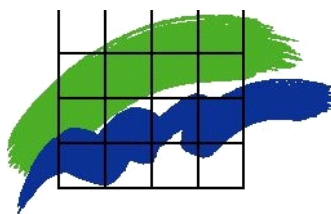


**norden**

Nordic Council of Ministers

Measurements of PM₁, PM_{2.5} and PM₁₀ in air at Nordic background stations using low-cost equipment

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B1791
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National Environmental Research Institute, Denmark

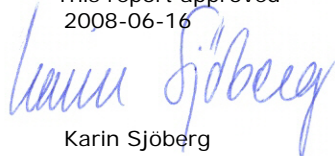


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<p>Title and subtitle of the report Measurements of PM₁, PM_{2.5} and PM₁₀ in air at Nordic background stations using low-cost equipment</p>	
<p>Summary Mass concentrations of PM₁, PM_{2.5} and PM₁₀ in air were measured at four EMEP stations in the Nordic countries during 2006. All stations used the same low-cost equipment for sampling PM₁, but used different techniques for the other size fractions. The PM₁ filters were analysed for inorganic ions for the first half of June. PM₁ constituted on average more than half of the PM_{2.5} concentrations, but was on average less than half of the PM₁₀ concentrations. There were two episodes of high PM₁ concentrations during the year, one in May-June and another one in August-September. The highest PM₁ concentrations were found during South-Easterly wind trajectories and lowest concentrations during northerly trajectories. Even though the annual average mass relations between the three size fractions were rather independent of the trajectory sectors, the fine and the coarse particle masses were not correlated on a daily basis. The PM_{2.5} concentration, which is the parameter that should be measured within EU, correlated fairly well with the concentration of accumulation mode particles (PM₁). In June only a minor fraction of PM₁ consisted of inorganic ions. Only ammonium and sulphate ions of the measured ions in PM₁ were well correlated with one another.</p>	
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Karin Sjöberg
Section Manager

To Jan Erik Hanssen who tragically died before the project was finished

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1 Introduction

1.1 Why study aerosols?

The tropospheric aerosol has become one of the most intensely studied topics within atmospheric sciences due to its impact on the global climate and its negative influence on human health.

1.2 Aerosol particle size - an important parameter

Size is regarded as the most fundamental parameter describing an aerosol particle. It is a key parameter concerning transport and removal, and it is essential in understanding the effects of the ambient aerosol. The aerosol is commonly defined by the aerodynamic diameter; i.e. *“that of a spherical particle of unit density (1 g cm^{-3}), having a settling velocity equal to that of the particle in question”*.

The size distribution of the tropospheric aerosol is commonly divided into three major modes (Whitby, 1978); the nuclei mode ($0.005 < d_p < 0.1 \text{ }\mu\text{m}$), the accumulation mode ($0.1 < d_p < 1.0 \text{ }\mu\text{m}$) and the coarse mode ($1.0 - 3.0 \text{ }\mu\text{m} < d_p$), all having different formation processes, leading to different characteristics of the aerosol. Subsequent physical and chemical processes may modify the size of the aerosol, thus the boundaries between the modes are not entirely fixed. Within each of the three modes mentioned, there could be several modes of different origin and composition.

1.3 Sources of aerosols

Tropospheric aerosol particles are either emitted directly or formed in the troposphere by oxidation of precursor gases, such as sulphur dioxide, nitrogen dioxide and volatile organic compounds, where the resulting oxidation products nucleate to form new particles or they condense on pre-existing ones. Particles formed through these two pathways are referred to as primary and secondary particles, respectively. The sources of tropospheric aerosols are plentiful, and arise from both natural (e.g. windborne dust, sea spray, volcanic activity, wild fires) and anthropogenic (e.g. fuel combustion, industrial processes, nonindustrial fugitive sources and transportation sources) activities. On a global scale the natural sources contribute the most, but regional variations in the man-made pollution can change this significantly in certain areas, especially in the Northern Hemisphere (Seinfeld and Pandis, 1998).

1.4 The accumulation mode

Small particles ($d_p < 1 \text{ }\mu\text{m}$) diffuse to the earth's surface, a process that becomes less efficient as the particle size increases, whereas larger particles ($d_p > 1 \text{ }\mu\text{m}$) settle gravitationally or by impaction on a surface, a process that becomes less efficient as the particle size decreases. In the size range $0.1 \text{ }\mu\text{m} < d_p < 1.0 \text{ }\mu\text{m}$, neither diffusion nor gravitational settling or impaction is efficient, thus aerosols tend to accumulate in this size range. The less efficient removal processes prolong the atmospheric residence time of the accumulation mode aerosols, thus increasing their long-range transport

potential. Accumulation mode aerosols are removed mainly by activation in clouds and subsequent precipitation.

1.5 Sampling of particulate matter (PM)

PM₁₀, PM_{2.5} and PM₁ should be sampled using inlets with a 50 % cut-off at 10 μm, 2.5 μm and 1 μm aerodynamic diameters respectively. Of these, PM₁ is the size fraction which most closely resembles the accumulation mode. The particles that pass the inlet with the greased impactor plate are collected on a filter medium. Filtration may, however, result in changes of the total collected particles mass. Adsorption of gases on the filter may increase the observed mass. Topochemical reactions i.e. particles of different origins that don't come in contact with one another in the atmosphere may come in contact on the filter and form gaseous compounds. Some particles will also be surrounded by air of reduced pressure due to the pressure drop over the filter resulting in a disturbed equilibrium between gas and particle phases. There is no way to avoid all these artefacts. It is therefore necessary to standardize the sampling procedure. The weighing is made at different temperature and humidity than during sampling. The weighing must therefore also be standardized. In Europe there are standards for PM₁₀ (CEN, 1998) and PM_{2.5} (CEN, 2005), but not yet for PM₁. Sampling of PM₁ was therefore in this project made using the same equipment and filter material at all sites. Sampling should according to the standards be made at ambient temperature and the filters should be equilibrated at 20 °C and 50 % r.h. before they are weighed. Sampling at ambient temperature as well as weighing at 50 % r.h. has made real-time measurements of PM₁₀, PM_{2.5} and PM₁ difficult. Correction terms therefore often have to be used in order to give comparable results with volumetric sampling (reference method).

It has been well documented that Scandinavia is subject to long-range transport of particulate matter pollution from the European continent. By measuring the PM₁ mass (μg m⁻³), we are more likely to identify the long-range transported aerosols. However, there are exceptions to this; given favourable meteorological conditions, coarse aerosols might also have a long-range transport potential; e.g. Saharan dust have been observed in Scandinavia at several occasions, whereas during wild fires, pyro-convection can lift coarse aerosols to such altitudes (into the stratosphere) that they can be subjected to transboundary transport.

1.6 Formation of accumulation mode aerosols

Continued condensation of Aitken mode particles (0.01 μm - 0.1 μm) and coagulation will eventually lead to accumulation of particles in the accumulation mode, and is regarded as the main mechanism transferring particles from the nuclei mode to the accumulation mode (Seinfeld and Pandis, 1998). Another way of accumulating secondary organic aerosols in the accumulation mode is through condensation on primary particles emitted in that size range (0.1 μm < d_p < 1.0 μm), typically coming from incomplete combustion of wood, oil, coal, gasoline and other fuels. These processes will account for the condensation mode, which is one of the two modes commonly seen in the accumulation mode, peaking at 0.2 μm (John, 2001).

Aqueous phase reactions taking place in cloud and fog droplets, and in aerosols experiencing relative humidities approaching 100 %, is another way of adding mass to the accumulation mode. Once a droplet is formed, gaseous compounds (e.g. SO₂) can enter the water phase and be oxidized (e.g. H₂SO₄). When the droplet evaporates, the residual particle is larger than the original particle. Activation of condensation mode particles, followed by aqueous phase chemistry and droplet

evaporation is a plausible pathway of the droplet mode, which is the second mode of the accumulation mode, peaking at 0.7 μm .

1.7 Chemical composition of accumulation mode aerosols

The accumulation mode accounts for the majority of PM_{2.5}, thus there are number of studies from which the chemical composition of the accumulation mode particles can be addressed. Sulphate, ammonium, organic carbon, elemental carbon and certain transition metals (e.g. Pb, Cd, V, Ni, Cu, Zn, Mn, Fe, As, Sb) are the most predominant species found in the fine mode. There are also number of species that can be found in both the fine and the coarse modes, such as certain elements (V, Cu, Mn, Ni, Cr, Co, Se) and nitrate. Fine nitrate is usually in the form ammonium nitrate, following the reaction between nitric acid and ammonia. Organic matter (OM = OC x conversion factor) or SO₄²⁻ is typically the major contributor to the aerosol mass.

1.8 Aim of the study

In Scandinavia, the regional background concentration of PM is demonstrated to make a substantial contribution even to the urban level of PM (Forsberg et al., 2005). A considerable part of the regional PM level is attributed to long-range transported PM. By measuring PM₁ at Scandinavian EMEP sites, we are more likely to isolate a larger fraction of the long-range transported aerosols than by measuring PM_{2.5}, which might be influenced by mechanically generated aerosols of local origin. Subsequent chemical analysis of PM₁ will provide additional important information about long-range transported PM. In the present study, PM₁ was measured at EMEP sites, which currently measure PM_{2.5} and PM₁₀, for a period of one year. Chemical analysis of the major anions (SO₄²⁻, NO₃⁻, Cl⁻) and cations (NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺), corresponding to the recommendations made by EMEP for level 1 sites, were performed on a subset of the samples.

2 Experimental

Measurements of PM were carried out at four Nordic EMEP stations (see Fig. 1). Sampling of PM₁, PM_{2.5} and PM₁₀ was performed on a 24 h basis (shifting 06:00 GMT) or in real-time with storage of hourly means. The measurements should cover one year, but started at different times on different stations.

PM₁ was collected using the same equipment (IVL, PModell S1) at all sites. The sampling inlet (Fig. 2) has been developed at IVL in collaboration with Lund Technical University. It is developed for a flow rate of 17.8 l min⁻¹. A 25 mm PTFE membrane disk filter (TF 1000) was used at all sites because of low background concentration and reasonable pressure drop. Its performance in the urban background environment has previously been compared to that of the EU reference method (Persson *et al.*, 2002), showing excellent results (Fig. 3). Impaction was used to remove unwanted particles in all sampling equipment used in this study. The air stream is then accelerated in a nozzle before it hits the impactor plate. The diameter of the nozzle has to be decreased with the aerodynamic diameter of the particle that should be removed. The smaller aerodynamic particles diameter you want to collect from the air, the more particle mass has to be removed by the impactor at the same time as the diameter of the nozzle (and the greased spot of the impactor) has

to be smaller. This can be a problem when sampling PM₁. If the greased spot becomes covered with particles, particle bounce-off may occur. A pre-separator has been constructed for the IVL sampling head to account for this, however, this feature seems to be necessary only for the high aerosol loading experienced in heavily trafficked streets. Insects can sometimes be found on the filter, but this occurred rarely.

PM_{2.5} and PM₁₀ was, however, measured with different techniques at different sites.

Lille Valby (Denmark)

PM₁₀ particles were collected on mixed cellulose ester filters with an SM200 beta attenuation monitor (Opsi, Sweden) at a flow rate 16.7 l min⁻¹. PM_{2.5} was measured using a TEOM monitor (Thermo Electron Corporation, USA) operating at 50 °C and a flow rate of 3 l min⁻¹ and a bypass flow of 13.7 l min⁻¹. No correction factor was used. Based on PM₁₀ measurements with TEOM, it is estimated that up to 9 µg m⁻³ is lost due to evaporation of volatiles on an annual basis.

Birkenes (Norway)

PM_{2.5} and PM₁₀ aerosol filter samples were provided using two low volume samplers from Derenda (LVS 3.1), operating at a flow rate of 38 l min⁻¹. The samples were collected according to a 6 + 1 day sampling scheme, and on a weekly frequency.

All samplers were operated using pre-baked (850°C for 3.5 hours) quartz fibre filters (Whatman QM-A, 47 mm). The filters were picked from the same batch number in order to minimize differences in adsorptive capacity (Kirchstetter *et al.*, 2001). Field blanks were assigned to each fourth day of sampling and were treated in exactly the same manner regarding preparation, handling, transport and storage, as the filters being exposed. The filters were conditioned at 20 °C and 50 % RH for 48 hours prior to and after exposure.

Aspvreten (Sweden)

PM₁₀ was analysed by a continuous TEOM 1400A with a Rupprecht and Pataschnick PM₁₀-inlet (conventional type). Data was recorded as one hour averages and aggregated to 24-hour data. A function was used to correct for losses of semi-volatile components and make results comparable with the EU reference gravimetric filter method.

$$PM_{10} \text{ (EU-ref)} = 1.26 \times PM_{10} \text{ (TEOM)} + 3.6$$

PM_{2.5} was collected synchronously with PM₁ on fibre film filters (heat resistant borosilicate glass fibre coated with fluorocarbon, TFE) using IVLs sampling head (IVL, PModell S2.5). Filters were weighed at 50% r.h. and 20°C.

Virolahti (Finland)

PM₁₀ particles were collected on polytetrafluoroethylene (PTFE, Teflon) filters, using the Digital D PM₁₀/2.3/01 sampling head (flow rate of 38 l min⁻¹). PM_{2.5} was sampled with a MCZ PM_{2.5} - sampling head. Filters were weighed at normal room temperature and humidity. Only data from filter sampling are used here. In addition to the filter samplers, there were also PM₁₀ and PM_{2.5} monitors at Virolahti. The correlation between the PM₁₀ masses measured with the monitor (Thermo ESM Andersen FH 62 I-R, correlation factor 1,31) and the filter sampler was good (PM₁₀ (monitor) = 1.12* PM₁₀ (filter), r= 0.97, n=50).



Figure 1. Map showing the locations of the stations.

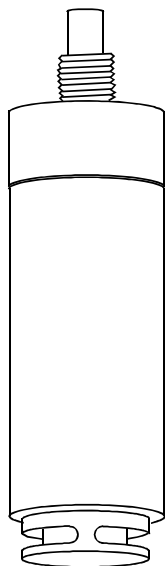


Figure 2. The PM_{10} sampling inlet used in the present study.

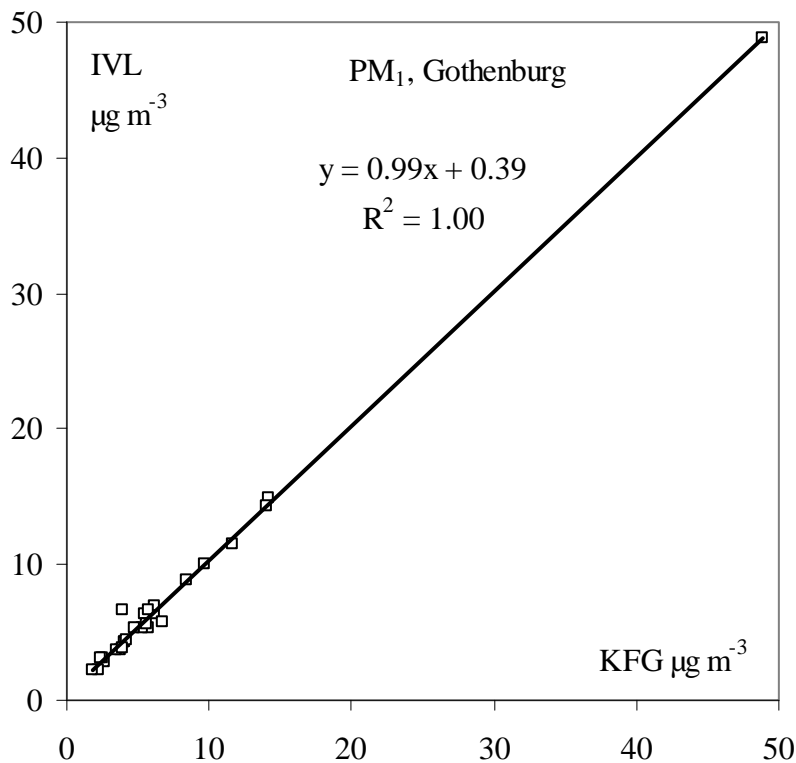


Figure 3. Scatter plot showing concentrations of PM₁ in an urban environment obtained using the IVL-head (inlet) and the reference method. (KFG = Kleinfiltergerät).

2.1 Filter weighing at low relative humidities

To estimate the water content of particles, the filters should be equilibrated at humidities well below the deliquescent point before weighing. There were a lot of problems with weighing the filters at low relative humidities. Decreasing the humidity implies that the water content decreases and the concentration of dissolved ions increases. This may increase the loss of ammonium nitrate as ammonia and nitric acid. It was therefore decided not to decrease the humidity before weighing and analysing the filters.

3 Results and discussion

3.1 Average PM₁, PM_{2.5} and PM₁₀ concentrations

In several occasions, the PM mass concentration measured was found to be close to the detection limit (ca 0.5 μg m⁻³), thus increasing the relative uncertainty of the data. In other cases, the difference between the PM fractions was close to the accuracy of the measurements. As a consequence of these two situations, concentrations of PM₁ were sometimes found to be higher than PM_{2.5}, and concentrations of PM_{2.5} sometimes higher than PM₁₀ which is obscure. For PM_{2.5}

and PM₁₀, part of the uncertainty could also be attributed to different samplers being used at the various sites. For comparison of the different PM size fractions, obscure results were removed from the dataset. As the accuracy of the measurements is estimated to be around $\pm 10\%$, only measurements when $PM_1 < 1.1 \cdot PM_{2.5}$ and $PM_{2.5} < 1.1 \cdot PM_{10}$ were used (see Table 1).

Table 1. Annual mean concentrations of PM₁, PM_{2.5} and PM₁₀ ($\mu\text{g m}^{-3}$) at the Scandinavian EMEP sites during 2006.

	PM ₁	PM _{2.5}	PM ₁₀
Lille Valby	8.1	11.3	25.6
Birkenes	5.4	6.6	10.6
Aspvreten	4.7	7.3	11.8
Virolahti	4.9	9.4	11.5

The average PM₁ concentration varies from 50 % (Virolahti) to 80 % (Birkenes) of the average PM_{2.5} concentrations. The PM₁/PM_{2.5} fraction may, however, be affected by the measurement technique. The average PM₁ concentration varies from 30 % (Lille Valby) to 50 % (Birkenes) of the average PM₁₀ concentrations.

3.2 Variations in PM₁ concentrations

The average, minimum, and maximum concentrations of PM₁ on a monthly basis are shown in Figures 4-7. There are two maxima during the year, one in May-June and another one in August-September. The monthly average concentrations seem to be influenced by the maximum of the month. When there is a high maximum concentration of a month, this month usually have several days with high concentrations. The lowest PM₁ monthly mean concentration was observed for December at all sites.

At Birkenes, the period with high concentrations of PM₁₀ in September lasted for 2 weeks and the weekly mean concentration for these two weeks was $23 \mu\text{g m}^{-3}$ and $26 \mu\text{g m}^{-3}$.

According to present EU-directive the PM₁₀ mass should not exceed $50 \mu\text{g m}^{-3}$ as a daily average concentration more than 37 days per year (90 percentile). There is no similar limit for PM_{2.5}, but according to a new EU-directive the PM_{2.5} mass should not exceed $25 \mu\text{g m}^{-3}$ as an annual average.

Exceedances are given in Table 2. The absence of exceeding concentrations at Birkenes might depend on the fact that only one 24h sampling of PM_{2.5} and PM₁₀ was performed per week.

Table 2. Number of days when PM_{2.5} concentration exceeded $25 \mu\text{g m}^{-3}$ and PM₁₀ concentration exceeded $50 \mu\text{g m}^{-3}$. The average PM₁/PM_{2.5} ratio for concurrent samples of PM₁ and PM_{2.5} is also given.

	PM _{2.5}	PM ₁₀	PM ₁ /PM _{2.5}
Lille Valby	13	19	79%
Birkenes	0	0	
Aspvreten	12	1	66%
Virolahti	19	2	51%

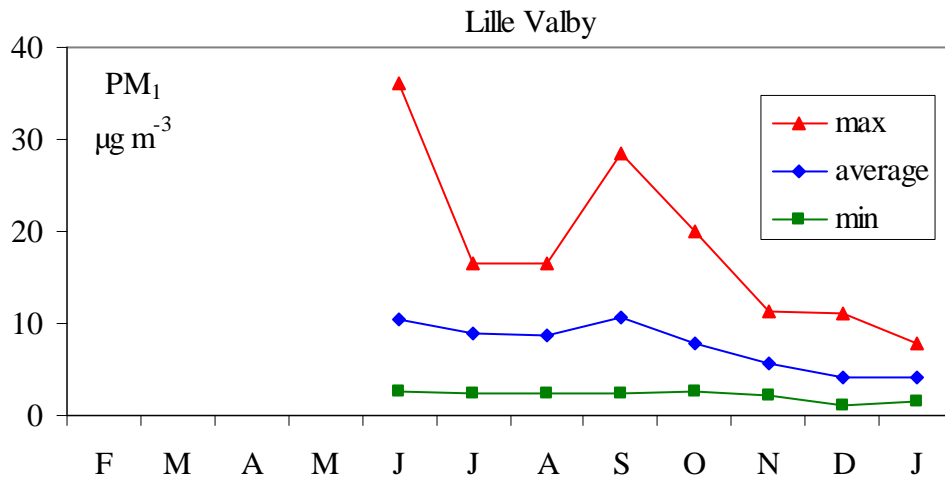


Figure 4. Minimum, average and maximum PM₁ concentrations at Lille Valby.

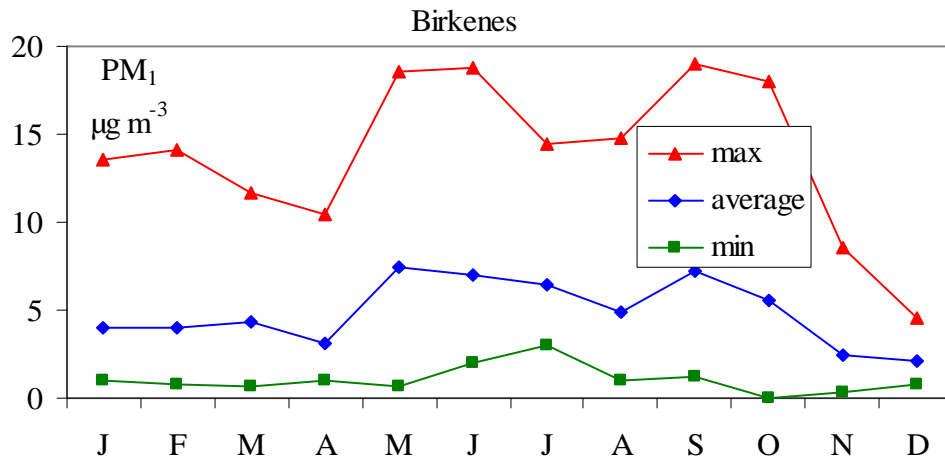


Figure 5. Minimum, average and maximum PM₁ concentrations at Birkenes.

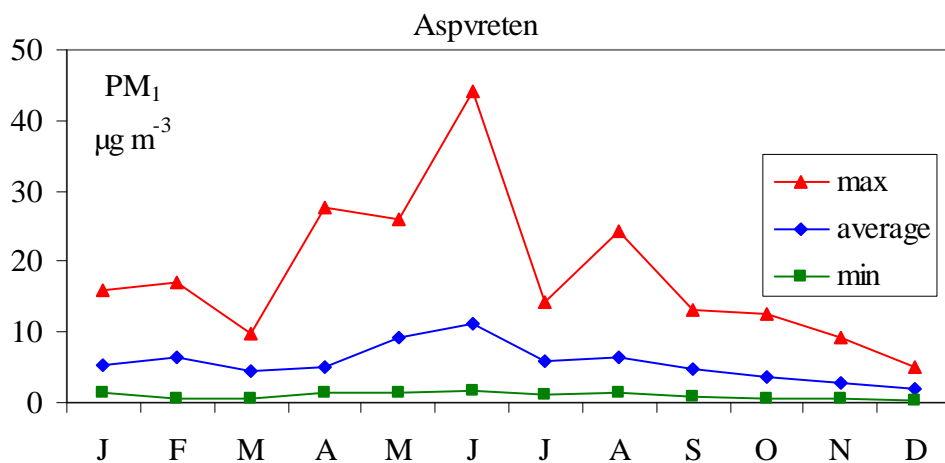


Figure 6. Minimum, average and maximum PM₁ concentrations at Aspvreten.

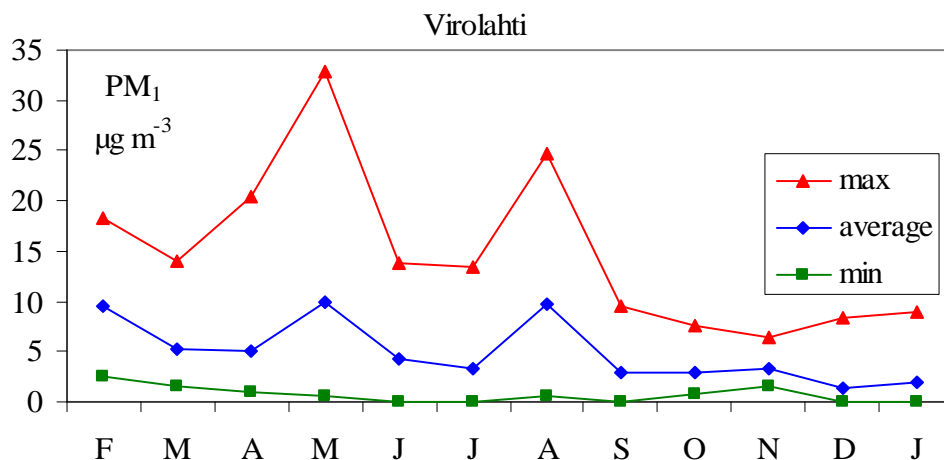


Figure 7. Minimum, average and maximum PM₁ concentrations at Virolahti.

3.3 Episodes of high and low PM₁ concentrations

Daily PM₁ concentrations observed during 2006 are shown in Fig. 8. Concentrations that are more than three times higher than the annual average have been marked with red bars, whereas concentrations less than 30 % of the annual average have been marked with green bars.

In the beginning of May 2006 there was an episode of elevated PM concentrations observed at all four sites, which was caused by massive wild and prescribed fires in western parts of Russia, Belarus, Ukraine and the Baltic states. Witham and Manning (2007) have studied how this episode affected the PM₁₀ concentrations in the UK. During the last years wild fires have been detected in Russia, Belarus and Ukraine every year. The MODIS fire maps, which have been available since 2001, show that such episodes of biomass combustion in March-April occur annually. However, the duration of the episode in spring 2006 was exceptionally long-lasting and the concentrations measured were unusually high.

Anttila *et al.*, (2007) have studied the effect of two biomass burning episodes with respect to air quality at Virolahti in 2006. The first episode occurred in April-May and the other one in August. The air quality in Virolahti was severely affected by these wild fire events. The daily PM₁₀ values exceeded 50 µg/m³ on the 3rd and 5th May and on the 13th August. The measured hourly PM₁₀ values exceeded 200 µg/m³ which is the highest concentration observed since the beginning of the PM₁₀ measurements in Virolahti in 2002. In spring 2006, the biomass burning aerosol detected at Virolahti originated from south and south-east from distances of even hundreds of kilometres. The high concentrations of particles, trace elements and ions were caused by a mixture of biomass burning aerosol and other sources. Elevated PAH concentration occurred in concurrence with the most intense biomass burning episode (Makkonen *et al.*, 2007). During the episode in August there were biomass fire sources rather close to Virolahti (50-100 km) causing record high particle concentrations. During the episode also the concentrations of PAH were elevated reaching values typical of urban wintertime environments.

An episode of low concentrations observed for all sites in December, with winds from west and northwest. This time of the year is typically the cleanest period regarding particulate pollution in Scandinavia.

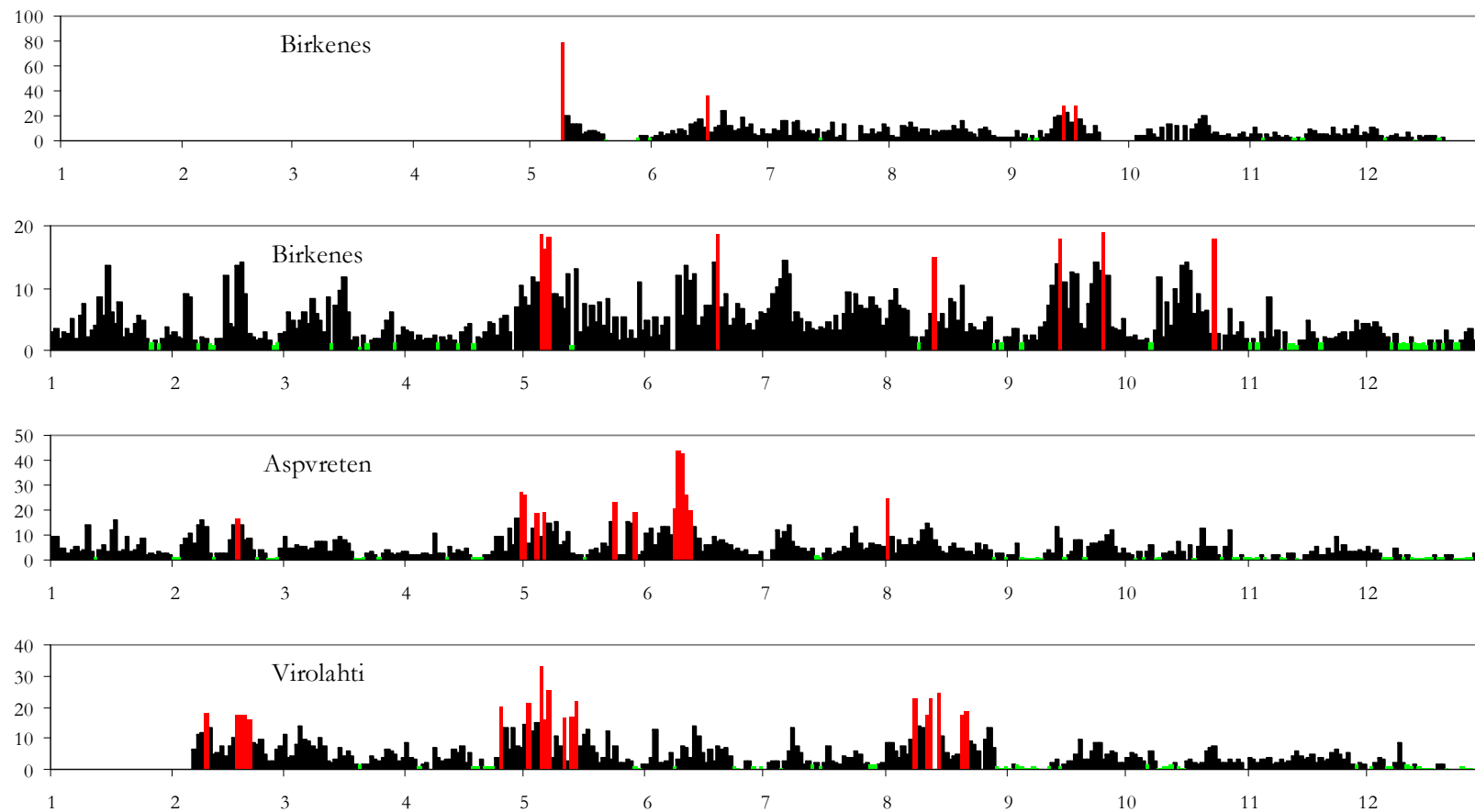


Figure 8. PM₁ concentrations during 2006. The numbers mark the starting point of each month. Red bars represent daily concentrations exceeding the annual average by a factor of three, whereas the green bars show daily concentrations less than 30 % of the annual average concentration.

3.4 Trajectory sectors analysis

Classified daily sector trajectories were obtained from Meteorological Synthesizing Centre – West (http://www.emep.int/Traj_data/traj2D.html). The trajectories were allocated to eight different sectors centred on the cardinals. Average concentrations in each sector are plotted for all four stations during 2006 for all three PM-fractions in Figures 9-12. The average concentrations for each of the three PM-fractions were surprisingly well correlated at all four sites.

It looks as though the ratios between the different size fractions are rather independent of the origin of the air mass.

The size distributions were, however, different at different sites. The correlation between the average PM_{2.5} concentrations and the average PM₁₀ concentrations for different sectors was particularly good. The average PM-concentrations (all three fractions) were highest in the south or south-east sectors and lowest in the north or north-west sectors.

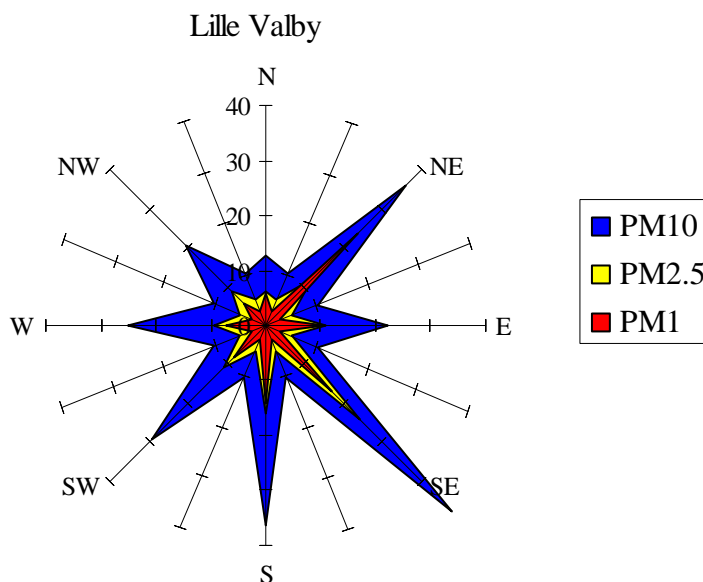


Figure 9. Average PM₁, PM_{2.5} and PM₁₀ concentrations ($\mu\text{g m}^{-3}$) at Lille Valby, when data for all three PM-fractions are available and reasonable simultaneously, as a function of sector for the wind trajectory.

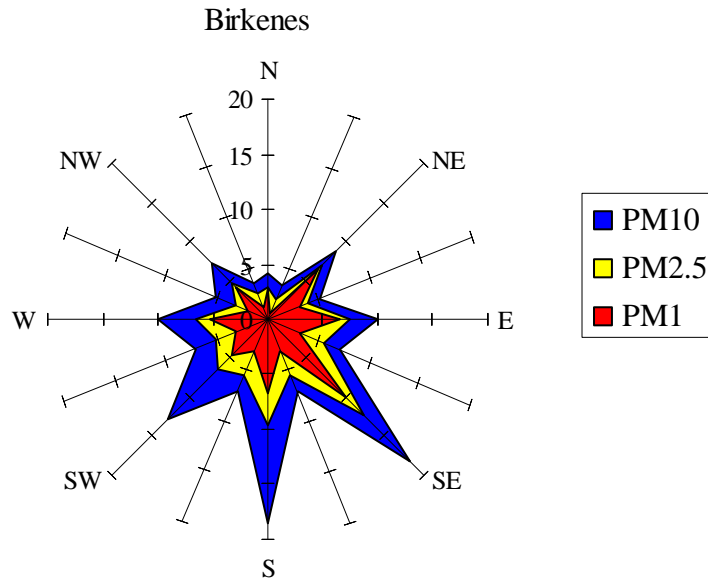


Figure 10. Average PM_1 , $PM_{2.5}$ and PM_{10} concentrations ($\mu g m^{-3}$) at Birkenes, when data for all three PM -fractions are available and reasonable simultaneously, as a function of sector for the wind trajectory.

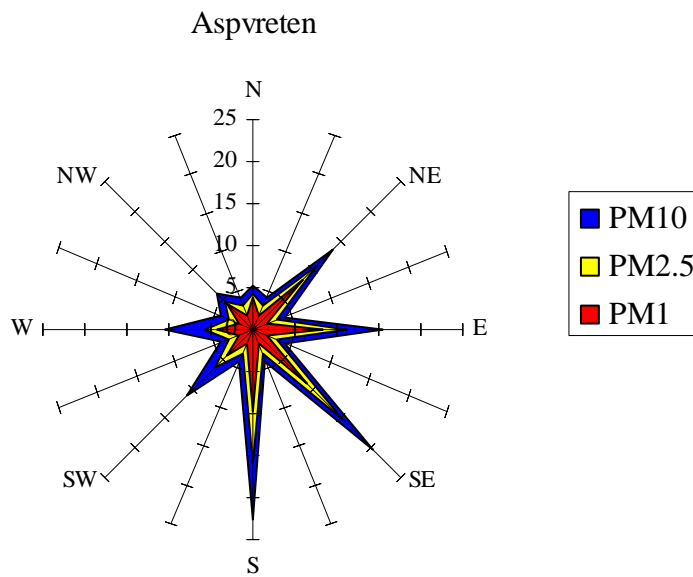


Figure 11. Average PM_1 , $PM_{2.5}$ and PM_{10} concentrations ($\mu g m^{-3}$) at Aspvreten, when data for all three PM -fractions are available and reasonable simultaneously, as a function of sector for the wind trajectory.

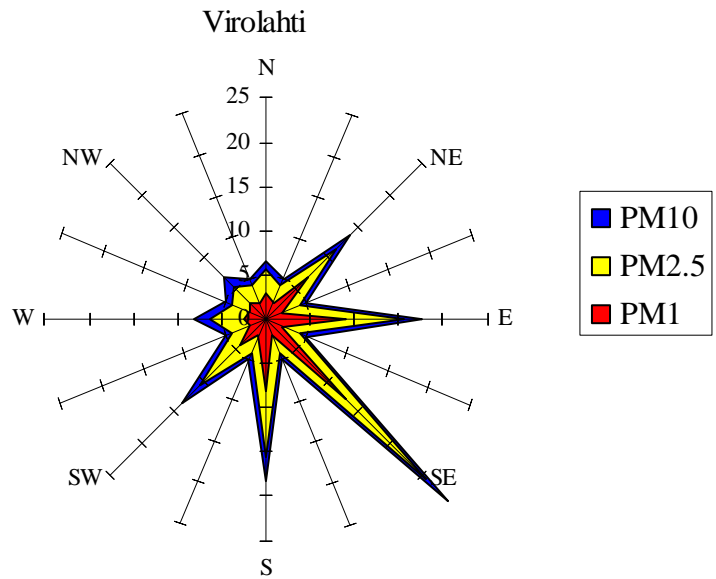


Figure 12. Average PM₁, PM_{2.5} and PM₁₀ concentrations ($\mu\text{g m}^{-3}$) at Virolahti, when data for all three PM-fractions are available and reasonable simultaneously, as a function of sector for the wind trajectory.

3.5 Seasonal variation

The monthly average concentrations for each fraction are shown in Figures 13-16. The concentrations were for all three fractions highest in September in Lille Valby and Birkenes. Aspvreten had a maximum for PM₁₀ in September, but for PM₁ and PM_{2.5} in June. Virolahti had the maximum concentrations in August. All stations had their minimum concentrations in December 2006 or January 2007. It is not known if this seasonal pattern is the same every year or specific for 2006.

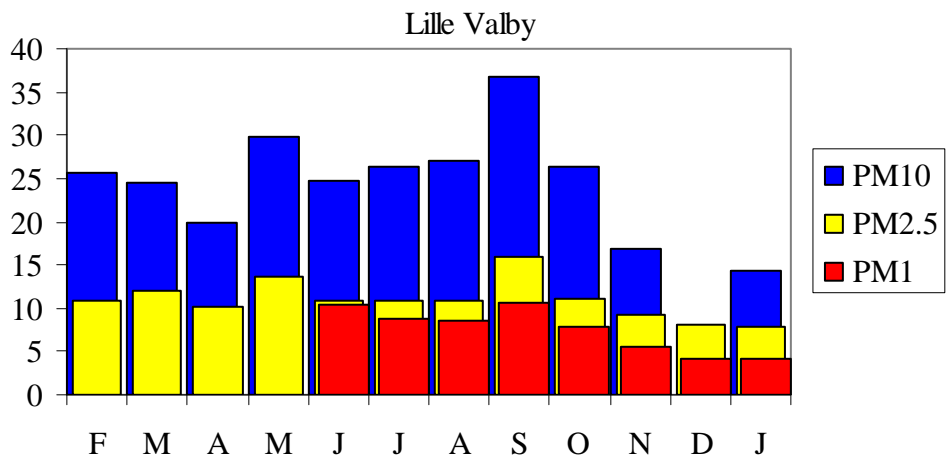


Figure 13. Average PM₁, PM_{2.5} and PM₁₀ concentrations ($\mu\text{g m}^{-3}$) at Lille Valby.

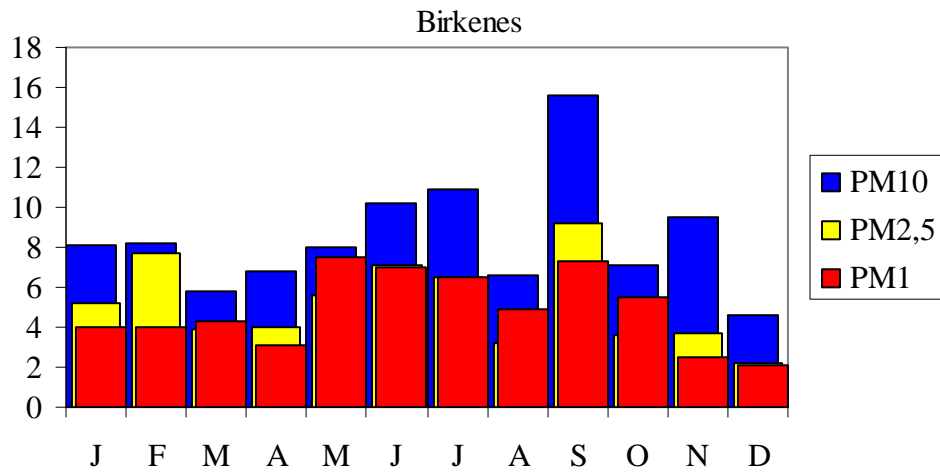


Figure 14. Average PM₁, PM_{2.5} and PM₁₀ concentrations (µg m⁻³) at Birkenes.

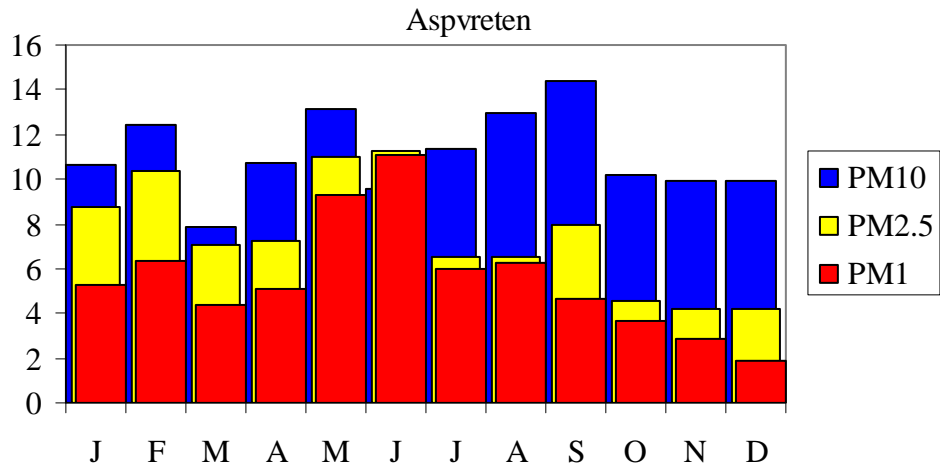


Figure 15. Average PM₁, PM_{2.5} and PM₁₀ concentrations (µg m⁻³) at Aspveten.

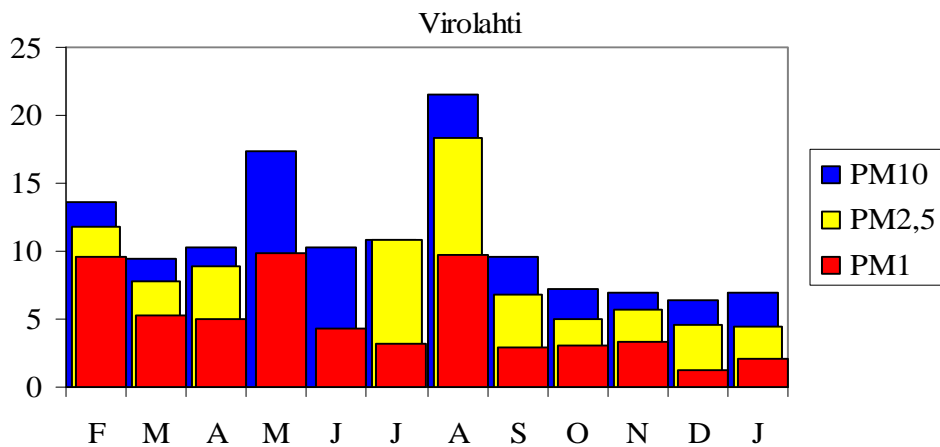


Figure 16. Average PM₁, PM_{2.5} and PM₁₀ concentrations (µg m⁻³) at Virolahti.

3.6 Correlation between accumulation and coarse modes

The two particle modes have different origin and should therefore not be correlated if it is not for meteorological reasons. From Figures 9-12 it looks as though the two modes have similar geographical origins. PM_{10} only represent the accumulation mode. Since both $PM_{2.5}$ and PM_{10} contain both modes their difference was here used to represent the coarse fraction. $PM_{10} - PM_{2.5}$ is plotted versus PM_{10} in Figures 17 – 20. The coarse mode ($PM_{10} - PM_{2.5}$) is highest in comparison with the accumulation mode (PM_{10}) in Lille Valby. It decreases in the order Birkenes, Aspvreten and Virolahti. The reason for the different behaviour at Lille Valby is quite obviously that $PM_{2.5}$ has not been corrected for the losses of volatile material in the TEOM monitor. If some of the volatile material belongs to the PM_{10} fraction, this will increase both the slope of the regression line and the correlation coefficient.

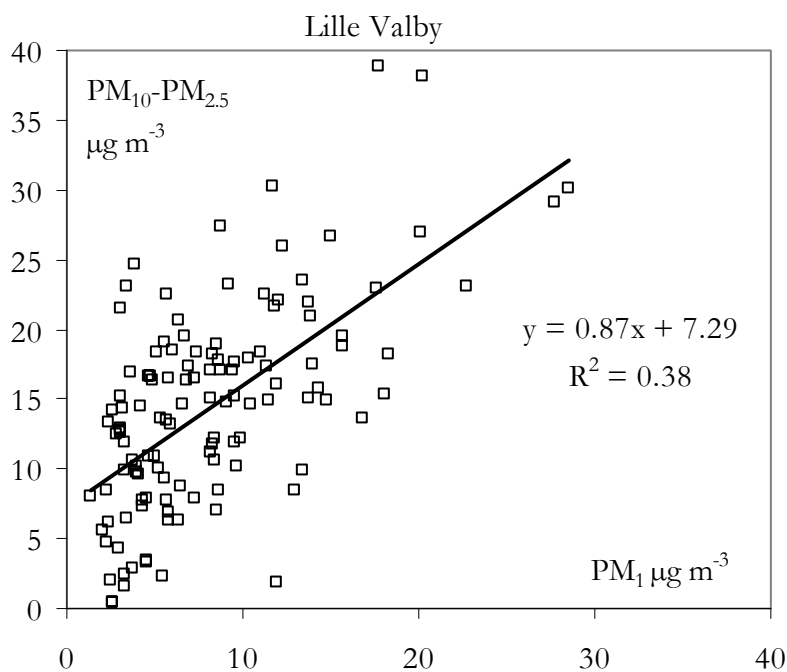


Figure 17. Mass concentration of coarse particle mode as a function of accumulation mode at Lille Valby. (PM_{10} was measured with beta attenuation monitor and $PM_{2.5}$ with TEOM).

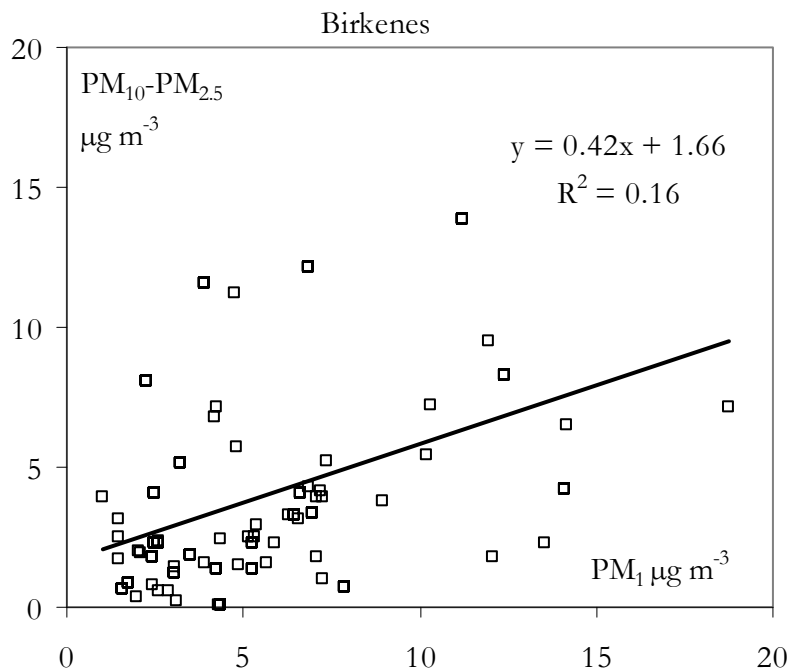


Figure 18. Mass concentration of coarse particle mode as a function of accumulation mode at Birkenes. PM₁₀ and PM_{2.5} were both measured using filter sampling.

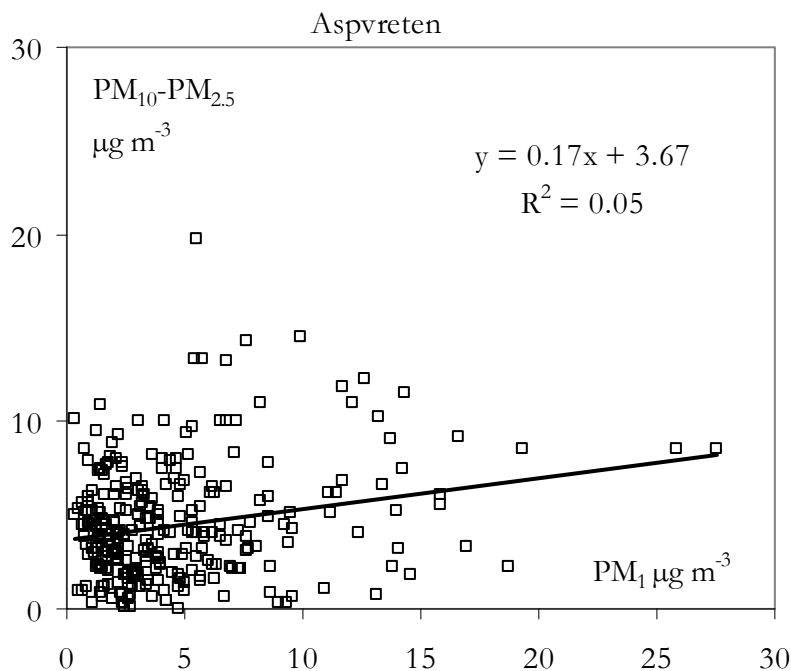


Figure 19. Mass concentration of coarse particle mode as a function of accumulation mode at Aspvreten. PM₁₀ was measured with TEOM and PM_{2.5} using filter sampling.

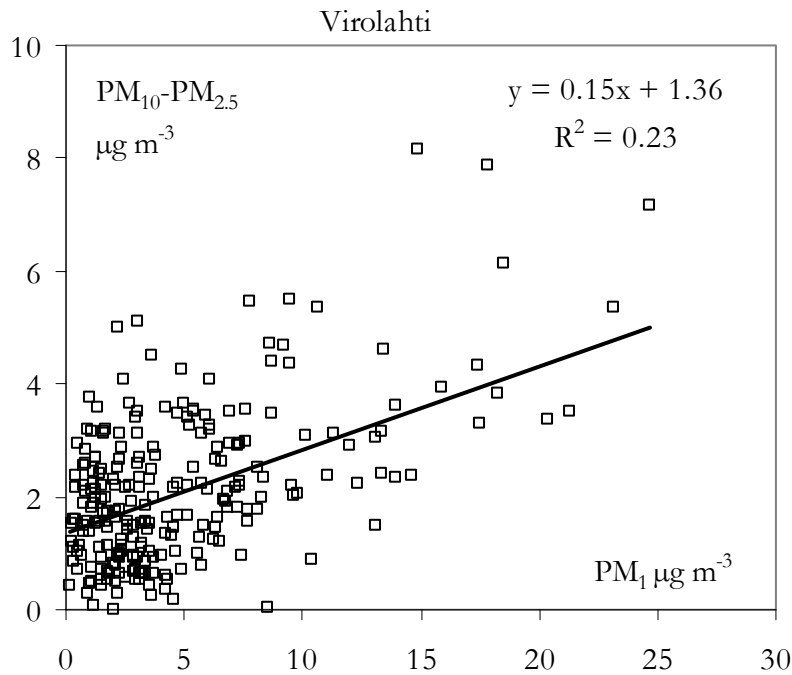


Figure 20. Mass concentration of coarse particle mode as a function of accumulation mode at Virolahti. PM₁₀ and PM_{2.5} were sampled using filter technique.

As can be seen from the Figures there are very poor correlation between the two modes.

3.7 How well does PM_{2.5} represent the accumulation mode?

Since EU wants the member states to measure PM_{2.5} which consists of the accumulation mode and a small fraction of the coarse mode, it is of interest to see how well PM_{2.5} and PM₁ are correlated. In the Figures 21-24 below, the same criteria as earlier was used ($PM_1 < 1.1 \cdot PM_{2.5}$ and $PM_{2.5} < 1.1 \cdot PM_{10}$). The PM_{2.5} in Lille Valby was measured with a TEOM monitor at 50 °C. A comparison with the scatter plots from Birkenes, Aspvreten, and Virolahti indicates that the TEOM values needs to be considerably corrected maybe with a factor of 1.2-1.5.

As can be seen from the Figures, the correlations are reasonable good (r^2 is in the range 0.73 to 0.89).

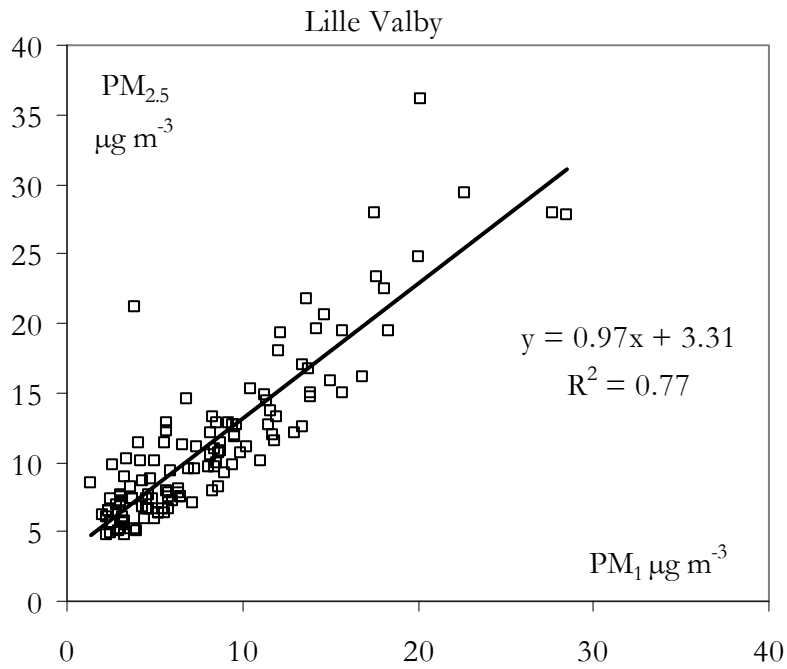


Figure 21. Mass concentration of PM_{2.5} (TEOM) as a function of PM₁ when all PM_x data are reasonable at Lille Valby.

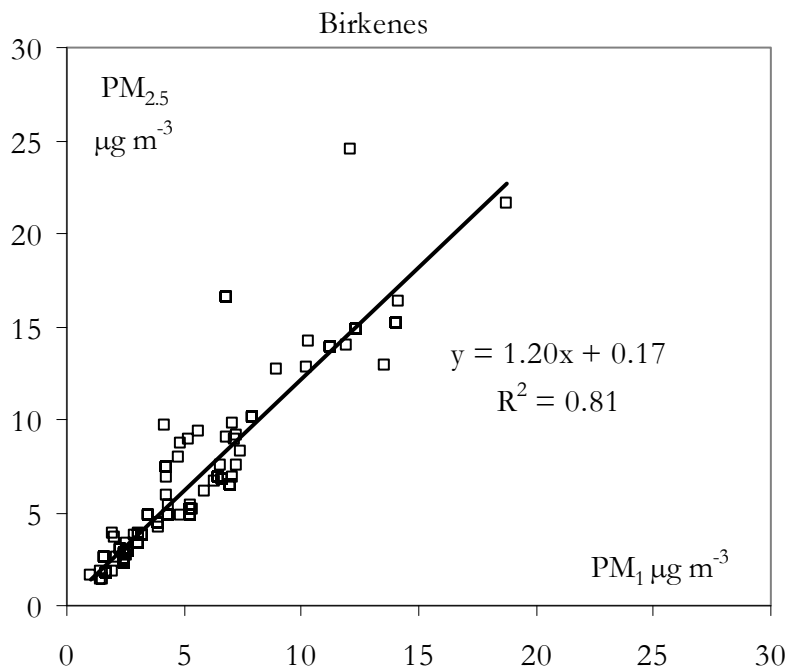


Figure 22. Mass concentration of PM_{2.5} (filter sampling) as a function of PM₁ when all PM_x data have been reasonable at Birkenes.

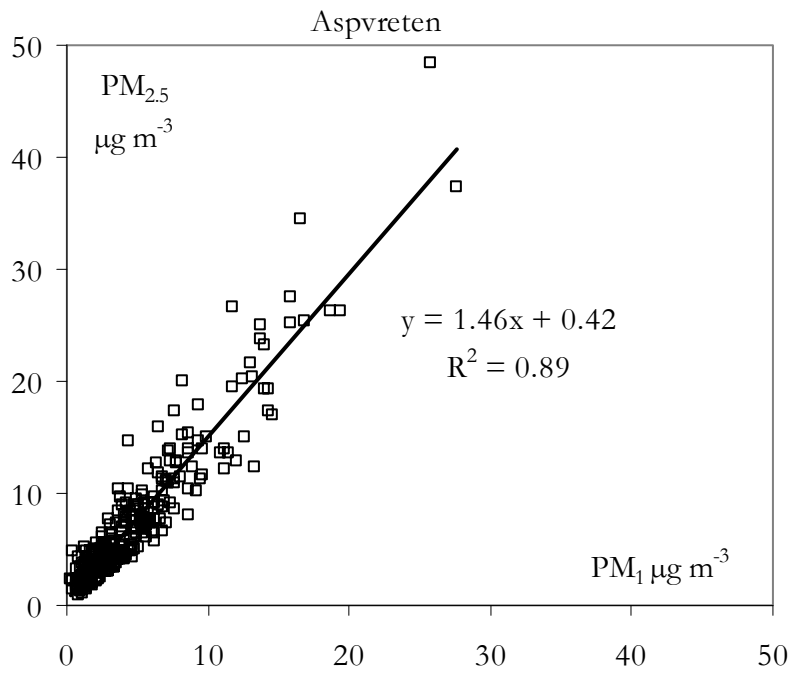


Figure 23. Mass concentration of PM_{2.5} (filter sampling) as a function of PM₁ when all PM_x data have been reasonable at Aspvreten.

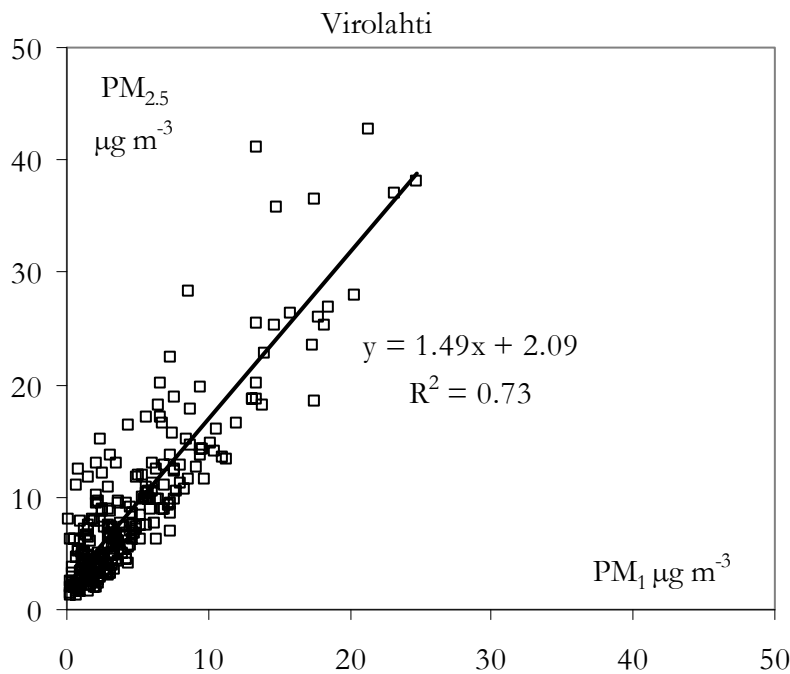


Figure 24. Mass concentration of PM_{2.5} (filter sampling) as a function of PM₁ when all PM_x data have been reasonable at Virolahti.

3.8 Chemical analysis of inorganic ions in PM₁ fraction

June was chosen for chemical analysis as it is one of the EMEP intensive measurement campaigns. Funding was received for 60 days and the first half of June was chosen for all four sites. The results can be found in the appendix. Average concentrations are given in Table 3.

Table 3. Average concentrations of water soluble inorganic ions in the PM₁ fraction for the period 1-15 June and the sum of all analysed ions divided by the total mass concentration. Daily concentrations can be found in the appendix. Unit $\mu\text{g m}^{-3}$.

	mass	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	water soluble
Lille Valby	10	0.03	0.25	0.86	0.44	0.16	0.01	0.06	0.03	18%
Birkenes	7	0.11	0.21	1.11	0.27	0.04	0.00	0.05	0.01	27%
Aspvreten	17	0.01	0.04	0.92	0.34	0.01	0.01	0.01	0.16	9%
Virolahti	5	0.00	0.02	0.65	0.19	0.01	0.00	0.01	0.03	18%

Ammonium and sulphate are very well correlated with each other at all sites, but no other ions correlated well with each other. At Aspvreten there was probably a pollen episode June 9-11. Filters were yellow-green and the potassium concentration was high. Even though pollen grains are very large, their aerodynamic diameter can be small.

For 2006, the aerosol content of elemental carbon (EC), organic carbon (OC) and total carbon (TC) was quantified in aerosol filter samples from Birkenes having a PM₁₀ and PM_{2.5} cut-off (SFT, 2007).

Large particles, with an unspecified cut-off, were collected at Aspvreten during 2006. OC and EC analysis were made on a weekly (4-14 days, but usually 7 days) basis. The OC, but not the EC concentrations were well correlated with the PM₁ concentration during winter (January to mid May and mid September to January).

Trace elements and polyaromatic hydrocarbons were analysed from the PM₁₀, PM_{2.5} and PM₁ samples collected in Virolahti in August 2006 (Makkonen *et al.*, 2007).

The PM₁₀, PM_{2.5} and PM₁ concentrations has also been measured at other sites in Sweden during 2006 (Sjöberg and Persson, 2007).

4 Conclusions

PM₁ constituted on average more than half of the PM_{2.5} concentrations, but was on average less than half of the PM₁₀ concentrations at the four EMEP sites during 2006. There were two episodes of high PM₁ concentrations during the year, one in May-June and another one in August-September. The highest PM₁ concentrations were found during South-Easterly wind trajectories and the lowest concentrations during Northerly trajectories.

Even though the annual average mass relations between the three size fractions at any station were rather independent of the trajectory sectors, the fine and the coarse particle masses were not correlated on a daily basis. The PM_{2.5} concentration, which is the parameter that should be measured within EU, correlates fairly well with the concentration of accumulation mode particles

(PM₁). In June only a minor fraction of PM₁ consisted of inorganic ions. Only ammonium and sulphate ions were well correlated of the measured ions in PM₁.

5 Acknowledgement

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6 References

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Appendix

Concentrations found at Lille Valby

start	stop	PM ₁ µg m ⁻³								
		mass	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
2006-06-01	2006-06-02	3	0.01	0.03	0.17	0.09	0.00	0.00	0.03	0.01
2006-06-02	2006-06-03	4	0.05	0.19	0.30	0.13	0.01	0.01	0.08	0.03
2006-06-03	2006-06-04	7	0.08	0.19	0.73	0.37	0.01	0.01	0.14	0.03
2006-06-04	2006-06-05	4	0.04	0.09	0.31	0.15	0.00	0.00	0.08	0.02
2006-06-05	2006-06-06	6	0.02	0.05	0.25	0.09	0.01	0.00	0.04	0.02
2006-06-06	2006-06-07	8	0.03	0.11	0.28	0.09	0.02	0.01	0.05	0.04
2006-06-07	2006-06-08	6	0.05	0.77	1.72	1.16	0.01	0.01	0.06	0.03
2006-06-08	2006-06-09	10	0.01	0.24	0.55	0.34	0.00	0.00	0.03	0.01
2006-06-09	2006-06-10	8	0.02	0.71	1.62	1.07	0.00	0.00	0.03	0.03
2006-06-10	2006-06-11	4	0.01	0.15	0.40	0.21	0.01	0.00	0.04	0.02
2006-06-11	2006-06-12	13	0.01	0.15	1.36	0.71	0.04	0.01	0.04	0.05
2006-06-12	2006-06-13	15	0.02	0.29	1.53	0.62	0.41	0.01	0.04	0.04
2006-06-13	2006-06-14	17	0.02	0.21	1.44	0.70	0.18	0.01	0.04	0.04
2006-06-14	2006-06-15	11	0.02	0.09	1.08	0.59	0.02	0.01	0.07	0.03
2006-06-15	2006-06-16	36	0.07	0.46	1.10	0.31	1.65	0.04	0.07	0.04

Concentrations found at Birkenes

start	stop	PM ₁ µg m ⁻³								
		mass	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
2006-06-01	2006-06-02	5	0.16	0.225	0.34	0.02	0.046	0.007	0.045	0.005
2006-06-02	2006-06-03	2	0.14	0.225	0.25	0.01	0.064	0.007	0.006	
2006-06-03	2006-06-04	5	0.16	0.18	0.40	0.02	0.034	0.006	0.047	0.001
2006-06-04	2006-06-05	2	0.14	0.18	0.31	0.01	0.053	0.006	0.034	
2006-06-05	2006-06-06	4	0.15	0.18	0.31	0.01	0.056	0.004	0.037	
2006-06-06	2006-06-07	5	0.13	0.18	0.64	0.09	0.039	0.005	0.031	0.006
2006-06-07	2006-06-08		0.11	0.18	0.86	0.15	0.024	0.003	0.058	0.007
2006-06-08	2006-06-09		0.09	0.225	1.29	0.32		0.003	0.047	0.012
2006-06-09	2006-06-10	12	0.15	0.18	1.29	0.32	0.046	0.004	0.082	0.009
2006-06-10	2006-06-11	6	0.05	0.225	1.90	0.50	0.038	0.005	0.079	0.008
2006-06-11	2006-06-12	14	0.03	0.27	2.51	0.75	0.034	0.002	0.073	0.015
2006-06-12	2006-06-13	11	0.03	0.27	3.00	0.97	0.021	0.003	0.075	0.022
2006-06-13	2006-06-14	12	0.02	0.315	2.48	0.77	0.021	0.004	0.069	0.016
2006-06-14	2006-06-15	4	0.18	0.18	0.37	0.04	0.028	0.004	0.041	
2006-06-15	2006-06-16	5	0.12	0.18	0.80	0.13	0.052	0.005	0.066	0.006

Concentrations found at Aspvreten

start	stop	PM ₁ µg m ⁻³								
		mass	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
2006-06-01	2006-06-02	11	0.04	0.02	0.51	0.20	0.02	0.00	0.03	0.18
2006-06-02	2006-06-03	12	0.02	0.04	0.55	0.20	0.00	0.01	0.02	0.20
2006-06-03	2006-06-04	6	0.00	0.02	0.42	0.19	0.00	0.00	0.02	0.07
2006-06-04	2006-06-05	11	0.01	0.02	0.16	0.07	0.00	0.00	0.01	0.13
2006-06-05	2006-06-06	14	0.00	0.01	0.29	0.12	0.00	0.00	0.01	0.10
2006-06-06	2006-06-07	13	0.01	0.02	0.44	0.18	0.00	0.01	0.01	0.16
2006-06-07	2006-06-08	10	0.01	0.03	0.58	0.24	0.00	0.00	0.01	0.10
2006-06-08	2006-06-09	21	0.01	0.05	0.54	0.21	0.01	0.01	0.00	0.20
2006-06-09	2006-06-10	44	0.02	0.12	2.06	0.63	0.02	0.02	0.01	0.39
2006-06-10	2006-06-11	43	0.01	0.06	0.52	0.21	0.00	0.01	0.01	0.44
2006-06-11	2006-06-12	26	0.02	0.04	1.53	0.50	0.01	0.01	0.02	0.21
2006-06-12	2006-06-13	20	0.01	0.06	2.32	0.92	0.01	0.01	0.01	0.14
2006-06-13	2006-06-14	13	0.00	0.03	2.37	0.91	0.01	0.00	0.01	0.08
2006-06-14	2006-06-15	9	0.00	0.02	1.25	0.51	0.01	0.00	0.02	0.05
2006-06-15	2006-06-16	3	0.00	0.02	0.23	0.09	0.01	0.00	0.03	0.03

Concentrations found at Virolahti

		PM ₁ µg m ⁻³								
start	stop	mass	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
2006-06-01	2006-06-02	2	0.00	0.00	0.59	0.21	0.00	0.00	0.01	0.02
2006-06-02	2006-06-03	4	0.00	0.02	0.44	0.16	0.00	0.00	0.01	0.04
2006-06-03	2006-06-04		0.00	0.03	0.08	0.01	0.01	0.00	0.02	0.01
2006-06-04	2006-06-05	2	0.00	0.00	0.81	0.24	0.00	0.00	0.01	0.01
2006-06-05	2006-06-06	2	0.00	0.00	0.38	0.10	0.01	0.00	0.00	0.01
2006-06-06	2006-06-07	3	0.00	0.00	0.71	0.11	0.01	0.00	0.00	0.01
2006-06-07	2006-06-08	5	0.00	0.01	1.22	0.28	0.01	0.00	0.01	0.03
2006-06-08	2006-06-09	1	0.00	0.00	0.71	0.14	0.00	0.00	0.01	0.01
2006-06-09	2006-06-10	3	0.00	0.00	0.72	0.21	0.01	0.00	0.01	0.03
2006-06-10	2006-06-11	8	0.00	0.01	0.17	0.06	0.01	0.00	0.01	0.06
2006-06-11	2006-06-12	7	0.00	0.02	0.41	0.13	0.01	0.00	0.01	0.05
2006-06-12	2006-06-13	4	0.00	0.03	0.52	0.18	0.01	0.00	0.01	0.03
2006-06-13	2006-06-14	14	0.00	0.06	1.65	0.61	0.02	0.01	0.01	
2006-06-14	2006-06-15	11	0.00	0.04	1.10	0.40	0.03	0.01	0.01	
2006-06-15	2006-06-16	5	0.00	0.04	0.27	0.08	0.02	0.00	0.02	0.03