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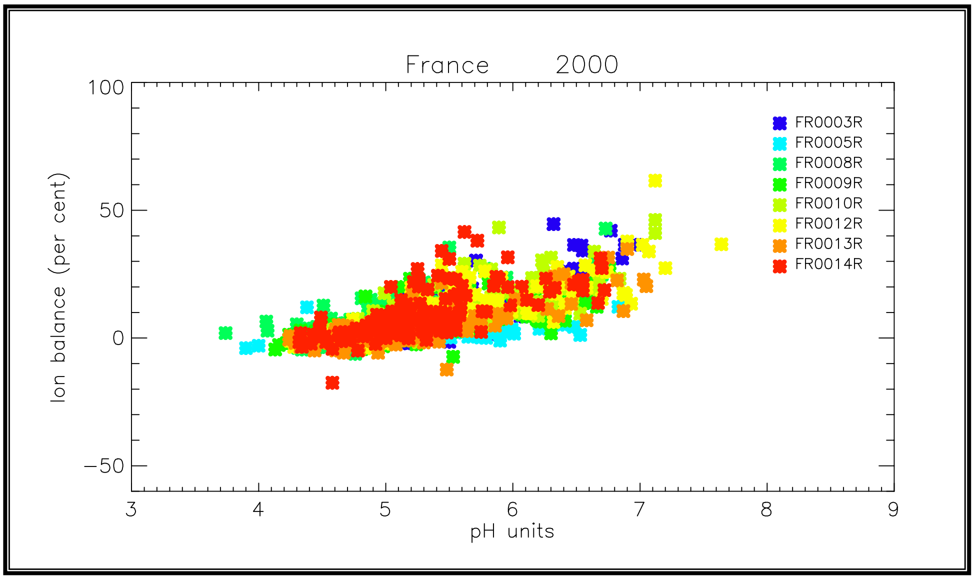
EMEP Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe

Data quality 2000, quality assurance, and field comparisons

**Wenche Aas, Anne-Gunn Hjellbrekke, Stein Manø,
Jan Schaug, Sverre Solberg and Hilde Th. Uggerud**



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Summary

This report is mainly concerned with the quality of the 2000 measurement data and new results from field and laboratory comparisons. Reports in this series have in the past focused mostly on components from the acid deposition part of EMEP's measurement programme, but the aim is to include all QA/QC activities for all the parameters in EMEP's measurements program.

The precipitation data quality is discussed on the basis of data completeness, ion balances, and performance in laboratory comparisons. The data quality objectives are given in Annex 1. However, the classification of data into four different quality groups as performed the last three years is not done. The reason is that CCC is working on criteria to flag both old and future EMEP data following objective measures. This work will be completed in the near future and the new flags will be used in the next annual report.

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

Field comparison at Zarra (ES12) in Spain measuring the main air components reveals problems with the SO_2 and NO_2 measurements; the sulphate and sum of nitrate measurements are however satisfactory. The field comparison of weekly wet-only measurements with daily bulk measurements in Norway is completed and presented here. In addition, in Diabla Gora (PL05) there was a parallel sampling of bulk and wet only due to change in sampling collectors. Both these comparisons show good correlation between the different samplers. But as expected dry deposition influence the bulk measurements so that the concentrations are generally higher than for wet-only measurements. This is more pronounced in Diabla Gora than at the Birkenes site.

In 2000 NILU and UBA carried out a carbonyl comparison at Waldhof (DE02). There is an overall good agreement between the two laboratories' data although UBA's values are systematically higher for formaldehyde and acetaldehyde. Furthermore, the results indicate that the agreement between the time series improved during the year. As UBA started their carbonyl analyses at the end of 1999, the data from 2000 should be regarded as preliminary. In the beginning of December 2001 CCC visited the Waldhof site and the UBA laboratory in Berlin.

The main conclusion is that the Waldhof site and the UBA laboratory perform carbonyl measurements of comparable quality as CCC.

Laboratory comparison of the main components in precipitation is carried out as usual. 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 now. The results are generally satisfactory with a few exceptions. There have also been two intercomparisons for POPs, one synthetic sample and one natural. In August 2000 ampoules containing solutions to be analysed in round 1 of the first EMEP POP laboratory comparison were shipped to 27 laboratories that had expressed their interest in participating in the exercise. The last results from round 1 were received in May 2001.

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 2000, 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 data of year 2000.

The three last years, the data of the main components in air and precipitation was classified into four different quality groups, A B C D, using information from laboratory and field comparisons as well as ion balance plots and data completeness. In the assessment work going on in EMEP it is also a need to quantify the uncertainty of the historical data. In that respect CCC is working on objective criteria to flag data with uncertain quality, and this work will finish this autumn. For the 2000 data there will therefore not be any classification using either the old or new approach.

Traditionally this report has focused on the acidifying and eutrophying components, but the aim is include all the information we have on data quality for all the components in the EMEP measurement program. Some of the information found in this report is therefore also found in the separate technical reports for the various compounds.

Parts of the information given here is collected from the participating laboratories, this being data on detection limits and precision. EMEP Laboratory intercomparison and results from field comparisons with reference instrumentation provide important information of the data quality. Calculations of ion balances in precipitation samples are important supplements to the organised comparisons. In addition are audit activities organized by CCC when needed.

The two last years we have included information from the countries regarding ozone calibration, maintenance of instruments and site surrounding to document the data quality of the ozone measurements. This information will be available at the EMEP homepage with a direct link from each monitoring station. New and updated information of the routines should be sent to CCC, and the forms can be downloaded from internet, http://www.nilu.no/projects/ccc/qa/ozone_questionnaire.doc.

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 2000 is given in Table 1. It is now an opening for weekly precipitation sampling even though daily sampling is still preferable. There are a few sites with weekly precipitation sampling (CH04, CZ01, EE09, EE11, SE05, SE11) or two samples a month (DK05, DK08, DK22). All participating countries, except Iceland and Lithuania had complete measurement programmes for the main components in precipitation in 2000. The data completeness should be at least 90 per cent (Annex 1) and as seen from Table 2, most participants met this requirement for the precipitation components.

For the air component the completeness 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. Therefore it is highly desirable that more sites start measuring all nitrogen components in the programme.

Table 1: EMEP's measurement programme for 2000.

	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	8 hours	twice weekly
	Hg	24 hours	weekly
Particles	SO_4^{2-}, Particulate matter (PM)	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)	to be decided	to be decided
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)	to be decided	to be decided

Measurements of PM_{10}, VOC, heavy metals and POPs are made at a small number of sites only.

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. This is 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 concentration; however, only sites in Hungary 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 was 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.

It is few countries reporting data on PM_{10} for 2000, only CH, ES and DE. However, an increasing number of sites have started PM_{10} measurements so this situation will probably change in the near future. It is also very few countries measuring Na, Mg, Ca, Cl and K in particles. It is however recommended to include these ions at least at the sites measuring PM_{10}. The number of sites with VOC measurements is also very small although the number of sites with carbonyls increased in 2000.

Table 2: Completeness for precipitation components, 2000.

Code	mm	mm off	SO_4	NH_4	NO_3	Na	Mg	Cl	Ca	pH	H^+	K	cond
AT02	100.0	-	100.0	100.0	100.0	100.0	100.0	99.3	100.0	100.0	-	100.0	100.0
AT04	100.0	-	92.4	90.8	92.3	88.3	87.8	92.4	92.4	100.0	-	73.1	100.0
AT05	100.0	-	99.9	98.8	99.9	98.2	99.7	93.9	99.9	100.0	-	90.8	100.0
CH02	99.7	-	97.9	97.9	97.9	97.9	97.9	97.9	97.9	99.6	-	97.9	99.6
CH04	85.2	-	99.8	99.8	99.8	99.8	99.8	99.8	99.8	100.0	-	99.8	100.0
CH05	99.7	-	98.9	98.9	98.9	98.9	98.9	98.9	98.9	99.7	-	98.9	99.7
CZ01	95.9	-	93.7	93.7	93.7	88.8	93.7	93.7	93.7	97.0	-	93.7	97.0
CZ03	100.0	-	98.1	98.7	97.9	96.2	94.3	90.0	93.4	98.8	-	95.8	98.2
DE02	100.0	-	97.7	96.6	97.7	97.5	97.5	97.7	97.6	97.5	-	97.5	97.5
DE04	100.0	-	99.5	99.4	99.5	99.6	99.6	99.5	99.6	99.0	-	99.6	99.3
DK05	99.7	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0
DK08	99.7	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0
DK22	83.1	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0
EE09	99.5	-	97.4	96.7	92.6	96.6	96.6	97.4	90.4	97.4	-	96.6	95.4
EE11	99.5	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0
ES01	46.7	-	98.2	97.9	98.2	97.1	97.1	98.2	97.1	99.1	-	97.1	99.0
ES03	44.3	-	99.7	98.8	99.7	77.6	77.6	99.7	77.6	100.0	-	77.6	100.0
ES04	100.0	-	91.9	90.4	91.9	88.1	88.1	92.1	88.1	94.5	-	88.1	94.1
ES05	40.7	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0
ES07	100.0	-	97.4	97.0	97.4	96.2	96.2	97.4	96.2	97.6	-	96.2	97.6
ES08	100.0	-	99.1	98.8	99.1	98.2	98.2	99.1	98.2	99.1	-	98.2	99.1
ES09	100.0	-	96.2	94.3	96.2	92.8	92.8	95.6	92.8	97.3	-	93.0	97.0
ES10	100.0	-	86.1	86.0	86.1	84.4	84.4	86.1	84.4	86.2	-	84.4	86.2
ES11	100.0	-	92.8	92.7	92.8	92.3	92.3	92.8	92.3	93.3	-	92.3	93.3
ES12	100.0	-	97.3	97.1	97.3	95.9	95.9	97.3	95.9	98.3	-	95.9	98.3
ES13	100.0	-	98.8	97.3	98.8	94.6	94.6	98.8	94.6	99.1	-	94.6	99.1
ES14	100.0	-	95.1	93.5	95.1	92.7	92.7	95.1	92.7	95.6	-	92.7	95.6
ES15	99.5	-	95.3	94.7	95.3	87.2	87.2	95.3	87.2	95.3	-	87.2	95.3
FI04	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0
FI09	100.0	100.0	93.6	93.6	93.6	93.6	93.6	93.6	93.6	94.0	-	93.6	94.0
FI17	100.0	100.0	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.8	-	99.5	99.8
FI22	100.0	100.0	99.3	99.3	99.3	99.3	99.3	99.3	99.3	99.8	-	99.3	99.8

Table 2, cont.

Code	mm	mm off	SO_4	NH_4	NO_3	Na	Mg	Cl	Ca	pH	H^+	K	cond
FR03	100.0	-	72.7	73.5	72.7	72.4	72.7	72.2	67.3	72.0	-	72.6	73.9
FR05	100.0	-	88.0	88.3	87.6	87.8	87.8	87.8	88.0	89.4	-	87.8	89.6
FR08	100.0	-	91.8	91.8	91.6	91.3	91.7	91.5	91.3	90.3	-	91.2	92.2
FR09	100.0	-	89.6	90.4	89.2	89.8	89.8	89.8	88.0	90.3	-	89.6	92.1
FR10	100.0	-	96.7	96.9	96.7	96.7	96.7	96.7	95.6	97.5	-	95.3	98.6
FR12	100.0	-	86.6	86.8	86.6	86.6	86.6	86.6	85.8	88.4	-	86.4	88.7
FR13	100.0	-	97.1	97.0	96.7	96.9	97.1	96.9	96.5	97.1	-	97.0	97.6
FR14	100.0	-	95.6	95.9	95.6	95.3	95.3	95.3	95.4	96.4	-	95.6	96.4
GB02	100.0	-	98.3	98.3	98.3	95.4	98.3	95.4	98.3	-	-	98.3	98.2
HU02	100.0	-	100.0	98.6	100.0	99.9	99.9	100.0	99.9	93.2	-	99.9	93.2
IE02	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.6	-	100.0	99.6
IE03	100.0	-	100.0	100.0	100.0	99.6	100.0	99.6	100.0	99.5	-	100.0	99.5
IE04	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0
IS02	100.0	-	100.0	-	-	100.0	-	-	-	100.0	-	-	-
IT01	100.0	-	100.0	96.1	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0
IT04	100.0	-	99.1	99.1	99.1	99.1	99.1	99.1	99.1	99.0	-	99.1	99.1
LT15	100.0	-	99.1	99.1	99.1	99.1	-	99.1	99.1	99.1	-	99.1	99.1
LV10	100.0	-	98.8	99.1	98.8	98.8	98.8	98.0	98.8	99.5	-	98.0	99.5
LV16	100.0	-	96.0	96.7	96.0	95.8	95.2	92.8	95.8	98.8	-	96.0	98.8
NL09	100.0	-	90.8	89.3	90.8	88.1	88.1	90.8	88.1	91.4	91.3	88.1	5.3
NO01	100.0	-	99.3	99.0	99.3	99.3	99.3	99.3	99.3	99.3	-	99.0	99.6
NO08	100.0	-	99.4	99.1	99.4	99.3	99.4	99.3	98.4	98.5	-	99.1	99.7
NO15	100.0	-	97.2	92.7	96.7	97.3	97.3	97.2	94.8	94.4	-	92.7	99.2
NO39	100.0	-	98.9	98.4	98.9	98.9	98.9	98.9	98.5	98.4	-	98.4	100.0
NO41	100.0	-	98.9	96.5	98.9	98.9	98.5	98.9	98.5	96.6	-	96.5	99.0
NO55	100.0	-	89.6	86.2	89.6	89.2	88.8	89.2	87.9	91.4	-	84.8	96.4
NO99	100.0	-	98.6	97.6	98.6	98.6	98.6	98.6	98.4	98.4	-	98.6	99.5
PL02	100.0	-	99.2	99.2	99.2	98.9	98.9	99.2	98.9	99.3	-	98.9	99.3
PL03	100.0	-	98.3	98.3	98.3	98.2	98.2	98.3	98.2	98.3	-	98.2	98.3
PL04	100.0	-	98.2	98.2	98.2	98.2	98.2	98.2	98.2	98.2	-	98.2	98.2
PL05	100.0	99.7	99.5	99.6	99.7	97.7	97.8	98.0	97.8	99.8	-	97.1	90.5
PT01	-	100.0	81.8	81.8	81.8	81.8	81.8	81.8	81.8	81.8	-	81.8	81.8
PT03	-	100.0	91.6	91.6	91.6	91.6	91.6	91.6	91.6	91.4	-	91.6	91.6
PT04	-	100.0	89.2	88.8	88.8	88.8	88.8	88.8	88.8	88.8	-	88.8	88.8
RU01	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0
RU13	100.0	-	100.0	100.0	100.0	100.0	98.1	100.0	98.1	100.0	-	100.0	100.0
RU16	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	99.9	100.0	-	100.0	100.0
RU18	100.0	-	100.0	100.0	100.0	100.0	94.0	100.0	94.0	99.8	-	100.0	99.7
SE02	100.0	-	99.9	99.5	99.9	98.6	99.8	99.9	99.8	100.0	-	99.8	98.2
SE05	100.0	-	100.0	100.0	100.0	99.9	99.9	100.0	99.9	100.0	-	99.9	99.8
SE11	100.0	-	97.3	97.3	97.3	97.3	97.3	97.3	97.3	97.3	-	97.3	97.3
SE12	33.1	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	97.9
SK02	100.0	-	96.1	96.1	96.1	96.1	96.1	95.9	95.9	94.5	-	96.1	96.1
SK04	100.0	-	98.7	98.7	98.7	98.7	98.7	98.7	98.7	97.4	-	98.7	98.7
SK05	100.0	-	97.2	97.2	97.2	97.2	97.2	97.2	97.2	96.6	-	97.2	97.2
SK06	100.0	-	95.4	95.4	95.4	95.4	95.4	95.4	95.4	95.4	-	95.4	95.4
TR01	100.0	-	98.6	98.6	98.6	99.0	99.0	98.6	94.5	100.0	-	99.0	100.0
YU05	100.0	-	99.8	98.5	97.8	90.4	90.4	96.3	90.1	100.0	-	90.4	100.0
YU08	100.0	-	100.0	99.7	99.4	99.6	99.6	96.9	99.6	100.0	-	99.6	100.0

Table 3: Completeness for air components, 2000.

Code	SO_2	SO_4	O_3	NO_2	HNO_3	NO_3	$sumNO_3$	NH_3	NH_4	$sumNH_3$	H^+	PM_{10}	SPM	Na	Mg	Cl	Ca	K
AT02	94.0	87.4	95.6	99.5	-	-	87.4	-	-	87.2	-	-	-	-	-	-	-	-
AT04	99.5	-	95.2	97.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT05	98.9	-	94.9	98.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT30	-	-	95.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT32	-	-	98.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT33	-	-	91.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT34	-	-	96.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT37	-	-	97.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT38	-	-	86.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT40	-	-	95.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT41	-	-	99.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT42	-	-	93.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT43	-	-	95.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT44	-	-	98.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT45	-	-	94.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT46	-	-	96.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AT47	-	-	95.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BE01	-	-	92.3	97.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BE32	-	-	94.7	98.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BE35	-	-	95.2	95.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH01	98.4	99.5	-	82.8	-	-	-	-	-	-	-	97.8	-	-	-	-	-	-
CH02	93.7	98.9	92.7	94.8	-	-	-	-	-	-	-	97.3	-	-	-	-	-	-
CH03	-	-	94.7	97.3	-	-	-	-	-	-	-	99.5	-	-	-	-	-	-
CH04	97.0	-	92.7	94.8	-	-	-	-	-	-	-	100.0	-	-	-	-	-	-
CH05	97.0	99.2	93.5	96.2	-	-	99.5	-	-	99.5	-	99.5	-	-	-	-	-	-
CZ01	98.4	-	98.9	92.1	99.5	99.5	99.5	99.5	99.5	99.5	-	-	-	-	-	-	-	-
CZ03	98.9	-	99.9	98.1	98.9	100.0	98.9	100.0	100.0	100.0	-	-	-	-	-	-	-	-
DE01	0.0	-	97.8	99.2	-	-	-	-	-	-	-	92.6	-	-	-	-	-	-
DE02	97.8	50.0	92.1	99.2	-	-	-	-	-	-	-	98.9	-	-	-	-	-	-
DE03	82.5	-	96.4	98.4	-	-	-	-	-	-	-	91.5	-	-	-	-	-	-
DE04	99.7	46.4	74.0	100.0	-	-	-	-	-	-	-	98.9	-	-	-	-	-	-
DE05	100.0	-	90.6	100.0	-	-	-	-	-	-	-	100.0	-	-	-	-	-	-
DE07	100.0	-	94.0	99.7	-	-	-	-	-	-	-	95.4	-	-	-	-	-	-
DE08	99.2	-	95.9	99.5	-	-	-	-	-	-	-	99.5	-	-	-	-	-	-
DE09	100.0	-	98.6	100.0	-	-	-	-	-	-	-	93.2	-	-	-	-	-	-
DE12	-	-	95.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DE17	-	-	86.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DE26	-	-	95.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DE35	-	-	91.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DE39	-	-	92.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DK03	89.6	89.3	-	-	-	-	89.3	-	-	89.6	-	-	-	89.6	-	-	-	-
DK05	98.4	98.4	-	-	-	-	98.1	-	-	98.1	-	-	-	98.1	-	-	-	-
DK08	97.0	97.0	-	95.6	-	-	97.0	-	-	97.0	-	-	-	97.0	-	-	-	-
DK31	-	-	96.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DK32	-	-	97.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
EE09	99.2	99.5	99.5	99.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-
EE11	97.5	-	94.8	7.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ES01	45.6	45.1	42.5	45.1	-	-	46.4	-	45.1	46.4	45.1	44.8	-	-	-	-	-	-
ES03	43.7	42.4	41.1	43.7	-	-	44.3	-	42.4	43.7	42.4	42.4	-	-	-	-	-	-
ES04	98.6	93.4	91.8	98.4	-	-	96.2	-	93.4	96.2	93.4	91.3	-	-	-	-	-	-
ES05	43.2	39.6	40.8	43.2	-	-	40.2	-	39.6	39.6	39.6	39.3	-	-	-	-	-	-
ES07	99.5	97.3	93.2	99.5	-	-	95.4	-	97.3	94.0	97.0	94.3	-	-	-	-	-	-
ES08	100.0	98.1	94.3	99.7	-	-	100.0	-	98.1	99.7	98.1	94.3	-	-	-	-	-	-
ES09	97.5	95.6	88.6	97.3	-	-	99.2	-	95.6	98.9	95.6	91.0	-	-	-	-	-	-
ES10	99.5	95.6	93.5	99.5	-	-	96.4	-	95.6	93.4	95.6	91.8	-	-	-	-	-	-
ES11	98.1	95.9	92.7	97.8	-	-	98.9	-	95.9	95.4	95.9	91.5	-	-	-	-	-	-
ES12	100.0	98.4	94.9	99.7	-	-	99.2	-	98.4	99.2	98.4	96.7	-	-	-	-	-	-
ES13	41.5	42.4	39.4	41.5	-	-	43.7	-	42.4	40.7	42.4	41.3	-	-	-	-	-	-
ES14	16.7	23.2	15.3	16.7	-	-	24.0	-	23.2	24.9	23.2	23.2	-	-	-	-	-	-
ES15	15.8	20.2	14.5	15.6	-	-	22.1	-	20.2	21.0	20.2	19.9	-	-	-	-	-	-
FI09	100.0	100.0	99.0	-	-	-	100.0	-	-	99.7	-	-	-	-	-	-	-	-
FI17	99.7	100.0	98.9	-	-	-	99.7	-	-	100.0	-	-	-	-	-	-	-	-
FI22	99.5	99.5	99.5	-	-	-	99.5	-	-	99.2	-	-	-	-	-	-	-	-
FI37	100.0	98.1	99.4	-	-	-	98.1	-	-	99.7	-	-	-	-	-	-	-	-
FR03	89.1	91.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FR05	89.1	89.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FR08	97.0	97.5	98.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FR09	95.9	94.0	99.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FR10	79.8	80.6	93.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FR12	94.8	95.4	87.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FR13	99.2	99.5	97.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FR14	98.9	99.5	94.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB02	91.8	94.3	98.8	-	-	-	92.1	-	-	91.8	-	-	-	-	-	-	-	-
GB04	94.8	92.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB06	95.9	98.4	90.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB07	90.4	94.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 3, cont.

Code	SO_2	SO_4	O_3	NO_2	HNO_3	NO_3	sumNO_3	NH_3	NH_4	sumNH_3	H^+	PM_{10}	SPM	Na	Mg	Cl	Ca	K
GB13	93.4	92.6	81.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB14	96.2	97.8	94.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB15	97.8	100.0	96.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB16	95.1	98.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB31	-	-	90.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB32	-	-	99.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB33	-	-	92.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB34	-	-	75.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB36	-	-	97.6	85.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB37	-	-	95.4	94.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB38	-	-	90.3	90.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB39	-	-	91.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB43	-	-	72.3	73.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB44	-	-	92.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GB45	-	-	76.2	84.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GR01	51.4	27.3	46.2	60.1	-	27.3	-	-	-	-	-	-	-	-	-	-	-	-
GR03	-	-	60.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HU02	94.8	95.1	97.6	98.4	95.1	95.1	95.1	95.1	95.1	95.1	-	-	-	-	-	-	-	-
IE02	-	93.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IE03	-	86.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IE04	-	95.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IE31	-	-	97.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IS02	-	94.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IT01	94.3	94.3	86.5	85.5	94.3	94.3	-	94.3	94.3	-	-	-	-	-	-	-	-	-
IT04	96.4	89.1	97.2	98.6	-	89.1	-	-	89.1	-	89.1	-	-	-	-	-	-	-
LT15	98.4	98.4	84.8	98.9	-	-	97.5	-	-	98.1	-	-	-	-	-	-	-	-
LV10	100.0	100.0	93.6	100.0	-	100.0	100.0	-	100.0	100.0	-	-	-	-	-	-	-	-
LV16	94.5	94.5	-	96.7	-	94.3	94.3	-	96.2	96.4	-	-	-	-	-	-	-	-
MT01	-	-	99.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NL09	96.4	86.3	98.1	98.1	-	86.3	-	-	86.3	-	-	-	-	-	-	-	-	-
NL10	97.8	91.3	94.0	98.1	-	91.3	-	74.6	91.3	-	-	-	-	-	-	-	-	-
NO01	100.0	100.0	99.7	100.0	-	-	100.0	-	-	100.0	-	-	-	100.0	100.0	100.0	100.0	100.0
NO08	94.8	95.4	-	99.2	-	-	94.8	-	-	95.1	-	-	-	95.1	95.1	95.4	95.1	94.8
NO15	100.0	99.7	99.7	99.7	-	-	99.7	-	-	99.5	-	-	-	99.7	99.7	99.7	99.7	99.7
NO39	98.6	97.0	99.9	100.0	-	-	96.4	-	-	98.4	-	-	-	98.6	98.6	97.8	98.6	98.6
NO41	94.8	95.1	99.4	99.7	-	-	94.3	-	-	94.8	-	-	-	94.8	94.8	94.5	94.8	94.8
NO42	97.5	96.4	86.6	-	-	-	94.3	-	-	95.1	-	-	-	96.2	96.2	96.4	96.2	96.2
NO43	-	-	98.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NO45	-	-	92.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NO48	-	-	99.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NO52	-	-	95.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NO55	99.7	99.7	99.3	99.5	-	-	99.7	-	-	99.5	-	-	-	99.7	99.7	99.7	99.7	99.7
NO56	-	-	98.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PL02	98.4	98.4	88.2	96.4	-	97.5	97.8	-	98.4	98.6	-	-	-	-	-	-	-	-
PL03	100.0	100.0	99.9	100.0	-	100.0	100.0	-	100.0	100.0	-	-	-	-	-	-	-	-
PL04	98.9	100.0	98.1	99.7	-	100.0	99.7	-	100.0	99.7	-	-	-	-	-	-	-	-
PL05	96.2	96.7	97.7	93.4	-	-	96.7	-	-	97.3	-	-	-	-	-	-	-	-
PT04	-	-	67.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
RU01	80.3	80.3	-	-	-	80.3	-	-	80.3	-	-	-	-	-	-	-	-	-
RU13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
RU16	94.5	94.3	64.4	-	-	94.3	-	-	-	-	-	-	-	-	-	-	-	-
RU18	89.1	89.1	80.1	-	-	88.8	-	-	89.1	-	-	-	-	-	-	-	-	-
SE02	98.4	98.6	99.8	98.1	-	-	98.4	-	-	98.6	-	-	98.9	-	-	-	-	-
SE05	98.1	98.1	-	98.1	-	-	97.3	-	-	98.4	-	-	98.6	-	-	-	-	-
SE08	100.0	-	-	98.9	-	-	-	-	-	-	-	-	98.1	-	-	-	-	-
SE11	98.4	98.6	98.7	98.1	-	-	98.4	-	-	92.3	-	-	98.1	-	-	-	-	-
SE12	24.6	24.9	84.0	24.6	-	-	24.6	-	-	24.6	-	-	-	-	-	-	-	-
SE13	-	-	99.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SE32	-	-	99.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SE35	-	-	97.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SI08	99.7	99.7	90.3	-	-	-	99.7	-	-	99.5	-	-	-	-	-	-	-	-
SI31	-	-	91.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SI32	-	-	95.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SI33	-	-	91.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SK02	98.1	97.5	73.2	97.5	98.1	97.5	97.5	-	-	-	-	-	-	-	-	-	-	-
SK04	97.8	97.5	94.1	100.0	97.8	97.5	97.5	-	-	-	-	-	-	-	-	-	-	-
SK05	100.0	100.0	-	100.0	100.0	100.0	100.0	-	-	-	-	-	-	-	-	-	-	-
SK06	99.5	99.5	92.1	100.0	99.5	99.5	99.2	-	-	-	-	-	-	-	-	-	-	-
SK07	-	-	91.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
TR01	60.4	88.0	-	87.7	60.4	-	-	59.3	-	12.3	-	-	-	-	-	-	-	-
YU05	80.1	-	-	21.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-
YU08	96.2	-	-	29.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 4: Completeness for heavy metals in precipitation, 2000.

Code	mm	mm off	Cd	Pb	Cu	Zn	As	Cr	Ni	Hg	Fe	Co	V	Mn	Al
BE04	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	-	-	-	-
CZ01	97.3	-	91.0	91.8	-	-	-	-	81.3	-	-	-	-	-	-
CZ03	95.9	-	98.3	99.7	-	-	-	-	92.0	-	-	-	-	-	-
DE01	85.9	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0	-
DE04	99.7	-	99.5	99.5	98.4	99.5	99.5	-	99.5	-	99.5	99.5	99.5	99.5	-
DE09	85.9	-	99.8	99.8	99.8	99.8	99.8	99.8	96.2	99.8	99.8	99.8	99.8	99.8	-
DK08	99.8	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	-	-	-	-	-
DK20	91.6	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	-	-	-	-	-
DK31	83.4	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	-	-	-	-	-
EE09	100.0	-	100.0	100.0	100.0	59.3	100.0	-	-	-	-	-	-	-	-
EE11	100.0	-	80.7	80.7	80.7	80.7	80.7	-	-	-	-	-	-	-	-
FI08	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	-	100.0	100.0	-
FI09	100.0	-	99.8	99.8	99.8	99.8	99.8	99.8	99.8	-	-	-	-	99.8	-
FI17	100.0	-	100.0	100.0	100.0	100.0	100.0	-	100.0	-	100.0	-	100.0	100.0	-
FI22	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	-	100.0	100.0	-
FI53	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	-	100.0	100.0	-
FI92	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	-	100.0	100.0	-
FI93	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	-	100.0	100.0	-
FI96	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	-	100.0	100.0	-
FR90	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	-	-	-	-	-
GB14	99.9	-	100.0	96.5	96.5	100.0	100.0	96.5	96.5	-	-	-	-	-	-
GB90	100.0	-	96.9	100.0	96.9	100.0	96.9	93.8	96.9	-	-	-	-	-	-
GB91	92.3	-	100.0	100.0	96.8	97.8	100.0	100.0	93.6	-	-	-	-	-	-
IE01	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	-	100.0	100.0	100.0
IE02	100.0	-	82.8	82.8	82.8	82.8	82.8	82.8	82.8	82.8	-	-	82.8	82.8	82.8
IS02	99.5	-	99.9	99.9	99.9	99.9	99.9	99.9	99.9	-	99.9	-	99.9	99.9	99.9
IS90	99.3	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	-	100.0	100.0	100.0
LT15	99.9	-	100.0	100.0	100.0	100.0	-	-	-	-	-	-	-	-	-
LV10	83.1	-	100.0	100.0	100.0	100.0	-	-	-	-	-	-	-	-	-
LV16	83.1	-	100.0	100.0	100.0	100.0	-	-	-	-	-	-	-	-	-
NL09	81.7	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	-	-	-	-	-
NL91	97.0	-	94.7	94.7	94.7	94.7	94.7	94.7	94.7	99.1	-	-	-	-	-
NO01	100.0	-	99.9	99.9	-	99.9	-	-	-	-	-	-	-	-	-
NO39	100.0	-	98.4	98.4	-	98.4	-	-	-	-	-	-	-	-	-
NO41	100.0	-	99.7	99.7	-	99.7	-	-	-	-	-	-	-	-	-
NO47	100.0	-	99.7	99.7	99.7	99.7	99.7	99.7	99.7	-	-	99.7	-	-	-
NO55	100.0	-	99.0	99.0	-	99.0	-	-	-	-	-	-	-	-	-
NO56	100.0	-	98.2	98.2	-	100.0	-	-	-	-	-	-	-	-	-
NO92	100.0	-	100.0	99.9	100.0	100.0	99.7	99.9	100.0	-	99.8	100.0	99.8	99.8	-
NO93	100.0	-	99.8	99.8	91.9	91.9	91.9	91.9	91.9	-	91.9	99.8	99.8	99.8	-
NO94	100.0	-	99.9	99.9	99.9	99.9	99.9	99.9	99.9	-	99.9	99.9	99.9	99.9	-
NO95	100.0	-	99.9	100.0	99.8	99.9	99.9	99.8	99.9	-	100.0	100.0	100.0	100.0	-
NO99	100.0	-	99.9	99.9	99.9	99.9	99.9	99.9	99.9	-	-	99.9	99.9	-	-
PT01	-	100.0	81.8	81.8	81.8	81.8	-	-	81.8	-	-	-	-	81.8	-
PT03	-	100.0	91.6	91.6	91.6	91.6	-	-	91.6	-	-	-	-	91.6	-
PT04	-	100.0	88.8	88.8	88.8	88.8	-	-	88.8	-	-	-	-	88.8	-
PT10	-	98.7	98.2	98.2	98.2	98.2	-	-	98.2	-	-	-	-	98.2	-
SE02	96.7	-	-	-	-	-	-	-	-	100.0	-	-	-	-	-
SE05	99.2	-	94.4	100.0	94.4	82.8	100.0	100.0	100.0	100.0	-	100.0	100.0	82.8	-
SE11	96.7	-	-	-	-	-	-	-	-	100.0	-	-	-	-	-
SE12	40.7	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	-	100.0	100.0	100.0	-
SE51	99.7	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	-	100.0	100.0	100.0	-
SE97	100.0	-	100.0	100.0	-	100.0	100.0	100.0	100.0	-	-	-	-	-	-
SK02	100.0	-	100.0	100.0	-	100.0	-	-	-	-	78.8	-	-	100.0	100.0
SK04	100.0	-	100.0	100.0	-	79.7	-	-	-	-	59.4	-	-	100.0	100.0
SK05	100.0	-	100.0	100.0	-	100.0	-	-	-	-	60.0	-	-	100.0	100.0
SK06	100.0	-	74.9	100.0	-	94.6	-	-	-	-	68.4	-	-	100.0	100.0
SK07	99.7	-	85.5	100.0	-	93.4	-	-	-	-	69.3	-	-	100.0	100.0

Table 5: Completeness for heavy metals in air, 2000.

Code	Cd	Pb	Cu	Zn	As	Cr	Ni	Hg	reHg	Fe	Co	V	Mn	Al	Se
BE04	-	100.0	100.0	100.0	-	-	100.0	-	-	-	-	-	-	-	-
CZ01	15.8	15.8	-	-	-	-	-	-	-	-	-	-	-	-	-
CZ03	15.6	15.6	-	-	-	-	-	-	-	-	-	-	-	-	-
DE01	-	100.0	-	-	-	-	-	-	-	-	-	-	-	-	-
DE03	-	100.0	-	-	-	-	-	-	-	-	-	-	-	-	-
DE04	-	100.0	-	-	-	-	-	-	-	-	-	-	-	-	-
DE05	-	100.0	-	-	-	-	-	-	-	-	-	-	-	-	-
DE07	-	100.0	-	-	-	-	-	-	-	-	-	-	-	-	-
DE08	-	100.0	-	-	-	-	-	-	-	-	-	-	-	-	-
DE09	-	100.0	-	-	-	-	-	-	-	-	-	-	-	-	-
DK03	95.1	95.1	95.1	95.1	95.1	95.1	95.1	-	-	95.1	-	-	95.1	-	-
DK05	97.8	98.1	98.1	98.1	98.1	98.1	98.1	-	-	98.1	-	-	98.1	-	-
DK08	99.7	100.0	100.0	100.0	100.0	100.0	100.0	-	-	100.0	-	-	100.0	-	-
DK10	-	86.6	86.6	86.6	86.6	86.6	86.6	62.7	-	-	-	-	86.6	86.6	86.6
DK15	-	-	-	-	-	-	-	59.3	-	-	-	-	-	-	-
DK31	99.5	99.7	99.7	99.7	99.7	99.7	99.7	-	-	99.7	-	-	99.7	-	-
FI96	99.3	99.3	99.3	99.3	99.3	99.3	99.3	13.1	-	99.3	-	99.3	99.3	-	-
GB14	99.9	92.2	99.9	99.9	99.9	99.9	91.2	-	-	-	-	-	-	-	-
GB90	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	-	-	-	-	-	-	-
GB91	92.3	92.3	-	92.3	92.3	90.6	85.2	-	-	-	-	-	-	-	-
IE31	-	-	-	-	-	-	-	86.1	-	-	-	-	-	-	-
IS91	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	-	100.0	100.0	100.0	-
LT15	99.7	99.7	99.7	99.7	-	-	-	-	-	-	-	-	-	-	-
LV10	98.2	98.2	98.2	98.2	-	-	-	-	-	-	-	-	-	-	-
LV16	94.0	94.0	94.0	94.0	-	-	-	-	-	-	-	-	-	-	-
NL09	24.9	24.9	-	24.9	24.9	-	-	-	-	-	-	-	-	-	-
NO42	28.1	28.1	28.1	28.1	28.1	28.1	28.1	84.4	-	-	28.1	28.1	28.1	-	-
NO99	93.7	93.7	93.7	93.7	93.7	86.1	93.7	5.2	-	-	93.7	93.7	-	-	-
SE02	-	-	-	-	-	-	-	25.7	-	-	-	-	-	-	-
SK02	73.8	72.2	73.8	-	-	73.8	73.8	-	-	-	-	-	73.8	-	-
SK04	85.2	85.2	85.2	-	-	85.2	85.2	-	-	-	-	-	85.2	-	-
SK05	85.5	85.5	85.5	-	-	85.5	85.5	-	-	-	-	-	85.5	-	-
SK06	62.6	62.6	62.6	-	-	62.6	62.6	-	-	-	-	-	62.6	-	-
SK07	65.1	65.1	65.1	-	-	64.6	65.1	-	-	-	-	-	65.1	-	-

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 2000 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 the Czech Republic, France and Norway. In other countries e.g. in Denmark and the Netherlands the systematic anion deficit do not occur.

The reason for the poor ion balances at pH values above 5–6 is not totally apparent. 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 weak 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), Table 2.

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

Since many countries use methods that deviate from the recommended methods for measurements of air components, it is of particular interest to see if this leads to systematic differences in the reported concentrations. To quantify the accuracy of the EMEP measurements, 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). The results from Spain were not finalized in last year report and will be concluded here. Field comparisons in the Netherlands, Slovenia and Switzerland are uncompleted and will therefore be presented next year.

A co-located measurement with reference instrumentation is a very direct method for determining the actual quality of the routinely reported EMEP data. The comparisons are carried out at the EMEP site using a set of reference instruments, which correspond 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 also 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 of practical reasons.

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 absorbing agent, which is added to glass sinter frits contained in glass bulbs. The methods are described in more detail in the EMEP Manual for Sampling and Chemical Analysis (EMEP, 1996).

5.1.3 Comparison at Zarra (ES12)

The comparison in Zarra started in May 2000 and continued for one year. The analyses and evaluation is now finished, but the main part of the results was also presented in last year report. At this station there are both manual and automatic equipment. The manual methods are analysed at Instituto de Salud Carlos III in Madrid and these results are the official data reported to EMEP. The automatic procedures for NO_2 and SO_2 are taken care of by MCV, S.A. in Barcelona. For SO_2 the manual method is H_2O_2 absorbing solution analysed using the Thorin method and the automatic method is UV-fluorescence. NO_2 is determined manually using a trietanolamin absorbing solution analysed by spectrophotometry, and the automatic method is chemifluorescence. The particulate sulphate is determined using a high volume sampler analysed using IC, and the sum of nitrate is sampled using impregnated filters and analysed using IC.

The results are summarised in Table 6 and the measurements are illustrated in Figure 1 – Figure 4. For 2000, Spain has reported both their manual and monitor data from all the Spanish sites. To illustrate the difference between the two methods, all the 2000 data for Zarra is included in the figures from the field intercomparison.

The results for particulate sulphate are satisfactory, less than 10% error is good. The error is somewhat larger for the sum of nitrate. The correlation is quite ok as seen in Figure 2, but the reference is somewhat higher than the national measurement. This bias is possibly due to a field blank problem.

Table 6: Results of co-located sampling at Zarra, ES12.

SO_2-S	ref.	H_2O_2 abs
Mean:	0.45	0.45
Median:	0.40	0.25
Num pairs:	86	
Average of diff.:	0	
Median of diff.:	0.03	
M.MAD:	0.27	
CoV:	67 %	

SO_2-S	ref.	monitor
Mean:	0.45	0.52
Median:	0.40	0.45
Num pairs:	85	
Average of diff.:	-0.08	
Median of diff.:	-0.07	
M.MAD:	0.25	
CoV:	63 %	

NO_2-N	ref.	TEA abs
Mean:	0.42	2.48
Median:	0.40	1.00
Num pairs:	95	
Average of diff.:	-2.06	
Median of diff.:	-0.65	
M.MAD:	1.34	
CoV:	339 %	

NO_2-N	ref.	monitor
Mean:	0.42	0.88
Median:	0.40	0.84
Num pairs:	93	
Average of diff.:	-0.45	
Median of diff.:	-0.41	
M.MAD:	0.22	
CoV:	54 %	

SO_4-S	ref.	ES12
Mean:	0.71	0.77
Median:	0.61	0.60
Num pairs:	84	
Average of diff.:	-0.06	
Median of diff.:	-0.05	
M.MAD:	0.06	
CoV:	10 %	

(HNO_3+ NO_3)-N	ref.	ES12
Mean:	0.47	0.31
Median:	0.36	0.27
Num pairs:	83	
Average of diff.:	0.16	
Median of diff.:	0.11	
M.MAD:	0.15	
CoV:	42 %	

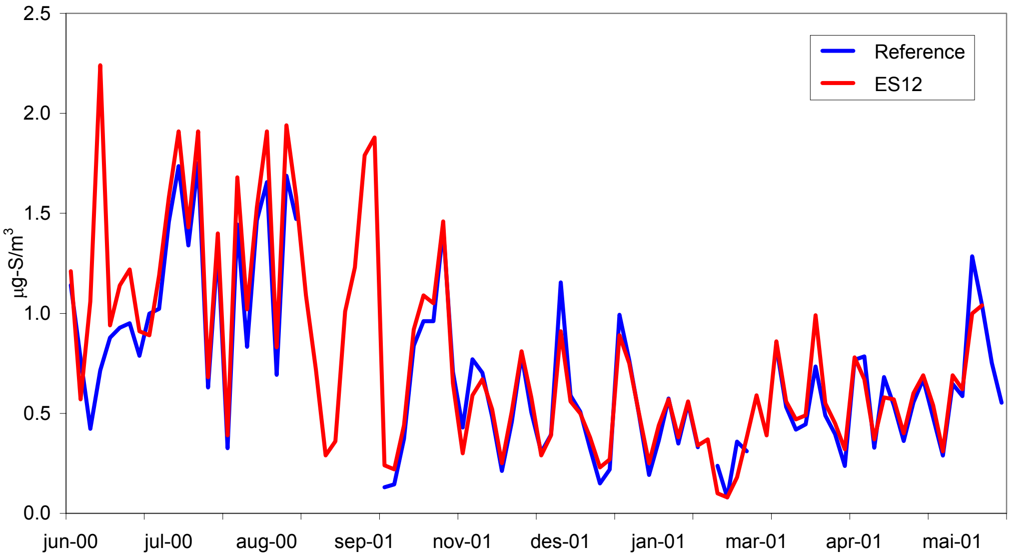

Figure 1: *Comparison of measurements at Zarra (ES12) with reference sampler; results for particulate sulphate.*

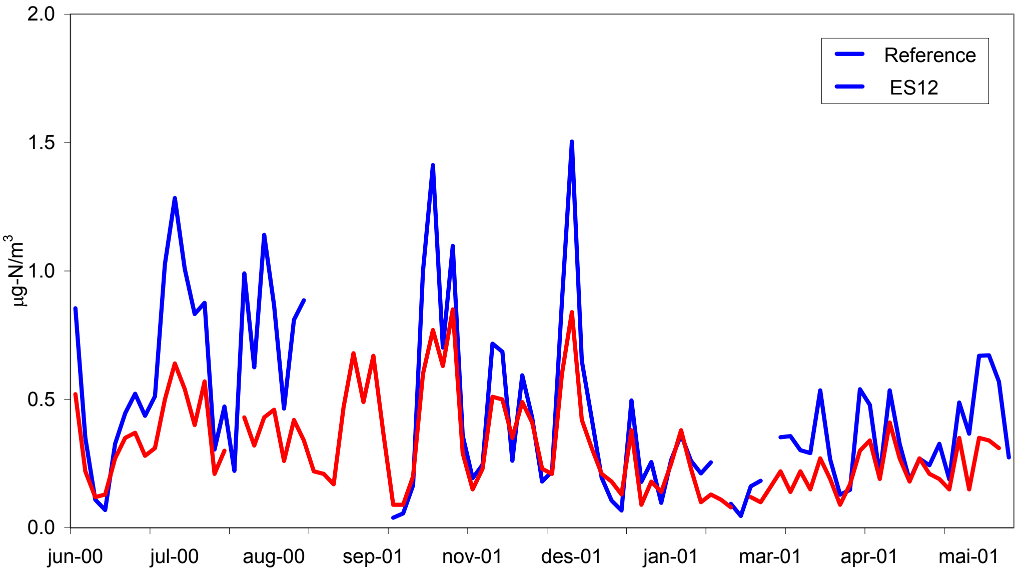

Figure 2: *Comparison of measurements at Zarra (ES12) with reference sampler; results for sum nitrates.*

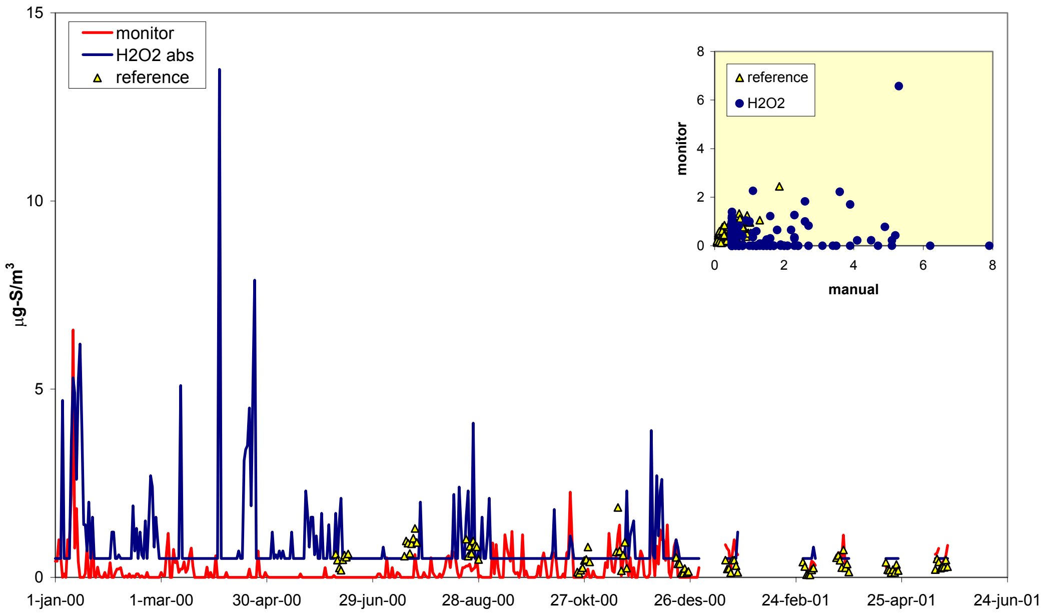

Figure 3: Comparison of measurements at Zarra (ES12) with reference sampler; results for sulphur dioxide.

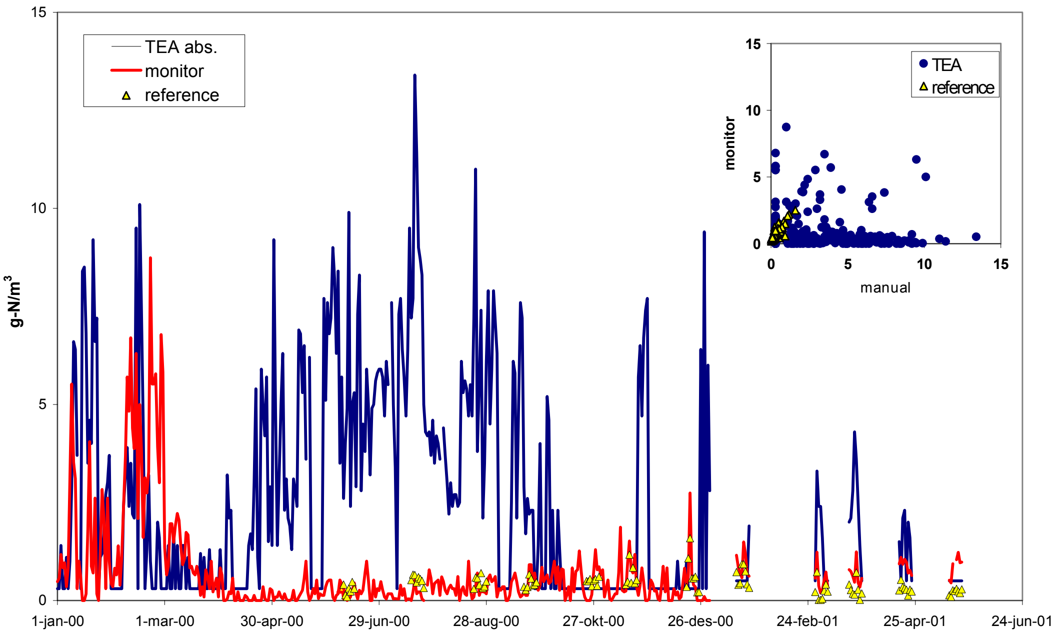

Figure 4: Comparison of measurements at Zarra (ES12) with reference sampler; results for nitrogen dioxide.

For the gaseous species the problems are more severe. The NO_2 manual absorption (trietanolamin) method is well known to have problems with instability at high temperature, sunlight, etc and it has low sensitivity. The differences between the methods are large. In the summertime the TEA method shows more than 10 times the values to the reference method and the monitor, but other part of the year much of the samples are below the detection limit (0.5 µg N/m^3), which in addition is too high for background areas. Half the detection limit is used when calculating the statistics. The comparison between the monitor and the reference is better. The correlation to the reference measurements is ok; the chemiluminescence is however higher by a factor of two compared to the NaI method. Probably this is a calibration and maintenance problem, a general difficulty when using monitors in background areas. It is highly recommended to consider changing methodology in Spain by e.g. using the reference NaI method.

The SO_2 measurements are also disappointing. The manual absorption method (H_2O_2) has many values below the detection limit and the peak values have little correlation with the reference method (NaOH impr. filters). Half the detection limit (0.25 µg S/m^3) is used when calculating the statistics. Accidentally the average between the manual absorption method and the reference is equal, but the plots and the M.MAD reveal that there are problems. When looking into historical data from Spain at several EMEP station, much of the measurements are below the detection limit. This means that this method is not suitable for background stations with low SO_2 concentration. To get reliable averages, at least 75% of the dataset should be above the detection limit. The hydrogen peroxide method works ok at other sites, like in Eskdalemuir (GB2) and Donon (FR8) (Schaug et al., 1998; Aas et al., 1999) where the correlation is acceptable, although, the H_2O_2 method generally overestimates the SO_2 concentration somewhat. The reason why it works poorly in Spain might be due to the warmer climate. The UV-fluorescence method shows better correlation with the reference method, but as for the NO_2 monitor it is biased maybe due to the uncertain baseline. Since the results of sulphate is very good it indicates that the laboratory works well and changing the method to impregnated filter will improve the measurements considerably, this is highly recommended.

In consequence of the results from this field intercomparison, CCC has decided to use the monitor data for SO_2 and NO_2 as the official data for Spain in 2000.

5.2 Main components in precipitation

5.2.1 Introduction

Since there is an opening for doing weekly precipitation sampling in EMEP, there has been a need to thoroughly document possible implication of this. In addition, there are many EMEP sites using bulk collector instead of the recommended wet only collector. It is thus a need to quantify the difference between these collectors at the sites using bulk collectors. In Košetice were several collectors compared and these results were presented by Aas et al. (2000). Similar comparisons have now been done at Birkenes (NO01) in the south of Norway and Diabla Gora (PL05) in Poland.

5.2.2 Comparison at Birkenes (NO01)

A bulk collector sampling on a daily frequency was compared with a wet only from Meteorological Institute Stockholm University (MISU) on weekly sampling frequency. The comparison started 1st September 2000 and lasted for one year. The concentrations from the bulk sampler were averaged into weekly volume-weighted averages to compare the results from the wet only collector.

Generally, there is a good correlation between the measurements in bulk and wet only precipitation at Birkenes. The differences are only a few mg/l for all components, which is about the uncertainty of the measurements. The difference in deposition at Birkenes is lower than 7% except for potassium and calcium. Potassium has two high episodes in the bulk collector indication dry deposition of local dust either from re-suspended soil or probably from pollen or plant debris. The contribution of calcium is often smaller in the bulk compared to wet only because of larger influence of dry deposition in the bulk collector, this is also seen here; however, the difference is within what is acceptable. At background sites with this little influence of dry deposition it will not have any large consequences using bulk collector instead of the recommended wet only collector.

Table 7: Results from intercomparison at Birkenes, (NO1).

Concentrations, mg/l											
	pH	H^+ (from pH)	Cl	NO_3-N	SO_4-S tot	SO_4-S ssc	Na	K	Ca	Mg	NH_4-N
vol w. mean (WO):	4.55	28	2.46	0.44	0.51	0.46	1.32	0.07	0.08	0.17	0.37
vol w. mean (bulk):	4.58	26	2.40	0.43	0.53	0.42	1.32	0.08	0.09	0.16	0.38
% difference:		-7 %	-3 %	-2 %	4 %	-9 %	0.1 %	17 %	12 %	-3 %	3 %
Num pairs:	52	52	49	49	49	49	49	49	49	49	49
M.MAD:	0.1	4.66	0.16	0.03	0.06	0.03	0.09	0.03	0.03	0.01	0.06
CoV:	2%	19%	22%	8%	13%	7%	22%	59%	59%	30%	20%
M.MAD and CoV are calculated from the arithmetic medians.											
Deposition, mg/m²											
	mm	H^+ (from pH)	Cl	NO_3-N	SO_4-S tot	SO_4-S ssc	Na	K	Ca	Mg	NH_4-N
Total (MISU):	1958	55	4819	855	991	899	2581	136	164	327	725
Total (NILU):	2010	52	4820	864	1058	837	2653	164	188	326	765
% difference:	3%	-5%	0.02%	1%	7%	-7%	3%	20%	15%	-1%	6%

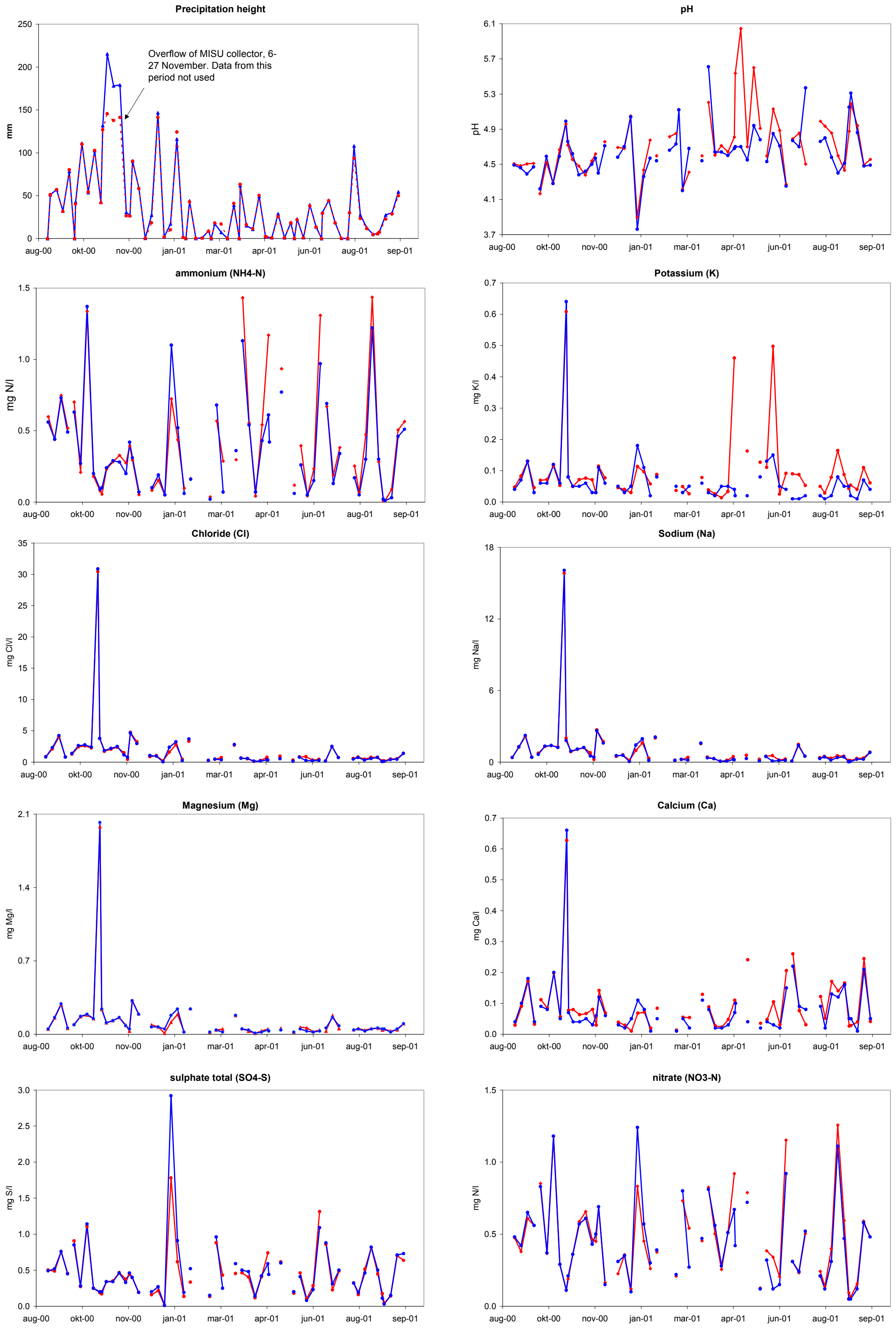

Figure 5: Results from at Birkenes (NO01), red line is NILU-RS bulk and blue line is MISU wet only collector.

5.2.3 Comparison at Diabla Gora (PL05)

In Diabla Gora (PL05) they have recently changed methodology using a local bulk collector to a wet only collector from Eigenbrodt. These samplers were compared for half a year, starting in June 2001, and the results so far are presented here. These measurements also include heavy metals in addition to the main components in precipitation. The wet only samples were collected every day but mixed and analyzed as weekly samples. The daily bulk samples were volume weighted to weekly averages to compare with the wet only samples. At Diabla Gora there is also an official rain gauge, which will be compared with the precipitation volumes from the two other precipitation collectors, the results are presented in Table 8.

At Diabla Gora the difference between the two collectors is somewhat higher compared with what was seen at Birkenes. As seen in Figure 6, the red line showing the measurements from the bulk collector lies generally above the blue line (wet only collector). The highest differences are for the ions often associated with larger particles (e.g. K and Mg), for sulphate there is little difference. The relatively high percentage difference for some of the ions is also related to the low concentration level. The total deposition of the main components is higher in the bulk collector, because of somewhat larger precipitation amount as well as dry deposition.

For heavy metals the situation is different, there is higher deposition and volume weighted mean concentrations in the wet-only collector. Looking at Figure 7 it is apparent that a few episodes have large impacts on the deposition levels since most of the concentrations in the bulk collector are higher than in the wet only. These “episodes” must be either local contamination from field or lab, and should probably be deleted from the dataset. It is only shown data for the elements where the concentrations were mainly above the detection limit.

The result from this intercomparison clearly shows that dry deposition has influence on the results at Diabla Gora when using bulk collector, and it is therefore a site where a wet only collector is preferred.

Table 8: Results from intercomparison at Diabla Gora, (PL05).

Concentrations, mg/l

	pH	H^+ (from pH)	SO_4-S	NO_3-N	NH_4-N	Cl	Na	K	Mg	Ca
vol w. mean (WO):	4.77	16.99	0.65	0.39	0.44	0.37	0.15	0.07	0.04	0.19
vol w. mean (bulk):	4.78	16.45	0.64	0.40	0.54	0.54	0.21	0.13	0.05	0.23
% difference		-3%	-2%	3%	24%	45%	33%	77%	36%	25%
Num pairs:	27	27	28	28	28	28	26	26	26	26
M.MAD:	0.16	5.53	0.06	0.09	0.11	0.18	0.02	0.05	0.02	0.07
CoV:	3%	38%	10%	21%	26%	56%	24%	91%	47%	55%

M.MAD and CoV are calculated from the arithmetic medians.

Concentrations, µg/l

	Al	Ba	Cu	Fe	Mn	Si	Sr	Zn
vol w. mean (WO):	30	1.3	1.5	32	3.5	46	0.9	21
vol w. mean (bulk):	15	1.0	1.7	17	2.2	35	0.6	8
% difference	-50%	-28%	11%	-45%	-38%	-23%	-29%	-62%
Num pairs:	26	26	25	26	26	26	26	25
M.MAD:	12	0.3	0.7	9	0.9	28	0.2	8
CoV:	113%	42%	53%	72%	66%	91%	45%	109%

M.MAD and CoV are calculated from the arithmetic medians.

Deposition, mg/m²

	mm	H^+ (from pH)	SO_4-S	NO_3-N	NH_4-N	Cl	Na	K	Mg	Ca
Official rain gauge	473									
Total (Eigenbrodt):	444	7542	289	174	195	166	69	33	18	83
Total (bulk):	477	7839	304	193	259	259	98	63	26	111
% difference:	-6 & 0.9%	4%	5%	11%	33%	56%	43%	90%	47%	34%

Deposition, µg/m²

	Al	Ba	Cu	Fe	Mn	Si	Sr	Zn
Total (Eigenbrodt):	13228	594	687	14073	1544	20265	384	9395
Total (bulk):	7172	460	820	8317	1025	16710	292	3852
% difference:	-46%	-23%	19%	-41%	-34%	-18%	-24%	-59%

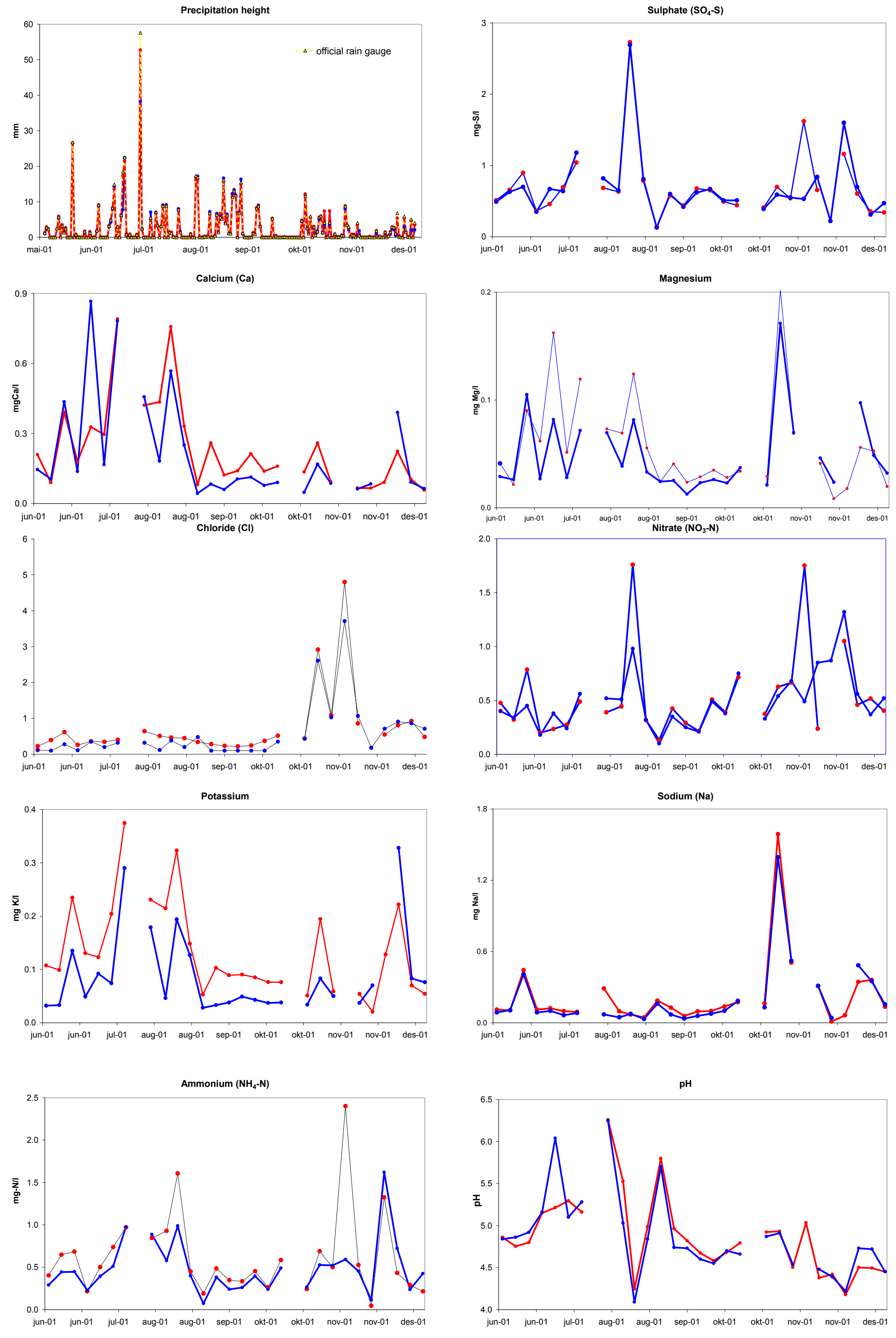

Figure 6: Results from at Diabla Gora (PL05), red line is bulk and blue line is Eigenbrodt wet only collector.

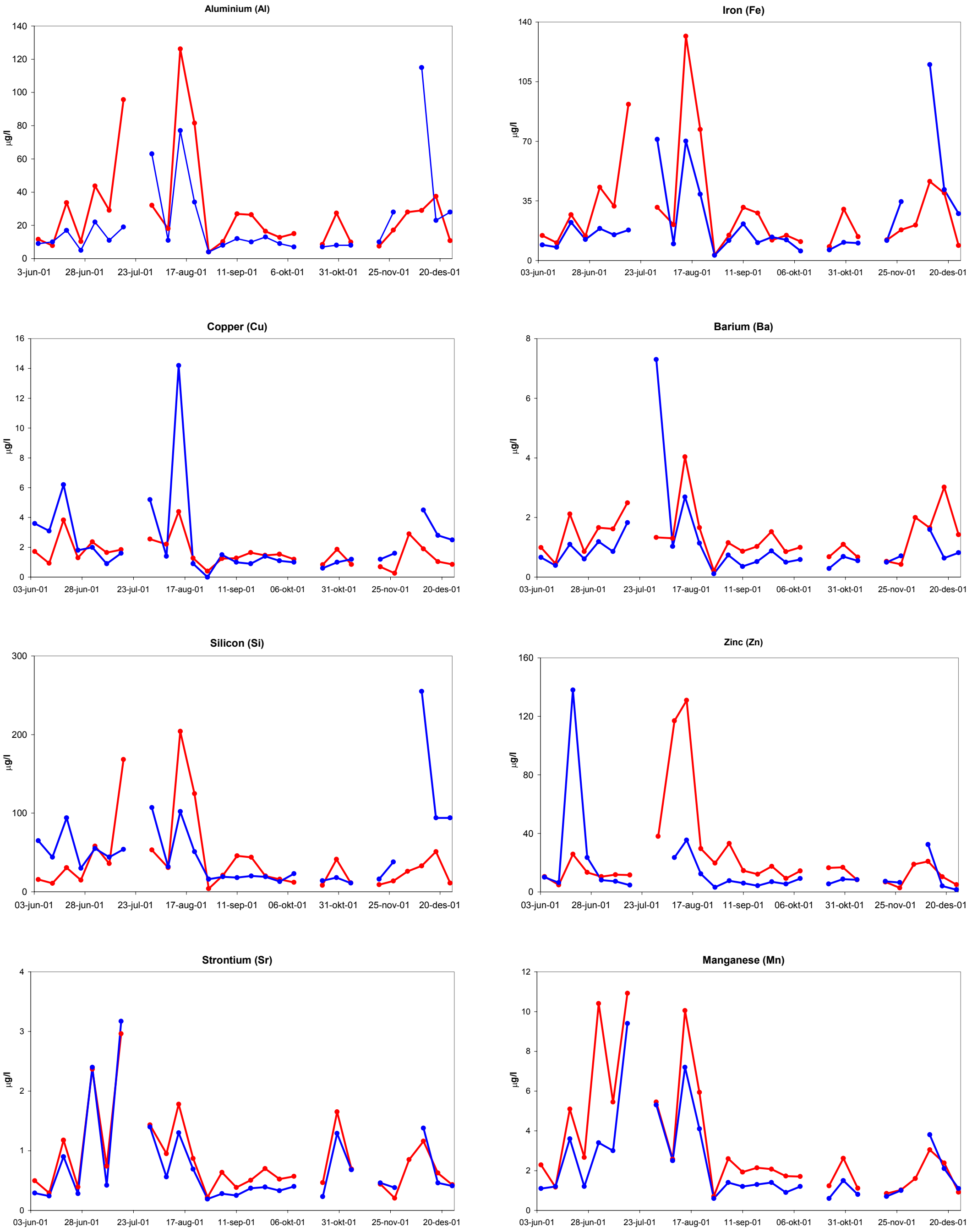

Figure 7: Results from heavy metals inter-comparison at Diabla Gora (PL05), red line is bulk and blue line is Eigenbrodt wet only collector.

5.3 VOC

5.3.1 Hydrocarbon comparison at Waldhof (DE02)

Parallel sampling and analysis of hydrocarbons by NILU and UBA at Waldhof (DE02) started in 1997 and was continued until June 1999. Some of these data was presented in last year QA report (Aas, 2002), and a continued discussion of the results is done by Solberg et al. (2002). A summary is given here.

The evaluation of the comparison between the two institutes should be based on the data quality objective (DQO) as well as on the principal limitations of the sampling procedure and the analysis method in connection with the physio-chemical properties of the individual substance under consideration:

As the DQO for the hydrocarbon analysis has not been finally decided within EMEP, the DQO assumed here is ±25% for concentrations above 100 ppt and ±25 ppt for concentrations below 100 ppt. This choice takes into account, that an overall fractional error does not make sense near the detection limit, and is in agreement with expert recommendations.

Regarding analysis, the GC-method is specified for C_2 to C_5 hydrocarbons and is useful up to C_7, but fails for C_8 and higher. Therefore larger differences are expected for hydrocarbons with more than 7 C-atoms.

Furthermore, the individual hydrocarbons differ considerably in atmospheric concentration: Alkenes in general have much lower concentrations than alkanes or aromatics. Additionally, at least the higher alkenes are more reactive than alkanes and therefore are more susceptible to concentration changes in the sampling canister. Therefore, larger differences are expected for alkenes than for alkanes.

Regarding sampling procedure, in contrast to 1998, where the same sample was analysed by the two institutes, in 1999 two samples where taken, one of which was analysed at UBA, the other one at NILU. The samples where taken “almost” parallel, which means, that the sampling was started within about 5 minutes. If concentrations have a large variability with time, differences between the two samples are expected.

The results show that both institutes are in general in agreement within the DQO-limits for most of the data. Discrepancies occur where they are expected from the discussion above. Biases and deviations from a slope of 1, which has been observed in 1998 for some hydrocarbons, are not present in the 1999 data. The agreement found for butanes and pentanes can be attributed as nearly perfect. Although within the DQO-limits, larger scatter is observed for ethane, ethene, and propene. Some deviations are visible for the butenes, which may be attributed to the low concentrations, analytical reasons or to stability problems in the sampling canisters.

Large discrepancies are expected for hydrocarbons with more than 7 C-atoms, as the method is not adapted here. This was actually the case for ethylbenzene and the xylenes. In conclusion, the agreement between the hydrocarbon measurements of NILU and UBA is within the range that can reasonably be expected.

5.3.2 Carbonyl comparison at Waldhof (DE02)

Figure 8 shows the results of the parallel analysis of formaldehyde, acetaldehyde and acetone at Waldhof by NILU's and UBA's laboratories in 2000. A few results with extreme values of acetone from UBA's analyses during the first three months of 2000 were removed from the dataset.

As indicated by Figure 8, there is an overall good agreement between the two laboratories' data although UBA's values are systematically higher for formaldehyde and acetaldehyde. Furthermore, the results indicate that the agreement between the time series improved during the year. Whereas a marked bias is evident during February-May, the bias is clearly reduced after May. UBA started their carbonyl measurements in the last months of 1999 and was still in a learning and development phase by the beginning of 2000 and the data should be regarded as preliminary.

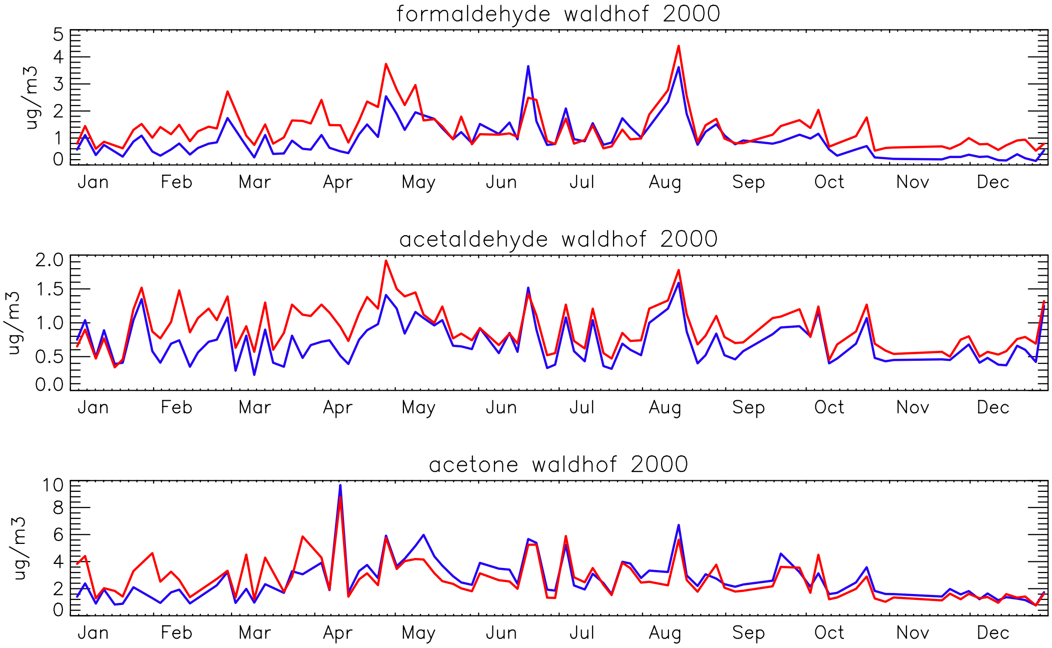

Figure 8: Results of parallel sampling and analyses of carbonyl compounds at Waldhof by NILU (blue line) and UBA (red line) in 2000.

6. Results from laboratory intercomparison

6.1 Main components

The nineteenth intercomparison of main component in precipitation and air is found in a separate report (Uggerud et al, 2002). In Table 9 a summary of the results in precipitation is given. Latvia and Ireland have not participated in the 19th laboratory intercomparison.

Table 9: Results from the 19th laboratory intercalibration of precipitation, average percent error compared with expected value, for 'pH diff' it is shown average deviation in pH unit from expected value.

Lab \ component	SO_4-S	NO_3-N	NH_4-N	Mg	Na	Cl	Ca	K	Cond.	pH diff	pH (H^+)
1 AT	1.1	1.0	1.6	4.3	5.8	14	8.2	5.0	3.7	0.03	7.2
3 CS	1.6	4.4	10	1.1	1.2	11	3.5	2.3	1.3	0.06	12
4 DK	1.2	1.0	0.9	6.3	7.8	3.9	4.5	11	3.3	0.05	11
5 FI	1.1	1.2	1.4	1.5	0.3	1.6	0.9	8.7	1.7	0.02	4.5
6 FR	1.1	2.1	8.2	17	3.6	5.2	17	9.0	5.3	0.01	4.3
7 DE(Leip.)	4.1	3.7	3.1	2.6	0.5	8.4	2.2	3.7	3.7	0.05	11
8 DE(Schau.)	0.8	0.6	4.5	1.5	2.0	3.3	2.6	1.1			
10 HU	1.8	1.6	3.8	15	28	9.2	25	19	0.7	0.16	31
11 IS	2.8	9.4	1.6	3.8	9.9	7.4	2.1	10	9.6	0.02	5.5
12 IE (MET)	0.6	0.6	35	1.6	2.4	5.1	7.3	7.7	2.8	0.01	2.8
13 IT-CNR	9.2	3.1	2.7	1.5	17	3.2	2.9	6.1	5.4	0.06	14
14 NL	1.7	1.5	4.1	2.6	1.8	2.9	1.4	4.1	2.2	0.11	23
15 NO	3.6	4.2	2.9	3.1	3.4	2.4	4.7	3.4	1.3	0.06	13
16 PL	2.2	4.2	4.2	1.1	3.2	5.9	2.1	7.1	1.7	0.02	5.9
17 PT	6.6	3.4	11	6.5	4.9	1.7	16	51	5.5	0.11	23
18 RO	8.9		68			12			15	0.11	28
19 ES	1.6	3.6	9.5	0.6	3.4	9.6	5.6	4.7	4.2	0.21	38
20 SE	15	1.0	0.4	20	9.3	5.7	12	12	4.8	0.02	5.4
21 CH	1.3	0.8	2.5	0.4	1.4	1.8	2.4	10	0.4	0.05	11
22 RU	4.5	4.1	2.8	6.7	5.8	32	22	8.5	7.4	0.07	15
23 GB	0.9	0.9	1.9	0.9	3.6	1.3	1.6	11	2.6	0.06	14
24 YU		124	20	1.8	4.6	51	3.4	7.7	12	0.11	29
26 CA	2.5	1.7	1.3	3.0	0.3	0.6	4.7	5.6		0.03	6.1
27 US-I	0.6	0.5	6.9	5.2	2.2	1.4	0.5	5.4	1.5	0.04	9.8
30 IT(ISP)	0.4	1.2	1.5	4.3	1.1	5.5	4.2	9.7	3.5	0.01	2.2
31 SK	1.2	1.8	4.1	3.9	3.3	2.6	1.1	2.9	3.1	0.04	9.3
32 LT											
33 LV	1.0	0.8	2.2	2.2	5.6	84	15	5.2	3.4	0.0002	6.7
34 TR	0.6	0.7	3.0	19	2.2	6.0	111	16	6.3	0.05	11
35 CR	1.8	1.3	1.9	1.3	1.6	2.9	3.2	3.3	7.6	0.09	18
36 SI	2.0	2.6	1.0	1.7	0.3	3.4	0.5	1.5	16	0.25	40
37 IE (ESB)											
38 EE	8.5	15	3.5	7.2	6.7	43	24	3.4	4.4	0.002	6.1
39 PL (Env.)	6.3	4.7	9.4	1.9	0.7	6.5	1.4	1.2	11	0.01	7.4
40 MK		50	5.2	9.9	38	21	8.4	49	13	0.52	235

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As seen the results are generally relatively good, except for some elements where there is room for improvements, especially for potassium and chloride. 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 9 is given at 0.05, 0.1 and 0.2 average pH units difference from expected value. As seen from the table most of the laboratories are within the DQO.

In Table 10 there is an overview of the result for the main air components. Also here the situation is quite acceptable, even though some elements need improvements at a few laboratories.

Table 10: Results from the 19th laboratory intercalibration of main components in air, average percent error compared with expected value.

Lab \ component	SO_2 impr	SO_2 abs	HNO_3	NH_3	NO_2
3 CS	1.1		0.6		4.2
4 DK	5.2		3.7	6.4	4.4
5 FI	0.5		0.8	3.1	
6 FR		12			
8 DE	4.0		0.7		
10 HU				29	2.8
11 IS	12		17	0.2	
12 IE	0.7				4.4
13 IT	0.4		0.9	3.5	
15 NO	3.4	12	3.7	5.7	0.1
16 PL	4.2		4.4	15	2.7
17 PT		9.6			
19 ES	1.2	19	13	9.6	1370
20 SE	2.0		4.4	2.7	1.4
21 CH		5.5			
22 RU	12		11	11	1.5
23 UK	3.6	0.3			5.5
24 YU					1.1
30 IT				3.4	
31 SK	4.2		1.1	40	11
33 LV	25		30	43	6.7
34 TU	3.9		11		3.2
35 HR					0.3
36 SI	4.8		6.3		3.5
38 EE	33				2.0
39 PL Env.	2.7		2.6	2.8	4.6

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🟩 5-10%
🟨 10-20%
🟧 >20%

CCC has carried out laboratory intercomparison since 1988, and the information from all these intercalibrations will be used for evaluating historical data. Data from laboratories showing unsatisfactory performance in the intercalibration will be flagged, see also introduction chapter 1.

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). In the laboratory intercomparison there are used four samples, two with relatively low and two with high concentrations. L and T represent the laboratories' and the expected concentrations respectively, and D is the difference. The difference for the lowest concentration is

$$D_1 = T_1 - L_1 \tag{1}$$

and the differences are D_1, D_2, D_3, D_4 in increasing order. Given a triangular distribution (Eurachem, 2000; Uggerud et al., 2002) the relative standard uncertainty (RSD) for 4 samples is given by

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

95 per cent of the laboratory results are expected to be within ±2·RSD and if the 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% for S and N containing components and 15% for other components, Annex 1). Correspondingly, the values 2·RSD should therefore be less than 10 or 15 per cent in order to comply with the DQO. Further discussion on how these calculations are done is found in Uggerud et al. (2002) and will also be documented further in EMEP's assessment work.

In Table 11 it is shown two times the RSD from intercomparison of sulphate in precipitation, the blue and green colours represent data within the DQO. In recent years almost all data satisfy this criteria. It is also clearly seen that the performance has improved since the first years.

6.2 Heavy metals

The results from the analytical intercomparison of heavy metals in precipitation are presented in a separate report (Uggerud and Skjelmoen, 2002), but a summary of the main findings is found in Table 12. The results are divided in high and low concentration samples because the performance may vary with concentrations. In general the results are better for high concentration samples. The DQO also 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, blue and green for high concentrations and blue, green and orange for low concentrations, Table 12. However, there are some laboratories that should evaluate their routines.

Table 11: Results from laboratory intercalibration of sulphate in precipitation, two times relative standard deviation (2RSD%) calculated using triangular distribution.

Lab. \ int.number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
1 AT	9.2		25	5.6	28	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	14			82	15		4.6	1.8	4.3	2.2	3	1							
3 CS			28	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		34	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	12			14	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			14	7.7	16	14	5.1	2.1	5.3	1.5	5.6	4.2		6.5	4.8	2.8		
10 HU	23			23	5.6	8.9	17	8.9	12	9.3	17	10	1.7	17	10	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	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		18	7.2	22	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		15	4	1.5	2.7	9.5	14	4.9	0.8	26	1.5	1.3	2.1	12	1.4
18 RO									15						20	15	5.6	25	8.8
19 ES									0.9	1		1.2	29	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				21	394			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				14	22	2.8	13	4.5	3.6	5.7	11	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	25		111	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	
33 LV													5.9	12	13	2.2	2.1	3.7	0.9
34 TR													3.7	0.8	0.7	1.4	26	2	1
35 HR													9.8	5.8	4.9	1	0.9	0.6	0.5
36 SI													12	5.4	2.1	0.3	2.5	1.1	1.3
37 IE EPA/EBS								2.4						12	2.1	0.9	3.7	6.6	
38 EE														6.6	21	2.9	2.4	1.5	2.2
39 PL (Env.)															4.7	3.5		20	1.8
40 MK																			
19 TNO				6.7	21	0.4	3	3.3											

🟦 <5% 🟩 5-10% 🟨 10-20% 🟧 >20%

Table 12: Results from the laboratory intercalibration of heavy metals in precipitation 2001, average percent error compared with expected value 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	0.4	1	3	1	1	3	5	5	6	4		3	1	1
3 CZ	75	14	51	2	6	4	3	3	0.3	7	10	7	12	3
5 FI	37	23	17	14	14	14	12	8	19	17	18	13	13	9
6 FR		16		4	17	13	71	1	40	25		2		1
8 DE	5	1	7	1	0.1	1	14	16	10	4	5	4	5	1
14 NL	25	13		1	1	3	11	2	15	3	10	32		0.2
15 NO	3	2	20	6	8	4	3	1	8	6	8	1	7	6
16 PL			6	1	8	3	20	8			5		10	5
23 GB	2	7	7	4	7	6	24	6	1	9	5	9	4	5
26 CA	2	3		2	3	4	6	2	10	2		3	5	3
31 SK	12	2	59	6	8	0	8		8	1	3	5	14	1
33 LV					59	11	20	8	3	3	10	12	10	1
34 TR			20	2	51	51	0	89			483	28	11	8
36 SI		6		4	8	3	12	11		2		14	10	5
38 EE		12	198	12	11	7		55		33		4		17

🟦 <5% 🟩 5-15% 🟨 15-25% 🟧 >25%

6.3 POPs

In August 2000, ampoules containing solutions to be analysed in round 1 of the first EMEP POP laboratory comparison were shipped to the participating laboratories. The sets sent to most of the participants contained:

- One standard solution of known PAHs and one standard solution of PAHs of unknown concentration
- One standard solution of known chlorinated compounds (pesticides and PCBs) and one standard solution of chlorinated compounds of unknown concentration.

The participants were asked to analyse the unknown solutions using their own quantification standard and to report the results by February 15th 2001.

The known standard could be used to check (optional) the quantification standard. Sets were sent to 27 labs in 20 different countries. Of all the labs, 18 returned results. Some labs reported results only for one of the two compound groups (PAH and chlorinated POPs). The last results were received on the May 7th 2001. A data report for round 1 was sent to the participants. An extended version of this report will be included in a draft report after round 2 of the comparison. The results from both rounds will be discussed in a workshop during winter 2002/2003 before the final report of the comparison is published. The overall impression from round 1 was positive, showing the competence of the labs participating (see Figure 9 and Figure 10).

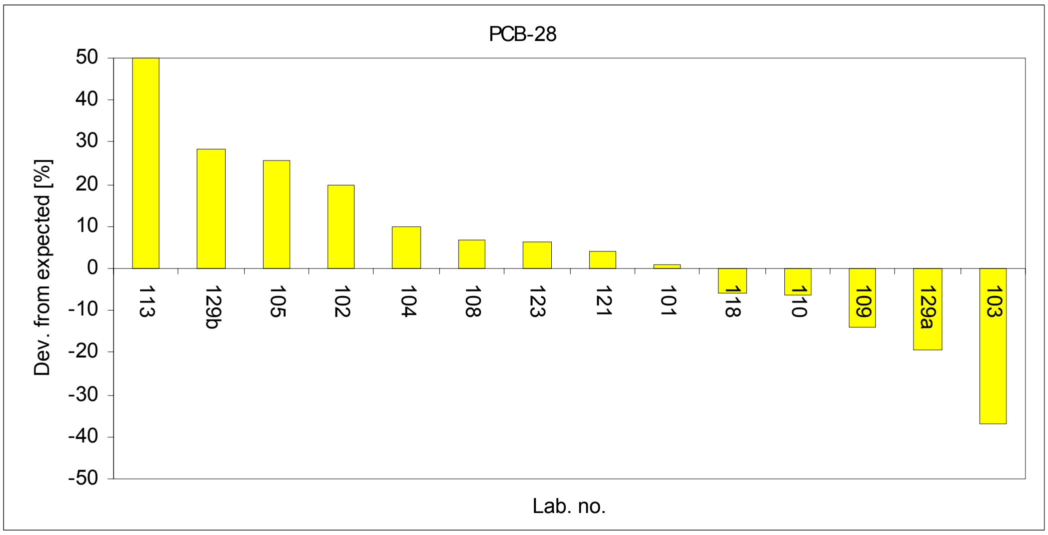

Figure 9: Results reported from 13 labs for the parameter PCB 28 at a concentration of 36 pg/µl.

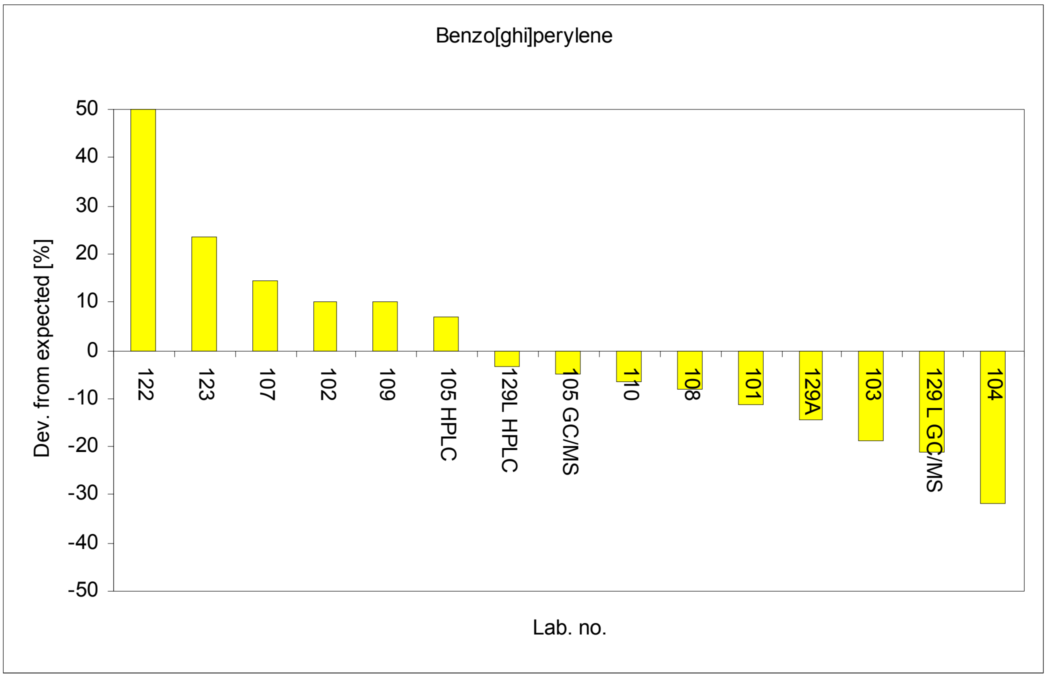

Figure 10: Results reported from 15 labs for the parameter Benzo[ghi]perylene at a concentration of 1,0 ng/µl.

6.4 VOC

For carbonyls, the concentrations of methyl-vinyl-ketone, meth-acrolein, 2-butanone and butanal have for many years been difficult to interpret. No systematic and explainable pattern has been found, and laboratory intercomparisons between EMD, UBA and NILU have indicated analytical problems. Laboratory studies at CCC indicate that unsaturated carbonyl compounds are not chemical stable in the prepared sample solution. Ongoing studies will provide a validation of the EMEP-method performance against unsaturated carbonyl compounds. Furthermore, LC/MS studies indicate possibilities of chromatographic interference in the C4 carbonyl compound range. Ongoing studies will provide a validation of the chromatographic performance of the EMEP-method.

7. Audits

7.1 Introduction

Audit is not being done regularly from CCC, but will be done when needed, as for VOC, see next chapter, 7.2. It is recommended regular audits at all EMEP sites, with at least one internal audit every year, but also with external auditions every 3-5 years. For ozone sites more frequent visits are necessary for calibration and maintenance (EMEP, 1996). 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.

7.2 Visit to UBA

Carbonyl measurements

In beginning of December 2001, CCC visited the Waldhof site and the UBA laboratory in Berlin. The intention by the visit was to discuss routines and protocols on the sampling site and the laboratory. The main conclusion is that the Waldhof site and the UBA laboratory perform carbonyl measurements at the same level as CCC. The agreement between the results from UBA's and CCC's laboratories is very satisfactory.

A number of points regarding the sampling and analyses were raised, though. Firstly, a problem with the ozone scrubber was discovered for the last part of the 2000 samples. The ozone scrubber prepared by CCC was for some months by a mistake not replaced according to the interval stated in the manual, while UBA's scrubber was running properly during the same period. As a routine, at Waldhof the scrubbers are tested against ozone scrubbing effect before discarding, and CCC's scrubber running on overtime did still perform satisfactory in ozone scrubbing when it was discarded. However, there are indications of altered performance as the scrubber tended to be active on carbonyl scrubbing due to systematic low carbonyl concentrations in the actual time. When a new ozone scrubber from CCC was installed a good agreement between the two data sets was re-established

Then, secondly, it was realized and agreed that the use of a so-called *ternary gradient* (in the chromatogram analyses) at UBA will make UBA's chromatograms and NILU's chromatograms more comparable. Furthermore, this will also lead to a better chromatographic resolution for C_4 carbonyl compounds. In addition, better resolution between the reagent peak and the formaldehyde peak will be achieved.

Thirdly, it was agreed that parallel sampling should be performed as a part of the QA work during two to four campaigns (6-8 samples) each year to compare UBA's measurements with NILU's measurements.

C_2-C_9 hydrocarbons

December 2001 CCC visited UBA's site Schmücke where UBA is performing measurements of C_2-C_9 hydrocarbons in canisters from five different sites (Schmücke, Zugspitze, Waldhof, Brotjacklriegel and Zingst). Every Thursday the instrument is used to do online measurements at Schmücke for a period of 24 hours.

During the audit the instrumentation for both canister sampling and canister cleaning was discussed. For the cleaning procedure a slight change for further cleaning of the purge gas was suggested and agreed on.

The routines for maintenance work like changing of drying tubes and CO_2 scrubber where discussed as well as calibration routines.

The synthetic standard gas is from NPL (UK) – concentrations of the individual hydrocarbons are between 1 and 8 ppb. 50 ml of the standard mixture is used for daily calibration – once a month a 500 ml aliquot is analysed. For on-line analysis or canister sampling 500 ml of air is analysed. Because of the fact that different volumes of standard and sample are analysed the precision and reproducibility of the volume measurements done by mass flow controllers are crucial.

The chromatograms of the instrument indicated one minor problem. Too much methane from the sample was pre-concentrated resulting in ethane being "rider peak" in the end of a big methane peak. This problem could be solved just by adjusting the temperatures for the pre-concentration step.

The results of parallel measurements between UBA and NILU were discussed. The results did agree very well.

The overall impression of the staff, the site, the instrumentation and the routines as well as the achieved results were very good.

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Uggerud, H.Th. and Skjelmoen, J.E. (2002) Analytical intercomparison of heavy metals in precipitation, 2001. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 2/2002).

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

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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.

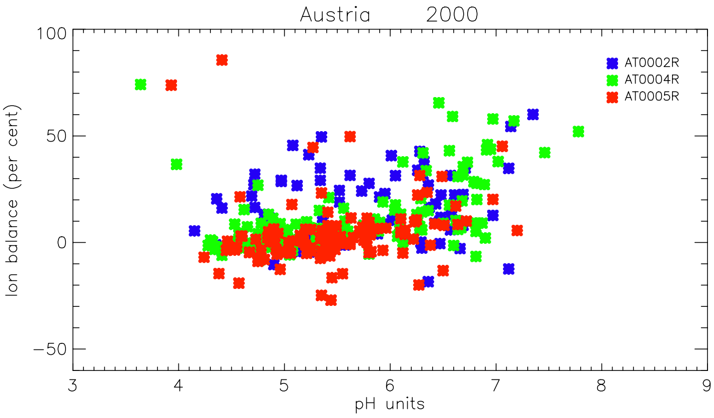
DQO for heavy metals

- 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 2000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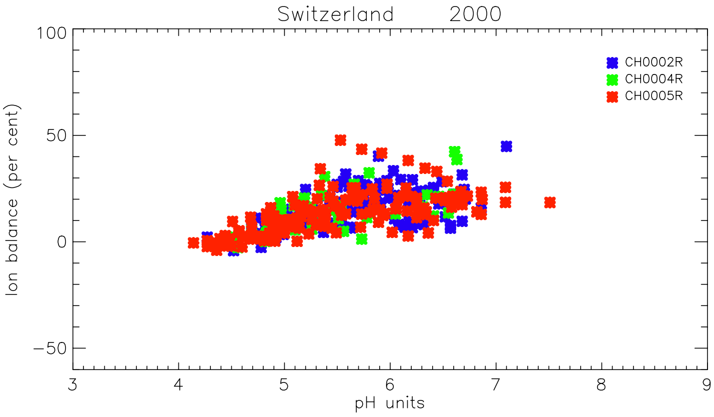
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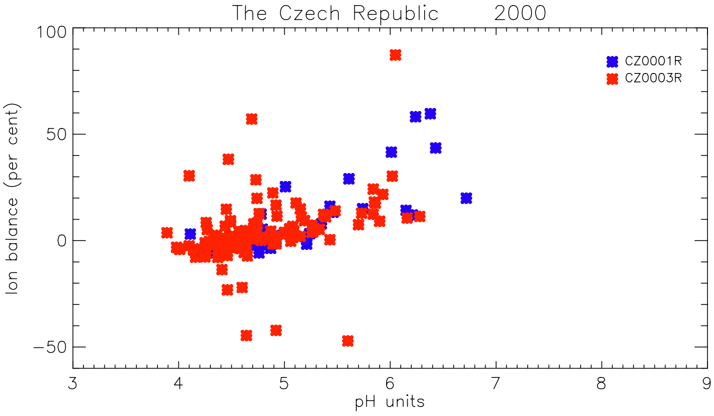
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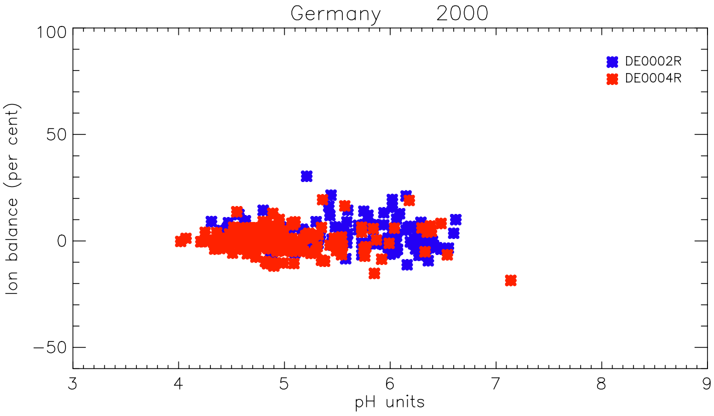
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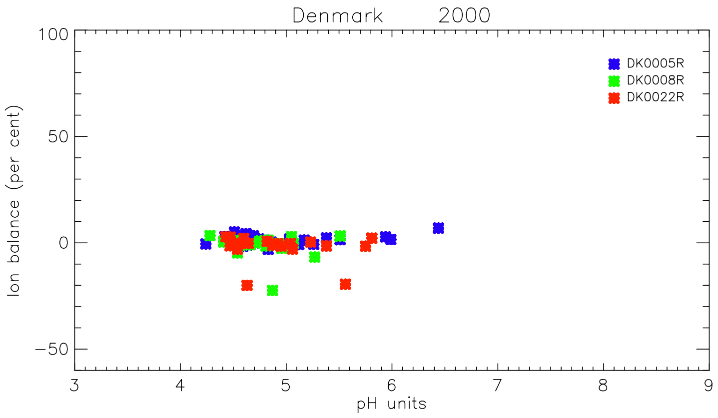
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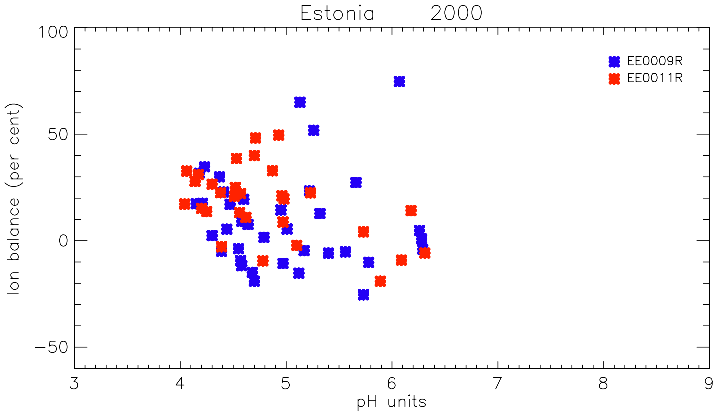
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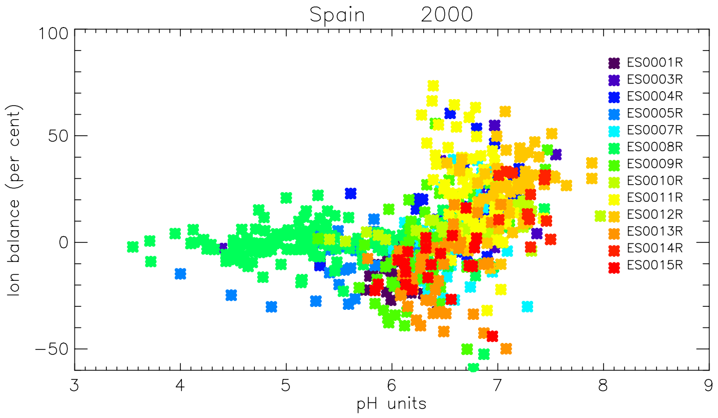
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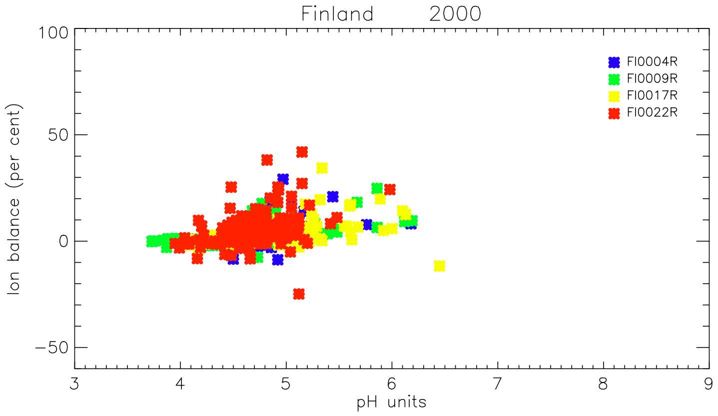
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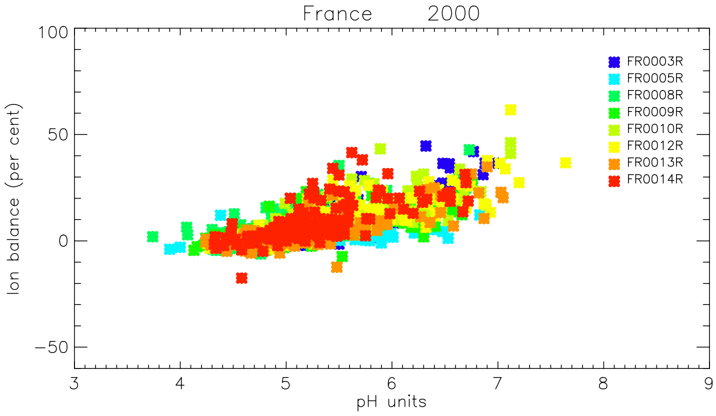
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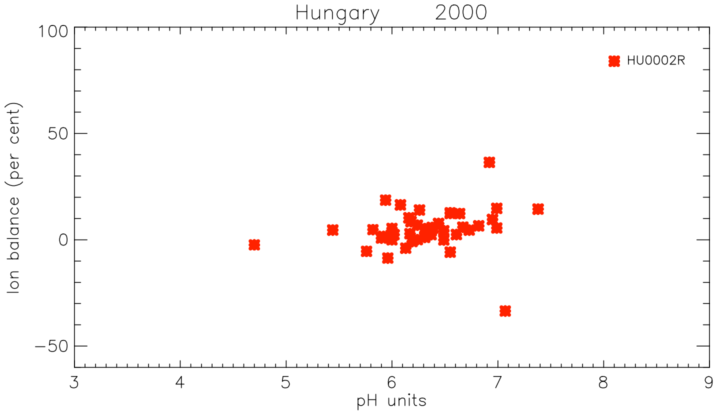
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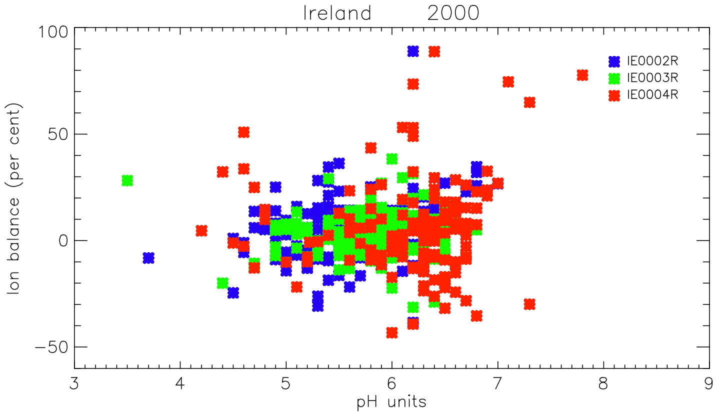
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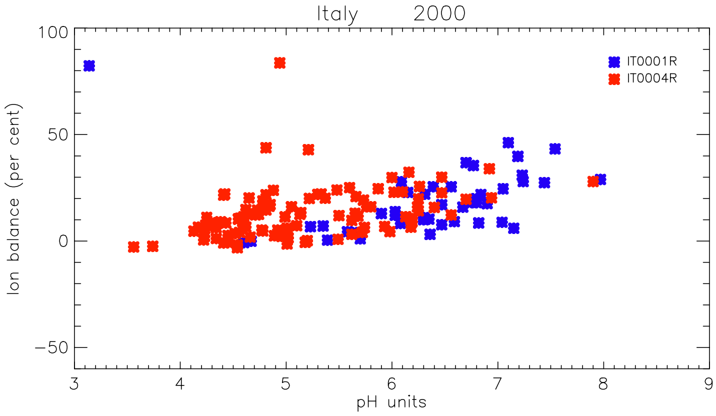
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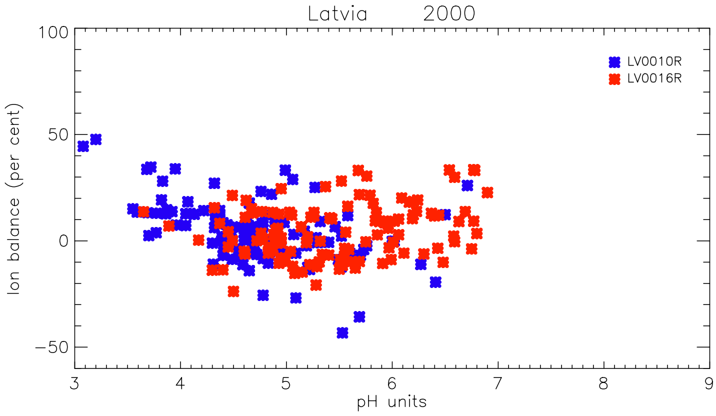
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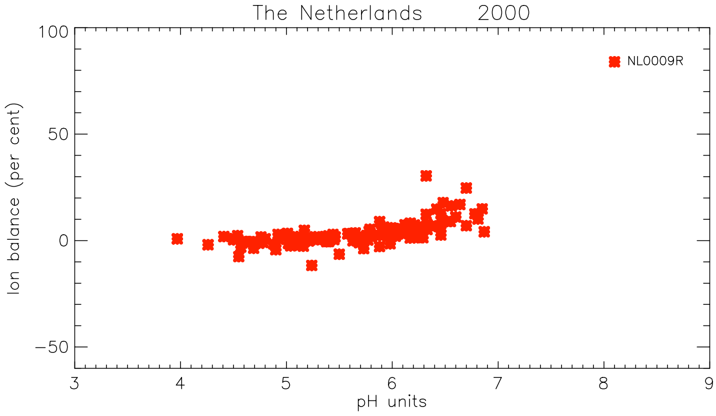
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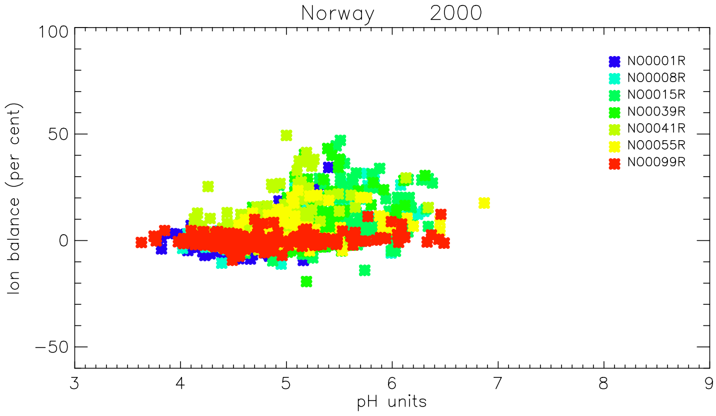
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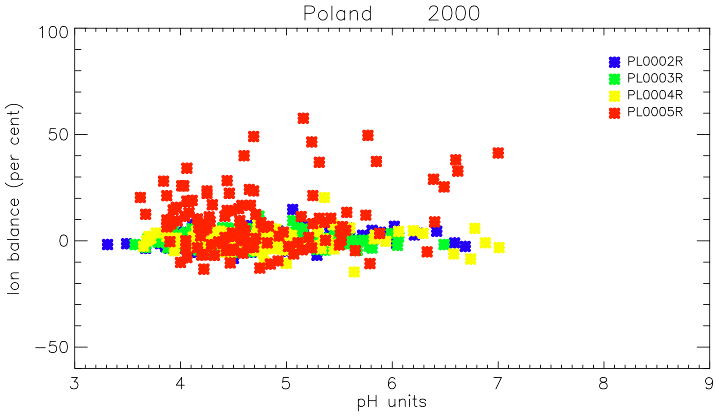
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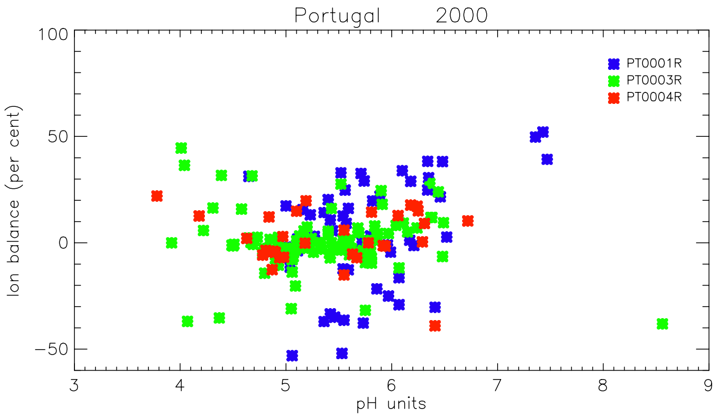
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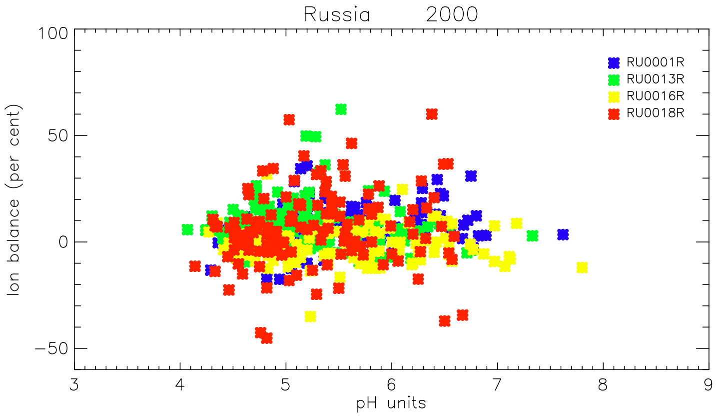
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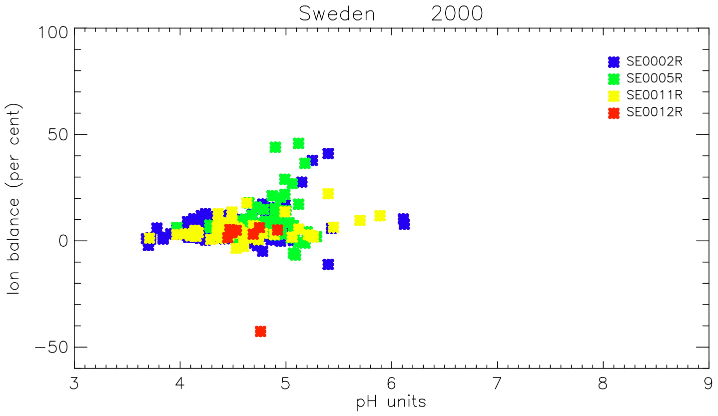
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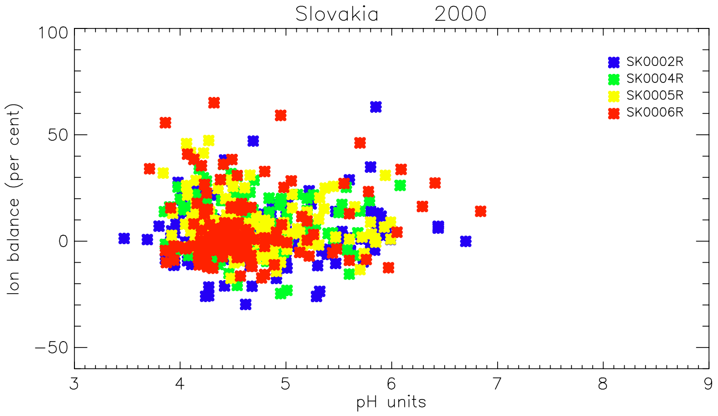
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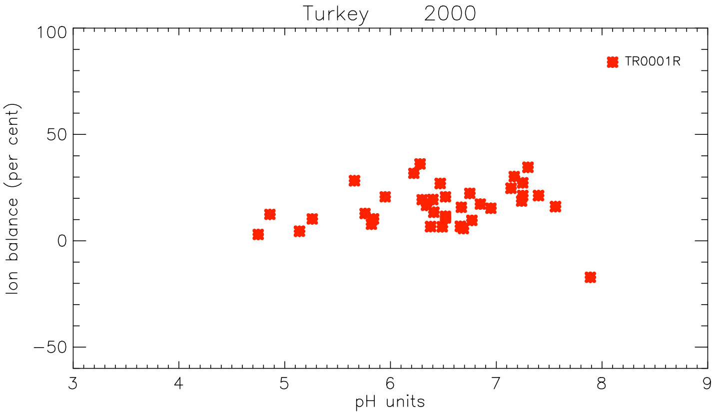
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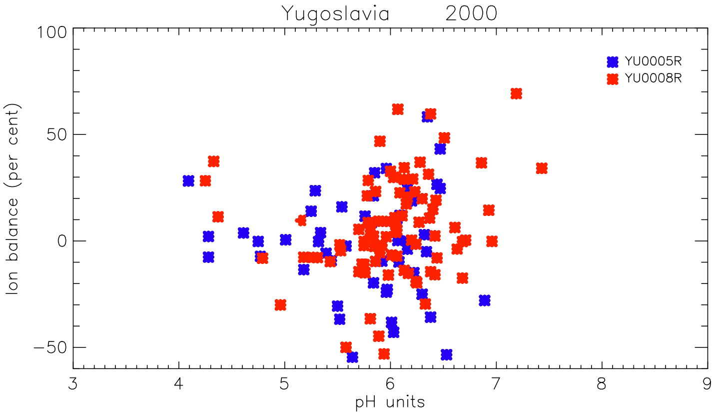
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pH units
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Annex 3

Detection limits and precision

Table 3.1: Detection limits and precision of ozone.

Country	Precision	Detection limit	Instrument
Austria AT02,04 AT05	1 ppb	0.4 ppb 0.5 ppb	Horiba APOA 350E Horiba APOA 360
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 FI17 FI22 FI37	2 µg/m^3	2 µg/m^3	Dasibi Environmental corp., DAS 1008 PC Environnement SA, Env. O3 41 M Dasibi Environmental corp., DAS 1008 AH Thermo Environmental Instruments, TEI 49 C
France FR08,10,13 FR09,10	2 µg/m^3	2 µg/m^3	Environnement SA, O341M SERES, OZ2000
Germany		2.0 µg/m^3	
Hungary			Thermo Environmental Instrument,M49
Irland (IE01)			API Model400
Italy (IT01)	2 µg/m^3	1 µg/m3	API Model400
Italy, EU (IT04)	2 ppb	2 ppb	Thermo Environmental Instruments 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 PL05	2µg or 1%, whichever is greater RSD 4.7%	2 µg/m^3 1 ppb	Monitor Labs Inc. ML-9810 Monitor Labs Inc. ML-9810
Slovakia	2 µg/m^3		TEI M49 (at SK02, 06); M49C (at SK04)
Slovenia, SI08,32 SI31,33			Thermo Environmental Model 49 C Monitor Labs, Model 8810
Spain			MCV, S.A. Model 48 AUV and 0341 M
Sweden, SE02,11,12 SE32,35	1 ppb 2 ppb	0.5 ppb 2 ppb	Monitor Labs, ML 9810 (ML 9810 B at SE 12) Monitor Labs, ML 8810
Switzerland, CH02,04,05 CH3	3.4 µg O$_3$/m^3 (c < 85 hourly mean) 4% (c > 85 hourly mean) 3.9 µg O$_3$ / m^3 (c< 85, hourly mean) 6% (c > 85, hourly mean)	1 ppb 1 ppb	Thermo Environmental Instruments TEI 49C Monitor Labs 9810
UK, all sites except: GB32 GB43 GB44	2 ppb		Monitor Labs, ML 8810 TECO, TE49 Ambirack API Model 400

Data from ES, UK and IT04 are taken from earlier years.

Table 3.2: Detection limits and precision of sulphur dioxide.

Country	Measurements		Laboratory	
	Precision	**Detection limit µgS/m^3**	**Precision**	**Detection limit**
[1]Austria	0.7 ppb	0.1 ppb		
Czech Republic	M.MAD: 0.16; CoV: 14%	0.1	1.5	0.1 mgS/l
Denmark	M.MAD: 0.02; CoV: 5%	0.02	M.MAD: 0,01 µgS/m^3; CoV: 1,8 %	0,01 µgS/m^3
Estonia		0.9		
Finland			c=0.65 mg S/l; 7.1% RSD c=1.6 mg S/l; 2.6% RSD	0.03 mgS/l
France			0.01<c<0,1 mgS/L: 8-12 % 0.1<c<0,5 mgS/l: 1-3%	0.1 mgS/L
Germany	M.MAD: < 0.02			0.01 µg/m^3
Hungary	0.28	<0.1	<10%	ca. 0.03
Italy (IT01)	RSD: 7.2 % at 2.0 µgS/m^3	0.1		
[2]Italy, EU (IT04)	0.5 ppb	1 ppb		
Latvia		0.2	CoV: 1.4%	0.1
Lithuania		0.02	c<0.7 µgS/m^3 2.4 % RSD; c>0.7 µgS/m^3: 0.5-1.0 % RSD	0.017 mgS/l
Netherlands	1 %	3		
Norway	M.MAD 0.04; CoV: 12%	0.03		0.01 µgS/m^3
Poland		0.2		0.04 mgS/l
PL05		0.1		0.5 mgS/l
Russia		RU1: 0.05; RU16: 0.10; RU18: 0.07		
Slovakia			RSD: 3.3%	0.040 mg/l
Slovenia		0.12		
Spain		0.5	4.30 %	1 µg S/sample
Sweden	RSD: 13%	0.02	2%	0.04
Switzerland	0.02 µgS/m^3 (Range <0.2 µgS/m^3), 10% (Range >0.2 µgS/m^3)	0.03		0.03 µgS/m^3
[3]CH02	1 µg SO_2 / m^3 (Range <10 µg SO_2 /m^3), 9 % (Range >10 µg SO_2 /m^3)	1 ppb		
[3]CH04, CH05		0.2 ppb		
Turkey		0.13	M.MAD: 0.014; 2.6%	0.016
Yugoslavia				0.005 mgSO_2/m^3

[1] AT, Monitor, (TEI 43 C trace level/TEI 43 S)
[2] IT04. Monitor Environment SA, AF 21M
[3] CH02: Monitor Labs 8850S, from 28.6.02 TEI 43C TL; CH04, Thermo Environmental Instruments TEI 43C TL; CH05: Thermo Environmental Instruments TEI 43BS

Data from ES and IT04 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**
[1]Austria	1 ppb	0.5 ppb		
Czech Republic	RSD: 12%	0.07	3.4	0.001 mgNO$_2$/l
Denmark		0.06	M.MAD: 0.03; CoV: 2.6%	0.06 µgN/m^3
Estonia		0.01		
Finland	0.3 µgN/m^3	0.3		
Hungary		<0.25	ca. 5%	ca. 0.15
Italy (IT01)	0.6 µgN/m^3	0.3		
[2]Italy, EU (IT04)	0.5 ppb	0.5 ppb		
Latvia		0.1	CoV: 1.3%	0.04
Lithuania		0.17	c<2.0 µgN/m^3: 4-7% RSD;	0.03 mgN/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 mgN/l
Poland		0.2	RSD: 1.0% at 0.3 mgN/l RSD: 5.9 % at 0.015 mgN/l	0.008 mgN/l
PL05		0.1		0.002 mgN/l
Slovakia			RSD: 4.5%	5.6 µg/l
Spain		1	1.5%	1 µg N/sample
Sweden	RSD: 12%	0.2	2%	0.05
[3]Switzerland	For ML9841: 3.5 µgN/m^3 at c <35 µgN/m^3 10% at c >35 µgN/m^3	CH04,05 : 0.5 ppb CH02,03: 1 ppb CH01: 0.05 ppb		
Turkey		0.13	M.MAD: 0.07; 11%	0.02
Yugoslavia				0.003mg NO$_2$/m^3

[1]AT: Monitor, HORIBA APNA 360
[2]IT04: Monitor, Thermo Environment 42C
[3]CH04: Monitor Labs 9841A; CH05:Monitor Labs 8841, from 5.4.2000 Monitor Labs 9841A; CH02 and CH03: Eco Physics CLD 700AL; CH01: Eco Physics CLD 770AL ppt + PLC 760

Data from ES, IT04 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: 0.04 DK05, DK08: 0.03		
Estonia		0.3		
Finland			c= 0.65 mg S/l; 4.0% RSD c= 1.6 mg S/l; 2.6% RSD	0.02 mg S/l
France			0.01<c<0.1 mgS/L: 8-12 % 0.1<c<0.5 mgS/l: 1-3%	0.2 µgS/filter
Germany	M.MAD < 0.02 µg/m^3			0.01 µg/m^3
Greece			M.MAD = 0.095; CoV = 7.8%	
Hungary	0.28 µgS/m^3	<0.1	<10%	ca. 0.03 µgS/m^3
Italy (IT01)	RSD: 1.4% at 1 µgS/m^3	0.01		
Italy, EU (IT04)		0.066 ppm	M.MAD. 0.01 ppm; CoV: 1.3%	
Latvia		0.10-0.15	CoV: 1.4%	0.1 mg/l
Lithuania		0.024	c<1.0 µgS/m^3: 7.2% RSD; c>1.0 mgS/m^3: 1.0% RSD	0.024 mgS/l
Netherlands			SD: 0.2	0.8 µg/m^3
Norway	M.MAD 0.009 µgS/m^3 at c<2.4 µgS/m^3	0.01		
Poland		0.18		0.04 mgS/l
PL05		0.1		0.5 mgS/l
Russia		RU01: 0.03; RU16: 0.05; RU18: 0.067		
Slovakia			RSD: 3.1%	0.062 mg/l
Slovenia		0.015 µgS/ml	RSD: 5.3%	0.013 mg S/l
Spain		0.01	1.36%	3,5 µg S/sample
Sweden	RSD: 13%	0.005	2%	0.005
Switzerland	0.25 µgS/m3	0.04		0.04 µgS/m^3
Turkey		0.05	M.MAD: 0.03; 4,9%	0.014
UK			RSD: 2%	0.01 mgS/l

*Data from ES, 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 µgN/m^3 CoV: 7,3%	DK03,08: 0.05 DK05: 0.07	M.MAD: 0,01 µgN/m^3 CoV: 0.9%	0.01 µgN/m^3
Finland			NO3: c=0.35 mgN/l; 5% RSD c=0.9 mgN/l; 3.0% RSD HNO3:c=0.35 mgN/l; 4% RSD c=0.9 mg N/l; 2.6% RSD	NO3: 0.01 mgN/l HNO3: 0.01 mgN/l
Germany	< 0.02 µg/m^3 M.MAD			0.01 µg/m^3
Greece				
Hungary	0.05	<0.1	<10%	ca. 0.03
Italy (IT01)	HNO3: RSD: 5.3 % at 0.25 µgN/m^3 NO3: RSD: 1 % at 1 µgN/m^3	HNO3: 0.01 NO3: 0.01		
Italy, EU, IT04		0.246 ppm	M.MAD: 0.01 ppm CoV: 1.2%	
Latvia		NO3: 0.01-0.02	NO3: CoV: 2.1%	NO3: 0.05 mg/l
Lithuania		0.014	c=0.3-1.0 μgN/m^3 0.5-1.2% RSD;	0.013 mgN/l
Netherlands			NO3, SD: 0.1	NO3: 0.7 ug/m^3
Norway	M.MAD 0.012 at <1.6 µgN/m^3	0.02		
Poland		0.02		NO3: 0.01 mgN/l
PL05		0.2		0.05 mgN/l
Russia		NO3: RU01,16: 0.01; RU18: 0.02		
Slovakia			HNO3, RSD 4.7% NO3 RSD: 2.6%	HNO3: 0.010 mg/l NO3: 0.026 mg/l
Slovenia		HNO3: 0.010 NO3: 0.011	NO3: RSD: 7.7%	NO3: 0.009 mgN/l
Spain		0.06		2 µg N/sample
Sweden	RSD: 12%	NO3: 0.002; HNO3: 0.004	2%	NO3: 0.002; HNO3 0.005
Switzerland	0.13 µgN/m^3	0.06		0.06 µgN/m^3
Turkey		0.04	NO3: 10%, M.MAD: 0,01; HNO3: 13%, M.MAD: 0.007	0.03

Data from ES 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%	DK03: 0.05 DK05: 8: 0.04	NH4: M.MAD: 0.02; CoV: 1.8% NH3: M.MAD: 0.01; CoV: 1.6%	0,01 µgN/m^3
Finland			c=0.22 mg N/l; 7.3% RSD c=0.72 mg N/l; 2.7% RSD c=1.42 mg N/l; 2.8% RSD	0.02 mgN/l
Germany	M.MAD < 0.02 µg/m^3			0.01 µg/m^3
Hungary	NH3: 0.18 NH4: 0.30	NH3: ca.0.05 NH4: <0.1	<10 %	ca. 0.04
Italy (IT01)	NH3: RSD: 3.5% at 1 µgN/m^3 NH4: RSD: 4.8% at 2 µgN/m^3	0.1		
Italy, EU (IT04)		0.061 ppm		
Latvia		NH4: 0.15-0.02	NH4: CoV: 2.1%	NH4: 0.06 mgN/l
Lithuania		0.027	c<1.0 mgN/m^3: 4.0 % RSD c>1.0 mgN/m^3: 0.6-1.8 % RSD	0.04 mgN/l
Netherlands	NH3: <2%	NH3: 0.12	NH4, SD: 0.03	NH4: 0.1 µg/m^3
Norway	M.MAD 0.04 at c <3.2 µgN/m^3	0.05		
Poland PL05		0.08 0.03		NH4: 0.03 mgN/l 0.01 mgN/l
Russia		NH4: RU01: 0.11; RU16: 0.21; RU18: 0.17		
Slovenia		NH4: 0.010 NH3: 0.037	NH4 RSD: 4.7%	NH4: 0.012 mgN/l
Spain		0.03	2.68 %	1 µg N/sample
Sweden	RSD: 13%	0.03	3%	NH4: 0.017 NH3: 0.03
Switzerland	0.45 µgN/m^3	0.2		0.2 µgN/m^3
Turkey		NH4: 0.037 NH3: 0.05		NH4: 0.022 NH3: 0.015

Data from ES 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	RSD: 1.5%	0.009	RSD: 1.3%	0.002
Czech Republic	M.MAD: 0.17		RSD: 11%	0.02
Denmark			M.MAD: 0.01; CoV: 1.6%	0.03
Estonia		0.2		
Finland			c=0.65 mg S/l; 2.4% RSD c=1.6 mg S/l; 2.1% RSD	0.02
France			c<0.2mgS/L: 5-10% 0.2<c<0.5mgS/L: 3-5% 0.5<c<5mgS/L: 1-3%	0.02
Germany				0.01
Hungary		ca. 0.03	<10%	ca. 0.03
Italy (IT01)	RSD: 1.3% at 1 mgS/l	0.01	RSD: 0.6% at 0.5 mg S/l RSD: 1.6% at 0.05 mg S/l	0.002
Latvia			CoV: 2.9%	0.01
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: 0.4 % at 6.7 mgS/l RSD: 1.6 % at 0.67 mgS/l RSD: 1.9 % at 0.33 mgS/l	0.03
PL05	M.MAD: 0.02; CoV: 4.2%	0.1	M.MAD: 0.02; CoV: 4.8%	0.1
Portugal			0.75%	0.15
Russia			CoV: 4%; M.MAD: 0.02	0.02
Slovakia			RSD: 1.1%	0.01
Spain			1.4 %	0.07
Sweden	RSD: 5%	0.004	2%	0.004
Switzerland	M.MAD: 0.01	0.03		0.03
Turkey			M.MAD: 0.03; 3.2%	0.025
UK			2%	0.04
Yugoslavia				0.16

Data from PT, ES, 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	RSD: 1.2%	0.03	RSD: 0.7%	0.001
Czech Republic	M.MAD: 0.164		RSD: 14%	0.03
Denmark			M.MAD: 0.02; CoV: 1.6%	0.03
Estonia		0.5		
Finland			c=0.35 mg N/l; 3.1% RSD c=0.9 mg N/l; 2.5% RSD	0.01
France			c<0.2 mgN/L: 5-10% 0,2<c<0.5 mgN/L: 3-5% 0.5<c<5 mgN/L: 1-3%	0.02
Germany				0.01
Hungary		ca. 0.03	<10%	ca. 0.03
Italy (IT01)	RSD: 1.4% at 1 mgN/l	0.01	RSD: 0.6% at 0.5 mgN/l RSD: 1.5% at 0.05 mgN/l	0.002
Italy, EU (IT04)				0.011 ppm
Latvia			CoV: 2.7%	0.01
Lithuania			c<0.5 mgN/l: 5.1% RSD c>0.5 mgN/l: 1.8% RSD	0.013
Netherlands			SD: 0.5	2 umol/l
Norway	M.MAD: 0.03, CoV: 8%		SD: 0.023 at c=0.86 mgN/ml SD: 0.016 at c=0.39 mgN/ml	0.01
Poland			RSD: 0.4% at 4.5 mgN/l RSD: 1.7% at 0.45 mgN/l RSD: 2.1% at 0.23 mgN/l	0.015
PL05	M.MAD: 0.04; CoV: 8.1%	0.05	M.MAD: 0.02; CoV: 7.2%	0.05
Portugal			0.25 %	0.09
Russia			CoV: 3%; MAD: 0.01	0.01
Slovakia			RSD: 0.7%	0.006
Spain			1.2%	0.08
Sweden	RSD: 5%	0.002	2%	0.002
Switzerland	M.MAD: 0.01	0.02		0.02
Turkey			M.MAD: 0.006; 2.2%	0.02
UK			4 %	0.03
Yugoslavia				0.02

Data from PT, ES, UK, IT04 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	RSD 2.4%	0.01	RSD 3.7%	0.007
Czech Republic	M.MAD: 0.043	0.01	RSD: 6.3%	0.02
Denmark			M.MAD: 0.01 CoV: 1.7%	0.02
Estonia		0.1		
Finland			c=0.23 mg N/l; 2.6% RSD c=0.70 mg N/l; 2.8% RSD	0.002
France			c<0.2mgN/L: 5-10% 0.2<c<0,5mgN/L: 3-5% 0.5<c<5mgN/L: 1-3%	0.03
Germany				0.01
Hungary		ca. 0.04	5-10%	ca. 0.04
Italy (IT01)	RSD: 0.9 % at 0.5 mg N/l	0.005	RSD: 0.6 % at 0.5 mg N / l RSD: 2.0 % at 0.05 mg N / l	0.001
Latvia			CoV: 1%	0.008
Lithuania			c<1.0 mgN/l: 3.3% RSD c>1.0 mgN/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: 0.16; CoV: 31%	0.01	M.MAD: 0.06; COV: 13%	0.01
Portugal			0.79 %	0.04
Russia			CoV: 5%; MAD: 0.01	0.02
Slovakia			RSD: 3%	0.16
Spain			2.7%	0.08
Sweden	RSD: 5%	0.02	3%	0.02
Switzerland	M.MAD: 0.02	0.02		0.02
Turkey			M.MAD: 0.014; 3.2%	0.038
UK			10 %	0.03
Yugoslavia				0.03

Data from PT, ES, 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	RSD: 1%	0.09	RSD: 2%	0.003
Czech Republic	M.MAD: 0.06		RSD 13%	0.02
Denmark			M.MAD: 0.02; CoV: 5.8%	0.02
Estonia		0.2		
Finland			c=0.20 mg Ca/l; 4.9% RSD c=0.61 mg Ca/l; 1.8% RSD	0.005
France			c<0,2mg/L: 10-20% 0,2<c<0,5mg/L: 5-10% 0,5<c<5mg/L: 1-5%	0.02
Germany				0.01
Hungary		ca. 0.01	< 5%	ca. 0.01
Italy (IT01)	RSD: 1.7% at 1 mg/l	0.01	RSD: 1.1% at 0.5 mg/l RSD: 3.3% at 0.05 mg/l	0.002
Latvia			CoV: 5.2%	0.086
Lithuania			c<0.2mgCa/l: 5.5% RSD c>0.2 mgCa/l: 1.5% RSD	0.02
Netherlands			SD: 0.4	1.5 umol/l
Norway	M.MAD: 0.03		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% at 0.7 mg/l RSD: 1.5% at 0.35 mg/l	0.03
PL05	M.MAD: 0.01; 4.2%	0.001	M.MAD: 0.005; CoV: 5.3%	0.001
Portugal			1.31 %	0.06
Russia			CoV: 15%; MAD: 0.04	0.05
Slovakia			RSD: 1.8%	0.007
Spain			7.4%	0.04
Sweden	RSD: 8%	0.05	5%	0.04
Switzerland	M.MAD: 0.02	0.05		0.05
Turkey			M.MAD: 0.009; 0.8%	0.03
UK			5%	0.05
Yugoslavia			19%	0.005

Data from PT, ES, 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	RSD: 5.4%	0.008	RSD: 2.3%	0.005
Czech Republic	M.MAD: 0.022		RSD: 12%	0.003
Denmark			M.MAD: 0,01; CoV: 4,3 %	0.04
Estonia				
Finland			c=0.12 mg K/l; 6.0% RSD c=0.36 mg K/l; 3.6% RSD	0.006
France			c<0,2mg/L: 10-20% 0,2<c<0,5mg/L: 5-10% 0,5<c<5mg/L: 1-5%	0.02
Germany				0.01
Hungary		ca. 0.01	< 5%	ca. 0.01
Italy (IT01)	RSD: 1.2 % at 1 mg/l	0.01	RSD: 1.5 % at 0.5 mg/l RSD: 3.1 % at 0.05 mg/l	0.002
Latvia			CoV: 5.3%	0.04
Lithuania			RSD: 8.1% at c<0.5mg/l	0.02
Netherlands			SD: 0.2	1 umol/l
Norway	M.MAD: 0.03		SD: 0.027; c=0.61 mg/l SD: 0.015; c=0.20 mg/l	0.01
Poland			RSD: 1.0 % at 0.45 mg/l RSD: 1.8 % at 0.16 mg/l RSD: 1.3 % at 0.09 mg/l	0.02
PL05	M.MAD: 0.015; CoV: 11%	0.002	M.MAD: 0.003; CoV: 7.7%	0.002
Portugal			1.7 %	0.077
Russia			CoV: 9%; MAD: 0.03	0.03
Slovakia			RSD: 2%	0.004
Spain			18%	0.05
Sweden	RSD: 14%	0.05	8%	0.05
Switzerland	M.MAD: 0.01	0.03		0.03
Turkey			M.MAD: 0.007; 2.4%	0.02
UK			6%	0.05
Yugoslavia			2%	0.015

Data from PT, ES, 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	RSD 2.9%	0.024	RSD: 3.6%	0.009
Czech Republic	M.MAD: 0.071		RSD: 16 %	0.02
Denmark			M.MAD: 0,07; CoV: 2,3%	0,09
Estonia		0.1		
Finland			c=0.5 mg Cl/l; 3.2% RSD c=1.2mg Cl/l; 2.3% RSD	0.01
France			c<0.2mg/L: 10-20 % 0.2<c<0.5mg/L: 5-10 % 0.5<c<5mg/L: 1-5 %	0.05
Germany				0.01
Hungary		ca. 0.10	<10%	ca. 0.1
Italy (IT01)	RSD: 0.8 % at 0.5 mg/l	0.005	RSD: 0.7% at 0.5 mg/l RSD: 1.2% at 0.05 mg/l	0.001
Italy, EU (IT04)				0.032 ppm
Latvia				0.011
Lithuania			RSD: 4.7% at c<0.5 mg/l RSD: 2.3% at c>0.5 mg/l	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: 0.5% at 10 mg/L RSD: 1.3% at 1 mg/L RSD: 1.8% at 0.5 mg/L	0.02
PL05	M.MAD: 0.04; CoV: 19%	0.1	M.MAD: 0.01; CoV: 9%	0.1
Portugal			0.53%	0.03
Russia			CoV: 11%; M.MAD: 0.09	0.03
Slovakia			RSD: 1%	0.005
Spain			5%	0.31
Sweden	RSD: 8%	0.05	2%	0.05
Switzerland	M.MAD: 0.02	0.05		0.05
Turkey			M.MAD: 0.016; 2.5%	0.026
UK			3%	0.05
Yugoslavia				0.05

Data from PT, ES, UK, IT04 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	RSD 1.3%	0.023	RSD: 1.2%	0.002
Czech Republic	M.MAD: 0.004		RSD: 17%	0.001
Denmark			M.MAD: 0.03; CoV: 3.7%	0.02
Estonia		0.01		
Finland			c=0.04 mg/l; 4.5% RSD c=0.66 mg/l; 1.7% RSD	0.003
France			c<0.2mg/L: 10-20% 0.2<c<0,5mg/L: 5-10% 0,.5<c<5mg/L: 1-5%	0.02
Germany				0.01
Hungary		ca. 0.01	< 5%	ca. 0.01
Italy (IT01)	RSD: 1.4% at 0.5 mg/l	0.005	RSD: 0.8% at 0.5 mg/l RSD: 3.4% at 0.05 mg/l	0.001
Latvia			CoV: 5.9%	0.095
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: 0.8 % at 0.27 mg/l RSD: 5.5 % at 0.1 mg/l RSD: 1.5 % at 0.35 mg/l	0.007
PL05	M.MAD: 0.002; 3.6%	0.001	M.MAD: 0.001; CoV: 4.1%	0.001
Portugal			0.60%	0.03
Russia			CoV: 3%; MAD: 0.002	0.001
Slovakia			RSD: 2.5%	0.01
Spain			7.2%	0.02
Sweden	RSD: 5%	0.02	3%	0.01
Switzerland	M.MAD: 0.01	0.01		0.01
Turkey			M.MAD: 0.007; 5.6%	0.012
UK			3.5%	0.05
Yugoslavia			0.5%	0.002

Data from PT, ES, UK and YU are taken from earlier years.

Table 3.14: Detection limits and precision of sodium in precipitation

	Measurements		**Laboratory**	
Country	**Precision**	**Detection limit, mg/l**	**Precision**	**Detection limit, mg/l**
Austria	RSD: 0.8%	0.014	RSD: 1.2%	0.003
Czech Republic	M.MAD: 0.023		RSD: 14%	0.002
Denmark			M.MAD: 0.04; CoV: 1.9%	0.07
Estonia				
Finland			RSD: 5.7% at c=0.22 mg/l RSD: 1.7% at c=0.66 mg/l	0.002
France			c<0.2mg/L: 10-20% 0.2<c<0.5mg/L: 5-10% 0.5<c<5mg/L: 1-5%	0.02
Germany				0.01
Hungary		ca. 0.01	< 5%	ca. 0.01
Italy (IT01)	RSD: 0.9% at 0.5 mg/ l	0.005	RSD: 1.0% at 0.5 mg / l RSD: 1.9% at 0.05 mg / l	0.001
Latvia			CoV: 1.7%	0.06
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: 0.9% at 1 mg/l RSD: 1.3% at 0.4 mg/l RSD: 1.0% at 0.2 mg/l	0.02
PL05	M.MAD: 0.019; CoV: 22%	0.002	M.MAD: 0.002; CoV: 6.8%	0.002
Portugal			0.54%	0.025
Russia			CoV: 5%; MAD: 0.02	0.01
Slovakia			RSD: 2.8%	0.01
Spain			14 %	0.1
Sweden	RSD 12%	0.05	4%	0.05
Switzerland	M.MAD: 0.02	0.02		0.02
Turkey			M.MAD: 0.01; 1.6%	0.023
UK			3.5%	0.03
Yugoslavia			1.8%	0.001

Data from PT, ES, 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			RSD: 3.9% at c=10 μg /l	0.006
Norway				0.1

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	M.MAD: 0.019		RSD: 20%	0.1
Estonia		0.01		
Finland			RSD: 3.5% at c=1 ug /l	0.002
Latvia			CoV: 6.8%	0.05
Slovakia			RSD: 1%	0.01
Netherlands			0.00007	0.0003 μmol/l
Norway				0.005

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			RSD: 8.6% at c=1 μg/l	0.02
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			RSD: 6.2% at c=1 ug/l	0.05
Latvia			CoV: 9.1%	0.14
Poland (PL05)	M.MAD: 0.3; CoV: 19%	0.3	M.MAD: 0.1; CoV: 18%	0.3
Netherlands			0.0014	0.006 μmol/l
Norway				0.1

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	M.MAD: 0.02		RSD: 33%	50
Netherlands			0.09	0.4 μmol/l
Norway				10

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	M.MAD: 1.3		RSD: 20%	1
Slovakia			RSD: 3%	0.017
Norway				0.5

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	M.MAD: 0.26		RSD: 31%	2
Estonia				
Finland			RSD: 4.9% at c=1 μg/l	0.02
Norway				0.2

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	M.MAD: 0.68		RSD: 21%	2
Estonia		0.6		
Finland			RSD: 4.7% at c=1 μg/l	0.03
Latvia			CoV: 0.7%	0.6
Slovakia			RSD: 2.2%	0.004
Netherlands			0.0005	0.002 μmol/l
Norway				0.01

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	M.MAD: 5.9		RSD: 37%	10
Finland			RSD: 4.7% at c=10 µg/l	0.03
Latvia			CoV: 3.1%	0.3
Poland (PL05)	M.MAD: 2.8 µg/l; CoV: 24%	0.2	M.MAD: 0.4; CoV 5.6%	0.2
Slovakia			RSD: 2.2%	1.69
Netherlands			0.014	0.06 µmol/l
Norway				0.1

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

Country	Measurements		Laboratory	
	Precision	**Detection limit, ng/m^3**	**Precision**	**Detection limit**
Slovakia	RSD: 1.9%	0.007 µg/l	CoV: 2.7%	
Netherlands			0.04	0.2 ng/m^3
Norway, NO42		0.03		
NO99				0.02 ng/m^3

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: 7.4%			0.05 µg/l
Latvia		0.02	CoV: 2.9%	1.5 µg/l
Slovakia			RSD: 1.4%	0.009 µg/l
Netherlands			0.01	0.04 ng/m^3
Norway, NO42		0.01		
NO99				0.002 ng/m^3

Table 3.26: Detection limits and precision of chromium in air.

Country	Measurements		Laboratory	
	Precision	**Detection limit, ng/m^3**	**Precision**	**Detection limit**
Slovakia			RSD: 2.4%	0.044 µg/l
Norway, NO42		3		
NO99				0.02 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**
Slovakia			RSD: 2.6%	0.020 µg/l
Norway, NO42		0.01		
NO99				1.1 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
Slovakia			RSD: 1.5%	0.050 µg/l
Norway, NO42		0.02		

Table 3.29: Detection limits and precision of nickel in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Slovakia			RSD: 1.7%	0.090 µg/l
Norway, NO42		0.03		
NO99				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: 4.4%			0.8 µg/l
Latvia		2.39	CoV: 6.8%	0.6 µg/l
Slovakia			RSD: 1.2%	0.09 µg/l
Netherlands			0.06	0.2 ng/m^3
Norway, NO42		0.01		
NO99				0.04 ng/m^3

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

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Lativia		2.1	CoV: 4.6%	42
Slovakia			RSD: 2.1%	1.8 µg/l
Netherlands			3.6	15 ng/m^3
Norway, NO42		0.01		
NO99				1.1 ng/m^3

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

Country	Precision	Detection limit
Germany (PM10)		1 µg/m^3
Slovakia (TSP)	RSD: 1.1%	0.2 µg
Switzerland (PM10)	SD: 5%	1 µg/m^3
Norway (PM10)	SD: 5%	0.2 µg/m^3

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

Compound	**Laboratory detection limit [ppb**			
	Czech Republic	**France**	**Germany**	**Finland**
VOC (general)		0.01	0.01	
Ethane	0.055			0.008
Ethene	0.020			0.009
Ethyne	0.041			0.011
Propane	0.008			0.006
Propene	0.011			0.007
Propyne	0.003			0.004
N-butane	0.003			0.005
2-methyl propane (i-butane)	0.005			0.005
2-methyl propene (i-butene)	0.006			0.006
1-butene	0.009			0.005
Trans-2-butene	0.004			0.005
Cis-2-butene	0.008			0.006
1,3-butadiene	0.009			0.006
N-pentane	0.003			0.005
2-methyl butane (i-pentane)	0.008			0.005
Trans-2-pentene	0.012			0.005
Cis-2-pentene	0.009			0.006
2-methyl pentane	0.003			0.006
3-methyl pentane	0.012			0.006
Isoprene	0.006			0.008
N-hexane	0.011			0.006
Cyclohexane	0.003			0.006
N-heptane	0.023			0.004
Benzene	0.012			0.003
Methyl benzene (toluene)	0.021			0.004
Ethyl benzene	0.019			
1,3-dimethyl benzene (m-xylene)	0.058			
1,2-dimethyl benzene (o-xylene)	0.013			
1,3,5-trimethyl benzene	0.013			
1,2,4-trimethyl benzene	0.007			
2 and 3-methyl pentane (combined areas)	5.8			
		in $\mu g/m^3$		
methanal		0.015		
ethanal		0.06		
propanone		0.3		
propenal		0.008		
propanal		0.01		
butenal +MVK		0.01		
butanal + isobutanal		0.009		
benzaldehyd		0.011		
isopentanal		0.012		
pentanal + o-tolualdehyde		0.016		
m+p tolualdehyde		0.015		
2,5 demethylbenzaldehyde		0.015		
hexanal		0.012		

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

Compound	**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
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	