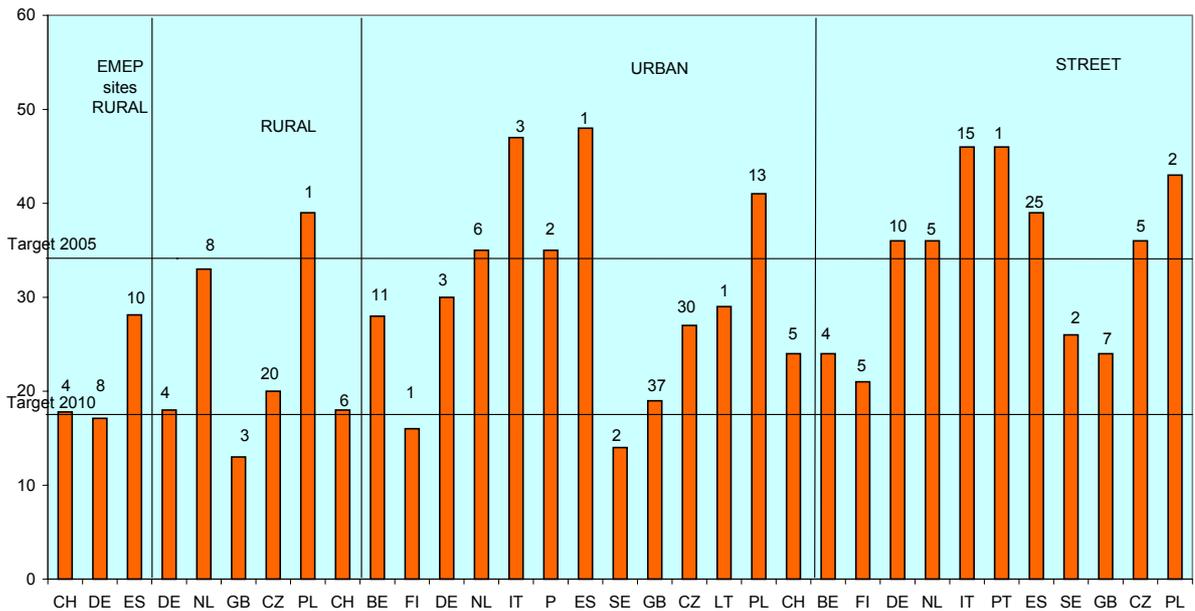


Measurements of Particulate Matter in EMEP

1999 PM10 data
Summary (Annual Average)



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

**Measurements of Particulate Matter
in EMEP**

Edited by Mihalis Lazaridis

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Measurements of Particulate Matter in EMEP

1. Introduction

Airborne particulate matter is the visible element of air pollution with very diverse effects ranging from human health to climate forcing. Fine particles have intrinsically low sedimentation and deposition velocities, and their atmospheric residence time are of the order of days. Particulate pollutants from source regions in Europe and Russia have been observed in the Arctic, at Svalbard, and even in Arctic Canada and Alaska. Furthermore, emissions of particulate matter from other continents reach the European domain. An important example is transport of the Saharan dust from northern Africa to southern parts of Europe.

Recently, concern has been raised with respect to the effect of particulate pollutants on human health, following a number of epidemiological studies in cities with different pollutant levels (Dockery and Pope, 1994; Schwartz, 1994; Lippman and Ito, 1995; Vedal, 1997). These studies show clear correlations between particulate pollutant concentration levels and adverse health effects. Toxicological studies also show an effect to human health from suspended particulate matter but for concentrations much higher than these encountered in air (Schlesinger, 1995).

Long-range transboundary transport is responsible for a significant fraction of the particulate pollution in European cities (WHO/UN, 1999). A major part of this contribution is secondary particulate matter in the form of sulphate, nitrate, ammonium and organic aerosol particles formed by the oxidation of sulphur dioxide, nitrogen oxides and organic gaseous species. It is apparent that particulate matter is not a single pollutant and its mass includes a mixture of many pollutants distributed differently at different sizes. A comprehensive description of the atmospheric particles requires the evaluation of particle number, surface and volume distributions in addition to the mass chemical composition. Size distribution measurements combined with chemical speciation are necessary for identifying also the sources of atmospheric particulate matter.

The concentration levels of sulphate and nitrate aerosol particles are already described in the EMEP programmes directed towards acidification and eutrophication. More work needs to be done, however, with respect to particulate matter emissions, the long range transport of primary particulate matter and the formation of secondary organic particulate matter from natural and anthropogenic emissions. Particulate matter from natural sources also need to be quantified and integrated. This includes sea-salt aerosol and Aeolian dust from Sahara in Southern Europe. Figure 1 shows a satellite image above the Mediterranean area on August 25th 2000 where Saharan dust is transported over large areas of southern Europe. The data are based on the TOMS satellite measurements of aerosol index (see <http://jwocky.gsfc.nasa.gov>). More subtle effects are also due to resuspension of dust in dry areas, particles of biogenic origin and forest fires during the summer period.

The traditional EMEP approach is to find how the air quality and the deposition of pollutants are affected by emissions in the different countries in Europe. This involves emission inventories, emission-based model simulation of atmospheric processes, transport and deposition, and verification and assessment by observations and measurements. This approach will be followed also for the long-range transport of particulate matter, although the elements of this programme are not fully developed yet. In particular, observations and measurements at appropriate located EMEP sites are still to be implemented in many countries. EMEP should give priority to PM₁₀ gravimetric measurements as specified at the EMEP-WMO fine particulate workshop (Hanssen et al., 2000; Lazaridis et al., 2000).

It is apparent that considerable gaps in the scientific knowledge concerning consistent and reliable measurements of physico-chemical properties of atmospheric aerosols still exist. The EMEP programme aims to provide a reliable, quality controlled monitoring information for atmospheric particles in Europe (mapping of their physico-chemical properties at regional level) based on state-of-the-art scientific knowledge.

Chemical speciation is a necessary component of monitoring strategy of particulate matter since this will give information for emission sources and will highlight the chemical components associated with human exposure. Soil dust is emitted from semi-arid rural areas and from motorways and urban areas by wind and mechanical resuspension (Prospero and Nees, 1986). In addition, primary particles are emitted from industrial dust with estimates globally between 100-200 Tg/yr (Wolf and Hidy, 1997). Sea salt is generated by several physical processes, mainly from the sea surface from bursting of air bubbles during whitecap formation (Smith et al., 1993). Carbonaceous aerosols are from many sources but mainly from combustion sources (vehicles, industry, biomass burning) and are also formed secondary from atmospheric oxidation of hydrocarbons (Andreae and Crutzen, 1997; Seinfeld and Pandis, 1998). Sulphates are mainly produced by oxidation of sulphur dioxide emitted from power plants and also from marine biogenic DMS (Lelieveld et al., 1997). Volcanic eruptions are another natural source for sulphate aerosols but with very uncertain temporal and spatial characteristics (IPCC, 1994). Nitrate is produced secondary from oxidation of nitrogen oxides emitted by combustion sources. Ammonia emissions from agriculture are associated with nitrate and sulphate aerosols resulting to their neutralization (Adams et al., 1999).

Dust particles are mainly concentrated in the coarse mode as illustrated in Figure 2, where the size distribution of particles from different sources is presented. Combustion sources emit predominantly fine particles that are concentrated in sizes below 2.5 micrometers. The importance of particle size distribution data for a comprehensive evaluation of their sources is evident. In addition, there exist other properties of aerosols that are also interesting to be monitored connected with their number size distribution and surface area. These properties are related closely with climate and visibility research.

Light scattering is one of two attenuating effects of aerosols on solar radiation (the other being absorption) and can be quantified directly by means of scattering

coefficients. Absorption is the other main radiative property of aerosols, and is strongly related to the aerosol Black Carbon (BC) content. In fact, BC is considered to be almost exclusively responsible for all light absorption by aerosols (Horvath, 1993), although absorption by large dust particles (diameter up to $\sim 16 \mu\text{m}$) is also significant. Figure 3 shows the number concentration and extinction coefficient (scattering and absorption) that is correlated to visibility (Kneizys et al., 1990) from research measurements performed in July 2000 on the island of Crete, Greece (Colbeck et al., 2001).



Figure 1: TOMS satellite measurements of aerosol index above the Mediterranean area on August 25th 2000.

Measurements were conducted in the $0.1 \mu\text{m}$ – $3 \mu\text{m}$ range using a multiwave nephelometer (TSI 3563) and a laser aerosol spectrometer (LASX, Particle Measuring Systems). Highest concentrations of up to $9500 \text{ particles cm}^{-3}$ were recorded at the $0.1 \mu\text{m}$ level, although concentrations of 1500 – $4000 \text{ particles cm}^{-1}$ were more typical for land based data. There was a strong diurnal variation evident at the $0.1 \mu\text{m}$ and $0.15 \mu\text{m}$ levels with peak concentrations occurring at about 15:00 and minimum concentrations at about 06:00. The same variation occurs to a lesser degree for the coarser size fractions. It is theorised that this variation resulted from a combination of solar influenced convective conditions and photochemical aerosol production.

In the study of the long-range transport of particulate matter there is a critical need to study the vertical exchange processes involved and the vertical profile of aerosol species. This information will further elucidate the advection and transport of atmospheric aerosols at long distances due to turbulence and prevailing meteorological patterns. It is also very important the understanding of the

different aerosol characteristics at different altitudes and their spatial and temporal characteristics.

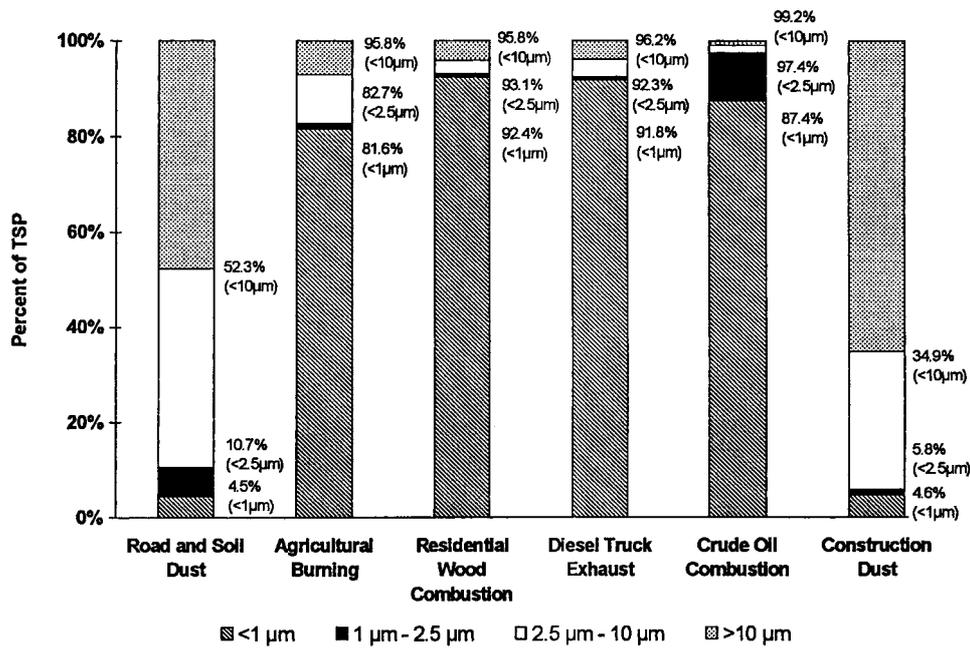


Figure 2: Size distribution of specific particulate matter emissions. (Adapted from Chow and Watson, 1998. Data from Ahuja et al., 1989; Houck et al., 1989.)

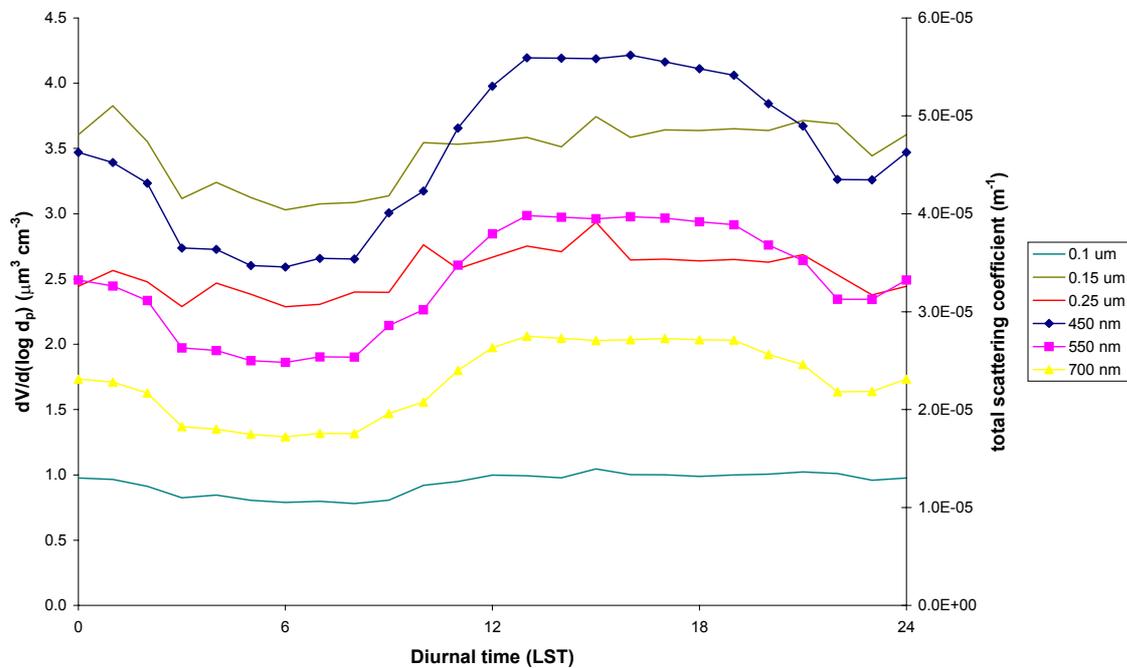


Figure 3: Nephelometer and LASX measurements during July 2000 at the Finokalia station, Greece.

The complex vertical structure of the planetary boundary layer above the North Adriatic is shown in Figure 4. The pictures are obtained from an experimental campaign in the northern part of the Adriatic Sea onboard the DLR CMET research aircraft (Eleftheriadis et al., 2000). Heavy aerosol load dominates the area up to an altitude of 4 Km. The marine boundary layer (MBL) is clearly recognized as a dense aerosol layer at 250 m above the sea surface. A second aerosol layer is observed up to a height of 2 Km. From the synoptic data it is deduced that this is advected from the Italian mainland. It is therefore critical for understanding the aerosol physico-chemical characteristics to consider the variation of aerosol composition and size distribution with altitude and its effect on the transport of pollutants in Europe. The three wavelength lidar was operated in downward-looking mode. It makes use of a flashlamp-pumped Nd:YAG laser with a fundamental wavelength of 1064 nm. Frequency doubling and tripling provides simultaneous output at 532 nm and 355 nm. The depolarisation (see Figure 4) contains information about the asphericity of the back-scattering particles which allows to characterise different aerosol or cloud particle types. The ratio of the orthogonal and parallel (to the incident beam) polarised 532 nm signals $\beta_{\perp} / \beta_{\parallel}$ i.e. the depolarisation of the light by the scattering particles contains information about their sphericity. Clouds with *only* spherical (liquid) particles may cause volume depolarisation below 1.4% since they increase only the intensity in the parallel channel.

The boundary layer (BL) appears to extend up to 1700 - 2100 m above surface level which is corroborated by lidar pictures (Eleftheriadis et al., 2000). These indicate a marine boundary layer (MBL) extending up to 200 - 400 m, overlain with an advected convective boundary layer (CBL) reaching to the BL top.

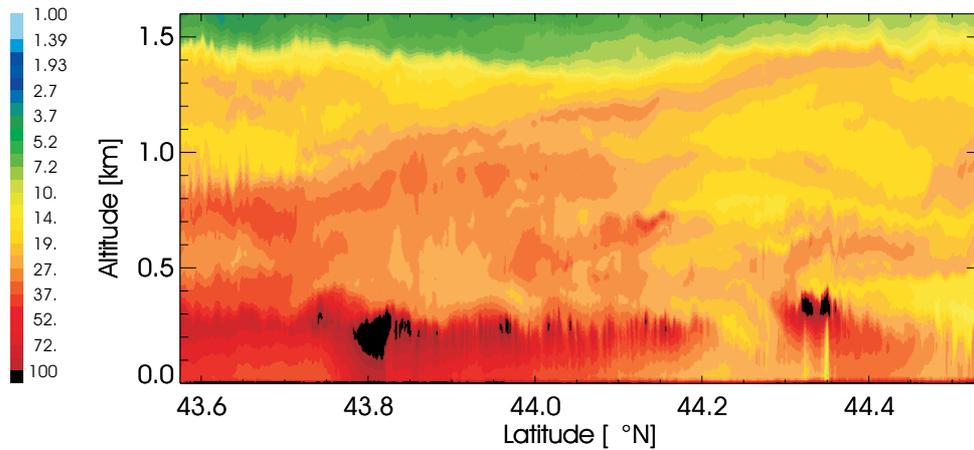
Another interesting aspect of the vertical profile characteristics is the variation in composition with altitude (see e.g. Eleftheriadis et al., 2000; Nyeki et al., 2000). Vertical profiles of aerosol physico-chemical characteristics is a valuable input to the EMEP monitoring measurements since it will provide a more integrated picture of the vertical and spatial dynamics of particulate matter in the European frame.

In the current report we focused mainly on recent PM₁₀ measurement data from the EMEP framework, chemical analysis data concerning total sulphate and nitrate, measurements from urban sites in Europe and ongoing research and monitoring measurement programs in Switzerland, Norway and Greece. In addition, particulate matter data from countries outside Europe are presented for giving an overview of their distribution at global level at both rural and urban sites. The current available data on particulate matter concentrations and their associated chemical composition at European level, appears to substantiate their spatial-temporal variability and starts to highlight their main emission sources. A challenging task remains to construct a comprehensive picture of the particulate matter physico-chemical characteristics in Europe over a substantial number of years and associate it with emission data. An additional task remains to assess the specific contribution and individual sources from the European Countries and their importance on the long range component of atmospheric aerosols. These tasks can only be achieved under the framework of a harmonised measurement programme with detailed chemical analysis, with modelling of the atmospheric dispersion.

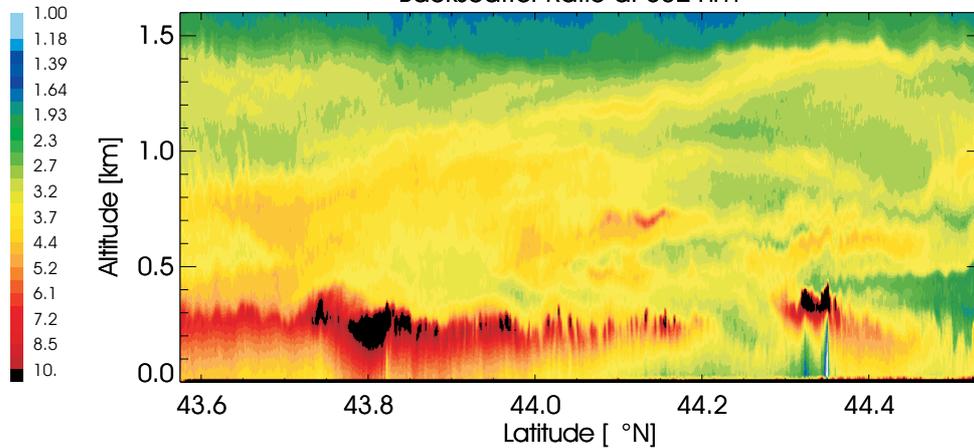


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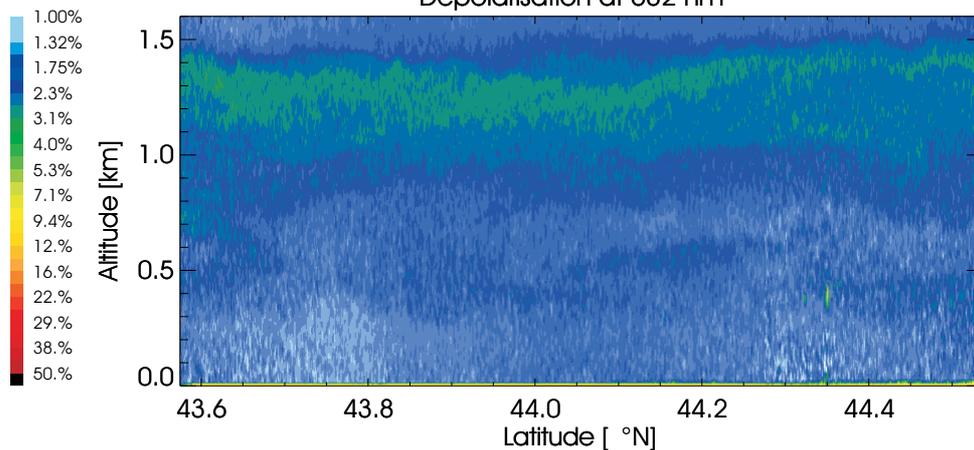
Backscatter Ratio at 1064 nm



Backscatter Ratio at 532 nm



Depolarisation at 532 nm



Time [UTC]

12:35:00

12:30:00

12:25:00

12:20:00

Figure 4: MBL structure and overlying layer in the North Adriatic at midday 24/09/99.

2. Overview on particulate matter measurements in Europe

2.1 Measurement Methods

According to the EU Directive 1999/30/EC, the first Daughter Directive of the Air Quality Framework Directive 1996/62/EC, the Member States (incl. Norway and other EEA-Member-States) have to start monitoring, among other pollutants, ambient air PM_{10} . The Directive requires that the measurements have to be performed according to the CEN standard EN12341, which means by use of one of the 3 reference methods described in the standard or with a method shown to be equivalent to one of the reference methods, or display a consistent relationship to one of the references (CEN, 1998). The EMEP monitoring programme has started to prepare its measurement requirements for mass and chemical analysis of aerosol filters (EMEP, 2000). A comprehensive monitoring programme for atmospheric particulate matter in EMEP is foreseen in the near future. In the United States there is currently a lot of work under progress for the evaluation and field performance of $PM_{2.5}$ samples (Peters et al., 2001; Noble et al., 2001). In Europe similar work is under progress.

Many national intercomparison studies have been arranged (EC Working Group on Particulate Matter, 2001) and further studies are in progress in Europe. As an example a study going on in Norway is described below. In urban air monitoring programmes in Norway, different methods have been used for PM_{10} (and $PM_{2.5}$) during several years. In recent years the use of the Tapered Element Oscillating Micro-balance (TEOM)-monitor from R&P have been widespread due to its continuous output. In order to test if the TEOM-monitor and other monitors and sampling methods meet the equivalence criteria given in the Standard under Norwegian conditions, a programme sponsored by the Nordic Council of Ministers (NMR) and some of the instrument manufacturers was set up.

According to the CEN standard, measurements will be performed in different typical areas and seasons. In Norway PM_{10} intercomparison is under progress. The sampling sites are a road station in Oslo, a city background station in Oslo, an area with wood burning (Elverum) and possibly a rural station (e.g. Birkenes). Sampling will be performed both during winter and spring/summer.

The sampling in the first phase was performed at the Oslo Road site situated a few meters from a heavily trafficked road leading out from Oslo Centre to the North. Samples were taken with the different filter samplers 4 days each week from 16 January to 7 March 2001, while the monitors were run continuously during the same period. Normally 23-hour samples were taken from 1300h to 1200h the next day (see Table 1). The samplers and monitors included are shown in Table 1.

Since no official report to the sponsors has been issued, only results from instruments owned by NILU in addition to samplers from Swedish Environmental Research Institute (IVL) are shown.

Table 1: *Samples and monitors used in the intercomparison PM₁₀ measurements in Oslo, Norway during winter 2001.*

Samplers	Filter type	Flow rate m ³ /24h
KleinfILTERgerät (Reference 1)	Quartz fibre Whatman QM-A 47 mm	55
PM10 High-vol. Andersen (Reference 2)	Quartz fibre Whatman QM-A 8x10 inches	1630
PM10 IVL 1	Teflon-covered glass fibre Pall Fiberfilm 47 mm	25.6
PM10 IVL 2	Teflon-covered glass fibre Pall Fiberfilm 47 mm	25.6
PM10 Partisol (R&P) (Sequential)	Teflon Pall Gelman Zefluor 47 mm	24
PM10 Gent 1	Teflon Pall Gelman Zefluor 47 mm	21.6
PM10 Gent 2	Teflon Pall Gelman Zefluor 47 mm	21.6
PM10 NILU 1	Teflon Pall Gelman Zefluor 47 mm	14.4
PM10 NILU 2	Teflon Pall Gelman Zefluor 47 mm	14.4
TSP High vol. (Andersen)	Quartz fibre Whatman QM-A 8x10 inches	1630
Monitor	Principle	
TEOM 1	Tapered element oscillating monitor with Nafion dryer 30°C	
TEOM 2	Tapered element oscillating monitor with Nafion dryer 30°C	
TEOM 3	Standard Tapered element oscillating monitor 50°C	
Eberline 1	β absorption	
Eberline 2	β absorption	
Grimm 1	Laser light scattering	
Grimm 2	Laser light scattering	

A NILU-filter pack sampler as used at the Norwegian EMEP sites is also included. This sampler is added for the determination of most of the main inorganic part of the gases and aerosols in the air. The main advantage of this sampler is its possibility to measure the sum of particulate and gaseous forms of nitrate and ammonium, in order to have an idea of the amount of semivolatile inorganic compounds, which may cause sampling artefacts in the different monitors and samplers. In addition to the particulate air samplers, an automatic weather station was used to collect different meteorological parameters.

The two reference samplers used are the KleinfILTERgerät with PM₁₀ intake (described in EN 12341) from Ing. Büro Norbert Derenda, and the Thermo Andersen GMW PM10 High Volume Air Sampler. These samplers are constructed according to EN 12341.

The two PM₁₀ NILU samplers use a NILU PM₁₀ pre-impactor designed by Risto Hillamo, Finnish Meteorological Institute. The air intake consists of an aluminum tube. In the end of the tube there are two plates, one with 5 circular holes around the periphery followed by one at a distance of 10 mm with a circular hole in the center. The surface of the outer part of the last plate is made sticky with a thin layer of grease. Air is drawn upwards into the tube, through the five holes and then through the central hole before entering the NILU filter holder on which the pre-impactor is fastened. Aerosol particles larger than 10 µm EQD are fastened on the sticky surface behind the peripheral holes while smaller aerosol particles follow the air-stream into the filter holder. The upper plate can be removed from

the tube with a special tool to be cleaned and re-greased to avoid a build-up of particles. The filter holder used is an open face one-stage NILU filter holder.

The two PM₁₀ Gent samplers consist of the Gent Stacked Filter Unit (SFU) described by Hopke et al. (1997). This has a PM₁₀ pre-impactor, also designed by Risto Hillamo, Finnish Meteorological Institute. The filter holder used in the sampler is a NILU two-stage open face filterholder where only the first filter stage is used. The second stage is filled with a dummy filter. The flow rate is maintained constant at 15 l/min. by a needle valve. A gas meter in the end of the sampling line measures the sample volume.

The two PM₁₀ IVL samplers had a flow rate constant at about 17 l/min that is maintained by a capillary kept at ambient temperature.

In Table 2 some results of the first phase of the intercomparison is shown by mean values, regression equations and regression coefficients together with the number of days with measured concentrations higher than 50 µg/m³. TSP-values during the measurement period varied from 32.9 to 195.9 µg/m³, with a mean value of 86.3 and 82.3 µg/m³ for the 25 and 30 days with parallel sampling shown in Table 2. This means that the PM₁₀ intakes for the different samplers really had a challenge. The results shows that all of the non-commercial samplers tested in this first phase of the intercomparison meet the criteria for giving equivalent data according to EN 12341, although the number of days exceeding the EU limit value are always smaller than for the reference samplers.

Table 2: Instrument intercomparison among the various instruments used at the Oslo road station.

Candidate	Reference	Mean Candidate µg/m ³	Mean Reference µg/m ³	Regression Equation Cand.=b*Ref. + a	r ² value and sample size	No. of Exceedances (50 µg/m ³) Cand.	No. of Exceedances (50 µg/m ³) Ref.
NILU A	Klein	38.5	40.8	y=1.03x + 3.52	0.95 (n= 25)	4	6
NILU B	Klein	38.8	40.8	y=0.98x - 0.98	0.93 (n= 25)	4	6
NILU mean	Klein	38.7	40.8	y=1.00x - 2.25	0.96 (n= 25)	4	6
Gent A	Klein	40.1	40.8	y=1.08x - 3.79	0.95 (n= 25)	5	6
Gent B	Klein	40.4	40.8	y=1.03x - 1.45	0.92 (n= 25)	5	6
Gent mean	Klein	40.2	40.8	y=1.05x - 2.62	0.96 (n= 25)	5	6
IVL A	Klein	39.1	40.8	y=1.08x - 3.79	0.95 (n= 31)	5	7
IVL B	Klein	39.4	40.8	y=1.03x - 1.45	0.92 (n= 31)	5	7
IVL mean	Klein	39.2	40.8	y=1.05x - 2.62	0.96 (n= 31)	5	7
NILU A	Hi-vol PM10	38.5	41.1	y=1.02x + 3.50	0.94 (n= 25)	4	7
NILU B	Hi-vol PM10	38.8	41.1	y=0.98x - 1.39	0.94 (n= 25)	4	7
NILU mean	Hi-vol PM10	38.7	41.1	y=1.00x - 2.45	0.95 (n= 25)	4	7
Gent A	Hi-vol PM10	40.1	41.1	y=1.08x - 4.30	0.95 (n= 25)	5	7
Gent B	Hi-vol PM10	40.4	41.1	y=1.04x - 2.16	0.94 (n= 25)	5	7
Gent mean	Hi-vol PM10	40.2	41.1	y=1.06x - 3.23	0.95 (n= 25)	5	7
IVL A	Hi-vol PM10	39.1	39.7	y=1.02x - 2.88	0.98 (n= 30)	4	7
IVL B	Hi-vol PM10	39.4	39.7	y=1.04x - 3.14	0.98 (n= 30)	4	7
IVL mean	Hi-vol PM10	39.2	39.7	y=1.03x - 3.01	0.98 (n= 30)	4	7

In Figure 5 and Figure 6 measurements between the two NILU filter packs and also between the NILU filter pack and the PM₁₀ IVL sampler is presented. The agreement between the two similar samplers and between the NILU and IVL samplers is quite acceptable.

Harmonization of measurements is needed. The measurements of PM₁₀ at urban concentration level appear to be straightforward and reproducible. However, this may not be the case at rural concentration levels with concentrations lower than 10 µg/m³. Therefore field intercomparison studies for PM₁₀ and PM_{2.5} instruments at different geographical locations and seasons in Europe is a necessary component for the performance of harmonized measurements and for understanding the instrument limitations.

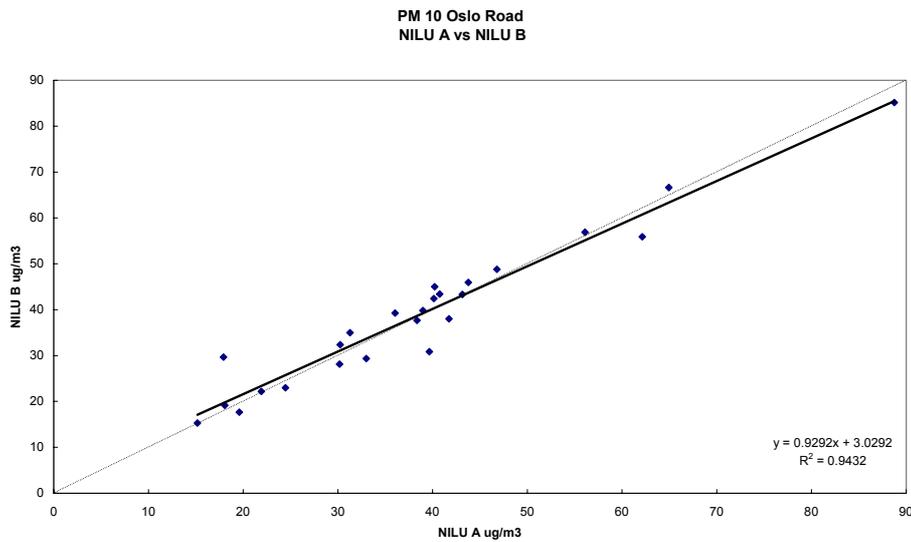


Figure 5: Comparison between the two NILU filter packs in the winter 2001 intercomparison PM₁₀ campaign.

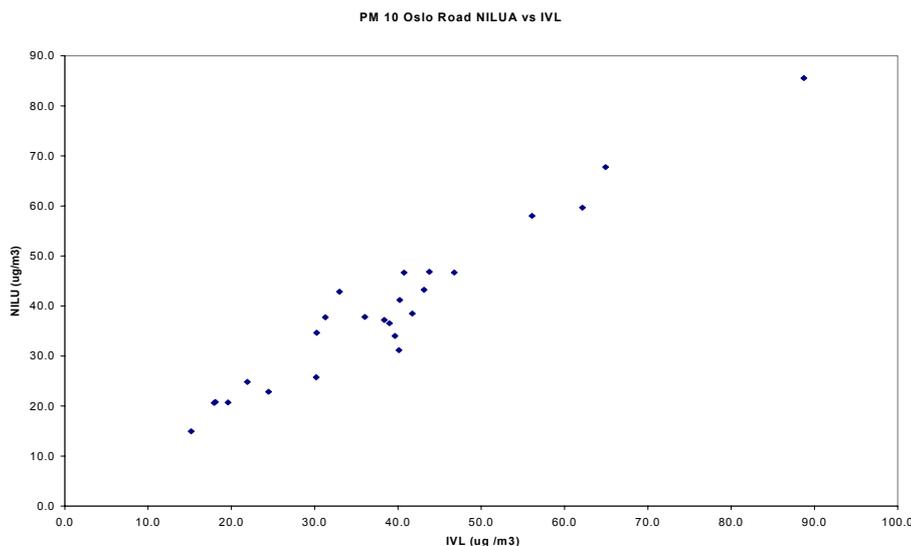


Figure 6: Comparison between the NILU filter pack and the IVL sampler in the winter 2001 intercomparison PM₁₀ campaign.

2.2 Particulate measurements inside the EMEP framework

Switzerland, Germany, Spain and Italy performed particulate matter measurements during the 1999 using gravimetric measurement methods. Italy reports TSP data from only one station located at Ispra. Spain started at 1999 to report PM₁₀ data from 10 stations across the Country. In addition, Germany (8 stations) and Switzerland (5 stations) continued to report PM₁₀ data following gravimetric methods.

Annual average concentrations from the EMEP stations for the 1998 and 1999 are presented in Figure 7 and Figure 8, respectively. The annual average concentrations for both 1998 and 1999 are similar. Annual averages for the period 1997-1999 in the EMEP stations are shown in Appendix 1. Concentrations in Germany for 1999 show an annual average of 19.5 µg/m³ similar to Switzerland (20.5 µg/m³). The station of Jungfraujoch at height of 3500 m has an annual average of 3.7 µg/m³ for 1999 since it is located usually above the boundary layer height with episodic higher concentrations when the boundary layer moves above the station. Time series of the particulate matter measurements in the EMEP stations are presented in Appendix 2.

In Switzerland, PM concentrations in 1999 are higher during winter than other seasons in agreement with observations from previous years. In Spain, higher PM concentrations are observed in summer, but as in previous years, there is no consistent seasonal variability. There is also no consistent seasonal variability in Germany but a number of stations exhibit higher concentrations during the winter.

As a conclusion of the particulate matter measurements inside the EMEP programme it is evident that the measurement network have been improved and the number of sites with available data increased. However, there is still not a harmonized network which provides an overview of PM₁₀ levels across Europe, similar to the EMEP network for sulphate and sulphur dioxide.

Daily measurements of particulate matter sulphate and total nitrate are performed within the EMEP framework. Figure 9 and Figure 10 show annual average concentrations for sulphate and nitrate (elemental S and elemental N) at the monitoring stations for 1999. Sulphate is determined at the majority of EMEP sites. Sulphate concentrations were higher in central and Southern Europe with annual average values close to 1 µg/m³ (as sulphur) whereas in northern Europe and Scandinavia annual average values close to 0.4 µg/m³ were observed.

Nitrate is measured as total nitrate. The measurement of nitrate and nitric acid with filter packs together with ammonia and ammonium gives biased results for the different species due to chemical reactions and volatilisation from the filters. Therefore the sums (HNO₃+NO₃) and (NH₃+NH₄) are often reported. In this aspect a number of sites in Hungary, the Netherlands and Italy have started to use denuders to separate particle and gaseous components. Total nitrate annual average concentrations close to 0.4 µg/m³ (as nitrogen) were measured in Scandinavia, U.K. and parts of Spain whereas in northern Germany and Denmark annual concentrations close to 1 µg/m³ were measured.

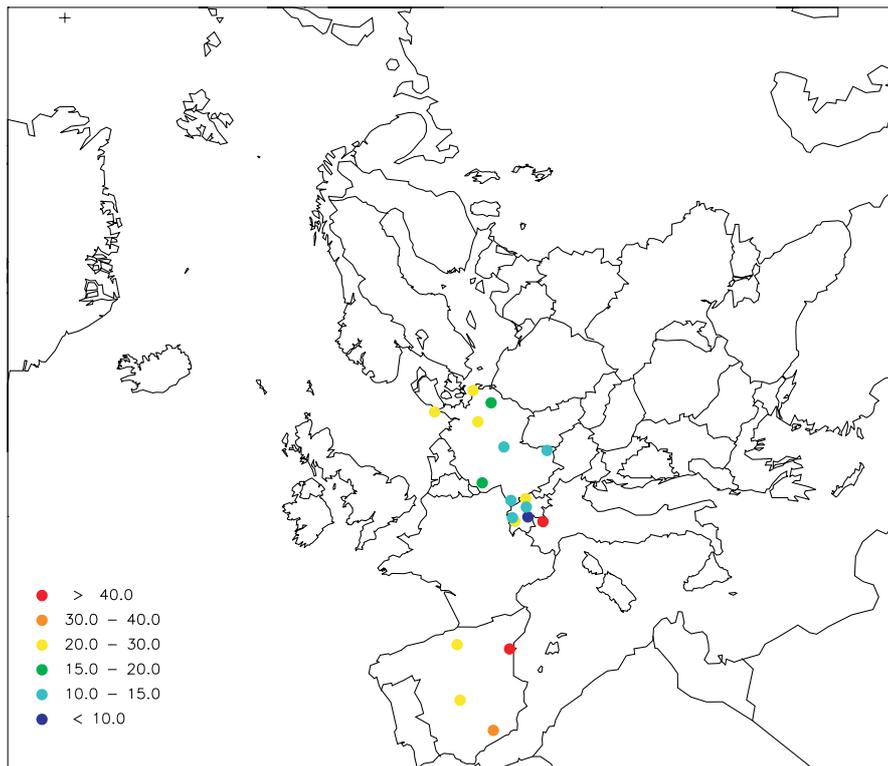


Figure 7: Annual average PM_{10} concentrations ($\mu\text{g}/\text{m}^3$) from the EMEP monitoring framework for 1998.

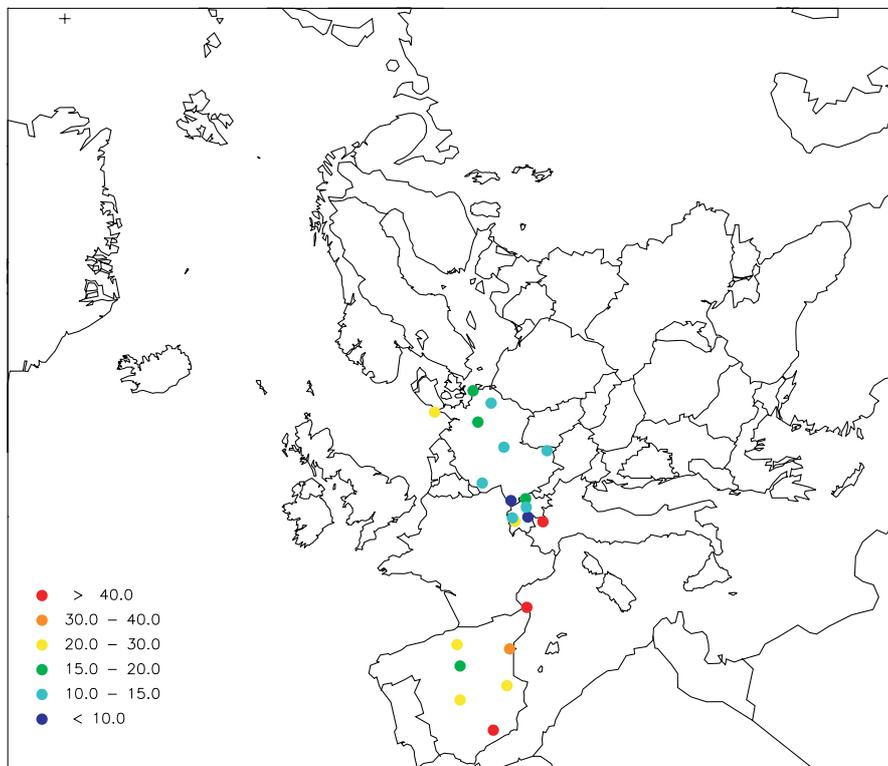


Figure 8: Annual average PM_{10} concentrations ($\mu\text{g}/\text{m}^3$) from the EMEP monitoring framework for 1999.

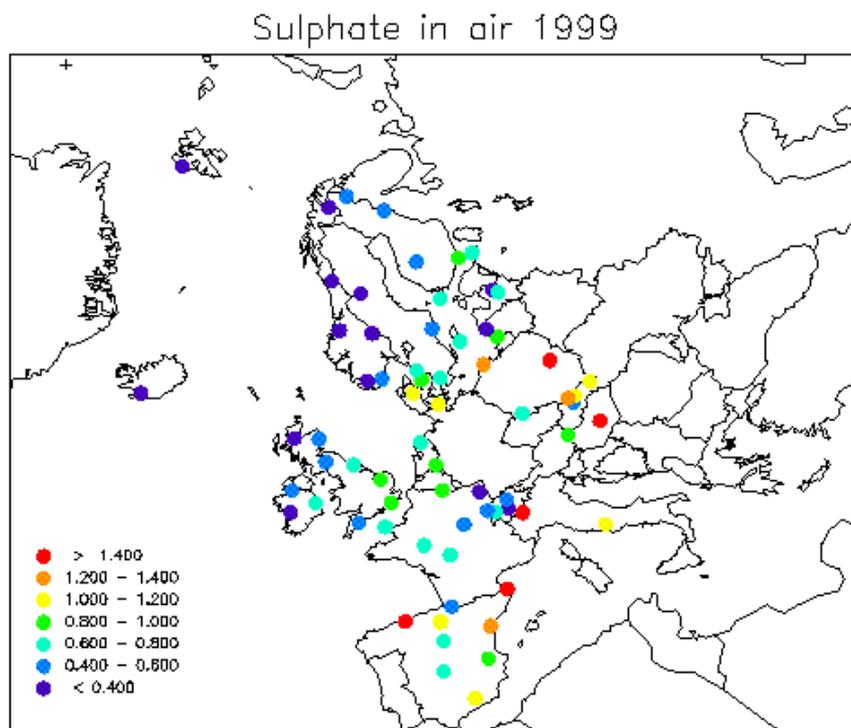


Figure 9: Annual average sulphate concentrations ($\mu\text{g S}/\text{m}^3$) from the EMEP framework for 1999.

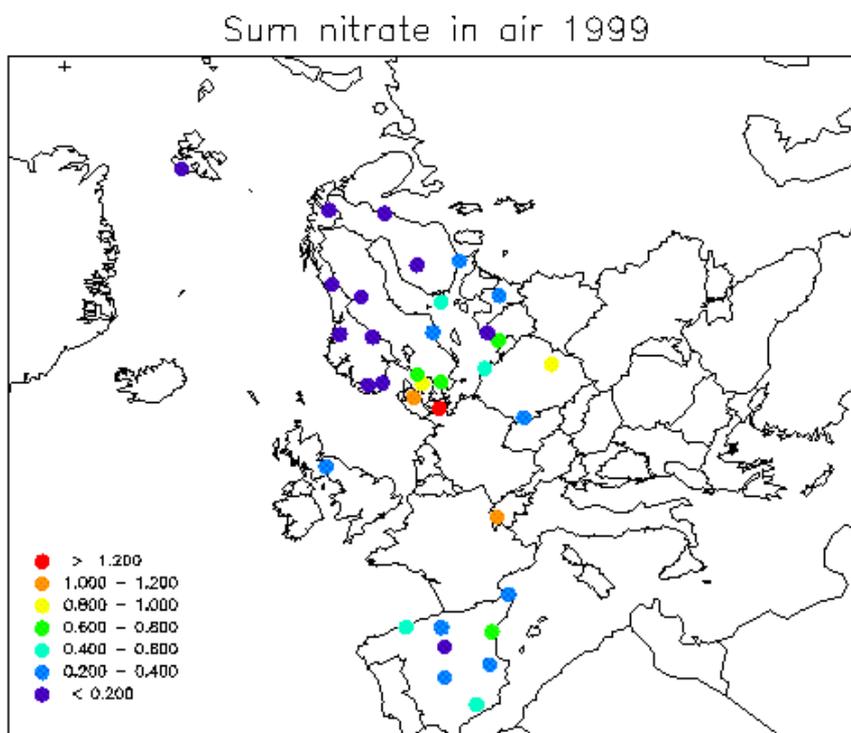


Figure 10: Annual average total nitrate concentrations ($\mu\text{g N}/\text{m}^3$) from the EMEP framework for 1999.

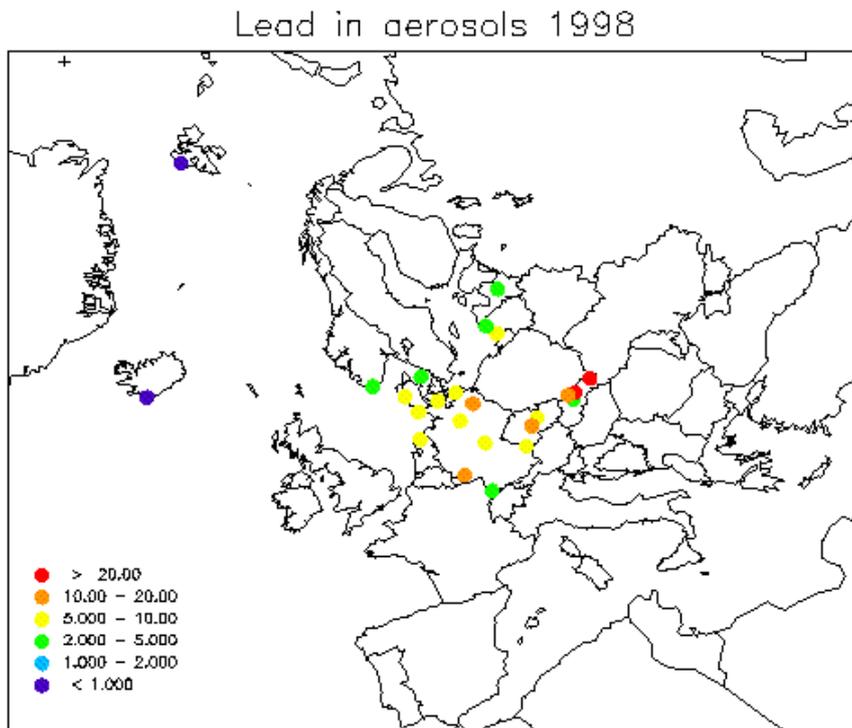


Figure 11: Annual average concentrations (ng/m^3) for lead in aerosols (1998).

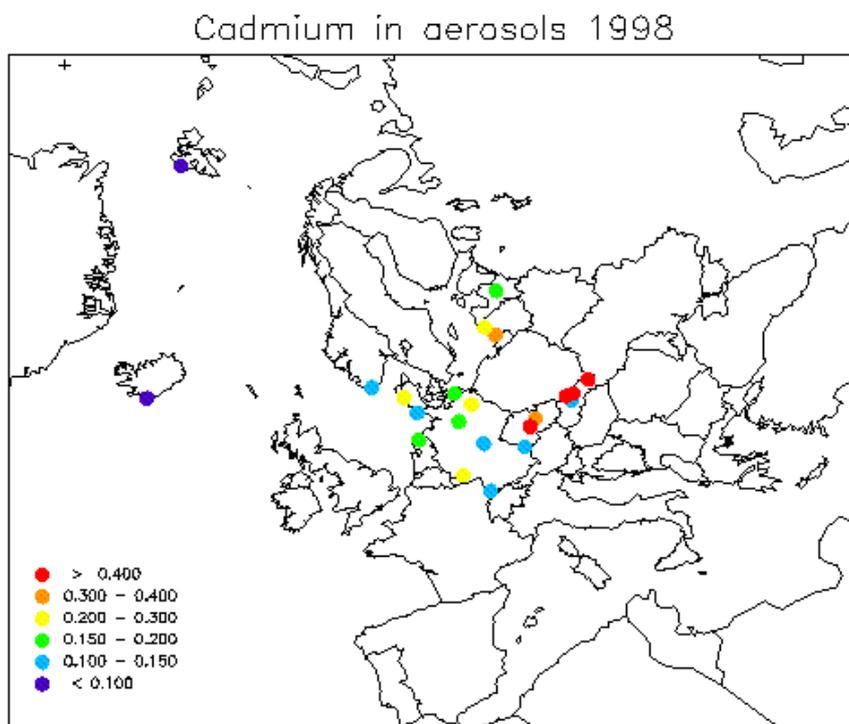


Figure 12: Annual average concentrations (ng/m^3) for cadmium in aerosols (1998).

In addition to sulphate and nitrate measurements heavy metals in aerosols are also determined in the EMEP programme. Annual average concentrations of lead and cadmium for 1998 in aerosols are shown in Figure 11 and Figure 12. The lowest concentrations of lead (below 1 ng Pb/m³) have been observed at Svalbard and Iceland. Maximum concentrations have been measured at the Slovak stations with annual means close to 20 ng Pb/m³. Cadmium shows a similar trend with higher concentrations at Slovak sites. A detailed description of heavy metal concentrations in Europe has recently been presented by EMEP (Berg et al., 2000).

2.3 Particulate measurements from European research and monitoring programmes

In this chapter particulate matter air quality data from 1998 and 1999 both from rural and urban sites are presented. The data have been obtained from EMEP measurement sites, from European countries that transmit their data in the framework of the “Exchange of Information” Decision (97/101/EC) and from research programmes. Data from 1997 from both EMEP and ETC/ACC have already been reported (Lazaridis et al., 2000) and data for the years 1998 and 1999 are presented here.

Figure 13 and Figure 14 show the measured levels of PM_{10} at rural, urban and roadside sites for 1998 and 1999 respectively. Data outside the EMEP framework were obtained from the European Topic Centre under contract from the European Environmental Agency (EEA).

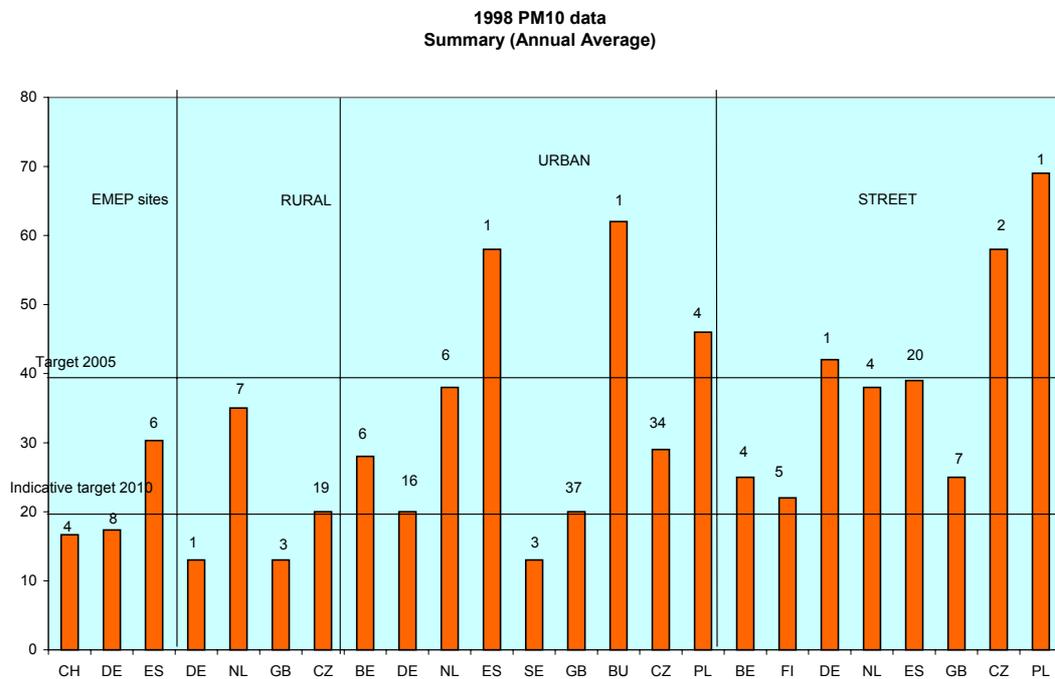


Figure 13: Annual average PM_{10} concentrations in different European countries for various site types (units: $\mu g/m^3$) during 1998.

It is evident that different measurement methods have been used to quantify aerosol levels in different European Countries and at different locations. Therefore, a comparison of data is not straightforward and only qualitative results can be obtained from this figure. In addition, for some countries the number of urban and street sites is very limited.

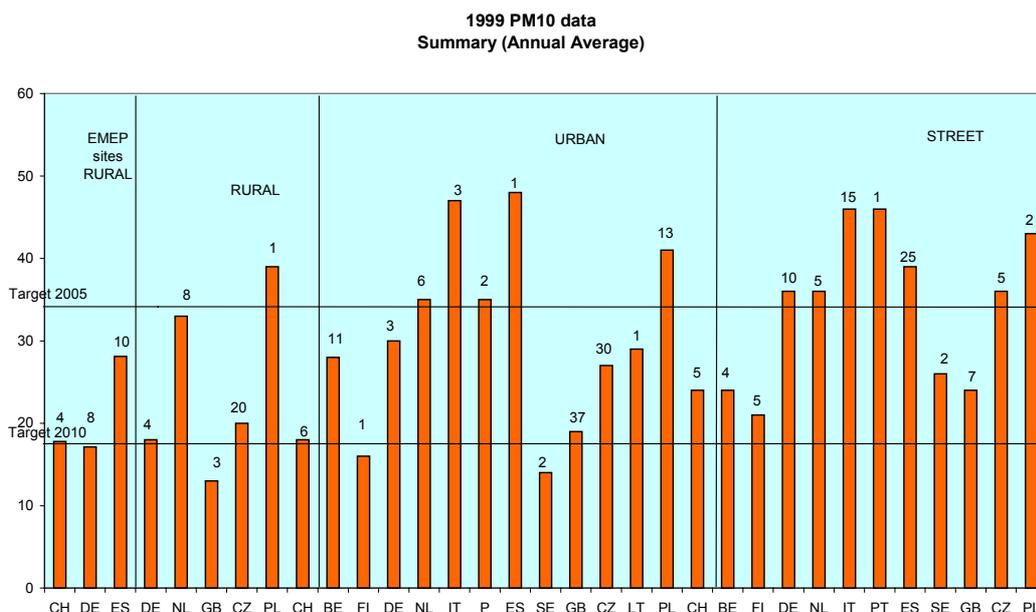


Figure 14: Annual average PM₁₀ concentrations in different European countries for various site types (units: µg/m³) during 1999.

Figure 15 illustrates the geographical distribution of measured particulate mass concentrations for 1998 from the ETC/ACC database system AIRBASE. Although measurements are not comparable between countries (see also Lazaridis et al., 2000) there are some interesting patterns with relatively high concentrations in the most populated areas of Europe in agreement with the data from 1997. Concentrations in Scandinavia and northern Europe are lower but it is interesting to point out the higher TSP concentrations in southern countries such as Italy and Spain. It is expected that resuspended dust contribute part of the TSP mass in these cases due to dry conditions.

A more detailed picture of the annual average concentration for PM₁₀ measurements in Europe from ETC/ACC¹ is shown in Figure 16 – Figure 19. Figure 16 and Figure 17 present PM₁₀ concentration from rural stations in Europe for 1998 and 1999 respectively whereas Figure 18 and Figure 19 show the PM₁₀ concentrations for urban sites.

¹ Figures 17-19 were produced by Jaroslav Fiala and Hana Livorova (Czech Hydrometeorological Office) from data obtained by the ETC/ACC (European Environmental Agency).

Particulate matter

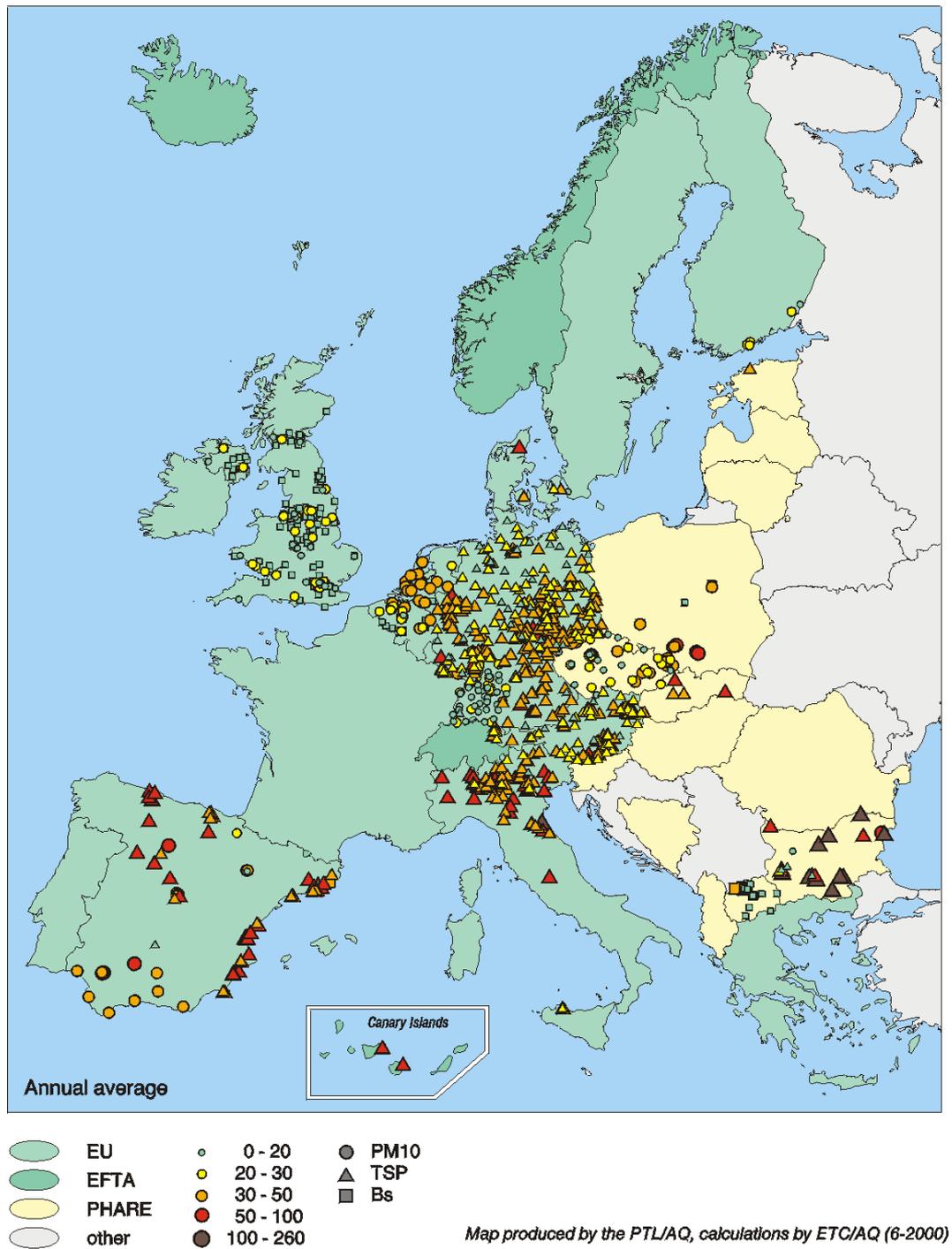


Figure 15: Particulate matter annual average of 24-hour concentrations ($\mu\text{g}/\text{m}^3$), 1998.

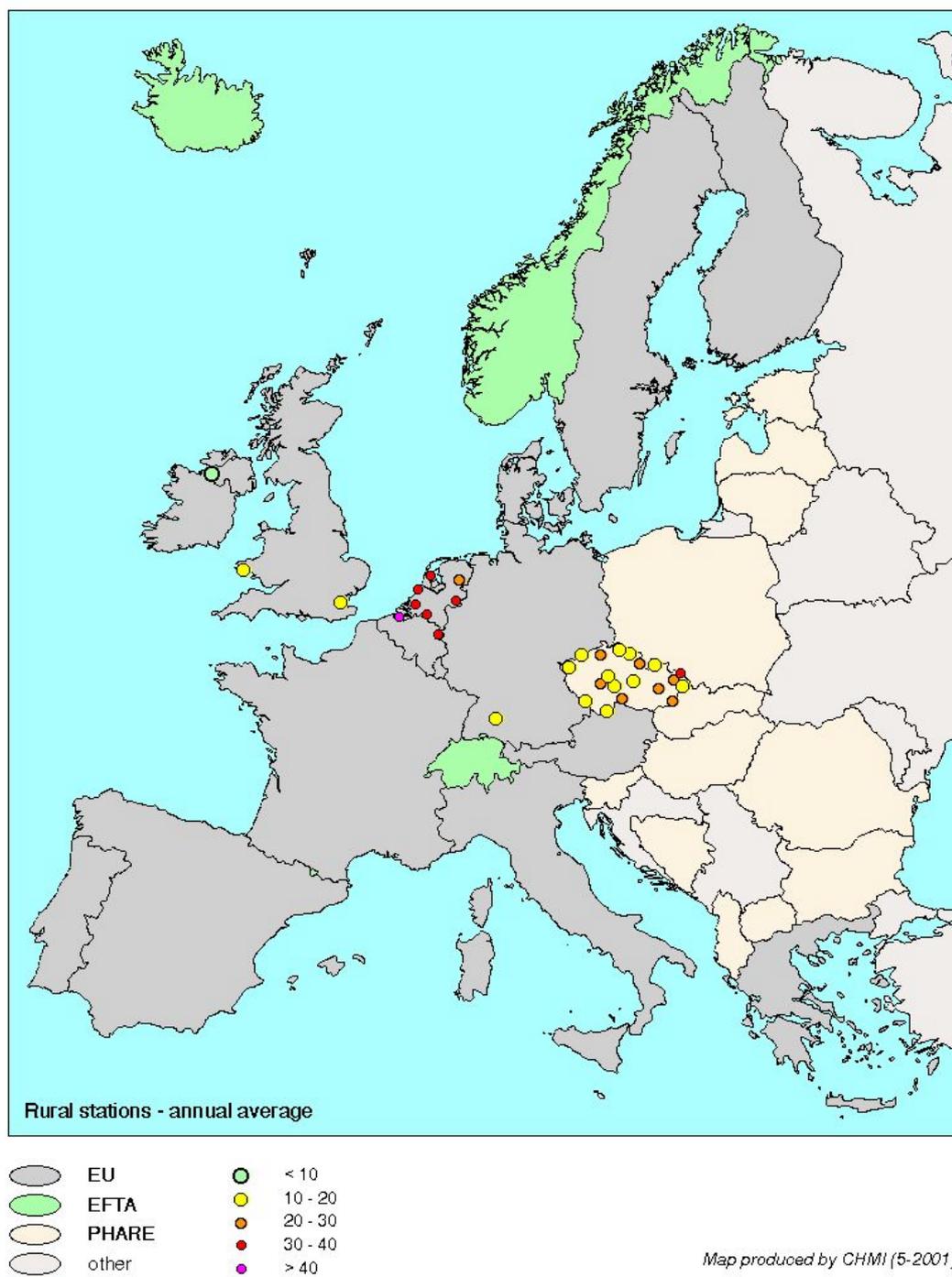
PM₁₀ - 1998

Figure 16: Particulate matter (PM₁₀) annual average (1998) of 24-hour concentrations from rural stations under the AIRBASE framework ($\mu\text{g}/\text{m}^3$).

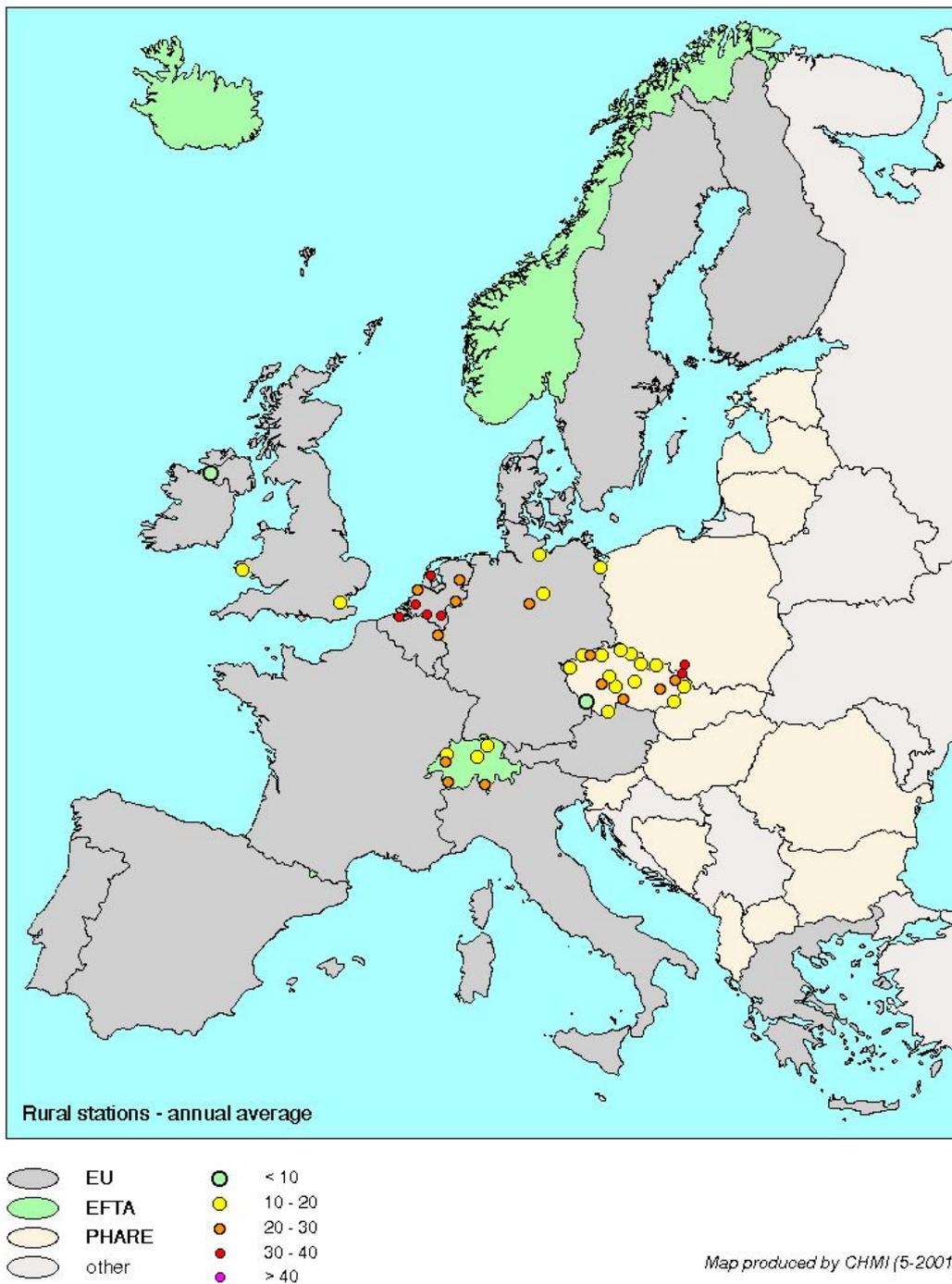
PM₁₀ - 1999

Figure 17: Particulate matter (PM₁₀) annual average (1999) of 24-hour concentrations from rural stations under the AIRBASE framework ($\mu\text{g}/\text{m}^3$).

PM₁₀ - 1998

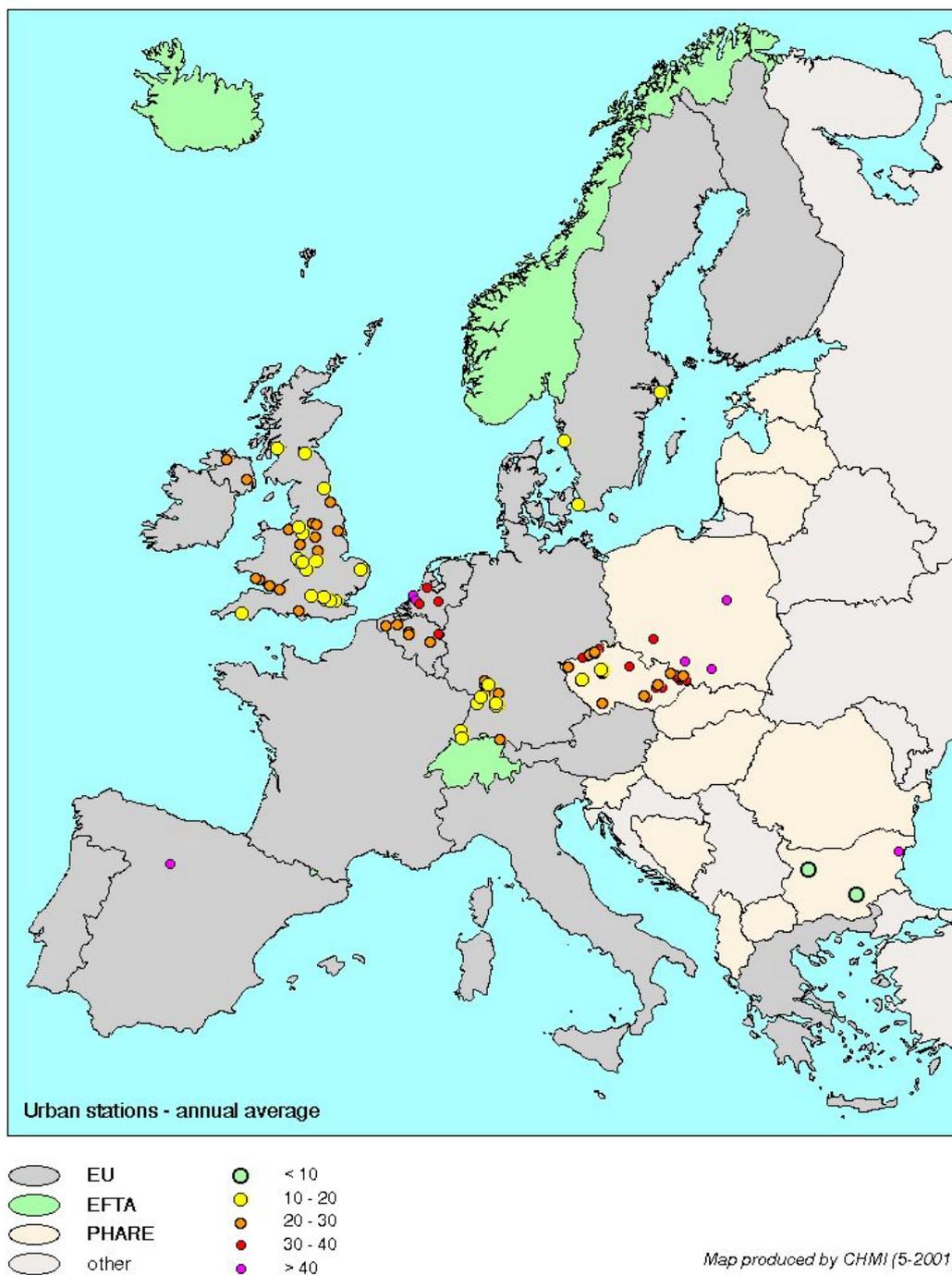


Figure 18: Particulate matter (PM₁₀) annual average (1998) of 24-hour concentrations from urban stations under the AIRBASE framework ($\mu\text{g}/\text{m}^3$).

PM₁₀ - 1999

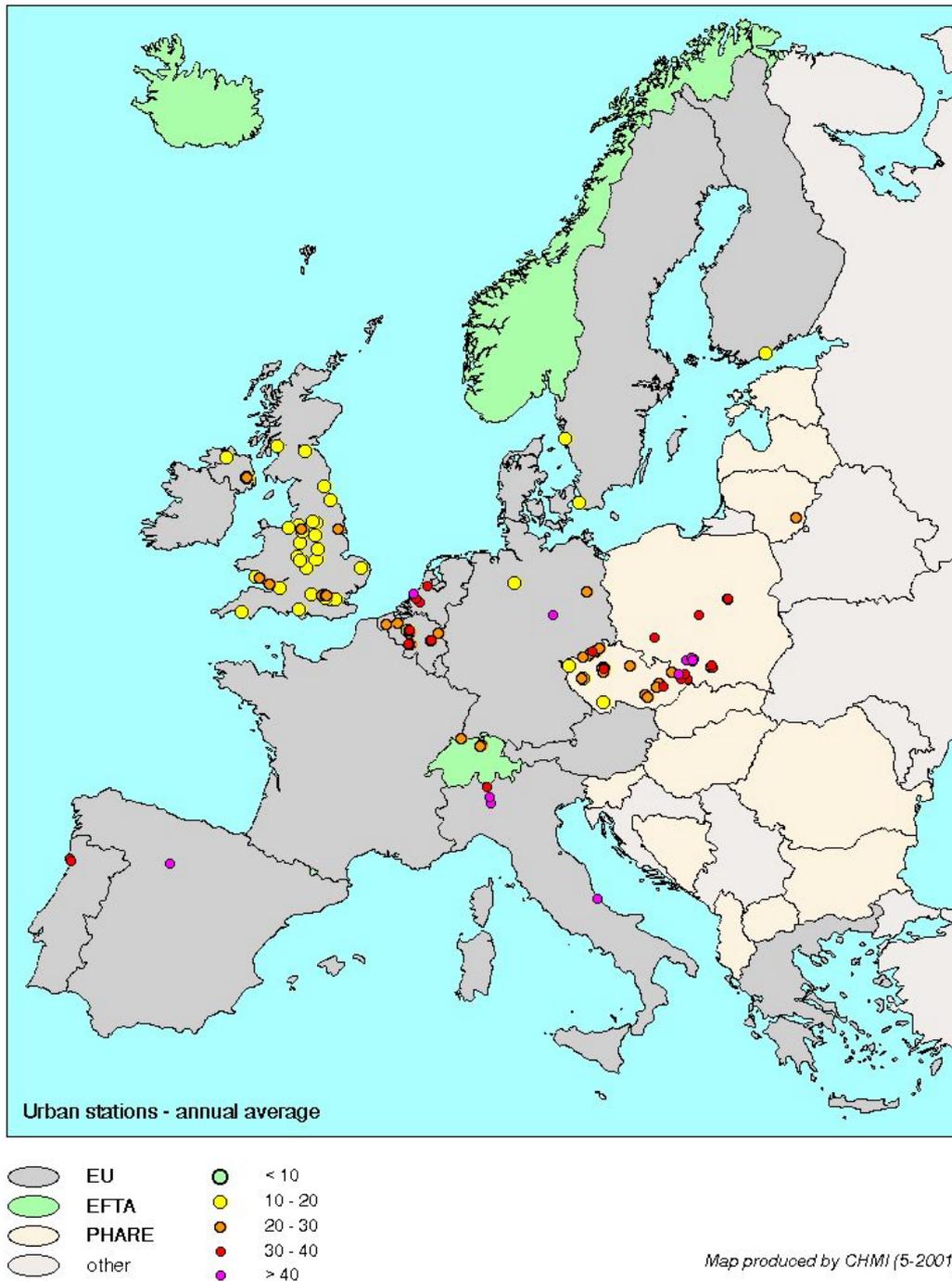


Figure 19: Particulate matter (PM₁₀) annual average (1999) of 24-hour concentrations from urban stations under the AIRBASE framework ($\mu\text{g}/\text{m}^3$).

It is apparent from the above measurement data and previous studies (Lazaridis et al., 2000) that more precise, harmonised and quality controlled measurements are needed to obtain a comprehensive picture of geographical and seasonal characteristics of particulate matter in Europe. Additional data with more detailed physico-chemical characterization of ambient aerosols including measurements of

their mass/chemical size distribution characteristics is a necessary aspect in understanding their dynamics at urban and rural locations in Europe. In this framework ambient aerosol data from measurements in the metropolitan area of Athens, Greece are briefly presented. The data are from measurement campaigns during the years 1997 and 2000. The 1997 data were obtained at the boundaries of the greater Athens Metropolitan area. The 1997 data were measured at the boundaries of the greater Athens Metropolitan area. Two sampling sites were selected at the coast and inland along the NE-SW axis. The latter coincides with the main surface wind flow pattern over the area. The coastal site was located atop the Castella hill (90 m a.s.l.) in Pireaus and the inland site on the edge of the Ag. Stefanos residential area. The distance between the two sampling sites is 22 km (see Figure 20). Cascade impactor (5l/min flow rate) was set-up to operate over concurrent 24-hour periods at each site.

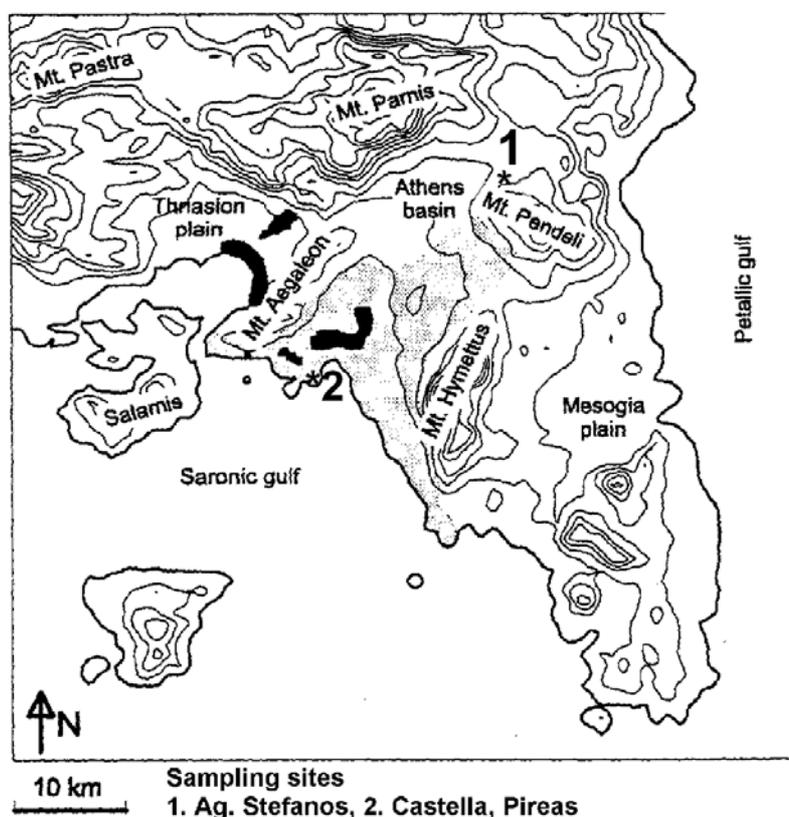


Figure 20: Map of the Athens metropolitan area displaying the positions of sampling sites. Shaded areas correspond to urban regions, and dark areas to industrial regions (from "Athens 2004 air quality").

Samples were analysed in a Dionex 2000i/SP conductivity ion chromatograph (IC) for Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+} . Average size distributions for NO_3 and SO_4 were calculated from a three week sampling period in July and August 1997 and are shown in Figure 21 and Figure 22. It is observed that sulphate displays a bimodal distribution with an increased coarse fraction near the coast, while nitrate appears to exist mainly in the coarse fraction at both sites (Eleftheriadis et. al., 1999).

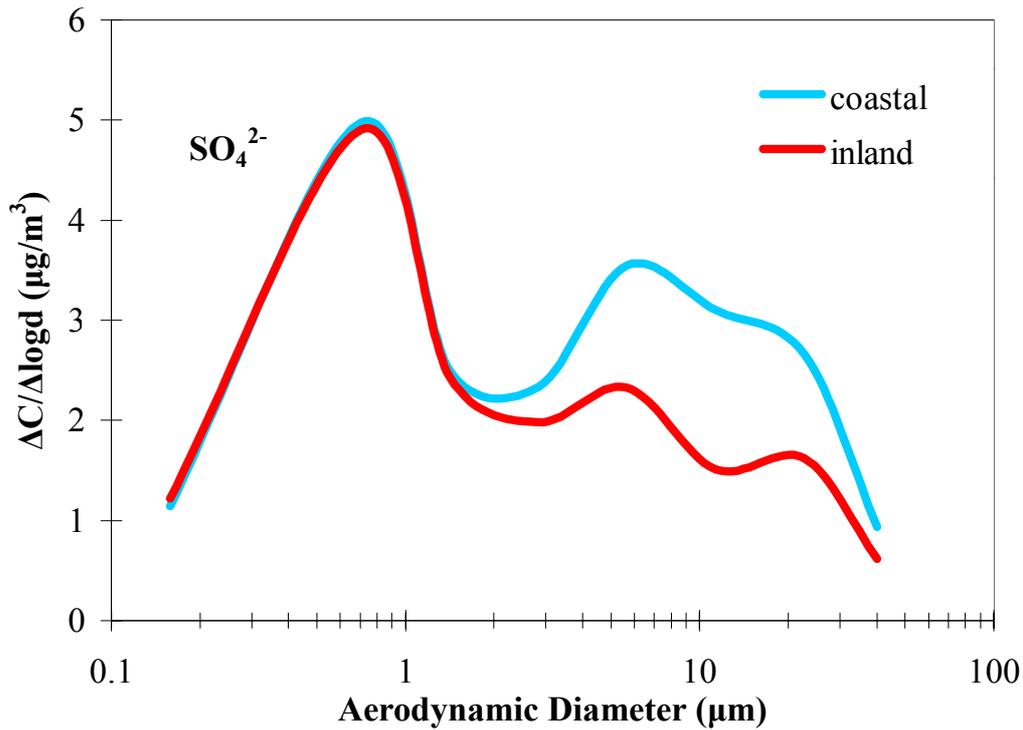


Figure 21: Typical mass size distribution of particulate sulphate from measurements in the Athens metropolitan area at two sites (coastal and inland) during summer 1997.

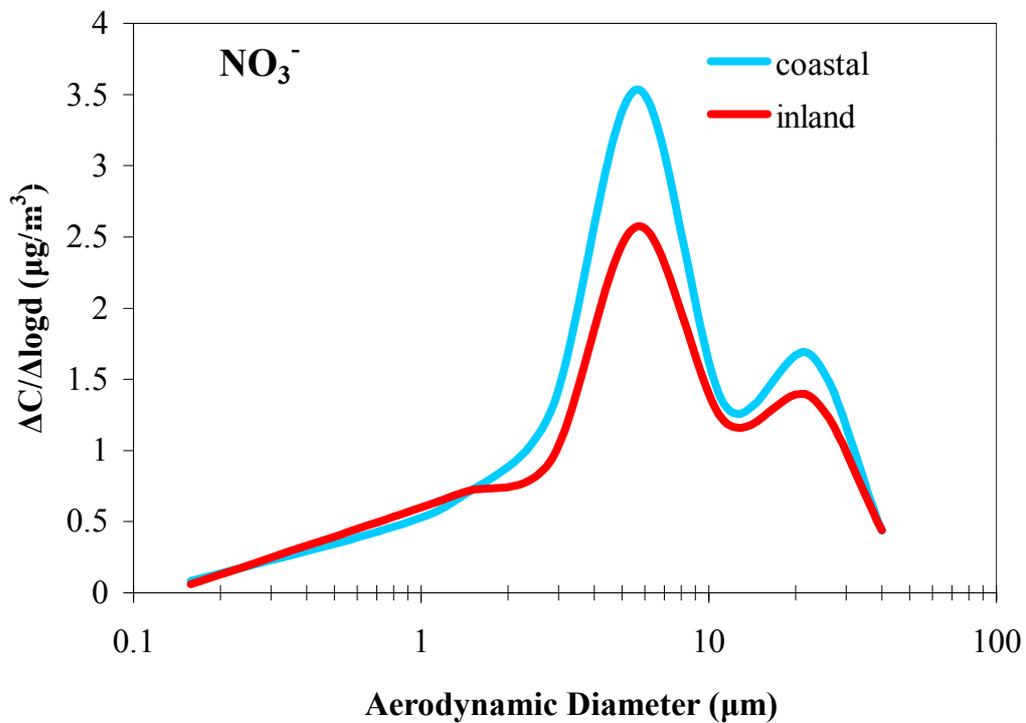


Figure 22: Typical mass size distribution of particulate nitrate from measurements in the Athens metropolitan area at two sites (one coastal and one inland) during summer 1997.

Measurements of the aerosol mass size distribution in Athens have been also conducted during July 2000, by means of Berner cascade impactors. Sampling was performed at a suburban inland site (N.C.S.R. Demokritos). Results for the 1st and 2nd of July are presented in Figure 23. The mass size distribution is bimodal with PM₁₀ mass concentrations close to 50 µg/m³.

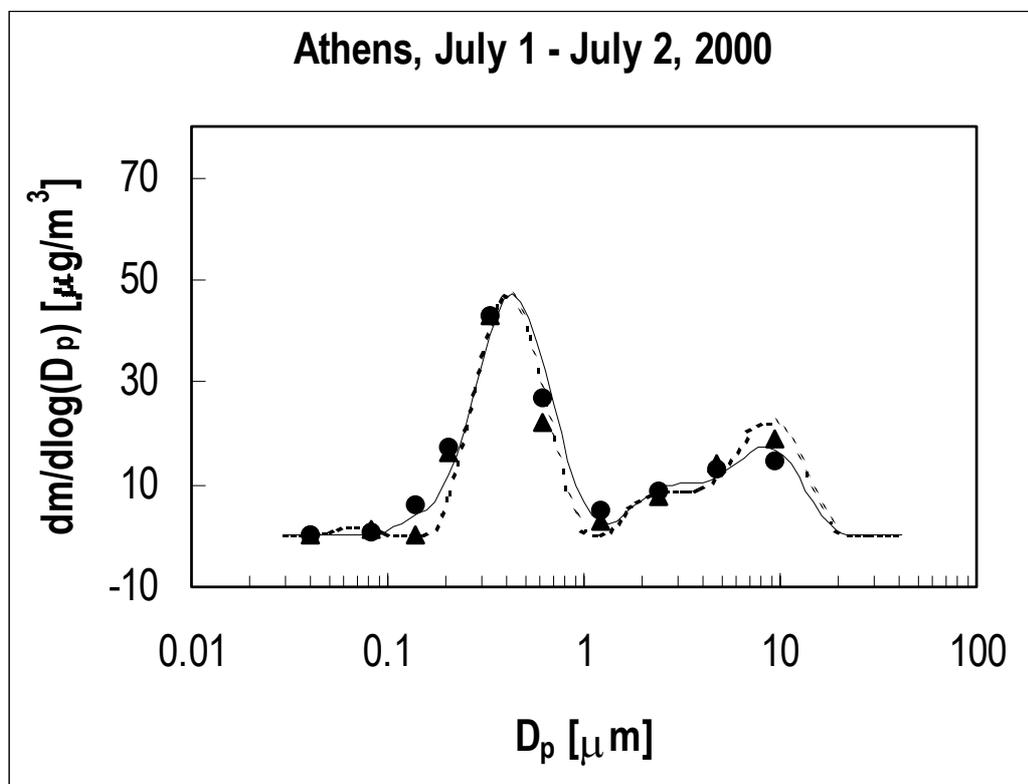


Figure 23: Typical mass size distribution in the Athens Metropolitan area measured by Berner impactors.

3. Extensive measurement campaigns from Switzerland, Norway and Greece

The data above are mainly PM₁₀ mass concentrations, and additional sulphate and nitrate at EMEP sites. More comprehensive chemical and physical characterisation is not yet available in the EMEP and the AIRNET data bases, although improvements and extensions have been proposed.

However, some data are available from national and scientific studies. In the following, data are presented which focus on chemical composition and source apportionment. Switzerland has undertaken a very comprehensive national study, both with respect to emissions and measurements, and their interpretation. Birkenes, Norway, is one of the best documented EMEP sites with extensive measurement records, and serves also as a site for the testing of new recommended measurement methods in EMEP. The high PM₁₀ concentration levels in the Mediterranean area, and the proximity of this area to Africa and the Sahara desert is a particular challenge in relation to PM source apportionment. This is the reason for including a special study from Crete, which also comprise more detailed physical characterisation of the fine particles at the site Finokalia.

3.1 Concentrations, composition and sources of PM₁₀ and PM_{2.5} in Switzerland

PM₁₀ and PM_{2.5} measurements were performed within the framework of the Swiss National Air Monitoring Network (NABEL) at selected sites in 1997 which represent important air pollution situations in Switzerland. In addition the chemical composition of a considerable number of ambient particle samples was analyzed in detail. The relatively small differences between urban and rural PM_{2.5} concentrations as well as the high content of secondary inorganic aerosols in PM_{2.5} underlines the importance of long-range transport for fine particles. A source attribution for PM₁₀ and partly also for PM_{2.5} was carried out with a receptor model. Road traffic turned out to be an important source for PM₁₀ accounting for about 35% at urban or suburban sites and for about 50% at sites which are directly exposed to nearby road traffic.

There are indications from recent epidemiological studies that elevated concentrations of fine suspended particles can be responsible for adverse health effects (BUWAL, 1996; WHO/UN, 1999). These findings were taken into account in the last revision of the Swiss clean air act with new limit values for PM₁₀, replacing the old limit values for TSP (total suspended particles). The measurements of PM₁₀ which started in 1997 within the framework of the Swiss National Air Monitoring Network (NABEL) show that the limit values (20 µg/m³ for annual means and max. 50 µg/m³ for daily values) are not attained in large parts of Switzerland.

In addition, there is at present an increasing interest in the finer particle fraction PM_{2.5}. Although there are no limit values for PM_{2.5} in Switzerland so far, there are also clear indications for adverse health effects related to the PM_{2.5} fraction. Therefore, additional PM_{2.5} measurements have been performed at a few selected sites of the NABEL network since 1998.

In order to develop effective reduction scenarios, the sources of fine particles need to be characterised as well as their quantitative contribution to ambient air concentrations. Up to now the sources of PM₁₀ and PM_{2.5} have not been sufficiently identified and quantified in Switzerland. It was, therefore, the main goal of a study within the scope of the Swiss National Research Programme "Transport and Environment" to identify the most important sources of fine particles and to quantify their contributions to the ambient air concentrations (Hüglin, 2000). According to the main purpose of the national research programme, the contribution of road traffic was considered in particular detail. The elevated concentrations of fine particles near busy roads as measured in the NABEL network show that road traffic is indeed an important source of atmospheric particles. The particle emissions of road traffic stem from different contributions. Primary particles as well as gaseous precursors for secondary particles are emitted by vehicles. In addition, road traffic contributes to the fine particle load of the atmosphere by abrasion and resuspension of particles (street dust, tyre wear, brake wear).

Measurement programme and methods

The mass concentrations of PM₁₀ and PM_{2.5} were measured with a gravimetric procedure which is compatible with the reference method according to EN12341 (CEN, 1998). High volume samplers (Digitel DHA-80) with a PM₁₀ or PM_{2.5} sampling inlet (impactor) were used for sampling. An ambient air volume of 720 m³ was drawn through glass fibre filters (Ederol 227/1/60) or quartz fibre filters (Schleicher und Schuell QF20) over a 24-hour period. Chemical analysis included:

- Water soluble inorganic ions NH₄⁺, NO₃⁻, SO₄²⁻, Na⁺, K⁺, Mg²⁺, Cl⁻ (Ion chromatography). The sum of the concentrations of NH₄⁺, NO₃⁻ and SO₄²⁻ represents the secondary inorganic particle fraction.
- Elemental and organic carbon EC and OC (coulometric carbon analysis, VDI 1996).
- Trace elements Al, As, Ba, Br, Ca, Ce, Cd, Cu, Fe, Ga, K, La, Mg, Mn, Mo, Nd, Ni, Pb, Rh, Sb, Se, Tl, V, Y (plasma mass spectrometry, ICP-MS).
- Biogenic particles (bio assays, microscopy)

Selection of sites and sampling procedures

Most of the sampling was performed within the scope of the NABEL network. The sites were selected according to important and representative pollution situations in Switzerland. During the period from 01.02.98 to 31.03.99 a number of PM₁₀ and PM_{2.5} samples from the sites Basel, Bern, Chaumont and Zürich-Kasernenhof were chemically analysed in detail. An additional site in Zürich-Wiedikon was included in the study because of its extreme exposure to traffic. Table 3 shows the characteristics of the investigated sites. Figure 24 gives the position of the sites within Switzerland.

Table 3: Characteristics of the investigated sites.

Site	Site characteristics	Elevation (m asl.)
Dübendorf	suburban	430
Basel	suburban	320
Bern	city centre, kerbside	540
Chaumont	rural	1140
Lugano	city centre south of the alps, in courtyard ("urban background")	280
Payerne	rural	490
Zürich-Kasernenhof	city centre, in courtyard ("urban background")	410
Zürich-Wiedikon	city centre, kerbside	410

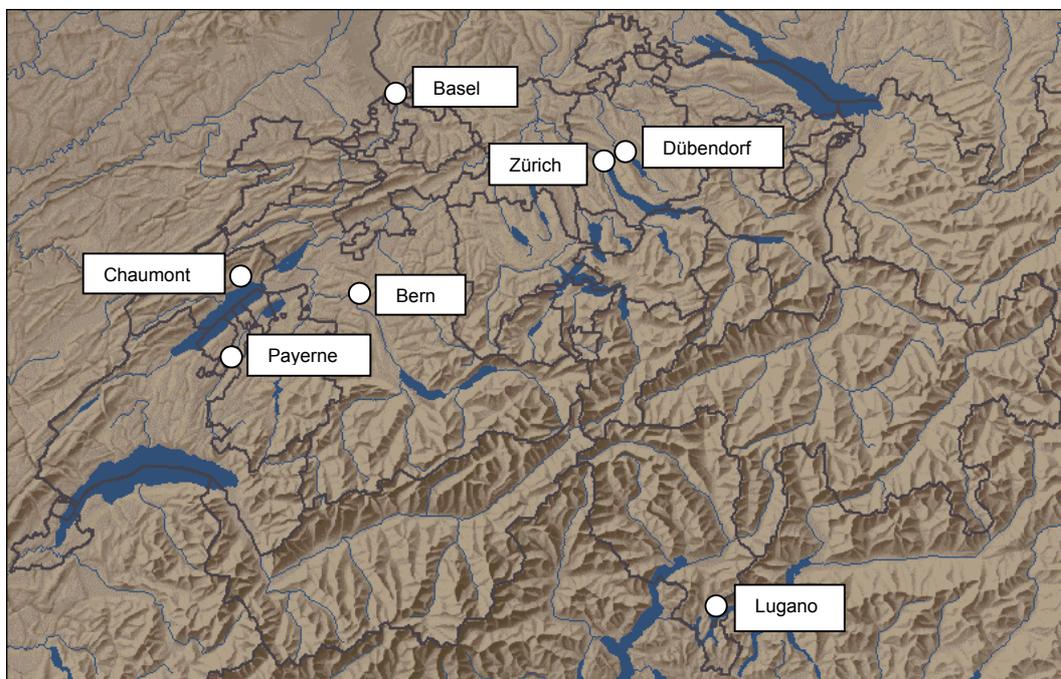


Figure 24: Site map.

Mass concentrations of PM₁₀ and PM_{2.5}

Table 4 gives an overview of the annual mean concentrations of PM₁₀ and PM_{2.5} at the investigated sites (without Zürich-Wiedikon, where only measurements from two special campaigns are available). There seems to be a decrease in concentrations of PM₁₀ at most sites (Figure 25). The annual mean concentrations for PM_{2.5} of the different stations vary only in a surprisingly small range, with the exception of the mountain site Chaumont. Table 5 shows that the ratios for PM_{2.5}/PM₁₀ do not vary much between the sites with the exception of the Bern which is directly exposed to traffic and therefore has a considerable amount of relatively coarse particles (abrasion and resuspension). The small variability in the PM_{2.5}/PM₁₀ ratio shows, that at some distance from direct emission sources fine particles tend to be quite homogeneously distributed over large areas, showing

also the importance of long-range transport for this parameter. This finding is also confirmed by an analysis of the correlations between the daily values of $PM_{2.5}$ at the different sites (Table 6). It shows quite high correlations between the sites Dübendorf, Basel, Zürich, Bern and Payerne which all are situated north of the alps. Lower correlations are found for Lugano (south of the alps) and Chaumont (mountain site) which are exposed to different air masses due to geographical and meteorological reasons.

Table 4: Annual mean concentrations of PM_{10} and $PM_{2.5}$.

	PM_{10} ($\mu\text{g}/\text{m}^3$)				$PM_{2.5}$ ($\mu\text{g}/\text{m}^3$)		
	1997	1998	1999	2000	1998	1999	2000
Dübendorf	30	27	24	21	20		
Basel	30	24	23	21	18	18	16
Bern	43	40	38	33	23	20	19
Chaumont	14	11	12	10	8	9	7
Lugano	37	36	31	34		24	25
Payerne	26	23	21	20		16	15
Zürich	31	24	25	23	19	19	17

Table 5: Mean $PM_{2.5}/PM_{10}$ ratios of the daily concentrations.

	1998	1999	2000	1998-2000
Dübendorf	0.74			0.74
Basel	0.72	0.77	0.75	0.75
Bern	0.58	0.55	0.59	0.57
Chaumont	0.74	0.79	0.74	0.76
Lugano		0.77	0.72	0.74
Payerne		0.78	0.72	0.75
Zürich	0.76	0.75	0.73	0.75

Table 6: Correlation coefficients (r) of the daily values for $PM_{2.5}$.

	Dübendorf	Basel	Bern	Chaumont	Lugano	Payerne
Dübendorf	1.00					
Basel	0.92	1.00				
Bern	0.88	0.84	1.00			
Chaumont	0.33	0.43	0.36	1.00		
Lugano		0.33	0.38	0.19	1.00	
Payerne		0.84	0.83	0.50	0.42	1.00
Zürich	0.98	0.90	0.85	0.41	0.33	0.79

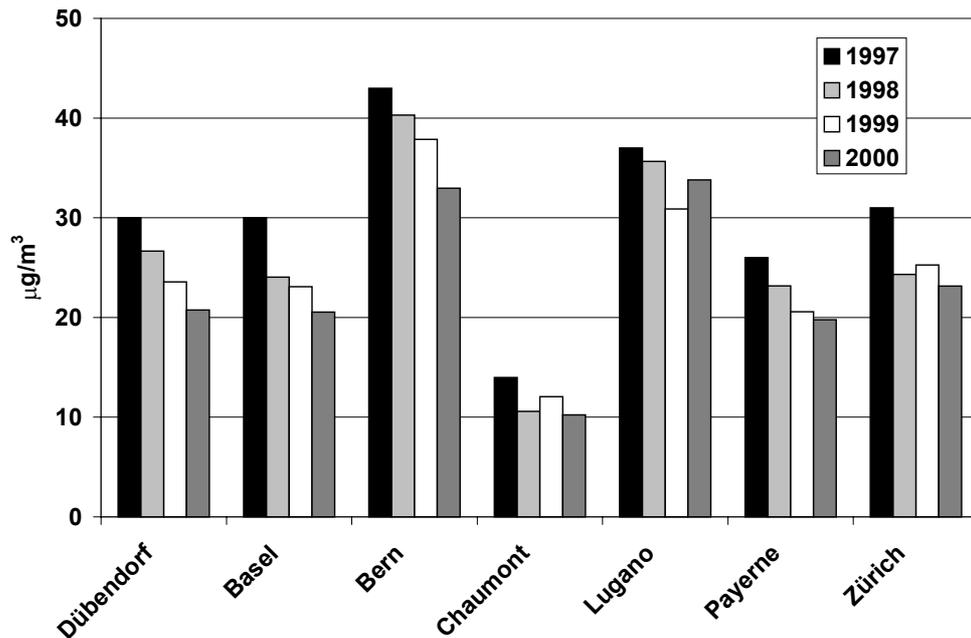


Figure 25: Annual mean concentrations of PM₁₀.

If local sources of coarse dust are absent, the correlation of the daily values of PM_{2.5} and PM₁₀ at a specific site is very high. Figure 26 shows as an example the scatterplot for the urban background site Zürich-Kasernenhof and compares it with the situation at the kerbside site Bern.

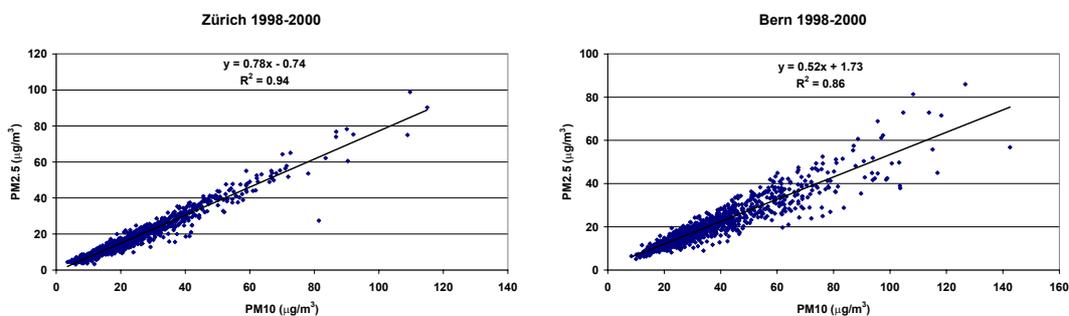


Figure 26: Scatter plots of daily PM_{2.5} versus PM₁₀.

Chemical composition of the fine particles

The analytical measurement programme comprised all components of the fine particle fraction which contribute considerably to the mass. Table 7 gives an overview of the composition of the investigated fine particle samples at the different sites. The sum of all analysed components should therefore equal the gravimetrically determined mass given in the first data column.

Table 7: Mean chemical composition of PM_{10} and $PM_{2.5}$ at the selected sites. Annual mean values (01.04.98–31.03.99), except for Zürich-Wiedikon and Payerne. All results are in $\mu\text{g}/\text{m}^3$. (EC=elemental carbon, OM=organic material =1.4 x organic carbon, PM grav. = gravimetrically measured particle concentration.)

Site	PM grav.	NH_4^+	NO_3^-	SO_4^{2-}	EC	OM	Mineral dust	Trace elements	unidentified
Basel PM_{10}	24.0	1.9	3.1	3.9	1.9	4.7	2.0	1.0	5.5
Bern PM_{10}	39.7	1.4	3.3	3.3	5.6	8.9	6.7	2.1	8.4
Chaumont PM_{10}	10.1	0.8	0.8	2.0	0.6	1.7	1.3	0.4	2.6
Zürich-Kasernenhof PM_{10}	24.1	2.0	3.3	3.7	2.0	5.0	2.2	0.7	5.4
Zürich-Wiedikon PM_{10}^a	43.0	2.6	4.7	4.2	7.7	9.0	4.9	2.4	7.6
Payerne PM_{10}^b	13.6	1.0	1.1	2.2	1.3	3.4	1.7	0.5	2.4
Basel $PM_{2.5}^c$	17.7	1.9	2.5	3.8	1.5	4.0	1.0	0.6	2.4
Bern $PM_{2.5}^c$	22.0	1.4	2.3	2.7	3.8	6.5	0.9	0.5	3.8
Chaumont $PM_{2.5}^c$	8.4	0.9	0.5	2.4	0.4	1.7	0.6	0.3	1.6
Zürich-Kasernenhof $PM_{2.5}^c$	18.6	1.9	2.7	3.3	1.6	4.4	0.9	0.4	3.5

^a Mean of 59 daily samples from two measurement campaigns (July/August 1998 and January/February 1999).

^b Mean of totally 17 daily samples from May-July 1998 and September-November 1998.

^c Annual mean. April to July 3 daily samples per month, else 8-9 daily samples per month. Samples from April to July are weighed by a factor 3.

The unidentified part in the last data column of Table 7 can mainly be attributed to the water content of the particles which is weighed in the gravimetric procedure but not involved in the analytical programme and to biogenic particles which are not always correctly quantified with the applied coulometric method for carbonaceous aerosols. Spot measurements of the humidity of selected samples showed a mean water content of 16% in the warm season and 6% in the cold season. Specific analysis of the mass of biogenic particles turned out to be very difficult. The applied methods did not allow an accurate quantification. The Bradford assay had a high detection limit, and the protein contents of all investigated samples were below the limit. From the known detection limit and the assumption of an average protein content of biogenic particles it can be concluded that the concentrations of biogenic particles in the investigated samples were always below $3.5 \mu\text{g}/\text{m}^3$. However, microscopic analysis of a limited number of samples (8 samples per site) clearly showed the presence of biogenic particles. As expected, the number of the identified biogenic particles was higher during the vegetation period. Conversion of particle number to mass concentration is generally very difficult because many uncertain assumptions about shape and

density of the particles have to be made. A rough estimate leads to a mean mass concentration for biogenic particles of approximately 1–1.5 $\mu\text{g}/\text{m}^3$.

Source attribution for primary aerosols

The attribution of the primary aerosols was performed with a receptor model (Hüglin, 2000). Detailed measurements of the chemical composition of the fine particle fraction at the investigated site (receptor) are needed as input data for receptor models. Of special interest are constituents which can be used as an indicator for emissions from a certain source or whose fluctuations in time are at least different from other sources in order to obtain information on the contributions of the emission sources. No detailed emission data are needed for the application of receptor models. As a result the applied model gives factors which explain a certain amount of the total variance of the constituents of the aerosols (Hopke, 1991). From the knowledge of typical combinations of constituents for certain emission sources and the comparison with the composition of the found factors, sources or groups of sources can be attributed to the statistically obtained factors. In addition to these so-called source profiles, the source activities can also be estimated. From the relation of the source activities with different weekdays or seasons and from the enrichment factors additional information for the identification of sources can be obtained.

With this method the following sources and source groups could be attributed to the factors which were obtained from the receptor model: Waste incineration and bio mass burning, thallium containing dust (cement production), road traffic (mainly tailpipe emissions), street dust, street dust containing salt. It is advisable to summarize the latter three factors to a common source "road traffic" because a complete separation of the factors seems to be unlikely due to the high correlation between these different road traffic contributions.

Table 8 shows the attribution of sources of the fine particle mass (PM_{10}) to the mentioned factors obtained from the receptor model. The receptor model does not give exactly the same factors (resp. separation of the sources) for all sites, which makes the direct comparison of the sites somewhat uncomfortable. Although daily samples with $\text{PM}_{10} > 8 \mu\text{g}/\text{m}^3$ for Chaumont were included into the statistical analysis, no detailed separation of the factors could be obtained. Therefore, the contribution of the road traffic could not be quantified at this site.

Table 8: Source attribution of the mean PM_{10} ambient air concentrations ($\mu\text{g}/\text{m}^3$) to the factors obtained with the receptor model. Only days with $PM_{10} > 8 \mu\text{g}/\text{m}^3$ were used for Chaumont.

	Basel	Bern	Chaumont	Zürich-Kasernenhof	Zürich-Wiedikon
Total PM_{10} (measured)	25.0	39.6	16.5	24.5	42.6
Tail pipe emissions of road traffic (incl. Off road)	4.9	7.6		3.4	17.8
Road dust (as far as not contained in the factors tail pipe emissions and road salt)	1.8	6.4		2.5	3.2
Road salt (incl. simultaneously resuspended road dust)	0.9	3.1	0.3	0.8	3.3
Waste incineration, biomass burning	2.7				
Waste incineration, biomass burning, long-range transport		8.2		4.8	5.4
Long-range transport, TI-factor ^a	2.9				
TI-factor ^a		1.4		1.6	
Mineral dust (not traffic related))	2.0	2.3	2.7	1.6	1.6
Diverse anthropogenic sources			4.3		
Other non identified sources	2.4	4.4	3.6	2.0	0.2
Secondary aerosols traffic related part	9.3 1.9	8.0 1.8	5.5 0.5	9.1 1.9	11.1 2.5

^a Probably from cement production

Source attribution of secondary inorganic aerosols

With the receptor model only emitted components of the particles which remain unchanged during transport to the receptor can be treated. Therefore the source attribution of the secondary inorganic aerosols was based on the data of the European emission inventory for the gaseous precursors NH_3 , NO_x and SO_2 (CORINAIR 1994) and the long range transport modelling of the secondary inorganic aerosol fraction within the scope of the EMEP programme (EMEP 1998). Agriculture is the main source of ammonia and contributes therefore considerably to the ambient air concentrations of ammonium. Road traffic is the main cause for nitrate formation. Emissions of fossil power plants and other industrial and non-industrial combustion processes as well as biogenic emissions are important emitters of SO_2 and contribute therefore to the sulphate formation. Based on the data of precursor emissions the contribution to the secondary inorganic PM_{10} can be estimated for the investigated sites.

The model results of EMEP agree quite well with the measurements performed in this study (EMEP, 1998). For Switzerland an annual mean value for the concentrations of secondary inorganic aerosols of 10-15 $\mu\text{g}/\text{m}^3$ was calculated. Our measured values at Basel, Bern and Zurich are somewhat below 10 $\mu\text{g}/\text{m}^3$. It has, however, to be kept in mind that the measurements underestimate the true ammonium and nitrate concentrations due to sampling losses.

Secondary organic aerosols

The measurements performed within the scope of this study show that secondary organic aerosols do not contribute significantly to the PM_{10} (and $\text{PM}_{2.5}$) mass considering long term means. However, elevated concentrations can be observed on specific days with high photochemical activity. From a detailed analysis of a photochemically active episode in Zurich a contribution of secondary organic aerosols of up to 3 $\mu\text{g}/\text{m}^3$ could be found. No attempt to attribute these generally small amounts to specific sources was made.

Overview of the source attribution for ambient air particle concentrations

Figure 27 shows the contributions of the different source groups to the PM_{10} concentrations at the four sites where the receptor model gave sufficiently resolved factors. The factors in connection with road traffic were added to get the total contribution of road traffic. In addition also the contribution of the secondary aerosol is included, split into a traffic related part and a non traffic related part.

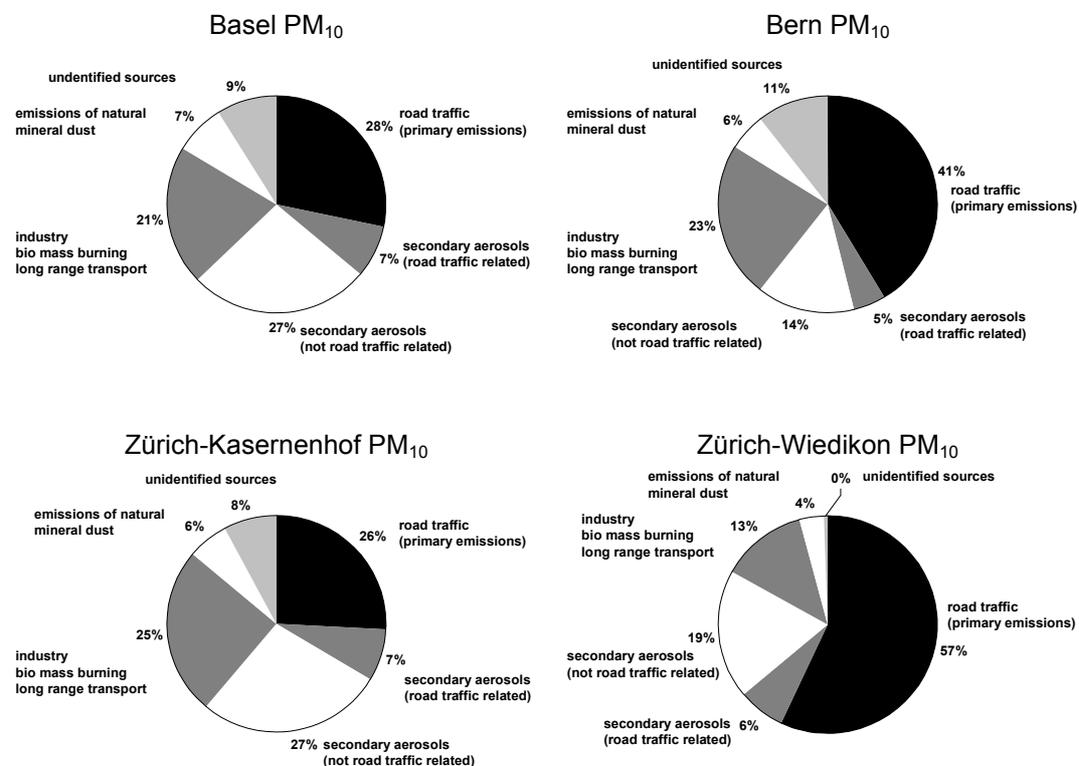


Figure 27: Contributions of the identified sources and source categories to PM_{10} at some sites with different pollution levels.

Conclusions and open problems

For some typical Swiss pollution situations the source contributions (in particular the traffic related part) to the PM_{10} and partly also to $PM_{2.5}$ were quantified by receptor modelling. The selection of rather polluted sites (in the range from extremely traffic influenced to urban background and suburban) led to the characterization of scenarios which are potentially harmful. For rural sites with low pollution levels (Chaumont) the receptor model did not allow to quantify the different sources with sufficient reliability. The values presented in this study are therefore representative for the exposition of an urban and suburban population but do not represent a Swiss mean exposition.

The limitations of the receptor model became clearly visible. A detailed speciation of the source contributions (e.g. distinction between light and heavy duty vehicles) was not possible. Also the determination of the contributions of the different industrial sources was only possible in a rather lumped way. The unsatisfactory separation of sources is a general problem involved with the use of receptor models for source attribution. In order to obtain a complete separation of the source contributions, specific tracers would be needed for all sources which in addition must be stable during the transport from the source to the receptor. Such tracers, however, are very difficult to find and often even more difficult to analyse.

As an open problem remain the contributions of the off road emissions in general. Due to the very similar chemical composition these emissions are not separated from the traffic related factors in the receptor model. It can be assumed, however, that at the selected sites the off road contributions are quantitatively not important because no typical off road sources as heavy construction machines, tractors or diesel powered rail engines were active near the sites. But this does not mean that off road emissions are in general not important as they can cause locally very high particle concentrations.

The contributions of domestic heating (oil and gas) could also not be separated due to the similar chemical composition. Nevertheless, it can be assumed that these emissions are not important at all for the particle concentrations at the selected sites because the emission factors of these heating devices are well known to be very low. The more difficult to assess is particle emissions of wood combustion are contained in the factor "biomass burning".

The measurements cannot distinguish between local and more distant sources, or the long range transported fraction. However, the secondary inorganic aerosol fraction is likely originate mainly from emissions outside Switzerland, as well as a significant part of the road-traffic-related fraction.

3.2 Study of the atmospheric aerosol composition and mass concentration at Birkenes, Norway

The site Birkenes was established in 1971 and has since operated with continuously sampling of precipitation chemistry. Gaseous and particulate sulphur species in air was added in 1973, and later other parameters have been included to the measurement programme, either on a long-term basis or during shorter research campaigns. With few local emission sources, the site has been proven well suited to monitor long-range transport of atmospheric pollution from European source regions to Southern Norway. The site is situated approximately 20 km from the Skagerrak coast (for site description see www.nilu.no/projects/ccc/index.html).

In 1999 the monitoring programme at Birkenes was extended to include aerosol mass of particles less than 10 µm (PM₁₀) using the Sierra Hi-vol. sampler. In 2000 the sampling method was changed to the KleinfILTERGERÄT (medium volume) (see sections 3.2.1 and 3.2.2 for details). At the same time also PM_{2.5} was added to the monitoring programme. Here, a brief summary of the results is presented.

Monthly means of the mass concentration for PM₁₀ during year 2000 are given in Table 9, showing very low concentrations during January – March and with increased levels during spring and autumn. During July-August and November - December the concentrations were also rather low.

Table 9: Monthly means of mass concentration of PM₁₀ for 2000 for Birkenes, including maximum- and minimum values.

Month	Mass concentration (PM ₁₀)	
	Mean	(min – max)
January	2.2 ¹⁾	(0.1 – 7.2)
February	2.2	(0.4 – 7.7)
March	3.0	(0.3 – 8.6)
April	11.6	(0.6 – 28.1)
May	11.4	(3.5 – 30.0)
June	9.5	(1.7 – 27.0)
July	5.4 ²⁾	(1.6 – 10.3)
August	4.6	(1.5 – 15.9)
September	10.0	(3.2 – 32.6)
October	10.1 ³⁾	(3.0 – 26.7)
November	6.1	(1.1 – 14.2)
December	6.5	(0.4 – 15.7)

All values in µg/m³

1) Mean based on a total of 23 samples.

2) Mean based on a total of 21 samples.

3) Mean based on a total of 13 samples. Two different sampling devices have been used (Appendix).

The monthly means for January and February are remarkably low. For a number of days (8 days) even negative values were seen, indicating problems in the mass determination. Non-exposed filters used as field blanks were however low or only slightly negative (one very high value is excluded). Loss of filter material during sampling may partly explain the low values observed. The results for January and February should therefore be used with caution. On the other hand, previous results from the period 1991 – 1996 show that mass concentration of PM₁₀ often tend to be rather low in January and February.

The highest monthly mean is seen during April and May and co-insides with the onset of spring. Several plants and trees generate pollen in a size range lower than the sampling cut-off of 10 μm and may give a significant contribution to PM_{10} of primary organic compounds from biogenic sources. As seen in Table 3, OC concentrations were also the highest during May. However, the concentration of secondary inorganic aerosols (SIA) has also a maximum in April indicating contribution from anthropogenic sources. Also the mineral fraction is reported to be at their highest concentration levels during spring and early summer (Amundsen et al. (1992); Maenhaut et al. (2000)). One important PM source during this season is wind mobilisation of soil particles from agricultural areas.

Mass concentration of PM_{10} seen in July and August are not as high as during spring, though considerably higher than in January, February and March. Except for a period of 2 – 3 days ultimo August, mass concentrations are rather low and stable this month. The low concentrations may be explained by the fact that air masses reaching Birkenes mainly came in from the Norwegian Sea. September exhibit a rather high mass concentration in regard to the two previous months and has the highest daily mean for the total sampling period (32.6 $\mu\text{g}/\text{m}^3$). The monthly mean for October is also relatively high, but it is strongly influenced by the fact that it is based on only 13 samples and that an episode of long-range atmospheric transport is included within this period. Former studies (Amundsen, et al., 1992) confirm that that long-range atmospheric transport to Southern Norway is favoured during autumn and springtime. For November and December concentrations decreases considerably, with levels being approximately half the concentrations of September and October.

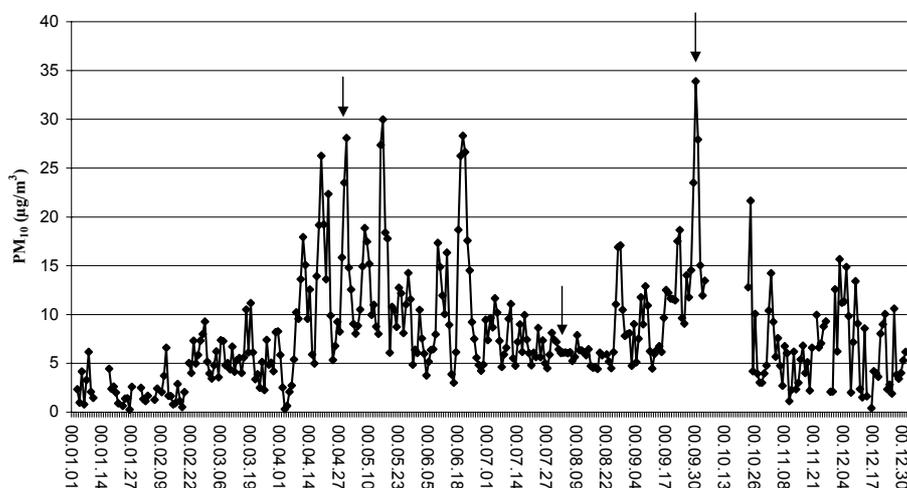


Figure 28: Time series for mass concentration of PM_{10} for Birkenes based upon daily means in 2000. Negative values have not been included in the figure. Arrows highlight days where trajectories have been shown in figures 29-31 (30.04, 08.08 and 30.09). No sampling was done in the period 05.10.00 – 22.10.00.

Although the air quality guideline set by EU for PM_{10} (50 $\mu\text{g}/\text{m}^3$ as a 24h mean) is not exceeded at Birkenes, the data show that the regional concentration of PM_{10} may contribute up to 65% of the limit value.

Trajectories, HYSPLIT4 (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model, 1997 NOAA Air Resources Laboratory, Silver Spring, MD, have been used to study the origin of air masses as they arrive Birkenes to give a better understanding of the corresponding concentrations of PM_{10} observed. 72 hours back trajectories for the altitudes 500, 1000 and 3000 m.a.s.l. for the days: 30.04, 30.09 and 08.08 are shown in Figure 29, Figure 30 and Figure 31, respectively.

Figure 29: 72 hours back trajectories for 30.04.00 (Birkenes).

Mass concentration of PM_{10} = $28.1 \mu\text{g}/\text{m}^3$.

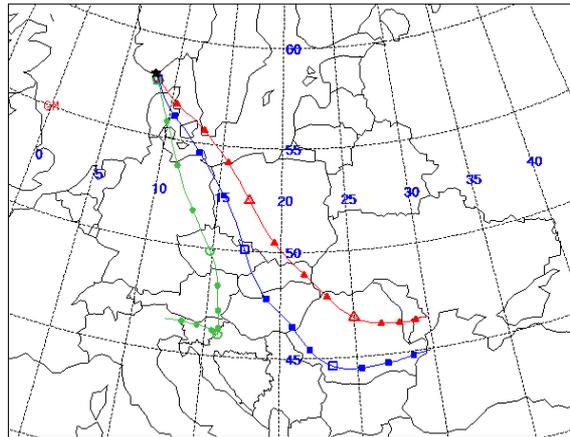


Figure 30: 72 hours back trajectories for 30.09.00 (Birkenes).

Mass concentration of PM_{10} = $32.6 \mu\text{g}/\text{m}^3$.

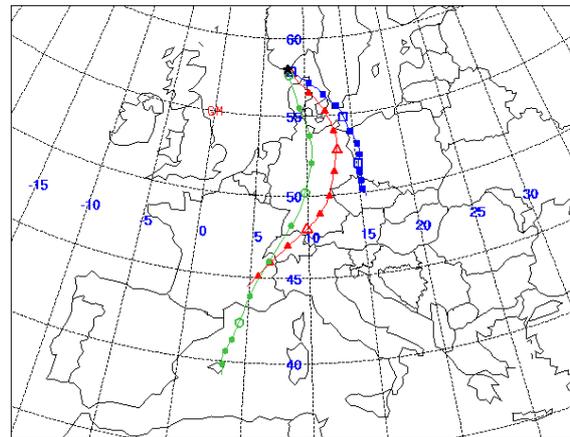
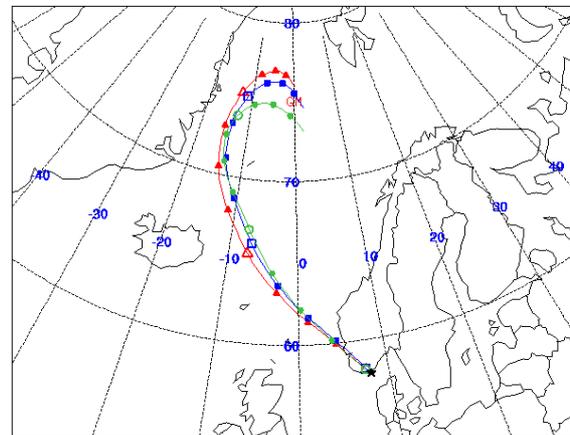
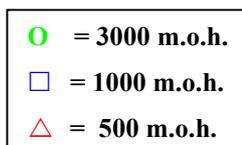


Figure 31: 72 hours back trajectories for 08.08.00 (Birkenes).

Mass concentration of PM_{10} = $2.6 \mu\text{g}/\text{m}^3$.



At the 30.04.00 and 30.09.00 there is a good correspondence between air passage over major source areas for precursors of secondary inorganic aerosols and the observed mass-concentrations of PM₁₀ at Birkenes. This is illustrated in Figure 29 and Figure 30. Figure 31 shows the geographically history of a typical air masses with low concentrations (08.08.00).

There is a good correlation between mass concentration of PM₁₀ and mass concentration of secondary inorganic compounds, and sulphate alone represent approximately 19% of PM₁₀ for the total sampling period. This finding confirms that long-range atmospheric transport has a considerable influence at Birkenes.

A significant loss of mass concentration may occur for some semi-volatile compounds like SVOCs and ammonium nitrate. Adsorption of gasses on to the filter may add mass, while evaporation may result in underestimation of the PM mass. Such artefacts are important sources of error and must be considered along with other possible errors in sampling, transport, storage and during conditioning of the filters. Some blanks showed rather high levels after 08.03.00. This is most probably due to elevated levels of humidity, which occurred during conditioning of the filters. This artefact might have resulted in slightly higher mass concentration for the samples being exposed to ambient air concentrations.

It should be noted that during periods with low anthropogenic influence the ambient concentrations are very low and in a range for which the determination of mass by weighing of filters is relatively uncertain.

The chemical analyses in this study do not include sufficient number of parameters to provide a total chemical mass closure. As seen from Figure 32 and Table 10 there is a significant and varying discrepancy between mass concentration of PM₁₀ and the sum of the chemical compounds over the year.

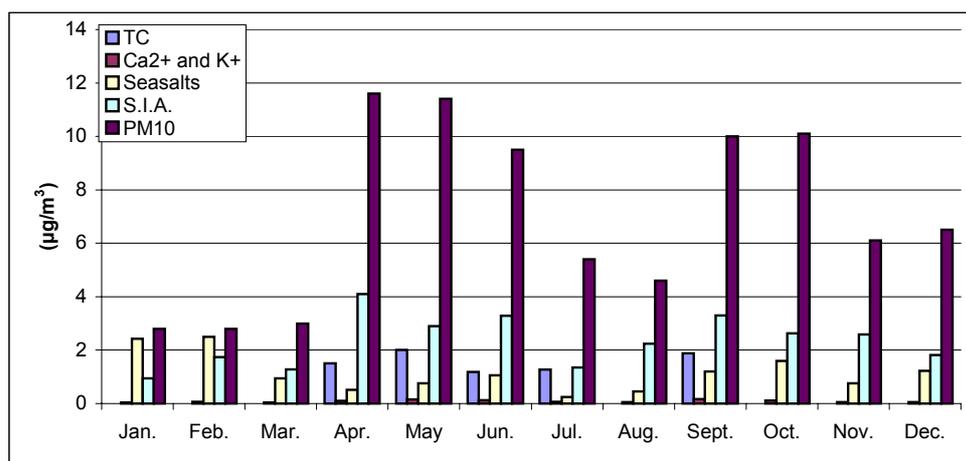


Figure 32: Mass concentration and chemical speciation of the PM₁₀ fraction at Birkenes during the period 01.01.00 - 31.12.00. Negative values and not reported values for mass concentration of PM₁₀ and corresponding values of the chemical compounds are not included in the figure.

Table 10: Mass concentration and chemical speciation of the PM₁₀ fraction at Birkenes during the period 01.01.00 – 31.12.00. Negative values and not reported values for mass concentration of PM₁₀ and corresponding values of the chemical compounds are not included in the table.

Month	PM ₁₀	Total carbon	Ca ²⁺ and K ⁺	Seasalts	Sec. Inorg. Aerosols	Not identified	Identified (%)
(January)	2.2 ¹⁾		0.05	2.43	0.95	-0.63	122.5 ⁴⁾
(February)	2.2		0.07	2.50	1.74	-1.51	153.9 ⁴⁾
March	3.0		0.05	0.94	1.28	0.73	75.6
April	11.6	1.68	0.10	0.51	4.10	5.21	55.1
May	11.4	2.27	0.15	0.76	2.90	5.32	53.4
June	9.5	1.33	0.12	1.06	3.29	3.70	61.1
July	5.4 ²⁾	1.32	0.07	0.25	1.35	2.41	55.3
August	4.6		0.06	0.46	2.24	1.84	60.0
September	10.0	1.88	0.17	1.20	3.30	3.45	65.5
October	10.1 ³⁾		0.11	1.59	2.63	5.77	42.9
November	6.1		0.05	0.76	2.58	2.72	55.6
December	6.5		0.06	1.23	1.82	3.37	47.9

All values in µg/m³ unless else is given.

- 1) Mean based on a total of 23 samples
- 2) Mean based on a total of 21 samples
- 3) Mean based on a total of 13 samples
- 4) Discussed in text

Attempts were made to estimate the contribution of the mineral fraction to the fine- and coarse mass fraction at Birkenes during the period 1991 – 1996 based upon two different models (Maenhaut/NILU, not published). The results showed that the mineral fraction could contribute to as much as 28% of the total PM₁₀ mass concentration (monthly means). The inclusion of the mineral fraction to the monitoring programme would therefore probably have contributed significantly in achieving a more total mass closure also for year 2000.

During 2000 approximately 57% of the total mass could be identified (Table 10) (for both January and February the sum of the chemical compounds exceed the mass concentration of PM₁₀ and these months were not included here). This compare well with the calculations for the period 1991 – 1996 where approx. 60% of the mass concentration of PM₁₀ could be identified (Maenhaut/NILU, not published).

The total carbon (TC) content was quantified during the period 01.01.00 – 30.09.00. During these periods two different types of filter (quartz and glass fibre) were used. The glass fibre filters gave high blank values and is a probable explanation to the discrepancy between mass concentration of PM₁₀ and the sum of the chemical compounds (Figure 32 and Table 10).

Total carbon concentrations during 5 months in 2000 is given in Table 11, showing that the organic fraction makes up for about 86-95% of TC during this period. The increase in TC from April to May is due to an increase in OC (organic carbon) probably due to emissions of biogenic compounds at this time of the year. During summer concentrations of TC are relatively low while for September the concentration of TC increases again, mainly due to OC, but also EC (elementary carbon) increase considerably. The observed increase of EC, produced during

combustion, is indicative of anthropogenic emissions and long-range atmospheric contribution.

A high correlation between OC and EC for April and September may also indicate air transport from common source areas. A poorer correlation during May, June and July may be due to less frequent episodes with transport from such areas.

Table 11: Monthly mean, minimum and maximum of OC, EC and TC for Birkenes 2000.

Month	OC		EC		TC	
	Mean	(min-max)	mean	(min-max)	mean	(min-max)
April	1.45	(0.36–5.07)	0.23	(0.03–0.63)	1.68	(0.41–5.69)
May	2.08	(0.84–5.02)	0.19	(0.01–0.77)	2.27	(0.89–5.79)
June	1.20	(0.26–4.10)	0.13 ²⁾	(n.d.–0.64)	1.33	(0.26–4.73)
July	1.25 ¹⁾	(0.42–2.52)	0.07 ³⁾	(n.d.–0.27)	1.32	(0.42–2.55)
September	1.65	(0.57–7.53)	0.25 ⁴⁾	(0.01–1.09)	1.88	(0.57–8.56)

n.d. = not detected

All values in $\mu\text{g}/\text{m}^3$

1) Mean based on a total of 21 samples

2) Mean based on a total of 26 samples

3) Mean based on a total of 20 samples

4) Mean based on a total of 27 samples

Figure 33 presents weekly mean concentrations of PM_{10} for the coastal site Lista (100 km SW of Birkenes). It should be noted that Lista is by far more influenced by sea salts which results in a higher mean of PM_{10} at Lista compared with Birkenes, and particularly during winter. Peaks like those highlighted in Figure 28 will not be displayed in Figure 33 as the sampling period for Lista is one week compared with 24 hours at Birkenes. Taken into account the influence of sea salts at Lista, Figure 32, seems to correlate rather well with Birkenes strongly suggesting that the atmospheric levels in southern Norway is due to long-range transport.

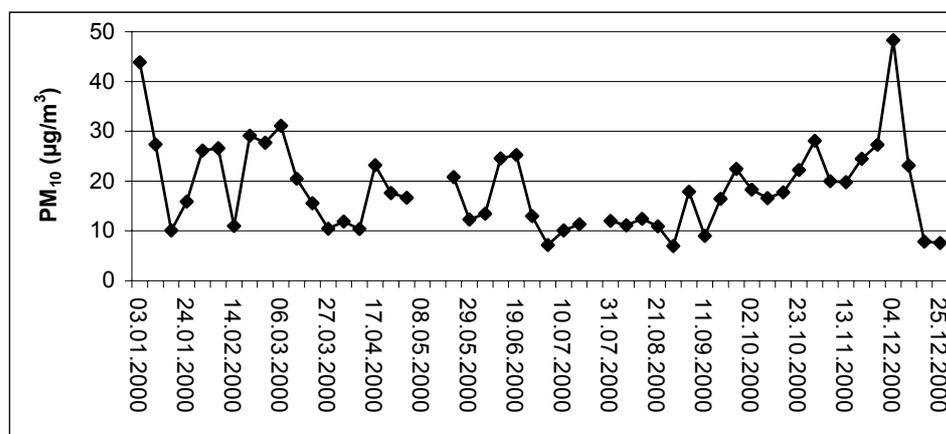


Figure 33: Mass concentration of PM_{10} for Lista based upon weekly means in 2000. No sampling was performed during the period 08.05.00 – 22.05.00 and 24.07.00 – 31.07.00.

3.2.1 Sampling instrumentation used at Birkenes

Sampling was performed with the Thermo Andersen PM₁₀ High Volume sampler on a 24 hours basis with a flow rate of 1630 m³/24 h during the period 01.01.00 – 04.10.00. During the periods 01.01.00- 29.03.00 and 22.07.00 – 21.08.00 glass fibre filters (Munktel MG 160; 8 x 10 inches) were used and during 29.03.00 – 20.04.00 quartz fibre filters were used (Munktel MK 360; 8 x 10 inches). During the periods 20.04.00 - 22.07.00 and 22.08.00 – 05.10.00 a second type of quartz fibre filters were used (Whatman QM-A; 8 x 10 inches).

During the period 04.10.00 – 31.12.00 sampling was performed with the Rupprecht & Patashnick Dichotomous Partisol-Plus (both PM₁₀ and PM_{2.5}) model 2025 operating with a flow rate of 24 m³/24 h. Teflon filters were used (Pall Gelman Zefluor; 47 mm).

Quantification of mass (PM₁₀) was done gravimetrically with filters being prepared at 20°C at 50% RH before and after exposure.

Quantification of elemental carbon, organic carbon and total carbon was performed using the Thermo Optical EC/OC method (Sunset laboratories Inc.)

3.2.2 Sampling instrumentation used at Lista

Sampling was performed with a Gent Stacked Filter Unit. PM₁₀ impactor inlet and two Nucleopore filters in a NILU filter container/holder. The first filter has a pore size of 8µm.

At a flow rate of 15-16 lpm this give a 50% efficiency cut-off at 2 µm EAD (equivalent aerodynamic diameter).

3.3 Measurements of physico-chemical aerosol characteristics at the Finokalia station, Crete, Greece

The measurements from Greece presented here aim to provide some first results from a characterisation study of atmospheric aerosols in the Eastern Mediterranean area where few data exist. High concentrations of PM₁₀ mass during summer has been observed correlated with photochemical activity and a considerable contribution of natural sources, such as Saharan dust, local dust resuspension and forest fires. It is very interesting to note the good correlation between very high PM₁₀ concentrations and elevated silica and iron concentrations, indicating Saharan dust events.

The atmospheric measurements from Greece presented in the current report refer to a detailed aerosol characterization experiment that was performed during 4 weeks in July 2000 and 1 week in January 2001 at a remote coastal site on the Greek Island of Crete. The sampling station at Finokalia is situated 70 km east of Heraklion at the top of a hilly elevation (130m a.s.l.). Details on the meteorological conditions encountered at Finokalia are given by Mihalopoulos et al (1997) and Kouvarakis et al. (2000). The main objective of the research work was to characterise the formation, accumulation, fate, and effects of ozone (O₃), other photochemical oxidants and fine particulate matter at different spatial and temporal scales in the Mediterranean area. The research project is financed by the European Commission under grant ENVK2-1999-00052 (SUB-AERO).

Aerosol scattering coefficients were measured with a three-wavelength integrating nephelometer (TSI model 3563). An aethalometer (Magee Sci.-Andersen Instruments) was used to determine black carbon (BC) concentrations in the winter period. In the summer period a Particle Soot Absorption Photometer (PSAP; Radiative Research, Seattle, WA, USA) was used for the BC measurements. The laser aerosol spectrometer (LASX, Particle Measuring Systems) was also used with 3-min time intervals throughout the summer and winter Finokalia campaigns. Detailed gaseous phase measurements for a number of photo-oxidants were continuously performed but in the current report only selected data from the aerosol studies are reported.

Berner Cascade Impactors with 10 impaction stages were employed, as well as a High Volume Impactor (Andersen GS2312 BL) for collection of size fractionated aerosol samples. The latter was deployed at a location 2 km inland from the main Finokalia sampling site. A number of micro-meteorological parameters were measured by a Vaisala portable weather station at Finokalia. The parameters included temperature, wind speed and humidity. Detailed characterization of the particulate matter (PM) physico-chemical characteristics was performed and the chemical analysis reveals the importance of specific components in the PM mass. Nucleation events were observed more often in the winter period compared to the summer and the aerosol mass concentration was lower in winter compared to summer data. High time resolution data for photo-oxidant species and aerosols are already available for determination of their dynamics in Eastern Mediterranean and for model comparison.

Particle size distribution in the aerosol submicron range (8-350) nm was measured with a Scanning Mobility Particle Sizer (SMPS). An example of results indicating

nucleation events is shown in Figure. Sampling of size fractionated ambient aerosol was performed by two Berner Cascade Impactors.

A standard Scanning Mobility Particle Sizer (TSI, Inc.), consisting of a TSI 3071 Electrostatic Classifier and TSI 3022 low flow rate Condensation Particle Counter was used. During the summer season the SMPS was set to sheath and inlet airflow rate of 9.0 and 0.9 l/min, respectively, to provide size range bounds 7.8–327 nm. In winter season sheath and inlet airflow rate of 10 and 1.0 l/min was used, respectively, which corresponds to size range bounds 7.5–316 nm. In both cases a preimpactor with nozzle 0.457 mm was used, giving 360 nm (summer) or 338 nm (winter) cut diameter. The instrument worked periodically with 60 s upward data scan, followed by 30 s downward scan. Using this procedure about 20.000 and 7.000 particle number size distributions were obtained for summer and winter season, respectively. The distributions were corrected for multiple charging (TSI SMPS software, Version 3.0).

During the summer campaign particle number concentration varied from $1-2 \times 10^3 \text{ cm}^{-3}$. The particle distributions were monomodal with concentration maximum around $d = 80-120 \text{ nm}$. The exception was July 14–15 where modes with maximum around $d = 40 \text{ nm}$ (July 14 in the morning) and 20 nm (July 15 in the afternoon) appeared, which lasted for several hours. Number distributions measured during the winter season were predominantly bimodal. Particle concentrations varied from 5×10^2 to $5 \times 10^3 \text{ cm}^{-3}$ with maxima around $d = 20-40$ and $d = 80-200 \text{ nm}$, respectively. As an example the number size distribution from July 14-15 is shown in Figure 35. The x- and y-axis show the time of day and the particle diameter d_p respectively. The z-component represents the number concentration. Number size distribution data from the winter campaign (January 9-10, 2001) are presented in Figure 36. During the winter period nucleation events were more often observed compared to the summer campaign and the background aerosol size distribution was considerable lower that in the summer.

Samples of atmospheric particles were collected and size segregated into ten size fractions by a Berner low-pressure cascade impactor (model 25/0.018/2). The inlet to the impactor provided an approximately $15 \mu\text{m}$ upper cut-off particle size. Samples were collected on Nuclepore foils greased by Apiezone L. Sampling was carried out in 24-hour intervals. During the period 10 – 19 July two impactors of the same type were used alternately (ICPF, Prague and “Demokritos”, Athens), after that the impactor from Prague was used until the end of campaign. Prior to the measurements both impactors were compared during two days of measurement of mass size distribution of urban aerosol in Athens. The agreement was very good. A typical size distribution from the summer measurements with the Berner impactor are shown in Figure 36. Concentration of PM_{10} close to $30 \mu\text{g}/\text{m}^3$ daily occurred during the summer period. Figure 37 shows a typical size distribution data from the winter period on the island of Crete. Much lower concentrations are observed during the winter mainly due to lower dust and Saharan dust contributions as well as due to lower photochemical activity and smaller local emissions on the island of Crete. In the winter period concentrations close to $20 \mu\text{g}/\text{m}^3$ are observed (see Figure 37).

A total of 21 mass size distributions were obtained. The distributions were predominantly bimodal with mode mean diameters around $0.3 \mu\text{m}$ and $5 \mu\text{m}$. In several cases an additional mode appeared at around $1 \mu\text{m}$. The raw size data were inverted into smooth size distributions by the MICRON code. The inverted distributions were integrated to obtain PM_{10} , $\text{PM}_{2.5}$, and PM_{10} . The results for the whole three week period are shown in Figure 38, whereas typical mass size distributions for the summer and winter periods at Finokalia are shown in Figures 39-40, respectively.

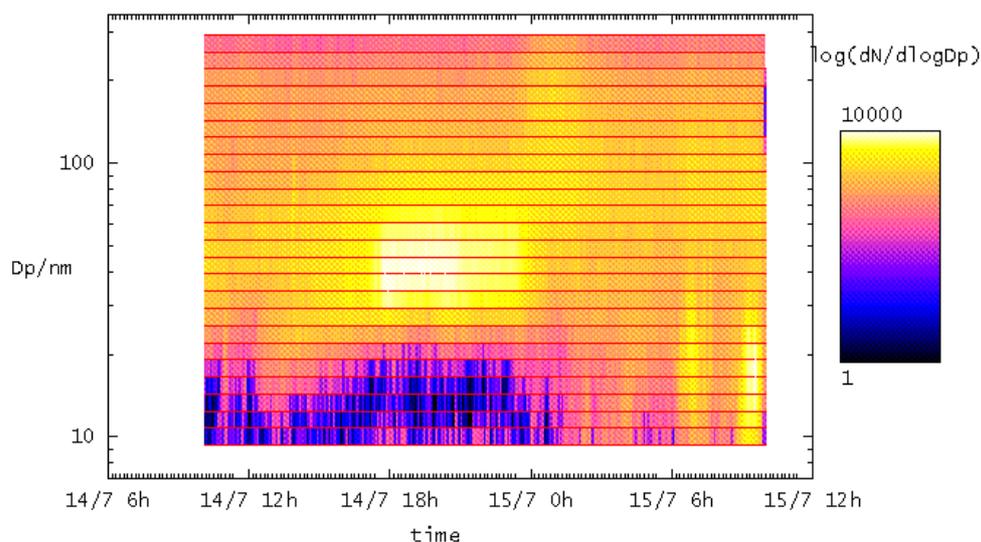


Figure 34: Plot of the particle number size distribution (Finokalia, from 10:00 h July 14, 2000 to 10:00 h July 15, 2000) where nucleation events are present.

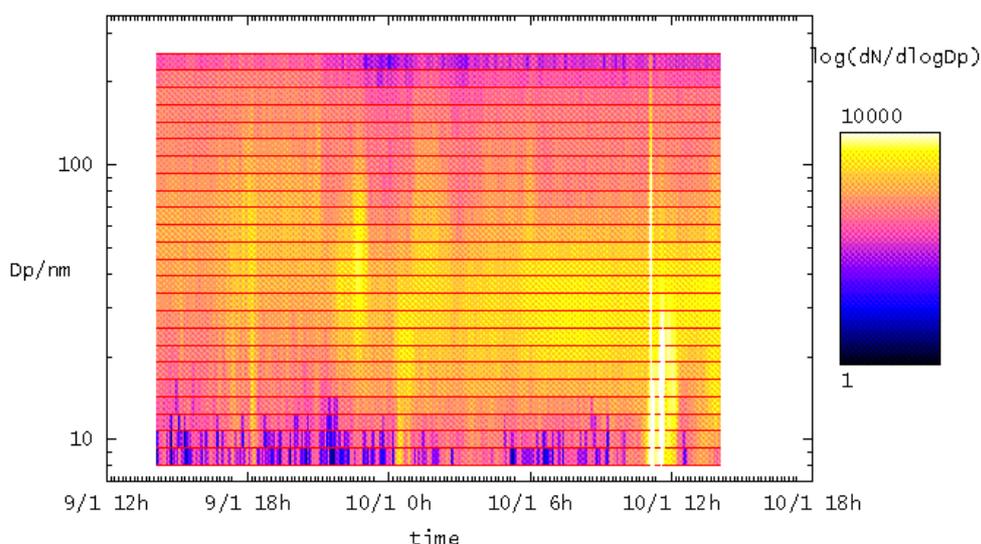


Figure 35: Plot of the particle number size distribution (Finokalia, from 12:00 h January 9, 2001 to 12:00 h January 10 2001) where nucleation events are present.

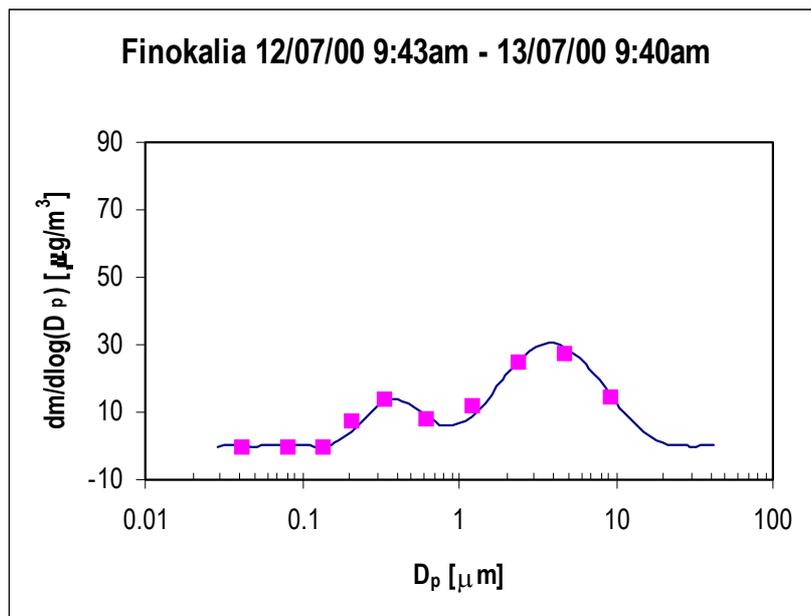


Figure 36: Typical particulate mass size distribution during the summer period on the island of Crete, Greece.

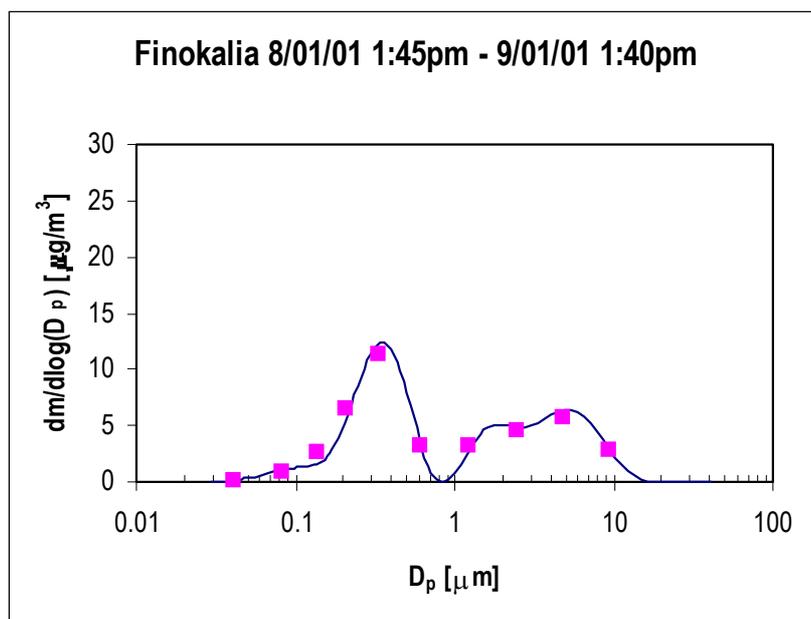


Figure 37: Typical particulate mass size distribution during the winter period on the island of Crete, Greece.

Measurements of the aerosol number size distribution were also performed with the use of a laser aerosol spectrometer (LASX) and a time series profile is shown in Figure 39.

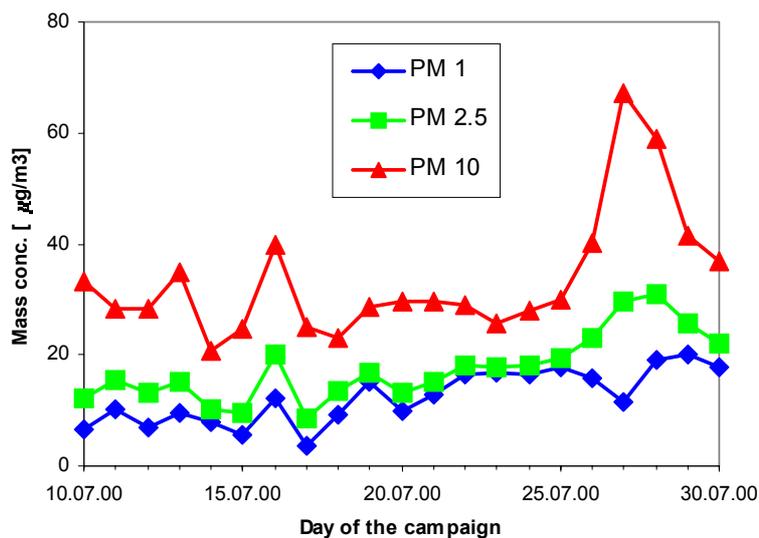


Figure 38: Particulate mass concentration as a function of sampling date.

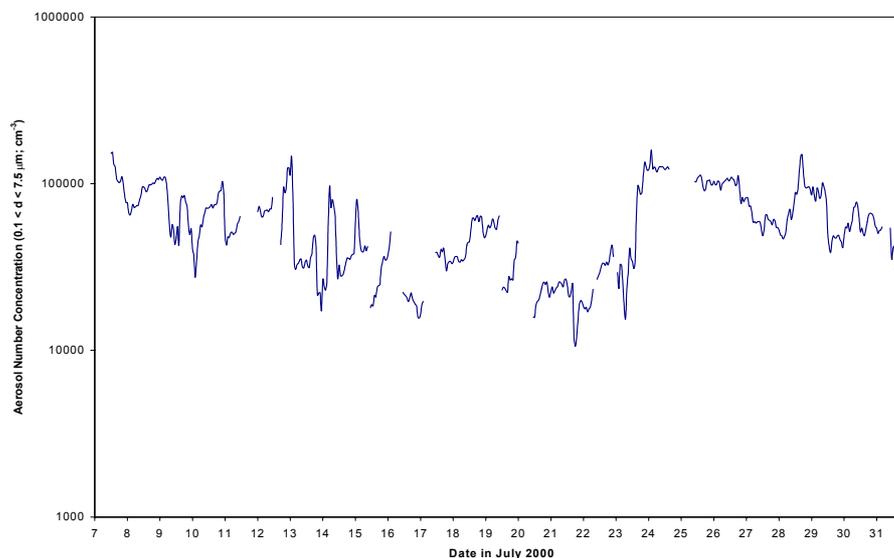


Figure 39: Number size distribution concentrations measured with a LASEX as a function of sampling date.

A detailed chemical analysis from the campaign is under progress for both the inorganic and organic part of the particulate matter characteristics. In Figure elementary (EC) and organic matter (OC) concentrations from TSP sampling on the island of Crete is presented. The EC/OC ratio is close to 0.2 which implies considerable emissions of primary organic matter (see Figure 40).

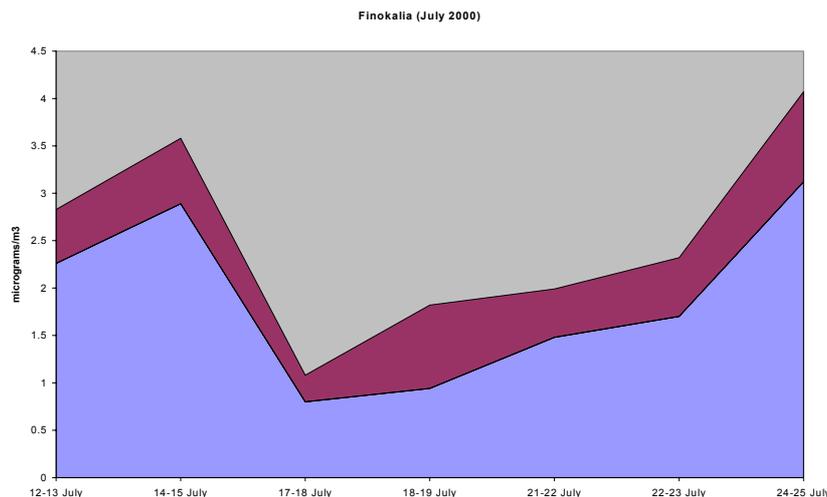


Figure 40: Elementary (brown) and organic carbon (blue) concentrations at the Finokalia station from Total Suspended Mass samples.

Particulate matter mass closure studies and chemical identification of the mass in the different sizes are very important components for the understanding of their sources and dynamics. A detailed chemical characterization study is under progress (see preliminary data from IC results in Figure 48 and Figure 49), however, preliminary results from PIXE measurements are presented. The samples were obtained from impactor measurements at Finokalia and were corrected for deposit thickness. Figure 41 shows the mass balance for different particle fractions where only a number of elemental oxides (Al_2O_3 , CaCO_3 , NaCl , Fe_2O_3 , K_2O , SO_3 , SiO_2 , TiO_2 , V_2O_5 , O, C, Na) were considered in this comparison. The results from the mass closure comparison with the gravimetric data are quite reasonable. It is expected that with the addition of inorganics that mass closure will be good.

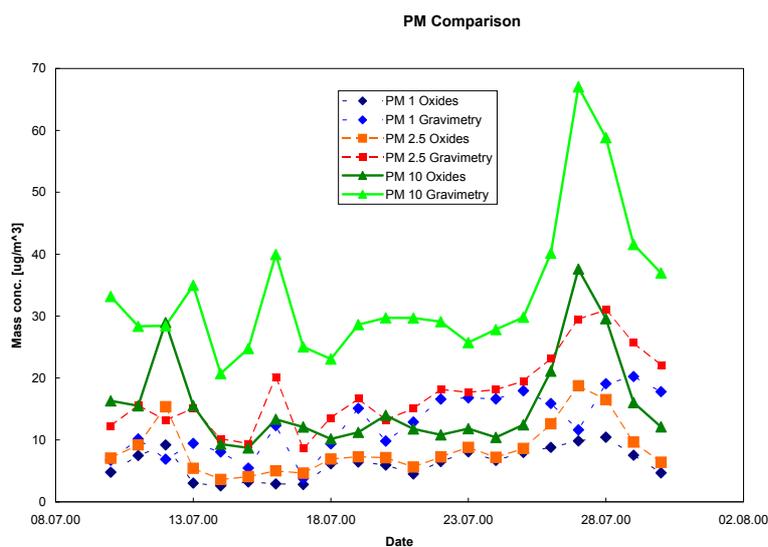


Figure 41: Mass closure between mass gravimetric measurements from impactors and PIXE analysis for a number of chemical species from the Finokalia station on the island of Crete, Greece.

In addition the mass size distribution (PM_{10} , $PM_{2.5}$, PM_{1}) for a number of chemical species is presented in Figure 42 – Figure 48 for measurements at Finokalia. The chemical analysis was also performed with the PIXE method. It is very interesting to note the high concentration of sulphur and chlorine (sea salt) as well as high concentrations of iron and silica in two periods close to 13 and 28 July 2000 where Saharan dust episodes occurred. The existence of trace species as heavy metals (lead) in the area is also evident.

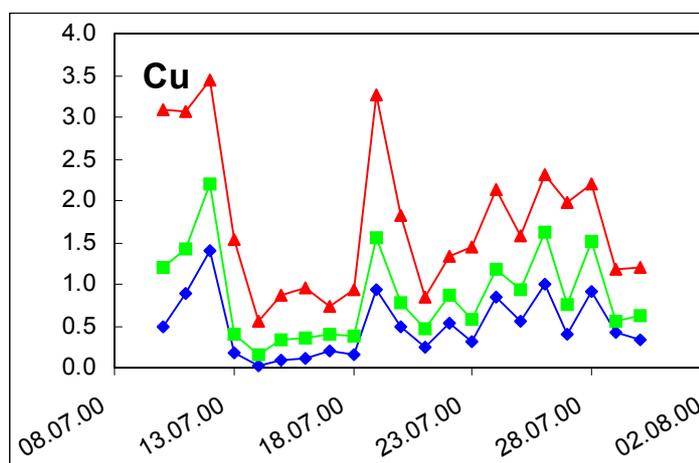


Figure 42: Mass size distribution of Cu at different sizes (PM_{10} : red; $PM_{2.5}$: green; PM_1 : blue) (ng/m^3).

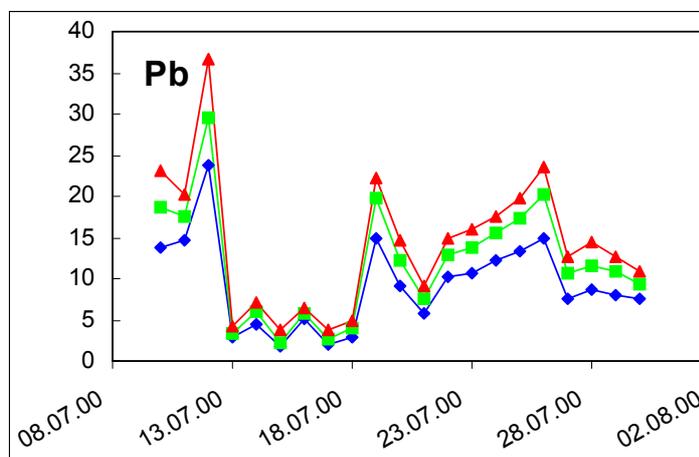


Figure 43: Mass size distribution of Pb at different sizes (PM_{10} : red; $PM_{2.5}$: green; PM_1 : blue) (ng/m^3).

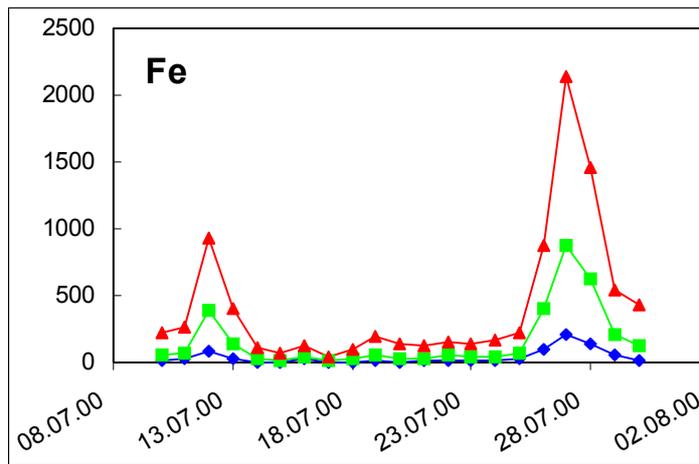


Figure 44: Mass size distribution of Fe at different sizes (PM_1 : blue; $PM_{2.5}$: green; PM_{10} : red) (ng/m^3).

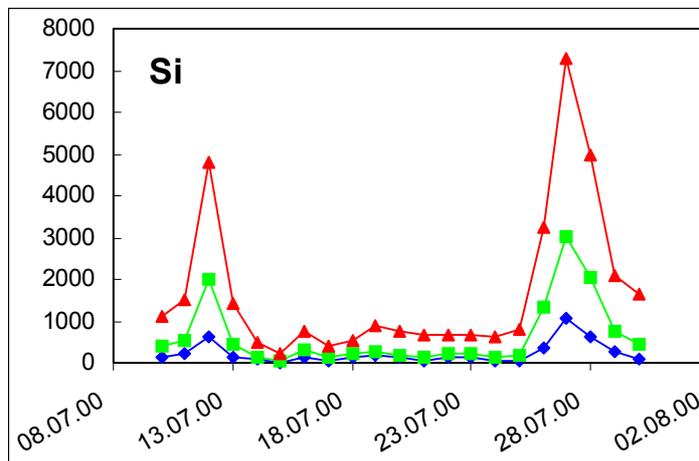


Figure 45: Mass size distribution of Si at different sizes (PM_1 : blue; $PM_{2.5}$: green; PM_{10} : red) (ng/m^3).

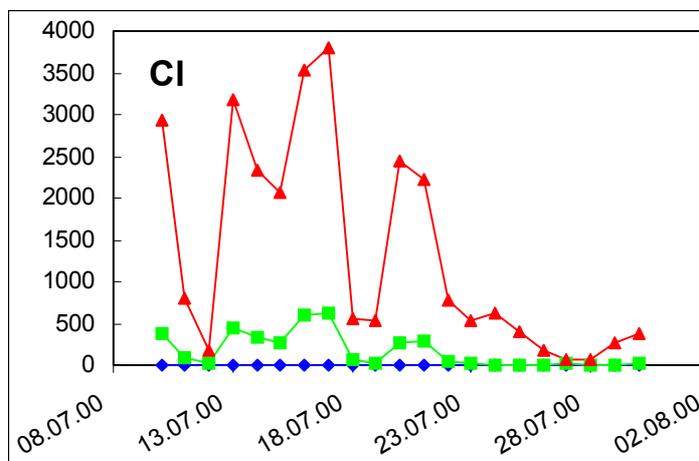


Figure 46: Mass size distribution of Cl at different sizes (PM_1 : blue; $PM_{2.5}$: green; PM_{10} : red) (ng/m^3).

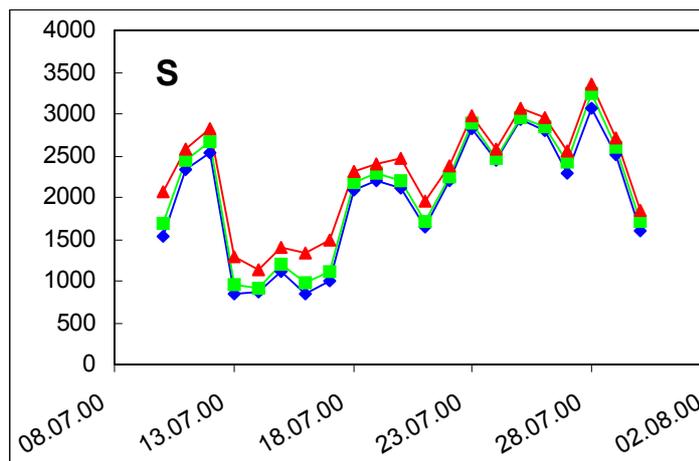


Figure 47: Mass size distribution of S at different sizes (PM_{1} : blue; $PM_{2.5}$: green; PM_{10} : red) (ng/m^3).

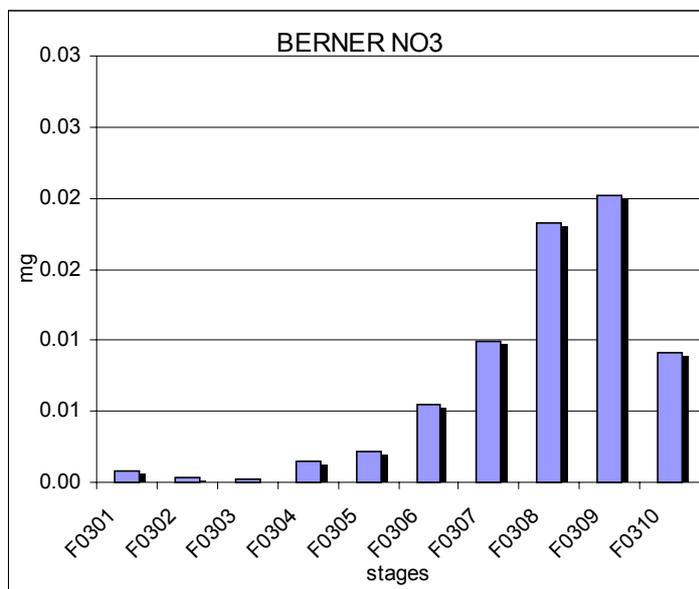


Figure 48: Typical Nitrate mass size distribution derived from IC analysis at the Finokalia station, Crete, Greece (summer 2000).

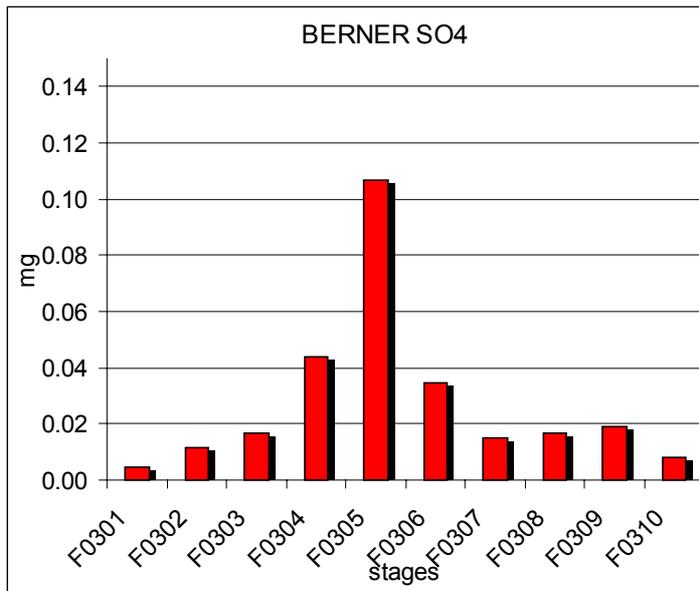


Figure 49: Typical Sulphate mass size distribution derived from IC analysis at the Finokalia station, Crete, Greece (summer 2000).

The data presented here give an insight into the aerosol characteristics in the Eastern Mediterranean area from which valuable information can be obtained for the EMEP programme. The detailed data set from the experimental campaign can be used for model evaluation studies and for the understanding of particulate matter emissions and their sources in the Mediterranean region.

4. Global Particulate Matter characteristics – An assessment of Particulate Matter Sources

The EMEP programme studies the particulate matter characteristics in Europe. However, there are a large number of studies outside the European framework from which valuable information can be obtained. From this perspective particulate matter measurements from United States and also some global aerosol physico-chemical characteristics are presented here. Furthermore, aerosols are a global issue and anthropogenic activities in Europe are closely paralleled in Northern America (NA), and the findings in NA may apply also to Europe.

Particulate matter in the atmosphere arises from both natural and anthropogenic sources. A significant amount of fine particulate matter concentrations is due to emissions from anthropogenic primary sources and due to secondary formation from gaseous precursors.

Particulate matter characteristics in the United States are presented in Figure 50. The California region shows considerably higher concentrations compared to other parts of the United States. PM_{10} concentrations are close to $30 \mu\text{g}/\text{m}^3$ throughout most of the US whereas $PM_{2.5}$ concentrations are higher in the Eastern and the industrialized part of the country with lower values in the Southwest and Upper Midwest. Chemical mass closure data for different areas in the US are presented in Figure 51 (EPA, 1996).

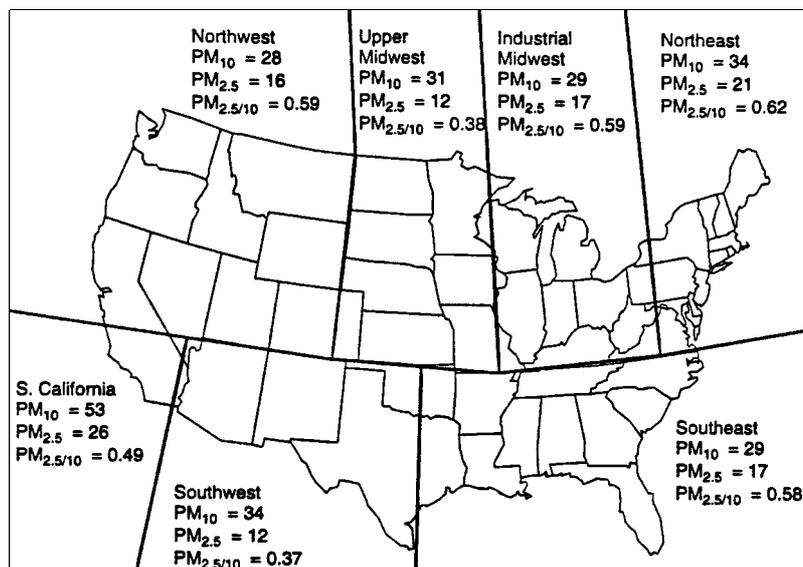


Figure 50: Particulate matter concentrations (PM_{10} and $PM_{2.5}$) in various parts of the United States (Adapted from McClellan and Miller, 1997. Data from U. S. EPA, 1996) (units $\mu\text{g}/\text{m}^3$).

The EMEP programme aims to produce similar mass closure figures for different European areas and identify differences in the chemical composition between high populated and industrialised areas in the central, northern and southern parts of Europe and the Mediterranean area.

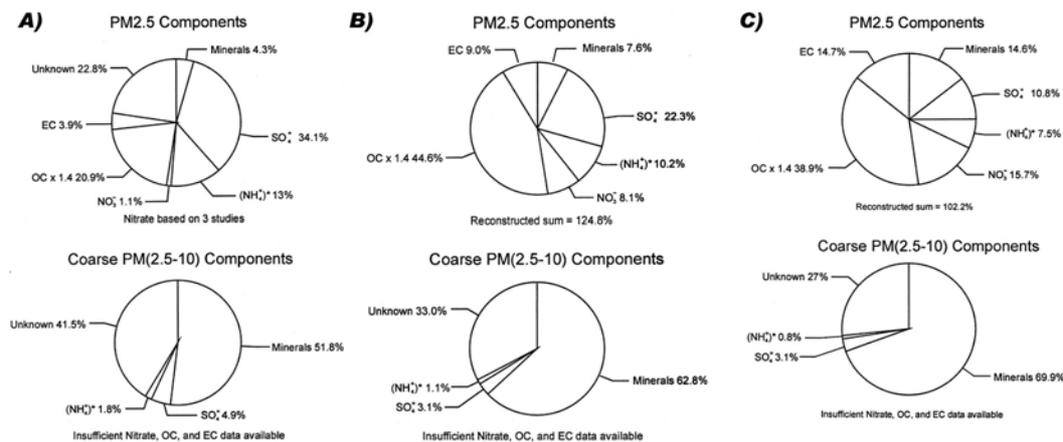


Figure 51: Chemical mass closure for particulate matter in the United States. $(NH_4^+)^*$ represents the concentration of NH_4^+ that would be required if all SO_4^- were present as $(NH_4)_2SO_4$ and all NO_3^- as NH_4NO_3 . The $(NH_4^+)^*$ represents an upper limit of NH_4^+ (A) Eastern (B) Central (C) Western (adapted from EPA, 1996).

Furthermore, it is interesting to compare the aerosol characteristics in different urban and rural sites around the globe as valuable information on their sources, transport, lifetime and dynamics can be determined. Figure 52 summarises data on aerosol mass measurements at different places around the world at both urban and rural sites. Different measurements methods were used and part of the data refer to TSP values and others refer to PM_{10} concentrations. Therefore the data have to be seen not as absolute values but mainly as order of magnitude concentration levels.

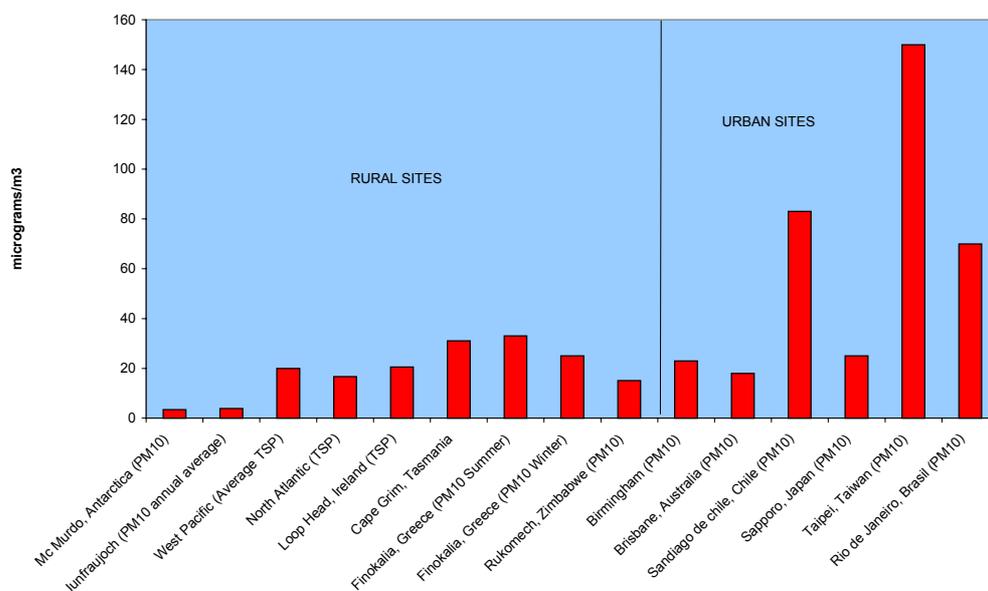


Figure 52: Particulate matter mass concentration at different urban and rural sites in the world (data from Mazzera et al., 2001; Pruppacher and Klett, 1997; Harrison et al., 2000; Rojas et al., 1990; Chen et al., 1997; Lazaridis et al., 2000; Colbeck et al., 2001).

It is evident that urban concentrations at mega-cities in Asia and south America are much higher than the U.S., European and Australian levels. Concentrations in rural areas at different global locations show similar levels of aerosol mass concentration whereas very low levels of aerosol mass were observed at remote sites such as Antarctica and the Jungfrauoch.

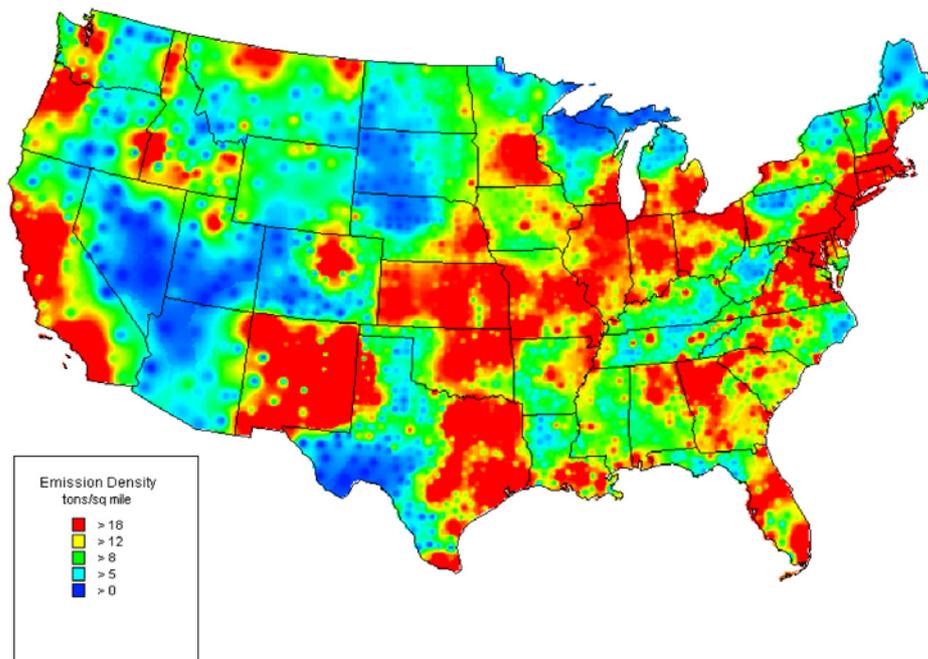


Figure 53: Density map of 1998 particulate matter (PM_{10}) emissions by County (EPA, 2000).

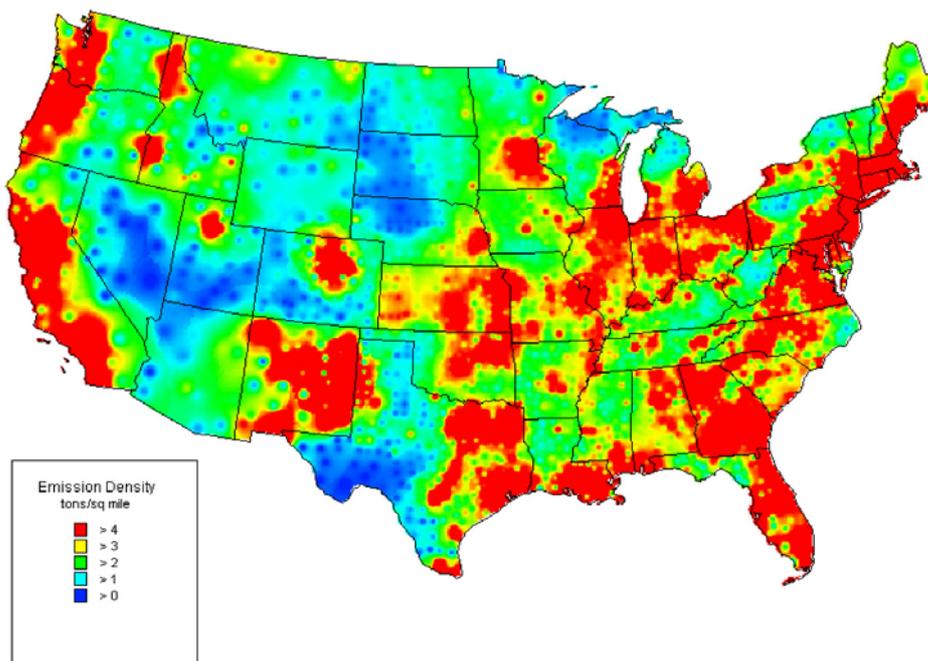


Figure 54: Density map of 1998 particulate matter ($PM_{2.5}$) emissions by County (EPA, 2000).

The understanding of the chemical composition/size distribution characteristics of particulate matter in the atmosphere and its relation to their sources and emission characteristics is important due to the fact that the chemical complexity of atmospheric aerosols requires consideration of their composition and sources and also due to a high degree of uncertainty about the size and composition of the particles that may be responsible for potential human health risk. Primary emissions are one aspect of the problem since secondary particles are the most important contribution to the ambient concentrations of particulate matter. For example primary emissions for PM₁₀ and PM_{2.5} in the United States for 1998 are presented in Figure 53 - Figure 54.

An understanding of atmospheric aerosol source apportionment is crucial for legislation since control costs for reduction of PM emissions are potentially very high. However, the source apportionment task for particulate matter is more complex than for gaseous species since a considerable fraction of atmospheric aerosol mass is formed via secondary processes in the atmosphere, which arise from the emission of anthropogenic and biogenic precursors.

In addition to the standard monitoring programme in EMEP it is necessary to perform more detailed studies on size distribution characteristics and chemical composition. The size distribution of aerosols is a critical factor influencing the extent to which particles penetrate into the respiratory tract. In addition, chemical characterization of PM is a critical factor that possibly influences their health implications.

The general methodology to apportion sources of contaminants in the atmosphere using a mass conservation and mass balance analysis is referred to as receptor modelling. Receptor models are based on the mass balance principle and consequently mass balance analysis with the scope to identify and quantify sources of pollutants in the atmosphere. An extensive dataset of chemical characteristics from ambient samples is needed for determining the contribution of various sources to ambient concentrations using receptor models. After the dataset is constructed a mass balance equation can be written for the m chemical species in the n samples originating from p independent sources (Hopke, 1997).

Seigneur et al. (1997) reviews in detail the recent status on receptor modelling and groups the receptor models into three major categories:

- Models that apportion primary PM using source information.
- Models that apportion primary PM without using source information.
- Models that apportion primary and secondary PM.

There are many techniques available in the different categories including US EPA regulatory tools for PM apportionment (CMB and PCA) as well as recent powerful research tools (e.g. Positive Matrix Factorization, Hybrid methods). Hybrid methods have been applied to apportion the secondary components of PM. Gray and Cass (1998) have combined modelling of air trajectories combined with receptor modelling to apportion the atmospheric fine carbon particle concentrations in the Los Angeles area. Additionally, ambient data have been used through inverse modelling to improve emission source inventories (Kleeman and Cass, 1999).

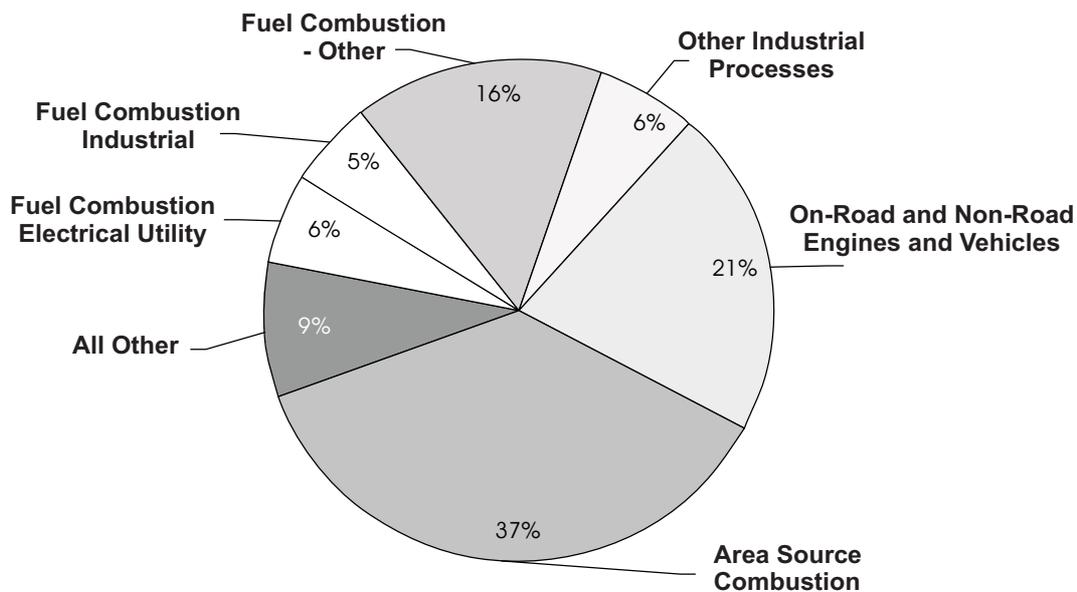


Figure 55: Primary particulate matter PM_{10} emissions by principal source categories for 1998 for non-fugitive dust sources (EPA, 2000).

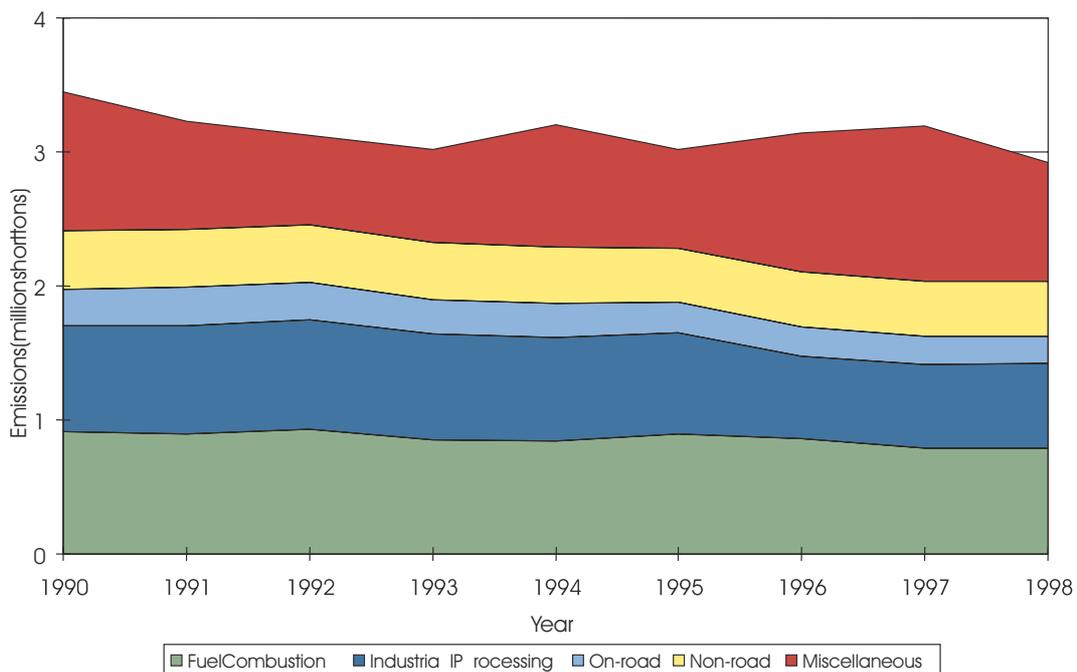


Figure 56: Particulate Matter ($PM_{2.5}$) trends in direct emissions excluding fugitive dust sources from 1990 to 1998 in the United States (EPA, 2000).

In the US EPA's Office of Air Quality Planning and Standards (OAQPS) there are two recommended methods for the PM-10 SIP (State Implementation Plan) guidance document. One important requirement for receptor models is the construction and update of databases on source profiles as well as speciated PM data for PM_{2.5} and PM₁₀. Source apportionment studies in the European framework will be a useful tool in the understanding of the emission characteristics and their contribution on the ambient particulate matter concentration.

In two recent documents from the U.S. EPA (EPA, 1996; EPA, 2000) a comprehensive study on particulate matter emission characteristics and source identification was performed for the United States. Figure 55 presents a pie chart for 1998 PM₁₀ emissions by source category in the United States. In this figure the fugitive dust contribution is not included. Interesting information on PM emissions in United States by sector are presented recently by the US EPA (EPA; 2000) where also trends in specific emission categories are included (see Figure 56). The same information on PM emissions and source apportionment in Europe will be a valuable input for the EMEP framework for further providing quantitative information on the effect of country emissions on the regional aerosol concentrations and their chemical characteristics.

An overview of particulate matter source strength (PM_{2.5}) is shown in Figure 57. The main emission sources of particulate matter in the atmosphere can be separated into two main groups. First, the primary organic particles which originate directly from anthropogenic and biogenic sources and secondly, secondary organic particles that arise from oxidation or photochemically induced transformations. Sulphate particles arise from anthropogenic sources such as power plants whereas there is a biogenic production through the dimethyl sulphide (DMS) production (Lovelock et al., 1972). In addition resuspended dust (Rodriguez et al., 2001), forest fires (Wotawa and Trainer, 2000) and sea salt (Smith et al., 1993) are also important sources of ambient aerosol concentrations and their impact on the total optical depth. In addition, the aerosol optical depth and Angstrom exponent from Polder satellite data are presented in a global picture in Figure 58. The Angstrom exponent are presented in a global picture from data of the POLDER satellite. The Angstrom exponent gives the wavelength dependence of scattered light between 670 and 865 nm. It is evident from the satellite pictures that continental transport of aerosols may contribute to aerosol mass concentration and this has to be considered in the study of the aerosol levels in Europe through the EMEP programme.

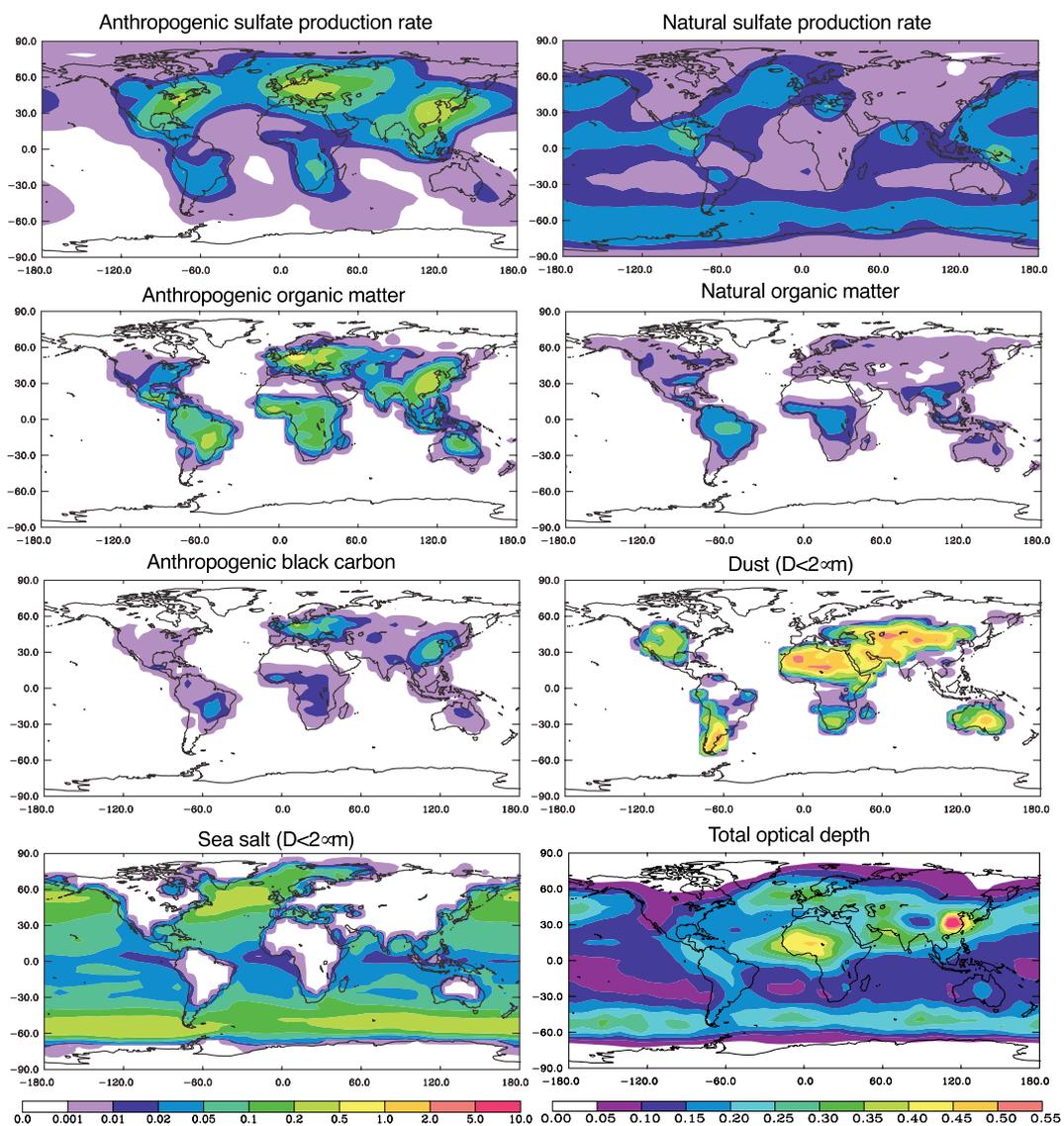
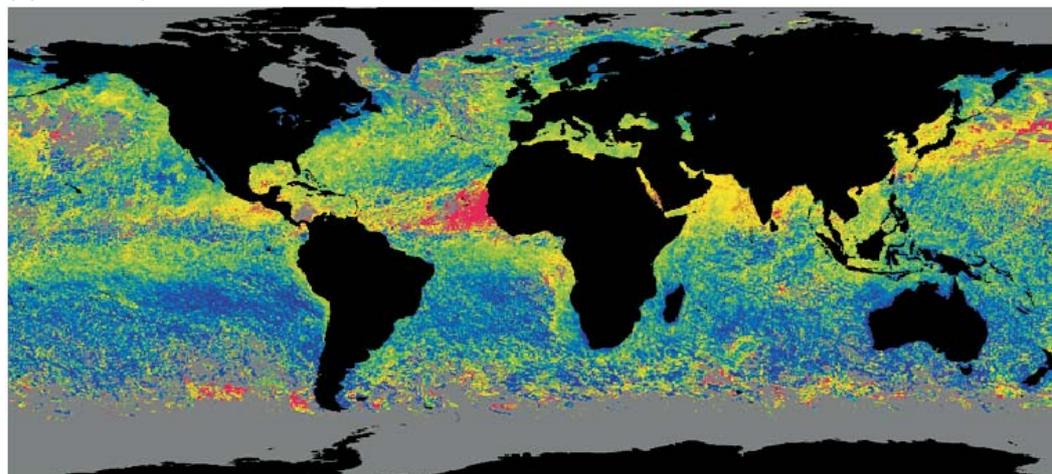


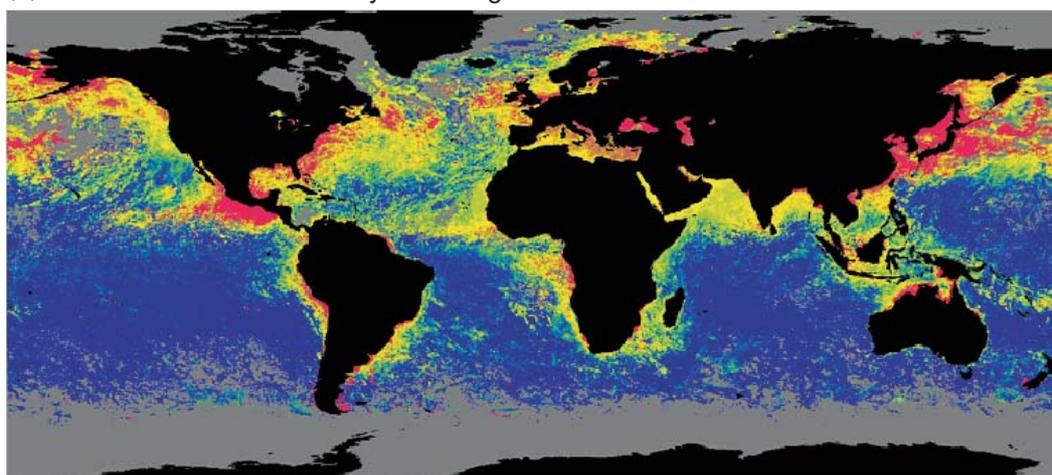
Figure 57: Source strength (Kg m⁻² hr⁻¹) as an annual average from a number of aerosol sources (Cooke et al., 1999; Gong et al., 1997; Lioussé et al., 1996; Penner et al., 1999; Prospero, 1999). The total optical depth is evaluated from the ECHAM/GRANTOUR model (Penner et al., 1999).

(a) May 1997 Aerosol optical depth at 865 nm from Polder on ADEOS



0.00.5 0.10.20.30.4

(b) May 1997 Angstrom coefficient



-0.21.2 0.00.20.40.60.81.0

POLDER data: CNES/NASDA; Processing: LOA/ LSCE

Figure 58: Aerosol optical depth and Angstrom exponent from Polder satellite data in May 1997 (Deuze et al., 1999). Dust from North Africa exhibits the largest optical depth. The Angstrom exponent aims to quantify the size difference of the aerosols where a large Angstrom exponent suggests small aerosols. The area around the continents show this feature whereas Saharan dust that is comprised of coarse particles has a small Angstrom exponent (Deuze et al., 1999).

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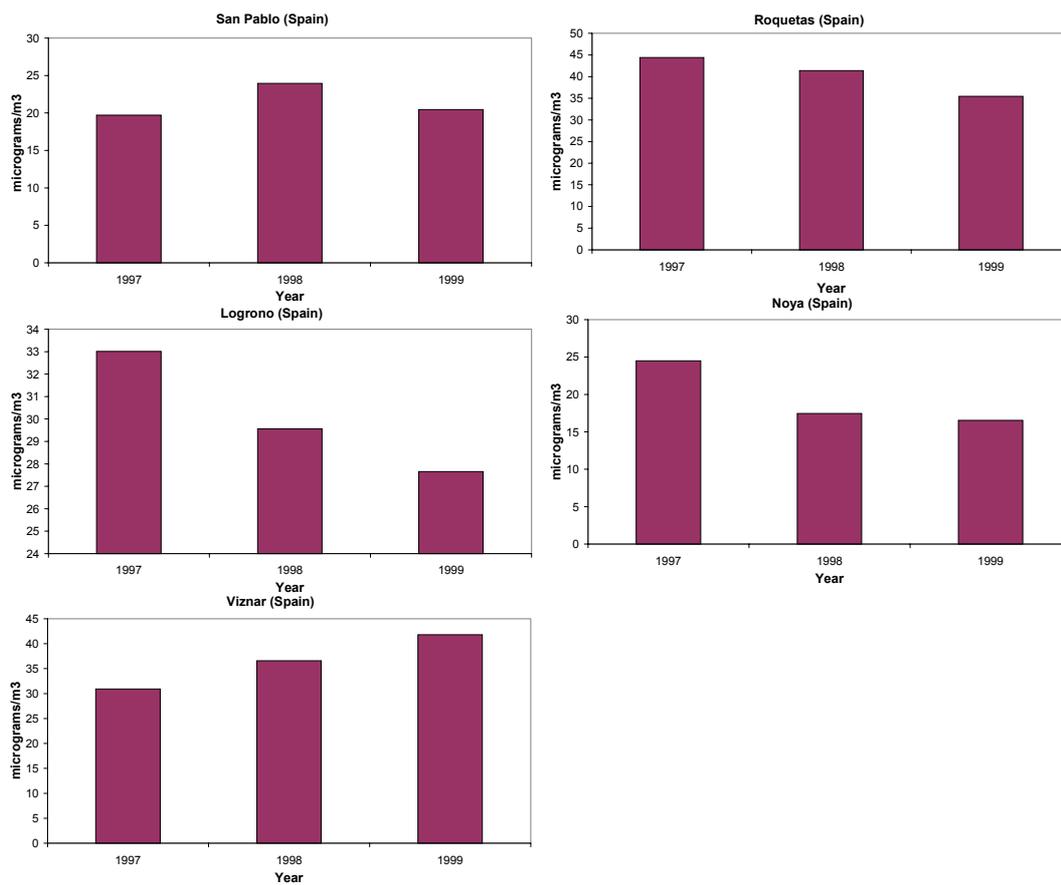
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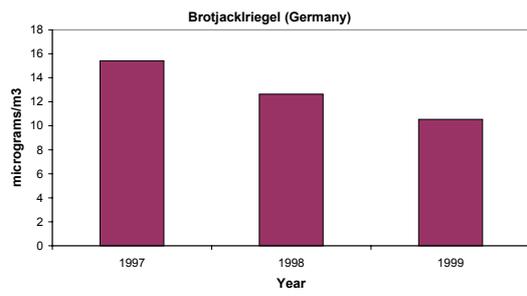
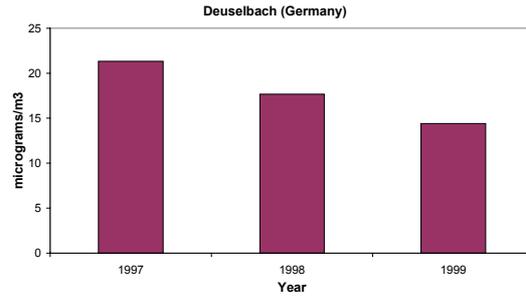
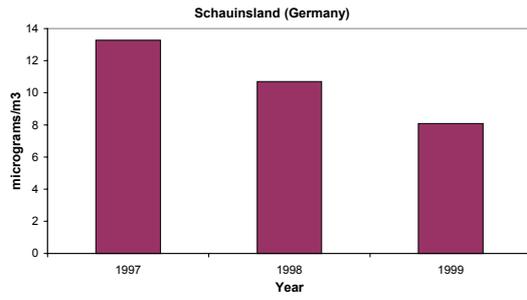
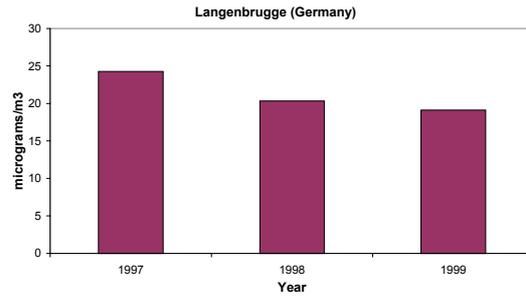
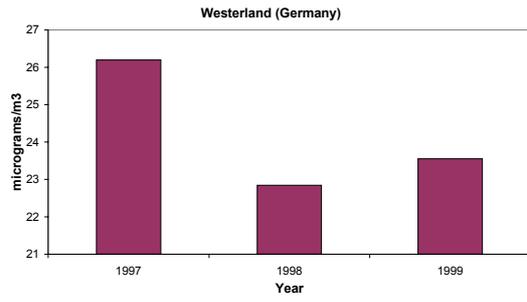
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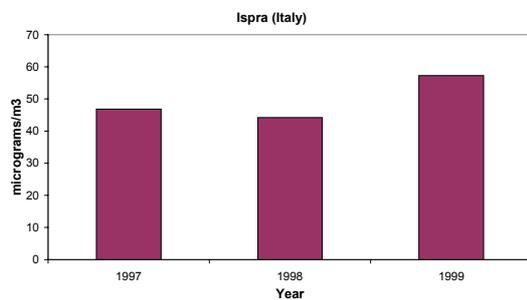
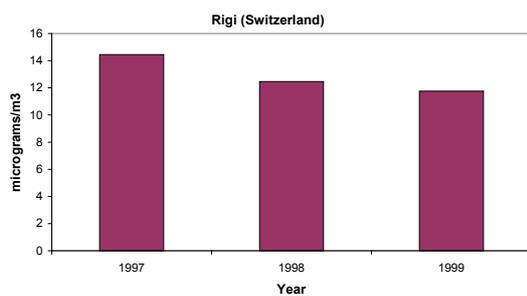
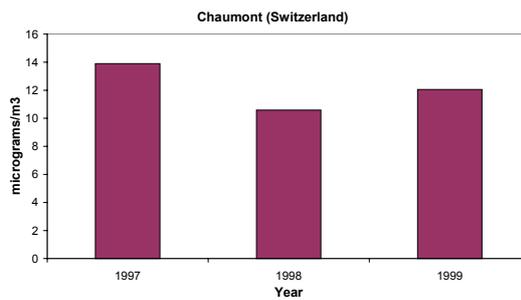
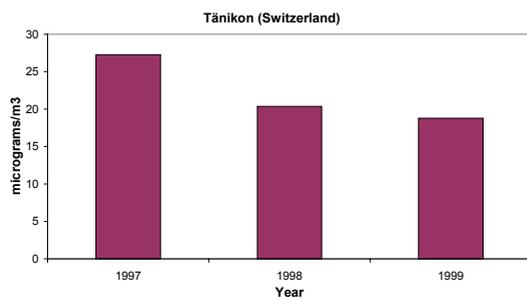
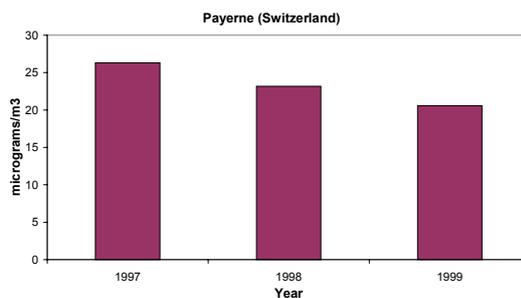
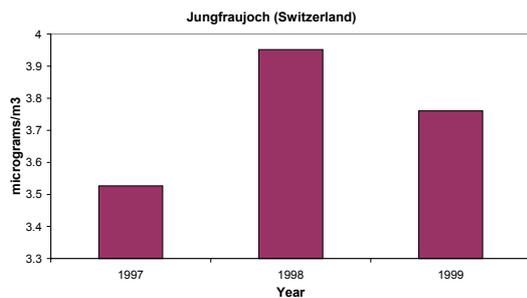
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Appendix 1

Annual average PM data from EMEP stations in the period 1997-1999







Appendix 2

Time Series of Particulate Matter Concentrations ($\mu\text{g}/\text{m}^3$) at EMEP Stations (1999)

