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Convention on Long-range Transboundary Air Pollution (CLRTAP)

International Co-operative Programme on Assessment and
Monitoring of Air Pollution Effects on Forests (ICP Forests)

MANUAL

on

methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests

Part XV

Monitoring of Air Quality

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1 Introduction

It is important to assess ambient air quality at the intensive monitoring plots for two reasons. Firstly, air pollutants may cause adverse effects to forest trees and forest ecosystems via direct effects, and secondly, the knowledge of pollutant concentrations in the atmosphere will improve estimates of dry deposition to the forest plots.

Measurements of air pollution deposition to forest trees are mandatory in the Intensive Monitoring Programme, and a large number of sites measuring throughfall and wet deposition have been established throughout Europe. However, throughfall measurements provide insufficient information to provide reliable estimates of dry deposition of nitrogen compounds, and additional modeling procedures must be carried out. Air pollutants of interest for this purpose are nitrogen dioxide, ammonia and other gaseous and particulate nitrogen species.

Air pollutants of interest for direct effects on vegetation include ozone (O_3), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and ammonia (NH_3). Ozone however, is of primary interest due to its phytotoxicity at ambient concentrations, and widespread occurrence in Europe, particularly in the Mediterranean area.

Ambient air quality at the site can be estimated by modeling or by interpolation of monitoring data from near-by sites. In most areas, however, representative local monitoring stations, that could provide the necessary data, are not available. For this reason, there is a lack of sufficient information that prevents most modeling approaches.

Real time air quality monitoring will provide the most detailed information, as a result of its high temporal resolution. However, such measurements are costly, and because of the necessary infrastructure requirements, these active monitoring sites are generally scarce in background areas.

Passive sampling for compounds such as ozone, sulfur dioxide, nitrogen dioxide and ammonia has been proved to be a valuable method in many areas. This is particularly the case in remote sites, where the availability of a power supply is often limited, and accurate determinations of ambient air concentration can be achieved at relatively low cost. The disadvantage of passive monitoring is the low temporal resolution (from one week to one month, mainly dependent on the magnitude of air concentrations).

The choice of method depends on the need for high temporal resolution, the frequency of on-going visits to the monitoring sites and the resources available. Passive sampling is recommended as the main method within the ICP Forests programme on sites that do not currently monitor ozone using active samplers. For validation purposes, at selected Level II sites (or in near-by monitoring stations, e.g. EMEP stations), the passive samplers should be combined with real time measurements.

As methods for estimating AOT40 from passive samplers and ozone flux modeling have been developed in recent times, measurement requirements and additional data needs will be taken into account to assure the applicability of such methods at selected plots.

2 Scope and application

This Part of the Manual aims at providing a consistent methodology to collect high quality, harmonized, and comparable data on pollutants concentrations at the intensive Level II plots of the monitoring programme, with special emphasis on passive sampling (Table 1). Harmonization of procedures is essential to ensure data comparability. To have their pollutant data used in the international database and evaluations, National Focal Centers and their scientific partners participating to the UNECE ICP Forests programme have to follow the methods described here.

Table 1: Quick reference of variables to be measured with passive and active samplers for the air quality monitoring programme

Form	Variable	Report. unit	Level II	Level II core	Level I	Value *	DQO	DQL
AQP	O_3	µg m^{-3}	o	m**	n	MC	±30%	75%
AQP	NH_3	µg m^{-3}	o	o	n	MC	±30% ***	75%
AQP	NO_2	µg m^{-3}	o	o	n	MC	±30% ***	75%
AQP	SO_2	µg m^{-3}	o	o	n	MC	±30% ***	75%
AQA	O_3	µg m^{-3}	o****	o****	n	hourly data	-	-
AQA	NH_3	µg m^{-3}	o	o	n	hourly data	-	-
AQA	NO_2	µg m^{-3}	o	o	n	hourly data	-	-
AQA	SO_2	µg m^{-3}	o	o	n	hourly data	-	-

o = optional; m = mandatory; n = not measured
* MC = Mean concentration
** For plots with active measurements, additional passive samplers are optional.
*** For values > 3 μg m^{-3}
**** Active ozone measurements are recommended to be combined with hourly meteorological measurements for ozone flux modelling
DQO: Data Quality Objective (minimum acceptable accuracy) for measurements, also referred to MQO (Measurement Quality Objective) (see Table 6)
DQL: Data Quality Limits (minimum frequency of data that must fit the DQO), i.e. the threshold for validating the data set (see Table 5)

3 Objectives

The main objectives of measuring the concentrations of tropospheric ozone, sulfur dioxide, nitrogen dioxide and ammonia at the Level II sites are to contribute to a better understanding and quantification of immission processes to European forest ecosystems.

Specific aims are set as follows:

- Quantification of annual immissions of ozone, sulfur dioxide, nitrogen dioxide and ammonia with an accuracy level of ±30% and a data completeness of 80% within the pollutant-specific measurement period (see Table 5).
- Detection of temporal trends of tropospheric ozone, sulfur dioxide, nitrogen dioxide and ammonia on a plot (significant changes within 10 years with a 95% significance level).
- Detection of spatial trends of tropospheric ozone, sulfur dioxide, nitrogen dioxide and ammonia across Europe (significant trends with a 95% significance level).

4 Location of measurements and sampling

Ambient air quality monitoring must be site-specific and should be carried out on Level II sites where meteorology and deposition data are available.

4.1 Sampling design

Given the nature of air concentration measurement, no formal statistical sampling design is proposed. Rather, proper criteria are provided for selecting the most appropriate site for the location of the open meteorological station.

4.1.1 Location of the sampling site

Air pollution concentrations should be measured near, but outside the forest. Samplers/monitors should be installed at the open field plot, either where the samplers for wet deposition and/or the meteorological equipment are installed. Choose the site that is closer to the nearby forest edge (see Meteorological measurements and Sampling and Analysis of Deposition, Parts VI and VII). In addition, where ongoing measurements are, or could be carried out above canopy level, it is recommended that such measurements are continued or initiated.

4.1.2 Use of shelter and number of replicates

Use protective shelters in order to reduce possible environmental disturbances (e.g. some passive samplers are sensitive to wind, overestimating in windy places if not exposed with shelters). Expose at least two replicates simultaneously at each site. For better data quality, three replicates are recommended.

4.1.3 Sampling height

Passive samplers should be installed at 2 m above soil level in the open-field plot (where ground vegetation is cut). If deposition and/or meteorological parameters are measured above forest canopy, they can also be installed above canopy. Optionally, complementary measurement points may be established at different heights. The inlet heights of active monitoring instruments should comply with the recommendations of EU Directive 2008/50 CE and the requirements necessary to study flux-gradient relationships (aerodynamic gradient method)

4.2 Sampling equipment

The countries are free to select the type of passive sampling device that is used. However, it should be guaranteed that both the samplers and the applied procedure, comply with additional measurements that are conducted for reference. For quality assurance, it is recommended to run the samplers in parallel with either one or several of the following reference methods:

- Reference methods established for the different pollutants in Directive 2008/50 CE of the European Parliament and Council of 21 May 2008 on Ambient Air Quality and Cleaner Air for Europe and European Norms referred to herein.
- Instrument run at an EMEP site in accordance to the EMEP Manual (EMEP/CCC/Report 1/15, NILU, Norway);
- To participate in intercomparison tests of different types of passive samplers.

4.3 Frequency of sampling and sampling period

For ozone, the sampling is carried out on a 2-week basis and covers the period of 1 April - 30 September. For Mediterranean conditions it is recommended to cover all 12 months of the year. If possible, change ozone passive samplers during even (e.g, 22, 24, 26, …) calendar weeks in order to synchronize measuring periods throughout Europe. For the other pollutants, the minimum sampling frequency is 4 weeks or monthly, preferably in coordination with collection of deposition samples, and should cover all 12 months of the year.

4.4 Sample collection, transport and storage

Transport and storage of the passive samplers before and after being exposed in the field, may have an influence on the chemical analysis, affecting the results. Therefore, it is important to strictly follow the guidelines of the passive sampler manufacturer in order to minimize possible disturbing effects by e.g. temperature. For quality control, at least four blank samplers per season (ozone) or year (the other pollutants) should be included in the standard transport- and storage-procedure. If passive samplers are transported or mailed to the different field plots using separate routes, randomly select one of them each time.

5 Measurements

5.1 Variables measured and reporting units

Ozone concentrations have to be measured at Level II core plots, either by passive or/and active sampling (the latter method is preferred). For the rest of standard Level II plots, measurement of this pollutant is optional. Measurement of the other pollutants (NO_2, SO_2, NH_3) at Level II plots, either by passive or active sampling, is also optional.

The variables measured with passive and active samplers and their units are reported in the following tables:

Table 2: Variables and units measured with passive samplers for the monitoring of air quality

Variable	Reporting unit
O_3 concentration*	µg m^{-3}
NH_3 concentration	µg m^{-3}
NO_2 concentration	µg m^{-3}
SO_2 concentration	µg m^{-3}

* at standard temperature and pressure

Table 3: Variables and units measured with active monitors for the monitoring of air quality

Variable	Reporting unit
Hourly O_3 concentration	µg m^{-3}
Hourly NH_3 concentration	µg m^{-3}
Hourly NO_2 concentration	µg m^{-3}
Hourly SO_2 concentration	µg m^{-3}

5.1.1 Analysis

The analytical procedure is directly linked to sample preparation. As mentioned in section 4.2, individual countries are free in their choice of manufacture and methodology for passive sampler, as long as the criteria for quality assurance (chapter 5.2) are met. It is recommended that all samplers, or at least all samplers measuring the same variable, are analyzed at the same laboratory per country. The laboratory should use and document well-defined sample handling and analytical procedures, according to either national and/or European standards for good laboratory practices (e.g., CEN/TC 264/WG11).

5.2 Quality Assurance and Quality Control

Individual countries are free in their choice of manufacture and methodology for passive sampler, as long as the criteria for quality assurance are met. As the comparability of results is essential for the further use of data in the ICP Forests programme, as well as in all other national and European networks, a strict quality assurance system must be applied in order to reach the objectives (chapter 3).

Regular inter-comparison tests between and among the different samplers used and reference methods are necessary in order to determine whether there are significant differences in accuracy under varying environmental conditions (temperature, wind speed, and pollutant concentrations).

The aim of the quality assurance is to avoid disturbing effects on the samplers and systematic monitoring errors as far as possible. For this, both the documentation of analytical methods (techniques used, detection limits, etc.) and of all actions and incidents during sample preparation, sample handling – in the field (sample exposure) and in the laboratory (sample analysis) –, transportation, and storage should be described in the DAR-Q form.

To ensure continuing consistency of the collected data when monitoring sites or procedures are changed, parallel measurements for at least one month before and after the change should be conducted to detect systematic differences between sites or manufacture-specific procedures.

Data can be checked with respect to quality as follows:

- Submitted data from passive samplers are checked for plausibility and compared to known concentration ranges and variability from the same region (see chapter 5.2.1). Additional plausibility tests are made with other national results in respect to ambient air quality;
- Submitted data are checked for completeness (see chapter 5.2.2).
- Results from duplicate (and triplet) passive samplers are compared;
- Results from passive samplers are checked against those from active samplers;
- Field blanks are included in the entire transport- and storage-process and analyzed to test for disturbing factors during preparation, transport, handling, and storage.

5.2.1 Plausibility limits

Plausibility limits for the passive samplers are provided in Table 4.

Table 4: Upper and lower plausibility limits for passive monitoring of air quality at Level II sites

Pollutant (units)	Lower Limit	Upper limit
O_3 (µg m^{-3})	5	200
NH_3 (µg m^{-3})	0.1	40
NO_2 (µg m^{-3})	0.2	40
SO_2 (µg m^{-3})	0.2	40

5.2.2 Data completeness

Data completeness requirements for the passive samplers are provided in Table 5.

Table 5: Data completeness and measurement period for passive monitoring of air quality at Level II sites

Pollutant	Data completeness for measurement period
O_3	80% April-September
NH_3	80% whole year
NO_2	80% whole year
SO_2	80% whole year

5.2.3 Data quality objectives or tolerable limits

Data quality objectives and tolerable limits are provided in Table 6.

Table 6: Data quality objectives (DQO) for passive monitoring of air quality at Level II sites

Pollutant	Type of measurement	Data Quality objectives
All pollutants	Field measurements	Data completeness ≥ 80%
All pollutants	Passive samplers co-located with active monitors	Data within ± 30% of reference value*
All pollutants	Intercomparison tests for passive samplers	Data within ± 30% of reference value*
All pollutants	Coefficient of variation among replicates	≤10%

* for values >3 µg m^{-3}; Reference value = value from co-located active monitor.

5.2.4 Data quality limits

Data quality limits are provided in Table 7.

Table 7: Lower data quality limit (DQL) for passive monitoring of air quality at Level II sites

Pollutant	Type of measurement	Lower Data Quality Limit
All pollutants	Field measurements	Data completeness ≥ 80% in at least 80% of the reported plots per country
All pollutants	In passive samplers co-located with active monitors	75% of the data within ± 30% of reference value*
All pollutants	Intercomparison tests for passive samplers	75% of the data within ± 30% of reference value*
O_3, NO_2, SO_2	Coefficient of variation among replicates	≤10% in at least 80% of the reported plots per country
NH_3	Coefficient of variation among replicates	≤20% in at least 80% of the reported plots per country

* for values >3 µg m^{-3}; Reference value = value from co-located active monitor.

6 Data handling

6.1 Data submission procedures

All validated data must be submitted in electronic format to the central data base at the ICP Forests Programme Co-ordinating Centre (PCC), using the forms that are provided by ICP Forests as soon as possible but in the calendar year following the observations at the latest.

Explanatory items, dictionaries, and information on forms for data upload can be found at http://www.icp-forests.org/documentation/.

Additional information on local conditions, sampling, transportation and storage procedures, analytical procedures, and interpretation of the results should be reported in DAR-Q form. The detailed time schedule is provided by the relevant bodies of PCC. The person responsible for the national database should inform the National Focal Centres about the different methods of electronic data submission.

6.2 Data validation

Data will be checked for plausibility, completeness and variability among replicates according to DQO and DQL limits established in chapter 5.2. Results of intercomparison exercises and of co-located passive samplers with active monitors will also be used as complementary information for data validation.

6.3 Transmission to co-ordinating centre

Every year, all validated data should be submitted to the central data storage facility at the ICP Forests Programme Coordinating Centre (PCC). Detailed time schedules and submission dead lines are provided by the relevant bodies.

6.4 Data processing guidelines

For passive samplers, seasonal or annual means will be calculated as weighted means (i.e., taking into account possible differences in the duration of the exposure period). AOT40 (in ppb h) will be calculated as the sum of the difference between hourly concentrations greater than 40 ppb over a given period using only the one-hour values measured between 8:00 and 20:00 Central European Time (CET) (i.e., between 7:00 and 19:00 UTC) each day (EU Directive 2008/50 CE). In cases where not all possible measured data are available (e.g., 9% of hourly data [8:00 to 20:00] missing for the period April-September), the following factor shall be used to calculate AOT40 values: $AOT40_{estimated} = AOT40_{measured} \times$ (total possible number of hours/number of measured hourly values) (EU Directive 2008/50 CE). However, it should be kept in mind, that for regions with longer periods of high radiation, the EU Directive 2008/50 CE approach may be conservative and underestimate AOT40 compared to the approach that is based on radiation (> 50 W m^{-2}).

Hourly ozone concentrations needed for AOT40 and ozone flux calculations are directly measured with active monitors. However, they can also be modeled from passive samplers. Of the different methods proposed for estimating AOT40 from passive samplers, the approach by Gerosa et al. (2007) has already been applied in Level II plots. This approach requires plot co-ordinates and elevation data. AOT40 has also been estimated by applying a simple linear regression model developed by Ferretti et al. (2012) (Schaub et al., 2015). Hourly ozone concentrations (measured or modeled), together with additional hourly meteorological data and (at least daily) soil water content measurements, can be used to calculate ozone fluxes (Schaub et al., 2007). Ozone flux modeling methods, as well as the recommended parameterizations for different species, are described in detail in ICP Modelling and Mapping (2004).

The different ozone metrics (means, AOT40, fluxes; measured or estimated) can be subsequently used for correlative studies with visible injury (see ICP Forests Manual Part VIII on the Assessment of Ozone Injury) and for risk assessment in relation with the current critical levels (EU Directive 2008/50 CE, ICP Modelling and Mapping, 2004).

6.5 Data reporting

All validated data should be sent to the National Focal Centre and submitted annually to the transnational central data storage. The respective submission forms are provided in the forms document available at the ICP Forests web page. An overview of the submission forms is given in Table 8.

Table 8: Abbreviation and content of the submission forms for monitoring of air quality at Level II sites.

Form abbreviation	Content description
PPS	Plot information for passive samplers
AQP	Measurement data from passive samplers
PAC	Plot information for active monitoring
AQA	Hourly data from active monitoring
AQB	Values from blank, i.e. not-exposed passive samplers for QA/QC
COL	Measurement data from passive samplers co-located with active monitors for QA/QC

Two of these forms (AQB and COL) are for quality assurance/quality control. Other complementary information needs to be documented in an annual DAR-Q: relevant local conditions for air quality (exposure to local emission sources and local land use, location in relation to forest edges etc.), information on the passive samplers (brands, methods, laboratories) and active monitors (measurement site, brands, …), irregularities found (e.g. missing data and errors encountered in the validation). DAR-Q document will also include a description of the sampling and analytical procedures, an interpretation of the results, and quality assurance results.

Note: For passive samplers, if measured values are below the limit of quantification, use the code "-1" (in field "Value" of forms AQP and AQB) and report this limit under the field "Other observations".

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Annex I – Conversion factor between *µ*g m^{-3} and ppb ozone

1 µg m^{-3} = 0.50937 ppb (at standard conditions, P = 1013 mbar, T = 25ºC)

Annex II – Minor changes after 2020

Date	Minor change to latest published version in 2020	Affected sections of this document