1. Introduction

The "Cooperative programme for monitoring and evaluation of long-range transmission of air pollutants in Europe" (EMEP) was launched in 1977 as a response to the growing concern over the effects on the environment caused by acid deposition. EMEP was organized under the auspices of the United Nations Economic Commission for Europe (ECE). Today EMEP is an integral component of the cooperation under the Convention on Long-range Transboundary Air Pollution.

The main objective of EMEP is to provide governments with information on deposition and concentration of air pollutants, as well as on the quantity and significance of long-range transmission of pollutants and transboundary fluxes. The programme includes three main elements: emission data, measurements of air and precipitation quality, and atmospheric dispersion models. The work is co-ordinated by three international centres: two centres for modelling activities and one Chemical Co-ordinating Centre (CCC) for coordination of the chemical measurements.

This manual describes the standard recommended methods for sampling and chemical analysis for the EMEP measurement network. The methods and procedures are generally derived from the development and experience gained within EMEP as well as information provided by similar programmes in North America, World Meteorological Organization, various research programmes and numerous EMEP workshops.

The measurements within EMEP are carried out by national laboratories, reporting the results to a common data base at the CCC. Experience has shown that measurements should be standardized as much as possible to obtain data which are comparable and of sufficient quality to allow meaningful comparisons with model calculations, calculation of trends and other statistical evaluations. In addition, quality assurance has to be carried out on both the national level and by the CCC to ensure satisfactory data quality. This applies both to individual samples and particularly to long-term aggregated values, such as seasonal or yearly mean values and trends. It is particularly important to avoid errors which may result in systematically too low or too high results, and undefined changes in the data quality over time, which may cause problems in trend analyses.

For the majority of the methods, the necessary quality assurance is facilitated by a combination of simple and robust sampling techniques with well-described sampling equipment, and use of synthetic control samples for the chemical analyses.

The representativity of a site is a highly relevant question for a measurement network such as EMEP. This can only be determined in relation to the purpose of the measurements. For EMEP the site must be positioned in such a way that the air quality and the precipitation is representative of a larger region. In order for the site to be representative, influences and contamination from local sources must be avoided.

During the period of EMEP operations, considerable improvements have taken place with respect to the development of instrumentation for chemical analysis.

EMEP's measurement programme and recommended methods described in the manual

Components	Measurement period	Measurement frequency	Sampling methods in field	Methods in laboratory
Gas				
SO_2	24 hours	daily	KOH impregnated filters	IC / (Thorin)
NO_2	24 hours	daily	NaI impregnated glass frit	IC / Griess
O_3	hourly means stored	continuously	UV absorption	
HNO_3	24 hours	daily	denuder	IC / Griess after reduction
NH_3	24 hours	daily	denuder	IC / Indophenol
Light hydrocarbons C2-C7	10-15 mins	twice weekly	steel canisters	GC
Ketones and aldehydes (VOC)	8 hours	twice weekly	DNPH cartridge	HPLC
Hg	24 hours	weekly	Gold traps	CV-AFS
Particles				
SO_4^{2-}	24 hours	Daily	aerosol filter	IC / (Thorin)
NO_3^-	24 hours	Daily	aerosol filter after denuder	IC / Griess after reduction
NH_4^+	24 hours	Daily	aerosol filter after denuder	IC / Indophenol
Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^-	24 hours	Daily	aerosol filter	IC / AAS / AES
PM_{10}	24 hours	Daily	EN 12341	micro balance
PMx	24 hours	Daily	To be decided	micro balance
Mineral dust	24 hours	Daily	EN 12341	INAA, PIXE, XRF
EC and OC	24 hours	Daily	EN 12341	Thermo desorption and oxidation
OC-speciation	24 hours	once a week	EN 12341	LC-MS
Cd, Pb (first priority), Cu, Zn, As, Cr, Ni (second priority)	weekly	weekly	EN 12341	ICP-MS / GF-AAS
Gas + particles				
$HNO_3(g)+NO_3^-(p)$,	24 hours	daily	Filter pack	IC / Griess after reduction
$NH_3(g)+NH_4^-(p)$	25 hours	daily	Filter pack	IC / Indophenol
POPs (PAH, PCB, HCB, chlordane, lindane, a-HCH, DDT/DDE)	to be decided	to be decided	PUF (polyurethane foam) sampler	GC-MS

Components	Measurement period	Measurement frequency	Sampling methods in field	Methods in laboratory
Precipitation				
Amount	24 hours (weekly)	daily (weekly)	rain gauge	By weight
SO_4^{2-}	24 hours (weekly)	daily (weekly)	wet only	IC
H^+	24 hours (weekly)	daily (weekly)	wet only	titration
pH	24 hours (weekly)	daily (weekly)	wet only	pH meter
NH_4^+	24 hours (weekly)	daily (weekly)	wet only	IC / Indophenol
NO_3^-	24 hours (weekly)	daily (weekly)	wet only	IC / Griess after reduction
Na^+	24 hours (weekly)	daily (weekly)	wet only	IC / AES
Mg^{2+}	24 hours (weekly)	daily (weekly)	wet only	IC / AAS
Cl^-	24 hours (weekly)	daily (weekly)	wet only	IC / Thiocyanate
Ca^{2+}	24 hours (weekly)	daily (weekly)	wet only	IC / AAS
K^+	24 hours (weekly)	daily (weekly)	wet only	IC / AES
κ (conductivity)	24 hours (weekly)	daily (weekly)	wet only	Cond-meter
Cd, Pb (first priority)	weekly	weekly	wet-only	ICP-MS / GF-AAS
Cu, Zn, As, Cr, Ni (second priority)	weekly	weekly		
Hg^{2+}	weekly (1 sampler) (or monthly (2 samplers)	weekly (or monthly)	wet only IVL sampler	CV-AFS
POPs (PAH, PCB, HCB, chlordane, lindane, a-HCH, DDT/DDE)	to be decided	to be decided	wet-only	

2. Siting criteria

2.1 Representativeness within an area

The site chosen for sampling and measurements should be representative of a larger area. The size of this area is determined by the variability of the air and precipitation quality, and the desired spatial resolution in the concentration and deposition fields. Urban and industrial areas, and the areas immediately outside such areas are not to be included, because these make up a very small fraction of the total area covered by EMEP, and the higher concentrations in such areas are caused by national emissions. The purpose of EMEP is to provide Parties with information on the deposition and concentration of air pollutants, as well as on the quantity and significance of the long-range transmission of pollutants and fluxes across national boundaries.

The size of the site's area of representativeness should be larger than the size resolution of the atmospheric dispersion models which are available for the evaluation of the long-range transmission and deposition of air pollutants. EMEP models and emission surveys have up to now employed a grid sizes of $150*150$ km^2, this spatial resolution is now being improved to $50*50$ km^2 in some models.

When the major part of the emissions influencing the air quality in an area are situated outside that area, selection of the site involves mainly consideration of the effects of the immediate surroundings and emissions within the nearest 20 km. These local emissions should not be allowed to result in unrepresentative measured air concentrations or precipitation chemistry at the site, which means that their influence must be evaluated and compared with the measurements. In practice, emissions of sulphur dioxide and nitrogen dioxide within the nearest 100 m should be avoided, emissions within the nearest 2 km should be less than 100 kg/year, and emissions within the nearest 20 km less than 1000 kg/year. In addition, consideration of local meteorological conditions, such as prevailing wind directions and formation of stagnant air should be considered.

The situation is more complicated if the site is located within an area of major emissions. In principle, the representativeness of a particular site within such an area can be determined by the use of models, provided that the models are adequate and the emissions and the meteorology are known in adequate detail. Since the distribution of emissions is uneven, the distributions of ambient concentrations at ground level are skewed, with median concentrations typically less than the area mean values. Variations in airborne concentrations within a given grid are caused by both short-term random fluctuations in the meteorological parameters responsible for dispersion and advection, by deposition processes and interactions with the surface, and by differences in the exposure towards dominating emissions in the long term. Seilkop (1994) used daily measured values for clusters of 3-5 neighbouring sites in 6 areas of the eastern USA to determine 95% confidence limits for these values, assuming that these reflect the spatial representativeness of the sites. As could be expected, for areas where the main source of sulphur dioxide is emissions from large power plants, daily variabilities were quite high for sulphur dioxide. In this situation no single site can be expected to reflect an area mean value on a day-to-day basis. Other papers presented at the

EMEP-WMO workshop in Passau (EMEP/CCC-Report 2/94) also show the difficulty in explaining or predicting individual high concentrations at individual sites on a daily basis by existing models. However, on a more long-term basis, inter-grid variabilities are generally much smaller. Sites within areas with large emission sources should therefore be expected to be representative only on a monthly or yearly averaging period.

Representativeness is more readily achieved for secondary pollutants such as sulphate aerosol and ozone.

Ammonia is a special problem, since the emissions are mainly linked with animal husbandry and agricultural activities. Stabling of animals, storage and application of manure, and grazing of fertilized pasture by cattle, are important emission sources, and should be avoided in the nearest surroundings of the site.

For precipitation, local emission sources of sulphur dioxide or nitrogen oxides are generally of less importance, but sources of dust and ammonia should be avoided. Even if a wet-only precipitation collector is used, a dusty environment may cause serious contamination problems.

Guidelines specifying minimum distances to emission sources have been given in the EMEP Quality Assurance Plan (Schaug, 1988). These were based on similar guidelines from North American monitoring programmes. Table 2.1.1 sums up these recommendations:

Table 2.1.1:   Minimum distance to emission and contamination sources.

Type	Minimum distance	Comment
Large pollution sources (towns, power plants, major motorways)	50 km	Depending on prevailing wind directions
Small scale domestic heating with coal, fuel oil or wood	100 m	Only one emission source at minimum distance
Minor roads	100 m	Up to 50 vehicles/day
Main roads	500 m	Up to 500 vehicles/day
Application of manure, stabling of animals.	2 km	Depending on the number of animals and size of fertilized field or pastures
Grazing by domestic animals on fertilized pasture	500 m	Depending on the number of animals and size of fertilized field or pastures

The distances given in this table should be taken only as indicative, an appraisal of local emissions' influence on the air and precipitation chemistry at the site must be made on the basis of considerations of meteorological and topographic conditions, and the estimated emissions from the activities mentioned above.

2.2 Representativeness with respect to topographic features

The site must be representative also with respect to exposure to the air mass. Valleys or other locations which are subject to formation of stagnant air under inversion conditions should be avoided, also mountaintops and passes (cols). The ideal is a well exposed site in moderately undulating terrain, or, if valleys cannot be avoided, on the side of the valley above the most pronounced night-time inversion layer. Coastal sites with pronounced diurnal wind variations due to land-sea breeze effects are also not recommended. Vegetation is a sink for many air pollutants, and it is important to avoid situations where sheltering by vegetation, e.g. by a stand of trees, results in lowered concentration when the wind is blowing from a particular direction.

The choice of a site, and the proper location of the precipitation collector is also important in order to ensure that the precipitation samples are representative for precipitation over a larger area. The collector should not be exposed to strong winds, but should also not be sheltered by tall trees or buildings. The annual precipitation amount at the site, as measured by an ordinary meteorological precipitation gauge, should not differ markedly from the precipitation amounts at adjacent sites in the national precipitation network, and the daily precipitation amounts should also be correlated with those from the adjacent sites.

The location of the sampler should conform to WMO site requirements for precipitation gauges (WMO, 1971). There should be no obstacles, such as trees, above 30° from the rim of the precipitation collector, and buildings, hedges, or topographical features which may give rise to updraughts or downdraughts should be avoided. Consideration of the prevailing wind directions during precipitation events is recommended in connection with locating the sampler.

Of particular concern is potential contamination from sedimentation of soil dust particles from the immediate surroundings. Gravel roads, farmyards, and tilled agricultural fields within a distance of 100 m to 1 km should be avoided. The ground cover should preferably be short grass.

2.2.1 Technical facilities

Air sampling and monitoring equipment requires a small building, or shed, and supply of electricity. The room containing pumps and control units should prefer-ably be kept at approximately 20°C. A refrigerator must also be available for storage of samples. A telephone line is useful for the transfer of ozone measure-ment data via a modem from a data logger. Access to the site by car should be limited to the persons directly in charge of the sampling and the measurements.

2.2.2 Documentation

The land use, and the topography of the immediate surroundings, and preferably also the meteorological conditions(wind rose, climatological data) should be available in the form of maps, tables and diagrams.

An inventory of emissions in the nearest 20 km is also required.

In order to evaluate the representativeness of the site, information on the air quality and deposition for several sites within the same area is generally required. Such information may be provided by detailed mathematical modelling if the sources of air pollutants are known in sufficient detail. Another possibility is to run measurements at several sites for a limited time period. Simple and relatively inexpensive measurement techniques are now available for the determination of long-term average concentrations of sulphur dioxide, nitrogen dioxide and ammonia, using passive samplers. For precipitation, weekly or even monthly sample collection at a number of sites within the same area will serve to determine the representativeness of the chosen site.

2.2.3 Distance between sites

The maximum distance between adjacent sites within the EMEP network should be carefully considered. This again depends on the size resolution of the models which are being used, and the spatial gradients in the concentration fields which are due to large-scale transport, transformation and deposition effects.

The (spatial) correlation between measured concentrations of air pollutants in Europe is highly anisotropic, and depends on the position and strength of emission sources, wind directions, topography and the chemical and physical properties of the various pollutants. An recent evaluation by the EMEP Bureau recommended a distance between the sites of 150–200 km in central parts of Europe, and about 300 km in areas which are mainly influenced by emissions more than 500 km away. Spatial covariance analyses of annual average concentration values give rather variable ranges of covariance from one year to another, but the range is usually 300–600 km.

2.3 References

WMO (1971) Guide to meteorological instrument and observing practices. Geneva, World Meteorological Organization (WMO No. 8 TP 3).

Seilkop, S.V. (1994) Representativeness of surface site air concentrations relative to an 80 km grid. To appear in Proceedings of the conference on regional photochemical measurement and modeling studies.

Berge, E., Schaug, J., Sandnes, H. and Kvalvågnes, I. (1994) A comparison of results from the EMEP/MSC-W acid deposition model and the EMEP monitoring sites during the four seasons of 1989. In: *EMEP Workshop on the Accuracy of Measurements. Passau 1993.* Edited by T. Berg and J. Schaug. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 2/94). pp. 209–266.

EMEP(1994) The status of monitoring within EMEP: Distribution of monitoring sites and implementation of measurement programme. Note by the Bureau (EB.AIR/GE.1/R.90).