CHAPTER 5

Characterization of PM2.5 in Flanders

Fine particulate matter is a hot item in the scientific society nowadays. Besides the uncertainty about its influence on our global climate, the lack of profound information about its possible health effects makes it to be the challenge of the next decennia. Our research group carried out several projects for the Flemish environmental governmental administration in order to characterize the PM2.5 fraction. A variety of analytical techniques, among which TW-EPMA, was applied 1) to compare different popular and new methods for determining PM2.5 concentrations, and 2) to compare the composition of the air (gases and particles) at different locations in Flanders.

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1. Introduction

1.1 TSP, PM10 and PM2.5

'Total suspended particulates' (TSP) and 'particulate matter' (PM) are frequently used terms in aerosol research. The first is defined as the total of all the suspended particles or droplets in a sampled air volume; in other words, the TSP mass concentration represents the total mass of the aerosol particles in a sampled air volume. The second expression, PM, is used to denote only a specific fraction within TSP. Aerodynamic diameters (in µm) are added at the end of the abbreviation to exactly indicate which fractions. PM2.5 is the fraction that represents the particles with aerodynamic diameters smaller than or equal to 2.5 µm, while PM10 is larger than PM2.5, since it also contains the fraction PM10-2.5 in order to represent all particles with diameters smaller than or equal to 10 µm. Therefore, one could say that TSP corresponds to PM∞.

The need for referring to specific particle size fractions has a reason. Since we inhale 15 to 17 m³ of air per day on average, it is vital to assess the quality of our daily portion of air, and especially the composition of the fine particles is important. For the last decades, medical research and epidemiological studies in particular have provided strong indications that the smaller particle fractions have huge impact on human health. Fine to ultra-fine particle fractions are connected to acute mortality and morbidity effects, increased incidence of immune-inflammatory diseases (like allergy and asthma), increased incidence of lung cancer and cardiovascular diseases. [1,2,3] The smaller the particles, the deeper they can penetrate into the respiratory and cardiovascular systems, where they can trigger respiratory infections (in the lung tissue) and increase the plasmoviscosity and coagulability (in the blood stream), as illustrated in the figure below.

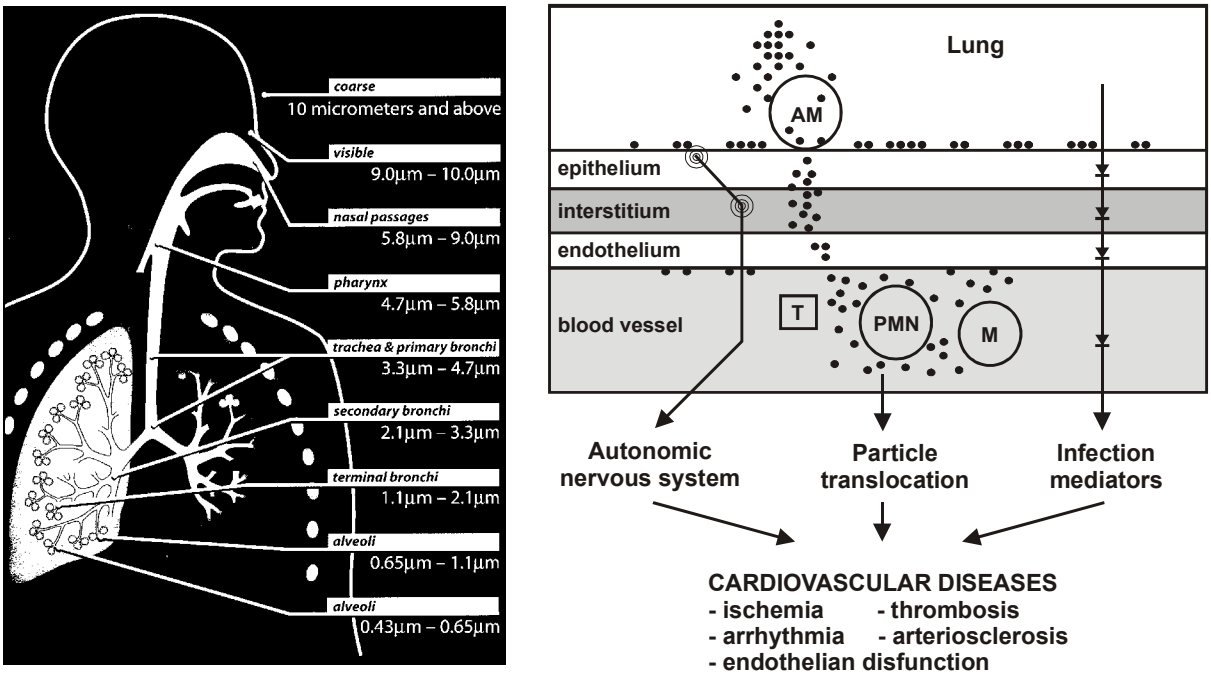


Figure 1: Schematic model of particle-body interactions leading to cardiovascular diseases
(made after [4,5]; AM = alveolar macrophage, T = thrombocyte, PMN = neutrophyle granulocyte, M = monocyte)

The health effects of long-term exposure to PM2.5 could eventually result in a loss of life expectancy. According to recent calculations, the life expectancy in Belgium, the Netherlands and Hungary was reduced with more than one year due to PM2.5 pollution.[6,7] A prognosis based on the expected evolution of PM2.5 towards 2010 and 2020 (due to reduction measures) shows that the impact of PM2.5 will decrease, but Belgium will probably still have one of the worst 'scores' within the EU.

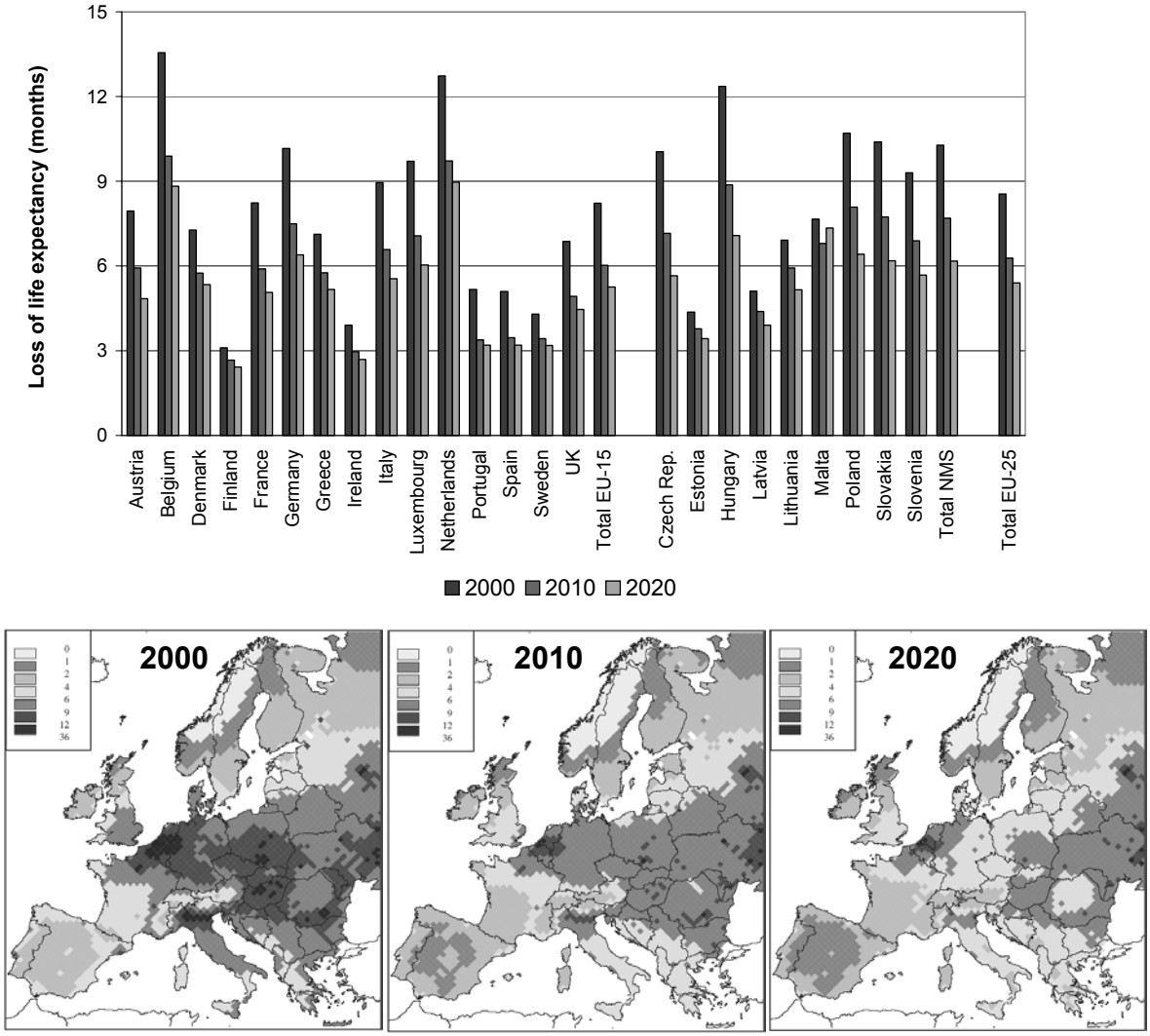


Figure 2: Loss of life expectancy (in months) due to anthropogenic PM2.5 in the EU [6]

Researchers ranked the different causes of loss of life expectancy in the Netherlands, and they found that the exposure to particulates is a major contributor.[6] Their ranking is as follows: 1) domestic accidents, 2) ***long-term exposure to particulates***, 3) traffic accidents, 4) noise pollution, 5) lead in drinking water, 6) food-borne causes, 7) *passive tobacco smoking*, 8) ***short-term exposure to particulates***, 9) indoor radon, 10) damp houses. The ranking in Flanders and Belgium is probably not much different.

The economic cost of the air pollution by PM2.5 can also be calculated. The cost of PM2.5 is estimated to be 14 000 euro/ton, which is much higher than the cost for other common air pollutants (e.g. 5 200 euro/ton SO_2 and 4 200 euro/ton NO_x).[8] The additional damage due to PM2.5 deposition in cities or urban areas is 33 000 euro/ton. The total economic cost of PM2.5 for Flanders in 2003 was estimated at 1.1 billion euro (0.8% of the GNP).[9,10]

Over the years, researchers little by little discovered that the health and economical effects of the exposure to fine particulates are enormous. Therefore, the focus of aerosol research and sampler development has gradually shifted from TSP over PM10 to PM2.5.

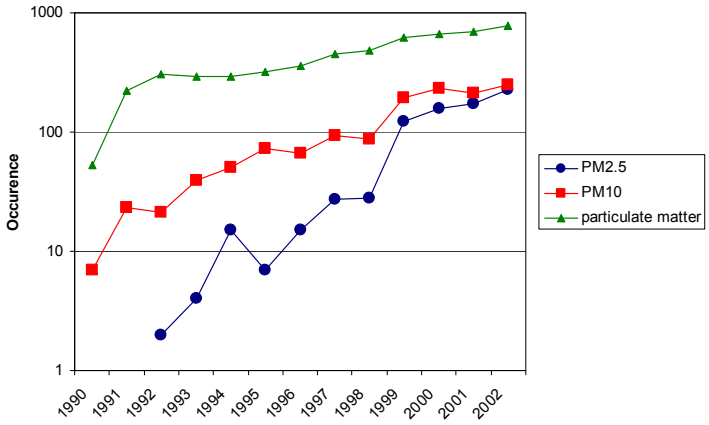


Figure 3: 'Particulate Matter', PM10 and PM2.5 in literature

The figure above shows the results of a search action in the Current Contents database of peer-refereed scientific articles. The keywords for our search were 'particulate matter', PM10 and PM2.5. If we assume that the citation of these terms corresponds to their importance for the scientific world, it can be observed that 'particulate matter' has indeed become an important item in literature, and that PM2.5 has caught up with PM10 over the last few years. It is expected that PM1 and PM0.1 are next in line, from the moment adequate samplers and analysis techniques have been developed.[2]

A similar trend can be found in environmental legislation and air quality guidelines. The focus in European legislation is now set on PM10, but a shift towards PM2.5 is to be expected within the next years. However, it is important to mention that the EU is not focused on PM2.5 only. The EU has decided to attack the problem of air pollution by a multi-pollutant and multi-effect approach, since all major air pollutants are connected to each other.[11] In other words, each pollutant should not be dealt with individually, but within a bigger framework. For example, NO_x, SO_2 and NH_3 are well-known for their role in acidification that causes damage to ecosystems, cultural heritage, etc. However, they are also major precursors for secondary particles in gas-to-particle conversions, so actions to reduce their emissions also have effects towards PM2.5 formation.

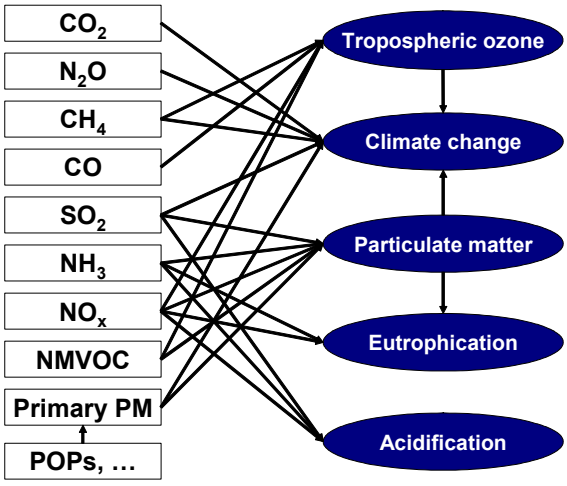


Figure 4: Illustration of multi-pollutant and multi-effect relationships

1.2 PM2.5 in Flanders

In order to comply with European directives, the Flemish government has to take actions to reduce the emission of several air pollutants. In 2001 strict national emission ceilings (NEC) were established for NO_x, NH_3, SO_2 and VOC (volatile organic compounds) that have to be met with in 2010 by the European member states.[12] At the same time, a European project called "Clean Air For Europe" (CAFE) started investigating which measures should be taken to control particulate matter. The effect of PM10 air quality guidelines, which were set in 1999, was to be evaluated, and the possibilities for new PM2.5 guidelines were to be investigated.
In Belgium, environmental legislation lies in the powers of Flanders, Brussels and Walloon, so the national emission quotas were distributed among these communities. In a joint-agreement, each of the communities decided to make the required efforts for reducing their individual emissions.[13] The reduction of traffic emissions is the only exception, since traffic is considered to be an (inter)national phenomenon, and therefore, its effects should be dealt with on the federal level. In Flanders, a research programme was started to investigate all of the possible policy scenarios for the emission reduction of air pollutants. The Flemish government decided that a diverse approach would be necessary to meet the emission ceilings, and that the first step would be to determine which sources were present in each of the different social sectors (agricultural, industrial, public, service). Afterwards, the main goal would be to find the highest reduction potentials at minimal costs.
After several sector studies were started, the Administration for Science and Innovation (AWI) set up another project to study PM2.5 in Flanders as well. The Flemish Institute for Technological Research (VITO) was asked to coordinate this project, called "Evaluation of policy scenarios related to fine dust (PM2.5)", but several Flemish authorities and the University of Antwerp were also involved.[9]

The main task of this project was to work out different *no-regret* policies to efficiently reduce the impact of PM2.5 in Flanders, taking into account existing uncertainties in our knowledge about particulate matter. Several subtasks were defined:

- Task 1: To give a critical survey of the international knowledge on the effects and mechanisms of PM2.5. This would lead to different impact scenarios (i.e. which pollution, reduction or any other action would lead to which reduction).
- Task 2: To make an inventory of the sources of PM2.5 (emission) and their effect on air quality (immission). An evaluation of the available knowledge would indicate the validity of the impact scenarios, and would enable to define gaps in the available knowledge.
- Task 3: To carry out additional immission measurements of PM2.5 in Flanders. This task would be an important support for the validation and refinement of task 2.
- Task 4: To define different policy scenarios, taking into account the possible impact scenarios and the known sources. Finally, the Flemish environmental authorities would be able to identify no-regret measures.

Unfortunately, task 3 could not be funded with the available budget. Nevertheless, this task was a key issue of the project, so other funds had to be found. Although the Flemish Environmental Agency for Water and Air (VMM) has a sophisticated network for monitoring air quality, it only just started to analyze PM2.5 at a small selection of monitoring stations.[14] Besides this limited experience, almost no experimental data could be found in literature about PM2.5 in Flanders.

Therefore, the University of Antwerp and the Flemish Institute for Technological Research (VITO, group of Dr. Berghmans) were asked to set up an extensive sampling and measurement campaign for the characterization of PM2.5 in Flanders. This project was titled "Measurement of PM2.5 in Flanders" and ran parallel with the AWI-project from 2001 until 2003. [15]
Shortly before this period, the UA had already been involved in another study about artefacts in Tapered Element Oscillating Microbalance (TEOM), a popular technique for the automated monitoring of particulate matter.[16] The VMM had discovered considerable differences between the measurements by TEOM and the classical gravimetric methods in some monitoring stations, which could not be explained. Although this first project led to hypotheses about possible local causes and effects, it was clear that an extensive sampling campaign would be required to enhance our knowledge about the problem. The new project with VITO in the period 2001-2003 was the right opportunity to do so, and it has produced results and conclusions that will discussed here.

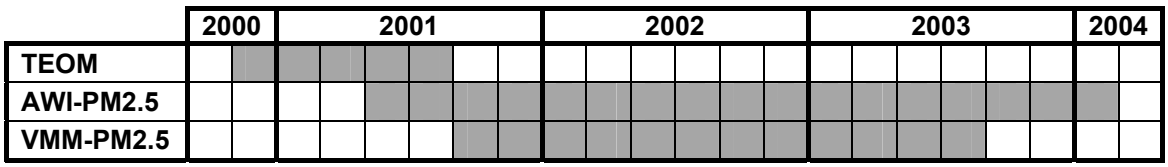


Figure 5: Time schedule of the different projects related to fine particulate matter

1.3 This chapter

The above-mentioned projects, to which the group of Prof. Van Grieken has contributed, resulted in bulky reports containing much detailed information. Since one of the goals of this thesis is to illustrate the use of TW-EPMA as a valuable technique in environmental analysis, especially in the study of atmospheric particles, it was not our purpose to copy all of the data in these reports, but to pick out some representative cases and to summarize the most important conclusions.
An interesting item throughout these projects was of course the methodology for the measurement of PM2.5 mass concentrations, and especially the problematic differences between the TEOM and other methods. This might seem less relevant in view of TW-EPMA; however, it is a hot topic in environmental monitoring, and it has to cope with strikingly similar problems as the ones TW-EPMA has to deal with. Therefore, it could not be omitted from this thesis.
Of course, the application of electron microscopy will also be discussed as part of our multi-analytical approach to study PM2.5 in Flanders. As will be explained below, only one of the six different locations where we have monitored and characterized PM2.5, was selected for a detailed discussion in this chapter. However, a final conclusion at the end of this chapter will thoroughly summarize all of the results of the VMM-PM2.5 project, and it will show the reader the importance of our study.

2. Scope of the PM2.5 project

2.1 Aim of the project

The main goals of the PM2.5 project for VMM were:
- to carry out a number of specific measurement campaigns for the determination of certain components of fine dust (like soot, heavy metals and some organic or inorganic pollutants);
- to evaluate the efficiency of certain measurement techniques for the quantitative mass determination and the chemical characterization of fine dust;
- to process all of the obtained data in view the spatial distribution or manifestation of fine dust emitted by local and distant sources.

Therefore, a huge collection of devices was used to sample fine particles and to monitor specific air pollutants on six different locations with diverse characteristics (urban, industrial or agricultural). Afterwards, the sampled particulates were characterized by different physical and chemical speciation techniques, and the obtained insights in the composition of atmospheric aerosols were linked to the existing knowledge about the nature of particles emitted by specific sources.

The results obtained by applying these techniques are also assumed to be of great help to air quality research and environmental policy making, for example:
- the implementation of a PM2.5 standard (air quality level) by using the data as an input for air quality models;
- the search for correlations between the concentration of certain PM2.5 components and effects on human health or the environment;
- the development of a Flemish monitoring network for PM2.5, based on the gained experience and knowledge.

2.2 Sampling locations

Six different locations were selected as sampling stations for the project: Wingene, Zelzate, Petroleumkaai and Borgerhout (both in Antwerp), Mechelen and Hasselt.

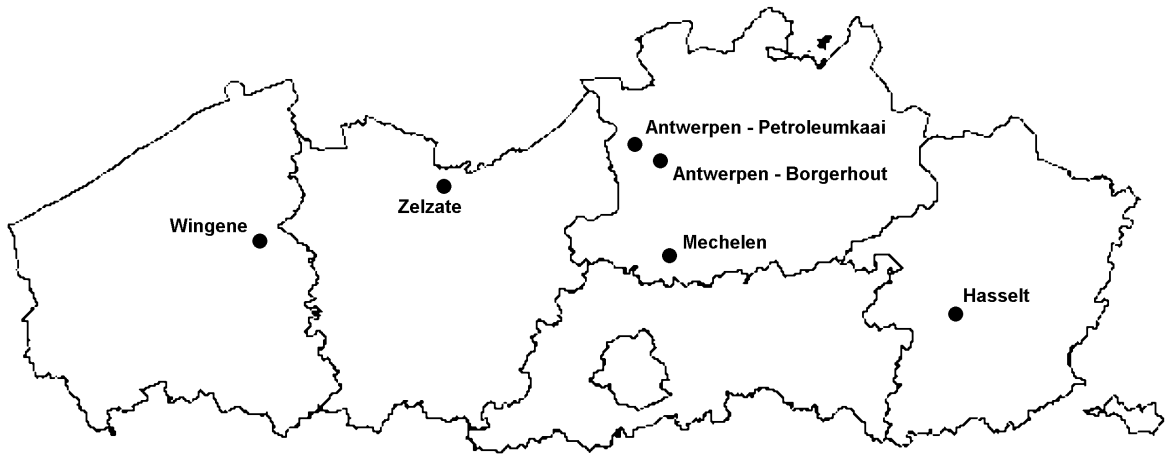


Figure 6: Sampling locations

Besides technical criteria like the availability of power supplies, the most important criterion for the selection of these stations was of course the local environment and the sources that are present in the surrounding area. Except for Wingene, all of the sampling locations were also monitoring stations in the VMM network, so additional monitoring data were available. Especially meteorological information was of great help during data processing and interpretation. Relevant parameters were of course wind direction and wind speed, but also precipitation, relative humidity, air pressure and temperature, but a thorough discussion will follow later.

Table 1: Sampling locations

	Area type	Station
Wingene	Rural (agriculture)	Military property
Hasselt	Suburban	VMM-station 42N045
Mechelen	Suburban	VMM-station 40ML01
Antwerpen - Borgerhout	Urban, heavy traffic	VMM-station 42R801
Antwerpen - Petroleumkaai	Industrial	VMM-station 42R822
Zelzate	Industrial, heavy traffic	VMM-station 44R750

Every location was visited twice and each time in a different period of the year, in order to study seasonal variations. Sometimes it was hard to stick to the original time schedule due to technical problems with equipments and power supplies, but the sampling periods at each locations lasted at least six weeks.

Table 2: Sampling periods

	Location	Sampling periods		
Campaign 1	Petroleumkaai	18/09/01	29/10/01	(Su-Au)
	Borgerhout	06/11/01	10/12/01	(Au)
	Zelzate	11/12/01	30/01/02	(Au-Wi)
	Hasselt	01/02/02	26/03/02	(Wi)
	Wingene	27/03/02	15/05/02	(Wi-Sp)
	Mechelen	16/05/02	26/06/02	(Sp)
Campaign 2	Wingene	27/06/02	12/08/02	(Su)
	Zelzate	13/08/02	26/09/02	(Su)
	Hasselt	27/09/02	04/11/02	(Su-Au)
	Mechelen	05/11/02	03/01/03	(Au)
	Petroleumkaai	19/12/02	23/02/03	(Au-Wi)
	Borgerhout	10/02/03	07/04/03	(Wi-Sp)

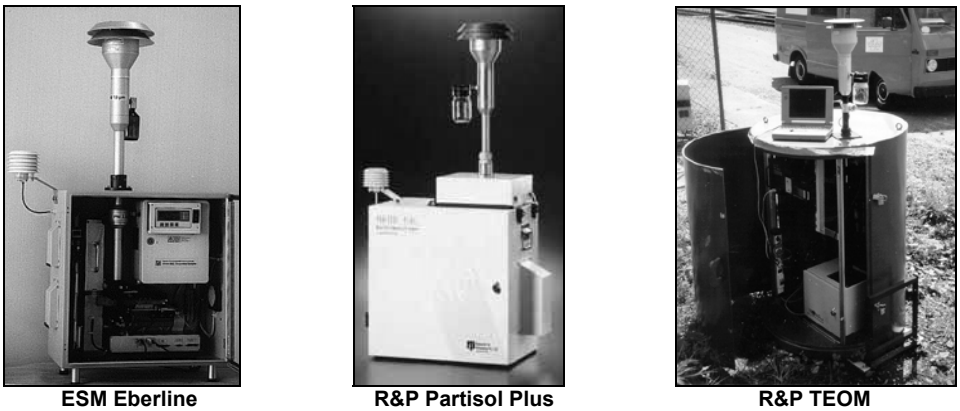
Sp = spring, Su = summer, Au = autumn, Wi = Winter

In the discussion of the extensive characterization of PM2.5, Borgerhout was selected as a case study for this thesis, which is one of the two stations in the city of Antwerp. A more detailed explanation about why this location was chosen, will be given in section 4. For the discussion in section 3 about the methodology for the determination of PM2.5 mass concentrations, a selection of the results for all stations will be discussed.

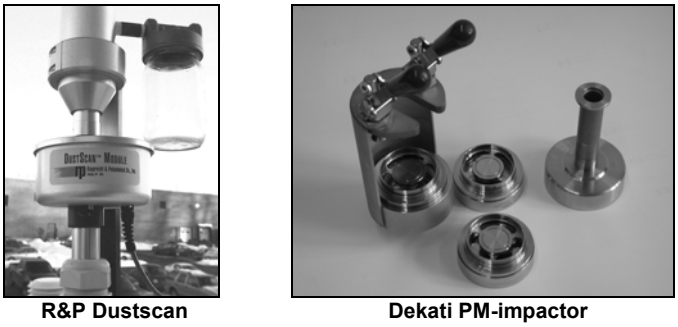
Figure 7: Typical set-up at Antwerpen-Petroleumkaai

2.3 Methodology for sampling, monitoring and analysis

A detailed explanation of all the applied sampling, monitoring and analysis techniques would lead us too far. This short summary will be confined to the most important aspects only, but more information will be given in the next sections when required.



ESM Eberline | R&P Partisol Plus | R&P TEOM

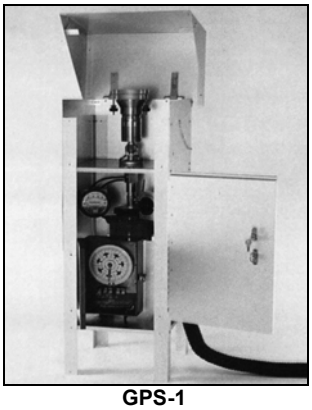


R&P Dustscan | Dekati PM-impactor

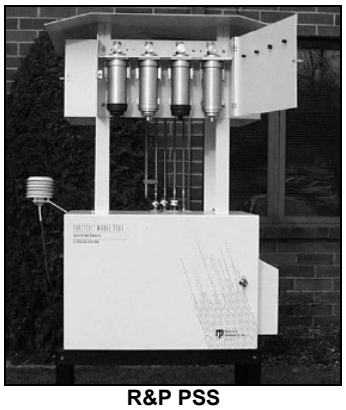
Figure 8: Equipment for sampling particulate matter

A crucial part of the sampling campaign consisted of comparing different methods for sampling PM2.5. VITO owns a large collection of equipments for the automated sampling of fine particulate matter, which was of course put into action for this project.
A Tapered Element Oscillating Microbalance (TEOM) from Rupprecht & Patashnik (R&P) was used for the automated, continuous measurement of PM2.5. The technique samples air on a dispensable filter through a glass tube. Both the tube and the filter oscillate with a known initial frequency which will be altered when dust is collected on the filter. The change in frequency is a measure for the sampled mass. In this case, a sharp cut cyclone was used for the selection of PM2.5.

Several automated R&P Partisol Plus samplers and a similar device from ESM Eberline were used for the sampling of PM2.5 on filters. These instruments can be programmed to sample several filters after each other, using a pneumatic system for moving the filters from a cassette to the actual filter holder or to another storage cassette after sampling. They have the huge advantage of decreasing the number of man hours required for an extensive sampling campaign, since up to 16 filters can be successively sampled. The flow rate through the machine is 1 m^3/h, allowing for 24h-samples to be taken without any problems under normal conditions. Different sampling heads were used i.e. for either PM10 or PM2.5, and different filter types were used as well. The filters were analyzed by gravimetry, followed by either ion chromatography (Dionex 1200 IC; AS 14 or CS 12A columns) or X-ray fluorescence (TRACOR Spectrace 5000 EDX).
An R&P Dust Monitor and a TSI Particle Sizer (TSI Inc.) were used for optical monitoring. When particles in an air stream pass a laser beam, the resulting diffraction is used to calculate the corresponding particle sizes. The R&P monitor can be installed on an R&P Partisol sampler, between the filter and the sampling head.
A Dekati impactor was used for the manual sampling of particulate matter, i.e. at each location, several impactor samples were taken during 24h. The impactor contains three stages and a back-up filter, corresponding to particle fractions >PM10, PM2.5-PM10, PM1-PM2.5 and PM1. The samples taken with this Dekati impactor were analyzed by gravimetric analysis in order to get an idea of the particle distribution over these different size fractions.


GPS-1

R&P ACPM


R&P PSS


VITO Honeycomb denuder

Figure 9: Other sampling equipment

Polyaromatic hydrocarbons (PAH) were sampled with a so-called GPS-1 device, that collects them either as particulate matter on quartz filters, or as gaseous species on a polyurethane foam (PUF). Both fractions were analyzed by the VMM using high performance liquid chromatography (Waters HPLC; Vydac 201 TP column; Perkin Elmers LC 240 fluorescence) after sample preparation by accelerated solvent extraction (ASE).

The Ambient Carbon Particulate Monitor 5400 (R&P ACPM) was used for the continuous monitoring of particulate carbon. Air is sampled at a conditioned temperature of 50°C for avoiding adsorption of volatile organics to the inner parts of the device. The analysis consists of two parts: 1) the samples are heated up to 350°C to burn organic species, 2) followed by afterburning at 750°C. After each part the CO2 content is measured by a non-dispersive infrared detector and the carbon content is calculated; the first concentration corresponds to the organic fraction, while the second concentration additionally contains the fraction of inorganic carbon.

Inorganic gaseous species were analyzed by two denuder systems: the VITO-made honeycomb denuder and the R&P Partisol Speciation Sampler. A gas flow is sampled over a coated set of tubes that adsorb the compounds, so that their concentrations can be determined by ion chromatography analysis after extraction of the coating.

Samples for analysis by electron microscopy, were taken with the Berner impactor that was also used for the experiments in previous chapters, in combination with conventional filter samplers (pump + filter holder). The Berner impactor samples were analyzed by TW-EPMA, as described before (JEOL JXA-733; 10 kV, 1 nA). The Nuclepore filter samples were analyzed by conventional SEM (JEOL JSM-6300; 20 kV, 1 nA) after coating with a conductive carbon film.

3. PM2.5 concentration measurements

During the sampling campaigns, PM2.5 mass concentrations were determined in parallel by continuous, semi-continuous or discontinuous methods. Dustscan and TEOM are automated, continuous and online techniques, in which the mass concentrations of particulate fractions in an air stream are determined at specific time intervals. On the other hand, the automated subsequent 24h-sampling on filters in Partisol or Eberline instruments should be considered as semi-continuous, since the filters have to be changed and analyzed offline afterwards. The Dekati samples were only taken on a limited number of occasions, so this method is certainly not continuous or online. From this point of view, the TEOM and Dustscan techniques certainly have a huge advantage over the other methods. As fast, online and standalone methods, they don't require as many man-hours. However, time and money are of course not the only criteria for evaluation, as will be shown below. Figure 15 shows the results of the different methods (the first letter of the graph identification stands for the location, the number for the campaign). Some signs have been put on the graphs to mark some of the problems that will be discussed below.

3.1 Optical versus gravimetric methods

The difference between the PM2.5 values of the Dustscan and the results of the other methods is striking. The reason for the fact that the Dustscan values are extremely high, is to be found in calibration errors. Optical methods are calibrated using standard aerosols, but in reality there is no such thing as a 'standard' aerosol. The morphology and composition of real sampled aerosols can differ strongly from location to location or from time to time, and the optical signal will vary depending on these properties. Since the optical signal is used to determine the size and mass of the sampled particles, the result will obviously be wrong. So it is right to say that if an instrument is calibrated with a certain standard aerosol, it only responds relative to that standard. Therefore, the Dustscan only shows trends in concentration variability and no absolute values. It is clear that the Dustscan curves run parallel with those of other methods and so they can be seen as an additional confirmation of the other results.

3.2 Dekati problems

The Dekati results do not always match the results obtained by Partisol, although their filters were analysed by the same gravimetric methods. The reason for the lower Dekati values is to be found in the back-up stage of the Dekati. The filter on this stage, for which the sampled particle fraction corresponds to PM1, is tightly positioned between two plastic rings during sampling. When the filter has to be removed after sampling, it often occurs that the filter is damaged. The slightest filter damage will results in a lower filter mass and particle concentration. Moreover, not only the PM1 fraction will be lower than it should, but also all other fractions.

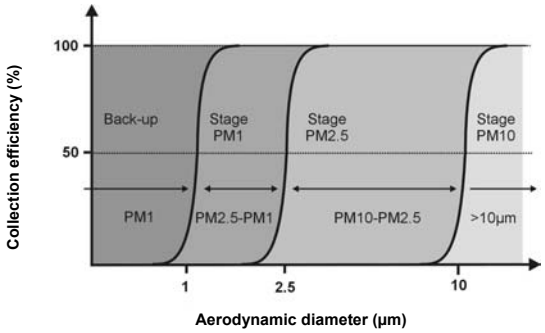


Figure 10: Dekati stages and particulate mass fractions

The PM2.5 fraction is built up of the PM1 fraction and the fraction 'PM2.5-PM1' (as can be seen in the picture above), so it should be calculated based on the result of the PM1 fraction. For this reason some negative measurements due to large filter losses were ignored. This problem is purely due to technical problems, but it illustrates a possible source of errors in gravimetry.

3.3 Influence of filter type on gravimetry

The Eberline PM10 measurements for the first locations that were visited in the first campaign (Petroleumkaai, Borgerhout and Zelzate) appeared to behave strangely, since they even often were lower than the PM2.5 values. At the start of the sampling campaign, cellulose-acetate filters were used, but after a while VITO discovered that the gravimetry or weighing of these filters was influenced by electrostatic charging. The charging of the filters resulted of course in deviations in filter masses. Therefore, the PM10 results of the first campaigns only show a rough trend or pattern instead of an absolute result. Starting from the campaign in Hasselt, Teflon filters were used instead that showed to be less vulnerable to electrostatic charging. So it is quite clear that the choice of filter materials is crucial for gravimetric analysis. On the other hand, filter materials also have to be selected as a function of the analyses after gravimetry as well. The filter type for Partisol sampling was selected on its blank value for X-ray fluorescence and ion chromatography: respectively cellulose-acetatate/nitrate and Teflon. For this reason, only the gravimetric results for Tefon-filters were taken in consideration in this discussion.

3.4 TEOM versus gravimetry

First a more detailed description of both methods is appropriate. In gravimetry according to specific European and/or international standards (EN12341), the sampled filters are first conditioned to an ambient temperature of 20°C ± 1°C and a relative humidity of 50% ± 5% in especially designed clean rooms, and then weighed using sensitive microbalances. TEOM is based on online microbalance measurements in a conditioned device at a certain temperature, which is typically fixed to 40 or 50°C according tot the original design by R&P. The air flow passes a very sensitive element that oscillates proportionally to the particle mass in the stream. The results obtained by gravimetry and TEOM are shown in the tables below, and it is quite obvious that gravimetry comes to much higher values than TEOM.

Table 3: PM2.5-data from gravimetry (24h-sampling on Teflon)

	PM2.5 CONCENTRATIONS (µg/m³)					
	CAMPAIGN 1			*CAMPAIGN 2*		
LOCATION	*Min.*	*Max.*	*Average*	*Min.*	*Max.*	*Average*
Antwerpen-Petroleumkaai	7.9	59.5	20 ± 11	6.3	61.6	21 ± 12
Antwerpen-Borgerhout	0.2	62.7	29 ± 15	13.8	99.7	45 ± 22
Zelzate	1.6	67.7	26 ± 16	5.9	43.8	16 ± 8
Hasselt	5.5	59.0	19 ± 13	4.4	38.5	16 ± 8
Wingene	7.0	63.9	28 ± 16	5.2	23.2	11 ± 4
Mechelen	7.1	21.3	12 ± 7	9.2	60.1	24 ± 13

Table 4: PM2.5-data from VMM-TEOM (24h-averages)

	PM2.5 CONCENTRATIONS (µg/m³)					
	CAMPAIGN 1			*CAMPAIGN 2*		
LOCATION	*Min.*	*Max.*	*Average*	*Min.*	*Max.*	*Average*
Mechelen	8	27	13 ± 4	8	51	22 ± 10

Table 5: PM2.5-data from VITO-TEOM (24h-averages)

	PM2.5 CONCENTRATIONS (µg/m³)					
	CAMPAIGN 1			*CAMPAIGN 2*		
LOCATION	*Min.*	*Max.*	*Average*	*Min.*	*Max.*	*Average*
Antwerpen-Petroleumkaai	8.2	30.8	17 ± 6	8.3	31.9	16 ± 6
Antwerpen-Borgerhout	6.2	34.9	20 ± 8	12.0	47.0	28 ± 11
Zelzate	6.2	53.1	21 ± 11	5.7	30.1	16 ± 7
Hasselt	6.8	34.4	13 ± 6	6.8	30.8	15 ± 6
Wingene	6.5	45.1	20 ± 10	6.5	27.2	13 ± 5
Mechelen	7.4	26.7	14 ± 5	9.9	44.5	21 ± 9

Many publications in different articles have concluded that TEOM measurements are often lower than those of classical weighing methods. The conditioning of the air stream to relatively high temperatures is seen as the main cause of the problem. The heating-up of the air causes some volatile compounds to evaporate, even at temperatures around 30°C. [17, 18] These compounds could go from ammonium nitrate to volatile organic compounds, as was confirmed directly and indirectly by us and by other researchers. For example, the VMM encountered most of their problems with TEOM devices in Oostrozebeke, which is a Flemish town known for the presence of wood industry. During our TEOM project we often experienced ourselves the strong smell of formaldehyde around the VMM monitoring station in that place. Chipboard manufacturers commonly use the organic in their production process, and it would be of no surprise to anybody if this quite volatile compound would form the base for the large artefacts in the determination of particulate mass concentrations. However, the quite abundant inorganic ammonium nitrate is also expected to have a negative influence on TEOM measurements, so the problem should not only be connected to volatile organics.

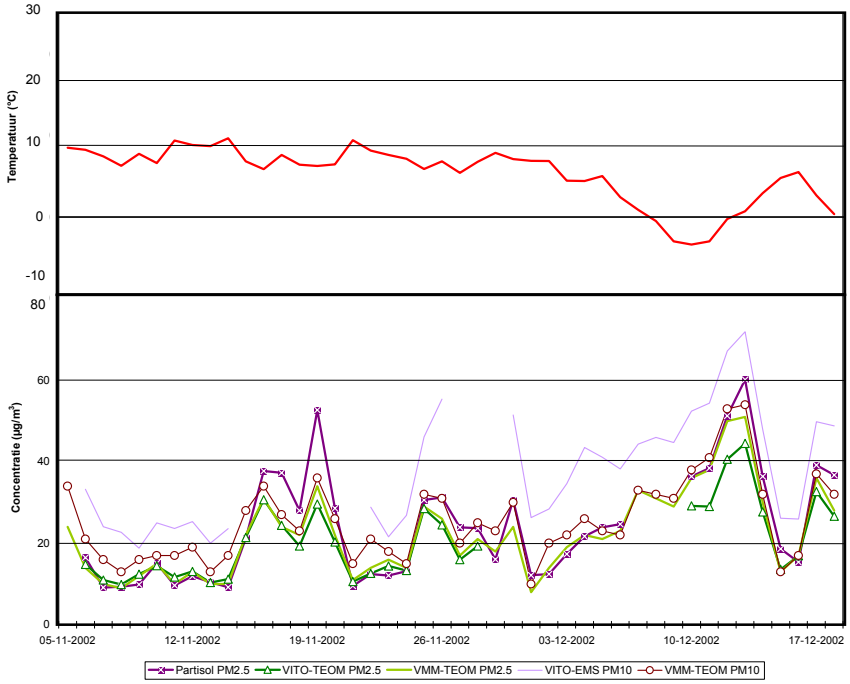


Figure 11: PM fraction and average daily temperature during Mechelen-2

The results for the second campaign in Mechelen appear to confirm these conclusions. Mechelen is the ideal location to draw well-founded conclusions, since two TEOM instruments were used: one from VITO and one from VMM. When we have a look at the PM2.5 results from both instruments, which were conditioned at respectively 50°C and 40°C, it is obvious that most results behave according to the following simple logic: VITO-TEOM < VMM-TEOM < Partisol. This confirms the influence of the measurement or conditioning temperature (50°C < 40°C < 20°C), as was concluded for measurements in winter and spring campaigns by other researchers.[19] Both TEOM instruments for PM2.5 measurements clearly produce lower values than the gravimetric method for PM2.5. Even the PM10-TEOM from VMM measured lower concentrations than the PM2.5 concentrations obtained by gravimetry (applied to the Partisol samples).
However, the results of the first campaign in Mechelen show that the phenomenon is more complex than expected. It is obvious that on most measurement days, the PM2.5 concentrations show the reverse pattern which is a contradiction to the previous statements. The same can be seen in Petroleumkaai-1, Wingene-2 and Zelzate-2 (though here we only have data for the VITO-TEOM). On the other hand, the PM10-concentrations of the VMM-TEOM and the VITO-Eberline do seem to behave similarly.

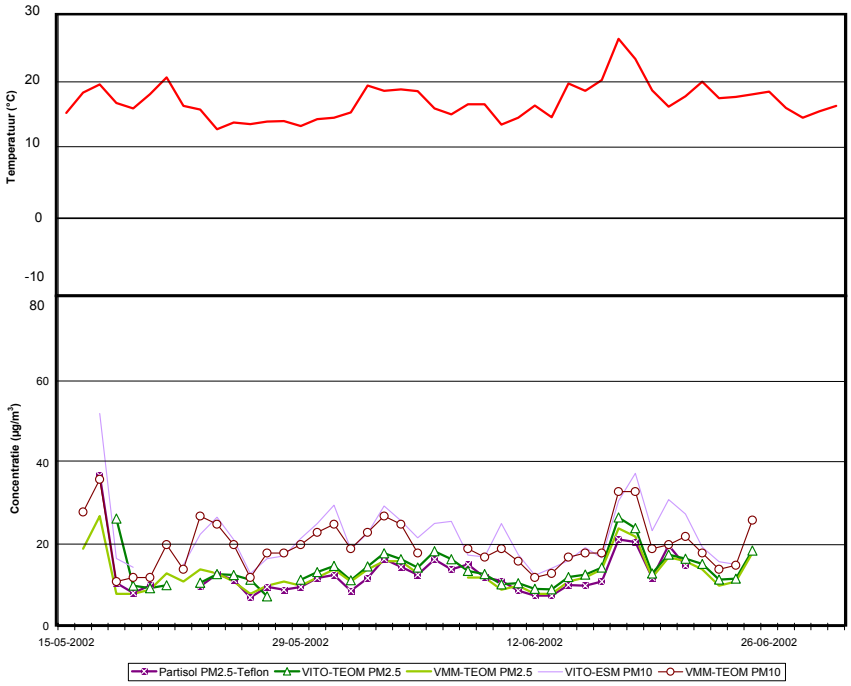


Figure 12: PM fraction and average daily temperature during Mechelen-1

Meteorological conditions could offer a possible explanation, since it can be see that on days where the expected trend does not occur, the 24h-average temperature is higher than 15°C. Instantaneous measurements within the VITO-TEOM show daily maxima of 28°C or more. That leads us to the following hypothesis:

1) If the ambient temperature during sampling is high (24-average > 15°C), most volatile compounds will have evaporated before sampling and the effect of temperature conditioning will be less or even nihil. Therefore, the TEOM measurements at 40°C or 50°C will also not differ very much. Since the Partisol filters are measured at some time after the sampling (sometimes two weeks after sampling), the filter is longer exposed to high temperatures. This causes additional evaporation, leading to values that are even lower than those from TEOM.

2) If the 24h-average temperature is lower than 15°C, the conditioning effect in TEOM is larger and Partisol filters are preserved much better.
3) The fact that PM10 concentrations are less dependent of the 24h-temperature during summer campaigns, could be explained by the fact that relatively more coarse particles are present in the air due to the dry, warm weather (more blown up soil dust, etc.). These coarse particles are more present in the PM10-PM2.5 fraction and they are less volatile than most fine particles in the PM2.5 fraction. That's why their mass will influence the PM10 measurements more heavily, and therefore, the influence of the ambient temperature will not be noticed as clearly. In cold periods with much precipitation, like in Mechelen-2, less coarse particles will be present in the air. The PM10 mass fraction will evidently be more influence by evaporation effects.

If the proposed hypothesis indeed explains the conclusions, then this leads to the following conclusions about the methodological difference between TEOM and gravimetry:

1) The weighing procedure for gravimetry is strictly standardised, so it is considered to be the reference technique for comparing with many other methods. However, it was shown that the way in which the sampled filters are stored and transported to the laboratory should also be strictly controlled in order to prevent exposure to high temperatures. Evaporation of volatile species should be prevented at all times, and this has some implications for the development of automated sampling devices like Partisol and Eberline, where filters are only removed after several days of subsequent filter sampling. Besides TEOM conditioning effects one should also take into consideration possible artefacts in case of gravimetry of filters that were stored during warm weather.
2) Many publications refer to fixed correction factors to take into account evaporation effects in TEOM measurements (e.g. the factor of 1.3 determined by the Environmental Protection Agency in the USA). These factors are calculated based on the comparison of TEOM with gravimetric results. However, one could wonder if these correction factors should not be dependent on the ambient temperature during sampling. A fixed factor will overestimate the required correction in warm summer periods, while in cold winters the correction will be an underestimation. A temperature-dependent correction would be better, though it is clear that it will not be evident to develop such a correction method. To make things more complex, one could also wonder if the function shouldn't be dependent of the presence of certain volatile compounds (and therefore it would often be dependent of the sampling location as well).

While looking for solutions to this problem, R&P introduced a new technique called 'FDMS' that is claimed to solve evaporation artefacts.

3.5 TEOM-FDMS

The Filter Dynamics Measurements System (FDMS) is an additional unit for R&P TEOM devices, which is claimed to deal with evaporation problems.[20] We were able to test this method for a short while in Borgerhout, since R&P were so kind to put one of their devices to our disposal. The FDMS calculates PM-concentrations based on separate air and reference measurements. Using a splitter, the sampled air is alternately send for six minutes to the measurement (at the fixed conditioning temperature of 30-50°C), either directly or else after filtration at 4°C. When a loss in filter mass is found after comparison of both measurements, the lost mass is accounted for in the calculated mass concentration. Every six minutes the average PM-concentration is re-evaluated, and in this way short-term (1h) as well as the long-term (24h) measurements can be performed.

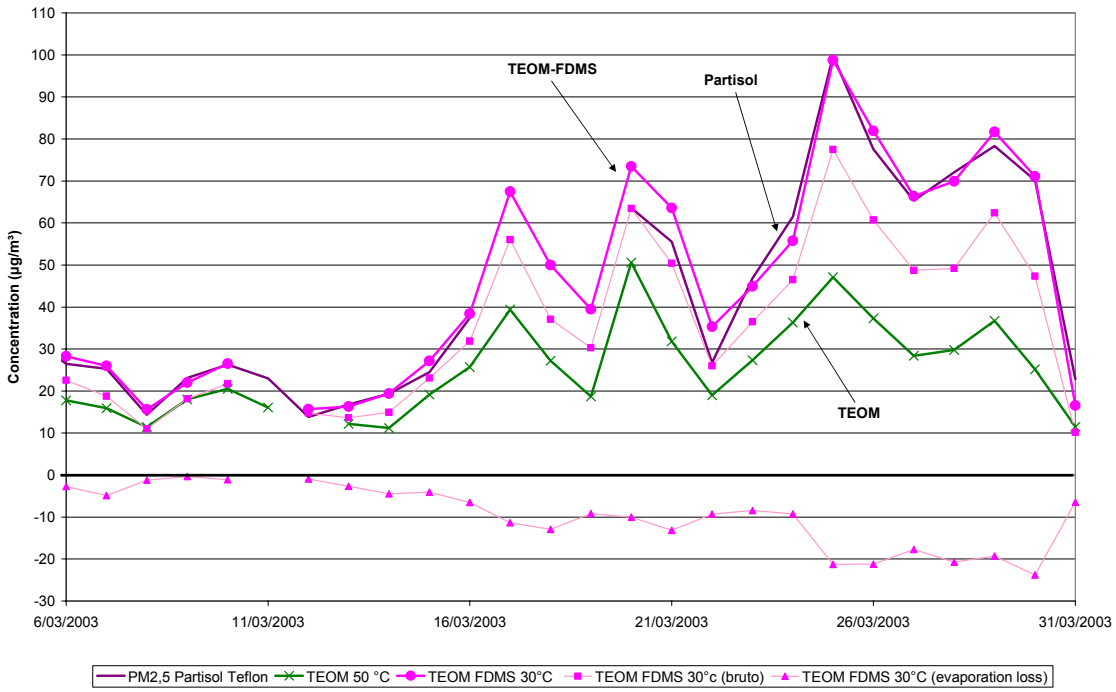


Figure 13: Comparison of TEOM, TEOM-FDMS and gravimetry

In the correlation graph (Figure 14), one could clearly recognize the previous trend again between classical TEOM (at 50°C) and gravimetry. When we consider TEOM-FDMS (30°C), it is clear that its final result is almost identical to that from gravimetry and certainly has the best correlation value, while the uncorrected value would indeed again be much lower than the expected value. Although the method was not tested during hot weather, there is no reason to assume that FDMS would not work as correctly as it did in the current testing period.

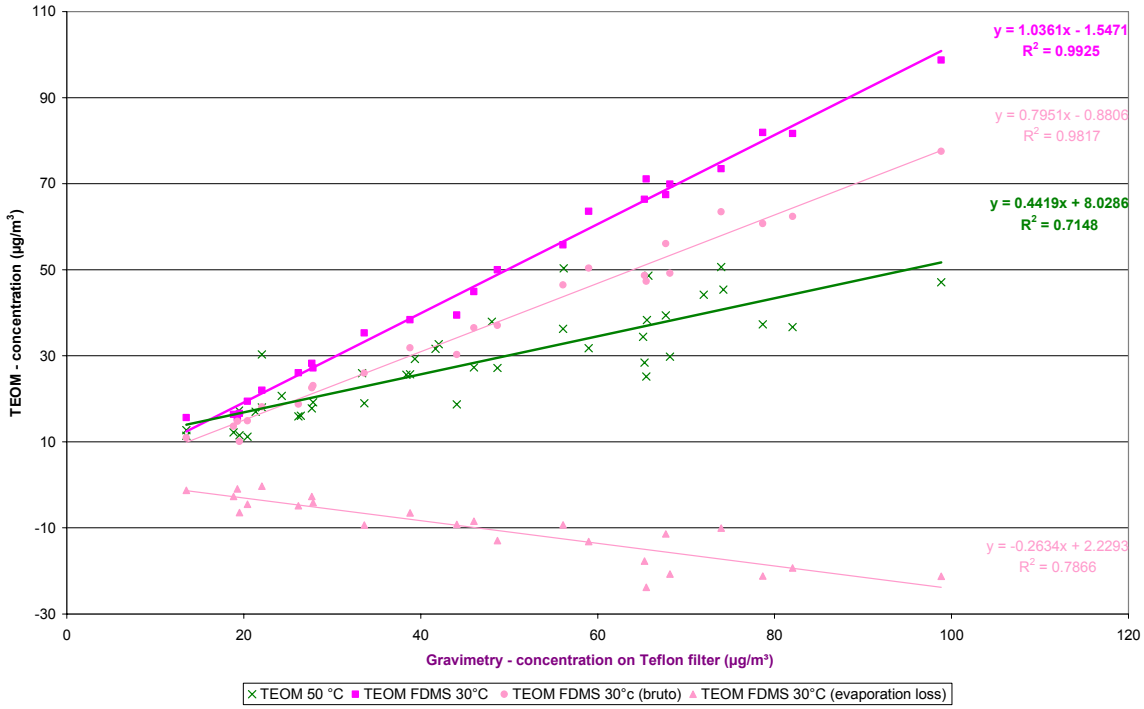


Figure 14: Correlation between TEOM or TEOM-FDMS with gravimetry

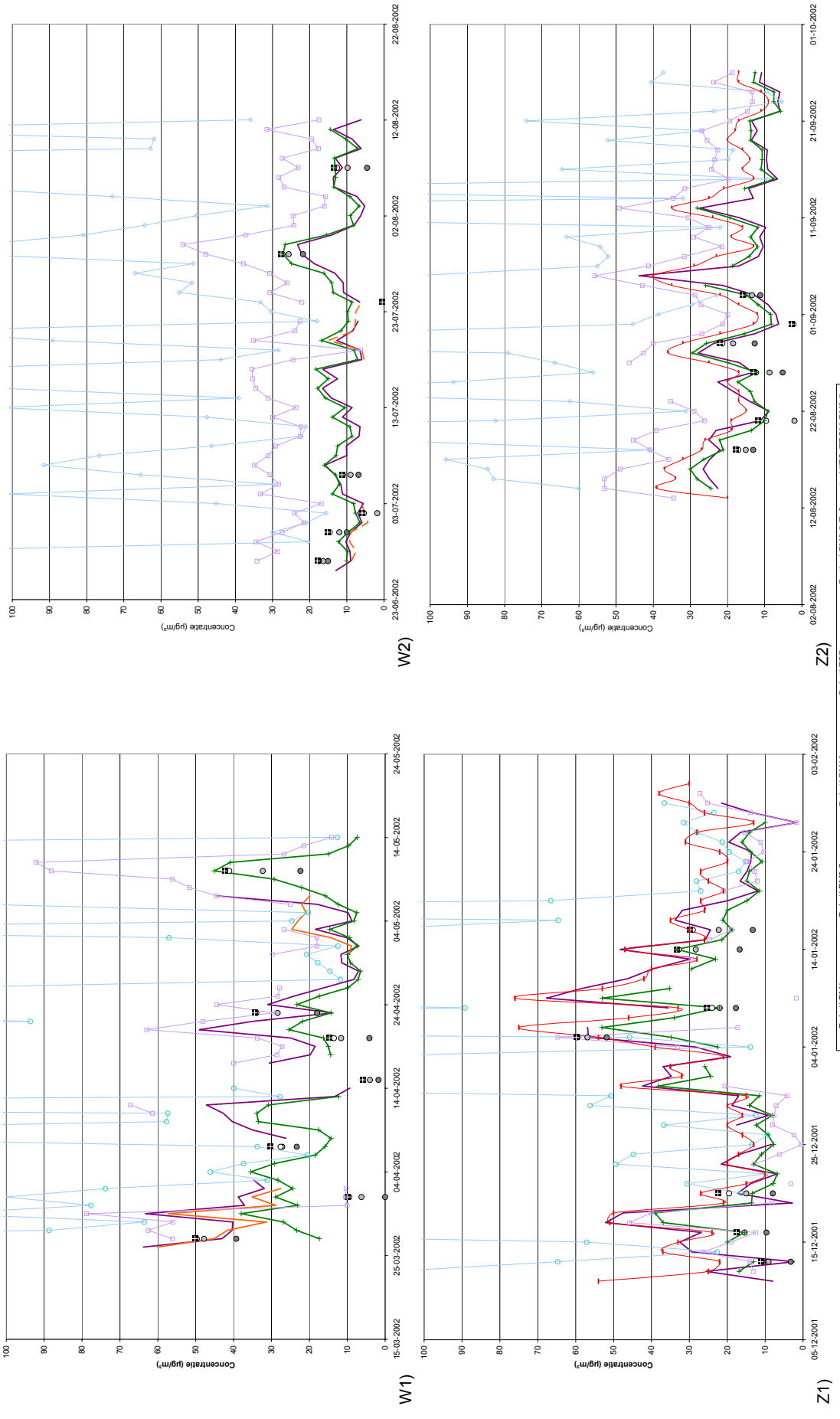


Figure 15: PM-concentrations for different locations during two campaigns

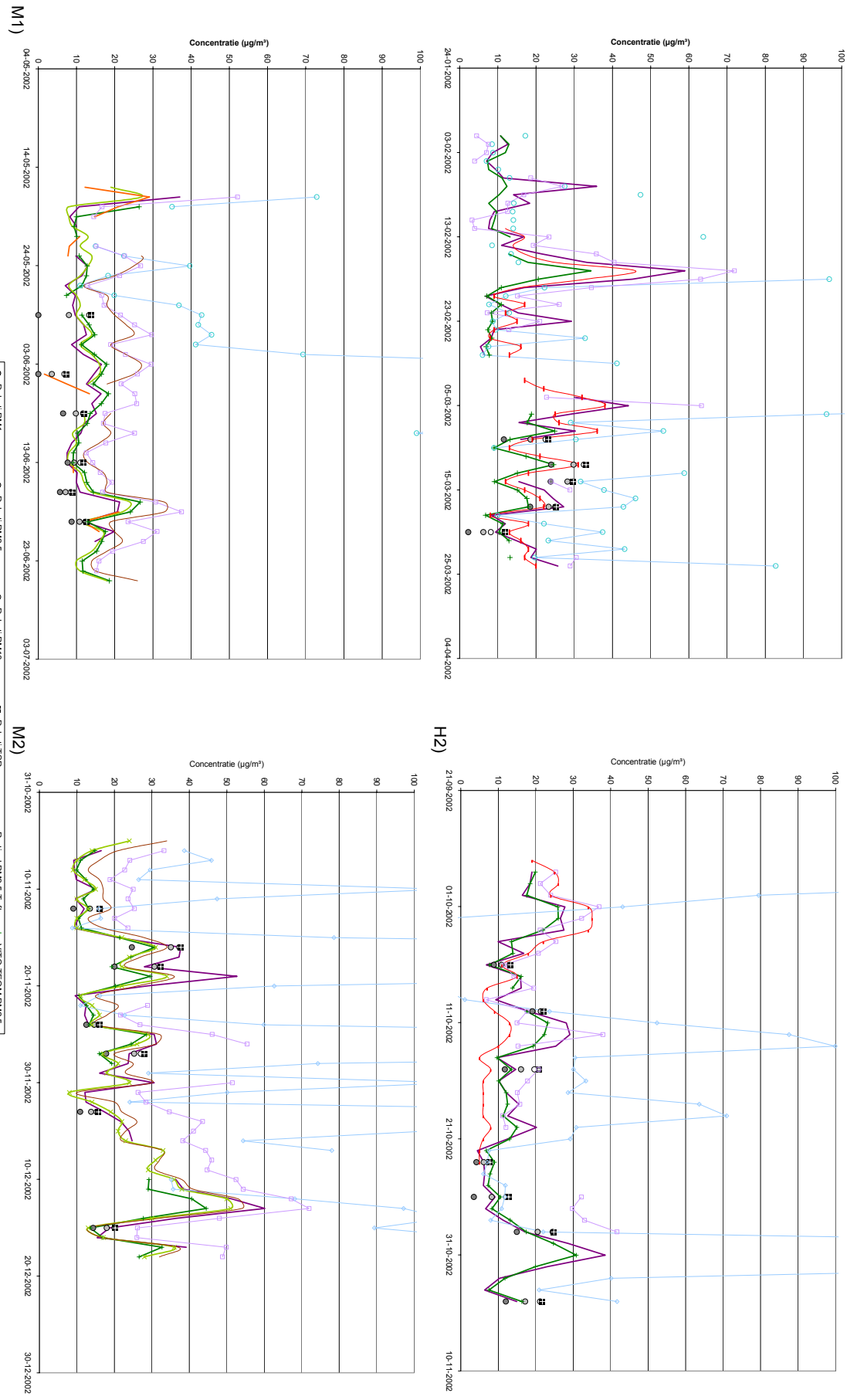


Figure 15 (continued): PM-concentrations for different locations during two campaigns

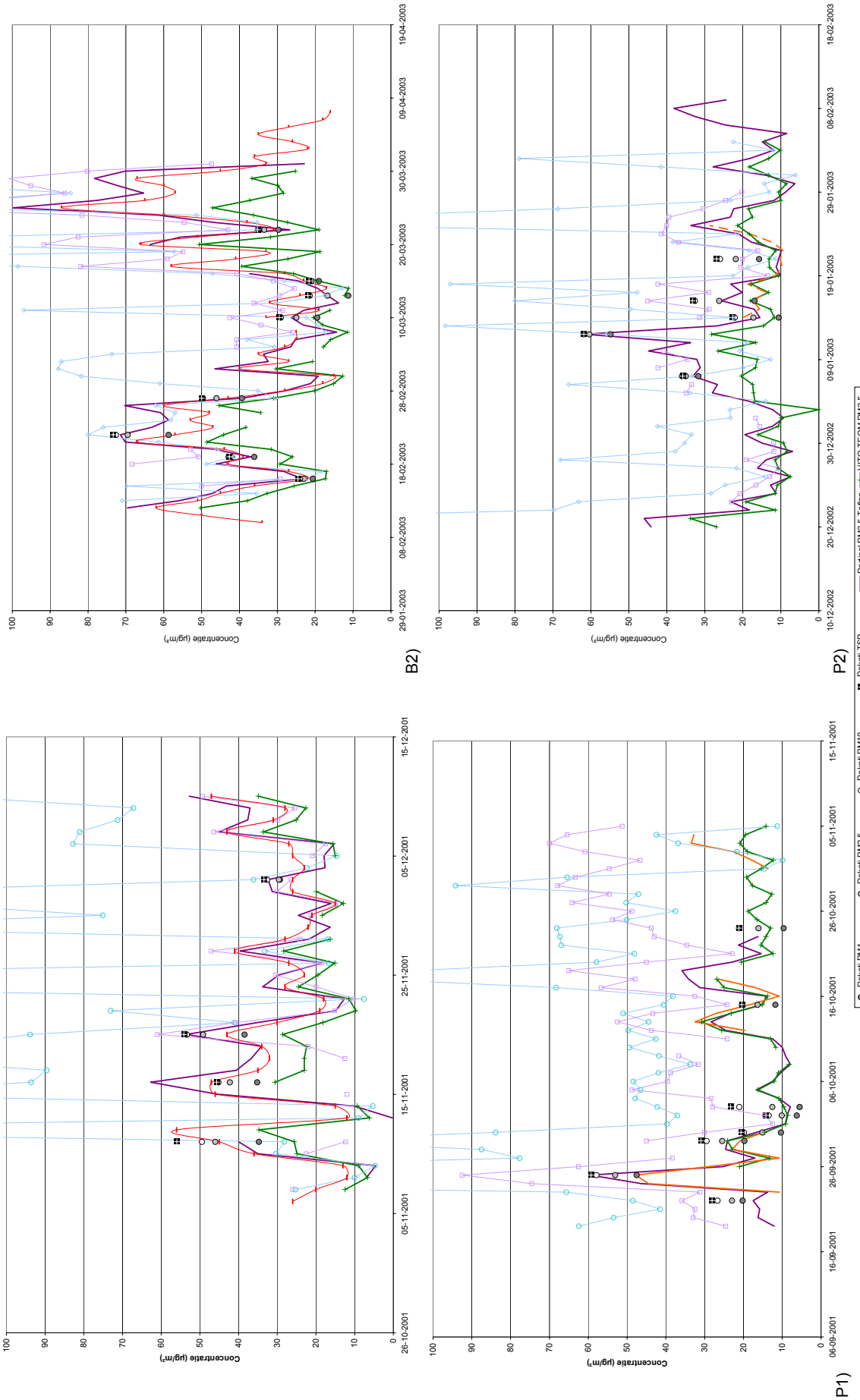


Figure 15 (continued): PM-concentrations for different locations during two campaigns

4. Characterization of the PM2.5 fraction

4.1 The case of Antwerp-Borgerhout

Borgerhout is a typical urban location in the city of Antwerp. The VMM monitoring station is located in one of the busiest access roads to the city centre (Plantin en Moretuslei) and very near the inner and outer ring roads surrounding it. A train station and other types of public traffic (mainly busses) are nearby. Within 500 m, we find a public school, several banks, a petrol station, a large supermarket and a hotel. The station itself is positioned at less than 15 m from the road.

Figure 16: Location of Antwerp-Borgerhout

As for all other locations, two campaigns were carried out. The first lasted from November 6 until December 10, 2001 (late autumn, early winter), while the second took place between February 10 and April 7, 2003 (late winter, early spring).

The **weather conditions** for the two campaigns were recorded at another station in the north of Antwerp (Luchtbal). Wind roses are given in the figure below, showing that southwestern wind prevailed in the first campaign, while eastern winds dominated most of the second campaign.

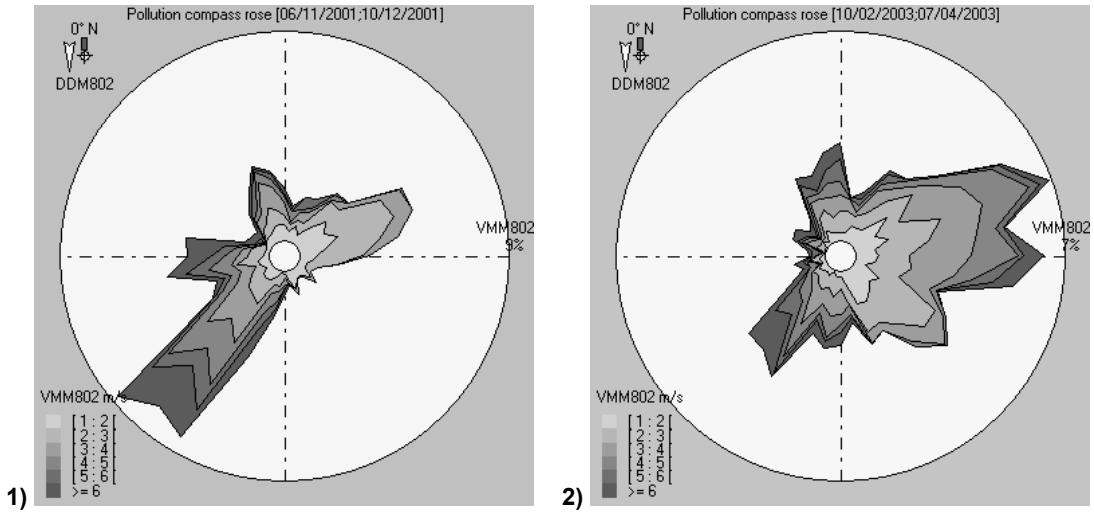
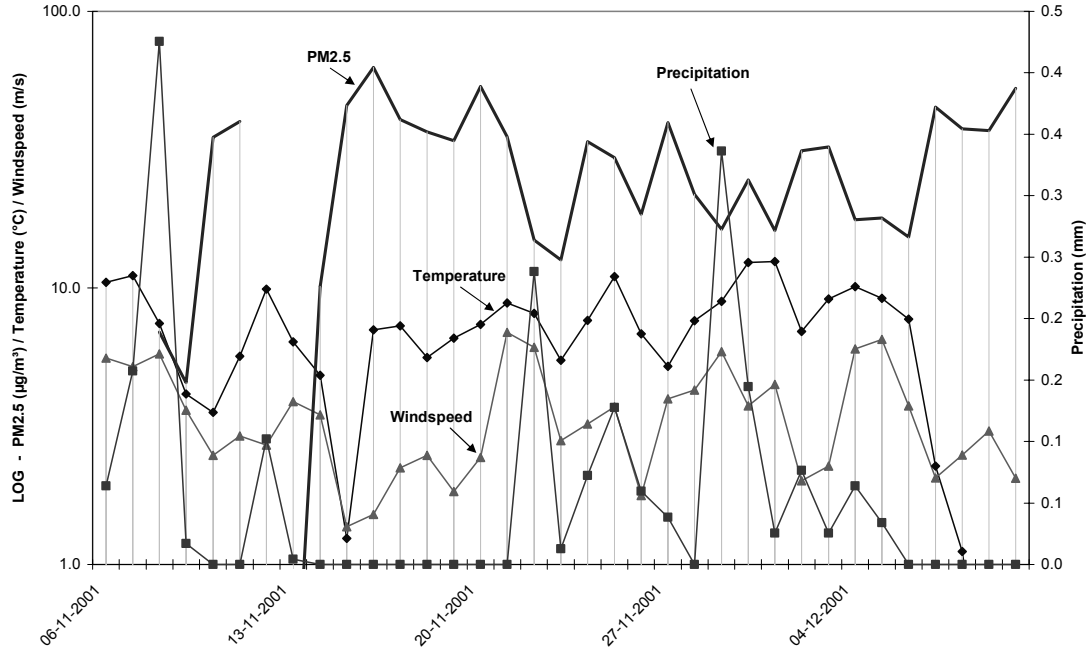


Figure 17: Wind roses for both campaigns in Borgerhout

Figure 18 shows precipitation, temperature, windspeed and PM2.5 curves for both campaigns.



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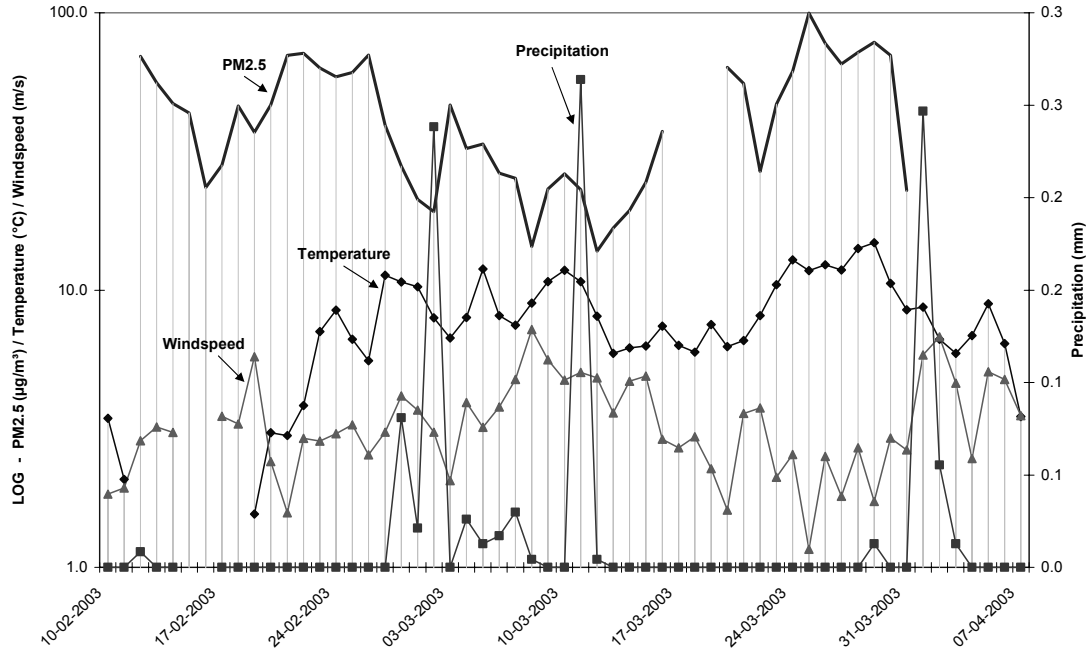

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Figure 18: Weather conditions versus PM2.5 concentrations for both campaigns

Both graphs clearly show the influences that meteorological conditions have on **PM2.5 mass concentrations**. First of all, concentrations drop whenever precipitation occurs, due to the so-called 'wash-out effect' (particles are captured in falling rain drops so that they are literally washed out). Wind speed is a measure for turbulence in the air, and the faster the wind, the more diluted the air will be and particle concentrations will drop. Links with temperature are more difficult to find, since the effects are expected to depend more on the composition of the particles. If the particles consist of volatile compounds, their concentrations might drop during warm periods due to evaporation. However, this drop in concentration doesn't tell much about air quality, since the species are still present, but in another form. In the meteorological station, air pressure and relative humidity were also recorded, but no clear relations were found.

These meteorological influences have major impact on the concentrations of particulate matter in the air. Most increases or decreases in concentrations in Borgerhout could be linked to the effect of weather conditions. However, this does not mean that the effects of local sources were not found in our measurements. For example, the influence of traffic can clearly be observed in the weekly and daily variation of PM2.5 concentrations. Figure 19 shows the concentrations during two weeks in the second campaign at Borgerhout. The peaks that often occur during the day happen to correspond to traffic rush hours. On weekdays, peaks were observed around morning and evening peak hours (8h-10h and 17h-20h, respectively). On Wednesdays, the morning peaks also occured, but the concentration behaviour in the afternoon was less predictable (probably due to the fact that most schools take half a day off). During weekends, the curves are quite fanciful, but again this might be related to the fact that most people don't work in the weekends and traffic is less regular. During weekends, peaks related to nightlife activities were also encountered.

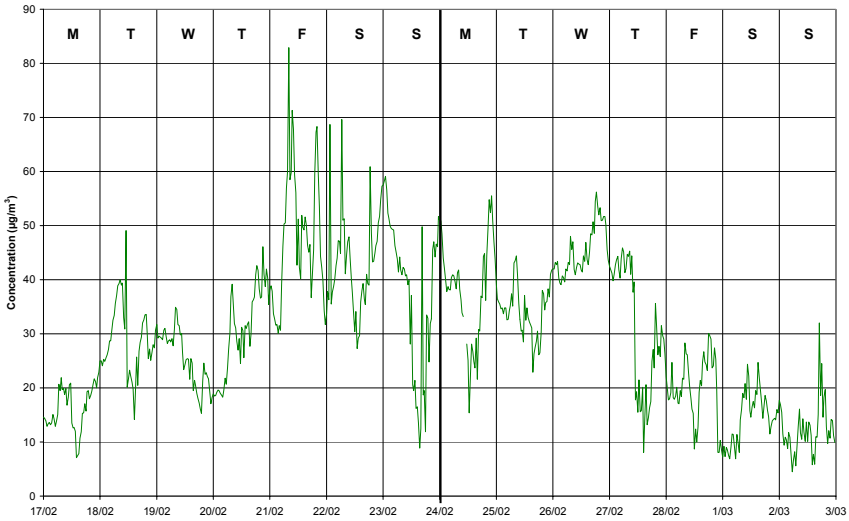
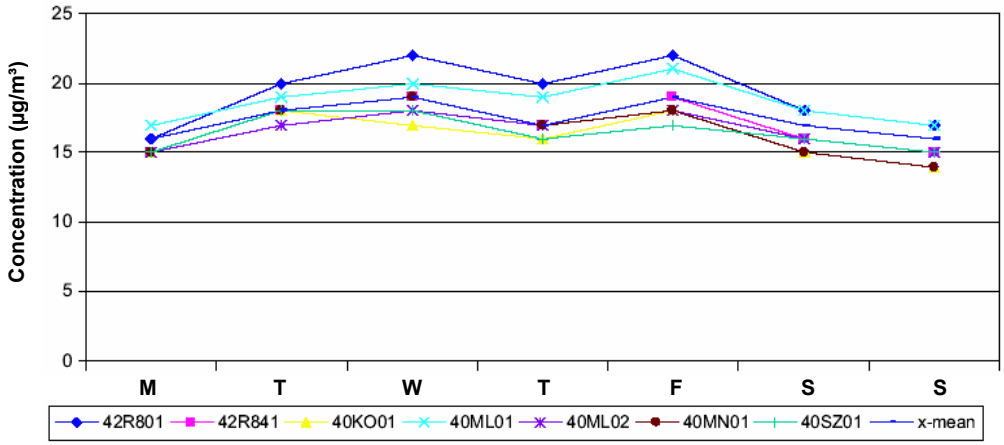


Figure 19: Example of daily and weekly variation in PM2.5 (Borgerhout-2)

Although it is not entirely clear in the graph above, a general trend was also found in the average daily concentrations that was also observed at the current PM2.5 measuring stations of VMM. The average concentrations in 2003 showed the following trend (the station in Borgerhout has number 42R801).[14]



The concentrations on Wednesdays, Thursdays and Fridays were higher than the weekly average, while Monday and Sunday showed the lowest concentrations.

Over all VMM sampling locations, the highest concentrations of PM2.5 were measured in Borgerhout (29 µg/m³ and 45µg/m³ for the first and second campaign respectively). The highest concentration of PM2.5 was also measured in Borgerhout (99.7 µg/m³ during the second campaign; 24h-sampling). We found that PM2.5 contributions to PM10 were the highest in Borgerhout (from 71% on average; 92% maximum), which means that most particles in Borgerhout belong to the fine to ultra-fine particle range.

In view of possible new European directives, it might be interesting to evaluate the measured concentrations and to check if they meet the first proposals for PM2.5 limit values.[6] The Clean Air for Europe (CAFE) project has investigated the following proposal:

1) a limit value of 20 µg/m³ (daily average);
2) a maximum number of 35 values per year exceeding a concentration of 35 µg/m³.

Since we only sampled and measured for maximum 3 months at each location during our campaigns, it was not possible to immediately check if the locations met the current proposal on a yearly basis, but it was possible to make a prediction based on extrapolation using the results that we had. Looking at our data, we could clearly see that we already exceeded the average concentration and number of allowed exceeding values within the short campaign period (76 days). The average PM2.5 concentration was 38.2 µg/m³ and 37 validated concentrations exceeded 35 µg/m³.

Table 6: Average PM2.5 concentration and number of exceeding values

LOCATIONS	*Days*	*PM2.5 concentration TEOM (µg/m³)*	*PM2.5 concentration Partisol (µg/m³)*	*Number of values > 35 µg/m³*
Petroleumkaai	89	14.6	20.9	9
Borgerhout	76	21.5	38.2	37
Zelzate	91	16.9	21.7	13
Hasselt	82	13.8	17.3	5
Wingene	94	17.3	19.8	17
Mechelen	71	16.4	19.3	11

Using the following formula, it was possible to extrapolate the values above to know the values for a whole year. The average year concentration of PM2.5 at a certain location was calculated using the average concentration during the short sampling period and a correction factor based on proportion of the average concentrations measured by VMM during the same period and over a whole year at other reference locations (average values are denoted by the accent marks <>).

$$\langle local\ PM2.5 \rangle_{YEAR} = \langle local\ PM2.5 \rangle_{PERIOD\ X} \times \frac{\langle VMM\ PM2.5 \rangle_{YEAR}}{\langle VMM\ PM2.5 \rangle_{PERIOD\ X}}$$

In this way, it was possible to avoid over- or underestimations due to unforeseen, general seasonal variations. The yearly average PM2.5 concentration was determined from VMM data for three locations in 2002: 16.1 µg/m³; the average for the same period as in Borgerhout was calculated: 21.5 µg/m³. Therefore, we could already assume that the very high value of 38.2 µg/m³ in Borgerhout was due to measurements that were carried out accidentally in a selective period of very high concentrations. The yearly average for Borgerhout was therefore expected to be lower than 38.2 µg/m³.

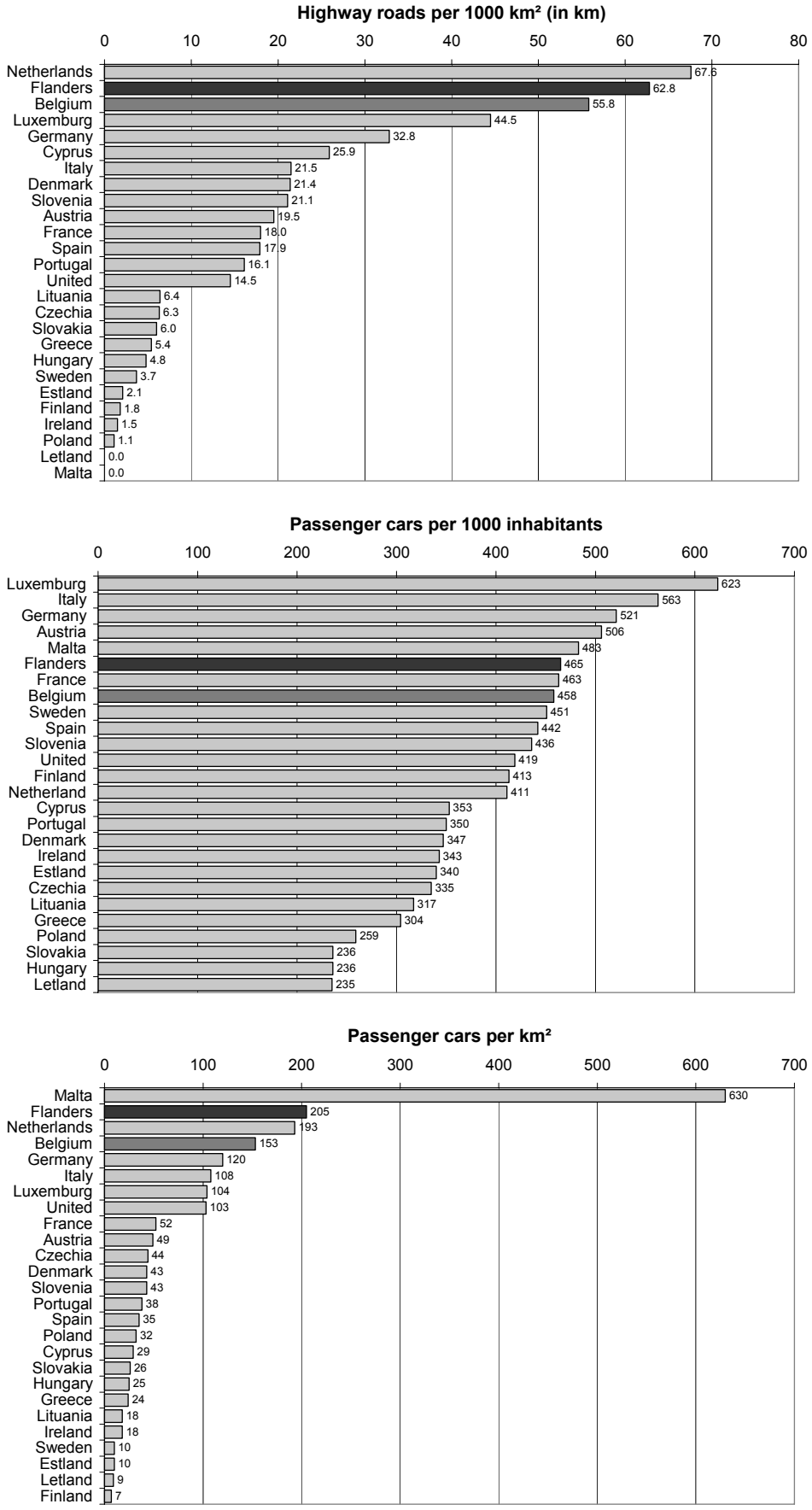


Figure 20: Statistic comparison of road and car density in Europe (after [21])

Effects of traffic were also found by our monitor for organic and elementary carbon (**ACPM**). Figure 21 shows the hourly variation of total carbon concentrations during some days in the first campaign. Although the rough variations of the concentrations are probably related to the meteorological influences, some small peaks can clearly be observed. Again, morning and evening rush hours result in concentration peaks at 8h-10h and 17h-20h. Some peaks occured at 4h in the morning, but it seems fair enough to assume that most peaks correspond to daily traffic jam. This is a very important conclusion in view of the effects of PM2.5 on human health, as we will explain later.

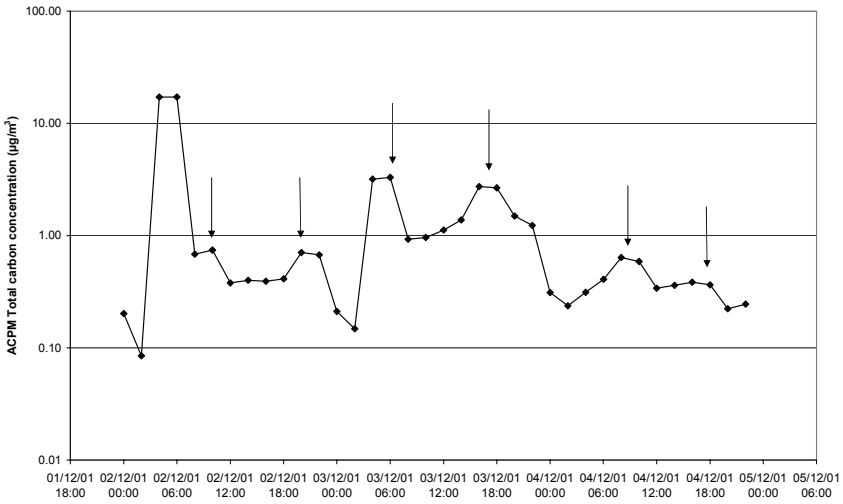
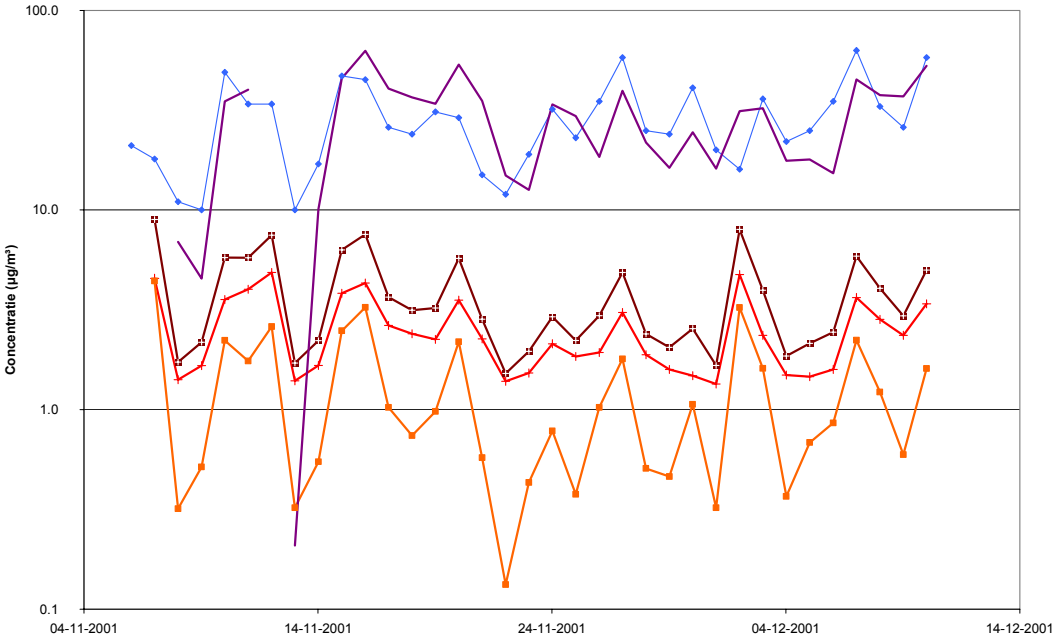


Figure 21: Hourly variation of carbon concentrations in Borgerhout

If we look at the whole set of data related to soot and carbon, it is important to notice that the curves representing these concentrations run parallel with the PM2.5 curves. For a clear interpretation of the graphs, we need to point out that we encountered a problem that is similar to the one with the optical Dustscan monitor. VMM and VITO have determined so-called black smoke or soot concentrations using a standardized optical method based on the black staining of loaded filters (reflectometry). Although VMM measurements were carried out for the totally suspended particulate fraction (TSP) and VITO used PM2.5 filters, both black smoke concentrations almost equal the PM2.5 concentrations, which is not logical, since PM2.5 must consist of much more species than 'black smoke' or 'soot'. As expected, this can again be explained by the calibration of the measurements. The ACPM results showed to be more consistent, so we preferred to work with these data instead, but the black smoke results did confirm the trends in our results. Borgerhout appeared to have the highest concentrations of elementary carbon measured at the six monitoring stations. This confirms again the influence of traffic, which produces high amounts of so-called carbon particles. For example, Petroleumkaai had much higher concentrations of organic carbon, which is logical, since it is located near petroleum refineries in the harbour of Antwerp that emit various organics. The average contribution in Borgerhout of elementary and organic carbon to PM2.5 was 12% and 14% for the first and second campaign respectively, which is lower than at other stations (the highest total contributions were found in Mechelen and Petroleumkaai).
The results for all locations are summarized in the tables and figures below. If data appear to be missing for some stations, this means that the involved instruments were not deployed there.

Table 8: Minima, maxima and averages of ACPM 24h-averages

	Elementary carbon (µg/m³)			*Organic carbon (µg/m³)*		
LOCATION	*Min.*	*Max.*	*Average*	*Min.*	*Max.*	*Average*
Antwerpen-Petroleumkaai-1	0.2	3.3	1.1 ± 0.8	2.0	7.3	4.1 ± 1.3
Antwerpen-Petroleumkaai-2	0.1	1.1	0.4 ± 0.3	0.7	7.6	2.3 ± 1.3
Antwerpen-Borgerhout-1	0.1	4.4	1.3 ± 1.0	1.3	4.9	2.5 ± 1.1
Antwerpen-Borgerhout-2	0.5	3.1	1.5 ± 0.6	1.0	5.6	2.9 ± 1.3
Zelzate-1	0.0	1.9	0.6 ± 0.5	1.1	5.9	2.6 ± 1.5
Hasselt-2	0.1	1.1	0.3 ± 0.2	1.3	5.6	2.7 ± 1.1
Mechelen-2	0.1	1.5	0.5 ± 0.3	2.0	10.2	4.2 ± 1.6



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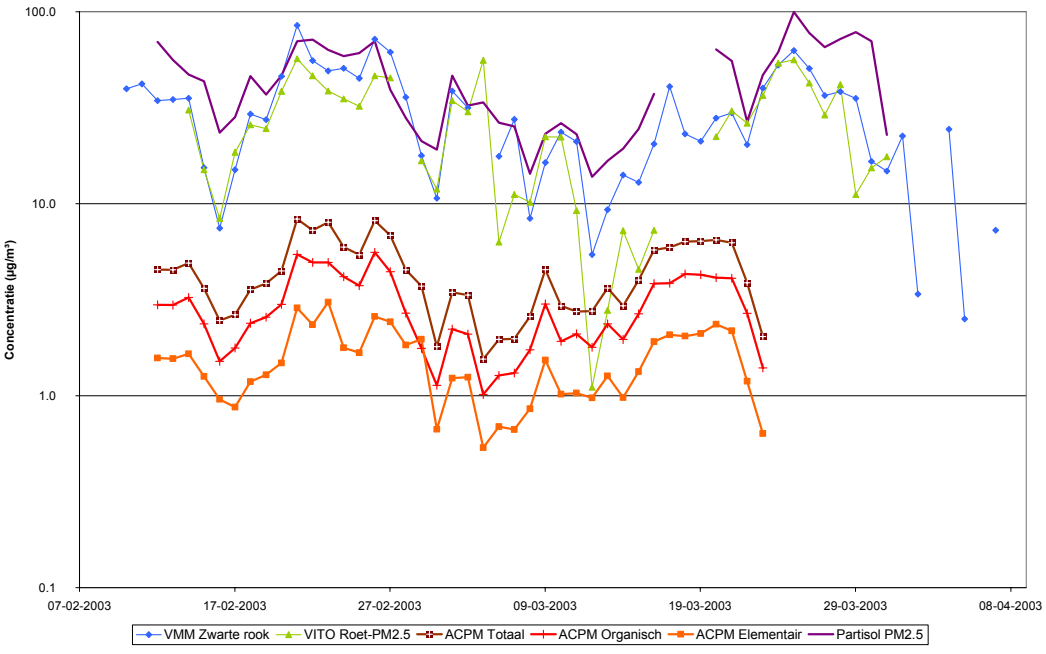
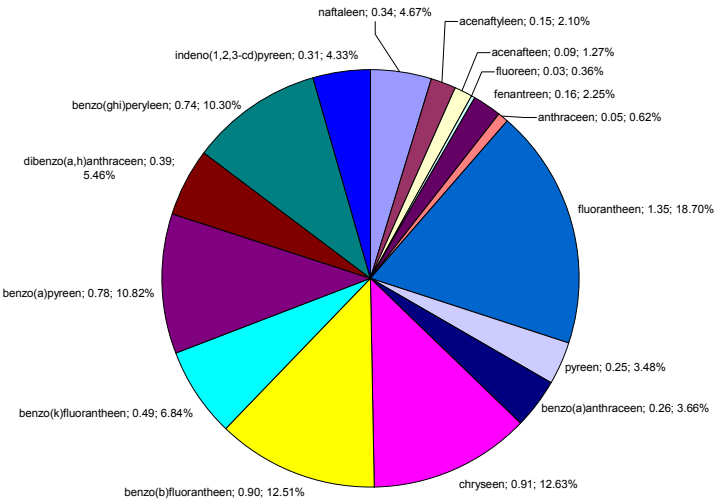


2)

Figure 22: Graphs of the carbon and black smoke measurements in Borgerhout

To have a better idea of at least one relevant fraction of the organic matter in the PM2.5 fraction, we also sampled polyaromatic hydrocarbons, for which concentrations were determined by **HPLC** in the VMM laboratory in Ghent. PAH are formed during combustion or in some industrial processes (like petroleum refining, cokes production or aluminium production). Background concentrations are reported to be 0.02-1.20 ng/m³ for rural areas and 0.15-19.30 for (sub)urban areas. Although legislation doesn't foresee any standards for air quality, PAH are known to be toxic; some are known to be mutagenic or carcinogenic. Benzo(a)pyrene is commonly accepted to be the most dangerous one and in the Netherlands a maximum of 1 ng/m³ is set as a limit value (yearly average). PAH could occur as gaseous species, but they could also be present in particulate form.
We found the second largest concentrations of particulate PAH for both campaigns in Borgerhout, namely 7.23 and 9.21 ng/m³, or 12 and 21% respectively. Consequently, Borgerhout also showed lower gaseous PAH in both campaigns.



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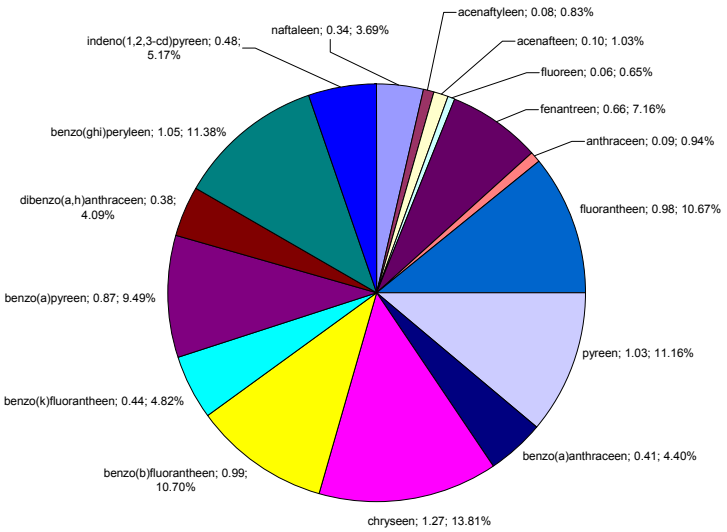

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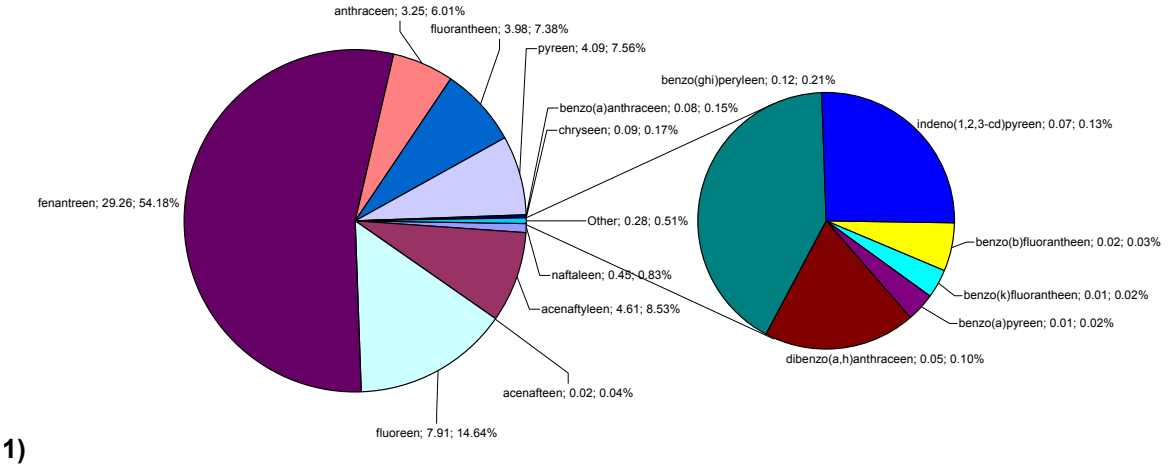
Figure 23: Absolute and relative concentrations of particulate PAH in Borgerhout

Besides the influence of traffic, there is another important source of particulate organic and elementary carbon, namely domestic heating. However, we could not clearly trace back this source in our measurements, since both campaigns in Borgerhout took place during quite cold periods in late autumn and early spring.

Therefore, it was not possible to detect some contrasts between both campaigns in regard of this aspect. However, the contrast with the rural, remote location in Wingene shows that combustion processes in areas with more industry or busier traffic are indeed responsible for the presence of observed PAH. The highest benzo(a)pyrene concentrations were encountered during cold periods, especially during Zelzate-1 (winter) and Mechelen-2 (autumn) for which the average 24-concentration of benzo(a)pyrene was higher than 1 ng/m³. In Borgerhout, only four 24h-measurement were found to exceed this value (one during the first campaign, three during the second).



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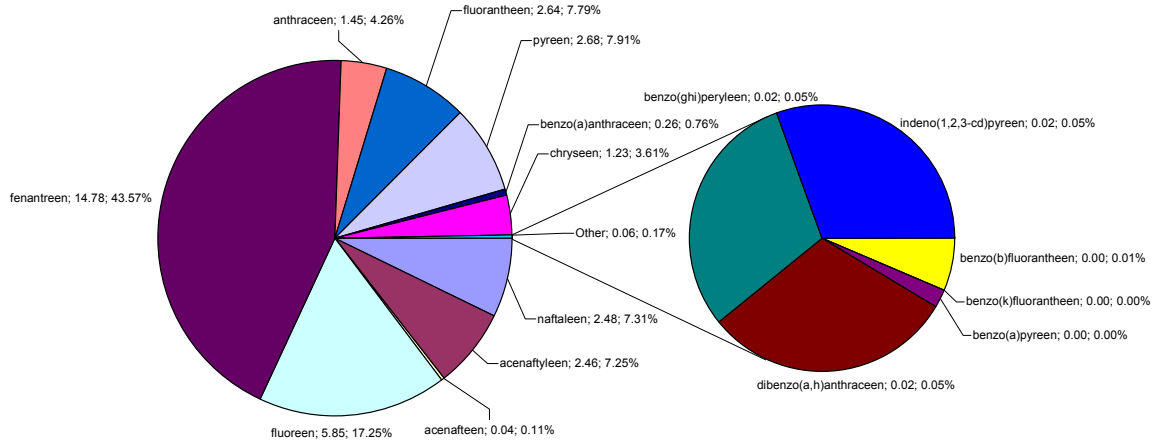

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Figure 24: Absolute and relative concentrations of gaseous PAH in Borgerhout

The total contribution of all PAH concentrations is less than 0.1% for all locations, so it is very difficult to say anything about the possible impact on human health from this point of view. As we described before, the toxic character of some PAH is well-known, but it is very difficult to assess their impact due to their diverse and complex nature.

Particulate inorganic species on our filters (like sodium or ammonium nitrates and sulfates) were determined by **ion chromatography**. First the filters were leached using water in an ultrasonic bath, after which the water-soluble particulate fraction was characterized. Gaseous inorganic species (like SO_2 and NH_3) were sampled using denuder tubes that were coated with adsorbing layers. After extraction of the chemi-adsorbed compounds, ion chromatography was able to determine specific ions for which the concentration is proportional to the concentration of the sampled gases in the air. Unfortunately, no gaseous species were determined using denuders in Borgerhout, but monitoring measurements were put to our disposal by VMM.

The high nitrate and ammonium content, as well as the high concentrations of NO and NO_2 during both campaigns in Borgerhout prove once more that the impact of traffic on air quality is unmistakably high. The gaseous exhaust of motor vehicles mainly exists of NO_x (due to the oxidization of nitrogen during combustion) and organics. These compounds may react with other species to form particulates, in particular nitrates and in a second phase ammonium.
The highest total ionic concentration was found during the second campaign in Borgerhout (48.77 µg/m³), while the average concentration consisted of 7.63 µg/m³ NO_3^- and 4.94 µg/m³ NH_4^+ (the highest concentrations measured over all locations). The concentrations in the first campaign were less pronounced, but still quite high (the relative contribution to the total PM2.5 concentration, however, was not the highest in Borgerhout (35% and 38% for the first and second campaign respectively). Sulphate concentrations were also found to be quite high (4.23 and 4.30 µg/m³ respectively), but less pronounced as in Petroleumkaai.

The average NO_2 concentrations were 53 and 61 µg/m³ for the first and second campaign respectively; NO concentrations were 58 and 38 µg/m³. Again SO_2 concentrations were quite high, but less than in Petroleumkaai and Zelzate (17 and 18 µg/m³ for the first and second campaign). The SO_4^{2-} and SO_2 might be related to domestic heating during the cold sampling periods, but again this cannot be proven unambiguously. Fuel for vehicles also contains sulphur, but less than in the past, and it is also difficult to trace back if the sulphur containing compounds come from combustion in motor vehicles. The influence of traffic is much more explicitly visible under the form of nitrates and NO_x, as can be seen in the tables below (*n.d.* means that the species were not detected or that they had concentrations below the detection limit).

Table 9: Average ionic concentrations (24h, µg/m³)

LOCATION	Na^+	$NH4^+$	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
Petroleumkaai-1	0.29	1.69	n.d.	n.d.	n.d.	0.01	0.01	0.74	4.00
Petroleumkaai-2	1.21	2.47	0.13	n.d.	n.d.	n.d.	0.10	3.15	2.69
Borgerhout-1	0.54	2.40	0.14	0.01	0.03	0.01	0.13	3.22	4.23
Borgerhout-2	1.12	4.94	0.24	0.01	0.05	n.d.	0.05	7.63	4.30
Zelzate-1	0.72	2.65	0.34	0.40	0.45	0.39	0.66	3.47	4.55
Zelzate-2	0.52	1.25	0.09	n.d.	0.01	0.01	0.01	0.58	3.30
Hasselt-1	0.50	1.46	0.10	0.04	0.03	0.01	0.20	2.76	2.31
Hasselt-2	0.72	1.31	0.08	n.d.	n.d.	0.02	0.06	1.72	2.53
Wingene-1	0.40	3.54	0.17	0.01	0.03	0.02	0.19	6.53	0.79
Wingene-2	0.42	1.31	0.11	n.d.	n.d.	n.d.	0.01	0.34	3.26
Mechelen-1	0.38	0.89	0.06	0.01	n.d.	0.02	0.16	0.40	0.43
Mechelen-2	0.78	2.06	0.19	n.d.	n.d.	n.d.	0.03	2.51	3.48

Table 10: Average gas concentrations (denuders, µg/m³)

LOCATION	HNO_2	HNO_3	SO_2	NH_3
Petroleumkaai-1	3 ± 1	0.4 ± 0.2	29 ± 15	5 ± 2
Petroleumkaai-2	4 ± 2	0.2 ± 0.2	51 ± 32	6 ± 3
Wingene-1	0.5 ± 0.3	0.3 ± 0.2	3 ± 3	6 ± 4
Wingene-2	0.3 ± 0.1	0.3 ± 0.1	1.4 ± 0.6	5 ± 2
Mechelen-1	0.8 ± 0.3	1.0 ± 0.7	3 ± 2	4 ± 1
Mechelen-2	2 ± 2	0.3 ± 0.2	6 ± 6	2 + 3

Table 11: Average gas concentrations (VMM, µg/m³)

LOCATION	*NO*	*NO_2*	*SO_2*
Petroleumkaai-1	24 ± 16	42 ± 11	26 ± 14
Petroleumkaai-2	35 ± 34	46 ± 15	34 ± 24
Borgerhout-1	58 ± 49	53 ± 10	17 ± 8
Borgerhout-2	38 ± 32	61 ± 20	18 ± 12
Zelzate-1	30 ± 41	37 ± 15	19 ± 9
Zelzate-2	12 ± 12	31 ± 9	6 ± 4
Hasselt-1	-	-	5 ± 4
Hasselt-2	-	-	5 ± 2
Mechelen-1	8 ± 4	32 ± 8	6 ± 3
Mechelen-2	30 ± 28	45 ± 13	8 ± 6

The results of **X-ray fluorescence** measurements on PM2.5 filters showed that the particulate fraction in Borgerhout contains quite high absolute lead concentrations (28 and 49 ng/m³ for the first and second campaign respectively). This is surprisingly high compared to the concentrations at the other locations, especially if one considers the efforts that were undertaken in the past to reduce the lead content in fuel. This means that either the lead content in petrol is still high enough to be noticed in our measurements, or else there is another source of lead near Borgerhout. The last option was not ruled out, but we could not find any possible sources in the area. The iron and potassium concentrations are also quite high (the latter might indicate wood combustion, but it might also be coming from other biogenic particles). The aluminium and silicon content indicate the presence of soil dust in the particle fraction. Although absolute concentrations are quite high, the relative contribution of these metals to the PM2.5 fraction is not so high compared to those at other locations (only 3% and 2%). The table below summarizes the results (*n.d.* again means that the elements were not detected or that the concentrations were below the detection limits).

Table 12: Average elemental concentrations (XRF; ng/m³)

LOCATION	*K*	*Ca*	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Rb*	*Sr*	*Pb*	*Al*	*Si*
Petroleumkaai-1	122	104	11	9	2	9	188	6	6	57	n.d.	n.d.	13	122	366
Petroleumkaai-2	139	3	5	16	1	4	66	7	4	31	1	n.d.	26	83	58
Borgerhout-1	175	79	2	5	2	11	197	8	10	70	n.d.	n.d.	28	55	186
Borgerhout-2	269	78	8	9	3	10	253	6	13	83	2	n.d.	49	106	118
Zelzate-1	247	111	6	6	1	13	279	9	7	84	1	1	24	60	302
Zelzate-2	104	63	6	8	1	3	95	4	5	20	1	n.d.	15	51	181
Hasselt-1	93	32	2	n.d.	n.d.	4	56	3	3	33	n.d.	n.d.	8	21	74
Hasselt-2	239	91	3	4	3	8	144	9	7	65	2	n.d.	26	55	42
Wingene-1	85	21	1	7	1	4	57	3	2	22	2	n.d.	13	34	66
Wingene-2	66	20	1	5	1	3	31	3	1	14	1	n.d.	10	28	38
Mechelen-1	69	34	1	1	2	5	60	4	5	31	1	n.d.	8	29	74
Mechelen-2	183	91	3	3	3	9	127	8	9	66	2	n.d.	30	46	35

Now, what does **electron microscopy** offer to this study? First of all, it is obvious that the different concept of single particle analysis compared to bulk analysis should offer us a look at how the different encountered species are distributed on the level of individual particles. Secondly it should at least confirm some of the previous conclusions from other techniques. As explained before, we carried out conventional SEM as well as TW-EPMA.
For the first technique, filters were taken using a simple setup of a filter unit connected to a pump. Before analysis, the filters were coated with a carbon layer for preventing charging effects. The analysis itself was split up into two parts. In a first run, only the 'coarse' particles with diameters above 2.5 µm were analyzed; in a second run, the smaller 'fine' particles were analyzed as well. For TW-EPMA, samples were collected using a Berner impactor. Silicon was used on stages 3 and 4, while silver was used on stages 5 to 8. Analyses were carried out as optimized (see chapters 2 and 3). Of course, we need to take into account the lower detection limit of 0.2 µm for particle size detection in both techniques.
The results for the conventional SEM anamysis of samples from Borgerhout samples are shown in Figure 25. The results for coarse and fine particles are given separately. The applied cluster identification table was given before in chapter 3. Similar particles type were given the same basic colour: blue for metal-containing particles, grey for low-*Z* particles, green for Ca/Mg-rich particles, and brown for Si-rich particles.

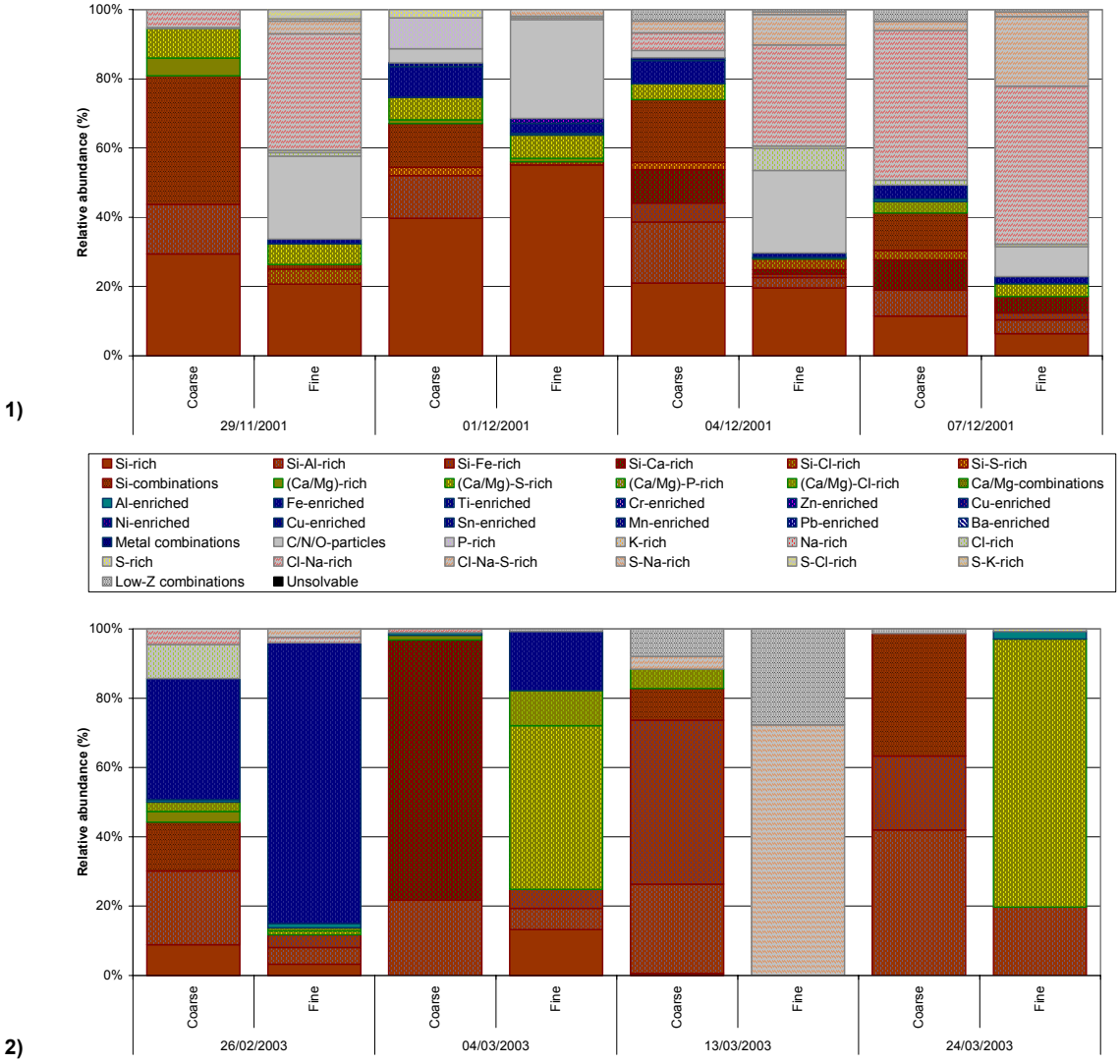


Figure 25: Results of conventional SEM analysis of Borgerhout samples (2 campaigns)

An indicative calculation of absolute particulate concentration, expressed as the number of particles per m³, confirms the previous conclusion about the huge number of fine particles: 15.2 x 10^6 fine versus 1.3 x 10^6 coarse particles per m³ in the first campaign; 1.3 x 10^6 fine versus 0.8 x 10^6 coarse particles in the second campaign. Especially in the first campaign, the fine fraction was enormously large compared to the coarse fraction, but both coarse and fine concentrations were extremely high compared to those of the samples from the other locations. In the second campaign, however, only the coarse fraction is the highest; the fine fraction is less abundant compared to the first campaign.
With one fast look at the graphs above one could say that, as expected, the contribution of silicon-containing particles is higher in the coarse fraction, since it consists mainly of soil dust that is lifted into the air by the wind. On the other hand, low-*Z* contributions are much more important in the fine fractions (especially on March 13, 2003). In the second campaign the number of sodium-chloride particles is smaller, which confirms the results from ion chromatography (lower chloride concentration in the second campaign). Special attention is required for the low-*Z* identification type 'C/N/O-particles', since it could contain organic and ammonium nitrate particles. The abundance of this type is higher in the first campaign, although we must stress that 1) these concentrations are relative, 2) the other (low-*Z*) groups might also contain the same type of particles without being noticed in particular. However, a thorough interpretation of the results is difficult due to the fact that a simple representation in graphs is almost impossible.
The table below gives a less-detailed summary of the average results for the main particle groups and for all locations over the two campaigns. It first appeared as if some of the results are in contradiction with those of other techniques.

Table 13: Average abundances (%) of the grouped particle types

	Borgerhout	Zelzate	Hasselt	Wingene	Mechelen	Petroleumkaai
Si/Soil dust	20.8	19.4	14.3	36.2	20.4	52.3
Ca/Mg	19.0	3.1	34.9	14.8	13.5	1.8
Metal	13.7	11.4	5.1	16.8	23.4	11.6
Low-*Z*	42.5	59.3	44.9	30.4	38.6	34.1

Although metal particles were expected due to the presence of a non-ferro industrial site that is located near to the VMM station, Zelzate appears to have one of the lowest abundances for metal-containing particle clusters. We must, however, remind the reader that the clustering technique and the applied regrouping are not so straightforward, and quite a lot of details are lost while reducing the datasets. The applied identification is based on the elements with the highest abundance within each cluster. The name of the particle type does not exclude any other elements to be present in the particles belonging to that type. Fact is that the results in Zelzate showed that many of the collected particles indeed contained concentrations of copper and iron, but these were too low to be identified as copper-rich or iron-rich. Therefore, it is clear that the overall cluster names after the (re)grouping are too general in case one is looking for species that are only present in small concentrations. It should always be remembered that the names of the particle clusters only indicate the main composition of the particle. For example, in order to evaluate the specific presence of heavy metals and their involved health risks, one should not only check the groups that have been given names containing a toxic heavy metal, but the presence of the element in the total dataset should also be evaluated. Elements that are present in an outer layer of a particle will have lower concentrations and will not be considered in the classification, although the toxicological effects might be high as well. Therefore, it was clear to us that, depending on the aim of the analysis, single particle analysis should indeed be done on the individual particle level, even during data interpretation.

As could be seen in the graphs representing the SEM results for Borgerhout, low-Z particles are quite abundant. The importance of these particles in Borgerhout and in the other locations is confirmed by TW-EPMA, but with this technique we can now also study the low-Z composition in much more detail. The results of the applied hierarchical cluster analysis are shown in Figure 27 (identification according to the table in chapter 3). A large number of clusters were found to contain carbon and oxygen, often combined with nitrogen and sulphur. Carbon and oxygen are of course linked to organic or carbon-containing species, which might again be connected to traffic emissions or any other combustion sources. Nitrogen and sulphur indicate the possible presence of ammonium nitrate and/or sulphate, which can also be traced back to traffic and combustion, since they originate from NO_x (especially on the lowest stages, as expected). In the first campaign, we also found clusters with less carbon, indicating pure ammonium nitrate and sulphate particles. In the second campaign the overall presence of aged sea salt, biogenic (potassium-containing) particles, alumino-silicates and calcium-containing particles was much higher than in the first campaign. In both campaigns we found iron-containing particles, in the second campaign even pure iron oxides.
The application of the expert system to the different datasets showed that at all locations a large number of particles could be assigned as 'carbon-rich', especially at the urban and industrial sites with heavy traffic, which confirms the results of the soot monitoring (Hasselt 12%, Wingene 17%, Petroleumkaai 33%, Borgerhout 36%, Mechelen 38%, Zelzate 41%). Other inorganic species were of course found as well (especially aged sea-salt particles), but it is more difficult to specifically trace these back to traffic or to other anthropogenic sources near the stations.
Some differences between the locations could be found in the images taken during analysis. In the samples of the first campaign in Mechelen and Hasselt, we could observe different spots containing long-shaped particles which turned out to be calcium/magnesium carbonate and sulphates. Most other particles were found to be more round-shaped, but even there we could see some remarkable particle characteristics. Many particles (often beam sensitive) appeared to have a core-shell structure, which could often be seen in images. One could recognize them as crystal-like particles, surrounded by a dark amorphous, almost fluid mass. In other cases, one could find groups of similar particles in a 'Stonehenge' kind of configuration, clearly indicating that they had 'splashed' onto the surface of the substrate. This shows that many particles are quite wet during sampling and that some chemical transformations that started during transport in the air, might be studied with our cryogenic, low-Z method, also in combination with the multiple-voltage technique. The later was, however, not used in this research.

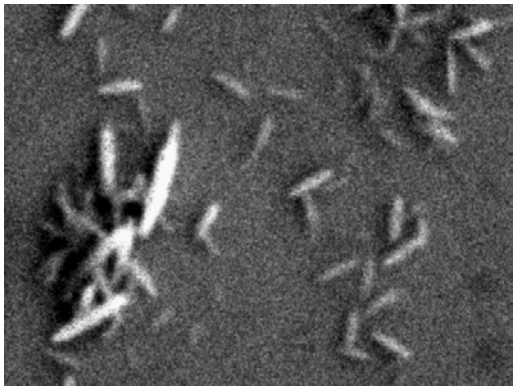
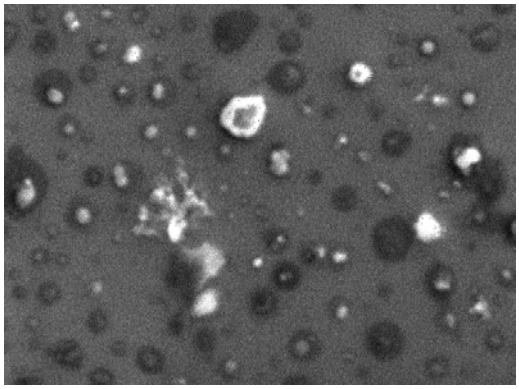
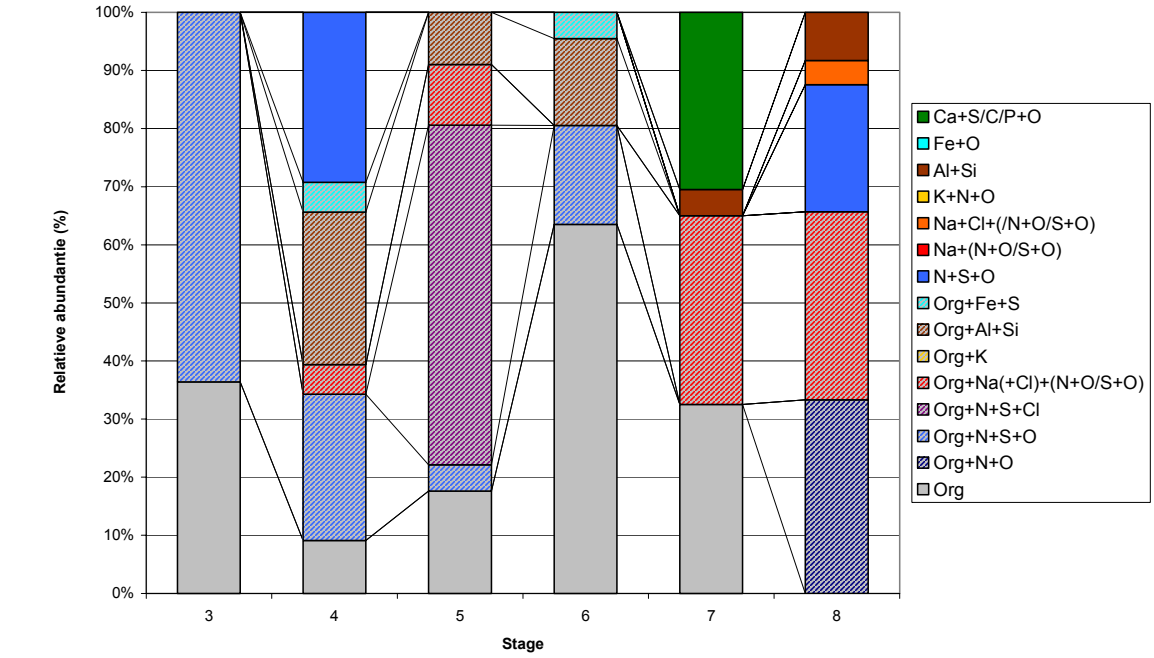
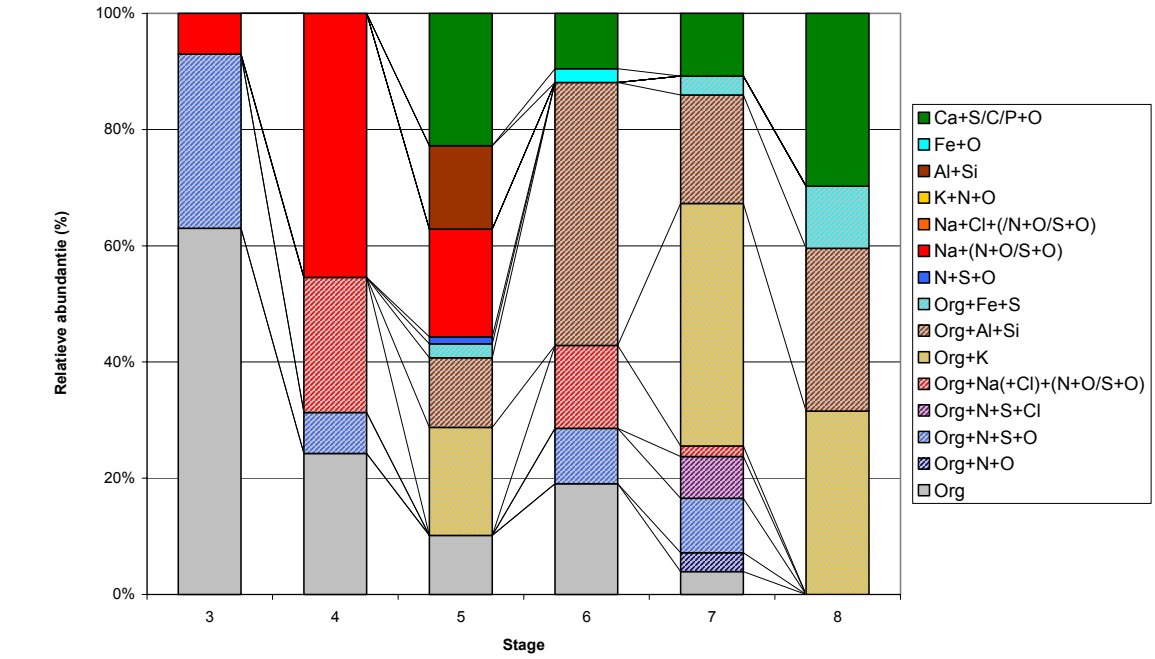
a)  b) 

Figure 26: Pictures of typical particles in samples from a) Mechelen, b) Borgerhout



1)



2)

Figure 27: Results of TW-EPMA analysis of Borgerhout samples (2 campaigns)

In this section, we saw that the samples in Borgerhout clearly showed its urban character and the influences of road traffic. The daily variation in the PM and carbon concentrations matched periods with and without traffic jam. The concentrations of sulphate, nitrate, ammonium and organic compounds (PAH) were quite high in both campaigns, which were confirmed in the SEM/EPMA measurements. The results of the other locations will be summarized in the next section. The main highlights of each location will be briefly discussed, after which the Flemish results will be compared with those found in literature for other European cities.

4.2 Other locations and conclusions

Zelzate is also located in the vicinity of rather busy roads (though the monitioring station is not as close to these roads as in Borgerhout) and near an industrial site. Measurements by XRF and SEM clearly showed the presence of metallurgical activities (steel manufacturing), especially in the first campaign. PAH concentrations were found to be high as well.
SEM/EPMA applied to the samples taken in **Hasselt** showed pronounced abundances of biogenic particles. All other species were quite average over both campaigns.
Wingene could be designated as 'rural' and 'remote'. In the IC results of the first campaign, clear influences of fertilization were found (nitrates, ammonium, ammonia). This influence was not seen in the second campaign, and particle distributions by APS confirmed that the size-variations in both campaigns were quite different. This is most likely due to the fact that manuring activities were lower in the second campaign. Fertilization obviously caused a high peak in the size distributions for particles with particle diameters > 10 µm, as can bee seen in the figure below (note the scale difference).

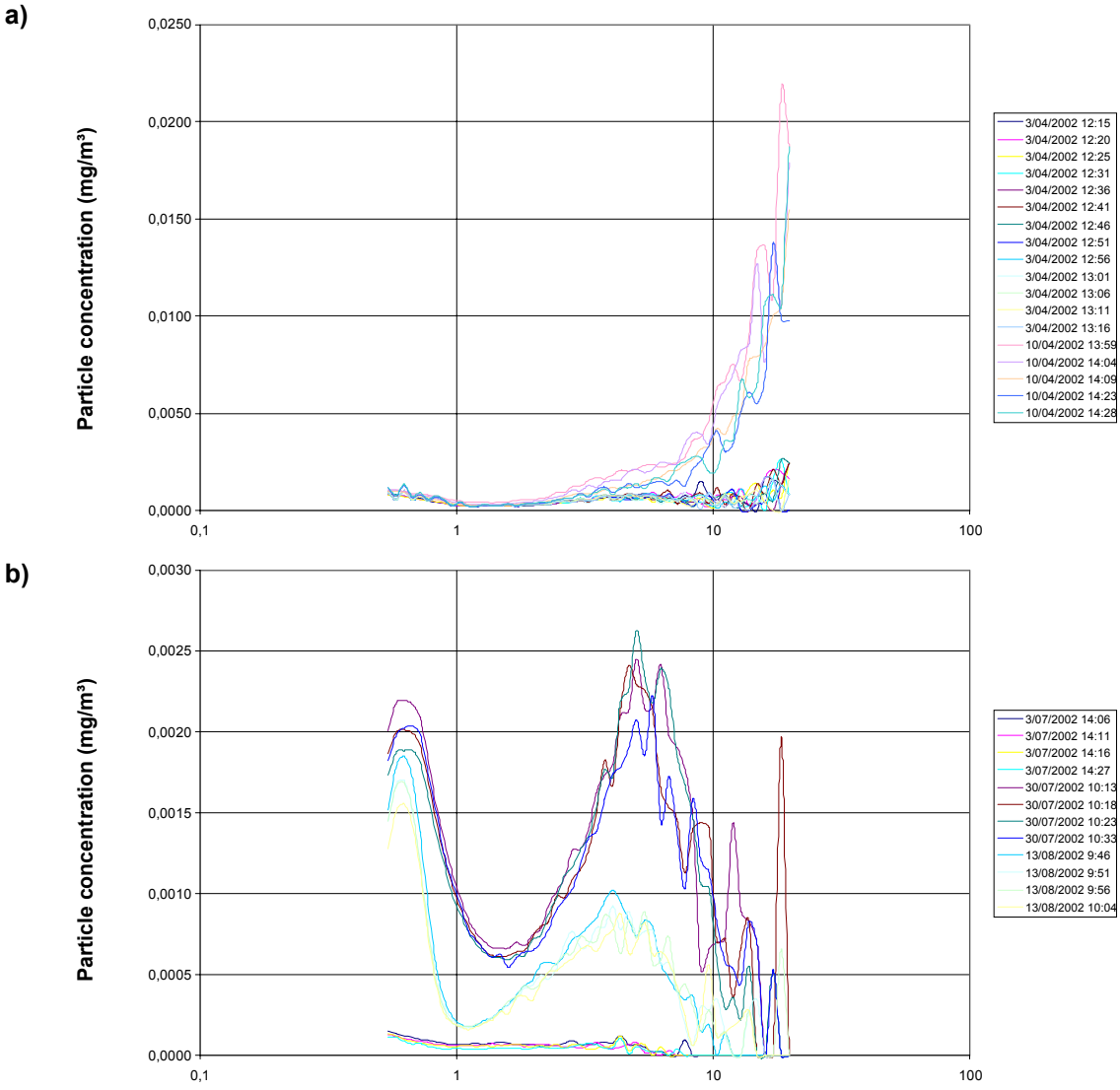


Figure 28: Particle size distributions in a) the first and b) the second Wingene campaign (based on number distribution and assumed density of 1 g/cm³)

The influence of the Antwerp petroleum industry and harbour near the location at **Petroleumkaai** was found in high sulphur, sulphur dioxide and sulphate concentrations. HPLC analysis also showed high gaseous PAH concentrations.
The first campaign in **Mechelen** was quite problematic due to the weather conditions, which made the interpretation of the results quite difficult, e.g. the PM composition was heavily influenced by wash-out. In the second campaign the (sub)urban character of the location was more pronounced (influences of traffic and industry).
Seasonal variations were found at all locations in the sulphate concentrations that were very high during summer periods. Indirectly, the difference between both campaigns in Wingene is also time-related, since fertilization occurs only in specific periods of the year.

The contributions of carbon and important ionic species to the total PM2.5 concentrations form the best criteria to compare the different Flemish locations and they are also interesting in view of Flemish and European reduction strategies. Therefore we determined the nitrate, sulphate, ammonium and carbon contributions for our six locations (as an average over both locations, if data were available), and we compared them to values found in literature for other European locations.[6] Graphs for the different locations can be found in Figure 29 and Figure 30. The ionic contributions 'sulphate', 'nitrate' and 'ammonium' speak for themselves; 'EC' and 'OC' respectively stand for the contributions of elementary and organic carbon, as measured with ACPM.

From a literature summary by the Clean Air For Europe workgroup (CAFE), we selected data for a few locations with rural or urban/traffic influences in and around European cities: Berlin in Germany (references from 1998 and 2000); Madrid and Barcelona in Spain (references respectively from 1999 and 2001); London and Birmingham in the United Kingdom (average values were reported for different locations in a reference from 2003; only carbon data available); Bemantes in Spain (reference from 2001).[23,24,25,26,27,28]
Bemantes is the only rural location with useful data. The CAFE publication contained more results for other cities, but it was found that the presented data were not always comparable. For locations in Sweden, only PM concentrations were reported. Results for locations in the Netherlands contained PM concentrations and its contributions due to sea salt, traffic and soil dust (in $\mu g/m^3$). Probably, literature sources could provide us with more data, but it is important to note that there is clearly a lack of uniform and comparible data for different locations in (and outside of) Europe.
Even for the selected locations, a thorough comparision is hampered by the differences in the applied analytical methods and in the way results are reported. The CAFE report even does not provide any information about time period during which samples were taken at the other locations, while it is clear from our campaigns in Flanders that time and seasons do play an important role. The carbon contributions were probably the least comparable criteria that we encountered in our attempt to find parallels between the literature references. For Berlin and the locations in the United Kingdom, 'organic matter' ('OM') was reported instead of 'OC', including of course much more than just the carbon content. The values of the United Kingdom were explained to be calculated as 1.4 x OC , but for the Berlin samples no explanations were given. For other locations, we only found the total carbon contributions without distinction between elemental and organic carbon. The ionic contributions didn't cause much problems, though we must say that for Berlin a distnction was made for sulphate originating from aged sea salt and from other sources (sulphate vs. non-sea-salt or nss-sulphate).

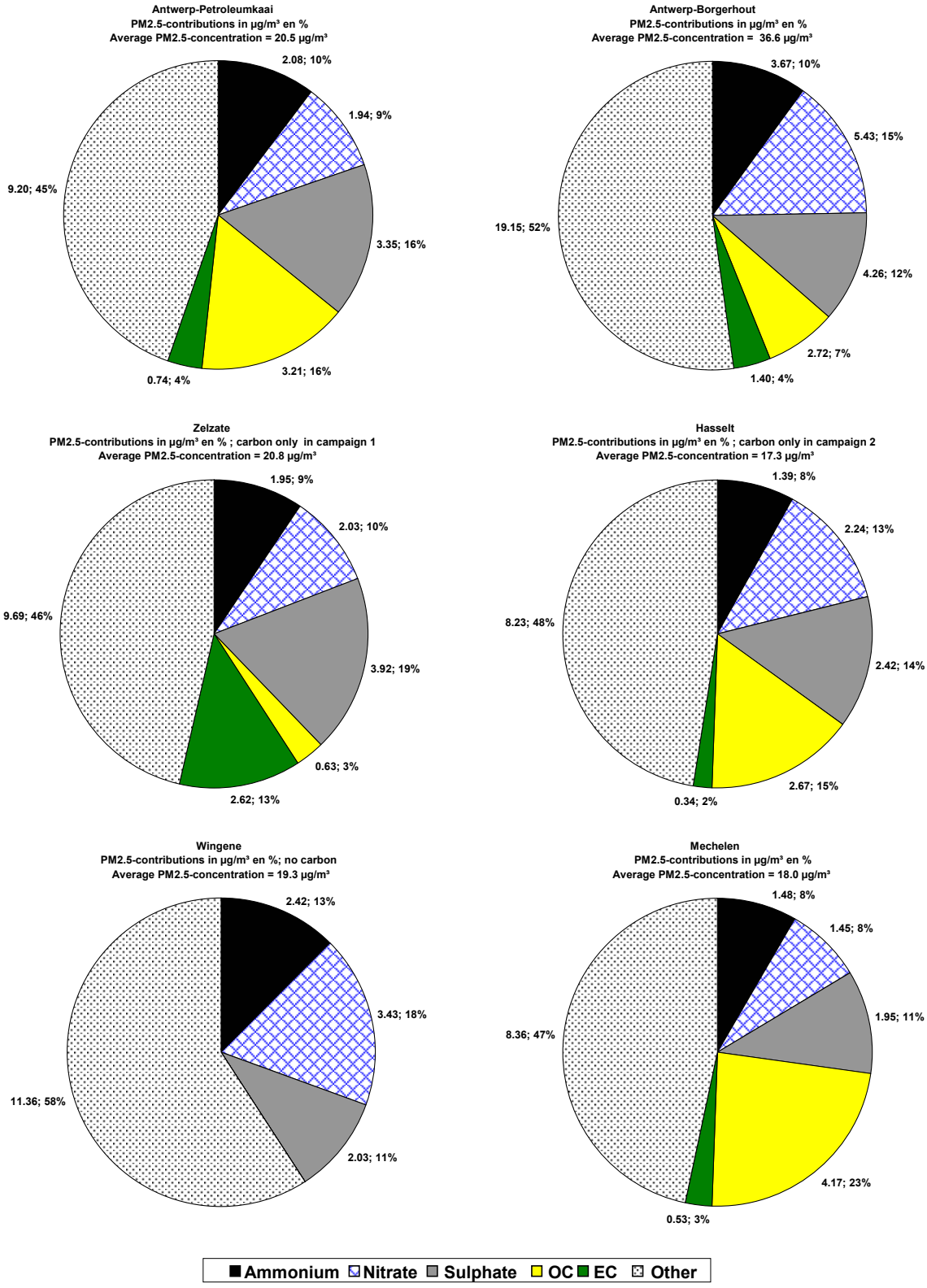


Figure 29: Average composition of PM2.5 at the different Flemish sampling locations

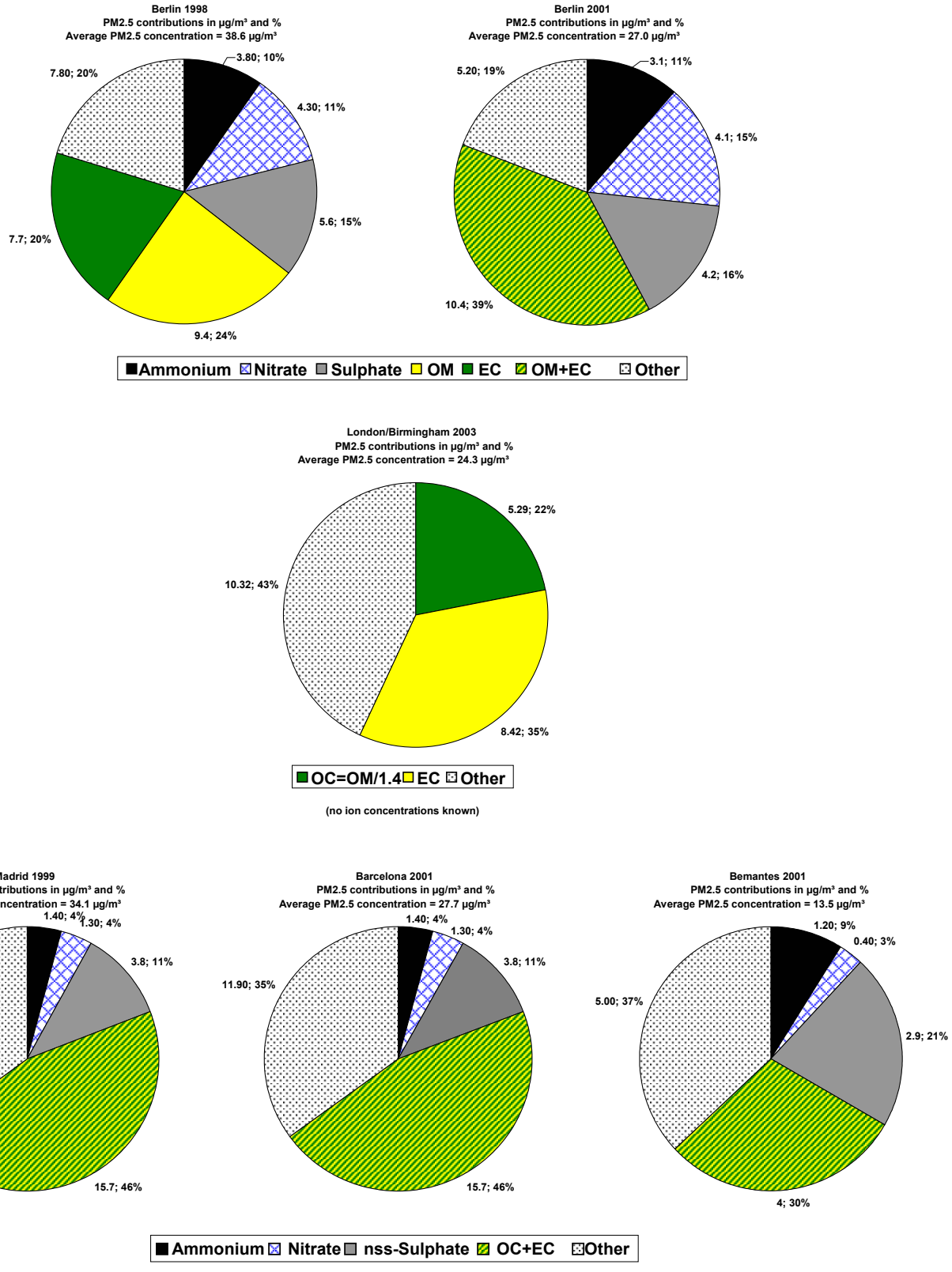


Figure 30: Composition of PM2.5 in other cities in Europe

It is clear that the measurements in Flanders produce similar results for relative ionic contributions (27-41% in Flanders compared to 19-42% elsewhere) and absolute PM2.5 concentrations (17-37 µg/m³ in Flanders compared to 14-39 µg/m³). There is, however, a huge difference between the total carbon contributions, calculated or given as 'OC+EC', 'OM+EC' oor '(OM/1.4)+EC': 11-26% in Flanders compared to 30-57% in other locations. Although the selected locations outside of Flanders predominantly had urban or traffic influences, an explanation of the lower percentages is probably not to be found in loaction or seasonal differences. As was shown in our own measurements of soot, carbon and black smoke, there are huge differences between the results of different analytical methods (optical, thermal or both) and this has consequenses in view of reporting and interpretation. Therefore, the carbon concentrations in Flanders are probably not lower, but the measurement results by ACPM are, because even in the rural station of Bemantes a higher concentration was found. Therefore, the most important conclusion of this study in view of future policy making is that international agreements should be made about the right and consistent application of measurement equipment and analytical methods, in addition to the uniform interpretation and reporting of results. It would be impossible to develop effective reduction strategies for PM2.5, if they would be based on false or ill-considered knowledge.

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