EMEP/CCC-Report 1/2000

Status report with respect to measurements of particulate matter in EMEP

**Mihalis Lazaridis, Arne Semb, Steinar Larssen,
Anne-Gunn Hjellbrekke, Øystein Hov, Jan Erik Hanssen,
Jan Schaug, Leonor Tarrason, Svetlana Tsyro**

NILU: EMEP/CCC-Report 1/2000
REFERENCE: O-98134
DATE: JULY 2000

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

Status report with respect to measurements of particulate matter in EMEP

Mihalis Lazaridis, Arne Semb, Steinar Larssen,
Anne-Gunn Hjellbrekke, Øystein Hov, Jan Erik Hanssen,
Jan Schaug, Leonor Tarrason*, Svetlana Tsyro*

Norwegian Institute for Air Research
P.O. Box 100, N-2027 Kjeller, Norway

*

Norwegian Meteorological Institute
P.O. Box 43 Blindern, N-0313 Oslo, Norway

Contents

1. Introduction 5

2. Particulate matter measurements 8
- 2.1 Particulate mass (PM_{10}) 8
- 2.2 EN-12341 Method for determining the PM_{10} fraction of suspended particulate matter 10
- 2.3 Chemical speciation 13

3. Particulate measurements in Europe 17
- 3.1 Particulate measurements inside the EMEP framework 17
- 3.2 Chemical composition of PM inside the EMEP framework 30
  - 3.2.1 Sulphate, nitrate and ammonium measurements 33
  - 3.2.2 Trends in measured airborne particulate matter concentrations in the EMEP measurement framework 39
  - 3.2.3 Heavy metals associated with particulate matter 41
- 3.3 Particulate measurements from European research programmes 42
  - 3.3.1 European Topic Centre on Air Quality (ETC/AQ) – AIRBASE data 42
  - 3.3.2 Measurements in Birkenes – Skreådalen (Norway) 48

4. References 53

Status report with respect to measurements of particulate matter in EMEP

1. Introduction

EMEP, which is an acronym for the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (or the European Monitoring and Evaluation Programme), is an activity under the Convention on Long-range Transboundary Air Pollution (CLRTAP). EMEP was organised within the framework of the United Nation's Economic Commission for Europe, and has been in operation since the autumn 1977. The main objectives are to provide quantitative information on the transport of air pollutants across national boundaries and on the deposition and concentration levels caused by this transport. EMEP's work in the past has been related to acid precipitation and photochemical oxidant formation, and lately heavy metals and persistent organic compounds have been included.

Particulate matter has become a new priority pollutant in the EMEP programme. The reason for this is the adverse effects of airborne particulate matter on public health (EPA, 1996; WHO, 1999), effects on sensitive ecosystems, and effects on climate (Andreae and Crutzen, 1997). In addition, particulate matter is important as vector of transport and deposition of sulphur, nitrate, heavy metals, and persistent organic compounds, and in relation to visibility (EPA, 1996; EU, 1996, 1997), as discussed at the two EMEP/WMO workshops on monitoring strategy (Ed.: Schaug and Uhse, 1997) and on fine particulates in 1999 (report in preparation).

Recent studies strongly support a significant contribution of the particulate matter (PM) long-range transport component to the regional particle mass and number size distribution. This is a result from the atmospheric residence time of PM which is ranging from a few days to a few weeks. As a consequence there exist small differences in the average total mass of $PM_{2.5}$ between urban and non-urban continental aerosols (Heintzenberg, 1989). Airborne particulate matter is a complex mixture of many different chemical species originating from a variety of sources with sizes ranging from few nanometers to several hundred micrometers (Finlayson-Pitts and Pitts, 1986; Seinfeld and Pandis, 1998; EPA, 1996; Position Paper on Particles, 1998).

Although long-range transport of sulphur and nitrogen compounds and other air pollutants has been studied extensively in Europe (e.g. Eliassen and Saltbones, 1983) there has been no systematic study on regional particulate matter in EMEP. A preliminary study (EMEP-WMO, 1999) indicated that the long-range component of particulate matter, measured as PM_{10}, is highly significant in relation to ambient concentration levels in Europe. There is an urgent need for more detailed investigations, and in particular the understanding of the regional composition/size distribution characteristics of particulate matter and its relation to human health is important:

- The chemical complexity of atmospheric aerosols requires a consideration of their composition and sources.
- There is a high degree of uncertainty about the size and composition of the particles that may be responsible for potential human health risk.
- Control costs for reduction of PM emissions are potentially very high.
- The size distribution of aerosols is a critical factor influencing the extent to which particles penetrate into the respiratory tract. In addition, chemical characterisation of PM is a critical factor that possibly influences their health implications.

The new EMEP programme aims at providing long-term validated information on the air concentrations of atmospheric particles. The results are designed to support the formulation and enforcement of emission reduction strategies at European level, to be useful for the assessment of adverse health effects, and they should provide information on the source allocation of the observed concentrations. For the assessment of effects, information on the chemical composition and size distribution of atmospheric particles is necessary.

With respect to the PM regional research in Europe EMEP should provide a basis for a quantitative assessment of the long-range transported aerosol component, and the rural concentration levels. Although this information is already available for the secondary inorganic aerosol particulate matter, which is a significant part of the long-range transported aerosol, very little is known about the European-wide distribution of other components of particulate matter. In addition, measurements of aerosol particulate mass have mainly been made in urban environments. Consequently, the current report is mainly a status report, bringing together existing information and outlining the progress towards a better understanding of regional PM in the Europe.

Measurement methods for PM are available, both for total particulate matter and for specific chemical components, but limited results are so far available at European level (Lazaridis et al., 1999). Furthermore, a preliminary emission inventory for the whole European region (TNO, 1997) has been used for an initial appraisal of the emissions of primary particulates from anthropogenic sources. This indicates that particles are emitted from a number of combustion sources, industrial processes and other activities, particularly within the transport sector. Steps have been taken to improve this emission inventory, and to update the estimates to the present situation. At the same time, countries are expected to check these estimates, and to provide supplementary information and corrections.

The ambient concentrations of ammonium sulphate and ammonium nitrate, which typically account for 20-50% of PM_{10} mass, and an even larger fraction of the fine particles, have been part of the modelling of sulphur and nitrogen deposition within EMEP. Using the preliminary emission inventory, the fraction resulting from primary anthropogenic emissions of particulate matter has also been estimated. Future improvements in the EMEP models will include modelling of the formation of secondary organic particulate matter, and inclusion of more detailed atmospheric physical processes which determine the size distributions and the mixing of the different components of atmospheric particulate matter.

A better quantification and understanding of the regional PM component in Europe will be accomplished by incorporating continuous daily measurements and detailed chemical characterisation of the PM constituents combined with regional modelling using the 3-D Eulerian EMEP model. In addition, as recommended from the EMEP-WMO (1999) workshop on fine particulates, “superstations” for PM measurements should be set up in co-operation with other scientific organisations and programmes. These could be used for a number of chemical and physical measurements that go beyond the scope of the “normal” EMEP site, e.g. for determination of some of the organic compounds, size distribution, detailed size fractionated chemical speciation, optical properties, water uptake, cloud condensation nuclei, vertical distribution and better time resolution (1 hour) for some parameters.

In the current report we are mainly concentrated on the reference methods, methodologies and available measurement data of particulate matter in Europe as well as providing recommendations for future work. Available information on recommended measurement methods for PM_{10} in Europe, PM characteristics from the EMEP measurement program and ongoing research measurement programs has therefore been included in this report. In addition, a preliminary assessment on PM emission inventory in European level based on recent emission data is presented. Detailed information on PM physical-chemical characteristics, modelling and European trends and emissions can by found in the work by Lazaridis et al. (1999). Table 1 presents data on ambient suspended particulate mass from the European Environmental Agency’s AIRNET database and from the EMEP sites.

Table 1: Some annual averages of measured particulate mass concentration levels (1997).

	EMEP sites			AIRNET data								
	Rural			Rural			Urban					
Country	CH	DE	ES	CZ	NL	GB	CZ	BE	NL	GB	IE	NO
SPM, µg/m^3	**21**	**24**	**30**	**25**	**39**	**14**	**38**	**32**	**41**	**23**	**17**	**19**
No. sites	4	5	4	19	9	3	34	6	6	36	1	3

Only some of these sites use the recommended CEN12341 reference method, or have corrected the data using the procedure recommended by CEN and the CEC (CEN, 1998). Based on experience we can therefore expect that there could be systematic differences of the order of ±20-30% between the measurement series in different countries (WHO, 1998). These results show, however, the order of magnitude of the aerosol particle mass concentrations, and that the difference between rural and urban concentration levels is rather small. This is particularly the case in continental Europe, where the regional emission levels appear to be more important than the relative modest urban emissions.

Total particulate sulphate and nitrate are the dominant components, with ammonium nitrate prevailing in Western Europe and particulate sulphate (mainly as ammonium sulphate) prevailing in Eastern Europe (see Van der Zee et al., 1998; Zappoli et al., 1999). Together with the secondary inorganics, primary aerosols, largely organic and elemental carbon, minerals and crustal material, explain a major part of the particulate mass concentration levels in Table 1. Recent studies (e.g. Heintzenberg et al., 1998) emphasise the importance of organic compounds, whereas minerals from fly ash apparently have decreased strongly. With respect to primary particles, the emission estimates at present are relatively uncertain, and the measurements do not provide any validation of the emission data, nor of the model estimates. It is difficult to derive significant conclusions on the actual variations in particulate matter observed over Europe because differences in the sampling and analytical methods can be of the same order of magnitude as regional variations.

Harmonised measurements of PM_{10} and more detailed chemical analyses of the particulate matter contribution to PM_{10} and $PM_{2.5}$ are required to support the formulation of environmental policies to reduce ambient PM concentrations (McMurry, 2000). The chemical analyses need to include elementary and organic carbon (EC/OC), as well as other parameters that may help to identify primary and secondary organic matter, and natural aerosol components (Turpin et al., 2000). The preliminary emission estimates need to be refined, particularly with respect to chemical composition of the primary particles from different source categories. The final emission data will also require active participation from research groups from all European countries. Future modelling should include interactions between different components of aerosol particulate matter, formation of secondary aerosol particles and growth of particles by coagulation and condensation processes, since these influence size distributions and deposition processes.

2. Particulate matter measurements

2.1 Particulate mass (PM_{10})

A number of different methods have been used to quantify the concentration of particulate matter in ambient air. These may either be based on the sampling of air through a suitable filter and subsequent weighing, or on other methods, such as by monitoring the absorption of β-radiation through the filter (Wedding and Weigard, 1993), or the monitoring of frequency of an oscillating tapered element with a filter at the tip (Patashnick and Rupprecht, 1991). Other methods are based on light scattering, or counting of particles with different mass through electrical charging and determining their mobilities. All these methods can and will give different results, and the European Standardisation Organisation (CEN) has therefore designed three different reference methods for determination of the mass of particulate matter with aerodynamic equivalent diameter <10 μm (CEN, 1998). Methods for the measurements of particulate mass and results from comparative testing of different methods have been reviewed in a workshop meeting by the WHO (1999).

Direct recording instruments can be used if they have been shown to provide consistent results compared with gravimetric methods. The main problem with the monitoring instruments is that heating to remove water contained in the aerosol particles will also lead to the evaporation of ammonium nitrate and volatile organic compounds. When these substances constitute a large fraction of the aerosol mass, some of the monitoring instruments will give erroneously low readings. The gravimetric method will also be subject to sampling artefacts, and losses of ammonium nitrate may also occur during sampling and when filters are suspended in a weighing room for 48 hours at 25 degrees C and 50% R.H. These artefacts will be addressed in separate tests and investigations that are now going on in several European countries in the preparations for a new European $PM_{2.5}$ standard.

Limiting the sampling to particles <10 µm is justified by the wish to study only particles which have an effect on human health. This has the added advantage that it reduces the effects caused by resuspension of soil particles from the ground, and it also removes artefacts in sampling at high wind speeds. However, comparison of measurements of PM_{10} and total suspended particulate show that the contribution of particles >10 µm to TSP is moderate in most places in Europe (EMEP-WMO, 1999). Quartz fibre filters are specified for the gravimetric determination of particulate matter. These have good retention properties with low pressure drop even for very high sampling rates. Absorption of gases on the filter material is also a limited problem. Water vapour retention by the quartz fibre material requires very careful conditioning of the filters before weighing. CEN (1998) specifies at least 48 hours at 25 ±2°C and 50 ±5 % relative humidity. This should also remove any water of hydration associated with watersoluble salts such as ammonium nitrate and ammonium sulphate. However, the conditioning may also result in loss of volatile components, such as ammonium nitrate and absorption of organic vapours on the quartz surface.

Following the recommendations made in the EMEP-WMO fine particulate workshop (EMEP-WMO, 1999) EMEP should give first priority to PM_{10} measurements. For this purpose the gravimetric method is the preferred method, particularly because the filters allow subsequent chemical analysis for quantification of different compounds. Monitors are acceptable if they have been shown to give equivalent results for the specific site and for all seasons. EMEP sites should also determine secondary inorganic particulate matter, i.e. ammonium sulphate and ammonium nitrate, as well as other water-soluble ions when these make up a significant part of PM_{10} mass.

Additional recommendations include the point that measurements of particles with an aerodynamic diameter less than 2.5 or 1 µm should be carried out in the near future when the definition of the European reference method is in place. More detailed size fractionated chemical speciation would be desirable and should be done in the context of scientific projects. Furthermore, for chemical characterisation, determination of elemental and organic carbon is highly desirable. The subsequent determination of organic and elemental carbon by thermo-desorption and oxidation is subject to artefacts, and care has to be taken to avoid results that are not comparable. There are also sampling artefacts related to organic compounds and EMEP will need to consult with other bodies on these issues. If they can be resolved, centralised laboratories for the determination of elemental and organic carbon should be established for the analysis of samples from EMEP sites.

According to Community Directive 96/62/EC on ambient air quality assessment and management and Directive 1999/30/EC relating to the establishment of limit values, inter alia also for particulate matter, all member states of the EU are obliged to report PM_{10} and $PM_{2.5}$ data. In order to assess air quality across Europe on a consistent basis the measurements need to be performed with standarized techniques. Therefore the European Commission has mandated the European Standardisation Committee (CEN) to establish reference methods for measurement of PM_{10} and $PM_{2.5}$ and to define requirements for alternative methods to be considered as equivalent methods.

The work for PM_{10} is now completed and has led to the standard EN-12341 while the work on $PM_{2.5}$ is still in its beginning phase. As for PM_{10}, a manual gravimetric reference method will most probably be defined for $PM_{2.5}$. With this procedure Europe is in line with the corresponding methods defined by the EPA for USA.

The EMEP monitoring program will adopt a gravimetric method based on the standard EN12341 for measuring PM_{10} which gives the possibility for further chemical analysis of the filters. In the next subsection the EN-12341 measurement standard for PM_{10} is briefly presented.

2.2 EN-12341 Method for determining the PM_{10} fraction of suspended particulate matter

A detailed description of the EN 12341 method is presented by the European Committee for Standardisation (CEN, 1998). The gravimetric method consists of a PM_{10} sampling inlet, directly coupled with a filter substrate and a regulated flow device. The PM_{10} mass collected on the filter can be determined gravimetrically. Filters have to be weighed before and after sampling.

Either a low- (Low Volume system: the LVS-PM_{10} sampler, see Figure 1), high- (High Volume system: the HVS-PM_{10} sampler, see Figure 2) or superhigh- (Superhigh Volume system: the WRAC-PM_{10} sampler, see Figures 3-4) volume system can be employed. For compatibility other sampling equipment must have PM_{10} inlet, constant flow and precision of sample volume measurement better than ±3%.

As indicated also in the CEN (1998) document the impactor nozzles and impaction surface shall be cleaned regularly. Greasing is also an important element of the measurement methodology. Furthermore the CEN (1998) report indicates that “the sampling instrument shall be able to withstand external weather conditions. E.g. sampling inlet and filter holder can be made of anodised aluminium and stainless steel; the filter holder can also be made of plastic material, like polycarbonate”. Quartz fibre filters should be used. These have very good filtration characteristics with high flow and low pressure drop, and their collection efficiency for small particles is excellent. The problem with the quartz fibre filters is their very large surface, and their adsorption of water vapour and other gases. Adsorption of sulphur dioxide is not a serious problem when quartz fibre filters are used, but glass fibre filters should not be used because of this possibility. It is required by CEN 12341 that the filters are equilibrated, at 25° C

(±2) and 50% R.H. (±5), for 48 hours. This equilibration should be performed before the filters are weighed previous to the sample collection, and after sampling, before the filter is weighed again with the collected sample. The filters are brittle, so special precautions should be taken in their handling. Exposed sample filters should be folded, wrapped in aluminium foil, and labelled before they are transferred to the laboratory for weighing. Disposable polyethylene gloves should be used during handling. Filters from the high-volume sampler (1630 m^3/24h) should be weighed to the nearest ± 1 mg, preferably to the nearest 0.1 mg. For the medium-volume sampler (~55 m^3/24h), a balance capable of weighing to the nearest 1 µg (preferably to the nearest 0.1 µg) should be used. Care should be taken to avoid electrostatic effects. It will be an advantage if the filters can be positioned in an upright position on the balance when the weighing is performed.

More detailed specification of accuracy is given in the reports from the co-located measurements with the three reference instruments. Standard least-squares statistics indicate an absolute precision of ± 2-3 µg/m^3, which is also satisfactory in relation to EMEP, considering that annual averages for PM_{10} at background sites will typically be in the range 10-50.

The three methods are all recommended reference methods. CEN and EU also specify that alternative methods have to be tested in co-located measurements at sites representative of where these methods are to be used, and that their precision should be at least ± 3%. The testing requirement also specifies how results from alternative measurements should be corrected with a constant factor.

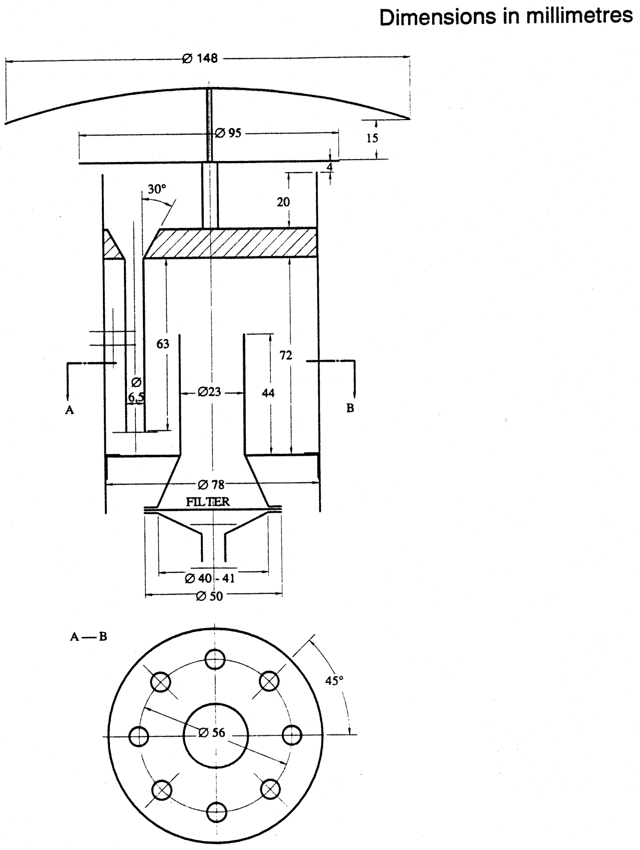


Figure 1: Design of 2,3 m^3/h LVS-PM_{10} sampling inlet (CEN, 1998).

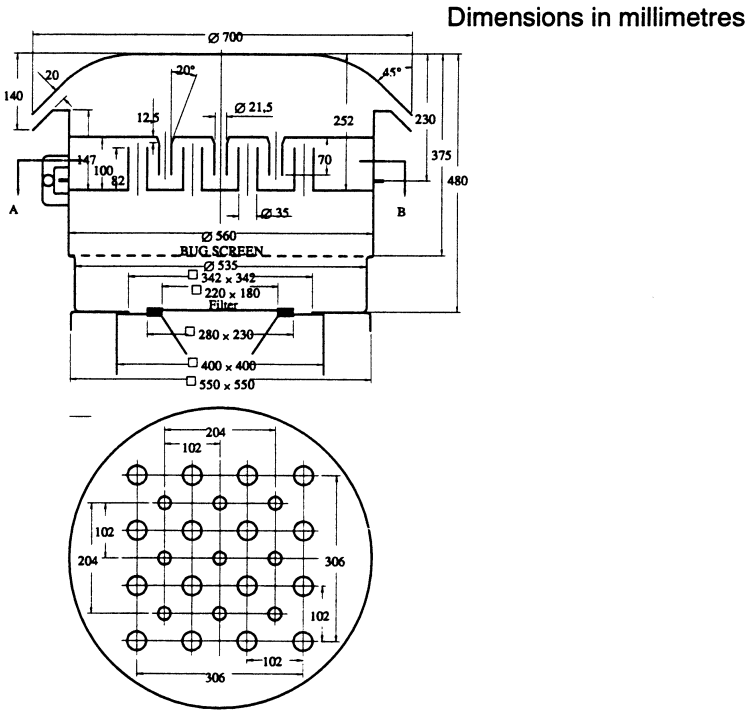


Figure 2: Design of 68 m^3/h HVS-PM_{10} sampling inlet (CEN, 1998).

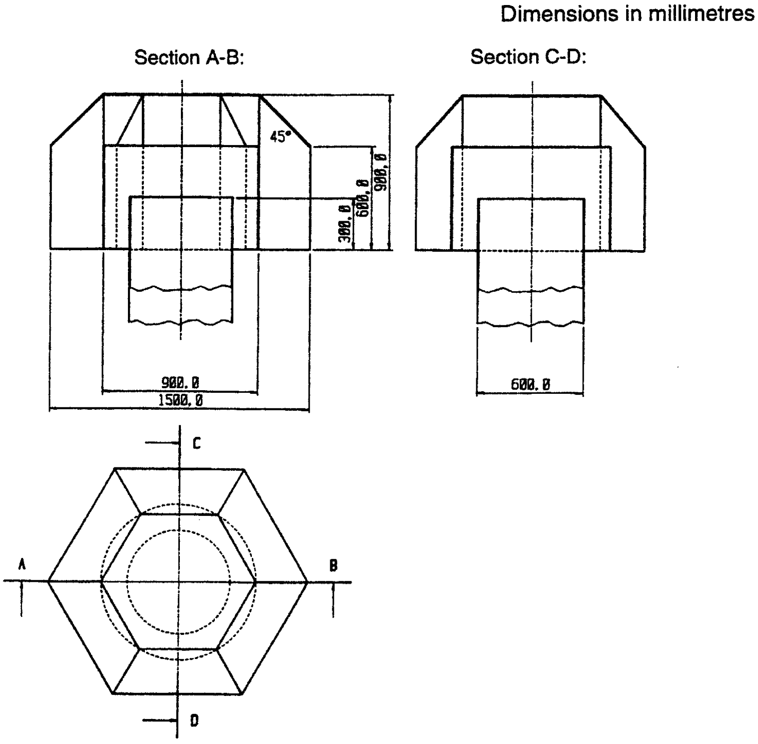


Figure 3: Design of WRAC inlet (CEN, 1998).

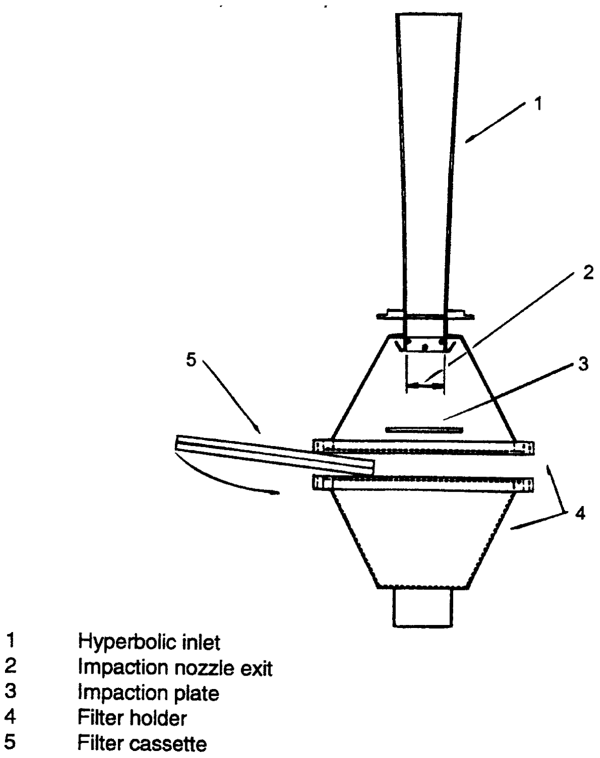


Figure 4: Design of WRAC PM_{10} stage (CEN, 1998).

2.3 Chemical speciation

An important aspect of aerosols is connected with their chemical composition and their chemical balance closure (Heintzenberg et al., 1998; Harrison and Yiu, 2000). The latter implies the necessity to identify all the major chemical constituents that compose the total aerosol mass.

Following the recommendations from the EMEP-WMO fine particulate workshop (EMEP-WMO, 1999) chemical constituents of the aerosol mass collected on the filter can be analysed for determining:

- Water-soluble inorganic components: Analyses of extracts from PM_{10} filters, or separate sampling. Analysis for the water-insoluble inorganic components is not recommended. Loss of ammonium nitrate and other volatile species is definitely an important concern during the weighing procedure and sampling.
- Elementary carbon. Elementary carbon should be determined together with organic carbon.
- Determination of specific organic compounds or groups of compounds. Up to 4000 individual organic compounds may be identified following liquid extraction from a sample of atmospheric aerosol particles. Together, these are not likely to explain more than 40% of the organic carbon. Although insignificant in connection with total mass, some of the individual organic compounds may be valuable quantitative indicators of important emission sources or processes, e.g. burning of biomass or formation of secondary

organic particulate matter. Determination of individual compounds will be regarded as a research activity until such relationships are proven and found valuable on European basis.

In the current EMEP measurement framework water-soluble ions (SO_4^{--}, NO_3^-, and NH_4^+) collected on filters are already reported. In some cases, only the sums of NO_3^- and HNO_3 and of NH_4^+ and NH_3 are reported. However, since the aerosol filters and the impregnated filters are separately leached and analysed, NO_3^- and NH_4^+ should be reported separately also in these cases. It is assumed that sampling artefacts are the same for all filter collection methods. Leaching and ion chromatographic analysis of the extracts from the aerosol filter will also give data for sea-salt aerosol, calcium and potassium. Alternatively, the weighed PM_{10} filters may be leached and analysed. It is most convenient to punch a smaller part of the sample filter for such analyses. The chemical analysis is straightforward, but care has to be taken to avoid clogging of the ion chromatograph with quartz fibres.

For extraction of water-soluble constituents from the quartz filters, it is recommended to use a punch to remove an accurately defined part of the exposed area of the sample filter. The diameter should be chosen so that it will also allow for a similar sub-sample to be taken for the determination of elementary and organic carbon. A suitable size would be a circular punch, of diameter 3-5 cm. The extraction volume should be at least 10 ml. Attention is also needed to avoid breaking up the filter by unnecessary stirring, because loose fibres in the solution does not go well with the ion chromatograph. Filtration of the extract may be necessary.

The quantification of elementary carbon and organic compounds (EC/OC) in aerosol particles is of considerable interest. Elementary carbon is present in the form of chain aggregates of small soot globules, and is responsible for the light absorption of the material collected on filters. Unfortunately this light absorption depends on the size distribution of the soot particles and on the association of the soot particles with other substances in the aerosol particles and on sample filters. Optical methods to determine EC are therefore only semi-quantitative, and calibration factors may vary from one situation to another (e.g. Liousse et al., 1993).

The recommended method to determine elementary carbon is therefore by successive volatilization and oxidation of the sample, and to determine the evolved CO_2, either directly or after conversion to CH_4 by a flame ionization detector (FID). This procedure also gives the total carbon content, and a quantification of the amount of organic materials through the organic carbon content of the aerosol particles. The method is not free of artefacts, particularly the charring or incomplete removal of organic compounds may lead to the overestimation of EC. To compensate for this, optical detection of a darkening of the filter during the last stage of the OC volatilization is recommended (Huntzicker et al., 1983; Chow et al., 1993). This method is now part of the USEPA programme, and the equipment described by Birch and Cary (1996) is commercially available (Sunset Laboratory Inc., USA). CCC of EMEP can analyse samples collected on quartz fibre filters and the equipment is also available in other laboratories in Europe. A factor of 1.4 is tentatively recommended to convert the measured OC content to total organic particulate mass.

Chemical analyses for further speciation of the organic component in aerosol particle samples are much more demanding, although some advances have been made in determining the water-soluble organic aerosol mass, and specific fractions of this mass. Quantification of selected chemical compounds by gas chromatography and other methods is also possible, but the number of individual compounds is very large, and chemical analyses should therefore be directed to determination of ”signature” compounds, which are indicative of certain groups or specific emission sources (e.g. wood combustion).

The quartz filter is less suitable for the determination of the insoluble inorganic mineral fraction, which mainly consist of silicates and oxides of silicium, aluminium and iron. To determine this fraction, it is more useful to use membrane filters and instrumental methods of analysis, such as x-ray fluorescence (XRF), neutron activation analysis (INAA), and proton-induced x-ray emission analysis (PIXE). A useful set-up for the determination of several inorganic elements in two separate size fractions has been described by Hopke et al. (1997).

In Figures 5-7 we present a chemical balance closure for aerosol concentrations in three different European countries (Hungary, Italy and Sweden). These results were taken from a recently published scientific paper (Zappoli et al., 1999) and are derived from sampling fine particles ($d_p < 1$ μm) at those rural sites for a period of two months in 1997. Because of this, care should be taken not to regard these results as representative of a longer period. The results indicate that the composition is complex, emphasising the importance of the secondary inorganic component (SO_4^{--}, NO_3^-, NH_4^+) and the water-soluble and water-insoluble organic components. The high relative proportion of water soluble organic components may be result of secondary organic aerosol formation.

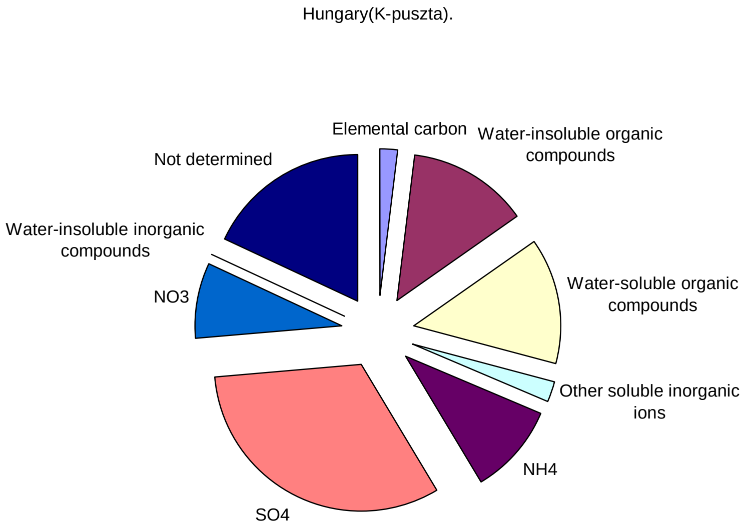


Figure 5: Chemical balance on element constituents of aerosol mass in Hungary (Zappoli et al., 1999).

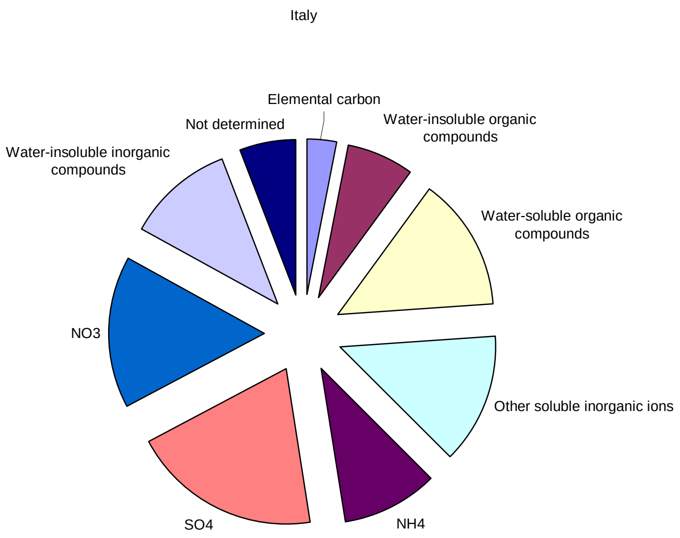


Figure 6: Chemical balance on element constituents of aerosol mass in Italy (Zappoli et al., 1999).

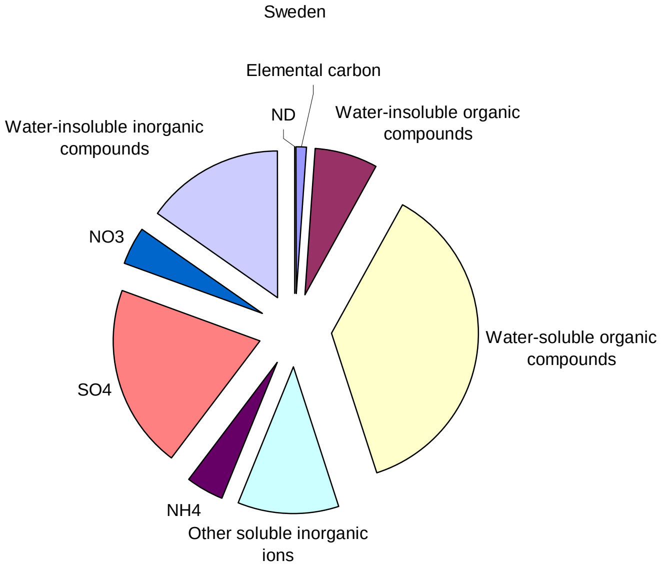


Figure 7: Chemical balance on element constituents of aerosol mass in Sweden (Zappoli et al., 1999).

It is apparent the importance of the chemical speciation in understanding the PM properties and trends in conjunction with their size distribution.

In addition to existing chemical speciation analysis inside the EMEP programme, a chemical analysis for determining the ratio of elementary to organic carbon (EC/OC) is highly desirable.

Many laboratories have extensive experience with the determination of different chemical elements of non-water soluble inorganic components by a variety of instrumental methods, such as atomic spectroscopy, mass spectroscopy, x-ray fluorescence, proton induced x-ray emission spectroscopy and nuclear activation analysis. In terms of particulate mass, however, the main contributors are silicates with composition typical of igneous or sedimentary rocks, and some iron oxide. Determination of silicon, aluminium, and iron gives a good basis for the quantification of this component.

These component are not sufficient to determine the full chemical mass balance. For this purpose, it is also necessary to include also the hydrogen, oxygen, nitrogen and other elements associated with the carbon in the organic fraction. Experience also indicates that some water is associated with the water-soluble fraction even after conditioning at 50% R.H. However, by multiplying the organic carbon with a factor of 1.4, and calculating the full weight of all the other components, reasonable agreement with the PM_{10} figure should be attained.

More detailed characterisation of the organic fraction, particularly in relation to different sources of organic particulate material (e.g. combustion, secondary organic particulate formation from both natural and anthropogenic VOC emissions) must be regarded as a highly relevant research topic.

3. Particulate measurements in Europe

Standardised measurement method for PM_{10} or $PM_{2.5}$ has not yet been implemented on an international basis in Europe. However, as explained in the previous chapter, the European Commission has selected two reference samplers for airborne particles, both with a size-selective inlet with a cut-off at 10 µm. One of these is a high-volume sampler with a sampling rate of 64 m^3/h, the other is a low-volume sampler with a sampling rate of 2.3 m^3/h, developed by the Institute for Water, Soil and Air Hygiene in Berlin. Both samplers have been extensively tested by the European Committee for Standardisation (CEN, 1998). In both cases the quantification is based on the weighing of filters after conditioning at 20°C and 50% relative humidity for at least 48 hours. This procedure is necessary to obtain consistent results with glass fibre filters, owing to the uptake of water by the glass fibres. The countries will have to make preparations for PM measurements in their sites based on the above recommended reference procedures.

3.1 Particulate measurements inside the EMEP framework

Only Switzerland, Germany and Spain report measured concentrations of suspended particulate matter at their EMEP stations in 1997, using gravimetric measurement methods. Germany reports TSP data, using a special high-volume sampler. These measurements were started before 1980 at several of the Umweltbundesamt's stations. During 1999 the samplers have been modified with new PM_{10} inlets. Switzerland reports PM_{10} data since 1997, before 1997, TSP data have been reported. Extensive co-located measurement data with TSP, PM_{10} and $PM_{2.5}$ samplers are available for the Swiss stations (EMEP-WMO, 1999). Spain has also reported TSP data since 1989. The Netherlands have measured particulate aerosol mass at several sites, including the EMEP sites Vredepeel (NL09), Eibergen (NL02) and Witteven (NL07). A monitoring instrument (FAG FH 621-N) based on β-ray absorption is used, this give systematically too low results according to work performed in Germany (EMEP-WMO, 1999). In order to compensate for this, the results presented have been multiplied with a constant factor of 1.33 (Buijsman and van Elzakker, 1996). The same instrumentation is used at the German UBA stations, without corrections the results are typically 30-40% lower than the results obtained with the LIS sampler. Measurements with a β-ray absorption instrument are also carried out in the Czech Republic at several rural stations, including Kosetice (CZ03). It is not clear if any correction factors are being used in the Czech network. Some rural concentration data are also available from the United Kingdom, these measurements have been made with TEOM instruments, which may underestimate PM_{10} concentration relative to the reference methods by as much as 30%. Again, German investigations support this (EMEP-WMO, 1999), but there is a reasonable good correlation between TEOM and PM_{10} on a daily basis, suggesting that a constant correction factor may be acceptable.

Inside the European national networks gravimetric methods based on the weighing of filters, automatic methods based on β-ray absorption or frequency attenuation of an oscillating tapered element (TEOM) are widely used.

For example, in Switzerland all measurements are performed with DIGITEL high volume samplers on glass fiber filters (Binzer 227/1/60). In the stations of Payerne, Rigi, Tänikon and Chaumont there are measurements of PM_{10} starting from January 1997 with flow rate of 30 m^3/h. Previous measurements were performed for TSP (total suspended particles) up to 30 µm with flow rate of 40 m^3/h. At Jungfraujoch the measurements performed are of TSP with two day samples.

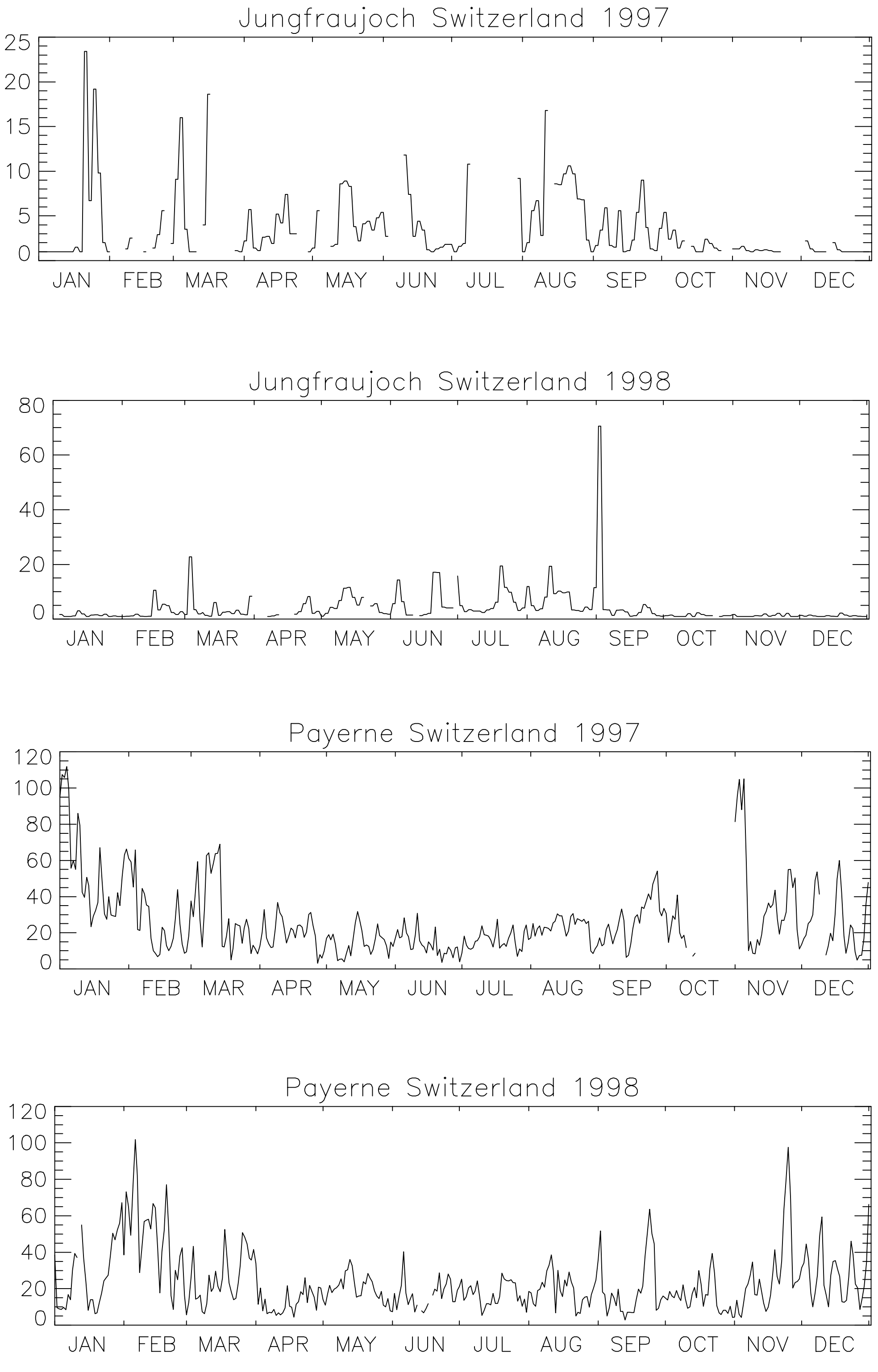
Annual averages are presented in Table 2, below. Measurements of SPM from the sites Aspvreten (SE12), Kollumerwaard (NL09) and Vredepeel (NL10) have been obtained directly from national authorities. The measured values may not be directly comparable, because of different measurement methods and procedures. This is partly because of differences in the air intakes, but also because of other sampling artefacts, particularly evaporation of ammonium nitrate and other volatile constituents from filters during sampling. This is particularly serious in the heated filters used in TEOM and β-absorption instruments (Allen et al., 1997; Patashnik, 1998).

In Figures 8-17 time series of measured PM concentrations for the 1997 and 1998 from EMEP stations in Switzerland, Germany and Spain are presented. Concentrations in Switzerland show an annual average of 21 µg/m^3 (excluding the Jungfraujoch measurements, height of 3,500 m) similar to Germany (24 µg/m^3). Spain shows higher concentrations with an annual average of 30 µg/m^3 in accordance with expectations due to the dry climatic conditions. Some Spanish sites have high summer PM concentrations, but there is no consistent seasonal variability. At Jungfraujoch the concentrations are generally very low (close to few µg/m^3), but high concentrations are observed in cases when the atmospheric boundary layer reaches the elevation of the station.

In Switzerland the PM concentrations are generally higher in winter than in the other seasons. An overview of the location of the EMEP stations and their current measurement capabilities is presented in Appendix 1.

Table 2: Measured aerosol particle concentrations at some EMEP sites.

Site	SPM, µg/m^3	Method
CH01 Jungfraujoch	3.5	PM$_{10}$
CH02 Payerne	26.3	
CH03 Tänikon	27.3	
CH04 Chaumont	13.9	
CH05 Rigi	14.4	
DE01 Westerland	26.2	LIS
DE02 Waldhof	24.3	
DE03 Schauinsland	13.3	
DE04 Deuselbach	20.7	
DE05 Brotjacklriegel	15.4	
DE07 Neuglobsow	23.1	
DE08 Schmücke	17.3	
DE09 Zingst	23.8	
ES01 Toledo	19.7	TSP
ES03 Roquetas	44.4	
ES04 Logrono	33.0	
ES05 Noya	24.5	
ES06 Mahon	28.4	
ES07 Viznar	30.9	
IT04 Ispra	46.8	
NL02 Witteven	(35)	β-abs.
NL10 Vreedepeel	(44)	β-abs.
SE12 Aspvreten	(9.5)	TEOM



Jungfraujoch Switzerland 1997

Jungfraujoch Switzerland 1998

Payerne Switzerland 1997

Payerne Switzerland 1998

Figure 8: Time series for ambient particulate matter concentrations (µg/m^3) in the EMEP stations of Jungfraujoch and Payerne (Switzerland) during 1997–1998.

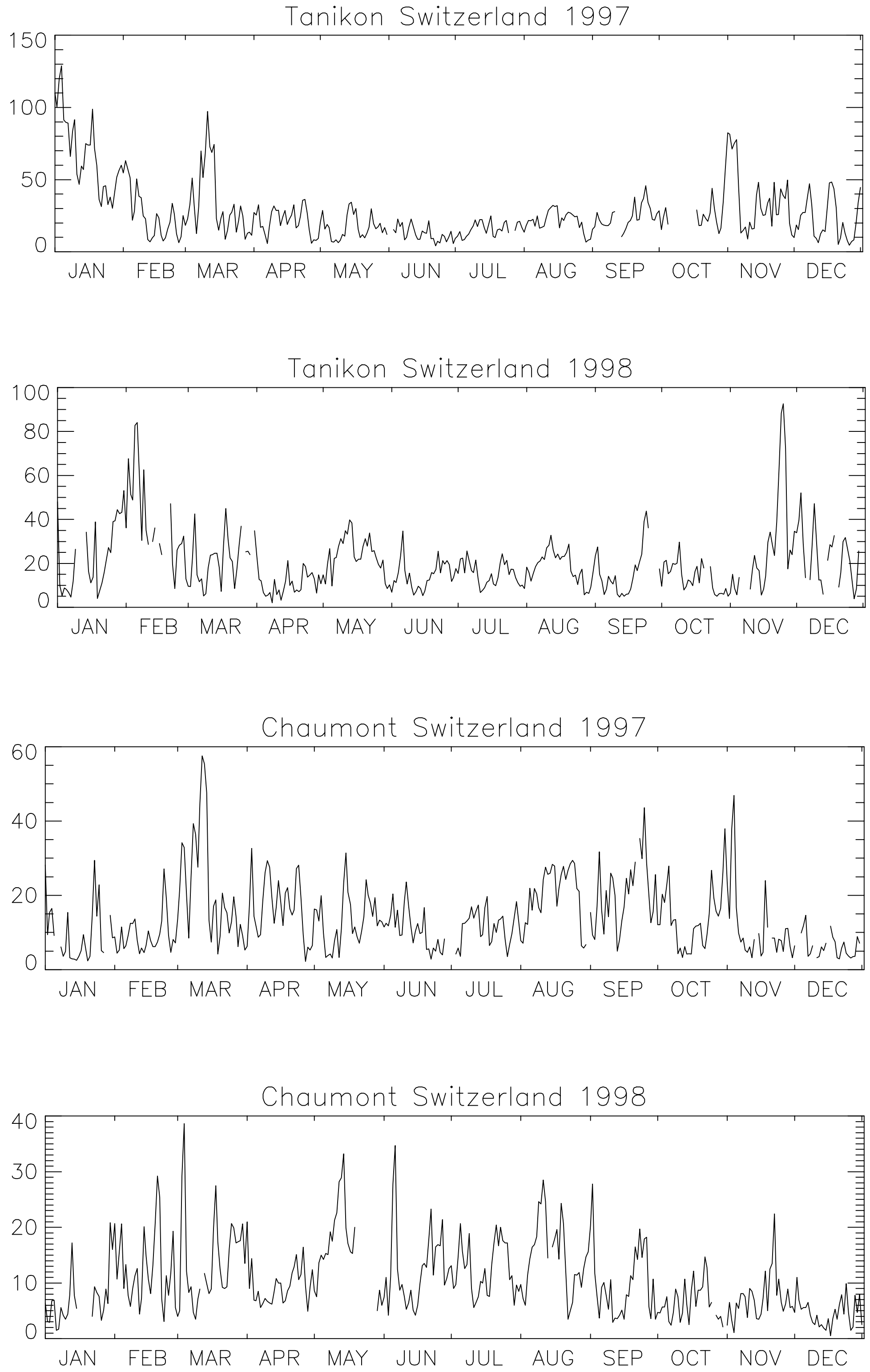


Figure 9: Time series for ambient particulate matter concentrations (µg/m^3) in the EMEP stations of Tanikon and Chaumont (Switzerland) during 1997–1998.

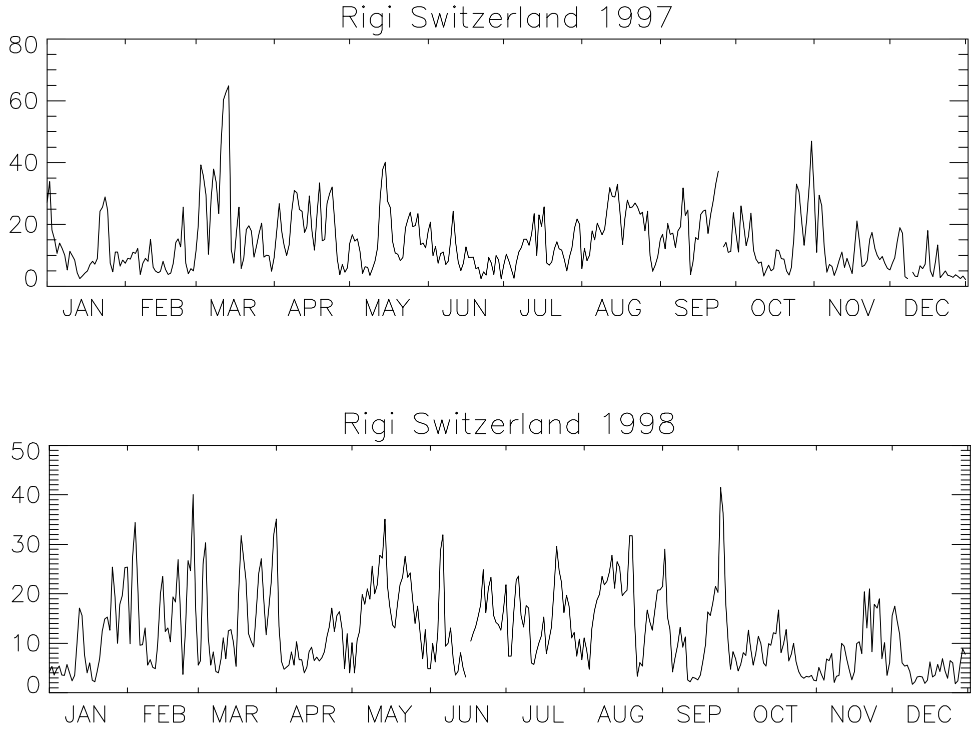


Figure 10: Time series for ambient particulate matter concentrations (µg/m^3) in the EMEP station of Rigi (Switzerland) during 1997–1998.

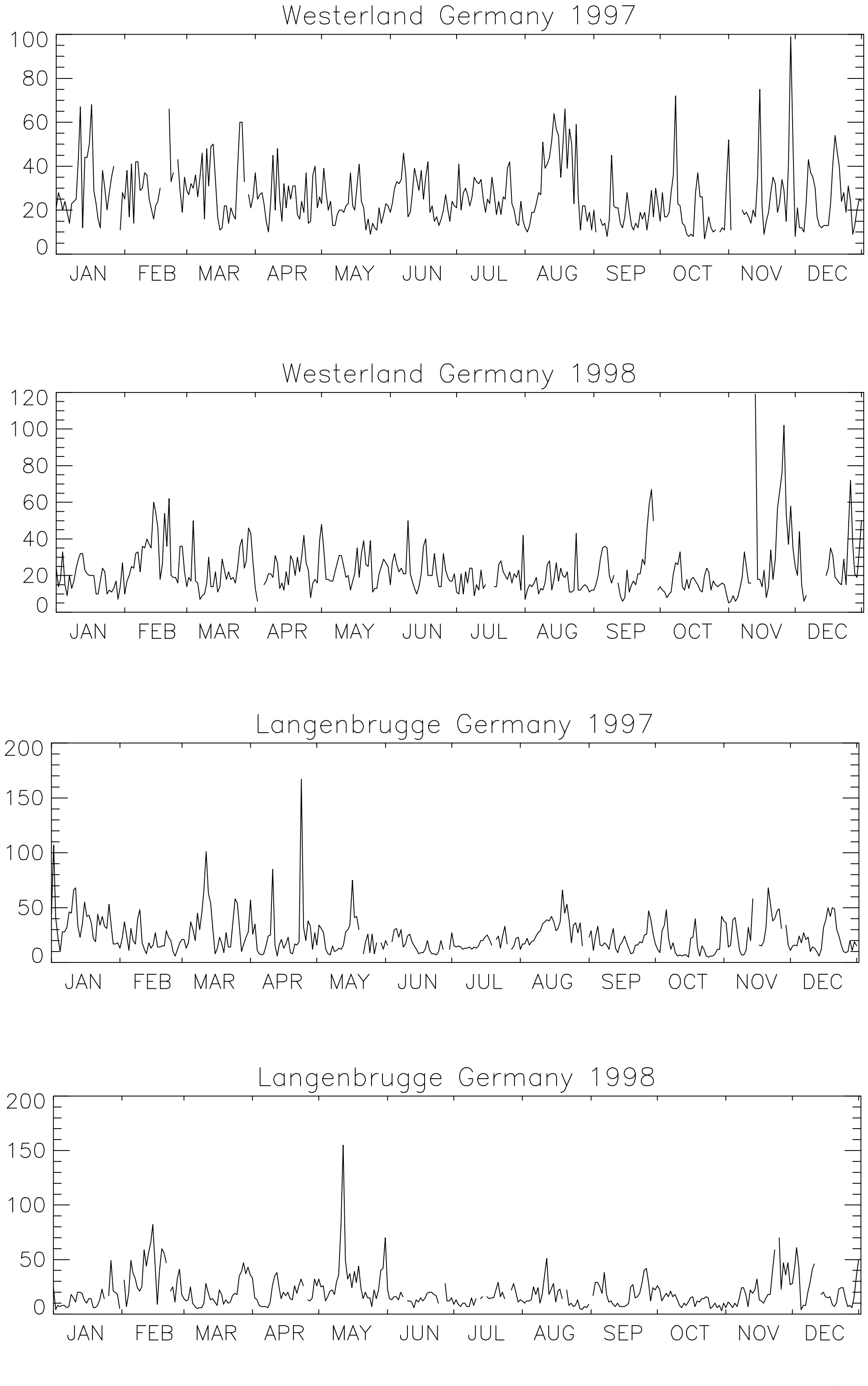


Figure 11: Time series for ambient particulate matter concentrations (μg/m^3) in the EMEP stations of Westerland and Langenbrugge (Germany) during 1997–1998.

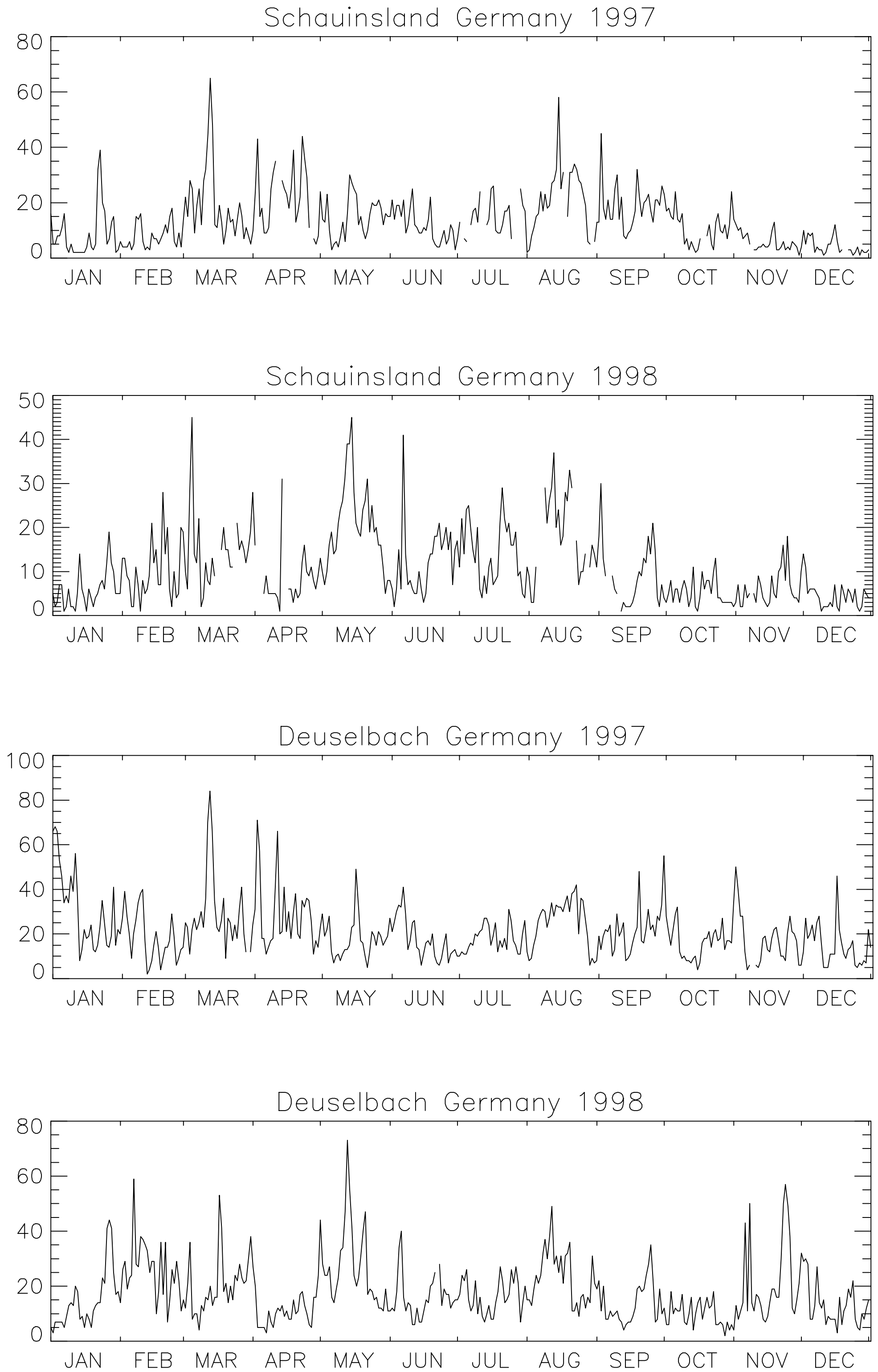


Figure 12: Time series for ambient particulate matter concentrations (µg/m^3) in the EMEP stations of Schauinsland and Deuselbach (Germany) during 1997–1998.

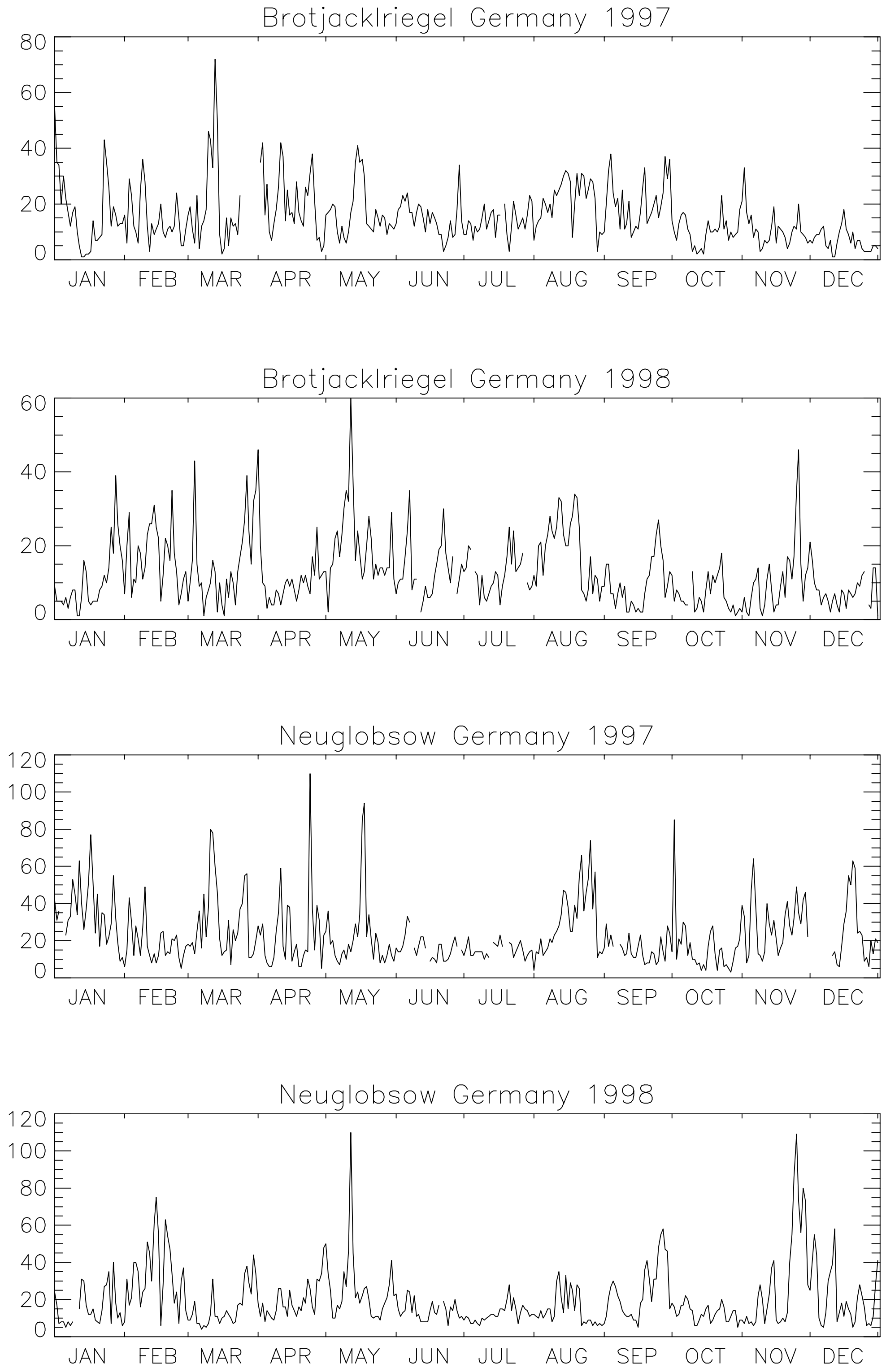


Figure 13: Time series for ambient particulate matter concentrations (µg/m^3) in the EMEP stations of Brotjaklriegel and Neuglobsow (Germany) during 1997–1998.

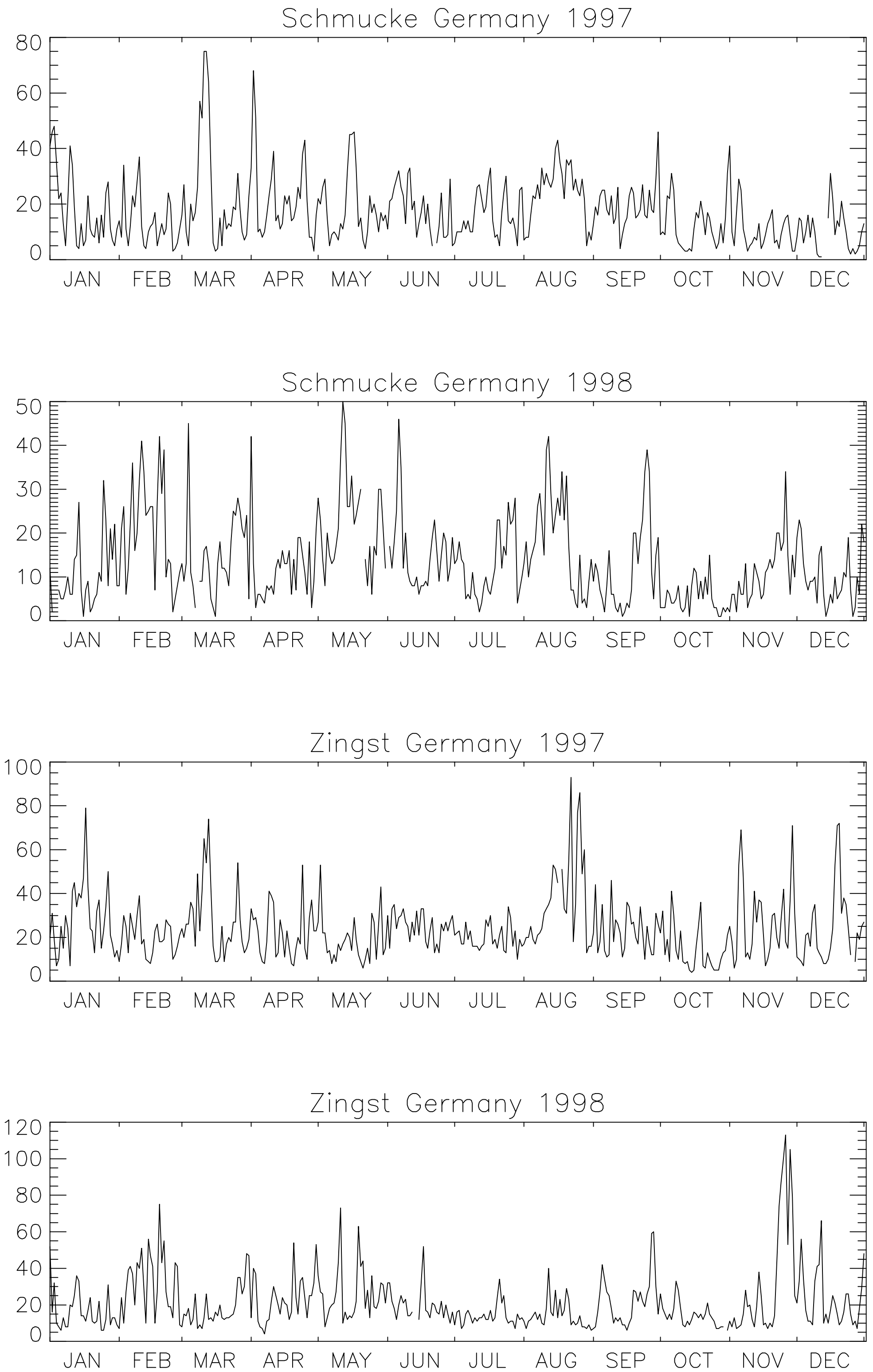


Figure 14: Time series for ambient particulate matter concentrations (µg/m^3) in the EMEP stations of Schmucke and Zingst (Germany) during 1997-1998.

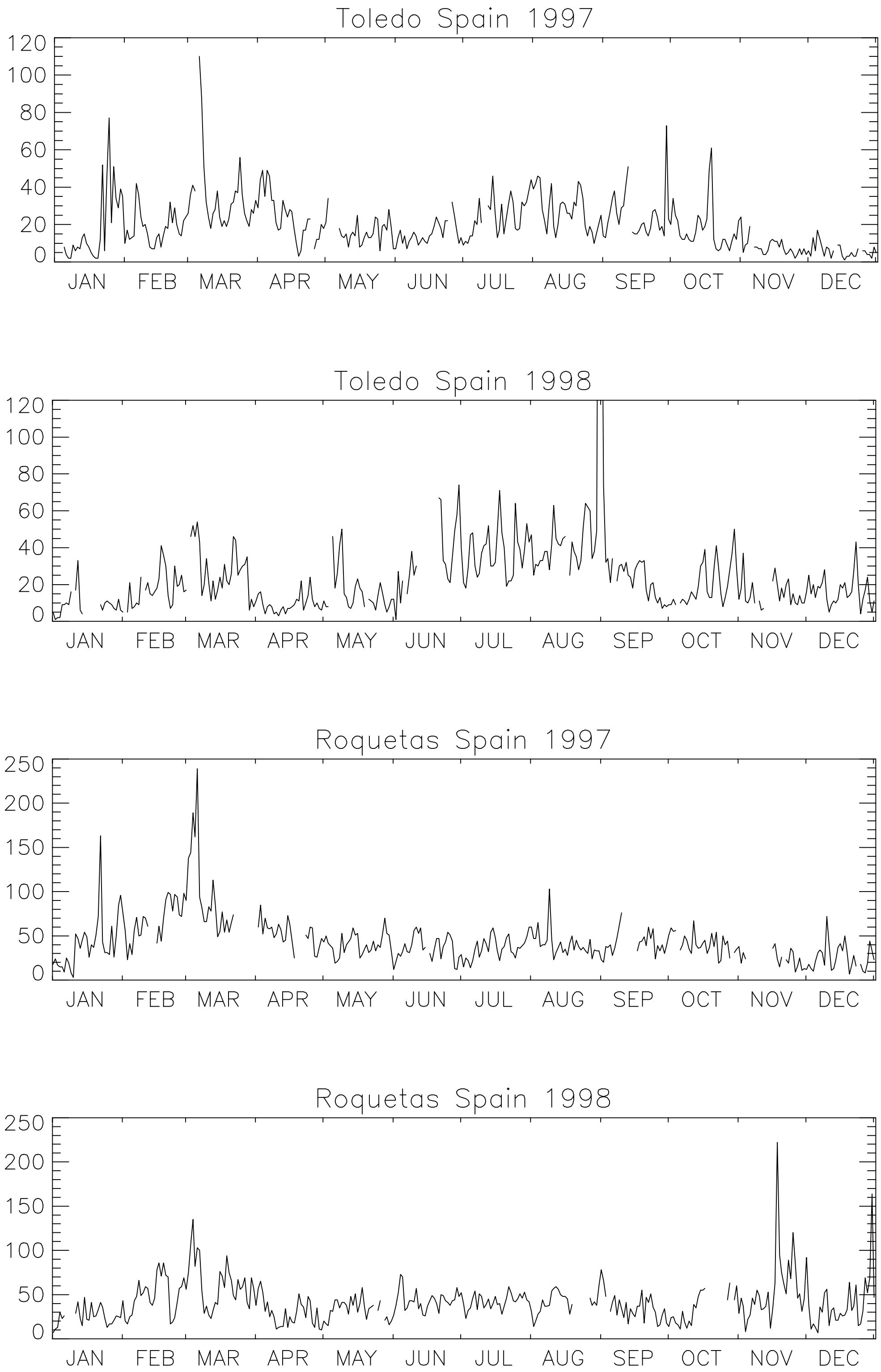


Figure 15: Time series for ambient particulate matter concentrations (µg/m^3) in the EMEP stations of Toledo and Roquetas (Spain) during 1997-1998. Maximum value for Toledo in 1998 was 342 µg/m^3.

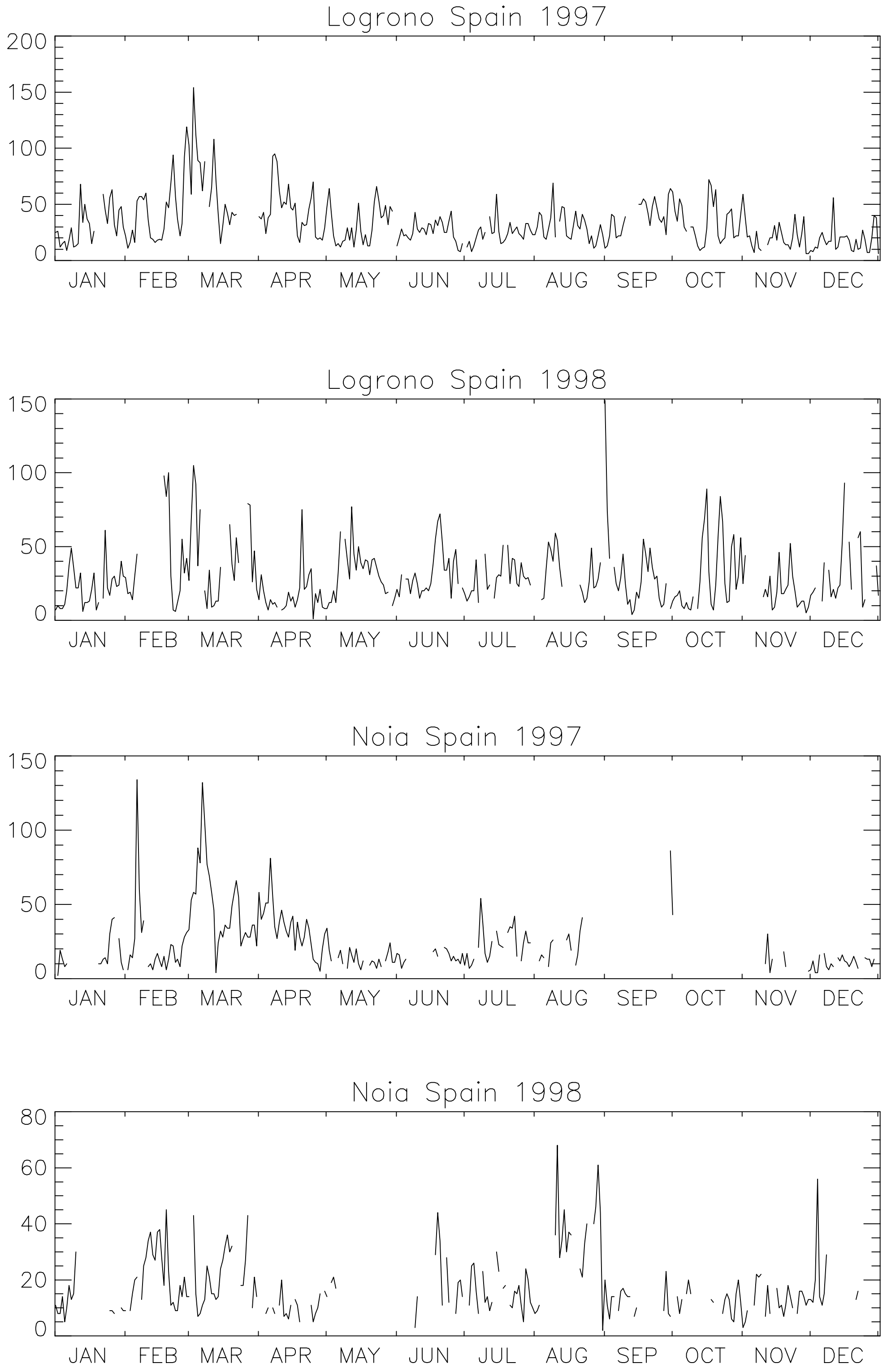


Figure 16: Time series for ambient particulate matter concentrations (µg/m^3) in the EMEP stations of Logrono and Noia (Spain) during 1997–1998.

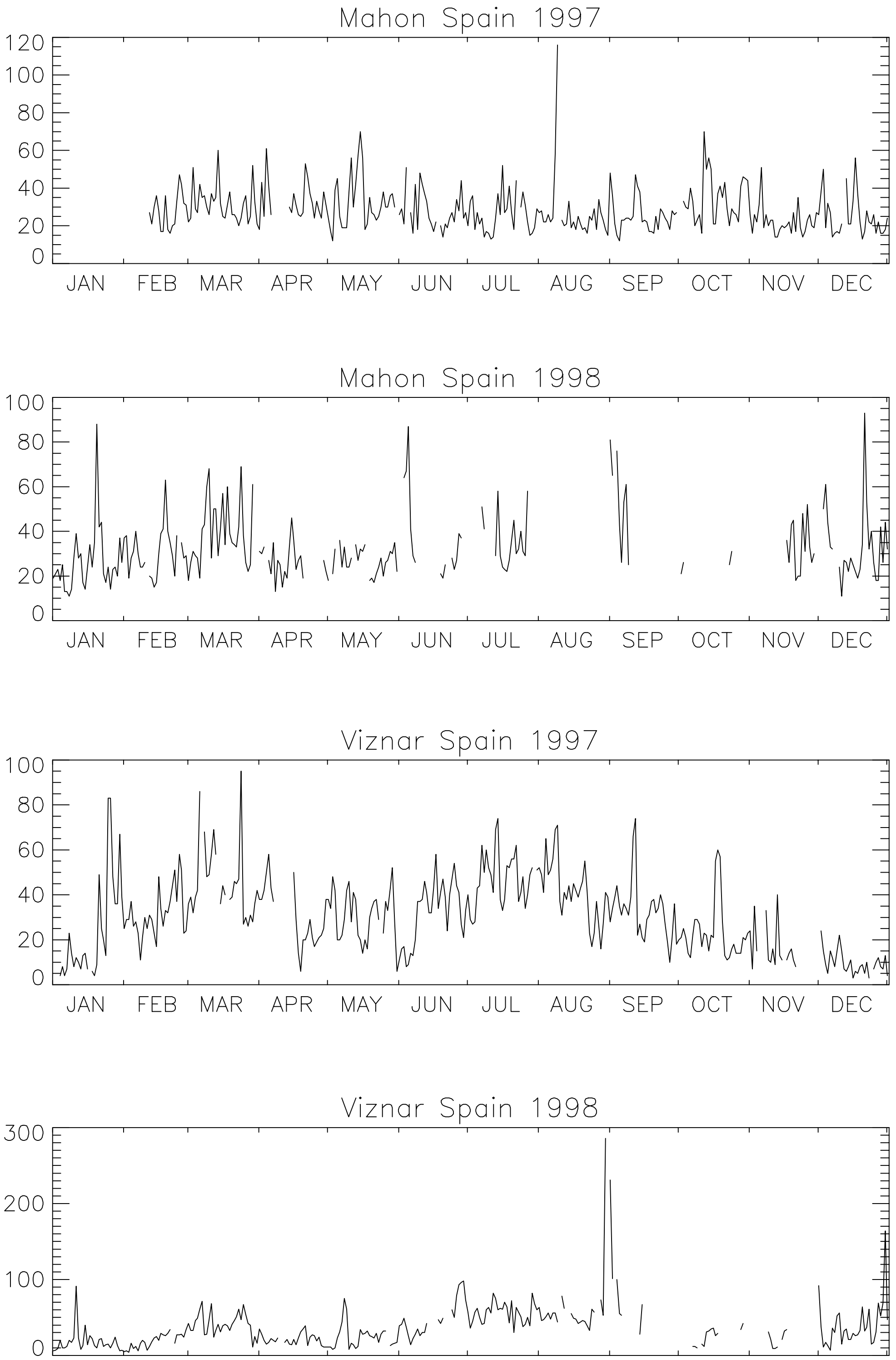


Figure 17: Time series for ambient particulate matter concentrations (μg/m^3) in the EMEP stations of Mahon and Viznar (Spain) during 1997–1998.

3.2 Chemical composition of PM inside the EMEP framework

Only a few sites reporting TSP or PM_{10} carry out EMEP's complete measurement programme. Sulphate is determined at the majority of the sites, ammonium and nitrate are at present often reported as the sum of ammonia and ammonium, and the sum of nitrate and nitric acid, respectively. However, experience has shown that ammonium associated with particles is generally explained as ammonium sulphate and ammonium nitrate. This may not be entirely justified, particularly not in Spain, where a significant fraction of both sulphate and nitrate may also be associated with alkaline soil dust particles. The ratio of nitrate associated with particles to the sum of nitrate and (gaseous) nitric acid has been studied in measurement campaigns carried out within EMEP in 1993 (Semb et al., 1998; see also Figure 18).

The results from the measurement campaign also show that the fraction of gaseous nitric acid is typically 20-30%, relative to the sum of nitrate and nitric acid. The lowest relative concentration of nitric acid is found in areas with high ground-level concentrations of ammonia, and relatively low temperatures. It was found that ammonia was not generally limiting the formation of ammonium nitrate, since the sulphur dioxide emissions and sulphate concentrations have been reduced.

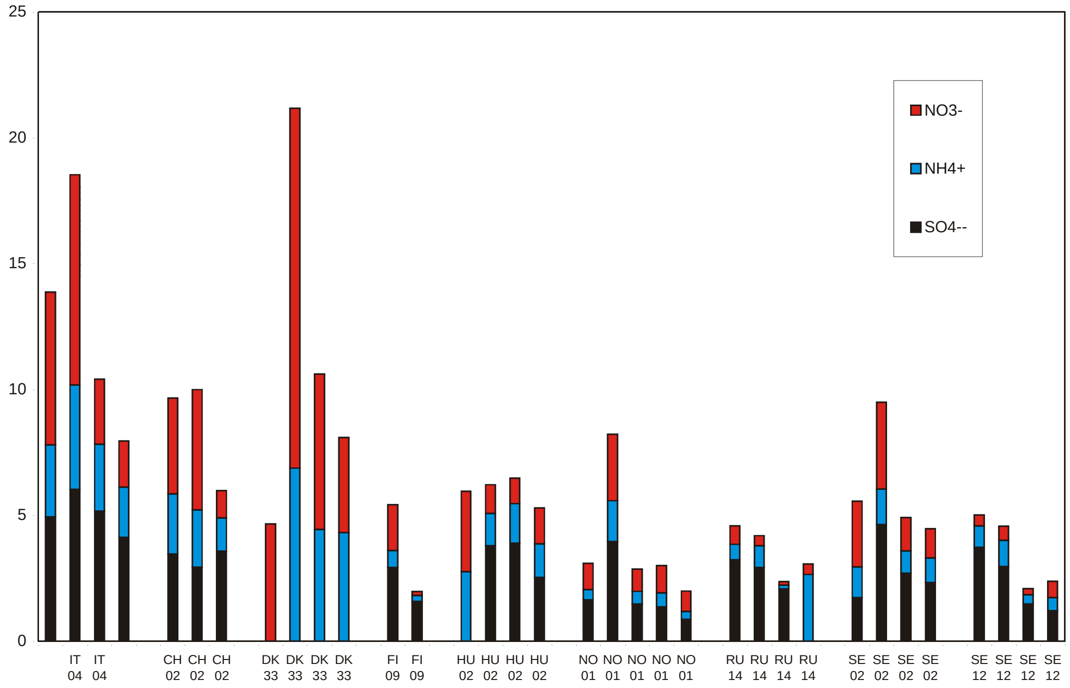


Figure 18: Concentrations of particulate sulphate, nitrate and ammonium from denuder measurements during the EMEP measurement campaign. Measurements were performed for periods of 4-5 weeks. Concentrations are given in weight equivalents for comparison with PM_{10} concentration levels.

Closing the mass balance also requires the determination of elementary carbon (soot particles) and organic compounds. The latter consist of a very large number of individual compounds, and the identified compounds or groups of compounds only account for some 15-20% of the organic fraction (e.g. Rogge et al., 1993; Liousse et al., 1993). Elementary carbon is typically 5-10% of total carbon. Examples of chemical composition of fine particles at three rural stations, in Italy, Hungary and Sweden are given by Zappoli et al., 1999. Two of these sites (K-puszta and Aspvreten) are also EMEP sites. Care should be taken with respect to the representativity of these results, since they only represent 2 months of sampling at three sites. The contribution of both water-soluble and -insoluble organic carbon to the fine particulate mass is remarkable. A very high contribution of water-soluble organic carbon to the mass at Aspvreten may be related to the time of the year and the low fine particulate mass concentration.

The importance of organic compounds for the particulate mass is also emphasised by Heintzenberg et al. (1998), who reported on extensive measurements from Melpitz, near Leipzig in south-eastern Germany. The concentration of coarse particles consisting mainly of inorganic minerals and fly ash particles has decreased strongly since 1993, and now represent only about 20% of total particulate mass, or PM_{10}.

There is relatively good correlation between observed TSP concentrations and concentrations of aerosol sulphate (and nitrate) at many of the sites, even if the sulphate and nitrate concentrations account only for 20%-40% of the aerosol mass. This indicates that the aerosol particle mass concentrations are part of a long-range transported or regional air pollution components, which also includes particles which are emitted from various anthropogenic sources, such as stationary combustion sources, mobile sources and industrial processes.

Only limited information is available with respect to the other chemical components in the aerosol particles. The contents of inorganic elements have been studied with various instrumental methods of chemical analysis, mainly focussed on the chemical signatures and the occurrence of particular trace elements which may be used to indicate source types and geographical regions. The elements which contribute most to the particulate mass are the elements most common in the earth’s crust, viz. silicon, aluminium, iron, calcium, a.o. Given that the concentration of these three or four elements have been determined, a good estimate of the contribution from inorganic primary particulate emissions may be made. Sea-salt concentrations are similarly inferred from the measured concentrations of sodium and chloride, chloride is often depleted in aerosol filter samples because of interactions with acid aerosols, or nitric acid. Available information on the concentration of inorganic elements in aerosol particles are reviewed by Pakkanen et al. (1996) and by Maenhaut et al. (1993). Figure 19 below shows the development with time of the concentrations of some elements at Birkenes, Norway from 1973 to 1996. It is seen that the concentrations have been decreasing strongly, particularly for sulphate and for the inorganic mineral elements. This is in accordance with emission reductions, and with similar observations concerning the decrease in deposition of base cations in precipitation (Hedin et al., 1994).

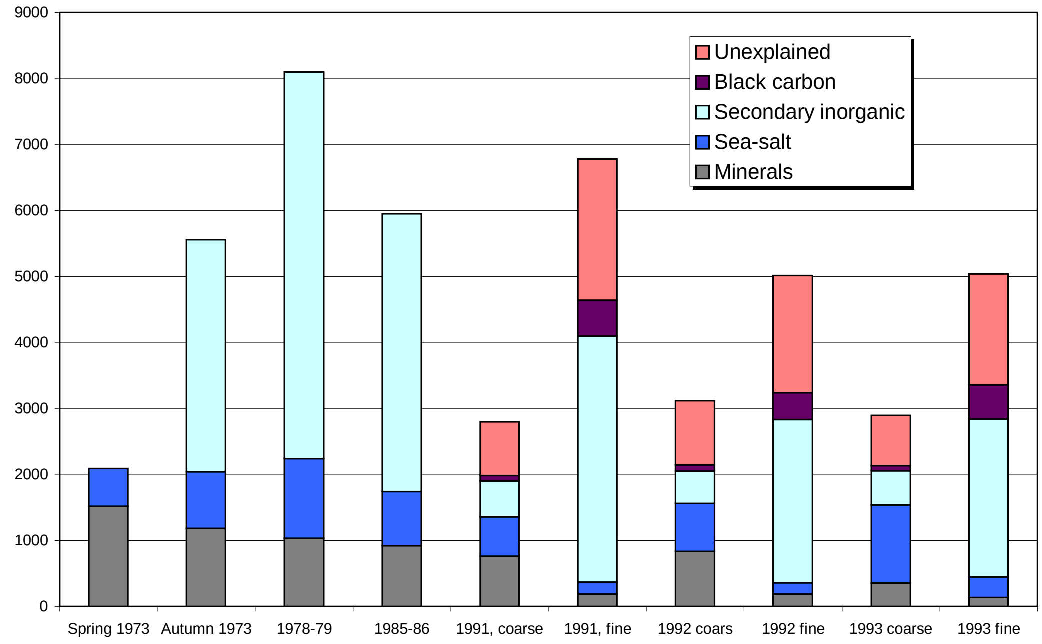


Figure 19: Chemical speciation (ng/m^3) of suspended particulate matter in Birkenes (Norway) in the 1973-1993 time period.

The total mass of the inorganic mineral elements has also been estimated, together with the mass of ammonium sulphate estimated from the sulphur content, and the mass of sea-spray aerosol particles. When these are compared with the total mass, determined by weighing of the membrane filters prior to the chemical analyses, a significant part remains, typically about 30-40% of the total mass, which consists of organic material and elementary carbon. Measurements of the optical absorption indicate that the elementary, or black carbon concentration level is about 0.5-1 µg/m^3. This corresponds well with other measurements of the chemical composition of aerosol particles in Europe, as shown before (Figures 5-7). Of particular interest is the relatively high proportion of water-soluble organic material, which may be attributed to chemical transformations in the atmosphere, either in the particles or by transformation of gaseous organic material that is subsequently absorbed in the aerosol particles. The formation of secondary organic aerosol has been the subject of extensive laboratory studies, and occur both with the oxidation of naturally emitted terpenes and with anthropogenic VOC, particularly VOCs with high molecular weight. Of the groups of compounds which can be identified, hydroxylic, carbonylic and carboxylic acid derivatives of both aliphatic and aromatic compounds are all present.

The content of organic materials in aerosol particles and their relationship with both primary emissions and atmospheric processes is a considerable challenge, more so because the other components of atmospheric particulate matter are declining because of emission reductions. Heintzenberg et al. (1998) have summarised the experience from research and observations of atmospheric particles in the Leipzig area, and find that the fine aerosols (<1-2 µm) consist almost exclusively of organic and secondary inorganic particulate material.

Previous studies indicate (Semb et al., 1998; Semb et al., 1995) that the contribution from secondary inorganic aerosol components, *viz.* ammonium sulphate and ammonium nitrate, is between 20 and 40%, 30% is rather typical of northern Europe. If the sampling was restricted to fine particles, i.e. particles less than 2.5 μm diameter, the weight percentage of the secondary inorganic aerosol component should increase.

Methods used to obtain aerosol mass concentrations by sampling on filters will always to some extent be ambiguous. Loss of volatile species during sampling has been mentioned, another artefact is related to water uptake by deliquescent salts. Most water-soluble inorganic salts will take up water at relative humidity above 60-70%, and aerosols will usually contain substantial amounts of water, which will be retained even at lower relative humidity, because crystallisation of the pure salts is inhibited.

Full chemical analysis of particles sampled on filters is also not straightforward, mainly because of the many different organic compounds. It is possible to determine some key components, which may be valuable if these components are specific indicators of important emission categories or processes. Determination of carbon following stage-wise thermo-desorption and oxidation may be used to quantify the amounts of elementary and organic carbon (e.g. Cachier et al., 1989). It is more technically demanding to separate different classes of compounds by selective extraction. The fraction of the organic compounds which is water-soluble may be quantified in this way, however.

Good analytical methods exist for the determination of inorganic elements, and there is a large body of information concerning the inorganic elemental composition of aerosol particles, dating from the 1970’s. (e.g. Pacyna et al., 1984; Lannefors et al., 1983; Amundsen et al., 1992; Pakkanen et al., 1996). These studies also show, however, that the concentration of inorganic minerals in aerosols have been declined over this period.

3.2.1 Sulphate, nitrate and ammonium measurements

Representative results from individual measurements concerning average concentrations of gaseous nitric acid, particulate nitrate, gaseous ammonia, and particulate ammonium, on a daily basis are shown in Figures 20-24. The concentrations of sulphate aerosol are also given when available. A detailed study on nitrogen pilot measurements in the EMEP programme is presented by Semb et al. (1998).

The measured concentrations of gaseous nitric acid were generally much lower than the concentrations of particulate nitrate. At the sites IT04 (Ispra), CH02 (Payerne) and DK33 (Lille Valby), relatively high concentrations of gaseous ammonia are effective in converting nitric acid to ammonium nitrate and suppressing ammonium nitrate dissociation. The relative amount of gaseous nitric acid to nitrate in particles increase during the summer months at these sites. Relatively high concentrations of gaseous ammonia are also measured at HU02 (K-puszta), but here the measured concentrations of nitric acid are comparable to the concentration of nitrate particles.

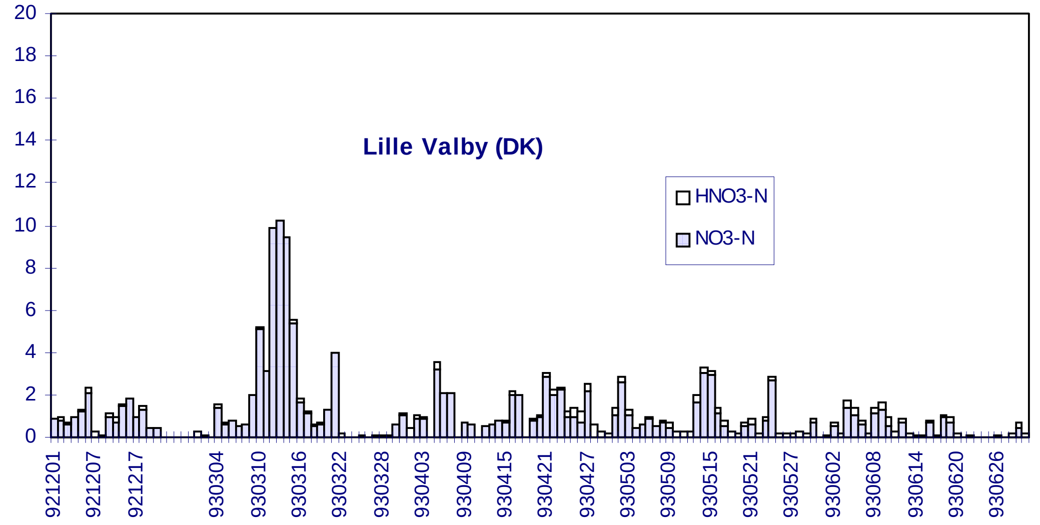
Concentrations of ammonia are low, but still measurable at SE02 (Rörvik) and NO01 (Birkenes) as shown in Figures 21 and 23. However, the concentrations of gaseous nitric acid relative to the concentrations of particulate nitrate at these sites were on average only 21 and 16%. At SE12 (Aspvreten) (see Figure 22) concentrations of ammonia were very low. Nitric acid and nitrate concentrations were also low, however.

Particulate ammonium is usually associated with particulate sulphate as ammonium sulphate. Ammonium nitrate and gaseous ammonia can only occur when sulphate particles are fully neutralised (as $(NH_4)_2SO_4$). Comparison of the concentrations of particulate sulphate, particulate ammonium and particulate nitrate can therefore be used to test if the particulate nitrate is in the form of ammonium nitrate or as other salts.

It is seen that there is generally good correlation between particulate ammonium and particulate sulphate. At IT04 (Ispra) the measurements indicate that ammonium nitrate is an important ammonium compound, but the excess of ammonium over the amount corresponding to ammonium sulphate is often too low to explain the particulate nitrate concentrations. As there is also an excess of ammonia, chemical absorption of nitric acid onto alkaline aerosol particles is the most likely explanation. Sulphate concentration data are not available from the Danish station Lille Valby, but it would appear likely that ammonium nitrate is a major component, together with ammonium sulphate.

At SE02 and NO01, the highest nitrate concentrations seem to be ammonium nitrate, but low and moderate concentrations of nitrate appear to be associated with other cations. This is in accordance with previous observations, which show that nitrate is often associated with sea-salt particles.

The low concentrations at SE12 makes it difficult to draw firm conclusions, but it appears that ammonia/ammonium concentrations levels are insufficient in relation to the formation of ammonium sulphate, and that any nitrates present may be connected with other cations than ammonium.



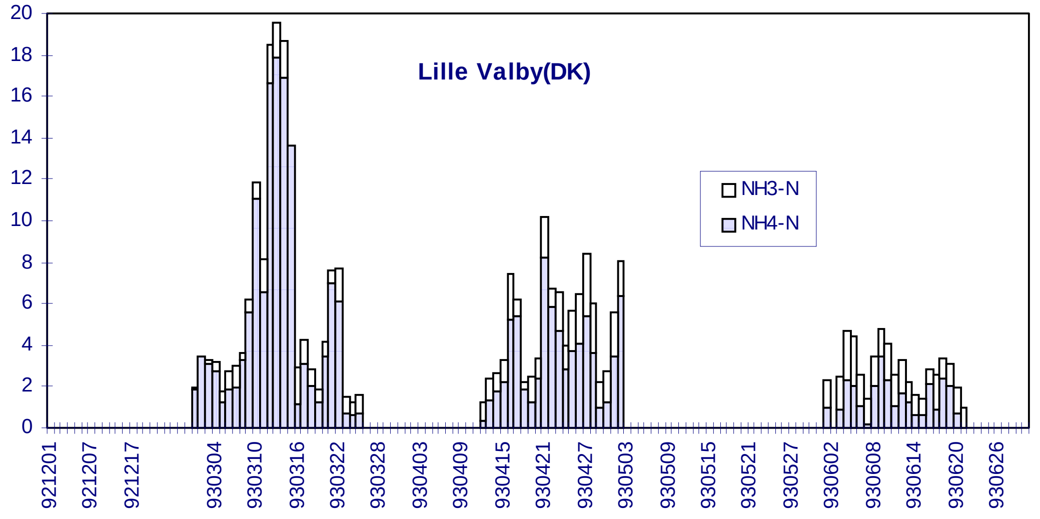
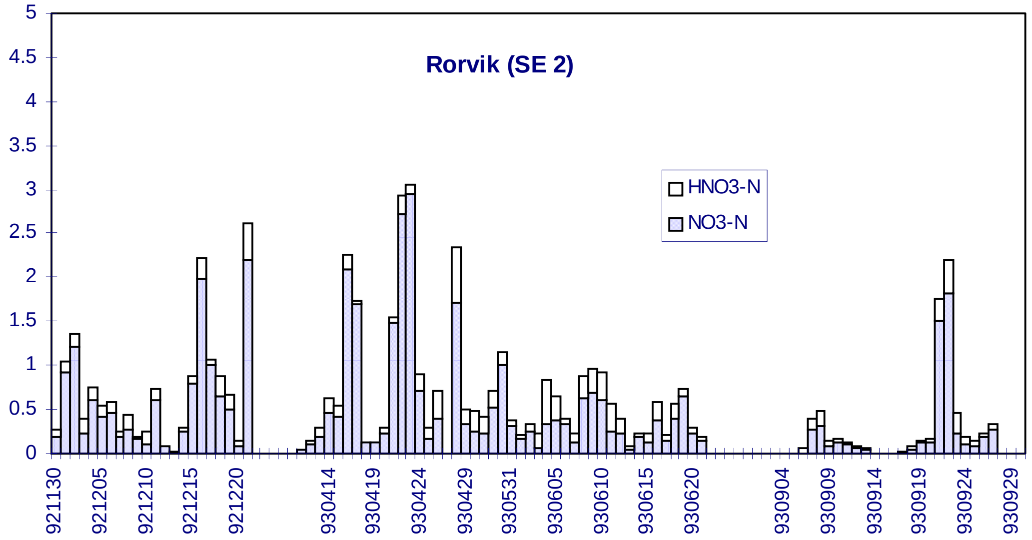


Figure 20: Measurement results from Lille Valby (DK33).



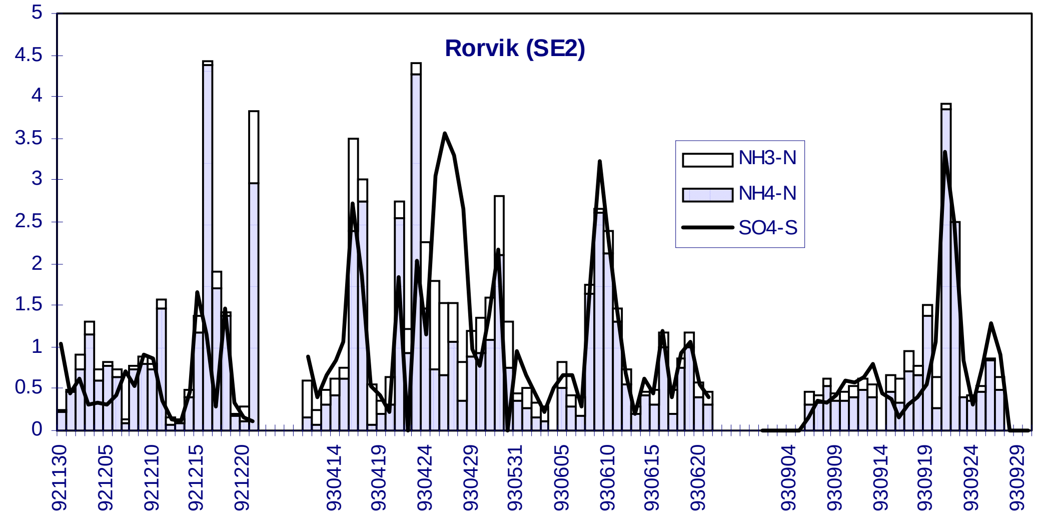


Figure 21: Measurement results from Rörvik (SE02).

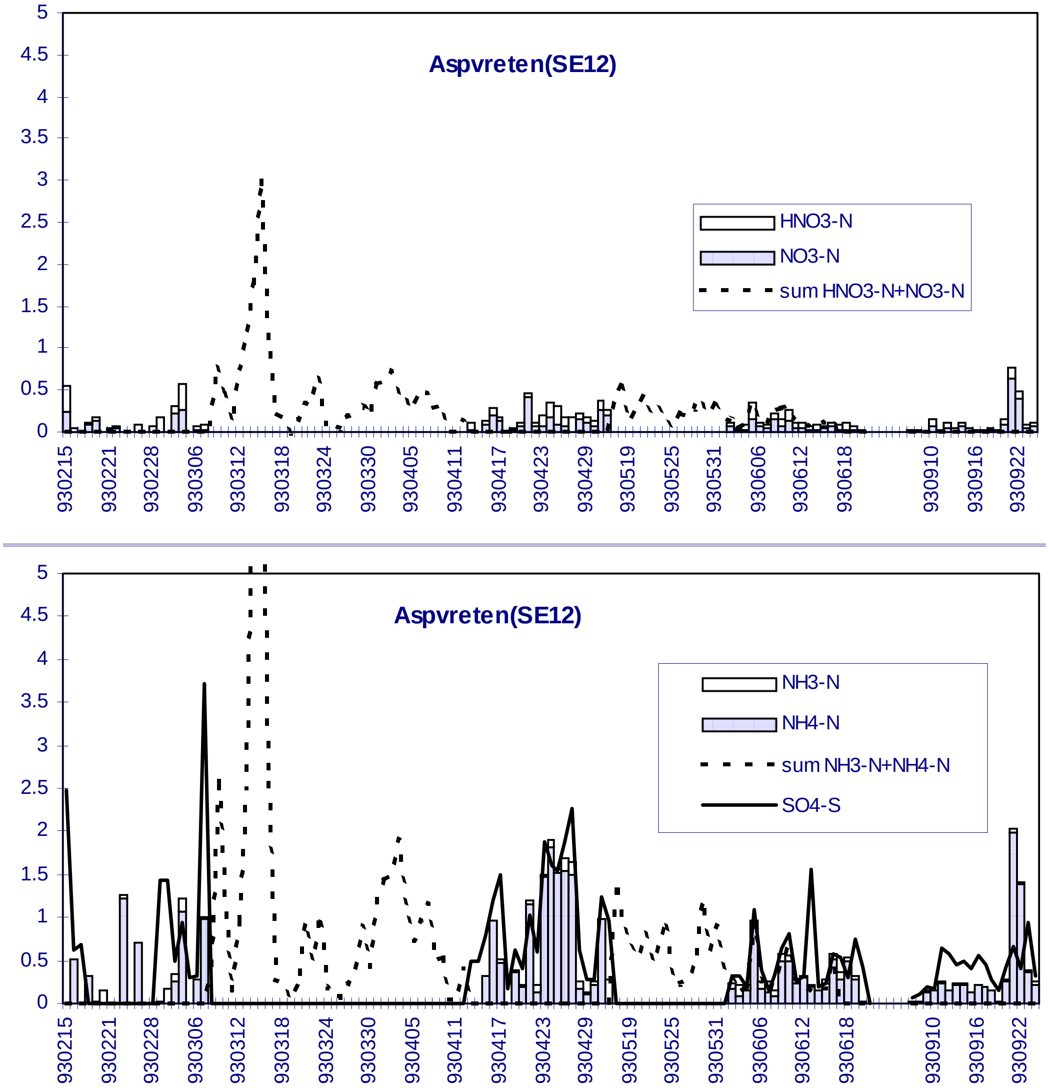


Figure 22: Measurement results from Aspvreten (SE12).

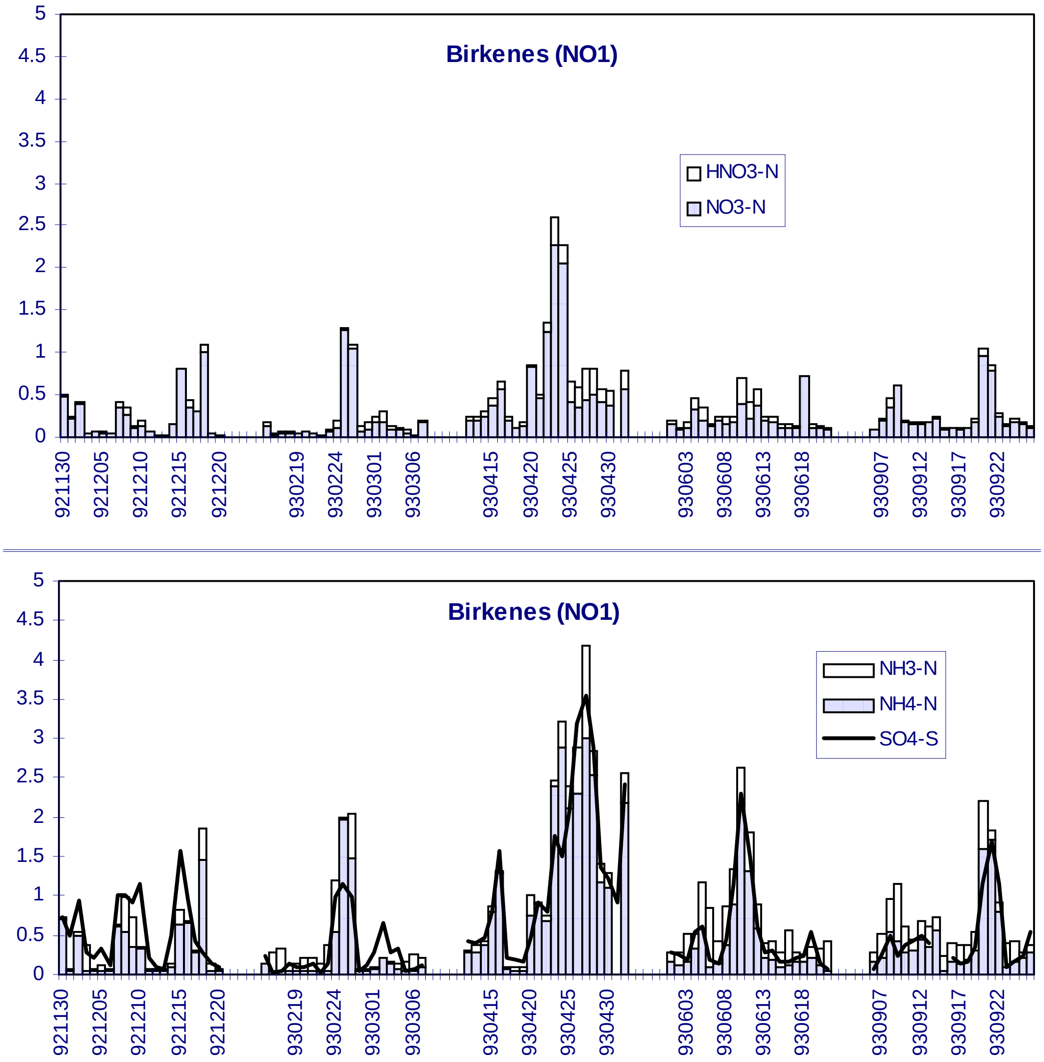


Figure 23: Measurement results from Birkenes (NO01).

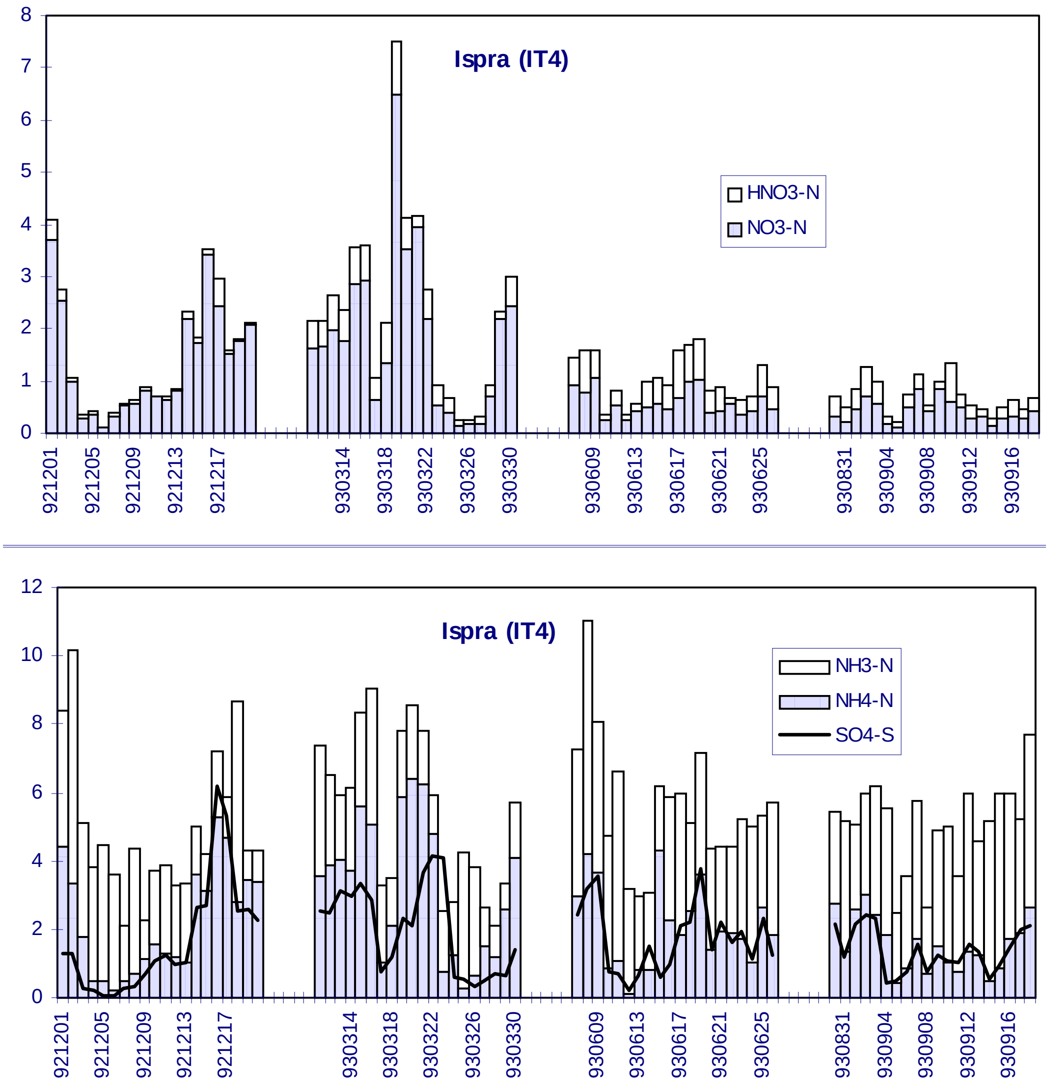


Figure 24: Measurement results from Ispra (IT04).

3.2.2 Trends in measured airborne particulate matter concentrations in the EMEP measurement framework

The strong reductions in the sulphur dioxide emissions in Europe during the past 15 years are reflected in corresponding observed decreases in the concentrations of airborne sulphur dioxide and sulphate aerosol, and in the sulphate concentrations and the acidity in precipitation samples. These changes are most pronounced in at sites which are influenced most strongly by the largest emission reductions, i.e. in western and northern Europe (see also Figures 25-26).

Available data inside EMEP indicate also that a reduction in the airborne sulphate concentrations is also seen at Ispra in Northern Italy, while there is no significant trend at Spanish or Portuguese sites. These countries have not reduced their emissions either.

In southern Scandinavia, where rain and snow are the main deposition mechanisms, sulphate concentrations are reduced by 50-70%, resulting in corresponding decreases in the acidity (see Figure 25). The concentrations of oxidised nitrogen components in air and precipitation have been reduced to a smaller extent in southern Scandinavia and central Europe (EMEP, 2000).

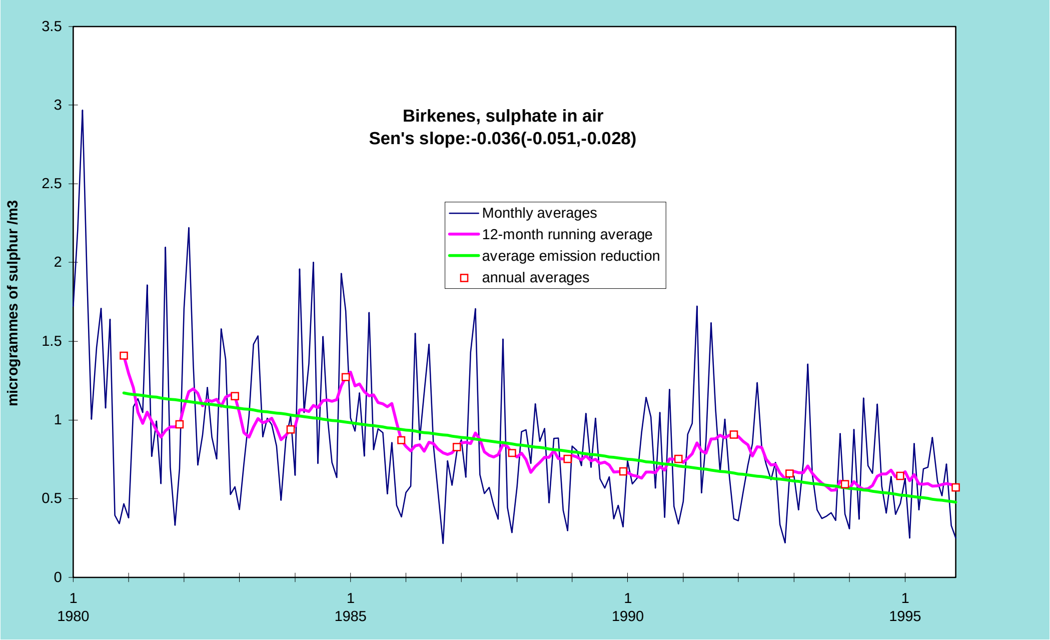


Figure 25: Trends in the concentration of ambient sulphate at Birkenes, Norway.

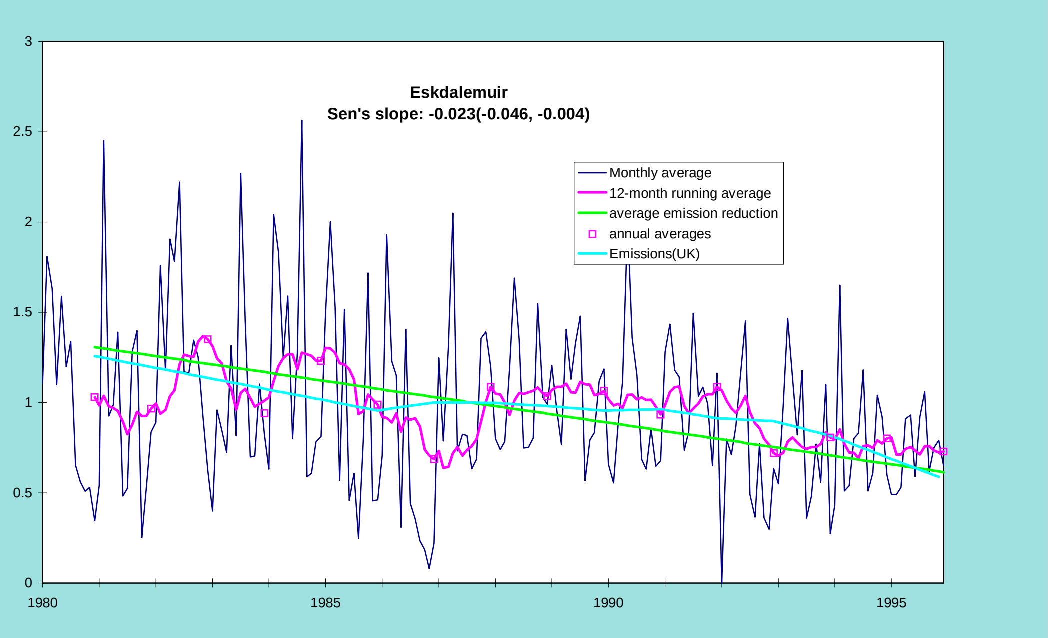


Figure 26: Trends in the concentration of ambient sulphate at Eskdalemuir.

3.2.3 *Heavy metals associated with particulate matter*

Airborne particulate matter includes small quantities of trace components such as heavy metals. Measurements of heavy metals in aerosols are already included as a main task in the EMEP programme. In the current document we briefly summarise the EMEP findings for ambient concentrations of lead and cadmium in aerosols in Europe during 1997 (Berg and Hjellbrekke, 1999). It should be noted that the maps presented in Figures 27 and 28 are based on relatively few measurement points and give only a coarse picture of the concentration distribution.

Figure 27 presents the annual averages of Pb in air in 1997. The lowest concentrations (below 1 ng Pb/m^3) can be seen at Spitzbergen (NO42) and at Iceland. A region with concentrations between 8 and 12 ng Pb/m^3 can be seen in central parts of Europe. A concentration maximum is seen in Belgium where there was an annual mean around 40 ng Pb/m^3. It should be noticed that, with the exception of the Baltic States, there are no data reported from southern- and eastern Europe.

Cadmium in aerosols is presented in Figure 28. As for Pb the lowest concentrations (below 0.05 ng Cd/m^3) are reported from Spitzbergen and Iceland. An increasing gradient can be seen south-eastward, with the highest concentration maxima in the Baltic States. No data are reported for the rest of eastern and southern Europe.

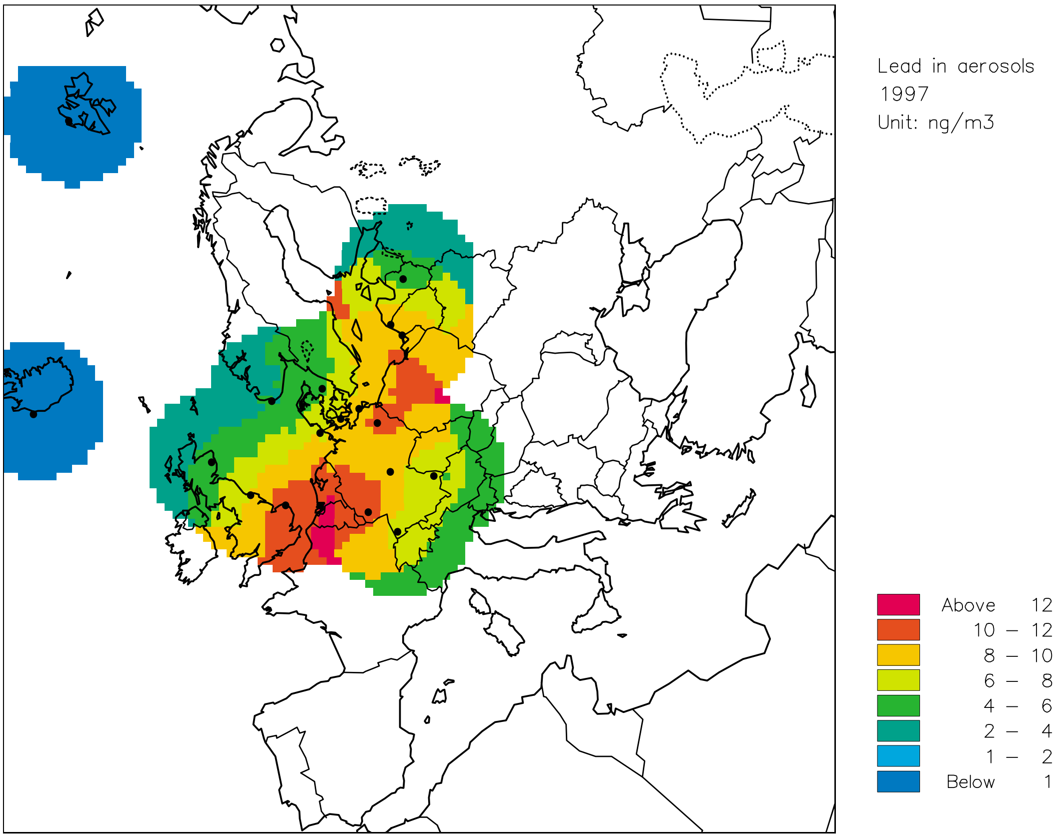


Figure 27: Kriged map of lead in aerosols, 1997 (ng/m^3).

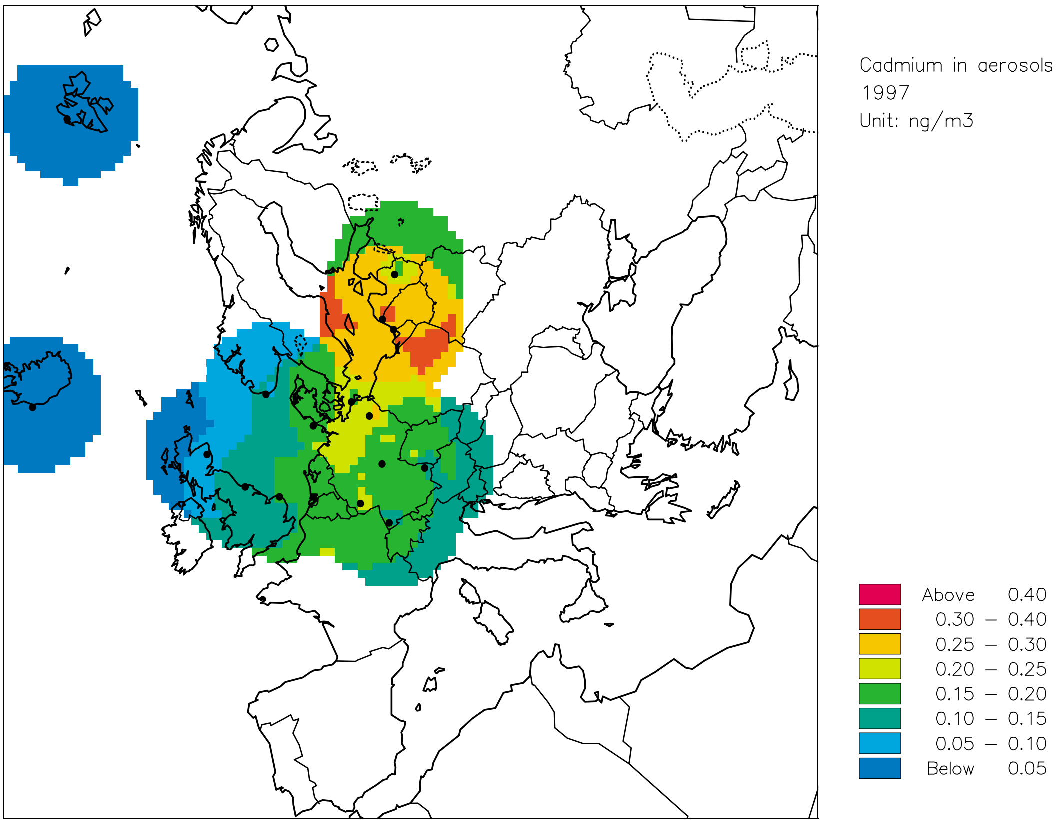


Figure 28: Kriged map of cadmium in aerosols, 1997 (ng/m^3).

3.3 Particulate measurements from European research programmes

3.3.1 European Topic Centre on Air Quality (ETC/AQ) – AIRBASE data

In this chapter we include PM air quality data for 1997 in Europe transmitted by countries on a voluntary basis in the framework of the "Exchange of Information" Decision (97/101/EC) as well as data from EMEP sites. This kind of data reporting is essential for summarising the collected information and outlining the underlying trends in air quality in Europe (Larssen and Lazaridis, 1998).

The European Topic Centre on Air Quality (ETC-AQ), under contract from EEA (European Environment Agency) is managing the database system AIRBASE. In this chapter we present summarised air quality data on PM concentrations from the AIRBASE and EMEP databases. In Figure 29 we show the measured levels of PM_{10} at rural, urban and roadside sites. Data from rural areas are from both the AIRBASE and EMEP databases. Different measurement methods have been used to quantify the particulate mass concentration levels on this Figure. The term “high” refers to the highest value among the stations. The Netherlands and the Czech Republic use beta-gauges, while the United Kingdom uses TEOM instruments. Both beta-ray absorption monitors and TEOM give low results compared to the CEN 12341 gravimetric reference method for PM_{10}, The Netherlands uses a constant factor to correct for this. The Figure, however, clearly indicates that the rural concentration levels of particulate mass are not much lower (10-30%) than the urban and roadside concentrations.

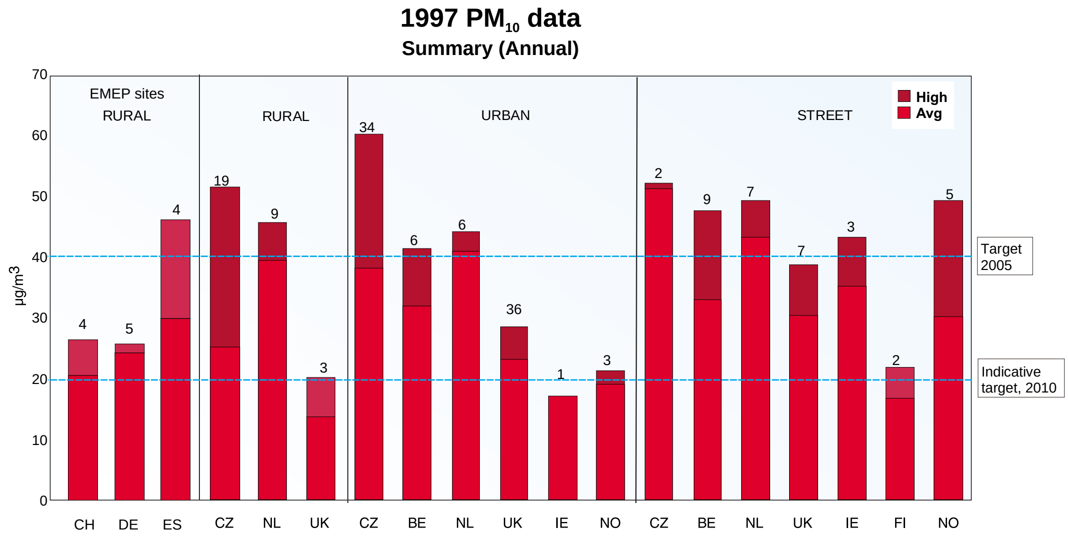


Figure 29: Annual averages of the PM_{10} concentrations in different countries in Europe for various site types.

In addition, Figure 30 is showing the geographical distribution of measured particulate mass concentrations: Although measurements are not comparable between countries (-30% – +50%), there is a clear pattern, with relatively high concentrations in the most densely populated areas of Europe, from England across the Low Countries, Germany and Central Europe. There is also a tendency towards higher concentrations in central and eastern Europe, although emissions have been decreasing in this area during the past 10 years. Measurements in Scandinavia are not shown in this figure: rural concentration levels range from about 15 µg/m3 in Scania (Malmö) to 10 µg/m3 near Stockholm, 8 µg/m3 in southern Norway (Birkenes) and less than 5 µg/m3 in northern Norway and Sweden. In order to provide a check on model estimates of the relative contributions to particulate mass from different sources and countries, more precise and specific measurements are clearly needed.

Particulate matter concentrations are reported either as PM_{10}, total suspended particulate (TSP) or black smoke. PM_{10} data were reported from 72 stations in 4 EU countries and from 73 stations in 3 non EU countries according to the annual average statistics. TSP data were reported from 460 stations in 3 EU countries and from 33 stations in 4 non EU countries. Black smoke data were reported from 244 stations in 5 EU countries and from 33 stations in 2 non EU countries. All together particulate matter data were reported from 776 stations in 9 EU countries and from 139 stations in 7 non EU countries (see Figure 30). The annual average and 24 hour maximum values (µg/m^3) of particulate matter concentrations in the AIRBASE framework have been presented in figures 31-32.

Table 3 presents annual average concentrations by country and station type.

Table 3: Average, minimum and maximum annual particulate matter concentrations (µg/m^3) in 1997. Figures between brackets refer to the number of stations.

		Annual average including range				
Country	measured as:	rural	urban	street	other	non-defined
Belgium	PM10		33 27-41(5)	30 24-34(4)	39 34-47(3)	
Finland	PM10			22(1)		
Netherlands	PM10	39 32-45(8)	40 38-44(6)	44 42-49(5)		
United Kingdom	PM10	15 10-20(3)	23 18-28(30)	29 24-32(5)	21 19-22(2)	
Austria	TSP	25 1-42(24)	33 16-65(43)	33 8-65(26)	37 23-79(13)	
Denmark	TSP	26(1)		54 47-61(3)		
Germany	TSP	22 6-42(21)	38 20-60(66)	46 27-89(91)	43 32-59(10)	35 13-75(162)
Belgium	Black S.	12 8-15(5)	16 9-27(32)	22 13-37(6)	13 9-19(6)	18 15-22(2)
Greece	Black S.					27(1)
Netherlands	Black S.	10 7-13(8)	14 12-14(3)	30 22-44(3)		
Sweden	Black S.	2 1-2(3)				
United Kingdom	Black S.		11 2-25(166)	53 23-102(5)	8 5-10(2)	12 9-15(2)
Non EU countries						
Czech Republic	PM10	25 13-51(19)	38 24-60(34)	51 50-52(2)	38(1)	
Poland	PM10		48 34-59(5)	77(1)	65 57-73(2)	
Switzerland	PM10	32(1)	29 19-37(5)	34 29-43(3)		
Estonia	TSP			36(1)		
Hungary	TSP		55 48-59(3)	53 44-65(4)	68(1)	
Slovak Republic	TSP		51 36-74(8)	49 21-65(6)	44 31-90(9)	
Switzerland	TSP	25(1)				
F.Y.R.O.M.	Black S.		23 5-42(15)	29 11-48(8)	25 12-36(4)	
Poland	Black S.		23 10-35(6)			

The EU TSP annual limit value of 150 µg/m^3 was not exceeded on any station in EU and non EU countries. There is no EU limit 98 percentile 24 hour value for TSP. The 95 percentile limit value is 300 µg/m^3. Only one station reported TSP 98 percentile value above 300 µg/m^3 (in a non EU country). There is no EU maximum limit value for TSP.

Reported annual black smoke concentrations were in general below the lower limit of the EU guide value of 40 µg/m^3, with the exception of some stations in two EU countries and one non EU country. The 98 percentile 24 hour black smoke 24 hour limit value of 250 µg/m^3 was not exceeded on any station. The EU guide value for 24 hour maximum black smoke of 100-150 µg/m^3 was exceeded on many stations in EU and non EU countries.

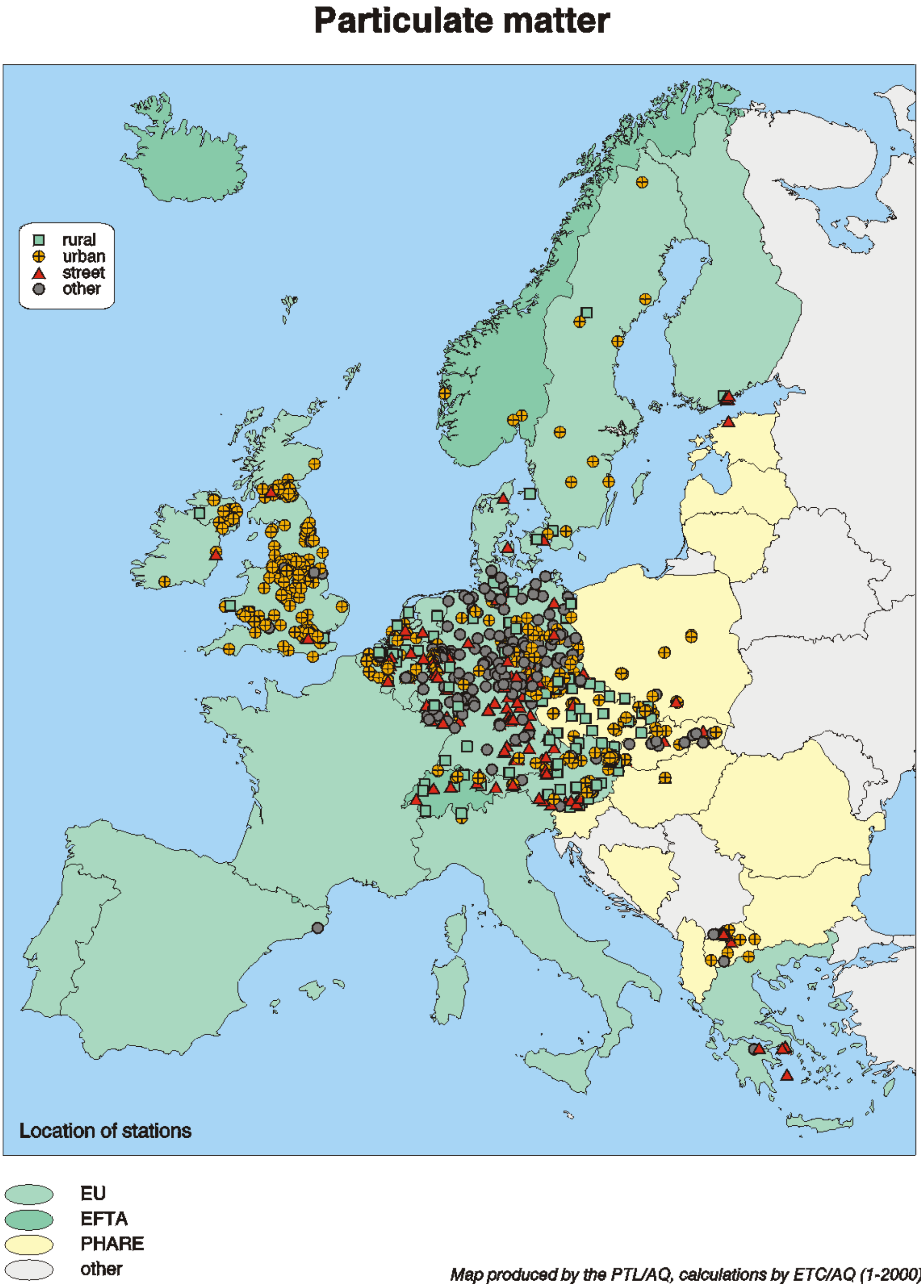


Figure 30: Location of stations and station type that measure particulate matter concentrations under the AIRBASE framework.

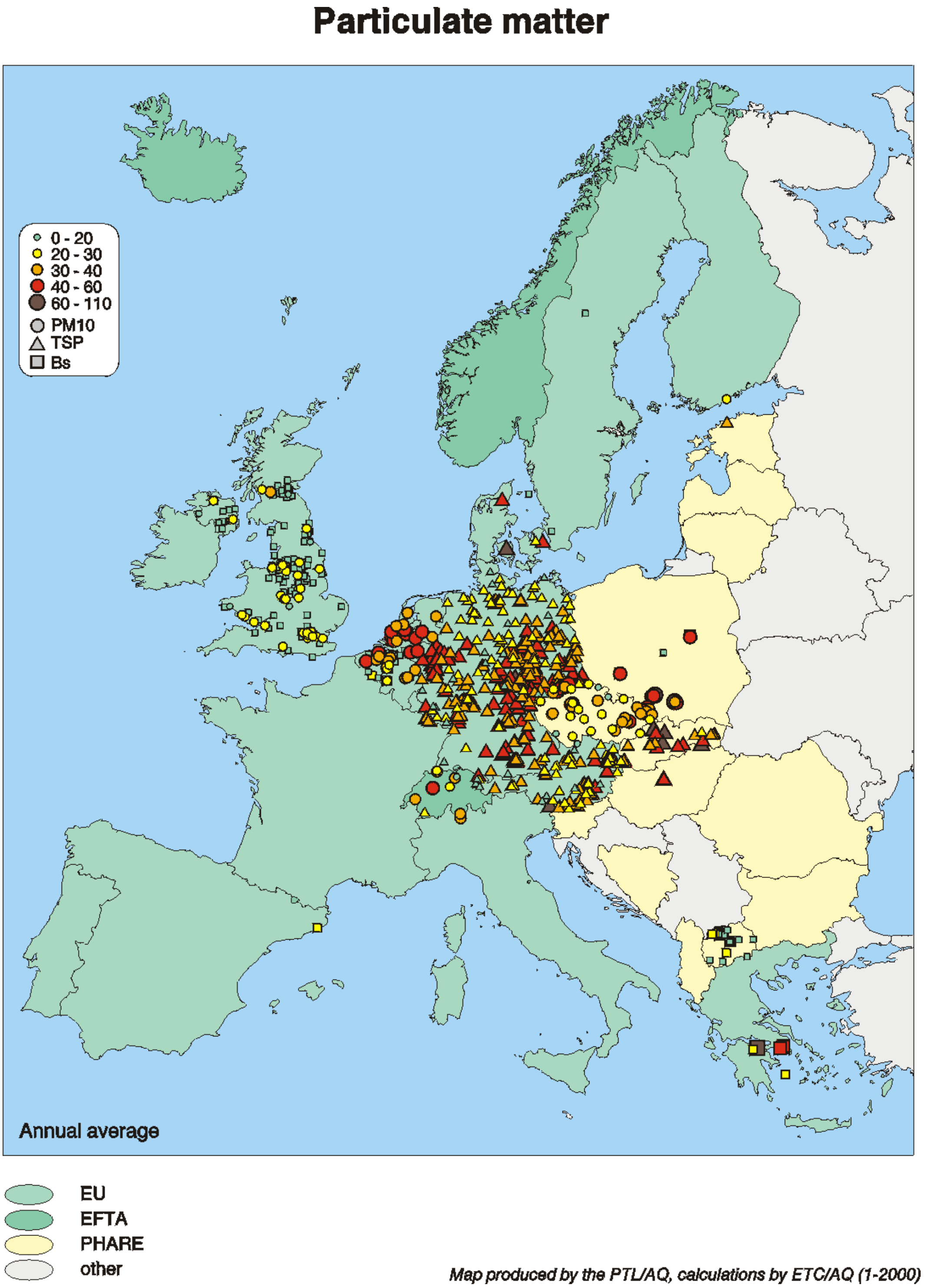
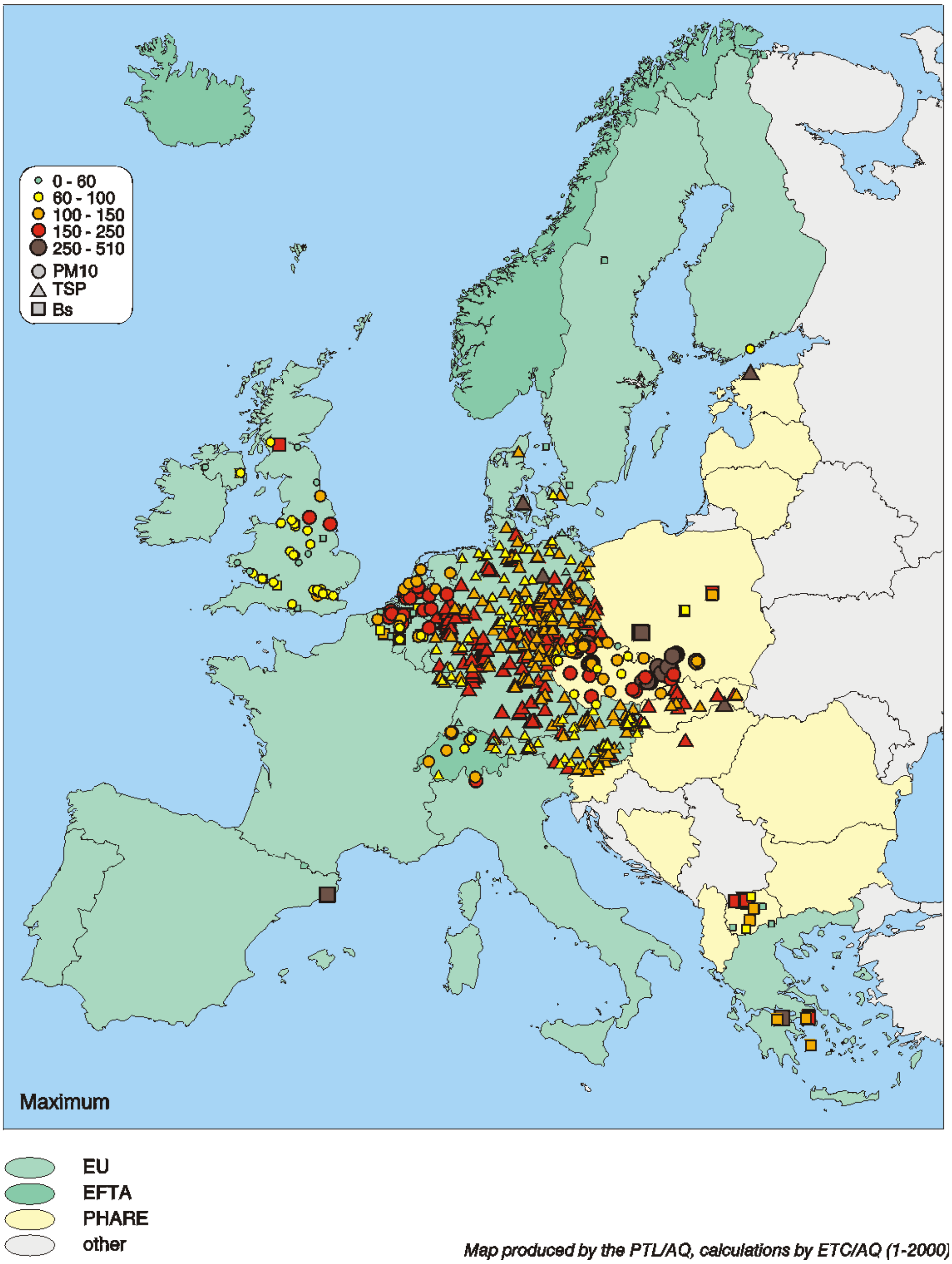


Figure 31: Annual average particulate matter concentrations under the AIRBASE framework.

Particulate matter



Map produced by the PTL/AQ, calculations by ETC/AQ (1-2000)

Figure 32: Maximum observed 24 hour values (µg/m^3) concentrations of particulate matter concentrations under the AIRBASE framework.

3.3.2 Measurements in Birkenes – Skreådalen (Norway)

In this section we present an outline of research measurements on particulate matter PM_{10} and $PM_{2.5}$ concentration and chemical composition in Birkenes and Skreådalen (Norway) from the early 1970 until recently.

The sampling in the campaigns before 1991 was performed with high-volume samplers, whereas the chemical analyses were done with neutron activation, atomic absorption and other chemical analyses. In the period between 1991–1995 the sampling was done with the "Gent" stacked filter unit, PM_{10} impactor inlet, followed by two Nucleopore filters in a NILU filter holder. The first Nucleopore filter ("coarse") has a 8µm nominal pore size. At a flow rate of 15-16 lpm, this gives a 50% efficiency cut-off at 2 µm EAD. The second filter is also a Nucleopore filter with a nominal pore size of 0.4.

Annual averages for Birkenes are indicated in Table 4. There has been a clear reduction in the concentration of inorganic aerosol constituents, particularly the elements associated with dust and fly ash emissions from process industries and solid fuel combustion. Emissions of heavy metals have also been reduced, and the concentration of ammonium sulphate is reduced since 1980. It is interesting to discuss the results in terms of different contributions to the total mass. For this purpose the following components have been defined:

Inorganic minerals.

The ratio between Si, Al, Fe and Ca is not very different from the average composition of the earth's crust, but Fe and Ca may be somewhat higher due to emissions from iron and steel industries, and from cement works. Potassium occurs in much higher concentrations than expected, and is particularly enriched in the $PM_{2.5}$ fraction.

Sea-salt.

The marine aerosol consists mainly Na and Cl, with minor amounts of Mg, Ca, K, and SO_4^{--}. The samples are always depleted with respect to Cl, this is particularly the case for the $PM_{2.5}$ fractions. Bromine is enriched in the fine fraction, so is iodine. Neither make any significant contribution to the particulate mass.

Secondary inorganic aerosol.

Only sulphur has been determined by PIXE. Other measurements have shown that sulphate is mainly present as ammonium sulphate, and that nitrate at Birkenes occurs in the coarse particle fraction, in association with sea-salt particles. The contribution of ammonium sulphate to the $PM_{2.5}$ mass is very substantial.

Elementary and organic carbon.

Only elementary carbon has been determined with an optical method, which is not an absolute method. Nevertheless, the measured average concentration at 0.5-0.6 µg/m^3 is close to expected values.

Table 4: Overview of aerosol concentrations at Birkenes, 1973-1993. All concentrations are given in nanogrammes/m^3*. Inferred values in italics. Spring 1973 and Autumn 1973 are neutron activation data by Rahn, compiled by Semb (1978); 1978-1979 data are from Pacyna et al., 1984b; 1985-1986 data are from Amundsen et al., 1992; data from 1991 onwards are from Maenhaut et al., 1993.*

	Spring 1973	Autumn 1973	1978-79	1985-86	1991, coarse	1991, fine	1992 coarse	1992 fine	1993 coarse	1993 fine
Si	433	323	304	277	115	68	131	46	66	33
Al	114	85	80	73	58	14	64	14	26	10
Fe	96	95	84	61	35	14	41	13	17	10
Ca	80	74			47	11	47	12	31	11
nss Ca	*65*				*37*	*7*	*35*	*8*	*13*	*4*
K	138	-			37	36	39	24	29	28
nss K	*123*				*27*	*32*	*27*	*20*	*12*	*22*
Zn	29	35		15	2	6	1.5	4.2	1.7	6.4
Pb		23	18	11	1	4	1.10	3.20	0.70	3.50
Minerals	*1658*	*1090*	*1019*	*908*	*561*	*257*	*620*	*195*	*280*	*148*
Na	403	478	508	350	273	116	329	118	464	179
Cl	60	256	566	380	258	33	316	17	600	84
Br			4.7	5.3			1.03	2.55	1.29	2.68
I							0.2	0.8		0.72
Sea-salt	*568*	*858*	*1206*	*821*	*602*	*179*	*730*	*165*	*1185*	*310*
SO_4		2560	4260	3060	393	2712	354	1797	378	1740
nss SO_4		2520	4217	3031	370	2702	326	1787	339	1725
NO_3		n.a.	n.a.	n.a.		n.a.	n.a.			
NH_4		*960*	*1598*	*1148*	*147*	*1017*	*133*	*674*	*142*	*653*
Secondary inorganic		*3480*	*5815*	*4178*	*518*	*3719*	*459*	*2461*	*481*	*2378*
Black carbon					80	544	90	410	80	514
Sum quantified components		*5429*	*8040*	*5907*	*1760*	*4699*	*1899*	*3231*	*2026*	*3349*
Measured					2800	6780	3120	5018	2898	5037
Unexplained					*1040*	*2081*	*1221*	*1787*	*872*	*1688*

Undefined components.

The difference between the calculated contributions from the components which have been quantified on the basis of chemical analyses, and the particulate mass determined by weighing of the sample filters, have been labelled “undefined”.

Both primary particulate matter and secondary organic particulate matter also contribute to the total mass of the $PM_{2.5}$ fraction. On the basis of measurements in urban areas, organic aerosol concentrations should be expected to be at least twice the concentration of elementary carbon. It is important to quantify these contributions properly. Primary particulate matter of biological origin (bioaerosols, organic debris) may be a significant contributor to the 2.5<PM<10 fraction.

The contribution from minerals, determined on the basis of Si, Al, Fe and Ca, is highly episodic. The high concentrations in May-June 1992 are associated with trajectories across southern Sweden from the Baltic countries, possibly implicating emission sources in the Narva-Leningrad region. It is expected that the minerals are from anthropogenic emissions, combustion of solid fuels, cement production, iron and steel industry (see Figure 33).

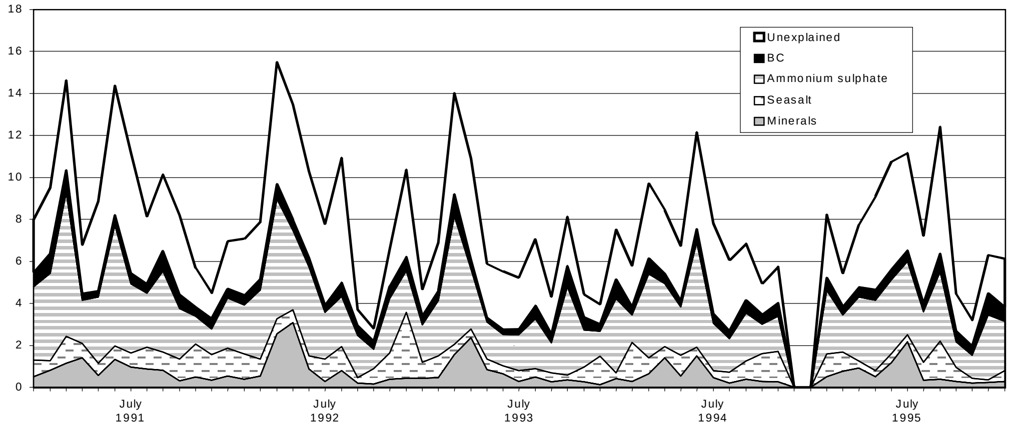


Figure 33: Measured PM_{10} mass concentrations at Birkenes for the period February 1991-February 1996, together with inferred masses of specific components from chemical analyses.

Sea-salt is also a main contributor to the coarse particle fraction. Chloride is depleted relative to sodium in most of the samples, particularly in the fine particle fraction. Part of the depletion is caused by reaction of nitric acid with the sea-salt particles, displacing hydrochloric acid. However, these data are not suitable for establishing a quantitative relationship.

A number of elements are “enriched” in aerosols relative to their abundance in the earth’s crust or in seawater. These are mainly found in the fine fraction, and include elements such as lead, cadmium, zinc, arsen, antimony, selenium, bromine and iodine. Neither of these contribute significantly to the particle mass, and, since lead-free petrol has become common, none are no longer valuable as tracers of particular emission sources either.

The main constituents in the fine fraction appears to be ammonium sulphate, elementary carbon and organic compounds. Clearly, good analytical methods for the two latter components are desirable for the full quantification of the fine particle fraction, although minerals and sea-salts are also of some importance.

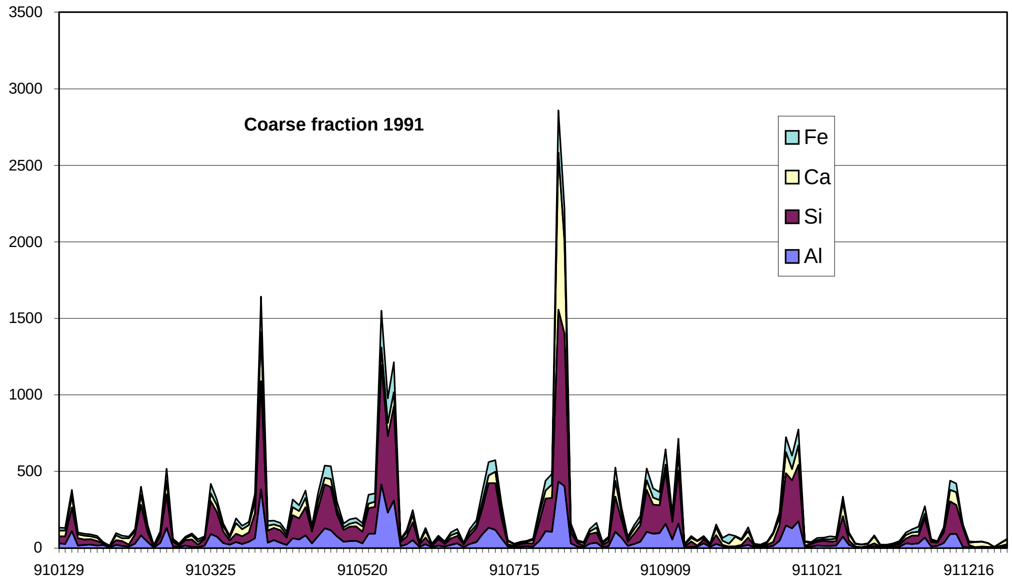


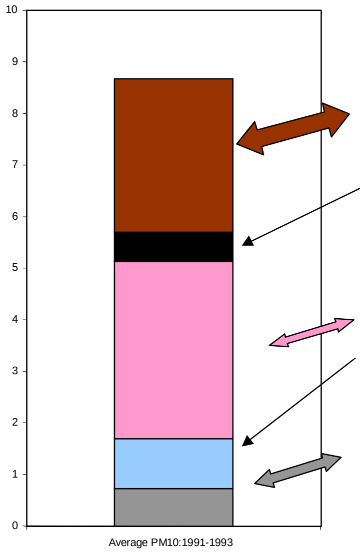
Figure 34: Aerosol coarse fraction concentration during 1991 for a number of inorganic compounds.

The measurements of the fine particle mass are quite consistent in time, with good correlation between the total mass and the identified components. A number of tentative conclusions can be reached from the above studies. The Ghent stacked filter unit is useful for quantifying PM_{10} and $PM_{2.5}$, and can provide samples for subsequent chemical analyses. The low air volumes make the weighing somewhat demanding, and the membrane filters are also subject to electrostatic charging. On the other hand, these filters do not need the careful "conditioning" which has to be carried out when weighing glass fibre filters.

In addition, secondary inorganic particulate matter is the main constituent in the $PM_{2.5}$ fraction at background sites, explaining 30-50% of the total mass. The second most important component in the $PM_{2.5}$ fraction is black carbon or soot, with associated organic compounds from combustion processes. Quantification of this component, preferably with more detailed characterisation of the organic fraction, is the key to understanding the composition and properties of $PM_{2.5}$, including the formation of secondary organic aerosols.

Sea-salt components and minerals are of minor importance for the $PM_{2.5}$ fraction but account for a major part of the PM_{10} - $PM_{2.5}$. These are important in connection with deposition of sea-salt ions, and alkaline base cations. In Figure 35 we present an outline of the chemical composition of PM_{10} measurements at Birkenes from measurements performed after 1991.

There exist an extensive set of data from aerosol measurements at Birkenes and Skreådalen stations in southern Norway from 1973 until today. In Figures 36-37 we present available data for sulphate in aerosol mass and PM_{10} for selected periods during 1995 and 1996 respectively.



The unidentified component is poorly quantified, being the difference between the total mass and the identified components below. Black carbon, determined with an optical reflectance or transmittance method, is subject to a calibration error of at least 50%. Direct determination of elementary and organic carbon is higly desirable in order to improve our understanding of aerosol mass and chemical compositoon

Ammonium sulphate and ammonium nitrate account for 30-50% of PM10 and an even larger percentage of fine particles

Sea-salt particles.

Silicates and other primary minerals are a minor component of PM10, and even more insignificant in fine particles. This component has declined markedly in Europe, mainly because of better emission controls in the last 10-20 years.

Figure 35: Chemical composition of PM_{10} (micrograms per m^3) at Birkenes in Southern Norway. (Data from W. Maenhaut, Univ. of Gent, and NILU.)

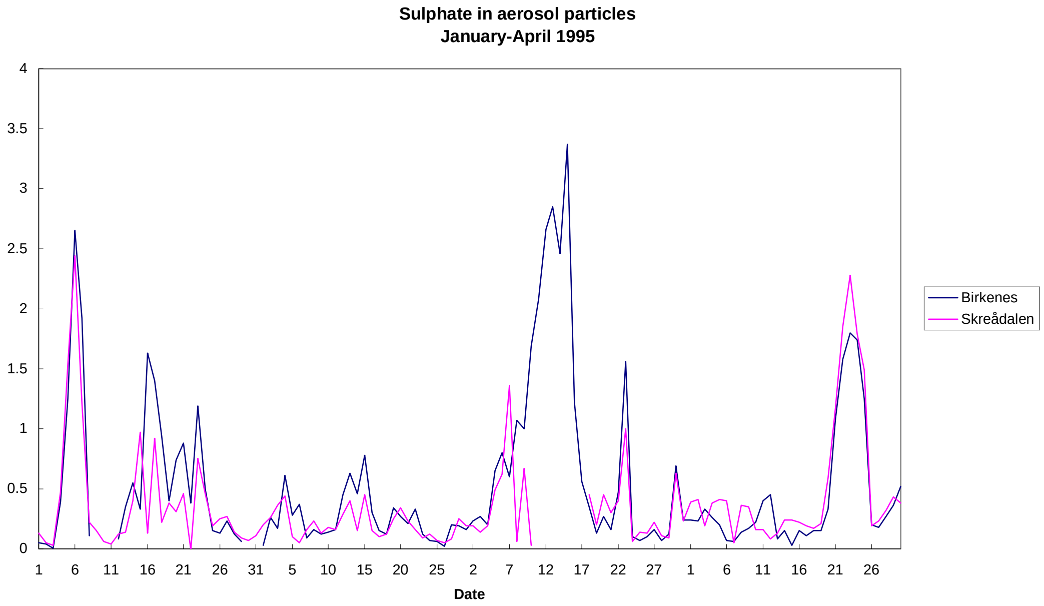


Figure 36: Sulphate concentration in the aerosol mass at Birkenes and Skreådalen stations between January and April 1995.

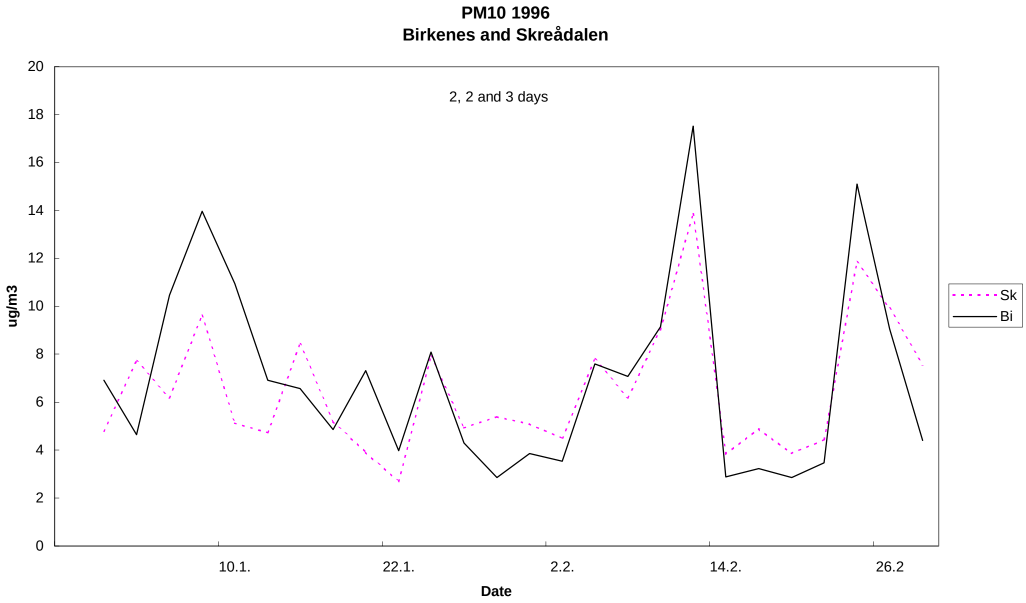


Figure 37: Ambient concentration of PM_{10} at Birkenes and Skreådalen stations during January and February 1996.

4. References

Ackermann, I.J., Hass, H., Memmesheimer, M., Ebel, A., Binkowski, F.S. and Shankar, U. (1998) Modal aerosol dynamics model for Europe: Development and first applications. *Atmos. Environ., 32*, 2981-2999.

Allen, G., Sioutas, C., Koutrakis, P., Reiss, R., Lurmann, F.W., and Roberts, P.T. (1997) Evaluation of the TEOM method for measurement of ambient particulate mass in urban areas. *J. Air Waste Manage. Assoc., 47*, 682-689.

Amundsen, C.E., Hanssen, J.E., Semb, A., and Steinnes, E. (1992) Long-range transport of trace elements to southern Norway. *Atmos. Environ., 26A*, 1309-1324.

Andreae, M.O. and Crutzen, P.J. (1997) Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry. *Science, 276*, 1052-1058.

Berdowski, J.J.M., Mulder, W., Veldt, C., Visschedijk, A.J.H. and Zandveld, P.Y.J. (1998) Particulate emissions (PM_{10}-$PM_{2.5}$-$PM_{0.1}$) in Europe in 1990 and 1993. Bilthoven, RIVM.

Berg, T. and Hjellbrekke, A.-G. (1999) Heavy metals and POPs within the ECE region 1997. Kjeller, Norwegian Institute for Air Research (EMEP/CCC Report 7/99).

Birch, M.E., and Cary, R.A. (1996) Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci. Technol., 25*, 221-241.

Buijsman, E. and van Elzakker, B.G. (1996) Meetaktiviteiten in 1996 in het kader van het Landelijk Meetnet Luchtkwaliteit. Bilthoven (RIVM Report 723101 022).

Cachier, H., Bremond, M.-P. and Buat-Ménard, P. (1989) Determination of atmospheric soot carbon with a simple thermal metod. *Tellus, 41B,* 379-390.

CEN (1998) Air quality – Determination of the PM_{10} fraction of suspended particulate matter – Reference method and field test procedure to demonstrate reference equivalence of measurement methods. European Committee for Standardization (European Standard EN 12341).

Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A. and Purcell, R.G. (1993) The DRI thermal/optical reflectance carbon analysis system: description, evaluation and application in U.S. air quality studies. *Atmos. Environ., 27A,* 1185-1201.

Commission of the European Communities (1996) Ambient Air Pollution by Particulate Matter, Executive Summary.

Commission of the European Communities (1997) Proposal for a council directive relating to limit values for sulphur dioxide, oxides of nitrogen, particulate matter and lead in ambient air. Luxembourg, Office for Official Publications of the European Communities. (Documents/Commission of the European Communities) (COM(97) 500 final) (CB-CO-97-525-EU-C).

Eliassen, A. and Saltbones, J. (1983) Modelling of long range transport of sulphur over Europe: a two year model run and some model experiments. *Atmos. Environ., 17,* 1457-1473.

EMEP (2000) Transboundary acid deposition in Europe. EMEP Summary report 2000. Oslo, Norwegian Meteorological Institute (EMEP Report 1/00).

EMEP/CORINAIR (1996) Atmospheric emission inventory guidebook. Copenhagen, European Environment Agency.

EMEP-WMO (1999) Workshop on Fine Particles - Emissions, Modelling and Measurements. Proceedings Interlaken, Switzerland. Kjeller, Norwegian Institute for Air Research (in preparation).

EPA (1996) Air quality criteria for particulate matter. Washington, U.S. Environmental Protection Agency (EPA 600/P-95-001).

Finlayson-Pitts, B.J. and Pitts, J.N. (1986) Atmospheric chemistry: fundamentals and experimental techniques. New York, Wiley.

Harrison, R.M. and Yin, J. (2000) Particulate matter in the atmosphere: which particle properties are important for its effects on health? *Sci. Total Environ., 249,* 85-101.

Hedin, L.O., Granat, L., Likens, G.E., Buishand, T.A., Galloway, J.N., Butler, T.N. and Rodhe, H. (1994) Steep declines in atmospheric base cations in regions of Europe and North America. *Nature, 367,* 351-354.

Heintzenberg, J. (1989) Fine particles in the global troposphere - a review. *Tellus, 41B,* 149-160.

Heintzenberg, J., Müller, K., Birmili, W., Spindler, G. and Wiedensohler, A. (1998) Mass-related aerosol properties over the Leipzig basin*. J. Geophys. Res., 103,* 13125-13135.

Hinds, W.C. (1999) Aerosol Technology. Properties, behavior, and measurement of airborne particles. New York, Wiley.

Hopke, P.K., Ying Xie, Raunemaa, T., Biegalski, S., Landsberger, S., Maenhaut, W., Artaxo, P. and Cohen, D. (1997) Characterisation of the Gent Stacked Filter Unit PM10 Sampler. *Aerosol Sci. Technol., 27,* 726-735.

Hutzincker, J.J., Hoffmann, R.S. and Cary, R.A. (1984) Aerosol sulfur episodes in St. Louis, Missouri. *Environ. Sci. Technol., 18,* 962-967.

Lannefors, H., Hansson, H.-C. and Granat, L. (1983) Background aerosol composition in southern Sweden – Fourteen micro and macro constituents measured in seven particle size intervals at one site during one year. *Atmos. Environ., 17,* 87-111.

Larssen, S. and Lazaridis, M. (1998) EUROAIRNET site selection 1998. Copenhagen, European Environment Agency (Technical report 16).

Lazaridis, M., Semb, A. and Hov, Ø. (1999) Long-range transport of aerosol particles. A literature review. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 8/99).

Liousse, C., Cachier, H. and Jennings, S.G. (1993) Optical and thermal measurements of black carbon aerosol in different environments. *Atmos. Environ., 27A,* 1203-1211.

Liu, B.Y.H. and Pui, D.Y.H. (1981) Aerosol sampling inlets and inhalable particles. *Atmos. Environ., 15,* 589-600.

Maenhaut, W., Francois, F. and Cafmeyer, J. (1993) First Research Co-ordination Meeting of the International Atomic Energy Agency (IAEA): Co-ordinated Research Programme on Applied Research on Air Pollution using Nuclear-Related Analytical Techniques. Vienna, Austria, 20 March-2 April. Proceedings.

McMurry, P. H. (2000). A review of atmospheric aerosol measurements. *Atmos. Environ., 34,* 1959-1999.

Pakkanen, T.A., Hillamo, R.E., Keronen, P., Maenhaut, W., Ducastel, G. and Pacyna, J.M. (1996) Sources and physico-chemical characteristics of the atmospheric aerosol in Southern Norway. *Atmos. Environ., 30*, 1391-1405.

Pacyna, J.M., Semb, A. and Hanssen, J.E. (1984a) Emission and long range transport of trace elements in Europe. *Tellus*, *36B*, 163-178.

Pacyna, J.M., Ottar, B., Hanssen, J.E. and Kemp, K. (1984b) The chemical composition of aerosols measured in Southern Scandinavia. Lillestrøm (NILU OR 66/84).

Patashnik, H. (1998) Letter to the Editor. *J. Air Waste Manage. Assoc., 48*, 195-197.

Patashnik, H. and Rupprecht, E.G. (1991) Continuous PM_{10} measurements using the tapered element oscillating microbalance. *J. Air Waste Manage. Assoc., 41*, 1079-1083.

Position Paper on Particles (1998) Ambient Air Pollution by Particulate Matter, Technical Working Group on Particles.

Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R. and Simoneit, B.R.T. (1993) Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation. *Atmos. Environ., 27,* 1309-1330.

Schaug, J. and Uhse, K. (1997) EMEP-WMO Workshop on strategies for monitoring of regional air pollution in relation to the need within EMEP, GAW and other international bodies, Lerum, Sweden, June 2-4, 1997. Kjeller, Norwegian Institute for Air Research (EMEP/CCC Report 10/97).

Seinfeld and Pandis (1998) Atmospheric chemistry and physics of air pollution: from air pollution to climate change. New York, Wiley.

Semb, A. (1978) Deposition of trace elemeents from the atmosphere in Norway. SNSF Projeckt, Ås, Norway. (SNSF FR 13/78).

Semb, A., Hanssen, J.E., Francois, F., Maenhaut, W. and Pacyna, J.M. (1995) Long range transport and deposition of mineral matter as a source for base cations. *Water Air Soil Pollut., 85,* 1933-1940.

Semb, A., Bartonova, A., Schaug, J., Lükeville, A. and Tørseth, K. (1998) Pilot measurements of nitrogen containing species in air. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 5/98).

Tarrason, L. and Tsyro, S. (1998) Long-range transport of fine secondary particles, as presently estimated by the EMEP Lagrangian model. EMEP/MSC-W Note 2/98. Oslo (EMEP/MSC-W note 2/98) (Norwegian Meteorological Institute research report 69).

Turpin, B. J., Saxena, P. and Andrews, E. (2000). Measuring and simulating particulate organics in the atmosphere: problems and prospects. *Atmos. Environ., 34,* 2983-3013.

Tørseth, K., Hanssen, J.E. and Semb, A. (1999) Temporal and spatial variations of airborne Mg, Cl, Na, Ca and K in rural areas of Norway. *Sci. Total Environ., 234,* 75-85.

Wedding, J.B. and Weigand, M.A. (1993) An automatic particle sampler with beta gauging. *J. Air Waste Manage. Assoc., 43,* 475-479.

WHO (1999) Particulate matter (PM_{10} and $PM_{2.5}$). Results of intercomparison studies. Report on a WHO Workshop, Berlin 3-5 September 1998. Copenhagen, WHO Regional Office for Europe (EUR/ICP/EHB1040102, E62010, 10-13).

WHO (1996) Revised WHO Air Quality Guidelines. Copenhagen, WHO Regional Office for Europe.

Van der Zee, S.K., Hoek, G., Harssema, H. and Brunekreef, B. (1998) Characterization of particulate air pollution in urban and non-urban areas in the Netherlands. *Atmos. Environ., 32,* 3717-3729.

Zappoli, S., Andracchio, A., Fuzzi, S., Facchini, M.C., Gelencser, A., Kiss, G., Krivacsy, Z., Molnar, A., Meszaros, E., Hansson, H.-C., Rosman, K. and Zebuhr, Y. (1999) Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility. *Atmos. Environ., 33,* 2733-2743.

Appendix 1

Location and measurement characteristics in the EMEP station framework

Table 1.1: Location and measurement characteristics in the EMEP station framework.

Site name	Lat.	Long.	Elev.	Sulphate µg S/m^3		Nitrate µg N/m^3		Ammonium µg N/m^3		Acidity ne H+/m^3		SPM µg/m^3		EMEP code
				start	end	start	end	start	end	start	end	start	end	
Austria														
Illmitz	47.46	16.46	117	7801	cont									AT 2
Belarus														
Vysokoe	52.20	23.26	163	7911	9110	8608	9110	8201	9110					BY 4
Belgium														
Offagne	49.53	5.12	420	7808	9112									BE 1
Croatia														
Puntijarka	45.54	15.58	988									9401	9412	HR 2
Zavizan	44.49	14.59	1594									9401	9412	HR 4
Czech Republic														
Svratouch	49.44	16.02	737	8905	cont	8904	cont	8904	cont					CS 1
Kosetice	49.35	15.05	633	8901	cont	9005	cont	9005	cont					CS 3
Denmark														
Tange	56.21	9.36	13	7804	cont			7804	8901	7804	8012			DK 3
Keldsnor	54.44	10.44	9	7804	cont			7804	8901	7804	8012			DK 5
Faroe Isl., Akraberg	61.24	-6.40	90	7811	9103			7811	8912	7811	8012			DK 7
Anholt	56.43	11.31	40	9101	9512									DK 8
Estonia														
Syrve	57.57	22.06	2	7911	8810	8608	8810	8201	8810					EE 2
Lahemaa	59.30	25.54	32	8608	9012	8608	9012	8608	9012					EE 9
				9501	9512									EE 9
Vilsandy	58.23	21.49	6	8903	9010	8903	9010	8903	9010					EE11
Finland														
Aehtari	62.33	24.13	162	7710	cont									FI 4
Koekar	59.55	20.55	10	7710	7909									FI 6
Virolahti	60.31	27.41	8	7710	8812									FI 7
Virolahti II	60.31	27.41	4	8901	cont									FI17
Utoe	59.47	21.23	7	8001	cont									FI 9
Oulanka	66.19	29.24	310	9001	cont									FI22
France														
Vert-le-Petit	48.32	2.22	64	7801	8709									FR 1
La Crouzille	45.50-	1.16	497	7801	8307									FR 3
				8602	cont									FR 3
La Hague	49.37	-1.50	133	7801	cont									FR 5
Valduc	47.35	4.52	470	7801	8408									FR 6
Lodeve	43.42	3.20	252	7802	8402									FR 7
Donon	48.30	7.08	775	9001	cont									FR 8
Revin	49.54	4.38	390	9202	cont									FR 9
Morvan	47.16	4.05	620	9001	cont									FR 10
Bonnevaux	46.49	6.11	836	9001	cont									FR 11
Iraty	43.02	-1.05	1300	9001	cont									FR 12

Table 1.1, cont.

Site name	Lat.	Long.	Elev.	Sulphate µg S/m^3		Nitrate µg N/m^3		Ammonium µg N/m^3		Acidity ne H+/m^3		SPM µg/m^3		EMEP code
				start	end	start	end	start	end	start	end	start	end	
Germany														
Arkona	54.41	13.26	42	8101	9012									DD 1
Westerland	54.55	8.18	12	7801	cont							7710	cont	DE 1
Langenbruegge	52.48	10.45	74	7801	cont							7710	cont	DE 2
Schauinsland	47.55	7.54	1205	7801	cont							7710	cont	DE 3
Deuselbach	49.46	7.03	480	7801	cont							7710	cont	DE 4
Brotjacklriegel	48.49	13.13	1016	7801	cont							7710	cont	DE 5
Neuglobsow	53.09	13.02	62	8101	cont							9301	cont	DE 7
Schmuecke	50.39	10.46	937	9101	cont							9101	cont	DE 8
Zingst	54.26	12.44	1	9301	cont							9301	cont	DE 9
Hohenwestedt	54.06	9.40	75	7801	8609							7710	8609	DE11
Bassum	52.51	8.43	52	7801	9512							7710	9512	DE12
Rodenberg	52.19	9.22	148	7801	9212							7710	9212	DE13
Meinerzhagen	51.07	7.38	510	7801	9512							7710	9512	DE14
Usingen	50.20	8.32	485	7801	9312							7710	9312	DE15
Bad Kreuznach	49.50	7.52	230	7801	9003							7710	9003	DE16
Ansbach	49.18	10.34	481	7801	9512							7710	9512	DE17
Rottenburg	48.29	8.56	427	7801	9512							7710	9512	DE18
Starnberg	48.01	11.21	729	7801	9412							7710	9412	DE19
Hof	50.18	11.53	568	8007	9312							8007	9312	DE20
Greece														
Aliartos (1)	38.22	23.05	110	7802	cont									GR 1
Hungary														
Kecskemet Komlosi	46.58	19.35	125	7710	8103			7710	8103	7710	8103	7710	8103	HU 1
K-puszta	46.58	19.35	125	8104	cont	8603	9612	8104	cont	8104	cont	8104	9512	HU 2
Iceland														
Rjupnahaed	64.05	-21.51	120	7810	7912									IS 1
Irafoss	64.05	-21.01	61	8001	cont									IS 2
Ireland														
Valentia Observatory	51.56	-10.15	9	8008	cont									IE 1
Turlough Hill	53.02	-6.24	420	9104	cont									IE 2
The Burren	53.00	-7.27	90	9701	cont									IE 3
Ridge of Capard	53.07	-9.20	340	9701	cont									IE 4
Italy														
Montelibretti	42.06	12.38	48	8310	cont	8709	cont	8311	cont			8310	8512	IT 1
Stelvio	46.21	10.23	1415	8409	8904			8409	8512			8409	8508	IT 2
Vallombrosa	43.44	11.33	1000	8407	8512			8407	8512			8407	8512	IT 3
Ispra (2)	45.48	8.38	209	8601	cont	8601	cont	8601	cont	8601	cont	8601	cont	IT 4
Arabba	46.31	11.53	2030	8601	9312							8601	9312	IT 5
Latvia														
Rucava	56.13	21.13	18	8609	cont	8609	cont	8609	cont					LV10
Zoseni	57.08	25.55	183	9401	9612	9401	9612	9401	9612					LV16
Lithuania														
Nida	55.21	21.04	17	8005	9012	8608	9012	8608	9012					LT 3
Preila	55.21	21.04	5	9101	9612	9101	cont	9101	cont					LT15
Moldova, Republic of Leovo	46.30	28.16	156	8801	9112	8801	9110	8801	9110					MD12

Table 1.1, cont.

Site name	Lat.	Long.	Elev.	Sulphate µg S/m^3		Nitrate µg N/m^3		Ammonium µg N/m^3		Acidity ne H+/m^3		SPM µg/m^3		EMEP code
				start	end	start	end	start	end	start	end	start	end	
Netherlands														
Witteveen	52.49	6.40	18	7710	9312	8201	9312	9201	9312			8104	9205	NL 2
Rekken	52.06	6.43	25	7710	8305	8201	8309					7710	8309	NL 5
Appelscha	52.57	6.43	10	7710	8103							7710	8103	NL 6
Eibergen	52.05	6.34	20	8310	8708	8310	8708					8310	8706	NL 7
Bilthofen	52.07	5.12	5	8709	9212	8709	9212	9201	9212			8802	9212	NL 8
Kollumerwaard	53.20	6.17	0	9401	cont	9401	cont	9401	cont					NL 9
Vreedepeel	51.32	5.51	28	9301	cont	9301	cont	9301	cont					NL10
Norway														
Birkenes	58.23	8.15	190	7710	cont									NO 1
Skreaadalen	58.49	6.43	475	7710	cont									NO 8
Tustervatn	65.50	13.55	439	7806	cont									NO15
Jergul	69.24	24.36	255	7710	9612									NO30
Hummelfjell	62.27	11.16	1539	7710	8712									NO36
Bear Island	74.31	19.01	20	7710	8812									NO37
Kaarvatn	62.47	8.53	210	7805	cont									NO39
Osen	61.15	11.47	440	8801	cont									NO41
Zeppelin Mountain	78.54	11.53	474	9001	cont									NO42
Karasjok	69.28	25.30	333	9701	cont									NO55
Portugal														
Braganca (1)	41.49	-6.46	691	7908	9512	9501	9512	9501	9512	9501	9512	9501	9512	PT 1
Faro (1)	37.01	-7.58	8	7908	9512							9501	9512	PT 2
V. do Castello (1)	40.25	-7.33	16	8706	9007									PT 3
Monte Velho (1)	38.05	-8.48	43	8801	9512									PT 4
Foia (1)	37.19	-8.54	902	9007	9312									PT 5
Poland														
Suwalki	54.08	22.57	184	7805	9312			7901	9312					PL 1
Jarczew	51.49	21.59	180	8501	cont	9401	cont	8501	cont	9501	9512	9501	9512	PL 2
Sniezka	50.44	15.44	1604	9101	cont	9401	cont	9501	cont	9501	9512	9501	9512	PL 3
Leba	54.45	17.32	2	9301	cont	9401	cont	9301	cont	9501	9512	9501	9512	PL 4
Diabla Gora	54.09	22.04	157	9301	cont	9301	9512	9301	9512					PL 5
Russian Federation														
Janiskoski	68.56	28.51	118	7911	cont	8608	cont	8201	cont					RU 1
Lesogorsky	61.00	28.58	39	7911	8501			8201	8501					RU 8
Pinega	64.70	43.40	28	9101	cont	9101	cont	9101	cont					RU13
Pushkinskie Gory	57.00	28.54	103	9005	9611	9005	9612	9005	9602					RU14
Shepeljovo	59.58	29.07	4	9401	cont	9401	cont	9401	cont					RU16
Slovakia														
Chopok	48.56	19.35	2008	7801	cont	9301	cont							SK 2
Stara Lesna	49.09	20.17	808	9301	cont	9301	cont							SK 4
Liesek	49.22	19.41	892	9301	cont	9301	cont							SK 5
Starina	49.03	22.16	345	9401	cont	9401	cont							SK 6
Slovenia														
Iskrba	45.34	14.52	520	9605	cont									SI 8

Table 1.1, cont.

Site name	**Lat.**	**Long.**	**Elev.**	**Sulphate µg S/m^3**		**Nitrate µg N/m^3**		**Ammonium µg N/m^3**		**Acidity ne H+/m^3**		**SPM µg/m^3**		**EMEP code**
				start	**end**	**start**	**end**	**start**	**end**	**start**	**end**	**start**	**end**	
Spain														
San Pablo	39.33	-4.21	917	8601	cont			8502	cont	8606	cont	8601	cont	ES 1
La Cartuja	37.12	-3.36	720	8701	9512			8701	9512	8701	9512	8701	9512	ES 2
Roqietas	40.49	-0.30	50	8706	cont			8706	cont	8706	cont	8706	cont	ES 3
Logrono	42.27	-2.30	445	8801	cont			8801	cont	8801	cont	8801	cont	ES 4
Noya	42.44	-8.55	685	9301	cont			9301	cont	9301	cont	9301	cont	ES 5
Mahon	39.54	4.15	78	9501	cont			9501	cont	9501	cont	9501	cont	ES 6
Viznar	37.14	-3.32	1265	9501	cont			9501	cont	9501	cont	9501	cont	ES 7
Sweden														
Ekeroed	55.54	13.43	140	8001	8401									SE 1
Roervik	57.25	11.56	10	7711	cont									SE 2
Velen	58.46	14.18	124	7908	9006									SE 3
Bredkaelen	63.51	15.20	404	7908	cont									SE 5
Hoburg	56.55	18.09	58	7809	cont									SE 8
Vavihill	56.01	13.09	172	8409	cont									SE11
Aspvreten	58.48	17.23	20	8405	cont	8601	8612	8405	8612	8601	8612			SE12
Esrange	67.53	21.04	475	9008	cont							9101	9412	SE13
Switzerland														
Jungfraujoch	46.33	7.59	3573	8009	cont							8009	cont	CH 1
Payerne	46.48	6.57	510	7904	cont							7904	cont	CH 2
Taenikon	47.29	8.54	540	9203	9612							9201	cont	CH 3
Chaumont	47.03	6.59	1130	9207	9612							9201	cont	CH 4
Rigi	47.04	8.28	1030	9207	cont							9201	cont	CH 5
Turkey														
Cubuk II	40.30	33.00	1169	9301	cont	9301	cont	9301	cont					TR 1
Ukraine														
Svityaz	51.31	23.53	164	7911	9110	8608	9110	8201	9110					UA 5
Rava-Russkaya	50.15	23.38	249	7911	9110	8608	9110	8201	9110					UA 6
Beregovo	48.15	22.41	112	7911	8909	8608	8909	8201	8909					UA 7
United Kingdom														
Eskdalemuir	55.19	-3.12	243	7712	cont									GB 2
Goonhilly	50.03	-5.11	108	7909	8804									GB 3
Stoke Ferry	52.34	0.30	15	8108	cont									GB 4
Ludlow	52.22	-2.38	190	8105	8703			8307	8703					GB 5
Lough Navar	54.26	-7.54	126	8501	cont			8501	8503					GB 6
Barcombe Mills	50.52	-0.02	8	8504	cont									GB 7
Yarner Wood	50.36	-3.43	119	8701	cont									GB13
High Muffles	54.20	-0.48	267	8701	cont									GB14
Strath Vaich Dam	57.44	-4.46	270	8701	cont									GB15
Glen Dye	56.58	-2.25	85	8701	cont									GB16

(1) Low completeness.

(2) Operated by the European Commission. (Other sites are operated by national institutions). EMEP sites codes are those currently used and they will indicate the present borders. Sites inside former Soviet Union, Yugoslavia, Czechoslovakia and German Democratic Republic all had different site codes in the past. Longer data series than those above will frequently be available. The start point given here is often October 1977 which was the start of EMEP's preparatory phase. One example is the site at Birkenes, Norway which has data series from October 1969. The sampling method used is by filter with various filter types and air volumes. One exception is Montelibretti, Italy where annular denuders are used consistently.