EMEP/CCC-Report 6/2003

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

Data quality 2001, quality assurance, and field comparisons

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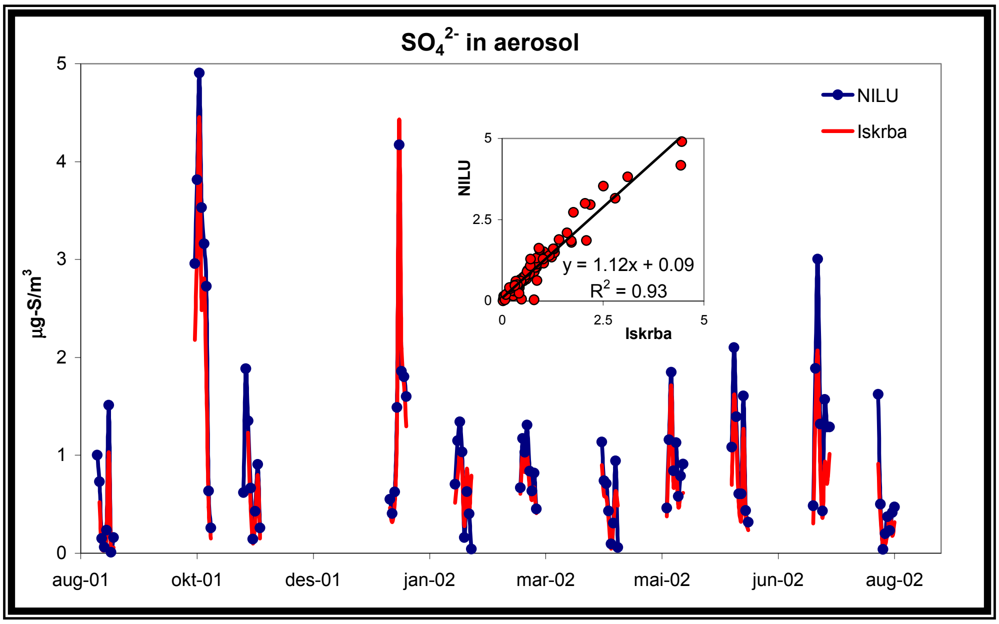

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Contents

Summary

This report is mainly concerned with the quality of the 2001 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 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, and the results are generally satisfactory with a few exceptions.

Results from the field comparisons in the Netherlands, Slovenia and Switzerland are presented in this report. In Dübendorf (CH) the monitors and reference measurements has fairly good correlation but are heavily biased. The monitors give higher concentrations than the reference for both SO_2 and NO_2. In Bilthoven (NL) the SO_2 monitor works satisfactory, but the NO_2 measurements were well correlated the first five months only followed by heavily biased results. In Iskrba (SI) the field intercomparison went well except for contamination problems for sumNH_4 and sumNO_3 during five months.

National organized field comparison of SO_2 have been performed in Germany and Turkey to compared the old TCM method and the recommended filterpack method. All these intercomparisons show that the TCM method underestimate the concentrations. There are major problems using the TCM method at very low concentrations as in Schauinsland. Results from parallel sampling of SO_2 at Illmitz (AT02) in 2001 using filterpack and UV fluorescence methods show that the monitor works satisfactory in Austria.

A new system has been developed to flag the main components in air and precipitation. The DQ flag has been divided in two two-digit numbers, one describing the performance in field intercomparisons and one describing the quality of the laboratory results. Each two-digit flag is furthermore defined by

letting the first digit represent the systematic error and the second digit the random error.

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 2001, 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 2001 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 to develop a new flagging system for all historical EMEP data 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 is 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

Since the start in 1978, the measurement frequency for all air and precipitation measurements of the main components has been daily; EMEP's measurement programme in 2001 is given in Table 1. It is now an opening for weekly precipitation sampling even though daily sampling still is preferable. There are a few sites with weekly precipitation sampling and even some with monthly data collection, which is not recommended. Further details on the sampling program and measurement frequency at the different sites are found in the data reports (Hjellbrekke, 2003). All participating countries, except Iceland and Lithuania, had complete measurement programmes for the main components in precipitation in 2001. The data completeness should be at least 90 per cent (Annex 1) and as seen from Table 2, most participants broadly met this requirement for the precipitation components.

The data completeness for the air components is less satisfactory. The main problem is evident from Table 3; the number of sites providing measurements of nitrogen components is far too low. Monitoring of nitrogen components is becoming increasingly important since the large reduction of sulphur dioxide emissions in Europe has increased the relative importance of nitrogen components as acidifying agents. Furthermore, nitrogen compounds do not only contribute to the acidification and eutrophication of ecosystems but are precursors of tropospheric ozone and they contribute to the total particulate matter. It is consequently highly desirable that more sites take up measurements of all nitrogen components in the programme.

Table 1: EMEP's measurement programme for 2001.

	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}	24 hours	daily
	Cd, Pb (first priority), Cu, Zn, As, Cr, Ni (second priority)	weekly	weekly
Gas + particles	$HNO_3(g)+NO_3^-(p)$, $NH_3(g)+NH_4^+(p)$	24 hours	daily
	POPs (PAH, PCB, HCB, chlordane, lindane, α-HCH, DDT/DDE)	48 hours	weekly
Precipitation	Amount, SO_4^{2-}, NO_3^-, Cl^-, pH, NH_4^+, Na^+, Mg^{2+}, Ca^{2+}, K^+, conductivity	24 hours/weekly	daily/weekly
	Hg, Cd, Pb (first priority), Cu, Zn, As, Cr, Ni (second priority)	weekly	weekly
	POPs (PAH, PCB, HCB, chlordane, lindane, α-HCH, DDT/DDE)	weekly	weekly

It is well known that filterpacks normally will give biased results for NO_3^-, HNO_3, NH_4^+ and NH_3, due to chemical reactions and loss of volatile substances from the aerosol filter, followed by a corresponding increase of substance on the impregnated filter. The concentrations of the individual components should therefore be used critically. In Table 3 it is seen that several countries report the individual concentrations; however, only sites in Hungary, the Netherlands (only for ammonia), and Italy use denuders where a quantitative separation of gas and particle is possible. It is highly recommended that more sites use denuders to separate particle and gas components.

Ozone measurements were carried out at "normal" EMEP sites but also at sites designated for ozone alone or in combination with other measurements not included in EMEP's programme.

Few Parties reported data on PM_{10} in 2001: AT, CH, DE, ES, NO and CEC. An increasing number of sites have, however, started PM_{10} measurements so this situation will probably change in the near future. Even less countries measure Na, Mg, Ca, Cl, and K in particles. It is, however, recommended to take up measurements of these ions, at least at the sites measuring PM_{10}.

For heavy metals the data capture is lower than for the main components, especially for air samples. However, several countries analyze heavy metals in air on one or two samples weekly from daily PM_{10} aerosol samples. 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.

Table 2: Completeness for precipitation components, 2001.

Code	mm	mm off	pH	SO_4	XSO_4	NH_4	NO_3	Na	Mg	Cl	Ca	K	cond
AT0002R	100.0	-	99.9	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.6	96.1	99.8
AT0004R	100.0	-	99.9	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8
AT0005R	100.0	-	91.8	91.7	91.7	91.8	91.7	91.8	91.8	91.7	91.7	90.4	91.8
CH0002R	100.0	-	99.8	94.3	94.3	94.3	94.3	94.3	94.3	94.3	94.3	94.3	99.6
CH0004R	99.7	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
CH0005R	100.0	-	99.8	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0	99.6
CZ0001R	99.7	-	99.9	99.6	99.6	99.8	99.6	91.3	91.3	99.6	99.8	91.3	99.8
CZ0003R	100.0	-	97.5	97.0	96.9	97.9	97.0	99.2	97.8	97.0	97.8	99.2	98.9
DE0001R	99.7	-	99.4	99.4	99.4	99.4	99.4	99.4	99.4	99.4	99.4	99.4	99.4
DE0002R	100.0	-	96.5	95.7	95.7	95.7	95.7	95.7	95.7	95.7	95.7	95.7	96.5
DE0003R	95.9	-	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8
DE0004R	100.0	-	98.7	99.3	99.3	99.3	99.3	99.3	99.3	99.3	99.3	99.3	98.7
DE0005R	99.7	-	99.7	99.7	99.7	99.7	99.7	99.7	99.7	99.7	99.7	99.7	99.7
DE0008R	99.7	-	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8
DE0009R	99.7	-	81.2	81.2	81.2	81.2	81.2	81.2	81.2	81.2	81.2	81.2	81.0
DK0005R	99.7	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	97.1	100.0	100.0
DK0008R	99.7	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.1	100.0	100.0
DK0022R	99.7	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	95.3	100.0	100.0
EE0009R	100.0	-	100.0	99.7	99.7	99.2	99.7	99.7	99.7	99.7	99.7	99.7	100.0
EE0011R	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
ES0007R	100.0	-	98.0	96.9	96.9	96.5	96.9	95.3	95.3	96.9	95.3	95.3	98.0
ES0008R	100.0	-	99.0	98.8	98.8	94.8	98.8	94.6	94.6	98.8	94.6	94.6	99.0
ES0009R	100.0	-	93.5	92.7	92.7	90.9	92.7	89.8	89.8	92.7	89.8	89.8	93.5
ES0010R	100.0	-	72.0	72.0	72.0	71.6	72.0	69.6	69.6	72.0	69.6	69.6	72.0
ES0011R	100.0	-	97.8	97.8	97.8	97.8	97.8	97.5	97.5	97.8	97.5	97.5	97.8
ES0012R	100.0	-	98.9	98.9	98.9	98.8	98.9	98.7	98.7	98.9	98.7	98.7	98.9
ES0013R	100.0	-	97.3	96.2	96.2	96.0	96.2	95.4	95.4	96.2	95.4	95.4	97.3
ES0014R	100.0	-	77.9	77.7	77.7	75.7	77.7	74.0	74.0	77.7	74.0	74.0	77.9
ES0015R	100.0	-	91.2	91.2	91.2	84.6	91.2	79.5	79.5	91.2	79.5	79.5	91.2
ES0016R	100.0	-	97.7	97.4	97.4	97.0	97.4	94.2	94.2	97.4	94.2	94.2	97.7
FI0004R	100.0	100.0	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5
FI0009R	99.7	100.0	99.6	99.4	99.4	97.8	99.4	99.4	99.4	99.4	99.4	99.4	99.6
FI0017R	100.0	100.0	99.6	99.4	99.4	99.4	99.4	99.4	99.4	99.4	99.4	99.4	99.6
FI0022R	100.0	100.0	99.7	98.8	98.8	98.8	98.8	98.8	98.8	98.8	98.8	98.8	99.7
FR0003R	100.0	-	89.7	87.9	87.9	88.0	87.9	87.9	87.9	87.9	87.9	87.9	89.7
FR0005R	100.0	-	93.7	91.9	91.9	92.1	91.9	91.9	91.9	91.9	91.9	91.9	93.7
FR0008R	100.0	-	97.7	97.6	97.6	97.6	97.6	97.6	97.6	97.6	97.6	97.6	97.7
FR0009R	100.0	-	96.5	94.5	94.5	95.3	94.5	94.5	94.5	94.5	94.5	94.5	96.5
FR0010R	100.0	-	93.2	92.3	92.3	92.7	92.3	92.3	92.3	92.3	92.3	92.3	93.2
FR0012R	100.0	-	93.6	92.0	92.0	92.4	92.0	92.0	92.0	92.0	92.0	92.0	93.6
FR0013R	100.0	-	97.9	96.0	96.0	97.1	96.0	96.0	96.0	96.0	96.0	96.0	97.9
FR0014R	100.0	-	96.7	95.6	95.6	95.9	95.6	95.6	95.6	95.6	94.3	95.6	96.7

Table 2, cont.

Code	mm	mm off	pH	SO_4	XSO_4	NH_4	NO_3	Na	Mg	Cl	Ca	K	cond
GB0002R	99.7	-	99.1	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
GB0006R	100.0	-	99.1	99.1	99.1	99.1	99.1	99.1	99.1	99.1	99.1	99.1	98.9
GB0013R	99.7	-	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.6
GB0014R	100.1	-	98.5	98.5	98.5	99.3	99.3	98.5	98.5	98.5	98.5	98.5	98.5
GB0015R	99.7	-	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.0
HR0002R	100.0	-	97.8	97.3	96.9	96.0	97.3	95.9	95.9	96.9	95.9	95.9	97.8
HR0004R	100.0	-	99.2	99.0	99.0	98.9	99.0	98.7	98.7	99.0	98.1	98.7	99.2
HU0002R	100.0	100.0	100.0	98.7	98.7	98.7	98.7	100.0	100.0	100.0	100.0	100.0	100.0
IE0001R	-	100.0	95.1	95.1	95.1	95.1	95.1	95.1	95.1	95.1	95.1	95.1	95.1
IE0002R	23.0	-	97.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	97.0
IE0003R	83.3	-	99.5	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.5
IE0004R	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
IS0002R	100.0	40.5	100.0	100.0	100.0	-	-	100.0	-	-	-	-	-
IT0001R	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
IT0004R	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
LT0015R	100.0	-	99.6	99.8	99.8	99.2	98.4	99.7	-	99.2	99.7	99.7	98.9
LV0010R	100.0	-	99.6	98.7	98.7	99.5	98.7	99.0	99.4	98.3	99.4	95.4	99.1
LV0016R	100.0	-	99.3	96.9	96.9	98.3	97.1	90.8	88.4	97.1	88.3	85.8	99.0
NL0009R	100.0	-	95.4	94.8	94.8	93.7	94.8	91.6	91.6	94.8	91.6	91.6	91.6
NO0001R	100.0	-	99.5	98.6	98.6	98.6	98.6	98.6	98.6	98.6	98.6	98.6	99.5
NO0008R	100.0	-	97.7	99.0	99.0	97.7	99.0	99.0	99.0	99.0	98.5	97.6	99.5
NO0015R	100.0	-	95.4	98.1	98.1	95.1	98.1	98.2	98.2	98.1	96.3	95.0	98.8
NO0039R	99.7	-	99.4	99.2	99.2	98.9	99.2	99.2	99.1	99.2	99.1	98.9	99.7
NO0041R	100.0	-	97.7	99.7	99.7	99.5	99.7	99.7	99.7	99.7	99.7	99.5	97.8
NO0055R	100.0	-	95.5	94.0	94.0	92.3	94.0	94.0	94.0	94.0	93.7	92.1	97.7
NO0099R	100.0	-	99.4	99.0	99.0	99.0	99.0	99.0	99.0	99.0	99.0	99.0	99.4
PL0002R	100.0	-	97.7	97.6	97.6	97.2	97.6	96.8	96.8	97.6	96.8	96.8	97.7
PL0003R	100.0	-	95.8	96.7	96.7	96.7	96.7	96.7	96.7	96.7	96.7	96.7	96.7
PL0004R	100.0	-	98.7	98.7	98.7	98.7	98.7	98.4	98.4	98.7	98.4	98.4	98.7
PL0005R	100.0	99.7	99.4	96.3	96.3	94.2	96.3	94.3	95.4	96.2	90.6	94.4	91.2
PT0001R	-	100.0	89.7	89.7	89.7	89.7	89.7	89.7	89.7	89.7	89.7	89.7	89.7
PT0003R	-	100.0	94.9	94.9	94.9	94.9	94.9	94.9	94.9	94.9	94.9	94.9	94.9
PT0004R	-	100.0	88.1	88.1	88.1	88.1	88.1	88.1	88.1	88.1	88.1	88.1	88.1
RU0001R	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	95.5	100.0	95.5	100.0	100.0
RU0013R	100.0	-	99.8	100.0	100.0	100.0	100.0	100.0	93.2	100.0	93.2	100.0	100.0
RU0016R	100.0	-	99.9	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
RU0018R	100.0	-	99.1	100.0	100.0	100.0	100.0	100.0	76.8	100.0	76.9	100.0	100.0
SE0002R	100.0	-	99.9	98.4	98.4	99.3	98.4	99.5	99.5	98.4	99.5	99.5	96.5
SE0005R	99.7	-	100.0	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.5
SE0011R	99.7	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.3
SK0002R	100.0	-	94.0	93.6	93.6	92.3	93.9	93.6	93.6	93.9	93.4	93.4	94.0
SK0004R	100.0	-	96.4	96.4	96.4	95.6	96.4	97.1	97.1	96.4	97.1	97.1	97.1
SK0005R	100.0	-	95.0	94.5	94.3	94.7	94.5	95.2	95.2	93.9	94.6	95.2	95.1
SK0006R	100.0	-	98.3	92.4	92.4	95.9	92.1	95.9	95.9	92.4	95.9	95.9	98.3
SK0007R	100.0	-	98.4	98.4	98.4	98.2	98.4	98.6	98.6	98.4	98.6	98.6	98.6
TR0001R	91.8	-	97.6	99.8	99.8	98.1	99.8	98.5	98.6	99.8	98.5	98.2	97.6
YU0005R	100.0	-	100.0	100.0	98.9	100.0	100.0	96.2	96.2	98.8	96.2	96.2	100.0
YU0008R	100.0	-	100.0	100.0	99.4	99.8	98.1	96.7	95.2	99.0	96.7	83.3	100.0

Table 3: Completeness for air components, 2001.

Code	SO_2	NO_2	O_3	SO_4	XSO_4	SNO_3	NO_3	HNO_3	SNH_4	NH_4	NH_3	PM_{10}	$PM_{2.5}$	SPM	Na	Ca	Mg	K	Cl
AT0002R	98.9	99.2	96.2	97.5	-	98.1	-	-	98.1	-	-	98.6	87.9	-	-	-	-	-	-
AT0004R	98.4	98.4	93.7	-	-	-	-	-	-	-	-	98.4	-	-	-	-	-	-	-
AT0005R	99.5	99.7	96.0	-	-	-	-	-	-	-	-	98.9	-	-	-	-	-	-	-
AT0030R	95.3	-	95.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0032R	-	-	99.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0033R	-	-	93.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0034G	-	-	93.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0037R	-	-	94.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0038R	-	-	97.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0040R	-	-	95.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0041R	-	-	99.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0042R	-	-	95.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0043R	-	-	95.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0044R	-	-	85.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0045R	-	-	95.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0046R	-	-	92.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT0047R	-	-	96.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BE0001R	-	76.9	92.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BE0032R	-	90.2	93.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BE0035R	-	91.0	94.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH0001G	80.8	71.0	-	100.0	-	-	-	-	-	-	-	-	-	92.3	-	-	-	-	-
CH0002R	98.1	99.2	94.7	97.5	-	-	-	-	-	-	-	99.5	100.0	-	-	-	-	-	-
CH0003R	-	98.9	95.1	-	-	-	-	-	-	-	-	100.0	-	-	-	-	-	-	-
CH0004R	100.0	100.0	95.2	-	-	-	-	-	-	-	-	99.5	99.7	-	-	-	-	-	-
CH0005R	97.5	97.3	93.4	99.5	-	99.7	-	-	99.7	-	-	100.0	-	-	-	-	-	-	-
CZ0001R	99.5	99.5	98.1	16.4	-	99.7	-	-	100.0	-	-	-	-	-	-	-	-	-	-
CZ0003R	100.0	95.3	98.5	16.7	-	99.7	-	-	98.9	-	-	-	-	-	-	-	-	-	-
DE0001R	48.5	97.8	88.3	48.5	-	48.5	-	-	48.5	-	-	93.4	-	-	-	-	-	-	-
DE0002R	58.9	48.8	92.4	-	-	-	-	-	-	-	-	95.3	95.1	-	-	-	-	-	-
DE0003R	96.4	-	95.2	96.4	-	95.9	-	-	96.2	-	-	93.4	80.5	-	-	-	-	-	-
DE0004R	50.1	99.7	94.8	54.5	-	50.1	-	-	50.1	-	-	98.4	97.3	-	-	-	-	-	-
DE0005R	48.5	-	95.9	-	-	-	-	-	-	-	-	99.5	-	-	-	-	-	-	-
DE0007R	96.7	91.5	95.6	98.9	-	96.7	-	-	98.4	-	-	97.8	-	-	-	-	-	-	-
DE0008R	72.1	99.5	95.5	-	-	-	-	-	-	-	-	97.8	-	-	-	-	-	-	-
DE0009R	99.7	96.7	96.7	99.5	-	99.5	-	-	97.0	-	-	99.7	-	-	-	-	-	-	-
DE0012R	-	-	77.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DE0017R	-	-	4.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DE0026R	-	-	92.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DE0035R	-	-	93.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DE0039R	-	-	90.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DE0042R	-	-	40.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DK0003R	81.9	-	-	81.4	80.8	75.6	-	-	81.4	-	-	-	-	-	81.1	-	-	-	-
DK0005R	93.7	-	99.4	93.2	92.9	92.6	-	-	93.4	-	-	-	-	-	93.4	-	-	-	-
DK0008R	96.4	98.1	-	94.5	94.5	94.8	-	-	95.9	-	-	-	-	-	94.8	-	-	-	-
DK0031R	-	-	96.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DK0032R	-	-	94.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DK0041R	-	-	98.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
EE0009R	95.3	97.5	98.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
EE0011R	96.4	94.2	95.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ES0007R	97.9	97.4	97.1	96.4	-	95.1	-	-	95.6	-	-	78.4	77.0	93.4	-	-	-	-	-
ES0008R	98.1	97.9	97.8	93.7	-	96.2	-	-	94.2	-	-	69.9	70.1	89.0	-	-	-	-	-
ES0009R	97.5	96.8	97.2	97.0	-	99.2	-	-	98.9	-	-	77.3	70.1	87.7	-	-	-	-	-
ES0010R	97.1	96.6	95.6	95.6	-	95.6	-	-	94.2	-	-	70.7	70.7	93.7	-	-	-	-	-
ES0011R	97.6	97.2	97.6	97.5	-	99.2	-	-	97.0	-	-	76.7	75.1	90.7	-	-	-	-	-
ES0012R	98.5	98.2	98.5	98.4	-	97.0	-	-	98.6	-	-	79.7	77.8	95.3	-	-	-	-	-
ES0013R	97.8	96.7	97.3	92.6	-	97.5	-	-	98.1	-	-	74.5	70.4	89.6	-	-	-	-	-
ES0014R	98.0	97.1	97.8	94.0	-	97.3	-	-	96.7	-	-	75.6	75.1	93.4	-	-	-	-	-
ES0015R	95.3	93.3	94.9	78.4	-	88.2	-	-	86.0	-	-	67.1	66.0	75.1	-	-	-	-	-
ES0016R	80.8	78.4	79.7	76.4	-	81.1	-	-	75.3	-	-	74.8	66.0	68.2	-	-	-	-	-
FI0009R	99.5	92.6	79.9	99.5	-	99.5	-	-	99.7	-	-	-	-	-	-	-	-	-	-
FI0017R	76.2	75.5	75.8	76.2	-	76.2	-	-	75.9	-	-	-	-	-	-	-	-	-	-
FI0022R	85.2	97.3	96.5	85.2	-	85.2	-	-	99.7	-	-	-	-	-	-	-	-	-	-
FI0037R	98.6	97.0	96.9	98.9	-	98.6	-	-	99.5	-	-	-	-	-	-	-	-	-	-
FR0003R	73.2	-	-	74.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FR0005R	99.7	-	-	97.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FR0008R	98.1	-	99.2	97.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FR0009R	99.2	-	96.1	95.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FR0010R	99.7	-	97.3	99.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FR0012R	92.3	-	91.6	91.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FR0013R	94.0	-	96.5	94.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FR0014R	100.0	-	86.1	98.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0002R	61.1	-	99.3	99.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0004R	64.9	-	-	83.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0006R	80.5	-	98.9	98.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0007R	64.9	-	-	81.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0013R	53.2	-	96.5	98.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0014R	57.5	-	79.4	97.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0015R	82.5	-	58.5	80.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0016R	53.4	-	-	66.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0031R	-	-	82.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0032R	-	-	99.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0033R	-	-	98.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0034R	-	-	97.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0036R	-	84.0	96.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0037R	-	88.4	53.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0038R	-	93.5	97.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0039R	-	-	98.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0043R	-	64.0	93.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0044R	-	-	97.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB0045R	-	87.5	90.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 3, cont.

Code	SO_2	NO_2	O_3	SO_4	XSO_4	SNO_3	NO_3	HNO_3	SNH_4	NH_4	NH_3	PM_{10}	$PM_{2.5}$	SPM	Na	Ca	Mg	K	Cl
GR0001R	90.1	88.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GR0002R	-	-	74.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HU0002R	95.1	98.1	92.9	95.3	-	-	95.3	95.3	-	95.3	95.3	-	-	-	-	-	-	-	-
IE0001R	99.7	100.0	-	99.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IE0002R	92.1	-	-	91.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IE0003R	-	-	-	57.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IE0004R	-	-	-	49.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IE0031R	-	-	99.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IS0002R	-	-	-	97.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IT0001R	94.8	95.6	90.6	94.8	-	-	94.8	94.8	-	94.8	94.8	-	-	-	-	-	-	-	-
IT0004R	100.0	98.1	98.7	62.2	-	-	62.2	-	-	61.4	-	62.2	62.2	61.4	-	-	-	-	-
LT0015R	98.6	99.2	98.9	-	-	98.4	-	-	98.9	-	-	-	-	-	-	-	-	-	-
LV0010R	96.4	99.7	80.4	99.7	-	99.7	99.7	-	98.9	98.9	-	-	-	-	-	-	-	-	-
LV0016R	88.8	92.3	-	92.3	-	90.7	92.3	-	92.3	92.3	-	-	-	-	-	-	-	-	-
MT0001R	-	-	92.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NL0009R	99.7	87.9	90.6	89.6	-	-	89.6	-	-	89.6	-	-	-	-	-	45.2	-	-	-
NL0010R	97.5	90.4	91.5	94.0	-	-	94.0	-	-	94.0	56.7	-	-	-	-	-	-	-	-
NO0001R	98.1	99.7	99.4	98.9	98.9	69.9	71.0	98.4	73.4	73.7	98.1	99.5	99.5	-	97.8	98.1	98.1	97.8	94.2
NO0008R	98.6	100.0	-	96.7	96.7	70.1	70.1	98.6	71.2	73.4	96.4	-	-	-	98.6	98.4	98.6	98.1	97.5
NO0015R	100.0	98.4	99.9	99.5	99.5	69.3	69.3	100.0	74.8	74.8	100.0	-	-	-	100.0	100.0	100.0	99.7	95.9
NO0039R	97.8	100.0	99.4	97.5	97.5	71.0	71.0	98.4	72.9	72.9	96.9	-	-	-	96.7	96.7	96.7	96.4	94.2
NO0041R	96.2	99.2	98.8	95.3	95.3	69.9	70.1	96.2	69.9	73.2	93.2	-	-	-	95.9	95.9	95.9	95.9	86.0
NO0042G	100.0	-	96.7	98.9	98.9	66.3	66.3	99.7	74.8	74.8	100.0	-	-	-	99.7	99.7	99.7	98.9	94.2
NO0043R	-	-	98.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NO0045R	-	-	97.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NO0048R	-	-	99.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NO0052R	-	-	99.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NO0055R	99.5	99.7	99.9	98.9	98.9	67.9	67.9	99.5	71.5	74.2	96.7	-	-	-	99.5	99.5	99.5	99.2	95.6
NO0056R	-	-	96.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NO0099R	-	-	-	-	-	-	-	-	-	-	-	88.4	96.1	-	-	-	-	-	-
PL0002R	95.1	78.1	99.7	95.1	-	94.8	95.1	-	88.5	88.5	-	-	-	-	-	-	-	-	-
PL0003R	100.0	100.0	99.7	100.0	-	100.0	100.0	-	100.0	100.0	-	-	-	-	-	-	-	-	-
PL0004R	100.0	100.0	99.9	100.0	-	99.7	100.0	-	100.0	100.0	-	-	-	-	-	-	-	-	-
PL0005R	96.4	98.4	96.6	98.9	-	99.2	-	-	99.5	-	-	-	-	-	-	-	-	-	-
PT0004R	-	-	93.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
RU0001R	87.4	-	-	89.9	-	-	89.9	-	-	89.9	-	-	-	-	-	-	-	-	-
RU0016R	92.6	-	70.6	93.2	-	-	93.2	-	-	93.2	-	-	-	-	-	-	-	-	-
RU0018R	81.4	-	49.5	81.4	-	-	81.4	-	-	81.4	-	-	-	-	-	-	-	-	-
SE0002R	99.7	99.5	97.5	99.7	-	97.5	-	-	98.6	-	-	-	-	100.0	-	-	-	-	-
SE0005R	99.7	99.7	-	98.1	-	98.4	-	-	99.7	-	-	-	-	100.0	-	-	-	-	-
SE0008R	100.0	99.2	-	98.4	-	-	-	-	-	-	-	-	-	97.8	-	-	-	-	-
SE0011R	97.3	99.2	99.7	99.5	-	97.5	-	-	96.7	-	-	-	-	99.2	-	-	-	-	-
SE0012R	-	-	87.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SE0013R	-	-	99.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SE0032R	-	-	95.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SE0035R	-	-	99.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SE0039R	-	-	96.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SI0008R	98.6	-	89.5	98.9	-	98.6	-	-	98.9	-	-	-	-	-	-	-	-	-	-
SI0031R	-	-	89.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SI0032R	-	-	94.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SI0033R	-	-	84.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SK0002R	99.2	98.1	-	99.2	-	-	99.2	99.2	-	-	-	-	-	-	-	-	-	-	-
SK0004R	98.6	99.7	98.0	99.7	-	-	99.7	98.6	-	-	-	-	-	-	-	-	-	-	-
SK0005R	98.1	99.5	-	99.5	-	-	99.5	98.1	-	-	-	-	-	-	-	-	-	-	-
SK0006R	93.4	97.5	97.0	98.1	-	-	98.4	93.4	-	-	-	-	-	-	-	-	-	-	-
SK0007R	98.1	99.5	77.8	99.5	-	-	99.5	98.1	-	-	-	-	-	-	-	-	-	-	-
TR0001R	71.5	69.9	-	71.5	-	71.5	71.5	71.5	-	71.2	68.5	-	-	-	-	-	-	-	-
YU0005R	90.4	88.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
YU0008R	93.4	83.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 4: Completeness for heavy metals in precipitation, 2001.

Code	mm	mm off	Cd	Pb	Cu	Zn	As	Cr	Ni	Fe	Co	V	Mn	Al	Hg
CZ0001R	99.7	-	92.2	97.8	-	-	-	-	97.8	-	-	-	-	-	-
CZ0003R	99.7	-	97.9	97.9	-	-	-	-	97.9	-	-	-	-	-	-
DE0001R	85.5	-	97.1	97.1	97.1	97.1	97.1	96.8	97.1	97.1	97.1	97.1	97.1	-	99.8
DE0002R	100.0	-	95.0	95.0	94.4	95.0	95.0	95.0	94.6	95.0	95.0	95.0	95.0	-	-
DE0004R	85.8	-	99.7	99.7	99.7	99.7	99.7	99.7	99.7	99.7	99.7	99.7	99.7	-	-
DE0009R	85.5	-	96.2	96.2	96.2	96.2	96.2	96.2	96.2	96.2	96.2	96.2	96.2	-	98.7
EE0009R	100.0	-	100.0	100.0	100.0	100.0	100.0	-	-	-	-	-	-	-	-
EE0011R	100.0	-	90.5	90.5	90.5	90.5	90.5	-	-	-	-	-	-	-	-
FI0009R	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0	-	-
FI0017R	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0	-	-
FI0053R	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0	-	-
FI0096R	96.7	-	-	-	-	-	-	-	-	-	-	-	-	-	100.0
IE0001R	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	-	100.0	100.0	100.0	100.0
IE0002R	100.0	-	-	76.9	-	76.9	-	-	76.9	-	-	76.9	76.9	-	-
IS0002R	40.5	-	98.4	98.4	98.4	98.4	98.4	98.4	98.4	98.4	-	98.4	98.4	-	-
IS0090R	99.8	-	-	97.8	97.8	97.8	97.8	97.8	97.8	97.8	-	97.8	97.8	-	-
LT0015R	100.0	-	100.0	100.0	100.0	100.0	-	-	-	-	-	-	-	-	-
LV0010R	100.0	-	100.0	100.0	100.0	100.0	-	-	-	-	-	-	-	-	-
LV0016R	100.0	-	100.0	100.0	100.0	100.0	-	-	-	-	-	-	-	-	-
NL0009R	81.1	-	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	-	-	-
NO0001R	100.0	-	99.9	99.9	-	99.9	-	-	-	-	-	-	-	-	-
NO0039R	100.0	-	100.0	100.0	-	100.0	-	-	-	-	-	-	-	-	-
NO0041R	100.0	-	99.9	99.9	-	99.9	-	-	-	-	-	-	-	-	-
NO0047R	94.8	-	99.4	99.4	99.4	98.4	99.4	99.4	99.4	-	99.4	-	-	-	-
NO0055R	98.1	-	99.9	99.9	-	99.9	-	-	-	-	-	-	-	-	-
NO0056R	100.0	-	97.7	99.9	-	99.9	-	-	-	-	-	-	-	-	-
NO0099R	100.0	-	99.2	99.2	99.2	99.2	99.2	99.2	99.2	-	99.2	99.2	-	-	100.0
PT0001R	-	100.0	28.0	28.0	28.0	28.0	-	-	28.0	-	-	-	28.0	-	-
PT0003R	-	100.0	36.9	36.9	36.9	36.9	-	-	36.9	-	-	-	36.9	-	-
PT0004R	-	100.0	40.0	40.0	40.0	40.0	-	-	40.0	-	-	-	40.0	-	-
SE0002R	96.7	-	-	-	-	-	-	-	-	-	-	-	-	-	100.0
SE0005R	100.0	-	93.9	100.0	93.9	93.9	100.0	100.0	100.0	-	-	100.0	93.9	-	100.0
SE0011R	96.7	-	-	-	-	-	-	-	-	-	-	-	-	-	100.0
SE0051R	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	-	100.0	-	-	-
SE0097R	98.9	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0	100.0	-	-
SK0002R	100.0	-	63.2	100.0	-	86.3	-	-	-	58.1	-	-	100.0	100.0	-
SK0004R	100.0	-	94.9	94.9	-	94.9	-	-	-	51.5	-	-	94.9	94.9	-
SK0005R	100.0	-	100.0	100.0	-	100.0	-	-	-	50.8	-	-	100.0	100.0	-
SK0006R	100.0	-	100.0	100.0	-	100.0	-	-	-	61.3	-	-	100.0	100.0	-
SK0007R	100.0	-	100.0	100.0	-	100.0	-	-	-	79.0	-	-	100.0	100.0	-

Table 5: Completeness for heavy metals in air, 2001.

Code	Cd	Pb	Cu	Zn	As	Cr	Ni	Fe	Co	V	Mn	Al	Hg	reHg
AT0002R	16.7	16.7	-	-	-	-	-	-	-	-	-	-	-	-
AT0004R	16.7	15.3	-	-	-	-	-	-	-	-	-	-	-	-
AT0005R	16.7	16.7	-	-	-	-	-	-	-	-	-	-	-	-
CZ0001R	15.9	15.9	-	-	-	-	-	-	-	-	-	-	-	-
CZ0003R	16.4	16.4	-	-	-	-	-	-	-	-	-	-	-	-
DE0001R	87.7	84.9	87.7	-	84.9	-	84.9	-	-	-	87.7	-	-	-
DE0002R	87.7	87.7	90.1	-	87.7	-	90.1	87.7	-	-	90.1	-	-	-
DE0003R	87.7	87.7	65.5	-	-	-	85.8	-	-	-	87.7	-	-	-
DE0004R	90.1	90.1	87.4	-	-	-	87.4	90.1	-	-	90.1	-	-	-
DE0005R	90.1	87.7	87.7	-	-	-	90.1	-	-	-	87.7	-	-	-
DE0007R	87.7	87.7	87.7	-	85.2	-	87.7	-	-	-	87.7	-	-	-
DE0008R	90.1	90.1	87.7	-	-	-	87.4	-	-	-	90.1	-	-	-
DE0009R	84.9	87.4	87.7	-	87.7	-	90.1	-	-	-	87.4	-	-	-
DK0003R	96.2	96.2	96.2	96.2	96.2	96.2	96.2	96.2	-	-	96.2	-	-	-
DK0005R	93.7	93.7	93.7	93.7	-	93.7	93.7	93.7	-	-	-	-	-	-
DK0008R	95.9	95.9	95.9	95.9	95.9	95.9	95.9	95.9	-	-	95.9	-	-	-
ES0008R	10.1	10.1	9.0	-	-	-	-	-	-	-	-	-	-	-
ES0009R	10.1	10.1	9.0	-	-	-	-	-	-	-	-	-	-	-
FI0036R	98.3	98.3	98.3	98.3	98.3	98.3	98.3	98.3	-	98.3	98.3	-	-	-
FI0096R	-	-	-	-	-	-	-	-	-	-	-	-	26.0	-
IS0091R	100.0	100.0	100.0	99.3	100.0	100.0	100.0	100.0	-	99.3	100.0	100.0	100.0	-
LT0015R	99.7	99.7	99.7	99.7	-	-	-	-	-	-	-	-	-	-
LV0010R	100.0	100.0	100.0	100.0	-	-	91.8	-	-	-	-	-	-	-
LV0016R	94.2	94.2	94.2	94.2	-	-	86.3	-	-	-	-	-	-	-
NL0009R	49.6	49.6	-	49.6	49.6	-	-	-	-	-	-	-	-	-
NO0042G	27.2	27.2	27.2	27.2	27.2	27.2	27.2	-	27.2	27.2	27.2	-	90.2	3.8
NO0099R	96.1	96.1	96.1	96.1	96.1	96.1	96.1	-	96.1	96.1	-	-	5.5	-
SE0002R	-	-	-	-	-	-	-	-	-	-	-	-	28.8	-
SK0002R	73.2	73.2	73.2	73.2	-	71.5	71.5	-	-	-	73.2	-	-	-
SK0004R	80.8	80.8	80.8	80.0	-	80.8	80.8	-	-	-	80.8	-	-	-
SK0005R	81.6	81.6	81.6	81.6	-	80.0	81.6	-	-	-	81.6	-	-	-
SK0006R	74.2	74.2	74.2	74.2	-	72.6	72.6	-	-	-	74.2	-	-	-
SK0007R	81.6	81.6	81.6	76.7	-	80.0	78.4	-	-	-	80.0	-	-	-

Data capture for POPs and VOC is not included in this report, but this information is found in the different data reports (Aas and Hjellbrekke, 2003; Solberg, 2003).

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 2001 are presented in Annex 2, 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 and Norway. In other countries, e.g. in Denmark and the Netherlands, 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, Netherlands (NL09).

In Annex 7 it is further discussed how CCC will flag data based on the ion balance test.

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 3.

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, more recent, field studies have been 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 and Spain (Schaug et al., 1998; Aas et al., 1999, 2000, 2001, 2002). Field comparisons in the Netherlands, Slovenia and Switzerland 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. For air measurements, the reference samples were collected two days every week, or in some cases during one week every month for practical reasons.

Large-scale field intercomparisons have additionally been organized in different campaigns with several countries sampling in parallel at one site. All the field intercomparisons performed so far in EMEP are summarized in Chapter 5.4.

Furthermore, results from field comparison done nationally are presented. Germany has measured SO_2 in parallel at DE3, DE7 and DE9 using the old TCM absorption technique and the filterpack method, which now is being used at most German sites. The same is the case for the Turkish EMEP site, Cubuk II where similar parallel measurements have been carried out. Moreover results from parallel sampling of SO_2 at Illmitz (AT02) in 2001 using filterpack and UV monitor will be presented.

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 Dübendorf, Switzerland

A field intercomparison at a Swiss EMEP site turned out to be difficult to accomplish because these sites are not visited as frequent as necessary to run the reference methods. A comparison of SO_2 and NO_2 was therefore performed at EMPA in Dübendorf. This is not a background site fulfilling the EMEP siting criteria, but it is one way of testing the methods used by Switzerland. This is not an active site and measurement instruments were installed solely for this field comparison. The method for measuring SO_2 and NO_2 (TEI 43C TL) at the Swiss EMEP sites are similar to the one tested in Dübendorf, i.e. UV-fluorescence and chemiluminescence (Horiba APNA 360) monitors respectively. Zero and span checks were performed daily (automatic), and the instruments were calibrated every second week.

The results from this comparison are found in Figure 1, Figure 2 and Table 6.

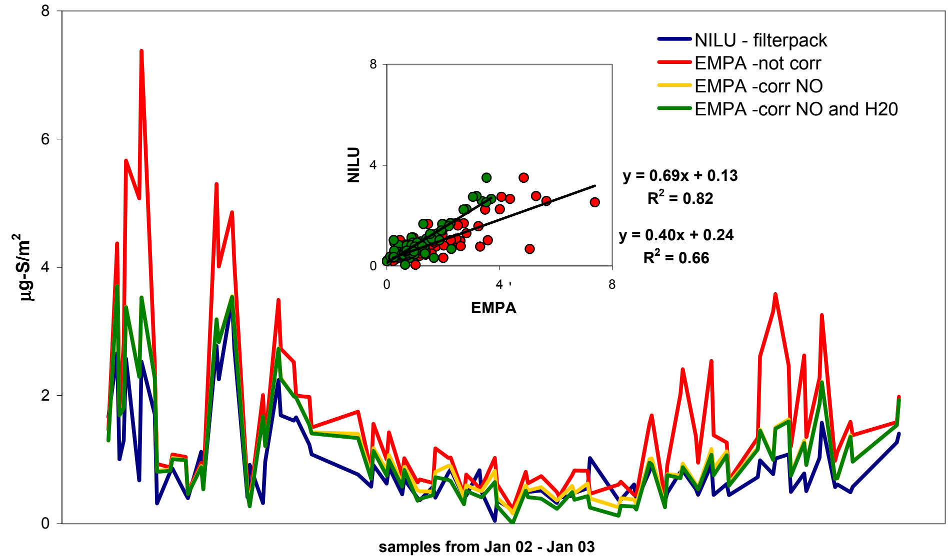

Figure 1: Comparison of the co-located SO_2 measurements at Dübendorf.

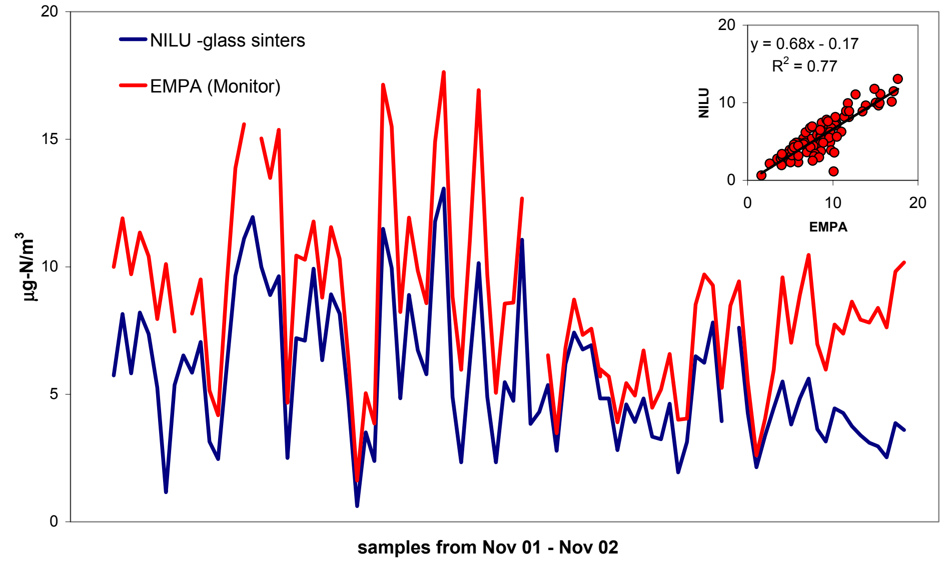

Figure 2: Comparison of the co-located NO_2 measurements at Dübendorf.

Table 6: Summary of results of co-located measurements at Dübendorf, in µg/m³.

	SO_2-S			NO_2-N
	not corrected	corr. for NO	corr. for NO & H2O	
Mean NILU	0.89	0.89	0.89	5.55
Mean EMPA:	1.64	1.16	1.10	8.45
Median NILU	0.68	0.68	0.68	4.90
Median EMPA:	1.17	0.90	0.83	8.39
Num pairs:	91	91	91	89
Average diff:	-0.75	-0.26	-0.21	-2.90
Median diff:	-0.50	-0.19	-0.13	-2.78
M.MAD:	0.52	0.29	0.36	1.91
CoV:	77 %	43 %	53 %	39 %

The SO_2 monitor has interference with NO and H_2O. A correction for this has been done. As clearly seen in Figure 1, NO has large influence on the results.

The monitors show higher concentrations for both NO_2 and SO_2. The concentrations are relatively high compared to a typical EMEP site and there should not be any problems with e.g. too high detection limit. In addition, the concentrations are not too high giving problems with the absorption capacity. For NO_2, the bias may to some extent be explained by the non-specific NO_2 detection with molybdenum converters. At EMEP sites it is recommended to determine NO_2 specifically as i.e. for the Cranox system used at Rigi and Jungfraujoch. For SO_2, the bias can possibly be due to interference from also other species than NO and H_2O (which is emitted from cars). E.g. m-xylene has shown to give interferences. Neither of these interferences is expected to have large influence on an EMEP background site.

5.1.4 Comparison at Bilthoven, the Netherlands

A field intercomparison at a Dutch EMEP site turned out be equally difficult to accomplish since these sites are not visited as frequently as necessary to run the reference methods from CCC. A comparison of SO_2, SO_4^{2-}, NO_2 and NO_3^- were therefore performed in Bilthoven where RIVM is situated. This is not a background site fulfilling the EMEP siting criteria, but it is one way of testing the methods in use by the Netherlands. The Dutch measurements of SO_2 and NO_2 are done using UV-fluorescence and chemiluminescence monitors respectively. The analysis of SO_4^{2-} and NO_3^- are done on PM_{10} aerosol samples.

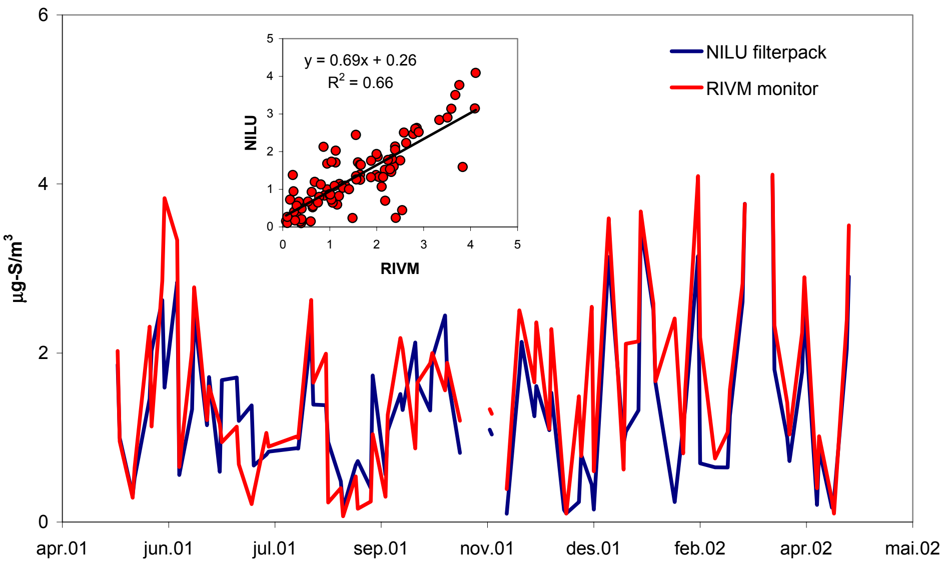

Figure 3: Comparison of the co-located SO_2 measurements at Bilthoven.

The regression between the two SO_2 measurements is acceptable when excluding the largest outliers. This gives a slope of 0.82 and not 0.69 as seen in Figure 3 for all data. The difference in the medians is about 15%, which is quite acceptable. The spread is somewhat higher, with a variation coefficient at 28%.

The comparison of the SO_4^{2-} measurements gives good results as seen in Figure 4. The difference in the average concentration is 16% and the spread, given as CoV, is 20%.

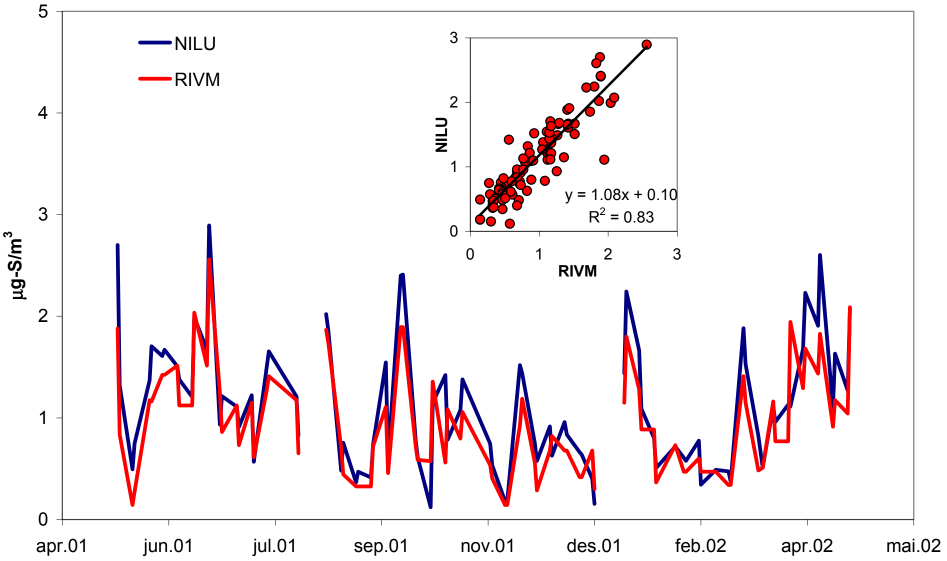

Figure 4: Comparison of the co-located SO_4^{2-} measurements at Bilthoven.

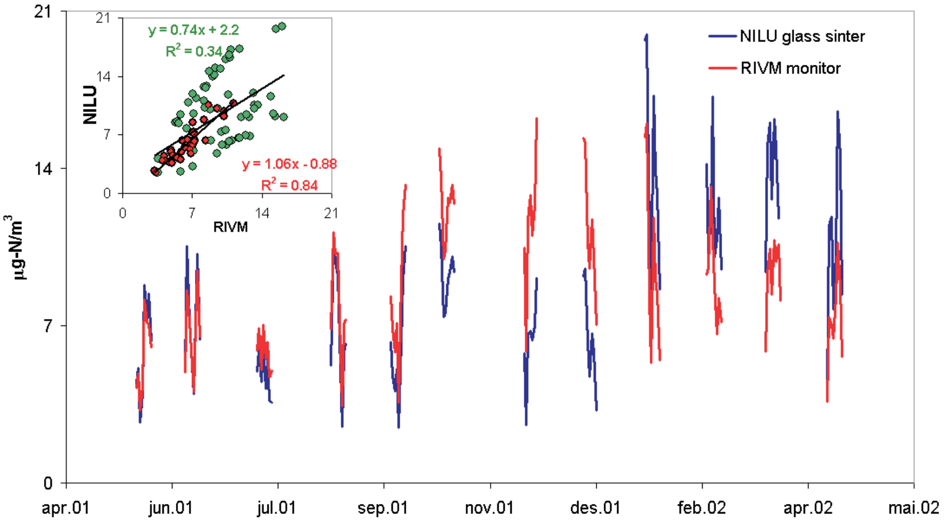

Figure 5: Comparison of the co-located NO_2 measurements at Bilthoven.

The NO_2 comparison went very well the five first months with almost 1:1 ratio between the two samplers; shown by red dots in the xy plot in Figure 5. During the next three months there was an overestimation by the monitor, which changed to underestimating the reference data the last four months. The over- and underestimations are equalizing each other and the average values are not much different from each other (Table 7). The spread and the average of the differences are large. The reason for the monitor behaviour is unclear, but there could have been a calibration problem in October 2001.

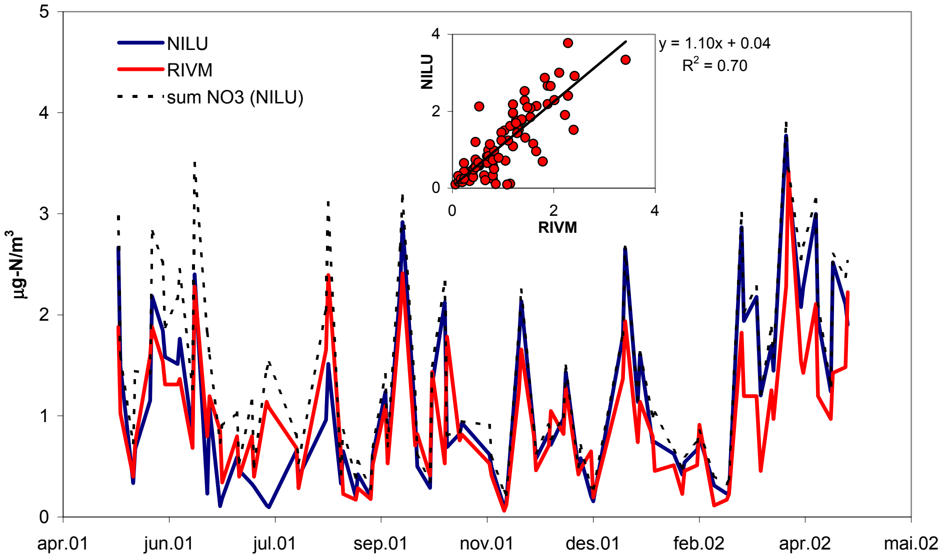

Figure 6: Comparison of the co-located NO_3^{2-} measurements at Bilthoven.

The correlation between the two series of NO_3^- aerosol concentrations is quite good as seen in Figure 6. The sum of nitrate and nitric acid from the impregnated filter in the reference is also included in the Figure. NO_3^- measurements on aerosol filters can be biased due to the volatile nature of NH_4NO_3, and it is seen that some of the large differences between the Dutch and the reference method for NO_3^- occur on days with the highest concentrations of nitric acid on the impregnated filter.

Table 7: Summary of results of co-located measurements at Bilthoven, in µg/m³.

SO2-S	filterpack		monitor
Mean ref:	1.35		1.57
Median ref:	1.25		1.41
Num pairs:		89	
Average of diff:		-0.22	
Median of diff:		-0.19	
M.MAD:		0.35	
CoV:		28%	

SO4-S	filterpack		RIVM
Mean ref:	1.13		0.95
Median ref:	1.08		0.85
Num pairs:		90	
Average of diff:		0.18	
Median of diff:		0.18	
M.MAD:		0.22	
CoV:		20 %	

NO2-N	filterpack		monitor
Mean ref:	8.63		8.74
Median ref:	8.41		8.35
Num pairs:		92	
Average of diff:		-0.11	
Median of diff:		-0.45	
M.MAD:		3.53	
CoV:		42%	

NO3-N	filterpack		RIVM
Mean ref:	1.14		1.00
Median ref:	0.83		0.82
Num pairs:		90	
Average of diff:		0.14	
Median of diff:		0.11	
M.MAD:		0.32	
CoV:		39 %	

5.1.5 Comparison at Iskrba, Slovenia

Slovenia has relatively recently started to measure main components in air using the reference methodology. A field comparison between the Slovenian filterpack sampler and a reference sampler from the CCC was organised from August 2001 to August 2002 in order to ensure that these measurements are running as intended. The results are found in Figure 7 to Figure 10 and in Table 8.

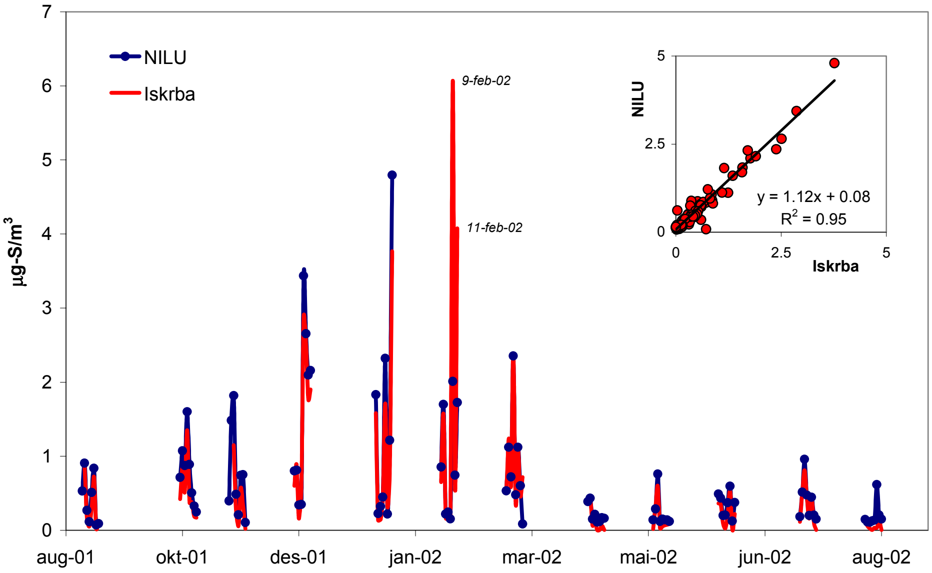

Figure 7: Comparison of the co-located SO_2 measurements at Iskrba.

The correlation between the two SO_2 measurements is good. There were two big outliers, 9th and 11th February, that are not included in the statistical calculations. The SO_4 comparison likewise gave satisfactory results as seen from Figure 8 and Table 8.

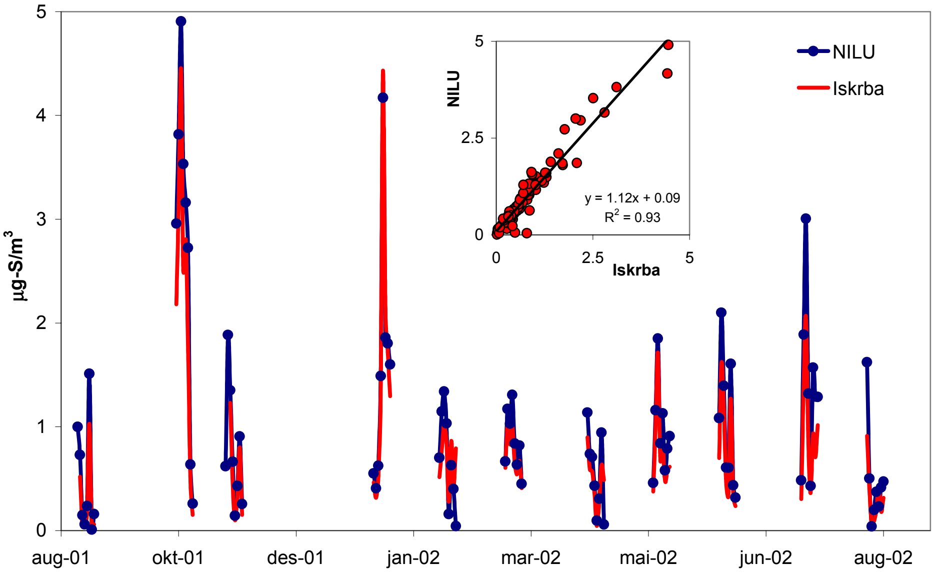

Figure 8: Comparison of the co-located SO_4 measurements at Iskrba.

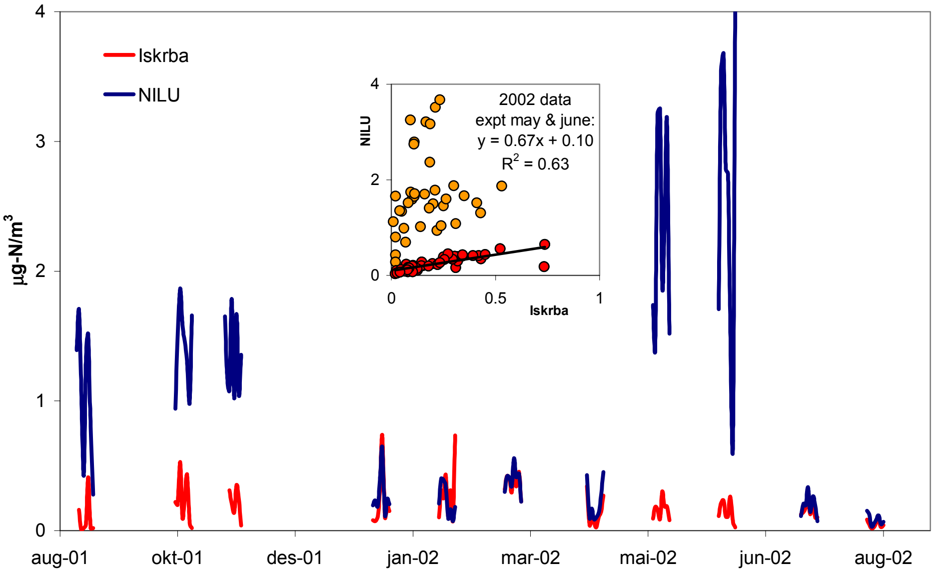

Figure 9: Comparison of the co-located sumNO₃ measurements at Iskrba.

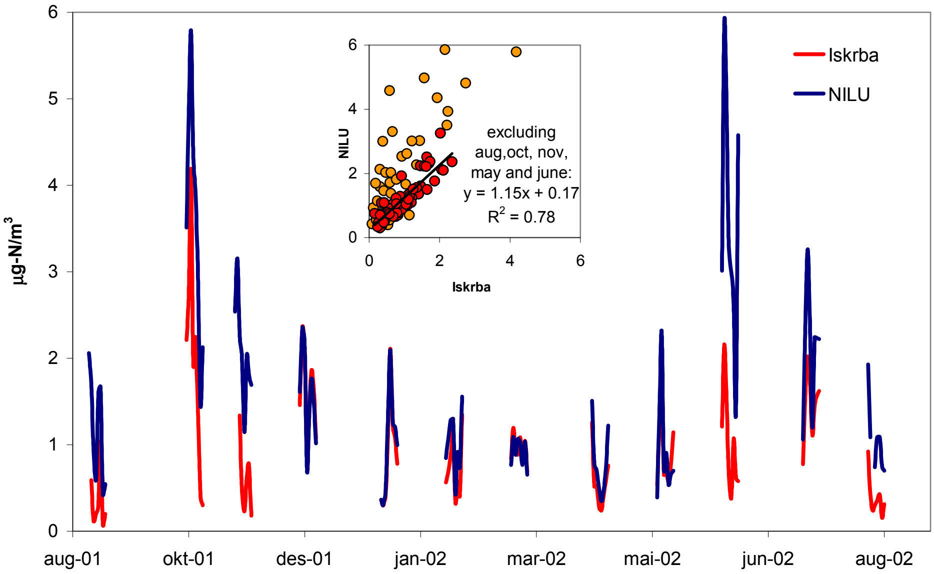

Figure 10: Comparison of the co-located sumNH$_x$ measurements at Iskrba.

The comparison of sumNH$_x$ and sumNO$_3$ gave CCC results that were much higher than the national in 2001 and in May–June in 2002, Figure 9. There has been a contamination at the CCC, this is seen from the field blanks for NO$_3^-$ and NH$_4^+$ these months. Consequently, the statistic evaluation of the comparison is based only on the months with normal field blank values.

Table 8: Summary of results of co-located measurements at Iskrba, in μg/m^3.

SO2-S	NILU	Iskrba
Mean ref:	0.65	0.51
Median ref:	0.38	0.30
Num pairs:	92	
Average of diff:	0.14	
Median of diff:	0.11	
M.MAD:	0.09	
CoV:	24 %	

SO4-S	NILU	Iskrba
Mean ref:	1.04	0.85
Median ref:	0.72	0.59
Num pairs:	86	
Average of diff:	0.19	
Median of diff:	0.15	
M.MAD:	0.12	
CoV:	15 %	

sum NH4-N*	NILU	Iskrba
Mean ref:	1.21	0.96
Median ref:	1.07	0.88
Num pairs:	55	
Average of diff:	0.25	
Median of diff:	0.18	
M.MAD:	0.28	
CoV:	26 %	

* Only 7 month of the data is used

sum NO3-N*	NILU	Iskrba
Mean ref:	0.23	0.20
Median ref:	0.20	0.13
Num pairs:	48	
Average of diff:	0.03	
Median of diff:	0.04	
M.MAD:	0.06	
CoV:	30 %	

* Only 6 month of the data is used

5.2 Comparison at of SO_2 measurements (filterpack and UV fluorescence monitor) at Illmitz, Austria, 2001

Austria started the recommended filterpack method at Illmitz in 2001. Additionally they have a TEI 43BS UV-fluorescence monitor in parallel to fulfil their obligations to the EU directives, changed to TE43 CTL December 15th. At the other Austrian sites they have monitors only, and this parallel sampling at AT02 is therefore very useful to document the performance of the Austrian SO_2 measurements. The SO_2 monitors have daily zero and span checks (automatic). Routine visits of the station are biweekly, calibration including linearity checks is minimum twice a year.

As seen in Figure 11 and Table 9 the correlation between the measurements is good. The averaging periods were eight hours different; the filterpack sampled from 08.00 to 08.00 and the UV-fluorescence measurements were averaged from 00.00 to 00.00. The slope is nevertheless very good, but there is a general underestimation of the concentrations by the monitor. The spread is somewhat high, but parts of this can be explained by the different averaging periods.

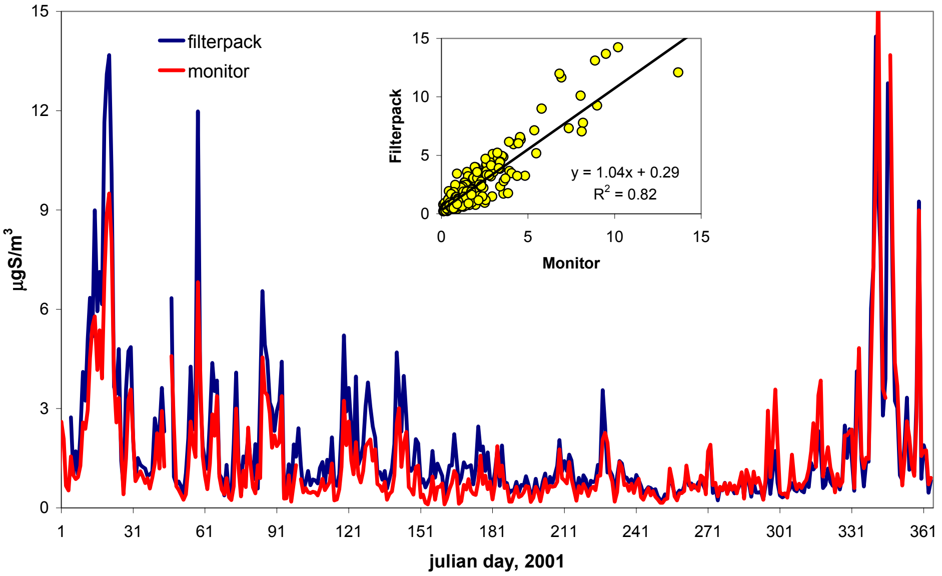

Figure 11: Comparison of the co-located SO_2 measurements at Illmitz.

Table 9: Summary of results of co-located SO_2 measurements at AT02, in $\mu gS/m^3$.

	Recommended filterpack	TEI 43BS
Mean:	1.86	1.50
Median	1.09	0.87
Num pairs:	354	
Average of diff:	0.36	
Median of diff:	0.24	
M.MAD:	0.46	
CoV:	42 %	

5.3 Comparison of SO_2 measurements (filterpack and TCM) in Germany and Turkey

Both Germany and Turkey have used the TCM absorption technique for measuring SO_2 in air. The German SO_2 data are among the longest SO_2 records in Europe and gives a valuable documentation of the regional changes in the concentrations of this component on the Continent; the extraction of reliable information from these data series is therefore most important.

There are two problems with the TCM data; firstly they have a detection limit that seems to reach 2–3 µg S/m^3 with noise and random concentrations below the detection limit. Secondly the TCM absorbing solution is unstable during the warm season giving concentrations close to zero, e.g. as demonstrated by the Schauinsland field comparison in 1998 (Aas et al., 1999).

Both Germany and Turkey apply the recommended filterpack method at their EMEP sites today. In connection with the change of method both countries carried out parallel measurements for one year, Germany at three sites, Schauinsland (DE3), Neuglobsow (DE07) and Zingst (DE9); and Turkey at Cubuk II.

The results are presented as time series in Figure 12–Figure 15, and in Table 10. All comparison results show that the TCM method underestimates the concentrations when compared with the filterpack results for complete years. The Schauinsland results in Figure 12 demonstrate the problems with the TCM method. The results from Neuglobsow and Zingst compare better with the filterpack results even at low concentrations.

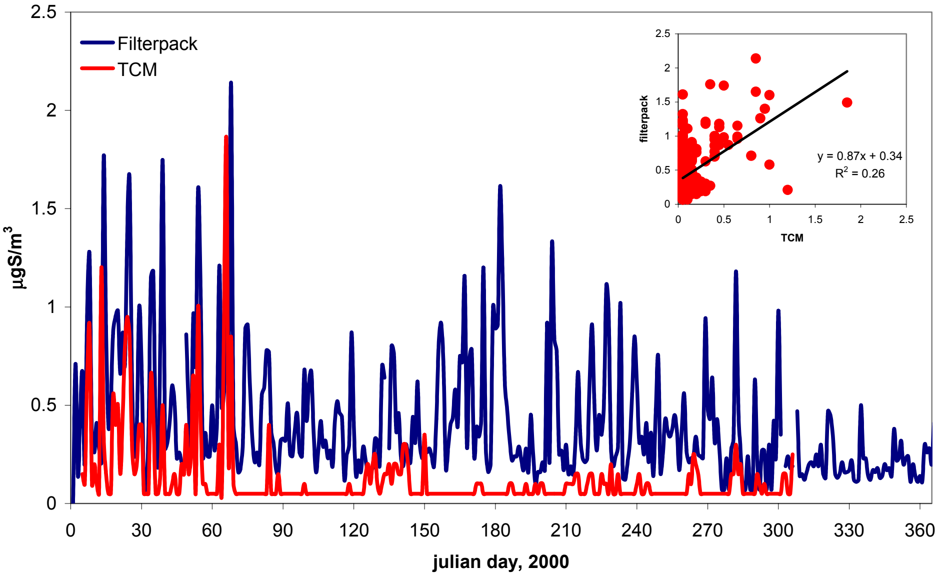

Figure 12: Comparison of the parallel SO_2 measurements at Schauinsland, DE03.

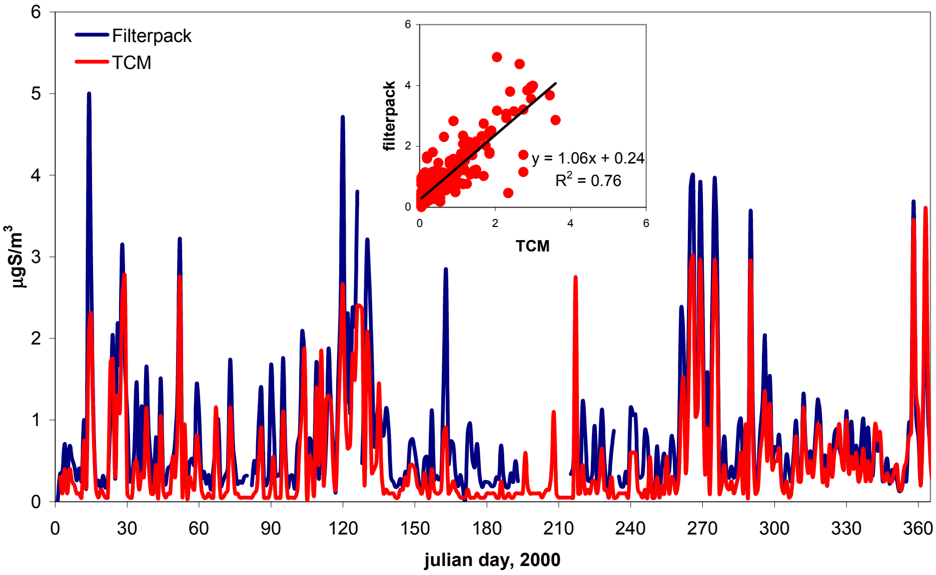

Figure 13: Comparison of the parallel SO_2 measurements at Neuglobsow, DE07.

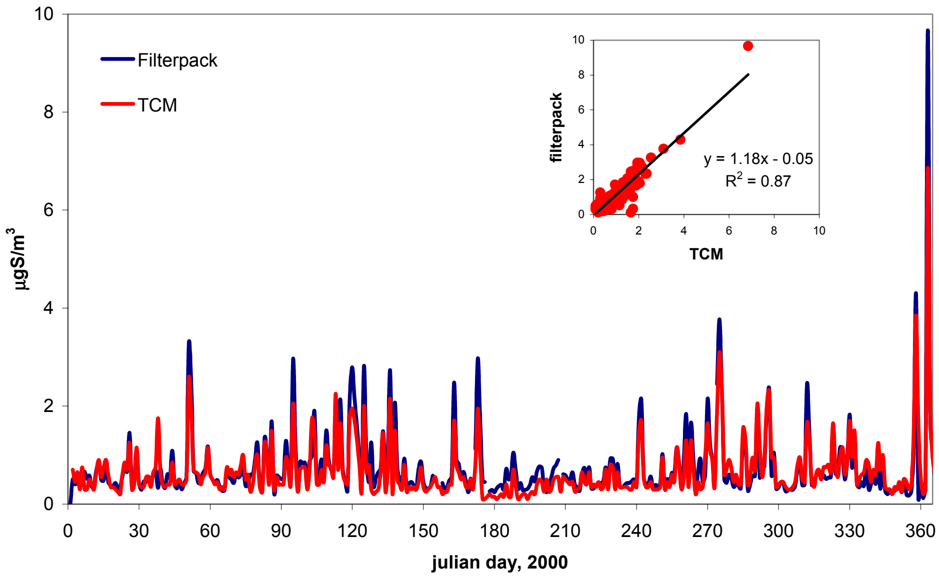

Figure 14: Comparison of the parallel SO_2 measurements at Zingst, DE09.

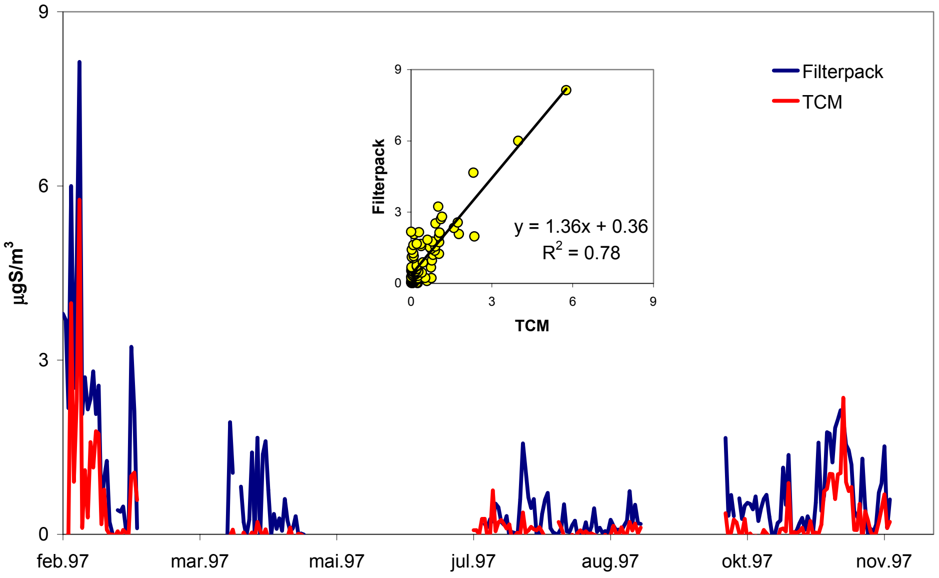

Figure 15: Comparison of the parallel SO_2 measurements at Cubuk II, TR01.

Table 10: Summary of results of co-located SO_2 measurements at in Germany and Turkey, in µgS/m^3.

	DE3		DE7		DE9		TR1	
	all data	data > DL	all data	data > DL	all data	data > DL	all data	data > DL
Mean filterpack:	0.46	0.56	0.80	0.91	0.75	0.75	0.98	1.33
Mean TCM:	0.13	0.27	0.52	0.63	0.68	0.68	0.46	0.74
Percent difference	72 %	52 %	35 %	31 %	9 %	9 %	53 %	44 %
Median filterpack:	0.33	0.37	0.50	0.65	0.52	0.52	0.51	0.93
Median TCM:	0.05	0.15	0.25	0.35	0.50	0.50	0.13	0.39
Percent difference	85 %	59 %	50 %	46 %	4 %	4 %	75 %	58 %
Num pairs:	299	108	341	281	357	357	101	60
Average of diff:	0.33	0.28	0.28	0.29	0.07	0.07	0.52	0.59
Median of diff:	0.25	0.20	0.22	0.22	0.05	0.05	0.32	0.36
M.MAD:	0.21	0.22	0.18	0.24	0.16	0.16	0.47	0.60
CoV:	63 %	61 %	36 %	36 %	31 %	31 %	93 %	65 %

The problem using the TCM method is more severe in the summer, clearly seen at TR01.

The Langenbrügge field comparison (Nodop and Hanssen, 1986) organised during the winter 1984–1985 indicated that the TCM method compared very well with the filterpack methods under the concentration levels and outdoor temperatures at that time. The concentrations during this period were hardly below 2 µg/m^3. Winter data from periods when the SO_2 concentrations were higher than today could therefore be acceptable without corrections. Clean winter historical data sets could probably be extracted by use of time-series graphs and histograms. Summer data and data from sites with very low concentrations as at Schauinsland the recent years should probably not be used. Wallasch (Annex 5) has proposed a factor (1.46) to be applied on all historical German (TCM) SO_2 data.

5.4 Summary of the results from the field comparisons

Two large-scale field comparisons of SO_2 and SO_4 in air have been organized by EMEP, at Langenbrügge (DE2) in northern Germany in 1985 (Nodop and Hanssen, 1986) and at Vavihill (SE11) in southern Sweden in 1990 (Semb et al., 1991). One large intercomparison of NO_2 was held in Kleiner Feldberg in Germany in 1991 (Fähnrich et al., 1993). 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 as described in the previous Chapters. Additional field comparisons organised by the Parties also give highly valuable documentation on the measurement data quality. The comparisons presented in this Chapter are used for flagging the air measurements in EMEP as described in Chapter 7.2.2.

Table 11: A summary of all the field comparisons of SO_2 measurements.

Langenbrügge, **1986** *Ref. method is NILU's measurements, outliers are not included*

Country:	DK	HU	DE	GB	FI	SE	FR
Method	KOHimp	TCM abs	TCM abs	H202 abs	H202 abs	H202 abs	H202 abs
Mean (ref):	11.93	11.59	11.72	11.87	12.43	11.59	16.52
Mean:	13.00	9.38	13.1	12.10	14.02	12.82	13.93
Median (ref):	5.80	5.80	5.90	6.00	5.50	5.80	10.50
Median:	7.90	5.60	8.00	7.20	8.10	5.90	8.20
Num pairs:	67	71	70	69	70	71	45
Average of diff:	-1.07	2.20	-1.38	-0.23	-1.58	-1.23	2.59
Median of diff:	-0.60	0.80	-1.05	-0.80	-1.60	0	1.70
median % err	-10 %	14 %	-18 %	-13 %	-29 %	0 %	16 %
M.MAD:	1.19	2.22	1.41	1.04	2.22	1.93	2.37
CoV:	20 %	38 %	24 %	17 %	40 %	33 %	23 %
slope:	1.03	1.38	1.01	0.88	1.04	1.17	1.11

National internal field intercomparions *Ref. method is the filterpack sampler*

Country:	NO	FI		TR		DE		AT
methods and year	FP/FP 1996	UV/FP all data	1993-2000 data >DL	TCM/FP, 1997 all data	data >DL	TCM/FP, 2000 all data	data >DL	UV/FP 2001
Mean (ref):	0.47	0.84	0.99	0.98	1.33	0.65	0.76	1.86
Mean:	0.53	0.87	1.07	0.46	0.74	0.44	0.59	1.50
Median (ref):	0.33	0.37	0.40	0.51	0.93	0.44	0.52	1.09
Median:	0.38	0.40	0.45	0.13	0.39	0.25	0.40	0.87
Num pairs:	16	7210	6734	101	60	846	607	354
Average of diff:		-0.02	-0.08	0.52	0.59	0.22	0.18	0.36
Median of diff:		-0.04	-0.05	0.32	0.36	0.17	0.11	0.24
median % err		-11 %	-13 %	63 %	39 %	39 %	21 %	22 %
M.MAD:	0.04	0.13	0.12	0.47	0.60	0.22	0.22	0.46
CoV:	12 %	36 %	30 %	93 %	65 %	50 %	43 %	42 %
slope:		0.86	0.86	1.36	1.39	1.03	1.10	1.04

Table 11, cont.

Vavihill, 1991 *Ref. method is the median of all the impr. filter samplers*

Country	AT	CZ	CZ,2	DE	ES	GB	IR	IT	NO	NO,2	SE	SE,2	SF	SF,2	SU
method	H202 abs	Impr filter	Impr filter	TCM abs	H202 abs	H202 abs	Impr filter	denuder	Impr filter	Impr filter	H202 abs	Impr filter	H202 abs	Impr filter	Impr filter
Mean (ref):	3.23	3.26	3.26	3.29	3.19	3.13	3.26	3.91	3.13	3.13	3.13	3.26	3.17	3.32	3.31
Mean:	4.59	2.85	2.93	3.84	4.13	4.35	3.65	4.59	3.14	3.26	5.12	3.38	4.38	3.70	2.98
Median (ref):	2.08	2.07	2.07	2.08	1.77	2.07	2.07	2.72	2.07	2.07	2.07	2.07	2.07	2.08	2.05
Median:	3.08	1.89	1.87	2.53	2.05	3.25	2.48	3.15	2.10	2.27	3.85	2.31	3.38	2.35	1.75
Num pairs:	49	42	42	47	38	51	42	33	51	51	51	42	50	41	40
Average of diff:	-1.36	0.41	0.33	-0.55	-0.94	-1.22	-0.39	-0.68	-0.01	-0.13	-1.99	-0.13	-1.21	-0.38	0.32
Median of diff:	-1.01	0.24	0.23	-0.4	-0.74	-1.03	-0.41	-0.49	-0.07	-0.05	-1.57	-0.08	-1.11	-0.31	0.23
median % err	-49 %	12 %	11 %	-19 %	-42 %	-50 %	-20 %	-18 %	-3 %	-2 %	-76 %	-4 %	-54 %	-15 %	11 %
M.MAD:	0.56	0.22	0.21	1.05	0.76	0.76	0.44	0.44	0.22	0.22	0.95	0.35	0.5	0.31	0.62
CoV:	27 %	11 %	10 %	51 %	43 %	37 %	21 %	16 %	11 %	11 %	46 %	17 %	24 %	15 %	30 %
slope:	0.76	1.12	1.05	0.66	0.84	0.82	0.91	0.89	0.93	0.92	0.72	0.94	0.78	0.93	1.14

Co-located sampling, reference method (impr. filters) compared with national method at the EMEP site

Site	GB2	IE2	PL5	PT4	DE3	DE3	FR8	CZ3	HR04	ES12	ES12	NL	SI08	CH
method at site	H202 abs	Impr filter	Impr filter	H202 abs	Impr filter	TCM abs	H202 abs	Impr filter	TCM abs	H202 abs	monitor	monitor	Impr filter	monitor
year	1997	1997	1998	1997	1998	1998	1998	1999	2000	2000	2000	2001	2001	2002
Mean (ref):	0.62	0.60	1.39	1.79	0.54	0.54	0.74	1.57	0.72	0.45	0.45	1.35	0.65	0.89
Mean:	0.86	0.57	1.22	2.69	0.64	0.21	0.81	2.21	0.15	0.45	0.52	1.57	0.51	1.10
Median (ref):	0.31	0.22	0.68	0.98	0.36	0.36	0.44	0.95	0.50	0.40	0.40	1.25	0.38	0.68
Median:	0.43	0.29	0.70	1.60	0.38	0.05	0.57	1.56	-	0.25	0.45	1.41	0.30	0.83
Num pairs:	63	87	95	101	93	88	94	79	77	86	85	89	92	91
Average of diff:	-0.24	0.03	0.16	-0.90	-0.1	0.33	-0.07	-0.63	0.57	0	-0.08	-0.22	0.14	-0.21
Median of diff:	-0.12	-0.02	-0.03	-0.54	-0.08	0.27	-0.07	-0.51	0.36	0.03	-0.07	-0.19	0.11	-0.13
median % err	-39 %	-9 %	-4 %	-55 %	-22 %	75 %	-16 %	-54 %	72 %	8 %	-18 %	-15 %	29 %	-19 %
M.MAD:	0.10	0.11	0.16	0.96	0.09	0.30	0.23	0.46	0.52	0.27	0.25	0.35	0.09	0.36
CoV:	32 %	49 %	23 %	98 %	25 %	84 %	52 %	48 %	104 %	67 %	63 %	28 %	24 %	53 %
slope:	0.48	1.04	1.31	0.66	0.86	0.98	0.85	0.14	-	0.07	0.62	0.69	0.69	0.69
slope without outliers	0.90	1.04	1.14	0.72	0.86	0.14	0.85	0.14	-	-	0.64	0.82	1.12	

Table 12: A summary of all the field comparisons of SO_4^{2-} *aerosol measurements.*

Langenbrügge, 1986 *Ref method is NILUs measurements using IC*

country:	DK	HU	DE	SE	FI	GB
lab method	Sulfonazo	IDA	XRF	XRF	XRF	XRF
Mean (ref):	3.32	3.23	3.06	3.23	3.24	3.29
Mean:	3.79	2.11	2.77	3.53	3.53	3.31
Median (ref):	2.10	2.00	2.05	2.00	2.00	2.10
Median:	2.40	1.40	1.70	1.60	1.80	2.10
Num pairs:	71	75	72	75	74	73
Average of diff:	-0.47	1.12	0.29	-0.31	-0.28	-0.02
Median of diff:	-0.30	0.60	0.40	0.40	0	0
median % err	-14 %	30 %	20 %	20 %		
M.MAD:	0.44	0.89	0.44	0.74	0.44	0.44
CoV:	21 %	44 %	22 %	37 %	22 %	21 %
slope:	0.86	1.70	1.00	0.62	0.73	1.06

Vavihill, 1991 *Average concentration is used as reference*

country:	AT	CS	CS,2	DE	ES	GB	IR	NO	NO, 2	SE	SF	SF, 2	SU
Mean (ref):	1.13	1.15	1.15	1.12	1.15	1.11	1.15	1.15	1.15	1.15	1.18	1.15	1.14
Mean:	0.88	1.24	1.15	1.05	1.08	1.2	1.01	1.17	1.22	1.2	1.14	1.31	1.42
Median (ref):	0.91	0.99	0.99	0.95	0.99	0.91	0.99	0.97	0.97	0.99	0.99	0.99	0.96
Median:	0.76	1.06	0.99	0.87	0.97	1.07	0.76	0.96	1.06	1.04	0.93	1.15	1.27
Num pairs:	57	42	42	47	42	59	42	51	51	42	48	42	40
Average of diff:	0.24	-0.09	0	0.07	0.07	-0.09	0.14	-0.02	-0.08	-0.05	0.04	-0.16	-0.28
Median of diff:	0.18	-0.06	0	0.08	-0.08	-0.08	0.14	0	-0.08	-0.03	0.03	-0.12	-0.24
median % err	20 %	-6 %	0 %	8 %	-8 %	-9 %	14 %	0 %	-8 %	-3 %	3 %	-12 %	-25 %
M.MAD:	0.16	0.08	0.09	0.13	0.19	0.15	0.2	0.13	0.15	0.11	0.06	0.14	0.16
CoV:	18 %	8 %	9 %	14 %	19 %	16 %	20 %	14 %	15 %	11 %	6 %	14 %	17 %
slope:	0.94	0.91	0.93	0.86	0.67	0.99	0.75	0.85	0.92	0.90	0.86	0.87	0.85

Table 12, cont.

Co-located sampling

Site	GB2	IE2	PT4	DE3	PL5	FR8	CZ3	ES12	NL	SI08
year	1997	1997	1997	1998	1998	1998	1999	2000	2001	2001
Mean (ref):	0.63	0.86	1.56	0.61	1.02	0.84	1.09	0.71	1.13	1.04
Mean:	0.65	0.78	1.77	0.66	1.24	0.6	1.24	0.77	0.95	0.85
Median (ref):	0.44	0.58	1	0.47	0.78	0.69	0.81	0.61	1.08	0.72
Median:	0.43	0.57	1.07	0.53	1.02	0.46	1	0.6	0.85	0.59
Num pairs:	63	87	100	93	94	90	39	84	90	86
Average of diff:	-0.01	0.08	-0.21	-0.05	-0.22	0.24	-0.16	-0.06	0.18	0.19
Median of diff:	-0.01	0.05	-0.06	-0.04	-0.23	0.22	-0.23	-0.05	0.18	0.15
median % err	-2 %	9 %	-6 %	-9 %	-29 %	32 %	-28 %	-8 %	17 %	21 %
M.MAD:	0.07	0.09	0.51	0.1	0.37	0.25	0.25	0.06	0.22	0.12
CoV:	17 %	16 %	51 %	20 %	48 %	36 %	31 %	10 %	20 %	17 %
slope:	0.97	1.13	0.72	1.02	0.75	1.09	1.09	0.78	1.08	1.12

Table 13: A summary of all the field comparisons of NO_2 measurements.

Kleiner Feldberg 1991

country	CS (SK)	CS (CZ)	DE (DDR)	DE (FRD)	DE (DDR)	DE (FRD)	DK	HU	IT	NO	NO	PL	RO
Method	bubbler (NEDA)	impr filter	saltzman	saltzman	monitor	monitor	impr glas	bubbler (TEA)	denuder	bubbler (TGS)	impr glas	bubbler (TGS)	impr glas
Mean (ref):	3.21	3.09	3.10	2.96	3.25	3.20	3.16	3.20	3.13	3.23	3.26	3.16	3.29
Mean:	2.79	2.71	2.77	2.64	2.75	2.71	2.75	2.79	2.75	2.79	3.15	2.77	3.15
Median (ref):	2.45	3.67	3.07	3.23	3.47	5.55	2.98	2.54	2.15	4.65	3.25	2.97	2.42
Median:	2.66	3.44	2.85	2.91	3.51	4.80	2.74	2.57	2.07	4.45	3.04	2.99	2.39
Num pairs:	66	57	72	50	46	35	74	70	70	79	78	76	70
Average of diff:	0.76	-0.59	0.03	-0.27	-0.21	-2.35	0.18	0.66	0.98	-1.42	0.01	0.19	0.87
Median of diff:	0.75	-0.69	-0.04	-0.16	-0.03	-2.03	0.07	0.56	0.76	-1.23	0	0.01	0.69
median % err	31 %	-19 %	-1 %	-5 %	-1 %	-37 %	2 %	22 %	35 %	-26 %	0 %	0 %	29 %
M.MAD:	1.28	1.16	0.30	0.61	1.07	1.66	0.10	1.08	0.50	0.76	0.06	0.72	1.01
CoV:	46 %	43 %	11 %	23 %	39 %	61 %	4 %	39 %	18 %	27 %	2 %	26 %	32 %
slope:	0.66	0.95	1.18	0.68	0.85	0.42	1.09	0.85	1.31	0.77	0.91	1.25	1.19

Kleiner Feldberg cont.

country	SE	SE	SU	YU	AT	AT	CH	CH	NL	UK	UK	UK
Method	impr glas	DOAS	impr glas	bubbler (TGS)	mon (Horiba)	monitor	mon (Cranox)	monitor	monitor	monitor	monitor	luminol
Mean (ref):	3.19	2.59	3.18	3.06	3.21	3.21	2.96	3.00	3.06	3.19	3.19	3.08
Mean:	2.75	2.53	2.79	2.75	2.79	2.79	2.73	2.97	2.73	2.95	2.95	2.68
Median (ref):	3.40	3.39	3.56	3.86	4.77	4.87	3.12	4.45	4.62	4.15	4.06	3.38
Median:	3.37	3.30	3.47	3.93	4.58	4.73	3.16	4.48	4.23	3.80	3.63	3.14
Num pairs:	74	52	82	64	78	78	48	56	68	80	80	66
Average of diff:	-0.21	-0.80	-0.38	-0.80	-1.57	-1.66	-0.16	-1.46	-1.56	-0.96	-0.87	-0.31
Median of diff:	-0.07	-0.67	-0.34	-1.16	-1.41	-1.55	-0.12	-1.51	-1.70	-0.84	-0.73	-0.42
median % err	-2 %	-20 %	-10 %	-30 %	-30 %	-32 %	-4 %	-34 %	-37 %	-20 %	-18 %	-12 %
M.MAD:	0.10	0.46	0.19	0.87	0.65	0.70	0.49	1.16	1.51	1.18	1.36	0.59
CoV:	4 %	18 %	7 %	32 %	23 %	25 %	18 %	39 %	55 %	40 %	46 %	22 %
slope:	0.89	0.69	0.94	0.52	0.94	0.83	0.76	0.73	0.64	0.68	0.69	1.26

Table 13, cont.

Co-located sampling

site	CZ3	DE3	ES12	ES12	IE2	PL5	PT4	NL	CH
method	impr filter	satzman	abs (TEA)	monitor	bubbler (TGS)	bubbler (TGS)	monitor	monitor	monitor
Mean (ref):	1.61	1.00	0.42	0.42	0.53	0.89	0.99	8.63	5.55
Mean:	2.50	1.13	2.48	0.88	0.64	0.94	1.04	8.74	4.90
Median (ref):	1.39	0.77	0.40	0.40	0.36	0.63	0.80	8.41	8.45
Median:	2.22	1.00	1.00	0.84	0.40	0.58	0.81	8.35	8.39
Num pairs:	75	83	95	93	74	87	94	92	89
Average of diff:	-0.89	-0.13	-2.06	-0.45	-0.12	-0.05	-0.05	-0.11	-2.90
Median of diff:	-0.69	-0.20	-0.65	-0.41	-0.11	0.01	0.02	-0.45	-2.78
median % err	-50 %	-26 %	-163 %	-103 %	-31 %	2 %	3 %	-5 %	-33 %
M.MAD:	0.74	0.41	1.34	0.22	0.15	0.32	0.36	3.53	1.91
CoV:	53 %	53 %	339 %	54 %	42 %	52 %	45 %	42 %	39 %
slope:	0.29	1.14	0.03	0.74	0.59	0.61	0.64	0.74 (1.06)	0.68

6. Results from laboratory comparisons

6.1 Main components

The twentieth intercomparison of main component in precipitation and air is reported separately (Uggerud et al., 2003). Table 14 gives a summary of the precipitation results. The CEC laboratory at Ispra did not participate in the 20th laboratory intercomparison. Appendix 4 is a summary of all previous 19 laboratory comparison results used for flagging the EMEP data (Chapter 7).

Table 14: Results from the 20th laboratory inter-calibration of precipitation; absolute value of the average percent error.
'pH diff' is the average deviation in pH unit from expected value.

Lab \ component	SO4-S	NO3-N	NH4-N	Mg	Na	Cl	Ca	K	Cond.	pH diff	pH (H+)
1 AT	3.7	2.0	3.8	8.6	8.0	7.5	9.7	23.5	1.8	0.03	6.9
3 CS	0.9	2.6	18.1	1.4	3.3	6.0	1.7	2.0	2.5	0.01	1.9
4 DK	3.7	3.2	3.5	11.0	8.7	3.6	1.8	45.9	4.6	0.03	7.4
5 FI	1.7	1.9	3.3	2.3	0.9	1.4	8.3	1.4	0.5	0.03	6.4
6 FR	2.7	3.8	0.2	8.9	0.9	5.0	3.7	6.0	3.9	0.01	2.1
7 DE(Leip.)	4.9	1.4	1.8	13.0	0.3	3.5	6.5	1.4	11.5	0.03	5.8
8 DE(Schau.)	0.2	2.3	3.4	1.0	1.1	2.0	2.5	1.6	2.7	0.05	10.5
10 HU	2.8	0.5	5.2	2.5	16.9	24.0	10.9	7.5	0.6	0.04	9.4
11 IS	1.5	3.0		4.4		21.5	5.4	34.3	4.5	0.08	17.0
12 IE (MET)	0.3	0.5	4.0	1.2	1.1	1.5	5.6	5.3	4.4	0.01	2.5
13 IT-CNR	1.7	0.8	2.1	4.2	49.0	0.8	6.0	1.4	2.6	0.03	6.9
14 NL	11.0	0.8	1.7	7.1	8.1	2.8	7.7	3.9	4.4	0.10	19.8
15 NO	1.3	1.2	2.9	5.7	1.3	3.0	6.4	2.1	3.4	0.05	10.6
16 PL	1.6	3.0	4.8	4.9	1.8	2.7	1.3	4.4	1.4	0.01	3.3
17 PT	6.1	0.7	14.7	2.5	22.9	69.2	20.2		2.6	0.13	20.2
18 RO			15.0			10.7			5.2	0.11	29.3
19 ES	1.3	1.5	19.7	0.4	4.7	50.8	1.5	1.5	0.5	0.10	19.8
20 SE	0.3	1.0	2.6	13.2	2.7	4.3	4.4	12.6	11.1	0.09	18.4
21 CH	4.0	0.4	1.8	0.5	1.6	1.0	3.4	6.4	2.1	0.04	8.0
22 RU	10.5	5.4	4.8	7.2	26.9	29.5	15.3	16.0	5.5	0.06	13.0
23 GB	0.5	3.2	4.6	3.3	11.3	3.2	2.8	8.1	13.0	0.02	4.9
24 YU	27.0	31.5		31.5	3.2	31.9	36.1	1.8	35.5	0.07	14.1
26 CA	1.1	1.5	2.0	0.7	0.6	0.9	0.8	2.5		0.05	10.6
27 US-I	2.0	1.2	5.8	2.2	1.0	0.9	3.4	1.9	1.4	0.05	11.6
30 IT(ISP)											
31 SK	1.0	1.6	3.5	0.8	3.0	5.1	3.8	2.3	1.0	0.01	2.3
32 LT	8.2	1.1	5.0		11.1	8.3	40.2	4.3	2.6	0.05	11.6
33 LV	2.6	1.6	8.2	0.8	0.8	3.3	1.4	3.1	1.6	0.05	11.1
34 TR	0.5	3.4	3.1	1.8	7.0	5.5	6.7	17.6	3.3	0.04	9.6
35 CR	4.1	3.2	2.2	0.6	0.8	1.3	1.7	2.2	2.6		15.6
36 SI	2.3	0.8	3.2	3.2	1.7	2.0	0.9	2.5	6.3	0.05	10.5
37 IE (ESB)	2.2	1.8	11.3	25.7	2.2	10.1	16.0	22.7	3.8	0.14	39.1
38 EE	9.2	6.8	3.5	20.1	10.1	7.4	6.1	12.8	53.4	0.07	14.5
39 PL (Env.)	5.6	3.2	12.2	1.0	1.3	10.3	1.6	1.3	8.1	0.07	14.1
40 MK		55.1	79.2	9.0	8.2		8.9	25.6	32.1		

🟦 <5% 🟩 5-10% 🟨 10-20% 🟥 >20%

The results in Table 14 are mostly good, except for some elements where there is room for improvements, for potassium and chloride particularly. Furthermore, pH is a difficult parameter and only a few laboratories are within 5 per cent error, however, the data quality objectives (DQO) for pH is 0.1 unit (Annex 1). The colour limits for pH in Table 14 is given at 0.05, 0.1 and 0.2 average pH units difference from expected value. As seen from the Table, most laboratories are within the DQO.

Table 15 gives a corresponding overview of the result for the main air components. The results are quite acceptable, even though some components need improvements at a few laboratories.

Table 15: Results from the 20th laboratory intercalibration of main components in air; the absolute value of the average percent error.

Lab \ component	SO_2 impr.	SO_2 abs.	HNO_3	NH_3	NO_2
3 CS	4.5		2.0		4.9
4 DK	5.2		1.9	17.1	4.4
5 FI	8.4		3.3	3.3	
6 FR		0.9			
8 DE	9.3		3.0	5.2	5.4
10 HU				36.2	3.5
11 IS	18.1		34.4	12.7	
12 IE					1.1
15 NO	2.4	12.7	4.6	6.1	9.6
16 PL	13.1		5.9	15.4	2.3
17 PT		20.3			
19 ES		17.4			8.2
20 SE	17.8			6.6	1.3
21 CH		2.4			
22 RU	38.2		24.1		6.1
23 UK		6.9			3.0
31 SK	4.5		3.4		21.3
32 LT					1.2
33 LV	17.6		3.5	9.6	2.8
34 TU	8.2		5.2		2.6
35 HR					2.8
36 SI	23.4				0.5
38 EE	24.0				0.7
39 PL Env.	2.4		1.8	10.8	6.4

🟦	<5%
🟩	5-10%
🟨	10-20%
🟥	>20%

6.2 Heavy metals

The results from the analytical comparison of heavy metals in precipitation are presented in a separate report (Uggerud and Skjelmoen, 2003), but a summary of the main findings is found in Table 16. The results are divided in high and low concentration samples because the performance may vary with concentrations. In general the results are best for the high concentration samples. The DQO differentiate between high and low concentrations (Annex 1); the accuracy in the laboratory should be better than 15% and 25% for high and low concentrations respectively.

Most of the results are within the DQO, i.e. blue and green for high concentrations and blue, green and orange for low concentrations (Table 16). Some of the laboratories need, as seen, to improve their routines.

Table 16: Results from the laboratory intercalibration of heavy metals in precipitation 2002; average percent absolute error in high and low concentrations samples.

Lab \ comp	Cr		Ni		Cu		Zn		As		Cd		Pb	
	low	high	low	high	low	high	low	high	low	high	low	high	low	high
1 AT	8	2	5	4	1	4	4	7		5	5	4	3	2
3 CS	10	5	25	8	10	4	1	4	3	2	17	3		3
5 FI	20	9	14	9	7	4	5	4	19	15	7	8	7	7
6 FR		5		7	3	2	21	4		24		1	13	5
7 DE (Leip.)	1	5	1	0.4	4	3	4	3	20	9	3	1	3	2
8 DE (Schau.)	3	1	5	1	2	1	10	6	4	4	6	2	2	0.4
14 NL	25	2		3	9	3		4	5	1	3	2	7	5
15 NO	2	5	1	4		1	2		7	3	9	7	2	4
16 PL	15			3	13	3	31	5						15
23 GB	4	26	7	3	9	3	11	8	3	3	6	5	6	7
31 SK	1	1	22	3	4	1		2	11	4	43	1	2	1
32 LT	4	7	40	1	13	2	6	1	11	31	32	13	7	4
33 LV	23	14	15	6	9	13	4	4	20	11	2	3	11	2
34 TR	24		23	20	9	10	48	6			8	3	10	7
38 EE		1	143	12	7	5		13		40	13	12		2
39 PL Env.	15	2		7	18	15	14	4			5	13		4

🟦 <5% 🟩 5-15% 🟨 15-25% 🟥 >25%

6.3 Laboratory comparison of POPs

An EMEP POP laboratory comparison with standards and extracts of real air samples of PAH and chlororganic compounds was organised during 2000 to 2002. A draft report of the results will be sent to the participants during the autumn 2003. A small work meeting involving the analytical chemists that returned results will take place at NILU in November this year.

7. New flags

7.1 Introduction

The EMEP network consists of a co-operation between a large number of participating laboratories and the data quality of the network is complex and varies from one national data set to the next. For the dataset 1996-1999 CCC classified the main components into four different quality groups using information from laboratory and field comparisons as well as ion balance plots, data completeness and information on detection limits. This system has now been revised and the EMEP data series will be given quality flags, mainly based on results from laboratory and field comparisons, see Chapter 7.2.

The participants may flag their data in the NASA/Ames files they use today to report data to the CCC that has a corresponding possibility to flag the data. These data flags are pasted to single measurements or sometimes to all data from a sample. The data flags may, e.g. be found on the CCC homepage. The CCC has attempted to add more substance to the flagging based on the ion balance taking into account high pH and/or low ionic strength, in Chapter 7.3.

7.2 Quality (DQ) flags

The DQ flag has been 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.

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.

The DQ flag-codes applied for the performance in the laboratory comparisons and in field comparisons are found in Table 17 and Table 18, respectively. The data series flagged with any of the red flags will be classified as invalid data. The rest of the data are classified as valid data although those marked with a green colour is by CCC considered as the most accurate data in the EMEP database.

7.2.1 Flags based on laboratory comparison

The EMEP laboratory intercomparisons started in 1977 and have been performed annually since then with a few exceptions, and are a very valuable basis for estimation of the uncertainty in the EMEP data. It should be kept in mind that test samples usually will be treated differently than the routine samples in the laboratories, and that the laboratory comparison results therefore could reflect a best, rather than the typical, data quality.

The systematic and random errors are calculated using a triangular distribution (Eurochem, 2000). The theory is described in Annex 6.

Table 17: Criteria used for classification of data quality based on field comparison results.

	M.MAD	≤ 0.25 µg S/m^3		≤ 0.50 µg S/m^3		> 0.50 µg S/m^3 and
	CoV		[0, 25 %]		< 25%, 50 %]	< 50%, → >
Regression slope (a) Ref = a^{x}Lab	< 1.30, → >	**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**
	< ←, 0.70 >	**50**	**51**	**52**	**53**	**54**

Table 18: 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**

7.2.2 The flags based on field comparison

A summary of the field comparisons is given in Chapter 5.4. 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 since 1978. 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. The present DQ flags and their use should therefore be further evaluated and discussed with the participants.

The random errors are calculated using the modified median absolute difference (M.MAD) and the coefficient of variation (CoV), defined in Chapter 4. The systematic errors are estimated using the regression slope between the reference and the national samples, i.e. the product of national mean values and the slopes should improve the comparability of the means.

7.3 Ion balance flags

The ion balance (IB) gives an indication of precipitation data quality since the concentrations of all negatively charged ions in a sample necessarily will have to equal the sum of the positively charged ions. When the concentrations of all major ions in a precipitation sample have been measured, a poor IB *may* therefore indicate a poor data quality, and the sample results are proposed flagged as described below.

This proposal aims at flagging data that are considered to have a quality less good than could be expected from EMEP's Data Quality Objectives (DQO). The flagged data are divided into two groups; data that are considered to have a quality sufficiently high to be useful for EMEP and therefore are considered valid and should be used, and secondly data that are considered invalid. The criteria are summarised in Figure 16.

A good IB is not a guarantee for a high data quality. It is important to bear in mind that even though a general good IB indicates adequate sample handling and a high analytical chemical skill in the laboratory, other factors may reduce the data applicability for EMEP and the overall data quality; e.g. local sources or sampling problems. Even a sample contamination will not necessarily be detected through an ion balance calculation, i.e. when the contamination takes place before the analyses have been started.

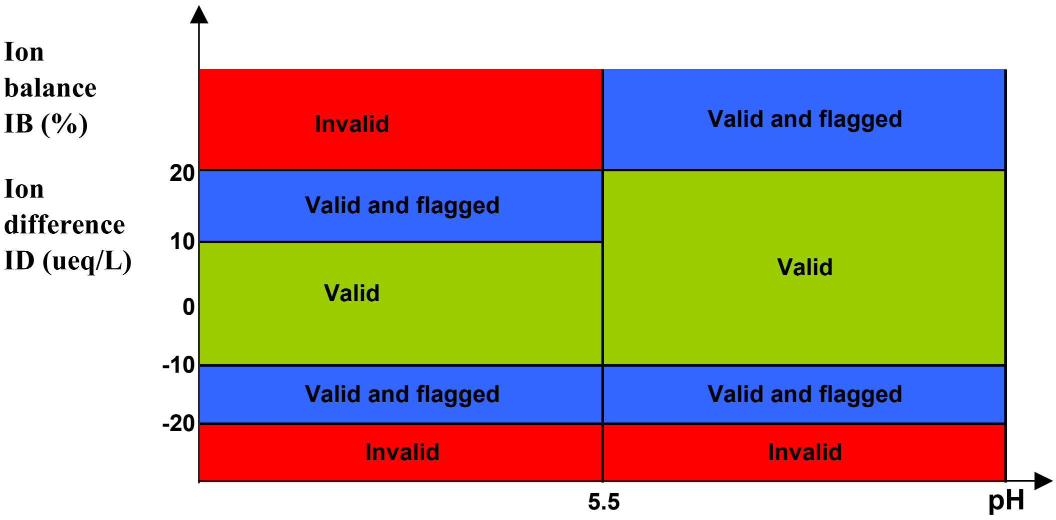

Figure 16: Criteria when the sum of ions IS >= 100 ueq/L is based on the ion balance in per cent. Criteria when the sum of ions IS < 100 ueq/L is based on the difference between cation and anion concentrations in ueq/L.

The flags are suggested linked to each result from a specific precipitation sample. Other information about the sample results may, however, override the IB flagging, and validate some of the results.

The complete description of the ion balance flags is given in Annex 7.

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 external auditing are reported to CCC.

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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.

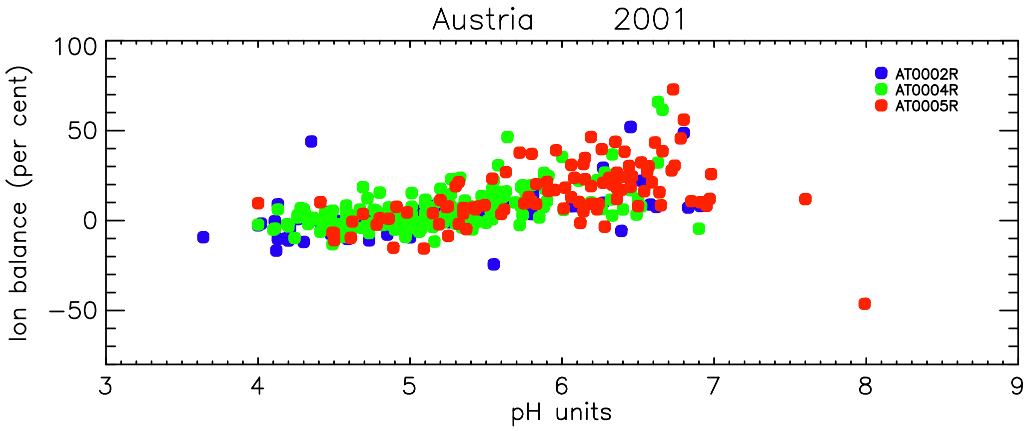
DQO for heavy metals

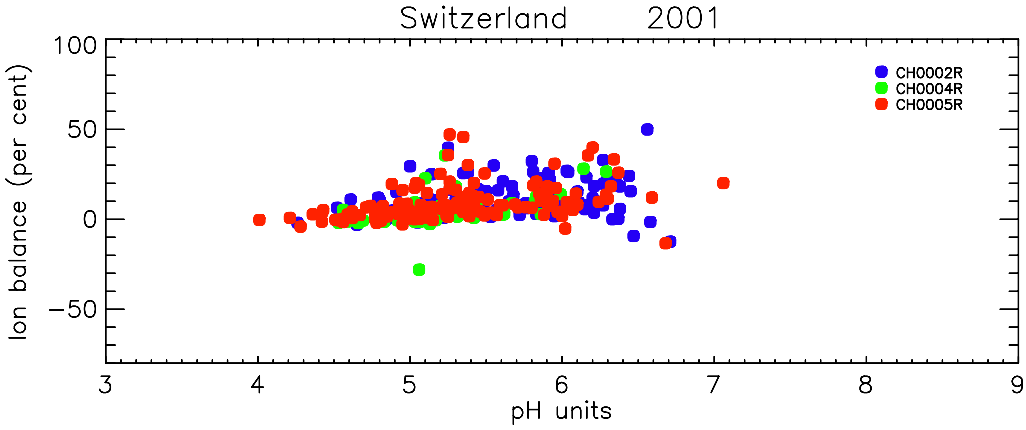
- 90% completeness
- 30% accuracy in annual average
- Accuracy in laboratory (c= concentration):

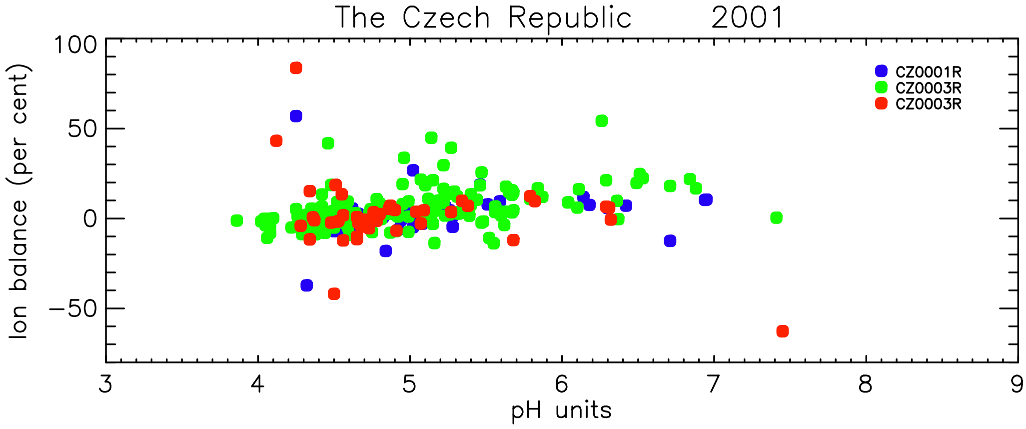
Pb:	15%	if c > 1 µg Pb/l
	25%	if c < 1 µg Pb/l
Cd:	15%	if c > 0.5 µg Cd/l
	25%	if c < 0.5 µg Cd/l
Cr:	15%	if c > 1 µg Cr/l
	25%	if c < 1 µg Cr/l
Ni:	15%	if c > 1 µg Ni/l
	25%	if c < 1 µg Ni/l
Cu:	15%	if c > 2 µg Cu/l
	25%	if c < 2 µg Cu/l
Zn:	15%	if c > 10 µg Zn/l
	25%	if c < 10 µg Zn/l
As:	15%	if c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

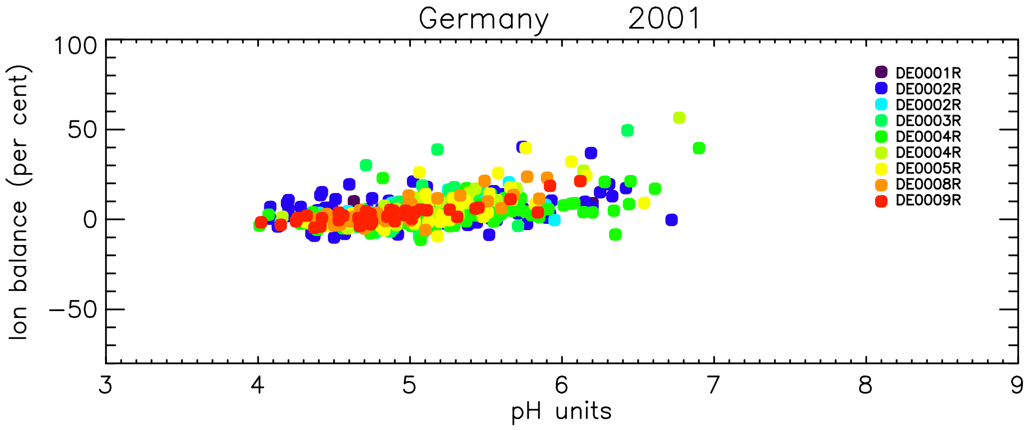
Annex 2

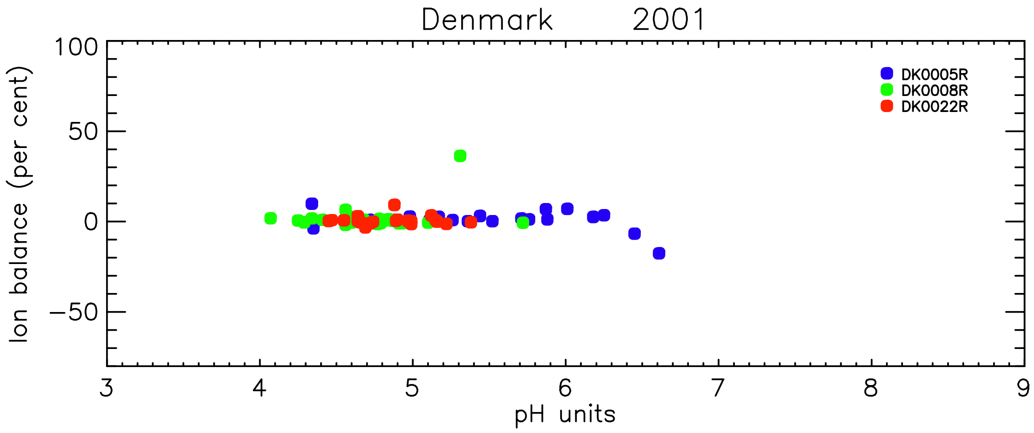
Ion balances in precipitation samples 2001

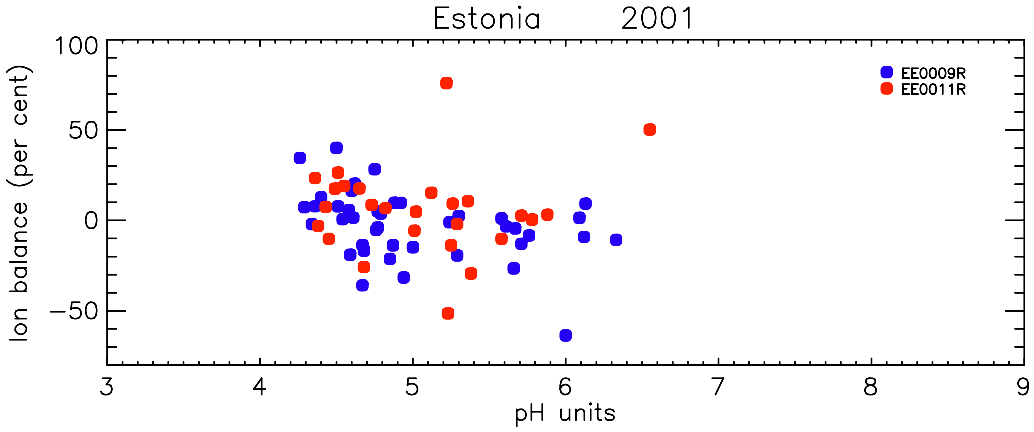

Austria 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
AT0002R
AT0004R
AT0005R

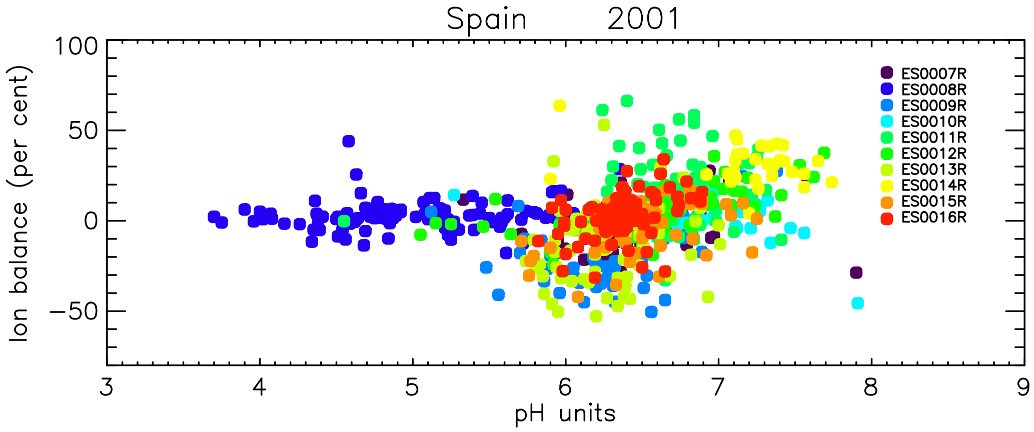

Switzerland 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
CH0002R
CH0004R
CH0005R

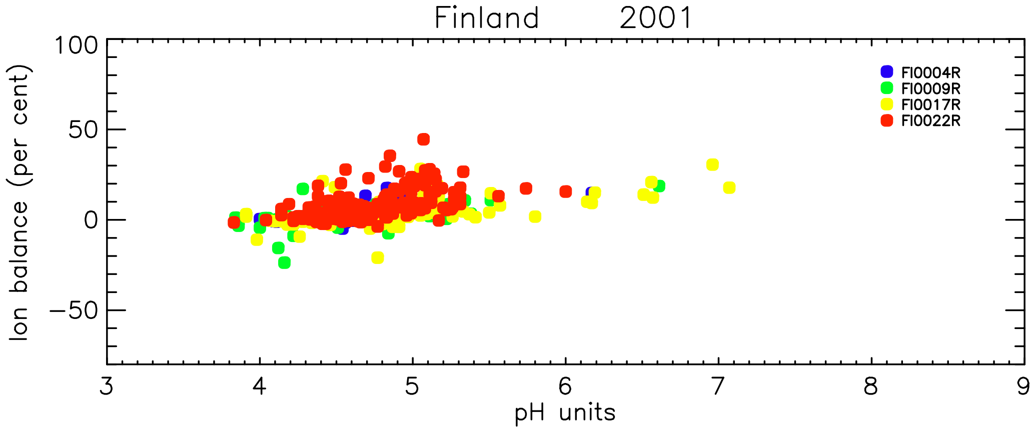

The Czech Republic 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
CZ0001R
CZ0003R
CZ0003R

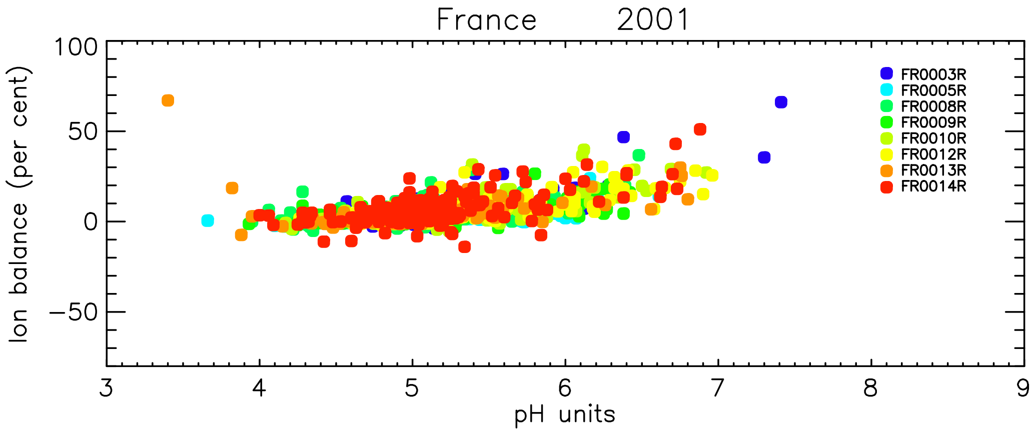

Germany 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
DE0001R
DE0002R
DE0002R
DE0003R
DE0004R
DE0004R
DE0005R
DE0008R
DE0009R

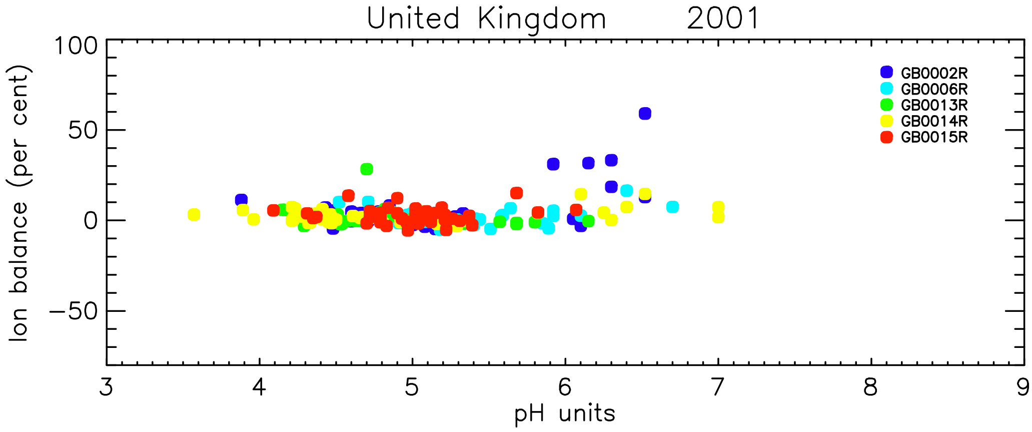

Denmark 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
DK0005R
DK0008R
DK0022R

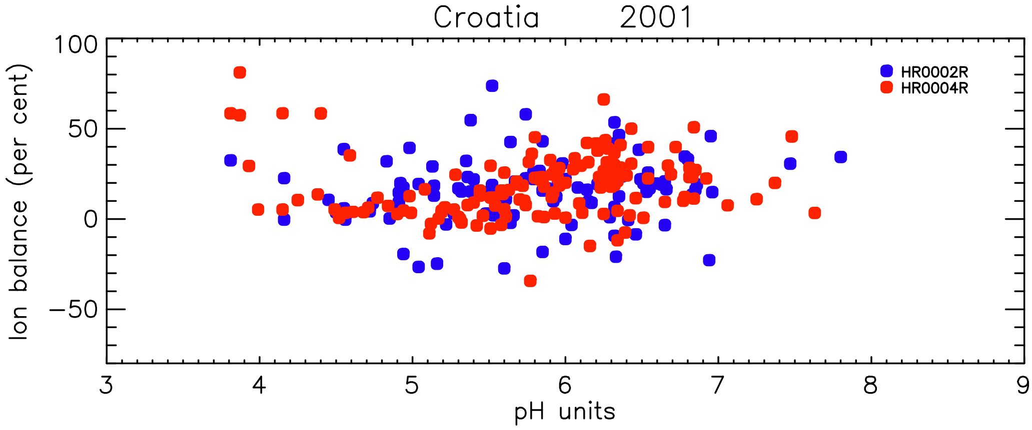

Estonia 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
EE0009R
EE0011R

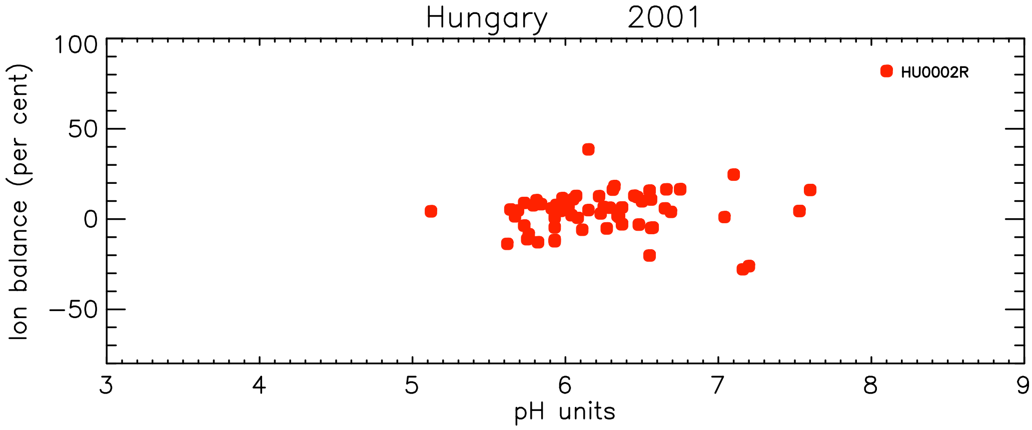

Spain 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
ES0007R
ES0008R
ES0009R
ES0010R
ES0011R
ES0012R
ES0013R
ES0014R
ES0015R
ES0016R

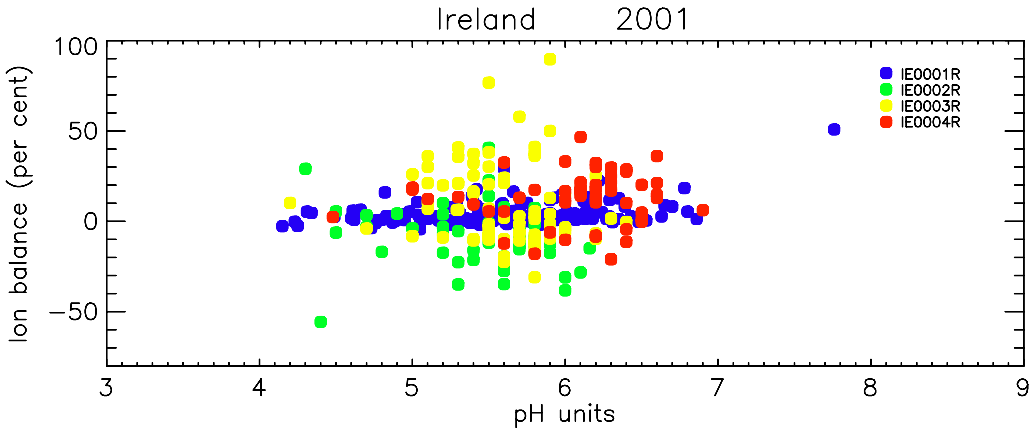

Finland 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
FI0004R
FI0009R
FI0017R
FI0022R

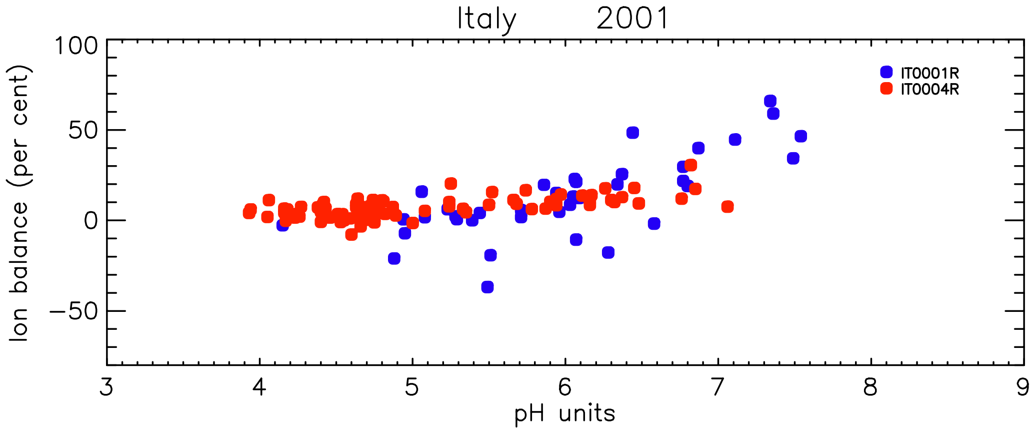

France 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
FR0003R
FR0005R
FR0008R
FR0009R
FR0010R
FR0012R
FR0013R
FR0014R

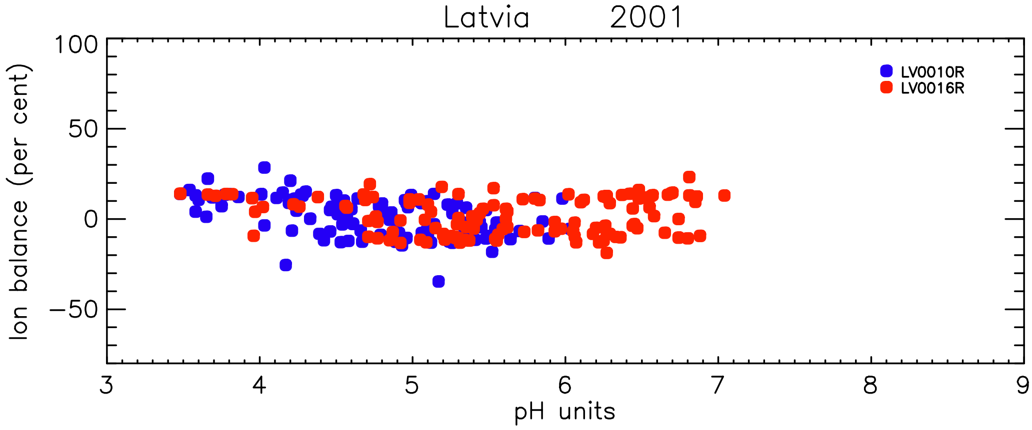

United Kingdom 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
GB0002R
GB0006R
GB0013R
GB0014R
GB0015R

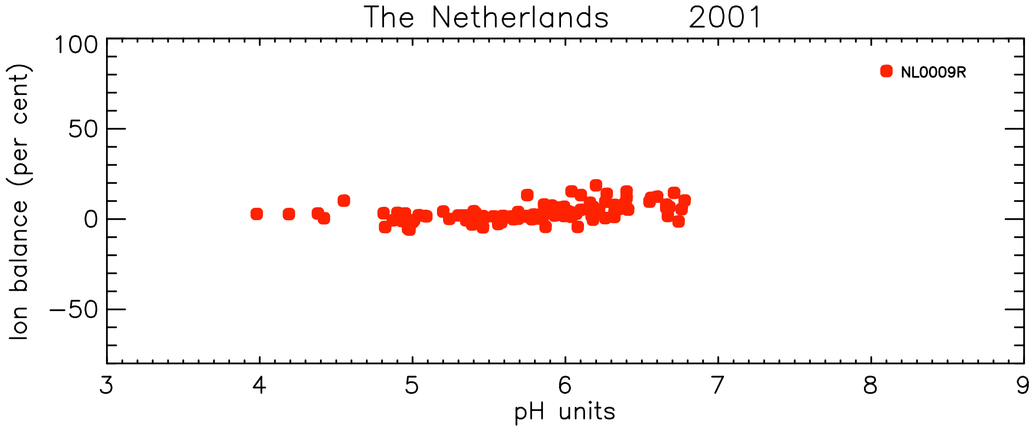

Croatia 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
HR0002R
HR0004R

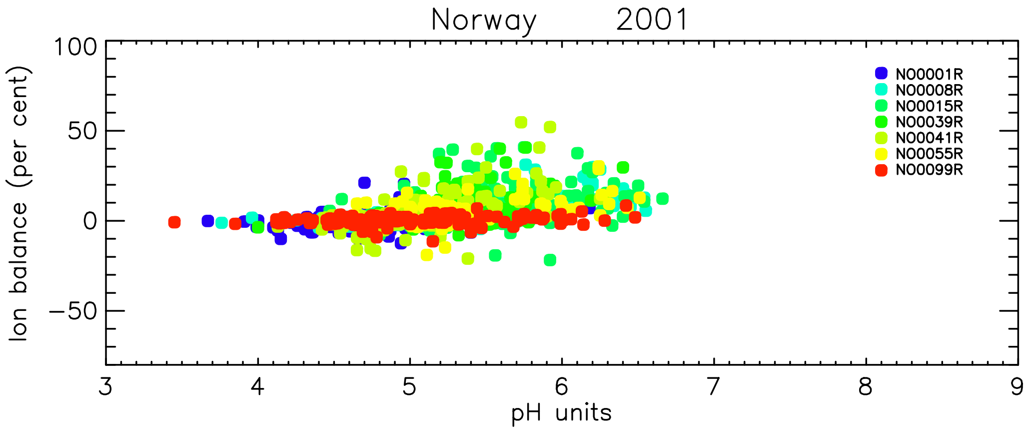

Hungary 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
HU0002R

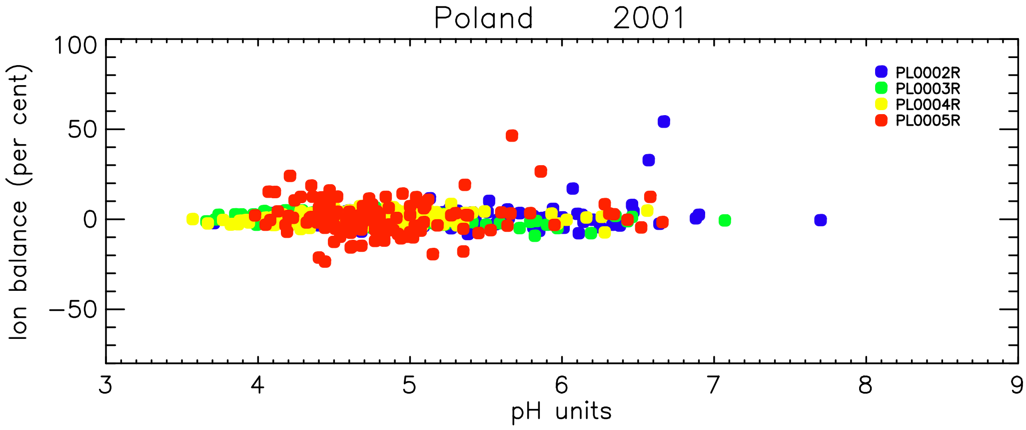

Ireland 2001

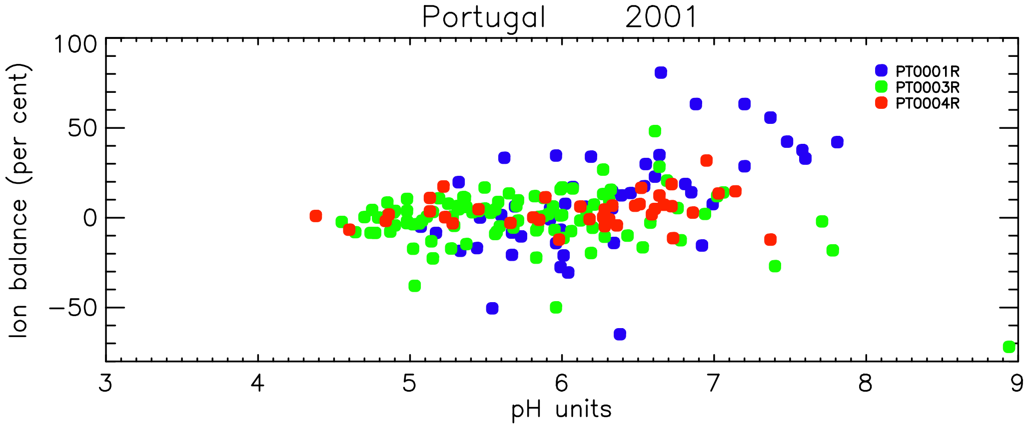

Italy 2001

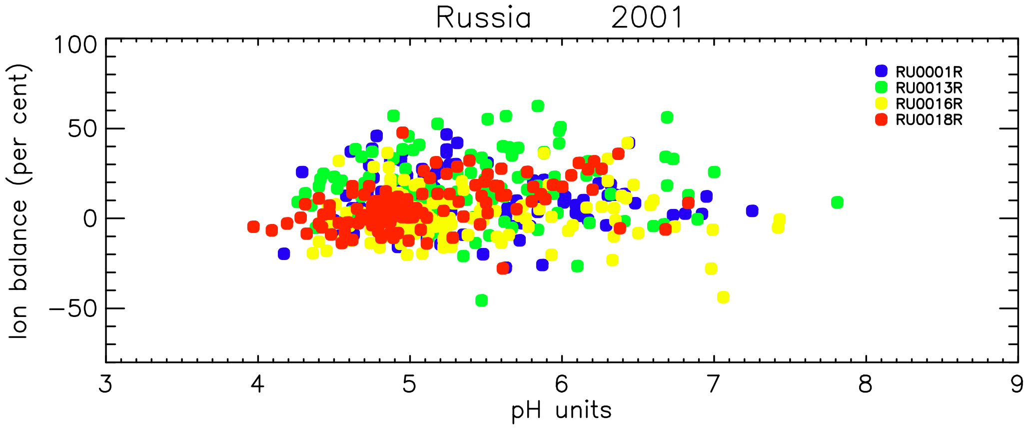

Latvia 2001

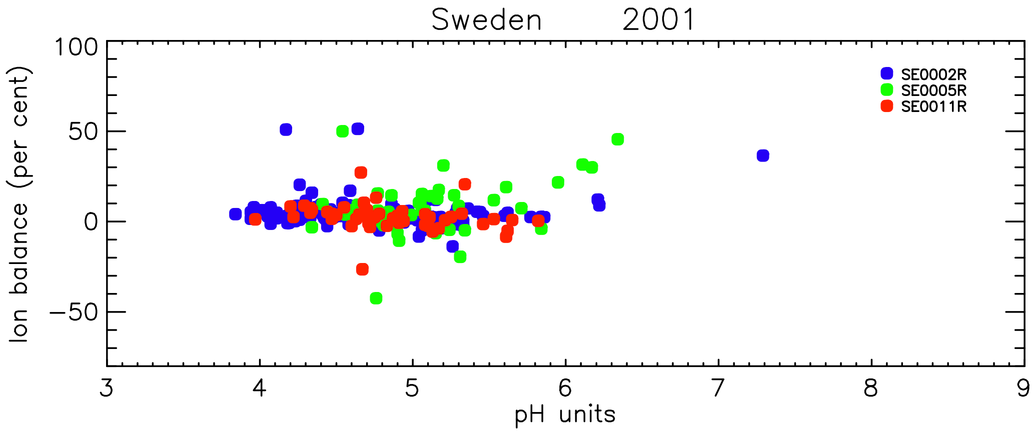

The Netherlands 2001

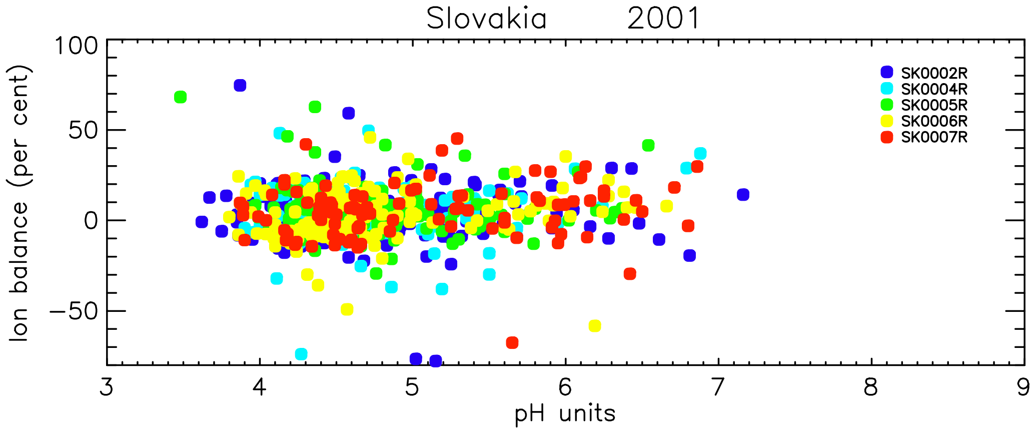

Norway 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
NO0001R
NO0008R
NO0015R
NO0039R
NO0041R
NO0055R
NO0099R

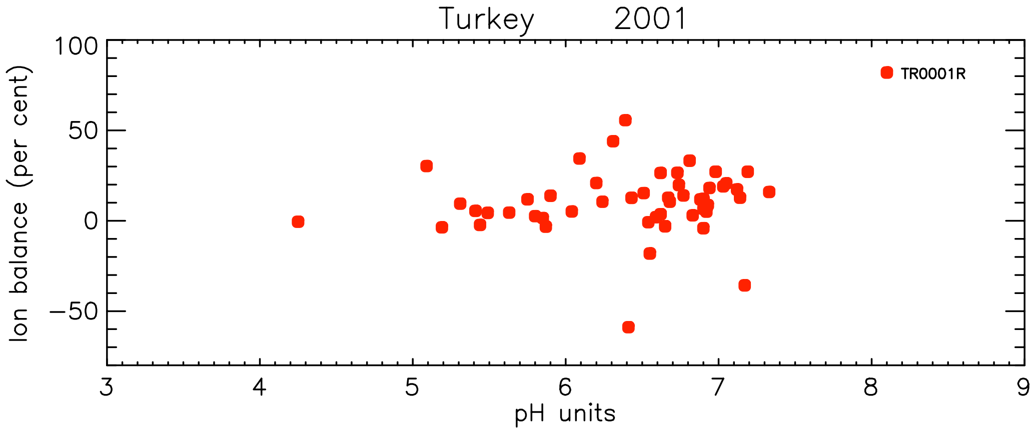

Poland 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
PL0002R
PL0003R
PL0004R
PL0005R

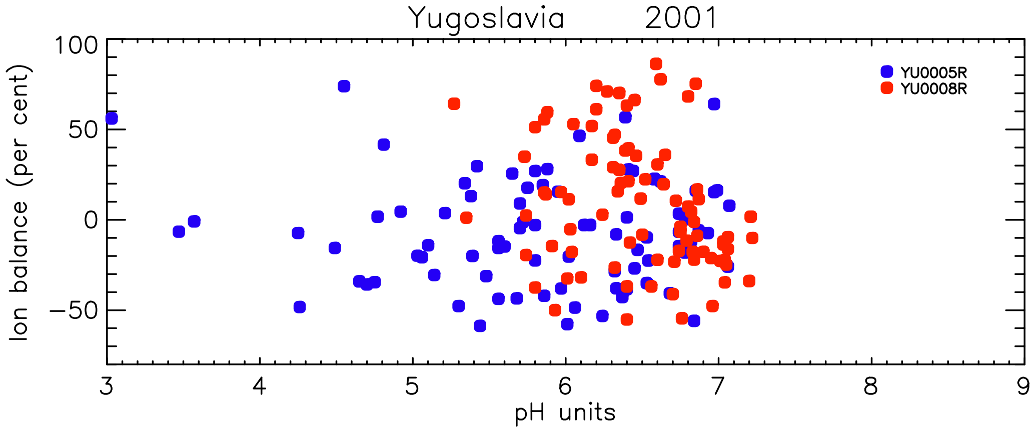

Portugal 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
PT0001R
PT0003R
PT0004R


Russia 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
RU0001R
RU0013R
RU0016R
RU0018R


Sweden 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
● SE0002R
● SE0005R
● SE0011R


Slovakia 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
● SK0002R
● SK0004R
● SK0005R
● SK0006R
● SK0007R


Turkey 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
● TR0001R


Yugoslavia 2001
Ion balance (per cent)
100
50
0
−50
3
4
5
6
7
8
9
pH units
● YU0005R
● YU0008R

Annex 3

Detection limits and precision

Table 3.1: 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
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 FI09	2 µg/m^3	2 µg/m^3	Dasibi Environmental corp., DAS 1008 PC
FI17			Environnement SA, Env. O3 41 M
FI22			Dasibi Environmental corp., DAS 1008 AH
FI37			Thermo Environmental Instruments, TEI 49 C
France FR08,10,13	2 µg/m^3	2 µg/m^3	Environnement SA, O341M
FR09,10			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/m3	API Model400
Italy, EU (IT04)	2 ppb	2 ppb	Thermo Environmental Instrument, Model 49
Latvia		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 2.2%	1 ppb	Monitor Labs Inc. ML-9810
Slovakia	2 µg/m^3		TEI M49 (at SK02, 06); M49C (at SK04)
Slovenia, SI08,32			Thermo Environmental Model 49 C
SI31,33			Monitor Labs, Model 8810
Spain			MCV, S.A. Model 48 AUV and 0341 M
Sweden, SE02,11,12	1 ppb	0.5 ppb	Monitor Labs, ML 9810 (ML 9810 B at SE 12)
SE32,35	2 ppb	2 ppb	Monitor Labs, ML 8810
Switzerland, CH02,04,05	1 ppb	1 ppb	Thermo Environmental Instruments TEI 49C
CH3	2 ppb	1 ppb	Monitor Labs 9810
UK, all sites except:	2 ppb		Monitor Labs, ML 8810
GB32			TECO, TE49
GB43			Ambirack
GB44			API Model 400

Table 3.2: 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	RSD : 14.0%, CoV : 11.0% M.MAD : 0.175 µg/m^3	0.03 µg SO$_2$/m^3	RSD : 2.7%	0.039 mg SO$_4^2$/l
Denmark	M.MAD: 0.02 ; CoV: 5 %	DK3: 0.02; DK5,DK8: 0.03	M.MAD: 0.01 µg S/m^3; CoV: 1.8 %	0.01 µg S/m^3
Estonia		0.48		
Finland		0.04 µg S/m^3	M.MAD: 0.003 µg S/m^3 CoV: 1.0%	0.01 µg S/m^3
France			at C=0.31: RSD=0.8%; CoV=2.57%	0.1 mg S/L
Germany	M.MAD: < 0.02			0.01 µg/m^3
Hungary		2.58		
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		0.1-0.14		
Lithuania		0.021 mg S/m^3	at c<0.7 mg S/m^3: 2.4% RSD; 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 ugS/m3
Poland		0.2		
PL05	M.MAD = 0.13; CoV= 11.2%	0.1	RSD: 0.73%	0.5 mgS/l
Russia	RU01: M.MAD 0.01; CoV= 3% RU18: M.MAD 0.01; CoV= 12%			
Serbia and Montenegro *				0.005 mg SO$_2$/m^3
Slovakia			1.25%	0.1 mg S/l
Slovenia		0.219 mg S/l		0.015 mg S/l
Spain				(0.5 µg S/m^3)[4]
Sweden *	uncertainty (95% conf. int): 13%	0.02	R: 2%	0.04
Switzerland	RSD: 4%	0.06		
[3]CH02, CH04, CH05	RSD: 5%	0.2 ppb		
Turkey		0.140	M.MAD: 0.0215; CoV: 2.85%	0.016 mgS/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
[4] Official data from Spain is from UV fluorescence monitor, lab.det. limit is from det abs.solution method which also is reported to CCC.

*Data from IT04, SE and YU are taken from earlier years

Table 3.3: Detection limits and precision of nitrogen dioxide.

	Measurements		Laboratory	
Country	**Precision**	**Detection limit, µgN/m^3**	**Precision**	**Detection limit**
Austria[1]	1 ppb	0.5 ppb		
Czech Republic	RSD: 12%	0.07 mg N/m^3	RSD: 3.4%	0.001 mg NO$_2$/l
Denmark		DK08: 0.07	M.MAD: 0.01; CoV: 2.1%	0.01 µg N/m^3
Estonia		0.07		
Finland	0.3 µg N/m^3	0.3		
Hungary		0.09	M.MAD: 0.001; CoV: 0.949%	
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		0.1	CoV: 1.3%	0.05 mg N/l
Lithuania		0.17	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 RSD: 4.6% at c=0.17 mgN/l RSD: 4.2% at c=0.08 mgN/l	0.0045 mg N/l
Poland		0.2	RSD: 1.0% at 0.304 mgN/l RSD: 5.9 % at 0.015 mgN/l	0.008 mg N/l
PL05	M.MAD: 0.13; CoV: 5%	0.2	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				(1 µg N/m^3)[4]
Sweden*	uncertainty (95% conf.int.): 12%	0.2	R: 2%	0.048
Switzerland[3]				
CH04, CH05	RSD: 5%	0.5 ppb		
CH02, CH03	RSD: 3%	0.5 ppb		
CH01		0.05 ppb		
Turkey	M.MAD: 0.0503; CoV: 12.29%	0.114	M.MAD: 0.0553; CoV: 6.26%	0.02 mg N/l

[1] AT: Monitor, HORIBA APNA 360

[2] IT04: Monitor, Thermo Environment 42C

[3] CH04 and CH05: Monitor Labs 9841A; CH02 and CH03: APNA 360; CH01: Eco Physics CLD 770AL ppt + PLC 760

[4] Official data from Spain is from Chemiluminescence monitor. Lab.det. limit is from the abs.solution method which also is reported to CCC.

Data from IT04, SE and YU are taken from earlier years.

Table 3.4: Detection limits and precision of sulphate in air.

Country	Measurements		Laboratory	
	Precision	**Detection limit, µgS/m^3**	**Precision**	**Detection limit**
Czech Republic*	0.062 M.MAD, 6.3% CoV	0.003		
Denmark	M.MAD: 0.05 µgS/m^3 CoV: 6,5 %	DK03, DK05: 0.03 DK08: 0.02		
Estonia		0.53		
Finland		0.04 µg S/m^3	M.MAD: 0.002 µg S/m^3; CoV: 0.5%	0.01 µg S/m^3
France			at c=0.31: RSD=0.8%; CoV= 2.57%	0.2 µg S/filter
Germany	M.MAD < 0.02 µg/m^3			0.01 µg/m^3
Hungary		0.07		
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)*		0.066 ppm	M.MAD. 0.01 ppm; CoV: 1.3%	
Latvia		0.1-0.14	CoV: 1.4%	0.1 mg S/l
Lithuania		0.024 µg S/m^3	at c<1.0 µgS/m^3: 7.2% RSD; 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 at c<2.4 µg S/m^3	0.01		
Poland		0.18		
PL05		0.1	RSD: 4%	0.5 mg S/l
Russia	RU01: M.MAD 0.01; CoV=2.5% RU16: M.MAD 0.02; CoV=7.5% RU18: M.MAD 0.01; CoV=2.3%			
Slovakia			2.12%	0.02 mg S/l
Slovenia				0.015 mg S/l
Spain				0.01 µg S/m^3
Sweden*	uncertainty (95% conf. int.): 113%	0.005	R: 2%	0.005
Switzerland	RSD: 10%	0.04		
Turkey		0.04	M.MAD: 0.0225; CoV: 4.11%	0.014 mg S/l
UK*			RSD: 2%	0.01 mg S/l

*Data from CZ, SE, UK and IT04 are taken from earlier years.

Table 3.5: Detection limits and precision of nitrate and nitric acid in air.

Country	Measurements		Laboratory	
	Precision	**Detection limit, µgN/m3**	**Precision**	**Detection limit**
Denmark	M.MAD: 0.04 µg N/m^3 CoV: 7,3%	DK05,08: 0.02 DK03: 0.04	M.MAD: 0,01 µg N/m^3 CoV: 1.0%	0.01 µg N/m^3
Finland		0.02 µg N/m^3	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$_3$: 0.08; NO$_3$: 0.03		0.002 mg N/l
Italy (IT01)	HNO$_3$: RSD: 6.2% at 0.25 µg N/m^3 NO$_3$: RSD: 1.5% at 1 µg N/m^3	HNO$_3$: 0.01 NO$_3$: 0.01		0.002 mg N/l
Italy, EU (IT04)*		0.246 ppm	M.MAD: 0.01 ppm CoV: 1.2%	
Latvia		NO$_3$: 0.015-0.020	CoV (NO$_3$): 2.2%	0.1 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		
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%			
Slovakia			HNO$_3$:1.71%; NO$_3$: 1.36	HNO$_3$: 0.02 mg N/l; NO$_3$: 0.01 mg N/l
Slovenia		NO$_3$: 0.006 mg N/l		0.01 mg N/l
Spain				0.06 µg N/m^3
Sweden*	uncertainty (95% conf. int.): 112%	NO$_3$: 0.002; HNO$_3$: 0.004	R: 2%	NO$_3$: 0.002; HNO$_3$: 0.005
Switzerland	RSD: 8%	0.06		
Turkey		NO$_3$: 0.055 HNO$_3$: 0.075	NO$_3$: M.MAD: 0.0073; CoV: 5.73% HNO$_3$: M.MAD: 0.0073; CoV: 16.87%	0.03 mg N/l

Data from SE and IT04 are taken from earlier years

Table 3.6: Detection limits and precision of ammonia and ammonium in air.

	Measurements		**Laboratory**	
Country	**Precision**	**Detection limit, µgN/m^3**	**Precision**	**Detection limit**
Denmark	M.MAD: 0.13 CoV: 6.6%	0.04	NH_4: M.MAD: 0.02; CoV: 1.1% NH_3: M.MAD: 0.01; CoV: 1.2%	NH_4: 0.01 µg N/m^3 NH_3: 0.02 µg N/m^3
Finland		0.04 µg N/m^3	M.MAD: 0.004 µg N/m^3; CoV: 1.5%	0.01 µg/m^3
Germany	M.MAD < 0.02 µg/m^3			0.01 µg/m^3
Hungary		NH_3: 0.43; NH_4: 2.58		
Italy (IT01)	NH_3: RSD: 3.9% at 1 µg N/m^3 NH_4: RSD: 4.2% at 2 µg N/m^3	0.1		
Italy, EU (IT04)*		0.061 ppm		
Latvia		NH_4: 0.15-0.17	CoV (NH_4): 2.1%	0.05 mg N/l
Lithuania		0.027	at c<1.0 µg N/m^3: 4.0% RSD 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		0.08		
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% NH_4: RU16: M.MAD 0.01; CoV=3.5% NH_4: RU18: M.MAD 0.01; CoV=2.1%			
Slovenia		NH_4: 0.018 mg N/l; NH_3: 0.084 mg N/l		0.008 mg N/l
Spain		0.03	2.68 %	0.03 µg N/m^3
Sweden*	uncertainty (95% conf. int.): 113%	0.03	R: 3%	NH_4: 0.017; NH_3: 0.03
Switzerland	RSD: 7%	0.2		
Turkey		NH_4: 0.16 NH_3: 0.084	NH_4: M.MAD: 0.1080; CoV: 14.96% NH_3: M.MAD: 0.0210; CoV: 7.74%	NH_4: 0.04 NH_3: 0.05

* Data from SE and IT04 are taken from earlier years.

Table 3.7: Detection limits and precision of sulphate in precipitation.

Country	**Measurements**		**Laboratory**	
	Precision	**Detection limit, mgS/l**	**Precision**	**Detection limit, mgS/l**
Austria		0.012	RSD: 1.3%	0.002
Czech Republic	RSD: 8.6%; CoV: 7.9% M.MAD: 0.231 mg/l	0.02	RSD: 1.4%	0.02
Denmark			M.MAD: 0.01; CoV: 1.6%	0.04
Estonia		0.347		0.221
Finland			M.MAD: 0.006 mg S/l; CoV: 2.0%	0.02
France			at c=0.262: RSD=0.64%; CoV=2.43% at c=1.322: RSD=2.31%; CoV=1.75%	0.02
Germany				0.01
Hungary			M.MAD=0.081; CoV=3.79%	ca. 0.03
Italy (IT01)	RSD: 1.1% at 1 mg S/l	0.01 mg S/l	RSD: 0.8% at 0.5 mg S/l RSD: 1.6% at 0.05 mg S/l	0.002
Latvia			CoV: 1.7%	0.030
Lithuania			c<0.5 mgS/l: 3.4% RSD 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 SD: 0.019 at c=0.85 mgS/l	0.01
Poland			RSD: 1% at 6.7 mg S/l RSD: 1.8% at 0.67 mg S/l RSD: 2% at 0.33 mgS/l	0.03
PL05	M.MAD: 0.03; CoV: 3.7%	0.1	M.MAD: 0.03; CoV: 7%	0.1
Portugal			0.75%	0.15
Russia			CoV: 5.5%; M.MAD: 0.02	0.02
Serbia and Montenegro*				0.16
Slovakia			3.13%	0.01
Spain			CoV: 1.4 %	0.07
Sweden*	uncertainty (95% conf. int.): 15%	0.004	R: 2%	0.004
Switzerland	M.MAD: 0.01			0.02
Turkey			M.MAD: 0.0178; CoV: 1.83%	0.040
UK*				0.16

* Data from SE, UK and YU are taken from earlier years.

Table 3.8: Detection limits and precision of nitrate in precipitation.

Country	Measurements		Laboratory	
	Precision	**Detection limit mgN/l**	**Precision**	**Detection limit mgN/l**
Austria		0.013	RSD: 0.7%	0.001
Czech Republic	RSD: 9.21%; CoV: 4.3% M.MAD: 0.104 mg/l	0.03 mg/l	RSD: 0.9%	0.03
Denmark			M.MAD: 0.02; CoV: 1.7%	0.02
Estonia		0.302		0.167
Finland			M.MAD: 0.003 mg N/l; CoV: 1.5%	0.01
France			at c=0.351: RSD=0.65%; CoV=1.85% at c=2.371: RSD=3.2%; CoV=1.37%	0.02
Germany				0.01
Hungary			M.MAD=0.047; CoV=2.78%	ca. 0.03
Italy (IT01)	RSD: 1.4% at 1 mgN/l	0.01	RSD: 0.7% at 0.5 mgN/l RSD: 1.5% at 0.05 mgN/l	0.002
Italy, EU (IT04)*				0.011 ppm
Latvia			CoV: 2%	0.060
Lithuania			c<0.5 mgN/l: 5.1% RSD c>0.5 mgN/l: 1.8% RSD	0.013
Netherlands			SD: 0.5	2 µmol/l
Norway	M.MAD: 0.03, CoV: 8%		SD: 0.023 at c=0.86 mg N/ml SD: 0.016 at c=0.39 mg N/ml	0.01
Poland			RSD: 1.7% at 4.5 mg N/l RSD: 1.9% at 0.45 mg N/l RSD: 2.0% at 0.23 mg N/l	0.015
PL05	M.MAD: 0.01; CoV: 2.1%	0.1	M.MAD: 0.03; CoV: 7.4%	0.1
Portugal			0.25%	0.02
Russia			CoV: 1.2%; MAD: 0.01	0.01
Serbia and Montenegro*				0.02
Slovakia			0.59%	0.01
Spain			CoV: 1.2%	0.08
Sweden*	uncertainty (95% conf. int.): 15%	0.002	R: 2%	0.002
Switzerland			M.MAD: 0.01	0.05
Turkey			M.MAD: 0.0047; CoV: 1.08%	0.030
UK*			4%	0.03

* Data from IT04 SE, UK and YU are taken from earlier years.

Table 3.9: Detection limits and precision of ammonium in precipitation.

Country	Measurements		Laboratory	
	Precision	**Detection limit, mgN/l**	**Precision**	**Detection limit, mgN/l**
Austria		0.013	RSD 3.7%	0.007
Czech Republic	RSD: 12.4%; CoV: 6.6% M.MAD: 0.075 mg/l	0.02 mg/l	RSD: 2.2%	0.02
Denmark			M.MAD: 0.01; CoV: 1.3%	0.01
Estonia		0.064		0.077
Finland			M.MAD: 0.001 mg N/l; CoV: 0.5%	0.002
France			at c<0.207: RSD=2.04%; CoV=9.86%	0.03
Germany				0.01
Hungary			M.MAD=0.003; CoV=1.07%	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 RSD: 1.8% at 0.05 mg N/l	0.001
Latvia			CoV: 0.7%	0.007
Lithuania			c<1.0 mg N/l: 3.3% RSD 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 SD: 0.013 at c=0.32 mgN/l	0.01
Poland			RSD: 2.7% at 1 mg/l RSD: 4.6% at 0.1 mg/l	0.03
PL05	M.MAD: 0.094; CoV: 18%	0.01	M.MAD: 0.05; CoV: 10%	0.01
Portugal			0.79%	0.04
Russia			CoV: 6.1%; MAD: 0.01	0.02
Serbia and Montenegro*				0.03
Slovakia			1.97%	0.01
Spain			CoV: 2.7%	0.08
Sweden*	uncertainty (95% conf.int.): 15%	0.02	R: 3%	0.02
Switzerland			M.MAD: 0.02	0.02
Turkey			M.MAD: 0.0105; CoV: 2.61%	0.038
UK*			10%	0.03

* Data from SE, UK and YU are taken from earlier years.

Table 3.10: Detection limits and precision of calcium in precipitation.

	Measurements		**Laboratory**	
Country	**Precision**	**Detection limit, mg/l**	**Precision**	**Detection limit, mg/l**
Austria		0.11	RSD: 2%	0.003
Czech Republic	RSD: 7.0%; CoV: 4.5% M.MAD: 0.109 mg/l	0.014	RSD: 2.0%	0.014
Denmark			M.MAD: 0.01; CoV: 3.8%	0.13
Estonia		0.407		0.382
Finland			M.MAD: 0.001 mg/l; CoV: 2.2%	0.005
France			at c=0.264: RSD=2.83%; CoV=10.72% at c=1.197: RSD=3.72%; CoV=3.11%	0.02
Germany				0.01
Hungary			M.MAD: 0.003; CoV: 1.33%	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 RSD: 3.6% at 0.05 mg Ca/l	0.002
Latvia			CoV: 4.1%	0.095
Lithuania			c<0.2mgCa/l: 5.5% RSD 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 SD: 0.006 at c=0.15 mg/l	0.01
Poland			RSD: 0.9% at 2 mg/l RSD: 1.8% at 0.8 mg/l RSD: 2.1% at 0.4 mg/l	0.03
PL05	M.MAD: 0.019; CoV: 13%	0.02	M.MAD: 0.002; CoV: 1.6%	0.001
Portugal			1.31%	0.06
Russia			CoV: 10.7%; MAD: 0.03	0.05
Serbia and Montenegro*			81%	0.005
Slovakia			0.91%	0.02
Spain			CoV: 7.4%	0.04
Sweden*	uncertainty (95% conf. int.): 18%	0.05	R: 5%	0.04
Switzerland			M.MAD: 0.02	0.02
Turkey			M.MAD: 0.0199; CoV: 2.10%	0.032
UK*			5%	0.05

* Data from SE, UK and YU are taken from earlier years.

Table 3.11: Detection limits and precision of potassium in precipitation.

Country	Measurements		Laboratory	
	Precision	**Detection limit, mg/l**	**Precision**	**Detection limit, mg/l**
Austria		0.015	RSD: 2.3%	0.005
Czech Republic	RSD: 18.7%; CoV: 5.1% M.MAD: 0.003 mg/l		RSD: 10.2%	0.008
Denmark			M.MAD: 0.01; CoV: 2.5%	0.06
Estonia		0.095		0.1
Finland			M.MAD: 0.002 mg/l; CoV: 3.5%	0.006
France			at c=0.183: RSD=2.1%; CoV=11.51% at c=0.996: RSD=4.23%; CoV=4.25%	0.02
Germany				0.01
Hungary			M.MAD: 0.003; CoV: 2.24%	ca. 0.01
Italy (IT01)	RSD: 1.4% at 1 mg K/l	0.01	RSD: 1.5% at 0.5 mg K/l RSD: 3.0% at 0.05 mg K/l	0.002
Latvia			CoV: 5.5%	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 SD: 0.015; c=0.20 mg/l	0.01
Poland			RSD: 1.0% at 0.5 mg/l RSD: 2.9% at 0.1 mg/l RSD: 2.4% at 0.05 mg/l	0.02
PL05	M.MAD: 0.006; CoV: 15.5%	0.04	M.MAD: 0.001; CoV: 0.8%	0.002
Portugal			1.69%	0.077
Russia			CoV: 9%; MAD: 0.03	0.03
Serbia and Montenegro*			98%	0.015
Slovakia			2.13%	0.03
Spain			CoV: 18%	0.05
Sweden*	uncertainty (95% conf. int.): 114%	0.05	R: 8%	0.05
Switzerland			M.MAD: 0.01	0.02
Turkey			M.MAD: 0.0063; CoV: 2.62%	0.019
UK*			6%	0.05

* Data from SE, UK and YU are taken from earlier years.

Table 3.12: Detection limits and precision of chloride in precipitation.

Country	Measurements		Laboratory	
	Precision	**Detection limit, mg/l**	**Precision**	**Detection limit, mg/l**
Austria		0.037	RSD: 3.6%	0.009
Czech Republic	RSD: 12.6%; CoV: 11.1% M.MAD: 0.047 mg/l	0.02	RSD: 1.4%	0.02
Denmark			M.MAD: 0.07; CoV: 2.3%	0.06
Estonia		0.463		0.155
Finland			M.MAD: 0.003 mg/l; CoV: 1.4%	0.01
France			at c=0.604: RSD=1.43%; CoV=2.37% at c=2.984: RSD=6.03%; CoV=2.02%	0.02
Germany				0.01
Hungary			M.MAD: 0.092; CoV: 24%	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 RSD: 1.1% at 0.05 mg Cl/l	0.001
Italy, EU (IT04)*				0.032 ppm
Latvia			CoV: 2.09%	0.084
Lithuania			c<0.5 mg Cl/l: 4.7% RSD 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 SD: 0.02 at c=0.46 mg/l	0.01
Poland			RSD: 1.9% at 10 mg/L RSD: 2% at 1 mg/L RSD: 2.6% at 0.5 mg/L	0.02
PL05	M.MAD: 0.02; CoV: 3.9%	0.1	M.MAD: 0.04; CoV: 9.2%	0.1
Portugal			0.53%	0.03
Russia			CoV: 12%; M.MAD: 0.01	0.03
Serbia and Montenegro*				0.05
Slovakia			0.66%	0.04
Spain			CoV: 4.9%	0.31
Sweden*	uncertainty (95% conf. int.): 18%	0.05	R: 2%	0.05
Switzerland			M.MAD: 0.02	0.01
Turkey			M.MAD: 0.063; CoV: 13.68%	0.050
UK*			3%	0.05

* Data from IT04, SE, UK and YU are taken from earlier years.

Table 3.13: Detection limits and precision of magnesium in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, mg/l	Precision	Detection limit, mg/l
Austria		0.034	RSD: 1.2%	0.002
Czech Republic	RSD: 13.8%; CoV: 8.9% M.MAD: 0.01 mg/l	0.002	RSD: 3.6%	0.002
Denmark			M.MAD: 0.02; CoV: 2.8%	0.01
Estonia		0.077		0.089
Finland			M.MAD: 0.001 mg/l; CoV: 2.1%	0.003
France			at c=0.213; RSD=1.17%; CoV=5.5% at c=1.05: RSD=2%; CoV=1.91%	0.02
Germany				0.01
Hungary			M.MAD: 0.003; CoV: 3%	ca. 0.01
Ireland				0.05
Italy (IT01)	RSD: 1.1% at 0.5 mg Mg/l	0.005	RSD: 0.8% at 0.5 mg Mg/l RSD: 3.2% at 0.05 mg Mg/l	0.001
Latvia			CoV: 3.9%	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 SD: 0.007; c=0.19 mg/l	0.01
Poland			RSD: 1.0% at 0.25mg/l RSD: 1.0% at 0.1 mg/l RSD: 2.4% at 0.025 mg/l	0.007
PL05	M.MAD: 0.002; 7%	0.01	M.MAD: 0.001; CoV: 3.5%	0.001
Portugal			0.60%	0.03
Russia			CoV: 31%; MAD: 0.02	0.001
Serbia and Montenegro*			99.5%	0.002
Slovakia			1.56%	0.03
Spain			CoV: 7.2%	0.02
Sweden*	uncertainty (95% conf. int.): 15%	0.02	R: 3%	0.01
Switzerland			M.MAD: 0.01	0.03
Turkey			M.MAD: 0.0033; CoV: 4.37%	0.012
UK*			3.5%	0.05

* Data from SE, UK and YU are taken from earlier years.

Table 3.14: Detection limits and precision of sodium in precipitation.

Country	Measurements		Laboratory	
	Precision	**Detection limit, mg/l**	**Precision**	**Detection limit, mg/l**
Austria		0.021	RSD: 1.2%	0.003
Czech Republic	RSD: 13.4%; CoV: 6.8% M.MAD: 0.007 mg/l	0.007	RSD: 2.6%	0.007
Denmark			M.MAD: 0.06; CoV: 3.1%	0.07
Estonia		0.095		0.1
Finland			M.MAD: 0.001 mg/l; CoV: 0.9%	0.002
France			at c=0.561; RSD=1.64%; CoV=2.92% at c=3.872: RSD=7.79%; CoV=2.01%	0.02
Germany				0.01
Hungary			M.MAD: 0.004%; CoV: 1.07%	ca. 0.01
Ireland				0.05
Italy (IT01)	RSD: 0.9% at 0.5 mg Na/l	0.005	RSD: 1.3% at 0.5 mg Na/l RSD: 2.0% at 0.05 mg Na/l	0.001
Latvia			CoV: 1.5%	0.053
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 SD: 0.011 at c=0.30 mg/l	0.01
Poland			RSD: 0.8% at 1 mg/l RSD: 1.4% at 0.4 mg/l RSD: 2.3% at 0.2 mg/l	0.02
PL05	M.MAD: 0.011; CoV: 13.9%	0.02	M.MAD: 0.002; CoV: 2.0%	0.002
Portugal			0.54%	0.025
Russia			CoV: 5.6%; MAD: 0.02	0.01
Serbia and Montenegro*			98.25%	0.001
Slovakia			1.28%	0.04
Spain			CoV: 14%	0.1
Sweden*	uncertainty (95% conf. int.): 112%	0.05	R: 4%	0.05
Switzerland			M.MAD: 0.02	0.03
Turkey			M.MAD: 0.0063; CoV: 1.98%	0.023
UK*			3.50%	0.03

" Data from SE, UK and YU are taken from earlier years.

Table 3.15: Detection limits and precision of arsenic in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, μg/l	Precision	Detection limit, μg/l
Estonia *		0.2		
Finland			M.MAD: 0.008 μg/l; CoV: 10.5%	0.006
Germany				0.004
Slovakia			1.99%	0.5
Norway				0.1

* Data from EE is taken from earlier years.

Table 3.16: Detection limits and precision of cadmium in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, μg/l	Precision	Detection limit, μg/l
Czech Republic	RSD: 9.5%; CoV: 10.9% M.MAD : 0.028 μg/l	0.04	RSD : 8.5%	0.04
Estonia *		0.01		
Finland			M.MAD: 0.002 μg/l CoV: 3.0%	0.002
Germany				0.003
Latvia			CoV: 12.3%	0.052
Slovakia			2.01 %	0.1
Netherlands			SD: 0.00007	0.0003 umol/l
Norway				0.005

* Data from EE is taken from earlier years.

Table 3.17: Detection limits and precision of chromium in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, μg/l	Precision	Detection limit, μg/l
Finland			M.MAD: 0.04 μg/l; CoV: 21.8%	0.02
Germany				0.01
Slovakia			1.58 %	0.04
Norway				0.2

Table 3.18: Detection limits and precision of copper in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, μg/l	Precision	Detection limit, μg/l
Estonia *		26		
Finland			M.MAD: 0.057 μg/l; CoV: 4.7%	0.05
Germany				0.01
Latvia			CoV: 12.7%	0.2
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
Slovakia			1.83 %	0.2

* Data from EE is taken from earlier years.

Table 3.19: 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% M.MAD : 0.02mg/l	6	RSD: 9.4%	6
Finland			M.MAD: 3.21 µg/l CoV: 9.6%	1.5
Germany				0.5
Netherlands			SD: 0.09	0.4 µmol/l

Table 3.20: 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% M.MAD : 2.15 µg/l	0.5	RSD : 5.2%	0.5
Finland			M.MAD: 0.073 µg/l CoV: 3.4%	0.005
Slovakia			2.96%	0.05

Table 3.21: Detection limits and precision of nickel in precipitation.

Country	Measurements		Laboratory	
	Precision	**Detection limit, µg/l**	**Precision**	**Detection limit, µg/l**
Czech Republic	RSD: 8.1% CoV: 7.6% M.MAD : 0.175 µg/l	1.0	RSD : 4.1%	1.0
Finland			M.MAD: 0.04 µg/l CoV: 15.5%	0.02
Germany				0.2
Norway				0.2
Slovakia			2.34 %	0.1

Table 3.22: Detection limits and precision of lead in precipitation.

Country	Measurements		Laboratory	
	Precision	**Detection limit, µg/l**	**Precision**	**Detection limit, µg/l**
Czech Republic	RSD: 9.0%; CoV: 7.0% M.MAD: 0.471 µg/l	0.7	RSD: 8.2%	0.7
Estonia*		0.6		
Finland			M.MAD: 0.049 µg/l CoV: 3.7%	0.03
Germany				0.002
Latvia			CoV: 10.4%	0.56
Netherlands			SD: 0.0005	0.002 µmol/l
Norway				0.01
Slovakia			3.52%	0.2

* Data from EE is taken from earlier years.

Table 3.23: 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% M.MAD: 0.003 mg/l	3	RSD: 7.4%	3
Finland			M.MAD: 0.183 µg/l CoV: 3.1%	0.03
Germany				0.2
Latvia			CoV: 2.2%	0.95
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

Table 3.24: Detection limits and precision of arsenic in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Czech Republic	RSD: 13.3%; CoV: 11.8% M.MAD: 0.15 ng/m^3	0.2 ng/m^3	RSD: 8.7%	0.75 µg/l
Germany				0.004 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; coarse: 0.24 ng/m^3

* Data from NL is taken from earlier years.

Table 3.25: Detection limits and precision of cadmium in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Czech Republic	RSD: 10.7%; CoV: 13.7% M.MAD: 0.042 ng/m^3	0.01 ng/m^3	RSD: 4.1%	0.05 µg/l
Germany				0.003 µg/l
Lativia		0.015	CoV: 1.6%	0.77 µg/l
Slovakia			1.44 %	0.04 µg/l
Netherlands *			0.01	0.04 ng/m^3
Norway, NO42				0.002 ng/m^3
NO99				fine: 0.002 ng/m^3; coarse: 0.001 ng/m^3

* Data from NL is taken from earlier years.

Table 3.26: *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; coarse: 0.6 ng/m^3

Table 3.27: *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				17 µg/l
Slovakia			1.41%	0.5 µg/l
Norway, NO42				0.01 ng/m^3
NO99				fine: 0.04 ng/m^3; coarse: 0.02 ng/m^3

Table 3.28: *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		0.15	CoV: 2.2%	5.9 µg/l
Slovakia			3.06%	0.1 µg/l
Norway, NO42				0.07 ng/m^3

Table 3.29: *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		0.22	CoV: 1.1%	7.5 µg/l
Slovakia			1.32%	0.4 µg/l
Norway, NO42				0.02 ng/m^3
NO99				fine: 0.008 ng/m^3; coarse: 0.02 ng/m^3

Table 3.30: Detection limits and precision of lead in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Czech Republic	RSD: 10.2%; CoV: 10.6% M.MAD: 0.8 ng/m^3	0.2 ng/m^3	RSD: 2.1%	0.78 µg/l
Germany				0.002 µg/l
Lativia		0.29000	CoV: 3.6%	5 µg/l
Slovakia			1.96%	0.4 µg/l
Netherlands *			0.06	0.2 ng/m^3
Norway, NO42				0.007 ng/m^3
NO99				fine: 0.008 ng/m^3; coarse: 0.004 ng/m^3

* Data from NL is taken from earlier years.

Table 3.31: Detection limits and precision of zinc in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Lativia		1.5	CoV: 2.7%	13 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; coarse: 0.02 ng/m^3

* Data from NL is taken from earlier years.

Table 3.32: Detection limits and precision of measurements of particulate matter.

Country	Precision	Detection limit
Germany (PM10)		1 µg/m^3
Slovakia (TSP)	2.00%	0.2 µg/m^3
Switzerland (PM10)	RSD: 7%	1 µg/m^3
Norway (PM10)	RSD: 5%	0.2 µg/m^3

Table 3.33: Detection limits and precision of volatile organic carbons, VOC.

	Laboratory detection limit. [ppb]				
Compund	**Czech Republic ***	**France**	**Germany**	**Finland***	**Spain**
VOC (general)		0.01	0.01		
Ethane	0.055			0.008	0.33
Ethene	0.020			0.009	0.35
Ethyne	0.041			0.011	
Propane	0.008			0.006	0.89
Propene	0.011			0.007	3.38
Propyne	0.003			0.004	
N-butane	0.003			0.005	0.59
2-methyl propane (i-butane)	0.005			0.005	1.81
2-methyl propene (i-butene)	0.006			0.006	
1-butene	0.009			0.005	0.52
Trans-2-butene	0.004			0.005	0.52
Cis-2-butene	0.008			0.006	0.57
1,3-butadiene	0.009			0.006	0.23
N-pentane	0.003			0.005	1.39
2-methyl butane (i-pentane)	0.008			0.005	
1-pentene					0.51
Trans-2-pentene	0.012			0.005	0.45
Cis-2-pentene	0.009			0.006	1.15
2-methyl pentane	0.003			0.006	
3-methyl pentane	0.012			0.006	
Isoprene	0.006			0.008	0.58
N-hexane	0.011			0.006	0.4
Hexene					0.54
Cyclohexane	0.003			0.006	
N-heptane	0.023			0.004	0.94
Benzene	0.012			0.003	0.75
Methyl benzene (toluene)	0.021			0.004	1.49
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			

* Data form CZ and FI are taken from earlier reports.

Table 3.34: Detection limits and precision of persistent organic pollutants (POP).

Compund	**Laboratory detection limit, pg/m^3**	
	Czech Republic	**Norway**
PCB 28	2	0.7
PCB 31		0.5
PCB 52	2	0.2
PCB 101	2	0.06
PCB 105		0.01
PCB 118	2	0.05
PCB 138	1	0.05
PCB 153	1	0.05
PCB 153		0.01
PCB 180	1	0.02
alfa-HCH	1	0.1
beta-HCH	3	
gama-HCH	1	0.3
delta-HCH	1	
HCB		0.8
p,p'-DDE	1	
p,p'-DDD	1	
p,p'-DDT	1	0.01
Hexachlorbenzen	1	
Pentachlorbenzen	1	
tr-kordan		0.08
cis-kordan		0.04
tr-nonaklor		0.02
tr-nonaklor		
PAH (general)		1
Naftalen	5	
Acenaftylen	5	
Acenaften	5	
Fluoren	5	
Fenantren	5	
Antracen	5	
Fluoranten	5	
Pyren	5	
Benz[a]antracen	10	
Chrysen	10	
Benzo[b]fluoranten	10	
Benzo[k]fluoranten	10	
Benzo[a]pyren	10	
Indeno[123cd]pyren	10	
Dibenz[ah]antracen	10	
Benzo[ghi]perylen	10	

* Data form CZ is taken from earlier reports.

Annex 4

Random and systematic errors in the lab intercomparisons

✓ The random errors are given in 2RSD% and the colors code correspond to:

🟨 1-2 DQO 🟥 >2 DQO

✓ The systematic errors are given in RB% and the colour codes corresponds to:

🟪 <-20% 🟧 <-20,-10>% 🟨 <10,20>% 🟥 >20%

🟦 systematic, i.e. all four samples have either positive or negative error

Table 4.1: Random error (2RSD%) for SO_4 in precipitation, in the different laboratory intercomparisons.

	SO4 prec		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
			1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT		9.2		25.1	5.6	28.2	3.3	6.8	5.3	1.8	2.6	1.8	1.7	0.6	1.3	0.8	1.4		1.3	0.5
2	BE		13.5			82.1	15.4		4.6	1.8	4.3	2.2	3	1							
3	CS				27.6	3.1	2.7	0.9	8.1	0.5	0.5	1.1	0.9	2.4	0.2	0.8	0.5	1.7	1.2	0.7	0.5
4	DK		2.3		3.3	4	2.5	2.6	2.7	1.1	1.4	0.9	0.9	0.3	0.6	0.6	0.4	0.2	0.2	0.5	1.5
5	FI		1.3		1.7	1.3	1.9	2.2	1.7	0.7	5.3	0.5	0.9	1.7	0.8	1.1	1	0.6	1	0.4	0.8
6	FR		3.1		33.5	3.1	3.8	9.2	2.4	2.4	0.7	1.4	5.6	0.9	0.2	0.6	0.2	2.7	0.8	0.1	0.4
7	DDLeip										8.7	2.8	3.8				0.4	0.4	2.1	8.2	1.6
8	DE		11.6			13.7	2.7	5.4	5.9	1.1	1.4	0.7	1.4	0.4	0.5	0.3	1.3	0.5	0.4	0.7	0.5
9	GR		16.4			13.7	7.7	16.3	14.3	5.1	2.1	5.3	1.5	5.6	4.2		6.5	4.8	2.8		
10	HU		22.8			23.4	5.6	8.9	17.3	8.9	11.9	9.3	16.6	10.2	1.7	16.9	10.4	1.7	2.9	0.6	1.9
11	IS					2.3	3.8	1.8	3.8	6	3.9	2.2	5.8	0.2	2.3	0.9	1.5	1.7	7	2.3	3
12	IE	Met					2.9	9.2	2.1	2.2	5.2	6	8.4	5.2	1.2	1.4	2.1	0.4	0.3	0.1	0.6
13	IT	CNR								3.1	17.4	1	1.8	1.4	5	3	1.4	0.9	0.2	2.5	7
14	NL		1		3.3	3.1	1.2	5.9	1.6	1.5	2.7	0.9	1.3	2.6	1.2	0.6	1	0.7	2.4	0.4	2.9
15	NO		4.9		3.3	2	1	1.3	3.3	1.1	0.7	0.5	2.2	0.8	0.5	0.9	2.2	2.4	0.9	2.6	1.2
16	PL	Met.	8.9		17.6	7.2	21.5	3.9	7.1			3.9	4.1	5.9	2	3.3	1.8	0.8	1.4	1.9	0.1
17	PT					2.2		14.8	4	1.5	2.7	9.5	13.6	4.9	0.8	25.9	1.5	1.3	2.1	11.8	1.4
18	RO										15.1						19.8	14.7	5.6	25.4	8.8
19	ES										0.9	1		1.2	28.9	3.9	2.6	2.7	5.6	4	1.6
20	SE	IVL	7.4		7.5	4.7	2.3	7.6	4.6	1.5	3.7	1.7	0.3	0.7	2.9	0.4	2.3	8.8	1.5	2.4	4.8
21	CH		1.3		1.7		1.9	1.8	1.9	2.5	4.3	0.8	1.3	0.4	0.1	0.4	0.5	0.1	4.5	1.6	0.6
22	SOV/RU					20.5	393.8			8.9	3.2	2.6	3.6	0.5	1	4.1	2.6	2.5	0.2	3	4.1
23	GB		4.5		6.7	2.3	1.9	5.2	4	1.6	0.9	0.5	0.8	1	1.4	1.6	1.1	4	7.5	0.4	1
24	YU					13.7	21.5	2.8	12.5	4.5	3.6	5.7	10.7	1.9	9.7	8.5	9	7.8		6.8	
25	SE	SNV									1.4	1.9	1.5						0.5		
26	CA	AES	24.5		110.5	2.3	1.9	2.2	1.1		2	1.9	0.5	0.4	2.4	1	0.6	1.6	0.6	0.7	0.9
27	US	ILL.								1.8	0.4	1.2	1.1	0.2	0.8	0.6	0.4	0.3		0.2	0.4
28	US	EPA								0.7	0.4	0.3	1.9	0.4							
29	CA	CONC.									1.6	3.9	3						0.6		
30	IT	ISPRA										0.7	1	0.6	0.4	0.5	0.2	0.4	0.8	1.1	0.5
31	SK													6.5	2.6	5.8	2.5	0.6	1.7	0.4	0.6
32	LT														8.6	6.8	4.4	2.2	11.2	2	
33	LV														5.9	11.5	12.7	2.2	2.1	3.7	0.9
34	TR														3.7	0.8	0.7	1.4	25.7	2	1
35	HR														9.8	5.8	4.9	1	0.9	0.6	0.5
36	SI														11.6	5.4	2.1	0.3	2.5	1.1	1.3
37	IE	EPA/EBS								2.4						11.7	2.1	0.9	3.7	6.6	
38	EE															6.6	21.3	2.9	2.4	1.5	2.2
39	PL (Env.)																4.7	3.5		20.2	1.8
40	MK																				
Gml.	19 TNO					6.7	21.1	0.4	3	3.3											

Table 4.2: Systematic error (RB%) for SO_4 in precipitation, in the different laboratory intercomparisons.

	SO4 prec	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
		1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT	6.3		2.1	-20.5	-32.5	0.0	-1.7	10.2	-5.0	-6.9	-3.9	-5.0	3.3	0.4	3.5	-1.6		-0.1	1.1
2	BE	-11.3			44.8	30.6		4.1	2.0	-4.1	-2.9	2.7	2.5							
3	CS			34.9	-2.2	-2.8	-0.7	-1.4	-0.2	3.1	-1.2	-1.0	1.0	0.7	-1.0	-2.7	-1.4	-0.4	-0.6	-1.5
4	DK	-5.3		19.5	2.2	-1.6	-0.7	0.6	-3.1	-0.2	-2.7	-2.1	-2.1	-1.8	-4.2	-1.1	0.6	-0.3	-1.5	0.0
5	FI	0.6		7.2	1.3	0.0	-1.8	-1.6	3.6	0.9	-1.0	-4.2	0.1	0.2	-0.1	1.3	1.4	0.6	0.4	1.1
6	FR	9.0		34.9	3.5	7.1	4.3	1.4	2.2	-0.9	-2.9	-22.7	1.3	0.3	-1.4	0.9	0.3	1.7	-0.2	-1.0
7	DDLeip									-2.0	-2.6	-0.9				-0.3	2.0	5.4	38.1	-4.3
8	DE	-26.2			-44.5	3.5	-6.8	-9.7	0.9	4.8	0.7	2.7	0.4	0.4	-0.2	-8.1	-0.3	-0.6	-1.5	0.8
9	GR	-3.0			-14.8	56.5	-13.3	-10.5	16.5	2.6	0.5	-20.0	18.7	-3.6		-1.9	-3.1	19.3		
10	HU	-3.7			-27.1	-9.4	-14.3	7.2	-28.7	1.5	24.7	-46.7	-31.8	-12.2	11.8	-14.3	6.1	-2.1	1.5	-0.8
11	IS				2.2	4.7	-1.4	-0.2	19.4	5.7	-8.6	-3.2	2.9	7.1	1.3	-1.2	-2.5	-1.8	-1.0	1.4
12	IE Met					-0.9	-12.7	6.6	-0.7	-0.2	-12.3	-10.3	-19.7	-4.7	-2.0	-7.6	-1.8	-0.4	-0.2	-0.5
13	IT CNR								-0.4	1.3	-3.8	-1.4	2.2	11.6	4.9	2.0	3.2	-1.0	2.9	5.9
14	NL	-1.2		1.0	-1.8	2.1	-0.7	0.2	1.6	-4.6	-1.8	3.0	8.5	0.3	-0.2	-3.3	0.2	-3.7	-0.6	0.2
15	NO	1.6		6.2	-2.9	-2.4	-2.5	4.1	-1.1	2.2	-2.1	5.0	1.4	0.3	3.9	-5.7	-3.2	-2.4	-4.9	-4.1
16	PL Met.	1.3		25.6	0.0	13.6	7.7	-1.0			-9.1	2.8	-6.4	7.6	-4.1	-5.0	-0.8	-2.0	1.3	-2.1
17	PT				8.2		-11.5	-11.1	2.0	0.2	-61.9	-16.0	12.4	-0.3	-5.1	-5.4	-1.7	-12.4	4.4	6.8
18	RO									-71.5						-48.3	1.2	-6.1	99.5	7.8
19	ES									0.2	-2.3		-15.6	0.2	-0.9	5.7	3.0	3.5	-5.4	1.1
20	SE IVL	3.0		-4.1	-3.1	-0.2	16.7	7.8	1.8	-2.0	35.0	-1.0	0.5	4.2	-1.0	2.4	4.7	3.0	-6.0	-15.5
21	CH	-1.6		-3.1		0.0	-1.4	-1.6	-7.6	-6.8	2.5	0.4	0.4	0.6	0.6	0.5	1.2	-1.8	2.9	1.4
22	SOV/RU				-3.7	471			-2.4	-2.2	1.8	-1.5	-6.0	-8.4	-3.0	1.4	0.0	0.7	-9.8	0.7
23	GB	-6.6		-5.1	-3.1	-4.7	-0.2	-2.5	2.0	1.5	1.1	1.7	3.9	4.7	3.6	2.8	-1.8	10.8	1.5	-0.4
24	YU				0.7	3.5	17.9	-17.3	33.0	3.5	-61.7	40.5	3.8	-15.2	31.4	5.9	0.5		5.4	
25	SE SNV									-3.3	4.2	0.5						-1.4		
26	CA AES	0.6		181.5	4.4	-7.8	-17.6	2.3		0.7	-3.7	-2.8	-1.2	-4.4	-1.2	-1.5	-4.7	1.6	-1.6	-2.5
27	US ILL.								-3.1	2.8	5.8	1.4	1.5	1.7	0.4	0.3	0.4		0.5	-0.5
28	US EPA								0.4	1.5	-1.6	4.5	1.7							
29	CA CONC.									-1.3	-1.8	-12.7						1.4		
30	IT ISPRA										-0.7	0.2	-0.7	0.8	-0.1	-1.1	-0.3	1.2	2.4	-0.2
31	SK												-3.1	-1.2	-0.3	3.7	-4.5	5.9	-1.0	-1.2
32	LT													30.1	0.2	6.8	-7.9	8.4	-6.4	
33	LV													-28.6	20.7	23.7	1.4	2.8	3.1	0.8
34	TR													1.2	-2.9	-3.6	1.8	12.9	1.4	0.1
35	HR													-7.6	-6.6	-29.0	-14.7	-1.8	-0.1	1.8
36	SI													12.1	6.0	-1.2	-2.1	0.6	0.8	-1.5
37	IE EPA/EB	S							-8.0						0.0	-3.6	-1.5	6.4	0.1	
38	EE														-12.0	37.3	-4.5	2.0	2.2	-9.4
39	PL (Env.)															4.8	9.8		18.8	6.4
40	MK																			
Gml.	19 TNO				-11.0	-16.5	-1.8	5.4	18.9											

Table 4.3: Random error (2RSD%) for NO_3 in precipitation, in the different laboratory intercomparisons.

	NO3 prec		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
			1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT		3.7		23.9	5.6	8	5.2	4.7	3.2	11.5	4.7	2.6	1.4	0.6	0.7	2.4	0.4		0.9	1
2	BE		4.8			7.6		15	4.7	1.6	7.7	3	1.5	1.7							
3	CS				14.4	2.8	1.8	5.7	3.6	1.1	1.6	0.9	0.5	1.3	0.6	0.7	0.9	0.4	0.4	0.4	0.8
4	DK		2.9		4.2	10.4	4.3	3.1	2.1	1.6	1.1	0.9	2.6	0.4	1	1.4	0.6	1.2	1.8	1.6	1.1
5	FI						1.8	3.6	1	1.6	2.7	8.5	0.6	1	1.1	0.5	0.7	0.6	0.7	0.3	1
6	FR		10.1		4.6	1.4	10.4	1.6	2.6	2.7	7.7	0.4	0.8	0.9	2.8	0.4	0.7	0.6	0.9	0.9	0.5
7	DD										3.3	2.6	15.3				0.7	0.8	3.9	1.1	0.9
8	DE		335				1.8	3.1	4.1	2.7	1.6	0.4	0.5	0.6	0.6	0.7	2.2	0.4	0.3	0.9	0.8
9	GR											9.3		2.5	7.8			9.6	0.4		
10	HU		13.8		9.9	5.6	1.8	6.7	5.7	1.1	61.4	6.3	2.6	5.4	4.7	2.5	2.7	2.4	4.5	1.6	1.4
11	IS						6.8						5	1.8	1.8	2	1.4	1.2	1.8	3	3.6
12	IE											5.4	5.5	3.2	0.6	0.7	1.5	1.2		1.2	0.4
13	IT	CNR								4.3	7.7	2.6	1.8	8.1	0.6	1.7	1.5	0.8	0.3	2	2.7
14	NL		1.8		21.1	6.3	4.9	6.3	1.6	2	0	1.6	0.5	0.7	1.2	4.3	2.2	0.5	0.9	0.8	1
15	NO		6.8		4.2	2.1	1.8	5.7	1.6	0.5	0.5	0.7	2.7	0.8	2.9	0.8	2	0.6	2.2	2.2	1.5
16	PL		5		8.4	4.2	17.2	6.7	4.7			5.8	2	4.8	2.9	1.7	2.2	0.8	1.9	0.3	0.3
17	PT									2.7	3.3	19.5	11	19.1	0.7	1.1	3.7	1.8	1.4	0.9	1
18	RO										18.1						23.6	14.8		1.5	
19	ES										1.6	3.2		0.4	0.5	0.5	1.1	2.2	4.5	4.8	1.5
20	SE	IVL	8.6		35.2	42.4	3.5	5.9	6.7	2.1	2.2	5.2	0.2	0.4	0.6	0.4	0.6	0.3	1.3	0.7	0.8
21	CH		11		2.8		3.1	8.3	4.1	1.6	8.8	0.4	0.7	1.4	0.1	0.8	2	0.5	1.1	0.2	0.6
22	RU									4.8	6.6	5.4	2.6	0.8	0.6	5.7	2.2	4.8	4.9	3.1	4.7
23	GB		34.9		7	3.5	2.5	3.6	3.6	0	2.2	0.4	0.2	0.2	1.7	3.1	2.6	2.2	0.5	3.8	0.9
24	YU					13.9	16.6		10.4	9	7.7	11.8	16.5	5	5.8	4.9	2.1	8.1	3.2	19.2	38.8
25	SE	SNV									3.3	1.5	2								
26	CA		18		1.8	0.7	3.7	0	4.7		1.1	1.5	0.8	0.1	0.6	1.1	1	1.5	0.7	1.3	0.8
27	US-I									0.2	0.5	1	0.8	0.9	1.1	0.8	1.3	1.2	0.9	0.8	0.6
28	US-E									0.5	1	0.5	1.4	0.5							
29	CA	CONC.									3.8	4.7	3.4								
30	IT	ISPRA										1.3	1.5	0.9	0.6	0.7	2.2	0.4	0.5	0.4	1.5
31	SK													2.5	2.6	1.6	0.6	2	1	1.8	1.7
32	LT														3.6	1	3.5	2.2	0.3	1.2	
33	LV														3.4	6.9	6.3	8.9	5.7	1.2	0.6
34	TU														0.9	0.4	2.1	2.9	1.2	0.6	0.6
35	HR														1.7	2.7	1.7	1.2	9.7	2.3	1.2
36	SI														1.2	4.6	2	0.4	1.1	2.6	1
37	IE (EPA)															1	2.2	1.3	1.8	27.7	
38	EE															7	3.1	1.8	2.9	1.1	10.6
39	PL (Env.)																4.4	2.6	1.2	3.5	2.3
40	MK																		5.8	10.8	8.1
41	EE Tartu																	6.1			
42	IS Ork																	0.4			
Gml. 19	NL	TNO					8.6	3.6	3.6	5.9											

Table 4.4: Systematic error (RB%) for NO_3 in precipitation, measurements in the different laboratory intercomparisons.

	NO3 prec	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
		1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT	6.7		-29.3 🟦	6.8	9.0 🟦	-4.4	-8.3 🟦	3.3 🟦	-11.4 🟦	2.4	-0.3	-5.1 🟦	2.5 🟦	1.2 🟦	5.0 🟦	-4.0 🟦		1.7 🟦	1.0
2	BE	4.5 🟦			-0.9		-12.1	2.5 🟦	4.6 🟦	0.0	-5.8 🟦	0.4	-6.8 🟦							
3	CS			-4.1	0.9	9.0 🟦	-3.8 🟦	-3.8 🟦	-1.3	2.0	0.3	-1.1 🟦	1.1	0.8	0.6	-2.5 🟦	0.3	-1.9 🟦	-3.0 🟦	-4.5 🟦
4	DK	-1.3		-3.4	-10.2 🟦	-5.3 🟦	-1.3	0.0	-0.7	-0.7	0.5	-4.6 🟦	-3.9 🟦	1.2	-3.1 🟦	0.6	-1.8 🟦	2.0 🟦	2.5	0.6
5	FI					0.8	2.5 🟦	3.8 🟦	-1.3	-2.7 🟦	1.5	-4.9 🟦	-1.0 🟦	3.5 🟦	1.7 🟦	-2.3 🟦	2.2 🟦	0.4	1.0 🟦	1.4
6	FR	-9.0		-4.8	-0.9	-2.3	1.3	3.2	-2.6	6.7 🟦	0.2	-2.5 🟦	1.5 🟦	1.0	0.4	0.9	-2.7 🟦	0.2	-0.7	-2.0 🟦
7	DD									-2.8	-4.6 🟦	17.3				-2.0 🟦	0.3	-7.1 🟦	-4.3 🟦	-3.7 🟦
8	DE	234.6 🟦				3.8 🟦	0.6	-1.9	6.5 🟦	0.7	2.2 🟦	1.7 🟦	0.5	-0.4 🟦	-0.7	-9.7 🟦	1.1 🟦	2.4 🟦	-0.8	0.2
9	GR										8.0		-5.8 🟦	-4.8			-14.2	-1.6 🟦		
10	HU	11.2		13.8 🟦	4.3	2.3	6.3	7.6 🟦	6.5 🟦	-10.1	5.8	3.3 🟦	-0.9	-9.6 🟦	9.2 🟦	-12.6 🟦	4.0 🟦	-1.4	0.9	-1.4
11	IS					0.8						-10.4 🟦	2.9 🟦	-2.5 🟦	-0.4	3.4 🟦	-2.0 🟦	0.2	4.0 🟦	10.4 🟦
12	IE										-5.3	-0.3	-3.8 🟦	-0.4 🟦	-0.7	-0.9 🟦	-0.5		-1.8	0.2
13	IT CNR								1.3	-4.0	0.5	-2.7 🟦	-0.8	8.1 🟦	1.2	1.6	1.5 🟦	-2.3 🟦	4.4 🟦	1.0
14	NL	0.2		1.7	10.2	12.8 🟦	13.2	5.1 🟦	-4.0 🟦	-1.3 🟦	0.9	-1.6 🟦	1.0	-1.1	-5.1	-1.8 🟦	0.3	-1.2	-0.6 🟦	-1.0 🟦
15	NO	-7.4		-5.2 🟦	-3.4 🟦	0.0	9.5 🟦	10.2 🟦	0.7	0.0	0.8	5.5 🟦	1.7 🟦	0.3	6.1 🟦	-3.9 🟦	-1.9 🟦	-1.9	-0.6	-4.1 🟦
16	PL	6.1		-5.2	5.1	-15.8	-5.7	7.0			-10.9 🟦	0.4	-9.7 🟦	-5.3 🟦	13.2 🟦	-8.6 🟦	-2.7 🟦	-3.8 🟦	-0.4	-3.9 🟦
17	PT								-4.6 🟦	10.1 🟦	-78.3 🟦	-1.0	18.6	-1.1	-2.9 🟦	-8.4 🟦	1.9	-2.6 🟦	3.0 🟦	3.6 🟦
18	RO									-16.8						20.4	-81.4 🟦		-16.9 🟦	
19	ES									2.0	2.6		-1.5 🟦	-3.2 🟦	-0.7	0.9	4.8 🟦	-2.4	-2.9	3.9 🟦
20	SE IVL	-9.4		-3.4	-9.4 🟦	2.3	5.0 🟦	1.9	1.3	-2.7	18.5 🟦	-1.7 🟦	0.9 🟦	2.4 🟦	2.2 🟦	-0.9 🟦	0.6 🟦	0.6	1.0 🟦	1.0
21	CH	-3.4		-1.7		-1.5	4.4	-1.3	-3.9 🟦	-10.7 🟦	2.5 🟦	1.3 🟦	0.2	1.0 🟦	0.6	0.2	1.2 🟦	-0.1	0.1	-0.5 🟦
22	RU								-10.4 🟦	6.7 🟦	-3.3	-3.2 🟦	-4.8 🟦	-3.7 🟦	5.2	1.6	6.2	-0.1	-5.0 🟦	-1.6
23	GB	-6.7		-8.6 🟦	1.7	-1.5	-0.6	8.9 🟦	-2.6 🟦	0.0	0.2	2.6 🟦	1.6 🟦	3.1	3.3	6.5 🟦	-3.6 🟦	1.9 🟦	-1.1	-0.5
24	YU				-3.4	6.0 🟦		-12.7 🟦	-8.5	3.4	-38.0 🟦	-1.4	-1.0	-29.3 🟦	-12.4 🟦	17.9 🟦	-28.8 🟦	-7.9 🟦	3.4	134.0 🟦
25	SE SNV									-1.3	3.1 🟦	-1.0								
26	CA	-0.9		-1.9	-1.7 🟦	-3.8	0.0	-8.3 🟦		-0.7	-3.3 🟦	-1.7 🟦	-3.7 🟦	-1.8 🟦	-2.3 🟦	0.3	-4.6 🟦	-0.9	-1.4	-2.1 🟦
27	US-I								-0.1	2.7 🟦	2.2 🟦	-0.3	2.7 🟦	3.1 🟦	2.0 🟦	2.3 🟦	1.2	0.9	1.4 🟦	0.2
28	US-E								1.3	0.3	-1.4 🟦	0.5 🟦	-0.9							
29	CA CONC.									2.7	0.7	21.9 🟦								
30	IT ISPRA										-1.2	1.9	0.2	-0.4	-0.3	-1.8	-2.4 🟦	1.0 🟦	0.7 🟦	-0.1
31	SK												-6.3 🟦	6.2 🟦	-2.3 🟦	1.6 🟦	-14.3 🟦	-0.3	1.4	-1.4
32	LT													-3.7	0.9 🟦	7.4 🟦	0.9	1.4 🟦	-3.8 🟦	
33	LV													-7.5 🟦	-19.1 🟦	9.9	3.0	-12.2 🟦	-2.8 🟦	-0.6
34	TU													-1.3 🟦	-2.8 🟦	-4.8 🟦	0.0	0.9	-1.8 🟦	-0.6
35	HR													-0.4	6.4 🟦	2.0 🟦	-1.6 🟦	6.4 🟦	0.0	0.8
36	SI													8.1 🟦	4.1 🟦	-2.1	-1.7 🟦	-2.7	-1.7	-2.5 🟦
37	IE (EPA)														0.3	-3.4 🟦	-2.8 🟦	4.3 🟦	-0.8	
38	EE														-0.3	2.3 🟦	1.0	5.9 🟦	3.4 🟦	-16.0 🟦
39	PL (Env.)															-1.4	5.3 🟦	1.8	11.1 🟦	3.5 🟦
40	MK																	-32.5 🟦	14.1	46.8 🟦
41	EE Tartu																10.7 🟦			
42	IS Ork																-4 🟦			
Gml. 19	NL TNO					7.5	-5.1	1.3	-0.7											
Gml. 25	IE ESB Dubl																			

Table 4.5: *Random error (2RSD%) for NH_4 in precipitation in the different laboratory intercomparisons.*

	NH4 prec		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
			1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT		26.0		23.3	19.0	19.2	12.5	2.8	15.6	26.9	8.4	38.4	5.3	2.9	2.3	3.6	4.0		3.0	0.3
2	BE		26.0			21.5	7.0	20.9	6.7	3.4	11.4	2.5	5.7	4.0							
3	CS				13.1	1.9	3.2	2.6	2.0	5.4	0.6	1.2	1.5	3.1	1.1	2.7	4.7	2.9	3.9	2.9	1.6
4	DK		13.6		18.1	3.7	3.5	17.2	1.6	4.8	3.0	1.2	6.0	4.0	1.7	2.8	0.9	0.4	1.5	1.1	0.8
5	FI				5.8	15.8	2.3	10.7	1.6	2.7	3.0	0.7	2.3	0.9	0.3	0.9	2.8	0.4	2.1	1.4	1.1
6	FR		17.4		25.4	13.3	9.0	30.6	11.1	40.8	9.0	10.4	6.8	7.8	7.8	2.9	1.2	0.8	6.3	1.1	5.0
7	DD/DE (Leip.)										3.0	1.4	4.5				5.1	4.0	0.8	1.0	0.9
8	DE		9.7					1.9	12.7	1.6	1.2	1.8	4.4	1.9	1.0	1.5	4.4	1.7	1.4	1.7	0.9
9	GR											13.9		12.0	2.0			25.2	5.7		
10	HU		20.6		65.6	10.8	11.6	7.0	2.8	13.6	15.6	1.5	6.8	26.2	2.9	11.3	9.4	4.0	3.5	1.0	0.1
11	IS												3.1	9.7	1.5	3.5	3.6	2.5	4.2	7.9	1.8
12	IE	Met, serv										4.4	5.7	3.9	1.9	1.6	3.6	2.5			39.7
13	IT	CNR								7.5	31.1	15.4	7.9	19.4	2.9	6.8	17.0	4.8	0.5	3.9	4.1
14	NL		1.0		33.5	7.6	4.6	7.5	1.2	1.4	2.4	0.3	2.3	12.6	1.0	1.6	2.0	0.9	2.6	2.3	0.4
15	NO		10.9		8.7	4.4	1.2	3.7	8.7	8.2	3.0	1.1	1.1	4.9	1.9	0.8	2.6	0.1	0.8	5.9	0.0
16	PL	Met.	2.0		20.4	7.6	2.9	10.2	9.1			3.4	21.5	4.9	5.8	6.1	2.4	1.7	2.4	2.6	3.9
17	PT								12.3	2.0	1.2	6.3	20.4	7.8	1.9	29.3	5.1	4.1	1.1	2.4	3.0
18	RO										11.4						12.6	0.6	4.4	5.3	17.3
19	ES										19.7	5.6		15.4	3.9	4.4	10.3	5.7	2.3	1.0	0.5
20	SE	IVL	4.6		11.7	24.7	3.8	3.7	1.9	0.7	0.5	3.0	1.1	1.9	1.0	2.9	2.7	0.3	1.8	0.6	0.6
21	CH		10.2		122.2		8.7	6.5	8.3	10.2	6.0	2.1	4.5	0.1	2.9	3.1	3.2	0.5	0.9	1.8	0.7
22	SOV/RU									40.1	4.2	16.3	3.4	5.8	0.8	8.4		1.7	3.5	5.7	0.5
23	GB		3.6		8.7	13.3	2.3	13.0	6.7	4.1	7.2	0.8	2.3	9.7	1.0	3.1	8.3	2.8	1.0	0.9	0.8
24	YU					27.8	6.4	1.9	16.2	57.8	3.0	6.3	14.1	6.7	13.0	7.4	4.7	0.1	9.1	3.8	4.7
25	SE	SNV									1.8	2.4	9.0								
26	CA	AES	18.0		12.5	20.9	9.1	8.4	13.5		1.7	0.3	2.1	3.1	2.7	1.7	2.3	0.5	1.9	0.6	0.7
27	US	ILL.								1.6	1.8	1.9	4.5	1.1	1.0	3.8	2.0	0.9	2.1	2.1	2.0
28	US	EPA								1.4	2.1	0.8	1.1	4.1							
29	CA	CONC.																			
30	IT	ISPRA										1.5	3.4	10.7	1.9	0.8	5.9	0.7	1.0	2.0	1.6
31	SK													3.9	1.3	4.5	4.2	3.3	7.2	3.2	3.4
32	LT														2.0	4.4	5.9	1.0	2.0	2.5	
33	LV														2.9	0.8	8.3	6.6	1.0	3.3	2.6
34	TR														1.7	2.6	2.4	1.1	1.6	1.5	1.3
35	HR														5.8	6.0	3.8	2.1	1.6	1.9	3.4
36	SI														3.9	3.7	2.6	0.6	0.4	1.7	0.9
37	IE	EPA/E	BS													1.6	3.1	0.8	2.1	23.5	
38	EE															2.2	1.8	3.3	1.0	4.0	2.0
39	PL (Env.)																4.7	1.6	0.6	1.5	2.5
40	MK																		3.1	16.8	5.3
41	Estonia (Tartu		)																0.5		
42	Iceland (Ork.)																		0.9		
Gml.19	TNO					3.2	5.8	8.8	2.0	4.1											

Table 4.6: Systematic error (RB%) for NH_4 in precipitation in the different laboratory intercomparisons.

	NH4 prec	1 1977	2 1978	3 1978	4 1979	5 1980	6 1981	7 1982	8 1984	9 1986	10 1987	11 1989	12 1991	13 1993	14 1994	15 1995	16 1997	17 1999	18 2000	19 2001
1	AT	1.2		7.1	4.7	18.5	4.0	-4.4	4.2	44.0	-11.1	45.4	-0.4	9.3	-1.2	-1.0	5.7		-8.6	-1.3
2	BE	1.5			5.4	2.1	-25.0	-7.7	7.5	28.6	-9.2	-12.7	9.3							
3	CS			-36.4	0.0	-2.1	-4.0	-3.4	0.0	-2.2	5.7	-5.0	-10.6	-0.2	-1.3	-3.9	0.9	-14.8	-5.3	-9.5
4	DK	-1.5		0.0	-0.6	9.3	16.5	1.5	0.8	1.5	4.9	1.0	-4.0	2.7	0.6	2.8	1.1	0.1	2.9	-0.5
5	FI			-7.1	17.8	2.8	7.4	0.5	-4.2	-1.5	-0.8	-3.0	-0.2	-3.2	-7.5	-2.0	-0.2	2.8	-1.8	-1.7
6	FR	-2.2		-7.5	-0.8	8.9	-3.4	5.8	30.0	7.3	9.9	-25.2	-8.7	21.1	12.7	-15.5	-0.2	2.3	-2.6	8.3
7	DD/DE (Leip.)									-	4.8	0.8	0.3			-	4.4	1.8 -	1.8 -	0.0
8	DE	1.9					-1.7	-30.0	-6.7	-5.1	-2.5	-4.3	-7.5	-1.4	-5.0	-5.8	4.7	-1.2	2.6	-4.5
9	GR										-11.7		-8.2	12.9			64.8	-2.7		
10	HU	-30.4		-8.9	34.1	-14.9	-6.8	-4.8	-10.8	-25.6	-6.9	-4.4	-31.2	16.4	-6.6	3.8	14.8	9.1	-12.4	-3.6
11	IS											-0.6	-2.7	0.7	-3.1	2.6	0.4	7.4	-0.2	-0.5
12	IE MetServ										8.4	-1.7	-2.7	6.9	-3.0	-1.0	-2.3			-11.2
13	IT CNR								-10.0	3.7	34.5	-3.0	2.0	16.4	-13.3	-14.5	22.6	0.1	13.8	0.1
14	NL	1.4		-41.1	0.0	7.1	-9.1	-1.0	-4.5	-7.3	1.7	1.1	-2.7	2.1	-4.0	1.5	-1.3	-4.2	-4.4	-4.0
15	NO	2.2		-10.7	5.4	-3.6	1.7	11.6	8.3	-2.9	-5.0	-3.0	-6.2	14.0	5.4	-7.4	-0.3	1.9	-5.2	-2.7
16	PL Met.	-1.1		-49.6	-7.8	1.4	-4.5	-9.7			-27.7	-47.4	-19.2	4.5	-2.1	1.9	-1.6	1.5	-1.4	2.6
17	PT							28.1	2.5	-1.5	-7.5	-26.6	2.0	5.7	9.5	-9.4	3.5	3.7	1.7	-10.6
18	RO									-44.0						-41.0	-20.1	0.6	-25.5	-68.7
19	ES									47.6	23.4		-12.1	-3.8	-24.3	-26.1	-7.6	3.8	5.5	-8.8
20	SE IVL	1.9		-14.3	18.6	0.8	-2.0	4.1	0.7	-4.5	13.4	-0.3	0.8	7.4	1.4	0.0	2.2	-3.3	-2.4	-0.1
21	CH	5.0		-35.7		15.7	-13.1	3.9	18.3	-4.4	0.8	-1.7	-2.6	5.7	-1.2	2.9	-1.9	1.8	0.1	2.1
22	SOV/RU								-51.7	-4.4	1.8	-4.4	-9.9	-9.7	-9.1		-2.4	-4.7	0.8	-2.7
23	GB	1.7		-32.1	3.9	0.7	8.5	-1.0	-2.5	-19.8	0.2	1.1	4.4	9.3	0.6	7.7	-18.1	-3.1	-0.2	-1.6
24	YU				6.2	4.3	-2.3	-11.1	-1.7	-6.6	17.0	-5.0	-8.5	7.4	-20.5	24.8	14.9	-3.1	1.6	-19.1
25	SE SNV									0.7	2.4	-5.8								
26	CA AES	-16.4		-42.5	-5.0	0.2	1.2	-6.8		-5.1	2.4	-2.4	-4.7	0.1	-1.9	0.6	-1.7	1.5	-1.0	-0.9
27	US ILL.								-4.9	-7.3	3.5	-0.3	-7.4	-1.4	-3.0	0.0	-0.3	-4.1	-7.4	-6.3
28	US EPA								-7.5	-5.6	-0.3	-8.7	-5.6							
29	CA CONC.																			
30	IT ISPRA										-3.5	-0.3	-5.1	-0.2	-7.7	-1.0	-1.0	2.3	2.0	0.6
31	SK												-11.0	12.5	-22.0	10.3	1.0	12.0	-1.8	-3.8
32	LT													5.8	-13.1	0.4	2.9	8.8	0.6	
33	LV													5.7	3.5	4.8	5.7	-5.4	5.6	1.9
34	TR													15.3	1.8	-3.7	5.7	-0.1	1.4	2.6
35	HR													-13.3	13.6	-3.9	21.8	0.5	-0.7	-0.1
36	SI													16.4	25.6	10.6	1.3	2.2	-1.0	-0.1
37	IE EPA/EBS														-2.1	12.3	4.2	-0.3	8.8	
38	EE														7.1	1.2	-1.3	4.9	2.2	-3.9
39	PL (Env.)															7.7	1.8	-2.9	2.8	9.4
40	MK																	-9.2	65.0	1.0
41	Estonia (Tartu)																	0.7		
42	Iceland (Ork.)																	3.7		
Gml. 19	TNO				3.1	-12.8	-6.3	-1	-7.5											

Table 4.7: Random error (2RSD%) for K in precipitation in the different laboratory intercomparisons.

	K prec		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
			1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT													0.8	3.3	3.0	4.6	3.5		2.9	8.0
2	BE											40.1									
3	CS									2.4	3.5	12.0	1.2	13.1	1.0	1.8	0.6	4.6	3.6	4.8	1.7
4	DK											1.1	6.6	1.5	2.1	6.6	6.6	1.6	3.6	1.9	6.8
5	FI									2.4	1.8	0.7	4.0	0.3	0.8	2.3	4.2	2.7	2.5	2.1	9.1
6	FR									18.3	96.6	17.1	2.8	1.4	2.6	0.7	3.6	1.6	2.3	2.9	1.6
7	DD/DE Lei										10.5	4.9	7.6				2.4	0.7	2.8	2.7	2.9
8	DE									1.2	1.8	0.7	1.9	1.3	1.8	7.3	2.2	1.6	12.8	3.9	1.6
9	GR																	29.5	5.7		
10	HU									12.2	35.1	7.8	13.5	11.6	22.7	30.2	21.7	8.2	3.2	172.4	8.2
11	IS											2.5	14.7	3.3	2.1	11.0	2.6	5.9	54.3	6.8	7.2
12	IE	MetServ										4.8	4.0	1.5		2.1	2.6	1.5			2.7
13	IT	CNR								6.1	14.0	4.0	21.6	18.6	3.0	8.9	14.4	10.3	0.9	1.9	1.0
14	NL									11.0	0.0	2.7	2.8	4.8	2.6	8.0	3.4	8.4	7.9	3.9	2.3
15	NO									4.9	12.3	5.8	4.0	3.3	7.7	2.7	1.0	3.3	0.6	11.2	3.7
16	PL	Met.										4.3	9.0	2.6	2.6	7.1	6.4	1.6	5.7	9.7	4.7
17	PT											60.9	30.6		3.9	27.9	4.2	1.3	0.9	8.1	5.6
18	RO										17.6						7.4	13.4	50.0		
19	ES										33.4	12.0		14.5	17.2	33.6	7.6	4.2	0.6	2.9	4.3
20	SE	IVL									5.3	2.2	4.3	0.3	1.8	2.1	2.4	4.8	6.6	1.7	5.6
21	CH									9.7	28.1	5.3	6.4	2.6	1.8	4.3	2.4	1.3	7.5	12.0	9.7
22	SOV/RU										5.3	16.6	25.6	10.4	2.6	180.0	7.2	9.9	12.6	43.4	8.4
23	GB										1.8	4.4	3.1	5.6	1.9	16.2	11.6	10.6	1.1	1.2	4.1
24	YU										36.9	4.9	3.1	3.5	17.1	4.3	9.8	1.8	7.5	5.2	3.7
25	SE	SNV									1.8	9.1	2.1								
26	CA	AES									1.8	1.5	2.8	1.0	1.8	2.7	2.0	0.5	1.3	2.7	1.0
27	US	ILL.								2.1	5.4	0.8	2.1	3.0	9.0	1.1	1.4	0.7	0.8	0.6	4.3
28	US	EPA								3.7	1.2	4.6	2.8	1.3							
29	CA	CONC.																			
30	IT	ISPRA										3.8	4.0	2.1	3.9	7.5	1.8	3.1	0.6	4.3	1.7
31	SK													11.3	1.3	9.8	6.4	6.0	12.1	5.2	2.5
32	LT														12.5	6.6	4.6	4.0	5.8	12.2	
33	LV														4.0	6.6	10.6	2.7	2.1	2.3	3.7
34	TR														4.3	1.8	6.0	3.7	2.1	33.1	13.2
35	HR														5.5	22.4	4.4	1.6	1.9	6.8	2.9
36	SI														16.0	15.8	16.5	5.7	3.2	2.7	1.6
37	IE	EPA/EBS								3.7						49.6	7.2	33.9	6.2	9.9	
38	EE															27.7	20.3	4.2	5.5	1.9	3.7
39	PL (Env.)																1.0	1.3	0.6	0.8	0.8
40	MK																		23.8	18.0	19.2
41	EE (Tartu)																	1.0	5.0		
42	IS (Ork.)																				
Gml. 19	TNO									2.4											

Table 4.8: Systematic error (RB%) for K in precipitation in the different laboratory intercomparisons.

	K prec	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
		1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT												-2.5	0.1	0.8	-16.5	-2.5		-13.2	-2.1
2	BE										30.4									
3	CS								0.0	2.2	-4.7	-1.7	4.1	-1.3	-1.7	0.7	-6.7	-3.0	1.5	-2.1
4	DK										-1.3	-7.6	-1.8	3.9	-2.0	-18.9	-4.7	-12.7	-6.8	-11.2
5	FI								-1.5	4.3	1.0	-2.9	-1.8	-1.6	-1.1	0.5	-5.8	-4.6	-0.5	-8.1
6	FR								20.9	68.8	-7.8	9.9	-11.8	-5.7	-2.0	-6.9	-22.6	-3.2	7.1	-7.4
7	DD/DE Lei									-17.2	7.1	2.3				-11.8	-1.6	-3.9	-3.8	-2.9
8	DE								4.5	0.0	0.2	-1.7	-7.2	-7.6	-2.2	3.2	-0.2	-9.7	-6.8	-0.7
9	GR																259.0	-10.4		
10	HU								-52.2	71.0	-29.4	63.7	-4.6	82.0	76.8	42.3	2.0	-11.5	-3.0	-18.1
11	IS										-8.9	8.1	-1.5	-1.9	25.5	3.2	-3.1	-24.2	60.3	6.4
12	IE MetServ										-1.6	3.8	-3.2		-12.6	-16.5	-15.2			-7.6
13	IT CNR								10.4	19.4	0.2	-5.5	-1.7	18.6	7.0	1.0	1.3	-1.2	-1.8	-5.0
14	NL								16.4	-4.3	4.1	-3.5	1.1	1.6	0.3	-4.9	0.0	-0.2	6.6	-2.1
15	NO								0.0	28.0	4.5	0.9	-4.9	15.7	0.6	-2.5	-1.8	0.2	22.3	0.7
16	PL Met.										2.9	-19.2	-14.4	-7.7	9.2	-3.9	-0.4	-5.8	-18.5	-8.8
17	PT										67.4	52.6		-18.0	6.2	-13.0	0.4	-7.9	-38.2	40.0
18	RO									-38.7						25.1	34.8	106.0		
19	ES									-4.3	24.7		31.8	49.2	54.1	54.5	-0.4	5.3	1.5	-5.0
20	SE IVL									-21.5	-4.2	1.2	1.0	-6.1	14.3	0.5	20.2	25.2	8.4	-11.2
21	CH								9.0	28.0	-3.2	-4.9	-1.8	4.1	3.1	1.0	5.6	-9.7	-16.5	-10.5
22	SOV/RU									-17.2	13.6	28.5	-5.8	-18.2	93.8	-9.8	27.6	6.9	17.5	6.7
23	GB									17.2	-5.5	-14.8	11.1	-14.7	-16.5	2.9	0.2	-5.1	-3.5	-10.5
24	YU									-86.0	-19.6	-3.2	15.0	-19.1	-7.0	-21.6	2.9	-10.2	-5.8	-7.6
25	SE SNV									-2.2	3.9	6.1								
26	CA AES									4.3	0.6	2.3	-0.3	-1.7	4.8	2.2	-2.0	-0.9	0.3	4.5
27	US ILL.								-1.2	3.0	0.2	7.6	-8.6	1.0	3.4	0.5	-1.6	0.7	0.8	-4.0
28	US EPA								0.0	2.8	-3.3	-9.6	4.6							
29	CA CONC.																			
30	IT ISPRA										-2.7	-42.7	2.5	-7.9	12.0	-4.7	-3.1	3.9	-6.8	-8.8
31	SK												5.5	0.7	11.2	15.5	-4.9	28.4	2.3	-2.9
32	LT													14.3	19.9	-14.0	13.9	-1.2	-11.1	
33	LV													-4.5	6.4	3.2	6.5	-4.8	-4.8	-4.0
34	TR													0.0	0.8	5.4	-4.9	-0.9	446.8	11.0
35	HR													21.7	40.3	-11.8	-2.9	10.6	5.1	-4.0
36	SI													-17.7	-1.4	2.2	6.7	-0.7	-4.6	1.0
37	IE EPA/EBS								-3.0						143.7	9.8	14.3	3.9	22.0	
38	EE														12.0	-26.3	-14.1	-7.6	-1.8	0.7
39	PL (Env.)															0.0	-0.4	-0.2	0.0	-1.2
40	MK																	59.6	-24.8	-49.0
41	EE (Tartu)																1.0			
42	IS (Ork.)																			
Gml.	19 TNO								0											

Table 4.9: Random error (2RSD%) for Ca in precipitation in the different laboratory intercomparisons.

	Ca prec		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
			1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT											2.4	28.7	0.5	0.9	1.8	3.6	1.2		1.6	1.1
2	BE										12.2	15.6									
3	CS									1.7	1.6	1.5	2.5	2.5	1.2	1.3	2.3	2	4.6	2	1.6
4	DK										5.7	3.4	8.2	2.9	6.6	7.2	3.4	1.6	2.9	3.4	2.3
5	FI									2.8	2.4	2	1.4	2.3	0.8	1.3	0.7	0.3	1.8	0.9	1.1
6	FR									1.7	7.3	2	38.9	1.3	4.9	3.3	3.4	5.4	2.9	4.5	5.5
7	DDLeip										8.9	2	11.5				3.4	2.1	9.2	4.7	2.4
8	DE									9	1.6	1	3.5	0.6	1.4	2.4	1.1	0.9	8.5	4.2	0.5
9	GR																	28.1	5.3		
10	HU									7.3	7.3	14.1	22.4		11.8	20.3	18.4	8	3.5	7.4	5.8
11	IS											3.9	10.4	2.8	3	14.8	18.8	2.1	2.8	2.4	2
12	IE	Met CNR									2.4	5.8	1.6	1.7		3.3	0.8	2.9		18.9	0.9
13	IT									1.7		4.4	7.1	11.7	5.7	7.5	3.6	11.8	5.5	4.5	4.6
14	NL									10.7	7.3	4.5	6.1	8.5	1.2	1	1.2	0.8	1.4	0.9	1.9
15	NO	Met.								1.7	3.2	0.5	3.3	1.6	2.3	2.7	1	1.4	1.9	3.2	5
16	PL											2.4		8	3.8	6	1.8	3.1	5.5	6	0.5
17	PT											15.2	38.4	3.9	1.6	10.6	9.5	2.2	2.9	6.7	5.6
18	RO										15.4						7.1	71.2			
19	ES	IVL									12.2	16.2		4.4	16.9	15.8	13.9	1	1.8	1.8	1.7
20	SE										16.2	5.8	4.5	4.2	0.9	3.5	4.8	3.5	5.5	8.1	8.7
21	CH									2.3	11.4	1	1.2	1.6	7.5	5.3	3.4	0.7	5.9	8.5	2.3
22	SOV/RU									18.6	16.2	10.2		9.8	22.2	14.1	6.5	20.2	11.5	23.5	19.5
23	GB									2.8	3.2	2.5	7	0.8	5.7	9.5	10.3	6.5	24.8	1.6	1.1
24	YU	SNV									19.5	7.3	8.2	4.5	148.2	695.2	23.2	4.7	5.1	6.7	2
25	SE	AES								7.3	11.4	7.2	2.4								
26	CA	ILL.									0.8	0.9	1.6	0.7	1.2	0.7	0.4	0.6	2	1.1	1.2
27	US	EPA								3.9	0.8	0.7	0.7	1.6	0.4	0.4	1.2	1.2	1.3	0.7	0.4
28	US	CONC.								0.5	1	0.6	1.6	1.1							
29	CA	ISPRA																			
30	IT											2.8	4.7	2	2.3	2.4	2.1	3.5	14.7	8.4	4.4
31	SK													3.2	3.5	14.1	10.6	1	3.9	5.4	0.4
32	LT														25.4	5.8		4.4	11.7	20.2	
33	LV														12.5	37.3	9.5	2.9	12	22.8	4.4
34	TR														16	8	3.3	3.7	4	16.4	129.6
35	HR														5.6	23.1	11.4	7.6	3.1	2	1.1
36	SI	EPA/EBS													3.3	29.7	9.1	0.5	1.3	1.7	0.4
37	IE																1.9	3.3	3.1	5.6	
38	EE																13.1	4.1	11.9	5.8	5
39	PL (Env.)																0.5	0.5	2.1	1.4	0.9
40	MK																		21.4	6.7	6
41	EETartu																				
42	IS (Ork.)																	2.9			
Gml. 19	TNO									1.7											

Table 4.10: Systematic error (RB%) for Ca in precipitation in the different laboratory intercomparisons.

	Ca prec		8	9	10	11	12	13	14	15	16	17	18	19
			1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT				-10.1	-15.9	-2.1	1.7	0.5	-1.7	-2.0		-3.5	-7.9
2	BE			-14.9	21.0									
3	CS		0.0	0.0	1.4	-9.1	1.6	0.2	3.3	-1.2	6.5	-4.0	-14.3	-3.9
4	DK			0.0	-7.7	0.0	6.5	-9.4	-4.3	-12.0	4.7	1.4	-5.5	-5.4
5	FI		-13.1	-1.0	2.0	3.5	-4.5	1.8	1.7	2.7	2.8	3.1	3.1	-0.5
6	FR		2.8	27.9	-0.5	-77.9	-8.4	-1.1	-6.4	3.2	-12.4	2.9	-8.0	19.1
7	DDLeip			18.9	3.1	-6.1				-17.0	-2.0	-4.1	11.7	-0.8
8	DE		4.1	1.0	0.8	8.7	-0.2	1.3	-2.3	-1.3	3.8	2.2	7.7	2.8
9	GR										43.3	-19.2		
10	HU		10.3	107.5	16.2	31.7		-14.7	79.5	47.1	-12.3	0.8	-23.2	-26.8
11	IS				3.1	17.0	7.1	-10.6	-7.5	0.3	2.4	2.2	2.7	-1.8
12	IE	Met CNR		-2.0	-7.1	5.2	3.6		-11.0	-10.1	-16.9		-100	-7.1
13	IT		2.8		8.0	-21.6	-22.2	1.1	12.7	10.1	22.2	9.2	5.3	0.2
14	NL		-11.7	-2.0	3.7	2.6	0.7	3.4	4.2	4.7	3.7	2.6	1.4	-0.5
15	NO	Met.	3.4	6.0	3.1	4.0	-3.6	7.5	6.1	1.2	1.0	0.3	9.3	-3.8
16	PL				-7.1		-12.1	1.1	4.9	5.6	-10.4	-5.5	-8.4	-2.1
17	PT				-18.5	116.9	8.9	8.1	14.8	15.5	2.7	4.1	-4.0	16.0
18	RO			-10.9						-19.0	171.3			
19	ES	IVL		-18.9	9.1		-7.7	-11.7	-32.2	-46.3	0.8	6.1	0.8	4.9
20	SE			-21.9	-5.8	-4.6	-7.6	-6.8	-4.3	-3.5	6.2	23.2	-4.8	8.4
21	CH		-4.8	-6.0	3.7	4.3	0.5	-2.1	4.7	-1.9	-0.1	1.4	12.1	-0.3
22	SOV/RU		21.4	1.0	-4.7		8	23.0	-11.5	-8.2	-11.2	16.3	16.6	23.5
23	GB		-6.2	-4.0	-3.9	-6.3	1.0	9.6	11.7	8.2	17.4	36.4	-1.3	-1.3
24	YU	SNV		-20.9	23.4	30.3	3.7	72.6	457.6	-28.3	-11.2	-2.6	-18.3	-3.6
25	SE	AES	3.4	-11.9	-11.3	4.3								
26	CA	ILL.		3.0	1.3	3.8	0.6	3.2	4.2	3.2	-1.4	-1.4	3.1	-4.9
27	US	EPA	-8.3	-0.2	-1.9	2.6	-2.6	1.2	1.2	-1.3	-1.3	-0.2	2.6	-0.5
28	US	CONC.	-0.6	-0.8	0.5	1.4	1.1							
29	CA	ISPRA												
30	IT				3.1	4.3	7.2	2.3	3.0	-1.9	-0.3	29.0	11.3	-2.1
31	SK						1.5	3.6	0.9	-22.9	-4.8	-1.5	-9.2	-0.8
32	LT							-5.2	-30.4		-4.7	-17.1	-16.7	
33	LV							-14.9	67.3	24.4	-1.4	-27.6	-22.8	-17.4
34	TR							54.5	-7.3	5.7	5.2	5.2	28.3	67.6
35	HR							-6.4	13.4	-62.6	-62.8	-20.1	-38.3	2.6
36	SI	EPA/EBS						0.6	105.2	-11.1	3.0	5.8	3.7	-0.2
37	IE									8.1	13.7	-27.5	4.0	
38	EE									-14.5	-2.7	-0.5	15.4	-23.5
39	PL (Env.)									0.3	1.7	-0.8	3.2	1.6
40	MK											8.9	-20.6	-9.7
41	EETartu													
42	IS (Ork.)										22.6			
Gml.	19 TNO		-8.3											

Table 4.11: Random error (2RSD%) for Na in precipitation in the different laboratory intercomparisons.

	Na prec		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
			1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT													4.5	1.5	0.4	1.6	1.3		3.5	1.4
2	BE		28.6					4.6			1.5	1	3.2	2.1							
3	CS				8	0.9	1.3	0.5	1.6	1.5	0.5	1.8	5.2	0.5	0.8	2.3	0.9	1.7	1.1	1.9	1.1
4	DK		9.4									0.7	8	2.1	7.5	2.5	3.4	4.1	1.9	4.5	4.3
5	FI				9.1		0	2.5	0.6	5.7	0.6	1.3	2.7	0.3	1.9	0.7	1.4	1.4	0.7	2.9	0.5
6	FR		3.3		15.6	13.8	1.7	6.1	2.2	1.8	0.9	2.7	3.2	1.6	2.2	5.2	3.1	0.9	1.6	1.8	0.5
7	DDLeip										5.2	1.7	2.7				1.5	0.2	0.4	0.6	0.8
8	DE		15.6					9.5	1.9	3	2.3	0.5	3.2	0.8	1.1	0.7	2	2	1.9	0.8	2.1
9	GR																	59.9	3.4		
10	HU		13.9		6.9	16.3	8.7		11.3	4.2	3.9	1.4	3.7	7.5	24.9	36.8	13.5	15	1.6	8.6	4.2
11	IS					3.6	2.6	13.1	176.5	8.9	4	0.4	3.2	6.3	1.1	5.9	1.5	5.2		0.7	2.8
12	IE	Met						1.1	1.9	1.3	1.5	1.5	17.7	1.3		2.5	2.1	1.3			1.1
13	IT	CNR								8.2	1.5	6.2	1	3.6	7.8	3.7	3.1	1.5	1.2	0.8	2.4
14	NL		9		11.4	0.5	0.9	1	4.6	1.7	0.6	1.5	2.8	0.7	0.6	0.4	1.1	0.9	0.7	0.9	0.3
15	NO		3.6		6.9	4.5	0.7	14.7	2.3	0.4	1.2	2.2	3.6	0.6	6.4	0.8	0.8	0.5	0.7	1.3	0.6
16	PL	Met.	6.3		10.3	3.6	2.4	8.5	4.6			2.3	7	3.1	5.7	2.8	1.4	3.8	2.8	5.5	1.2
17	PT											4.1	4.7	3.2	11.9	13.9	2	2.5	5.2	6.3	0.4
18	RO										5.2						3.1	20.2			
19	ES										15.9	0.5		1.1	2.7	1.9	3.8	3.4	1.7	3.4	2
20	SE	IVL									1.9	0.9	7.3	1.1	1.5	7.3	4.7	3.2	4.7	7.2	6.2
21	CH		3.5				18	0.5		1.3	1.5	0.2	2.2	1.1	4	1.2	1.5	0.3	1.6	0.9	1.6
22	SOV/RU									1.5	0.9	2.7	25.8	7.5	1.9	24.5	0.3	6.2	4.5	13.8	1.2
23	GB		2.1		6.9	5.4	2.6	5	4	1.6	2.3	0.1	3.2	9.1	1.9	1.7	1.6	0.9	0.8	0.4	0.5
24	YU						5.3	2.9	3.4		16.2	4.9	3.2	2	3.3	2.9	2.2	1.5	6.2	3.1	2.1
25	SE	SNV									0.8	1.4	2.8								
26	CA	AES	25.5		8	1.8	0.7	0.2	1		0.6	0.4	3.2	0.4	1.5	0.4	1.2	0.5	0.5	0.6	0.4
27	US	ILL.								1.8	0.2	0.4	3.2	1.5	0.4	0.3	0.6	0.5	1.3	0.7	1.5
28	US	EPA								0.9	1.4	1.5	2.1	1.4							
29	CA	CONC.																			
30	IT	ISPRA										0.9	2.4	1.2	4.2	1.1	2.5	2.4	3.9	3.1	1
31	SK													0.6	2.2	4	4.6	4.1	1.5	2.5	2.1
32	LT														8.9	4.7	4	2	7.3	8.6	
33	LV														4.7	1.6	2.6	3.8	2.6	1.3	3.4
34	TR														2.3	1.4	1.9	3	1.4	2.4	2.9
35	HR														6.1	5.9	5.2	3	1.2	1.3	0.5
36	SI														6.1	11.2	3.5	0.3	1.1	1.3	0.3
37	IE	EPA/EBS								2.2						19.1	4.7	1.6	5.5	60.5	
38	EE															10.9	25.4	2	3.5	0.6	3.4
39	PL (Env.)																1.2	0.3	0.3	1.3	0.8
40	MK																		8.5	27.6	8.8
41	EETartu																				
42	IS(Ork.)																	0.9			
Gml. 19	TNO					1.1	14.5	8.3	31.3	0.9											

Table 4.12: Systematic error (RB%) for Na in precipitation in the different laboratory intercomparisons.

	Na prec		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
			1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT													-2.2	1.5	0.5	2.7	-1.6		-2.6	-5.2
2	BE		-42.6					-10.0			-10.4	-4.6	-1.2	-4.4							
3	CS				9.8	0.7	-1.1	-0.3	-1.4	0.0	-1.3	2.3	-15.1	0.5	-1.0	-14.8	-2.9	-4.7	-0.9	3.3	-0.8
4	DK		-1.3									-0.4	-1.9	-4.4	12.0	11.6	-1.8	-1.9	1.3	6.4	7.2
5	FI				8.4		0.0	-5.1	-0.4	0.4	3.6	-1.8	1.2	0.1	0.7	0.4	0.9	1.9	1.1	3.2	0.1
6	FR		5.4		40.7	4.4	2.1	-4.5	-2.4	4.0	7.4	2.1	-9.0	-9.9	0.1	5.6	6.9	-7.7	0.1	4.8	-3.4
7	DDLeip										-8.1	-2.9	-9.1				-11.2	-2.1	-1.4	1.3	0.0
8	DE		-14.7					-8.6	-4.8	-6.4	-11.3	0.6	0.3	0.7	-4.0	-3.6	-0.1	-6.4	-0.6	-1.3	-2.0
9	GR																	79.6	-8.1		
10	HU		-4.8		7.0	0.9	-6.1		7.2	-1.6	-3.8	-25.7	-17.9	17.6	-26.8	34.1	-31.6	-12.5	-1.0	-19.5	-27.4
11	IS					-2.4	-3.2	0.7	452.9	-1.3	-9.3	-9.3	2.9	4.7	1.6	-6.2	-4.8	-12.8		-2.6	-10.4
12	IE	Met						0.0	0.7	-2.0	0.8	2.9	4.8	-6.0		-5.7	-6.3	-5.1			-2.1
13	IT	CNR								15.2	-6.6	-5.5	0.8	6.4	20.0	-10.0	-0.7	0.7	1.0	-0.2	-1.2
14	NL		9.6		-1.4	1.5	-0.6	1.8	5.7	1.4	0.8	3.3	-2.8	1.4	2.4	-0.9	0.8	-0.1	-0.1	-1.5	-1.6
15	NO		4.4		8.4	-5.5	0.0	19.0	-7.1	-3.3	-0.2	3.1	1.3	0.1	16.6	4.5	-0.7	-0.1	-0.3	0.3	-3.4
16	PL	Met.	16.4		1.4	-0.2	-1.1	-7.0	-0.7			-16.3	-0.9	-6.9	-11.0	15.5	17.2	5.1	-3.0	-7.0	-2.9
17	PT											-0.9	18.7	-15.0	-12.9	-7.9	-15.5	-6.0	-12.9	-7.6	4.6
18	RO										33.8						7.7	-47.9			
19	ES										-27.2	14.2		4.0	33.0	15.9	-19.7	3.9	7.3	-3.9	3.5
20	SE	IVL									-4.7	-0.3	-2.4	-0.2	-6.1	-18.8	-15.2	-5.1	0.0	0.3	9.6
21	CH		-1.1				10.5	1.5		-4.4	-6.6	-1.4	-0.9	0.1	4.3	0.5	-2.2	0.4	-0.1	1.6	0.1
22	SOV/RU									-1.3	-1.7	-1.5	-5.2	-20.1	-7.7	4.1	-0.1	-5.5	-2.9	1.5	-5.3
23	GB		-2.6		26.6	6.6	8.1	-5.4	-0.4	-2.0	-0.2	-1.7	-2.3	14.2	0.1	-0.6	2.7	-5.5	-2.9	-2.6	-3.4
24	YU						38.7	0.3	1.3		1.5	-6.2	0.8	-1.3	-2.0	5.1	-20.7	3.7	1.1	-4.9	-4.6
25	SE	SNV									1.7	3.0	2.4								
26	CA	AES	-2.2		16.8	0.4	-1.1	-0.6	-3.8		-2.5	1.3	1.3	1.4	-1.9	-0.1	2.3	-1.5	-0.6	0.3	-0.2
27	US	ILL.								-3.5	-1.3	-1.4	0.1	-8.4	1.0	1.2	0.5	-0.9	0.6	1.4	-2.0
28	US	EPA								0.7	-0.2	-6.6	1.7	0.7							
29	CA	CONC.																			
30	IT	ISPRA										4.5	0.3	3.8	12.6	0.3	1.6	0.4	4.8	0.7	-1.0
31	SK													1.3	0.1	-8.3	-2.8	17.6	-0.6	1.8	-3.3
32	LT														10.6	7.1	-17.7	1.6	-1.4	9.3	
33	LV														-37.9	6.2	-1.9	5.2	-6.7	-3.9	-5.9
34	TR														-36.9	-3.8	7.0	4.5	2.8	11.3	0.4
35	HR														8.1	-12.3	-6.7	-26.1	0.4	-4.1	-4.0
36	SI														-3.8	17.9	2.0	1.9	3.7	1.6	-0.3
37	IE	EPA/EB	S							8.4						19.0	13.7	4.3	-2.9	8.4	
38	EE															22.2	57.9	-6.4	-7.2	-1.9	-6.8
39	PL (Env.)																-3.3	0.7	1.0	-1.2	-0.7
40	MK																		-21.7	-50.2	-38.8
41	EETartu																				
42	IS(Ork.)																	0.3			
Gml. 19	TNO					-4.6	-11.3	-26	-30.1	-1.1											

Table 4.13: Random error (2RSD%) for Mg in precipitation in the different laboratory intercomparisons.

	Mg prec		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
			1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT											6.7	9.4	0.5	1.2	0.9	2.7	2		1.7	1.5
2	BE		179.8					9.1			3.2	30.3									
3	CS				4.1	0.9	0.5	0.9	3.7	1.7	2.7	1.7	2.2	2.3	0.8	1.8	1.2	1	0.5	1.2	0.9
4	DK		7.1									3.3	4.6	0.9	2.2	3.2	3.7	1.6	2.9	1.9	5.7
5	FI		3.9		5.8	4.6	2.1	1.8	3.3	6.3	1.6	4.3	1.1	0.9	0.4	0.5	0.7	0.6	0.7	0.5	0.6
6	FR		3.2		2.3	3.6	9.5	0.9	0.8	1.6	6.4	1.4	34.8	1.2	0.8	2.1	3.7	2.8	1.9	1.7	2.7
7	DDLeip										9.1	2.6	3				13	2.2	1.7	1.9	2.1
8	DE		15.9					0.9	2.5	22	3.2	1.7	1.9	1.2	1.8	0.9	2.2	1.4	2.9	1.7	0.9
9	GR																	6.1	8.2		
10	HU		2.6		58.3	6.4	6.3	5.4	4.9	17.3	21.6	8.3			6.9			1	1.4	1.9	3.9
11	IS					2.7						1.7	2.4	1.9	1.2	2.5	5.1	1.6	1.7	1	3.9
12	IE	Met										2.4	2.7	2.8	0.6	1.4	2.7	3			0.9
13	IT	CNR								2.4		7.9	7.8	6	3.7	10.1	3.7	2	2.9	3.1	1.5
14	NL		2.9		5.8	1.8	2.1	2.7	1.6	5.5	3.2	3.8	4.6	2.6	5.3	4.1	2.2	2	2.4	4.3	2.7
15	NO		1.4		11.7	0.9	3.2	0.9	1.6	1.6	3.2	0.7	1.1	0.9	3.5	3.2	0.7	1.4	0.7	1.7	
16	PL	Met.	0.6		5.8	8.2	6.3	16.3	9.1			5	8.4	2.6	0.8	2.5	2.5	1.6	3.8	2.4	1.2
17	PT											6	49.4	9.7	0.8	2.5	2.7	1.4	1.2	2.4	2.7
18	RO										4.8						2.7	14.2	11.3		
19	ES										27.2	14.5		2.6	6.9	3	8.6	0.4	0.2	4.3	0.3
20	SE	IVL									1.6	3.3	3	3.7	1.6	0.9	1.2	0.8	2.9	3.4	5.1
21	CH		2.9				4	2.4	3.6	3	4.8	1.4	3.2	1.6	3.7	3.2	2.7	1	3.1	5.5	0.3
22	SOV/RU									17.3		46.5		1.2	9.5	4.6	6.9	4.7	2.4	2.4	3.6
23	GB		7.8		5.8	8.2	15.8	4.5	3.3	11	3.2	1.7	3.2	1.9	5.5	5.3	9.8	2.4	14.6	0.5	0.6
24	YU						6.3	1.8	8.2	1.6	11.2	5.7	1.1	4.4	74.9	25.5	11.8	0.8	3.1	6.2	1.5
25	SE	SNV									9.6	5	3								
26	CA	AES	17.5		11.7	3.6	2.1	0.9	10.7		3.2	1.7	2.7	0.2	1.6	0.5	1	0.2	1	0.5	0.3
27	US	ILL.								2	1.8	0.7	1.1	2.1	1.2	0.7	1.2	1	1.4	1.7	1.5
28	US	EPA								3.1	2.1	1.7	5.7	1.4							
29	CA	CONC.																			
30	IT	ISPRA										1.4	1.1	0.9	4.3	3	0.7	3.4	6.7	4.3	1.5
31	SK													2.3	2.4	0.9	2.5	1.4	2.9	3.6	1.2
32	LT														22.3						
33	LV																	2.4	7.2	153.7	2.7
34	TR														1.6	1.1	0.2	1.8	5.5	1.7	31
35	HR														2.2	6.2	11	4.5	1.2	0.7	1.8
36	SI														9.3	3.9	4.9	0.8	1.2	1	0.6
37	IE	EPA/EBS								4.7						22.2	1	1.2	5.3	17.7	
38	EE																0.5	1.6	6.5	1.7	3.9
39	PL (Env.)																1	0.4	0.5	1.4	0.3
40	MK																		3.8	5.5	9.9
41	EE (Tartu)																				
42	IS (Ork.)																	1.6			
Gml. 19	TNO					12.8	11.6	10	3.3	3.1											

Table 4.14: Systematic error (RB%) for Mg in precipitation in the different laboratory intercomparisons.

	Mg prec	1	2	3	4	5	6	7	8	9	10	11	1	13	14	15	16	17	18	19
		1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT										-5.0	-2.3	0.0	3.0	0.8	3.9	-15.4		-1.8	-4.1
2	BE	253.2					6.3			-29.4	19.9									
3	CS			10.7	1.1	-1.2	-0.8	2.2	1.7	-0.6	-0.6	-4.0	0.0	-0.5	-1.1	0.9	5.5	-1.8	-0.3	0.4
4	DK	-6.1									-3.8	-0.7	1.0	0.2	1.1	-7.5	-3.2	-9.1	-6.2	-7.4
5	FI	-2.6		7.1	8.9	0.0	-1.6	-3.0	-5.8	-3.9	-13.7	2.3	-3.0	-2.7	1.1	0.6	3.2	1.5	1.8	1.5
6	FR	1.5		-0.7	-5.6	1.3	2.4	0.0	0.0	11.8	-3.8	107.1	-1.0	-10.4	-6.5	-4.5	-21.1	2.6	-14.7	-15.1
7	DDLeip									11.4	9.3	8.3				-26.4	-8.2	-3.8	7.3	3.0
8	DE	25.4					1.6	3.0	-3.8	0.0	-0.6	-0.7	-1.0	10.2	-1.7	-0.3	-0.5	2.6	-2.9	1.5
9	GR																18.9	2.6		
10	HU	-8.3		114.3	3.4	-1.3	1.6	-3.0	-39.4	-40.2	-9.9			-32.8			-0.5	0.6	-12.0	-15.9
11	IS				2.2						-7.9	-1.7	-2.0	-7.5	-7.9	-1.8	-16.1	-11.7	1.5	-1.1
12	IE Met										-5.3	-2.3	-4.0	-2.7	-8.1	-14.1	-14.2			-1.1
13	IT CNR								0.0		-3.5	24.5	-11.0	9.5	20.8	13.5	0.5	2.3	0.0	-0.7
14	NL	4.2		-7.1	0.0	-1.3	0.8	-10.1	-9.6	0.0	-0.9	-4.0	1.0	-0.5	-2.5	2.1	5.7	-0.9	4.7	0.7
15	NO	2.4		-28.6	-2.2	-3.9	-0.8	1.0	-3.8	0.0	2.9	2.3	-7.0	7.2	6.7	-0.6	0.5	1.8	-2.9	
16	PL Met.	0.0		-14.3	-4.5	-9.0	-23.0	-6.1			6.4	-8.6	-3.0	-5.5	-2.5	-3.0	-4.2	1.2	-3.2	-0.7
17	PT										-7.0	98.5	52.0	-0.5	-0.8	-3.9	2.7	2.9	5.6	6.3
18	RO									-15.7						3.6	46.5	5.9		
19	ES									-15.7	50.2		-7.0	-8.0	-15.4	-10.5	-0.7	-0.6	-1.2	-0.7
20	SE IVL									-5.9	-9.6	-5.3	-1.0	2.0	-1.7	7.5	10.7	6.2	-2.3	17.0
21	CH	0.1				-1.8	2.5	-0.5	-2.5	-15.7	-3.2	-7.9	0.0	2.0	6.7	-0.3	-3.2	3.8	10.0	0.0
22	SOV/RU								38.5		7.6		3.0	-34.3	-9.3	-0.9	1.7	-4.1	-4.4	-4.4
23	GB	-9.0		-21.4	-5.6	-18.1	2.4	5.1	-9.6	-5.9	-7.3	9.6	4.0	4.7	12.6	6.0	4.2	16.4	-3.2	-1.1
24	YU					23.2	1.6	11.1	3.8	-11.8	2.0	2.3	-5.0	80.8	55.1	-5.1	5.2	12.6	-12.6	-1.5
25	SE SNV									-13.7	3.5	1.3								
26	CA AES	2.4		0.0	-3.4	2.6	-1.6	-1.0		-5.9	-0.6	-3.0	0.0	2.0	5.1	-0.6	0.2	0.0	-0.6	3.0
27	US ILL.								-3.3	-2.4	-2.3	-1.0	-1.0	3.2	0.8	0.3	-2.2	-3.2	-5.6	-4.8
28	US EPA								-1.9	-3.9	-1.2	10.9	3.0							
29	CA CONC.																			
30	IT ISPRA										2.0	-4.3	0.0	0.2	-0.8	-1.5	-2.5	5.6	7.3	-4.1
31	SK												-1.0	0.5	2.0	0.3	0.2	1.5	-1.5	3.3
32	LT													-28.1						
33	LV																13.2	-7.0	141.6	-1.5
34	TR													3.7	0.3	-0.6	6.5	5.0	5.6	6.6
35	HR													5.2	14.9	-28.5	-36.5	-6.2	-7.9	2.2
36	SI													56.7	-7.6	-6.9	-2.0	-0.9	0.9	-1.8
37	IE EPA/EB	S							-3.8						-21.6	5.7	7.0	-15.0	8.8	
38	EE															2.4	-6.7	23.5	-7.6	-8.5
39	PL (Env.)															0.3	1.0	0.3	-3.2	-1.8
40	MK																	-20.6	-32.6	-8.5
41	EE (Tartu)																			
42	IS (Ork.)																3.2			
Gml. 19	TNO				-6.7	0	-14.3	-3	-7.7											

Table 4.15: Random error (2RSD%) for Cl in precipitation in the different laboratory intercomparisons.

	Cl prec		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
			1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT										4.2	2.4	2.4	14	4.1	2.1	1.3	4.1		4.2	5.3
2	BE		31.1					26.4	2	1.4	2.1	6.2	0.9	3.8							
3	CS				2.3	3.9	4.6	1.2	0.6	0.8		1.8	6.9	2.7	0.7	1.6	0.5	1.3	1.3	1.1	2.1
4	DK		10.2		8.3	1.7	0.7	0.3	0.4	1.6	1.4	0.3	2.3	4.8	2.4	0.9	3.5	1.2	2.5	1.5	4
5	FI				4.5	18	19	2.2		1.1	0.8	0.6	1.4	1.9	2	1.1	0.8	0.7	0.5	2.2	2
6	FR		7.3		6	8.8	29.1	2.5	19.6	1		4	5.7	3.2	9.3	0.8	1.6	2.1	5.1	1.9	2.3
7	DDLeip										1.2	4.7	10.3				0.8	2.5	1.2	0.9	1.9
8	DE		6.7				2.1	0.5	2.5	0.8	0.8	0.7	0.7	3.5	0.4	2.1	3.2	2.1	5	5.8	2
9	GR										4.7	1.8		17.7	62.1			35.8	11.5		
10	HU		12.8		14.3	11.3	10	5.2	3.7	1.1	11.4	2.3	24	17.6	24.3	11.9	6.7	3.2	3.8	2.8	4.6
11	IS										10.8	0.5	2.5	6.1	10.2	25.2	1.6	7.3	11.4	5.6	2
12	IE	Met									5					3.1	2.6	2.3		0.8	0.5
13	IT	CNR								5.7	0.2	0.7	1.7	2.6	2.1	1.3	2.8	3.3	2.5	2.6	1.4
14	NL		5.4		13.5	2.3	9.1	0.9	5.7	1.6	0.3	3	1.9	3	2.1	12.9	1.7	17.6	0.5	5.6	4.1
15	NO		3.8		4.5	2.8	1.4	1.5	1	2.5	4.6	0.4	1.9	2.2	3.4	1.3	1.8	0.7	2	0.5	1.2
16	PL	Met.	4.4		15.1	0.3	8.6	1.5	1.1		2.6	3.8	9	4.8	2.7	12.6	2.6	2.4	5.1	2.9	7
17	PT							3.7	10		2.9		18.4	12.1	2.9	21.1	3.5	4.6	3.4	1.3	1
18	RO										2.7						3.2	48.2	6.1	14.5	8.4
19	ES										4.2	2.2		14.4	19.3	7.9	2.2	1.3	11.7	13.5	17.2
20	SE	IVL	3.9		6.8	22.7	1.9	3.6	10.6	2.4	7.6	1.3	0.9	0.7	1.2	2.1	0.8	0.7	2.7	1.5	5.9
21	CH		10.1		25.6		12.5	2.9	1.3	5.2		4.9	0.9	0.6	1.1	3.1	0.6	0.1	1	2.4	1.8
22	SOV/RU									9		1.3	4.4	22.3	10.9	21	5.4	7.3	17.7	7.2	12.7
23	GB		3.1		4.5	10.1	5.5	3.8	2.8	1.6	4.4	0.2	1.7	2.4	7.5	25.8	2.9	6.5	7.8	8.1	0.8
24	YU					6.4	9.7	7.4	7.6	0.8	2	1.6	16.7	16.4	10.1	14.3	8.3	11.4	6.9	16.3	18.7
25	SE	SNV									6.2	2.4	0.4								
26	CA	AES	15		5.3	1.1	11.1	2.2	1.4			1.1	2.4	5.2	2.1	2.7	2	4.4	1.3	1.4	0.4
27	US	ILL.								0.3	0.9	0.4	0.8	0.5	1.4	2.9	1.3	0.8	1.2	0.8	0.5
28	US	EPA								0.5	1.5	0.1	0.6	0.6							
29	CA	CONC.										4.5	0.9								
30	IT	ISPRA										0.7	1.9	1.9	1.1	6.9	1.1	1.1	3.4	5.4	1.8
31	SK													2	10.2	12.6	2.9	2.6	3.5	4.1	2.6
32	LT														4.8	12.8	2.6	5.4	0.9	1.5	
33	LV																	8.5	24.4	0.3	5.6
34	TR															1.1	1.9	0.4	3.1	9	3.1
35	HR														13.5	8.5	6.6	4.7	8.8	2.5	0.4
36	SI														2.3	18.9	4.7	0.5	3.8	0.8	1.8
37	IE	EPA/EBS								0.8	1.4					8.9	2.2	0.7	10.5	47.2	
38	EE																19.4	3.5	6.5	4	12.5
39	PL (Env.)																3.1	2.5	14.3	11.9	3.1
40	MK																				23.1
41	EETartu																	10			
42	ISOrk																	2.3			
Gml. 19	TNO					2.6	1.4	1.7	2.8	1.7											

Table 4.16: Systematic error (RB%) for Cl in precipitation in the different laboratory intercomparisons.

	Cl prec		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
			1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT										-18.6	-24.5	-3.4	-4.0	2.5	-2.2	0.1	-8.1		-6.0	-13.8
2	BE		55.0					15.7	-3.2	-3.5	-3.0	2.2	-21.7	-13.5							
3	CS				9.2	-4.8	-5.6	0.8	-2.0	0.2		-1.5	3.5	-1.4	-7.1	0.0	-2.9	-0.4	-6.1	-8.7	-9.5
4	DK		-1.4		-11.1	-2.3	-1.4	-2.7	-2.2	-2.5	3.5	-10.1	10.9	3.6	-0.4	3.9	-6.6	-5.0	-4.2	-3.5	2.2
5	FI				11.1	49.7	36.1	-16.8		-1.2	0.6	-0.5	-4.9	-2.4	-3.6	3.0	0.6	0.3	-0.8	-1.8	-1.0
6	FR		6.7		0.0	-7.2	-11.9	-5.9	29.9	1.0		-2.8	-13.6	-4.3	-5.3	-1.6	2.6	-7.8	-6.9	-3.2	-5.3
7	DDLeip										2.8	-3.4	9.4				-1.6	13.2	-2.9	-2.7	-7.2
8	DE		-4.2				-1.7	-4.7	0.7	-8.4	1.7	1.4	-2.8	-5.3	-2.5	-1.2	-14.1	-0.9	-6.8	-2.4	-3.8
9	GR										0.7	0.4		-16.1	36.1			207.4	-7.5		
10	HU		16.3		34.1	2.8	-7.1	13.4	-5.5	6.2	-10.6	-4.1	-28.8	-57.5	-3.4	41.1	-32.2	8.9	-10.4	16.8	3.2
11	IS										36.2	-7.0	-4.1	7.2	-13.5	10.0	-0.8	-1.2	-0.1	-9.0	6.8
12	IE	Met									-2.8					-6.3	-7.5	-13.6		-5.2	3.7
13	IT	CNR								-10.1	0.0	6.6	-2.2	-10.4	8.6	-3.2	0.4	8.4	3.2	6.0	-3.3
14	NL		10.4		-41.5	-6.9	-2.2	-4.1	4.6	15.5	-4.1	-0.2	-4.1	-2.0	-1.5	-4.5	-2.8	-0.5	-3.9	0.7	-0.6
15	NO		-4.4		-6.5	-1.4	-6.8	-1.0	-0.7	-1.6	2.6	-4.5	-3.5	0.9	1.5	8.7	0.3	-4.0	-5.2	-4.8	-2.6
16	PL	Met.	-8.0		22.1	1.4	-4.2	-4.1	-3.1		0.4	-8.8	4.6	13.5	9.4	32.4	-9.7	-0.9	0.3	-4.7	-5.2
17	PT							-4.5	-21.6		-10.6		-9.1	-21.5	-1.9	-29.4	-4.1	-1.7	-7.3	-5.6	1.8
18	RO										17.7						-6.5	26.9	-6.8	11.8	0.0
19	ES										-2.6	-9.9		-0.9	25.7	13.4	15.9	-3.9	52.9	52.8	-29.1
20	SE	IVL	-4.3		-61.8	34.8	-5.1	7.3	15.6	1.0	-17.3	-4.9	-1.5	-0.9	-2.5	0.8	-0.1	0.5	-5.9	-6.1	-7.3
21	CH		-8.8		9.2		-5.1	-4.1	2.1	3.3		1.6	1.2	-2.0	0.3	1.6	0.7	0.8	-0.9	-5.8	-0.5
22	SOV/RU									25.9		-6.6	-34.9	-64.6	-33.5	-34.8	-4.4	-12.8	8.1	-10.4	-22.4
23	GB		7.6		11.1	6.9	0.0	15.7	1.1	2.5	-0.6	-0.7	1.2	-5.0	10.7	27.0	0.9	-2.4	25.5	19.6	0.2
24	YU					1.8	-8.0	-9.4	-6.6	-4.5	2.8	-18.8	40.2	14.5	18.4	1.8	-2.8	34.8	32.6	-7.7	-47.5
25	SE	SNV									6.7	-3.4	-1.3								
26	CA	AES	1.0		-0.9	5.5	-10.2	4.4	2.0			-4.9	-2.8	-2.0	-4.6	0.2	-1.2	-4.5	-0.2	0.4	-0.6
27	US	ILL.								0.0	0.2	1.8	-1.1	0.4	-1.3	1.8	0.9	-0.7	1.7	-1.0	-1.2
28	US	EPA								-1.7	-0.4	-1.7	2.7	1.5							
29	CA	CONC.										-2.8	-9.3								
30	IT	ISPRA										-3.9	-9.6	2.9	2.3	0.8	-0.6	0.2	-12.1	2.6	-4.1
31	SK													-0.5	-24.7	1.2	7.9	-11.7	-5.3	-8.6	-1.0
32	LT														-4.5	-1.5	-1.8	-19.3	-0.9	-3.5	
33	LV																	-15.2	27.4	-3.8	61.2
34	TR															-4.3	-7.6	-0.2	4.0	-6.7	-6.0
35	HR														41.9	50.1	-22.8	-13.7	8.8	-1.6	-3.9
36	SI														13.0	44.2	-2.1	0.0	-3.3	-1.0	-3.8
37	IE	EPA/EBS								-3.3	-4.1					18.2	-6.2	-14.2	-20.2	-3.2	
38	EE																-39.9	0.9	-6.0	-18.0	25.9
39	PL (Env.)																0.1	2.1	-22.8	11.0	-4.7
40	MK																				-6.7
41	EETartu																	1.0			
42	ISOrk																	-6.7			
Gml. 19	TNO					6.9	3.4	-4.1	3	1.4											

Table 4.17: Random error (2RSD%) for pH in precipitation in the different laboratory intercomparisons.

	pH prec (H+)		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
			1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT		10.8		16.8	16.5	24.4	1.6	9	1.2	19.4	7.4	15.6	7.2	2	3.9	11.5	4.7		8.2	3.2
2	BE		10.9			34.4	21.4	11.5	29.2	3.8	11.2	13	22.2	20.3							
3	CS				26.9	6	6.9	4.9	4.6	2.2	4.2	2.1	5.3	2.9	3.8	4	7.6	5	4.4	8.1	7.8
4	DK		3		15.5	7.6	12.6	12.8	11.5	13.8	15.1	10.9	13.2	5.4	5.2	11	5.2	1.9	6.6	7.8	4.7
5	FI		5.8		20.7	7.8	8.2	10.7	7.2	7.7	3.8	1.6	4.4	3.4	1.1	3.1	3.7	0.7	2.1	2.7	1.8
6	FR		26.9		30	2.2	8.6	8.2	10.2	7.5	12.7	7.5	3.8	11.9	1.6	8.5	4.9	3.1	7.9	7.5	5.4
7	DD/Leip										17.8	4.8	2.8				10.3	6	4	8.2	5.6
8	DE		32.1					6	16.8	13.8	9	5.7	5.5	5.9	3.1	6.5	7.6	8.4	10.3	10.2	
9	GR		123.2		290.8	462.5	83.5	27.6	20	10.7	22	17.9	20.1	8.3	11.1		18.8	8.7	4.1		
10	HU		33.4		75.4	181.3	23.6	20.8	8.2	26.7	6.1	7.8	124.6	73.2	7.9	91.4	54.3	4.2	10.9	7.6	14.3
11	IS					15.4	5.2		5	39.9		6.4	5.5	2.5	4.1	14.9	3.9	2.4	11.5	30.9	2.9
12	IE	Met					7.2	5.8	1.5	3.4	1.8	0	3.5	1.2	1.5	3.6	8.9	8.1		2.9	1.6
13	IT	CNR								4.1	44.7	22.3	7.8	17.7	21.2	89.4	114.8	3.5	23.1	8	5
14	NL		6.2		48.5	18.5	16.2	11.3	8.5	3.6	8.8	1.6	2.5	8.1	10.8	10.9	4	4	3.6	4.5	6.8
15	NO		15.8		20.1	22.4	16.1	4.3	4.4	4.9	5.2	3.5	3.7	2.5	5.2	7.8	3.3	3.5	6.2	5.8	5
16	PL	Met.	33		31.6	10.7	3.4	8.7	5.7			13.4	4.6	10.2	6.7	13.7	4.8	1.1	4.6	12.2	5.6
17	PT					3.9		3.2	18.8	23.8	26.3	17.4	15.8	16.9	3.8	12.8	12.8	2.2	5.4	17	8.7
18	RO										22.8						2.2	6.3	3.8	11.6	10.4
19	ES										12.1	5.1		6.3	12.3	15.1	17.7	3.2	10.1	10.3	11.6
20	SE	IVL	5.5		20.1		3.4	7.7	23.8	3.3	13.7	1.2	3.4	4.1	1.7	4.1	2.4	2.7	1.7	3	2
21	CH		8.9		17.6		9.8	15.8	10.4	7.1	14.9	5.2	4.8	2	2.9	6	4.3	3.5	0.5	1.7	4.7
22	SOV/RU									14		7.5	11.7	8.4	6.9	9.6	4.2	4.7	5.5	3.5	6.8
23	GB		46.8		11.9	7	29.5	8.7	13.5	2.4	6.2	0	2.6	4.6	8.4	12.1	6.6	1.5	7.9	26.5	0.5
24	YU					13.5	7.4	13.7	20.1	8.1	3	14.7	4.5	8.8	16.8	6.8	8.9	3.6	8.5	4.2	18.8
25	SE	SNV									5.4	1.3	8.8								
26	CA	AES	23.9		18.2	7.9	4.4	16.5	5		3	4.8	8.6	2.4	1.3	6.7	7.6	4.7	5.7	4	3.7
27	US	ILL.								6.3	5.7	2.7	4.8	3.6	2.8	9.1	5.7	5.2	7	5	5.2
28	US	EPA								4.8	4.6	2	4.5	2.7							
29	CA	CONC.									8.1										
30	IT	ISPRA										3.7	10.2	3.2	1	8.2	4.4	2.5	9.6	9.2	1.8
31	SK													10.5	6.5	35.2	13.2	12.5	3.6	9.2	9.4
32	LT														5.5	15.9	9	0.3	7.3	5.9	
33	LV														23.8	14.5	4.5	3.2	7.4	4.9	9.6
34	TR														13.6	8	3.9	14	16	4.8	5.3
35	HR														2.5	24.9	7.1	1.3	7.8	1.3	5.1
36	SI														6.9	10	6.1	1.1	8.1	8.9	7.1
37	IE	EPA/EBS								24						36.8	4.8	4.5	7.9	7.3	
38	EE															33.3	11.2	13	7.8	11.1	5.7
39	PL (Env.)																8.4	4	7.8	26.1	9.2
40	MK																		4.4	43.2	42.8
41	EETartu																	33.2			
42	ISOrk																	6.8			
Gml. 19	TNO					17.4	3	7.2	3.1	26											

Table 4.18: Systematic error (RB%) for pH in precipitation in the different laboratory intercomparisons.

	pH prec	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
		1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT	-10.2		10.3	19.3	46.1	0.6	21.6	14.9	94.1	-17.5	32.6	16.5	3.3	2.5	-7.1	-10.6		-20.4	-7.2
2	BE	-1.8			-44.4	-11.3	20.8	-32.6	8.7	0.5	-17.2	-52.5	-18.9							
3	CS			20.1	-9.9	-8.4	1.9	-1.5	6.3	11.9	-12.7	-3.1	-2.6	-9.3	7.9	-7.1	-11.0	-6.9	-9.8	-12.5
4	DK	0.4		7.2	-4.3	-23.4	-21.4	-10.9	-16.5	-12.1	-21.5	-18.7	-8.2	-16.3	-9.9	0.8	-1.2	-14.1	-14.6	-10.0
5	FI	-3.0		-16.6	-22.2	-15.8	-21.4	-9.5	-7.3	23.4	-4.5	-9.5	-5.2	2.4	9.3	9.6	0.1	-2.2	-4.2	-4.3
6	FR	18.0		-8.8	-1.7	-11.6	-3.1	19.6	34.7	11.9	-18.7	-8.2	23.3	-7.8	6.7	12.4	-4.2	-12.7	4.0	-2.8
7	DDLeip									-18.5	-10.8	-3.6				-0.6	-16.4	-7.7	-13.5	-9.6
8	DE	4.5					-17.5	0.6	-14.9	6.3	-10.8	-10.3	8.3	-0.9	11.3	-3.3	-19.7	-17.9	-12.6	
9	GR	121.8		287.4	1627	-87.5	-30.4	35.3	10.3	-6.1	4.5	91.6	-4.1	38.1		1.0	-15.3	-5.0		
10	HU	11.2		49.2	92.7	59.9	-4.9	33.2	61.0	44.1	28.5	276.0	336.3	19.6	184.5	123.5	-15.2	-18.9	-19.4	-31.0
11	IS				15.1	18.0		9.6	57.6		-9.5	-9.5	0.3	-7.7	-6.4	14.7	-1.9	-9.2	-10.0	-5.9
12	IE Met					-2.8	-5.8	7.6	4.6	16.5	0.0	-3.3	2.7	-3.3	6.7	24.7	30.9		1.7	-3.0
13	IT CNR								10.2	151.4	44.3	5.4	50.7	37.2	195.0	196.6	36.6	17.8	-15.4	-14.0
14	NL	3.0		51.2	-25.7	0.2	-38.6	-2.0	4.1	-0.2	-6.9	0.0	-23.3	-25.7	1.0	-10.0	-15.2	-9.6	-15.7	-21.9
15	NO	-11.1		38.1	28.6	8.8	-3.9	4.2	5.5	27.8	5.7	-5.5	-2.5	-13.2	4.6	2.0	-7.8	-9.2	2.7	-11.5
16	PL Met.	-28.9		-3.4	-29.2	-22.0	-15.8	3.7			-6.4	-6.8	3.0	3.3	3.5	-10.8	0.1	-2.1	15.2	-5.9
17	PT				-17.5		-7.0	-22.2	8.5	0.2	47.8	-36.4	-19.3	-7.9	17.3	5.7	-5.8	-8.6	25.6	-22.4
18	RO									55.2						17.3	-16.5	-5.7	25.7	21.9
19	ES									-5.1	-8.8		-37.0	-16.6	39.1	-3.1	9.1	-26.7	-26.9	-34.5
20	SE IVL	19.3		38.1		-7.1	-12.8	5.8	-0.2	8.7	2.2	-5.1	-3.9	-1.0	1.3	-9.9	2.1	-0.5	-3.1	4.7
21	CH	51.0		26.3		-19.9	5.8	-1.1	-8.7	5.2	-1.6	-7.1	0.5	-5.6	-3.1	-5.4	-9.2	2.1	-2.9	-10.6
22	SOV/RU								-24.7		-4.6	-15.9	-17.6	-20.5	-8.7	4.6	-21.8	-17.9	-11.3	-10.7
23	GB	4.3		4.0	8.4	52.8	-6.2	33.7	4.3	14.3	0.0	-1.6	9.4	-5.9	3.7	10.4	-2.9	-14.5	54.3	11.8
24	YU				-7.9	-20.1	-20.2	-0.3	-3.0	9.3	-13.6	7.2	-2.2	15.0	-6.2	9.4	-13.4	-12.9	11.5	26.3
25	SE SNV									34.7	0.0	-5.5								
26	CA AES	-27.3		18.3	-10.9	3.2	-8.5	9.6		21.9	-5.2	-7.1	-3.9	1.3	-3.1	-6.7	-11.9	-4.9	-6.6	-6.5
27	US ILL.								-4.0	11.1	-0.7	-4.7	-3.8	-4.7	1.1	-1.8	-9.2	-13.1	-7.9	-9.9
28	US EPA								0.0	11.0	-0.7	-3.1	5.6							
29	CA CONC.									3.6										
30	IT ISPRA										5.1	22.7	-0.8	-4.0	-5.2	0.0	-1.2	-13.6	13.5	-2.3
31	SK												-6.1	-17.1	-22.0	12.8	48.4	-1.1	-8.3	-9.9
32	LT													1.6	30.7	-8.3	-7.3	-9.1	-4.0	
33	LV													-25.5	-12.5	-13.8	-17.6	-13.2	-9.9	0.8
34	TR													22.7	-1.5	4.0	46.5	36.8	-11.8	-10.1
35	HR													-5.4	64.7	-4.7	-7.3	-10.2	-7.2	-17.9
36	SI													-7.6	-1.5	-4.1	2.1	-17.2	-7.7	-31.3
37	IE EPA/ESB								69.3						100.8	7.7	-25.5	-15.1	-14.6	
38	EE														-54.6	-13.8	4.0	-8.6	27.4	-2.8
39	PL (Env.)															17.2	-12.7	-11.7	60.6	-0.1
40	MK																	-12.4	165.1	200.1
41	EETartu																-20.2			
42	ISOrk																-20.2			
Gml. 19	TNO				-27.9	-9.2	-24.8	17.4	38.7											

Table 4.19: Random error (2RSD%) for SO_2 in air in impregnated filter in the different laboratory intercomparisons.

	SO2 air (imp)		1	2	3	4	5	6	7	8	9	10	11	12	13	14_avg	15_avg	16_avg	17_avg	18	19
			1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT																				
2	BE																				
3	CS						75.8		2.5	1.6	14	2.9	5.3	4.6	2.3	1.9	4.5	5.8	1.1		2.2
4	DK			8.3	4.2	1	6.1	2.6	9.9	2.2	3.8	2	3.9	1	2.8	3.05	0.85	1.2	1.05		1
5	FI												4.5	2	1.2	1.1	0.9	7.85	1.85		0.7
6	FR																				
7	DD																				
8	DE																				1
9	GR																				
10	HU														2.5	11.1	10.5	3.1			
11	IS													0.9	4.5	7.75	6.1	8.5	4.7		3.6
12	IE						14	9.3	6	5.7	5.9	2.8	6.3	6.2	4.1	4.15	2.6	2			1.8
13	IT	CNR											5.5	9.7	7.2		3.95	4.5			1.7
14	NL																				
15	NO			3.6	5.2	6.5	3.5	6.8	1.7	1	6.2	0.4	1.5	5.2	0.8	2.65	1.25	1.85	2.1		2.8
16	PL													3.3	14	23.3	2.4	5.1	2.55		3
17	PT																				
18	RO																				
19	ES																				7.1
20	SE	IVL													2.3	3.15	1.8	3.85	0.9		2.7
21	CH																				
22	RU													4.4	6	8.05	1.85	2.65	2.6		5.7
23	GB																				4.2
24	YU																				
25	SE	SNV									2.7	0.4	1.3								
26	CA			1.8	1.6	2.1	43.3	3.8			1.3	2.1	2	1.4		1.7	1.7	2.6	0.75		
27	US-I																				
28	US-E									6.4	2.7	0.1	2.2	0.1							
29	CA	CONC.									9.2		3.8								
30	IT	ISPRA										0.5		1	2	2.45	1.15	1.05			
31	SK													4.7	2.1	6.25	2.15	3.7	4.6		2.8
32	LT														15.1	8.05	40	10.8	0.8		
33	LV														3.5	23		8.9	6.9		12.7
34	TU														12.3	2.25		22.2	1.2		1.9
35	HR																				
36	SI														11.6	25.1		2	6.5		1.8
37	IE (EPA)															3.1		10.6			
38	EE															7.2		5.35	13.1		9.2
39	Pl Env.																	3.6	5.85		1.2
40																					
41																					
42																		30			
Gml. 19	NL	TNO																			

Table 4.20: Systematic error (RB%) for SO_2 in air in impregnated filter in the different laboratory intercomparisons.

	SO2 imp		2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	19
			1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2001
1	AT																		
2	BE																		
3	CS					51.4		5.2 🟦	-4.3 🟦	1.2	-10.1 🟦	1.0	8.2 🟦	-3.0	3.7	14.1 🟦	9.9 🟦	7.7 🟦	5.6 🟦
4	DK		24.7 🟦	-18.7 🟦	-2.1 🟦	-1.6	7.6 🟦	0.4	2.3 🟦	-7.7 🟦	-2.7 🟦	0.1	3.1 🟦	-8.9 🟦	-0.9	-2.7 🟦	-3.2	-2.8 🟦	-1.0 🟦
5	FI											-19.6 🟦	-8.6 🟦	-1.5 🟦	-0.7	-5.7 🟦	6.1	-2.1	2.0 🟦
6	FR																		
7	DD																		
8	DE																		1.3 🟦
9	GR																		
10	HU													5.3 🟦	34.9 🟦	18.6	0.6		
11	IS												-1.5 🟦	-11.8 🟦	-8.2	-12.5 🟦	0.2	-1.0	-8.6 🟦
12	IE					-10.2 🟦	-9.5 🟦	13.0 🟦	-0.5	-5.3	-0.8	4.8 🟦	-9.2	-3.2	-0.9	-1.0	-2.2		3.1 🟦
13	IT	CNR										-1.9	12.4	-13.4 🟦		0.9	0.8		-0.3
14	NL																		
15	NO		-5.1	-9.1 🟦	-5.2	-6.4 🟦	-6.5	-4.2 🟦	-3.2 🟦	-17.3 🟦	-3.4 🟦	-0.4	-1.3	-1.2 🟦	1.1	1.3	2.3	-0.9	-1.6
16	PL												-8.2 🟦	18.5	11.6	-4.2	6.5	-7.3 🟦	-1.2
17	PT																		
18	RO																		
19	ES																		13.6 🟦
20	SE	IVL												-0.7	-2.1	-2.5	-1.3	-15.6 🟦	-2.9
21	CH																		
22	RU												1.3	-18.9 🟦	-19.7	2.4 🟦	-3.6 🟦	-8.4	-11.2
23	GB																		3.9 🟦
24	YU																		
25	SE	SNV								-3.7 🟦	2.5 🟦	2.2 🟦							
26	CA		-5.8 🟦	1.7	-1.0	7.8	8.7 🟦			-1.9	3.2 🟦	1.6	-1.7 🟦		-0.4	-0.4	1.2	-5.1 🟦	
27	US-I																		
28	US-E								-12.2 🟦	-7.3 🟦	0.5 🟦	2.8 🟦	1.0 🟦						
29	CA	CONC.								9.6		-3.3							
30	IT	ISPRA									0.5		-11.7 🟦	-10.4 🟦	3.8 🟦	-6.6 🟦	0.4		
31	SK												-2.6	-5.0 🟦	-17.6	-9.7 🟦	-0.3	-1.6	6.8 🟦
32	LT													-21.3 🟦	7.6	60.4 🟦	14.8	3.9 🟦	
33	LV													-13.0 🟦	13.8		-4.9	-14.8 🟦	-22.4 🟦
34	TU													-24.3 🟦	-0.6	-4.4	5.0	-2.1	1.6
35	HR																		
36	SI													-11.4	-40.0 🟦	2.6 🟦	-1.7	10.0	3.5 🟦
37	IE (EPA)														-9.8 🟦	-19.6 🟦	-11.5 🟦		
38	EE														-29.0 🟦	-14.7	-16.3	-15.5	-17.0 🟦
39	PI Env.															-17.7 🟦	-3.3 🟦	-7.8	-2.5 🟦
40																			
41																			
42																	10.55 🟦		
Gml. 19	NL	TNO																	
Gml. 25	IE	ESB Dubl.																	

Table 4.21: Random error (2RSD%) for SO_2 in air in absorbing solution in the different laboratory intercomparisons.

	SO2 abs		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
			1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2000	2001
1	AT		21.5	6.5	2.4	5.1	15.6	2.9	1.6	5.9	8.2	4.3	2.5	3.1	12.9	3.4					
2	BE		30.5																		
3	CS				13.7	3.6															
4	DK																				
5	FI		1.5	2.4	3	1.8	1.6	1.8	1.3	1.7	2.2	3.4	4.6								
6	FR		12.1	6.5	3.9	7.3	3.1	5	2.1	2.8	8.2	3.4	13.3	2.5	3	3.4	1.5	2.1	11.9		1.6
7	DD																				
8	DE		27.8			8.3	3	2.4	9.2												
9	GR		52.8	59.7	7.7	3.6	6.6	8	17.2	8.7	6	2.7	10.1	1.5	25.2		11.1	55.6	26.7		
10	HU					5.4	16.6	13.5	5.8		38.3										
11	IS					1.8	3.1	4.7	2.6	5.2	1.7	4.3	3.3	1.8							
12	IE																				
13	IT	CNR									3.9	3.8									
14	NL		1	3.9	1.1	0.5	2	3.3	0.7	2.7	2.2	1.2									
15	NO		7.7	0.9	1.5	2.9	1.2	6.3	7.2	2.1	1.7	0.8	3.6	0.2	0.9	1.9	2.4	1.7	4		5
16	PL		8.5	15.2	5	12	3	4.2	4.5			5.1	35.1								
17	PT					0.9					5.2	7.4	59		6.3	11.9	12.9	2.9	5.3		15.2
18	RO																				
19	ES										2.2	3.4		5.2	2.1	4.4	4.2	11.6	12.6		16.7
20	SE	IVL	9.2	3.9		18.3	2.3	5.8	1.8	5.2	10.3	5.3	1.7	2.8							
21	CH		13.3	2.2	4.5		7.8	1.8	5.3	0.3	1.7	2.2	2.4	1.8	0.4	3.3	3.1	1.4	1		0.7
22	SOV/RU										1.7										
23	GB		50.6	2.4	14.8	1.8	2.3	13	2.9	2.1	1.7	11	5.4	2	3.5	1.7	2.9	1.4	3.3		2.8
24	YU																				
25	SE	SNV																			
26	CA		37.7																		
27	US	ILL.																			
28	US	EPA								7.7											
29	CA	CONC.																			
30	IT	ISPRA																			
31	SK																				
Gml. 19	NL	TNO				14.5	4.7	1.6	3.4	18.2											
Gml. 25	IE	ESB								3.8											

Table 4.22: Systematic error (RB%) for SO_2 in air absorbing solution in the different laboratory intercomparisons.

	SO2 abs		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	19
			1977	1978	1978	1979	1980	1981	1982	1984	1986	1987	1989	1991	1993	1994	1995	1997	1999	2001
1	AT		-0.1	-6.7	17.1 🟦	6.0	7.4	3.4 🟦	3.4	-4.3	-3.2	-6.8 🟦	3.1	-2.8	12.0 🟦	-0.8				
2	BE		-6.7 🟦																	
3	CS				1.5	3.3 🟦														
4	DK																			
5	FI		-0.4	5.3 🟦	3.6	6.7 🟦	-1.9	-0.6	0.0	0.9	0.0	2.6	-1.7							
6	FR		0.3	0.0	13.5 🟦	8.9	2.9	9.3 🟦	4.7	0.9	10.6 🟦	13.0 🟦	-19.3 🟦	-3.0	18.1 🟦	7.3 🟦	-2.0	-3.5 🟦	-12.7	-5.3 🟦
7	DD																			
8	DE		-6.6 🟦			-43.1 🟦	4.2 🟦	-0.6	-7.9											
9	GR		-0.2	-12.8	1.5	-5.6 🟦	-19.0 🟦	-9.1	-28.3	-3.4	3.2	-16.6 🟦	-19.2 🟦	7.4 🟦	23.3		31.8 🟦	18.1 🟦	13.4	
10	HU					4.0	-19.2	-16.9 🟦	-4.5		7.4									
11	IS					0.0	4.8	-4.6	0.0	9.4 🟦	10.0 🟦	-9.1 🟦	-2.4	2.1						
12	IE																			
13	IT	CNR									-8.4 🟦	-4.0								
14	NL		-1.0 🟦	4.9 🟦	2.3 🟦	1.3	1.3	-2.9	1.0	6.3 🟦	-1.1	-4.0 🟦								
15	NO		-1.4	1.1	0.0	4.2 🟦	-1.5	-3.6	-3.7	6.0 🟦	1.1	0.3	3.0 🟦	-0.4 🟦	0.5	3.5	-4.4 🟦	-0.2	1.6	-4.4 🟦
16	PL		-6.3	13.3 🟦	-0.4	0.0	2.9 🟦	-0.8	-4.8			-3.0	9.9							
17	PT					1.3 🟦					3.2	-4.2	-6.4		5.4 🟦	-22.5 🟦	-33.8 🟦	7.3 🟦	11.7 🟦	10.8
18	RO																			
19	ES										5.8 🟦	11.1 🟦		17.8 🟦	-2.1	1.5	3.4	4.6 🟦	-38.5 🟦	-7.4
20	SE	IVL	2.7	1.3		6.4	3.2 🟦	8.9 🟦	2.6 🟦	3.0	12.1	12.5 🟦	6.0 🟦	6.8 🟦						
21	CH		-2.4	2.4	1.8		1.9	3.4 🟦	1.3	3.0 🟦	3.7 🟦	5.5 🟦	10.6 🟦	-1.2	2.3 🟦	0.0	-2.9	3.4 🟦	1.9 🟦	0.2
22	SOV/RU										6.3 🟦									
23	GB		-4.3 🟦	-4.5 🟦	-3.6	2.2 🟦	3.8 🟦	18.3 🟦	2.4	3.0 🟦	1.6	20.3 🟦	2.1	1.0	12.8 🟦	3.6 🟦	16.3 🟦	-1.1 🟦	10.3 🟦	6.6 🟦
24	YU																			
25	SE	SNV																		
26	CA		0.6																	
27	US	ILL.																		
28	US	EPA								11.6 🟦										
29	CA	CONC.																		
30	IT	ISPRA																		
31	SK																			
Gml. 19	NL	TNO				40.0 🟦	-3.8	-0.8 🟦	6.9 🟦	31.3 🟦										
Gml. 25	IE	ESB								-0.4										

Table 4.23: Random error (2RSD%) for NO_2 in air in the different laboratory intercomparisons.

	NO2 air		11 1989	12 1991	13 1993	14 1994	15 1995	16 1997	17 1999	18 2000	19 2001
1	AT										
2	BE										
3	CS		0.7	10.9	1.8	2.2	2.8	0.4	1.3		14
4	DK				1.3	0.9	1	1.8	0.7		1.1
5	FI										
6	FR										
7	DD/DE (Leip.)										
8	DE		1.6	3.1	0.9	1.5	0.4	0.7	1.7		
9	GR			5.1	2.9	2	1.7	2.8	2.7		
10	HU		7.5	4.5	17.9	41.2	22.8	0.5	4		1.1
11	IS										
12	IE	MetServ	2.3	9.6	4.1	4.6	4.6	3.2	5.4		1.4
13	IT	CNR			3.7						
14	NL										
15	NO		3.3	3.9	5.1	1.1	1.2	6.7	1.7		1.8
16	PL	Met.	7	5	4.2	4.1	2	2.8	5		1.8
17	PT										
18	RO						12.6	16.7			
19	ES			12.1	17	16.2	4.3	0.1	1		347.1
20	SE	IVL	3.3	2.8	1.2	4	0.3	0.2	2.7		1.4
21	CH										
22	SOV/RU		8.3	20.1	6.8	3.2	3.9	3.4	1.3		1.8
23	GB					1.2	1.8	0.2	3		4
24	YU			3.5	4	2.1	3.3	3.7	5.4		3.2
25	SE	SNV			0.7						
26	CA	AES									
27	US	ILL.									
28	US	EPA									
29	CA	CONC.									
30	IT	ISPRA									
31	SK			7.3		5.5	3.4	4.8	4.4		2.9
32	LT				6.1	4.3	2.5	3	3.4		
33	LV					2.8	3.7	3.6	3.7		5.4
34	TR				2.9	1.7	3.4	3	4.7		3.2
35	HR						6.1	0.4	1.3		1.4
36	SI				4.1	2.4	1	0.6	4.4		0.7
37	IE	EPA/EBS	2.2								
38	EE								1.7		1.1
39	PL (Env.)						2.2	10.1	3.7		2.9
40	MK										
41	EE Tartu							5.3			
42	IS (Ork.)										
Gml. 19	TNO										

Table 4.24: Systematic error (RB%) for NO_2 in air in the different laboratory intercomparisons.

	NO2 air		11 1989	12 1991	13 1993	14 1994	15 1995	16 1997	17 1999	18 2000	19 2001
1	AT										
2	BE										
3	CS		-6.0 🟦	-24.1 🟦	-2.1 🟦	-4.6 🟦	0.6	-0.8 🟦	-6.6 🟦		-7.0
4	DK				3.2 🟦	-3.2 🟦	-1.4	-0.5	-1.6 🟦		-4.4 🟦
5	FI										
6	FR										
7	DD/DE (Leip.)										
8	DE		-3.7 🟦	-4.9 🟦	-1.0 🟦	-2.8	0.0	1.7 🟦	2.9 🟦		
9	GR			-8.6 🟦	-2.9	-3.9	-2.0	7.8 🟦	-2.5 🟦		
10	HU		19.3 🟦	-10.9 🟦	-42.5 🟦	-48.1	-39.2 🟦	-1.0 🟦	0.4		-2.6 🟦
11	IS										
12	IE	MetServ	-3.0 🟦	-14.7 🟦	0.6	16.9 🟦	1.2	8.3 🟦	2.9		4.0 🟦
13	IT	CNR			-3.7 🟦						
14	NL										
15	NO		-6.3 🟦	-5.0 🟦	-13.8 🟦	1.6	-4.8 🟦	-14.1 🟦	-1.6 🟦		-0.4
16	PL	Met.	12.4 🟦	-13.3 🟦	-0.2	-1.9	2.8 🟦	-4.7 🟦	2.5		-3.1
17	PT										
18	RO						54.6 🟦	62.2 🟦			
19	ES			1.5	-15.0	20.1	-8.2 🟦	-5.3 🟦	-2.9 🟦		1318.5 🟦
20	SE	IVL	0.3	-9.1 🟦	-3.7 🟦	-8.2 🟦	-1.0 🟦	0.2	-2.9 🟦		-1.8
21	CH										
22	SOV/RU		-28.0 🟦	-44.8 🟦	-8.9 🟦	-9.4 🟦	-7	-3.1	9.0 🟦		1.8
23	GB					4.6 🟦	4.0 🟦	-0.9 🟦	-5.7 🟦		4.4 🟦
24	YU			-1.3	9.9 🟦	7.7 🟦	7.2 🟦	7.2	-3.7		-0.9
25	SE	SNV			0.7						
26	CA	AES									
27	US	ILL.									
28	US	EPA									
29	CA	CONC.									
30	IT	ISPRA									
31	SK			-11.5 🟦		-12.1 🟦	-8.9 🟦	-10.5 🟦	-14.4 🟦		-11.0 🟦
32	LT				-0.7	-7.4 🟦	4.4	-0.4	-3.7		
33	LV					11.7 🟦	-1.8 🟦	-3.4	-5.7 🟦		-7.5 🟦
34	TR				-6.5 🟦	-3.1 🟦	-4.6	-6.4 🟦	6.6 🟦		-3.5
35	HR						24.5 🟦	-3.6 🟦	-0.8		-0.4
36	SI				-15.4 🟦	8.3 🟦	1.7	6.6 🟦	7.4 🟦		-3.5 🟦
37	IE	EPA/EBS	6.3 🟦								
38	EE								2.5 🟦		-2.2 🟦
39	PL (Env.)						-6.8 🟦	6.7	-5.7 🟦		3.1 🟦
40	MK										
41	EE Tartu							5.0			
42	IS (Ork.)										
Gml.1	9 TNO										

Annex 5

Note to be attached to the German EMEP data (by Markus Wallasch, QA–Manager)

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 !

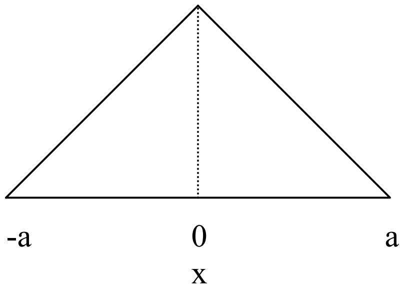
for Sulfur in Particles : Y = 1.50 X

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

Annex 6

Estimating errors from laboratory comparisons

Systematic errors or bias in the laboratory analyses give a constant shift in the results from the expected ones at a particular concentration level. It is assumed that laboratories taking part in comparisons will obtain results near the expected ones when this bias is removed, and that the differences between expected and obtained results more often will be close to zero than not. A triangular distribution, based upon this assumption, can be used to quantify the random errors in the laboratory results (Eurachem, 2000).



The triangle distribution is symmetric with a baseline 2a. The height in the triangle will be 1/a when the triangle area equals 1. The standard uncertainty is given by

$$u(x) = \frac{a}{\sqrt{6}} \qquad (1)$$

and more than 95 % of the data will be within $\pm 2 \cdot u(x)$. The distance from –a to a (i.e. 2a) is called the range. When applied on the laboratory comparison results, the range equals the distance between the largest and smallest of the four differences between expected and found concentrations. As long as the bias can be assumed to be constant for the samples in the comparison of a specific component, it cannot have an effect on the distance corresponding to 2a. The bias may be dependent upon the concentrations, but can be considered approximate constant for the concentrations used here in the comparison of the main components in precipitation, since the differences between the concentrations are small.

L and T represent the laboratories' and the expected concentrations respectively, and D is the difference. The difference for the lowest concentration is

$$D_1 = L_1 - T_1 \qquad (2)$$

and the differences are D_1, D_2, D_3, D_4 in increasing order assuming 4 test samples.

The range is $D_4 - D_1$ and the standard uncertainty for the differences u(D) becomes

$$u(D) = \frac{(D_4 - D_1)}{(2 \cdot \sqrt{6})}. \qquad (3)$$

The average expected concentration T for the four samples is given by

$$T = \frac{(T_1 + T_2 + T_3 + T_4)}{4} \tag{4}$$

The relative standard uncertainty, RSD, for 4 samples is given by $\frac{u(D)}{T}$, or

$$RSD = \frac{2 \cdot (D_4 - D_1 \cdot 100)}{\sqrt{6} \cdot (T_1 + T_2 + T_3 + T_4)}\%, \tag{5}$$

and 95 per cent of the laboratory results in this comparison are expected to be within ±2 · RSD.

If the data quality objectives (DQO) likewise are looked upon as 95 percentiles, then 95 per cent of the laboratory analytical results should not be more than 10 or 15 per cent from the correct values (10 per cent for S and N containing components and 15 per cent for other components).

Correspondingly, the values 2·RSD should therefore be less than 10 or 15 per cent in order to comply with the DQO.

An estimation of bias in single measurements requires a long data series, and four samples as we normally have in laboratory comparison, are merely able to give an indication of the bias or a very coarse estimate.

Calculating the systematic error (RB%)

Coarse estimates may be performed in the cases where the four samples had similar concentrations and where all four laboratory results were either higher or lower than the expected concentrations. The median of the differences D_i, as defined above, was taken as a measure of the bias, B, in these cases.

$$B = \text{median}[D_i] \tag{6}$$

A relative bias, RB, was also calculated based upon the average expected concentration T, as defined in (4).

$$RB = \frac{4 \cdot \text{median}[D_i] \cdot 100}{(T_1 + T_2 + T_3 + T_4)}\% \tag{7}$$

Annex 4 gives the results from the first 19th laboratory intercomparison divided in systematic and random errors. The calculated errors (2RSD% and 2RB) have been further translated into a flag number as defined in Table 17.

Annex 7

Ion balance flags

The ion balance (IB) gives an indication of precipitation data quality since the concentrations of all negatively charged ions in a sample necessarily will have to equal the sum of the positively charged ions. When the concentrations of all major ions in a precipitation sample have been measured, a poor IB *may* therefore indicate a poor data quality, and the sample results are proposed flagged as described below.

This proposal aims at flagging data that are considered to have a quality less good than could be expected from EMEP's Data Quality Objectives (DQO). The flagged data are divided into two groups; data that are considered to have a quality sufficiently high to be useful for EMEP and therefore are considered valid and should be used, and secondly data that are considered invalid. The criteria are summarised in Figure A7.2.

A good IB is not a guarantee for a high data quality. It is important to bear in mind that even though a general good IB indicates adequate sample handling and a high analytical chemical skill in the laboratory, other factors may reduce the data applicability for EMEP and the overall data quality; e.g. local sources or sampling problems. Even a sample contamination will not necessarily be detected through an ion balance calculation, i.e. when the contamination takes place before the analyses have been started.

The flags described below are suggested linked to each result from a specific precipitation sample. Other information about the sample results may, however, override the IB flagging, and validate some of the results.

Random errors have been used below as a basis for the criteria. Systematic errors are considered either to be insignificant or already corrected for.

Definitions

C_i is the concentration of ion type *i* in a specific sample, expressed in μe/L. No index has been used for sample number below. IS is the sum of all ion concentrations, and ID is the difference between the sum of the cation concentrations and the sum of the anion concentrations. Both IS and ID are expressed in μe/L. ID would in ideal cases be zero. The ion balance, IB, expresses this difference ID in per cent of the sum of all concentrations IS.

$$IS = \sum_{\text{cations}} C_i + \sum_{\text{anions}} C_i \qquad (1)$$

$$ID = \sum_{\text{cations}} C_i - \sum_{\text{anions}} C_i \qquad (2)$$

$$IB = (ID/IS) \cdot 10^2 \qquad (3)$$

All measurements have in reality some errors attached them, both systematic and random, and the ion difference ID and the balance IB will never be exactly zero. S_{ci} is defined as the standard uncertainty in the concentration of ion type *i* for a large number of samples or analyses at concentration C_i and is expressed in μe/L.

S_{IB} is the corresponding standard uncertainty in IB that can be calculated from the uncertainties S_{ci}. S_{IB}'s unit is as IB's per cent, and is given by

$$S_{IB}^2 = (1/IS^2)\ \{\sum_{\text{anions}}(IB + 100)^2\ S_{ci}^2 + \sum_{\text{cations}}(IB - 100)^2\ S_{ci}^2\} \qquad (4)$$

The standard uncertainty in the concentrations, S_{ci}, normally increases with the concentrations themselves. S_{IB} will depend on the composition and concentrations in the sample and increases as IS decreases, i.e. S_{IB} will be high when concentrations are low.

Since it is assumed that all ions have been analysed and all systematic errors removed, IB equals zero and equation (4) is reduced to

$$S_{IB} = (\ (\sum_{\text{all ions}} S_{ci}^2)^{1/2}/IS\ ) \cdot 10^2 \qquad (5)$$

Normal distributions have been assumed below, and S_{ci} may be estimated from repeated analysis of the sample.

Ion balance in data complying with the DQO

Instead of estimating S_{ci} from analyses, S_{IB} can be estimated from the DQO if S_{ci} can be expressed by the DQO. The DQO, which give the maximum errors in the analytical chemical work, will therefore now be considered as 95 per cent confidence limits for each chemical specie rather than strict upper limits. The DQO for a specific ion *i* will in this case span an interval of concentrations equal to ± 1.96 S_{ci}, assuming normal distribution. This assumption obviously relaxes the requirements to analytical accuracy somewhat since 5 per cent of the values will be outside the DQO.

The requirements given in the DQO (EMEP/CCC-Report 1/95) are that a concentration of component *i*, C_i , should be within $C_i \pm a \cdot C_i$ where a is either 0.10 or 0.15 (except for the very lowest concentrations).

When combining this with the assumptions in the preceding paragraph,

$$a \cdot C_i = 1.96 \cdot S_{ci}\ ,\ \text{or} \qquad (6)$$

$$S_{ci} = (a/1.96) \cdot C_i \qquad (7)$$

where a=0.10 for SO_4^{2-} and NO_3^-, and a=0.15 for all other ions.

Equations (7) and (5) can be used to estimate the expected uncertainty in IB, i.e. the limits for IB for measurements that comply with the DQO, given the assumptions above.

Calculations of ion balance in data complying with the DQO

Estimations of S_{IB} have been carried out for a series of different concentrations and compositions from the DQO. The calculations demonstrate that S_{IB} depends on the composition of the sample as well as on the concentrations, and that S_{IB} obtains its highest values for two-component samples e.g. of ammonium sulphate with other components at the detection limit. The lowest S_{IB} occurs in samples with approximately equal concentrations of all ions (i.e. for EMEP, concentrations of sulphate, nitrate and chloride all being equal and twice the concentrations of ammonium, hydrogen ions, sodium, magnesium calcium, and potassium). Figure A7.1 presents the approximate 95 % confidence limits (i.e. $\pm 2\ S_{IB}$), which can be expected from the DQO for two different sample types.

Assuming negligible systematic errors, the 95% confidence interval ($\approx 2 \cdot S_{IB}$) is expected to correspond to 7.1 to 10.8 per cent for a sum of concentrations (IS) at 100 µe/L (Figure A7.1) for the two compositions above. At IS equal to 1000 µe/L, the confidence interval correspond to ±4.6 to ±9.0 per cent. For IS less than 100 µe/L, S_{IB}, increases strongly.

Ion balance in samples with pH larger than 5.5

It is well known that samples having pH values above 5.5–6.0 often have an apparent deficit of anions (e.g. Schaug et al., 1997). This seems to differ from one measurement site to the next and is not yet well understood. Obviously this could be explained by components with weak acidic functional groups that are not analysed, e.g. such as organic substances. The estimations above can therefore often not easily be applied to precipitation samples with pH above 5.5. Separate criteria for samples with and without pH > 5.5 have therefore been proposed below.

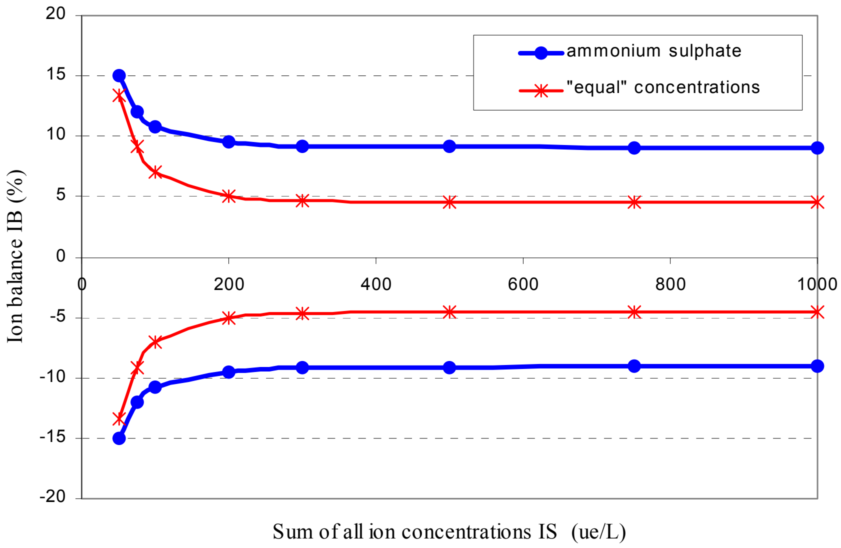


Figure A7.1: 95-confidence interval for the ion balance for data complying with the DQO. Upper and lower graphs for a solution of ammonium sulphate with other components at the detection limit. The two other graphs are based on a solution with "equal" concentrations as defined above. It is assumed that all components have been measured and that any significant bias has been removed.

Criteria for flagging ion balances in precipitation samples with pH ≤ 5.5

The estimated standard uncertainties S_{IB} and confidence intervals making use of the two compositions in Figure A7.1 have been used to set quality criteria for precipitation samples, a distinction was, however, made between samples with an ion sum IS higher and lower than 100 µe/L.

IS ≥ 100 µe/l
Samples with an ion balance within ± 10% can be considered to contain valid data in accordance with the DQO. *Valid, non-flagged precipitation data should therefore have an ion balance within ± 10%.*

Correspondingly its suggested that samples within an ion balance twice the limits in Figure A7.1 should be considered valid, but should be flagged to indicate that the quality is expected to be lower than targeted. *Valid but flagged data should have an ion balance between –20 to –10% or +10 to +20%.*

Results from samples outside 20% can be considered invalid. 20% corresponds approximately to the confidence limits for data within 2 DQO.
IS < 100 µe/L
When the sum of all ion concentrations is less than 100 µe/L, the criteria have been based on the ion difference ID (in µe/L) rather than IB due to the strong increase in IB with decreasing IS. When IS is exactly 100 µe/L, the IB limits 10 and 20% correspond exactly to ID equal to 10 and 20 µe/L, as seen from (3).

For IS < 100 µe/L these limits at 10 and 20 µe/L are suggested kept unchanged, i.e.a. *sample with an ion difference within ±10 µe/L can be considered valid, and within ±20 µe/L as valid, but is to be flagged.*

Samples with ion differences outside ±20 µe/L are considered to contain invalid data.

Criteria for flagging ion balances in precipitation samples with pH > 5.5

As mentioned above there is often an apparent anion deficit that is not well understood, and the size of the deficit is seen different from one site to the next. Relaxed criteria should therefore be applied at present. The criteria have been based on the discussion above as well as on inspection of today's ion balances. They should take care of the ion balance differences EMEP have, and take care of major errors without excluding too much data.

IS ≥ 100 µe/L
Since there is an apparent deficit of anions ("too much cations"), the criterion for valid non-flagged data has been made less strict when this occurs. *It is suggested to set an upper limit at IB +20% for valid non-flagged data.* The corresponding limit at lower pH values (above) was 10%. *The criteria for valid non-flagged data is suggested to be kept at IB ≥ -10% as for pH < 5.5 on the "negative IB side".*

When the ion balance is larger than +20%, the data still have been suggested valid, but should be flagged. This means that data will not be proposed invalidated due to a high ion balance alone.

On the "negative IB side" the criterion have been proposed kept unchanged, i.e. if -20% ≤ IB ≤ -10 % data can be considered valid, but will be flagged.

If IB < -20% the data are considered invalid.

IS < 100 µe/L
For low concentration samples with IS < 100 µe/L the criteria can be set similar to samples with IS ≥ 100 µe/L, but replacing the ion balance IB with the difference ID.

The criteria are summarised in Figure A7.2.

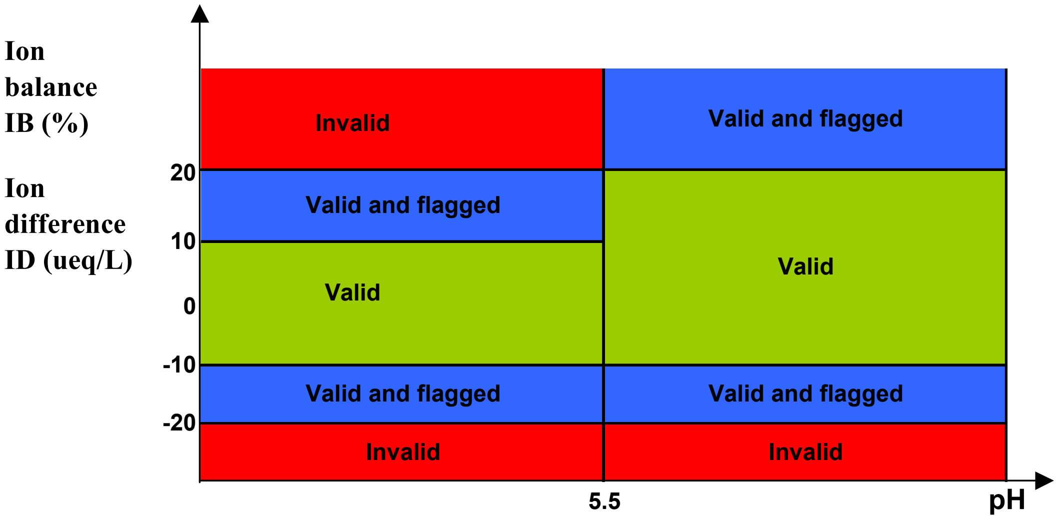


Figure A7.2: Criteria when the sum of ions IS >= 100 ueq/L is based on the ion balance in per cent. Criteria when the sum of ions IS < 100 ueq/L is based on the difference between cation and anion concentrations in ueq/L.

References

Schaug, J., Semb, A., Hjellbrekke, A.-G., Hanssen, J.E. and Pedersen, A. (1997) Data quality and quality assurance report. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 8/97).