EMEP – PM Assessment Report

Content

1 PM Assessment Report – Austria

1.1 PM measurement in Austria

1.1.1 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 (1^{st} 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.

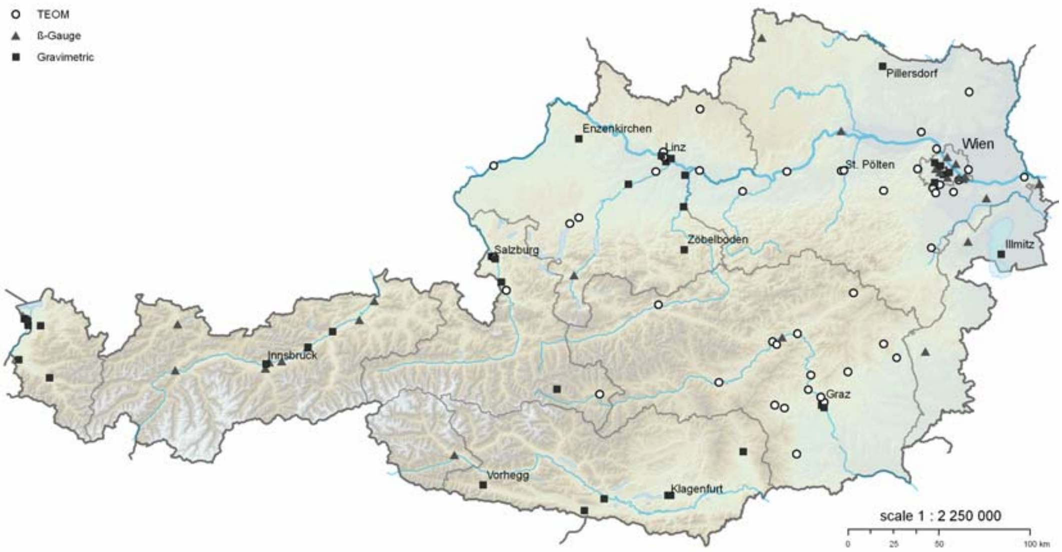

Figure 1.1: PM_{10} monitoring network in Austria, 2005.

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.

1.2 PM pollution level in Austria

1.2.1 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 1.1).

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 1.1: 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

1.2.2 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 1.2: 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 1.2 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 1.2 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.

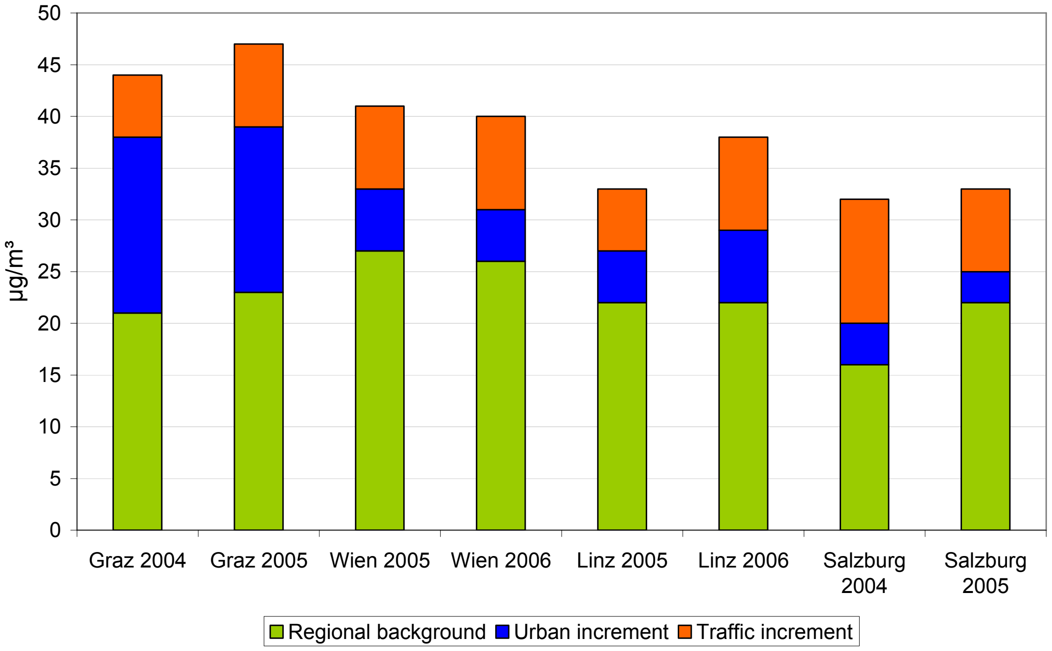

Figure 1.2: Estimation of urban increment PM_{10} concentration (annual means) in Graz, Wien, Linz and Salzburg.

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/.

1.2.3 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 1.3 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 1.3 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 inceases slightly in the morning, which is caused by advection of polluted air from below when the nocturnal inversion layer is lifted.

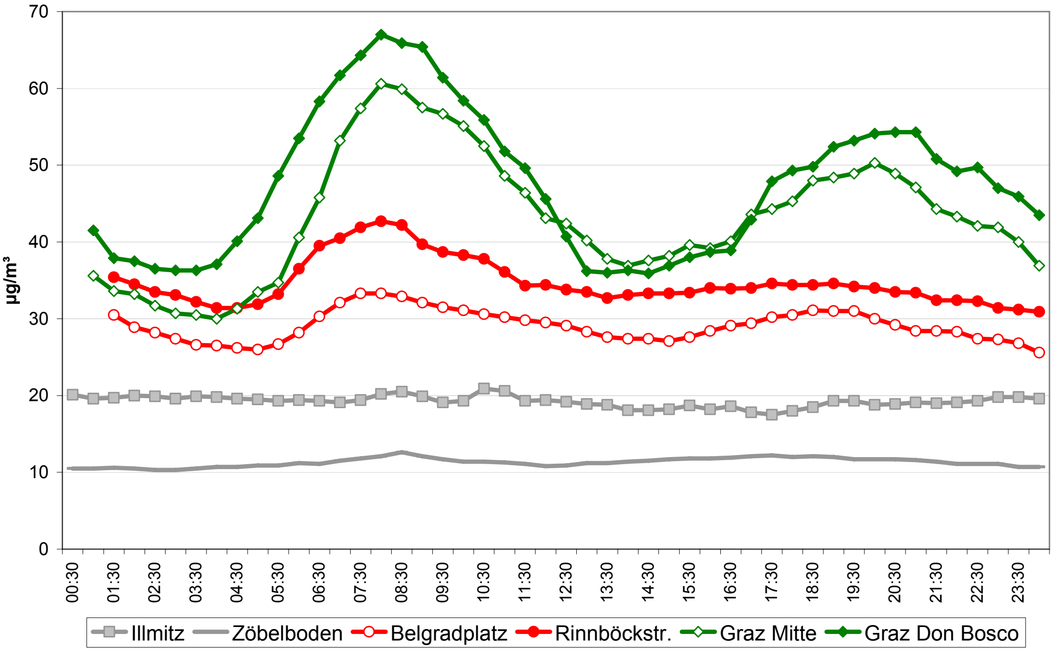

Figure 1.3: Average diurnal variation of PM_{10} concentrations at rural background sites and selected sites in Wien and Graz, 2005.

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 1.4 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.

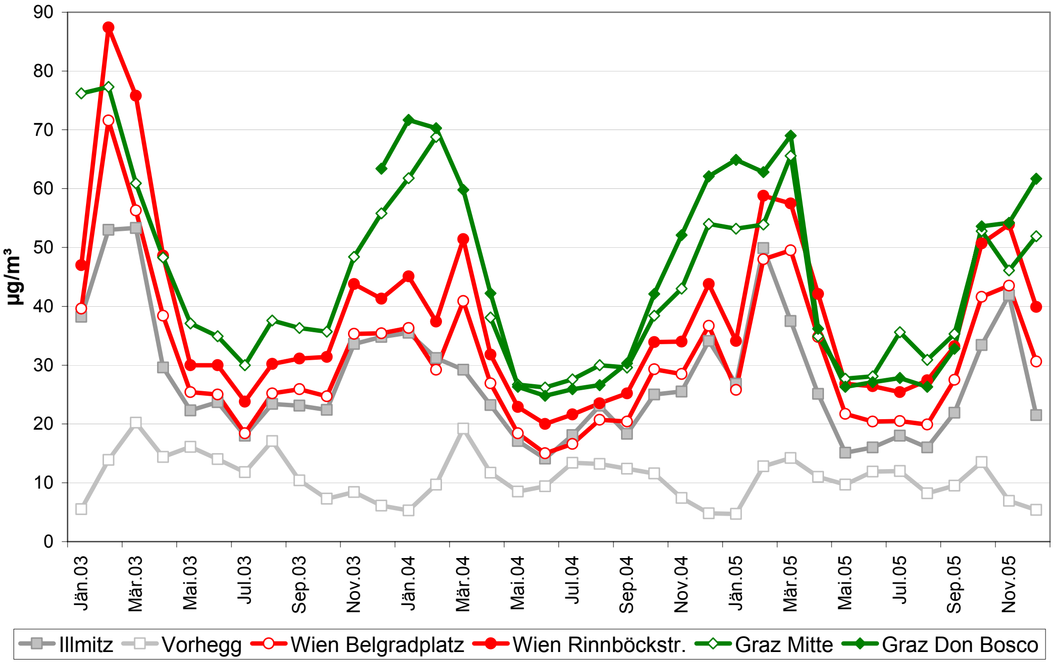

Figure 1.4: PM_{10} monthly mean values at rural background sites and selected sites in Wien and Graz, 2003 – 2005.

Figure 1.4 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.

1.3 Sources of PM_{10}

1.3.1 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 1.5. 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.

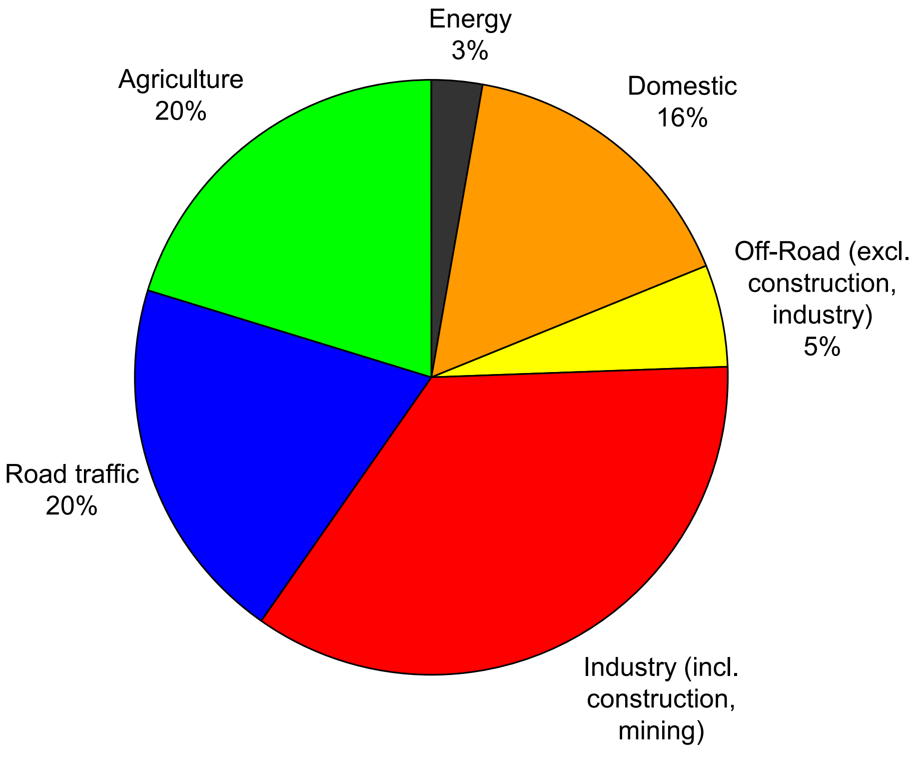

Figure 1.5: PM_{10} emissions in Austria by sector, 2004.

1.3.2 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 1.3.1. Since the sectoral distribution of PM_{10} emissions per year (Figure 1.5) 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 1.5), 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 1.6 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.

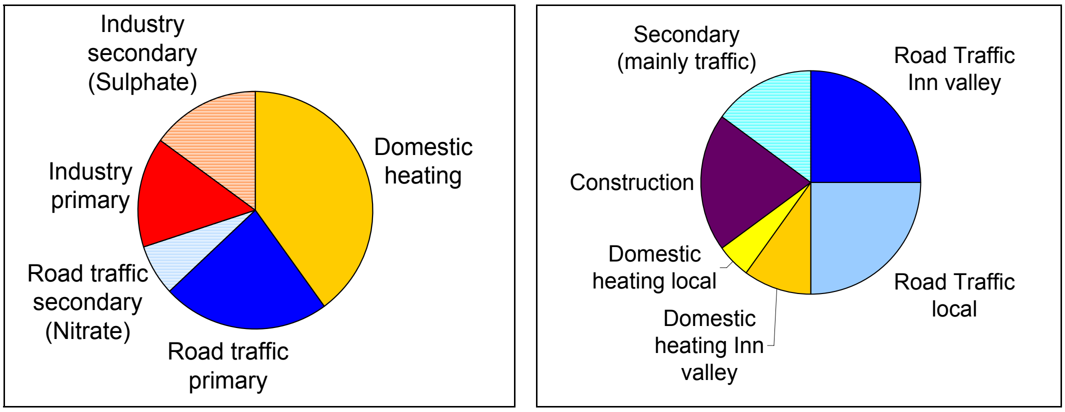

Figure 1.6: Source attribution for elevated PM_{10} concentrations in Wolfsberg (province of Carinthia), left, and Imst (province of Tyrol), right.

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.

1.3.3 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 1.7 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.

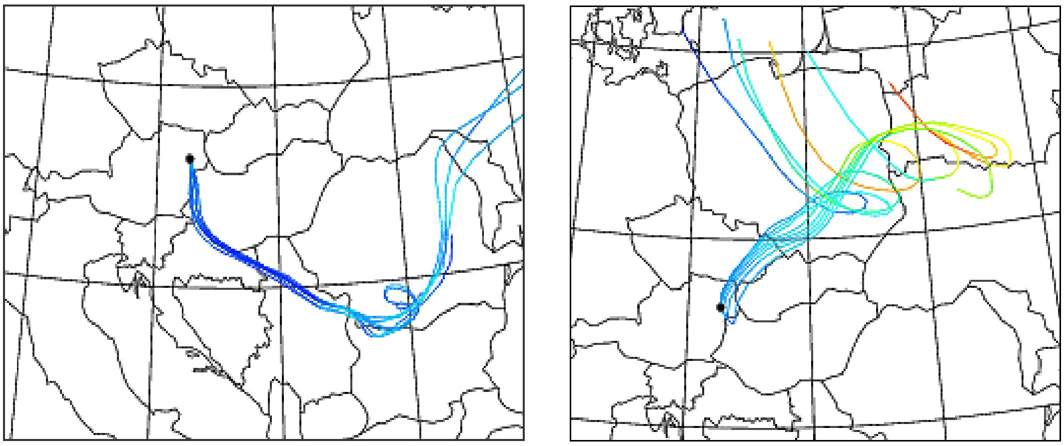

Figure 1.7: Backward trajectories for typical situations with elevated PM_{10} levels in Wien. Long-range transport from southern Romania and northern Serbia (left, February 9th, 2005) and southern Poland and northern Moravia (Czech Republic) (right, February 5th, 2005) The colour indicates the altitude of the air masses (blue < 900 m amsl, yellow > 1600 m).

Figure 1.8 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[1].

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[1] 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.

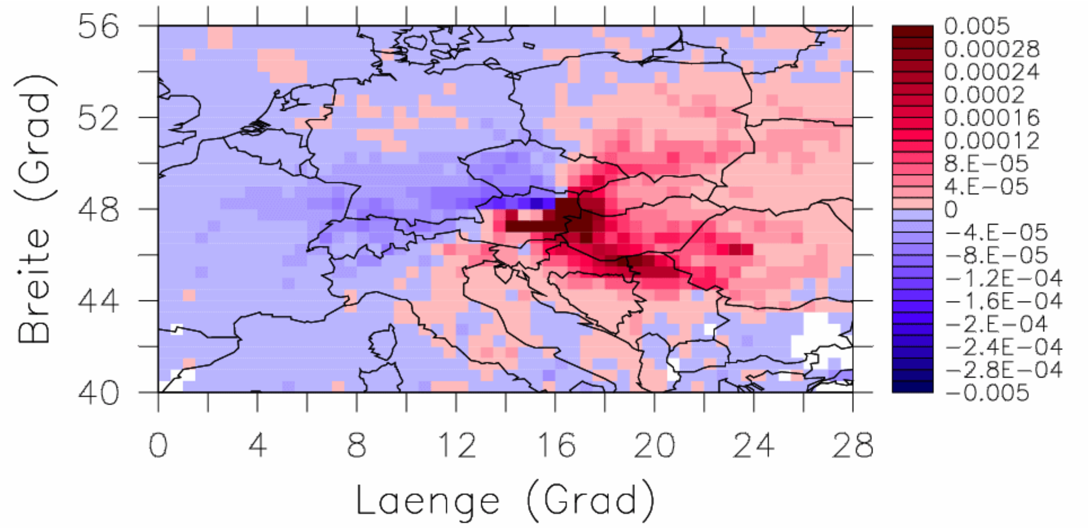

Figure 1.8: Trajectory statistics based on concentration weighted residence time, PM_{10} background concentration in Wien, 2003 (red: above average concentrations, blue: below average concentrations).

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 1.9. 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 1.10 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.

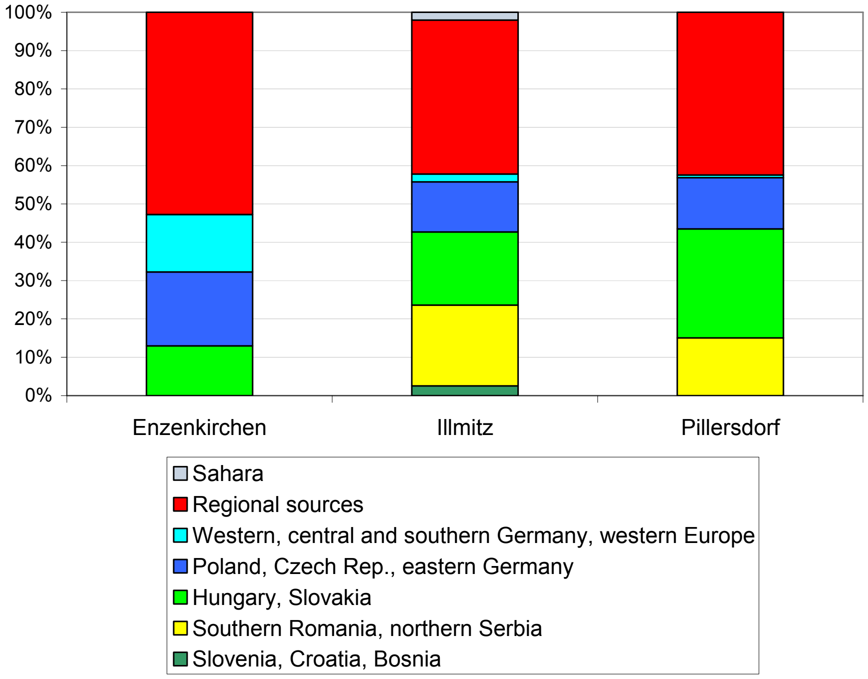

Figure 1.9: Contributions of different source regions to PM_{10} concentrations (above 50 µg/m³) at the rural background sites Enzenkirchen (North-western Austria), Illmitz(Eastern Austria) and Pillersdorf (Northern Austria), data 1999/2000, 2003-2005.

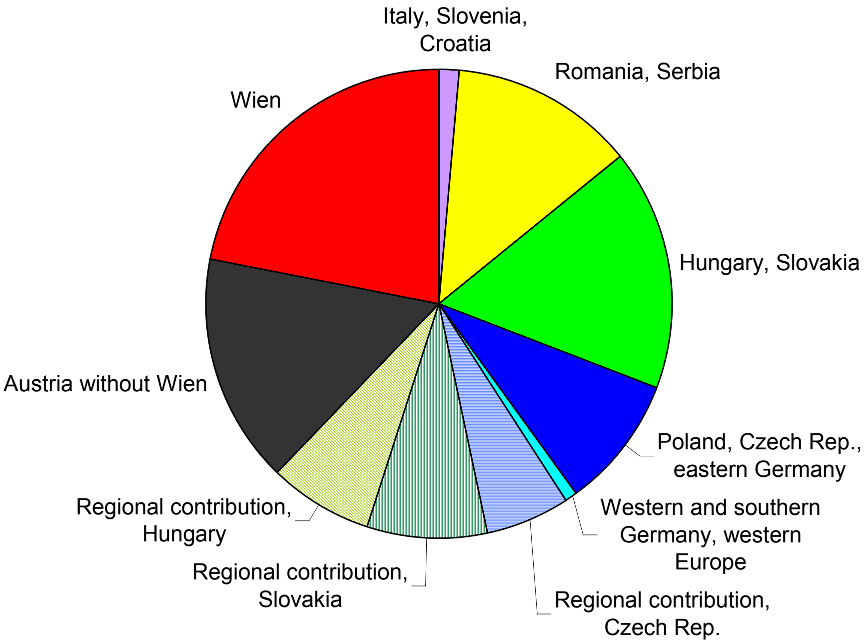

Figure 1.10: Contributions of different source regions to PM_{10} concentrations (above 50 µg/m³) to the urban background in Wien (data 1999/2000, 2003-2005).

1.4 $PM_{2.5}$ 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 1.3 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 1.3: $PM_{2.5}$ 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[2]	0.5
Illmitz	2004	25	19	0.78	14	0.5
Illmitz	2005	27	22	0.80	16	0.6
Illmitz	2006	26	21	0.77	15	0.5
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	0.6
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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[2] PM1 since April 2004; PM_{10} average over PM_1 measurement period: 25.7 µg/m³.

1.5 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 1.4 gives an overview of the chemical composition of PM_{10} in Austria, covering the major constituents elemental carbon (EC), organic matter[3] (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 1.4: 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*[4]	Rural	2004+	14	7 %	26 %	13 %	9 %	15 %		3 %	6 %
Arnoldstein*[5]	rural, medium industrial	March 99 – Feb. 00	22	6 %	31 %	18 %	8 %	8 %	3 %		
Bockberg*[4]	Rural	Dec. 03 – Dec.04+	25	8 %	31 %	14 %	8 %	12 %		5 %	2 %
Graz Don Bosco*[4]	Central urban traffic	Dec. 03 – Jan. 05+	45	14 %	39 %	8 %	4 %	7 %		4 %	7 %
Graz Süd*[6]	suburban, medium commercial	June 00 – May 01	33	14 %	24 %	13 %	7 %	5 %	3 %		
Graz Süd*[4]	Suburban, commercial	Dec. 03 – Jan.05+	38	12 %	42 %	9 %	4 %	7 %		7 %	6 %
Illmitz**[7]	rural background++	Oct. 99 – Nov. 00	24,2	8 %	23 %	18 %	11 %	8 %	4 %		
Linz ORF-Zentrum*[6]	central urban, medium industrial	June 00 – May 01	34	11 %	16 %	15 %	11 %	7 %	3 %		
Salzburg Lehen*[4]	Suburban background	2004+	18	12 %	29 %	10 %	6 %	11 %		9 %	5 %
Salzburg Rudolfspl.*[4]	Central urban traffic	2004+	28	23 %	32 %	7 %	3 %	7 %		9 %	6 %
Streithofen*[6]	rural	June 99 – May 00	23,7	8 %	25 %	16 %	17 %	11 %	3 %		
Unterloibach*[5]	rural	March 99 – Feb. 00	20	5 %	27 %	18 %	9 %	10 %	2 %		
Wien AKH*[6]	central urban background	June 99 – May 00	30,4	12 %	26 %	15 %	13 %	8 %	5 %		

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

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

[5] LAVRIC (2001)

[6] AUPHEP (2004)

[7] UMWELTBUNDESAMT (2002)

Site	Site type	Period	PM_{10}	EC	OM	Sul-phate	Nitrate	Ammo-nium	Metals	Silicates	Carbo-nates
Wien Kendlerstr.*[4]	Urban background	2004+	28	10 %	28 %	12 %	7 %	11 %		16 %	9 %
Wien Liesing*[8]	Suburban, commercial	Nov. 01 – Oct. 02	49,7	10 %	24 %	12 %	11 %	7 %	8 %		
Wien Lobau*[4]	Suburban forest	2004+	22	8 %	29 %	17 %	8 %	12 %			3 %
Wien Rinnböckstr.*[4]	Suburban, medium traffic	2004+	33	11 %	28 %	12 %	6 %	12 %		16 %	7 %
Wien Schafbergbad *[8]	Suburban background	Nov. 01 – Oct. 02	35,7	10 %	23 %	17 %	14 %	10 %	4 %		
Wien Schafbergbad *[4]	Suburban background	2004+	21	8 %	28 %	15 %	8 %	12 %		13 %	3 %
Wien Spittelauer Lände**[7]	central urban traffic++	Oct. 99 – Nov. 00	53,4	20 %	20 %	9 %	8 %	4 %	9 %		
Episode sampling											
Innsbruck Zentrum[9]	urban, medium traffic	Sept.03/Nov.03	26	20 %	32 %	8 %	5 %	3 %	5 %		
Klagengurt Völkermarkter str.[10]	urban traffic	Dec 02/Jan.03	64	17 %	29 %	8 %	9 %	5 %	4 %		
Lienz[11]	small town, traffic	Dec. 02	49	25 %	34 %	6 %	6 %	2 %	4 %		
Wien Belgradplatz[12]	central urban background	Feb./March 03, Jan./Feb. 04	93	9 %	20 %	16 %	17 %	8 %	4 %		
Wolfsberg[13]	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 1.11 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.

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

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 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.

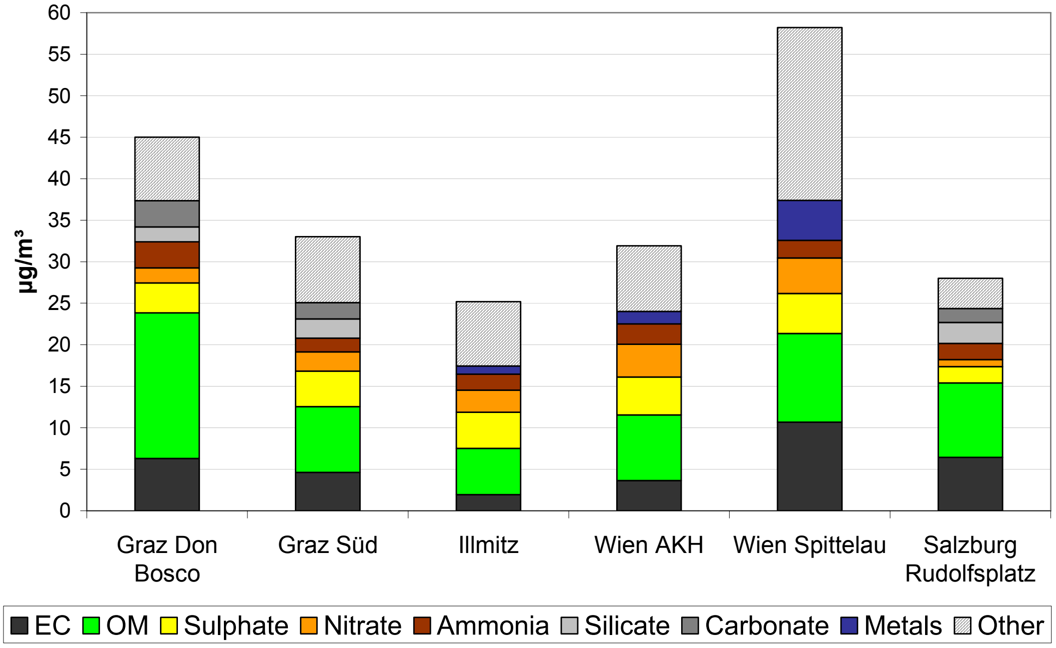

Figure 1.11: Chemical composition of PM_{10} at sites in Graz, Wien, Illmitz and Salzburg.

1.6 Literature

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2 Atmospheric particulate matter in Belgium

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2.1 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).

2.2 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 2.1. 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.

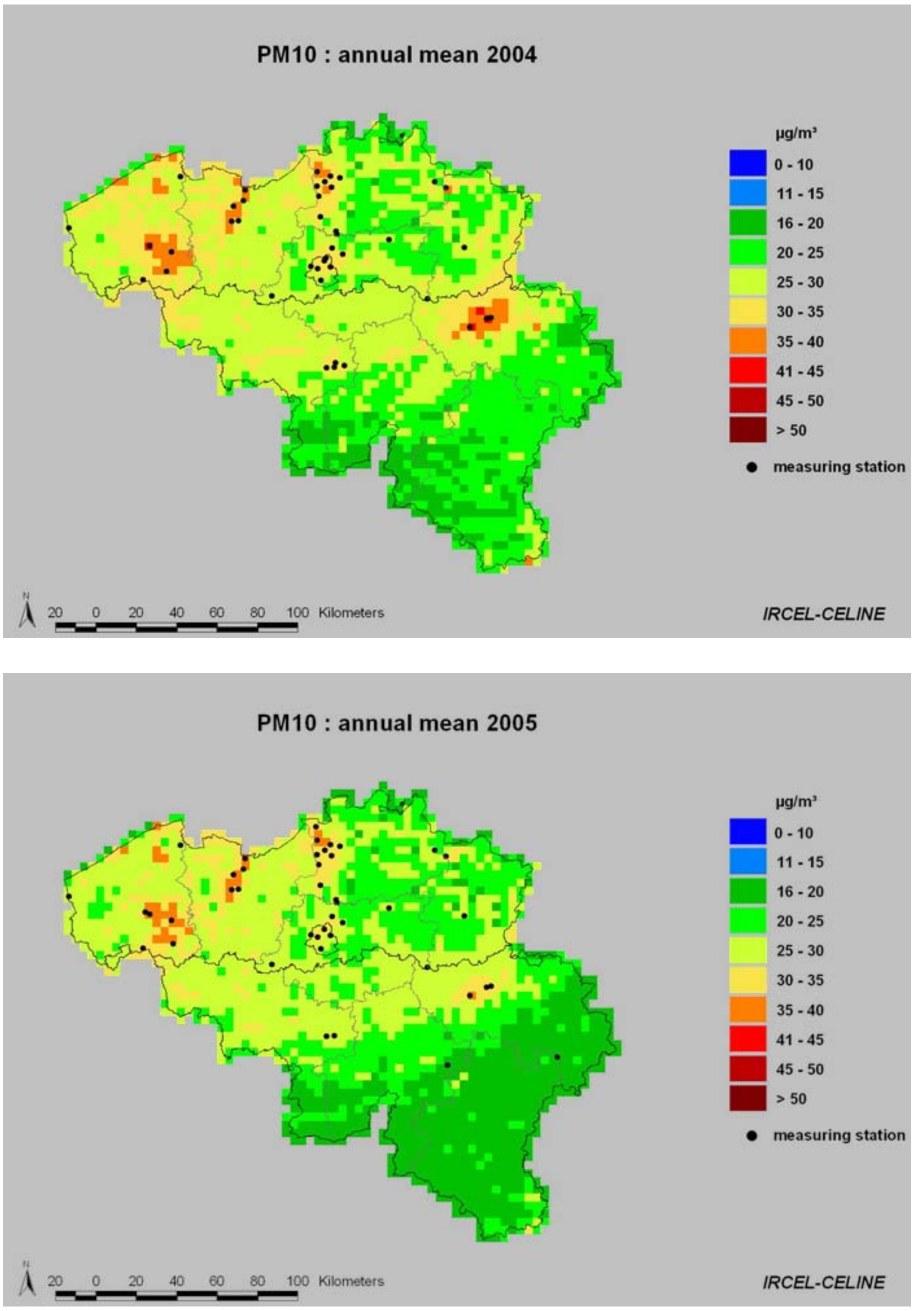

Figure 2.1: Annual mean PM_{10} concentration data for Belgium in the years 2004 and 2005.
Flanders is in the north and its provinces are from left to right: West Flanders, East Flanders, Antwerp (top) and Flemish Brabant (around Brussels), and Limburg. The Walloon region is in the south and its provinces are from left to right: Hainaut, Walloon Brabant (top) and Namur (bottom), and Liège (top) and Luxemburg (bottom).

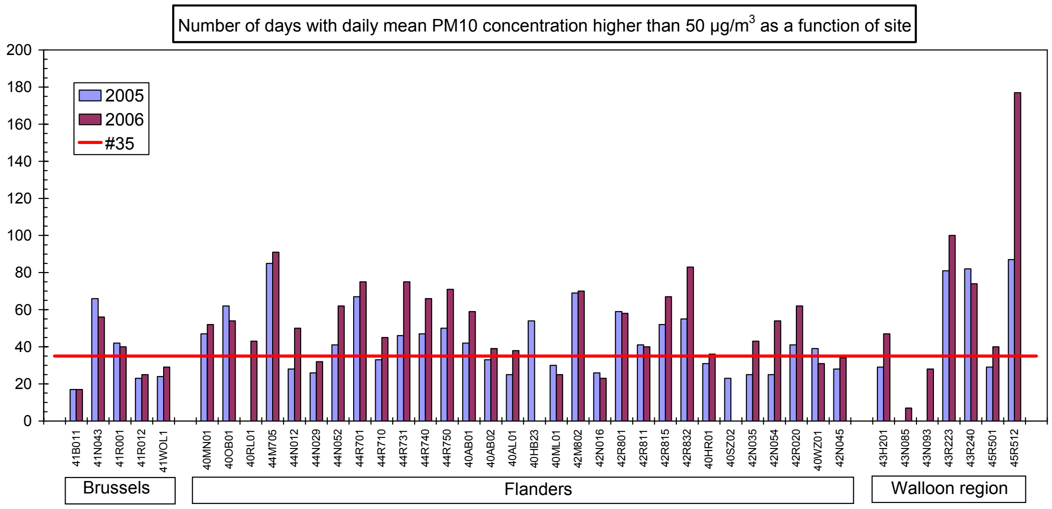

Figure 2.2: Compliance with the EU directive of less than 35 days with daily mean PM_{10} concentration higher than 50 µg/m^3 for the stations in the networks. The data for 2006 are not validated.

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 2.2).

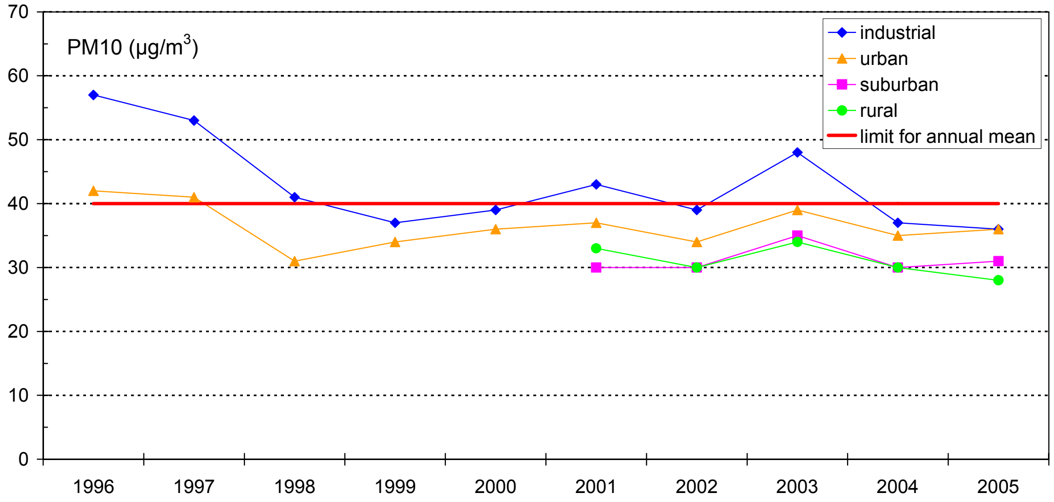

Figure 2.3: Annual mean PM_{10} concentration for different types of stations in the Flemish networks; the EU limit of 40 µg/m^3 (valid since 2005) is also indicated.

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 2.3, 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.

2.3 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.

2.4 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}.

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

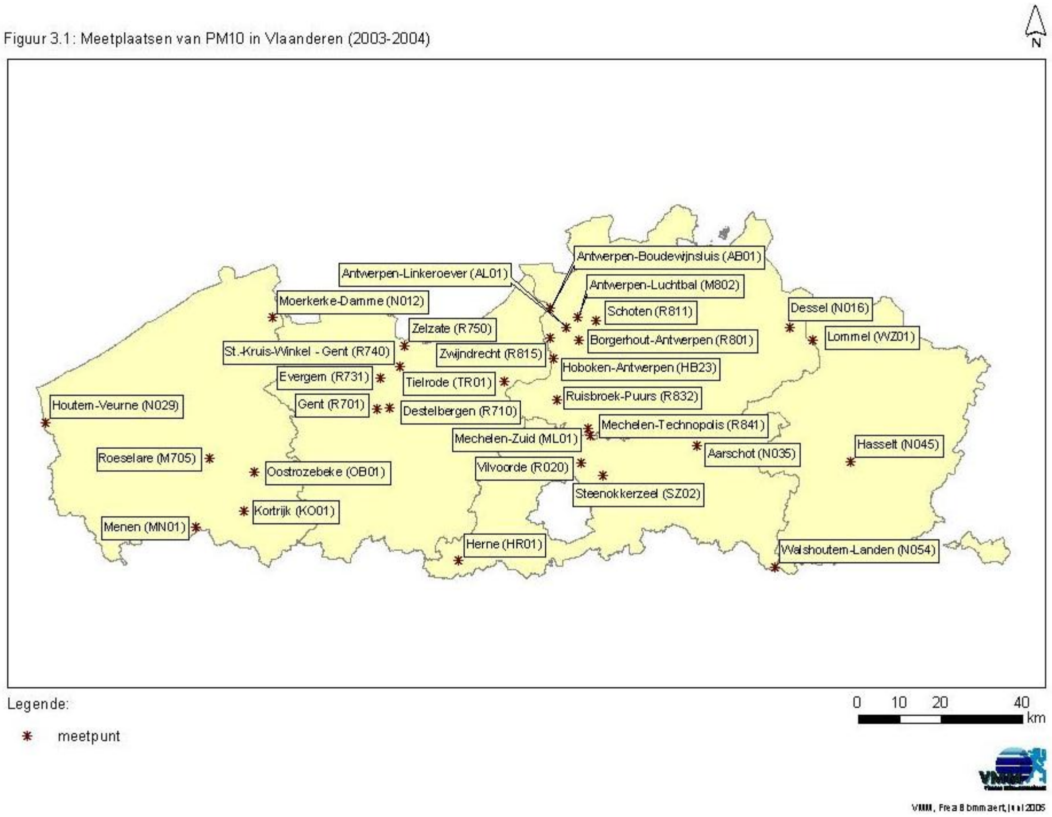

Figure 2.4: Location of the PM_{10} monitoring sites in Flanders.

Table 2.1: 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 2.1 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 2.4.

The total absence of correlation for the site WZ01 (Lommel) in Table 2.1 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.

2.6 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 2.5. 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.

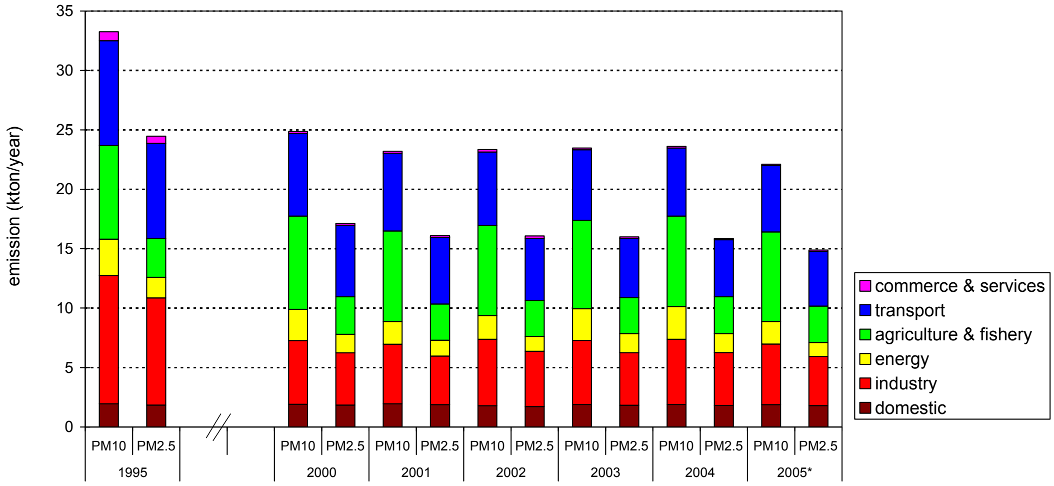

Figure 2.5: Emission of primary PM_{10} and $PM_{2.5}$ in Flanders. Note that the data for 2005 are preliminary.

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 2.6.

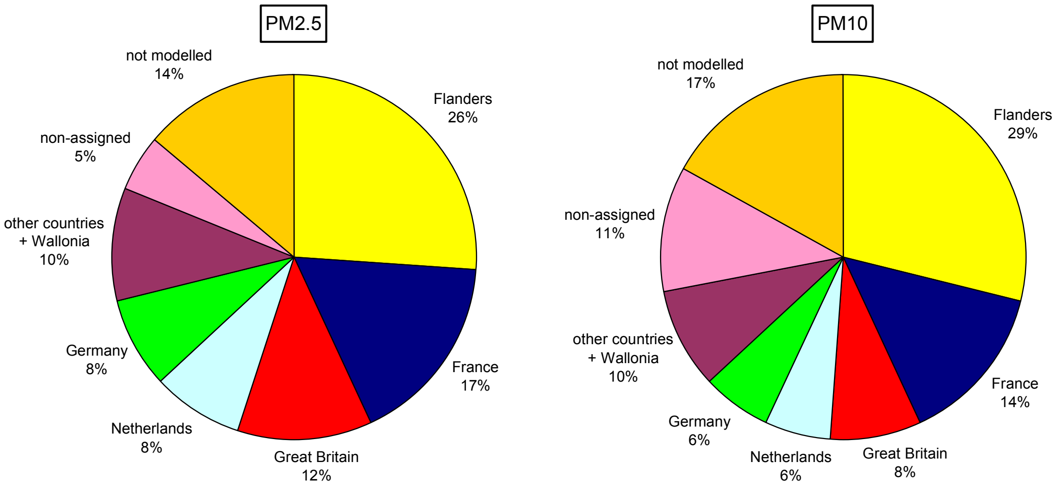

Figure 2.6: Modelled contributions to the $PM_{2.5}$ and PM_{10} levels for Flanders in 2002.

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 2.7. 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.

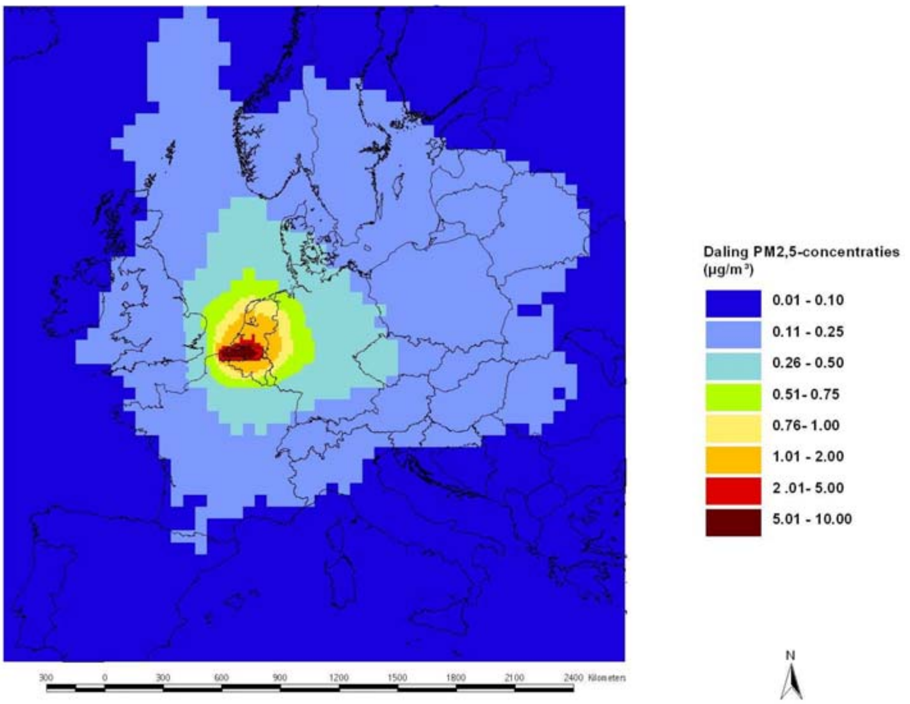

Figure 2.7: Modelled decrease of the $PM_{2.5}$ concentrations in Flanders and Europe when the emissions in Flanders are shut off (calculations for the year 2002).

2.7 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 2.8. Note that the 7 campaigns were not conducted simultaneously.

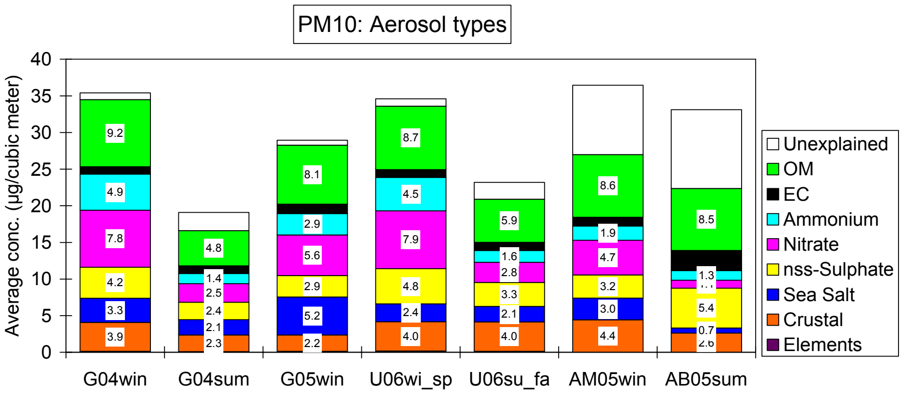

Figure 2.8: Average concentrations of 8 aerosol types in PM_{10} and of the unexplained gravimetric PM_{10} mass during 7 sampling campaigns [G04win, G04sum, and G05win stand for Ghent 2004 winter, Ghent 2004 summer, and Ghent 2005 winter, resp., and the samplings took place at INW; U06wi_sp and U06su_fa 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).

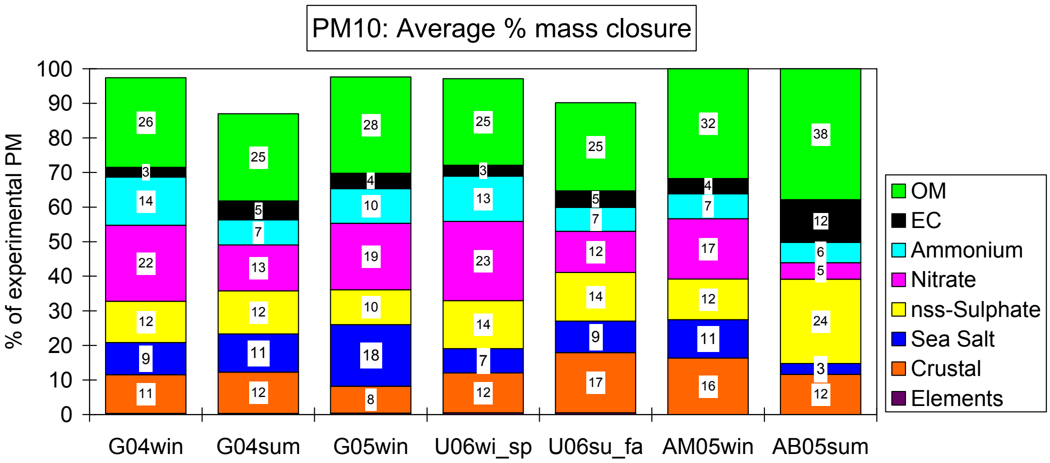

Figure 2.9: Average percentages of 8 aerosol types as % of the mean gravimetric PM_{10} mass (and for the two sites in Antwerp as % of the sum of the components); for additional explanation, see caption of Figure 2.8.

In order to better examine the differences in PM_{10} aerosol composition between the various sites and seasons, the data from Figure 2.8 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 2.9. 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 2.8, 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 2.9 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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3 PM trends in the Czech Republic

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3.1 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.

3.2 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.

3.3 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 3.1.

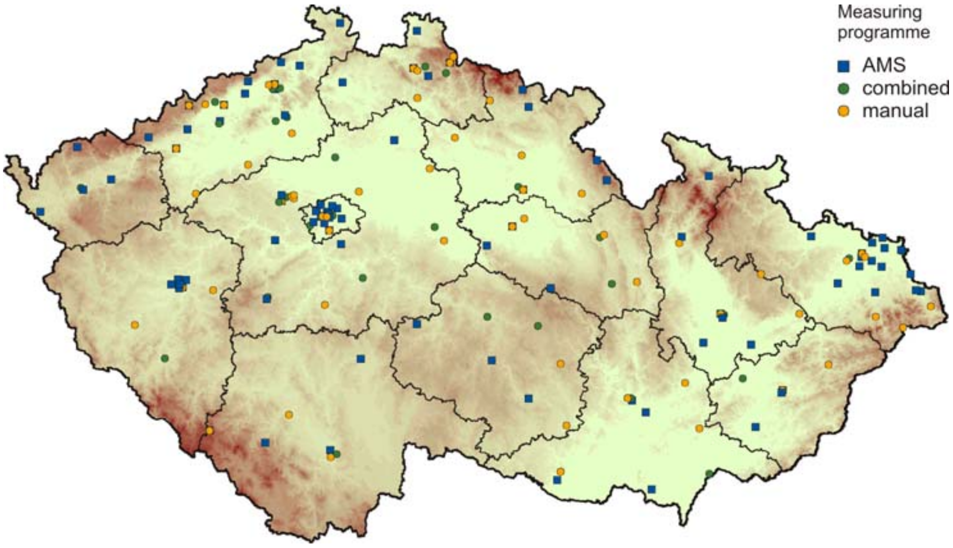

Figure 3.1: PM_{10} station network in the Czech Republic, 2005.

In 2005 measurements of the fine fraction of suspended particles ($PM_{2,5}$) began in 25 localities (Figure 3.2).

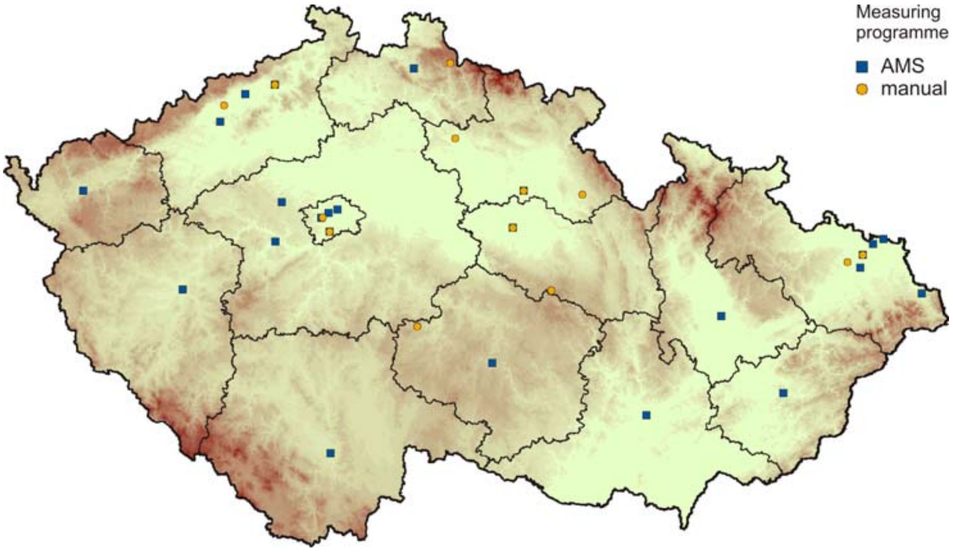

Figure 3.2: $PM_{2,5}$ stations in the Czech Republic, 2005.

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.

3.4 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 3.3).

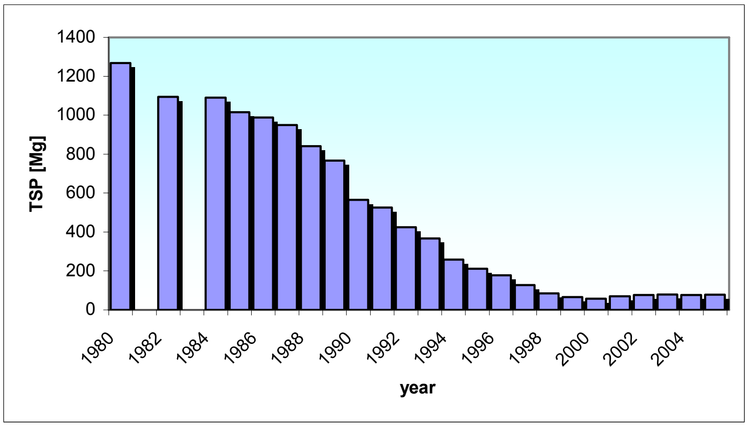

Figure 3.3: Trend of TSP emissions in The Czech Republic 1980-2005.

3.5 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 3.4). 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.

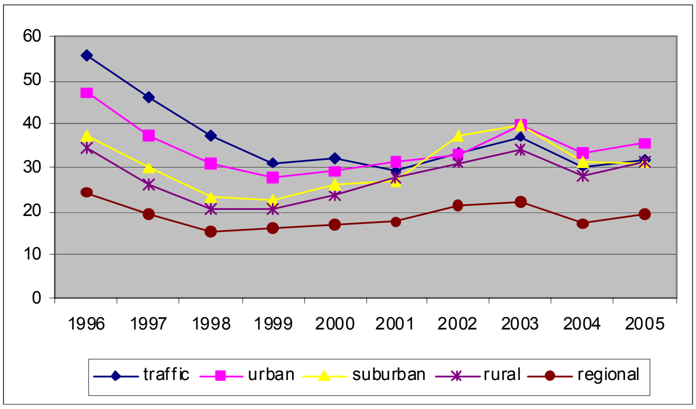

Figure 3.4: Trend of PM_{10} concentrations in the Czech Republic (1996-2005) at different types of stations ($\mu g.m^{-3}$).

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 3.5). The Moravian - Silesian region on the Czech-Polish border belongs to the most polluted regions by PM in Europe.

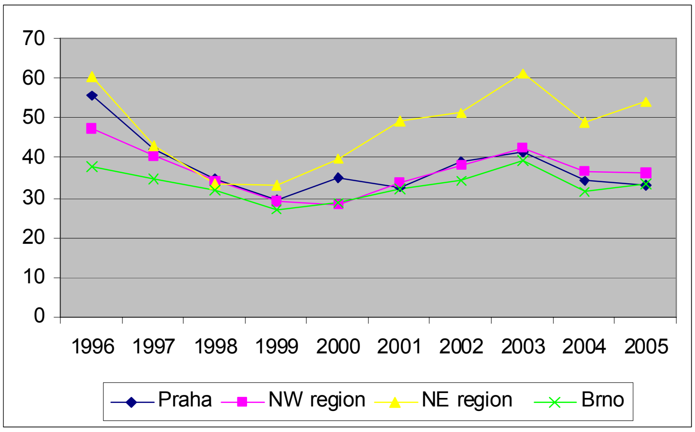

Figure 3.5: Trend of PM_{10} concentrations in agglomerations ($\mu g.m^{-3}$).

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 3.6).

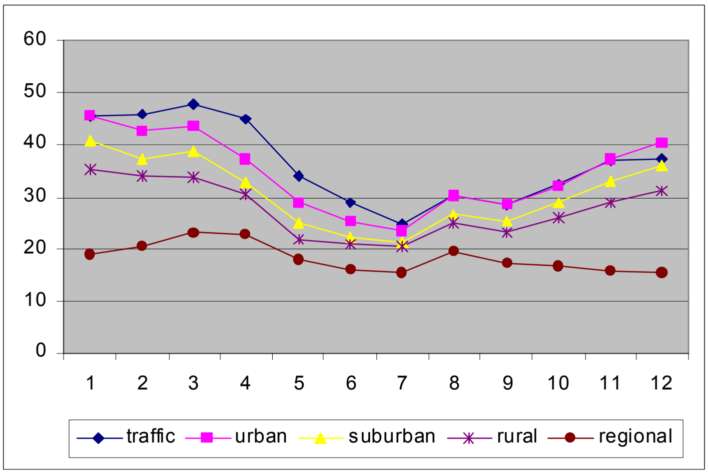

Figure 3.6: PM_{10} annual variation in the Czech Republic (1996-2005) at different types of stations (µg.m^{-3}).

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 3.7.).

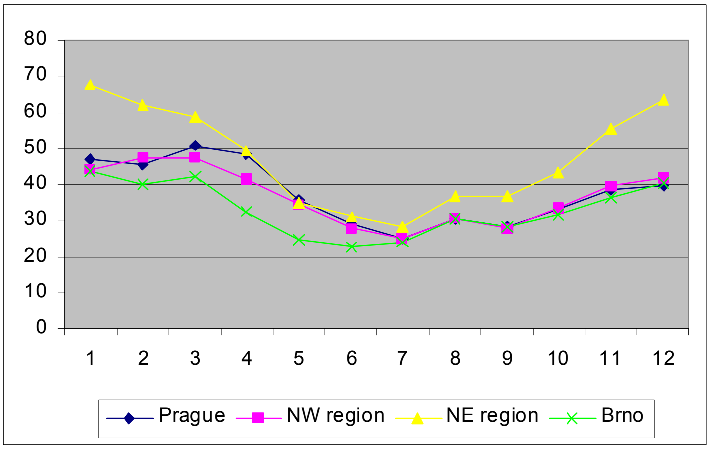

Figure 3.7: PM_{10} annual variation in agglomerations (µg.m^{-3}).

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 3.8). Figure 3.9 clearly shows much higher morning and evening PM_{10} concentrations in Ostrava-Karviná region compared to other agglomerations.

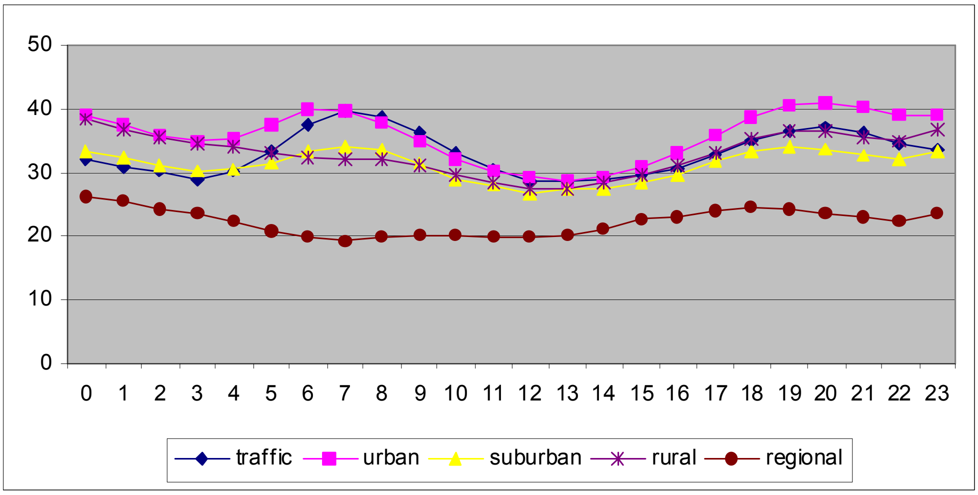

Figure 3.8: PM_{10} Diurnal variation at different types of stations ($\mu g.m^{-3}$).

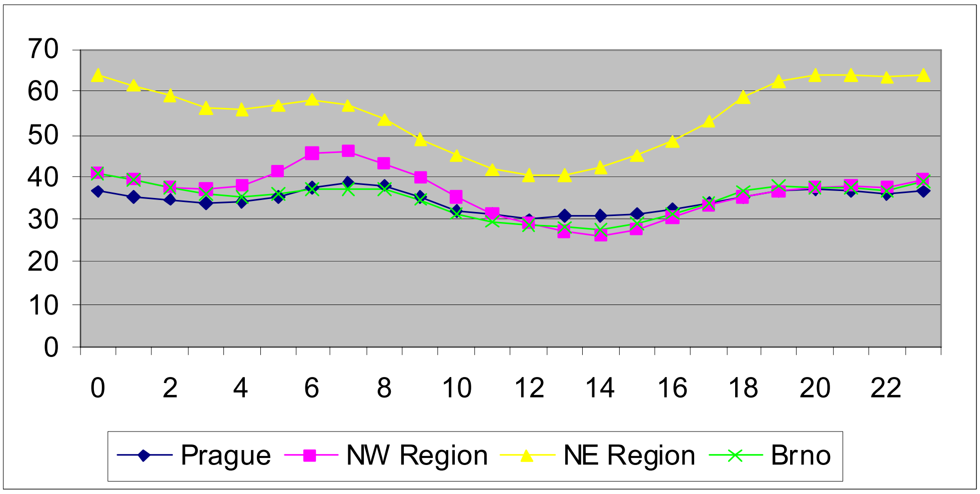

Figure 3.9: PM_{10} diurnal variation in agglomerations ($\mu g.m^{-3}$).

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 3.10).

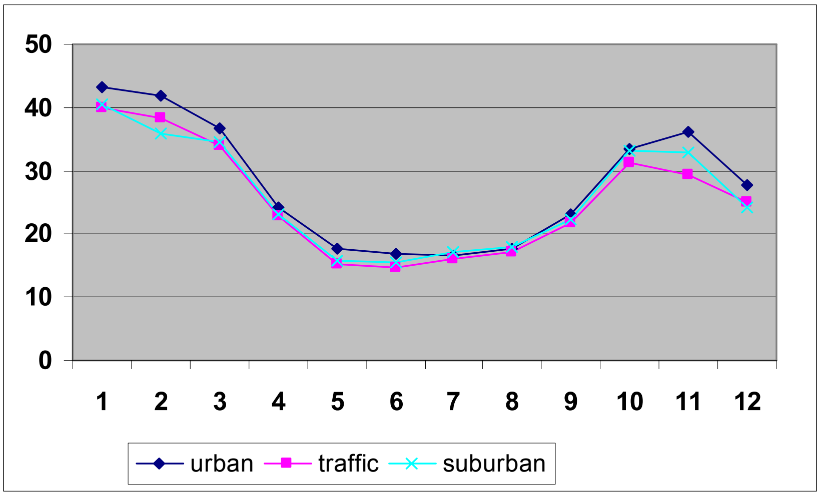

Figure 3.10: $PM_{2,5}$ annual variation in the Czech Republic (2005) at different types of stations ($\mu g.m^{-3}$).

The seasonal course of the ratio between $PM_{2,5}$ and PM_{10} (Figure 3.11) 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.

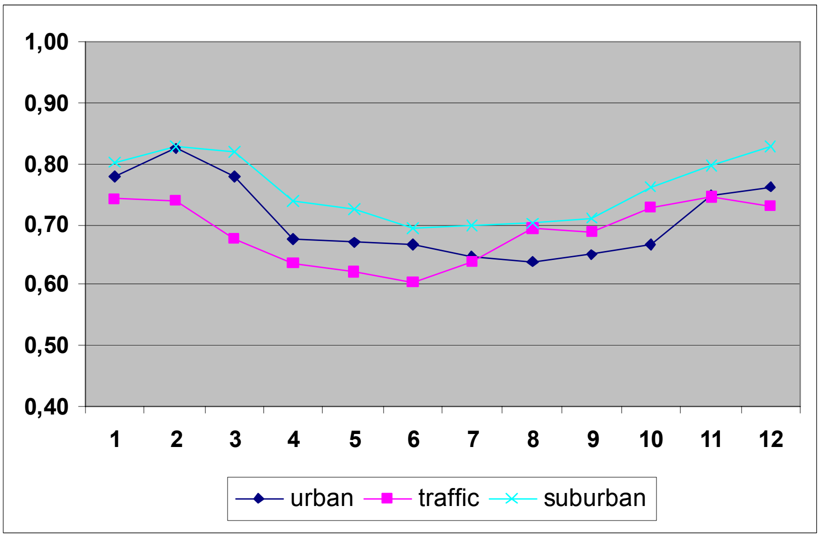

Figure 3.11: The seasonal course of the ratio between $PM_{2,5}$ and PM_{10} in 2005 at different types of stations.

$PM_{2,5}$ diurnal variation displays the same patterns as by PM_{10} (Figure 3.12). The difference between the situation in Ostrava-Karviná region and agglomerations is even higher than in the case of PM_{10} (Figure 3.13).

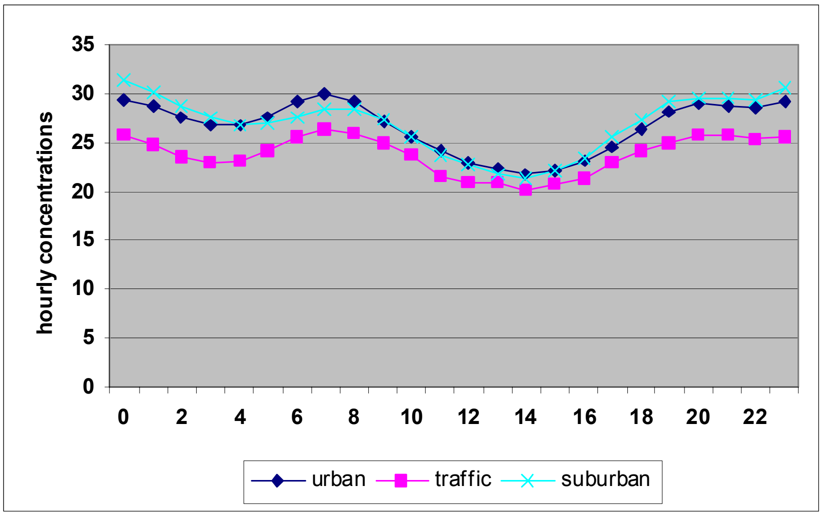

Figure 3.12: $PM_{2,5}$ diurnal variation at different types of stations ($\mu g.m^{-3}$).

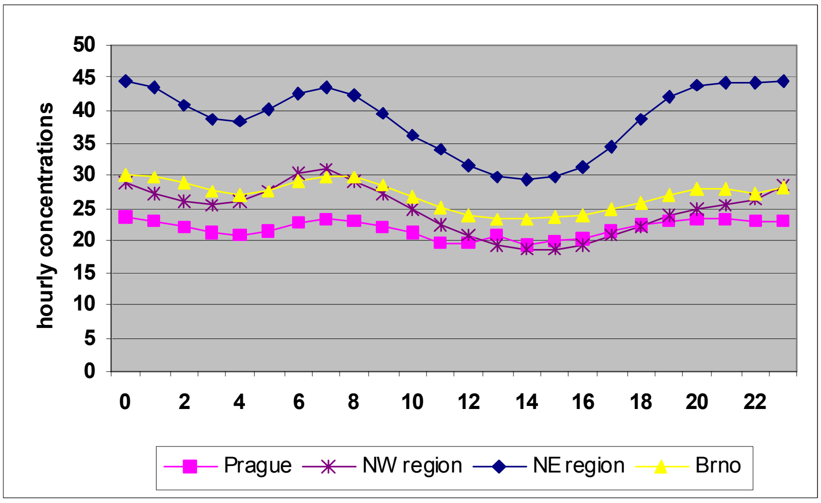

Figure 3.13: $PM_{2,5}$ diurnal variation in agglomerations ($\mu g.m^{-3}$).

3.6 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 3.14). The limit value for annual concentration was exceeded in 1,5% of territory (Figure 3.15). In the areas, where the PM_{10} concentrations exceed the air pollution limit values, live more than 65% of the population.

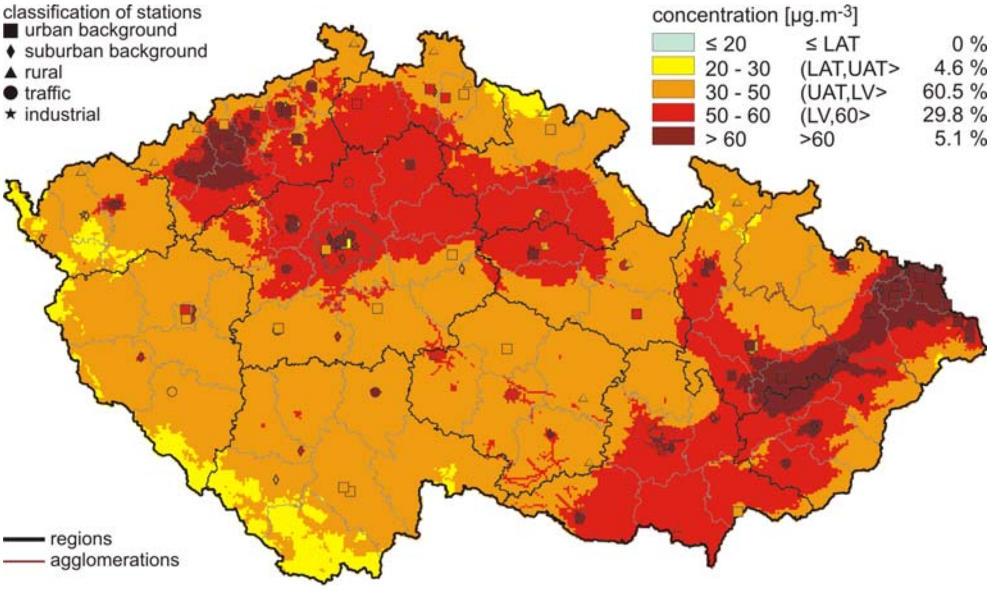

Figure 3.14: Field of the 36th highest 24-hour concentration of PM_{10} in 2005.

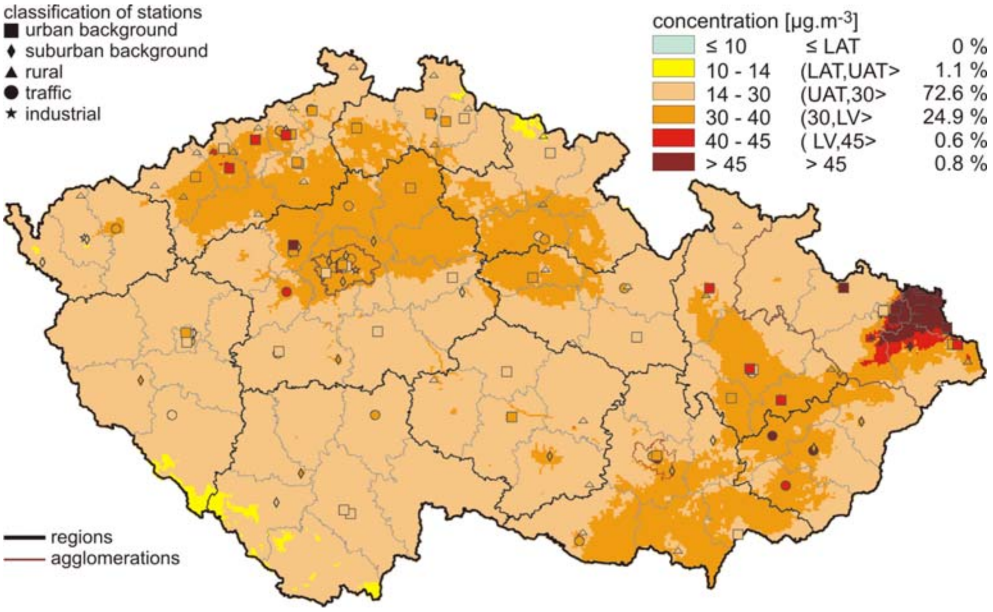

Figure 3.15: Field of annual average concentrations of PM_{10} in 2005.

3.7 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 3.16)

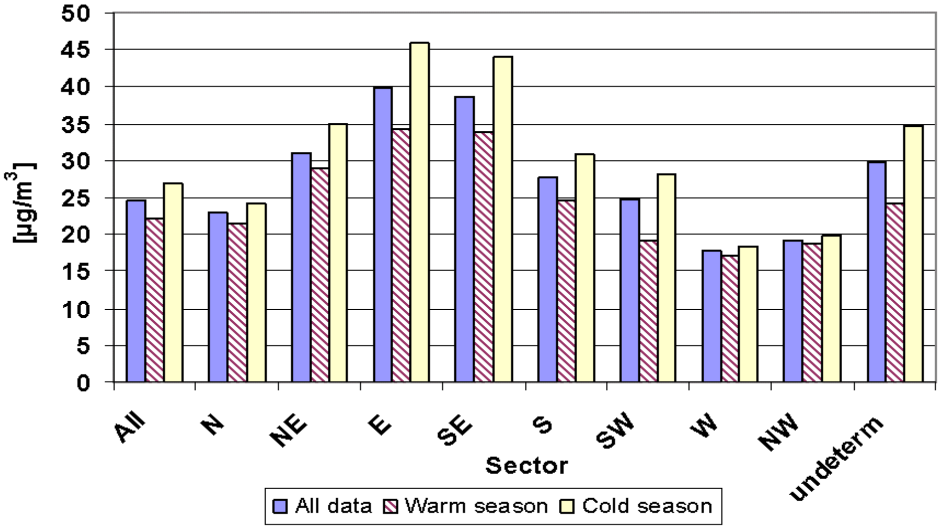

Figure 3.16: Sector distribution of PM_{10} concentrations (Košetice 1995-2004, $\mu g.m^{-3}$).

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 3.17). The increase after 2000 corresponds with the rising trend in Moravian-Silesian region located in this direction.

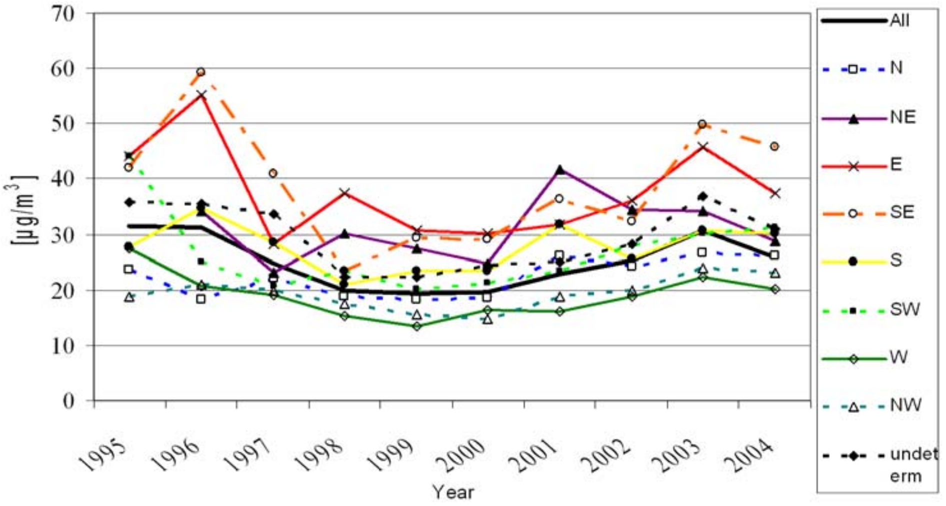

Figure 3.17: Sector distribution trend of PM_{10} concentrations (Košetice 1995-2004, $\mu g.m^{-3}$).

Significant difference was found between trends in summer and winter period. While the trend of winter concentrations is comparable with general trend (Figure 3.18), 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 3.19).

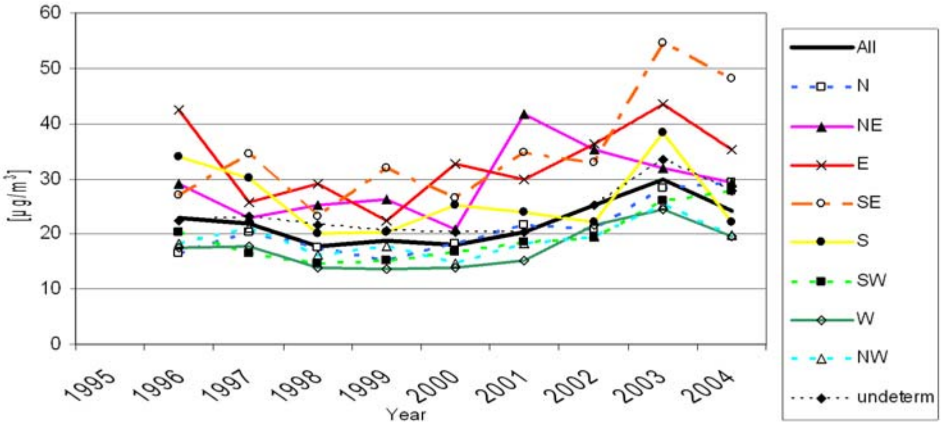

Figure 3.18: Sector distribution trend of PM_{10} *concentrations – warm period (Košetice 1995-2004,* $\mu g.m^{-3}$*).*

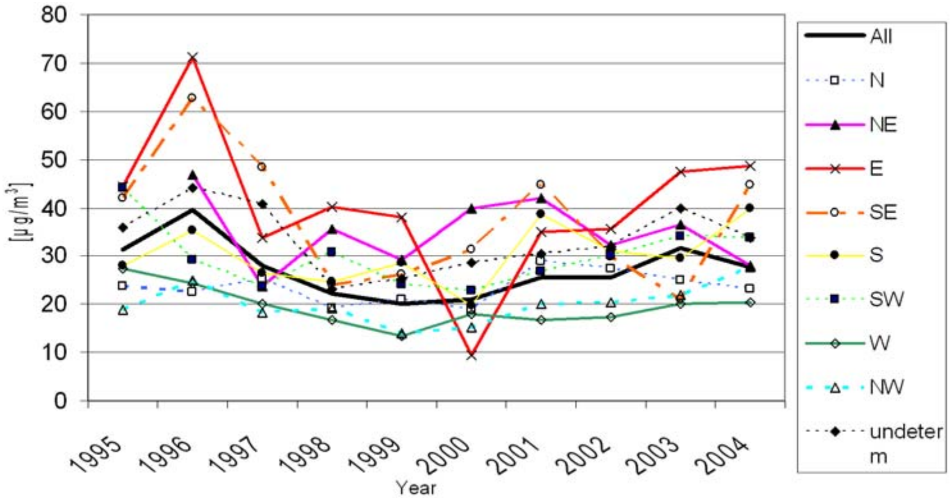

Figure 3.19: Sector distribution trend of PM_{10} *concentrations – cold period (Košetice 1995-2004,* $\mu g.m^{-3}$*).*

Figure 3.20 and Figure 3.21, based of the Košetice data, show the relation of PM data and meteorological conditions. The highest concentrations are measured in calm and dry periods.

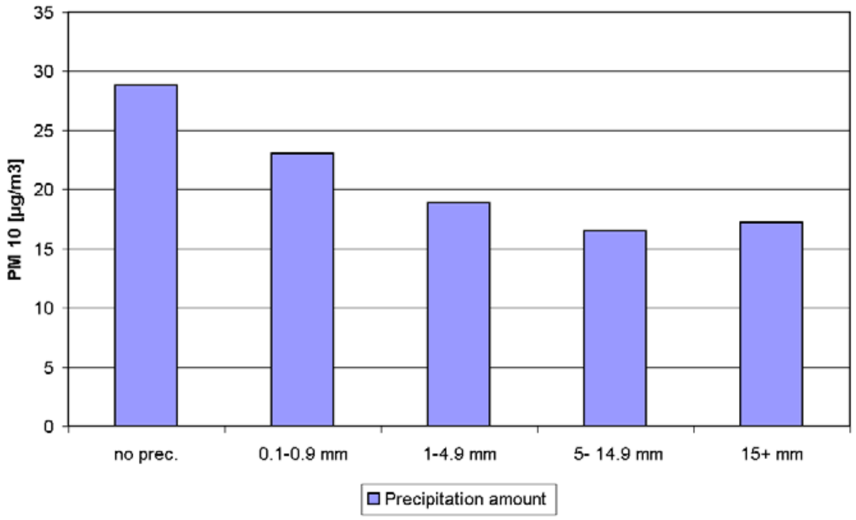

Figure 3.20: PM_{10} concentrations relation to precipitation amount (Košetice 1995-2005).

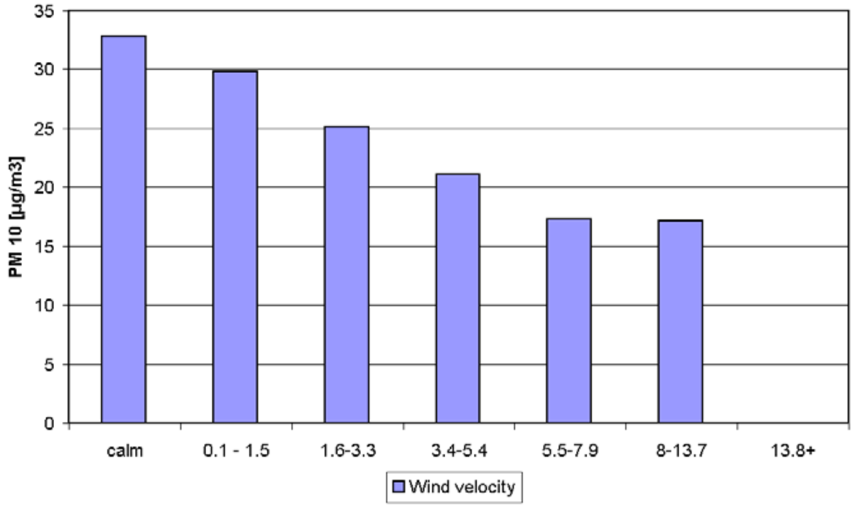

Figure 3.21: PM_{10} concentrations relation to wind velocity (Košetice 1995-2005).

3.8 Chemical composition

Selected metals are analyzed from the PM_{10} samples (arsenic, cadmium, manganese, copper, nickel and lead). Figure 3.22 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 3.22: 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 3.23). This situation is caused first of all due to the emissions from local glassworks.

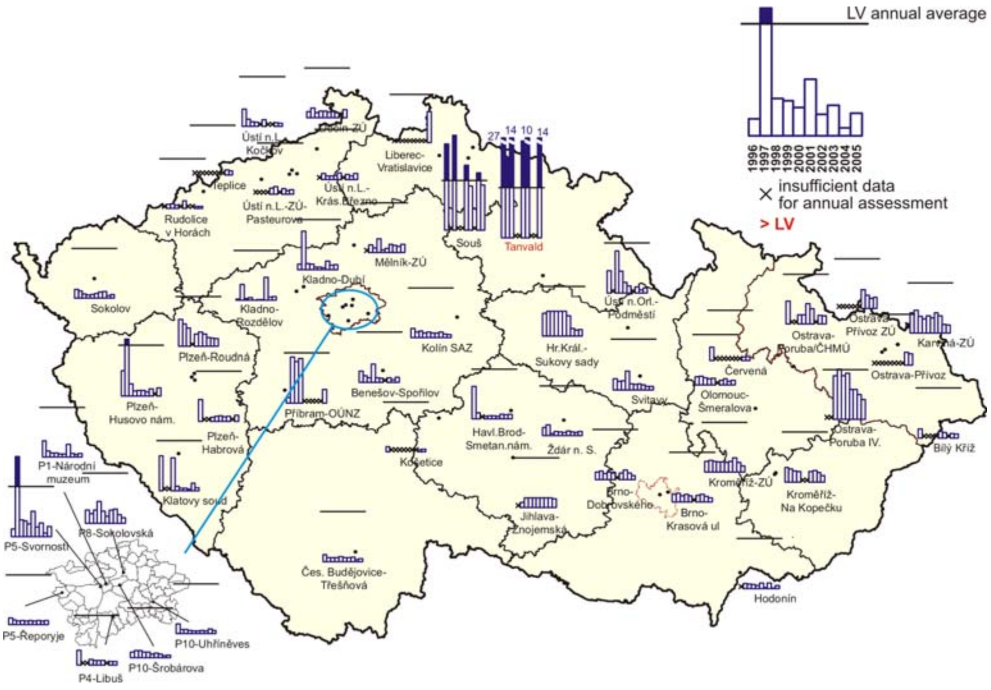

Figure 3.23: Mean annual concentrations of cadmium in PM_{10} in the ambient air 1996-2005.

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}.

3.9 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 3.24) 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 3.25) 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.

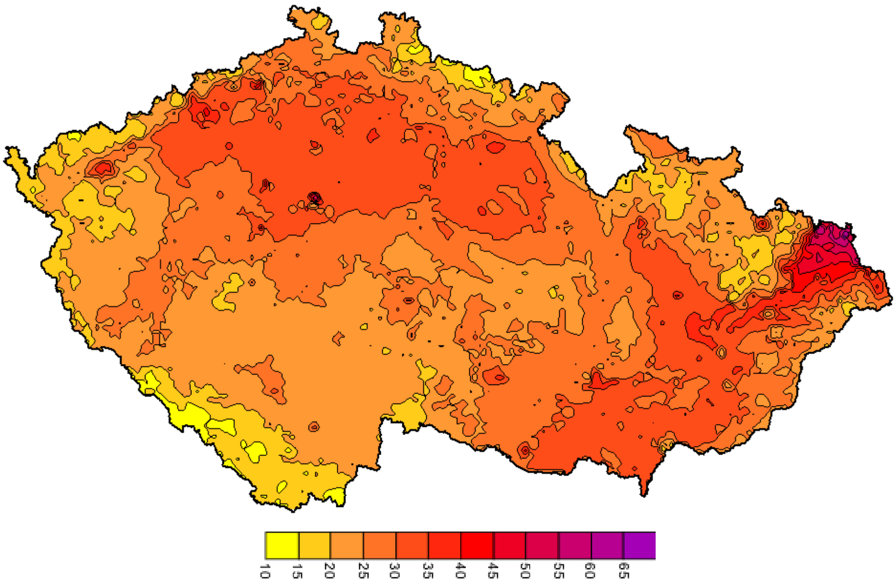

Figure 3.24: 2004 PM_{10} concentrations (µg.m^{-3}) – monitoring network.

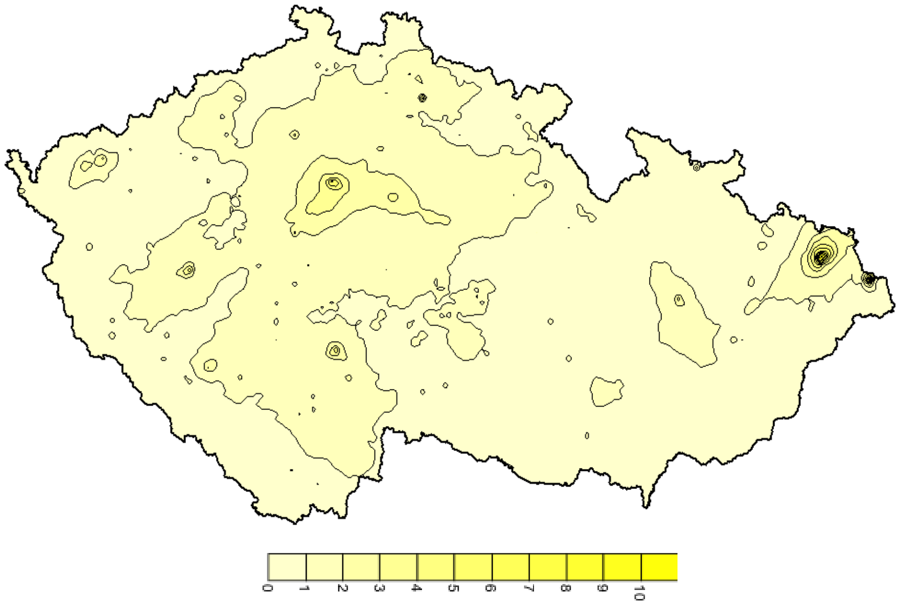

Figure 3.25: 2004 PM_{10} concentrations ($\mu g.m^{-3}$) - Model SYMOS 97.

Ratio between SYMOS'97 model outputs and measurements is presented in Figure 3.26. 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.

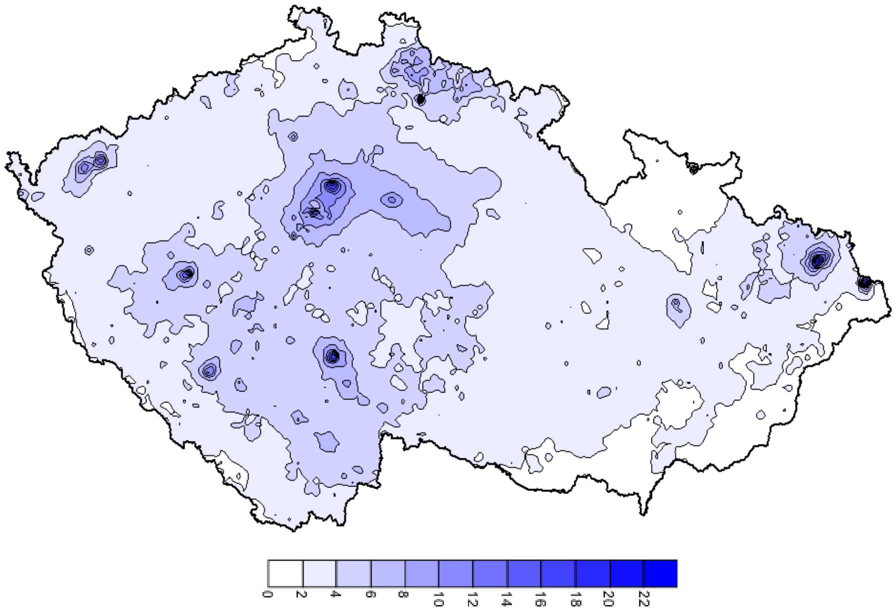

Figure 3.26: Model x measurement PM_{10} concentrations.

Annual PM_{10} concentrations based on 2000 EMEP model outputs are presented in Figure 3.27. 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).

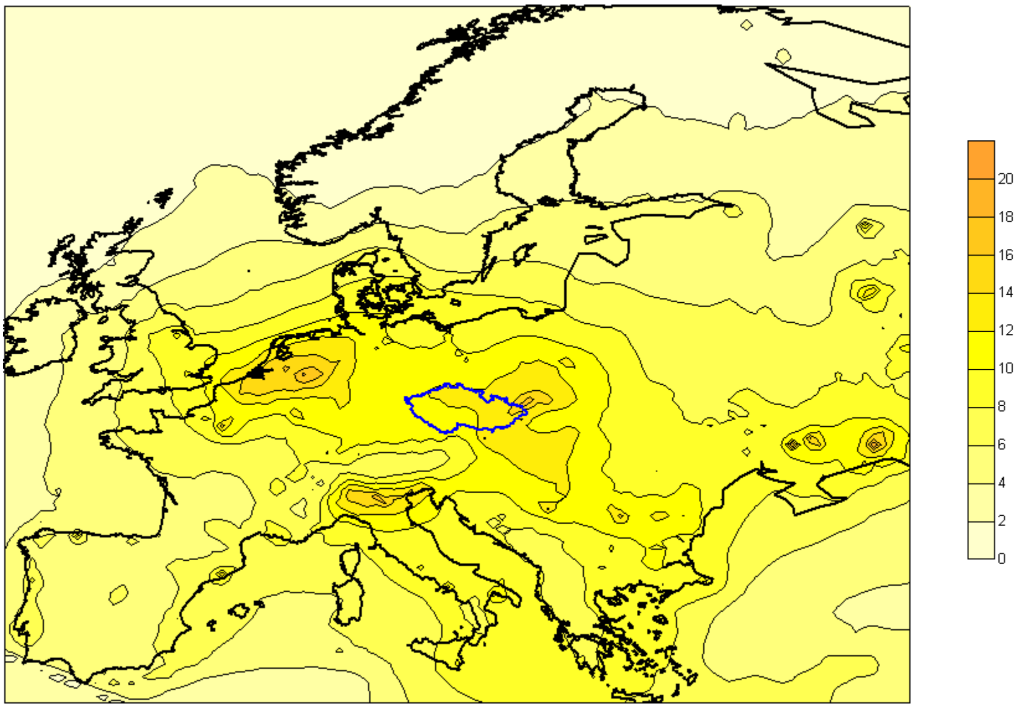

Figure 3.27: Model PM_{10} concentrations in 2000 – EMEP model (µg.m^{-3}).

3.10 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.

3.11 References

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

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4.1 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 site near Leipzig in Eastern Germany, coming down from an annual mean of 38 $\mu g/m^3$ in 1993 to about 20 $\mu g/m^3$ 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.

4.2 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 4.1 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.

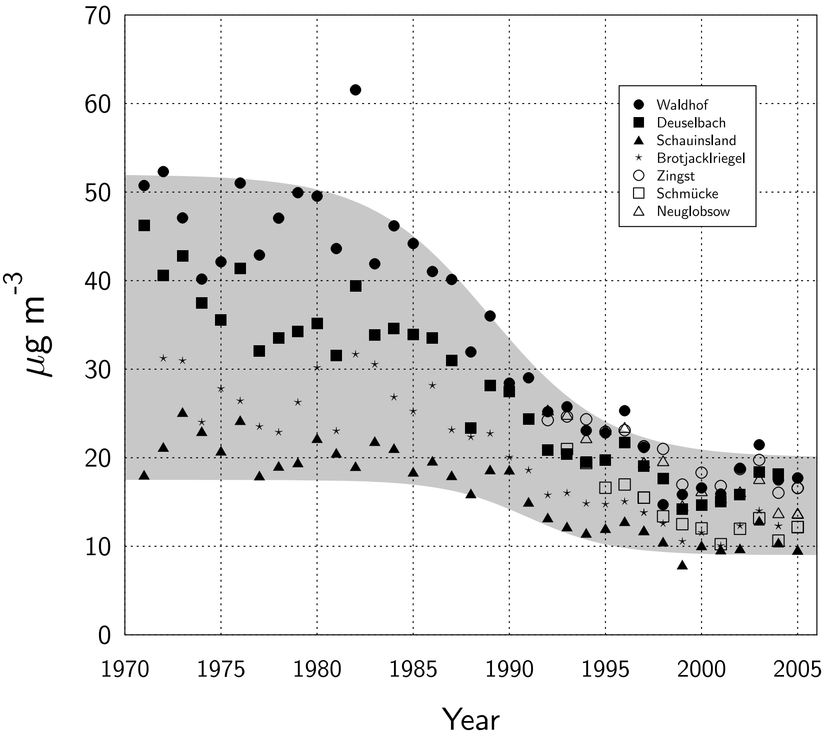

Figure 4.1: Annual average PM_{10}[14]-concentrations at German EMEP sites. The shaded area has been fitted visually to the envelope of the data.

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

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[14] Sampling heads with an aerodynamic cut off diameter of approximately 50 µm were in use before 1998. Since 1998 samples are taken with PM_{10}--inlets. A factor of 0.9 (obtained from parallel measurements) was applied to the values prior to 1998 to estimate the PM_{10} concentrations.

Melpitz up to the early 90s, decreasing to current PM_{10} levels of about 20 µg/m³. 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 4.2.

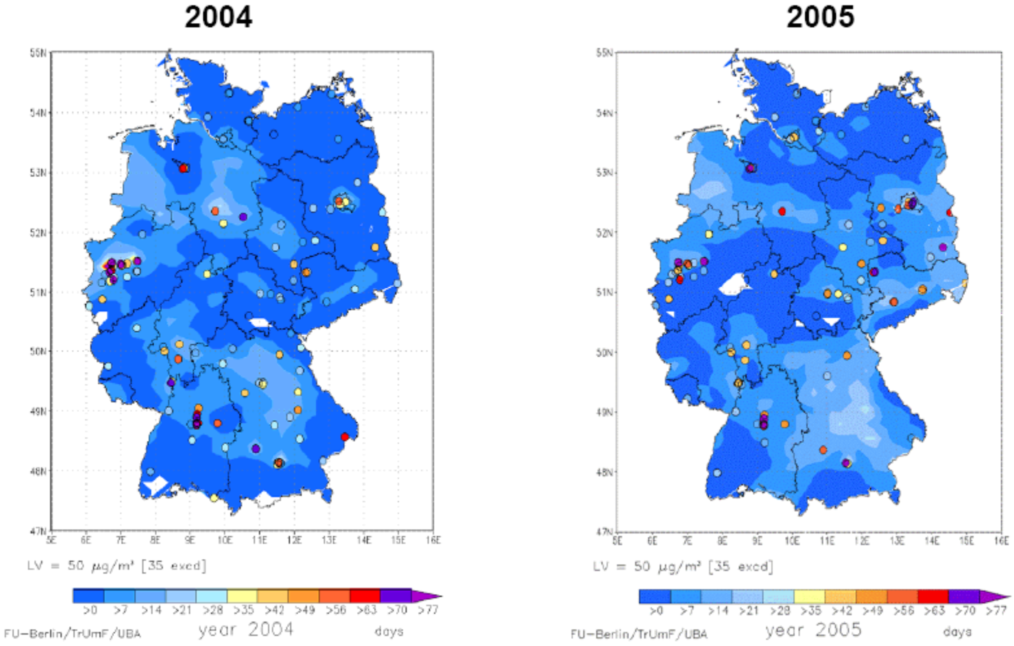


Figure 4.2 Number of PM_{10} daily means > 50 µg/m³ in Germany.

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.

4.3 Data Evaluation

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

4.3.1.1 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 4.3: 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.

4.3.1.2 Results

The general weekly concentration/time pattern (Figure 4.4, 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 4.4, right diagram) become more pronounced.

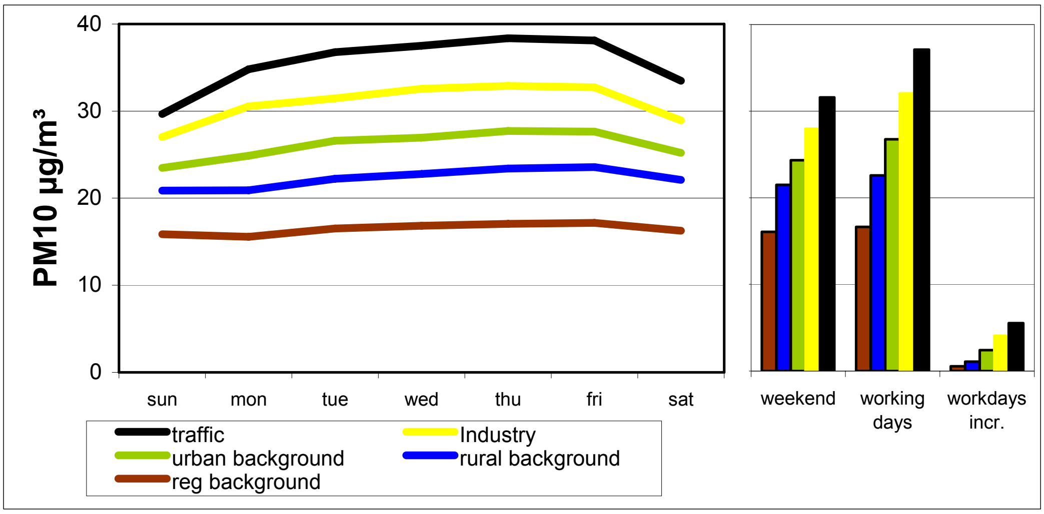


Figure 4.4: Weekly variation of PM_{10} *concentrations at different site types (mean values for all considered sites and years) and comparison for weekend and workdays averages*

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 4.3.

Significant differences may exist with respect to industrial and traffic sites. An example is illustrated in Figure 4.5 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.

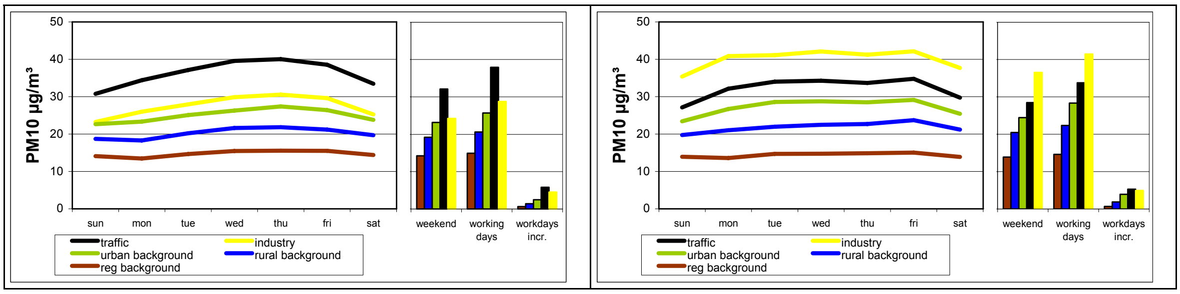


Figure 4.5: Weekly variation of PM_{10} *concentrations at different site types for the agglomerations Ludwigshafen/Mannheim (left diagram) and Ruhr-District.*

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 4.6. 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 4.1. Due to prior averaging for the considered years, the minimum and maximum values defining the ranges given in Table 4.1 are not identical with those shown in Figure 4.6.

Table 4.1: 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.

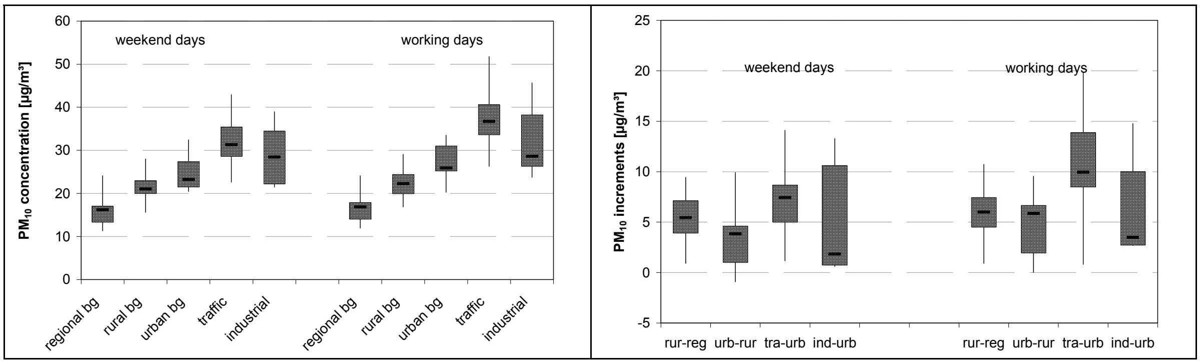


Figure 4.6: Box-whisker diagrams showing the minimum and maximum (whiskers), 25-and 75-percentiles (box) and median (bar) of PM_{10} concentrations (left side) and increments (right side).

The increments shown in Figure 4.6 (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/m^3 is obvious for traffic sites on working days, while industrial sites again add ca 5 µg/m^3 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 4.2 summarises the ranges of increment concentrations, regression coefficients and ratios of daily means observed for the year 2005.

Table 4.2: 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 4.6 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 4.7, there are only slight and probably insignificant differences.

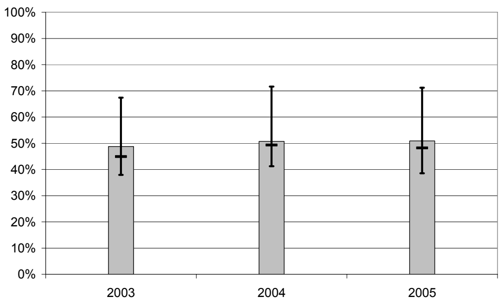


Figure 4.7: Regional background contributions to PM_{10} concentrations at traffic hot spot sites for the years 2003, 2004, and 2005 (Column: mean, bar: median, whiskers:min/max).

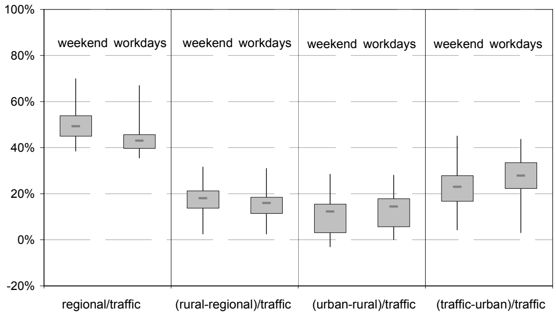


Figure 4.8:Fraction of traffic-site PM_{10} determined by the regional background concentrations and increments.

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 4.8. 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 4.9. 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.

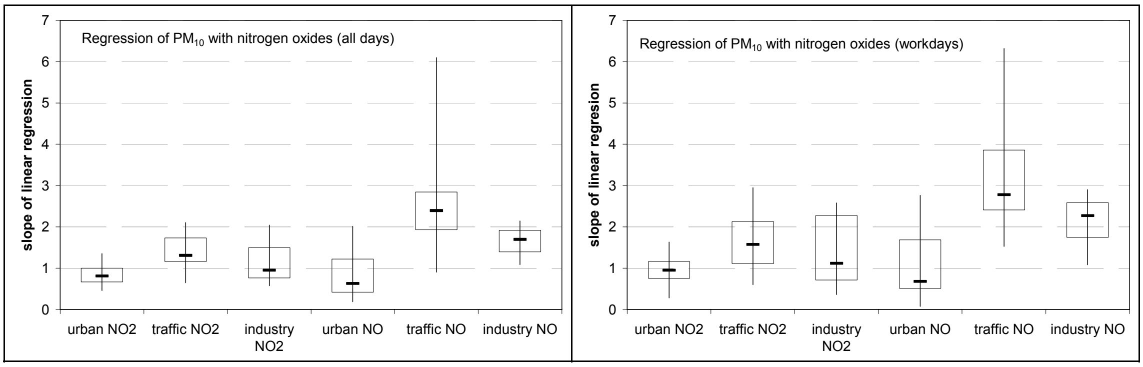


Figure 4.9:Box-plot diagrams showing the minimum, 25-,50- and 75-pecentiale and maximum of regression slopes NO_2/PM_{10} and NO/PM_{10} for all days (left side) and workdays (right side).

4.3.2 Part II: PM components

4.3.2.1 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 4.3, the corresponding locations are shown in Figure 4.10.

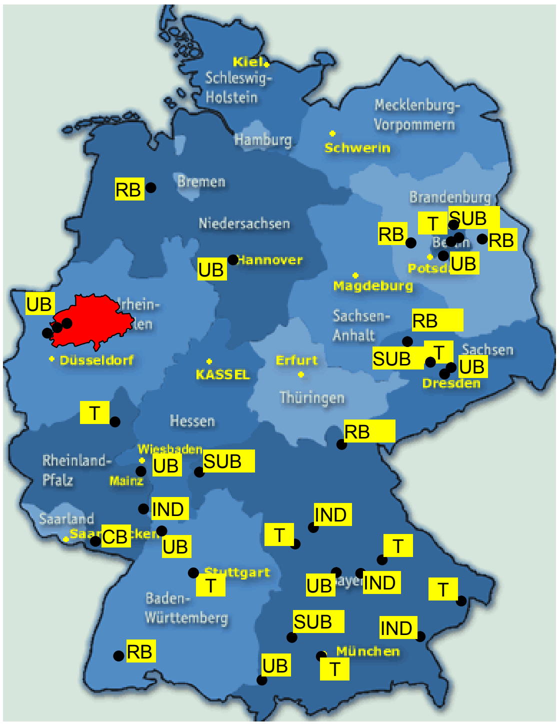


Figure 4.10: Map showing the sites with available PM composition measurements.

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 ratio of Si to Ti.

Table 4.3: 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 selsected 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 cam-paigns 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	UBA long-term measurement 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

4.3.2.2 Results

Averaged data from the reports listed in Table 4.3 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 4.11 and Figure 4.12. Both figures include the corresponding PM_{10} mass concentration plots (which are identical in both figures) for comparison.

From Figure 4.11 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 4.12. 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.

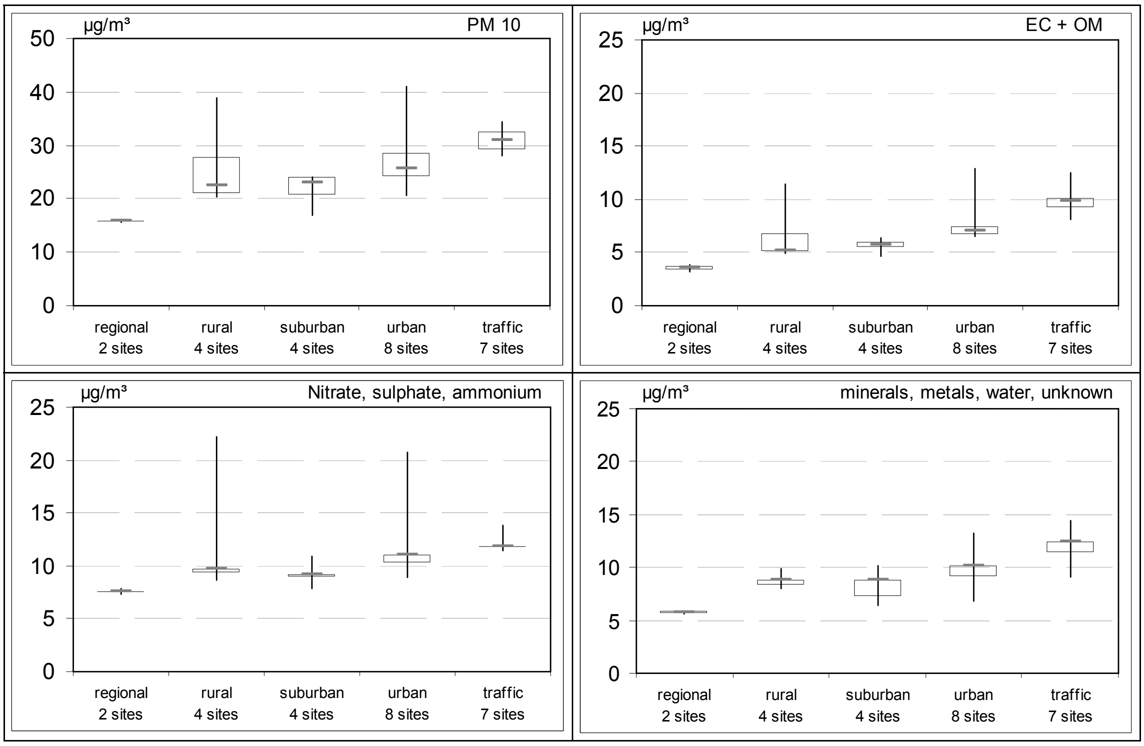


Figure 4.11: Boxplots for concentrations of PM_{10} and main compound groups.

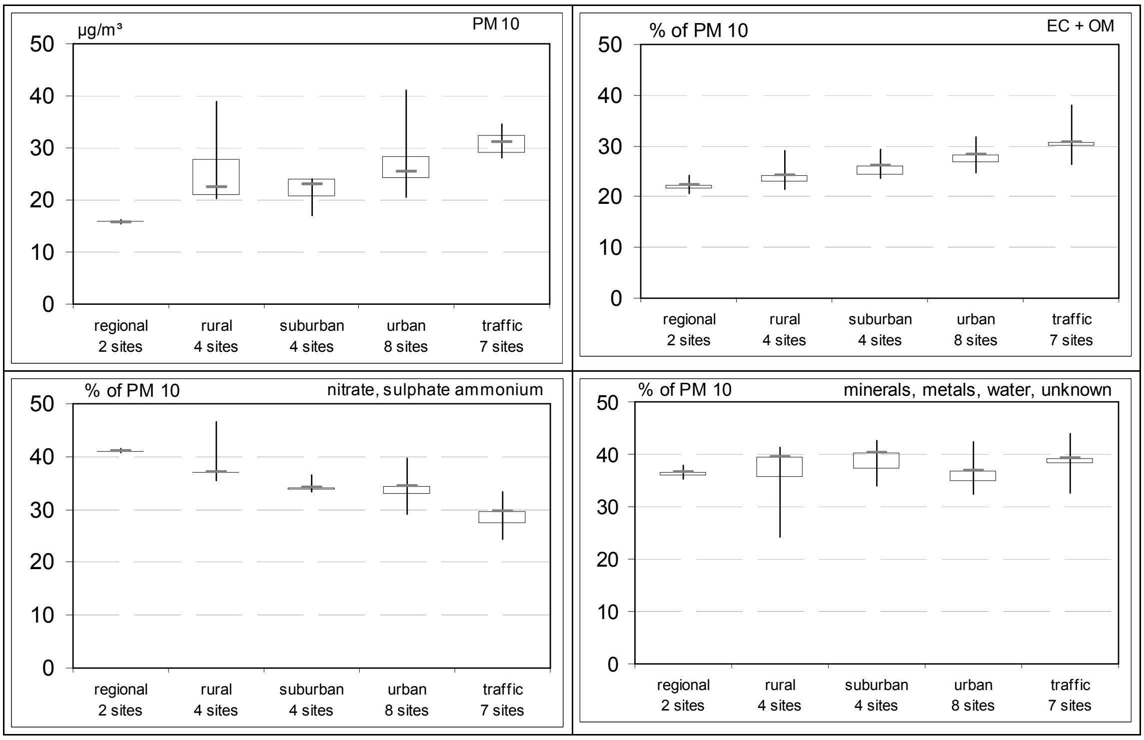


Figure 4.12: Boxplots for PM_{10} concentration and percentage contribution of main compound groups.

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 negligible 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 $Q^X > 1$.

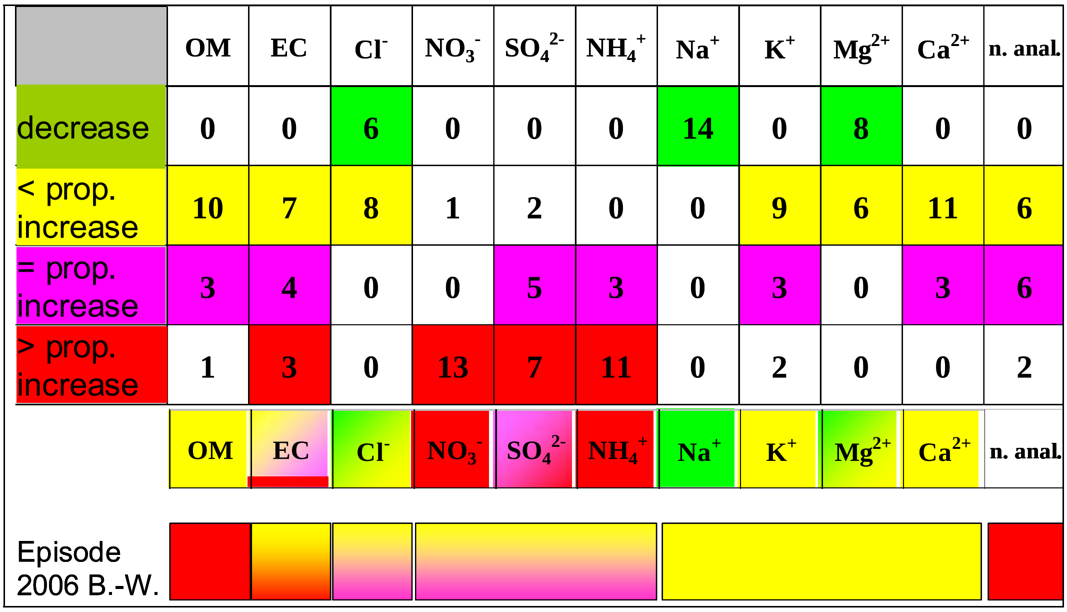
The underlying hypothesis for such evaluation is that a high PM_{10} episode being solely driven by air mass exchange conditions (e.g. inversion) should result in a pure accumulation of PM_{10} without chemical changes and therefore exhibit a more or less proportionate increase of PM_{10} compounds with 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 4.13 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
	OM	EC	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	n. anal.
Episode 2006 B.-W.											

Figure 4.13: 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 4.13, 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 $\mu g/m^3$ (N=6) at a Stuttgart traffic site were compared with those days (N=2) still having lower concentrations at the episode start-up. 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.

4.4 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/m³, 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/m³
Rural background:~ 22 µg/m³
Urban background:~ 27 µg/m³
Traffic site: ~ 32/37 µg/m³ (weekend/working days)
Industrial urban site :~ 32 µg/m³

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/m³ 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 Northwest due to agriculture and North Sea influence [v, vi], respectively.

From the intensive long-term measurements carried out at the UBA 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.

4.5 References

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ANNEX : Data from the UBA research site at Melpitz/Saxonia

5 Particulate Matter (PM_{10}) in Ireland

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5.1 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) 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.

5.2 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 Rathmines site, Dublin.

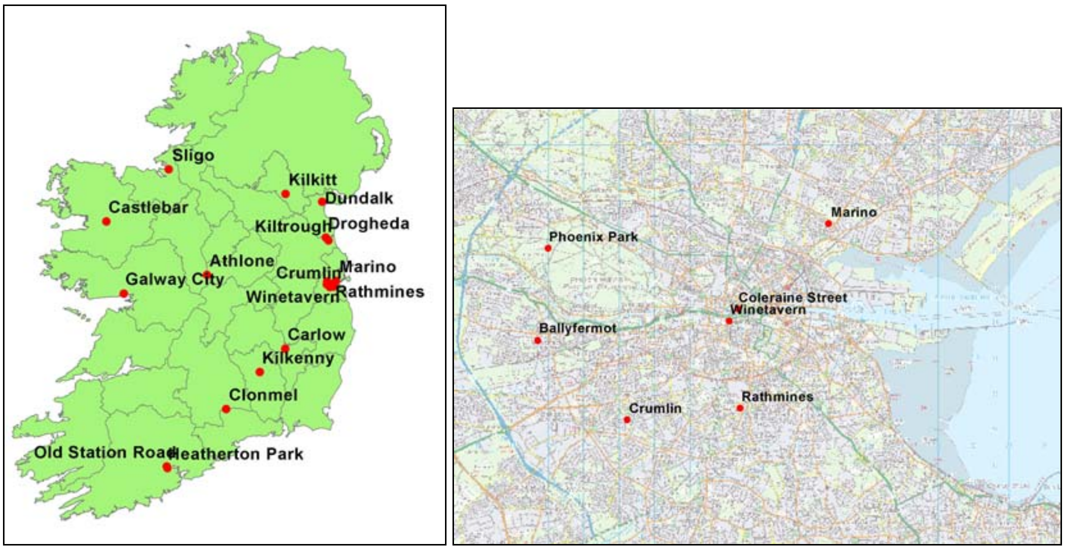

Figure 5.1: Location of the PM_{10} sites in Ireland, and in the Dublin area.

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 5.1. Seven of the sites are located in the Dublin area, as shown in Figure 5.1 (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 the Table 5.1, 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. Kilkitt site has data available for 2006 only; it is a rural background site, and therefore included here.

Table 5.1: Site statistics for all daily PM_{10} 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

5.3 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 5.2.

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 5.2. Also included is a Dublin kerbside site, and a rural background site, from a study by Jennings et al. (2006), based on measurements in 2002. Figure 5.2 shows annual averages for those stations that have data available for at least three of the four years (2002 to 2005).

Table 5.2: Annual PM_{10} means for the PM_{10} sites in Ireland.

µg/m^3	Range of annual means, and number	Median of annual means
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

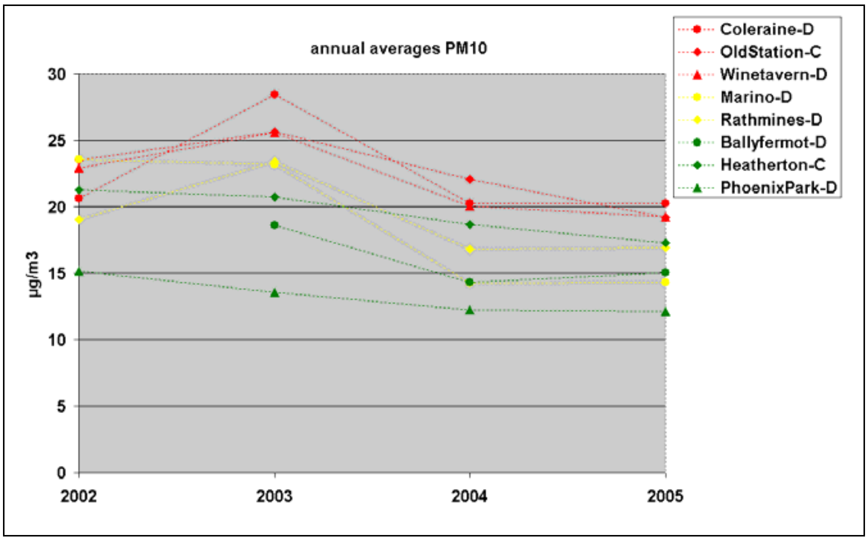

Figure 5.2: Annual averages for sites with at least three of the four years 2002 to 2005.

5.4 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 5.3.

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.

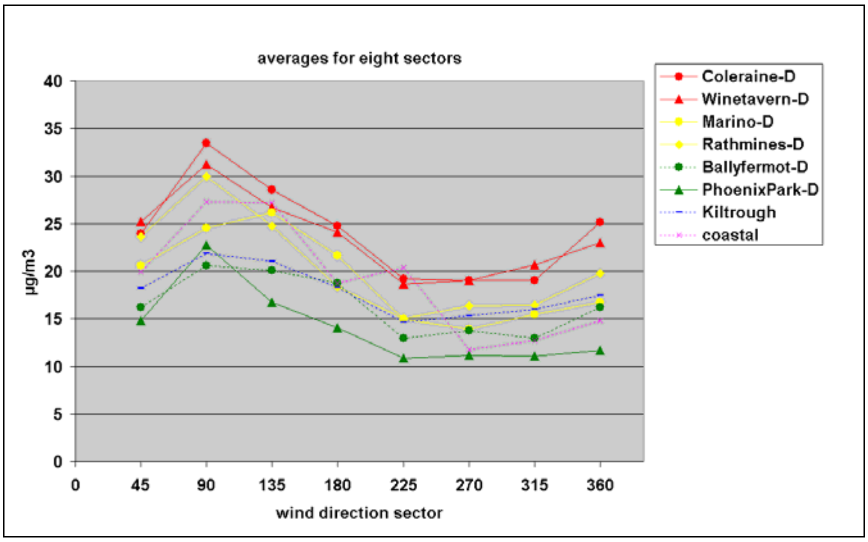

Figure 5.3: PM_{10} levels depending on wind direction, for eight sectors.

The sites shown in Figure 5.3 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).

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%.

5.5 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 µg/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, separated 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 5.4.

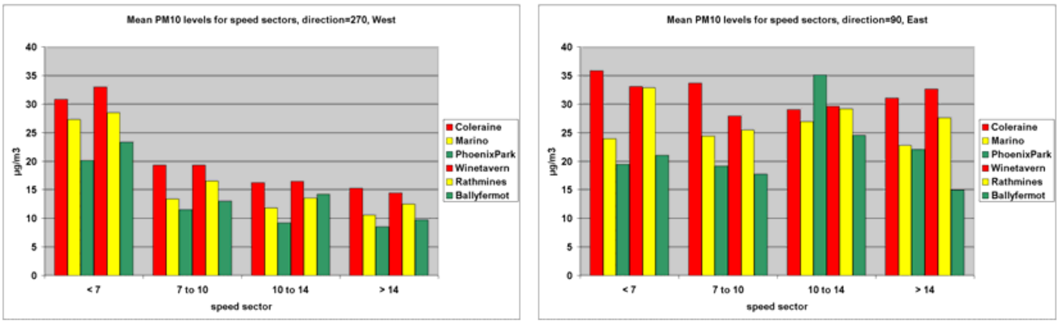

Figure 5.4: PM_{10} concentration for westerly and easterly wind directions and four wind speed sectors.

The data in Figure 5.4 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.

5.6 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 5.5. 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.

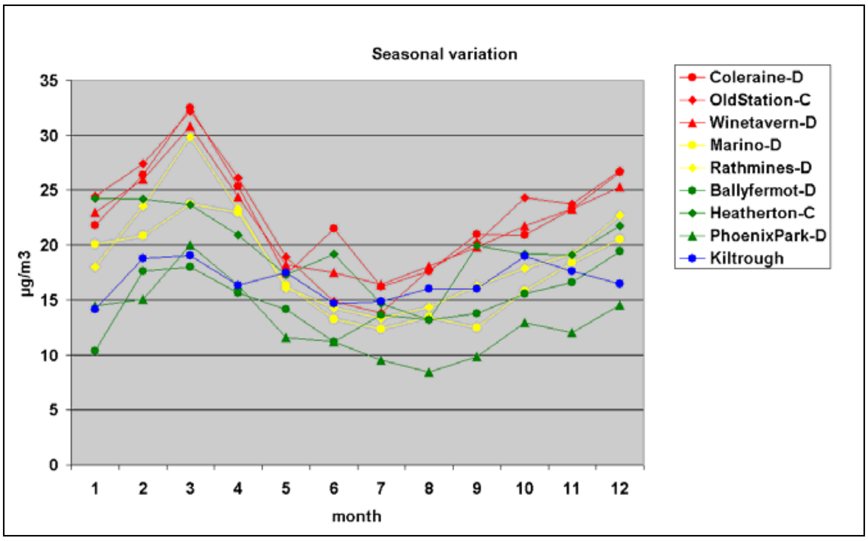

Figure 5.5: Seasonal variation of PM_{10} concentration.

5.7 PM$_{2.5}$/PM$_{10}$ ratios

Figure 5.6: 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. (2006) 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 5.6. 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. PM$_{2.5}$/PM$_{10}$ ratios were found to be between 50 and 60%.

Both the results from OldStationRoad in Cork and from the aforementioned study (for 2002) are summarised in Table 5.3.

Table 5.3: 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)	22-24	11.5-12.5	52%
Coastal site (C)	20	12.5	63%
Rural background (D)	10.5	6.3	60%

5.8 Urban increment

There are very few background measurements to derive an urban increment from. Based on the campaign carried out by Jennings et al. (2006) in 2001 and 2002, the urban increment of the annual mean is about 12 to 14 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. A PM$_{10}$ kerbside increment for the annual mean of an additional 13 µg/m^3 over urban traffic sites was observed during the same campaign, for PM$_{10}$, and of 9 to 10 µg/m^3 for PM$_{2.5}$. Kerbside levels, however, depend strongly on the exact location of the site.

5.9 PM_{10} chemistry and sea salt

Figure 5.7: EMEP sites measuring PM_{10} chemical compounds

At three background air quality monitoring sites (EMEP sites), in Malin Head, Carnsore Point, and Oak Park, PM_{10} is collected on filters, using digital 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 till September. Annual means for sulphate, nitrate, and non-sea-salt sulphate are shown in Table 5.4.

Table 5.4: Chemical compounds in PM_{10} in 2005 and 2006, annual mean values.

	2005			2006		
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 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 5.5. 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.

Table 5.5: Sea salt concentration in PM_{10} 2005 and 2006 (for Valentia and Mace Head in total PM).

µg/m^3	2005			2006		
	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				

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.

5.10 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 PM10 chemistry, for 2005 and 2006
3. A study carried out by NUI Galway in 2002 (S.G. Jennings et al., 2006)
4. Data from Valentia Observatory (operated by MetEireann) and Mace Head (operated by NUI Galway)

5.11 References

S. G. Jennings, D. Ceburnis, A. G. Allen, J. Yin, R. M. Harrison, M. Fitzpatrick, E. Wright, J. Wenger, J. Moriarty, J. R. Sodeau, E. Barry; Nature and Origin of PM_{10} and Smaller Particulate Matter in Urban Air; Final Report (2006); published by the Environmental Protection Agency, Ireland; ISBN: 1-84095-191-5

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;

6 EMEP – PM assessment report National contribution of Italy

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6.1 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 6.1; 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.

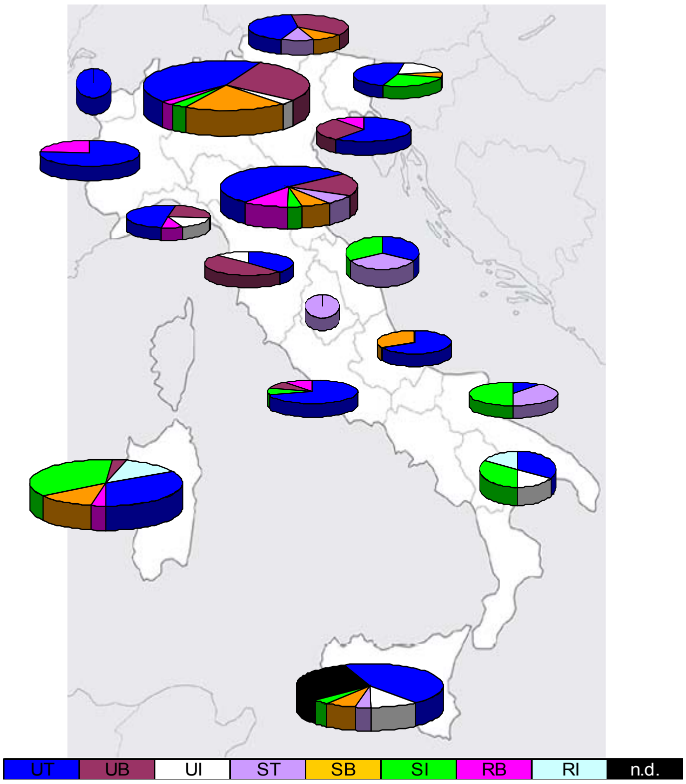


Figure 6.1: PM_{10} monitoring network in Italy (data source: Apat, ARPA, Regions and Autonomous Provinces).

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 6.2, 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.

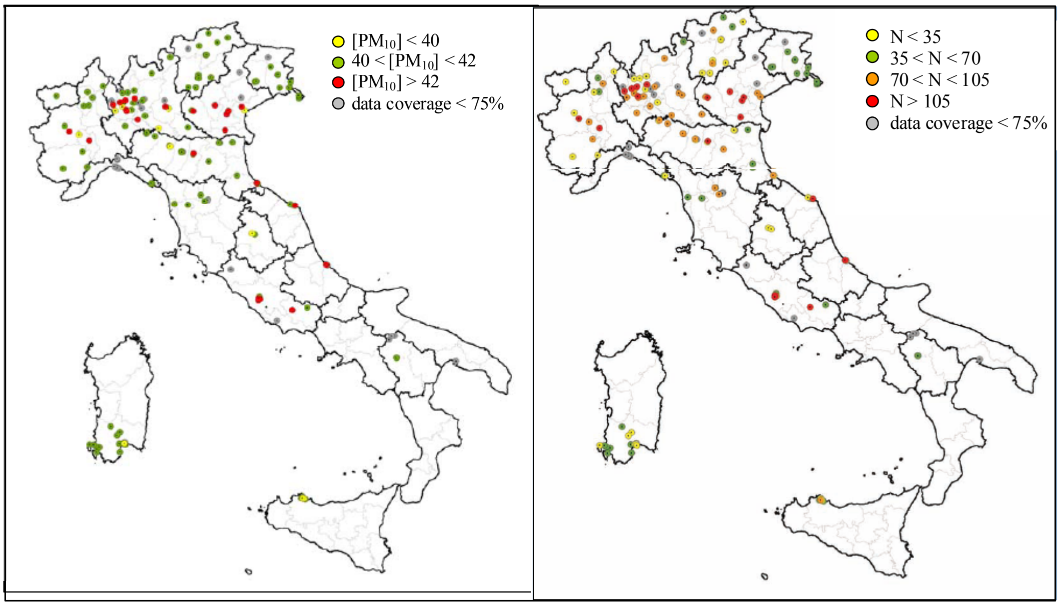


Figure 6.2: Classification of PM$_{10}$ stations according to the annual mean concentration (left graph) and to the number of exceedances of the daily EU limit value (right graph). Year: 2004. Data source: APAT, 2006.

The temporal pattern of PM$_{10}$ in some major Italian cities during the period 2000 – 2006, reported in Figure 6.3, 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).

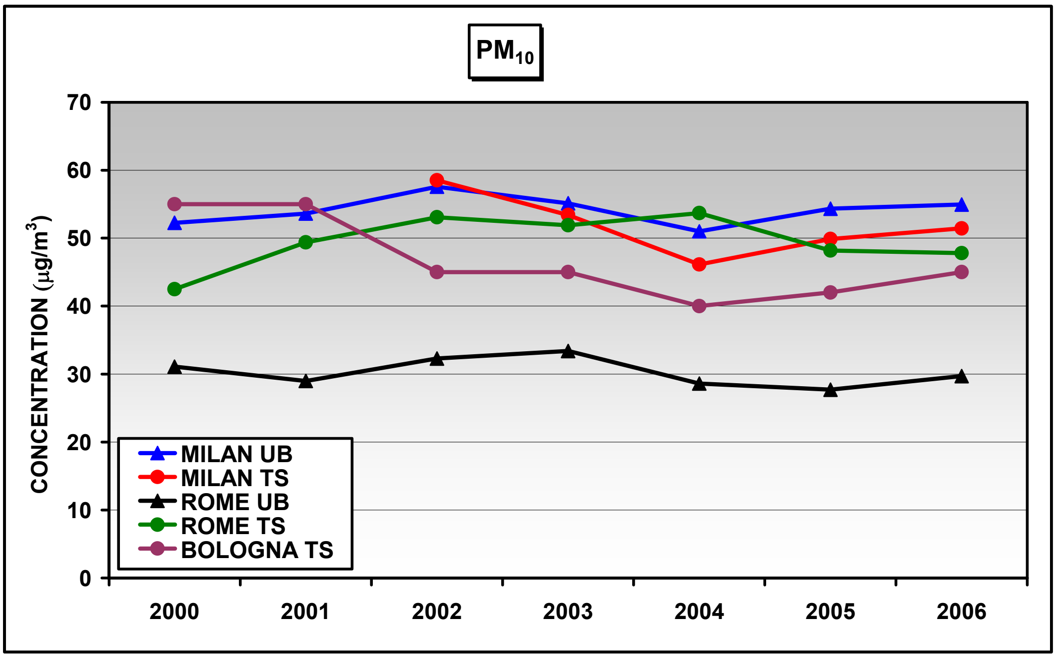


Figure 6.3: Inter-annual variations of the PM_{10} concentration in Milan, Rome and Bologna. UB: urban background station; UT: traffic station. Data source: APAT, regional ARPAs.

The frequency distribution of PM_{10} at a traffic station in Milan (north), Rome (center) and Palermo (Sicily, south) are shown in Figure 6.4 (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.

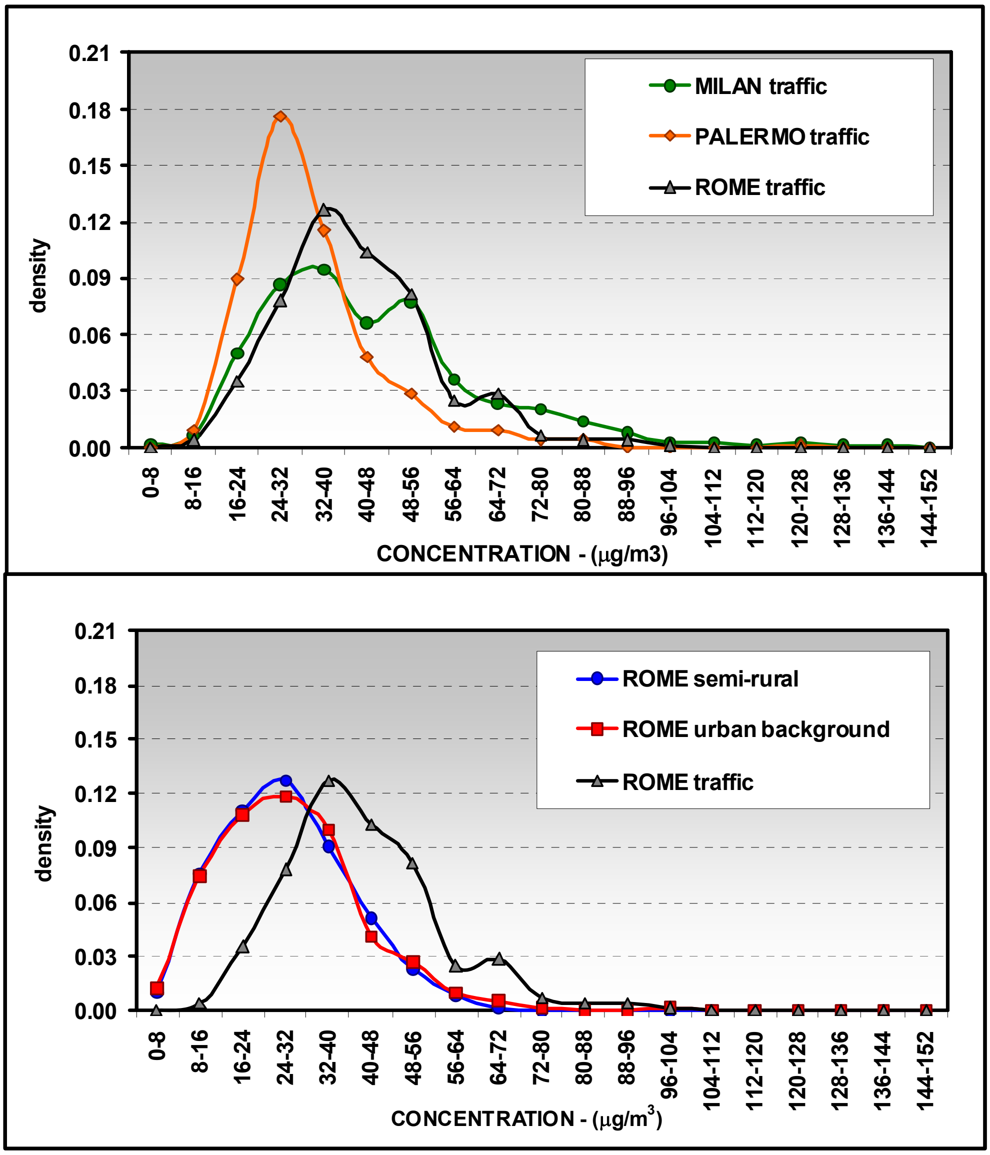


Figure 6.4: Frequency distribution of PM_{10} at Milan, Rome and Palermo traffic stations (upper graph) and at semi-rural, urban background and traffic stations in the area of Rome (year 2003).

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 $\mu g/m^3$, 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 6.5, 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.

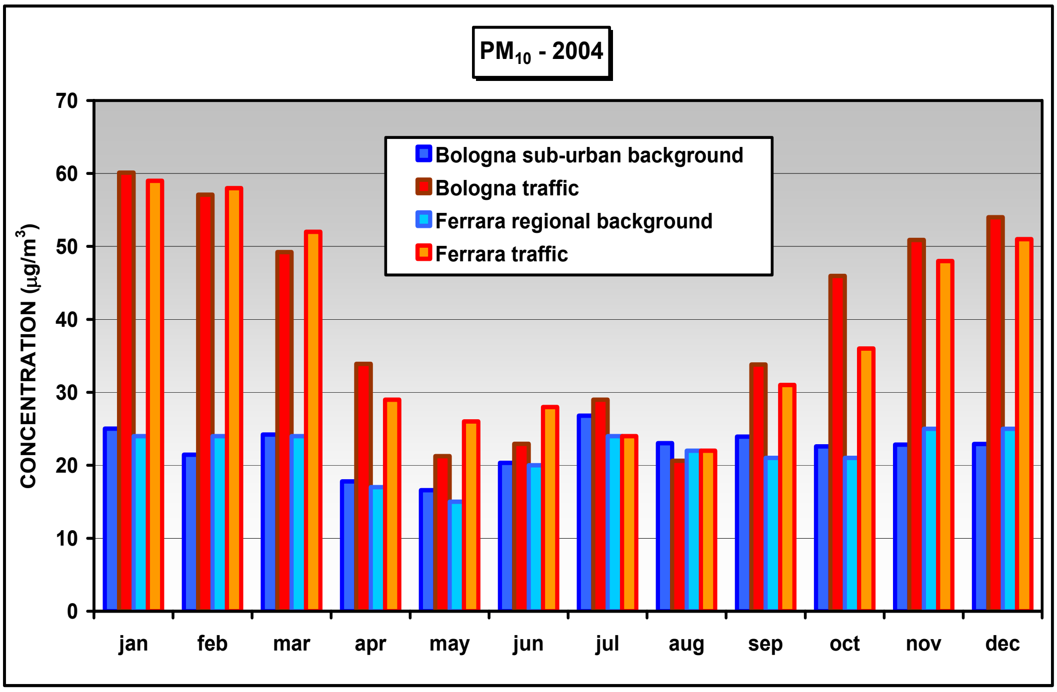


Figure 6.5: Monthly variation of PM_{10} concentration during 2004 at a traffic station and a sub-urban background station in Bologna (Porta S. Felice and Monte Cuccolino), at a traffic station in Ferrara (C. Isonzo) and at a regional background station in the area of Ferrara (Gherardi). Data source: ARPAER.

The seasonal variations of PM_{10} during the year 2005 at traffic sites of many Italian cities are reported in Figure 6.6. 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 6.6: Seasonal variation of PM_{10} at urban traffic stations of different Italian cities during 2005. Maximum PM_{10} concentration is 100 µg/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 6.7. 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.

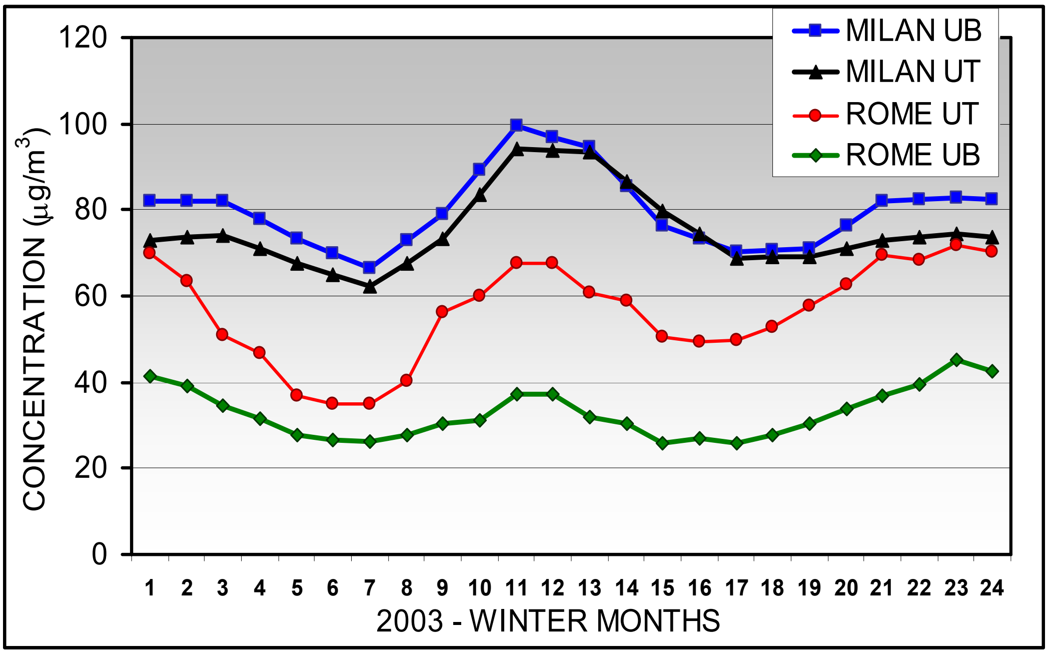


Figure 6.7: Average diurnal variation of PM_{10} *concentration during the wintertime.*

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).

6.2 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 6.8. They are dominated by the transport sector, mainly road transport.

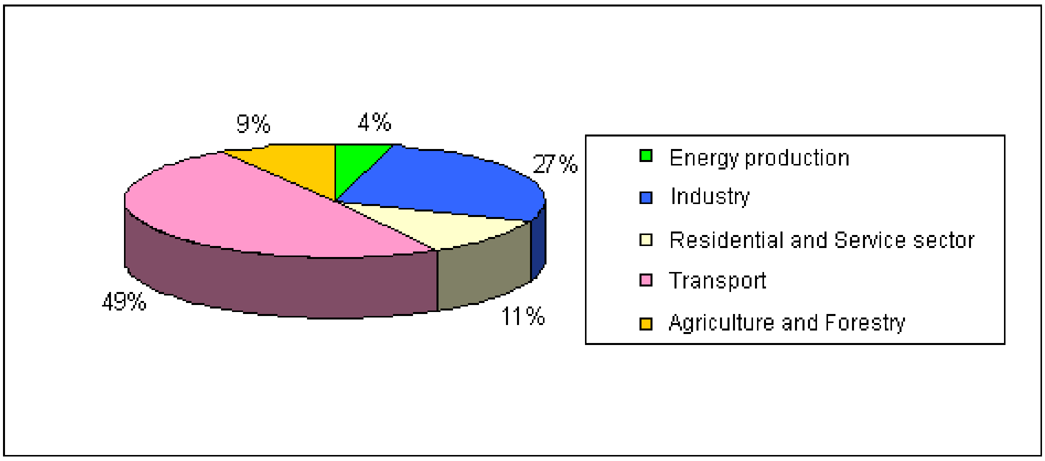


Figure 6.8: Per cent distribution of primary PM emission in 2003 (total amount: 172.7 tons). Data source: APAT.

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.

6.3 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).

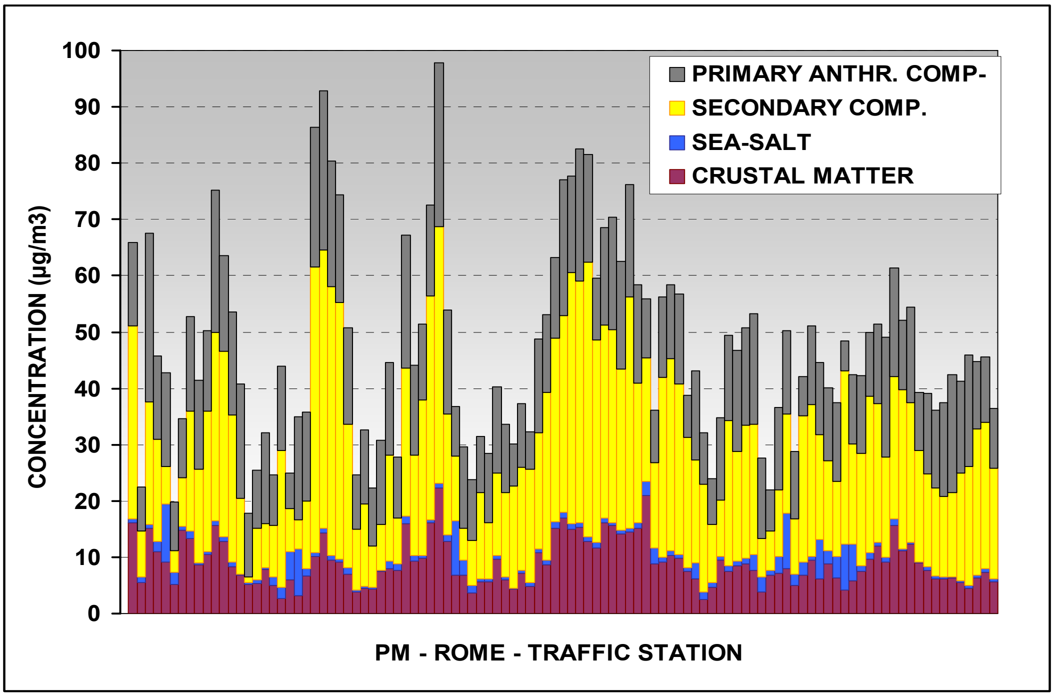


Figure 6.9: Chemical composition of PM_{10} *during October 2004 – July 2005 at a traffic station in Rome.*

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 6.9. 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 6.10 (average of the same days of Figure 6.9). 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).

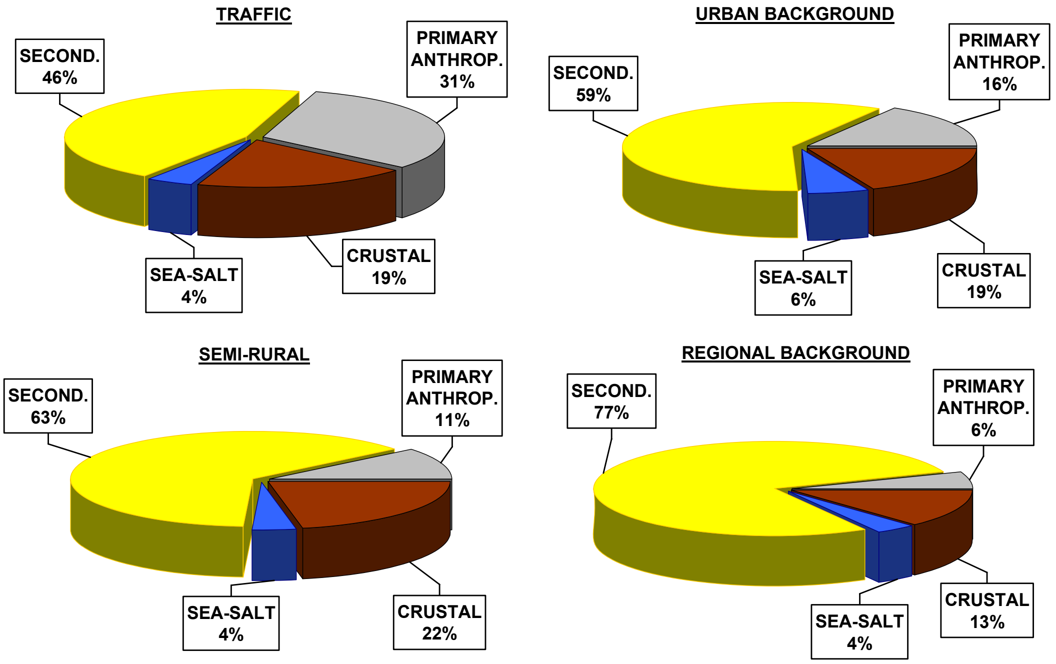


Figure 6.10: Per cent chemical composition of PM_{10} during October 2004 – July 2005 at four stations in the Lazio region.

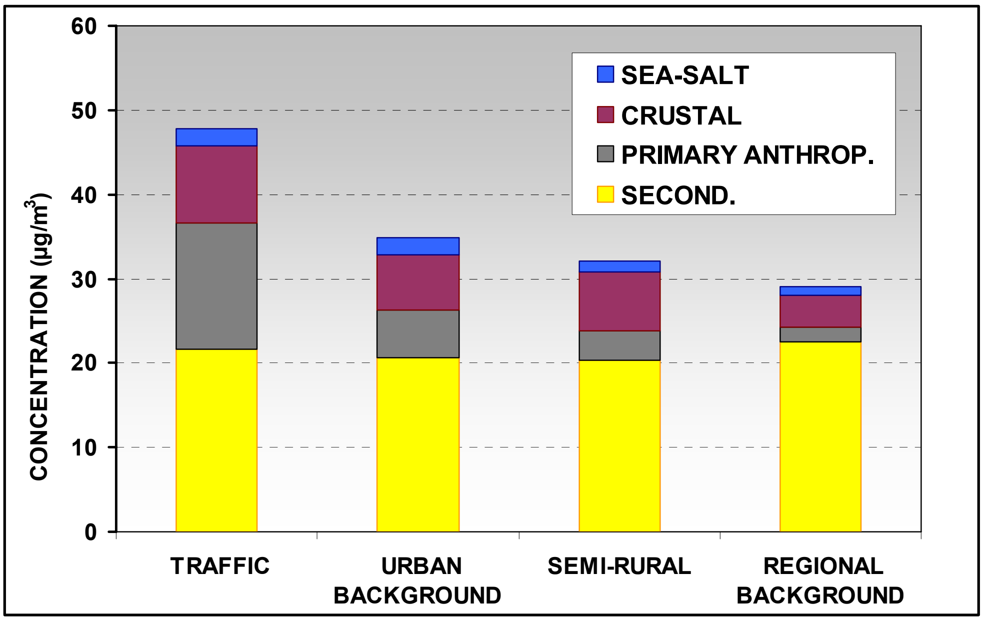


Figure 6.11: Chemical composition of PM_{10} during October 2004 – July 2005 in the Lazio region.

In terms of mass concentration, Figure 6.11 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.

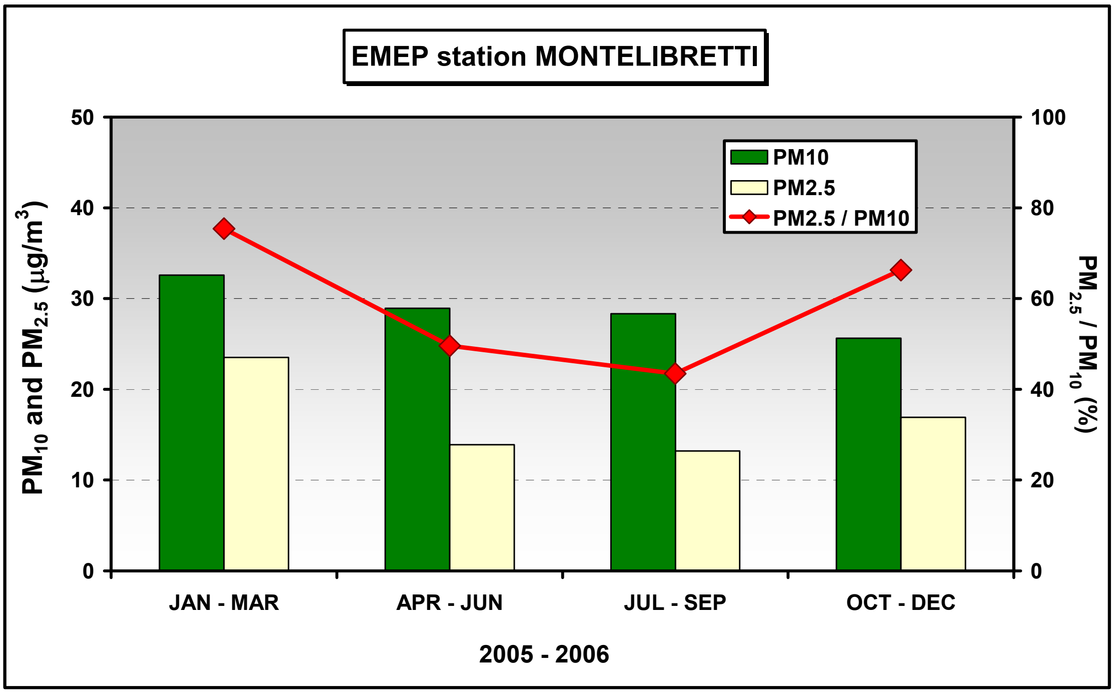


Figure 6.12: PM_{10}, $PM_{2.5}$ concentration and ratio at the Montelibretti station during 2005 - 2006.

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 6.12. 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 6.14).

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 6.13, 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 6.4).

Table 6.1: 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

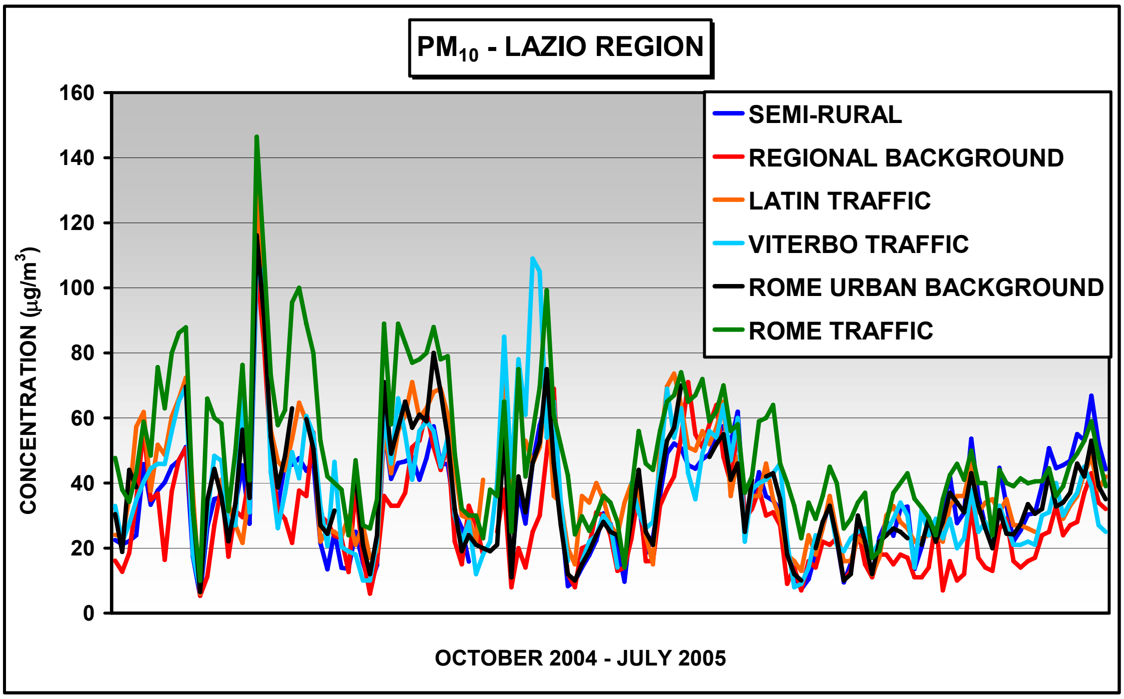


Figure 6.13: PM_{10} concentration at six stations in the Lazio region during October 2005 – July 2006.

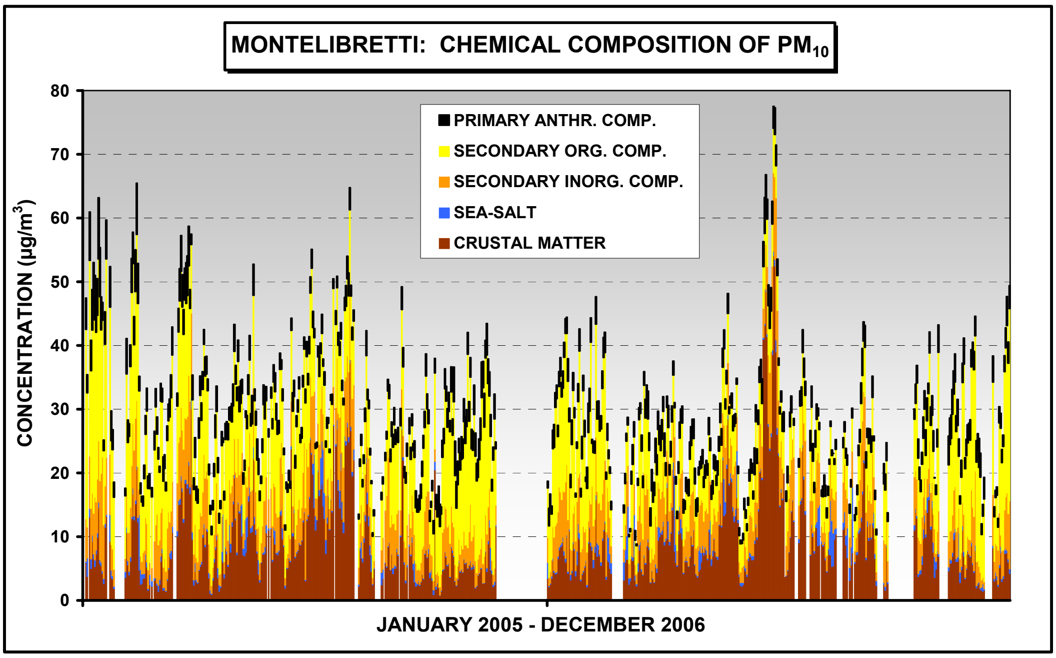


Figure 6.14: Chemical speciation of PM_{10} at the semi-rural EMEP site of Montelibretti.

The chemical composition of PM_{10} at Montelibretti during the years 2005 and 2006 is reported in Figure 6.14. 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 6.15, 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 $\mu g/m^3$) and the summer (32 $\mu g/m^3$) than during the intermediate seasons (27 $\mu g/m^3$ during the spring, 25 $\mu g/m^3$ during the autumn).

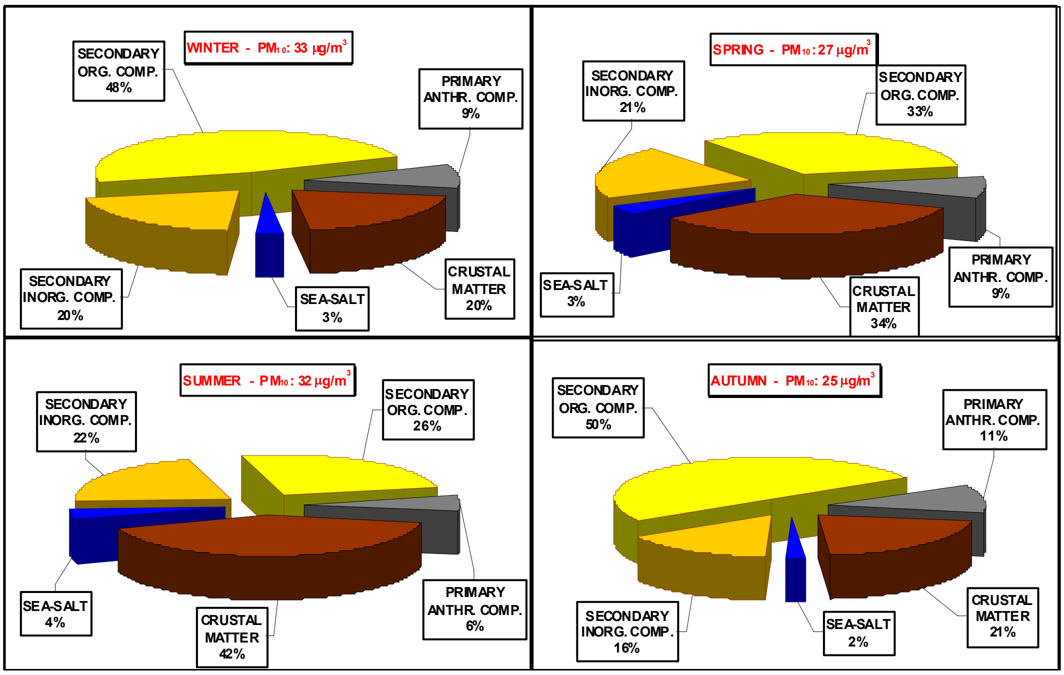


Figure 6.15: Seasonal variation of the PM_{10} composition at the semi-rural EMEP site of Montelibretti during 2005 and 2006.

6.4 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.

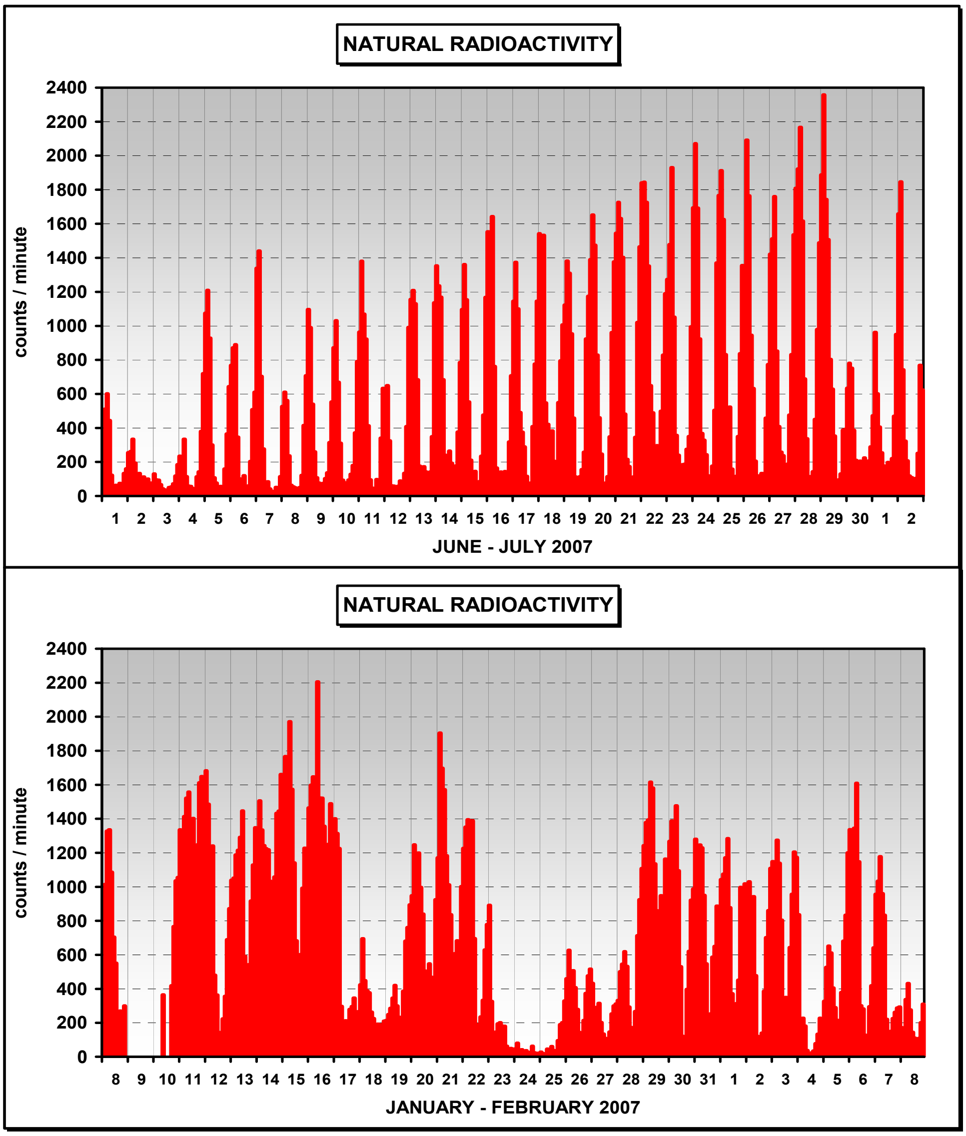


Figure 6.16: Natural radioactivity measurements during the two intensive campaigns.

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 6.16. 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).

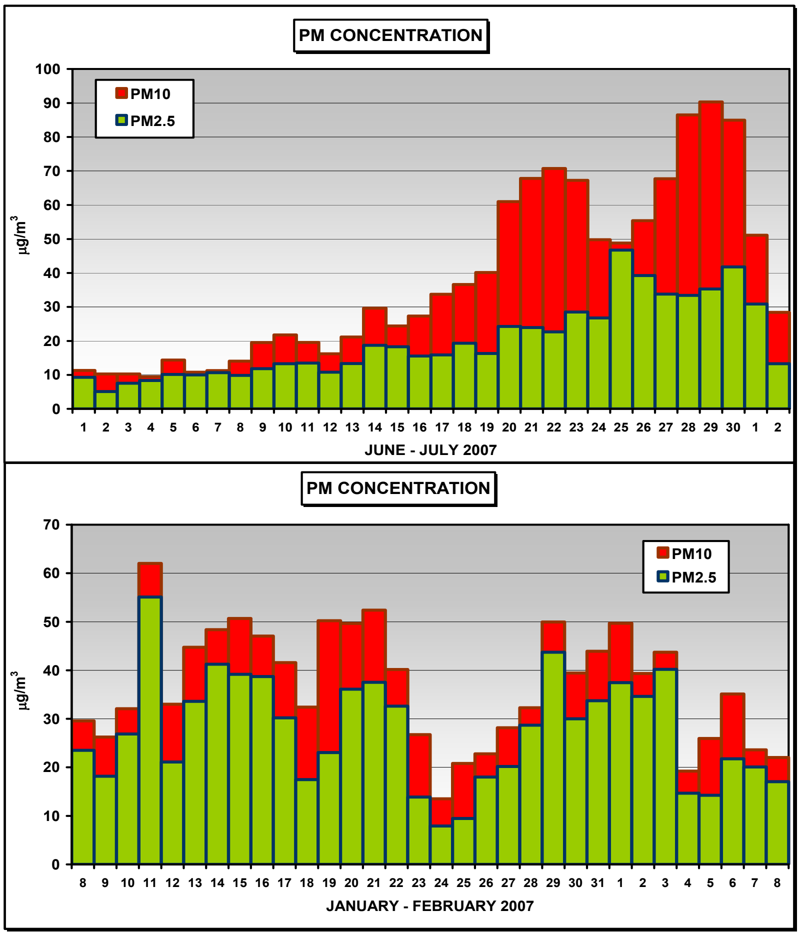


Figure 6.17: PM_{10} and $PM_{2.5}$ mass concentration during the two intensive campaigns.

These differences in the dilution properties of the lower boundary layer result in a different modulation of the particle concentration (Figure 6.172). 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.

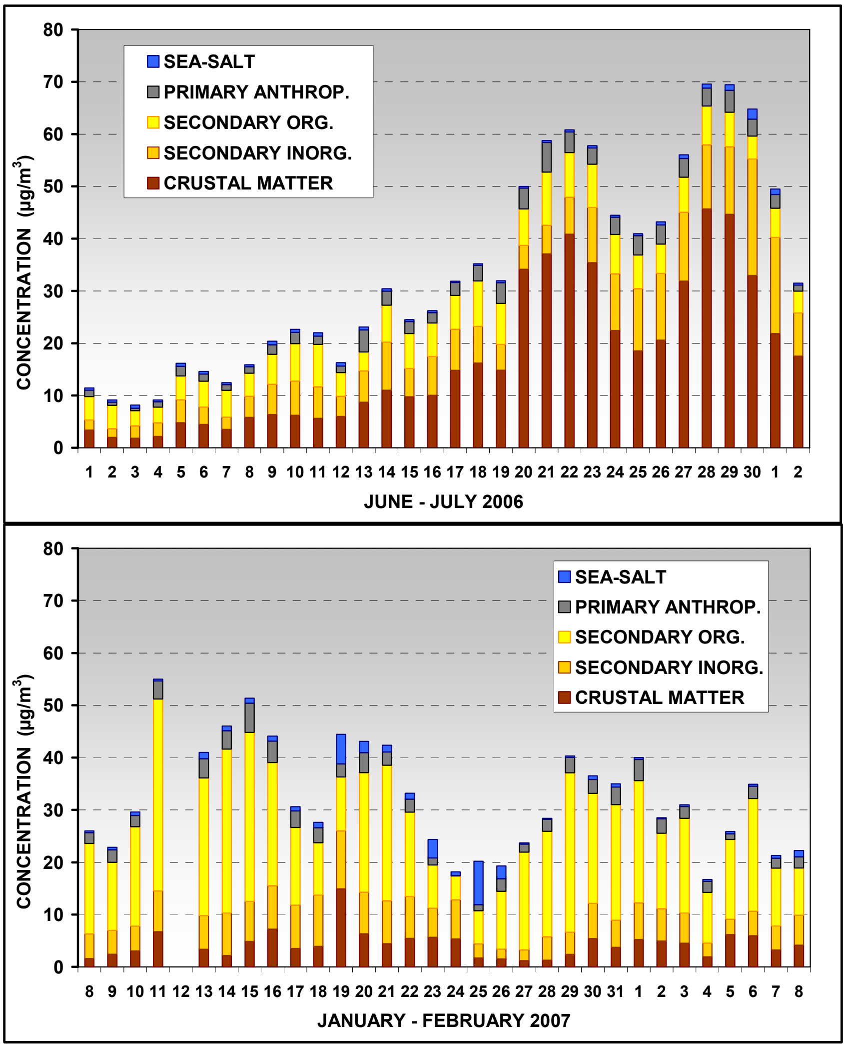


Figure 6.18: Chemical composition of PM_{10} during the two intensive campaigns.

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 6.18, 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 µg/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 6.19, 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.

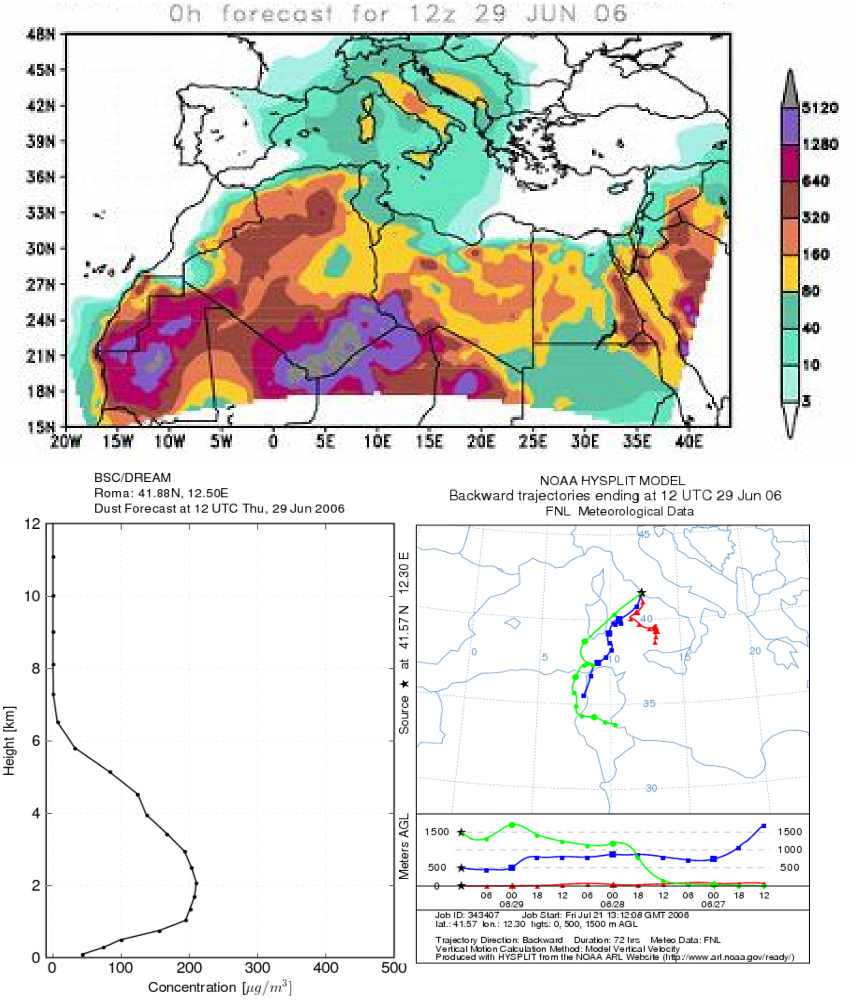


Figure 6.19: Dust loading and vertical profile over Rome by the ICoD DREAM model and back-trajectories by the Hysplit NOAA model on June 29th, 2006.

The per cent composition of PM_{10}, of $PM_{2.5}$ and if the coarse fraction ($PM_{10-2.5}$) is reported in Figure 6.20. 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%).

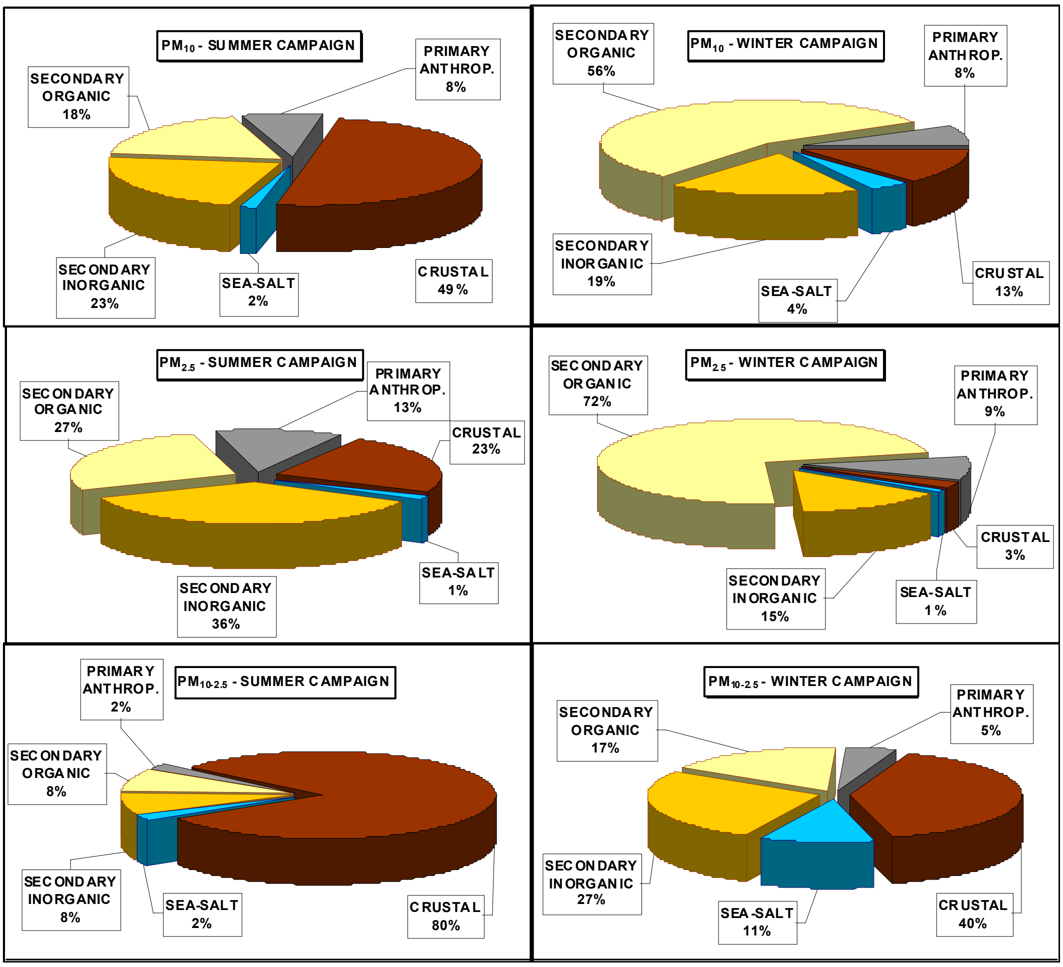


Figure 6.20: Chemical composition of PM_{10}*,* $PM_{2.5}$ *and* $PM_{10-2.5}$ *during the two intensive campaigns.*

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.

6.5 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.

6.5.1 A northern Italy region assessment

GAMES (Gas Aerosol Modelling Evaluation System) (Volta and Finzi, 2006) modelling system integrates (Figure 6.21):

- 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.

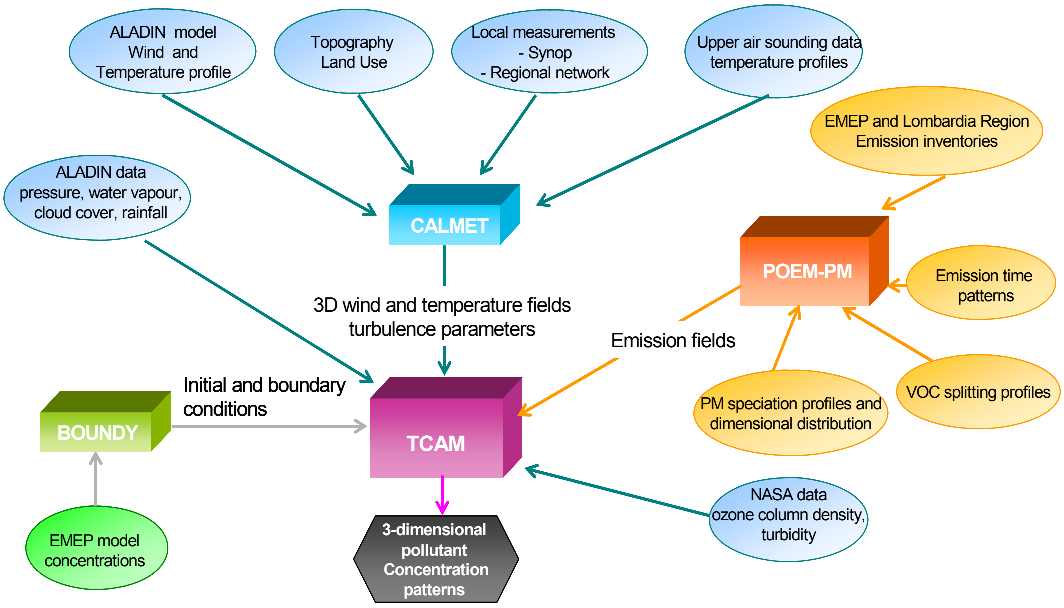


Figure 6.21: Scheme of the GAMES modelling system.

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 6.22). 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.

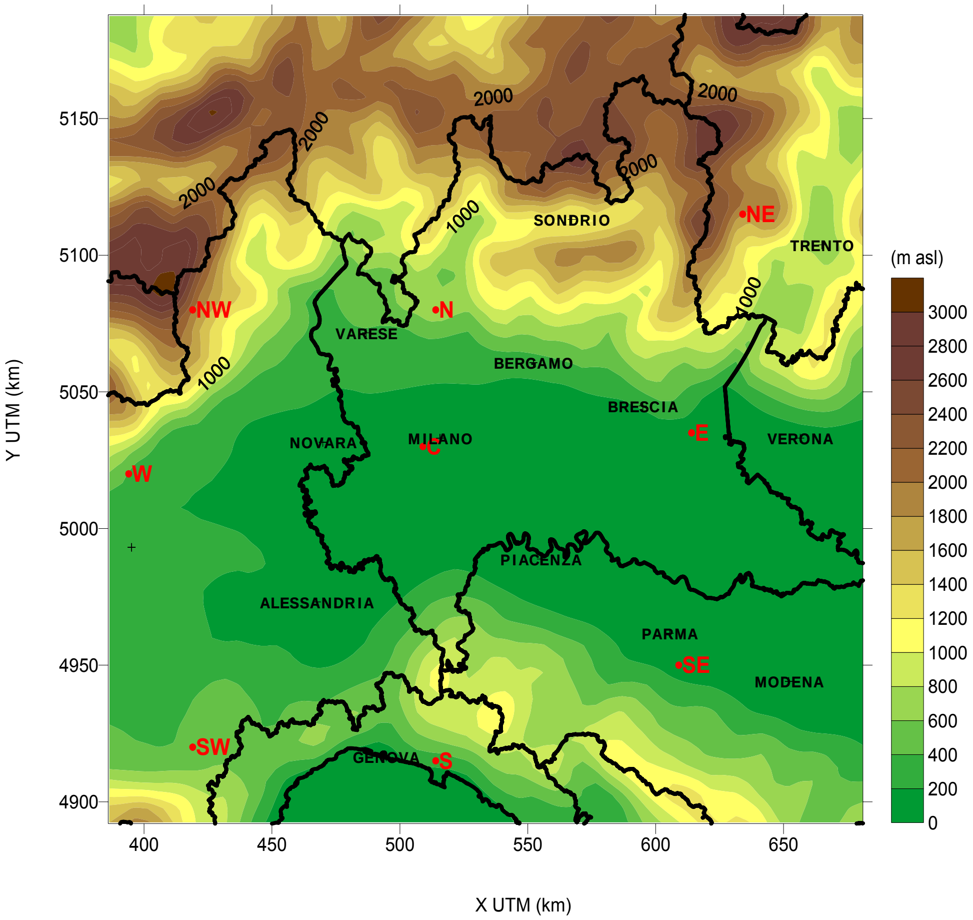


Figure 6.22: The simulation domain.

The model has been driven by emission (Figure 6.23) 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 6.22), chosen as significantly representative of the meteorological and emission regimes on the domain.

In Figure 6.24 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.

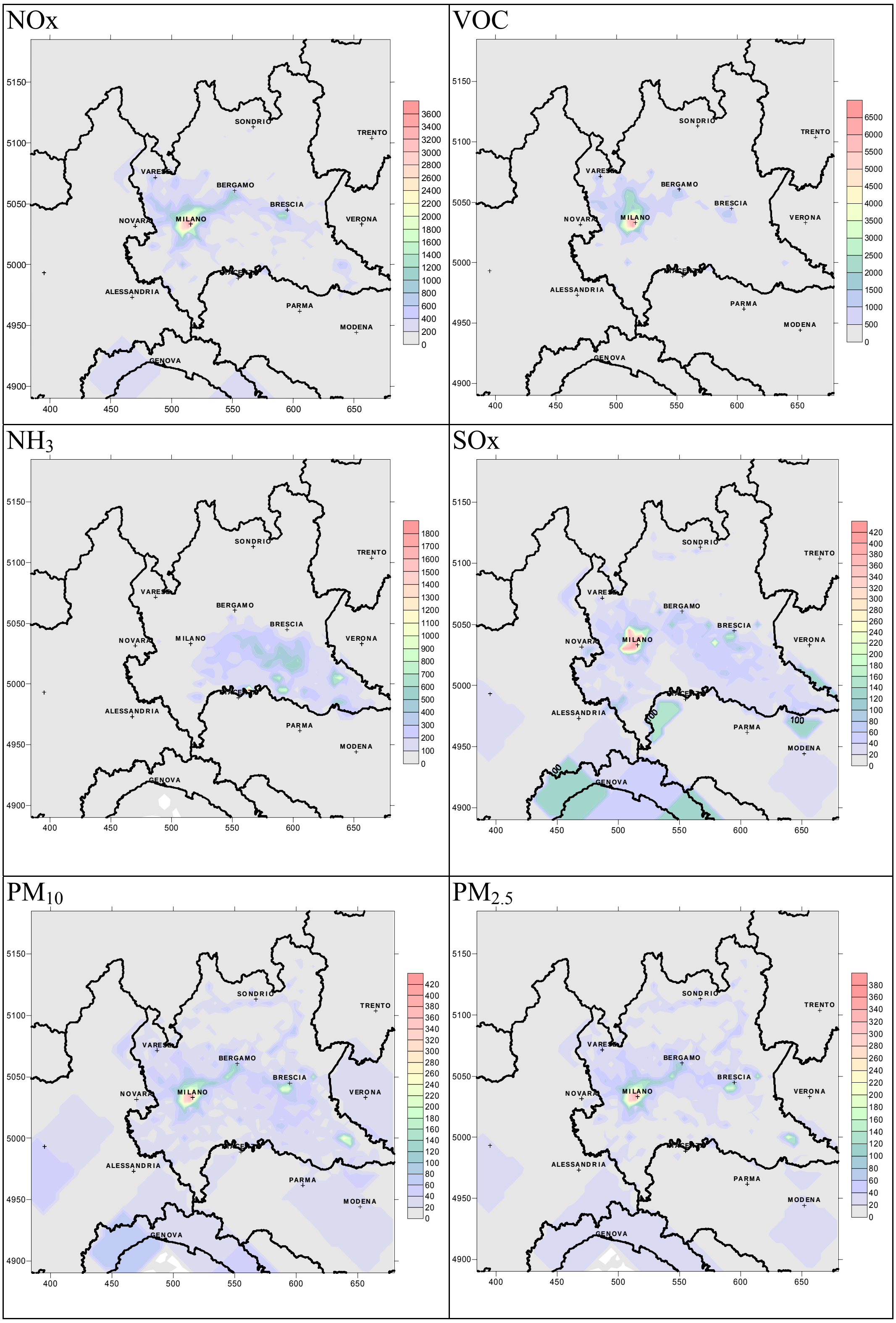

NOx
VOC
NH_3
SOx
PM_{10}
$PM_{2.5}$

Figure 6.23: PM_{10} precursor emissions (ton/year).

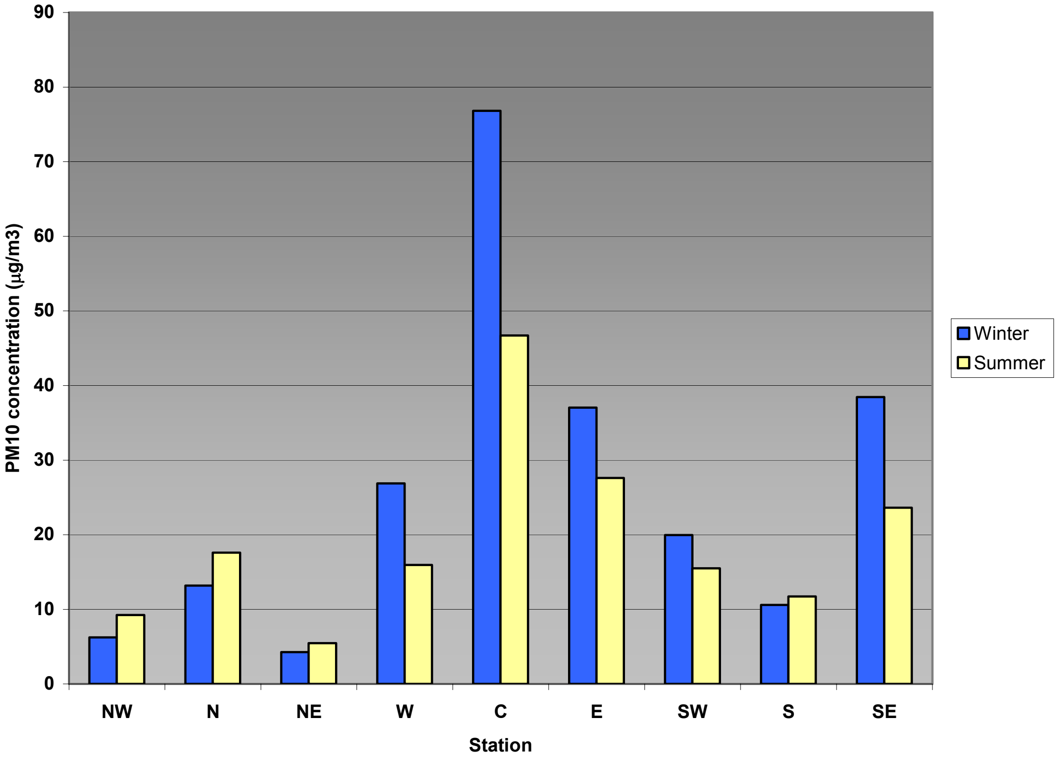


Figure 6.24: Simulated PM_{10} *in the 9 selected station in winter (blue) and summer (yellow).*

Figure 6.25 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 6.23). 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.

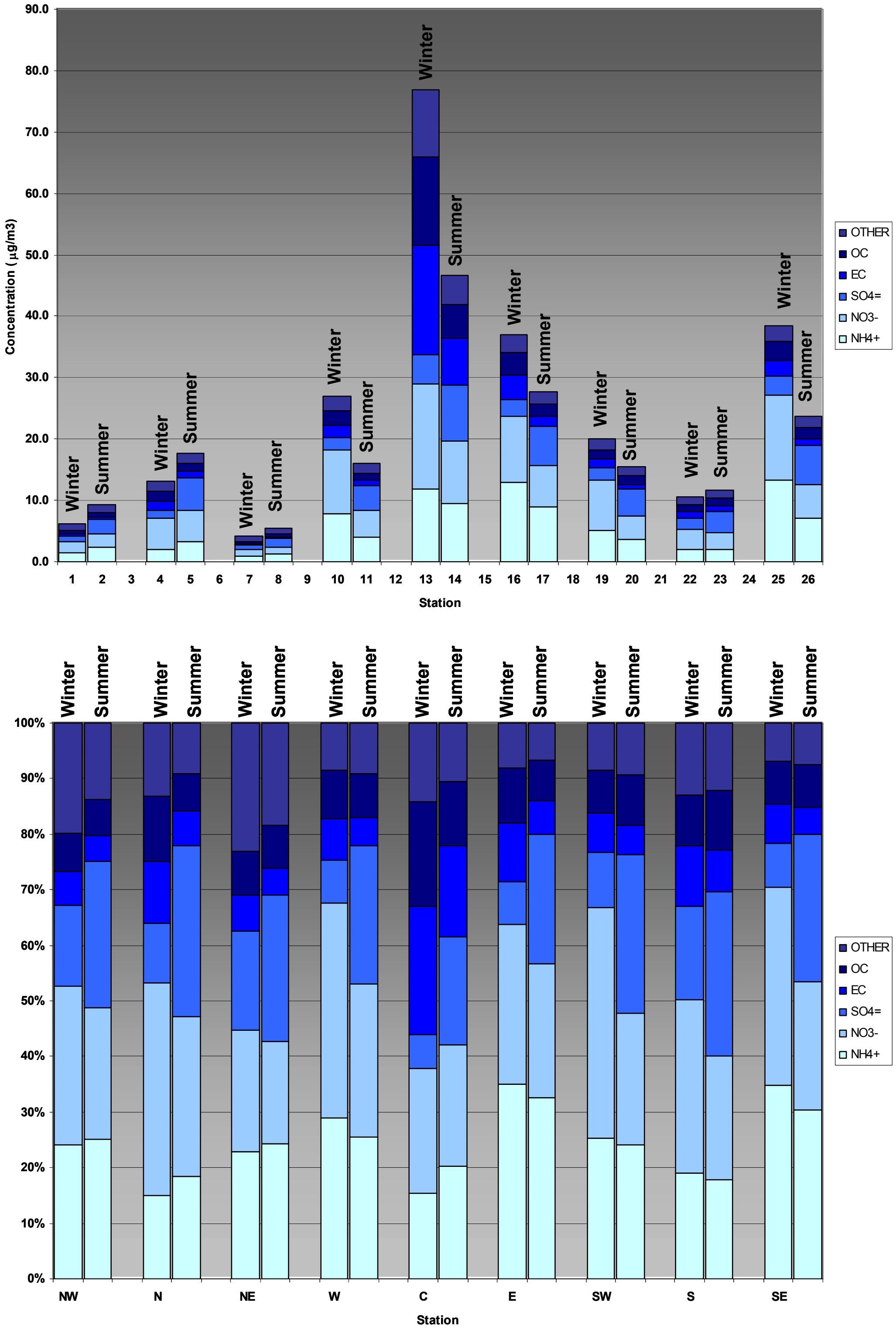


Figure 6.25: Chemical composition of PM_{10} in the 9 selected points for summer and winter months in µg/m3 (upper) and in percentage (lower).

The simulated *ammonium* contribution is higher in the rural area in the south-east of the domain (E and SE point in Figure 6.22), where the most important ammonia sources are located (Figure 6.23). The spatial distribution of *nitrates* concentrations (Figure 6.25) 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

6.5.2 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 6.26) 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.

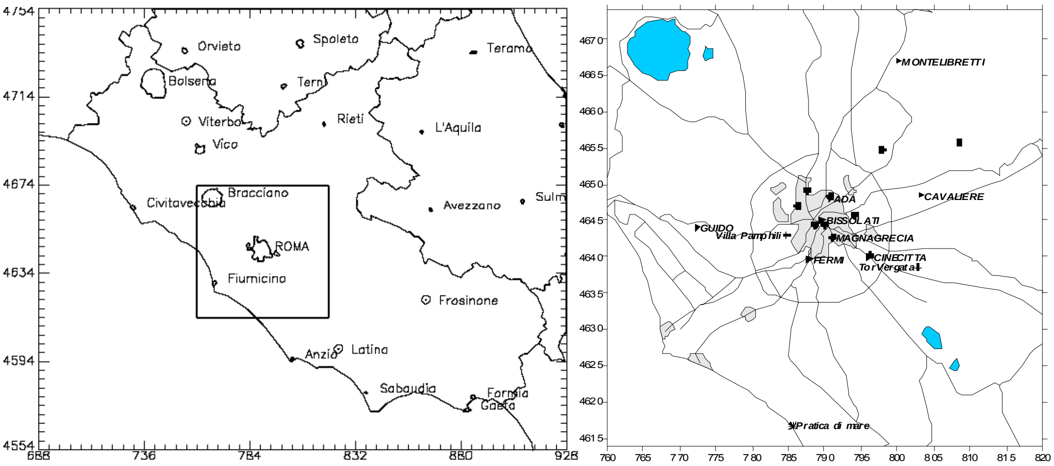


Figure 6.26: The nested modelling domains (the inner domain is expanded on the right side) and location of main meteorological and air quality measurement sites.

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 6.27). 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.

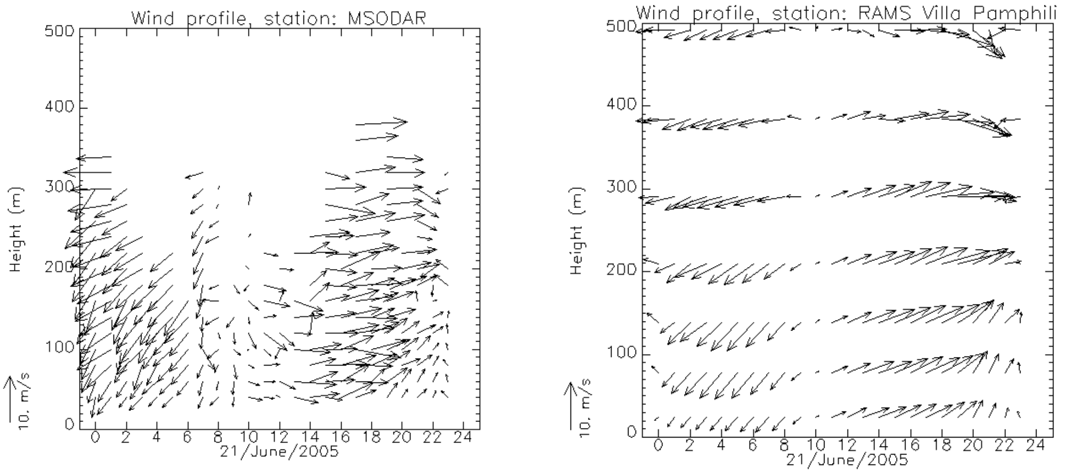
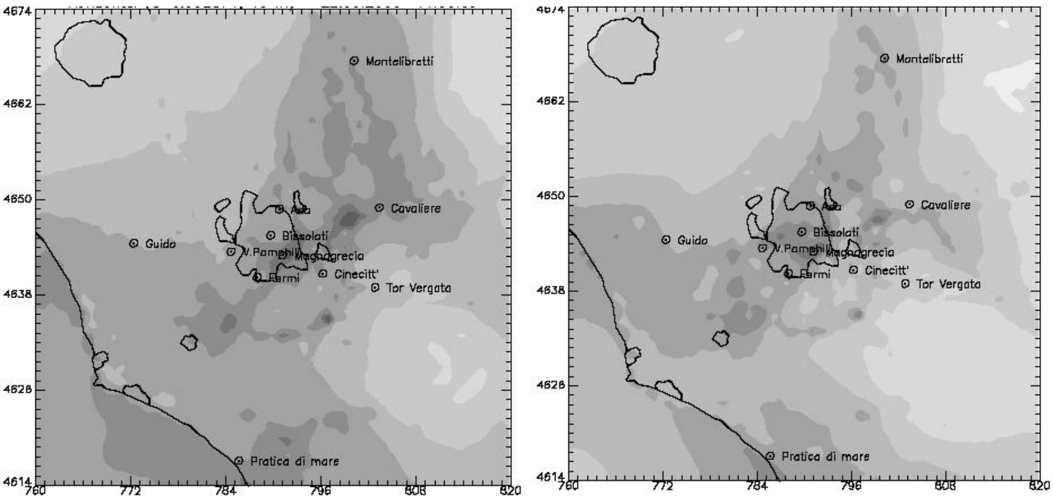
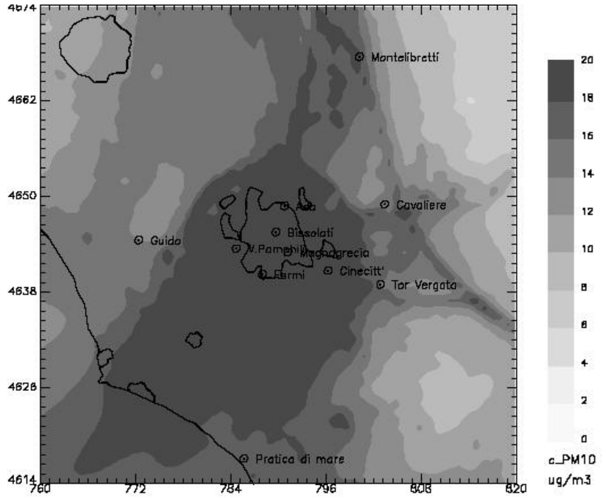


Figure 6.27: Comparison of SODAR measured (left) and RAMS modeled (right) vertical wind profile on June 21 2005 at the Villa Pamphili station (Rome).

The chemical transport model FARM has been employed to describe pollutant dispersion and chemical transformation over the two inner domains (Figure 6.26) 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 6.28 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

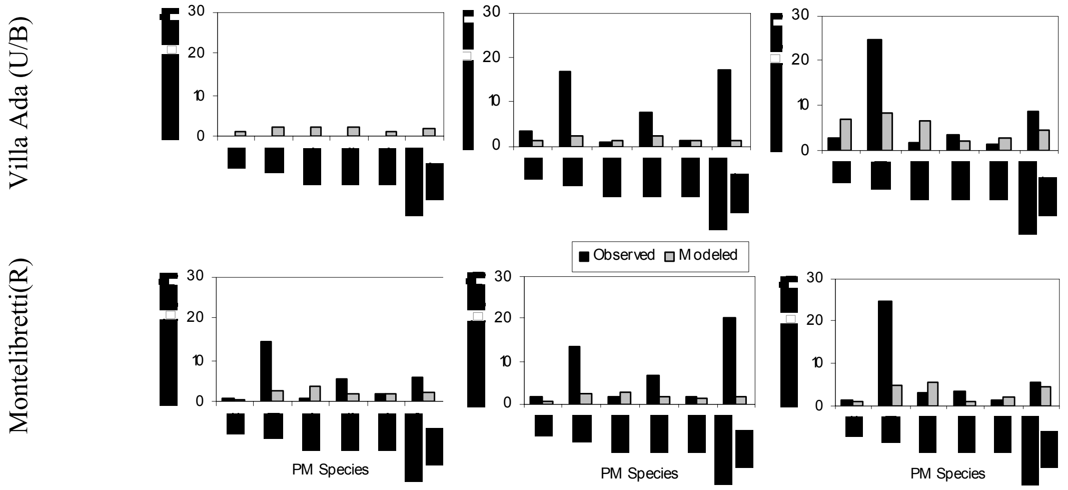


c) 9-13 January 2006

Figure 6.28: 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 μg/m^3. The winter map shows a large area with an average PM_{10} concentration of 20 μg/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 μg/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 6.29 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 6.29: 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.).

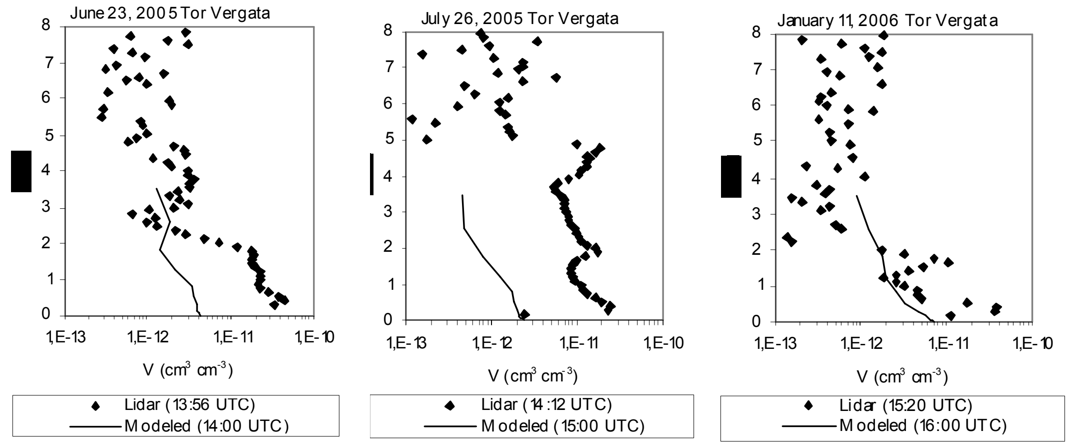


Figure 6.30: Comparison of modeled and Lidar observed atmospheric aerosol volume profiles at Tor Vergata site on June 23, 2005 (left), July 26, 005 (middle), January 11, 2006 (right).

The other component that results to be significant underestimated is the soil (and sea salt) component for which the analysis of Figure 6.29 evidences a good agreement for the winter episode (Figure 6.29c), a non negligible underestimation at Montelibretti for June episode (Figure 6.29a – Villa Ada data were not available -) and a significant underestimation during the July 2005 episode (Figure 6.29b). The use of Lidar data is very useful to understand the reasons for these results. Figure 6.29 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 6.30 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 6.30 left); D > 10% and R > 1.5 for July (Figure 6.30 middle) and non-dust conditions for January (Figure 6.30 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 6.29c at Montelibretti) or its underestimation is reduced (Figure 6.29c at Villa Ada).

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7 Analysis of particulate matter (PM_{10}) concentrations in Latvia

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7.1 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.

7.2 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 7.1 and Table 7.1.

Figure 7.1: Geographical position of PM_{10} monitoring stations in Latvia, (yellow- operated stations, blue – planned stations).

Table 7.1: 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.

7.3 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 7.2).

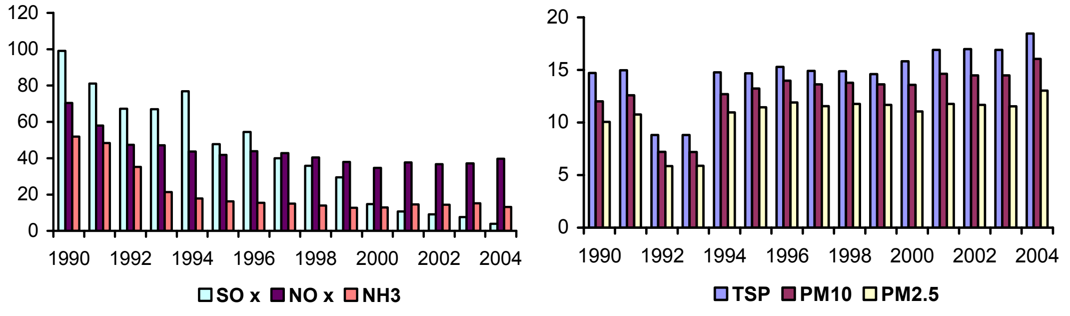

Figure 7.2: Total emissions of gaseous pollutants and particulate matter in Latvia, Gg.

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.

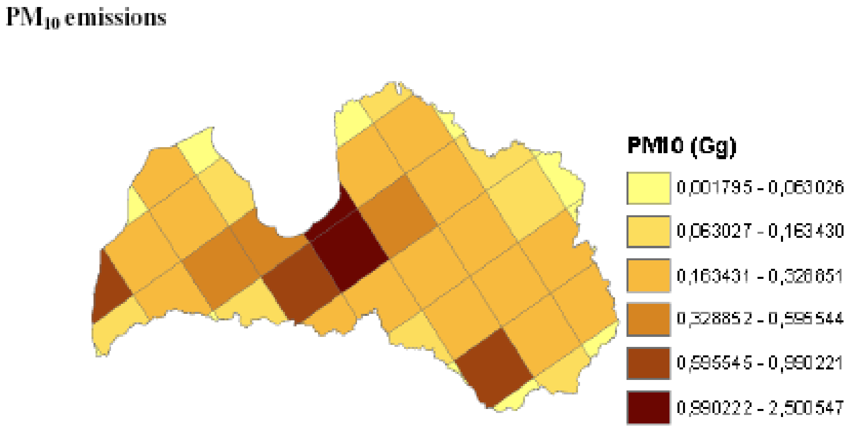

Figure 7.3: Total PM_{10} emission within EMEP grid cells (50x50 km^2), 2000.

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.

7.4 Results

7.4.1 Exceedance of EU limit values

The monitoring results are presented in Table 2 and clearly testify to the fact that PM_{10} is one of the problematic pollutants for the whole area of Latvia.

A 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 7.2: Results of particulate matter (PM_{10}) monitoring.

No	Measurement site	Year	Frequency of observation	Annual mean value, µg/m³	Daily maximum value, µg/m³	Hourly maximum value, µg/m³	Number of exceedances of 50 µg/m³ value
1.	Riga, centre	2000	daily	59*	116	n.d.	*
		2001		54	176		92
		2002		58	215		109
2.	Riga, Brivibas	2003	daily	56	156	n.d.	105
		2004		52	106		99
		2005		54*	137		*
3.	Riga, Valdemara	2003	hourly	54	229		139
		2004		48	109		137
		2005		48	166		124
4.	Riga, Tvaika	2003	daily	27*	61	n.d.	*
		2004		31	99		23
		2005		32	92		32
5.	Liepaja	2000	daily	41*	103	n.d.	*
		2001		41	126		65
		2002		44*	138		*
		2003		49	172		78
		2004		45	149		86
		2005		43	99		69
6.	Ventspils	2002	daily	25	78	n.d.	20
		2003		16	127		3
		2004		15	48		0
		2005		18	55		3
7.	Rezekne	2001	daily	36*	158	n.d.	*
		2002		51*	250		*
		2003		39	185		35
		2004		38*	98		*
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/m³ limit value but in 34 % of cases this limit value was exceeded (Figure 7.4).

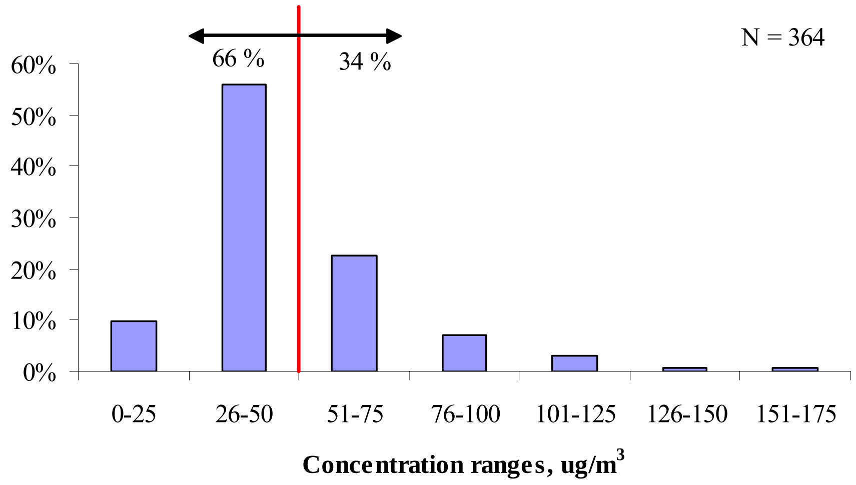

Figure 7.4: Distribution of PM_{10} concentration at station Riga, Valdemara, 2005.

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 ug/m^3 (Figure 7.5).

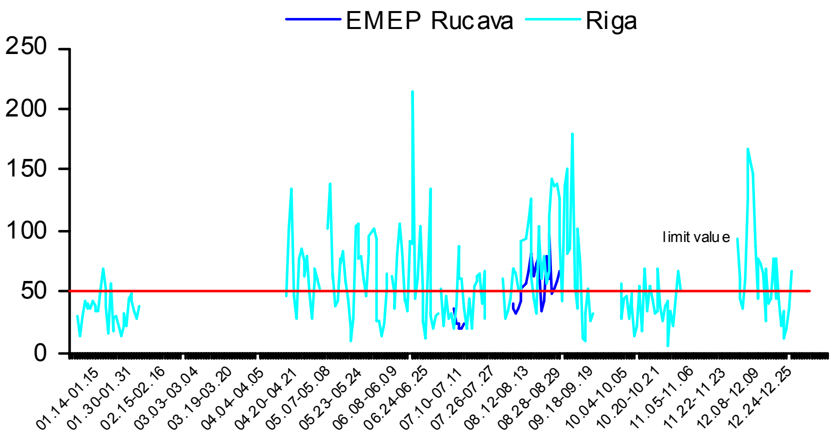

Figure 7.5: Dynamics of PM_{10} daily (µg/m3) concentrations at EMEP (Rucava) and traffic (Riga) stations, 2002.

Annual average transboundary concentrations of PM_{10} in Latvia in 2004, calculated with the Unified EMEP model ranged within 5 to 10 ug/m^3.

The PM_{10} annual average concentration for the traffic stations in Latvia was in generally higher compared to other European countries (Figure 7.6).

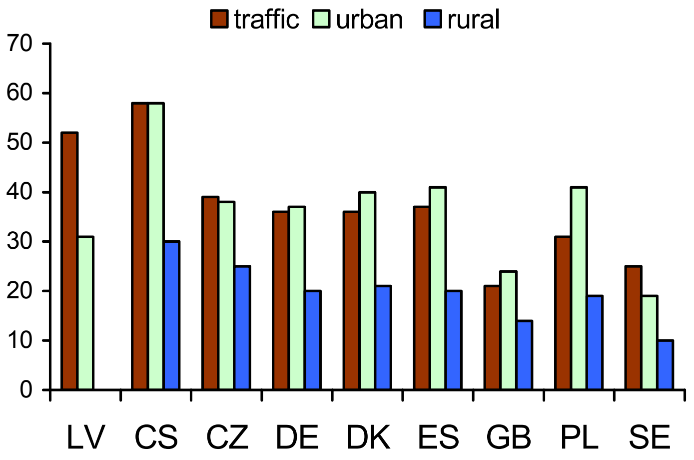

Figure 7.6: Annual average concentrations of PM_{10} (ug/m3) in Latvia and other European countries, 2004.

7.4.2 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 weekdays and on weekend (Figure 7.7). The situation was alike at other stations.

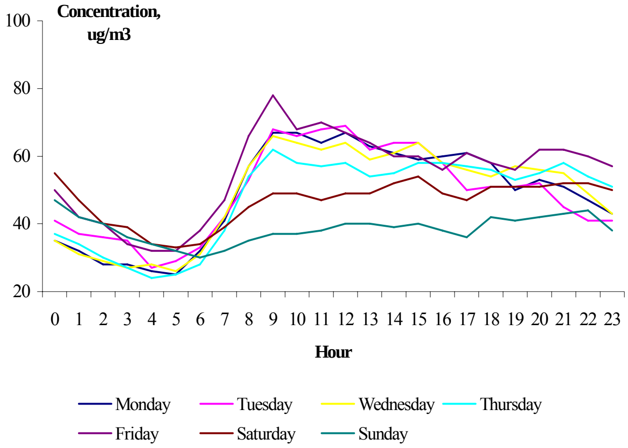

Figure 7.7: PM$_{10}$ hourly and daily variations at station Riga, Valdemara, 2004.

An analysis of monthly variations showed the highest values during February-April (Figure 7.8).

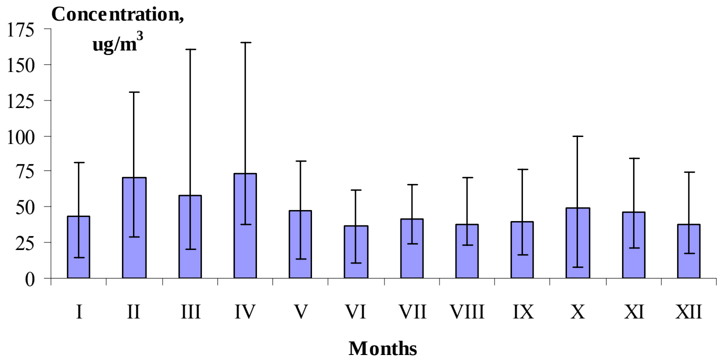

Figure 7.8: PM$_{10}$ monthly variations at station Riga, Valdemara, 2005.

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.

The highest concentrations and variation range of PM$_{10}$ were observed in the spring and winter (Figure 7.9).

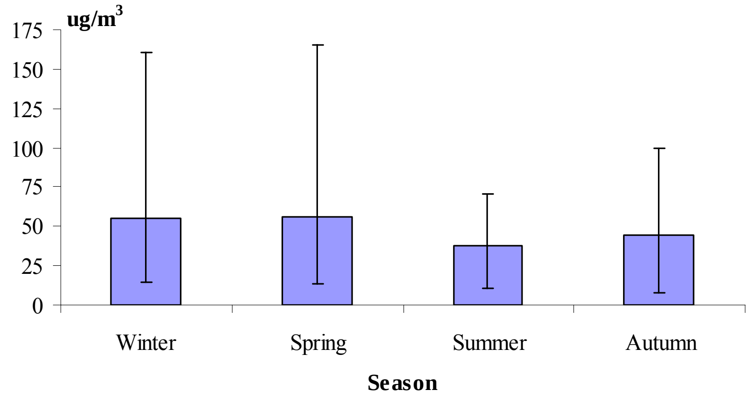

Figure 7.9: PM_{10} seasonal variations at station Riga, Valdemara , 2005.

7.4.3 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 7.10).

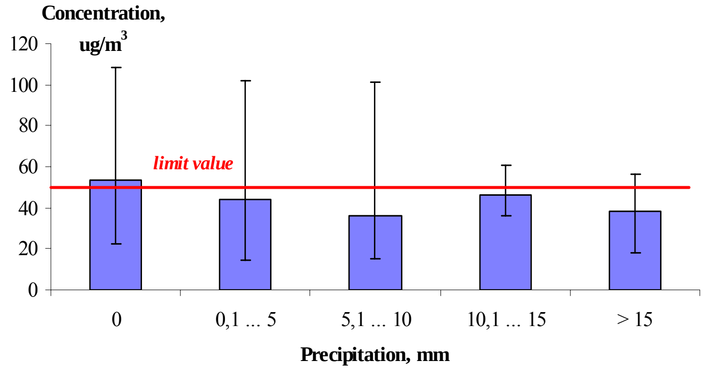

Figure 7.10: PM_{10} daily concentrations on days with and without precipitation at station Riga, Valdemara, 2004.

On the so-called dry days (days without or poor precipitation), the daily limit value was exceeded in 94 % of the cases (Figure 7.11).

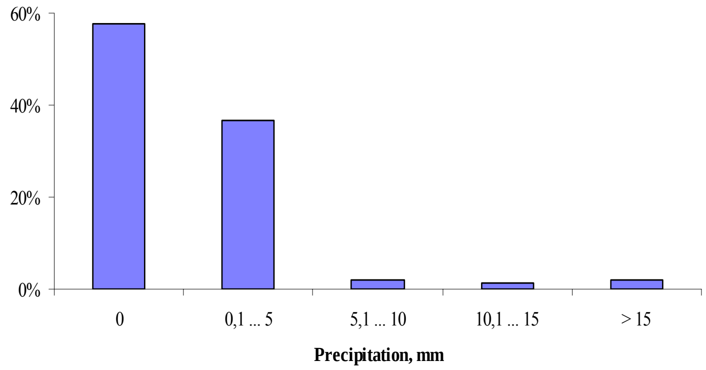

Figure 7.11: Cases of exceedance of PM_{10} of the daily limit value on days with and without precipitation at station Riga, Valdemara, 2004.

The wind is one of the dominant factors that affect 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.

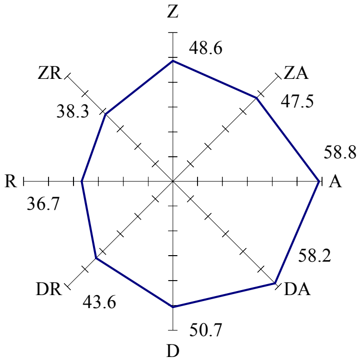

Figure 7.12: Wind rose of PM_{10} concentrations at station Riga, Valdemara, 2004.

Concentrations of over 100 µg/m^3 of PM_{10} increases in a wind speed of 5.5-7.9 m/s (Figure 7.13).

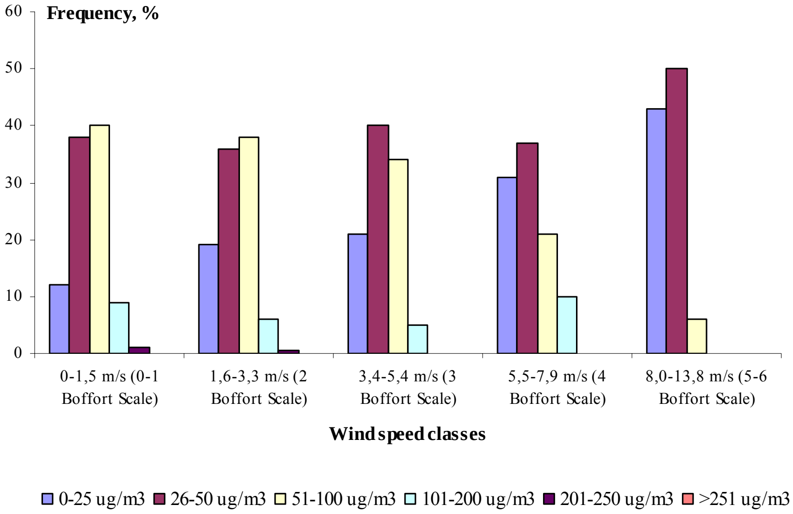

Figure 7.13: Dependence of PM_{10} concentration on the wind speed week days at station Riga, Valdemara, 2004.

During spring time some relationship was found between PM_{10} 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 7.14).

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 7.15). Normally, such meteorological conditions have occurred 15 times per year, with 14 of them in spring.

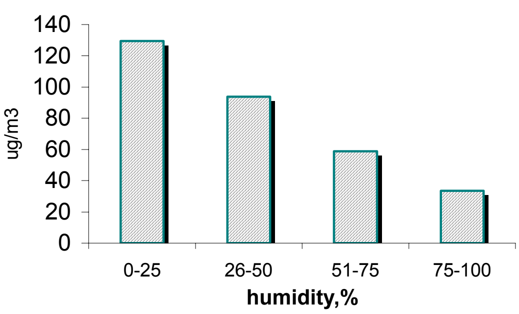

Figure 7.14: Spring PM_{10} average concentrations versus relative humidity (wind speed 5.5-7.9 m/s).

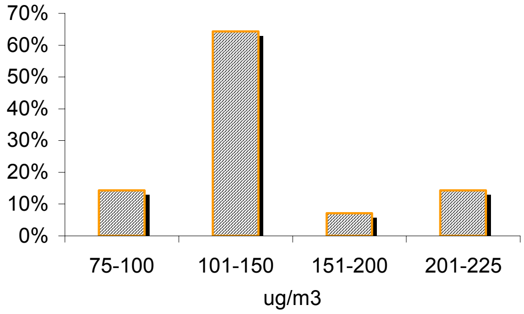

Figure 7.15: Spring PM_{10} concentration distribution (wind speed 5.5-7.9 m/s, relative humidity 0-25 %).

Correlation coefficients of main pollutants and meteorological parameters were estimates as linear best to fit coefficients (Table 7.3).

Table 7.3: Correlation coefficients of main pollutants and meteorological parameters in Riga at Valdemara Street (2004).

	PM_{10}	Benzene	NO_x	O_3	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

7.5 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 $\mu g/m^3$ for PM_{10} and daily limit value of 50 $\mu g/m^3$ 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 have significant influence to PM_{10} pollution levels at some particular cases (specially at high pollution episodes), only strong direct relationship was not 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 $\mu g/m^3$. 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 NO_x was stated, the highest of them – NO_x ($R^2 = 0.35$).

7.6 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.

8 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.

8.1 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 $\mu g/m^3$ /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 $\mu g/m^3$.
- 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.

8.2 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 8.1–Figure 8.4).

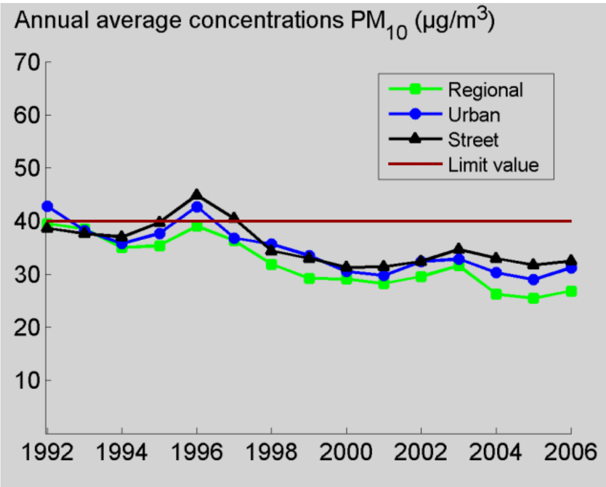

Figure 8.1: Measured annual average particulate matter concentrations in the Netherlands from 1992- 2006. The trend lines indicate the average of the stations in the corresponding group.

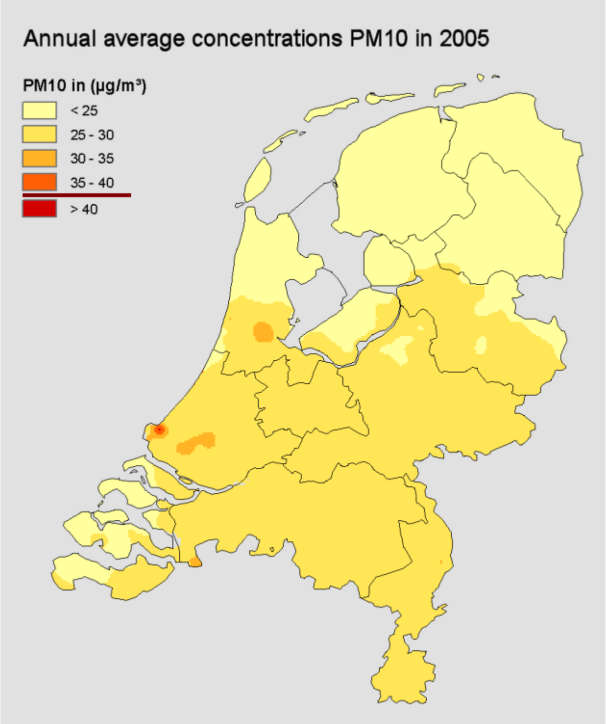

Figure 8.2: Annual average concentration of PM$_{10}$ in 2005. The map for the annual average concentrations was obtained from measurement results from the Dutch National Air Quality Monitoring Network combined with model calculations.

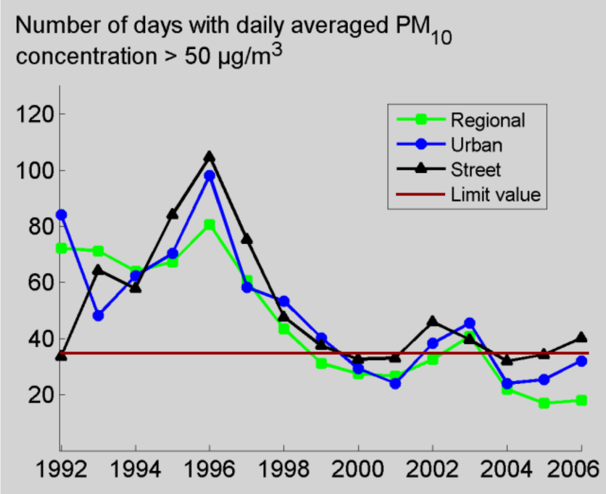

Figure 8.3: The number of days with a 24-hour average above 50 µg/m3 in the Netherlands in the period 1992-2006 at three types of measurement stations.

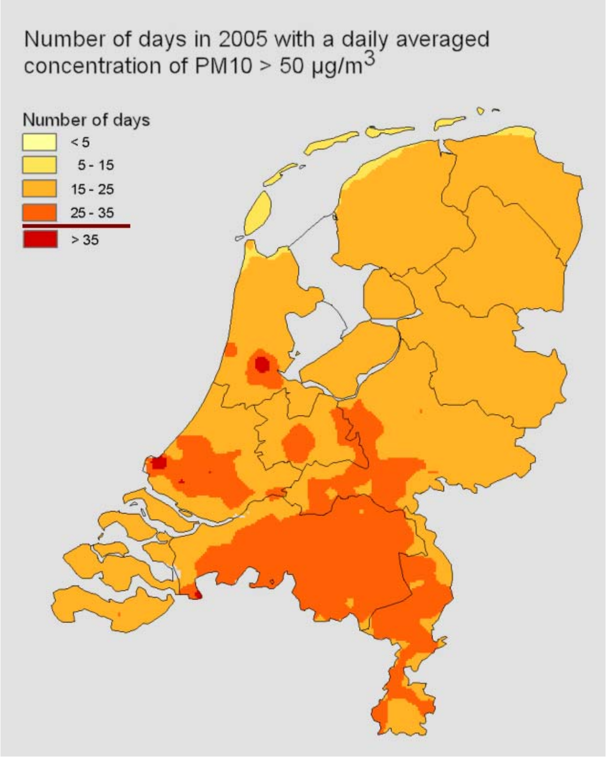

Figure 8.4: The map for the number of days exceeds the 50 µg/m3. The plot is based upon the relation between annual average concentration and the number of days with a daily average > 50 µm/m3. The compliance problems concerning the limit value for the 24-hour average are concentrated on some spots/cities.

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 8.1. In the period 2004-2006 the average levels are shown in Table 8.1. 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 8.1: 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

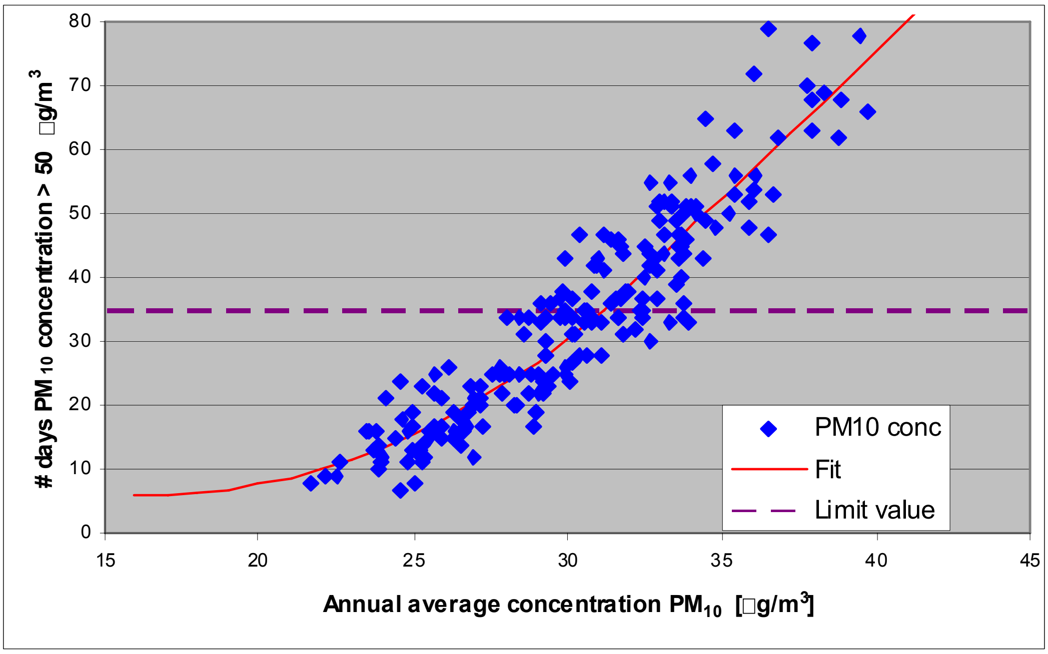

Figure 8.5: Relationship between the annual average particulate matter concentration and the number of days with a 24-hour average above 50 $\mu g/m^3$. In the linear part of the relationship, high concentrations, every additional microgram of particulate matter results in five more days that exceed 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 8.3). 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.

8.3 Trends in the concentration

Figure 8.6 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.

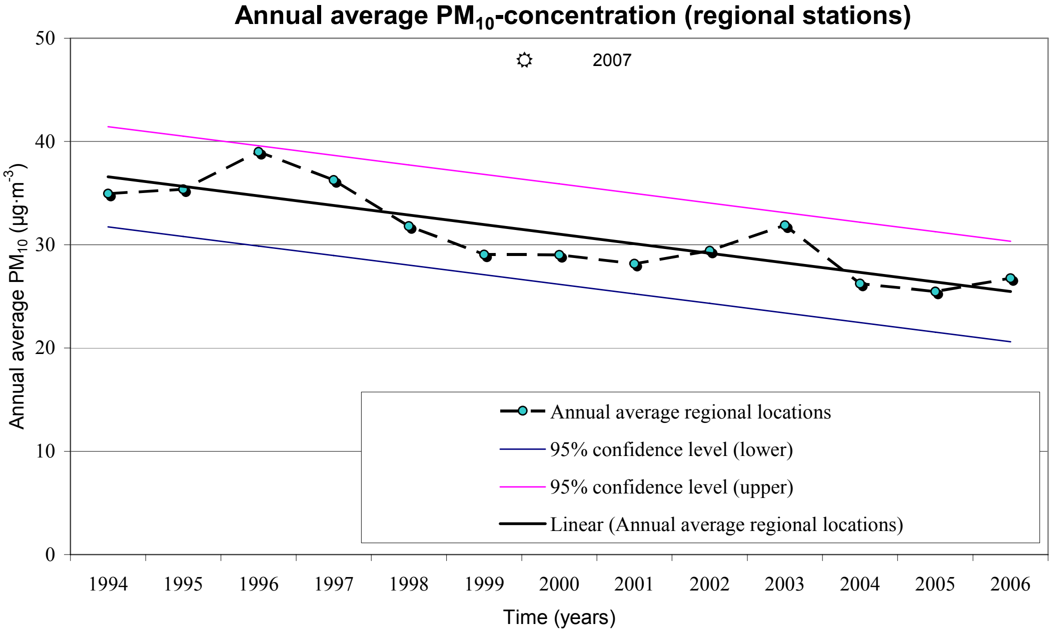

Figure 8.6: Measured trend in the annual average particulate matter concentration at the regional stations of the Dutch National Air Quality Monitoring Network. The figure shows variations of the annual average particulate matter concentration up to 5 µg/m3 (95 % confidence interval).

8.4 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[15], in Amsterdam comprises five monitoring stations.

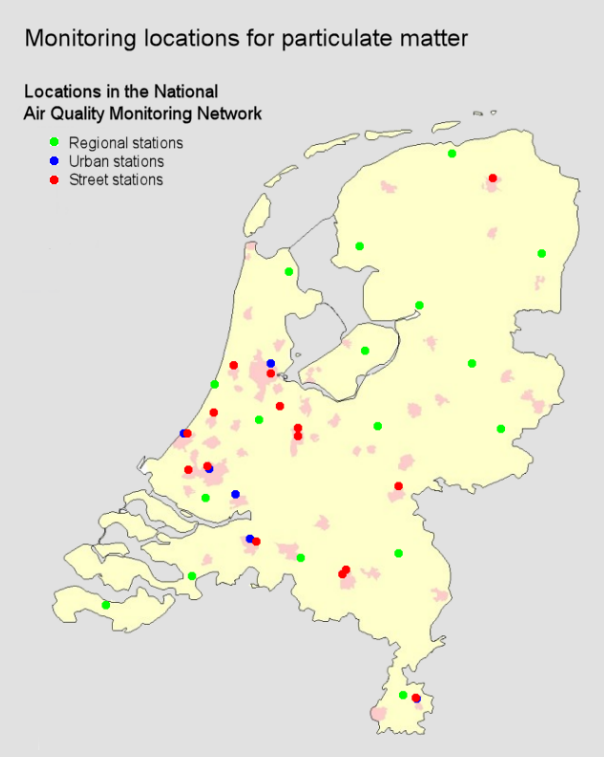

Figure 8.7: Monitoring locations for particulate matter (PM$_{10}$) in the Dutch National Air Quality Monitoring Network 2006. Local monitoring networks for particulate matter are not shown.

8.5 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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[15] 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.

8.6 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 8.8). 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.

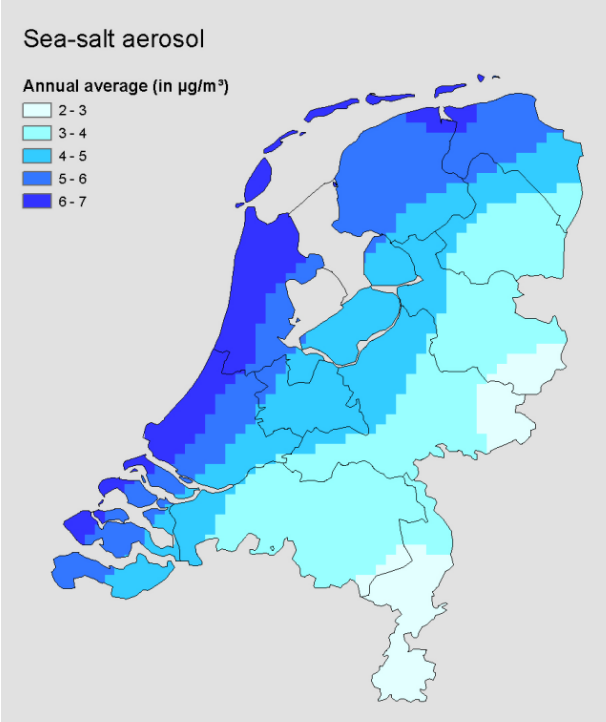

Figure 8.8: Annual average contribution of sea salt aerosol to the particulate matter concentration in the Netherlands. The estimate is based on interpolation of monitoring results and has been combined with assumptions about the distribution of sea salt along the Dutch coast (Eerens et al., 1998).

8.7 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.

8.8 References

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9 Particulate matter gradients in the Amsterdam area

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9.1 PM network data for Amsterdam for 2002-2005

The Amsterdam Air Quality Network[16] 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[17] (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 9.1 summarizes the annual mean concentrations for the various sites over the 2002-2005 period.

Table 9.1: 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 9.1 and visually summarized in Figure 9.1. Averaged over the 2002-2005 period the Amsterdam increment for PM_{10} is 2.3 µg/m^3. PM_{10} traffic increments range from 4.2 µg/m^3 (road) to 7.1 µg/m^3 (motorway). The total increment in the PM_{10} data (from regional background to the motorway) is 9.4 µg/m^3.

For PM_1 traffic increments are 2.4 µg/m^3 (from urban background to road traffic) and 2.9 µg/m^3 (urban background to motorway traffic).

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[16] operated by the Department of Air Quality of the Municipal Health Centre of Amsterdam.

[17] owned by the Provincial Authority of Noord-Holland and maintained by the Amsterdam Network organization.

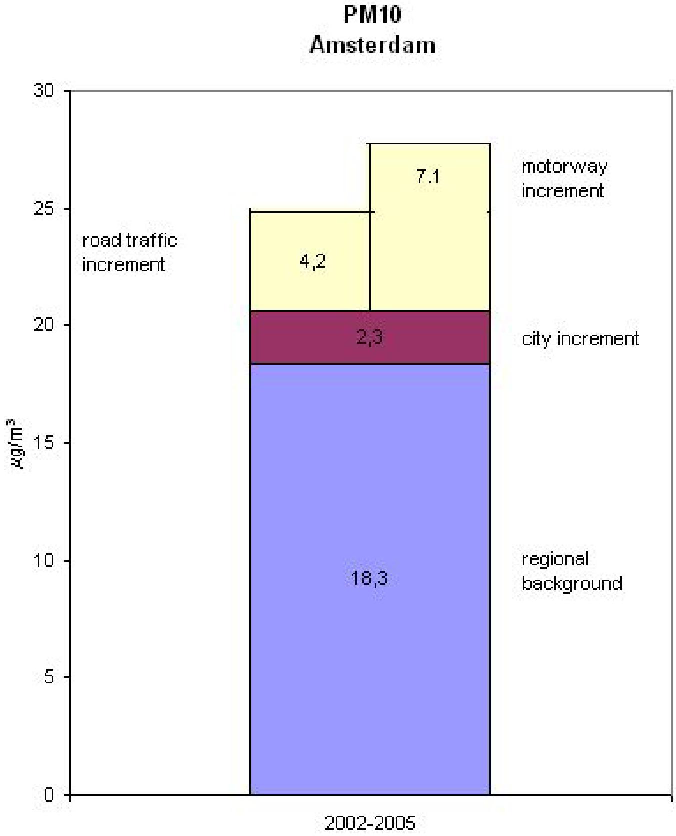


Figure 9.1: Urban and traffic increments for PM_{10} ($\mu g/m^3$) in Amsterdam with respect to regional background (De Rijp) averaged over 2002-2005.

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 9.2 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.

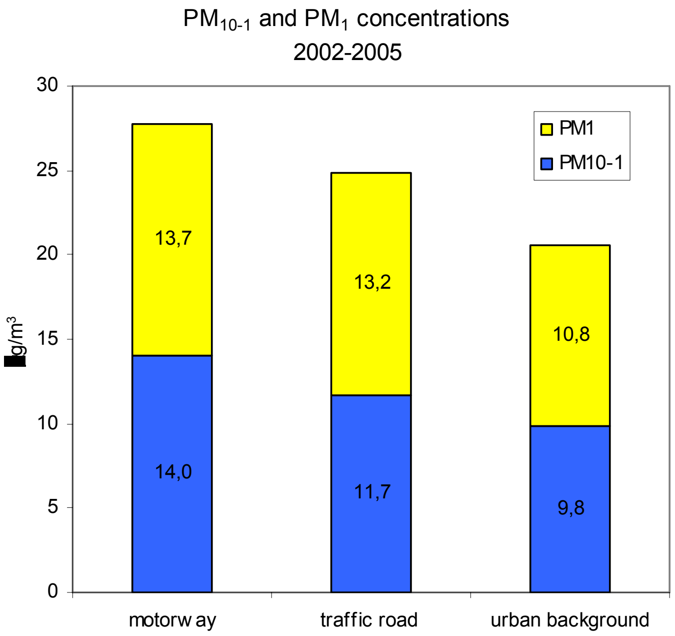


Figure 9.2: Annual mean PM_{10}, PM_1 and PM_{10-1} concentrations for 2002-2005 in the Amsterdam Air Quality Network.

9.2 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 9.2. 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 9.2: 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

9.3 Correlations between sites

Correlation coefficients between stations are given in Table 9.3 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 9.3: 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 9.3 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.

9.4 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 9.3) 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.

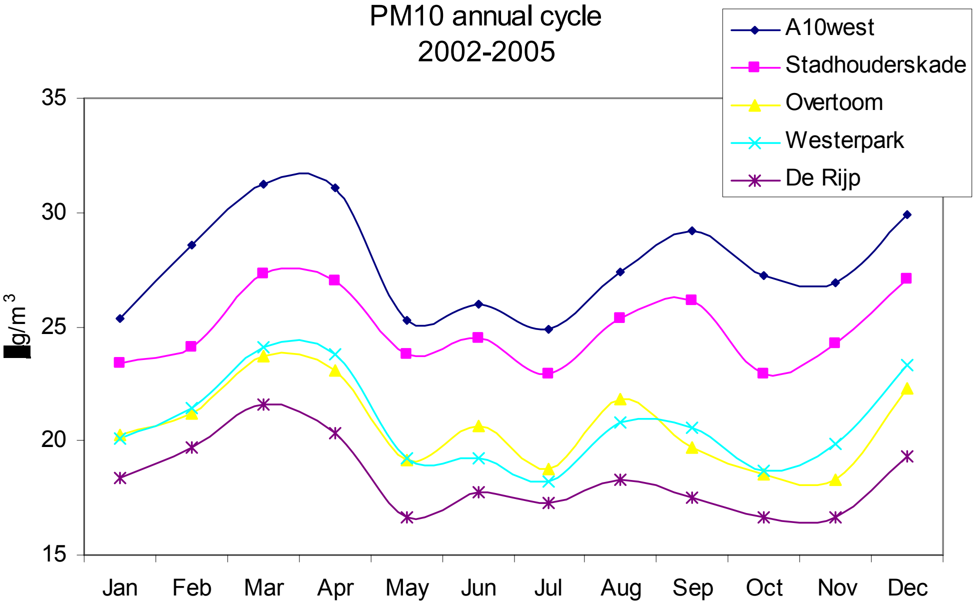


Figure 9.3: Annual variation for monthly averaged PM_{10} concentrations (Amsterdam Network; De Rijp; 2002-2005).

9.5 Wind direction dependent variation of PM_{10}, PM_1 and $PM_{10\text{-}1}$

Figure 9.4 shows the mean PM_{10}, PM_1 and $PM_{10\text{-}1}$ 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 $PM_{10\text{-}1}$ 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.

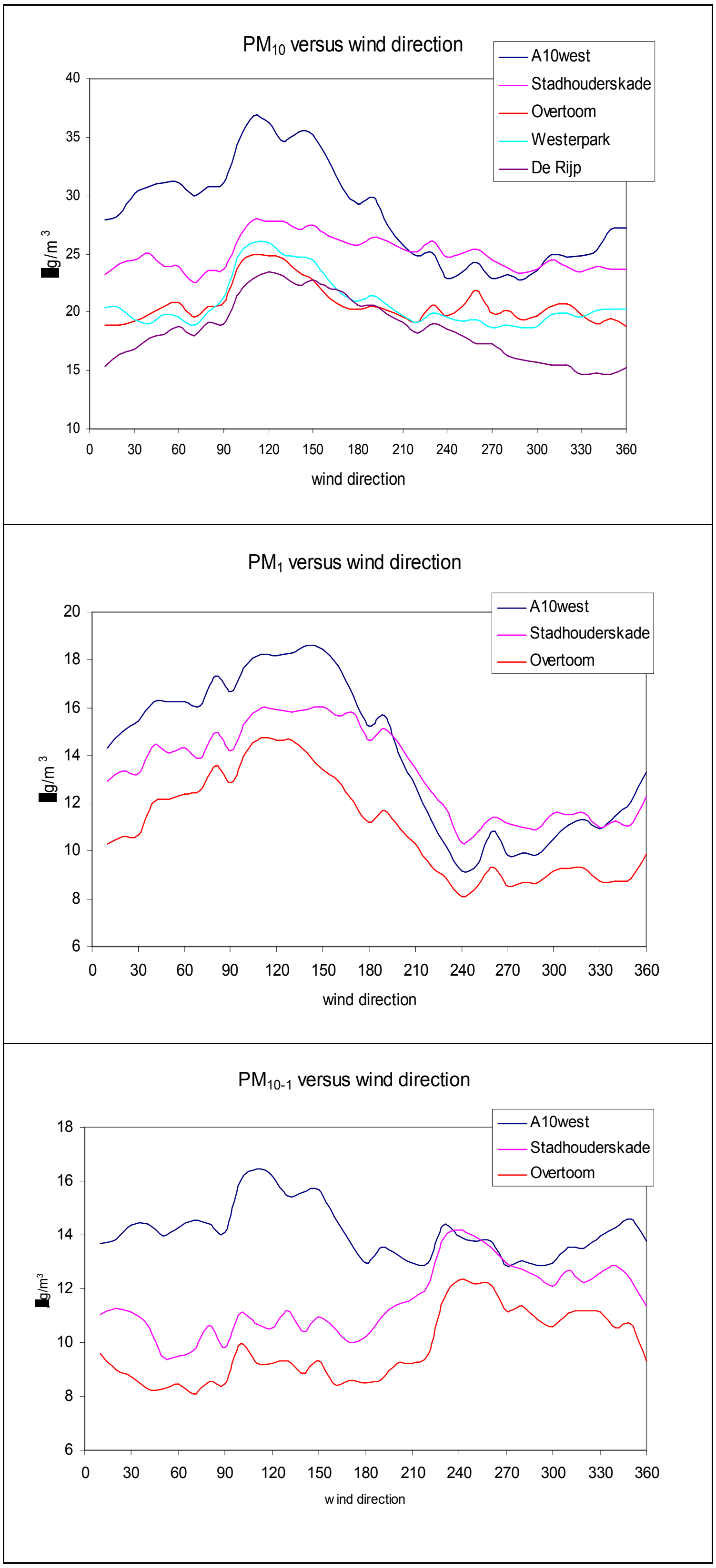
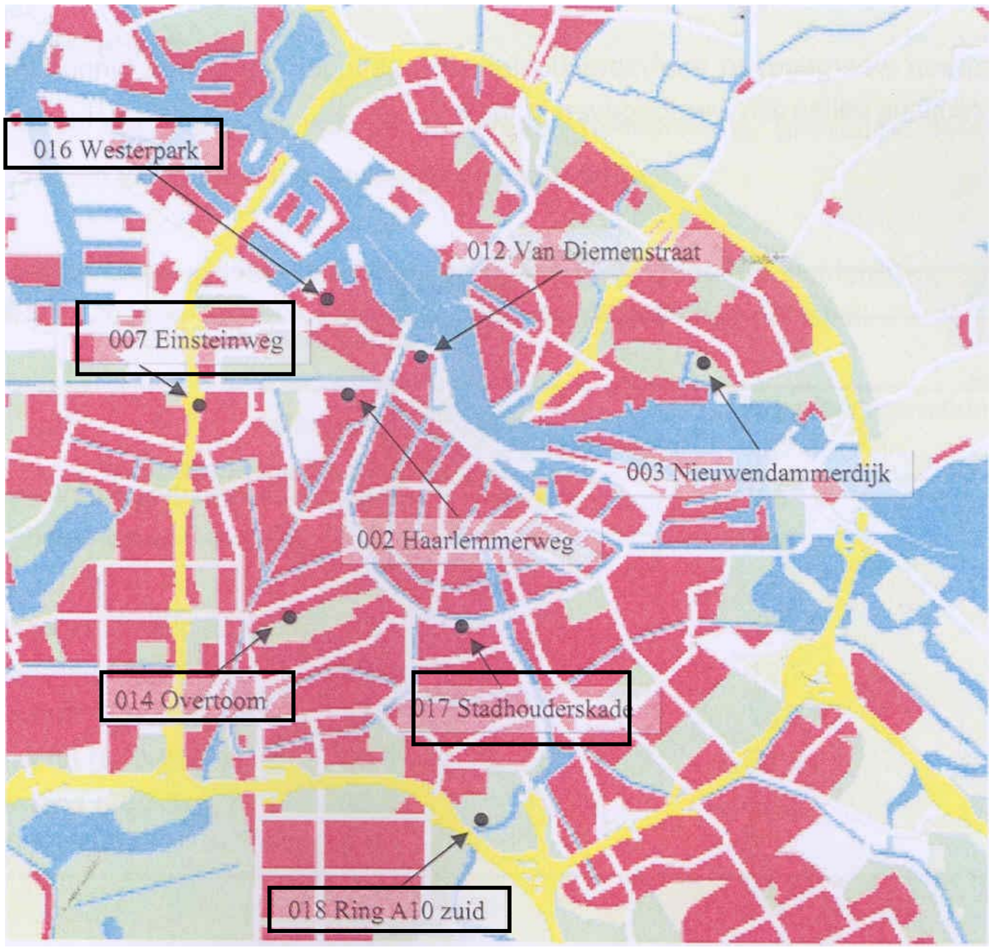


Figure 9.4: PM$_{10}$, PM$_1$ and PM$_{10-1}$ concentrations observed as function of wind direction sector at various monitoring stations.

Appendix A



Locations of the PM measuring stations of the Amsterdam network.

10 Concentrations of particulate matter (PM_{10}, $PM_{2.5}$) in Norway Annual and seasonal trends and spatial variability

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10.1 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 10.1.

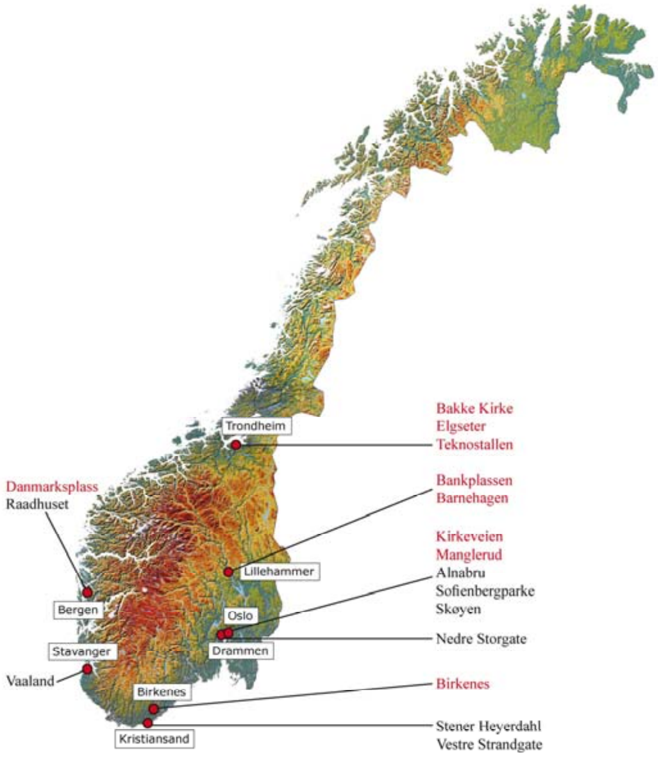

Figure 10.1: Geographical situation of the rural background, urban background, and traffic sites, in Norway reporting measurements of PM in 2005. Black text indicates measurements of PM_{10}, whereas red text means measurements of both PM_{10} and $PM_{2.5}$.

10.2 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).

10.3 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 $\mu g\ m^{-3}$ for the period 2000 - 2005 (Figure 10.2a), 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 10.2b, 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.

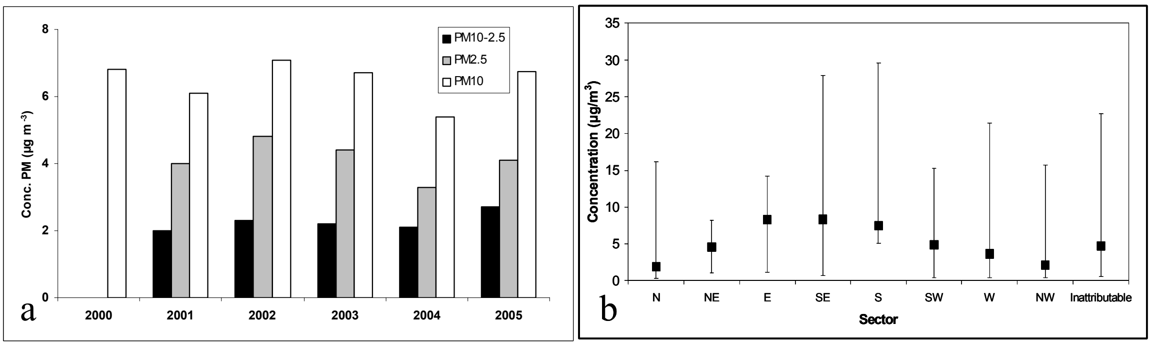

Figure 10.2: Annual mean concentration of PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$ at Birkenes for the period 2000 – 2005 (a); Concentrations of $PM_{2.5}$ at Birkenes as a function of wind direction (b).

$PM_{2.5}$ 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 10.3). 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 10.2).

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 10.3).

10.4 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 10.1a 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 10.1a: 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 10.1b: 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 10.3b). 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 10.1a 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 10.3a).

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.

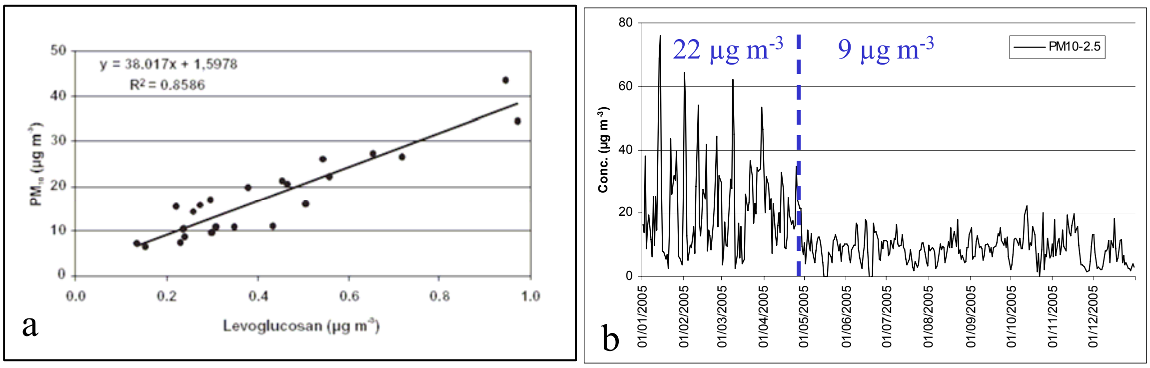

Figure 10.3: High concentrations of levoglucosan are reported for Norwegian cities and towns in winter (here: Elverum). The high correlation reported for levoglucosan vs PM underlines the importance of wood burning for residential heating as a source of PM in winter (Figure is taken from Yttri et al., 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).

10.5 $PM_{2.5}/PM_{10}$ 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 10.2).

Table 10.2: 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 10.2, the frequency distribution of the $PM_{2.5}/PM_{10}$ ratio can be quite different for summer and winter. Figure 10.4b 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 10.2 and that seen in Figure 10.4a.

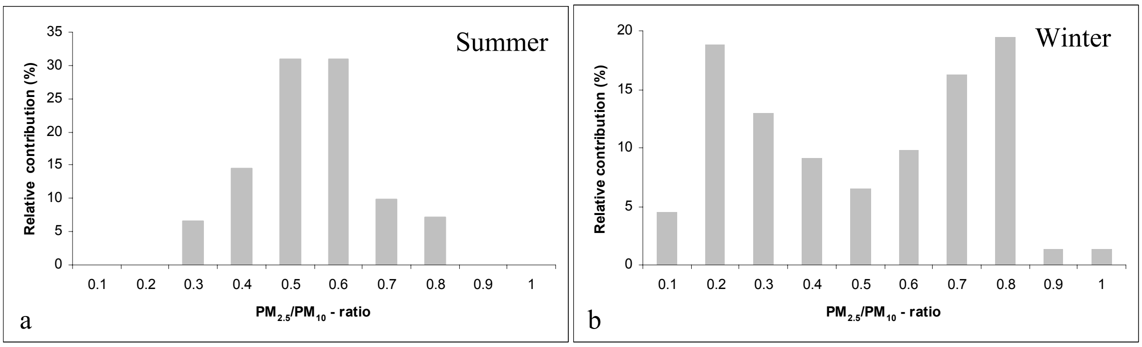

Figure 10.4: Frequency distribution of the $PM_{2.5}/PM_{10}$ ratio for the "Bankplassen" site in the city of Lillehammer in Summer (a) and winter (b), emphasizing that the $PM_{2.5}/PM_{10}$ ratio typically is either very low (resuspension of road dust) or very high (residential wood burning) in winter.

10.6 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 10.3). 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 10.1 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 10.3: 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)

10.7 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 10.5a) is dominated by SO_4^{2-}, NO_3^- and NH_4^+, and organic carbon (OC), which are constituents typically associated with this source.

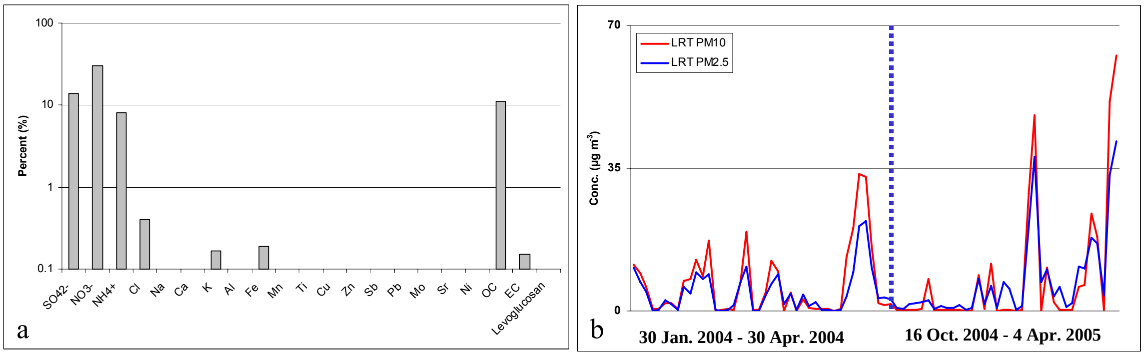

Figure 10.5: Source profile for LRT PM_{10} obtained for a traffic site in Oslo winter 2004 and winter 2004/2005 using positive matrix factorisation (a); Calculated concentrations of LRT PM_{10} and LRT $PM_{2.5}$ at a traffic site in Oslo (30 Jan. – 30 Apr. 2004 and 16 Oct. – 4 Apr. 2005) using positive 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 10.1a 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 10.1a, 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.

10.8 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 10.6). 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.

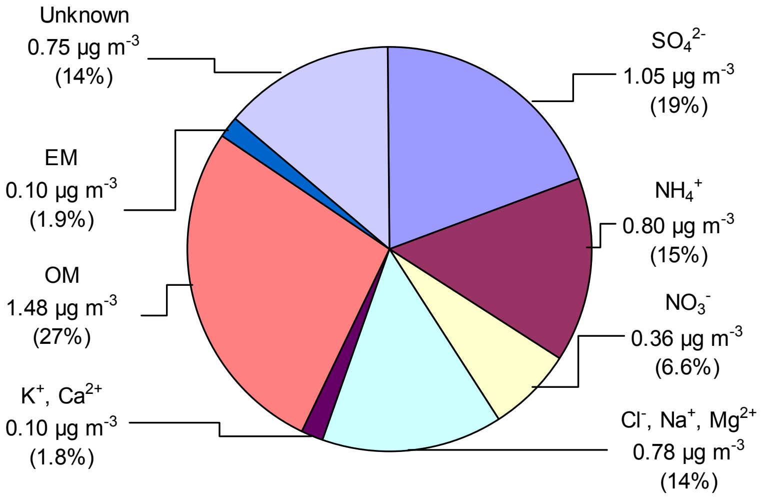

Figure 10.6: Mass closure of PM_{10} (5.4 µg m^{-3}) at the rural background site Birkenes (2004).

Figure 10.7a 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 10.2). 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 10.7b). 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.

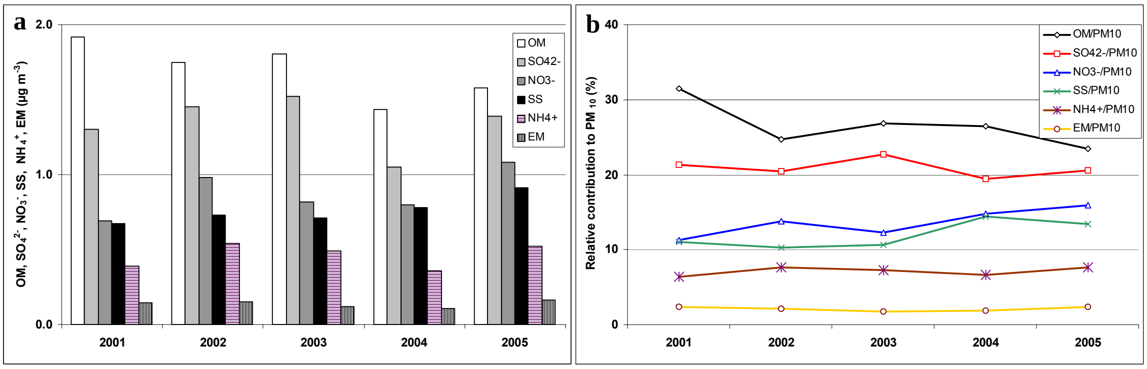

Figure 10.7: Annual variation of secondary inorganic constituents (SO_4^{2-}, NO_3^-, and NH_4^+), carbonaceous material (OM and EM), and sea-salts (Na^+, Cl^-, and Mg^{2+}) for the period 2001 – 2005 at the rural site Birkenes (µg m^{-3}) (a): Relative contribution of secondary inorganic constituents, 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}.

10.9 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 10.4).

Table 10.4: 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 matter1)	16.6	24	11.7	43	1.2	16
Elemental matter2)	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 10.8 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} .

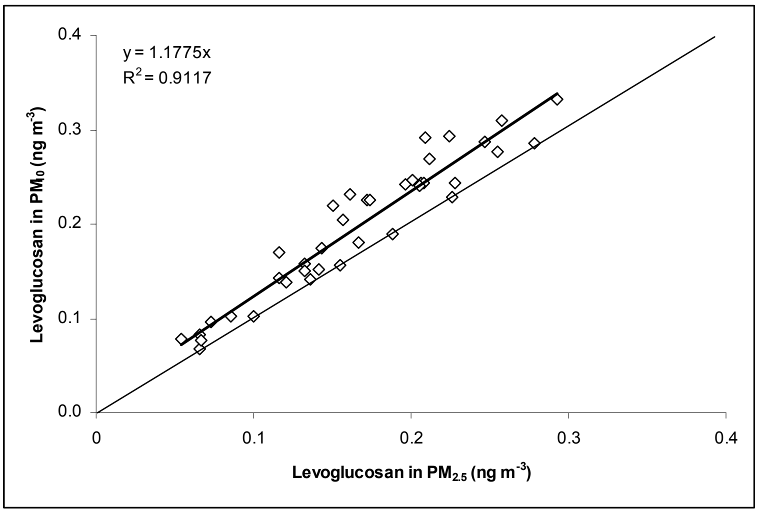

Figure 10.8: Scatter plot of levoglucosan in PM_{10} and $PM_{2.5}$ at Riksvei 4 (traffic site) in Oslo during the period 16 October 2004 - 4 April 2005.

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 10.4).

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 10.4). 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}.

10.10 Source apportionment of particulate matter by positive matrix factorization

Based on the chemical data summarized in Table 10.4, 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 10.5.

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 10.5: 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 10.5) 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 10.8, 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”).

10.11 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

11 National PM assessment report – Slovak Republic

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11.1 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 11.1. 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).

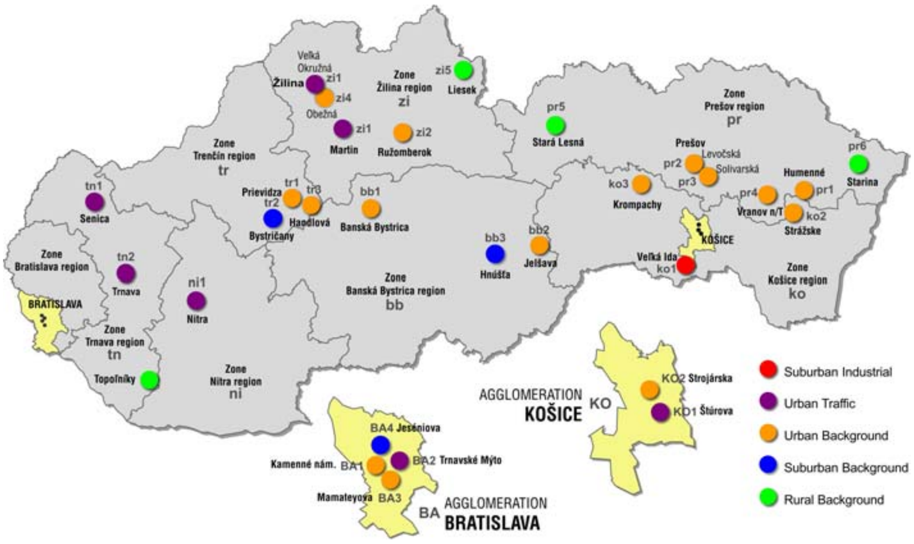

Figure 11.1: National air quality monitoring network in Slovakia (status in 2005).

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.

11.2 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 11.2. 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 11.1) 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 11.1: 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

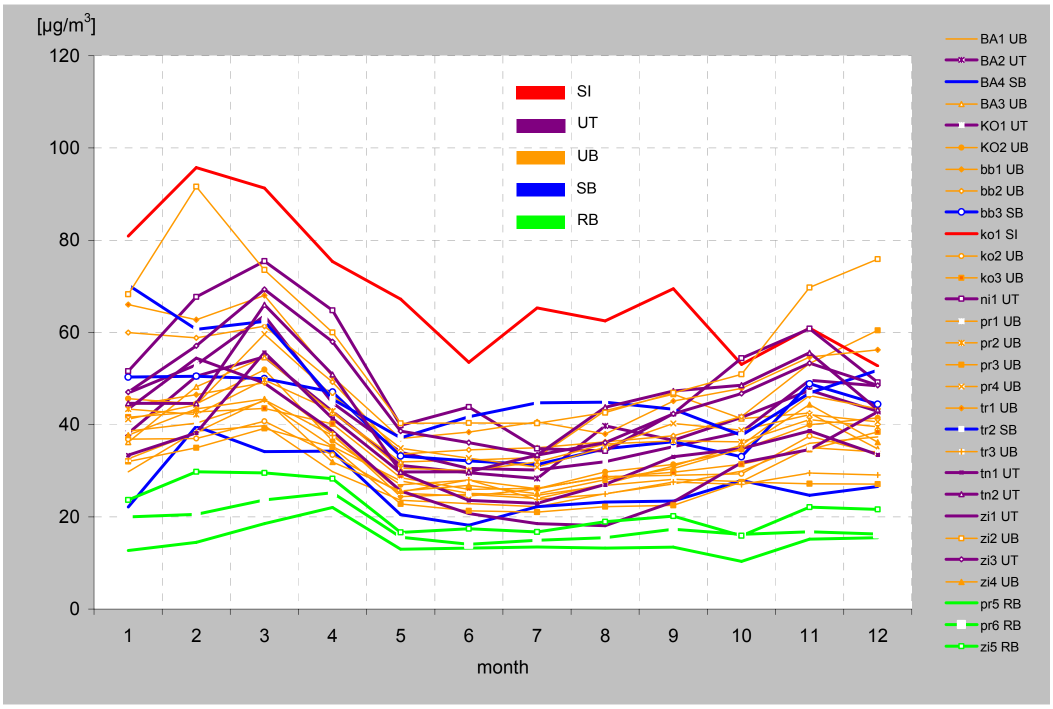

Figure 11.2: Monthly course of PM$_{10}$ concentration in Slovakia (2003-2005 average).

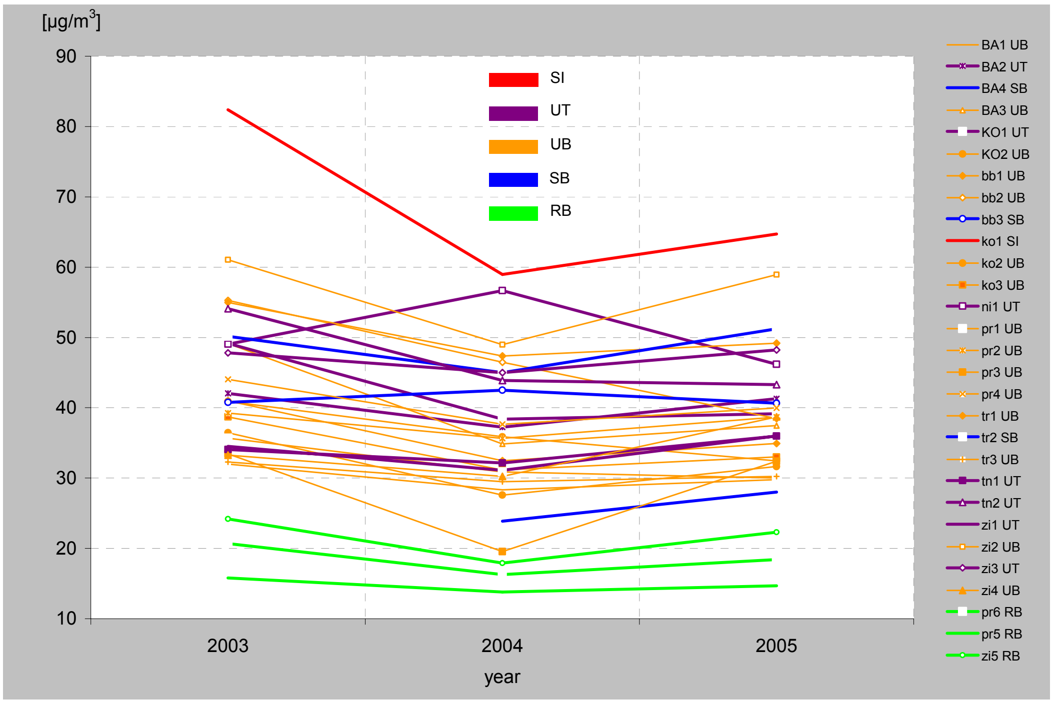

Figure 11.3: Yearly course of PM$_{10}$ concentration at the Slovak monitoring stations.

11.3 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 11.4 and Figure 11.5.

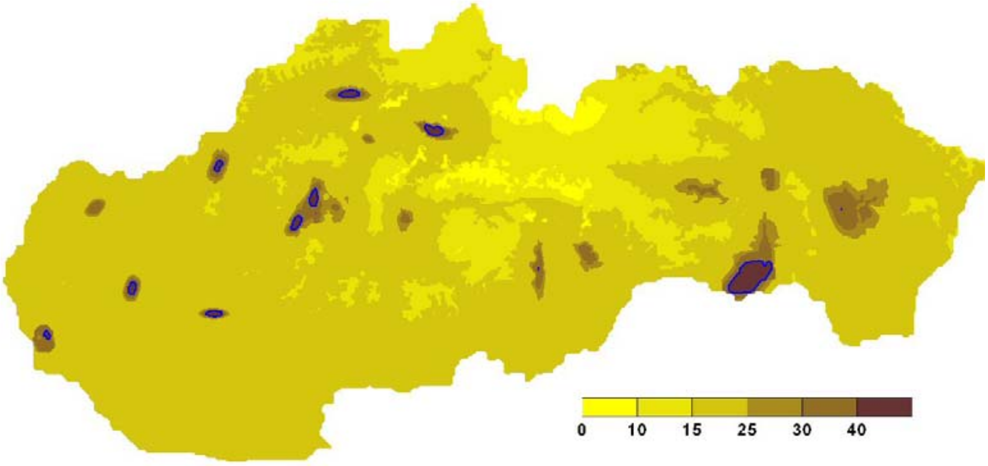

Figure 11.4: Annual average concentration of PM_{10} [$\mu g.m^{-3}$] – Slovakia, 2005.

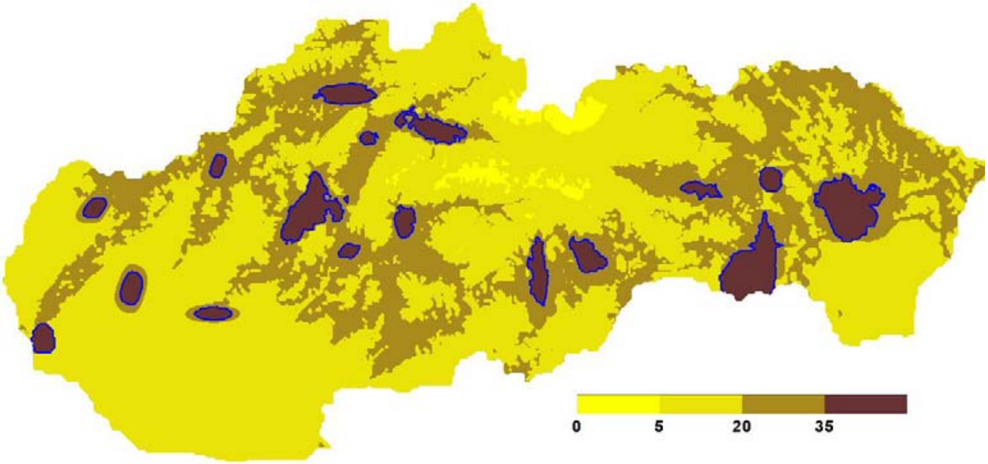

Figure 11.5: Exceedance (in days) of 24-h concentration of PM_{10} (50 $\mu g.m^{-3}$) - Slovakia, 2005.

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).

11.4 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 11.2). 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 11.2: Sulphate and nitrate concentrations in PM at some Slovak EMEP stations.

EMEP station		SO_4 [$\mu g.m^{-3}$]			NO_3 [$\mu g.m^{-3}$]			SO_4/PM_{10} [%]			NO_3/PM_{10} [%]		
		2003	2004	2005	2003	2004	2005	2003	2004	2005	2003	2004	2005
Starina	SK06	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

11.5 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 “noncontrollable” 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.

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12 Atmospheric particulate matter in Spain: levels, composition and source origin

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12.1 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.

12.2 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.

12.3 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 12.1 and Table 12.1.

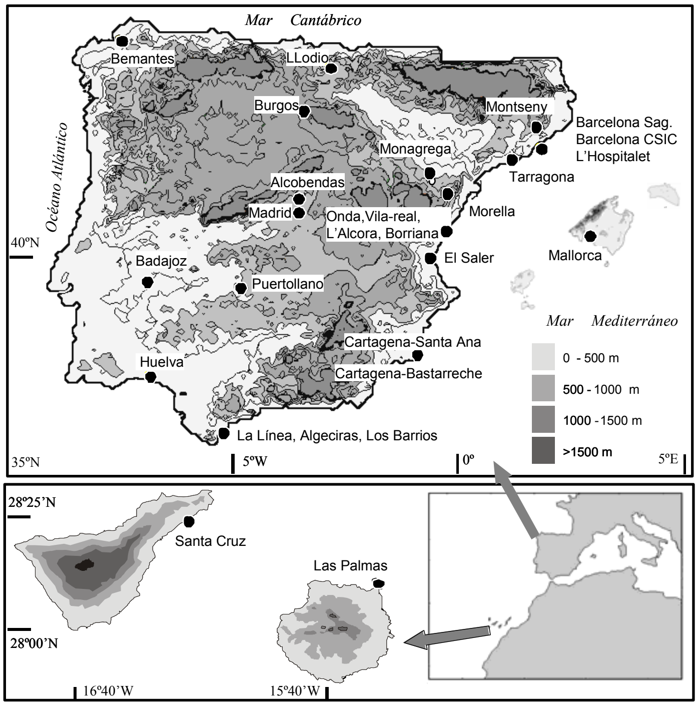


Figure 12.1: Location map of all monitoring stations across Spain discussed in this study.

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 12.2. 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 12.1: 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

12.4 Results and interpretation

12.4.1 PM levels

According to the character of each monitoring site, PM_{10} and $PM_{2.5}$ concentrations (in µg/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 12.2 and Table 12.2). $PM_{2.5}$ concentrations are usually 40-75% those of PM_{10} at any given site. The $PM_{2.5}/PM_{10}$ ratios (Figure 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 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 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 exceedences (>50 µg/m^3) at this monitoring regional background site over this period were caused by North African dust outbreaks. The oposite 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 12.2: 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
MEP stations	13-21	ND	ND	--	2-4	1-2	ND		
ural 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%)
rban 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%)
rban –industrial ackground	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%)		
raffic 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
MEP stations	8-14	ND	ND	--	ND	ND	ND		
ural 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%)
rban 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%)
rban –industrial ackground	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%)		
raffic 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 12.4 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 12.4 also shows that the 25 $\mu gPM_{2.5}/m^3$ 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 12.4).

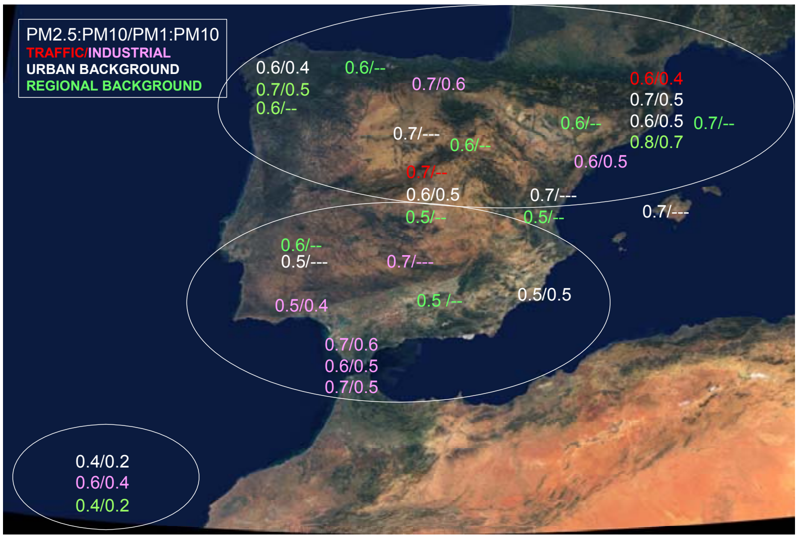


Figure 12.2: Average $PM_{2.5}/PM_{10}$ and PM_1/PM_{10} ratios indicating their regional, urban or traffic/industrial setting. Regional background data includes Spanish EMEP stations.

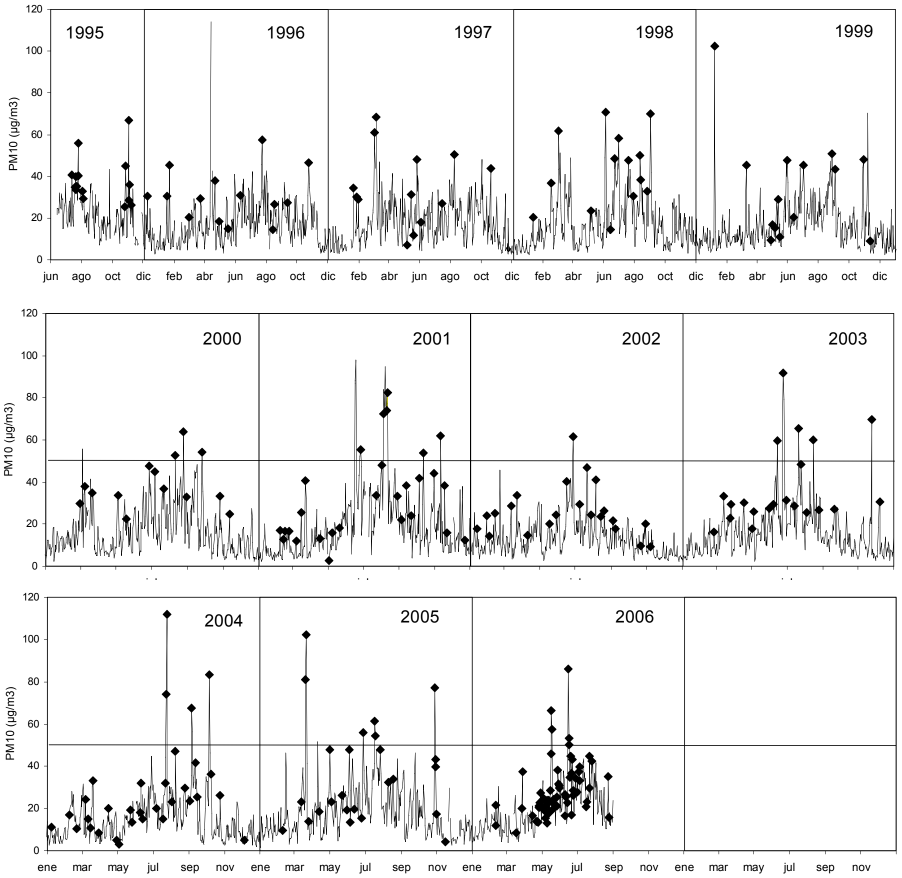


Figure 12.3: PM_{10} levels recorded from 1995 to 2006 at the Monagrega Regional background station and their relationship with the occurrence of African dust outbreaks (black rhombus), frequent during summer and in the February-March months. 54 out of 64 exceedances in these years were related to dust outbreaks. DLV: daily limit value.

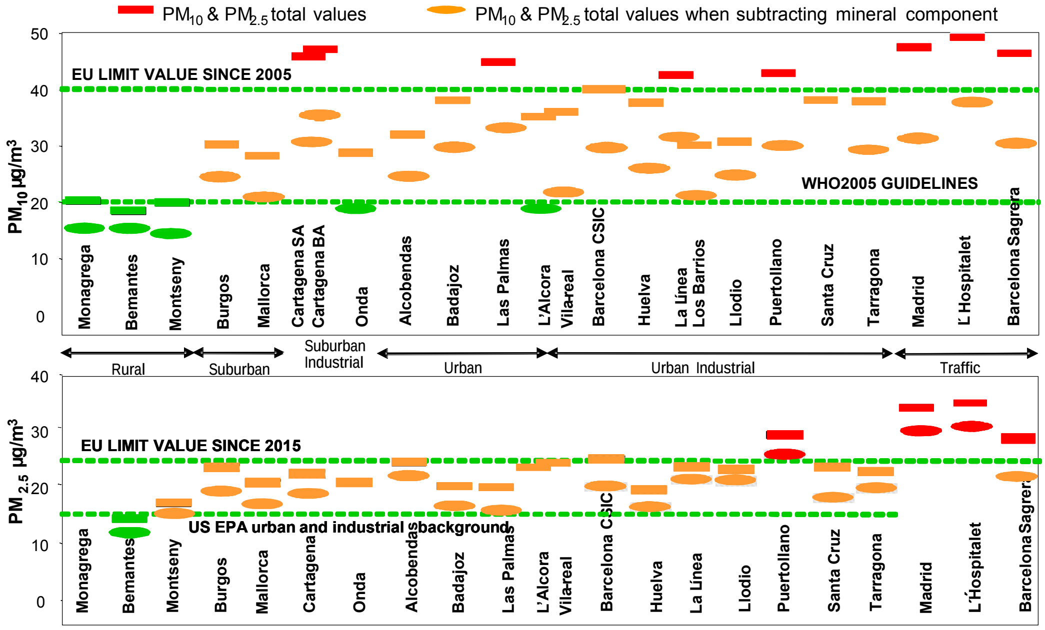


Figure 12.4: Top) Annual average PM_{10} values for each area studied across the country depending on the character of the site and compared with the allowed values for 2005 and the WHO 2005 air quality guidelines. Bottom) Same for the $PM_{2.5}$ values compared with the proposed limit value for 2015 and the US EPA limit value.

As we have discussed in previous publications (Querol et al., 2004c), and as is further illustrated by Figure 12.5, the current legislative daily PM_{10} limit value is more demanding than the annual limit value. Figure 12.5 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 exceedences/year (currently 35 or 90.4 percentile) equivalent to the annual limit value of 40 $\mu gPM_{10}/m^3$ should be well over 60-65 $\mu gPM_{10}/m^3$, instead of the current 50 $\mu gPM_{10}/m^3$. Or in other words: a) to meet the requirement of 35 exceedances of the daily value of 50 $\mu gPM_{10}/m^3$, an annual mean of around 30 $\mu gPM_{10}/m^3$ should not be exceeded; or b) the number of annual exceedances of the 50 $\mu gPM_{10}/m^3$ daily limit value recorded by stations measuring 40 $\mu gPM_{10}/m^3$ 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 $\mu g/m^3$ and a 90.4 percentile of around 60 $\mu g/m^3$ 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.

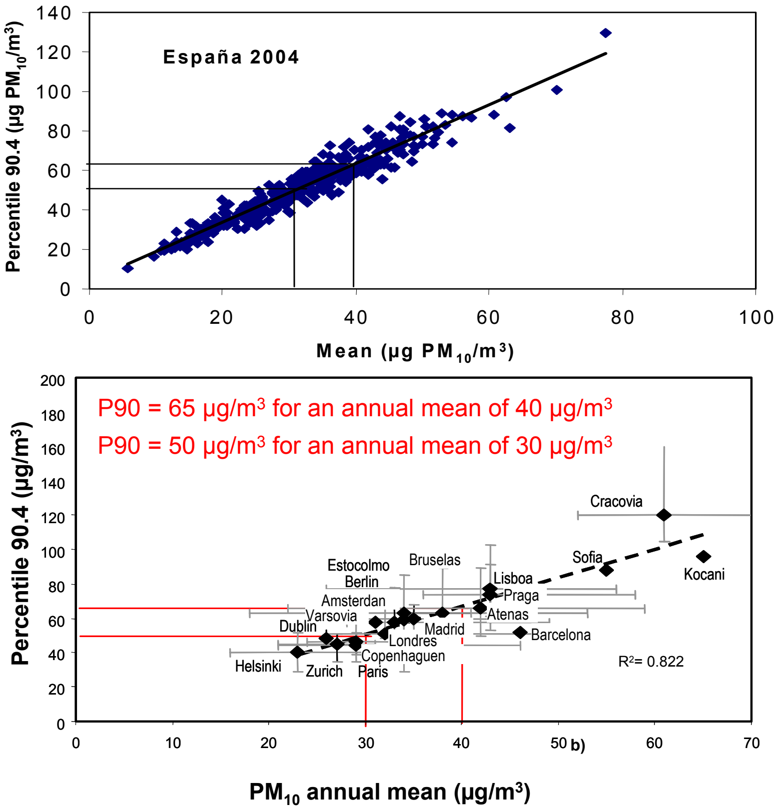
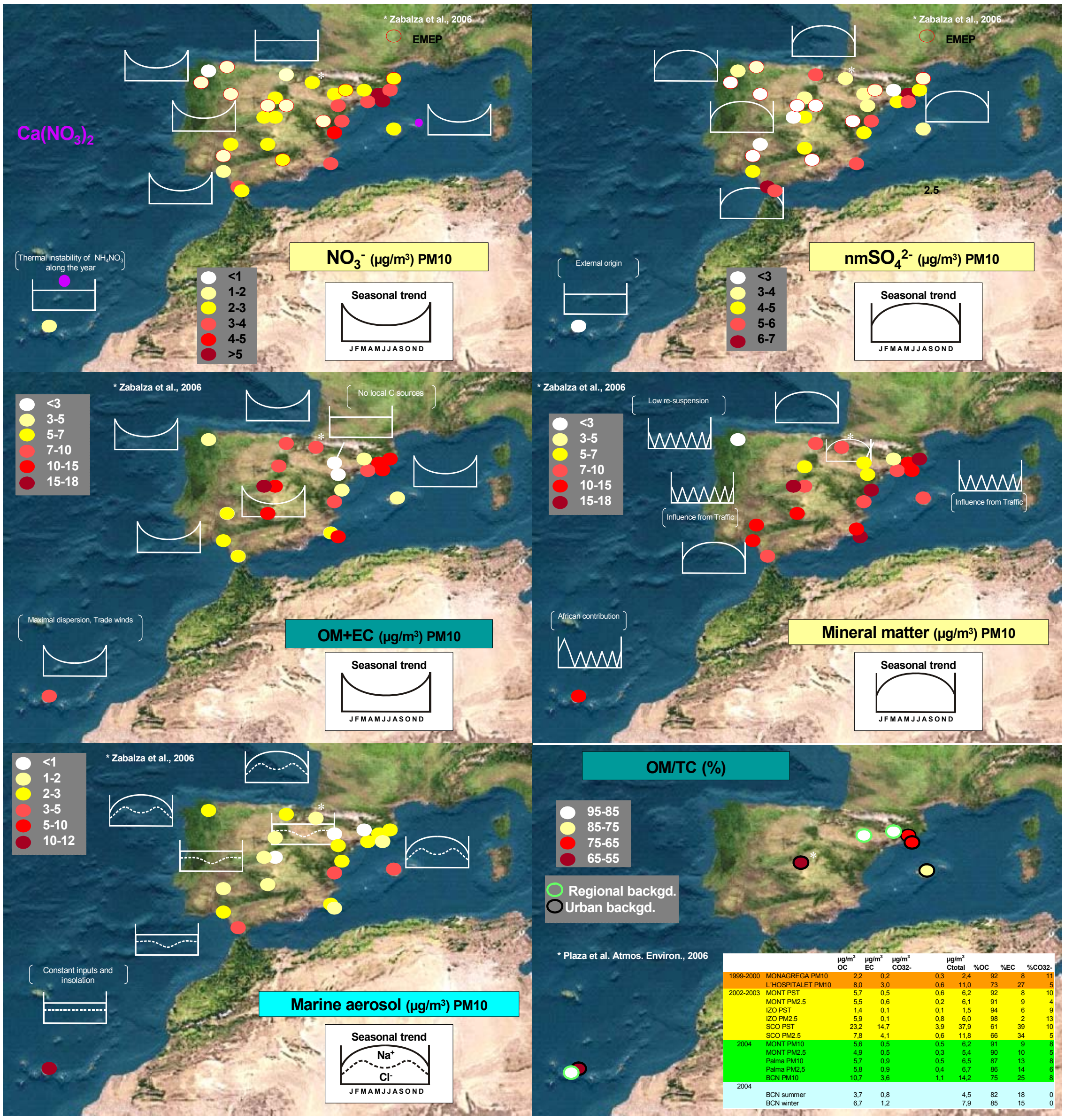


Figure 12.5: PM_{10} annual average levels against the percentile 90.4 values for a) all monitoring stations in Spain in 2004, and b) other main European stations (all data from Airbase, http://air-climate.eionet.eu.int/databases/airbase/index_html). See discussion in the text.

12.4.2 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 12.6 and Table 12.2). 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 12.6 and Table 12.2), 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 12.6a: 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.

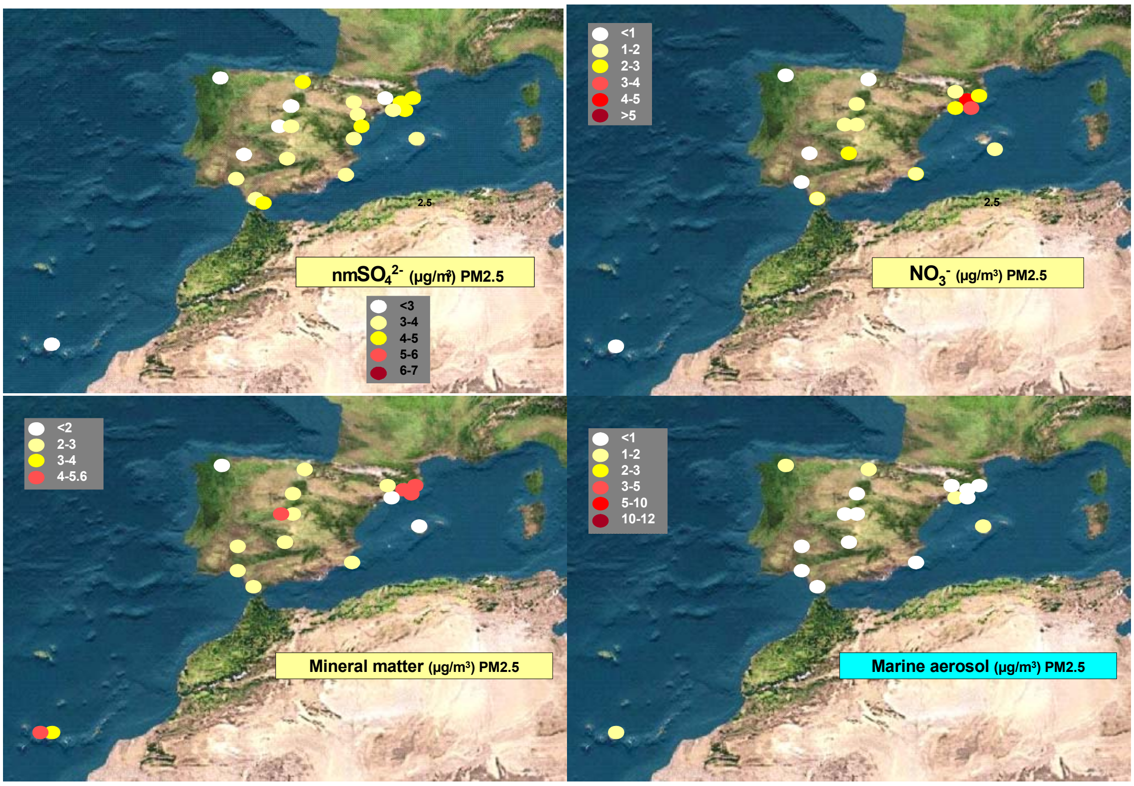


Figure 12.6b. Distribution of NO_3^-*, non marine* SO_4^{2-}*, mineral matter and marine aerosol (sea spray) levels (µg/m*^{3}*) across the country for* $PM_{2.5}$*. Seasonal tendencies are also shown when applicable.*

Figure 12.7 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 aplicable 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 12.8) 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).

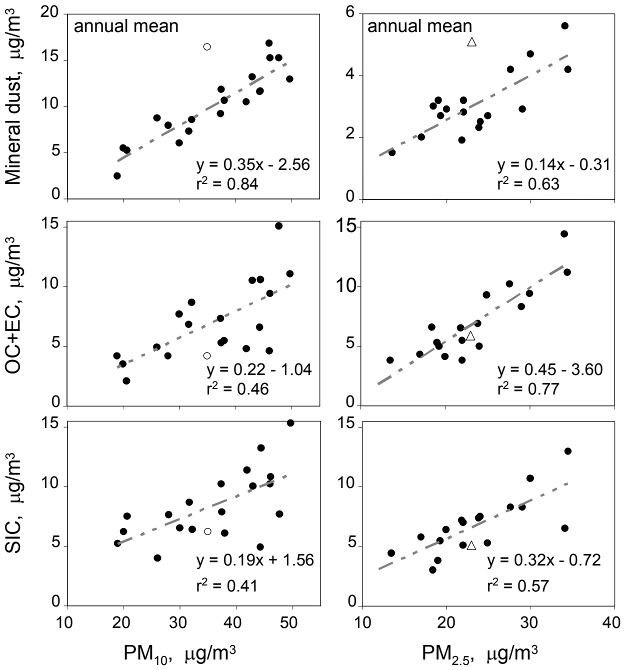


Figure 12.7: Annual mean levels of PM components versus PM_{10} and $PM_{2.5}$ levels across Spain (O: L'Alcora-industrial area of ceramic production and △: Santa Cruz de Tenerife urban-industrial background, none of them considered in the regression analysis).

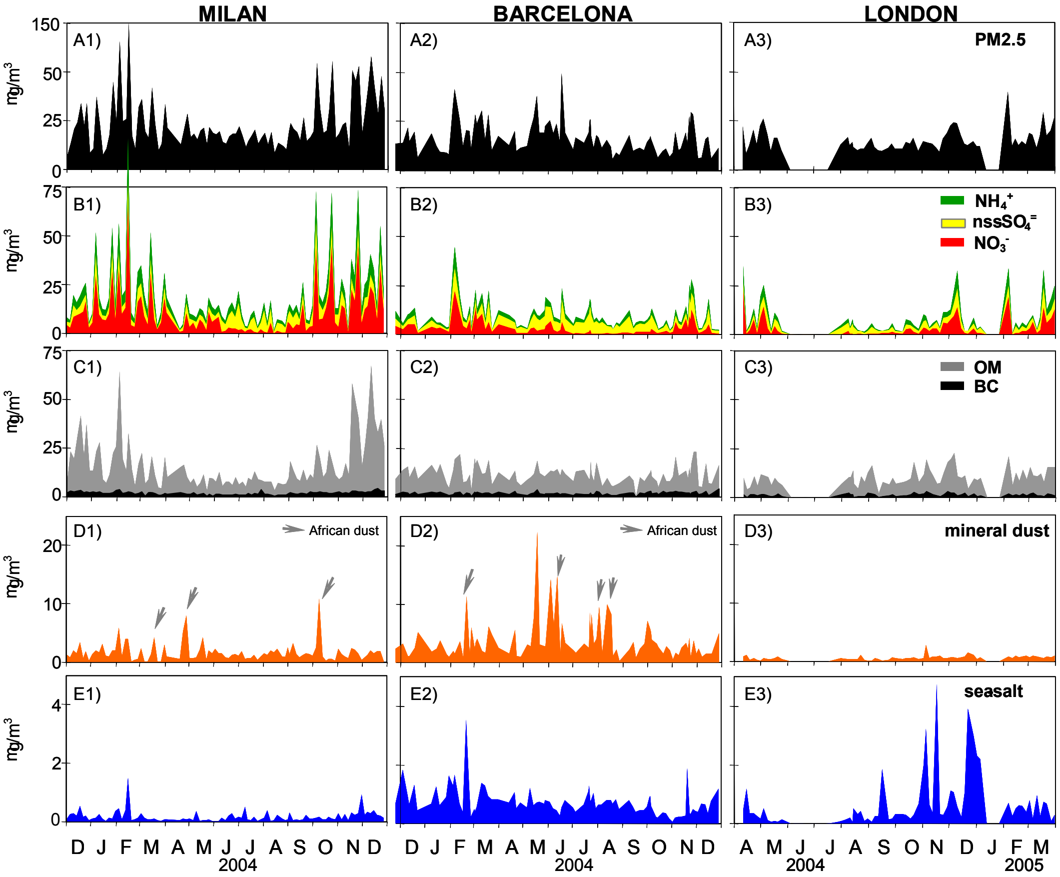


Figure 12.8: Comparison of PM2.5 speciation data from Milan, Barcelona and London obtained with the same methodology (Rodríguez et al., 2007), note the high mineral matter load at Barcelona, but the similarity of levels for the other PM components when compared with London.

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 12.6 and Table 12.2). 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 12.9 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 12.6 and Table 12.2). 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 12.9), 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.

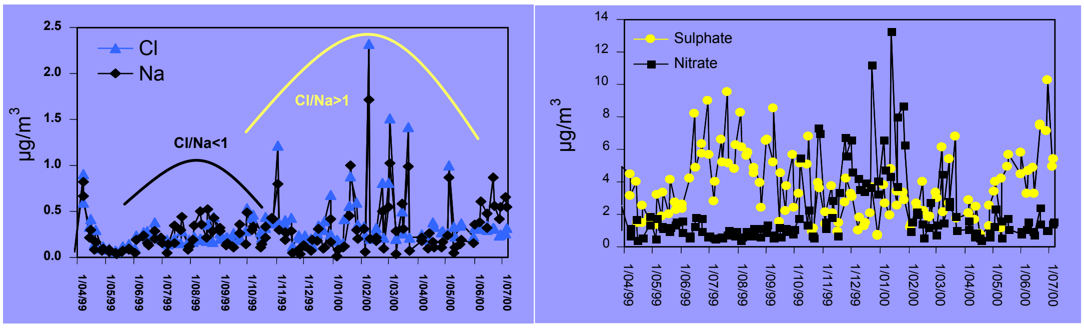


Figure 12.9: Levels of marine components, sulphate and nitrate at the Monagrega inland regional background station registered from April 1999 to July 2000.

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 12.6). 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 12.8). 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 µg/m^3 (Table 12.3) 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 12.3 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 12.3: 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 this 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.

12.4.3 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 12.4), 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 $\mu g/m^3$), but only 3–15% in the Peninsula (0.7–3.4 $\mu g/m^3$). In the Central regions (Madrid and Monagrega), this fraction contributes with only 0.5–1.0 $\mu g/m^3$ whereas in the coastal areas it reaches 2–3 $\mu g/m^3$. 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 $\mu g/m^3$. 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 $\mu g/m^3$). 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 $\mu g/m^3$).

Table 12.4: 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.

12.4.4 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 $\mu gPM_1/m^3$, much reduced than in $PM_{2.5}$ (2-6 $\mu gPM_{2.5}/m^3$). 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 $PM_{2.5-1}$ 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 12.10, 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 $PM_1/PM_{2-5-1}/PM_{2.5-10}$, fractions respectively).

c) Conversely, mineral dust and sea spray aerosols are mainly coarse in size (10/20-25/65-70% in the $PM_1/PM_{2-5-1}/PM_{2.5-10}$, 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 $PM_1/PM_{2-5-1}/PM_{2.5-10}$, 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 $PM_1/PM_{2-5-1}/PM_{2.5-10}$, 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 $PM_1/PM_{2-5-1}/PM_{2.5-10}$, 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 $PM_1/PM_{2-5-1}/PM_{2.5-10}$, fractions respectively). These species are very hydrophilic and tend to accumulate water (the main cause of the unaccounted determination).

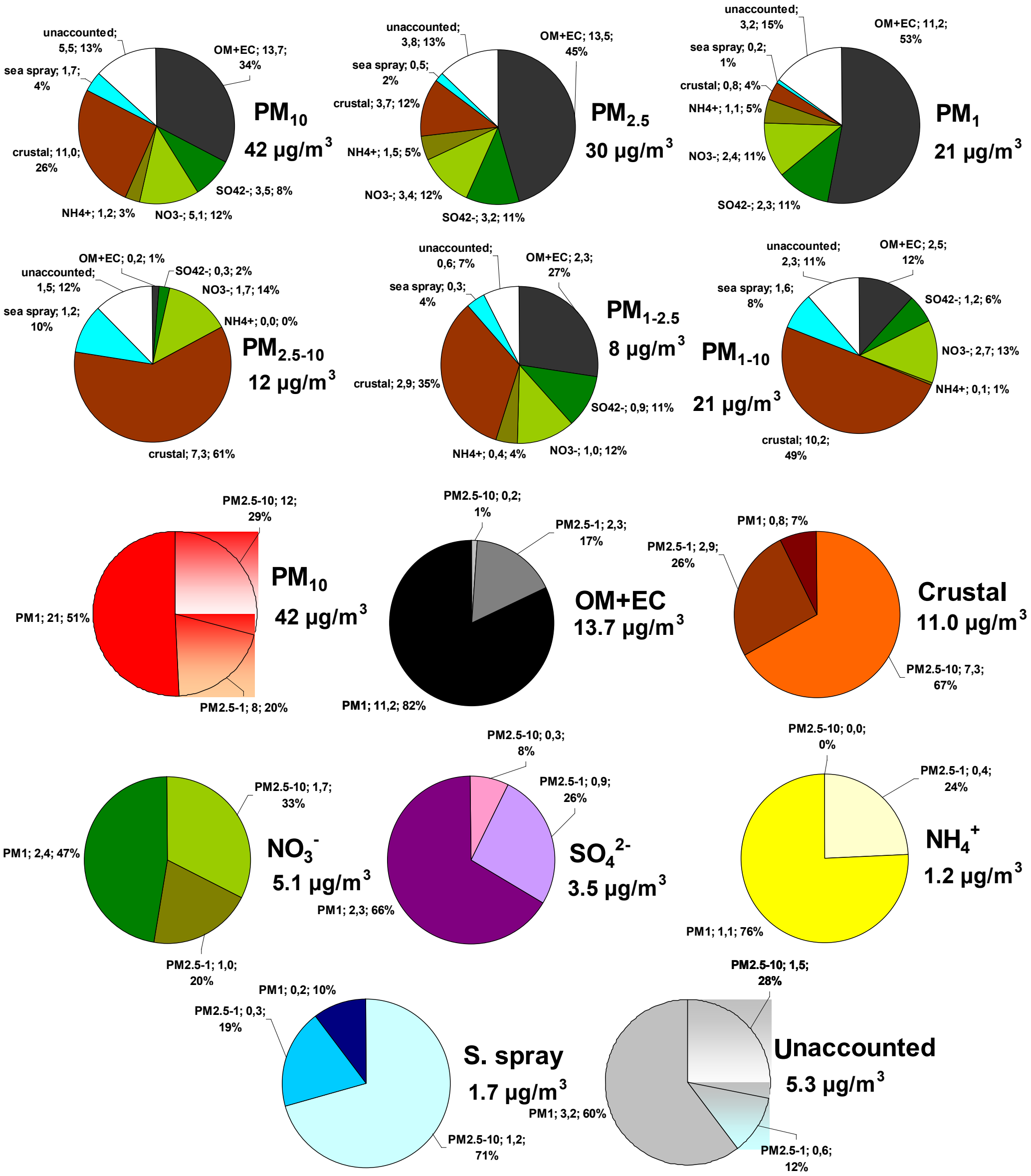


Figure 12.10:Mean speciation data for PM_{10}, $PM_{2.5}$ and PM_1 obtained at an urban background site of Barcelona, from 10-10-2005 to 08-01-2006, n=22 samples for each of the 3 PM fractions obtained simultaneously. $PM_{2.5-10}$ and $PM_{1-2.5}$ obtained by difference.

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13 PM$_{10}$ and PM$_{2.5}$ gradients through rural and urban areas in Sweden

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13.1 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/m^3 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/m^3 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.

13.2 Measurement methods and network

13.2.1 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.

13.2.2 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[18], Sveavägen[19] and Norrlandsgatan[20]) and one urban background station at roof level; ~20 meter above street (Rosenlundsgatan[21]) in the city.

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[18] Hornsgatan is 24 meter wide street canyon with 24 meter buildings and 35 000 vehicles/day.

[19] Sveavägen is a 30 meter wide street canyon with 24 meter buildings and around 35 000 vehicles per day.

[20] Norrlandsgatan is 15 meter wide with 20 meter high buildings and around 10 000 vehicles per day.

[21] 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).

13.3 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 13.1 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 13.2 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 µg/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.

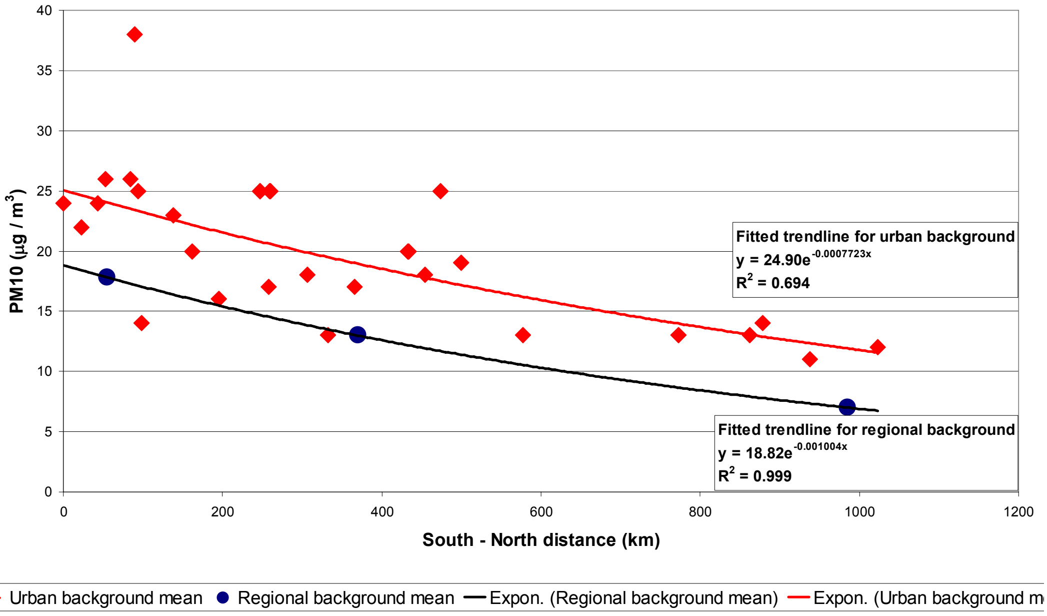

Figure 13.1: Winter half-year mean PM_{10} concentrations for urban and regional background sites are shown versus the distance from the very south of Sweden. Exponential curves have been fitted separately for the urban and regional background concentrations versus distance (with the southernmost station 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.

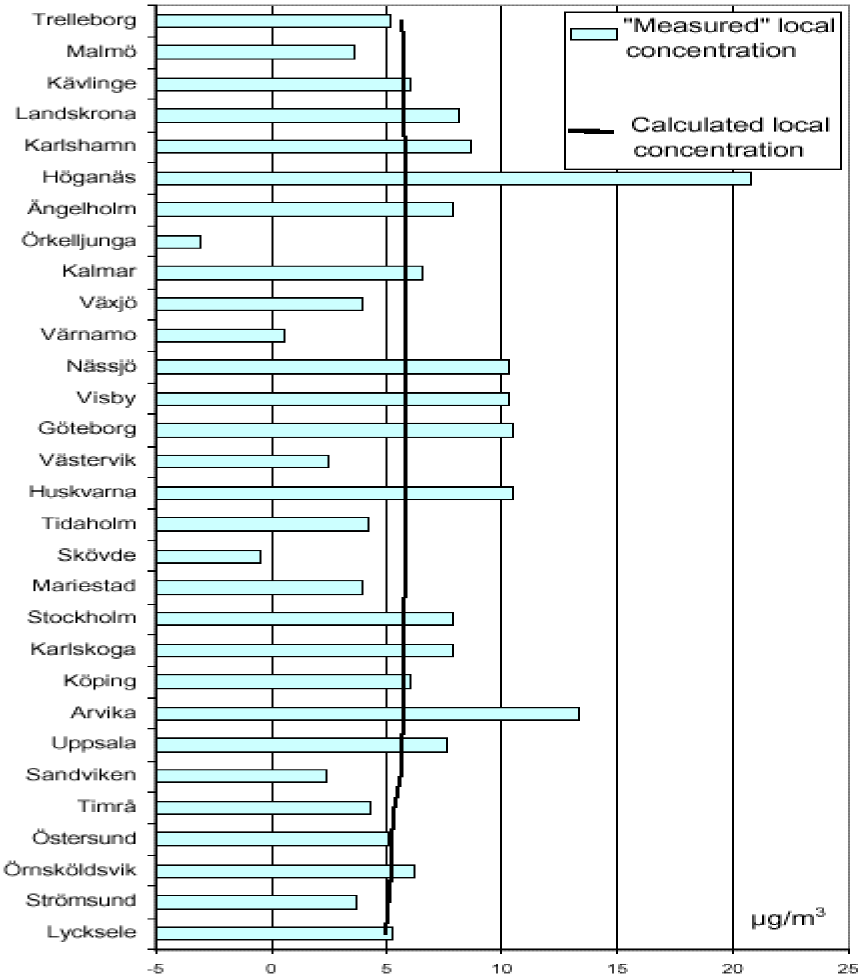

Figure 13.2: The calculated local PM_{10} contribution compared with the measured urban PM_{10} concentration when the rural background particle PM_{10} concentration is subtracted (from Forsberg et al., 2005).

13.4 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 13.3. 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.

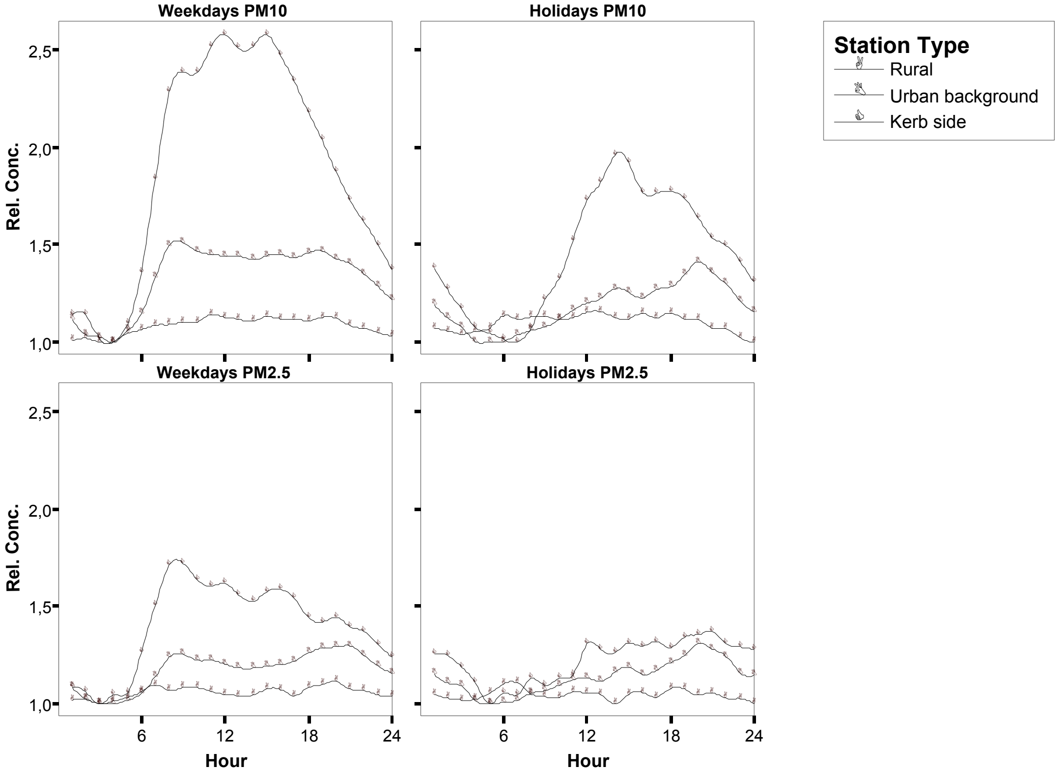

Figure 13.3: Diurnal variation of PM_{10} and $PM_{2.5}$ during weekdays and holidays at rural, urban background and kerb side sites. The concentrations are given in relative units, where the daily minimum (one hour average) for each site type is 1.0.

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 13.4). 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 13.10).

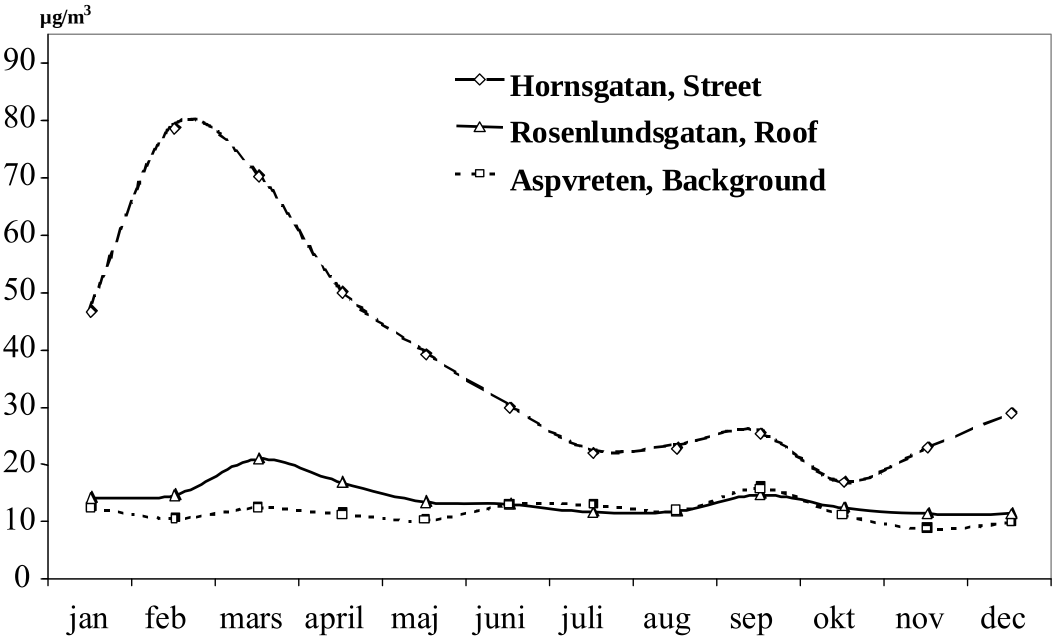

Figure 13.4: Monthly mean concentrations of PM_{10} at kerbside (Stockholm), urban background (Stockholm) and a rural site (70 km's south of Stockholm) during a year

13.5 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 13.5). 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 ($PM_{2.5}$).

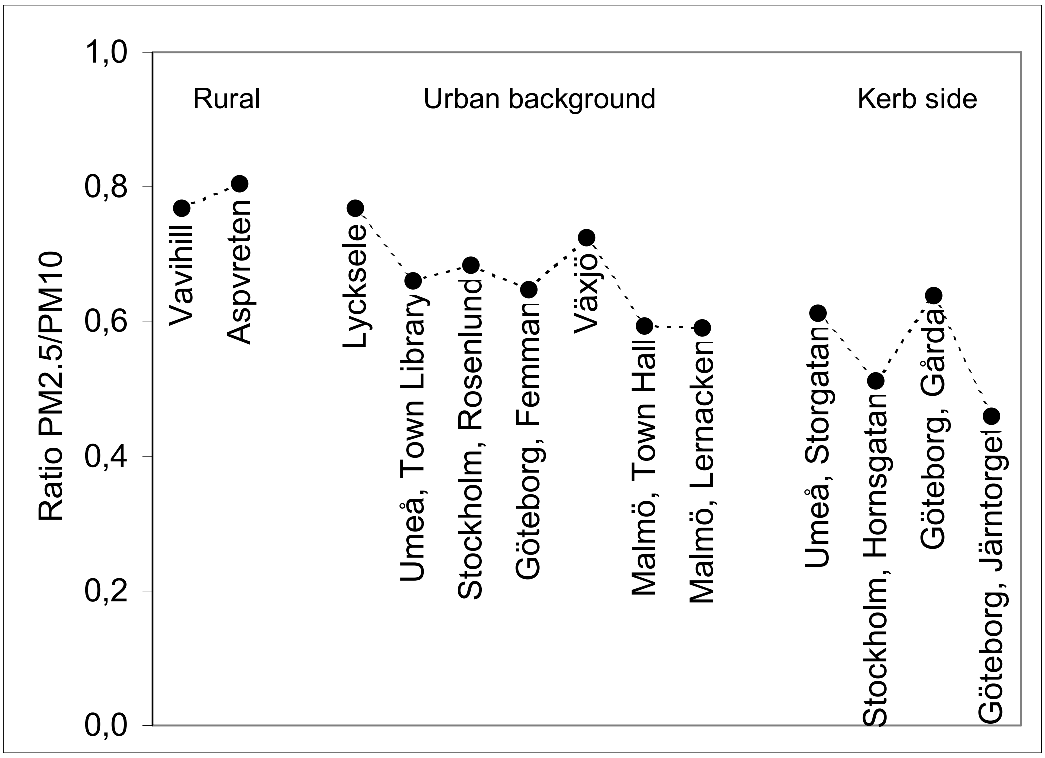

Figure 13.5. Average ratio $PM_{2.5}/PM_{10}$ at thirteen Swedish sites.

13.6 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.

13.6.1 Temporal variation of PM_{10} and PNC

Figure 13.6 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 springtime 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).

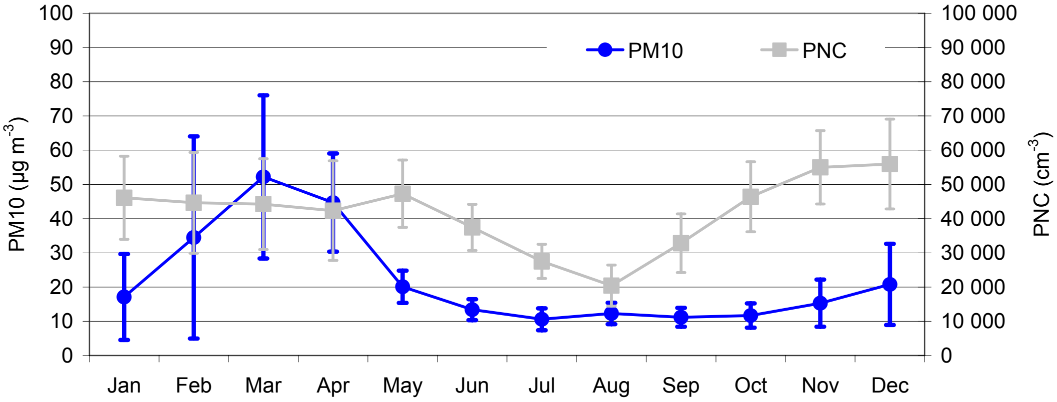

Figure 13.6: Monthly average total particle number (PNC) and PM_{10} concentrations at Hornsgatan in central Stockholm (street canyon). The concentrations represent the contribution from the local traffic on this street since the measured urban background concentrations of PM_{10} and PNC have been subtracted. 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 13.8 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.

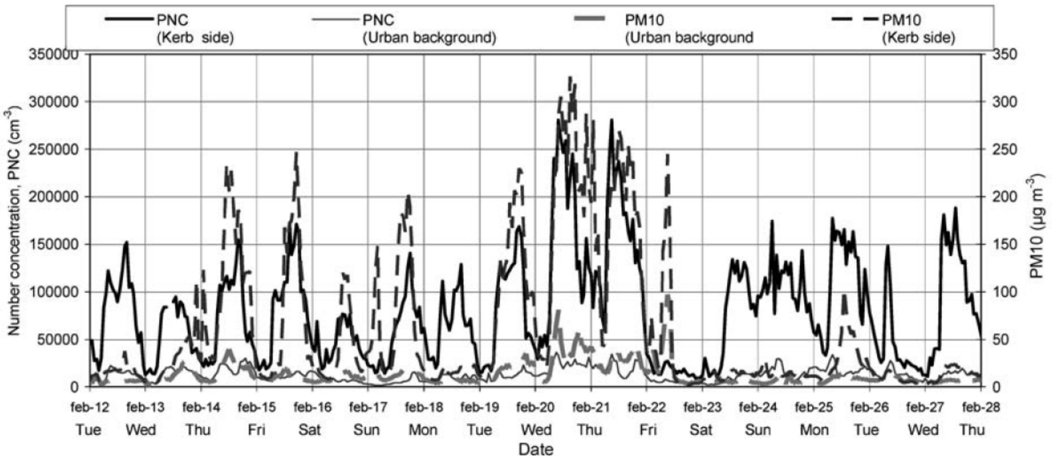

Figure 13.7: Total particle number (PNC) and PM_{10} concentrations at kerb-side and urban background in central Stockholm (from Johansson et al., 2006).

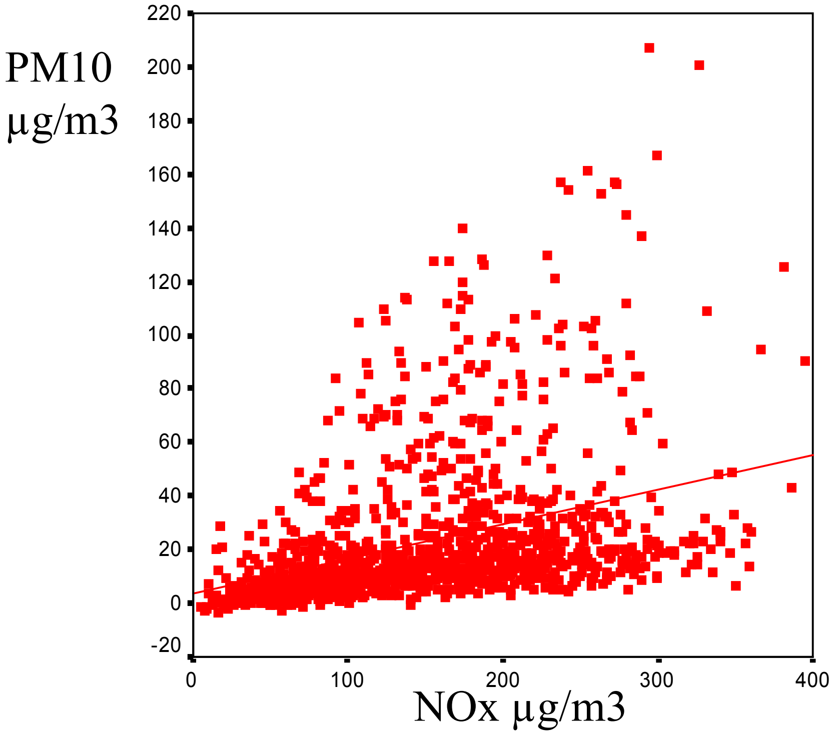

Figure 13.8: Daily average PM_{10} concentration plotted versus NO_x. Concentrations refer to street canyon of Hornsgatan (3 m above street) and the roof top concentrations have been withdrawn, so that only the local street traffic contributions are included.

In Figure 13.9 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.

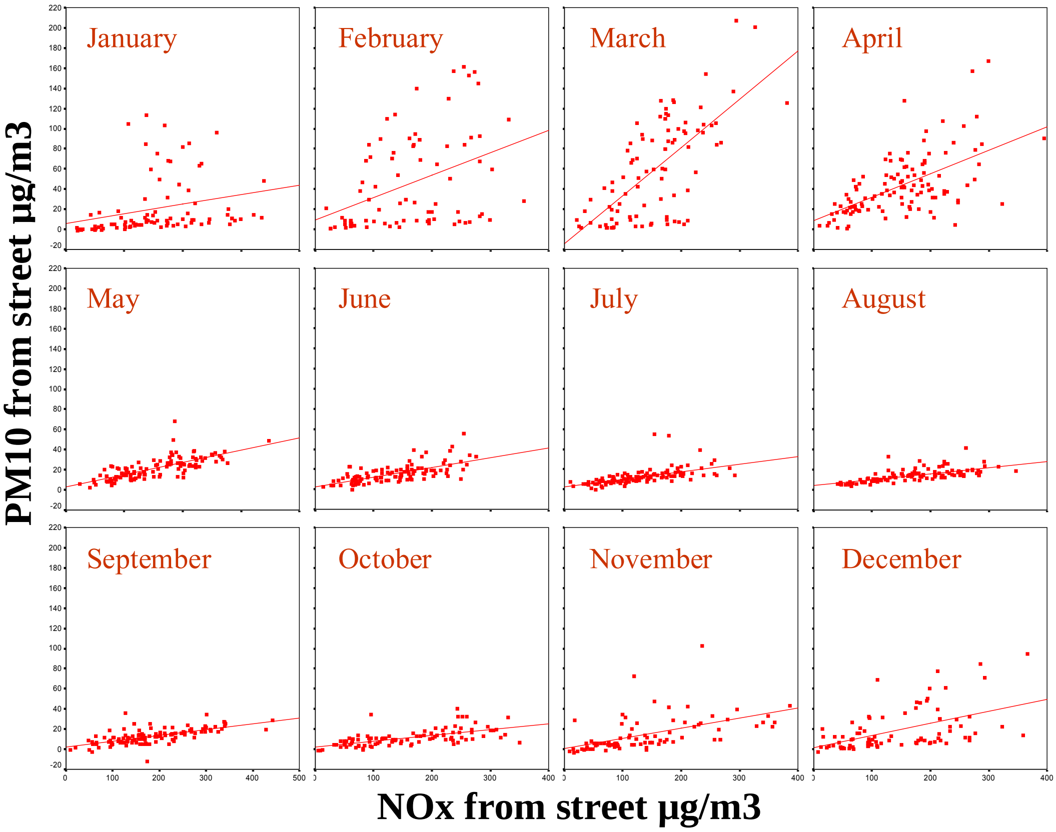

Figure 13.9: Scatter plots of PM_{10} versus NO_x. Data from Hornsgatan in Stockholm. The data are daily averages of the concentrations at the street minus the concentration at the roof top, indicating the contribution only from the local traffic in the street.

Measurements of the particle size distribution in different urban environments of Stockholm revealed the influence of different sources (See Figure 13.10). 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.

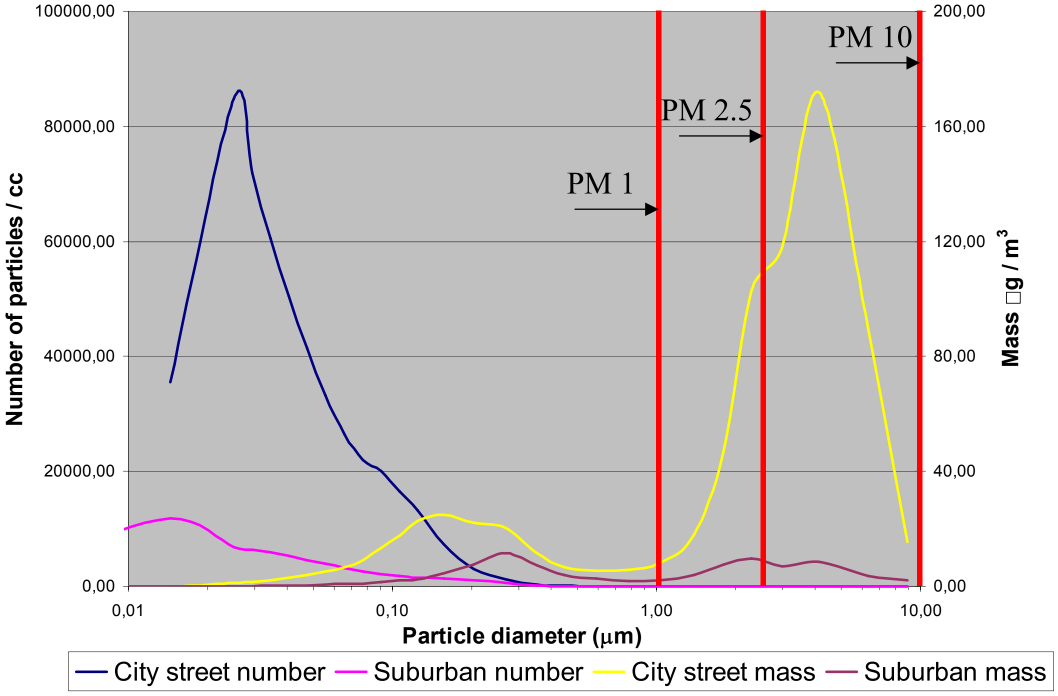

Figure 13.10: Mass and number particle size distributions from a highly trafficked street canyon and one suburban back road in Stockholm.

13.6.2 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 13.1; 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 13.11 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 13.1: 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	

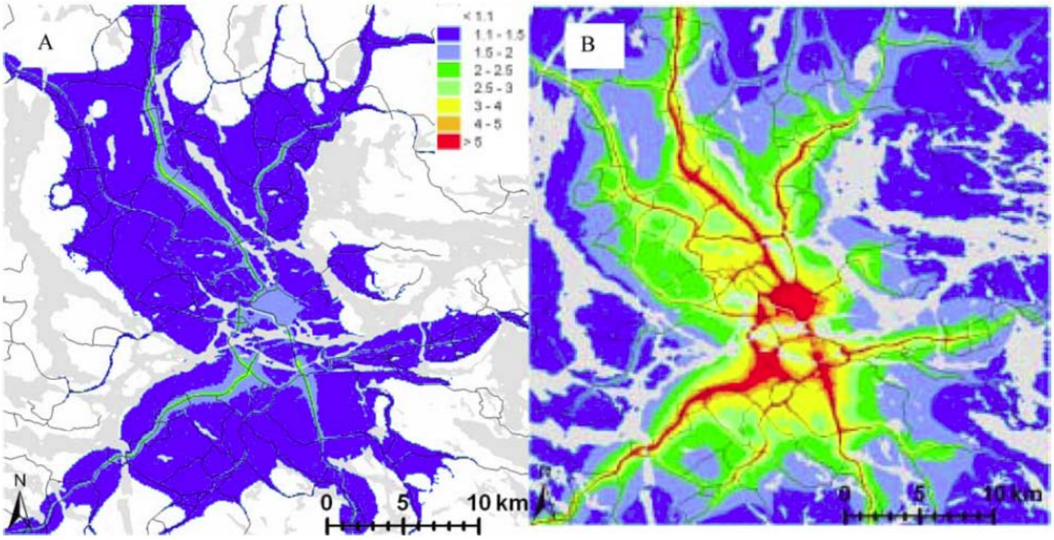

Figure 13.11: Model calculated relative spatial variation of annual mean concentrations of A) PM_{10} and B) PNC (total particle number concentration) in Greater Stockholm area (35 km x 35 km). The colours indicate the increase above rural background (10 µg m^{-3} for PM_{10} and 3500 cm^{-3} for PNC) due to local traffic emissions in the area. From Johansson et al. (2006).

13.7 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.

13.8 References

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14 PM_{10} and $PM_{2.5}$ gradients through London

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14.1 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 14.1 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 14.1 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 14.1: 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}.

14.2 $PM_{2.5}$ 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 14.2. 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 14.2: 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.

14.3 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 14.3. 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 14.3: 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.

14.4 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 14.4 and Table 14.5. 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 14.4: 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 14.5 for $PM_{2.5}$ are larger than those for PM_{10} in Table 14.4. 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 14.5: 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

14.5 4. 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.

14.6 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.

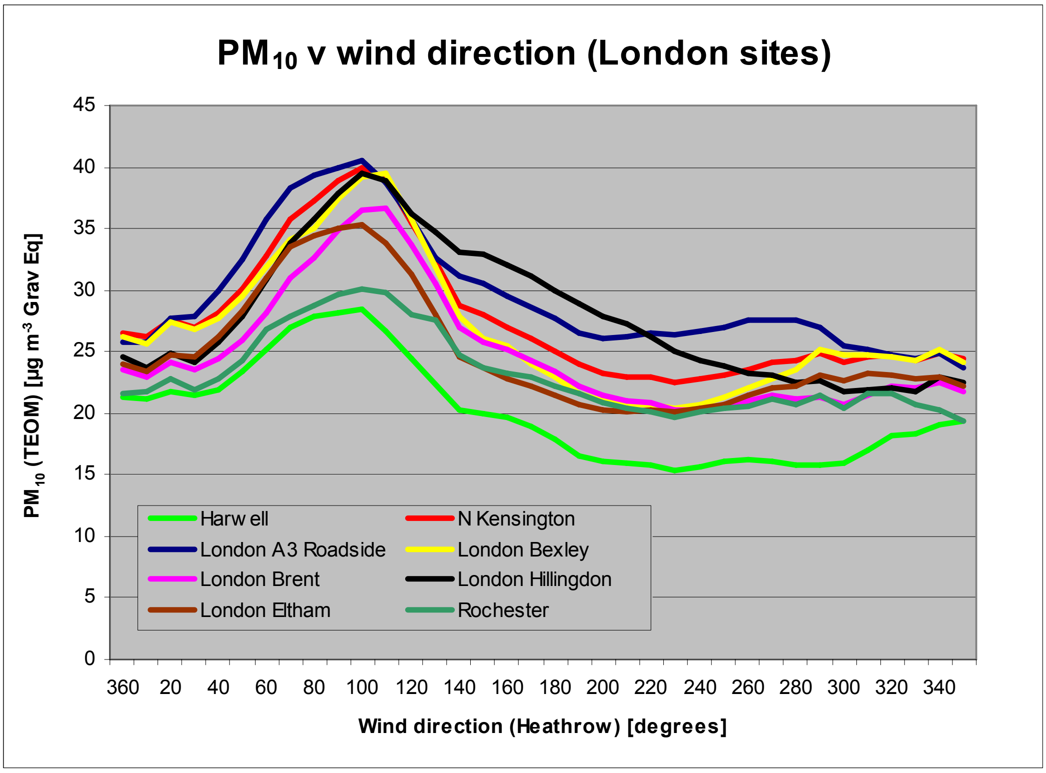

Figure 14.1: Mean PM_{10} concentrations at a range of monitoring sites across London plotted against wind direction sector.

Figure 14.1 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.

14.7 6. 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 14.6 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 14.6: 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 14.7 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 14.7: 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

14.8 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 14.2. Annual mean concentrations fell steadily from about 30 $\mu g\ m^{-3}$ in 1992 to about 22 $\mu g\ m^{-3}$ in 2000 and have remained rather constant during the 2000-2006 period. Figure 14.2 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 14.2: 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.

14.9 Acknowledgements

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