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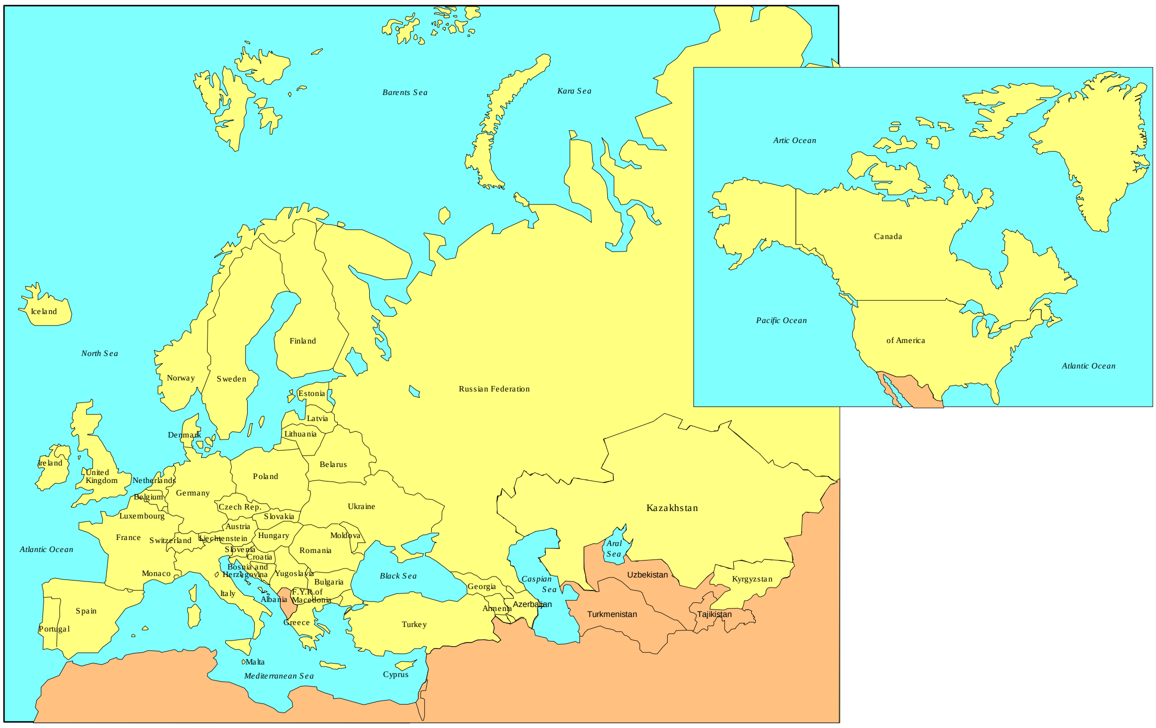
EMEP Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe

EMEP Particulate Matter Assessment Report



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

EMEP Particulate Matter Assessment Report

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Executive Summary

This EMEP PM Assessment Report addresses the adequacy and completeness of the underpinning science upon which models currently used for policy development have been built. An important issue has been to strike a balance between the need to resolve a number of key scientific uncertainties and the desire to make progress with the integrated assessment modelling. It has been recognised that striking this balance is important for policy-making within the Working Group on Strategies and Review. The purpose of the report is to inform the policy process about the state of current understanding on PM issues and the level of confidence in PM models.

The PM models currently used in policy development underestimate total PM_{10} and $PM_{2.5}$ and none currently achieve mass closure. The main reason for this is that some PM components are not included at all in models and some others are treated in a simplified ways. There are large uncertainties in the emissions inventories of the primary PM components especially with respect to the coarse PM fraction and of some PM precursors. Confidence in the PM models ultimately rests on the comparison of model predictions with observations. Currently there are too few observations for satisfactory model verification.

There is a high degree of confidence that SO_2 sources can be linked to the observed levels of particulate sulphate. Over the years, most of the important uncertainties in SO_2 emission inventories have been tackled and a few outstanding problems remain, such as domestic coal burning and ship emissions. Observations of particulate sulphate have the necessary reliability and spatial coverage for model verification purposes. Long-running time series are available to check model calculated trends with observed trends over the last two decades.

There is a reasonable level of confidence that NO_x sources can be linked to the observed levels of particulate nitrate. Too few measurements for particulate nitrate have been made using techniques that are artefact-free and some of the outstanding problems with the evaporation of ammonium nitrate still have not been solved. Intensive field campaigns have been organised using continuous instruments to overcome these shortcomings. There are still some uncertainties associated with ammonia emissions that when taken together with the non-linearities in the formation of ammonium nitrate could limit our confidence in particulate nitrate modelling, especially during episodes, and its response to ammonia and NO_x emission reductions.

Uncertainties in European models for particulate sulphate are currently judged to be of the order of ± 15 – 20%, on an annual average basis. The corresponding uncertainties in model particulate nitrate are somewhat larger at about ± 40%. Measurement uncertainties in particulate sulphate and nitrate are comparable to those in models. This situation is considered acceptable for the policy purpose of assessing the outcome of different control measures for SO_2 and NO_x on the regional component of particulate sulphate and nitrate.

Uncertainties in model results for elemental carbon and organic matter PM are large. Many of our current difficulties with elemental carbon and organic carbon particulates stem from difficulties with their measurement methods, the lack of a reference method and the lack of consistency between the existing European measurements. The split between elemental and organic carbon depends on the method and is influenced by charring, leading to elemental carbon measurements that may differ by up to a factor of two when comparing the two most commonly used protocols. Measurements are therefore considered to have limited reliability.

Many of the remaining difficulties with elemental carbon and organic PM stem from problems with emission inventories. Emission inventories for primary PM components are of relatively recent development. Reliability, size and spatial resolution, coverage of the different source categories and PM species coverage still remain crucial issues for PM emission inventories. Emission inventories for elemental carbon need substantial improvement in terms of accuracy and coverage of source categories particularly those of road traffic, wood combustion and residential heating. Improvements are required in spatial resolution at the European scale and in the representation of diurnal, weekly and seasonal emission profiles.

Without these improvements in the emission inventories for primary carbonaceous PM, confidence is limited in the regional scale distributions of primary carbonaceous PM calculated with the current PM models used in policy development.

The review of the Unified EMEP model noted that confidence in the understanding of the mechanism of the formation of secondary organic aerosol was so low that it had not been included in the EMEP model, leading to underestimates for PM_{10} and $PM_{2.5}$. There are major problems with emission inventories and with the representation of the main atmospheric processes that control the distribution of particulate organic matter across Europe. Uncertainties in measurement data and their general paucity, preclude any quantification of model uncertainty for these PM components. As a consequence, it is difficult to link VOC emissions and their control to secondary organic PM in the PM models currently used for policy development.

There are major difficulties in the representation of mineral dust in PM models which stem from a range of causes mainly due to the lack of knowledge on their emissions and of the soil databases with which to characterise them.

Uncertainties in current model predictions for natural PM components such as mineral dust, sea salt and biogenic primary organic matter are large and difficult to assess.

On this basis, we have a high level of confidence that the PM models currently used for policy development can address the regional scale impacts of SO_2 and NO_x emission reductions on PM mass concentrations, for the purposes of integrated assessment modelling. However, there are uncertainties with ammonia emissions that when taken together with the non-linear chemical production pathways to form ammonium nitrate, could limit our confidence in the representation of ammonia and NO_x emission reductions on PM mass. Nevertheless, it should be noted that current model performance against observed particulate nitrate concentrations is quite satisfactory. Because of outstanding problems with the emission inventories for elemental and organic PM carbon, the

PM models have difficulties with the simulation of carbonaceous PM compounds. Consequently, when they are used for policy development to describe the urban and traffic increments in $PM_{2.5}$ that are required for integrated assessment modelling and for policy assessments of urban health effects, their results must be interpreted carefully.

The model uncertainties in reproducing absolute PM concentrations, hamper their use for quantitative assessment against target and limit values for PM. But, current PM models used in policy development are considered adequate for the assessment of the relative magnitudes of emission reductions of some PM components and their precursors on PM mass concentrations.

There is currently a significant level of effort being undertaken by the Parties to the Convention and by the EMEP Centres that is focussed on improving PM emission inventories, improving PM observations, carrying out targeted field campaigns and enhancing PM models. These activities should be encouraged within the EMEP framework and will over time bring increased confidence in our understanding of PM and its representation in PM models.

Part A

European Perspective

EMEP Particulate Matter Assessment Report

Part A : European Perspective

1 Introduction

1. An important issue for the Parties to the Long-range Transboundary Air Pollution LRTAP Convention for consideration in the review of the Gothenburg Protocol is the status of knowledge on particulate matter PM. An underlying issue is the level of scientific confidence that we have in our understanding of PM and in PM models used for policy development and the nature and formulation of a policy instrument that could be supported within the LRTAP Convention. The Working Group on Strategies and Review WGSR asked for technical input from the EMEP Steering Body on the current level of confidence in the modelling of PM in the Unified Eulerian EMEP model (ECE, 2006).

2. This EMEP PM Assessment Report addresses the adequacy and completeness of the underpinning science upon which the current PM models used for policy development have been built. An important issue has been to strike a balance between the need to resolve a number of key scientific uncertainties and the desire to make progress with the integrated assessment modelling. The Task Force on Measurement and Modelling TFMM recognised that striking this balance is important for policy-making within the WGSR but wished to inform the policy process as clearly as it could about the state of current understanding on PM issues and the level of confidence in PM models as currently seen at the TFMM level.

3. The EMEP PM Assessment Report was commissioned by the EMEP Steering Body at its 29th Session in September 2005. The 7th Session of the Task Force on Measurement and Modelling hosted by the Finnish Meteorological Institute and held in Helsinki, Finland discussed this commission and laid out the framework and remit of the EMEP PM Assessment Report. It proposed a structure with a Part A addressing EMEP-wide issues and a Part B composed of national contributions describing PM monitoring and assessment carried out by the Parties. The TFMM proposed a question and answer format for Part A and posed 9 questions:

1. Are there significant differences in the PM climate across Europe?
2. To what extent is PM a transboundary problem?
3. How well do we understand the major PM components and their origins?
4. How important are natural PM sources?
5. To what extent do sources outside of Europe contribute to European PM?
6. How important is regional PM for urban PM levels?
7. How well can we link sources to observed PM levels with atmospheric models?
8. How large are the uncertainties in PM measurements and model predictions?
9. What improvements are required in PM monitoring, modelling and basic scientific understanding for the assessment of health and climate impacts of PM?

4. These questions and the two part structure for the PM Assessment Report were approved by the EMEP Steering Body at its 30th Session in September 2006. The drafting of Part A was begun at a Workshop in Paris hosted by ADEME and INERIS during November 2006. The workshop participants split into three groups with Chairpersons: Ms Sonja Vidic, Ms Laurence Rouil and Mr Jean-Philippe Putaud and with Rapporteurs: Ms Nathalie Poisson, Mr Karl-Espen Yttri and Mr Peter Bruckmann. Each group addressed three questions and their answers to the nine questions formed the text of Part A. The finished text was assembled by the Chairpersons of the Task Force on Measurement and Modelling.

5. Inspiration for the national contributions in Part B came from the presentations at the 7th TFMM meeting by Mr Andres Alastuey (Spain), Mr Robert Gehrig (Switzerland), Mr Risto Hillamo (Finland), Ms Cinzia Perrino (Italy) and Mr Jean-Philippe Putaud (JRC Ispra). Further outlines of national contributions were presented at the Workshop in Paris by Mr Peter Bruckmann (Germany), Mr Dick Derwent (United Kingdom), Ms Giovanna Finzi (Italy), Mr Hans-Christen Hansson (Sweden), Mr Ronald Hoogerbrugge (The Netherlands), Mr Savva Kleanthous (Cyprus), Mr Steinar Larssen (Norway, ETC/ACC), Mr Frank de Leeuw (The Netherlands. ETC/ACC), Mr Stephan Leinert (Ireland), Ms Marta Mitosinkova (Slovak Republic), Mr Finn Palmgren (Denmark), Mr Ulrich Quass (Germany), Ms Laurence Rouil (France), Mr Xavier Querol (Spain), Mr Gerald Spindler (Germany), Mr Milan Vana (Czech Republic), Ms Sonja Vidic (Croatia), Mr Markus Wallasch (Germany) and Mr Karl-Espen Yttri (Norway).

2 Questions and answers concerning particulate matter in Europe

Q1. Are there significant differences in the PM climate across Europe?

6. The behaviour of a trace gas is usually completely described by its concentration but this is not the case for PM. The PM climate across Europe can be described in terms of PM mass concentrations, size distribution and chemical composition and by physical properties, such as optical characteristics. The national contributions in Part B of this report summarise a great deal of information on PM mass concentrations, size distributions and chemical composition with which PM climates can be constructed.

Q1.1. Are there significant differences in PM mass concentrations across Europe?

7. Annual mean PM concentrations show large differences across Europe. To facilitate comparisons, national PM monitoring data are stratified according to site types such as rural background, suburban, urban background, industrial- and traffic-influenced. At remote, rural (EMEP) monitoring sites during 2004, annual mean $PM_{2.5}$ concentrations ranged from 3.3 µg m^{-3} in Norway to 28.3 µg m^{-3} in Italy, whereas for PM_{10} the concentrations ranged from 5.3 to 34.7 µg m^{-3} (Yttri and Aas, 2006). At traffic-influenced locations, annual mean $PM_{2.5}$ concentrations for 2004 ranged from 8 µg m^{-3} for the average of three sites in Finland to 56 µg m^{-3} for two sites in Bulgaria (Larssen et al., 2006).

8. There is a general tendency for annual mean $PM_{2.5}$ concentrations to increase from west to east across Europe, reflecting the progressive addition of man-made PM to Atlantic air masses and the different dispersion conditions between the oceanic and continental regions. Putaud et al. (2004) describe a European continental PM background of 7.0 ± 4.1 ug m^{-3} PM_{10} and 4.8 ± 2.4 ug m^{-3} $PM_{2.5}$, respectively, inferred from rural and near-city background monitoring site 5%-percentile values. Urban and traffic-influenced PM increments can then be characterised on top of these continental and regional background levels.

9. Differences in mean PM levels across Europe may also be inferred from satellite measurements of light extinction through the whole atmosphere, aerosol optical depth AOD or of light back-scattering at ground level from satellite-borne LIDAR instruments. Satellite imagery has been particularly useful in the detection and forecasting of Saharan dust outbreaks.

10. Among the factors controlling the regional-scale variations in PM mass concentrations and hence PM climate, the most important are:

- Pollutant dispersion, together with topography and meteorology, (both local and synoptic scale),
- Primary PM emissions (local scale) and those of the PM precursors (regional scale),
- Long-range and transboundary PM transport (synoptic scale).

11. As a result of the interactions between the above factors, a number of distinct PM climates can be distinguished across Europe. Locations along the Atlantic Ocean sea-board observe PM contributions that are heavily influenced by

the natural sea spray source (Visser et al., 2001). Dry, arid conditions during summertime lead to elevated rural levels in southern and central Europe (Rodriguez et al., 2003; Yttri and Aas, 2006). These arid conditions are especially important in the Western Mediterranean, where the lowest precipitation rates in Europe are registered (Rodriguez et al., 2007). Locations in southern Europe are heavily influenced by natural Saharan dust outbreaks (Rodriguez et al., 2001; Escudero et al., 2005; Querol et al., 2004a). Wintertime wood burning and road wear by studded vehicle tyres lead to elevated urban and traffic-influenced levels in Scandinavia (Larssen et al., 2006). During wintertime, the European Arctic is strongly impacted during wintertime by long range transport and experiences the so-called Arctic haze phenomenon.

Q1.2. Are there significant differences in PM size distributions across Europe?

12. Atmospheric particles are polydisperse, that is to say have differing sizes, ranging over more than three orders of magnitude in their diameters. Hence their number, surface and volume (mass) distributions versus particle size differ a great deal. Most particles are found below 0.1 µm diameter, whereas most of the volume (mass) is found above that size. So, for example, Saharan dust events can lead to a dominating mass distribution in the above 1 µm diameter size range, despite a small number of particles in that size range. As predominant particle number and mass refer to different fractions of the size distribution, they are necessarily governed by different processes. This implies that, in general, no simple correlation can be expected between particle number and particle volume (or mass) unless both are heavily influenced by particular emissions from the same source or meteorological events (van Dingenen et al., 2004).

13. Compared with observations of PM mass, there are relatively few long term measurements of PM particle size distributions. Van Dingenen et al. (2004) summarise the available information for 15 locations covering the free troposphere, continental background, rural, suburban, urban and traffic-influenced sites. During summertime, morning particle size distributions are expected to be largely influenced by traffic and afternoons by atmospheric photochemistry. Nucleation processes may occur under certain circumstances. Wintertime particle size distributions are shifted towards larger numbers and diameters, reflecting reduced vertical dispersion and the condensation of semi-volatile species onto the ambient particles, favoured by the colder temperatures.

14. For rural background sites in Scandinavia, higher particle number concentrations are observed during summer compared to winter conditions. This behaviour becomes more evident the further north the sites are within Scandinavia and may well result from the reduced impact of man-made sources, favouring the formation of new particles from the nucleation of condensable species of biogenic origins.

15. The national contributions in Part B of this report summarise a great deal of information on PM mass size distributions, mainly in the form of PM_1, $PM_{2.5}$ and PM_{10} ratios by mass. Although limited in scope, this information is highly relevant to defining PM climates across Europe.

16. Generally speaking, $PM_{2.5}$ and PM_{10} mass concentrations are well correlated at a given site whether rural or urban on an hourly and daily basis. However,

$PM_{2.5}$ and PM_{coarse} = $PM_{2.5\text{-}10}$ mass concentrations are not always well correlated, reflecting the different sources contributing to the different PM measures. Annual mean $PM_{2.5}/PM_{10}$ ratios range from 0.5 to 0.8 and are significantly lower at sites where specific sources of coarse particles such as coarse mineral dust and sea spray particles are important. Such locations may include the Mediterranean basin (Saharan dust), the Atlantic Ocean sea-board (sea salt) or those heavily influenced by motor vehicle traffic (resuspension) or specific industrial or mining emissions (Querol et al., 2004b).

17. Sea-spray is unquestionably a natural PM source. Mineral dust may be a natural PM source when its occurrence is driven by strong winds or by long-range transport from, for example, the Saharan region. Mineral dusts may be classed as human-influenced when man-made coarse particles are blown up and transported by strong winds or when natural or man-made particles are resuspended by human activities such as agricultural activities or road traffic.

18. However, $PM_{2.5}/PM_{10}$ ratios may show significant day-to-day and seasonal variability and this confirms the view that different sources contribute to the different PM size fractions during particular episodes. Seasonal variations are closely related to meteorology and particular synoptic situations bringing mineral dust from arid regions, local strong winds causing soil dust resuspension and sea-spray production. Due to the short lifetime of PM_{coarse}, $PM_{2.5}/PM_{10}$ ratios can change due to specific events such as precipitation, traffic congestion, road construction and building demolition and construction.

19. Large differences have been reported in the particle number and size distributions across Europe (van Dingenen et al., 2004). Such differences may have important health-effect consequences because the smallest particles are the most numerous and have the largest contact surface area. Seasonally-averaged $PM_{2.5}$ mass concentrations at similar sites may be associated with particle numbers differing by a factor of two or more in different regions across Europe (van Dingenen et al., 2004).

Q1.3. Are there significant differences in PM composition across Europe?

20. Although nitrate, sulphate, ammonium, sea salt, organic matter and elemental carbon, the predominant PM constituents, are almost ubiquitous across Europe, their relative contributions vary significantly both spatially and temporally. These variations are sufficiently large to define different ‘PM climates’ across Europe. However, full chemical characterisation of PM is rarely achieved due to the wide range of detection and measurement methods required to quantify the different PM components. Also the distribution of the main PM constituents in the fine and coarse particle size fractions, varies substantially throughout Europe.

21. Mineral compounds and sea salt contribute more to the coarse fraction whereas ammonium, sulphate and organic matter contribute more to the fine fraction. Elemental carbon and nitrate contribute more to the fine fraction but their contributions to the coarse fraction vary significantly, both spatially and temporally. Organic matter in the fine fractions may result from combustion processes or from the oxidation of volatile organic compounds, whilst that in the coarse fraction may also comprise mechanically-generated particles including biological debris. Nitrate in the fine fraction is bound to ammonium and

evaporates from particles under warm conditions in summer, whereas that in the coarse fraction is bound to sea-salt or mineral dust particles and is not semi-volatile (Putaud et al., 2004). In southern Europe, coarse particle nitrate levels may exceed those of fine (Querol et al., 2004b).

22. The national contributions in Part B of this report show that, generally speaking, PM nitrate to PM sulphate ratios decline from west to east and from north to south. Certainly, PM nitrate to PM sulphate ratios are low in Arctic haze, probably due to the shift of nitrate to coarse particles and the preferential dry deposition of the larger nitrate particles over the long transport time scales to the Arctic. The contribution of mineral dust to PM_{10} on an annual average basis increases from 5 to 25% from north to south, showing the influence of drier summertime conditions in southern Europe and the frequency of Saharan dust outbreaks. The contribution of particulate organic matter to PM increases significantly in regions with wood and agricultural waste burning (Gelencser et al., 2007). The Carbosol project has shown that the ratio of particulate organic matter to secondary inorganic PM ranges from 0.5 in south-west Europe to 1.2 in north east Europe. Ratios of particulate organic matter to elemental carbon vary from 5 to 11 in Carbosol studies (Pio et al., 2007) and reach 15 in Spain (Querol et al., 2006). In the EMEP carbonaceous aerosol campaign 2002-2003, the ratios of elemental carbon to total PM mass ranged from 1 – 5% and those of particulate organic matter to total PM mass from 9 – 37% (Yttri et al., 2006).

23. Because the regional background PM contributes significantly to the PM observed at urban background and traffic-influenced sites, it follows that changes in regional background composition will be manifested in changes in chemical composition at urban sites. Rural and urban sites therefore tend to observe similar absolute levels of particulate sulphate that is due mainly to regional pollution. In contrast, particulate organic matter and elemental carbon show large differences between urban and traffic-influenced sites and rural levels. In addition, large urban and traffic excess concentrations of road dust and resuspended dust are observed in most cities, particularly in wintertime when road salt and road sand are applied and studded tyres are fitted to motor vehicles. These sources affect the composition of both $PM_{2.5}$ and PM_{10}.

24. The robustness of the answers to the above questions depends crucially on the reliability of the observations that have been used. An important issue is their adequacy and completeness and the impact of measurement artefacts. Measurements of PM mass concentrations may not necessarily be comparable across Europe because of a number of issues:

- The comparability of the different methods, including TEOM, FDMS-TEOM, β-gauge, gravimetry. Correction factors are applied to the measurements to make them comparable with reference methods but these factors are not always robust and accurate.
- The classification of sites as rural, suburban, urban background, traffic-influenced sites may not be harmonised throughout the different countries of Europe.

25. It should also be borne in mind that the standard method for determining PM mass concentrations EN 12341 which also serves as the reference method under EU air quality directives may be biased by sampling artefacts (see below)

and analytical artefacts, namely the amount of water remaining at 50% relative humidity as required by EN 12341 (CEN, 1998). This analytical artefact depends on the filter history and on the hygroscopicity of the sample, linked to its chemical composition of the PM. Notwithstanding, this reference method has been adopted as the basis for the PM limit and target values in the air quality Directives promulgated by the European Union (CEN, 1998). Experiments performed within the EMEP network and elsewhere (Schwela et al., 2002; Putaud et al., 2006) demonstrated that at about 50% relative humidity, the percentage of PM mass due to PM-bound water may range from about 10 – 30%, depending on the location, reflecting changes in PM composition.

26. Sampling artefacts, both positive and negative may affect most measurements of semi-volatile particulate components such as ammonium nitrate and organic matter. The best understood artefact is the loss of ammonium nitrate from the filters by volatilisation when ambient temperatures exceed 20^oC. Both laboratory and field experiments showed that up to 100% of the ammonium nitrate may be lost from filters, leading, for example, to an underestimation of up to 15 µg m^{-3} of the PM mass concentration in Northern Italy (Schaap et al., 2004).

27. There are also a number of specific analytical issues that may hamper the comparison of PM composition measurements, including:

- The splitting between organic carbon and elemental carbon is method-dependent and influenced by charring, leading to elemental carbon mass concentrations that may differ by up to a factor of two, comparing the two most commonly used thermal-optical protocols (NIOSH and IMPROVE),
- Most instruments that measure organic matter and elemental carbon report C whilst adjustments are required for the presence of other atoms (H, O, N etc.). These adjustment or scaling factors may generally range from 1.2 to 2.1 (Turpin and Lim, 2001).
- Mineral dust is often not directly quantified but inferred from measurements of Al, Ca, Fe and Ti etc. using scaling factors. These scaling factors are often not reported.

Q2. To what extent is PM a transboundary problem?

28. The long-range transport of PM is a transboundary problem that can have significant impacts on PM_{10} and $PM_{2.5}$ levels in remote, rural and urban areas. National contributions in Part B of this report clearly identify a regional-scale background contribution to urban PM levels and a further traffic contribution on top of urban background levels at traffic-influenced sites. This regional background may contribute between 60 – 90% of urban background PM_{10} and $PM_{2.5}$ levels on an annual basis. The questions addressed here are: what is the extent of the contribution from long-range transboundary transport to the regional background of PM_{10} and $PM_{2.5}$ and how may this contribution be quantified?

29. The contribution from long-range transboundary transport to urban PM levels depends on many factors. Each of the PM size fractions has a different atmospheric lifetime because of the manner in which dry deposition velocities and wash-out through wet deposition vary with particle diameter. Ultrafine and coarse particles are removed more readily than the larger particles within the PM_1 and $PM_{2.5}$ size fractions by Brownian impaction and coagulation for ultrafine particles

and by deposition for coarse, respectively. The larger particles with soluble fractions are also more likely to form droplets and to be washed out in precipitation. There is therefore a preferential removal of the very small and larger particles with increasing transport distance which would generate a largely uniform submicron particle size distribution as seen in the Arctic haze. Nevertheless, the coarse fraction of PM_{10} still has a significant transboundary component despite its shorter mean transport distance compared with $PM_{2.5}$.

30. All PM fractions have the potential to be transported over the long-range distance scale but there are situations where the contribution of local pollution to $PM_{2.5}$ levels can be large. Particle size is therefore not the sole determinant of the extent of the long-range transboundary transport of PM because of the influence of local pollution sources and local pollution episodes. Any assessment of the extent of PM long-range transboundary transport at a particular location should take into account weather conditions on the local and synoptic scales, seasonal variations in meteorology and the geographical disposition of PM sources. Attention should be given to the influence of pollution episodes, whether they are local or regional in scale.

31. Clearly, when considering the extent of the contribution from long-range transboundary transport at a particular location, geography plays an important role. If the location is close to a border with a neighbouring country, then transboundary transport will necessarily appear more important than if the location is in the centre of that country. Equally well, the size of a country is an important factor since transboundary transport will seem relatively more important for small countries compared with large countries.

32. Location within Europe is also an important issue for the characterisation of ‘PM climates’. Rural PM_{10} and $PM_{2.5}$ levels show an increasing trend across Europe, lower in the west and higher in the east, reflecting the progressive addition of man-made PM sources and the difference in atmospheric dispersion conditions between oceanic and continental sites. There is also a strong gradient in precipitation from west to east and from north to south across Europe. All other factors being equal, these factors would lead to a steadily increasing contribution from long-range transboundary transport when moving from west to east. The spatial pattern of man-made PM sources is markedly different in north west Europe compared with southern Europe, and also for western and eastern Europe, and this may also lead to different perceptions of the importance of long-range transboundary transport.

33. Back-track air mass trajectories are a useful tool in distinguishing between regional-scale and long-range PM transport. Pollution wind-roses also provide a simple, visual means of characterising contributions from long-range transport. National contributions in Part B of this report show that large-scale pollution episodes can be the result of both local PM sources and of long-range transport, in response to variations in regional climate and geography. An example is that of the Melpitz site in Germany as shown in Part B of this report where over a short period in time, PM episodes were characterised from both local and long-range transport. For the specific case of Saharan dust outbreaks, a number of tools such as satellite imagery, back-track air mass analyses and modelling tools such as SKIRON, DREAM and NAAPS have been employed to detect and forecast dust outbreaks.

34. The analysis of the long-range transport contribution to rural and urban PM levels under episode conditions or average pollution levels is therefore not a straightforward task. Episodes with high PM levels may have different properties and hence long-range transport may contribute differently to episodes compared to the average situation.

35. In some parts of Europe, chemical composition and PM composition wind roses may provide a clear indication of the extent of transboundary transport, for example, in the UK for $PM_{2.5}$, sulphate, nitrate and elemental carbon. Saharan dust is a clear indicator of long-range transport in the Mediterranean basin and in southern Europe. A large proportion of the exceedances of the EU PM_{10} daily limit values in southern Europe may be attributed to long-range transport and Saharan dust outbreaks, in this way, see Figure 1.

36. The extent of long-range transport of the different PM components varies in different regions of Europe. Ammonium nitrate is a good indicator for long-range transport in north west Europe; sulphate is a good indicator in eastern and central Europe of long-range transport. A high contribution from mineral dust indicates transport of Saharan desert dust to southern Europe and the Mediterranean basin.

37. Long-range transboundary transport can be best characterised at rural and EMEP sites where the influence of local PM sources in minimal. However, the contribution of transboundary transport to PM levels at suburban and urban background sites is more relevant to policy and human health effects. Transboundary transport can be best characterised for $PM_{2.5}$ but care must be taken to recognise the influence of local contributions to $PM_{2.5}$ levels when quantifying the transboundary and long-range transport contributions to PM levels.

38. Quantification of the extent of PM transboundary transport should take into account different meteorological conditions, back-track air mass trajectories, synoptic weather patterns, large-scale phenomena, temperature inversions and conditions of poor atmospheric dispersion. It should also take into account the differences in deposition velocities and hence transport distance scales for the different particle sizes and hence different PM components, particularly PM sulphate and nitrate. Any analysis should address both PM_{10} and $PM_{2.5}$ and $PM_{2.5}/PM_{10}$ ratios. It should also be combined with model results and cover the relevant area. Quantification studies should cover both winter and summer seasons because of important changes in the dominant PM emission sources.

Q3. How well do we understand the major PM components and their origins?

39. PM is not a unique chemical compound (such as ozone) but a generic term for or a complex mixture of various compounds that differ widely in their physical and chemical characteristics. PM is defined by the different measurement methods. Each measurement method has its own biases, artefacts, standardisation, harmonisation and complexity issues.

40. There is still a great lack of understanding of some of the major PM components. There seems to be an apparent discrepancy between decreasing PM emissions during the 2000s and observed $PM_{2.5}$ and PM_{10} levels that have remained more or less unchanged over the same period in many parts of Europe.

An example of this behaviour is illustrated in the contribution from Germany to Part B of this report. This discrepancy may reflect deficiencies in our understanding of PM emissions and atmospheric chemistry. Meteorological variability may explain the increase in PM levels between 1999 and 2003 (Tarrason et al., 2005) but PM levels have remained unchanged beyond these years.

41. Some of the major PM components are well understood and these include particulate sulphate and nitrate and to a lesser extent, particulate ammonium. There are uncertainties with ammonia emissions, that when taken together with its non-linear chemical production pathways, limit confidence in the understanding of ammonium nitrate. Some PM components are poorly understood because they are difficult to measure, carbonaceous particles and particle-bound water, for example, and some because they are not widely measured, particularly the crustal minerals, for example. Much further work is required to characterise organic matter, whether natural or man-made and whether primary or secondary in origin. On a research basis, using a wide range of experimental techniques about 90% or more mass closure can be reached. Such levels of mass closure cannot be achieved on a routine basis.

42. The composition and origins of particulate organic matter are poorly understood. Particulate organic matter is difficult to analyse, except the total mass of carbon, as it is comprised of hundreds of individual organic compounds. Without some understanding of which are the major compounds present in particulate organic matter it is impossible to apportion accurately it into primary versus secondary origins and to classify it according to whether it has been derived from man-made versus natural biogenic sources. Analyses of the ^{14}C content of organic matter will assist in the differentiation between contemporary, largely natural biogenic, and fossil, largely man-made, sources.

43. Single-particle mass spectrometry is a novel but expensive method for the identification of the type, composition and origins of ambient particles. Operating these instruments is a research activity as they are not suitable for unattended operation in pollution monitoring networks. Single-particle mass spectrometry has been included in the recent EMEP intensive monitoring campaigns. When the results from these campaigns become available, they will add significantly to our understanding of the origins of particulate organic matter, in particular, and ambient particles, in general.

44. Particle monitoring super-sites, together with measurement programmes analysing size distributions and the number and chemical composition of particles, are important ways of extending our understanding of PM. It is recommended that the location of these supersites should be carefully considered to ensure that they are representative of the main regions of the European PM climate. Harmonisation and standardisation of research monitoring methods is essential if the results are to be comparable across Europe. Super-sites should also be established in urban background locations for the identification of the PM constituents most relevant for urban air pollution and therefore for policy purposes.

Q4. How important are natural PM sources?

45. Generally, natural sources are important for both $PM_{2.5}$ and PM_{10}, but their fractional contribution to total PM is significantly greater for PM_{10} compared with $PM_{2.5}$ since natural PM is mainly mineral dust and sea-spray. Nevertheless, natural biogenic secondary organic aerosol is predominantly in the $PM_{2.5}$ size fraction. A number of natural sources of PM have been identified at various sites across Europe and these are described in the paragraphs below.

46. Long-range transport of Saharan dust can cause daily mean mineral dust PM_{10} levels in excess of 500 µg m^{-3} in the Mediterranean basin, leading to 30 – 35 exceedances of the EU daily mean air quality limit value per year (Rodriguez et al. 2001; Querol et al., 2004a; Escudero et al., 2005). Annual mean dust PM_{10} concentrations are up to 15 µg m^{-3} in Cyprus, 2 – 4 µg m^{-3} in the Mediterranean basin and about 1 µg m^{-3} north of the Pyrenees and Alps. In the Mediterranean basin and the Canary Islands, daily PM_{10} and $PM_{2.5}$ levels around 600 and 70 µg m^{-3}, respectively, have been reported for African dust outbreaks (Querol et al., 2004a), with $PM_{2.5}/PM_{10}$ ratios close to 0.3 – 0.4. It is clear that $PM_{2.5}$ is influenced by Saharan dust outbreaks though this is not always recognised in the literature. In the specific case of Cyprus, hourly mean PM_{10} concentrations of up to 1500 µg m^{-3} have been reported. Saharan dust events have been observed in the British Isles leading to peak hourly PM_{10} level of up to 290 µg m^{-3} during one episode during March 2000. Hourly peak $PM_{2.5}$ levels were generally 40 – 60 µg m^{-3}, and reached about one half of the PM_{10} levels (AQEG, 2005).

47. Strong winds and storms at sea can lead to elevated daily mean sea salt PM_{10} levels at exposed coastal sites of up to 35 µg m^{-3} on the Atlantic Ocean sea-board of Europe. Annual mean sea salt PM_{10} levels are 10 – 12 µg m^{-3} in the Canary Islands as measured by Querol et al., (2004a) at a coastal site in Gran Canaria, about 7 µg m^{-3} at coastal sites in the Netherlands (Visser et al., 2001) and less than 1 µg m^{-3} at inland continental sites. The sea-salt contribution to $PM_{2.5}$ is clearly diminished relative to PM_{10}, with levels of the former usually less than 1 – 2 µg m^{-3} even at Atlantic Ocean coastal sites.

48. Particulate organic matter POM of natural biogenic origins may be of primary or secondary origin. Natural primary organic matter may include spores, bacteria and biological cell debris. Natural secondary organic matter may include semi-volatile organic compounds resulting from the oxidation of biogenic organic compounds such as isoprene, terpenes and sesquiterpenes. Secondary organic particulate matter can also be formed from the oxidation of man-made VOCs, particularly aromatic compounds, and so it is difficult to classify secondary organic particulate matter as either natural or man-made.

49. There is no analytical method able to separate the ambient aerosol content of natural organic carbon from that of man-made origins. However, by using state-of-the-art radiocarbon measurement and organic tracer analysis, the organic carbon fraction that originates from fossil fuel combustion and biogenic sources can be distinguished from each other and quantified. In a recent study using the ^{14}C-methodology, it was demonstrated that about 60% of the particulate organic carbon at an urban background site in Zurich, Switzerland could be attributed to biogenic sources during summer, whereas the corresponding percentage during winter was about 27% (Szidat et al., 2006). The majority of the biogenic fraction in that study was attributed to secondary organic aerosols, whereas plant debris

accounted for 2 – 19% of the biogenic organic matter. Particulate organic matter from biogenic VOCs may contribute up to about 30% of the total organic carbon in winter at city background sites and about 60% in summer. In Finland, secondary organic carbon from biogenic VOCs can reach up to 2 µg m^{-3}.

50. Water typically contributes about 50% of the aerosol mass in a clean atmosphere. A significant amount of this water remains bound to the particulate matter on the filters under the conditions of 50% relative humidity prescribed in the reference method for gravimetric PM_{10} analyses (EN 12341). Typically water may account for between 10 and 30% of the aerosol mass in a gravimetric analysis carried out using the reference method. This water is chemically bound to the hygroscopic constituents of the particulate matter collected on the filters, including sea salts and ammonium salts, mainly sulphates and water-soluble organic compounds. Further information is available in Gnauk et al., (2005), Neususs et al., (2002) and Metzger and Lelieveld (2007).

51. A number of measurement issues have been identified that are related to the quantification of the contribution of natural sources to PM_{10} and $PM_{2.5}$ levels, including:

- Mineral dust: chemical analyses are costly but cannot always distinguish between wind blown or desert dusts (natural) and dusts resuspended by vehicular traffic (man-made),
- Particulate organic matter: requires sophisticated ^{14}C determination or levoglucosan tracer measurements that are too expensive for routine monitoring,
- Particle-bound water: direct measurements are difficult.

Q5. To what extent do sources from outside Europe contribute to European PM?

52. This is a difficult question to answer based on observations alone. Satellite imagery can demonstrate the occurrence of long-range transport of desert dust and biomass burning plumes from outside of Europe but it cannot provide quantitative information. Chemistry-transport models can answer these questions by switching off emissions from outside of Europe (Park et al., 2004), as long as emission inventories and atmospheric process descriptions are accurate enough.

53. In principle, observations should provide the most cogent evidence that sources outside of Europe contribute to European PM. The contributions from sources outside of Europe can be roughly assessed by looking at the concentrations observed at sites located at the borders of continental Europe when they are upwind of the Continent. In this way, it has been estimated that about 1 µg m^{-3} PM arrive from North America and reach the Netherlands (Visser et al., 2001). Putaud et al. (2003) estimate that just less than 1 µg m^{-3} reach Izana in the Canary Islands from North America. PM levels in Scandinavia, Finland, UK, Germany and Poland have been affected by large-scale forest fires in Siberia. Smoke particles from large-scale fires in Canada have been detected over Germany (Muller et al., 2005).

54. Intercontinental ship traffic emissions may be considered as a source of PM which is outside of Europe. Certainly, such emissions were not initially

considered in the EU CAFÉ programme and by the UN ECE Convention on Long-range transboundary air pollution. Emission inventories show that shipping is and will be an important future source of PM precursors (such as SO_2) and of primary PM (particularly elemental carbon) as land-based emissions are reduced by regional pollution control actions. There is also the special situation in harbours where there are contributions to emissions from international non-EU ships.

55. The extent to which sources from outside of Europe contribute to European PM is amenable to study through atmospheric modelling. Park et al. (2004) used the GEOS-CHEM 3-D coupled oxidant – aerosol model to estimate trans-Atlantic influences on sulphate – nitrate – ammonium aerosol concentrations in Europe. They reported an enhancement due to North American pollution sources of 0.1 – 0.2 µg m^{-3} in particulate sulphate in Europe and close to zero for nitrate and ammonium. The EMEP Task Force on the Hemispheric Transport of Air Pollution is currently addressing the importance of intercontinental transport for a number of pollutants, PM included. The TF HTAP is due to produce an interim assessment during 2007 that will bring together the information required on emissions of PM precursors, atmospheric processes and chemistry-transport models, to address these issues.

Q6. How important is regional PM for urban PM levels?

56. National contributions in Part B of this report, identify the regional background contribution to urban background $PM_{2.5}$ and PM_{10} levels as typically in the range from 60 – 90%. In some regions of southern Europe, this percentage may be even lower, 30 – 50%, when most PM pollution is produced in large urban agglomerations. At traffic- or industrially-influenced sites with high local emissions, the regional contribution will be lower. In densely populated areas, such as in the Benelux countries or the Ruhr region of Germany, with numerous local source contributions, the clear discrimination between rural and urban PM levels may be difficult. In isolated towns and cities in rural areas, the regional contribution may towards the lower end of the range.

57. The concepts of urban and traffic PM increments are useful in the analysis of PM observations (Lenschow et al., 2001). They are best derived from carefully chosen pairs or groups of monitoring stations. Both stations should be in the same geographical region with distance separations of up to 50 km. One station should be in an urban background location and the other in a rural location in the surrounding regions. Urban and traffic increments should be expressed in µg m^{-3} and not as percentage increments. The local environments and monitoring heights should be similar at the two stations.

58. Regional PM background concentrations arise from long-range transport, regional sources such as city plumes and from regional accumulation during low wind situations. They do not necessarily represent directly the extent of long-range or transboundary PM transport. Quantification of the extent of transboundary PM transport required further analysis of the origins of the PM levels during average and episodic conditions.

59. The local traffic increment, measured as the excess in PM concentrations at a heavily traffic-influenced location or "hot spot" above the urban background level, strongly depends on the precise location of the monitoring site with respect

to the local traffic emissions. Traffic increments are therefore unlikely to be comparable within a city or across Europe unless care is taken to harmonise the siting criteria for urban monitoring sites. Climate differences may also account for large variations in PM levels and PM composition for a given traffic flow and siting criteria. At traffic sites with high rainfall, wash-out of road dust will lead to decreased PM levels. Whereas, if rainfall is scarce, mineral road dust will be continuously resuspended, leading to increased PM levels and increased mineral matter loadings.

Q7. How well can we link sources to observed PM levels with atmospheric models?

60. It is important to make some general observations about the current state of PM modelling in Europe. All models currently underestimate total PM_{10} and $PM_{2.5}$ and therefore do not achieve mass closure. There are several reasons for this state of affairs. Some PM components are not included at all in models and some others are treated in simplified ways. There are large uncertainties in the emissions inventories of the primary PM components and of some PM precursors. Our confidence in the PM models ultimately rests on the comparison of model predictions with observations. Currently there are only few observations of the numerous PM constituents for model verification purposes. This may be because for some PM components our understanding is limited and the measurements are too expensive and difficult for routine operation. Many of these observational challenges have been addressed in the EMEP monitoring strategy and it is important that this strategy is fully implemented without further delay in order to increase our confidence in the application of PM models on the different scales. Also further observations in urban environments are needed for improved understanding of the sources relevant to human exposure.

Q7.1. How well can we link SO_2 sources to observed levels of particulate sulphate with atmospheric models?

61. We have a high degree of confidence that we can link SO_2 sources to the observed levels of particulate sulphate. Over the years, most of the important uncertainties in SO_2 emission inventories have been tackled and few outstanding problems remain, except for domestic coal burning and ships in harbours. Observations of particulate sulphate have the necessary reliability and spatial coverage for model verification purposes. Long-running time series are available to check model calculated trends with observed trends over the last two decades.

62. The review of the Unified EMEP model (TFMM, 2004) remarked that there was a high level of confidence in the model’s ability to represent the broad spatial pattern of particulate sulphate across Europe, its trends and the role played by its long-range transport in providing the regional background levels required as an input to urban health impact studies.

63. Further improvements in the representation of particulate sulphate in current PM models are to be encouraged. The more detailed representations of cloud chemistry processes is an area where improvements are still possible. The evaporation of cloud droplets is a major source of particulate sulphate in the background atmosphere (Raes et al., 2000). Wet removal of particulate sulphate is a further area when improvement is necessary to provide a better match with

observed sulphur deposition fields. In this context, it is relevant also to investigate dry deposition processes, such as the co-deposition of SO_2 and NH_3.

Q7.2. How well can we link NO_x sources to observed levels of particulate nitrate with atmospheric models?

64. We have a reasonable level of confidence that we can link NO_x sources to the observed levels of particulate nitrate. As with SO_2 emissions, few outstanding problems remain with NO_x emission inventories for land-based sources and we can be confident that they adequately represent the atmospheric sources of NO_x. There are major questions concerning the adequacy and completeness of NH_3 emissions, particularly from agriculture, and the influence that they have on the assessment of particulate nitrate model performance. The uncertainties in ammonia emissions, when taken with the non-linear chemical production pathways, limit our confidence in the ability of models to represent particulate ammonium nitrate formation.

65. The few measurements that are available in Europe for particulate nitrate have been made using filter-based techniques and the outstanding problems with evaporation of the ammonium nitrate still have not been solved. Few high (hourly) time resolution measurements are available for particulate nitrate with which to verify the atmospheric process descriptions employed in the models. Difficulties remain with how to translate measurements by filters into results that provide an adequate check on particulate nitrate model performance. The atmospheric processes that control the levels of particulate nitrate are highly sensitive to meteorological parameters. Temperature and humidity control the formation and evaporation of ammonium nitrate.

66. There is also an important coupling between nitric acid and ammonia that controls the gas-particle partitioning of ammonia and oxidised nitrogen compounds. Hence, there is an important requirement for concomitant measurements of ammonia, nitric acid and nitrogen dioxide with those of particulate nitrate. This need was incorporated into the EMEP monitoring strategy (Tørseth and Hov, 2003) and intensive field campaigns have been organised. The results concerning the gas-particle partitioning of ammonia and oxidised nitrogen compounds will be of vital importance of particulate nitrate model development when they become available during 2007.

67. The review of the Unified EMEP model (TFMM, 2004) remarked that there were insufficient particulate nitrate and ammonium measurements available to provide an adequate test of the model performance for particulate nitrate. However, it was concluded that the EMEP model was able to calculate the regional component of particulate nitrate with enough accuracy to assess the effects of different control measures.

68. Improvements in the model performance for particulate nitrate and hence increasing confidence in the model predictions will arise from the results of the intensive monitoring campaigns on the gas-particle partitioning of ammonia and oxidised nitrogen compounds. Such improvements are not considered as a priority for modelling because model results are currently satisfactory but will nevertheless be welcomed and will be important for building confidence in the model predictions.

Q7.3. How well can we link sources of elemental carbon and organic PM to observed levels with atmospheric models?

69. Currently, we have little confidence that we can link sources of elemental carbon and organic carbonaceous PM to observations with models because of the complexities involved in the formation of secondary organic aerosol, the importance of biomass burning, the importance of primary sources of both natural and man-made carbonaceous PM and because of their relatively large contribution to $PM_{2.5}$ and PM_{10} mass.

70. Many of our current difficulties with elemental carbon and organic carbon particulates stem from difficulties with their measurement methods, the lack of a reference method and the lack of consistency between the existing European measurements. The split between elemental and organic carbon depends on the method and is influenced by charring, leading to elemental carbon measurements that may differ by up to a factor of two when comparing the two most commonly used protocols, that is NIOSH and IMPROVE. Most instruments that measure elemental carbon and organic PM report their results as elemental C and so adjustments are required for the presence of other atoms (H,O,N etc.) to calculate and report as $PM_{2.5}$ or PM_{10}. These adjustment factors generally range from 1.2 to 2.1 in published studies and have yet to be harmonised. Monitoring results could be expressed on a total carbon basis and hence would be more directly comparable with model results. However, this would not help in the identification of the mass contributions to $PM_{2.5}$ and PM_{10} from primary and secondary organic matter sources and biogenic versus man-made sources. Many of these monitoring problems could be resolved by further harmonisation and standardisation. There is an important requirement to use identical harmonised and standardised procedures in the measurement of elemental carbon and organic PM emissions.

71. Many of the remaining difficulties with elemental carbon and organic PM, stem from problems with emission inventories. Emission inventories for primary PM components are of relatively recent development. Reliability, size and spatial resolution, coverage of the different source categories and PM species coverage still remain crucial issues for PM emission inventories. Emission inventories for elemental carbon need substantial improvement in terms of accuracy and coverage of source categories particularly those of road traffic, wood combustion and residential heating. Improvements are required in spatial resolution at the European scale and in the representation of diurnal, weekly and seasonal emission profiles. Levoglucosan acts as an excellent tracer for wood burning and this could be used in source-receptor modelling to quantify an important missing source from the PM inventories. Agricultural waste burning and forest fires are also important sources of elemental carbon and organic PM. Harmonised and standardised measurement procedures should be implemented in the emission measurements used to compile emission factors to ensure consistency between the models and observations.

72. Improvements in VOC emission inventories are also urgently required to improve model descriptions of the formation of secondary organic PM. The improvements need to address the speciation of both man-made and natural biogenic VOC sources and the formation mechanisms of the semi-volatile and other organic PM precursor species.

73. The review of the Unified EMEP model (TFMM, 2004) noted that the confidence in the understanding of the mechanism of the formation of secondary organic aerosols was so low that they had not been included in the EMEP model, leading to underestimations for PM_{10} and $PM_{2.5}$. The Unified EMEP model is thus unable to assess the impacts of VOC emission control measures on secondary organic aerosol mass. Understanding will grow steadily in the quantification of primary particle emissions and this will lead eventually to increased confidence in the estimation of regional levels of primary particles emitted, thereby improving the assessment of $PM_{2.5}$ and PM_{10}. However, the model is able to calculate the regional component of some primary PM species with enough accuracy to assess the effect of different control measures.

74. Developments in current PM models to improve the description of atmospheric processes and to address uncertainties in PM emission inventories are thus urgently needed. These developments are severely hampered by the lack of measurement data. They remain of crucial importance to policy because elemental carbon and organic PM could represent 30 – 50% of the total PM composition by mass.

75. Whilst there is some confidence in the ability of models to represent the regional component of some primary PM components, there is little confidence that they are ready to describe the urban or traffic increments in $PM_{2.5}$ that are required for integrated assessment models and for policy assessments of urban health effects. As noted in the review of the Unified EMEP model (TFMM, 2004), the ability of current PM models is limited to the simulation of the relative impacts of different emission scenarios, taking carefully their limitations and uncertainties into account. As a consequence, it is not straightforward to use current PM models for the investigation of compliance with air quality standards, targets and limit values.

Q7.4. How well can we link sources of mineral dust to observed levels with atmospheric models?

76. There are major difficulties in the representation of mineral dust in PM models. Mineral dust components of PM_{10} and $PM_{2.5}$ are often not directly quantified by chemical analyses but are inferred from measurements of elements such as Al, Ca etc. using scaling factors. These scaling factors are often not reported and are not necessarily harmonised with other literature studies. Measurements of mineral dust, which may originate from deserts or from local wind erosion, do not distinguish natural resuspension from man-made resuspension by road traffic or agricultural activities. The parameterisations used in models to represent mineral dust are driven by local weather conditions and require a great deal of information about soils and land use. Results of dust measurements in large urban agglomerations show differences between hot-spots and urban background levels, demonstrating a high degree of variability. The emission patterns are complex because of the influence of road traffic, demolition, construction, traffic resuspension and the long dry periods in southern Europe. As a result they have large uncertainties and there is a paucity of measurement data with which to verify their accuracy. Nevertheless, their inclusion in PM models does bring a measure of improvement in model performance.

Q8. How large are the uncertainties in PM measurements and models?

77. Uncertainties in European models for particulate sulphate are currently judged to be of the order of ± 15 – 20%, on an annual average basis. The corresponding uncertainties in model particulate nitrate are somewhat larger at about ± 40%. Measurement uncertainties in particulate sulphate and nitrate are comparable to those in models. This situation is considered acceptable for the policy purpose of assessing the effect of different control measures for SO_2 and NO_x on the regional component of particulate sulphate and nitrate as noted in the Unified EMEP model review (TFMM, 2004).

78. Uncertainties in current model predictions for natural PM components such as mineral dust, sea salt and biogenic primary organic matter are large and difficult to assess. Currently, these sources are not included the PM models used for policy development and hence they do not achieve mass closure. As a consequence these PM models cannot be used for testing compliance with air quality standards, targets and guidelines for PM.

79. Uncertainties in model results for elemental and organic PM are also large. There are major problems with emission inventories and with the representation of the main atmospheric processes controlling their distributions across Europe. Uncertainties in measurement data and their general paucity, preclude any quantification of model uncertainty for these PM components. Nevertheless, this is an area where significant progress may be expected in the foreseeable future and secondary organic aerosol may well be represented in future PM policy models.

80. Whilst there is limited confidence in the ability of models to represent the regional component of some primary PM species such as elemental carbon, there is little confidence that they are ready to describe the urban or traffic increments in $PM_{2.5}$ that are required for integrated assessment models and for policy assessments of urban health effects.

81. A number of recommendations can be made that would help to reduce the uncertainties in models and to increase confidence in their predictions:

- To develop a standardised method to check the ability of models to represent the different chemical regimes in Europe. By chemical regimes, we mean NO_x-limited versus VOC-limited regimes for ground level ozone formation or NH_3-limited versus NO_y limited regimes for PM nitrate and ammonium formation.
- To employ the models to compare emissions and policy scenarios for their impacts on regional PM mass concentrations rather than to determine exceedances of air quality limit values, guidelines and standards but in a relative sense for comparing scenarios for their relative impacts on regional PM levels.
- To gather relevant measurements at relevant sites. The EMEP monitoring strategy should be promptly and widely implemented to help to reduce model uncertainty and to help increase confidence in model predictions.

82. Deficiencies in the EU reference method for PM_{10} (EN 12341) are well recognised and include large, variable water content and sampling artefacts.

'Reference' PM measurements have therefore a high level of uncertainty, while non-reference methods such as TEOM-based continuous samplers are more self-consistent but measure something different. Any interpretations and assessments of model PM results against observations must take these uncertainties into account.

Q9. What improvements are required in PM monitoring, modelling and basic understanding for the assessment of health and climate impacts of PM?

83. Current assessments of the health and climate impacts of PM across Europe are severely hampered by the lack of comparability in the measurement methods for PM mass and its composition. Reference methods should be defined and used where possible and practical, scaling factors should be documented and instrumental methods and procedures should be harmonised and standardised. Improvements are required in the description and classification of monitoring sites to ensure maximum comparability in the definitions of rural, urban background and traffic-influenced sites. Common issues between the PM air quality, climate change and human health impacts research communities have recently been authoritatively reviewed (Hansson and Dowd, 2006; WHO, 2006).

84. A general requirement is better quantification of PM emission inventories. This concerns not only primary PM emissions but also PM precursors. Special attention should be given to those source sectors and activities where there is a paucity of specific emission factors, such as residential heating, wood combustion and wind-blown dust.

85. PM models, like all other chemistry-transport models, require accurate meteorological input data to drive them. Further improvements are to be expected in the accuracy, temporal and spatial resolution of meteorological datasets, especially for clouds and precipitation. With the increased availability of global meteorological datasets and global chemistry-transport models, we can anticipate improved representation of atmospheric boundary conditions and of intercontinental transport in regional PM models.

86. The measurement of the vertical profiles of meteorological parameters and atmospheric composition should be promoted. This would help to improve the global performance of models by ensuring a more realistic vertical distribution of PM mass and composition. It would also allow a better quantification of vertical dispersion, a key parameter during PM pollution episodes.

87. Data assimilation already plays an important role in numerical weather prediction and has substantially increased the quality of meteorological predictions. Data assimilation will increasingly be applied in PM models using satellite observations of aerosol optical depth, for example.

88. Improvements are urgently required in the modelling of PM components at the urban scale. Currently integrated assessment models use urban PM increments to describe the relationship between $PM_{2.5}$ concentrations on the urban and regional scales. It is important to review and assess the model approaches for the quantification of urban increments and hence of urban health effects and to check whether they are fit-for-purpose in the policy context. Further work is required to provide measurement data from which urban increments can be more reliably inferred.

89. The measurement of particle size distributions should be encouraged at more monitoring sites across Europe. This would be useful for model evaluation and for the better quantification of PM health impacts. Continuous measurements of PM components would also allow for better model evaluation.

3 Summary and conclusions

90. This EMEP PM Assessment Report addresses the adequacy and completeness of the underpinning science upon which models currently used for policy development have been built. An important issue has been to strike a balance between the need to resolve a number of key scientific uncertainties and the desire to make progress with the integrated assessment modelling. It has been recognised that striking this balance is important for policy-making within the Working Group on Strategies and Review. The purpose of the report is to inform the policy process about the state of current understanding on PM issues and the level of confidence in PM models.

91. Annual mean PM concentrations show large differences across Europe when stratified according to site types such as rural background, suburban, urban background, industrial- and traffic-influenced. At remote, rural (EMEP) monitoring sites during 2004, annual mean $PM_{2.5}$ concentrations ranged from just above 3 µg m^{-3} in Norway to 28 µg m^{-3} in Italy, whereas for PM_{10} the concentrations ranged from 5 to close to 35 µg m^{-3}. At traffic-influenced locations, annual mean $PM_{2.5}$ concentrations ranged from 8 µg m^{-3} for the average of three sites in Finland to above 55 µg m^{-3} for two sites in Bulgaria.

92. There is a general tendency for annual mean $PM_{2.5}$ concentrations to increase from west to east across Europe, reflecting the progressive addition of man-made PM to Atlantic air masses and the different dispersion conditions between the oceanic and continental regions. Dry, arid conditions during summertime lead to elevated rural levels in southern and central Europe due to wind-blown and resuspended dust. These arid conditions are especially important in the Western Mediterranean, where the lowest precipitation rates in Europe are registered. Wintertime wood burning and road-wear due to studded vehicle tyres lead to elevated urban and traffic-influenced levels in Scandinavia.

93. The long-range transport of PM is a transboundary problem that can have significant impacts on PM_{10} and $PM_{2.5}$ levels in remote, rural and urban areas. National contributions in Part B of this report clearly identify a regional-scale background contribution to urban PM levels and a further traffic contribution on top of urban background levels at traffic-influenced sites. This regional background typically contributes between 60 – 90% of urban background PM_{10} and $PM_{2.5}$ levels on an annual basis. It may be lower, 35-50%, in southern Europe where most man-made PM pollution is generally caused by concentrated large agglomerations.

94. Long-range transboundary transport can be best characterised at rural and EMEP sites where the influence of local PM sources in minimal. However, the contribution of transboundary transport to PM levels at suburban and urban background sites is more relevant to policy and human health effects. Transboundary transport can be best characterised for $PM_{2.5}$ but care must be taken to minimise the influence of episodes with large local contributions to $PM_{2.5}$ levels when quantifying the transboundary and long-range transport contributions to PM levels.

95. There is still a great lack of understanding of some of the major PM components. There seems to be an apparent discrepancy between decreasing PM

emissions during the 2000s and observed $PM_{2.5}$ and PM_{10} levels that have remained more or less unchanged over the same period in many parts of Europe. An example of this behaviour is illustrated in the contribution from Germany to Part B of this report. This discrepancy may reflect deficiencies in our understanding of PM emissions and atmospheric chemistry. Meteorological variability may explain the increase in PM levels between 1999 and 2003 but PM levels have remained largely unchanged beyond these years.

96. Current knowledge on PM levels and speciation are hampered by shortcomings in monitoring and modelling. Measurements of PM mass concentrations are not directly comparable across Europe because of the comparability of the different methods, because of differences in the correction factors applied to the measurements to make them comparable with reference methods and because of a number of specific analytical issues that may hamper the comparison of PM composition measurements. Furthermore, there are difficulties associated with the harmonisation of siting criteria for urban monitoring sites across Europe.

97. The PM models currently used in policy development underestimate total PM_{10} and $PM_{2.5}$ and none currently achieve mass closure. The main reason for this is that some PM components are not included at all in models and some others are treated in a simplified ways. There are large uncertainties in the emissions inventories of the primary PM components especially with respect to the coarse PM fraction and of some PM precursors. Confidence in the PM models ultimately rests on the comparison of model predictions with observations. Currently there are too few observations for satisfactory model verification. Model intercomparison activities such as EURODELTA have contributed much towards improving confidence in PM model predictions.

98. There is a high degree of confidence that SO_2 sources can be linked to the observed levels of particulate sulphate. Over the years, most of the important uncertainties in SO_2 emission inventories have been tackled and a few outstanding problems remain, such as domestic coal burning and ship emissions. Observations of particulate sulphate have the necessary reliability and spatial coverage for model verification purposes. Long-running time series are available to check model calculated trends with observed trends over the last two decades.

99. There is a reasonable level of confidence that NO_x sources can be linked to the observed levels of particulate nitrate. Too few measurements for particulate nitrate have been made using techniques that are artefact-free and some of the outstanding problems with evaporation of the ammonium nitrate still have not been solved. Intensive field campaigns have been organised using continuous instruments to overcome these shortcomings. There are uncertainties associated with ammonia emissions that when taken together with the non-linearities in the formation of ammonium nitrate limit our confidence in particulate nitrate modelling and its response to ammonia and NO_x emission reductions.

100. Uncertainties in European models for particulate sulphate are currently judged to be of the order of ± 15 – 20%, on an annual average basis. The corresponding uncertainties in model particulate nitrate are somewhat larger at about ± 40%. Measurement uncertainties in particulate sulphate and nitrate are comparable to those in models. This situation is considered acceptable for the

policy purpose of assessing the outcome of different control measures for SO_2 and NO_x on the regional component of particulate sulphate and nitrate.

101. Uncertainties in model results for elemental carbon and organic matter PM are large. Many of our current difficulties with elemental carbon and organic carbon particulates stem from difficulties with their measurement methods, the lack of a reference method and the lack of consistency between the existing European measurements. The split between elemental and organic carbon depends on the method and is influenced by charring, leading to elemental carbon measurements that may differ by up to a factor of two when comparing the two most commonly used protocols. Measurements are therefore considered to have limited reliability.

102. Many of the remaining difficulties with elemental carbon and organic PM stem from problems with emission inventories. Emission inventories for primary PM components are of relatively recent development. Reliability, size and spatial resolution, coverage of the different source categories and PM species coverage still remain crucial issues for PM emission inventories. Emission inventories for elemental carbon need substantial improvement in terms of accuracy and coverage of source categories particularly those of road traffic, wood combustion and residential heating. Improvements are required in spatial resolution at the European scale and in the representation of diurnal, weekly and seasonal emission profiles.

103. Without these improvements in the emission inventories for primary carbonaceous PM, confidence is limited in the regional scale distributions of primary carbonaceous PM calculated with the current PM models used in policy development.

104. The review of the Unified EMEP model noted that confidence in the understanding of the mechanism of the formation of secondary organic aerosol was so low that it had not been included in the EMEP model, leading to underestimates for PM_{10} and $PM_{2.5}$. There are major problems with emission inventories and with the representation of the main atmospheric processes that control the distribution of particulate organic matter across Europe. Uncertainties in measurement data and their general paucity, preclude any quantification of model uncertainty for these PM components. As a consequence, it is not possible to link VOC emissions and their control to secondary organic PM in the PM models currently used for policy development.

105. There are major difficulties in the representation of mineral dust in PM models which stem from a range of causes mainly due to the lack of knowledge on their emissions and of the soil databases with which to characterise them.

106. Uncertainties in current model predictions for natural PM components such as mineral dust, sea salt and biogenic primary organic matter are large and difficult to assess.

107. On this basis, we have a high level of confidence that the PM models currently used for policy development can address the regional scale impacts of SO_2 emission reductions on PM mass concentrations, for the purposes of integrated assessment modelling. There are uncertainties with ammonia emissions

that when taken together with the non-linear chemical production pathways to form ammonium nitrate, limit our confidence in the representation of ammonia and NO_x emission reductions on PM mass. Because of outstanding problems with the emission inventories for elemental and organic PM carbon, there is little confidence that the PM models currently used for policy development are ready to describe accurately the urban and traffic increments in $PM_{2.5}$ that are required for integrated assessment modelling and for policy assessments of urban health effects. Current PM models used in policy development may thus be adequate for the assessment of the relative magnitudes of emission reductions of some PM components and their precursors on PM mass concentrations but not necessarily for their quantitative assessment against target and limit values for PM.

108. There is currently a significant level of effort being undertaken by the Parties to the Convention and by the EMEP Centres that is focussed on improving PM emission inventories, improving PM observations, carrying out targeted field campaigns and enhancing PM models. These activities should be encouraged within the EMEP framework and will over time bring increased confidence in our understanding of PM and its representation in PM models.

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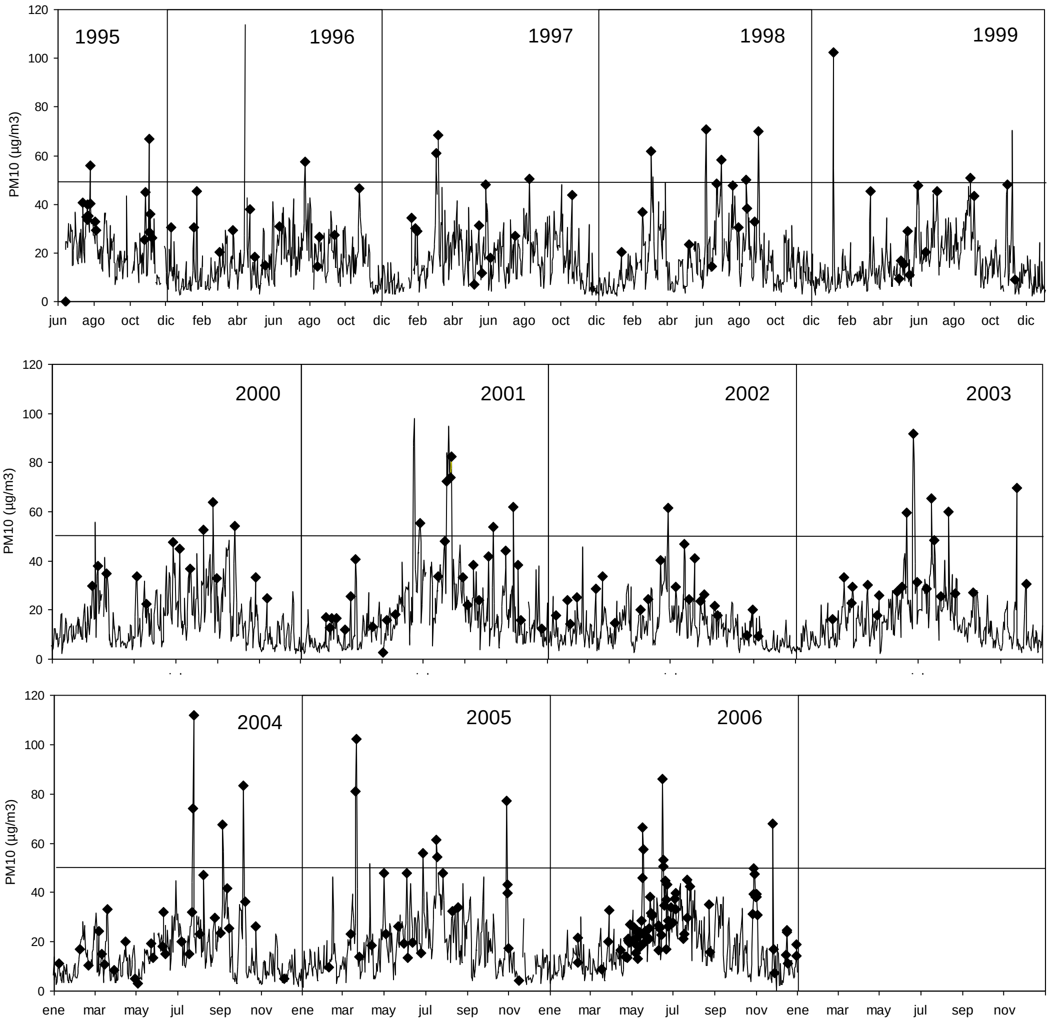

Figure 1: Levels of PM$_{10}$ measured (June 1995 to December 2006) at a rural site of NE Spain (Monagrega). Notice that African dust outbreaks (black rhombus) cause >90 % of the exceedances of the EU PM$_{10}$ daily limit value at this rural site (modified from Querol et al., 2007).

Part B

National contributions

1 PM_{10} and $PM_{2.5}$ concentrations in Europe as assessed from monitoring data reported to AirBase. ETC/ACC contribution to the EMEP PM assessment report

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1.1 Summary

This contribution gives an assessment of PM concentrations in Europe, present (2005) and during the previous 9 years, based upon the data reported to the European Commission and AirBase by Member Countries of the European Environment Agency (EEA). It also draws information from other projects carried out by the EEA, European Topic Centre on Air and Climate Change (EEA-ETC/ACC).

PM_{10} concentrations were reported from more than 2200 monitoring stations in 32 countries in Europe for 2005. The number of stations reporting data to AirBase has increased steadily from only a few hundred stations in 1997. For 2005 $PM_{2.5}$ concentration data was reported from 268 stations in 18 countries, and very few stations have $PM_{2.5}$ time series for more than a few years.

Annual average PM_{10} concentrations in 2005 averaged to be 20.2 $\mu g/m^3$ at 180 rural stations, 26.0 $\mu g/m^3$ at 742 urban background stations, and 31.2 $\mu g/m^3$ at 477 street stations. Thus the rural background contribution to urban background PM_{10} levels is on the average approximately 78%, and approximately 65% on the average for street stations. From analysis using station pairs, the average urban increment was 5.6 $\mu g/m^3$ (based upon 101 rural-urban station pairs in the data set for 2002) and the average street increment over urban background was also 5.6 $\mu g/m^3$ (based upon 49 station pairs within a 20 km distance from each other within the same city, in the 2002 data set).

The EU PM_{10} limit value for annual average was exceeded in 2005 at 5, 89 and 107 rural, urban and street stations respectively. The short-term (24-hour) limit value was exceeded much more extensively, for instance at approximately 30% and 55% of the urban and street stations, respectively. The most pronounced exceedances were observed in Silesia and Northern Bohemia, in the Milan/Po valley area and in the Southern part of Spain. BeNeLux and Eastern Europe areas were also affected.

The spatial coverage of $PM_{2.5}$ monitoring data is still sparse in Europe. Annual average $PM_{2.5}$ concentrations in 2005 averaged to be 12.9 $\mu g/m^3$ at 33 rural stations, 16.9 $\mu g/m^3$ at 72 urban background stations and 19.7 $\mu g/m^3$ at 55 street stations. Thus the contribution of rural $PM_{2.5}$ to the urban background and traffic levels is similar as in the case of PM_{10}: 76% and 65%, respectively. The correlation between co-located $PM_{2.5}$ and PM_{10} measurements is high and is, like the $PM_{2.5}/PM_{10}$ concentration ratio, similar for 2004 and 2005. The $PM_{2.5}/PM_{10}$ ratio (average per station) varies from 0.4 to 0.8 and shows a dependency on station type and region. The ratio is lower at sites where sources of coarse

particles (PM_{10} minus $PM_{2.5}$) are important. Stations with an annual average above the proposed cap value (25 µg/m^3) can be found in many European regions, many of them in the Czech Republic and Silesia.

The PM_{10} time series from 1997 to 2005, which is based upon a rather limited data set, does not show an overall tendency upwards or downwards since 1997 (Figure 1.9). In this period the reported primary PM_{10} emissions decreased by 7% while the emissions of the precursors SO_2 and NO_X decreased by 65% and 20% respectively. The reported ammonia emissions were reduced by less than 5%. It has been shown that the development during the period 1997-2004 can to a large extent be explained by inter-annual meteorological variability (see section 1.2.5). The shorter time series (2001-2005) based upon a much larger data set show similar variability as the longer series, although less pronounced. Urban and rural background concentrations trends follow each other closely, the rural background concentration providing the dominating contribution to total urban background PM_{10}, and about 2/3 of the PM_{10} measured at street stations.

The development as well as the dominance of the rural contribution varies considerable between countries, see examples from the Netherlands, UK and the Czech Republic in Figure 1.10).

The ensemble of PM_{10} data in AirBase indicate two separate tendencies since 1999-2000:

- Increasing rural concentrations in central-eastern European areas (extending to Sweden, with an indication of additional increases in urban contributions).
- Decreasing or unchanging rural concentrations in the west to north-west (France, Belgium, Netherlands, UK); except an increase in all areas from 2002 to 2003.
- The tendencies in most of the cities with long time series data do not deviate from the overall European picture: decreasing concentrations towards 2000 and increasing thereafter with a drop in 2004.

The contribution to PM concentrations near streets from suspension of road dust has been investigated in the EEA-ETC/ACC ‘Street Emission Ceilings’ (SEC) project. Based upon the analyses carried out at 9 station pairs, the conclusion is that for streets where no studded tyres are used, the coarse fraction emission factor, which is dominated by road dust suspension, varies for the locations included in the analysis, between 1 and 4 times the emission factor for fine particles (which is dominated by exhaust particle emissions), as an average for a winter or summer season. In Scandinavian streets where studded tyres are used in the winter, the coarse fraction emission factor is 3-10 times the fine fraction emission factor, as winter average. The contribution from road dust suspension to the fine fraction is also significant, while still not well quantified. In Hornsgatan in Stockholm, this contribution is about 1/3 of the exhaust particle contribution.

Methodological factors of PM sampling and monitoring are important, and need to be taken into account when assessing concentrations across Europe. Correction factors (CF) for PM_{10} concentrations, when measured with automatic monitors and used by countries to correct their data, have been reported to AirBase to some extent. The reported CFs are typically within 1.0-1.3, although some countries have established even higher CFs.

1.2 PM_{10} concentrations in Europe, 1997-2005

The number of stations reporting PM_{10} data to AirBase has increased steadily for many years. 1997 was the first year with a fairly substantial number of stations reporting PM_{10} concentrations to AirBase (about 200 stations). In 2005, PM_{10} was reported for more than 2200 stations in 32 countries (Table 1.2). 1880 of these stations had annual data coverage higher than 70%. There were 235 stations in rural areas and 969 urban/suburban background stations. Of all hot spot stations, 673 were traffic stations (16 in rural areas) and 353 industrial stations (93 in rural areas). The rest of the stations were not properly classified.

In the following, summaries and overviews of the PM_{10} data in AirBase are presented. These overviews focus on 2003, 2004 or 2005, as well as developments in PM concentrations since 1997. 2003 and 2004 overviews are taken from the 'Air Pollution in Europe 1997-2004' report (Larssen et al., 2007) and the 2005 data summary report of AirBase (Mol et al., 2007), while some 2005 overviews have been compiled for this contribution.

PM measured by automatic methods typically have to be corrected in order to correspond with measurement results obtained by applying the respective reference method. This is done by using correction factors, which have to be determined based on comparison studies in each country. Chapter 1.6 gives an overview of the monitoring methods used in the various European countries, and a summary of CFs used the those countries. Many countries have station-specific CFs, and for a few stations even season-specific CFs are used. It is not completely clarified yet, however, how the CFs are implemented in the data that are contained in AirBase.

1.2.1 Overview of PM_{10} concentrations

Country-wise annual average PM_{10} concentrations measured at stations in 2004, reported to AirBase, are shown in Figure 1.1. There are separate bars for three types of stations: rural background, urban/suburban background, and street stations. The countries are placed in a sequence from north-western Europe (Iceland, Norway, etc.), sweeping through the central and towards the south-eastern parts of Europe, and then towards the south-west (Spain and Portugal). The Figure shows elevated/high rural/urban levels in BeNeLux and eastern/south-eastern areas (from Poland and Czech Republic, towards FYROM, Greece and Cyprus, and to a lesser extent in the Mediterranean countries). Concentrations at street stations can be high in all countries.

The PM_{10} concentrations in Europe in 2004, averaged over all stations of a certain category, were (number of stations with data in brackets)[1]:

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[1] The EU has set an annual limit value for PM_{10} of 40 µg/m$^{3.}$. The limit value for daily mean concentarins is set at 50 µg/m^{3,} this level may be exceeded on 35 days per year. Thus, if the 36th highest daily mean is above 50 µg/m^3 the limit value is exceeded.

- annual average:	at rural stations:	20.2 $\mu g/m^3$	(180)
	at urban background:	26.0 $\mu g/m^3$	(742)
	at street stations:	31.2 $\mu g/m^3$	(477)
- 36th highest day:	at rural stations:	34.4 $\mu g/m^3$	(176)
	at urban background:	43.3 $\mu g/m^3$	(717)
	at street stations:	51.4 $\mu g/m^3$	(459)

These numbers, as well as the Figure 1.1 and Figure 1.2, show clearly that the rural concentration level contributes considerably to the concentration levels at urban locations, and even to the concentrations at street level stations. Concentrations at the industrial stations did not deviate much from the typical urban/traffic hot spot concentrations: they averaged 46.6 $\mu g/m^3$ (36th highest day), with a maximum value of 129 $\mu g/m^3$ at one station.

The annual average concentration at the 180 rural stations was about 78% of the average concentration at the 742 urban background stations, and about 65% of the concentration at the 477 street stations. The urban increment calculated using this data set was 5.8 $\mu g/m^3$ and the average street increment above the urban background was 5.2 $\mu g/m^3$.

Urban and street increments are better assessed when looking at stations pairs, located in such a way that the larger scale representative station of a pair (the rural or urban station) is fairly close to and represents the background concentration at the smaller scale representative station of the pair (the urban or street station). Station pair data has been extracted from AirBase: Rural-urban station pairs have been chosen if they are closer than 20 km from each other, while street-urban station pairs have been identified for two cases: Stations that are closer than 10 km from each other, or 20 km from each other (within the same city).

101 such rural-urban station pair combinations were found. The average urban increment for those station pairs was 5.6 $\mu g/m^3$. For 16 street-urban pairs within 10 km distance from each other, the street increment was 6.9 $\mu g/m^3$, while for 49 street-urban pairs within 20 km distance, the street increment was 5.6 $\mu g/m^3$ (Larssen, 2007). These increments are a bit higher than those calculated using the full data set without applying any criteria for station locations relative to each others. This assessment includes a variety of European urban and street traffic situations, and is an estimate of the average urban and street increments in Europe.

Figure 1.2, representing 2005 data, presents the Airbase data in a different way, showing the total extent of exceedances of limit values. It shows the number of stations and average PM_{10} concentrations for three station categories (rural background, urban/suburban background and urban/suburban traffic/street). Displayed are the annual average concentrations and the 36th highest day values, according to three criteria: all stations, the stations which are above the limit value, and the station with the highest concentration.

The limit value for annual average was exceeded at 5, 89 and 107 rural, urban and street stations respectively. The short term limit value (represented by the 35th highest daily value) was exceeded at urban stations (256 stations, more than 30% of the stations) and at traffic stations (302 stations, more than 55% of the stations).

At rural stations exceedances are observed at 17% of the stations. The highest measured concentrations were 3-4 times the limit values.

The concentrations in 2005 were slightly higher than in 2004 but not as high as in 2003.

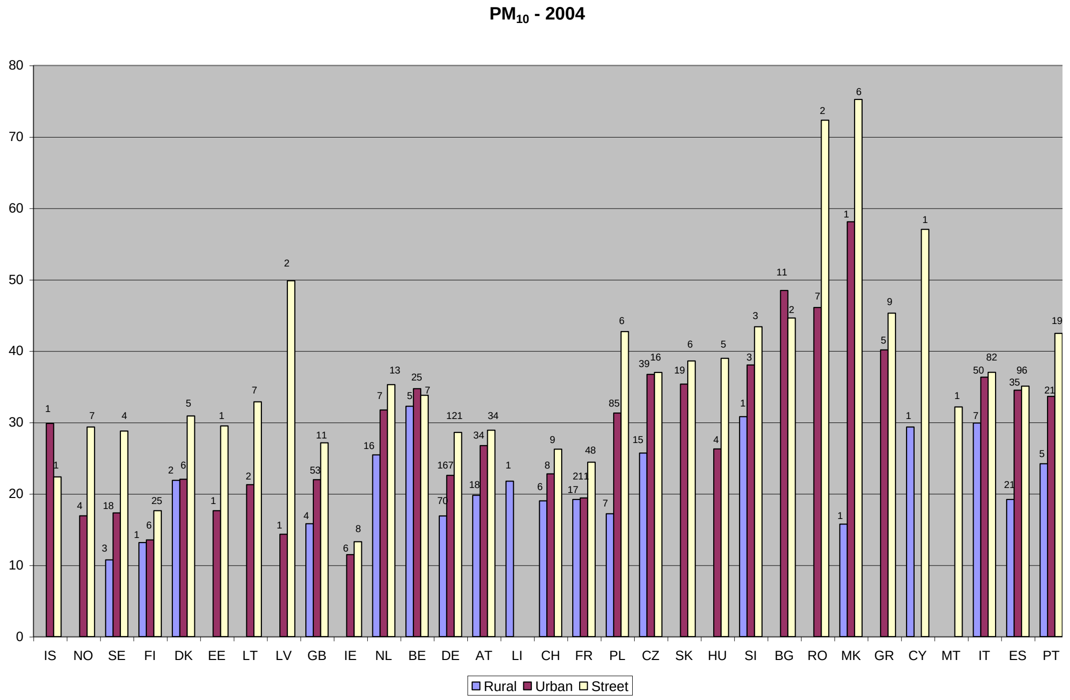

Figure 1.1: Overview of PM_{10} data in AirBase, 2004: country-wise annual averages per station type. Number of stations on top of bars.

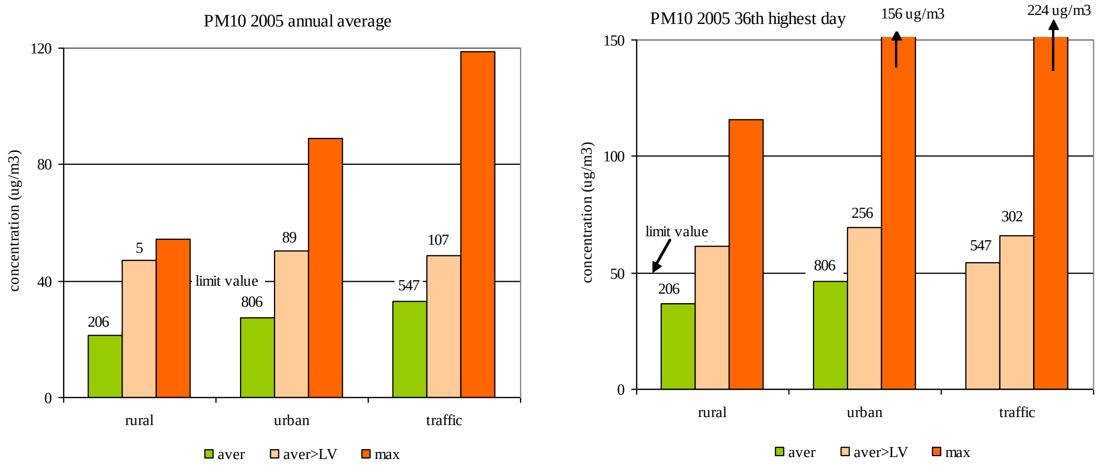

Figure 1.2: Overview of PM_{10} data in AirBase, 2005: average concentrations, average at stations exceeding Limit Values and number of stations, in each category; maximum concentrations (one station).

1.2.2 Mapping of PM$_{10}$ across Europe, 2003 and 2004

Figure 1.3 and Figure 1.4 show assimilated maps of PM$_{10}$ concentrations across Europe, where EMEP model results have been combined with data from the monitoring stations in rural and urban background areas, as well as with other parameters (EEA-ETC/ACC, 2005). Results are shown both for 2003 and 2004, indicating the situation in a year with high concentrations (2003) and in a more typical year (2004). Figure 1.3 shows annual average concentrations, and Figure 1.4 shows the 36th highest daily values.

Rural areas

Rural PM$_{10}$ concentrations are generally higher in some central, eastern and southern areas of Europe than in western parts of Europe (see also Figure 1.1). Spain and Portugal may experience elevated PM values due to dry conditions and the influence of Saharan dust, while BeNeLux and East England are possibly affected by air pollutant transport from central Europe in addition to emissions from local sources.

The PM$_{10}$ limit value for annual average, 40 $\mu g/m^3$, is exceeded in several larger and small areas across Europe (Figure 1.3). The highest exceedances can be found in Silesia, North Bohemia, the Milan-Po Valley area and the southern tip of Spain. For 2005, the measurement results indicate that 5 rural stations in the Czech Republic, Italy and Spain show annual average concentrations above the limit value (Figure 1.6). At 15 stations concentrations were higher than 35 $\mu g/m^3$.

The PM$_{10}$ short term limit value (max 35 days above 50 $\mu g/m^3$) was exceeded to a larger extent than the annual average limit value (Figure 1.3 and Figure 1.4). In 2003, the year with very high pollution levels, large areas in the Benelux countries, northern Italy, eastern Europe as well as in Portugal were above this limit value. The same areas showed also high levels in 2004. The southern tip of Spain had exceedances in 2004, presumably due to Saharan influence.

Urban background

Figure 1.3, Figure 1.4 and Figure 1.7 show that the PM$_{10}$ concentrations at urban background locations are high in many cities across Europe. The 2004 summary in Figure 1.1 and Figure 1.2 shows that exceedances of the annual average limit value were measured at 69 (in 2005: 89) urban stations, and at 191(in 2005: 256) urban stations for the short-term limit value.

The highest urban background concentrations were measured in cities in central, eastern and southern European countries (such as Bulgaria, Romania, Poland, Italy, Czech Republic, Slovakia; see Figure 1.7).

Traffic hot-spots

Figure 1.5 and Figure 1.8 show that concentrations at urban street stations are exceeding the PM$_{10}$ short term limit value extensively at many street sites in Europe. Figure 1.5 shows the situation in 2004 when the annual average limit value was exceeded at 81 street stations (in 2005: at 107 stations). In 2004 the short term limit value was exceeded at 224 street stations (in 2005: at 302 stations; see Figure 1.2). The highest concentrations measured in 2004 were typically about the double of the limit value (except for a station in Skopje which reported an annual average about 4 times the limit value). Concentrations were even higher in 2003 (as indicated in Figure 1.9).

Similar to urban concentrations, the highest traffic related concentrations were measured in cities in central, eastern and southern European countries (Macedonia, Poland, Italy, Spain, Romania, Czech Republic, Greece; see Figure 1.8). In some cases special conditions were responsible for exceedances, such as suspended dust in Spain and studded winter tyres in Nordic countries.

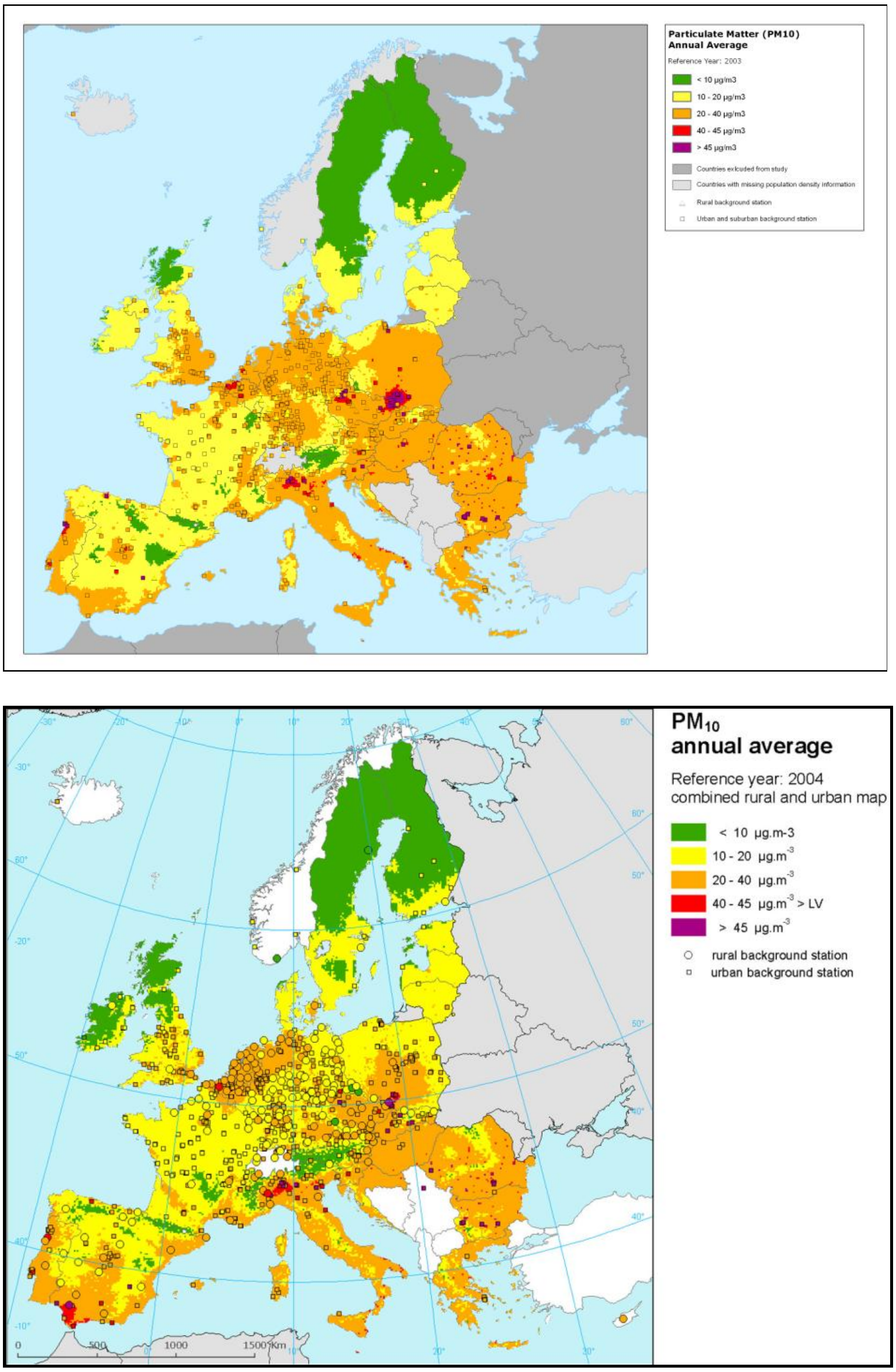

Figure 1.3: Annual average PM_{10} concentrations in Europe 2003 and 2004. Figures constructed from combining measurements and model calculations (ETC/ACC, 2005).

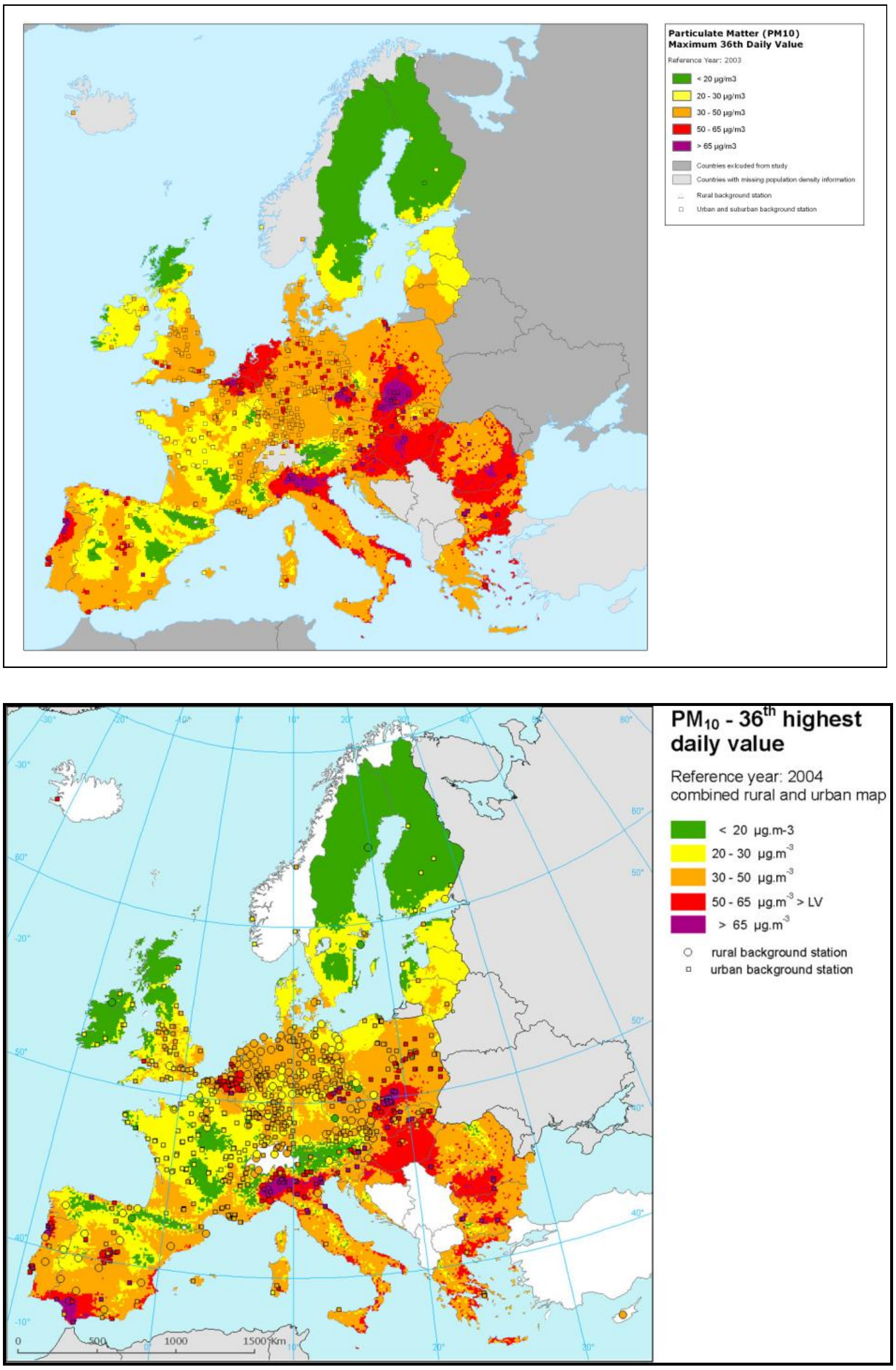

Figure 1.4: PM_{10} concentrations in Europe 2004 and 2003, showing the 36th highest daily value. Figures constructed from combining measurements and model calculations (ETC/ACC, 2005).

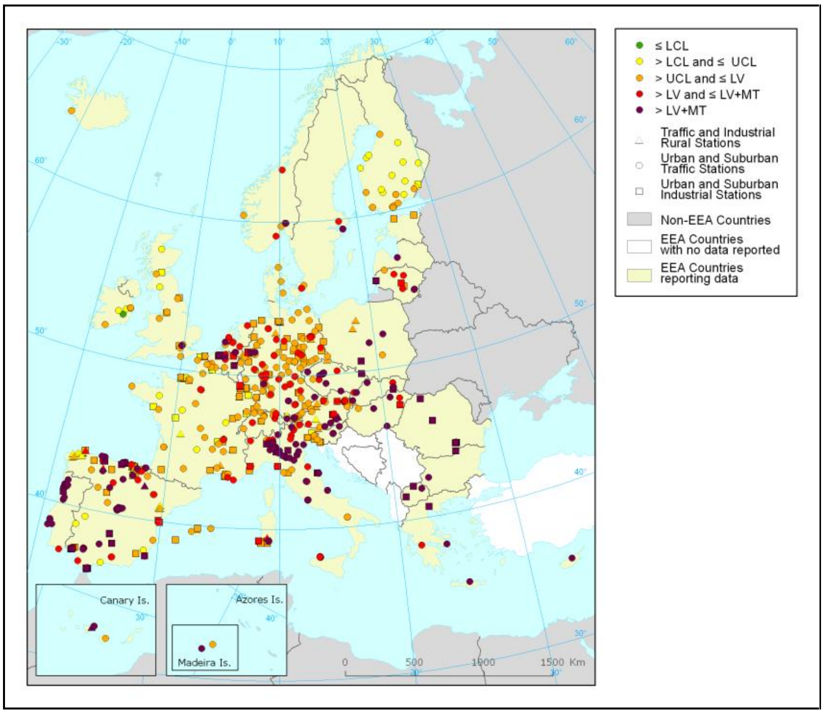

Figure 1.5: PM$_{10}$ concentrations at hot-spot stations, 2004.
36th highest daily value (EEA, 2007).
Limit value (LV): 50 μg/m^3.
Upper (UCL) / lower (LCL) classification levels: 30 / 20 μg/m^3.
Margin of Tolerance (MT), 2004: 5 μg/m^3.

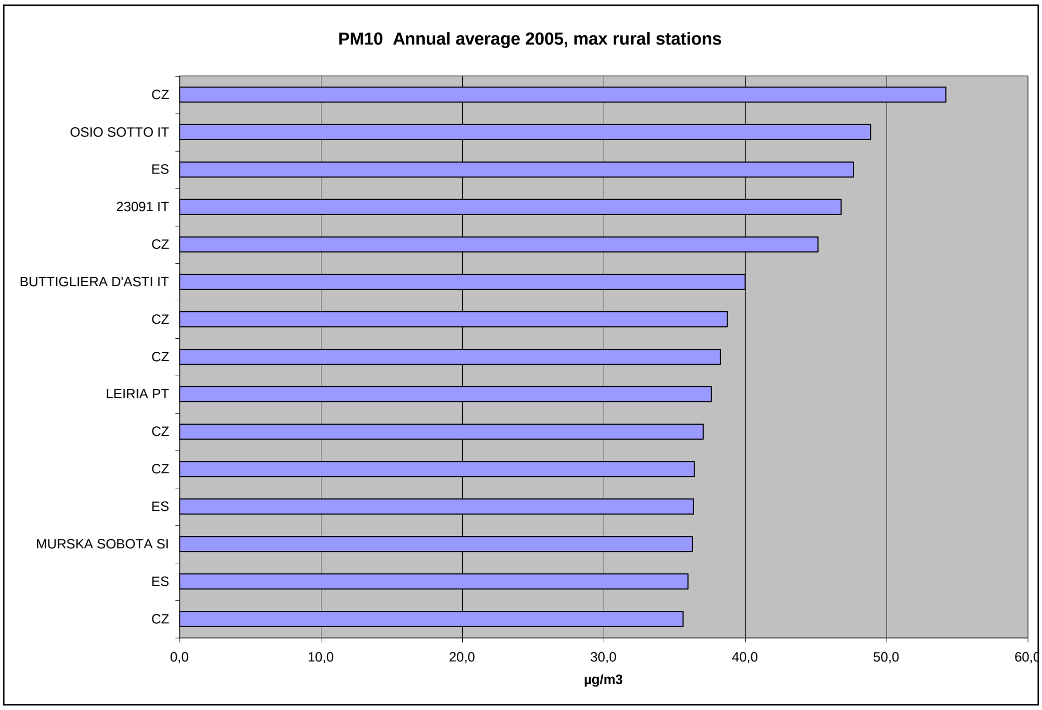

Figure 1.6: PM$_{10}$ annual average concentrations, 2005. Rural stations with the highest concentrations measured, reported to AirBase.

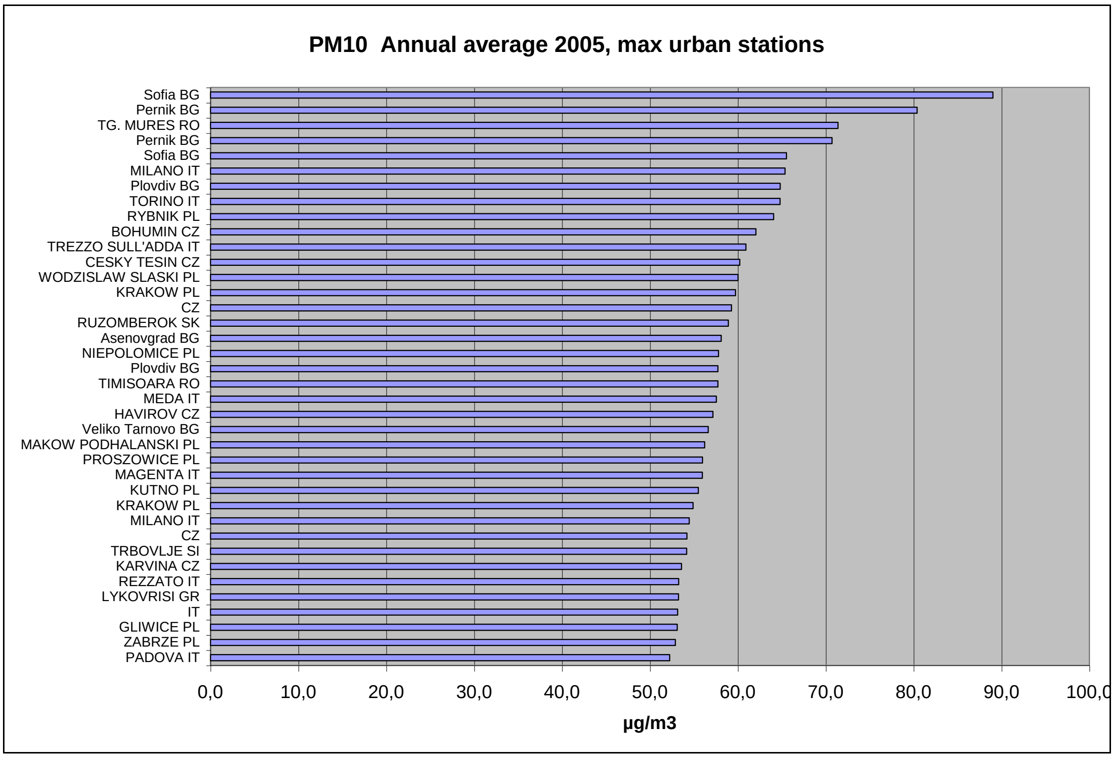

Figure 1.7: PM_{10} annual average concentrations, 2005. Urban/suburban background stations with the highest concentrations measured, reported to AirBase.

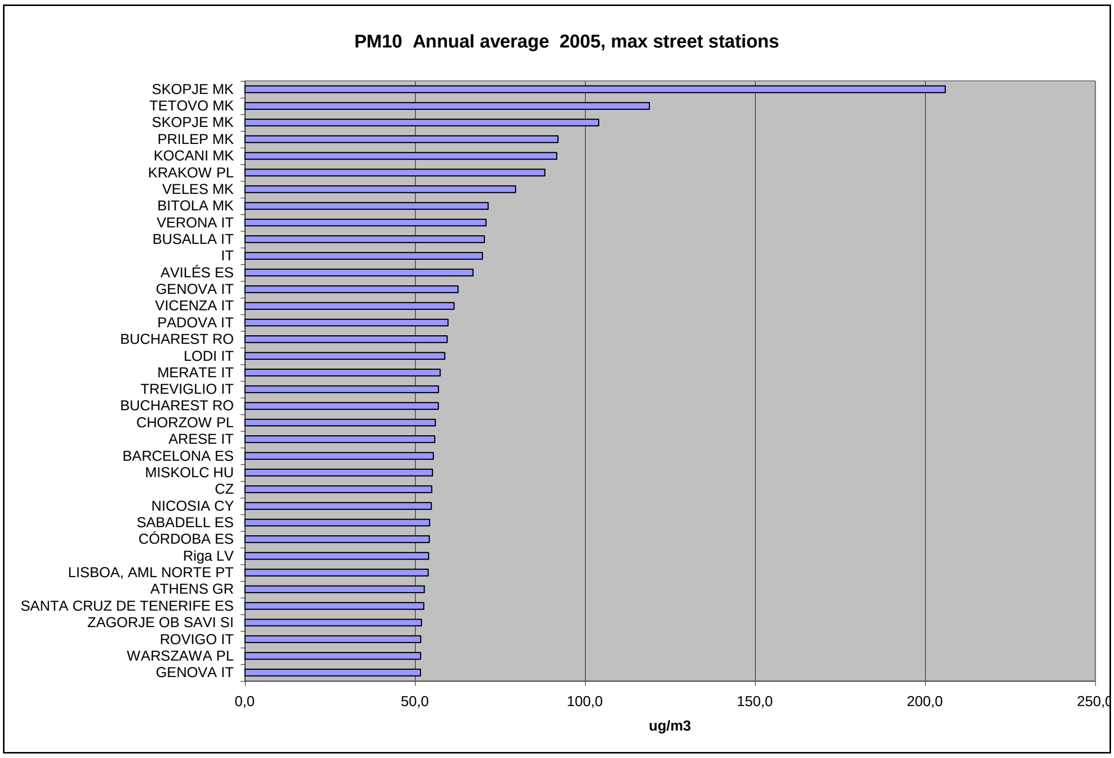

Figure 1.8: PM_{10} annual average concentrations, 2005. Street stations with the highest concentrations measured, reported to AirBase.

1.2.3 Changes 1997-2005

Europe-wide developments

Figure 1.9 shows the tendencies in annual average PM_{10} concentrations for 1997-2005, based upon 202 stations in 12 countries where data for at least seven years were available. The figure shows separate graphs for rural background (32 stations), urban/suburban background (90 stations) and traffic stations (57 stations); 23 others stations (industrial, not-defined) are not included. Figure 1.9 includes also the same information for the period 2001-2005 only, based upon a much larger data set (565 stations: 64 rural, 267 urban background, 166 traffic and 68 ‘other’ - in 21 countries).

It should be noted that the different station types do not necessarily represent the same areas (e.g. the rural stations are not necessarily in the same areas as the urban stations, and similar, the street stations are not necessarily in cities where urban background stations can also be found, although this is the case for many of the cities). Thus, the differences in concentrations in rural, urban and street locations shown in the figures do not fully represent the ‘real’ differences between such locations in Europe. This has already been discussed for the 2005 data set in section 1.3. Figure 1.9, which is based on data from all European regions, may thus mask the differences in concentration developments and urban/street increments in different countries.

The 1997-2005 series, which is based upon a rather limited data set, does not show an overall tendency upwards or downwards since 1997. Between 1997 and 2005 the reported primary PM_{10} emissions decreased by 7% while the emissions of the precursors SO_2 and NO_X decreased by 43% and 16% respectively. Ammonia emissions were reduced by less than 5%. The development during the period 1997-2004 can partly be explained by inter-annual meteorological variability (see section 1.2.5; Larssen et al., 2007). The shorter time series (2001-2005) based upon a much larger data set shows similar variability as the longer series, although less pronounced. Urban and rural background concentrations trends follow each other closely. The rural background concentration provides the main contribution to total urban background PM_{10}, and accounts for approximately 2/3 of the PM_{10} measured at street stations. The urban increment above the rural background, calculated by using the total 2001-2005 data set, is about 6 $\mu g/m^3$, and the street increment over the urban background is about 5 $\mu g/m^3$.

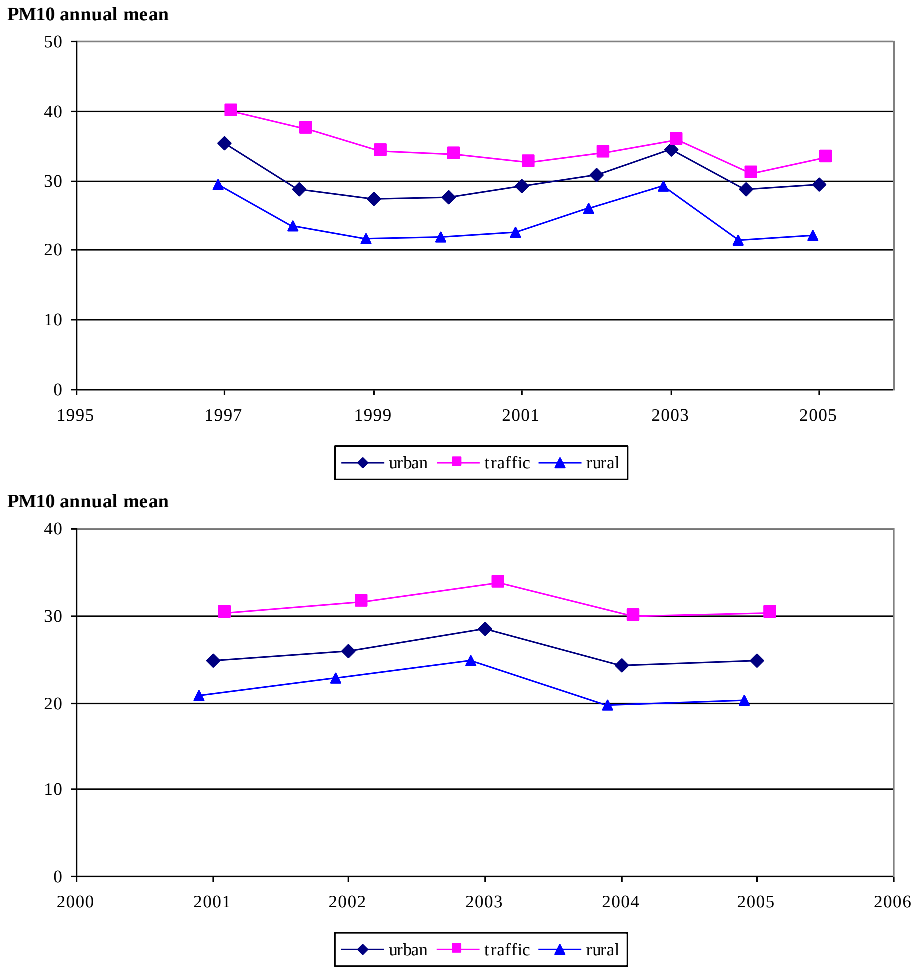

Figure 1.9: Changes in PM_{10} air quality (based on annual mean concentrations) over the period 1997-2005 (based on 202 stations in 8 countries) and over 2001-2005 (based on 565 stations in 19 countries).

1.2.4 Differences between countries, and tendencies in specific cities

Whilst the general background concentrations of PM as observed at rural background stations dominate developments, Figure 1.10 shows that its contribution does vary between countries, both in absolute and relative terms. Figure 1.10 shows the development of PM_{10} concentrations for selected cities with long monitoring series.

In some areas, e.g. the Netherlands (as seen already in Figure 1.3), the existing rural background is very high, and the urban areas increase the concentrations only very little; in the Czech Republic the lower rural background makes up about 75% of the urban concentration. The UK is here represented by only one rural station, thus a representative figure of the rural contribution cannot be given. Street level contributions to total PM_{10} are in general limited, however, in streets with high traffic intensity the contribution is more substantial. The street contribution to PM_{10} levels are due to both exhaust particles, abrasion particles from brake linings and tyres, as well as suspended street dust particles.

Factors behind the differences in rural background concentrations include the extent and scale of long-range atmospheric transport of PM_{10} to a country (dependent upon location and neighbour country emissions), importance of natural sources (e.g. sea salt, desert dust), size of cities/agglomerations, distance to neighbouring large cities as well as density of traffic in the area, main PM sources in the urban area in addition to road traffic (e.g. domestic heating), national PM control, and the extent of ‘secondary’ PM formed within a country by chemical reactions between emitted PM precursor gases.

The ensemble of PM_{10} data in AirBase indicate two separate tendencies since 1999-2000:

- Increasing rural concentrations in central-eastern areas (extending to Sweden, with an indication of additional increase in urban contributions). For instance, the Czech Republic has had a very substantial increase in background rural PM_{10} since 1999, a large urban contribution, and indications of an increase in this urban contribution. Upward tendencies are also seen in Germany, Switzerland, Poland, and Sweden.
- Decreasing or unchanging rural concentrations in the west to north-west (France, Belgium, Netherlands, UK); except an increase in all areas from 2002 to 2003. Urban contributions vary a lot between cities, but have also been rather constant.
- The tendencies in most of the cities with long measurement time series do not deviate from the overall European picture: decreasing concentrations towards 2000 and increasing thereafter with a drop in 2004 (Figure 1.10).

Station numbers elsewhere in Europe are too small, and time series too short for clear conclusions. Slight decreases in PM_{10} concentrations at Spanish and Slovakian stations can be observed, although limited data quantity makes it difficult to come to clear conclusions concerning the spatial representativeness of the available monitoring results.

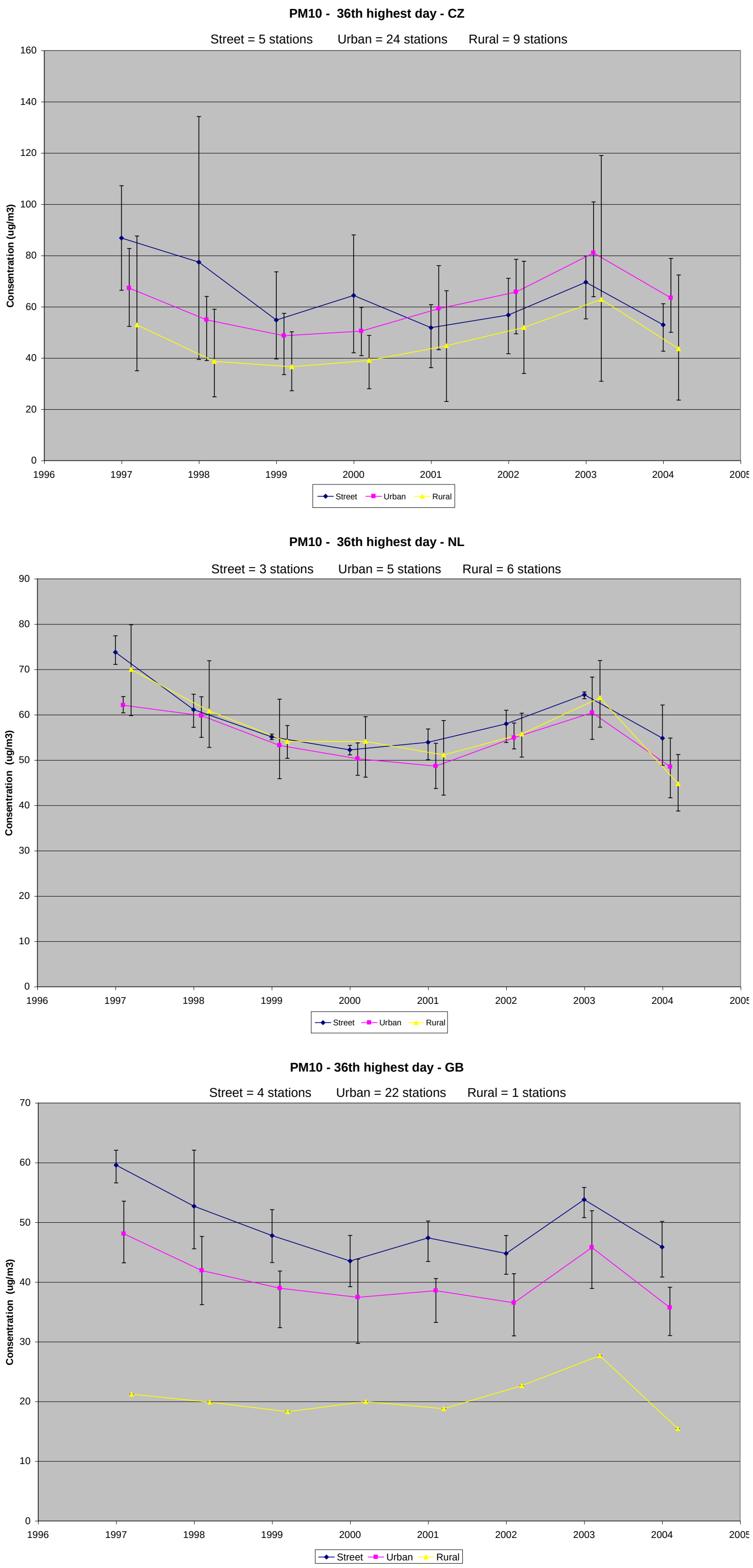

Figure 1.10: Interannual variations of mean daily PM_{10} concentrations, 1997–2004. Example countries: Czech Republic, Netherlands, UK. Vertical bars: 10th/90th percentiles.

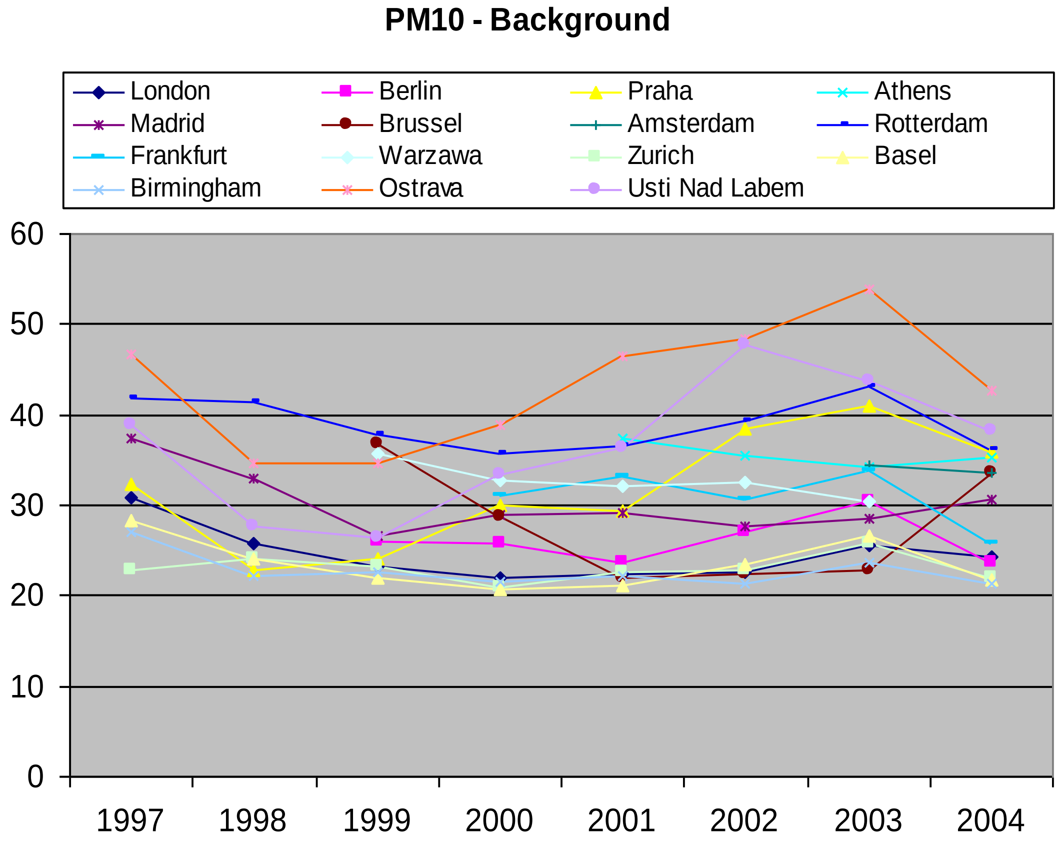

Figure 1.11: PM_{10} annual average interannual variations, 1997–2004, selected cities. Urban Background. Cities with minimum 2 stations all years.

1.2.5 Analysis of effect of meteorological variability on annual average PM_{10} concentrations

Observed PM_{10} levels during 1997-2004 show decreases from 1997 towards 1999, then an increasing tendency towards 2003 with very high concentrations in 2003, and then a decreasing tendency again in 2004 and 2005 (see section 1.2.3). Concentrations depend both on emissions and atmospheric factors, with inter-annual variations in meteorology affecting pollutant concentrations.

The effect of meteorological variability on PM concentrations can be estimated through computer modelling scenarios. In an exercise conducted for the ‘Air Pollution in Europe 1990-2004’ report the Unified EMEP model was used for such an analysis (Larssen et al., 2007). Emissions were held constant for the years 1997-2004, however, yearly changes in meteorological conditions included in the model were considered. While such a comparative exercise can circumvent the problems of underestimation absolute concentration levels, difficulties remain in representing urban/street concentrations below the 50 km spatial resolution of the EMEP model.

Together with observed PM_{10} air concentrations, model estimates using both actual reported emissions and a scenario of constant emissions throughout the period 1997-2004 are presented in Figure 1.12 for rural, urban background and street sites. The model reproduces the main signals in observations: a decrease towards 1999-2000, with a subsequent increase in 2002 and 2003 regardless of emission changes. A decline is once again resumed in 2004. This strong signal suggests that high observed concentrations in 2002 and 2003 may (partly) be explained by changes in meteorological conditions. Indeed, the fact that the modelled rise in concentrations, with emissions held constant, was greater than the increase observed by measurement results suggests that emissions have actually decreased in 2002-2003, in line with the emission estimates for this period. On the other hand, observed concentrations have increased steeper than the concentrations modelled by using reported yearly emissions. Possible meteorological explanations for the increased observed PM_{10} levels in 2002 and 2003 are reduced precipitation with reduced washout of particulate material (thus higher air concentrations), warmer early-year temperatures in parts of Europe encouraging greater formation of secondary particulates, and relatively stable atmospheric conditions leading to reduced deposition, thus higher PM concentrations in the air.

The ratio between the maximum modelled yearly average concentrations in the two periods 2002-2003 and 1997-2001 (assuming constant emissions) is also mapped in Figure 1.12. The Figure indicates that in large areas of western and south-western Europe the PM_{10} levels have actually been reduced. AirBase stations are often located in areas with rather high modelled PM_{10} concentrations for 2002-2003. This suggests that observations represent the areas which are particularly influenced by meteorological conditions.

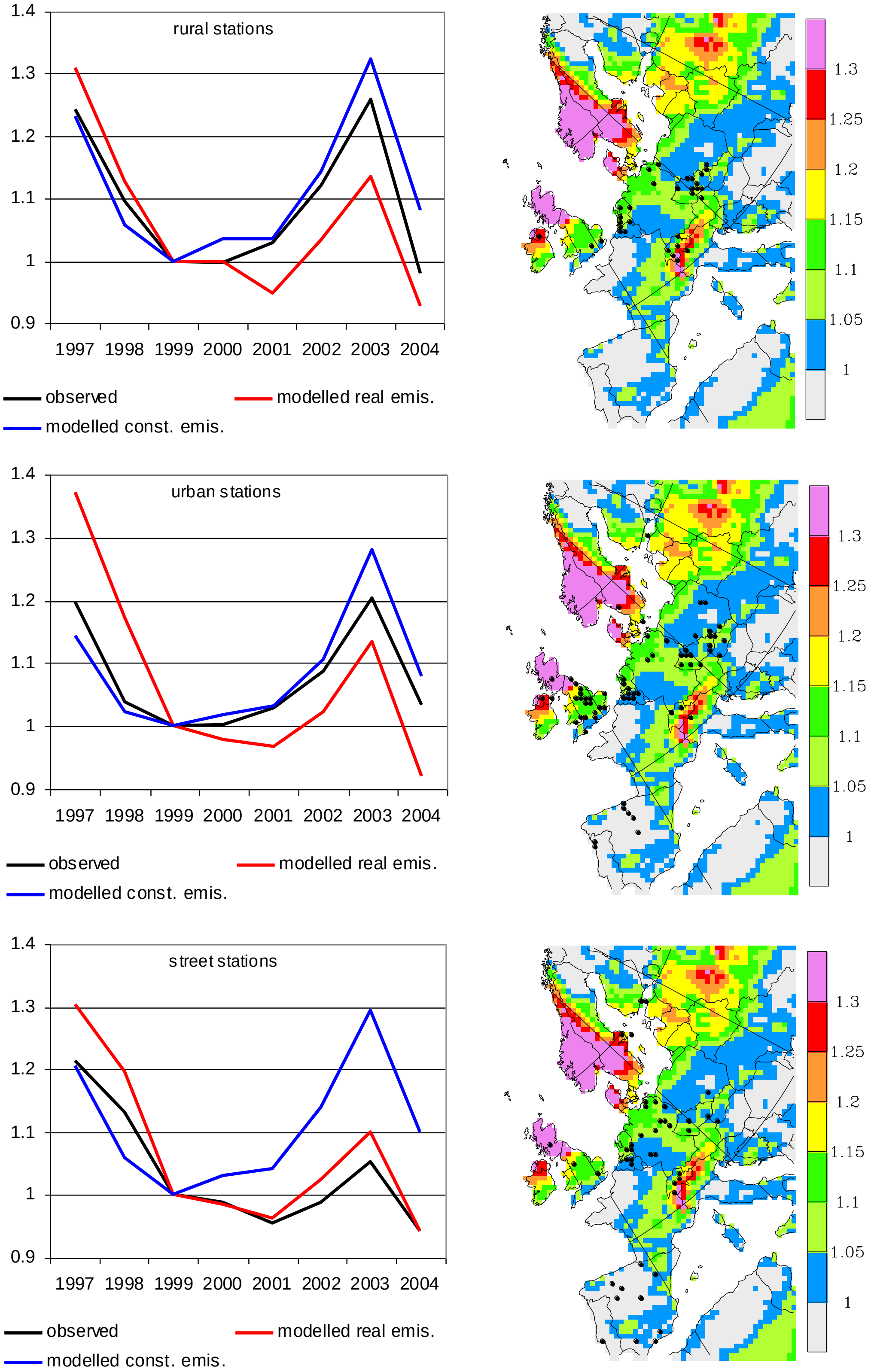

Figure 1.12: Left panels: observed and modelled PM_{10} concentrations relative to 1999.
Right panels: ratio of the max. modelled yearly concentrations for 2002-2003 to 1997-2001.
Dots indicate the measurement sites.

1.3 $PM_{2.5}$ concentrations in Europe

The routine monitoring of $PM_{2.5}$ is still in an initial phase in most European countries. Whereas in 2004 a total of 195 stations reported $PM_{2.5}$ concentration to AirBase, this number increased to 268 in 2005. However, the $PM_{2.5}$ equipment seems to be less reliable than PM_{10} instruments. The data coverage is much lower than for PM_{10}: in 2004 25% of the $PM_{2.5}$ stations failed having coverage of 75% or more; in 2005 this number was even 35%. For PM_{10} 19% of all stations had a data coverage of less than 75% in 2004 (in 2005: 18%).

In Figure 1.13 and Figure 1.14, $PM_{2.5}$ concentrations (annual average) are shown for all stations with >75% data coverage in 2005. Stations with annual average above the proposed cap value (25 $\mu g/m^3$) exist in many regions, many of them in the Czech Republic and Silesia. Annual mean $PM_{2.5}$ concentrations in 2005 averaged to be 12.9 $\mu g/m^3$ at 33 rural stations, 16.9 $\mu g/m^3$ at 72 urban background stations and 19.7 $\mu g/m^3$ at 55 street stations. The data suggest that the contribution of rural $PM_{2.5}$ to the urban background and traffic levels is similar as for PM_{10}: 76% and 65%, respectively.

There are still only very few stations with a time series covering a number of years. Figure 1.15 is based on nine stations for which data were reported for the whole 5-year period 2001-2005. These nine stations include one traffic station (London), five (sub)urban background stations (three stations in France, one in Finland and one in the UK) and three rural background stations (one in Austria and two in the UK). Obviously, it cannot be claimed that Figure 1.14 is representative for the $PM_{2.5}$ concentration development in Europe in general. However, the figure bears some resemblance to Figure 1.9, indicating similar results as for PM_{10}.

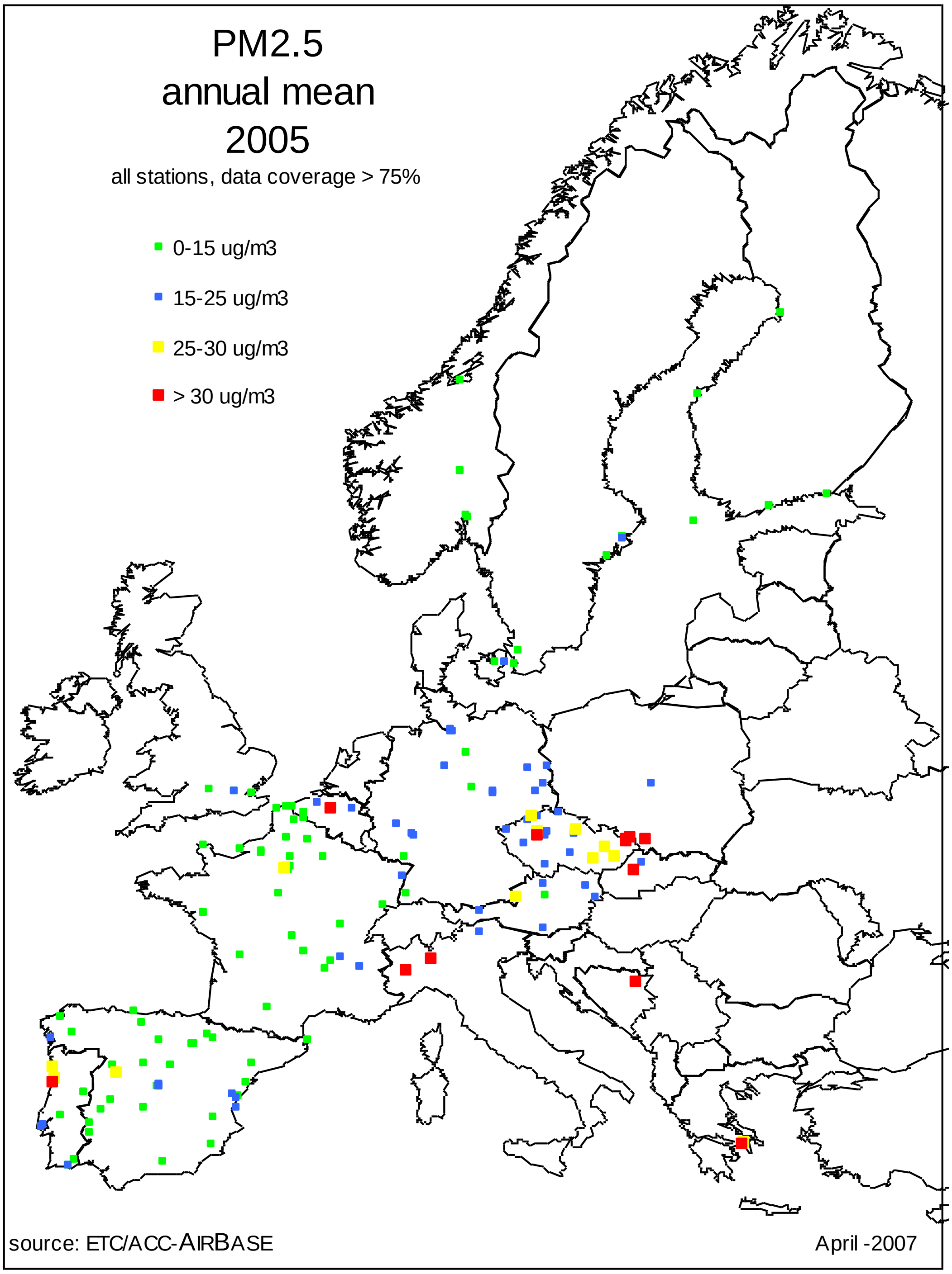

Figure 1.13: PM$_{2.5}$ concentrations (annual mean) all stations with a data coverage of more than 75% are included.

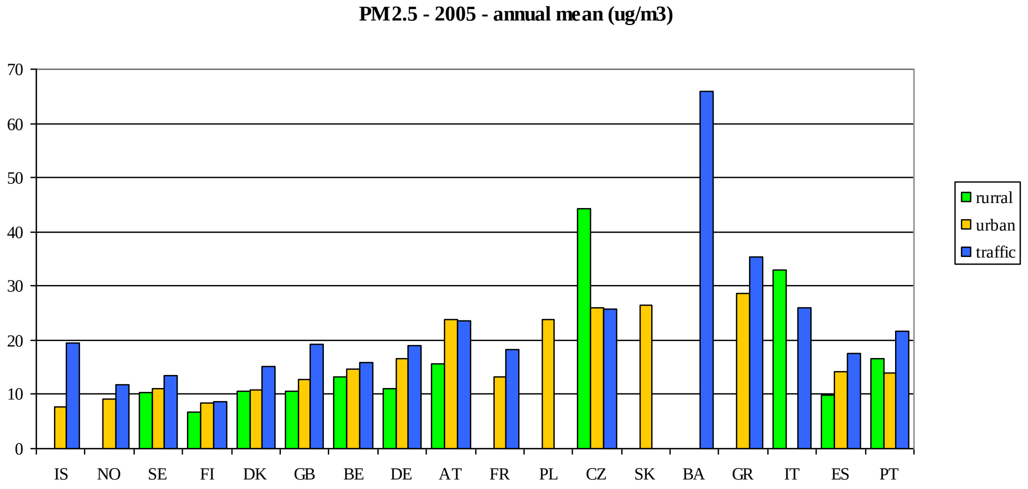

Figure 1.14: Measured $PM_{2.5}$ concentrations, 2005 ($\mu g/m^3$, annual average) for several countries. Each bar represents the average concentrations for each station type.

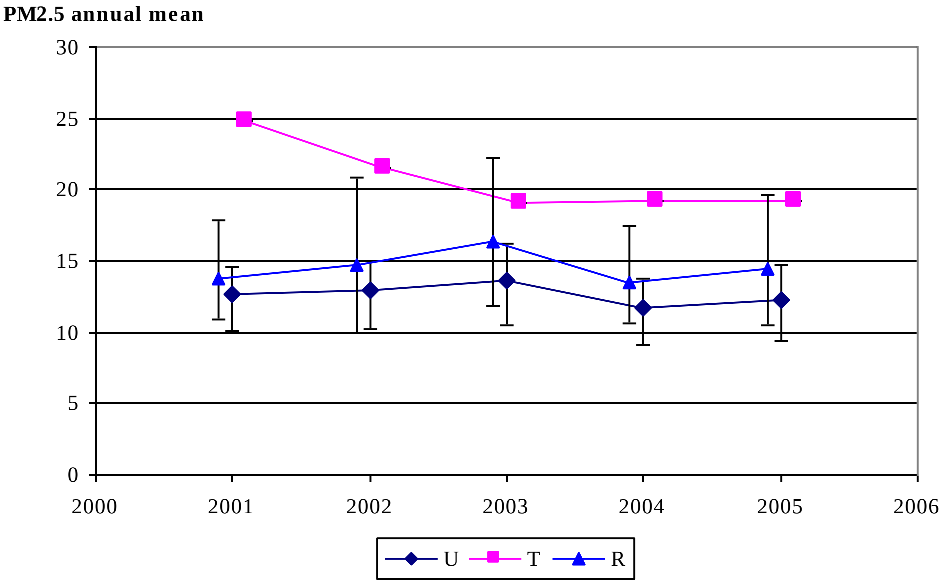

Figure 1.15: Annual variability of $PM_{2.5}$ annual mean concentrations. Number of stations represented by each line:

- Traffic (T) stations: 1

- Urban (U) stations: 5

- Rural (R) stations: 3.

1.4 $PM_{2.5}$ in relation to PM_{10}

In 2004 and 2005 co-located $PM_{2.5}$ and PM_{10} measurements were reported for 274 stations. However, data submission does not cover the full two-year period for all stations. The data available from AirBase were used as reported, i.e., it was assumed that PM values had been corrected if a non-reference measurement method had been applied. Information on PM_{10} measurement methods and correction factors is given in Chapter 1.6; information on the applied $PM_{2.5}$ correction factors is yet not available in Airbase. This lack of information hampers the comparison of results between countries. Any conclusion regarding $PM_{2.5}$ / PM_{10} relations should be handled witch caution against the background of this uncertainty. 2004 and 2005 data with minimum annual data coverage of 75% on a daily basis has been analysed.

The correlation between co-located $PM_{2.5}$ and PM_{10} measurements is generally high: R=0.86 (2004) and R=0.88 (2005), averaged over all stations. The inter-annual variations in correlations are small. There are striking differences between countries. The Nordic countries (Denmark, Finland, Iceland, Norway, and Sweden) show a correlation which is clearly lower than that in countries further south. The more frequent use of studded tyres and winter sanding in the Nordic countries leads to increases of the coarse PM fraction during parts of the year, affecting the correlation between $PM_{2.5}$ and PM_{10}. Although there are only two (2004) or three (2005) operational rural background stations in the Nordic region, these two stations show a better correlation than found at the five (2004) or six (2005) (sub)urban background stations and at the eleven traffic stations.

For all available stations, the correlation at (sub)urban background stations (R = 0.89) and rural background stations (R = 0.89) is similar and better than at traffic stations (R = 0.81).

In Figure 1.16 the annual mean concentrations of PM_{10} and $PM_{2.5}$ are given as function of the station classification. The figure indicates a wide spread in $PM_{2.5}$ / PM_{10} ratios; the ratio clearly depends on the type of station.

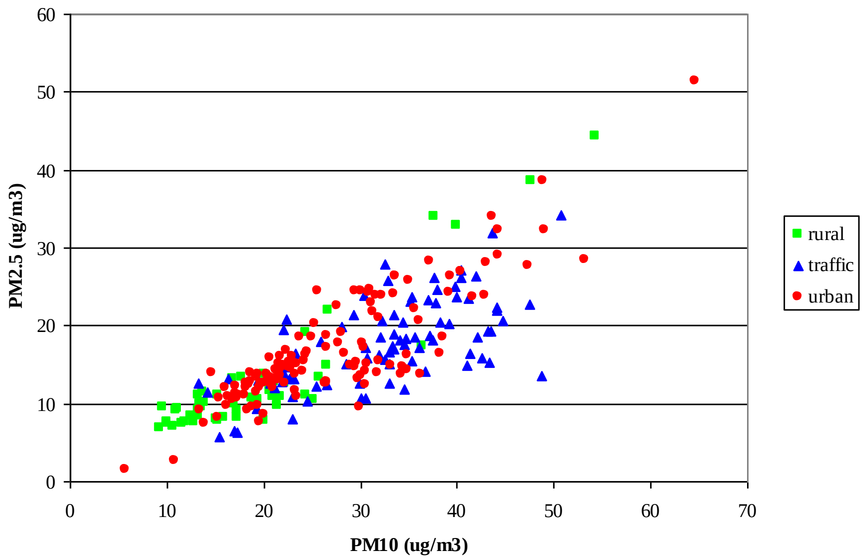

Figure 1.16: Annual mean concentrations of PM_{10} and $PM_{2.5}$ (period 2004-2005).

There are various options to calculate the $PM_{2.5}$ / PM_{10} ratio. The **simplest approach** (M1) is to calculate the ratio by using the annual mean values:

$$ratio = \overline{C}_{PM25} \Big/ \overline{C}_{PM10} \quad \text{or} \quad ratio = \frac{1}{n}\sum C_{PM25} \Big/ \frac{1}{m}\sum C_{PM10} \qquad [M1]$$

where $\overline{C}$ is the annual mean value. The averaging is over n and m days, respectively. The number of days is not necessarily the same for PM_{10} and $PM_{2.5}$.

A **second approach** (M2) is to estimate the ratio as the slope of a linear regression of daily concentrations:

$$C_{PM25} = ratio C_{PM10} + b$$

where C is the daily mean value and b is the intercept which could – optionally – be forced to zero. In this case, the ratio is obtained from:

$$ratio = \frac{1}{k}\sum C_{PM25} \cdot C_{PM10} \Big/ \frac{1}{k}\sum C^2{}_{PM10} \qquad \text{[M2]}$$

where the averaging is over the k days with simultaneous measurements of PM_{10} and $PM_{2.5}$.

In the **third approach** (M3) the ratio is calculated on a daily basis and next averaged over the full year:

$$ratio = \frac{1}{k}\sum \left(C_{PM25} / C_{PM10} \right) \qquad \text{[M3]}$$

During further data analysis, two stations were excluded as preliminary calculations indicated unrealistic ratios of more than 1.1 or smaller than 0.07. Calculations for each of the two years showed that the inter-annual variations in ratios are small. The results of the two years were therefore combined in further data processing.

Comparing the three methods generally results in similar ratios, see Figure 1.17. The largest differences are found when in method M1 the data coverage of $PM_{2.5}$ and PM_{10} show relatively large differences. Method M2 will result in the best fit between $PM_{2.5}$ and PM_{10} concentrations and should therefore be preferred.

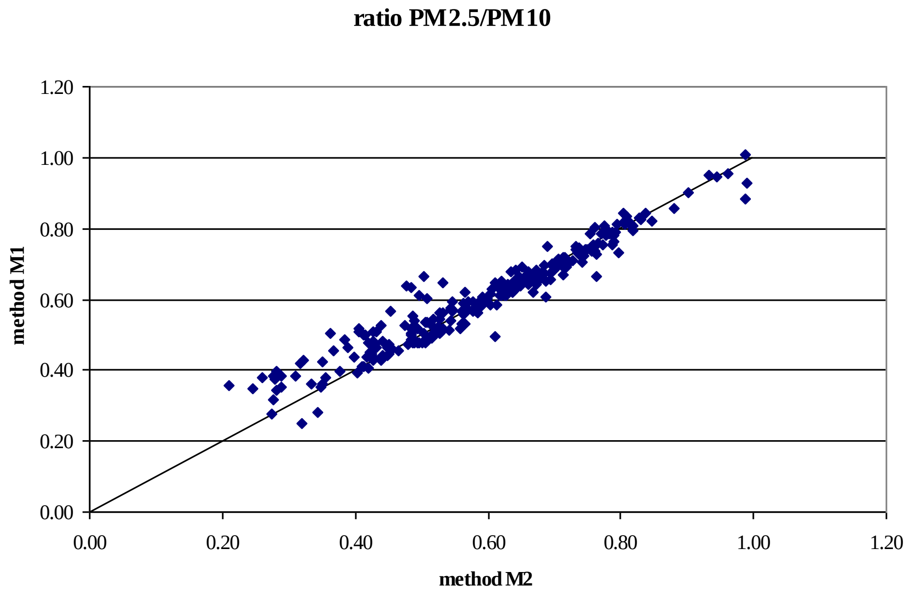

Figure 1.17: Comparison between method M1 and M2 in calculating the $PM_{2.5}$ / PM_{10} ratio. The line corresponds to the 1:1 line.

A closer look at the ratios suggests, besides the dependency on station type, a geographical dependency. To evaluate this phenomenon, Europe was divided into four regions. Not all countries have reported valid paired $PM_{2.5}$ and PM_{10} time series. Countries not included in the analyses presented here are marked *italic*:

1. Northern Europe: Norway, Sweden, Finland, Estonia, *Lithuania*, *Latvia*, Denmark and Iceland
2. North-western Europe: United Kingdom, Ireland, *the Netherlands*, Belgium, *Luxembourg*, France north of the 45 degrees latitude
3. Central and Eastern Europe: Germany, Poland, Czech Republic, Slovakia, Hungary, Austria, *Switzerland, Liechtenstein*
4. Southern Europe: France south of the 45 degrees latitude, Portugal, Spain, *Andorra*, *Monaco*, Italy, *San Marino*, *Slovenia*, *Croatia*, Greece, *Cyprus*, *Malta*.

Results (method M2) are presented in Table 1.1 and Figure 1.18. The ratios are in the range of 0.4 to 0.8. In the north and the central-east of Europe there is a clear tendency to lower ratios, in the order from rural to urban to traffic stations. This indicates an increasing contribution of locally emitted coarse particles at urban and traffic sites. In Southern Europe no such significant tendency can be observed. The rural stations in North-Western Europe (4 time series in the UK, one in Belgium) show a ratio which is surprisingly low compared to the ratio at urban and traffic sites in this region. The low number of time series may play a role.

The ratio at rural stations is much lower in North-Western and Southern Europe than in the northern and central-eastern parts of Europe. A possible explanation is the importance of sea spray particles (NW Europe) and mineral (Sahara) dust (S Europe).

Table 1.1: $PM_{2.5}$ / PM_{10} ratios and available number of time series as function of region and station type.

	$PM_{2.5}$ / PM_{10} ratio			number of time series		
region	rural	urban	traffic	rural	urban	traffic
North	0.78	0.46	0.39	5	11	22
North-West	0.53	0.61	0.59	5	54	17
Central-East	0.76	0.70	0.64	13	45	22
South	0.56	0.55	0.54	28	19	24
Total	0.63	0.62	0.54	51	129	85

The ratios presented here indicate some clear dependencies. However, as uncertainties in the ratios are large, one should be careful to draw conclusions. As mentioned above, detailed information on how measurements using a non-reference method are treated is still lacking; different procedures and methods used for $PM_{2.5}$ and PM_{10} monitoring are probably reflected in variations in the ratios. Further, ratios show large station-to-station variability (see the standard deviations plotted in Figure 1.18). For each station type the number and location of stations differs widely within a region (and also within a country). For example, in North-Western Europe, 4 (out of 5) rural time series are from stations located in the UK while 43 (out of 54) urban time series are from French stations. The use of a $PM_{2.5}$ / PM_{10} ratio to generate "pseudo" $PM_{2.5}$ data from the widely available PM_{10} measurements is not recommended.

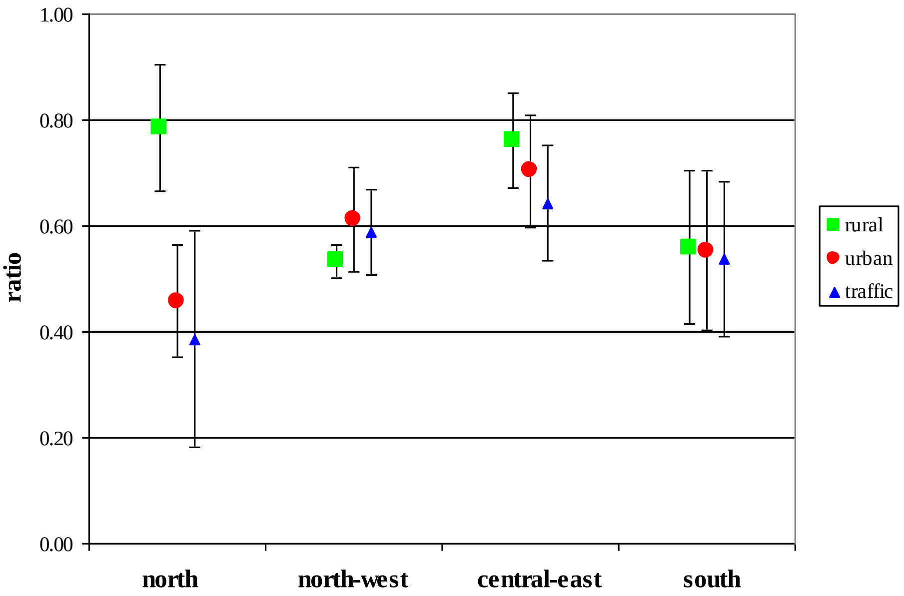

Figure 1.18: $PM_{2.5}$ / PM_{10} ratios averaged per region and station type. The error bars indicate plus/minus one standard deviation.

1.5 The street dust suspension source

Within the 'Street Emissions Ceiling (SEC)' project of the EEA-ETC/ACC, data from selected street/urban background station pairs were analysed. One purpose was to assess the contribution of street dust suspension to PM air pollution. Station pairs were identified where annual (or several months) data series of NO_X, NO_2, PM_{10} and $PM_{2.5}$ were available. Hourly PM concentration values together with meteorological data as well as traffic counts were used. Such fairly complete data sets were available for 9 station pairs, e.g. for London-Marylebone street, Stockholm-Hornsgatan, Berlin-Frankfurter Avenue, Oslo-RV4 road, Helsinki-Runeberg Street (Larssen et.al., 2007).

The street dust suspension situation differs considerably between streets in Nordic countries where studded tyres (and sanding in some cases) are used in winter and streets in other parts of Europe where such tyres are not in use.

Figure 1.19 and Figure 1.20show examples of the results obtained by analysing the station pairs: for Marylebone Street in London (data provided by David Green at King's College London), where studded tyres are not used, and for Hornsgatan in Stockholm (data provided by Christer Johansson at ITM Air Pollution Laboratory at Stockholm University), where studded tyres are used in winter. The figures show ratios between PM (as well as NO_2) increments and NO_X increments (over urban background), called 'delta ratios'. Ratios are shown for summer and winter, and workday and weekend conditions, respectively.

In Marylebone Street in London the ratios are about the same in winter and summer, and on workdays and during weekends. The PM_{10} ratio above NO_X is close to 2 times the $PM_{2.5}$ ratio, which indicates that the coarse fraction source, i.e. mainly the suspension source, has about the same strength as the exhaust source, both in winter and summer. Hornsgatan in Stockholm shows quite a different picture: In winter the importance of the studded tyre road dust suspension source is obvious. Average winter $PM_{2.5}$ concentrations reach values of approximately 30% above the non-suspension source (mainly exhaust particles), and are approximately 3 times higher than the summer PM_{10} concentrations (the NO_X emissions in the street are considered to be about the same during summer and winter).

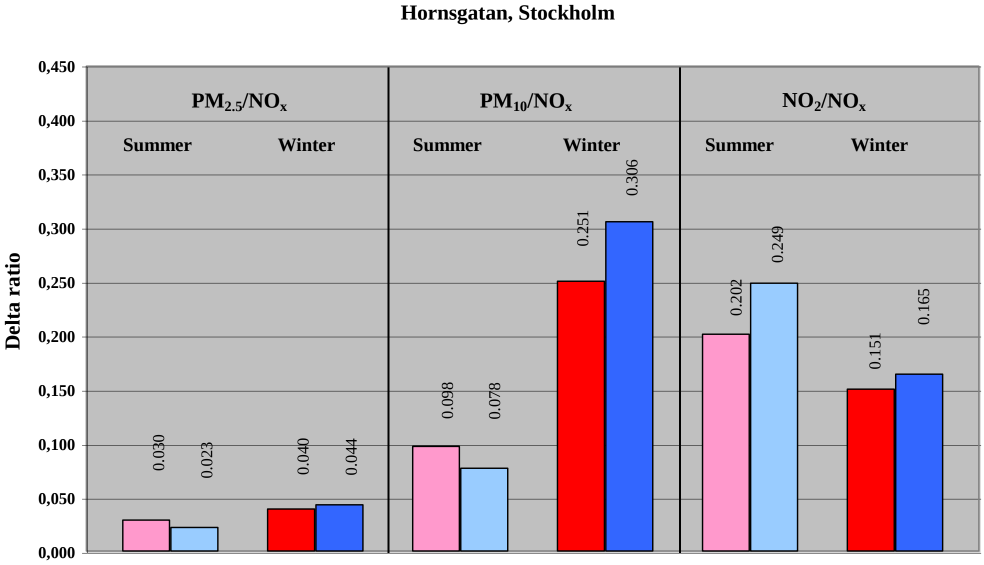

Figure 1.19: Delta ratios for the Hornsgatan station pair in Stockholm, 2000. Red columns: workdays. Blue columns: weekend days.

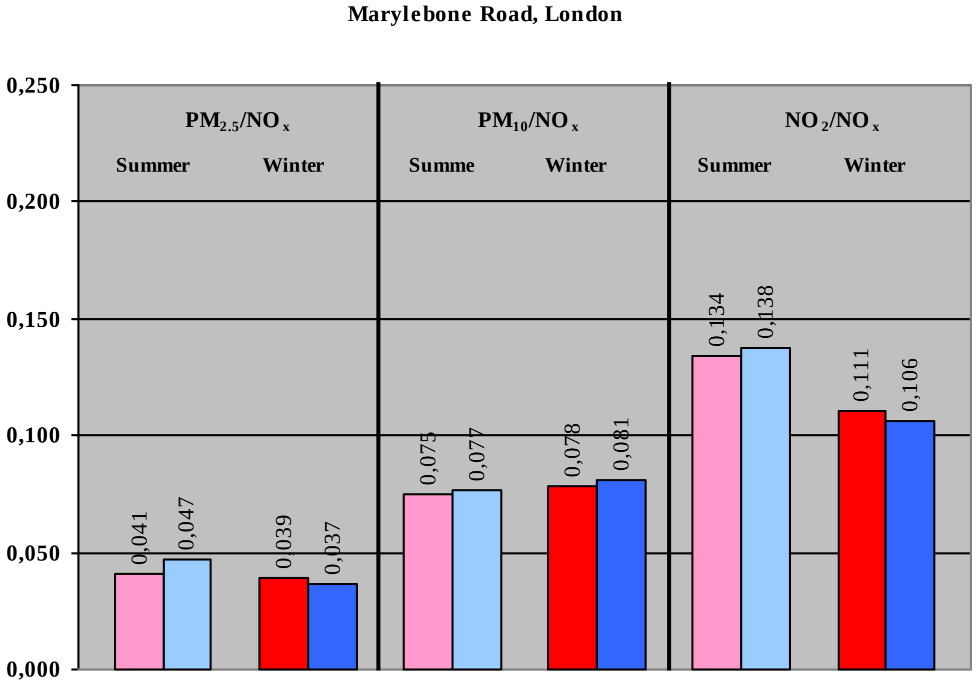

Figure 1.20: Delta ratios for the Marylebone Road station pair in London, 2000.

Based upon the analyses carried out for all 9 station pairs, the conclusion was that for streets **where no studded tyres were used** the coarse fraction emission factor, which is dominated by road dust suspension, is 1 to 4 times the emission factor for fine particles (which is dominated by exhaust particle emissions), varying between the street cases analysed. These results refer to an average for a winter or summer season. In Scandinavian streets **where studded tyres are used in winter**, the coarse fraction emission factor is 3-10 times higher than the fine fraction emission factor, as average over a winter season. The fine fraction contribution from road dust suspension is also significant, while in general still not well quantified. In Hornsgatan in Stockholm, this contribution is about 1/3 of the exhaust particle contribution.

Based upon the analyses carried out for all the 9 station pairs, the conclusion was that for streets where studded tyres are not used, the coarse fraction emission factor, which is dominated by road dust suspension, varies for the locations included in the analysis, between 1 and 4 times the emission factor for fine particles (which is dominated by exhaust particle emissions), as an average for a winter or summer season. In Scandinavian streets where studded tyres are used in the winter, the coarse fraction emission factor is 3-10 times the fine fraction emission factor, as winter average. The fine fraction contribution from road dust suspension is also significant, while still not well quantified. In Hornsgatan in Stockholm, this contribution is about 1/3 of the exhaust particle contribution.

1.6 Methodological aspects of PM mass measurement, and correction factors

PM mass is measured with different methods and instrument across Europe. The prevailing methods are:

- Gravimetry (sampling on filters with subsequent filter weighing in the laboratory), according to, or similar to, the CEN reference method.
- Automatic instruments using the beta ray absorption method (referred to as BAM method)
- Automatic instruments using the tapered element oscillating method (referred to as the TEOM method).

All methods require that acceptable QA/QC procedures are applied by the operating institution to provide quality data according to the requirements to accuracy set in the EU AQ Directive.

It is also established that the automatic instrumental methods need to be compared with the reference sampling method in order to provide comparable results, and that in most areas in Europe, results from the automatic methods need to be corrected.

Table 1.2 and Table 1.3 show the mix of methods used for PM_{10} and $PM_{2.5}$ monitoring respectively in the various countries reporting data to AirBase.

For both PM_{10} and $PM_{2.5}$, the gravimetric methods, for PM_{10} presumably conforming to the reference method, are used at about 20% of the stations reporting data to AirBase. The beta attenuation method (BAM) is the most widely used method for PM_{10}, used at 950 (42%) of the 2272 stations, while TEOM is most prominent at the $PM_{2.5}$ stations, used at 83 (31%) of the 268 stations. For some of the stations the method used has not been reported to AirBase.

Table 1.2: PM_{10} mass measurement methods per country, for stations reported to AirBase.

Country	Gravimetry	BAM	TEOM	Unknown	Total
AT	34	34	39		107
BE		20	27		47
BG	14	14			28
CH	17		4	1	22
CS		1			1
CY			2		2
CZ	35	84			119
DE	66	227	77	58	428
DK	9		3		12
EE		4			4
ES	54	114	167	50	385
FI		14	18		32
FR		66	287	5	358
GB	7	1	63		71
GR		10			10
HU		18	1		19
IE	11		3		14
IS		2			2
IT	39	173	17	6	235
LI		2			2
LT		12			12
LV		3			3
MK		14			14
MT		1	1		2
NL		38			38
NO	1	5	13		19
PL	85	38	28	1	152
PT	4	50			54
RO	15				15
SE	15		12		27
SI			10		10
SK	1	5	22		28
Total	**407**	**950**	**794**	**121**	**2272**

BAM: Beta attenuation method
TEOM: Tapered element oscillation method

Table 1.3: $PM_{2.5}$ mass measurement methods per country, for stations reported to AirBase.

Country	Gravimetry	BAM	TEOM	Unknown	Total
AT	7				7
BA		2			2
BE	1		8		9
CZ	7	24			31
DE	8	7	5	4	24
DK			3		3
ES	18	19	5	28	70
FI	1	4	1		6
FR			56	3	59
GB			4		4
GR		2			2
IS		2			2
IT	3	8	1		12
NO			8		8
PL	2				2
PT	4	13			17
SE			7		7
SK		2	1		3
Total	51	83	99	35	268

Most countries have been or are investigating the correction factors (CF) to use for their PM mass measurements, according to the CEN 12341 standard methodology. Full information on the respective CFs used in different countries has not yet penetrated into AirBase, although many countries have already reported corrected concentration values to the database. Overviews of the CFs in AirBase are summarised in Table 1.4 and in EEA-ETC/ACC Technical papers (see Buijsman and de Leeuw, 2004) and de Leeuw, 2005.) The CFs vary largely between 1.0 and 1.3. Many countries have station-specific CFs. The TEOM CFs are typically somewhat higher than the BAM CFs. Belgium is using the largest CFs.

Although a reference method has not yet been set for $PM_{2.5}$, some countries have reported CFs for some of their $PM_{2.5}$ stations to AirBase. This concerns Germany, Spain, Hungary and Slovenia, and these countries are typically using the same CFs for $PM_{2.5}$ as they use for PM_{10}.

The work to clarify the status of setting and implementing CFs for data in AirBase is not yet completed. We don’t have the full overview of which countries have or have not implemented CFs for all years for which data have been reported to AirBase. This work is in progress.

Table 1.4: Correction factors for PM_{10} reported to AirBase.

Country	BAM	TEOM	Unknown
AT	1.3 Seasonally variable at 7 stations	1.0-1.3	
BE	1.37 1.08 at 1 station	1.47	
DE	1.1-1.3	1.2-1.26	
DK		1.23-1.36	
EE	1.15		
ES	0.84-1.2 ~0.7*b at some stations	1.0-1.3	1.0-1.56
FI	1.0	1.0	
FR	1.0	1.0	
HU	1.0-1.31	1.0	
IT	-	- 1.3 at 1 station	
LV	1.0		
MT	1.3	1.3	
NL	1.3		
PT	1.11-1-18	1.1-1.2	
SI		1.12-1.3	
SK	1.3	1.3-1.3+	
UK		1.3	

1.7 References

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2 PM Assessment Report – Austria

2.1 PM measurement in Austria

2.1.1 PM monitoring network

The ambient concentration of particulate matter was measured for the last decades as „total suspended particulates“ at about 140 sites in Austria. These were usually equipped with ß-gauge instruments with Laskus-inlet.

The introduction of PM_{10} limit and target values by EC legislation (1st Daughter Directive 1999/30/EC) induced the start of PM_{10} measurement in Austria in 1999. In 2001, legal limit values for PM_{10} came into force in Austria and 67 PM_{10} monitoring sites were in operation. By 2005 the number of PM_{10} monitoring sites reached 111. At 41 of these sites the gravimetric method (Digitel High Volume Sampler, glass fibre filters) is being applied, 90 sites are equipped with continuous measurement (ß-gauge or TEOM), which include 20 sites with parallel measurement by gravimetry and continuous devices. The correction factor for continuous PM_{10} data covers a range between 1.0 and 1.42. In one Austrian monitoring network, the city of Vienna (Wien), a correction function with seasonally varying coefficients for offset and slope is applied.

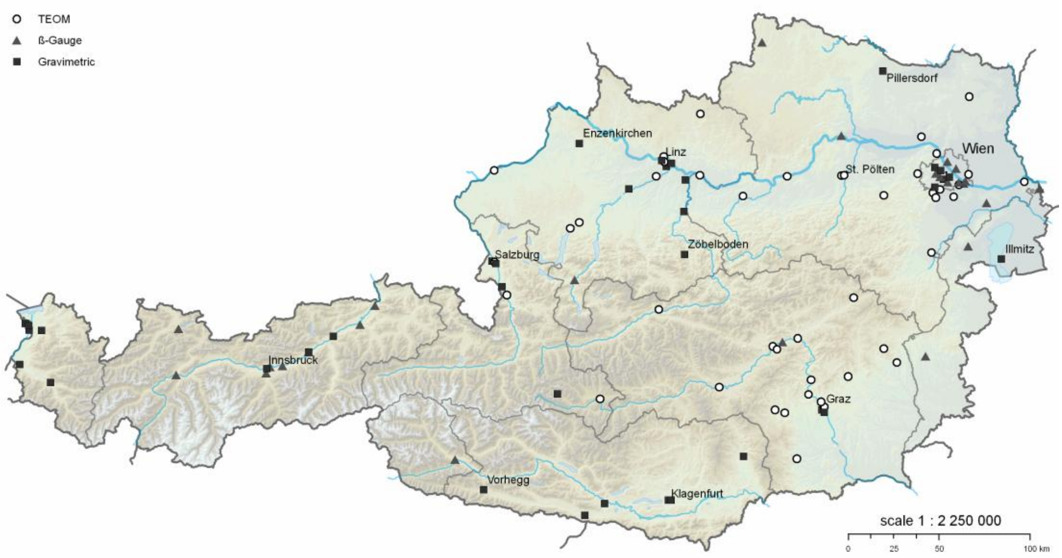

Figure 2.1: PM_{10} monitoring network in Austria, 2005.

Other PM fractions have been measured only at a small number of sites during recent years, including the EMEP site Illmitz ($PM_{2.5}$ and PM_1). As a legal requirement, in 2005 $PM_{2.5}$ measurement was started at background sites in the larger cities.

$PM_{2.5}$ and PM_1 are measured by the gravimetric method only.

2.2 PM pollution level in Austria

2.2.1 PM_{10} – Rural concentrations

Large-scale rural background concentrations are measured by the background monitoring network run by the Umweltbundesamt, which includes the three EMEP sites. At all monitoring sites, gravimetric PM_{10} data are used for assessment (the location of these sites can be found in Figure 2.1).

The monitoring sites in the flat and hilly extra-alpine regions show a fairly uniform and quite high PM_{10} concentration level. In eastern Austria, the limit value according to Dir 1999/30/EC for the daily mean is exceeded.

Rural PM_{10} concentrations show a distinct vertical gradient. Mountainous sites at an altitude around 1000 m measure almost no daily mean values above 50 µg/m³ and an average concentration between 40 and 50 % of that observed in the lowlands. At the mountainous sites exceedances of 50 µg/m³ as daily mean are caused by Saharian dust events, up to four days per year.

Table 2.1: Annual mean PM_{10} concentrations at rural background sites in Austria (µg/m³). Gravimetric data.

	Enzenkirchen	Illmitz	Pillersdorf	St. Koloman	Vorhegg	Zöbelboden
altitude (m)	525	117	315	1020	1020	899
2000		27.3				
2001		26.2		11.4	10.6	
2002		29.1		12.1	11.2	
2003		31.1		13.6	12.3	14.0
2004	21.7	24.5	23.0		10.4	10.9
2005	22.0	26.7	26.6		10.0	11.1
2006	22.1	25.6	26.2		10.0	10.0

2.2.2 PM_{10} – urban concentrations

Urban background PM_{10} levels cover a wide concentration range, depending on the topographic and climatic situation of the town.

Distinctly high PM_{10} levels are observed in the south-eastern pre-alpine lowlands and hilly regions (Styria) and in the basins and valley south of the central Alpine ridge; these regions are affected by adverse meteorological conditions, especially in winter due to shading from oceanic air masses by the Alps.

In Graz, much higher PM_{10} background levels are observed in the central urban area compared to suburban locations, whereas in other cities and agglomerations – with more favourable dispersion conditions – background concentrations are spaially more uniform.

Urban hot spot sites – usually kerb side locations – observe only moderately higher annual average PM_{10} concentrations compared to the background sites. Nevertheless, it has to be noted that the PM_{10} monitoring network does not necessarily cover the highest polluted locations. The “increment” of the annual mean, compared to background sites, is between 2 and above 20 µg/m³.

Table 2.2: Annual mean PM_{10} concentrations at urban background sites in large Austrian cities, 2003 – 2006, µg/m³.

	2003	2004	2005	2006
Wien	33 – 35	25 – 28	30 – 32	29 – 32
Graz	37 – 48	31 – 41	33 – 43	35 – 40
Linz	30 – 38	25 - 30	27 – 32	29 – 34
Salzburg	26	23	25	26
Innsbruck	29	27	29	32
Klagenfurt		27	26	29
St. Pölten	34	26	29	28

The urban and kerb side increment of the annual mean PM_{10} concentration is estimated in Figure 2.2 for Graz, Wien, Linz and Salzburg for different years and, depending on availability of PM_{10} data, for different combinations of monitoring stations. The results are possibly not completely representative due to the location of “background” sites. Traffic sites are located somehow deliberately and it cannot be assessed if they represent an average or maximum traffic impact. Figure 2.2 not only shows different urban and traffic impacts, which might depend on the specific location of the monitoring sites, but also inter-annual variations.

A major conclusion of the investigation is, in any case, that the specific location of the urban monitoring sites used for the assessment is, of course, of high importance, but may not be comparable in different cities. It is not clear in any case which site is really “background”. Further it has to be considered that urban background concentrations may vary within a city.

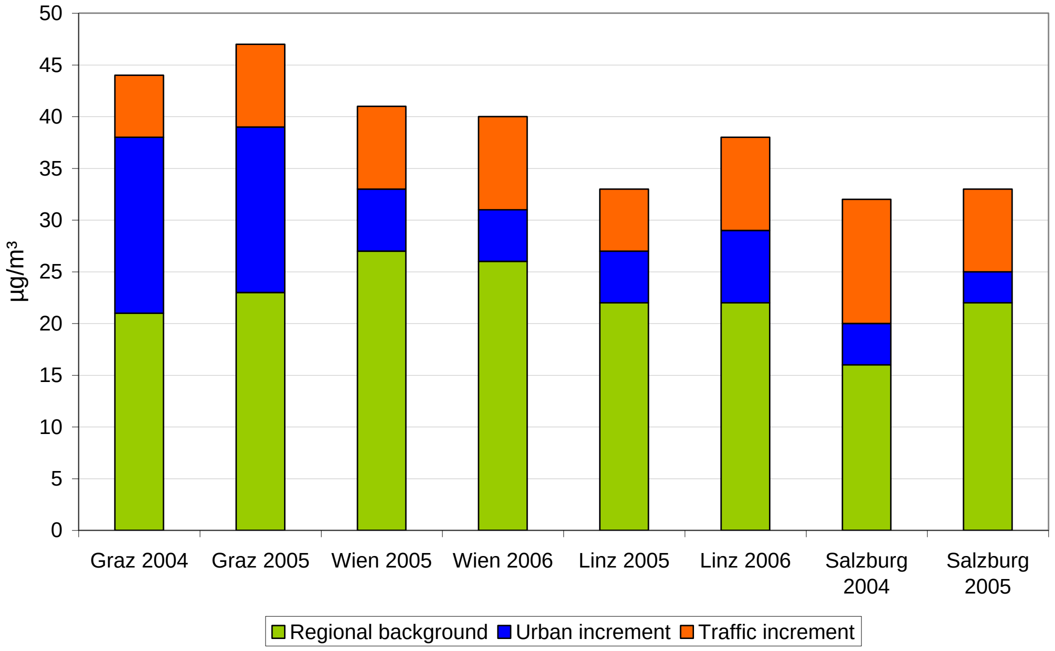

Figure 2.2: Estimation of urban increment PM_{10} concentration (annual means) in Graz, Wien, Linz and Salzburg.

A complete documentation of PM_{10} concentrations and trends in Austria can be found in the annual reports on air quality in Austria: **http://www.umweltbundesamt.at/jahresberichte/**.

2.2.3 Diurnal, seasonal and inter-annual variations

At urban sites, PM_{10} concentrations show a distinct daily variation which is due to the daily variation of emissions – mainly triggered by road traffic, but also from domestic heating – and the dispersion conditions. Figure 2.3 shows the average daily variation of PM_{10} concentrations at the two rural background sites Illmitz (117 m) and Zöbelboden (900 m), two sites in Wien (Belgradplatz, urban background, and Rinnböcktraße, traffic influence) and two sites in Graz (Graz Mitte, central urban background, and Graz Don Bosco, high traffic influence).

High emissions from road traffic during the morning induce peak PM_{10} levels at this time, coinciding with adverse dispersion conditions, especially in winter. Figure 2.3 clearly shows much higher morning PM_{10} levels in Graz compared to Wien, which is due to the much more unfavourable dispersion conditions in Graz, situated in a basin at the south-eastern fringe of the Alps – usually the ground inversion is lifted only during short period around noon in winter. This effect of different local dispersion conditions also triggers the high evening PM_{10} levels in Graz, whereas there is only a slight increase in PM_{10} levels in Wien in the evening. A further reason for higher PM_{10} levels in Graz in the evening is the comparably higher contribution of domestic heating emissions in Graz.

Rural sites show almost no daily variation. In Illmitz (flat terrain), a very slight decrease during the afternoon is caused by more favourable dispersion conditions. At elevated sites (e.g. Zöbelboden, 900 m) the PM_{10} concentration increases slightly in the morning, which is caused by advection of polluted air from below when the nocturnal inversion layer is lifted.

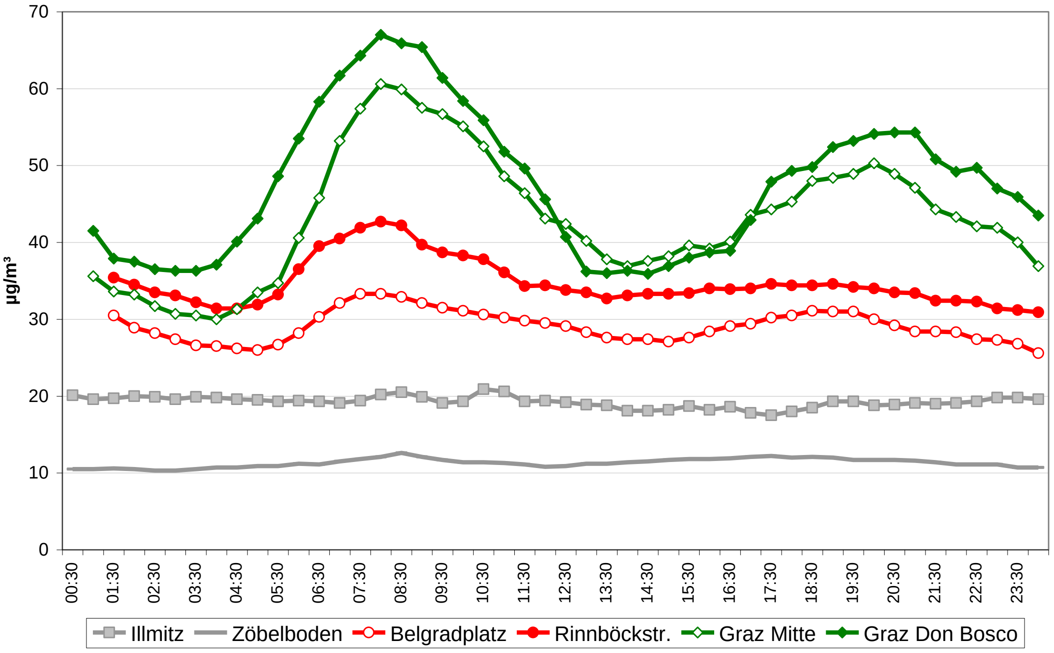

Figure 2.3: Average diurnal variation of PM_{10} concentrations at rural background sites and selected sites in Wien and Graz, 2005.

The extra-alpine sites and those in alpine valleys and basins observe distinct annual variations in PM_{10} levels. During winter, PM_{10} concentrations are 2 to 3 times higher compared to summer. Figure 2.4 shows the monthly mean PM_{10} concentrations at the two rural background sites Illmitz and Vorhegg (1020 m), two sites in Wien (Belgradplatz and Rinnböckstraße) and two sites in Graz (Graz Mitte and Graz Don Bosco) for the years 2003 to 2005. The highest average PM_{10} concentrations are most frequently observed during late winter at these sites, which can be attributed to the following reasons:

- higher emissions of primary PM_{10} from domestic heating (including district heating and electric power generation) and resuspension of winter sanding;
- higher emissions of SO_2 and NO_x from domestic heating and power plants as precursors for ammonium nitrate and ammonium sulphate;
- adverse dispersion conditions, especially during long lasting high pressure situations;
- higher concentrations of ammonium nitrate, which is not present in summer due to high temperatures.

In contrast, the background site Vorhegg at about 1000 m shows no clear seasonal variation. These altitudes usually are situated above the ground inversion layer during winter and therefore only slightly affected by emissions in the lowlands and valleys.

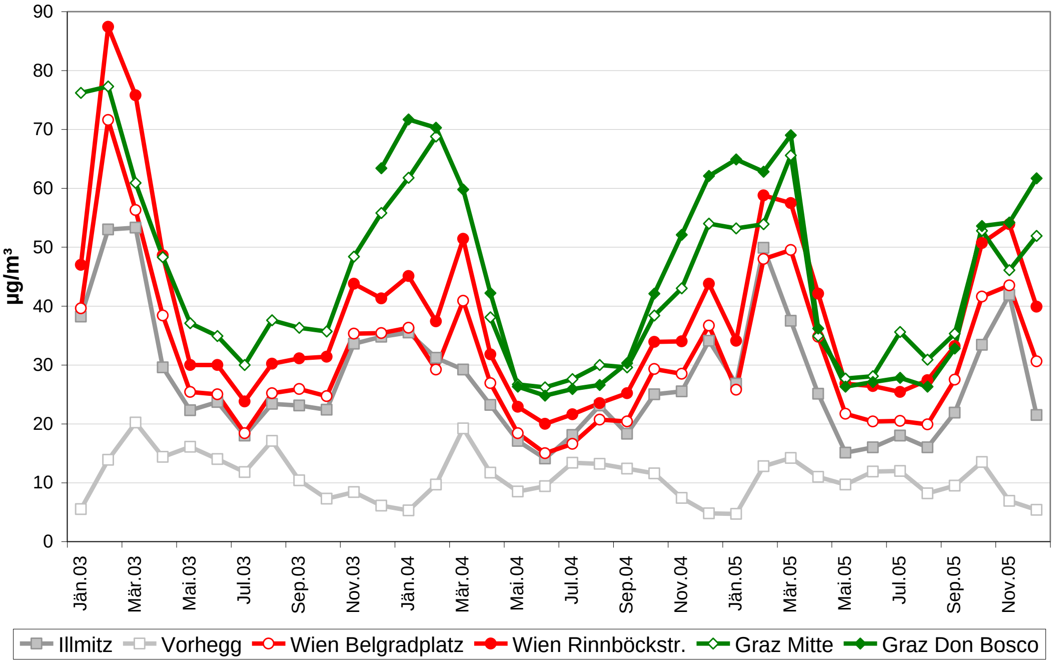

Figure 2.4: PM_{10} monthly mean values at rural background sites and selected sites in Wien and Graz, 2003 – 2005.

Figure 2.4 also gives a glance at the inter-annual variations of PM_{10} concentrations. High annual averages of PM_{10} in 2003, compared to other years, were caused by extraordinarily high concentrations especially in February and March. Long-lasting high-pressure situations with very low temperatures characterised these months, triggering both local and regional PM_{10} accumulation as well as frequent regional to long-range transport from eastern central Europe.

The meteorological conditions seem to be the key factor for the inter-annual variations and any medium-term trends of PM_{10} concentrations.

2.3 Sources of PM_{10}

2.3.1 PM_{10} emissions in Austria

Total PM_{10} emissions in Austria are calculated to be 46,700 t in 2004 and have not changed significantly in the past 15 years (UMWELTBUNDESAMT 2001, 2006b). It has to be noted that estimates for fugitive emissions (industry), mining, resuspension (road traffic) and agriculture are still affected by large uncertainties. The sectoral distribution is depicted in Figure 2.5. Emissions from road traffic – exhaust, abrasion and resuspension – have increased by 32 % since 1990, caused mainly by a general increase in traffic volume and by a distinct increase in Diesel passenger car numbers (induced by low taxes on Diesel fuel). Domestic emissions are mainly caused by wood and coal burning. The contribution of this sector has decreased by 18 % since 1990.

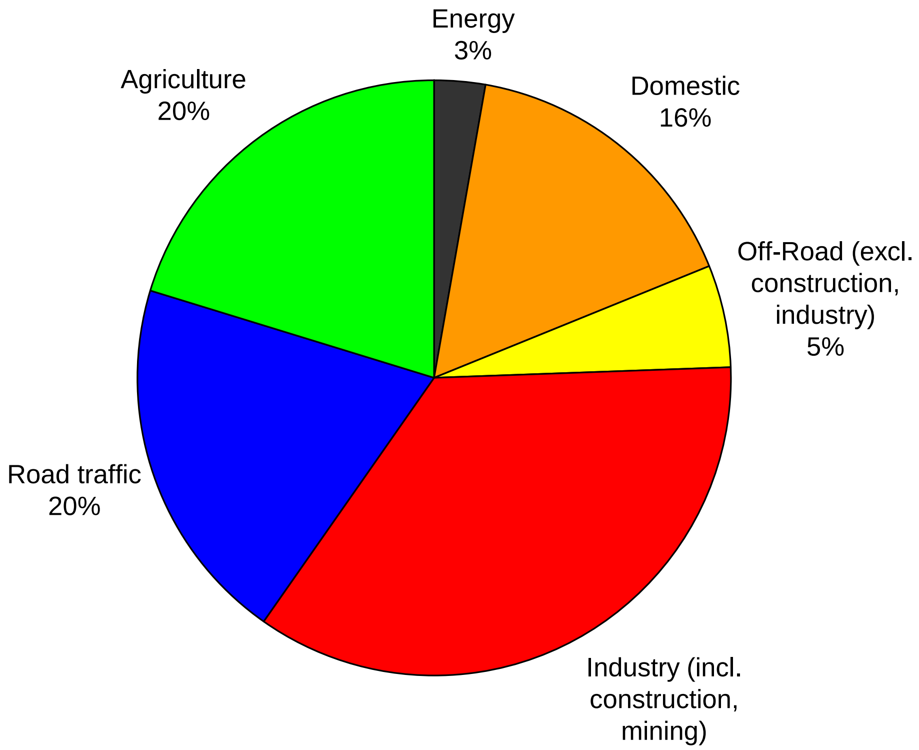

Figure 2.5: PM_{10} emissions in Austria by sector, 2004.

2.3.2 Source attribution for Austrian monitoring stations

The attribution of elevated PM_{10} levels to sources of PM_{10} (and to sources of precursors of secondary particles), including their sectoral and spatial allocation, was subject of several studies, most of which have been conducted to investigate exceedances of limit values (primarily concerning daily means > 50 µg/m³).

These studies focussed on days or periods with elevated concentrations, not on the annual mean; since exceedances of 50 µg/m³ as daily mean mainly occur in winter, the sectoral distribution of emissions differs from the annual sum presented in chapter 2.3.1. Since the sectoral distribution of PM_{10} emissions per year (Figure 2.5) reflects a temporal and spatial average for Austria, the actual contributions at certain locations or monitoring stations can be quite different. During winter, emissions from domestic heating, district heating and electric power generation are distinctly higher than in the annual average, and resuspension emissions are increased by winter sanding. On the other hand, emissions from agriculture are low during winter, and mining emissions and industrial fugitive emissions as well as (natural) soil erosion are reduced by frozen or wet ground or snow cover.

Especially in urban and road side locations, the relative contribution from road traffic and domestic heating to elevated PM_{10} concentrations in winter is much higher than the average percentages to total PM_{10} emissions (Figure 2.5), due to low emission heights and high emission densities in cities.

Industrial emissions and construction (including resuspension from dirty roads) can contribute a large share at specific locations.

Figure 2.6 gives examples for a source attribution for different sites with high PM_{10} levels. Wolfsberg (left) is located in a broad Alpine valley with distinctly high PM_{10} and SO_2 emissions from industry, and high emissions from wood burning in domestic heating. The valley is shaded from advection from other valleys and from outside the alpine region by mountains and does suffer from frequent ground inversion situations.

Imst (right) is located in the Inn valley. The monitoring site is affected by a very high contribution from road traffic emissions. A distinction between local and regional contribution was attempted. Construction works were a specific problem at this location, which influenced PM_{10} levels mainly by dirt dispersed on adjacent roads by lorries and machinery and then resuspended by regular traffic.

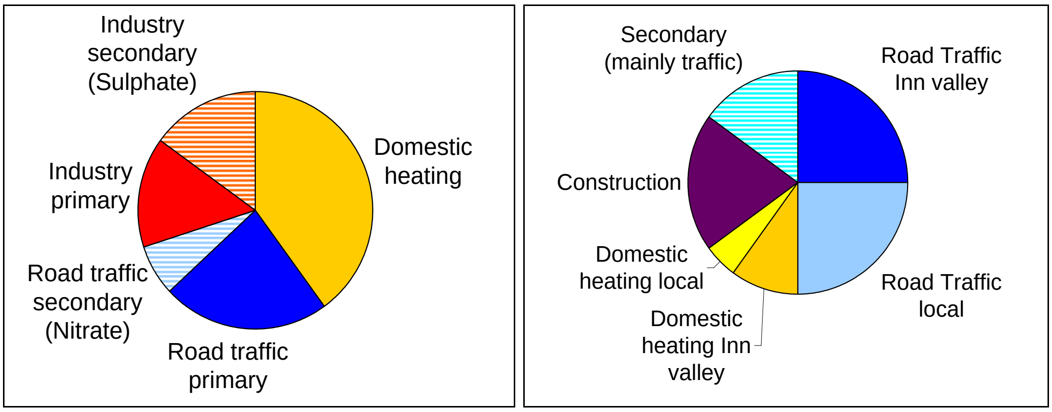

Figure 2.6: Source attribution for elevated PM_{10} concentrations in Wolfsberg (province of Carinthia), left, and Imst (province of Tyrol), right.

Agriculture, mining and natural soil erosion could not be identified as significant sources of elevated PM_{10} concentrations.

Long-range transport of Sahara dust causes PM_{10} daily mean values above 50 µg/m³ on one day per year on average in Austria.

2.3.3 Regional and long-range transport and accumulation

As already mentioned above, PM_{10} levels and their temporal variation are influenced by the combination of emissions and meteorological circumstances, which trigger accumulation as well as transport. Due to the long atmospheric life time of PM_{10} of several days, PM_{10} can be advected over distances of several hundreds of kilometres, and can be accumulated over several days during stable high pressure situations.

Regional transport and accumulation of PM_{10} and long-range transport were investigated for the eastern and northern parts of Austria using backward trajectories (UMWELTBUNDESAMT 2004, 2005, 2006a). Figure 2.7 depicts examples of typical situations with long-range transport from high-emission regions in southern Poland and northern Moravia (Czech Republic) (February 5th, 2005) and in southern Romania and northern Serbia (February 9th, 2005) coinciding with high PM_{10} concentrations in north-eastern Austria.

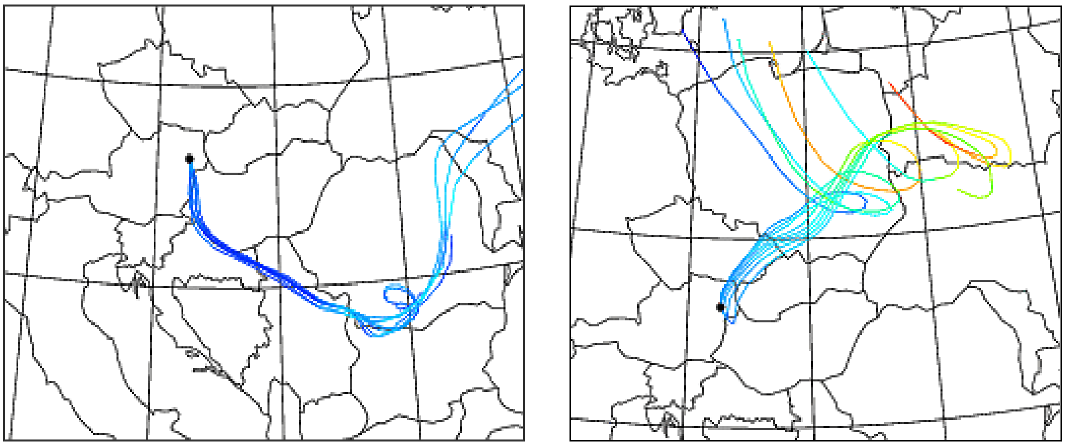

Figure 2.7: Backward trajectories for typical situations with elevated PM_{10} levels in Wien. Long-range transport from southern Romania and northern Serbia (left, February 9th, 2005) and southern Poland and northern Moravia (Czech Republic) (right, February 5th, 2005). The colour indicates the altitude of the air masses (blue < 900 m amsl, yellow > 1600 m).

Figure 2.8 gives an example of a source analysis of PM_{10} data from Wien (urban background) 2003 (documentation of method and details in Umweltbundesamt 2005) based on concentration-weighted trajectory residence time statistics. Advection of highly polluted air masses from the south-east and north-east can be clearly identified[2].

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[2] The „source region“ of highly polluted air over the eastern Alps represents subsidence during high pressure situations, when the trajectories are not representative for the highly polluted ground layer.

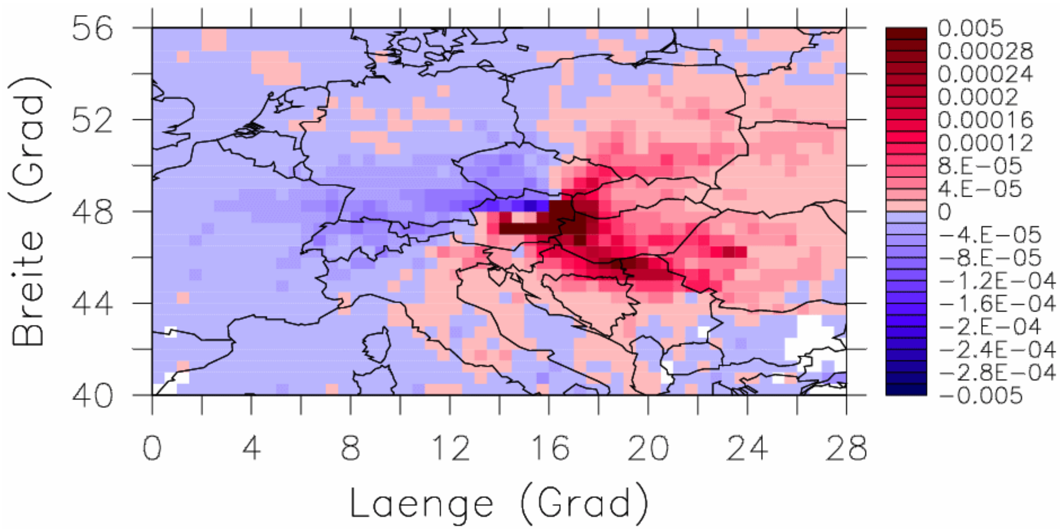

Figure 2.8: Trajectory statistics based on concentration weighted residence time, PM_{10} background concentration in Wien, 2003 (red: above average concentrations, blue: below average concentrations).

To achieve a semi-quantitative attribution of highly polluted air masses to certain source regions, the backward trajectories for days with daily mean PM_{10} values above 50 µg/m³ were classified and combined with the EMEP emission inventory for primary PM_{10} and SO_2 (as precursos for sulphate). Results for the rural background sites of Enzenkirchen, Illmitz and Pillersdorf (data 2003-2005, Illmitz also 1999/2000) are presented in Figure 2.9. Rural background PM_{10} concentrations in eastern Austria are influenced by regional and long-range transport from Serbia, Romania, Hungary and Slovakia to a major extent. In north-western Austria, the contribution from the north (Poland, Czech Republic) is higher, but also from regional emissions. Long-range transport from high-emission regions in north-western central Europe give comparably low contribution, as transport from these regions is mostly associated with favourable dispersion conditions in oceanic air masses. In contrast, regional to long-range transport from the east and north coincides with the advection of continental air masses with adverse dispersion conditions.

Figure 2.10 gives the assessment of the contributions of different source regions (primary and precursors of secondary PM_{10}) to the urban background concentration in Wien. With respect to the high regional background, the contribution of emissions in Wien is relatively low (about 20 %). Nevertheless, it has to be noted that kerb-side locations in Wien measure much higher PM_{10} levels with local contributions of 30 % or more.

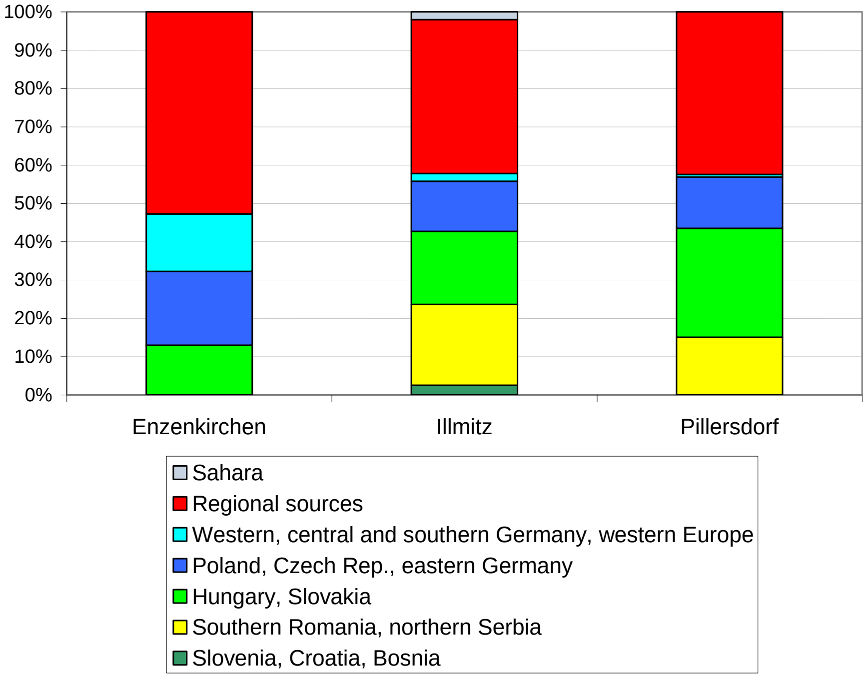

Figure 2.9: Contributions of different source regions to PM_{10} concentrations (above 50 µg/m³) at the rural background sites Enzenkirchen (North-western Austria), Illmitz(Eastern Austria) and Pillersdorf (Northern Austria), data 1999/2000, 2003-2005.

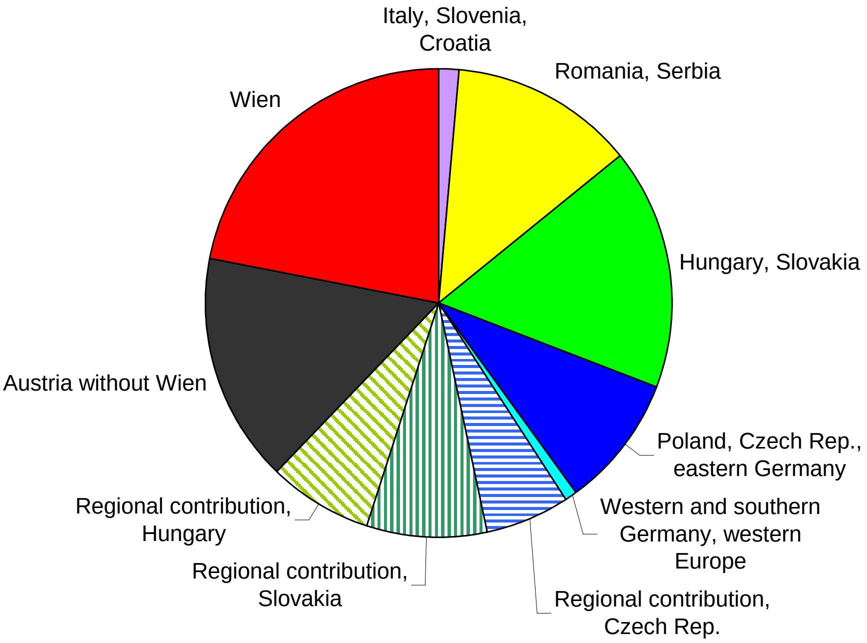

Figure 2.10: Contributions of different source regions to PM_{10} concentrations (above 50 µg/m³) to the urban background in Wien (data 1999/2000, 2003-2005).

2.4 $PM_{2.5}$ and PM_1

Measurements of PM fractions other than PM_{10} were conducted at selected sites only in the last years; the longest measurement series of $PM_{2.5}$ and PM_1 is available at the EMEP site Illmitz. Urban $PM_{2.5}$ measurements started on a legal basis in 2005 in the larger cities.

Table 2.3 lists all available $PM_{2.5}$ and PM_1 monitoring data in Austria.

Both at rural and urban background sites, $PM_{2.5}$ annual mean concentrations between 19 and 25 µg/m³ were observed in recent years. The highest annual means were observed at urban traffic locations with up to 38 µg/m³ (temporal traffic site in Vienna).

$PM_{2.5}/PM_{10}$ ratios cover a quite narrow range between 0.64 and 0.85. Lower $PM_{2.5}/PM_{10}$ ratios are observed at urban sites compared to rural locations (UMWELTBUNDESAMT 2006).

$PM_{2.5}/PM_{10}$ and PM_1/PM_{10} ratios seem to be rather constant over time (on the basis of annual means); the $PM_{2.5}/PM_{10}$ ratio in Illmitz varies between 0.77 and 0.80 during the last years.

Table 2.3: $PM_{2.5}$ and PM_1 concentrations and $PM_{2.5}/PM_{10}$ and PM_1/PM_{10} ratios at Austrian monitoring sites.

Monitoring site	Period	PM_{10} (µg/m³)	$PM_{2.5}$ (µg/m³)	$PM_{2.5}/PM_{10}$	PM_1 (µg/m³)	PM_1/PM_{10}
Graz Süd (suburban)	Oct. 00–Sept. 01	33	22	0.68		
Illmitz (rural)	Oct. 99–Oct. 00	26	20	0.77		
Illmitz	2001 (since 1.3.)	24	19	0.77		
Illmitz	2002	30	23	0.79		
Illmitz	2003	31	25	0.77	14[3]	0.55
Illmitz	2004	25	19	0.78	14	0.59
Illmitz	2005	27	22	0.80	16	0.60
Illmitz	2006	26	21	0.77	15	0.57
Innsbruck Zentrum (central urban background)	2005	29	21	0.73		
Klagenfurt (urban traffic)	2005 (since 8.3.)	33	23	0.71		
Linz Neue Welt (urban industrial)	2005	32	24	0.72		
Linz ORF-Zentrum (central urban)	Oct. 00–Sept. 01	34	22	0.64	19	0.60
Salzburg (urban traffic)	2005 (since 4.2.)	33	26	0.78		
Streithofen (rural)	June 99–May 00	24	18	0.73		
Wien Erdberg (urban traffic)	May 01–May 02	43	29	0.68		
Wien Spittelau (urban traffic)	Oct. 99–Oct. 00	53	38	0.72		
Wien Währinger Gürtel (urban background)	June 99–May 00	30	22	0.69		
Wien Währinger Gürtel	2005	30	24	0.76		
Zöbelboden (rural)	2004 (since 14.2.)	11	9	0.78		
Zöbelboden	2005	11	9	0.85		

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[3] PM1 since April 2004; PM_{10} average over PM_1 measurement period: 25.7 µg/m³.

2.5 Chemical composition of PM in Austria

Measurement campaigns including chemical analyses of PM_{10} and $PM_{2.5}$ have been conducted at different sites in Austria since 1999, but the information they yield is still fragmentary.

Table 2.4 gives an overview of the chemical composition of PM_{10} in Austria, covering the major constituents elemental carbon (EC), organic matter[4] (OM), sulphate, nitrate, ammonium, and (soluble) metals for most sites. Only the AQUELLA measurement programme (2003-2005) covers also silicates and carbonates.

Compounds not analysed cover water (adsorbed mainly to sulphate) and mineral dust for the analyses without silicate and carbonate and can account for 20 to 30 % of the total PM_{10} mass. But also the AQUELLA analyses cover only 80 to 90 % of the total PM_{10} mass.

Table 2.4: Major PM_{10} constituents at measurement campaigns in Austria. PM_{10} concentrations in µg/m³, chemical composition in %.

Site	**Site type**	**Period**	**PM_{10}**	**EC**	**OM**	**Sulphate**	**Nitrate**	**Ammonium**	**Metals**	**Silicates**	**Carbonates**
Sampling approx. 12 months											
Anthering*[5]	Rural	2004+	14	7 %	26 %	13 %	9 %	15 %		3 %	6 %
Arnoldstein*[6]	rural, medium industrial	March 99 – Feb. 00	22	6 %	31 %	18 %	8 %	8 %	3 %		
Bockberg*[5]	Rural	Dec. 03 – Dec.04+	25	8 %	31 %	14 %	8 %	12 %		5 %	2 %
Graz Don Bosco*[5]	Central urban traffic	Dec. 03 – Jan. 05+	45	14 %	39 %	8 %	4 %	7 %		4 %	7 %
Graz Süd*[7]	suburban, medium commercial	June 00 – May 01	33	14 %	24 %	13 %	7 %	5 %	3 %		
Graz Süd*[5]	Suburban, commercial	Dec. 03 – Jan.05+	38	12 %	42 %	9 %	4 %	7 %		7 %	6 %
Illmitz**[8]	rural background++	Oct. 99 – Nov. 00	24,2	8 %	23 %	18 %	11 %	8 %	4 %		
Linz ORF-Zentrum*[7]	central urban, medium industrial	June 00 – May 01	34	11 %	16 %	15 %	11 %	7 %	3 %		
Salzburg Lehen*[5]	Suburban background	2004+	18	12 %	29 %	10 %	6 %	11 %		9 %	5 %
Salzburg Rudolfspl.*[5]	Central urban traffic	2004+	28	23 %	32 %	7 %	3 %	7 %		9 %	6 %
Streithofen*[7]	rural	June 99 – May 00	23,7	8 %	25 %	16 %	17 %	11 %	3 %		
Unterloibach*[6]	rural	March 99 – Feb. 00	20	5 %	27 %	18 %	9 %	10 %	2 %		
Wien AKH*[7]	central urban background	June 99 – May 00	30,4	12 %	26 %	15 %	13 %	8 %	5 %		
Wien Kendlerstr.*[5]	Urban background	2004+	28	10 %	28 %	12 %	7 %	11 %		16 %	9 %

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[4] Calculated from organic carbon with a factor of 1.7 for the AQUELLA analyses and a factor of 1.4 for earlier analyses.

[5] AQUELLA (BAUER 2005, PUXBAUM 2004, 2006)

[6] LAVRIC (2001)

[7] AUPHEP (2004)

[8] Umweltbundesamt (2002)

Site	Site type	Period	PM_{10}	EC	OM	Sul-phate	Nitrate	Ammo-nium	Metals	Silicates	Carbo-nates
Wien Liesing*[9]	Suburban, commercial	Nov. 01 – Oct. 02	49,7	10 %	24 %	12 %	11 %	7 %	8 %		
Wien Lobau*[5]	Suburban forest	2004+	22	8 %	29 %	17 %	8 %	12 %			3 %
Wien Rinnböckstr.* [5]	Suburban, medium traffic	2004+	33	11 %	28 %	12 %	6 %	12 %		16 %	7 %
Wien Schafbergbad *[9]	Suburban background	Nov. 01 – Oct. 02	35,7	10 %	23 %	17 %	14 %	10 %	4 %		
Wien Schafbergbad *[5]	Suburban background	2004+	21	8 %	28 %	15 %	8 %	12 %		13 %	3 %
Wien Spittelauer Lände**[8]	central urban traffic++	Oct. 99 – Nov. 00	53,4	20 %	20 %	9 %	8 %	4 %	9 %		
Episode sampling											
Innsbruck Zentrum[10]	urban, medium traffic	Sept.03/Nov.03	26	20 %	32 %	8 %	5 %	3 %	5 %		
Klagengurt Völkermarkter str.[11]	urban traffic	Dec 02/Jan.03	64	17 %	29 %	8 %	9 %	5 %	4 %		
Lienz[12]	small town, traffic	Dec. 02	49	25 %	34 %	6 %	6 %	2 %	4 %		
Wien Belgradplatz[13]	central urban background	Feb./March 03, Jan./Feb. 04	93	9 %	20 %	16 %	17 %	8 %	4 %		
Wolfsberg[14]	small town, traffic	Dec.04/Jan.05	74	14 %	31 %	9 %	7 %	4 %	4 %		

* Technical University Wien, Institute for Chemical Technology and Analytics.
**Umweltbundesamt (note: possible overestimation of EC)
\+ Average over months of January, April, July and October.
\+\+ Sampling every 6th day.

As an example, Figure 2.11 shows the average chemical composition of PM_{10} at two sites in Graz (Graz Don Bosco, traffic, Graz Süd, background), Illmitz (rural background in eastern Austria, representative for Wien), Wien AKH (urban background) and Wien Spittelau (traffic) and Salzburg Rudolfsplatz (traffic).

The quantitatively most important “chemical species” is organic matter, especially in alpine – rural as well as urban – locations. OM can account for 30 to 40 % of the PM_{10} concentration. Major sources of OM are wood and coal burning in domestic single stoves, but these, as source apportionment by certain tracers indicate, do not account for the whole OM mass.

Elemental carbon, the major source of which is road traffic (exhaust), account for up to more than 20 % of PM_{10} at traffic related sites, but about 5 % at rural locations.

The absolute concentrations of sulphate vary largely, the highest values are observed in eastern Austria and can be attributed to long-range transport from central eastern and south-eastern Europe. Sulphate concentrations are quite

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[9] BAUER (2002)
[10] Umweltbundesamt (2004a)
[11] Umweltbundesamt (2003)
[12] Umweltbundesamt (2003a)
[13] Umweltbundesamt (2004)
[14] Umweltbundesamt (2005b)

uniform in the non-alpine regions, but low in most alpine valleys and basins due to the absence of major SO_2 sources.

High nitrate concentrations are observed especially in Wien and the surrounding region and can be attributed to high NO_x emissions in this region. Long-range transport of nitrate seems to be of minor importance. In alpine valleys and basins, nitrate concentrations are lower than in the non-alpine regions, but cover a larger share of the inorganic secondary aerosols, compared to sulphate.

The contribution of mineral dust (silicate, carbonate) is around 10 % for most sites; higher concentrations are observed in Wien. High carbonate concentrations in January can be attributed to winter sanding, but silicate concentrations show no distinct annual variation and obviously originate from other – not yet identified – sources.

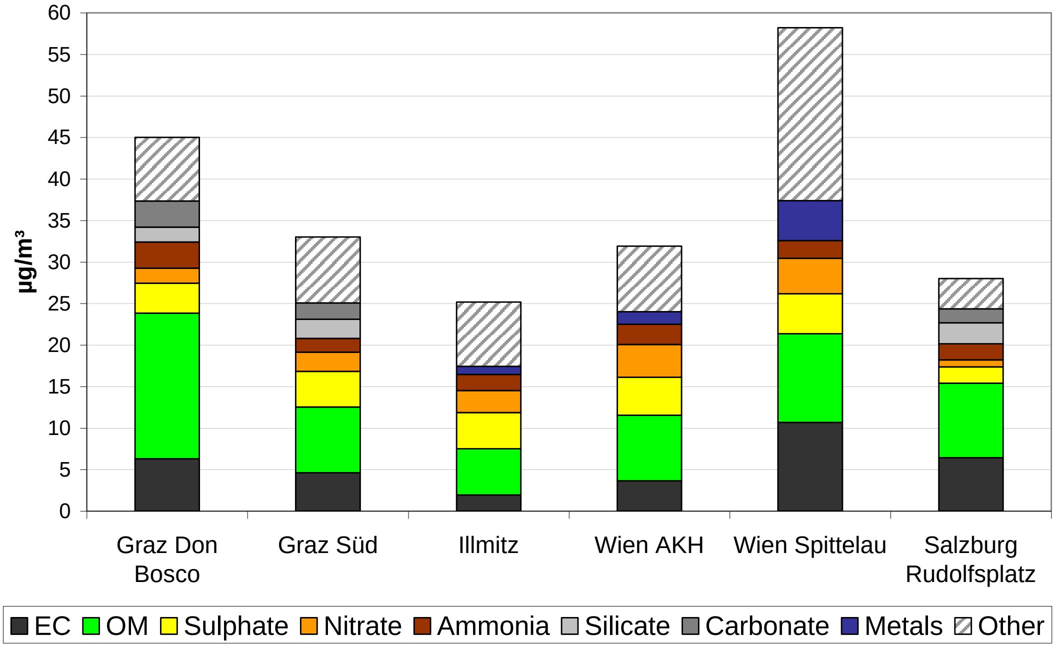

Figure 2.11: Chemical composition of PM_{10} at sites in Graz, Wien, Illmitz and Salzburg.

2.6 Literature

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3 Atmospheric particulate matter in Belgium

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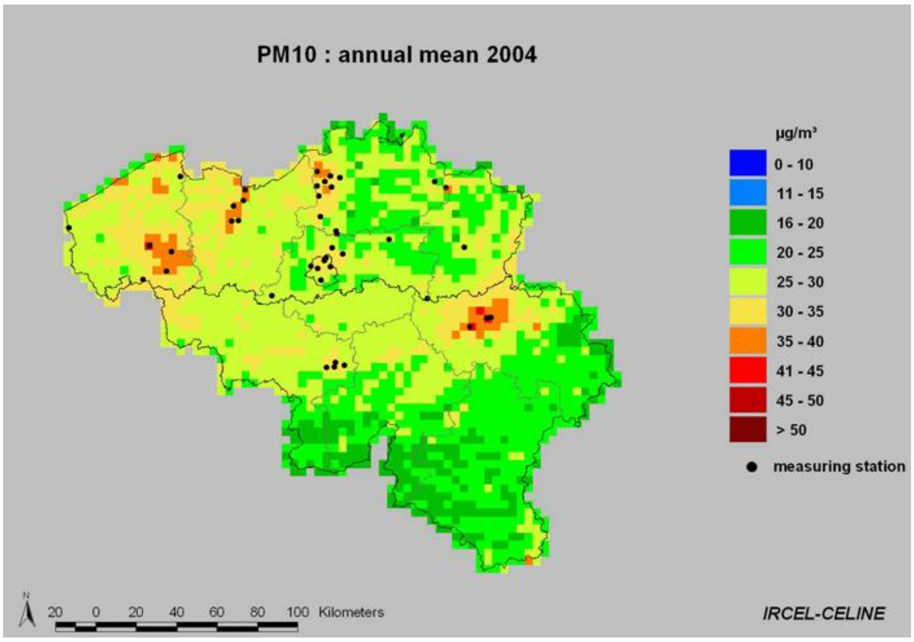
3.1 Introduction

This text deals with atmospheric particulate matter (PM, mostly PM_{10}) in Belgium. Belgium consists of 3 regions (Brussels, Flanders, and the Walloon region). The PM concentration data presented here originate from the Belgian Interregional Environmental Agency (IRCEL - CELINE; http://www.irceline.be), which compiles the results of the monitoring networks of the 3 regional agencies. The 3 agencies are "Bruxelles Environnement - Leefmilieu Brussel" (http://www.ibgebim.be), the "Vlaamse Milieumaatschappij" (VMM; http://www.vmm.be), and the "Ministère de la Région wallonne" (http://mrw.wallonie.be/dgrne/eew). The 3 agencies perform the PM measurements on a continuous basis using automated instruments with high time resolution, including ESM monitors based on β-absorption, regular TEOM monitors with the filter kept at 50ºC, TEOM-FDMS instruments and Grimm monitors. For the ESM and regular TEOM monitors correction factors (of 1.37 and 1.47) are applied to convert the PM10 results to data that are equivalent to the European norm EN12341. For the interpretation and discussion of the PM data, I relied heavily on reports (in Dutch) from the VMM and the Brussels region. Besides the PM data and their discussion, also data of chemical composition of the PM are presented in this text. The latter data were all obtained by my own research group in a number of sampling campaigns, some of which were performed by the VMM. The aerosol collection time in these campaigns was 24 hours; a variety of filter devices and filter types were used, the PM mass was determined by gravimetry (at 50% relative humidity and 20ºC) and the samples were analysed (using a thermal-optical transmission method, ion chromatography, and particle-induced X-ray emission spectrometry) for organic and elemental carbon, major anionic and cationic species, and a suite of elements [Maenhaut et al., 2002]. The chemical data were used to examine differences in composition between summer and winter and among sites, and to assess to which extent aerosol chemical mass closure could be obtained (that is to examine to which extent the sum of the measured components added up to the gravimetric PM mass).

3.2 PM_{10} concentrations in Belgium and relation with limit values of the EU directives

The networks have (as of 1 February 2007) 47 stations measuring PM_{10} (5 in Brussels, 32 in Flanders, and 10 in the Walloon region) and 12 stations measuring $PM_{2.5}$ (4 in Brussels and 8 in Flanders). Using the PM_{10} data from the various stations, maps of the yearly average PM_{10} concentration over the entire country are produced using an "Inverse Distance Weighting" (IDW) interpolation method [Ircel, 2005]. The maps for the years 2004 and 2005 are shown in Figure 3.1. There is clearly a tendency for lower concentrations in 2005 than in 2004. The figure also shows that, for Flanders, the highest levels are noted in the provinces East and West Flanders and in the west of the province of Antwerp; for the Walloon region the highest levels are observed in its northern part, especially in the northern part of the province of Liège. It should be noted that the maps are influenced by the locations of the stations. For example, for East Flanders all stations are in Ghent and to the north of it, where there is a large industrial area, and some stations in the south-eastern part of West Flanders are impacted by nearby industries.



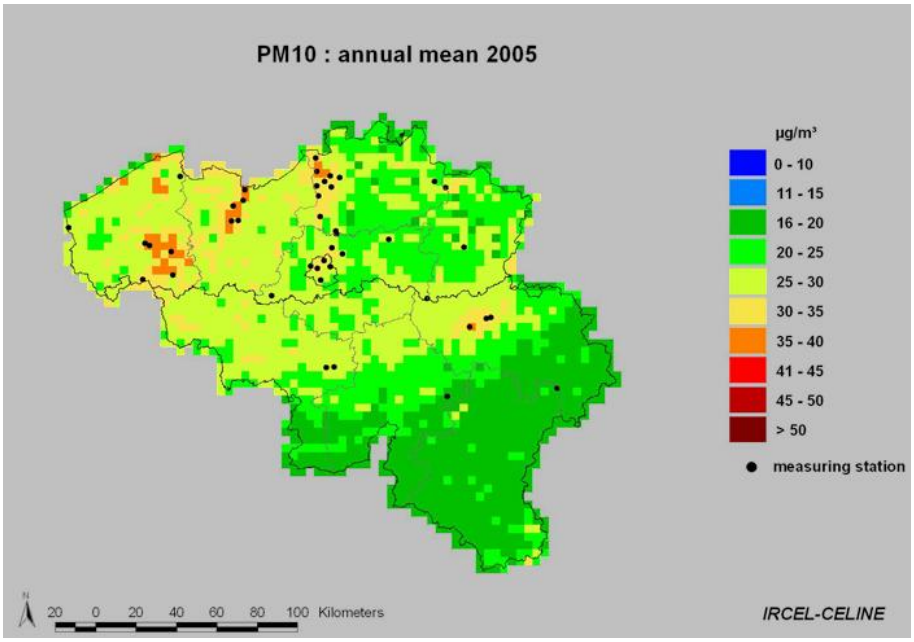


Figure 3.1: Annual mean PM$_{10}$ *concentration data for Belgium in the years 2004 and 2005.*
Flanders is in the north and its provinces are from left to right: West Flanders, East Flanders, Antwerp (top) and Flemish Brabant (around Brussels), and Limburg. The Walloon region is in the south and its provinces are from left to right: Hainaut, Walloon Brabant (top) and Namur (bottom), and Liège (top) and Luxemburg (bottom).

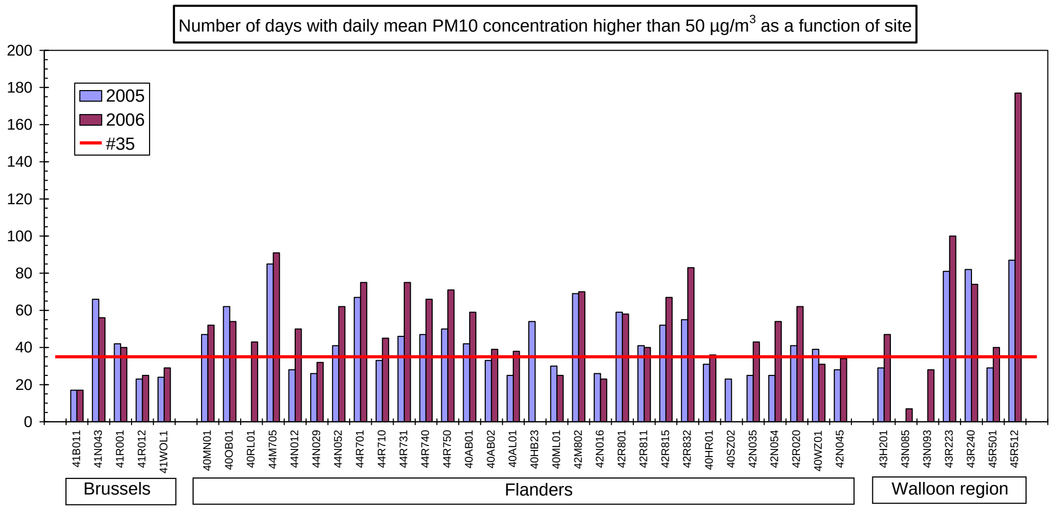


Figure 3.2: Compliance with the EU directive of less than 35 days with daily mean PM$_{10}$ concentration higher than 50 µg/m^3 for the stations in the networks. The data for 2006 are not validated.

With regard to compliance with the limit values of the EU directive: That there should be no more than 35 exceedances of the daily mean PM$_{10}$ concentration of 50 µg/m^3 was not observed for about half of the stations in 2005, and for 2006 the situation was even worse (see Figure 3.2).

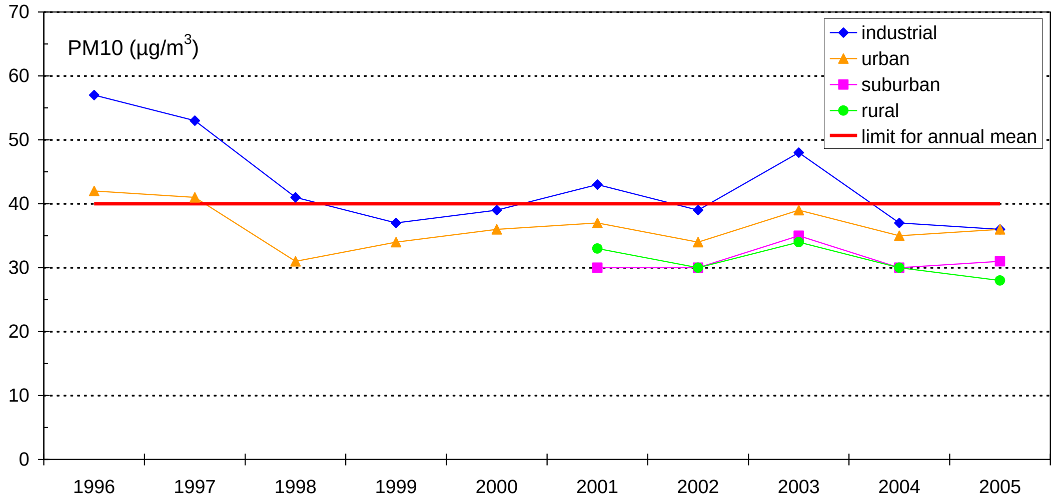


Figure 3.3: Annual mean PM$_{10}$ concentration for different types of stations in the Flemish networks; the EU limit of 40 µg/m^3 (valid since 2005) is also indicated.

There are clearly less problems with observing the EU directive of not exceeding the annual mean PM$_{10}$ concentration of 40 µg/m^3. This is illustrated in Figure 3.3, which presents the annual mean PM10 data for Flanders as a function of year (since 1996) for different types of sites. As to the 31 individual stations within the Flemish networks, in 2004 there were only exceedances in 2 of them and in 2005 in none of them.

3.3 PM concentrations in relation to meteorological conditions

The text in this section 3 (and also in section 4) is entirely based on the Summary of the VMM report “Zwevend stof in Vlaanderen: Periode 2003 en 2004” [VMM, 2005].

Episodes with elevated PM_{10} levels (pollution episodes) coincide mainly with dry weather. Important precipitation is only noted at the end of such episodes. Pollution episodes are mostly characterised by continental air, lower wind speed or both. There are also frequently temperature inversions during such episodes.

Days with ozone smog coincide with periods of elevated PM levels. The enhanced PM levels may be due to increased photochemical activity. On the other hand, during such days we have mostly meteorological conditions which favour, independently of photochemical activity, enhanced PM levels.

Periods with low PM_{10} levels coincide mostly with maritime air. Maritime air is mostly accompanied with precipitation and higher daily averaged wind speeds. Temperature inversions are also absent or rare during such periods.

Elevated PM_{10} levels are mostly noted for low wind speeds. This is even more pronounced for $PM_{2.5}$. The levels of coarse PM ($PM_{10-2.5}$) decrease slightly with wind speed or remain rather constant. The mass ratio of $PM_{2.5}/PM_{10}$ is consequently largest at lower wind speeds. At higher wind speeds a larger fraction of PM_{10} therefore consists of coarser particles. Apparently, for the coarser aerosol, with increasing wind speed there is not only the dilution effect, but also increased resuspension.

During episodes of PM_{10} and ozone smog, the wind speed is also lower than average. Possibly, there is an impact from the wind speed also then.

The pollution roses for PM_{10} and $PM_{2.5}$ indicated (for most of the stations) elevated levels for winds from the NE to SE. This may be caused by the advection of continental air. Pollution episodes often coincide with winds from that direction. When comparing the pollution roses of 2003 and 2004, there is for nearly all stations in 2003 a NNW component, which is not seen in 2004. During the pollution episode of the first half of August 2003, NNW winds were frequent. Most stations exhibit the highest relative contribution of coarse PM for westerly wind sectors.

3.4 Variations in PM levels with season, day of the week, and time of day

For $PM_{2.5}$ lower levels are noted in the summer months than in the winter months. For PM_{10} the same was true in 2004, but the 2003 summer levels were for many stations higher or equal to the winter 2002-2003 and/or winter 2003-2004 levels. The levels of coarse aerosol show less variation with season.

The mass ratio $PM_{2.5}/PM_{10}$ is in winter mostly larger than in summer. Consequently, in winter, $PM_{2.5}$ makes up for a larger fraction of PM_{10}.

During most of the PM_{10} pollution episodes, the mass ratio $PM_{2.5}/PM_{10}$ is larger than the average $PM_{2.5}/PM_{10}$ mass ratio of either winter or summer. The mass ratio $PM_{2.5}/PM_{10}$ is mostly also larger during days with elevated ozone levels than during the other days in summer. The wind speed in summer is lower than that in winter.

At nearly all stations lower levels of PM_{10}, $PM_{2.5}$ and coarse PM are observed in the weekend than during workdays. When comparing the 2 weekend days with each other, the lowest levels are noted on Sundays. The Sunday PM_{10} levels were in 2003 and 2004, on average, 9 and 5 µg/m³ lower than the average weekday levels. For Saturday, the PM_{10} levels were, in 2003 and 2004, 6 and 3 µg/m³ lower than the average weekday levels. In all stations, the contribution from coarse PM to PM_{10} is larger on workdays than in the weekend and larger on Saturday than on Sunday.

The diurnal pattern for PM_{10} and $PM_{2.5}$ is mostly as follows: the levels rise in the morning, subsequently they decrease to exhibit a second maximum in the evening. At nearly all stations higher night levels (during 1 or a few hours) are noted in the weekend than during the workdays. The levels of coarse PM are highest during the day and/or in the late evening. The same applies to the relative contribution of coarse PM to PM_{10}.

3.5 Correlation between PM concentrations of different sites in Flanders in the years 2003 and 2004

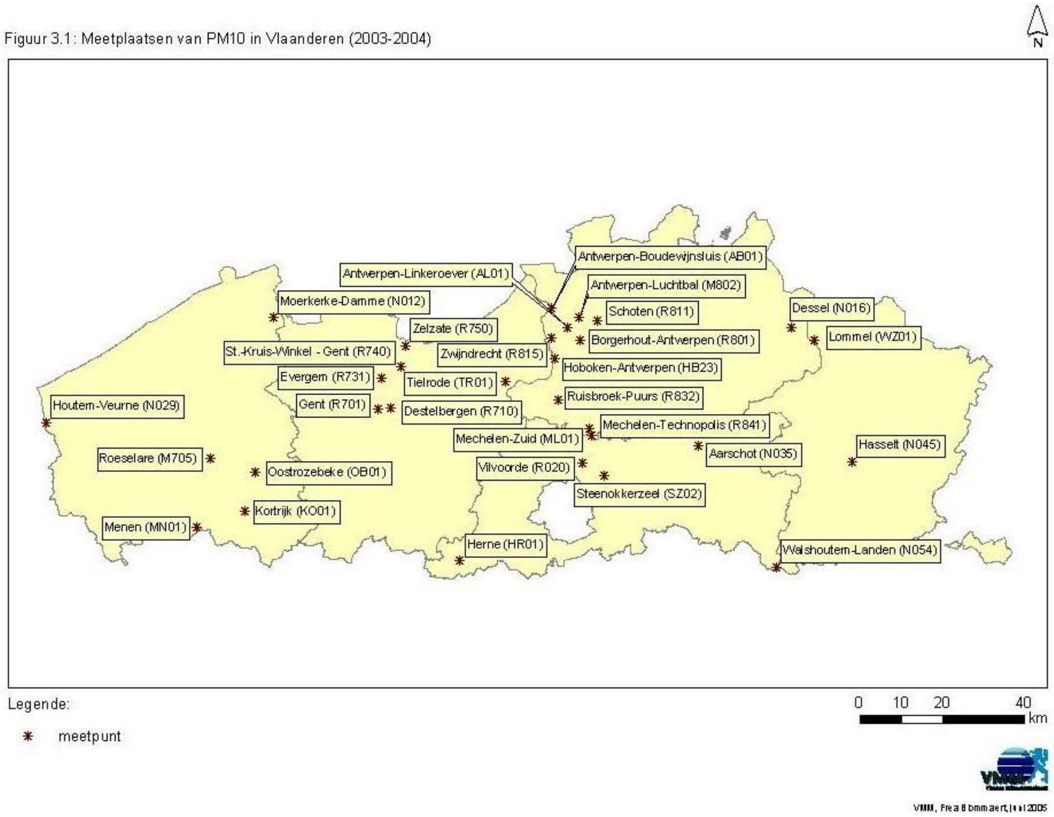


Figure 3.4: Location of the PM_{10} monitoring sites in Flanders.

Table 3.1: Correlation (R^2 values) between the daily averaged PM_{10} data of the monitoring sites in Flanders in 2004; R^2 values larger or equal than 0.60 are highlighted in yellow.

N016	N035	N045	N054	R020	R801	R811	R815	R832	R841	M705	N012	N029	R701	R710	R731	R740	R750	AB01	AL01	HB23	HR01	KO01	ML01	MN01	M802	OB01	SZ02	WZ01	Code	Location
1	0.90	0.85	0.76	0.81	0.76	0.85	0.81	0.77	0.83	0.56	0.71	0.50	0.74	0.77	0.76	0.67	0.59	0.55	0.74	0.56	0.53	0.58	0.72	0.45	0.56	0.27	0.66	0	N016	Dessel
	1	0.86	0.85	0.85	0.76	0.83	0.77	0.85	0.88	0.62	0.69	0.52	0.79	0.81	0.79	0.69	0.58	0.56	0.76	0.61	0.59	0.64	0.76	0.49	0.58	0.29	0.69	0	N035	Aarschot
		1	0.81	0.76	0.74	0.81	0.76	0.77	0.79	0.50	0.62	0.42	0.69	0.74	0.71	0.64	0.53	0.50	0.69	0.61	0.53	0.55	0.69	0.45	0.56	0.26	0.64	0	N045	Hasselt
			1	0.69	0.61	0.66	0.61	0.74	0.79	0.53	0.58	0.50	0.69	0.66	0.67	0.62	0.46	0.41	0.62	0.49	0.52	0.55	0.58	0.41	0.46	0.24	0.58	0	N054	Walshoutem
				1	0.83	0.86	0.83	0.86	0.88	0.62	0.69	0.50	0.79	0.85	0.79	0.69	0.62	0.64	0.83	0.69	0.62	0.69	0.85	0.56	0.67	0.36	0.79	0	R020	Vilvoorde
					1	0.88	0.85	0.81	0.76	0.58	0.71	0.46	0.77	0.81	0.76	0.67	0.64	0.72	0.85	0.69	0.56	0.64	0.81	0.59	0.76	0.41	0.74	0	R801	Borgerhout
						1	0.90	0.81	0.83	0.56	0.76	0.48	0.76	0.86	0.79	0.67	0.66	0.67	0.83	0.67	0.55	0.64	0.83	0.53	0.72	0.36	0.71	0.01	R811	Schoten
							1	0.79	0.76	0.56	0.72	0.41	0.77	0.85	0.77	0.66	0.66	0.64	0.79	0.58	0.49	0.64	0.76	0.50	0.67	0.35	0.66	0	R815	Zwijndrecht
								1	0.86	0.66	0.69	0.55	0.85	0.79	0.79	0.74	0.62	0.62	0.79	0.62	0.53	0.66	0.77	0.56	0.62	0.34	0.66	0	R832	Ruisbroek
									1	0.62	0.67	0.55	0.77	0.81	0.77	0.71	0.58	0.52	0.79	0.59	0.56	0.64	0.77	0.49	0.56	0.30	0.71	0	R841	Mechelen-Techn.
										1	0.69	0.69	0.74	0.67	0.76	0.58	0.49	0.55	0.61	0.37	0.49	0.76	0.55	0.55	0.46	0.35	0.46	0	M705	Roeselare
											1	0.72	0.74	0.79	0.77	0.66	0.67	0.64	0.67	0.52	0.44	0.62	0.66	0.55	0.50	0.31	0.52	0	N012	Moerkerke
												1	0.59	0.53	0.58	0.50	0.44	0.49	0.49	0.37	0.37	0.50	0.45	0.44	0.35	0.24	0.36	0	N029	Houtem
													1	0.86	0.85	0.79	0.66	0.59	0.77	0.56	0.59	0.77	0.72	0.59	0.61	0.41	0.64	0	R701	Gent
														1	0.85	0.81	0.76	0.61	0.79	0.59	0.55	0.77	0.74	0.55	0.62	0.45	0.64	0	R710	Destelbergen
															1	0.72	0.64	0.64	0.79	0.56	0.56	0.77	0.72	0.62	0.62	0.41	0.67	0	R731	Evergem
																1	0.66	0.52	0.71	0.66	0.46	0.59	0.62	0.53	0.52	0.41	0.55	0.03	R740	St.-Kruis-Winkel
																	1	0.59	0.61	0.58	0.34	0.55	0.66	0.55	0.45	0.36	0.44	0	R750	Zelzate
																		1	0.76	0.64	0.40	0.56	0.74	0.58	0.59	0.38	0.61	0.01	AB01	Antwerpen-Boud.
																			1	0.72	0.58	0.72	0.85	0.59	0.71	0.44	0.79	0	AL01	Antwerpen-LO
																				1	0.53	0.46	0.71	0.52	0.59	0.59	0.69	0.04	HB23	Hoboken
																					1	0.59	0.58	0.46	0.64	0.38	0.67	0.04	HR01	Herne
																						1	0.66	0.72	0.59	0.53	0.64	0	KO01	Kortrijk
																							1	0.59	0.66	0.42	0.79	0	ML01	Mechelen-Zuid
																								1	0.49	0.52	0.58	0.01	MN01	Menen
																									1	0.38	0.69	0.01	M802	Antwerpen-Lucht.
																										1	0.44	0.03	OB01	Oostrozebeke
																											1	0.01	SZ02	Steenokkerzeel
																												1	WZ01	Lommel

For both PM_{10} and $PM_{2.5}$ the data of the different stations in Flanders are fairly well correlated with each other. The correlations are in general better for the year 2003 than for 2004. The correlations between the different $PM_{2.5}$ stations are mostly larger than those between the PM_{10} stations. In interpreting the latter observation, one has to be cautious, though, as there are many more PM_{10} stations than $PM_{2.5}$ stations. The correlations between the coarse PM data are lower than those between the PM_{10} or $PM_{2.5}$ data.

To illustrate the good coherence between the PM data, Table 3.1 shows the correlation matrix (R^2 values) between the different PM_{10} sites in Flanders during the year 2004. The location of the sites is shown in Figure 3.4.

The total absence of correlation for the site WZ01 (Lommel) in Table 3.1 is due to soil sanitation works, which converted the surroundings of this site into a bare sand area, which has influenced the measurements at that location in 2004.

Also the correlations between PM_{10} and $PM_{2.5}$ are large. The correlations between PM_{10} and coarse PM and those between $PM_{2.5}$ and coarse PM are substantially lower. There is virtually no correlation between $PM_{2.5}$ and coarse PM.

The correlations between PM_{10} and $PM_{2.5}$ are larger in winter than in summer.

3.6 Sources of PM and contribution from other countries to the PM levels in Flanders

Modelling of the sources of the PM in Flanders is done by the Flemish Institute for Technology (VITO; http://www.vito.be) and the VMM, and is incorporated in the MIRA VMM reports (http://www.milieurapport.be), e.g., Deutsch et al. [2006].

For a particular site, the PM levels are assumed to be made up by various contributions. For example for a kerbside, these contributions are from (a) local traffic, (b) the city, (c) Flanders, (d) foreign countries (including Wallonia), and (e) other sources. The contributions of (b), (c) and (d) are derived from belEUROS model simulations [Deutsch et al., 2004]. As an example, for an urban site in Antwerp in 2002, it was derived that the major contribution (43%) came from foreign countries (including Wallonia), followed by Flanders (28%); the contribution from local traffic was 8%, that from the city 6%, and the non-modelled contribution 14% [Deutsch et al., 2006].

With regard to the atmospheric PM, a distinction has to be made between primary PM, which consists of PM that is emitted by the sources in the particulate form, and secondary PM, which is formed within the atmosphere from gaseous precursors (mainly SO_2, NO_x, NH_3 and volatile organic compounds (VOCs)).

The emissions of primary PM from anthropogenic sources in Flanders, as based on emission inventories, are shown in Figure 3.5. Since 2001 there is no significant decrease anymore in the emissions. In 2005, agriculture is still the major anthropogenic emitter of primary PM_{10}, followed by transport and industry, whereas for primary $PM_{2.5}$ the major anthropogenic emitter is transport, followed by industry and agriculture.

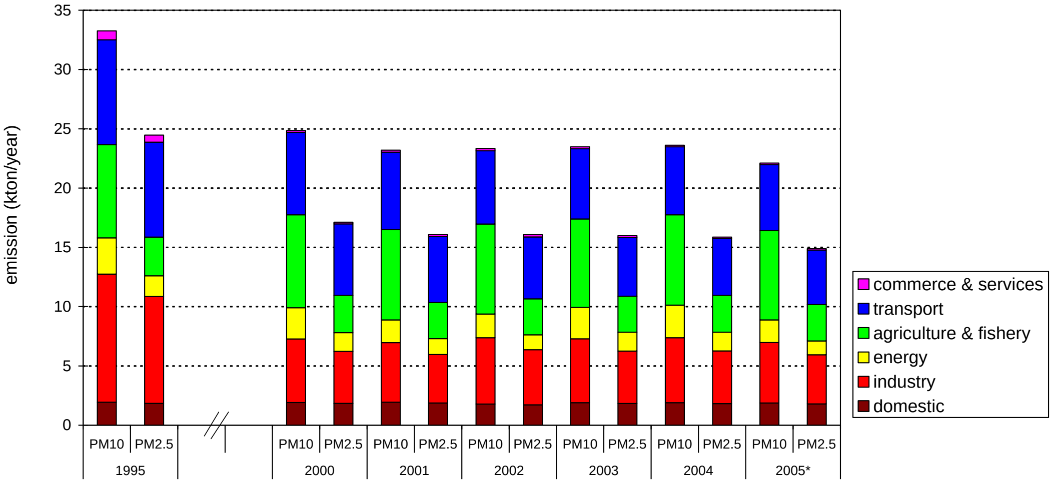


Figure 3.5: Emission of primary PM_{10} and $PM_{2.5}$ in Flanders. Note that the data for 2005 are preliminary.

Using the belEUROS model mentioned above, contributions were not only derived for individual sites, but also for Flanders as a whole. The results obtained for the year 2002 are shown in Figure 3.6.

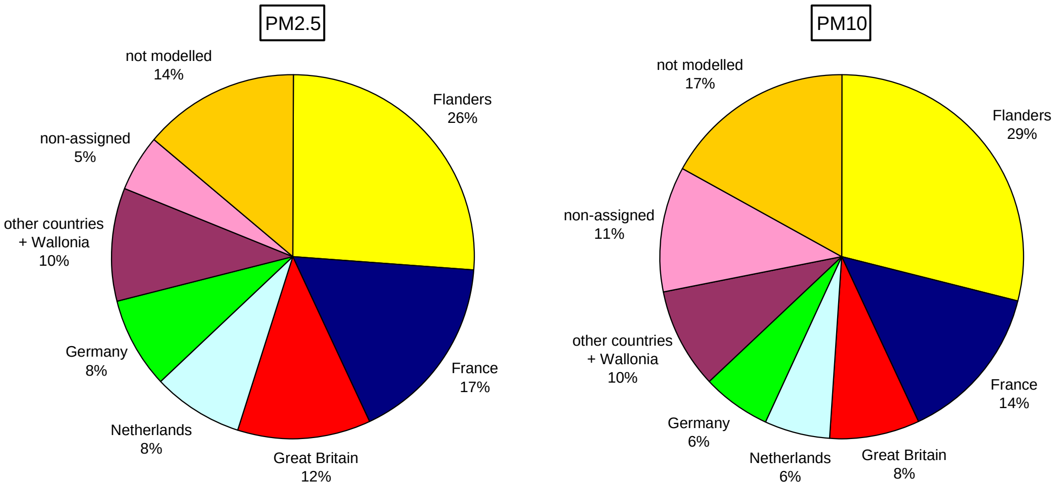


Figure 3.6: Modelled contributions to the $PM_{2.5}$ and PM_{10} levels for Flanders in 2002.

The large contributions from France (17% and 14% for $PM_{2.5}$ and PM_{10}, respectively) are due to the prevailing SW winds and the relatively high emissions in the north of France, close to the border with Belgium. Also the contributions from Great Britain are to a large extent due to the prevailing winds.

However, transboundary transport of PM is not only a matter of transport from other countries to Flanders and Belgium, but also of the latter to other countries. Using belEUROS with emission and meteorological data of 2002, it was estimated what the decrease in annual mean $PM_{2.5}$ concentration would be if there would be no Flemish emissions. The results of this modelling exercise are shown in Figure 3.7. For the neighbouring countries or regions, i.e., the Netherlands, Wallonia and the western part of Germany, shutting off the Flemish emissions would result in a decrease in the annual mean $PM_{2.5}$ level of typically between 0.76 and 2 µg/m^3. For far away countries, such as the Baltic states and the southern parts of the Scandinavian countries, the Flemish emissions still make a difference of 0.11 to 0.25 µg/m^3.

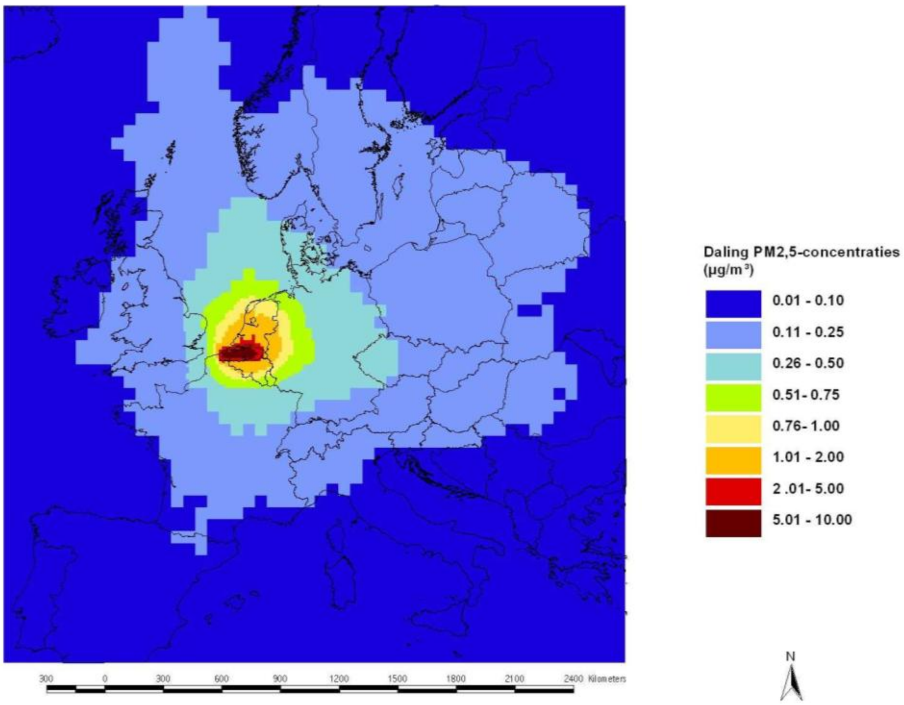


Figure 3.7: Modelled decrease of the $PM_{2.5}$ concentrations in Flanders and Europe when the emissions in Flanders are shut off (calculations for the year 2002).

3.7 Chemical composition and mass closure for PM and sources of major PM components

Determination of the chemical composition of the PM gives clues on its sources and allows one to assess the relative importance of primary and secondary PM. If the chemical analysis includes a measurement of the various major PM components (or of markers for these components), the data can also be used for aerosol chemical mass closure (that is to examine to which extent the sum of the measured components adds up to the gravimetric PM mass). Within the 3 agencies that take care of monitoring networks in Belgium, chemical analysis of the PM on a routine basis is only done for selected compounds, such as heavy metals and polyaromatic hydrocarbons (PAHs). More detailed analyses are performed by the agencies within special studies. The VMM does the latter typically with co-operation of the VITO and Flemish universities, including the University of Antwerp and Ghent University. On the other hand, within the latter two universities, research groups are involved in studies on atmospheric aerosols and their composition, and these groups have their own research projects (independently of the 3 agencies).

Here, I present recent chemical composition and mass closure data for PM that were obtained by my own research group, whereby some of the projects were done in co-operation with others or were even commissioned by the VMM. The PM samples for this work were obtained in campaigns of typically one month duration and in different seasons (typically summer and winter). The sampling sites for the campaigns were the Institute for Nuclear Sciences (INW) in Ghent, the Royal Meteorological Institute (RMI) of Belgium in Uccle (Brussels), and two sites within the city of Antwerp. The INW and RMI sites can be classified as urban background sites, and the two sites in Antwerp as kerbsides. For the INW and RMI sites, the PM samplers (and filters) were provided by my research group and the gravimetric PM measurements and chemical analyses were also done by my group [Wang et al., 2005; Maenhaut et al., 2006b; Chi et al., 2007]. For the campaigns in Antwerp, which was commissioned by the VMM, the PM samplers (and filters) were provided by VITO, the gravimetric PM measurements were also done by VITO, and the chemical composition measurements by my group [Maenhaut et al., 2006a]. From the chemical composition data, the concentrations of the following 8 aerosol types (components) were derived (on an individual sample basis): (1) organic matter [OM; estimated as 1.4 times particulate organic carbon (OC)], (2) elemental carbon (EC), (3) ammonium, (4) nitrate, (5) non-sea-salt sulphate, (6) sea salt, (7) crustal matter, and (8) other non-sea-salt/non-crustal elements [Maenhaut et al., 2002]. Note that only one of these 8 components (i.e., sea salt) is purely natural; EC, ammonium, nitrate, non-sea-salt sulphate and other elements are in Flanders essentially from anthropogenic origin, and OM and crustal matter are probably also mostly due to anthropogenic sources (For the last component there are contributions from road dust and agriculture). The concentrations of the 8 components were then averaged per campaign, the averages were summed up and compared with the average gravimetric PM of the campaign, and the difference is then referred to as unexplained mass. The results for PM_{10} in 7 sampling campaigns are shown in Figure 3.8. Note that the 7 campaigns were not conducted simultaneously.

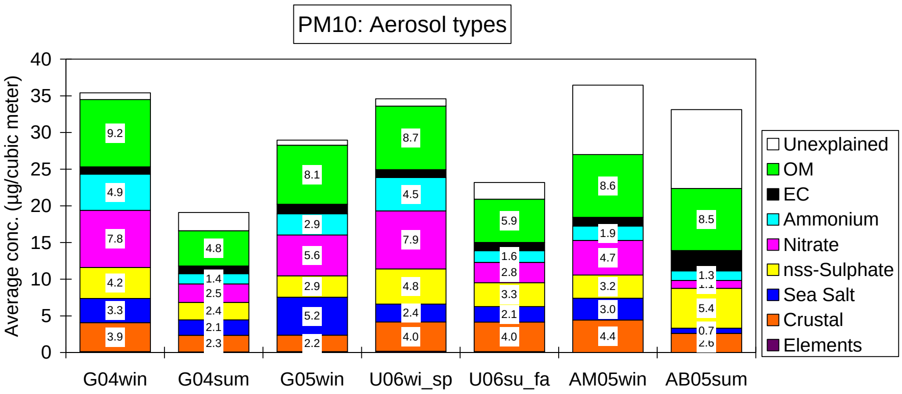


Figure 3.8: Average concentrations of 8 aerosol types in PM_{10} and of the unexplained gravimetric PM_{10} mass during 7 sampling campaigns [G04win, G04sum, and G05win stand for Ghent 2004 winter, Ghent 2004 summer, and Ghent 2005 winter, resp., and the samplings took place at INW; U06wi_sp and U06su_fa stand for Uccle 2006 winter-spring and Uccle 2006 summer-fall, resp., with samplings at RMI; AM05win stands for Antwerp 2005 winter (with samplings at the Mechelse steenweg) and AB05sum for Antwerp 2005 summer (with samplings in Borgerhout)].

Noteworthy is that the unexplained PM_{10} mass is much larger for the two campaigns in Antwerp than in the other 5 campaigns. There were difficulties with the gravimetric PM determinations for these two campaigns. Also the gravimetric PM data were derived from low-volume quartz fibre filters for these 2 campaigns and from low-volume Pall Gelman Teflo and/or Nuclepore polycarbonate filters in the other 5 campaigns and substantially higher PM data for low-volume quartz fibre filters than for the other filter types have been observed before [Maenhaut et al., 2002; Hitzenberger et al., 2004]. It is thought that there may be a substantial positive artefact for the PM data of the low low-volume quartz fibre filters, and therefore the PM data from these filters are considered less reliable.

In agreement with what was indicated in section 4 above, there is a tendency for higher PM_{10} levels in winter than in summer. Particularly for nitrate, much higher concentrations are observed in winter than in summer. This finding is in agreement with the findings of the European Aerosol Phenomenology study [Putaud et al., 2004]. The low nitrate values in summer are due to the fact that the volatile ammonium nitrate is rather in the gas phase than in the particulate phase within the atmosphere during this season (Volatilisation of nitrate from the aerosol collected on the filter may also play a role).

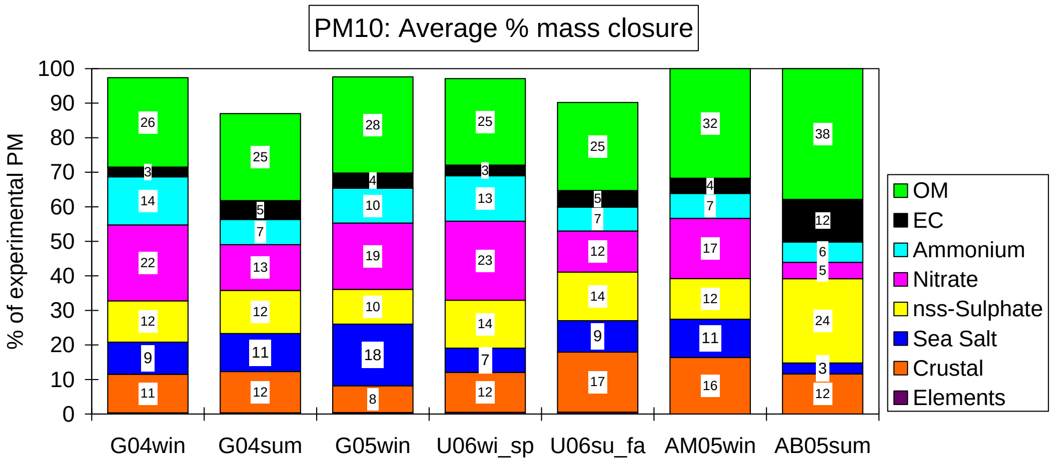


Figure 3.9: Average percentages of 8 aerosol types as % of the mean gravimetric PM_{10} mass (and for the two sites in Antwerp as % of the sum of the components); for additional explanation, see caption of Figure 3.8.

In order to better examine the differences in PM_{10} aerosol composition between the various sites and seasons, the data from Figure 3.8 were expressed as percentage of the gravimetric PM_{10} mass (and for the two campaigns in Antwerp as percentage of the sum of the components). The results of this calculation are shown in Figure 3.9. Even expressed as % instead of as absolute concentrations, there are clearly differences for nitrate between winter and summer, with lower percentages in summer. It further appears that the average PM_{10} aerosol composition is fairly similar for the 4 winter campaigns. The most noteworthy difference is observed for the sea-salt component, with a percentage as high as 18% for Ghent 2005 winter. In Figure 3.8, it can be seen that also the absolute concentration of the sea-salt component was high during this campaign, and that, on the other hand, the average PM_{10} level was on the low side. Examination of the data for the individual samples of this campaign indicated that the percentage contribution of sea salt to the PM_{10} mass was especially high for samples with low PM_{10} mass concentration and was low for samples with high PM_{10} mass concentration [Viana et al., 2007]. The individual data from the various campaigns clearly indicated that sea salt cannot really be invoked as cause for exceedance of the daily PM_{10} EU limit value of 50 $\mu g/m^3$. When such exceedances occur, both the absolute concentrations of sea salt and the percentages of sea salt in the PM_{10} aerosol are quite low.

Figure 3.9 further indicates that there is a large contribution of secondary aerosol to the PM_{10} mass. Ammonium, nitrate and non-sea-salt sulphate are all secondary inorganic aerosol (SIA) components. In winter, the sum of these 3 components accounts, on average, for 40% or more of the PM_{10} mass. For $PM_{2.5}$ even larger percentage contributions of SIA were observed. Also a substantial fraction of the OM may consist of secondary aerosol and thus be secondary organic aerosol (SOA), especially in summer. The total contribution of secondary aerosol is likely over 50% in all seasons.

The SIA components in the PM in Belgium are undoubtedly predominantly from anthropogenic origin, whereby the precursor gases (NH_3, NO_x and SO_2) are not only emitted within Belgium, but also in neighbouring countries and in the rest of Europe. As far as the emissions in Flanders are concerned, agricultural activities, in particular intensive cattle breeding and storage and spread of animal manure, is the major source of NH_3; NO_x originates mainly from combustion processes associated with traffic, electricity production and industry (which contributed with 47%, 14%, and 21%, resp., of the total NO_x emission in 2005); and SO_2 is predominantly due to the combustion of fossil fuels (oil and coal), with 78% of the total SO_2 emissions in 2005 originating from industry, refineries and electricity production combined [Anonymous, 2005; VMM, 2006].

In contrast to SIA, the sources of the OM in the PM in Belgium are much less clear and it is also highly uncertain which fraction of the OM is SOA. While a substantial fraction of the primary OM (and most of the EC) is likely derived from traffic, other anthropogenic sources and emissions from the biosphere (especially the vegetation) also contribute to both the primary OM and SOA. Several particulate organic compounds within the PM are quite useful for identifying certain sources or source types (or even the formation of SOA) and in assessing their contribution. In a co-operation between the research group of Magda Claeys of the University of Antwerp and my own team, work has been (and is being) done on these topics [Kubátová et al., 2002; Zdráhal et al., 2002; Pashynska et al., 2002; Claeys et al., 2004, 2007]. By using levoglucosan as a tracer, it was estimated that wood burning was responsible for 35% of the particulate OC in PM_{10} in Ghent during winter 1998 [Zdráhal et al., 2002]. By measuring other saccharidic compounds, including arabitol, mannitol, fructose and sucrose, in PM_{10} samples from winter and summer campaigns at Ghent [Pashynska et al., 2002], it was found that their concentrations were much higher during summer than during winter, which indicates larger concentrations of primary biogenic aerosols (e.g., plant pollen and fungal spores) during summer. Currently, work is being done on the use of particulate-phase photo-oxidation products of biogenic VOCs, in particular isoprene [Claeys et al., 2004] and monoterpenes [Claeys et al., 2007], to estimate the contribution of biogenic SOA to the OM.

Acknowledgments

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4 PM trends in the Czech Republic

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4.1 Abstract

The aim of this study is the assessment of 1996-2005 PM data from the Czech air quality monitoring network. Gradual decline in emissions of PM after 1989 in the Czech Republic was caused by general decrease of industrial production and reduction in electricity generation in conventional thermal power stations. In the beginning of new millennium the decreasing trend was interrupted and the emissions slightly increased. Decreasing trend of PM_{10} concentration was registered in the period 1996-1999 at all types of stations (traffic, urban, suburban, rural and regional), but this trend was stopped in the beginning of this century and the concentrations slightly increased and the differences between types of stations became smaller. The most serious situation is in the Moravian-Silesian region. This is caused by the fact that in this area, in addition to transport and local sources of PM significant contribution is made by further emission sources (metallurgy, fuel processing). Regional transfer from Poland (heavily industrialized Katowice region) is also very significant. The PM_{10} concentrations in winter are higher than in the summer, the most significant annual variation was found at traffic stations. In 2005 measurements of $PM_{2,5}$ began at 25 localities. The results show significant contribution of $PM_{2,5}$ fractions to air pollution situation in the Czech Republic. The proposed annual air pollution limit would be exceeded in more than 10 sites, mainly in the Moravian-Silesian region. The ratio between $PM_{2,5}$ and PM_{10} shows certain seasonal course that is connected with the seasonal character of several emission sources. Emissions from combustion sources show higher shares of $PM_{2,5}$ fractions than emissions from agriculture and reemission during dry and windy weather. The fraction ratio ranged between 0,69 and 0,85 in 2005. The highest PM_{10} concentrations at the background station Košetice (EMEP, GAW) are measured when the air masses from eastern directions predominate and the lowest values are measured when they come from the west.

4.2 Introduction

The impact on human health by atmospheric particles was recognized to be one of the most serious environmental problems in the last decade. Aerosols also affect the radiative balance and thus contribute to climate change. The preliminary assessment by WHO-EMEP indicated a significant association between the long range component of particulate matter, measured as the total mass of PM_{10}, and a wide range of health damaging effects. The most recent review based on a number of more recent panel studies has concluded that fine particles ($PM_{2.5}$) are more hazardous in terms of mortality and cardiovascular and respiratory endpoints.

The particles contained in the ambient air can be divided into primary and secondary particles. The primary particles are emitted directly into the atmosphere, both from natural and anthropogenic sources. Secondary particles are mostly of anthropogenic origin and are creating by oxidation and consequent reactions of gaseous compounds in the atmosphere. Similarly as in the whole Europe, most emissions in the Czech Republic are of anthropogenic origin, the main sources include: transport, power stations, combustion sources, fugitive emissions from industry, loading/unloading, mining and building activities.

4.3 Monitoring network and measurement methods

National ambient air pollution monitoring network in the Czech Republic is operated by Czech Hydrometeorological Institute (CHMI). This network is continuously upgraded in accordance with the requirements of EU Directives and Act No. 86/2002 on Air Quality Control.

The concentrations of particulate matter were measured since the eighties as TSP (total suspended particulates). The measurement of PM_{10} fraction was started in 1996. The PM_{10} monitoring network in 2005 is presented in Figure 4.1.

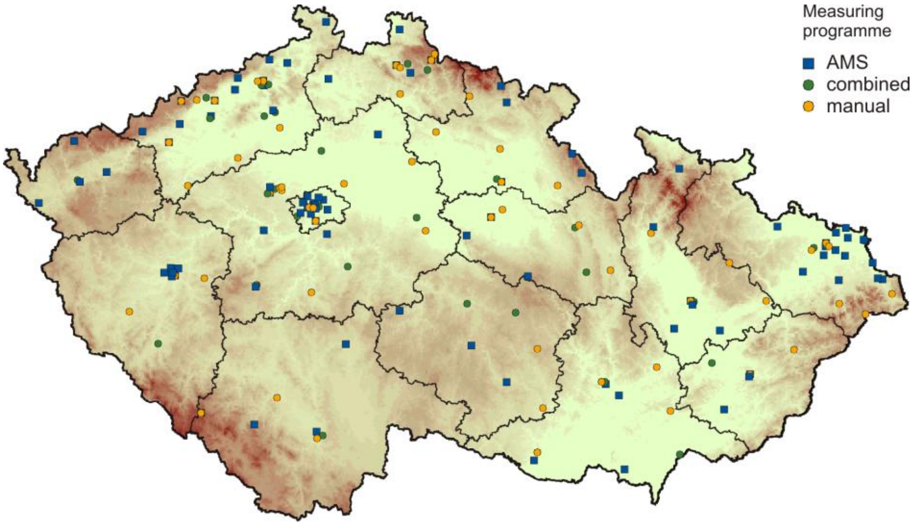

Figure 4.1: PM_{10} station network in the Czech Republic, 2005.

In 2005 measurements of the fine fraction of suspended particles ($PM_{2,5}$) began in 25 localities (Figure 4.2).

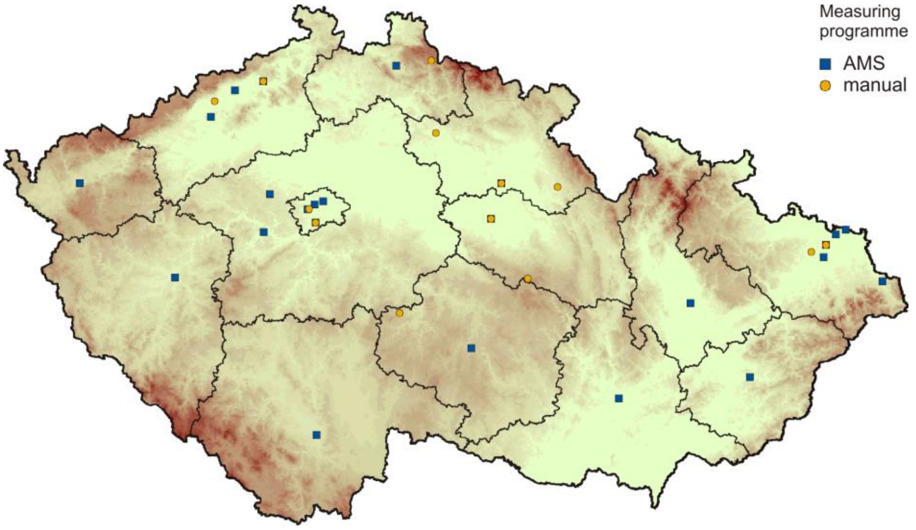

Figure 4.2: $PM_{2,5}$ stations in the Czech Republic, 2005.

In the CHMI monitoring network two ways of PM detection are used:

Radiometry: It stands on beta-ray absorption in a sample captured on filtering material, which is proportional to the mass of the captured suspended particulate matter, gives the information on its concentration.

Gravimetry: The sample is taken through continuous filtration of ambient air on selected filtering material (Millipore filters 1,2 µg with diameter 47 mm are used for detecting PM_{10} and $PM_{2,5}$). The difference between the weight of the filter prior to and after the exposure is determined gravimetrically.

Selected metals are analyzed from the samples (arsenic, cadmium, manganese, copper, nickel and lead). Filters are mineralized at 220°C in solution of nitric acid and hydrogen dioxide in high pressure microwave digestion system before chemical analysis. The analysis is carried out on the inductively coupled plasma – mass spectrometry system. For requirements of QA/QC is along the analysis also measured (by the same way mineralized) certified reference material NIST 1648 – Urban Particulate Matter – and its results are monitored in control charts.

Analytical method is periodically controlled in interlaboratory comparison tests. The whole process including sampling is accredited by the Czech Institute for Accreditation. Parallel samplers are installed at two manual stations for quality control purposes of sampling, weighting and analysis.

4.4 Emissions

Based on the total annual emissions data of the principal pollutants between 1980 and 2004, TSPs was (together with sulphur dioxide) obviously the pollutant that caused the most serious emissions in that period. Gradual decline in TSP emissions after the political changes in the beginning of the nineties was caused by general decrease of industrial production, by the reduction in electricity generation in conventional thermal power stations and increasing electricity generation in nuclear power plants. Between 1990 and 1999, total suspended particles emissions dropped by nearly 88%. Since 2001 Czech emission inventory contains tyre and brake wear emissions and road abrasion emissions. Due to this fact emissions have been slightly increasing since in the period 2001-2005 (Figure 4.3).

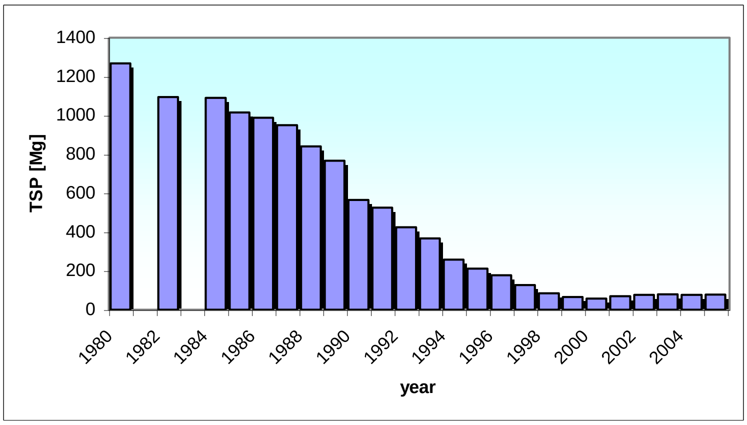

Figure 4.3: Trend of TSP emissions in The Czech Republic 1980-2005.

4.5 PM trends in the Czech Republic

Decreasing trend of PM_{10} concentration was registered in the period 1996-1999 at all types of stations (Figure 4.4). This trend was stopped in the beginning of this century and the concentrations slightly increased and the differences between types of stations became smaller (with an exception of regional stations). The increase of PM_{10} concentrations at rural stations was caused mainly due to combustion practices of inhabitants in small villages. Hand in hand with increasing prices of oil and natural gas, the people in villages and small towns tend to return back to traditional cool and wood burning.

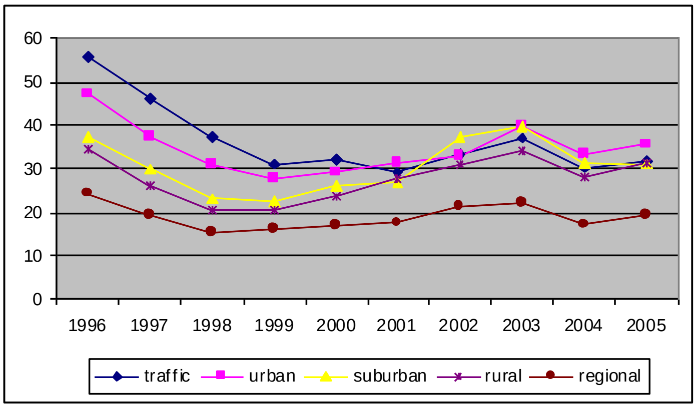

Figure 4.4: Trend of PM_{10} concentrations in the Czech Republic (1996-2005) at different types of stations ($\mu g.m^{-3}$).

The most serious air pollution situation caused by suspended particles is in the Moravian-Silesian region (Ostrava-Karviná agglomeration). This is caused by the fact that in this area, in addition to transport and local sources of PM significant contribution is made by further emission sources (metallurgy, fuel processing). Air pollution of this area is also influenced by regional transfer from Poland (heavily industrialized Katowice region). The PM_{10} trend in this region was quite different in comparison with other industrial regions in the Czech Republic (Figure 4.5). The Moravian - Silesian region on the Czech-Polish border belongs to the most polluted regions by PM in Europe.

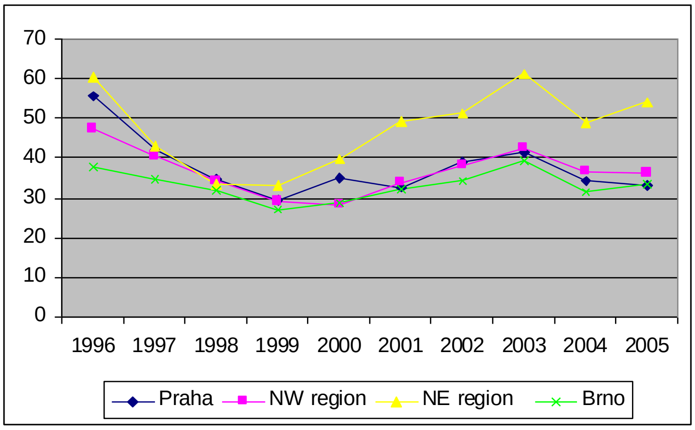

Figure 4.5: Trend of PM_{10} concentrations in agglomerations ($\mu g.m^{-3}$).

The PM_{10} concentrations in winter are higher than in the warm period (in average about 20 µg.m^{-3}). The most significant annual variation was found at traffic stations; on the other hand almost no annual variation was found at regional stations (Figure 4.6).

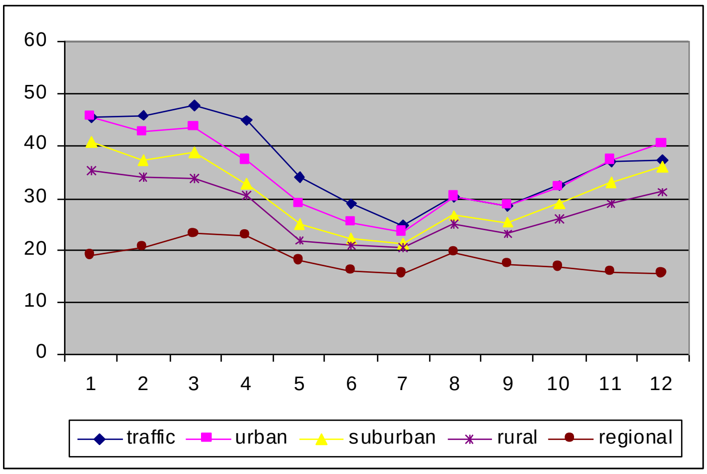

Figure 4.6: *PM_{10} annual variation in the Czech Republic (1996-2005) at different types of stations (µg.m^{-3}).*

Summer level of air pollution caused by PM_{10} is similar in all main agglomerations, the difference between Moravian-Silesian region, where critical levels are exceeded in winter season, and the other agglomerations, is significant (Figure 4.7.).

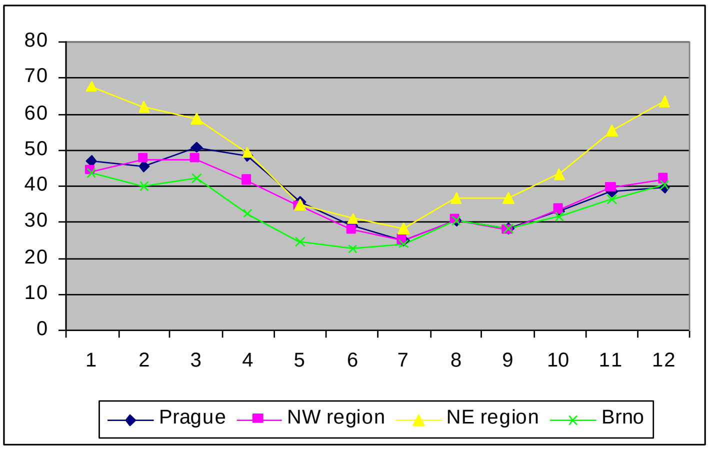

Figure 4.7: *PM_{10} annual variation in agglomerations (µg.m^{-3}).*

The PM_{10} concentrations at urban sites show a distinct diurnal variation with peaks in rush hours in the morning and in the evening. This variation is caused by daily emission changes (stimulated by traffic, but also by local heating) and dispersion conditions. The situation at suburban stations is similar to urban conditions, but diurnal variation is not so significant. Only minimal daily variation was found at the regional scale (Figure 4.8). Figure 4.9 clearly shows much higher morning and evening PM_{10} concentrations in Ostrava-Karviná region compared to other agglomerations.

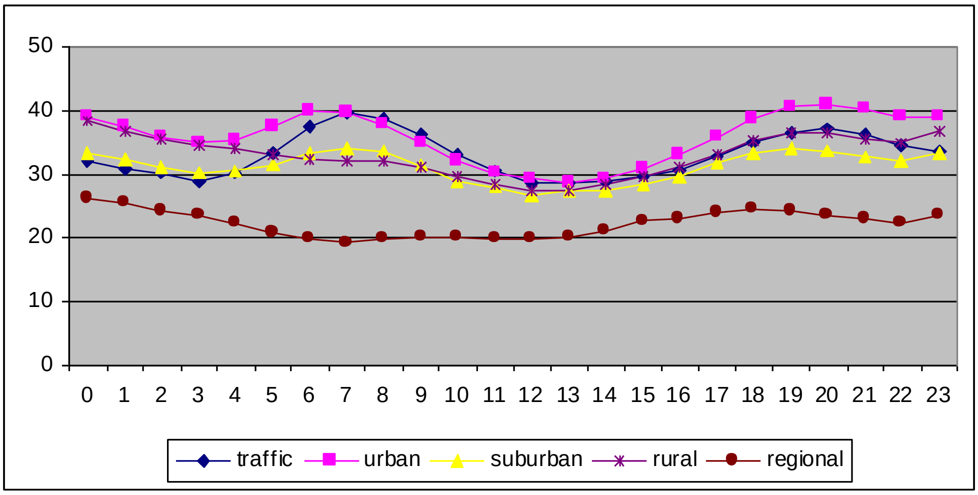

Figure 4.8: PM_{10} Diurnal variation at different types of stations ($\mu g.m^{-3}$).

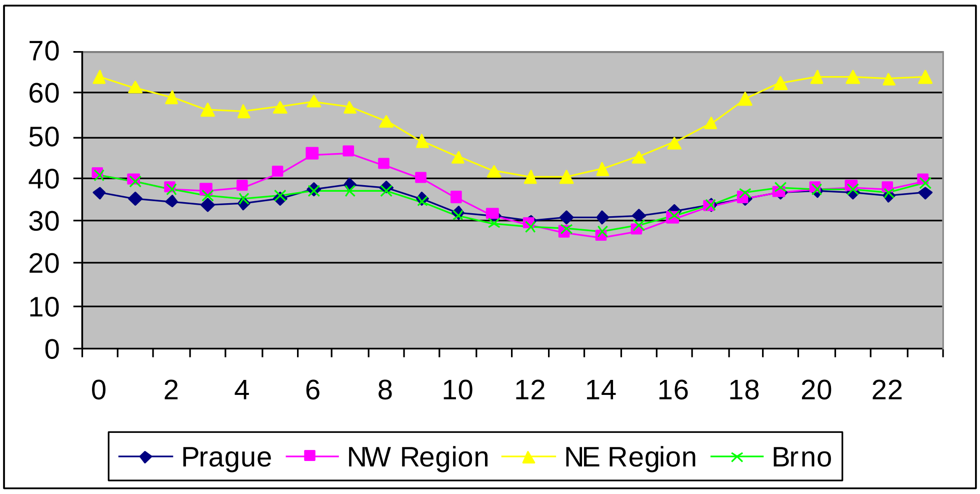

Figure 4.9: PM_{10} diurnal variation in agglomerations ($\mu g.m^{-3}$).

In 2005, pursuant to EU recommendations ensuing from 199/30/EC Directive, the monitoring of the fine fraction of suspended particles ($PM_{2,5}$) began in 25 localities. The prevailing source of $PM_{2,5}$ fractions are combustion processes, producing secondary particles originating as a result of chemical reactions between the gaseous compounds and condensation of hot gases and vapour. The results show significant contribution of $PM_{2,5}$ fractions to air pollution situation in the territory of the Czech Republic. When comparing the results with the proposed annual air pollution limit value, the limit value would be exceeded in more than 10 sites, mainly in the Ostrava agglomeration region. Annual variation at different types of stations is more significant that in the case of PM_{10} (Figure 4.10).

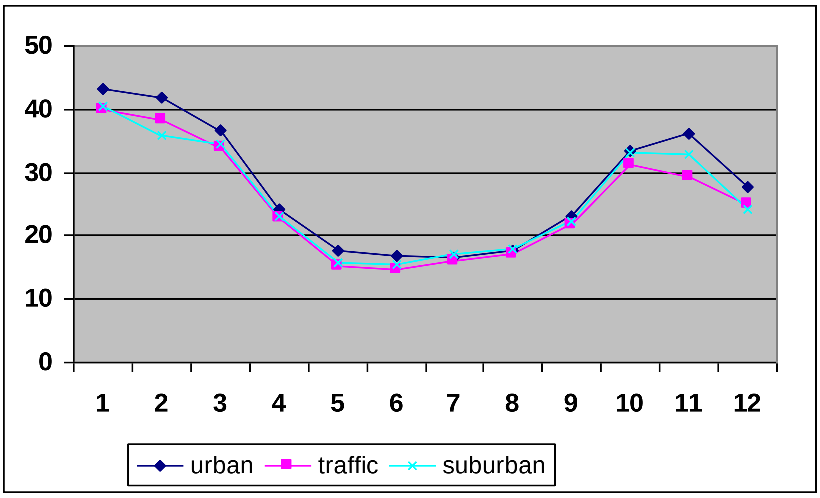

Figure 4.10: PM$_{2,5}$ annual variation in the Czech Republic (2005) at different types of stations (µg.m^{-3}).

The seasonal course of the ratio between PM$_{2,5}$ and PM$_{10}$ (Figure 4.11) shows certain seasonal course that is connected with the seasonal character of several emission sources. Emissions from combustion sources show higher shares of PM$_{2,5}$ fraction than for instance emissions from agriculture and reemission during dry and windy weather. Consequently, heating in the cold period can cause the higher share of PM$_{2,5}$. The fraction ratio ranges between 0,69-0,85 in 2005. The 2004-2005 ratio at the EMEP station Košetice is 0,87.

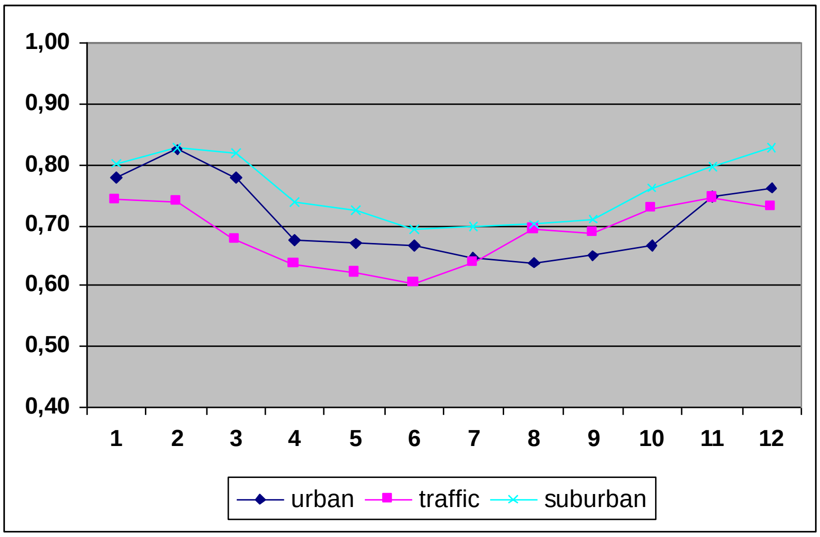

Figure 4.11: The seasonal course of the ratio between PM$_{2,5}$ and PM$_{10}$ in 2005 at different types of stations.

PM$_{2,5}$ diurnal variation displays the same patterns as by PM$_{10}$ (Figure 4.12). The difference between the situation in Ostrava-Karviná region and agglomerations is even higher than in the case of PM$_{10}$ (Figure 4.13).

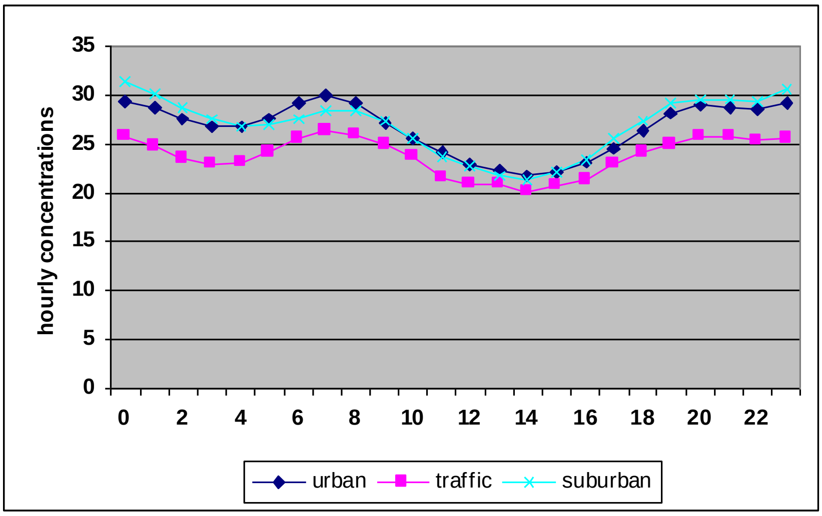

Figure 4.12: PM$_{2,5}$ diurnal variation at different types of stations (µg.m^{-3}).

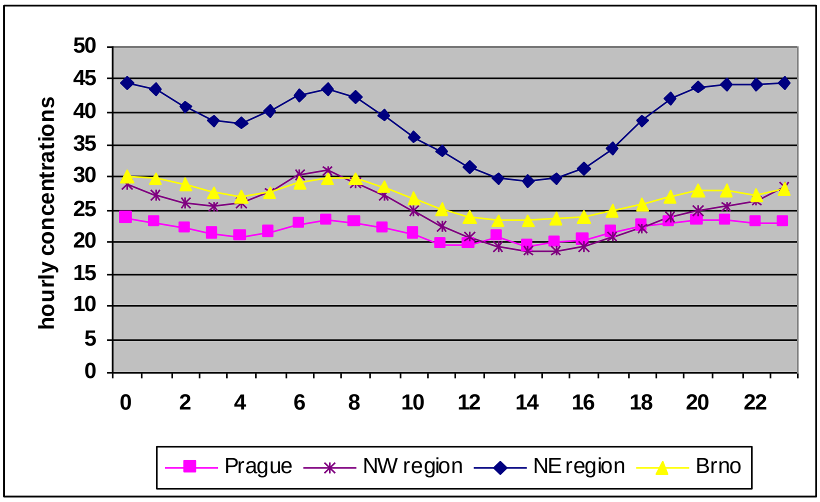

Figure 4.13: PM$_{2,5}$ diurnal variation in agglomerations (µg.m^{-3}).

4.6 Critical levels

Air pollution caused by PM$_{10}$ fraction exceeded limit values in the whole period 2000-2005. In 2005 the limit values for 24-hour PM$_{10}$ concentrations were exceeded in 35% of the territory (Figure 4.14). The limit value for annual concentration was exceeded in 1,5% of territory (Figure 4.15). In the areas, where the PM$_{10}$ concentrations exceed the air pollution limit values, live more than 65% of the population.

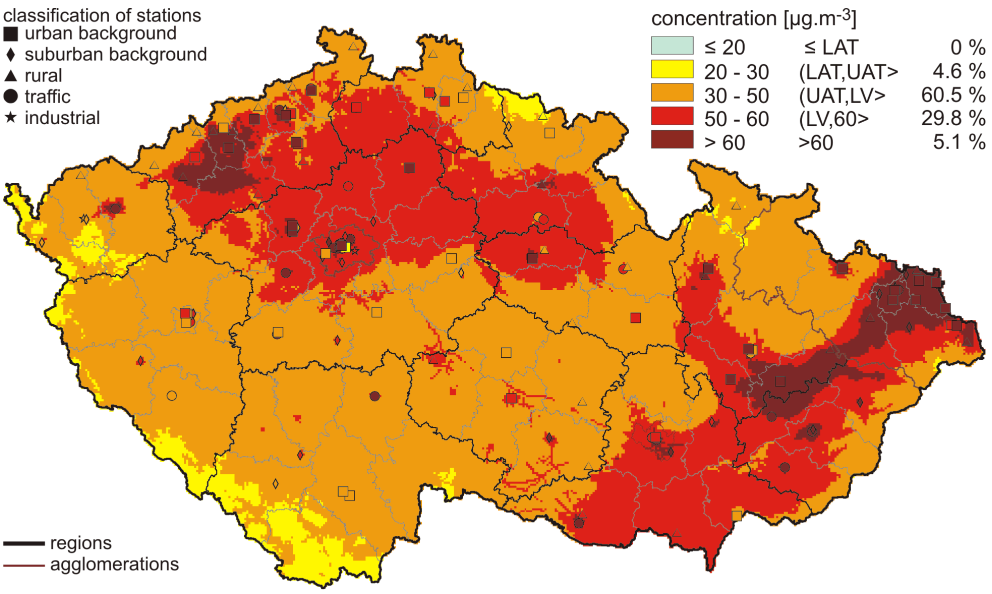

Figure 4.14: Field of the 36th highest 24-hour concentration of PM$_{10}$ in 2005.

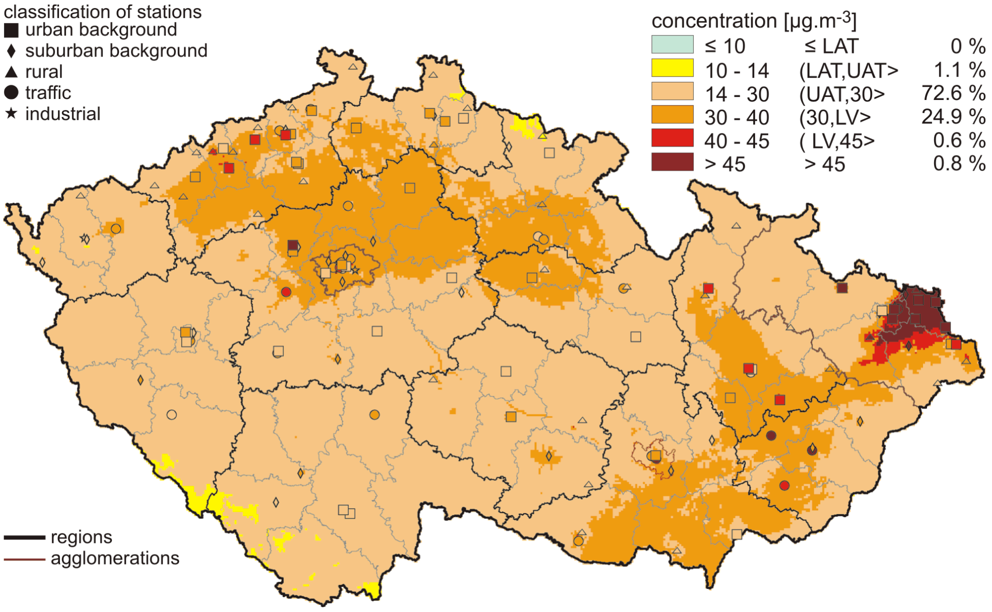

Figure 4.15: Field of annual average concentrations of PM$_{10}$ in 2005.

4.7 Meteorological aspects

2D trajectories (NILU, 2002-2006) were used for sector analysis of PM$_{10}$ data from EMEP and GAW station Košetice Observatory. The highest concentrations are measured when the air masses from eastern directions predominate and the lowest values are measured when they come from the west (Figure 4.16)

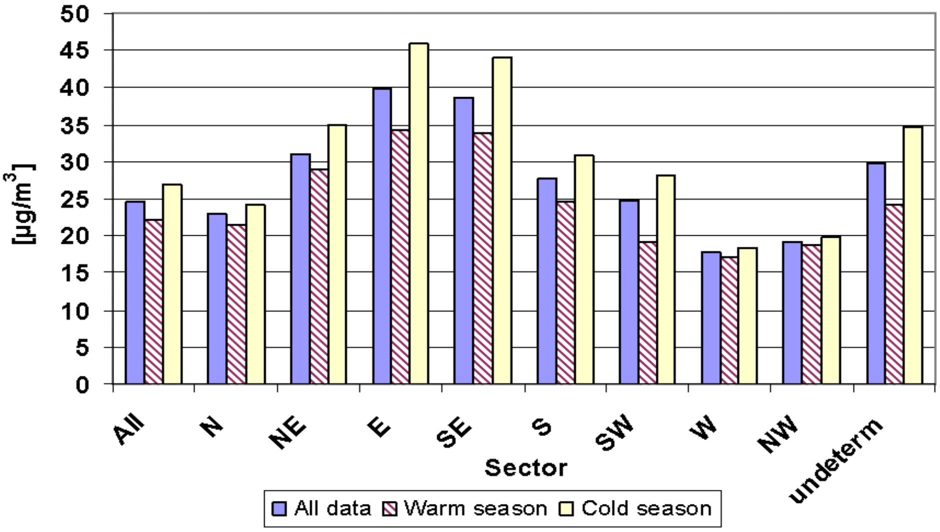

Figure 4.16: Sector distribution of PM_{10} concentrations (Košetice 1995-2004, $\mu g.m^{-3}$).

Trend evaluation of sector analyses shows that the highest concentrations and year by year variability were measured in the air masses from eastern directions in the whole period under review (Figure 4.17). The increase after 2000 corresponds with the rising trend in Moravian-Silesian region located in this direction.

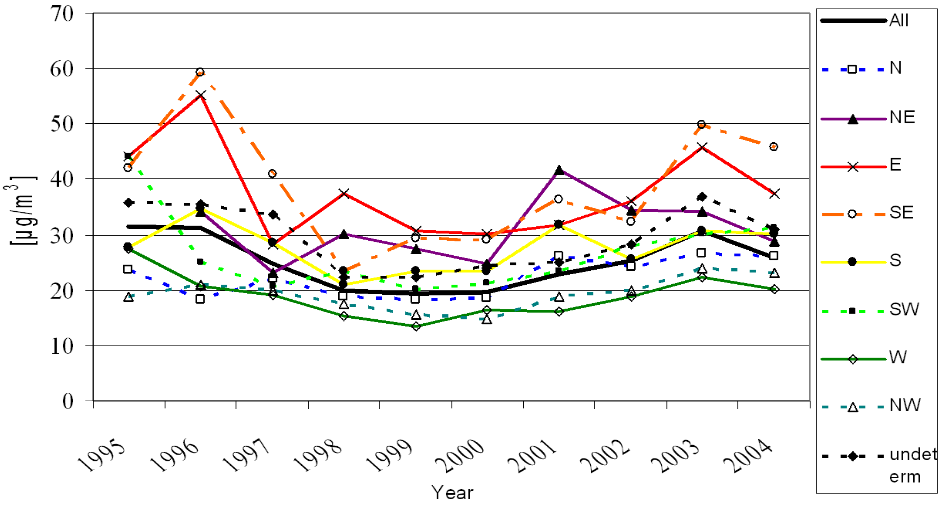

Figure 4.17: Sector distribution trend of PM_{10} concentrations (Košetice 1995-2004, $\mu g.m^{-3}$).

Significant difference was found between trends in summer and winter period. While the trend of winter concentrations is comparable with general trend (Figure 4.18), there is a rapid increase of summer concentrations throughout the period under review, especially when in the air masses with origin in eastern sectors (Figure 4.19).

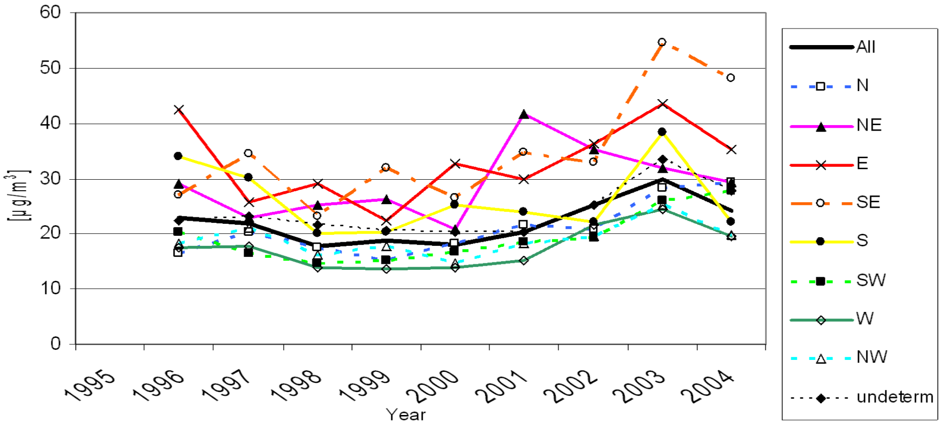

Figure 4.18: Sector distribution trend of PM_{10} concentrations – warm period (Košetice 1995-2004, μg.m^{-3}).

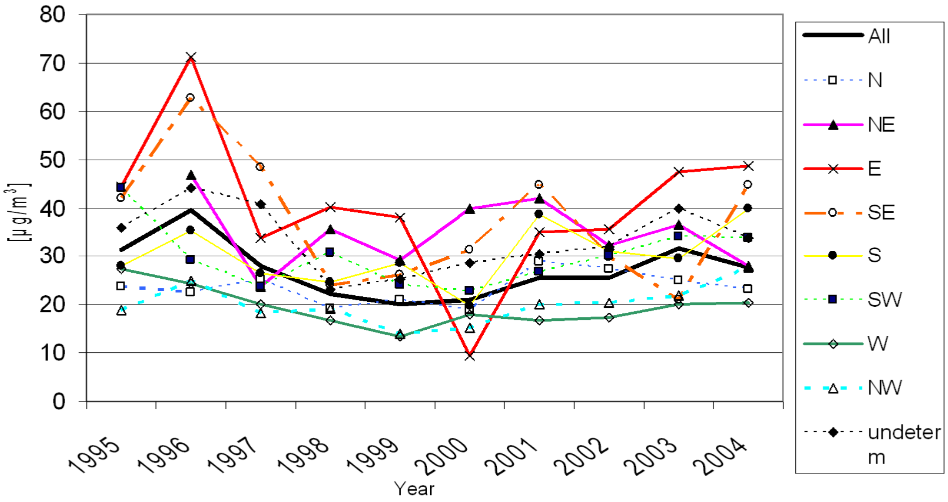

Figure 4.19: Sector distribution trend of PM_{10} concentrations – cold period (Košetice 1995-2004, μg.m^{-3}).

Figure 4.20 and Figure 4.21, based of the Košetice data, show the relation of PM data and meteorological conditions. The highest concentrations are measured in calm and dry periods.

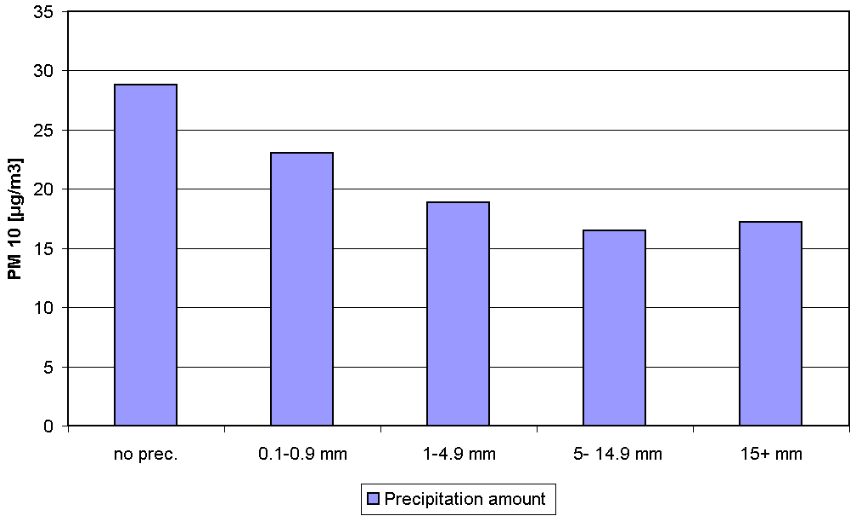

Figure 4.20: PM_{10} concentrations relation to precipitation amount (Košetice 1995-2005).

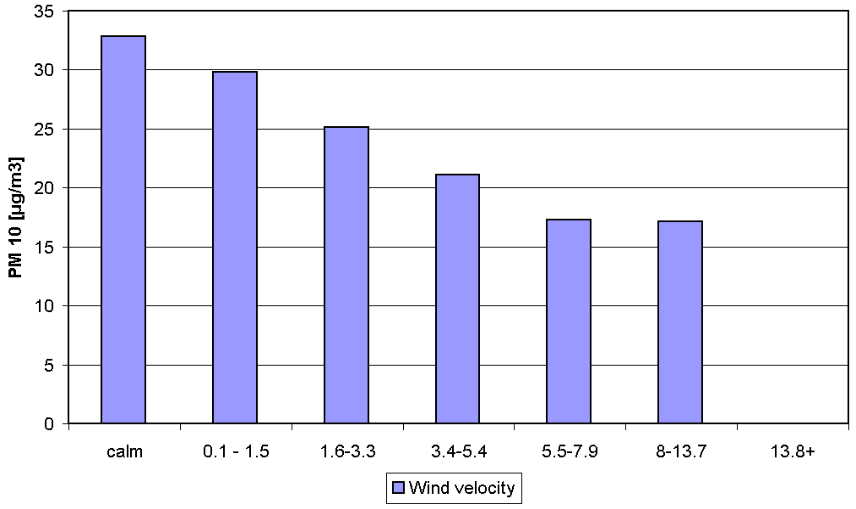

Figure 4.21: PM_{10} concentrations relation to wind velocity (Košetice 1995-2005).

4.8 Chemical composition

Selected metals are analyzed from the PM_{10} samples (arsenic, cadmium, manganese, copper, nickel and lead). Figure 4.22 shows the generally decreasing trend of lead concentrations in PM_{10} in the Czech Republic. The lead levels at the majority of The Czech Republic area do not reach the limit value in the long terms.

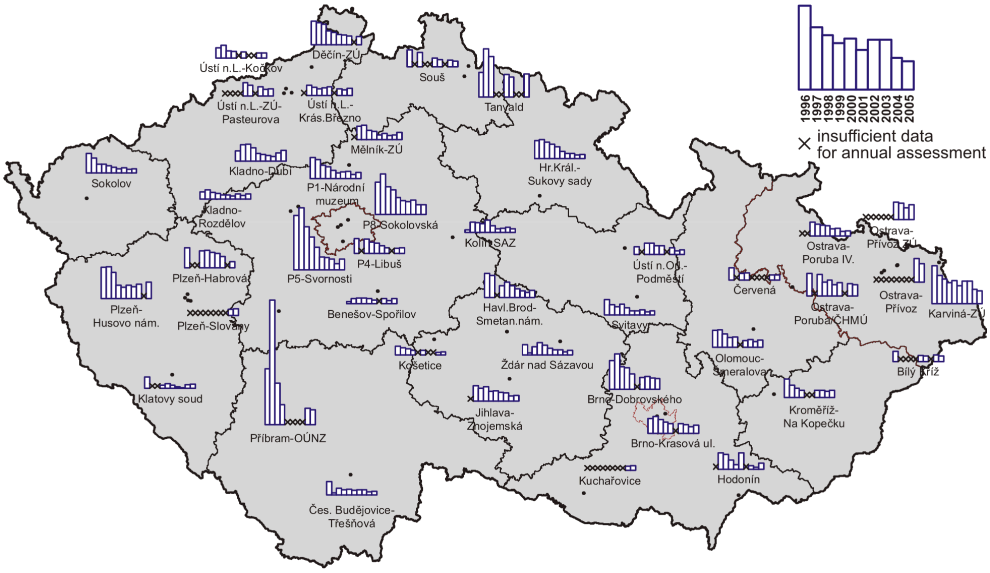

Figure 4.22: Mean annual concentrations of lead in PM_{10} in the ambient air 1996-2005.

The heaviest load of cadmium concentrations is recorded in Northern Bohemia (Liberec region), where the mean annual concentrations reach high levels in the long term (Figure 4.23). This situation is caused first of all due to the emissions from local glassworks.

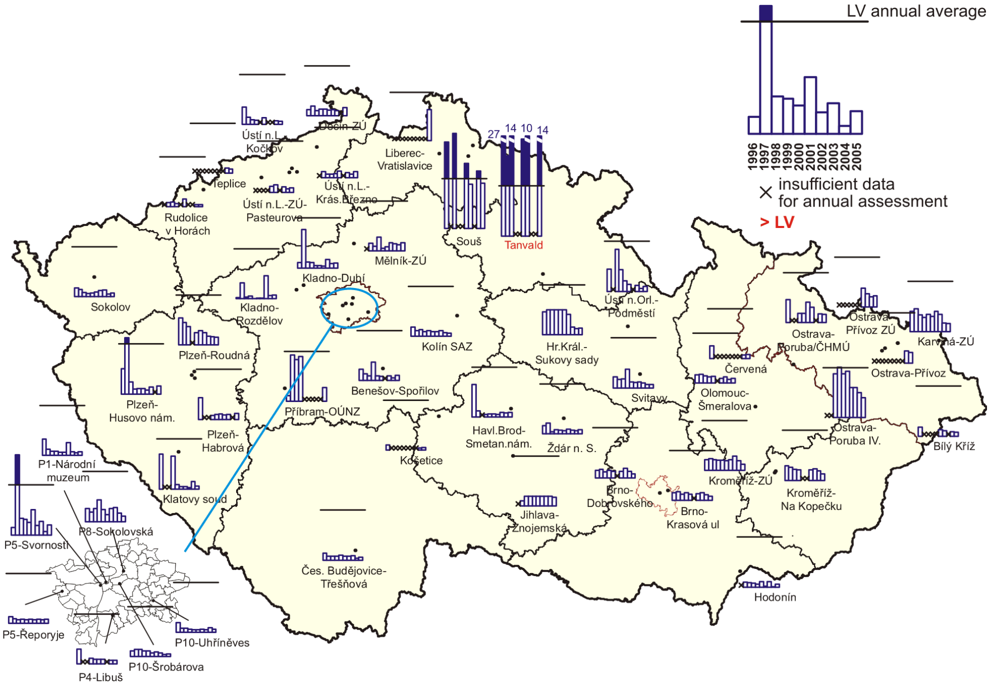

Figure 4.23: Mean annual concentrations of cadmium in PM_{10} in the ambient air 1996-2005.

In 2005, heavy metals were analyzed also from the $PM_{2,5}$ samples at a limited number of sites. The first results show that the lead concentrations in $PM_{2,5}$

samples at the regional level, represented by EMEP and GAW station Košetice (6-7 ng.m^{-3}) is only slightly lower than at suburban background of Prague (8-10 ng.m^{-3}). The highest values are measured in Ostrava – Karviná agglomeration (40-55 ng.m^{-3}). In the case of cadmium, the results from EMEP station and suburb of Prague are on very similar level (0,2-0,3 ng.m^{-3}), the concentrations in Ostrava – Karviná exceed 1 ng.m^{-3}.

4.9 Comparison of measured data with model results

Following results were used for comparison:

1. 2004 PM_{10} data from air pollution monitoring network in the Czech Republic. Values were spatially interpolated using interpolation techniques including dispersion model.
2. 2004 SYMOS'97 model outputs (only primarily emissions used)
3. 2000 EMEP model outputs

Model SYMOS'97 (System for Modelling of Stationary Sources) is the reference method for dispersion studies processing in the Czech Republic (Gauss model modified for using in complex terrain).

Mean 2004 annual PM_{10} concentrations (Figure 4.24) ranged from 20 to 30 µg.m^{-3} in the majority of the Czech Republic area. Higher values (40 – 60 µg.m^{-3}) were registered especially in the Moravian-Silesian region and also in other industrial agglomerations (Northern Bohemia, Prague). SYMOS'97 model results (Figure 4.25) identify as the most polluted areas Central Bohemia and Moravian-Silesian region. Calculated concentrations in these regions reach 10 µg.m^{-3}. In the rest of the Czech Republic area the concentrations drop bellow 4 µg.m^{-3}.

Only primarily emissions of PM from stationary sources and mobile sources originated from exhaust gases were used in model. On the other hand, emissions of secondary particles, wear tire and brake were not included.

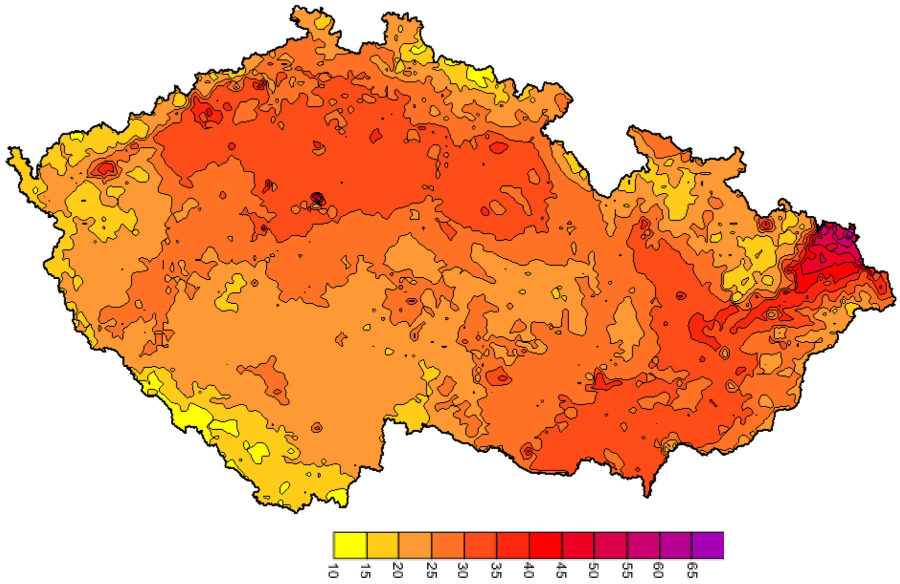

Figure 4.24: 2004 PM_{10} concentrations (µg.m^{-3}) – monitoring network.

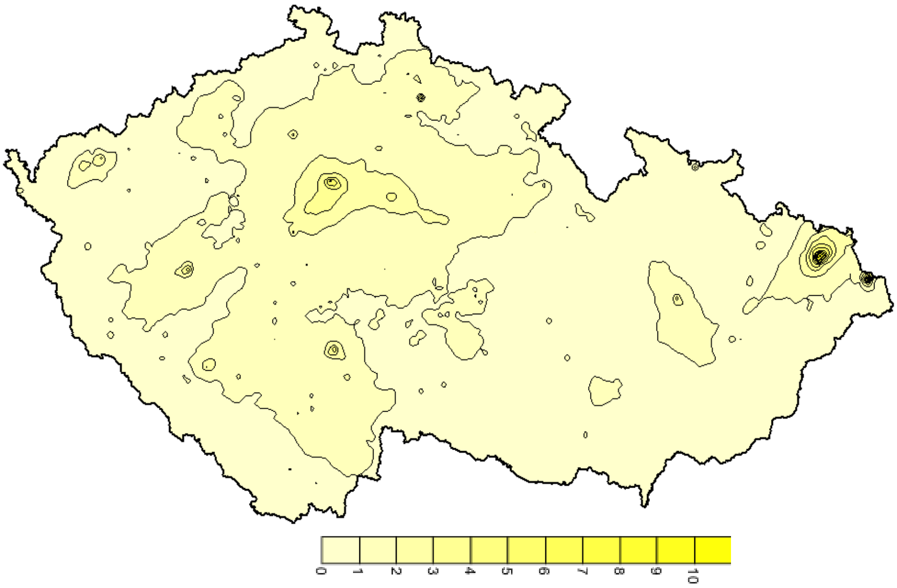

Figure 4.25: 2004 PM_{10} *concentrations* ($\mu g.m^{-3}$) *- Model SYMOS 97.*

Ratio between SYMOS’97 model outputs and measurements is presented in Figure 4.26. Model concentrations (caused by primarily sources) represent only units of measured concentrations in the most of the area of the Czech Republic. The ration of primarily sources is higher (about 20%) only in large industrial agglomeration with higher density of stationary sources (Prague, Moravian-Silesian region). Despite SYMOS model probably underestimate the contribution of primarily sources, it is evident, that SYMOS model is able to cover only a small part of total PM emissions in the atmosphere. Secondary particles formation by chemical reactions was not taken into account in the model, which caused significant underestimation of real concentrations. In rural areas, resuspended particles from Earth's surface play an important role.

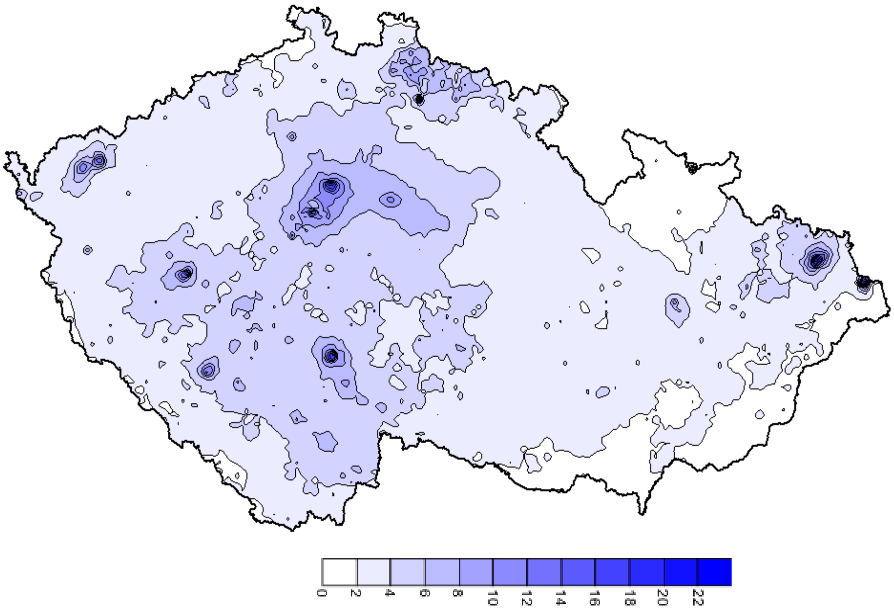

Figure 4.26: Model x measurement PM_{10} *concentrations.*

Annual PM_{10} concentrations based on 2000 EMEP model outputs are presented in Figure 4.27. Model results reflect better the reality. The concentrations amount to one third of measured data (10 – 15 µg.m^{-3}). The model reflects the increased concentrations in north and northeast of the Czech Republic. High concentrations in agglomerations are not fit due to relatively rough scale of EMEP model (50 km).

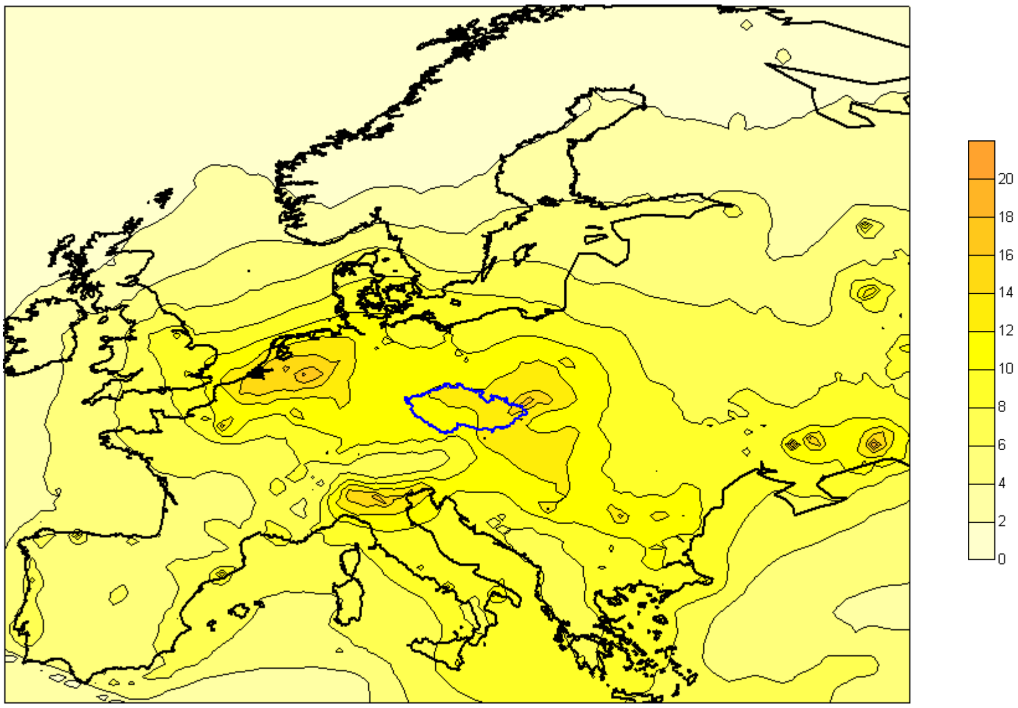

Figure 4.27: Model PM_{10} concentrations in 2000 – EMEP model (µg.m^{-3}).

4.10 Conclusions

- Decreasing trend of PM_{10} concentration in the period 1996-1999 was found at all types of stations. This trend was stopped in the beginning of this century and the concentrations slightly increased and the differences between types of stations are smaller.
- Increase of PM_{10} concentrations at rural stations was cause first of all by combustion practices in small towns and villages. There is a strong tendency to come back to traditional cool and wood burning.
- The most serious air pollution situation caused by suspended particles is in the Moravian-Silesian region. In addition to transport and local sources of PM significant contribution is made by further emission sources (metallurgy, fuel processing). Regional transfer from Poland (heavily industrialized Katowice region) is significant.
- Certain seasonal course of the ratio between $PM_{2,5}$ and PM_{10}, that is connected with the seasonal character of several emission sources. Emissions from combustion sources show higher shares of $PM_{2,5}$ fractions than for instance emissions from agriculture and reemission during dry and windy weather. Consequently, heating in the cold period can cause the higher share of $PM_{2,5}$.
- The fraction ratio ranges between 0, 69-0, and 85 in 2005. The 2004-2005 ratio at the EMEP station Košetice is 0, 87.

- The highest PM_{10} concentrations at the background station Košetice (EMEP, GAW) are measured when the air masses from eastern directions predominate and the lowest values are measured when they come from the west.
- The highest concentrations and the year by year variability were measured in the air masses from eastern directions in the whole period under review. The increase after 2000 corresponds with the rising trend in Moravian-Silesian region located in this direction.
- Significant difference was found between trends in summer and winter period. While the trend of winter concentrations is comparable with general trend, there is a quite rapid increase of summer concentrations throughout the period under review, especially when in the air masses with origin in eastern sectors.
- Dispersion models that don’t take into account chemical reactions in the atmosphere, underestimate the real PM_{10} concentration level significantly. Primarily particles emitted directly from the sources produce 10 – 30 % total emission load, secondary particles 30 – 50 % and resuspended particles 20 – 40 %. It is necessary to include all three mentioned processes into models predicting creation and behaviour of fine particles in the atmosphere.

4.11 References

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5 PM pollution in Denmark

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5.1 Air quality monitoring network

Air quality monitoring is carried out under the National Air Quality Monitoring Network (NOVANA) in urban and rural areas in Denmark, Figure 5.1. The programme provides i.a air quality data from the four largest urban areas and the rural background areas in Denmark (NERI, 2006 and Kemp et al., 2006). The monitoring is supplemented by data from a special particle research programme. The objective of the Danish particle programme is to provide new and broader knowledge on the adverse health effects of atmospheric particles with the aim to develop strategies to reduce the adverse health effects of man-made air pollution. We focus on characterisation of particles and their sources.

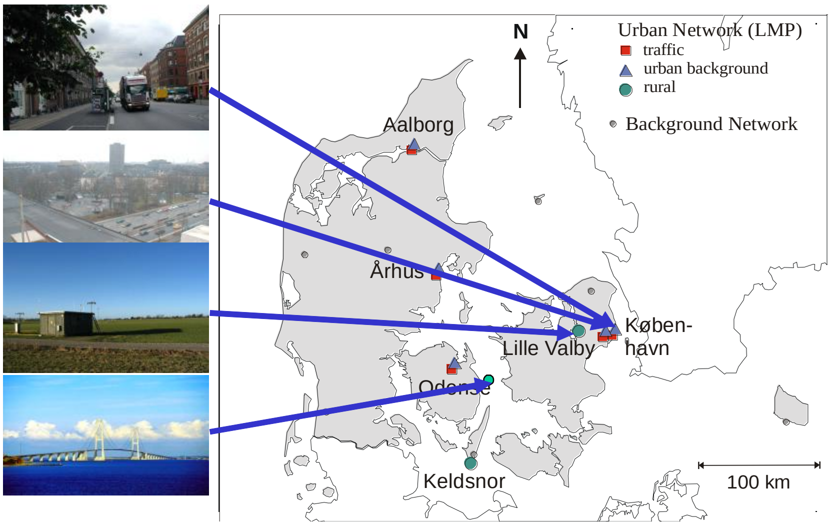


Figure 5.1: Air quality monitoring in Denmark at streets, urban background, rural and remote stations.

Air quality monitoring is carried out under the National Air Quality Monitoring Network (NOVANA) in urban and rural areas in Denmark, Figure 5.1. The programme provides i.a air quality data from the four largest urban areas and the rural background areas in Denmark (NERI, 2006 and Kemp et al., 2006). The monitoring is supplemented by data from a special particle research programme. The objective of the Danish particle programme is to provide new and broader knowledge on the adverse health effects of atmospheric particles with the aim to develop strategies to reduce the adverse health effects of man-made air pollution. We focus on characterisation of particles and their sources.

The trends of TSP and PM_{10} for traffic sites are shown in

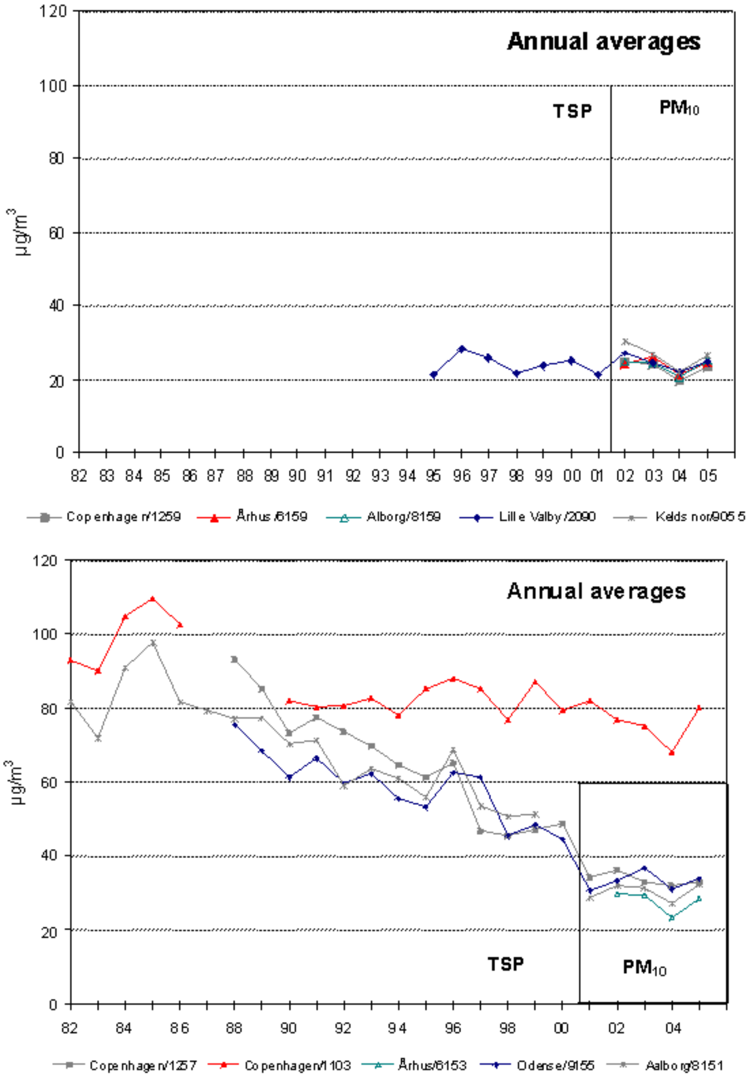


Figure 5.2. Regular PM_{10} monitoring was introduced in 2000, using a gravimetric method, supplemented by β-absorption. The urban background level of PM_{10} (and TSP) was generally very close to the rural background level. A clear decreasing trend was observed at all traffic sites except at street in central Copenhagen (H.C. Andersen's Boulevard), which is a street with dense traffic (67,000 vehicles per day). The PM_{10} limit value, 40 $\mu g/m^3$, will probably be exceeded in 2010 at the most densely trafficked streets.

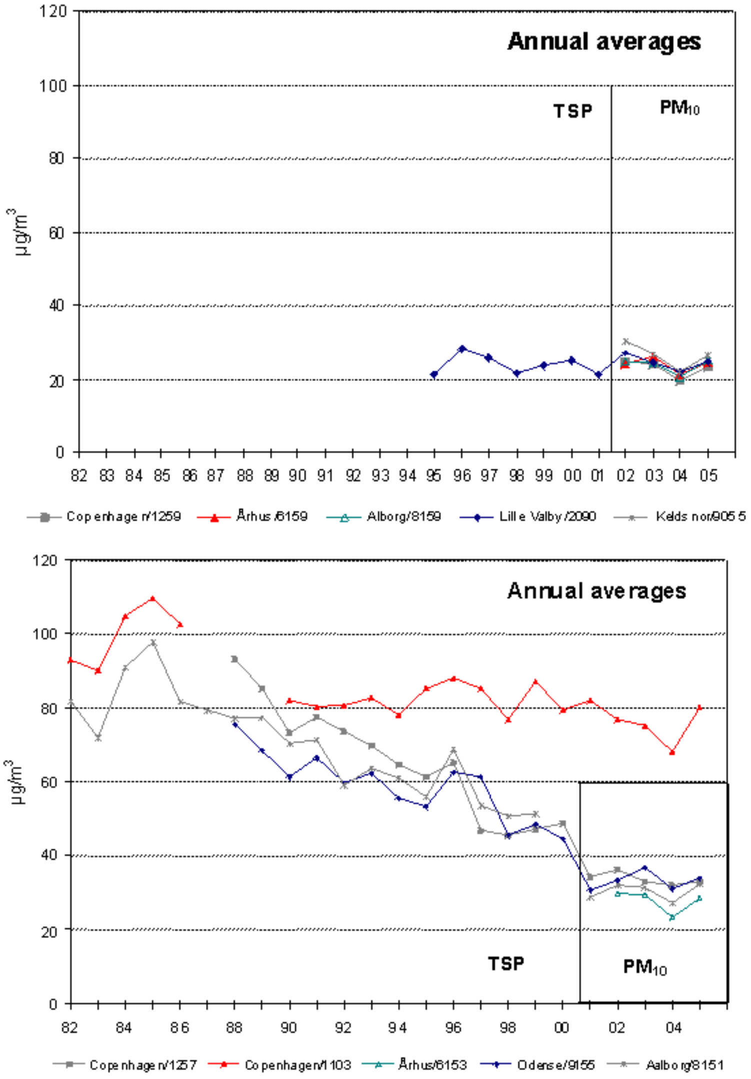
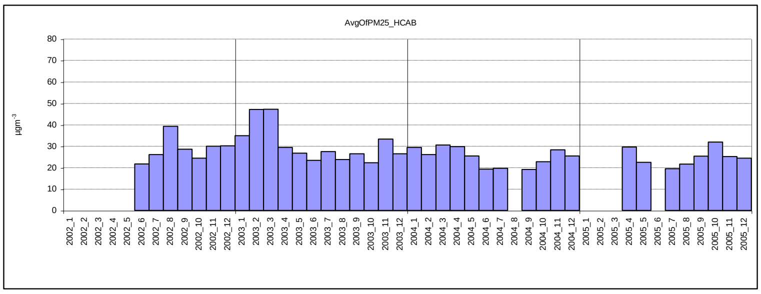


Figure 5.2: The trends of TSP and PM_{10} at rural and urban background (upper graph) and traffic (lower graph) locations in Denmark.

$PM_{2.5}$ has been measured at a few sites by TEOM, but the time series are still rather short, Figure 5.3. The correction of the TEOM data due to evaporation/ decomposition of i.a. ammonium nitrate, organics and perhaps water was performed using simultaneous gravimetric PM_{10} measurements. The TEOM losses for $PM_{2.5}$ at traffic sites are generally the same as at urban background sites. The ratio between gravimetric measurements and TEOM measurements depends therefore strongly on the type of site, and varies between approx. 1.5 at traffic sites and 1.9 at urban background sites in Copenhagen.



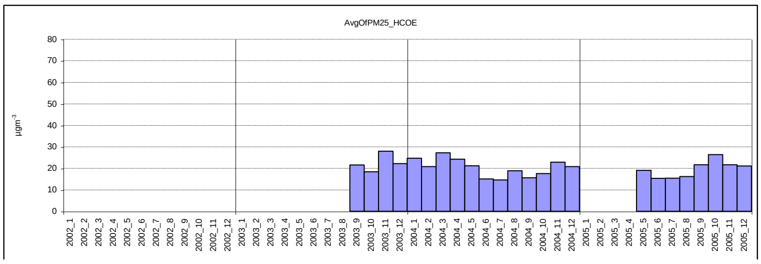


Figure 5.3: $PM_{2.5}$ results ($\mu g/m^3$) at street (upper graph) and urban background (lower graph) sites in Copenhagen measured by TEOM after correction for losses.

A summary of the Danish PM data in 2005 is given in Table 5.1 and Table 5.2 and table 2. The data confirm that the urban background levels are very close to the rural background levels, which means that the urban increment is very low in Denmark for PM_{10} as well as for $PM_{2.5}$.

Table 5.1: Summary of Danish PM_{10} data from 2005 ($\mu g/m^3$). The numbers in red indicate exceedances of limit value. Gravimetric method.

Location	Average	36. highest	Max.
Traffic:			
Copenhagen/1257	33	**53**	110
Århus/6153	29	45	83
Odense/9155	34	**55**	140
Aalborg/8151	33	49	189
Urban background:			
Copenhagen/1259	23	37	67
Århus/6159	24	39	112
Odense/9159	27	43	79
Aalborg/8159	25	39	88
Rural background:			
Ll. Valby/2090	25	40	69
Keldsnor/9055	26	37	63
Limit value	40	50	-

Table 5.2: Summary of Danish $PM_{2.5}$ data from 2005 ($\mu g/m^3$). TEOM method.

Location	Average	36. highest
Traffic:		
Copenhagen/1103	15	22
Urban backgr.:		
Copenhagen/1259	11	18
Rural:		
Lille Valby/2090	11	16

5.2 The special particle studies

The particle research is mainly taking outset in the Danish nationwide air quality monitoring programme, with long time series of the main pollutants, including PM_{10} at all stations and other PM parameters (e.g. soot, ultrafine PM, $PM_{2.5}$, EC/OC) at selected stations. The particle studies included measurement campaigns supported by data from the monitoring programme. The combination of long time series of traditional pollutants and the special particle campaigns permits establishment of relationships between sources and the properties of the particles. The experimental studies of PM_{10}, $PM_{2.5}$ and ultrafine particles were performed in busy street canyons, urban background and rural locations, and included chemical composition, e.g. the content of elemental carbon, PAHs and other organic compounds and size distributions (10-700 nm).

Receptor modelling of $PM_{2.5}$ has been carried out based on all available data, i.e. chemical composition and sizes of the particles and concentration data on gaseous pollutants. An example of preliminary results is shown in Figure 5.4, which include data from a very densely trafficked street in Copenhagen and the corresponding urban background site. At present the new $PM_{2.5}$ limit value, 25 $\mu g/m^3$, may be exceeded at the most densely trafficked streets in the largest cities (hot spots), but we expect compliance with the limit value in 2015. The dominating contribution to $PM_{2.5}$ is secondary regional particles. The secondary inorganic particles comprise ammonium nitrate and ammonium sulphate formed due to NO_x and SO_2 emissions in Europe and from international ships. A large part of the secondary particles include organic components and is to a certain degree unknown, both with respect to chemical composition and origin. The local traffic contribution is rather well described and consists of exhaust from the road traffic and particles from brakes, road, tires and road salt (used in Denmark slippery road abatement).

Long-range transported particles, i.e. primary particles and secondary particles formed by oxidation of SO_2 and NO_x emitted at the European continent are dominating in urban background and comparable with the traffic contribution in busy streets (mass concentration, $PM_{10}/PM_{2.5}$). The local contributions at urban background sites in Danish urban areas are less than 2% of the total $PM_{2.5}$ pollution.

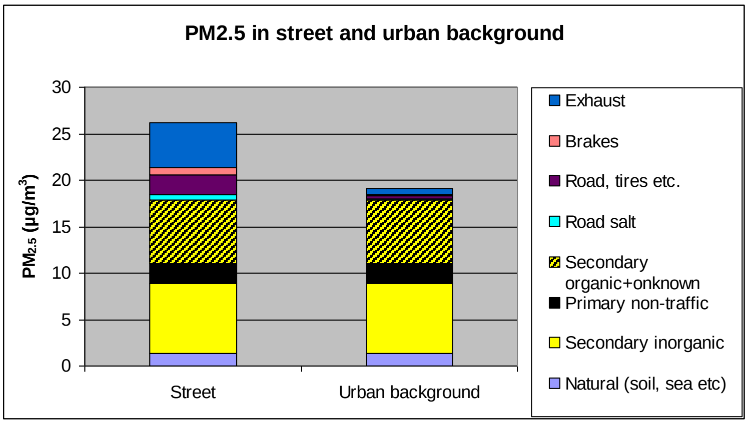


Figure 5.4: Schematic presentation of the main contributions to PM$_{2.5}$ in a busy street and at an urban background site in Copenhagen.

The road traffic (Wåhlin et al. 2003) and wood stoves (Glasius et al. 2005) are the most important local particle sources in Denmark. They cause the highest outdoor human exposure due to high emissions at low release heights and in urban areas where the population lives. Figure 5.5 shows road traffic contribution separated in fine (PM$_{2.5}$) and coarse (PM$_{10}$-PM$_{2.5}$) particles from exhaust, brakes, road and road salt. The results may be dominated by winter data.

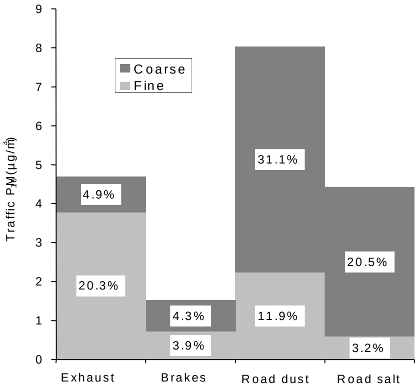


Figure 5.5: Road traffic contributions to fine and coarse particles in a street in Copenhagen (67,000 vehicles/day) based on two one week campaigns.

Diesel vehicles are the dominating source of nano-particles and ultrafine particles. The highest emissions of particles take place from traditional diesel vehicles without filters or catalysts. The particle filters are generally very efficient (>95%) for all particles including nano particles and ultrafine particles. In addition to the tailpipe, the non-exhaust emissions from wear of road surfaces, tires, brakes etc contributes significantly to the PM$_{10}$ pollution from diesel as well as from petrol vehicles (Wåhlin et al. 2006).

5.3 Size distribution of particles

Times series of particle size distributions have been recorded by continuous measurements by DMPS (Differential Mobility Particle Sizer) at traffic, urban background and rural sites. The size range was 10-700 nm. Figure 5.6 shows the average weekly variation of the traffic contribution in a busy street. The “condensates with sulphur” particles are very small particles, especially emitted from modern diesel cars with oxidizing catalysts. They are probably mainly sulphur nuclei, perhaps with organic compounds. The dominating number contributions are the condensates, which are volatile particles less than 30 nm. The dominating mass contributions are soot from diesel engines centred on 200 nm and secondary particles (long range transport) centred around 500 nm. The mass concentration corresponds approximately to $PM_{0.7}$. Results are published (Palmgren et al. 2005).

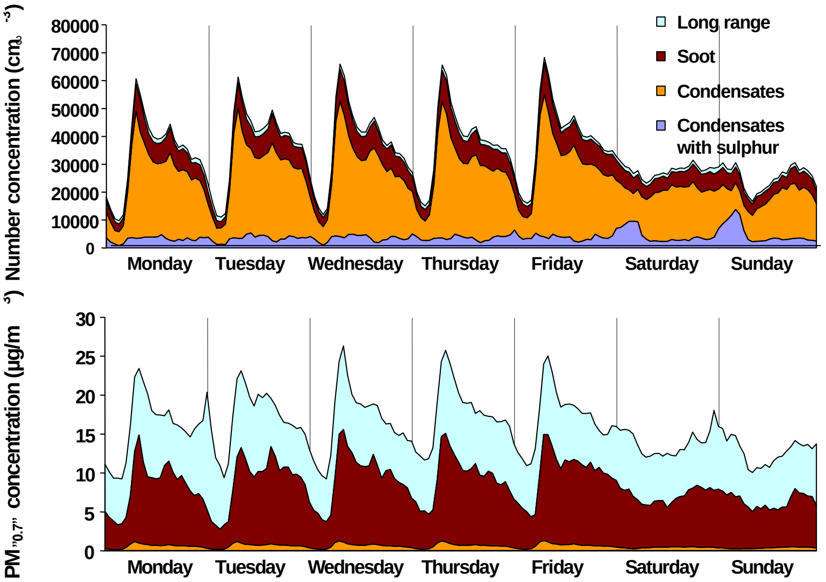


Figure 5.6: Average weekly variation of the traffic contribution. The upper graph is the number concentration and the lower graph is the volume (approx. mass) concentration,

5.4 References

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6 Aerosol measurements and modeling. Some recent advances in Finland

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6.1 The spatial and temporal variation of measured urban PM mass in the Helsinki Metropolitan Area in 1997-99

[Pohjola, M A, Kousa, A, Kukkonen, J, Härkönen, J, Karppinen, A, Aarnio, P, Koskentalo, T, 2002. The Spatial and Temporal Variation of Measured Urban PM10 and PM2.5 concentrations in the Helsinki Metropolitan Area. International journal on Water, Air and Soil Pollution: Focus 2 (5-6), pp. 189-201.]

6.1.1 Measurements

Figure 6.1 shows the location of the air quality monitoring stations in the Helsinki metropolitan area and the pollutants monitored in 1999. The network contains six permanent multicomponent stations; these are located in Helsinki city districts (Töölö, Vallila and Kallio 2), in suburban in the cities of Espoo and Vantaa centres (Leppävaara and Tikkurila), and in a rural area in Espoo (Luukki). The stations used in this study represent urban (Töölö and Vallila) and suburban traffic environments (Leppävaara), together with the urban background (Kallio 2). Regional background concentrations were monitored in a rural environment in Luukki, approximately 20 km to the north-west of downtown Helsinki. Two urban monitoring stations, Töölö and Vallila, are located in the Helsinki downtown area.

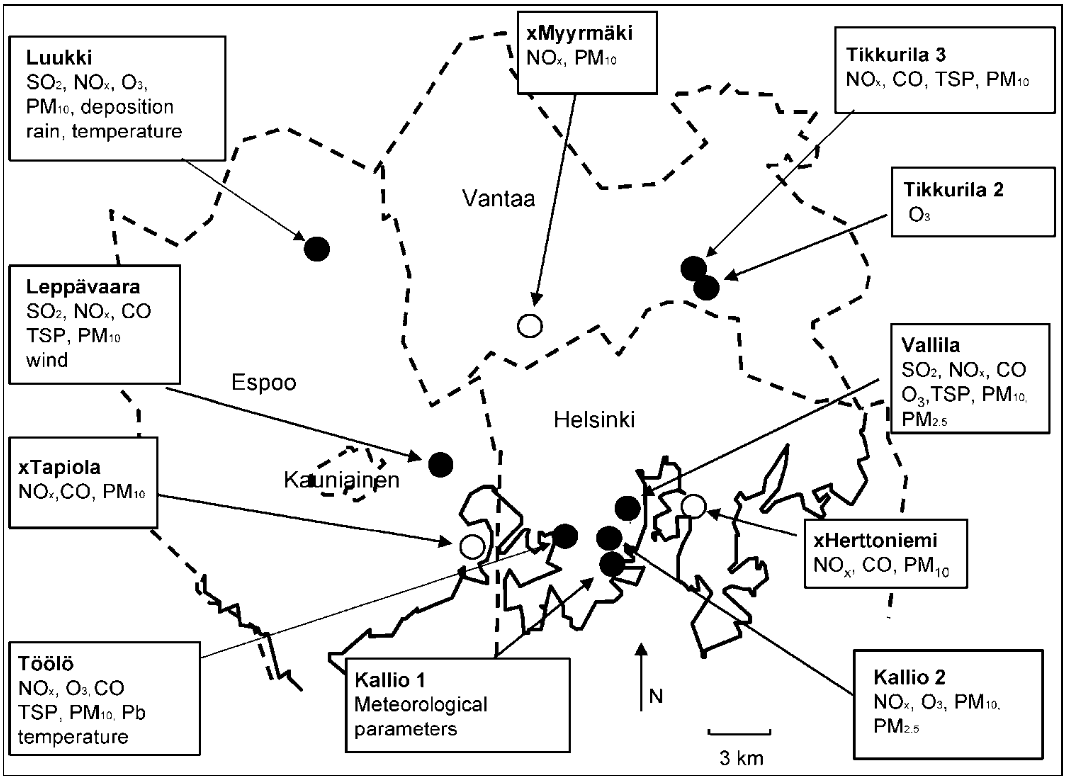


Figure 6.1: Urban air quality monitoring network in the Helsinki Metropolitan Area in 1999. The legends show the name of the station and the pollutants measured. X indicates a mobile station.

6.1.2 Diurnal variation of PM concentrations

Data has been compiled on the diurnal variation of the PM_{10} and $PM_{2.5}$ concentrations at the various monitoring stations during 1997–1999. As an example, we have presented the diurnal variation of PM_{10} concentrations at the various stations in Figure 6.2a–c, averaged over each of the years 1997–1999, and $PM_{2.5}$ concentrations at Vallila averaged over the same years and additionally at Kallio 2 in 1999 in Figure 6.3a–b. Clearly, the diurnal variation of traffic-originated pollutant concentrations depends on the day of the week; for these figures we have selected data from working days (Monday–Friday) only. The concentrations of PM_{10} show a clear diurnal variation. The concentrations increase continuously during the morning rush hours, from approximately 6 to 8 a.m.; as expected, this increase took place irrespective of the year (during the period 1997–1999) and the season of the year. Subsequently the concentrations decrease slowly during the rest of the daytime hours, also showing in some cases peak values during the afternoon rush hours, from approximately 3 to 6 p.m. The more moderate diurnal variation of the PM_{10} concentrations, compared with the traffic flows, could be caused by resuspension of PM from street surfaces. Resuspended PM increases with increasing traffic flow; however, it can reach a saturated state, in which a further increase of traffic cannot cause any more resuspension.

During working days, there is a very clear diurnal variation of local vehicular traffic. Despite this, the $PM_{2.5}$ concentrations are temporally fairly uniform during working days, except for a moderate increase during the morning rush hours. The diurnal variation of local vehicular traffic flows seems to have no substantial correlation with the $PM_{2.5}$ concentrations. In 1999, the temporal variation of $PM_{2.5}$ concentrations at both monitoring stations was also very similar. This indicates that the PM resuspended from street surfaces and other sources has only a minor effect on the $PM_{2.5}$ concentrations, and that a large fraction of the $PM_{2.5}$ concentrations most likely originates from regional or long-range scale sources.

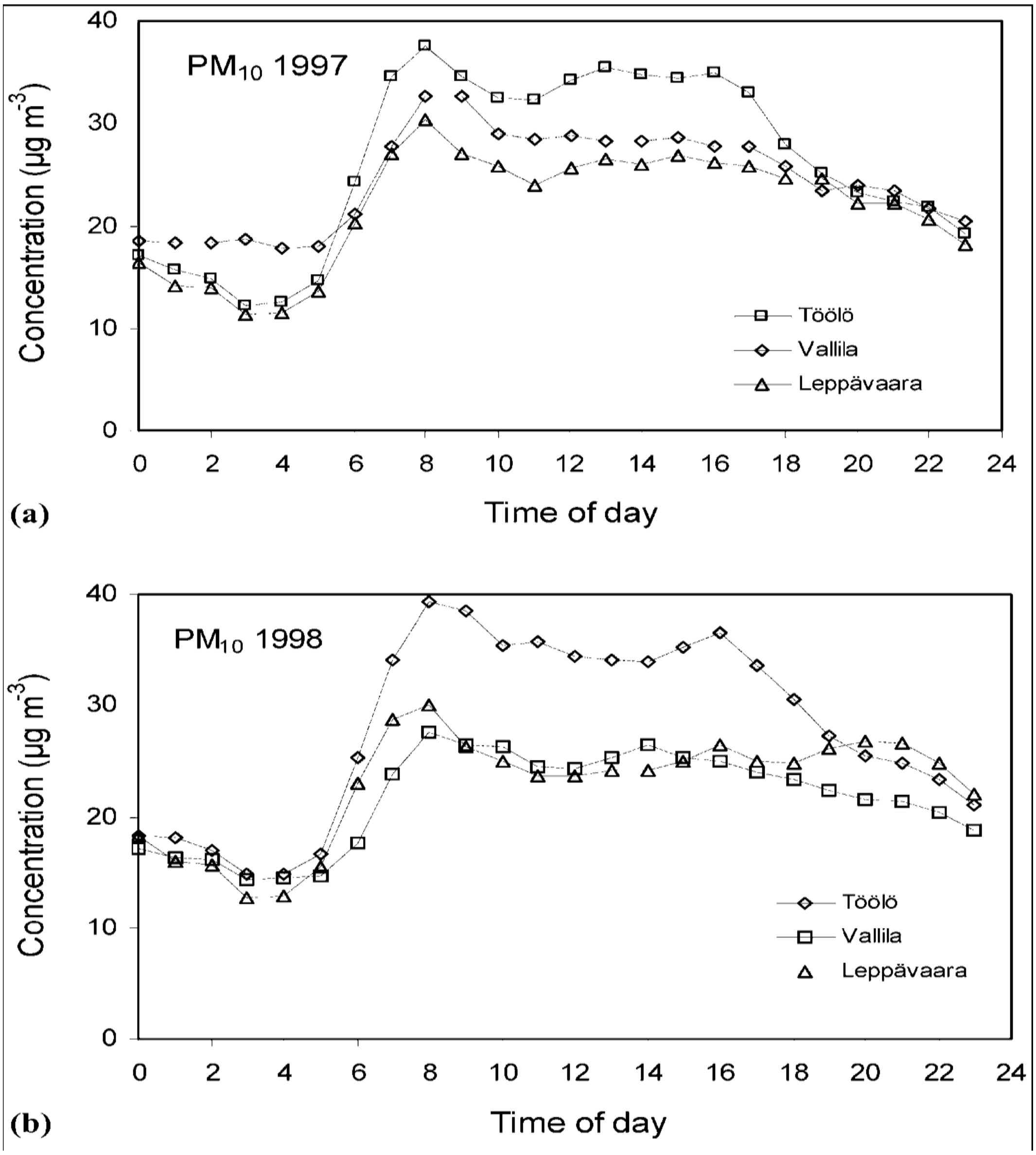


Figure 6.2: The diurnal variation of PM_{10} concentrations at the stations of Töölö, Vallila and Leppävaara during 1997–1999, and at the station of Luukki, during 1999. Figures include data from working days only.

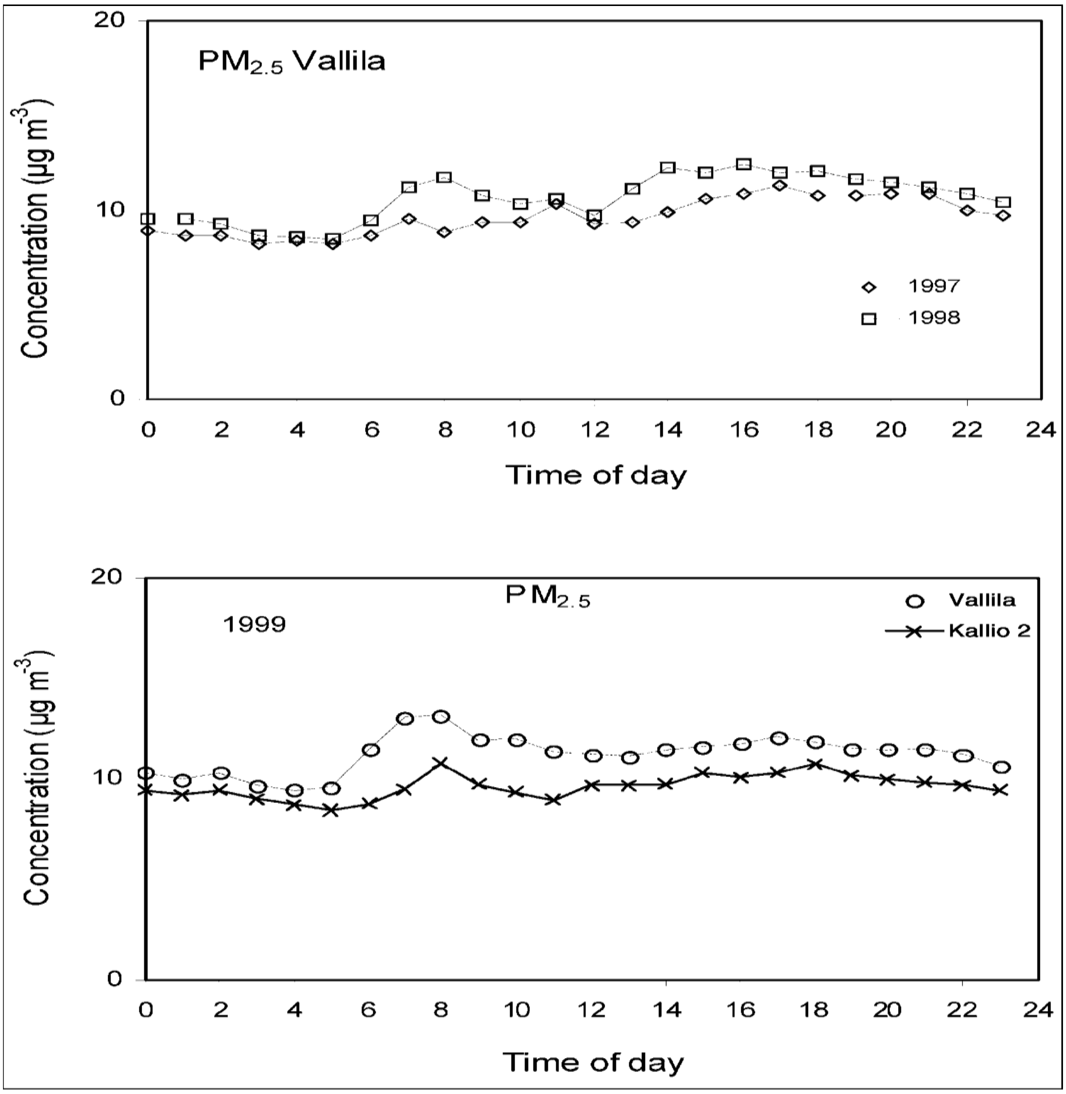


Figure 6.3: The diurnal variation of $PM_{2.5}$ concentrations at the station of Vallila during 1997–1998, and at the stations of Vallila and Kallio 2 during 1999. Figures include data from working days only.

6.1.3 Conclusions

The diurnal variation of the PM_{10} concentrations was clear, irrespective of the year and the season of the year. This variation partly follows the corresponding variation of local vehicular traffic flows. On the other hand, both the spatial and temporal variation of the fine particle ($PM_{2.5}$) concentrations was moderate. The results provide indirect evidence indicating that the PM_{10} concentrations are originated mainly from local vehicular traffic (direct emissions and resuspension), while the $PM_{2.5}$ concentrations are mostly of regionally and long-range transported origin. This result is qualitatively in agreement with source apportionment studies in the same area

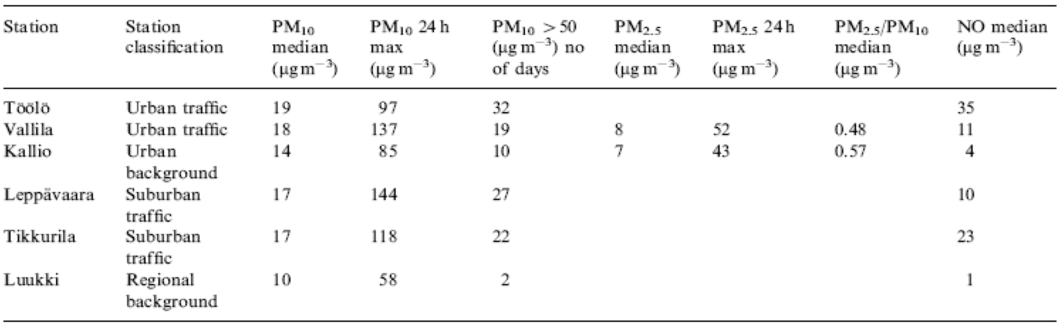
6.2 Analysis and evaluation of selected PM_{10} pollution episodes in the Helsinki Metropolitan Area in 2002

[Päivi Aarnio, Jyrki Martikainen, Tareq Hussein, Ilkka Valkama, Hanna Vehkamäki, Larisa Sogacheva, Jari Härkönen, Ari Karppinen, Tarja Koskentalo, Jaakko Kukkonen, Markku Kulmala, 2007. Atm. Env., doi:10.1016/j.atmosenv.2007.02.008].

We developed methods to distinguish the long-range transport (LRT) episodes from local pollution (LP) episodes. The first method is based on particle number concentrations ratio between accumulation mode (diameter >90 nm) and Aitken mode (diameter 25–90 nm). The second method is based on a proxy variable (interpolated ion sum) for long-range transported $PM_{2.5}$. The ion-sum is available from the measurements of sulphate, nitrate and ammonium at the nearest EMEP stations. We also utilised synoptic meteorological weather charts, locally measured meteorological data, and air mass back-trajectories to support the evaluation of these methods.

We selected nine time periods (i.e. episodes) with daily average $PM_{10} > 50$ μgm^{-3} in the Helsinki Metropolitan Area during year 2002. We characterized the episodes in terms of PM_{10} and $PM_{2.5}$ concentrations and the fraction of fine particles in PM_{10} at an urban traffic and regional background air quality monitoring sites. Three of these episodes were clearly of local origin. They were characterized by a low average fraction of $PM_{2.5}$ (<0.2) in PM_{10} at the urban traffic monitoring site, low ratio between PM_{10} concentrations at the regional background site and at the urban traffic site (<0.2), low average ion sums (1.5–2.5 μgm^{-3}) and low accumulation to Aitken mode ratios (0.13–0.26). Four of the episodes had distinct LRT characteristics: a high fraction of fine particles in PM_{10} (0.5–0.6) at the urban traffic site, a high ratio between PM_{10} concentrations at the regional background site and at the urban traffic site (0.7–0.8), high interpolated values for the ion sum (6.6–11.9 μgm^{-3}), and high accumulation to Aitken mode ratios (0.75–0.85). During the remaining two episodes there was significant contribution from both local sources and LRT. A detailed analysis of meteorological variables and air mass back-trajectories gave support to these findings.

Table 6.1: PM and NO concentration at the air quality monitoring sites in the Helsinki Metropolitan Area in 2002.



Station	Station classification	PM_{10} median (μg m^{-3})	PM_{10} 24 h max (μg m^{-3})	$PM_{10} > 50$ (μg m^{-3}) no of days	$PM_{2.5}$ median (μg m^{-3})	$PM_{2.5}$ 24 h max (μg m^{-3})	$PM_{2.5}/PM_{10}$ median (μg m^{-3})	NO median (μg m^{-3})
Töölö	Urban traffic	19	97	32				35
Vallila	Urban traffic	18	137	19	8	52	0.48	11
Kallio	Urban background	14	85	10	7	43	0.57	4
Leppävaara	Suburban traffic	17	144	27				10
Tikkurila	Suburban traffic	17	118	22				23
Luukki	Regional background	10	58	2				1

These characteristics can be utilised in a simple procedure to distinguish between LRT and LP episodes. Further quantitative investigations to these characteristics provide an indication to the episode strength. There was a good correlation between the 24-h averages of $PM_{2.5}/PM_{10}$ at the urban traffic site (Vallila) and the accumulation to Aitken mode ratio at the urban background site (Kumpula). There was a moderate to good correlation also between $PM_{2.5}/PM_{10}$ ratio and the interpolated ion sum, and between the ion sum and the accumulation to Aitken mode ratio. The scatter plots for these correlations are shown in Figure 6.4 , which also show the grouping of the different types of episodes. The quantitative results presented in the current study are applicable to the Helsinki Metropolitan Area and similar cities. Nevertheless, developing these methods for other cities require analyses of the meteorological conditions, behaviour of the PM concentrations, and air-mass back trajectories for that specific city.

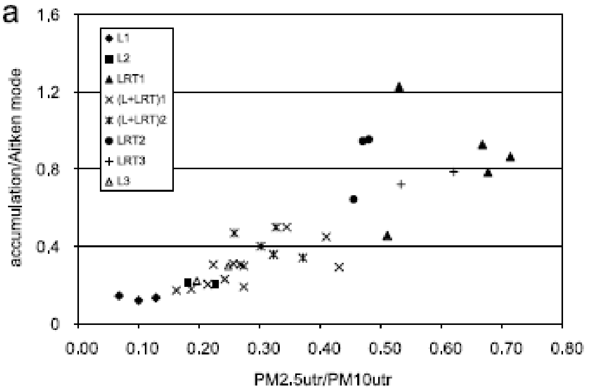
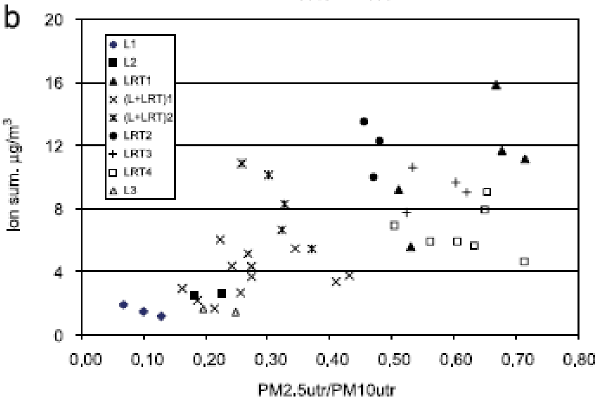
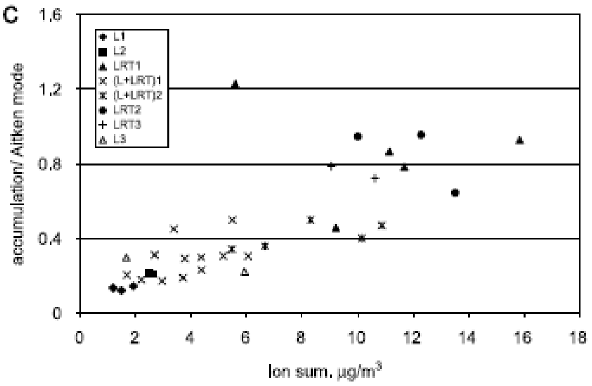


Figure 6.4 (a)
The $PM_{2.5}/PM_{10}$ ratios at the urban traffic monitoring site vs. accumulation to Aitken mode ratios measured at the urban background site.



(b)
$PM_{2.5}/PM_{10}$ ratios at the urban traffic monitoring site vs. the ion sums.



(c)
ion sums vs. the accumu-lation to Aitken mode ratio.

6.3 Temporal and spatial patterns of PM mass in Finland

[Pia Anttila and Timo Salmi, 2006. Characterizing temporal and spatial patterns of urban PM_{10} using six years of Finnish monitoring data. *Boreal Env. Res.* 11: 463–479]

Six years (1998-2003) of continuous PM_{10} mass concentration measurements from 25 stations in 20 cities in different parts of Finland were used to examine the temporal and spatial patterns of urban PM_{10} in Finland (Anttila and Salmi 2006). PM_{10} data was extracted from the Finnish Meteorological Institute's Air Quality Monitoring Data Management System (ILSE). PM_{10} was measured with automatic analyzers based either on the tapered element oscillating microbalance or the beta-attenuation method.

Long term means of PM_{10} at twenty five Finnish urban stations vary between 11-24 µg m^{-3}, the highly trafficked urban centers tending to have higher concentrations than the suburban stations or small towns (Figure 6.5). Year to year variation at each station is very low, typically only 2-4 µg m^{-3}. The national background concentration was estimated to be about 5 µg m^{-3}, and there is some indication that when traffic influence is eliminated a decreasing trend of PM_{10} from south/southeast to north emerges.

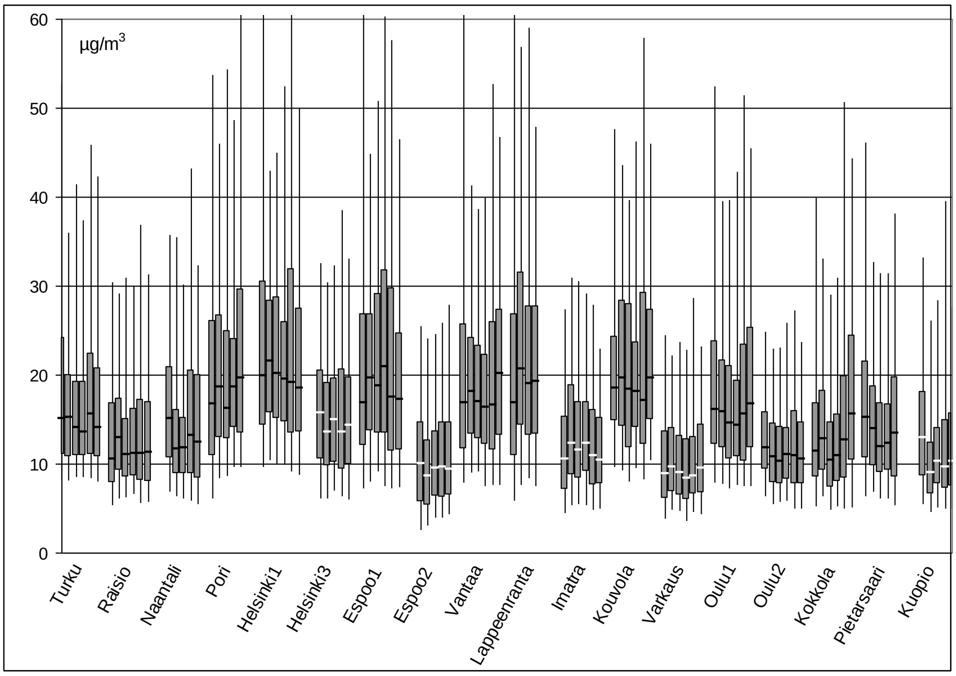


Figure 6.5: Annual distribution of 24-hr average PM_{10} concentrations from 1998 to 2003 at 18 stations. Values for the 5th, 25th, 50th, 75th and 95th percentiles are shown. At the non-traffic stations the medians are denoted with white horizontal lines.

The seasonal variation of PM_{10} at all stations is dominated by the maximum during spring; in March-April the PM_{10} concentrations are about twice as high as during the rest of the year. This spring peak of PM_{10} covers practically the whole snowmelt period, which also is the driest period of the year.

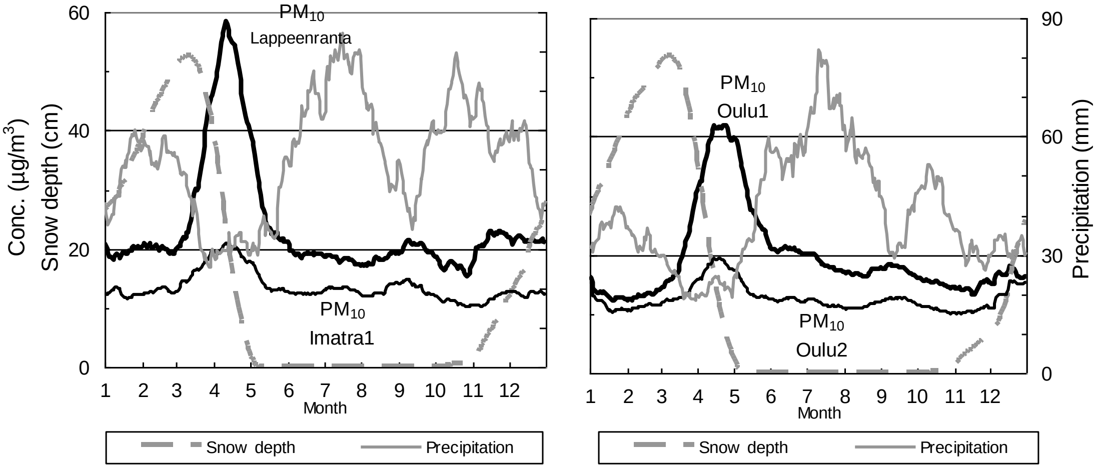


Figure 6.6: Annual variation of the PM_{10} concentration (black lines, left axis) and snow depth (grey dashed line, left axis) and precipitation (grey line, right axis) averaged over years 1998-2003 in southwestern Finland (Lappeenranta and Imatra1) and norhern Finland (Oulu1 and Oulu2). Meteorological data are from Lappeenranta and Oulu airport synoptic stations.

In spring also the Sunday concentrations at all urban stations are significantly lower (from 13% to 40%) than the weekday concentrations which implies a strong traffic influence on the PM_{10} concentrations. The spring time dry period with increasing temperatures, radiation and evaporation enables the effective suspension of the dust accumulated from multiple sources to road surfaces and shoulders and initiates the elevation of PM_{10} concentrations. However, the highly synchronized day to day variation at a variety of sites across the country highlights the role of large scale weather patterns also in the formation of spring episodes. In March and April the exceedances of 50 µg/m^3 as a daily mean are frequent at almost all urban stations, however the EU limit value (35 exceedances) is exceeded only at the most trafficked street canyons in Helsinki.

Every year, most often in August, September and October, there are also 1-5 irregular regional PM_{10} episodes, lasting from one day to six days and being most likely originated from long range transported particles. During these regional events the PM_{10} concentrations may well reach the typical spring peak concentration levels. Similar regional LTR-events are probable also in spring but they get masked behind the overwhelming road influence.

Long term fine particle ($PM_{2.5}$) mass measurements are still scarce in Finland. Longest time series are from Helsinki metropolitan area and Oulu (since 2002) and from the FMI background station Virolahti (since 2004). Figure 3 shows the monthly means of $PM_{2.5}$ from these stations during 2002-2005 together with the co-located PM_{10} measurements. At the Virolahti rural background station the distinctive spring maximum of the PM_{10} is missing and the ratio $PM_{2.5}$ to PM_{10} typically varies between 0.6 to 0.8 being highest in early spring February and March. At the urban stations the ratio of $PM_{2.5}$ to PM_{10} drops to 0.2 in spring being in the midwinter at its highest 0.7. From site to site the fine particle concentrations vary much lesser than the thoracic particles. The study period

(Figure 6.7) mean of the fine particles in Virolahti is 7.3 µg/m^3 and in Oulu 8.5 µg/m^3.

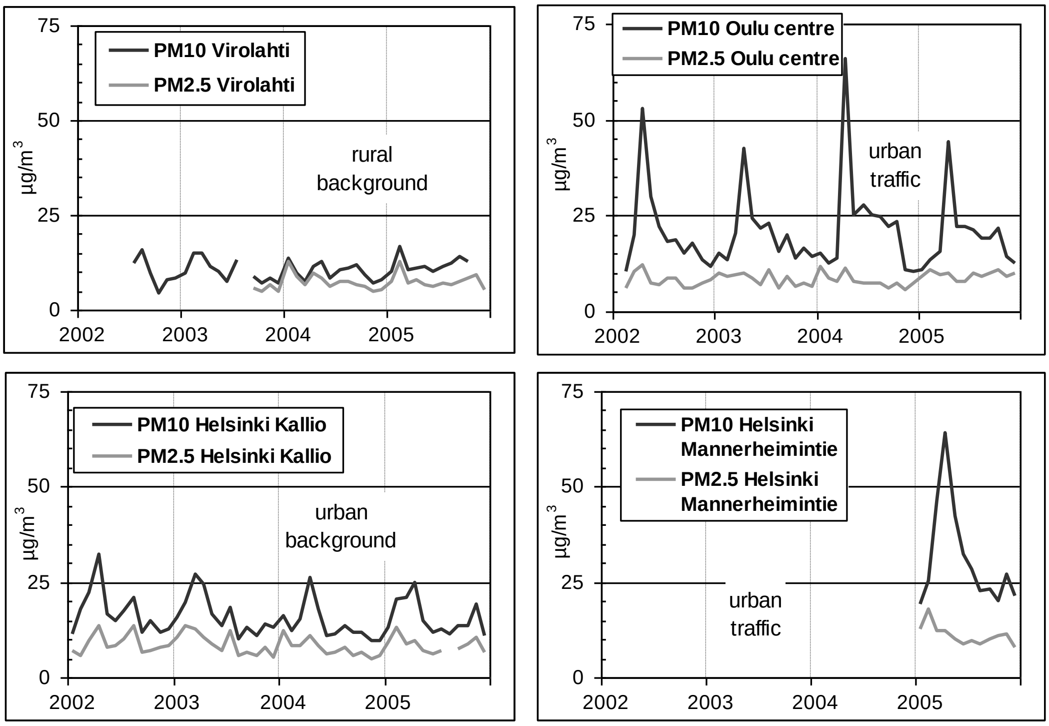


Figure 6.7: Monthly means of PM$_{10}$ and PM$_{2.5}$ masses at different types of monitoring stations in 2002-2005.

6.4 Modelling fine particle concentrations in Helsinki metropolitan area

[Kauhaniemi, M., Karppinen, A., Härkönen, J., Kousa, A ., Koskentalo, T., Aarnio, P. and Kukkonen, J., 2007. Refinement And Statistical Evaluation Of A Modelling System For Predicting Fine Particle Concentrations In Urban Areas. In: Ranjeet S. Sokhi and Marina Neophytou (eds): Proceedings of the 6th International Conference on Urban Air Quality, Limassol, Cyprus, 27-29 March 2007, CD-disk: ISBN 978-1-905313-46-4, University of Hertfordshire and University of Cyprus (pp. 68-71)]

We present a combined modelling system that addresses particulate matter on an urban scale and long-range transported aerosols (LRT). We have evaluated the advantages and limitations of the statistical model (Karppinen et al., 2004) for computing the LRT'ed contribution to PM$_{2.5}$ in U.K. and in Finland (Kukkonen et al., 2007). We also aim to evaluate the performance of the combined modelling system against measured PM$_{2.5}$ data in Helsinki.

6.4.1 Meteorological and Air Quality Measurements

The relevant meteorological parameters for the models are evaluated using data produced by a meteorological pre-processing model (Karppinen et al., 1997, 1998). The location of the study area, the meteorological stations and the background air quality measurement stations are presented in Figures 1a and b. We used a combination of the data from the stations at Helsinki-Vantaa airport and Helsinki-Isosaari. The mixing height of the atmospheric boundary layer was evaluated using the meteorological pre-processor, based on the sounding observations at Jokioinen (90 km northwest) and the routine meteorological observations.

The EMEP stations (‘Co-operative programme for monitoring and evaluating of the long-range transmission of air pollutants in Europe’) that are located nearest to Helsinki are shown in Figure 6.8a; these are Utö, Ähtäri and Virolahti. The following concentrations are measured daily at the EMEP stations: (i) SO_4^{2-} (sulphate), (ii) the sum of NO_3^- (nitrate) and HNO_3 (nitrogen acid), and (iii) the sum of NH_4^+ (ammonium) and NH_3 (ammonia). The fine particle ($PM_{2.5}$) measurements of the Helsinki Metropolitan Area Council (YTV) monitoring stations at Vallila and Kallio were used. The location of the YTV monitoring stations in Helsinki metropolitan area is shown in Figure 6.8b. Monitoring station of Vallila represents urban roadside conditions. The Kallio station is an urban background monitoring station.

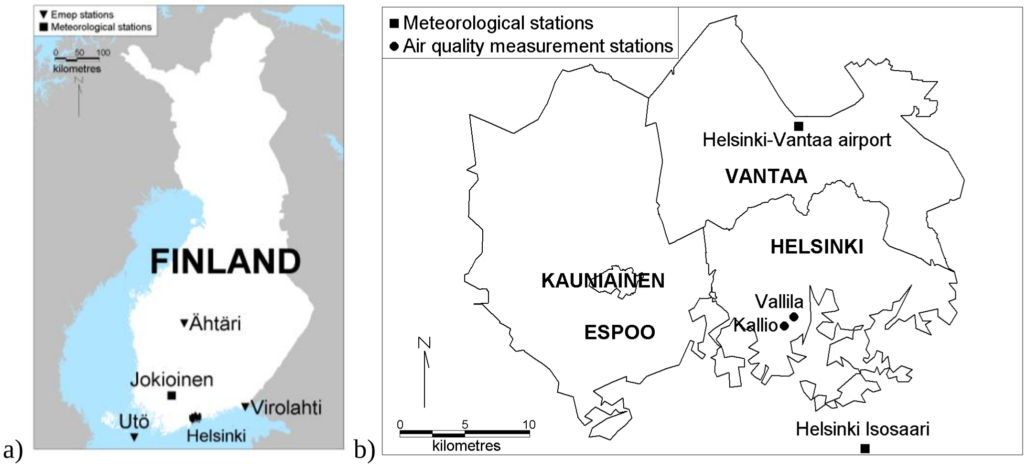


Figure 6.8: The meteorological and air quality monitoring stations in the Helsinki metropolitan area in 2002 (edited YTV, 2003).

6.4.2 Modelling System

The atmospheric dispersion of vehicular emissions is evaluated using a roadside dispersion model, CAR-FMI (Härkönen, 2002). The dispersion equation is based on an analytic solution of the Gaussian dilution equation for a finite line source. The dispersion parameters are modelled as function of the Monin-Obukhov length, the friction velocity and the mixing height. Traffic-originated turbulence is modelled with a semi-empirical treatment. The model includes the basic reactions of nitrogen oxides, oxygen and ozone, and the dry deposition of the fine particles. The model also takes into account the effect of the non-exhaust vehicular emissions and particulate matter suspended from the street surfaces, using empirical correlations.

The long-range transported contribution to urban particulate matter was evaluated with a statistical model (Kukkonen et al., 2007) that utilises, as input values, the daily sulphate, nitrate and ammonium ion concentrations measured at the EMEP stations. Currently, there is also an option to use representative regional background $PM_{2.5}$ concentration measurements in the Helsinki Metropolitan area. The regional background $PM_{2.5}$ concentrations can also be determined using the

European-scale computations using the regional and continental-scale dispersion model SILAM (Sofiev et al, 2006).

6.4.3 Results

The mean, the maximum and the standard deviation, together with the statistical parameters for the predicted and observed daily average time series of $PM_{2.5}$ concentrations in 2002, for Vallila and Kallio monitoring stations are presented in Table 6.2.

Table 6.2: The statistical analysis of the predicted and observed daily average time series of $PM_{2.5}$ concentrations at the Vallila and Kallio monitoring stations for 2002 (the days 01.01.02 and 31.12.02 are omitted).

Statistical Parameter	Vallila		Kallio	
	Predicted	Observed	Predicted	Observed
Mean (µg/m^3)	11.2	9.90	7.92	8.64
Maximum (µg/m^3)	39.0	52.0	35.2	42.5
Standard deviation (µg/m^3)	5.31	6.75	4.80	5.89
Index of agreement (IA)	0.83		0.86	
Pearson's correlation coefficient (COR)	0.74		0.77	
Normalised mean square error (NMSE)	0.16		0.16	
Fractional bias (FB)	0.13		-0.09	
Number of data	360	360	358	358

At both stations the predicted $PM_{2.5}$ concentrations agree fairly well with the measured data. The model has slight over prediction for the station at Vallila and minor under prediction for the station at Kallio. The scatter plots of the predictions and observations at Vallila and Kallio in 2002 is presented in Figure 6.9a and b.

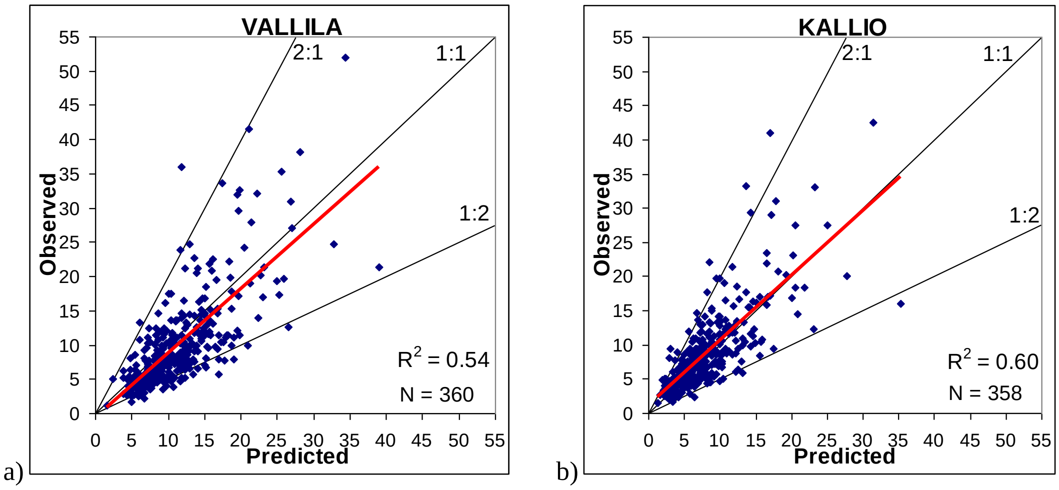


Figure 6.9: The scatter plots and the correlation coefficient squared (R^2) values of the predicted and observed daily average $PM_{2.5}$ concentrations in 2002, for the monitoring stations at Vallila (a) and Kallio (b).

Predicted total annual average concentration of $PM_{2.5}$ in the Helsinki metropolitan area and Helsinki city centre are presented in Figure 6.10a and b, respectively. On a yearly basis, the estimated contribution from regional and long-range transported origin to the observed $PM_{2.5}$ varies from 40 % at the most trafficked areas in Helsinki to nearly 100 % in the outskirts of the metropolitan area.

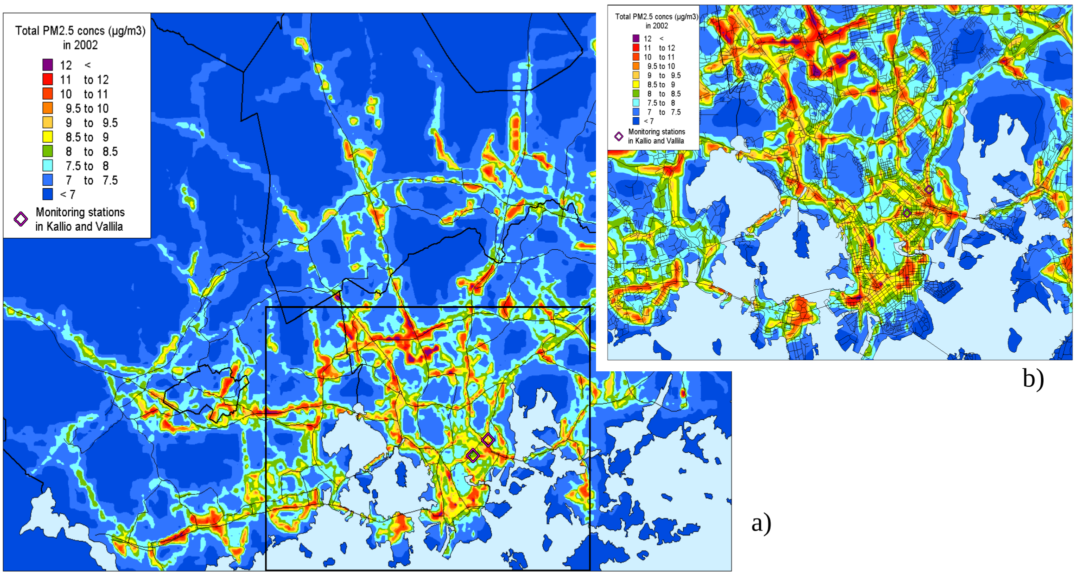


Figure 6.10: Predicted total annual average $PM_{2.5}$ concentrations [$\mu g/m^3$] in 2002, in the Helsinki metropolitan area (a) and in the centre of Helsinki (b). The main road and street network, and the monitoring stations of $PM_{2.5}$ are also presented in the figure.

6.4.4 Conclusions

The comparison of the modelled daily averaged values with the corresponding measurements showed a fairly good agreement. The results show that the statistical LRT model is a useful and simple tool for the assessment of LTR'ed $PM_{2.5}$ that is applicable within a fairly good accuracy. Clearly, the model also has inherent limitations. The accuracy of the model presented depends on the chemical composition of $PM_{2.5}$, especially the content of carbonaceous species; however, measurements of these species at the EMEP stations have not been published. The ion sum parameter defined also contains in part the measurements of two gaseous substances (HNO_3, NH_3). If their concentrations were high, compared to the concentrations of the corresponding compounds in particulate form, there could be substantial inaccuracies in the model predictions.

6.4.5 References

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6.5 Regional scale dispersion modeling of fine particulate matter (SILAM)

[Sofiev M., Jourden E., Pirjola L., Kangas L., Karvosenoja N., Karppinen, A. and Kukkonen J, 2007. Dispersion modelling of the concentrations of fine particulate matter in Europe, *Proceedings ot the 28th NATO/CCMS, ITM on Air pollution Modelling and its Applications,* May 15-19, 2006, Leipzig, Germany].

6.5.1 Introduction

The results presented are based on a research project "An integrated model for evaluating the emissions, atmospheric dispersion and risks caused by ambient air fine particulate matter" (KOPRA) of Finnish Finding Agency for Technology and Innovation (TEKES). An overall goal of the project was to evaluate the whole cycle of aerosol air pollution in Finland including emission of particulate matter and its pre-cursors, their dispersion, transformation and deposition, resulting contamination patterns and their impact to public health, as well as possible ways to reduce the aerosol atmospheric concentrations. In this paper, we concentrate of dispersion simulations performed with the Finnish emergency and air quality model SILAM at Finnish Meteorological Institute. The main goal of these simulations was to assess a link between the Finnish and European emissions of various gaseous and particulate species and resulting aerosol contamination of northern Europe. A specific goal was to build as complete budget for the aerosol composition over Finland as possible and compare the resulting bulk values with the observations. Separate verification was performed for some specific substances, such as aerosol precursors, primary PM, sea salt, etc.

6.5.2 Input data and modelling tools

Input data for the simulations were combined from several sources. European-wide anthropogenic emission of particulate matter (with a split to $PM_{2.5}$ and $PM_{2.5\text{-}10}$), as well as of sulphur oxides, was adopted from the WebDab database of European Monitoring and Evaluation Programme EMEP (www.emep.int). The information was available at annual level and with spatial resolution of 50 km. Temporal disaggregating to hourly fluxes was made on a country-by-country basis using the results of EUROTRACGENEMIS project (Lennart *et al.*, 1997). Vertical distribution of emission followed the EMEP methodology based on 11 emission source categories and characteristic injection heights for each of them (Simpson *et al*., 2003). The European information was complemented with a high-resolution Finnish national emission inventory with detailed chemical and size-segregation splits: emission of primary particles was considered for 5 size classes ($PM_{0.1}$, $PM_{0.1\text{-}1}$, $PM_{1\text{-}2.5}$, $PM_{2.5\text{-}10}$, $PM_{10\text{-}TPM}$) and included separate estimates for the following compounds: black carbon, organic carbon, dust, sulphates, and total PM. Emission of pre-cursors included SO_2, NO_x, NH_3, and anthropogenic VOC. The dataset included spatially distributed emission with a resolution of 1 km and over 250 point sources with physical stack characteristics. Temporal dis-aggregating was performed following the same GENEMIS methodology. Vertical injection height for area sources was assumed to be within the lowest 100 m, while the plumes from point sources were parameterised using actual stack heights though made independent from actual meteorological conditions to reduce the computation costs. Meteorological information and necessary geophysical and land cover maps were taken from the FMI-HIRLAM and ECMWF meteorological models. All input data covered the period of 2000-2002 and the simulations were also targeting this time interval. The main modelling tool used for regional- and meso-scale simulations was the Finnish Emergency and Qir Quality Modelling System SILAM (Sofiev *et al*, 2006). It is a lagrangian particle model with Monte-Carlo random-walk mechanism representing the vertical and horizontal turbulent diffusion. The system includes a sophisticated meteorological pre-processor for evaluation of basic features of boundary layer and free troposphere using the meteorological fields provided by NWP models. In implementation, SILAM assumes well-mixed boundary layer and fixed turbulent diffusion coefficients in free troposphere. Exchange between them is mainly driven by temporal variation of the top of boundary layer. A physico-chemical module of SILAM covers up to 496 radioactive nuclides, sulphur oxides, primary particles of various types as well as probability (used for evaluation of area of risk and for solution of inverse-problems). The system accepts an arbitrary definition of the particle size spectrum described in the current study via a set of bins. Chemical transformations of SO_x follow the scheme of DMAT model (Sofiev, 2000). A local-scale model CAR-FMI (Kukkonen *et al*., 2001a,b) was used for evaluation of Helsinki city-scale pollution levels. Evaluation of the influence of aerosol dynamics is done using the aerosol dynamics model MONO32 (Pirjola and Kulmala, 2000; Pirjola *et al.*, 2003). MONO32 is a box model covering gas-phase chemistry and aerosol dynamics. The model uses monodisperse representation for particle size distribution with an optional number of size modes. In this work, five modes are used: nucleation, Aitken, accumulation, and two coarse modes. All particles in a certain mode are characterised by the same size and composition, and they can consist of sulphuric acid, ammonium sulphate, ammonium nitrate, organic carbon, elemental carbon, sodium chloride, and mineral dust. Water content of aerosols is calculated separately. Particles can be emitted as primary particles or formed in the atmosphere by nucleation. Size and composition of particles in any class can change due to multicomponent condensation of sulphuric acid and organic vapours as well as due to coagulation between particles. A specific model, simulation setup, and input data were needed for evaluation of the desert dust pollution. Due to highly episodic character of this phenomenon as well as its strong inter-annual variability, computations over a single or a few years would be insufficient to catch even an order of magnitude of its contribution to aerosol concentrations over Finland. Therefore, we utilised a simplified but computationally efficient model DMAT (Sofiev, 2000), which was forced by pre-processed NCAR 22-years long meteorological re-analysis over the Northern Hemisphere. More information on this study can be found in (Hongisto & Sofiev, 2004).

6.5.3 Results and discussion

Following the strategy outlines above, four sets of simulations have been performed: at the European-scale – for primary $PM_{2.5}$, $PM_{2.5\text{-}10}$, sea salt, and SO_x; at regional scale – for primary $PM_{0.1}$, $PM_{0.1\text{-}1}$, $PM_{1\text{-}2.5}$, $PM_{2.5\text{-}10}$, PM-coarse (over 10 μm size), and SO_x; for Helsinki area – $PM_{2.5}$, PM_{10} and NO_x; finally, the wind-blown dust was computed for the Northern Hemisphere. European-scale resolution was 30 km with daily averaging, regional simulations provided 5 km daily output fields while hemispheric runs were made with 150 km grid and provided monthly-mean values. The reference year was 2000; most of simulations were also performed for 2001 and 2002; hemispheric simulations were made for the period 1967-1988 in order to obtain a climatologically representative dataset. There were also a few case studies in the adjacent years (1999, 2003) made for the periods of observational campaigns. An example of the simulation results is presented in Figure 1 for primary $PM_{2.5}$, which characteristic level in 2000 was about 1 μg m^{-3} over large areas of Europe with several highconcentration areas. This is in a good agreement with the aerosol model simulations by EMEP Western Centre (Kanhert & Tarrason (eds), 2003). However, nearly twice better spatial resolution of current simulations allowed for more detailed patterns over strongly polluted areas, such as Po Valley, Scandinavian capitals, etc. Improved resolution over Finland and, further, over Helsinki area also highlighted local-scale distributions – both as urban vs. regional background (visible at 5-km map) and over specific parts of the city (local-scale map). It should be pointed out that the 5 km map in Figure 6.11 is presented without the European background, which would bring the total level of primary $PM_{2.5}$ concentrations over southern Finland to the level of about 1-2 μg PM m^{-3}. Direct comparison of primary particles with observations was not performed because in 2000 there were practically no representative observations resolving the chemical composition of aerosol and thus capable of separating the primary PM from secondary inorganic aerosol (sulphates, nitrates and ammonia), sea salt and mineral dust. The second part of aerosol budget constitutes from the secondary inorganic aerosol.

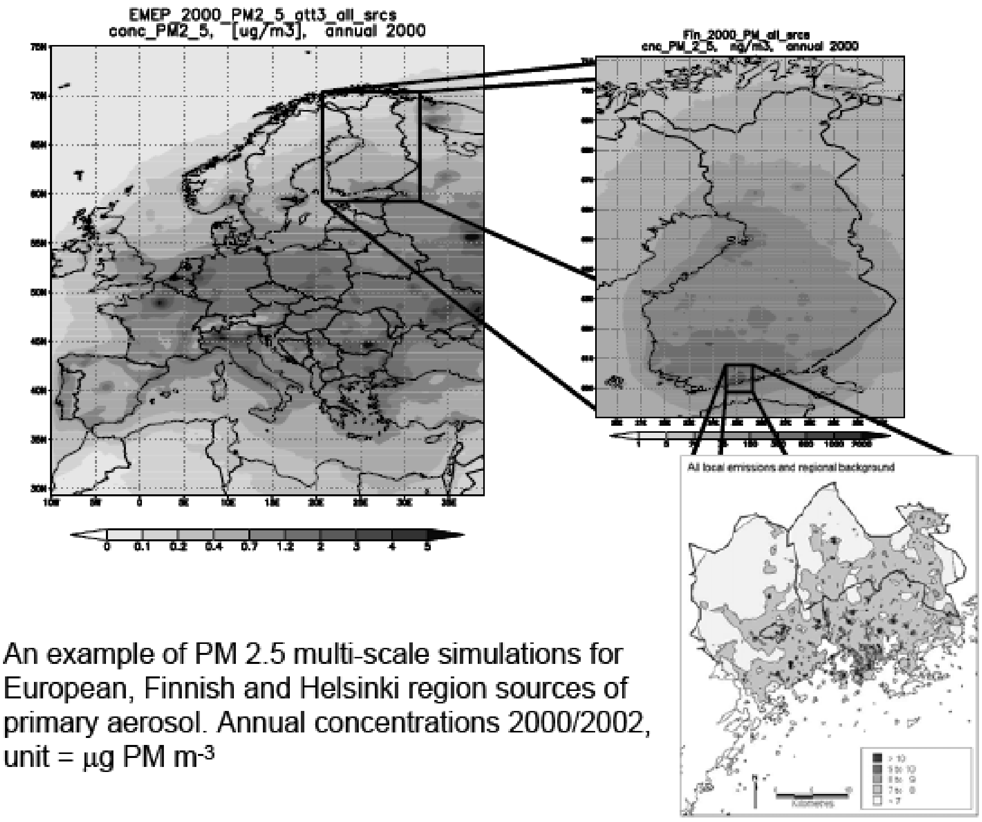

Figure 6.11: An example of three-scale off-line nested simulations for primary $PM_{2.5}$.

Comparison of sulphates and SO_2 with airborne measurements of e.g. EMEP network as well as with other models is quite straightforward. According to that, the SILAM simulations have “standard” accuracy: the model tends to slightly underestimate sulphates being otherwise within a factor of two from the most of observations. Simulations for two more components of the atmospheric aerosol are – sea salt and windblown dust – are shown in Figure 6.12a and 2b, respectively. Near-surface concentrations of the wind-blown dust do not make much sense over Scandinavia because most of such aerosol flies over thousands of kilometres before reaching the region, which implies a wide and often uneven distribution along the vertical of the arrived masses. Therefore, the only representative parameter for that component is the vertically integrated column burden. Observations of the sea salt are quite scarce and can be performed either via comparison of vertically integrated aerosol optical depth observed by satellites or by comparing some chemical components specific for this type of aerosol, for example, Na+, which constitutes about 30% of the sea salt mass. Comparison with Na+ observations at Mace Head showed that the model tends to under-estimate the overall level of concentrations by a factor of 2-3, closely capturing the summer low-salt periods and being significantly lower than measurements over winter periods when strong storms inflate the salt concentrations by 3-5 times. This seasonality in the model is less pronounced. The present sea salt emission module in SILAM is based on improved scheme of Monahan *et* al. (1986). It is known to somewhat under-produce the sub-micron particles, which have the longest transport distance. The other feature of the scheme – strong over-production of particles smaller than 0.05 µm was corrected during implementation. Finally, SILAM emission module neglects the mechanism of production of coarse particles (over 10 µm) as they have no impact on regional and long-range transport. However, they can still significantly affect observations at Mace Head.

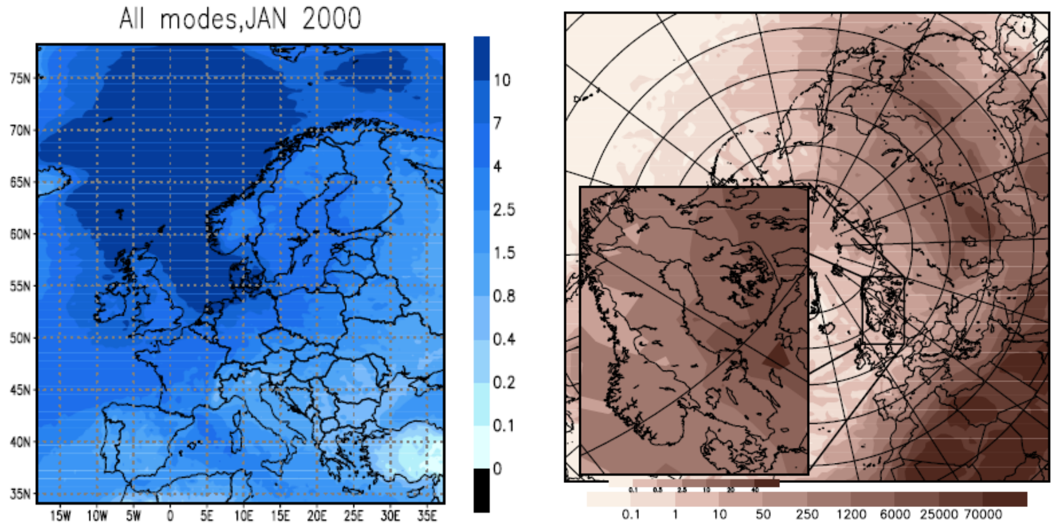

Figure 6.12: a) Mean Jan 2000 concentration of sea salt (all size classes). Unit µg PM m^{-3}. b) Mean 1967-1988 vertically integrated wind-blown dust concentration in air column. Unit: mg PM m^{-2}. Obs different scales!

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7 PM atmospheric concentrations in France : analysis and key findings

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7.1 Introduction

Since the year 2000, a significant effort has been provided in France for enhancing the air quality monitoring structure devoted to the Particulate Matter measurement Although PM_{10} was the priority, the assessment of the $PM_{2.5}$ concentrations has not been neglected because of their adverse effects on human health. Research partners together with national and local organisations in charge of air quality monitoring have developed skills and experience related to the behaviour of PM emissions and concentrations in the air. In 2007, it seems feasible to establish a first assessment of the PM situation in France, compiling data issued from several types of information:

- Emission inventories allow to analyse source apportionment, to assess the efficiency of control measures, and to feed air quality models. Development of PM (and their precursors) emission inventories is a crucial and difficult task, still hampered by the lack of knowledge related to the sources and the processes. However results considered as reasonably relevant are now published.
- In 2006, more than 300 PM_{10} measurement stations and 65 $PM_{2.5}$ stations were implemented in France. This is the result of more than 15 years devoted to the development of the PM monitoring strategy in France. Most of them are TEOM or beta gauge devices which allow to get high temporal and spatial resolutions. With such a dense network, a database workable for reporting on the PM situation and for trend analysis has been built. More information is provided by research projects, supersites, and field campaigns devoted to a better characterisation of the aerosol composition and the origin of PM events.
- Although particulate modelling is still a science under development, a dynamic research policy in that field, allowed the implementation of PM models dedicated to air quality forecasting and to a comprehensive analysis of the aerosol phenomenology. Thus modelling is considered as a part of the whole PM monitoring system implemented in France.

The present report compiles the information currently available from the French PM monitoring system and provides an interpretation of the PM situation in the country. A first section is dedicated to the PM emissions status. The second part describes the PM measurement network and specific field campaigns. Results and trends issued from these data are presented in a third section. Before concluding, an interpretation of the PM phenomenology in France based on measurement and modelling is proposed.

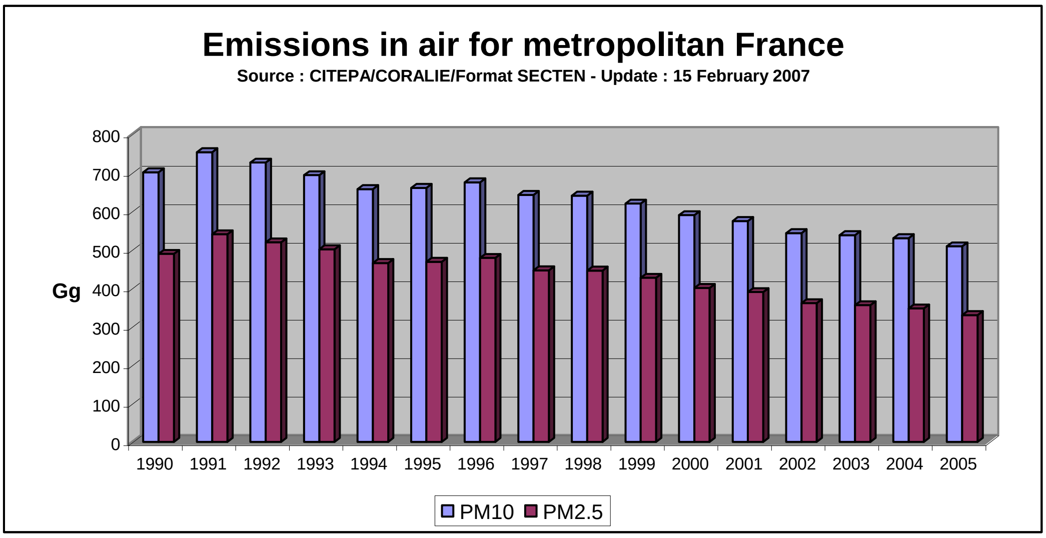
7.2 PM emission inventories

Emission data related to PM_{10} and $PM_{2.5}$ from 1990 to 2005, and recently updated, are given below.

PM EMISSIONS IN AIR FOR METROPOLITAN FRANCE (units Gg = kt)

Source CITEPA / CORALIE / format SECTEN Update : 15 February 2007

Année	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005
PM10	**701**	**753**	**726**	**693**	**657**	**660**	**674**	**642**	**640**	**619**	**589**	**574**	**542**	**537**	**529**	**508**
PM2.5	**489**	**540**	**519**	**500**	**465**	**468**	**478**	**446**	**445**	**427**	**400**	**389**	**360**	**355**	**347**	**329**



In 2005, **emissions of PM_{10}** in metropolitan France are **508 Gg**. These emissions decreased by about 28% from 1990 to 2005, despite the high emission level in 1991. The main contributors to these emissions are, by order of importance:

- Agriculture and forestry (29%), especially ploughing
- Manufacturing industry (28%), especially quarrying and building sites
- Residential/tertiary (28%), especially wood, coal, and fuel combustion.

Emissions of $PM_{2.5}$ in metropolitan France are **329 Gg** in 2005. These emissions decreased by about 33% from 1990 to 2005.

The main contributors to these emissions are, by order of importance:
- Residential/tertiary (41%), especially wood, coal, and fuel combustion
- Manufacturing industry (26%), especially quarrying and building sites
- Agriculture and forestry (17%), especially ploughing.

Both PM_{10} and $PM_{2.5}$ emissions decreased in all sectors except in transport activities (not including road transport). This is partially due to progress in dust removal techniques, but also comes from structural effects such as technological improvements in biomass combustion.

7.3 Description of the French PM measurement networks

Intensive work related to the measurement of PM concentrations has been realised these last years in France. A quite dense operational network devoted to reporting, monitoring and public information has been implemented, together with supersites devoted to research purposes and PM monitoring following the highest levels of requirement of the EMEP strategy. Field campaigns allow to get a complementary information, and to insure the equivalence of the automatic methods with the reference one (gravimetry HVS DA-80) described by the norm CEN/TC264, 2005.

7.3.1 Regulatory network implemented for monitoring purposes

Figure 7.1 presents the location of PM_{10} measurement stations in 2006. The stations are operated by local associations in charge of air quality monitoring (AASQA), acting with the agreement of the Ministry of Ecology. The observations are compiled in two databases implemented and maintained by the Agency in charge of the Environment and the Energy (ADEME): near real time unvalidated data are stored in the BASTER database when validated data are compiled following a longer term process in the BDQA database.

All the PM monitoring stations are based on automatic devices (85% TEOM - Tapered Element Oscillating Microbalance - and 15% beta gauges - β ray attenuation monitor) which allow high temporal resolution.

PM_{10} stations are distributed throughout the country in the following way: about 72% in urban and suburban areas, 2.5% in rural areas. Near emissions sources, about 13% of the number of sites are traffic ones and 12.5% are industrial stations.

$PM_{2.5}$ stations are mainly located at urban and suburban locations (79 %), 19% at traffic sites and the difference concerns industrial sites.

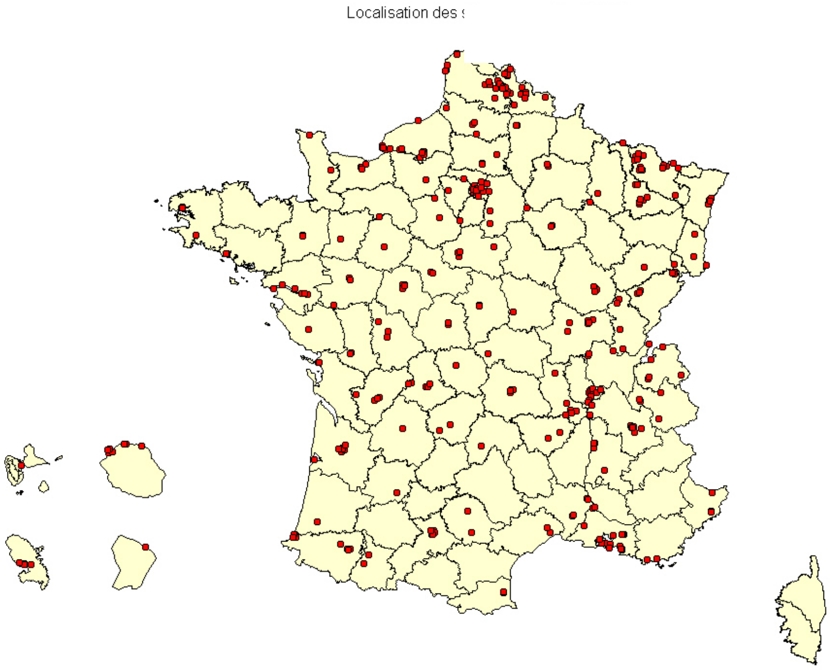


Figure 7.1: PM_{10} measurement network in France (2006).

7.3.2 *Field campaigns*

As far as air quality monitoring is concerned, the main field campaigns from 2002 up to now are listed below:

Objectives	material	where	When	results	Ref
Demonstration of equivalence of the TEOM-FDMS PM_{10} and $PM_{2.5}$	Partisol 2025 TEOM-FDMS	Paris (Bobigny)	2005	TEOM-FDMS ok for PM_{10} and $PM_{2.5}$	[Le Bihan, 2005 and 2006] [Mathe, 2006)
		Marseille	2006		
Demonstration of equivalence of the Beta Gauge MP101M-RST PM_{10}	Partisol 2025, MP101M-RST	Paris (Bobigny), 2005	2005	MP101M-RST ok for PM_{10}	
		Marseille, 2006	2006		
		Italy (b)	2003		
		Belgium (a)	2006		
Preliminary test of the TEOM-FDMS PM_{10}	Partisol 2025, TEOM-FDMS	Paris	2003, 2004	High correlation between FDMS and the reference method for PM_{10}	[Bessagnet, 2004]
PM_{10} chemical composition	Partisol 2025	Paris, Rouen	2002	Confirmation of the TEOM 50°C under-estimation of PM_{10} mass	[Blanchard, 2002]

(a) : French participation to a program led by Belgium.
(b) : Intercomparison test performed by CNR-IIA (Italy)

7.3.3 *EMEP remote stations and research supersites*

In the framework of the EMEP monitoring strategy, two french remote stations of the French Background Air Pollution Monitoring Network (MERA) have been recently equiped to measure PM_{10} (Figure 7.2). The sampling method used is the automatic system TEOM.

A 1-year measurement campaign, started in June 2006, is running in another EMEP-MERA site (FR09 Revin) with the objective to evaluate the equivalence of the automatic method with the reference one. The first preliminary results already show the necessity of TEOM FDMS.

Nitrates and ammonium daily concentrations are also measured at the two sites and could help out in the interpretation.

The Puy de Dôme supersite is operated by the Observatoire de Physique du Globe de Clermont-Ferrand. The site is located in the Auvergne region (Central France) at 1465 m high, far away from emission sources. The sampling site is influenced by both long-range transport of gas and particles from the free troposphere and by the more regional boundary layer air.

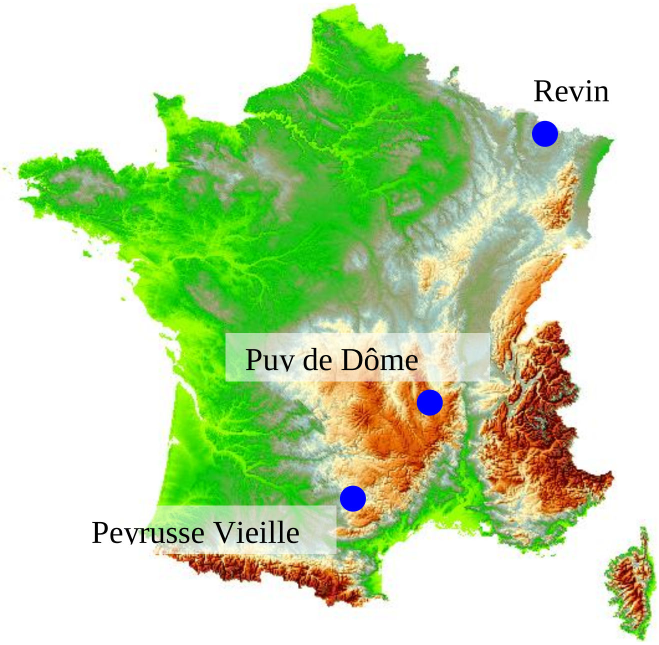


Figure 7.2: Location of EMEP supersites and Puy-de-Dome PM station.

The site is equipped with complete instrumentation to characterize aerosol properties:

- ❑ Aerosol Chemistry : low volume samplers for IC and OC/EC chemistry (PM_{10}) since 2003
- ❑ Aerosol Chemistry : High volume sampler for IC and organic speciation (PM_{10}- CARBOSOL program) since 2004
- ❑ Aerosol Size segregated Chemistry since 2006
- ❑ Size distribution since 2005
- ❑ Optical properties : scattering (nephelometer) since 2006 and absorption (aethalometer) coefficients since 2000
- ❑ Hygroscopic properties : HTDMA during research campaigns in 2006
- ❑ Aerosol Mass –(RH-Controlled gravimetry on aerosol filters PM_{10}) since 2006 and number concentrations (CN counter) since 2003

Finally, it should be noted that puy de Dôme is now a part of the EUSAAR network. The objective of the project EUSAAR is the integration of measurements of atmospheric aerosol properties performed in a distributed network of 20 high quality European ground-based stations (Supersites). This integration contributes to a sustainable and reliable operational service in support of policy issues on air quality, long-range transport of pollutants and climate change. The project is coordinated by CNRS in Clermont-Ferrand.

7.3.4 Issues related to the use of TEOM and beta gauge devices

The reference method for sampling and measurement of PM_{10} as mentioned in the 1st Daughter Directive 99/30/EC is described in EN 12341:1999 standard. It is based on 24 hours sampling of PM_{10} on filters followed by filters weighting under controlled humidity and temperature conditions. However, this method is not sufficiently operational for routine monitoring. The main difficulties encountered when using this method are:

- delicacy of filter handling procedures;
- impossibility to provide real-time data for public information (daily basis prescribed in Directive)
- -high running costs (weighting room with controlled atmosphere, whole measurement process).

Automatic tools such as TEOM or beta gauges bring a solution to these difficulties. However, the 90's version of such devices does not measure correctly the PM semi-volatile compounds. Consequently, the use of these techniques leads to an underestimation of PM levels compared with the reference method.

The main reason for that was clearly identified as the volatilisation of some PM_{10} compounds in the instrument. This is illustrated in the Figure 7.3 for the TEOM: TEOM measurements need to be corrected with volatilised compounds (ammonium nitrate in this case). This underestimation is an important point because it makes the TEOM measurement and beta gauge methods not equivalent to the reference method.

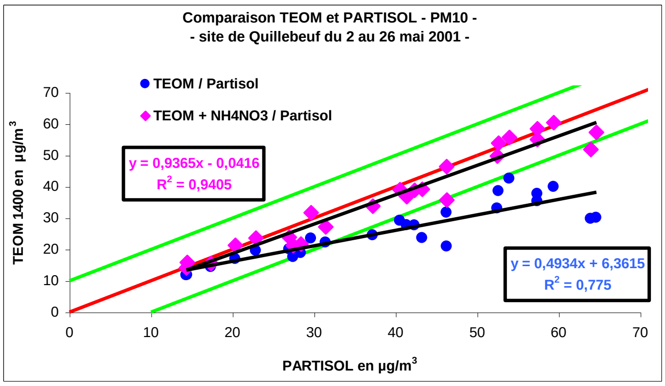


Figure 7.3: Correlation between TEOM and reference method (blue), and TEOM corrected with NH_4NO_3 and reference method (pink), for PM_{10} measurements.

The first option examined to tackle this problem was to correct TEOM measurements with a conversion factor. However, field operations have demonstrated that this conversion factor is highly variable in time and space. Table 7.1 show that this factor ranged between 1.0 and 1.5 for monthly averages, and can exceed 2 for daily values.

Looking for an instrumental option, two technical solutions have been identified and tested: for the MP101M beta gauge, the RST module (Regulated Sampling Tube); for the TEOM, the FDMS (Filter Dynamics Measurement System). These additional modules dry and master the particles in such a way that the measurements are comparable to the reference method.

Table 7.1: Relation between TEOM and reference method for PM$_{10}$ measurement for different sites and seasons. n is the number of daily samples.

Site	**Typology**	**Period**	**n**	**PARTISOL/TEOM** PM$_{10}$ **µg/m^3**	**Mean ratio**	**Ratio [min - max]**
Auteuil	Traffic	summer	30	43,6 / 43,8	1,0	0,9 – 1,1
		winter	30	40,5 / 36,4	1,1	0,9 – 1,3
Gennevilliers	Urban background	summer	23	24,0 / 22,0	1,1	1,0 – 1,3
		winter	30	24,5 / 18,7	1,3	0,8 – 1,7
PA 18	Traffic	summer	34	23,9 / 21,9	1,1	0,9 – 1,3
		winter	31	30,4 / 21,9	1,4	0,9 – 1,8
Vitry sur Seine	Urban background	summer	29	20,6 / 19,8	1,0	0,9 – 1,3
		winter	28	30,5 / 21,3	1,4	0,7 – 2,0
Quillebeuf	Industrial	summer	32	35,5 / 23,9	1,5	1,1 – 2,2
Le Havre	Urban background	summer	29	23,3 / 19,9	1,2	0,9 – 1,7

To demonstrate the equivalence with the reference method, by the end of 2004, field operations started to obtained necessary data with respect to the European Commission "guidance on the demonstration of equivalence". These field campaigns have been carried out in France, or in Belgium in collaboration with European partners.

An example of intercomparison result is proposed in Figure 7.4. Table 7.2 gives a summary of the all data obtained.

Results for the two automatic monitoring methods show that the following meet the equivalence criteria set out: TEOM retrofitted with FDMS (for PM$_{10}$ and PM$_{2.5}$); and beta gauge MP101M-RST (for PM$_{10}$). The equivalence criteria is respected without the application of correction for slope and/or intercept.

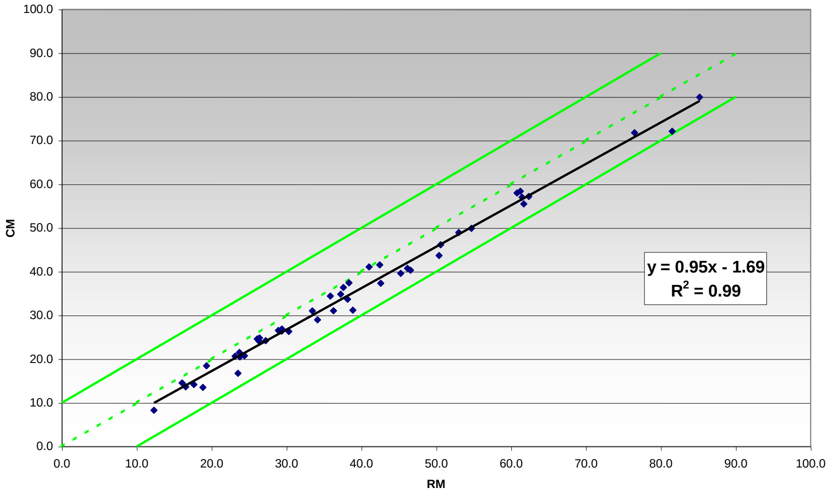


Figure 7.4: Correlation between PM$_{10}$ measurement with the reference method (RM) and FDMS (CM) in Paris (urban background site of Bobigny, winter 2005, 49 daily samples.

Table 7.2: Field campaigns devoted to the equivalence checking.

Candidate method	Trial site location	Time period	Equivalence criteria met?
Thermo R&P TEOM-FDMS PM_{10} series 8500 version b [(a)]	Bobigny (France)	25/01 to 17/04/2005	**Yes**
	Marseille (France	21/12/2005 to 13/04/2006	
Thermo R&P TEOM-FDMS $PM_{2.5}$ series 8500 version b [(a)]	Bobigny (France)	25/01 to 17/04/2005	**Yes**
	Marseille (France	21/12/2005 to 13/04/2006	
Environnement SA MP101M-RST PM_{10} [(b)]	Bobigny (France)	25/01 to 17/04/2005	**Yes**
	Marseille (France	21/12/2005 to 13/04/2006	
	Aarschot (Belgium)	10/05 to 24/06/2006	
	Monterotondo (Italy)	24/06 to 19/08/2003 & 10/12/2003 to 11/01/2004	

(a) 1h-step time measurement
(b) 24h-step time measurement

Due to the variability of test sites (in time and space) involving different composition of ambient air and meteorological conditions, it can be assumed that equivalence for equipment tested under the used configuration is valid anywhere else in France under ambient conditions.

Once the equivalence procedure has been conclusive, 2006 spring has been dedicated to define an implementation strategy all over the French territory, to produce validated PM_{10} measurements, including the volatile fraction of PM_{10}. The system calibrated to produce corrected data is based on a network of reference sites, where PM_{10} are measured simultaneously with usual TEOM and TEOM-FDMS. The difference between the two measurements is used on a scale defined by the user (regional in most cases) to adjust TEOM measurements on sites where FDMS are not yet installed.

By now, about 50 reference sites are producing real-time corrections.

7.4 Results and trends for PM_{10} and $PM_{2.5}$ concentrations

Note : the results presented below are issued from non corrected measurement data (prior to 2006). The volatile fraction of the particles should not been taken into account.

7.4.1 Basic statistics

Figure 7.5 and Figure 7.6 show the trends of PM_{10} concentrations since 1998. Since 2004, concentrations get the same level; a slight increase can even be noted in 2006. The exceptional events observed in summer 2003 with the heat wave are also visible on PM concentrations.

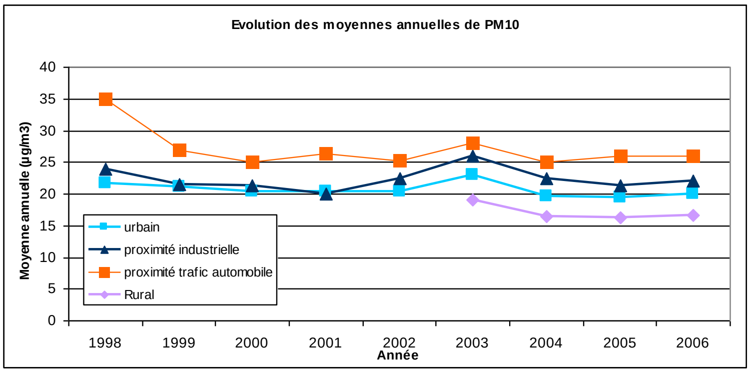


Figure 7.5: PM_{10} concentrations in France since 1996.

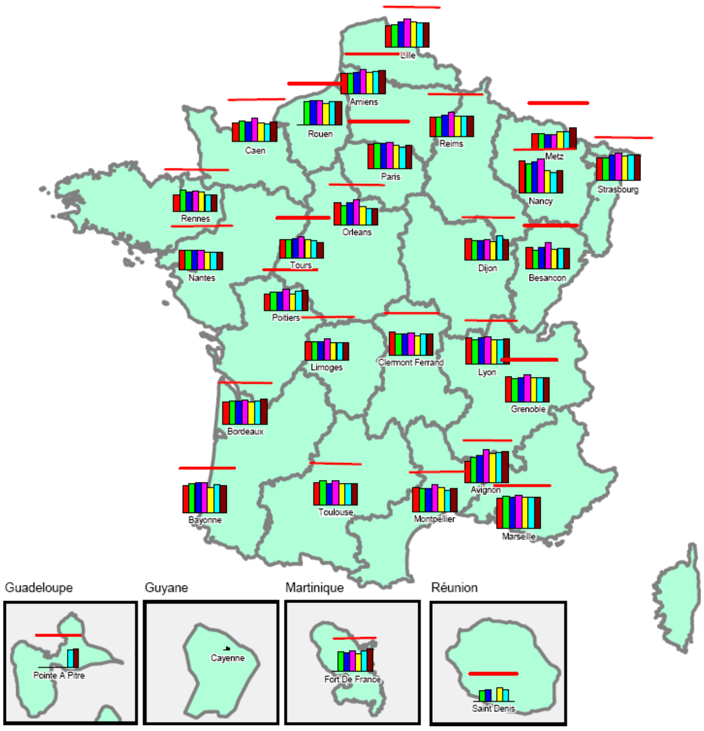


Figure 7.6: PM_{10} concentrations in the French cities.

The annual averages of $PM_{2.5}$ and PM_{10} concentrations in different regions are presented in Figure 7.7. Highest concentrations are measured at traffic stations for both pollutants.

In urban areas, highest $PM_{2.5}$ concentrations (15 to 18 µg/m^3) are found in the South-East (Provence-Alpes Cote d'Azur), and in the Eastern side of the country (Alsace, Rhone-Alpes). The western part is not concerned by such concentration levels. Areas near the Atlantic side get $PM_{2.5}$ concentrations 5 to 7 µg/m^3 lower than those measured at the eastern sites. The north, the Centre of the country as well as Paris area get median concentrations levels (12 to 14 µg/m^3).

The East/West gradient noted for $PM_{2.5}$5 concentrations also holds for PM_{10} concentrations. Mediterranean area is still the most exposed and Nantes, a city located on the Atlantic coast the less one. Paris area and the North show quite high PM_{10} concentrations, generally higher than those observed in Alsace and Rhone-Alpes regions.

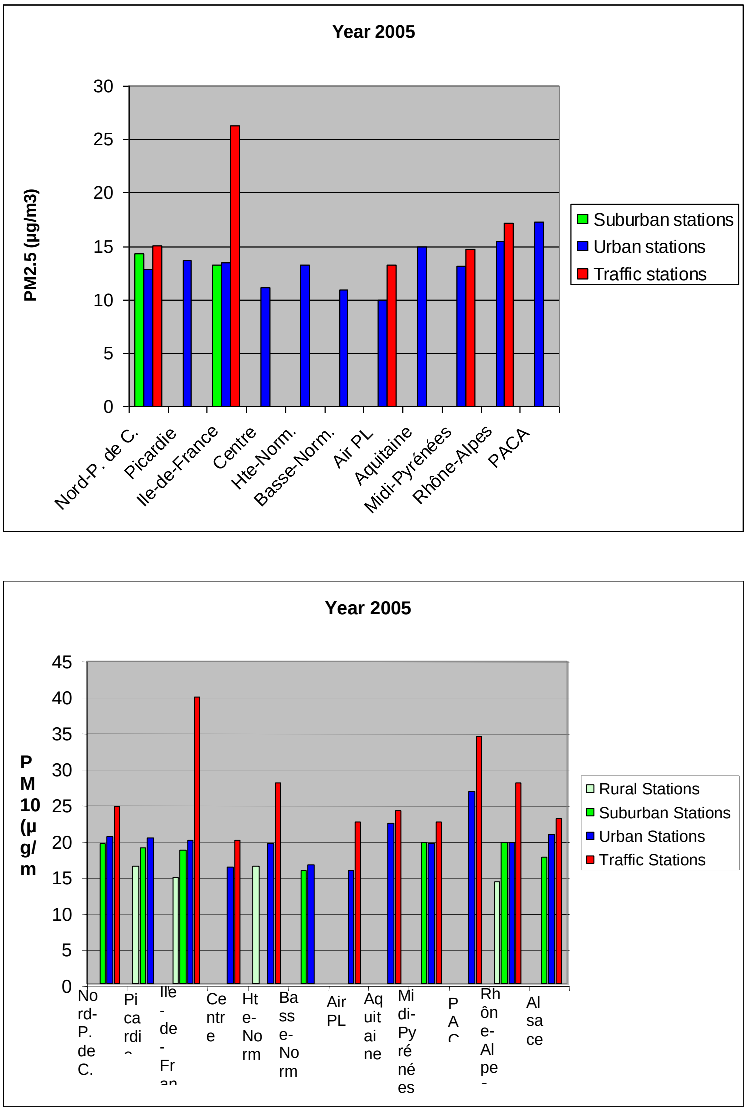


Figure 7.7: $PM_{2.5}$ and PM_{10} annual means in French regions.

It should be noted (not shown) that $PM_{2.5}$ and PM_{10} concentrations were particularly high everywhere during summer 2003, when the heat wave occurred in Europe. High photochemical activity could help to explain this phenomenon.

Comparable levels of concentration have been observed at remote sites (EMEP sites) located at Peyrusse-Vieille (FR13 EMEP site) in the South of France and Revin in the North. In 2006-2007 the daily mean concentrations were respectively 15.3 µg/m^3 (Aug 06 to Feb 07, average daily data, 9h-9h TU)) with a maximum daily value at 60 µg/m^3 and 13.8 µg/m^3 (Aug 06 to Feb 07, average daily data, 9h-9h TU) with a maximum value of 46 µg/m^3 (Figure 7.9).

Except for this period, analysis of seasonal variability demonstrates the following statements:

- $PM_{2.5}$ concentrations are higher in March/April and November/December than the rest of the year;
- They are the lowest in summer;
- Seasonal variability of urban $PM_{2.5}$ is more or less sharpened depending on the cities considered (see Figure 7.8 with a clear difference between summer and winter at Grenoble and Strasbourg).
- No seasonal trend is observed for PM_{10} concentrations. In some cases, they are higher in winter than in summer, in other situations the contrary is true. In most cases concentrations averaged over both periods are rather comparable.

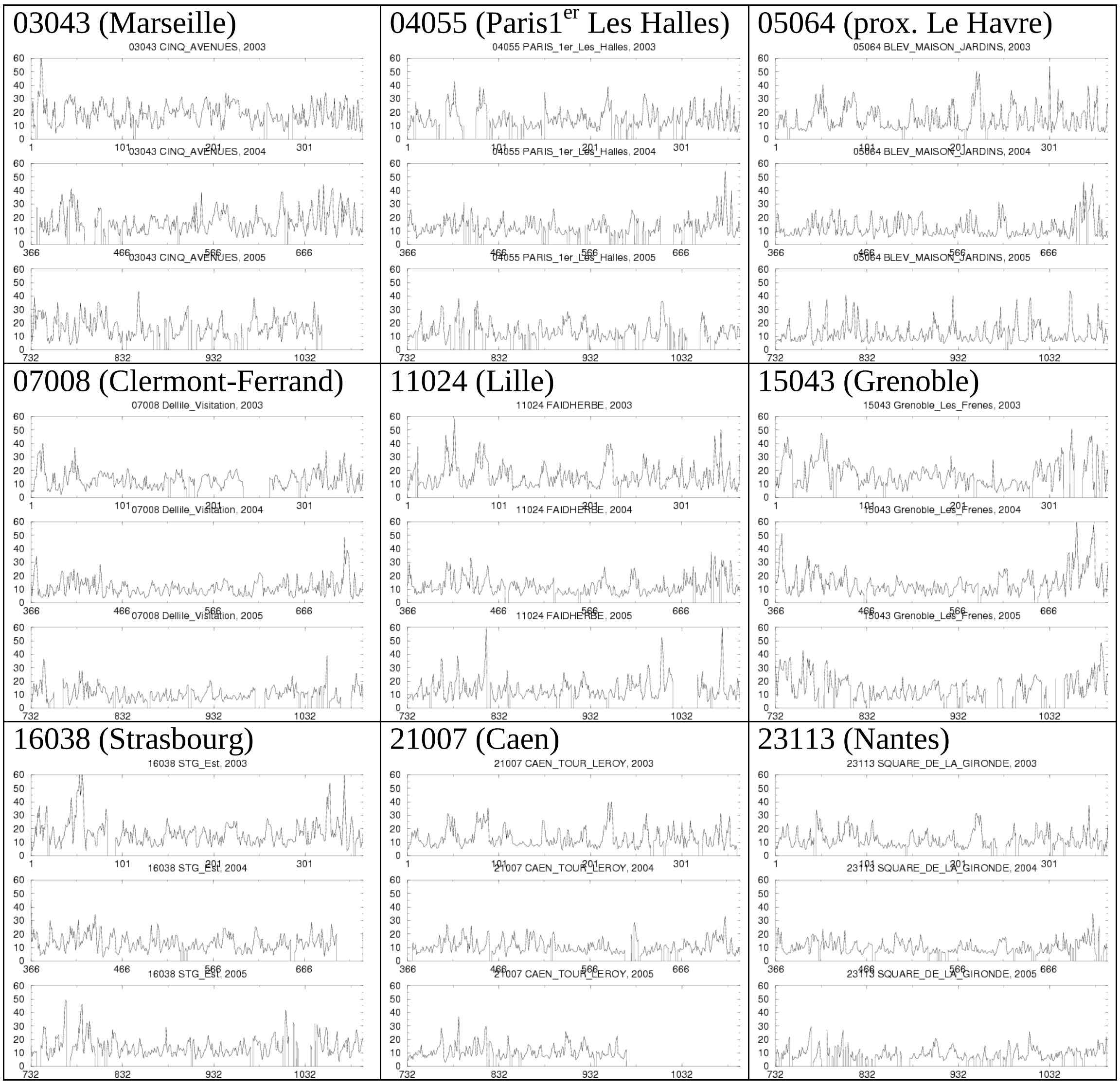


Figure 7.8: $PM_{2.5}$ concentrations time series for few French cities.

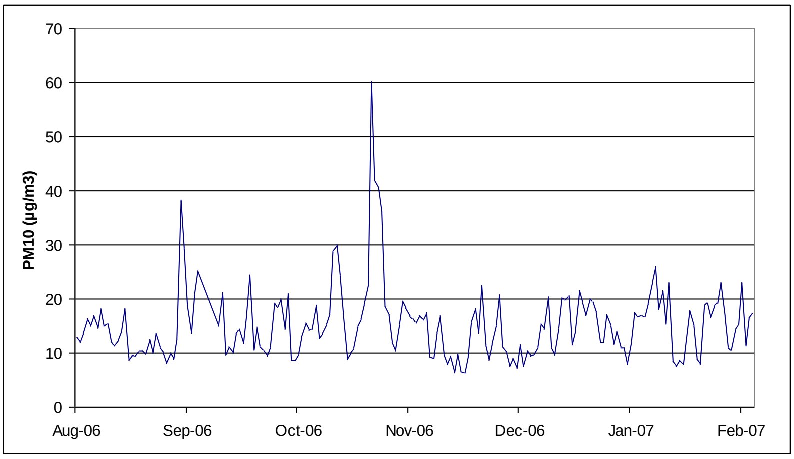


Figure 7.9: PM_{10} concentrations (µg/m^3, daily value) measured at Peyrusse Vieille (FR13, EMEP station) from July 2006 to February 2007.

7.4.2 PM characteristics

Characteristics of PM are thoroughly investigated at the Puy-de-Dome supersite. A large panel of indicators is evaluated helping in a better understanding of the rural background composition. PM mass composition at urban and suburban sites has been analyzed during the equivalence campaigns which held in Paris and in the Normandy regions (see Section 7.3.2).

7.4.2.1 Puy-de-Dome situation

Concentrations measured at the site show that the site is typical of the natural background. Average PM_{10} mass is slightly lower than 5 µg/m^3 (daily average) with minimum values lower than 1 µg/m^3 (free tropospheric background) and maximum values close to 30 µg/m^3 (Saharan dust episodes).

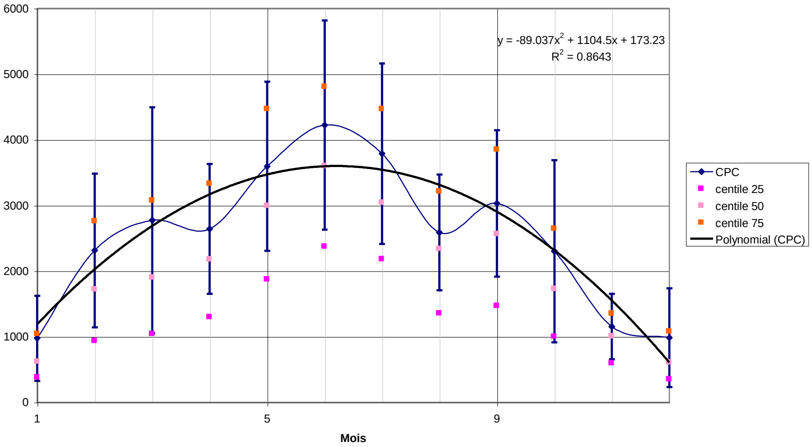


Figure 7.10: Max, Min and percentile (25%, 50% and 75%) of the particle number concentration at Puy de Dôme for each month.

The number concentration also shows high variability, mostly linked to seasonal variability (Figure 7.10) with highest values in summer (4000 part. cm^{-3} – hourly average) and lowest values in winter (1000 part cm^{-3} – hourly average). Such variability is obviously linked to both change in boundary layer height and in the origin of air masses advected to the site. This signal is also influenced by nucleation episodes as discussed thereafter.

The evolution of the particle size distribution is seen on a daily basis at Puy de Dôme. The mode of the size distribution lies around 50 nm during background periods regardless of seasons and the distribution is mono-modal. During summer months, an additional source of particle is present, due to mixing with boundary layer air, leading to bimodal size distribution with both Aitken (30 nm) and accumulation (80 nm) modes. Figure 7.11 shows typical daily variation during different seasons at Puy de Dôme.

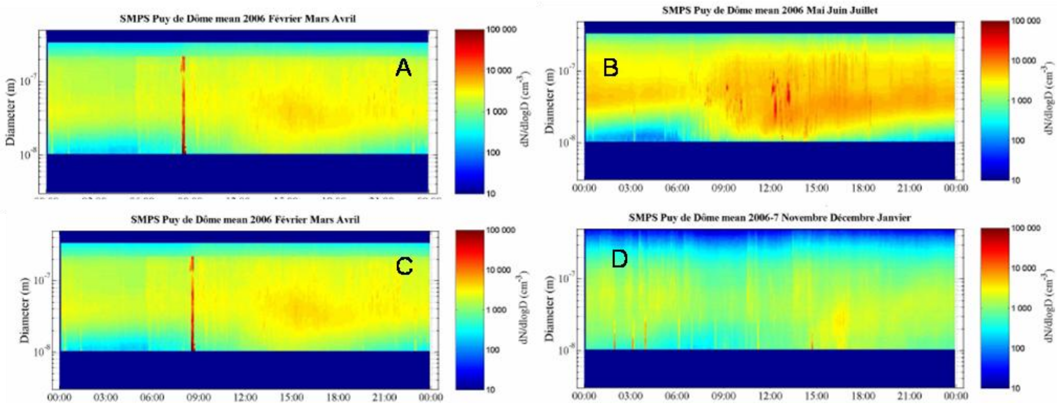


Figure 7.11: Average daily size distribution of aerosol particles measured at Puy de Dôme for Spring (A), Summer (B) Autumn (C) and Winter (D) periods.

As mentioned earlier, the variability of the size distribution signal is also linked to nucleation episodes. The occurrence of these episodes is higher during spring time and early summer and usually takes place during clear-sky conditions, at the interface between free-tropospheric and boundary layer air masses.

The mechanisms of particle nucleation at Puy de Dôme has been reviewed by Venzac et al. (2007) showing that most of the episodes are connected with increases in the ion background in the atmosphere. Nucleation events are likely to be one of the most efficient processes controlling particle concentrations in the free troposphere over Europe.

The weekly averaged concentration is close to 3 µg/m^3. On average, the OC fraction accounts for less than 1 µg/m^3 although weekly averages can be higher than 1.5 µg/m^3.

Average proportions of inorganic and organic compounds are shown in Figure 7.12.

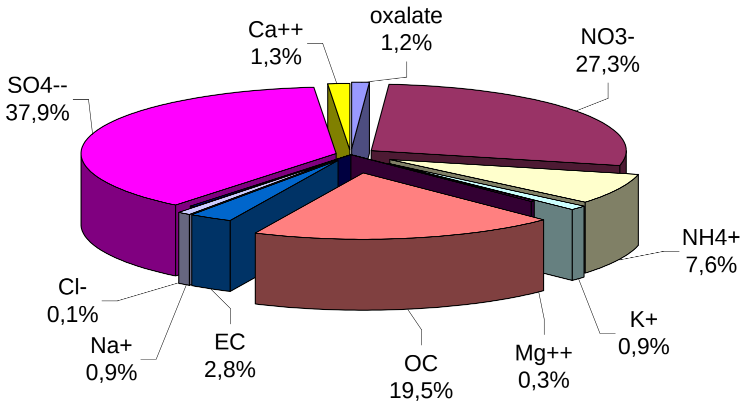


Figure 7.12: Average fractions of inorganic and organic components of aerosol at puy de Dôme. Note that the NO_3-fraction.

7.4.2.2 Urban PM speciation

The field campaigns organised to assess the volatile part lost by automatic devices allowed to described the PM_{10} mass composition in winter and in summer for different types of sites. Figure 7.13 shows some of these results.

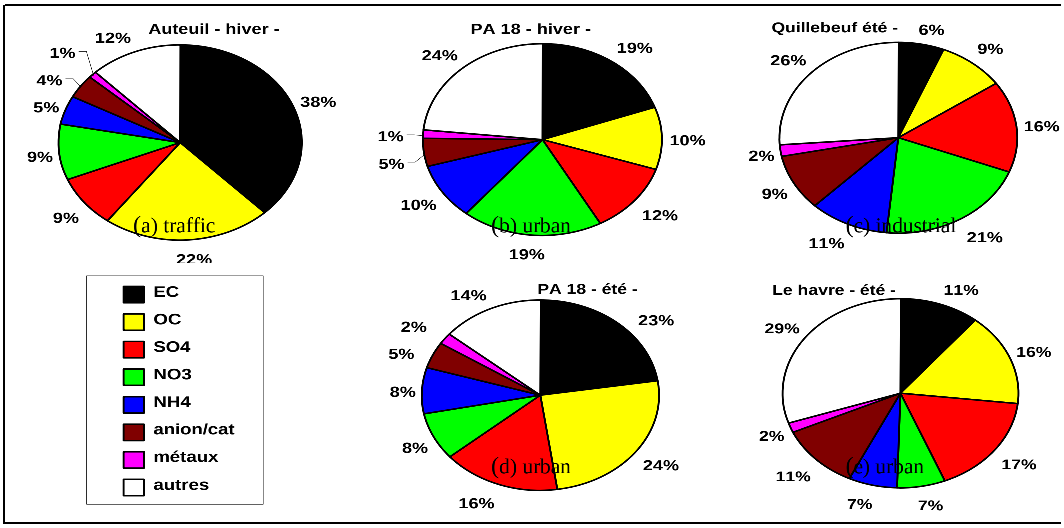


Figure 7.13: PM_{10} mass composition for different situations in winter (a and b) and in summer (c to e).

7.4.3 Relationships between PM_{10} and $PM_{2.5}$ concentrations

7.4.3.1 Correlation between PM_{10} and $PM_{2.5}$ mass concentrations

Correlation between PM_{10} and $PM_{2.5}$ mass concentrations is excellent everywhere, higher than 75% (minimum in the South-West region) (Figure 7.14). The score of 85% is often exceeded, with better results in winter or in summer depending on the geographic area. Correlation is higher in winter in Paris areas, in the North and in the Rhone-Alpes (Centre-East) regions.

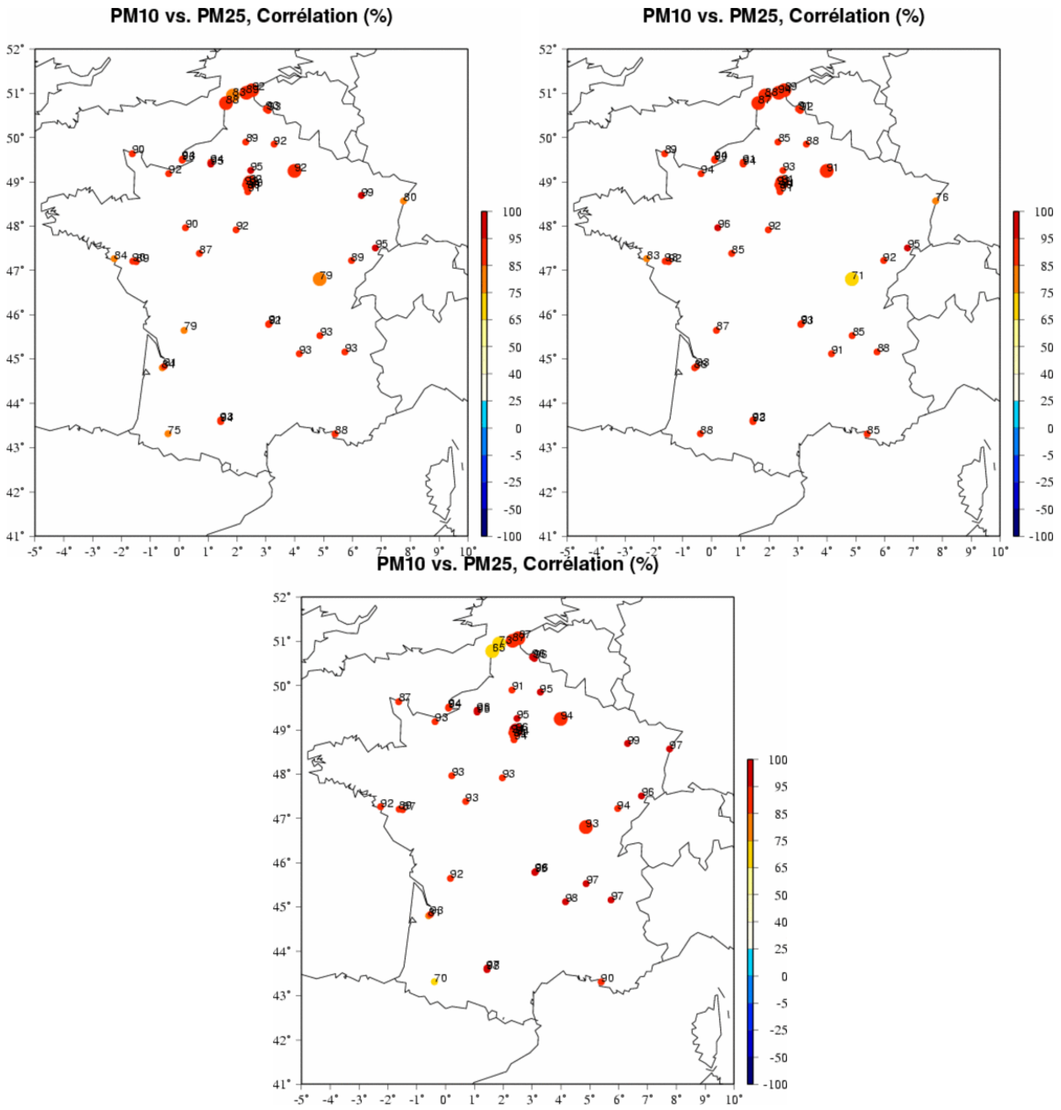


Figure 7.14: Correlation between PM_{10} and $PM_{2.5}$ concentrations. Suburban stations (large circles) and urban (small circles) are drawn for the 2003-2005 period (top left); summers 2003 to 2005 (top right) and winter 2003 to 2005 (bottom left).

7.4.3.2 Ratio $PM_{2.5}/PM_{10}$

Figure 7.15 shows ratios $PM_{2.5}/PM_{10}$ mass concentrations. This indicator varies depending on the geographic area considered. Highest ratios (72 to 84%) are seen in the eastern part of the country (Loraine, Vosges, Bourgogne), excepted in Alsace (65%). In Paris area $PM_{2.5}/PM_{10}$ ratio varies from 64 to 71%. It is quite homogeneous in the mid-south of France: from 63 to 69%. Ratios are lower at sites located in the western and northern coasts (53% at Nantes and 58-59% at Calais, Dunkerque).

$PM_{2.5}/PM_{10}$ ratio is almost higher in winter than in summer with a 5 to 10% increase compared to the average mean.

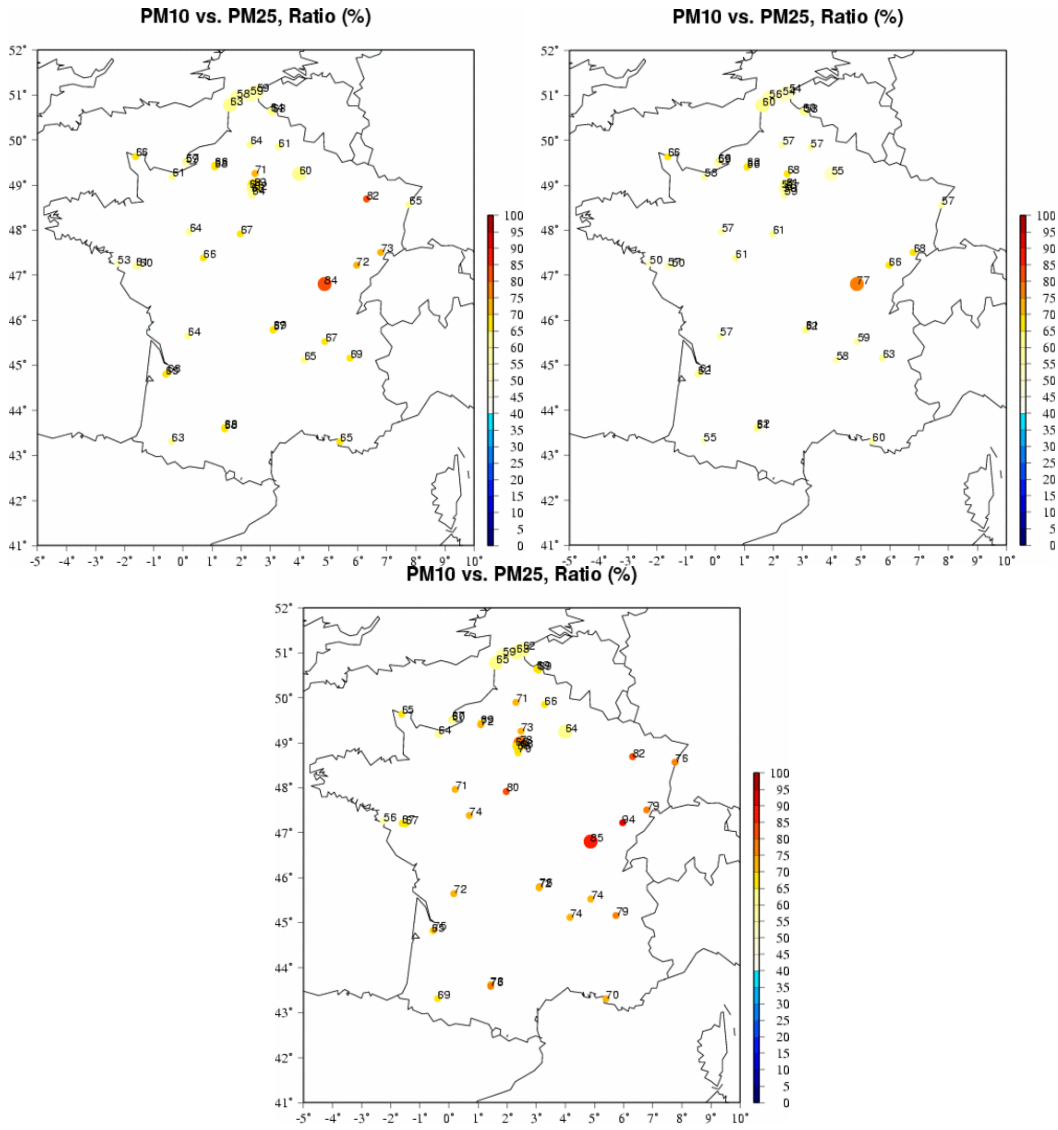


Figure 7.15: PM$_{2.5}$/PM$_{10}$ ratios. Suburban stations (large circles) and urban (small circles) are drawn for the 2003-2005 period (top left); summers 2003 to 2005 (top right) and winter 2003 to 2005 (bottom left).

7.5 PM climatology in France

The Puy-de-Dome rural supersite helps to investigate the long range transport contribution to PM concentrations. It is clearly detected during advection of anthropogenic, marine and Saharan dust air masses to the sampling site. The contribution of the specific emission area is difficult to estimate without detailed modelling of transport mechanisms. Available measurements show that contribution of marine aerosol (from the Atlantic Ocean) to the free troposphere in France remains extremely limited far from the Coastal areas. On average, we can consider that this contribution never gets above 0.1 µg/m^3, that is, at the most, a few % of the total PM$_{10}$ mass.

On the contrary, Saharan dust episodes have potentially a higher impact on the average PM_{10} mass measured at Puy de Dôme. During Saharan dust episodes, the contribution of dust (mostly found onto large particles) reaches a few µg/m^3 (2-6), and contributes to a substantial fraction of PM. It should be noted that the dust is mostly formed by Ca-containing material but also provides a surface for condensing HNO_3 vapour that in turn will contribute to increasing PM. The contribution of NO_3 condensed onto large particles can reach several tens of % of the total aerosol mass.

Finally, high concentration of particles is also measured during advection of air masses from Northern Europe (including the Paris area). These episodes are most intense following cold front when cyclonic conditions favour Northerly winds to the site. However, a precise contribution of long-range transport from anthropogenic activities is difficult to estimate due to the fact that the contribution of boundary layer air is embedded in the bulk filter (and impactor measurements). We can estimate that long range transport from Northern Europe increases the aerosol mass at the Puy-de-Dome supersite by a few µg/m^3 and is mostly composed of nitrate, sulphate and organic material.

Model experiments allow to represent the impact in France of particulate pollution episodes mainly due to inorganic particulate formation. The CHIMERE model [Bessagnet , 2005] has been developed to simulate primary and secondary PM concentrations. Its results have been assessed against observations and during European model intercomparison exercises [Cuvelier, 2006]. Provided that the emissions are reliable, confidence is built in model results especially for inorganic compounds. Thus, CHIMERE is able to correctly detect ammonium nitrate episodes . This capacity is used in the PREV'AIR system (www.prevair.org) , which is the french air quality forecasting platform (Figure 7.16).

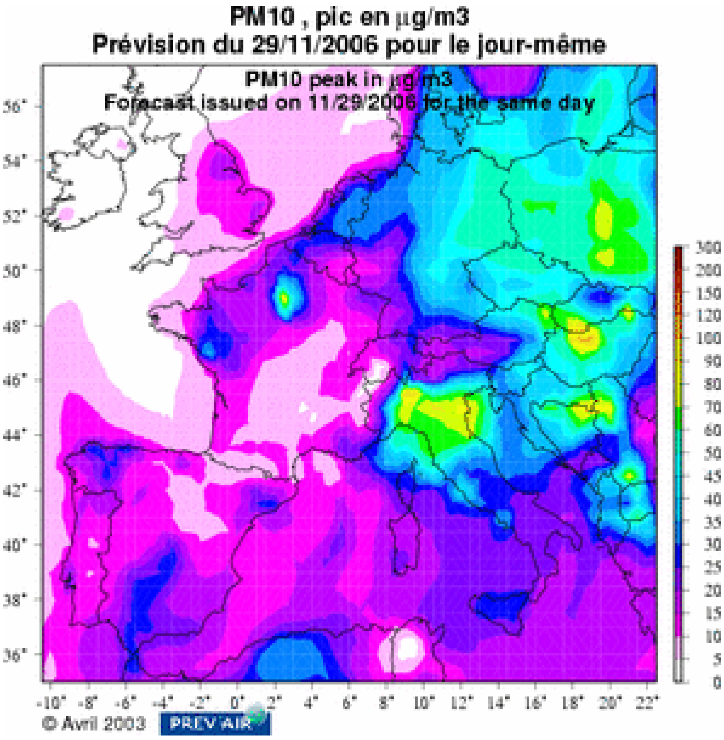
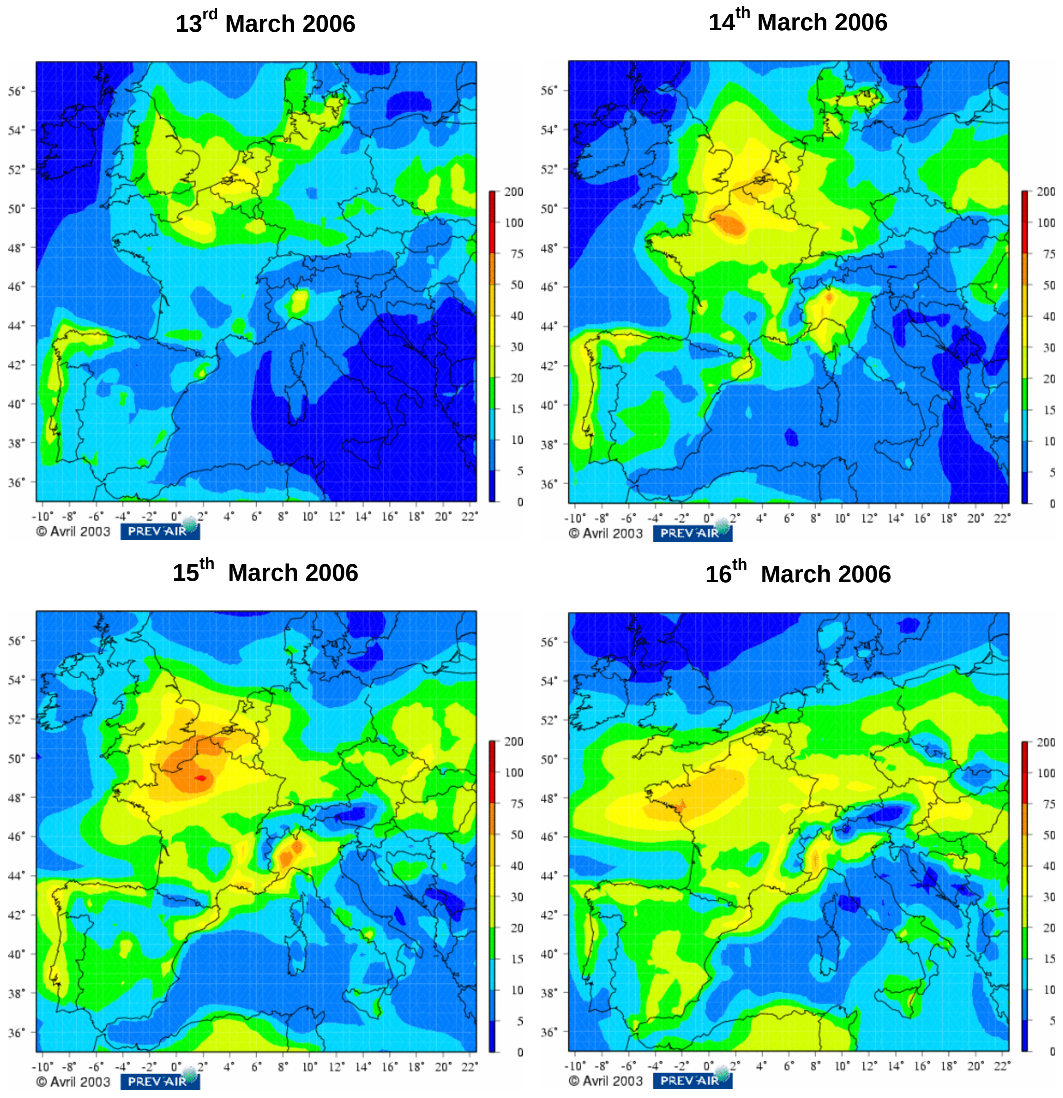


Figure 7.16: PREV'AIR PM_{10} forecast.

An example of ammonium nitrate episode simulated by CHIMERE is given in Figure 7.17. Such episodes occurs several times a year, especially in spring because of favourable meteorological conditions and higher emissions of ammonium in the northern part of Europe.


13rd March 2006

14th March 2006

15th March 2006

16th March 2006

Figure 7.17: Ammonium nitrate episode simulated with the CHIMERE model (March 2006).

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8 PM mass concentrations, trends, gradients, and components in Germany

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8.1 Abstract

Recent data on PM_{10} concentrations available from UBA monitoring sites and selected German State air quality control networks are reviewed and evaluated for time trends, variations in particle composition, and gradients between regional, rural, urban background and hot-spot sites.

A significant decrease of PM_{10} concentrations by ca. 50% is evident as from 1985 based on the long-term TSP-PM_{10} measurements carried out at the UBA EMEP sites. However, this does not correspond with the 85% decrease in primary particle emissions during the same time period, indicating the importance of secondary particle formation and transboundary transport on ambient PM concentrations.

A detailed evaluation of PM_{10} gradients observed during the years 2003-2005 in and around agglomeration areas was conducted. The importance of regional background contributions to urban PM_{10} concentrations is evident from this analysis. Nevertheless, the weekly PM_{10} variation indicates a substantial increment due to urban combustion processes, mainly traffic.

In particular cases, PM gradients can be inversed with rural sites exhibiting higher PM_{10} concentrations than the urban agglomeration background. In one of these cases it may be attributed to agricultural activities (chicken farming) in the vicinity of the rural background station.

Data on PM composition obtained from various measurement campaigns and source apportionment studies in Germany show the increasing importance of carbonaceous aerosol fraction from regional background to urban sites with the highest effect at traffic hot spots. Secondary aerosols, being dominant in the regional background, become less important based on mass percent in urban and hot-spot areas. However, secondary aerosols may often (but not always) be the driving factor during episodes of high PM_{10} concentrations since their concentration increase was shown to be disproportionately high compared to the overall PM_{10} increase.

An example for a quite special situation is the observation of a considerable decrease of PM_{10} concentrations at the Melpitz research site near Leipzig in Eastern Germany, coming down from an annual mean of 38 µg/m³ in 1993 to about 20 µg/m³ in 2005. Large changes in industrial structure and domestic fuel consumptions as a consequence of the German reunification have reduced the contribution of local emissions to PM ambient air concentrations. At present, high PM episodes are frequently associated with long-range transport of particles from Eastern Europe as e.g. evidenced by high $PM_{2.5}/PM_{10}$ ratios (up to 0.9). While

similar high $PM_{2.5}/PM_{10}$ ratios can be observed for single days also in Western Germany, the median ratio for longer periods appears to be lower (~0.7) and almost independent of site location.

8.2 Introduction

PM concentration measurements are part of the program of German background air quality monitoring network since its beginnings almost 40 years ago. Reliable data sets are available since 1971. This German network became part of the EMEP network and although PM measurements became part of the EMEP monitoring program not until 1999, PM measurements were continued over the whole period. This data set now allows a continuous and consistent assessment of background PM concentration changes in Germany during the last 35 years.

The time trend of PM concentrations obtained from the data shown in Figure 8.1 shows a drop of the average annual PM concentrations from about (35 ± 17) µg m^{-3} in the 1970's to (15 ± 5) µg m^{-3} in rural areas nowadays. The major changes in mass concentration occurred between 1985 and 1995 and no clear trends are evident for the periods before 1980 and after 2000. The decrease is presumably caused by reduction of primary particles emissions and gaseous precursors.

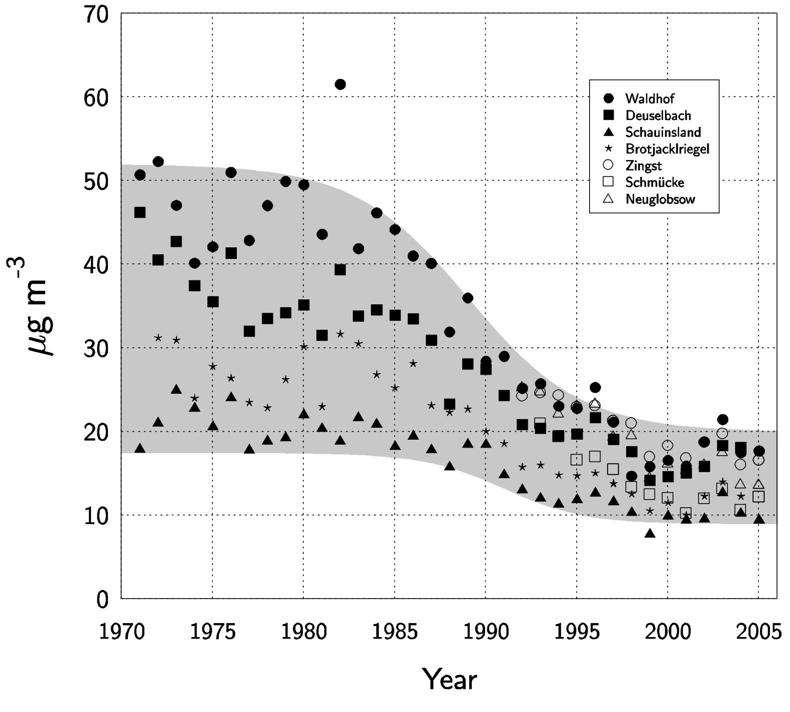

Figure 8.1: Annual average PM_{10}[15]-concentrations at German EMEP sites. The shaded area has been fitted visually to the envelope of the data.

Similar information is also derived from observations made in Saxony. TSP concentrations of ca. 70 µg/m³ were measured at the rural background site at Melpitz up to the early 90s, decreasing to current PM_{10} levels of about 20 µg/m³.

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[15] Sampling heads with an aerodynamic cut off diameter of approximately 50 µm were in use before 1998. Since 1998 samples are taken with PM10-inlets. A factor of 0.9 (obtained from parallel measurements) was applied to the values prior to 1998 to estimate the PM10 concentrations.

More detailed investigations into the different particle fractions and their composition e.g. give hints to naturally emitted particle precursors in summertime samples. In general data indicate that with decreasing anthropogenic emissions the importance of long-range transport became more important (at this site particularly associated with wintertime and Eastern wind direction). These influences are mirrored by short-term $PM_{2.5}/PM_{10}$ ratios as high as 90%. [i, Annex A], whereas measurements of $PM_{2.5}$ carried out in recent years in the urban background (Ruhr-Area) typically show ratios of about 0.7 [iv].

Comparing the 85%-decrease in (national) primary particle emissions [ii] between 1985 and 1995 with the observed 50%-decrease of PM concentration during the same period, it is obvious that both do not match well in magnitude. Likely reasons for this divergence might be that there is increasing importance of secondary particle formation and long range transport on PM concentrations and that there are still national primary particle emissions less well addressed by mitigation, e.g. fugitive emissions and abrasion processes.

The German Laender are responsible for air quality monitoring and air quality assessment among others for PM_{10} and also for $PM_{2.5}$ since recently. They operate their own air quality monitoring networks at hot spots, in agglomerations and in rural areas to fit with European and German legal requirements in air quality control.

The overall situation for PM_{10} in Germany is shown by maps for the years 2004 and 2005 in Figure 8.2.

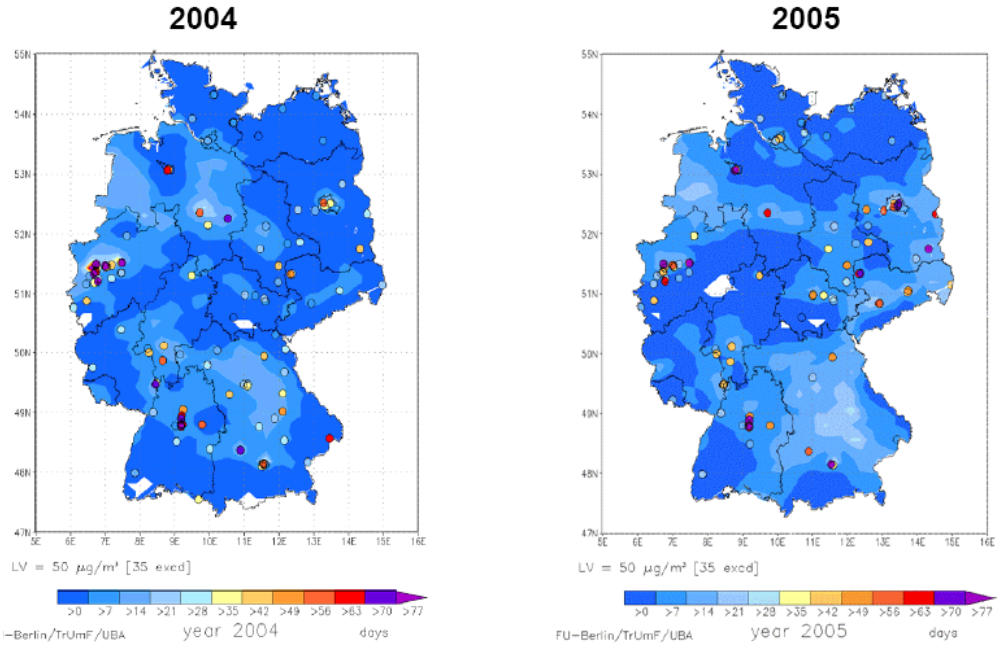


Figure 8.2: Number of PM_{10} daily means > 50 µg/m³ in Germany.

From German monitoring network data it can be concluded:

- Exceedances of PM_{10} limit values don't occur in the rural background.
- The limit value for the annual mean is exceeded very rarely only at hot spots.

Exceedances of the 24-hour limit value more than 35 times in a calendar year are observed predominantly in agglomerations where increased traffic volume is a significant local characteristic.

Nevertheless, long range transport of (secondary) PM contributes to the local situation by a considerable amount.

In order to assess this background contribution to the urban environment and obtain data on the PM_{10} concentration gradients and increments further evaluation of network measurement data is presented in the following.

8.3 Data Evaluation

8.3.1 Part I: PM_{10} gradients for major German agglomerations (2003-2005)

8.3.1.1 Methodology

Nine major urban agglomeration areas were selected in order to cover different regions and situations in Germany. These comprise the metropoles Berlin, Hamburg and Munich, large cities such as Stuttgart, Frankfurt and Hannover and intermediate conurbations (Leipzig/Dreseden, Bremen) as well as the cities of Dortmund and Duisburg representing the Eastern and Western border of the Ruhr-Area agglomeration.

Figure 8.3: Location of German agglomerations and conurbations considered for PM_{10} gradient evaluation.

A set of monitoring sites from the Laender and UBA networks was compiled for each of these agglomerations representing the regional (= minimal local influence), rural (= outside agglomerations) and urban background as far as possible. Two sites were chosen for each type. Further, traffic and industrial hot-spot sites were added. However, not all networks comprise sites of all types. Therefore combinations of sites from different networks were used in several cases. E.g. urban/hot spot sites were taken from Bremen together with regional sites from UBA network and rural sites operated by the State of Lower Saxony).

PM_{10} data comprised measurement data from the Laender and UBA monitoring networks. A considerable number of such data sets (105) had previously been used [iii] and thus was already subject to a thorough quality assurance procedure. Further data sets selected for the present evaluation could not be treated in the same way; however, an outlier routine was applied to eliminate all values higher than 5 times the median. German Laender in most cases report measurement data as 0.5h averages; however, in certain cases lower time resolution and/or moving average methods were applied by the Laender networks. Therefore, all measurement data of a given set of sites were converted to the lowest time resolution prior to further evaluation.

Average weekly concentration variations/time pattern (CTP) were calculated based on these data, hence reducing the data set of a monitoring station to a time series of e.g. 336 values in case of 0.5h resolution per year. The CTPs of the two corresponding background sites were averaged (separately for regional/rural/ urban) and from these the time patterns of concentration increments (rural-regional, urban-rural) were calculated. No averaging was carried out in the case of hot-spot sites to maintain the information of individual local features (e.g. street canyon).

The information on the weekly pattern was further condensed by calculating the daily averages of concentrations and increments for each weekday, and further processed to give the averages of working and of weekend days. These averages, obtained separately for each year, is the basic data used for further evaluation, i.e. to obtain the workday increments as an indicator for the influence of local and urban activities on the pollutant concentrations.

Finally, the linear regression slopes NO/PM_{10} and NO_2/PM_{10} were investigated to assess the possible influence of local traffic on PM_{10} concentrations measured at industrial hot spot sites.

8.3.1.2 Results

The general weekly concentration/time pattern (Figure 8.4, left diagram), averaged for all agglomerations and years, was derived using the arithmetic means of the site-type specific weekly variations as calculated for each agglomeration. Obviously, with higher PM_{10} concentration (increased influence of anthropogenic activities) the weekly profile and differences between weekend and workdays (Figure 8.4, right diagram) become more pronounced.

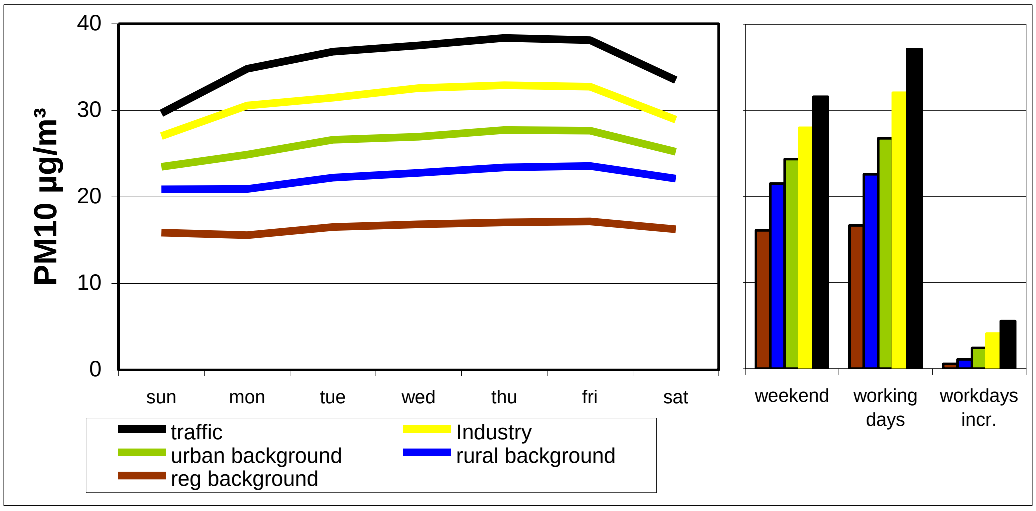


Figure 8.4: weekly variation of PM_{10} concentrations at different site types (mean values for all considered sites and years) and comparison for weekend and workdays averages.

The shape of the weekly profiles and also the levels of PM_{10} concentrations revealed to be quite similar for all agglomerations if only background sites are considered. It also can be noted that a slight, maybe not significant increase in PM_{10} concentrations can be observed from Monday to Friday in Figure 8.3.

Significant differences may exist with respect to industrial and traffic sites. An example is illustrated in Figure 8.5 comparing the weekly profiles obtained for the Ruhr-Area with those belonging to the area of Ludwigshafen/Mannheim. The industrial site chosen in Ludwigshafen/ Mannheim is much closer to the urban background site with respect to the PM_{10} concentrations than the one chosen for the Ruhr-Area.

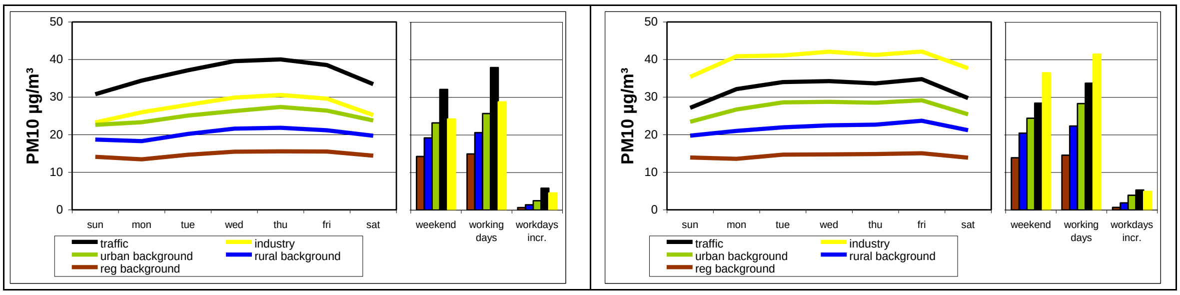


Figure 8.5: weekly variation of PM_{10} concentrations at different site types for the agglomerations Ludwigshafen/Mannheim (left diagram) and Ruhr-District.

In another peculiar case (Bremen), an opposite gradient was observed indicating higher pollution at a rural site compared to an urban background site. The reason is most probably the influence of agricultural emissions (e.g. chicken farming) at the rural background site.

The distribution of the calculated concentrations and increments is shown as box-whisker-plots in Figure 8.6. Minimum/maximum values refer to the lowest/ highest value occurring in one of the three years considered.

Averages of PM_{10} concentrations and increments for all years are compiled in Table 8.1. Due to prior averaging for the considered years, the minimum and maximum values defining the ranges given in Table 8.1 are not identical with those shown in Figure 8.6.

Table 8.1: Concentrations and increments for PM_{10} calculated based on weekly concentration/time profiles (averaged for 2003-2005).

PM10 concentrations	**µg/m³**							
header concentrations			regional bg (2 sites)	rural bg (2 sites)	urban bg (2 sites)	traffic 1	traffic 2	industrial
header increments				rur-reg	urb-rur	traf 1-urb	traf 2-urb	ind-urb
Berlin	Concentrations *)	weekend	16	22	28	34	33	
		working days	16	22	29	39	38	
	Increments	weekend		7	6	6	5	
		working days		6	7	10	9	
Bremen	Concentrations	weekend	18	24	25	38	34	
		working days	18	25	27	43	42	
	Increments	weekend		7	1	13	9	
		working days		7	2	16	15	
Frankfurt	Concentrations	weekend	12	21	24	27	30	
		working days	13	22	27	30	35	
	Increments	weekend		8	3	3	6	
		working days		9	5	2	8	
Hamburg	Concentrations	weekend	21	22	23	30	31	24
		working days	21	22	23	32	32	26
	Increments	weekend		2	<1	7	8	2
		working days		1	1	9	10	3
Hannover	Concentrations	weekend	18	24	25	38	34	
		working days	18	25	27	43	42	
	Increments	weekend		7	1	13	9	
		working days		17	2	16	15	
Leipzig/Dresden	Concentrations	weekend	18	21	26	33	34	
		working days	19	23	30	42	42	
	Increments	weekend		3	5	7	8	
		working days		5	6	13	12	
Ludwigshafen/Mannheim	Concentrations	weekend	14	19	23		32	24
		working days	15	21	26		38	29
	Increments	weekend		5	4		9	1
		working days		6	5		12	3
Munich	Concentrations	weekend	14	18	25	34	29	
		working days	15	20	28	41	34	
	Increments	weekend		4	7	9	4	
		working days		5	7	13	7	
Ruhr-District	Concentrations	weekend	14	20	24	29	28	37
		working days	15	22	28	34	33	41
	Increments	weekend		7	4	4	4	12
		working days		8	6	6	5	13
Range	Concentrations	weekend	12 - 21	18 - 24	23 - 28	27 - 38		24 - 37
		working days	13 - 21	20 - 25	23 - 30	30 - 43		26 - 41
	Increments	weekend		2 - 8	<1 - 7	3 - 13		1 - 12
		working days		1 - 17	1 - 7	2 - 16		3 - 13

*) averaged for 2003, 2004 and 2005

Clear concentration gradients exist between the regional background and urban conditions with traffic sites exhibiting further increased concentrations. The increase is lower for the industrially influenced sites selected for the present analysis. Gradients are steeper during workdays compared to weekend days for urban, traffic and industrial sites. This effect would be even more pronounced if weekdays were compared to the Sundays alone because considerable traffic activity still exists on Saturdays which may last up to the early morning hours of Sundays. To evaluate the maximum influence of traffic and other anthropogenic sources with a regular weekly time pattern it might be advisable to generate an "idealised" Sunday comprising the early hours of Mondays (e.g. 0:00 to 4:00 a.m.) and the complementary Sunday hours between 4:00 a.m. and 12:00 p.m.

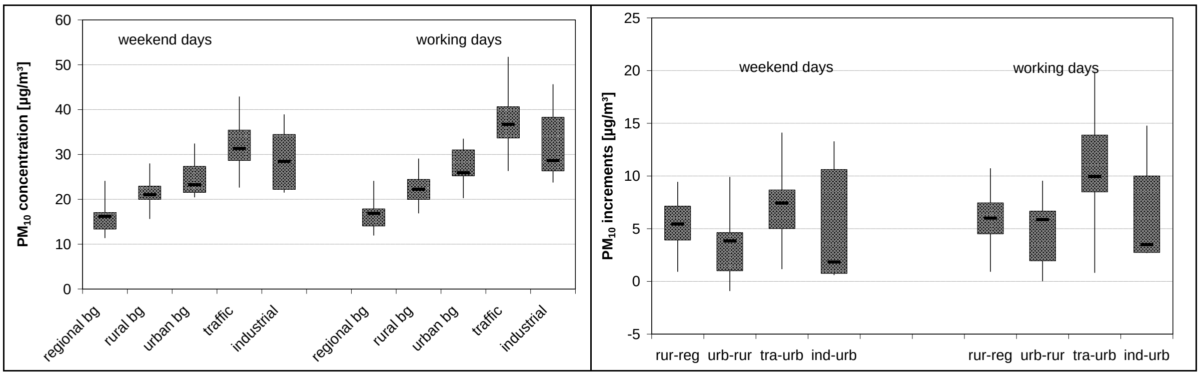


Figure 8.6: Box-whisker diagrams showing the minimum and maximum (whiskers), 25-and 75-percentiles (box) and median (bar) of PM$_{10}$ concentrations (left side) and increments (right side).

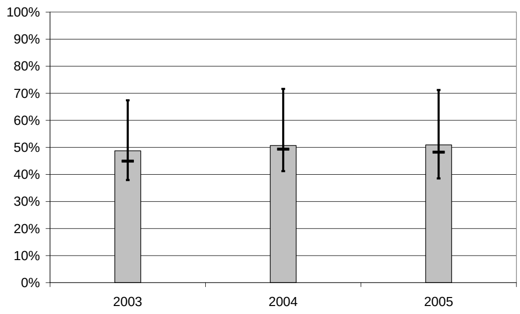
The increments shown in Figure 8.6 (right side) appear to be rather constant at around 5 µg/m^3 for the regional, rural, and urban background for both, weekend and working days. A substantially increasing increment of more than 10 µg/m³ is obvious for traffic sites on working days, while industrial sites again add ca 5 µg/m³ to the urban background.

These findings are supported by independent analyses carried out by the North Rhine-Westphalian Environment Protection Agency[iv] which were based on daily mean concentrations. Table 8.2 summarises the ranges of increment concentrations, regression coefficients and ratios of daily means observed for the year 2005.

Table 8.2: Summary of increments from adjacent North Rhine Westphalian monitoring sites

sites	increments (µg/m³)	r²	ratio of daily means (av.)
Rural background/regional	5 - 7		
Urban background/regional (medium sized cities)	4 -9	0.2 – 0.7	1.10 – 1.60
Urban background/regional (conurbation)	2 - 6	0.7 – 0.9	
Traffic-exposed/urban background	3 - 7	0.7 – 0.9	1.1 – 1.4
Kerbside/urban background	8 - 15	0.7 – 0.8	1.3 – 1.6
Industrial/urban background	6 - 15	0.4 – 0.6	1.2 – 1.5

From Figure 8.6 it can be concluded that the regional background contribution to PM$_{10}$ concentrations at traffic hot-spots is roughly 50%. Since the analysed data set comprised three years with substantial differences in meteorological conditions (“centennial summer” in 2003), it was checked, if this background contribution varies between the years. As shown by Figure 8.7, there are only slight and probably insignificant differences.



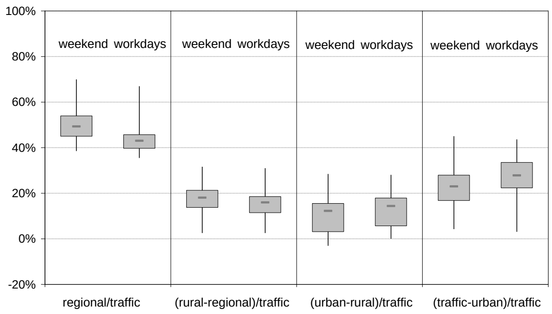


Figure 8.7: Regional background contributions to PM_{10} concentrations at traffic hot spot sites for the years 2003, 2004, and 2005 (Column: mean, bar: median, whiskers: min/max).

Figure 8.8:Fraction of traffic-site PM_{10} determined by the regional background concentrations and increments.

Using the increments, the question can be answered which fraction of the PM_{10} concentrations measured at an urban traffic hot spot already is determined by background influence and which fraction is caused by local emissions. To illustrate this, the variations of the ratios between regional background concentrations and increments to the traffic site concentrations are shown in Figure 8.8. Referring to the median values shown, the regional background contributes by about 49%/43% (weekend/workdays), and rural and urban increments by ca. 18%/16% and 12%/14%, respectively. The local increment, presumably to the largest part caused by traffic emissions, makes up 23% for the weekend and 28% on workdays.

The lower but still obvious increase of PM_{10} at sites influenced by industry gives rise to the question whether this observation also indicates traffic influence or is primarily due to emissions from industrial facilities. Nitrogen oxide concentrations were included in the analysis and regression analyses have been made comparing the measurement data of PM_{10} with both NO_2 and NO values to tackle this question. The assumption for this analysis is NO/PM_{10} or NO_2/PM_{10} ratios from urban to hot-spot sites will be significantly lower for industrial compared to traffic sites.

The results of the calculations are shown in Figure 8.9. There is only a slight and probably insignificant difference of the NO_2/PM_{10} regression slopes for urban background and industry sites, whereas the slope for traffic sites appears significantly increased. In case of NO, the slopes found for industrial sites are between those for urban and traffic sites. On workdays these differences are slightly more pronounced. Thus, we do see increased ratios of NO to PM_{10} but being more pronounced for the traffic than for the industrial sites. For NO_2 only a slight tendency towards the same trend is detected. This result indicates that

a) combustion, possibly traffic, is still a significant contributor to elevated PM_{10} concentrations at industrial sites, and
b) other sources than combustion significantly contribute to PM_{10} concentrations at the industrial sites.

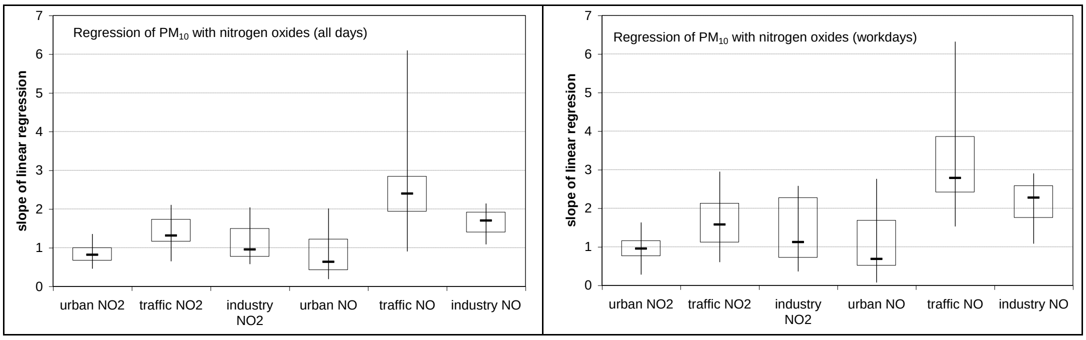


Figure 8.9: Box-plot diagrams showing the minimum, 25-,50- and 75-pecentiale and maximum of regression slopes NO_2/PM_{10} and NO/PM_{10} for all days (left side) and workdays (right side).

8.3.2 Part II: PM components

8.3.2.1 Methodology and data overview

Information on the composition of PM_{10} and other PM fractions is available from various studies mainly related to studies investigating source contributions. Such studies are not repeated on a regular basis due to the high effort linked to the sampling and chemical analysis of dust samples. Depending on the study design, also data on composition gradients between different types of sites is obtained. Studies carried out in Germany in recent years are listed in Table 8.3, the corresponding locations are shown in Figure 8.10.

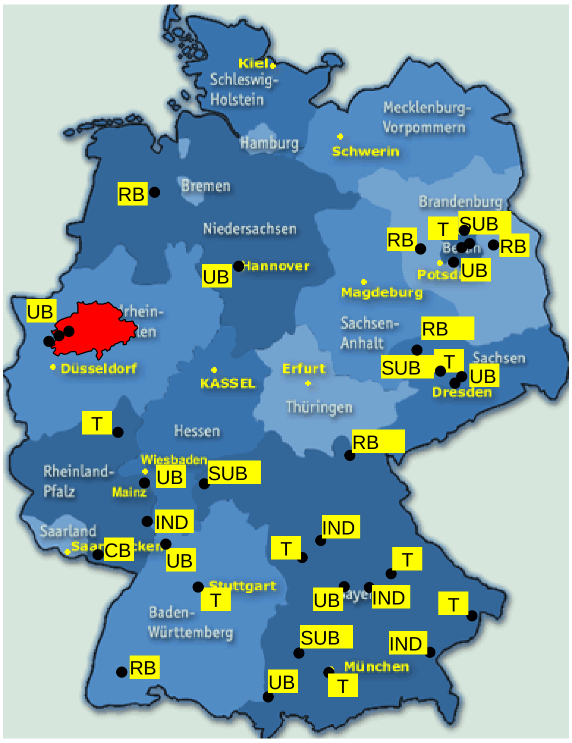


Figure 8.10: Map showing the sites with available PM composition measurements.

In some cases additional data treatment of the originally reported information was necessary for the comparisons given here. This concerns the conversion of organic carbon (OC) to organic matter (OM) by applying a factor of 1.4 to account for other elements present in organic compounds. Moreover, it has to be noted that the fraction of PM mass denoted “unknown” was treated differently in the various studies. Due to the use of quartz fibre filters in most cases, silicates could not be analysed and thus were part of the unknown fraction as well as water and carbonates. However, the fraction of SiO_2 may be estimated from typical ratios between Si and Ti, in cases where the latter is analysed. Such estimates are given for example in the report from Saxony [ix], where a factor of 40 is used for the for ratio of Si to Ti.

Table 8.3: German studies providing information on chemical constituents of PM samples.

State/region	Period	PM fractions	no./type of sites	Remarks	Reference
North Rhine Westphalia/Ruhr-Area (Duisburg)	1 year; spring 2002-2003	PM_{10}/ $PM_{2.5}$/ PM_1	3 urban background	Central site all fractions for 1 year; satellite sites 2 campaigns in spring and autumn ($PM_{10/2.5}$)	v
Lower Saxony Bösel and Hannover	1 year; spring 2002-2003	PM_{10}	1 rural 1 urban bg	Ca. 80 samples of days with high PM_{10} mass concentration selected for analysis	vi
Rhineland-Palatinate	1 year spring 2002-2003	PM_{10}	1 regional bg 1 urban bg 1 traffic 1 industrial		vii
Berlin	1 year autumn 2001-2002	PM_{10}	1 regional bg 2 rural bg 2 suburban bg 1 urban bg 2 traffic	2 sites operated for entire period, other for shorter time; regional bg site on suburban tower (324 m)	viii
Saxony Dresden	1 year summer 2003-2004	PM_{10}	1 suburban bg 1 urban bg 1 traffic	Traffic site 1 year every 2nd day; all sites during campaigns in winter 02/04 and summer 04	ix
Saxony Melpitz	2 years; Spring 2004 - 2006	PM_{10}/ $PM_{2.5}$/ PM_1	1 rural bg	long-term research site; main ions analysed from filter samples, add. components from impactor samples	i, see Annex A
Baden-Württemberg	Jan/Feb 2006	PM_{10}	1 regional bg 1 traffic	Investigation of particular inversion episode, measurements continued throughout entire year (data not yet published)	x
Bavaria	1 year; spring 2003-2004	PM_{10}	3 industrial (rural, suburban, urban) 2 urban bg 2 suburban bg 1 rural bg 4 traffic (all urban)	Analyses from pooled samples: EC, OC, PAK: monthly Sec. compounds/Trace metals: quarterly:	xi

8.3.2.2 Results

Averaged data from the reports listed in Table 8.3 and being assessed to be representative for a whole year was used for further evaluation of three major composition groups, e.g. the

1. carbonaceous fraction (EC +OM)
2. secondary fraction (nitrate, sulphate, ammonium)
3. mass difference to measured PM_{10} mass comprising minerals, metals, water and unknown compounds (further denoted to “mineral” fraction).

The distribution of concentrations and contributions are shown for these composition groups and the measurement site types as box-plots in Figure 8.11 and Figure 8.12. Both figures include the corresponding PM_{10} mass concentration plots (which are identical in both figures) for comparison.

From Figure 8.11 it can be concluded that the positive gradient of PM_{10} mass concentration corresponds to similar trends of all three composition groups. However, the gradient slopes are different, leading to a dissimilar picture when looking at the relative contributions in Figure 8.12. While the contribution of the carbonaceous fraction still increases with rising PM_{10} mass concentrations, an opposite gradient is observed for the secondary aerosols and the “mineral” fraction exhibits almost constant contributions independent of the site type.

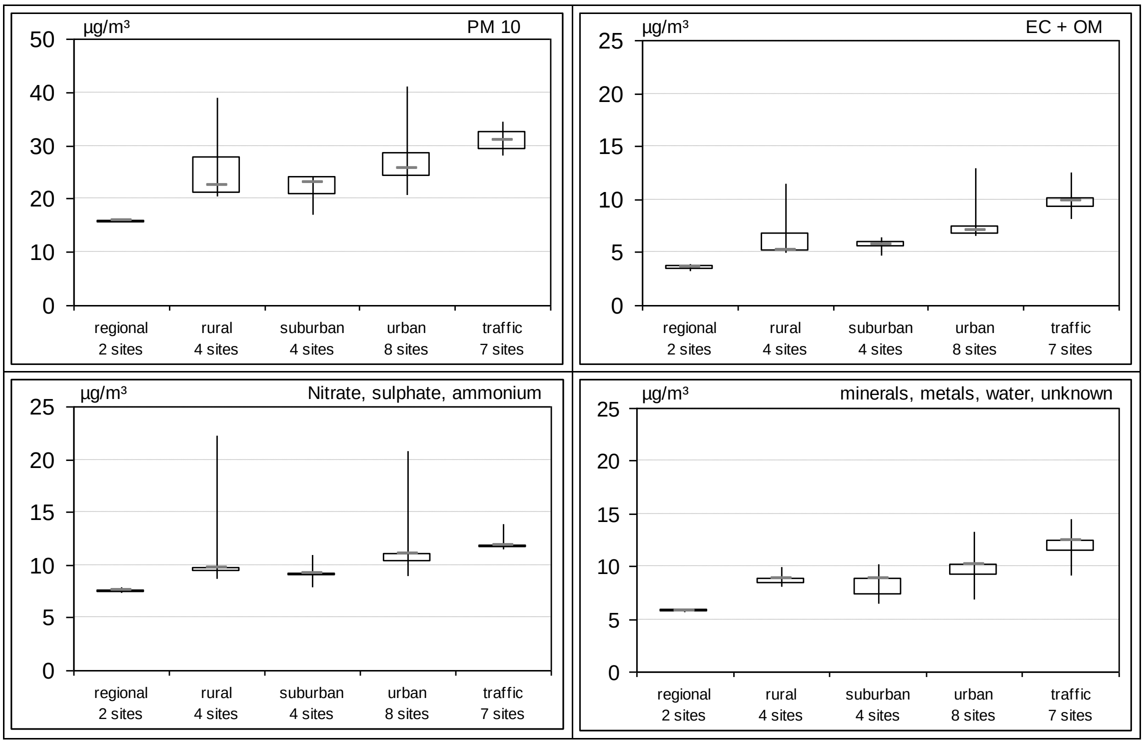


Figure 8.11: Boxplots for concentrations of PM_{10} and main compound groups.

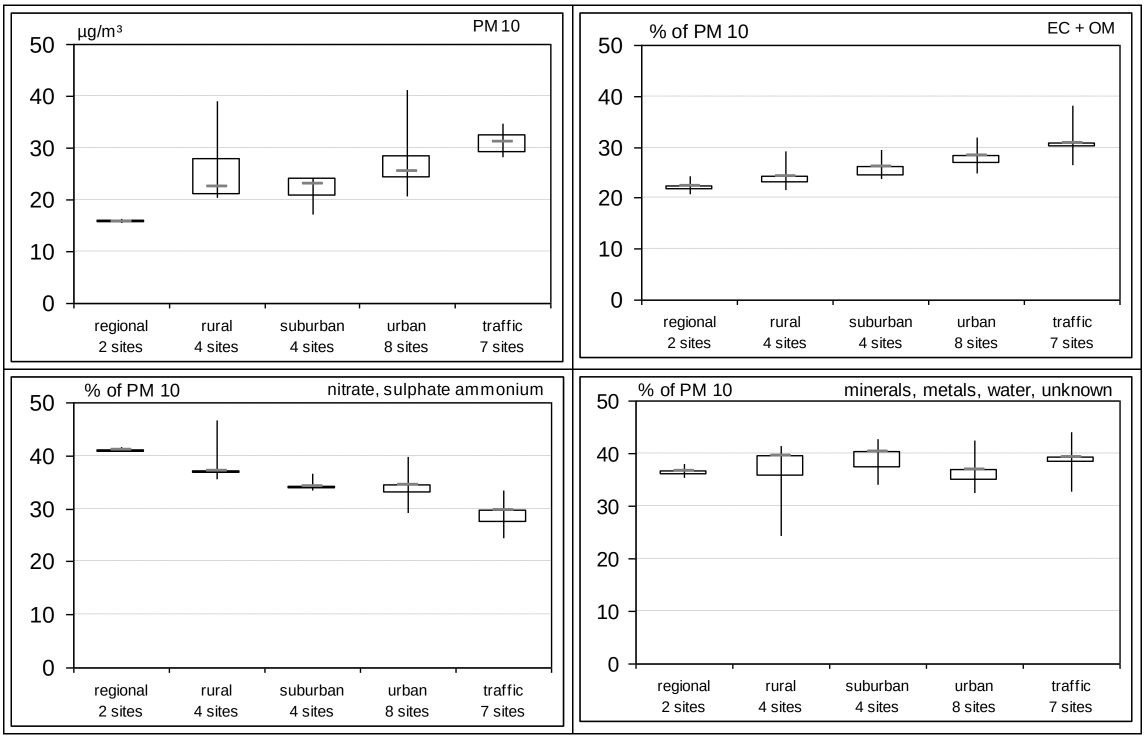


Figure 8.12: Boxplots for PM_{10} concentration and percentage contribution of main compound groups.

The increasing contribution of combustion emissions to the urban and traffic related areas is evident from the increase in carbonaceous matter as percent of the total PM_{10} mass concentrations. The constant contribution of the "mineral" fraction independent from the site type also indicates a significant increase due to local emissions (e.g. resuspension and abrasion processes). Secondary aerosols appear to be part of the background aerosol, being on the one hand accumulated in the urban regions due to specific dispersion conditions (increasing roughness length, fumigation and down-mixing) but on the other hand loosing relative importance since no or neglible additional local formation occurs.

It should be stressed that these conclusions have been derived from a *spatial* (= inter-site) comparison and apply only to the average PM_{10} mass composition being representative for periods covering more or less all seasons and days with high and low PM_{10} mass concentrations. However, a different view on the effects on the composition can be made when doing an intra-site *temporal* comparison comparing periods of high and low PM_{10} mass concentrations.

The question is whether there are compounds which show increased enrichment during episodes of high PM_{10} concentrations in comparison to periods with low pollution. In order to differentiate those compounds which show different behaviour of concentration changes with rising PM_{10} mass concentrations it is helpful to calculate the relative excess concentrations q of both, the compound X and PM_{10}, and to compare these:

$$Q^X = \frac{q^X}{q^{PM_{10}}} \qquad \text{with} \qquad q = \frac{c_{episode} - c_{nonepisode}}{c_{nonepisode}}$$

The advantage of this calculation is that there are 4 regimes to differentiate easily:

1. for a compound X exhibiting decreasing concentrations despite of growing PM_{10}, q will become negative (because $c_{episode} < c_{nonepisode}$). Since $q^{PM_{10}}$ is always positive (by definition of q) also the ratio Q^X becomes < 1 for decreasing compound concentrations;
2. in case the concentration compound X does increase with increasing PM_{10}, but less than proportionate, Q^X will be between 0 and 1;
3. for a proportionate growth of X with PM_{10} the ratio Q^X is expected to equal 1;
4. finally, compounds increasing disproportionately high will result in $Q^X > 1$.

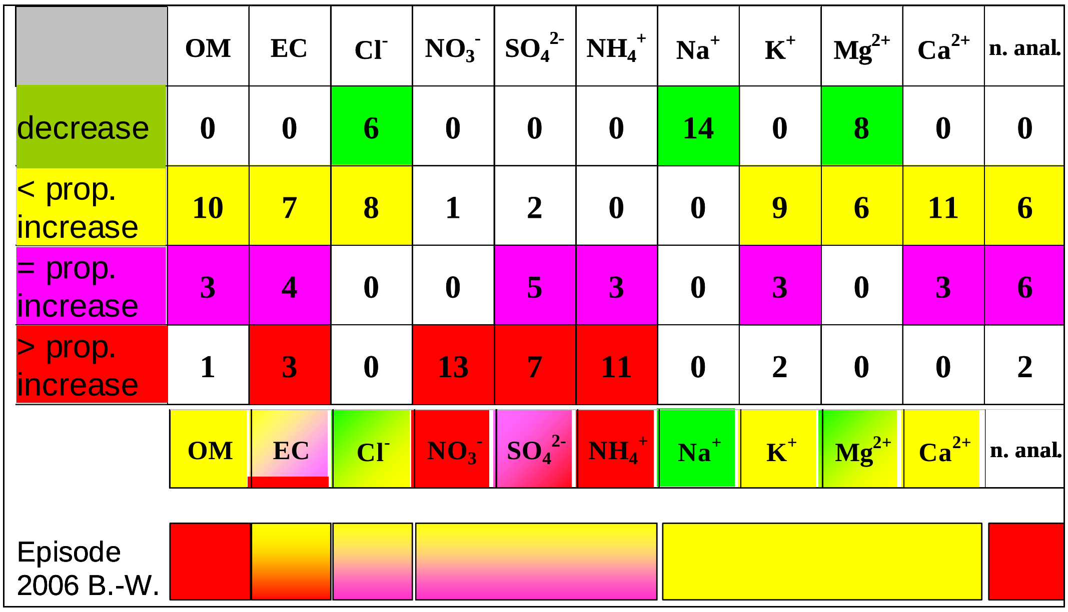
The underlying hypothesis for such evaluation is that a high PM_{10} episode being solely driven by air mass exchange conditions (e.g. inversion) should result in a pure accumulation of PM_{10} without chemical changes and therefore exhibit a more or less proportionate increase of PM_{10} compounds with increasing PM_{10} concentrations. On the contrary, if changes of source strength, source types or sinks efficiencies (also) play a role for the rise in PM_{10} considerable differences should be observable in dependence of the investigated PM_{10} compound.

Such an evaluation was conducted for only some of the available data since detailed day-by-day- composition information was needed. Figure 8.13 shows in its upper part the result of the comparison for periods with PM_{10} concentrations being < 30 µg/m³ and > 50 µg/m³ based on the measurements in the projects [v, vii, viii] overall comprising 14 sites. It shows the number of sites for which the specific compound falls into one of the 4 regimes (thus, the sum in each column equals 14).

To further explain the results the case of sea-salt compounds may be highlighted. For sodium ions (Na^+) at all sites decreasing concentrations have been found. For about 50% of the sites this was also observed for the other typical sea-salt compounds (Cl^- and Mg^{2+}) which otherwise grow disproportionately low. Hence, during high PM_{10} episodes sea salt was clearly depleted.

On the other hand, secondary aerosol compounds (NO_3^-, NH_4^+) showed disproportionate high concentration increases at the majority of sites, for sulphate a mixed behaviour with 50% proportionate and 50% higher concentration growth was found.

In conclusion, this indicates that – at least for the sites and periods considered here – exceedance of the PM_{10} daily limit is often driven by large scale processes leading to intensified formation of background secondary aerosols during usually low dispersion conditions. The precursors of the secondary aerosol component are expected to be emitted within an area of about 400 km from the measurement site based on the meteorological conditions during such episodes (from back trajectory analyses).



	OM	EC	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	n. anal.
decrease	0	0	6	0	0	0	14	0	8	0	0
< prop. increase	10	7	8	1	2	0	0	9	6	11	6
= prop. increase	3	4	0	0	5	3	0	3	0	3	6
> prop. increase	1	3	0	13	7	11	0	2	0	0	2

Figure 8.13: Number of sites assigned to different compound concentration change patterns for episodes with PM_{10} high mass concentrations.

However, there are indications that this rule does not apply always or everywhere. At the bottom of Figure 8.13, the outcome of a similar evaluation is presented for the data obtained from Baden-Württemberg for a winter episode in 2006. In this case, the days with PM_{10} above 100 µg/m³ (N=6) at a Stuttgart traffic site were compared with those days (N=2) still having lower concentrations at the episode startup. Thus the statistical population is much smaller than that analysed before. Moreover, the chemical composition was reported only for compound groups which therefore had to be treated together.

Nevertheless, a disproportionate high increase was observed for organic material, the unaccounted (water, silicates-) fraction and partly for elemental carbon, while secondary aerosols at most accumulated and the contribution of mineral compounds lowered. Hence, this episode appeared to be more driven by compounds emitted locally. Indeed, the episode was characterised by a very stable and low inversion layer at low temperatures which may have caused increased domestic heating activities.

8.4 Discussion and Conclusions

Long-term records of PM measurements in Germany at regional background sites show a general decrease in concentrations of about 50% during the last three decades. This concentration decrease can be linked to the reductions in primary particle emissions in Germany during the same time period. But comparing the decrease in ambient PM_{10} concentrations of 50% with the reduction of primary particle emissions by approximately 80 % a gap exists hinting at PM_{10} sources less well addressed, e.g. formation of secondary aerosols from gaseous precursors and transboundary transport, as well as fugitive dust emissions which might have been inadequately addressed to abatement measures so far.

The evaluation of average PM_{10} gradients analysed and presented in this report shows a considerable contribution of background aerosol to urban traffic sites of one third to 50%. This is different to e.g. nitrogen dioxide which can be found in the regional background only at levels near the detection limits and strongly increases in direction to the more populated and congested areas.

PM$_{10}$ increments between the different types of sites are quite constant in the order of 5 µg/m^3, except for the traffic/urban background increment on working days which is about twice that value. The typical PM$_{10}$ concentration (annual averages) sequence for Germany was calculated to be

Regional background: ~ 17 µg/m^3
Rural background: ~ 22 µg/m^3
Urban background: ~ 27 µg/m^3
Traffic site: ~ 32/37 µg/m^3 (weekend/working days)
Industrial urban site : ~ 32 µg/m^3

PM$_{10}$ concentrations of course may be considerably higher in street canyon situations than given here for a general traffic site situation [iv].

Differences between weekends and working days increments are also apparent for urban-rural and industrial-urban site increments but are less pronounced than for traffic sites.

Relatively few data is available in Germany with regard to PM$_{10}$ composition. Data sets covering about one year have been analysed for this report. On the long-term average, they indicate absolute concentration gradients for all of the main compound groups (carbonaceous compounds, minerals, secondary aerosols) in correspondence to the PM$_{10}$ gradients with increases from regional background to hot-spot sites. However, despite the absolute concentrations increase observed for all compound groups, their relative contributions change. The carbonaceous fraction which concentrations grow disproportionately high thus gains a higher importance, most probably due to combustion related primary emissions (traffic, heating). This is balanced by a lowering relative contribution of secondary aerosols. Hence, for these compounds transport from background into the urban environment can be assessed to be the major process. The sum of all other PM constituents, mainly mineral compounds, remains at nearly constant percentages in the increasing PM$_{10}$ mass., which means that still significant local emissions of such compounds take place.

On the other hand, short-term episodes of high PM$_{10}$ concentrations exceeding the daily limit value of 50 µg/m^3 frequently are driven by large scale meteorology which may cause both, accumulation of primary emissions and enhanced formation of secondary aerosols.

Overall, the PM$_{10}$ pollution situation in Germany appears to be rather similar throughout the country. At the borders some peculiarities may be observed, as e.g. a stronger influence of secondary and sea-salt aerosol constituents in the North-West due to agriculture and North Sea influence [v, vi], respectively.

From the intensive long-term measurements carried out at the research site in Melpitz (Sachsen) it follows that Eastern Germany may be influenced episodically by air masses from south-eastern Europe transporting aerosols with a high

$PM_{2.5}/PM_{10}$ ratio [i, see Annex]. PM_{10} concentrations in this area are generally increased at wind directions from east compared to situations with westerly winds.

8.5 References

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ANNEX A

Data from the research site at Melpitz/Saxonia

Size-segregated physical and chemical long-time characterization of particles depending from air mass origin at German lowlands (Saxony, Melpitz site)

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Summary

In the 1980s and 1990s the region around the city of Leipzig (West-Saxony) was one of the most polluted regions in central Europe. There were a number of sources contributing to the pollution during that period: emission from brown coal open mining, environmentally irresponsible industry, old power plants, old fashioned heating systems and mostly cars with two stroke engines without efficient exhaust fume cleaning techniques. The TSP concentrations in these periods show a large scatter with a mean value about 75 µg/m³. Since the re-unification of Germany in 1990, a continuous decrease in PM_{10} *concentration till 1998/99 was observed.*

Long-time measurements of PM_{10} *has started in 1993 at the IfT-research site Melpitz located in the lee side of the Leipzig conurbation in Saxony near the city of Torgau (12°56'E, 51°32'N, 86 m above sea level). The mean wind direction is Southwest; the second-class wind direction is East.*

The measured PM_{10} *concentration in 1993 was about 38 µg/m³ in summertime and about 44 µg/m³ in wintertime. The* PM_{10} *level decreased to 24 µg/m³ and 28 µg/m³ for winter and summer in 1998 and 1999, respectively. The yearly variation of the mean concentration was lower in summer than in winter.*

Since 1995 weekly low volume samples of $PM_{2.5}$ *(since 1999 also* PM_1*) show that the percentage of coarse particle (*PM_{10}*-*$PM_{2.5}$*) in summer is higher than in winter with an increasing trend till the end of the 1990s. This is a hint for an increasing influence of local emissions caused by agriculture and wind blowing dust from dry surfaces in summer. The particle mode between* PM_1 *and* $PM_{2.5}$ *mostly accounts for the highest percentage of the* PM_{10} *during winter months. The concentration of the particles between* PM_1*-*$PM_{2.5}$ *together with the fraction smaller than* PM_1 *can reach higher than 80% of the* PM_{10} *in wintertime. This is a hint of the influence of long range transport.*

With the decrease of anthropogenic emissions in the Saxon cities and whose direct surroundings at end of 1990s the influence of the long-range transport especially with air masses from the East during high pressure situation with low mixing heights in winter became more and more evident and is the cause for distinctive episodes with elevated particle concentrations in wider areas. The mean sources regions for wintertime anthropgenically influenced air masses are inside and outside of the European Union. The mean concentrations in the Melpitz area for PM_{10}*,* $PM_{2.5}$ *and* PM_1 *was 19.9, 15.2 and 12.7 µg/m³ in 2004 and 22.4, 17.6 and 12.9 µg/m³ in 2005, respectively.*

Therefore, particles were physically and chemically characterized for two years after size-segregated sampling in a project between the German Environmental Protection Agency (Umweltbundesamt, UBA) and the Leibniz-Institute for Tropospheric Research (IfT). The main results of the project the differences in the mean particle mass concentration, the chemical distribution and the physical properties of particles distinguished for air masses transported from West or East in summer and winter by classification of the daily results. These differences show the possible influence of long-

range transport from the east, mostly in wintertime, to the region of Saxony near the Polish boarder. In the winters 2004/05 and 2005/06 the PM_{10} mass concentration at the rural Melpitz site exceeded the limit value of 50 µg/m³ for 8 and 9 days, respectively. These concentrations were mostly accompanied with a strong elevated percentage of $PM_{2.5}$ in PM_{10}. These days contributed to the 35 days with exceeding the limit value of 50 µg/m³ allowed in cities. The detailed investigations also give clues to naturally emitted precursors for secondary particle mass formation especially in summer. A single event in May 2006 shows the strong influence of forest fires in Russia on the particle concentrations in wide areas of Germany with a strongly elevated percentage of $PM_{2.5}$ in PM_{10}.

1. Introduction

In the 1980s and 1990s the region around the city of Leipzig (West-Saxony) was one of the most polluted regions in central Europe. There were chemical industry and power plants without efficient waste gas cleaning systems, wide open coal mines with large erosion areas and domestic heating systems mostly based on brown coal briquettes. After the German reunification in 1990 fast and comprehensive modernization of power plants was initiated. Many old factories and metal processing facilities were closed. The remaining industry and a large fraction of the household heating systems were reconstructed within the last decade. Now the main sources for anthropogenic air pollutants are the traffic, the remaining brown coal open mining areas, power plants, households, and agricultural activities leading to primary particle emissions from surface erosion and secondary particle mass formation.

Long-time characterization of particles starts at the research site of the Leibniz-Institute for Tropospheric Research (IfT) Melpitz in 1993 with PM_{10} high volume samplers (Müller, 1999). Low volume samplers for PM_{10} and $PM_{2.5}$ were added in 1995 and for PM_1 in 1999. Figure 1 shows the particle concentrations before the German reunification and the decrease after the reunification in Saxony (Spindler et al., 1999 and 2004).

With the dramatic decrease of anthropogenic emissions in the Saxon cities and their direct surroundings at the end of 1990s the influence of long-range transport of trace gases and particles, especially from Eastern Europe became more and more apparent as a cause for distinctive episodes with elevated particle concentrations, mostly in wintertime. During high-pressure conditions dry air masses may be transported over long distances to Saxony, often with moderate wind velocity and low precipitation. The main source regions for these air masses are located outside (Russia, Belarus and Ukraine) and inside (Poland, Czech Republic and Slovakia) the European Union. Such situation with long-range transport from the east (continental air masses) can occur particularly in wintertime with daily PM_{10} concentrations > 50 $\mu g m^{-3}$. Long-range transport during these meteorological conditions can increase the number of days with mean PM_{10} concentrations > 50 $\mu g/m^3$ (limited to 35, EU-Commission, 1999) in wide areas and Saxon cities. Under the dominating wind direction (SW to NW) the particle concentrations are low in Saxony, because continental air masses from the European Union or maritime air masses from the Atlantic Ocean with showers are transported, often during low pressure conditions with high turbulence to Saxony. Because of the long distance to the sea the influence of sea salt particles is low.

In a two year joint study (2004-07-01 until 2006-06-30) between the Umweltbundesamt (UBA) and the IfT, size-segregated particles were characterized chemically and physically using high-volume samplers, five stage BERNER-type impactors and physical online instruments at Melpitz site. The main aim of the project is to show the differences in particle mass concentration, chemical distribution and physical properties by classification of daily particle characterization results for air masses from west (maritime and/or continentally influenced) and east (continentally influenced) with a distinction between winter and summertime. The PM size distributions from 3 nm to 10 µm was also investigated to address the toxicological aspects of PM (Samoli et al., 2005)

The IfT took part in the EMEP summer campaign in June 2006, with daily high-volume measurements of PM_1, $PM_{2.5}$ and PM_{10} and five stage BERNER type impactor measurements. The particles were analyzed for water soluble ions, organic carbon and elemental carbon (OC/EC). The size distributions and the absorption of the particles were continuously monitored using a tandem differential mobility particle sizer (TDMPS) system and a Multi Angle Absorption Photometer (MAAP), respectively. The EMEP winter campaign for January 2007 with identical instrumentation to the EMEP summer campaign is part of a one year continuation of the joint project with the UBA.

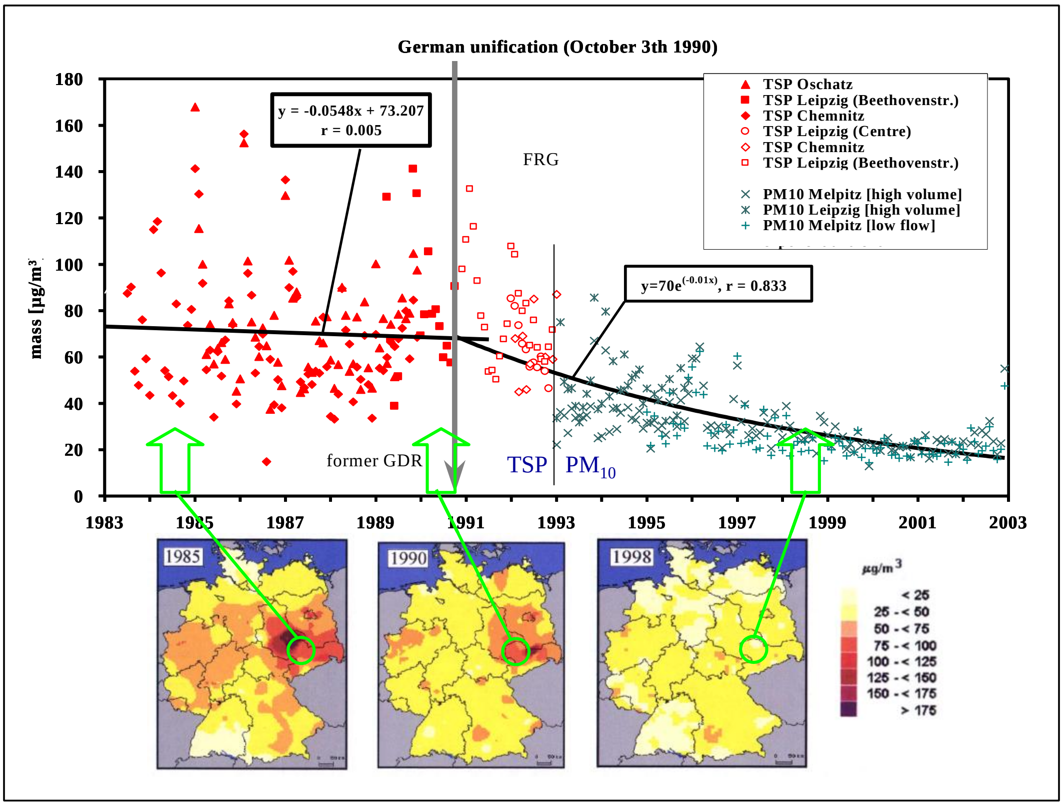

Figure 1 Mean aerosol mass concentration during 1993-2002 for west Saxony. The data shown are monthly means (1983-1992, TSP from different places in Saxony, source: SLUG, Sächsisches Landesamt für Umwelt und Geologie, 1992-2002 own high-volume PM_{10} measurements from Leipzig and Melpitz). The model calculations for 1985, 1990 and 1998 are from the Umweltbundesamt (UBA).

2. Measurement site, sampling methods, analysis, and determination of air mass origin

Measurement site

All measurements described in this report were performed at the IfT-research station Melpitz (12°56’E, 51°32’N, 86 m a.s.l.). IfT and the research station Melpitz are integrated in the new EU activities ACCENT (Atmospheric Composition Change, the European Network of Excellence) and EUSAAR (European Supersites for Atmospheric Aerosol Research, Flossmann et al., 2006) (Figure 2). Melpitz is located about 50 km in north-easterly direction from the city centre of Leipzig near Torgau, between the *Dübener Heide* and the *Dahlener Heide* in a representative region for rural sites of the German low lands. There are no major anthropogenic sources of PM near the site (Figure 3). During several national and international projects of the IfT the site was characterized meteorologically (Spindler et al., 1996, Brüggemann and Spindler, 1999, Erisman, et al., 2001, Stratmann et al., 2003), for trace gases (Gnauk et al., 1997, Spindler et al., 2001, Spindler et al., 2003) and for PM concentrations (Heintzenberg et al., 1998, Spindler, et al., 1999, Müller, 1999, Neusüss et al. 2002, Plewka et al., 2004, Spindler et al., 2004a, Herrmann et al., 2006, Engler et al. 2006). Comparisons to other European sites are given in Putaud et al., 2004, Van Dingenen et al., 2004 and MacDougall et al., 2005. Long-time measurements since 1993 and an intensive joint test project with the UBA in November and December 2003 (Spindler et al., 2004b) have shown that Melpitz is a representative site for a continuous size-segregated physical and chemical PM characterization and is suitable for the classification of days with different origins and history of air masses.

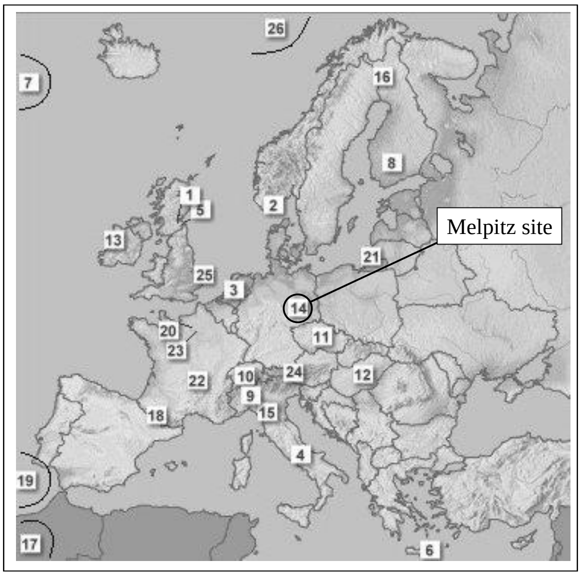

Figure 2 Location of the Melpitz site in Europe (EUSAAR network).

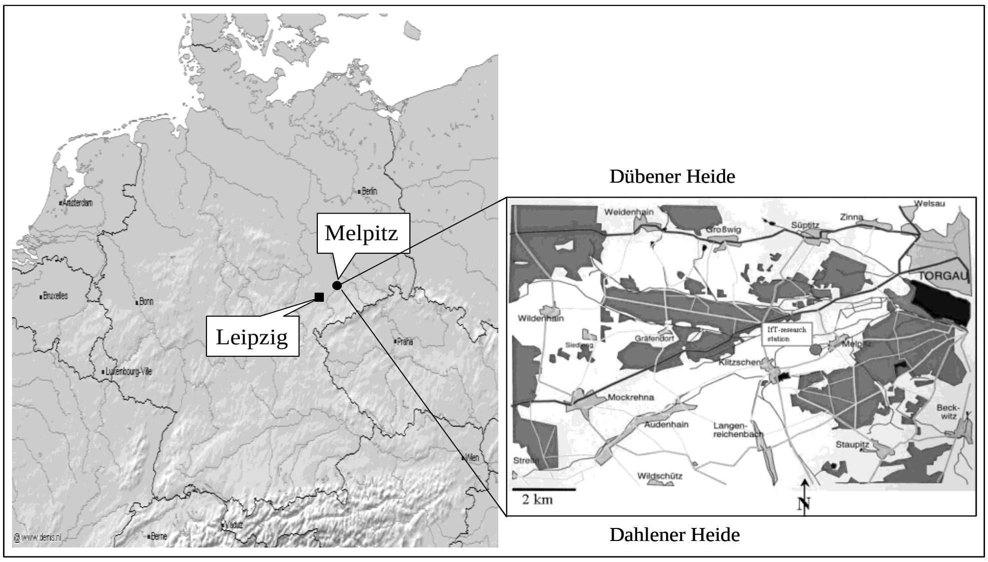

Figure 3 Location of the Melpitz site in Germany and surroundings

Long-time measurements

For the long-time measurements (Müller 1999, Spindler et al. 2004), the daily samples were taken by a modified Sierra-Anderson-PM_{10} high volume sampler (Anderson Samplers Inc., USA). The sampling volume was approximately 1340 m³. The filters were rectangular quartz fibre filters (MUNKTELL, Sweden). Since 1995 weekly filter samples for PM_{10} and $PM_{2.5}$ were taken using a low-volume sampler ('Partisol 2000', Rupprecht & Patashnik Co. Inc., USA) with 47 mm diameter Teflon filters (Type 4700, 3 µm pore size, Millipore, USA). The low volume sampling starts every Monday 12:00 MEZ. Since 1999 a PM_1 sample was taken simultaneously.

Two years intensive measurements

The PM size spectrum from 10 µm down to 3 nm was investigated for two years (winters 04/05 and 05/06 and summers 05 and 06) using different sampling systems combined with physical-chemical off-line analysis and physical on-line instruments.

High-volume sampling

Three identical samplers, DIGITEL DHA-80 (Walter Riemer Messtechnik, Germany), were used to determine PM_{10}, $PM_{2.5}$ and PM_1 (Gnauk et al. 2005). The sampling velocity was 30 m³/h for all systems. The filter was made from quartz fibre (MK 360, MUNKTELL, Sweden). The sampling time for each filter was 24 hours. The automatic filter change took place at midnight. PM_{10} and $PM_{2.5}$ were measured every day and PM_1 every sixth day (except during intensive measuring campaigns, e.g., EMEP in June 2006, when PM_1 was measured daily too).

BERNER-type impactors

In parallel to the filter sampling, size-segregated PM sampling using five-stage BERNER type impactors was carried out with a sampling velocity of 75 l/min for selected days. The impactors consist of six successive impactor stages with decreasing cut-off diameters (D_{pa}: 10, 3.5, 1.2, 0.42, 0.14, and 0.05 µm). Aluminum foils were used as a substrate (Gnauk et al. 2005). Particle mass and chemical size distributions were determined by weighing the mass of particles impacted on the stages and from the analysis of the particle phase chemical composition. On stage 1 (0.05-0.14 µm) freshly emitted particles were typically found (e.g., traffic emitted soot). On stages 2 and 3 aged particles were found though the particles from other sources were also found (e.g., long-range transport particles or from domestic heating). In the coarse mode fractions 4 and 5 the sea salt particles, primary biogenic material, and resuspended crustal material were found. The chemical composition of the particles in different size classes varied with sources of PM and the meteorological conditions during the sampling periods.

High time resulution measurements with TEOM®

Additionally, a high time resolution PM_{10} concentration (half-hourly-means) were measured using a TEOM® 1400a (Rupprecht & Patashnick Co., Inc., USA). The TEOM operates at 50°C and quasi-continuously measures PM_{10} mass by collecting particles on an oscillating microbalance. The air stream is regulated by a mass flow controller. The relatively high operating temperature (50 °C) for the TEOM microbalance is necessary to avoid the condensation of water vapor (positive artifact) but can also generates systematic errors by evaporating volatile compounds (negative artifacts) such as ammonium nitrate (Charron et al., 2004). The TEOM is used only for the monitoring of short time effects. The mean mass for 24 hours would be corrected by a daily comparison with the PM_{10} data from high-volume sampler (DIGITEL DHA-80).

Mass determination and Ion-chromatography

The mass, the concentrations of main ionic species (Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}), the elemental carbon (EC) and the organic carbon (OC) in all size fractions were determined from impactor samples and the PM_1, $PM_{2.5}$ and PM_{10} samples. The impactor foils and filters were equilibrated for 48 hours in the weighing room under controlled temperature and relative humidity (20°C and 50% RH.). The impactor foils were weighed using a microbalance UMT-2 and an AT-261 for filters (both Mettler-Toledo GmbH, Germany). Anions and cations from filter samples were analyzed by ion chromatography (Metrohm, Switzerland) after two hours extraction in Milli-Q grade water. Different procedures were used for anion determination from the impactor samples and the filter samples. Cations in the impactor samples were analyzed using IC but the anions in the impactor samples were analyzed by capillary zone electrophoresis (Spectra Phoresis 1000-Thermo Separation Products, USA).

OC and EC determination

OC/EC separation can be achieved in different ways as reviewed by Penner and Novakov (1996). In this study the particulate carbon fraction was determined by a two step thermographic method using a carbon analyzer C-mat 5500 (Ströhlein, Germany). The method applied in this study is a variation of the German official VDI guideline (VDI 2465, Part 2, 1999). In a first step nitrogen was used as carrier gas for the OC volatilization at 650°C for eight minutes. Those carbon compounds that evaporate under N_2 atmosphere at 650°C conditions and converted to CO_2 by a catalyst are addressed as OC in this study. In a second step the remaining carbon was transformed to CO_2 by combustion under oxygen for eight minutes at 650°C and detected by IR absorption is addressed as EC in this study. A NDIR detector was used for the detection of CO_2. This temperature was selected to avoid melting of the aluminum substrates, decomposition of carbonates (Petzold and Nießner, 1996) as well as to minimize charring processes during the volatilization step. The method discussed in detail can be found in Neusüß et al. (2002) and Plewka et al. (2004). The method was involved in the Germany-internal VDI/DIN - comparison experiment (Neuroth et al., 1999) as well as the International Round Robin Test Carbon Shoot out Stage I (Schmid et al., 2001) and Stage II (Puxbaum, TU Vienna, unpublished).

Carbon preference index (CPI)

The determination of selected non-polar semivolatile organic species was carried out by CPP-GC-MS (Curiepoint pyrolysis gas chromatography mass spectrometry) directly from the impactor foils. The CPP system (JPS-350, Japan Analytical Industry, Ltd.) acts as a fast thermal desorption injector. The evaporation of species occurs at 500 °C under helium after adding internal standards (two deuterated alkanes). The detection limits are in the lower pg/m³ range for the most compounds.

The concentration of n-alkanes is used to distinguish biogenic and anthropogenic sources of carbonaceous PM. The CPI (Carbon preference index) is determined as follows:

$$\mathrm{CPI}_{odd} = \frac{\text{mass concentration of odd n-alkanes } (C_{21} - C_{33})}{\text{mass concentration of even n-alkanes } (C_{20} - C_{32})}$$

Alkanes from anthropogenic sources have the CPI close to 1 and the CPI of alkanes from biogenic origins is typically between 5 and 20. Additionally to the CPI index, the mode where alkanes are found can give information on the sources. For example, plant waxes have been found typically in coarse mode PM (Sicre et al., 1990; Kavouras et al., 1998) but fresh traffic emission PM, e.g., is found in the submicron PM.

TDMPS/APS-system with thermodenuder

A tandem differential mobility particle sizer (TDMPS) was used for continuous online particle number concentration determination in the size range 3 to 800 nm (twin differential mobility particle sizer,Birmili et al., 1999) in combination with a thermodenuder (TD). This system is suitable to measure dry number size distributions of ambient aerosol particles and those of non volatile particle fraction in an alternating manner. The system is equipped with automatic valves which enable measurements with and without TD. The valves are switched computer controlled. The TDMPS system consists of two Hauke type DMAs (differential mobility analyzer) in combination with two CPCs (condensation particle counter). One DMA (ultrafine DMA) is operated at an aerosol flow rate of 2 lpm, a sheath air flow of 20 lpm and it measures particle size between 3 and 22 nm (mobility size). The number concentration of the quasi monodisperse aerosol fraction behind the UDMA is measured by an ultrafine CPC (UCPC, model 3025, TSI Inc., USA). The second DMA is operated at an aerosol flow rate of 0.5 lpm, a sheath air flow of 5 lpm and it measures particles between 22 and 800 nm. The particle number concentration was measured behind the DMA by a CPC (model 3010, TSI Inc., USA). The measurements are controlled by LabView®-based software. Both systems start the measurements overlapping at 22 nm and continue stepwise up- and downwards to their upper and lower limits with a size resolution of 16 channels per decade. The system measures a complete size distribution from 3 to 800 nm within 10 min, thus there are 3 measurements with and without TD available per hour. An inversion routine is used afterwards to calculate the real number size distributions using the real DMA transfer function (e,g, Stratmann and Wiedensohler, 1996). The TD removes a volatile fraction of particles by thermal desorption (Wehner et al., 2002). The TD consists of two units, a heating and a cooling section. In the first part of the instrument, particles are heated to a certain temperature (maximum ~ 300 °C) where all the volatile material is evaporated. The subsequent cooling tube is filled with active carbon for the adsorption of evaporated gas phase compounds. The aerosol flow inside the heating section is maintained at constant temperature and controlled and regulated using a thermal resistor (Pt 100) which is placed halfway along the aerosol line on the outside of the stainless steel tube. A second Pt 100 is located at the entrance of the cooling section to monitor the temperature of the aerosol flow downstream of the heater. The aerosol tube (stainless steel, 20 mm ID) is surrounded by a second tube (copper, 35 mm ID) filled with fine sand to maintain a homogeneous and uniform temperature distribution between wall and aerosol line. The tubing inside the cooling unit consists of stainless steel gauze which permits the gases to transfer to the carbon section. It is supplied with a thin-walled stainless steel tubing system wrapped spirally around the aerosol line to actively cool the aerosol flow if needed.

The number size distribution between 0.8 and 10 µm was measured using an aerodynamic particle sizer (APS, model 3321, TSI Inc, St. Paul, USA). Within the APS particles are separated according to their inertia. The sample flow is accelerated through a critical orifice and the following time of flight measurement provides the aerodynamic diameter. The time resolution of the APS is identical to the TDMPS system 10 min, but measurements have been performed with ambient aerosol (without TD) only.

Figure 4 shows the size cuts of high volume samplers, the impactor, the TDMPS and the APS, which took part in this study.

Determination of air mass origin

A determination of air mass origin of measurement days was carried out because particle mass concentration, physical and chemical properties and their size distribution depends mainly on the air mass history, the origin, and the seasons (winter or summer). The classification was based on 96-hour backward trajectories from the NOAA-Hysplit-Modell (source: http://www.arl.noaa.gov/ ready/hysplit4.htm). Backward trajectories were plotted twice a day (10:00 and 18:00 CET) and for 200, 500 and 1500 m above ground level for the measurement periods (winters 04/05, 05/06 and summers 05 and 06). The measurement days from May to October were assigned to the summertime and measurement days from November to April were assigned to wintertime. The days with westerly air mass transport was classified as continental and/or maritime and the days with easterly air mass transport was classified as continental. Figure 5 shows the two broad sectors used for the classification of long-range transported air masses by backward trajectories. The days with low wind velocity and more local influences and the days with air mass transported from North or South were not considered in the different means for air masses from West (maritime and/or continentally influenced) and from East (continentally influenced).

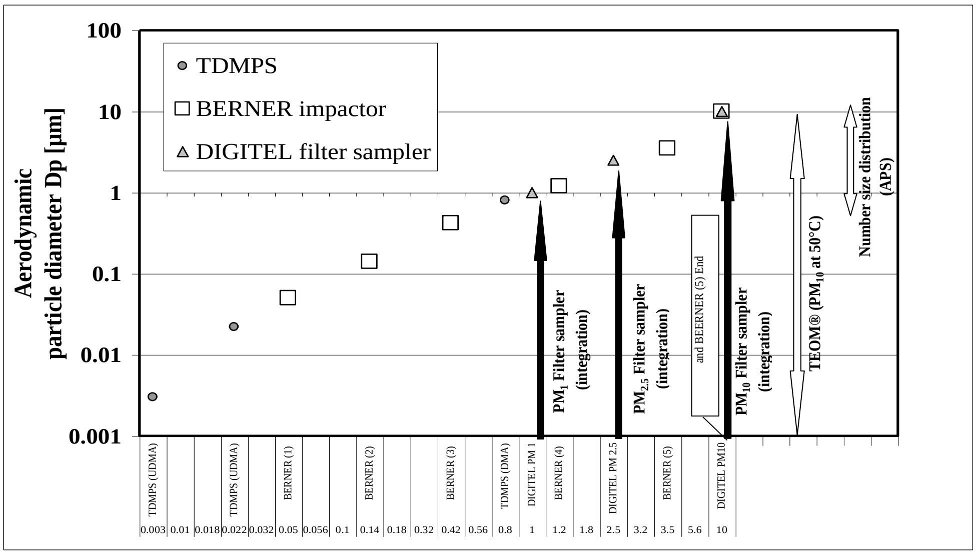

Figure 4 Size-segregated chemical and physical characterization of particles with different sampling systems and online devices.

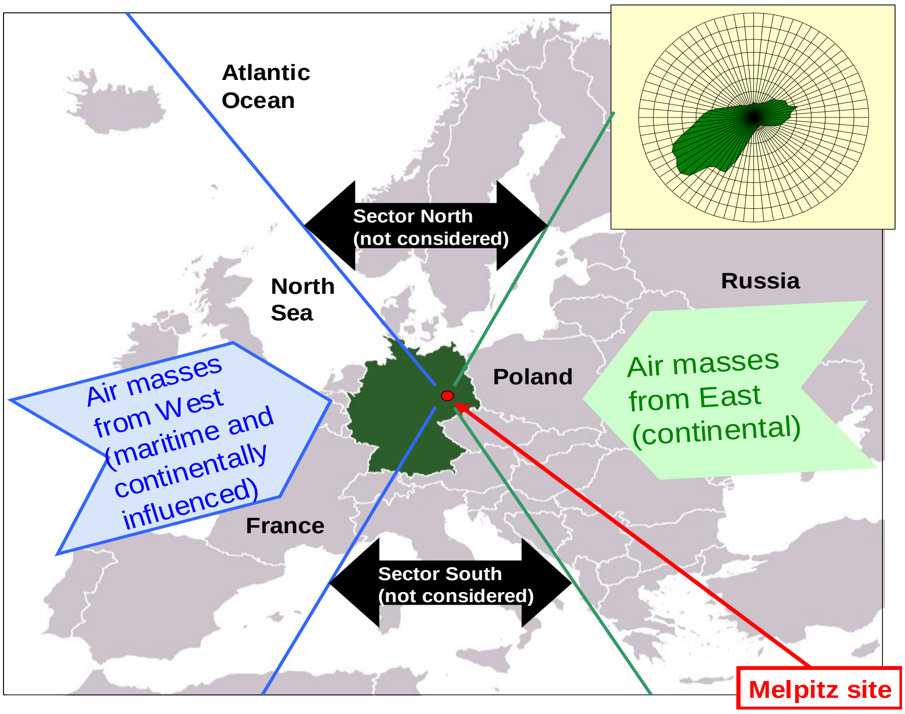

Figure 5 Classification of daily samples for two major long-range transport patterns - air masses from West (maritime and/or continentally influenced) and air masses from East (continentally influenced) and wind rose for the Melpitz site (more than 4.2 million 5 min averages considered, calm wind velocity < 0.5 ms^{-1} in 12 m above ground is 8.6% of the measurement time).

3. Results

3.1. Long-time measurements

Long-time characterization of particles started at the Melpitz site in 1993 with PM_{10} high volume sampling. Figure 6 shows the course of average half-yearly particle mass concentration of PM_{10} for winter and summer combined with the half-yearly means of precipitation sum over 14 years. The elevated PM_{10}-concentration (1993 till 1997) was mostly caused from local emission in the Saxon cities and surroundings A decreasing PM_{10}-mass concentration can be observed till about 1998/99.. From about 1999 up to now the influence of the long-range transport of particles, especially from Eastern Europe became apparent. This is now the major cause for distinctive high PM episodes in wide regions in Saxony. The winters show the higher inter annual pattern caused by lower turbulence as in the summers. This means the general influence of different meteorological conditions is more pronounced in winter ($r^2 = 0.47$), than in summer ($r^2 = 0.90$). The correlation with the total precipitation is weak but winters with relatively high mass concentrations show low total precipitations, these are hints of a more continentally influenced climate in these winters with a low mixing height during cold high pressure weather situations.

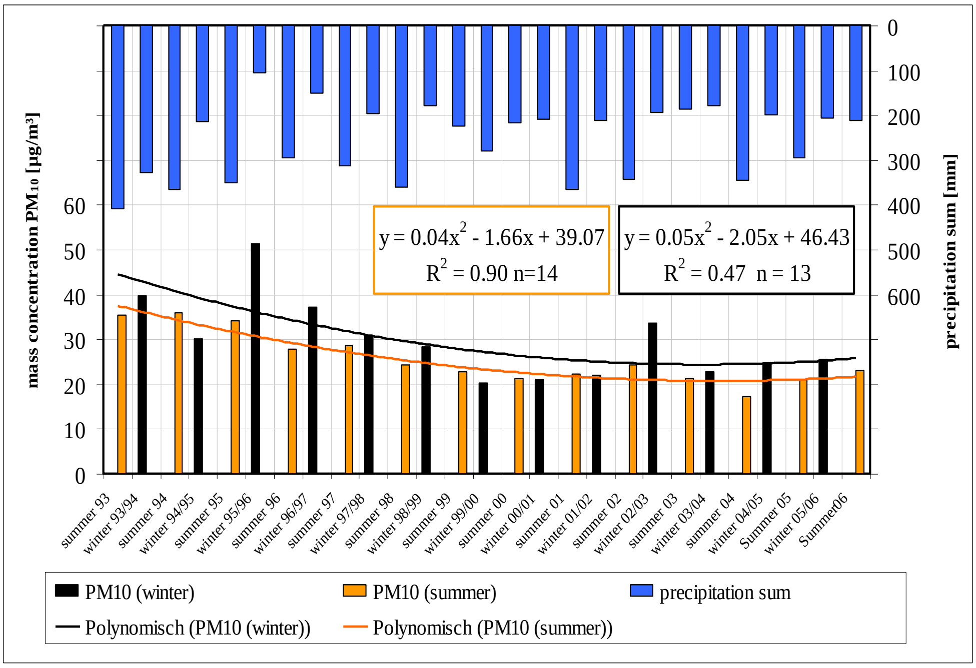

Figure 6 Evolution of half-hourly PM_{10}-mass concentration and precipitation in winter (November until April) and summer (May until October) at Melpitz site in the least 14 years. The half yearly precipitation sum is plotted as inverse.

Weekly low-volume filter samplers for PM_{10} and $PM_{2.5}$ since 1995 and PM_1 since 1999 are available for a size-segregated chemical characterization at Melpitz site. The percentage of PM_{10}-$PM_{2.5}$ concentration in PM_{10} since 1995 and the relative parts of $PM_{2.5}$-PM_{10} and PM_1-$PM_{2.5}$ concentrations in PM_{10} since 1999 are plotted in Figure 7. These size segregated measurements show a typical pattern with significantly higher percentages of coarse particles PM_{10}-$PM_{2.5}$ in summers. The reason is, at one hand, the regional re-suspension of coarse particles from dry surfaces in summer by agricultural activity and/or blowing wind. On the other hand, the particles smaller than $PM_{2.5}$ were emitted from domestic heating systems in winter which were transported over long distances. The re-suspension of coarse mode particles from wet or snow-covered surfaces is depressed in winter. The increase of the percentage of coarse mode particles PM_{10}-$PM_{2.5}$ from 1995 till 1998 may be caused by decreasing emissions of coarse particles in the surroundings. This means that local course mode emissions account comparably higher fractions of the coarse mode now than the time when the site was influenced by much worse pollution episodes.

Additionally, the particle fraction $PM_{2.5}$-PM_1 is available since 1999 (Figure 7). These particles are mostly from long range transport. Generally, higher percentages of fine particles $PM_{2.5}$-PM_1 were detected in winter than summer. The percentage of the particles smaller than PM_1 and the fine particles $PM_{2.5}$-PM_1 can reach more than 80 % of PM_{10} especially during times with snow covered surfaces and with low mixing heights in winter. Low contribution of PM_{10}-$PM_{2.5}$ can be explained by negligible coarse particle emissions in the near surroundings. This means that high PM_{10} particle mass concentrations in winter outside a conurbation are made of 80 % or higher $PM_{2.5}$ masses (compare chapter 3.2.1. and 3.2.3.).

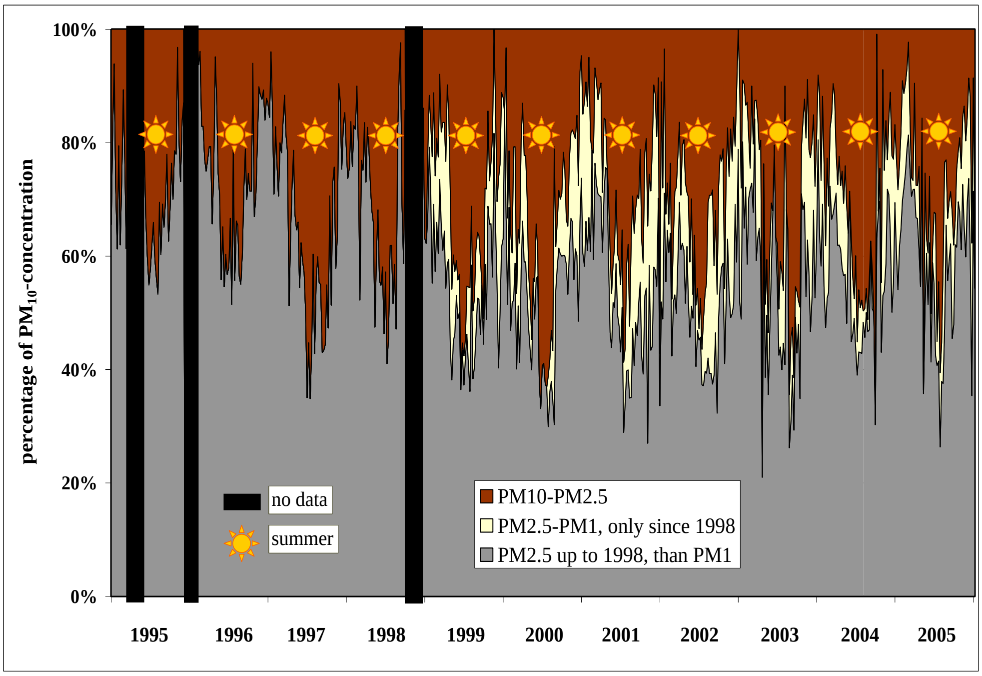

Figure 7 Time series of the percentage of PM_{10}-$PM_{2.5}$ and $PM_{2.5}$-PM_1 mass concentration in PM_{10} since 1995 at Melpitz site (from 1995-98 only PM_{10}-$PM_{2.5}$). The data are weekly averages.

3.2. Characterization of particles – comparison for air mass transport from West and East in winter and summer

3.2.1. PM_1, $PM_{2.5}$ and PM_{10} measurements with high-volume samplers

Three identical high volume samplers (DIGITEL) were used to determine PM_{10}, $PM_{2.5}$ and PM_1 since May 2004 till now. PM_{10} and $PM_{2.5}$ were measured every day and PM_1 every six days (expect during intensive campaigns with daily PM_1 measurements). The yearly mean concentrations for PM_{10}, $PM_{2.5}$ and PM_1 were 19.9, 15.2 and 12.7 µg/m³ in 2004 and 22.4, 17.6 and 12.9 µg/m³ in 2005, respectively. The time series since May 2004 together with an indicator for air mass direction from West or East are plotted in Figure 8.

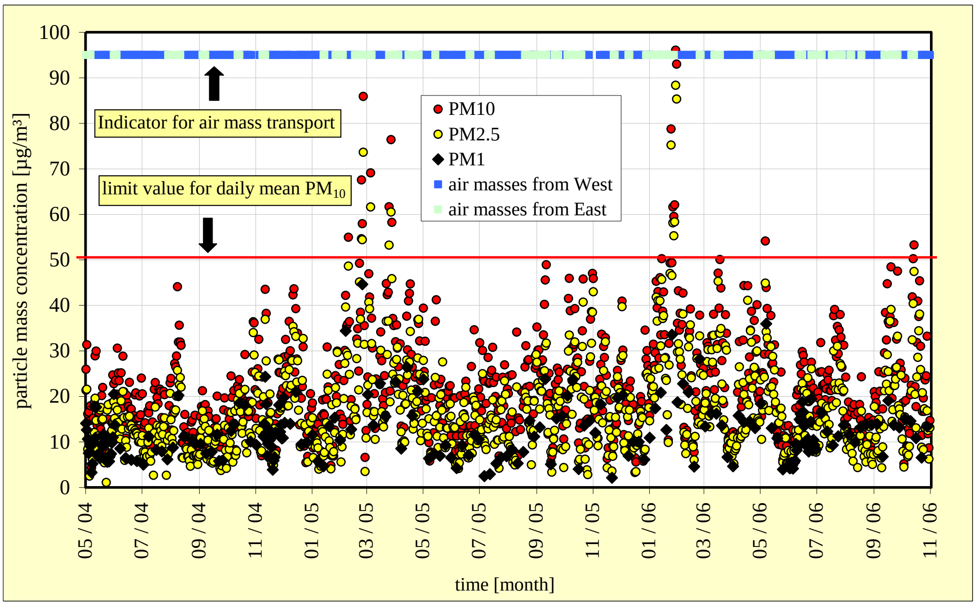

Figure 8 Time series of daily particle mass concentration PM_1, $PM_{2.5}$ and PM_{10} (May 2004 until October 2006) with indicator for air mass origin.

In winters the PM_{10} but also the $PM_{2.5}$ particle mass concentrations at the rural Melpitz site exceed the limit value of 50 µg/m³ for PM_{10} (8 times in winter 04/05 and 9 times in winter 05/06). These numbers of days with large area exceedings of the PM_{10} concentration limit of 50 µg/m³ contribute to the limit number of 35 days in cities nearby the Melpitz site. Additionally, the numerous days with elevated background concentrations higher than 30 µg/m³ are a problem in view of the limits. The elevated PM_{10} values for the very hot and dry July 2006 in Germany and the warm and dry October 2006 are also recognizeable. The high PM concentrations in May 2006 were caused by a long-range transport from partly anthropogenically caused vegetation fires in Russia. During this episode from May 5-9 in 2006, when the particle mass concentration exceeded 50 µg/m³ in wider areas, the percentage of the $PM_{2.5}$ fraction in PM_{10} was strongly elevated and reaches 84%, typical for long range transport episodes. Figure 9 illustrates this special situation. From the data plotted in Figure 8, the daily and monthly percentage of $PM_{2.5}$ in PM_{10} was calculated and plotted in Figure 10. As Figure 10 shows, the higher percentages for $PM_{2.5}$ in winter can be also caused by long range transport, especially during air mass transport from east during dry high pressure situations with low mixing height.

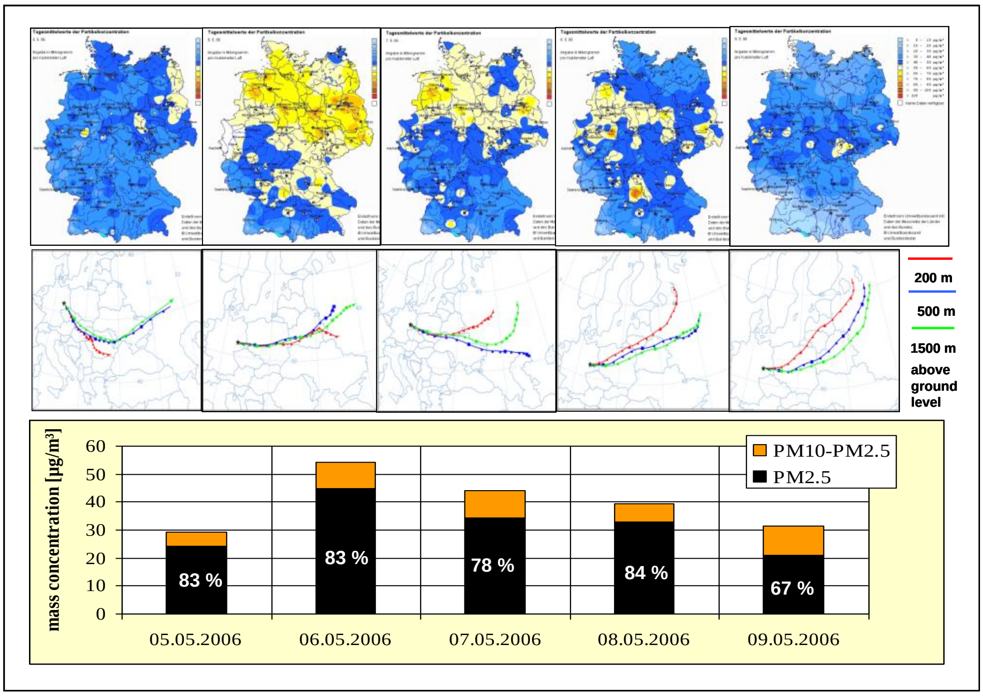

Figure 9 PM_{10} concentrations in Germany with a high percentage of $PM_{2.5}$ at five days in May 2006 caused by long-range transport from East. (sources: concentration maps, Umweltbundesamt, 96-hour backward trajectories, NOAA-Hysplit-Model).

The highest percentage of $PM_{2.5}$ in PM_{10} at Melpitz was between 92 and 96% during a smog episode over Germany in winter 2006 (January 22 till February 7). At the same time the mean percentage of $PM_{2.5}$ in PM_{10} was 67.4% (average of 6 sites) in North-Rhine-Westphalia (Bruckmann et al. 2006). These data show that the air masses near the Polish border were negligibly influenced by locally caused coarse particle emissions and the percentage of $PM_{2.5}$ in PM_{10} decreased over Germany because locally produced coarse particle were added to the air masses during the transport from East to West. Figure 11 shows the time series of daily particle mass concentration of the main ions (nitrate, sulfate and ammonium) and the total carbon content (TC) in PM_1, $PM_{2.5}$ and PM_{10}. The concentrations in winter samples were higher than in summer samples for all species. The secondary aerosol components (NH_4^+, SO_4^{2-} and NO_3^-) were a significant fraction of PM and dominated in the samples which had influence of the long range transport (compare also with Figure 12). The strong variation of the ammonium nitrate concentrations between summer and winter can be explained by the vapor pressure of ammonium nitrate over the corresponding particles (Hildemann et al., 1984). Ammonium nitrate shows a temperature and relative humidity dependent phase distribution (Lammel and Leip, 2005, Plessow et al., 2005, Vayenas, et al., 2005) but also volatilization from filters in summer is possible.

Ammonium, hydrogen sulfate and sulfate can exist as NH_4HSO_4 and $(NH_4)_2SO_4$ in the condensed phase, therefore a reasonable concentration of NH_4^+ and SO_4^{2-} was observed in the condensed phase in summer. The TC concentration in the winter was often strongly elevated and corresponded to the episodes of high particle mass concentration (see Figure 9). The reason is the air mass transport from East, especially in winter.

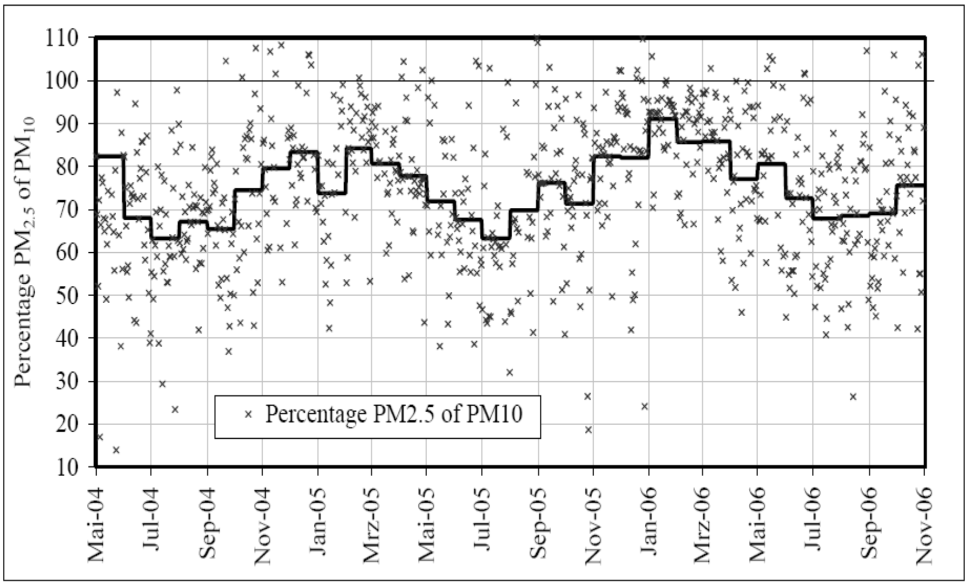

Figure 10 Time series of daily and monthly percentage of $PM_{2.5}$ in PM_{10} (May 2004 until October 2006).
(Values greater than 100 % can be calculated in the range of spreading.)

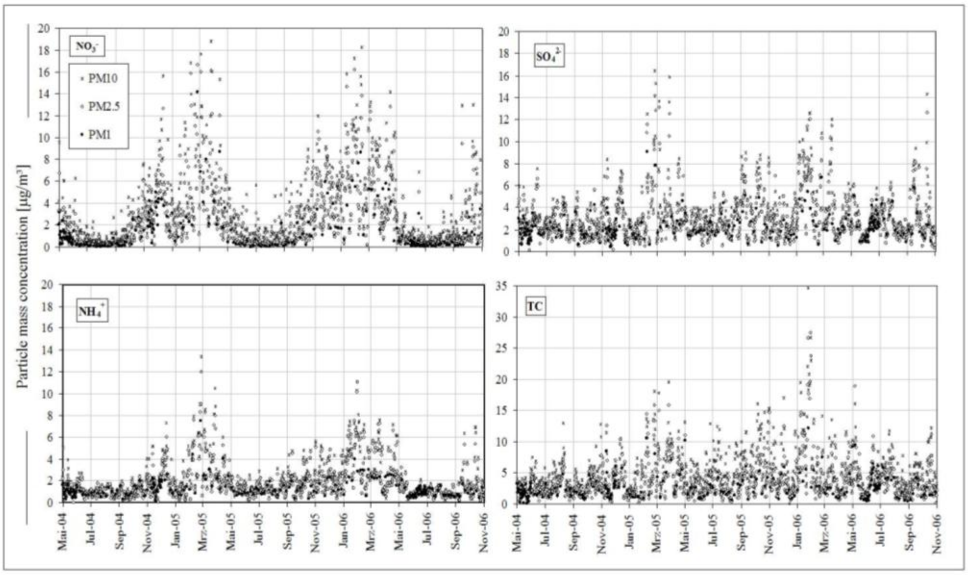

Figure 11 Time series of daily particle mass concentrations PM_1, $PM_{2.5}$ and PM_{10} for the main ions (nitrate, sulfate and ammonium) and total carbon content (TC).

Figure 12 shows the average summer and winter particle phase mass concentrations of the main water soluble ions (nitrate, sulfate and ammonium) and organic and elemental carbon (OC and EC) in PM_1, $PM_{2.5}$ and PM_{10} for days with air mass transported explicitly from East or West. The average particle mass concentrations in Melpitz were higher in winter than in summer. The highest PM concentrations were observed during air mass transport from East (continentally influenced) in winter, caused from long range transport but also from a low mixing high pronounced during high pressure situations. The air masses from East were mostly dry and stable. The main source regions for these air masses are located in Russia, Belarus, Ukraine, Poland, Czech Republic and Slovakia. The high contents of sulfate, OC and EC indicate that there were also from anthropogenic emissions (power plants, industry, households and older automobiles). The wintertime OC/EC ratio was lower than in summer (i.e. higher EC fractions in winter), especially for the air masses from East, possibly caused by additional emissions from combustion processes. This observation is not valid for nitrate because the main source of nitrate is the NO_x-emission of cars. The difference in nitrate concentration between winter and summer was caused by the volatility of ammonium nitrate in summers.

The unidentified mass was mostly mineral dust. Unlike unidentified mass, the fraction of water soluble ions was higher in PM_1 than PM_{10} and also was higher in the summer samples than in the winter samples. One reason is the re-suspension of coarse particles from agricultural activities and wind blowing dust in the surroundings. The re-emission is preferred in the summer as surfaces are drier and also dry much more faster after precipitation events than in winter. Generally, the PM concentration is lower under air mass transports from West (maritime and/or continentally influenced) because they are often combined with precipitation (wet deposition) and higher mixing volumes in more turbulent air masses.

3.2.2. PM_{10} measurements with TEOM®

With a TEOM® a high time resolution PM_{10} time series can be monitored additionally. Possible positive or negative sampling artifacts of the devise were corrected daily in this project by a comparison with PM_{10} data from the PM_{10} high volume sampler.

The investigations of the high time resolution time series confirm the results discussed in chapter 3.2.1. Figure 13 shows the mean diurnal variation of half-hourly PM_{10} measurements for air masses transport from West and East, and for winter and summer. In Figure 14 the relative frequency distributions of half-hourly PM_{10} concentrations are plotted. The mean daily time series for days with air mass transported from East in winter shows the highest half-hourly PM_{10} concentration, with a negligible variation, which is typical for long range transport. In summer the concentrations were lower for the air mass transported from east with a weak daily variation (lowest mean concentration in the early morning about 21 µg/m³) and highest in the late afternoon about 33 µg/m³). Also the concentrations during air mass transported from West in summer were observed at a level that is about 10-15 µg/m³ lower than in the winter with a weak daily variation (lowest mean concentration in early morning about 14 µg/m³ and highest in the late afternoon, about 18 µg/m³). A reason for this variation can be found in the re-suspension of particles from dry surfaces in the surroundings of the Melpitz site in summertime. The mean concentration time series for the air mass transported from West in winter was about 20 µg/m³ lower than for the air mass transported from East and was also nearly equal over the whole day. This is a hint for pronounced long range transport.

In consequence the relative frequency distributions (Figure 14) show clearly the higher percentage for elevated PM_{10} concentrations especially for wintertime and air mass transported from the East. The smallest frequency distribution was observed from the measurements during air mass transported from west in summer.

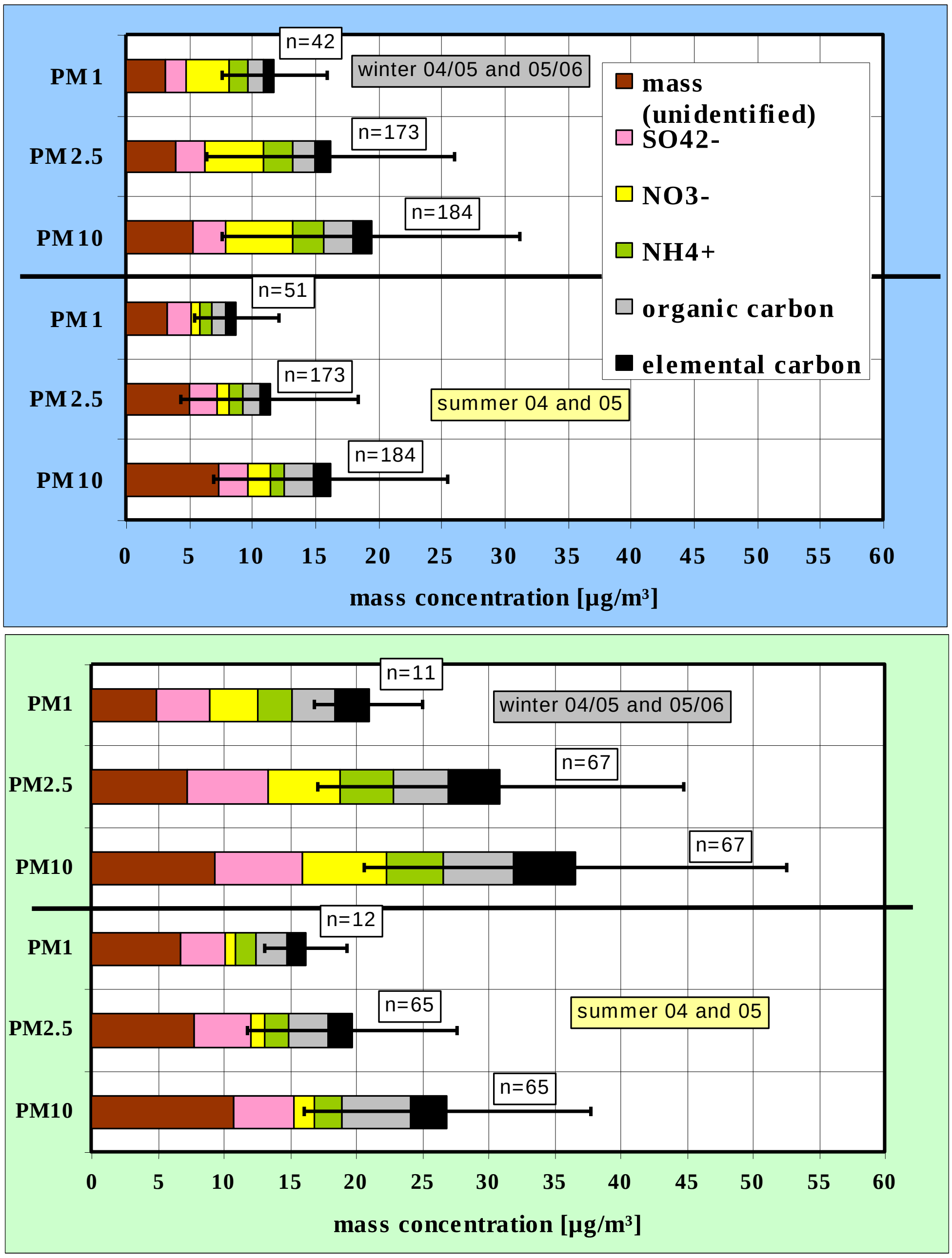

Figure 12 Mean PM_1, $PM_{2.5}$ and PM_{10} mass concentrations and the concentrations of the main ions (nitrate, sulfate and ammonium) and organic and elemental carbon content (OC and EC) in winter and summer. Only days with air mass transport explicitly from West (blue frame) or from East (green frame) are considered.
The error bars are the standard deviation for the particle mass concentration. "n" is the number of days. Averages of two winters (2004/05 and 2005/06 and two summers (2005 and 2006) are shown.

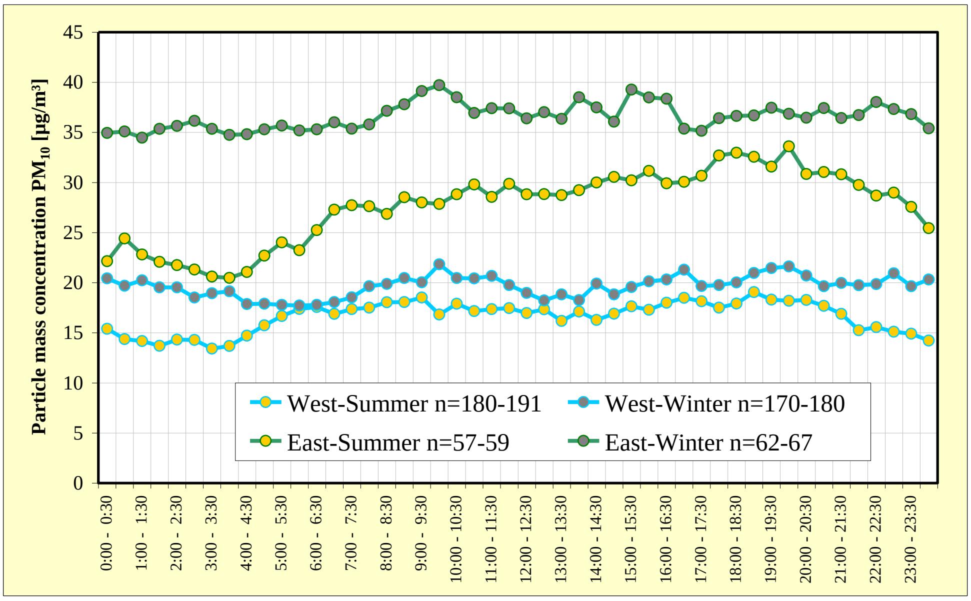

Figure 13 Mean daily time series of half-hourly PM_{10} measurements with a TEOM®, divided for winter and summertime. Only days with air mass transported explicitly from West or from East are considered.

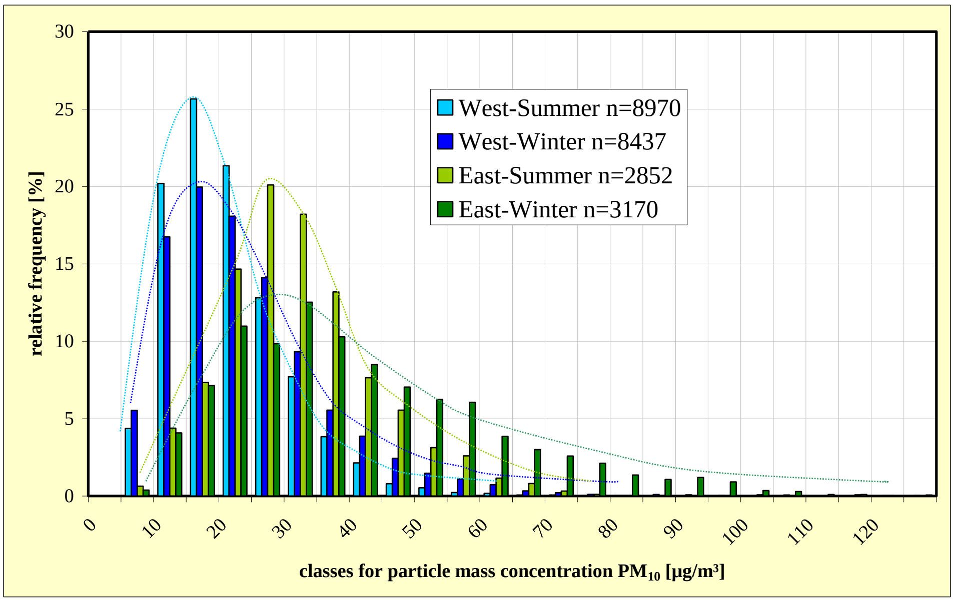

Figure 14 Relative frequency distributions of half-hourly PM_{10} measurements from Figure 13.

3.2.3. PM characterization with five stage BERNER-type impactor

Selection of measuring days

PM sampling using the impactors was carried out during selected dry days with stable maritime and stable continental air mass transports according to the definition made in Figure 5. The impactor samples were taken over 24 hours. The days were selected by the weather forecast and the origin of air masses which was determined by 96-hours back trajectories. During the two years of the measurements 14 maritime and 8 continental summer days and 12 maritime and 12 continental winter days have been selected for mass determination and chemical analysis.

Mass, content of water soluble ions, OC/EC, and organic species

For these measurements all the above mentioned samples have been used. The Figure 15 shows the means of the determined mass of the size classes for summer and winter and air mass transported from West and East. Differences between seasons and source regions are evident. Summer concentrations are lower than winter concentrations and air masses transported from Eastern Europe carry higher amounts of PM. The highest concentration of PM was typically found in the size fraction 0.42-1.2 µm which is known for their atmospheric stability. This PM fraction is characteristic for long range transported particles. During wintertime also aged PM from domestic heating using coal was found mainly in this fraction. The percentage of coarse mode particles (size fraction 3.5-10 µm) was higher during summers because of the natural re-suspension by turbulence and the anthropogenic re-suspension of PM from dry surfaces by agricultural activities near the sampling site.

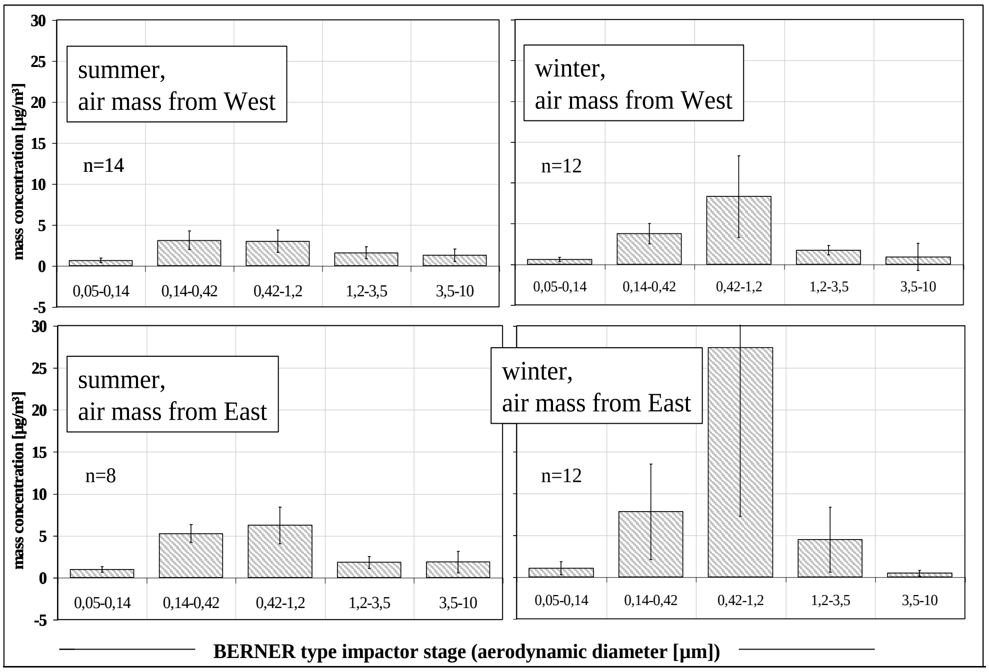

Figure 15 Mean PM mass concentration from the five stages of BERNER type impactor, divided for winter and summer days and air mass transported from West (continentally and/or maritime influenced) or East (continentally influenced). The error bars are the standard deviation, n is the number of days used for the average in winters 04/05 and 05/06, and summers 05 and 06.

In Figure 16 striking differences were found in the relative constitution of PM in the five size classes. During the summertime the non-resolved part of PM (mainly mineral dust) was the major fraction in all size classes for both source regions. Sulfate was found only in fine particles during summers but during winter sulfate was observed also in super-micron particles and in higher concentration in continentally influenced samples. The concentration of sulfate in winter often reached 10 µg/m³ in stage 3 particles. Similar patterns are seen for the other main ionic components such as ammonium, nitrate and chloride but not for the metal ions such as sodium, magnesium and calcium. Their content in PM is mainly influenced by sea salt. During winters chloride was also emitted by burning processes and by re-suspension of KCl from roads. Nitrate was the major ionic component (NH_4NO_3 in PM < 1 µm and $NaNO_3$ in coarse mode PM) during winter sampling periods with maritime air masses whereas nitrate was found at a similar concentration to sulfate in PM of continental origin. In the summer samples nitrate was found mainly in the coarse mode particles, typically as the stable $NaNO_3$ whereas NH_4NO_3 decomposes to ammonia and nitric acid during summers leading to smaller fractions. Sodium nitrate was formed from sea salt by the exchange of chloride by nitric acid. Ammonium concentrations were low in coarse mode particles but in fine PM only ammonium sulfate was found in summer. However, both ammonium nitrate and ammonium sulfate were found in PM in winter.

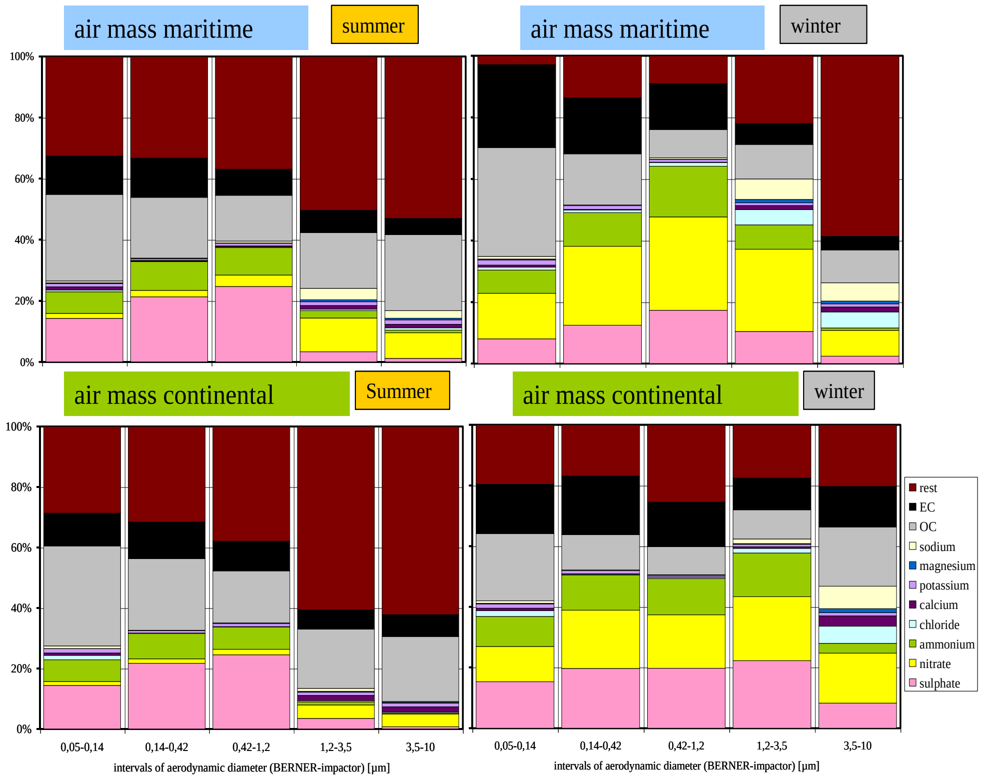

Figure 16 Percentage of mass of water soluble ion mass concentrations, mass concentration for organic carbon (OC) and elemental carbon (EC) and unidentified mass (rest) from the five stages of BERNER type impactor, divided for winter and summer days and air mass transported from East or West. Average values for winters 2004/05 and 2005/06 and summers 2005 and 2006.

The concentrations of organic carbon (OC) and elemental carbon (EC) show the identical behavior to sulfate because they have identical sources – all types of burning processes. The size distribution of EC and OC typically shows highest concentration at stage 3. Notable is the high percentage of OC/EC in the smallest particle which was mainly influenced by local or regional traffic emissions and SOA (secondary organic aerosol) from gas to particle conversion. The relatively high percentage of OC in coarse mode summer samples had the origin in biogenic material. Figure 17 shows the CPI values as a measure for biogenic hydrocarbons.

In summer samples the CPI increases with the size of PM independently from the source region. The small differences have their origin in the traffic which is the influence from the Leipzig-Halle region. CPI from winter samples (near 1) indicates the anthropogenic origin of the alkanes because the biogenic material was clearly only a minor part of the alkanes and most of hydrocarbons were released from domestic heating and traffic.

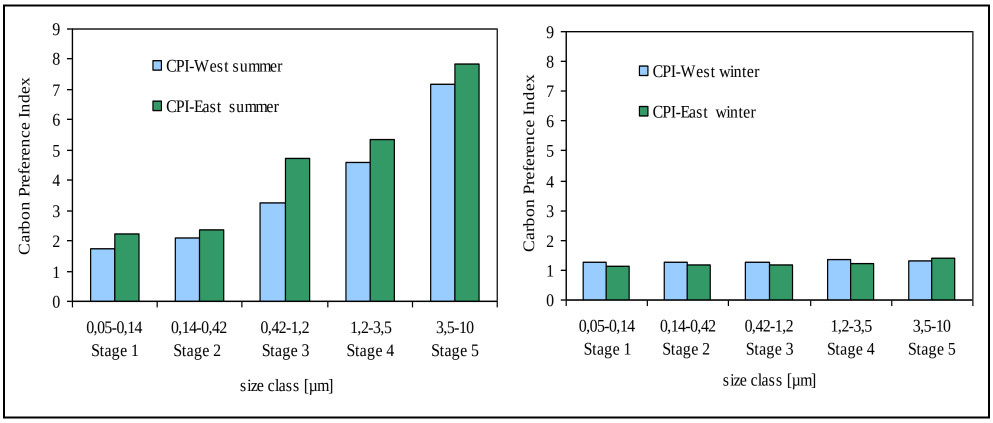

Figure 17 Carbon Preference Indices (CPI) from winter and summer and source regions in the West and in the East.

3.2.4. PM characterization by TDMPS/APS

The TDMPS system measures number size distributions for particle diameters from 3 to 800 nm alternating with and without thermodenuder. The time resolution for one scan is 10 min, thus every 20 min a number size distribution for ambient and non-volatile aerosols is available. Larger particles (0.8 – 10 µm) are measured using an APS but for ambient aerosols only. The diurnal variation of the number size distributions was averaged for days with air mass transport from West and East and for summer- and wintertime. Results are shown in Figure 19. The variation of number size distributions shows significant differences. This was caused by variations in natural and anthropogenic aerosol sources but also in variations in meteorology. Air masses arriving from western directions (continentally and/or maritime influenced) are typically characterized by higher wind speeds and higher chance for precipitation compared to continental air masses coming from the East (continentally influenced). Continental air masses are usually connected with weather conditions dominated by long term high pressure influence without precipitation, higher amplitude of the temperature cycle between day and night and also dry air. Such high pressure systems occur also in wintertime and cause frequently a low mixing layer height during the cold season.

During summer months the measurements show higher concentration of coarse particles due to re-suspension of crustal material from dry areas (compare Chapter 3.2.1. and 3.2.2.). These particles appear within the range of APS measurements (> 800 nm). Concentrations of very small particles (< 10 nm) show on average a maximum around noon time and represents the so-called new particle formation events which occur frequently mainly under influence of solar radiation, i.e. on days with only little cloud coverage. In summer the new particles were measured after a well mixed boundary layer has been developed and the nocturnal inversion has been removed (9:00 – 10:00 CET). Later on the particles grow up to sizes of 100 nm in diameter. This phenomenon has been also observed after the thermodenuder but at smaller diameters meaning the newly formed particles contain some non-volatile material. In air masses from West the number concentration after thermodenuder seems to be decreased significantly, but for continental air masses number concentration if newly formed particles seem to be nearly identical. Since this process is connected with intensity of global radiation it is not clearly recognizable for wintertime. But the general observation that particles after the thermodenuder appear at smaller size is valid for winter and summer and both types of air masses.

In winter sometimes another phenomenon was observed: when the size distribution without thermodenuder was unimodal it was split into two modes after the thermodenuder. The mean plots are not suitable to show this behavior very clearly but it is still recognizable for winter and air mass transport from West. The mean maximum diameter in wintertime is shifted to larger sizes compared to summer months.

Figure 18 shows mean number size distributions averaged over whole days in summer and winter between July 2004 and June 2006 divided into air mass from West and air mass from East. The most significant difference is the higher number concentration in continental air masses at diameters between 50 and 1000 nm. This is the size range where mainly anthropogenic and aged anthropogenic aerosols appear and thus the result indicates that more polluted air was advected from eastern directions. This is in agreement with the results for the high-volume samplers, the TEOM® and the Berner type impactor.

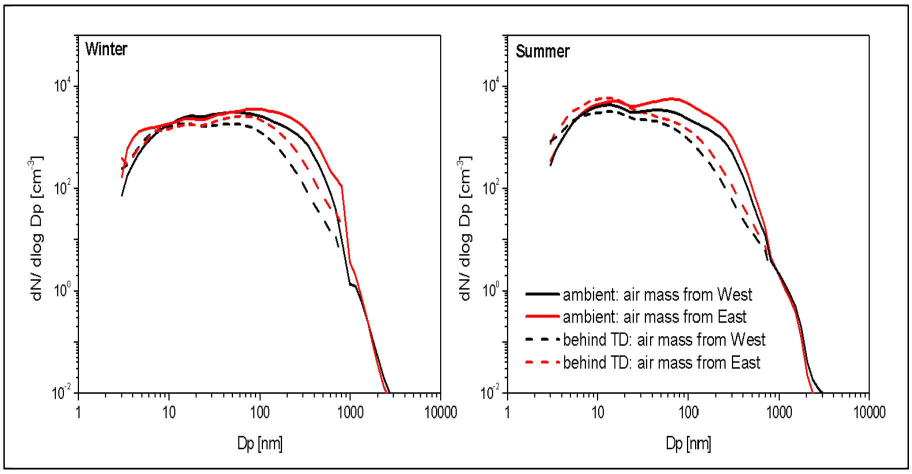

Figure 18 Mean number size distributions averaged for days in summer and winter divided into air mass from West and from East. Means for winters 04/05 and 05/06 and summers 05 and 06.

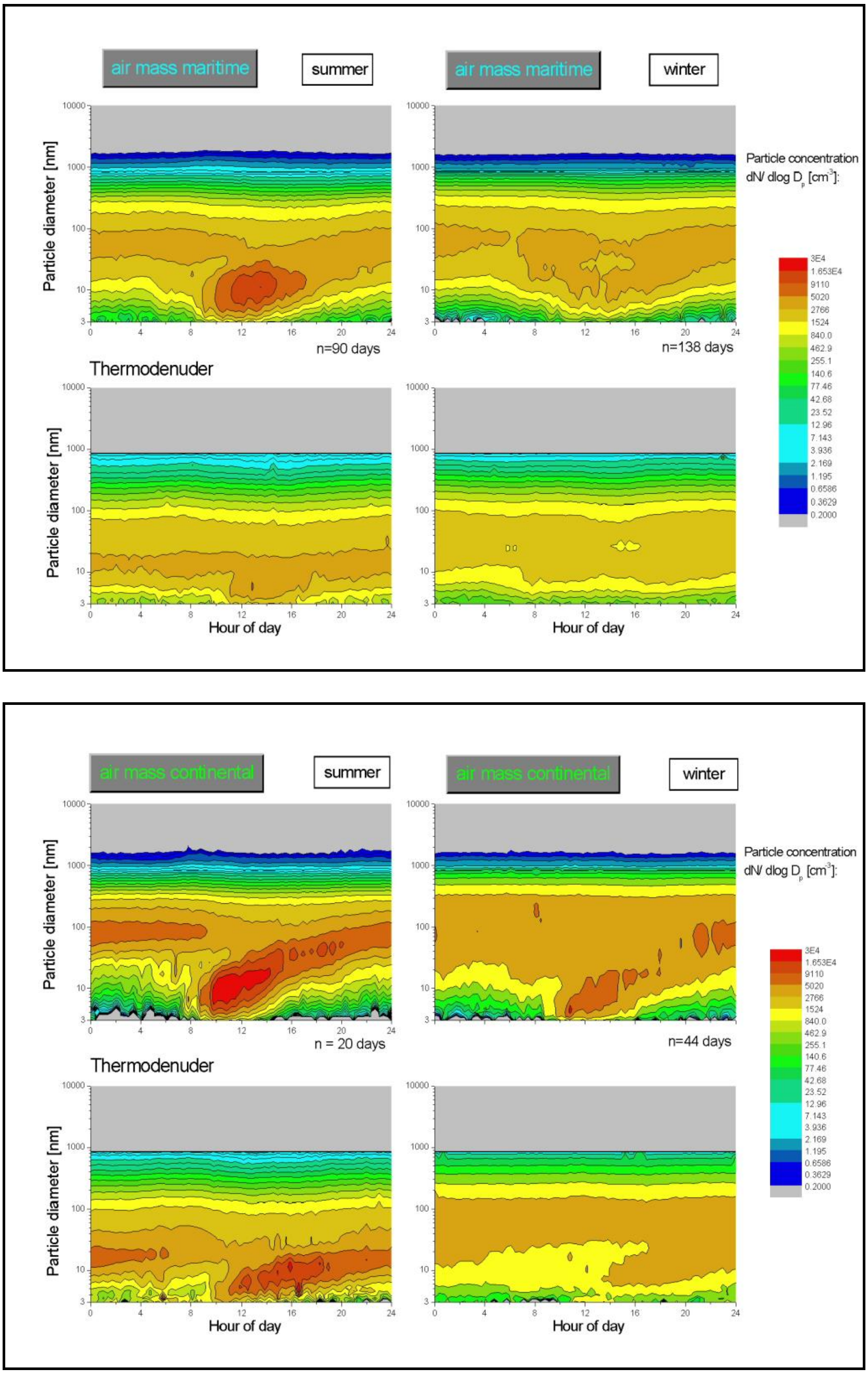

Figure 19 Evolution of number size distributions of ambient aerosols (upper figures) and of non-volatile particle fractions behind the thermodenuder (lower figures) for air mass from West (upper Plot) and air mass from East (lower Plot) divided for summer and winter days. Means for winters 04/05 and 05/06 and summers 05 and 06.

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9 Particulate Matter (PM_{10}) in Ireland

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9.1 Abstract

PM_{10} data for Ireland, for the years 2002 to 2005 are presented here. PM_{10} levels were analysed with respect to annual means, differences between site types, annual variation, and dependency on wind sector and speed.

The PM_{10} annual level increases from rural background (10 μg/m^3), to background suburban (15 μg/m^3), to traffic suburban (19 μg/m^3), to traffic urban (21 μg/m^3), and to kerbside (35 μg/m^3). PM_{10} levels are highest for easterly wind directions, and lowest for westerly directions. Annual variation shows highest PM_{10} levels in March, and lowest levels in June/July.

The $PM_{2.5}/PM_{10}$ ratio usually varied between about 50% and 60%. Thus, $PM_{2.5}$ usually makes up about half or more of PM_{10}, although the annual ratio was 41% for Cork City for the year 2004.

The urban increment for annual PM_{10} levels is about 12 μg/m^3 for traffic urban sites in comparison with rural background sites, and an increment of 14 μg/m^3 for a kerbside location compared to traffic urban sites.

Dublin and Cork traffic urban sites show very similar behaviour both in mean PM_{10} levels, annual variation and in variation of PM_{10} levels with wind direction.

Background sites show high PM_{10} levels of sea salt, with an annual mean of about 6 to 8 μg/m^3 for coastal sites, and 2 μg/m^3 for an inland site. Daily sea salt contributions to PM_{10} for coastal sites showed levels of 38 μg/m^3 and higher.

Currently, the available routine measurement network does not allow for mass closure to be evaluated.

9.2 PM_{10} network data for Ireland

PM_{10} gravimetric data are measured in a network run by the EPA and local authorities. Several types of samplers are used in the Irish PM_{10} network: Partisol 2025, Dichotomous Partisol, Leckel sequential sampler, Opsis SM-200. Filters are weighed before and after exposure. Weighing takes place after equilibration at 20° C and at a relative humidity of 50%.

Two of the presented sites (Kiltrough, Clonmel) are using TEOMs (Tapered Element Oscillating Microbalance) for PM_{10} mass determination; a factor of 1.3 is applied to the raw data. TEOM data shown here include the factor of 1.3. The factor was derived by the EPA Air Quality Monitoring team by operating a TEOM and gravimetric method (Partisol) in parallel at the Rathmines site, Dublin.

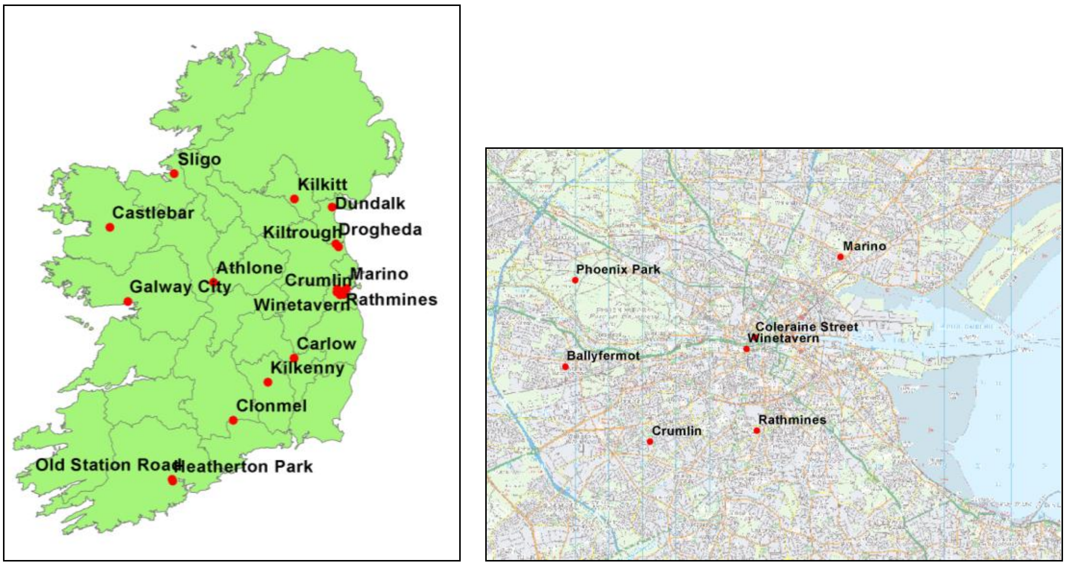

Figure 9.1: Location of the PM_{10} sites in Ireland, and in the Dublin area.

Fixed sites are running continuously, with a sampling time coverage of usually above 90% (Coleraine, OldStation, Winetavern, Marino, Rathmines, Ballyfermot, Heatherton, PhoenixPark, Kiltrough, Castlebar, Kilkitt). Mobile instrumentation is typically deployed for a period of several months (Carlow, Crumlin, Drogheda, Dundalk, Galway, Sligo, Athlone, Clonmel, Kilkenny).

Location of the measurement sites for Ireland are shown in Figure 9.1. Seven of the sites are located in the Dublin area, as shown in Figure 9.1 (right). This study includes a total of 20 sites.

PM_{10} data for the period 2002 to 2005 are presented here. Statistics for 20 sites are summarised in Table 9.1, giving the mean value (for all days with data available in 2002 to 2005), standard deviation, and median, for all sites. Also, the type of instrument deployed at the sites is given, as well as the number of days contributing to the data set. Mobile sites are marked as ‘(mobile)’ in the Table. The Kilkitt site has data available for 2006 only; it is a rural background site, and is therefore included here.

Table 9.1: Site statistics for all daily PM10 values available in the years 2002 to 2005.

Site	Type of instrument/site	Mean±std, all days	Median	Days of data
Traffic urban				
Coleraine (Dublin)	Partisol	22.3±15.6	18.1	1321
OldStation (Cork)	Dichot. Partisol	22.6±13.1	18.8	1323
Winetavern (Dublin)	Partisol	22.0±13.8	18.5	1350
Traffic suburban				
Carlow	Opsis (mobile)	16.7±10.3	14.6	142
Crumlin (Dublin)	Opsis (mobile)	20.8±13.6	16.7	262
Drogheda	Opsis (mobile)	32.4±15.1	30.1	100
Dundalk	Opsis (mobile)	20.1±10.8	17.4	107
Galway	Opsis (mobile)	23.4±11.2	21.0	191
Marino (Dublin)	Partisol	17.7±13.7	13.6	1137
Rathmines (Dublin)	Partisol	19.0±13.6	15.1	1341
Sligo	Opsis (mobile)	17.7±12.0	14.2	184
Industrial rural				
Kiltrough (TEOM)	TEOM	16.7±6.5	15.3	691
Background suburban				
Athlone	Opsis (mobile)	21.4±17.9	15.1	159
Ballyfermot (Dublin)	Partisol	15.2±10.8	12.5	782
Castlebar	Leckel	15.5±9.6	13.5	169
Clonmel	TEOM (mobile)	20.2±8.7	18.1	204
Heatherton (Cork)	Partisol	19.6±10.4	17.5	1186
Kilkenny	Opsis (mobile)	12.8±8.2	10.8	147
PhoenixPark (Dublin)	Partisol	13.2±12.2	10.2	1213
Background rural				
Kilkitt (2006)	Partisol	10.2±9.8	7.7	260

9.3 Annual PM_{10} averages

Annual PM_{10} averages were calculated for each year and for each station. Some stations have data available for each of the four years, whereas other sites were operated for a few months only and contribute only one average. This yields a total of 45 annual averages for the 20 sites. A summary is shown in Table 9.2.

There is a clear gradient between the types of sites, i.e. background suburban site data display the lowest concentrations of PM_{10} while the highest concentrations were recorded at the urban traffic sites. The range within one category is broad at about 9 $\mu g/m^3$ (traffic suburban includes one outlier, Drogheda 2002 with 32.4 $\mu g/m^3$). An overview of the annual mean values for different site types is given in Table 9.2. Also included are a Dublin kerbside site, and a rural background site, from a study by Jennings et al. (2006), based on measurements in 2002. Figure 9.2 shows annual averages for those stations that have data available for at least three of the four years (2002 to 2005).

Table 9.2: Annual PM_{10} means for the PM_{10} sites in Ireland.

Site	Range of annual means (µg/m^3), and number	Median of annual means (µg/m^3)
Dublin kerbside	35.4 (1)	35.4
Traffic urban	19.2 – 28.4 (12)	21.3
Traffic suburban	14.3 – 32.4 (15)	19.0
Industrial rural	16.7 – 16.8 (2)	16.7
Background suburban	12.1 – 21.4 (15)	15.5
Rural background	10.2 – 10.5 (2)	10.4

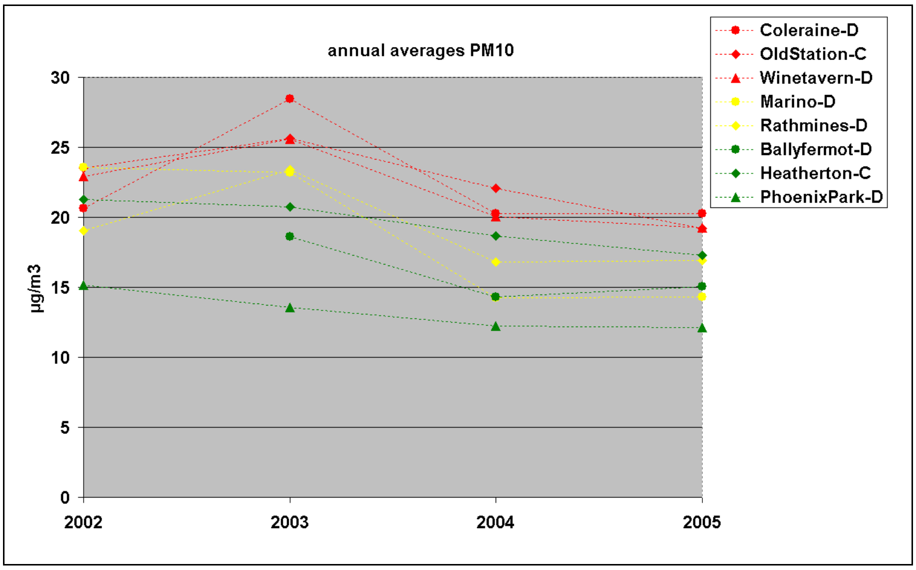

Figure 9.2: Annual averages for sites with at least three of the four years 2002 to 2005.

9.4 Dependence of PM_{10} levels on wind direction/sector

The PM_{10} data from Dublin sites and Kiltrough were averaged for wind direction sectors (eight sectors, multiples of 45 degrees; e.g. 45±22.5), for those sites with at least two years of data available in the 2002 to 2005 period. The plots for individual stations can have different number of daily data feeding into the wind direction distribution. Wind direction is based on Dublin airport wind data for all sites. The data is shown in Figure 9.3.

For comparison, a coastal site is included, from the study by Jennings et al. (2006). The coastal site is located about 40 km south of Dublin. Samples were taken every other day. Data shown for the coastal site is for 2002.

The sites shown in Figure 9.3 have between 1186 and 1350 daily values contributing to the distribution (except for Ballyfermot with 782 days, Kiltrough with 691 days, and the coastal site with 162 days – these sites are shown with dotted lines). The sites are situated in the Dublin area (except for Kiltrough, ca. 50 km north of Dublin, and a coastal site, about 40 km south of Dublin).

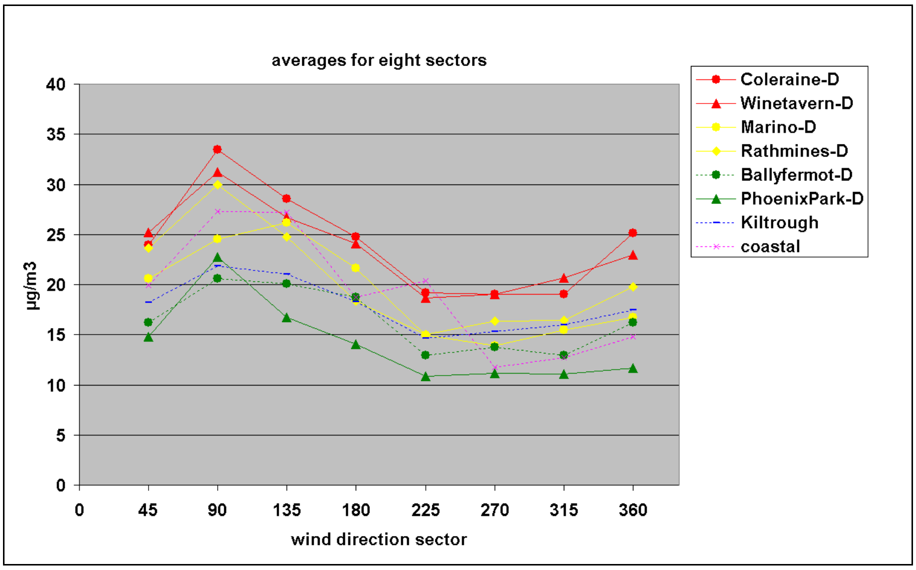

Figure 9.3: PM_{10} levels depending on wind direction, for eight sectors.

Highest mean values are observed for easterly wind directions, whereas lowest values are observed for westerly directions. This is considered to indicate that, on average, during easterly conditions the background PM_{10} level is increased due to transboundary air pollution contributions. Different meteorological conditions associated with easterly wind directions could also contribute to the effect.

In the years 2002 to 2005, wind at Dublin airport was in the easterly sector (90±22.5 degrees) for 122 days, which accounts to about 8% of days, whereas it was in the westerly sector (270±22.5 degrees) for 355 days, which is equivalent to about 24%.

9.5 Dependence of PM_{10} levels on wind speed

PM_{10} levels for Dublin sites were analysed for wind speed dependency, with wind speed measured at Dublin Airport. There is no clear correlation between wind speed and PM_{10} levels. Low levels are observed at any wind speed. High PM_{10} levels (above 50 $\mu g/m^3$) are observed mostly for low wind speeds (e.g. below 10 knots). This indicates that any PM_{10} increasing effect of high wind speeds, e.g. particle resuspension, is offset by increased dilution at high wind speeds.

PM_{10} levels were analysed with respect to wind direction sectors: for easterly winds (wind direction = 90±22.5 degrees) and westerly winds (wind direction = 270±22.5 degrees), and for four wind speed sectors: wind speed <7 knots, wind speed 7 to 10 knots, 10 to 14 knots, and >14 knots. For low wind speeds, less than 7 knots, the mean PM_{10} levels are similar, whereas for higher wind speed sectors, mean PM_{10} levels are lower for the westerly wind direction. The comparison is shown in Figure 9.4.

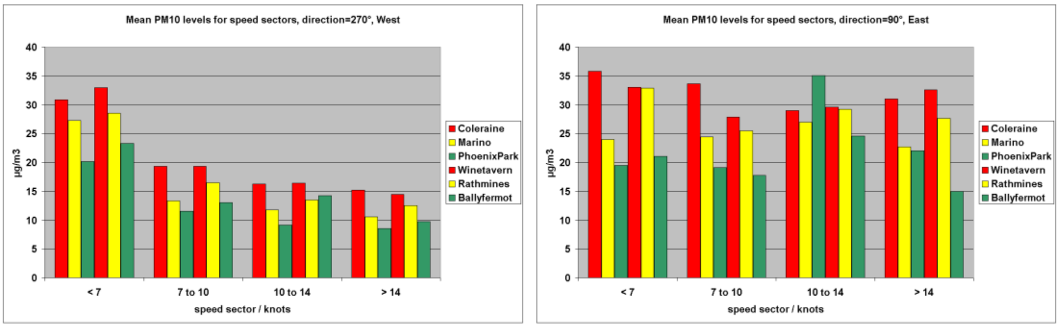

Figure 9.4: PM_{10} concentration for westerly and easterly wind directions and four wind speed sectors

The data in Figure 9.4 for the westerly wind sector is based on about 40 to 50 days for wind speeds below 7 knots, 70 to 90 days for 7-10 knots, 90 to 100 days for 10-14 knots, and 80 to 90 days for >14 knots. For easterly winds, the data include about 40 to 50 days for wind speeds below 7 knots, about 24 days for 7-10 knots, about 20 days for 10-14 knots, and 10 days for wind speeds >14 knots. The exact number of days contributing to the statistics depends on the individual sites. For Ballyfermot, the number of days is about half of the number for other sites.

9.6 Seasonal variation of PM_{10}

The sites with data available for at least two of the years 2002 to 2005 were used to calculate monthly means. Means were calculated averaging over all daily values available for a specific site for a specific month, for all four years (2002 to 2005) combined. Results are shown in Figure 9.5. Highest PM_{10} levels were found in spring (February to April), with the maximum in March. Both Dublin and Cork show very similar annual variation.

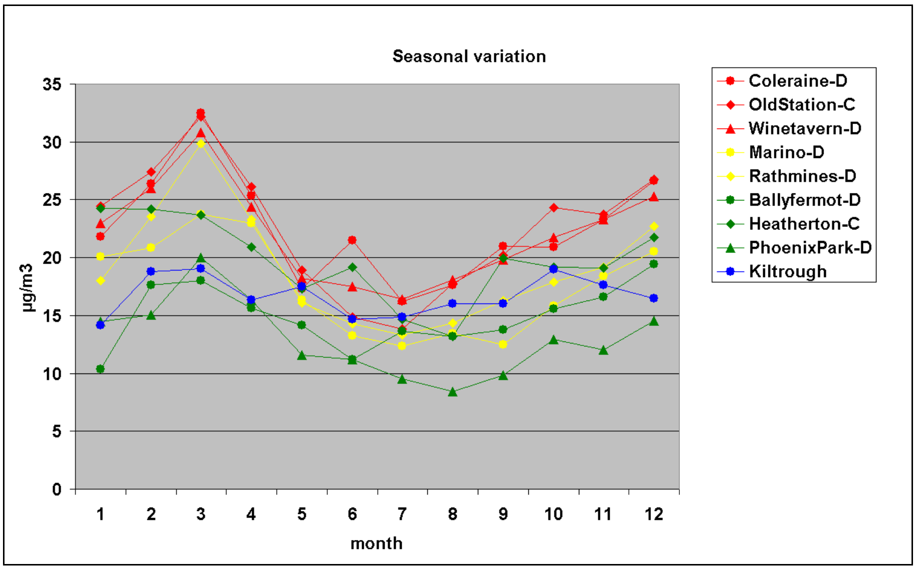

Figure 9.5: Seasonal variation of PM_{10} concentration.

9.7 $PM_{2.5}/PM_{10}$ ratios

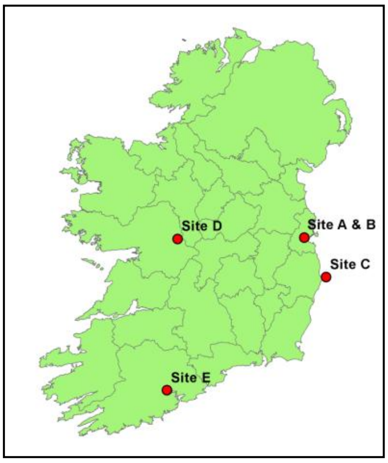

Figure 9.6: Sites used in 2002 for the study by Jennings et al. (2006).

Currently, OldStationRoad in Cork is the only site in Ireland routinely measuring $PM_{2.5}$ and PM_{10}. The ratio between annual $PM_{2.5}$ and annual PM_{10} averages ranges from 0.4 to about 0.6 in the years 2002 to 2005. Usually, $PM_{2.5}$ contributes half or more to PM_{10} levels.

A study by Jennings et al. (2006a) measured $PM_{2.5}/PM_{10}$ ratios at several sites in Ireland from July 2001 to December 2002. The location of the sites is shown in Figure 6. Sites included a kerbside site (A), an urban traffic site in Dublin (B) and Cork (E), a coastal site (C), and a rural background site (D). $PM_{2.5}/PM_{10}$ ratios were found to be between 40% and 60%.

Both the results from OldStationRoad in Cork and from the aforementioned study (for 2002) are summarised in Table 9.3.

Table 9.3: $PM_{2.5}/PM_{10}$ ratios.

Annual means, µg/m^3	PM_{10}	$PM_{2.5}$	$PM_{2.5}/PM_{10}$
OldStation 2002	23.5	12.3	52%
OldStation 2003	25.6	13.8	54%
OldStation 2004	22.1	9.0	41%
OldStation 2005	19.2	11.0	57%
Annual means 2002, µg/m^3	PM_{10}	$PM_{2.5}$	$PM_{2.5}/PM_{10}$
Dublin kerbside (A)	35.4	21.5	61%
Dublin (B)/Cork City (E)	21.5/23.9	11.5/12.6	53%/53%
Coastal site (C)	19.9	8.0	40%
Rural background (D)	10.5	6.3	60%

9.8 Urban increment

There are very few background measurements from which to derive an urban increment. Based on the campaign carried out by Jennings et al. (2006a) in 2001 and 2002, the urban increment of the annual mean is about 11 to 13 µg/m^3, for urban traffic sites as compared to a rural background site. For $PM_{2.5}$, the increment is about 5 to 6 µg/m^3. The annual mean for the Dublin kerbside site shows an additional increment over the Dublin traffic site of 14 µg/m^3 for PM_{10}, and 10 µg/m^3 for $PM_{2.5}$.

9.9 PM_{10} chemistry and sea salt

At three background air quality monitoring sites (EMEP sites), in Malin Head, Carnsore Point, and Oak Park, PM_{10} is collected on filters, using digitel DHA-80 high volume samplers, at a flow rate of 500 lpm (720 m^3/day), one filter a day. Filters are analysed in MetEireann laboratories. These sites provide PM_{10} chemistry data. Data are available starting in January 2005 for Malin Head and Oak Park, and starting in May 2005 for Carnsore Point. 2006 data cover the period until September. Annual means for sulphate, nitrate, and non-sea-salt sulphate are shown in Table 9.4.

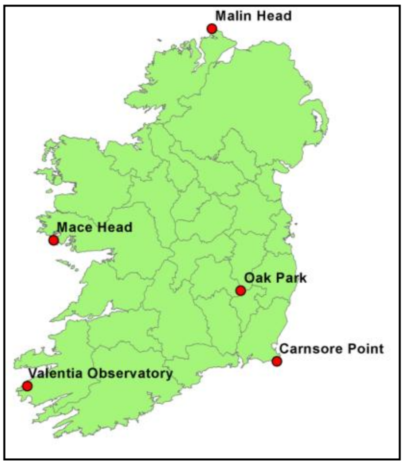

Figure 9.7: EMEP sites measuring PM_{10} chemical compounds.

Table 9.4: Chemical compounds in PM_{10} in 2005 and 2006, annual mean values.

Site	2005			2006		
	(µg/m^3)			(µg/m^3)		
	SO_4	NO_3	nss SO_4	SO_4	NO_3	nss SO_4
Malin Head	1.4	1.2	0.9	1.7	1.1	1.1
Oak Park	1.3	1.4	1.2	1.7	1.6	1.5
Carnsore Point	2.1	1.7	1.4	2.4	1.8	1.6

Sea-salt is a major contribution to PM_{10} levels in Ireland. Sea-salt contribution to PM_{10} is high at coastal sites (Malin Head, Carnsore Point) at about 6 to 8 µg/m^3 as an annual mean. The inland site Oak Park still shows about 2 µg/m^3. Daily values for sea -salt contribution to PM_{10} were up to 38 µg/m^3 and higher. Results are summarised in Table 9.5. Also added are sea-salt concentrations measured at Valentia Observatory, with EMEP filter packs (no PM_{10} cut off), and Mace Head (no PM_{10} cut off). Sea -salt is calculated as 2.54*Na.

Data from Mace Head is based on samples taken from 1988 to 1994 during the AEROCE campaign, co-ordinated by Joe Prospero (University of Miami). Samples were taken unsectored and for clean marine sector only. The sampler did not have a PM_{10} cut off. Sea salt contribution to TSP in the clean sector was above 30 µg/m^3 for about 7.5% of the time, and above 40 µg/m^3 for about 2.5% of the time.

A study at Mace Head by Jennings et al. (2006b) found a strong seasonal variation of sea salt contribution to TSP. For 2003, the average sea salt level in TSP for the clean sector in summer (June/July/August) was 7.3 µg/m^3, whereas in winter (December/ January/February) it was 22.5 µg/m^3.

Table 9.5: Sea salt concentration in PM_{10} 2005 and 2006 (for Valentia and Mace Head for total PM).

Site	2005			2006		
	(µg/m^3)			(µg/m^3)		
	mean ± std	median	max	mean ± std	median	max
Malin Head	6.2 ± 5.5	4.9	29	6.0 ± 4.3	4.9	24.6
Oak Park	1.8 ± 1.5	1.4	10.3	2.3 ± 1.7	1.9	8.2
Carnsore Point	7.3 ± 6.2	5.5	38	8.3 ± 6.9	5.7	39
Valentia Obs.	4.4 ± 4.4	2.9	34	5.3 ± 4.5	3.9	24
	1988-1994, clean marine					
Mace Head	14.5 ± 12	12.4				

9.10 Data sources

Data in this report are taken from four different sources:

1. The air quality monitoring network, run by EPA and local authorities; data shown here is for 2002 to 2005.
2. Three EMEP sites (Oak Park, Malin Head, Carnsore Point) monitoring PM_{10} chemistry, for 2005 and 2006.
3. A study carried out by NUI Galway in 2002 (S.G. Jennings et al., 2006a).
4. Data from Valentia Observatory (operated by MetEireann) and Mace Head (operated by NUI Galway; S.G. Jennings et al., 2006b).

9.11 References

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S.G. Jennings, D. Ceburnis, B.M. Kelly, T.G. Spain, D.L. Savoie; Study of the composition, sources and radiative properties of aerosols at a west coast location; Final Report (2006b); Environmental Protection Agency, Ireland.

10 EMEP – PM assessment report, National contribution of Italy

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10.1 PM monitoring network in Italy

The Italian network for PM monitoring in ambient air is composed of more than 200 stations managed by regional and local administrations. Some of them are used in order to implement Council Decision 97/107/EC, as amended by Council Decision 2001/752/EC, establishing a reciprocal Exchange of Information (EoI) and data from networks and individual stations measuring ambient air pollution within the Member States. In 2005, according to EoI data, the PM stations were distributed in 17 out of the 20 administrative regions of the national territory and they were 133 stations in Northern Italy, 25 in Central Italy and 78 in the South. The distribution of the PM_{10} stations over the Italian territory in 2005 is depicted in Figure 10.1; it shows that many stations are used for the determination of hot spots levels and are directly influenced by traffic and industrial emission sources.

UT: uban traffic;

UB: urban background,

UI: urban industrial;

ST: suburban traffic;

SB: suburban background;

SI: suburban industrial;

RB: rural background;

RI: rural industrial;

n.d.: not determined.

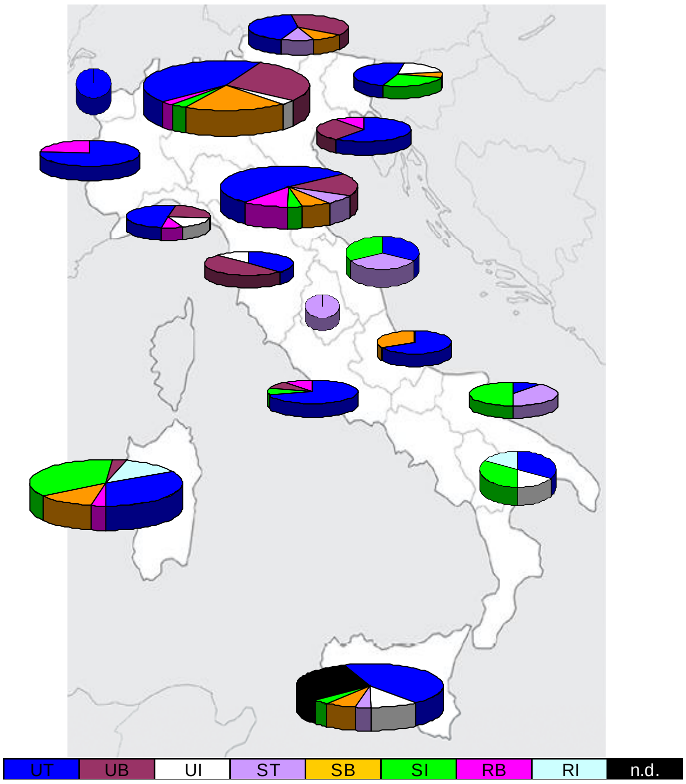


Figure 10.1: PM_{10} monitoring network in Italy (data source: Apat, ARPA, Regions and Autonomous Provinces).

The monitoring network includes also 12 $PM_{2,5}$ stations (in 2005, there were 10 stations in Northern and 2 in Central Italy). Measurements of other PM fractions are sparse and generally carried out in the framework of research projects.

The classification of the 170 PM_{10} stations participating to the EoI (Exchange of Information) network during 2004 is reported in Figure 10.2, as far as the annual mean concentration (left graph) and number of exceedances of the daily limit value (right graph) are concerned. The limit value of 40 µg/m^3 (as yearly average) was exceeded in 28% of the stations; only 30% of the stations exceeded the daily limit value of 50 µg/m^3 less than 35 times, as stated by the EU Directive, while a number of exceedances between 35 and 70 was recorded in another 31% of the stations, 25% of the stations recorded a number of exceedances between 70 and 105 and 13% of the stations experienced a number of exceedances higher than 105.

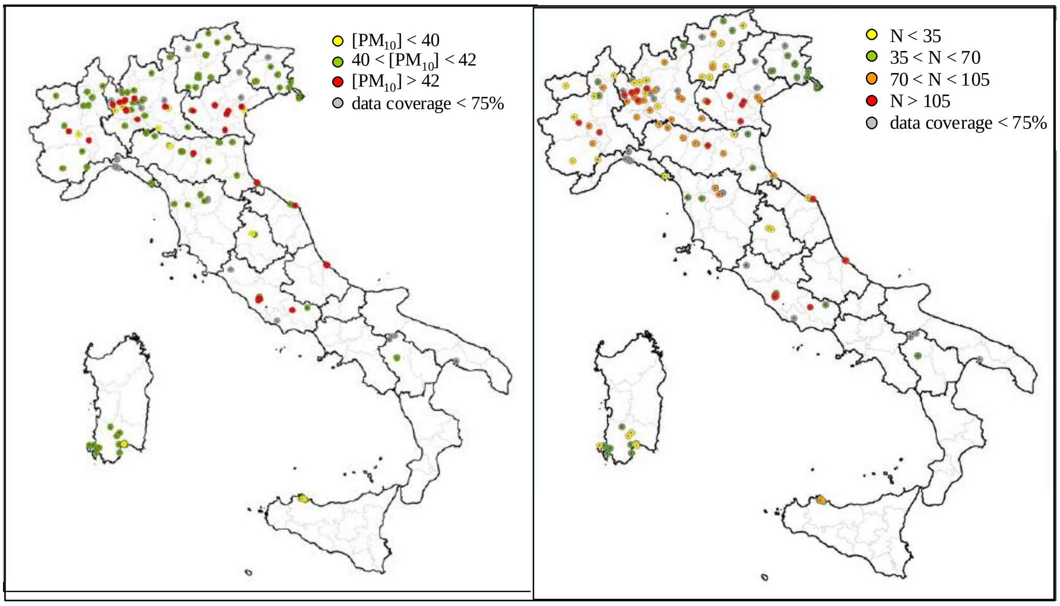


Figure 10.2: Classification of PM_{10} stations according to the annual mean concentration (left graph) and to the number of exceedances of the daily EU limit value (right graph). Year: 2004. Data source: APAT, 2006.

The temporal pattern of PM_{10} in some major Italian cities during the period 2000–2006, reported in Figure 10.3, does not show any relevant concentration decrease, specially as far as the background stations in Rome and Milan are concerned. All data, with the exception of the urban background station in Rome, sited inside the major green area of the city, exceed the annual EU limit value of 40 µg/m^3. The traffic station in Bologna seems to show a downward pattern but all the trends need to be confirmed by further data, since any variation in the air quality may be easily masked by the inter-annual variations of the meteorological situation, which play a major role in determining pollution dispersion (see the similarity between the patterns of the traffic stations in Milan and Bologna, both sited in Northern Italy).

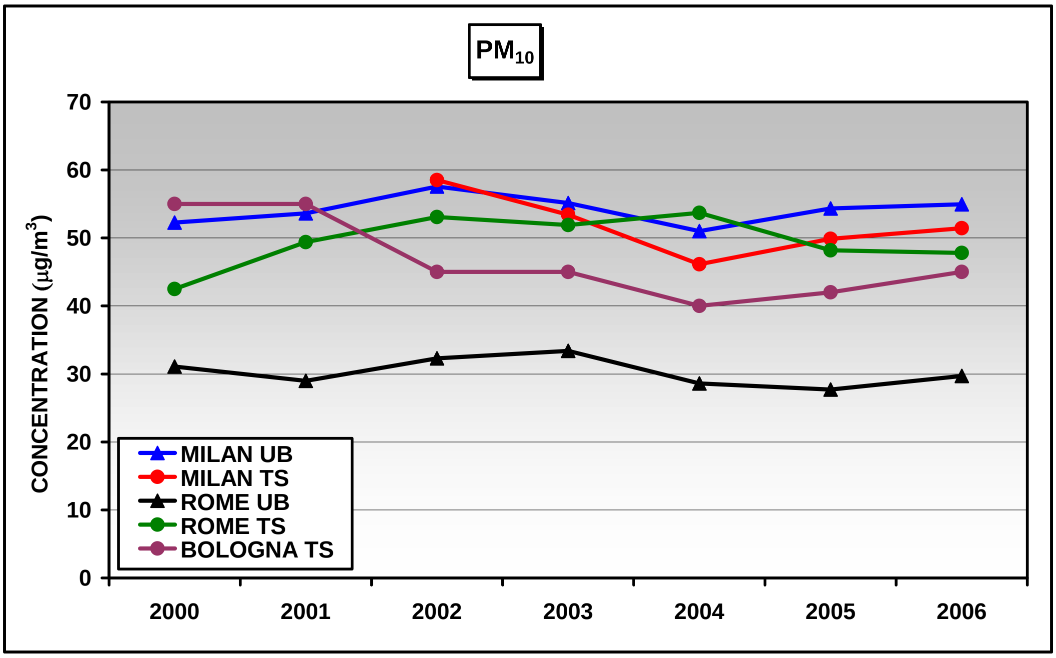


Figure 10.3: Inter-annual variations of the PM$_{10}$ concentration in Milan, Rome and Bologna. UB: urban background station; UT: traffic station. Data source: APAT, regional ARPAs.

The frequency distribution of PM$_{10}$ at a traffic station in Milan (north), Rome (center) and Palermo (Sicily, south) are shown in Figure 10.4 (upper graph), together with the frequency distribution at the background station and a traffic station in Rome and at the semi-rural station of Montelibretti, 25 km from the city (lower graph). These data show that concentration values from the semi-rural and urban background stations seem to be mainly grouped in one mode, while the traffic stations in Milan and in Rome shows a three-mode pattern. At the traffic station in the south of Italy the second and third mode are much less pronounced. The distribution at the urban background station and the semi-rural station in the area of Rome are almost identical.

For the case of Rome, the concentration increment during 2005 between the regional background station and the semi-rural station was about 6 µg/m^3 (22 and 28 µg/m^3, respectively), there was no perceptible difference between the semi-rural and the urban background station, and the increment between the urban background and the traffic station was of the order of 20 µg/m^3.

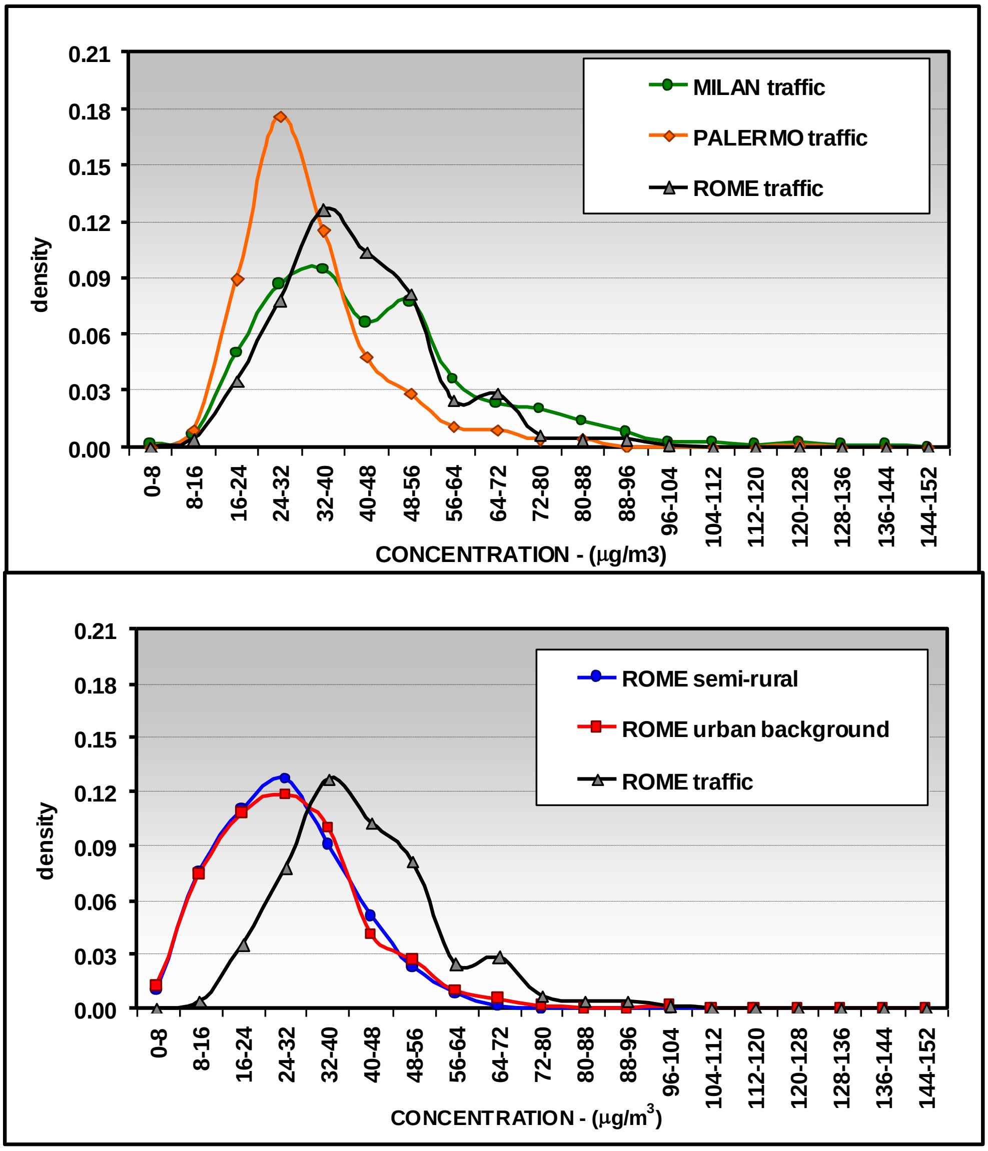


Figure 10.4: Frequency distribution of PM_{10} at Milan, Rome and Palermo traffic stations (upper graph) and at semi-rural, urban background and traffic stations in the area of Rome (year 2003).

For the case of the Emilia Romagna region, located in Northern Italy (Po valley), the increment in PM_{10} concentration between rural stations and traffic stations during the period 2004–2006 was of the order of 15–20 µg/m^3, with small variations dependent on the year and location. It is interesting to note that the increment is recorded almost only during the winter period: the data of 2004 reported in Figure 10.5, which refer to the cities of Bologna and Parma, both sited in the Emilia Romagna region, show that PM_{10} concentration at the rural stations does not show any significant variation during the year, while at the traffic stations PM_{10} concentration during the wintertime can be also twice as much as the summer values.

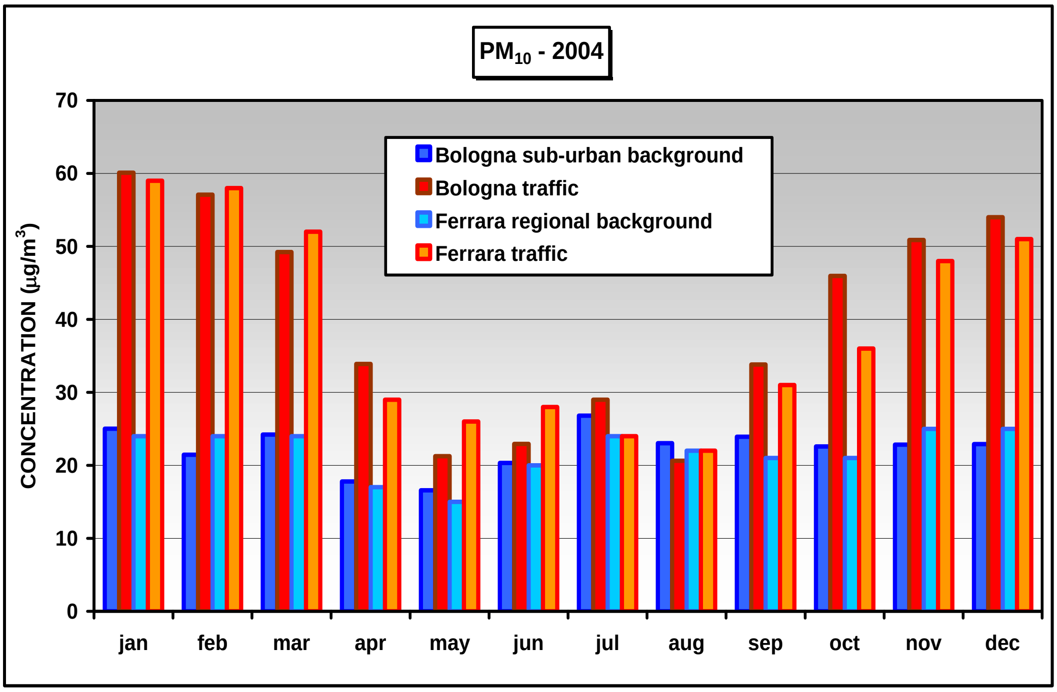


Figure 10.5: Monthly variation of PM_{10} concentration during 2004 at a traffic station and a sub-urban background station in Bologna (Porta S. Felice and Monte Cuccolino), at a traffic station in Ferrara (C. Isonzo) and at a regional background station in the area of Ferrara (Gherardi). Data source: ARPAER.

The seasonal variations of PM_{10} during the year 2005 at traffic sites of many Italian cities are reported in Figure 10.6. In this case, the situation is very different when moving from the north towards the south of Italy. In areas sited inland of Northern and Central Italy PM_{10} concentration shows a concave seasonal pattern, with distinctly higher values during the winter periods (A, B, D, F). This pattern is mainly due to the prevalence of stability conditions during the cold months, which cause a sharp and significant increase of PM concentration. In coastal area of Northern Italy (C, E), where the stability is mitigated by the presence of the sea, this pattern is smoothed.

In Central Italy, coastal cities (G, H) show lower values during the cold season with respect to inland northern areas, but the warmer and drier climate causes higher summer values due to photochemical smog formation and particulate re-suspension. As a consequence, the pattern of PM_{10} shows a nearly flat appearance. In Southern cities (I, L, M) these last phenomena prevail with respect to the wintertime stability and the seasonal pattern of PM_{10} concentration shows a convex appearance.

Figure 10.6: Seasonal variation of PM_{10} at urban traffic stations of different Italian cities during 2005. Maximum PM_{10} concentration is 100 $\mu g/m^3$ in all graphs. A: Torino Consolata; B: Milano Verziere; C: Gorizia; D: Bologna S Felice; E: Genova Europa; F: Prato Po Roma; G: Pescara Grue; H: Roma Arenula; I: Potenza Firenze; L: Cagliari La Plaja; M: Palermo Indipendenza.

The average daily variation of PM_{10} at four urban stations (one traffic and one urban background station in Milan and in Rome) during the winter of 2003 (January, February and December) is reported in Figure 10.7. The pattern shows two periods when PM concentration increases: during the night, because of the unfavourable dispersion conditions, and during the late morning. A similar, less pronounced, trend is shown during the rest of the year.

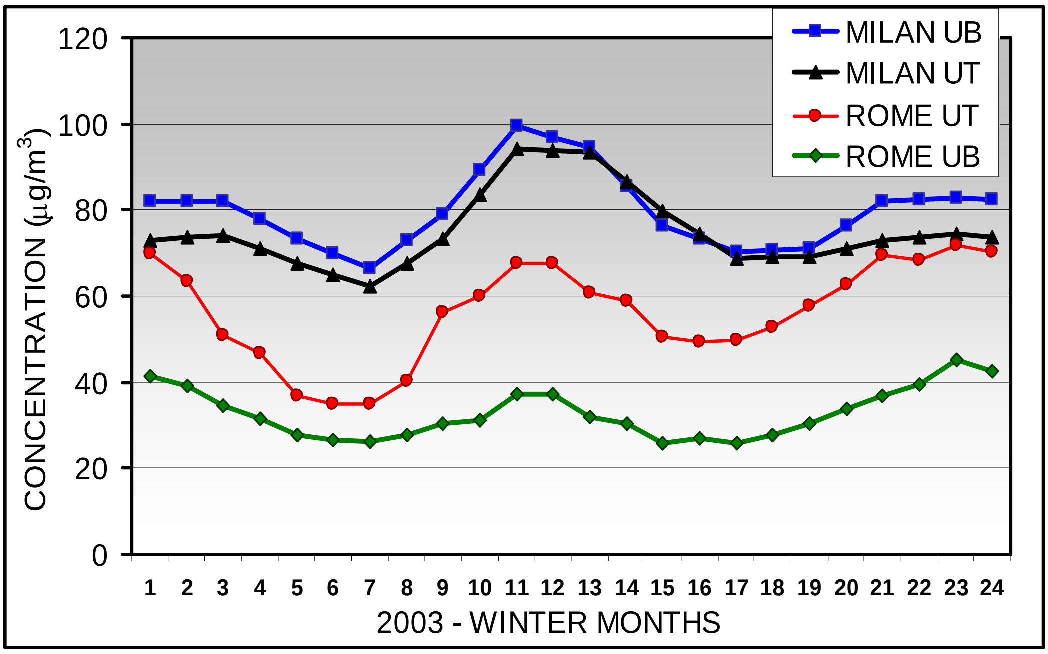


Figure 10.7: Average diurnal variation of PM_{10} concentration during the wintertime.

From the above overview it results that PM_{10} concentrations in urban areas of Italy are generally higher than the EU limits, in terms of both annual and daily average. Daily exceedances are mainly recorded during the winter season, due to poor atmospheric dispersion conditions (ground-based inversions), but in the peninsular area they are also not infrequent during the spring, due to Saharan dust episodes, and during the summer, due to photochemical smog formation. At most sites, no significant yearly time variations are observed for PM_{10} during the last few years, but more observation are needed to get sound conclusions about mid-term PM trend. Diurnal variation of PM hourly concentration, as well as day-to-day variations, are linked to the meteorological situation, and especially to the mixing properties of the lower boundary layer, which are the main factor influencing the concentration of pollutants.

Regional background pollution accounts for more than half of the urban PM concentration, indicating a major role of secondary compounds (see Chapter 6.3).

10.2 Sources of PM

In 2003, total PM emissions in Italy have been calculated to be 172.7 tons. Ten years before, in 1993, they were 242.5 tons and this noticeable decrease is mainly due to improvements in the sectors of energy production (from 42.8 to 7.7 tons), industry (from 56.7 to 46.1 tons) and forest and agriculture (from 27.3 to 15.9 tons). The per cent decrease in the transport sector is lower, but this sector accounts for about one half of the total PM emission and also a smaller reduction (from 100.9 to 84.5 tons) may have a relevant impact on the environment. The residential heating sector shows, instead, an increase from 14.6 to 18.5 tons, mainly due to an increase in consumptions. The emission reduction in the sector of energy production is due to the enforcement of the legislative decree about the emission limits in power plants, to the use of better fuels and improved abatement technologies. The reduction in the transport sector is due to the enforcement of the EU Directives about car emissions and about fuels.

The per cent distribution of PM emissions in 2003 is shown in Figure 10.8. They are dominated by the transport sector, mainly road transport.

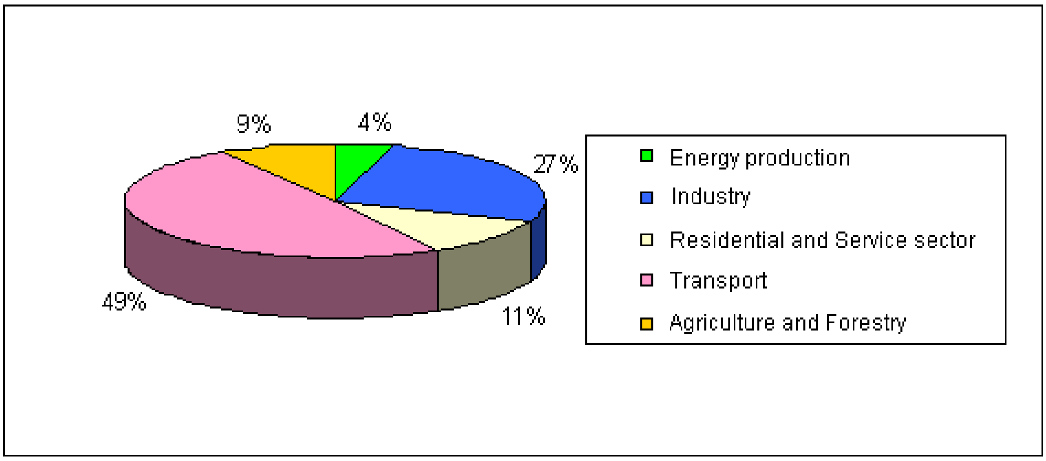


Figure 10.8: Per cent distribution of primary PM emission in 2003 (total amount: 172.7 tons). Data source: APAT.

It is worth stressing that this inventory takes into account only primary emissions, and that locally generated and long-range transported secondary particles, (not included in the inventory) accounts for a very relevant fraction of PM concentration, generally more than 50% at regional background, semi-rural and urban background stations (for the case of Rome and the Lazio region, see chapters 3 and 4). Also, the evaluation of non-exhaust road emission needs a more precise estimation, to be obtained in further source apportionment studies.

10.3 PM composition in the Lazio region

The first comprehensive picture of the chemical composition of PM_{10} and $PM_{2.5}$ in the Lazio region (Central Italy) has been determined in the framework of a research project carried out between October 2004 and July 2005 and aimed to determine the frequency and quantitative relevance of PM natural events. The measurements have been carried out at six stations, having characteristics of traffic, urban background, semi-rural and regional background stations. The method provides the daily collection of PM_{10} and $PM_{2.5}$ fractions on both Teflon and quartz filter membranes and the determination of their mass concentration, on Teflon filters, by the beta attenuation method. After the sampling, quartz filter are analysed for their elemental carbon and organic carbon content (EC/OC) by means of a thermo-optical analyser. Teflon filters are analysed for their metal content (Al, Si, Fe, Mg, Ca, Ti, S) by energy-dispersion X-ray fluorescence, then extracted in a water solution and analysed for their anionic (Cl^-, NO_3^-, $SO_4^=$) and cationic (Na^+, $NH4^+$, K^+, Mg^{++} Ca^{++}) content by ion chromatography. By following this procedure, the components of PM typically accounting for more than 1% of the total mass can be identified and quantified and a general picture of the aerosol composition obtained (Perrino et al., 2006).

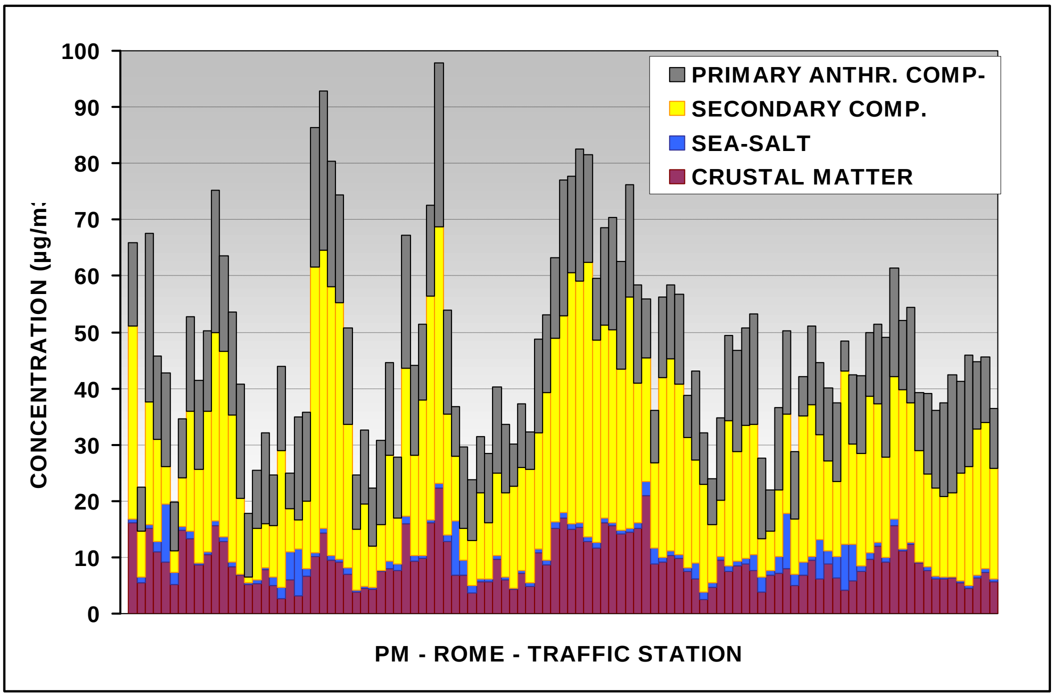


Figure 10.9: Chemical composition of PM_{10} during October 2004 – July 2005 at a traffic station in Rome.

The main chemical components of PM (ions, metals and EC/OC) have been grouped into four classes: crustal matter (calculated as the sum of Al, Si, Fe, K, Ca, Mg and Na oxides - Chan et al., 1997), sea-salt aerosol (calculated from Na^+ and Cl^-), primary anthropogenic pollutants (calculated as EC plus an equivalent amount of OC – Viidanoja et al., 2002) and secondary compounds. These have been calculated as the sum of nitrate, sulphate, ammonium and the remaining amount of OC multiplied by a factor that takes into account the non-carbon content of organic molecules; this factor ranges from 1.6 in traffic locations to 2.1 in background sites (Turpin and Lim, 2001). A typical time pattern of the mass concentration of the four groups of components at a traffic station in Rome (140 selected days between October 2004 and July 2005), showing the predominance of secondary compounds, is reported in Figure 10.9. Comparison with gravimetrically determined mass concentration shows that at all stations the chemical speciation accounted for more than 90% of the collected mass.

The per cent composition of PM_{10} at a traffic station in Rome, the urban background station in Rome, the semi-rural EMEP site of Montelibretti and the regional background station is reported in Figure 10.10 (average of the same days of Figure 10.9). The data show that the percentage of secondary compounds increases from 46% to 59%, 63% and 77% when moving from the traffic to the urban background, the semi-rural, the regional background station; the percentage of primary anthropogenic compounds, instead, decrease when going away from the urban traffic area (31%, 16%, 11% and 6% at the traffic, urban background, semi-rural and regional background station, respectively).

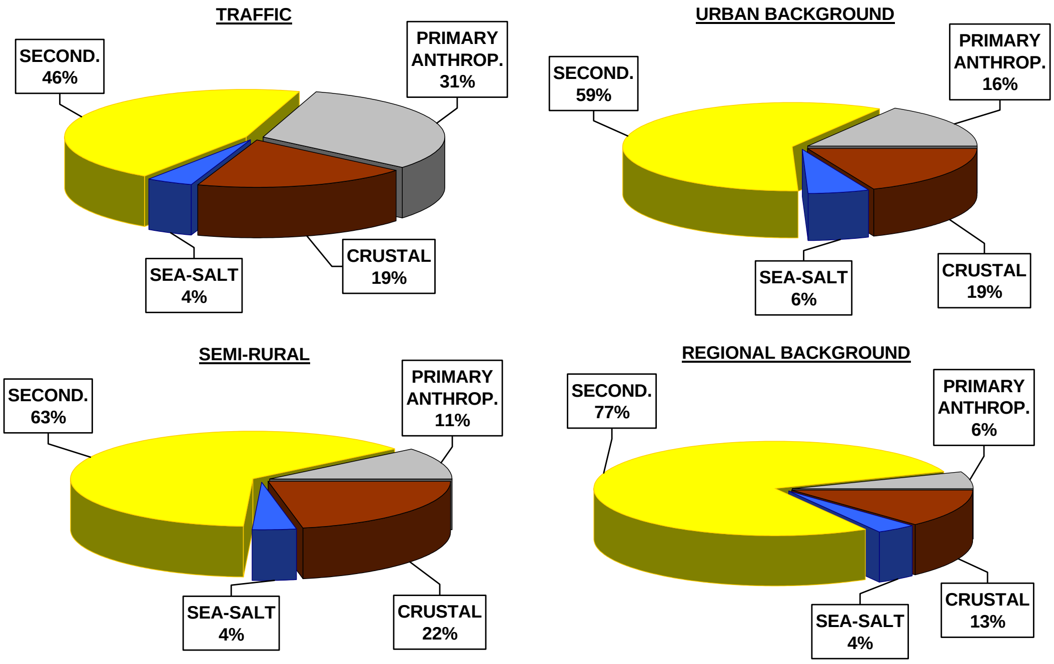


Figure 10.10:Per cent chemical composition of PM_{10} during October 2004 – July 2005 at four stations in the Lazio region.

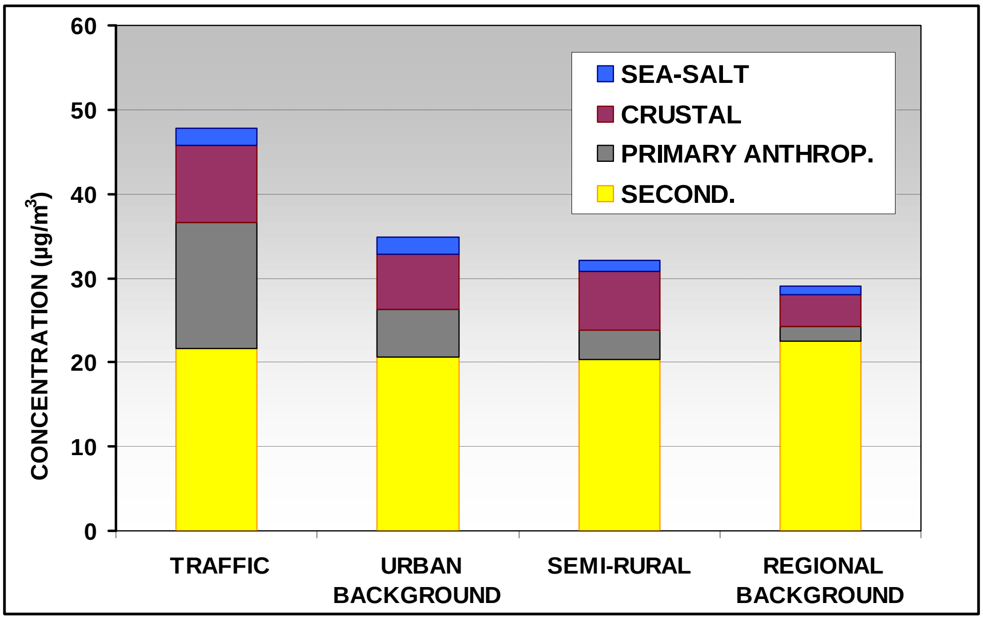


Figure 10.11:Chemical composition of PM_{10} during October 2004 – July 2005 in the Lazio region.

In terms of mass concentration, Figure 10.11 shows that a constant concentration of secondary species slightly higher than 20 µg/m^3 is recorded through the whole region, while the concentration of primary anthropogenic components manifestly decreases when moving from the traffic station towards the urban background, the semi-rural and the regional background station. Crustal components are slightly lower at the regional background station with respect to the other sites, probably because of the lower impact of traffic-generated re-suspension of particles. Sea-salt concentration also decreases when moving from Rome, which is about 20 km from the coast, to Montelibretti and to the regional background station, sited inland.

The results of this study have also shown that natural events have a non-negligible influence on PM concentration in the Lazio region and in all Central and Southern Italy. During sea-salt events, an increase of the ratio between coarse and fine particles is observed and the contribution of sea aerosol in PM_{10} may rise from 1-2% to 20-40%. Since the air masses coming from the sea are generally not much polluted, during these events PM_{10} keeps moderately low values. Consequently, as the concentration increment due to sea aerosol does not generally exceed 10 $\mu g/m^3$, in Central Italy sea-salt events are not responsible for exceedances of the daily PM_{10} EU limit value of 50 $\mu g/m^3$.

During Saharan dust events, instead, PM_{10} concentration area much higher and crustal components may increase from the regular 10-20% to more than 50% of PM_{10}. During these events values higher than 100 ug/m^3 as daily average of PM_{10} at the urban stations are not unusual, and multi-day exceedances of the EU limit value of 50 $\mu g/m^3$ are very often recorded.

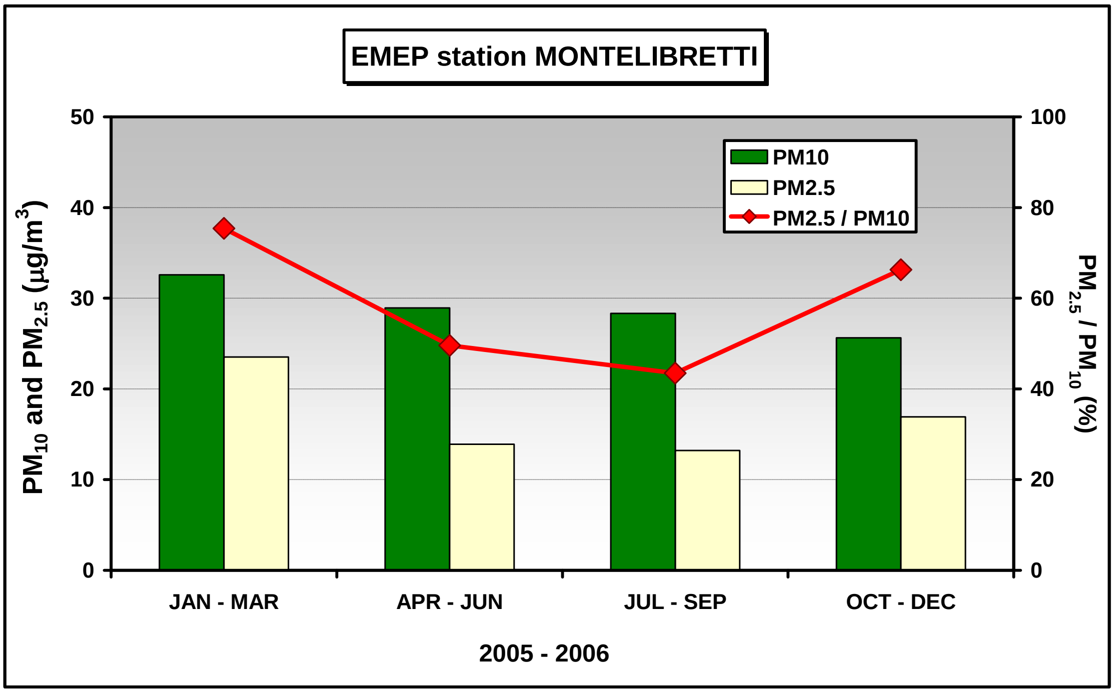


Figure 10.12:PM_{10}, $PM_{2.5}$ concentration and ratio at the Montelibretti station during 2005 - 2006.

Much information about the mechanisms that cause the increase in PM concentration can be obtained by studying the variations of the chemical composition of PM along the year. The time series of PM_{10} concentration at the semi-rural station of Montelibretti started in 2002; $PM_{2.5}$ measurements were added on July 2004 and the database containing the chemical speciation of PM_{10} is available for 2005 and 2006. During these two last years the average PM_{10}

concentrations were 28.7 and 29.2 μg/m^3, respectively, while the values of $PM_{2.5}$ were 16.2 and 17.6 μg/m^3. Seasonal variations were not relevant for PM_{10} (29.1 and 28.6 μg/m^3 as average values of the periods October – March and April – September of the two years, respectively), while they were significant for $PM_{2.5}$ (20.2 μg/m^3 during the winter and 13.6 μg/m^3 during the summer). $PM_{2.5}$ constituted 47% of PM_{10} during the summer and 75% during the winter. More detailed seasonal values are reported in Figure 10.12. The correlation between PM_{10} and $PM_{2.5}$ is very good during the winter ($R^2 = 0.78$) and lower during the summer ($R^2 = 0.42$).

The comparison between the concentration of PM_{10} at the semi-rural site of Montelibretti, about 25 km from Rome, and at the urban background site of Rome, site inside the green park of Villa Ada, is available for the five-year period 2002 – 2006. The data, reported in table I, show that the PM_{10} concentration levels at the two stations were very close to each other, with a five-year average value of 29.1 μg/m^3 at the semi-rural site and 30.1 μg/m^3 at the urban background site. The average PM_{10} concentration at a traffic site in Rome was about 40% higher. This finding indicates a quantitative relevance of the secondary components of PM, which are almost homogeneously distributed over the region. An estimate of the concentration of secondary inorganic species (nitrate, sulphate and ammonium), calculated by the results of the measurements carried out in Montelibretti in the framework of the EMEP program by means of diffusion denuder lines, indicates that secondary inorganic components account for 25-30% of the PM_{10} mass concentration. A similar, even higher, percentage may be considered for secondary organic species (see Figure 10.14).

A good agreement is also obtained between PM_{10} data at Montelibretti and at the traffic stations in Rome: during 2004, for example, the regressions between the values at Montelibretti and at the traffic stations M. Grecia and Fermi yielded R^2= 0.61 and R^2= 0.65, respectively. The very good agreement in the time pattern of PM_{10} between all the measurement stations in the Lazio region, shown for the period October 2004 – July 2005 in Figure 10.13, indicates, again, the relevance of secondary components, and also highlights that that the driving force in determining particulate pollution level is the meteorology, and specifically the mixing properties of the lower atmosphere, which determine the accumulation or dilution of pollutants and their daily fluctuations (see Chapter 10.4).

Table 10.1: Concentration of PM_{10} at a traffic station, at the urban background station of Rome and at the semi-rural station of Montelibretti: secondary inorganic compounds at Montelibretti as a percentage of PM_{10}.

	Traffic st. PM_{10} (μg/m^3)	Urban background st. PM_{10} (μg/m^3)	Semi-rural st. PM_{10} (μg/m^3)	Semi-rural st. sec. inorg. (%)
2002	53.1	32.3	32.6	32.6
2003	51.9	33.4	29.2	31.2
2004	53.7	28.6	29.5	28.2
2005	48.2	27.7	28.4	25.4
2006	47.8	29.7	28.9	25.3

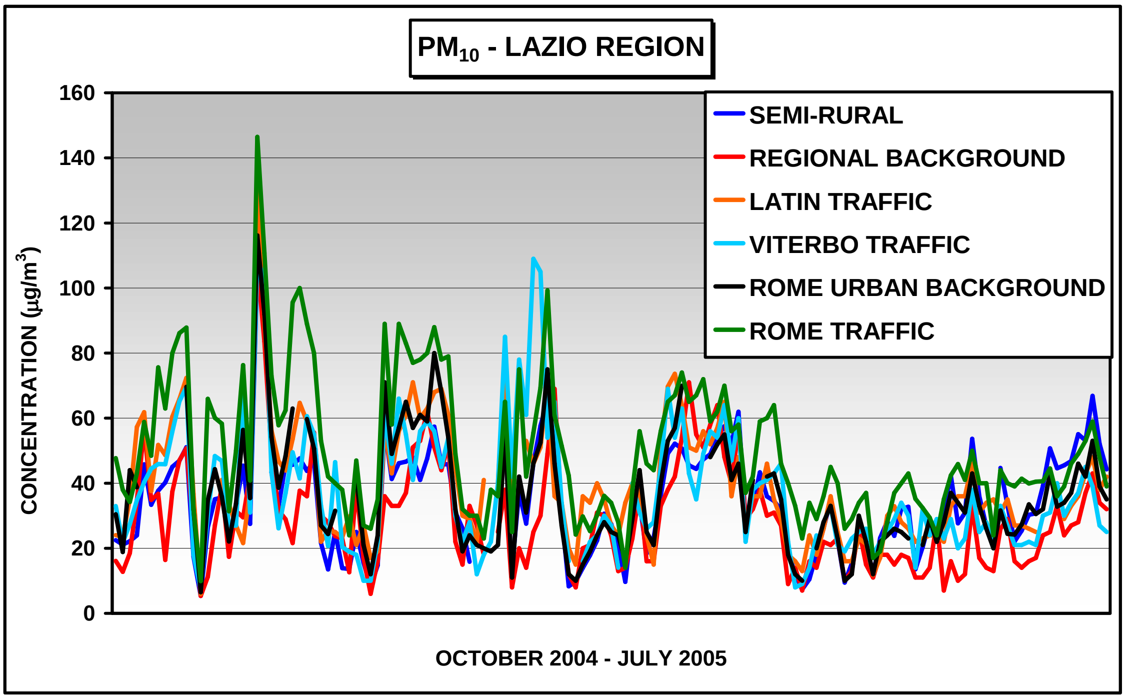


Figure 10.13:PM$_{10}$ concentration at six stations in the Lazio region during October 2005 – July 2006.

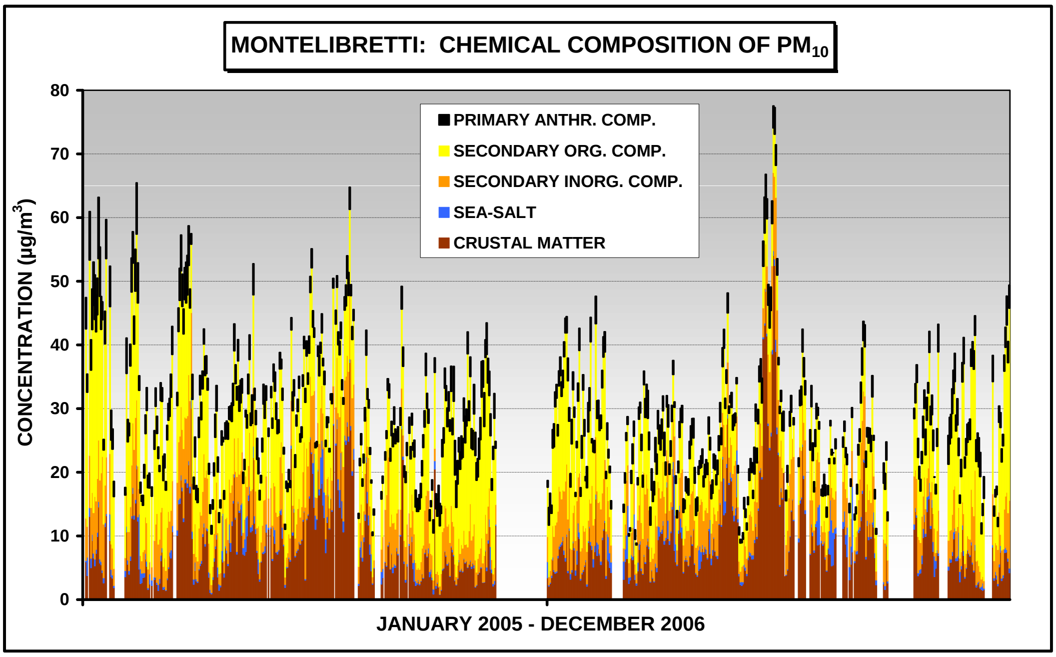


Figure 10.14:Chemical speciation of PM$_{10}$ at the semi-rural EMEP site of Montelibretti.

The chemical composition of PM$_{10}$ at Montelibretti during the years 2005 and 2006 is reported in Figure 10.14. PM$_{10}$ is generally dominated by secondary compounds, (roughly, 20% inorganic and 38% organic), but a relevant contribution is also given by crustal matter (30%) sea-salt (3%) and anthropogenic compounds (9%) contribute at a less extent. The contribution of the most important Saharan dust event, occurred on June 2006, during the summer EMEP intensive campaign, is apparent.

The seasonal variations in the composition of PM$_{10}$, shown in Figure 10.15, indicate a different composition during the cold season (autumn – winter), with a predominance of secondary organic compound over inorganic species, and during the warm season (spring – summer), with a predominance of crustal matter and an equivalence of organic and inorganic secondary species. Mass concentration are higher during the winter (33 µg/m^3) and the summer (32 µg/m^3) than during the intermediate seasons (27 µg/m^3 during the spring, 25 µg/m^3 during the autumn).

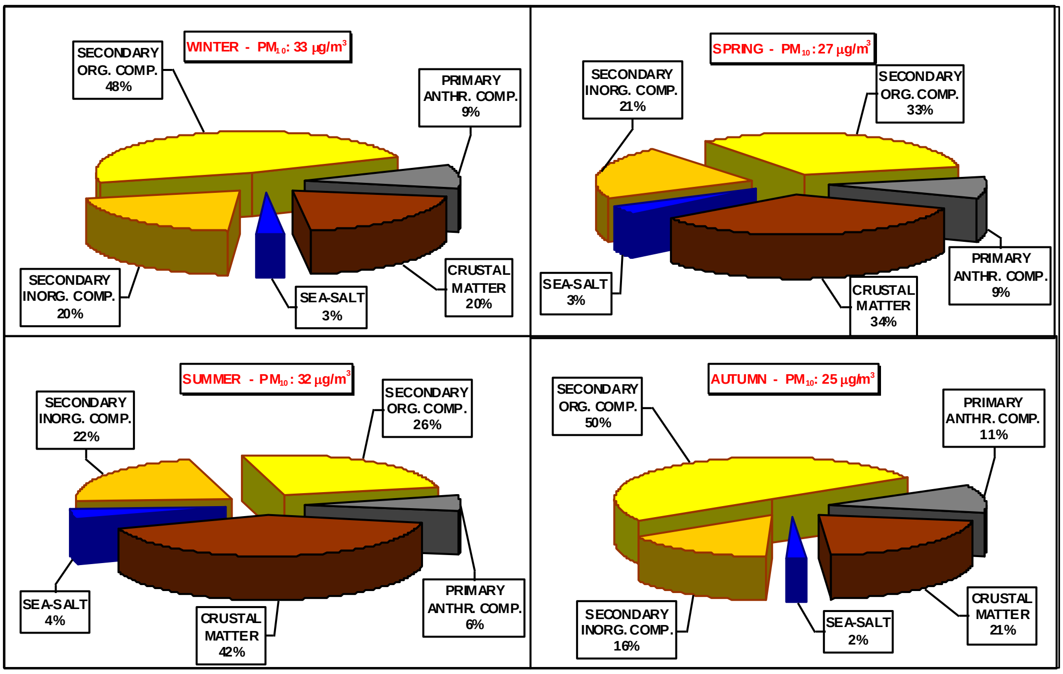


Figure 10.15:Seasonal variation of the PM$_{10}$ composition at the semi-rural EMEP site of Montelibretti during 2005 and 2006.

10.4 EMEP intensive campaigns in Montelibretti

The summer and winter EMEP intensive campaigns have been carried out at the Montelibretti station on June 1st – July 2nd 2006 and January 8th – February 8th 2007, respectively.

During both campaigns semi-continuous measurements of natural radioactivity have been carried out in order to trace the dilution properties of the lower atmosphere. This technique is based on the following assumptions: Radon is supplied by the Earth's crust; its emission flow into the atmosphere depends on the type, porosity, dampness and temperature of the soil (Nagaraja et al., 2003); for a given geographical location and for the time scale of our observation (weeks) the emission flux of Radon can be considered to be constant; the air concentration of ^{222}Radon and of its short-lived daughters (^{218}Po, ^{214}Pb, ^{214}Bi and ^{214}Po) depends only on the dilution factor (Shweikani et al., 1995, Porstendorfer, 1991); by monitoring natural radioactivity we can obtain a reliable picture of the dispersion properties of the boundary layer.

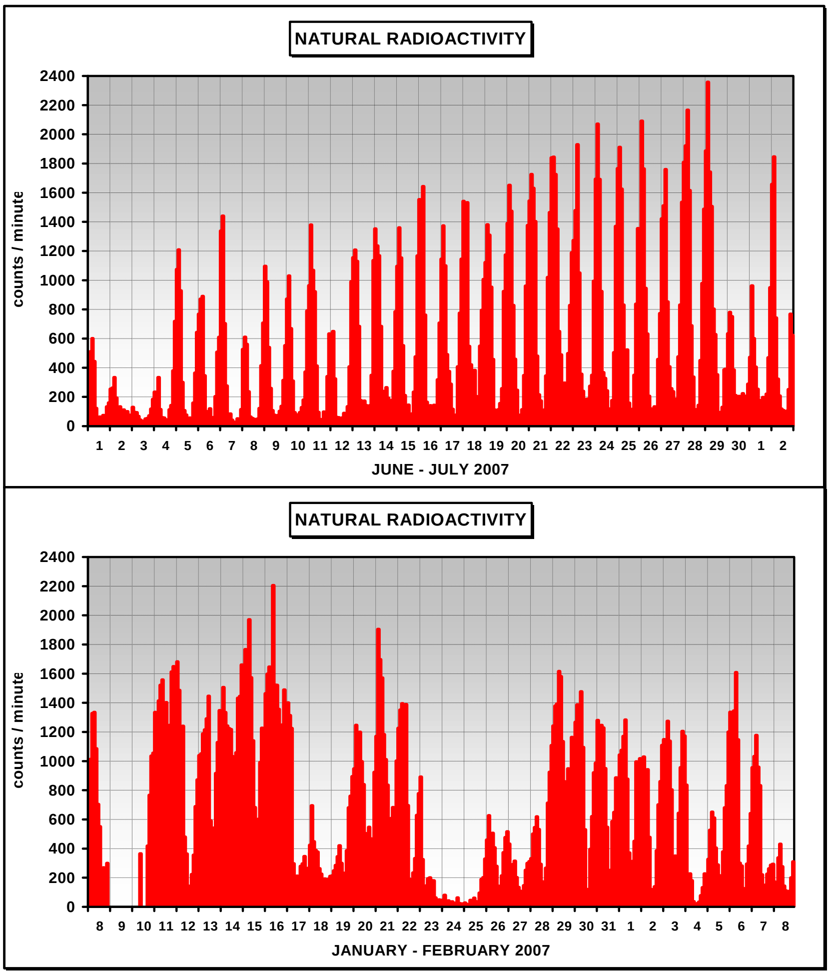


Figure 10.16:Natural radioactivity measurements during the two intensive campaigns.

Natural radioactivity was measured by means of an automated stability monitor (PBL Mixing Monitor, FAI Instruments, Fontenuova, RM-I) that basically consists of a particulate matter sampler equipped with a Geiger–Muller counter for determining the total beta activity of the short-lived Radon progeny. The instrument is automatic and operates on two filters at the same time: sampling is performed on the first filter for a 1-h sampling duration, then this filter undergoes the beta measurement phase while a second filter undergoes the sampling phase. These instrumental features assure that the short-lived beta activity of the particles is determined continuously over an integration time of 1 h with a beta measurement period long enough to guarantee a good accuracy of the results.

By using this method, we can identify periods characterised by atmospheric stability, which favours the build-up of pollution, and periods characterised by advection, which favours the dispersion of locally emitted pollutants (Perrino et al., 2001, Sesana et al., 2003, Vecchi et al., 2007).

The time pattern of natural radioactivity during the two intensive campaigns is reported in Figure 10.16. The difference between the two graphs reflects the difference in the mixing properties of the lower atmosphere between warm and cold months: during the summer atmospheric stability during the night, with high values of natural radioactivity, regularly alternates to convective mixing during the day, with low values of natural radioactivity (see the period between June 5th and 28th). During the winter, instead, multi-day advection periods, with constantly low values of natural radioactivity (January 17th-19th, 23rd-25th and February 4th) alternate to multi-day stability periods, with low mixing of the atmosphere during the night but also during the day (particularly on January 11th, 13th-16th, 20th-21st, 29th and February 3rd).

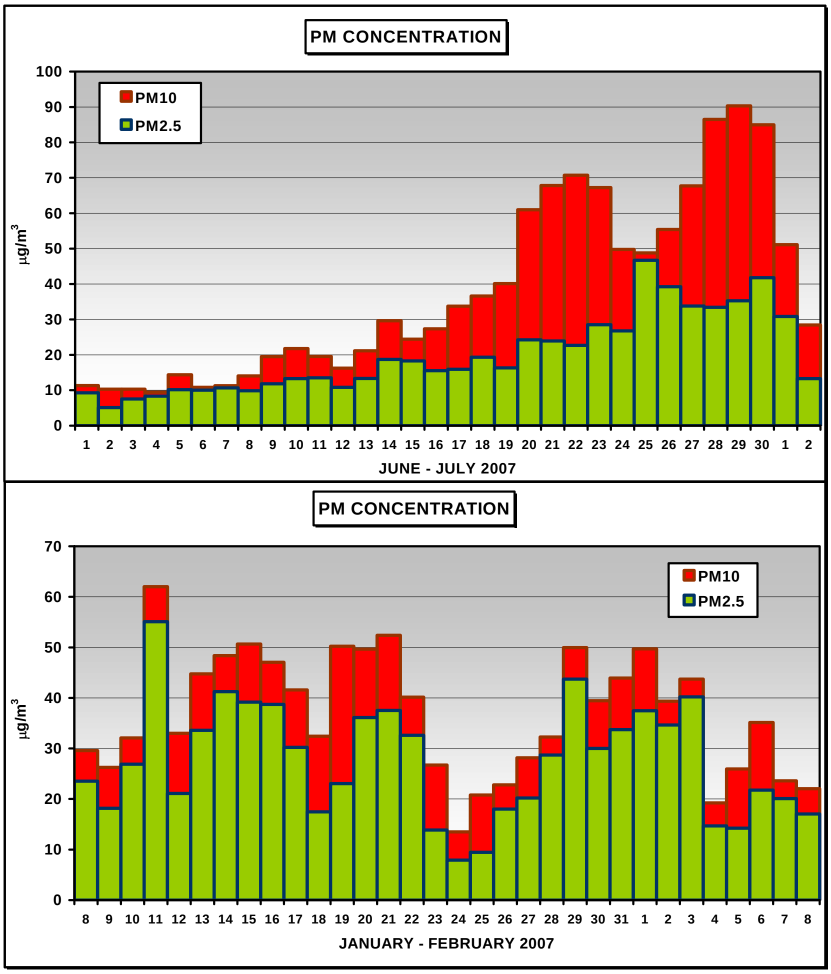


Figure 10.17:PM_{10} and $PM_{2.5}$ mass concentration during the two intensive campaigns.

These differences in the dilution properties of the lower boundary layer result in a different modulation of the particle concentration (Figure 10.17). Considering $PM_{2.5}$ during the winter campaign, we observe a sharp increase in its concentration during the days when the mixing of the atmosphere was poor, particularly during the daytime, that is, when natural radioactivity daytime minima were high (January 11th, 13th-16th, 20th-21st, 29th, February 3rd). Low values were recorded during advection (e.g. 23rd – 25th). On average, $PM_{2.5}$ constituted 73±13 % of PM_{10}. The lower values of the ratio $PM_{2.5}$ / PM_{10} were recorded on January 19th and 25th (0.46 and 0.45, respectively); low values of this ratio indicate a predominance of the coarse fraction and the occurrence of a natural event. The type of event (sea-salt or Saharan dust) can only be determined by running the chemical analyses of the collected particles.

During the summer campaign, instead, the ratio $PM_{2.5}$ / PM_{10} was 0.71±13 during the first two weeks and 0.50±16 during the last two weeks; this indicates that the whole second half of the study was characterised by an important natural event.

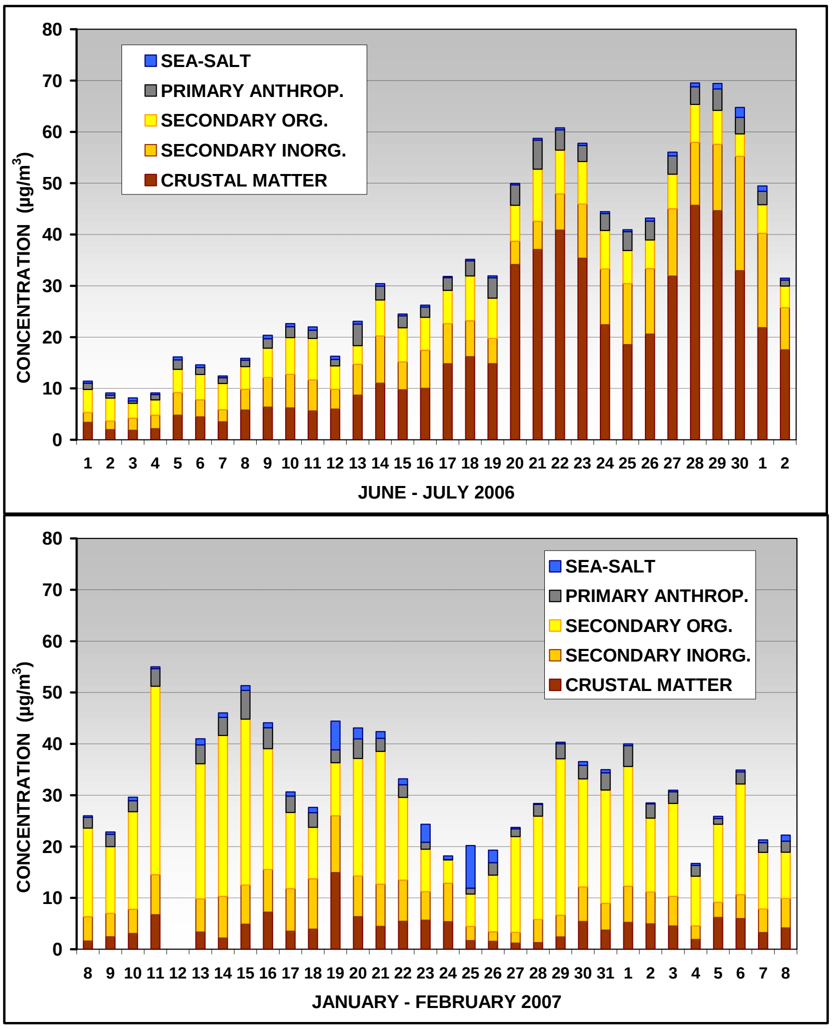


Figure 10.18:Chemical composition of PM_{10} during the two intensive campaigns.

The chemical analysis of PM (elements, ions, elemental and organic carbon) allowed reconstructing more than 90% of the collected mass. The study of the composition of PM_{10} and $PM_{2.5}$, shown in Figure 10.18, reveals that a relevant increase of the crustal fraction was recorded during the second half of the summer campaign. During this event (June 20th – July 1st), the crustal fraction, on average, constituted 56% of the PM_{10} and accounted for a mass concentration of 32 $\mu g/m^3$. These very high values can be common in Central and Southern Italy, which are often affected by Saharan dust intrusions. The dust loading over the Mediterranean and the vertical profile over Rome, calculated by the Dust Regional Atmospheric Model (DREAM) of the Centre on Insular Coastal Dynamics, and the back-trajectories of the air masses, calculated by the Hysplit model of NOAA, reported in Figure 10.19, show the intensity of the episode, which caused ten exceedances of the PM_{10} daily concentration limit.

During the winter campaign, instead, the composition of PM_{10} was dominated by secondary species, with the exception of the natural events of January 19th, a mixed dust – sea-salt event, and January 25th, a sea-salt event.

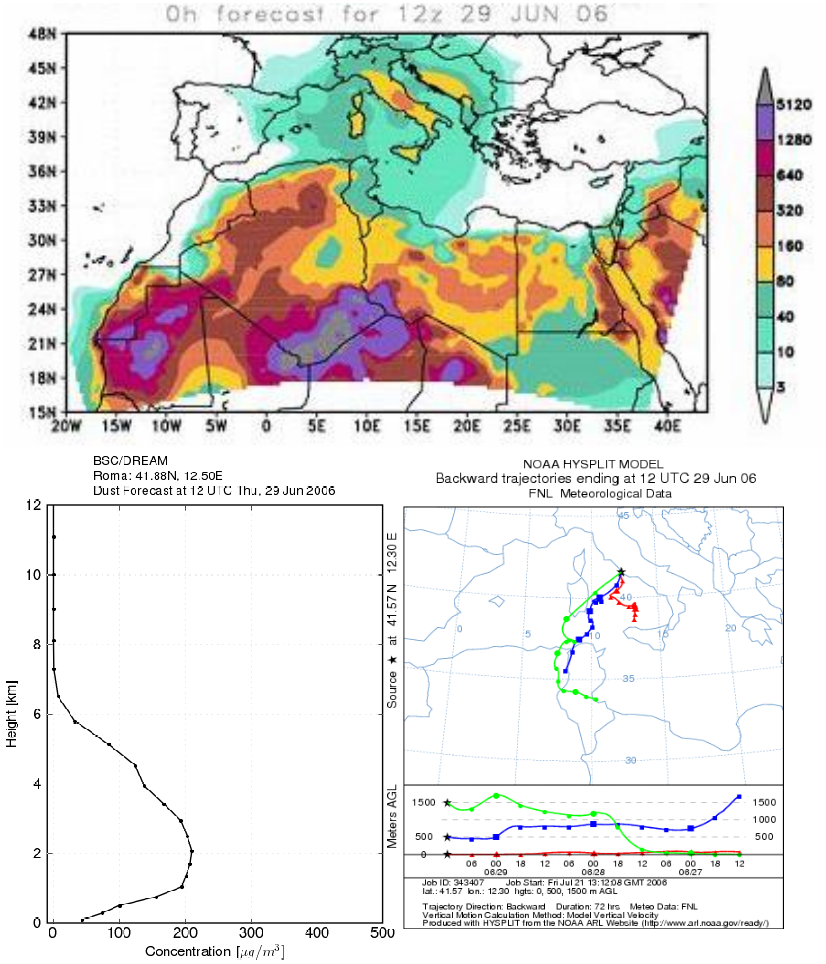


Figure 10.19:Dust loading and vertical profile over Rome by the ICoD DREAM model and back-trajectories by the Hysplit NOAA model on June 29th, 2006.

The per cent composition of PM_{10}, of $PM_{2.5}$ and if the coarse fraction ($PM_{10-2.5}$) is reported in Figure 10.20. During the summer campaign the coarse fraction and also the PM_{10} fraction are dominated by the crustal component. $PM_{2.5}$, instead, is composed mainly of inorganic and organic secondary compounds. Among inorganic species, about 80% is constituted by sulphate, while nitrate constitutes only 4% of $PM_{2.5}$. During the winter campaign, crustal matter prevails only in the coarse fraction, while both PM_{10} and $PM_{2.5}$ are dominated by secondary organic compounds. In this period, inorganic components were more equally distributed between sulphate (60%) and nitrate ammonium (20%).

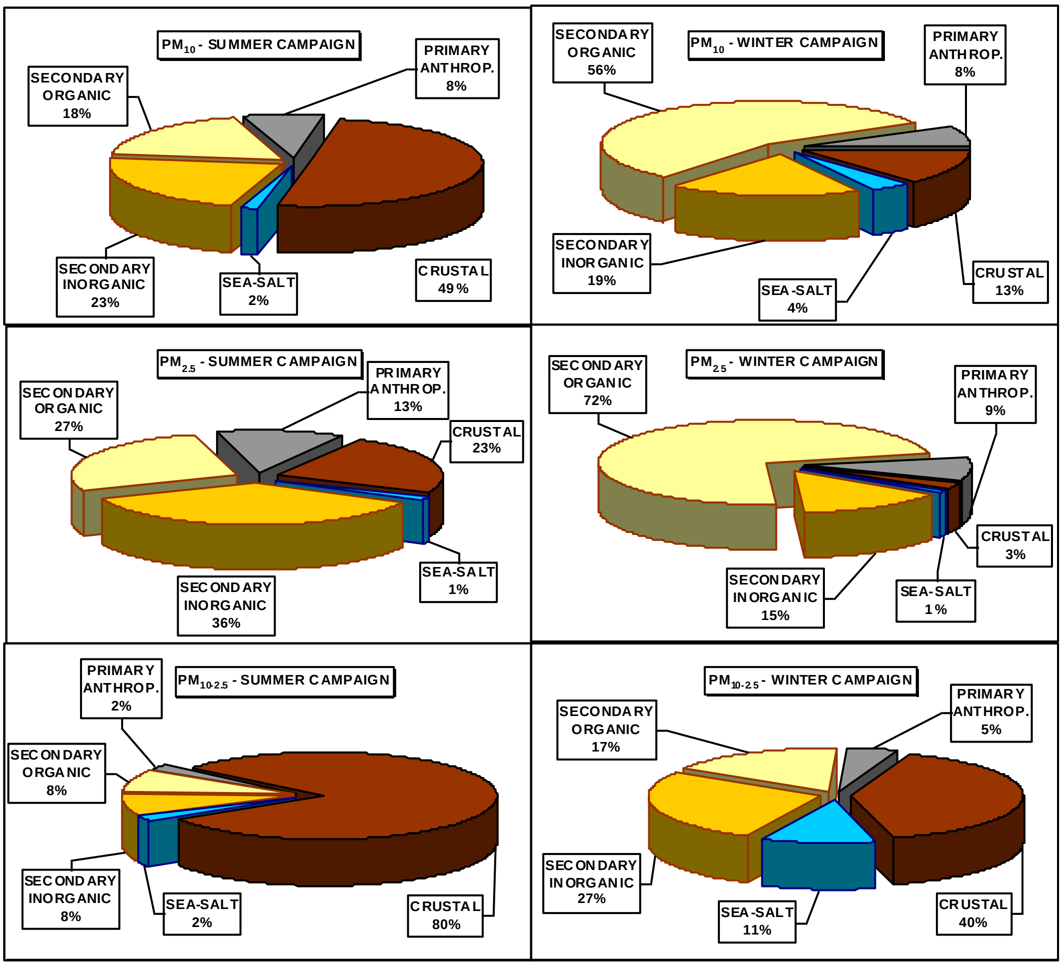


Figure 10.20:Chemical composition of PM_{10}, $PM_{2.5}$ and $PM_{10\text{-}2.5}$ during the two intensive campaigns.

It is important to stress that the determination of the nitrate content of PM suffers from a relevant bias when the sampling is carried out by using a single filter, as in the case of most air quality networks. The comparison of the nitrate and sulphate content of $PM_{2.5}$ as determined by the Teflon filter and by the co-located diffusion denuder lines (a combination of diffusion denuders and a filterpack where the Teflon filter is followed by two back-up filters for the recovery of evolved ammonium salts) shows that for sulphate the difference between the two sampling systems is of the order of 10-15%. For nitrate, instead, the value obtained by the collection on one single Teflon filter is only 20% of the value obtained by the diffusion lines during the winter campaign and 40% during the summer campaign.

10.5 Modelling evaluation of PM_{10} chemical composition

Monitoring campaigns provide punctual air quality measurements representative of the area where the instruments are placed and the physical-chemical details are often bounded by associated costs. So modelling system simulations may integrate air quality assessment, both allowing the description of pollutant temporal and spatial evolution over the simulation domain and evaluating the chemical physical properties of pollutants. In the particular case of PM, it is quite interesting to estimate the different chemical components of the atmospheric aerosol, characterized by different impacts on human health and ecosystems.

In the following, the applications of two modelling systems will be presented, focusing on the evaluation of PM_{10} chemical composition in the Milan and Rome regions.

10.5.1 A northern Italy region assessment

GAMES (Gas Aerosol Modelling Evaluation System) (Volta and Finzi, 2006) modelling system integrates (Figure 10.21):

the TCAM (Transport Chemical Aerosol Model) multiphase model:
the POEM-PM (Carnevale et al., 2006) emission pre-processor;
a meteorological chain, based on the prognostic Aladin (Bubnova et al., 1993) output and the diagnostic CALMET (Scire et al., 1990) model;
an initial and boundary condition pre-processor.

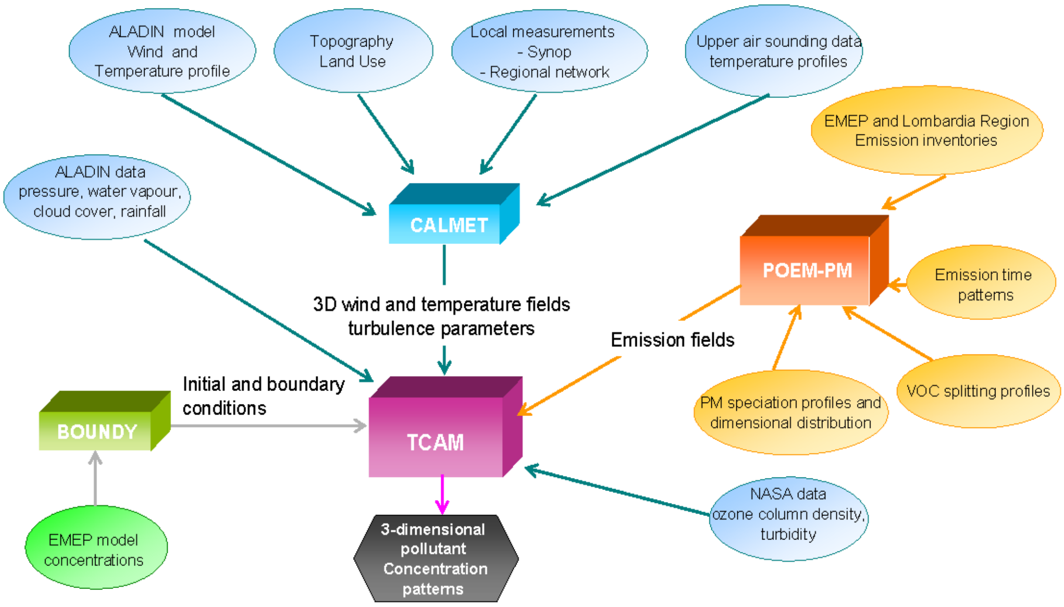


Figure 10.21:Scheme of the GAMES modelling system.

TCAM (Carnevale et al., 2005, http://pandora.meng.auth.gr/mds/) is a multiphase three-dimensional Eulerian grid model, expressed in terrain-following co-ordinate system. The model formalizes the physical and chemical phenomena involved in the formation of secondary air pollution; it solves a mass balance equation system, taking into account transport, diffusion, dry and wet deposition, multiphase chemistry and aerosol processes by means of a split operator technique.

In particular, TCAM includes and harmonizes a module describing the main aerosol processes: the condensation, the evaporation, the nucleation of H_2SO_4 and the aqueous oxidation of SO_2. The aerosol module describes the dynamics of 21 chemical compounds: the inorganic species are 12 (H_2O, $SO_4^=$, NH_4^+, Cl^-, NO_3^-, Na^+, H^+, $SO_2(aq)$, $H_2O_2(aq)$, $O_3(aq)$, elemental carbon and the other class, mainly including crustal material), while the organic species are 9, namely a generic primary one and 8 classes of secondary organic species.

The model has been applied to a northern Italy 300 x 300 km^2 domain (Figure 10.22). The domain is centred on Milan and it includes a large part of the

Po Valley, surrounded by mountains. The site is characterized by complex terrain, high industrial and urban emissions and a close road net. The domain has been divided horizontally into 5x5 km^2 grid cells and vertically in 11 varying levels ranging from 20 to 3900 meters above ground level. The grid resolution allows the model to reproduce both urban and regional circulation and chemical phenomena, as highlighted by the validation procedure performed in the frame of the CityDelta project (http://aqm.jrc.it/citydelta/). The performed simulation concerns the entire year 2004.

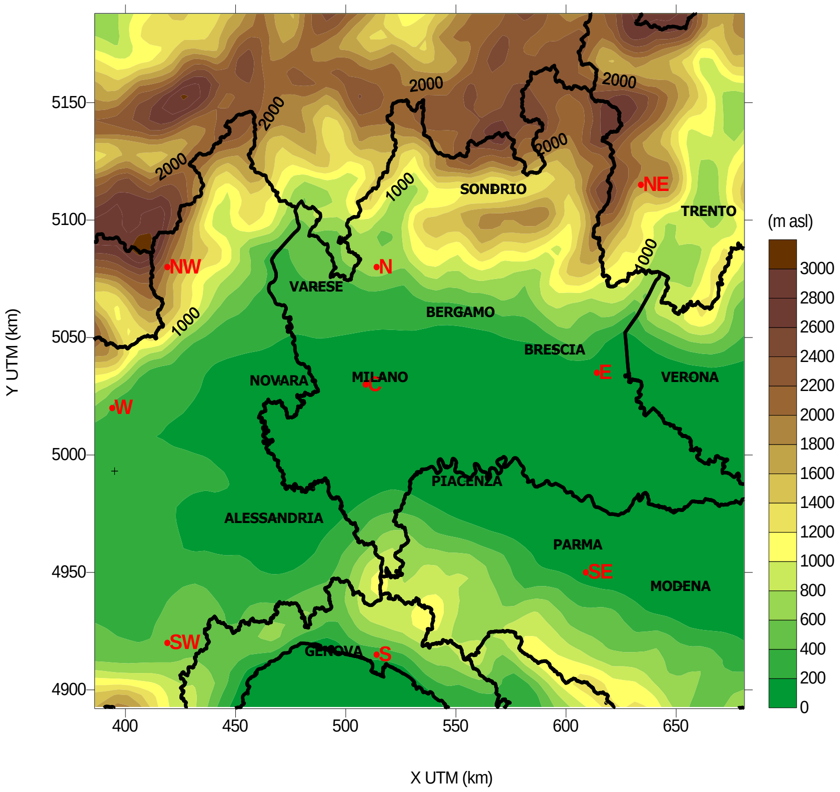


Figure 10.22:The simulation domain.

The model has been driven by emission (Figure 10.23) and meteorological fields, initial and boundary conditions provided by JRC-IES in the frame of CityDelta exercise.

The evaluation of the chemical composition of atmospheric aerosol simulated by GAMES are presented in terms of estimated mean concentrations in 9 points (NW, N, NE, W, C, E, SW, S, SE) (Figure 10.22), chosen as significantly representative of the meteorological and emission regimes on the domain.

In Figure 10.24 the simulated PM_{10} concentration for winter (January-March, October-December) and summer (April-September) is presented. In general, concentrations are higher in winter than in summer and the gap increases with the increasing of concentrations; so Milan urban area (point C) presents winter concentrations close to the double of the summer ones.

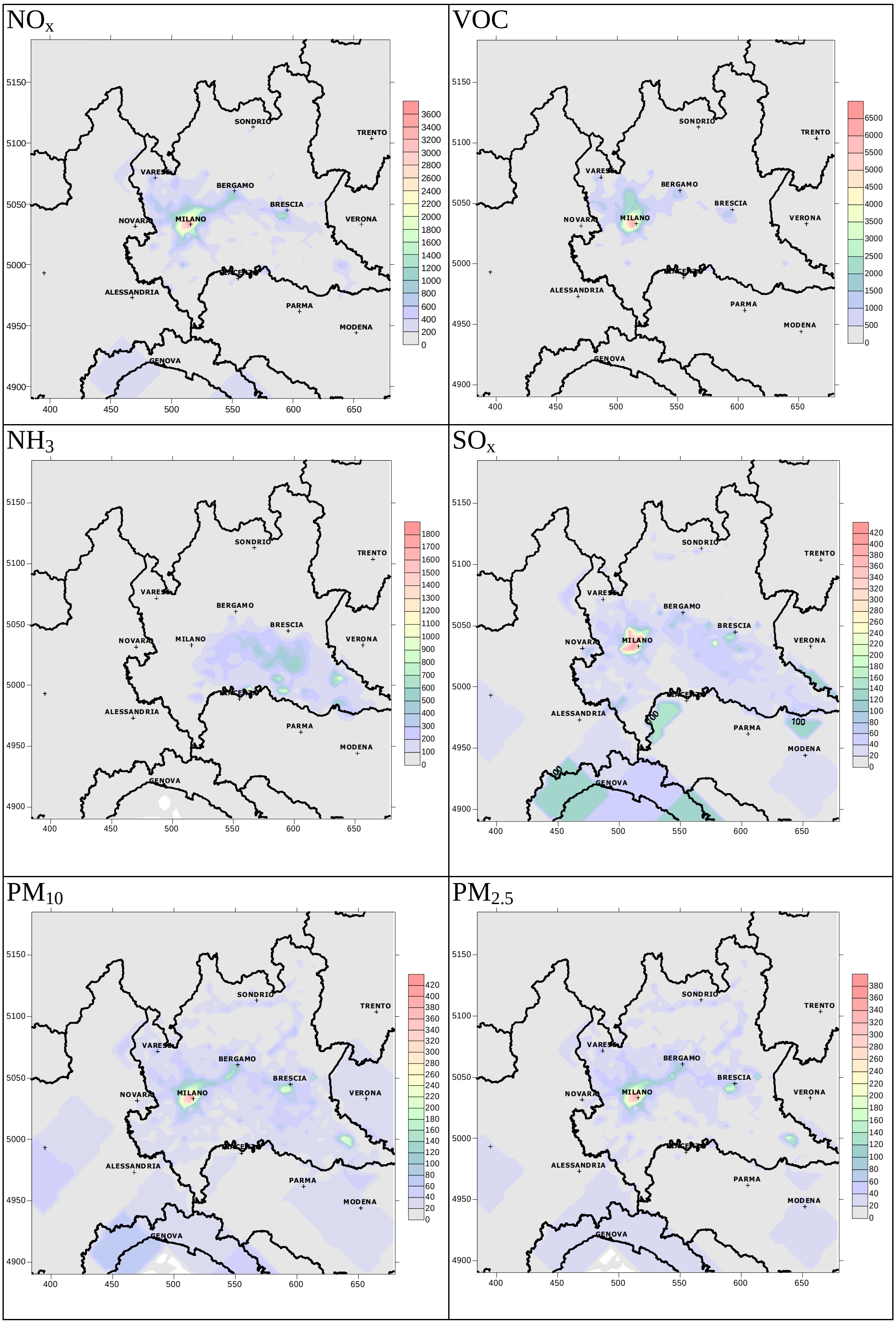


Figure 10.23:PM$_{10}$ precursor emissions (ton/year).

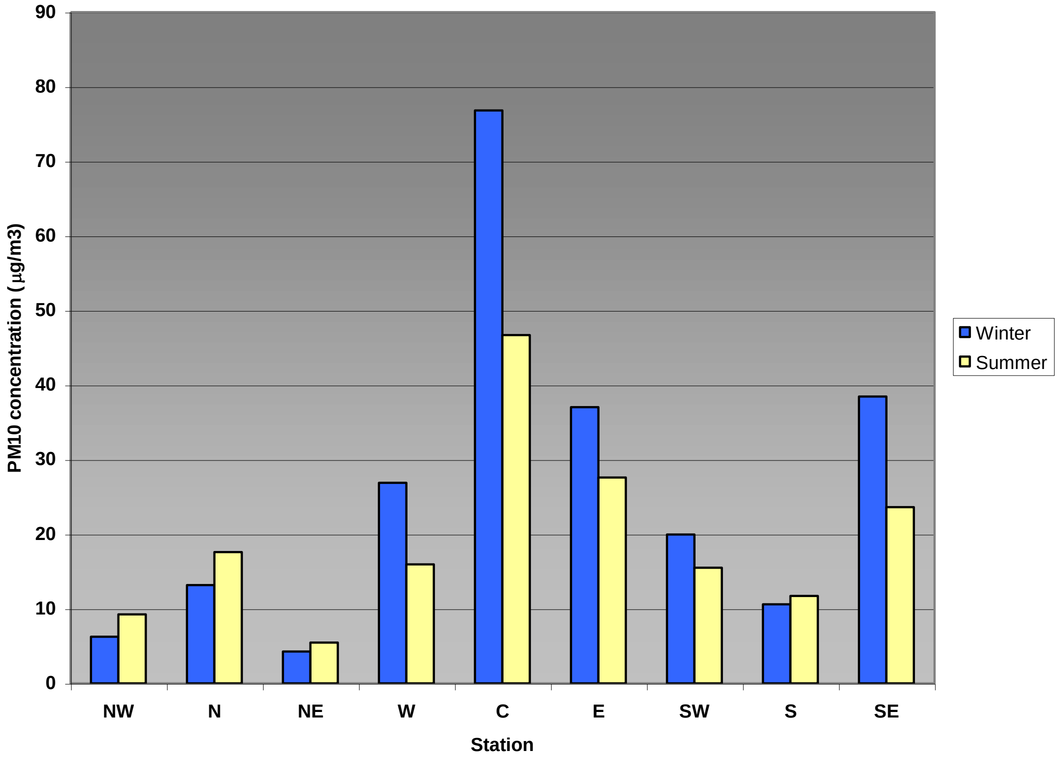


Figure 10.24:Simulated PM_{10} *in the 9 selected station in winter (blue) and summer (yellow).*

Figure 10.25 shows the analysis of PM_{10} chemical composition for the two seasons. As for winter, in the areas with highest PM_{10} and NOx emissions (point C, Milan city) the aerosol is mainly composed by primary (“elemental carbon” and “other” classes) and organic species, while the contribution of inorganic secondary compounds is limited to 44%.

The *organic* fraction decreases far off urban areas, reaching its minimum in the southern rural area, where primary PM_{10} and VOC emissions are lower (Figure 10.23). Simulated organic and primary fractions are in good agreement with experimental data made available in Van Dingenen et al. (2004). Moreover the estimated organic and elemental carbon fractions are higher during winter, when the reduced photochemical activity leads to a higher availability of VOC and the low temperature increases the condensation ratio of the organic species.

The contribution of *inorganic* compounds reaches the 70%, with high ammonium and nitrates fractions, except for Milan urban area. The winter inorganic concentrations are in general significantly higher than the summer ones due to the reaction between gas phase ammonia and nitric acid to form aerosol phase ammonium nitrate, favoured by the low ambient temperature of winter. Otherwise the percentage contribution is higher during summer, when the lower PM emissions and the photochemical activity reduce the organic (both primary and secondary) fraction in aerosol phase.

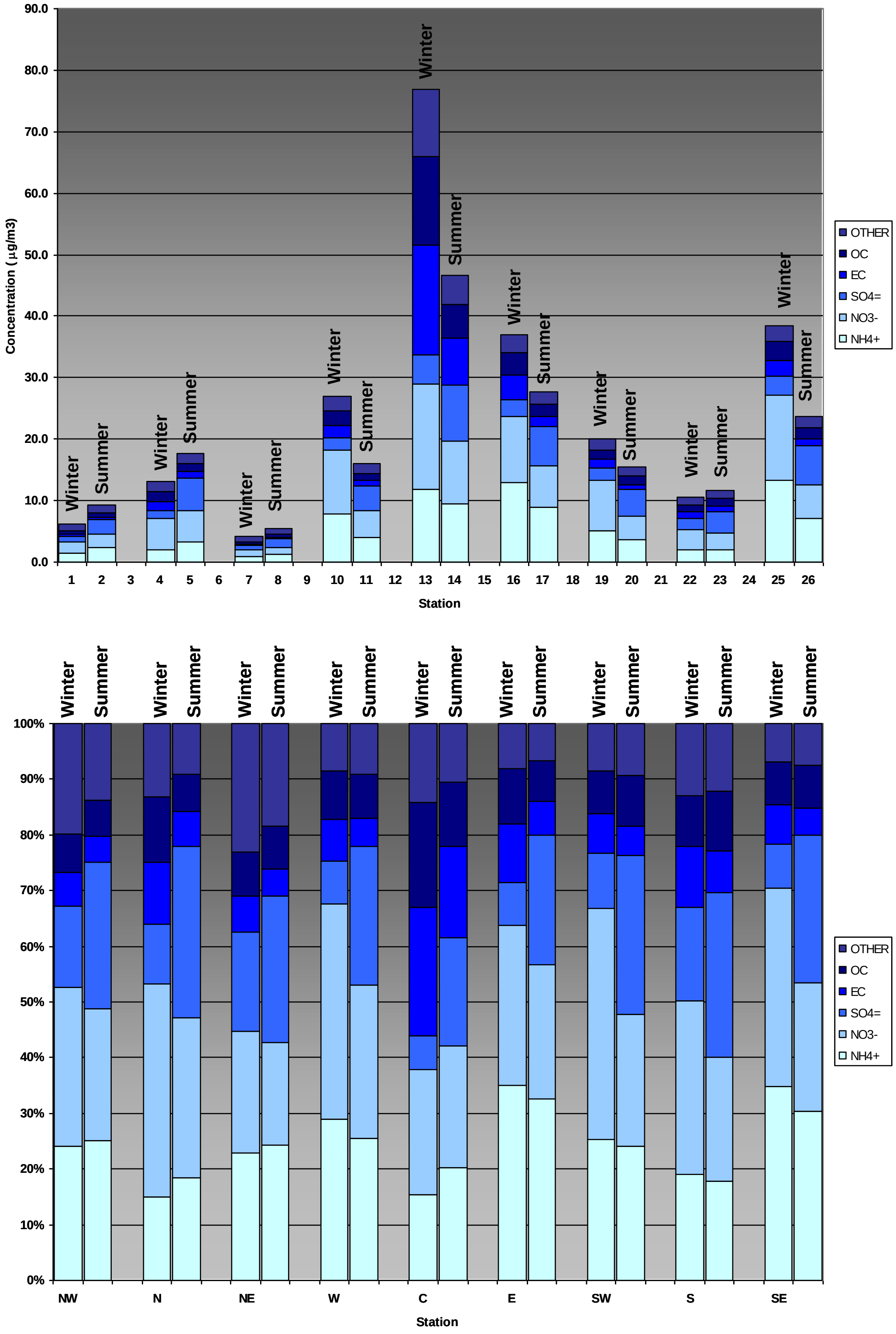


Figure 10.25:Chemical composition of PM$_{10}$ in the 9 selected points for summer and winter months in µg/m3 (upper) and in percentage (lower).

The simulated *ammonium* contribution is higher in the rural area in the south-east of the domain (E and SE point in Figure 10.22), where the most important ammonia sources are located (Figure 10.23). The spatial distribution of *nitrates* concentrations (Figure 10.25) shows a higher contribution near the relevant metropolitan NO_x sources, in particular in the north of Milan. Due to the domestic heating NO_x emissions and to the low temperature the winter nitrate contribution is heavily greater than the summer one.

Severe *sulphate* concentrations are simulated near SO_x stack emissions in the domain, suggesting that sulphate formation in the other areas of the dominion is mainly driven by trans-boundary pollution

10.5.2 The case of Rome urban area

In the following the application and evaluation of a modelling system based on FARM Chemical Transport Model (Silibello *et al., 2007*) over Rome urban area is presented.

Chemical transport model simulations over Lazio Region and Rome urban area (Figure 10.26) were performed to identify the areas concerned by the highest air pollutant concentrations during summer and winter severe air pollution episodes. The modelling analysis was supported by data gathered during meteorological and air quality field campaigns carried out from June 2005 to June 2006 (see paragraphs 3-4), to enhance routinely available observations space coverage and to add information on vertical profiles and particle matter composition.

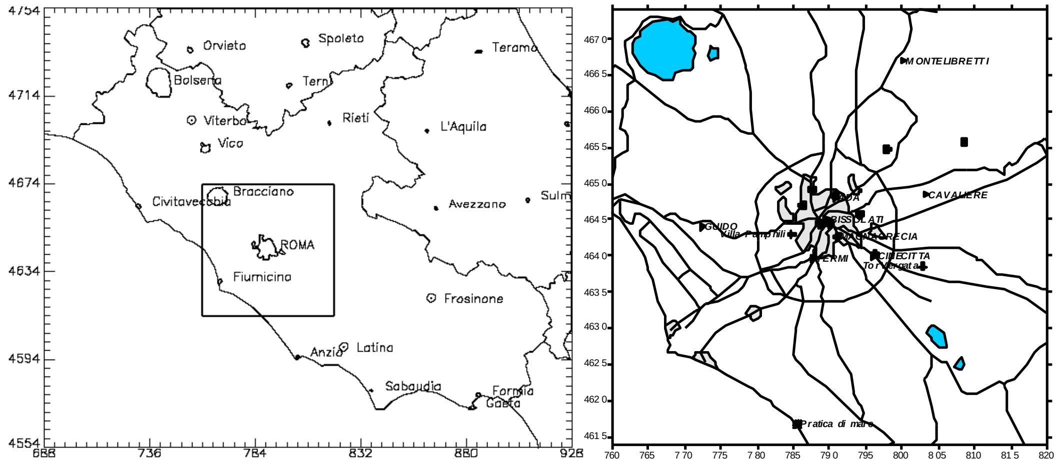


Figure 10.26:The nested modelling domains (the inner domain is expanded on the right side) and location of main meteorological and air quality measurement sites.

Three episodes were selected for the modelling study. High ozone peaks were detected during the first two episodes (20-24 June and 25-29 July 2005), related to summer Mediterranean circulation conditions but associated with different synoptic forcing: the first one was characterized by the eastward expansion of the Azores anticyclone in the lower layers and an high pressure ridge centred on the Iberian peninsula aloft; the second one was dominated by an high pressure ridge of African origin over central Mediterranean. The third period (9-13 January 2006) was otherwise characterized by PM_{10} peaks, mainly induced by stagnant meteorological conditions with consequent pollutants accumulation, under the influence of a persisting high pressure system centred over north-eastern Europe.

The simulations have been performed using a comprehensive modelling system, including module for the treatment of meteorology, traffic, emissions and the atmospheric dispersion and transformation of air pollutants.

The mesoscale meteorological model RAMS (Cotton et al., 2003) has been used to reconstruct the atmospheric flow with three nested domains: Italy, Centre Italy and Rome urban area at 16, 4 and 1 km resolution respectively. The vertical structure and the daily cycle of the atmospheric circulation have been correctly reconstructed by RAMS (Figure 10.27). Surface wind speed was correctly reconstructed for stations exposed to the main flow (e.g. Rome hilltop stations) or located above the urban canopy, while some overestimation of wind speed and underestimation of temperature has been obtained within urban canopy, probably due to the lack of a proper treatment of urban meteorology. Local scale atmospheric circulation description has been enhanced using data assimilation techniques with RAMS simulations. Over Rome domain, to better reproduce the fluxes induced by the presence of the urban area, the background wind field produced by RAMS have been further adjusted, using measured values, by means of the mass consistent model MINERVE (Aria Technologies, 2001). The meteorological and air quality models are connected by means of SURFPRO interface module (Arianet, 2004; D'Allura et al., 2004).

The emission inventory was developed by combining different sources of information: the Italian national inventory, largest industrial facilities emissions data, directly estimation of traffic sources emission from vehicles flows. Hour-by-hour traffic data, related to more than 9000 links making up the 700 Km of the primary road network of Rome, have been produced by a traffic assignment model based on source-destination approach for the selected episodes, and then used to estimate emissions. Emissions for each road link of Rome network were calculated by means of TREFIC model (Nanni et al., 2004), based upon the COPERT III methodology. Hourly gridded emission rates were then generated through Emission Manager/EMMA module, using gridded proxies for spatial disaggregation and activity-specific time patterns. Sea salt and wind blown soil surface erosion emissions were calculated by SURPRO interface module.

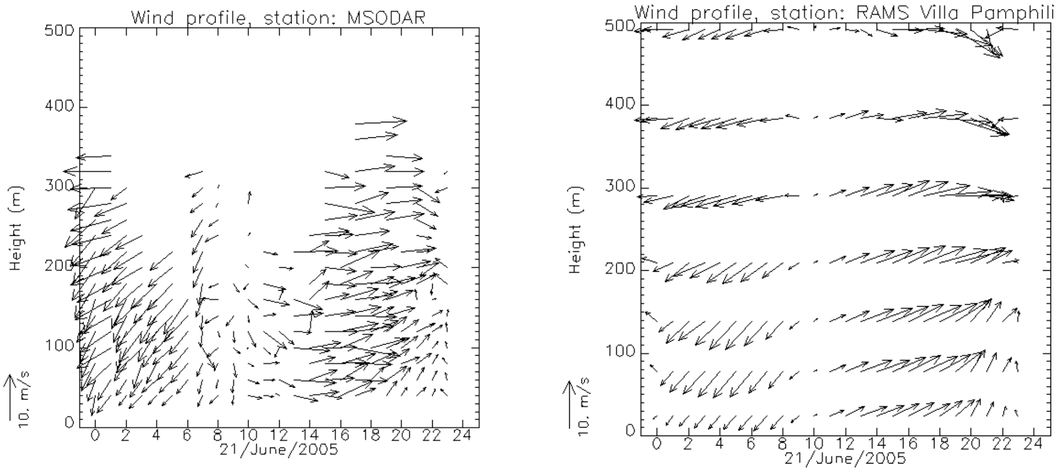
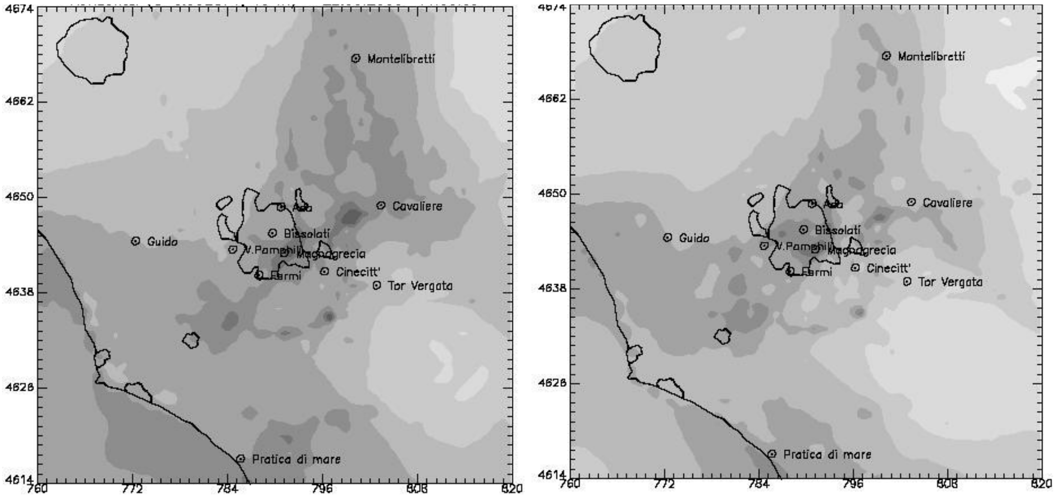
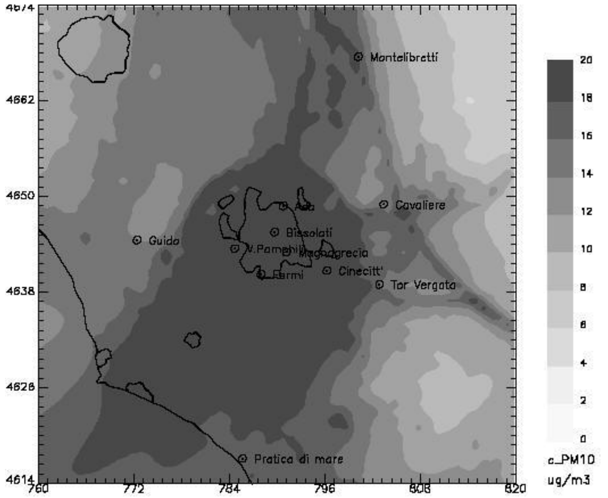


Figure 10.27:Comparison of SODAR measured (left) and RAMS modeled (right) vertical wind profile on June 21 2005 at the Villa Pamphili station (Rome).

The chemical transport model FARM has been employed to describe pollutant dispersion and chemical transformation over the two inner domains (Figure 10.26) using 2-way nesting approach. FARM is an Eulerian model dealing with multiphase chemistry of pollutants in the atmosphere. Photochemical reactions are described by means of SAPRC-90 chemical scheme, while the CMAQ aero-3 module (Binkowski and Roselle, 2003), based on a modal approach, is employed for particulate matter. Figure 10.28 shows the average PM_{10} concentration maps during the June 2005, July 2005 and January 2006 episodes evidencing the typical seasonal behaviour, with higher concentrations during winter and lower levels in summer. The summer average concentrations in the Rome urban core and around it are about 10-12 $\mu g/m^3$, with peaks of 14-16 $\mu g/m^3$ spatially limited at specific locations. Clearly evident is the influence of the highway road ring (GRA) around Rome.



a) 20-24 June 2005 b) 25-29 July 2005

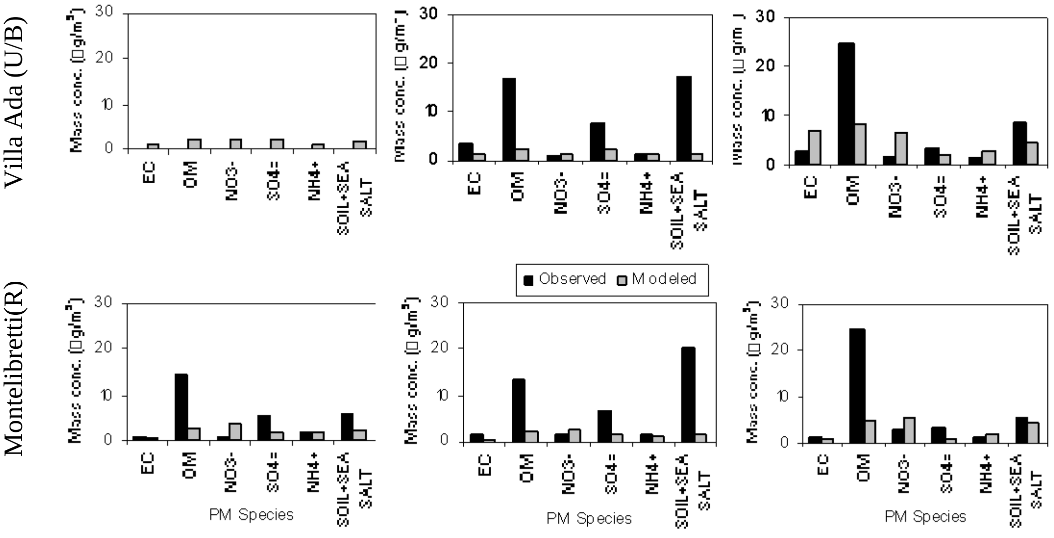


c) 9-13 January 2006

Figure 10.28:Average PM_{10} ground concentration maps in the target urban domain during the June (a), July (b) and January (c) episodes.

At summertime the breeze effect transports PM and the other compounds to the north-east part of the territory. Both coastland and inland parts are also affected by PM_{10}, with concentrations up to 12 $\mu g/m^3$. The winter map shows a large area with an average PM_{10} concentration of 20 $\mu g/m^3$ covering Rome, its surroundings and the south-east part until the coastline. This effect is produced by a high-pressure system, characterized by persistent north-northeast weak winds and often calm conditions, slowly transporting to south-southeast pollutants emitted or produced in Rome area. As for the summer results, the south-east hillside part of the domain seems to be less influenced by PM_{10}, probably due to its elevation. Highest PM_{10} concentration maps produced for each episodes (not shown) exhibit large areas with values up to 40 $\mu g/m^3$, mainly detected at night-time when PBL heights are lower and consequently higher concentrations are reached.

To further investigate the model capability to reproduce the different PM components and to better understand the reasons of model underestimations in predicting the PM concentrations, daily data of PM_{10} compositions collected at Villa Ada and Montelibretti were used. Speciated PM_{10} data of sulphates, nitrates, ammonium, elemental carbon, organic matter, crustal matter and sea salts were available for the three modelled episodes. Crustal and sea-salts components were then aggregated, to be compared with the correspondent species calculated by the FARM model. Figure 10.29 shows a comparison between modelled and measured PM species at Montelibretti and Villa Ada sites, averaged over each simulated episode.



a) 20-24 June 2005 b) 25-29 July 2005 c) 9-13 January 2006

Figure 10.29:Average concentrations of modelled/observed PM_{10} and its compositions at Villa Ada and Montelibretti sites during the June (a), July (b) and January (c) episodes.

The analysis of this figure evidences good results for elemental carbon (EC), nitrate (NO_3^-) and ammonium (NH_4^+) particular at Montelibretti station. A moderate overestimation is detected for nitrate with larger differences during the winter episode, while for the sulphate ($SO_4^=$) modelled results indicate underestimation of the observed concentrations. As for inorganic ions, it can be assumed that these results are consistent with the current performance expected from most other air quality models, although some relevant processes could be improved such as the nitrate formation due to condensation and aqueous-phase chemistry. The analysis of organic matter component (OM) shows a significant underestimation of observed levels partially explaining the model underestimation of PM_{10} concentrations. This result is coherent with those found by different authors (Tesche et al., 2006; Zhang et al., 2006) which detected underestimations up to 80% for the OM content in $PM_{2.5}$. They found that both primary OM emissions and model treatments of chemistry and thermodynamics of organic components are responsible for this OM underestimation. Similar conclusions are reported in Part A: European Perspective regarding uncertainties in model results for elemental carbon and organic matter (uncertainties in emission inventories, difficulties with measurements methods, SOA formation, etc.).

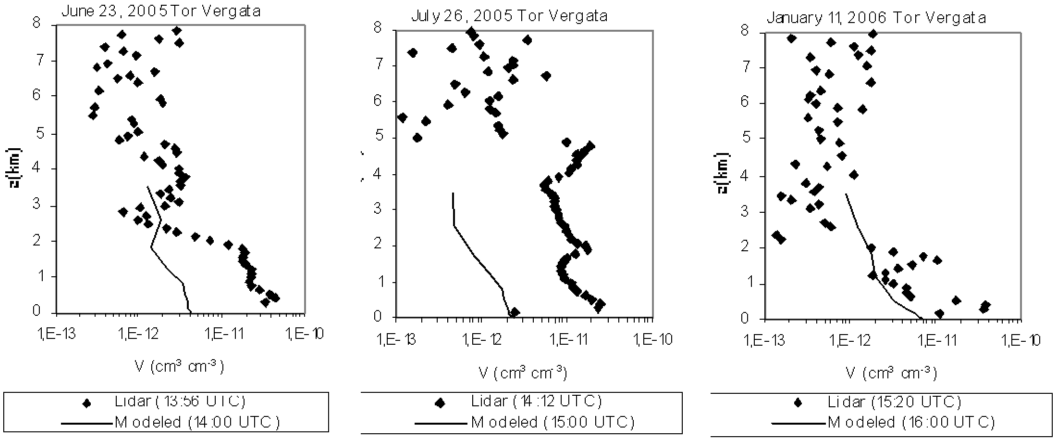


Figure 10.30:Comparison of modeled and Lidar observed atmospheric aerosol volume profiles at Tor Vergata site on June 23, 2005 (left), July 26, 005 (middle), January 11, 2006 (right).

The other component that results to be significant underestimated is the soil (and sea salt) component for which the analysis of Figure 10.29 evidences a good agreement for the winter episode (Figure 10.29c), a non negligible underestimation at Montelibretti for June episode (Figure 10.29a – Villa Ada data were not available -) and a significant underestimation during the July 2005 episode (Figure 10.29b). The use of Lidar data is very useful to understand the reasons for these results. Figure 10.29 shows an example of modelled and measured dust volume vertical profiles obtained at the Tor Vergata site at specific times for each considered episode. The analysis of this figure evidences that the model underestimates Lidar data, for about one order of magnitude, during both June and July episodes while it provides more reliable results for the winter episode, at least in terms of magnitude (Figure 10.30 right). According to Barnaba and Gobbi (2001), the combination of lidar depolarisation trace (D) and backscatter ratio (R) permits to discriminate between dust (typically D> 10% and R > 1.5) and nondust conditions (typically D < 10%). For the profiles shown in Figure 5.10 following values are estimated for D and R: 4.7< D < 11.7% and R > 1.5 for June (Figure 10.30 left); D > 10% and R > 1.5 for July (Figure 10.30 middle) and non-dust conditions for January (Figure 10.30 right). These results are confirmed by the analysis of back-trajectories that indicates, for the July 2005 episode the existence of air masses proceeding from West, mainly from Southern Spain and North Africa, confirming the significant contribution of Saharan dusts to PM_{10} observed levels. Also the June 20-24 episode follows an intense Saharan dust advection phenomena lasted from 13 until 19 June, 2005. When this long-range effect is absent, as during the January 2006 episode, this component is better reproduced (see Figure 10.29c at Montelibretti) or its underestimation is reduced (Figure 10.29c at Villa Ada).

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11 Analysis of particulate matter (PM_{10}) concentrations in Latvia

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Latvian Environment, Geology and Meteorology Agency

11.1 Introduction

The national assessment of the Latvia's particulate matter (PM_{10}) data covers the emissions of gaseous pollutants and particulate matter and the PM_{10} concentrations in urban and traffic areas over 2000-2005. The concentrations have been recorded at the air quality monitoring stations of the Latvian Environment, Geology and Meteorology Agency and Riga City Council.

Exceedances of PM_{10} concentration were closely looked at against short- and long-term air quality limit values, specified in European directives. With this in mind, and human health in particular, the quantitative and qualitative impacts of meteorological parameters were analyzed.

The assessment provides an analysis of the relationship of meteorological parameters and PM_{10} levels in urban and traffic areas. Meteorological conditions were analyzed, with special emphasis on the air pollution episodes caused by the wind (speed and direction), temperature, humidity, rainfalls, and daily and seasonal variations. The study was performed in order to identify the meteorological conditions that would cause extremely high particulate matter concentrations in agglomerations and urban areas in particular.

11.2 Measurement network and methods

Particulate matter (PM_{10}) monitoring started in 2000. Since then, the observational network has been greatly improved. The geographical position of the monitoring stations and a description of the sites and the changes are shown in Figure 11.1 and Table 11.1.

Figure 11.1: Geographical position of PM_{10} monitoring stations in Latvia, (yellow- operated stations, blue – planned stations).

Table 11.1: Measurement sites, Latvia.

No	Measurement site	Period of observations	Site type	Method, equipment
1	Riga, Centre	2000 - 2002	Traffic station	Beta gauge, SM200
2	Riga, Brivibas	2003 - 2005*	Traffic station	Beta gauge, SM200
3.	Riga, Tvaika	2003 - 2005*	Urban-industrial	Beta gauge, SM200
4	Riga , Valdemara	2003 - 2005*	Traffic station	Beta gauge, Horiba
5.	Liepaja	2000 - 2005*	Traffic station	Beta gauge, SM200
6.	Ventspils	2000 - 2005*	Urban background	Beta gauge, SM200
7.	Rezekne	2001 - 2004	Urban background	Beta gauge, SM200
8.	Rucava	2002	Rural background	Beta gauge, SM200

* monitoring is being continued

At present, 5 urban stations are carrying out monitoring of PM$_{10}$, with 3 of them (traffic and urban-industrial stations) in the capital city of Riga (764329 inhabitants) and 2 in the western part of Latvia, in the biggest towns of Ventspils (43928 inhabitants) (urban-background station) and Liepaja (89448 inhabitants) (traffic station).

The PM$_{10}$ measurements at the EMEP station Rucava were performed in the period from July to August 2002. The measurements were stopped because of a technical problem.

In order to meet the requirements of EU Directives, it is planned to resume the measurements at Rezekne and Rucava, Zoseni (EMEP), the rural station at Nigrande and the urban background station in Riga.

11.3 Pollution sources

During the last 15 years, a significant decrease in total emission of gaseous pollutants has been observed. In 1990 -2004, the total SO$_2$ emission has decreased by 96.1%, NO$_X$ by 42.9% and NH$_3$ by 72%. The reduction occurred mainly due to the use of fuels with a lower sulphur concentration as well as switching from solid and liquid fuels to natural gas and biomass, significant changes in industrial activity (Figure 11.2).

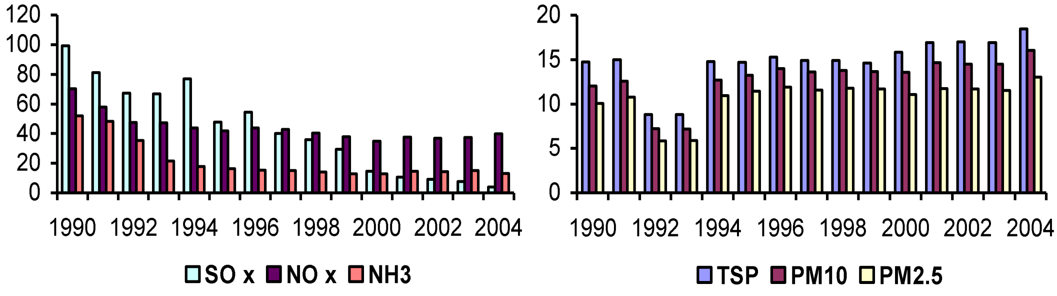

Figure 11.2: Total emissions of gaseous pollutants and particulate matter in Latvia ,Gg.

Primary particulate matter emission has no significant changes, from 2000 to 2004 particulate matter emission have increased by 15% it is because amount of used fuel is increased as well as number of livestock.

The assessment of the PM_{10} emission was carried out according to the EMEP 50x50 km^2 grid for 8 emission source categories. It has show that most of pollution sources are situated in the central (capital city included), south-western (Liepaja) and south-eastern (Daugavpils) parts of Latvia.

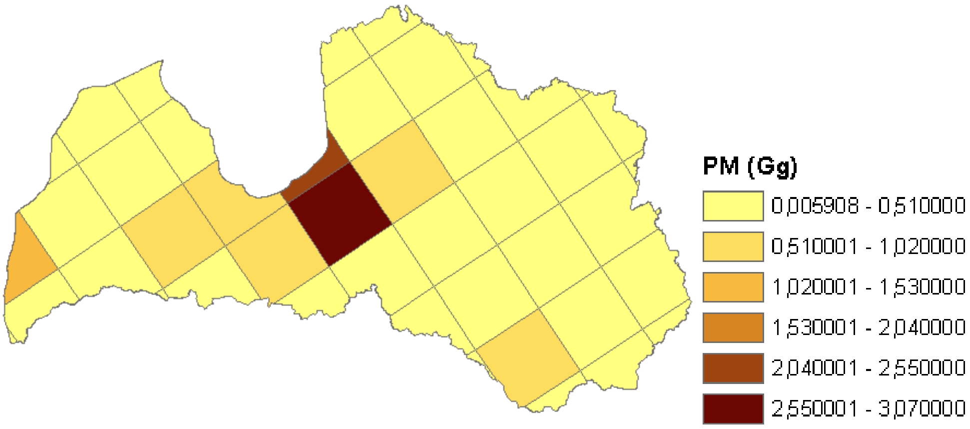

Figure 11.3: Total PM_{10} emission within EMEP grid cells (50x50 km^2), 2005.

The main sources of PM_{10} emissions are the commercial and residential sectors. Combustion of wood and wood products accounts for 71.7% of total PM_{10} emission, against 10.2% (industries), 8.9% (transport) and 5.8% (agriculture).

The long-range pollution transport significantly contributes to PM_{10} pollution level due to the geographical position of the country (entry of pollution from the major polluting areas in central Europe) and close proximity of the sea. The main pollutants are nitrates, sulphates, ammonium compounds as well as the primary particulate matter. The secondary particulates forming by oxidation of SO_2 and NO_X and in reactions with ammonia. The long-range pollution transport accounts for 80% of oxidized sulphur, 75% of oxidized and reduced nitrogen of total deposition of pollutants onto the territory of Latvia.

In addition, there has been a large contribution from natural sources, e.g. soil dust and sea spray.

11.4 Results

11.4.1 Exceedance of EU limit values

The monitoring results are presented in Table 11.2 and clearly testify to the fact that PM_{10} is one of the problematic pollutants for the whole area of Latvia.

An EU annual limit value of 40 $\mu g/m^3$ of PM_{10} and a limit value of 50 $\mu g/m^3$ for daily average of PM_{10} for more than 35 days was exceeded at the observation stations in Riga and Liepaja during 2000-2005. At all other stations, annual average concentrations exceeded an upper assessment limit of 14 $\mu g/m^3$.

Table 11.2: Results of particulate matter (PM_{10}) monitoring.

No	Measurement site	Year	Frequency of observation	Annual mean value, µg/m^3	Daily maximum value, µg/m^3	Hourly maximum value, µg/m^3	Number of exceedances of 50 µg/m^3 value
1.	Riga, centre	2000 2001 2002	daily	59* 54 58	116 176 215	n.d.	* 92 109
2.	Riga, Brivibas	2003 2004 2005	daily	56 52 54*	156 106 137	n.d.	105 99 *
3.	Riga, Valdemara	2003 2004 2005	hourly	54 48 48	229 109 166		139 137 124
4.	Riga, Tvaika	2003 2004 2005	daily	27* 31 32	61 99 92	n.d.	* 23 32
5.	Liepaja	2000 2001 2002 2003 2004 2005	daily	41* 41 44* 49 45 43	103 126 138 172 149 99	n.d.	* 65 * 78 86 69
6.	Ventspils	2002 2003 2004 2005	daily	25 16 15 18	78 127 48 55	n.d.	20 3 0 3
7.	Rezekne	2001 2002 2003 2004	daily	36* 51* 39 38*	158 250 185 98	n.d.	* * 35 *
8.	Rucava	2002	daily	52*	99	n.d.	

n.d. – no data
* less than 50 % of measurements

During the 2005-year 66% of PM_{10} concentrations were under 50 µg/m^3 limit value but in 34% of cases this limit value was exceeded (Figure 11.4).

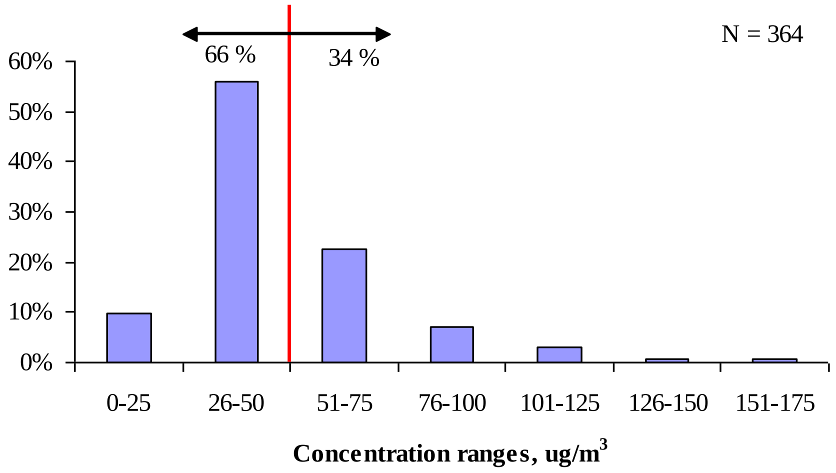

Figure 11.4: Distribution of PM_{10} concentration at station Riga, Valdemara, 2005.

Random PM_{10} measurements at the EMEP station in Rucava in July-August 2002 showed the levels similar to those at the traffic stations in Riga, with an average value of 48 μg/m^3 (Figure 11.5).

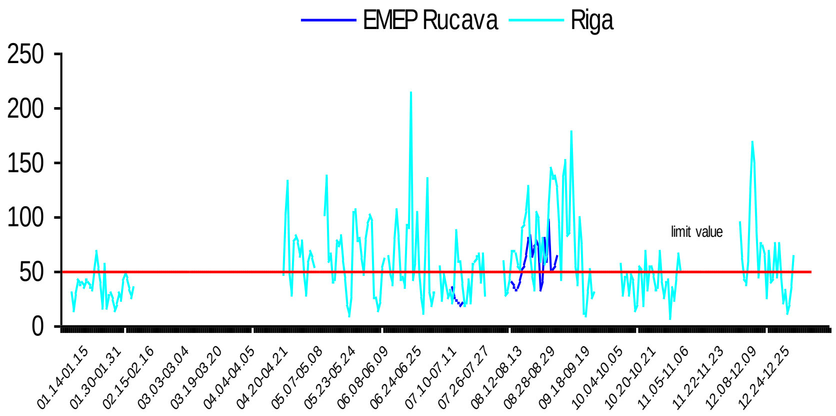

Figure 11.5: Dynamics of PM_{10} daily (μg/m^3) concentrations at EMEP (Rucava) and traffic (Riga) stations, 2002.

Annual average transboundary concentrations of PM_{10} in Latvia in 2004, calculated with the Unified EMEP model ranged within 5 to 10 μg/m^3.

The PM_{10} annual average concentration for the traffic stations in Latvia was in generally higher compared to other European countries (Figure 11.6).

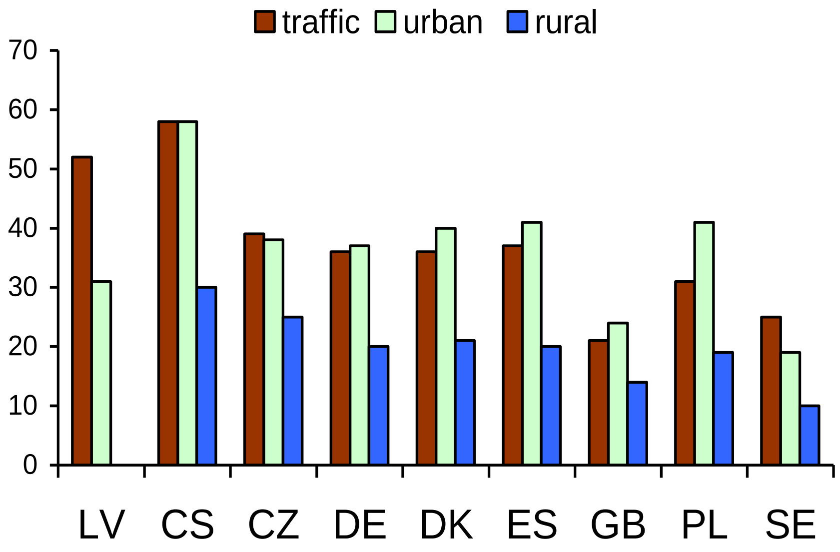

Figure 11.6: Annual average concentrations of PM_{10} (μg/m^3) in Latvia and other European countries, 2004.

11.4.2 *Hourly, daily and monthly variations*

The causes of daily variations between the heavy polluted days and the days of good air quality were analyzed. The analysis involved testing of each individual variable; identification of the mathematical expression of the relationship and compilation of a list of key indicators that cause particulate matter pollution.

In comparing the hourly and daily variations at the station in Riga (Valdemara), concentration maxima were recorded in the morning, with a stable decreasing tendency over the rest of the day. Some differences (37% on average) were identified during the week days and on weekend (Figure 7). The situation was alike at other stations.

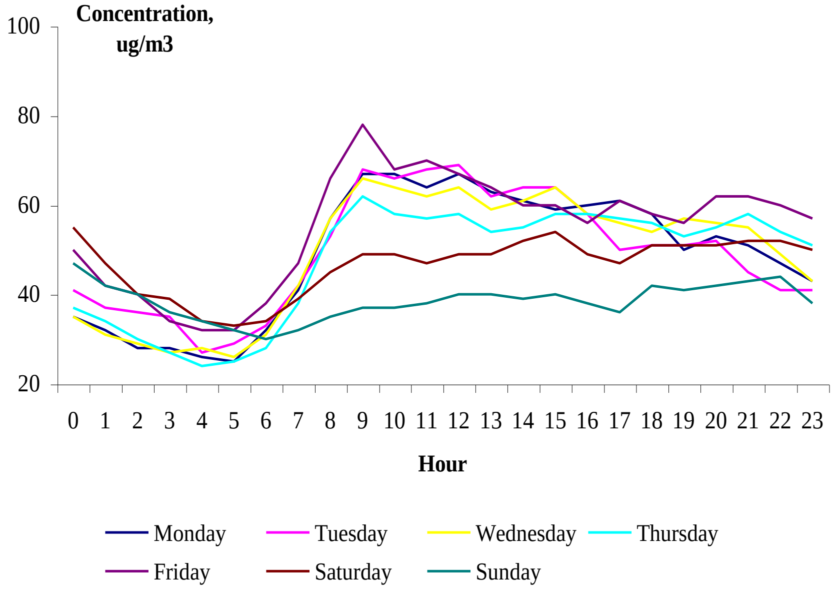

Figure 11.7: PM_{10} hourly and daily variations at station Riga, Valdemara, 2004.

An analysis of monthly variations showed the highest values during February-April (Figure 11.8).

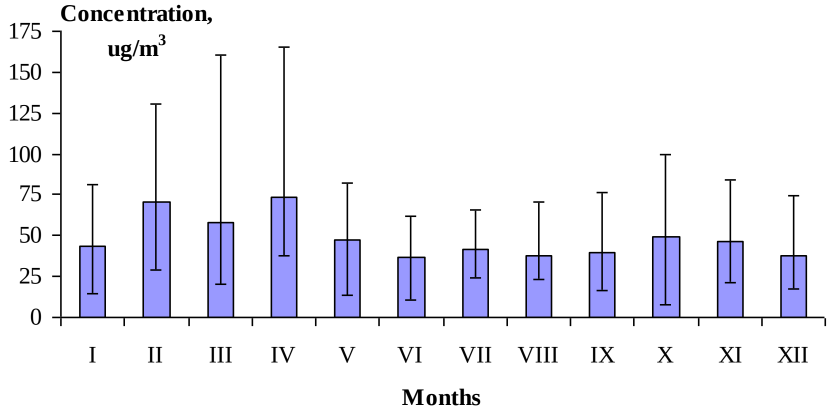

Figure 11.8: PM_{10} monthly variations at station Riga, Valdemara, 2005.

The seasonal variations were calculated for the astronomical seasons: winter: from December, 22 till March, 20; spring: from March, 21 till June, 21; summer : from June, 22 till September 22; autumn: from September, 23 till December, 21.

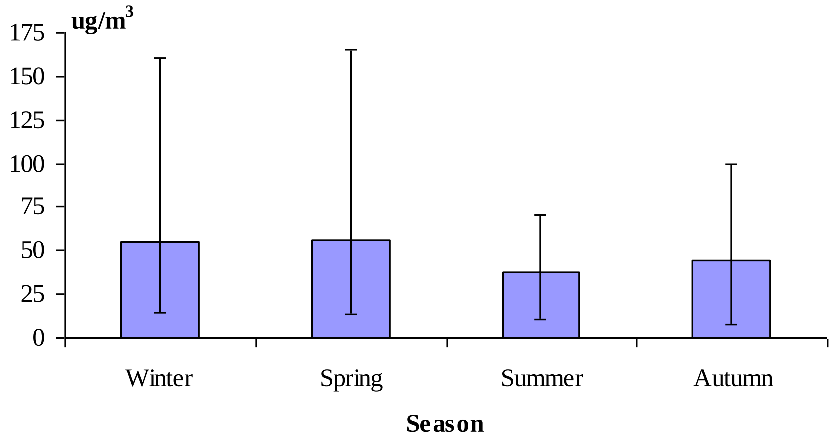

Figure 11.9: PM$_{10}$ seasonal variations at station Riga, Valdemara , 2005

The highest concentrations and variation range of PM$_{10}$ were observed in the spring and winter (Figure 11.9).

11.4.3 Influence of meteorological parameters

Precipitation significantly influences the particulate matter pollution levels. On days with precipitation, particulate matter concentrations are lower comparing to clear sky days (Figure 11.10).

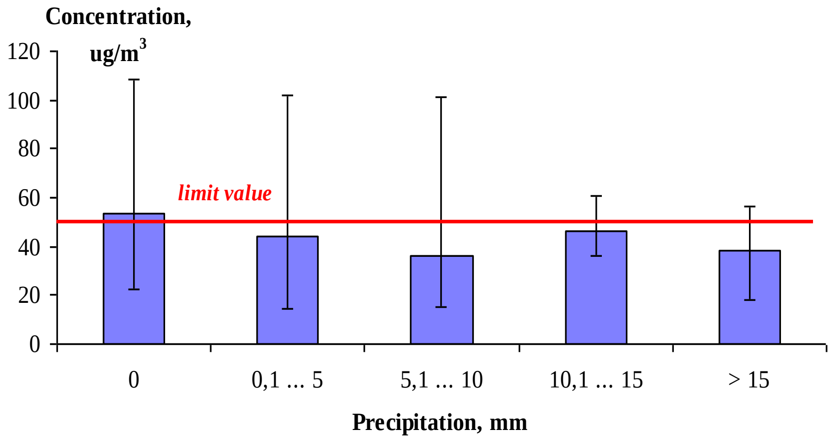

Figure 11.10:PM$_{10}$ daily concentrations on days with and without precipitation at station Riga, Valdemara, 2004.

On the so-called dry days (days without or poor precipitation), the daily limit value was exceeded in 94% of the cases (Figure 11.11).

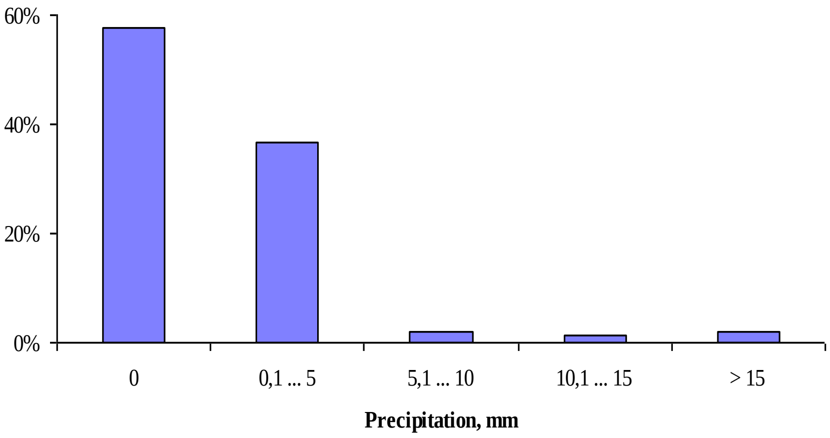

Figure 11.11:Cases of exceedance of PM_{10} *of the daily limit value on days with and without precipitation at station Riga, Valdemara, 2004.*

The wind is one of the dominant factors that effect the particulate matter pollution level. In East, South-East, and South winds (direct impact of traffic, because station is located at the left border of the street, the PM_{10} concentrations exceeded the daily limit value.

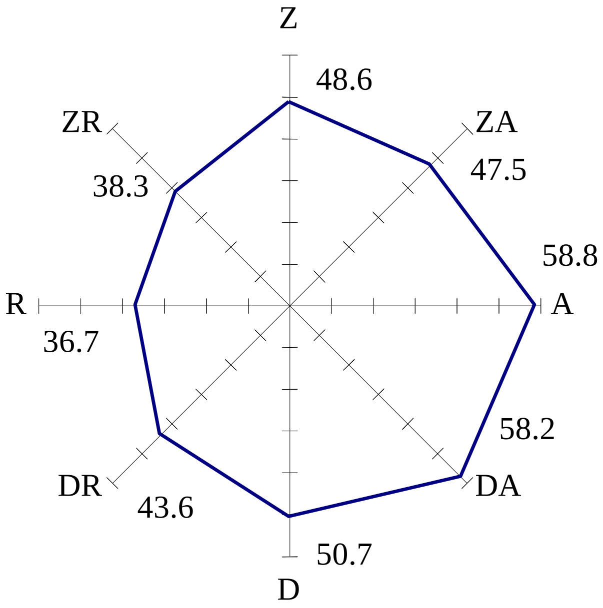

Figure 11.12:Wind rose of PM_{10} *concentrations at station Riga, Valdemara, 2004.*

Concentrations of over 100 µg/m^3 of PM_{10} increases in a wind speed of 5.5-7.9 m/s (Figure 11.13).

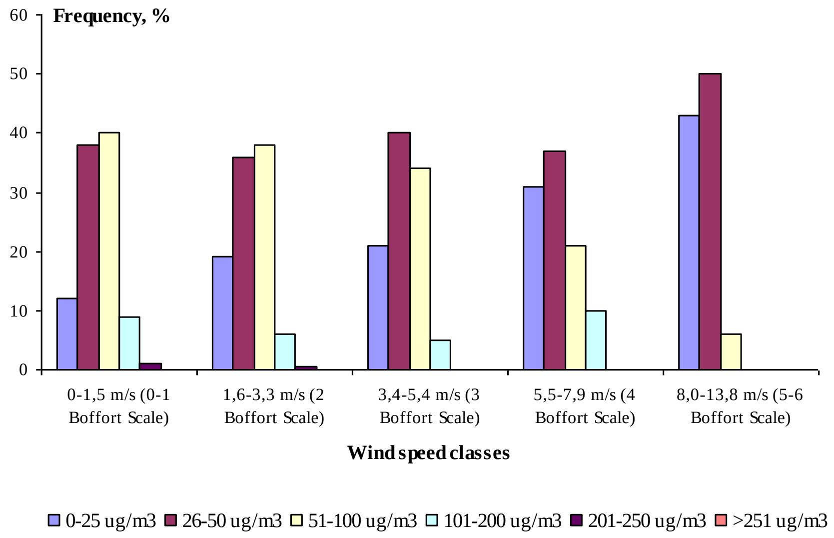

Figure 11.13:Dependence of PM_{10} concentration on the wind speed week days at station Riga, Valdemara, 2004.

During spring time some relationship was found between PM10 concentrations and relative humidity for one particular wind speed diapason (5.5-7.9 m/s), which has been selected as a transition switch for concentration specific weight changes from lower to higher one (Figure 11.14).

The lowest PM_{10} hourly concentration under definite meteorological conditions (wind speed of 5.5-7.9 m/s, relative humidity of 0-25 %) is 89 mkg/m^3 (Figure 11.15). Normally, such meteorological conditions have occurred 15 times per year, with 14 of them in spring.

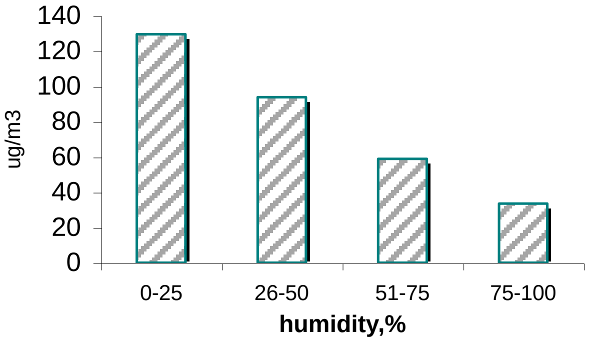

Figure 11.14: Spring PM_{10} average concentrations versus relative humidity (wind speed 5.5-7.9 m/s).

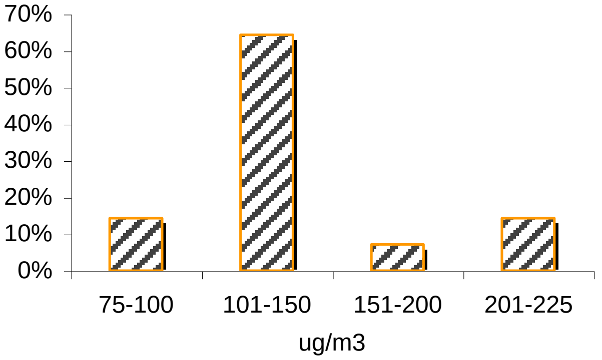

Figure 11.15: Spring PM_{10} concentration distribution (wind speed 5.5-7.9 m/s, relative humidity 0-25%).

Correlation coefficients of main pollutants and meteorological parameters were estimates as linear best to fit coefficients (Table 11.3).

Table 11.3: Correlation coefficients of main pollutants and meteorological parameters in Riga at Valdemara Street (2004).

	PM_{10}	Benzene	NOx	O3	Xylene	Toluene	Wind speed	Wind direction	Temperature	Global radiation	Relative humidity	Atmospheric pressure
PM_{10}		0.29	0.35	0.16	0.20	0.22	0.01	0.01	0.001	0.02	0.06	0.02

11.5 Conclusions

- PM_{10} is one of the pollutants of great concern for the whole of Latvia. Despite the decreasing tendency for gaseous pollutant emissions, stable and high PM_{10} pollutions levels have been determined for 2002-2005. EU annual limit value of 40 µg/m^3 for PM_{10} and daily limit value of 50 µg/m^3 was exceeded during last years.
- Concentrations of PM_{10} at rural background (EMEP) station Rucava in July-August of 2002 were at the levels measured in urbanized territories.
- Meteorological parameters such as precipitation, wind speed and direction has significant influence to PM_{10} pollution levels at some particular cases (especially at high pollution episodes), only strong direct relationship wasn't found. On dry days (days without or poor precipitation), the daily limit value was exceeded in 94% of the cases. During the spring time when wind speed varies between 5.5-7.9 m/s and relative humidity is very low (0-25%) hourly PM_{10} pollution levels could increase till 100-150 µg/m^3. Normally 15 such specific meteorological conditions have occurred per year with 14 of them during the spring.
- Some linear relationship between PM_{10} concentrations BTX and NOx was stated, the highest of them – NO_x ($R^2 = 0.35$).

11.6 References

1. Central Statistical Bureau (CSB) in Latvia, 2006.
2. Latvian's informative inventory report, submission of Latvian CLRTAP data in 2006.
3. Transboundary particulate matter in Europe, Status report 4/2006, CCC&MSC-W, 2006.

12 Particulate matter: an update of the PM_{10} levels in The Netherlands

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In 2005 the Netherlands Environmental Assessment Agency (MNP) and the National Institute for Public Health and the Environment published a comprehensive overview on the Dutch state of affairs on the particulate matter.
http://www.rivm.nl/bibliotheek/rapporten/500037011.pdf
This paper presents an update of the chapter 4 concerning the measurement data of particulate matter.

12.1 Summary

The measured concentrations of particulate matter in the Netherlands are presented with exceedances of the two European limit values and the relationship between these limit values. In addition, information about the infrastructure used for measurements, about the measurements themselves and about the measured components of particulate matter is given.

- The measured annual average concentration of particulate matter decreased with approximately 1 µg/m^3 /year.
- In the Netherlands, the limit value for the annual average concentration and that for the 24-hour average are both being exceeded. Measurements show that the limit value for the 24-hour average is exceeded more often than the limit value of the annual average concentration. The limit value for the 24-hour average therefore appears to be more stringent than the limit value for the annual average concentration.
- Particulate matter concentrations are measured in the Netherlands equivalent to the methodology prescribed in European legislation. Measurements of PM_{10} are conducted in the Netherlands at 39 locations; 22 of these locations are in urban surroundings.
- Components of particulate matter are: inorganic secondary components, components that contain carbon, sea salt, oxides of metals and silicon and water. Sea salt and soil dust are important components of particulate matter; on an annual average basis, they amount to 20% to 30% of total particulate matter.
- Meteorological influences can lead to fluctuations in the annual average particulate matter concentration of around 5 µg/m^3.
- Subtracting the contribution of sea-salt aerosol from the total particulate matter concentration has little effect on how often the limit value for the 24-hour concentration is exceeded. On average for the Netherlands, it is estimated that subtracting sea-salt aerosol results in six fewer days when the limit value for the 24-hour average is exceeded.

12.2 Concentrations in the Netherlands

The air quality regarding particulate matter in the Netherlands has improved during the past decade. The annual average concentrations have declined by 25%

in ten years. During the same period, the number of days with a 24-hour average concentration above 50 µg/m^3 declined by 50%. Nevertheless, both limit values are still exceeded in the Netherlands. It appears that the limit value for the 24-hour average is exceeded more often than the limit value for the annual average concentration (Figure 12.1–Figure 12.4).

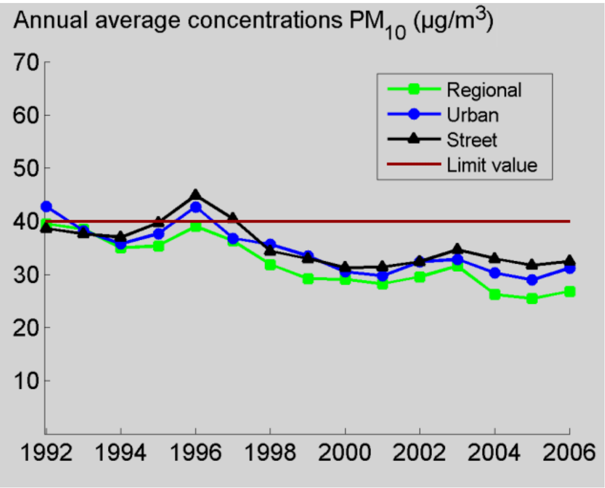

Figure 12.1: Measured annual average particulate matter concentrations in the Netherlands from 1992- 2006. The trend lines indicate the average of the stations in the corresponding group.

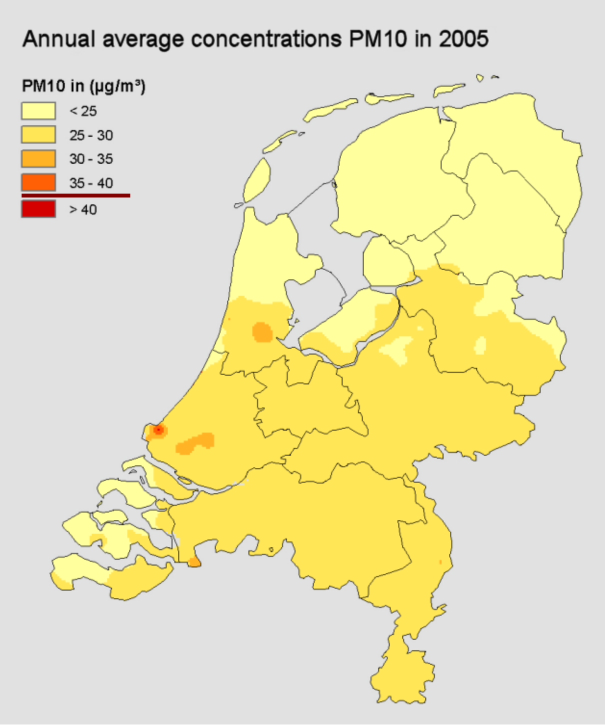

Figure 12.2: Annual average concentration of PM$_{10}$ in 2005. The map for the annual average concentrations was obtained from measurement results from the Dutch National Air Quality Monitoring Network combined with model calculations.

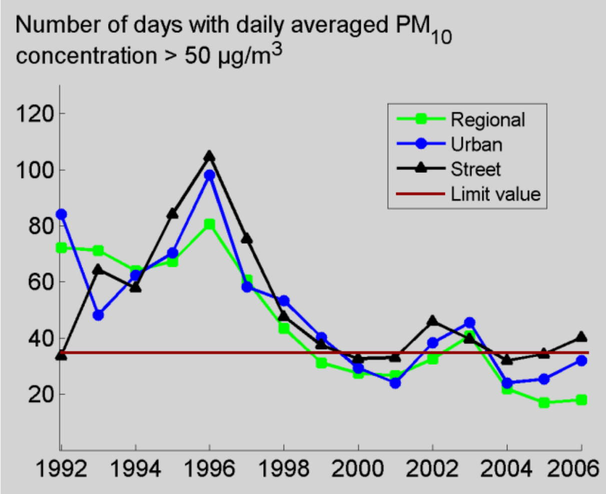

Figure 12.3: The number of days with a 24-hour average above 50 µg/m³ in the Netherlands in the period 1992-2006 at three types of measurement stations.

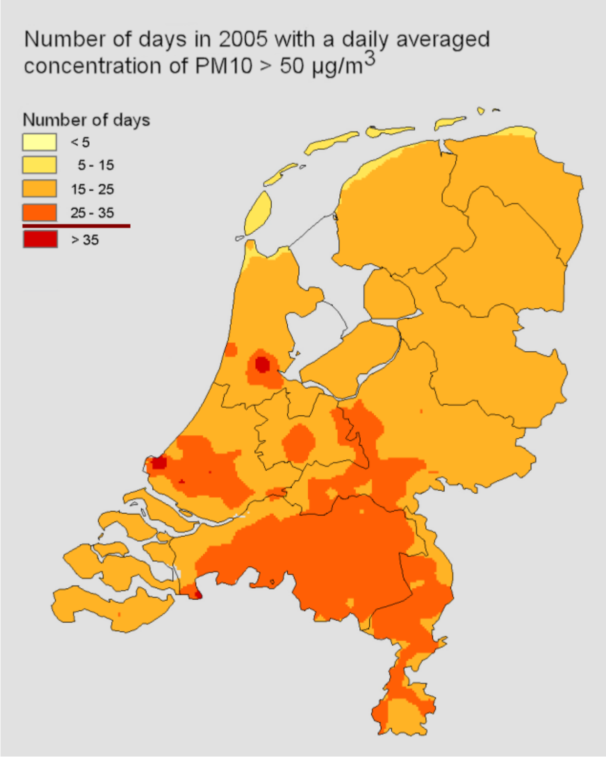

Figure 12.4: The map for the number of days exceeds the 50 µg/m³. The plot is based upon the relation between annual average concentration and the number of days with a daily average > 50 µm/m³. The compliance problems concerning the limit value for the 24-hour average are concentrated on some spots/cities.

Urban increment

A simple approach to study the typical increment of PM_{10} levels in Dutch cities is to calculate the difference between the average levels of PM_{10} in the three type of monitoring stations as shown in Figure 12.1. In the period 2004-2006 the average levels are shown in Table 12.1. The distribution of PM_{10} monitoring stations across the country is distributed quite homogeneously for the regional stations while city-background stations are concentrated in the Southern/Western (SW) part of the country. On average levels at urban background locations are about 3 $\mu g/m^3$ higher than the regional stations in the same area. Note that the average of the SW subset is only about 1 $\mu g/m^3$ higher than the national average indicating that the gradient of background levels over the Netherlands is quite small.

Table 12.1: Annual average PM_{10} levels in $\mu g/m^3$ for the various types of stations.

	Regional (all)	**Regional (subset SW)**	**Urban background**	**Urban background increment**	**street**
2004	26	27	30	3	33
2005	25	26	29	3	32
2006	27	27	31	4	32
average	26	27	30	3	32

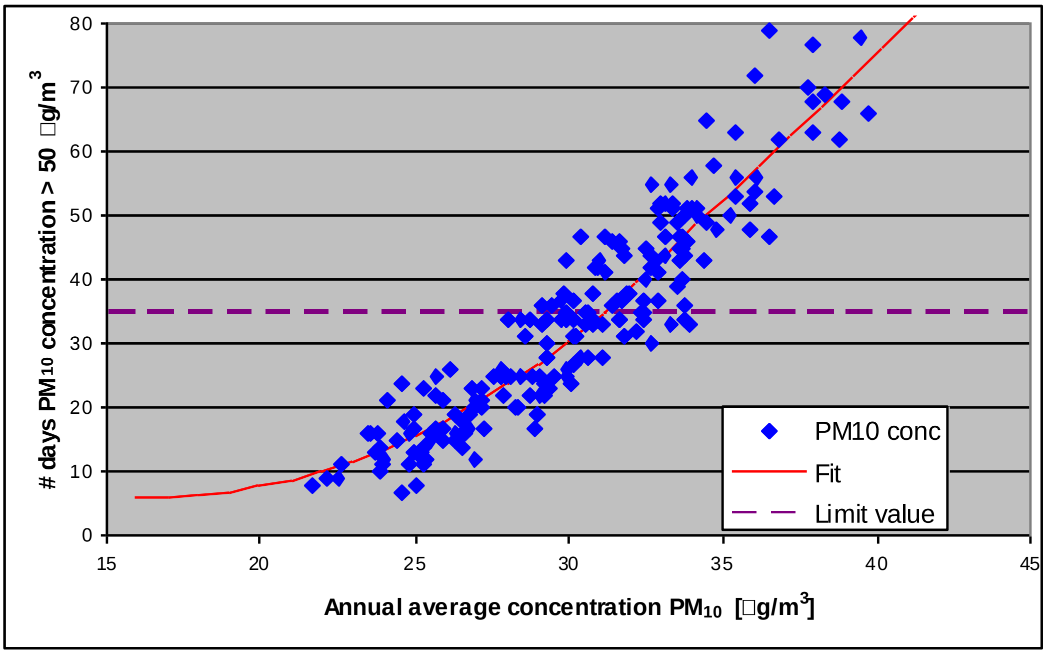

Figure 12.5: Relationship between the annual average particulate matter concentration and the number of days with a 24-hour average above 50 $\mu g/m^3$. In the linear part of the relationship, high concentrations, every additional microgram of particulate matter results in five more days that exceed the limit value for the 24-hour average concentration. According to this relationship, an annual average concentration of 31 $\mu g/m^3$, corresponds to 35 days with a 24-hour average concentration of 50 $\mu g/m^3$.

The measurement results for particulate matter also show the relationship between the two European limit values: the limit value for the annual average concentration, 40 µg/m^3, and the limit value for the 24-hour average; the latter is a maximum of 35 days per year with a 24-hour average concentration above 50 µg/m^3 (Figure 12.3). This relationship shows that the limit value for the 24-hour average corresponds with an annual average particulate matter concentration of approximately 31 µg/m^3. The limit value for the 24-hour average is therefore significantly more stringent than the limit value for the annual average concentration.

12.3 Trends in the concentration

Figure 12.6 shows the trend in the annual average particulate matter concentration at the regional stations of the Dutch National Air Quality Monitoring Network. Assuming a linear relation the figure shows an approximated annual decreasement of 1 µg/m^3. The figure shows variations of the annual average particulate matter concentration up to 5 µg/m^3 which is most likely due to variation in meteorology-cal conditions.

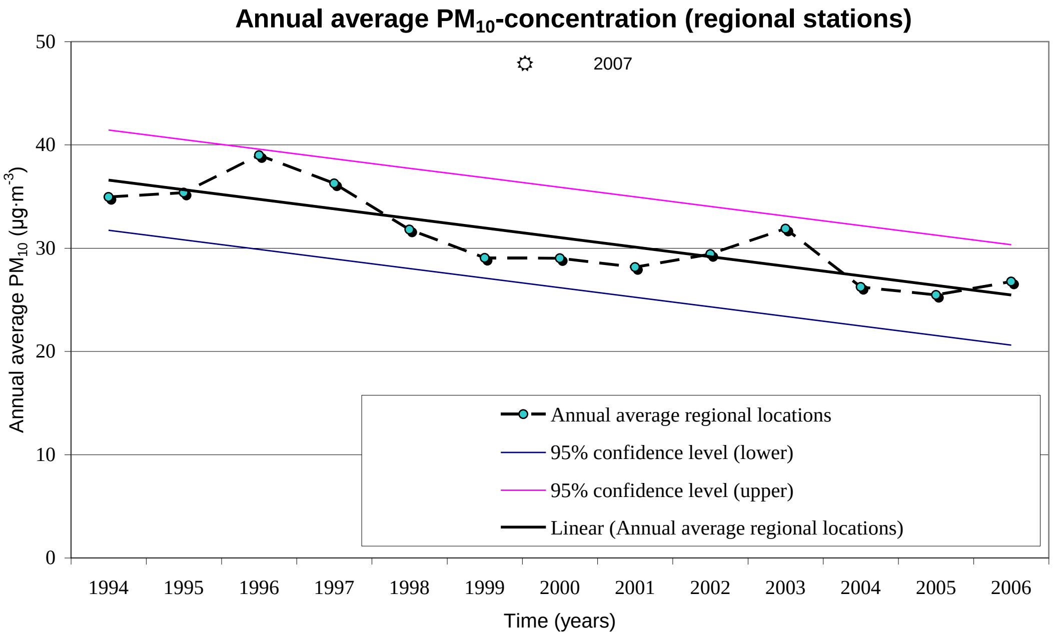

Figure 12.6: Measured trend in the annual average particulate matter concentration at the regional stations of the Dutch National Air Quality Monitoring Network. The figure shows variations of the annual average particulate matter concentration up to 5 µg/m3 (95 % confidence interval).

12.4 Monitoring infrastructure

The monitoring of particulate matter concentrations has taken place in the Netherlands since 1992 (Van Elzakker, 2001). Initially, there were 19 monitoring stations in the monitoring network for particulate matter in the Netherlands. The Netherlands has chosen the numbers of monitoring stations in such a way that it is possible on the basis of the measurement results alone – therefore without the use of models – to provide a representative picture of the air quality for particulate matter in the Netherlands.

Beginning 2007, there were 17 regional stations, 7 urban background stations and 15 street stations in the monitoring network for particulate matter. One more street station is planned this year. This will bring the total number of monitoring stations for particulate matter up to the intended number of 40. In 2006 no exceedances of the annual average concentration were found. Exceedances of the number of days above 50 µg/m^3 were in 2006 not observed at regional stations and at approximately 50 % of the urban background stations and 60 % of the street stations.

In the Netherlands, there are also a number of regional and local authorities which monitor particulate matter. The provinces of Limburg and North Holland have monitoring networks with two and six monitoring stations, respectively. The monitoring network of the DCMR Environmental Protection Agency in the Rotterdam region, has three monitoring stations, and the monitoring network of the GGD, Municipal Health Centre[16], in Amsterdam comprises five monitoring stations.

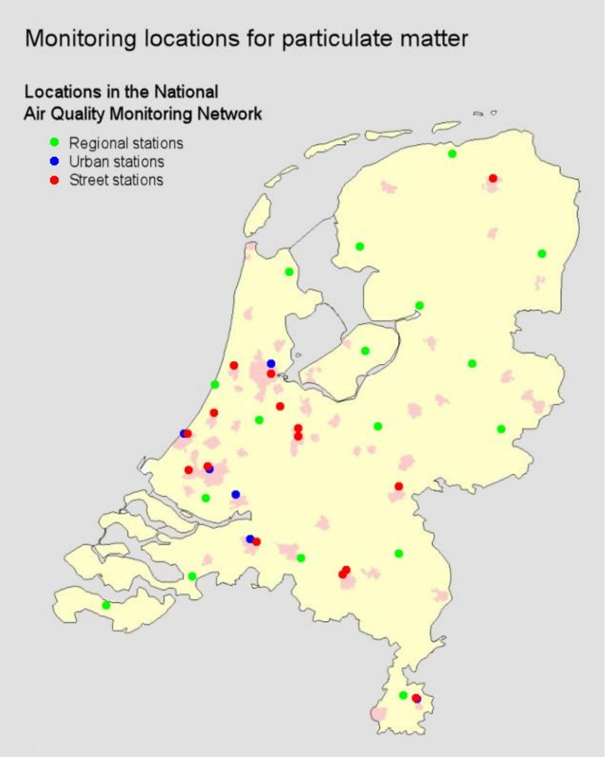

Figure 12.7: Monitoring locations for particulate matter (PM$_{10}$) in the Dutch National Air Quality Monitoring Network 2006. Local monitoring networks for particulate matter are not shown.

12.5 Measurement method

The particulate matter measurements are conducted in the Netherlands with automatic monitoring apparatus that works according to the principle of the attenuation of beta radiation. At the end of 2006 the number of comparison

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[16] See also contribution from Ernie Wijers and Saskia van der Zee on PM gradients in the Amsterdam area

measurements was sufficient for calibration of the automatic measurements to the reference method and equivalence was demonstrated [Beijk *et al* (2007)].

Before 1992, particulate air pollution was monitored in the Netherlands only in the form of black smoke (Van Elzakker, 2001). However, black smoke is only a portion of particulate matter (and $PM_{2.5}$). Therefore, statements about a possible trend in particulate matter concentrations can only be made on the basis of data from 1992 onwards.

12.6 Components of particulate matter

The measurement of particulate matter with the beta attenuation method is given in terms of mass per unit volume. It does not provide any information about the chemical composition of the particulate matter. Research has shown that the most important components of particulate matter are inorganic secondary components, carbon containing components, sea salt, oxides of metals and silicon and water (Visser et al., 2001). Sea salt and soil dust are important components of particulate matter: on a yearly average, they amount to 20% to 30% of total particulate matter. Between 25% and 50% of the sea salt aerosol is composed of particles in the $PM_{2.5}$ fraction (Visser et al., 2001). Sea salt and the natural component of soil dust cannot be influenced by policy measures. Moreover, it is very probable that sea salt does not have any health effects. In current European legislation for particulate matter, however, the total concentration, therefore including fractions of natural origin, is regulated. As a result, a discussion is now taking place in the Clean Air for Europe (CAFE) programme about the possibility of making a statutory exception for components in particulate matter of natural origin which are also viewed as non-hazardous. An important question is: what is the relationship between the concentrations of sea salt and soil dust on the one hand and non-compliance with the limit values on the other? To answer this question, an initial estimate of the long-term average contribution of sea-salt aerosol to the particulate matter concentration in the Netherlands was made. This contribution was estimated at 4 - 5 $\mu g/m^3$. Measurements have shown that the annual average sea-salt aerosol concentration on the coast is between 5 and 8 $\mu g/m^3$; in the southern province of Limburg and on the eastern border of the Netherlands, this value is 3 $\mu g/m^3$ (Figure 12.8). Measurements of sea salt aerosol in the German federal state of Nordrhein- Westfalen indicate an average concentration of 1 to 2 $\mu g/m^3$. These figures support the assumed distribution across the Netherlands.

Tentative estimates indicate that subtracting the contribution of sea-salt aerosol would bring the particulate matter concentration below the limit value for the annual average concentration of 40 $\mu g/m^3$ (under average meteorological conditions). It is expected that this limit value would then only be exceeded locally, due to local traffic contributions. Non-compliance with the limit value for the 24-hour average is the most acute problem concerning the air quality regulations for particulate matter. However, the subtracting of the contribution of the sea-salt aerosol will have little effect on bringing the Netherlands into compliance with the limit value for the 24-hour average. This is because high particulate matter concentrations generally occur due to air movement from continental Europe. Under such conditions, the share of sea-salt aerosol in the particulate matter concentration is quite small. The relationship between exceeding the limit value for the 24-hour average particulate matter concentration and the concentration of sea-salt aerosol has been investigated based on several measurements. It is estimated that subtracting the sea-salt aerosol will lead, on average for the Netherlands, to six fewer days when the value for the 24-hour average is exceeded. This estimate has a 50% uncertainty.

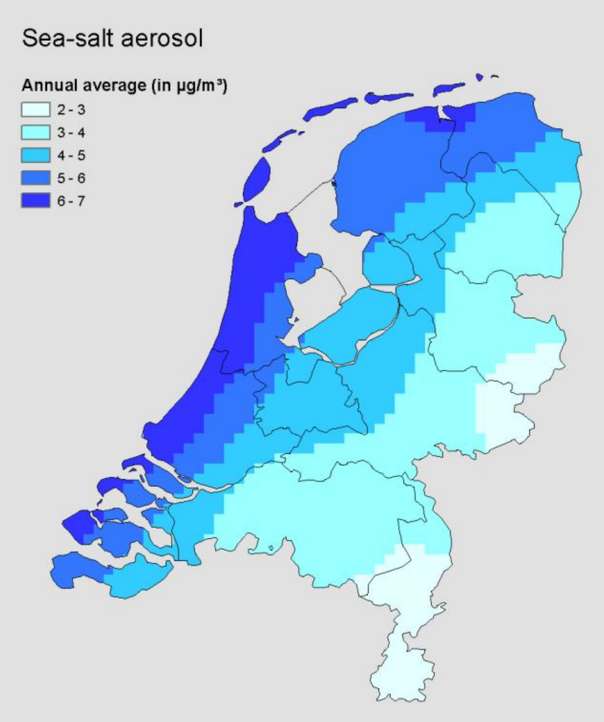

Figure 12.8: Annual average contribution of sea salt aerosol to the particulate matter concentration in the Netherlands. The estimate is based on interpolation of monitoring results and has been combined with assumptions about the distribution of sea salt along the Dutch coast (Eerens et al., 1998).

12.7 Chemical composition of particulate matter in the Netherlands

Recent measurements of the chemical composition of particulate matter in the Netherlands have led to a good understanding of the average composition of particulate matter (Visser et al., 2001). The components are the following:

Inorganic secondary components. This primarily concerns sulphate (SO_4), nitrate (NO_3) and ammonium (NH_4) aerosol. These particles are formed in the atmosphere from the gases sulphur dioxide (SO_2), nitrogen oxides (NO_x) and ammonium (NH_3). The contributions in terms of mass of these components to the annual average concentration is around 10 µg/m^3. Approximately 90% of these components are found in the $PM_{2.5}$ fraction. Virtually all these secondary components are of anthropogenic origin.

Carbon-containing components. This primarily concerns elementary carbon and organic compounds. The majority of these compounds are emitted directly into the atmosphere. The contribution in terms of mass of these components is 5 µg/m^3, of which 1 µg/m^3 is elementary carbon and 4 µg/m^3 comprises organic compounds. Soot is composed of a mixture of elementary carbon and organically bound carbon. A small portion of the carbon-containing components is formed in the air by a chemical reaction; this is the secondary organic aerosol. Of the carbon-containing components, 90% are found in the $PM_{2.5}$ fraction. This group also contains a very small (in terms of mass) quantity of polycyclic aromatic hydrocarbons (PAHs). The elementary carbon and the PAHs are entirely of anthropogenic origin, while the other organic compounds are partly of natural origin and partly of anthropogenic origin.

Sea salt. Sea salt is composed primarily of sodium chloride (table salt) with a smaller contribution from magnesium, calcium and potassium compounds. Sea-salt aerosol is of natural origin and is formed in the air when the wind blows over the sea's surface. On average across the Netherlands, the contribution in terms of mass of sea salt is 4-5 $\mu g/m^3$. Between 25% and 50% of the sea salt is found in the $PM_{2.5}$ fraction.

Oxides of metals and silicon. This primarily concerns oxides of silicon, aluminium, calcium, iron and potassium. This can be largely attributed to windblown soil dust. This soil dust comes into the air primarily as the result of human activities. The total soil dust concentration is on the order of 4 $\mu g/m^3$ on average across the Netherlands. Soil dust is largely comprised (70% to 90%) of particles larger than $PM_{2.5}$.

Water. Components of particulate matter, especially inorganic secondary components, can contain chemically-bound water. The contribution of chemically-bound water is estimated at 10% to 15% of the total particulate matter concentration. The share of water in the $PM_{2.5}$ fraction is larger because water is bound especially to inorganic secondary components.

12.8 References

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13 Particulate matter gradients in the Amsterdam area

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13.1 PM network data for Amsterdam for 2002-2005

The Amsterdam Air Quality Network[17] provides daily PM_{10}, $PM_{2.5}$ and PM_1 air quality data across various sites through Amsterdam. The PM network consists of two urban background sites, one roadside station, and one kerbside motorway station. For an overview of the locations see Appendix A. In this study daily PM_{10} data of the rural station De Rijp[18] (35 km north of Amsterdam) were also available.

The data reported here have been provided by TEOM instruments *without* gravimetric correction (i.e. the data have *not* been adjusted for underestimation of the volatile fraction). Table 13.1 summarizes the annual mean concentrations for the various sites over the 2002-2005 period.

Table 13.1: Annual mean PM data for 2002-2005 for sites taken from the Amsterdam Air Quality Network and the urban background station De Rijp.

annual mean	**2002-2005**		
site	**PM_{10}**	**$PM_{2.5}$**	**PM_1**
kerbside motorway			
Ringweg A10west	27.8		13.7
roadside			
Stadhouderskade	24.9		13.2
urban background			
Overtoom	20.6	13.7	10.8
Westerpark	20.8	13.4	
rural			
De Rijp	18.3		

The presence of a rural level with superimposed Amsterdam and traffic increments to PM is apparent from Table 13.1 and visually summarized in Figure 13.1. Averaged over the 2002-2005 period the Amsterdam increment for PM_{10} is 2.3 $\mu g/m^3$. PM_{10} traffic increments range from 4.2 $\mu g/m^3$ (road) to 7.1 $\mu g/m^3$ (motorway). The total increment in the PM_{10} data (from regional background to the motorway) is 9.4 $\mu g/m^3$.

For PM_1 traffic increments are 2.4 $\mu g/m^3$ (from urban background to road traffic) and 2.9 $\mu g/m^3$ (urban background to motorway traffic).

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[17] operated by the Department of Air Quality of the Municipal Health Centre of Amsterdam.

[18] owned by the Provincial Authority of Noord-Holland and maintained by the Amsterdam Network organization.

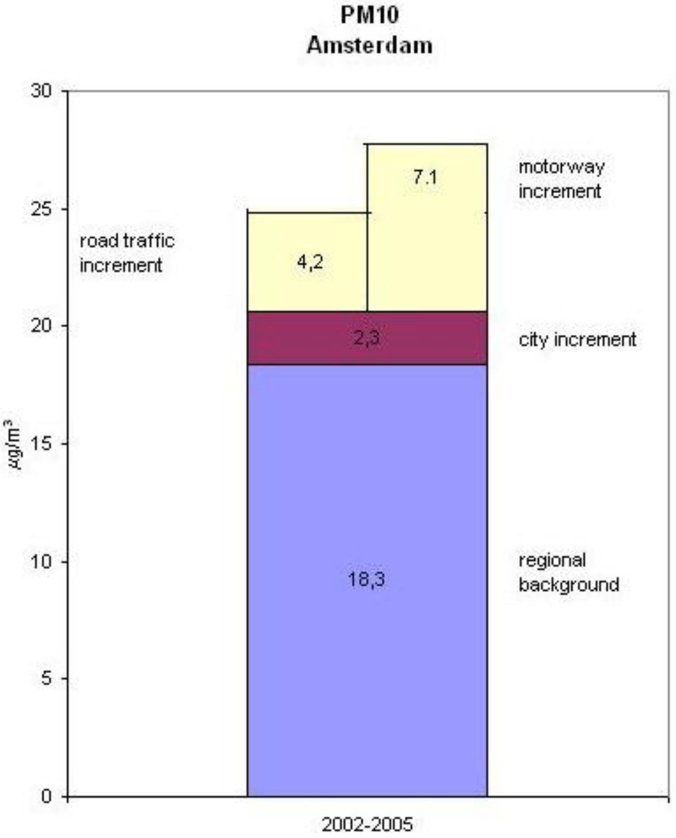


Figure 13.1: Urban and traffic increments for PM_{10} ($\mu g/m^3$) in Amsterdam with respect to regional background (De Rijp) averaged over 2002-2005.

Based on the average of the daily ratios between sites, the Amsterdam background PM_{10} concentration appears 14% higher than the rural background concentrations; the PM_{10} concentrations at the Amsterdam roadside and motorway stations are 25% and 38% higher than the urban background level, respectively. The largest increase (difference observed between the motorway and rural background level) is 57%.

Figure 13.2 displays corresponding changes in the PM_1 ("fine") and PM_{10-1} ("coarse") fractions. It is concluded that:

a) the road traffic increment (+4.2 $\mu g/m^3$) is due to an increase of the PM_1 fraction with 2.4 $\mu g/m^3$ and an increase of PM_{10-1} fraction with 1.9 $\mu g/m^3$,

b) the motorway increment in PM_{10} (+7.1 $\mu g/m^3$) is predominantly due to an increase in the coarse fraction (PM_{10-1}) with 4.2 $\mu g/m^3$, most likely caused by higher traffic-induced emissions from abrasion and more resuspension from the motorway.

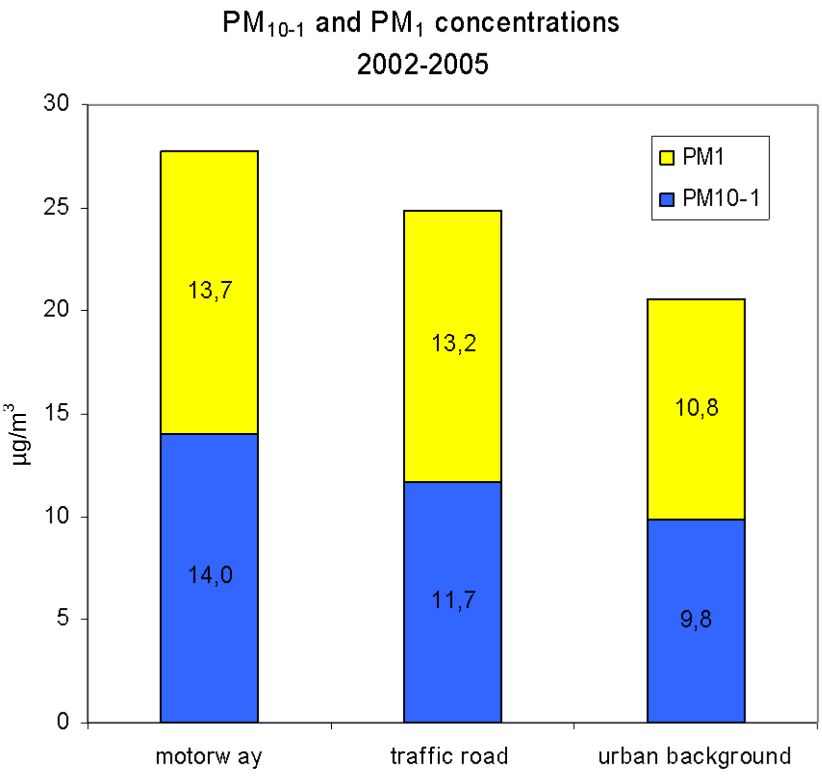


Figure 13.2: Annual mean PM_{10}, PM_1 and PM_{10-1} concentrations for 2002-2005 in the Amsterdam Air Quality Network.

13.2 Correlations between PM_{10}, $PM_{2.5}$ and PM_1

Correlation coefficients R^2 and regression slopes (with zero intercepts) between daily mean PM_{10}, $PM_{2.5}$ and PM_1 concentrations are given in Table 13.2. In general, correlations are good. It is concluded that the fine particles, $PM_{2.5}$, constitute at least 65% of PM_{10} at the urban background stations; for PM_1 this is around 53%. The regression slope for PM_1/PM_{10} is lowest at the A10west motorway site due to traffic-induced emissions from abrasion and resuspension. For PM_1 the similarity between Stadhouderskade and Overtoom is remarkable.

Table 13.2: Correlation coefficients and regression slopes between PM_{10} and $PM_{2.5}$ at Overtoom and Westerpark (urban background), and between PM_{10} and PM_1 at Ringweg A10west (motorway), Stadhouderskade (roadside) and Overtoom during 2002-2005.

Site	**R^2**	**regression slope $PM_{2.5}/PM_{10}$**
Overtoom	0.77	0.67
Westerpark	0.80	0.66
Site	**R^2**	**regression slope PM_1/PM_{10}**
Ringweg A10west	0.81	0.50
Stadhouderskade	0.69	0.53
Overtoom	0.69	0.53

13.3 Correlations between sites

Correlation coefficients between stations are given in Table 13.3 for PM$_{10}$, PM$_{2.5}$ and PM$_{1}$, respectively. In general, the daily time series at the various stations are clearly correlated. A strong correlation is found for both PM$_{10}$ and PM$_{2.5}$ at the urban background stations Overtoom and Westerpark (0.84, 0.85). Both sites also have a strong correlation for PM$_{10}$ with the rural site De Rijp (0.79). This indicates that the day-to-day variations in PM$_{10}$ are strongly influenced by day-to-day variations in meteorology. The same pattern of meteorological variability influences these sites to a similar extent.

Somewhat weaker correlations are found between the daily mean concentrations of PM$_{10}$ at the motorway site A10west and road site Stadhouderskade, and the regional background station (de Rijp): 0.63 and 0.71, respectively, indicating the effect of local traffic sources which appears stronger at A10west. A strong correlation for PM$_{10}$ exists for Stadhouderskade with the urban background stations (0.83-0.84), comparable with the correlation between the urban background stations (0.85).

Table 13.3: Correlation coefficients (R2) between daily mean mass concentrations during 2002-2005.

PM$_{10}$	A10west	Stadhouderskade	Overtoom	Westerpark
A10west	1			
Stadhouderskade	0.75	1		
Overtoom	0.74	0.83	1	
Westerpark	0.79	0.84	0.85	1
De Rijp	0,63	0,71	0,79	0,80

PM$_{2.5}$	Overtoom	Westerpark
Overtoom	1	
Westerpark	0.85	1

PM$_{1}$	A10west	Stadhouderskade	Overtoom
A10west	1		
Stadhouderskade	0.85	1	
Overtoom	0.84	0.89	1

Correlation coefficients in Table 13.3 for PM$_{1}$ are larger than those for PM$_{10}$, probably due to the large variability in the vehicle resuspension contribution to PM$_{10}$ which is absent in PM$_{1}$. Summarizing, PM concentration levels appear dominated by prevailing meteorology. The strongest local contribution is seen at the motorway site, most likely due to resuspension and abrasion.

13.4 Annual variation of PM$_{10}$

The correlations between the daily mean PM concentrations monitored at the different stations across Amsterdam and at De Rijp suggest that the day-to-day variations in PM levels are mainly caused by meteorology. PM levels are affected by meteorology in two ways:

1. similar meteorological influences act upon different local sources at the various sites and act to produce coordinated variations in PM levels locally, and
2. similar meteorological influences bring similar contributions from distant sources to the urban sites.

The annual variation of PM_{10} concentration at various stations (Figure 13.3) clearly illustrates the meteorological influence. All stations have a similar variation. The highest concentrations occur in the period February-April (due to conditions characterised by low wind speed and low amounts of rainfall), the lowest in the period May-July and October-November. The relatively high levels in December are caused by firework.

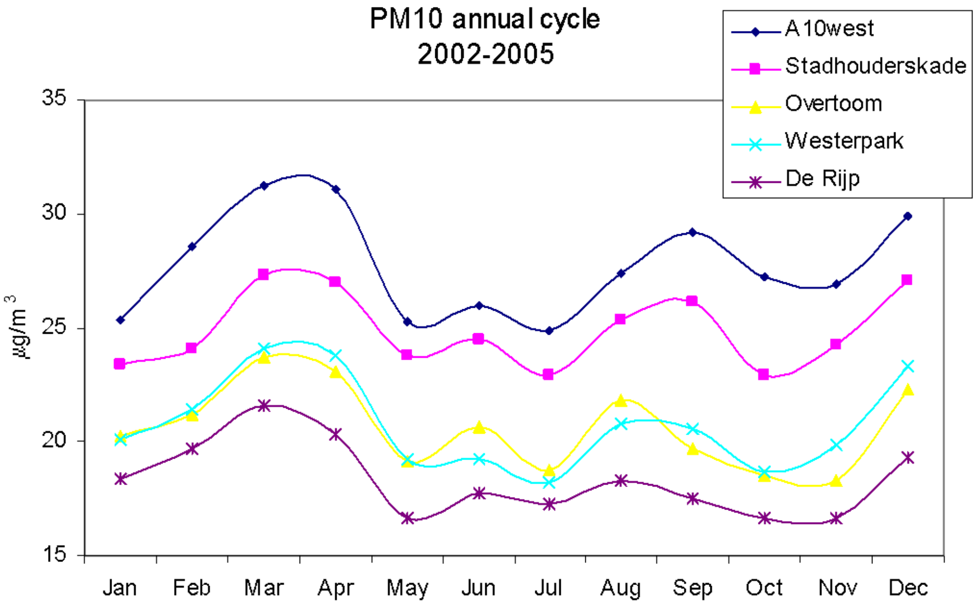


Figure 13.3: Annual variation for monthly averaged PM_{10} concentrations (Amsterdam Network; De Rijp; 2002-2005).

13.5 Wind direction dependent variation of PM_{10}, PM_1 and PM_{10-1}

Figure 13.4 shows the mean PM_{10}, PM_1 and PM_{10-1} concentrations as function of wind direction sector. Clearly, these pollution roses show evidence of increased PM contributions originating from certain wind directions: the maximum PM_{10} and PM_1 values occur when the wind direction is between East and South. All stations (including the background station De Rijp) have a similar pattern indicating the dominance of larger-scale transport of polluted air masses. The largest variation is measured at the motorway station A10west which should be due to additional contributions of emissions in the city (A10west lies in the western part of Amsterdam) and a rather large superimposed vehicular contribution.

The coarse fraction PM_{10-1} shows a different behaviour at Stadhouderskade and Overtoom: higher levels during western air transport. This generally coincides with higher wind speeds leading to more resuspension.

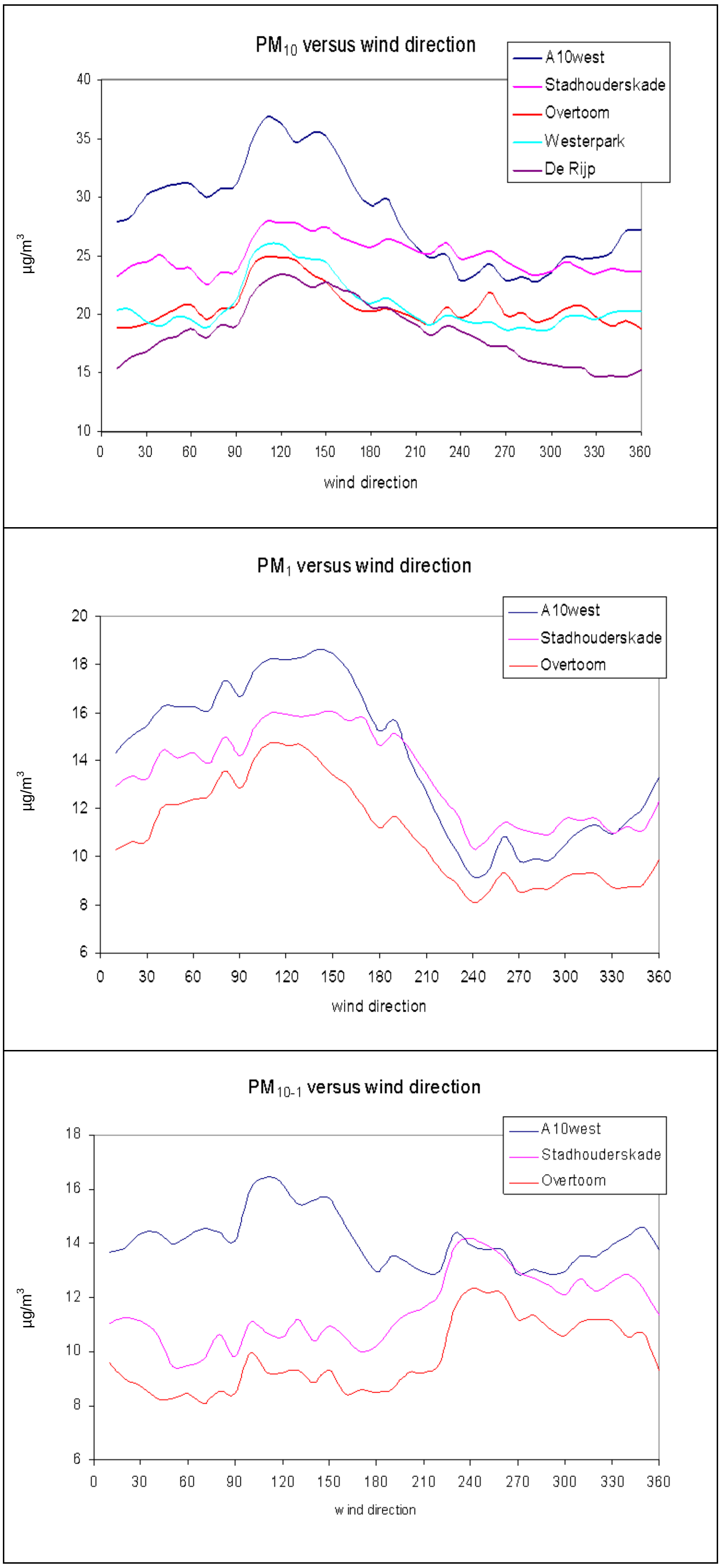
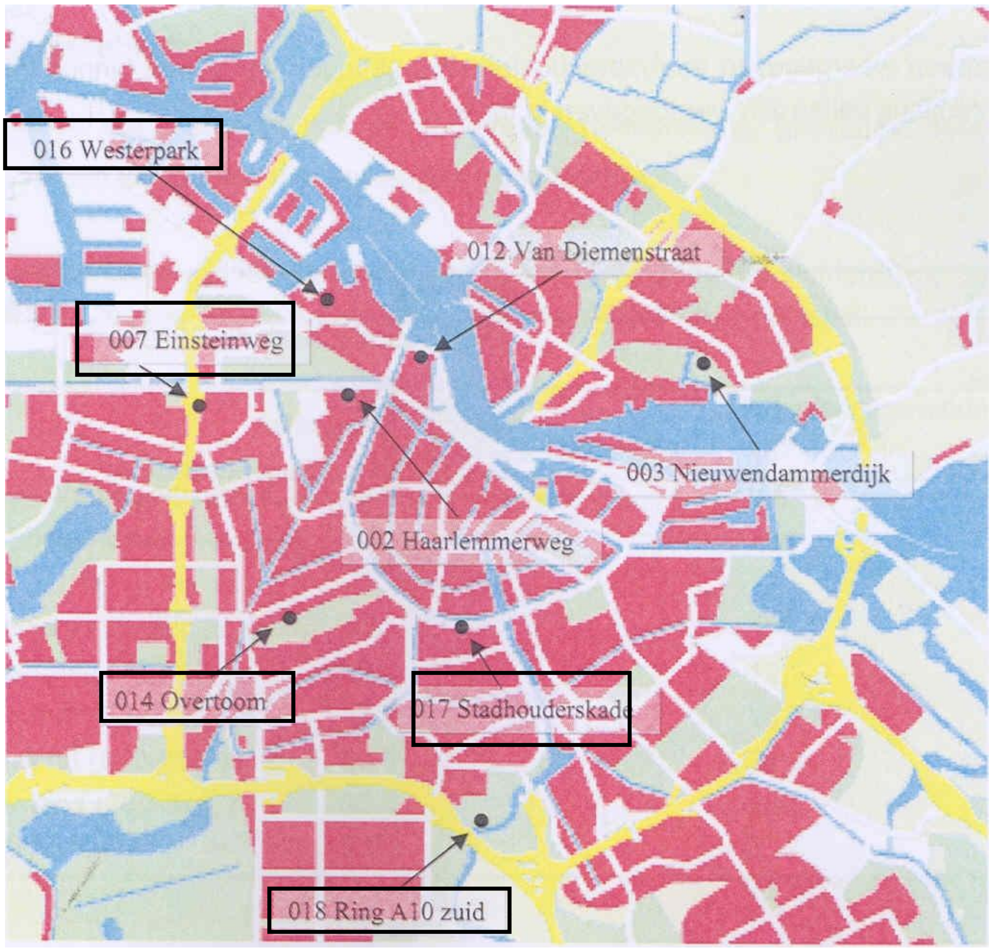


Figure 13.4: PM$_{10}$, PM$_1$ and PM$_{10-1}$ concentrations observed as function of wind direction sector at various monitoring stations.

Appendix A

Location of the PM measuring stations of the Amsterdam network



14 Concentrations of particulate matter (PM_{10}, $PM_{2.5}$) in Norway Annual and seasonal trends and spatial variability

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14.1 PM data for Norway

Norway has only one rural background site that measure mass concentrations of PM, Birkenes. The site is located approximately 20 km from the Skagerak coast, 190 m a.s.l., in the southern part of Norway, and is frequently influenced by episodes of transboundary air pollution from continental Europe. At Birkenes, daily concentrations of PM_{10} have been reported since 2000, while $PM_{10-2.5}$ and $PM_{2.5}$ was added in 2001.

Sampling of PM_{10} is performed in several urban areas in Norway, but unfortunately not always on a continuous basis at all sites. Typically, the data coverage during summer is poorer than in winter. In 2005, annual sampling was performed at nine traffic sites and at seven urban background sites in seven Norwegian sites. Measurements of $PM_{2.5}$ were performed at six traffic sites and at only two urban background sites in four cities. All sites were located at altitudes below 350 m a.s.l. The geographical situation of the sites is shown in Figure 14.1.

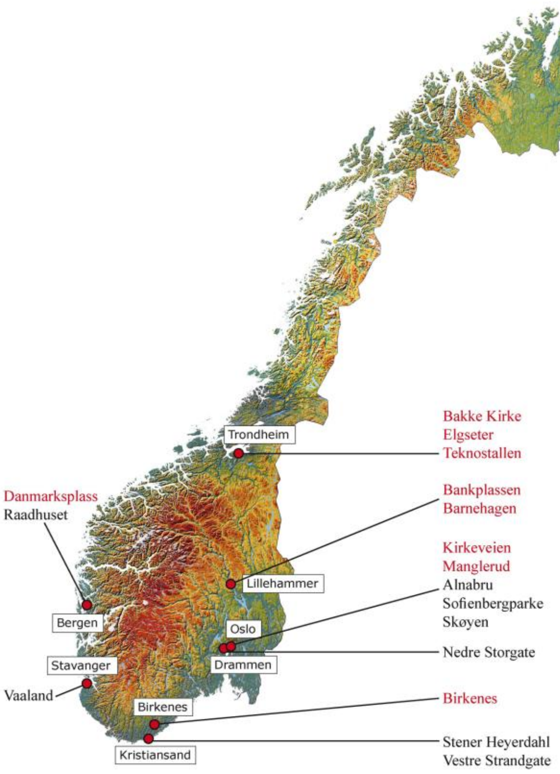

Figure 14.1: Geographical situation of the rural background, urban background, and traffic sites, in Norway reporting measurements of PM in 2005. Black text indicates measurements of PM_{10}, whereas red text means measurements of both PM_{10} and $PM_{2.5}$.

14.2 Sampling methodology

At the rural background site, $PM_{10-2.5}$ and $PM_{2.5}$ aerosol filter samples are collected using a Partisol DICHO 2025, which mass concentrations subsequently are decided gravimetrically. From 2001, the mass concentration of PM_{10} is obtained by adding those of $PM_{2.5}$ and $PM_{10-2.5}$. At the urban background and the traffic sites, concentrations of PM_{10} and $PM_{2.5}$ are measured using monitors, either Beta Gauge or TEOM technology (Tapered Element Oscillating Microbalance). The TEOM monitors use a correction factor of 1.1).

14.3 PM_{10} and $PM_{2.5}$ concentrations at the rural background site

At the rural background site Birkenes, the annual mean concentration of PM_{10} ranges from 5.4 - 7.1 µg m^{-3} for the period 2000 - 2005 (Figure 14.2a), and there are typically minor variations from year to year. The highest concentrations occur during spring, and coincide with more frequent episodes of long-range transport from the European continent. This is evidenced in Figure 14.2b, showing that Birkenes is experiencing elevated PM concentrations when the air masses arrive from a south-easterly direction. During such events the daily mean concentrations can be seven times higher than the annual mean concentration. From spring on, the concentration decline throughout the year, only interrupted by a moderate increase in late summer. Higher concentrations of PM_{10} are observed in summer (May - October) compared to winter (November - April), and are consistent with increased concentrations of major aerosol constituents such as SIA, in particular SO_4^{2-}, and organic carbon at this site during summer.

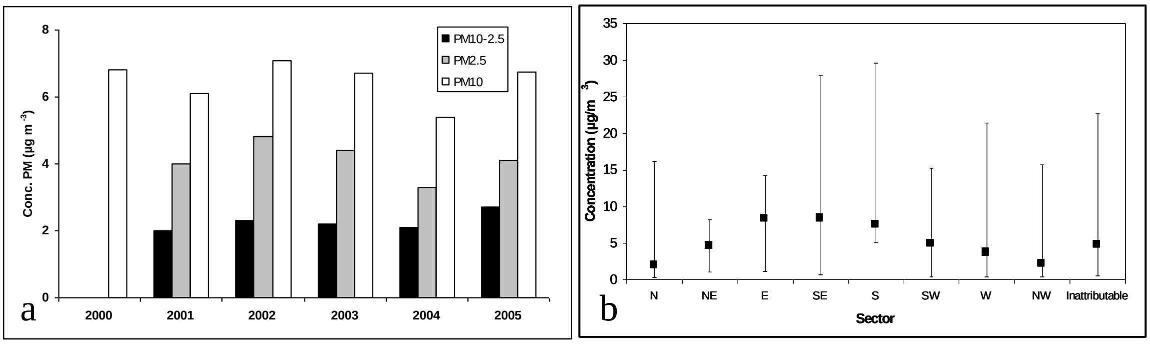

Figure 14.2: Annual mean concentration of PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$ at Birkenes for the period 2000 – 2005 (a); Concentrations of $PM_{2.5}$ at Birkenes as a function of wind direction (b).

$PM_{2.5}$ is the major size fraction of PM_{10}, accounting for 59 % of PM_{10} for the period 2001 - 2005, hence PM_{10} and $PM_{2.5}$ are also highly correlated ($r_p = 0.88$) (Table 14.3). The seasonal variation for $PM_{2.5}$, and for $PM_{10-2.5}$, quite closely resembles that of PM_{10}. The mean $PM_{2.5}/PM_{10}$ ratio, based on daily samples, is slightly lower in summer compared to winter at Birkenes for the period 2001 – 2005 (Table 14.2).

There are no significant differences in the correlation coefficient for PM_{10} versus $PM_{2.5}$, when comparing summer and wintertime measurements (r_p = 0.87 in summer; r_p = 0.89 in winter) (Table 14.3).

14.4 PM_{10} and $PM_{2.5}$ concentrations at urban background and traffic sites

The annual mean PM_{10} concentrations reported for the urban background sites and the traffic sites in 2005, are on average three and four times higher than that recorded at the rural background site (Table 14.1a and b). For $PM_{2.5}$ the difference is less pronounced than for PM_{10}; two times higher for the urban background sites and three times higher for the traffic sites.

Table 14.1a: Annual, summertime and wintertime mean concentrations of PM_{10} at rural background, urban background, and traffic sites in Norway in 2005.

City	Site	Site Category	Size fraction	Annual mean	Summer mean	Winter mean
Bergen	Raadhuset	Urb. Back.	PM_{10}	19	16	20
Kristiansand	Stener Heyerdahl	Urb. Back.	PM_{10}	21	18	24
Lillehammer	Barnehagen	Urb. Back.	PM_{10}	20	13	25
Oslo	Skøyen	Urb. Back.	PM_{10}	26	20	32
Oslo	Sofienbergparken	Urb. Back.	PM_{10}	26	24	29
Stavanger	Vaaland	Urb. Back.	PM_{10}	17	14	19
Trondheim	Teknostallen	Urb. Back.	PM_{10}	19	15	21
			Mean ± SD	**21 ± 4**	**17 ± 4**	**24 ± 5**
Bergen	Danmarksplass	Traffic	PM_{10}	27	20	34
Drammen	Bangeløkka	Traffic	PM_{10}	35	26	49
Kristiansand	Vestre Strandgate	Traffic	PM_{10}	17	14	19
Lillehammer	Bankplassen	Traffic	PM_{10}	30	17	41
Oslo	Alnabru	Traffic	PM_{10}	29	22	36
Oslo	Kirkeveien	Traffic	PM_{10}	26	20	31
Oslo	Manglerud	Traffic	PM_{10}	30	21	39
Trondheim	Bakke Kirke	Traffic	PM_{10}	27	23	30
Trondheim	Elgeseter	Traffic	PM_{10}	31	26	33
			Mean ± SD	**28 ± 5**	**21 ± 4**	**35 ± 8**
S. Norway	Birkenes	Rur. Back.	PM_{10}	6.6	7.5	5.6

Table 14.1b: Annual, summertime and wintertime mean concentrations of $PM_{2.5}$ at rural background, urban background, and traffic sites in Norway in 2005.

City	Site	Site Category	Size fraction	Annual mean	Summer mean	Winter mean
Lillehammer	Barnehagen	Urb. Back.	$PM_{2.5}$	8.6	6.7	10
Trondheim	Teknostallen	Urb. Back.	$PM_{2.5}$	9.5	7.7	11
			Mean ± SD	**9.1 ± 0.6**	**7.2 ± 0.7**	**10 ± 0.1**
Bergen	Danmarksplass	Traffic	$PM_{2.5}$	15	-	15
Lillehammer	Bankplassen	Traffic	$PM_{2.5}$	11	8	13
Oslo	Kirkeveien	Traffic	$PM_{2.5}$	12	11	14
Oslo	Manglerud	Traffic	$PM_{2.5}$	13	11	14
Trondheim	Bakke Kirke	Traffic	$PM_{2.5}$	12	10	13
Trondheim	Elgeseter	Traffic	$PM_{2.5}$	14	13	16
			Mean ± SD	**13 ± 2**	**10 ± 1**	**14 ± 1**
S. Norway	Birkenes	Rur. Back.	$PM_{2.5}$	4.1	4.5	3.6

Unlike the rural background site, higher concentrations of PM_{10} and $PM_{2.5}$ are reported during winter than for summer for the urban background sites and the traffic sites, hence the difference in PM concentration grows larger during winter and becomes less in summer. It is likely that this can be attributed to increased PM emissions from residential heating and from resuspension of road dust in urban areas in winter. In Norway, resuspension of road dust contributes considerably to the coarse fraction of PM_{10} due to the use of studded tires in wintertime (Figure 14.3b). This could also explain why the difference is more severe between the traffic sites and the rural background site, than for the urban background sites (Table 14.1a and b).

While resuspension of road dust mainly contributes to $PM_{10-2.5}$, emissions from residential wood burning is a major contributor to $PM_{2.5}$. In Norway, emissions from residential wood burning is supposed to account for approximately 70 % of the total annual emission of PM_{10}, even though this is a source which only is active during winter. Indeed, elevated concentrations of levoglucosan, which is a highly specific tracer of wood burning, have been reported for Norwegian towns and cities in winter, confirming the influence of this source (Yttri et al., 2005) (Figure 14.3a).

It should be noted that the increased concentrations of fine PM from residential wood burning and the resuspension of coarse road dust experienced in winter, could be considerably reinforced by meteorological conditions, such as temperature inversions, which can be quite strong and frequent in wintertime.

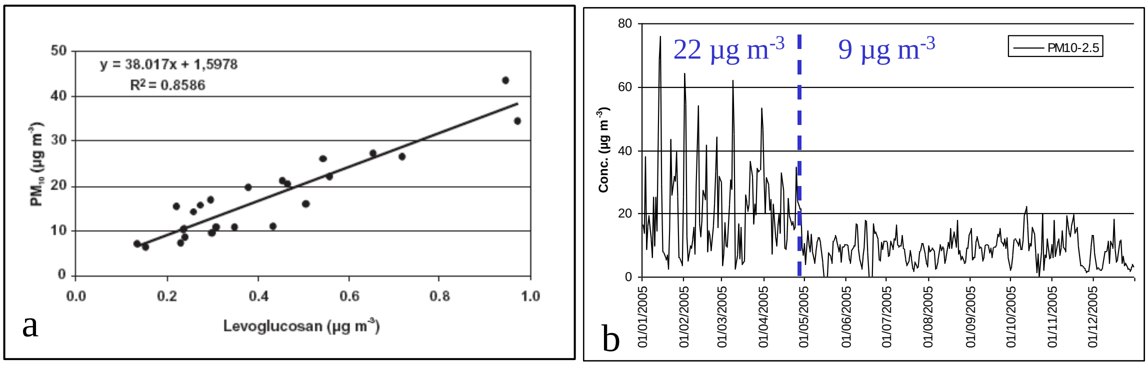

Figure 14.3: High concentrations of levoglucosan are reported for Norwegian cities and towns in winter (here: Elverum). The high correlation reported for levoglucosan vs PM underlines the importance of wood burning for residential heating as a source of PM in winter (Figure is taken from Yttri et al., 2005, J. Air & Waste Manage Assoc. 55, 1169-1177) (a); Studded tires severely affects the concentration of $PM_{10-2.5}$ in winter (22 µg m^{-3}) compared to summer (9 µg m^{-3}) (b).

14.5 $PM_{2.5}/PM_{10}$ ratios

For the urban background sites and traffic sites reporting concurrent measurements of PM_{10} and $PM_{2.5}$, $PM_{2.5}$ tend to be the dominant fraction by a very short margin based on the annual mean $PM_{2.5}/PM_{10}$ ratio of the daily values (Table 14.2).

Table 14.2: Annual mean $PM_{2.5}$ /PM_{10} ratios based on daily measurements at rural background, urban background, and traffic sites in Norway in 2005.

City	Site	Site Category	Annual mean	Summer mean	Winter mean
Lillehammer	Barnehagen	Urb. Back.	0.49	0.53	0.47
Trondheim	Teknostallen	Urb. Back.	0.55	0.52	0.57
Bergen	Danmarksplass	Traffic	0.52	0.66	0.51
Lillehammer	Bankplassen	Traffic	0.47	0.49	0.45
Oslo	Kirkeveien	Traffic	0.52	0.54	0.50
Oslo	Manglerud	Traffic	0.48	0.52	0.43
Trondheim	Bakke kirke	Traffic	0.50	0.46	0.52
S. Norway	Birkenes	Rur. Back.	0.59	0.56	0.62

Although no obvious indication of a seasonal variation can be drawn from the mean seasonal ratios listed in Table 14.2, the frequency distribution of the $PM_{2.5}$/PM_{10} ratio can be quite different for summer and winter. Figure 14.4b shows very well how either low (resuspension of road dust) or high (residential wood burning) $PM_{2.5}$/PM_{10} ratios dominate in winter at the Bankplassen site in the city of Lillehammer. In summertime, however, there is a consistency between the ratio reported for $PM_{2.5}$/PM_{10} in Table 14.2 and that seen in Figure 14.4a.

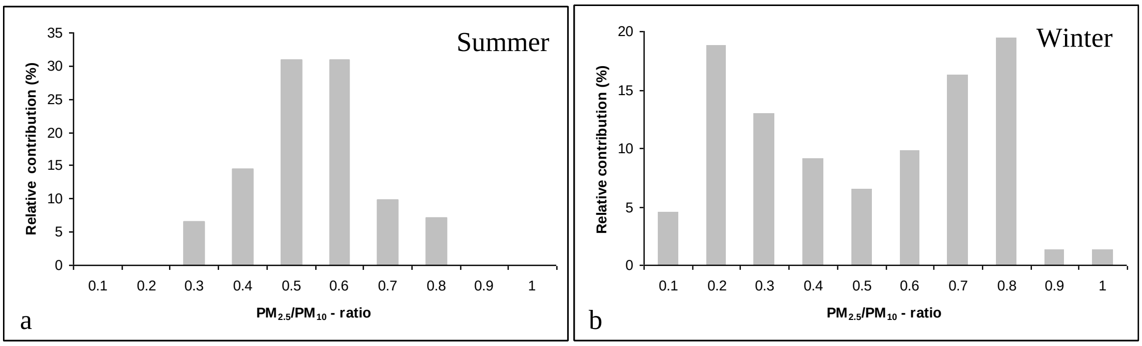

Figure 14.4: Frequency distribution of the $PM_{2.5}$/PM_{10} ratio for the "Bankplassen" site in the city of Lillehammer in Summer (a) and winter (b), emphasizing that the $PM_{2.5}$/PM_{10} ratio typically is either very low (resuspension of road dust) or very high (residential wood burning) in winter.

14.6 Correlation PM_{10} vs $PM_{2.5}$

For the traffic sites and urban background sites reporting concurrent measurements of PM_{10} and $PM_{2.5}$ in 2005, it is observed that the Pearson correlation coefficient for PM_{10} vs $PM_{2.5}$ is considerably higher during summer ($r_p = 0.85 \pm 0.08$) (Mean ± SD) (May - October) than for winter ($r_p = 0.53 \pm 0.12$) (November - April) (Table 14.3). This can be explained by the absence of residential wood burning and resuspension of road dust in summer, which contributes to the fine and the coarse fraction of PM_{10}, respectively, in winter. The relatively high correlation observed in summer could be an indication of a common source. Several of the traffic and urban background sites listed in Table 14.1 experience elevated concentrations of $PM_{2.5}$ in summer when air masses arrive from a southerly and or southeasterly wind direction, which might indicate long-range transport. On the other hand, this feature is not always evident for all sites within the same city, suggesting the influence of local topography and local sources.

Table 14.3: Pearson correlation coefficient for PM_{10} vs $PM_{2.5}$ based on daily values for rural background, urban background, and traffic sites in Norway for 2004 - 2005.

City	Site	Site category	Year	Annual	Summer	Winter
Lillehammer	Barnehagen	Urban background	2005	0.53	0.86	0.38
Trondheim	Teknostallen	Urban background	2005	0.63	0.89	0.55
Bergen$^{1)}$	Danmarksplass	Traffic	2005	0.74	0.94	0.74
Lillehammer	Bankplassen	Traffic	2005	0.49	0.74	0.38
Oslo	Kirkeveien	Traffic	2005	0.66	0.92	0.55
Oslo	Manglerud	Traffic	2005	0.61	0.91	0.54
Trondheim	Bakke Kirke	Traffic	2005	0.57	0.75	0.52
Trondheim	Elgeseter	Traffic	2005	0.63	0.81	0.61
Trondheim	Teknostallen	Urban background	2004	0.63	0.91	0.53
Oslo	Kirkeveien	Traffic	2004	0.52	0.70	0.40
Oslo	Løren	Traffic	2004	0.59	0.85	0.49
Trondheim	Elgeseter	Traffic	2004	0.65	0.94	0.60
S. Norway	Birkenes	Rural background	2005	0.93	0.95	0.89
S. Norway	Birkenes	Rural background	2001-2005	0.88	0.87	0.90

1) Danmarksplass is affected by the low number of samples collected in summer (n = 25)

14.7 Correlation of PM between sites

Located in the southernmost part of Norway, which is the region most influenced by long-range transport of PM, Birkenes is not an optimal site with respect to address the rural background concentrations of PM in western and northern parts of Norway. It is likely that the rural background concentration will decline along a northern transect in Norway due to less influence form long-range transport. At least, such a finding has been made for Norway's neighboring country, Sweden (Forsberg et al., 2005). Further, northern and western Norway is separated from the southern part by high mountain ranges. Birkenes is also situated a fairly long distance, approximately 300 km, from Oslo, which along with its surrounding areas is the most densely populated area in Norway.

Indeed, Table A1.1a-c and Table A1.2a-c (Appendix) shows that the Pearson correlation coefficient (r_p) for 24 h concentrations of PM_{10} and $PM_{2.5}$ between Birkenes and the traffic and urban background sites is rather low on an annual basis, and that the r_p is higher in summer compared to winter. In general, r_p is somewhat higher for $PM_{2.5}$ than for PM_{10} on the annual basis and during summer, while they are equally low in winter. The highest correlation coefficients are observed between Birkenes and the sites situated in Southern (Kristiansand) and Eastern (Drammen, Lillehammer, Oslo) parts of Southern Norway. In addition to the wide geographical distribution of the sites, the low correlation observed in winter could be explained by the contribution from local sources (residential wood burning and resuspended road dust).

A crude estimate of the urban background and the traffic increment in PM can be estimated from the intercept in the scatter plot of the daily mean concentrations at the urban background/traffic sites and the rural background site. However, this approach requires a high correlation coefficient, which is not the case given the strong impact of local sources in Norwegian cities in winter. Hence, Positive Matrix Factorisation was attempted to quantify the long-range transport (LRT) contribution to PM_{10} and $PM_{2.5}$ at a traffic site in Oslo in winter 2004 and winter 2004/2005 (Hagen et al., 2005). The source profile obtained for LRT in PM_{10} (Figure 14.5a) is dominated by SO_4^{2-}, NO_3^- and NH_4^+, and organic carbon (OC), which are constituents typically associated with this source.

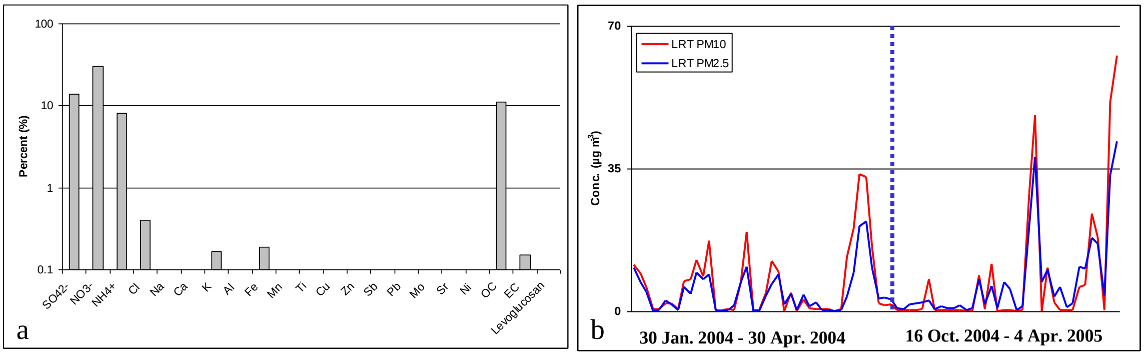

Figure 14.5: Source profile for LRT PM_{10} obtained for a traffic site in Oslo winter 2004 and winter 2004/2005 using positive matrix factorisation (a); Calculated concentrations of LRT PM_{10} and LRT $PM_{2.5}$ at a traffic site in Oslo (30 Jan.–30 Apr. 2004 and 16 Oct.–4 Apr. 2005) using positive matrix factorisation (b). From Hagen et al. (2005)

LRT PM was mainly found in the fine fraction. The contribution of PM from LRT to $PM_{2.5}$ was 5.9 µg m^{-3} and 7.2 µg m^{-3} for PM_{10}, which account for 22.6 % of $PM_{2.5}$ and 9.5 % of PM_{10}. The mean concentrations of LRT PM calculated for the traffic site in Oslo matched rather well with the PM concentration measured at Birkenes during the same period, being 15 % and 2 % higher for $PM_{2.5}$ and PM_{10}, respectively. The LRT PM concentrations calculated for Oslo were to a certain degree correlated with those recorded at the rural background site Birkenes. For $PM_{2.5}$ $r_p = 0.64$, whereas $r_p = 0.61$ for PM_{10}.

These findings suggests that Birkenes can be used for monitoring of LRT PM to Oslo, at least in winter. Assuming that Birkenes is equally well suited in summer, a crude estimated of the urban increment can be provided by a simple subtraction on the basis of the data presented in Table 14.1a and b. This approach estimates that the traffic site concentration of PM_{10} in Oslo is ~ 22 µg m^{-3} above the rural background concentration on an annual basis. Likewise can it be estimated that the urban background increment is ~ 19 µg m^{-3}. Performing a similar subtraction with respect to season provides a traffic site increment of 13 µg m^{-3} during summer and 30 µg m^{-3} in winter for Oslo. The urban background increment with respect to season is estimated to be 14 µg m^{-3} in summer and 25 µg m^{-3} in winter. For $PM_{2.5}$ the traffic increment for Oslo is estimated to be 8.4 µg m^{-3} on an annual basis, 6.5 µg m^{-3} in summer, and 10.5 µg m^{-3} in winter.

Attempt has not been made to calculate the LRT PM concentration by PMF to other cities than Oslo. Thus, we cannot validate how well such a simple subtraction method is for other sites in other cities.

According to Table 14.1a, the concentrations at urban background sites in Oslo are somewhat higher than for the surrounding cities. Thus, the estimated urban background (~ 13 µg m^{-3}) increment for PM$_{10}$ for the other cities is somewhat lower, while for the traffic sites it is more or less the same (~ 21 µg m^{-3}). It should be noted though that a considerably lower concentration is observed for the traffic site Vestre Strandgate in Kristiansand (17 µg m^{-3}), hence the increment for this site would be only 10 µg m^{-3}. For PM$_{2.5}$, the estimated urban background increment was ~ 5 µg m^{-3}, whereas it was ~ 9 µg m^{-3} for the traffic sites.

High correlation coefficients are typically reported between sites in the same city, but are also seen for "neighboring cities" such as Drammen, Kristiansand, Lillehammer and Oslo. This is particularly obvious for PM$_{2.5}$ in summer.

14.8 Chemical speciation of particulate matter in Norway

In Norway, extensive measurements of the ambient aerosol chemical composition are performed at the rural background site Birkenes, as part of the national monitoring programme. Such analysis is only performed on a campaign basis in the major cities.

The aerosols constituents analysed in filter samples collected at Birkenes account for approximately 85 % of the PM$_{10}$ mass concentration on an annual basis (2004) (Figure 14.6). Organic matter (OM = OC x 1.7) is the major fraction (27 %), whereas SO_4^{2-} is the most abundant single compound (19 %), followed by NH_4^+ (14 %) and NO_3^- (6.6 %). Together, Na$^+$, Cl$^-$ and Mg^{2+} account for 14 %, whereas the base cations Ca^{2+} and K$^+$, and elemental matter (EM = EC x 1.1) contribute with less than 2 %. The heavy metals As, Cd, Cr, Co, Cu, Pb, Ni, V and Zn account for less than 0.5 %. The 15 % of the PM$_{10}$ mass concentration, which is not accounted for, could be attributed to mineral dust, and water, which is associated with the aerosol matrix and the filter material.

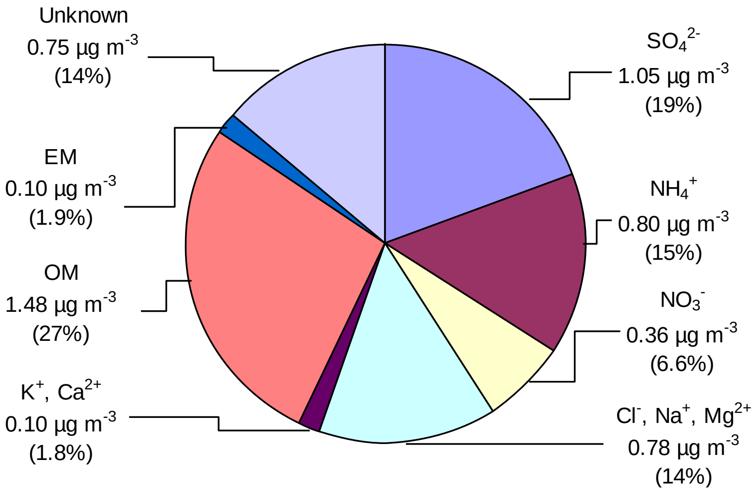

Figure 14.6: Mass closure of PM$_{10}$ (5.4 µg m^{-3}) at the rural background site Birkenes (2004).

Figure 14.7a shows the annual variation in concentration of secondary inorganic constituents (SO_4^{2-}, NO_3^-, and NH_4^+), carbonaceous material (OM and EM), and sea salts for the period 2001 – 2005 at Birkenes. Characteristic for this period is the drop in concentration in 2004 for all constituents and fractions, except from the sea salts. This drop reflects the observation made for PM_{10} and $PM_{2.5}$ for the same site (Figure 14.2). No conclusions of a downward or upward trend for the relative contribution of chemical constituents and fractions to PM_{10} can be based on only five years of sampling (Figure 14.7b). Typically, a rather small variation in the relative contribution can be observed on a year-to-year basis for this period (2001–2005). The largest variation is seen for sea salts and NO_3^-, for which the relative contribution seems to increase over the actual period.

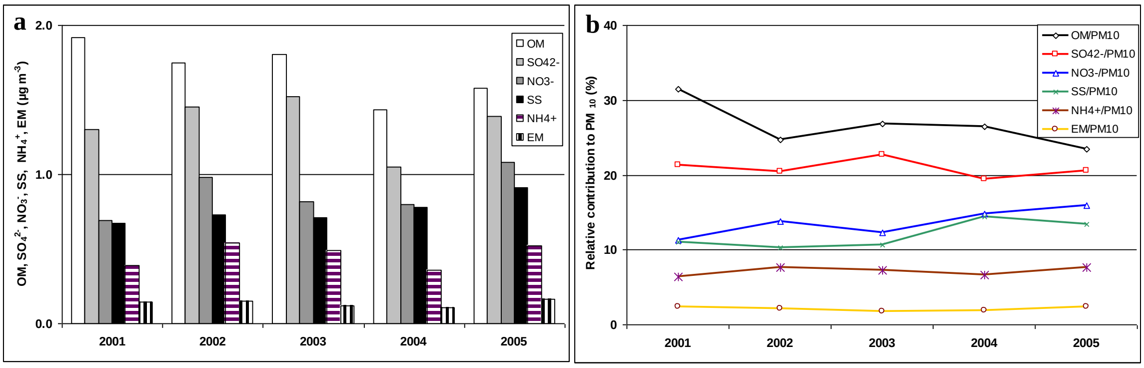

Figure 14.7: Annual variation of secondary inorganic constituents (SO_4^{2-}, NO_3^-, and NH_4^+), carbonaceous material (OM and EM), and sea-salts (Na^+, Cl^-, and Mg^{2+}) for the period 2001 – 2005 at the rural site Birkenes (µg m^{-3}) (a): Relative contribution of secondary inorganic constituents, carbonaceous material, and sea-salts for the period 2001 – 2005 (%) (b).

EC and OC are the only fractions measured in both PM_{10} and $PM_{2.5}$ at the Birkenes site. These concurrent measurements have shown that the majority of the carbonaceous material is associated with the fine aerosol on an annual basis. This is most pronounced for EC ($EC_{PM2.5}/EC_{PM10}$ = 0.84 ± 0.07). The corresponding ratio for OC is somewhat less ($OC_{PM2.5}/OC_{PM10}$ 0.76 ± 0.05). For OC a considerable increase in the coarse fraction is observed during the vegetative season, most likely due to the influence of primary biological aerosol particles, equalling the fine OC content of PM_{10}.

14.9 Comparison of the PM chemical composition at a traffic site and at a rural background site

Concurrent measurements at a traffic site (Riksvei 4) in Oslo and at the rural background site (Birkenes) during two winter periods (30 January–30 April 2004 and 16 October 2004–4 April 2005) show that the PM chemical constituents and fractions are higher by a factor of 1.5–46 in Oslo compared to Birkenes (Table 14.4).

Table 14.4: Concurrent measurement of the particulate matter chemical composition at the traffic site Riksvei 4 in Oslo and at the rural background site Birkenes during winter 2004 and winter 2004/5, along with the relative contribution of the chemical constituents and fractions to the PM mass concentration.

Chemical Composition	**Traffic site**				**Rural site**	
	PM_{10} (µg m^{-3})	**Rel. cont. to PM_{10} (%)**	**$PM_{2.5}$ (µg m^{-3})**	**Rel. cont. to $PM_{2.5}$ (%)**	**FP/PM_{10}[3)] (µg m^{-3})**	**Rel. cont. to PM_{10} (%)**
Organic matter[1)]	16.6	24	11.7	43	1.2	16
Elemental matter[2)]	5.5	8.0	4.1	15	0.1	1.6
Cl^-	4.7	6.9	0.5	1.9	0.4	5.7
Al, Fe	4.2	6.1	0.5	2.0		
NO_3^-	3.6	5.3	2.7	9.9	1.3	17
Na^+	3.1	4.5	0.4	1.6	0.4	5.5
SO_4^{2-}	2.9	4.2	2.4	8.7	1.4	18
K^+, Ca^{2+}	2.2	3.2	0.5	1.9	0.1	1.6
NH_4^+	0.9	1.3	1.0	3.7	0.6	8.1
Mg^{2+}					0.1	0.8
Other heavy metals	0.5	0.7	0.1	0.5	0.03	0.4
Sum chemical composition	44.2	64	23.9	88	5.8	76
Unknown mass	24.5	36	3.1	12	1.8	24
PM mass concentration	68.7		27.0		7.6	

1. (OM = OC x 1.6)
2. (EM = EC x 1.1)
3. FP = Filterpack (EMEP) with a non-defined cut off size

The largest difference is seen for EM (EM = EC x 1.1), which is a typical anthropogenic compound, originating from incomplete combustion of fossil fuel in gasoline and diesel cars, as well as from residential wood burning, which is quite common in Oslo in winter. The impact of residential wood burning at the traffic site is mirrored by the levels of levoglucosan, ranging from 11 – 494 ng m^{-3} (mean con. 142 ng m^{-3}) for the period in question. From Figure 14.8 it can be seen that PM from residential wood burning by far (< 80 %) contribute to the fine PM fraction at the traffic site. During winter the sources of organic matter (OM = OC x 1.7) and EM in Norway are *expected* to be more or less the same, as biogenic secondary organic aerosol formation and contribution of primary biogenics is supposed to be very low or absent. Still, the concentrations of OM are no more than 15 times higher at the traffic site compared to the rural background site. The relative importance of EC at the traffic site compared to the rural background site also becomes obvious when looking at the EC/TC ratio, which is 32 ± 8 % at the traffic site and 13 ± 4 % at the rural background site, both for PM_{10}.

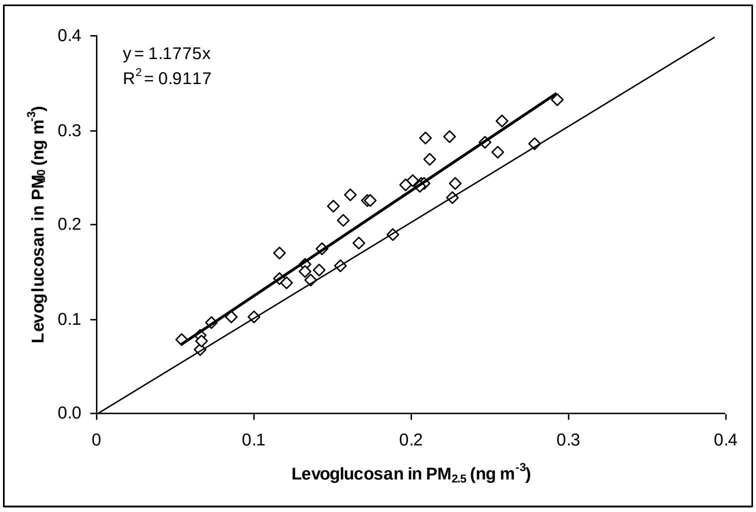

Figure 14.8: Scatter plot of levoglucosan in PM_{10} and $PM_{2.5}$ at Riksvei 4 (traffic site) in Oslo during the period 16 October 2004 - 4 April 2005.

While virtually all EM is associated with fine aerosols at the rural site (not shown), the corresponding $PM_{2.5}/PM_{10}$ for EM at the traffic site is 0.74. The corresponding ratio for OM at the traffic site is 0.70 whereas it is 0.87 at the rural site. It could be speculated that the lower ratios seen at the traffic site could be attributed to traffic-induced resuspension of EM and OM that is agglomerated to larger particles.

For the secondary inorganic constituents (SIA) (SO_4^{2-}, NO_3^-, NH_4^+), only minor differences in concentrations are observed between Birkenes and Oslo (1.4 – 2.7). This can be explained by the fact that these are constituents associated with long-range transport, hence they tend to be more widely distributed, which is underlined by the fact that they are mainly associated with the fine aerosols (Table 14.4).

The mean concentration of chloride is 11 times higher in Oslo compared to Birkenes, whereas it is seven times higher for sodium. The aerosols content of Cl^- and Na^+ could be attributed to sea salts at Birkenes, while use of NaCl for road salting is the main source in Oslo. Road salting typically generates Na^+ and Cl^- containing particulate matter that contributes to the coarse fraction of PM_{10}, which also is the case for Na^+ and Cl^- originating from sea spray.

Levels of Ca^{2+} and K^+ were 17 times higher in Oslo compared to Birkenes, while the corresponding number for “other heavy metals” was 15. Calcium could be attributed to road dust following from the extensive wearing of the road surface in winter due to the use of studded tires, hence explaining the prevalence of Ca^{2+} in the coarse fraction ($Ca^{2+}_{PM2.5}/Ca^{2+}_{PM10}$ Ca^{2+} = 75 %). Potassium is mainly associated with fine aerosols ($K^+_{PM2.5}/K^+_{PM10}$ = 80 %), which could indicate that it mainly originates from residential wood burning.

64 % of PM_{10} at the traffic site could be accounted for based on the chemical analysis performed, whereas for $PM_{2.5}$ the percentage is 88 (Table 14.4). The lower percentage for PM_{10} is mainly due to silicon (Si) not being analysed. Si is typically the most abundant element of mineral/road dust, which contributes

significantly to the coarse fraction of PM_{10}, in particular in winter, as a result of vehicles using studded tires. For the actual period, OM is the major identified fraction in both PM_{10} (24 %) and $PM_{2.5}$ (43 %) at the traffic site, being three times higher than the second most abundant fraction, which in both cases is EM. This finding clearly emphasizes the abundance of carbonaceous material in urban particulate matter in winter.

76 % of the PM_{10} mass concentration could be accounted for at the rural background site Birkenes during the same period. Unlike the traffic site, OM was not the major fraction, although its contribution to PM_{10} (16 %) was only marginally lower than for SO_4^{2-} (18 %) and NO_3^- (17 %), which was the most abundant constituents. It is worth nothing that Cl^- and Na^+ together account for more than 11 % of PM_{10} at both the traffic site and the rural site.

Al, Ca, Fe, Mn, and Ti are all important constituents of crustal material, and some of them are also present in the studs used in studded tires. At the traffic site, these constituents are all highly correlated ($R^2 = 0.72 \pm 0.18$) pointing towards abrasion of tires and the road surface. Together, this non-tailpipe vehicle-derived constituents account for 9.3 % of PM_{10}.

14.10 Source apportionment of particulate matter by positive matrix factorization

Based on the chemical data summarized in Table 14.4, positive matrix factorisation (PMF) was used to apportion the sources contributing to PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$ at the traffic site riksvei 4. The results from this exercise are presented in Table 14.5.

Comparing the measured concentrations of PM_{10}, $PM_{2.5}$, and $PM_{10-2.5}$ with those obtained by the PMF approach show that the performance of this statistical approach is good for all three size fractions. The mean concentration obtained by the PMF approach differ by less than 3.5 % compared to the measured concentration, and the correlation was found to be rather good; R^2 ranging between 0.70 - 0.81.

Table 14.5: Mean and relative contribution of PM from various sources to PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$ at the traffic site Riksvei 4 during winter 2004 and 2004/5, obtained by positive matrix factorisation.

Source	PM_{10} (µg m^{-3})	(%)	$PM_{2.5}$ (µg m^{-3})	(%)	$PM_{10-2.5}$ (µg m^{-3})	(%)
Road dust	20.2	26.8	3.6	13.8	17.4	36.2
Road dust + NaCl	15.2	20.1	1.1	4.0	15.8	32.8
Petrol cars + studded tires	14.9	19.7	5.5	21.2		
Wood burning	14.8	19.6	7.0	26.9		
Long-range transport	7.2	9.5	5.9	22.6		
Diesel cars	3.2	4.2	3.0	11.4		
Resuspended dust high in biological material					11.3	23.4
Non-attributed					3.7	7.7
Measured concentration	76.2		26.8		49.6	
Calculated concentration	75.5		26.1		48.1	
R^2 measured vs. calculated	0.81		0.70		0.79	

Road dust, with (26.8 %) and without NaCl (20.1 %), dominates PM_{10}, and the majority seems to be associated with the coarse fraction. Residential wood burning contributes significantly to both PM_{10} (19.6 %) and $PM_{2.5}$ (26.9 %). It is somewhat surprising though that wood burning seems to distribute equally between the coarse and the fine fraction of PM_{10} (14.8 µg m^{-3} in PM_{10} and 7.0 µg m^{-3} in $PM_{2.5}$) (Table 14.5) although it is not apportioned as a separate source for $PM_{10-2.5}$. This finding does also fail to reproduce the result, which can be deducted from Figure 14.8, showing that more than 80 % of levoglucosan, which is a highly specific tracer for wood burning, could be attributed to fine aerosols.

Separating tail-pipe emissions from petrol and diesel cars is not straightforward. Here PM concentrations, which can be attributed to combustion of diesel, account for 11.4 % of $PM_{2.5}$, whereas the corresponding percentage for cars with petrol engines is 21.2 %. Unfortunately, the latter source was not separated from PM originating from the wearing of studs in studded tires. This becomes quite obvious when looking at the PM_{10} fraction, to which this mixed source contributes with 14.9 µg m^{-3} compared to 3.2 µg m^{-3} for diesel cars. It is likely that the PM originating from tail pipe exhaust from petrol cars contributes to the fine fraction of PM_{10}, whereas the studs contributes to the coarse fraction. The contribution of PM from long-range transport is discussed more in detail in a previous sub chapter ("Correlation of PM between sites").

14.11 References

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Appendix 1

Table A1.1a: Pearson correlation coefficients (rp) for daily measurements of PM2.5 at rural background, urban background, and traffic sites in Norway in 2005.

	Danmarksplass	Bankplassen	Barnehagen	Kirkeveien	Manglerud	Bakke Kirke	Elgeseter	Teknostallen	Birkenes
Danmarksplass		0.25	0.28	-0.01	0.13	0.31	0.25	0.30	0.05
Bankplassen			0.93	0.77	0.78	0.43	0.42	0.48	0.43
Barnehagen				0.74	0.71	0.46	0.48	0.52	0.43
Kirkeveien					0.87	0.32	0.29	0.41	0.45
Manglerud						0.42	0.37	0.49	0.45
Bakke Kirke							0.88	0.90	0.33
Elgeseter								0.88	0.18
Teknostallen									0.26
Birkenes									

Table A1.1b: Pearson correlation coefficients (r_p) for daily measurements of $PM_{2.5}$ during summer at rural background, urban background, and traffic sites in Norway in 2005.

	Danmarksplass	Bankplassen	Barnehagen	Kirkeveien	Manglerud	Bakke Kirke	Elgeseter	Teknostallen	Birkenes
Danmarksplass		0.04	-0.02	0.03	0.18	0.42	0.15	0.34	-0.04
Bankplassen			0.97	0.89	0.88	0.61	0.60	0.72	0.68
Barnehagen				0.89	0.86	0.62	0.58	0.70	0.74
Kirkeveien					0.90	0.65	0.63	0.72	0.74
Manglerud						0.68	0.61	0.74	0.68
Bakke Kirke							0.83	0.93	0.50
Elgeseter								0.88	0.35
Teknostallen									0.50
Birkenes									

Table A1.1c: Pearson correlation coefficients (r_p) for daily measurements of $PM_{2.5}$ during winter at rural background, urban background, and traffic sites in Norway in 2005.

	Danmarksplass	Bankplassen	Barnehagen	Kirkeveien	Manglerud	Bakke Kirke	Elgeseter	Teknostallen	Birkenes
Danmarksplass		0.28	0.33	-0.02	0.12	0.30	0.26	0.30	0.08
Bankplassen			0.89	0.69	0.69	0.33	0.20	0.37	0.34
Barnehagen				0.60	0.58	0.41	0.34	0.46	0.34
Kirkeveien					0.83	0.20	0.14	0.31	0.28
Manglerud						0.32	0.25	0.40	0.29
Bakke Kirke							0.90	0.88	0.38
Elgeseter								0.88	0.24
Teknostallen									0.24
Birkenes									

Table A1.2a: Pearson correlation coefficients (r_p) for daily measurements of PM_{10} at rural background, urban background, and traffic sites in Norway in 2005.

	Raadhuset	Bangeløkka	Stener Heyerdahl	Bankplassen	Barnehagen	Alnabru	Kirkeveien	Manglerud	Skøyen	Sofienbergparken	Vaaland	Bakke Kirke	Elgeseter	Teknostallen	Birkenes	Vestre Strandgate
Danmarksplass	0.82	0.42	-0.04	0.25	0.27	0.15	0.12	0.21	0.05	0.10	0.29	0.18	0.05	0.29	-0.02	0.01
Raadhuset		0.41	0.14	0.25	0.31	0.16	0.15	0.17	0.12	0.21	0.41	0.24	0.12	0.33	0.18	0.11
Bangeløkka			0.35	0.69	0.70	0.79	0.77	0.71	0.65	0.58	0.37	0.35	0.23	0.39	0.12	0.39
Stener Heyerdahl				0.35	0.35	0.48	0.47	0.28	0.63	0.43	0.53	0.26	0.33	0.32	0.60	0.84
Bankplassen					0.86	0.56	0.51	0.54	0.48	0.38	0.46	0.40	0.19	0.38	0.11	0.42
Barnehagen						0.61	0.56	0.50	0.59	0.49	0.40	0.40	0.21	0.42	0.19	0.51
Alnabru							0.78	0.74	0.67	0.62	0.33	0.20	0.12	0.26	0.18	0.52
Kirkeveien								0.80	0.81	0.69	0.35	0.17	0.02	0.23	0.25	0.44
Manglerud									0.62	0.53	0.27	0.11	-0.06	0.18	0.06	0.31
Skøyen										0.75	0.45	0.28	0.11	0.32	0.37	0.56
Sofienbergparken											0.36	0.27	0.11	0.32	0.33	0.39
Vaaland												0.23	0.14	0.29	0.38	0.41
Bakke Kirke													0.78	0.84	0.34	0.27
Elgeseter														0.75	0.31	0.29
Teknostallen															0.32	0.29
Birkenes																0.49

Table A1.2b: Pearson correlation coefficients (r_p) for daily measurements of PM_{10} in summer at rural background, urban background, and traffic sites in Norway in 2005.

	Raadhuset	Bangeløkka	Stener Heyerdahl	Bankplassen	Barnehagen	Alnabru	Kirkeveien	Manglerud	Skøyen	Sofienbergparken	Vaaland	Bakke Kirke	Elgeseter	Teknostallen	Birkenes	Vestre Strandgate
Danmarksplass	0.83	0.33	0.02	0.54	0.46	0.50	0.37	0.53	0.23	0.31	0.74	0.31	0.27	0.44	0.11	0.20
Raadhuset		0.41	0.37	0.56	0.60	0.60	0.58	0.62	0.45	0.50	0.85	0.42	0.40	0.57	0.42	0.45
Bangeløkka			0.54	0.83	0.78	0.41	0.74	0.66	0.64	0.46	0.25	0.27	0.22	0.34	0.38	0.59
Stener Heyerdahl				0.53	0.53	0.66	0.73	0.60	0.77	0.41	0.54	0.30	0.42	0.41	0.86	0.93
Bankplassen					0.88	0.79	0.74	0.75	0.53	0.39	0.35	0.17	0.12	0.32	0.41	0.67
Barnehagen						0.80	0.83	0.79	0.70	0.59	0.24	0.24	0.20	0.44	0.57	0.68
Alnabru							0.87	0.84	0.72	0.47	0.39	0.42	0.47	0.59	0.53	0.71
Kirkeveien								0.81	0.81	0.63	0.39	0.35	0.35	0.51	0.67	0.73
Manglerud									0.64	0.49	0.28	0.42	0.47	0.57	0.52	0.57
Skøyen										0.71	0.35	0.47	0.45	0.52	0.70	0.75
Sofienbergparken											0.26	0.27	0.24	0.33	0.43	0.36
Vaaland												0.29	0.46	0.37	0.53	0.53
Bakke Kirke													0.85	0.89	0.25	0.29
Elgeseter														0.86	0.27	0.36
Teknostallen															0.34	0.41
Birkenes																0.75

Table A1.2c: Pearson correlation coefficients (r_p) for daily measurements of PM_{10} in winter at rural background, urban background, and traffic sites in Norway in 2005.

	Raadhuset	Bangeløkka	Stener Heyerdahl	Bankplassen	Barnehagen	Alnabru	Kirkeveien	Manglerud	Skøyen	Sofienbergparken	Vaaland	Bakke Kirke	Elgeseter	Teknostallen	Birkenes	Vestre Strandgate
Danmarksplass	0.82	0.32	-0.07	0.17	0.19	0.02	0.00	0.07	-0.08	0.00	0.22	0.12	-0.05	0.23	0.09	-0.03
Raadhuset		0.36	0.08	0.19	0.23	0.03	0.03	0.04	0.00	0.10	0.35	0.19	-0.02	0.27	0.21	0.03
Bangeløkka			0.26	0.48	0.48	0.36	0.70	0.60	0.53	0.64	0.23	0.26	0.03	0.33	0.15	0.29
Stener Heyerdahl				0.30	0.30	0.34	0.32	0.13	0.60	0.43	0.45	0.26	0.29	0.29	0.42	0.76
Bankplassen					0.83	0.45	0.34	0.35	0.34	0.39	0.34	0.40	0.06	0.38	0.28	0.39
Barnehagen						0.47	0.37	0.29	0.45	0.48	0.40	0.40	0.03	0.41	0.35	0.46
Alnabru							0.71	0.68	0.60	0.69	0.19	0.11	-0.09	0.14	0.11	0.39
Kirkeveien								0.76	0.78	0.73	0.23	0.09	-0.18	0.12	0.16	0.27
Manglerud									0.54	0.54	0.14	-0.01	-0.27	0.04	0.04	0.18
Skøyen										0.74	0.38	0.20	-0.10	0.22	0.42	0.47
Sofienbergparken											0.38	0.24	-0.12	0.28	0.37	0.39
Vaaland												0.17	-0.04	0.23	0.43	0.28
Bakke Kirke													0.85	0.82	0.54	0.26
Elgeseter														0.79	0.21	0.31
Teknostallen															0.46	0.26
Birkenes																0.41

15 National PM assessment report – Slovak Republic

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15.1 History of PM monitoring

The Slovak Hydrometeorological Institute (SHMU) is state organization, supervised by the Ministry of Environment, authorized for air quality monitoring, assessment and reporting on a national level and thus provide basic input for the development and fulfilment of national reporting obligations, mitigation plans and programs.

The current state of the Slovak national air quality monitoring network is presented in Figure 15.1. PM_{10} measurements started in 2002 and in 2005 the 28 real-time PM_{10} monitoring stations were in operation in urban/suburban areas. Results from 26 of these stations are presented in this report. PM_{10} inlet systems originate from several renowned European and US producers. At the real-time monitoring stations TEOM instruments were installed using default correction factor 1.3. At 18 TEOMs the FDMS modules were installed last year. Studies from other countries proved that these measurements provide equivalence with the reference method and therefore no correction factor was applied. The rural background PM is monitored at five EMEP sites, but PM_{10} only at three of them Stará Lesná SK04, Liesek SK05 and Starina SK06. At the EMEP stations the sampling period is one week. The EMEP station Topoľníky SK07 in Danube lowlands started the real-time PM_{10} and $PM_{2.5}$ (TEOMs) measurements only recently as well as PM_{10} in weekly interval. The $PM_{2.5}$ was measured in Slovakia in 2005 on three urban traffic station (TEOMs).

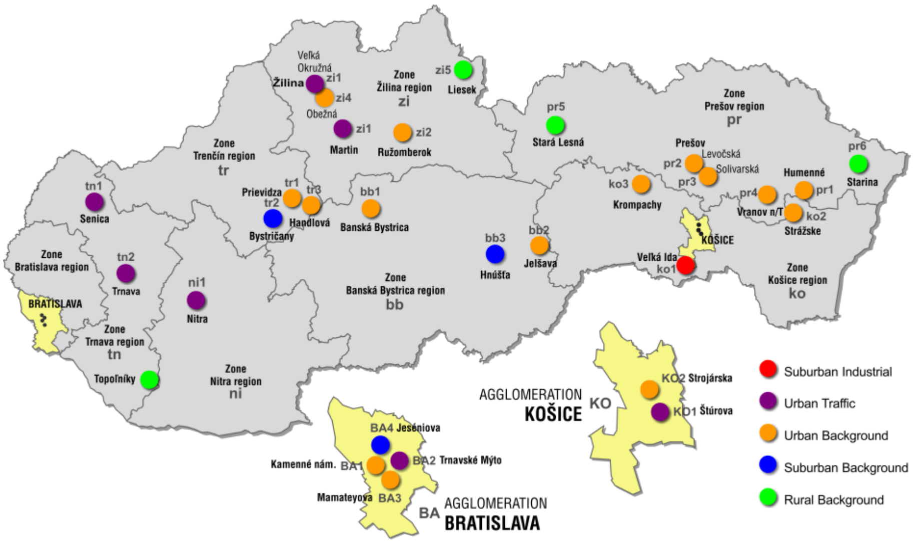

Figure 15.1: National air quality monitoring network in Slovakia (status in 2005).

For improvement of PM data quality, the QA/QC procedures have to be fully implemented at all stations. In the forthcoming year the process of accreditation in air quality monitoring network will start which will result in improvements of maintenance system, calibration processes, demonstration of equivalence to reference method, uncertainty estimates etc. Weighing room and weighing procedures have been already prepared for accreditation. The parallel in-situ measurements (according to EN 12341, resp. EN 14907) with mobile unit have been prepared and are going to start also this year. The quality of $PM_{2.5}$ measurements has to be improved significantly as well which is underlined also by the fact that expected $PM_{2.5}$ limit values will be approved in 2007.

15.2 Data assessment

For the time being the available PM_{10} data were assessed and reported only according to the EU AQ obligations. More detailed, scientific assessment of measurements has not been completed yet. However, the present estimates clearly indicate, that PM rural background, especially the share of long-range transboundary transport, play very important role especially for fine particles.

Typical annual PM_{10} averages for Slovakia in 2005

- rural background (EMEP)15–25µg.m^{-3} (in dependence on altitude)
- urban/suburban background30–35µg.m^{-3}
- urban/suburban all types30–65µg.m^{-3}
- primary anthropogenic particles*3–10µg.m^{-3} (at some industrial stations even more)

**Model estimation based on national PM emission inventory data (registration of small, medium, large and mobile anthropogenic sources).*

Monthly course of PM_{10} concentrations from all monitoring station is shown in Figure 15.2. The highest values were registered at the industrial station Velka Ida situated very close to US Steel factory while the lowest values were recorded at rural background stations. Cross correlations of daily concentrations was estimated for 25 real-time stations indicating high correlation exists among all monitoring stations at the whole territory of Slovakia (Table 15.1) documenting clearly the rural background (transboundary) aspect of PM_{10} pollution level. As expected the lowest correlation was found out for industrial station Velka Ida at which the local PM_{10} sources play decisive role.

Table 15.1: Correlation matrix of PM_{10} daily concentrations – Slovakia, 2005.

AGGLOMERATION / zone			BA			KO		bb			ko			ni	pr				tr			tn		zi			
		Station	1	2	3	1	2	1	2	3	1	2	3	1	1	2	3	4	1	2	3	1	2	1	2	3	4
BA	1	Bratislava, Kam. nám.	1																								
	2	Bratislava, Trnav. mýto	**0.86**	1																							
	3	Bratislava, Mamateyova.	**0.80**	**0.83**	1																						
KO	1	Košice, Štúrova	0.58	0.56	0.52	1																					
	2	Košice, Strojárska	0.53	0.54	0.50	**0.93**	1																				
bb	1	Ban. Bystrica, Nám.slob.	0.71	0.71	0.63	0.74	0.72	1																			
	2	Jelšava, Jesenského	0.48	0.48	0.43	0.74	0.77	**0.73**	1																		
	3	Hnúšťa, Hlavná	0.56	0.55	0.56	0.75	0.75	**0.75**	**0.81**	1																	
ko	1	Veľká Ida, pri ŽSR	0.19	0.23	0.30	0.15	0.17	0.25	0.10	0.15	1																
	2	Strážske, Mierová	0.50	0.50	0.47	0.85	0.80	0.68	0.63	0.59	**0.16**	1															
	3	Krompachy, Lorenzova	0.57	0.58	0.56	0.83	0.85	0.77	0.76	0.77	**0.23**	**0.73**	1														
ni	1	Nitra, Štefánikova	0.64	0.74	0.71	0.66	0.64	0.71	0.58	0.63	0.22	0.54	0.65	1													
pr	1	Humenné, Nám. slobody	0.50	0.50	0.47	0.83	0.79	0.71	0.67	0.65	0.23	0.94	0.76	0.58	1												
	2	Prešov, Levočská	0.54	0.54	0.55	0.88	0.88	0.70	0.72	0.74	0.20	0.84	0.84	0.63	**0.84**	1											
	3	Prešov, Solivarská	0.51	0.53	0.57	0.79	0.71	0.62	0.59	0.61	0.20	0.78	0.70	0.62	**0.76**	**0.84**	1										
	4	Vranov n/T, M.R.Štefan.	0.52	0.52	0.54	0.83	0.81	0.66	0.64	0.65	0.19	0.87	0.78	0.58	**0.85**	**0.88**	**0.78**	1									
tr	1	Prievidza, J. Hollého	0.64	0.65	0.62	0.72	0.70	0.82	0.64	0.74	0.17	0.66	0.71	0.72	0.68	0.71	0.59	0.66	1								
	2	Bystričany, Roz. SSE	0.54	0.61	0.62	0.55	0.59	0.65	0.55	0.63	0.20	0.52	0.62	0.68	0.52	0.61	0.48	0.54	**0.77**	1							
	3	Handlová, Morov.cesta	0.66	0.71	0.68	0.65	0.62	0.79	0.62	0.70	0.25	0.59	0.69	0.72	0.64	0.70	0.60	0.71	**0.81**	**0.69**	1						
tn	1	Senica, Hviezdoslavova	0.78	0.83	0.82	0.66	0.59	0.74	0.53	0.58	0.27	0.59	0.61	0.84	0.62	0.62	0.65	0.63	0.71	0.62	0.76	1					
	2	Trnava, Kollárova	0.69	0.78	0.75	0.58	0.52	0.66	0.48	0.54	0.23	0.51	0.52	0.78	0.53	0.58	0.62	0.60	0.66	0.58	0.77	**0.87**	1				
zi	1	Martin, Jesenského	0.51	0.55	0.54	0.63	0.63	0.62	0.52	0.58	0.17	0.47	0.71	0.73	0.51	0.52	0.48	0.49	0.61	0.58	0.52	0.56	0.45	1			
	2	Ružomberok, Riadok	0.61	0.63	0.58	0.67	0.64	0.80	0.59	0.59	0.21	0.61	0.75	0.71	0.65	0.59	0.55	0.58	0.71	0.61	0.63	0.67	0.54	**0.81**	1		
	3	Žilina, Veľká Okružná	0.72	0.74	0.71	0.66	0.62	0.80	0.63	0.63	0.18	0.59	0.66	0.71	0.61	0.66	0.67	0.66	0.72	0.59	0.78	0.81	0.75	**0.53**	**0.72**	1	
	4	Žilina, Obežná	0.70	0.71	0.75	0.71	0.66	0.84	0.67	0.69	0.26	0.69	0.73	0.74	0.70	0.70	0.72	0.67	0.77	0.68	0.75	0.81	0.71	**0.66**	**0.81**	**0.86**	1

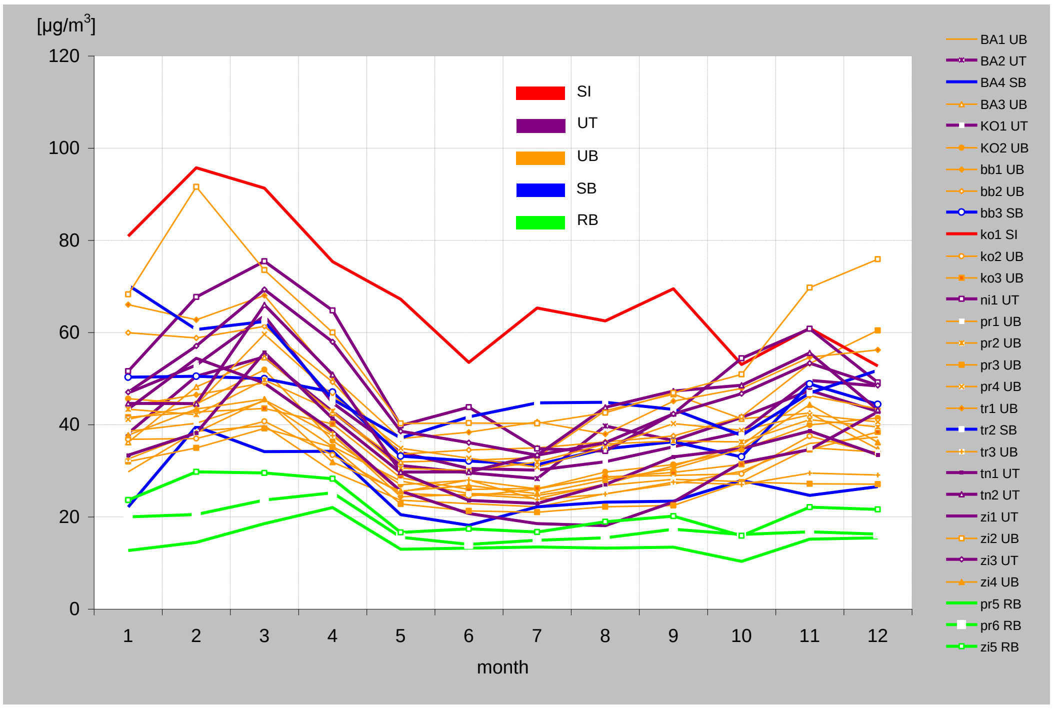

Figure 15.2: Monthly course of PM_{10} concentration in Slovakia (2003-2005 average).

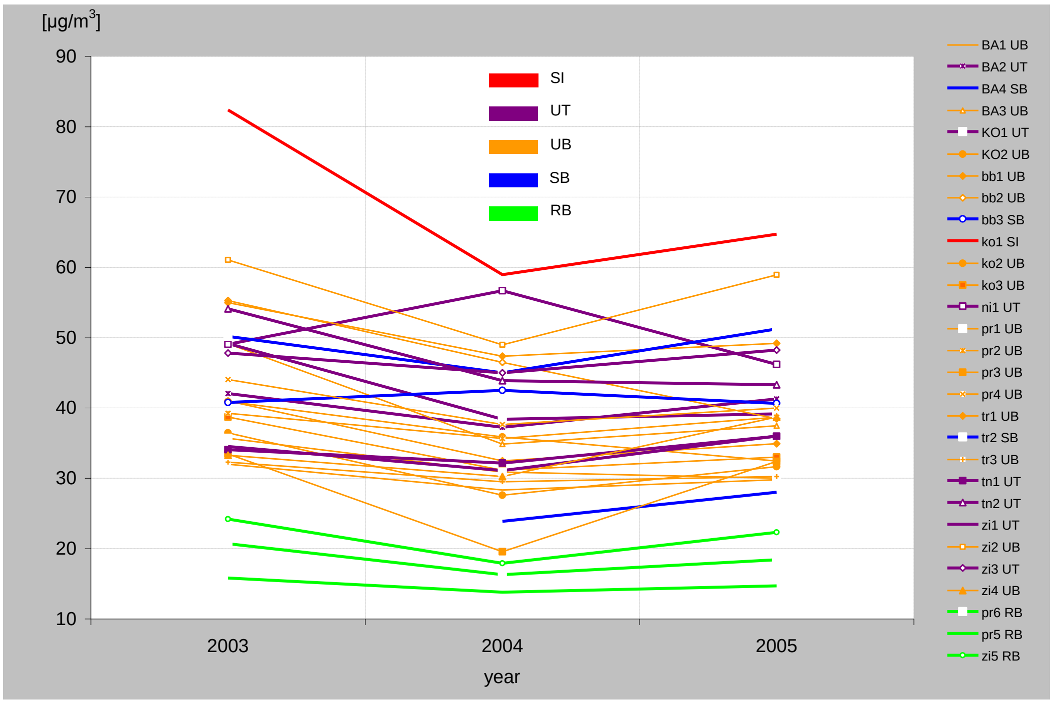

Figure 15.3: Yearly course of PM_{10} concentration at the Slovak monitoring stations.

15.3 Modelling activities

High statistical relationships of PM_{10} concentration among stations enabled to implement 3D interpolation anisotropic model IDWA (Szabó 2004, 2005). An interpolation scheme was proposed, based on an inverse weighting distance between monitoring stations and grid points. The distance used in the interpolation routine is anisotropically re-scaled. The anisotropy ratio respects local conditions. It is determined by a wind rose representative for each grid point. The interpolation scheme contains an empirical altitude dependent function of concentration derived from real rural background measurements (EMEP). Results for the year 2005 are presented in Figure 15.4 and Figure 15.5.

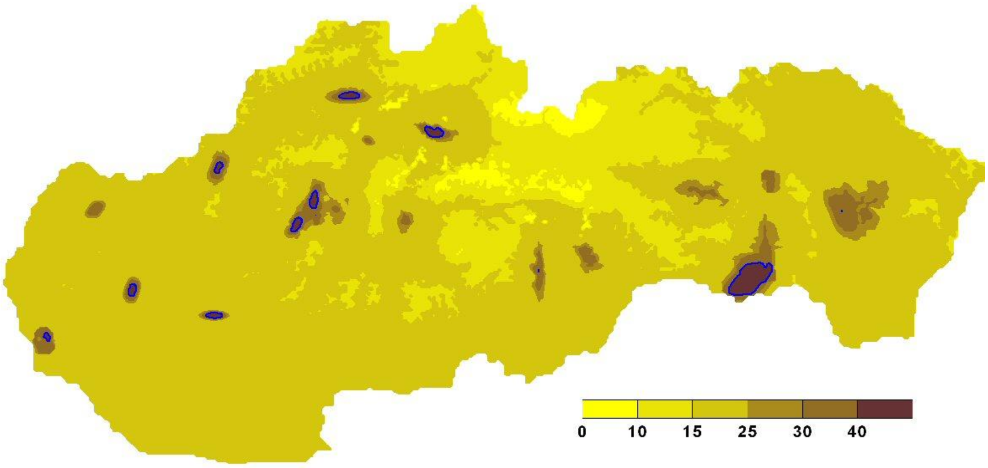

Figure 15.4: Annual average concentration of PM_{10} [µg.m^{-3}] – Slovakia, 2005.

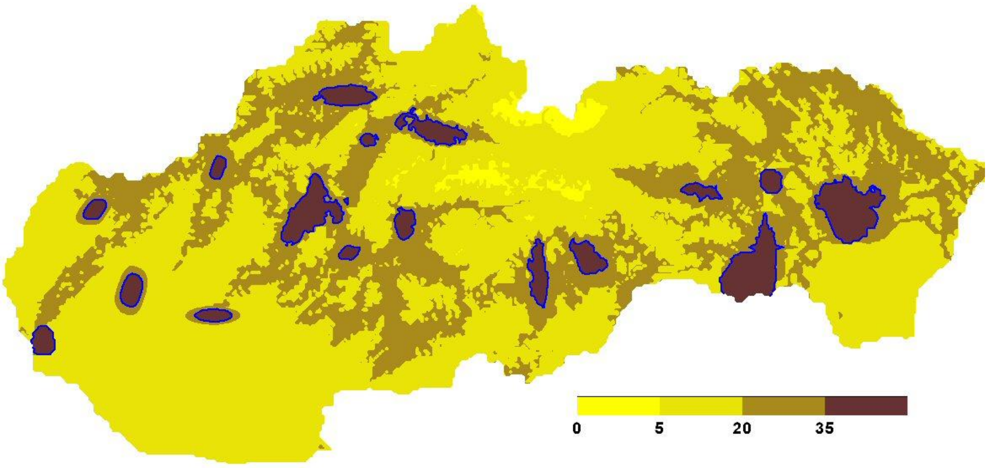

Figure 15.5: Exceedance (in days) of 24-h concentration of PM_{10} (50 µg.m^{-3}) - Slovakia, 2005.

Within the framework of the Holland-Slovak bilateral project “Improving of some pollutant monitoring within the Slovak Republic territory” (PPA03/SK/SK/7/7) the Dutch model LOTOS-EUROS was applied. For the years 1999 and 2003 two model runs were carried out (Szabó, 2006). In both cases two alternatives were taken into account: with and without inclusion of the all Slovak registered emission sources. Sequential 1-hour concentrations of all basic pollutants, including PM_{10}, were computed. The LOTOS outputs are box averages (grid-distance about 30 km), which better reflect the regional background level. Because the fugitive emissions such as wind blown dust and particle water were not taken into account the LOTOS data generally underestimated the monitored data. The year 1999 was close to climatological normal than extremely warm and dry year 2003, when the highest averages were recorded. For 2003 a little higher concentration level was estimated as for 1999 contrary to the national PM emission decrease about 30 % in the period 1999-2003. These facts document the importance of transboundary transport and highlight that PM_{10} problem overcrosses the European scale. The importance role of meteorological factors at PM_{10} pollution indicates also the yearly course of particular matter. There is clear decrease of annual concentrations at almost all stations (28) in 2004, the only exception is traffic station Nitra-Štefánikova, due to of influence new local sources. The share of registered national emissions on the formation of rural background PM_{10} level in Slovakia was estimated less than 20 % on average and share of the transboundary part over 60 % (Szabo, 2006; Ytrri and Aas, 2006).

15.4 PM composition

There is only little information concerning PM composition in Slovakia. Sulphates and nitrates are regularly monitored at EMEP stations. The share of sulphates in PM at Slovak background stations ranges between 15-25 % and of nitrate 6-11 %, depending on location and year (Table 15.2). Together with ammonium (the analysis of NH_4 in PM_{10} started in July 2005 on EMEP station SK04) the total contribution in the Slovak PM rural background is over 30 %. Heavy metals in PM_{10} are regularly measured at 26 urban/rural locations, but total HM mass contributions to PM_{10} is below 0.5 %. EC/OC in PM_{10} was measured at EMEP station SK04 during one year campaign 2002/2003 organised by NILU, CNR and National University of Ireland (Yttri et al., 2006). Annual concentration of EC 0.80 $\mu g.m^{-3}$ and OC 4.32 $\mu g.m^{-3}$ was reported for this station. The higher OC concentration observed during summer compared to winter at SK04 site was attributed to the influence of biogenic sources and forest fires (Yttri et al., 2006). Total carbonaceous material in SK04 station accounted for 36 % of PM_{10}. Data from urban area are still missing. Contribution of mineral dust in Slovakia is assumed to be high, especially in lowlands due to agriculture activities, some industrial activities, construction works, etc. Re-suspension and winter sanding may play significant role along roads, mainly in urban areas. However, all fugitive emissions as well as natural emissions have not been assessed in Slovakia until now. Episodes of Saharan dust or dust from other arid regions are sporadically observed, but generally such contribution supposed to be small in Slovakia. The contribution of marine aerosol for Central Europe was estimated about 1 $\mu g.m^{-3}$.

Table 15.2: Sulphate and nitrate concentrations in PM at some Slovak EMEP stations.

EMEP station	SO_4 [µg.m^{-3}]			NO_3 [µg.m^{-3}]			SO_4/PM_{10} [%]			NO_3/PM_{10} [%]		
	2003	2004	2005	2003	2004	2005	2003	2004	2005	2003	2004	2005
StarinaSK06	3.24	3.27	3.27	1.20	1.51	1.59	15.6	20.1	17.8	5.8	9.3	8.6
Stará Lesna SK04	2.76	3.51	2.55	1.15	1.06	1.15	17.5	25.4	17.3	7.2	7.7	7.8
Liesek SK05	3.51	3.00	3.42	2.13	2.04	2.39	14.5	16.8	15.3	8.8	11.4	10.7

15.5 Conclusions

1. Slovakia is a small country in Central Europe. The total national anthropogenic (registered) PM emission decreased from 290 kt in 1990 to 51 kt in 2004. Further reduction of this emission is limited. Transboundary transport of PM (of anthropogenic and natural origin) and “noncontrolable” national sources of particles play decisive role. Urban background is largely affected by traffic emission (diesel engines), resuspension, construction works and winter sanding. Consumption of coal in Slovakia is relatively very low. Unfortunately supportive scientific studies in Slovakia are still missing.
2. PM concentrations are increasing with increasing aridity, in Europe generally from the West to the East. Therefore some geographical factors should be introduced.
3. PM is typically transboundary problem given by lifetime of particles. Data among all Slovak PM_{10} stations correlate very well. Exceedances of daily limit values can be episodically observed direct on national border, e.g. in winter persistent anticyclones.
4. Knowledge on PM components and their origin in Slovakia is very poor.
5. The share of PM natural sources (primary and secondary) and area fugitive sources including wind blown dust, wild fires and biomass burning in Slovakia has not been estimated yet.
6. Contribution of rural background PM_{10} to urban background level is about 60 % with exception of some industrial and traffic stations.
7. Model computations based only on national primary PM emission inventory data underestimate very significantly the observed concentrations.
8. Further improvement of QA/QC process of PM monitoring and assessment, introduction of regular analysis of PM composition and improvement of modelling tools are needed in Slovakia.
9. The EU and in particular updated WHO guidelines introduced PM_{10} limit values and proposed $PM_{2.5}$ limit values are very strict for Slovakia. To meet these limits in inland Central and Eastern European countries is unreal (transboundary transport, natural sources, etc.). Therefore, the possibilities of national PM mitigation policy in Slovakia are very limited.

15.6 References

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16 Atmospheric particulate matter in Spain: levels, composition and source origin

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16.1 Abstract

Average ranges of PM_{10} and $PM_{2.5}$ concentrations and chemical composition in Spain show significant variations across the country, with current PM_{10} levels at several industrial and traffic hotspots exceeding recommended pollution limits. Such variations and exceedences are linked to patterns of anthropogenic and natural PM emissions, climate, and reactivity/stability of particulate species. PM_{10} and $PM_{2.5}$ concentrations reach 13-21µgPM_{10}/m^3 and 8-14µg$PM_{2.5}$/m^3 in EMEP type regional background sites, 19-21µgPM_{10}/m^3 and 12-17µg$PM_{2.5}$/m^3 in most rural sites, 28-32µgPM_{10}/m^3 and 18-25µg$PM_{2.5}$/m^3 in suburban sites, 28-47µgPM_{10}/m^3 and 19-29µg$PM_{2.5}$/m^3 in urban background and industrial sites, and 46-50µgPM_{10}/m^3 and 28-35µg$PM_{2.5}$/m^3 in heavy traffic hotpots. Spatial distributions show sulphate and carbon particle levels reaching maximum values in industrialised areas and large cities (where traffic emissions are higher), and nitrate levels increasing from the Atlantic to the Mediterranean coast (independently of the regional NO_x emissions). African dust outbreaks have an influence on the number of exceedances of the daily limit value, but their additional load on the mean annual PM_{10} levels is only highly significant in Southern Iberia and the Canary and Balearic islands. The marine aerosol contribution is near one order of magnitude higher in the Canaries compared to the other regions. Important temporal influences include PM intrusion events from Africa (more abundant in February-March and spring-summer), regional scale pollution episodes, and weekday *vs.* weekend activity. Higher summer insolation enhances $(NH_4)_2SO_4$ levels but depletes particulate NO_3^- (as a consequence of the thermal instability of ammonium nitrate in summer) and Cl^- (due to HCl volatilisation resulting from the interaction of gaseous HNO_3 with the marine NaCl), and it is also related to a general increase of dry dust resuspension under a semi-arid climate conditions. Average trace metal particle concentrations show the highest levels at industrial and traffic hotspots sites, sometimes exceeding rural background levels by over an order of magnitude (Ti, Cr, Mn, Cu, Zn, As, Sn, W and Pb). Levels of Cu and Sb are relatively high in urban areas when compared with industrialised regions. This is probably due to the fact that in urban areas important PM emissions arise from brake abrasion from road traffic. Cu, Sb, Fe and Zn are major constituents of brakes in vehicles. Levels of Cr, Mn, Ni, Zn, Mo, Se, Sn and Pb are higher in areas with steel production. Levels of As, Bi and Cu are relatively higher in areas with copper metallurgy industry. The levels of Zn are relatively high around zinc metallurgy hotspots. Levels of V and Ni are relatively high only in one of the areas with petrochemical plants, but probably have a low relationship with such plants and are likely to be emitted from fuel oil combustion. These conclusions may be also valid for other petrochemical hotspots

with power plants. Levels of Zn, As, Se, Zr, Cs, Tl y Pb are relatively higher in the ceramic production areas studied. Source apportionment studies show high variability according to the type of sampling station. Between 4 and 6 PM sources were identified by means of the source contribution analysis, with the majority of the sources such as the crustal, industrial (with different chemical profiles according to the site), marine (only in the PM_{10} samples) and traffic factors being common to all stations. At some sites there is a "combustion" factor, which accounts for the emissions from power plants, and/or an "external or regional" factor. The latter case includes emissions which are not generated locally with two different scenarios depending on the location: a) emissions from long distance transport, mainly characterised by the presence of ammonium sulphate and b) regional emissions, mostly defined by secondary inorganic aerosols, OM+EC and different trace metals.

16.2 Introduction

Due to the strong climatic and orographic contrasts found across the different regions in Spain, from the continental and mountainous interior to the Mediterranean and Atlantic coastlines and archipelagos (Canaries and Balearics), the composition and seasonal patterns of atmospheric particulate pollutants in urban areas of these regions can vary significantly. The factors controlling the variations of ambient air PM levels in Spain are of particular concern. PM_{10} levels in Spain contain a high proportion of resuspended anthropogenic and natural particles (Querol et al., 2004a).

The location of monitoring stations in the different EU state members is based on different strategies designed by each country, so that the number of stations in rural, urban, traffic or industrial sites varies greatly. According to Airbase data from 2001 to 2004 (http://air-climate.eionet.eu.int/), between 70-80% of the monitoring sites in Spain are located in hotspots, while in other EU state Members the average is 40-45%, although the average can be lower than 16% in some cases. As an obvious result of this, Spain, with a higher proportion of traffic and industrial hotspots monitoring sites, will present average annual PM_{10} levels and number of exceedences of the daily limit value higher than those countries with more rural and urban background monitoring sites. The difference is attributable to the fact that the monitoring of air quality in Spain was initially focused on the control of maximum exposure levels in urban environments, this explaining why the measuring sites were located in hotspots (i.e. places with a very high level of PM such as those close to heavy traffic and industrial emissions). The new directive, however, tries to evaluate the level of PM to which a representative population of 250,000 inhabitants is exposed. Nevertheless, it seems that the proposed $PM_{2.5}$ target/limit value is relatively permissive compared with the US $PM_{2.5}$ limit value, although it is very important to note that in EU the limit/target value also applies for hotspots.

With these current challenges and changes to European pollution law in mind (Putaud et al., 2004), this paper presents a summary of the results obtained from the PM pollution data collected over a period of 6 years (1999-2005) from a wide range of sites across Spain, greatly increasing the database used in previous investigations (Querol et al., 2004a) and better illustrating the factors controlling the flux of particulate matter across the country. A full report is publisher by the Spanish Ministry of the Environment (2006) in Spanish and English.

16.3 Methodology

The monitoring sites registered for the 1999-2005 time period were distributed across mainland Spain and the Canary and Balearic Islands, trying to cover all main types of different climatic conditions and anthropogenic activities. The areas located in the Iberian Peninsula include Galicia in the northwest, the Basque Country in the north, the eastern area bordering the Mediterranean sea, the central plateaux (both north and south interior Mesetas), Andalucía as the southernmost region of the Peninsula in the Atlantic-Mediterranean inter-phase and Extremadura in the central-western area next to Portugal. Both the Canary and Balearic islands were also selected, the former for their proximity to the Sahara desert, and the latter to illustrate PM levels at island locations in the Western Mediterranean. The study includes 28 sites as described by Figure 16.1 and Table 16.1.

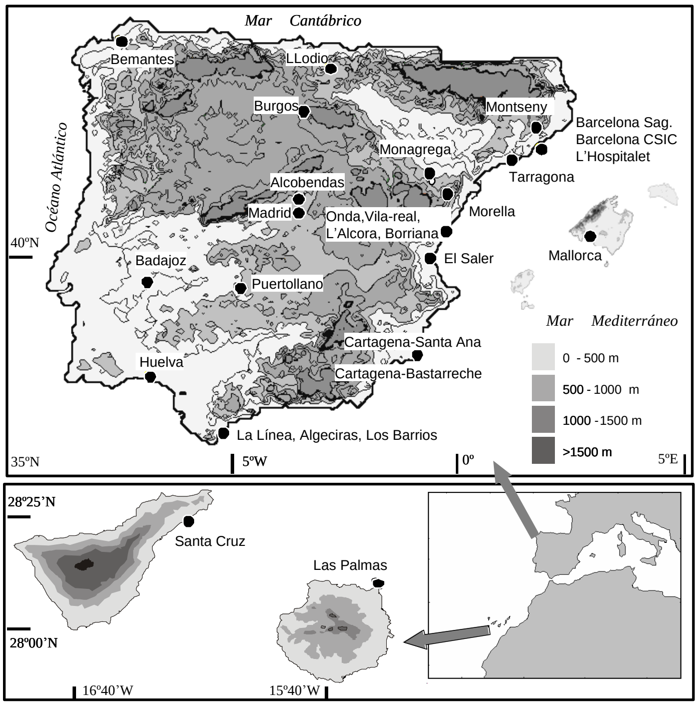


Figure 16.1: Location map of all monitoring stations across Spain discussed in this study.

The data were obtained using manual gravimetric PM_{10} high volume captors (in most cases the EU PM_{10} reference method EN12341 was used), and high or low volume samplers equipped with $PM_{2.5}$ inlets and quartz micro-fibre filters. The range of mean annual levels are summarised in Table 16.2. Following sampling, PM_{10} and $PM_{2.5}$ filters were analysed for major and trace elements and compounds, with a total of 57 determinations per sample (for specific conditions see Querol et al., 2004a). During this study the chemical components were grouped as: a) crustal (sum of Al_2O_3, SiO_2, CO_3^{2-}, Ca, Fe, K, Mg, Mn, Ti and P); b) marine (sum of Cl^-, Na^+ and marine sulphate); c) OM+EC or organic matter plus elemental carbon (value obtained after applying a 1.2 factor to the OC+EC concentrations for urban sites and 1.4 for regional background sites); and d) secondary inorganic species (SIC, as the sum of the non marine SO_4^{2-}, NO_3^- and NH_4^+ concentrations).

Receptor modelling techniques based on principal component analysis (PCA) and on a subsequent multilinear regression analysis (MLRA) were applied to the data bases for source apportionment analices at each sampling site following the methodology proponed by Thurston and Spengler (1985).

The influence of atmospheric transport scenarios on the levels of particulate matter was investigated by means of atmospheric back-trajectory analysis using the Hysplit model (Draxler and Rolph, 2003) and information obtained from TOMS-NASA, NRL, SKIRON and ICoD-DREAM aerosol and dust maps (TOMS, http://jwocky.gsfc.nasa.gov; NRL, http://www.nrlmry.navy.mil/aerosol; SKIRON: DREAM: http://forecast.uoa.gr; http://www.icod.org.mt/aerosol/dust, currently http://www.bsc.es/projects/earthscience/DREAM), and satellite images provided by the NASA SeaWIFS project (http://seawifs.gsfc.nasa.gov/SEAWIFS.html).

Table 16.1: Location and characteristics of the 28 measurement stations selected for the study.

Site	Longitude	Latitude	Altitude (m.a.s.l.)	Station Type	Sampling period
Alcobendas	03º 37' 39" W	40º 32' 42" N	667	Urban	2001
Algeciras	05º 27' 07" W	36º 08' 16" N	24	Urban-Industrial	2003-2004
Badajoz	06º 34' 48" W	38º 31' 48" N	188	Urban	2004
Barcelona-CSIC	02º 07' 09" E	41º 23' 05" N	68	Urban-Industrial	2002-2006
Barcelona-Sagrera	02º 11' 22" E	41º 25' 21" N	24	Traffic-Industrial	2001
Bemantes	08º 10' 50" W	43º 20' 15" N	170	Rural	2001
Borriana	00º 05' 10" W	39º 53' 38" N	20	Urban-industrial	2005
Burgos	03º 38' 15" W	42º 20' 06" N	889	Suburban	2004
Cartagena-Santa Ana	01º 00' 40" W	37º 39' 10" N	15	Suburban-Industrial	2004
Cartagena-Bastarreche	00º 58' 28" W	37º 36' 14" N	20	Urban-Industrial	2004
Huelva	05º 56' 24" W	37º 15' 21" N	10	Urban-Industrial	2001
L'Alcora	00º 12' 43" W	40º 04' 07" N	175	**Urban-industrial**	2002-2005
L'Hospitalet	02º 06' 40" W	41º 22' 23" N	70	Traffic-Industrial	1999-2000
La Línea	05º 20' 49" W	36º 09' 37" N	1	Urban-Industrial	2003-2004
Las Palmas	15º 24' 49" W	28º 08' 04" N	20	Urban	2001
Llodio	02º 57' 44" W	43º 08' 42" N	122	Urban-Industrial	2001
Los Barrios	05º 28' 55" W	36º 11' 02" N	45	Urban –Industrial	2003-2004
Madrid	03º 40' 52" W	40º 25' 32" N	672	Traffic	1999-2000
Mallorca	02º 35' 24" E	39º 35' 24" N	20	Suburban	2004
Monagrega	00º 19' 15" W	40º 56' 23" N	600	Rural	1999-2000
Montseny	02º 22' 40" E	41º 46' 47" N	730	Rural	2002-2006
Morella	00º 05' 34" W	40º 38' 10" N	1154	Rural	2004
Onda	00º 15' 09" W	39º 57' 44" N	163	Suburban-Industrial	2002-2005
Puertollano	04º 05' 19" W	38º 41' 64" N	670	Urban-Industrial	2004
Santa Cruz	16º 14' 51" W	28º 28' 21" N	52	Urban	2002-2006
Tarragona	01º 14' 52" E	41º 07' 29" N	20	Urban-Industrial	2001
Valencia- El Saler	00º 19' 08" W	30º 20' 46" N	7	Suburban coastal	2003-2004
Vila-real	00º 06' 21" W	39º 56' 30" N	60	Urban-Industrial	2002-2005

16.4 Results and interpretation

16.4.1 PM levels

According to the character of each monitoring site, PM_{10} and $PM_{2.5}$ concentrations (in $\mu g/m^3$ measured gravimetrically or corrected real time measurements) rise from: 13-21 and 8-14 (EMEP stations), 19-21 and 12-17 (rural), 28-32 and 18-25 (urban), 28-47 and 19-29 (urban-industrial background) to 46-50 and 28-35 (heavy traffic hotspots) (Figure 16.2 and Table 16.2). $PM_{2.5}$ concentrations are usually 40-75% those of PM_{10} at any given site. The $PM_{2.5}/PM_{10}$ ratios (Figure 16.2) measured at most sites of northern, north-western, north-eastern and central Spain fall in the range 0.6-0.7, with the highest ratios obtained in areas with higher pollution. This ratio decreases to 0.5 and 0.4 for most urban and rural sites of Southern Iberia and the Canary Islands, respectively, although again levels rise above this at heavily industrialised sites (0.6-0.7). The coarser grain size distribution trend shown in Figure 16.2 is probably the result of the higher mineral load in PM_{10} as a consequence of the drier climate and the proximity to the African desert regions.

At rural and regional background sites PM levels show concentration peaks coinciding with the intrusion of African air masses, regional atmospheric stagnation, and local contamination episodes, with a clear trend towards higher levels in summer due to resuspension, less precipitation and a higher frequency of African dust and regional episodes (Millán et al., 1997; Viana et al., 2002; Escudero et al., 2005). The latter trend is illustrated by Figure 16.3 which shows the regular occurrence of a summer PM_{10} maximum over the last 11 years at our Monagrega site in east central Spain, as well as the common occurrence of a spring peak and a winter minimum (Rodríguez et al., 2001, 2004; Moreno et al., 2005). We calculate that 85% of all PM_{10} daily exceedances (>50 µg/m^3) at this monitoring regional background site over this period were caused by North African dust outbreaks. The opposite situation is observed in industrial and urban areas where, in most cases, around 70-80% of the exceedances are due exclusively to local anthropogenic sources. In these areas, the seasonal trend for PM levels is reverse to the one described above for the regional background, with higher winter levels as a consequence of the prevalence of atmospheric stagnation.

Table 16.2: Typical ranges of mean annual values (in µg/m^3 and in % in brackets) for PM_{10} and $PM_{2.5}$, and different components in Spain.

	PM_{10}	Crustal	OM+EC	SIC	SO_4^{2-}	NO_3^-	NH_4^+	Marine aerosol	
EMEP stations	13-21	ND	ND	--	2-4	1-2	ND		
Rural background	19-21	2-5 (13-25%)	3-6 (13-29%)	5-8 (27-36%)	3-4 (15-18%)	1-3 (5-12%)	1.2-1.3 (6-7%)	Inland	0.7-1.7 (2-5%)
Urban background	28-32*	6-9* (21-28%)	5-10 (18-33%)	5-8 (18-27%)	2-4 (8-14%)	1.9-2.5 (6-8%)	1.1-1.6 (3-6%)	Coast & Balearic Islands	1.5-4.9 (3-12%)
Urban – industrial background	28-47	7-16+ (20-47%)	4-12 (12-26%)	6-13 (19-33%)	4-7 (12-19%)	1.1-5.5 (4-11%)	0.7-2.4 (2-6%)		
Traffic hotspots	46-50	13-15 (26-33%)	11-18 (25-37%)	8-15 (16-31%)	4-7 (9-14%)	2-6 (4-12%)	1.2-2.7 (3-5%)	Canary Islands	10-12 (25-27%)
	$PM_{2.5}$	Crustal	OM+EC	SIC	SO_4^{2-}	NO_3^-	NH_4^+	Marine aerosol	
EMEP stations	8-14	ND	ND	--	ND	ND	ND		
Rural background	12-17	1.5-2.1 (11-12%)	4-5 (27%)	4-6 (31-36%)	2-3 (17-21%)	0.5-2 (3-11%)	1.2-1.4 (8-9%)	Inland	0.5-0.8 (1-4%)
Urban background	18-25	2-3 (11-17%)	5-9 (25-37%)	4-6 (21-36%)	2-4 (11-20%)	0.4-1.3 (2-6%)	0.7-1.9 (4-11%)	Coast & Balearic Islands	0.3-1.7 (2-5%)
Urban – industrial background	19-29	2-5 (9-22%)	4-11 (18-35%)	5-11 (22-33%)	4-5 (13-20%)	0.5-3.5 (3-10%)	0.9-2.5 (4-9%)		
Traffic hotspots	28-35	4-6 (12-16%)	12-17 (38-51%)	7-13 (19-37%)	4-6 (11-17%)	1-4 (4-11%)	1.4-3.2 (4-9%)	Canary Islands	1.4-1.6 (6-9%)

* Las Palmas de Gran Canaria excluded (44 µgPM_{10}/m^3) due to the high mineral load (12µg/m^3) caused by the frequent African dust outbreaks, as well as the high sea spray load (11 µg/m^3). Also excluded crustal contribution at Cartagena-Sta Ana, due to construction works around the monitoring site during the study period. + crustal load 7-12µg/m^3 (20-34%) if excluded ceramic area.

Figure 16.4 summarises the average annual PM_{10} concentrations registered for the 6 year recording period. Also shown on this diagram is the maximum annual limit value set by the European directive for 2005 (EU Directive 1999/30/EC). It can be seen that one third of the sites, with the 1999-2005 data, already exceed 2005 limit values, and only the rural background sites would meet the intended indicative limit values suggested by WHO (2005). Figure 16.4 also shows that the 25 µg $PM_{2.5}/m^3$ target value, proposed in the new directive and to be met from January 2010, is currently exceeded in a significant number of traffic and several industrial hotspots. If the mineral dust load, mainly of an anthropogenic origin but with higher levels in Spain compared with most central and northern EU state members (Querol et al., 2004b) due to the accumulation on roads by climatic causes such as low rainfall, is subtracted from the annual PM_{10} and $PM_{2.5}$ means, all the measurements performed in the 28 sites meet the requirements of the current and forthcoming EU directives, with the exception of 2 traffic and 1 industrial hotspots (Figure 16.4).

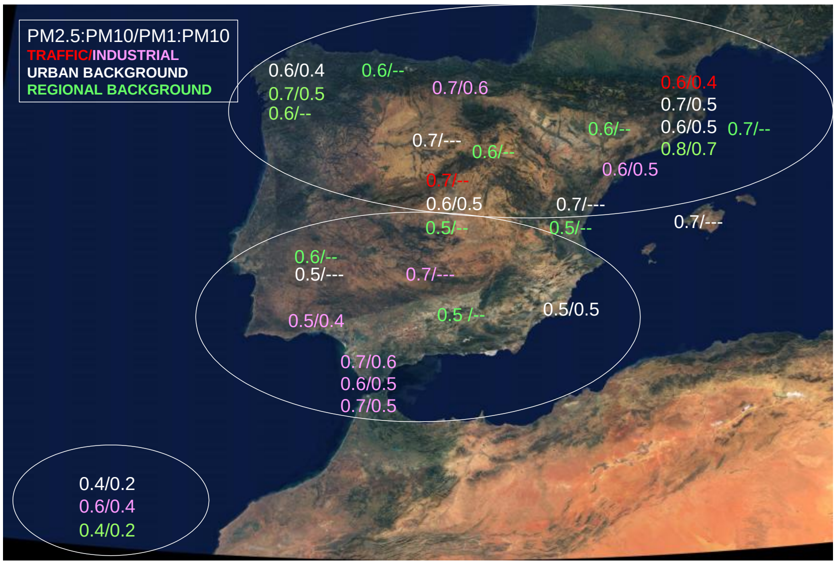


Figure 16.2: Average $PM_{2.5}/PM_{10}$ and PM_1/PM_{10} ratios indicating their regional, urban or traffic/industrial setting. Regional background data includes Spanish EMEP stations.

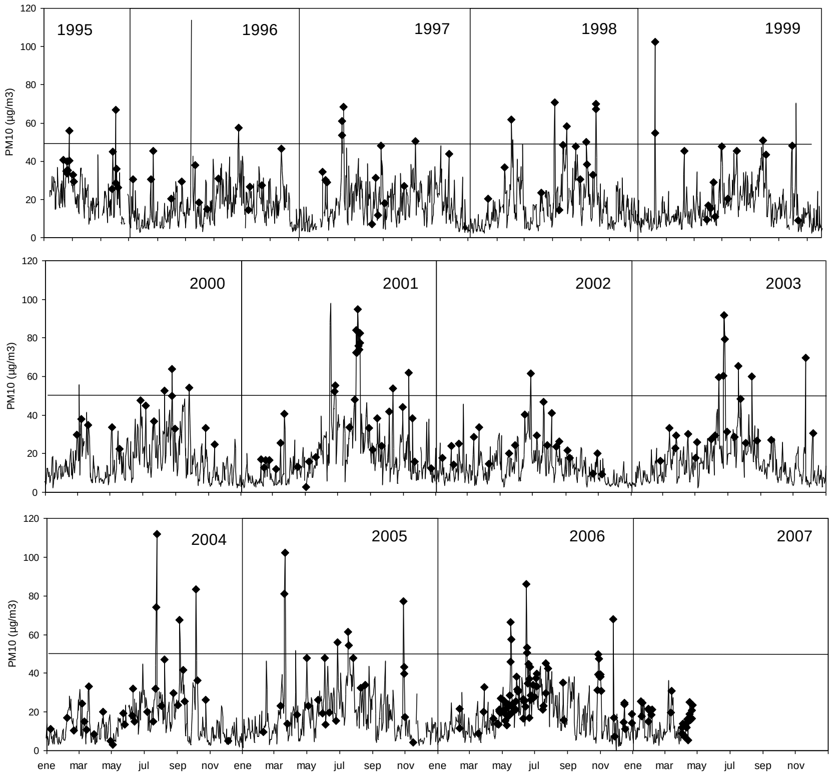


Figure 16.3: PM_{10} levels recorded from 1995 to 2007 at the Monagrega Regional background station and their relationship with the occurrence of African dust outbreaks (black rhombus), frequent during summer and in the February-March months. 54 out of 64 exceedances in these years were related to dust outbreaks. DLV: daily limit value.

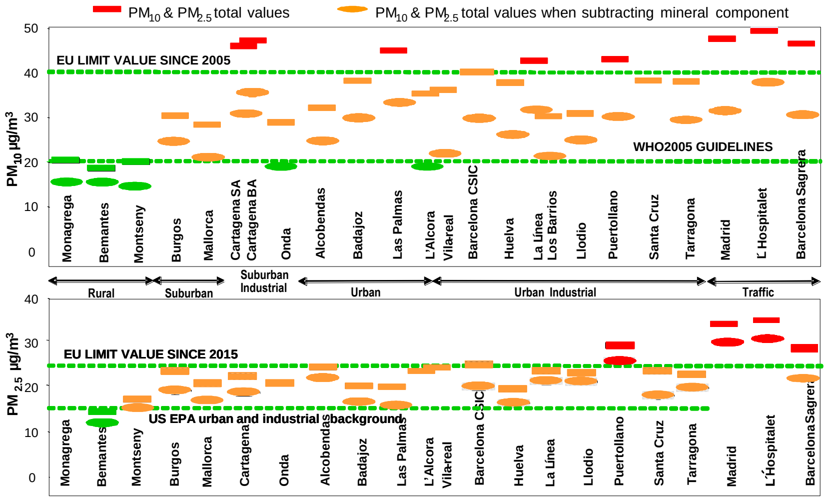


Figure 16.4: Top) Annual average PM_{10} values for each area studied across the country depending on the character of the site and compared with the allowed values for 2005 and the WHO 2005 air quality guidelines. Bottom) Same for the $PM_{2.5}$ values compared with the proposed limit value for 2015 and the US EPA limit value.

As we have discussed in previous publications (Querol et al., 2004c), and as is further illustrated by Figure 16.5, the current legislative daily PM$_{10}$ limit value is more demanding than the annual limit value. Figure 16.5 plots all data on the annual PM$_{10}$ and the values of the 90.4 percentile obtained in all PM monitoring sites of Spain in 2004 (a) and gives comparative data for elsewhere in Europe obtained from Airbase 2003 (b). The Figure unequivocally demonstrates how proposed limits on numbers of daily exceedances/year (currently 35 or 90.4 percentile) equivalent to the annual limit value of 40 µgPM$_{10}$/m^3 should be well over 60-65 µgPM$_{10}$/m^3, instead of the current 50 µgPM$_{10}$/m^3. Or in other words: a) to meet the requirement of 35 exceedances of the daily value of 50 µgPM$_{10}$/m^3, an annual mean of around 30 µgPM$_{10}$/m^3 should not be exceeded; or b) the number of annual exceedances of the 50 µgPM$_{10}$/m^3 daily limit value recorded by stations measuring 40 µgPM$_{10}$/m^3 as an annual mean is around 80, instead of 35. The 90.4 percentile and the annual mean are thus not independent variables and consequently only one of them should be standardised. If both of them are, however, to be standardised, then an annual mean of 40 µg/m^3 and a 90.4 percentile of around 60 µg/m^3 should be established. The fact that the same linear relationship is observed throughout Europe, with not very different slopes (1.356 for Spain in 2003, and 1.564 throughout Europe), indicates that the above discussion could be extrapolated across the rest of EU territory.

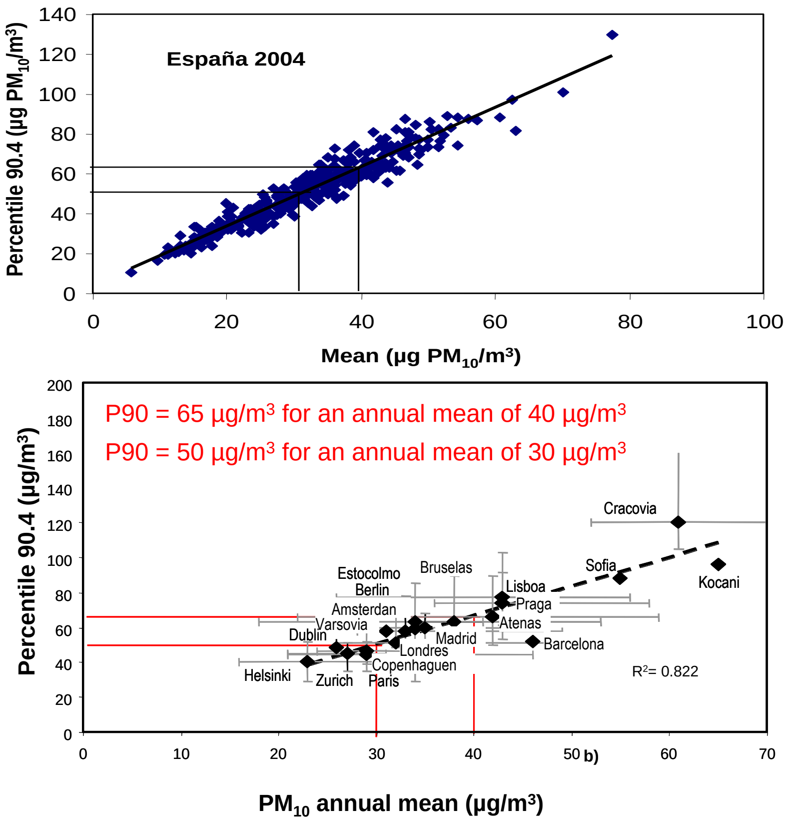
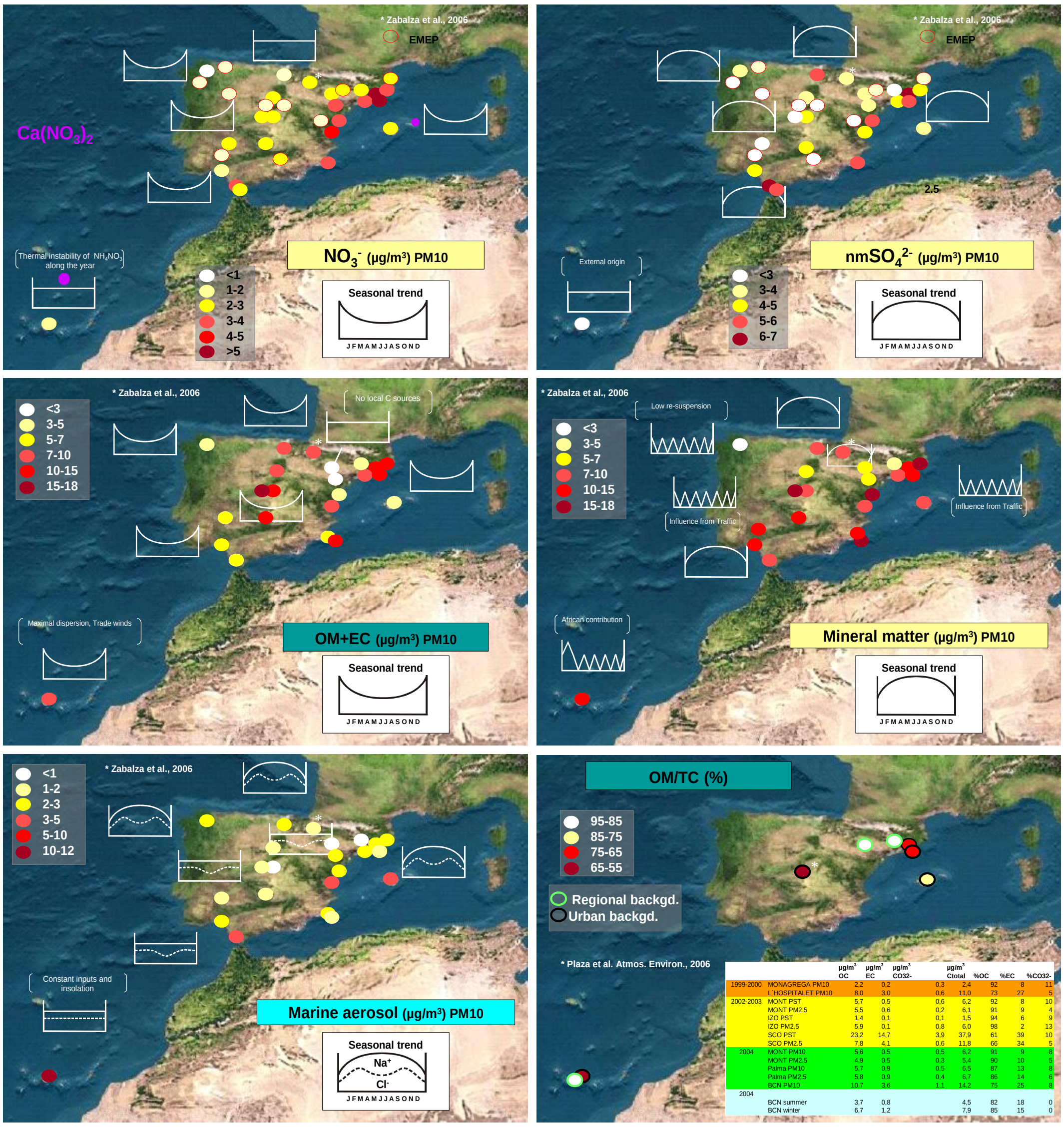


Figure 16.5: PM$_{10}$ annual average levels against the percentile 90.4 values for a) all monitoring stations in Spain in 2004, and b) other main European stations (all data from Airbase, http://air-climate.eionet.eu.int/databases/airbase/index_html). See discussion in the text.

16.4.2 Major PM components

Carbonaceous particle concentrations (organic matter and elemental carbon) for both coarser and finer fractions rise from minimal background levels of 3-6 µg/m^3 (rural) to 5-10 µg/m^3 for most suburban and urban sites, except for the city traffic hotspots (up to 15 µg/m^3 in Madrid) and the petrochemical and coal mining town of Puertollano, where levels commonly exceed 10 µg/m^3. The highest levels are measured at traffic hotspots (Madrid and Barcelona: Figure 16.6 and Table 16.2). In addition to this obvious traffic and industrial influence, there are seasonal variations discernable at virtually all stations, with a carbonaceous particulate winter maximum (in both fractions) related to the low dispersive atmospheric conditions typical of that time of the year. This can be contrasted with a notable summer minimum, attributed to lower traffic flows and enhanced mixing conditions, which is also observed in the Canary Islands due in this case to the strengthening of trade winds enhancing dispersion of local pollutants. The OC/(OC+EC) ratios in urban sites of Spain are very high (0.6-0.8). If diesel vehicles are a major road traffic emission source and the OC/EC ratio of the PM emissions of these vehicles is usually low, a mismatch between the theoretical impact of these emissions on PM levels and the PM speciation is found.

In marked contrast to the finer size fractionation of carbonaceous particles, those elements normally associated with **mineral particles**, such as silicates, carbonates, oxides and phosphates (“crustal mineral particles”), are notably more abundant in the coarser fraction ($PM_{2.5-10}$). These PM_{10} components increase from <6 µg/m^3 in rural background stations, to 6-8 µg/m^3 at surburban sites, to >8 µg/m^3 at virtually all of the other sites (Figure 16.6 and Table 16.2), except for the ceramic industrial area (Onda, Vila-real, Borriana and L’Alcora), where 9 to 16 µg/m^3 of crustal load was measured as an annual mean. The highest values (13-15 µg/m^3) are reached at the urban traffic hotspots and near primary industrial emission sources. The $PM_{2.5}$ mineral fraction is also clearly elevated near heavy traffic and specific industrial sites (4-6 µg/m^3 $PM_{2.5}$), although concentrations are always much lower than in the PM_{10} (13-15µg/m^3 PM_{10}). However, despite this decrease, it is important to emphasise the still high concentrations of fine ($PM_{2.5}$, and therefore more readily inhaled) crustal particles at traffic-rich and urban background sites, where levels range from 4 to 6 and 2 to 3 µg/m^3, respectively, as well as in some urban background monitoring stations in the Canaries (close to African dust emissions sources) which have recorded values of 3-5 µg/m^3.



		µg/m³ OC	µg/m³ EC	µg/m³ CO32-	µg/m³ Ctotal	%OC	%EC	%CO32-
1999-2000	MONAGREGA PM10	2,2	0,2	0,3	2,4	92	8	11
	L´HOSPITALET PM10	8,0	3,0	0,6	11,0	73	27	5
2002-2003	MONT PST	5,7	0,5	0,6	6,2	92	8	10
	MONT PM2.5	5,5	0,6	0,2	6,1	91	9	4
	IZO PST	1,4	0,1	0,1	1,5	94	6	9
	IZO PM2.5	5,9	0,1	0,8	6,0	98	2	13
	SCO PST	23,2	14,7	3,9	37,9	61	39	10
	SCO PM2.5	7,8	4,1	0,6	11,8	66	34	5
2004	MONT PM10	5,6	0,5	0,5	6,2	91	9	8
	MONT PM2.5	4,9	0,5	0,3	5,4	90	10	5
	Palma PM10	5,7	0,9	0,5	6,5	87	13	8
	Palma PM2,5	5,8	0,9	0,4	6,7	86	14	6
	BCN PM10	10,7	3,6	1,1	14,2	75	25	8
2004								
	BCN summer	3,7	0,8		4,5	82	18	0
	BCN winter	6,7	1,2		7,9	85	15	0

Figure 16.6: Distribution of NO_3^-, non marine SO_4^{2-}, OC+EC, mineral matter and marine aerosol (sea spray) levels (µg/m^3) and OM/TC ratio (TC=OM+EC) across the country for PM_{10}. Seasonal trends are also shown when applicable.

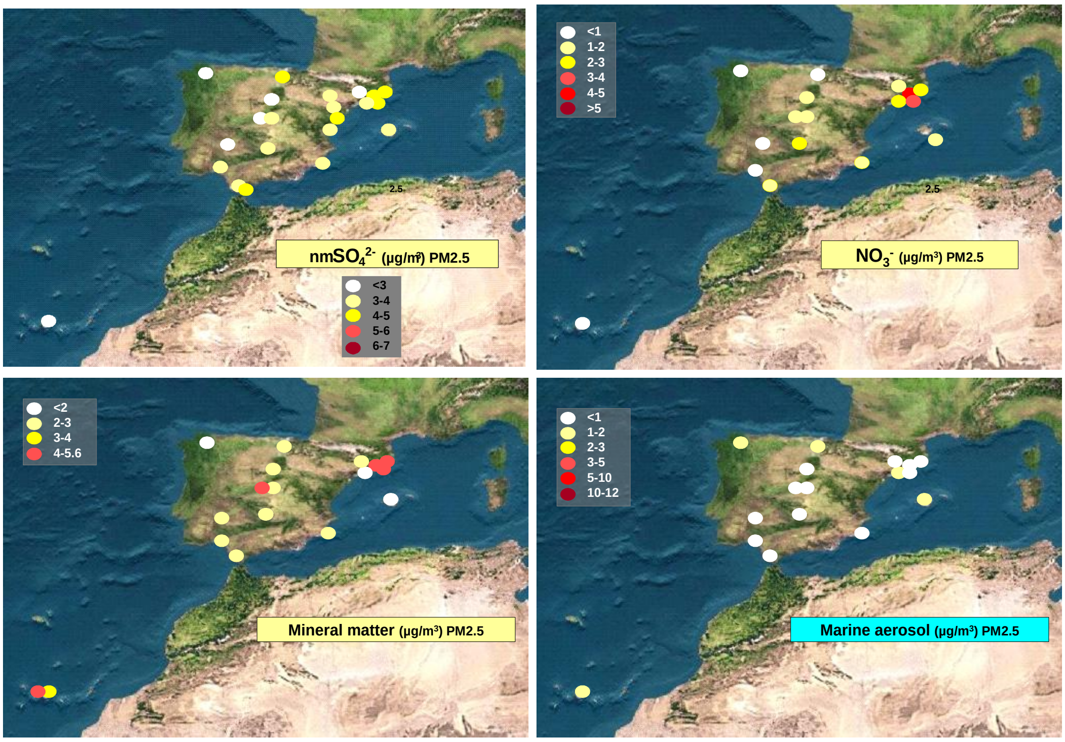


Figure 16.6b. Distribution of NO_3^-*, non marine* SO_4^{2-}*, mineral matter and marine aerosol (sea spray) levels (µg/m*^{3}*) across the country for* $PM_{2.5}$*. Seasonal tendencies are also shown when applicable.*

Figure 16.7 shows the annual mean concentrations of the major PM components versus PM_{10} and $PM_{2.5}$ levels. Notice how mineral dust is the PM component exhibiting the highest influence on the annual mean PM_{10} levels: it is the only component that always increases with increasing PM_{10} levels (from rural to suburban, urban-background, industrial and road traffic sites), and its contribution is as important as that (often higher than) of OC+EC and the sum of the SIC. The results indicate that as an average across the country, the increases in annual mean PM_{10} levels from rural to urban sites are mainly due to the increase in mineral dust load and OC+EC in PM_{10}. In the $PM_{2.5}$ fraction, all components exhibit an increasing trend with increasing general PM levels, but it is important to highlight that at the urban background sites and at the traffic hotspots the mean annual mineral levels in $PM_{2.5}$ reach 2-3 and 4-5 µg/m^3. This feature is not applicable to most European regions as reported by Querol et al., (2004c) and recently confirmed by Rodríguez et al., (2007) using the same methodology (see Figure 16.8) in a Milan-London-Barcelona compartive $PM_{2.5}$ study. At London, mineral dust in $PM_{2.5}$ reached an annual mean of 0.8 µg/m^3, whereas at Barcelona, with a lower traffic flor this contribution reached 5 µg/m^3. At the urban areas, the high mineral dust load results from two main contributions: 1) mainly from high resuspension rates of road dust, and other dust sources such as demolition and construction, after its accumulation on roads because of the lower rainfall rates in Spain in comparison with central and northern EU regions, 2) in a much lower proportion from African dust events and natural resuspension on arid soils.

It has been demonstrated that the dust outbreaks have a high influence in the number of exceedances (Rodriguez et al., 2001; Querol et al., 2004a), but the present study indicates a lower influence on the annual means (<3 µgPM_{10}/m^3 of the annual mean), except for the Spanish regions close to Africa (southern and eastern Iberia, Canaries, Balearic) where the annual means are also highly influenced by natural contributions (3-5 µgPM_{10}/m^3 of the annual mean).

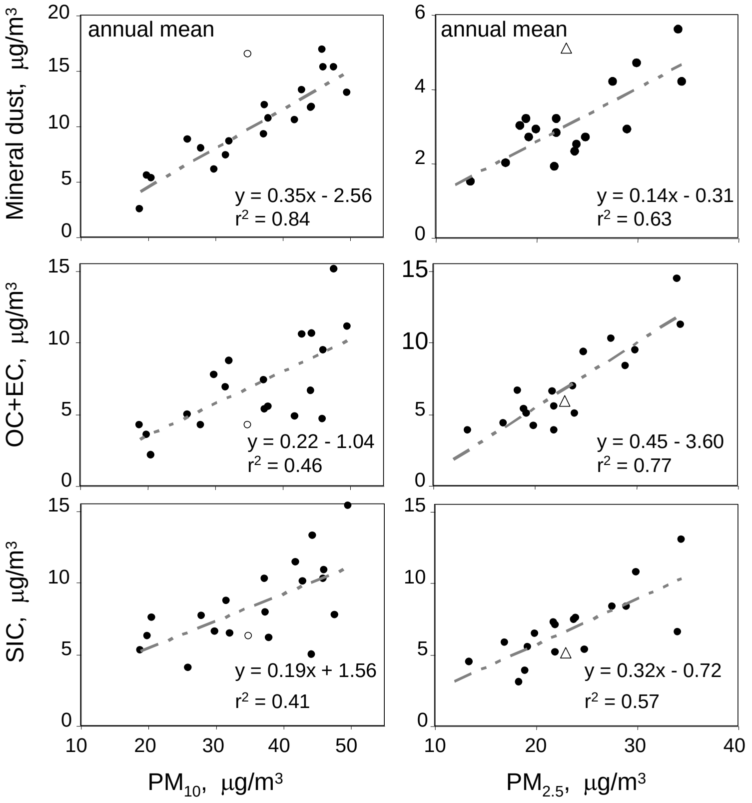


Figure 16.7: Annual mean levels of PM components versus PM_{10} and $PM_{2.5}$ levels across Spain (○: L'Alcora-industrial area of ceramic production and △: Santa Cruz de Tenerife urban-industrial background, none of them considered in the regression analysis).

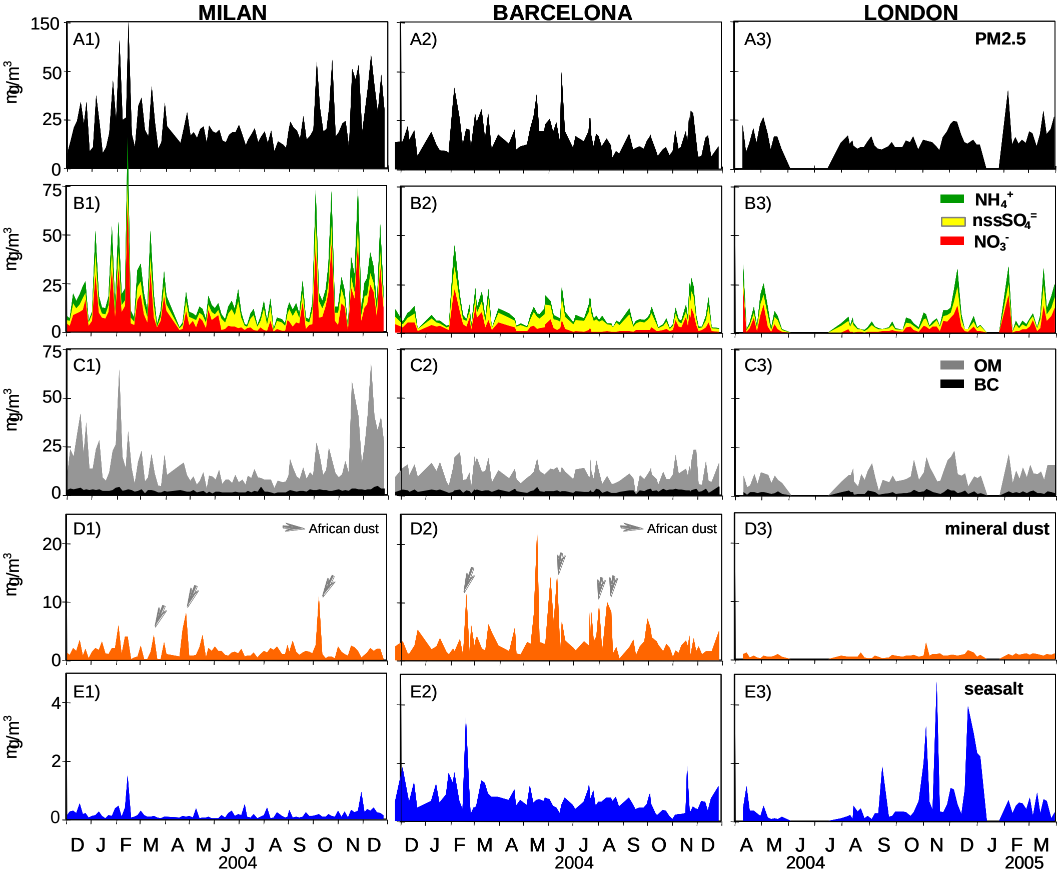


Figure 16.8: Comparison of $PM_{2.5}$ speciation data from Milan, Barcelona and London obtained with the same methodology (Rodríguez et al., 2007), note the high mineral matter load at Barcelona, but the similarity of levels for the other PM components when compared with London.

The same preference for the coarser fraction is displayed by **sea spray**, which is predictably extremely low (around 1 µg/m^3 or less for PM_{10}) for inland sites, but more than double at the coast, reaching 11.5 µg/m^3 in the Canary Islands site at Las Palmas (Figure 16.6 and Table 16.2). The load of marine aerosols in PM_{10} in the Atlantic coastal sites is much higher than in the Mediterranean coast, with levels reaching up to 7 µg/m^3, as an annual mean contribution (Visser et al., 2001). PM_{10} measurements of Na^+ and Cl^- in the Canaries once again show the characteristic lack of seasonal variability, a clear difference from those recorded in the Peninsula where there are two distinct patterns. The first of these patterns is shown in the coastal sites (except Huelva) where Na^+ ions are at their maximum in summer due to the stronger influence of sea breezes, whereas Cl^- levels decrease during the summer months as a consequence of their volatilisation as HCl during the formation of $NaNO_3$ from gaseous HNO_3 and marine NaCl. The second pattern is observed in the sites located within the continental interior (Madrid and Monagrega) where the arrival of Na^+ and Cl^- as marine aerosol in areas far away from the coast occurs in a constant manner throughout the year, especially associated with the entrance of Atlantic fronts. In such places Cl^-/Na^+ ratios decrease during the summer months as a consequence of Cl^- volatilisation as HCl, as illustrated by Figure 16.9 which shows the typical Cl^-/Na^+ summer depletion in an inland site (Monagrega).

Levels of **secondary inorganic compounds** (sulphate, nitrate and ammonium salts) in PM_{10} measure <8 µg/m^3 at the majority of sampling stations, but exceed 10 µg/m^3 at several of the industrial and traffic hotspots, with the content in $PM_{2.5}$ being higher than the content in the coarse fraction (usually 65-85% of the content in PM_{10} is present in $PM_{2.5}$, Figure 16.6 and Table 16.2). Non-marine sulphate PM_{10} levels (mostly $(NH_4)_2SO_4$) are lower (<4 µg/m^3) in rural, suburban and urban background monitoring stations compared with traffic and industrial hotspots (4-7 µg/m^3), with the percentage of sulphate in $PM_{2.5}$ fraction always being higher than in the coarse (70% in $PM_{2.5}$). Within the Iberian Peninsula $(NH_4)_2SO_4$ levels are at their maximum in summer (Figure 16.9), because of the stronger insolation and therefore the higher oxidation of SO_2 to SO_4^{2-}. In the Canary Islands on the other hand, an elevated percentage of sulphate levels is not local in origin but due to emissions from urban and industrial sources in Europe having been rapidly transported over the ocean by the north-easterly trade winds (McGovern et al, 2002). Thus, sulphate aerosols in the Canaries are mostly externally derived and therefore lack seasonal variability.

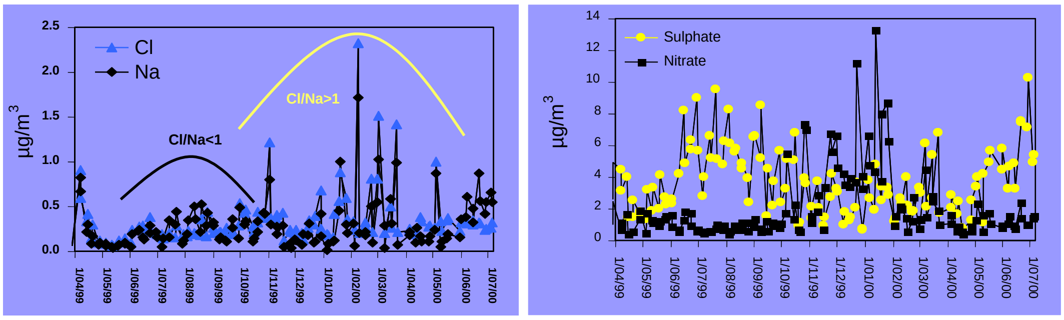


Figure 16.9: Levels of marine components, sulphate and nitrate at the Monagrega inland regional background station registered from April 1999 to July 2000.

Nitrate levels are characterised by a clear spatial gradient in concentrations across the Peninsula towards the Mediterranean region, (independently of the relevance of the regional/local emissions of NO_3^- precursors) (Figure 16.6). This trend is observed independently of the type of monitoring site studied, with sites under similar industrial emissions (like Huelva and Tarragona) showing very different average nitrate levels (2 versus 4 µg/m^3 in PM_{10} respectively). A possible cause of this spatial pattern is the higher ammonia levels along the Mediterranean coast, above all in the northeast of Spain, caused by emissions from intensive cultivation and farming (EPER, 2001). However, traffic NH_3 emisssions in urban areas with high humidity (coastal areas in our case) may also give rise high ammonium nitrate levels. Within this context maximum levels (4-6 µg/m^3) are associated with the highly industrialised areas of the Mediterranean coast, while in the rest of industrial (the Atlantic sites of Huelva and Llodio), regional and urban background sites, nitrate levels vary between 2-3 µg/m^3, and the lowest values occur in the rural background site in North Spain (Bemantes, 1 µg/m^3). Seasonal variations show increased nitrate levels during winter, the opposite pattern to that shown by non-marine sulphates (Figure 16.8). This is probably due to the low thermal stability on NH_4NO_3 in summer, when under the prevalent warm conditions of most of the Iberian Peninsula, the formation of HNO_3 instead of NH_4NO_3 is favoured (Adams et al., 1999, Pakkanen et al., 1999; Schaap et al., 2002). This interpretation is supported by the lack of a seasonal pattern in northern Iberia and the Canary Islands due probably to mild summer and winter ambient conditions, respectively, compared with other regions of Spain.

A very peculiar feature is the large proportion of nitrate found in the coarse fraction of PM_{10} compared with other studies carried out in central and northern Europe (EC, 2004). The presence of gaseous HNO_3 and the possible interaction of this pollutant with mineral Ca carbonate and sea salt may account for the increase of the coarse nitrate proportion. The $PM_{2.5}$ nitrate fraction is always significantly lower than the coarser component (usually between 25-75%), this being due to the preference of $NaNO_3$ and $Ca(NO_3)_2$ for the coarser fraction (2.5-5.0 µm, Querol et al., 1998). In the Canary Islands, given the high ambient levels of NaCl, most of the nitrate is normally present as sodium (rather than ammonium) nitrate. Canarian nitrate levels are similar to those registered in the western Peninsula, and once again seasonal variation is less pronounced.

Levels of **ammonium** in both PM_{10} and $PM_{2.5}$ fractions register <2 $\mu g/m^3$ (Table 16.3) in all sites except those in Barcelona and Puertollano, and, unlike in most other elements described above, there is no preferential concentration in either fraction. As previously described, ammonium nitrate concentrations register minimum levels in summer in most of the sites, due to the thermal instability of ammonium nitrate and the corresponding presence of gaseous nitric acid and ammonia as the dominant phases. In winter, on the other hand, this compound is stable as a particulate aerosol, and its accumulation is favoured by less dispersive conditions in the atmosphere.

As an important conclusion of this study Table 16.3 shows the trace element concentration ranges measured for the elements studied in the 3 rural sites, 9 urban background sites and a number of industrial sites with different industrial influences. These concentration ranges may be of great value to evaluate the air quality in industrial areas concerning the concentration levels of some trace elements of environmental concern without limit or target values, or even to identify possible emissions of hazardous elements from a given industrial activity.

At the least polluted rural sites (Monagrega, Bemantes and Montseny), most trace metal concentrations lie within the range of 0.1-10 ng/m^3, with only Zr, Mo, Ni, V, Ti, Ba, Cu, Pb, Zn (in increasing order of abundance) exceeding 1 ng/m^3. Concentrations rise with increasing anthropogenic contamination, in the most extreme cases multiplying values to over x10 rural background for Ti, Cr, Mn, Cu, Zn, As, Sn, W and Pb.

Table 16.3: Concentration ranges for annual trace element levels (ng/m^3) in PM$_{10}$ measured in rural and urban background sites of Spain, and in areas with different types of industry. Bold numbers are marked to highlight the trace markers from each type of environment.

ng/m^3	Rural background		Urban background		Steel	Stainless steel	Copper metallurgy	Zinc metallurgy	Petrochemical estates		Ceramic estates	
	min	max	min	max	mean	mean	mean	mean	min	max	min	max
Li	0.1	0.3	0.2	0.7	0.4	0.6	0.2	0,4	0.2	1.0	0.6	1.3
Be	0.01	0.02	0.02	0.05	0.06	0.03	0.07	0.06	0.01	0.07	0.02	0.05
Sc	0.1	0.1	0.1	0.3	0.1	0.2	0.1	0.10	0.1	0.3	0.3	0.5
Ti	7	22	18	**83**	24	36	60	31	23	62	33	57
V	2	5	2	15	8	**28**	7	11	7	**25**	4	5
Cr	1	2	2	8	**25**	**24**	2	2.9	2	6	3	8
Mn	5	5	4	23	**87**	17	11	12	8	11	6	8
Co	0.1	0.1	0.2	0.5	0.5	0.6	0.4	0.3	0.2	0.8	0.4	0.7
Ni	2	3	2	7	**33**	**20**	3	6.7	3	**11**	3	5
Cu	4	8	7	**81**	33	11	**70**	18	23	33	4	10
Zn	16	30	14	**106**	**417**	73	51	**504**	35	54	45	**183**
Ga	0.1	0.2	0.1	0.3	0.4	0.2	0.3	0.2	0.2	0.4	0.2	0.3
Ge	0.1	0.3	0.04	0.3	0.2	0.3	0.1	0.04	0.1	0.2	0.03	0.1
As	0.3	0.4	0.3	1.5	1.8	0.9	**5**	1.0	0.5	1.9	1.7	**5**
Se	0.3	0.5	0.3	1.1	**3**	0.8	1.5	0.6	0.5	0.6	1.0	**3**
Rb	0.5	0.6	0.5	1.8	1.1	0.8	1.5	0.9	0.6	1.6	1.2	2.4
Sr	1	5	3	**10**	3	6	4	7.8	4	5	3	5
Y	0.1	0.1	0.1	0.4	0.1	0.3	0.3	0.1	0.1	0.3	0.2	0.3
Zr	4	4	2	10	2	5	2	1.7	2	6	10	**20**
Nb	0.04	0.1	0.05	0.4	0.1	0.2	0.2	0.1	0.1	0.3	0.2	0.3
Mo	2	3	2	5	**15**	**15**	2	1.7	2	7	1	2
Cd	0.2	0.2	0.1	0.7	1.2	0.3	0.8	0.7	0.1	0.8	0.6	1.5
Sn	1	2	1	6	**38**	1	2	2.0	2	2	1	1
Sb	0.6	0.6	1	**11**	4	1	3	3.4	1	7	1	6
Cs	0.01	0.04	0.03	0.13	0.1	0.1	0.1	0.06	0.04	**0.2**	0.1	**0.3**
Ba	5	11	4	**41**	14	15	16	16	12	16	12	16
La	0.1	0.2	0.2	0.6	0.3	0.6	0.5	0.3	0.3	0.9	0.3	0.6
Ce	0.2	0.4	0.4	1.3	0.4	0.7	0.9	0.7	0.5	1.2	0.7	1.9
Pr	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.08	0.1	0.2	0.1	0.2
Hf	0.1	0.2	0.1	0.3	0.1	0.2	0.2	0.3	0.1	0.2	0.2	0.4
W	0.01	0.03	0.05	0.6	0.7	0.2	0.06	0.07	0.04	0.2	0.10	0.3
Tl	0.1	0.1	0.05	0.4	0.3	0.01	0.2	0.1	0.03	0.3	0.5	**2.8**
Pb	5	10	7	57	**102**	13	37	20	8	37	35	**103**
Bi	0.1	0.1	0.1	1.0	0.5	0.1	**1.6**	0.2	0.1	0.2	0.4	**1.5**
Th	0.1	0.2	0.1	0.3	0.1	0.1	0.4	0.1	0.1	0.4	0.1	0.2
U	0.1	0.2	0.1	0.3	0.3	0.1	0.3	0.2	0.1	0.3	0.1	0.1

The comparison of the usual concentration range for trace elements in urban areas and those measured at the above list of industrial regions allowed us to conclude the following evidences:

- Levels of Ba, Cu, Sb, Sr, Ti and Zn are relatively high in urban areas when compared with industrialised regions. This is probably due to the fact that in urban areas important PM emissions arise from brake (Cu, Fe, Zn, Sb), tyre (Ba and Zn) and road pavement (Sr and Ti) abrasion.

- Levels of Cr, Mn, Ni, Zn, Mo, Se, Sn and Pb are relatively high in steel production areas.
- Levels of V, Cr, Ni and Mo are relatively higher in areas where stainless steel is produced. Levels of V and Ni in this area (La Línea and Algeciras) may be also highly influenced by the petrochemical industry and fuel oil combustion (power generation and shipping emissions).
- Levels of As, Bi and Cu are relatively higher in areas with copper metallurgy industry.
- Leviels of Zn are relatively high at the zinc metallurgy hotspot (Cartagena). At this site leveles of V and Ni are also slightly high compared with other areas, but this is attributed to the emissions from a petrochemical estate or a fuel-oil power plant loscated in the same area.
- Levels of V and Ni are relatively high only in one of the areas with petrochemical plants (Algeciras-La Línea), but not in the others (Cartagena, Huelva, Puertollano and Tarragona) where the levels measured for these two elements fall in the usual range measured at urban sites. As previously stated the higher V and Ni levels measured at Algeciras and La Línea may be also attributed to fuel oil combustion: power generation and the intensive shipping emissions from the Gibraltar strait.
- The ceramic production area is characterised by a number of trace elements present in relatively high levels when compared with the usual range found in urban sites and also around other industrial activities. These elements are Zn, As, Se, Zr, Cs, Tl and Pb, and the reason for the higher concentrations is probably due to the frit, enamel and pigment production and applications.

Thus atmospheric metal particle mixtures from our sites tend to each have their own characteristic chemical signature. Furthermore, it is interesting to note that the ambient air levels of crustal related trace elements (Cs, Sr, Ti among others) measured as $PM_{2.5}$ reach only 20-40% the levels of PM_{10}, a percentage that in contrast increases up to 60, 65, 70 and 80% for As, Ni, Pb and Cd.

From the data available in thi study, we do not expect there will be major problems in the near future in meeting requirements from EU air quality directives concerning levels of metals in ambient air, out of a few specific industrial hotspots.

16.4.3 Source apportionment

Following the source apportionment analysis strategy described by Thurston and Spengler (1985), the different sources which contribute to the levels of PM_{10} and $PM_{2.5}$ were identified (Table 16.4), and their contributions have been quantified on a daily and annual basis for both samples at each station. Between 4 and 6 PM sources were identified by means of the source contribution analysis, the majority of the sources such as the crustal, industrial (with different chemical profiles according to the site), marine (only in the PM_{10} samples) and traffic factors were common to all stations. The crustal and traffic sources account for the same type of emissions at the different sites, whereas the industrial sources at sites such as Llodio, Huelva, Bastarreche, Palma de Mallorca and Puertollano depend on the different industrial activities. Furthermore, at four sites (A Coruña, Barcelona, Canaries and Puertollano) a "combustion" factor was defined, which accounts for the emissions from power plants. At the Llodio and Las Palmas (Canaries) stations, a factor defined as "external" was determined, which includes emissions which are not generated locally and are mainly characterised by the presence of ammonium sulfate (tracer of regional and long-range transport). Also a secondary-regional factor, not easily linked to any specific emission source, was defined at Burgos, Badajoz, Santa Ana, Bastarreche and Puertollano mostly defined by secondary inorganic aerosols, different trace metals and OM+EC, depending on each site.

As expected, the contribution of the different sources is highly variable according to the type of sampling station. The results obtained at the sites in the Iberian Peninsula are also very different from those obtained in the Canary Islands. The results of the source apportionment analysis of particulate matter are presented as an example of the outputs of the studies performed. Main points may be summarised as follows:

- Direct road traffic contributions reach from 30-48% of the PM_{10} annual load in urban sites, not including secondary aerosols which are formed from gaseous precursors from traffic. These values can be lower (e.g. 21%) in some urban sites such as Badajoz where crustal and secondary particles are predominant.
- Industrial contributions reach, in most industrial areas, loads close to 30% of the PM_{10} annual values. Exceptional high values can be registered at sites with high industrial influence (44% in Puertollano).
- There is an important and constantly identified source of crustal composition which is in fact not a single source but includes a mixture of natural and anthropogenic mineral matter (road dust, demolition and construction dust among others) deposited in urban areas and constantly being resuspended by traffic and wind. This load represents 25 to 35% of the PM_{10} mass in urban areas, but can reach up to 50% around industrial areas with primary particulate emissions (ceramics). It is important to note the marked North to South increasing gradient found when looking at mineral matter levels in PM_{10} as aridity (caused by low rainfall rates) and proximity to Africa increases.
- The marine contribution is limited to 3-5% in continental sites, 4-10% in coastal sites, but reaches 30-35% in urban sites of the Canary Islands on an mean annual basis. These high percentages are due to a relatively low PM_{10} concentrations and high Atlantic wind speeds.
- There is a large contribution of unaccounted mass for model outputs obtained for regional background sites. This is attributed to the relatively high proportion of water contained in PM_{10} which is still not extracted from the sample under 25 or 50% humidity chambers after 48 h of equilibrium. This artefact is inherent to the filter sampling strategy and is more important in remote sites due to the lower ambient concentrations of actual PM components compared with absorbed water with respect to the polluted sites.
- Another limitation we found from our source apportionment studies is the frequent identification of a secondary inorganic aerosol (SIA) regional contribution source resulting in lower loadings of other components. This may account for up to 30% of the PM_{10} levels and is in fact a regional or

external source stemming from a mixture of contributions, not a single source. The relative load of this mixed sources component is lower in polluted sites because part of its contribution is assigned by modelling to local emission sources that are partially associated with SIA and with defined chemical tracers.

- There is an increasing gradient from the lower levels of the Atlantic side to relatively higher levels in the Mediterranean coast of Spain concerning the SIA load on a regional scale. This is attributed to lower dispersion of pollutants, lower rainfall, and probably to higher NH_3 levels (due to agricultural emissions) in the eastern part of the country. Thus the origin of this higher secondary inorganic load is due to relatively high NO_x and SO_2 emissions from industry and urban sources, to the higher NH_3 agricultural emissions, and probably to the higher humidity in eastern Spain.

Natural sources have a much higher influence on PM$_{10}$ levels in the Canary Islands than in the Peninsula. The marine source represents 35% of the PM$_{10}$ mass in the Canaries (12 µg/m^3), but only 3–15% in the Peninsula (0.7–3.4 µg/m^3). In the Central regions (Madrid and Monagrega), this fraction contributes with only 0.5–1.0 µg/m^3 whereas in the coastal areas it reaches 2–3 µg/m^3. Finally, the crustal load in PM$_{10}$ ranges from 16–36% at all sites, including the one in the Canary Islands (33%). However, in absolute values, the contribution of the crustal factor is maximal in the Canary Islands 11–15 µg/m^3. In this case, a high proportion of the crustal contribution has an African origin (mean daily dust loads reaching 100–600 µg PM$_{10}$/m^3 are often recorded during the frequent African episodes, known locally as "calima"). The crustal component at the Barcelona and Puertollano stations attained similar values (15 µg/m^3). However, this is due to road dust resuspension and other mineral emissions rather than to African contributions. Moreover, crustal contributions at urban stations (Escuelas Aguirre-Madrid, Huelva, Tarragona, Llodio, L'Hospitalet, Badajoz) are high (8–12 µg/m^3).

Table 16.4: Results of the source apportionment analysis (% contribution to mean annual PM mass levels) performed for PM$_{10}$ (top) and PM$_{2.5}$ (bottom) in different monitoring sites of Spain.

PM$_{10}$	Montseny	Monagrega	Bemantes	Palma	Huelva	Alcobendas	Llodio	Las Palmas	Tarragona
Crustal	23	26	12	16	27	31	26	33	32
Regional	58	26	24	20	<1	22	19	10	<1
Traffic	<1	13	25	31	33	34	22	5	30
Marine	9	5	14	16	5	6	7	35	9
Industrial	<1	<1	17	15	32	6	15	10	28
Not det.	8	30	8	2	3	1	11	7	1

PM$_{10}$	Madrid	L'Hospitalet	Barcelona	Cart. Bast.	Burgos	Badajoz	Puertollano	Los Barrios	Algeciras
Crustal	26	24	32	25	24	32	36	27	25
Regional	18	<1	<1	17	26	20	<1	<1	<1
Traffic	48	35	32	19	10	21	<1	26	18
Marine	3	4	5	3	3	4	9	15	17
Industrial	<1	24	30	5	23	9	44	31	37
Not det.	5	13	1	31	14	14	11	1	3

PM$_{2.5}$	Badajoz	Palma	L'Hospitalet	Burgos	Carta. S.A.	Puertollano	Badajoz
Crustal	22	19	9	14	9	6	22
Regional	30	30	<1	30	<1	<1	30
Traffic	28	21	53	9	40	<1	28
Marine	<1	<1	<1	<1	2	<1	<1
Industrial	3	8	35	20	27	59	3
Not det.	17	22	3	27	22	35	17

The crustal load for days with African dust outbreaks at remote sites is much higher (12-15 and 2.5-5 µg/m^3 for PM_{10} and $PM_{2.5}$, respectively as annual means) than the annual mean 3-5.5 and 1.3-3 µg/m^3 for PM_{10} and $PM_{2.5}$) and especially than for non African days (1-4 and 1-2 µg/m^3 for PM_{10} and $PM_{2.5}$). With these data one may calculate that the regional soil resuspension may account for around 1-4 and 1-2 µg/m^3 as annual PM_{10} and $PM_{2.5}$ means, whereas the African dust contribution to the mean annual levels may reach 1-2 and 0.3-1 µg/m^3 for PM_{10} and $PM_{2.5}$, in central and northern Iberia. Higher African dust contributions are expected for the Balearic and Canary Islands and Southern Iberia.

If we subtract the 5.5 µg/m^3 crustal contribution detected at the Monagrega rural station (regional dust resuspensión: local and African) from the urban background levels of crustal material, it may be concluded that there is a local urban crustal contribution of 2–7 µg/m^3 at urban sites. This contribution is therefore related to the mineral city background arising from anthropogenic activities (demolition, construction, road works, traffic). If we subtract the levels of crustal components recorded at urban background from those attained at roadside sites it can be concluded that the local pavement erosion of the monitored road accounts for 3–5 µg/m^3 of crustal input to the annual PM_{10} mean levels. Thus, an important proportion of the crustal load quantified with the receptor modelling may be attributed to urban anthropogenic sources such as traffic. Road dust may be deposited onto the pavement and, in the absence of rain episodes, the resuspension of this dust could increase the crustal load of PM_{10}. The source receptor model will not always associate this dust with traffic tracers such as nitrate or carbonaceous aerosols.

The same emission sources found to be responsible for major variations of PM_{10} levels were identified for $PM_{2.5}$ using the factor analysis. However, as discussed above, the marine and the crustal factor contributions were markedly reduced with respect to PM_{10}. However, in relative values, the crustal contribution may still account for around 20% of the $PM_{2.5}$ mass, especially at kerbside sites.

16.5 Additional remarks: PM_{10}, $PM_{2.5}$ and PM_1

The coarse fraction ($PM_{10-2.5}$) is dominantly made up of mineral dust (with variable origin) and marine aerosol, although variable relative minor proportions of SIA (Na, Ca, K, Mg sulphate and nitrate) and carbonaceous material may be also present. It is evidenced from several studies that at drier and warmer regions of Europe the coarse/fine fraction of SIA increases with respect to the cooler and wet regions.

The mass of marine aerosol and mineral dust is reduced in the $PM_{2.5}$ fraction with respect to PM_{10}, specially the first one. However, in drier and warm regions of Europe the contribution of mineral dust to $PM_{2.5}$ may still reach 15-20%. Most of the carbonaceous components presents in PM_{10} fall also in the $PM_{2.5}$ range, but as previously stated a fraction of the sulphate, and specially sulphate, loads of PM_{10} is coarse, and consequently is not present in $PM_{2.5}$. Thus, $PM_{2.5}$ is still a mixture of SIA, carbonaceous material and variable proportions of mineral dust depending on the region of Europe. In industrial hotspots with important primary PM emissions, the mineral load in $PM_{2.5}$ may still be very high (up to 40% of the bulk PM2.5 mass around cement, ceramic production areas or mining activity).

The mineral dust load is markedly reduced if PM_1, thus even in Southern Europe, the mineral matter load in PM1 measured at urban sites is lower than 1 µgPM_1/m^3, much reduced than in $PM_{2.5}$ (2-6 µg$PM_{2.5}/m^3$). Around 80-90% of the carbonaceous material present in $PM_{2.5}$ is still present in PM_1. However, SIA (especially nitrate levels) are reduced from $PM_{2.5}$ to PM_1 by a 20-30%. Thus, the $PM_{2.5\text{-}1}$ fraction is made up mineral dust and SIA, with a minor fraction of carbonaceous matter.

As a summary, it can be stated that in most urban areas of Europe (see Figure 16.10, showing data from Barcelona, Spain, as an example):

a) PM_1/PM_{10} and $PM_{2.5}/PM_{10}$ proportions vary widely across Europe, but in most urban areas these falls in the ranges: 40-60 % and 60-75%, respectively.

b) Carbonaceous material it is mainly present in the fine fraction (80/20/<1% in the $PM_1/PM_{2\text{-}5\text{-}1}/PM_{2.5\text{-}10}$, fractions respectively).

c) Conversely, mineral dust and sea spray aerosols are mainly coarse in size (10/20-25/65-70% in the $PM_1/PM_{2\text{-}5\text{-}1}/PM_{2.5\text{-}10}$, fractions respectively, in both cases).

d) Sulphate is distributed among the three PM fractions with a prevalent fine grain size (65-70/20-25/10% in the $PM_1/PM_{2\text{-}5\text{-}1}/PM_{2.5\text{-}10}$, fractions respectively), as a consequence of the prevalence of ammonium sulphate (fine aerosols) versus the coarser Ca, Na or Mg sulphate species.

e) Nitrate shows a similar size distribution to sulphate, with a shift towards the coarse fractions (45-60/20-25/20-35% in the $PM_1/PM_{2\text{-}5\text{-}1}/PM_{2.5\text{-}10}$, fractions respectively). The slightly coarser size distribution is due to the prevalence of fine ammonium nitrate, but coarser Na and Ca nitrate also occur in appreciable levels.

f) Ammonium shows a fine size distribution (75-80/20-25/<5% in the $PM_1/PM_{2\text{-}5\text{-}1}/PM_{2.5\text{-}10}$, fractions respectively) as a consequence of the fine grain size of ammonium sulphate and nitrate.

g) The unaccounted mass follows a very similar size distribution to that reported for nitrate and sulphate (50-70/10-15/20-40% in the $PM_1/PM_{2\text{-}5\text{-}1}/PM_{2.5\text{-}10}$, fractions respectively). These species are very hydrophilic and tend to accumulate water (the main cause of the unaccounted determination).

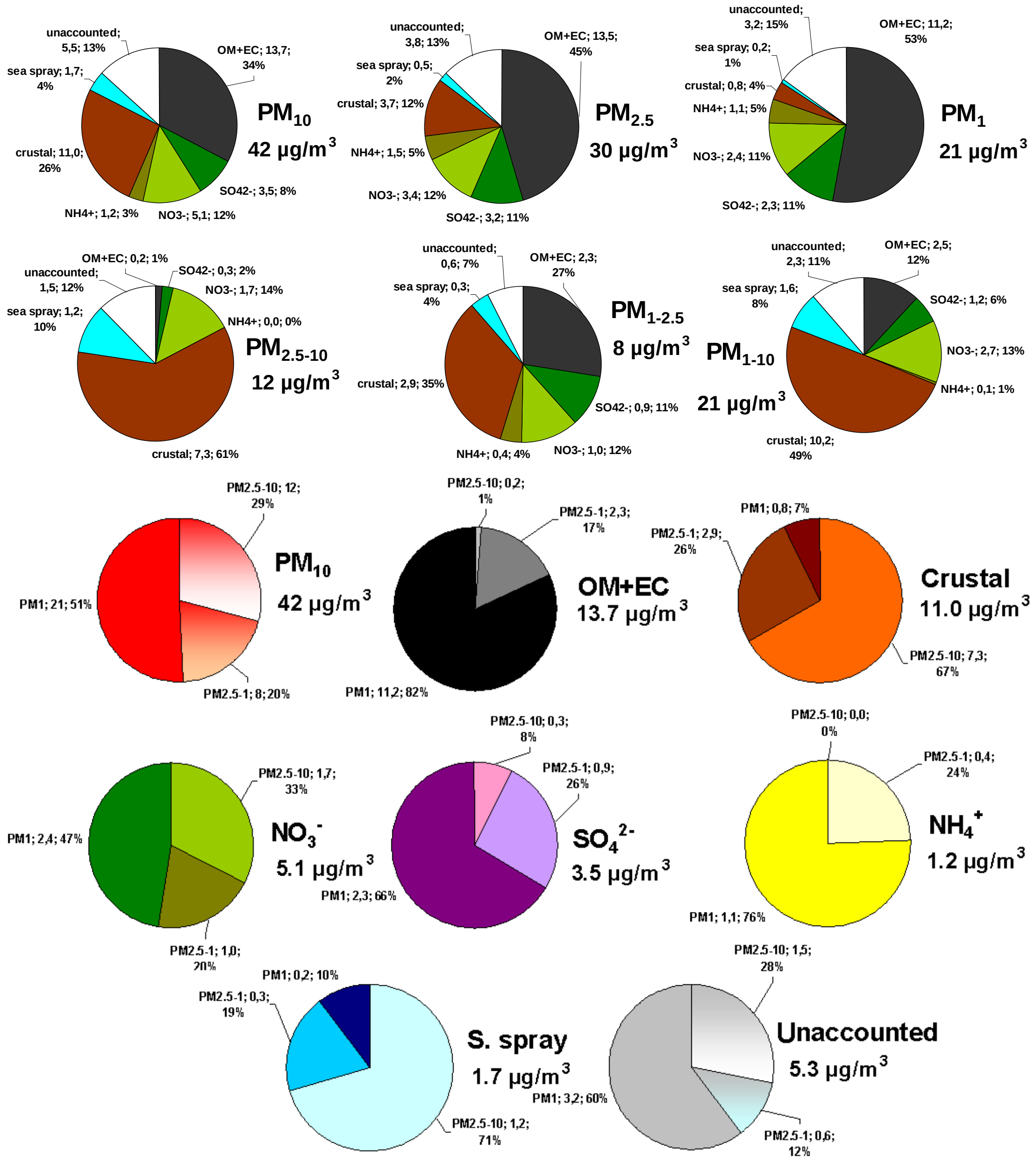


Figure 16.10: Mean speciation data for PM_{10}, $PM_{2.5}$ and PM_1 obtained at an urban background site of Barcelona, from 10-10-2005 to 08-01-2006, n=22 samples for each of the 3 PM fractions obtained simultaneously. $PM_{2.5\text{-}10}$ and $PM_{1\text{-}2.5}$ obtained by difference.

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17 PM_{10} and $PM_{2.5}$ gradients through rural and urban areas in Sweden

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17.1 Abstract

In Sweden long distance transport of particles has been shown to be substantial giving an annual mean PM_{10} contribution in the **rural background** of around 13-19 µg/m^3 in Southern Sweden and 5-9 µg/m³ in the north. This large decrease is due to the increasing distance from the sources on the continent when going from southern to northern Sweden. Fine particles, $PM_{2.5}$, constitute around 80% of PM_{10} in rural areas.

Measurements in the **urban background** of 30 cities have shown an average contribution to PM_{10} levels due to local sources of is about 20-40 % of the total level, which is in the range 12-25 µg/m3 as an annual average. The higher concentrations and the lower fraction of local contribution are found in the south. As the influence of long distance transport is decreasing the total concentration decrease and the local contribution increase. There is no obvious relation between the local contribution and the size of the city. In larger cities (>100 000 inhabitants) the local sources contribute with 4-10 µg/m^3. Around 60% to 70% of PM_{10} in urban background is fine particles.

The most important local sources in urban areas are due to road wear and incomplete combustion of wood in residential areas. Road wear gives annual mean contributions to PM_{10} with up to 20 µg/m³ at densely trafficked **kerb-side** sites. Road wear contribute mainly to the coarse particle fraction but there is also a substantial contribution to $PM_{2.5}$. The ratio of $PM_{2.5}/PM_{10}$ is around 0.4 to 0.6 at kerb-side. Other local sources are of less importance on an annual basis, with the exception of the contribution from wood burning mainly in urban areas situated in the inland of Northern Sweden, where wood is commonly used for residential heating and where the cold winter climate lead to frequent situations with very stable meteorological conditions. Measurements at an inland urban site of northern Sweden have shown that hourly PM_{10} levels may be 50 times higher than the annual average levels during periods with strongly stable conditions, which mainly occur during winter-time. Wood burning is the main source of PM_{10} and $PM_{2.5}$ in these areas but road wear may also contribute during the spring.

As a case study for PM gradients from kerbside through to urban background, suburban and rural locations we have focused on Stockholm were there are more detailed information from measurements and model calculations. Stockholm has very high daily mean PM_{10} levels as compared to many large cities in Europe and the EU limit value is exceeded on many of the streets. The main reason is the use of studded tires that may increase the PM_{10} emission due to road wear by a factor of 30 to 50 compared to using winter tires without studs. The road wear is higher during wet road conditions but subsequent suspension of particles occurs mainly during dry road conditions. Accumulation of particles along roads may occur during the winter with mostly wet conditions. During the spring when roads are

dry, suspension increase giving very high PM_{10} levels along busy roads. Monthly mean values during spring (February – April) may be 5 to 10 times higher at kerb-side as compared to rural levels during this period.

Using NO_x as tracer for road traffic exhaust it has been shown that the annually averaged emission factor for non-exhaust particles is about 10 times the emission of exhaust particles. For $PM_{2.5}$ the non-exhaust particle emission is about 2 times higher. This means that exhaust emission control measures in Sweden will have little or no effect on future PM_{10} levels in urban areas of Sweden. The only local measures that would result in lower PM_{10} levels is connected with the coarse particle generation.

PM_{10} and $PM_{2.5}$ particle fractions in rural areas consist mainly of particulate organic compounds of both anthropogenic and natural origin, followed by sulphate, nitrate and ammonium. In urban areas the average composition is similar but with additional contributions to PM_{10} from soil minerals and minor additional contributions of particulate organic compounds, elemental carbon and possibly some carbonate.

17.2 Measurement methods and network

17.2.1 Urban and rural $PM_{10}/PM_{2.5}$ networks in Sweden

Concentrations of PM_{10} and $PM_{2.5}$ are in Sweden mainly measured within two different networks; an urban network and a rural network. The urban network includes 30 urban background sites in cities and towns from the very south to far north covering a total distance of more than 1000 km (Sjöberg et al., 2004). At these sites a gravimetric filter method is used (Ferm & Hansson, 2004). The rural network includes three background stations representative for southern, middle and northern Sweden (Areskoug et al, 2004). At these stations automatic TEOM instruments (Tapered Element Oscillating Microbalance, model 1400, Rupprecht and Pataschnik; Patashnick et al., 1991) equipped with PM_{10} and $PM_{2.5}$ inlets. In urban areas there is not so much data on $PM_{2.5}$ as for PM_{10}, as there is no limit values set yet. Some few cites, mainly the three major cities in Sweden, have been measuring $PM_{2.5}$ for periods longer than one year.

17.2.2 $PM_{10}/PM_{2.5}$ measurements and model calculations in Stockholm

In this report we present more detailed information on the gradients in the concentrations of PM_{10} and $PM_{2.5}$ in an urban area is given from measurements and modelling in the city of Stockholm (Johansson et al., 2006). Particle mass concentration measurements were performed by the Environment and Health Administration of Stockholm using automatic TEOM instruments (see Johansson et al., 2006). Measurement stations were located in street canyons with busy streets (10000-35000 vehicles/day) in central Stockholm (Hornsgatan[19], Sveavägen[20] and Norrlandsgatan[21]) and one urban background station at roof level; ~20 meter above street (Rosenlundsgatan[22]) in the city.

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[19] Hornsgatan is 24 meter wide street canyon with 24 meter buildings and 35 000 vehicles/day.

[20] Sveavägen is a 30 meter wide street canyon with 24 meter buildings and around 35 000 vehicles per day.

[21] Norrlandsgatan is 15 meter wide with 20 meter high buildings and around 10 000 vehicles per day.

[22] Rosenlundsgatan is a roof top site in central Stockholm that can be regarded as representative for the urban background since it is not directly affected by nearby local vehicle emission. This is also verified by urban scale modelling of particle number concentrations by Gidhagen et al. (2005).

17.3 Countrywide gradients in rural and urban background in Sweden

The regional background in Sweden is mainly due to long distant transport from the large sources on the continent, both of primary particles and gaseous precursors (Areskoug et a, 2004; Forsberg et al., 2005). The presentation below follows that given by Forsberg et al. (2005).

All processes causing deposition of particles can be approximated as proportional to the actual concentrations. Accordingly this will cause an exponential decay of the concentration with distance from the major sources. As the major sources contributing to the anthropogenic part of the regional background is upstream, i.e. south of Sweden the concentrations ought to follow a exponential decay curve. In Figure 17.1 the concentrations are plotted versus the distance from the most southern site. Both the urban background concentrations and regional background are fitted with exponential curves. The regional background concentrations follow the exponential curve very nicely.

The local contributions to the measured urban background concentrations may be estimated using the rural background concentrations throughout Sweden. In Figure 17.2 the local contribution is estimated for different sites by subtracting the estimated regional concentrations from measured PM_{10} urban concentrations giving a mean local contribution of about 6.3 $\mu g/m^3$. The local contribution constitutes generally roughly 29 % of the total concentrations, with a somewhat lower influence in the south while in the north it grows to almost 50% as the influence of the long distance transport decreases.

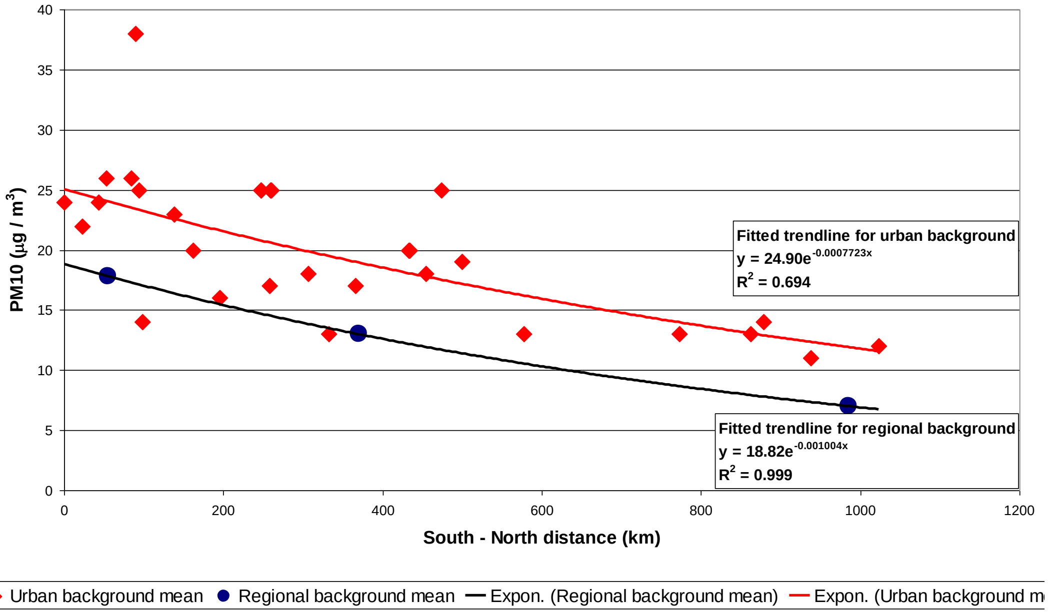

Figure 17.1: Winter half-year mean PM_{10} concentrations for urban and regional background sites are shown versus the distance from the very south of Sweden. Exponential curves have been fitted separately for the urban and regional background concentrations versus distance (with the southernmost station as zero) (from Forsberg et al., 2005).

However, considerable deviation from the mean is found on a few sites. There is one site with a local influence of about 21 µg/m^3, in a total of 38 µg/m^3. This indicates a strong local source dominating the sampling site. Another site has a local influence of about 13 µg/m^3, also indicating a strong local influence. There are also 3 sites showing negligible or no local influence. Else the local influence is found in the concentration range 3 – 11 µg/m^3, with somewhat higher concentrations in the south compared to the very north. These results compare well with the findings of Areskoug et al. (2004), giving a general estimate of the local influence of about 6 µg/m^3 on the urban background concentrations.

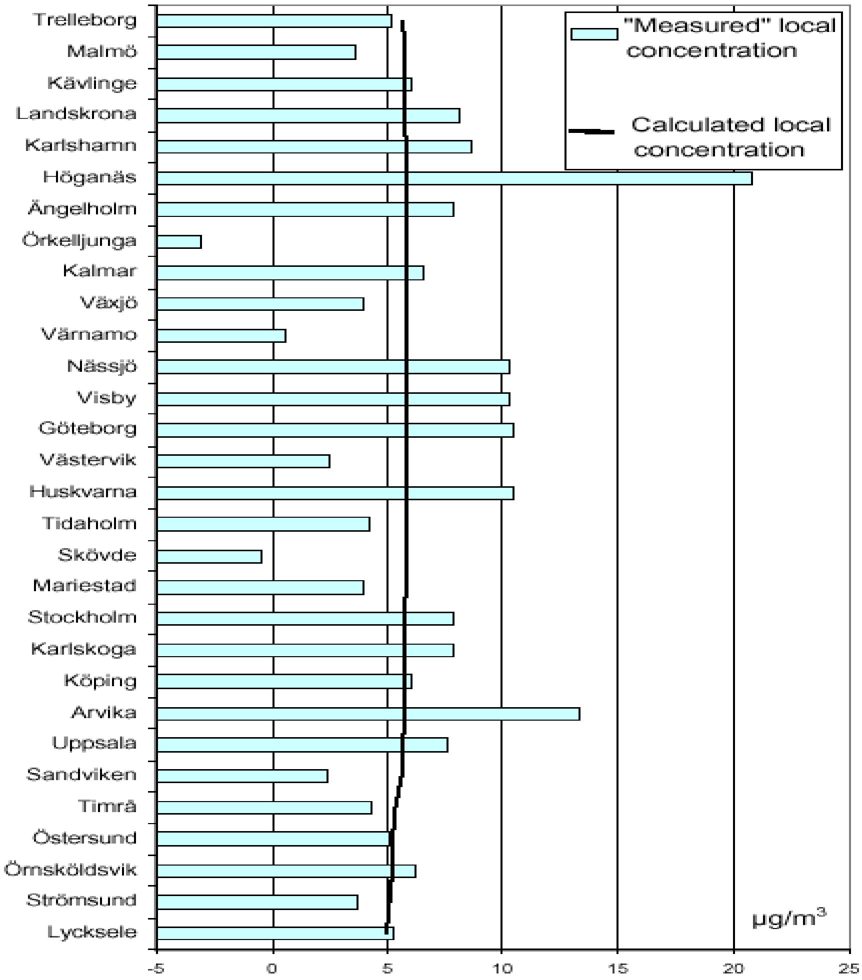

Figure 17.2: The calculated local PM_{10} contribution compared with the measured urban PM_{10} concentration when the rural background particle PM_{10} concentration is subtracted (from Forsberg et al., 2005).

17.4 Diurnal and seasonal variations

The diurnal and seasonal concentrations and their variations were investigated in a study including the three major Swedish cities, 3 smaller cities and 3 rural background sites. The mean diurnal variation of PM_{10} is strong at the kerb side sites, especially during weekdays, see Figure 17.3. The concentrations are about 2 to 3 times higher at noon (37 µg/m^3) than in the early morning (15 µg/m^3). During holidays, the daily maximum is about two times the minimum. The concentrations of PM_{10} raises rapidly during the weekday mornings at the kerb-side sites, but considerably slower during holidays. This reflects the difference in traffic emissions between weekdays and holidays. It should be noted that this is the mean diurnal variation for the whole measurement period. The diurnal variation at the urban background sites shows a similar pattern as at the kerb side, but the daily maximum hourly mean concentration (16 µg/m³) is only about 1.5 times the minimum (11 µg/m³) during weekdays and about 1.4 times during holidays.

A slight diurnal variation can also be seen at the rural sites. The daytime maximum (13 µg/m³) is about 10% higher compared to the minimum (11.5 µg/m³). This could be due to stronger winds during daytime, especially in spring and summer, cause suspension of soil dust. Long-range transport even for larger particle is stronger especially during spring due to strong winds and low precipitation. The local sources increase PM_{10} at the kerb side sites with about 17 µg/m³ and 11 µg/m³ during weekdays and holidays respectively. In the urban background, the local sources increases PM_{10} with 4 and 2 µg/m³ during weekdays and holidays respectively.

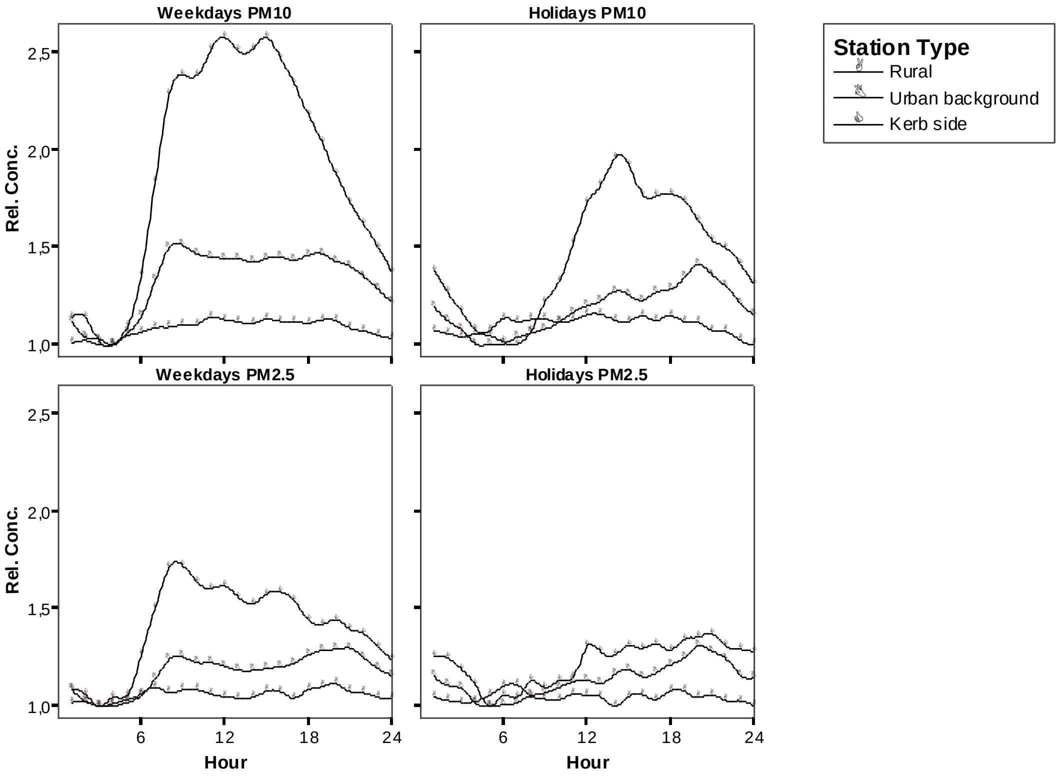

Figure 17.3: Diurnal variation of PM_{10} and $PM_{2.5}$ during weekdays and holidays at rural, urban background and kerb side sites. The concentrations are given in relative units, where the daily minimum (one hour average) for each site type is 1.0.

The diurnal variation of $PM_{2.5}$ is much less pronounced than for PM_{10}. A significant variation can only be seen at the kerb side sites during weekdays. The maximum (15 µg/m³), recorded at 8:00 – 9:00, is about 70% higher than the daily minimum. Smaller diurnal variation; the maximums being about 25% higher than the minimum, can also be seen during weekdays and holidays in the urban background and the kerb-side sites. The local sources increase the average concentrations of $PM_{2.5}$ with about 5 µg/m³ and 3 µg/m³ at the kerb-side during weekdays and holidays respectively. The increase at the urban background sites is about 1.5 and 1 µg/m³ during weekdays and holidays respectively.

The data on the diurnal variation presented above represents an average for the whole measurement period. However, the difference between seasons is substantial (Figure 17.4). The difference between the daytime concentrations of PM_{10} (average concentration at 13:00 – 14:00) and the minimum concentrations in the early morning (average concentration at 04:00 – 05:00) is 30 – 40 µg/m³ in February – May, but only about 10 in July to September at kerb-side sites. The reason for the high PM_{10} levels found at kerb-side during spring is suspension of road dust particles from the road surfaces. This process is most important when the roads are dry during spring and before the sand has been removed and before the studded tires have been removed from the vehicles.

For both PM_{10} and $PM_{2.5}$ the seasonal variation is much less pronounced at all other sites. A similar variation, but much less, as for PM_{10} at the kerb-side, can be seen for PM_{10} at the urban background sites and for $PM_{2.5}$ at the kerb-side sites. The increased levels during daytime at the urban background in spring are also due to road dust. Some of the suspended particles are small enough to be sampled as $PM_{2.5}$ (see Figure 17.10).

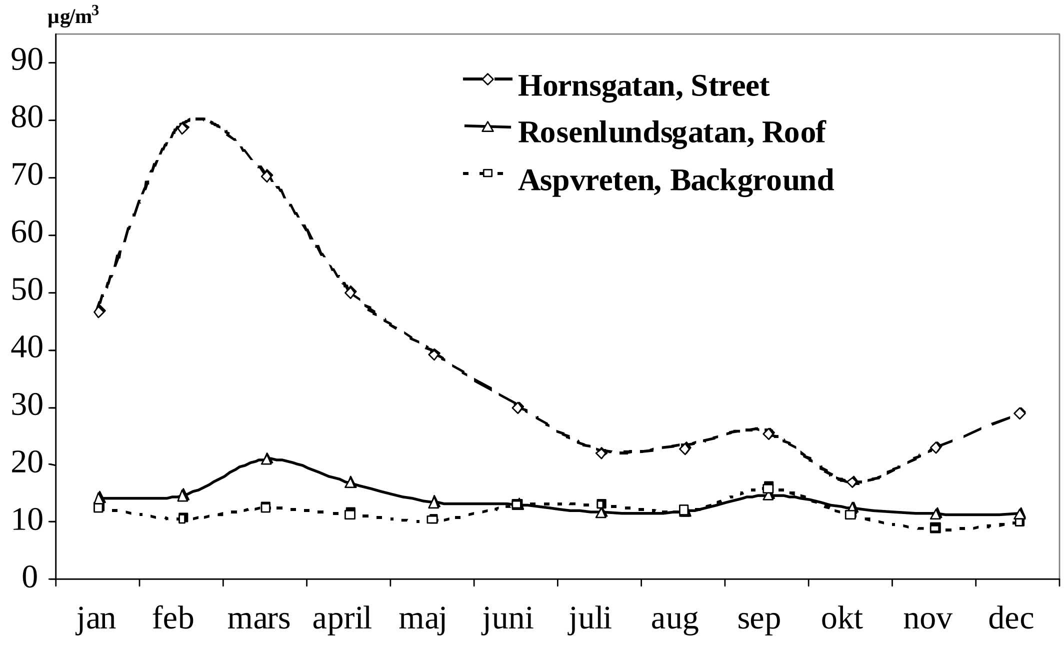

Figure 17.4: Monthly mean concentrations of PM_{10} at kerbside (Stockholm), urban background (Stockholm) and a rural site (70 km's south of Stockholm) during a year

17.5 Fraction $PM_{2.5}$ of PM_{10}

The fine particle mass, $PM_{2.5}$, constitutes a large fraction, about 80%, of PM_{10} at the rural sites (see Figure 17.5). There is a general trend that the ratios $PM_{2.5}/PM_{10}$ are lower at the urban background sites (0.6 – 0.7) than at the rural sites and even lower (0.6 – 0.4) at the kerb side sites. Local sources of coarse particles (PM_{10}-$PM_{2.5}$) are much more important than local sources of fine particles ($PM_{2.5}$).

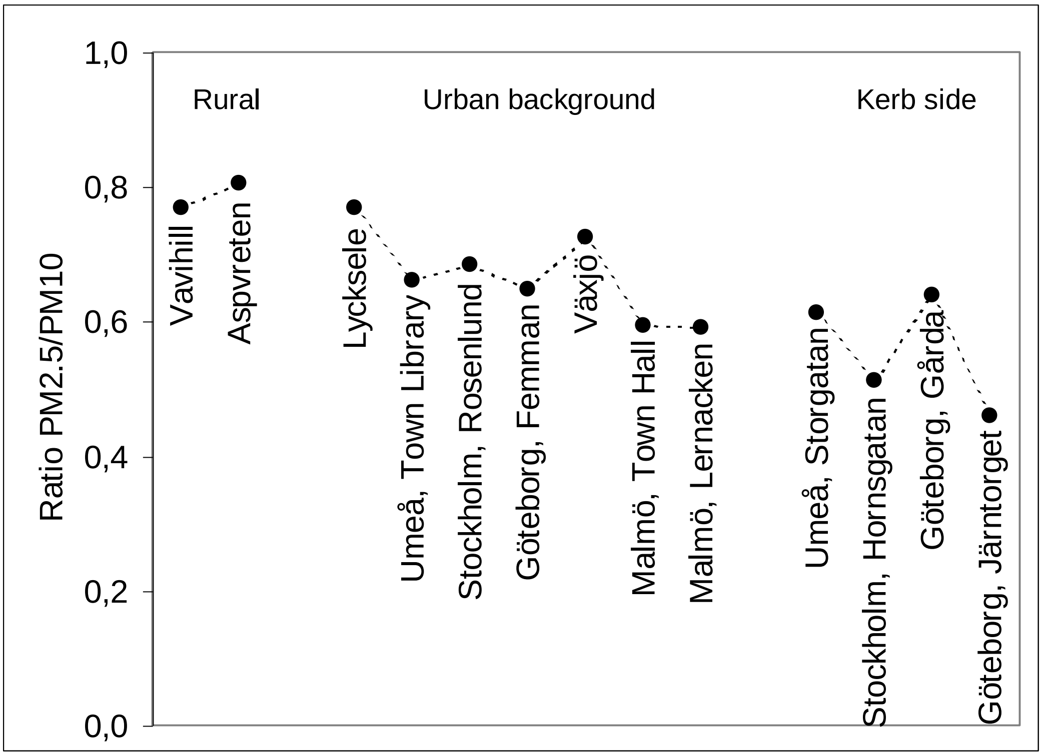

Figure 17.5. Average ratio $PM_{2.5}/PM_{10}$ at thirteen Swedish sites.

17.6 Comparison of PM_{10} levels with NO_x and particle number concentrations in Stockholm

For PM_{10}, concentrations are not affected by vehicle exhaust but on factors that control road dust generation (Norman and Johansson, 2006; Omstedt et al., 2005). In Stockholm road wear is more important for PM_{10} concentrations than in other countries where the use of studded tires is not so common. Approximately 70 % of all light duty vehicles use studded tires in Stockholm during wintertime, November to March (Norman and Johansson, 2006). Concentrations of NO_x and total particle number are good tracers of vehicle exhaust and can therefore be used to illustrate the impact of exhaust versus non-exhaust particles for PM_{10} and $PM_{2.5}$ levels.

17.6.1 Temporal variation of PM_{10} and PNC

Figure 17.6 shows monthly average PNC (total particle number concentration) and PM_{10} concentrations due to local traffic emissions at Hornsgatan (street canyon) in central Stockholm. For both PNC and PM_{10} there is a strong seasonal variation. However, the PM_{10} levels peak during spring, March to April, whereas the PNC is highest during the winter season, November to February. The spring-time peak in PM_{10} is caused by direct emissions due to use of studded tires causing increased road wear and also increased suspension of road wear particles during more dry conditions in spring (Omstedt et al., 2005).

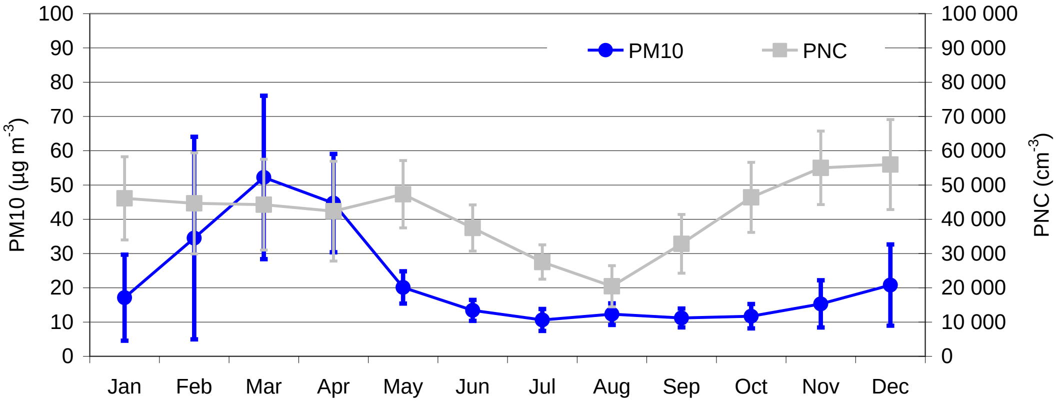

Figure 17.6: Monthly average total particle number (PNC) and PM_{10} concentrations at Hornsgatan in central Stockholm (street canyon). The concentrations represent the contribution from the local traffic on this street since the measured urban background concentrations of PM_{10} and PNC have been subtracted. The monthly mean values were obtained from hourly measurements taken from January 2001 to May 2005. Vertical bars indicate standard deviation of diurnal averages. Only months with data covering more than 50% of the time have been included (for PM_{10} the averages are based on between 111 and 149 days; for PNC the averages are based on between 24 and 94 days). From Johansson et al. (2006).

The suspension of road dust can increase both $PM_{2.5}$ and PM_{10} to very high levels during the spring. Hourly mean PM_{10} concentrations may reach 500 – 900 µg/m³ at the kerb sites in Stockholm. Similar concentrations have also been recorded in Göteborg and Umeå. In Stockholm it is mainly during these episode that the EU directive of 50 µg/m³ as daily average is exceeded. Most exceedances occur during March to April. Only during these two months between 10 and 20 days have values higher than 50 µg/m³. It is also during these months that the monthly mean values maximise.

On a given street, the meteorological conditions are of the greatest importance. If the street surface is wet, the amount of re-suspended particles can be reduced to practically zero, whilst dry conditions and dust on the road surface increases PM in the air to high concentrations. In contrast to this the temporal variation of PNC is independent of the street conditions (Johansson et al., 2006). The concentration of coarse particles, PM_{10} – $PM_{2.5}$, at the kerb side site Hornsgatan in Stockholm hourly averages exceed 100 µg/m³ on many days during the spring.

The impact of non-exhaust versus exhaust particles is also well illustrated by plotting PM_{10} versus NO_x concentrations (tracer for exhaust emissions). Figure 17.8 shows all daily averages during 4 years of the NO_x and PM_{10} concentration in the street canyon of Hornsgatan. Note that the concentrations refer to the difference between the street and roof level, i. e. they represent the contribution of the local traffic at the street. Taking all values there is a very large scatter in the data, indicating that there are different sources of NO_x and PM_{10} in the street canyon. If both NO_x and PM_{10} originated from vehicle exhaust one would expect much less scatter in the data.

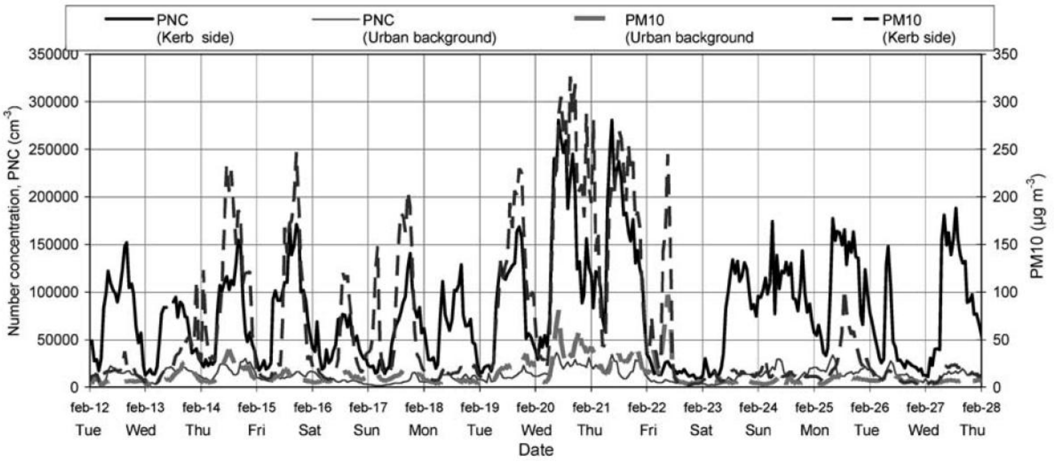

Figure 17.7: Total particle number (PNC) and PM_{10} concentrations at kerb-side and urban background in central Stockholm (from Johansson et al., 2006).

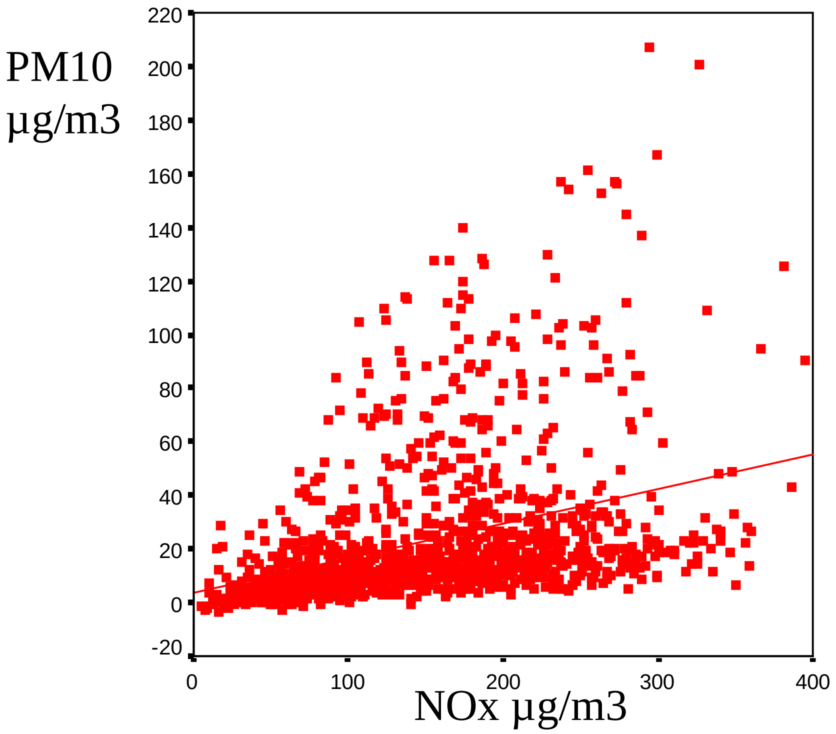

Figure 17.8: Daily average PM_{10} concentration plotted versus NO_x. Concentrations refer to street canyon of Hornsgatan (3 m above street) and the roof top concentrations have been withdrawn, so that only the local street traffic contributions are included.

In Figure 17.9 the data have been divided into different months of the year. During November, December and January to April there are several days with substantially elevated PM_{10} levels than expected if the only source would be exhaust emissions.

But during May to October there is a nice linear relationship between PM_{10} and NO_x indicating that most PM_{10} is due to local traffic exhaust emissions during these periods. The slope of the regression ranges from 480 mg PM_{10}/g NO_x in March to 57 mg PM_{10}/g NO_x in October.

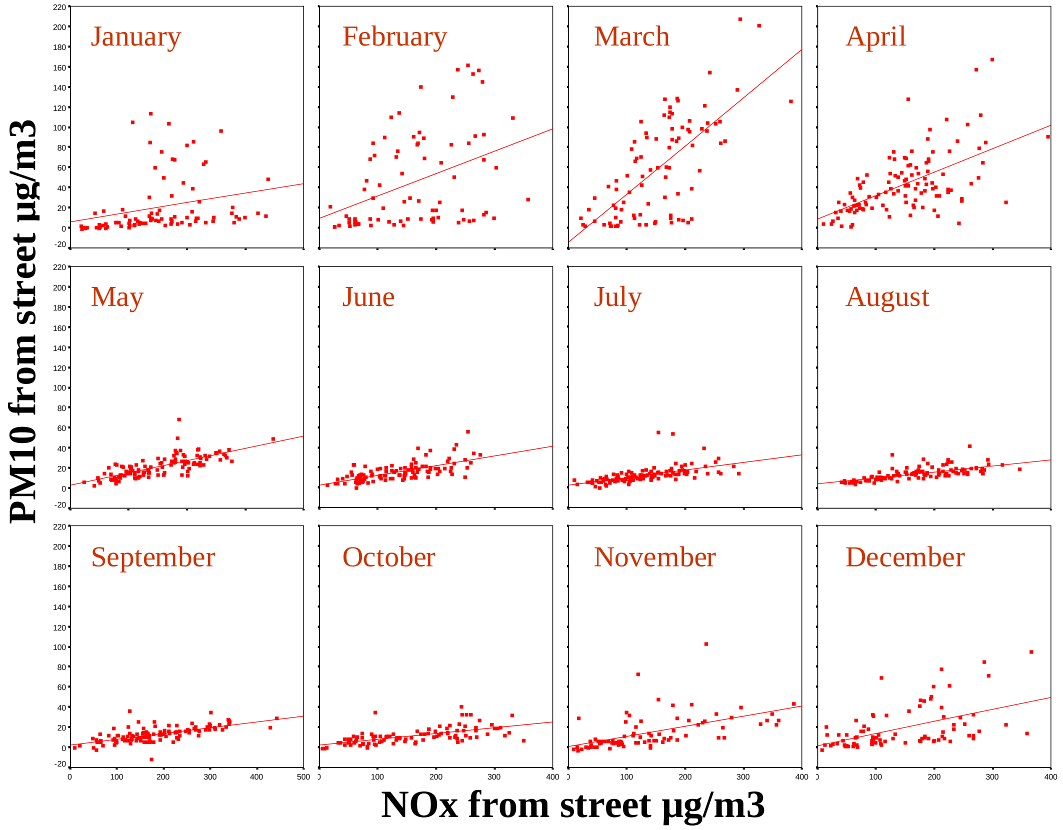

Figure 17.9: Scatter plots of PM_{10} versus NO_x. Data from Hornsgatan in Stockholm. The data are daily averages of the concentrations at the street minus the concentration at the roof top, indicating the contribution only from the local traffic in the street.

Measurements of the particle size distribution in different urban environments of Stockholm revealed the influence of different sources (See Figure 17.10). Particles below 0.2 µm are dominated by vehicle exhaust as seen in the difference between a highly trafficked city street and the suburban house road. The long-range transported particles are found in the size range 0.2 – 0.4 µm.

The road dust emissions in the city street give a strong contribution to particle sizes larger than 1 µm and also to mass compared with the exhaust and long-range transported particles.

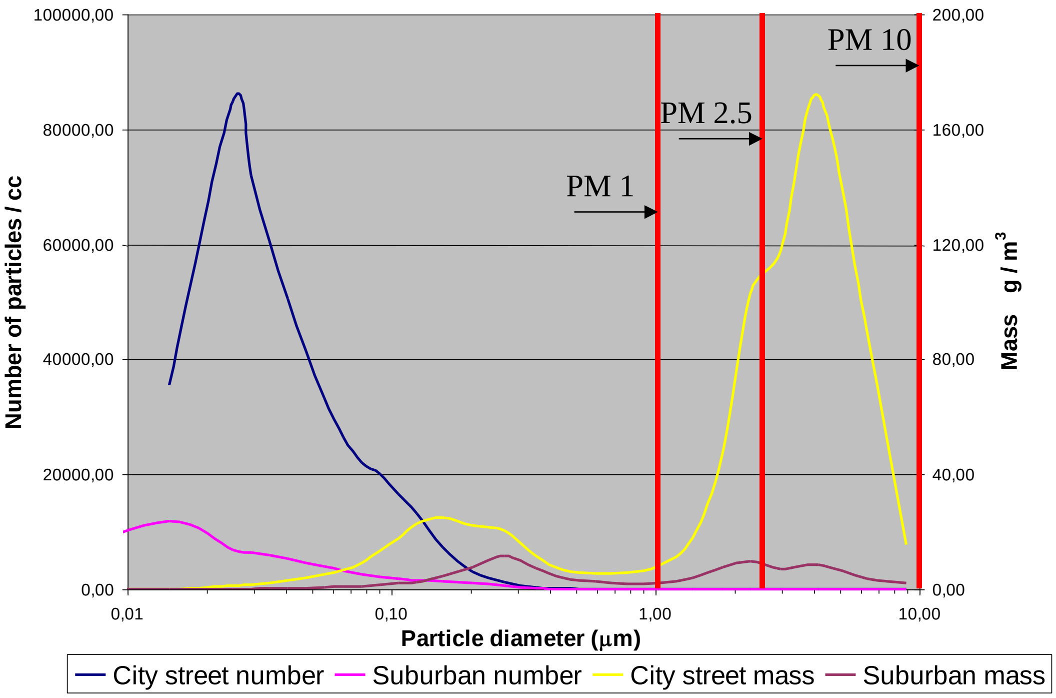

Figure 17.10:Mass and number particle size distributions from a highly trafficked street canyon and one suburban back road in Stockholm.

17.6.2 Spatial variation of PM_{10} and PNC

The ratio of the total concentration measured at kerb side locations to that measured at roof indicates the importance of local road traffic emissions versus influence of other emissions and background concentrations (Table 17.1; Johansson et al., 2006). For PM_{10} kerb side concentrations are 2 to 3 times higher than urban roof level. For NO_x and PNC kerb side concentrations are 4.5 to 8.2 times the roof concentrations, indicating a much higher influence of local traffic exhaust emissions compared to road wear (PM_{10}).

Thus, long-range transport is much more important for the urban and kerb-side PM_{10} annual mean levels as compared to PNC (Johansson et al., 2006). Figure 17.11 shows the calculated relative variation of the annual mean urban background concentrations of PNC and PM_{10} in the Greater Stockholm area (35 km^2, 100 meter spatial resolution).

Table 17.1: Annual mean ratio of kerb-side and urban background concentrations (roof at a height of ca 20 meters) for PM_{10}, NO_x and PNC (from Johansson et al., 2006).

	Mean ratio Kerb-side/Roof ± Standard deviation		
Street average number of vehicles	PM_{10}	NO_x	PNC
Hornsgatan 35 000 veh/day	2.5 ± 1.5	8.2 ± 3.3	5.6 ± 2.1
Norrlandsgatan 10 000 veh/day	2.0 ± 1.3	4.5 ± 2.3	
Sveavägen 30 000 veh/day	2.1 ± 1.5	4.6 ± 2.5	

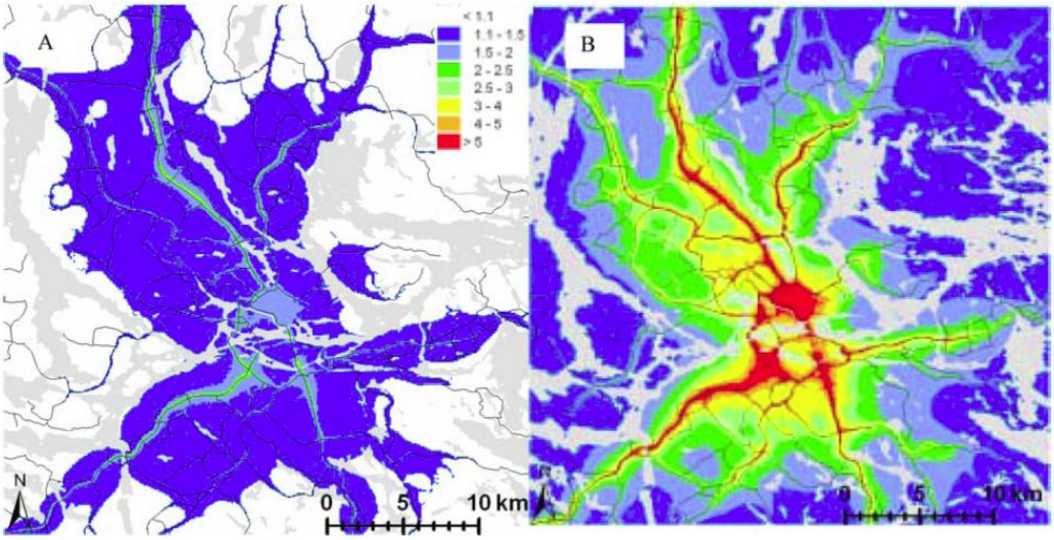

Figure 17.11: Model calculated relative spatial variation of annual mean concentrations of A) PM_{10} and B) PNC (total particle number concentration) in Greater Stockholm area (35 km x 35 km). The colours indicate the increase above rural background (10 µg m^{-3} for PM_{10} and 3500 cm^{-3} for PNC) due to local traffic emissions in the area. From Johansson et al. (2006).

17.7 Chemical composition

PM_{10} and $PM_{2.5}$ particle fractions in rural areas consist mainly of particulate organic compounds of both anthropogenic and natural origin. At the rural site Aspvreten EC and OC has been analysed on collected filters using a thermo-optical technique (TOT, Sunset lab). Measurements have been performed since September 2004. Around 30% of $PM_{2.5}$ consists of organic material if average OC levels (around 2 µg/m^3) are converted to particulate organic material assuming a factor of 1.4 accounting for other elements than organic carbon. Elemental carbon is around 2% (mean level 0.2 µg/m^3). The sum of sulphate, nitrate and ammonium contribute with around 40% to $PM_{2.5}$. The rest is soil minerals, sea salt and some water.

In urban areas the average composition is similar but with additional contributions to PM_{10} from soil minerals and minor additional contributions of particulate organic compounds, elemental carbon and possibly some carbonate.

17.8 References

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18 Concentrations of particulate matter (PM_{10}, $PM_{2.5}$, PM_1) in Switzerland, Annual and seasonal trends and spatial variability

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18.1 Abstract

Extensive long-term parallel measurements of PM_{10}, $PM_{2.5}$ and PM_1 have been performed at several sites with different exposition characteristics within the Swiss National Monitoring Network (NABEL). This data set forms a unique data basis for investigating the temporal and spatial behaviour of PM_1 and $PM_{2.5}$ compared to PM_{10}. From an analysis of the data the following conclusions were drawn:

At all sites the concentrations of the different size fractions were highly correlated on the level of daily values. Unless strong and variable local sources of coarse particles are present, parallel measurements of PM_1, $PM_{2.5}$ and PM_{10} seem to provide only limited additional information. Therefore, parallel measurements can be restricted to a few carefully selected sites in a monitoring network.

The comparison of daily PM values from different sites often show quite high correlation also. The analysis of the Swiss data indicates that this has primarily meteorological reasons. Even distant sites show good correlations if they are situated in an area with similar meteorological conditions. However, the correlations drop drastically if this is not the case i.e. if the sites are divided by high topographical obstacles (Alps) or by an inversion layer. High correlations of PM could be expected due to a homogenous distribution of long-range transported PM over large areas. However, this would not explain the high daily variability of the PM concentrations because on a regional scale the daily variability of the PM emissions is quite small. In fact, no matter whether the particles are locally emitted or long-range transported, it is mainly the meteorology (wind speeds, turbulence, vertical mixing, inversions etc.) which causes more or less effective dilution of the emitted pollutants and thus the daily fluctuation of the concentrations.

18.2 Introduction

Measurements of PM_{10}, which is considered to represent the thoracic fraction of the ambient particles (ISO 1995), have been performed within the Swiss National Monitoring Network (NABEL) already since 1997. Due to the increasing public interest for the finer alveolar fraction ($PM_{2.5}$), the measurement programme of the network has been extended to include $PM_{2.5}$ measurements at seven sites in 1998. A preliminary comparison of these parallel measurements has already been published earlier (Gehrig and Buchmann 2003). From 2003 also PM_1 measurements were added to the measurement programme. This fraction provides, better than $PM_{2.5}$, information on the particle sources, as PM_1 represents in reasonable approximation combustion particles and secondary aerosol, while PM_{10-1} can be attributed to mechanically produced and geogenic particles. Long-term data sets of parallel measurements of the different PM fractions are still scarce if not lacking for Europe. Therefore, the Swiss data set forms a unique data basis for investigating the temporal and spatial behaviour of PM_1 and $PM_{2.5}$ compared to PM_{10}. It includes meanwhile eight years of parallel $PM_{2.5}$ and PM_{10} data and three years of parallel PM_1 and PM_{10} data at various sites and site categories important with respect to human PM exposure. population. This paper gives an overview of the measured concentrations and compares the temporal and spatial behaviour of the different size fractions.

18.3 Measurement programme and methods

Table 18.1 lists the seven sites where the parallel PM measurements have been performed, including their site category. The PM concentration recorded at the two rural sites, Chaumont and Payerne, are reported to EMEP. The map in Figure 18.1 shows the geographical position of the sites within Switzerland. All particle samplings were conducted with high-volume-samplers Digitel DA 80 (VDI 1996). The sampling inlet is operated at a flow of 30 m^3/h and meets the requirements of EN 12341 for reference equivalency (UMEG 1999). For $PM_{2.5}$ and PM_1 the same kind of instrument was used, but with correspondingly adapted sampling heads. Glass fibre filters of the type Ederol 227/1/60 were used for particle collection. The measurement uncertainty for the PM_{10} measurements has been quantified from collocated parallel measurements to be 10% (95% confidence interval for single daily values) in the concentration range 10–30 $\mu g/m^3$. The detection limit was determined from the standard deviation of field blanks to be 1 $\mu g/m^3$. Because the only difference between the applied method for PM_{10} and $PM_{2.5}$ or PM_1 is the number and diameter of the nozzles in the sampling heads, the same measurement uncertainty can be assumed for the $PM_{2.5}$ and PM_1 measurements.

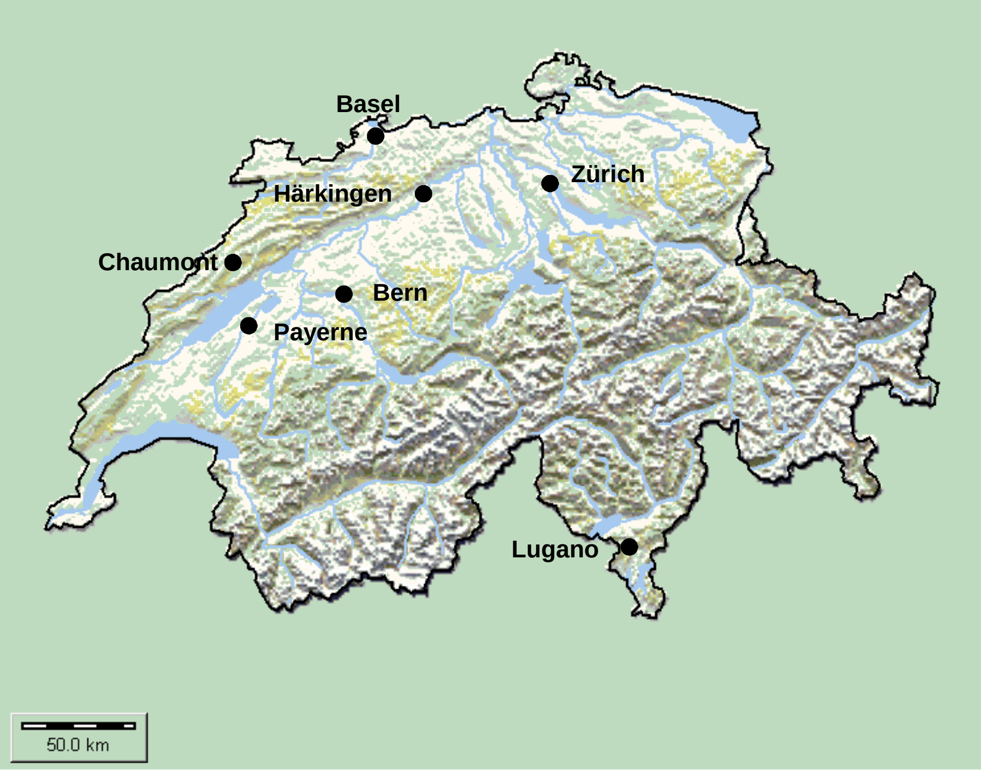

Figure 18.1: Geographical position of the seven investigated sites of the Swiss National Monitoring Network (NABEL).

Table 18.1: Characterisation of the measurement sites.

Basel	Suburban
Bern	Kerbside, street canyon
Chaumont	Rural, 1140 m a.s.l.
Härkingen	20 m from motorway
Lugano	Urban background
Payerne	Rural, 490 m a.s.l.
Zürich	Urban background

18.4 Results and discussion

18.4.1 Comparison of PM_{10}, $PM_{2.5}$ and PM_1 concentrations

Figure 18.2 shows at a glance the annual mean concentrations of the measured size fractions. From Table 18.2 it can be seen that the variability of the long-term $PM_{2.5}/PM_{10}$ as well as the PM_1/PM_{10} ratios is very low. The only exception is the street canyon site Bern, where the local traffic forms a considerable source of coarse dust, which results in clearly lower ratios Figure 18.3 shows the seasonal variations of the mass concentrations for the period 2003-2006. It can be seen that for all sites, with the exception of the elevated site of Chaumont, a characteristic seasonal variation can be observed for all mass fractions with elevated concentrations during the cold season. The reasons for this are not primarily caused by seasonal fluctuations of the emissions, but rather by meteorological effects. This is already well known from similar variations of other parameters such as sulphur dioxide and nitrogen oxide (frequent inversions during winter and good vertical mixing during summer). In contrast, Chaumont shows the lowest values in winter. This also shows the dominating influence of the meteorology. The site is situated on an altitude of 1140 m a.s.l. and, therefore, during wintertime most of the time above the inversion layer, thus protected from the emissions of the lowlands of the Swiss basin. From April to September the variations at Chaumont follow that of the other sites, though on a lower concentration level, due to the better vertical mixing of the lower atmosphere during the warmer season.

Table 18.3 shows, that there is a high correlation of PM_{10} with $PM_{2.5}$ at all sites. With the exceptions of the still high correlations at Bern (r=0.92) and Chaumont (r=0.91), all correlations were 0.95 or higher. The lower correlation at Bern reveals that the traffic induced coarse particles from abrasion and resuspension contained in PM_{10} follow different temporal emission patterns than $PM_{2.5}$ and PM_1, which are dominated by exhaust pipe emissions. This is plausible because mechanically produced particles, and in particular resuspension, depend not only on the vehicle frequency but also on the condition of the road surface (e.g. clean/dirty, wet/ dry). At the site of Chaumont, the lower correlation can be explained with the generally lower concentrations and the correspondingly higher relative measurement uncertainties.

The correlation coefficients between PM_1 and PM_{10} are similarly high. For the reasons already explained, also here with somewhat lower values at Bern and Chaumont.

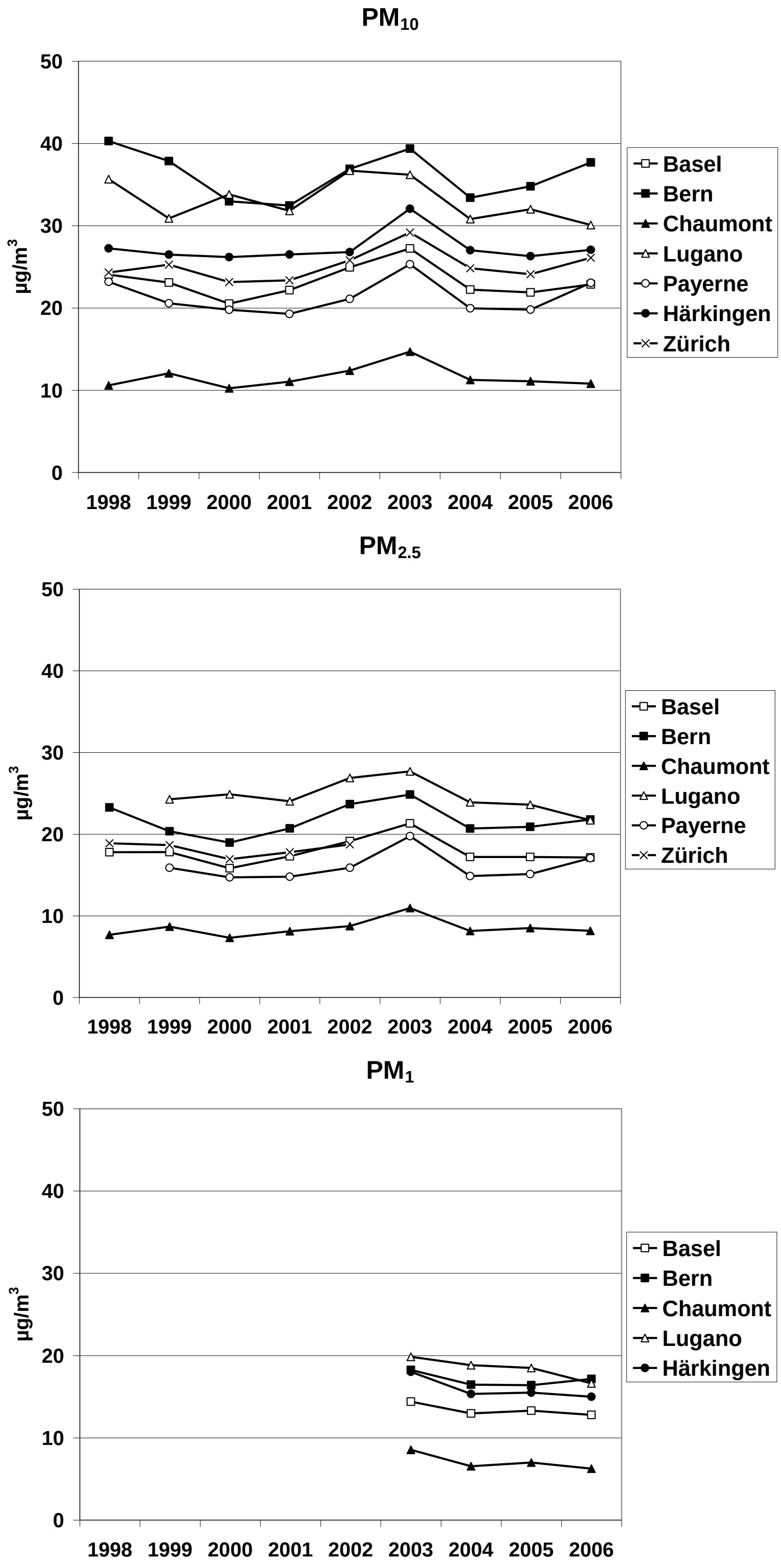

Figure 18.2: Annual mean concentrations of PM$_{10}$, PM$_{2.5}$ and PM$_1$.

Table 18.2: Mean $PM_{2.5}$/PM10 and PM_1/PM_{10} ratios of the daily values for 2003-2006.

	$PM_{2.5}/PM_{10}$	PM_1/PM_{10}
Basel (Suburban)	0.75	0.58
Lugano (Urban background)	0.73	0.59
Zürich (Urban background)	0.75	
Payerne (Rural, 490 m a.s.l.)	0.74	
Chaumont (Rural, 1140 m a.s.l.)	0.76	0.65
Härkingen (Motorway)		0.59
Bern (Kerbside, street canyon)	0.61	0.50

Table 18.3: Pearson correlation coefficient (r) for PM_{10} vs $PM_{2.5}$ and PM_{10} vs PM_1 (daily values).

	PM2.5	PM1
Basel (Suburban)	0.95	0.92
Lugano (Urban background)	0.95	0.92
Zürich (Urban background)	0.97	
Payerne (Rural, 490 m a.s.l.)	0.97	
Chaumont (Rural, 1140 m a.s.l.)	0.91	0.89
Härkingen (Motorway)		0.92
Bern (Kerbside, street canyon)	0.92	0.88

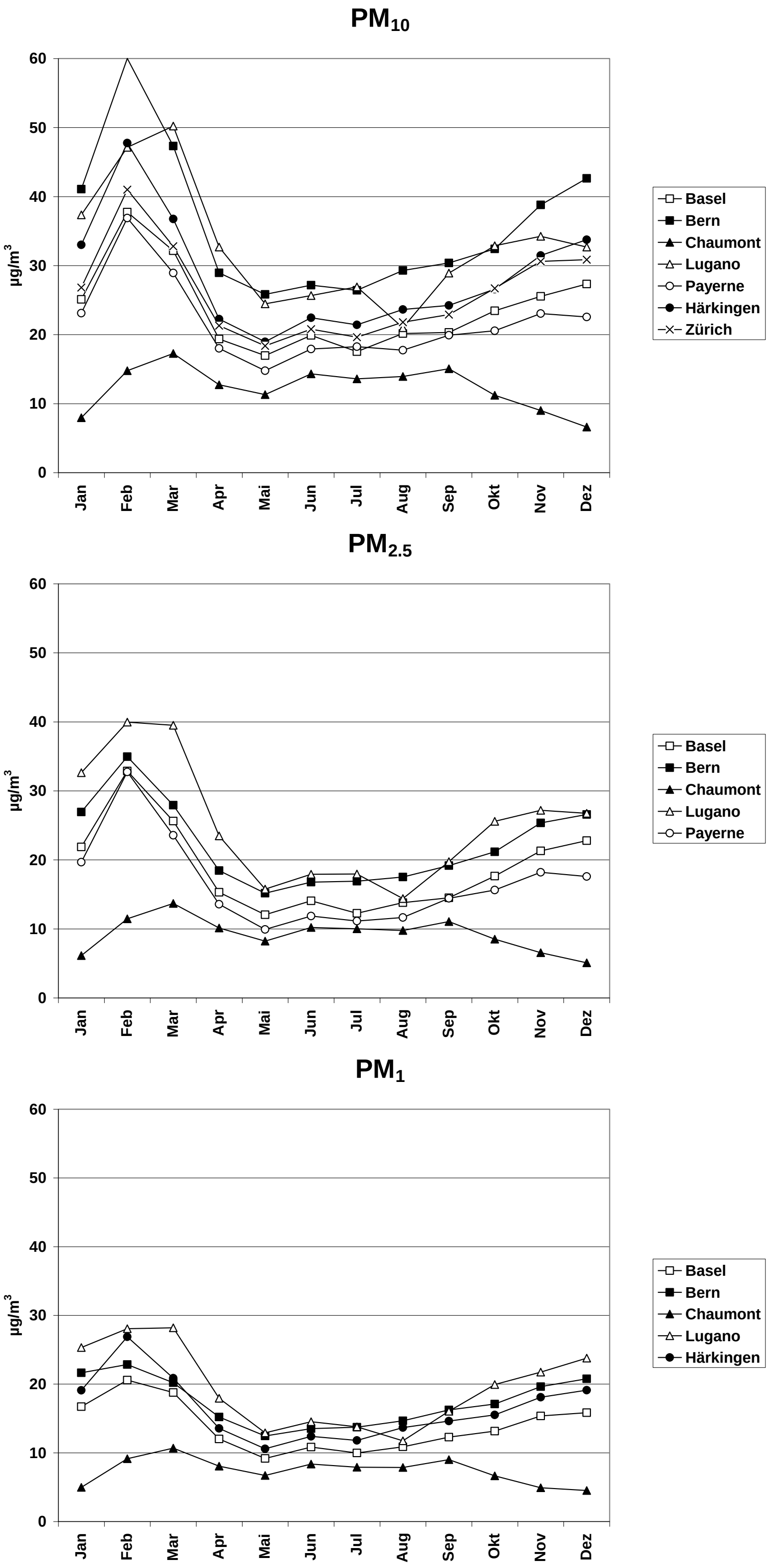

Figure 18.3: Seasonal variations of monthly means for PM_{10}, $PM_{2.5}$ and PM_1 for the period 2003-2006.

18.4.2 Spatial variability of PM_{10}, $PM_{2.5}$ and PM_1 concentrations

Interesting information about the spatial variability of PM concentrations can be obtained from an analysis of the correlations of the PM concentration data between the different sites of the NABEL network. Table 18.4 shows the Pearson correlation coefficients r for the comparison of the daily values of different sites. It can be seen that the correlation coefficients for all mass fractions (PM_{10}, $PM_{2.5}$ and PM_1) between the sites situated north of the Alps at moderate altitude (Basel, Bern, Payerne and Härkingen) are quite high, i.e. in the range of 0.84-0.92. This indicates that the variability of the daily concentrations is not primarily influenced by local events and sources, but are rather determined by meteorological conditions. Chaumont, which is often situated above the inversion layer and Lugano, which is separated by the Alps show (not surprisingly) much lower correlations. This is elaborated in some more detail with the following three examples, which differentiate between summer (June-August) and winter (December-February). Figure 18.4 shows the correlation for PM_{10} between the sites Basel and Payerne. Though the distance between these two sites is 95 km and they are separated by the 600-800m high Jura Mountains, good correlation can be observed in particular in winter, but also during summer.

Figure 18.5 compares Basel, north of the Alps with Lugano, south of the Alps. As expected, no correlation can be observed during wintertime. During summertime the correlation is somewhat higher, but still very low. This shows clearly that the high mountains of the Alps form an efficient obstacle for the distribution and homogenisation of fine particles.

Figure 18.6 shows a comparison of the two sites Payerne and Chaumont for $PM_{2.5}$. The sites are located quite close together (distance 24 km) but on different altitudes. Chaumont is situated 650 m higher than Payerne. A high correlation can be observed during summertime when the vertical mixing of the lower atmosphere is generally good and the absolute concentration level of the mountain site is only about 20% lower than at Payerne, which is situated within the Swiss basin in a rural environment. However, during wintertime, when the meteorology is characterised by frequent inversions, the observed $PM_{2.5}$ levels are largely decoupled. The correlation is very low and the absolute concentration level at the mountain site Chaumont reaches only about 25% of that of Payerne.

*Table 18.4: Pearson correlation coefficients (r) of the daily values of PM_{10}, $PM_{2.5}$ and PM_1 measured simultaneously at different sites (2003-2005)***.**

PM_{10}

	Basel	Bern	Chaumont	Lugano	Payerne
Basel	1.00				
Bern	0.84	1.00			
Chaumont	0.60	0.45	1.00		
Lugano	0.48	0.49	0.31	1.00	
Payerne	0.89	0.88	0.60	0.51	1.00
Härkingen	0.88	0.89	0.47	0.50	0.89

$PM_{2.5}$

	Basel	Bern	Chaumont	Lugano
Basel	1.00			
Bern	0.89	1.00		
Chaumont	0.55	0.52	1.00	
Lugano	0.51	0.52	0.27	1.00
Payerne	0.90	0.92	0.58	0.52

PM_1

	Basel	Bern	Chaumont	Lugano
Basel	1.00			
Bern	0.85	1.00		
Chaumont	0.55	0.46	1.00	
Lugano	0.52	0.55	0.22	1.00
Härkingen	0.89	0.90	0.48	0.53

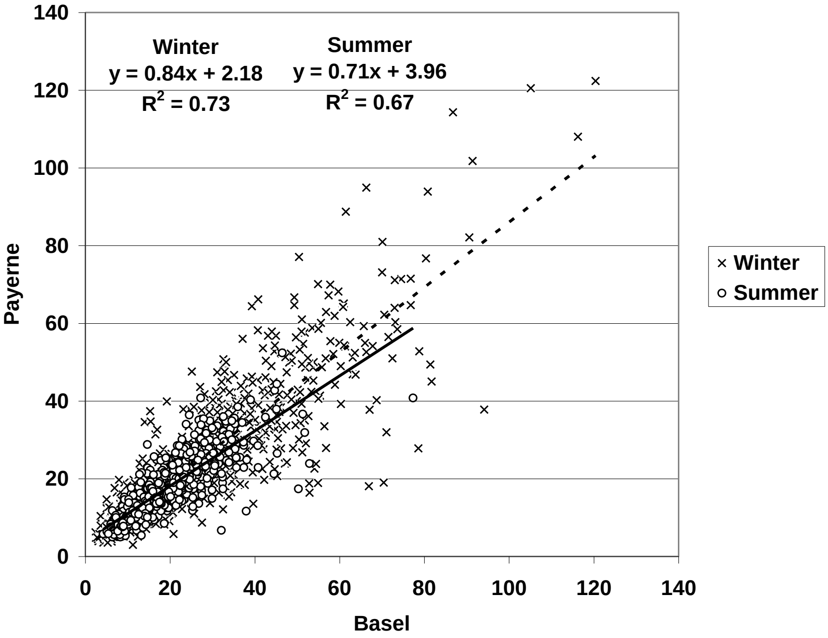

Figure 18.4: Scatterplot and linear regression of the daily values (1998-2005) of PM_{10} ($\mu g/m^3$) at Basel and Payerne during summer (June to August) and during winter (December–February). Dotted line: winter; solid line: summer.

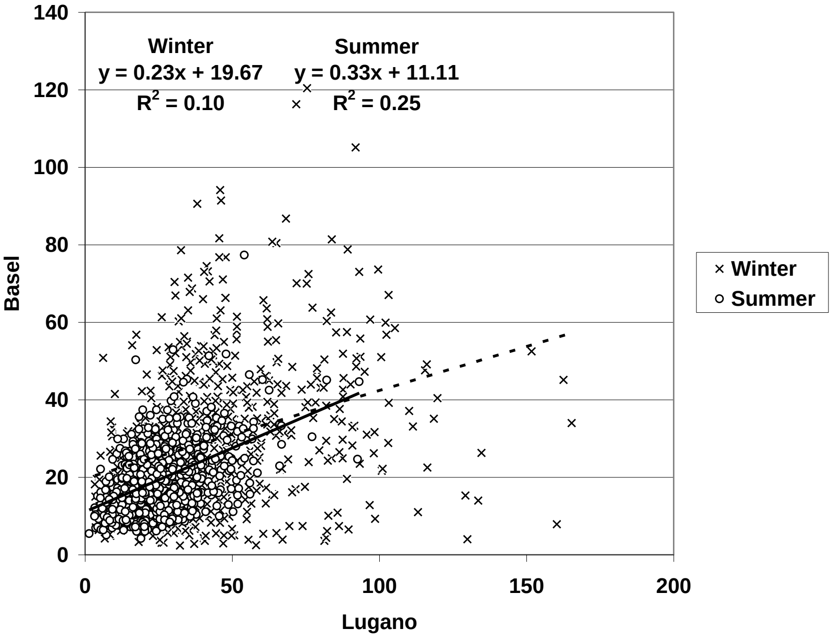

Figure 18.5: Scatterplot and linear regression of the daily values (1998-2005) of PM_{10} ($\mu g/m^3$) at Basel and Lugano during summer (June to August) and during winter (December–February). Dotted line: winter; solid line: summer.

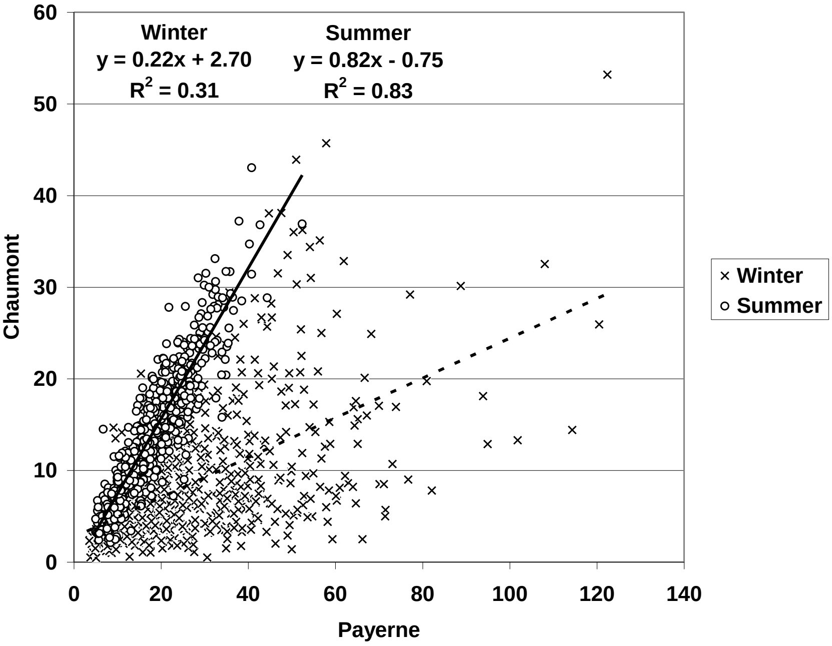

Figure 18.6: Scatterplot and linear regression of the daily values (1998-2005) of PM_{10} ($\mu g/m^3$) at Chaumont and Payerne during summer (June to August) and during winter (December–February). Dotted line: winter; solid line: summer.

18.5 Conclusions

From the presented analysis of long-term parallel measurements of PM_1, $PM_{2.5}$ and PM_{10} concentrations in Switzerland the following conclusions can be drawn:

- At all sites the concentrations of the different size fractions were highly correlated on the level of daily values. Unless strong and variable local sources of coarse particles are present, parallel measurements of PM_1, $PM_{2.5}$ and PM_{10} provide only limited additional information. In order to make efficient use of the financial and personal resources, such parallel measurements can be restricted to a few carefully selected sites in a monitoring network.

- Also the comparison of daily PM values from different sites often show quite high correlation. The analysis of the Swiss data indicates that this has primarily meteorological reasons. Even distant sites show good correlations if they are situated in an area with similar meteorological conditions. However, the correlations drop drastically if this is not the case i.e. if the sites are divided by high topographical obstacles (Alps) or by an inversion layer. Particle transport modelling shows clearly the relevance of long-range transport of fine particles though robust quantification still seems to be difficult (EMEP, 2004). Therefore, high correlations of PM at even distant sites could be expected due to a relatively homogenous distribution of long-range transported PM over large areas. However, the high daily variability of the PM concentrations can not be explained with long-range transport because on a regional scale the daily variability of the PM emissions is quite small. In fact, no matter whether the particles are locally emitted or long-range transported, it is mainly the meteorology (wind speeds, turbulence, vertical mixing, inversions etc.) which causes more or less effective dilution of the emitted pollutants and thus the daily fluctuation of the concentrations.

18.6 References

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19 PM_{10} and $PM_{2.5}$ gradients through London

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19.1 PM_{10} network data for London for 2000-2005

The London Air Quality Network LAQN provides PM_{10} air quality data across a range of site types and provides evidence for PM_{10} gradients through London. Table 19.1 summarises the air quality data for 64 sites over the 2002–2004 period. These data have been provided by TEOM instruments and the data are reported in Table 19.1 with gravimetric correction, that is to say, these data have been scaled by a factor of 1.3. Also shown in Table 1 are results from the UK DEFRA AURN network for key rural sites for 2000–2005 to establish the PM_{10} concentrations gradients through London.

Table 19.1: Annual mean PM_{10} data for 2000–2005 for a range of site types taken from the LAQN and DEFRA AURN monitoring networks.

Site type	2000	2001	2002	2003	2004	2005
Kerbside sites						
Marylebone Rd	48	44	45	48	43	43
Average 5 sites			43	43	40	
Roadside sites						
Average 29 sites			35	39	34	
Urban background						
Bloomsbury	28	29			26	27
N Kensington	26	26	25	29	24	25
Average 19 sites			29	31	26	
Suburban sites						
Bexley	24	24	25	27	24	
Average 9 sites			26	30	27	
Rural sites						
Harwell	18	19	17	20	19	19
Rochester	22	21		25	21	21
Increments						
Traffic	21	17	19	18	18	17
London	7	8	8	7	5	6

Notes:
a. Gravimetric scaling has been applied to these data.
b. Traffic increments are defined by subtracting the average of London Bloomsbury and London North Kensington concentrations from those at Marylebone Road.
c. London increments are defined by subtracting the average of Harwell and Rochester concentrations from the average of London Bloomsbury and London North Kensington.

The presence of rural levels, with superimposed London and traffic increments are apparent from this Table. London increments in PM_{10} concentrations range from 5–8 µg m^{-3} and traffic increments from 17–21 µg m^{-3}.

19.2 $PM_{2.5}$ data for a transect through London

$PM_{2.5}$ monitoring is not as widespread across London as that for PM_{10} and the available data are summarised in Table 19.2. All these data are from TEOM instruments and the results are tabulated as provided by the instrument without scaling. The presence of rural levels, with superimposed London and traffic increments are apparent from this Table. London increments in $PM_{2.5}$ appear to be about 1.9–4.1 µg m^{-3} and traffic increments about 4.9–11.7 µg m^{-3}.

Table 19.2: Annual mean $PM_{2.5}$ data for 2000–2005 for a range of site types taken from the LAQN and DEFRA AURN monitoring networks.

Site type	2000	2001	2002	2003	2004	2005
Kerbside sites						
Marylebone Rd	25.5	24.7	21.5	19.0	19.3	19.3
Roadside sites						
Average 3 sites				18.4	16.5	
Urban background						
Bloomsbury	14.6	13.0	13.6	14.1	12.7	12.9
Hackney				17.7	12.5	
Suburban sites						
Bexley				13.3	11.7	
Rural sites						
Harwell	10.1	10.6	9.7	11.8	10.6	10.3
Rochester	10.9	11.4	11.4	12.6	10.9	11.4
Increments						
Traffic	10.9	11.7	7.9	4.9	6.7	6.4
London	4.1	2.0	3.1	1.9	1.9	2.3

Notes:

a. Raw TEOM data and no gravimetric scaling has been applied to these data.

b. Traffic increments are defined by subtracting London Bloomsbury concentrations from those at Marylebone Road.

c. London increments are defined by subtracting the average of Harwell and Rochester concentrations from those at London Bloomsbury.

19.3 Correlations between PM_{10} and $PM_{2.5}$

The correlations between daily mean PM_{10} and $PM_{2.5}$ concentrations are generally good at most sites and during most years. The correlation coefficients R^2 and orthogonal regression slopes for the sites on a transect through London are given in Table 19.3. The correlation coefficient at the rural EMEP (Harwell) site is slightly smaller than those at the London urban background (Bloomsbury) and London kerbside (Marylebone Road) sites because of the generally lower concentrations and higher measurement uncertainties. The orthogonal regression slopes are lowest at the London kerbside site because of the local influence of traffic-induced emissions from abrasion and resuspension.

Table 19.3: Correlations between daily mean PM_{10} and $PM_{2.5}$ concentrations at three sites on a transect through London during 2004 and the slopes determined by orthogonal regression.

Site	R^2	Regression slope $PM_{2.5}/PM_{10}$
Marylebone Road	0.84	0.64 ± 0.02
Bloomsbury	0.85	0.72 ± 0.02
Harwell	0.79	0.76 ± 0.02

Notes:

a. $PM_{2.5}$ and PM_{10} data for 2004 were taken from the UK DEFRA Air Quality Archive without scaling.

19.4 Correlations between sites

Daily mean concentrations at the rural EMEP (Harwell) site and the London urban background site (Bloomsbury) are strongly correlated for both PM_{10} and $PM_{2.5}$, see Table 19.4 and Table 19.5. This indicates that both PM_{10} and $PM_{2.5}$ at these sites are not unduly influenced by local sources. Day-to-day variations in PM_{10} and $PM_{2.5}$ are strongly influenced by day-to-day variations in meteorology. The same pattern of meteorological variability influences both sites to a similar extent.

Table 19.4: Correlation coefficients R^2 between daily mean PM_{10} concentrations during 2005.

	Marylebone Road	Bloomsbury	Harwell
Marylebone Road	1		
Bloomsbury	0.24	1	
Harwell	0.13	0.62	1

In contrast, correlations between daily mean concentrations at the London kerbside (Marylebone Road) and London urban background (Bloomsbury) site for both PM_{10} and $PM_{2.5}$ are much weaker because of the influence of local traffic sources. Generally speaking, the correlation coefficients in Table 19.5 for $PM_{2.5}$ are larger than those for PM_{10} in Table 19.4. This is presumably due to the large inherent variability in the vehicle resuspension contribution to PM_{10} which is not present with $PM_{2.5}$.

Table 19.5: Correlation coefficients R^2 between daily mean $PM_{2.5}$ concentrations during 2005.

	Marylebone Road	Bloomsbury	Harwell
Marylebone Road	1		
Bloomsbury	0.46	1	
Harwell	0.30	0.71	1

19.5 Estimation of London and Traffic PM_{10} and $PM_{2.5}$ increments

Estimates can be made of the magnitude of the London increment in PM_{10} from the intercept in the scatter plot of the daily mean concentrations at the London urban background (Bloomsbury) and rural EMEP (Harwell) site. Using the 2005 data from the UK DEFRA Air Quality Archive which has a gravimetric scaling factor of 1.3 applied to PM$_{10}$, simple linear regression gives an intercept of about 6 µg m^{-3} with a slope that is close to unity. On this basis, 6 µg m^{-3} can be taken as an estimate of the mean elevation of the London urban background site above rural levels, the London increment. A corresponding analysis for PM$_{2.5}$ gives a London increment of about 1 µg m^{-3}.

By applying the same analysis to the daily mean PM data for a London kerbside site (Marylebone Road) and the London urban background (Bloomsbury) site, traffic increments of PM$_{10}$ of 20 µg m^{-3} and of PM$_{2.5}$ of 7 µg m^{-3} could be generated using 2005 data from the UK DEFRA Air Quality Archive.

19.6 Wind direction sector analyses for London sites

The good correlations between the daily mean PM concentrations monitored at different sites in a transect through London, suggests strongly that the day-to-day variations are caused by meteorology. It may be that similar meteorological influences act upon different local sources at the pairs of sites and act to produce coordinated variations in PM levels. Alternatively, it may be that similar meteorological influences bring similar contributions from distant sources to the pairs of sites. If meteorological variability acts by bringing contributions from distant sources, then pollution roses should show evidence of heightened PM contributions from particular wind direction sectors.

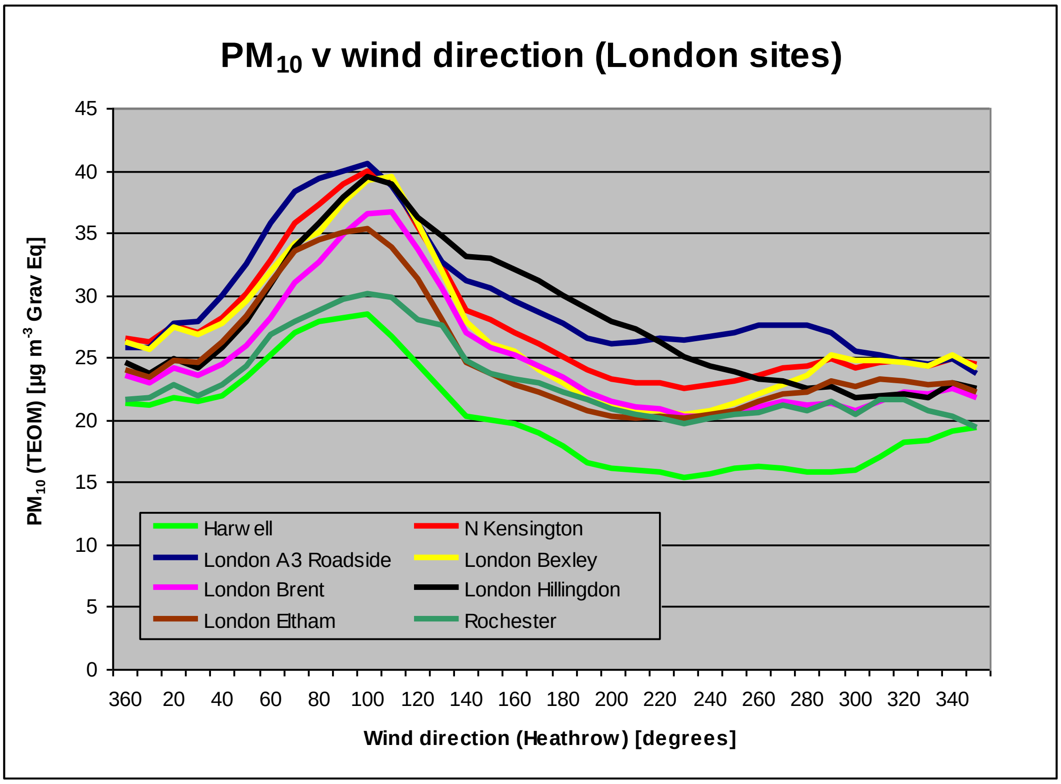

Figure 19.1: Mean PM$_{10}$ concentrations at a range of monitoring sites across London plotted against wind direction sector.

Figure 19.1 presents the mean PM$_{10}$ concentrations observed at a range of monitoring sites across London for different wind direction sectors. These data have been taken from the UK DEFRA Air Quality Archive and include the 1.3 gravimetric slope factor. There is clear evidence of maximum PM_{10} concentrations associated with easterly wind directions. Maxima are found in easterly wind directions for the rural sites at Harwell and Rochester and point to the influence of long-range transboundary transport from continental Europe. These easterly maxima are also evident at the London urban background sites (N Kensington, Hillingdon, Brent, Bexley, Eltham) and the London A3 roadside site. They are at a higher concentration level because of the addition of the London and traffic increments.

19.7 Site-specific PM modelling along a transect through London

Maps of background PM_{10} and $PM_{2.5}$ concentrations on a 1 km x 1 km grid for 2004 have been presented using a site-specific model (Stedman et al., Atmospheric Environment **41**, 161-172, 2007). These maps have been calculated by summing contributions from different sources:

- Secondary inorganic aerosol (derived by scaling measurements of SO_4, NO_3 and NH_4)
- Secondary organic aerosol (semi-volatile organic compounds formed by the oxidation of non-methane volatile organic compounds. Estimates derived from results from a Lagrangian model)
- Large point sources of primary particles (modelled using an air dispersion model and UK national emissions estimates, NAEI)
- Small point sources of primary particles (modelled using a small points model and emissions estimates from the NAEI)
- Regional primary particles (from results from a Lagrangian model and emissions estimates from the NAEI and EMEP, with local emissions within 20 km of the receptor excluded)
- Area sources of primary particles (modelled using a dispersion kernel, which is derived using an air dispersion model and emissions estimates from the NAEI)
- Sea salt (assumed to be a constant value)
- Residual (assumed to be a constant value)

The concentrations of these components have been estimated separately for the fine and coarse fraction. This enables a consistent method to be adopted for estimation of PM_{10} (the sum of the fine and coarse fractions) and $PM_{2.5}$ (fine fraction only).

The modelled value for each component has extracted for each of the monitoring site locations. The estimate of local primary PM concentration has been derived as the sum of the contribution from large and small point sources and area sources.

Table 19.6 presents the estimates of the concentrations of the different components of $PM_{2.5}$ for a range of sites along a transect through London. From the entries in this table, a value of the regional contribution to $PM_{2.5}$ concentrations in the London area of 12.5 $\mu g\ m^{-3}$ can be obtained, together with 4.3 $\mu g\ m^{-3}$ for the London increment above this regional contribution. Of this London increment, a contribution from local traffic of about 0.3 $\mu g\ m^{-3}$ can be ascertained from the site-specific modelling. This traffic increment rises considerably at heavily-trafficked locations.

Table 19.6: Regional background, regional primary and local primary contributions to total $PM_{2.5}$ concentrations for a range of locations along a transect through London ascertained from the site-specific PM model.

Site	Regional background $PM_{2.5}$, µg m^{-3}	Regional primary $PM_{2.5}$, µg m^{-3}	Local primary $PM_{2.5}$, µg m^{-3}	Total $PM_{2.5}$, µg m^{-3}
Rural sites				
Harwell	10.2	1.4	1.3	12.9
Stoke	10.8	1.6	1.4	13.8
Suburban sites				
Mean 3 sites	10.8	1.7	4.1	16.5
Urban background				
Mean 6 sites	10.8	1.7	4.1	16.5
Urban centre				
Mean 5 sites	10.8	1.8	4.2	16.8

Table 19.7 presents the corresponding estimates from the site-specific PM_{10} model for the same transect through London. On this basis, a regional contribution to PM_{10} concentrations of 17.4 µg m^{-3} can be calculated for the London area, together with a London increment of 6.3 µg m^{-3}. Of this London increment, a contribution from local traffic emissions of about 0.5 µg m^{-3} could be ascertained from the site-specific PM model.

Table 19.7: Regional background, regional primary and local primary contributions to total PM_{10} concentrations for a range of locations along a transect through London ascertained using a site-specific PM model.

Site	Regional background PM_{10}, µg m^{-3}	Regional primary PM_{10}, µg m^{-3}	Local primary PM_{10}, µg m^{-3}	Total PM_{10}, µg m^{-3}
Rural sites				
Harwell	15.8	1.4	2.1	19.3
Stoke	16.7	1.6	1.8	20.1
Suburban sites				
Mean 3 sites	16.6	1.7	6.2	24.5
Urban background				
Mean 6 sites	16.7	1.7	6.7	25.0
Urban centre				
Mean 5 sites	16.6	1.7	6.0	24.4

19.8 Trends in PM_{10} Concentrations for a London urban background site from 1992-2006

The time series of PM_{10} measurements for the London urban background site at Bloomsbury began in 1992 and continues through to 2006, see Figure 19.2. Annual mean concentrations fell steadily from about 30 µg m^{-3} in 1992 to about 22 µg m^{-3} in 2000 and have remained rather constant during the 2000-2006 period. Figure 19.2 shows that this behaviour is consistent with that found in the majority of the long-running urban background sites in other cities in the UK.

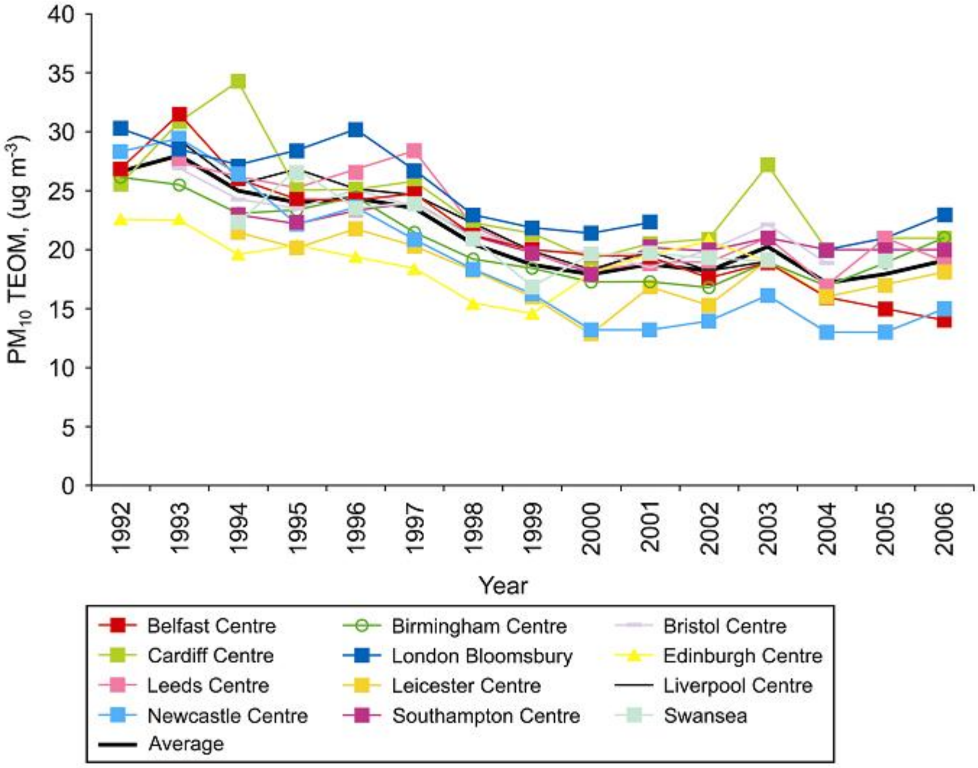

Figure 19.2: Time series of annual mean PM_{10} concentrations at the London Bloomsbury site together with those from long-running urban background sites in other UK cities from 1992 to 2006.

The observed fall in PM_{10} concentrations at the London urban background site over the 1992-2006 period amounts to about 30% whereas UK PM_{10} emissions have fallen by about 38% over the slightly shorter period of 1996-2004. Trends in annual mean PM_{10} concentrations in London are therefore not solely determined by trends in UK primary PM_{10} emissions. Other sources of PM_{10} must be influencing London's levels and their contribution must be showing an increasing or level trend so that the trend from primary PM emissions has been partially offset.

19.9 Acknowledgements

The support of the Air and Environmental Quality Division of the United Kingdom Department for Environment, Food and Rural Affairs is gratefully acknowledged.