

5. Quality assurance

General guidelines considering the quality assurance work within EMEP were given in the EMEP Quality Assurance Plan (EMEP/CCC-Report 1/88). While there have been considerable improvements in the quality assurance work within EMEP over the last years, there is still need for improvements. The EMEP/WMO workshop in Passau on accuracy of measurements (EMEP/CCC Report 2/94) gave a series of recommendations aiming at an improved quality assurance. These recommendations have been accepted by the EMEP Steering Body in 1994, and will form a basis for the QA programme within EMEP. Important steps in this programme are:

- Appointment of an EMEP QA Manager at the CCC, and a National QA manager in each of the participating countries. These will be responsible for implementing harmonized quality assurance systems within the countries, including documentation of standards and reference materials.
- Development of standardized operating procedures based on the recommendations in this Manual.
- Co-location experiments and instrument comparisons in the various countries to document precision and quantify internal network differences.
- Continuation of efforts towards site characterization.

It was also agreed to continue exchange of views and information with the WMO, since the WMO GAW network share a number of the stations and measured parameters. Since then further discussions have taken place between EMEP and WMO/GAW and there is a strong desire to harmonize and coordinate the efforts in order not to duplicate activities and efforts.

The implementation of the recommendations above will be a gradual process, starting with the establishment of responsible National QA managers.

Guidelines for the QA work are given in the following sections.

5.1 Job description for EMEP's National Quality Assurance Manager

The overall goal of the quality assurance activities is to provide data which meet the EMEP Data Quality Objectives (Section 5.2).

The EMEP quality management and quality system which will build further on the Quality Assurance Plan for EMEP and the Manual for Sampling and Chemical Analysis, will in general follow the guidelines in the ISO 9004 standards, and the guidance given in EN 45001, ISO/IEC Guide 25, and the WELAC Guidance Document No. WGD 2 or the updated version EAL-G4.

The quality assurance activities will therefore follow normal accepted standards and recommendations for good measurement practice. The quality system will, when fully implemented, ensure the targeted data quality.

The concept of quality system implementation requires that NQAM have the authority and full support at national level.

NQAM are then responsible for implementation of the EMEP quality system within his/her own country and for its supervision.

The responsibilities include among other duties:

- Preparation of standard operating procedures (SOP) based on EMEP's recommended methods, when the recommended methods are in use,
- to develop SOPs for other methods in use,
- to document that these other methods are at least as precise and accurate as EMEP's recommended methods, and have a corresponding low detection limit,
- to co-operate with the CCC in comparison experiments both with respect to comparison with reference equipment in order to quantify differences between the measurement systems, and with respect to two identical national measurement systems in order to quantify precision,
- the timely reporting of measurement data to the CCC,
- the reporting of quality assurance data, with the DQO, to the CCC which will compile this data in annual reports,

and in particular

- to perform audits in co-operation with the CCC,
- to document sites and site surroundings, measurements, and standards and reference materials used,
- the quality control including data checking and validation.

The NQAM shall have direct access to the highest level of management at which decisions are taken on measurement policy and on resources, and will work in close co-operation with the EMEP Quality Assurance Manager.

5.2 EMEP Data Quality Objectives (DQO)

5.2.1 DQO for the acidifying and eutrophying compounds

- 10% accuracy or better for oxidised sulphur and oxidised nitrogen in single analysis in the laboratory,
- 15 % accuracy or better for other components in the laboratory,
- 0.1 units for pH,
- 15–25% uncertainty for the combined sampling and chemical analysis (components to be specified later),
- 90 % data completeness of the daily values.
- The targets, with respect to accuracy in the laboratory, for the very lowest concentrations of the main components in precipitation follow the WMO GAW (1992) recommendations for regional stations:

	Accuracy	
SO ₄ ²⁻	0.032 mg S/l	(1 µmol/l)
NO ₃ ⁻	0.014 mg N/l	(1 µmol/l)
NH ₄ ⁺	0.028 mg N/l	(2 µmol/l)
Cl ⁻	0.107 mg Cl/l	(3 µmol/l)
Ca ²⁺	0.012 mg Ca/l	(0.3 µmol/l)
K ⁺	0.012 mg K/l	(0.3 µmol/l)
Mg ²⁺	0.007 mg Mg/l	(0.3 µmol/l)
Na ⁺	0.007 mg Na/l	(0.3 µmol/l)

The targets for the wet analysis of components extracted from air filters are the same as for precipitation. For SO₂ the limit above for sulphate is valid for the medium volume method with impregnated filter. For NO₂ determined as NO₂⁻ 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.

5.2.2 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 $c > 10 \mu\text{g Zn/l}$
 25% if $c < 10 \mu\text{g Zn/l}$

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

Hg: 15% if $c > 0.01 \mu\text{g Hg/l}$
 25% if $c < 0.01 \mu\text{g Hg/l}$

5.3 Quality Assurance Plan

The quality assurance plan was first discussed at EMEP's workshop in Freiburg, Germany in 1986, and later distributed as a separate CCC report (EMEP/CCC-Report 1/88). The objectives of the quality assurance is to make sure that the data accuracy satisfy the DQO and to document the sites, the measurements, and the quality of the collected measurement data. It consists of the following elements:

- All the monitoring stations should meet the siting criteria defined in Section 2. Any deviations from these criteria should be documented, and their effect on the measurements examined.
- Instrumentation, standard operating procedures for sample collection and handling, chemical analyses and data reporting should be at hand, and documents describing the equipment and procedures should be available to the operators and technicians responsible for the sampling and chemical analysis, and to the EMEP QA Manager. These documented procedures should be

followed in detail. All the involved personnel should be properly trained and instructed. Duties and responsibilities should be specified.

- Field blanks and control samples should be included in the sampling and analysis series to document the accuracy, precision and detection limit, as described elsewhere in this Manual.
- Co-location sampling and measurements should be carried out, either with identical equipment to define the over-all precision of the measurements, or with different equipment to obtain information on the additional uncertainty due to sampling methodology. Non-standard sampling equipment or measurement methods should be compared with standard reference instrumentation and methods to define inter-network inconsistencies.
- Procedures should be developed to avoid gaps in the measurement series due to instrument breakdown. These procedures will involve preventive maintenance, supplies of spare parts, and replacement of instruments.
- A report of the quality assurance work at the national level should be prepared annually, covering the points mentioned above.
- System audits should be carried out at regular intervals to see that the instrumentation and sampling equipment is adequate, that sampling and chemical analysis is carried out according to specifications in this Manual, and to written procedures available at the sites and in the laboratories.

5.4 Measurement sites

The siting criteria are given in Section 2. Precautions to be undertaken with respect to the individual component are also described in the sampling part in Section 3.

5.4.1 Information about a monitoring site

Information about the EMEP site surroundings was presented in EMEP/CCC-Report 1/81. Since then a large number of new stations have been established.

Rather comprehensive forms for sites and site surroundings including distances to emission sources have been filled in and returned to the CCC. The key information collected is stored in the EMEP data base. The forms for this type of information will be revised as a part of the QA activity and the new forms will be simpler and less time-consuming to fill in.

The site information is available from CCC's homepage,
<http://www.nilu.no/projects/ccc/network.html>.

5.5 Field and laboratory operations

5.5.1 *Common guidelines for field and laboratory activities*

When relevant for the measurements taken place in participating countries, the guidelines from the CCC should be translated before being passed on to the stations or laboratories.

The staff at the measurement sites and in the laboratories should have copies of the instructions for their work, their responsibilities and their delegated authority at hand. They should be familiar with these documents. The documents should be updated when needed.

The staff should be properly instructed before being assigned to the work, and should be given refresher courses at regular intervals, e.g. in combination with the national audits.

National resources should be sufficient to give the staff both in field and laboratory the equipment and accessories including spare parts and traceable standards, needed to perform their work in accordance with the EMEP quality assurance plan and recommendations.

Routines for handling, maintenance, and calibration of instruments and samplers at regular intervals, should be established, be at hand at the site and in the laboratories, and should be followed as intended.

Corrective routines should be established in order to have a high data completeness, and a stocks of the most used spare parts should be kept at the sites and in the laboratories.

Calibrations, maintenance etc. should be recorded in field journals and in laboratory journals. There should be one journal at hand next to each instrument.

It is strongly recommended that laboratories should apply for accreditation for compliance with EN 45001 or similar standards.

Any changes in instrumentation should be reported to the CCC.

5.5.1.1 *Audits*

Performance audits should be carried out by representatives of the technical staff from the institution operating the site once each year to see that the field operations work as intended. System audits should be carried out by the EMEP QA Manager in cooperation with the National QA Managers at regular intervals.

A detailed check-list to be filled in during these inspections should be worked out, and the WMO GAW check-list (WMO, 1994) may be used during audits of the wet deposition part of the measurements. The filled-in forms should be assessed by a scientist to ensure that the station operates as intended. The auditors should bring with them copies of the filled-in forms from the last visit when performing a site inspection. Corrective action should be taken immediately when necessary.

The system audits should:

- Check the quality system in general,
- inspect the sample locations and the site surroundings, and any changes since the last visit should be noted,
- follow the staff during their routines, and correct bad handling of equipment,
- check and calibrate the equipment and instruments,
- inspect the field journals,
- evaluate the need for improvements.

An audit plan and guidelines for the audit, should be worked out for this purpose.

5.5.2 Field operations

5.5.2.1 Instrumentation

Procurement of instrument or materials is the process of obtaining instruments and materials for field use, i.e. the instructions for contracting, purchasing, testing etc. The procurement procedures for instruments and materials should involve several quality assurance steps. The complexity and the number will usually be dependent upon how important the instrument or material is for the field operations.

Procurement has been treated by the US EPA (US EPA, 1976), procedures have for example been worked out for the Canadian Air and Precipitation Network (CAPMoN), see Vet and Onlock, 1983).

Each participant should have a preventive maintenance plan which covers all instruments used in the national network. The plan should list all instruments, the maintenance procedures for each instrument, and the preventive maintenance time schedule. The plan should further contain a list of replacement parts which may be needed, and a storage of tubes and other spare parts which easily can be changed at the site should be kept at the site in order to reduce the down period for instruments and to obtain a high data completeness.

The preventive maintenance should be carried out by the technical staff from the institution responsible for the site, or from the manufacturer of the instrument. Journals should be at hand for each instrument and records made for the preventive maintenance. Inspections for leaks in the tubes and connections should be a part of the daily sample exchange procedure. Low pressure readings in air sampling equipment may indicate leaks, and tubes appearing to be unclean need to be replaced with new tubes.

A calibration plan and calibration procedure covering the various instruments at the site must exist at all sites. For gaseous and aerosol components accurate volume readings are most important for the resulting measurements accuracy, and the volume meters may need frequent calibration. The accuracy of an air volume meter should be better than 5%. The results from the calibrations should also be kept in the journals. The need for calibration will normally be specified by the manufacturer. As a general rule a calibration at least twice a year is desirable but should under no circumstances be less frequent than once every year. The

institution responsible for the measurement may modify the calibration procedures or frequencies as more experience is gained with the instrument.

Written instructions for maintenance and calibration must be available at the site, and the operator should be familiar with the contents.

5.5.2.2 *Changing of samples at the site*

Detailed procedures for changing of samples for the recommended methods are parts of Section 2 in this Manual. Meter readings and other data of importance should be written into the field journal at the site, and copies of this information filled into the field reporting forms. Field reporting forms should follow the exposed samples and field blanks to the laboratory.

5.5.2.3 *Sample storage and transportation*

It is recommended to ship a one weeks supply from the laboratory to the site, and vice versa, once every week. There should be one blank sample every week.

Samples should be kept in a refrigerator, and once every week the field operator should fetch the seven exposed samples from the refrigerator as well as the one unexposed field blank, put the filter packs in the transportation box together with the site reporting form covering the past week. Field reporting forms should always be put in a separate plastic bag in case of accidental leaks from precipitation samples which may be contained in the same transportation box. In order to keep precipitation samples chilled during transportation, the boxes should be insulated and ice packs ("blue ice") follow the samples in the transportation boxes.

The samples should be kept in a refrigerator in the laboratory until the analysis is completed. The storage before the chemical analysis should in general be short. Aliquots of the samples should be stored for re-analysis until the quality checks of the data carried out at the responsible institutions are finished (e.g. three months).

Biological materials i.e. insects, leaves etc., and dust in precipitation samples will change the sample quality during storage and have an effect on the concentrations of hydronium ions, ammonium ions and other ion species in the sample. In order to detect any possible changes in the precipitation samples, pH or conductivity may be measured at the field site and compared with the results obtained after arrival in the laboratory. Samples which contain visual contamination should be filtrated in the laboratory as fast as possible.

5.5.2.4 *Field blanks*

A field blank sample is a sample which has been prepared, handled, and analysed as a normal sample in every way, except that it has not intentionally been exposed, and therefore should not contain the substance to be determined. Weekly field blank samples should be used in order to check possible sample contamination or sampling errors. Field blanks should be reported regularly to the CCC. Detection limits for the measurements are calculated from field blanks. A procedure for calculation of detection limits is given in Section 5.5.

Field blanks may be unexposed filterpacks, absorption solutions, containers for precipitation etc. which are returned unexposed to the laboratory from the site and analysed. The blank samples should be handled and stored like normal samples and for the normal time periods.

Some precipitation collecting systems make use of reusable equipment which are cleaned in the field with deionized water every day when the sample has been collected. Errors may then very easily be introduced. In such systems it is particularly important to make use of field blanks by pouring a known amount of deionized water into the sampler after cleaning, immediately take it out of the sampler, handle and transport it to the laboratory, exactly like a normal precipitation sample.

It is also recommended to investigate the influence of dust and gases on the precipitation sample. This may be done on days when no precipitation has occurred the preceding 24 hours, at the time when the sample should have been collected (7-9 am local time), by adding a known amount of deionized water into the collector. This field blank should then be handled, stored and transported, as mention above.

5.5.2.5 Comparison of different field instruments

Different methods for sampling of air constituents and different collectors for rain and snow are used in the EMEP network today. The efficiency and performance of the various precipitation collectors depend upon the type of precipitation (rain, snow, etc.), wind speed, temperature, and a number of intrinsic factors related to the construction and design of the collectors.

In contrast to a precipitation collector one air sampler can collect only some of the components in the EMEP measurement programme, and more than one sampler has to be used.

The consequence of the large number of different samplers for gases, aerosols, and precipitation is that comparisons with a reference sampler are necessary in order to assess the differences in the results i.e. the between-network biases. Three large-scale field comparisons have been carried out for samplers of gaseous components and aerosols, and a deeper understanding of the differences and their causes has been gained. Nevertheless the experience shows that a quantitative relations are not easily obtained from these large experiments due to sampler problems and failure, and consequently too short data periods.

Comparisons should cover longer periods, preferably two years in order to catch different meteorological conditions. Only a smaller (random) selection of the samples need, however, to be analysed in order to obtain a reasonable basis for a quantitative estimate since EMEP has daily measurements. The comparisons should be performed with a reference sampler and a national sampler at one site in each country. Results from these types of field intercomparisons can be found on <http://www.nilu.no/projects/ccc/>.

The problem with comparability also arises when changing from one type of air or precipitation sampler to another, within a participating country. The two collectors should therefore be run in parallel in the same way as briefly described above.

The recommended method for the calculations is taken from North American comparisons as described by Sirois and Vet (1994) in Section 5.6.1.

5.5.2.6 *Precision of field instruments and measurement systems*

Two identical samplers or collectors should be run in parallel over some period in order to assess the precision in the data. As above, it is recommended to allow a two year period of comparisons. Section 5.6.2 describes the calculations.

5.5.3 *Laboratory operations*

The chemical analysis of the samples should, as far as possible, not be divided between several institutions within one participating country in order at least to eliminate within-country inconsistencies.

The normal analytical laboratory procedures involve a series of precautions which have to be followed during the work in order to produce data with the required accuracy and precision. The precautions which seem to be specific to the recommended methods have been formulated in Section 4, Chemical analysis. More general aspects have been given in this Section in order to prevent unnecessary repetitions. Standard operating procedures should always be applied.

5.5.3.1 *Chemical analysis*

Calibration should be carried out in the beginning, and end of a series of samples, not to exceed 50, and at the end of the day at the latest. The average of the calibration before and after a sample series should be applied.

In order to quantify the precision and accuracy and detection limit in the laboratory:

- 5% of the samples should be split and the results used to quantify the analytical precision, for calculations of precision see Section 5.6.2,
- 5% of the samples should have known, and realistic, concentrations and should be run between the normal samples to control the performance of the analytical system,
- 5% of the samples should be blank samples used to quantify the analytical detection limit, for calculations of detection limit see Section 5.7.

5.6 Determination of accuracy

Accuracy of a chemical analysis in the laboratory is possible through internal checks against known concentrations and through the annual laboratory comparison exercises organized by the CCC (Hanssen and Skjelmoen, 1995). It is, however, in principle not possible to assess the accuracy in air concentration measurements carried out at a site when accuracy is defined as the deviation from the true, and unknown, concentration. Even the comparability of the data is a severe problem with a widespread monitoring network involving a large number of different sampling methods and laboratories. It is, however, possible to determine the systematic errors (bias) relative to a reference measurement system and also to determine the precision of the measurements. The bias relative to a standard system and the precision together determines the uncertainty of the measurements and will when assessed through the network, and used together with the routine data, give a comparable data set.

The basis for the assessment is parallel sampling, either by one reference method and one national measurement system giving the (relative) bias, or by running two identical national measurement systems giving the precision.

The samples should cover all seasons, and the experiment should preferably extend over two years in order, to some extent, represent different measurement conditions. For an evaluation of the results, however, only a selection of the samples needs to be analysed, and one or two samples every week selected at random may give a sufficient number of samples for an annual average. By selecting samples at random, possible systematic effects on the results from source differences during weekends compared to working days will be reduced. It will also reduce the autocorrelation in the data which simplifies some types of statistics. The bias and random errors in the measurements must be expected to depend upon several factors and the analysis of the data may necessitate a stratification of the material and more than one estimate of the bias difference or precision to be given, e.g. different results for each season. An inspection of the blanks including visualization in charts is strongly recommended before starting the calculations. For Canadian precipitation data Sirois and Vet (1994) concluded that precipitation depth, precipitation type, concentrations, location as well as season and year all influenced the precision. In this case a larger number of samples than indicated above may be necessary.

5.6.1 *Determination of systematic errors*

The basis for the assessment of the systematic errors (bias) relative to a reference analytical chemical method or a reference measurement system, e.g. the between-network bias, is the parallel sampling between two systems.

The importance of standard operating procedures which enables a reproduction of results should be emphasized once more, without them, clearly an effort with parallel sampling is wasted.

Following Sirois and Vet (1994) the overall difference between two measurement systems can be described by the average or median of the differences, the

variability in the differences through the modified median absolute difference estimator (M.MAD), and the coefficient of variation (CoV).

A simple model is applied for the measurements:

$$C_i^l = T_i + B_i^l + e_i^l$$

$$C_i^r = T_i + B_i^r + e_i^r$$

C_i^l and C_i^r are the concentrations obtained with the local or national measurement system and with the reference system respectively, in sample (day) i . T_i is the true and unknown concentration of the component examined which is independent of the measurement system applied. B_i^l and B_i^r are the possible biases in the two systems in sample i , and e_i^l and e_i^r contain the random errors in the data which are reflected in the precision. The random errors e_i are both assumed to have mean values equal to zero while the mean values of both B_i in general are different from zero.

The difference between the two measurements a specific day i gives:

$$C_i^l - C_i^r = (B_i^l - B_i^r) + (e_i^l - e_i^r)$$

and the average difference between the systematic errors for a year, or in a stratum, e.g. during the winter season, can be calculated. Assuming an average over a sufficient number of samples, the averages of the random errors e_i will approximate zero

$$\overline{D} = \frac{1}{n} \sum (C_i^l - C_i^r) = \frac{1}{n} \sum (B_i^l - B_i^r) + (0)$$

and the average of the differences, \overline{D} , between the systematic errors be assessed.

The arithmetic average is often replaced by the median of $C_i^l - C_i^r$ because the statistical distribution of the data frequently deviate from a normal distribution and the median is not influenced by a few extremely large or small measurements.

When $\varepsilon_i^{lr} = C_i^l - C_i^r$, the definition of M.MAD and CoV are

$$M.MAD = \frac{1}{0.6756} \text{median} \left(\left| \varepsilon_i^{lr} - \text{median}(\varepsilon_i^{lr}) \right| \right)$$

$$\text{CoV} = \frac{\text{median}(\varepsilon_i^{lr})}{\text{median}(C_i^r)}$$

The calculations should not include measurements which are considered to be extreme. Such results indicate a measurement problem which needs to be solved.

The experiment has to be repeated for all countries taking part in the network using the same standard measurement system as reference. Assuming that bias differences between sites within a country can be disregarded a correction of annual averages, or averages of possible strata as indicated above, of the routine data can be carried out.

It is necessary to complement the calculations on the parallel measurements with charts such as scatter plots and often also to include other statistical methods to further investigate the differences which may occur.

5.6.2 *Determination of precision*

The precision in the total measurement is more useful for a data user as a measure of the random errors than is the laboratory precision. The basis for an estimation of the measurement precision is a parallel sampling with two identical measurement devices following identical sampling and analytical procedures.

Several measures of precision may be used, e.g. the modified median absolute difference (M.MAD) which is used in the preceding section (Vet and McNaughton, 1994; Sirois and Vet, 1994) and which we will use. This is an estimator of the spread in the data which becomes equivalent to the standard deviation for normal distributions. In the latter case about 68 per cent of the data will be within one standard deviation from the average. The M.MAD is as in the preceding section based on the median of the differences between the corresponding measurements (i.e. usually daily results) which will be insensitive to the presence of a few extreme values.

The equations are similar to the ones in the preceding section. The statistical model for the measurements is given by

$$C_i^1 = T_i + B_i + e_i^1$$

$$C_i^2 = T_i + B_i + e_i^2$$

i is the sample number and C_i^1 the concentration obtained with one of the sampling systems. The true value day i is T_i , and the bias, assumed to be identical for the two measurement systems, is B_i . The random error is contained in e_i^1 which has mean value zero. The precision is then described by the spread in e_i . Assuming that e_i from each of the two samplers are drawn from the same distribution:

$$e_i = \frac{1}{\sqrt{2}} (C_i^1 - C_i^2) \text{ or}$$

$$e_i = \frac{1}{\sqrt{2}} (e_i^1 - e_i^2)$$

The factor in front of the parentheses is included because the errors e_i in the two measurements are assumed drawn from identical distributions.

$$M.MAD = \frac{1}{0.6745} \text{median} (|e_i - \text{median}(e_i)|)$$

The factor 1/0.6745 has been included to make the M.MAD equal the standard deviation for normal distributions.

The coefficient of variance is defined as

$$\text{CoV} = \frac{\text{M.MAD}}{\text{median}(\bar{C}_i)}$$

and where \bar{C} is the average of the two corresponding (usually daily) results.

$$\bar{C}_i = \frac{1}{2} (C_i^1 + C_i^2).$$

5.6.3 Calculation example for precision

The example below is from a series of parallel measurements of aldehyde/ketones carried out during the winter 1994–1995 at the Birkenes site (NO 1) in Norway. The methods for sampling and analysis are described elsewhere in this Manual, and the data are the concentrations of acetone (propanone). Volatile organics are sampled twice weekly in EMEP, usually Tuesdays and Thursdays.

The Tables 5.6.1 and 5.6.2 present the resulting precision expressed by the modified median absolute deviation (M.MAD) and the coefficient of variance (CoV) making use of the formulas in the preceding section with a spreadsheet as a basis for the calculations. The “Median (H)”, in the rightmost column of Table 5.6.2, gives the M.MAD when divided by 0.6745, and the CoV is obtained by division of the M.MAD with the “Median (\bar{C})” and multiplying with 100 in order to have the result in per cent.

Table 5.6.1: Precision of acetone measurements expressed by the modified median absolute deviation M.MAD, and the coefficient of variance CoV.

M.MAD µg/m ³	CoV per cent
0.042	4.5

Table 5.6.2: Calculation of precision. The two leftmost columns contain the 8-hour averages of acetone from two parallel measurements.

S 1 = Birkenes 1	S 2 = Birkenes 2	$\bar{C} = \frac{(S1 + S2)}{2}$		D = S1 - S2 Difference	$E = \frac{D}{\sqrt{2}}$		G = E - F	H = G	
		Average				F =			
1.57	2.49	2.030	Median (C)	-0.92	-0.6505	Median (E)	-0.6293	0.6293	Median (H)
1.37	1.42	1.395	= 0.9300	-0.05	-0.0354	= -0.0212	-0.0141	0.0141	= 0.0283
2.27	2.41	2.340		-0.14	-0.0990		-0.0778	0.0778	
2.16	2.23	2.195		-0.07	-0.0495		-0.0283	0.0283	
1.48	1.52	1.500		-0.04	-0.0283		-0.0071	0.0071	
4.09	4.22	4.155		-0.13	-0.0919		-0.0707	0.0707	
0.93	0.89	0.910		0.04	0.0283		0.0495	0.0495	
1.21	1.24	1.225		-0.03	-0.0212		0.0000	0.0000	
1.41	1.45	1.430		-0.04	-0.0283		-0.0071	0.0071	
3.54	2.46	3.000		1.08	0.7637		0.7849	0.7849	
1.80	1.94	1.870		-0.14	-0.0990		-0.0778	0.0778	
2.31	2.21	2.260		0.10	0.0707		0.0919	0.0919	
1.39	1.42	1.405		-0.03	-0.0212		0.0000	0.0000	
1.36	1.45	1.405		-0.09	-0.0636		-0.0424	0.0424	
0.81	0.90	0.855		-0.09	-0.0636		-0.0424	0.0424	
0.93	0.97	0.950		-0.04	-0.0283		-0.0071	0.0071	
0.69	0.76	0.725		-0.07	-0.0495		-0.0283	0.0283	
0.78	0.84	0.810		-0.06	-0.0424		-0.0212	0.0212	
0.57	0.56	0.565		0.01	0.0071		0.0283	0.0283	
0.78	0.83	0.805		-0.05	-0.0354		-0.0141	0.0141	
0.86	0.96	0.910		-0.10	-0.0707		-0.0495	0.0495	
0.63	0.74	0.685		-0.11	-0.0778		-0.0566	0.0566	
0.66	0.63	0.645		0.03	0.0212		0.0424	0.0424	
0.56	0.56	0.560		0.00	0.0000		0.0212	0.0212	
0.60	0.65	0.625		-0.05	-0.0354		-0.0141	0.0141	
1.01	1.00	1.005		0.01	0.0071		0.0283	0.0283	
0.54	0.55	0.545		-0.01	-0.0071		0.0141	0.0141	
0.63	0.63	0.630		0.00	0.0000		0.0212	0.0212	
0.75	0.73	0.740		0.02	0.0141		0.0354	0.0354	
1.00	0.95	0.975		0.05	0.0354		0.0566	0.0566	
0.55	0.51	0.530		0.04	0.0283		0.0495	0.0495	
0.41	0.44	0.425		-0.03	-0.0212		0.0000	0.0000	
0.42	0.44	0.430		-0.02	-0.0141		0.0071	0.0071	
0.62	0.62	0.620		0.00	0.0000		0.0212	0.0212	
0.87	0.93	0.900		-0.06	-0.0424		-0.0212	0.0212	
0.95	0.95	0.950		0.00	0.0000		0.0212	0.0212	
1.14	0.94	1.040		0.20	0.1414		0.1626	0.1626	
1.53	1.54	1.535		-0.01	-0.0071		0.0141	0.0141	

The temporal variation of the two parallels is given in Figure 5.6.1, and Figure 5.6.2 contains a scatterplot of the results.

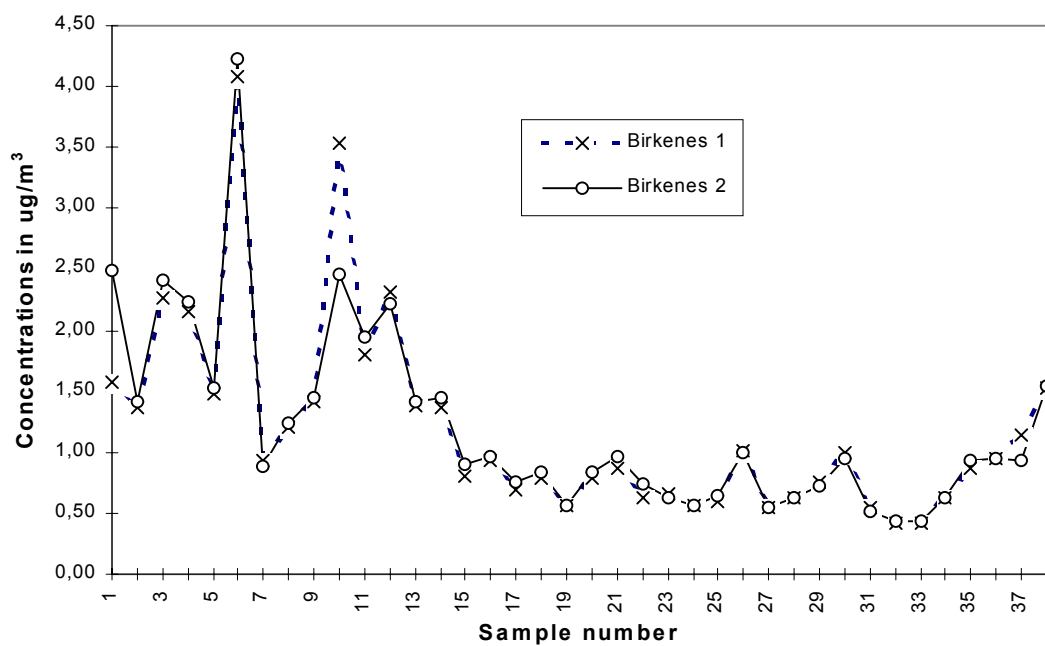


Figure 5.6.1: Temporal variation of acetone during the winter 1994–1995 at Birkenes (NO 1), measured in two parallels. Units in $\mu\text{g}/\text{m}^3$.

The correspondence is generally very good in the Figure above except for the results from sample pair 10 where a mistake has been made with one of the parallels.

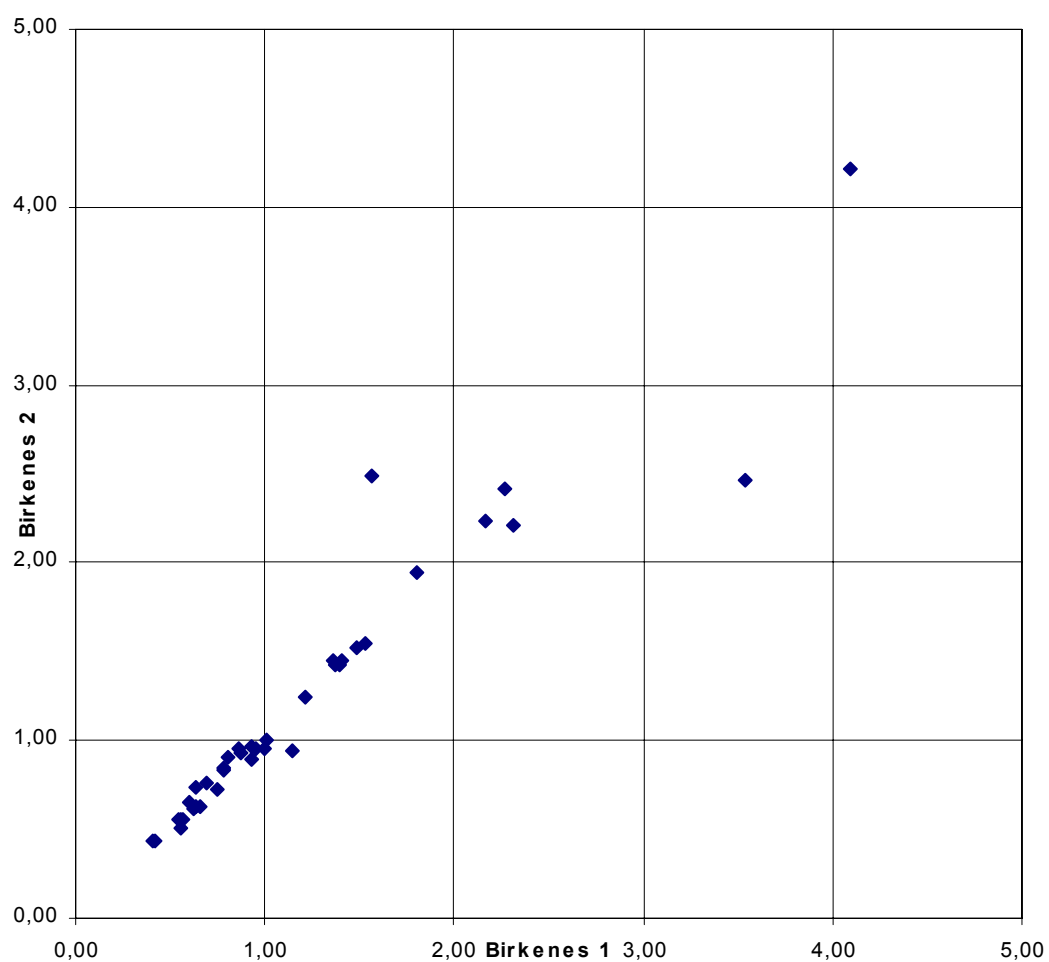


Figure 5.6.2: Scatterplot of the two parallel measurements of acetone at Birkenes (NO 1) during the winter 1994–1995. Units in $\mu\text{g}/\text{m}^3$.

5.7 Calculation of detection limit

Different definitions of detection limits can be found in the literature, and in the preliminary version of this manual, a statistical method after Currie (1968), Wilson (1973), and Kirchmer (1983) was described. One common definition of the detection limit is important because it will highly ease the use of the data, and also simplify the data documentation. As a result of discussions, and a desire to harmonize with WMO GAW, a method different from the one above was selected in the end. The method below and the method described by Currie (1968) and others, are both based on normal distributed data, and the numeric difference in the resulting detection limits comes from a different factor to be multiplied with the standard deviation. The method described by Currie (1968) will in our case give a detection limit about fifty percent higher than the one defined below.

In order to make a detection limit relevant to a complete measurement process, it must be calculated from field blank samples.

It should be emphasized that when concentrations become less than the detection limit, the calculated concentrations should still be reported when possible, and not given as “less than the detection limit”. A data user should normally be able to take such data into account, and at the same time be aware of their limitation.

5.7.1 *Basic assumption*

The reported EMEP data are assumed to be the differences between measurements made on normal exposed samples and blanks e.g. field blank samples. A field blank sample is defined as a sample which has been prepared, handled, transported, and analysed as a normal sample in every way, except that it has not intentionally been exposed, and therefore should not contain the substance to be measured.

The blank values should be aggregated to averages before used to correct measurement results. A possible seasonal variation of blank samples needs to be investigated, and if a variation is present, the blank samples should be aggregated as seasonal or half-yearly averages or better medians, rather than as annual averages before used in corrections.

Unexpected high blank values point at a measurement problem which has to be identified and solved. Such blank values shall not be used for corrections of measurements and calculations of detection limits. The related measurement results must be flagged as less accurate than normal. As an alternative to a complete rejection of the outliers, a “Winsorization” procedure is recommended.

It is assumed that the distribution of the blanks does not deviate too much from a normal distribution.

5.7.2 Statistical considerations

5.7.2.1 Data distribution

It is well known that air pollution data have skew distributions, usually closer to lognormal than to normal distributions. It was assumed above that the data have approximate normal distributions. This is a frequently made assumption when detection limits are discussed and simple statistics based on normal distributions give generally reasonable results even if the distribution is not normal in a strict sense.

The example presented in Figure 5.7.1 is based on field blanks of sulphur dioxide on impregnated filters from the Birkenes site in Norway in 1994. The distribution looks bimodal due to a pile up of blanks in the low-concentration end, around and partly below the detection limit of the analytical method applied (ion chromatography). This distribution is, however, accepted as a sample from a normal distribution when tested with Kolmogorov-Smirnov statistics. This only illustrates that assumptions about normal distributions of the blanks may be reasonable, although not generally valid.

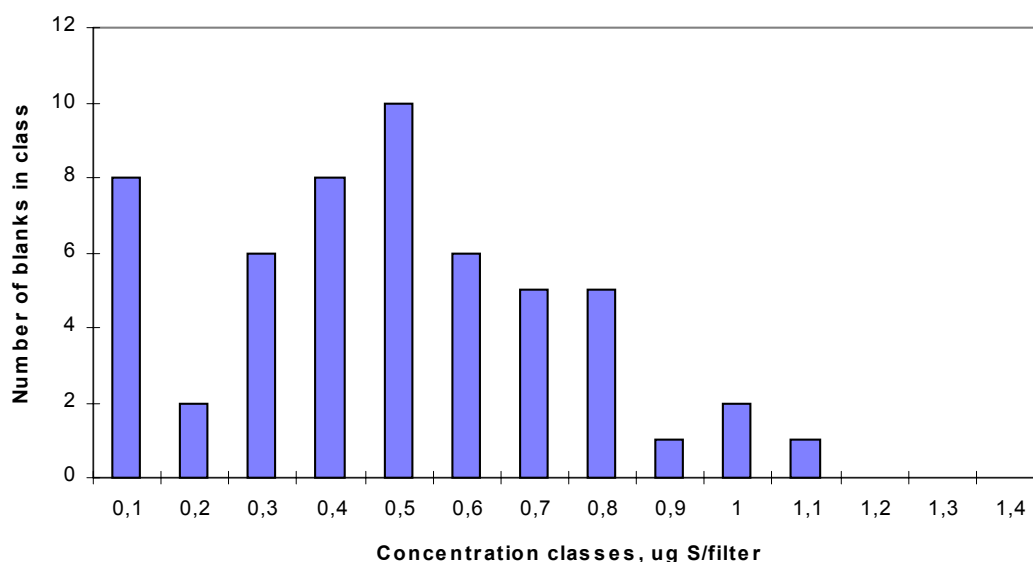


Figure 5.7.1: Frequency of field blanks for SO_2 at Birkenes in 1994.
Unit: $\mu\text{g S/KOH}$ impregnated filter.

5.7.2.2 Detection limit

The detection limit is taken to be three times the standard deviation of the blank results. The probability for having a blank of this size is less than 0.5 per cent.

The detection limit can be calculated:

$$L_d = 3.0 \cdot S_b$$

where the standard deviation is defined as

$$s_b = \left(\frac{1}{N-1} \sum_{i=1}^N (C_i - \bar{C})^2 \right)^{1/2}$$

N is the number of field blanks, C_i is the concentration of the relevant substance in the i^{th} field blank and \bar{C} is the field blank average after elimination of “extreme” blank values. M is the median value.

$$\bar{C} = \frac{1}{N} \cdot \sum_{i=1}^N C_i$$

5.7.2.3 Winsorization procedure

The following procedure may be followed to “Winsorize” outliers, e.g. see Gilbert (1987). The outliers may be identified by inspection and experience rather than by statistical procedures.

As an example, the occurrence of 2 extremely high blank values is assumed.

- Replace the 2 extreme high values with the next lower value.
- Replace the 2 lowest values with the next higher value.
- Calculate the average and the standard deviation of the new data set following Section 5.7.2.2.
- Calculate the Winsorized standard deviation.
- Apply the Winsorized standard deviation to calculate L_d in Section 5.7.2.2.

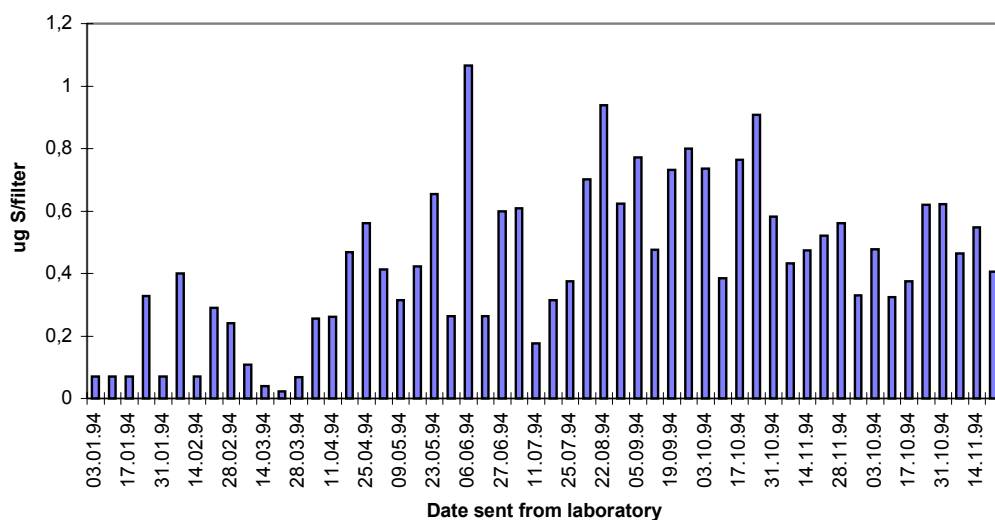
The Winsorized standard deviation, S_w , is

$$S_w = \frac{S_b (n-1)}{v-1}$$

where n is the number of blanks, S_b is the standard deviation of the new data set after the replacements described above. The number of data not replaced, $v = n-2k$, with k outliers (k is 2 in the example above).

5.7.3 Calculation example for air samples

Figure 5.7.1 present field blank results for sulphur dioxide measurements at Birkenes (NO1) in 1994. The unit is $\mu\text{g S/filter}$, the typical air volume is 24 m^3 , a normal air volume with the type of equipment used (NILU EK air sampler) at Norwegian sites. A one weeks supply of filterpacks is sent to the site every week and returned and analysed after one week. Figure 5.7.2 shows the variation of the concentrations of sulphur dioxide in the field blanks through 1994. It is recommended to perform a separate calculation for each quarter.



The results obtained with the data presented in Figure 5.7.2 are given in Table 5.7.1, based on 24 m³ air/day.

	jan-mar		apr-jun		jul-sep		oct-dec	
	µg/filter	µg/m ³	µg/filter	µg/m ³	µg/filter	µg/m ³	µg/filter	µg/m ³
\bar{C}	0.149	<0.01	0.418	0.02	0.574	0.02	0.544	0.02
S _b	0.129	<0.01	0.258	0.01	0.222	0.01	0.166	<0.01
M	0.071	<0.01	0.364	0.02	0.609	0.03	0.521	0.02
L _D	–	0.02	–	0.03	–	0.03	–	0.02

5.8 Training of personnel

Training courses may be organized by the CCC in cooperation with other institutions.

5.8.1 Training of station personnel

Proper training and instruction of site operators is of great importance of the data quality, and all new operators should receive their instructions directly from the scientist responsible for the performance of the station. The training and instruction should take place at the actual measuring station, if necessary after some basic instructions at the laboratory. The operators responsibilities at the site must correspond with his/hers technical qualifications, and the operation of complicated sampling equipment may require technical education.

5.8.2 Training of laboratory personnel

Laboratory personnel should be properly trained in sample handling and analytical work before they are allowed to carry out the routine analyses. Before being assigned on a routine basis to new instruments or methods, they should preferably work on split samples in order to ensure that the requirements to precision and accuracy are met.

5.9 References

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6. Data handling and data reporting

6.1 Data checking

Data checking or validation is based upon:

- experience with the data from earlier measurements,
- relations between chemical components in air and precipitation,
- knowledge about spatial variation,
- knowledge about temporal variation,
- comparisons between measurements and estimates from theory or models.

Records of old data can be used to create simple statistics including percentiles, mean values and standard deviations. Log-transformed data are often preferred. These statistics can be used in connection with control charts or in other comparisons of new data with aggregation of the old ones.

Relations between various chemical components should be utilized, this includes ion balances, relations between sea salt components, and relations between constituents in minerals and dust from other sources. Comparisons with measurements from neighbour stations can be useful, and plots of time-series, e.g. 4-5 year long series of monthly averages of each component can give indications about measurement problems. Estimates of conductivity should be compared with the measured ones. When pH is higher than 5-6 weak acids, which normally are not measured, will be present in the sample. This is a frequent problem in connection with precipitation samples at many EMEP sites.

In this case the ion balance test and comparisons with conductivity will fail unless the missing anions are measured, i.e. through titrations. It should additionally be noted that the equivalent conductivity of the hydronium ion is much higher than those of the other ions, and that a conductivity test of an acidic sample therefore tends to be a test on the pH determination.

6.1.1 Statistical tests

The statistical tests compare new measurements with data already stored in the data base. The tests are carried out to identify possible outliers and results which may be wrong. They can be based upon assumptions about the data distributions i.e. a lognormal distribution, or they can be based on comparisons with cumulative frequency distributions.

Gaseous, aerosol or precipitation components may be compared with all earlier data for each component making use of lognormal distributions. The data should then be split into data from different seasons or into winter and summer data. Data outside three or four times the standard deviations should be inspected manually by comparison with other components, concentrations the preceding and following days, and concentrations at neighbouring stations.

The distributions of the different types of data may deviate from a theoretical lognormal distribution. The deviation may be particularly notable in the low concentration part of the distribution where all concentrations less than the

detection limit will have to be set equal to a small value. Since the tests are used only to identify measurements which should be inspected more closely, minor deviations from a theoretical distribution function can be accepted.

One way to test if a set of data in fact follows a theoretical distribution function is to make use of the Kolmogorov-Smirnov one-sample, two-tailed test (Siegel, 1956).

Other useful statistical textbooks are Gilbert (1987) and Conover (1980).

6.1.2 Ion balance

The EMEP precipitation programme includes all main components in precipitation, and the difference of positive and negative ion concentrations expressed in microequivalents per litre should therefore be zero. Alternatively, the ratio between the anion and cation concentrations expressed in microequivalents per litre should be close to one.

The effect of minor components e.g. phosphates and organic acids, which are not included in the analysis, is usually negligible in acid precipitation.

Assuming equilibrium between carbon dioxide in air and carbonic acid in precipitation, the bicarbonate concentration is negligible when the pH is below 5 and will only contribute 5 e/l at pH=6. Bicarbonate ions dissociate into carbonate ions, but this is negligible below pH=8.

When pH is above 6 in a precipitation sample, experience shows that there apparently is present a large excess of anions in the sample which can not be accounted for. This may be the case even if the bicarbonate concentration, calculated from simple equilibrium conditions, are added.

The weak or strong acids were determined by a titration in the start of EMEP, and these results revealed for some sites large differences between the weak acid concentration measured and the bicarbonate concentrations as calculated from pH assuming equilibrium. It is possible that precipitation samples sometimes are supersaturated with carbon dioxide and therefore may contain more bicarbonate than expected. Clearly, if the pH in precipitation samples at a site frequently is above 6, a titration of the acid concentration should be performed on a routine basis in order to be able to control the precipitation data quality.

During storage, soil dust, organic material etc. may be dissolved or biological processes may occur under unfavourable conditions. Deviations in the ionic sum from zero may indicate this.

The ionic balance check should be carried out as soon as possible, while the chemical analysis can still be repeated. The DGO in Section 5.2 has 10–15% laboratory accuracy as target for the main components in precipitation. As a general guideline, based upon the difference and the sum of cation and anion concentrations, the ion concentration difference in per cent of the ion concentration sum should be lower than 10–15% (except for samples with ion

sums below 50 $\mu\text{e/l}$). If a complete chemical analysis is performed, the ionic balance test is equally useful for aerosol samples.

6.1.3 Conductivity

The conductivity of the precipitation samples should be measured, and compared with values calculated from the measured concentrations by adding the equivalent ionic conductivities. The conductivity measurements should be carried out at 25 °C. A correct determination of conductivity will reveal whether the ion concentration sum is too low or too high. When combined with ion balance calculation and other information, e.g. relations between sea salt components at marine influenced sites, it will identify a smaller group of components which are wrong.

It should be noted, however, that at low pH values ($\text{pH} < 4.0$) the conductivity of the solution will be dominated by the hydrogen ions. Errors in the concentrations of other ionic species will then not be easily detected.

Since this test is based on the ion concentrations as is the ionic balance test, the same limitations as above occur for $\text{pH} > 6$.

6.1.4 Calculation of ion balance and conductivity

Explanation of symbols

(A) Concentration of element A in mg/l. Primary precipitation parameter as reported in data base.

[A] Concentration of element A in $\mu\text{e/l}$ (micro-equivalents per litre). Used in computation of ionic sums and conductivity.

E_A Equivalent weight for ion species A in g/l.

F_A Equivalent ionic conductivity for ion species A in $\text{mho/cm} = \frac{S}{\text{cm}}$ (S = Siemens).

The equivalent conductivity F_A expresses the conductivity due to one equivalent of A per litre.

Conversion of concentration

To convert from (A) to [A] the following formula is used:

$$[A] = \frac{(A) \cdot 1000}{E_A} \quad (1)$$

The equivalent weight E_A for different ion species are given in Table 6.1.1 below.

It is seen from this table that parameter 4, H^+ , is an exception. It is reported in the unit $\mu\text{e/l}$ in the data base. Formula (1) is never applied to this species.

Table 6.1.1: Equivalent weights (E_A) and equivalent ionic conductivities (F_A) at infinite solution and 25°C for different species (WMO-GAW Report 85, CRC, 1985–1986).

Species	E_A	F_A
$\text{SO}_4^{2-}\text{-S}$	16.0	80.0
$\text{SO}_4^{2-}\text{-S (corr)}$	–	–
H^+	–	349.7
$\text{NH}_4^+\text{-N}$	14.0	73.5
$\text{NO}_3^-\text{-N}$	14.0	71.4
Na^+	23.0	50.1
Mg^{2+}	12.2	53.0
Cl^-	35.5	76.3
Ca^{2+}	20.0	59.5
pH	–	349.7
K^+	39.1	73.5
HCO_3^-	–	44.5

- Sulphate corrected for sea-salt is not used in computations of ionic sums and conductivity.
- is reported in $\mu\text{e/l}$, not in mg/l as for the other precipitation species. Thus no conversion factor E_A is given.
- pH cannot be used directly in conductivity computations. First $[\text{H}^+]$ is computed from pH. This value is then used with the F_A given for pH in the conductivity computations.
- Bicarbonate, HCO_3^- , is not a primary parameter in the data base. This is also computed from pH before computation of specific conductivity.

Sum of positive ions

The formula is:

$$\text{ISP} = [\text{H}^+] + [\text{NH}_4^+\text{-N}] + [\text{Na}^+] + [\text{Mg}^{2+}] + [\text{Ca}^{2+}] + [\text{K}^+] \quad (2)$$

If H^+ is measured by titration and is negative, it is set to zero in this computation (refer to the section on weak acids below).

If H^+ is not measured, but pH is determined with a legal value ($\text{pH} > 0$), the $[\text{H}^+]$ is substituted by:

$$[\text{H}^+_{\text{comp.}}] = 10^{(6.0-\text{pH})} \quad (3)$$

The remaining elements in formula (2) are computed by formula (1) if the species are reported, and otherwise set to zero.

Weak acids

If $[H^+]$ determined through a titration is negative, it no longer reflects the concentration of strong acids in the precipitation. Instead it now reflects the sum of concentrations of various weak acids, including the bicarbonate ion, HCO_3^- . When this condition is found, the following two steps are taken before ionic sums are computed:

$$[\text{Weak acids}] = -[H^+] \quad (4)$$

$$[H^+] = 0 \quad (5)$$

Sum of negative ions

The basic formula is:

$$ISN = [\text{Weak acids}] + [HCO_3^-] + [SO_4^{2-}-S] + [NO_3^- - N] + [Cl^-] \quad (6)$$

In this expression $[\text{Weak acids}]$ is defined by formula (4) above.

If $[\text{weak acids}]$ is not measured, the $[HCO_3^-]$ is taken into the calculation if $pH > 5.0$.

$$[H^+_{\text{comp.}}] = 10^{(6.0-pH)} \mu\text{e/l} \quad (3)$$

$$[HCO_3^-] = \frac{5.1}{[H^+_{\text{comp.}}]} \mu\text{e/l} \text{ (Topol et al., 1985)} \quad (7)$$

The remaining elements in (6) are computed by formula (1) if the corresponding species are reported.

Conductivity

The basic formula for the conductivity is:

$$\text{Cond} = 10^{-3} \cdot \sum_A [A] \cdot F_A \frac{\mu\text{S}}{\text{cm}} \quad (10)$$

The expression $[A]$ is as before computed by formula (1).

6.1.5 Use of time series plots in data checking

PCs and Unix systems have made graphical possibilities easy accessible which should be utilized in the data control. Although errors should be detected at an much earlier stage, plots of monthly average concentrations in three or four year long series, have revealed errors in EMEP data. This is strongly recommended as an additional test. Plots of daily concentrations or precipitation amounts should likewise be a part of the routine. The plots should be compared with historical

data divided into half-yearly, seasonal or even monthly aggregates. From the historical data good sets of 5- and 95-percentiles can be calculated since EMEP now possesses a vast amount of data. Data outside these limits should be inspected more closely as a routine.

6.1.6 Other methods for data check

Relations between components which are connected, e.g. sea salt components, should be utilized.

6.2 Rejection of data

No data should be rejected automatically by use of a computer programmes alone; manual inspection should always be carried out before this step is taken.

The purpose of the EMEP is to provide information about air pollution from distant anthropogenic sources, natural pollution and sources within the region (as far as this is in consistence with the criteria given for site location).

Data carrying other types of information, e.g. contaminated samples or careless handling of samples etc., should only be accepted in the data base when the effect of the contamination is considered to be negligible. These data need to be flagged.

6.3 Classification of precipitation samples

The QA plan for EMEP (EMEP/CCC Report 1/88) and the draft version of this Manual contained a classification of precipitation sample results based on ion balance tests and comparisons between measured and estimated conductivities. Having introduced Data Quality Objectives in EMEP, it seems reasonable to base a classification on the criteria given in Section 5.2. The classification given in the two previous reports should therefore not be used, and a new classification will be worked out for the next revision of this Manual.

6.4 Data flags

Several flags have in the past been used to give information about the quality of the data stored in the data base. These flags are revised and are currently under evaluation. The new data flag system contain the old flags, and it will be extended at need.

Some EMEP sites are located at the coast and are from time to time highly exposed to sea salt particles. This will of course affect several components in precipitation which should be flagged in the data base. In particular the “excess sulphate” in precipitation, which will be the difference between two large numbers, may have a high uncertainty and should be flagged.

The person responsible for the data reporting in each participating country is the data originator (DO). The DO will have access to NILU’s external computer and will take care of the future data transfer to the central data base at the CCC.

Flags are sorted according to severity. Flags above 250 indicate an exception that has invalidated or reduced the quality of the data element.

Flags below 250 indicate that the element is valid, even if it may fail simple validation tests. The value may for example be extreme, but has been tested and found correct.

The flag 100 is used to indicate that a value is valid even if an exception in the 999-250 range has also been flagged. In this case the 100 flag must appear before the other flags. In all other cases, the most severe flag should appear first if more than one flag is needed.

All flags are grouped in two categories: V (valid measurement) or I (invalid measurement).

6.4.1 Group 9: Missing

When a measurement is missing and no particular information is available, we cannot assign any numerical value to the measurement (no substitution value is applicable). The measurement value must have been replaced with the transfer file missing flag. For all flags in this group, the measurement is irrecoverably lost, and no substitution value may be computed or estimated. The DO assigns one of the following flags in the flag variable (in addition to setting the transfer file missing flag):

Flag Mnemonic	V/I	Description
999 MMU	I	Missing measurement, unspecified reason
990 MSN	I	Precipitation not measured due to snow-fall. Needed for historic data, should not be needed for new data
980 MZS	I	Missing due to calibration or zero/span check

6.4.2 Group 8: Undefined

In some cases a measurement may not be performed because the parameter to be measured is not defined. As mentioned above, the concentration of pollutants in precipitation is undefined when there is zero precipitation. In this situation the measurement is not missing, and the data availability is not reduced. It is not possible to compute or estimate a substitution value for a measurement that is undefined. The DO assigns one of the following flags:

Flag Mnemonic	V/I	Description
899 UUS	I	Measurement undefined, unspecified reason
890 UNP	I	Concentration in precipitation undefined, no precipitation

6.4.3 Group 7: Value unknown

This group of flags is assigned by the DO when the exact numerical value is unknown, but significant additional information is available. This situation exists when a measurement is below the detection limit of the instrument or method, or is considered to be less accurate than normal.

For many data users it is important to know that the value is low, even if a numerical value is not available. Some users may also need to use or create a substitution value. The substitution value may be based on the detection limit (if reported), or on some other estimate. Statisticians have described methods for using the distribution function of all reported values to estimate the average of the values that fall below the detection limit.

Flag Mnemonic	V/I	Description
799 MUE	I	Measurement missing (unspecified reason), data element contains estimated value
784 LPE	I	Low precipitation, concentration estimated
783 LPU	I	Low precipitation, concentration unknown
781 BDL	V	Value below detection limit, data element contains detection limit
780 BDE	V	Value below detection limit, data element contains estimated value.
771 ARL	V	Value above range, data element contains upper range limit
770 ARE	V	Value above range, data element contains estimated value
750 ALK	I	H+ not measured in alkaline sample
701 LAU	I	Less accurate than usual, unspecified reason. (Used only with old data, for new data see groups 6 and 5)

6.4.4 Group 6: Mechanical problem

This group of flags is assigned by the DO when a measurement value is less accurate than normal due to severe weather or instrument malfunction. The measured value is reported, but should be excluded from use when strict quality control is required.

Flag Mnemonic	V/I	Description
699 LMU	I	Mechanical problem, unspecified reason
679 LUM	V	Unspecified meteorological condition
678 LHU	V	Hurricane
677 LAI	I	Icing or hoar frost in the intake
659 LSA	I	Unspecified sampling anomaly
658 LSV	I	Too small air volume

657 LPO	V	Precipitation collector overflow. Heavy rain shower (squall)
656 LWB	V	Wet-only collector failure, operated as bulk collector
655 LMI	V	Two samples mixed due to late servicing of sampler. Estimated value created by averaging
654 LLS	V	Sampling period longer than normal, observed values reported
653 LSH	V	Sampling period shorter than normal, observed values reported
649 LTP	V	Temporary power fail has affected sampler operation

6.4.5 Group 5: Chemical problem

This group of flags is assigned by the DO when a measurement value is less accurate than normal due to some kind of chemical contamination of the sample. The measured value is reported, but should be excluded from use when strict quality control is required.

Flag Mnemonic	V/I	Description
599 LUC	I	Unspecified contamination or local influence
593 LNC	I	Industrial contamination
591 LAC	I	Agricultural contamination
578 LSS	I	Large sea salt contribution (ratio between marine and excess sulphate is larger than 2.0). Used for old data only. For newer data use 451/450.
568 LSC	I	Calcium invalid due to sand contamination
567 LIC	I	pH, NH ₄ and K invalid due to insect contamination
566 LBC	I	pH, NH ₄ and K invalid due to bird droppings
565 LPC	I	K invalid due to pollen and/or leaf contamination
558 SCV	V	Sand contamination, but considered valid
557 LIV	V	Insect contamination, but considered valid
556 LBV	V	Bird droppings, but considered valid
555 LPV	V	Pollen and/or leaf contamination, but considered valid
549 LCH	I	Impure chemicals
540 LSI	I	Spectral interference in laboratory analysis
532 LHB	V	Data less accurate than normal due to high field blank value
531 LLR	V	Low recovery, analysis inaccurate
521 LBA	V	Bactericide was added to sample for storage under warm climate. Considered valid

6.4.6 Group 4: Extreme or inconsistent values

This group of flags is assigned by the DO after evaluation of the credibility of the measured values. If a measured value is extremely high or low, it may in many cases be suspected to be wrong based on statistics alone. In a conservative presentation of the data set such elements should be excluded.

Some measurements are found to be inconsistent with other measurements or with computed parameters (ion balance, conductivity, etc.). As above, such measurements may be used with caution, but should be excluded from use when strict quality control is required.

Flag Mnemonic	V/I	Description
499 INU	V	Inconsistent with another unspecified measurement
478 IBA	I	Invalid due to inconsistency discovered through ion balance calculations
477 ICO	I	Invalid due to inconsistency between measured and estimated

		conductivity
476 IBV	V	Inconsistency discovered through ion balance calculations, but considered valid
475 COV	V	Inconsistency between measured and estimated conductivity, but considered valid
460 ISC	I	Contamination suspected
459 EUE	I	Extreme value, unspecified error
458 EXH	V	Extremely high value, outside four times standard deviation in a lognormal distribution
457 EXL	V	Extremely low value, outside four times standard deviation in a lognormal distribution
456 IDO	I	Invalidated by data originator
451 SSI	I	Invalid due to large sea salt contribution
450 SSV	V	Considerable sea salt contribution, but considered valid

6.4.7 Group 3

This group of flags (flags 301-399) is presently not defined.

6.4.8 Group 2: Exception flags assigned by the database co-ordinator

This group of flags is reserved for use by the database co-ordinator. The flags in this group are identical to group 4 above. They are only assigned by the database co-ordinator if an inconsistency is found, and the data originator has not previously flagged the condition.

Flag Mnemonic	V/I	Description
299 CNU	V	Inconsistent with another unspecified measurement
278 CBA	I	Invalid due to inconsistency discovered through ion balance calculations
277 CCO	I	Invalid due to inconsistency between measured and estimated conductivity
276 CIV	V	Inconsistency discovered through ion balance calculations, but considered valid
275 CCV	V	Inconsistency between measured and estimated conductivity, but considered valid
260 CSC	I	Contamination suspected
259 CUE	I	Unspecified error expected
258 CXH	V	Extremely high value, outside four times standard deviation in a log-normal distribution
257 CXL	V	Extremely low value, outside four times standard deviation in a log-normal distribution
251 CSI	I	Invalid due to large sea salt contribution
250 CSV	V	Considerable sea salt contribution, but considered valid
249 QDT	V	Apparent typing error corrected. Valid measurement
211 QDI	V	Irregular data checked and accepted by database co-ordinator. Valid measurement
210 QDE	V	Episode data checked and accepted by database co-ordinator. Valid measurement

6.4.9 Group 1: Exception flags for accepted, irregular data

Flag Mnemonic	V/I	Description
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147 QOD	V	Below theoretical detection limit or formal Q/A limit, but a value has been measured and reported and is considered valid
120 QOR	V	Sample reanalysed with similar results. Valid measurement
111 QOI	V	Irregular data checked and accepted by data originator. Valid measurement
110 QOE	V	Episode data checked and accepted by data originator. Valid measurement
100 QOU	V	Checked by data originator. Valid measurement

6.4.10 Group 0

This group of flags (flags 001-099) is presently not defined. The “flag” value 0 is not an error condition flag. It must be assigned to the flag variable for all measurements that are of normal quality. In this manner the DO confirm that the data element is valid (with no known exception that should have been flagged).

6.5 Data reporting

A new relational data base contains the concentrations or measurements with remarks/flags to the data, and the information about sites, instruments etc.

Data reporting forms have been worked out by the CCC in the past; three forms may be used for the reporting of concentrations, one for air, one for precipitation, one for air and precipitation components. Forms containing information about the sites were worked out in the past, and new less comprehensive will be worked out and distributed in 1996 together with information about the data reporting formats above.

The data reporting to be introduced in 1995 follows the NASA/AMES type 1001. Besides this format the ISO 7168 is still valid. Magnetic tapes should not be used. For users of NASA/AMES and ISO 7168 a data base will be created at NILU's external computer, and the users may transfer data directly into this data base using internet.

Data should be submitted to the CCC twice every year, in September data from January to June, and in March data from July to December. Data which are not received before the end of the following year may be excluded from the annual data reports from the CCC, due to the time-consuming calculations and long production time.

The procedure for submission of data are found in more detailed on CCC's homepage: <http://www.nilu.no/projects/ccc/submission.html>

Data are available from the CCC homepage <http://www.nilu.no/projects/ccc/emepdata.html>. Besides this annual and seasonal summaries are worked out and printed in reports.

Experience shows that errors are discovered even in the final data. When errors are discovered they are corrected as far as possible. The most correct data will therefore at any time be the data in the data base at the CCC. *New copies of this data should always be requested from the CCC for scientific use.*

6.6 References

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