0.32 | 0.30 | 0.21 | 0.37 |
| Difference | | 22% | -28% | 64% | 9% | 31% | 24% | 35% | 19% | 49% | 15% | 18% | 39% | 19% |
| **mm** | bulk | 52 | 87 | 37 | 58 | 52 | 41 | 168 | 153 | 21 | 69 | 81 | 38 | 858 |
| | wet only | 58 | 95 | 47 | 69 | 50 | 64 | 164 | 138 | 24 | 84 | 76 | 41 | 911 |
| Difference | | -9% | -8% | -21% | -16% | 4% | -37% | 3% | 11% | -13% | -18% | 5% | -8% | -6% |
| **mm Hg** | wet only | 59 | 95 | 46 | 67 | 48 | 60 | 165 | 128 | 22 | 84 | 76 | 41 | 890 |
| Difference | | -11% | -8% | -21% | -13% | 10% | -32% | 2% | 20% | -6% | -17% | 5% | -8% | -4% |

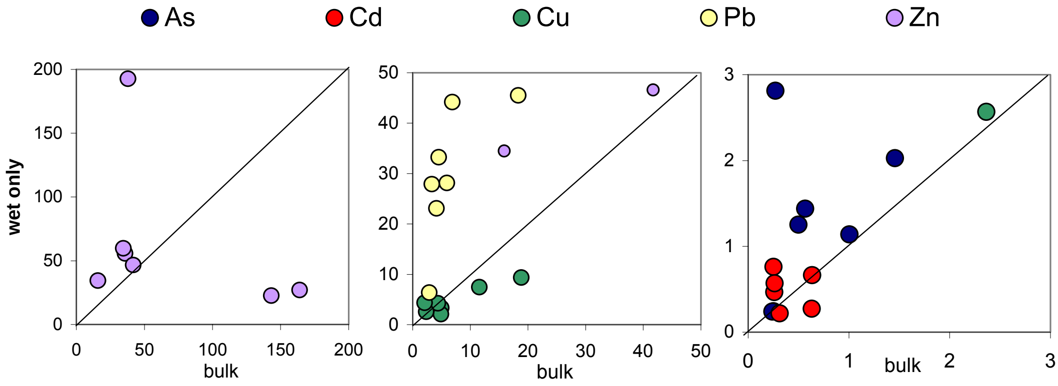


*Figure 18. Scatter plot of volume weighted annual average concentrations of heavy metals in precipitation at BE04 from 1996 to 2002, μg/l.*

# 6. Results from laboratory comparisons

## 6.1 Main components

The twentieth intercomparison (Uggerud et al., 2003) of main components in air and precipitation is relevant for the data reported for 2002. The results of the systematic and random errors are shown in Table 7 and Table 8, respectively. The details on how these calculations are done are found in last year QA report (Aas et al., 2003).

The results are mostly good. There are some elements that are more difficult than other and sometimes outliers can cause large deviations, but this is not necessarily the general performance for the laboratory. One should look at the performance for several years if one needs a general picture.

*Table 7: Random errors (2RSD%) in the 20th laboratory intercomparison for precipitation and air.*

| | Precipitation | | | | | | | | | | | Air | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SO_4$ | $NO_3$ | $NH_4$ | pH | H | Mg | Na | Cl | Ca | K | Cond | $NO_2$ | $SO_2$ | $HNO_3$ |
| AT | 1.1 | 1.6 | 4.4 | 7.2 | | 3.3 | 2.9 | 3.2 | 3.4 | 2.3 | 2.5 | | | |
| CZ | 0.5 | 0.4 | 2.4 | 2.1 | 2 | 1.1 | 1.8 | 1.5 | 1.8 | 1.8 | 1.5 | 4.4 | 1.4 | 2.4 |
| DK | 1.4 | 1.6 | 1.2 | 2.2 | | 1.8 | 8.9 | 2.6 | 2 | 50.5 | 2.3 | 1.6 | 1.5 | 2.3 |
| FI | 2 | 0.6 | 3.8 | 2.8 | | 0.4 | 0.4 | 1.1 | 3.3 | 1.2 | 0.5 | | 3.9 | 1.3 |
| FR | 0.3 | 0.5 | 0 | 2.1 | 8 | 0.4 | 0.9 | 4 | 2.9 | 2.8 | 1.3 | | | |
| DE(Leip.) | 1.3 | 0.5 | 1.8 | 4.1 | | 6.2 | 0.2 | 1.8 | 2.5 | 0.7 | 10.4 | | | |
| DE(Shau.) | 0.3 | 0.3 | 2 | 4.1 | | 0.7 | 0.9 | 1.2 | 2.9 | 0.7 | 2 | 0.8 | 2.3 | 2.7 |
| HU | 2 | 0.5 | 1 | 2.5 | | 3.3 | 5.7 | 20 | 7.4 | 2.1 | 0.8 | 1.2 | | |
| IS | 1.3 | 2.4 | 1.9 | 7.4 | | 1.1 | 5.7 | 8.7 | 0.8 | 8.9 | 2.1 | | 5.5 | 9.5 |
| IE (MET) | 0.3 | 0.7 | 3.6 | 1.5 | | 0.4 | 0.8 | 1.3 | 2 | 2.1 | 1.2 | 1.2 | | |
| IT-CNR | 1.5 | 1 | 2.3 | 2.8 | | 1.5 | 0.8 | 0.8 | 4.5 | 0.9 | 0.7 | | | |
| NL | 1.7 | 0.4 | 1.4 | 6.3 | 4 | 0.7 | 2.5 | 2.3 | 1.5 | 3.6 | 1.5 | | | |
| NO | 1.2 | 0.7 | 3.4 | 4 | | 0.7 | 1.2 | 3.4 | 1.6 | 1.4 | 2.1 | 0 | 2.6 | 2.1 |
| PL | 1.3 | 2.2 | 4.2 | 2.6 | | 2.5 | 1.6 | 2.8 | 1.4 | 1.6 | 0.7 | 1.6 | 2.2 | 5 |
| PT | 1.9 | 0.9 | 3.7 | 30.4 | | 2.2 | 3 | 65.6 | 1.1 | | 3.5 | | 21.4 | |
| RO | | | 14.1 | 7.8 | | | | 8.6 | | | 4 | | | |
| ES | 1 | 0.4 | 6 | 2.7 | | 0.4 | 1 | | 1 | 2 | 0.7 | 7.2 | 13.8 | |
| SE | 0.2 | 0.5 | 0.7 | 5.3 | | 3.3 | 2.8 | 0.7 | 2.3 | 3.9 | 5.3 | 1.2 | 4.2 | 2.3 |
| CH | 0.2 | 0.4 | 1.4 | 2.9 | | 0.7 | 1.1 | 1.3 | 0.8 | 2.1 | 0.6 | | 1.5 | |
| RU | 0.4 | 1.5 | 1.3 | 8 | | 1.8 | 10.6 | 15.3 | 2.5 | 15.3 | 1.5 | 2.8 | 5.9 | 16.3 |
| UK | 0.5 | 0.9 | 1.2 | 4.5 | | 0.7 | 0.6 | 0.5 | 3.1 | 1.6 | 2.7 | 1.2 | 0.8 | |
| YU | | | | 5.7 | | 10.9 | 2.3 | | 10.6 | 2.1 | 10.1 | | | |
| CA | 0.4 | 0.4 | 0.5 | 5.7 | | 0.7 | 0.5 | 0.9 | 0.7 | 1.8 | | | | |
| US-I | 0.4 | 0.7 | 1.7 | 4.4 | 4 | 0.7 | 0.7 | 0.5 | 0.3 | 2.7 | 0.6 | | | |
| SK | 0.8 | 1.4 | 3.8 | 3 | | 1.1 | 2.1 | 6 | 3.1 | 2.5 | 1.1 | 5.5 | 4.2 | 2.3 |
| LT | 0.9 | 0.1 | 2.4 | 5.2 | 5 | | 8.8 | 1.7 | 11.6 | 5.3 | 3.1 | 0.4 | 10.9 | 11.9 |
| LV | 1.4 | 1 | 2.9 | 4 | | 1.1 | 0.6 | 5.8 | 1.6 | 0.9 | 0.7 | 1.2 | 1.9 | 4.1 |
| TR | 0.3 | 0.4 | 3.6 | 3.7 | 3 | 1.5 | 5 | 4 | 4.4 | 5.9 | 4.3 | 2.4 | 2.5 | 2.7 |
| CR | 1.3 | 0.7 | 0.6 | 3 | 3 | 6.9 | 2.7 | 2.1 | 4.6 | 0.7 | 1.3 | 1.6 | | |
| SI | 1 | 0.5 | 3.2 | 5.9 | 6 | 1.1 | 0.7 | 0.5 | 0.4 | 0.7 | 1.3 | 0.8 | 5.5 | 1.1 |
| IE (ESB) | 1.6 | 2 | 1.6 | 22 | | 6.9 | 4.1 | 4.4 | 10.6 | 2.8 | 2.9 | | | |
| EE | 1 | 1.1 | 2.4 | 7.6 | | 4 | 3.4 | 6.6 | 3.3 | 3.9 | | 0.8 | 13.6 | |
| PL | 2.7 | 1.2 | 4.2 | 5.8 | | 0.7 | 0.8 | 5.2 | 1.4 | 1.1 | 3.1 | 7.6 | 2.6 | 2.7 |
| MK | | 17.7 | 6.1 | | | 8.4 | 6.2 | 25.2 | 0.3 | 3.2 | 4.9 | | | |

🟨 1-2 DQO　　🟥 > 2 DQO

*Table 8: Systematic error (RB%) in the 20th laboratory intercomparison for precipitation.*

| | Precipitation | | | | | | | | | | | Air | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SO_4$-S | $NO_3$-N | $NH_4$-N | pH | H | Mg | Na | Cl | Ca | K | Cond | $NO_2$ | $SO_2$ | $HNO_3$ |
| AT | 4 P | 2 | 3 | -5 | | -9 N | -7 N | -6 N | -9 N | -24 N | -1 | | | |
| CZ | 1 P | -3 N | -15 N | -2 | -2 | -2 | -4 N | -5 N | 1 P | 1 | -3 N | 6 | -4 N | -1 |
| DK | 3 P | 3 P | -3 N | -7 N | | -12 N | 2 | -4 N | -1 | -32 N | -4 N | 2 | -5 N | 1 |
| FI | -1 | 2 P | -1 | -6 N | | 2 P | 1 P | -2 | 8 P | 1 | 0 | | 5 P | 3 P |
| FR | -3 N | -4 N | 0 | -1 | -4 N | -9 N | -1 | -5 | 3 | -6 N | -4 N | | -1 | |
| DE(Leip.) | 5 P | 1 P | -1 | -5 N | | -9 N | 0 | -4 N | -7 N | -1 N | -13 | | | |
| DE(Shau.) | 0 | -2 N | 3 | -11 N | | 1 | -1 | -2 N | -2 | 1 P | -3 | -5 N | 7 P | 0 |
| HU | 3 | 0 | -5 N | 9 P | | 0 | -18 N | -3 | 10 P | -7 N | 0 | -3 N | | |
| IS | -1 N | 3 P | 2 | -18 N | | -5 N | -13 N | 10 P | -5 N | -38 N | -4 N | | -15 N | -36 N |
| IE (MET) | 0 | 0 | -5 N | -3 N | | -1 N | -1 N | -1 | -6 N | -6 N | 4 P | -1 | | |
| IT-CNR | 2 | 0 | 0 | -7 N | | 4 P | 1 | 0 | 5 P | 1 | 2 P | | | |
| NL | 11 P | 1 P | -2 | -21 N | -3 N | -7 N | -7 N | -2 N | -7 N | 2 | -5 N | | | |
| NO | 1 | -1 N | 1 | -11 N | | 6 P | 0 | -2 | 7 P | 2 P | -4 N | -9 N | 1 | 3 P |
| PL | -2 | -3 N | -5 N | 4 P | | -6 N | -2 | -2 | -1 | -4 N | -2 N | -2 | 7 P | -3 |
| PT | 6 P | 1 | 15 P | -7 N | | -2 | -21 N | 36 | -20 N | | -1 | | 15 | |
| RO | | | 12 P | 28 P | | | | -11 | | | 5 | | | |
| ES | -1 N | -2 N | 21 P | -19 N | | 0 | -5 N | | 1 P | 0 | 0 | -5 N | -11 | |
| SE | 0 | 1 P | -3 N | -19 N | | 14 P | -2 | -3 N | 4 P | 12 P | 10 P | -1 | 11 P | 0 |
| CH | 4 P | 0 | -2 N | -8 N | | 0 | -2 N | 0 | 3 P | -6 N | -2 N | | 3 | |
| RU | -10 N | -6 N | -5 N | -14 N | | -7 N | -25 N | -31 N | -15 N | -2 | -6 N | 6 P | -29 N | -24 N |
| GB | 0 | 3 P | -4 N | -4 | | -3 N | -10 N | -2 N | -2 | -8 N | 14 P | -3 N | 6 P | |
| YU | | | | -14 N | | -34 N | -4 N | | -36 N | -1 | -35 N | | | |
| CA | -1 N | -2 N | -2 N | -11 N | | 0 | 0 | -1 | 1 P | 2 | | | | |
| US-I | 2 P | 1 P | -6 N | -12 N | -12 N | -3 N | 1 | -1 | -3 N | 1 | 1 P | | | |
| SK | 1 P | -1 | -2 | -2 | | 0 | -3 N | 2 | 4 | 0 | -1 | -21 N | 0 | -1 |
| LT | -8 N | 1 P | 5 | -12 N | -12 N | | 10 P | -6 N | -41 N | 3 | 0 | 1 P | 6 P | 1 |
| LV | 3 P | 2 | 7 P | -11 N | | 0 | -1 | -1 N | 0 | -3 N | -2 N | 3 P | 12 P | -3 |
| TR | 0 | -3 N | -2 | -9 N | -10 N | 1 | 3 | -7 N | 9 | -17 N | -3 | -2 | -5 N | -6 N |
| HR | 4 P | 0 | -2 N | -15 N | -15 N | -53 N | -11 N | -3 | -46 N | -5 N | -3 N | 3 P | | |
| SI | -3 N | -1 N | 1 | -9 N | -9 N | -3 N | 1 P | -2 N | 1 P | -3 N | -6 N | 1 | 15 P | -2 N |
| IE (ESB) | -2 N | 1 | 10 P | 45 P | | -27 N | 0 | -8 N | -17 | -22 N | -3 N | | | |
| EE | -9 N | -7 N | -5 N | -13 N | | -20 N | -11 N | -8 N | -5 N | -13 N | | -1 | -13 N | |
| PL | 6 P | 3 P | 11 P | -14 N | | 1 | -1 | -9 N | 1 P | -1 N | -8 N | 4 | -2 | -1 |
| MK | | 64 P | 72 P | | | 0 | 7 | 26 | 9 P | -26 N | -33 N | | | |

P systematic positiv bias

N systematic negative bias

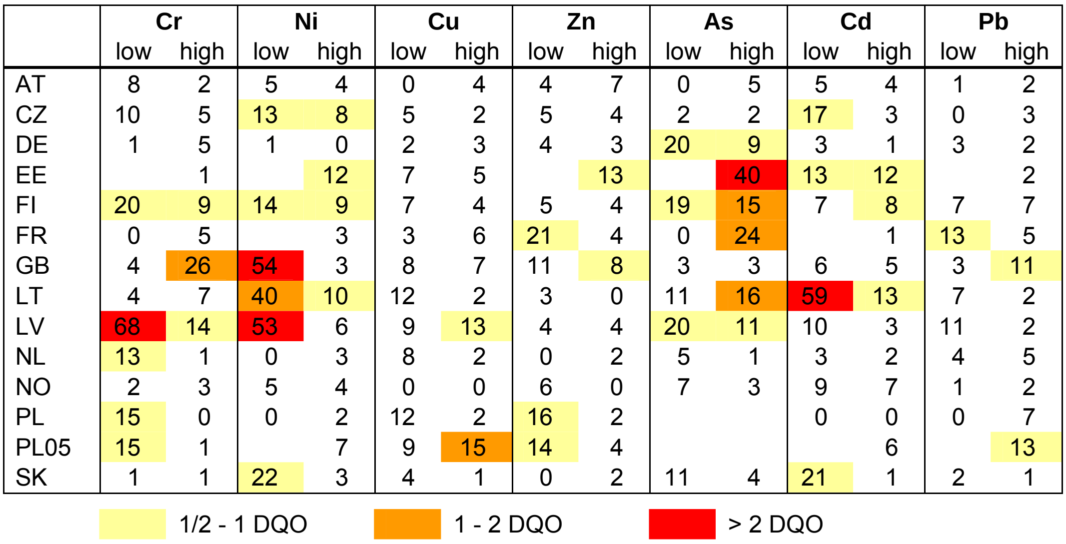
🟥 more than 20 % or less than -20% bias

🟨 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. 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 2002 data (Uggerud and Skjelmoen, 2003). In Table 9, there is a summary of the results from this laboratory intercomparison. Sweden, Denmark (precipitation) and Iceland were not participating because these measurements were analyzed in Norway. The measurements of high concentration samples are quite OK except for As maybe, however, at many EMEP sites these samples are not very representative. Several countries have some problems with measuring low concentration samples of Cr, Ni and Cd. In addition, there are some countries reporting measurement data without participating 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 9: Average per cent error (absolute) in low and high concentration samples, results from the heavy metal laboratory intercomparison in 2002.*



| | **Cr** | | **Ni** | | **Cu** | | **Zn** | | **As** | | **Cd** | | **Pb** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | low | high | low | high | low | high | low | high | low | high | low | high | low | high |
| AT | 8 | 2 | 5 | 4 | 0 | 4 | 4 | 7 | 0 | 5 | 5 | 4 | 1 | 2 |
| CZ | 10 | 5 | 13 | 8 | 5 | 2 | 5 | 4 | 2 | 2 | 17 | 3 | 0 | 3 |
| DE | 1 | 5 | 1 | 0 | 2 | 3 | 4 | 3 | 20 | 9 | 3 | 1 | 3 | 2 |
| EE | | 1 | | 12 | 7 | 5 | | 13 | | 40 | 13 | 12 | | 2 |
| FI | 20 | 9 | 14 | 9 | 7 | 4 | 5 | 4 | 19 | 15 | 7 | 8 | 7 | 7 |
| FR | 0 | 5 | | 3 | 3 | 6 | 21 | 4 | 0 | 24 | | 1 | 13 | 5 |
| GB | 4 | 26 | 54 | 3 | 8 | 7 | 11 | 8 | 3 | 3 | 6 | 5 | 3 | 11 |
| LT | 4 | 7 | 40 | 10 | 12 | 2 | 3 | 0 | 11 | 16 | 59 | 13 | 7 | 2 |
| LV | 68 | 14 | 53 | 6 | 9 | 13 | 4 | 4 | 20 | 11 | 10 | 3 | 11 | 2 |
| NL | 13 | 1 | 0 | 3 | 8 | 2 | 0 | 2 | 5 | 1 | 3 | 2 | 4 | 5 |
| NO | 2 | 3 | 5 | 4 | 0 | 0 | 6 | 0 | 7 | 3 | 9 | 7 | 1 | 2 |
| PL | 15 | 0 | 0 | 2 | 12 | 2 | 16 | 2 | | | 0 | 0 | 0 | 7 |
| PL05 | 15 | 1 | | 7 | 9 | 15 | 14 | 4 | | | | 6 | | 13 |
| SK | 1 | 1 | 22 | 3 | 4 | 1 | 0 | 2 | 11 | 4 | 21 | 1 | 2 | 1 |

🟨 1/2 - 1 DQO  🟧 1 - 2 DQO  🟥 > 2 DQO

## 6.3 POPs

The data quality of the POP measurements can to some extent be addressed by evaluating the results from the laboratory intercomparison in 2000-2002 (Manø and Schaug, 2003). The comparison was a two-step exercise: Round 1: Analysis of a mixture of standards of known composition but with unknown concentrations. Round 2: Analysis of two raw-extracts from filter and gas phase adsorbents after high volume air sampling. Two groups of POPs were investigated during the exercise: Organochlorine compounds including pesticides, hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). The second round showed the importance of using an analytical method and instrumentation able to cope with possible interferences without loss of analyte even while working at low concentrations, while round 1 mainly was a calibration exercise. To assess the data quality of the EMEP sites, it is therefore looked at the second round. Not all countries reporting data to EMEP took part in the laboratory intercomparison, these are Finland, Sweden, and Netherlands. In principle the data quality from these countries are unknown. Ireland did only participate in round 1, but their results are very crude because of instrument problems. Those EMEP laboratories that did participate in round 2 did in general satisfactory and are mostly within 50% of the average deviation from the median, Table 10. The Czech laboratory had some problems with insufficient cleaned silica during the comparison, which may explain the high deviation in the PCB analysis.

Table 10: *Average of the absolute percent deviation from the median in the POP laboratory intercomparison, round 2.*

**A) PAH compunds**

| Lab | Napht-alene | Acen-apht-ylene | Acen-aph-thene | Fluor-ene | Phen-an-threne | Anthra-cene | Fluor-anth-ene | Pyr-ene | B[a]A | Chrys-ene | B[b]F | B[k]F | B[a]P | Indeno-pyrene | DiB [a,h]A | B[ghi]P | B[e]P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BE | 24 | 7 | 94 | 48 | 0 | 7 | 1 | 45 | 89 | 1 | 25 | 15 | 0 | 11 | 68 | 55 | |
| CZ | 7 | 36 | 25 | 29 | 16 | 27 | 25 | 25 | 22 | 33 | 14 | 14 | 23 | 10 | 3 | 9 | |
| DE | 32 | | 34 | 25 | 24 | 435 | 23 | 2 | 21 | 10 | 22 | 25 | 13 | 16 | 26 | 1 | |
| LT | | | | | | | | | | | | | 66 | | | | |
| NO | 7 | 23 | 1 | 23 | 7 | 1 | 1 | 2 | 10 | 7 | 93 | | 14 | 1 | 8 | 1 | 17 |

**b) Organochlorine compounds**

| Lab | pp-DDT | pp'-DDE | g-Chlor-dane | a-Chlor-dane | g-HCH | a-HCH | HCB | PCB 28 | PCB 52 | PCB 101 | PCB 118 | PCB 138 | PCB 153 | PCB 180 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BE | | | | | 2 | 27 | 11 | | | | | | | |
| CZ | 64 | 19 | | 1 | 54 | 45 | 7 | 55 | 129 | 176 | 91 | 262 | 80 | 61 |
| DE | 27 | 176 | | | 18 | 25 | 12 | | | 1 | 71 | 303 | 162 | 397 |
| IS | 17 | 2 | 8 | 22 | 5 | 1 | 1 | 1 | 22 | 5 | 7 | 8 | 6 | 23 |
| NO | 19 | 13 | 9 | 13 | 15 | 5 | 24 | 17 | 10 | 7 | 10 | 6 | 7 | 33 |

🟩 < 25% 🟨 between 25 and 50% 🟥 >50%

# 7. QA flags

## 7.1 Introduction

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 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 understood 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 11 and Table 12 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.

*Table 11: Criteria used for classification of data quality based on field comparison results.*

| | **M.MAD** | ≤ 0.25 µg S/m$^3$ | | ≤ 0.50 µg S or N/m$^3$ | | > 0.50 µg S or N/m$^3$ and |
|---|---|---|---|---|---|---|
| | **CoV** | | [ 0, 25 % ] | | < 25%, 50 %] | < 50%, → > |
| **Regression slope (a) Ref = a$^x$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 12: 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 |

## 7.2 QA flags for 2002

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 Table 13 and Table 14 the flags relevant for 2002 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 20th laboratory intercomparison (Uggerud et al., 2003). 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. For the sum of nitrate and ammonium the flags are not included. The reason is the uncertainty in the field comparisons. Very often there has been large deviation because of very high blank values; these deviation may be both negative and positive and it is therefore difficult to say whether there are systematic deviations or not.

As seen there are very few measurements that should be considered invalid (marked in red); however, the B category is rather big and included measurements with quite high systematic error as well as low precision. 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 13: QA flag and category for main components in precipitation.*

| | $SO_4$ | | $NH_4$ | | $NO_3$ | | Ca | | Cl | | K | | Mg | | Na | | pH | | H | | Cond | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| AT | 00 | A | 00 | A | 00 | A | 20 | A | 20 | A | 60 | B | 20 | A | 20 | A | 00 | A | | | 00 | A |
| CH | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 20 | A | 00 | A | 00 | A | 20 | A | 00 | A | 00 | A |
| CZ | 00 | A | 40 | B | 00 | A | 00 | A | 20 | A | 00 | A | 00 | A | 00 | A | 00 | A | | | 00 | A |
| DE | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 40 | B | | | 00 | A |
| DK | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 62 | B | 40 | B | 00 | A | 20 | A | | | 00 | A |
| EE | 20 | A | 00 | A | 20 | A | 20 | A | 20 | A | 40 | B | 60 | B | 40 | B | 40 | B | | | | |
| ES | 00 | A | 50 | B | 00 | A | 00 | A | | | 00 | A | 00 | A | 00 | A | 40 | B | | | 00 | A |
| FI | 00 | A | 00 | A | 00 | A | 10 | A | 00 | A | 00 | A | 00 | A | 00 | A | 20 | A | | | 00 | A |
| FR | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 20 | A | 20 | A | 00 | A | 00 | A | 00 | A | 00 | A |
| GB | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 20 | A | 00 | A | 20 | A | 00 | A | | | 30 | B |
| HR | 00 | A | 00 | A | 00 | A | 80 | C | 00 | A | 00 | A | 80 | C | 40 | B | 40 | B | 40 | B | 00 | A |
| HU | 00 | A | 00 | A | 00 | A | 10 | A | 01 | A | 20 | A | 00 | A | 40 | B | 10 | A | | | 00 | A |
| IE0001 | 00 | A | 00 | A | 00 | A | 20 | A | 00 | A | 20 | A | 00 | A | 00 | A | 00 | A | | | 00 | A |
| IE (ESB) | 00 | A | 30 | B | 00 | A | 40 | B | 20 | A | 60 | B | 60 | B | 00 | A | 71 | C | | | 00 | A |
| IS | 00 | A | 00 | A | 00 | A | 20 | A | 30 | B | 60 | B | 00 | A | 40 | B | 40 | B | | | 00 | A |
| IT0001 | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 20 | A | | | 00 | A |
| LT | 20 | A | 10 | A | 00 | A | 80 | C | 20 | A | 00 | A | | | 30 | B | 40 | B | 40 | B | 00 | A |
| LV | 00 | A | 10 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 40 | B | | | 00 | A |
| MK | | | 70 | C | 71 | C | 10 | A | 51 | B | 60 | B | 00 | A | 10 | A | 60 | B | | | 60 | B |
| NL | 30 | B | 00 | A | 00 | A | 20 | A | 00 | A | 00 | A | 20 | A | 20 | A | | | 00 | A | 00 | A |
| NO | 00 | A | 00 | A | 00 | A | 10 | A | 00 | A | 00 | A | 10 | A | 00 | A | 40 | B | | | 00 | A |
| PL | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 20 | A | 00 | A | 00 | A | | | 00 | A |
| PL0005 | 10 | A | 30 | B | 00 | A | 00 | A | 20 | A | 00 | A | 00 | A | 00 | A | 40 | B | | | 20 | A |
| PT | 10 | A | 30 | B | 00 | A | 40 | B | 53 | C | | | 00 | A | 60 | B | 22 | B | | | 00 | A |
| RO | | | 30 | B | | | | | 40 | B | | | | | | B | 50 | B | | | 00 | A |
| RU | 20 | A | 00 | A | 20 | A | 40 | B | 61 | B | 01 | A | 20 | A | 60 | A | 40 | B | | | 20 | A |
| SE | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 30 | B | 30 | B | 00 | A | 40 | B | | | 10 | A |
| SI | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 20 | A | 20 | A | 20 | A |
| SK | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | 00 | A | | | 00 | A |
| TR | 00 | A | 00 | A | 00 | A | 10 | A | 20 | A | 40 | B | 00 | A | 00 | A | 20 | A | 20 | A | 00 | A |
| YU | | | | | | | 60 | B | | | 00 | A | 60 | B | 00 | | 40 | B | | | 60 | B |

*Table 14: QA flag and category for main components in precipitation.*

| | $NO_2$ | | | | $SO_2$ | | | | $SO_4$ | | sum $NO_3$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | field | | lab | | field | | lab | | field | | lab | |
| AT30 | | | | | 22 | B | | | | | | |
| CH01 | 31 | B | | | | | | | | | | |
| CH | 33 | B | | | 32 | B | 00 | A | | | | |
| CZ | 03 | B | 10 | A | 12 | B | 00 | A | 01 | A | 00 | A |
| DE | 23 | B | 20 | A | 01 | A | 10 | A | 00 | A | 00 | A |
| DK | 00 | A | 00 | A | 00 | A | 00 | A | 0 | A | 00 | A |
| EE | 62 | B | 00 | A | 12 | B | 41 | B | 82 | C | | |
| ES | 30 | B | 20 | A | 32 | B | 41 | B | 00 | A | | |
| FI | | | | | 01 | A | 00 | A | 00 | A | 00 | A |
| FR | | | | | 20 | B | 00 | A | 20 | B | | |
| GB | 53 | B | 00 | A | 10 | B | 10 | A | 00 | A | | |
| HR | | | 00 | A | | | | | | | | |
| HU | 13 | B | 00 | A | | | | | | | | |
| IE | 50 | B | 00 | A | 00 | A | | | | | | |
| IS | | | | | | | 40 | B | | | 60 | B |
| IT01 | | | | | 00 | A | 11 | B | 00 | A | | |
| LT | 32 | B | 00 | A | 10 | B | | | 10 | B | 01 | A |
| LV | 02 | B | 00 | A | 50 | B | 30 | B | 22 | B | 00 | A |
| NL | 03 | B | | | 11 | B | | | 00 | A | | |
| NO | 00 | A | 20 | A | 00 | A | 00 | A | 00 | A | 00 | A |
| PL | 43 | B | 00 | A | 00 | A | 10 | A | 01 | A | 00 | A |
| PL05 | 52 | B | 00 | A | 20 | B | 00 | A | 32 | B | 00 | A |
| PT | | | | | | | 32 | B | | | | |
| RU01 | | | | | 10 | A | 60 | B | | | | |
| RU | 00 | A | 10 | A | 23 | B | | | 00 | A | 61 | B |
| SE | 10 | B | 00 | A | 00 | A | 30 | B | 00 | A | 00 | A |
| SI | | | 00 | A | 00 | A | 30 | B | 20 | B | 00 | A |
| SK | 53 | B | 60 | B | | | 00 | A | | | 00 | A |
| TR | | | 00 | A | 00 | A | 20 | A | | | 20 | A |
| YU | 53 | B | | | | | | | | | | |

# 8. Audits

## 8.1 Introduction

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.

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# 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 | Vasiliki Smirnioudi |
| 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) | Frank Raes and Jean-Philippe Putaud |
| Latvia | Latvian Hydrometeorological Institute | Iraida Lyulko |
| Lithuania | Institute of Physics | Dalia Sopauskiene and<br>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<br>Institute of Environmental Protection | Grazyna Mitosek<br>and for PL05: Anna Degorska |
| Portugal | Instituto de Meteorologia | Amelia Lopes |
| Russia | Institute of Global Climate and Ecology | Alexey Ryaboshapko |
| Serbia and Montenegro | Federal Hydrometeorological Institute | Momcilo Zivkovic |
| Slovenia | Environment Agency - Slovenia | Brigita Jesenovec |
| Slovak Republic | Slovak Hydrometeorological Institute | Marta Mitosinkova |
| Spain | Subdirección General de Calidad Ambiental | Montserrat Fernández San Miguel |
| Sweden | Swedish Environmental Research Institute (IVL) | Karin Sjöberg |
| Switzerland | Swiss Federal Laboratory of testing Materials and Research (EMPA) | Robert Gehrig |
| Turkey | The Ministry of Health of the Republic of Turkey | Canan Yesilyurt |
| 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 accuracy in the laboratory, for the very lowest concentrations of the main components in precipitation follow the WMO GAW (1992) recommendations for regional stations:

| | Accuracy | |
|---|---|---|
| $SO_4^{2-}$ | 0.032 mg S/l | (1 µmol/l) |
| $NO_3^-$ | 0.014 mg N/l | (1 µmol/l) |
| $NH_4^+$ | 0.028 mg N/l | (2 µmol/l) |
| $Cl^-$ | 0.107 mg Cl/l | (3 µmol/l) |
| $Ca^{2+}$ | 0.012 mg Ca/l | (0.3 µmol/l) |
| $K^+$ | 0.012 mg K/l | (0.3 µmol/l) |
| $Mg^{2+}$ | 0.007 mg Mg/l | (0.3 µmol/l) |
| $Na^+$ | 0.007 mg Na/l | (0.3 µmol/l) |

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.

The aim for data completeness is valid for the current definition used by the CCC. This definition will, however, be harmonised with the WMO GAW definition and modified.

## 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 2002, 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 | 99 | 100 |
| AT0004R | 100 | - | 83 | 83 | 83 | 83 | 83 | 81 | 83 | 83 | 83 | 81 | 82 |
| AT0005R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 93 | 100 | 100 | 100 |
| BY0004R | 100 | - | 77 | 100 | 100 | 87 | 100 | 94 | 99 | 99 | 100 | 93 | 1 |
| CH0002R | 100 | - | 98 | 96 | 96 | 96 | 96 | 96 | 96 | 96 | 96 | 96 | 98 |
| CH0004R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| CH0005R | 100 | - | 99 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 99 |
| CZ0001R | 100 | - | 89 | 89 | 89 | 94 | 89 | 94 | 94 | 89 | 94 | 94 | 88 |
| CZ0003R | 100 | - | 98 | 98 | 96 | 96 | 98 | 97 | 97 | 98 | 97 | 97 | 96 |
| DE0001R | 98 | - | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 |
| DE0002R | 100 | - | 99 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 99 |
| DE0003R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| DE0004R | 100 | - | 99 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 99 |
| DE0005R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| DE0007R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| DE0008R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| DE0009R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 99 |
| DK0005R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| DK0008R | 100 | - | 91 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| DK0022R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| EE0009R | 100 | - | 100 | 100 | 100 | 99 | 100 | 99 | 99 | 100 | 99 | 99 | 100 |
| EE0011R | 100 | - | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 |
| ES0007R | 99 | - | 96 | 96 | 96 | 96 | 96 | 95 | 95 | 96 | 95 | 95 | 87 |
| ES0008R | 99 | - | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 98 |
| ES0009R | 97 | - | 97 | 96 | 96 | 95 | 96 | 94 | 94 | 96 | 94 | 94 | 90 |
| ES0011R | 99 | - | 97 | 97 | 97 | 97 | 97 | 97 | 97 | 97 | 97 | 97 | 97 |
| ES0012R | 97 | - | 99 | 99 | 99 | 98 | 99 | 98 | 98 | 99 | 98 | 98 | 99 |
| ES0013R | 98 | - | 99 | 99 | 99 | 98 | 99 | 98 | 98 | 99 | 98 | 98 | 90 |
| ES0014R | 100 | - | 91 | 91 | 91 | 90 | 91 | 89 | 89 | 91 | 89 | 89 | 91 |
| ES0015R | 97 | - | 86 | 85 | 85 | 85 | 85 | 83 | 83 | 85 | 83 | 83 | 85 |
| ES0016R | 92 | - | 99 | 98 | 98 | 97 | 98 | 97 | 97 | 98 | 97 | 97 | 92 |
| FI0004R | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| FI0009R | 100 | 100 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 |
| FI0017R | 100 | 100 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 |
| FI0022R | 100 | 100 | 99 | 99 | 99 | 97 | 99 | 99 | 99 | 99 | 99 | 99 | 99 |
| FR0003R | 100 | - | 60 | 58 | 58 | 58 | 58 | 58 | 58 | 58 | 58 | 58 | 60 |
| FR0005R | 100 | - | 92 | 91 | 91 | 91 | 91 | 91 | 91 | 91 | 91 | 91 | 92 |
| FR0008R | 100 | - | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 |
| FR0009R | 100 | - | 97 | 96 | 96 | 97 | 96 | 96 | 96 | 96 | 96 | 96 | 97 |
| FR0010R | 100 | - | 85 | 84 | 84 | 84 | 84 | 84 | 84 | 84 | 84 | 84 | 85 |
| FR0012R | 100 | - | 93 | 93 | 93 | 93 | 93 | 93 | 93 | 93 | 93 | 93 | 93 |
| FR0013R | 100 | - | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| FR0014R | 100 | - | 94 | 93 | 93 | 93 | 93 | 93 | 93 | 93 | 93 | 93 | 94 |
| FR0015R | 100 | - | 96 | 95 | 95 | 95 | 95 | 95 | 95 | 95 | 95 | 95 | 96 |
| FR0016R | 100 | - | 94 | 92 | 92 | 92 | 92 | 92 | 92 | 92 | 92 | 92 | 94 |
| GB0002R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| GB0006R | 102 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| GB0013R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| GB0014R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| GB0015R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| HU0002R | 100 | 100 | 88 | 89 | 89 | 99 | 89 | 99 | 99 | 89 | 99 | 99 | 88 |
| IE0001R | 100 | 100 | 99 | 99 | 99 | 98 | 99 | 99 | 99 | 99 | 99 | 99 | 99 |
| IE0002R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| IE0003R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| IS0091R | 95 | 100 | 97 | 97 | - | 97 | 97 | 97 | 97 | 97 | 97 | 97 | 97 |

*Table A2.1, cont.*

| Code | mm | mm off | pH | $SO_4$ | $XSO_4$ | $NH_4$ | $NO_3$ | Na | Mg | Cl | Ca | K | cond |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| IT0001R | 13 | - | 95 | 95 | 95 | 95 | 95 | 95 | 95 | 95 | 95 | 95 | 95 |
| IT0004R | 100 | - | 100 | 100 | 100 | 98 | 100 | 100 | 94 | 100 | 100 | 100 | 99 |
| LT0015R | 92 | - | 100 | 100 | 100 | 100 | 100 | 100 | - | 100 | 100 | 100 | 100 |
| LV0010R | 100 | - | 98 | 97 | 97 | 97 | 97 | 94 | 93 | 97 | 94 | 91 | 95 |
| LV0016R | 100 | - | 97 | 89 | 89 | 97 | 89 | 95 | 94 | 89 | 94 | 93 | 96 |
| NL0009R | 100 | - | 97 | 96 | 96 | 95 | 96 | 93 | 94 | 96 | 93 | 94 | 90 |
| NO0001R | 100 | - | 98 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 98 |
| NO0008R | 100 | - | 98 | 99 | 99 | 98 | 99 | 100 | 100 | 99 | 99 | 98 | 99 |
| NO0015R | 100 | - | 95 | 99 | 99 | 99 | 99 | 98 | 99 | 98 | 99 | 99 | 97 |
| NO0039R | 100 | - | 96 | 98 | 98 | 97 | 98 | 98 | 98 | 98 | 98 | 97 | 98 |
| NO0041R | 100 | - | 98 | 100 | 100 | 99 | 100 | 100 | 100 | 100 | 100 | 99 | 100 |
| NO0055R | 100 | - | 92 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 92 |
| NO0099R | 100 | - | 97 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 97 |
| PL0002R | 100 | - | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 |
| PL0003R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| PL0004R | 100 | - | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 |
| PL0005R | - | 100 | 98 | 98 | 98 | 95 | 98 | 96 | 95 | 95 | 96 | 96 | 85 |
| PT0001R | - | 100 | 77 | 77 | 77 | 77 | 77 | 77 | 77 | 77 | 77 | 77 | 77 |
| PT0003R | - | 100 | 82 | 82 | 82 | 82 | 82 | 82 | 82 | 82 | 82 | 82 | 82 |
| PT0004R | - | 100 | 92 | 92 | 92 | 92 | 92 | 92 | 92 | 92 | 92 | 92 | 92 |
| RU0001R | 100 | - | 97 | 100 | 100 | 100 | 100 | 100 | 99 | 100 | 99 | 100 | 100 |
| RU0013R | 100 | - | 98 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| RU0016R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| RU0018R | 100 | - | 99 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 98 | 100 |
| SE0005R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 99 |
| SE0011R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| SE0014R | 100 | - | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 96 |
| SK0002R | 100 | - | 86 | 93 | 93 | 92 | 93 | 92 | 92 | 93 | 92 | 92 | 86 |
| SK0004R | 100 | - | 94 | 96 | 96 | 96 | 96 | 96 | 96 | 96 | 96 | 96 | 94 |
| SK0005R | 100 | - | 91 | 95 | 95 | 96 | 95 | 96 | 96 | 95 | 96 | 96 | 91 |
| SK0006R | 100 | - | 94 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 98 | 94 |
| SK0007R | 100 | - | 91 | 96 | 96 | 95 | 96 | 95 | 95 | 96 | 95 | 95 | 91 |
| TR0001R | 90 | - | 94 | 100 | 100 | 99 | 100 | 99 | 99 | 100 | 99 | 99 | 98 |
| YU0005R | 100 | - | 100 | 100 | 100 | 99 | 100 | 99 | 99 | 100 | 99 | 99 | 100 |
| YU0008R | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

*Table A2.2: Data capture for main components in air in 2002, in per cent.*

| Code | $SO_2$ | $NO_2$ | $SO_4$ | $XSO_4$ | $SNO_3$ | $NO_3$ | $HNO_3$ | $SNH_4$ | $NH_4$ | $NH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| AT0002R | 100 | 99 | 100 | - | 100 | - | - | 99 | - | - |
| AT0004R | - | 100 | - | - | - | - | - | - | - | - |
| AT0005R | - | 99 | - | - | - | - | - | - | - | - |
| AT0030R | 95 | - | - | - | - | - | - | - | - | - |
| BE0001R | - | 86 | - | - | - | - | - | - | - | - |
| BE0032R | - | 94 | - | - | - | - | - | - | - | - |
| BE0035R | - | 78 | - | - | - | - | - | - | - | - |
| CH0001G | 81 | 82 | 100 | - | - | - | - | - | - | - |
| CH0002R | 100 | 100 | 100 | - | - | - | - | - | - | - |
| CH0003R | - | 100 | - | - | - | - | - | - | - | - |
| CH0004R | 100 | 99 | - | - | - | - | - | - | - | - |
| CH0005R | 100 | 96 | 100 | - | 100 | - | - | 100 | - | - |
| CZ0001R | 99 | 100 | 16 | - | 98 | - | - | 99 | - | - |
| CZ0003R | 99 | 99 | 16 | - | 99 | - | - | 100 | - | - |
| DE0001R | 100 | 98 | 100 | - | 100 | - | - | 100 | - | - |
| DE0002R | 100 | 69 | - | - | - | - | - | - | - | - |
| DE0003R | 97 | 95 | 97 | - | 96 | - | - | 96 | - | - |
| DE0004R | 99 | 97 | 99 | - | 99 | - | - | 99 | - | - |
| DE0005R | 99 | 82 | - | - | - | - | - | - | - | - |
| DE0007R | 98 | 97 | 98 | - | 98 | - | - | 97 | - | - |
| DE0008R | 98 | 92 | - | - | - | - | - | - | - | - |
| DE0009R | 99 | 99 | 99 | - | 99 | - | - | 99 | - | - |
| DK0003R | 97 | - | 96 | 95 | 96 | - | - | 95 | - | - |
| DK0005R | 99 | - | 97 | 97 | 98 | - | - | 99 | - | - |
| DK0008R | 99 | - | 99 | - | 99 | - | - | 99 | - | - |
| EE0009R | 98 | 97 | 98 | - | - | - | - | - | - | - |
| EE0011R | 99 | 96 | - | - | - | - | - | - | - | - |
| ES0007R | 98 | 98 | 96 | - | 96 | - | - | 98 | - | - |
| ES0008R | 96 | 97 | 92 | - | 97 | - | - | 96 | - | - |
| ES0009R | 97 | 95 | 98 | - | 98 | - | - | 99 | - | - |
| ES0010R | 97 | 96 | 93 | - | 91 | - | - | 89 | - | - |
| ES0011R | 98 | 97 | 98 | - | 99 | - | - | 100 | - | - |
| ES0012R | 98 | 97 | 96 | - | 94 | - | - | 95 | - | - |
| ES0013R | 98 | 96 | 96 | - | 99 | - | - | 99 | - | - |
| ES0014R | 98 | 99 | 90 | - | 96 | - | - | 96 | - | - |
| ES0015R | 97 | 97 | 76 | - | 93 | - | - | 86 | - | - |
| ES0016R | 94 | 92 | 92 | - | 96 | - | - | 93 | - | - |
| FI0009R | 98 | 90 | 98 | - | 98 | - | - | 100 | - | - |
| FI0017R | 100 | 96 | 100 | - | 100 | - | - | 100 | - | - |
| FI0022R | 100 | 98 | 100 | - | 100 | - | - | 99 | - | - |
| FI0037R | 100 | 74 | 98 | - | 98 | - | - | 100 | - | - |
| FR0003R | 50 | - | 49 | - | - | - | - | - | - | - |
| FR0005R | 100 | - | 95 | - | - | - | - | - | - | - |
| FR0008R | 97 | - | 96 | - | - | - | - | - | - | - |
| FR0009R | 100 | - | 100 | - | - | - | - | - | - | - |
| FR0010R | 100 | - | 100 | - | - | - | - | - | - | - |
| FR0012R | 96 | - | 96 | - | - | - | - | - | - | - |
| FR0013R | 98 | - | 95 | - | - | - | - | - | - | - |
| FR0014R | 89 | - | 88 | - | - | - | - | - | - | - |
| FR0015R | 99 | - | 99 | - | - | - | - | - | - | - |
| FR0016R | 94 | - | 94 | - | - | - | - | - | - | - |
| GB0002R | 96 | - | - | - | - | - | - | - | - | - |
| GB0006R | 100 | - | - | - | - | - | - | - | - | - |
| GB0013R | 92 | - | - | - | - | - | - | - | - | - |
| GB0014R | 96 | - | - | - | - | - | - | - | - | - |
| GB0015R | 100 | - | - | - | - | - | - | - | - | - |
| GB0036R | - | 98 | - | - | - | - | - | - | - | - |
| GB0037R | - | 97 | - | - | - | - | - | - | - | - |

*Table A2.2, cont.*

| Code | $SO_2$ | $NO_2$ | $SO_4$ | $XSO_4$ | $SNO_3$ | $NO_3$ | $HNO_3$ | $SNH_4$ | $NH_4$ | $NH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| GB0038R | - | 91 | - | - | - | - | - | - | - | - |
| GB0043R | - | 86 | - | - | - | - | - | - | - | - |
| GB0045R | - | 85 | - | - | - | - | - | - | - | - |
| HU0002R | 81 | 89 | 86 | - | - | 86 | 86 | - | 94 | 94 |
| IE0001R | 98 | 100 | 99 | - | - | - | - | - | - | - |
| IE0002R | 86 | - | 86 | - | - | - | - | - | - | - |
| IE0003R | - | - | 92 | - | - | - | - | - | - | - |
| IS0091R | - | - | 100 | - | - | 100 | - | - | - | - |
| IT0001R | 100 | 94 | 100 | - | - | 99 | 100 | - | 100 | 100 |
| IT0004R | 92 | 81 | 58 | - | - | 58 | - | - | 58 | - |
| LT0015R | 96 | 96 | 96 | - | 96 | - | - | 96 | - | - |
| LV0010R | 95 | 99 | 99 | - | 100 | 100 | - | 100 | 99 | - |
| LV0016R | 94 | 99 | 99 | - | 99 | 99 | - | 99 | 99 | - |
| NL0009R | 99 | 91 | 93 | - | - | 93 | - | - | 93 | - |
| NL0010R | 87 | 93 | 99 | - | - | 99 | - | - | 99 | 77 |
| NO0001R | 99 | 98 | 98 | 98 | 90 | 90 | 91 | 91 | 91 | 91 |
| NO0008R | 99 | 97 | 99 | 99 | 88 | 88 | 91 | 89 | 89 | 91 |
| NO0015R | 99 | 100 | 99 | 99 | 64 | 64 | 67 | 67 | 67 | 67 |
| NO0039R | 98 | 99 | 98 | 98 | 85 | 85 | 88 | 88 | 88 | 81 |
| NO0041R | 99 | 92 | 99 | 99 | 95 | 96 | 96 | 96 | 96 | 96 |
| NO0042G | 97 | - | 96 | 96 | 57 | 57 | 68 | 68 | 68 | 68 |
| NO0055R | 100 | 100 | 99 | 99 | 83 | 83 | 92 | 92 | 92 | - |
| PL0002R | 99 | 98 | 98 | - | 40 | 92 | - | 95 | 89 | - |
| PL0003R | 100 | 100 | 100 | - | 100 | 100 | - | 100 | 100 | - |
| PL0004R | 83 | 100 | 83 | - | 100 | 98 | - | 90 | 98 | - |
| PL0005R | 98 | 99 | 99 | - | 99 | - | - | 99 | - | - |
| RU0001R | 89 | - | 91 | - | - | 91 | - | - | 91 | - |
| RU0016R | 96 | - | 96 | - | - | 96 | - | - | 96 | - |
| RU0018R | 88 | - | 88 | - | - | 88 | - | - | 88 | - |
| SE0005R | 97 | 96 | 97 | - | 97 | - | - | 95 | - | - |
| SE0008R | 98 | 98 | 98 | - | - | - | - | - | - | - |
| SE0011R | 100 | 92 | 100 | - | 100 | - | - | 100 | - | - |
| SE0014R | 98 | 95 | 98 | - | 98 | - | - | 98 | - | - |
| SI0008R | 99 | - | 99 | - | 99 | - | - | 99 | - | - |
| SK0002R | 95 | 95 | 98 | - | - | 98 | 98 | - | - | - |
| SK0004R | 98 | 100 | 98 | - | - | 98 | 98 | - | - | - |
| SK0005R | 96 | 91 | 99 | - | - | 99 | 98 | - | - | - |
| SK0006R | 97 | 99 | 96 | - | - | 98 | 98 | - | - | - |
| SK0007R | 96 | 100 | 98 | - | - | 99 | 99 | - | - | - |
| TR0001R | 82 | 95 | 97 | - | 89 | 97 | 85 | 94 | 94 | 84 |
| YU0005R | 87 | 86 | - | - | - | - | - | - | - | - |
| YU0008R | 32 | 32 | - | - | - | - | - | - | - | - |

*Table A2.3: Data capture for heavy metals in precipitation in 2002, in per cent.*

| Code | Pb | Cd | Zn | Hg | Ni | As | Cu | Co | Cr | Mn | V | Fe | mm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BE0004R | 86 | 86 | 86 | 94 | 86 | 92 | 70 | - | 86 | - | - | - | 96 |
| CZ0001R | 99 | 99 | - | - | 99 | - | - | - | - | - | - | - | 100 |
| CZ0003R | 99 | 99 | - | - | 99 | - | - | - | - | - | - | - | 100 |
| DE0001R | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| DE0002R | 95 | 95 | 95 | 100 | 90 | 95 | 93 | 95 | 93 | 95 | 95 | 95 | 100 |
| DE0004R | 99 | 99 | 99 | - | 99 | 99 | 99 | 99 | 99 | 99 | 99 | - | 100 |
| DE0009R | 98 | 98 | 98 | 100 | 98 | 98 | 91 | 98 | 98 | 98 | 98 | 98 | 100 |
| DK0008R | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 | - | - | 100 | 100 |
| DK0020R | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 | - | - | 100 | 92 |
| DK0031R | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 | - | - | 100 | 100 |
| EE0009R | 100 | 100 | 100 | - | - | 100 | 100 | - | - | - | - | - | 100 |
| EE0011R | 72 | 72 | 69 | - | - | 72 | 72 | - | - | - | - | - | 100 |
| FI0008R | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 | 100 | 100 | 100 | 100 |
| FI0009R | 100 | 100 | 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 | 99 |
| FI0053R | 100 | 100 | - | - | 98 | 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 | 96 | 100 | 100 | 100 |
| FI0096R | - | - | - | 100 | - | - | - | - | - | - | - | - | 97 |
| FR0090R | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 | - | - | - | 100 |
| GB0014R | 92 | 100 | 100 | - | 100 | 100 | 100 | - | 100 | - | - | - | 100 |
| GB0090R | 100 | 100 | 100 | - | 100 | 97 | 100 | - | 100 | - | - | - | 98 |
| GB0091R | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 | - | - | - | 98 |
| IE0001R | 100 | 100 | 100 | 100 | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 |
| IE0002R | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 |
| IS0090R | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 | 100 | 100 | 100 | 99 |
| IS0091R | 100 | 100 | 100 | - | 100 | - | 100 | - | 100 | 100 | - | 100 | 96 |
| LT0015R | 94 | 93 | 99 | - | - | - | 99 | - | - | - | - | - | 99 |
| LV0010R | 100 | 100 | 100 | - | 100 | 100 | 100 | - | - | 100 | - | - | 83 |
| LV0016R | 100 | 100 | 100 | - | 100 | 100 | 100 | - | - | 100 | - | - | 83 |
| NL0009R | 72 | 70 | 70 | - | 72 | 72 | 72 | - | 72 | - | - | - | 96 |
| NL0091R | 100 | 100 | 96 | 100 | 96 | 100 | 100 | - | 100 | - | - | - | 100 |
| NO0001R | 100 | 100 | 100 | - | - | - | - | - | - | - | - | - | 100 |
| NO0039R | 100 | 100 | 100 | - | - | - | - | - | - | - | - | - | 100 |
| NO0041R | 100 | 100 | 100 | - | - | - | - | - | - | - | - | - | 100 |
| NO0047R | 98 | 98 | 98 | - | 98 | 98 | 98 | 98 | 98 | - | - | - | 96 |
| NO0055R | 100 | 100 | 100 | - | - | - | - | - | - | - | - | - | 100 |
| NO0056R | 95 | 95 | 95 | - | - | - | - | - | - | - | - | - | 100 |
| NO0099R | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | - | 100 | - | 83 |
| PL0004R | 100 | 100 | 100 | - | 100 | - | 100 | - | 100 | - | - | - | 100 |
| PL0005R | 97 | 97 | 97 | - | 97 | - | 97 | - | 97 | - | - | - | 100 |
| PT0001R | 77 | 77 | 77 | - | 77 | - | 77 | - | - | 77 | - | - | - |
| PT0003R | 82 | 82 | 82 | - | 82 | - | 82 | - | - | 82 | - | - | - |
| PT0004R | 92 | 92 | 92 | - | 92 | - | 92 | - | - | 92 | - | - | - |
| PT0010R | 92 | 92 | 92 | - | 92 | - | 92 | - | - | 92 | - | - | - |
| SE0005R | 100 | 100 | 100 | 100 | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 97 |
| SE0011R | - | - | - | 100 | - | - | - | - | - | - | - | - | 97 |
| SE0014R | - | - | - | 100 | - | - | - | - | - | - | - | - | 97 |
| SE0051R | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 |
| SE0097R | 100 | 100 | 100 | - | 100 | 100 | 100 | 100 | 100 | 100 | 100 | - | 97 |
| SK0002R | 100 | 100 | 78 | - | 100 | 100 | 100 | - | 100 | 100 | - | - | 100 |
| SK0004R | 100 | 100 | 81 | - | 100 | 100 | 100 | - | 100 | 100 | - | - | 100 |
| SK0005R | 100 | 100 | 94 | - | 100 | 100 | 100 | - | 100 | 100 | - | - | 100 |
| SK0006R | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 | 100 | - | - | 100 |
| SK0007R | 100 | 100 | 100 | - | 100 | - | 100 | - | 100 | 100 | - | - | 100 |

*Table A2.4: Data capture for heavy metals in air in 2002, in per cent.*

| Code | Pb | Cd | Zn | Hg | Ni | As | Cu | Co | Cr | Mn | V | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| AT0002R | 29 | 29 | - | - | 13 | 13 | - | - | - | - | - | - |
| AT0004R | 17 | 17 | - | - | - | - | - | - | - | - | - | - |
| AT0005R | 26 | 26 | - | - | 11 | 11 | - | - | - | - | - | - |
| BE0004R | 33 | 33 | 33 | - | 33 | - | 33 | - | - | - | - | - |
| CZ0001R | 17 | 17 | - | - | - | - | - | - | - | - | - | - |
| CZ0003R | 16 | 16 | - | - | - | - | - | - | - | - | - | - |
| DE0001R | 100 | 100 | - | - | 100 | 100 | 100 | - | - | 100 | - | 97 |
| DE0002R | 96 | 96 | 94 | 97 | 96 | 96 | 96 | - | - | 96 | - | 96 |
| DE0003R | 97 | 97 | - | - | - | 95 | 97 | - | - | 97 | - | - |
| DE0004R | 100 | 100 | - | - | 100 | 100 | 100 | - | - | 100 | - | - |
| DE0005R | 100 | 100 | - | - | - | 100 | 100 | - | - | - | - | 97 |
| DE0007R | 100 | 100 | - | - | 100 | 100 | - | - | - | 100 | - | 97 |
| DE0008R | 100 | 100 | - | - | 100 | 100 | 100 | - | - | 100 | - | 100 |
| DE0009R | 100 | 100 | - | - | 100 | 100 | 100 | - | - | 100 | - | 97 |
| DK0003R | 98 | 98 | 98 | - | 98 | 98 | 98 | - | 98 | 98 | - | 98 |
| DK0005R | 99 | 99 | 99 | - | 99 | 99 | 99 | - | 99 | 99 | - | 99 |
| DK0008R | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 | 100 | - | 100 |
| DK0031R | 99 | 99 | 100 | - | 99 | 99 | 99 | - | 99 | 99 | - | 99 |
| ES0008R | 12 | 12 | - | - | - | - | 12 | - | - | - | - | - |
| ES0009R | 12 | 12 | - | - | - | - | 12 | - | - | - | - | - |
| FI0036R | 96 | 96 | 96 | - | 96 | 96 | 96 | - | 96 | 96 | 96 | 96 |
| FI0096R | - | - | - | 83 | - | - | - | - | - | - | - | - |
| GB0014R | 100 | 100 | 100 | - | 100 | 100 | 100 | - | 100 | - | - | - |
| GB0090R | 100 | 100 | 100 | - | 92 | 100 | 100 | - | 100 | - | - | - |
| GB0091R | 99 | 99 | 99 | - | 99 | 99 | 99 | - | 99 | - | - | - |
| IS0091R | 100 | 100 | 100 | 100 | 100 | 100 | 100 | - | 100 | 100 | 100 | 100 |
| LT0015R | 99 | 99 | 99 | - | - | - | 99 | - | - | - | - | - |
| LV0010R | 96 | 96 | 96 | - | 96 | 96 | 96 | - | - | 96 | - | - |
| LV0016R | 95 | 95 | 95 | - | 95 | 95 | 95 | - | - | 95 | - | - |
| NL0009R | 50 | 50 | 50 | - | - | 50 | - | - | - | - | - | - |
| NO0042G | 25 | 25 | 25 | 78 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | - |
| NO0099R | 100 | 100 | 100 | 6 | 62 | 100 | 90 | 83 | 62 | - | 77 | - |
| SE0005R | 93 | 93 | - | - | 93 | 93 | - | - | - | - | - | - |
| SE0014R | 92 | 92 | - | 24 | 92 | 92 | - | - | - | - | - | - |
| SK0002R | 92 | 92 | 92 | - | 90 | 92 | 90 | - | 90 | 92 | - | - |
| SK0004R | 86 | 91 | 86 | - | 91 | 88 | 91 | - | 89 | 91 | - | - |
| SK0005R | 67 | 67 | 67 | - | 56 | 63 | 56 | - | 67 | 63 | - | - |
| SK0006R | 98 | 98 | 98 | - | 98 | 98 | 98 | - | 98 | 98 | - | - |
| SK0007R | 98 | 98 | 98 | - | 96 | 98 | 98 | - | 92 | 96 | - | - |

*Table A2.5: Data capture for ozone in 2002, in per cent.*

| Code | O3 | Code | O3 | Code | O3 | Code | O3 |
|---|---|---|---|---|---|---|---|
| AT0002R | 96 | DE0009R | 96 | FR0010R | 91 | NO0039R | 99 |
| AT0004R | 96 | DE0012R | 91 | FR0012R | 86 | NO0041R | 98 |
| AT0005R | 96 | DE0026R | 91 | FR0013R | 98 | NO0042G | 97 |
| AT0030R | 96 | DE0035R | 86 | FR0014R | 97 | NO0043R | 100 |
| AT0032R | 99 | DE0039R | 93 | FR0015R | 98 | NO0045R | 100 |
| AT0033R | 96 | DE0042R | 87 | FR0016R | 99 | NO0048R | 100 |
| AT0034G | 96 | DE0045R | 93 | GB0002R | 99 | NO0052R | 100 |
| AT0037R | 92 | DE0046R | 94 | GB0006R | 88 | NO0055R | 98 |
| AT0038R | 95 | DE0047R | 95 | GB0013R | 92 | NO0056R | 100 |
| AT0040R | 95 | DK0005R | 100 | GB0014R | 94 | NO0488R | 95 |
| AT0041R | 95 | DK0010G | 24 | GB0015R | 95 | NO0489R | 53 |
| AT0042R | 94 | DK0011G | 19 | GB0031R | 90 | NO0492R | 98 |
| AT0043R | 95 | DK0031R | 99 | GB0032R | 99 | PL0002R | 100 |
| AT0044R | 92 | DK0041R | 96 | GB0033R | 97 | PL0003R | 100 |
| AT0045R | 95 | EE0009R | 98 | GB0034R | 99 | PL0004R | 100 |
| AT0046R | 96 | EE0011R | 99 | GB0035R | 74 | PL0005R | 96 |
| AT0047R | 95 | ES0007R | 98 | GB0036R | 97 | PT0004R | 90 |
| BE0001R | 93 | ES0008R | 98 | GB0037R | 97 | RU0016R | 54 |
| BE0011R | 100 | ES0009R | 96 | GB0038R | 94 | RU0018R | 39 |
| BE0013R | 100 | ES0010R | 96 | GB0039R | 99 | SE0011R | 99 |
| BE0032R | 93 | ES0011R | 98 | GB0043R | 91 | SE0012R | 95 |
| BE0035R | 91 | ES0012R | 97 | GB0044R | 98 | SE0013R | 100 |
| CH0002R | 95 | ES0013R | 98 | GB0045R | 99 | SE0014R | 99 |
| CH0003R | 95 | ES0014R | 99 | GR0002R | 71 | SE0032R | 99 |
| CH0004R | 95 | ES0015R | 96 | HU0002R | 97 | SE0035R | 99 |
| CH0005R | 95 | ES0016R | 93 | IE0031R | 98 | SE0039R | 100 |
| CZ0001R | 98 | FI0009R | 74 | IT0001R | 92 | SI0008R | 91 |
| CZ0003R | 95 | FI0017R | 99 | IT0004R | 83 | SI0031R | 94 |
| DE0001R | 95 | FI0022R | 95 | LT0015R | 99 | SI0032R | 93 |
| DE0002R | 95 | FI0037R | 99 | LV0010R | 88 | SI0033R | 77 |
| DE0003R | 91 | FR0008R | 96 | MT0001R | 94 | SK0002R | 97 |
| DE0004R | 91 | FR0008R | 98 | NL0009R | 95 | SK0004R | 100 |
| DE0005R | 96 | FR0008R | 98 | NL0010R | 93 | SK0006R | 100 |
| DE0007R | 90 | FR0008R | 96 | NO0001R | 99 | SK0007R | 99 |
| DE0008R | 91 | FR0009R | 98 | NO0015R | 96 | | |

*Table A2.6: Number of valid (daily) samples of hydrocarbons and carbonyls (after inspection and removal of outliers).*

According to EMEP's recommendations, the samples should be taken twice a week, implying that 104 samples per year correspond to 100% data capture. A 90% data completeness is therefore 94 samples per year.

| Station | Number of samples | |
|---|---|---|
| | HC | Carb |
| Pallas | 96 | - |
| Utö | 89 | - |
| Zingst | 101 | 104 |
| Waldhof | 104 | 104 |
| Schmücke | 104 | 104 |
| Brotjacklriegel | 104 | 104 |
| Hohenpeissenberg | 337 | - |
| Košetice | 103 | - |
| Starina 2) | 80 | - |
| Rigi 1) | 314 | - |
| Donon | 91 | 75 |
| Peyrusse Vieille 2) | 79 | 28 |
| La Tardiere | 104 | 28 |
| Campisábalos | 97 | - |

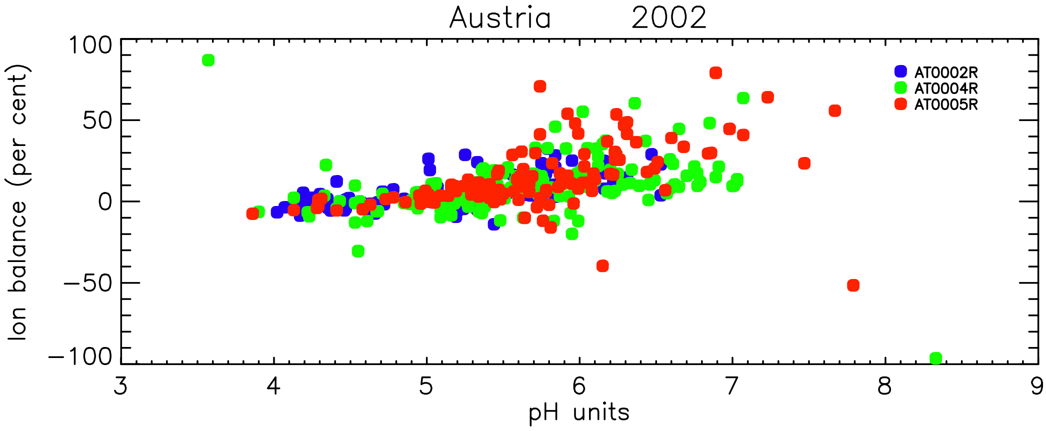
1) Refer to days with monitoring data
2) Renovation at the station

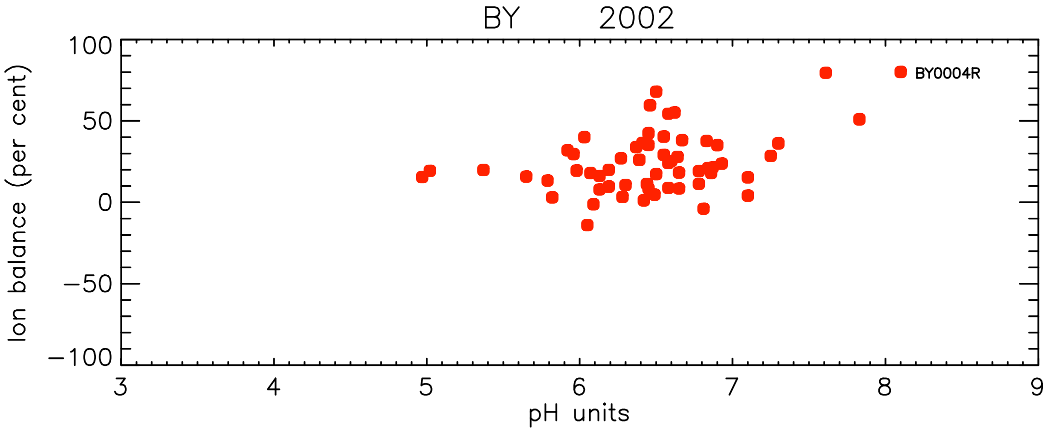
*Table A2.7: Data capture for POPs in 2002, in per cent.*

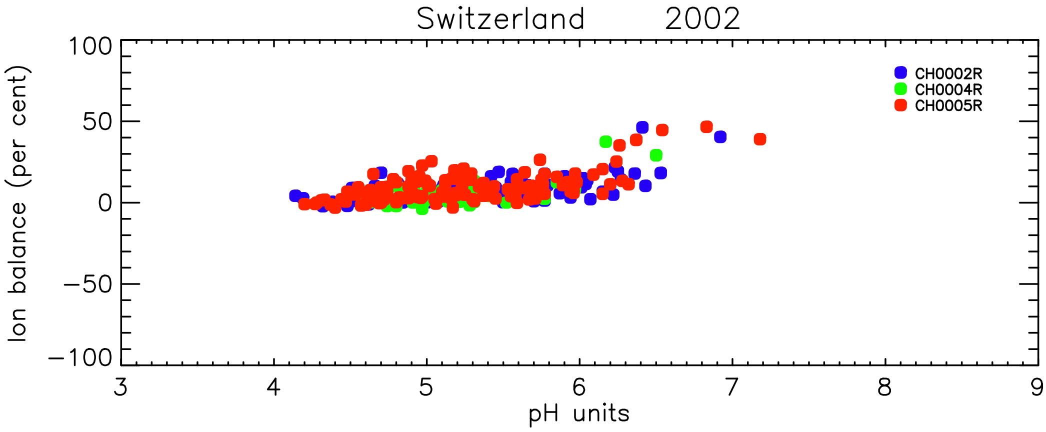
| | air (in %) | total dep (in %) | num samples | sampl frequenzy | precip (in %) |
|---|---|---|---|---|---|
| BE0004R | | | | | 100 |
| CZ0003R | 14 | | 52 | 1 day a week | |
| DE0001R | | | | | 100 |
| DE0009R | | | | | 85 |
| FI0096R | 23 | 23 | 12 | 1 week a month | |
| IE0002R | | | | | 70 |
| IS0091R | 100 | | 25 | biweekly | 100 |
| LT0015 | 100 | | 25 | monthly | |
| NL0091R | | | | | 100 |
| NO0042G | 32 | | 57 | 48h a week | |
| NO0099R | 14 | | 52 | 24h a week | 100 |
| SE0012R | 22 | 22 | 12 | 1 week a month | |
| SE0014R | 96 | 98 | 51 | weekly | |

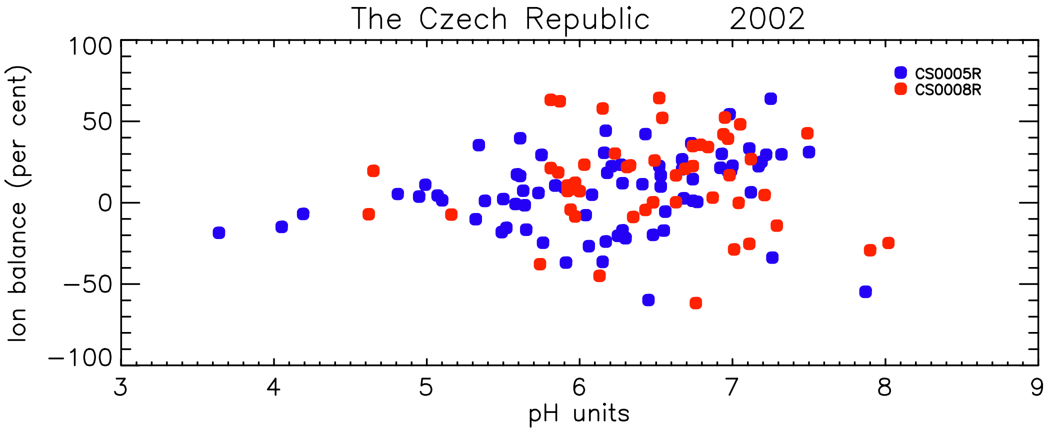
# Annex 3

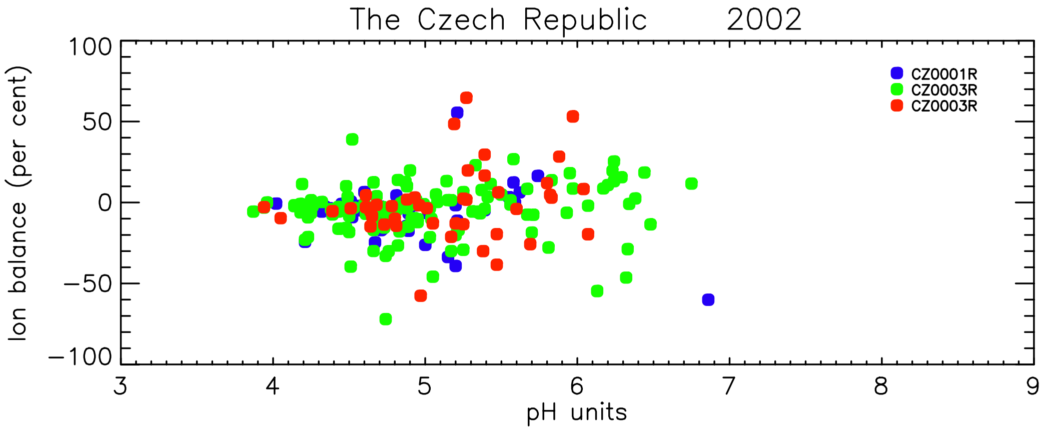
# Ion balances in precipitation samples 2002

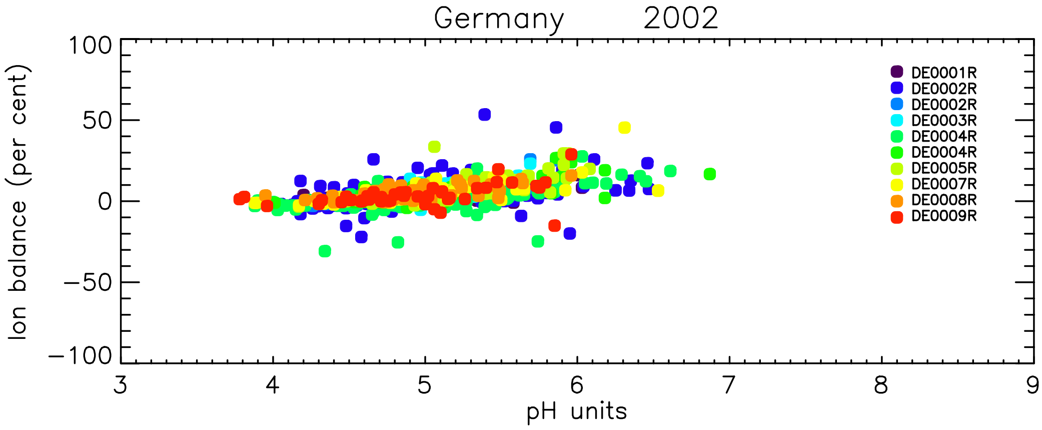

Austria 2002
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units
AT0002R
AT0004R
AT0005R

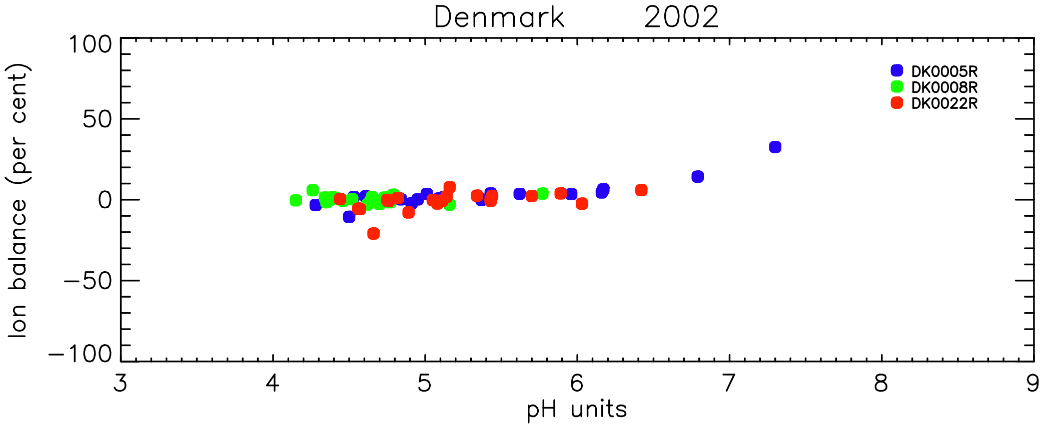

BY 2002
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units
BY0004R

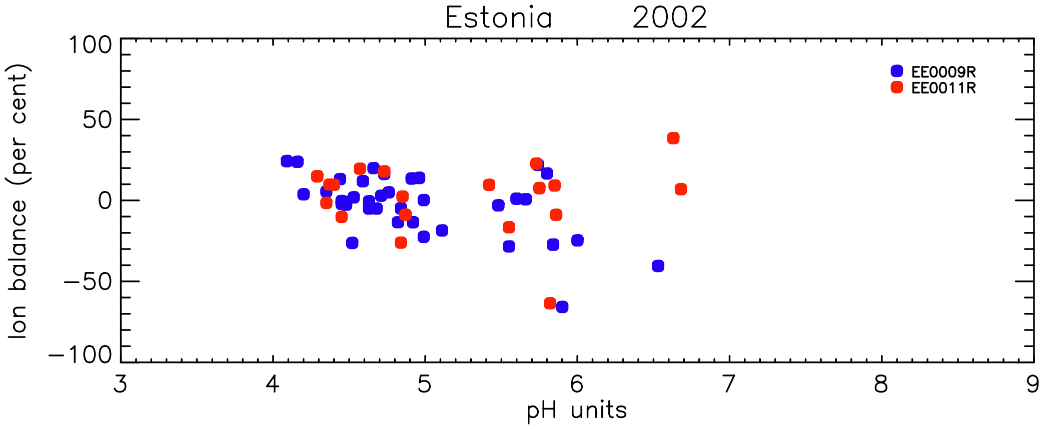

Switzerland 2002
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units
CH0002R
CH0004R
CH0005R

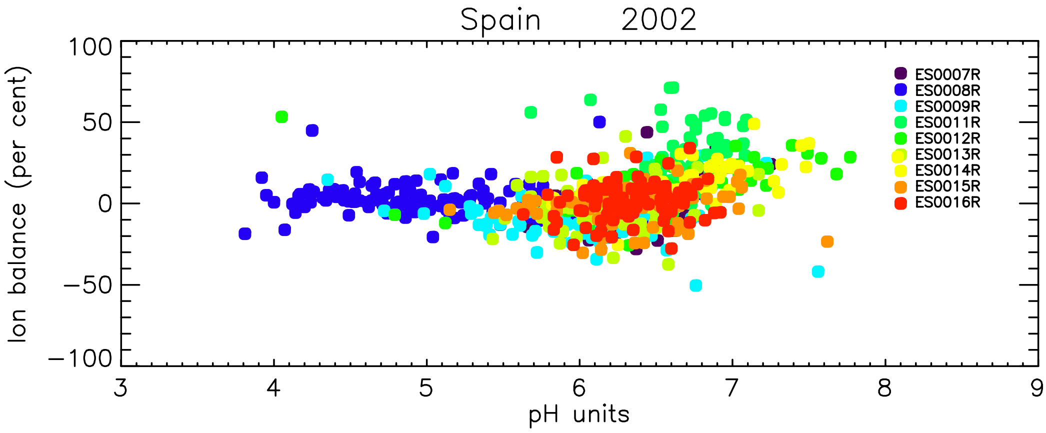

The Czech Republic 2002
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units
CS0005R
CS0008R

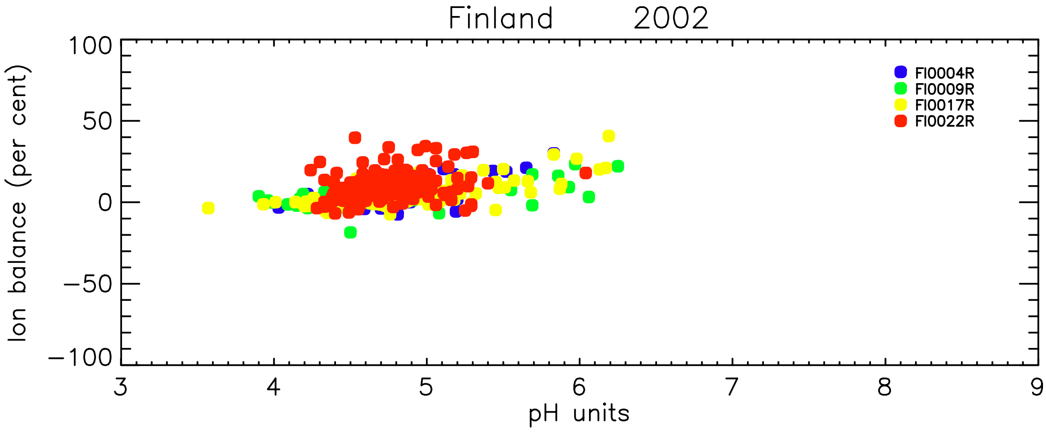

The Czech Republic 2002

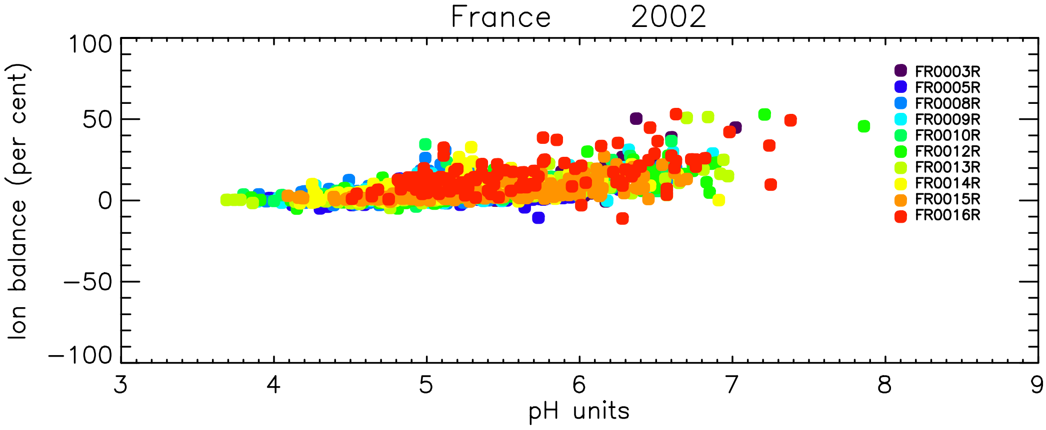

Germany 2002

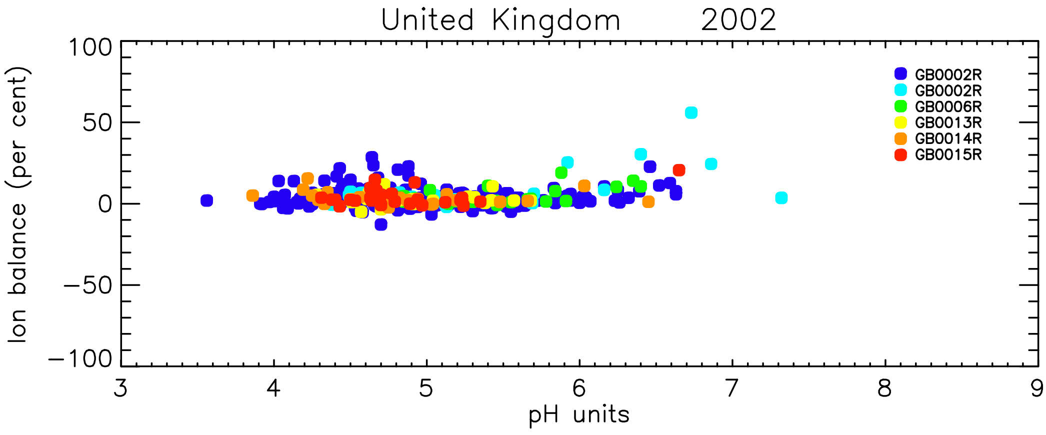

Denmark 2002

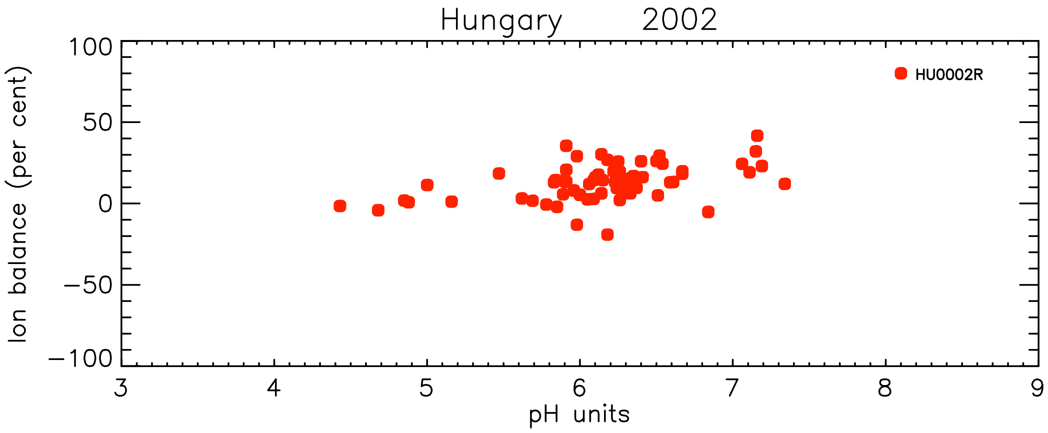

Estonia 2002

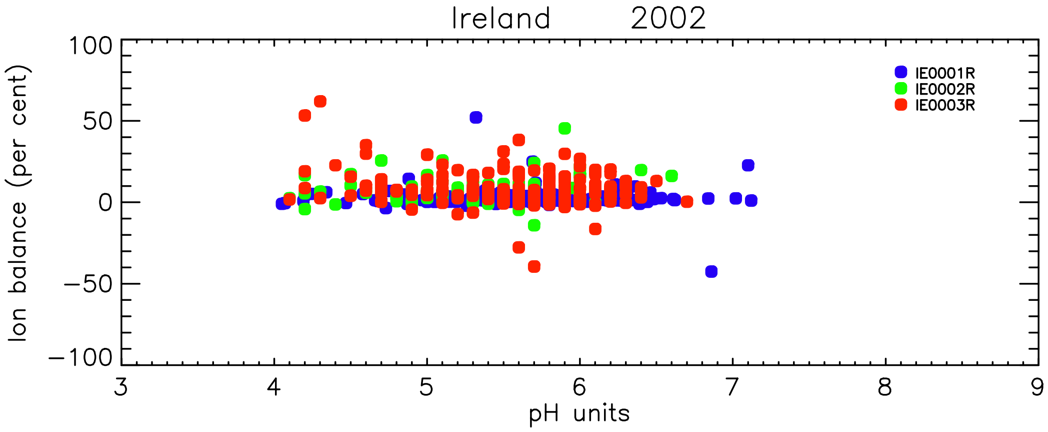

Spain 2002

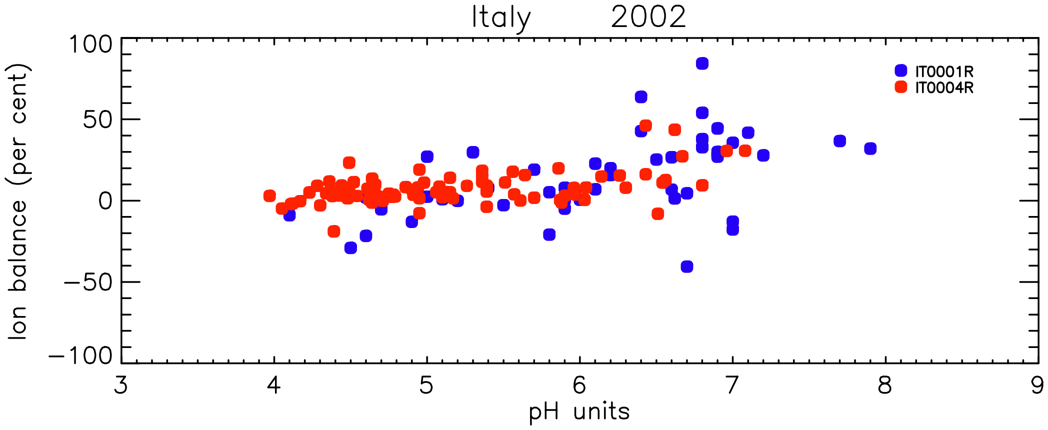

Finland 2002

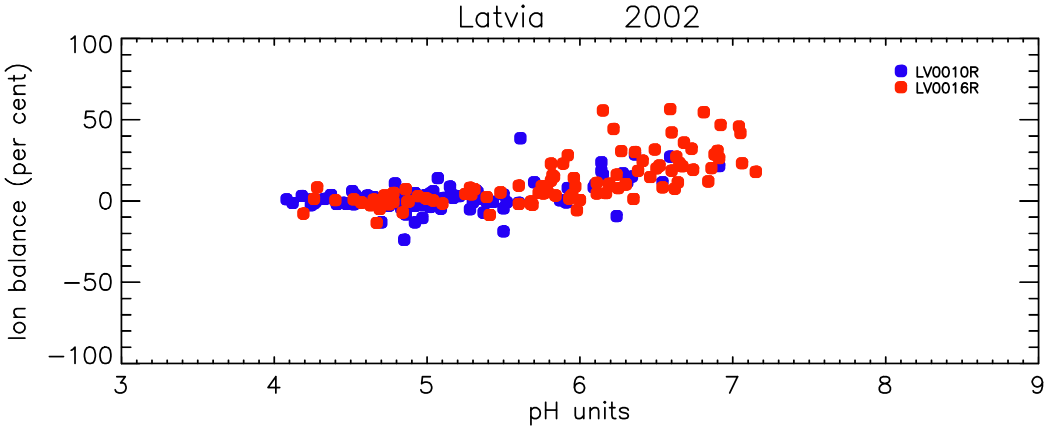

France 2002

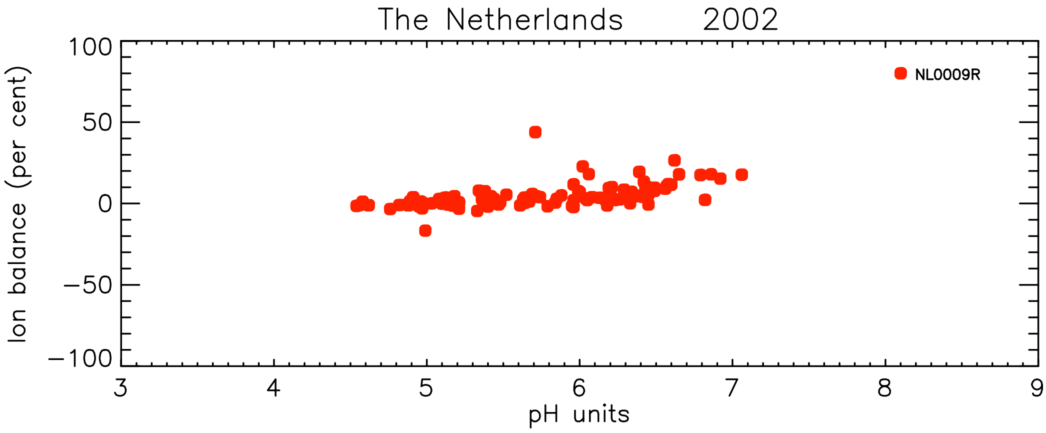

United Kingdom 2002

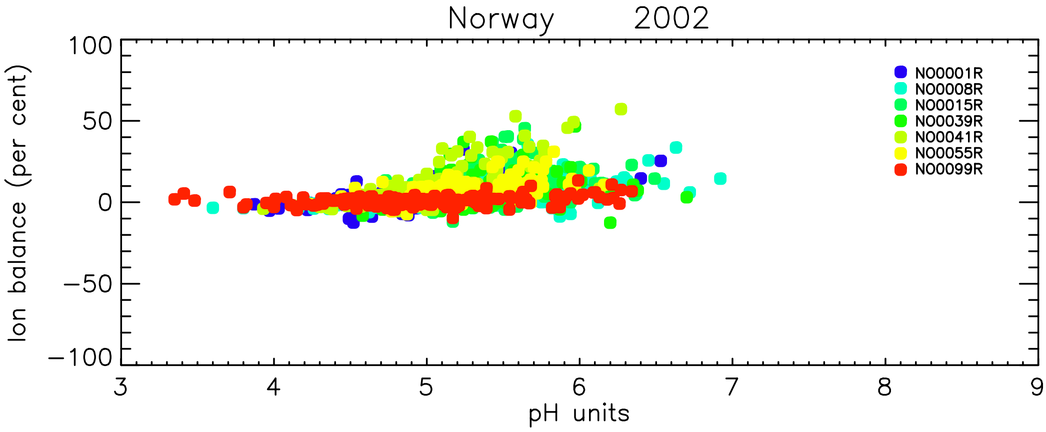

Hungary 2002
HU0002R
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units

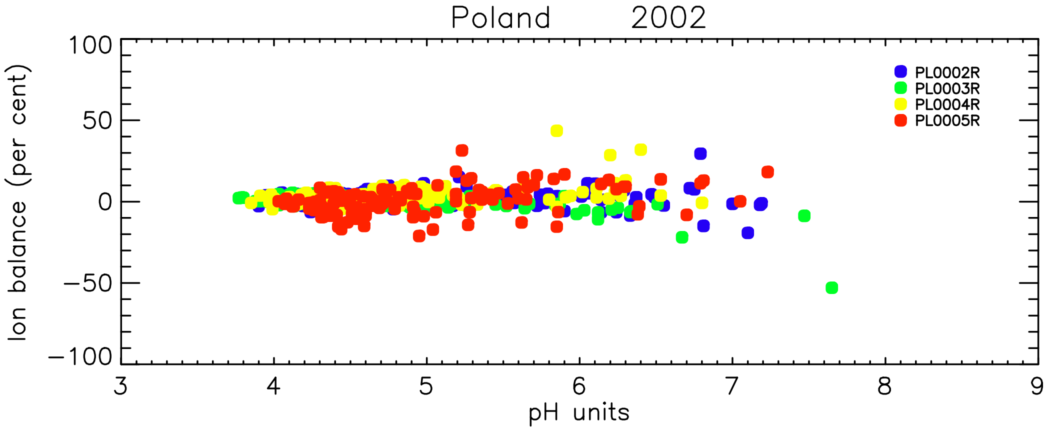

Ireland 2002
IE0001R
IE0002R
IE0003R
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units

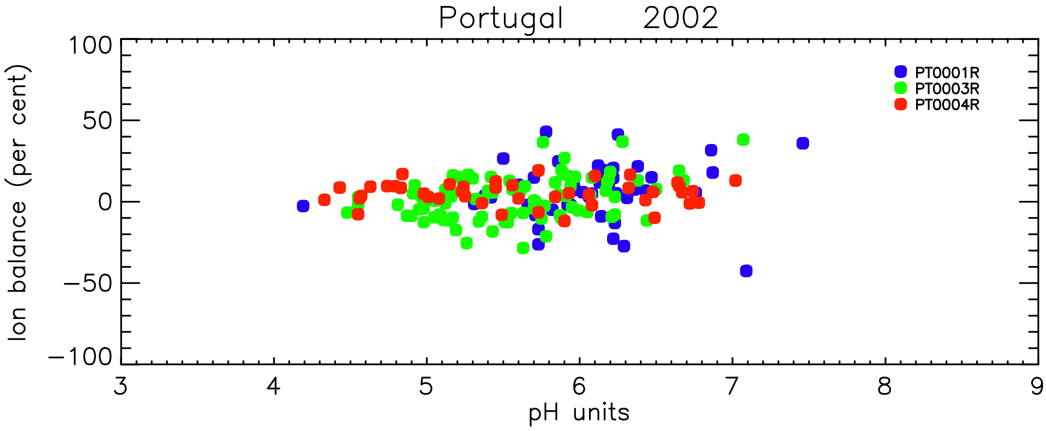

Italy 2002
IT0001R
IT0004R
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units

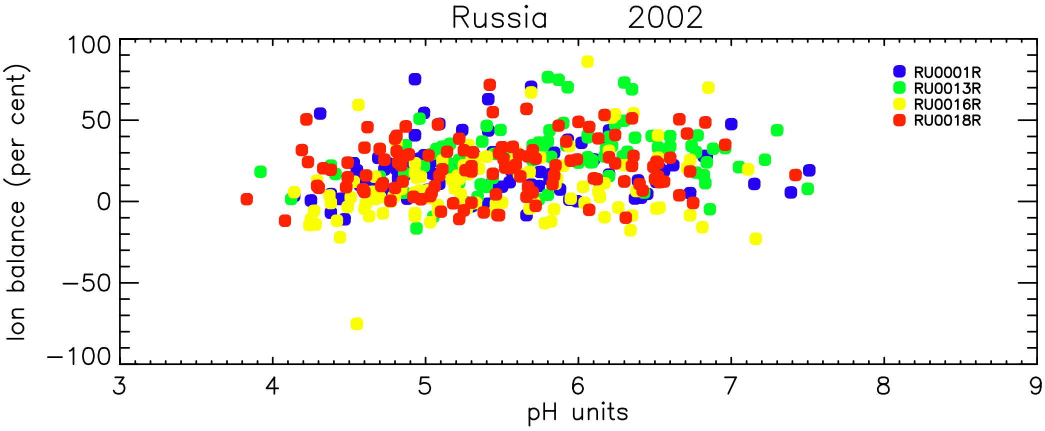

Latvia 2002
LV0010R
LV0016R
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units

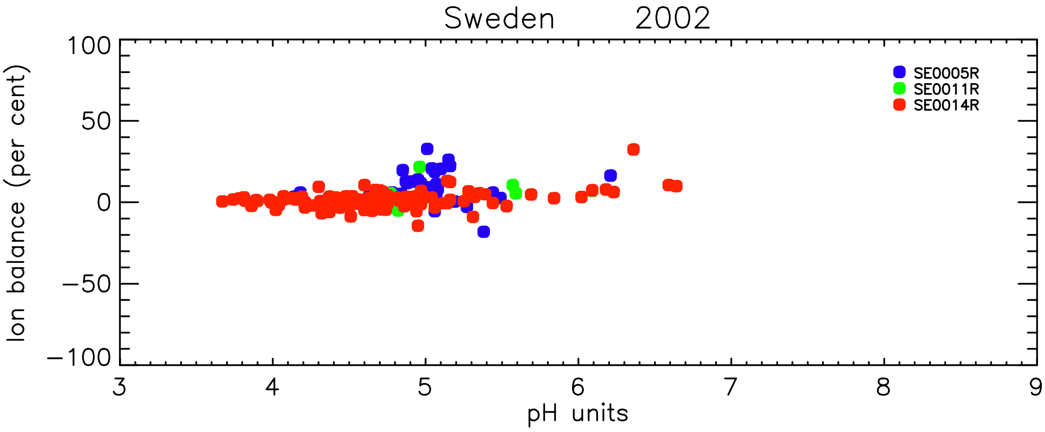

The Netherlands 2002
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units
NL0009R

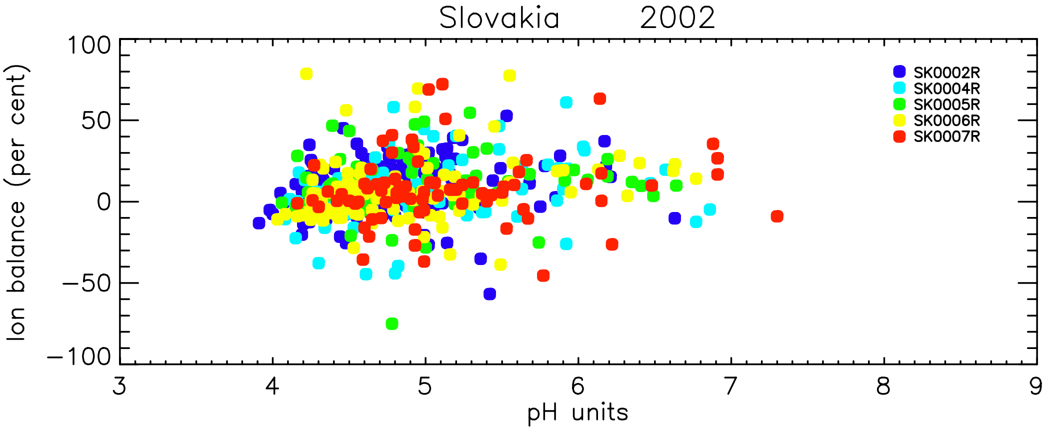

Norway 2002
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units
NO0001R
NO0008R
NO0015R
NO0039R
NO0041R
NO0055R
NO0099R

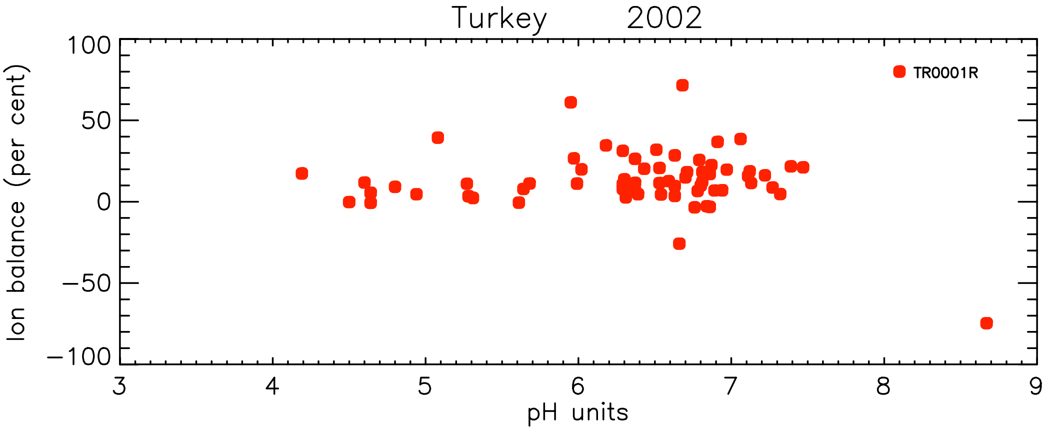

Poland 2002
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units
PL0002R
PL0003R
PL0004R
PL0005R


Portugal 2002
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units
PT0001R
PT0003R
PT0004R


Russia 2002
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units
RU0001R
RU0013R
RU0016R
RU0018R


Sweden 2002
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units
SE0005R
SE0011R
SE0014R


Slovakia 2002
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units
SK0002R
SK0004R
SK0005R
SK0006R
SK0007R


Turkey 2002
Ion balance (per cent)
100
50
0
−50
−100
3
4
5
6
7
8
9
pH units
TR0001R

# Annex 4

# Detection limits and precision

*Table A4.1: Detection limits and precision of ozone.*

| Country | Precision | Detection limit | Instrument |
|---|---|---|---|
| Austria AT02,04 | 1 ppb | 0.4 ppb | Horiba APOA 350E |
| AT05 | | 0.5 ppb | Horiba APOA 360 |
| Belgium | 1 ppb | 1 ppb | O341M Ozone Analyzer |
| | | 0.5 ppb | 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 | 2 µg/m$^3$ | 2 µg/m$^3$ | Thermo Environmental Instruments, TEI 49 C |
| FI09 | | | Dasibi Environmental corp., DAS 1008 PC |
| FI17 | | | Environnement SA, Env. O3 41 M |
| FI22 | | | Dasibi Environmental corp., DAS 1008 AH |
| France FR08,09,12,13,14,15,16 | 2 µg/m$^3$ | 2 µg/m$^3$ | Environnement SA, O341M |
| FR10 | | | SERES, OZ2000 |
| 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$^3$ | |
| Norway* | 2 µg/m$^3$ | 2 µg/m$^3$ | API Model 400 |
| Poland | 2 µg or 1%, whichever is greater | 2 µg/m$^3$ | Monitor Labs Inc. ML-9810 |
| PL05 | RSD 1.8% | 1 ppb | 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 (at SK02, 04, 06, 07) |
| Slovenia*, SI08,32 | | | Thermo Environmental Model 49 C |
| SI31,33 | | | Monitor Labs, Model 8810 |
| Spain | 2% | 1 ppb | MCV, S.A. Model 48 AUV |
| | 2 µg/m$^3$ | 2 µg/m$^3$ | MCV, S.A. Model 0341 M |
| Sweden, SE11,12,14 | 1 ppb | 1 ppb | Monitor Labs, ML 9810 (ML 9810 B at SE 12) |
| SE32 | 1 ppb | 1 ppb | Thermo Environmental Instrument, Model 49C |
| SE13,35,39 | 1 ppb | 1 ppb | Monitor Labs, ML 8810 |
| Switzerland, CH02,04,05 | RSD: 2% | 1 ppb | Thermo Environmental Instruments TEI 49C |
| CH03 | RSD: 3% | 1 ppb | Monitor Labs 9810 / from 15.03.04 TEI 49C |
| UK, all sites except: | 2 ppb | | Monitor Labs, ML 8810 |
| GB32 | | | TECO, TE49 |
| GB43 | | | Ambirack |
| GB44 | | | API Model 400 |

*Data from EE, FR, HU, NL, NO and SI are taken from earlier years

## *Table A4.2: Detection limits and precision of sulphur dioxide.*

| Country | Measurements | | Laboratory | |
|---|---|---|---|---|
| | **Precision** | **Detection limit; µg S/m3** | **Precision** | **Detection limit** |
| Austria[1] | 0.7 ppb | 0.1 ppb | | |
| Czech Republic | CoV: 26.4%<br>M.MAD : 0.308 µg $SO_2$/$m^3$ | 0.05 | S: RSD : 0.3% | 0.013 mg $SO_4^{2}$/l |
| Denmark | M.MAD: 0.02; CoV: 5 % | DK03: 0.02; DK05, DK08: 0.01 | M.MAD: 0.01 µg S/$m^3$; CoV: 3% | 0.02 µg S/$m^3$ |
| Estonia* | | 0.48 | | |
| Finland | | 0.04 | M.MAD: 0.003 µg S/$m^3$ CoV: 1.0% | 0.01 µg S/$m^3$ |
| France | | | at 0.01<c<0.1 mg S/l: RSD = 8-12%<br>at 0.1<c<0.5 mg S/l: RSD = 1-3% | 0.1 mg S/L |
| Germany | M.MAD: < 0.02 | | | 0.01 µg/$m^3$ |
| Hungary | | 2.20 | | 2.49 µg S/$m^3$ |
| Ireland | | | | 0.05 µgS/$m^3$ |
| Italy (IT01) | RSD: 7.0% at 2.0 µg S/$m^3$ | 0.1 | | 0.002 mg S/l |
| Italy, EU (IT04) [2] | 0.5 ppb | 1 ppb | | |
| Latvia | | 0.11 | RSD: 2.3% | 0.02 mg S/l |
| Lithuania | | 0.021 mg S/$m^3$ | at c<0.7 mg S/$m^3$: 2.4% RSD;<br>at c>0.7 mgS/m3: 0.5-1.0 % RSD | 0.017 mg S/l |
| Netherlands* | 1% | 3 | | |
| Norway* | M.MAD 0.04; CoV: 12% | 0.03 | | 0.01 µg S/m3 |
| Poland | | 0.2 | | 0.04 mg S/l |
| PL05 | M.MAD = 0.13; CoV= 11.2% | 0.1 | RSD: 0.73% | 0.5 mg S/l |
| Russia* | RU01: M.MAD 0.01; CoV= 3%<br>RU18: M.MAD 0.01; CoV= 12% | | | |
| Serbia and Montenegro* | | | | 0.005 mg $SO_2$/$m^3$ |
| Slovakia | | | 1.25% | 0.1 µg S/filter |
| Slovenia | | 0.097 | | 0.013 µg S/ml |
| Spain | 1% or 0.2 ppb | 0.06 ppb | | |
| Sweden | uncertainty (95% conf. int): 13% | 0.02 | R: 2% | 0.01 µg S/$m^3$ |
| Switzerland CH01 | RSD: 4% | 0.03 | | |
| [3]CH02, CH04, CH05 | RSD: 5% | 0.2 ppb | | |
| Turkey | | 0.11 | M.MAD: 0.015; CoV: 2.8% | 0.016 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: TEI 43C TL; CH05: TEI 43BS / from 21.08.02 TEI 43CTL

*Data from EE, NL, NO, RU, TR and YU are taken from earlier years

*Table A4.3: Detection limits and precision of nitrogen dioxide.*

| Country | Measurements | | Laboratory | |
|---|---|---|---|---|
| | **Precision** | **Detection limit, µg N/m$^3$** | **Precision** | **Detection limit** |
| Austria[1] | 1 ppb | 0.5 ppb | | |
| Belgium (BE01) | 0.6 µg N/m$^3$ | 0.3 | | |
| (BE02) | 1% | 0.5 ppb | | |
| Czech Republic | RSD: 12% | 0.07 | RSD: 3.4% | 0.001 mg NO$_2$/l |
| Denmark | | DK08: 0.07 | M.MAD: 0.01 µg N/m$^3$; CoV: 1.04% | 0.01 µg N/m$^3$ |
| Estonia* | | 0.07 | | |
| Finland** | 0.3 µg N/m$^3$ | 0.3 | | |
| Hungary | | 0.12 | M.MAD: 0.001; CoV: 6.846% | |
| Ireland | | | | 0.1 µg N/m$^3$ |
| Italy (IT01) | 0.6 µg N/m$^3$ | 0.3 | | |
| Italy, EU (IT04)[2] | 0.5 ppb | 0.5 ppb | | |
| Latvia | | 0.16 | RSD: 2.8% | 0.005 mg N/l |
| Lithuania | | 0.08 | at c<2.0 µg N/m$^3$: 3.75-6.9% RSD | 0.03 mg N/l |
| Netherlands* | 1% | 2 | | |
| Norway* | M.MAD: 0.13; CoV: 5% | 0.03 | RSD: 7.0% at c=0.03 mgN/l<br>RSD: 4.6% at c=0.17 mgN/l<br>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<br>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 | | | | 0.003 mg NO$_2$/m$^3$ |
| Slovakia | | | 3.51% | 0.003 mg N/l |
| Spain | 0.05 ppb | 0.05 ppb | | |
| Sweden | uncertainty (95% conf.int.): 6% | 0.3 | R: 2% | 0.02 mg N/l |
| Switzerland[3] | | | | |
| CH04, CH05 | RSD: 5% | 0.5 ppb | | |
| CH02, CH03 | RSD: 3% | 0.5 ppb | | |
| CH01 | | 0.05 ppb | | |
| Turkey | M.MAD: 0.078; CoV: 8% | 0.39 | M.MAD: 0.084; CoV: 9.7% | 0.02 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

* Data from EE, NL, NO, TR and YU are taken from earlier years.
** FI: Monitor, Thermo Environment 42TCL

*Table A4.4:Detection limits and precision of sulphate in air.*

| Country | Measurements | | Laboratory | |
|---|---|---|---|---|
| | **Precision** | **Detection limit, µg S/m$^3$** | **Precision** | **Detection limit** |
| Czech Republic | RSD: 18.5% | | | S: 2.6 ng/m$^3$ |
| Denmark | M.MAD: 0.05 µg S/m$^3$<br>CoV: 6.5% | DK03, 05, 08: 0.03 | | |
| Estonia* | | 0.53 | | |
| Finland | | 0.04 | M.MAD: 0.002 µg S/m$^3$;<br>CoV: 0.5% | 0.01 µg S/m$^3$ |
| France | | | at 0.01<c<0.1 mg S/l: RSD = 8-12%<br>at 0.1<c<0.5 mg S/l: RSD = 1-3% | 0.2 µg S/filter |
| Germany | M.MAD < 0.02 µg/m$^3$ | | | 0.01 µg/m$^3$ |
| Hungary | | 0.10 | | <0.01 µg S/m$^3$ |
| Ireland | | | | 0.05 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 | | 0.11 | RSD: 2.3% | 0.02 mg S/l |
| Lithuania | | 0.024 | at c<1.0 µgS/m$^3$: 7.2% RSD;<br>at c>1.0 mgS/m$^3$: 1.0% RSD | 0.024 mgS/l |
| Netherlands* | | | SD: 0.07 nmol/filter | 0.7 µmol/filter |
| Norway* | M.MAD 0.009 µg S/m$^3$<br>at c<2.4 µg S/m$^3$ | 0.01 | | |
| Poland | | 0.18 | | 0.04 mg S/l |
| PL05 | M.MAD: 0.08;<br>CoV=10.4% | 0.1 | RSD: 4% | 0.5 mg S/l |
| Russia | RU01: M.MAD 0.01; CoV=2.5%<br>RU16: M.MAD 0.02; CoV=7.5%<br>RU18: M.MAD 0.01; CoV=2.3% | | CoV: 1.75 µg/m$^3$ | 0.02 mg/l |
| Slovakia | | | 2.12% | 0.03 mg S/l |
| Slovenia | | | | 0.013 µg S/ml |
| Spain | | | | 0.01 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 | | 0.02 | M.MAD: 0.033; CoV: 4.4% | 0.014 mg S/l* |
| UK | | | RSD: 2% | 0.01 mg S/l |

*Data from EE, NL, NO and TR are taken from earlier years.

*Table A4.5: Detection limits and precision of nitrate and nitric acid in air.*

| Country | Measurements |  | Laboratory |  |
|---|---|---|---|---|
|  | **Precision** | **Detection limit, µg N/m3** | **Precision** | **Detection limit** |
| Czech Republic | M.MAD: 0.706; CoV 29.1% | 0.1 | $NO_3$: 2% | $NO_3$: 0.02 mg N/l |
| Denmark | M.MAD: 0.04 µg N/m$^3$<br>CoV: 7,3% | DK05,08: 0.05<br>DK03: 0.04 | M.MAD: 0,01 µg N/m$^3$<br>CoV: 1.0% | 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 |  | $HNO_3$: 0.06;<br>$NO_3$: 0.07 |  | $HNO_3$: <0.01;<br>$NO_3$: 0.09 |
| Italy (IT01) | $HNO_3$: RSD: 6.2% at 0.25 µg N/m$^3$<br>$NO_3$: RSD: 1.5% at 1 µg N/m$^3$ | $HNO_3$: 0.01<br>$NO_3$: 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: 2.6% | 0.011 mg N/l |
| Lithuania |  | 0.014 | c=0.3-1.0 µg N/m$^3$; 0.5-1.2% RSD | 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 | $NO_3$: RU18: M.MAD 0.01; CoV=4.9% |  |  | 0.01 mg/l |
| Slovakia |  |  | $HNO_3$: 1.71%;<br>$NO_3$: 1.36% | $HNO_3$: 0.01 mg N/l;<br>$NO_3$: 0.04 mg N/l |
| Slovenia |  | $NO_3$: 0.011 µg N/m$^3$ |  | 0.006 µg N/ml |
| Spain |  |  |  | 0.06 µg N/m$^3$ |
| Sweden | uncertainty (95% conf. int.): 12% | $NO_3$-N: 0.005;<br>$HNO_3$-N: 0.01 | R: 2% | $NO_3$-N: 0.005;<br>$HNO_3$-N: 0.01 mg N/l |
| Switzerland | RSD: 8% | 0.04 |  |  |
| Turkey |  | $NO_3$: 0.03<br>$HNO_3$: 0.07 | $NO_3$: M.MAD: 0.007; CoV: 8.2%<br>$HNO_3$: M.MAD: 0.008; CoV: 10.8% | 0.03 mg N/l* |

*Data from NO and TR are taken from earlier years.

*Table A4.6: Detection limits and precision of ammonia and ammonium in air.*

| | **Measurements** | | **Laboratory** | |
|---|---|---|---|---|
| **Country** | **Precision** | **Detection limit, µg N/m$^3$** | **Precision** | **Detection limit** |
| Czech Republic | $NH_4$: CoV: 27.2%<br>M.MAD: 0.441 $\mu$g/m$^3$ | 0.17 | N: RSD: 0.6% | 0.02 mg N/l |
| Denmark | M.MAD: 0.13 $\mu$g N/m$^3$<br>CoV: 6.6% | DK08: 0.04<br>DK03,05: 0.05 | $NH_4$: M.MAD: 0.02 $\mu$g N/m$^3$; CoV: 1.3%<br>$NH_3$: M.MAD: 0.01 $\mu$g N/m$^3$; CoV: 1.0% | $NH_4^+$: 0.01 $\mu$g N/m$^3$<br>$NH_3$: 0.02 $\mu$g N/m$^3$ |
| Finland | | 0.04 | M.MAD: 0.004 $\mu$g N/m$^3$; CoV: 1.5% | 0.01 $\mu$g/m$^3$ |
| Germany | M.MAD < 0.02 µg/m$^3$ | | | 0.01 µg/m$^3$ |
| Hungary | | $NH_3$: 0.72;<br>$NH_4$: 0.33 | | |
| Italy (IT01) | $NH_3$: RSD: 3.9% at 1 µg N/m$^3$<br>$NH_4$: RSD: 4.2% at 2 µg N/m$^3$ | 0.1 | | |
| Italy, EU (IT04) | | 0.17 | CoV: 2.4% | 0.074 mg N/l |
| Latvia | | $NH_3$: 0.43,<br>$NH_4$: 2.58 | RSD: $NH_4$: 4%; $NH_3$: 2% | $NH_4$; 0.03 mg N/l<br>$NH_3$: 0.02 mg N/l |
| Lithuania | | 0.027 | at c<1.0 $\mu$g N/m$^3$: 4.0% RSD<br>at c>1.0 mg N/m$^3$: 0.6-1.8% RSD | 0.04 mgN/l |
| Netherlands* | $NH_3$: RSD: <2% | $NH_3$: 0.12 | $NH_4$, SD: 0.0025 nmol/filter | $NH_4$: 0.4 µmol/filter |
| 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 0.01; CoV=4.5%<br>$NH_4$: RU16: M.MAD 0.01; CoV=3.5%<br>$NH_4$: RU18: M.MAD 0.01; CoV=2.1% | | $NH_4$: M.MAD: 0.01 $\mu$g/m$^3$<br>CoV: 3.39 $\mu$g/m$^3$ | $NH_4$: 0.02 mg/l |
| Slovenia | | $NH_4$: 0.014 $\mu$g N/m$^3$;<br>$NH_3$: 0.032 $\mu$g N/m$^3$ | | 0.009 $\mu$g N/m$^3$ |
| Spain | | 0.03 | 2.68 % | 0.03 $\mu$g N/m$^3$ |
| Sweden | uncertainty (95% conf. int.): 13% | $NH_3$-N: 0.03;<br>$NH_4$-N: 0.02 | R: 3% | $NH_4$: 0.017;<br>$NH_3$: 0.03<br>(N mg/l) |
| Switzerland | RSD: 7% | 0.1 | | |
| Turkey | | $NH_4$: 0.04<br>$NH_3$: 0.10 | $NH_4$: M.MAD: 0.026; CoV: 5.2%<br>$NH_3$: M.MAD: 0.034; CoV: 14% | $NH_4$: 0.04*<br>$NH_3$: 0.05* |

* Data from NL, NO and TR are taken from earlier years.

*Table A4.7: 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%<br>M.MAD: 0.153 mg/l | $SO_4$: 0.294 | RSD: 1.4% | 0.02 |
| Denmark | | | M.MAD: 0.01 mg S/l;<br>CoV: 1.6% | 0.04 |
| Estonia* | | 0.347 | | 0.221 |
| Finland | | | M.MAD: 0.006 mg S/l;<br>CoV: 2.0% | 0.02 |
| France | | | at c<0.2 mg S/l: RSD = 5-10%<br>at 0.2<c<0.5 mg S/l: RSD = 3-5%<br>at 0.5<c<5 mg S/l: RSD = 1-3% | 0.02 |
| Germany | | | | 0.01 |
| Hungary | | | M.MAD=0.019; CoV=1.25% | ca. 0.03* |
| Italy (IT01) | RSD: 1.1% at 1 mg S/l | 0.01 | RSD: 0.8% at 0.5 mg S/l<br>RSD: 1.6% at 0.05 mg S/l | 0.002 |
| Italy, EU (IT04) | | | CoV: 1.3% | 0.004 |
| Latvia | | | CoV: 3.3% | 0.011 |
| Lithuania | | | c<0.5 mgS/l: 3.4% RSD<br>c>0.5 mgS/l: 1.0% RSD | 0.02 |
| Netherlands* | | | SD: 0.2 | 1 µmol/l |
| Norway* | M.MAD: 0.03, CoV: 7% | | SD: 0.041 at c=2.23 mgS/l<br>SD: 0.019 at c=0.85 mgS/l | 0.01 |
| Poland | | | RSD: 1% at 6.7 mg S/l<br>RSD: 1.8% at 0.67 mg S/l<br>RSD: 2% at 0.33 mgS/l | 0.03 |
| PL05 | M.MAD: 0.01; CoV: 1.8% | 0.1 | M.MAD: 0.04; CoV: 7.3% | 0.1 |
| Portugal | | | 0.75% | 0.05 |
| Russia | | | CoV: 0.78% | 0.02 |
| Serbia and Montenegro* | | | | 0.16 |
| Slovakia | | | 3.13% | 0.01 |
| Spain | | | CoV: 1.4 % | 0.07 |
| Sweden Water | uncertainty (95% conf. int.): 5% (0.004-1 mg/l)<br>uncertainty (95% conf. int.): 1% (1-28 mg/l) | 0.004 | R: 2% | 0.004 |
| Switzerland | M.MAD: 0.01 mg S/l | | | 0.01 |
| Turkey | | | M.MAD: 0.023; CoV: 1.7% | 0.040* |
| UK | | | 1% | 0.01 |

* Data from EE, HU, NL, NO, TR and YU are taken from earlier years.

## *Table A4.8: 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%<br>M.MAD: 0.155 mg/l | 0.403 | RSD: 0.9% | 0.03 |
| Denmark | | | M.MAD: 0.02 mg N/l;<br>CoV: 2.6% | 0.02 |
| Estonia* | | 0.302 | | 0.167 |
| Finland | | | M.MAD: 0.003 mg N/l;<br>CoV: 1.5% | 0.01 |
| France | | | at c<0.2 mg N/l: RSD = 5-10%<br>at 0.2<c<0.5 mg N/l: RSD = 3-5%<br>at 0.5<c<5 mg N/l: RSD = 1-3% | 0.02 |
| Germany | | | | 0.01 |
| Hungary | | | M.MAD=0.003; CoV=0.25% | ca. 0.03* |
| Italy (IT01) | RSD: 1.4% at 1 mg N/l | 0.01 | RSD: 0.7% at 0.5 mg N/l<br>RSD: 1.5% at 0.05 mg N/l | 0.002 |
| Italy, EU (IT04) | | | CoV: 1.2% | 0.011 |
| Latvia | | | CoV: 0.2% | 0.001 |
| Lithuania | | | c<0.5 mg N/l: 5.1% RSD<br>c>0.5 mg N/l: 1.8% RSD | 0.013 |
| Netherlands* | | | SD: 0.5 | 2 $\mu$mol/l |
| Norway* | M.MAD: 0.03, CoV: 8% | | SD: 0.023 at c=0.86 mg N/ml<br>SD: 0.016 at c=0.39 mg N/ml | 0.01 |
| Poland | | | RSD: 1.7% at 4.5 mg N/l<br>RSD: 1.9% at 0.45 mg N/l<br>RSD: 2.0% at 0.23 mg N/l | 0.015 |
| PL05 | M.MAD: 0.03;<br>CoV: 7.1% | 0.1 | M.MAD: 0.02; CoV: 5.2% | 0.1 |
| Portugal | | | 0.25% | 0.02 |
| Russia | | | | 0.01 |
| Serbia and Montenegro* | | | | 0.02 |
| Slovakia | | | 0.59% | 0.01 |
| Spain | | | CoV: 1.2% | 0.08 |
| Sweden Water | uncertainty (95% conf. int.): 5% (0.002-1 mg/l)<br>uncertainty (95% conf. int.): 1% (1-6 mg/l) | 0.002 | R: 2% | 0.002 |
| Switzerland | M.MAD: 0.01 mg N/l | | | 0.01 |
| Turkey | | | M.MAD: 0.005; CoV: 1.1% | 0.030* |
| UK | | | 1% | 0.01 |

* Data from EE, HU, NL, NO, TR and YU are taken from earlier years.

*Table A4.9: 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%<br>M.MAD: 0.169 mg/l | 0.061 | RSD: 0.6% | 0.02 |
| Denmark | | | M.MAD: 0.01 mg N/l;<br>CoV: 1.7% | 0.01 |
| Estonia* | | 0.064 | | 0.077 |
| Finland | | | M.MAD: 0.001 mg N/l;<br>CoV: 0.5% | 0.002 |
| France | | | at c<0.2 mg N/l: RSD = 5-10%<br>at 0.2<c<0.5 mg N/l: RSD = 3-5%<br>at 0.5<c<5 mg N/l: RSD = 1-3% | 0.03 |
| Germany | | | | 0.01 |
| Hungary | | | M.MAD=0.002; CoV=0.61% | ca. 0.04* |
| Italy (IT01) | RSD: 0.8% at 0.5 mg N/l | 0.005 | RSD: 0.5% at 0.5 mg N/l<br>RSD: 1.8% at 0.05 mg N/l | 0.001 |
| Italy, EU (IT04) | | | CoV: 2.4% | 0.014 |
| Latvia | | | CoV: 2.9% | 0.015 |
| Lithuania | | | c<1.0 mg N/l: 3.3% RSD<br>c>1.0 mg N/l: 1.0% RSD | 0.04 |
| Netherlands* | | | SD: 0.2 | 1 μmol/l |
| Norway* | M.MAD: 0.06, CoV: 20% | | SD: 0.016 at c=0.64 mg/l<br>SD: 0.013 at c=0.32 mgN/l | 0.01 |
| Poland | | | RSD: 2.7% at 1 mg/l<br>RSD: 4.6% at 0.1 mg/l | 0.03 |
| PL05 | M.MAD: 0.05; CoV: 8.9% | 0.01 | M.MAD: 0.02; CoV: 3.4% | 0.01 |
| Portugal | | | 0.79% | 0.04 |
| Russia | | | CoV: 2.24%; M.MAD: 0.02 | 0.02 |
| Serbia and Montenegro* | | | | 0.03 |
| Slovakia | | | 1.97% | 0.015 |
| Spain | | | CoV: 2.7% | 0.08 |
| Sweden Water | uncertainty (95% conf. int.): 5% (0.01-1 mg/l)<br>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: 0.007; CoV: 1.6% | 0.038* |
| UK | | | 1% | 0.01 |

* Data from EE, HU, NL, NO, TR and YU are taken from earlier years.

*Table A4.10: Detection limits and precision of calcium in precipitation.*

| | **Measurements** | | **Laboratory** | |
|---|---|---|---|---|
| **Country** | **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%<br>M.MAD: 0.107 mg/l | 0.095 | RSD: 2.0% | 0.014 |
| Denmark | | | M.MAD: 0.01 mg/l;<br>CoV: 3.9% | 0.13 |
| Estonia* | | 0.407 | | 0.382 |
| Finland | | | M.MAD: 0.001 mg/l;<br>CoV: 2.2% | 0.005 |
| France | | | at c<0.2 mg/l: RSD = 10-20%<br>at 0.2<c<0.5 mg/l: RSD = 5-10%<br>at 0.5<c<5 mg/l: RSD = 1-5% | 0.02 |
| Germany | | | | 0.01 |
| Hungary | | | M.MAD: 0.008; CoV: 3.83% | ca. 0.01* |
| Ireland | | | | 0.05 |
| Italy (IT01) | RSD: 1.8% at 1 mg Ca/l | 0.01 | RSD: 1.2% at 0.5 mg Ca/l<br>RSD: 3.6% at 0.05 mg Ca/l | 0.002 |
| Italy, EU (IT04) | | | CoV: 16% | 0.014 |
| Latvia | | | CoV: 4.5% | 0.02 |
| Lithuania | | | c<0.2mgCa/l: 5.5% RSD<br>c>0.2 mgCa/l: 1.5% RSD | 0.02 |
| Netherlands* | | | SD: 0.4 | 1.5 µmol/l |
| Norway* | M.MAD: 0.03; CoV: 59% | | SD: 0.010 at c=0.27 mg/l<br>SD: 0.006 at c=0.15 mg/l | 0.01 |
| Poland | | | RSD: 0.9% at 2 mg/l<br>RSD: 1.8% at 0.8 mg/l<br>RSD: 2.1% at 0.4 mg/l | 0.03 |
| PL05 | M.MAD: 0.005;<br>CoV: 1.4% | 0.02 | M.MAD: 0.030; CoV: 11.8% | 0.001 |
| Portugal | | | 1.31% | 0.06 |
| Russia | | | CoV: 5.88%; M.MAD: 0.03 | 0.05 |
| Serbia and Montenegro* | | | 81% | 0.005 |
| Slovakia | | | 0.91% | 0.03 |
| 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 | | | 0.05 |
| Turkey | | | M.MAD: 0.019; CoV: 1.6% | 0.032* |
| UK | | | 1% | 0.02 |

* Data from EE, HU, NL, NO, TR and YU are taken from earlier years.

*Table A4.11: 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%<br>M.MAD: 0.015 mg/l | 0.074 | RSD: 10.2% | 0.008 |
| Denmark | | | M.MAD: 0.01 mg/l;<br>CoV: 3.6% | 0.054 |
| Estonia* | | 0.095 | | 0.1 |
| Finland | | | M.MAD: 0.002 mg/l;<br>CoV: 3.5% | 0.006 |
| France | | | at c<0.2 mg/l: RSD = 10-20%<br>at 0.2<c<0.5 mg/l: RSD = 5-10%<br>at 0.5<c<5 mg/l: RSD = 1-5% | 0.02 |
| Germany | | | | 0.01 |
| Hungary | | | M.MAD: 0.002;<br>CoV: 2.22% | ca. 0.01* |
| Italy (IT01) | RSD: 1.4% at 1 mg K/l | 0.01 | RSD: 1.5% at 0.5 mg K/l<br>RSD: 3.0% at 0.05 mg K/l | 0.03 |
| Italy, EU (IT04) | | | CoV: 3.7% | 0.005 |
| Latvia | | | CoV: 2.3% | 0.043 |
| Lithuania | | | RSD: 8.1% at c<0.5 mg K/l | 0.02 |
| Netherlands* | | | SD: 0.2 | 1 µmol/l |
| Norway* | M.MAD: 0.03; CoV: 59% | | SD: 0.027; c=0.61 mg/l<br>SD: 0.015; c=0.20 mg/l | 0.01 |
| Poland | | | RSD: 1.0% at 0.5 mg/l<br>RSD: 2.9% at 0.1 mg/l<br>RSD: 2.4% at 0.05 mg/l | 0.02 |
| PL05 | M.MAD: 0.005;<br>CoV: 5.7% | 0.04 | M.MAD: 0.017;<br>CoV: 14.9% | 0.002 |
| Portugal | | | 1.69% | 0.077 |
| Russia | | | CoV: 5.20%; M.MAD: 0.02 | 0.03 |
| Serbia and Montenegro* | | | 98% | 0.015 |
| Slovakia | | | 2.13% | 0.03 |
| Spain | | | CoV: 18% | 0.05 |
| Sweden | uncertainty (95% conf. int.): 10% (0.08-1 mg/l)<br>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;<br>CoV: 2.6% | 0.019* |
| UK | | | 1% | 0.02 |

* Data from EE, HU, NL, NO, TR and YU are taken from earlier years.

*Table A4.12: 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%<br>M.MAD: 0.072 mg/l | 0.157 | RSD: 1.4% | 0.02 |
| Denmark | | | M.MAD: 0.08 mg/l;<br>CoV: 3.7% | 0.08 |
| Estonia* | | 0.463 | | 0.155 |
| Finland | | | M.MAD: 0.003 mg/l;<br>CoV: 1.4% | 0.01 |
| France | | | at c<0.2 mg/l: RSD = 10-20%<br>at 0.2<c<0.5 mg/l: RSD = 5-10%<br>at 0.5<c<5 mg/l: RSD = 1-5% | 0.05 |
| Germany | | | | 0.01 |
| Hungary | | | M.MAD: 0.032; CoV: 13.17% | ca. 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<br>RSD: 1.1% at 0.05 mg Cl/l | 0.001 |
| Italy, EU (IT04) | | | CoV: 2.1% | 0.009 |
| Latvia | | | CoV: 3.7% | 0.013 |
| Lithuania | | | c<0.5 mg Cl/l: 4.7% RSD<br>c>0.5 mg Cl/l: 2.3% RSD | 0.01 |
| Netherlands* | | | SD: 0.7 | 3 µmol/l |
| Norway* | M.MAD: 0.16, CoV: 22% | | SD: 0.028 at c=1.16 mg/l<br>SD: 0.02 at c=0.46 mg/l | 0.01 |
| Poland | | | RSD: 1.9% at 10 mg/L<br>RSD: 2% at 1 mg/L<br>RSD: 2.6% at 0.5 mg/L | 0.02 |
| PL05 | M.MAD: 0.05;<br>CoV: 11.7% | 0.1 | M.MAD: 0.04; CoV: 11.2% | 0.1 |
| Portugal | | | 0.53% | 0.03 |
| Russia | | | | 0.03 |
| Serbia and Montenegro* | | | | 0.05 |
| Slovakia | | | 0.66% | 0.04 |
| Spain | | | CoV: 4.9% | 0.31 |
| Sweden | uncertainty (95% conf. int.): 8% (0.05-1 mg/l)<br>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: 0.054;<br>CoV: 7.5% | 0.050* |
| UK | | | 1% | 0.02 |

* Data from EE, HU, NL, NO, TR and YU are taken from earlier years.

## *Table A4.13: 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%<br>M.MAD: 0.015 mg/l | 0.01 | RSD: 3.6% | 0.002 |
| Denmark | | | M.MAD: 0.02 mg/l;<br>CoV: 7.0% | 0.02 |
| Estonia* | | 0.077 | | 0.089 |
| Finland | | | M.MAD: 0.001 mg/l;<br>CoV: 2.1% | 0.003 |
| France | | | at c<0.2 mg/l: RSD = 10-20%<br>at 0.2<c<0.5 mg/l: RSD = 5-10%<br>at 0.5<c<5 mg/l: RSD = 1-5% | 0.02 |
| Germany | | | | 0.01 |
| Hungary | | | M.MAD: 0.004; CoV: 6.85% | ca. 0.01* |
| Ireland | | | | 0.05 |
| Italy (IT01) | RSD:<br>1.1% at 0.5 mg Mg/l | 0.005 | RSD: 0.8% at 0.5 mg Mg/l<br>RSD: 3.2% at 0.05 mg Mg/l | 0.001 |
| Italy, EU (IT04) | | | CoV: 2.2% | 0.002 |
| Latvia | | | CoV: 4.1% | 0.020 |
| Netherlands* | | | SD: 0.2 | 1 μmol/l |
| Norway* | M.MAD: 0.01, CoV: 30% | | SD: 0.012 at c=0.31 mg/l<br>SD: 0.007; c=0.19 mg/l | 0.01 |
| Poland | | | RSD: 1.0% at 0.25mg/l<br>RSD: 1.0% at 0.1 mg/l<br>RSD: 2.4% at 0.025 mg/l | 0.007 |
| PL05 | M.MAD: 0.002;<br>CoV: 2.3% | 0.01 | M.MAD: 0.005; CoV: 8.7% | 0.001 |
| Portugal | | | 0.60% | 0.03 |
| Russia | | | CoV: 8.17%; M.MAD: 0.09 | 0.001 |
| Serbia and Montenegro* | | | 99.5% | 0.002 |
| Slovakia | | | 1.56% | 0.01 |
| Spain | | | CoV: 7.2% | 0.02 |
| Sweden | uncertainty (95% conf. int.): 20% (0.02-1 mg/l)<br>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: 0.006; CoV: 4.3% | 0.012* |
| UK | | | 1% | 0.01 |

* Data from EE, HU, NL, NO, TR and YU are taken from earlier years.

*Table A4.14: 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%<br>M.MAD: 0.019 mg/l | 0.066 | RSD: 2.6% | 0.007 |
| Denmark | | | M.MAD: 0.10 mg/l;<br>CoV: 3.2% | 0.06 |
| Estonia* | | 0.095 | | 0.1 |
| Finland | | | M.MAD: 0.001 mg/l;<br>CoV: 0.9% | 0.002 |
| France | | | at c<0.2 mg/l: RSD = 10-20%<br>at 0.2<c<0.5 mg/l: RSD = 5-10%<br>at 0.5<c<5 mg/l: RSD = 1-5% | 0.02 |
| Germany | | | | 0.01 |
| Hungary | | | M.MAD: 0.010%;<br>CoV: 4.71% | ca. 0.01* |
| Ireland | | | | 0.05 |
| Italy (IT01) | RSD:<br>0.9% at 0.5 mg Na/l | 0.005 | RSD: 1.3% at 0.5 mg Na/l<br>RSD: 2.0% at 0.05 mg Na/l | 0.001 |
| Italy, EU (IT04) | | | CoV: 2.1% | 0.011 |
| Latvia | | | CoV: 3.6% | 0.03 |
| Lithuania | | | RSD: 2.4-5.7% | 0.02 |
| Netherlands* | | | SD: 0.5 | 2 µmol/l |
| Norway* | M.MAD: 0.09, CoV: 22% | | SD: 0.025 at c=0.75 mg/l<br>SD: 0.011 at c=0.30 mg/l | 0.01 |
| Poland | | | RSD: 0.8% at 1 mg/l<br>RSD: 1.4% at 0.4 mg/l<br>RSD: 2.3% at 0.2 mg/l | 0.02 |
| PL05 | M.MAD: 0.002;<br>CoV: 2.3% | 0.02 | M.MAD: 0.012; CoV: 11% | 0.002 |
| Portugal | | | 0.54% | 0.025 |
| Russia | | | CoV: 0.45% | 0.01 |
| Serbia and Montenegro* | | | 98.25% | 0.001 |
| Slovakia | | | 1.28% | 0.04 |
| Spain | | | CoV: 14% | 0.1 |
| Sweden | uncertainty (95% conf. int.): 6% (0.12-1 mg/l)<br>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: 0.009;<br>CoV: 1.4% | 0.023* |
| UK | | | 1% | 0.01 |

* Data from EE, HU, NL, NO, TR and YU are taken from earlier years.

## *Table A4.15: 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;<br>CoV: 10.5% | 0.006 |
| Latvia | | | CoV: 6.5% | 0.7 mg/l |
| Germany | | | | 0.004 |
| Slovakia | | | 1.99% | 0.5 |
| Norway | | | | 0.1 |
| UK | | | | 0.04 mg/l |

* Data from EE is taken from earlier years.

## *Table A4.16: Detection limits and precision of cadmium in precipitation.*

| Country | Measurements | | Laboratory | |
|---|---|---|---|---|
| | Precision | Detection limit, µg/l | Precision | Detection limit, µg/l |
| Czech Republic | CoV: 11.5%<br>M.MAD: 0.019 µg/l | 0.06 | RSD: 8.5% | 0.04 |
| Estonia* | | 0.01 | | |
| Finland | | | M.MAD: 0.002 µg/l<br>CoV: 3.0% | 0.002 |
| Germany | | | | 0.003 |
| Latvia | | | CoV: 8.1% | 0.03 |
| Slovakia | | | 2.01 % | 0.03 |
| Netherlands* | | | SD: 0.00007 | 0.0003 umol/l |
| Norway | | | | 0.005 |
| UK | | | | 0.04 mg/l |

* Data from EE and NL are taken from earlier years.

## *Table A4.17: 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;<br>CoV: 21.8% | 0.02 |
| Germany | | | | 0.01 |
| Slovakia | | | 1.58 % | 0.04 |
| Norway | | | | 0.2 |
| UK | | | | 0.008 mg/l |

## *Table A4.18: 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;<br>CoV: 4.7% | 0.05 |
| Germany | | | | 0.01 |
| Latvia | | | CoV: 5.4% | 0.4 |
| Poland (PL05) | M.MAD: 0.2; CoV: 23.3% | 0.3 | M.MAD: 0.1; CoV:11% | 0.3 |
| Norway | | | | 0.1 |
| Netherlands* | | | SD: 0.0014 | 0.006 µmol/l |
| UK | | | | 0.003 mg/l |

* Data from EE and NL are taken from earlier years.

*Table A4.19: Detection limits and precision of iron in precipitation.*

| Country | Measurements |  | Laboratory |  |
|---|---|---|---|---|
|  | **Precision** | **Detection limit, µg/l** | **Precision** | **Detection limit, µg/l** |
| Czech Republic | RSD: 14.6%; CoV: 15.8%<br>M.MAD : 0.02mg/l | 6 | RSD: 9.4% | 6 |
| Finland |  |  | M.MAD: 3.21 µg/l<br>CoV: 9.6% | 1.5 |
| Germany |  |  |  | 0.5 |
| Netherlands* |  |  | SD: 0.09 | 0.4 µmol/l |

* Data from NL is taken from earlier years.

*Table A4.20: Detection limits and precision of manganese in precipitation.*

| Country | Measurements |  | Laboratory |  |
|---|---|---|---|---|
|  | **Precision** | **Detection limit, µg/l** | **Precision** | **Detection limit, µg/l** |
| Czech Republic | RSD: 9.1%; CoV: 7.6%<br>M.MAD : 2.15 µg/l | 0.5 | RSD : 5.2% | 0.5 |
| Finland |  |  | M.MAD: 0.073 µg/l<br>CoV: 3.4% | 0.005 |
| Latvia |  |  | CoV: 2.8% | 10 |
| Slovakia |  |  | 2.96% | 0.05 |

*Table A4.21: Detection limits and precision of nickel in precipitation.*

| Country | Measurements |  | Laboratory |  |
|---|---|---|---|---|
|  | **Precision** | **Detection limit, µg/l** | **Precision** | **Detection limit, µg/l** |
| Czech Republic | CoV: 17.3%<br>M.MAD: 0.189 µg/l | 3.1 | RSD: 4.1% | 1.0 |
| Finland |  |  | M.MAD: 0.04 µg/l<br>CoV: 15.5% | 0.02 |
| Germany |  |  |  | 0.2 |
| Latvia |  |  | CoV: 7.3% | 0.9 |
| Norway |  |  |  | 0.2 |
| Slovakia |  |  | 2.34 % | 0.1 |
| UK |  |  |  | 0.009 mg/l |

*Table A4.22: Detection limits and precision of lead in precipitation.*

| Country | Measurements |  | Laboratory |  |
|---|---|---|---|---|
|  | **Precision** | **Detection limit, µg/l** | **Precision** | **Detection limit, µg/l** |
| Czech Republic | CoV: 13.4%<br>M.MAD: 0.398 µg/l | 1.6 | RSD: 8.2% | 0.7 |
| Estonia* |  | 0.6 |  |  |
| Finland |  |  | M.MAD: 0.049 µg/l<br>CoV: 3.7% | 0.03 |
| Germany |  |  |  | 0.002 |
| Latvia |  |  | CoV: 4.7% | 0.4 |
| Netherlands* |  |  | SD: 0.0005 | 0.002 µmol/l |
| Norway |  |  |  | 0.01 |
| Slovakia |  |  | 3.52% | 0.2 |
| UK |  |  |  | 0.002 mg/l |

* Data from EE and NL are taken from earlier years.

## *Table A4.23: Detection limits and precision of zinc precipitation.*

| Country | Measurements | | Laboratory | |
|---|---|---|---|---|
| | **Precision** | **Detection limit, µg/l** | **Precision** | **Detection limit, µg/l** |
| Czech Republic | RSD: 11.3%; CoV: 9.4%<br>M.MAD: 0.003 mg/l | 3 | RSD: 7.4% | 3 |
| Finland | | | M.MAD: 0.183 µg/l<br>CoV: 3.1% | 0.03 |
| Germany | | | | 0.2 |
| Latvia | | | CoV: 2.3% | 20 |
| Netherlands* | | | SD: 0.014 | 0.06 µmol/l |
| Norway | | | | 0.1 |
| Poland (PL05) | M.MAD: 2.3 µg Zn/l; CoV: 24% | 0.2 | M.MAD: 0.2; CoV 1.9% | 0.2 |
| Slovakia | | | 3.17 % | 1.69 |
| UK | | | | 0.1 mg/l |

* Data from NL is taken from earlier years.

## *Table A4.24: Detection limits and precision of arsenic in air.*

| Country | Measurements | | Laboratory | |
|---|---|---|---|---|
| | **Precision** | **Detection limit, ng/m$^3$** | **Precision** | **Detection limit** |
| Czech Republic | CoV: 16.1%<br>M.MAD: 0.15 ng/m$^3$ | 0.2 | RSD: 8.7% | 0.75 µg/l |
| Germany | | | | 0.004 µg/l |
| Latvia | | 0.09 | CoV: 4.8% | 2.0 µg/l |
| Slovakia | | | 2.34 % | 0.7 µg/l |
| Netherlands* | | | 0.04 | 0.2 ng/m$^3$ |
| Norway, NO42 | | | | 0.005 ng/m$^3$ |
| NO99 | | | | fine: 0.9 ng/m$^3$;<br>coarse: 0.24 ng/m$^3$ |

* Data from NL is taken from earlier years.

## *Table A4.25: Detection limits and precision of cadmium in air.*

| Country | Measurements | | Laboratory | |
|---|---|---|---|---|
| | **Precision** | **Detection limit, ng/m$^3$** | **Precision** | **Detection limit** |
| Czech Republic | CoV: 7.9%<br>M.MAD: 0.018 ng/m$^3$ | 0.04 | RSD: 4.1% | 0.05 µg/l |
| Germany | | | | 0.003 µg/l |
| Lativia | | 0.005 | CoV: 1.9% | 0.13 µg/l |
| Slovakia | | | 1.44 % | 0.03 µg/l |
| Spain | | | | 0.01 ng/m$^3$ |
| Netherlands* | | | 0.01 | 0.04 ng/m$^3$ |
| Norway, NO42 | | | | 0.002 ng/m$^3$ |
| NO99 | | | | fine: 0.002 ng/m$^3$;<br>coarse: 0.001 ng/m$^3$ |

* Data from NL is taken from earlier years.

*Table A4.26: Detection limits and precision of chromium in air.*

| Country | Measurements | | Laboratory | |
|---|---|---|---|---|
| | Precision | Detection limit, ng/m$^3$ | Precision | Detection limit |
| Slovakia | | | 1.01 % | 0.4 µg/l |
| Norway, NO42 | | | | 0.02 ng/m$^3$ |
| NO99 | | | | fine: 0.3 ng/m$^3$;<br>coarse: 0.6 ng/m$^3$ |

*Table A4.27: 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 |
| Latvia | | 0.2 | CoV: 1.6% | 1.9 µg/l |
| Slovakia | | | 1.41% | 0.5 µg/l |
| Spain | | | | 0.18 ng/m$^3$ |
| Norway, NO42 | | | | 0.01 ng/m$^3$ |
| NO99 | | | | fine: 0.04 ng/m$^3$;<br>coarse: 0.02 ng/m$^3$ |

*Table A4.28: 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 |
| Latvia | | 0.21 | CoV: 1.7% | 6.0 µg/l |
| Slovakia | | | 3.06% | 0.1 µg/l |
| Norway, NO42 | | | | 0.07 ng/m$^3$ |

*Table A4.29: 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 |
| Latvia | | 0.26 | CoV: 3.2% | 2.9 µg/l |
| Slovakia | | | 1.32% | 0.4 µg/l |
| Norway, NO42 | | | | 0.02 ng/m$^3$ |
| NO99 | | | | fine: 0.008 ng/m$^3$;<br>coarse: 0.02 ng/m$^3$ |

*Table A4.30: Detection limits and precision of lead in air.*

| Country | Measurements | | Laboratory | |
|---|---|---|---|---|
| | **Precision** | **Detection limit, ng/m$^3$** | **Precision** | **Detection limit** |
| Czech Republic | CoV: 8.9%<br>M.MAD: 0.486 ng/m$^3$ | 0.5 | RSD: 2.1% | 0.78 μg/l |
| Germany | | | | 0.002 μg/l |
| Latvia | | 0.05 | CoV: 1.1% | 1.8 μg/l |
| Slovakia | | | 1.96% | 0.4 μg/l |
| Spain | | | | 0.4 ng/m$^3$ |
| Netherlands* | | | 0.06 | 0.2 ng/m$^3$ |
| Norway, NO42 | | | | 0.007 ng/m$^3$ |
| NO99 | | | | fine: 0.008 ng/m$^3$;<br>coarse: 0.004 ng/m$^3$ |

* Data from NL is taken from earlier years.

*Table A4.31: Detection limits and precision of zinc in air.*

| Country | Measurements | | Laboratory | |
|---|---|---|---|---|
| | **Precision** | **Detection limit, ng/m$^3$** | **Precision** | **Detection limit** |
| Lativia | | 0.7 | CoV: 2.2% | 12.0 μg/l |
| Slovakia | | | 3.53% | 4.6 μg/l |
| Netherlands* | | | 3.6 | 15 ng/m$^3$ |
| Norway, NO42 | | | | 0.01 ng/m$^3$ |
| NO99 | | | | fine: 0.05 ng/m$^3$;<br>coarse: 0.02 ng/m$^3$ |

* Data from NL is taken from earlier years.

*Table A4.32: Detection limits and precision of measurements of particulate matter.*

| Country | Precision | Detection limit |
|---|---|---|
| Germany (PM10) | | 1 μg/m$^3$ |
| Italy IT01 (PM10) | 2.00% | 2 μg/m$^3$ |
| Slovakia (TSP) | 2.00% | 1.0 μg/m$^3$ |
| Spain | 2.00% | 1 μg/m$^3$ |
| Switzerland (PM10) | RSD: 7% | 1 μg/m$^3$ |
| Norway (PM10) | RSD: 5% | 0.2 μg/$^{m3}$ |
| UK | 4 μg m$^{-3}$ | |

*Table A4.33: 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 | | | 0.008 | | |
| Ethene | 0.020 | | | 0.009 | | |
| Ethyne | 0.041 | | | 0.011 | | |
| Propane | 0.008 | | | 0.006 | | |
| Propene | 0.011 | | | 0.007 | | |
| Propyne | 0.003 | | | 0.004 | | |
| N-butane | 0.003 | | | 0.005 | | |
| 2-methyl propane (i-butane) | 0.005 | | | 0.005 | | |
| 2-methyl propene (i-butene) | 0.006 | | | 0.006 | | |
| 1-butene | 0.009 | | | 0.005 | | |
| Trans-2-butene | 0.004 | | | 0.005 | | |
| Cis-2-butene | 0.008 | | | 0.006 | | |
| 1,3-butadiene | 0.009 | | | 0.006 | | |
| N-pentane | 0.003 | | | 0.005 | | |
| 2-methyl butane (i-pentane) | 0.008 | | | 0.005 | | |
| 1-pentene | | | | | | |
| Trans-2-pentene | 0.012 | | | 0.005 | | |
| Cis-2-pentene | 0.009 | | | 0.006 | | |
| 2-methyl pentane | 0.003 | | | 0.006 | | |
| 3-methyl pentane | 0.012 | | | 0.006 | | |
| Isoprene | 0.006 | | | 0.008 | | |
| N-hexane | 0.011 | | | 0.006 | | |
| Hexene | | | | | | |
| Cyclohexane | 0.003 | | | 0.006 | | |
| N-heptane | 0.023 | | | 0.004 | | |
| Benzene | 0.012 | | | 0.003 | | |
| Methyl benzene (toluene) | 0.021 | | | 0.004 | | |
| 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 | | | | | |
| | | *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 A4.34: Detection limits and precision of persistent organic pollutants (POP).*

| **Compound** | **Laboratory detection limit, pg/m$^3$** | | |
|---|---|---|---|
| | **Czech Republic** | **Norway** | **UK** |
| PCB 28 | 0.5 | 0.05 | |
| PCB 31 | 0.5 | 0.05 | |
| PCB 52 | 0.5 | 0.05 | |
| PCB 101 | 0.5 | 0.05 | |
| PCB 105 | 0.5 | 0.05 | |
| PCB 118 | 0.5 | 0.05 | |
| PCB 138 | 0.5 | 0.05 | |
| PCB 153 | 0.5 | 0.05 | |
| PCB 153 | 0.5 | 0.05 | |
| PCB 180 | 0.5 | 0.05 | |
| alfa-HCH | 0.5 | 0.05 | |
| beta-HCH | 0.5 | | |
| gamma-HCH | 0.5 | 0.05 | |
| delta-HCH | 0.5 | | |
| HCB | 0.5 | 0.05 | |
| p,p'-DDE | 0.5 | 0.05 | |
| p,p'-DDD | 0.5 | 0.05 | |
| p,p'-DDT | 0.5 | 0.05 | |
| Hexachlorbenzene | 0.5 | 0.05 | |
| Pentachlorbenzene | 0.5 | | |
| tr-chlordane | | 0.05 | |
| cis-chlordane | | 0.05 | |
| tr-nonachlor | | 0.05 | |
| cis-nonachlor | | 0.05 | |
| | | | |
| PAH (general) | | 1 | |
| Naphtalene | 2.5 | | |
| Acenaphthylene | 2.5 | | |
| Acenaphthene | 2.5 | | |
| Fluorene | 2.5 | | |
| Phenanthrene | 2.5 | | |
| Anthracene | 2.5 | | |
| Fluoranthene | 2.5 | | |
| Pyrene | 2.5 | | |
| Benz[a]antracene | 2.5 | | |
| Chrysene | 2.5 | | |
| Benzo[b]fluorantene | 2.5 | | |
| Benzo[k]fluorantene | 2.5 | | |
| Benzo[a]pyrene | 2.5 | | < 10 |
| Indeno[123cd]pyrene | 2.5 | | |
| Dibenz[ah]anthracene | 2.5 | | |
| Benzo[ghi]perylene | 2.5 | | |

# Annex 5

# Sulphate in air and sulphur dioxide in EMEP, flags and comments

# Sulphate in air and sulphur dioxide in EMEP, flags and comments

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Results from laboratory and field comparisons for sulphate in air and sulphur dioxide have been used to flag data series in a quasi-quantitative way. More exact measures of data quality and comparability for EMEP's data would have required more frequent and longer field tests. The methodology applied when assigning flags to laboratory and field comparison results has been described elsewhere.

The data series have been flagged with four digits where the two leftmost digits give information on the complete measurements as judged from field comparisons alone while the two rightmost digits are based on the performance in inter-laboratory comparisons.

A good laboratory performance is a necessary, but not a sufficient requirement for high data quality. Sometimes the field and laboratory results are inconsistent, and in a few cases no recommendation has been given below. Except for this, the best flags, as far as one can judge, have been given in bold characters when a choice must be made whether to rely on the field or on the laboratory comparison results.

## Sulphate in air

### Measurement methods for sulphate concentrations in air

Different types of samplers have been used in EMEP for sulphate in aerosols, the most common being in-line low volume samplers (1–3 $m^3$/24 h) and medium volume open-face samplers (15–60 $m^3$/24 h), both without a specified cut-off. Spain has made use of a high volume sampler, and Italian measurements are by denuder.

Wet-chemical methods and quantification by X-ray fluorescence (XRF) have both been used for determining the sulphate concentrations on the filters. The laboratories have applied different calibration procedures for sulphur on filters by XRF. They have also made use of different types of filters for their EMEP measurements. The Thorin method (CCC, 1996) was recommended for chemical analysis from the start. It takes, however, both experience and dedication obtaining exact results with this method. Ion chromatography (IC) is now being applied by an increasing number of laboratories and gives generally much better data.

### Laboratory and field comparisons

A long series of laboratory comparisons with synthetic and exposed filter samples has been organized since EMEP's start (Thrane, 1978, 1980,1981; Hanssen, et al., 1983–1985, 1987, 1988, 1990, 1992, 1994–1997, 2001; Uggerud et al., 2001–2003).

A comparison between the Thorin method at the CCC at the Norwegian Institute for Air Research (NILU), with the XRF method at the reference laboratory for the XRF measurements (Institute for Energy Research, Kjeller, Norway) was organized in 1981. Filter samples generated with an aerosol generator equipped with a multi-channel open sampler were prepared for the 6th comparison. Most of the samples were analysed by the participating laboratories, but seven samples from each batch were analysed by the CCC with an automated Thorin method after extraction, and by the reference laboratory by XRF analyses. The differences between the CCC wet chemical results and the XRF results from the reference laboratory were always less than 10 per cent (Hanssen et al., 1983). Exposed filters, analysed for sulphur by XRF in the reference laboratory, were again distributed to the participants in the 7th exercise, and the results revealed that the average ratio between the reference and the national laboratories (both XRF) varied between 0.73 and 1.20. Different calibration procedures and filter types were noted as possible explanations. The corresponding ratio for reference (by XRF) to national by wet chemical analysis varied between 0.79 and 1.29.

Two large-scale field comparisons for sulphate in aerosols have been organized in EMEP, at Langenbrügge (DE 2) in northern Germany, November–January in 1985, and at Vavihill (SE 11) in southern Sweden, January–March in 1990 (Nodop and Hanssen, 1986; and Semb et al., 1991). All EMEP field studies, but the Vavihill exercise, have been comparisons of complete measurements where participating laboratories analysed their own samples.

One of the conclusions from the Vavihill field comparison (Semb et al., 1991) was that the choice of medium or low volume sampler for sulphate did not seem to be critical. It was noted that the medium volume sampler gave somewhat higher concentrations and that this could be due to impaction of particles in the tubes. The average difference was, however, only 0.15 μg S/m$^3$ over the sampling period. This was about 10 per cent of the average over that measurement period

Figure 1 compares the low, medium, and high volume results obtained at the Vavihill field comparison. The low and medium volume concentrations in the Figure are the medians of the low, respectively medium samplers' results. The high volume results are the Spanish results. High and medium volume samples were analysed by NILU and the low volume samples by the Swedish Environmental Research Institute (IVL), all samples by IC. The differences in Figure 1 between the sampler types are in the best group for systematic errors ( ±10%) used in the classification.

During the second half of the nineties a series of on-site comparisons of national measurements with reference instrumentation have been carried out in EMEP (Schaug et al., 1997 and 1998; Aas et al., 1999, 2000,2001, 2002, 2003). The reference instrumentation is a three-filter-pack method with an aerosol filter followed by a KOH impregnated filter for $SO_2$, and a third filter with oxalic acid for $NH_3$ sampling. The instrument has a mass flow control unit and operates at about 10 m$^3$/24 hours (e.g. Schaug et al., 1998).

Some countries never participated in field comparisons, and some countries changed their measurement method after participation in a field comparison.

Additionally some results were rather unsatisfactory, and there is a need to repeat some of the comparisons from the past to see if improvements have been made. The comparisons carried out so far are therefore far from sufficient to fully express the comparability of sulphate measurements since 1978.

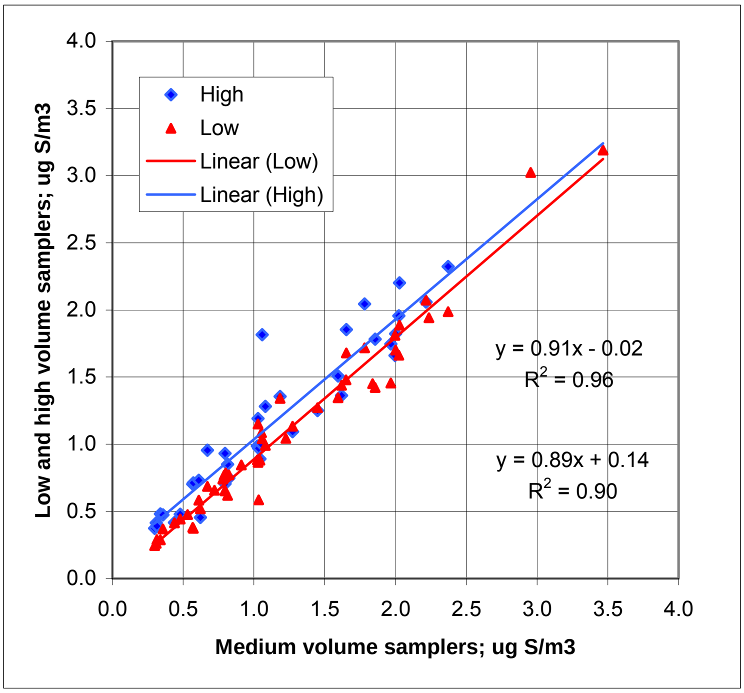

*Figure 1. Vavihill field comparison of sulphate in air; medium volume sampler concentrations compared with low volume and high volume results. Medium and low volume concentrations are the medians of medium samplers' results and low volume samplers' results respectively. 4 high volume outliers are not taken into account. High and medium volume samples were analysed by NILU, low volume samples by IVL, all samples by IC.*

The validation of the field comparison data has been based on the differences between national measurements and reference data by using non-parametric statistics; M.MAD, the coefficient of variation, and the median of the differences in order to detect random errors and bias. X-Y plots and regression lines and graphs of differences as function of reference measurements have also carefully been investigated for different concentration ranges as a further support.

Specific comments to some of the countries and quality flags for sulphate in air have been given in Annex 1.

## Sulphur dioxide

### *Measurement methods for sulphur dioxide in EMEP*

Four sampling principles have been used for SO2; the $H_2O_2$ absorbing solution method, the KOH or NaOH impregnated filter method, the tetrachloromercurate method (TCM), and mostly recently monitors based on UV fluorescence. CCC has recommended the two first methods in the Manual (CCC, 1996).

Several analytical chemical methods have been applied. The most sensitive UV monitors compare well with the impregnated filter method when care is taken (Finnish unpublished results, com. to CCC). Interferences from hydrocarbons and nitrogen monoxide may, however, occur and should be tested out. Some important results from comparisons of the three other methods have been given below.

### Laboratory and field comparisons

As for other components, a long, nearly annual, series of laboratory comparisons with synthetic $SO_2$ samples, has been organized by the CCC since EMEP's start in 1977. Frequently it can be seen that the performance in a field comparison can be explained by the results obtained in the most relevant inter-laboratory comparison. There are, however, also examples of the opposite; countries performing fairly well in laboratory comparisons may obtain rather unexplainable results in field exercises

Synthetic samples for the TCM method were never a part of the laboratory comparisons and $SO_2$ results obtained with this method must be judged from field comparisons alone.

Three central laboratories analysed the samples in the Vavihill comparison; IVL analysed the $H_2O_2$ absorbing solution samples, NILU analysed the impregnated filter samples while the nearby Swedish Laboratory for Cereals analysed the tetrachloromercurate (TCM) samples. Comparisons of IVL's and NILU's performance in the laboratory comparison most relevant for the Vavihill results, have been used to slightly correct the results. The Vavihill results have been used below to compare the $H_2O_2$ absorbing solution and the impregnated filter methods.

Table 1, and Figures 2 and 3 compare the daily medians of the Vavihill measurements as obtained with the participants modifications of the $H_2O_2$ absorbing solution method. (4 samplers) with the impregnated filter method (8 samplers). The samples were all analysed by IC.

*Table 1. Vavihill field comparison. Medians of results with the impregnated filter method (Y) versus the hydrogen peroxide absorbing solution results (X) in a linear regression. Slopes and intercepts with their 95 % confidence intervals, $R^2$ and number of data.*

| Concentration interval | Slope | Intercept | $R^2$ | N |
|---|---|---|---|---|
| 0 – 3 µg S/m$^3$ | 0.751<br>(0.732, 0.770) | -0.26<br>(-0.30, -0.22) | 0.91 | 24 |
| 3 – 20 µg S/m$^3$ | 0.904<br>(0.897, 0.911) | -0.55<br>(-0.60, -0.50) | 0.99 | 27 |

The peroxide absorbing solution is quite inaccurate at the lowest concentrations (Semb et al., 1994) and is thought to overestimate, but give more correct results at high concentrations. The slope for the 3–20 µg S/m$^3$ interval is within the [0.90, 1.10] interval that is the best class for systematic errors.

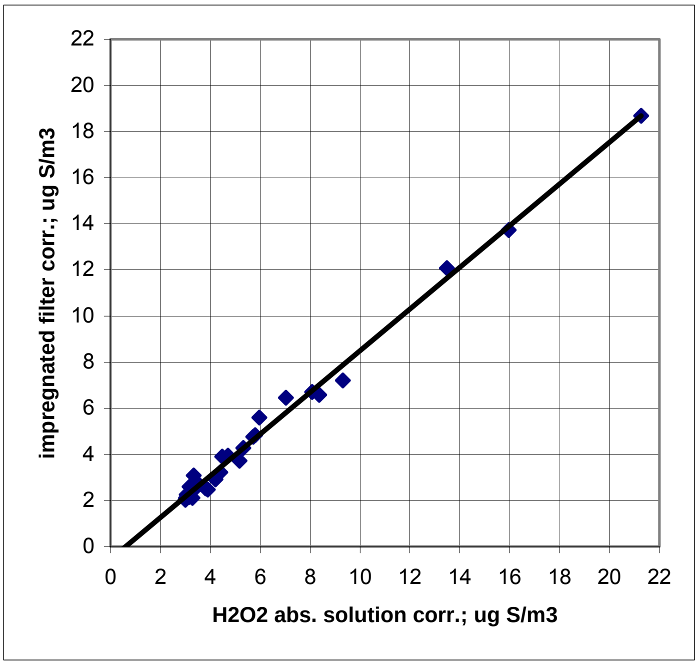

*Figure 2. Measurements of sulphur dioxide at Vavihill January–March 1990. Medians of daily measurements obtained with $H_2O_2$ absorbing solution against the corresponding medians of impregnated filter results.*
*$SO_2$ concentrations higher than 3 µg S/m$^3$.*

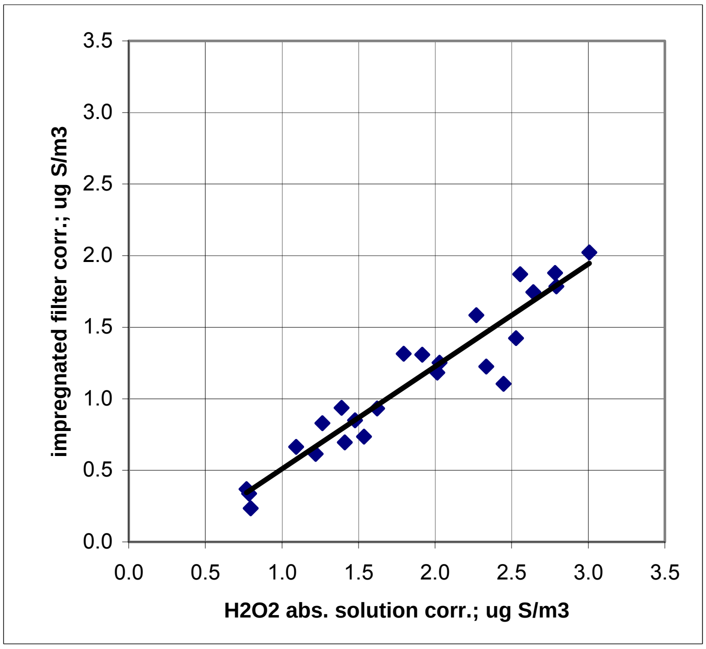

*Figure 3. As Figure 1. $SO_2$ concentrations up to 3 µg S/m$^3$.*

The slope and intercept for a specific participant when compared with reference instrumentation will depend on far more factors than the sampling method, e.g. the analytical chemical method applied and the QA procedures including air volume calibration. The results corresponded reasonably well with other comparisons e.g. carried out in the UK later in the nineties. A comparison between the two methods by using the Langenbrügge results obtained by NILU, the Danish National Environmental Research Institute (DMU), and Warren Spring Laboratory (WSL) in the UK gave a near 1:1 correspondence with $R^2$ at 0.98 for the 3–20 µg S/$m^3$ interval. Similar results were obtained for the lower concentrations with $R^2$ at 0.79. The three laboratories' results are considered to be accurate since they obtained very good results during the analytical comparison during this exercise and in the 9th laboratory comparison the following months. A comparison between the French sampler and the reference in the nineties showed an opposite relation; the reference data were higher than the French concentrations. The French results were, however, lower than impregnated filter results also during the Langenbrügge comparison thirteen years earlier, but this sampler was not tested during the Vavihill experiment.

Germany has long data series with the TCM method, and the Langenbrügge results have been used to compare the TCM method with both the $H_2O_2$ absorbing solution method and the impregnated filter result obtained by the three laboratories above. Figures 4 and 5 present the results.

The Figures shows that the TCM method gave slightly higher concentrations both for concentrations in the interval 3 – 20 µg S/$m^3$ and for the lowest concentrations (Figure 5).

Hungary and Turkey, besides Germany, previously applied the TCM method for EMEP measurements. Potential interferences in this method should have been minimized or eliminated by different means. If kept at 5 deg C after completion of sampling the solution should be stable for up to 30 days ( Scaringelli et al., 1967). The samples need to be shielded from direct sunlight.

The field comparison at Schauinsland (DE3) in 1998 (Aas et al., 1999) revealed that the TCM method gave too low results below 1 – 2 µg S/m3, at least during summer conditions. National comparisons carried out in Germany for complete years showed that the TCM method gave slightly lower results than the impregnated filter method during winter, in contrast to the Langenbrügge results presented above. The TCM summer data gave lower results than the impregnated filter method, and annual data set gave somewhat lower results than the impregnated filter method for complete years (Aas et al., 2003). National comparison in Turkey February - November (1997) showed low TCM results compared to corresponding impregnated filter data (Aas et al., 2003)

It seem that the TCM method gives quite acceptable results compared to the impregnated filter method and the $H_2O_2$ absorbing solution method during winter conditions with respect to systematic errors. The summer results are somewhat low compared to the impregnated filter method. This should be kept in mind when using the TCM data.

Specific comments to some of the countries and quality flags for sulphur dioxide are given in Chapter 2.

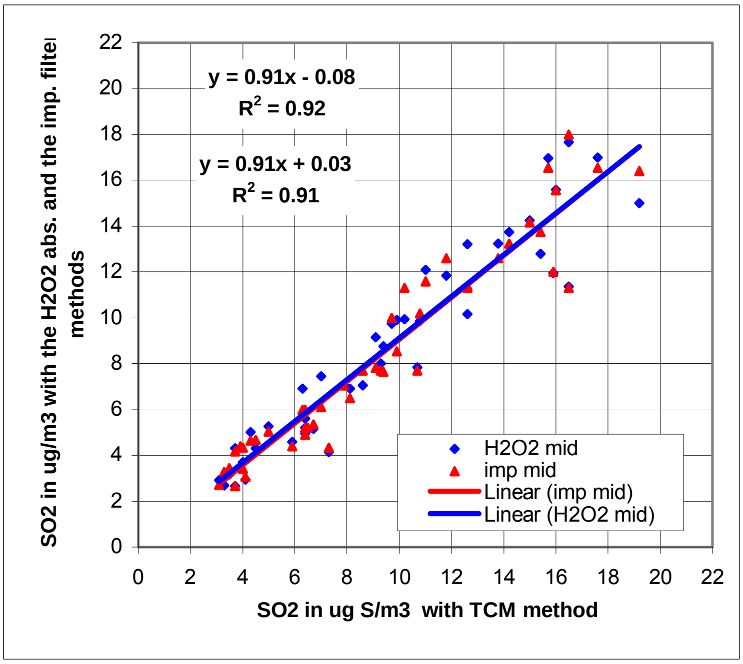

*Figure 4. Measurements of sulphur dioxide from the Langenbrügge field comparison*
*Results obtained with the TCM method of UBA, the $H_2O_2$ absorbing solution method of NILU and WSL, and the impregnated filter results of DMU and NILU. $SO_2$ concentrations 3–20 µg S/$m^3$.*

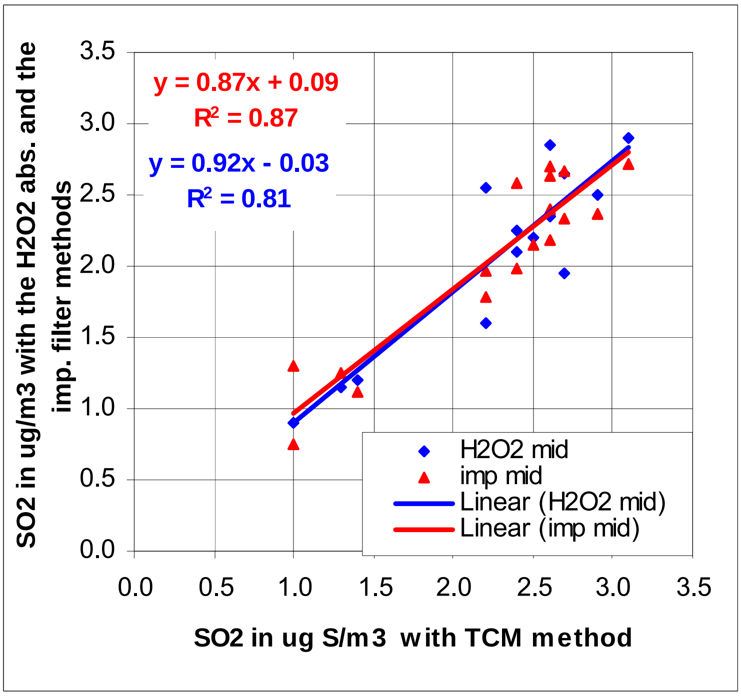

*Figure 5. As Figure 3 for concentrations up to 3 µg S/$m^3$.*

## Comments to some countries and quality flags

### Sulphate in air

### Czech republic and Czech part of the former Czechoslovakia

The sulphate data are invalid until 1989 due to a sampling error as explained for $SO_2$.

The Czech measurements were compared with other measurements at Langenbrügge (1985), Vavihill (1990) and at Košetice during 1998–1999. The error above was detected as a result of the Langenbrügge exercise. The Czech samplers performed excellent both with respect to precision and comparability with the other samplers in the Vavihill comparison.

The number of samples taken during the on-site comparison at Košetice in 1998–1999 was far too low to allow for firm conclusions on the data quality. However, the low concentrations seem to be of acceptable quality, but at concentrations above 2 $\mu g/m^3$ there are indications that the concentrations may be too low. Since the XRF method has not been compared since 1993 and the sampler performs well, the error sources could be connected to the XRF analysis.

### Germany

The Langenbrügge exercise (1985) revealed a spread in the measurements when compared with the reference data set, but the regression line had a slope close to 1. The Vavihill comparison confirmed a good correspondence with the reference measurements. The comparison in 1998 at Schauinsland showed a good agreement with the reference measurements with small random differences.

The German Democratic Republic (DDR) never took part in EMEP’s field comparison and the performance of their instrumentation. The laboratory comparison results were good except for the very first years from 1979 to 1982.

### France

The French background network was reorganized in 1989 as described for sulphur dioxide.

France took part in the Langenbrügge comparison in 1985 and an on-site comparison at Donon with reference instrumentation in 1998. The field comparison at Langenbrügge (1985) indicated systematic low results. The comparison at Donon (1998) revealed again large systematic deviations in the French measurements relative to the reference method.

French laboratories have taken part in laboratory comparisons from the start. IRCHA had very high systematic deviations from the reference laboratory until 1981/82. The random errors also seem to have been quite high until 1980. After 1982 there have been systematic low values by 10 to 20 per cent with random errors less than 20 per cent. The low laboratory results could fit with the low French results in the Langenbrügge field comparison two years later, in 1985.

The new laboratory had a good laboratory performance after 1991.

### Hungary

The Hungarian laboratory made use of the isotope dilution method until 1995 when ion chromatography took over. The laboratory participated in the Langenbrügge comparison and the results revealed large systematic low Hungarian measurements when compared with the reference. This corresponds with too low results in the most relevant laboratory comparison.

### Ireland

Ireland has three laboratories taking part in the analyses of the samples; they are the Meteorological Service of Ireland, the Environmental Protection Agency (EPA), and the Electricity Supply Board (ESB). The Met. Service is responsible for the oldest site, IE 1 at Valentia Observatory. EPA was responsible for the site IE2 during 1995–1997, but the analyses are now carried out by the ESB that also analyse samples from the other Irish sites IE3 and IE4.

The Met. Service took part in the Vavihill field comparison with the sampler, with satisfactory, but slightly low results. An on-site comparison took place during 1996–1997 with reference instrumentation at Valencia Observatory and gave similar results

Met. Service has taken part in the laboratory comparisons from the start while the EPA took part 1994–1997. The ESB has not until recently taken part in the comparisons.

### Italy

The denuder system from Istituto sull'Inquinamento Atmosferico, Consiglio Nazionale delle Ricerche (CNR) took part in the Vavihill comparison and obtained very good results when compared with the reference.

CNR is the only Italian laboratory having taken part in the comparisons and all other sulphate aerosol data therefore have an undocumented quality, the ISPRA site IT4, that is run by the Commission for the European Communities (CEC), not included.

### Portugal

An on-site comparison took place in Portugal in 1997, and the laboratory has taken part in most of the laboratory comparisons since 1981. The field comparison revealed a fairly large spread in data lower than 2 µg S/m$^3$. Most of the measurements fell unfortunately in this interval during the exercise. Concentrations above 4–5 µg S/m$^3$ were far too high. The most relevant laboratory comparison showed slightly high Portuguese data, the test solutions corresponded, however, all to concentrations lower than 4 µg S/m$^3$.

### Soviet Union

The samples from the Soviet network were divided between two laboratories as explained for sulphur dioxide. The Institute for Applied Geophysics, which is identical to today's Institute for Global Climate and Ecology in Moscow, took part in the laboratory comparisons. This institute analysed the samples from SU1, 5, and 9. The quality of the remaining Soviet samples remains unknown.

**Sweden**

Two sampling systems have been in operation, the low-volume and the currently used medium-volume system were both compared with other samplers, and performed very good, at the Vavihill exercise in 1990.

The low-volume sampler was also tested in the Langenbrügge comparison and showed Swedish results to be higher than other measurements with different analytical methods. The reason for this may be the calibration procedure for the XRF that was used at that time for analysis. Analytical comparisons carried out in Sweden in 1986–1987 gave different results. The XRF results were lower than those obtained by IC and should be multiplied with factors between 1.1 and 1.6 (Kindbom et al., 1994).

The National Swedish Environment Protection Board operated the site SE12 1984–1989 while the Swedish Environmental Research Institute was responsible for the remaining sites.

**United Kingdom**

Warren Spring Laboratory was responsible for the UK measurements until 1994 when AEA Technology took over.

### Notes applied with the $SO_4$ flags

UK: unknown
NR: not relevant
(1): field flag is based on less than 40 data and considered uncertain
(2): the sums of sulphur dioxide and aerosol sulphate concentrations are available
(3): See comments and proposals for corrections given by Dr. M. Wallasch
(4): concentrations $< 4$ µg $S/m^3$
(5): concentrations $\geq 4$ µg $S/m^3$
(6): all Soviet sites except SU1, SU5, SU9
(7): Swedish sites except SE12

Recommended quality flags are given in **bold numbers** below

### Austria

| | | |
|---|---|---|
| AT | 1978 | 20**20** |
| AT | 1979 | 20**00** |
| AT | 1980 | 20**10** |
| AT | 1981 | 20**01** |
| AT | 1982,1983 | 20**20** |
| AT | 1984,1985 | 20**40** |
| AT | 1986 | 20**00** |
| AT | 1987,1988 | 20**40** |
| AT | 1989 - 1994 | 20**61** |
| AT | 1995,1996 | 20**61** |
| AT | 1997 - 2000 | NPNP |

### Belgium

| | | |
|---|---|---|
| BE | 1979 - 1991 | NPNP |

### Czech republic and Czech part of the former Czechoslovakia

| | | |
|---|---|---|
| CZ | 1979 - 1988 | NRNR (2) |
| CZ | 1989,1993 | **00**00 |
| CZ | 1994 - 2000 | 01NP (1) |

### Denmark

| | | |
|---|---|---|
| DK | 1978 | 00**00** |
| DK | 1979,1980 | 00**10** |
| DK | 1981 | 00**21** |
| DK | 1982,1983 | 00**10** |
| DK | 1984 - 1986 | 00**00** |
| DK | 1987 - 1994 | 00**00** |
| DK | 1995 - 2000 | 00**00** |

### Estonia

| | | |
|---|---|---|
| EE | 1997,1998 | NP**71** |
| EE | 1999,2000 | NP**41** |

**Finland**

| | | |
|---|---|---|
| FI | 1977,1978 | 00**40** |
| FI | 1979,1980 | 00**51** |
| FI | 1981 - 1986 | 00**00** |
| FI | 1987 - 1990 | 00**20** |
| FI | 1991 - 1993 | 00**00** |
| FI | 1994 | 00**30** |
| FI | 1995 - 2000 | 00**00** |

**France**

| | | |
|---|---|---|
| FR | 1978 - 1980 | 6373 |
| FR | 1981 | 6371 |
| FR | 1982,1983 | 6360 |
| FR | 1984 | 6321 |
| FR | 1985 - 1987 | 63NP |
| FR | 1988,1989 | 6300 |
| FR | 1990 | 6372 |
| FR | 1991,1992 | 2020 |
| FR | 1993,1994 | 2000 |
| FR | 1995,1996 | 2000 |
| FR | 1997,1998 | 2020 |
| FR | 1999,2000 | 2000 |

**Germany (4)**

| | | |
|---|---|---|
| DE | 1978,1979 | **00**60 |
| DE | 1980 | **00**30 |
| DE | 1981 | **00**61 |
| DE | 1982,1983 | **00**40 |
| DE | 1984,1985 | **00**30 |
| DE | 1986 | **00**40 |
| DE | 1987,1988 | **00**30 |
| DE | 1989,1990 | **00**00 |
| DE | 1991,1992 | **00**30 |
| DE | 1993 | **00**41 |
| DE | 1994 | 00NP |
| DE | 1995 - 2000 | 00NP |

**German Democratic Republic**

| | | |
|---|---|---|
| DD | 1980 | NP02 |
| DD | 1981 | NP01 |
| DD | 1982,1983 | NP32 |
| DD | 1984,1985 | NP40 |
| DD | 1986 | NP00 |
| DD | 1987 - 1990 | NP31 |

**Greece**

| | | |
|---|---|---|
| GR | 1978,1979 | NP73 |
| GR | 1980 | NP83 |
| GR | 1981 | NP23 |
| GR | 1982,1983 | NP61 |

| | | |
|---|---|---|
| GR | 1984,1985 | NP20 |
| GR | 1986 - 1988 | NP40 |
| GR | 1989 - 1992 | NP21 |
| GR | 1993 | NP41 |
| GR | 1994 | NP71 |
| GR | 1995 - 1998 | NP73 |
| GR | 1999,2000 | NP20 |

**Hungary**

| | | |
|---|---|---|
| HU | 1977,1978 | NR22 |
| HU | 1979 | NR52 |
| HU | 1980 | NR62 |
| HU | 1981 | NR52 |
| HU | 1982,1983 | NR11 |
| HU | 1984,1985 | NR61 |
| HU | 1986 | NR21 |
| HU | 1987,1988 | NR61 |
| HU | 1989,1990 | NR82 |
| HU | 1991,1992 | NR62 |
| HU | 1993 | NR00 |
| HU | 1994 | NR71 |
| HU | 1995,1996 | NR51 |
| HU | 1997,1998 | NR10 |
| HU | 1999,2000 | NR00 |

**Iceland**

| | | |
|---|---|---|
| IS | 1979 - 1983 | NPNP |
| IS | 1984 | NP51 |
| IS | 1985,1986 | NPNP |
| IS | 1987,1988 | NP20 |
| IS | 1989 - 1991 | NP51 |
| IS | 1992 - 1994 | NP00 |
| IS | 1995,1996 | NP00 |
| IS | 1997,1998 | NP30 |
| IS | 1999,2000 | NP00 |

**Ireland**

| | | |
|---|---|---|
| IE0001 | 1980 | NP42 |
| IE0001 | 1981,1982 | NP41 |
| IE0001 | 1983 - 1986 | **20**20 |
| IE0001 | 1987,1988 | **20**40 |
| IE0001 | 1989,1990 | **20**20 |
| IE0001 | 1991,1992 | **20**41 |
| IE0001 | 1993,1994 | **20**00 |
| IE0001 | 1995 - 1998 | **20**00 |
| IE0001 | 1999,2000 | NPNP |
| IE0002 | 1991 - 1994 | NP00 |
| IE0002 | 1995 - 1997 | NP00 |
| IE0002 | 1998 - 2000 | NPNP |
| IE0003,IE0004 | 1997 - 2000 | NPNP |

**Italy**

| | | |
|---|---|---|
| IT0001 | 1983 - 1989 | NPNP |
| IT0001 | 1993 | 00**31** |
| IT0001 | 1994 - 1996 | 00**00** |
| IT0001 | 1997,1998 | 00**10** |
| IT0001 | 1999,2000 | 00**00** |
| IT0002,IT0003,IT0005 | 1977,1994 | NPNP |
| IT0002,IT0003,IT0005 | 1995,2000 | NPNP |
| IT0002,IT0003,IT0005 | 1995,2000 | NPNP |
| IT0004 | 1985 - 1990 | NP00 |
| IT0004 | 1991 - 1993 | NP20 |
| IT0004 | 1994 | NP10 |
| IT0004 | 1995 - 2000 | NP00 |

**Latvia**

| | | |
|---|---|---|
| LV0010 | 1991 | NPNP |
| LV0010 | 1992 | NP60 |
| LV | 1993 | NP60 |
| LV | 1994 | NP31 |
| LV | 1995 - 2000 | NP40 |

**Lithuania**

| | | |
|---|---|---|
| LT0015 | 1991 | NPNP |
| LT | 1992,1993 | NP20 |
| LT | 1994 | NP51 |
| LT | 1995,1996 | NP51 |
| LT | 1997 | NP20 |
| LT | 1998 - 2000 | NP00 |

**Netherlands**

| | | |
|---|---|---|
| NL | 1977 - 1979 | NP40 |
| NL | 1980 | NP61 |
| NL | 1981,1982 | NP40 |
| NL | 1983 - 1986 | NP40 |
| NL | 1987 - 1989 | NP30 |
| NL | 1990 - 1992 | 00**30** |
| NL | 1993 | 00**00** |
| NL | 1994 | 00**30** |
| NL | 1995,1996 | 00**00** |
| NL | 1997,1998 | 00**10** |
| NL | 1999,2000 | 00**00** |

**Norway**

| | | |
|---|---|---|
| NO | 1977,1978 | 00**01** |
| NO | 1979 | 00**00** |
| NO | 1980 | 00**01** |
| NO | 1981 | 00**42** |
| NO | 1982 - 1985 | 00**00** |
| NO | 1986 | 00**20** |
| NO | 1987 - 1993 | 00**00** |

| | | |
|---|---|---|
| NO | 1994 | 00**10** |
| NO | 1995,1996 | 00**50** |
| NO | 1997 - 2000 | 00**00** |

**Poland**

| | | |
|---|---|---|
| PL0001 - PL0004 | 1978 | 01**60** |
| PL0001 - PL0004 | 1979 | 01**40** |
| PL0001 - PL0004 | 1980 | 01**01** |
| PL0001 - PL0004 | 1981 | 01**61** |
| PL0001 - PL0004 | 1982 | 01**23** |
| PL0001 - PL0004 | 1983 - 1986 | 01NP |
| PL0001 - PL0004 | 1987 - 1990 | 01**71** |
| PL0001 - PL0004 | 1991 | 01**00** |
| PL0001 - PL0004 | 1992,1993 | 01**31** |
| PL0002 - PL0004 | 1994 | 01**00** |
| PL0002 - PL0004 | 1995,1996 | 01**00** |
| PL0002 - PL0004 | 1997 | 01**10** |
| PL0002 - PL0004 | 1998 - 2000 | 01**00** |
| PL0005 | 1995 - 2000 | 32**00** |

**Portugal**

| | | |
|---|---|---|
| PT | 1979 - 1981 | NP61 |
| PT | 1982 | NP40 |
| PT | 1983 - 1985 | NPNP |
| PT | 1986 | NP00 |
| PT | 1987,1988 | NPNP |
| PT | 1989 | NP73 |
| PT | 1990 | NPNP |
| PT | 1991,1992 | NP32 |
| PT | 1993 | NP00 |
| PT | 1994 | NPNP |
| PT | 1995,1996 | NP60 |
| PT | 1997,1998 | 0310 (4) |
| PT | 1997,1998 | 3410 (5) |
| PT | 1999,2000 | NP00 |

**Russian Federation**

| | | |
|---|---|---|
| RU | 1991,1992 | 00**11** |
| RU | 1993 | 00**20** |
| RU | 1994 | 00**30** |
| RU | 1995,1996 | 00**00** |
| RU | 1997,1998 | 00**20** |
| RU | 1999,2000 | 00**00** |

**Slovakia and Slovakian part of the former Czechoslovakia**

| | | |
|---|---|---|
| SK | 1978 - 1990 | NPNP |
| SK | 1991,1992 | NP01 |
| SK | 1993 | NP00 |
| SK | 1994 | NP10 |

| | | |
|---|---|---|
| SK | 1995,1996 | NP00 |
| SK | 1997 - 2000 | NP20 |

**Slovenia**

| | | |
|---|---|---|
| SI | 1996 - 1998 | NP00 |
| SI | 1999,2000 | 20NP |

**Soviet Union**

| | | |
|---|---|---|
| SU0001,SU0005,SU0009 | 1979 | NPID |
| SU0001,SU0005,SU0009 | 1980 | 00**83** |
| SU0001,SU0005,SU0009 | 1981 - 1983 | 00NP |
| SU0001,SU0005,SU0009 | 1984,1985 | 00**61** |
| SU0001,SU0005,SU0009 | 1986 | 00**21** |
| SU0001,SU0005,SU0009 | 1987 - 1991 | 00NP |
| SU | 1979 – 2000 | NPNP (6) |

**Spain**

| | | |
|---|---|---|
| ES | 1984,1985 | 00NP |
| ES | 1986 | 00**00** |
| ES | 1987,1988 | 00**32** |
| ES | 1989,1990 | 00NP |
| ES | 1991,1992 | 00**61** |
| ES | 1993 | 00**60** |
| ES | 1994 | 00**20** |
| ES | 1995 - 2000 | 00**00** |

**Sweden**

| | | |
|---|---|---|
| SE | 1978 | 3230 |
| SE | 1979 | 3200 |
| SE | 1980 | 3230 |
| SE | 1981 – 1983 | 3200 |
| SE | 1984 - 1985 | 3240 (8) |
| SE | 1986 | 3200 (8) |
| SE | 1987-1988 | 00NP(8) |
| SE | 1989 | 00**10** (8) |
| SE | 1990 – 1993 | 00**00** |
| SE | 1994 | 00**10** |
| SE | 1995 – 1999 | 00**00** |
| SE | 2000 | 00**10** |
| SE0012 | 1984 | 00NP |
| SE0012 | 1985 – 1986 | 00**00** |
| SE0012 | 1987 – 1988 | 00**10** |
| SE0012 | 1989 | 00**00** |

**Switzerland**

| | | |
|---|---|---|
| CH | 1978,1979 | NP30 |
| CH | 1980 | NP51 |
| CH | 1981,1982 | NP10 |
| CH | 1983 | NP51 |
| CH | 1984,1985 | NP10 |

| | | |
|---|---|---|
| CH | 1986 | NP30 |
| CH | 1987,1988 | NP10 |
| CH | 1989,1990 | NP00 |
| CH | 1991,1992 | NP30 |
| CH | 1993,1994 | NPNP |
| CH | 1995 - 2000 | NPNP |

**Turkey**

| | | |
|---|---|---|
| TR | 1993 | NP30 |
| TR | 1994 | NP40 |
| TR | 1995,1996 | NP20 |
| TR | 1997,1998 | NP40 |
| TR | 1999,2000 | NP00 |

**United Kingdom**

| | | |
|---|---|---|
| GB | 1977,1978 | 00**60** |
| GB | 1979 | 00**31** |
| GB | 1980 | 00**51** |
| GB | 1981,1982 | 00**00** |
| GB | 1983 | 00**51** |
| GB | 1984,1985 | 00**00** |
| GB | 1986 | 00**31** |
| GB | 1987,1988 | 00**20** |
| GB | 1989 - 1992 | 00**00** |
| GB | 1993 | 00**31** |
| GB | 1994 | 00**00** |
| GB | 1995,1996 | 00**00** |
| GB | 1997-2000 | 00**00** |

## Sulphur dioxide

### Czech Republic and the Czech sites in Czechoslovakia

The impregnated filter method has been applied for $SO_2$ from the start. The aerosol filter and the KOH impregnated filter were, however, not properly separated, which caused variable amounts of $SO_2$ to be absorbed in the aerosol filter. The data before 1989 are given as the sum of $SO_2$ and $SO_{4air}$ only, and can be found in the database.

### France

The French central laboratory was located at Institute National de Recherche Chimique Appliquee (IRCHA) until the summer 1990. After a reorganization of the network the responsibility was given to Ecole Nationale Superieure des Techniques Industrielles et des Mines de Douai.

Data before June 1990
The Langenbrügge comparison revealed a large spread in the data, particularly below 5 $\mu$g S/m$^3$. The laboratory applied the Thorin method for analysis at that time and changed to IC in 1988, which should have improved the results.

Data after June 1990
The $SO_2$ measurements were compared to the reference instrumentation through eleven months in 1998. The field comparison results indicate that the French data are too low for concentrations larger than 0.5 $\mu$g S/m$^3$, which corresponds to the performance in the laboratory comparison

### Germany, Fed. Rep.

The stability of exposed TCM samples is affected by temperature and light and have therefore been analysed at the various sampling sites shortly after exposure. This suggests that the data quality could be somewhat different from one site to the next. The winter data compare well with the $H_2O_2$ absorbing solution method and the KOH impregnated filter method. The TCM summer data gave lower results than this method, and annual data set gave somewhat lower results than the impregnated filter method for complete years (Aas et al., 2003).

### Hungary

Hungary applied the TCM method until 1997. Compared with the other results from the Langenbrügge comparison there was a systematic difference that increases rather strongly with concentration. Hungary did not take part in the Vavihill exercise, and comparisons with reference instrumentation at the Hungarian site are not yet initiated.

### Portugal

A on-site comparison took place 1996–1997. The results revealed rather high random errors. The field comparison indicated too high Portuguese measurements while the laboratory comparison suggested too low data.

### Russian Federation.

The measurements at RU 1 were carried out with an UV fluorescence monitor as a co-operation between Russian and Finnish scientists. Comparisons between the monitor and the Finnish filter-pack method, carried out at Finnish sites present a good correspondence.

**Soviet Union**

Most of the USSR EMEP samples were analysed in a central laboratory in Ventspils, in today’s Latvia. When the USSR was separated into independent states at the very beginning of the nineties, this laboratory was closed down permanently. The central laboratory in Ventspils never took part in the laboratory or field comparisons and the data quality therefore remains unknown for a larger part of the USSR sulphur dioxide measurements.

The samples from the sites SU 1, 5, and 9 were analysed by the Institute for Applied Physics which is today’s Institute of Global Climate and Ecology in Moscow.
The results from the Vavihill comparison were quite close the reference data set below 5 µg S/m$^3$. Above this concentration the Soviet/Russian results were about 20% too low. Both Russian and reference samples were analysed by NILU, and the error is therefore in the sampling device.

**Spain**

Spain took part in the Vavihill comparison with their $H_2O_2$ absorbing solution sampler. The data had more spread than expected.

A follow-up comparison at Zarra for about one year from May 2000 gave mostly data less than the detection limit at 0.5 µg S/m$^3$ from the Spanish laboratory while the reference measurements gave higher results. The Spanish results reported above the dl where far to high.

### Notes applied with the $SO_2$ flags

UK: unknown quality
NR: not relevant
NP: not participated
MoUV: Monitor, UV monitor
DOAS: DOAS has been applied, data should not be used
MoFP: Monitor flame photometry
(1): Consider to apply the Vavihill hydrogen peroxide/impregnated filter relation before the laboratory corrections.
(2): based on national comparisons
(3) the sums of sulphur dioxide and aerosol sulphate concentrations are available
(4): Based on the Langenbrügge data. For concentrations lower than 30 μg S/$m^3$.
(5): See comments and proposals for corrections given by Dr. M. Wallasch (see page 114).
(6): Based on the Langenbrügge data. For concentrations 5–50 μg S/$m^3$.

### Austria

| | |
|---|---|
| AT 1978 | 11**30** (1) |
| AT 1979,1980 | 11**11** (1) |
| AT 1981 - 1986 | 11**00** (1) |
| AT 1987,1988 | 11**20** (1) |
| AT 1989 - 1992 | 11**00** (1) |
| AT 1993 | 11**31** (1) |
| AT 1994 | 11**00** (1) |
| AT 1995 - 1998 | UKNR DOAS |
| AT0002 1999 - 2002 | NPNP |
| AT0030 1999 - 2003 | 22NR MoUV(2) |

### Belgium

| | |
|---|---|
| BE 1979 - 1991 | UKNR MoFP |

### Croatia

| | |
|---|---|
| HR 1991 - 1996 | 64NR |

### Czech republic and Czech part of the former Czechoslovakia

| | |
|---|---|
| CZ0001 1978 - 1988 | UKNR (3) |
| CZ 1989,1990 | 12**00** |
| CZ 1991 | 12**10** |
| CZ 1992 - 1994 | 12**00** |
| CZ 1995 - 1996 | 12**30** |
| CZ 1997 - 2001 | **12**10 |

### Denmark

| | |
|---|---|
| DK 1979,1980 | 01**00** |
| DK 1981 | 01**10** |
| DK 1982 - 1985 | 01**00** |
| DK 1986 | 01**20** |
| DK 1987 - 1992 | **00**00 |

| | |
|---|---|
| DK 1993 | **00**20 |
| DK 1994 - 2001 | **00**00 |

**Estonia**

| | |
|---|---|
| EE09 1997 - 2001 | NE**41** |
| EE11 1997 – 2001 | NRNR MoUV |

**Finland**

| | |
|---|---|
| FI 1978,1979 | 12**10** (1) |
| FI 1980 - 1988 | 12**00** (1) |
| FI 1989 | 12**40** (1) |
| FI 1990,1991 | 01**20** |
| FI 1992 - 1996 | 01**00** |
| FI 1997 | 01**11** |
| FI 1998 - 2001 | 01**00** |

**France**

| | |
|---|---|
| FR 1978 | 2330 (4) |
| FR 1979 | 2310 (4) |
| FR 1980 | 2300 (4) |
| FR 1981 | 2310 (4) |
| FR 1982 - 1985 | 2300 (4) |
| FR 1986 - 1988 | 2330 (4) |
| FR 1989,1990 | 2341 (4) |
| FR 1991,1992 | 20**00** (1) |
| FR 1993 | 20**30** (1) |
| FR 1994 | 20**10** (1) |
| FR 1995 - 1997 | 20**00** (1) |
| FR 1998 - 1999 | 20**41** (1) |
| FR 2000,2001 | 20**20** (1) |

**Germany (5)**

| | |
|---|---|
| DE 1978 – 2000 | 01NR |

**German Democratic Republic**

| | |
|---|---|
| DD 1978 - 1991 | NPNP |

**Greece**

| | |
|---|---|
| GR 1978,1979 | NP20 (1) |
| GR 1980 | NP40 (1) |
| GR 1981 | NP20 (1) |
| GR 1982,1983 | NP61 (1) |
| GR 1984 - 1986 | NP00 (1) |
| GR 1987,1988 | NP40 (1) |
| GR 1989,1990 | NP41 (1) |
| GR 1991 | NP10 (1) |
| GR 1992 | NP32 (1) |
| GR 1993 - 1995 | NP52 (1) |
| GR 1996 - 1999 | NP32 (1) |

### Hungary

| | |
|---|---|
| HU 1978 - 1996 | 63NR (6) |
| HU 1997 | NP00 |
| HU 1998 - 2001 | NPNP |

### Ireland

| | |
|---|---|
| IE0001 1980 | 01**41** |
| IE0001 1981 | 01**20** |
| IE0001 1982,1983 | 01**30** |
| IE0001 1984,1985 | 01**00** |
| IE0001 1986 | 01**20** |
| IE0001 1987 - 1990 | 01**00** |
| IE0001 1991 | 00**20** |
| IE0001 1992 - 2001 | **00**00 |
| IE0002 1991 - 1993 | NPNP |
| IE0002 1994 | NP20 |
| IE0002 1995 - 1997 | NP41 |
| IE0002 1998 - 2000 | NPNP |
| IE0002 2001 | NP00 |

### Italy

| | |
|---|---|
| IT0001 1983 - 1985 | NPNP |
| IT0001 1986 | NP20 |
| IT0001 1987 | NP00 |
| IT0001 1988 - 1990 | 00**00** |
| IT0001 1991,1992 | 00**30** |
| IT0001 1993,1994 | 00**40** |
| IT0001 1995 - 2001 | 00**00** |

### CEC

| | |
|---|---|
| IT0004 1985 - 1988 | NP**00** |
| IT0004 1989 - 2001 | NPNR MoUV |

### Lithuania

| | |
|---|---|
| LT 1991,1992 | NENP |
| LT 1993 | NE61 |
| LT 1994 | NE10 |
| LT 1995,1996 | NE73 |
| LT 1997,1998 | NE31 |
| LT 1999 | NE00 |

### Latvia

| | |
|---|---|
| LV 1991,1992 | NENP |
| LV 1993 | NE40 |
| LV 1994 | NE12 |
| LV 1995,1996 | NENP |
| LV 1997,1998 | NE21 |
| LV 1999,2000 | NE40 |
| LV 2001 | NE61 |

### Netherlands

| | |
|---|---|
| NL0002 1977 - 1985 | NP00 (1) |
| NL0002 1986 - 1993 | 11NR MoUV |
| NL0005 1977 - 1984 | NP00 (1) |
| NL0006 1977 - 1983 | NP00 (1) |
| NL0007 1983 - 1987 | NP00 (1) |
| NL0008 1987 | NPNP |
| NL0008 1988 - 1992 | 11NR MoUV |
| NL0009 1985 –1992 | 11NR MoUV |
| NL0010 1985 –1992 | 11NR MoUV |
| NL 1993 - 2001 | 11NR MoUV |

### Norway

| | |
|---|---|
| NO 1977 - 1981 | 00**20** |
| NO 1982 - 1985 | 00**00** |
| NO 1986 | 00**40** |
| NO 1987 - 2001 | 00**00** |

### Poland

| | |
|---|---|
| PL 1978 | NP11 (1) |
| PL 1979 | NP01 (1) |
| PL 1980 - 1983 | NP00 (1) |
| PL 1984,1985 | NPNP (1) |
| PL 1986 - 1990 | 00NP |
| PL 1991 | 00**20** |
| PL0001 - PL0003 1992 | 00**20** |
| PL0001 - PL0004 1993 | 00**31** |
| PL0002 - PL0004 1994 | 00**31** |
| PL0002 - PL0004 1995 - 1996 | 00**00** |
| PL0002 - PL0004 1997 - 1998 | 00**10** |
| PL0002 - PL0004 1999 - 2000 | 00**20** |
| PL0002 - PL0004 2001 | 00**00** |
| PL0005 1992 - 1994 | 20NP |
| PL0005 1995 - 1996 | **20**40 |
| PL0005 1997 - 1998 | **20**00 |
| PL0005 1999 - 2000 | **20**20 |
| PL0005 2001 | **20**00 |

### Portugal

| | |
|---|---|
| PT 1979 | 3400 |
| PT 1980 - 1985 | 34NP |
| PT 1986 - 1988 | 3400 |
| PT 1989 | 3423 |
| PT0001,PT0003,PT0005 1990 - 1992 | 34NP |
| PT0001,PT0003,PT0005 1993 | 3410 |
| PT0001,PT0003,PT0005 1994 - 1997 | 3461 |
| PT0004 1990 - 1997 | NPNR MoUV |

### Russian Federation

| | |
|---|---|
| RU0001 1992 - 2001 | **10**NR MoUV |

| | |
|---|---|
| RU0013 - RU0018 1992 | **23**20 |
| RU0013 - RU0018 1993 - 1994 | **23**40 |
| RU0013 - RU0018 1995 - 1998 | **23**00 |
| RU0013 - RU0018 1999,2000 | **23**20 |
| RU0013 - RU0018 2001 | **23**40 |

### Slovenia

| | |
|---|---|
| SI 1996 - 1998 | 00**00** |
| SI 1999,2000 | 00**11** |
| SI 2001 | 00**00** |

### Slovakia and Slovakian part of the former Czechoslovakia

| | |
|---|---|
| SK 1978 - 1988 | NPNP |
| SK 1989 - 2001 | NP00 |

### Soviet Union

| | |
|---|---|
| SU 1979 - 1989 | NPNR |
| SU0001 1989,1990 | 23NP |
| SU0001 1990,1991 | 10NR MoUV |
| SU0002 - SU0014 1990,1991 | 23NP |

### Spain

| | |
|---|---|
| ES 1986 | **34**10 |
| ES 1987 - 1992 | **34**30 |
| ES 1993 - 1996 | **34**00 |
| ES 1997,1998 | **34**01 |
| ES 1999 | **34**61 |
| ES 2000,2001 | **32**NR MoUV |

### Sweden

| | |
|---|---|
| SE 1977 - 1978 | 13**00** (1) |
| SE 1979 | 13**11** (1) |
| SE0001 - SE0008 1980 - 1984 | 13**00** (1) |
| SE0001 - SE0011 1985 - 1988 | 13**30** (1) |
| SE0002 - SE0011,SE0013 1989 - 1992 | 13**10** (1) |
| SE0002 - SE0011 1993 - 1998 | 00**00** |
| SE0002 - SE0011 1999 | 00**40** |
| SE0002 - SE0011 2000,2001 | 00**00** |
| SE0012 1984 | NPNP |
| SE0012 1985 - 1989 | 00**00** |

### Switzerland

| | |
|---|---|
| CH 1979 - 1987 | NP**00** (1) |
| CH0001 1988 | NP**10** (1) |
| CH0001 1989 | NP**30** (1) |
| CH0001 1990 - 2001 | NP**00** (1) |
| CH0002 1988 - 1991 | 32NR MoUV |
| CH0002 - CH0005 1992 - 2002 | 32NR MoUV |

### Turkey

| | |
|---|---|
| TR 1993- 1999 | 64NR |
| TR 2000,2001 | 00**00** (2) |

### United Kingdom

| | |
|---|---|
| GB 1977 | 10**03** |
| GB 1978 | 10**01** |
| GB 1979,1980 | 10**00** |
| GB 1981 | 10**31** |
| GB 1982 - 1986 | 10**00** |
| GB 1990 - 1992 | 10**00** |
| GB 1993 | 10**30** |
| GB 1994 | 10**00** |
| GB 1995 | 10**30** |
| GB 1996 - 1998 | 10**00** |
| GB 1999 | 10**30** |
| GB 2000,2001 | 10**10** |

### Yugoslavia

| | |
|---|---|
| YU 1977 - 1991 | 64NP |

## Comments to German EMEP data

### Note to be attached to the German EMEP data

author
Markus Wallasch (QA-Manager)
Langen (Germany), 07 March 2003

This note refers to:

- $SO_2$ measured by the TCM method for the period of time from the begin of measurements until end of year 2000.

- $NO_2$ measured by the Salzmann method the period of time from the begin of measurements until end of year 2001.

- Sulfur in Particles by the X-ray fluoreszens method in the period of time from the begin of measurements until 31. August 1999.

Parallel measurements over long periods suggest systematic errors for the above mentioned components. Therefore, it is recommended to rescale the data according to the equation given bellow before making comparisons with other measurements or model calculations. The details of the parallel measurements and on how the rescaling equations are derived will be given in an additional paper. It should be noted here, that these relations are to be understood in a statistical sense, i.e.they apply to a large ensemble with a considerable scatter of the "data points". So the rescaling may be most helpful, if one is interested in long term averages (for example, annual averages). They are of a more limited usefulness if individual values or short periods are considered. Therefore, it was decided to keep the data in the database as they are. Instead, it is left to the user of the data if he or she likes to follow the recommendation and rescale the data before use, as this decision may depend crucially on the purpose of the study.

Rescaling Equations:

for $SO_2$ : Y = 1.46 X

for $NO_2$ : Y = 1.50 X + ( 1.0 - 6.0 EXP( - 0.1 X^2 ) )
if negative values of Y occur, these must be discarded !

for Sulfur in Particles : Y = 1.50 X

where: X: old concentration in µg m^(-3), daily values
Y: new concentration in µg m^(-3), daily values
EXP: exponential function

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