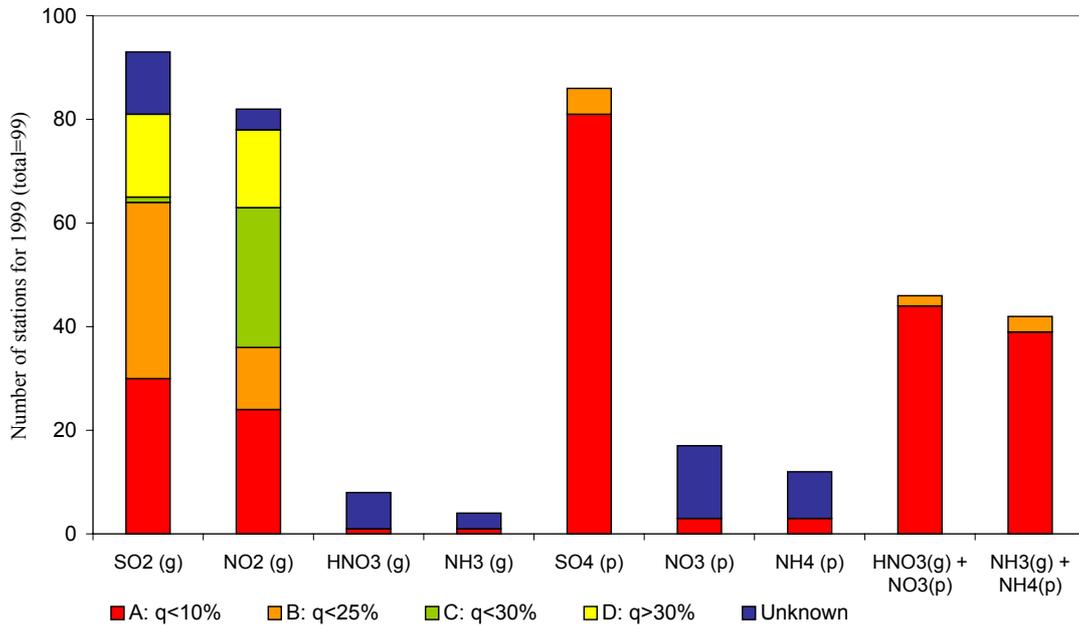


# Data quality 1999, quality assurance, and field comparisons

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Jan Schaug and Sverre Solberg





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

**Data quality 1999, quality assurance,  
and field comparisons**

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## Summary

This report is mainly concerned with the quality of the 1999 data and new results from field comparisons. Reports in this series have in the past focused mostly on components from the acid deposition part of EMEP's measurement programme, but in order to give a broader overview of the quality of data collected, ozone was included last year. This year's report is more comprehensive with respect to the quality of measurements of ozone and VOC, and also gives information on heavy metals.

Like the preceding years 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. 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 ion balance for many countries was within  $\pm 20$  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. This information and the results from laboratory comparisons were used to evaluate the quality of the measurements of main components in precipitation. It is, however emphasized that this does not give an exact assessment of the quality, but rather contains the best judgment based on tests and measurement results. The main message is that the precipitation data quality in general is satisfactory, but that there nevertheless is room for improvements for some components like chloride, magnesium, calcium, and potassium.

A comparison of weekly wet-only measurements with daily bulk measurements is underway in Norway. The results from the first four months show that the differences in the average concentrations are small and not larger than 0.03 concentration units, except for the three marine related components. The wet-only collector gave the highest concentrations and depositions of chloride, sodium, and magnesium.

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.

Results from two field comparisons, carried out in Spain and in Croatia, with measurements of sulphur dioxide, sulphate in aerosols, nitrogen dioxide, and the sum of nitric acid and particulate nitrate are given in this report. The comparison results from Spain cover only the first eight months of the exercise. The comparison of sulphate in particles in Spain shows good results and an excellent agreement during the last part of the comparison that is presented here. The comparison of the sum of nitric acid and nitrate in particles, where Spain applies the recommended method, is well correlated with the reference method during the last part of the period reported here. The results are however too low. The other

results from Spain were not satisfactory, particularly the measurements of sulphur and nitrogen dioxides are in a serious need for improvements. The reasons for the large deviations from the reference method are not clear.

Data from Croatia have not been reported after 1996, and at that time sulphur and nitrogen dioxides only were reported. The comparison results show that there is a need to change to recommended methods for the two components, and that the results obtained with the present methodology are not very useful for EMEP.

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.

Annex 4 contains an overview of the expected data quality for the stations' annual averages in 1999. As emphasized above, this does not give an exact assessment of the quality, but rather contains the best judgment based on tests and measurement results of air and precipitation components.

Laboratory comparisons of air and precipitation samples are reported separately and the results have not been included in this report.

Last year a questionnaire requesting information about the procedures applied for ozone monitoring was distributed. This information has been reexamined this year in order to try to give an estimate of the ozone data quality and to identify areas with need for improvement. The information given by the participants was compared with a set of criteria based on the recommendations in the EMEP manual on maintenance and calibration frequencies, and the use of standards. The results, given in Annex 4, e.g. show that most laboratories make use of transfer standards traceable to NIST, but that the calibration frequency at more than 50 per cent of the sites is lower than recommended. Nearby NO<sub>2</sub> sources also appear to be a rather common problem. The results summarized are based on a limited number of ozone sites only and therefore cannot give a complete picture of the ozone programme within EMEP.

This report also gives an overview of the recent laboratory and field comparisons of hydrocarbons, aldehydes and ketones. Hydrocarbon canister samples collected at Waldhof (DE02) during the first half of 1999 have been analysed both at UBA's laboratory and at the NILU/CCC laboratory. Except for some outliers the time series indicate a good correspondence and satisfactory results for most hydrocarbons. The results obtained for some components like acetylene are remarkably good, but the discrepancies for a few components, which are found at very low concentrations; butenes, xylenes, and ethylbenzene are rather large. Based on the results from this comparison and similar studies, it is proposed to work out a list of hydrocarbons, which the laboratories are able to analyse with good and comparable result, to be reported in the future to EMEP together with precision estimates.

A large number of laboratories took part in a parallel sampling and analysis of hydrocarbons during the EU FP5 project AMOHA. The results show that except

for a few laboratories the agreement is within  $\pm 25$  per cent of the median for light hydrocarbons. Further it is seen that the spread in the results are much less for laboratories using a NPL standard, and that much of the differences seen reflects the use of different calibration gases. When using the same NPL standard the results from the comparison are very satisfactory.

Parallel sampling and analysis of VOC was started in 1997 at Donon (FR08) and ended in 1999. The results from the hydrocarbon part of the comparison have been given in an earlier report in this series, and a brief analysis of the carbonyl results are given here. In one part of the comparison two identical samplers were run in parallel, and the carbonyl samples sent to, and analysed in, the laboratory at EMD and at NILU/CCC. The results show a good agreement for formaldehyde, but the results for other components have clear differences although correlations are seen for most components. For two components NILU/CCC measured all concentrations lower than the detection limit while EMD measured higher results. The results call for more detailed laboratory comparisons of carbonyl samples. One aim could be, as proposed for hydrocarbons, a selection of components which can be analysed with good and comparable results, to be reported to EMEP in the future.

This report emphasizes that the number of VOC monitoring sites still is very small, e.g. aldehydes and ketones are only measured at four sites. The recommendation made at the VOC workshop in Lindau in 1989 included 10–15 measurement sites for VOC.

Laboratory comparisons in 1999 and 2000 of trace metals have been reported separately. The conclusion from the two comparisons is that the results are generally satisfactory.



# **Data quality 1999, quality assurance, and field comparisons**

## **1. Introduction**

The aim of quality assurance is to provide data with sufficiently good and known quality, and this series of reports is intended to document the EMEP data quality and the progress made. The present report is relevant for the 1999 data.

Traditionally this report focused on the acidifying and eutrophying components, but last year ozone was included and this year results from a field comparison for VOC measurements will be presented as well and some comments from the heavy metal laboratory intercalibrations. The aim is include all the information we have on data quality for all the components in the EMEP measurement program. Part 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 inter-comparison and results from field comparisons with reference instrumentation are used for estimating the data quality. Calculations of ion balances in precipitation samples are important supplements to the organised comparisons.

## **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 1999 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 (SE05, SE11, SE12, DK08, CZ01 and LT15). All participating countries, except Iceland and Lithuania had complete measurement programmes for the main components in precipitation in 1999. The data completeness should be at least 90 per cent (Annex 1) and as seen from Table 2 this requirement was broadly met by most participants 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 1999.

	Components	Measurement period	Measurement frequency
Gas	SO <sub>2</sub> , NO <sub>2</sub>	24 hours	daily
	O <sub>3</sub>	hourly means stored	continuously
	Light hydrocarbons C <sub>2</sub> -C <sub>7</sub>	10-15 mins	twice weekly
	Ketones and aldehydes (VOC)	8 hours	twice weekly
	Hg	24 hours	weekly
Particles	SO <sub>4</sub> <sup>2-</sup>	24 hours	daily
	Cd, Pb (first priority), Cu, Zn, As, Cr, Ni (second priority)	weekly	weekly
Gas + particles	HNO <sub>3</sub> (g)+NO <sub>3</sub> <sup>-</sup> (p), NH <sub>3</sub> (g)+NH <sub>4</sub> <sup>+</sup> (p)	24 hours	daily
	POPs (PAH, PCB, HCB, chlordane, lindane, α-HCH, DDT/DDE)	to be decided	to be decided
Precipitation	Amount, SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , pH, NH <sub>4</sub> <sup>+</sup> , Na <sup>+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , K <sup>+</sup> , 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 VOC, heavy metals and POPs are made at a small number of sites only.

It is well known that filter packs normally will give biased results for NO<sub>3</sub><sup>-</sup>, HNO<sub>3</sub>, NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> 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 there are several countries reporting 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 desirable 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. The two rightmost columns in Table 3 give sites which report suspended particulate matter and soot and acidity in airborne particles, neither of which were elements of the measurements programme in 1999.

The monitoring program of VOC is commented in chapter 7.4, but details are found in the VOC measurements report (Solberg et. al 2001). The available data on heavy metals and POP measurements are reported separately (Berg et al., 2001).

Table 2: Completeness for precipitation components, 1999.

Code	mm	mm off	SO <sub>4</sub>	NH <sub>4</sub>	NO <sub>3</sub>	Na	Mg	Cl	Ca	pH	H <sup>+</sup>	K	cond
AT02	100.0	-	99.1	98.7	99.1	98.7	98.7	99.1	98.7	99.9	-	98.7	99.7
AT04	100.0	-	99.5	99.4	99.5	99.4	99.4	99.5	99.4	100.0	-	99.4	99.8
AT05	100.0	-	98.9	98.9	98.9	98.9	98.9	98.9	98.9	100.0	-	98.9	99.7
CH02	99.7	-	98.6	98.6	98.6	98.6	98.6	98.6	98.4	99.5	-	98.6	99.5
CH04	99.7	-	99.4	99.4	99.4	99.4	99.4	99.4	98.4	99.8	-	99.4	99.8
CH05	99.7	-	99.1	99.1	99.1	99.1	99.1	99.1	98.5	99.8	-	99.1	99.8
CZ01	102.2	-	96.0	94.6	96.0	92.6	94.1	94.6	94.1	100.0	-	94.1	100.0
CZ03	100.0	-	93.8	93.7	93.8	93.8	93.8	92.8	93.8	94.3	-	93.7	93.8
DE01	100.0	-	98.6	98.5	98.6	98.6	98.8	98.5	98.8	99.3	-	98.8	99.7
DE02	100.0	-	98.0	97.8	98.0	97.7	97.7	98.0	97.7	98.0	-	97.7	98.0
DE03	100.0	-	98.5	98.2	98.5	98.5	98.4	98.5	98.5	98.7	-	98.2	98.7
DE04	100.0	-	98.4	98.3	98.4	98.4	98.4	98.4	98.4	97.8	-	98.4	97.8
DE05	100.0	-	97.1	97.1	97.1	96.9	96.9	97.1	96.9	97.2	-	96.9	97.2
DE07	100.0	-	97.3	97.3	97.3	97.4	97.4	97.3	97.4	99.3	-	97.4	99.4
DE08	100.0	-	99.3	99.3	99.3	99.2	99.2	99.3	99.2	99.5	-	99.3	99.5
DE09	100.0	-	99.2	99.0	99.2	98.8	98.8	99.2	98.8	99.4	-	98.8	99.4
DK03	49.6	-	98.1	98.6	99.0	97.3	87.5	99.1	97.3	96.9	-	84.0	76.7
DK05	88.5	-	99.6	95.2	99.6	97.9	97.6	99.6	97.3	98.0	-	98.8	98.7
DK08	99.7	-	100.0	100.0	100.0	99.8	100.0	99.8	100.0	100.0	-	100.0	100.0
EE09	100.0	-	98.8	98.0	98.8	96.3	96.2	98.8	96.2	100.0	-	96.3	100.0
EE11	100.0	-	99.5	98.9	99.5	99.0	99.0	99.5	99.0	99.8	-	99.0	100.0
ES01	100.0	-	99.4	98.9	99.4	97.2	97.2	99.4	97.2	99.9	-	97.2	99.7
ES03	100.0	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-	0.0	0.0
ES04	100.0	-	98.6	97.3	98.1	96.5	96.5	98.9	96.5	100.0	-	96.5	99.7
ES05	100.0	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-	0.0	0.0
ES07	100.0	-	99.9	99.3	99.9	98.4	98.4	99.9	98.4	100.0	-	98.4	100.0
ES08	100.0	-	100.0	98.0	100.0	91.7	91.7	100.0	91.7	100.0	-	91.7	100.0
ES09	100.0	-	99.5	98.5	99.4	97.9	97.9	99.5	97.9	99.9	-	97.5	99.9
ES10	100.0	-	100.0	100.0	100.0	98.3	98.3	100.0	100.0	100.0	-	100.0	100.0
ES11	100.0	-	99.9	99.8	99.9	99.6	99.6	99.9	99.6	100.0	-	99.6	99.9
ES12	100.0	-	99.9	99.8	99.9	99.2	99.2	99.9	99.2	100.0	-	99.2	100.0
FI04	100.0	100.0	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.7	-	99.5	99.7
FI09	100.0	100.0	97.0	97.0	97.0	97.0	97.0	97.0	97.0	97.6	-	97.0	97.6
FI17	100.0	100.0	98.3	98.3	98.3	98.3	98.3	98.3	98.3	98.6	-	98.3	98.6
FI22	100.0	100.0	99.4	99.4	99.4	99.4	99.4	99.4	99.4	99.8	-	99.4	99.8
FR03	100.0	-	96.0	96.1	96.0	96.0	96.0	96.0	96.0	96.8	-	96.0	96.8
FR05	100.0	-	88.0	88.1	88.0	88.0	88.0	88.0	88.0	88.8	-	88.0	88.8
FR08	100.0	-	96.4	96.5	96.4	96.4	96.4	96.4	96.4	95.0	-	96.4	97.2
FR09	100.0	-	93.5	93.3	93.5	93.5	93.5	93.5	93.5	93.9	-	93.5	93.9
FR10	100.0	-	92.9	92.9	92.9	92.9	92.9	92.9	92.9	94.1	-	92.9	94.1
FR12	100.0	-	89.7	90.3	89.7	89.7	89.7	89.7	89.7	90.6	-	89.7	90.6
FR13	100.0	-	92.9	93.4	92.9	92.9	92.9	92.9	92.9	94.5	-	92.9	94.5
FR14	100.0	-	92.2	93.0	92.2	92.2	92.2	92.2	92.2	93.4	-	92.2	93.4
GB02	100.0	-	99.7	99.7	99.7	97.6	99.7	97.6	99.7	99.7	-	99.7	99.5
GB06	100.0	-	91.2	91.2	91.2	91.2	91.2	91.2	91.2	91.2	-	91.2	91.2
GB13	100.0	-	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	-	99.8	99.7
GB14	100.0	-	98.4	98.4	98.4	97.5	98.4	97.5	98.4	98.4	-	98.4	98.2
GB15	100.0	-	99.8	99.8	99.8	96.0	99.8	96.0	99.8	99.8	-	99.8	99.6

Table 2, cont.

Code	mm	mm off	SO <sub>4</sub>	NH <sub>4</sub>	NO <sub>3</sub>	Na	Mg	Cl	Ca	pH	H <sup>+</sup>	K	cond
HU02	100.0	100.0	98.5	95.9	98.5	89.0	88.4	98.5	89.0	98.4	-	89.0	98.5
IE02	100.0	-	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.6	-	99.8	99.6
IE03	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.8	-	100.0	99.8
IS02	100.0	-	100.0	-	-	100.0	-	-	-	100.0	-	-	-
IT01	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	48.0	-	100.0	48.0
IT04	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	99.7	-	99.7	99.7	99.7	-	99.7	99.7
LV10	100.0	-	98.9	99.3	98.9	98.9	98.7	98.5	98.9	99.8	-	97.9	99.8
LV16	100.0	-	98.2	99.2	98.3	94.0	96.1	95.0	96.4	99.6	-	96.4	99.5
NL09	100.0	-	95.7	94.4	95.7	92.4	92.2	95.7	92.4	96.2	96.2	92.4	88.8
NO01	100.0	-	98.6	98.6	98.6	98.6	98.5	98.6	96.6	97.5	-	98.6	99.5
NO08	100.0	-	99.3	99.1	99.3	99.3	99.3	99.3	98.8	99.0	-	99.1	99.8
NO15	100.0	-	90.4	89.3	90.2	90.4	90.4	90.4	89.6	90.7	-	89.7	92.6
NO39	100.0	-	99.3	99.3	99.3	99.3	99.3	99.3	99.3	99.9	-	99.3	100.0
NO41	100.0	-	97.9	93.7	97.5	97.9	97.9	97.9	97.5	95.3	-	93.2	99.2
NO55	100.0	-	93.5	88.1	93.3	90.5	93.5	90.5	91.0	90.0	-	90.3	98.0
PL02	100.0	-	98.7	98.6	98.7	98.3	98.3	98.6	98.3	98.7	-	98.2	98.7
PL03	100.0	-	99.0	99.0	99.0	96.1	96.1	99.0	96.1	99.0	-	96.1	99.0
PL04	100.0	-	97.6	97.6	97.6	97.6	97.6	97.6	97.6	97.6	-	97.6	97.6
PL05	100.0	100.0	98.8	100.0	98.8	94.7	94.9	98.8	98.3	99.6	-	99.1	91.7
PT01	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0
PT03	-	100.0	96.5	98.0	98.0	98.0	98.0	98.0	98.0	98.0	-	98.0	98.0
PT04	-	100.0	99.2	99.2	99.2	99.2	99.0	99.2	99.2	100.0	-	99.2	100.0
RU01	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.6	-	100.0	100.0
RU13	100.0	-	100.0	100.0	100.0	100.0	99.9	98.1	99.9	99.6	-	98.1	100.0
RU16	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	100.0
RU18	55.3	-	100.0	99.3	100.0	100.0	100.0	100.0	100.0	99.7	-	100.0	100.0
SE02	100.0	-	97.0	96.7	97.0	97.0	97.0	97.0	97.0	97.8	-	97.0	97.1
SE05	100.0	-	100.0	99.9	100.0	100.0	100.0	100.0	100.0	100.0	-	100.0	99.8
SE11	100.0	-	100.0	99.3	99.3	100.0	100.0	100.0	100.0	100.0	-	100.0	99.9
SE12	100.0	-	99.7	99.6	99.7	99.7	99.7	99.7	99.7	100.0	-	99.7	98.8
SK02	100.0	-	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.0	-	95.5	95.5
SK04	100.0	-	95.7	95.7	95.7	95.6	95.7	95.6	95.7	95.7	-	95.6	95.7
SK05	100.0	-	94.3	94.3	94.3	94.3	94.3	94.3	94.3	94.4	-	94.3	94.4
SK06	100.0	-	94.5	94.5	94.5	94.5	94.5	94.5	94.5	94.5	-	94.5	94.5
TR01	100.0	-	98.6	98.2	98.6	98.7	98.6	98.6	97.5	100.0	-	97.7	100.0
YU05	100.0	-	100.0	100.0	99.7	91.9	91.9	88.3	91.9	100.0	-	91.9	100.0
YU08	100.0	-	100.0	99.9	99.9	99.3	99.3	98.7	99.3	100.0	-	98.3	100.0

Table 3: Completeness of air components, 1999.

Code	SO2	SO4	O3	NO2	HNO3	NO3	sumNO3	NH3	NH4	sumNHx	H+	SPM
AT02	82.2	95.6	95.6	82.2	-	-	-	-	-	-	-	-
AT04	58.9	-	93.2	62.5	-	-	-	-	-	-	-	-
AT05	76.2	-	95.1	80.5	-	-	-	-	-	-	-	-
BE01	-	-	90.6	98.4	-	-	-	-	-	-	-	-
BE32	-	-	92.2	97.8	-	-	-	-	-	-	-	-
BE35	-	-	94.0	96.4	-	-	-	-	-	-	-	-
CH01	98.6	97.0	-	81.6	-	-	-	-	-	-	-	94.0
CH02	97.3	98.9	99.5	96.7	-	-	87.7	-	-	87.9	-	93.7
CH03	100.0	-	99.6	99.2	-	-	-	-	-	-	-	97.5
CH04	96.7	-	96.3	95.3	-	-	-	-	-	-	-	86.6
CH05	98.1	95.1	98.1	97.5	-	-	-	-	-	-	-	98.9
CZ01	99.2	14.5	99.2	87.1	100.0	100.0	100.0	95.6	100.0	95.6	-	-
CZ03	99.7	15.6	96.1	97.5	99.5	100.0	99.5	99.3	100.0	99.2	-	-
DE01	59.5	63.8	94.5	95.9	-	-	-	-	-	-	-	98.1
DE02	96.4	66.3	97.5	99.5	-	-	-	-	-	-	-	98.9
DE03	95.6	66.6	91.6	98.6	-	-	-	-	-	-	-	95.9
DE04	100.0	66.6	61.4	100.0	-	-	-	-	-	-	-	97.8
DE05	100.0	66.6	93.5	100.0	-	-	-	-	-	-	-	100.0
DE07	99.7	66.6	94.8	99.2	-	-	-	-	-	-	-	100.0
DE08	100.0	66.6	95.6	100.0	-	-	-	-	-	-	-	100.0
DE09	100.0	66.6	99.5	100.0	-	-	-	-	-	-	-	99.7
DE12	-	-	89.2	-	-	-	-	-	-	-	-	-
DE17	-	-	88.9	-	-	-	-	-	-	-	-	-
DE26	-	-	94.4	-	-	-	-	-	-	-	-	-
DE31	-	-	15.2	-	-	-	-	-	-	-	-	-
DE35	-	-	95.5	-	-	-	-	-	-	-	-	-
DE38	-	-	38.0	-	-	-	-	-	-	-	-	-
DE39	-	-	94.5	-	-	-	-	-	-	-	-	-
DK03	95.9	97.0	-	-	-	-	97.0	-	-	96.4	-	-
DK05	81.9	81.9	-	-	-	-	81.9	-	-	81.9	-	-
DK08	97.8	97.5	-	100.0	-	-	97.3	97.3	-	97.3	-	-
DK31	-	-	98.0	-	-	-	-	-	-	-	-	-
DK32	-	-	98.4	-	-	-	-	-	-	-	-	-
EE09	97.3	97.8	93.4	86.0	-	-	-	-	-	-	-	-
EE11	92.9	-	89.6	85.2	-	-	-	-	-	-	-	-
ES01	97.0	97.3	91.0	97.8	-	-	99.5	-	97.3	95.9	94.8	95.1
ES03	98.4	92.1	94.6	95.3	-	-	97.5	-	92.1	98.1	81.6	91.8
ES04	90.4	89.9	89.6	91.0	-	-	98.1	-	89.9	95.1	85.8	88.5
ES05	62.5	57.0	94.3	64.1	-	-	53.2	-	57.0	61.1	57.0	55.6
ES07	92.3	91.8	94.3	94.0	-	-	92.3	-	91.5	95.1	67.7	91.2
ES08	92.1	85.8	94.3	91.5	-	-	95.1	-	85.8	91.5	85.5	67.4
ES09	97.3	93.4	91.9	95.9	-	-	97.8	-	93.2	96.4	90.4	89.3
ES10	89.0	94.0	94.0	82.2	-	-	96.2	-	94.0	92.6	89.6	81.1
ES11	72.6	71.2	77.8	67.7	-	-	73.2	-	71.2	72.3	67.9	68.8
ES12	93.4	92.9	94.9	88.2	-	-	93.7	-	92.9	93.4	82.5	91.5
FI04	-	-	-	-	-	-	-	-	-	-	-	-
FI09	98.4	98.1	97.8	97.5	-	-	98.1	-	-	95.6	-	-
FI17	100.0	100.0	94.6	100.0	-	-	100.0	-	-	100.0	-	-
FI22	99.7	99.7	98.1	98.9	-	-	99.7	-	-	98.9	-	-
FI37	98.9	98.4	96.4	95.1	-	-	98.4	-	-	99.7	-	-
FR03	95.9	95.9	-	-	-	-	-	-	-	-	-	-
FR05	96.2	95.9	-	-	-	-	-	-	-	-	-	-
FR08	98.9	98.6	47.7	-	-	-	-	-	-	-	-	-
FR09	78.4	78.4	79.5	-	-	-	-	-	-	-	-	-
FR10	96.4	95.9	83.5	-	-	-	-	-	-	-	-	-

Table 3, cont.

Code	SO2	SO4	O3	NO2	HNO3	NO3	sumNO3	NH3	NH4	sumNHx	H+	SPM
FR12	96.7	95.9	76.1	-	-	-	-	-	-	-	-	-
FR13	96.4	96.4	98.0	-	-	-	-	-	-	-	-	-
FR14	97.3	97.0	95.9	-	-	-	-	-	-	-	-	-
GB02	93.2	92.9	95.5	-	-	-	99.2	-	-	99.7	-	-
GB04	92.9	92.6	-	-	-	-	-	-	-	-	-	-
GB06	99.2	98.1	87.6	-	-	-	-	-	-	-	-	-
GB07	100.0	96.7	-	-	-	-	-	-	-	-	-	-
GB13	88.8	88.5	98.3	-	-	-	-	-	-	-	-	-
GB14	98.4	99.2	99.2	-	-	-	26.3	-	-	26.3	-	-
GB15	100.0	98.9	94.1	-	-	-	-	-	-	-	-	-
GB16	99.5	97.5	-	-	-	-	-	-	-	-	-	-
GB31	-	-	99.1	-	-	-	-	-	-	-	-	-
GB32	-	-	95.5	-	-	-	-	-	-	-	-	-
GB33	-	-	96.8	-	-	-	-	-	-	-	-	-
GB34	-	-	94.4	-	-	-	-	-	-	-	-	-
GB36	-	-	91.1	52.1	-	-	-	-	-	-	-	-
GB37	-	-	97.5	87.1	-	-	-	-	-	-	-	-
GB38	-	-	96.9	63.8	-	-	-	-	-	-	-	-
GB39	-	-	95.1	-	-	-	-	-	-	-	-	-
GB43	-	-	83.7	63.6	-	-	-	-	-	-	-	-
GB44	-	-	98.8	-	-	-	-	-	-	-	-	-
GB45	-	-	95.4	86.3	-	-	-	-	-	-	-	-
GR01	72.6	74.5	81.6	82.2	-	74.8	-	-	-	-	-	-
GR02	-	-	73.0	-	-	-	-	-	-	-	-	-
HU02	95.6	95.9	92.4	95.6	95.6	95.6	95.3	95.6	95.9	93.2	-	-
IE02	91.8	95.6	-	-	-	-	-	-	-	-	-	-
IE03	-	95.9	-	-	-	-	-	-	-	-	-	-
IE31	-	-	99.7	-	-	-	-	-	-	-	-	-
IS02	-	97.8	-	-	-	-	-	-	-	-	-	-
IT01	91.2	91.2	97.7	97.3	91.2	91.2	91.2	91.2	91.2	91.2	-	-
IT04	99.7	99.5	98.1	98.9	-	99.5	-	-	99.5	-	99.5	99.5
LT15	98.6	98.4	81.4	97.5	-	-	98.9	-	-	98.6	-	-
LV10	89.3	89.9	80.8	90.4	-	89.9	89.9	-	89.3	82.5	-	-
LV16	93.7	93.7	-	98.9	-	93.7	94.0	-	96.2	96.2	-	-
NL09	100.0	98.9	99.7	97.8	-	98.9	-	-	98.9	-	-	-
NL10	99.2	99.7	94.3	85.5	-	99.7	-	-	99.7	-	-	-
NO01	99.7	100.0	99.7	100.0	-	-	99.7	-	-	100.0	-	-
NO08	76.4	76.7	-	97.3	-	-	76.2	-	-	76.2	-	-
NO15	99.7	100.0	99.9	97.8	-	-	99.7	-	-	100.0	-	-
NO39	95.9	96.7	99.9	100.0	-	-	95.6	-	-	96.4	-	-
NO41	99.2	99.2	99.8	95.3	-	-	99.2	-	-	99.2	-	-
NO42	99.2	99.2	99.2	-	-	-	99.2	-	-	93.4	-	-
NO43	-	-	99.4	-	-	-	-	-	-	-	-	-
NO45	-	-	99.6	-	-	-	-	-	-	-	-	-
NO48	-	-	99.7	-	-	-	-	-	-	-	-	-
NO52	-	-	99.8	-	-	-	-	-	-	-	-	-
NO55	99.5	99.5	96.8	99.5	-	-	99.5	-	-	99.2	-	-
NO56	-	-	99.7	-	-	-	-	-	-	-	-	-
PL02	97.3	96.7	97.9	93.7	-	97.0	97.3	-	95.9	95.9	-	-
PL03	99.7	99.7	98.2	99.7	-	99.7	99.7	-	99.7	99.7	-	-
PL04	98.6	98.6	98.7	98.4	-	98.6	97.8	-	98.6	98.6	-	-
PL05	74.2	73.2	98.5	73.4	-	-	72.6	-	-	74.8	-	-
PT04	-	-	76.2	-	-	-	-	-	-	-	-	-
RU01	77.0	77.0	-	-	-	77.0	-	-	77.0	76.7	-	-
RU13	-	-	-	-	-	-	-	-	-	-	-	-

Table 3, cont.

Code	SO2	SO4	O3	NO2	HNO3	NO3	sumNO3	NH3	NH4	sumNHx	H+	SPM
RU16	83.6	83.8	98.4	-	-	83.8	-	-	83.8	-	-	-
RU17	-	-	38.5	-	-	-	-	-	-	-	-	-
RU18	47.9	47.9	-	-	-	47.9	-	-	47.9	-	-	-
SE02	93.7	94.0	97.8	96.4	-	-	93.7	-	-	93.4	-	91.8
SE05	99.5	100.0	-	98.9	-	-	99.5	-	-	100.0	-	99.7
SE08	97.3	97.8	-	98.4	-	-	-	-	-	-	-	99.2
SE11	96.2	96.4	98.2	96.4	-	-	96.2	-	-	95.9	-	95.6
SE12	97.8	97.8	91.8	90.7	-	-	96.4	-	-	97.8	-	-
SE13	-	-	99.8	-	-	-	-	-	-	-	-	-
SE32	-	-	95.9	-	-	-	-	-	-	-	-	-
SE35	-	-	99.6	-	-	-	-	-	-	-	-	-
SI08	99.5	99.5	89.1	-	-	-	99.5	-	-	99.5	-	-
SI31	-	-	87.4	-	-	-	-	-	-	-	-	-
SI32	-	-	88.7	-	-	-	-	-	-	-	-	-
SI33	-	-	80.8	-	-	-	-	-	-	-	-	-
SK02	99.2	99.5	62.0	99.2	99.2	99.5	99.2	-	-	-	-	-
SK04	99.5	100.0	93.0	99.7	99.5	100.0	99.5	-	-	-	-	-
SK05	100.0	100.0	-	100.0	100.0	100.0	100.0	-	-	-	-	-
SK06	100.0	99.7	97.6	100.0	100.0	99.7	99.7	-	-	-	-	-
TR01	62.7	63.3	-	61.1	63.0	63.3	63.3	61.6	61.9	63.3	-	-
YU05	51.8	-	-	47.4	-	-	-	-	-	-	-	-
YU08	95.9	-	-	90.4	-	-	-	-	-	-	-	-

### 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 1999 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, United Kingdom and Norway. In other countries e.g. in Denmark and Russia the systematic anion deficit does 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 occur in other networks

in other parts of the world. The current situation with the very poor ion balances for samples with pH above 5 is highly unsatisfactory since we will only have limited information about the consistency of these results. Countries having weakly acidic samples as a larger fraction of their precipitation could supplement their current pH measurements with titration for determining weak acid concentrations, preferably as described in the Manual (EMEP, 1996). Only one sites do 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.

As seen in annex 3, there are various ways of defining the measurement and laboratory precision and detection limits. In addition, it is not always clear whether the values reported are describing the performance of the laboratory or the measurement. This makes the comparisons between countries difficult. The procedures for reporting are defined in the EMEP Manual (EMEP, 1996). To calculate precision in measurements, parallel sampling is necessary and the precision should be given as M.MAD and CoV. 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):

$$M.Mad = \frac{1}{0.6754} \text{median} (|e_i - \text{median}(e_i)|)$$

where  $e_i$  is the error in the two measurements

$$CoV = \frac{M.Mad}{\text{median}(\bar{C})} * 100\%$$

where  $\bar{C}$  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 of SO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>+HNO<sub>3</sub>

### 5.1 Introduction

Since many countries use methods that deviate from the recommended methods for measurements, 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 and the Czech Republic (Schaug et al., 1998; Aas et al., 1999; 2000). Results from Croatia and Spain are presented in this report.

A co-located measurement with reference instrumentation is a very direct method for determining the actual quality of the routinely reported EMEP data. It has been found most informative to carry out the comparisons at one site in each country, 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 about 100 measurements were considered necessary. The reference samples were collected two days every week, or in some cases during one week every month of practical reasons.

### 5.2 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).

### 5.3 Comparison in Zavizan (HR04)

The intercomparison in Zavizan (44°49'N; 14°59'E; 1594 m.a.s.l.) started in September 1999 and continued for one year. Croatia have not reported data to EMEP since 1996 and the aim of this intercomparison was also to determine the concentration level at this site since the methods in use have high detection limits. The methodology for SO<sub>2</sub> in Croatia is TCM absorbing solution with a detection limit of 2.5 µg S/m<sup>3</sup>. From Figure 1 it is seen that all the Croatian data are measured below the detection limit. Technically the concentration is set equal to half the detection limit, 1.25 µg S/m<sup>3</sup>, to give an average estimate. The median remains undetermined. This could have been written in the summary Table 4, but

it would not make the intercomparison results any better. The reference method does measure episode with higher values than the TCM's detection limit; however this is not detected. It is apparent that the method used today is useless at this site.

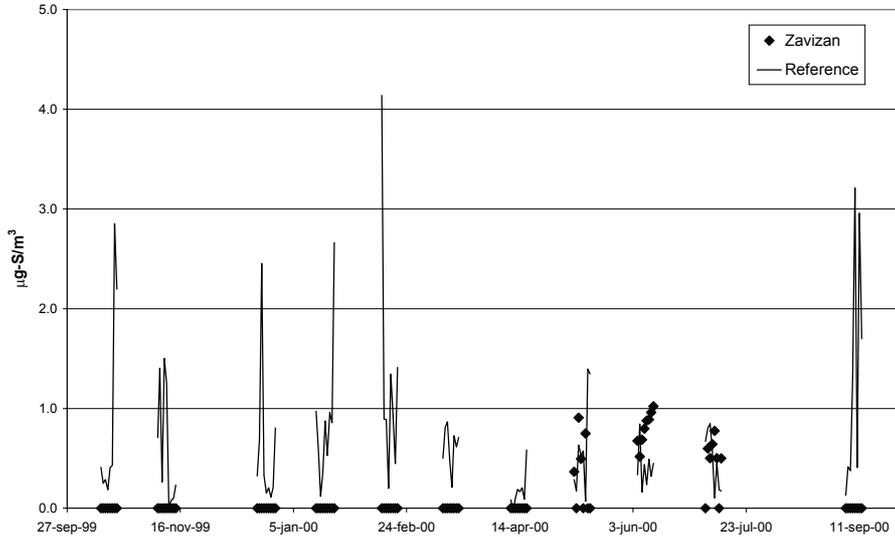


Figure 1: Comparison of measurements at Zavizan with reference sampler; results for sulphur dioxide.

NO<sub>2</sub> is determined using Trietanolamin absorbing solution. The average values are of the same magnitude with a difference of about 30%, but the correlation is poor, see Figure 2, and the method is not appropriate on a EMEP station.

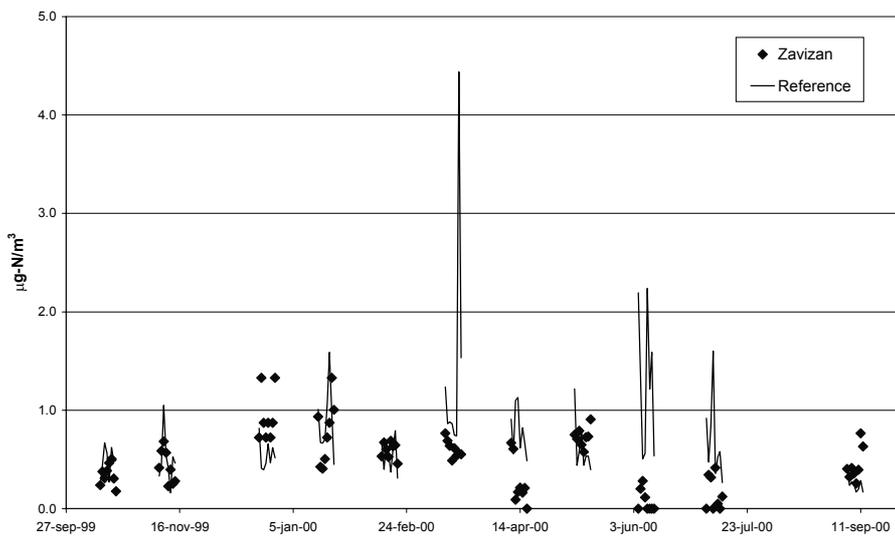


Figure 2: Comparison of measurements at Zavizan with reference sampler; results for nitrogen dioxide.

Table 4: Results of co-located sampling at Zavizan.

Sulphur dioxide (SO <sub>2</sub> -S)	Zavizan		Reference
Average	0.15		0.72
Median	–		0.50
Number of sample pairs		77	
Average difference		0.57	
Median difference		0.36	
M.MAD		0.52	

Nitrogen dioxide (NO <sub>2</sub> -N)	Zavizan		Reference
Average	0.50		0.75
Median	0.53		0.58
Number of sample pairs		74	
Average difference		0.25	
Median difference		0.15	
M.MAD		0.46	

Table 5: Average and median concentration of about 75 samples between September 1999 and September 2000, in µg/m<sup>3</sup>, sampled using EMEP reference methodology.

	SO <sub>2</sub> -S	NO <sub>2</sub> -N	SO <sub>4</sub> -S	(HNO <sub>3</sub> + NO <sub>3</sub> )-N
Average	0.72	0.75	0.66	0.33
Median	0.50	0.58	0.52	0.27

Zavizan station has a good location for an EMEP background station; it is therefore very much in interest that the methods are changed to the reference methods.

#### 5.4 Comparison in Zarra (ES12)

The comparison in Zarra (1°06'W; 39°05'N; 885 m.a.s.l.) started in May 2000 and continued for one year. The analyses and evaluation is not finished, but the main part of the results is presented here. Zarra is a new Spanish EMEP station, and started reporting data to EMEP from 1999. 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<sub>2</sub> and SO<sub>2</sub> are taken care of by MCV, S.A. in Barcelona. For SO<sub>2</sub> the manual method is H<sub>2</sub>O<sub>2</sub> absorbing solution analysed using the Thorin method and the automatic method is UV-fluorescence. NO<sub>2</sub> 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 illustrated in Figure 3–Figure 6. For SO<sub>2</sub> there are big differences between the methods; the manual absorption technique deviates from the reference with many samples below the detection limit, Figure 3. The average is calculated using half the detection limit (0.25 µg/m<sup>3</sup>) for samples below the detection limit, and accidentally this average is similar to the reference methodology; however the median and the M.MAD reveal that the comparison is not satisfactory. The comparison between the monitor and the reference method is better with 8% difference in the annual average, but with a large spread and a CoV of about 60%. This is also seen from Figure 2 with positive and negative systematic errors. The problem for the manual method is not clear, but the long transportation from site to laboratory might be one reason. Earlier field comparisons (Aas et al., 2000) has shown that the H<sub>2</sub>O<sub>2</sub> solution method tends to give too high results, but in addition there must be other factors contributing in a serious way. Since the manual and the automatic methods have been run in parallel for a longer time than this comparison it is recommended to compare the whole data-set to be able to evaluate the results better.

The comparison for particulate sulphate is much better, 11% difference in the total average. The spread is also good with a CoV of 15%, and as seen in Figure 4, and this is mainly due to a few samples in the beginning of the sampling period, the rest of the period shows excellent correlation.

The NO<sub>2</sub> data from Spain have for a long time been suspected to be erroneous, and they have shown very little correlation with the EMEP model. This comparison shows that the official NO<sub>2</sub> data are very poor, Figure 5 and Table 6. In the first part of the comparison the manual absorption techniques gives values far higher than the reference method and in the latter part most data are below the detection limit. This situation is of course highly unsatisfactory and these data are useless to EMEP. The monitor data have a better correlation with the reference method even though the difference is large and with almost 100% difference in the average values and a CoV of about 50%.

The comparison of the total nitrate in air shows good correlation, Figure 6, but there is a systematic deviation in the beginning of the comparison arising in a difference of 33% in the total average value. The comparison in the latter part of the period is, however, very good.

Further conclusions will be presented in the next year report when the evaluation of the whole data set is completed.

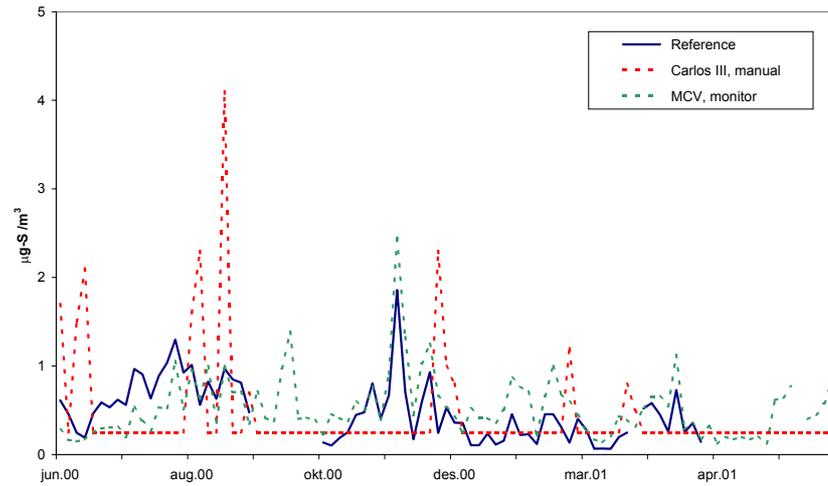


Figure 3: Comparison of measurements at Zarra (ES12) with reference sampler; results for sulphur dioxide.

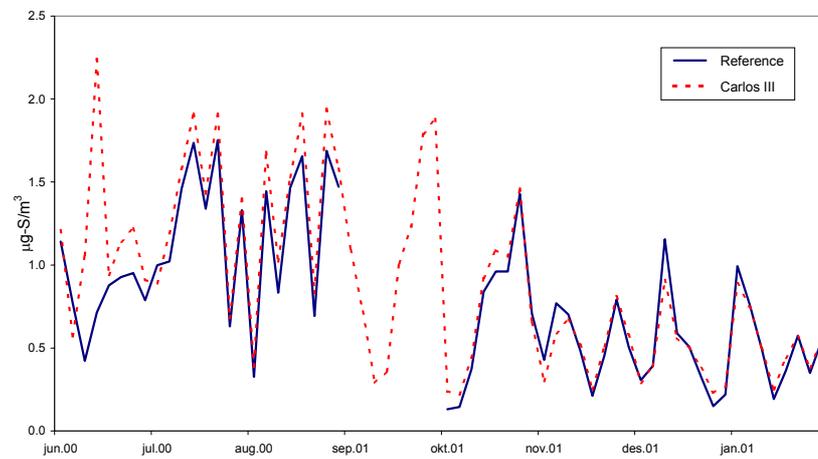


Figure 4: Comparison of measurements at Zarra (ES12) with reference sampler; results for particulate sulphate.

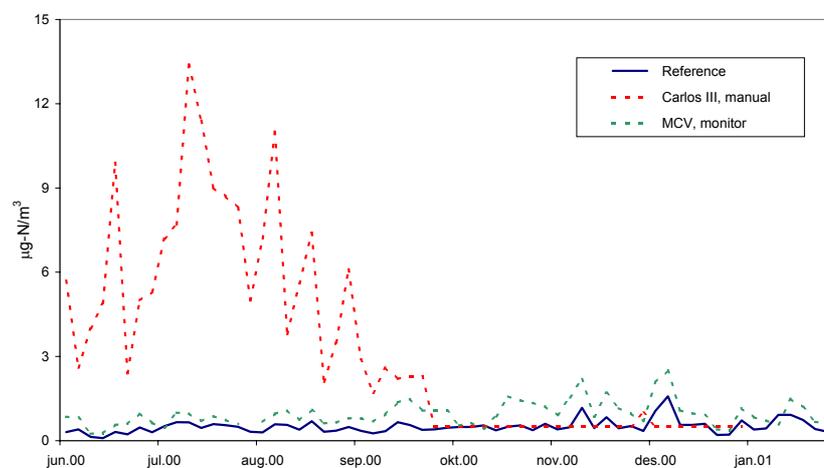


Figure 5: Comparison of measurements at Zarra (ES12) with reference sampler; results for nitrogen dioxide.

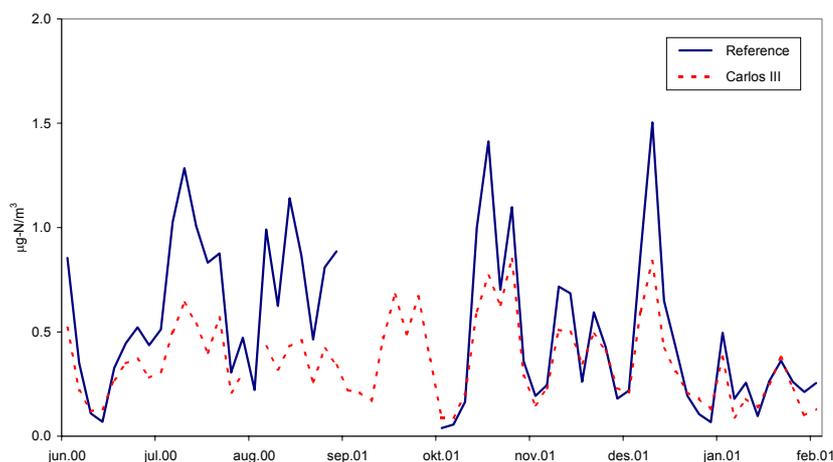


Figure 6: Comparison of measurements at Zarra (ES12) with reference sampler results for sum nitrates.

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

<b>Sulphur dioxide (SO<sub>2</sub>-S)</b>	Carlos III	Ref.	<b>Nitrogen dioxide (NO<sub>2</sub>-N)</b>	Carlos III	Ref.
Average	0.49	0.49	Average	3.30	0.50
Median	0.25	0.46	Median	2.15	0.48
Number of sample pairs		70	Number of sample pairs		56
Average difference		-0.01	Average difference		-2.80
Median difference		0.11	Median difference		-1.64
M.MAD		0.37	M.MAD		2.51
CoV		80%	CoV		520%

<b>Sulphur dioxide (SO<sub>2</sub>-S)</b>	MCV	Ref.	<b>Nitrogen dioxide (NO<sub>2</sub>-N)</b>	MCV	Ref.
Average	0.53	0.49	Average	0.96	0.50
Median	0.44	0.46	Median	0.91	0.48
Number of sample pairs		70	Number of sample pairs		55
Average difference		-0.07	Average difference		-0.47
Median difference		-0.07	Median difference		-0.41
M.MAD		0.28	M.MAD		0.23
CoV		60%	CoV		48%

<b>Sulphate aerosol (SO<sub>4</sub><sup>2-</sup>-S)</b>	Carlos III	Ref.	<b>sum nitrate (HNO<sub>3</sub>+NO<sub>3</sub><sup>-</sup>-N)</b>	Carlos III	Ref.
Average	0.88	0.79	Average	0.35	0.53
Median	0.78	0.74	Median	0.32	0.44
Number of sample pairs		56	Number of sample pairs		56
Average difference		-0.09	Average difference		0.18
Median difference		-0.06	Median difference		0.12
M.MAD		0.11	M.MAD		0.20
CoV		15%	CoV		45%

## 5.5 Comparison between daily bulk and weekly wet only precipitation measurements at Birkenes (NO01)

Since there is now an opening for doing weekly precipitation sampling in EMEP, there has been a need to thoroughly document possible implication of this. For example in the last year report (Aas et al., 2000) results were presented from Košetice where several collectors were compared. The conclusion was that there were no major differences in the average concentration when changing the sampling frequency when using wet-only sampler. This exercise has followed up a similar comparison at Birkenes station in the south of Norway. The bulk collector sampling on a daily frequency will be compared with a wet only from Meteorological Institute Stockholm University (MISU) one year from 1<sup>st</sup> September 2000. The first part of the results are presented here, but the final evaluation will be made in next year's report.

The averages from 1<sup>st</sup> September to 31<sup>st</sup> December and the percentage difference of these are presented in Table 7. There are small differences; all components except magnesium show a difference of less than 10%.

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

Parameter	NILU-RS		MISU		Percent difference	
	Total deposition	Volume weighted conc.	Total deposition	Volume weighted conc.	Total deposition	Volume weighted conc.
mm prec	1510		1642		8.7	
Cl	4701	3.11	5467	3.33	16.3	7.0
NO <sub>3</sub> <sup>-</sup>	714	0.15	773	0.14	8.3	6.8
SO <sub>4</sub> <sup>2-</sup> (tot)	800	1.12	889	1.15	11.1	2.6
SO <sub>4</sub> <sup>2-</sup> (cor)	592	0.74	654	0.74	10.5	0.5
Na <sup>+</sup>	2490	4.21	2805	4.29	12.7	1.9
K <sup>+</sup>	129	0.05	134	0.05	3.8	7.8
Ca <sup>2+</sup>	140	1.09	143	1.07	2.1	1.7
Mg <sup>2+</sup>	308	2.19	354	2.47	15.0	12.7
NH <sub>4</sub> <sup>+</sup>	483	1.57	548	1.55	13.5	1.3

## 6. Results from parallel analysis of VOC

### 6.1 Parallel analysis of hydrocarbons at Waldhof (DE02)

In the first half year of 1999 (until early June) the hydrocarbon canisters sampled at Waldhof were first analysed by UBA's laboratory and then shipped to CCC/NILU for a second analysis. The resulting parallel analyses are shown in Figure 7.

For most components and except for a few outliers, these time series indicate satisfactory results. Except for the data for 7 January the results indicate a close relationship between the two time series for ethene, propane, propene, acetylene, n-butane and i-butane. Also for n-pentane, i-pentane, n-hexane, isoprene, benzene and toluene the relationship indicated by these time series are good except for a

few more outliers. The results indicate a systematic difference in ethane during the first three months, with UBA's data being lower than NILU's, and good agreement after that. For the butenes, ethylbenzene and the xylenes the discrepancies are larger, indicating analytical difficulties for these compounds.

A statistical evaluation of the data is given in Table 8. The statistical parameters include the medians of the data from NILU and UBA and the median differences as well as the modified median absolute difference estimator, M.MAD and the coefficient of variation, CoV, defined as  $CoV = (M.MAD) / (\text{NILU's median})$ . In order to obtain CoV in per cent, as in Table 6, the figures in Table 8 must be multiplied with 100. The analyses from the laboratory at CCC/NILU were regarded the reference in these calculations.

As recommended (EMEP, 1996) some extremes were removed from the statistical analyses, thus the statistical results for o-xylene and ethylbenzene are not really representative as most of the analyses turned out to be highly different between the two laboratories.

The statistical calculations show that the CoV is less than 15% for a number of compounds. However, for ethene and propene the CoV is rather high even though the time series indicate a good agreement. The reason for this is probably that the concentrations span a wide range whereas the medians are low compared to the high values.

The conclusion from this evaluation is that for many of the components the agreement is satisfactory (and for some, as acetylene, remarkably good). The reason for the analytical problems with some of the aromats and alkenes should be studied further. The reason for the few outliers (i.e. totally different results between the laboratories) should also be cleared out. Based on such an evaluation supplied with similar studies for other laboratories, a list of selected hydrocarbons to report in the future accompanied with estimates of the total precision of each single component should be agreed on.

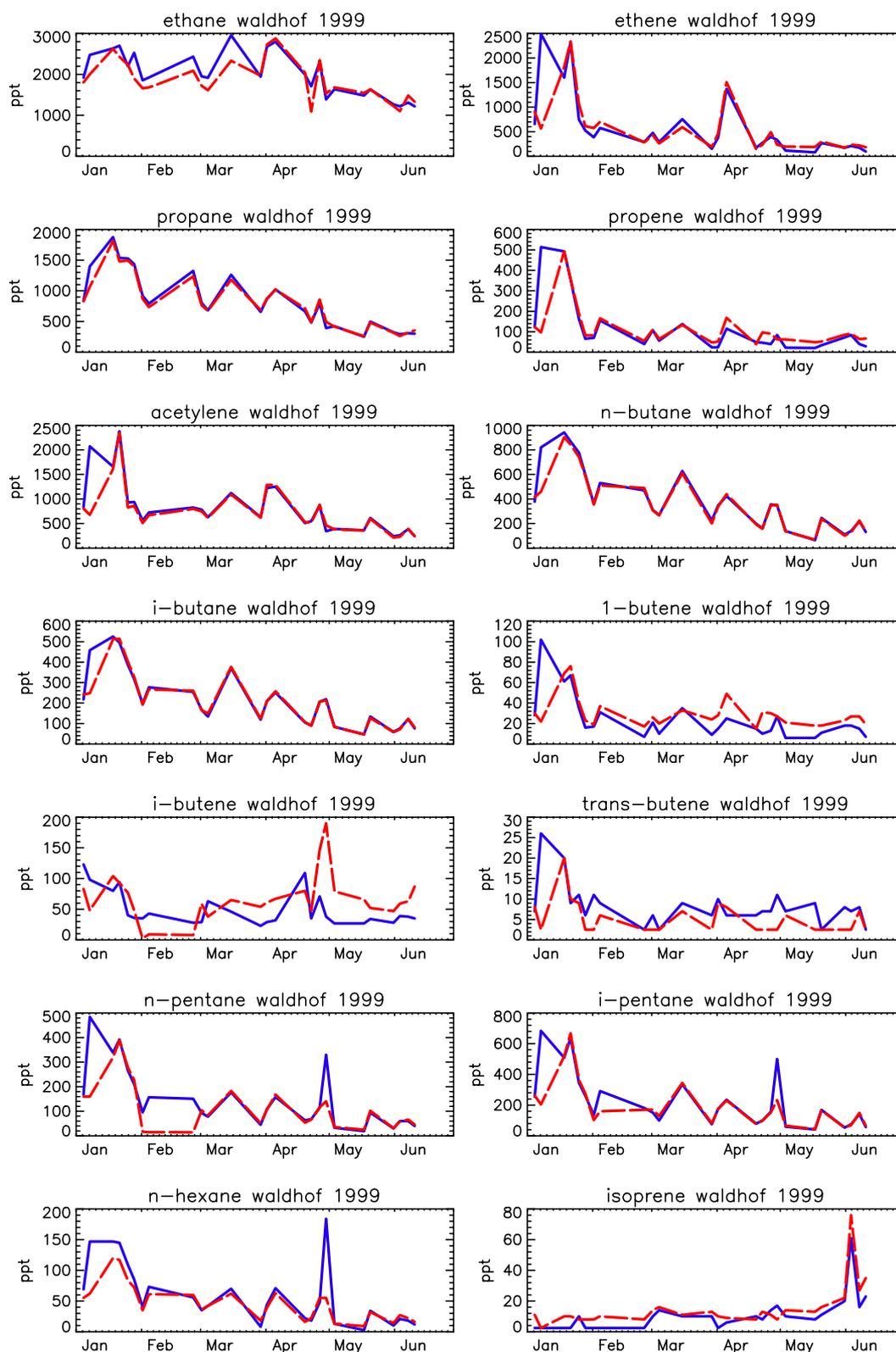


Figure 7: Results of parallel analyses of hydrocarbons at Waldhof in January – June 1999. Red dashed line marks canisters analysed by UBA. Blue full line marks the same canisters subsequently analysed by CCC/NILU. Unit: pptv.

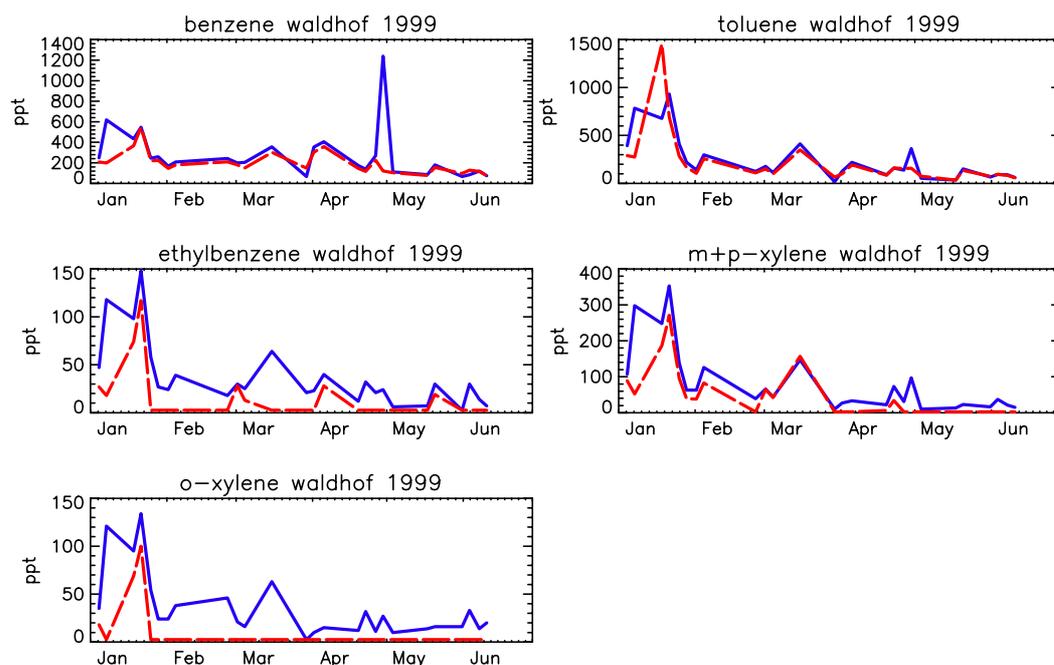


Figure 2, cont.

Table 8: Results from parallel analyses of hydrocarbons at Waldhof (DE02) during Jan-June 1999. Concentrations in ppt.

	median NILU	median UBA	median difference	M.MAD	CoV
ethane	1934	1765	-26.5	187	0.097
ethene	356	364	45.0	100	0.281
propane	793	748	-8.0	46.7	0.059
propene	68	84	14.0	18.5	0.273
acetylene	679	645	-27.0	33.4	0.049
n-butane	348	343	-6.5	15.6	0.045
i-butane	202	200	0.5	8.15	0.040
1-butene	16.5	26.5	8.5	5.19	0.314
i-butene	38.0	63.0	20.0	25.2	0.663
trans-butene	7.0	2.5	-2.0	2.97	0.424
n-pentane	95	103	2.0	6.67	0.071
i-pentane	163	163	0.5	12.6	0.077
n-hexane	43.0	40.5	-3.5	11.1	0.259
isoprene	10.0	11.0	5.0	3.71	0.371
benzene	205	179	-27.0	28.2	0.137
toluene	145	144	-16.0	31.9	0.220
ethylbenzene	27.5	15.5	-11.3	10.7	0.391
m-xylene	64.5	40.5	-17.0	18.2	0.282
o-xylene	14.5	2.5	-12.0	4.45	0.307

## 6.2 Parallel analysis of carbonyls at Donon (FR08)

Parallel sampling and analyses of VOC have been carried out at Donon, since the French laboratory at EMD (Ecole Mines des Douai) started VOC sampling in 1997. The parallels of hydrocarbons were ended in 1998, whereas the parallels of carbonyl compounds continued until mid April 1999 when CCC/NILU's sampling was ended. In 1999 the parallel measurements were carried out by using both parallel sampling and parallel analyses. Separate sampling devices and DNPH cartridges were mounted and the samples were taken for the same time periods. The exposed cartridges were then shipped to the responsible laboratories which analysed them independently.

The time series of the carbonyls analysed by NILU and EMD are given in Figure 8 and a statistical evaluation of the parallel data are given in Table 9, similar to the statistical evaluation for hydrocarbons at Waldhof in the previous section. The results from the laboratory at CCC/NILU were regarded the reference in these calculations as well.

One outlier was taken out of the statistical calculations for each of propanal, benzaldehyde and glyoxal although they are shown in Figure 8. The time series clearly shows best agreement between the two laboratories for formaldehyde. For other compounds the differences are larger although a clear correlation is seen for most of the components. For some compounds the comparison is not possible as different detection limits obviously have been applied by the two laboratories. This regards in particular methyl vinyl ketone and methacrolein. All NILU's data for methacrolein were below detection limit and this compound was thus let out of the statistical analyses. However, also for propenal, butanal, benzaldehyde and glyoxal a large number of the samples from the laboratory at CCC/NILU were flagged as below detection limit, whereas data values were provided by the French laboratory for the same days.

The results show higher values when measured by CCC/NILU than by EMD for formaldehyde, acetaldehyde, acetone and butanone. The CoV are smallest for hexanal, formaldehyde and butanone which all are below 15%. For the other compounds the CoV s in the range 15-100%. The precision of the carbonyl measurements (sampling and analyses) by NILU's laboratory on its own has been previously estimated at better than 15% for most compounds based on parallel sampling and analyses at Birkenes (NO01) (Solberg et. al, 1996b and 1998). It is of course not surprising that the differences are larger when using different sampling tubes and different laboratories.

Based on these results it is recommended to carry out a more detailed laboratory intercomparison for carbonyls taking into account all previous results for parallel sampling as well. As for the hydrocarbons, the aim should be to agree on detection limits and the selection of individual components to report to EMEP in the future.

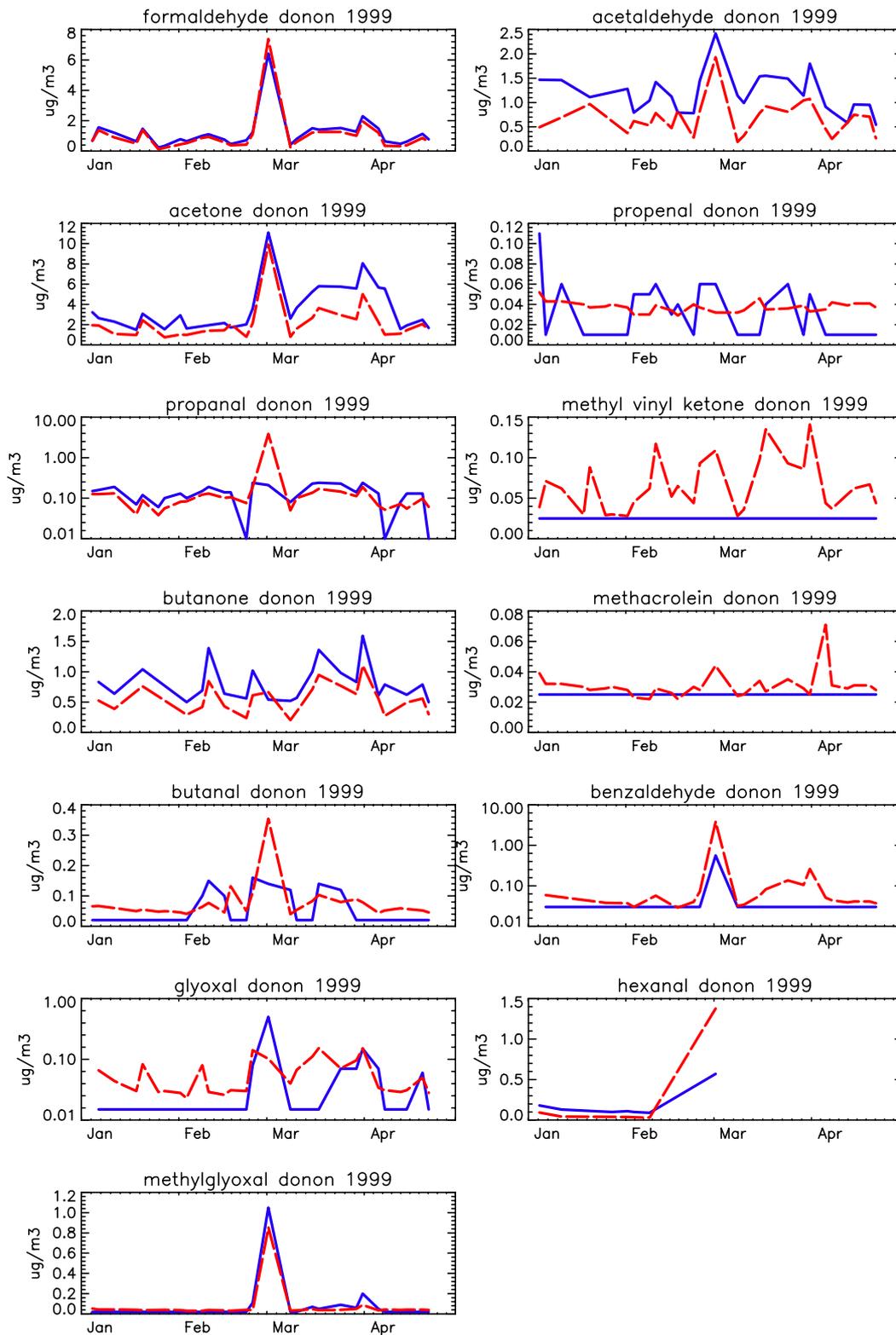


Figure 8: Results of parallel sampling and analyses of carbonyl compounds at Donon by NILU (blue full line) and EMD (red dashed line) in January–April 1999. Note the logarithmic axis for propanal, benzaldehyde and glyoxal (due to outliers for these compounds).

Table 9: Results from parallel sampling and analyses of carbonyl compounds at Donon (FR08) during Jan-April 1999.

	median NILU	median EMD	median difference	M.MAD	CoV
formaldehyde	0.800	0.690	-0.177	0.104	0.130
acetaldehyde	1.120	0.692	-0.561	0.291	0.259
acetone	2.625	1.529	-1.197	1.027	0.391
propenal	0.010	0.037	0.025	0.010	1.038
propanal	0.130	0.099	-0.033	0.025	0.194
mvk	0.025	0.062	0.037	0.037	1.483
butanone	0.740	0.540	-0.262	0.085	0.115
butanal	0.020	0.057	0.030	0.015	0.741
benzaldehyde	0.030	0.041	0.011	0.014	0.469
glyoxal	0.015	0.034	0.015	0.015	0.988
hexanal	0.110	0.040	-0.066	0.010	0.094
methylglyoxal	0.020	0.039	0.017	0.007	0.371

### 6.3 Results from the AMOHA project

In the EU FP5 project AMOHA (Accurate Measurements of Hydrocarbons in the Atmosphere) a large number of laboratories in Europe participated in parallel sampling and analyses of hydrocarbons in ambient air. Main results from the three different sampling periods (different times of the day) are shown in Figure 9 – Figure 11. The results show that except for a few laboratories the agreement is within  $\pm 25\%$  of the median for the lighter alkanes. For some aromats and unsaturated hydrocarbons as well as the C6-C7 alkanes a large spread in the values are seen, indicating measurement difficulties with these compounds. The spread in the results were, however, much less for laboratories using a NPL standard for calibration. This is seen in Figure 12 which shows the results from sampling period 2 only for the sites which use the same NPL standard for calibration. Thus, it may be concluded that a large part of the differences seen among the laboratories reflects the use of different calibration gases. When using the same NPL standard the results from this intercomparison are very satisfactory.

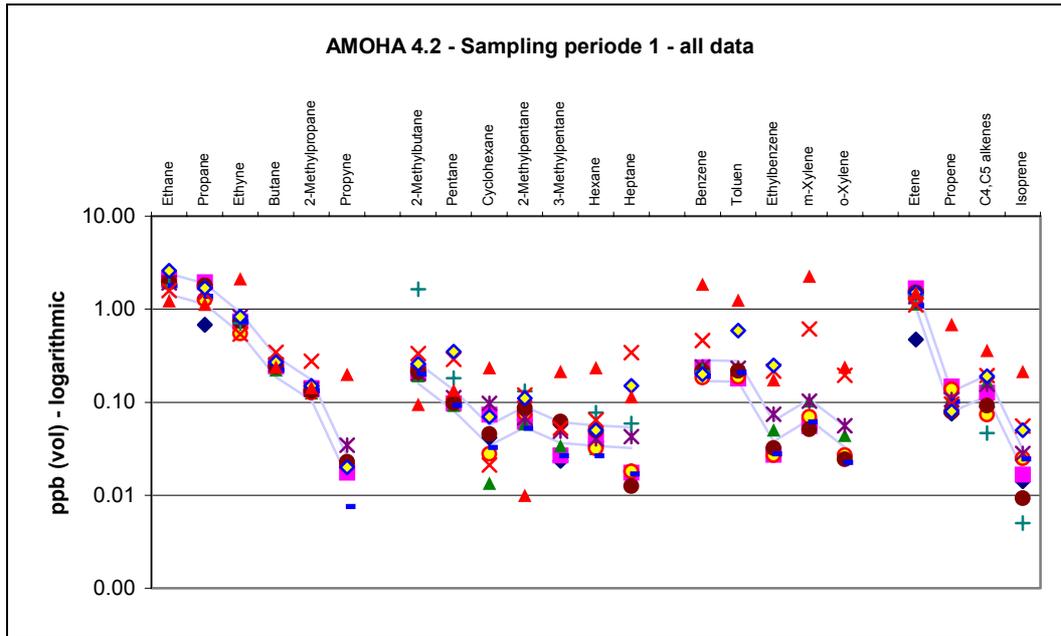


Figure 9: Results of the hydrocarbon measurement intercomparison (sampling period 1) in the EU FP5 project AMOHA. The symbols mark the average results from individual laboratories for a wide range of individual species given on top of the panel. The blue lines mark the median  $\pm$  25%.

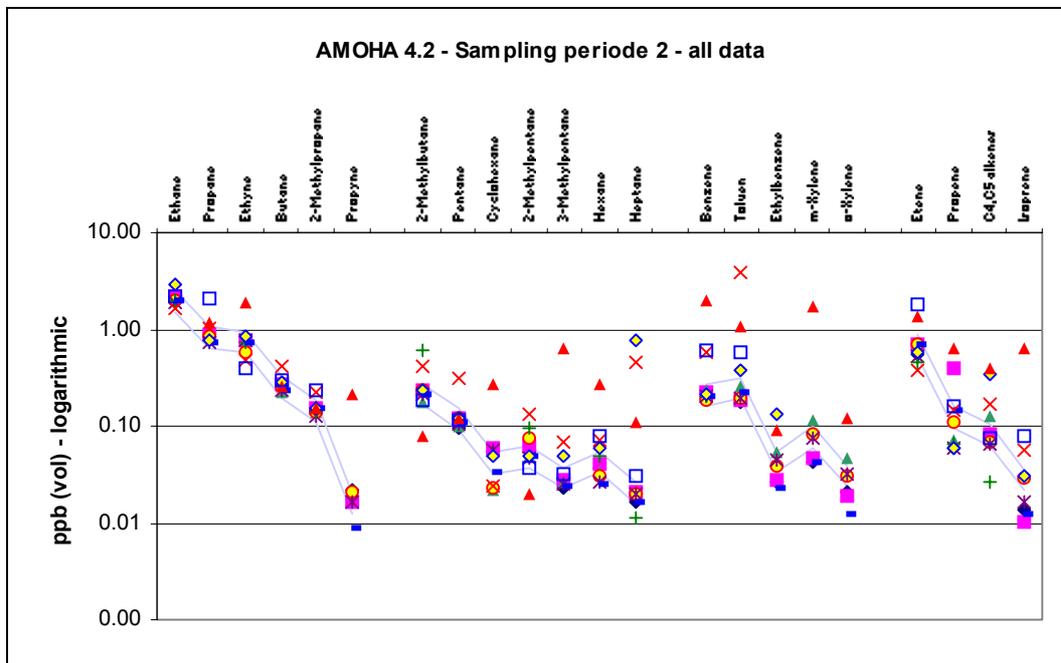


Figure 10: Same as Figure 9 for sampling period 2.

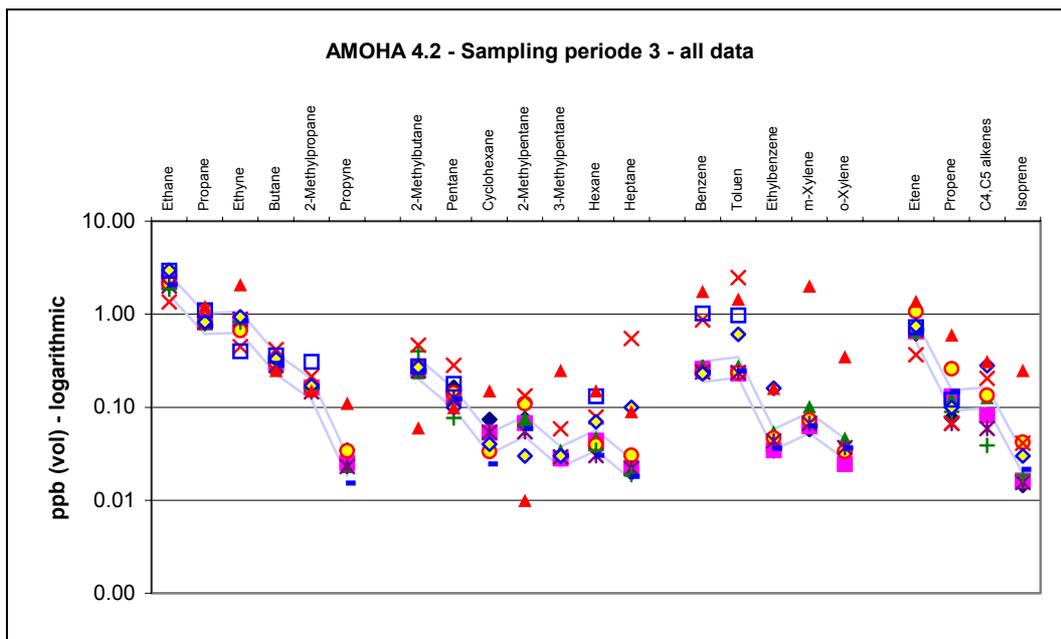


Figure 11: Same as Figure 9 for sampling period 3.

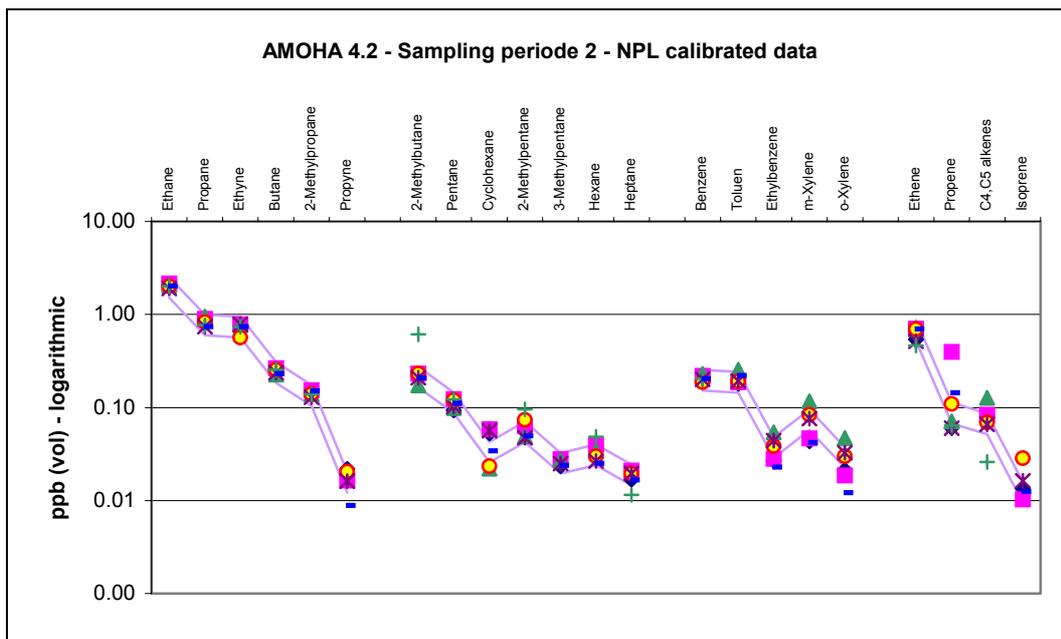


Figure 12: Same results as in Figure 10, but only for the laboratories which use a standard gas from NPL for calibration.

## 7. Quality of the 1999 measurements

### 7.1 Acid deposition components

The performance of the laboratories has been evaluated on the basis of the results obtained in the laboratory comparisons 17 and 18 from 1999 and 2000 (Hanssen and Skjelmoen, 2001 and Uggerud et al., 2001), which are the most relevant comparisons for the 1999 measurements. The laboratory comparisons contained the main components in precipitation, and comparison No. 17 also as usual samples for sulphur dioxide (impregnated filter and absorbing solution), nitrogen dioxide and sulphate samples on filter. Air samples were not included in the 18<sup>th</sup> comparison, this occurred due to a mistake only and air samples will be included in future laboratory comparisons. These will also be extended with filter samples of nitrate and ammonium.

The recommended EMEP methods have been given in the Manual (1996), and most participants make use of these. It is, however, a number of other methods in use in EMEP of different reasons, such as a lack of adequate equipment or sufficient funding, extraordinary long data series obtained with other methods which need careful parallel measurements with the new method over a long period before the old method can be replaced, or simply good experience with other methods and therefore a reluctance to change to the recommended ones.

The EMEP laboratory comparisons include samples for the recommended methods only; countries with alternative methods are consequently not tested in these exercises. The performance of the other measurements methods and the comparability with the recommended ones is a crucial point, and field comparisons have been organized for this reason.

Laboratories in the Czech Republic, Switzerland and Germany are using the XRF-method; samples for X-ray fluorescence are no longer included in the comparisons and these laboratories are consequently not tested for this component in the laboratory comparisons. Croatia, Germany and Yugoslavia use the TCM method for sulphur dioxide, which is not included in the comparisons. The TCM method has been compared with the recommended method (KOH impregnated filters) in field comparisons both in Germany and in Turkey (poster presentation at the Dubrovnik workshop, 1999). Based on the discouraging results obtained for the TCM method at today's concentration levels, Turkey today uses impregnated filter and Germany is in a process changing to the recommended method. Some laboratories use monitors giving continuous sulphur dioxide and nitrogen dioxide. For sulphur dioxide both very good and poor results have been obtained in field comparisons with the recommended method. It seems that the sulphur dioxide monitors are demanding with respect to calibration and maintenance, and the detection limit is higher than for the recommended method. There is a clear need to do more comparisons at different concentrations level, and for the time being the data quality is rated as "Unknown". Nitrogen dioxide monitors are not completely specific for this component; the exception being the type of monitor applied at Jungfraujoch in Switzerland (Cranox).

Netherlands has reported SO<sub>2</sub> data with very low precision. The detection limit is very high 1.5 µg S/m<sup>3</sup> and these data are therefore not satisfactory for EMEP.

Results from field comparisons have been used in addition to the laboratory comparisons to evaluate the 1999 data quality. A summary of the field comparisons carried out during the second half of the nineties is given in last year quality report (Aas et al., 2000). Besides the results from comparisons, plots of ion balance versus pH and the sum of concentration in precipitation (Annex 2) give strong indications about the data quality

The Annex 4 (Table 4.1) contains the results of the evaluation of the data quality with "A" indicating an expected accuracy in annual average better  $\pm 10\%$ , B  $< \pm 25\%$ , C  $< \pm 30\%$ , and D  $> \pm 30\%$ . "U" means an unknown quality due to a lack of documented comparisons with reference methods. It should be noted that the use of "U" and "D" is different from earlier reports where both a low quality and an unknown quality were contained in "D".

It should be emphasized that the present Tables do not give an exact assessment of data quality, but contain the best judgement based on tests and results.

An European wide overview of the 1999 data quality for the EMEP precipitation and air measurement networks is given in Figure 13 and Figure 14. The figures show the total number of stations for each component that has been included in the five different categories. In general the EMEP precipitation measurements are satisfactory. Nevertheless, the measurement quality of especially Cl, Mg, Ca and K can be improved at many sites.

Air components on the other hand have various qualities and particularly the quality of SO<sub>2</sub> and NO<sub>2</sub> measurements is variable. The main reasons for these variations are the different methodologies used; a further harmonization is therefore essential. From Figure 14 it is also very clear that many sites measure less than a full measurement program, especially the nitrogen part is incomplete. There are also very few countries using denuders for separating the gaseous and particulate compounds, and that is the reason that most of this data is classified as unknown.

This exercise was also carried out for the 1997 data (Tarrason and Schaug, 1999), and when comparing the results some differences are seen. There are more stations in 1999 (99) against 93 in 1997; the quality of the sulphate, ammonium (sum of ammonium in air) and nitrate (sum of nitrate in air) in both air and precipitation has improved, but the quality of the chloride and potassium measurements has somewhat decreased.

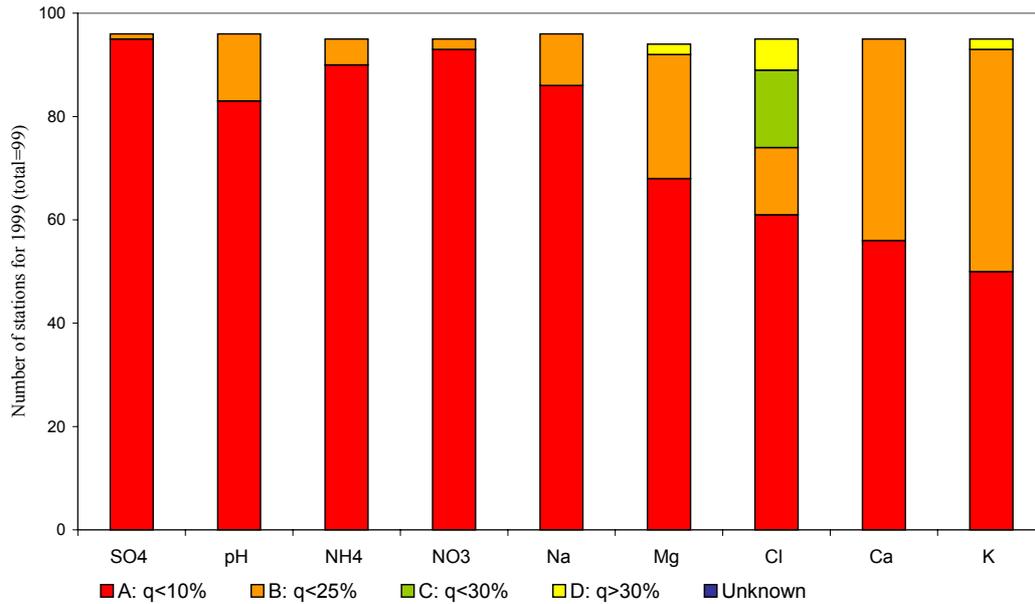


Figure 13: Classification of the 1999 precipitation data measurements.

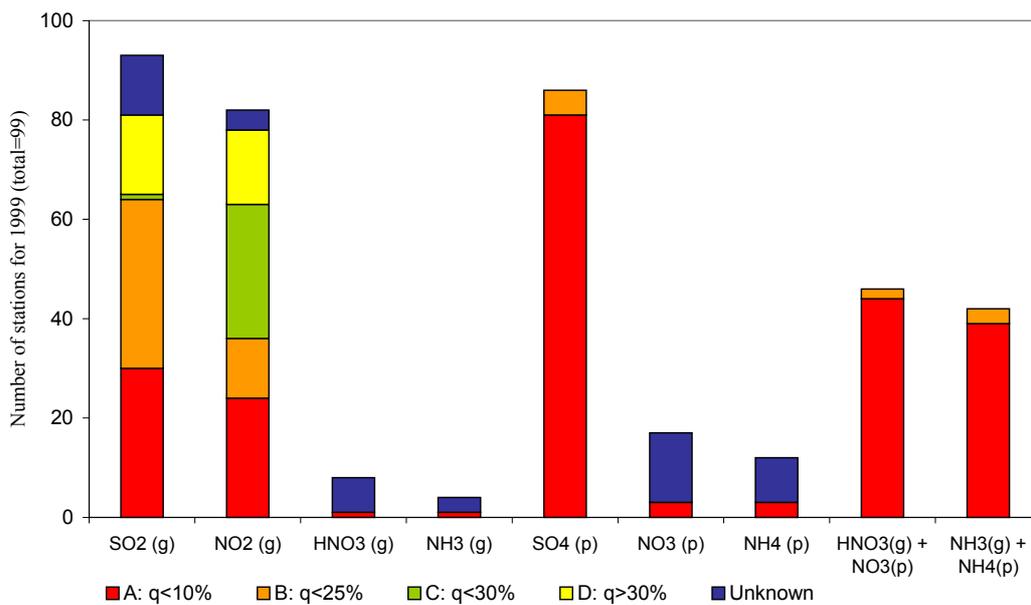


Figure 14: Classification of the 1999 air data measurements.

## 7.2 Ozone

A questionnaire requesting information about the applied procedures for ozone monitoring was distributed within EMEP last year. Summaries of local surroundings and emission sources of  $\text{NO}_x$  were also requested. This information was included in the data quality report last year (Aas et al., 2000) both in a complete version and as a summary table.

This year the same information was reviewed with reference to specified recommendations on ozone measurements given in the EMEP manual (EMEP, 1996) or elsewhere. The aim of this year's review was to identify areas for improvement as well as to give a general overview of the quality of the ozone-monitoring network for end users of this data. The information supplied by the laboratories was evaluated against the set of criteria given in Table 10 and the result for the reported stations are given in the Annex 4, Table 4.2. Note that this is entirely based on the information supplied in 2000, no updates or additions were asked for.

Criteria for calibration procedures and standards were based on the recommendations in the EMEP manual (EMEP, 1996). The EMEP manual does, however, not give quantitative requirements to the maintenance procedures, which should be in accordance with the producer's specifications, or better. The requirements to the maintenance procedures in Table 10 are based on CCC's view only; the producer's specifications may be different for different monitors. This should be kept in mind when using the results. Furthermore, the evaluation of local NO<sub>x</sub> sources is highly uncertain as it depends to a large extent on how this information is supplied from the local laboratories. More information is given in last year's data quality report (Aas et al., 2000). The questionnaire also asked for information on instrumentation and data validation. This turned out to be well taken care of in all countries and is not included.

The results are self-explaining, a few remarks may nevertheless be made; this evaluation identifies violations with the applied criteria in several ways; quality assurance procedures applied less frequent than the recommendations are seen at many stations both for calibration and maintenance procedures. This does not necessarily indicate poor data quality, but rather an elevated risk for technical errors and losing data.

*Table 10: The criteria used to evaluate the information supplied by the laboratories in the questionnaire in 2000 regarding ozone monitoring.*

Maintenance	Inlet filter exchange interval	3 months
	Leak test interval	3 months
	Freq. of checking the pressure transducer	1 year
	Freq. of checking the scrubber performance	1 year
Calibration	Freq. of zero and span checks	2 weeks
	Frequency of calibration against transfer standard	3 months
Standards	Is the transfer standard traceable to a NIST SRP?	Yes
	Freq. of calibration of transfer standard with NIST SRP	1 year

The results of the questionnaire for QA procedures for ozone as given in Table 10 and are summarized in Figure 15 indicating to what extent the applied procedures follow the recommendations within the EMEP ozone monitoring network. This shows that the recommended procedures for calibration are violated at many (more than 50%) of the sites. This reflects that local laboratories calibrate their monitors less frequent than the recommended 3 months interval. Furthermore,

problems of local NO<sub>x</sub> emissions are also a rather common problem. On the other hand, most laboratories use transfer standards which are traceable to a NIST standard. It should be noted that the results summarized in Figure 15 are based on a limited number of the ozone monitoring sites and is therefore not giving the complete picture of the ozone program within EMEP. Data for German sites are lacking and information of the local NO<sub>x</sub> sources at most UK sites were not supplied either. As mentioned elsewhere, the discrepancy relative to recommended procedures does not necessarily indicate poor data quality, but rather an increased risk of failures in the monitoring.

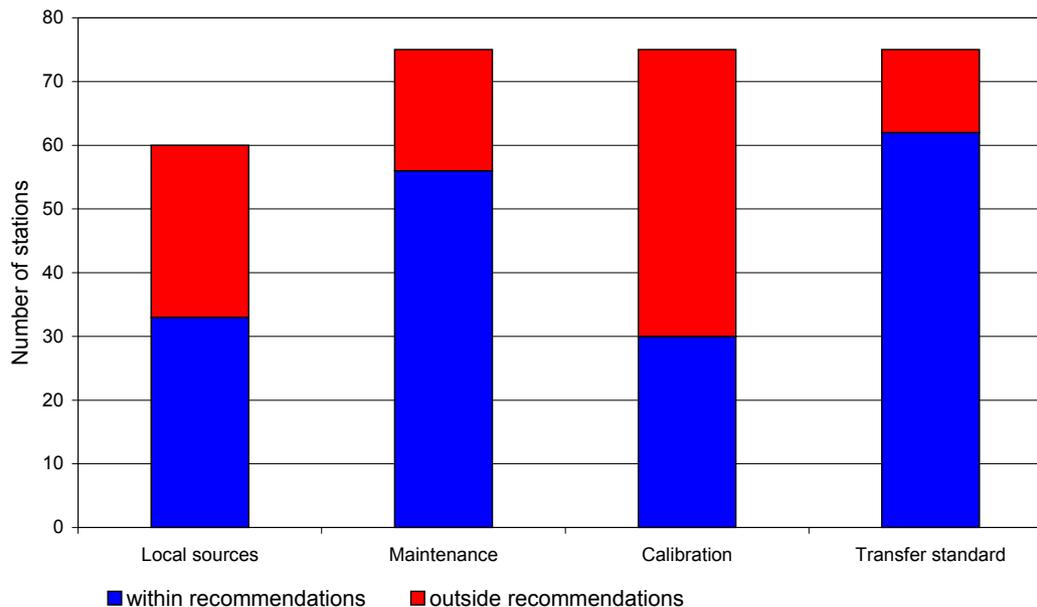


Figure 15: Classification of the 1999 ozone data measurements.

### 7.3 Heavy metals

From 1999 heavy metals have been a part of EMEP's measurement programme, and as a part of the quality assurance, analytical intercomparisons will be carried out on annual basis.

The laboratory intercomparisons in 1999 and 2000 are found in separate EMEP reports (Berg and Aas, 2000; Uggerud and Berg, 2001). Both of these are relevant for the data quality for the 1999 data.

The conclusion from the intercalibration in 1999 was that the analytical results were generally satisfactory. The results showed the following order of success: Cr > Pb > As > Cu > Cd > Ni > Zn. For all samples analysed the deviations from the theoretical values were calculated. The median deviations including all the laboratories were below 27% for all elements and concentration levels, but for the high concentration samples the average deviations were below 10%. It should be emphasised that most laboratories involved measure mainly concentrations similar to the high concentration samples in their monitoring networks, and are therefore less experienced with low concentrations. In the comparison performed in 2000,

the results were similar with Pb and Cr as the best elements and most problems with Cd.

An evaluation of the individual laboratories and methodology used will be done in future reports, similar as for the main components described in chapter 7.1.

#### 7.4 VOC

As indicated by Table 11, data for 11 measurement sites for VOC have been reported to CCC and 4 of these included ketones/aldehydes. These were also sampled at the Zeppelin Mountain (NO42) station in 1999, but the data were not available for publication. VOC measurements were started at Peyrusse Vieille (FR13) in France in July 1999.

*Table 11: Status of the VOC monitoring programme in 1999. The columns give the station names, site code, and the sampling frequencies for hydrocarbons (HC) and carbonyl compounds (Carb). The laboratory responsible for the chemical analyses is also given. Additional laboratories taking part in parallel measurements are indicated in parenthesis.*

Station	Code	HC <sup>1)</sup>	Lab. <sup>2)</sup>	Carb <sup>1)</sup>	Lab. <sup>2)</sup>	Comments
Zeppelin	NO042	Reg.	NILU			Only the first half year
Pallas	FI096	Reg.	FMI	n.m.	-	
Utö	FI009	Reg.	FMI	n.m.	-	(Carbonyl sampling started in April 2000)
Birkenes	NO001	Reg.	NILU	Reg.	NILU	
Waldhof	DE002	Reg.	UBA (NILU)	Reg.	NILU (UBA)	Parallel analyses of hydrocarbons first half year. Parallel analyses of carbonyls during all of 1999.
Schmücke	DE008	Reg.	UBA	n.m.	-	
Košetice	CS003	Reg.	CHMI	Reg.	NILU	
Starina	SK006	Reg.	SHMI	n.m.	-	
Donon	FR008	Reg.	EMD	Reg.	EMD (NILU)	Parallel analysis of carbonyls January-April
Peyrusse Vieille	FR013	Reg.	EMD	n.m.	-	Sampling of HC started in July. Sampling of carbonyls started in 2000.
Tänikon	CH003	Con.	EMPA	n.m.	-	

1) Reg. = regularly, Con. = continuous, n.m. = not measured.

2) NILU = Norwegian Institute for Air Research  
 FMI = Finnish Meteorological Institute  
 UBA = Umweltbundesamt  
 CHMI = Czech Hydrometeorological Institute  
 SHMI = Slovak Hydrometeorological Institute  
 EMD = Ecole des Mines de Douai (France)  
 EMPA = Swiss Federal Lab. for Materials Testing and Research

Extensive parallel sampling is carried out when the responsibility for chemical analyses are transferred to local laboratories. Long-term parallel sampling and/or analyses have been carried out at Starina (SK06), Košetice (CZ03), Waldhof

(DE02) and Donon (FR08) when the national laboratories took over the responsibility of the measurements. Thus, in 1999 there were no parallel measurements at Košetice or Starina, while at Donon and Waldhof the parallel analyses were carried out during the first part of the year only.

As in previous years, EMPA kindly shared their results from the continuous hydrocarbon monitoring at Tänikon with EMEP. A detailed comparison between the continuous monitoring and grab sampling at Tänikon was given by Solberg et al. (1996 and 1997).

Table 12 gives the sampling frequencies and the data coverage. The term 'raw data' refers to the total number of samples reported to the CCC, and the fraction of rejected data is relative to this number. Note that 'rejected data' in this context refers to samples which are classified as outliers and rejected by inspection of the CCC. Outliers may arise due to either local pollution episodes close to the monitoring site, contamination of the samples or errors in the chemical analyses. Normally the responsible laboratory removes samples which are wrong due to technical problems, thus there is always a screening (and rejection of samples) prior to the outlier detection carried out by the CCC.

*Table 12: The number of samples of hydrocarbons (HC) and carbonyls (Carb) in 1999 available to NILU/CCC, relative to a recommendation of two samples/week (raw data coverage), as well as the fraction of data rejected by CCC due to local contamination or analytical error. The percentage of concurrent sampling of hydrocarbons and carbonyls (i.e. on the same days) is also given.*

Station <sup>a)</sup>	Raw data coverage		Data rejected due to local contamination or analytical error		Net data coverage		Concurrence (HC and Carb)
	HC (%)	Carb	HC (%)	Carb	HC (%)	Carb	
Zeppelin <sup>a)</sup>	54	0	2	-	52	-	-
Pallas	92	-	0	-	92	-	-
Utö	98	-	1	-	97	-	-
Birkenes	132	80	2	3	130	77	89
Waldhof	84	106	0	0	84	106	82
Schmücke	98	-	1	-	97	-	-
Košetice	97	97	1	1	96	96	96
Starina <sup>b)</sup>	92	-	(100)	-	(0)	-	-
Peyrusse Vieille <sup>c)</sup>	37	0	1	0	36	0	-
Donon	100	96	0	0	100	96	100
Tänikon <sup>d)</sup>	con	-	0	-	con	-	-

- a) Only measurements during the first half year on Zeppelin  
 b) Preliminary data for Starina. Needs further evaluation  
 c) VOC measurements at Peyrusse Vieille started in July  
 d) Continuous monitoring at Tänikon

The net data coverage of Table 12 is the total number of samples reported from the responsible laboratories to the CCC subtracted the number of samples rejected by CCC. 'Concurrence', given in the last column of Table 12, denotes the fraction of hydrocarbon and carbonyl samples, which were collected at the same days relative to the maximum possible number (based on the raw data). According to EMEP's recommendations, the samples should be taken twice a week, and the hydrocarbons and carbonyls should be sampled on the same days. The data in Table 12 are given relative to this recommendation, i.e. 104 samples/year. In practice, however, the sampling frequency will vary at the sites due to the removal of outliers occurring as a result of e.g. local pollution episodes or technical problems.

The table shows that in general the VOC measurements are satisfactory both with regard to sampling frequency, outliers and the concurrent sampling of hydrocarbons and carbonyls. Compared to previous years there has been a general improvement in these parameters. A 90% data completeness of daily values is given as data quality objective according to the EMEP manual (EMEP, 1996) and that is fulfilled at most VOC sites. The sampling at Zeppelin Mountain is however, less frequent than recommended as it was carried out only the first half year. The hydrocarbon data reported for Starina was considered preliminary and awaits a further evaluation of sampling and analytical procedures.

The number of VOC monitoring sites is small. For hydrocarbons the number of sites is at the low end of the original recommendations of 10-15 set up in Lindau 1989 (EMEP, 1990). Carbonyls were only measured at four sites in 1999 which is much less than the recommendations. An effort to increase the number of carbonyl monitoring is therefore particularly needed. Carbonyl sampling has been started at Utö in 2000 with assistance from CCC as the responsible laboratory and a similar procedure could be applied at other sites.

For the EMEP VOC measurements in general, the quality control of the VOC measurements includes QA procedures at all stages from sampling to chemical analyses and integration. The QA procedures are described in the EMEP manual (EMEP, 1996) and are the laboratories' responsibility to follow up. In addition, data received from the individual laboratories are inspected before classified as valid or invalid by the EMEP/CCC. The routines for this is by visual inspection of plots and by several outlier tests as described in more detail in previous VOC reports (Solberg et al., 1997). First of all, seasonal or monthly average levels are compared with data from previous years and used to identify serious shifts in the general concentration levels. Then, provided that sufficient data exists, each concentration value for the year reported is checked against the centred running mean and standard deviation using the data for several previous years, and assuming a log-normal distribution. If the new value is found to be more than  $4\sigma$  from the running mean of the previous years' data, it is flagged as an outlier. Whether the data value then is rejected or kept varies from sample to sample. Samples are rejected if contamination or other problems are likely. Rejection of sample values are done in agreement with the laboratory providing the data. Additionally, the data for several years together are also checked by a Rosner's test (Gilbert, 1987), suitable for detecting multiple outliers. Cross-correlation plots are also used to detect outliers in individual components as previous experience

indicates well-marked correlations between pairs of hydrocarbons. The number of data rejected (classified as invalid) by these methods is indicated by Table 12.

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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,
- 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 <sub>4</sub> <sup>2-</sup>	0.032 mg S/l	(1 µmol/l)
NO <sub>3</sub> <sup>-</sup>	0.014 mg N/l	(1 µmol/l)
NH <sub>4</sub> <sup>+</sup>	0.028 mg N/l	(2 µmol/l)
Cl <sup>-</sup>	0.107 mg Cl/l	(3 µmol/l)
Ca <sup>2+</sup>	0.012 mg Ca/l	(0.3 µmol/l)
K <sup>+</sup>	0.012 mg K/l	(0.3 µmol/l)
Mg <sup>2+</sup>	0.007 mg Mg/l	(0.3 µmol/l)
Na <sup>+</sup>	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<sub>2</sub> the limit above for sulphate is valid for the medium volume method with impregnated filter. For NO<sub>2</sub> determined as NO<sub>2</sub><sup>-</sup> 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  $c > 1 \mu\text{g Pb/l}$   
          25%    if  $c < 1 \mu\text{g Pb/l}$

Cd:        15%    if  $c > 0.5 \mu\text{g Cd/l}$   
          25%    if  $c < 0.5 \mu\text{g Cd/l}$

Cr:        15%    if  $c > 1 \mu\text{g Cr/l}$   
          25%    if  $c < 1 \mu\text{g Cr/l}$

Ni:        15%    if  $c > 1 \mu\text{g Ni/l}$   
          25%    if  $c < 1 \mu\text{g Ni/l}$

Cu:        15%    if  $c > 2 \mu\text{g Cu/l}$   
          25%    if  $c < 2 \mu\text{g Cu/l}$

Zn:        15%    if  $c > 10 \mu\text{g Zn/l}$   
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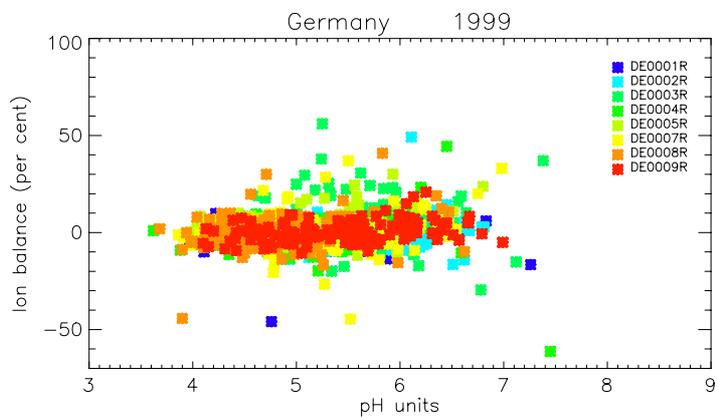
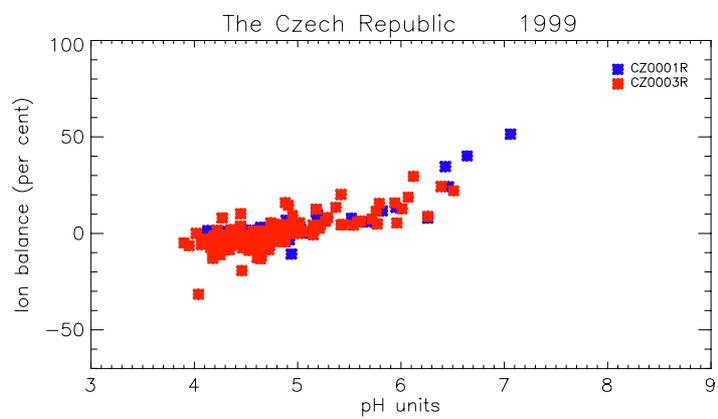
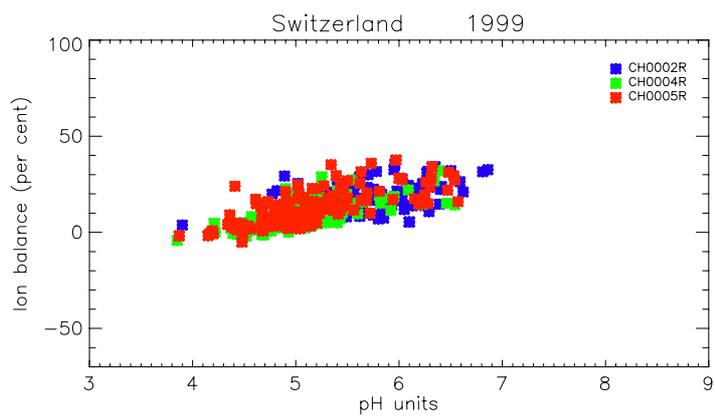
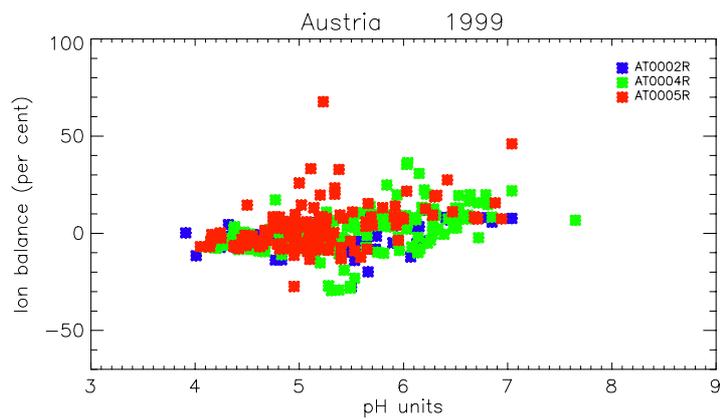
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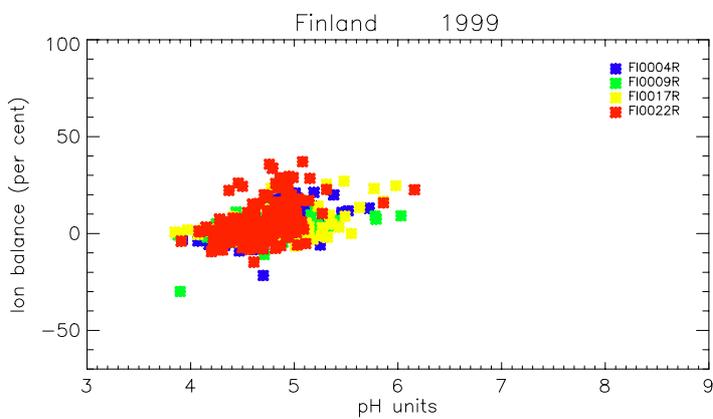
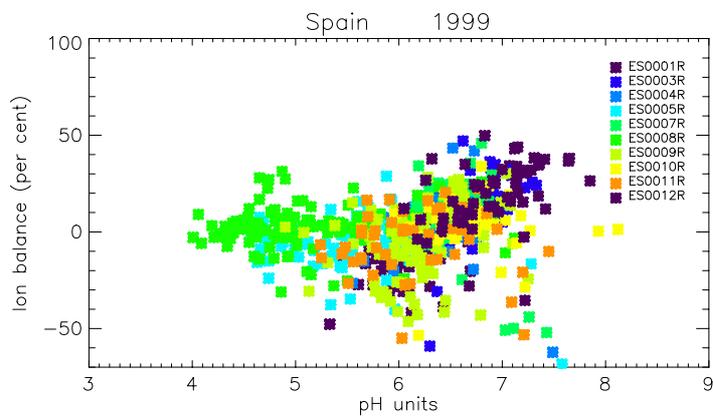
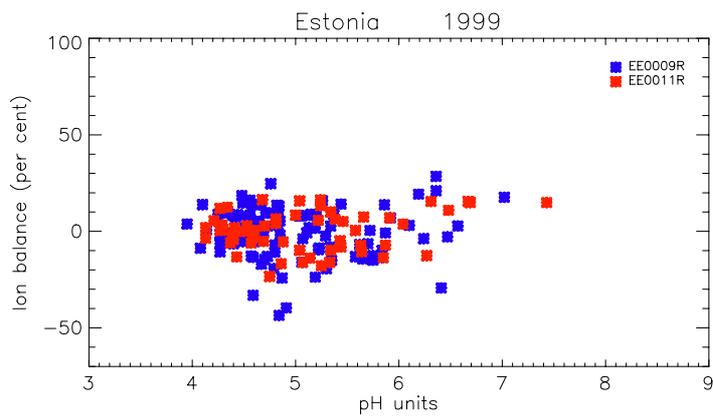
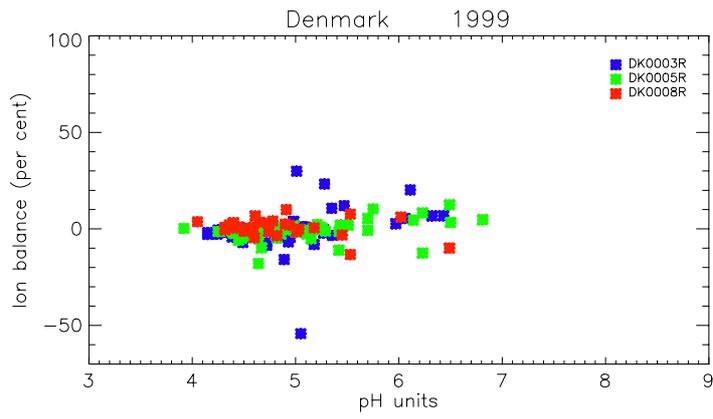
Hg:        15%    if  $c > 0.01 \mu\text{g Hg/l}$   
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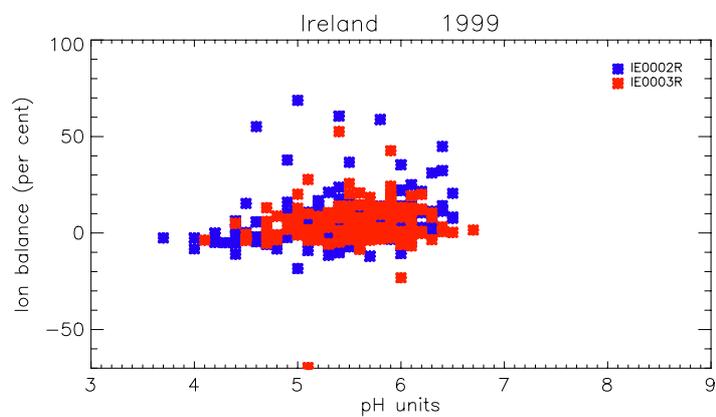
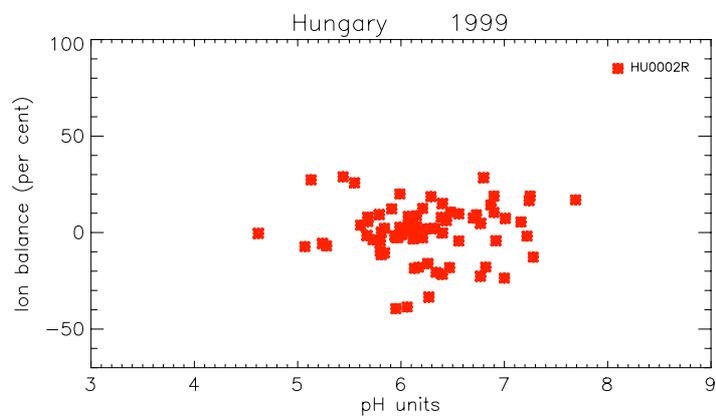
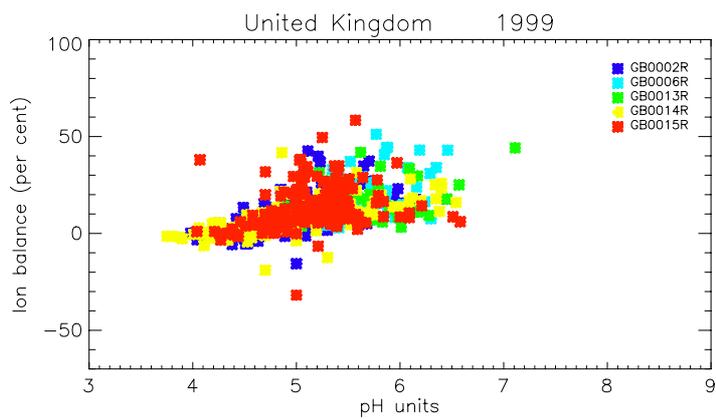
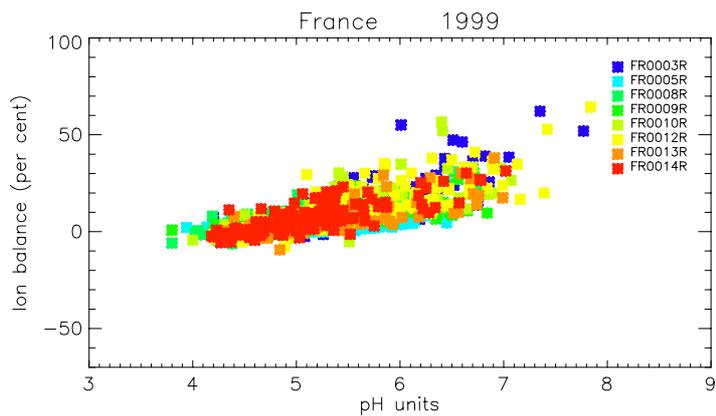
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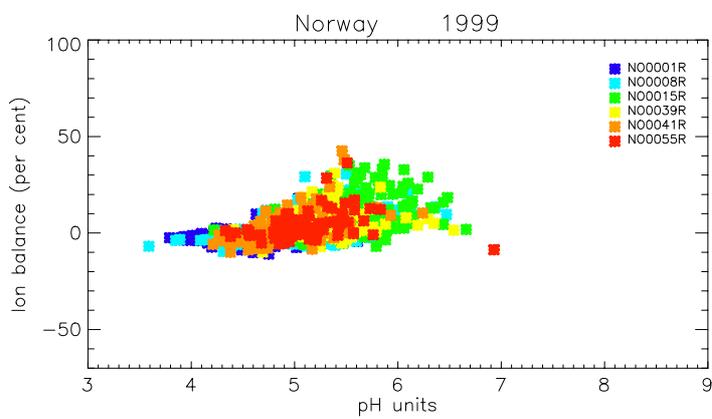
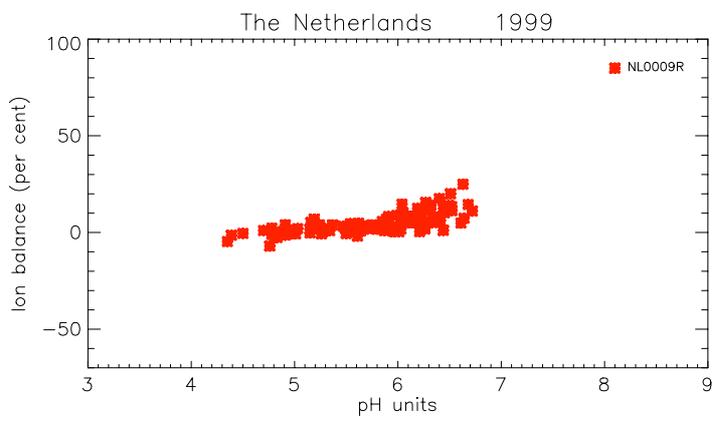
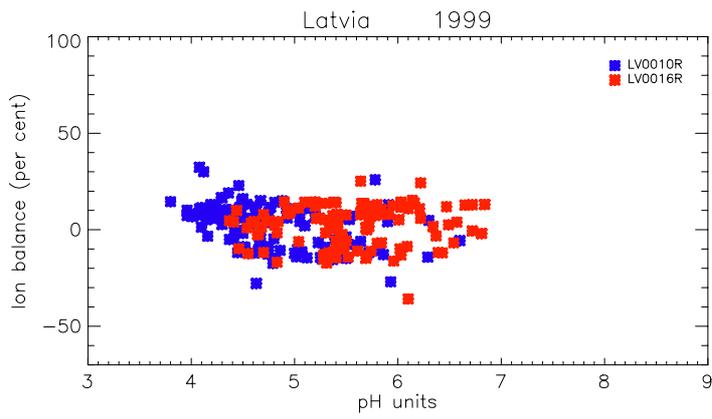
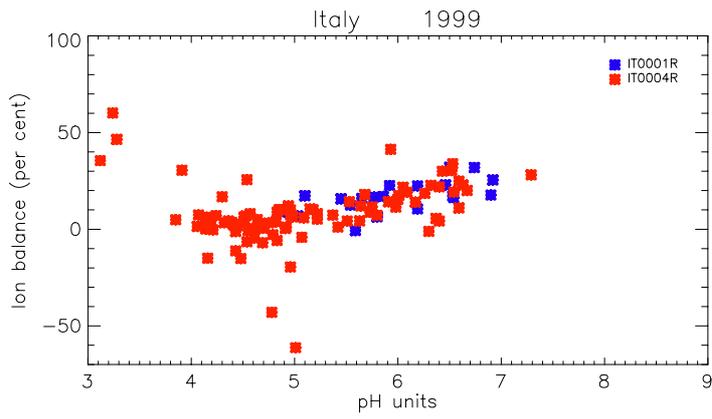
### **Ion balances in precipitation samples 1999**

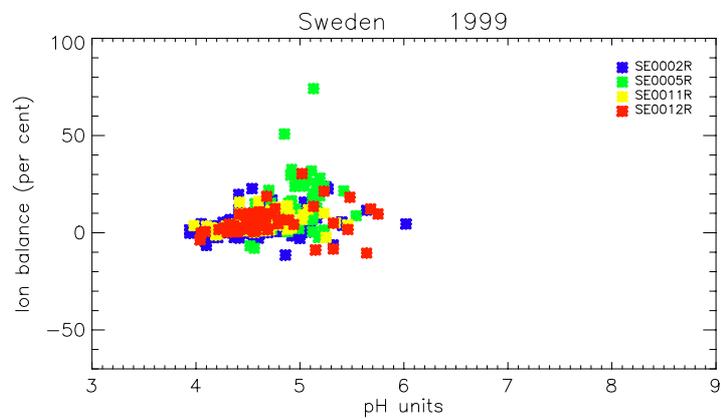
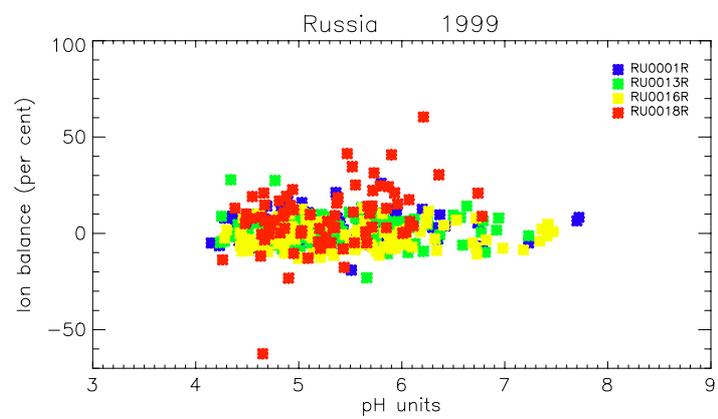
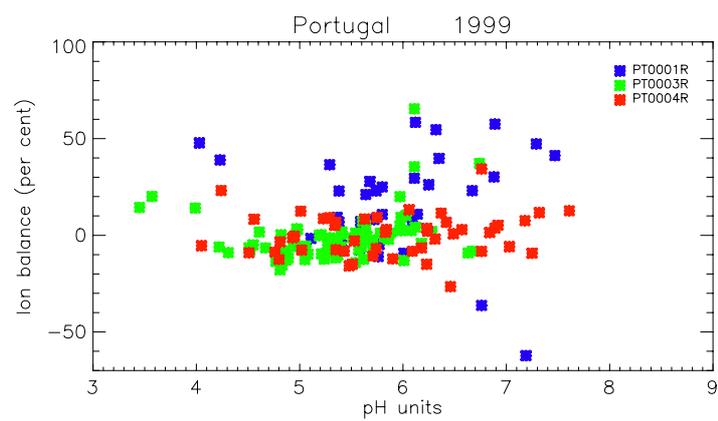
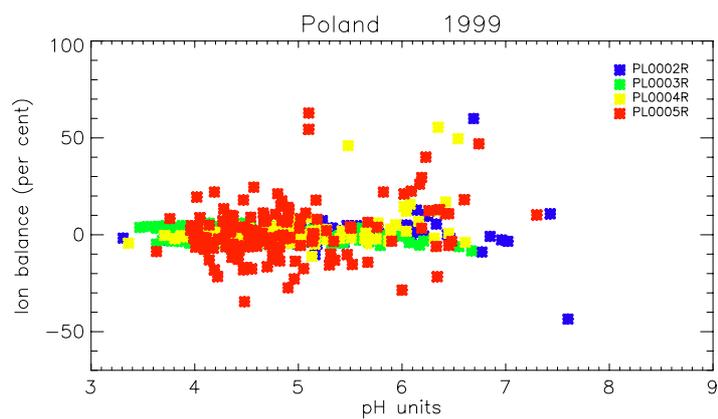


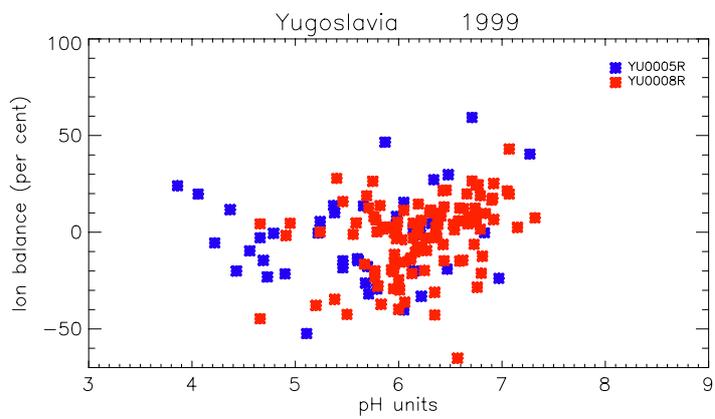
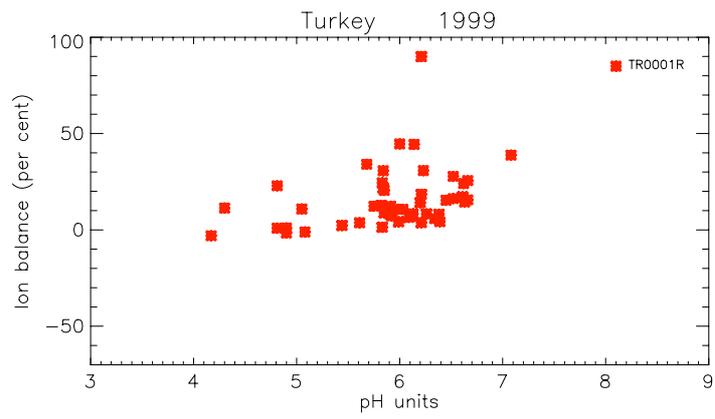
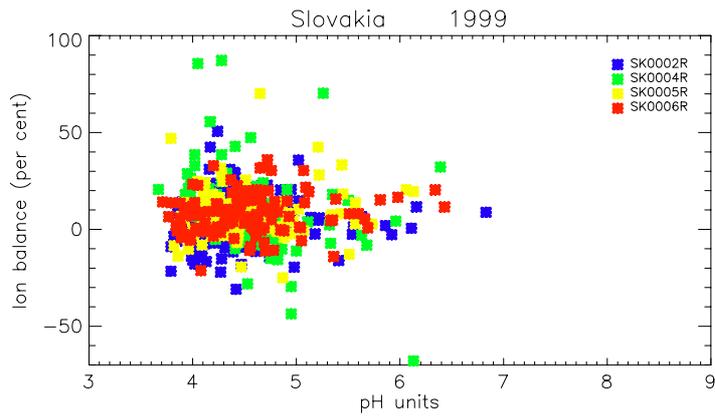












## **Annex 3**

### **Detection limits and precision**



Table 3.1: Detection limits and precision of ozone.

Country	Precision	Detection limit	Instrument
Austria	1 ppb	0,5 / 0,4 ppb	HORIBA APOA 360 / APOA 350E
Czech Republic			Thermo Electron Series 49
Denmark	2 ppb + 8 % of the measured value	1 ppb	API, either model M400 or M400A
Estonia	2 µg/m <sup>3</sup>	2 µg/m <sup>3</sup>	Thermo Environmental Instruments Inc. TEI 49 C
Finland, FI09	2 µg/m <sup>3</sup>	2 µg/m <sup>3</sup>	Dasibi Environmental corp., DAS 1008 PC
FI17			Environnement SA, Env. O3 41 M
FI22			Dasibi Environmental corp., DAS 1008 AH
FI37			Thermo Environmental Instruments, TEI 49 C
France, FR08, 10, 13	2 µg/m <sup>3</sup> ; CoV = 0.01 ppb	2 µg/m <sup>3</sup>	Environnement SA, O341M
FR9, 10			SERES, OZ2000
Germany		2.0 µg/m <sup>3</sup>	
Hungary			Thermo Environmental Model 49
Italy (IT1)	2 µg/m <sup>3</sup>	1 µg/m <sup>3</sup>	API Model 400
Italy, EU (IT4)	2 ppb	2 ppb	Thermo Environment Model 49
Latvia			O341M Ozone Analyzer
Netherlands	1%	4 µg/m <sup>3</sup>	
Norway	2 µg/m <sup>3</sup>	2 µg/m <sup>3</sup>	API Model 400
Poland	2 µg or 1% whichever is greater	2 µg/m <sup>3</sup>	Monitor Labs Inc. ML-9810
PL05			Monitor Labs Inc. ML-9810
Slovakia	2 µg/m <sup>3</sup>		TEI M49 (at SK02, 06); M49C (at SK04)
Slovenia, SI08, 32			Thermo Environmental Instruments, Model 49 C
SI31, 33			Monitor Labs, Model 8810
Spain			MCV, S.A. Model 48 AUV and O341 M
Sweden, SE02, 11, 12	1 ppb	0.5 ppb	Monitor Labs, ML 9810 (ML 9810 B at SE 12);
SE32,35	2 ppb	2 ppb	Monitor Labs, ML 8810
Switzerland, CH2, CH4	3.4 µg O <sub>3</sub> /m <sup>3</sup> (c < 85 hourly mean)	1 ppb	to 3.12.99 Monitor Labs 8810; from 4.12.99 TEI 49C
CH5	4% (c > 85 hourly mean)		Thermo Environmental Instruments TEI 49C
CH3	3.9 µg O <sub>3</sub> / m <sup>3</sup> (c < 85, hourly mean)	1 ppb	Monitor Labs 9810
	6% (c > 85, hourly mean)		
UK, all site except: GB32	2 ppb		Monitor Labs, ML 8810
GB43			TECO, TE49
GB44			Ambirack
			API Model 400

Table 3.2: Detection limits and precision of sulphur dioxide.

Country	Measurements		Laboratory	
	Precision	Detection limit	Precision	Detection limit
Austria <sup>1</sup>	0,7 ppb	0,1 ppb		
Czech Republic	0,63 M. MAD	0,1 mg S/m <sup>3</sup>	1.5	0.1 mg S/l
Denmark	M.MAD: 0.02 µg S/m <sup>3</sup> CoV: 5.0%	0.03 µg S/m <sup>3</sup>	M.MAD: 0.01 µg S/m <sup>3</sup> , CoV: 1.3%	
Estonia	1% of reading or 3 µg S/m <sup>3</sup>	0,03 µg S/m <sup>3</sup>		
Finland			RSD: 7.1% at c=0.65 mg S/l;; RSD: 2.6% at c=1.6 mg S/l;	0.05 mg S/l
France			0.01<c<0,1 mg S/l: 8-12% 0.1<c<0,5 mg S/l: 1-3%	0.1 mg S/l
Hungary	0.28 µg S/m <sup>3</sup>	<0.1	<10%	ca. 0.03 µg S/m <sup>3</sup>
Italy (IT1)	RSD: 7.2% at 2.0 µg S/m <sup>3</sup>	0.10 µg S/m <sup>3</sup>		
Italy <sup>2</sup> , EU (IT4)	0.5 ppb	1 ppb		
Latvia		0.2 µg S/m <sup>3</sup>		
Lithuania	c<1.5 mg S/m <sup>3</sup> ; 1.3-3.8% RSD c>1.5 mg S/m <sup>3</sup> ; 1.0% RSD	0.01 mg S/m <sup>3</sup>	c< 0.5 mg S/l; 1.3-3.8% RSD c> 1.5 mg S/l; 1.0% RSD	0.02 mg S/l
Netherlands	1%	3 µg /m <sup>3</sup>		
Norway	M.MAD 0.012 at c< 4.2 µg S/m <sup>3</sup>	0.03 µg S/m <sup>3</sup>		
Poland PL05		0.2 mg S/m <sup>3</sup> 0.1 mg S/m <sup>3</sup>		0.04 mg S/l 0.04 mg S/l
Russia, RU1 RU16 RU20	RU16: M.MAD = 0.01 CoV = 1.8%	0.06 mg S/m <sup>3</sup> ; 0.11 mg S/m <sup>3</sup> 0.10 mg S/m <sup>3</sup>		
Slovakia	0.75%	0.012 mg S/l		0.02 µg S/m <sup>-3</sup>
Slovenia	0,081 µg S/ml	0.114 µg S/m <sup>3</sup>		
Spain		0.5 µg S/m <sup>3</sup>	4.30%	1 µg S/sample
Sweden	CoV: 5%	0.02 µg/m <sup>3</sup>	2%	0.04 mg S/l
Switzerland CH2 <sup>3</sup> , CH3 CH4 <sup>3</sup> , CH5	0.02 µg S/m <sup>3</sup> (range <0.2 µg S/m <sup>3</sup> ), 10% (range >0.2 µg S/m <sup>3</sup> ) 1 µg SO <sub>2</sub> /m <sup>3</sup> (range <10 µg SO <sub>2</sub> /m <sup>3</sup> ), 9% (range >10 µg SO <sub>2</sub> /m <sup>3</sup> )	0.02 µg S/m <sup>3</sup>  1 ppb 0.2 ppb		0.02 µg S/m <sup>3</sup>
Turkey			M.MAD: 0.014; CoV: 0.026	3.6 µg S/sample
Yugoslavia				0.005 mg SO <sub>2</sub> /m <sup>3</sup>

<sup>1</sup> AT, Monitor, (TEI 43 C trace level/TEI 43 S)<sup>2</sup> IT4: Monitor Environment SA, AF 21M<sup>3</sup> CH2, CH3: Monitor Labs 8850S; CH5: Thermo Environmental Instruments TEI 43BS; CH4, Thermo Environmental Instruments TEI 43BS

Table 3.3: Detection limits and precision of nitrogen dioxide.

Country	Measurements		Laboratory	
	Precision	Detection limit	Precision	Detection limit
Austria <sup>1</sup>	1 ppb	0.5 ppb		
Czech Republic	RSD: 12.2%	0.07 µgN/m <sup>3</sup>	3.4	0.001 mgN/l
Denmark		DK8: 0.08 µg N/m <sup>3</sup>	M.MAD: 0.01 µg N/m <sup>3</sup> , CoV: 0,6%	0.01 mgN/l
Estonia	2 µg/m <sup>3</sup>	0.01 µg/m <sup>3</sup>		
Finland	0.3 µg N/m <sup>3</sup>	0.3 µg N/m <sup>3</sup>		
Hungary			ca. 5%	ca. 0.15 µg N/m <sup>3</sup>
Italy (IT1)	0.6 µg N/m <sup>3</sup>	0.3 µg N/m <sup>3</sup>		
Italy <sup>2</sup> , EU (IT4)	0.5 ppb	0.5 ppb		
Latvia		0.1 µg N/m <sup>3</sup>	RSD: 2.9%	0.1 mg N/l
Lithuania	8.2% RSD at c<1.0 µg N/m <sup>3</sup> ; 3.8% RSD at c>1.0 mg N/m <sup>3</sup>	0.08 µg N/m <sup>3</sup>	3.0 - 8.2% RSD at c= 0.02-0.06 mg N/l;	0.02 mg N/l
Netherlands	1%	2 ug/m3		
Norway			RSD: 7.0% at c=0.03 mg N/l RSD: 4.6% at c=0.17 mg N/l RSD: 4.2% at c=0.08 mg N/l	0.0045 mg N/l
Poland		0.2 µg N/m <sup>3</sup>	RSD: 1.0% at 0.3 mg N/l RSD: 5.9% at 0.015 mg N/l	0.008 mg N/l
PL05		0.1 µg N/m <sup>3</sup>		0.002 mg N/l
Spain		1 µg N/m <sup>3</sup>	1.5%	1 µg N/sample
Sweden	5% CoV	0.2 µg/m <sup>3</sup>	2%	0.048 mg N/l
Switzerland <sup>3</sup>	For ML9841: 3.5 µg N/m <sup>3</sup> at c <35 µg N/m <sup>3</sup> 10% at c >35 µg N/m <sup>3</sup>	CH4,CH5 : 0.5 ppb CH2, CH3: 1 ppb CH1: 0.05 ppb		
Turkey	M.MAD: 0.05; CoV: 12.8%	0.1 µg N/m <sup>3</sup>	M.MAD: 0.04; CoV: 11.1%	
Yugoslavia				0.003 mg NO <sub>2</sub> /m <sup>3</sup>

<sup>1</sup> AT: Monitor, HORIBA APNA 360

<sup>2</sup> IT4: Monitor, Thermo Environment 42C

<sup>3</sup> CH4: Monitor Labs 9841A; CH5: Monitor Labs 8841; CH2 and CH3: Eco Physics CLD 700AL; CH1: Eco Physics CLD 770AL ppt + PLC 760

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

Country	Measurements		Laboratory	
	Precision	Detection limit	Precision	Detection limit
Czech Republic	M.MAD 0.112	0.03 µg S/m <sup>3</sup>	< 1,5	0.3 mg S/filter
Denmark	M.MAD: 0.05 µg S/m <sup>3</sup> ; CoV: 6.5%	0.03 µg S/m <sup>3</sup>		
Finland			RSD: 4.0% at c= 0.65 mg S/l RSD: 2.6% at c= 1.6 mg S/l	0.02 mg S/l
France			0.01<c<0.1 mg S/L: 8-12% 0.1<c<0.5 mg S/l: 1-3%	0.2 µg S/filter
Greece			M.MAD = 0.095; CoV = 7.8%	
Hungary	0.28 µg S/m <sup>3</sup>	<0.1 µg S/m <sup>3</sup>	<10%	ca. 0.03 µg S/m <sup>3</sup>
Italy (IT1)	RSD: 1.4% at 1 µg S/m <sup>3</sup>	0.01 µg S/m <sup>3</sup>		
Italy, EU (IT4)		0.066 ppm	M.MAD. 0.01 ppm; CoV: 1.3%	
Latvia		0.1-0.15 µg/m <sup>3</sup>	RSD: 2.6%	0.2 mg S/l
Lithuania	RSD: 8% at c<0.6 µg S/m <sup>3</sup> RSD: 3.2% at c>0.6 µg S/m <sup>3</sup>	0.025 µg S/m <sup>3</sup>	RSD: 8% at c<0.5 µg S/m <sup>3</sup> RSD: 3.2% at c>0.5 µg S/m <sup>3</sup>	0.02 mg S/l
Netherlands			SD: 0.2	0.8 µg/m <sup>3</sup>
Norway	M.MAD 0.009 µg S/m <sup>3</sup> at c<2.4 µg S/m <sup>3</sup>	0.01 µg S/m <sup>3</sup>		
Poland PL05		0.18 µg S/m <sup>3</sup> 0.1 µg S/m <sup>3</sup>		0.04 mg S/l 0.04 mg S/l
Russia, RU1	M.MAD=0.01 µg S/m <sup>3</sup> ; CoV =3.2%	0.05 µg S/m <sup>3</sup>		
RU16	M.MAD=0.021 mg S/m <sup>3</sup> ; CoV =3.7%	0.1 µg S/m <sup>3</sup>		
RU20	M.MAD=0.01 mg S/m <sup>3</sup> ; CoV =3%	0.09 µg S/m <sup>3</sup>		
Slovakia	4.30%	0.07 mg S/l		0.088 µg S/m <sup>3</sup>
Slovenia	SD: 0.011 µg S/ml	0.034 µg S/m <sup>3</sup>	7%	0.033 mg S/l
Spain		0.01 µg S/m <sup>3</sup>	1.36%	3.5 µg S/sample
Sweden	CoV: 5%	0.005 µg S/m <sup>3</sup>	2%	0.005 mg/l
Switzerland	0.25 µg S/m <sup>3</sup>	0.04 µg S/m <sup>3</sup>		0.02 µg S/m <sup>3</sup>
Turkey		0.02 µg S/m <sup>3</sup>	M.MAD 0.14; CoV: 33%	
UK			RSD: 2%	0.01 mg S/l

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

Country	Measurements		Laboratory	
	Precision	Detection limit	Precision	Detection limit
Denmark	M.MAD: 0.04 µg N/m <sup>3</sup> ; CoV: 7.3%	0.05 µg N/m <sup>3</sup>	M.MAD: 0.01 µg N/m <sup>3</sup> , CoV: 1%	Sum: 0,01 mg N/l
Finland			NO <sub>3</sub> : c=0.35 mg N/l; 5.1% RSD c=0.9 mg N/l; 3.0% RSD HNO <sub>3</sub> : c=0.35 mg N/l; 4.3% RSD c=0.9 mg N/l; 2.6% RSD	NO <sub>3</sub> : 0.01 mg N/l HNO <sub>3</sub> : 0.03 mg N/l
Greece			M.MAD = 0.04 mg N/l; CoV = 7.9%	
Hungary	0.05 µg N/m <sup>3</sup>	<0.1 µg N/m <sup>3</sup>	<10%	ca. 0.03 µg N/m <sup>3</sup>
Italy (IT1)	HNO <sub>3</sub> : RSD: 6.5% at 0.25 µg N/m <sup>3</sup> NO <sub>3</sub> : RSD: 1.4% at 1 µg N/m <sup>3</sup>	HNO <sub>3</sub> : 0.01 µg N/m <sup>3</sup> NO <sub>3</sub> : 0.01 µg N/m <sup>3</sup>		
Italy, EU (IT4)		0.246 ppm	M.MAD: 0.01 ppm; CoV: 1.2%	
Latvia		NO <sub>3</sub> : 0.01-0.02 µg N/m <sup>3</sup>	NO <sub>3</sub> : RSD 2.4%	0.1 mg/l
Lithuania	RSD: 3.2% at c<1.25 µg N/m <sup>3</sup> ;	0.01 µg N/m <sup>3</sup>	c< 1.0 mg N/l; 3.2% RSD	0.02 mg N/l
Netherlands			NO <sub>3</sub> , SD: 0.2	NO <sub>3</sub> : 0.8 µg N/m <sup>3</sup>
Norway	M.MAD 0.012 µg N/m <sup>3</sup> at <1.6 µg N/m <sup>3</sup>	0.02 µg N/m <sup>3</sup>		
Poland PL05		0.2 µg N/m <sup>3</sup>		NO <sub>3</sub> : 0.01 mg N/l 0.05 mg N/l
Russia		0.04 µg N/m <sup>3</sup>		
Slovakia	3%	0.02 mg N / l		0.02 µg N/m <sup>3</sup>
Slovenia	SD, HNO <sub>3</sub> : 0.011 µg N/ml SD, NO <sub>3</sub> : 0.010 µg N/ml	HNO <sub>3</sub> : 0.015 µg N/m <sup>3</sup> ; NO <sub>3</sub> : 0.014 µg N/m <sup>3</sup>	9.5%	NO <sub>3</sub> : 0.009 mg N/l
Spain		0.06 µg N/m <sup>3</sup>		2 µg N/sample
Sweden	CoV: 3%	NO <sub>3</sub> : 0.002 µgN/m <sup>3</sup> HNO <sub>3</sub> : 0.004 µg N/m <sup>3</sup>	2%	NO <sub>3</sub> : 0.002 mg/l HNO <sub>3</sub> : 0.005 mg/l
Switzerland	0.13 µg N/m <sup>3</sup>	0.02 µg N/m <sup>3</sup>		0.02 µg N/m <sup>3</sup>
Turkey		0.04 µg N/m <sup>3</sup>	HNO <sub>3</sub> , M.MAD: 0.004; CoV: 5.8% NO <sub>3</sub> , M.MAD: 0.02; CoV: 24.8%	

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

Country	Measurements		Laboratory	
	Precision	Detection limit	Precision	Detection limit
Denmark	M.MAD: 0.134 $\mu\text{g N/m}^3$ CoV: 6.6 %	DK3: 0.06 $\mu\text{g N/m}^3$ DK5: 0.08 $\mu\text{g N/m}^3$ DK8: 0.06 $\mu\text{g N/m}^3$	NH <sub>4</sub> : M.MAD: 0.03 $\mu\text{g N/m}^3$ , CoV: 2.5 % NH <sub>3</sub> : M.MAD: 0.01 $\mu\text{g N/m}^3$ , CoV: 2.0 %	NH <sub>4</sub> : 0.02 mg N/l NH <sub>3</sub> : 0.02 mg N/l
Finland			RSD = 7.2% at c=0.22 mg N/l RSD: 2.7% at c=0.72 mg N/l RSD: 2.8% at c=1.42 mg N/l	0.02 mg N/l
Hungary	NH <sub>3</sub> : 0.18 $\mu\text{g N/m}^3$ ; NH <sub>4</sub> : 0.30 $\mu\text{g N/m}^3$	NH <sub>3</sub> : ca. 0.05 $\mu\text{g N/m}^3$ NH <sub>4</sub> : <0.1 $\mu\text{g N/m}^3$	<10 %	ca. 0.04 $\mu\text{g N/m}^3$
Italy (IT1)	NH <sub>3</sub> : RSD: 4.5 % at 1.0 $\mu\text{g N/m}^3$ NH <sub>4</sub> : RSD: 4.6 % at 2 $\mu\text{g N/m}^3$	0.1 $\mu\text{g N/m}^3$		
Italy, EU (IT4)		0.061 ppm		
Latvia		NH <sub>4</sub> : 0.25 $\mu\text{g N/m}^3$	NH <sub>4</sub> : RSD 2.5 %	0.02
Lithuania	c<1.25 $\mu\text{g N/m}^3$ ; 4.8% RSD	0.03 $\mu\text{g N/m}^3$	c< 1.2 mg N/l; 4.8% RSD	0.04 mg N/l
Netherlands	NH <sub>3</sub> : <2%	NH <sub>3</sub> : 0.12 $\mu\text{g/m}^3$	NH <sub>4</sub> , SD: 0.02	NH <sub>4</sub> : 0.1 $\mu\text{g/m}^3$
Norway	M.MAD 0.039 at <3.2 $\mu\text{g N/m}^3$	0.05 $\mu\text{g N/m}^3$		
Poland PL05		0.08 mg N/m <sup>3</sup> 0.03 mg N/m <sup>3</sup>		NH <sub>4</sub> : 0.03 mg N/l 0.01 mg N/l
Russia, RU1 RU16 RU20	M.MAD=0.01 $\mu\text{g N/m}^3$ ; CoV =4.8%. NH <sub>4</sub> : M.MAD=0.01 $\mu\text{g N/m}^3$ , CoV =2.7% NH <sub>4</sub> : M.MAD=0.01 $\mu\text{g N/m}^3$ , CoV =2.3%	0.07 $\mu\text{g N/m}^3$ NH <sub>3</sub> : 0.34 $\mu\text{g N/m}^3$ NH <sub>3</sub> : 0.20 $\mu\text{g N/m}^3$		
Slovenia	NH <sub>4</sub> , SD: 0.004 $\mu\text{g N/m}^3$ NH <sub>3</sub> , SD: 0.016 $\mu\text{g N/ml}$	NH <sub>4</sub> : 0.010 $\mu\text{g N/m}^3$ ; NH <sub>3</sub> : 0.025 $\mu\text{g N/m}^3$	NH <sub>4</sub> : 4.4%	NH <sub>4</sub> : 0.009 mg N/l
Spain		0.03 $\mu\text{g N/m}^3$	2.68 %	1 $\mu\text{g N/sample}$
Sweden	CoV: 3%	0.03 $\mu\text{g N/m}^3$	3 %	NH <sub>4</sub> : 0.017 mg/l NH <sub>3</sub> : 0.03 mg/l
Switzerland	0.45 $\mu\text{g N/m}^3$	0.2 $\mu\text{g N/m}^3$		0.2 $\mu\text{g N/m}^3$
Turkey		0.04 $\mu\text{g N/m}^3$		

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

Country	Measurements		Laboratory	
	Precision	Detection limit, [mg S/l]	Precision	Detection limit, [mg S/l]
Austria		0.010	2.4%	0.002
Czech Republic	0.14 M.MAD	0.02	RSD: 0.9%	0.02
Denmark			M.MAD: 0.005 mg S/l, CoV: 0.5%	0.002
Estonia			1%	0.1
Finland			c=0.65 mg S/l; 2.4% RSD c=1.6 mg S/l; 2.1% RSD	0.02
France			c<0.2 mg S/L: 5-10% 0.2<c<0.5 mg S/L: 3-5% 0.5<c<5 mg S/L: 1-3%	0.02
Germany				0.01
Hungary			<10%	ca. 0.03
Italy (IT1)	RSD: 1.0% at 1 mg S/l	0.01	RSD: 0.6% at 0.5 mg S/l RSD: 1.7% at 0.05 mg S/l	0.002
Latvia			15 RSD%	0.15
Lithuania	c<0.5mg S/l; 2-5% RSD c>0.5mg S/l; 1% RSD	0.1	c< 0.5 mg S/l; 2-5% RSD c> 0.5 mg S/l; 1% RSD	0.02
Netherlands			SD: 0.2	1 umol/l
Norway			SD: 0.041 at c=2.23 mg S/l SD: 0.019 at c=0.85 mg S/l	0.01
Poland			RSD: 0.6% at 6.7 mg S/l RSD: 1.5% at 0.67 mg-S/l RSD: 1.8% at 0.33 mg-S/l	0.04
PL05	M.MAD: 0.031 mg S/l; CoV: 4.4%	0.05	M.MAD: 0.03 mg S/l; CoV: 7.5%	0.05
Portugal			0.75%	0.15
Russia	RU1: M.MAD=0.01 mg S/l; CoV =2.8%. RU13: M.MAD=0.021 mg S/l; CoV =3.8% RU16: M.MAD=0.021 mg S/l; CoV =2% RU20: M.MAD=0.021 mg S/l CoV =3.9%			0.02
Slovakia				0.07
Spain			1.4%	0.07
Sweden	CoV: 4%	0.004	2%	0.004
Switzerland	0.04 M.MAD	0.03		0.03
Turkey			M.MAD: 0.02; CoV: 2.2%	
UK			2%	0.04
Yugoslavia				0.16

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

Country	Measurements		Laboratory	
	Precision	Detection limit, [mg/l]	Precision	Detection limit, [mg N/l]
Austria		0.005	1%	0.001
Czech Republic	0.1059 M.MAD	0.03	RSD: 2.1%	0.03
Denmark			M.MAD: 0.004 mg N/l, CoV: 0.6%	0.01
Estonia			2%	0.02
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 mg N/l: 5-10% 0.2<c<0.5 mg N/l: 3-5% 0.5<c<5 mg N/l: 1-3%	0.02
Germany				0.01
Hungary			<10%	ca. 0.03
Italy (IT1)			RSD: 0.7% at 0.5 mg N/l RSD: 1.6% at 0.05 mg N/l	0.002
Italy, EU (IT4)		0.001 ppm		
Latvia			RSD: 17%	0.1
Lithuania	c<0.5 mg N/l; 1.0% RSD c>0.5 mg N/l; 0.5% RSD	0.04	c< 0.5 mg N/l; 1.0% RSD c>0.5 mg N/l; 0.5% RSD	0.02
Netherlands			SD: 0.5	2 umol/l
Norway			SD: 0.023 at c=0.86 mg N/ml SD: 0.016 at c=0.39 mg N/ml	0.01
Poland			RSD: 0.6% at 4.5 mg N/l RSD: 1.5% at 0.45 mg N/l RSD: 1.9% at 0.23 mg N/l	0.01
PL05	M.MAD: 0.016 mg N/l; CoV: 3%	0.05	M.MAD: 0.02 mg N/l; CoV: 4.4	0.05
Portugal			0.25%	0.09
Russia	RU1:M.MAD=0.005 mg/l; CoV =5%. RU13: M.MAD=0.01 mg/l; CoV =5.8% RU16: M.MAD=0.01 mg/l; CoV =2.9% RU20: M.MAD=0.01 mg/l; CoV =3.9%			0.01
Slovakia	0.2-2.4%	0.01		0.05
Spain			1.2%	0.08
Sweden	CoV: 4%	0.002	2%	0.002
Switzerland	0.05 M.MAD	0.02		
Turkey			M.MAD: 0.008; CoV: 2.1%	
UK			4%	0.03
Yugoslavia				0.02

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

Country	Measurements		Laboratory	
	Precision	Detection limit, [mg/l]	Precision	Detection limit, [mg N/l]
Austria		0.023	3.7%	0.007
Czech Republic	0.0426 M.MAD	0.011	RSD: 6.3%	0.02
Switzerland	0.02 M.MAD	0.02		0.02
Denmark			M.MAD: 0.01 mg N/l, CoV: 2,0%	0.02
Estonia			6%	0.01
Finland			c=0.23 mg N/l; 2.6% RSD c=0.70 mg N/l; 2.8% RSD	0.002
France			c<0.2 mg N/l: 5-10% 0.2<c<0.5 mg N/l: 3-5% 0.5<c<5 mg N/l: 1-3%	0.03
Germany				0.01
Hungary			5-10%	ca. 0.04
Italy (IT1)	RSD: 0.8% at 0.5 mg N/l	0.005	RSD: 0.5% at 0.5 mg N/l RSD: 1.9% at 0.05 mg N/l	0.001
Italy, EU (IT4)		0.104 ppm		
Latvia			RSD: 9%	0.03
Lithuania	c<1.0 mg N/l; 4.8% RSD	0.06	c<1.0 mg N/l; 4.8% RSD	0.04
Netherlands			SD: 0.2	1 umol/l
Norway			SD: 0.016 at c=0.64 mg/l SD: 0.013 at c=0.32 mg N/l	0.01
Poland			RSD: 2.7% at 1 mg/l RSD: 4.6% at 0.1 mg/l	0.03
PL05	M.MAD: 0.055 mgN/l; CoV: 14%	0.01	M.MAD: 0.05 mg N/l; CoV: 15.1%	0.01
Portugal			0.79%	0.04
Romania				
Russia	M.MAD=0.01 mg/l; CoV =6.5%			0.02
Slovakia	2.4%	0.02		0.02
Spain			2.7%	0.08
Sweden	CoV: 3%	0.02	3%	0.02
Switzerland				
Turkey			M.MAD: 0.014; CoV: 1.9%	
UK			10%	0.03
Yugoslavia				0.03

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

Country	Measurements		Laboratory	
	Precision	Detection limit, [mg/l]	Precision	Detection limit, [mg/l]
Austria		0.028	2%	0.003
Czech Republic	0.148 M.MAD	0.001	5.8 RSD%	0.011
Denmark			M.MAD 0.02 mg/l, Cov: 6.2%	
Estonia			1%	2
Finland			c=0.20 mg Ca/l; 4.9% RSD c=0.61 mg Ca/l; 1.8% RSD	0.005
France			c<0.2 mg/l: 10-20% 0.2<c<0.5 mg/L: 5-10% 0.5<c<5 mg/L: 1-5%	0.02
Germany				0.01
Hungary			< 5%	ca. 0.01
Italy (IT1)	RSD: 1.6% at 1 mg/l	0.01	RSD: 1.2% at 0.5 mg/l RSD: 3.3% at 0.05 mg/l	0.002
Italy, EU (IT4)		0.123 ppm		
Latvia			RSD: 4%	0.02
Lithuania				0.02
Netherlands			SD: 0.07	0.3 umol/l
Norway			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: 10% at 0.2 mg/l	0.03
(PL05)	M.MAD 0.019 mg/l; CoV: 12%	0.001	M.MAD: 0.005 mg/l; CoV: 3.4%	0.001
Portugal			1.31%	0.06
Romania				
Russia, RU1	M.MAD= 0.016 mg/l; CoV =9.8%.			0.05
RU13	M.MAD = 0.042 mg/l; CoV =15.8%.			
RU16	M.MAD = 0.021 mg/l; CoV =2.3%			
RU20	M.MAD = 0.063 mg/l; CoV =16.8%			
Slovakia	5.0%	0.01		0.06
Spain			7.40%	0.04
Sweden	CoV: 4%	0.05	5%	0.04
Switzerland	0.02 M.MAD	0.05		0.05
Turkey			M.MAD: 0.034; CoV: 1.8%	
UK			5%	0.05
Yugoslavia			80.94%	0.005

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

Country	Measurements		Laboratory	
	Precision	Detection limit, [mg/l]	Precision	Detection limit, [mg/l]
Austria		0.018	2.3%	0.005
Czech Republic	0.046 M.MAD	0.003	2.24 RSD%	0.003
Denmark			M.MAD: 0.01 mg/l; CoV: 6.4%	
Estonia			3%	0.1
Finland			c=0.12 mg/l; 6.0% RSD c=0.36 mg/l; 3.6% RSD	0.006
France			c<0.2 mg/L: 10-20% 0.2<c<0,5 mg/l: 5-10% 0.5<c<5 mg/l: 1-5%	0.02
Germany				0.01
Hungary			< 5%	ca. 0.01
Italy (IT1)	RSD: 1.2% at 1 mg/l	0.01	RSD: 1.4% at 0.5 mg/l RSD: 2.8% at 0.05 mg/l	0.002
Latvia			RSD: 3%	0.019
Lithuania				0.02
Netherlands			SD: 0.2	1 umol/l
Norway			SD: 0.027; c=0.61 mg/l SD: 0.015; c=0.20 mg/l	0.01
Poland			RSD: 1.3% at 0.5 mg/l RSD: 10.8% at 0.05 mg/l	0.02
	PL05 M.MAD: 0.055 mg/l; CoV: 30%	0.003	M.MAD: 0.004 mg/l; CoV: 5.2%	0.003
Portugal			1.69%	0.077
Russia, RU1	M.MAD = 0.031 mg/l; CoV = 8.2%.			0.03
	RU13 M.MAD = 0.031 mg/l; CoV = 7.2%.			
	RU16 M.MAD = 0.021 mg/l; CoV = 5.1%			
	RU20 M.MAD = 0.021 mg/l; CoV = 7.1%			
Slovakia	2.3%	0.01		0.02
Spain			18%	0.05
Sweden	CoV: 14%	0.05	8%	0.05
Switzerland	0.01 M.MAD	0.01		0.01
Turkey			M.MAD: 0.019; CoV: 4.2%	
UK			6%	0.05
Yugoslavia			98.05%	0.015

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

Country	Measurements		Laboratory	
	Precision	Detection limit, [mg/l]	Precision	Detection limit, [mg/l]
Austria		0.034	3.5%	0.009
Czech Republic	0.0577 M.MAD	0.02	1.1 RSD%	0.02
Denmark			M.MAD: 0.04 mg/l, CoV: 0,9%	0.07
Estonia			1%	0.1
Finland			c=0.5 mg/l; 3.2% RSD c=1.2 mg/l; 2.3% RSD	0.01
France			c<0.2 mg/l: 10-20% 0.2<c<0.5 mg/l: 5-10% 0.5<c<5 mg/l: 1-5%	0.05
Germany				0.01
Hungary			<10%	ca. 0.1
Italy (IT1)	RSD: 0.8% at 0.5 mg/l	0.005	RSD: 0.6% at 0.5 mg /l RSD: 1.0% at 0.05 mg/l	0.001
Italy, EU (IT4)		0.032 ppm		
Latvia			14 RSD%	0.1
Lithuania	c<0.5 mg/l; 4.5% RSD c>0.5 mg/l; 2.3% RSD	0.29	c<0.5 mg/l; 4.5% RSD c>0.5 mg/l; 2.3% RSD	0.01
Netherlands			SD: 0.7	3 umol/l
Norway			SD: 0.028 at c=1.16 mg/l SD: 0.02 at c=0.46 mg/l	0.01
Poland			RSD: 0.6% at 10 mg/l RSD: 1.3% at 1 mg/L RSD: 1.8% at 0.5 mg/L	0.03
PL05	M.MAD: 0.1 mg/l; CoV: 13%	0.10	M.MAD: 0.08 mg/l; CoV: 20%	0.10
Portugal			0.53%	0.03
Russia, RU1	M.MAD=0.089 mg/l; CoV = 11.2%			0.03
RU13	M.MAD = 0.073 mg/l; CoV =9.5%.			
RU16	M.MAD = 0.017 mg/l; CoV =7.9%			
RU20	M.MAD = 0.042 mg/l; CoV =12.3%			
Slovakia	5.4%	0.01		0.09
Spain			4.9%	0.31
Sweden	CoV: 6%	0.05	2%	0.05
Switzerland	0.02 M. MAD	0.05		0.05
Turkey			M.MAD: 0.026; CoV: 1.6%	
UK			3%	0.05
Yugoslavia				0.05

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

Country	Measurements		Laboratory	
	Precision	Detection limit, [mg/l]	Precision	Detection limit, [mg/l]
Austria		0.035	1.2%	0.002
Czech Republic	0.01 M.MAD	0.026	RSD: 1.9%	0.001
Denmark			M.MAD: 0,01 mg/l, CoV: 5,5%	
Estonia			1%	1
Finland			c=0.04 mg/l; 4.5% RSD c=0.66 mg/l; 1.7% RSD	0.003
France			c<0.2 mg/l: 10-20% 0.2<c<0.5 mg/l: 5-10% 0,5<c<5 mg/l: 1-5%	0.02
Germany				0.01
Hungary			< 5%	ca. 0.01
Italy (IT1)	RSD: 1.0% at 0.5 mg/l	0.005	RSD: 0.7% at 0.5 mg/l RSD: 3.3% at 0.05 mg/l	0.001
Latvia			4 RSD%	0.010
Netherlands			SD: 0.4	1.5 umol/l
Norway			SD: 0.012 at c=0.31 mg/l SD: 0.007; c=0.19 mg/l	0.01
Poland			RSD: 0.6% at 0.25 mg/l RSD: 5.5% at 0.025 mg/l	0.007
PL05	M.MAD: 0.007 mg/l; CoV: 11%	0.001	M.MAD: 0.002 mg/l; CoV: 5.9%	0.001
Portugal			0.60%	0.03
Russia, RU1	M.MAD= 0.001 mg/l; CoV =9.9%			0.001
RU13	M.MAD = 0.003 mg/l; CoV =3.9%			
RU16	M.MAD = 0.004 mg/l; CoV =2.4%			
Slovakia	1.9%	0.01		0.02
Spain			7.20%	0.02
Sweden	CoV: 2%	0.02	3%	0.01
Switzerland	0.01 M.MAD	0.01		0.01
Turkey			M:MAD: 0.014; CoV: 6%	
UK			3.50%	0.05
Yugoslavia			99.54%	0.0015

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

Country	Measurements		Laboratory	
	Precision	Detection limit, [mg/l]	Precision	Detection limit, [mg/l]
Austria		0.010	1.2%	0.003
Czech Republic	0.038 M.MAD	0.002	RSD: 1.2%	0.002
Denmark			M.MAD 0.02 mg/l, CoV: 1,3%	
Estonia			3%	0.1
Finland			c=0.22 mg/l; 5.7% RSD c=0.66 mg/l; 1.7% RSD	0.002
France			c<0.2 mg/l: 10-20% 0.2<c<0.5 mg/l: 5-10% 1-5%	0.02
Germany				0.01
Greece				
Hungary			< 5%	ca. 0.01
Italy (IT1)	RSD: 0.8% at 0.5 mg/l	0.005	RSD: 1.2% at 0.5 mg/l RSD: 2.2% at 0.05 mg/l	0.001
Italy, EU (IT4)				
Latvia			RSD: 4%	0.018
Lithuania				0.02
Netherlands			SD: 0.4	1.5 umol/l
Norway			SD: 0.025; c=0.75 mg/l SD: 0.011 at c=0.30 mg/l	0.01
Poland			RSD: 0.6% at 1 mg/l RSD: 5.4% at 0.1 mg/l	0.02
PL05	M.MAD: 0.018 mg/l; CoV: 10.5%	0.003	M.MAD: 0.004 mg/l; CoV: 7.5%	0.003
Portugal			0.54%	0.025
Russia, RU1	M.MAD= 0.021 mg/l; CoV = 4.2%			0.01
RU13	M.MAD = 0.01 mg/l; CoV =2.7%			
RU16	M.MAD = 0.021 mg/l; CoV =1.9%			
RU20	M.MAD = 0.021 mg/l; CoV =7.1%			
Slovakia	2.7%	0.01		0.03
Spain			14%	0.1
Sweden	CoV: 12%	0.05	4%	0.05
Switzerland	0.02 M.MAD	0.02		0.02
Turkey			M.MAD: 0.018; CoV: 2.3%	
UK			3.50%	0.03
Yugoslavia			98.25%	0.001

## **Annex 4**

### **Expected data quality for the stations' annual averages in 1999**



Table 4.1: Expected data quality for acid components in air and precipitation.

Station Code and Name	SO <sub>4</sub> prec	pH prec	NH <sub>4</sub> prec	NO <sub>3</sub> prec	Na prec	Mg prec	Cl prec	Ca prec	K prec	SO <sub>2</sub> Air	NO <sub>2</sub> Air	HNO <sub>3</sub> Air	NH <sub>3</sub> Air	SO <sub>4</sub> Air	NO <sub>3</sub> Air	NH <sub>4</sub> Air	HNO <sub>3</sub> +NO <sub>3</sub> Air	NH <sub>3</sub> +NH <sub>4</sub> Air
AT2 Illmitz	A	B	A	A	A	A	A	A	B	U	U			A				
AT4 St. Koloman	A	B	A	A	A	A	A	A	B	U	U							
AT5 Vorhegg	A	B	A	A	A	A	A	A	B	U	U							
CH1 Jungfraujoch	A	A	A	A	A	B	A	A	B	B	A			A			A	A
CH2 Payerne	A	A	A	A	A	B	A	A	B	U	C			A				
CH3 Taernikon	A	A	A	A	A	B	A	A	B	U	C							
CH4 Chaumont	A	A	A	A	A	B	A	A	B	U	C							
CH5 Rigi	A	A	A	A	A	B	A	A	B	U	C			A				
CZ1 Svatouch	A	A	B	A	A	A	A	B	A	A	B	U	U		U		B	B
CZ3 Kosetice	A	A	B	A	A	A	A	B	A	A	B	U	U		U		B	B
DE1 Westerland	A	A	A	A	A	A	A	A	B	D	D			A				
DE2 Langenbruegge	A	A	A	A	A	A	A	A	B	D	D			A				
DE3 Schauinsland	A	A	A	A	A	A	A	A	B	D	D			A				
DE4 Deuselbach	A	A	A	A	A	A	A	A	B	D	D			A				
DE5 Brotjackriegel	A	A	A	A	A	A	A	A	B	D	D			A				
DE7 Neuglobsow	A	A	A	A	A	A	A	A	B	D	D			A				
DE8 Schmuecke	A	A	A	A	A	A	A	A	B	D	D			A				
DE9 Zingst	A	A	A	A	A	A	A	A	B	D	D			A				
DK3 Tange	A	A	A	A	A	A	A	A	B	A	A			A			A	A
DK5 Keldsnor	A	A	A	A	A	A	A	A	B	A	A			A			A	A
DK8 Anholt	A	A	A	A	A	A	A	A	B	A	A		U	A			A	A
EE9 Lahemaa	A	B	A	A	A	B	B	B	B	B	C			B				
EE11 Vilsandy	A	B	A	A	A	B	B	B	B	U	U			B				
ES1 San Pablo	A	B	A	A	A	A	D	A	A	D	D		U	A		U	A	A
ES3 Roquetas	A	B	A	A	A	A	D	A	A	D	D		U	A		U	A	A
ES4 Logrono	A	B	A	A	A	A	D	A	A	D	D		U	A		U	A	A
ES5 Noya	A	B	A	A	A	A	D	A	A	D	D		U	A		U	A	A

Table 4.1, cont.

Station Code and Name	SO <sub>4</sub> prec	pH prec	NH <sub>4</sub> prec	NO <sub>3</sub> prec	Na prec	Mg prec	Cl prec	Ca prec	K prec	SO <sub>2</sub> Air	NO <sub>2</sub> Air	HNO <sub>3</sub> Air	NH <sub>3</sub> Air	SO <sub>4</sub> Air	NO <sub>3</sub> Air	NH <sub>4</sub> Air	HNO <sub>3</sub> +NO <sub>3</sub> Air	NH <sub>3</sub> +NH <sub>4</sub> Air
ES6 Mahon	A	B	A	A	A	A	D	A	A	D	D		U	A		U	A	A
ES7 Viznar	A	B	A	A	A	A	D	A	A	D	D		U	A		U	A	A
ES8 Niembro	A	B	A	A	A	A	D	A	A	D	D		U	A		U	A	A
ES9 Campisabalos	A	B	A	A	A	A	D	A	A	D	D		U	A		U	A	A
ES10 Cabo de Creus	A	B	A	A	A	A	D	A	A	D	D		U	A		U	A	A
ES11 Barcarrola	A	B	A	A	A	A	D	A	A	D	D		U	A		U	A	A
ES12 Zarra	A	B	A	A	A	A	D	A	A	D	D		U	A		U	A	A
FI4 Ahtari	A	A	A	A	A	A	A	A	A	A	C			A			A	A
FI9 Utoe	A	A	A	A	A	A	A	A	A	A	C			A			A	A
FI17 Virolahti	A	A	A	A	A	A	A	A	A	A	C			A			A	A
FI22 Oulanka	A	A	A	A	A	A	A	A	A	A	C			A			A	A
FI37 Ahtari	A	A	A	A	A	A	A	A	A	A	C			A			A	A
FR3 La Crouzille	A	A	A	A	A	A	A	A	A	B				A				
FR5 La Hague	A	A	A	A	A	A	A	A	A	B				A				
FR8 Donon	A	A	A	A	A	A	A	A	A	B				A				
FR9 Revin	A	A	A	A	A	A	A	A	A	B				A				
FR10 Morvan	A	A	A	A	A	A	A	A	A	B				A				
FR11 Bonnevaux	A	A	A	A	A	A	A	A	A	B				A				
FR12 Iraty	A	A	A	A	A	A	A	A	A	B				A				
FR13 Peyrusse Vieille	A	A	A	A	A	A	A	A	A	B				A				
FR14 Montandon	A	A	A	A	A	A	A	A	A	B				A				
GB2 Eskdalemuir	A	A	A	A	A	B	C	B	A	B	C			A			A	A
GB4 Stoke Ferry	A	A	A	A	A	B	C	B	A	B	C			A				
GB6 Lough Navar	A	A	A	A	A	B	C	B	A	B	C			A				
GB7 Barcombe Mills	A	A	A	A	A	B	C	B	A	B	C			A				
GB13 Yarnar Wood	A	A	A	A	A	B	C	B	A	B	C			A				
GB14 High Muffles	A	A	A	A	A	B	C	B	A	B	C			A				

Table 4.1, cont.

Station Code and Name	SO <sub>4</sub> prec	pH prec	NH <sub>4</sub> prec	NO <sub>3</sub> prec	Na prec	Mg prec	Cl prec	Ca prec	K prec	SO <sub>2</sub> Air	NO <sub>2</sub> Air	HNO <sub>3</sub> Air	NH <sub>3</sub> Air	SO <sub>4</sub> Air	NO <sub>3</sub> Air	NH <sub>4</sub> Air	HNO <sub>3</sub> +NO <sub>3</sub> Air	NH <sub>3</sub> +NH <sub>4</sub> Air
GB15 Strath Vaich D.	A	A	A	A	A	B	C	B	A	B	C			A				
GB16 Glen Dye	A	A	A	A	A	B	C	B	A	B	C			A				
GB36 Harwell	A	A	A	A	A	B	C	B	A	B	C			A				
GB37 Ladybower	A	A	A	A	A	B	C	B	A	B	C			A				
GB38 Lullington Heath	A	A	A	A	A	B	C	B	A	B	C			A				
GB43 Narberth	A	A	A	A	A	B	C	B	A	B	C			A				
GB45 Wicken Fen	A	A	A	A	A	B	C	B	A	B	C			A				
GR 1 Aliartos										C	B			A	U			
HU2 K-puszta	A	A	B	A	B	A	B	B	D	A	A	U	U	A	U	U	A	B
IE2 Turrough Hill	A	A	B	A	B	B	B	B	B	A				A				
IE3 The Burren	A	A	B	A	B	B	B	B	B									
IS2 Irafoss	A	A			A									A				
IT1 Montelibretti	A	B	A	A	A	A	A	A	A	A	C	A	A	A	A	A		
IT4 Ispra	A	A	A	A	A	A	B	B	A	U	C			B	U	U		
LT15 Preila	A	A	A	A	A	-	A	B	A	A	A			A			A	A
LV10 Rucava	A	A	A	A	A	D	B	B	A	B	A			B	U	U	A	A
LV16 Zoseni	A	A	A	A	A	D	B	B	A	B	A			B	U	U	A	A
NL9 Kollumerwaard	A	A	A	A	A	A	A	A	A	U	C			A	A	A		
NL10 Vreedepeel										U	C			A	A	A		
NO1 Birkenes	A	A	A	A	A	A	A	A	B	A	A			A			A	A
NO8 Skreaadalen	A	A	A	A	A	A	A	A	B	A	A			A			A	A
NO15 Tustervatn	A	A	A	A	A	A	A	A	B	A	A			A			A	A
NO39 Kaarvatn	A	A	A	A	A	A	A	A	B	A	A			A			A	A
NO41 Osen	A	A	A	A	A	A	A	A	B	A	A			A			A	A
NO42 Spitzbergen, Z.																		
NO55 Karasjok	A	A	A	A	A	A	A	A	B	A	A			A			A	A

Table 4.1, cont.

Station Code and Name	SO <sub>4</sub> prec	pH prec	NH <sub>4</sub> prec	NO <sub>3</sub> prec	Na prec	Mg prec	Cl prec	Ca prec	K prec	SO <sub>2</sub> Air	NO <sub>2</sub> Air	HNO <sub>3</sub> Air	NH <sub>3</sub> Air	SO <sub>4</sub> Air	NO <sub>3</sub> Air	NH <sub>4</sub> Air	HNO <sub>3</sub> +NO <sub>3</sub> Air	NH <sub>3</sub> +NH <sub>4</sub> Air
PL2 Jarczew	A	A	A	A	A	A	A	B	A	A	B			A	U	U	A	A
PL3 Sniezka	A	A	A	A	A	A	A	B	A	A	B			A	U	U	A	A
PL4 Leba	A	A	A	A	A	A	A	B	A	A	B			A	U	U	A	A
PL5 Diabla Gora	B	B	A	A	A	A	B	A	A	A	A			A			A	A
PT1 Braganca	A	A	A	A	B	A	A	A	A									
PT3 V.d. Castelo	A	A	A	A	B	A	A	A	A									
PT4 Monte Velho	A	A	A	A	B	A	A	A	A									
RU1 Janiskoski	A	A	A	A	B	A	B	B	B	B	A			A	U	U	A	A
RU13 Pinega	A	A	A	A	B	A	B	B	B	B	A			A	U	U	A	A
RU16 Shepeljovo	A	A	A	A	B	A	B	B	B	B	A			A	U	U	A	A
RU18 Danki	A	A	A	A	B	A	B	B	B	B	A			A	U	U	A	A
SE2 Roerwik	A	A	A	A	A	A	A	B	B	B	A			A			A	A
SE5 Bredkaelen	A	A	A	A	A	A	A	B	B	B	A			A			A	A
SE8 Hoburg	A	A	A	A	A	A	A	B	B	B	A			A				
SE11 Vavihill	A	A	A	A	A	A	A	B	B	B	A			A			A	A
SE12 Aspvreten	A	A	A	A	A	A	A	B	B	B	A			A			A	A
SI8 Iskriba										A				A			A	
SK2 Chopok	A	A	A	A	A	A	A	A	B	A	B	U		A	U		A	
SK4 Stara Lesna	A	A	A	A	A	A	A	A	B	A	B	U		A	U		A	
SK5 Liesek	A	A	A	A	A	A	A	A	B	A	B	U		A	U		A	
SK6 Starina	A	A	A	A	A	A	A	A	B	A	B	U	U	A	U	U	A	
TR1 Cubuk11	A	A	A	A	A	A	A	B	D	U	D			A			A	A
YU5 Kamenicki vis	A	A	A	B	A	B	C	B	A	D	B							
YU8 Zabljak	A	A	A	B	A	B	C	B	A	D	B							

Table 4.2: Synthesis of the responses to the 2000 questionnaire regarding ozone monitoring procedures. '0' indicates 'ok' (within the criteria), whereas any marks indicate violation of the criteria.

Station Code and Name	Local NO <sub>x</sub> sources <sup>1)</sup>	Maintenance <sup>2)</sup>	Calibration <sup>3)</sup>	Transfer standard <sup>4)</sup>
AT02 Illmitz	0	0	0	0
AT04 St. Koloman	mw 8	0	0	0
AT05 Vorhegg	0	0	0	0
CH02 Payerne	s.tr.	nlt, infreq scrub	0	0
CH03 Tänikon	s.tr.	nlt	0	0
CH04 Chaumont	0	nlt, infreq scrub	0	0
CH05 Rigi	0	nlt, infreq scrub	0	0
CZ01 Svratouch				
CZ03 Kosetice				
DE all stations <sup>5)</sup>	?	?	?	?
DK05 Keldsnor	s.town 20	not reg	not reg	0
DK31 Ulborg	0	not reg	not reg	0
DK32 Fredriksborg	s.town 4	not reg	not reg	0
EE09 Lahemaa	0	infreq	infreq	no st
EE11 Vilsandy	0	infreq	infreq	no st
ES01 San Pablo	s.tr.	0	infreq	not trac
ES03 Roquetas	suburb	0	infreq	not trac
ES04 Logrono	suburb	0	infreq	not trac
ES05 Noia	tr	0	infreq	not trac
ES07 Viznar	city1-10	0	infreq	not trac
ES08 Niembro	s.tr., ppl10-50	0	infreq	not trac
ES09 Campisábalos	0	0	infreq	not trac
ES10 Cabo de Creus	l.tr.	0	infreq	not trac
ES11 Barcarrota	s.tr., psrc 22	0	infreq	not trac
ES12 Zarra	s.tr.	0	infreq	not trac
FI09 Utö	s.tr.	0	0	0
FI17 Virolahti	s.tr.	0	0	0
FI22 Oulanka	s.tr.	0	0	0
FI37 Ähtäri	0	0	0	0
FR08 Donon	0	npt	infreq sp	0
FR09 Revin	0	0	0	0
FR10 Morvan	0	0	0	0
FR13 Peyrusse Vieille	0	infreq lt	infreq sp	0
FR14 Montandon	0	infreq lt	0	0
GB02 Eskdalemuir	? <sup>6)</sup>	0	0	0
GB06 Lough Navar	? <sup>6)</sup>	0	0	0
GB13 Yarner Wood	? <sup>6)</sup>	0	0	0
GB14 High Muffles	? <sup>6)</sup>	0	0	0
GB15 Strath Vaich	? <sup>6)</sup>	0	0	0
GB31 Aston Hill	? <sup>6)</sup>	0	0	0
GB32 Bottesford	? <sup>6)</sup>	0	0	0
GB33 Bush	? <sup>6)</sup>	0	0	0
GB34 Glazerbury	? <sup>6)</sup>	0	0	0
GB35 Great Dun Fell	? <sup>6)</sup>	0	0	0
GB36 Harwell	? <sup>6)</sup>	0	0	0
GB38 Lullington Heath	? <sup>6)</sup>	0	0	0
GB39 Sibton	? <sup>6)</sup>	0	0	0
GB43 Narberth	s.tr.	0	0	0

Table 4.2, cont.

Station Code and Name	Local NO <sub>x</sub> sources <sup>1)</sup>	Maintenance <sup>2)</sup>	Calibration <sup>3)</sup>	Transfer standard <sup>4)</sup>
GB44 Somerton	? <sup>6)</sup>	0	0	0
GB45 Wicken Fen	? <sup>6)</sup>	0	0	0
GR01 Aliartos				
HU02 K-puszta	0	npt, nsc	infreq	0
IE031 Mace Head				
IT01 Montelibretti	s.tr.	nsc	infreq sp	0
IT04 Ispra				
LT15 Preila				
LV10 Rucava	0	infreq, npt, nsc	infreq	no st
NL09 Kollumerwaard				
NL10 Vreedepeel				
NO01 Birkenes	0	0	infreq	0
NO15 Tustervatn	0	0	infreq	0
NO39 Kaarvatn	0	0	infreq	0
NO41 Osen	0	0	infreq	0
NO42 Zeppelinfjellet	0	0	infreq	0
NO43 Prestebakke	0	0	infreq	0
NO45 Jeløya	s.tr.	0	infreq	0
NO48 Voss	0	0	infreq	0
NO52 Sandve	0	0	infreq	0
NO55 Karasjok	0	0	infreq	0
NO56 Hurdal	s.tr.	0	infreq	0
PL02 Jarczew				
PL03 Sniezka				
PL04 Leba				
PL05 Diabla Gora	s.tr.	0	infreq sp	0
PT04 Monte Velho				
RU01 Janiskoski				
RU13 Pinega				
RU16 Shepeljovo				
SE02 Rörvik	0	0	infreq, infreq sp	0
SE11 Vavihill	0	0	infreq, infreq sp	0
SE12 Aspvreten	0	0	infreq, infreq sp	0
SE13 Esrange	0	0	infreq, infreq sp	0
SE32 Norra Kvill	0	0	infreq, infreq sp	0
SE35 Vindeln	0	0	infreq, infreq sp	0
SI08 Iskrba	s.tr.	infreq lt	infreq	0
SI31 Zavodnje	ppl 8	infreq	infreq	0
SI32 Krvavec	some	infreq	infreq	0
SI33 Kovk	ppl 4	infreq lt	infreq	0
SK02 Chopok	0	0	infreq	0
SK04 Stara Lesna	s.tr.	0	infreq	0
SK06 Starina	0	0	infreq	0

<sup>1)</sup> mw <x>: Motorway <x> km away; s.tr.: some traffic; s.town: small town; ppl: power plant; tr: traffic; psrc: point source

<sup>2)</sup> nlt: No leak test; infreq scrub: infrequent scrubber test; not reg: not regularly; npt: No pressure transducer test; nsc: no scrubber test

<sup>3)</sup> not reg: Not regularly; infreq: infrequent; infreq sp: infrequent span and zero check

<sup>4)</sup> no st.: No standard; not trac: Presently not tracable to a NIST standard

<sup>5)</sup> Some information on the calibration was supplied for Germany, but the questionnaire was not answered

<sup>6)</sup> No information supplied