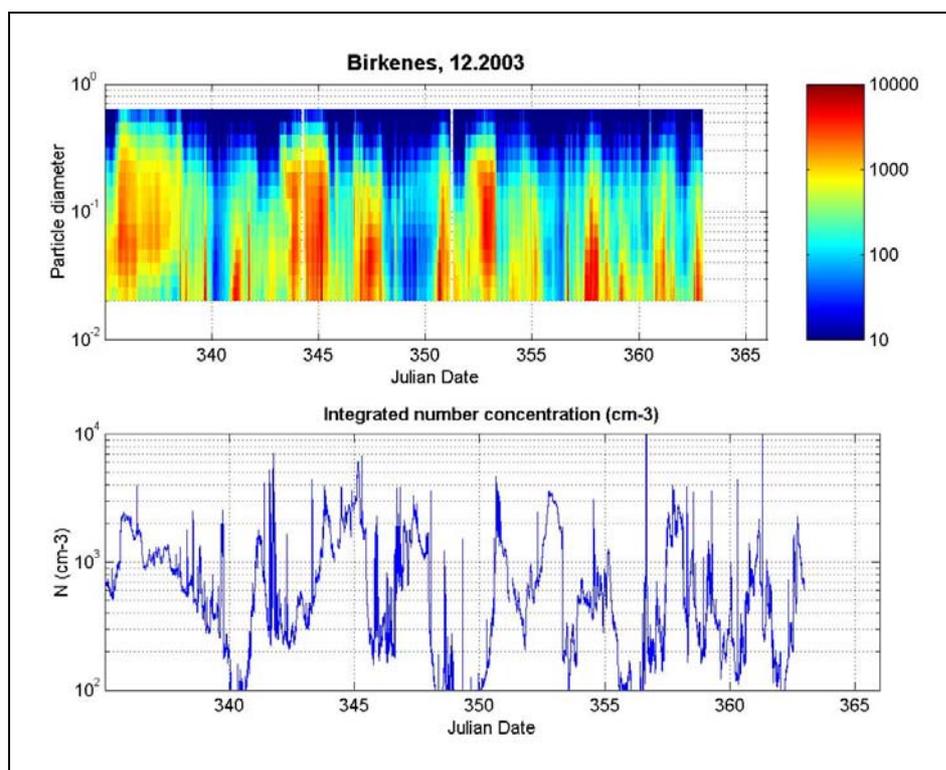


Measurements of Particulate Matter: Status Report 2004



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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:
Status Report 2004**



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Summary

This report contains six separate contributions on recent EMEP, or highly EMEP related activities with respect to airborne particles. A summary of the findings is given below.

Measurements of PM₁₀ within EMEP were taken up at two more sites in 2002 compared to the preceding year. Additionally weekly measurements of particulate suspended matter were started at four more sites. The total number of sites is, however, small and the sites cover a rather small part of Europe.

None of the EMEP sites exceeded the PM₁₀ annual limit value for the protection of human health, set by EU in the first Daughter Directive. The corresponding 24-hour limit, was slightly exceeded at a site in northern Italy in 2002.

All EMEP sites should be representative for a larger region, and are not necessarily background sites. It was emphasized in last year's status report that many countries such as Germany, Spain, United Kingdom, Poland, and Switzerland clearly had lower rural values of PM₁₀ than corresponding values at urban centres and hotspots indicating a significant contribution of local sources on a local scale. This points of course at a larger PM problem in Europe than that indicated by the EMEP sites. The European Environment Information and Observation Network (EIONET) of the EU is important in this connection, and consists of a large number of sites.

PM_{2.5} mass was measured at a subset of the EMEP PM₁₀ network during 2002. Several sites measured relative high PM_{2.5} concentrations compared to the corresponding PM₁₀ concentrations indicating large fractions of fine particles. No limit value has been set for PM_{2.5} mass in EU. PM_{2.5} standards from the United States EPA exist, however, and a site in Austria could have been in conflict with this standard in 2002.

Preliminary results from the carbon measurement campaign, which took place between 1st July 2002 and 1st July 2003, have been given in this year's status report. Fourteen EMEP sites took part in the sampling of PM₁₀ with CEN approved, or equivalent samplers. All samples were collected on pre-baked quartz-fibre filters, which were weighed before and after exposure, and analysed in one laboratory at NILU.

The main focus of the campaign was to address the level of carbonaceous material present in ambient aerosols at representative rural background sites in Europe, as there is a strong need for more knowledge concerning this parameter. An instrument that corrects for charring during analysis has been used to quantify elemental carbon (EC) and organic carbon (OC) for all samples collected. The chemical measurements will include analysis of the water-soluble organic carbon and the water-insoluble organic carbon as well as LC/MS analysis of levoglucosan for some of the samples. Levoglucosan is a tracer for aerosols emitted from biomass burning. These analyses are not yet completed and will be reported later.

The EC annual average for all sites in the campaign varied between 0.14–1.86 $\mu\text{g C m}^{-3}$. Taking into account the presence of approximately 10% hydrogen as well as trace levels of other elements, by multiplying the concentration of EC by a factor 1.1, EC was estimated to account for 1.1–5.4% of the PM_{10} mass on an annual basis.

In general the concentration of EC and the EC/TC ratio increased from summer to winter, TC being total carbon, i.e. EC+OC.

The annual mean concentration of OC for all sites in the campaign varied between 1.17–7.90 $\mu\text{g C m}^{-3}$. In order to take into account oxygen, nitrogen and hydrogen bound chemically to carbon and not included in the EC/OC analysis, the OC concentrations at the urban background sites and the “Near-city” site, were multiplied by a factor 1.6. A corresponding factor of 2.0 was applied for the rural background sites and the rural site. Organic matter (OM) was in this way estimated to account for 12.6–44.9% of the PM_{10} mass.

The concentrations of OM increased from summer to winter except at the Scandinavian sites and at the Slovakian site where OM concentrations were higher in summer than in winter.

The total carbonaceous material, EC+OM, accounted for 13.7–49.5% of the PM_{10} mass. As much as 61.6% of PM_{10} mass could, however, be accounted for by carbonaceous matter at the Portuguese site during winter. The lowest EC+OM contributions to the PM_{10} mass were found at the west coast of Ireland, not exceeding 15% in any season.

This report contains two contributions on particle number measurements, from southern Norway at Birkenes, and from Crete with measurements at the Finokalia site and onboard a vessel cruising in the eastern Mediterranean. Finokalia is a coastal remote site in the north of the island.

This report presents some of the results from 2003 obtained with the new Differential Mobility Particle Sizer (DMPS) instrument installed at Birkenes (NO01), which measures aerosol size distributions in the diameter range between 19.0 nm and 643.2 nm.

The report gives e.g. an example of repeated particle formation events at Birkenes during a 9-day period in early spring where high particle number concentrations are correlated with the appearance of new small Aitken particles, most likely due to local nucleation events. Also the dynamic growth of the Aitken particles to accumulation size on the time scale of 1-3 days was observed. Over a period of a day it is observed that the Aitken particles grow to accumulation size, repeatedly fuelled by newly appearing small particles. These nucleation events stop at night and resume in the morning of the next day. This diurnal variation in the production of new particles supports the hypothesis that these particles are of biogenic origin. During nighttime the growth process of the Aitken particles to accumulation size continues.

The frequency of nucleation events in 2003 at Birkenes was largest around spring and summertime. This seasonal variation has been observed at similar sites.

An episode probably dominated by long-range transport of aerosols to Birkenes is also presented. Only a few occurrences of small Aitken particles can be seen during this episode. The aerosols may have been primary particles that are locally emitted. However, as Birkenes is a regional background station far away from major emission sources, this is rather unlikely.

The particle number measurements in the eastern Mediterranean are parts of the EU funded SUB-AERO project. One of the objectives was investigating the new particle formation and particles' fate in the Mediterranean. Particle number concentration measurements were performed using a Scanning Mobility Particle Sizer (SMPS) and an optical particle counter (PMS Las-X) both in summer and winter.

The concentrations of ultrafine particles (< 30 nm) were highest during the winter with several peaks going up to about $1 \cdot 10^4 \text{ cm}^{-3}$. Corresponding concentrations measured during the summer campaign had an average value of about $1 \cdot 10^2 \text{ cm}^{-3}$ at Finokalia and an average value about $5 \cdot 10^1 \text{ cm}^{-3}$ aboard Aegeon vessel.

The particle concentrations for size fraction 30–100 nm were mostly around $1 \cdot 10^3 \text{ cm}^{-3}$ for all measurements but reached $5 \cdot 10^3 \text{ cm}^{-3}$ in the middle of the winter campaign.

The concentrations of the 100–300 nm size fraction were higher during the summer ranging from $1 \cdot 10^3$ to $5 \cdot 10^3 \text{ cm}^{-3}$ aboard the boat and from $2 \cdot 10^2$ to $2 \cdot 10^3 \text{ cm}^{-3}$ at Finokalia. Corresponding concentrations measured during the winter varied from $1 \cdot 10^2$ to $1 \cdot 10^3 \text{ cm}^{-3}$.

The particle distributions measured during the summer were typically monomodal with concentration maximum around 70–150 nm at Finokalia and around 100–220 nm aboard Aegeon. Number distributions measured during the winter were predominantly bimodal with modes around 40–100 and 120–220 nm, respectively.

Examples of nucleation events for both winter and summer have been given. Comparing the winter and summer periods the nucleation events were observed more frequently in winter (3 events during seven days) than in the summer (1 event during three weeks).

This is probably due to the lower concentration of PM_1 and PM_{10} observed in the winter period resulting in lower coagulation scavenging of small nuclei and also due to higher biogenic emissions from plants and higher humidity which increase the driving force for the particle growth. It is also noted that both in winter and summer the nucleation events were accompanied by a decrease of the Aitken mode position down to about 40 nm.

The second contribution from the eastern Mediterranean aims at a characterization of particulate matter including Saharan dust. Research studies have shown that

there is a consistent pattern of geographical variability in Europe with lower concentrations of particulate matter in the far north and higher concentrations in southern countries. This is due to natural emissions of unsaturated hydrocarbons (including isoprene) that are highly reactive, and high emissions of anthropogenic gaseous and aerosol pollutants in southern Europe. Furthermore, the Mediterranean region is characterized by North African desert dust besides sea spray.

The current study focus on the PM₁₀ and PM_{2.5} measurements between 2003 and 2004 at the Acrotiri research monitoring station in the north-western part of Crete. The average PM₁₀ mass concentration for the whole period was 35.1 µg/m³ with quite variable PM₁₀ summer concentrations reaching 80-90 µg/m³. During the winter period the PM₁₀ concentrations were in general lower and the variability smaller. However, a Saharan dust event in February led to an average PM₁₀ level of 193.2 µg/m³. The continuous monitor recorded 528 µg/m³ as maximum concentration during the episode.

It is evident from the PM₁₀ concentrations that high aerosol concentrations occur during specific short time intervals (1-3 days) due to the influence of southern winds originating from Africa.

The PM_{2.5} measurements were started much later than the PM₁₀ measurements and only 3 months of data have been available so far. The average PM_{2.5} concentration during this measurement period was 26.3 µg/m³. There were three periods in which the PM_{2.5} concentration reached high values, and which correspond to Saharan dust episodes in the area. The last Saharan dust episode was very intense with a considerable reduction in the visibility and with PM_{2.5} concentration reaching 454 µg/m³.

The origin of the particulate matter concentrations in the area of Crete has been studied using a statistical analysis of the data and back trajectory modelling using the HYSPLIT4 Model, developed by the Air Resources Laboratory of the National Oceanic and Atmospheric Administration (NOAA). Also a statistical analysis has been performed using the back-trajectory data for each day of the measurement period with maps for the origin of the air masses. Four segments have been used corresponding the north-west (NW), north-east (NE), south-west (SW) and south-east (SE) directions.

The results showed that the frequency of occurrence of the air masses from the south direction was very small during the summer period and consequently no significant contribution from this direction can be seen. During the autumn the PM₁₀ levels from the northern directions were lower than during summer, and there is an increase in the frequency of air masses from the southern directions with higher PM₁₀ concentration levels.

During winter the PM₁₀ concentration was low when air masses were transported from the northern directions and elevated with transport from the southern directions. In addition, during the spring period there was a general increase in the PM₁₀ concentration.

A non-metric Multi Dimensional Scaling (MDS) analysis was further applied to study the particulate matter. In the MDS analysis the particulate matter data have been organized in clusters with the same statistical characteristics of the meteorological parameters. The results strongly indicated three clusters. The high PM events have similarity with the outbreaks of African dust, the low PM events have similarity with high storm events, whereas the major part of the data can be organized in a third cluster in which typical meteorological conditions occurred with air masses originating from the northern directions.

The last contribution to the status report focus on the aerosol load from surface to the top of the atmosphere as expressed through the aerosol optical depth. The Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO) started a new global network of aerosol optical depth (AOD) observations in 1999 through the PMOD/WRC in Davos. These are measurements of direct solar radiation in four narrow spectral bands centred at 862, 500, 412 and 368 nm. The instrument measures the sun radiation and can only give results during clear non-cloudy daylight.

Data quality control includes instrumental tests, like detector temperature, solar pointing staying within specifications, and automated cloud screening by two different algorithms. Data that were applied had been filtered with a tight cloud and sun-tracking filter. Instruments are calibrated in a calibration hierarchy including laboratory standards and master instruments that are calibrated at high altitude sites like Jungfraujoch, Switzerland or Mauna Loa, Hawaii.

The aerosol optical depth at Ny-Ålesund is normally relatively high during the spring compared to the corresponding summer measurements. This is due to the Arctic haze phenomenon that has been observed for more than fifty years. Aerosol removal mechanisms are suppressed during winter and spring, and the cold and stable winter Arctic boundary layer may extend into the industrial sources in the south. In summer precipitation occurs resulting in a fast removal of aerosols as well as water-soluble gases

The observatory at Jungfraujoch is located at about 3600 m asl and is frequently in the free troposphere above the boundary layer. The aerosol optical depth is therefore normally extremely low permitting this site to be used for calibration of master sun photometers

The observatory at Hohenpeißenberg is located in the southern part of Germany about 60 km southwest of Munich and some 20 km north of the rising Alpine mountain range. The observatory's altitude is, however, nearly 1000 m asl and the observatory is above the polluted surface layer much of the time.

When comparing the AOD at 500 nm from the three sites it was seen that the AOD at Hohenpeißenberg was a factor of ten higher than at Jungfraujoch on one or two days in March and September, but during winter both observatories had very low and more equal aerosol optical depths. It is evident that the optical depth at 500 nm in the Arctic at Ny-Ålesund generally was lower than that at Hohenpeißenberg, but also much higher than at Jungfraujoch.

During March and September when all three sites had valid monthly averages, the Arctic AOD at 500 nm were about three to four times higher than the high altitude averages from Jungfrauoch and about one half to one third of the Hohenpeißenberg monthly averages in 2003.

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Measurements of Particulate Matter: Status Report 2004

1. Measurements of particulate matter in EMEP during 2002

by J. Schaug and A.-G. Hjellbrekke

Measurements of PM₁₀ were taken up at two more sites in 2002 compared to the preceding year. Italy replaced the sampling of suspended particulate matter (SPM) at Montelibretti (IT01) with daily PM₁₀ measurements. Also Slovakia started PM₁₀ measurements at Stará Lesná (SK04), sampling being weekly. Slovakia additionally took up weekly SPM measurements at four more sites. SPM measurements were continued at the high altitude site at Jungfrauoch (CH01), and at the Spanish sites. The Spanish SPM measurements are, however, supplemented with PM₁₀ data. Annual averages of PM₁₀ from 2002 are given in Figure 1.1. Sites with at least 75 per cent data coverage and daily sampling were included; results from the one Slovakian site (SK04) and the Norwegian measurements at Lista lighthouse (NO99) on the southern coast have therefore not been presented in Figure 1.1.

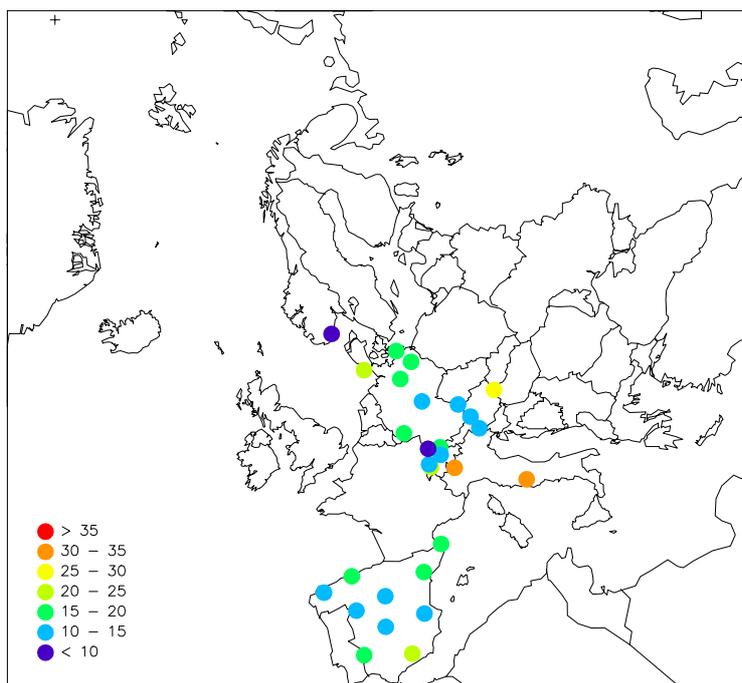


Figure 1.1: Annual 2002 averages of daily PM₁₀ mass measurements. Unit $\mu\text{g}/\text{m}^3$.

The carbon measurement campaign with measurements of elementary (EC) and organic carbon (OC) (Chapter 2) also included the PM₁₀ mass. The PM₁₀ results from the campaign are presented in Figure 1.2. This campaign started 1 July 2002 and continued for one year, the results in Figure 1.2 are therefore shifted a half

year compared to the results in Figure 1.1. The carbon measurements are described in Chapter 2.

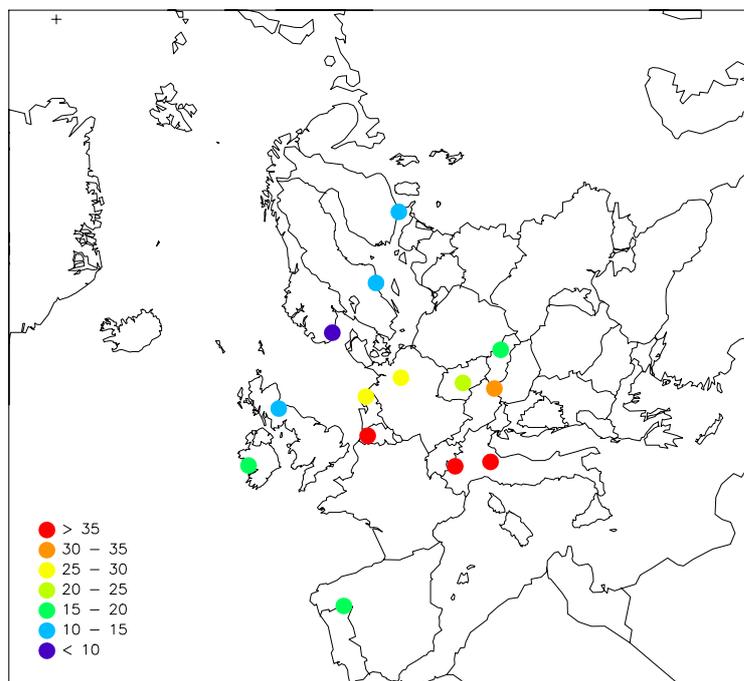


Figure 1.2: Annual averages of PM₁₀ mass measurements from the carbon campaign 1st July 2002–1st July 2003. Samples were taken 24 hours once every week. Unit µg/m³.

It should be noted that in addition to the comparatively small PM₁₀ EMEP network, a much larger network with rural stations, urban background sites as well as measurements in hotspots is run in Europe in the European Union (EIONET; <http://www.eionet.eu.int/>) and data collected in the AIRBASE data base. The network, together with the 2001 results, was presented in last year's report (Kahnert, 2003).

Table 1.1 gives the median values of particulate matter in air, mostly daily samples, from 2002. The location of sites as well as more statistics and metadata have been given by Hjellbrekke (2004).

None of the EMEP sites exceeded the annual limit value for the protection of human health, set by EU in the first Daughter Directive. This limit value is reduced every year and was 44.8 µg/m³ for 2002, taking the margin of tolerance into account. The corresponding 24-hour limit, which should not be exceeded more than 35 times a calendar year, was 65 µg/m³ in 2002, again margin of tolerance added. This limit was slightly exceeded in northern Italy at the Ispra site IT04 (37 higher values in 2002).

Table 1.1: Median of daily particulate matter measurements 2002. Sites included have at least 75% data capture. All sites with PM₁₀ measurements except the two below are given in Figure 1.1.*

| Site code | PM ₁₀ µg/m ³ | PM _{2.5} µg/m ³ | SPM µg/m ³ |
|-----------|---------------------------------------|--|--------------------------|
| AT0002 | 24.9 | 18.7 | |
| AT0004 | 9.9 | | |
| AT0005 | 9.7 | | |
| CH0001 | | | 2.1 |
| CH0002 | 18.2 | 13.2 | |
| CH0003 | 16.9 | | |
| CH0004 | 9.8 | 7.1 | |
| CH0005 | 10.6 | | |
| DE0001 | 17.0 | | |
| DE0002 | 16.0 | 11.0 | |
| DE0003 | 7.5 | 5.5 | |
| DE0004 | 13.0 | 10.0 | |
| DE0005 | 9.0 | | |
| DE0007 | 12.0 | | |
| DE0008 | 9.0 | | |
| DE0009 | 14.6 | | |
| ES0007 | 19.0 | 10.0 | 34.0 |
| ES0008 | 16.0 | 8.0 | 26.0 |
| ES0009 | 8.0 | 6.0 | 12.0 |
| ES0010 | 18.0 | 12.0 | 31.0 |
| ES0011 | 13.0 | 10.0 | 21.0 |
| ES0012 | 13.0 | 7.0 | 19.0 |
| ES0013 | 10.0 | 6.0 | 14.0 |
| ES0014 | 14.0 | 10.0 | 22.0 |
| ES0015 | 10.0 | 6.0 | |
| ES0016 | 10.0 | 7.0 | 16.0 |
| IT0001 | 31.0 | | |
| IT0004 | 27.7 | | |
| NO0001 | 5.3 | 4.3 | |
| NO0099* | 14.0 | 5.4 | |
| SK0002* | | | 12.4 |
| SK0004* | 15.3 | | |
| SK0006* | | | 14.4 |
| SK0007* | | | 22.3 |

* weekly samples

All EMEP sites should be representative for a larger region, but are not necessarily background sites. Kahnert (2003) noted last year that many countries such as Germany, Spain, United Kingdom, Poland, and Switzerland clearly had lower rural values of PM₁₀ than corresponding values at urban centres and hotspots indicating a significant contribution of local sources on a local scale. This points of course at a larger PM problem in Europe than that indicated by the EMEP sites.

Figure 1.3 presents the annual averages of $PM_{2.5}$ mass during 2002. The sites undertaking measurements of $PM_{2.5}$ mass during 2002 also reported data the preceding year; there were no changes in the network. The data from the Ispra site in Italy, IT04, had about 60 per cent data coverage during 2002 and the Norwegian site NO06 collects weekly samples; both sites are missing in Figure 1.3. The $PM_{2.5}$ mass at Ispra was about $23 \mu\text{g}/\text{m}^3$ indicating that the PM_{10} mass of $27.7 \mu\text{g}/\text{m}^3$ could contain a comparatively large fraction of fine particles. A comparative large amount of fine particles in the PM_{10} mass occurred at several sites as can be seen from the median values in Table 1.1.

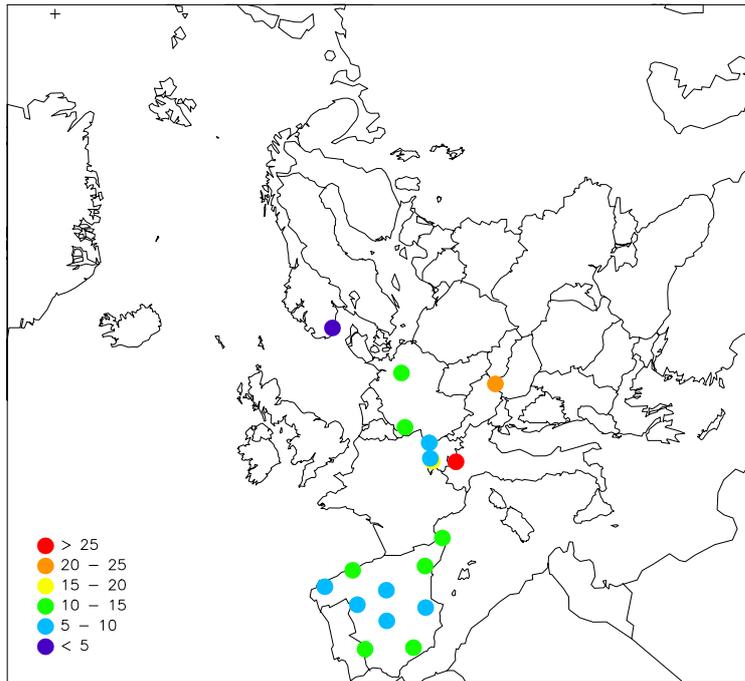


Figure 1.3: Annual 2002 averages of daily $PM_{2.5}$ mass measurements. Unit $\mu\text{g}/\text{m}^3$.

No limit value has so far been set for $PM_{2.5}$ concentrations in EU. The revised $PM_{2.5}$ standards from the United States EPA is $15 \mu\text{g}/\text{m}^3$ for annual arithmetic mean, allowing for an average of multiple community oriented monitors and averaged over 3 year. The corresponding standard for 24-hour averages is the 98th percentile concentration not to exceed $65 \mu\text{g}/\text{m}^3$, averaged over 3 years and maximum population oriented monitor in an area. The annual arithmetic average from the site Illmitz AT02, being $23.4 \mu\text{g}/\text{m}^3$, was higher than the annual limit value in the US standard. The 98th-ile of the 24-hour $PM_{2.5}$ concentration from this site in 2002 was slightly higher than the corresponding US standard.

2. Preliminary results from the EMEP EC/OC campaign

by K.E. Yttri and M. Kahnert

2.1 Summary

In this chapter preliminary results from the EMEP EC/OC campaign has been presented. The main focus of the campaign has been to address the level of carbonaceous material present in ambient aerosols at representative rural background sites in Europe, as there is a lack of knowledge concerning this parameter. The dataset is somewhat unique containing weekly concentrations of elemental carbon (EC), organic carbon (OC) and PM₁₀ for 14 sites in 13 European countries for an entire year. An instrument that correct for charring during analysis has been used to quantify EC and OC for all samples collected. The dataset will be extended by including analysis of the water-soluble organic carbon and the water-insoluble organic carbon as well as LC/MS analysis of levoglucosan for some of the samples in the dataset. Levoglucosan is a tracer used to address the contribution of aerosols emitted from biomass burning.

The annual average of EC for the sites included in the campaign varies between 0.14–1.86 $\mu\text{g C m}^{-3}$. By multiplying the concentration of EC ($\mu\text{g C m}^{-3}$) by a factor 1.1, taking into account the presence of approximately 10% hydrogen as well as trace levels of other elements, EC was found to account for 1.1–5.4% of PM₁₀ on an annual basis. In general the concentration of EC and the EC/TC ratio increased from summer to winter, TC being total carbon, i.e. EC+OC.

The annual average of OC for the sites included in the campaign varies between 1.17–7.90 $\mu\text{g C m}^{-3}$. In order to account for oxygen, nitrogen and hydrogen not included in the EC/OC analysis, the OC ($\mu\text{g C m}^{-3}$) concentration at the urban background sites and the “Near-city” site were multiplied by a factor 1.6. A factor of 2.0 was applied for the rural background sites and the rural site. Using these conversion factors OM (organic matter) was found to account for 12.6–44.9% of PM₁₀. The concentrations of OM increased from summer to winter except at the Scandinavian sites and at the Slovakian site where OM concentrations were higher in summer than in winter. Total carbonaceous material, EC+OM, accounted for 13.7–49.5% of the PM₁₀. However, as much as 61.6% of PM₁₀ could be accounted for by carbonaceous matter at the Portuguese site during winter. The lowest fraction of EC+OM in PM₁₀ was found for Ireland, not exceeding 15% in any season.

2.2 Introduction

Carbon species in aerosols are found in the form of organic carbon (OC), “elemental” or black carbon (EC or BC), and carbonates. OC compounds are observed both in the fine and in the coarse size fraction, EC mainly occurs in the fine fraction, whereas carbonates are mainly found in coarse particles. The contribution of OC to the total aerosol mass can be significant (Heintzenberg, 1989; Kahnert et al., 2004) and even dominant (Xu et al., 2000). Comprehensive reviews on organic atmospheric aerosols can be found in the articles by Jacobsen et al. (2000) and by Saxena and Hildemann (1996).

The environmental relevance of OC and EC comprises a large number of topics, such as human health, which is mainly a local and regional issue, and direct and indirect climate forcing, which mainly are global issues. Organic acids also play a role in rainwater acidification (Keene and Galloway, 1984), and organic peroxy radicals contribute to the ozone production by reacting with NO_x . Organic aerosols emitted from vegetation (Fehsenfeld et al., 1992) and other primary biological aerosol particles (PBAP) are significant for the formation of oxidants and the global carbon cycle.

In spite of its abundance and significance this fraction of the atmospheric aerosol remains poorly characterised, resulting in an incomplete picture of health effects and climate impact. The OC fraction can account for 10% to 70% (Turpin et al., 2000) of the fine particle mass, depending on the region (White, 1990). It consists of virtually thousands of different individual components, originating from a variety of anthropogenic and natural sources, and it occurs in aerosols with highly variable physical properties. This makes it difficult to obtain sufficient measurement information and to develop reliable model parameterisations.

Long-term monitoring information on EC and OC is not yet available on a regional scale, moreover, the importance of including EC and OC monitoring within EMEP has previously been emphasised by Kahnert et al. (2004). Monitoring of EC and OC needs to rely on both robust and cost-efficient techniques. In order to assess the feasibility of performing EC and OC monitoring on a regular basis and to obtain an overview on a regional scale of the spatial and temporal variability of EC and OC in Europe, a one-year campaign has been carried out at 14 sites in 13 European countries.

The EMEP EC/OC campaign was conducted for one full year (2002.07.01–2003.07.01). Table 2.1 gives an overview of the sampling sites included in the campaign, their site-category and the respective sampling equipment used. Aerosol sampling has been performed using CEN approved or equivalent PM_{10} gravimetric samplers, collecting one 24h sample every week (starting Tuesday mornings). Aerosols were collected on pre-heated quartz-fibre filters. After exposure the filters were sent back to NILU for analysis.

Sampling of atmospheric aerosols for subsequent analysis of the carbonaceous content has proven to be challenging. Semi-volatile OC condensed onto particles trapped by the filter, might evaporate during continued sampling. This is known as a negative artefact. Semi-volatile OC is known to adsorb onto filter-material during sampling and is recognized as a positive artefact as the amount of OC on the filter increases although no particulate OC has been added (Turpin et al., 1994; McDow and Huntzicker, 1990). The positive artefact is enhanced by the fact that pre-baked quartz fibre filters are used for sampling. Pre-baking the filters will activate them and facilitate the adsorption of semivolatile OC to the filter surface.

The positive artefact can be more pronounced in areas with low levels of particulate OC as the difference between the quartz-fibre filters capacity of adsorbing vaporous OC and the filter loading of particulate OC can be really small. This can be overcome by increasing the particulate OC loading on the filter

either by increasing the sampling time or the sampling volume. The positive artefact has been shown to decrease as the filter face velocity increases (McDow and Hunzicker, 1990). This should be kept in mind when comparing concentrations of OC obtained from samplers operating at different filter face velocities.

Both positive and negative artefacts may occur during integrated sampling, however there is no consensus concerning which effect prevails. There are several approaches to correct for negative and positive artefacts (McDow and Hunzicker, 1990; Mader et al., 2001) and the QBQ-approach (Quartz behind Quartz) (quantifying the positive artefact), described by McDow and Hunzicker (1990), is used in monitoring networks. However, it is beyond the scope of this EMEP EC/OC campaign to adapt any of these approaches due to economy, scientific benefit and infrastructure.

A number of different approaches exist for quantification of carbonaceous material associated with atmospheric aerosols. An intercomparison test (Schmid et al., 2001) has shown that levels of TC show rather low variability regardless of the analytical approach applied. Analysis of EC and OC show more variable results and only methods that correct for charring during analysis (TOT/TOR-methods) or prevent charring were recommended based on the intercomparison test reported by Schmid et al. (2001). In the present study quantification of EC and OC was performed using the Thermo Optical EC/OC method (Sunset laboratories Inc.). This instrument uses Thermo Optical Transmission to correct for charring during analysis. One instrument has been used to quantify all the samples collected in the campaign, in order to avoid systematic differences in the dataset.

In this chapter preliminary results, concentrations of EC, OC, TC and PM₁₀, from the EMEP EC/OC campaign are presented. WSOC (Water-soluble Organic Carbon) and WINSOC (Water-insoluble Organic Carbon) analysis are performed on selected parts of the dataset and analysis of functional groups will follow. Likely has LC/MS-analysis of levoglucosan been undertaken for parts of the dataset.

As seen in Table 2.1 the sampling sites are categorized into four different classes, and are likely influenced by different major sources. This should be kept in mind when comparing the results from the different sampling sites. The sites in Finland (Virolahti), Norway (Birkesnes), Sweden (Aspvreten) and Ireland (Mace Head) are all classified as rural background, whereas a “Near-city” site (JRC, Italy) and urban background sites (Ghent, Belgium and S.P.C, Italy) are amongst the sampling sites in the central parts of Europe. This might lead to the impression of a more pronounced north-south gradient than can be justified.

Table 2.1: Sampling sites in the EMEP EC/OC campaign, their site category and sampling equipment used.

| Country | Sampling site | Site category | Aerosol sampler | Filter size | Flow rate |
|-----------------|--------------------------------------|------------------|------------------|-------------|--------------------------|
| Austria | Illmitz (AT02) | Rural Background | Partisol | 47 mm | 16.7 l min ⁻¹ |
| Belgium | Ghent (BE02) | Urban Background | Gent Filter Unit | 47 mm | 17 l min ⁻¹ |
| Czech Republic | Košetice (CZ03) | Rural Background | FH 95 SEQ | 47 mm | 38 l min ⁻¹ |
| Finland | Virolahti (FI17) | Rural Background | KFG | 47 mm | 38 l min ⁻¹ |
| Germany | Langenbrügge (DE02) | Rural Background | Hi-Vol (Digitel) | 150 mm | 500 l min ⁻¹ |
| Ireland | Mace Head (IE31) | Rural Background | KFG | 47 mm | 38 l min ⁻¹ |
| Italy | Ispira (JRC) (IT04) | Near-city | KFG | 47 mm | 38 l min ⁻¹ |
| Italy | San Pietro Capofiume (S.P.C.) (IT08) | Urban Background | Gent Filter Unit | 47 mm | 17 l min ⁻¹ |
| The Netherlands | Kollumerwaard (NL09) | Rural Background | KFG | 47 mm | 38 l min ⁻¹ |
| Norway | Birkenes (NO01) | Rural Background | KFG | 47 mm | 38 l min ⁻¹ |
| Portugal | Braganza (PT01) | Rural Background | Hi-Vol (Sierra) | 8 x 10 inch | 1133 l min ⁻¹ |
| Sweden | Aspvreten (SE12) | Rural Background | Gent Filter Unit | 47 mm | 17 l min ⁻¹ |
| Slovakia | Stara Lesna (SK04) | Rural Background | Partisol | 47 mm | 16.7 l min ⁻¹ |
| United Kingdom | Penicuik (GB46) | Rural | Partisol | 47 mm | 16.7 l min ⁻¹ |

2.3 Elemental carbon

The annual mean concentration of EC varies by a factor of 13 between the site with the highest concentration of EC (Italy, JRC) ($EC_{\text{Annual mean}} = 1.86 \mu\text{g C m}^{-3}$) and the site with the lowest concentration of EC (Norway) ($EC_{\text{Annual mean}} = 0.14 \mu\text{g C m}^{-3}$), being a “Near-city” site and a rural background, respectively. The annual mean EC concentration exceed $1 \mu\text{g C m}^{-3}$ for only 5 of the 14 sites, namely the sites in Austria, Belgium, Czech Republic and Italy (JRC and S.P.C). The lowest concentrations are in general observed at the sites in Scandinavia and at the British Isles, whereas the highest ones are reported for the sites in the central, eastern and southern parts of Europe (Figure 2.1). Average EC concentrations of $1.3 \mu\text{g C m}^{-3}$ and $3.8 \mu\text{g C m}^{-3}$ have been reported in the United States for urban-influenced-rural sites and urban sites, respectively, whereas EC concentrations between $0.2\text{--}2.0 \mu\text{g m}^{-3}$ has been reported for remote and rural areas (Seinfeld and Pandis and references therein, 1998). As stated in Table 2.1 the sampling sites have been categorized into four different classes, this partly explaining the wide concentration range in the dataset. It is possible that the rural background sites in the central parts of Europe are more influenced by urban areas than those in outskirts of Europe.

For the two Italian sites (JRC and S.P.C.) and the Belgian site all had 95-percentiles higher than $3 \mu\text{g C m}^{-3}$, while the Scandinavian sites and Ireland had their corresponding 95-percentiles lower than $1 \mu\text{g C m}^{-3}$ (Figure 2.1). The other sites had 95-percentiles between $1 \mu\text{g C m}^{-3}$ and approx. $2 \mu\text{g C m}^{-3}$.

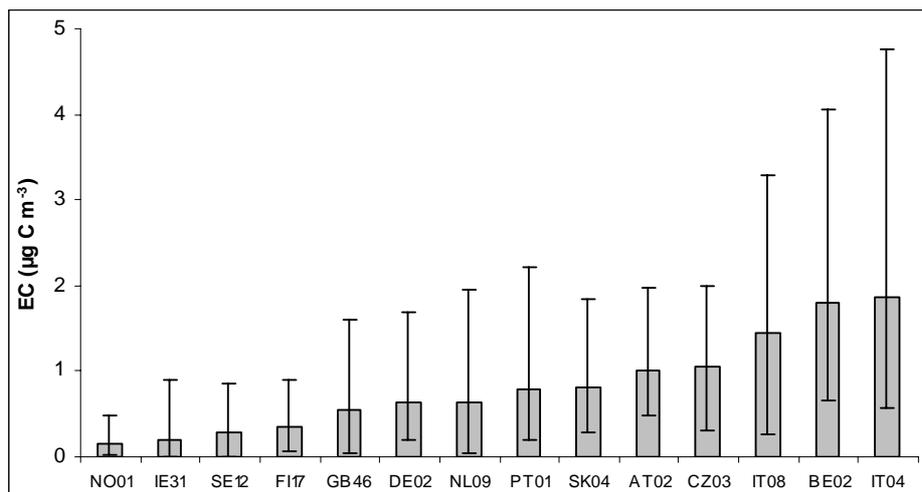


Figure 2.1: Annual mean concentration of EC including the 5% and 95% percentile. Sampling period 01.07.2002–01.07.2003.

2.4 Winter versus summer

Wintertime (October–March) concentrations of EC were found to be higher than those recorded during summer (April–September) for all sites, except at the Norwegian site ($EC_{\text{Winter}}/EC_{\text{Summer}} = 0.95$). For the sites in Austria, Belgium, Czech Republic, Finland, Ireland and Sweden, the $EC_{\text{Winter}}/EC_{\text{Summer}}$ ratio vary between 1.1–1.5, whereas it varies between 1.5–1.9 for the sites in United Kingdom, Italy (S.P.C.), Portugal and Slovakia. For the sites in Germany, The Netherlands and Italy (JRC), the EC concentration during winter was found to be a factor 2.1–2.5 higher than during summer. The increased levels of EC found during winter may be explained by increased emission from residential heating (coal, oil and wood) and traffic during winter (cold starts) and possibly more frequent inversions.

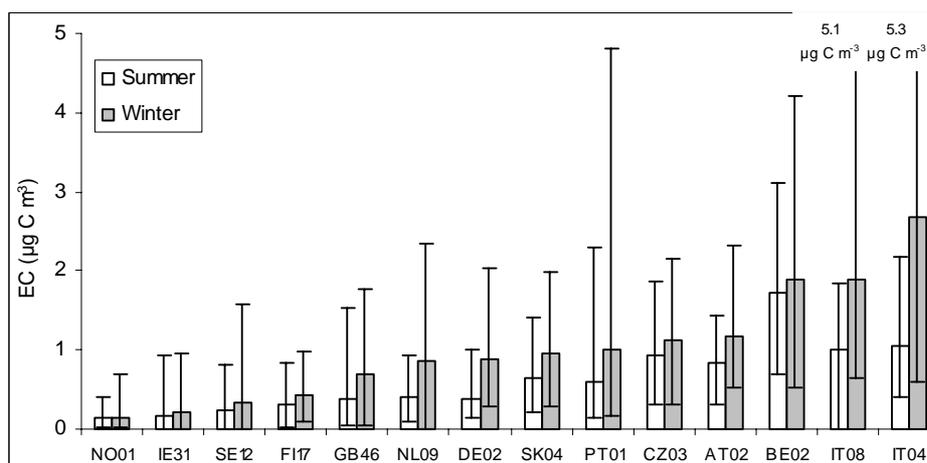


Figure 2.2: Concentrations of EC during summer (April–September) and winter (October–March) including the 5% and 95% percentile. Sampling period 01.07.2002–01.07.2003.

2.5 Elemental/total carbon ratio

The annual mean EC/TC ratios vary from 10% at the Irish site to 31% at the Belgian site, reflecting the relative impact of EC-rich sources. Rau (1989) reported EC/TC ratios between 0.14–0.27 for aerosols emitted from wood burning on conventional fireplaces, whereas traffic (primarily diesel vehicles) have EC/TC ratios as high as 0.6–0.7 (Williams et al., 1989). Aging of airmasses tend to lower the EC fraction of the aerosol as it is mixed with non-combustion particles, likewise will the EC/TC ratio decrease due to condensation of organic material from the gas phase. For the sites in Ireland, Norway and Sweden, low annual levels of EC are reflected in low EC/TC-ratios, whereas the sites in Belgium and Italy (JRC) are typical examples of the opposite. Modest levels of EC are reported for the sites in United Kingdom and The Netherlands in the present campaign (Figure 2.1), but the second highest (26%) and the fourth highest (20%) EC/TC_{Annual mean} ratio is found at these two sites, respectively (Figure 2.3). The UK site most likely has events of polluted airmasses reaching the site from the nearby urban areas of Edinburgh.

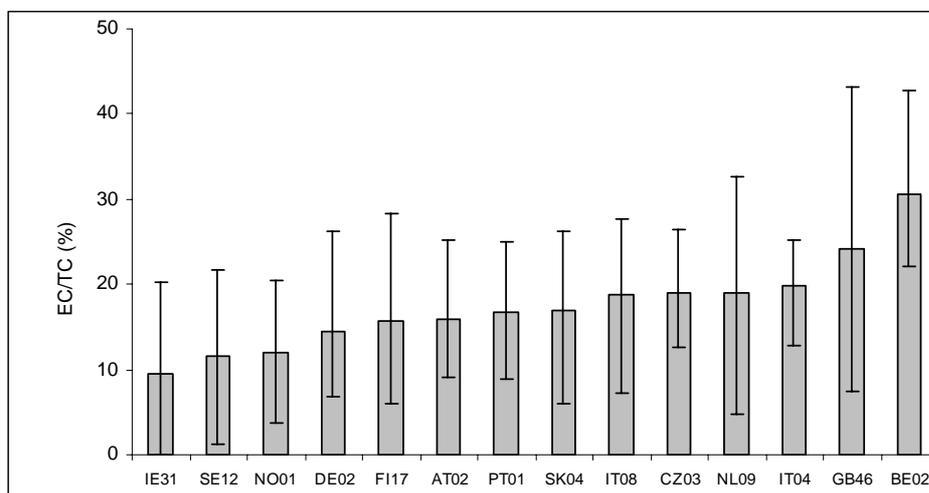


Figure 2.3: Annual mean of EC/TC-ratios including the 5% and 95% percentile. Sampling period 01.07.2002–01.07.2003.

2.6 Elemental/total carbon ratio; winter versus summer

Apart from the sites in Belgium and Portugal, EC accounts for a larger fraction of TC during winter than during summer. For the sites in Finland, Germany, United Kingdom, Norway, Sweden and Slovakia, the EC/TC ratio increases by a factor 1.5–1.8 from summer to winter. This can partly be explained by the general increase in concentration of EC during winter as seen in Figure 2.2. However, also the wintertime reduction in OC reported for the sites in Finland, Norway, Slovakia and Sweden (see Figure 2.6), contributes to the higher EC/TC ratio during winter.

For the remaining sites, apart from Belgium and Portugal, the EC/TC ratio increases by a factor ~1–1.5 from summer to winter. For these sites both the concentration of EC and OC is found to be higher during winter than summer. Whether this will lead to an increase in the EC/TC-ratio or the OC/TC ratio during

winter is dependent upon the relative increase of EC and OC from summer to winter.

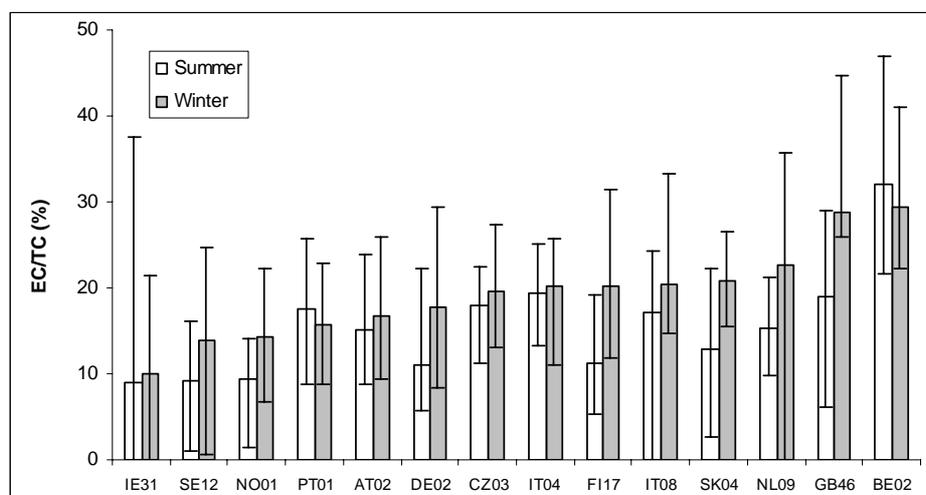


Figure 2.4: EC/TC-ratios during summer (April–September) and winter (October–March) including the 5% and 95% percentile. Sampling period 01.07.2002–01.07.2003.

2.7 Organic carbon

According to Seinfeld and Pandis (1998) (and reference therein), OC concentrations in rural locations can be found around $3.5 \mu\text{g C m}^{-3}$. In the EMEP EC/OC campaign the annual mean concentration of OC varies by a factor of about 7 between the site with the highest concentration of OC (Italy JRS) ($\text{OC}_{\text{Annual mean}} = 7.90 \mu\text{g C m}^{-3}$) and the site with the lowest concentration of OC (Norway) ($\text{OC}_{\text{Annual mean}} = 1.17 \mu\text{g C m}^{-3}$) (Figure 2.5). These sites are the same that reported the highest and lowest concentration of EC as well. Since the site in Italy (JRC) is classified as “Near-city” and the one in Norway as rural background, they are expected to be found in separate parts of the concentration range. The annual mean OC concentration exceeds $5 \mu\text{g C m}^{-3}$ for 3 of the 14 sites, namely the site in Austria and the two sites in Italy (JRC and S.P.C.). For the sites in Belgium, Czech Republic, Germany, Portugal and Slovakia, the annual mean concentration of OC is remarkably consistent (Figure 2.5). This finding is not observed for EC for the same sites. It should be emphasized that the Belgian site is an urban background site, while the others are classified as rural background sites. As for EC the lowest concentrations of OC are found at the sites in Scandinavia and at the British Isles, whereas higher concentrations are reported for the sites in the central, eastern and southern parts of Europe.

Maximum concentrations of OC of $30.5 \mu\text{g C m}^{-3}$ and $36.3 \mu\text{g C m}^{-3}$ were reported for the sites in Portugal and Italy (JRC), both during winter. LC/MS analysis of selected samples from the Portuguese site has revealed quite high ($>1 \mu\text{g m}^{-3}$) concentrations of levoglucosan during late fall and winter. This finding indicates that wood burning for residential heating is an important source influencing this rural background site during the cold season. This also suggests

that wood burning for residential heating can explain the maximum OC concentration reported for this site.

The maximum concentration for Italy (JRC) is most likely an episode of polluted air coming from the nearby city of Milan.

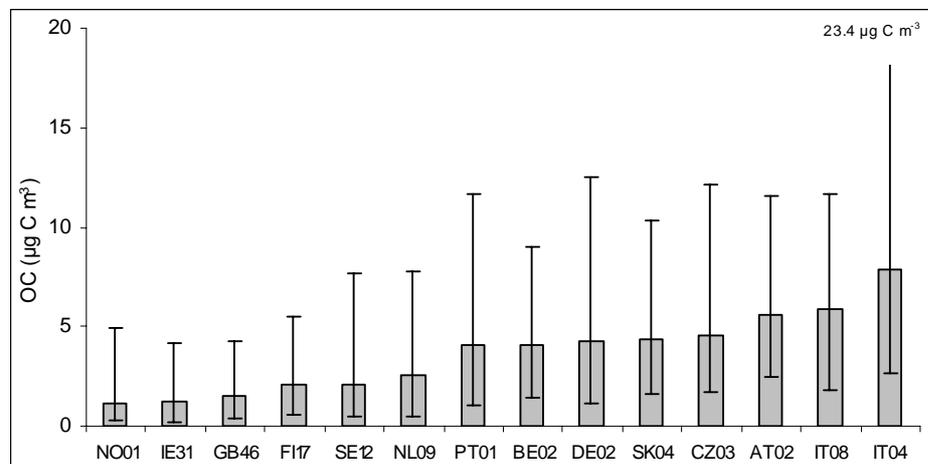


Figure 2.5: Annual mean concentration of OC including the 5% and 95% percentile. Sampling period 01.07.2002–01.07.2003.

2.8 Organic carbon; winter versus summer

At the three Scandinavian sites and at the site in Slovakia, the summertime (April, May, June, July, August, September) concentrations of OC were found to be a factor 1.4–1.6 higher than those recorded during winter (Figure 2.6). One possible explanation may be that this is due to biogenic OC and PBAP (Primary Biological Aerosol Particles) contributing to the OC fraction at these sites during summer. Together with low impact from anthropogenic derived OC, the sources mentioned might possibly explain the pronounced annual variation that is specific for the Scandinavian and Slovakian sites.

For the other sites the concentration of OC increases by a factor 1.2–2.7 (Italy JRC) from summer to winter. Most likely this can be explained by increased emissions from residential heating (coal, oil and wood) and traffic during winter (cold starts) as for EC. For the Portuguese site there are strong indications that the annual increase in OC from summer to winter is due to wood burning for residential heating, as high concentrations of levoglucosan has been found in samples collected during late fall and winter.

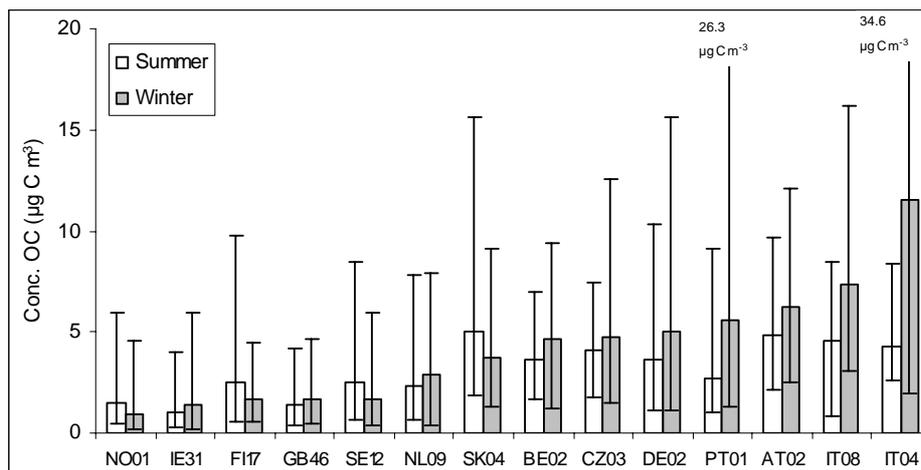


Figure 2.6: Concentrations of OC during summer (April–September) and winter (October–March) including the 5% and 95% percentile. Sampling period 01.07.2002–01.07.2003.

2.9 Organic/total carbon ratio

The annual mean OC/TC ratios vary from 69% at the Belgian site to 91% at the Irish site, emphasizing that OC is the dominating the carbonaceous fraction of the aerosol at all sampling sites. As there is a general increase in the EC/TC ratio from summer to winter for almost every site (see Figure 2.4) a decrease in the OC/TC ratio from summer to winter should be expected. The increased OC/TC ratio from summer to winter at the Portuguese site is as most probably due to wood burning for residential heating. Having a rather low EC/TC ratio, the vast amount of OC coming from this source might at least partly explain this annual variation seen.

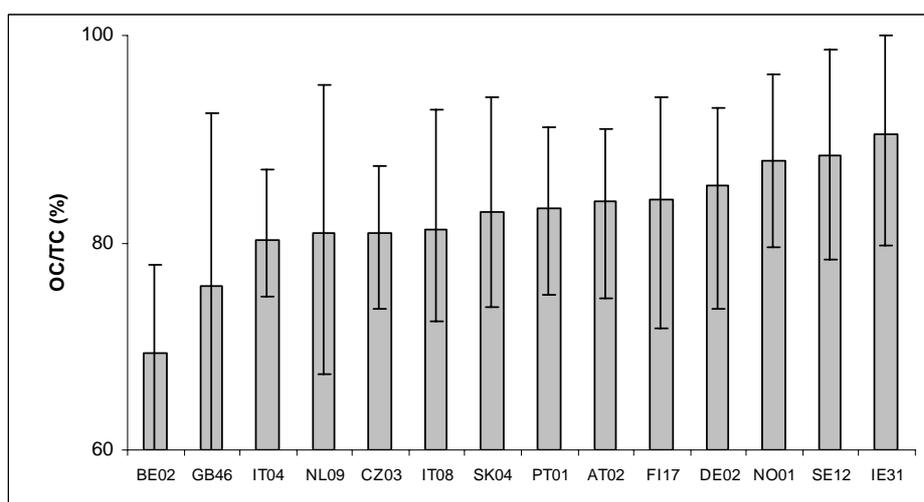


Figure 2.7: Annual mean of OC/TC ratios including the 5% and 95% percentile. Sampling period 01.07.2002–01.07.2003.

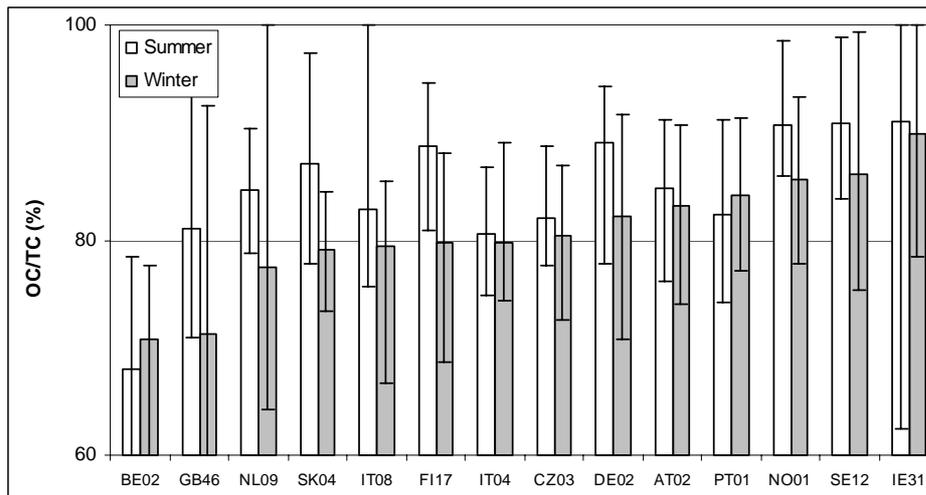


Figure 2.8: OC/TC ratios during summer (April–September) and winter (October–March) including the 5% and 95% percentile. Sampling period 01.07.2002–01.07.2003.

2.10 PM₁₀ measurements

The annual mean concentration of PM₁₀ varies from 7.4 $\mu\text{g m}^{-3}$ at the Norwegian site to 42.0 $\mu\text{g m}^{-3}$ at the Italian (JRC) site, whereas the annual mean for all the sites is 23.5 $\mu\text{g m}^{-3}$ (Figure 2.9). Both sites in Italy (JRS and S.P.C.) exceed the annual PM₁₀ limit set by the EU for 2005, which is 40 $\mu\text{g m}^{-3}$. Also the site in Belgium has a high annual PM₁₀ mean concentration of 37.0 $\mu\text{g m}^{-3}$. The lowest annual mean is reported for the sites in Scandinavia and in the United Kingdom, which are all lower than 15 $\mu\text{g m}^{-3}$. Annual maximum concentrations of PM₁₀ higher than 100 $\mu\text{g m}^{-3}$ were reported at four sites, (Belgium, 127.1 $\mu\text{g m}^{-3}$; Germany, 100 $\mu\text{g m}^{-3}$, Italy JRC, 157.5 $\mu\text{g m}^{-3}$, Italy S.P.C. 115.1 $\mu\text{g m}^{-3}$), and all were reported during winter.

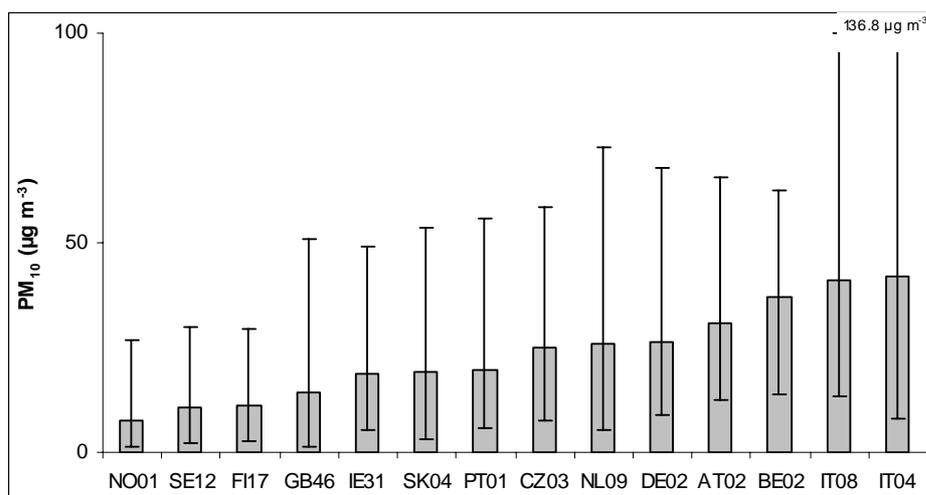


Figure 2.9: Annual mean concentration of PM₁₀ including the 5% and 95% percentile. Sampling period 01.07.2002–01.07.2003.

2.11 Total carbon/PM₁₀ ratio

The annual mean TC/PM₁₀ ratio varies from 4% at the Irish site to 27% at the Slovakian site (TC given in $\mu\text{g C m}^{-3}$). Disregarding the Irish site, the EC/TC ratio does not vary too much, only by a factor 2.7 (see Figure 2.10). However, this picture is somewhat misleading as only the carbon content of TC is accounted for.

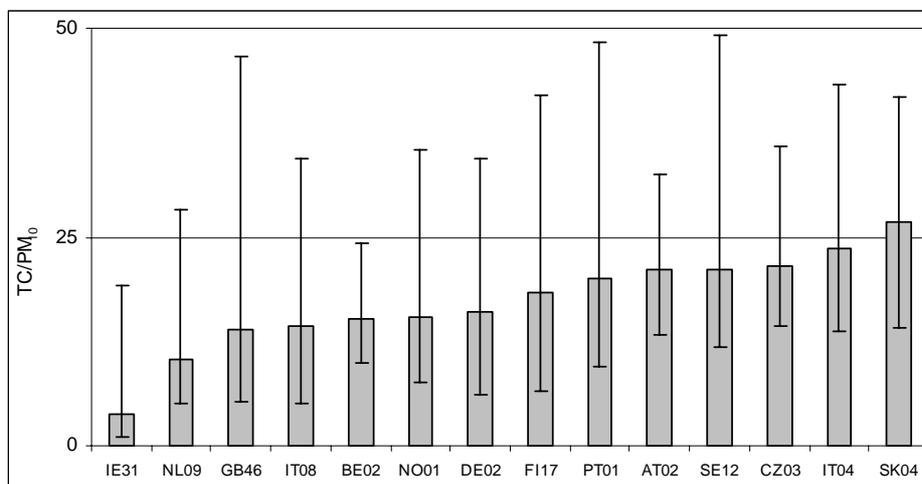


Figure 2.10: Annual mean of TC/PM₁₀ ratios including the 5% and 95% percentile. Sampling period 01.07.2002–01.07.2003.

Several studies apply a factor of 1.4 to convert OC ($\mu\text{g C m}^{-3}$) to OM (Organic Matter) ($\mu\text{g m}^{-3}$). The study by Turpin and Lim (2001) find this factor to be the lowest reasonable ratio applicable for urban sites, having a relatively larger percentage of water-insoluble organic material (WINSOC), and states that it is too low for areas influenced by sources like wood burning and aged aerosols. Turpin and Lim (2001) suggested a conversion factor of 1.6 for urban aerosols and 2.1 for aged and non-urban aerosols. For areas being heavily influenced by emission from biomass burning a conversion ratio of 2.2–2.6 was suggested. In the study by Kiss et al. (2002) a conversion factor of 1.9–2.0 was estimated, mostly based on experimental studies, for fine aerosols ($d_p < 1.5 \mu\text{m}$) collected at the rural site of K-pusztá Hungary. In the same study a conversion factor of 1.1 was estimated for EC. EC consists mainly of carbon atoms, but may contain 10% hydrogen as well as trace levels of other elements.

Without any previous knowledge of the OC fraction composition at a given site, choosing a suitable conversion factor is difficult. Due to the apparent diversity of the sites included in the present campaign, the major sources contributing with carbonaceous material most likely vary considerably from site to site, as well as their relative contribution may vary on an annual basis. For this reason using one conversion factor for all the sites is not an obvious approach. To give a rough estimate of how much of the aerosol can be accounted for by carbonaceous material, the annual mean, the wintertime mean and the summertime mean of EC ($\mu\text{g C m}^{-3}$) and OC ($\mu\text{g C m}^{-3}$) have been multiplied by the following conversion factors: For EC a conversion factor of 1.1 were used for all the sites in the campaign. For the urban background sites (Ghent, Belgium and S.P.C., Italy) and

the “Near-city” site (JRC, Italy), a conversion factor for OC to OM of 1.6 was applied, whereas for the rural background sites and the rural site a conversion factor of 2.0 was used.

On an annual basis EC accounts for 1.1–5.4% of PM₁₀ whereas 12.6–44.9% is attributed to OM, all site categories included (Table 2.2). The total carbonaceous material (EC+OM) varies between 13.7% at the Irish site and 49.5% at the Slovakian site. For the rural background sites the mean (EC+OM)/PM₁₀ ratio is approx. 37%, most likely being equally high or higher than SO₄²⁻/PM₁₀, emphasizing the importance of the carbonaceous fraction at this site category.

From Table 2.3 and Table 2.4 it can be seen that the EC/PM₁₀ ratio is higher during winter than during summer except at the Belgian and the Portuguese sites. For the Scandinavian sites and the Slovakian site there is a profound increase in the OM/PM₁₀ ratio from winter to summer (Finland approximately 17%, Sweden approximately 16%). As previously emphasized this can be due to biogenic OM and PBAP contributing significantly to these sites during the growth season. For the Portuguese site there is a significant decrease in the OM/PM₁₀ ratio from winter to summer (26.5%). It has previously been suggested that this is due to high levels of OC emitted from wood burning for residential heating during the cold season. The seasonal variation for the OM/PM₁₀ ratio has also an impact on the (EC+OM)/PM₁₀ ratio. For the sites in Finland, Slovakia and Sweden approximately 50% of PM₁₀ can be accounted for by carbonaceous material, whereas at the Portuguese site over 60% of PM₁₀ can be attributed to carbonaceous material during winter.

Table 2.2: Annual ambient concentrations of EC, OM and PM₁₀ and relative contribution of EC, OM, and the sum EC+OM to the PM₁₀ concentration. Sampling period 2002.07.01–2003.07.01.

| Site | Site category | EC ¹ µg m ⁻³ | OM ^{2,3} µg m ⁻³ | PM ₁₀ µg m ⁻³ | EC/PM ₁₀ % | OM/PM ₁₀ % | (EC+OM)/PM ₁₀ % |
|-----------------|---------------|---------------------------------------|---|--|--------------------------|--------------------------|-------------------------------|
| Austria | Rural Backgr. | 1.11 | 11.13 | 30.9 | 3.6 | 36.1 | 39.7 |
| Czech Republic | Rural Backgr. | 1.16 | 9.08 | 25.0 | 4.6 | 36.4 | 41.0 |
| Finland | Rural Backgr. | 0.40 | 4.16 | 11.0 | 3.6 | 37.8 | 41.4 |
| Germany | Rural Backgr. | 0.70 | 8.61 | 26.1 | 2.7 | 32.9 | 35.6 |
| The Netherlands | Rural Backgr. | 0.70 | 5.18 | 26.1 | 2.7 | 19.9 | 22.6 |
| Ireland | Rural Backgr. | 0.21 | 2.39 | 19.0 | 1.1 | 12.6 | 13.7 |
| Portugal | Rural Backgr. | 0.87 | 8.20 | 19.4 | 4.5 | 42.2 | 46.7 |
| Norway | Rural Backgr. | 0.16 | 2.33 | 7.4 | 2.1 | 31.4 | 33.5 |
| Slovakia | Rural Backgr. | 0.89 | 8.64 | 19.2 | 4.6 | 44.9 | 49.5 |
| Sweden | Rural Backgr. | 0.31 | 4.24 | 10.6 | 3.0 | 39.9 | 42.8 |
| United Kingdom | Rural | 0.60 | 3.06 | 14.3 | 4.2 | 21.3 | 25.5 |
| Belgium | Urban backgr. | 1.98 | 6.59 | 37.0 | 5.4 | 17.8 | 23.2 |
| Italy (S.P.C.) | Urban backgr. | 1.58 | 9.46 | 41.0 | 3.9 | 23.1 | 26.9 |
| Italy (JRC) | Near-city | 2.04 | 12.64 | 42.0 | 4.9 | 30.1 | 35.0 |

1) To account for hydrogen and trace levels of other elements, concentrations of EC (µg C m⁻³) have been multiplied by a factor of 1.1 for all sites.

2) To convert OC (µg C m⁻³) to OM (µg m⁻³) concentrations of OC (µg C m⁻³) have been multiplied by a factor of 2.0 for all the rural background sites and the rural site.

3) To convert OC (µg C m⁻³) to OM (µg m⁻³) concentrations of OC (µg C m⁻³) have been multiplied by a factor of 1.6 for all the urban background sites and the “Near-city” site.

Table 2.3: Ambient wintertime concentrations of EC, OM and PM₁₀ and relative contribution of EC, OM, and the sum EC+OM to the PM₁₀ concentration. Sampling period 2002.10.01–2003.04.01.

| Site | Site category | EC ¹ µg m ⁻³ | OM ^{2,3} µg m ⁻³ | PM ₁₀ µg m ⁻³ | EC/PM ₁₀ % | OM/PM ₁₀ % | (EC+OM)/PM ₁₀ % |
|-----------------|---------------|---------------------------------------|---|--|--------------------------|--------------------------|-------------------------------|
| Austria | Rural Backgr. | 1.30 | 12.55 | 34.7 | 3.8 | 36.2 | 40.0 |
| Czech Republic | Rural Backgr. | 1.23 | 9.55 | 26.2 | 4.7 | 36.5 | 41.2 |
| Finland | Rural Backgr. | 0.46 | 3.30 | 11.2 | 4.1 | 29.6 | 33.7 |
| Germany | Rural Backgr. | 0.97 | 9.96 | 30.6 | 3.2 | 32.6 | 35.7 |
| The Netherlands | Rural Backgr. | 0.94 | 5.70 | 31.6 | 3.0 | 18.0 | 21.0 |
| Ireland | Rural Backgr. | 0.25 | 2.80 | 23.4 | 1.1 | 12.0 | 13.0 |
| Portugal | Rural Backgr. | 1.10 | 11.14 | 20.1 | 5.5 | 55.6 | 61.1 |
| Norway | Rural Backgr. | 0.15 | 1.81 | 6.5 | 2.3 | 27.6 | 30.0 |
| Slovakia | Rural Backgr. | 1.06 | 7.36 | 18.1 | 5.9 | 40.7 | 46.6 |
| Sweden | Rural Backgr. | 0.37 | 3.37 | 10.6 | 3.5 | 31.9 | 35.4 |
| United Kingdom | Rural | 0.76 | 3.36 | 15.6 | 4.9 | 21.6 | 26.5 |
| Belgium | Urban backgr. | 2.08 | 7.38 | 41.1 | 5.1 | 18.0 | 23.1 |
| Italy (S.P.C.) | Urban backgr. | 2.09 | 11.83 | 51.9 | 4.0 | 22.8 | 26.8 |
| Italy (JRC) | Near-city | 2.93 | 18.48 | 57.7 | 5.1 | 32.1 | 37.1 |

1) To account for hydrogen and trace levels of other elements, concentrations of EC (µg C m⁻³) have been multiplied by a factor of 1.1 for all sites.

2) To convert OC (µg C m⁻³) to OM (µg m⁻³) concentrations of OC (µg C m⁻³) have been multiplied by a factor of 2.0 for all the rural background sites and the rural site.

3) To convert OC (µg C m⁻³) to OM (µg m⁻³) concentrations of OC (µg C m⁻³) have been multiplied by a factor of 1.6 for all the urban background sites and the “Near-city” site.

Table 2.4: Ambient summertime concentrations of EC, OM and PM₁₀ and relative contribution of EC, OM, and the sum EC+OM to the PM₁₀ concentration. Sampling period 2002.07.01–2002.10.01 and 2003.04.01–2003.07.01.

| Site | Site category | EC ¹ µg m ⁻³ | OM ^{2,3} µg m ⁻³ | PM ₁₀ µg m ⁻³ | EC/PM ₁₀ % | OM/PM ₁₀ % | (EC+OM)/PM ₁₀ % |
|-----------------|---------------|---------------------------------------|---|--|--------------------------|--------------------------|-------------------------------|
| Austria | Rural Backgr. | 0.92 | 9.66 | 26.9 | 3.4 | 35.9 | 39.3 |
| Czech Republic | Rural Backgr. | 1.02 | 8.17 | 22.6 | 4.5 | 36.1 | 40.6 |
| Finland | Rural Backgr. | 0.33 | 5.06 | 10.9 | 3.0 | 46.5 | 49.5 |
| Germany | Rural Backgr. | 0.42 | 7.26 | 21.7 | 2.0 | 33.4 | 35.4 |
| The Netherlands | Rural Backgr. | 0.44 | 4.65 | 20.3 | 2.2 | 22.9 | 25.0 |
| Ireland | Rural Backgr. | 0.18 | 2.03 | 15.0 | 1.2 | 13.5 | 14.7 |
| Portugal | Rural Backgr. | 0.65 | 5.49 | 18.9 | 3.5 | 29.1 | 32.6 |
| Norway | Rural Backgr. | 0.16 | 2.93 | 8.3 | 1.9 | 35.2 | 37.2 |
| Slovakia | Rural Backgr. | 0.70 | 9.96 | 20.4 | 3.4 | 48.8 | 52.2 |
| Sweden | Rural Backgr. | 0.26 | 5.11 | 10.7 | 2.4 | 47.7 | 50.2 |
| United Kingdom | Rural | 0.42 | 2.73 | 13.0 | 3.2 | 21.0 | 24.2 |
| Belgium | Urban backgr. | 1.88 | 5.80 | 32.9 | 5.7 | 17.6 | 23.3 |
| Italy (S.P.C.) | Urban backgr. | 1.12 | 7.28 | 31.0 | 3.6 | 23.4 | 27.0 |
| Italy (JRC) | Near-city | 1.15 | 6.79 | 24.9 | 4.6 | 27.2 | 31.9 |

1) To account for hydrogen and trace levels of other elements, concentrations of EC (µg C m⁻³) have been multiplied by a factor of 1.1 for all sites.

2) To convert OC (µg C m⁻³) to OM (µg m⁻³) concentrations of OC (µg C m⁻³) have been multiplied by a factor of 2.0 for all the rural background sites and the rural site.

3) To convert OC (µg C m⁻³) to OM (µg m⁻³) concentrations of OC (µg C m⁻³) have been multiplied by a factor of 1.6 for all the urban background sites and the “Near-city” site.

3. One year of boundary layer aerosol size distribution measurements at the EMEP site Birkenes (Norway)

by C. Lunder

As mentioned in the previous EMEP status report (EMEP/CCC, 2003) more emphasis needs to be placed on particle number distributions and on ultrafine particles (UFP). Particle mass is mostly determined by accumulation and coarse particles, whereas Aitken and nucleation particles make a negligible contribution to PM₁₀, PM_{2.5}, or even PM₁ mass. On the other hand, coarse particles contribute little to particle number densities. The main contribution to the particle number concentration comes from UFP, i.e. nucleation and Aitken particles, and to a less extent from accumulation particles. A better characterisation of Aitken particles is needed to facilitate our understanding of adverse health effects of aerosols, and of the dynamic growth of Aitken particles to accumulation mode particles by heterogeneous chemical processes. Accurate prediction of aerosol number concentrations is important for estimating the indirect climate forcing of aerosols.

The size distribution of aerosols is an important parameter that impacts the transport and deposition properties of particles in the atmosphere, their optical properties, and their ability to act as cloud condensation nuclei. The optical properties determine the direct climate effect of aerosols, whereas their role as cloud condensation nuclei is the origin of the indirect climate forcing effect of aerosols. Recent evidence suggests that the toxicological properties of particulate pollutants are strongly influenced by their sizes (Stone and Donaldson, 1998). Detailed information on particle size distributions can therefore provide valuable information for the validation of air pollution models (EMEP/CCC, 2003), for source attribution, and for understanding the formation, transport, and deposition of particles in the atmosphere (Tunved et al., 2003a). Size distribution data also are an indispensable input parameter for modelling the radiative effects of aerosols (Myhre and Stordal, 2001; Kahnert and Kylling, 2003).

Nucleation particles (smaller than 30 nm) are formed from precursor gases and quickly grow within a few hours by condensation of gases or by coagulation with larger particles. Aitken particles (between 30 nm and 100 nm) can originate from primary emission (e.g. diesel soot) or from growing nucleation particles. Accumulation particles (between 100 nm and 1000 nm) have the longest lifetime (up to 2 weeks). Most accumulation particles originate from Aitken particles, which grow within a few days to accumulation size (by heterogeneous liquid phase reactions, condensation, and coagulation). Most coarse mode particles (larger than 1000 nm) originate from primary emitted particles (mainly sea salt and mineral dust). However, precursor gases (e.g. H₂SO₄ and HNO₃) can chemically interact with coarse mode particles (e.g. NaCl, CaCO₃), thus adding mass (e.g. sulphate, nitrate) to the aerosols. Coarse mode particles have high deposition rates and thus short lifetimes in the atmosphere. Accumulation particles are most important for long-range transport due to their long lifetime, whereas nucleation and Aitken particles usually originate from local sources. Thus by investigating aerosol size distributions we can distinguish between locally formed particles and those originating from more distant source regions.

Few measurement data on particle number concentrations are available. One of the most extensive networks for measuring particle number distributions in Europe is a Nordic network comprising several Swedish and Finnish stations, and, since autumn 2002, the EMEP station at Birkenes. This report presents some of the results obtained with the new Differential Mobility Particle Sizer (DMPS) instrument installed at Birkenes, which measures aerosol size distributions in the diameter range between 19.0 nm and 643.2 nm.

Figure 3.1 and Figure 3.2 show time series of number size distributions (upper panel) and total number concentrations (lower panel) measured in December 2003 and July 2003, respectively. Particle numbers are considerably lower in winter than in summer, which is in nice agreement with published data from other Nordic background stations (Tunved et al., 2003b). Potential explanation for the seasonal variation in particle number concentration might be a higher biogenic activity in spring and summer, which produces larger amounts of organic vapours that contribute to the growth of aerosol particles by condensing onto existing particles, but can also be explained by seasonal changes in air masses, lower rate of incoming solar radiation and thus less new particle formation during the winter period and/or a higher rate of precipitation and overall cloudiness during the winter (Tunved et al., 2003b).

Figure 3.3 presents a 9-day period in early spring characterized by repeated particle formation events. High particle number concentrations (lower panel) are correlated with the appearance of new small Aitken particles, most likely due to local nucleation events. Also the dynamic growth of the Aitken particles to accumulation size on the time scale of 1-3 days is observed.

Diurnal variations were observed and most of the nucleation events were characterized by a sharp increase of nuclei mode number concentration around noon (Figure 3.3 and Figure 3.4). The frequency of nucleation events in 2003 at Birkenes has been shown to be largest around spring and summertime. This seasonal variation has been observed at similar sites (Tunved et al., 2003b).

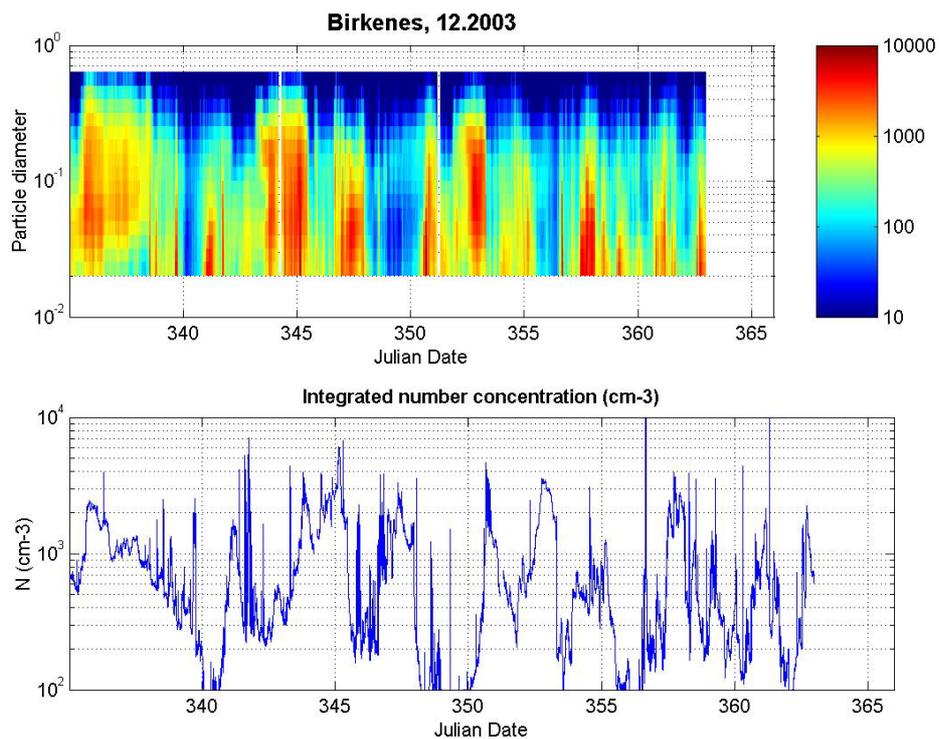


Figure 3.1: Spectral plot of aerosol number as a function of size distribution (μm) and Julian Day (upper panel) and time series of total number concentration (lower panel) at Birkenes in December 2003.

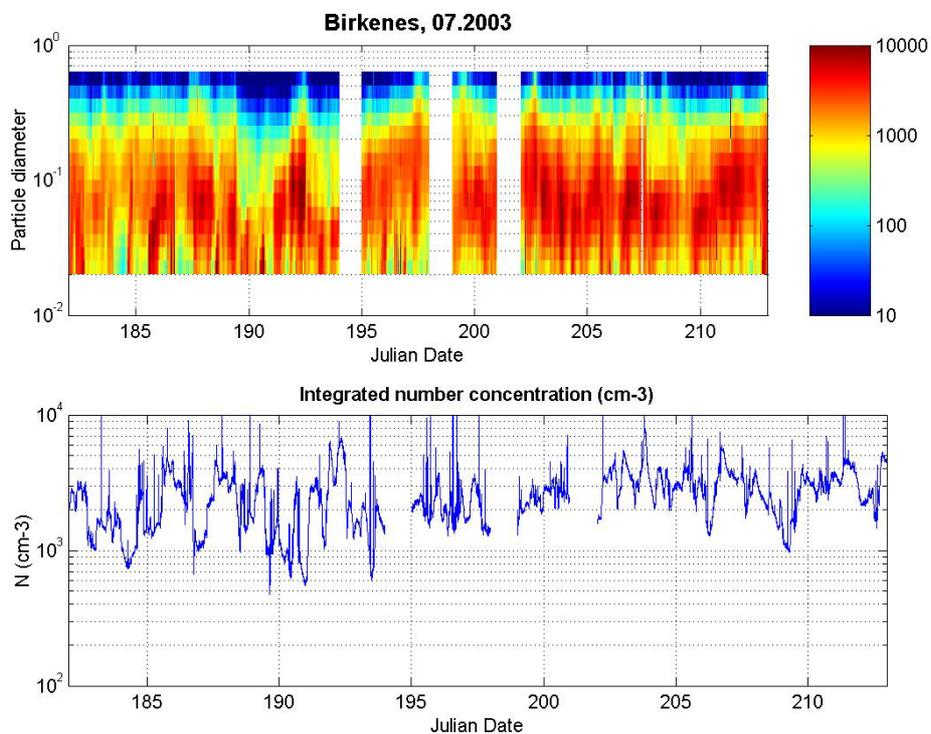


Figure 3.2: Spectral plot of aerosol number as a function of size distribution (μm) and Julian Day (upper panel) and time series of total number concentration (lower panel) at Birkenes in July 2003.

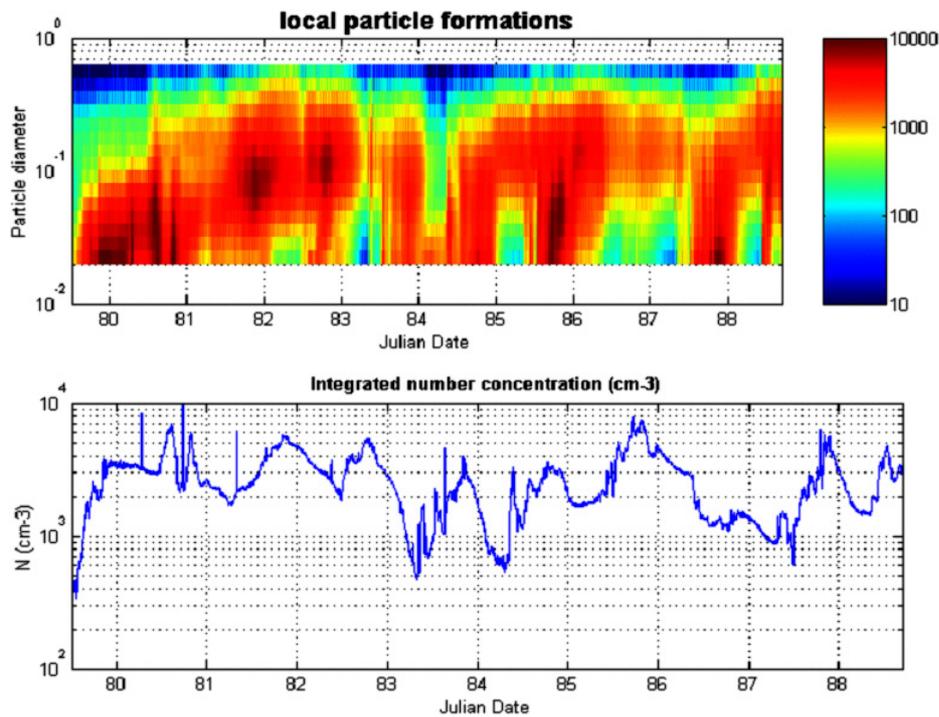


Figure 3.3: A 9-day period in early spring 2003 with repeated local particle formations and diurnal variations.

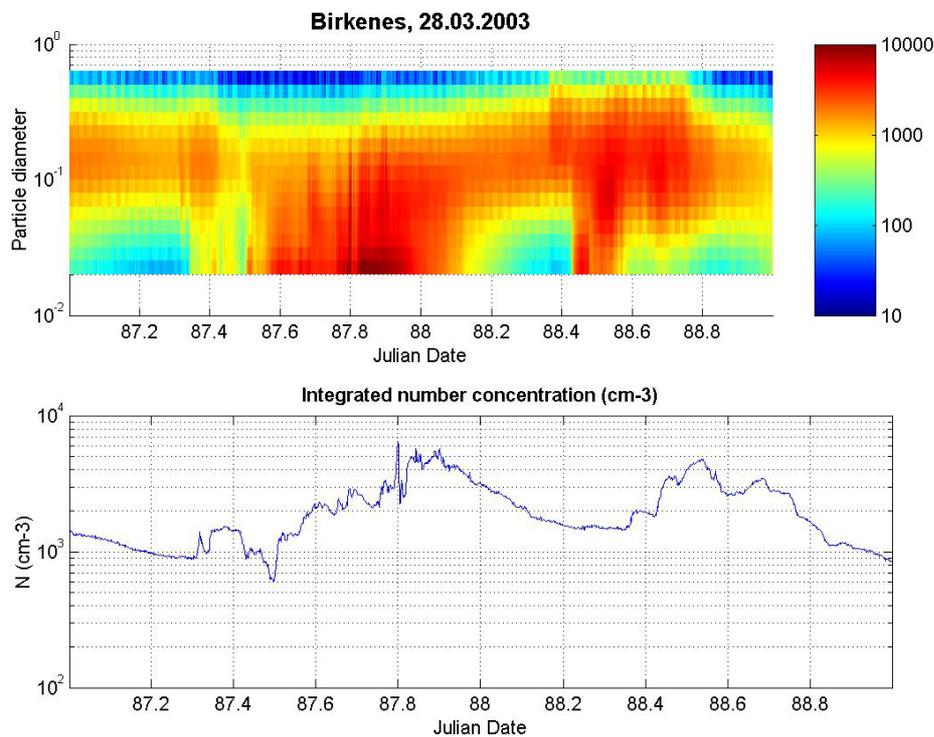


Figure 3.4: Example of typical nucleation events at Birkenes.

Figure 3.4 shows an episode of dynamic particle growth processes. At the beginning of the period (Julian day 87) small Aitken particles appear, which most

likely originate from the growth of nucleation mode particles. These particles come from local, possibly biogenic sources. Over a period of a day it is observed that the Aitken particles grow to accumulation size, repeatedly fuelled by newly appearing small particles, most likely due to local nucleation events. These nucleation events stop at night and resume in the morning of the next day. This diurnal variation in the production of new particles supports the hypothesis that these particles are of biogenic origin. During nighttime the growth process of the Aitken particles to accumulation size continues. The production of new particles continues on Julian day 88 throughout the day and stops again in the evening. Comparison of the upper and lower panel also shows that peaks in number concentrations are usually accompanied by the appearance of new small Aitken particles. This demonstrates that small particles make the dominant contribution to number concentrations. The reason for this is coagulation of particles, which is one of the important dynamic processes (Kerminen et al., 2001). Coagulation increases the average particle size while decreasing particle number concentration.

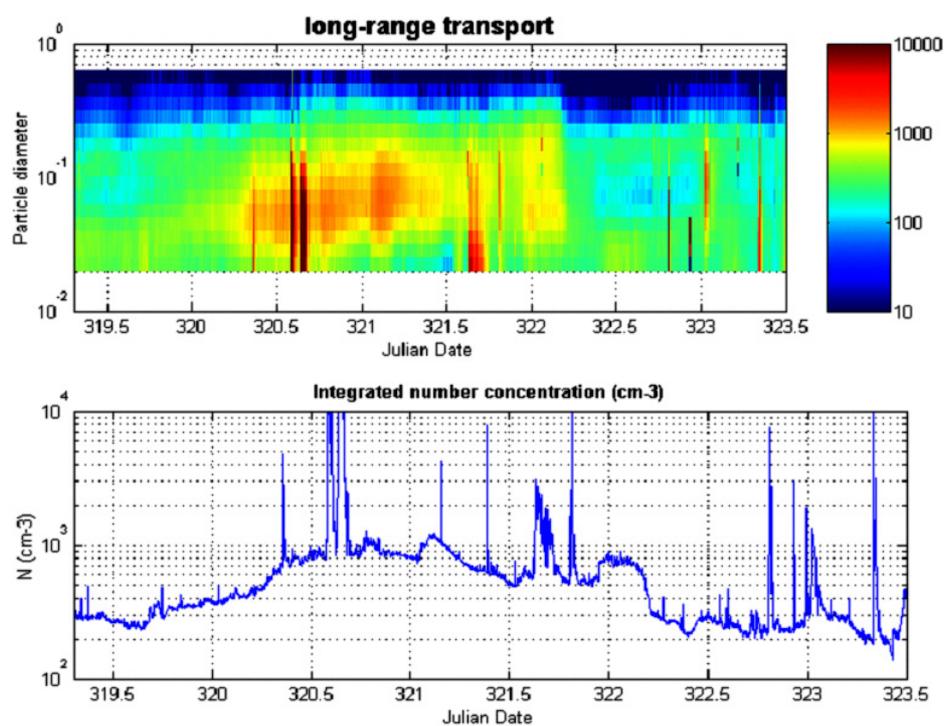


Figure 3.5: An episode of long-range transported aerosols which appears in the morning of Julian Day 320 in 2002 and disappears in the morning the following day.

In literature it is argued that the primary emissions from anthropogenic activities largely contribute to aerosols in the Aitken size range (Birmili et al., 2001). In contrast to those episodes dominated by local particle formation events, which were shown in the previous two Figures, Figure 3.5 presents an episode dominated by long-range transport of aerosols. Only few occurrences of small Aitken particles can be observed. The most prominent feature in the upper panel is a distribution of particles between roughly 30 nm and 110 nm, which appears in the morning of Julian day 320 in 2002 and disappears in the morning of the

following day. Unlike the episodes presented in Figure 3.3 and Figure 3.4, no appearance of smaller Aitken particles precedes the appearance of these aerosols. This leaves, in principle, two possible explanations. The aerosols may be primary particles that are locally emitted. However, as Birkenes is a regional background station far away from major emission sources, this is rather unlikely. It is more plausible that these particles are aged aerosols that originate from a more distant source region, and that these aerosols have undergone long-range transport in the atmosphere.

4. Submicron particle number concentrations measured during summer 2000 and winter 2001 in the Eastern Mediterranean

by J. Smolik, V. Zdimal and M. Lazaridis

One of the objectives of the European Union funded SUB-AERO project was the investigation of new particle formation and its fate in the Mediterranean area under different meteorological conditions and seasons (summer and winter) including their chemical composition. During the project two field campaigns were carried out at the Finokalia sampling site (10.–31.7.2000 and 7.–14.1.2001) and one campaign aboard the vessel Aegeon cruising in the Mediterranean Sea (25.–29.7.2000). This work included also mass and chemical size distributions of atmospheric aerosol collected by a low pressure cascade impactor at the Finokalia sampling site on Crete island and aboard the scientific boat Aegeon. Finokalia (35° 19' N, 25° 40' E) is a coastal remote site eastward Heraklion on the top of a hill (elevation 130m) facing the sea within the sector of 270° to 90°. Depending on the weather the air masses reaching the station originate from Europe to Africa.

Along with the characterization of the collected atmospheric particulate matter particle number concentration measurements were also performed using a Scanning Mobility Particle Sizer (SMPS) and an optical particle counter (PMS Las-X) both in summer and winter. Simultaneously, gaseous pollutants (NO₂, HONO, HONO₂, SO₂, O₃), temperature, humidity, and wind direction and velocity were monitored. The instruments were connected to the same sampling inlet located at about 4 m above the ground.

A standard Scanning Mobility Particle Sizer (TSI, Inc.), which consists of 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 the winter period 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 pre-impactor 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 the summer and the winter season, respectively. The distributions were corrected for multiple charging (TSI SMPS software, Version 3.0). To visualise the time development of the size distribution, raw data from each day have been exported from the SMPS native format into a text file. This text file has been further processed and the data displayed as colour maps. Further, in order to determine the location of the modes of the individual distributions and their temporal variation gnostic theory was used. This approach allowed both filtering of gross measurement errors and determination of distribution functions (Wagner et al., 2002).

Temporal variation of particle number concentrations for three size intervals corresponding approximately to the nucleation (< 30 nm), Aitken (30–100 nm), and accumulation (100–300 nm) modes are shown in Figure 4.1–Figure 4.3. As can be seen the concentrations of ultrafine particles (< 30nm) were highest during

the winter where the concentration varied mostly from $1 \cdot 10^2$ to $5 \cdot 10^2 \text{ cm}^{-3}$ with several peaks going up to about $1 \cdot 10^4 \text{ cm}^{-3}$. Corresponding concentrations measured during the summer campaign varied mostly from $1 \cdot 10^1$ to $1 \cdot 10^3 \text{ cm}^{-3}$ with an average value of about $1 \cdot 10^2 \text{ cm}^{-3}$ at Finokalia and from about $1 \cdot 10^1$ to $1 \cdot 10^2 \text{ cm}^{-3}$ with average value about $5 \cdot 10^1 \text{ cm}^{-3}$ aboard Aegeon vessel. The particle concentrations for size fraction 30–100 nm were mostly around $1 \cdot 10^3 \text{ cm}^{-3}$ for all measurements but increased up to $5 \cdot 10^3 \text{ cm}^{-3}$ in the middle of the winter campaign followed by a decrease to $5 \cdot 10^1 \text{ cm}^{-3}$. The concentrations of the 100–300 nm size fraction were higher during the summer ranging from $1 \cdot 10^3$ to $5 \cdot 10^3 \text{ cm}^{-3}$ aboard the boat and from $2 \cdot 10^2$ to $2 \cdot 10^3 \text{ cm}^{-3}$ at Finokalia. Corresponding concentrations measured during the winter varied from $1 \cdot 10^2$ to $1 \cdot 10^3 \text{ cm}^{-3}$.

The temporal variation of the mode diameter and the total particle number concentration measured by SMPS are shown in Figure 4.4–Figure 4.6. The particle distributions measured during the summer were typically monomodal with concentration maximum around 70–150 nm at Finokalia and around 100–220 nm aboard Aegeon. Number distributions measured during the winter were predominantly bimodal with modes around 40–100 and 120–220 nm, respectively. During the three nucleation events which were observed in the middle of the winter campaign another mode appeared at about 20 nm. Note that during the nucleation events the smaller mode fell down from about 80 nm to 40 nm while the higher mode has disappeared. Similar behaviour was observed during the summer (14–15 July 2004) where also a smaller mode at around 40 nm appeared in connection to an observed nucleation event. The evolution of nucleation event (10–11 January 2001) is shown in Figure 4.7.

A special effort on the interpretation of the nucleation events which were observed during three days in winter and one day in summer has been given. For these time series the meteorological conditions (wind direction and velocity, temperature, humidity) and the concentration of the gaseous pollutants (ozone, NO_2 , NO_x , HONO, HNO_3) were analysed. The results were compared with the temporal variation of the concentration of the different size fraction of submicron aerosols, measured by SMPS (8–320 nm) and with the time variation of the modes of the submicron particle size distribution. A correlation with the local values of the above-mentioned parameters has not been found.

Comparing the winter and summer periods the nucleation events were observed more frequently in winter (3 events during seven days) than in the summer (1 event during three weeks). This is probably due to the lower concentration of PM_{10} and PM_{10} observed in the winter period (Smolík et al., 2003) resulting in lower coagulation scavenging of small nuclei and also due to higher biogenic emissions from plants and higher humidity which increase the driving force for the particle growth (Kulmala et al., 2004). It has to be noted also that both in winter and summer the nucleation events were accompanied by a decrease of the Aitken mode position down to about 40 nm.

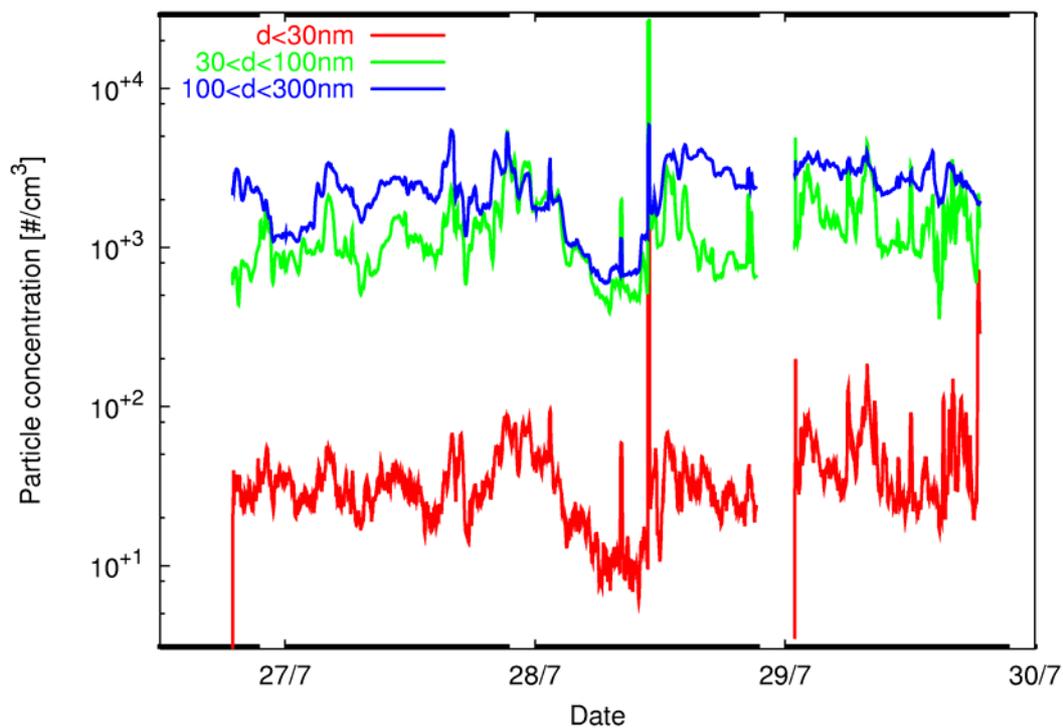


Figure 4.1: Temporal variation of the number concentration for three size intervals, onboard the research vessel Aegeon (27/07/00-29/07/00).

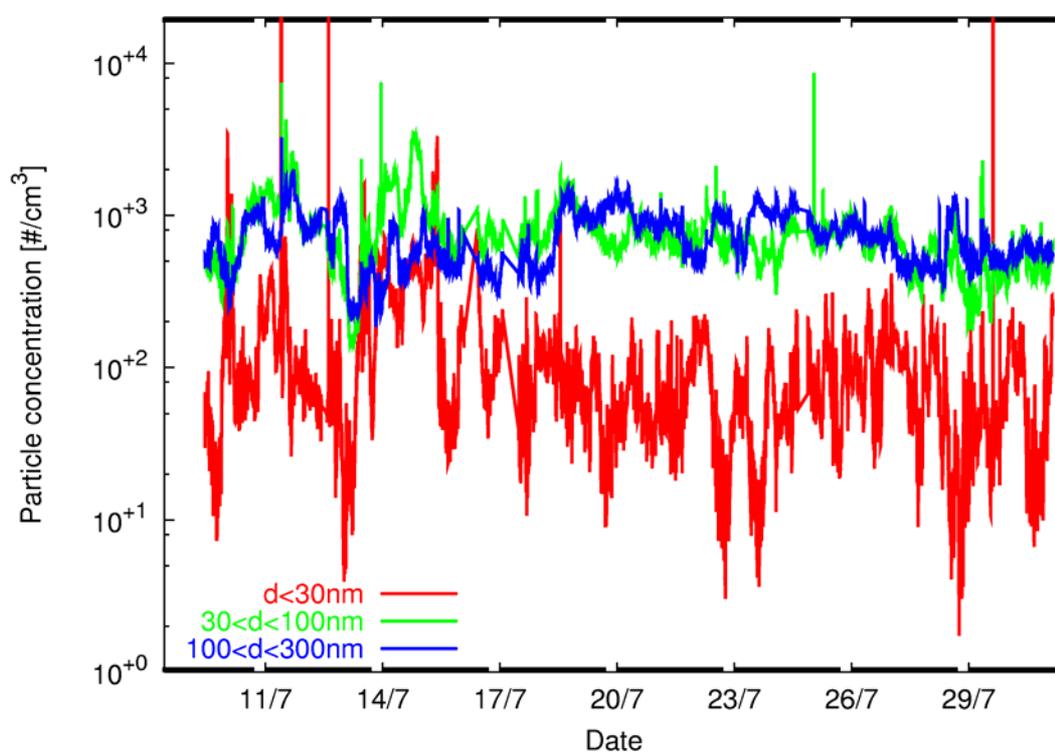


Figure 4.2: Temporal variation of the number concentration for three size intervals, at the Finokalia sampling site (10/07/00-31/07/00).

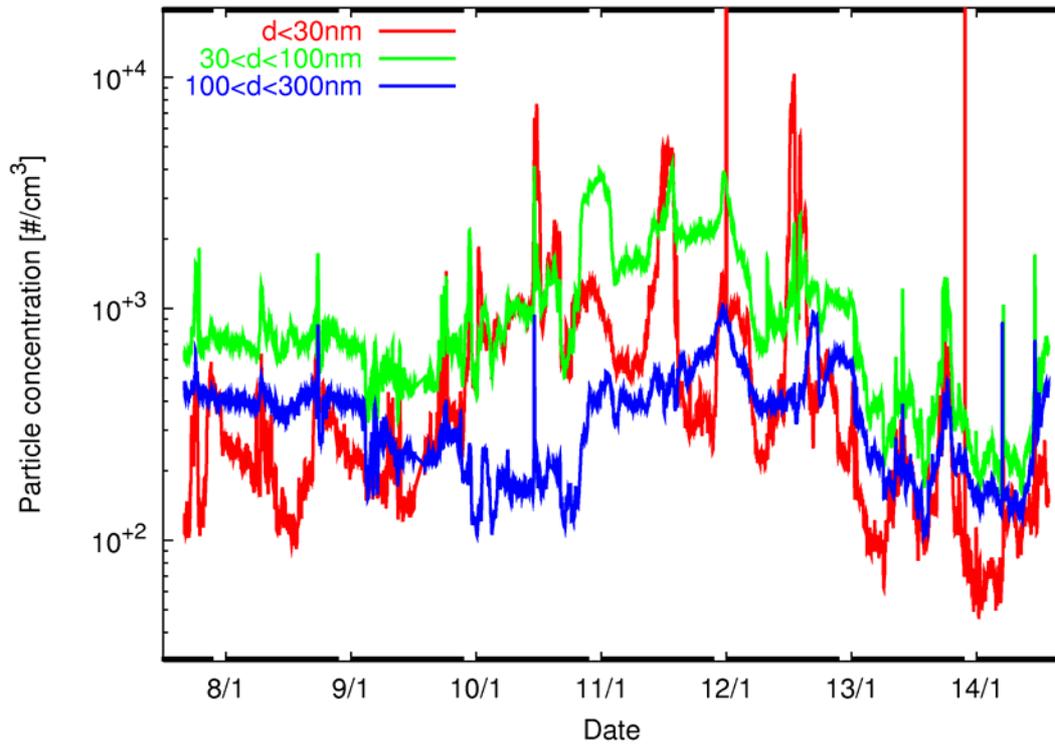


Figure 4.3: Temporal variation of the number concentration for three size intervals, at the Finokalia sampling site (07/01/01-14/01/01).

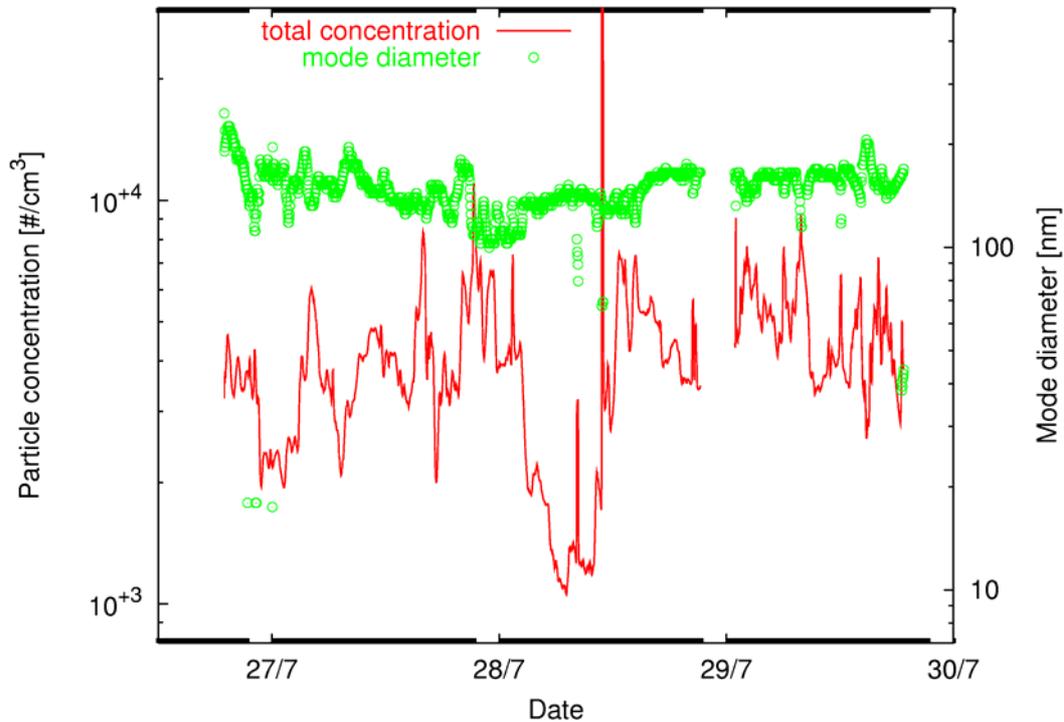


Figure 4.4: The temporal variation of the mode diameter and the total particle number concentration onboard the research vessel Aegeon (27/07/00-29/07/00).

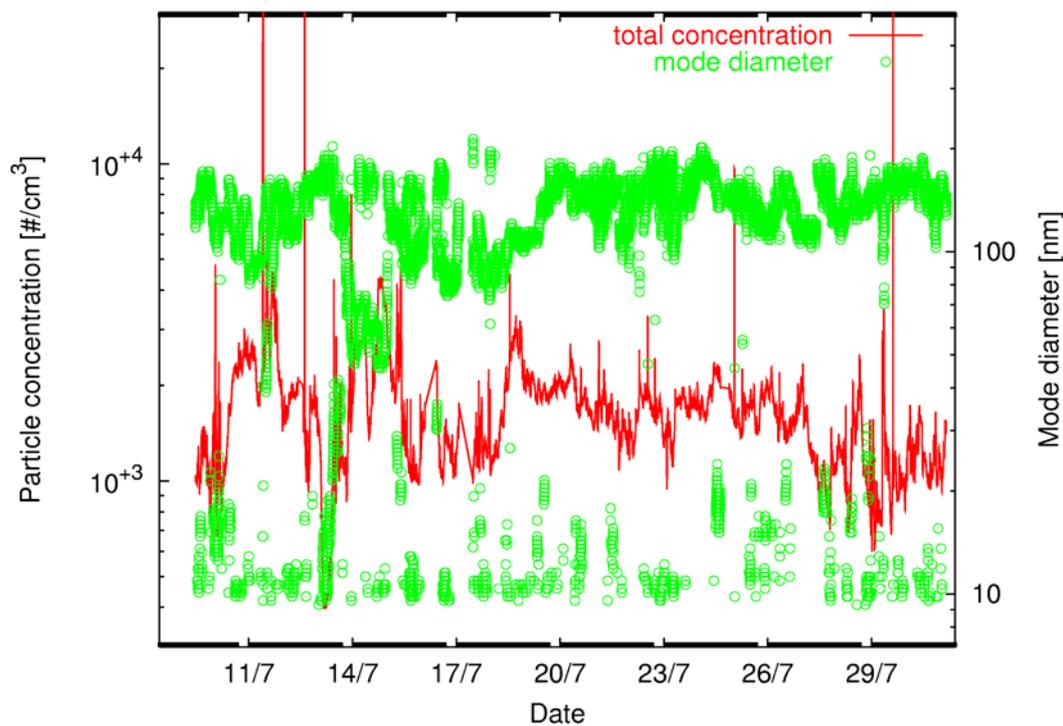


Figure 4.5: The temporal variation of the mode diameter and the total particle number concentration at the Finokalia sampling site (10/07/00-31/07/00).

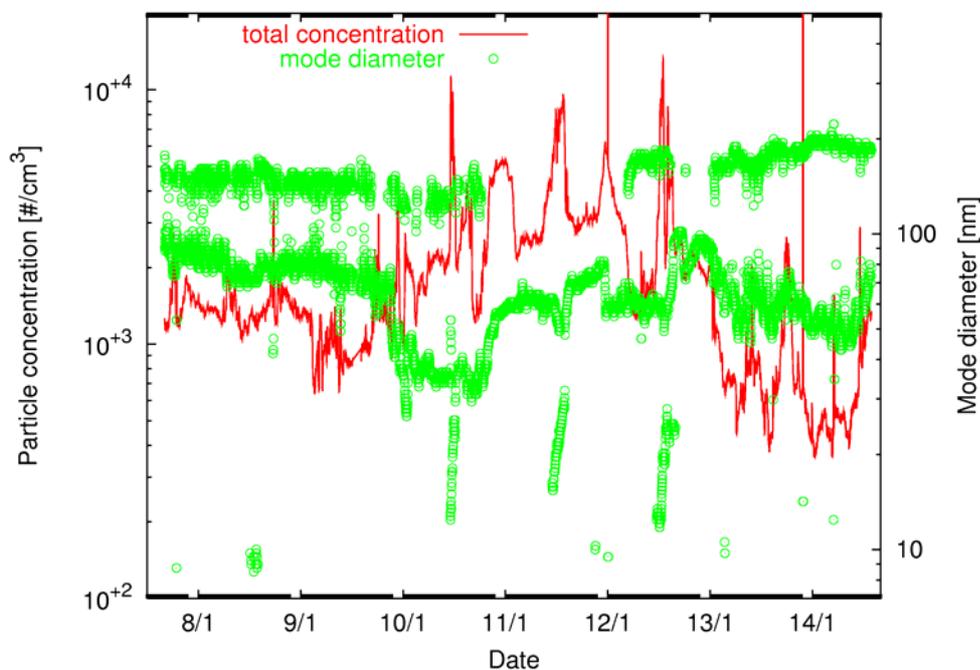


Figure 4.6: The temporal variation of the mode diameter and the total particle number concentration at the Finokalia sampling site (07/01/01-14/01/01).

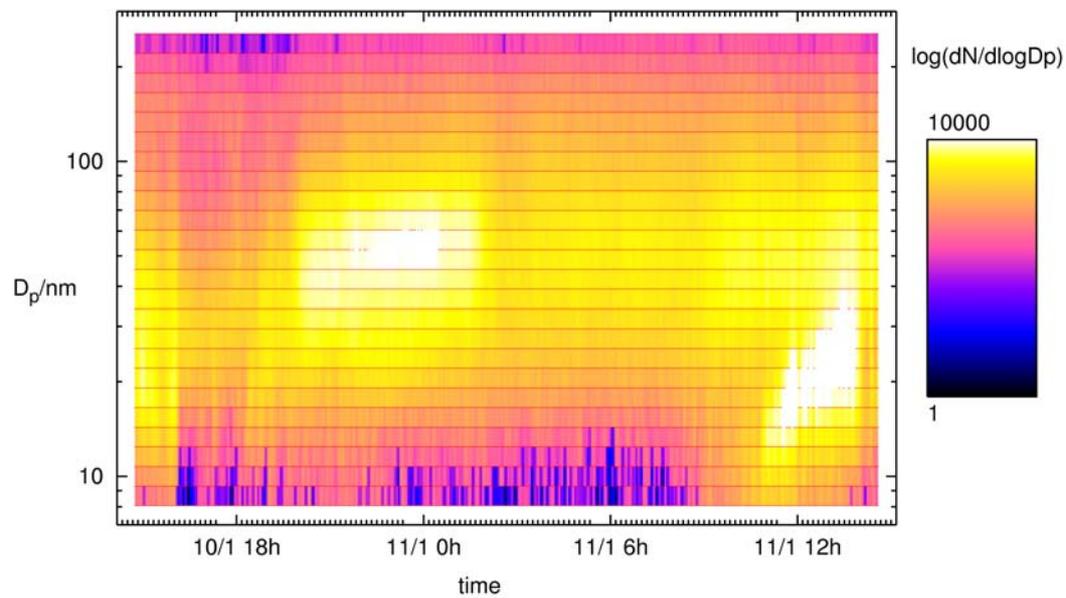


Figure 4.7: Evolution of a nucleation event at the Finokalia station during 10-11 January 2001.

5. Particulate matter characteristics in the Eastern Mediterranean – Saharan dust episodes

by A. Boulgarakis, T. Glytsos, Ø. Hov, K. Tørseth and M. Lazaridis

5.1 Introduction

Long-range transboundary transport is responsible for a significant fraction of the particulate pollution in European cities (WHO/UN, 1999; Position Paper, 2004). 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.

The measurements of sulphate and nitrate aerosol particles, already described in the EMEP programme (EMEP/CCC, 2003), are mainly directed towards acidification and eutrophication. There is also a strong need for more work to be done 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 needs to be quantified and integrated, such as sea-salt aerosol and Aeolian dust from the Sahara in Southern Europe. A study on the PM phenomenology in Europe has recently been published (Van Dingenen et al., 2004; Putaud et al., 2004).

Research studies show that there is a consistent pattern of geographical variability in Europe with lower concentrations of particulate matter in the far north and higher concentrations in southern countries. This is due to natural emissions of unsaturated hydrocarbons (including isoprene) that are highly reactive, and high emissions of anthropogenic gaseous and aerosol pollutants in Southern Europe (Hoffman et al., 1997). Aerosol yields obtained from experimental measurements and theoretical estimates also indicate that highly non-linear aspects are involved in the production of organic aerosols. Furthermore, the Mediterranean region is characterized by a specific natural aerosol load, namely sea spray and North African desert dust. These natural particulate emissions are involved in heterogeneous reactions with anthropogenic gaseous pollutants and may modify the processes leading to gas-to-particle conversion (Millan et al., 1997; Rodriguez et al., 2002; Bardouki et al., 2003).

In the current study the focus is on the PM₁₀ and PM_{2.5} levels at the Acrotiri research monitoring station on the island of Crete (Greece) (Figure 5.1) and the influence of African dust outbreaks on the particulate matter concentration. The work here presents one of the first studies of continuous aerosol monitoring at the Eastern Mediterranean.



Figure 5.1: Geographical location of the Acrotiri research station on the island of Crete.

5.2 Particulate Measurements at the Acrotiri research station

This study is based on particulate matter (PM_{10} and $PM_{2.5}$) measurements performed at a rural station on the island of Crete (Greece) in a period between 2003 and 2004. The measurements are performed with the FH 62 I-R continuous particulate monitor whereas continuous meteorological data are also monitored.

Figure 5.2 shows the average daily values for PM_{10} during the measurement period. The average value for the whole period is $35.1 \mu\text{g}/\text{m}^3$. There is a large variability of the PM_{10} values during the summer period with concentrations $80\text{-}90 \mu\text{g}/\text{m}^3$. During the winter period the PM_{10} concentrations are in general lower and the variability smaller. However, on the 27/02/04 a major Saharan dust event lead to an average PM_{10} level of $193.2 \mu\text{g}/\text{m}^3$. It is interesting to note that the PM_{10} levels in the evening between 9 and 12 p.m. reached $400 \mu\text{g}/\text{m}^3$ with the highest value of $528 \mu\text{g}/\text{m}^3$ around 11 p.m., which is a very high concentration even for typical Saharan dust episodes (Rodriguez et. al., 2001).

The lowest observed PM_{10} value during the measurement period was on 13/02/04 ($10 \mu\text{g}/\text{m}^3$) where a large storm influenced the area. It is evident from the PM_{10} concentrations that the high aerosol concentrations occur during specific short time intervals (1-3 days) due to the influence of southern winds originating from Africa.

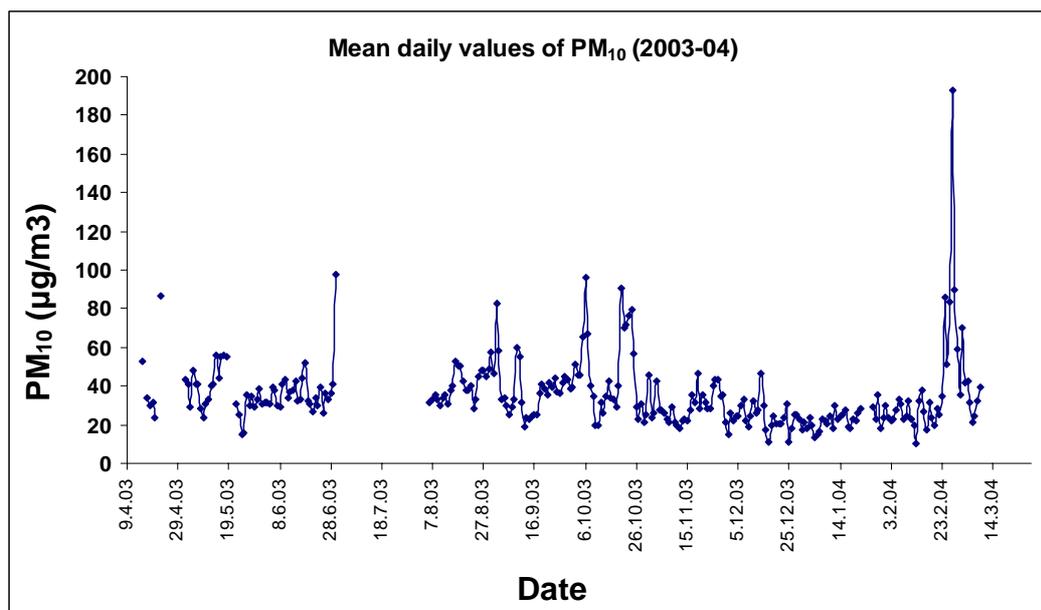


Figure 5.2: Daily average PM₁₀ concentration at the Acrotiri research station.

Figure 5.3 shows the average monthly PM₁₀ concentration during April 2003–March 2004. High aerosol concentrations were observed during the whole measurement period with an average concentration for October 2003 and February 2004 equal to 45.8 µg/m³ and 40 µg/m³ respectively. The reason for the elevated concentrations during these months is the outbreak of a number of Saharan dust episodes in the area.

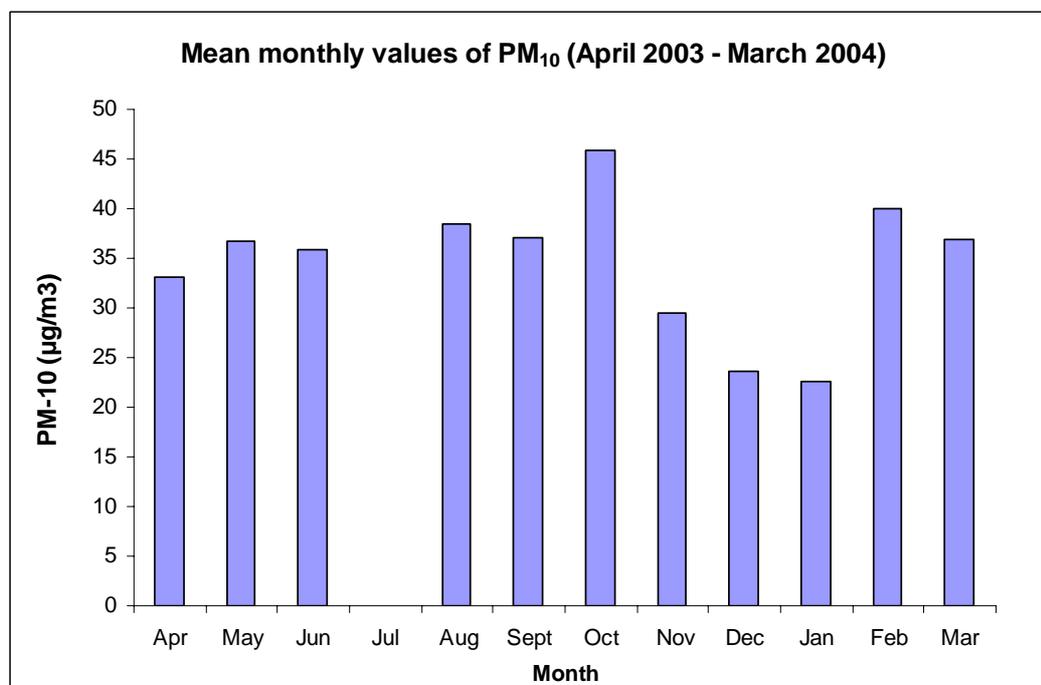


Figure 5.3: Mean PM₁₀ concentration during April 2003–March 2004 at the Acrotiri research station (Crete, Greece).

PM_{2.5} measurements were started 10/3/04 and the daily average concentrations until the 31/05/04 are shown in Figure 5.4.

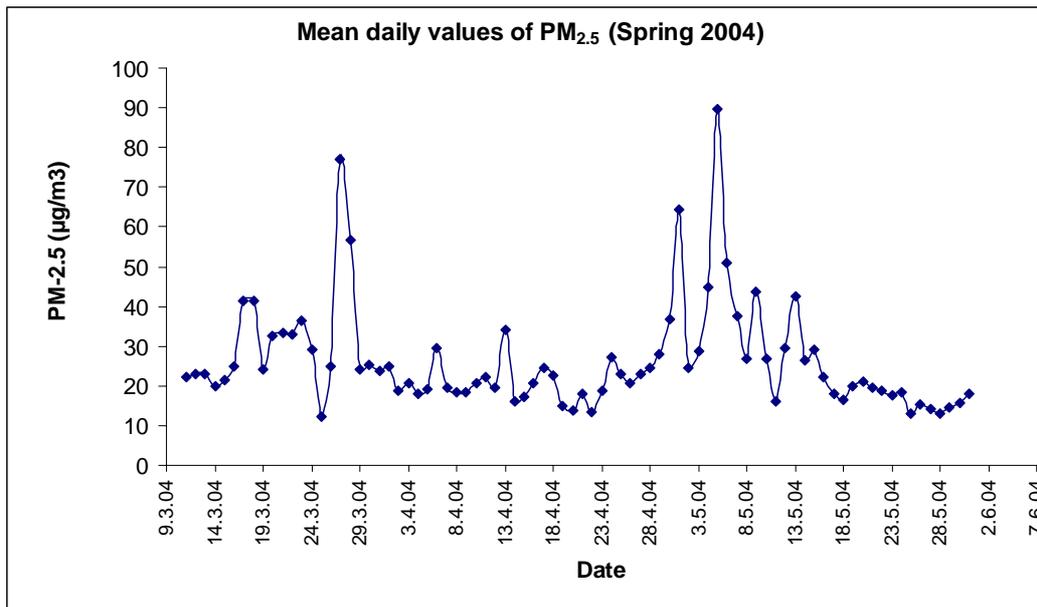


Figure 5.4: Daily average PM_{2.5} concentrations between 10/03/2004–31/05/04.

The average PM_{2.5} concentration during the measurement period is 26.3 µg/m³. There are three periods in which the PM_{2.5} concentration reached high values, which correspond to Saharan dust episodes in the area. On the 27/03/04 the average concentration was 77.1 µg/m³, on the 01/05/04 it was 64.5 µg/m³, and on the 05/05/04 the concentration reached 89.6 µg/m³. The last Saharan dust episode was very intense with a considerable reduction in the visibility. At 9 a.m. the 05/05/04 the PM_{2.5} concentration reached 454 µg/m³.

5.3 Analysis of the Particulate Matter Concentration sources

The origin of the particulate matter concentrations in the area of Crete has been studied using a statistical analysis of the data and back trajectory modelling. Trajectories were obtained using the HYSPLIT4 Model, developed by the Air Resources Laboratory of the National Oceanic and Atmospheric Administration (NOAA) (NOAA, 2002). The trajectories were computed for the coordinates 35.5N, 24.1 E which are the coordinates of the city of Chania. The total run time of the model was 120h (5 days).

The 27/2/04 is a day with very high PM₁₀ concentration values due to a Saharan dust episode (average PM₁₀ concentration 193.2 µg/m³, maximum value 528 µg/m³). In contrast to this, the lowest PM₁₀ concentration for the whole measurement period (average PM₁₀ concentration 10 µg/m³, maximum value 6 µg/m³) was observed on the 13/2/04. Figure 5.5a shows that the origin of the air masses on the 27/2/04 is from the northern Africa whereas in Figure 5.5b, 13/2/04, the origin of the air masses was from north. However, on the 27/2/04 a snowstorm occurred in the area of Crete, which can explain the low PM₁₀ concentration.

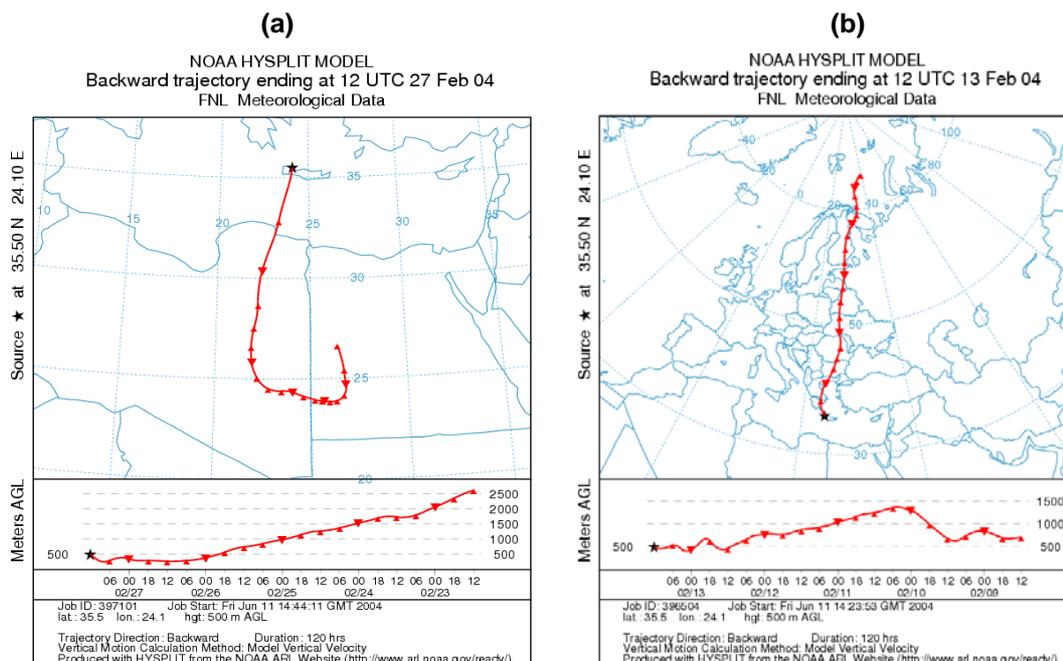


Figure 5.5: Back trajectories calculated by the HYSPLIT4 Model (NOAA, 2002) for (a) 27th February 2004 (b) 13th February 2004.

A statistical analysis has been performed using the back-trajectory data for each day of the measurement period with maps for the origin of the air masses. Four segments have been used corresponding the north-west (NW), north-east (NE), south-west (SW) and south-east (SE) directions.

During the summer period (Figure 5.6) the frequency of occurrence of the air masses from the south direction is very small and consequently no significant contribution can be seen. The average PM_{10} concentration is $42.3 \mu\text{g}/\text{m}^3$ and $35.6 \mu\text{g}/\text{m}^3$ for the NW and NE directions respectively. Figure 5.7 shows the frequency of occurrence of the air masses for the autumn period. During the autumn the PM_{10} levels from the northern directions are lower than the summer period (NW: $34.9 \mu\text{g}/\text{m}^3$, NE: $31.2 \mu\text{g}/\text{m}^3$). However, there is an increase in the frequency of air masses from the southern directions with higher PM_{10} concentration levels (SE: $55.4 \mu\text{g}/\text{m}^3$, SW: $55.5 \mu\text{g}/\text{m}^3$).

Figure 5.8–Figure 5.9 present the origin of the air masses for the periods of winter and spring respectively. During winter the PM_{10} concentration is low during air masses transport from the northern directions (NW: $23.5 \mu\text{g}/\text{m}^3$, NE: $25.5 \mu\text{g}/\text{m}^3$) and elevated with transport from the southern directions (SE: $43.7 \mu\text{g}/\text{m}^3$, SW: $42.1 \mu\text{g}/\text{m}^3$). In addition, during the spring period there is a general increase in the PM_{10} concentration. The air masses originating from the southern direction have elevated PM_{10} levels (SE: $55.7 \mu\text{g}/\text{m}^3$, SW: $70.2 \mu\text{g}/\text{m}^3$). In addition, the PM_{10} concentration from the northern directions is also high (NW: $31.0 \mu\text{g}/\text{m}^3$, NE: $48.0 \mu\text{g}/\text{m}^3$).

Summer period

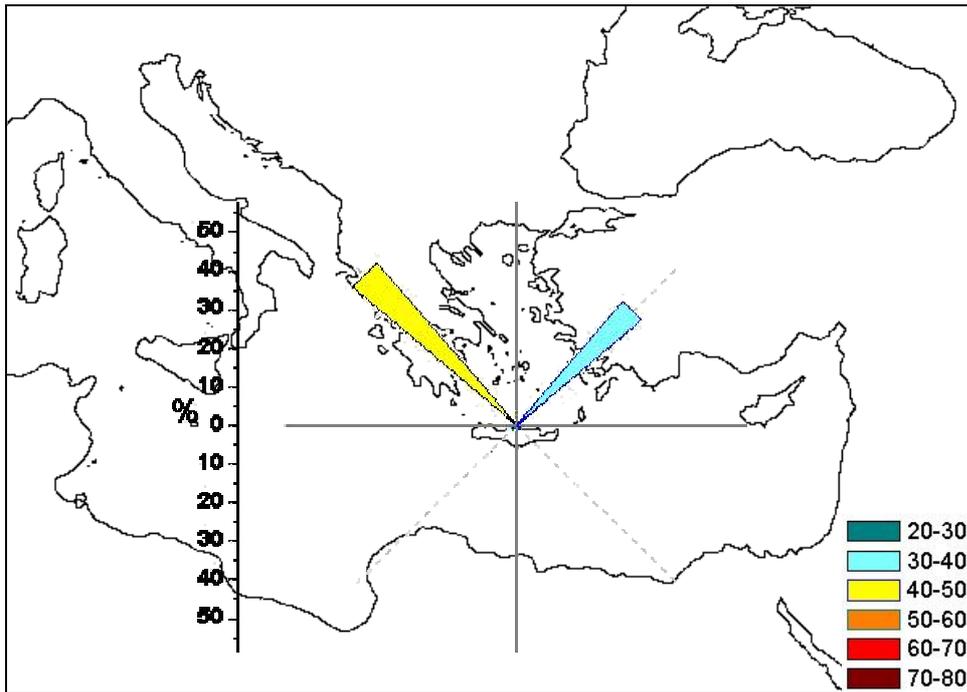


Figure 5.6: Origin of the air masses and corresponding average PM_{10} concentration ($\mu\text{g}/\text{m}^3$) for the summer period.

Autumn period

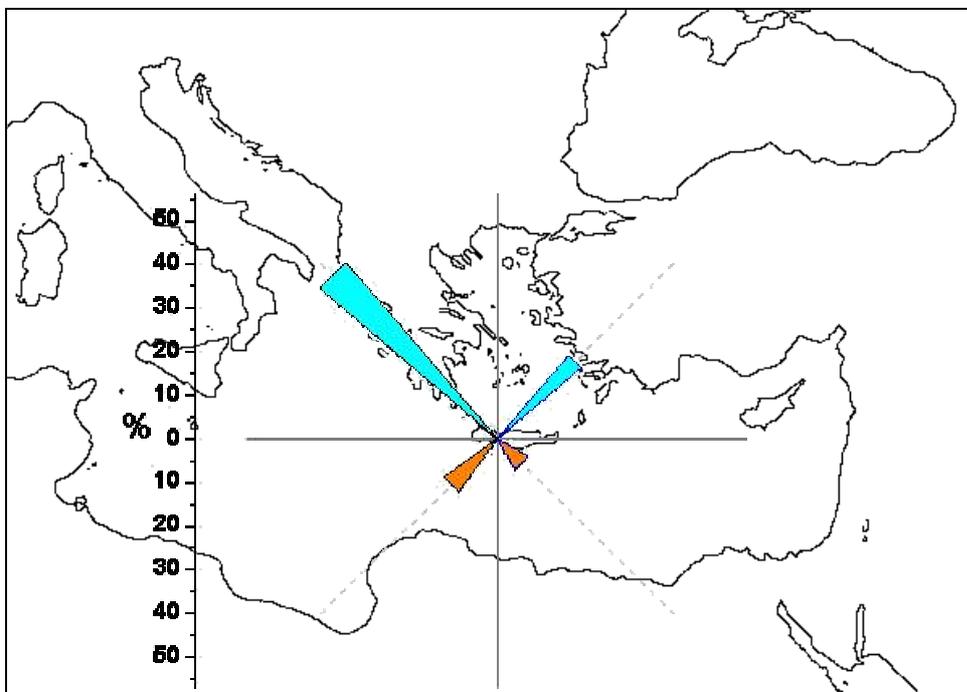


Figure 5.7: Origin of the air masses and corresponding average PM_{10} concentration ($\mu\text{g}/\text{m}^3$) for the autumn period.

Winter period

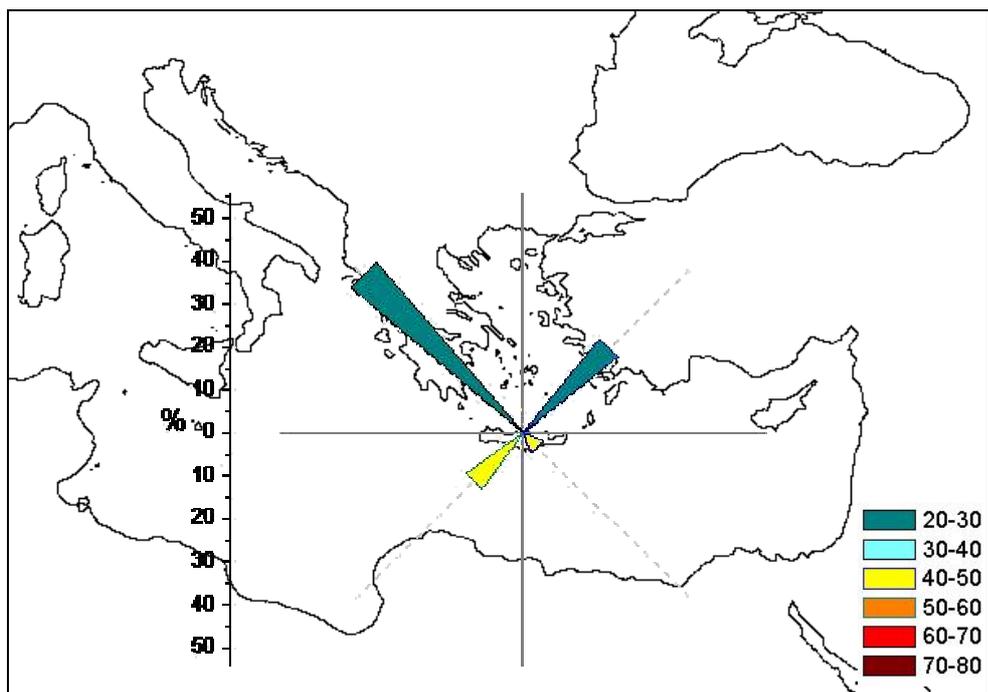


Figure 5.8: Origin of the air masses and corresponding average PM_{10} concentration ($\mu g/m^3$) for the winter period.

Spring period

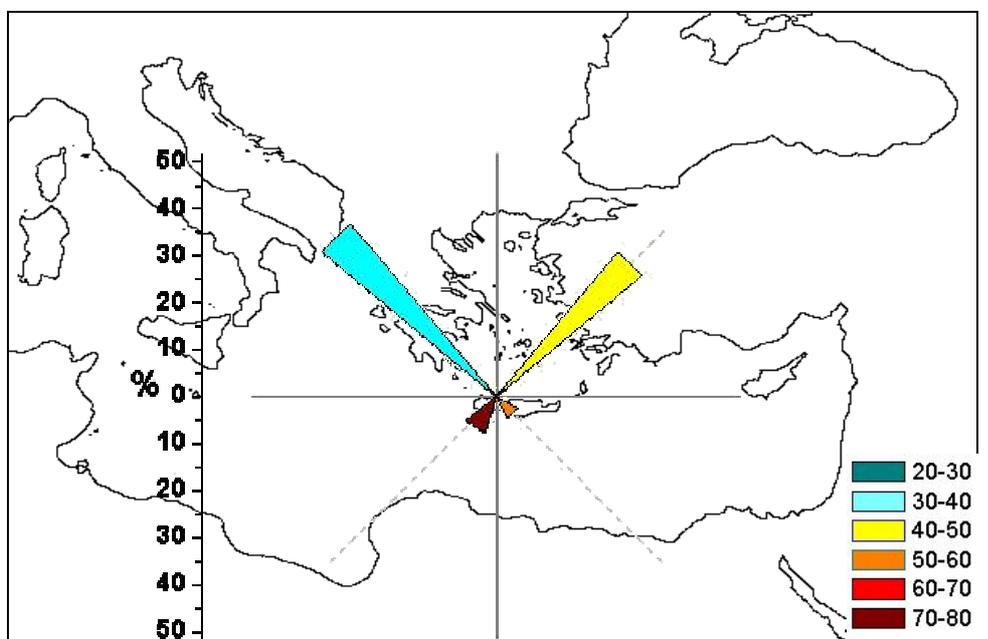


Figure 5.9: Origin of the air masses and corresponding average PM_{10} concentration ($\mu g/m^3$) for the spring period.

Finally, Figure 5.10 presents the frequency distribution of the PM_{2.5} concentration in the Acrotiri research station during the Spring 2004. The results for the PM_{2.5} levels are similar to those for PM₁₀. The PM_{2.5} concentrations originating from the southern directions are high (SE: 32.3 µg/m³, SW: 40.1 µg/m³), whereas elevated concentrations occurred from the northern directions (NW: 24.0 µg/m³, NE: 21.6 µg/m³).

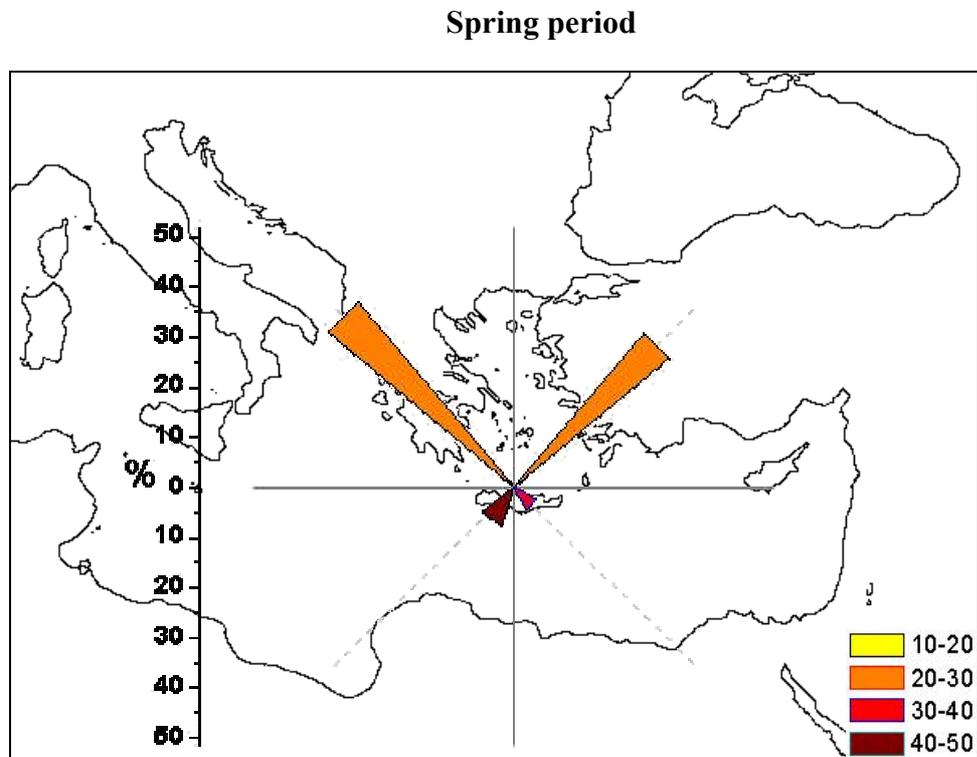


Figure 5.10: Origin of the air masses and corresponding average PM_{2.5} concentration (µg/m³) for the spring period.

5.4 Non-metric Multi Dimensional Scaling (MDS) Analysis

A non-metric Multi Dimensional Scaling (MDS) analysis has further been applied to study the similarity of the particulate matter concentration in connection with the meteorological data. In the MDS analysis the particulate matter data are organized in clusters with the same statistical characteristics in relation to the meteorological parameters. Figure 5.11 shows all the daily average values of PM₁₀ and the size of each circle depends on the particulate matter concentration. The results strongly indicate three clusters. The right cluster refers to high concentration values and is well correlated with Saharan dust episodes. The cluster at the left correlates with snowstorm events where the concentration values are very low. Finally, we have the middle cluster which refers to typical particulate matter concentrations in the area. We can therefore conclude with three distinctive clusters of particulate matter concentrations in the area. The high PM events have similarity with the outbreaks of African dust, the low PM events have similarity with the high storm events, whereas the major part of the data can be organized in a third cluster in which typical meteorological conditions occurred with air masses originating from the northern directions.

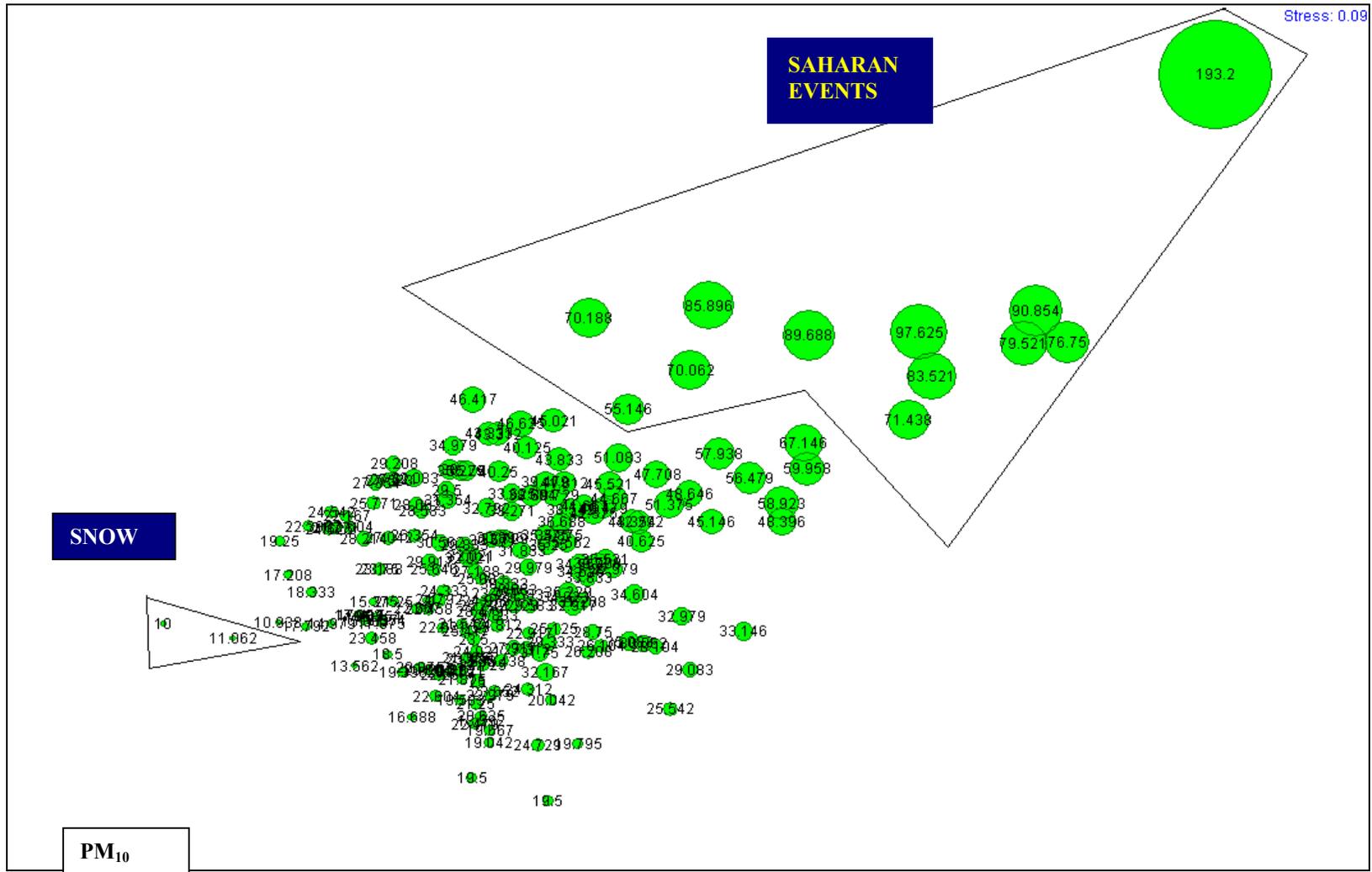


Figure 5.11: MDS bubble plot for the PM₁₀ ambient concentration at the Acrotiri research station between April 2003-03/04-March 2004.

5.5 Conclusions

The ambient PM₁₀ and PM_{2.5} concentration at the Acrotiri research station on Crete (Greece) show a large variability with elevated concentrations during Saharan dust episodes. The statistical analysis reveals that the high particulate matter concentrations in the area correlate well with air masses originating from Africa whereas the low PM events correlate with heavy storm episodes in the area of Crete.

The transport from the Greek mainland and the European continent contributes significantly to the particulate matter levels in the area since the north winds are dominant during the year. However, the particulate matter concentration at the Acrotiri during the transport of air masses from the northern Europe is elevated but considerable lower than the high concentrations during the outbreaks of African dust.

The annual average PM₁₀ standard of 40 µg/m³ is not exceeded in the area. However, the EU 2010 annual average PM₁₀ standard of 20 µg/m³ is exceeded. Furthermore, the US-EPA annual average PM_{2.5} standard of 15 µg/m³ seems to be exceeded in the area. Since the Acrotiri station measures PM_{2.5} levels from March 2004 only, no certain conclusion can, however, be drawn for the PM_{2.5} annual average concentration.

6. Sun photometer measurements within WMO GAW in Ny-Ålesund at Spitzbergen, and in continental Europe during 2003

by J. Schaug and C. Wehrli

The PFR measurements at Ny-Ålesund are part of a global network of aerosol optical depth (AOD) observations that was started in 1999 by PMOD/WRC on behalf of the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO). During an initial trial-phase, this network served as a test-bed for new instrumentation and methods of calibration and determination of AOD in GAW after WMO had recommended to abandon AOD observations in the former BAPMoN program following a critical review of measurement procedures and data quality assurance in 1994. A World Optical Depth Research and Calibration Center (WORCC) was established in 1996 at PMOD/WRC, based on a mandate recommended during a WMO meeting of experts in 1995, and has developed a robust, automated filter radiometer and a calibration hierarchy including laboratory standards and master instruments that are calibrated at high altitude sites like Jungfraujoch, Switzerland or Mauna Loa, Hawaii.

A limited number of 12 GAW stations were proposed by the GAW Scientific Advisory Group on Aerosols to participate in this trial network by operating a PFR radiometer on a solar tracker and making the data available to WORCC. The radiometers, but not the sun trackers, are provided by MeteoSwiss as a contribution to the GAW program.

Measurements of direct solar radiation in four narrow spectral bands centred at 862, 500, 412 and 368 nm from the network stations are collected off-line at WORCC for centralized evaluation of aerosol optical depth on a monthly basis. Data quality control includes instrumental tests, like detector temperature, solar pointing staying within specifications, and automated cloud screening by two different algorithms. Final results are delivered as hourly averages after statistical tests to the World Data Center for Aerosols (WDCA) in Ispra. Where atmospheric conditions permit, instruments are calibrated on-site, while for other sites they can be recalibrated by comparison to standard instruments maintained at WORCC, Davos. The high stability of the new PFR is typically better than 1% per year represent a significant improvement over instruments used in the former BAPMoN program.

By end of 2003, eight international stations were delivering data, 3 more stations have agreed to participate, but were, for lack of solar trackers, not yet operational. Figure 6.1 shows the geographical extent of the network. Ny-Ålesund is the station at highest latitude in this network, where routine AOD observations are scarce and thus of special interest.

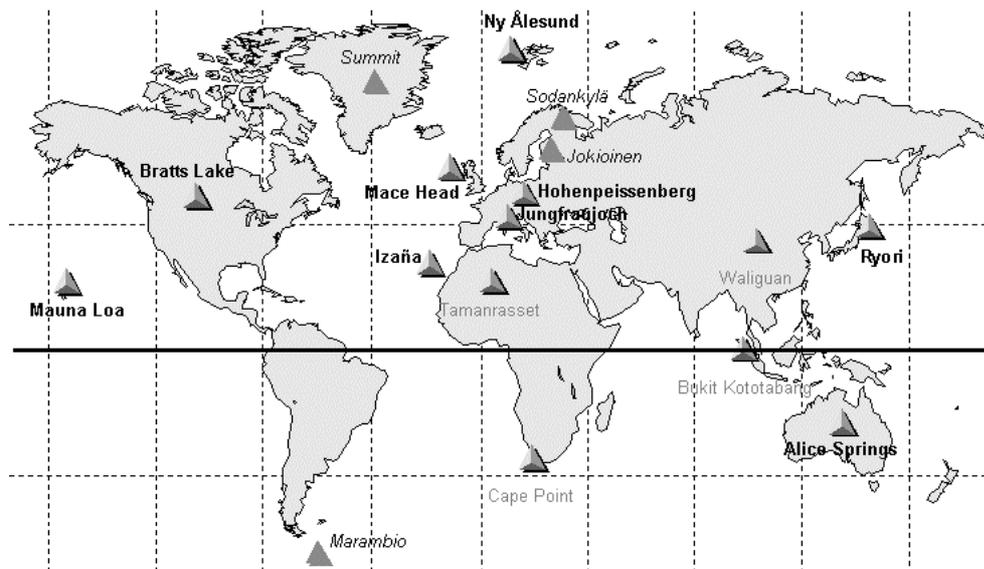


Figure 6.1: Map of GAWPFR network. Station names in **bold** are operational, in *grey* planned sites; names in italics indicate additional PFR's operated by FMI or ETHZ.

An presentation of the 2003 Ny-Ålesund results are given below and compared with the corresponding measurements from Hohenpeißenberg in the southern part of Germany at 985 m asl, and at Jungfrauoch at 3580 m asl in the Swiss Alps. The three sites are all different with respect to aerosol optical depth and also aerosol concentrations at the measurement site. The data presented have been filtered with a tight cloud and tracking filter, daily averages represent at least 90, and monthly averages at least 360 quality controlled records.

Ny-Ålesund

The sun photometers has sun trackers that direct the photometers to the sun disc and leads the spectrometers to follow the sun across the sky during the day. The sun photometers are passive instrument that records the sun irradiance only, and they cannot carry out measurements during dark hours or during foggy or cloudy conditions. Fog and low clouds often occur in Ny-Ålesund, and this reduces the data completeness seriously at this site. A relocation of the instrument at the Zeppelin mountain station (474 m asl) would give more results since the fog in this case often will be lower than the instrument, and the instrument could have a longer active period not being in the shade of surrounding mountains. So far, however, no sun tracker is available at the Zeppelin station. The polar night at Ny-Ålesund lasts from 26th October to 16th February, the measurement season is therefore much shorter than at the sites Hohenpeißenberg and Jungfrauoch, but offers a unique opportunity for annual recalibration of the instrument at WORCC, as done in 2003 and 2004.

2003 was not a good year with respect to data completeness at Ny-Ålesund since technical problems occurred in addition to fog and clouds conditions. The instrument temperature sensor failed in April, and the pointing of the sun

photometer to the sun disc fell frequently out of range from May to July causing data to be excluded from the present data set.

Figure 6.2 shows the aerosol optical depth measured at Ny-Ålesund from the middle of April to the beginning of October. The Figure also gives for comparison the sulphate concentrations in aerosols measured at the Zeppelin Mountain (475 m asl). The aerosol optical depth and the aerosol sulphate concentrations are normally relatively high during the spring compared to the corresponding summer measurements, and are due to the Arctic haze phenomenon that has been observed for more than fifty years. Aircraft measurements revealed that most of the wintertime Arctic haze was found in the boundary layer, but that distinct layers of haze also could be found at different altitudes up to 5 km (Ottar et al., 1986). Strong inversions inhibit the exchange of air between the layers during winter and prevent the formation of precipitation giving clouds.

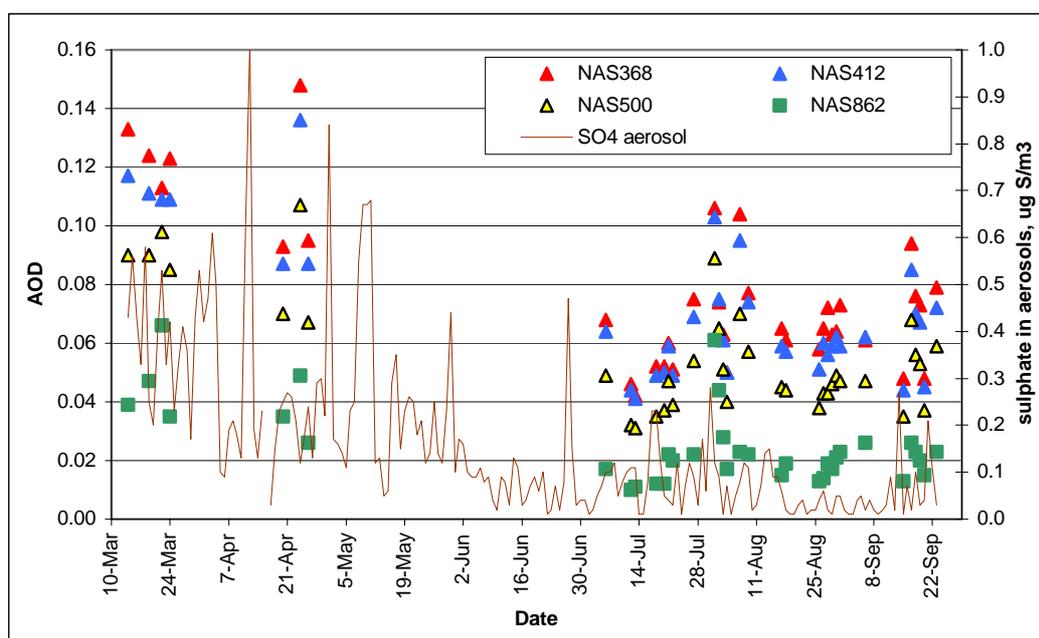


Figure 6.2: Daily AOD averages at 368, 412, 501, and 863 nm measured in Ny-Ålesund, applying a tight cloud and tracking filter. Daily averages concentrations of sulphate in airborne particles measured at the Zeppelin mountain site during 2003.

Removal mechanisms are therefore suppressed during winter and spring, and the cold and stable winter Arctic boundary layer may extend into the industrial sources in the south. In summer precipitation occurs resulting in a fast removal of aerosols as well as water-soluble gases. The Arctic haze is very well described by AMAP (1998) in the assessment report that additionally give a large number of references to related topics.

Jungfraujoch

The observatory at Jungfraujoch is located at about 3600 m asl and is frequently in the free troposphere above the boundary layer. The aerosol optical depth, as well as the particle concentration at the site, is therefore normally extremely low permitting this site to be used for calibration of master sun photometers. Figure 6.3 presents the daily AOD averages at the four wavelengths, together with the daily averages of suspended particulate matter (SPM) from the observatory during 2003. As seen the AOD results were all lower than 0.10 in this data set, and with the highest values during March–June in 2003.

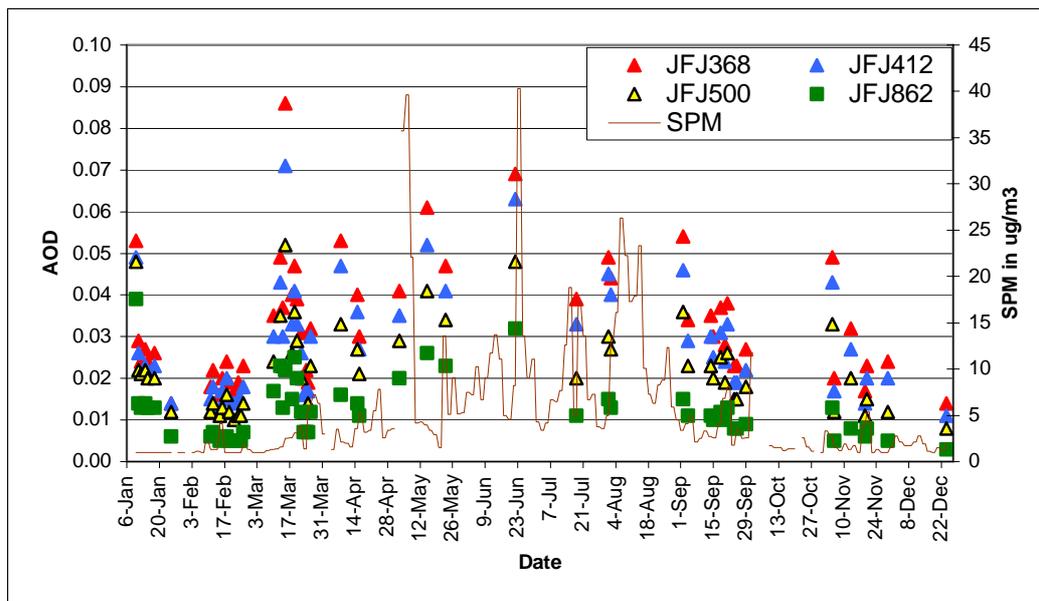


Figure 6.3: Daily AOD averages at 368, 412, 501, and 863 nm at Jungfraujoch during 2003, applying a tight cloud and tracking filter. SPM measurements at the observatory.

Hohenpeißenberg

The observatory at Hohenpeißenberg is located in the southern part of Germany about 60 km southwest of Munich and some 20 km north of the rising Alpine mountain range. The observatory's altitude is, however, nearly 1000 m asl and the observatory is above the polluted surface layer much of the time. Given a clear sky, this sun photometer can be operated all year around. The aerosol load and surface concentrations are generally higher at Hohenpeißenberg than at the two other sites. The highest aerosol optical depths were observed between late March and early May, but relatively high AODs were seen even in autumn. Figure 6.4 presents the daily averages measured at Hohenpeißenberg during 2003.

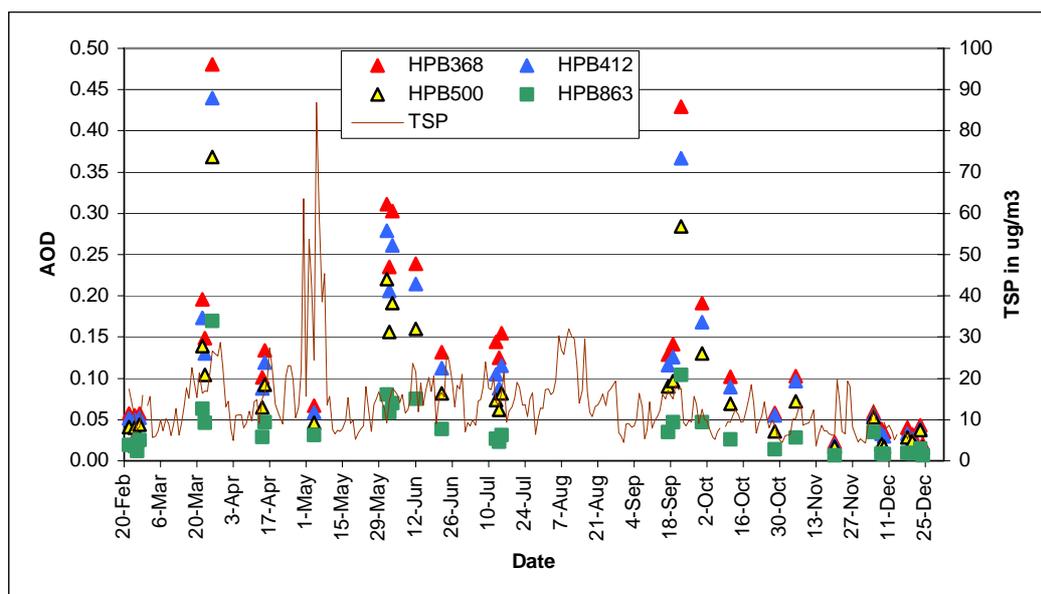


Figure 6.4: Daily AOD averages at 368, 412, 501, and 863 nm measured at Hohenpeißenberg during 2003, applying a tight cloud and tracking filter. TSP daily averages at the observatory (Kaminski, personal communication).

Figure 6.5 and Figure 6.6 compare the aerosol optical depth at 500 nm at the three sites by giving the monthly mean values and the daily averages respectively

The AOD at Hohenpeißenberg is seen to be about a factor of ten higher than at Jungfraujoch on one or two days in March and September, but during winter both observatories have very low and more equal aerosol optical depths. The Hohenpeißenberg monthly averages of AOD at 500 nm in Figure 6.5 were about 2-3 times higher than those at Jungfraujoch during November and February.

It is also evident from Figure 6.5 and Figure 6.6 that the optical depth at 500 nm in the Arctic at Ny-Ålesund generally was lower than that at Hohenpeißenberg, but much higher than at Jungfraujoch. During March and September when all three sites had valid monthly averages, the Arctic AOD at 500 nm were about three to four times higher than the high altitude averages from Jungfraujoch and about one half to one third of the Hohenpeißenberg monthly averages in 2003.

It should be noted that in order to obtain general and quantitative conclusion on the levels of the AODs at the three measurement sites, data from at least five years should be needed. This is particularly important when applying a tight cloud and tracking filter that, although including high quality data only, could exclude a large fraction of the measurements.

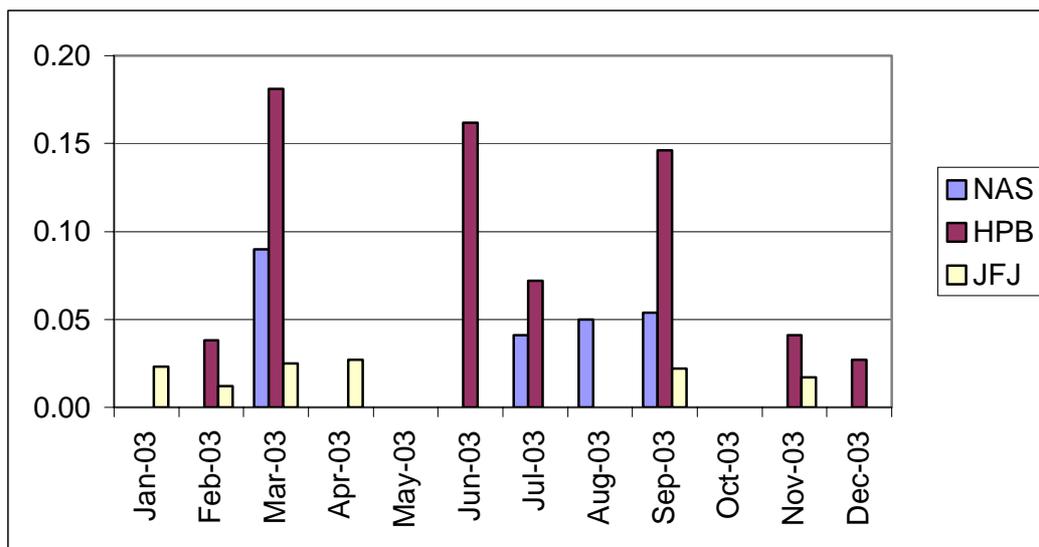


Figure 6.5: Monthly mean AOD at 500 nm measured at Ny-Ålesund (NAS), Hohenpeißenberg (HPB), and at Jungfraujoch (JFJ), applying a tight cloud and tracking filter.

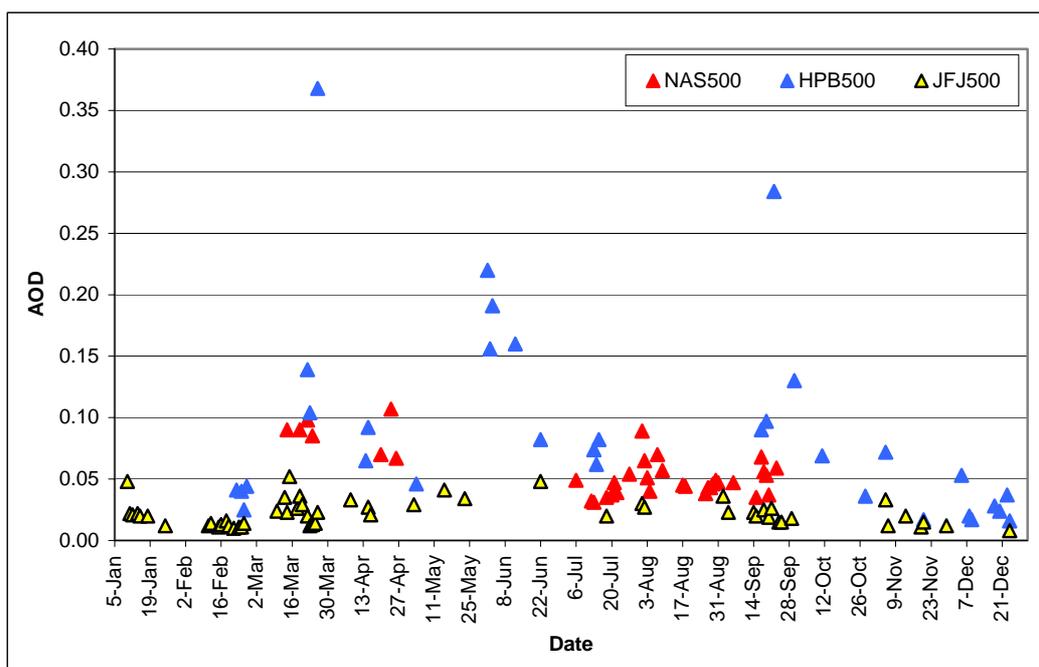


Figure 6.6: Daily averages of AOD at 500 nm measured at Ny-Ålesund (NAS), Hohenpeißenberg (HPB), and at Jungfraujoch (JFJ), applying a tight cloud and tracking filter.

Acknowledgement

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