Convention on Long-range Transboundary Air Pollution

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Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe

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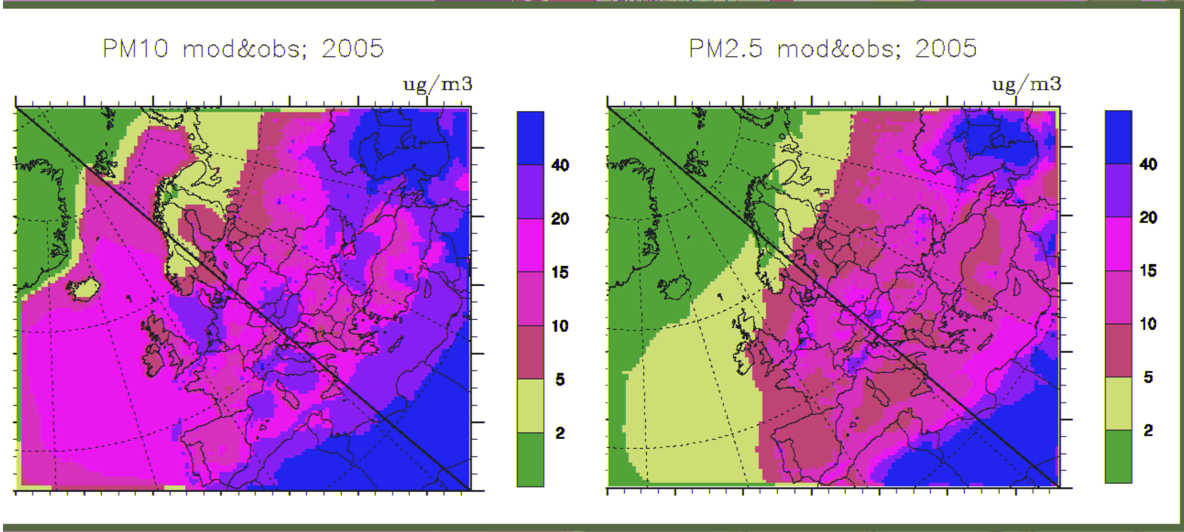

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EMEP Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe

Transboundary particulate matter in Europe
Status report 2007

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Executive Summary

The objective of the present report is to provide an updated assessment of the particulate matter concentrations in the European rural background environment, made available by measurements and modelling.

PM level in 2005

The number of countries performing and reporting measurements of PM_{10} and $PM_{2.5}$ mass concentrations at their EMEP sites in 2004 are 13 and 9 respectively (an increase by one country compared to 2004). There were 38 sites measuring PM_{10}, of which 22 measured $PM_{2.5}$ as well. This is a reduction of one site compared to 2004. Additionally, three of the sites measuring PM_{10} and $PM_{2.5}$ also performed measurements of PM_1. The inclusion of PM measurements at the Polish site (PL05), has improved the geographical coverage towards Eastern Europe, however a further extension eastwards is needed to provide a uniformly distributed PM monitoring network of rural background sites in Europe.

Assessment of PM levels, based on combined EMEP model calculations and EMEP observations, showed that the annual mean concentrations of regional background PM_{10} ranged from 5 to 20 µg m^{-3}, whereas the corresponding range for $PM_{2.5}$ was 2 to 15 µg/m^3 in 2005 over most of Europe. The lowest annual mean concentrations of PM_{10} were observed in the Scandinavian countries, as compared to the European mainland, ranging from 6.8 µg m^{-3} (NO01) to 40.4 µg m^{-3} (IT04). Enhanced concentration levels (above 15 µg/m^3 $PM_{2.5}$ and above 20 µg m^{-3} PM_{10}) were found for the Benelux countries, central and northern Italy, south of Spain, Central Europe (the Czech Republic, Slovakia, Hungary) and southern part of the Russian Federation. In general, European PM_{10} and $PM_{2.5}$ concentrations were 5 to 20% higher in 2005 compared to 2004, with the exception of only some regions in Sweden, northern Spain and Belgium. This spatial distribution of PM_{10} corresponds to that reported for previous years.

50 percent of the sites reported higher annual mean concentrations of PM_{10} in 2005 compared to 2004, and for the majority of these sites the increase was above 10%. The higher PM_{10} and $PM_{2.5}$ levels can only partly be explained by emission increases in a few countries, while the largest increase is due to meteorological conditions, i.e. by suppression of pollutants dispersion in the stable atmosphere over northern parts of Russia and by smaller wet scavenging due to less precipitation over most of Europe in 2005 compared to 2004.

Compared to EMEP observations in 2005, the model underestimates PM_{10} concentrations by 28% and $PM_{2.5}$ concentrations by 23%. The spatial correlations between calculated and measured concentrations are 0.68 for PM_{10} and 0.82 for $PM_{2.5}$; and the temporal correlation coefficients exceed 0.5 at most of the sites.

Exceedances of PM limit values

The EU annual limit value of 40 µg m^{-3} for PM_{10} concentrations was exceeded at the Italian site Ispra. More than 25% of the sites that reported annual mean concentrations of PM_{10} for 2005 above the WHO proposed Air Quality Guideline (AQG) of 20 µg m^{-3}. Exceedances of the proposed WHO PM_{10} level were observed for sites situated all over Europe, including Scandinavia. Model results show that the regional background PM_{10} concentrations were below the EU annual limit value in all of Europe, with the exception of the outmost southern areas of the model domain. At the same time, 2005 annual mean PM_{10} concentrations exceeded the WHO AQG in Benelux and in the Po Valley in northern Italy. In those regions, exceedances were mainly due to anthropogenic emissions, whereas in the south of Spain and the Russian Federation, eastern parts of Ukraine, Kazakhstan and in the Caucasus, the PM exceedances were largely due to the influence of windblown dust.

The Italian site Ispra was the only site exceeding the EU annual limit value of $PM_{2.5}$ (25 µg m^{-3}, to be valid from 2010), exceeding it by approximately 20%. 45% of the sites reporting annual mean concentrations of $PM_{2.5}$ in 2005 exceeded the WHO AQG of 10 µg m^{-3}. The modelled annual mean background concentrations of $PM_{2.5}$ in excess of 10 µg m^{-3} were found in most of Central and Eastern Europe, the Po Valley, the south of the Russian Federation and the EECCA (Eastern Europe, Caucasus, Central Asia) countries. In most of these areas, with the exception of the most southern ones, the exceedances of $PM_{2.5}$ can be attributed to anthropogenic emissions. Also, $PM_{2.5}$ levels exceeded 10 µg/m^3 along the main ship routes in the Mediterranean Sea.

The 24-hour limit value of 50 µg m^{-3} for PM_{10} not to be exceeded by more than 35 days, was exceeded at Ispra (99 days) and at the Austrian site Illmitz (40 days). Both sites experienced a 40% increase in the number of days exceeding the limit value compared to 2004. The model results show exceedances in the regional background PM_{10} for more than 35 days in Milan region, Moscow region, in eastern Ukraine and southern parts of the Russian Federation, in Kazakhstan and Caucasus area, but only exceedances in the cities of Milan and Moscow were due to anthropogenic emissions. The WHO daily AQGs for PM_{10} were exceeded in 4 and more days in Benelux, the Po Valley, in parts of Germany and the UK, in the south of Spain, in Eastern Europe, the Russian Federation and EECCA countries in 2005.

When comparing the daily values of $PM_{2.5}$ for 2005 with that of the WHO 24-hour guideline, *i.e.* the 99th percentile of the distribution of daily values should not exceed 25 µg m^{-3}, 19 of 22 sites exceeded the guideline. Modelled daily mean $PM_{2.5}$ exceeded AQGs for 4 and more days almost all over Europe, except for Scandinavia, north of the Russian Federation and central Spain.

Size distribution and chemical speciation

Distinct differences with respect to size distribution were observed for the three sites measuring all sizes ranges PM_{10}, $PM_{2.5}$ and PM_1 in 2005. At the Austrian site Illmitz (AT02) and the Swiss site Chaumont (CH04), PM_1 accounted for 60% of PM_{10} on an annual basis, while for the German site Langenbrügge (DE02) the relative contribution was only 40%. When examining the size distribution for the days with the highest (95-percentile) PM_{10} concentrations, PM_1 was the dominating fraction of PM_{10} at all three sites. For Illmitz and Chaumont, the relative contribution of PM_1 to PM_{10} was lower for the high-concentration events compared to the whole year, whereas it was the other way around for Langenbrügge. The relative contribution of $PM_{10-2.5}$ to PM_{10} increased considerably during summer at all three sites. This is mainly attributed to a decrease in concentration of $PM_{2.5}$ in summer, rather than increased levels of $PM_{10-2.5}$. This is a pattern observed for the sites in Central Europe in general.

The relative contribution of SO_4^{2-} and NO_3^- to PM_{10} accounted for 9-22% and 6-28% of PM_{10}, respectively. NH_4^+ always made a less contribution to PM_{10} than SO_4^{2-} and NO_3^- at those sites where concurrent measurements were available, the relative contribution ranged between 5-13%. The contribution of Ca varied with location, highest in south of Europe with a relative contribution of 5% to PM_{10}, lowest for northern sites with contributions below 1%. The sea salt content depends on the distance to the coast. The highest contribution of Na is seen at DE01 with 11%. More continental sites have less than 1% sea salt. The mean relative contribution of all the measured inorganic ions accounts for 44±8% of the PM_{10} mass. When accounting for the secondary inorganic constituents and the sea salts, the remaining aerosol mass consists of carbonaceous material, mineral dust and water. Only two sites measured carbonaceous material and mineral dust. In 2005, carbonaceous material was the major contributor to PM_{10} at the two sites performing such analysis, namely Ispra (53%) and Birkenes (26%). Timeseries of EC, OC, and TC in PM_{10} and $PM_{2.5}$ for the period 2001–2006 at Birkenes indicate that the trends of carbonaceous material resemble the evolution of total PM and secondary inorganic aerosol concentrations over the same period.

Model results show the contribution of primary constituents in PM_{10} and $PM_{2.5}$ is between 10 and 30% over most of Europe. SIA constitutes between 30 and 60% of PM_{10} and $PM_{2.5}$ concentrations, with the largest contributions over 50% in Central and Easter Europe and in the south of Sweden and the UK.

EC/OC

As indicated above, very few sites are compiling information of carbonaceous material routinely within EMEP yet. For progress in this area we are therefore dependent on specific campaigns and independent research projects. The CARBOSOL project is a good example. The project has contributed with important new information on sources of particulate carbonaceous matter in southern and central Europe. The most notable conclusion from CARBOSOL was the strong under-prediction of the biomass-burning components, and the SOA components. Unfortunately all the CARBOSOL sites are situated in south-central Europe. However, we can expect from the analysis of levoglucosan, BC and TC from the EMEP sites that different conclusions would be drawn in other parts of Europe. In particular, there is no evidence of a substantial under-prediction of wood-burning emissions at the Nordic sites. Further, the EMEP model tends to over-predict TC at these sites, suggesting that this scheme may generate too much rather than too little SOA.

Carbonaceous material sampling is hampered by the fact that various sampling approaches and analytical techniques are used to provide EC/OC data. Unfortunately, such data not easily compared, and thus hampers any attempt to establish a reliable pattern of the air pollution in Europe. This is a challenge not only troubling EMEP, but the entire scientific community, thus developing, validating, and establishing a unified protocol for sampling of OC and analysis of EC and OC is of high priority, and is currently undertaken by the EU funded project EUSAAR (*European Supersites for Atmospheric Aerosol Research*). Commercial denuders for trapping gaseous OC before they enter the filter have been validated and tested. Sorbents for collecting OC that evaporates from the filter have also been tested. The entire sampling train will be validated for various meteorological and pollution conditions, and will be completed no later than 2010. However, the denuder part of the sampling train is likely to be implemented in 2008. An optimised thermal-optical protocol for analysing EC and OC has been developed at JRC-Ispra and tested on filter samples collected at several EUSAAR sites. Feedbacks have been considered and will be used to develop a slightly revised protocol, which will be made available to the EMEP community by July 2007. Tentatively, this revised protocol could be taken into service in 2008. The methods currently used for determining EC and OC at various EUSAAR sites have been compared, and a report on this will be released by October 2007.

EMEP intensive measurement periods

The first preliminary results from the EMEP intensive measurement periods June 2006 and January 2007 have been analysed for this report. These data are very important for improving our current understanding of the temporal and spatial variation of PM and PM constituents in Europe, their sources and formation mechanisms, and for model validation.

Ten of the twenty-two sites participating in the EMEP intensive measurement periods collected filter samples for subsequent analysis of the aerosols content of carbonaceous material. Six sites accounted for the positive artefact of OC, while seven sites used thermal optical analysis (TOA) for quantification of EC and OC, which is a state-of-the-art type instrumentation that corrects for charring of OC during analysis. The number of sites quantifying EC and OC using TOA is highly encouraging with respect to implementation of the coming EUSAAR protocol, as well as for the potential number of sites reporting such data routinely to EMEP in the coming years. The positive sampling artefact of OC was found to be substantial, accounting for approximately 40% of OC in PM_{10} at those sites operating their samplers according to the QBQ-approach. The positive artefact was more substantial for fine aerosols than for PM_{10} due to the lower loadings, underlining the importance of sampling trains that correct for the artefacts.

For June 2006, the first of the two sampling periods, it was estimated that the particulate carbonaceous fraction accounted for 22-44% of $PM_{2.5}$ for the four sites reporting such data.

The initial comparison of model calculations with observation data from June 2006 EMEP intensive campaign for three stations (Birkenes, Melpitz and Montelibretti) has shown that the model underestimates PM mainly because it underestimates of carbonaceous particles and sulphate at these sites. It also shows that the model seems to be doing reasonably well calculating size distribution of sea salt and mineral dust (available only at Montelibretti) between the fine and the coarse fraction. But it appears to have problems reproducing concentrations of fine nitrate for Birkenes and Montelibretti and fine EC for Melpitz and Montelibretti. The temporal correlation between calculated and measured concentrations appears to decrease from north to south. In general, the temporal correlation is lower for $PM_{2.5}$ components than for PM_{10} components.

Further evaluation of these data is necessary and should allow a better understanding the reasons of the model performance that will be reported in due time.

Country contributions to PM assessment report

This year the Parties, as well as external experts, have done substantial amount of work to write an assessment report of particulate matter (EMEP/CCC report 8/2007). The PM assessment report provides a relevant status of the current knowledge and challenges ahead. The efforts by the individual countries to characterize PM levels and origins in their areas are compiled in Part B of the assessment report. The contributions by the Parties show that there are a great deal of activities in the different countries that can be very useful for the EMEP programme.

The EMEP centers, CCC and MSC_W, are presently engaged in the task of evaluating ways to make such national information and knowledge available to EMEP. This is a considerable task that involves further co-operation and bilateral consultations with the Parties. In particular, we are interested to determine to what extent measurement data that not necessarily have been reported to EMEP before, e.g. from rural background sites, may become more useful to EMEP. This is part of the new Monitoring Strategy of EMEP and will be essential to the further development of the programme now that EMEP modelling is extending to cover finer scales. We count on the co-operation of the Parties to identify the ways to facilitate this work.

1. Measurement of particulate matter in the European rural environment: Status in 2005

1.1 Concentrations, trends and exceedances

By Karl Espen Yttri and Wenche Aas

1.1.1 Introduction

Ambient particulate matter constitutes a complex mixture of various chemical compounds, which originates from a wide variety of sources, and their size varies over several orders of magnitude. The physical and chemical properties of PM vary with respect to time and place and they often inhibit a seasonal variability.

Particulate matter can cause a variety of negative effects on our environment. Currently, particulate matter is the most severe air contaminant encountered in Europe, causing about 300 000 excess deaths in Europe on an annual basis. The recent Air Quality Guidelines from WHO underlines the importance of PM as a severe air pollutant, calling for a significant decrease in the ambient PM level. PM also affects the Earth's temperature through scattering of solar radiation and absorption of solar and terrestrial radiation. In addition, aerosols influence the radiative balance indirectly by affecting the optical properties, frequencies and lifetimes of clouds.

In Europe, PM measurements are mainly performed in urban areas in order to monitor human exposure to PM, while PM measurements in rural areas is not that extensive as seen in the urban environment. However, such measurements are important, as it has been demonstrated that the concentration gap between rural and urban areas can be quite marginal for certain regions in Europe. The atmospheric lifetime of aerosols are of a magnitude allowing significant transboundary fluxes. Thus, measurement of particulate matter was specifically added to the EMEP work programme in 1998 in order to monitor long-range transport of PM in Europe and its long-term trends.

Since 1998, several countries have started PM measurements and by 2005 approximately 40 stations report such data to the EMEP database. At present, the sites reporting PM data does not constitute a uniformly distributed pattern in Europe. In particular, an extension eastwards would be important towards the goal of obtaining a comprehensive geographical overview of the rural PM levels in Europe.

This chapter briefly presents the available monitoring data of particulate matter reported during the year 2005. This includes annual levels of PM, exceedances of annual and 24-hours limit values and guidelines, and relative contributions by inorganic constituents to $PM_{10.}$

1.1.2 Data availability and methods

The number of countries reporting aerosol mass data to EMEP in 2005 was 13, which is one more than for 2004. In general there is a positive tendency for more sites measuring PM_{10} and $PM_{2.5}$, but it is still a long way to go in order to fulfil the goal of the EMEP monitoring strategy (EB.AIR/GE.1/2004/5), which is mass concentration measurements at all the EMEP sites. However, the number of sites and Parties that perform such measurements are likely higher than what is reflected in the EMEP database. This can be seen from the amount of data available in AirBase, the EEA database storing data for monitoring of PM performed under the Air Quality Directive. Belgium, Finland, Great Britain, the Netherlands, and Macedonia all report PM_{10} measurements performed at EMEP sites to AirBase, but not to EMEP. Also Austria, Germany and Denmark have measurements at EMEP sites not being reported to EMEP but to AirBase only. One reason can be that these additional measurements reported to AirBase do not fulfil EMEP recommendations or data quality objectives. The reporting of the data to AirBase via the DEM tool can also be used to report data to EMEP. However, it is necessary to include additional metadata information. Otherwise, EMEP will not get direct access to these data, and it will be unclear whether they are meant to be reported for both bodies or not. It seems like many Parties forget to include this type of information and thus some of the AirBase data are not forwarded to EMEP/CCC as they should be. Hence, the EMEP centers strongly insist on the Parties to ensure that their relevant data are reported to all the relevant bodies.

There are also relatively few sites that have a complete measurement program; only two sites report both inorganic and organic composition. However, several of the sites participating in the intensive measurement periods in June 2006 and January 2007 (see Chapter 5) performed chemical analysis of the ambient aerosol composition, even for several size fractions. Hopefully, several of these sites will include such measurements as part of their regular monitoring program.

Several sites report daily concentrations of $PM_{2.5}$ that are higher than concurrent measurements of PM_{10}. For days when fine aerosols dominate PM_{10} and when the PM loading is low, this may occasionally happen due to the uncertainties associated with measurements, handling of filters, weighing, and so forth. However, for certain sites we find that the daily concentrations of $PM_{2.5}$ are higher than PM_{10} for 40% of the days, which is way too high. We also observe that certain sites reporting data with an hourly time resolution, using monitors, more frequently experience this problem. However, this problem is less apparent when converting the data into daily average concentrations.

1.1.3 PM mass concentrations

The annual mean concentrations of PM_{10}, $PM_{2.5}$, and PM_1 for 2005 are presented in Table 1.1, whereas the spatial coverage of PM_{10} and $PM_{2.5}$ are presented in Figure 1.1.

For 2005, PM_{10} concentrations were reported for 38 sites, which is one less than for 2004. On the other hand, 2005 was the first year that PM_{10} measurements from Poland were reported, thus 13 countries are now reporting data directly to EMEP, which is one more than for 2004. The inclusion of PM measurements at the Polish site (PL05), has improved the geographical coverage towards Eastern Europe, however a further extension eastwards is needed to provide a uniformly distributed PM monitoring network of rural background sites in Europe. Of the 38 sites reporting concentration of PM_{10} in 2005, 15 were located in Central Europe, 14 in Southern Europe, five in Northern Europe, and four in Eastern

Europe. The sites in Southern Europe are totally dominated by those located in Spain (10 of 14 sites).

Figure 1.1 shows that the lowest concentrations of PM_{10} were observed in the Scandinavian countries, as compared to the European mainland. This spatial distribution of PM_{10} corresponds with that reported for previous years and reflects both population density and major anthropogenic sources. While vehicular traffic and industries are important sources for the entire European mainland, mineral dust from local sources and Saharan dust events are likely to grow more important for the Southern parts. The lowest annual mean concentration of PM_{10} was observed at the Norwegian site Birkenes (NO01) (6.8 µg m^{-3}), whereas the highest was recorded at the Italian site Ispra (IT04) (40.4 µg m^{-3}). The annual mean concentration of PM_{10} observed at the Polish site, and which was reported for the first time in 2005, reported the fourteenth highest concentration (18.9 µg m^{-3}). This is in the same range as observed for Slovakia, which is the other country in Eastern Europe reporting concentrations of PM_{10}.

50% of the sites listed in Table 1.1 reported higher annual mean concentrations of PM_{10} in 2005 compared to 2004, and for the majority of these sites the increase was above 10%. The most significant increase was observed at the Norwegian site Birkenes (NO01), reporting a substantial 27% increase from 2004. In general, the increase in PM_{10} experienced by 50% of the sites going from 2004 to 2005 could not be attributed to neither $PM_{2.5}$ nor $PM_{10-2.5}$. All but one of the five sites that reported a decrease of 10% or more in the annual mean concentration of PM_{10} from 2004 to 2005 was situated in Spain. The largest reduction, 24%, was observed at the Spanish site El Torms (ES14).

Table 1.1: Annual mean concentrations of PM_{10}, $PM_{2.5}$ and PM_1 at EMEP sites for 2005 (concentrations in µg/m^3).

Code	PM_{10}	$PM_{2.5}$	PM_1	Code	PM_{10}	$PM_{2.5}$	PM_1
AT0002R	26.7	21.9	15.7	ES0009R	11.9	7.7	
AT0005R	10.0			ES0010R	20.6	11.6	
AT0048R	11.1	9.3		ES0011R	19.0	10.2	
CH0002R	19.8	15.1		ES0012R	15.3	7.8	
CH0003R	18.4			ES0013R	12.9	7.7	
CH0004R	11.0	8.6	7.1	ES0014R	16.8	9.9	
CH0005R	11.8			ES0015R	15.2	8.0	
CY0002R	28.9			ES0016R	13.6	9.5	
CZ0001R	22.9			IT0001R	28.7		
CZ0003R	20.7	18.6		IT0004R	40.4	29.8	
DE0001R	19.6			NO0001R	6.8	4.1	
DE0002R	17.7	13.4	7.6	PL0005R	18.9		
DE0003R	9.7	7.3		SE0011R	15.2	10.9	
DE0007R	13.8			SE0012R	9.5	9.6	
DE0008R	12.2			SE0035R	7.8		
DE0009R	17.2			SI0008R	15.9	14.5	
DK0005R	24.6			SK0004R	14.7		
ES0007R	21.8	10.9		SK0005R	22.2		
ES0008R	17.3	9.0		SK0006R	18.4		

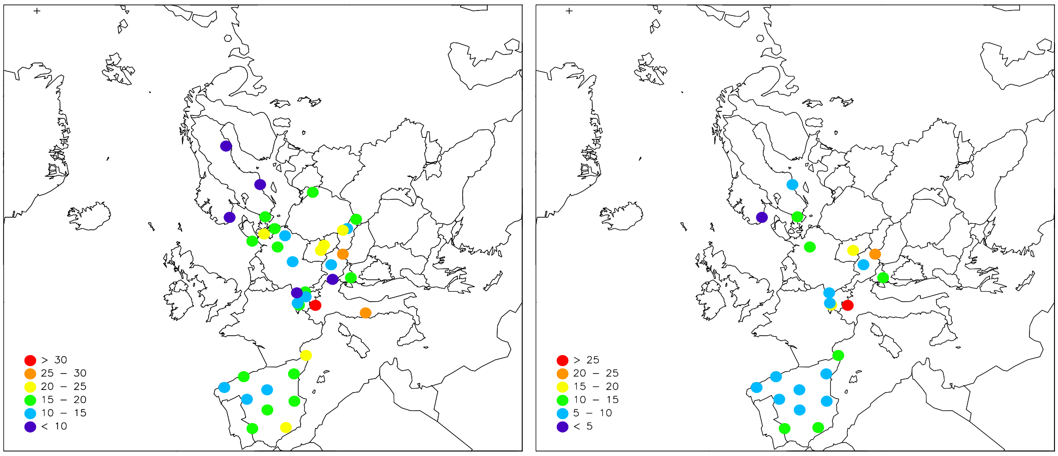


Figure 1.1: Annual mean concentrations of PM_{10} (left) and $PM_{2.5}$ (right) for 2005 ($\mu g/m^3$).

In 2005, there were 22 sites measuring concentrations of $PM_{2.5}$, which is one less than for 2004. However, 2005 was the first year that concentrations of $PM_{2.5}$ was reported for a Czech site (CZ03), hence there were nine countries reporting $PM_{2.5}$ data directly to EMEP, which is one more than for 2004. The majority of the sites are located in Southern Europe, Spain in particular, Central Europe, and in Scandinavia. From Figure 1.1 it can be seen that the highest annual mean concentrations were observed for sites situated in Central Europe, whereas the concentrations reported for Southern Europe, the Spanish sites, were in the same range as those observed for parts of Scandinavia (Sweden). As for PM_{10}, the highest concentration of $PM_{2.5}$ was observed for the Italian site Ispra (IT04) (29.8 µg m^{-3}), whereas the lowest was recorded at the Norwegian site Birkenes (NO01) (4.1 µg m^{-3}).

With the exception of the sites situated in Spain (except ES16), all sites measuring $PM_{2.5}$ in 2005 reported higher annual mean concentrations of $PM_{2.5}$ compared to 2004. The increase was most pronounced in Scandinavia, ranging from 12-37%. Quite a considerable increase of 15% was observed for the Austrian site Illmitz (AT02). With the exception of the Swiss site Chaumont (CH04), experiencing an increase in the annual mean $PM_{2.5}$ concentration of 6%, the remaining sites reported an increase of 5% or less. Nine of ten Spanish sites reported a decrease in the annual mean concentration of $PM_{2.5}$ by 2-21% from 2004-2005, but for eight of these the decrease was less than 10%. ES16 was the only site that reported an increase in the annual mean $PM_{2.5}$ concentration, although less than 5%.

Also the annual mean concentrations of PM_1 were found to be increased in 2005 compared to 2004. It should be noted though that only a limited number (n = 3) of sites reported such data for 2005. The most significant increase was observed for the Austrian site Illmitz (AT02) and the Swiss site Chaumont (CH04), where the increase was 12% and 9% respectively, whereas it was only 2% at the German site Langenbrügge (DE02).

1.1.4 Exceedances of limit values and guidelines

During 2005, the EU annual limit value of PM_{10} (40 µg m^{-3}) was exceeded at the Italian site Ispra (IT04) situated in Northern Italy, reporting an annual mean concentration of 40.4 µg m^{-3}. Although having reported annual mean concentrations in the range 35-40 µg m^{-3} since measurements started at this site in 2001, this is the first time the limit value of PM_{10}, set for urban areas, have been exceeded at any EMEP site since monitoring was initiated in 1999. The 16% increase in the annual mean PM_{10} concentration experienced from 2004 to 2005 at Ispra could mainly be attributed to the coarse fraction of PM_{10}.

More than 25% of the sites that reported annual mean concentrations of PM_{10} for 2005 exceeded the Air Quality Guideline for PM_{10} of 20 µg m^{-3} put forward by the WHO (2005). This was true for sites situated all over Europe, including Scandinavia. Those sites violating the guideline exceeded it by 29 ± 28% on average, underlining that there is a considerable effort ahead to cope with the guidelines for large parts of Europe, even in rural background areas.

The number of days for which the daily PM_{10} limit value was exceeded during 2005 is presented in Table 1.2. Nine sites experienced an increase in number of days exceeding the limit value for PM_{10} (50 µg m^{-3} > 35 days) in 2005 compared to 2004, while 15 sites reported a decrease. For the remaining eight sites there were no changes in number of exceedances. There was no pattern with respect to which part of Europe experienced a decrease versus decrease. For certain sites, such as the Czech sites (CZ01 and CZ03) and the two Spanish sites ES07 and ES14, the decrease was considerable; *e.g.* only three days exceeding the limit value was observed in 2005 compared to 20 in 2004 for CZ03.

The Italian site Ispra (IT04) (99 days) and the Austrian site Illmitz (AT02) (40 days) were the only two sites violating the daily limit value for PM_{10} in 2005. However, an increase in the number of exceedances by more than 40% was observed for 2005 compared to 2004 for the two sites. In fact, the number of exceedances observed at Ispra for 2005 was the highest recorded since the monitoring started in 2001 (Figure 1.2). Even the annual mean concentration of PM_{10} exceeded the air quality guideline for the 24-hour mean at Ispra. At Illmitz, the number of exceedances in 2005 was exceeded by the years 2002 (45 days) and 2003 (50 days).

Table 1.2: *Number of exceedances of the daily PM_{10} limit value (50 µg/m^3) during 2005.*

	Code	Number of exceedances of the daily limit value for PM_{10}				
		Total	Winter	Spring	Summer	Autumn
Central Europe	AT0002R	40	17	9	1	13
	AT0005R	0	0	0	0	0
	AT0048R	14	0	2	2	0
	CH0002R	5	4	1	0	0
	CH0003R	6	5	1	0	0
	CH0004R	0	0			
	CH0005R	0	0			
	CZ0001R	3	0	0	1	2
	CZ0003R	3	0	3	0	0
	DE0002R	3	2	1	0	0
	DE0003R	0	1	1		
	DE0007R	3	1	2	0	0
	DE0008R	0				
	DE0009R	5	3	0	0	2
	DE0001R	7	3	0	0	4
	PL00005	6	0	2	0	4
	SI00008	6	2	1	0	3
Southern Europe	CY0002R	23	7	11	1	4
	ES0007R	15	0	6	9	0
	ES0008R	7	0	4	1	2
	ES0009R	5	0	4	1	0
	ES0010R	2	0	2	0	0
	ES0011R	6	0	3	3	0
	ES0012R	6	0	4	1	1
	ES0013R	4	0	2	2	0
	ES0014R	3	0	1	2	0
	ES0015R	7	0	3	4	0
	ES0016R	5	0	4	1	0
	IT0001R	20	8	7	5	0
	IT0004R	99	48	25	1	25
Northern Europe	DK0005R	4	0	2	0	2
	NO0001R	0				

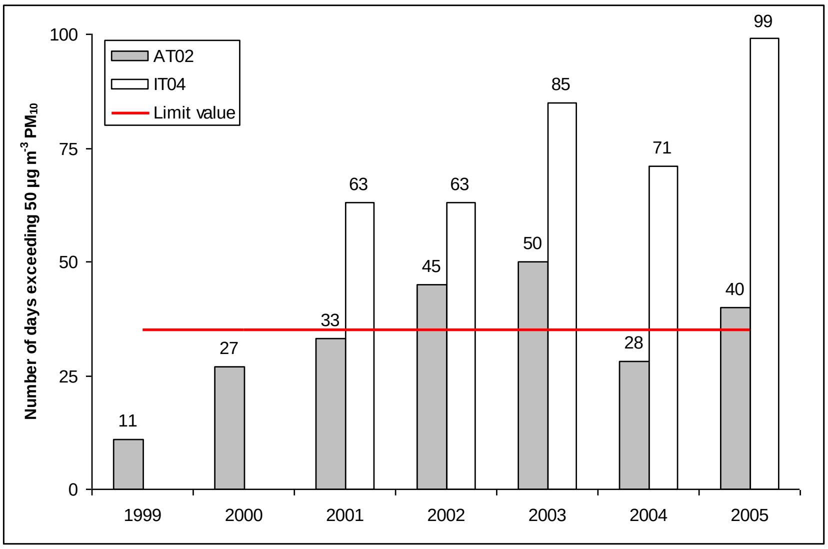


Figure 1.2: *Number of days exceeding the 24-hour mean limit value for PM_{10} at the Austrian site Illmitz (AT02) and the Italian site Ispra (IT04). For 2005, no more than 35 days are allowed.*

Table 1.2 also shows the number of exceedances of the 24-hour PM_{10} limit value for each station with respect to season. No common seasonal pattern could be observed for all sites, but common features were observed for the sites situates in the Mediterranean region (the sites in Spain, at Cyprus, and IT01) compared to the rest of Europe (the sites in Austria, Switzerland, The Czech Republic, Germany), mainly Central Europe. While approximately 80% of the exceedances occurred during spring and summer in the Mediterranean region, the corresponding percentage for the rest of Europe was approximately 30%. This suggests that exceedances at sites in Central Europe are associated with enhanced emissions from anthropogenic sources during winter combined with unfavourable dispersions conditions. In the Mediterranean region, exceedances of the daily limit value, and maximum concentrations, are observed during meteorological conditions that favour transport of mineral dust from the African continent. These Saharan dust events are characterized by coarse particles and the $PM_{2.5}/PM_{10}$ ratio observed is typically low (See Figure 1.3). Peak concentrations of PM_{10} associated with Saharian dust events are also observed in Central Europe, but the concentrations are lower.

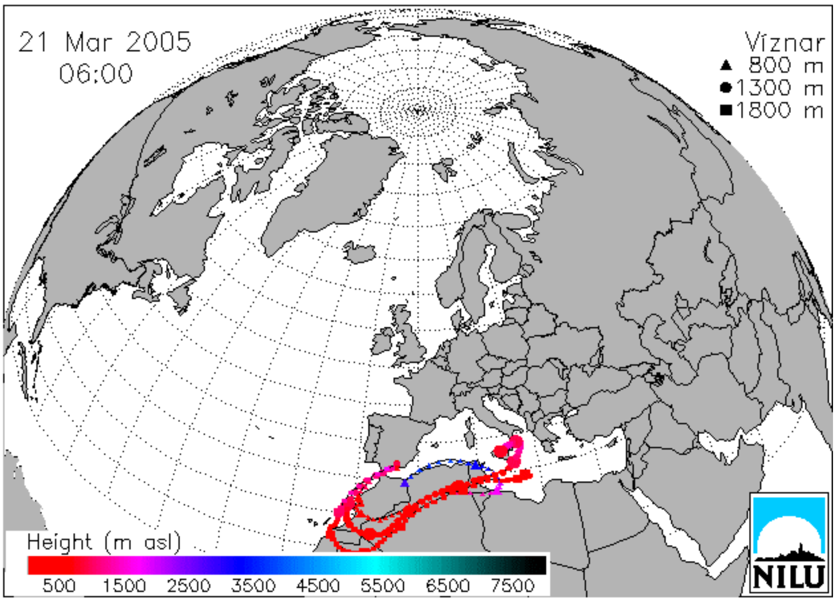


Figure 1.3: Back trajectories of air masses reaching the Viznar station (ES07) 06:00 at the 21 March 2005. The PM_{10} concentration for this date was 147 µg m^{-3} and the $PM_{2.5}/PM_{10}$ ratio was 0.27.

Ispra, reporting an annual mean $PM_{2.5}$ concentration of 29.8 µg m^{-3}, was the only site violating the EU annual limit value of $PM_{2.5}$ (25 µg m^{-3}) to be valid from 2010, exceeding it by approximately 20%. The 5% increase from 2004 to 2005 interrupts the downward trend observed in the time period from 2001 (32.01 µg m^{-3}) to 2004 (28.3 µg m^{-3}), suggesting that it still might take a while before being in compliance with the limit value.

45% of the sites reporting annual mean concentrations of $PM_{2.5}$ in 2005 exceeded the WHO Air Quality Guideline of 10 µg m^{-3}. This leaves no part of Europe unaffected by the guideline, including even the Scandinavian Peninsula. The sites violating the guideline exceeded it by 57±62% on average. For certain sites, Illmitz (AT), Chaumont (CH04), Košetice (CZ03) and Ispra (IT04), there is obviously a long way ahead before being in compliance with the WHO guideline, as they also exceed the WHO interim target three (IT-3) of 15 µg m^{-3}. The annual mean concentration of $PM_{2.5}$ at Ispra even exceeds the WHO interim target two (IT-2) of 25 µg m^{-3}. The interim targets have been defined in such a way that with successive and sustained abatement measures they will be achievable.

When comparing the daily values of $PM_{2.5}$ for 2005 with that of the WHO 24-hour guideline, *i.e.* the 99th percentile (corresponding to the fourth highest value of the year) of the distribution of daily values should not exceed 25 µg m^{-3}, 19 of 22 sites exceeded the guideline (Figure 1.4). The number of days exceeding the guideline is particularly high at certain sites in Central Europe, *e.g.* Ispra (IT04) (162 days) and Illmitz (AT02) (104 days). These two sites also fail to meet the interim target number one (IT-1) at 75 µg m^{-3}. One more site, SI08, fails to meet the IT-2 requirement at 50 µg m^{-3}, while a total of ten sites exceeds IT-3 (37.5 µg m^{-3}). The WHO has recommended *“that countries with areas not meeting these guideline values should take immediate action to achieve these levels in the shortest possible time.”* The three sites not violating the guideline were NO01, ES09, and ES12.

The seasonal pattern of exceedances of the WHO 24-hour air quality guideline for $PM_{2.5}$ is similar to that of PM_{10} and the EU limit value; while more than 70% of the exceedances takes place during spring and summer in the Mediterranean region the corresponding percentage for rest of Europe is 30%.

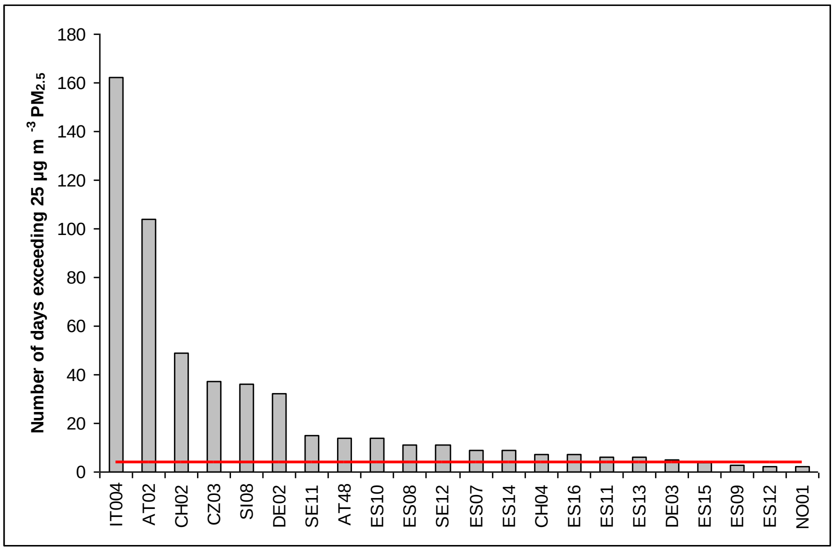


Figure 1.4: Number of days exceeding the WHO 24-hour air quality guideline for $PM_{2.5}$ at rural background sites in Europe. The guideline states that the 99th percentile of the distribution of daily values should not exceed 25 µg m^{-3}. The 99th percentile corresponds to the fourth highest daily value of the year.

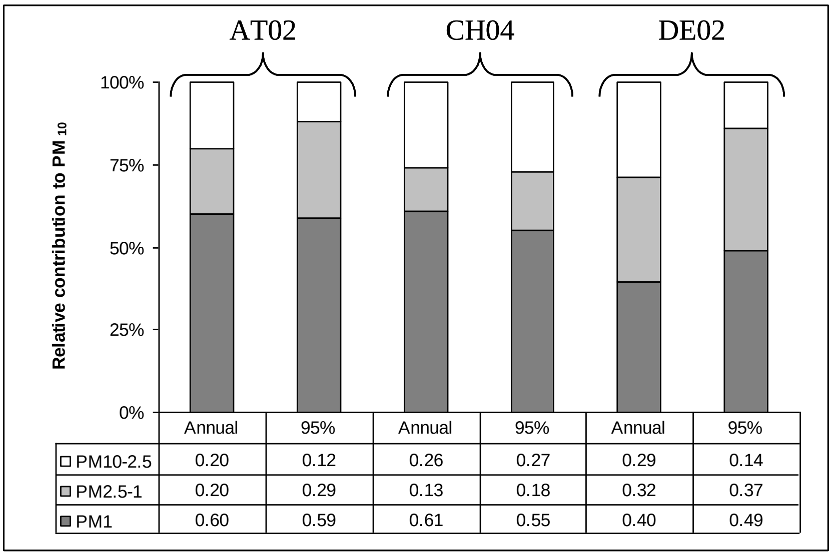
1.1.5 Ratios

Ratios of $PM_{2.5}$ to PM_{10}, PM_1 to PM_{10}, and PM_1 to $PM_{2.5}$ in 2005 are summarized in Table 1.3, showing that sites in Central Europe and Italy have rather high $PM_{2.5}/PM_{10}$ ratios (0.75 ± 0.04) compared to sites in Spain and Scandinavia (0.58 ± 0.07). This difference is probably associated with the high contribution of anthropogenic fine PM emissions to concentrations of PM_{10} in Central Europe. In addition, the PM_{10} concentration in Spain is influenced by dust from semi arid regions and deserts, whereas for certain Scandinavian sites the influence by marine aerosols (sea-salt) could be important. Hence, this could be a possible explanation for why a larger fraction of the particles in Spain and in the Scandinavian countries is found in the $PM_{10-2.5}$ fraction.

Table 1.3: PM concentration ratios in 2005.

		Code	$PM_{2.5}/PM_{10}$	PM_1/PM_{10}	$PM_1/PM_{2.5}$
Central Europe	Austria	AT0002R	0.80	0.60	0.75
		AT0048R	0.80		
	Switzerland	CH0002R	0.72		
		CH0004R	0.74	0.61	0.81
	Germany	DE0002R	0.72	0.40	0.55
		DE0003R	0.70		
Southern Europe	Spain	ES0007R	0.55		
		ES0008R	0.50		
		ES0009R	0.73		
		ES0010R	0.55		
		ES0011R	0.55		
		ES0012R	0.56		
		ES0013R	0.63		
		ES0014R	0.60		
		ES0015R	0.58		
		ES0016R	0.69		
	Italy	IT0004R	0.75		
Northern Europe	Norway	NO0001R	0.57		

For 2005, there were three sites performing simultaneous measurements of PM_1, $PM_{2.5}$, and PM_{10}, namely Chaumont (CH04) in Switzerland, Illmitz (AT02) in Austria, and Langenbrügge (DE02) in Germany. The annual mean size distribution for 2005 and the size distribution for selected periods, showing elevated concentrations of PM_{10} (95-percentile), are presented in Figure 1.5.



	Annual	95%	Annual	95%	Annual	95%
□ PM10-2.5	0.20	0.12	0.26	0.27	0.29	0.14
▨ PM2.5-1	0.20	0.29	0.13	0.18	0.32	0.37
■ PM1	0.60	0.59	0.61	0.55	0.40	0.49

Figure 1.5: Relative contribution of PM_1, $PM_{2.5-1}$ and $PM_{10-2.5}$ to PM_{10} at the sites Chaumont (CH04), Illmitz (AT02), and Langenbrügge (DE02) for the year 2005 and for the 95-percentile of PM_{10} in 2005.

On an annual basis, distinct differences could be observed with respect to the size distribution for the three sites. At AT02 and CH04, PM_1 was found to account for 60% and 61% of PM_{10}, respectively, while for DE02 the relative contribution was only 40%. However, the difference is much less when comparing the relative contribution of $PM_{2.5}$ to PM_{10} at the three sites. This shows that the difference could be attributed to the $PM_{2.5-1}$ fraction, which ranged from 13% at the Swiss site to 33% at the German site, while it accounted for 20% at the Austrian site. The relative contribution of the coarse fraction ($PM_{10-2.5}$) to PM_{10} ranged from 20% at AT02 to 29% at DE02.

Examining the size distribution for the days with the highest (95-percentile) PM_{10} concentrations, showed that PM_1 was the dominating fraction of PM_{10} at all three sites, exceeding 50% at Illmitz (59±10%) and Chaumont (55±14%), but just nearly at DE02 (49±9%). For the Austrian and the Swiss sites, the relative contribution of PM_1 to PM_{10} was lower for the high-concentration events compared to the whole year, although just barely for the Austrian site. For the German site it was the other way around.

The relative contribution of $PM_{2.5}$ to PM_{10} (86 ± 8%) was clearly elevated for the 95-percentile group compared to the annual mean (72 ± 13%) at DE02, while this was less pronounced at the Austrian and the Swiss sites. The coarse fraction accounted for an equally high amount of PM_{10} for the 95-percentile group as for the whole year at Chaumont, whereas it was two times lower for the German site.

At all three sites, the relative contribution of $PM_{10-2.5}$ to PM_{10} increased considerably during summer. This is exemplified for the Austrian site in Figure 1.6a, showing that the relative contribution starts to increase during spring and peaks in July. The figure also shows that this is a common pattern, which is experienced each year for the period 2001 – 2005. This finding is mainly attributed to the decrease in concentration of $PM_{2.5}$ during summer rather than increased levels of $PM_{10-2.5}$. This is a pattern observed for the sites in Central Europe in general.

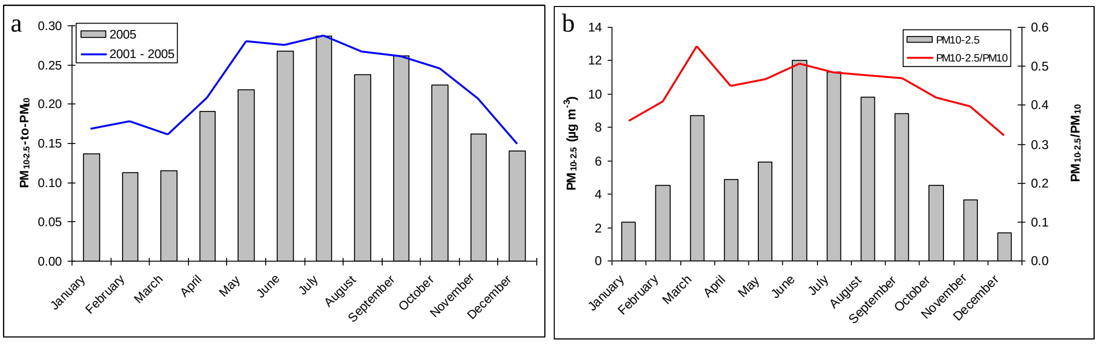


Figure 1.6: Relative contribution of $PM_{10-2.5}$ to PM_{10} for the year 2005 and for the period 2001 – 2005 at the Austrian site Illmitz (AT02) (a). Monthly mean concentrations of $PM_{10-2.5}$ and relative contribution of $PM_{10-2.5}$ to PM_{10} at the Spanish site Risco Llamo (ES15) for the period 2001 – 2005 (b).

About 50% of the Spanish sites experience an increase in the $PM_{10-2.5}$ to PM_{10} ratio in summer. Unlike the sites in Central Europe, nine of ten Spanish sites experienced a considerable increase in the $PM_{10-2.5}$ concentration during summer. However, a concurrent increase in the $PM_{2.5}$ concentration is observed as well, which occasionally cancels the relative increase in $PM_{10-2.5}$ to PM_{10} in summer.

There appears to be only moderate variations, 5-20%, in the relative contribution of $PM_{10-2.5}$ to PM_{10} between years. It should be underlined though that PM_{10} and $PM_{2.5}$ have been monitored concurrently only for a limited number of years at most sites, the longest concurrent time series of PM_{10} and $PM_{2.5}$ going back to 1998 (CH04).

1.1.6 Chemical composition of PM

At EMEP stations, speciation of the ambient particulate matter is mainly focused on the secondary inorganic constituent SO_4^{2-}, NO_3^- and NH_4^+. SO_4^{2-} is measured at the majority of the sites, while NO_3^- is reported as the sum of NO_3^- and HNO_3 and NH_4^+ as the sum of NH_4^+ and NH_3. The carbonaceous content of PM is only measured at a very few sites, and will discussed more closely in chapter 1.2.

In 2005, concurrent measurements of the major inorganic constituents of ambient PM and PM_{10} was performed at only a limited number of sites: 29 for SO_4^{2-}, 21 for NO_3^-, and 11 for NH_4^+ sites. This corresponds to 37%, 46% and 32% of the sites measuring SO_4^{2-}, NO_3^-, and NH_4^+, respectively. There were also 11 sites reporting PM_{10} in 2005, which did not report SO_4^{2-}, NO_3^-, or NH_4^+.

When calculating the relative contribution of the inorganic constituents to PM_{10}, the results could be confounded by the fact that the filterpack unit samples particulate matter larger than PM_{10}. However, SIA are mainly associated with fine aerosols, thus it is not likely that such an exercise will lead to any substantial overestimation of the relative contribution of these constituents. Another uncertainty relies on the fact that the filter pack method is not particularly reliable when it comes to separating the gaseous nitrous compounds NH_3 and HNO_3 from NH_4^+ and NO_3^-, respectively. NH_4 and NO_3 can be substantially underestimated, especially in warmer regions due to evaporation of NH_4NO_3. It can also be positive artefact of these ions under moist conditions when gases may adsorb on the aerosol filters.

Table 1.4 lists the relative contribution of the individual SIA to PM_{10} based on the data reported for 2005. SO_4^{2-} and NO_3^- contributed about equally to PM_{10}, accounting for 9-22% and 6-28% of PM_{10}, respectively. For those sites performing concurrent measurements of SO_4^{2-} and NO_3^- there was no consistency in whether sulphate or nitrate was the major constituent. The relative contribution of NH_4^+ to PM_{10} ranged between 5-13%. NH_4^+ always made a less contribution to PM_{10} than SO_4^{2-} and NO_3^- at those sites were concurrent measurements was available.

Table 1.4: Relative contribution of SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, K^+, Cl^-, Mg^{2+} and Na^+ to PM_{10} at EMEP sites for 2005 (%).

Station	**SO_4^{2-}/PM_{10}**	**NO_3^-/PM_{10}**	**NH_4^+/PM_{10}**	**Ca^{2+}/PM_{10}**	**K^+/PM_{10}**	**Cl^-/PM_{10}**	**Mg^+/PM_{10}**	**Na^+/PM_{10}**
AT02	12	6	5	0.7	0.8		0.1	0.3
CH02	11							
CH05	14							
CZ01	14							
CZ03	17							
DE01	13	18	5	1.1	1.7		1.7	11
DE02	15	13	6	0.8	0.8		0.4	2.2
DE03	20	14	6	2.2	0.6		0.4	1.4
DE07	19	17	7	1.1	0.9		0.6	3.0
DE09	22	28	10	1.3	0.7		0.8	4.4
DK05	10		7					
ES07	10	10						
ES08	20	11						
ES09	13	9	7	5.0	1.1	3.8	0.3	4.2
ES10	18	12						
ES11	12	8						
ES12	17	12						
ES13	15	10						
ES14	20	13						
ES15	12	10						
ES16	19	8						
IT01	9	9	5					
IT04	10	18	9					
NO01	20	16	13	0.9	0.8	5.8	0.8	6.8
PL05	10							
SE11	12							
SI08	16			0.8	1.0	0.2	0.2	0.4
SK05	16	11						
SK06	18	9						
Mean	**15**	**12**	**7**	**1.5**	**0.9**	**3.3**	**0.6**	**3.7**
SD	**4**	**5**	**2**	**1.4**	**0.3**	**2.9**	**0.5**	**3.4**

To acquire mass closure of the PM mass typically requires analysis of the secondary inorganic constituents, the carbonaceous fraction, and the mineral dust content. For sites frequently influenced by marine air masses the sea salt contribution should also be measured. In 2005 the chemical data reported from the EMEP sites included only inorganic components, with the exception of two sites measuring the carbonaceous content. No sites reported concentrations of Silicon (Si), Aluminium (Al), and Iron (Fe), which are the most abundant constituents of mineral dust, originating from the Earths crust. Ca was however measured at nine sites. The relative contribution varied between 0.7% and 5%. The highest level was observed at ES09, which occasionally experience high episodes of Saharan dust.

Measurements of all the major constituents of sea salt (Na, Cl and Mg), were only reported for two sites in 2005, NO01 and ES09. However, seven sites reported concentrations of one or two of the ions; in addition, the Danish sites DK05 performed measurements of Na from June 2005. When calculating the relative contribution of Na to PM_{10}, it was found to be less than 5% for all the sites except at NO01 and DE01, which both are located quite close to the coastline, the contribution was 7% and 11%, respectively (Table 1.4).

Potassium was measured at nine sites in 2005. Potassium made only a minor contribution to the mass concentration of PM_{10} on an annual basis, accounting for less than 1% at most sites: 1.7% at Westerland (DE01). At Illmitz, levels of potassium were found to be increased by a factor of three in winter compared to summer, probably reflecting increased emissions by residential wood burning in winter, whereas the relative contribution increased by approximately a factor of two. At Birkenes, the potassium concentration was slightly increased in summer compared to winter for the period 2000–2006, which also lead to a modest increase in the relative contribution of potassium to PM_{10}. The seasonal variation suggests that the increased concentrations in summer could be attributed to biological material, *e.g.* fungal spores.

The relative contribution of the individual SIA constituents to PM_{10} was examined for those sites reporting such data for a period of more than five years. For the five sites examined with respect to SO_4^{2-}, the relative contribution of was found to be highly consistent, typically changing less than 2% from year to year (Figure 1.7). For NO_3^- and NH_4^+ the number of datasets fulfilling this criterion is much less than for SO_4^{2-} trend data. For the sites Birkenes (NO01) and Ispra (IT04), the relative contribution of NO_3^- to PM_{10} were found to increase steadily from 11% in 2001 to 16% in 2005, and from 13% to 18%, respectively (Figure 1.8). The relative contribution of NH_4^+ to PM_{10} ranged between 6% and 8% at these two sites during the same period.

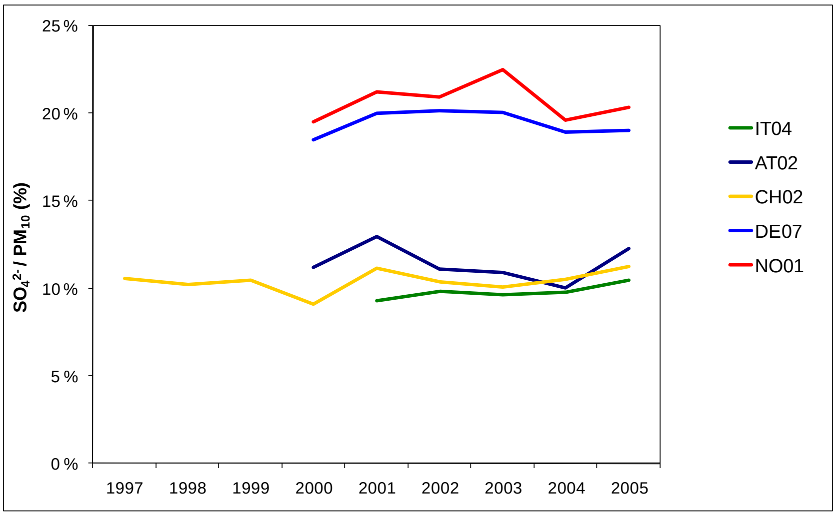


Figure 1.7: Relative contribution of SO_4^{2-} *to* PM_{10} *for the period 1997–2005.*

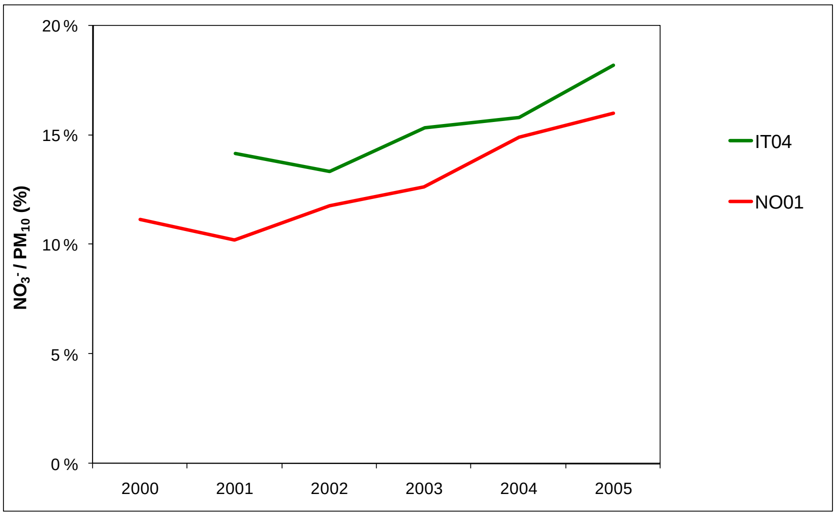


Figure 1.8: Relative contribution of NO_3^- *to* PM_{10} *for the period 2000–2005.*

In Figure 1.9a the average monthly mean concentration of the sum of Cl, Mg, and Na for the period 2000 - 2006 is presented for the Birkenes site. The results show that the concentrations obtained during winter are almost two times higher compared to summer. This can be attributed to the increased wind speed observed during winter. Birkenes is situated just 20 km from the Skagerrak coastline, thus it experiences a number of sea salt episodes in winter when there is moderate to strong winds from the southern sector. The episodic nature of the sea salt contribution in winter could also be deducted from the much higher standard deviations observed in winter compared to summer.

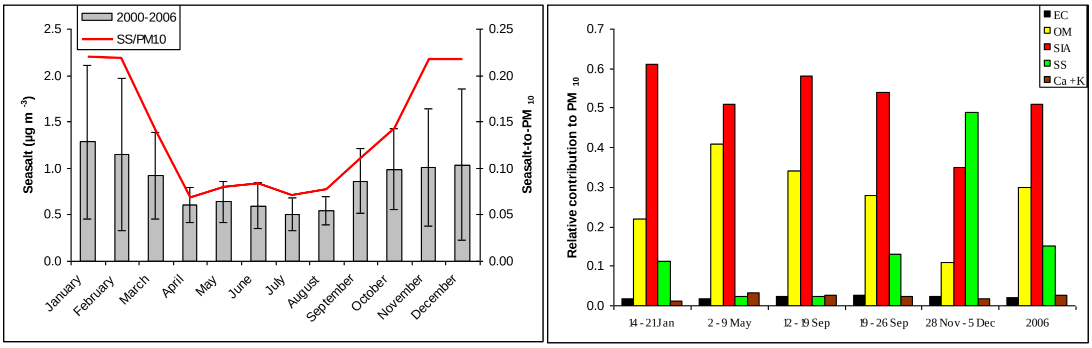


Figure 1.9: Monthly mean concentrations of sea salts (Na^+, Cl^-) and relative contribution of sea salts to PM_{10} at the Norwegian site Birkenes for the period 2000–2006 (a). Chemical composition of PM for the five weeks reporting the highest PM_{10} loading at Birkenes in 2006. Note that sea salt is the major fraction for the period 28 November – 5 December. On average, 75 ± 8% of PM_{10} could be accounted for by the chemical analysis performed (b).

The relative contribution of sea salts to PM_{10} has a similar seasonal variation as the sea salt concentration, accounting for 18 ± 11% in winter compared to 9 ± 4% in summer for the period 2000–2006. Hence, a substantial percentage of the PM_{10} loading could be attributed to natural sources, in particular in winter. Occasionally it is observed that PM dominated by sea salts actually contributes to the five weeks with the highest PM_{10} loading during the year, as shown the period 28 November to 5 December for Birkenes in 2006 (Figure 1.9b).

Figure 1.9 illustrates how natural sources of PM could be a considerable contributor to the ambient PM level, and emphasizes the importance of further sites reporting levels of sea salts, in particular in areas influenced by marine air masses.

1.1.7 Trends

12 of the 38 sites reporting concentrations of PM_{10} for 2005 have time series extending more than five years. None of these sites have a stepwise year-by-year reduction or increase in the PM_{10} concentration. The longest time series, going back to 1997, are reported for the four Swiss sites Payerne (CH02), Tänikon (CH03), Chaumont (CH04), and Rigi (CH05). Large inter annual variations are observed for this nine years period. From 1997 to 2000/2001, they all experience a 25-30% decrease in the PM_{10} concentration, after which the concentration increased by 25-45% till 2003. For 2004 and 2005, the concentrations were 15-25% lower compared to 2003.

Only four of the 22 sites reporting concentrations of $PM_{2.5}$ for 2005 have time series longer than five years. The longest time series are reported for Chaumont and Payerne, going back to 1998 and 1999, respectively. For both sites, the time series follow that of PM_{10} quite closely.

1.2 Monitoring of EC and OC within EMEP

By Karl Espen Yttri

1.2.1 Introduction

In Europe, long-term monitoring data of EC and OC is not yet available on the regional scale, although the importance of such data has been emphasized by e.g. Kahnert et al. (2004). Monitoring of EC and OC needs to rely on both robust and cost-efficient techniques, but at the same time a satisfactory quality of the data must be maintained. It has long been recognized that significant artefacts can be introduced during filter sampling of particulate matter for subsequent analysis of OC (McDow and Huntzicker, 1990), which can both grossly over and under-estimate the samples content of OC. Furthermore, great analytical challenges are associated with splitting the aerosols content of EC from OC (Schmid et al., 2001). The challenges associated with sampling of OC and the separation of EC and OC are more thoroughly discussed in chapter 1.3, which provides a progress report on the development and validation of standardised protocols for sampling of OC and analysis of EC and OC within the EMEP network.

1.2.2 Status of sampling and measurement, and quality of data

According to the EMEP monitoring strategy, quantifying the aerosols content of EC and OC is regarded as a level 2 activity. In Table 1.5, the two countries that reported concentrations of EC and OC in 2005 are listed. These sites are Birkenes (NO01) in Norway and Ispra (IT04) in Italy. At Birkenes, concentrations of EC and OC in PM_{10} and $PM_{2.5}$ have been reported since 2001, whereas Ispra took up such measurements in 2002.

Table 1.5: Sites reporting EC and OC to the EMEP database, including size fractions and sampling period.

Site (Country)	EC	OC	PM_1	$PM_{2.5}$	PM_{10}	Period
Birkenes (Norway)	x	x		x	x	2001, 2002, 2003, 2004, 2005
Ispra (Italy)	x	x		x	x	2002$^{1)}$, 2003, 2004, 2005

1) EMEP EC/OC campaign

Table 1.6 shows the sampling time and frequency, the filter face velocity, the sampling technique, and the analytical instrumentation used at Ispra and Birkenes. These parameters are the most crucial concerning the magnitude of the sampling artefact of OC and the split between EC and OC.

For 2005, different sampling time and sampling frequency were applied at the two sites. Neither of the samplers operated according to a sampling technique that corrected for, or quantified, the negative artefacts, while a denuder was used to account for the positive artefact at Ispra.

Table 1.6: Sampling equipment and analytical approach used at the sites reporting EC and OC to the EMEP database.

Site (Country)	Sampling time/frequency	Filter face velocity	Sampling equipment	Analytical approach
Birkenes (Norway)	(6+1) days, weekly	54 cm s^{-1}	Single filter (no correction)	Sunset TOT (quartz. par)
Ispra (Italy)	24 hr, daily	20 cm s^{-1}	Denuder (pos. artifact)	Multi-step flash heating$^{1)}$ and Sunset Dual Optical Analyser$^{2)}$

1) Two aliquots were analysed: one from the plain filter, the other one after baking for 2 hours in He/O_2 carrier gas at 340°C. Charring-free EC determined from the latter.
2) PM_{10} (Multi-step flash heating: January - April; Sunset Dual Optical Analyser: April - December)
$PM_{2.5}$ (Sunset Dual Optical Analyser: 2005)

Thermal optical analysis was used to quantify the samples content of EC and OC at the two sites in question, except for a period of four months for the PM_{10} samples at Ispra. According to Schmid et al. (2001) only methods that correct for charring during analysis, or that prevent charring to take place, should be recommended when it comes to splitting TC into EC and OC. Hence, both the approach used at Birkenes and at Ispra meet this requirement.

The differences between the two sites regarding sampling and analytical approach pinpoints the great challenges associated with monitoring of EC and OC in order to get comparable data. This lack of comparability makes the data less suited for model validation, for validation of the effectiveness of implementation of current air pollution legislations, and for revising and improving current policy. Despite that the results are not likely comparable, they still provide valuable information concerning seasonal variation, mass closure of PM, and time-trends at the respective sites.

1.2.3 EC and OC levels in Europe

There is a general lack of comparable EC/OC data in Europe, which makes it difficult to address the spatial and temporal variation of these parameters on the regional scale. Unfortunately this situation did not improve from 2004 to 2005. Currently there are only two datasets available that can be used to obtain such information, namely that of the EMEP EC/OC campaign, conducted during the period July 2002 to July 2003, and the CARBOSOL project, conducted during the period October 2002–July 2004. Both datasets are comprehensive and benefits from thermal-optical analysis being used to quantify EC and OC. A short summary of the EMEP EC/OC campaign can be found in the “Transboundary particulate matter in Europe” Status report 2006, and will not be repeated here. The interested reader could find more comprehensive information in Yttri et al. (2007a), describing the campaign and its results in detail. A thorough description of the EC/OC data in CARBOSOL could be found in the paper by Pio et al. (2007) and Legrand and Puxbaum (in press), whereas Simpson et al. (2007) used data from both datasets to validate the performance of the EMEP model with respect to OC and TC. A summary of the main findings from the paper of Simpson et al. (2007) is presented in Chapter 3.

To provide more information on EC/OC data in the European rural background environment, the Parties was encouraged to include such analysis in the EMEP intensive measurement periods that took place in June 2006 and January 2007. Some preliminary results and interpretations of the EC/OC data from these measurements are presented in Chapter 5.

1.2.4 EC and OC levels at the Norwegian site Birkenes (NO01)

The Birkenes atmospheric research station (58° 23’N, 8° 15’E, 190 m asl) is a joint supersite for EMEP and GAW and is situated approximately 20 km from the Skagerrak coast in the southern part of Norway The site is often influenced by episodes of transboundary air pollution from continental Europe and has frequently been used to study long-range air pollution. The station is located in a boreal forest with mixed conifer and deciduous trees. The station has been operational since 1971.

Figure 1.10a-c shows the annual mean concentrations of EC, OC, and TC in PM_{10}, $PM_{2.5}$ and $PM_{10\text{-}2.5}$ at Birkenes for the period 2001–2006. For this period, OC in PM_{10} ranged from 0.8 µg m^{-3} to 1.2 µg m^{-3}, whereas the corresponding range for OC in $PM_{2.5}$ was 0.6–1.0 µg m^{-3}. For $PM_{10\text{-}2.5}$ the annual mean concentration of OC ranged from 0.1–0.3 µg m^{-3}. For PM_{10} and $PM_{2.5}$, the annual mean concentrations of EC ranged between 0.1–0.2 µg m^{-3} for the period in question. For $PM_{10\text{-}2.5}$ the annual mean concentration of EC did not exceed 0.05 µg m^{-3}.

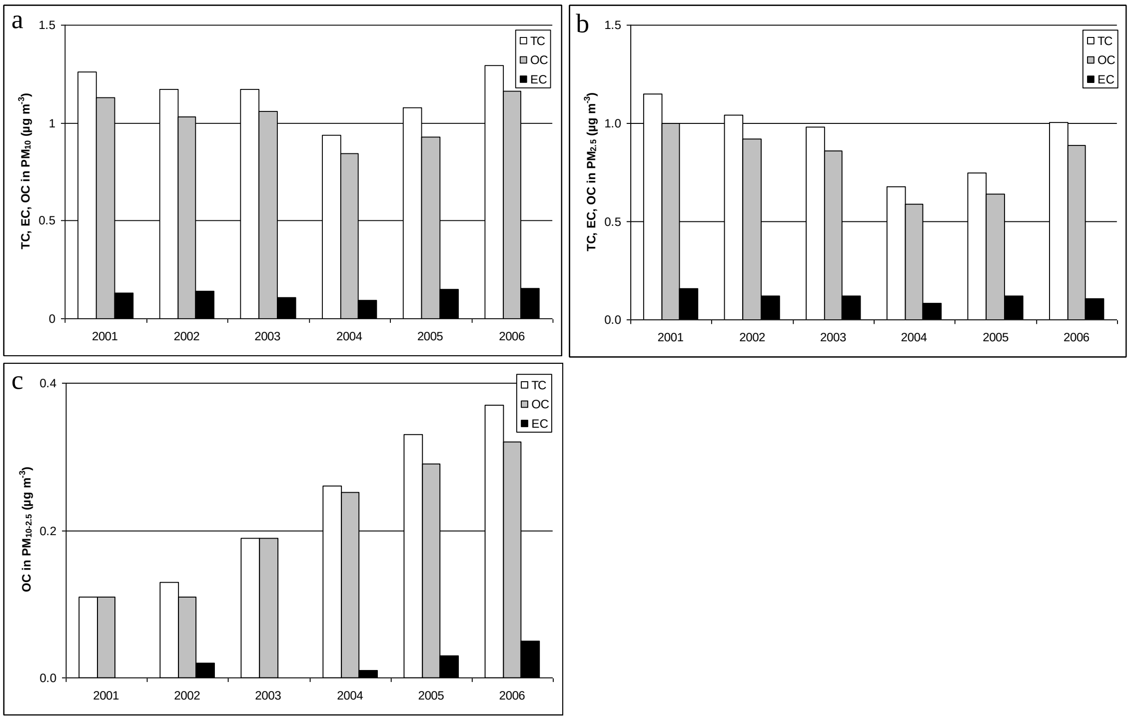


Figure 1.10: Annual mean concentrations of EC, OC and TC in PM_{10} (a), $PM_{2.5}$ (b) and $PM_{10\text{-}2.5}$ (c) at the Norwegian site Birkenes.

The concentration of OC in PM_{10} is always higher during summer compared to winter for the period 2001–2006 at Birkenes. This can be attributed to increased levels of $OC_{PM10-2.5}$ during summer. For $PM_{2.5}$, the increase of OC in summer is not as pronounced as for PM_{10}. For EC, the concentration tends to be higher in winter compared to summer for both PM_{10} and $PM_{2.5}$, but this is not a consistent pattern.

Table 1.7: Relative contributions of EC-to-TC and OC-to-TC for PM_{10} and $PM_{2.5}$ at the site Norwegian site Birkenes (NO01) and at the Italian site Ispra (IT04).

Site	**PM_{10}**		**$PM_{2.5}$**	
	EC/TC (%)	**OC/TC (%)**	**EC/TC (%)**	**OC/TC (%)**
Birkenes (NO01) (2001 - 2006)	11 ± 2	89 ± 2	13 ± 2	87 ± 1
Ispra (IT04) (2003 - 2005)	21 ± 6	79 ± 6	18 ± 3	82 ± 3

OC is always the dominant fraction of TC at Birkenes, regardless of size fraction (Table 1.7). For the period 2001–2006, OC accounted for 89 ± 2% of the TC fraction in PM_{10} on an annual basis, whereas the corresponding range for EC was 11 ± 2%. Only minor differences were observed for $PM_{2.5}$ with respect to the relative contribution of EC and OC to TC. The mean EC/TC ratio for the period 2001–2006 have an obvious seasonal variation both for PM_{10} and $PM_{2.5}$ (Figure 1.11). This reflects the somewhat decreased levels of EC in summer, but mainly the increased levels of OC in summer.

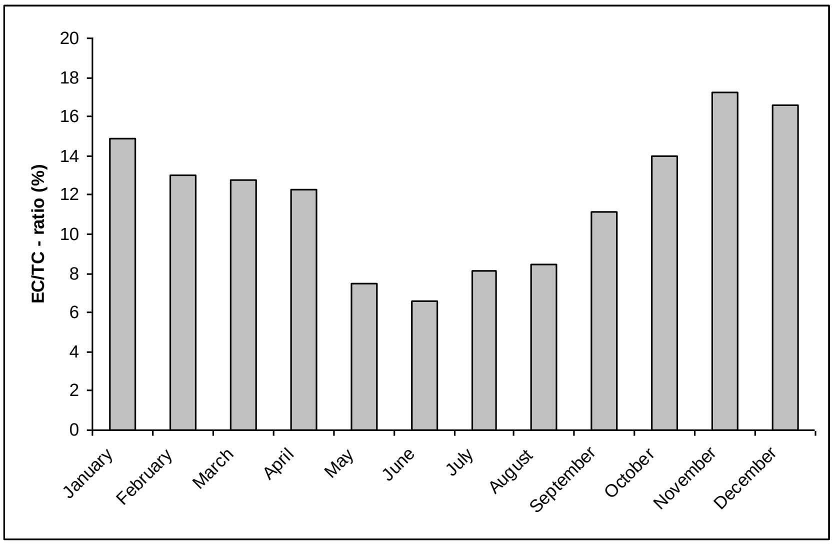


Figure 1.11: EC/TC ratio for PM_{10} at Birkenes for the period 2001–2006.

The majority of OC in PM_{10} can be attributed to the fine fraction, ranging from 67–88% on an annual basis for the period 2001–2006. For 2006 the relative contribution was 68%. Fine OC makes a less contribution to OC in PM_{10} in summer and fall. This seems to be attributed to the impact of primary biological aerosol particles in summer (Yttri et al., 2007a,b), which mainly is found in the coarse fraction of PM_{10}. During summer, coarse OC may be the major fraction, accounting for more than 50% of OC in PM_{10} even on a monthly basis. This finding is consistent also for 2006 and emphasizes the importance of monitoring OC in both $PM_{2.5}$ and PM_{10}.

Birkenes (NO01) is the only EMEP site that has a time series of EC, OC, and TC, for more than five years (2001–2006). While the concentrations of OC and TC decreased from 2001–2004, they have been increasing from 2004 to 2006. In fact, the highest annual mean concentration of OC and TC in PM_{10} was observed for 2006. Compared to 2005 the concentration of OC increased by approximately 30% for PM_{10} and 40% for $PM_{2.5}$. The less reduction for PM_{10} could be attributed to the fact that OC in $PM_{10-2.5}$ increased by 10% (Figure 1.10c). From 2001-2006 the concentration of OC in $PM_{10-2.5}$ have increased steadily from 0.13 µg m^{-3} to 0.32 µg m^{-3}. It could be speculated that this increase follow from climatic changes, such as dry and windy conditions and reduced snow cover, which would promote resuspension of coarse OC from the ground.

Concentrations of EC in PM_{10} decreased from 2005 to 2006, while for $PM_{2.5}$ the concentration increased.

Characteristic for the timeseries of EC, OC, and TC in PM_{10} and $PM_{2.5}$ is the decrease in concentration observed for 2004. This reflects what has been observed for PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$, as well as for the secondary inorganic aerosol (SIA) constituents at Birkenes (Figure 1.12), and also for several other EMEP sites measuring PM. The increased concentrations of OC and TC in 2006 compared to 2005 is also observed for PM and SIA.

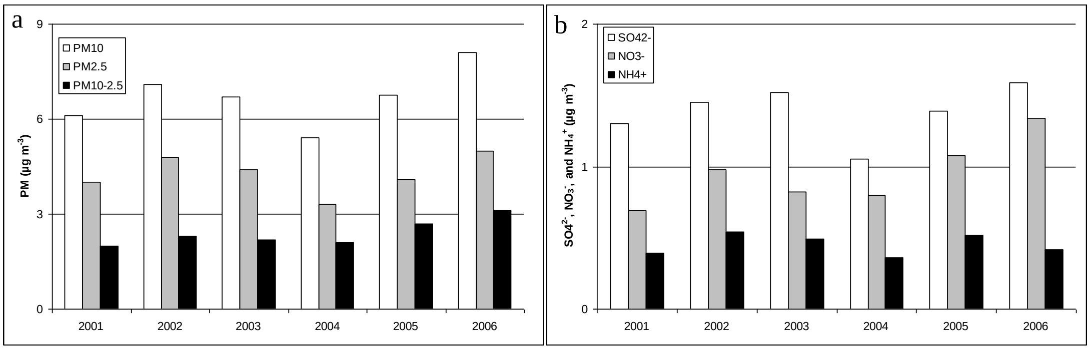


Figure 1.12: Annual mean concentration of PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$ (a), and SO_4^{2-}, NO_3^- and NH_4^+ at the Norwegian site Birkenes (NO01).

For the period in question, the relative contribution of TCM-to-PM_{10} [(TCM = Total carbonaceous matter (TCM = OC x 1.7 + EC x 1.1)] at Birkenes has decreased from 34% in 2001 to 26% in 2006 (Figure 1.13a). The relative contribution of TCM-to-$PM_{2.5}$ follows the same pattern as for TCM-to-PM_{10}, accounting for 47% in 2001 and 32% in 2006. A slight increase in TCM-to-$PM_{2.5}$ was observed for 2006 compared to 2005. The relative contribution of TCM to $PM_{10-2.5}$ ranged from 9–21% for the actual period. While TCM-to-$PM_{10-2.5}$ increased substantially from 2001–2004, corresponding to the major increase in the $OC_{PM10-2.5}$ concentration shown in Figure 1.10c, the figures have been stable for the last two years. Compared to SO_4^{2-}, NO_3^-, NH_4^+, and sea salt, TCM accounts for the greatest contribution of mass to PM_{10} at Birkenes (Figure 1.13b).

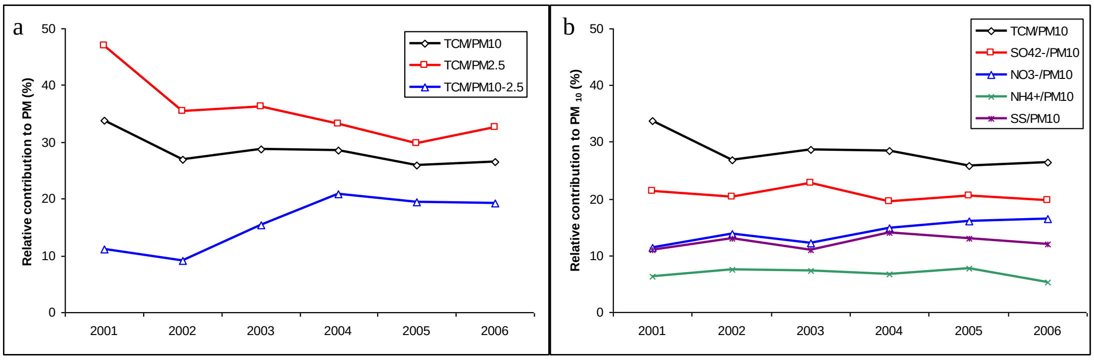


Figure 1.13: Relative contribution of TCM (Total Carbonaceous Matter) to PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$ (a) and relative contribution of TCM, SO_4^{2-}, NO_3^-, NH_4^+ and sea salt to PM_{10} (b).

1.2.5 EC and OC levels at the Italian site Ispra (IT04)

The other site reporting levels of EC, OC and TC for 2005 was the Italian site Ispra (IT04) (45° 49'N, 8° 38'E, 209 m asl) situated in the Po Valley in the north-western part of Italy. The site is representative for the rural parts of the densely populated central Europe and has been operational since 1985.

For 2005 the annual mean concentration of OC at Ispra was 12.7 µg m^{-3} for PM_{10} and 10.1 µg m^{-3} for $PM_{2.5}$, whereas the corresponding levels of EC were 4.1 µg m^{-3} (PM_{10}) and 2.4 µg m^{-3} ($PM_{2.5}$) (Table 1.8). The annual mean concentration of total carbon (TC) was 16.6 µg m^{-3} for PM_{10} and 12.5 µg m^{-3} for $PM_{2.5}$. For $PM_{10-2.5}$ the annual mean concentration of EC, OC and TC was 1.8 µg m^{-3}, 2.7 m^{-3} and 4.3 µg m^{-3}, respectively.

Table 1.8: Annual mean concentrations of EC, OC, and TC in PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$ at the Italian site Ispra (IT04) for the years 2003-2005 (µg m^{-3}).

Year	**PM_{10}**			**$PM_{2,5}$**			**$PM_{10-2.5}$**		
	EC	**OC**	**TC**	**EC**	**OC**	**TC**	**EC**	**OC**	**TC**
2003	1.7	8.3	10.1	1.3	6.6	7.8	0.46	1.8	2.3
2004	1.8	9.0	10.8	1.6	8.6	10.2	0.14	0.42	0.56
2005	4.1	12.7	16.6	2.4	10.1	12.5	1.8	2.7	4.3

The PM concentrations of EC, OC and TC for 2005 were all higher than for 2004. The increase was particularly high for PM_{10}. Increased levels were also observed for SIA and PM, although not as substantial as seen for PM_{10}, but in line with that of OC and TC in $PM_{2.5}$. This might indicate some kind of systematic error in the PM_{10} dataset for EC, OC and TC. It should also be noted that for part of the sampling period the $PM_{2.5}$ sampler was operated without a denuder and a sampling head, and that there was a change of samplers from two, collecting PM_{10} and $PM_{2.5}$, respectively, to one from which both parameters could be obtained. In addition, a new analytical instrument was introduced in 2005, providing 12% higher level of TC.

For 2005 the levels of EC and OC had an obvious seasonal variation with higher concentrations during winter compared to summer. This is in agreement with what was observed at Ispra in previous years (Figure 1.14).

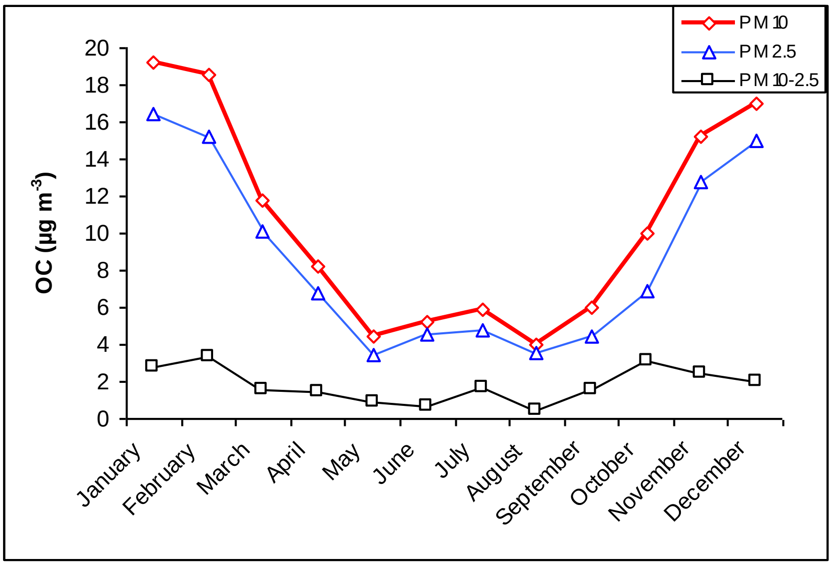


Figure 1.14: Monthly mean concentrations of OC in PM_{10}, $PM_{2.5}$ and $PM_{10-2.5}$ at the Italian site Ispra (IT04) for the period 2003–2005.

From Table 1.7 is can be seen that OC was the dominant fraction of TC at Ispra for the period 2003-2005, accounting for 79 ± 6% of TC in PM_{10} and for 82 ± 3% of TC in $PM_{2.5}$. The corresponding percentages for EC were 21 ± 6% (PM_{10}) and 18 ± 3% ($PM_{2.5}$). Higher EC/TC ratios was observed for 2005 compared to previous years.

Table 1.9: Annual mean $EC_{PM2.5}/EC_{PM10}$, $OC_{PM2.5}/OC_{PM10}$, and $TC_{PM2.5}/TC_{PM10}$ ratios at the Italian site Ispra for the period 2003–2005 (%).

Year	**$EC_{PM2.5}/EC_{PM10}$**	**$OC_{PM2.5}/OC_{PM10}$**	**$TC_{PM2.5}/TC_{PM10}$**
2003	68	84	84
2004	68	83	84
2005	57	80	74
Mean ± SD	**64 ± 6**	**82± 2**	**81 ± 6**

The majority of the carbonaceous material was associated with fine aerosols (Table 1.9). However, this was less pronounced for 2005 compared to previous years, and in particular for EC. This might stem from the irregularities concerning sampling in 2005. It should be mentioned though, that only days where data for both EC and OC existed, were included in the annual mean ratio. In addition, days with higher levels of EC, OC, and TC in the fine fraction compared to PM_{10} were excluded, which were quite a few.

For 2005 the annual mean concentration of TCM accounted for 53% of PM_{10} at Ispra (Figure 1.15), whereas it was slightly less for $PM_{2.5}$ (52%). These estimates are rather high in general, and for PM_{10} it was substantially higher than for the two preceding years. A conversion factor of 1.4 was used to convert OC to OM for all size fractions at Ispra, whereas a factor of 1.1 was used to account for hydrogen associated with EC (Kiss et al., 2002). The conversion factors for OC reported in literature range from 1.2-2.6, depending on the origin of the aerosols and to what extent they have been aged in the atmosphere (Turpin and Lim, 2001). For the EMEP EC/OC campaign, conversion factors for OC ranging from 1.4-1.8 was calculated for the sites participating, based on the relative contribution of WSOC and WINSOC to OC at the various sites (Yttri et al., 2007a). Without doubt, the use of such wide range of conversion factors might introduce a significant level of uncertainty to the TCM-to-PM estimates.

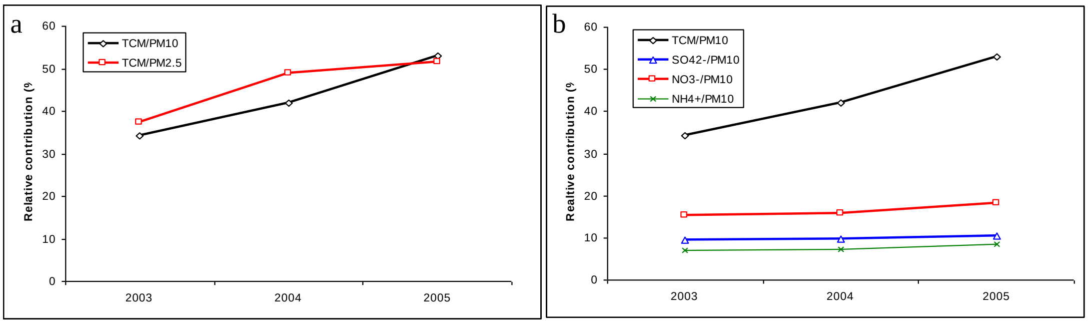


Figure 1.15: Relative contribution of TCM (Total Carbonaceous Matter) to PM_{10} and $PM_{2.5}$ (a) and relative contribution of TCM, SO_4^{2-}, NO_3^- and NH_4^+ to PM_{10} (b).

TCM accounted for the majority of the mass concentration of PM_{10} at Ispra in 2004, followed by NO_3^- (18%), SO_4^{2-} (10%), and NH_4^+ (9%). Whereas the relative contribution of TCM to PM_{10} increased significantly from 2004-2005, only minor changes were observed for the inorganic aerosol constituents. This collaborates to the indication that the levels of carbonaceous material might have been erroneously high for 2005.

1.3 Development and validation of standardised protocols for sampling OC and analysing EC and OC for the EMEP network

By Jean-Philippe Putaud and Fabrizia Cavalli

1.3.1 Introduction

The EMEP-monitoring data is supposed to provide high quality data to establish a reliable picture of the air pollution situation in Europe, for model validation, for validation of the effectiveness of implementation of current air pollution legislations, and for assessing the needs to revise and improve current policy. It is therefore essential that the measurements reflect air concentrations in a representative manner, i.e. that the methods applied are consistent and free of artefacts. In addition, long-term monitoring, in particular, requires that measurement series can be continued consistently for many years. This includes that changes in instrumentation should be avoided, unless the impact of changes are carefully evaluated and documented. Experience has also shown that measurements should be standardised as far as possible to obtain data that are comparable and of sufficient quality. These requirements are best met by a combination of simple and robust sampling techniques that are well described.

There is little doubt that several of those requirements listed above are still not met with respect to monitoring of EC and OC. This is a challenge not only troubling EMEP, but the entire scientific community. Development of standardised protocols for sampling of OC and analysing EC and OC should be of high priority. In the framework the EU funded project EUSAAR (European Supersites for Atmospheric Aerosol Research), which networks 20 stations across Europe (of which nine are EMEP sites), work devoted to the development and validation of standardised protocols for sampling OC and analysing EC and OC started in April 2006. A short progress report is presented here.

1.3.2 Objectives

The problem of sampling OC on filters is to a certain extent similar to that of sampling NH_4NO_3; semi-volatile organic carbon (SVOC) present in the gas phase in the atmosphere may condense on the filters, similarly to NH_3 and HNO_3, but can also evaporate from the filters, as NH_4NO_3 can. This topic is further complicated by the fact that SVOC consists of a large number of various molecules with different physical and chemical properties, which affects their volatility and affinity to filters.

Estimates of artefact contribution to the measured particulate organic carbon concentrations, range from – 80 to + 100%. Whether positive or negative artefacts prevail, depends on several parameters, e.g. meteorological conditions and the chemical composition of the OC mix. Various sampling trains exist that are supposed to account for the sampling artefacts of OC (e.g. Mader et al., 2003), but the performance of these approaches are disputed. “Artefact-free” sampling trains including denuder(s), filter(s), and sorbent(s) have been developed and used in the USA for the last 20 years. However, these sampling trains are still not well characterised with respect to their efficiency and lifetime hence they are not widely used, even at the US-EPA supersites. Further, it is not straightforward to extrapolate from results obtained at a limited number of sites in the USA to the various climatic and pollution environments encountered in Europe, simply because the carbonaceous aerosol mix is likely to differ substantially.

The analysis of EC and OC is also highly challenging, again because carbonaceous particulate matter consists of thousands of different molecules, ranging from semi-volatile to refractory species, which makes it impossible to define and produce suitable standards for atmospheric organic and elemental carbon.

In Europe, a concerted action regarding these issues has been undertaken within the frame of EUSAAR (***European Super-sites for Atmospheric Aerosol Research***), an EC-funded Integrated Infrastructure Initiative. The participation of EMEP sites in this project is particularly important with respect to the subsequent implementation of the standardised protocol to the EMEP monitoring network, and because sampling of particulate OC seems to pose particular challenges in areas with low aerosol loadings. The objectives of EUSAAR relative to the carbonaceous aerosol issues were listed as follows:

1- deliver a sampling train for particulate carbonaceous matter, well characterised with respect to particle trapping efficiency, positive and negative artefact assessment, lifetime, running cost, maintenance, etc…

2- define a standardised protocol for the thermal-optical analysis of EC and OC.

3- assess the comparability of this standard analytical method with the other methods used within the network and periodically check their consistency (intercomparisons)

4- design a standardised method for analysing the back up sorbents.

5- get the overall standardised procedure for EC and OC determination adopted by the EMEP task force on measurements and modelling, and by the WHO Global Atmospheric Watch scientific advisory group.

1.3.3 Status report

Here we present the status of the activities related to objectives 1-4 listed above.

1.3.3.1 Development of an artefact-free sampling train

A commercially available carbon monolith denuder has been successfully tested at the EMEP station IT04. The use of this denuder reduces the contribution of the adsorbed SVOC (i.e. the positive artefact) to the amount of Carbon collected by the quartz fibre filter to 2-10% for the entire range of concentrations observed. Three such denuders have been made available for testing at the sites Košetice in the Czech republic, Jungfraujoch in Switzerland, and Montseny in Spain. Several other stations have purchased these denuders for testing as well. Additional denuders purchased by JRC are to be made available to others by the end of July 2007. In addition, a denuder that is to be operated at a higher flow rate (38 l min^{-1}) than the original one, which operates at 16.7 l min^{-1}, will be tested as an alternative for parts of Europe experiencing low PM OC levels. Results of the tests performed at various sites across Europe will be available by October 2007.

The work on negative sampling artefacts has been delayed by the fact that the previously tested sorbent material (carbon impregnated glass fibre filters from Schleicher and Schuell) is no longer available on the market. Alternatives have been tested at IT04 under various meteorological and pollution situations in July 2007. The results from this testing will be available by October 2007. However, tests will be performed at other stations as well.

When a suitable sorbent have been found and thoroughly tested, this will lead to the definition of the best affordable sampling train, which will be fully characterised in term of efficiency, positive and negative artefacts, lifetime, running cost, maintenance, and so forth. This is scheduled for no later than 2010. It is likely though, that the denuder could be taken into service at an earlier stage, tentatively 2008, accounting for the positive artefact. It should be noted though that using a denuder without a backup sorbent is expected to increase the negative artefact. Alternatively, the quartz fibre filter behind quartz fibre filter approach (QBQ), as described in the interim recommendations (http://www.nilu.no/projects/ccc/manual/index.html), could be used to account for the positive artefact.

1.3.3.2 Optimisation of thermal-optical analysis of EC and OC

A comprehensive work has been undertaken at JRC-Ispra to develop an optimised thermal-optical protocol for EC and OC analysis. This protocol, called EUSAAR_1, aims at minimising the analytical artefacts inherent to the thermal-optical analytical technique, which currently is the most reliable method for determining EC and OC in ambient aerosol filter samples. The EUSAAR_1 protocol was designed to: (1) reduce pyrolysis to a minimum and to favour the volatilisation of organic carbon by prolonging the steps at lower temperatures, (2) minimize the underestimation of elemental carbon by limiting the release of light absorbing carbon at high temperatures in the He-mode, and (3) minimize the risk of overestimating elemental carbon due to the slipping of residual organic carbon into the He/O_2-mode. A report on this work has been made available to the EUSAAR community at www.eusaar.net.

EUSAAR_1 was developed based on PM samples collected at Ispra (IT04), and did not pretend to be ideal for every PM sample collected across Europe. Hence, the protocol was tested for various sample types by four other EUSAAR partners (University of Crete, The Finnish Meteorological Institute, Lund University, and the Norwegian Institute for Air Research). The feedback from this testing will be considered in order to define a slightly revised protocol, namely EUSAAR_2. The scheduled delivery time for EUSAAR_2 is end of July 2007. Testing of EUSAAR_2 will be performed during fall 2007 by those who provided feedback on EUSAAR_1. These results will be reported by October 2007. Given that this testing provides positive results, is likely that EUSAAR_2 could be taken into service in 2008.

1.3.3.3 *EC, OC, TC analysis – Round robin test*

Not all stations performing analysis of the ambient PM carbonaceous fraction have a thermal-optical instrument at their disposal. Furthermore, similar instrument can show discrepancies due to e.g. different technical settings. Therefore, periodic inter-comparisons of all the instruments used for EC and OC analyses within the EUSAAR network have been scheduled, based on distributing selected aerosol filters among EUSAAR partners and associates. A first set of eight samples was distributed in March 2007 and the results were to be delivered by May 2007. A preliminary interpretation of these results is that most instruments are able to determine TC with a good accuracy (Figure 1.16), whereas large discrepancies (> factor of 3) among instruments are observed with respect to the filters content of EC. However, less variation is observed when comparing results obtained by instruments operating according to thermal-optical analysis. Further, the two laboratories using the EUSAAR_1 protocol (FMI, JRC) found very similar results, which is highly encouraging. Among the laboratories using the instrument default protocol, discrepancies can be larger (factor of 2) though. The results from this Round robin test are to be presented and discussed in October 2007. It is expected that the use of a standardised protocol based on thermal-optical analysis will improve the consistency of EC determination.

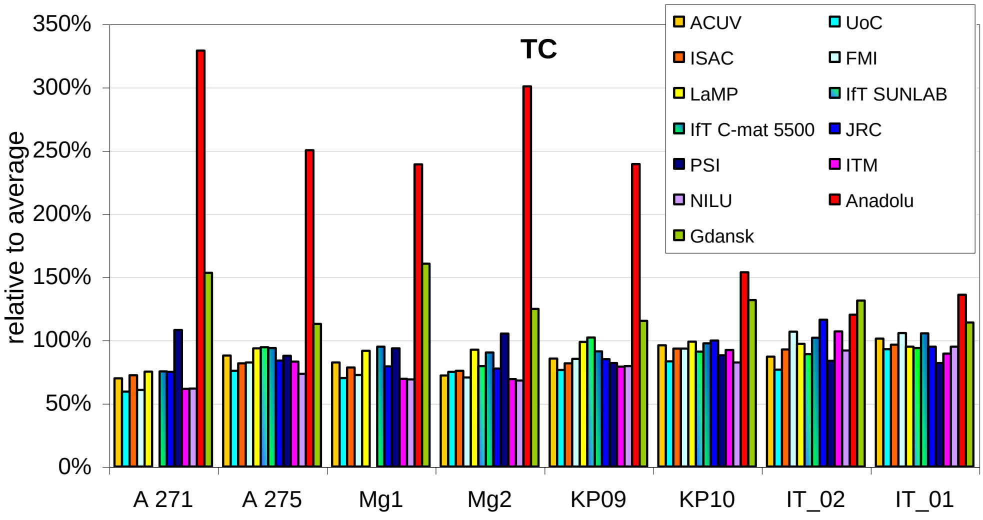


Figure 1.16: Preliminary result of the first carbonaceous aerosol analysis inter-comparison carried out within EUSAAR, based on eight ambient aerosol samples collected at four sites across Europe. Shown are results regarding the filters content of total carbon (TC).

1.3.3.4 *Method for analysing sorbent back-up filters*

A thermal protocol for analysing semi-volatile organic carbon trapped by the sorbent back up filter has been developed and tested at JRC. It is suitable for both Carbon based sorbents and XAD-impregnated filters. It is available to the EUSAAR community at www.eusaar.net, and may be provided to other EMEP stations on request.

1.3.4 Conclusions

A comprehensive work is going on within EUSAAR to develop and optimise a unified protocol on artefact-free sampling of OC and thermal-optical analysis of EC and OC. Commercial denuders for trapping gaseous OC/SVOC have been validated at IT04 and tested at several other sites. Results from this testing will be available by October 2007. Sorbents for collecting OC lost from the filter where particulate matter is sampled were tested at IT04. Results will be available by October 2007. The entire sampling train will be validated for various meteorological and pollution conditions, and will be completed no later than 2010. However, the denuder part of the sampling train is likely to be taken into service in 2008.

An optimised thermal-optical protocol for analysing EC and OC has been developed at JRC and tested on filter samples collected at four other EUSAAR sites. Feedbacks have been considered and will be used to develop a slightly revised protocol, which will be made available to the EUSAAR community by July 2007. Tentatively, this revised protocol could be taken into service in 2008. The methods currently used for determining EC and OC at various EUSAAR sites have been intercompared. A report on this Round robin test will be released by October 2007.

During the period while we await the finalization of the EUSAAR unified protocol, interim recommendations/guidelines concerning how to perform sampling for subsequent analysis of EC and OC and analysis of EC and OC can be found on the EMEP web pages (http://www.nilu.no/projects/ccc/manual/index.html).

2. PM emissions reported to EMEP

By Leonor Tarrasón and Vigdis Vestreng

2.1 Introduction

This chapter presents short summary of the status of PM emissions and precursors as reported to the Convention via the EMEP Programme. First, the status of emissions are presented, then differences between official emissions and the "best estimates' used for modelling are presented and finally, differences between 2004 estimates and the 2005 emissions are evaluated. It is important to note that the most significant uncertainties with emission data this year are related with the official reported emissions in EECCA countries.

2.2 Status of submissions in 2005

The number of Parties reporting emission data to the Convention has been quite constant since year 2000. This year, 37 of the 51 Parties to the Convention, corresponding to 73%, submitted emission data. 28 of these, corresponding to 55% of the Parties, reported the emission data within the deadline.

The number of Parties submitting emission data to EMEP has not increased during the last five years although the number of Parties to the Convention has increased from 46 to 51 in the period. However, as indicated in Figure 2.1, there has been a significant increase in the number of Parties reporting emissions within deadline. The increase is related to the extension of the submission deadline to 15th February after the 2002 Guidelines for Reporting Emissions were adopted (ECE/EB.AIR/80).

Since the time of adoption of the 2002 Guidelines, the actual emission information reported to EMEP has increased significantly, both with respect to sector specific emissions and with respect to gridded data. Every five years, Parties to the Convention are requested to provide additional information on gridded distributions of emissions, activity data and projections. This year, such information was required to the Parties for emissions in 2005.

It is encouraging to note that the availability of gridded sector data has increased considerably compared to previous years, as illustrated in Figure 2.2. It is also positive that the increase in data availability involves not only main pollutants but also PM, HMs and to a lower extent also POPs. Gridded sector data is particularly relevant to EMEP because the dispersion of pollution in the atmosphere is very dependent on the actual location of the sources. These data are direct input to EMEP modelling and their quality determines to a large extent the validity of the modelled results. It should still be noted however that despite this increase, 68% of all EMEP Party areas are still not covered by these data.

The status of submissions of emission data to the Convention in 2005, together with the results from the review process are presented in detail in Vestreng et al. (2007). Documentation of the data used for modelling at MSC-W and an analysis of differences with previous years follows below.

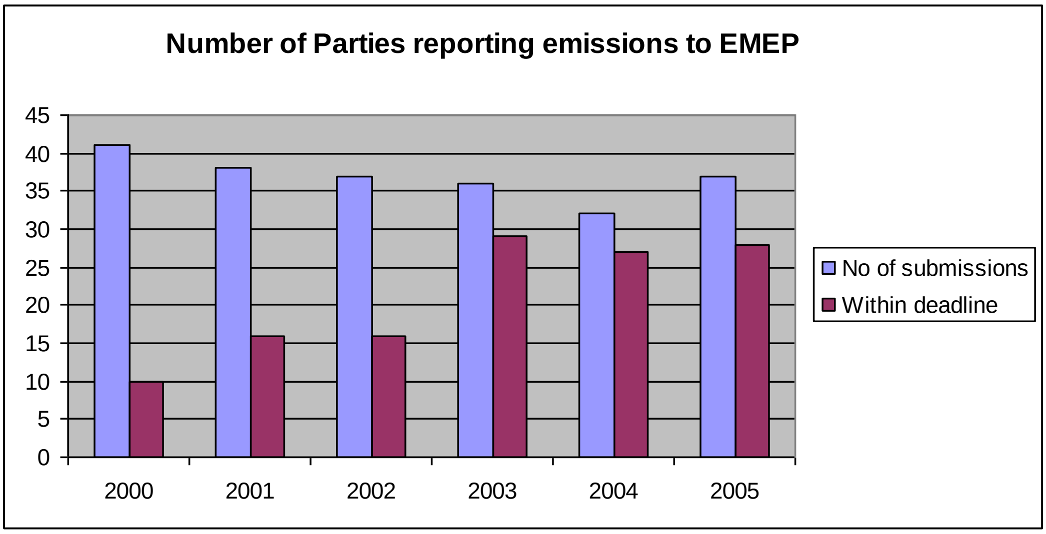


Figure 2.1: Number of Parties reporting emission data to EMEP since 2000. The total number of Parties has increased from 46 in 2000 to 51 in 2005.

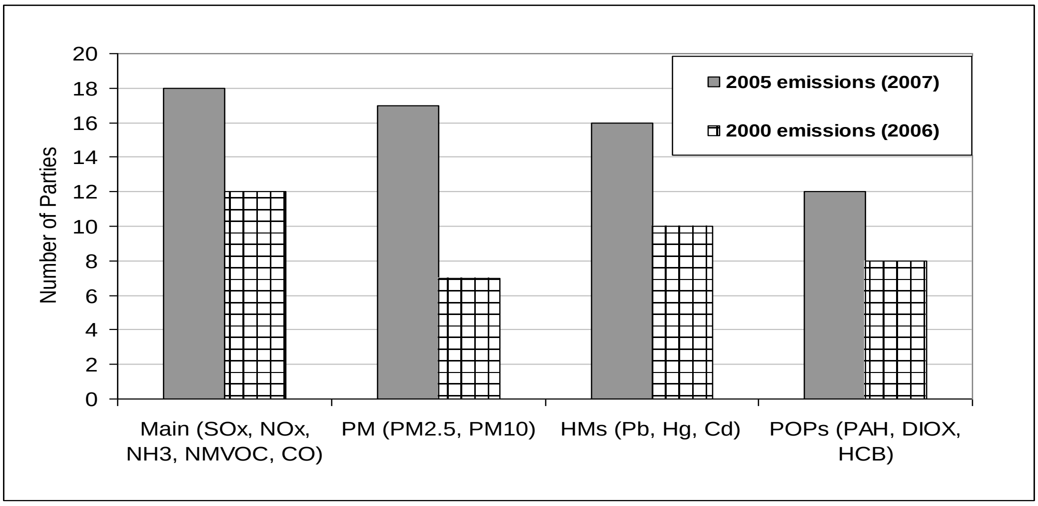


Figure 2.2: Number of Parties reporting gridded sector data to EMEP, increase since last year. Source: Vestreng et al. (2007).

2.3 Emission data used for modelling in 2005

EMEP/MSC-W uses officially reported emission data for modelling purposes when the official data is available for the simulation year (or a year close enough) and when the available data has fulfilled the QA/QC requirements of QA/QC of the annual emission review.

When official emission data is not available, EMEP/MSC-W uses instead non-Party estimates to complete the necessary emission input information.

When official emission data is available but has not passed the review requirements, EMEP/MSC-W substitutes the official data by an independent non-Party estimate.

An overview of the emission data used by country for 2005 calculations presented in this report is provided in Table 2.1. Official gridded sector data values have been used for twenty countries: Austria, Belarus, Germany, Denmark, Estonia, Finland, France (for 2000), Hungary, Ireland, Italy (for year 2000), Lithuania, Latvia, Netherlands (for 2000 emissions), Norway, Portugal (for 2004), Sweden, Slovenia, Spain, Switzerland and United Kingdom (for 2004).

Table 2.1: Overview of emission data used in EMEP/MSC-W modelling for 2005.

Country name	Official reports	Replacements	Non-Party estimates
Albania			CIAM report 1/2006 + MSCWgrid
Armenia			CIAM reports + MSCW grid
Austria	15/02/07	no	
Azerbaijan	30/03/03	For all sectors, for reported components	EDGAR + MSCW grid
Belarus	15/02/07	Yes, except for NH3	CIAM report 1/2006 + MSCWgrid
Belgium	23/03/07	no	MSCW grid
Bosnia Herzegovina			CIAM report 1/2006 + MSCWgrid
Bulgaria	16/02/07	no	MSCW grid
Croatia	2006	yes, for PM	CIAM report 1/2006 + MSCWgrid
Cyprus	16/02/07	no	MSCWgrid
Czech Republic	15/02/07	yes, for NMVOC	CIAM reports+ MSCWgrid
Denmark	15/02/07	no	
Estonia	15/02/07	no	
Finland	15/02/07	yes, for CO	CIAM reports+ MSCWgrid
France	15/02/07	no	
Georgia			CIAM report 1/2006 + MSCWgrid
Germany	15/02/07	no	
Greece	15/06/07	yes, for CO, S7	CIAM reports+ MSCWgrid
Hungary	15/02/07	yes, for PM	CIAM reports+ MSCWgrid
Iceland			EDGAR + MSCWgrid
Ireland	15/02/07	yes, for PM	CIAM reports + MSCWgrid
Italy	2006 and 2000	no	
Kazakhastan			EDGAR + MSCWgrid
Kyrgyzstan			EDGAR + MSCWgrid
Latvia	15/02/07	no	
Lithuania	15/02/07	yes, for PM	CIAM reports + MSCWgrid
Luxembourg	2006		CIAM reports+ MSCWgrid
Malta	22/02/07	no	CIAM reports + MSCWgrid
Moldova	14/02/07	yes, except for NMVOC and Nox	CIAM report 1/2006 + MSCWgrid
Montenegro			CIAM report 1/2006 + MSCWgrid
Netherlands	15/02/07 and 2000	no	
Norway	15/02/07	no	
Poland	15/03/07	no	MSCWgrid
Portugal	15/02/07 and 2004	no	
Romania	15/02/07	yes, except for SOx and PM	CIAM report 1/2006 + MSCWgrid
Russian Federation	13/02/07	yes, for all components	CIAM report 1/2006 + MSCWgrid
Serbia	13/02/07	yes, for NOx and SOx	CIAM report 1/2006 + MSCWgrid
Slovakia	15/05/07	yes, except for NOx and SOx	CIAM reports + MSCWgrid
Slovenia	14/02/07	yes, for NH3 and CO	CIAM reports
Spain	23/05/07	no	
Sweden	15/02/07	no	
Switzerland	15/02/07	no	
TFYROM	26/02/07	yes, for SOx,CO and NMVOC	CIAM report 1/2006 + MSCWgrid
Turkey			CIAM report 1/2006 + MSCWgrid
Ukraine	23/03/07	yes, except for PM	CIAM report 1/2006 + MSCWgrid
United Kingdom	15/02/07 and 2004	no	

For 9 countries, no official emission estimates are available and MSC-W has derived their own estimates from independent sources. In these cases, the main source of information for national emissions and sector data are the reports from CIAM, in particular the latest estimates by Cofala et al. (2006) prepared last year for the review of the Gothenburg Protocol. In few cases, where no information is available from CIAM, estimates by EDGAR (http://www.mnp.nl/edgar) or GEIA (http://www.geiacenter.org/). The methodology to distribute these sector emission spatially is described in Tarrason et al. (2004).

For 17 countries, official emissions have been replaced by information from the independent sources above, because the official data has not complied with the quality standard established in the EMEP emission review. The main reason to substitute official emission estimates is an incomplete reporting of sector sources by Parties.

For this years calculations, replacements of emission data have been made primarily for EECCA countries.

2.3.1 Differences in EECCA countries between official emissions and non-Party emissions

The geographical distribution and the magnitude of replacements are shown in Figure 2.3. With very few exceptions, the corrections of official emissions have been done mainly for EECCA countries. For Serbia and Montenegro, the substitution of official data is related to the need of allocating emissions from these two new independent countries.

For sulphur dioxide, the replacement of official emissions leads to 5% higher SO_2 emissions over the area. The most significant change is for Azerbaijan, where the official reported emissions are about a factor 10 lower than the non-Party EDGAR estimates. For the other countries with replacements, differences in national totals are very small for this component. The replacements have mostly addressed reallocation of sector emissions. For example, over the Russian Federation, the large differences in Figure 2.3 correspond mainly to redistribution of emissions of SO_2 reported as traffic and off-road emission to emissions in SNAP Sector 1, 2 and 4. The sector distribution for the EECCA countries used in the replacements follows the conclusions from Cofala et al. (2006). It is expected that the effects that this re-allocation of sources in different sectors will have a significant impact, in the atmospheric transport calculations. For the Russian Federation especially, emissions in the official estimates are considered as area (traffic) sources, while the replacements locate those sources in power and industrial plants and are treated by the model as point sources.

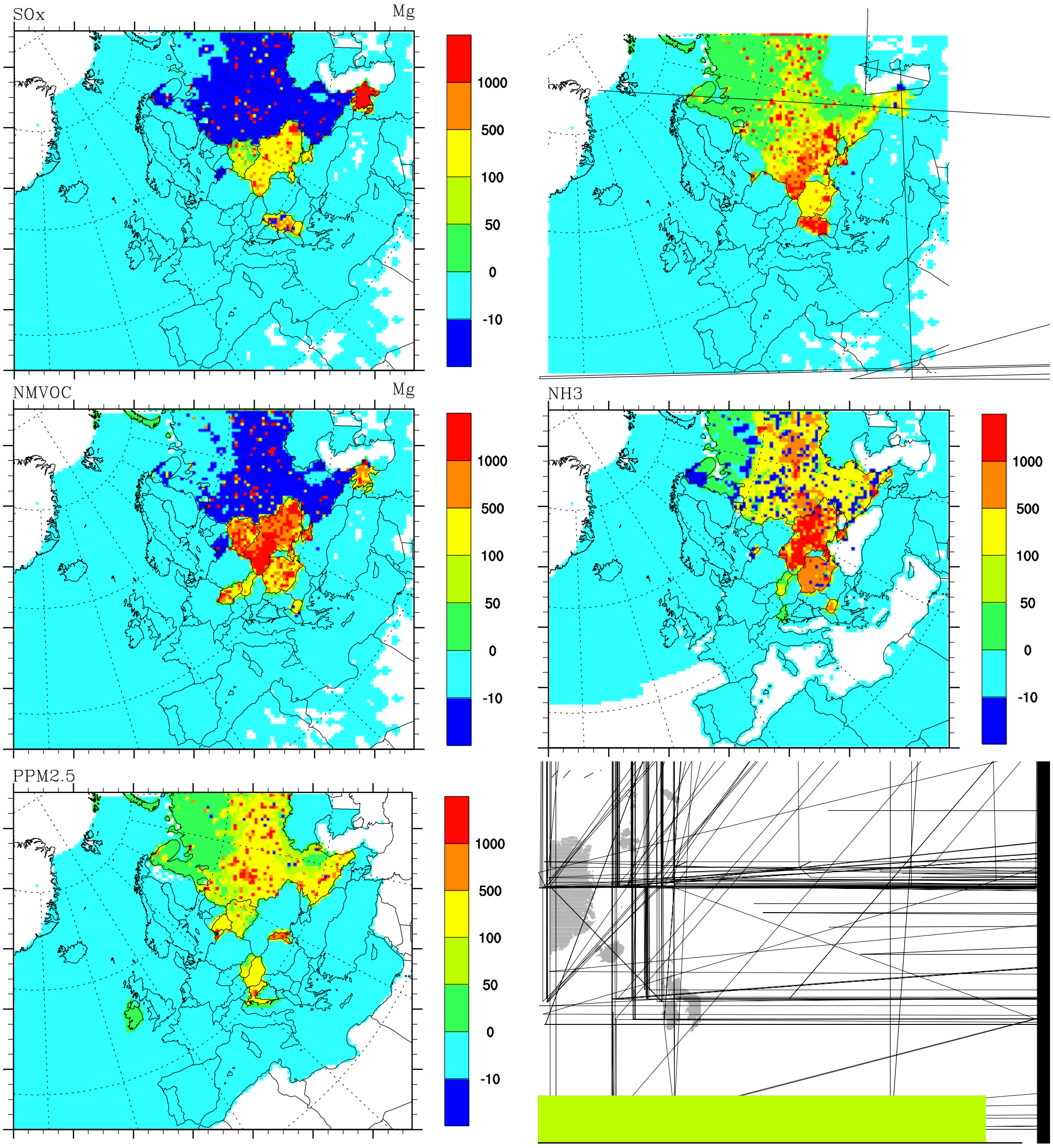


Figure 2.3: Differences between replacements and reported national total emissions (Unit: Mg)

For nitrogen dioxide, the replacement of official emissions leads to a considerable increase of the total emissions of the area, in all about 20% higher emissions. The replacements in this case are usually related to the addition of sources from SNAP Sector 2 (Non-industrial combustion plants) and in Sector 4 (Production processes) to the official reported values, which did not include emissions from these sources. The increase in NMVOC emissions due to the use of replacements leads also to 20% higher emissions in the area of the replacements. The largest increases are for Ukraine and in the case of the Russian Federation must of the changes are due to the redistribution of sources in Sector 3 (Combustion in Manufacturing Industry) to other sectors, and specially Sector 6 (Solvent Use).

For ammonia emissions, the replacement of official emissions implies also a significant increase in the ammonia emission estimates over the area, over 30% emission increase. The largest increases are for Ukraine, Romania and the Russian

Federation. Specially for the Russian Federation, the spatial distribution of ammonia is significantly different between the official estimates and the replacements. This is because emissions of ammonia are reported by the Russian Federation to be in SNAP Sector 8 (Other mobile source and off-road) and not in sector 10 (Agriculture). The spatial distribution of emissions from these two sectors are considerably different and that explains the differences illustrated in Figure 2.3.

The largest relative difference between official emission estimates and non-Party estimates is for primary PM emissions. The non-Party emissions are about double as large than those reported officially. The increases illustrated in Figure 2.3 are of the order of 50% for fine $PPM_{2.5}$ and of 60% for PPM_{coarse} emissions. The reason for these large differences between official and the independent non-Party estimates is incomplete reporting by the Parties. In most cases, the Parties have not included PM emissions from agricultural practices (SNAP Sector 10). These are relevant PM sources for PM and justify the large underestimation in the incomplete official reports. In some countries, in addition, PM sources from residential sources (Sector 2) and from production processes (Sector 4), also relevant PM activity sectors, are not included in the incomplete official reports.

This analysis indicates that the main reason for the replacements of official emission data is related to incomplete or erroneous allocation of sources in different activity sectors. In particular, over EECCA countries, bilateral communication between national experts and the EMEP centres should continue, but additional actions seem also necessary. Regular training courses and workshops with guidance on how to compile emission data should be carried out, in order to reduce the uncertainties of emission data in these countries.

2.3.2 Differences between 2005 and 2004 emissions

The differences presented here are for the 'best estimate' of emission data, after replacements have taken place. The trends of emission data for the different main components are given in Appendix A, for each individual country and area within EMEP.

For the whole EMEP area, emission changes between 2005 and 2004 are generally small, with averaged reductions of -0.5% for SO_2, -2.2% for NO_x, -0.4% for NH_3, -0.4% for $PPM_{2.5}$ and -3.8% for PPM_{coarse}, and no net significant changes for NMVOCs.

The individual country emissions change more significantly from 2005 and 2004, but these changes are different from country to country and region to region, as illustrated in Figure 2.4. The figure shows the variability of gridded emissions also within individual countries. The distribution of emissions per country and sector has changed significantly from 2004 to 2005, as a combined effect from differences in sector emissions and changes in the spatial distribution of sector emissions. It is interesting to note, however, that emission changes from 2004 to 2005 are not so large for the Russian Federation and Turkey as they are for other individual countries. This is simply because no data on gridded distribution of emissions has been reported from these countries and the same methodology has been used for allocating emissions in 2004 and 2005. The changes identified in Figure 2.4 for these countries arise from sector activity changes.

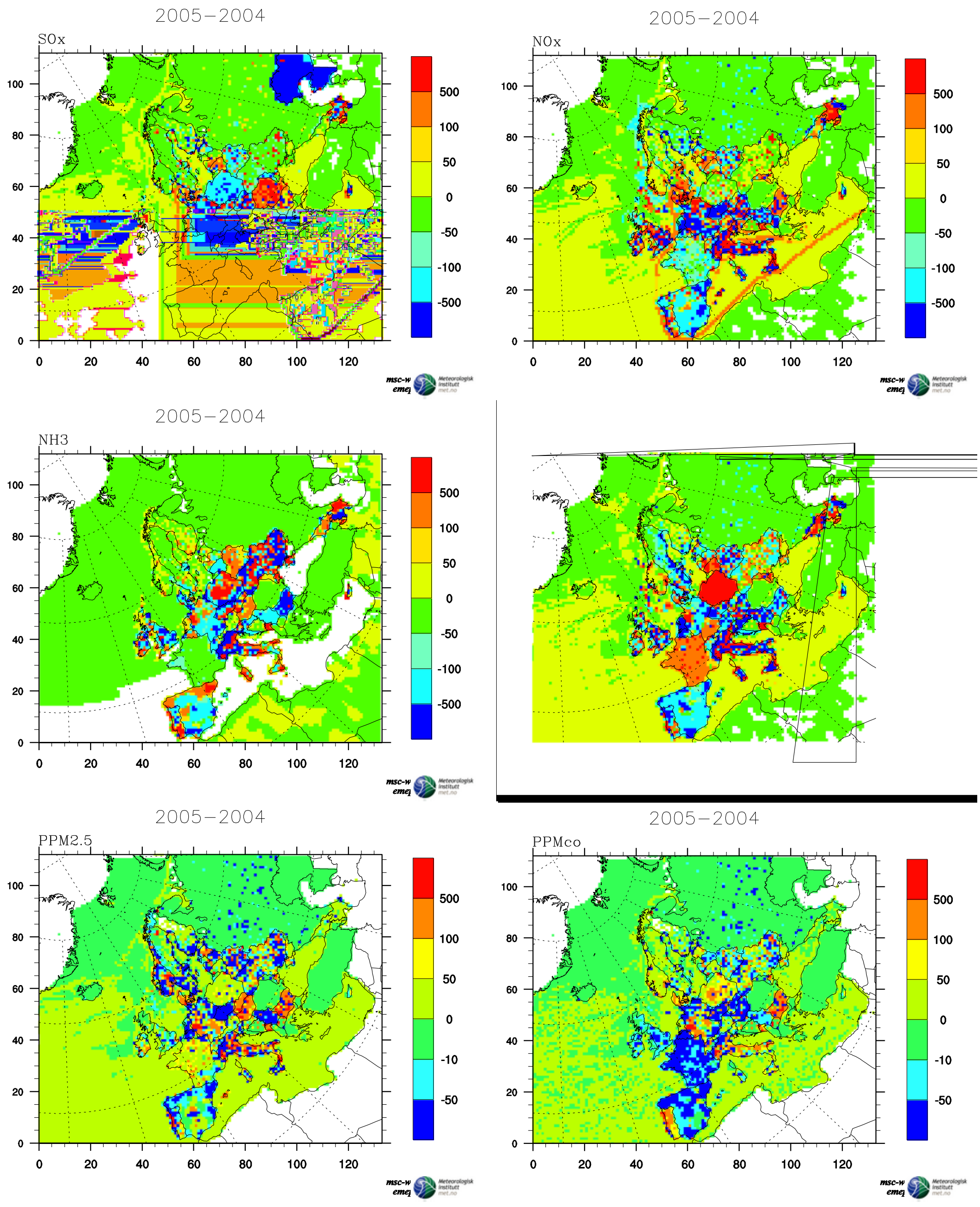


Figure 2.4: Differences in the spatial distribution of emissions between 2005 and 2004. Units: Mg.

The most significant changes in emissions from 2004 to 2005 are: a) the decrease of NO_x traffic emissions from EU countries, b) the general increase of ship traffic emissions and c) the reduction of primary PM_{coarse} emissions from agriculture. While the general reduction of NO_x emissions over the EMEP countries is about -2.2%, emission reduction of NO_x emissions in EU27 are on average -5.6% for traffic emissions in SNAP Sector 7 and of -8% for other mobile sources in SNAP Sector 8. This decrease is associated with the implementation of new EU regulations in 2005 in EU countries. The current estimate of trends in ship traffic emissions used in EMEP model calculations implies an increase of 2.5% increase per year for these emissions (Cofala et al., 2006). In comparison with the annual changes of other sector emissions reported to EMEP, this is a significant increase. Finally, for primary PM emissions, recalculations by individual countries have resulted in a significant reduction of PPM_{coarse} emissions, in particular emissions from SNAP Sector 10.

The spatial variability of the emission changes from 2004 to 2005 and the relatively small intensity of the emission changes suggest that these will have a limited effect in the calculations of air concentrations and depositions at long-range European scale. For more local pollution studies, however, these changes will be more relevant although they may be masked by meteorological variability.

More significant are the changes of 2005 with respect to year 2000. Based on the emission data per country given in the Appendix A, we have calculated the percentage change of emissions since year 2000 for different groups of countries. The results is shown in Figure 2.5 The countries are grouped as EECCA countries within EMEP, including Azerbaijan, Armenia, Belarus, Kazakhstan, Georgia, Republic of Moldova, Russian Federation and Ukraine, EU27 and OTHER, including Albania, Bosnia and Herzegovina, Croatia, Iceland, the FYR of Macedonia, Montenegro, Norway, Serbia, Switzerland and Turkey. In general, emissions have decreased in all Parties in the EMEP area by 5-15%, but the decrease is in most cases (except for SO_x) counterbalanced by a general increase in emissions in EECCA countries.

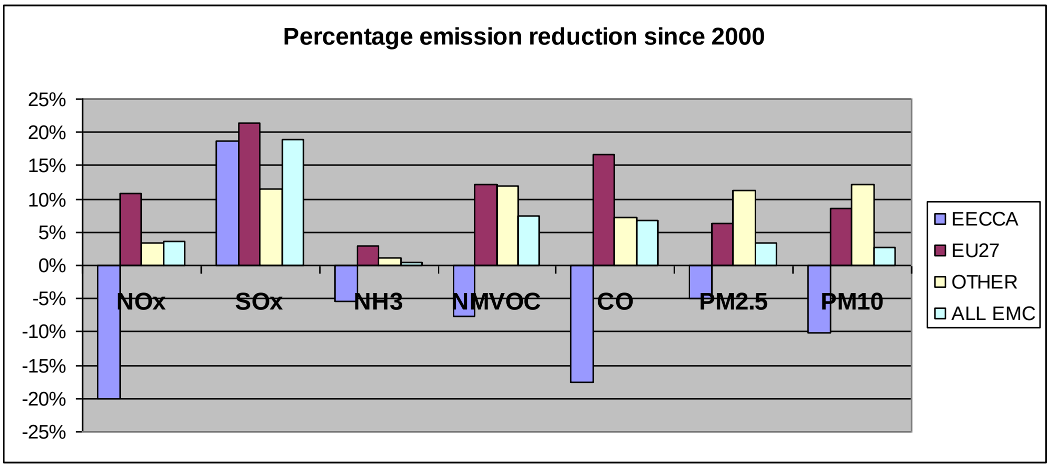


Figure 2.5: Percentage reduction of emissions for different groups of countries within EMEP from 2005 to2000.

3. Model assessment of particulate matter in Europe: Status in 2005

By Svetlana Tsyro

3.1 Introduction

In this chapter, we present an assessment of the concentration levels of transboundary particulate matter (PM) over Europe in 2005, based on both EMEP model results and EMEP observations. Characterisation of the composition of regional background PM is given through presenting the maps of model calculated concentrations of PM individual components. The discussion is based on the differences in the modelled concentrations of PM in 2004 compared to 2005. Included are the calculated exceedances of the WHO guideline values (WHO, 2005) for long-range transported PM_{10} and $PM_{2.5}$.

The calculations have been performed with the EMEP Unified model, documented in EMEP (2003), EMEP (2004) and EMEP (2005). An extended version of the model, which allows for description of the chemical composition of primary PM, has been used in this work (EMEP, 2003; EMEP, 2005; Tarrasón et al., 2006; Tsyro, 2005). The meteorological data for 2005 used to drive model simulations was produced with the HIRLAM-PS Weather prediction model. The calculations have been based on emissions of SO_x, NO_x, NH_3, PM_{10} and $PM_{2.5}$ for the year 2005 from the EMEP database. From primary $PM_{2.5}$ emissions, the emissions of elemental carbon (EC) and primary organic carbon (POC) have been derived using data from Kupiainen and Klimont (2007). The emissions of coarse EC have been derived from coarse PM emissions (which are the difference between PM_{10} and $PM_{2.5}$ emissions). The remaining fraction of primary $PM_{2.5}$ and coarse PM emissions were assigned to inorganic PM (e.g. mineral dust).

Evaluation results of the model performance with respect to PM_{10} and $PM_{2.5}$ and individual aerosol components based on EMEP observations in 2005 are also provided in this Chapter. The observation PM data, collected from the EMEP monitoring network in 2005, is discussed in Chapter 1.

3.2 PM_{10} and $PM_{2.5}$ in 2005

3.2.1 Annual mean PM_{10} and $PM_{2.5}$

Annual mean concentrations of PM_{10} and $PM_{2.5}$ in 2005 derived by combining EMEP model calculated fields and EMEP measurements are presented in Figure 3.1. The observations used in the merged maps are concentrations of PM_{10} and $PM_{2.5}$ measured at EMEP monitoring stations in 2005 (Chapter 1). Calculated PM_{10} and $PM_{2.5}$ include primary PM and secondary inorganic aerosols (SIA) from anthropogenic emissions, natural aerosols of sea-salt and wind blown dust and particle water. Particle water has been included in the calculated PM concentrations in order to account for the water in PM mass measured with gravimetric methods according to the CEN standard (Tsyro, 2005). Still, secondary organic aerosols (SOA) have not been incorporated in the standard model. For the most recent development and validation of SOA modelling in EMEP see Chapter 3 in this report and Simpson et al. (2007).

Annual mean concentrations of regional background PM_{10} ranged from 5 to 20 µg/m^3, whereas the corresponding range for $PM_{2.5}$ was from 2 to 15 µg/m^3 in 2005 over most of Europe. Enhanced concentration levels (above 15 µg/m^3 $PM_{2.5}$ and above 20 µg/m^3 PM_{10}) were found for the Benelux countries, central and northern Italy, south of Spain, Central Europe (the Czech Republic, Slovakia, Hungary) and southern part of the Russian Federation.

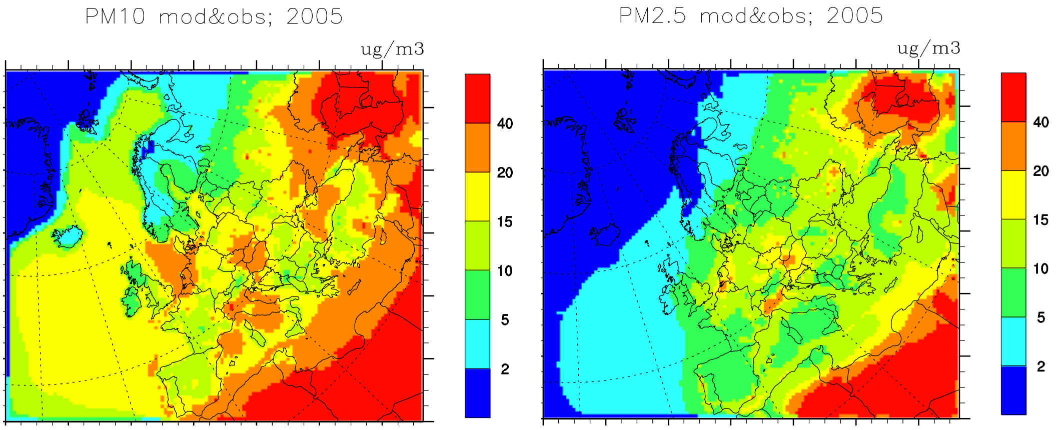


Figure 3.1: Annual mean concentrations of PM_{10} and $PM_{2.5}$ in 2005, derived from the EMEP model calculation results and EMEP observations.

3.2.2 PM composition

Annual mean concentration maps of primary PM_{10} and secondary inorganic aerosols (SIA) for 2005 are shown in Figure 3.2. In general, SIA concentrations exhibit a more smooth spatial distribution over Europe compared to primary PM. SIA dominates calculated PM_{10} and especially $PM_{2.5}$ concentrations in most areas, except in larger cities and industrial areas.

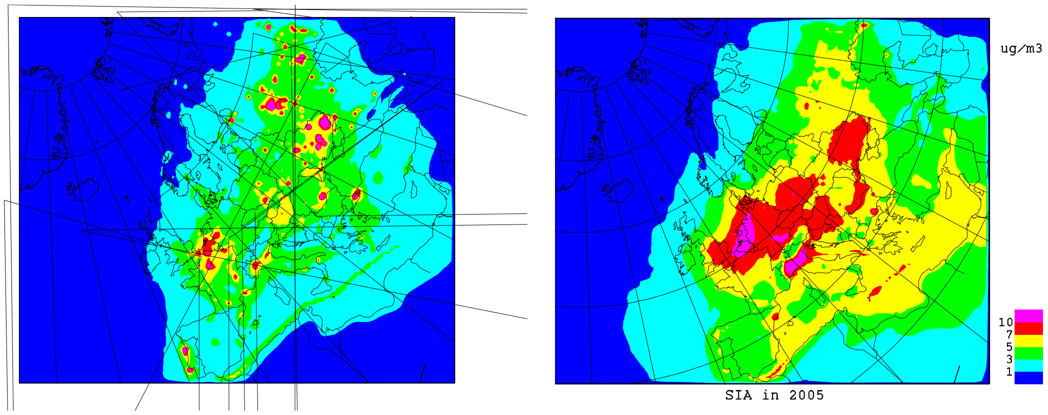


Figure 3.2: Calculated annual mean concentrations of primary PM_{10} (left) and, SIA (right) in 2005.

In most of Europe, the contribution of primary PM in PM_{10} and $PM_{2.5}$ concentrations is between 10 and 30% in 2005. SIA constitutes between 30 and

60% of PM_{10} and $PM_{2.5}$ concentrations, with the largest contributions over 50% in Central and Easter Europe and in the south of Sweden and the UK.

Annual mean concentration maps of PM constituents, i.e. SO_4^{2-}, NO_3^-, NH_4^+, EC, primary OC (POC) and natural particles (sea salt and mineral dust) are provided in Figure 3.3. Model results show that SO_4^{2-} is the main SIA component, which contribution to PM_{10} varies from 10-15% (in Western Europe) to 25%. NO_3^- contribution to PM_{10} is largest (20-35%) in Central and Western Europe, going down to 5-15% in the rest of Europe. NH_4^+ makes up about 10-15% of PM_{10} over Europe in 2005.

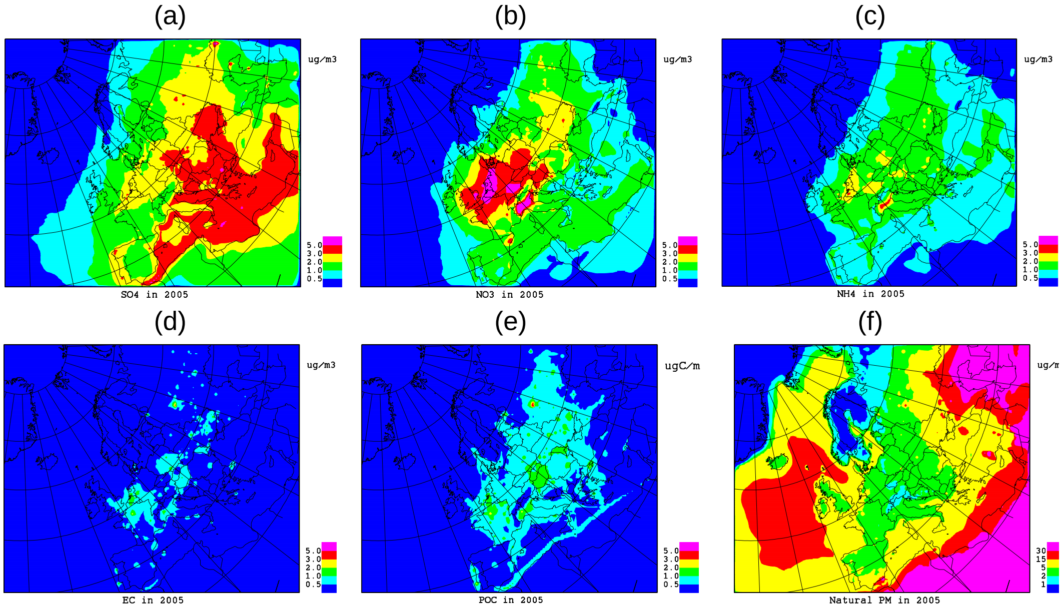


Figure 3.3: Calculated annual mean concentrations of aerosols: (a) sulphate, (b) nitrate, (c) ammonium, (d) elemental carbon, (f) primary organic carbon, (e) sea salt and mineral dust in 2005.

3.2.3 Model performance compared to observations in 2005

This chapter provides results of the evaluation of model performance for PM through comparison with observations obtained at the EMEP monitoring network in 2005. Table 3.1 summarises the comparison statistics of modelled concentrations of PM_{10}, $PM_{2.5}$, SIA and some individual aerosol components with observations at EMEP sites in 2005. The number of stations for which measurements of PM components were available in 2005 is shown in the second column (Nsite) of Table 3.1.

On average, the model calculated annual mean concentrations of PM_{10}, $PM_{2.5}$ and the considered individual PM components are within 35% of the measured values. The coefficients of spatial correlation between calculated and observed concentrations are between 0.68 and 0.98 for all of the components. In general, the model performance for 2005 is quite similar to its performance for 2004, presented last year. Scatter-plots for annual mean modelled and measured concentrations of PM_{10} and $PM_{2.5}$ (Figure 3.4) show that for 2005, the model underestimates observed PM_{10} concentrations by 28% and observed $PM_{2.5}$ concentrations by 23%. The spatial correlations between calculated and measured concentrations are 0.68 for PM_{10} and 0.82 for $PM_{2.5}$.

Table 3.1: Summary of the comparison statistics between model calculated and measured annual mean concentrations for PM_{10}, $PM_{2.5}$, SIA, SO_4^{2-}, NO_3^-, NH_4^+, and Na^+ at EMEP stations with observations in 2005.

Component	Nsite	Obs, µg/m^3	Mod, µg/m^3	Bias, %	RMSE	Corr
PM_{10}	33	16.64	12.02	-28	6.22	0.68
$PM_{2.5}$	22	11.61	8.99	-23	4.47	0.82
SIA	20	5.22	5.59	7	2.12	0.81
SO_4^{2-}	58	2.07	1.81	-13	0.71	0.74
NO_3^-	27	1.83	2.47	35	1.25	0.83
NH_4^+	24	1.03	1.27	24	0.47	0.85
Na^+	7	0.74	0.76	3	0.13	0.98

Here, Ns – the number of stations with measurements, Obs – the measured mean, Mod – the calculated mean, Bias is calculated as Σ(Mod-Obs)/Obs x 100%, RMSE – the Root mean Square Error= $[1/Ns\Sigma(\text{Mod-Obs})^2]^{1/2}$, Corr – the spatial correlation coefficient between modelled and measured concentrations.

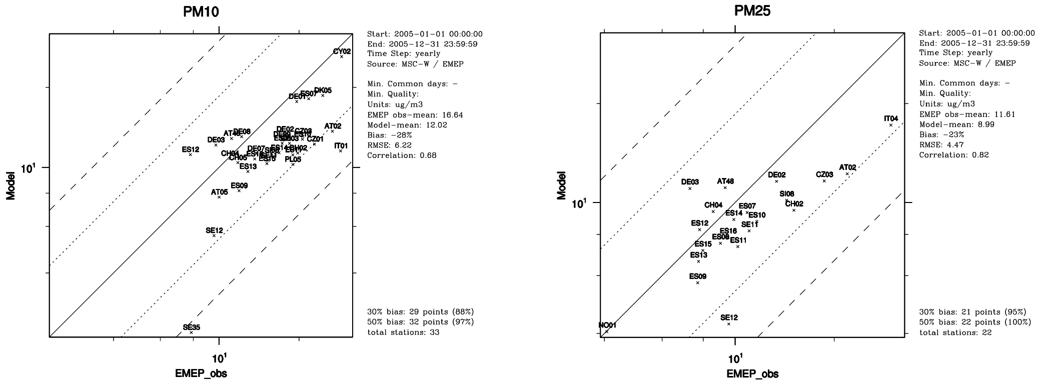


Figure 3.4: Scatter-plots for modelled versus observed annual mean concentrations of PM_{10} and $PM_{2.5}$ at EMEP stations for 2005.

Another way of depicting comparison of model results with observations is by mapping the interpolated differences between measured and calculated PM concentrations (Figure 2.4). The maps nicely visualise the geographical distribution and the magnitude of differences between the model and observations; and they also show the geographical coverage of available PM_{10} and $PM_{2.5}$ measurements in 2005.

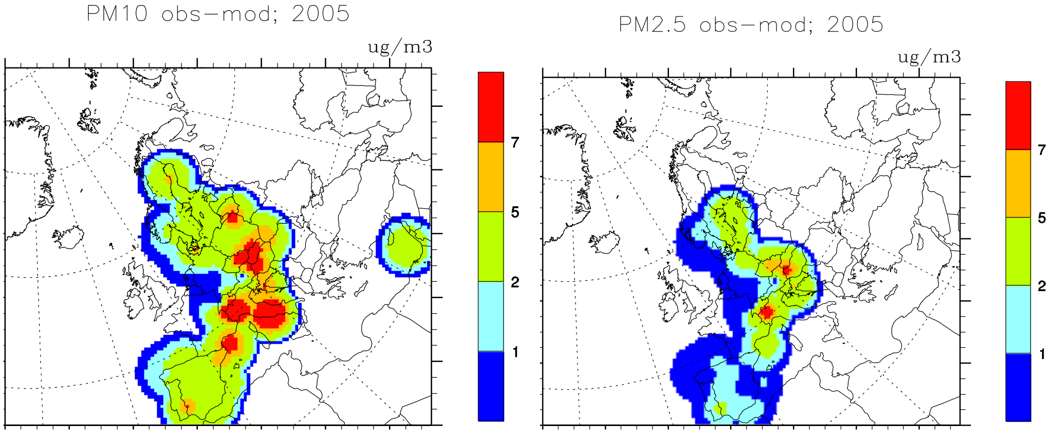


Figure 3.5: Interpolated differences between annual mean concentrations of PM_{10} and $PM_{2.5}$, observed at EMEP sites and modelled, for 2005.

Evaluation of the model performance for seasonal mean concentrations of PM_{10}, $PM_{2.5}$, SIA, SO_4^{2-}, NO_3^-, NH_4^+ and Na^+ for various seasons in 2005 is summarised in Table 3.2. Also, comparison between calculated and measured concentrations on a daily basis and at all sites has been analysed (shown in rows titled "Daily mean").

Finally, comparison statistics between calculated and observed daily PM_{10}, $PM_{2.5}$ and SIA concentrations for individual EMEP sites with PM measurements for 2005 are provided in Table 3.3. In this table, those statistical parameters, which verification improved compared to verification for 2004 (Tarrasón et al., 2006), are shadowed with grey. For quite a few sites, (e.g. CH02, IT01, NO01, Austrian, Swedish and some Spanish sites), a significant improvement in temporal correlation between calculated and measured PM is obtained for 2005 compared to 2004. At a number of stations, both the bias and the temporal correlation for either of the PM size fractions are better for 2005. Finally, at CH02, DE02, ES07, ES11, ES14, SE11 and SE12, both biases and correlations are better for 2005 compared to 2004 for both PM_{10} and $PM_{2.5}$. At least partly, this improvement in model results might be due to new spatial distributions of primary PM and gaseous precursors emissions, used in model calculations for 2005. Among others, recently reported gridded emissions from Austria, Germany, Italy, Norway, Sweden and Switzerland were included in the emissions spatial distribution for 2005.

Table 3.2: Annual and seasonal comparison statistics between EMEP model calculated and EMEP measured concentrations of PM_{10}, $PM_{2.5}$, *SIA,* SO_4^{2-}, NO_3^-, NH_4^+ *and* Na^+ *for 2005.*

Period	N sites	Obs (µg/m^3)	Mod (µg/m^3)	Bias	RMSE	Corr
PM_{10}						
Daily mean	33	16.34	11.93	-27	12.39	0.51
JanFeb	33	16.20	12.95	-20	13.99	0.53
spring	33	17.44	13.22	-24	13.53	0.56
summer	33	16.64	9.07	-45	11.27	0.55
autumn	33	16.44	12.86	-22	11.62	0.49
PM_{25}						
Daily mean	22	11.54	9.00	-22	9.93	0.53
JanFeb	22	13.23	10.10	-24	14.48	0.47
spring	22	12.20	9.87	-19	8.92	0.65
summer	22	10.73	6.67	-38	6.74	0.49
autumn	22	11.16	9.97	-11	9.61	0.57
SIA						
Daily mean	20	5.24	5.70	9	5.41	0.63
JanFeb	19	6.08	7.43	22	7.18	0.55
spring	19	5.83	6.10	5	5.53	0.66
summer	20	4.08	3.37	-17	2.99	0.65
autumn	20	5.53	6.39	16	5.64	0.65
SO_4						
Daily mean	62	2.09	1.82	-13	1.85	0.53
JanFeb	60	2.25	2.11	-6	2.55	0.50
spring	60	2.22	1.74	-22	1.76	0.55
summer	62	1.96	1.80	-8	1.40	0.56
autumn	62	2.12	1.76	-17	1.82	0.58
NO_3						
Daily mean	27	1.86	2.51	35	3.08	0.64
JanFeb	26	2.13	3.32	56	3.87	0.56
spring	26	2.28	2.82	24	3.19	0.64
summer	27	1.15	0.88	-24	1.35	0.58
autumn	27	1.99	3.12	57	3.42	0.67
NH_4						
Daily mean	24	1.04	1.29	24	1.17	0.68
JanFeb	22	1.10	1.55	41	1.46	0.67
spring	22	1.19	1.42	19	1.22	0.70
summer	24	0.74	0.79	7	0.62	0.68
autumn	24	1.18	1.49	27	1.30	0.67
Na						
Daily mean	7	0.71	0.72	2	1.22	0.59
JanFeb	6	1.27	0.98	-23	2.85	0.60
spring	6	0.48	0.58	20	0.54	0.70
summer	7	0.60	0.56	-6	0.48	0.78
autumn	7	0.72	0.79	9	0.65	0.75

Here, Ns – the number of stations, Obs – the measured mean, Mod – the calculated mean, Bias is calculated as Σ(Mod-Obs)/Obs x 100%, RMSE – the Root mean Square Error= $[1/Ns\Sigma(Mod-Obs)^2]^{1/2}$, Corr – the tempo-spatial correlation coefficient between modelled and measured daily concentrations and spatial correlation for seasonal mean concentrations.

Table 3.3: Comparison of modelled and measured concentrations of PM$_{10}$, PM$_{2.5}$ and SIA at the individual EMEP stations for 2005. Highlighted in bold are new data used for verification and shaded grey are improved statistical parameters compared to 2004.

	PM$_{10}$				**PM$_{2.5}$**				**SIA**		
Site	Obs	Mod	Bias	R	Obs	Mod	Bias	R	Obs	Mod	R
AT02	26.7	13.7	-49	0.52	21.9	12.2	-44	0.53	6.2	7.9	0.47
AT05	10.0	7.7	-23	0.47	**9.3**	**11.1**	**19**	**0.53**			
AT48	11.2	12.9	15	0.51							
CH02	19.8	11.4	-43	0.61	15.1	9.5	-37	0.62			
CH03	18.4	12.3	-33	0.56							
CH04	11.0	10.8	-2	*0.36*	8.6	9.4	10	0.49			
CH05	11.8	10.4	-11	0.38							
CY02	29.0	26.2	*-10*	*0.23*							
CZ01	**22.9**	**12.2**	**-47**	**0.46**							
CZ03	**20.7**	**13.1**	**-37**	**0.69**	**18.7**	**11.6**	**-38**	**0.69**			
DE01	19.6	17.7	-10	0.68					7.5	8.2	0.71
DE02	17.7	13.3	-25	0.62	13.4	11.6	-13	0.64	6.3	7.4	0.51
DE03	9.8	12.2	*25*	*0.22*	7.3	11.1	*52*	*0.26*	4.0	7.5	0.21
DE07	13.8	11.3	-18	0.62					5.7	6.9	0.64
DE08	12.2	13.1	7	0.42							
DE09	17.2	12.7	-26	0.63					7.4	7.2	0.7
DK05	24.6	18.7	*-24*	*0.58*							
ES07	21.8	18.2	-17	0.53	10.9	9.4	-14	0.47			
ES08	17.3	12.4	-29	0.63	9.0	7.5	-17	0.64			
ES09	11.9	8.2	-31	0.52	7.7	5.7	*-26*	*0.45*			
ES10	20.6	12.8	-38	0.54	11.7	8.8	-25	0.63			
ES11	19.0	11.2	-41	0.43	10.2	7.4	-28	0.55			
ES12	7.8	11.2	43	0.58	7.8	8.3	6	0.58			
ES13	12.9	9.7	-25	*0.48*	7.8	6.6	-14	0.5			
ES14	16.9	11.4	-33	0.56	9.9	8.9	-10	0.52			
ES15	15.2	10.4	*-32*	*0.39*	8.0	7.2	-10	0.38			
ES16	13.6	10.8	*-21*	*0.51*	9.5	7.9	-18	0.62			
IT01	28.7	11.5	*-60*	0.48							
IT04	(*)				]29.8	17.2	-42	0.34			
NO01	6.78	5.23	-23	0.73	4.1	4.1	-1	0.78			
PL05	**18.9**	**10.3**	**-46**	**0.58**							
SE11	15.3	10.6	-31	0.6	11.0	8.2	-26	0.65			
SE12	9.6	5.5	-42	0.66	9.6	4.3	-55	0.72			
SE35	7.9	2.4	-70	0.57							
SI08	**15.8**	**11.1**	**-30**	**0.46**	**14.4**	**10.2**	**-29**	**0.51**			

3.3 Difference analysis of modelled PM for 2004-2006

Changes in pollutant concentrations are driven by emission changes and by meteorological variability. For the year 2005, the model has been run twice, using officially reported emissions in one run and reviewed emission data in the second run. Model calculations have also been performed for meteorological conditions of 2006, using reviewed 2005 emissions. Here, we compare PM concentrations calculated for 2005 using two emission datasets, which are officially reported and reviewed, and the latter also are compared with PM calculated for meteorological conditions of 2006 and PM calculated for 2004 (presented in the last year report (Tarrasón et al., 2006)). The differences in calculated PM concentrations are explained in terms of the changes in both emissions and meteorology.

3.3.1 Officially reported emissions vs. emissions with replacement for 2005

As documented in Vestreng et al. (2007), two emission inventories for model runs have been prepared this year: 1. One based on officially reported data, complemented with expert estimates for not reporting countries, and 2. One based on only the reported data that passed review, complemented with expert estimates in the cases of incomplete or inconsistent reported data or missing emissions. In general, replacements of unreliable reported data lead to more than 30% higher emission totals. The main reason for that is that emissions of primary PM or gaseous precursors were not reported for all sectors in a number of countries. For some countries, emissions were replaced with larger values in some sectors (Vestreng et al., 2007). Subsequently, two model computations have been performed using these emission inventories for the year 2005. All model results presented so far in this report are based on the calculations with the reviewed emission data set. Here, we outline the main differences in model results using the officially reported and reviewed emissions.

Practically all emission replacements were for Eastern European countries and the Russian Federation. As a consequence of the replacements, large differences in calculated PM_{10} and $PM_{2.5}$ concentrations are found for the Russian Federation, Ukraine, Belarus, Moldova, Romania and Serbia (example for PM_{10} is given in Figure 3.6a, and the picture is quite similar for $PM_{2.5}$). In these countries, PM_{10} and $PM_{2.5}$ calculated with the reviewed emissions are between 5 and 20% higher than those with officially reported emissions. Applying officially reported emissions, we calculate 5-20% lower SIA concentrations and from 20 to more than 60% lower primary PM concentrations compared to results with reviewed emissions for these regions (Figure 3.6b-d).

The majority of stations with PM measurements are located outside the areas where calculated concentrations are efficiently affected by emission replacements. Therefore, we could not see any significant difference when comparing modelled PM calculated either with officially submitted emissions or with expert revised emissions with observations. In other words, verification of model results with currently available observations does not allow us drawing any firm conclusion concerning which of the emission dataset is more adequate.

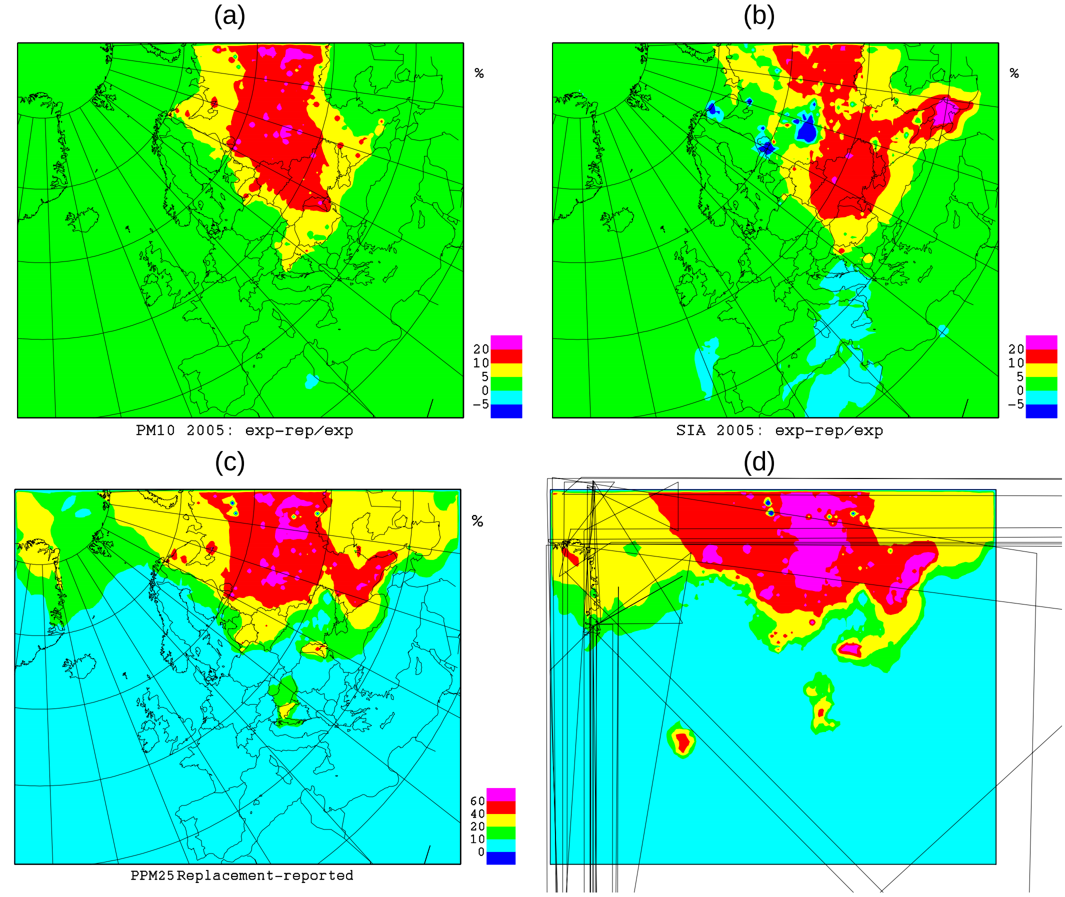


Figure 3.6: Relative differences between annual mean concentrations of PM_{10}, SIA and primary $PM_{2.5}$ and coarse PM, calculated using the reviewed and officially reported emissions for 2005.

3.3.2 2005 vs. 2004 PM: Emissions effect

PM_{10} and $PM_{2.5}$ concentrations, calculated with the model for 2005, are 5 to 20% higher compared to 2004 in most of Europe, with the exception of only a few regions (e.g. in Sweden, northern Spain and Belgium) (Figure 3.7a,b). Considering separately primary and secondary PM, reduction of primary $PM_{2.5}$ and PM_{10} emissions resulted in lower PPM concentrations in 2005 than in 2004 in a number of countries (i.e. Belgium, Check Republic, Germany, Spain, Finland, Sweden and Baltic countries) (Figure 3.7c,d). On the other hand, PPM concentrations in Denmark are higher in 2005 because Danish emissions of both $PM_{2.5}$ and coarse PM increased in 2005 compared to 2004. In Hungary and Slovakia, $PM_{2.5}$ emissions went down, whereas coarse PM emissions went up from 2004 to 2005. This is reflected in lower primary $PM_{2.5}$ concentrations and higher primary coarse PM concentrations calculated for 2005.

For most of Europe, calculated SIA concentrations are 5-25% higher in 2005 than in 2004 (Figure 3.7e). Formed in the atmosphere from gaseous precursors, changes in the SIA concentrations can be related to changes in the emissions of either SO_x, NO_x or NH_3, or all of them. Only for some areas, the increase in SIA concentrations can be associated with reported increase in the emissions of gaseous precursors in 2005 (e.g. increase of SO_x and NH_3 emissions in Belarus and of SO_x and NO_x emissions in the Kaliningrad region of Russia). In several countries (e.g. Denmark, Finland and Italy), increase in the emissions of one gaseous precursor was offset by emissions decrease of the other(s).

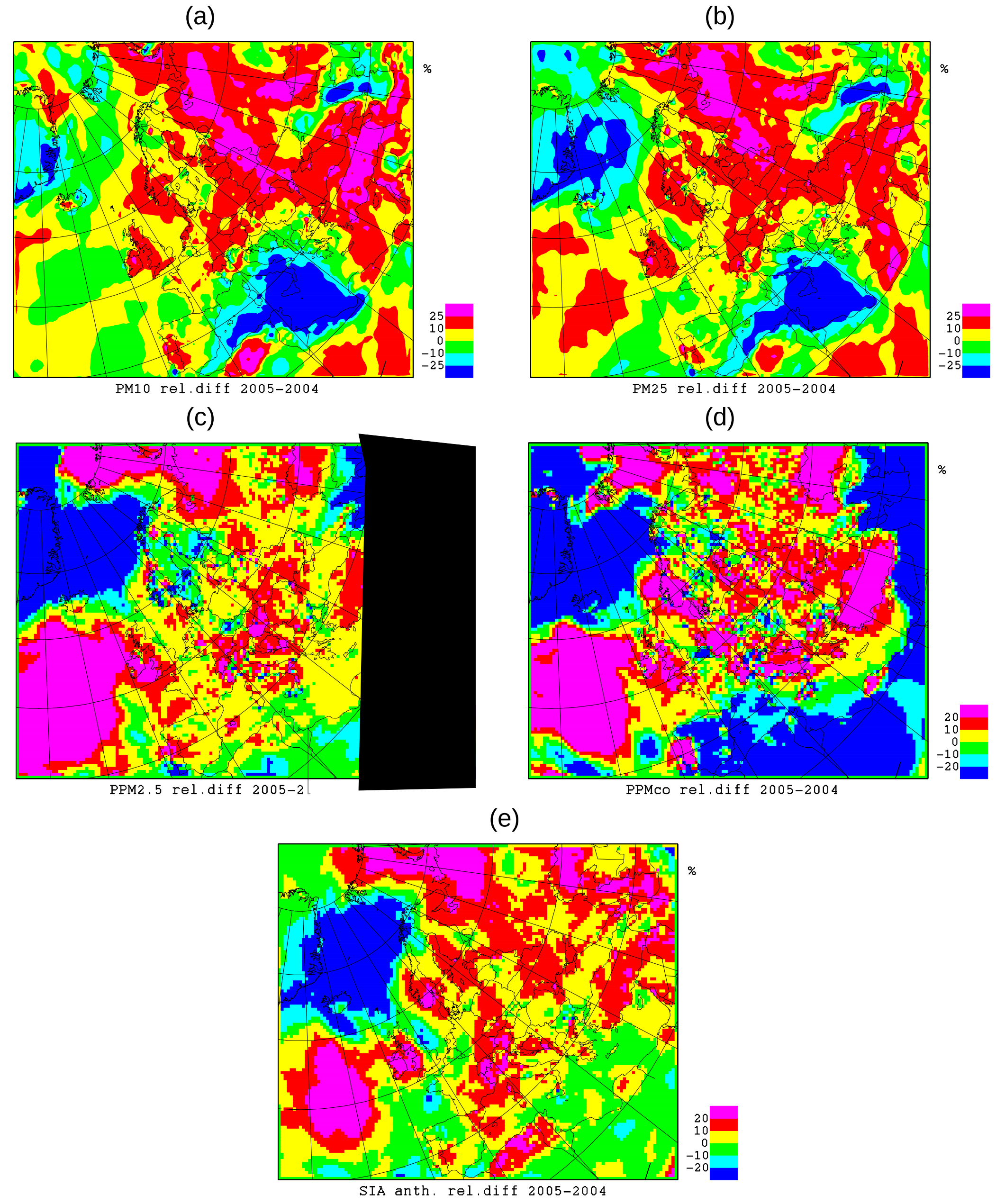


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Figure 3.7: Relative differences between calculated annual mean concentrations of PM_{10}, $PM_{2.5}$, primary $PM_{2.5}$ and coarse PM, and SIA in 2005 and 2004.

For the countries not mentioned above, emissions of primary PM and SIA gaseous precursors changed only slightly in 2005 compared to 2004. These changes in the emissions alone cannot explain why the general PM level is higher in 2005 than in 2004. It should be noted that not only national total emissions, but also their spatial distributions affect concentration fields of air pollutants. Spatial distribution of all emissions changed considerably in 2005 compared to 2004 as new reported and reviewed gridded and Large Point Sources (LPS) data were included this year (Vestreng et al., 2007).

3.3.3 2005 vs. 2004 PM: Meteorology effect

Meteorological conditions affect PM concentrations in the atmosphere by determining formation, dispersion and removal of atmospheric pollutants. Thus, year-to-year variability in PM concentration fields is partly due to the inter-annual meteorological variability, detailed analyses of which can be found in Tarrasón et al. (2007).

Compared to 2004, the year 2005 was on average characterised by warm high pressure system over northern Russia, which caused less efficient dispersion and dry deposition of pollutants in this area. At the same time, 2005 was in general a drier year than 2004 over most of Europe (except north-western Scandinavia and the south-east of Europe) (Figure 3.8, left). Since wet scavenging is the main removal process for atmospheric aerosols, less precipitation will result in more PM remaining in the air. Thus, higher overall levels of PM_{10} and $PM_{2.5}$ concentrations, which could not be due to solely the emissions changes, can be explained in terms of meteorological conditions, i.e. by suppression of pollutants dispersion in the stable atmosphere over northern parts of Russia and by smaller wet scavenging due to less precipitation over most of Europe in 2005 compared to 2004.

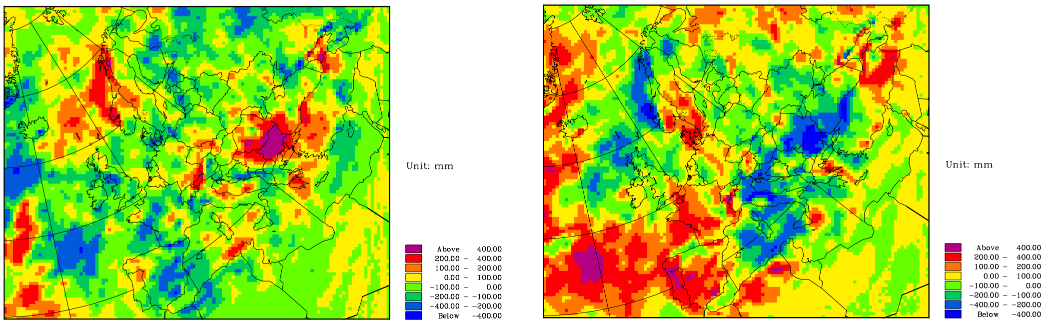


Figure 3.8: Differences in precipitation amount between 2005 and 2004 (left) and between 2006 and 2005 (right).

3.3.4 2005 vs. 2006: Meteorology effect

Model calculations for the meteorological conditions of 2006 have been performed with the same emissions as for the meteorological conditions of 2005. Therefore, the differences in model results are only due to the variability in meteorology in 2005 and 2006. Annual mean maps show that contrary to 2005, low pressure system was centred over Russia in 2006, accompanied with lower temperatures and larger precipitation amounts (Figure 3.8, right). Another low pressure was centred over the North Atlantic and covered much of Spain and France. This low was a cause of more precipitation in 2006 then in 2005 in these areas, which is the most important removal mechanism of PM from the air. On the other hand, high pressure, and thus more stable conditions over southern and Eastern Europe, resulted in considerably less precipitation in 2006 than in 2005.

Thus, in these regions, we expect slower wet and dry depositions and less efficient dispersion of PM.

These differences in the meteorological conditions explains 10-30% lower annual mean concentrations of $PM_{2.5}$ and PM_{10} (and individually primary PM and SIA) over Russia and 5-15% higher concentrations in the countries of southern and eastern Europe in 2006 compared to 2005. It is interesting to note that the pattern of differences of the precipitation amounts is particularly reflected in the concentrations differences of coarse PM in 2005 and 2006. This is because these particles are relatively short lived and therefore the local effect of wet scavenging of coarse PM is more important than their long-range transport. More precipitation in the northern Alps can explain the 5 to 25% lower calculated PM concentrations for 2006 compared to 2005. Finally, higher PM concentrations over Spain and Italy are also due to the higher concentrations of wind blown dust in 2006 than in 2005, as predicted by the model.

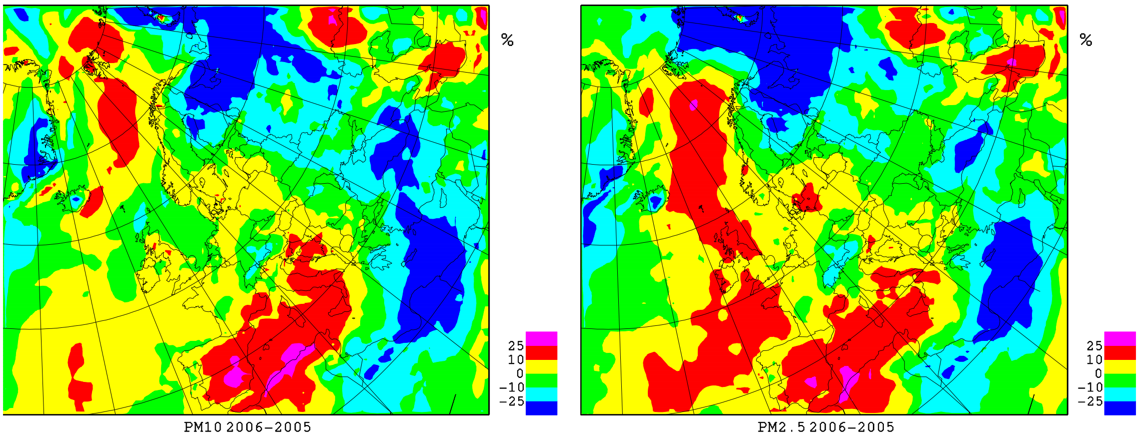


Figure 3.9: Relative differences between calculated annual mean concentrations of PM_{10} and $PM_{2.5}$ in 2006 and 2005.

3.4 Exceedances of AQG by long-range transported PM in 2005

In this section, we present model calculated exceedances of the EU limited values for PM_{10} and WHO Air Quality Guidelines (AQGs) for PM_{10} and for $PM_{2.5}$ for European regional background PM in 2005.

According to the Council Directive 1999/30/EC, annual mean PM_{10} concentrations should not exceed a limit value of 40 $\mu g/m^3$ and that daily PM_{10} concentrations should not exceed 50 $\mu g/m^3$ more than 35 times a calendar year.

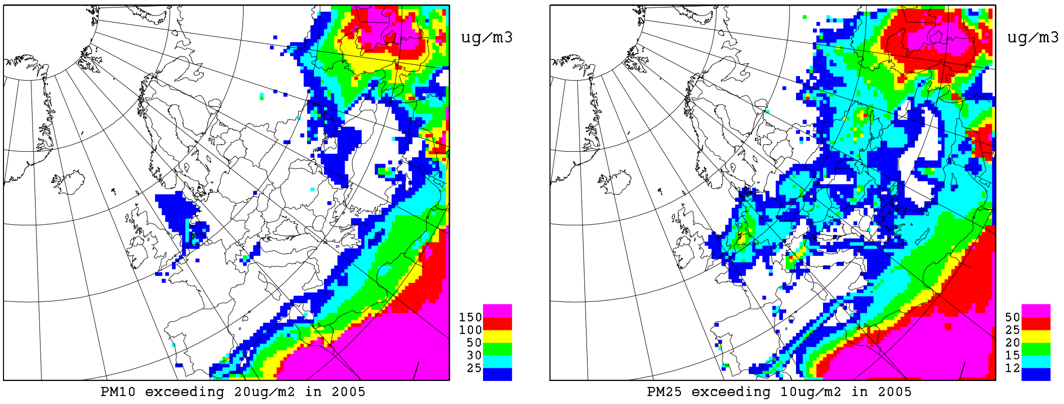
The WHO AQGs (WHO, 2005) are:

for PM_{10}: 20 $\mu g/m^3$ annual mean,
50 $\mu g/m^3$ 24-hour mean (99th percentile or 3 days per year)
for $PM_{2.5}$: 10 $\mu g/m^3$ annual mean,
25 $\mu g/m^3$ 24-hour mean (99th percentile or 3 days per year).

3.4.1 Annual mean exceedances

Model results show that in 2005, the regional background PM_{10} concentrations were below the EU annual limit value of 40 µg/m^3 in all of Europe, with the exception of the outmost southern areas of the model domain. The maps in Figure 3.10 show the areas where calculated regional PM_{10} and $PM_{2.5}$ concentrations exceeded the WHO annual mean guideline values of 20 µg/m^3 and 10 µg/m^3 respectively in 2005. Compared to 2004 (Tarrasón et al., 2006), the total area with PM_{10} and $PM_{2.5}$ exceedances of annual AQGs was somewhat larger in 2005, because of the generally higher levels of PM in 2005 (Section 3.3). In 2005, the annual mean PM_{10} exceeded 20 µg/m^3 in the Benelux countries and in the Po Valley in northern Italy, which was mainly due to anthropogenic emissions, whereas in the south of Spain and the Russian Federation, eastern parts of Ukraine, Kazakhstan and in the Caucasus, PM exceedances were also due to a large influence of windblown dust.

The calculated annual mean background concentrations of $PM_{2.5}$ exceeding 10 µg/m^3 were found in most of Central and Eastern Europe, the Po Valley, the south of the Russian Federation and the EECCA (Eastern Europe, Caucasus, Central Asia) countries. In most of these areas, with the exception of the most southern ones, the exceedances were found already for anthropogenic $PM_{2.5}$. Also, $PM_{2.5}$ exceeded 10 µg/m^3 along the main ship routs in the Mediterranean Sea. In the southern regions of the modelled domain, windblown dust contributed heavily to the $PM_{2.5}$ exceedances in 2005.



PM10 exceeding 20ug/m2 in 2005

PM25 exceeding 10ug/m2 in 2005

Figure 3.10: Calculated exceedances of the WHO AQGs for annual mean concentrations by long range transported PM_{10} (left) and $PM_{2.5}$ (right) in 2005 (only grid cells with exceedances are shown in colours).

3.4.2 Daily exceedances

The maps in Figure 3.11 show the number of days when exceedances of daily EU limits and WHO AQGs occurred for model calculated regional background PM_{10} and $PM_{2.5}$ in 2005. The upper and lower maps in Figure 3.11 show situations for the total and anthropogenic PM respectively.

In 2005, the EU daily limit value of PM_{10} of 50 µg/m^3 was exceeded by regional background PM_{10} more than 35 days in Milan region, Moscow region, in eastern Ukraine and southern parts of the Russian Federation, in Kazakhstan and Caucasus area (Figure 3.11 upper panel). As seen in Figure 3.11 (lower panel), only exceedances in the cities of Milan and Moscow were due to anthropogenic emissions.

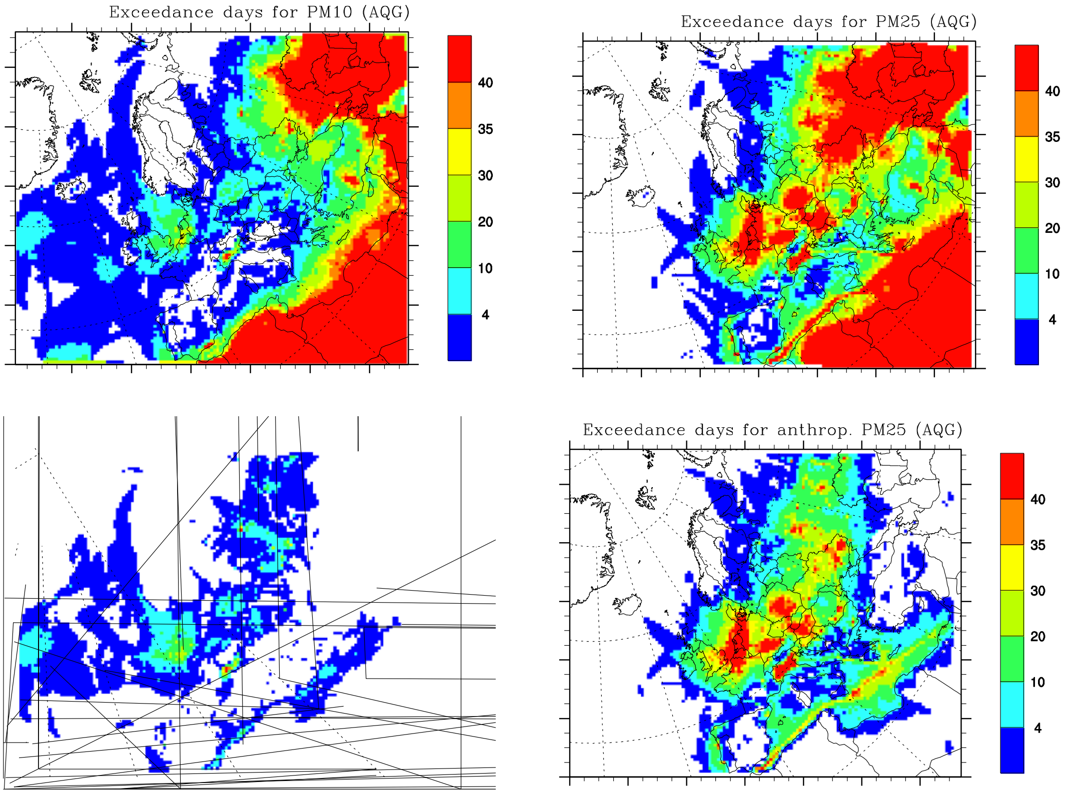


Figure 3.11: Calculated number of days with transboundary $PM_{2.5}$ concentrations exceeding the WHO updated 24-hour guideline value of 25 µg/m^3 in 2004.

According to the WHO AQGs, daily concentrations of 50 µg/m^3 for PM_{10} and 25 µg/m^3 for $PM_{2.5}$ should not be exceeded more than 3 days in a calendar year. In 2005, the daily AQGs for PM_{10} were exceeded in 4 and more days in Benelux, the Po Valley, in parts of Germany and the UK, in the south of Spain, in Eastern Europe, the Russian Federation and EECCA countries. Calculated daily mean $PM_{2.5}$ exceeded AQGs for 4 and more days almost all over Europe, except for Scandinavia, north of the Russian Federation and central Spain. Model calculations suggest that the emissions from anthropogenic sources were responsible to a large degree for the AQGs exceedances for PM_{10} and especially for $PM_{2.5}$ in the most of Central and Eastern Europe (Figure 3.11 lower panels). Whereas erosion dust episodes are expected to impair the air quality in southern regions.

4. Modelling carbonaceous aerosol over Europe. Recent results and status

By David Simpson

4.1 Introduction

This chapter briefly updates the discussion of modelling and measurement results associated with the EMEP EC/OC and EU CARBOSOL campaigns given in EMEP Report 4/2006. In particular, the CARBOSOL project (Present and retrospective state of organic versus inorganic aerosol over Europe: implications for climate) has now had a large number of papers accepted for a special issue of the Journal of Geophysical Research. These papers, already available electronically (through www.agu.org/pubs) for those with personal or library access, contribute important new information on the sources of particulate carbonaceous matter (PCM) in southern and central Europe. This information is significant, as PCM is believed to contribute to around 30% of PM levels at rural and natural background sites in Europe (Putaud et al., 2004), but recent reviews have highlighted its complexity in terms of known composition and formation mechanisms (Fuzzi et al., 2006; Kanakidou et al., 2005).

4.2 Measurements

The EMEP EC/OC campaign (2002-2003) measured elemental carbon (EC), organic carbon (OC), total carbon (TC=EC+OC) and particulate matter (PM) at 15 sites, and many of these sites have complementary measurements of other species. In addition, some of the samples from the EMEP campaign have been analysed for levoglucosan. Details of the EMEP EC/OC campaign can be found in Yttri et al. (2007a).

The EU CARBOSOL Project combined weekly measurements of EC, OC, inorganic ions, elemental composition, levoglucosan and radioactive tracers across a network of 6 sites in southern-central Europe. Analysis of ice and snow cores also gave information on historical changes in some organic species (Legrand et al., 2007). Further details of the CARBOSOL campaign can be found in Legrand and Puxbaum (2007), Pio et al. (2007), and references cited therein.

4.3 Emissions

The CARBOSOL work made use of a new inventory for annual national BC and OC emissions developed by Kupiainen and Klimont (2007). An important advantage of this inventory is that it includes details for a very large number of sources. In particular, we were able to extract the emissions from wood-burning sources separately, which allowed a verification against the levoglucosan measurements performed within EMEP and the CARBOSOL project. Figure 4.1 illustrates the emissions of EC and OM, highlighting the very significant contribution of wood-burning to annual emissions.

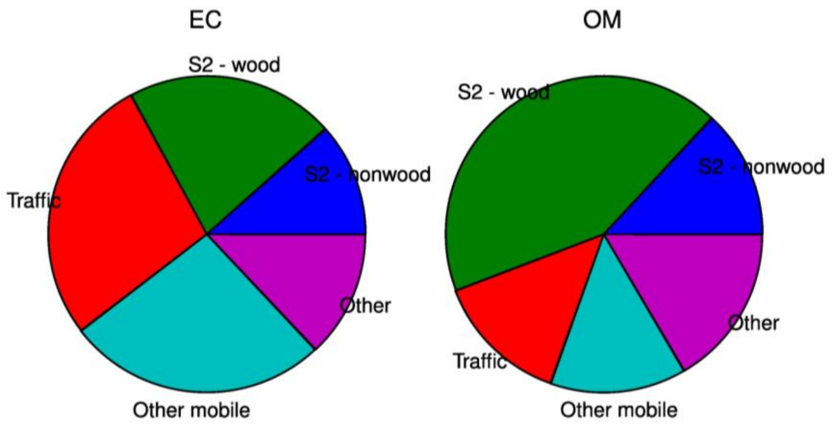


Figure 4.1: Emissions of sub-micron elemental carbon and organic matter in Europe, as given by Kupiainen and Klimont (2007).

4.4 CARBOSOL/EMEP Modelling Papers

Details of the modelling work carried out in CARBOSOL and for the EMEP EC/OC campaign can be found in Simpson et al. (2007) for PCM generally, and in Tsyro et al. (2007) and Fagerli et al. (2007) for EC.

The work of Fagerli et al. (2007) was mainly concerned with simulations of ice-core data from the French Alps. Modelled concentrations of sulphate and ammonium, based upon historical emission estimates, showed rather satisfactory comparison with summertime ice-core data for 1920-2003. This work was extended with EC, although recognising that the estimated EC emissions were much more uncertain than for sulphur. Indeed, patterns of emission changes were found to be very sensitive to assumptions concerning the time-variation of road-traffic emission factors (EFs, e.g. g EC/kg fuel used). An emission estimate which assumed that EFs were greater for older vehicles showed much better agreement with the ice-core data than an estimate assuming constant EFs.

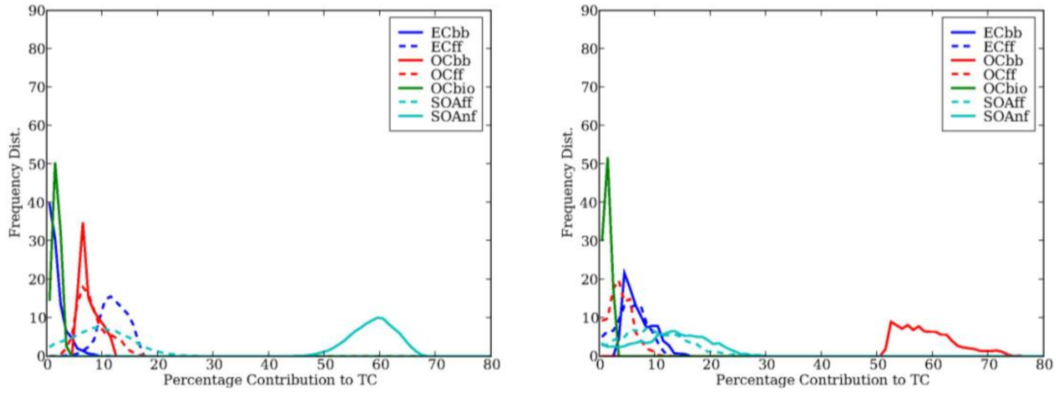
Simpson et al. (2007) presented detailed comparisons against data for TC, EC, levoglucosan and other compounds. Two versions of the EMEP SOA model were used. The Kam-2 version uses the gas/particle scheme as developed by Andersson-Sköld and Simpson (2001). An alternative version, Kam-2X, was also used, with the same basic scheme, but with lower vapour pressures for some compounds. This paper illustrates for example the dominant role of BSOA in determining PCM levels across much of Europe, and especially around the Nordic countries. This work confirms that the EMEP model does a good job of reproducing concentrations of pollutants with well-know emissions and chemistry, for example of sulphate. Further, in Northern Europe the model predicts TC levels which are in line with measured values, especially with the Kam-2X scheme. These predictions are dominated by modelled BSOA. However, in Southern Europe, including the CARBOSOL sites, both versions of the model significantly under-predict TC levels, especially in wintertime. This is further discussed in Section 3.5.

Tsyro et al. (2007) modelled EC across Europe, with particular focus on the sensitivity to assumptions concerning scavenging, and on the importance of forest fire emissions. They found that the model underestimated EC by 19% for the EMEP stations on average, although with large spatial variations. The results indicated large potential uncertainty in primary emission estimates, especially for residential emissions, but also likely from mobile source emissions. Wildfire emissions were found to contribute just 1-10% of total EC in most areas of Europe, although up to 20-30% in some areas. The need for better (time-resolved) estimates of such wildfire emissions was emphasised. Finally, EC wet scavenging ratios were found to have an appreciable effect on calculated EC, but they are still poorly known. Finally, this work recommended that the extension of the EC monitoring network was essential for a more accurate representation of the expected EC gradient and temporal variation across Europe.

4.5 Comparison with Source Apportionment Data

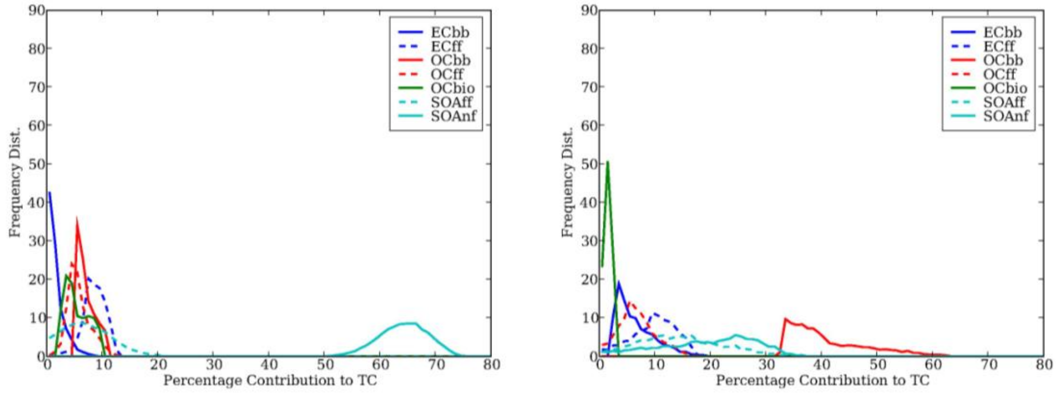
One of the main features of the CARBOSOL project was the sampling of many tracer species. Levoglucosan was used as a tracer of organic carbon from biomass-burning (OCbb), BC as a tracer (albeit crude) of primary OC emissions from fossil-fuel. Measurements of cellulose were used to determine the contribution of primary biogenic sources. Pooled filter-samples from summer and winter periods were also analysed for ^{14}C, in order to determine the percentage of modern carbon versus C from fossil-fuel sources. Gelencsér et al. (2007) combined all of these sources of information in an effort to calculate the relative contributions of the primary sources of C, and of the secondary sources, denoted SOAnf (SOA from non-fossil fuel sources, which included condensation of SVOC from biomass-burning as well as BSOA as used in the EMEP model) and SOAff (SOA from fossil-fuel sources, equivalent to ASOA as used in the EMEP model). Each step of this analysis, e.g. to estimate OCbb from levoglucosan, is of course very uncertain, so Gelencsér et al. (2007) defined both a central best-estimate value for each factor with a plausible range of uncertainty. Latin Hypercube Sampling (LHS), a form of Monte-Carlo analysis, was used to explore many possible combinations of these uncertain factors. In most cases, the results turned out to be rather robust, e.g. that SOAnf dominated TC levels at most sites in summertime, and that OCbb was often a major contributor in wintertime.

Figure 4.2 (from Gelencser et al., 2007) gives the results of these uncertainty calculations for two sites. In these plots, each curve represents the probability distribution of that component's contribution to the total carbon (TC). As an example, we discuss the results of the uncertainty calculations for Aveiro (AVE). There the likely contribution of SOAnf (non-fossil) to TC is seen to be very large in summertime (Figure 4.2a), with the calculations suggesting a contribution of between 50-70%. Other sources of C are clearly smaller but non-negligable. In wintertime (Figure 4.2b), the main contribution is clearly from biomass-burning, with OCbb likely accounting for between 50-70% of TC. Rather similar features were found for all the CARBOSOL sites, with high non-fossil (likely SOA) contributions in summer and high biomass-burning (likely domestic wood-comnbustion) contributions in winter. Further discussion can be found in Gelencser et al. (2007).



(a) AVE, Summer

(b) AVE, Winter



(c) KPZ, Summer

(d) KPZ, Winter

Figure 4.2: Probability distributions of source-contributions to TC for low-level sites Aveiro (Portugal), and for K-Puszta, Hungary, for summer and winter respectively. From Gelencser et al. (2007).

It is important to note that the main conclusions to be derived from Figure 4.2 are quite robust. For example, SOAnf (non-fossil) is clearly the biggest contributor to TC in summertime, whether we look at the central (most likely) estimates or the tails of the various curves (which represent possible but unlikely results of the LHS analysis). Given the wide range of uncertainties used in generating these figures, these results demonstrate that in general we can clearly identify the main contributors in the different seasons: the answer does not depend very much on our assumptions.

These results allow for the first time an evaluation of the components of the model's TC prediction, comparing primary and secondary, fossil-fuel and biogenically derived SOA for example. This type of comparison, illustrated in Table 4.1, is discussed in Simpson et al. (2007), and suggests that the model under-predicts both the biomass burning and SOA components of the measured TC at these sites.

Table 4.1: Comparison of Modelled Components of Summertime TC at K-Puszta, Hungary, with Observation-derived components (5^{th}-95^{th} percentile range) from CARBOSOL data (c.f. Figure 4.2). See Gelencsér et al. (2007) and Simpson et al. (2007) for details. Units: $\mu g\ C/m^3$.

	Obs.-Derived (5–95th %ile)	EMEP Model (Kam2 - Kam2X)
TC	5.2	1.6 – 2.7
WOOD	0.3 – 0.5	0.05
EC	0.4 – 0.7	0.4
FFUEL	0.2 – 0.5	0.4
BSOA	2.9 – 3.6	0.2 - 1.4
ASOA	0.05 – 0.7	0.03 - 0.04

One can ask the question: is the EMEP model at fault – is the SOA scheme just badly formulated? In fact, the underprediction of SOA discussed above seems to be in fact typical of, or if anything somewhat better than, all models today. Volkamer et al. (2006) presented a nice summary plot of recent studies, ranging from close-to-source studies in Mexico (own study) to free-tropospheric values from ACE-Asia (Heald et al., 2005). This comparison showed that the ratio of observed versus modelled SOA varied between 5-100, on timescales ranging from some minutes to some days. The discrepancy seemed to increase with photochemical age, although other factors may also play a role (e.g. temperature). Such poor results should not be surprising given that the basic formation processes of SOA formation are still poorly understood, and we still do not know which pathways are most important in atmospheric conditions (e.g. Fuzzi et al., 2006; Robinson et al., 2007; Volkamer et al., 2006).

4.6 Conclusions

A number of conclusions from the CARBOSOL and EMEP comparisons are given in detail in Simpson et al. (2007) and Tsyro et al. (2007). The most notable feature of the CARBOSOL comparisons was the strong under-prediction of (1) the biomass-burning components, and (2) the SOA components, especially for SOAff. Unfortunately all the CARBOSOL sites are situated in south-central Europe. However, we can conclude from the analysis of levoglucosan, BC and TC from the EMEP sites that different conclusions would be drawn in other parts of Europe. In particular, there is no evidence of a substantial under-prediction of wood-burning emissions at the Nordic sites. Further, the EMEP model tends to over-predict TC at these sites, suggesting that this scheme may generate too much rather than too little SOA.

The possible reasons for problems in modelling EC, SOA, biomass-burning and other emissions are discussed in detail in Simpson et al (2007) and Tsyro et al. (2007). Many problems, including the basic understanding of SOA formation, may require years of high-level research. However, Simpson et al. (2007) and Tsyro et al. (2007) identified a number of steps which could help to reduce at least some of the uncertainties in the near to medium term:

- Evaluation of the emissions of BVOC. These emissions are crucial to any attempt to model BSOA, but still very uncertain. Given the fact that emissions validation is possible with today's measurement methods, this step alone would significantly improve the most important input for PCM modelling
- Evaluation of the emissions of PM, including EC and OC fractions, from anthropogenic sources. Mobile sources as well as residential combustion emissions are still highly uncertain, but very amenable to near-source validation experiments.
- Improvement in wildfire emission estimates and treatment in the EMEP models.
- Evaluation of the emissions of heavy VOC from anthropogenic sources. A fraction of the non-primary TC classified as SOAnf or SOAff by Gelencsér et al. (2007) may consist of high-molecular weight compounds which are still volatile at the point and temperature of emission, but which quickly condense to the particle phase. These VOC may fall outside the scope of both VOC and PM inventories, but contribute to measured TC. Robinson et al. (2007) have highlighted similar problems.
- Further use of tracers, such as C14, levoglucosan and markers of primary biological OC (e.g. cellulose, sugars). Such tracers offer much greater possibilities to understand the sources of observed OC than measurements of simply the total OC or TC.

4.7 Acknowledgements

The work was supported by the EU project CARBOSOL, and by the EMEP project under UNECE, the Nordic Council of Ministers, and the Swedish MISTRA Project on Organic Aerosols. CARBOSOL colleagues, as well as K. Kupiainen (SYKE) and Z. Klimont (IIASA), and K.E. Yttri (NILU) are acknowledged for their ideas and support.

5. EMEP intensive measurement periods

By Karl Espen Yttri, Svetlana Tsyro and Wenche Aas

5.1 Introduction

In the EMEP Monitoring Strategy, advanced aerosol measurements at super sites (Level 2 and 3) should be included as a regular part of the monitoring programme in Europe. It is, however, not realistic to require daily chemical speciation or continuous measurements of all species 365 days a year. There are many scattered campaigns with these types of measurements, but to enhance the effect and use of these campaign data, coordinated intensive measurements have been recommended (EMEP/CCC-Report 2/2005). The purpose of performing intensive measurement periods within the framework of EMEP is to extend the standard measurement program with additional PM and PM related parameters. Such data is important for improving our current understanding of the temporal and spatial variation of PM and PM constituents in Europe, their sources and formation mechanisms, and for model validation. Such measurement periods also motivate and prepare the Parties to initiate new measurements stated in the EMEP monitoring strategy.

The first sampling periods were set for June 2006 and January 2007. The main focus was on size-resolved chemical speciation (*i.e.* PM_{10}, $PM_{2.5}$ and PM_1), size distribution and gas/particle partitioning. In Table 5.1 there is an overview of which measurements have been performed. In addition there has been a positive response from Hungary and Greece to participate with data from these intensive measurement periods.

The carbonaceous fraction of PM is a parameter reported only by a very few EMEP sites. There are several reasons for this, such as the great analytical challenges of separating EC from OC, the severe sampling artefacts of OC, and thus, the lack of a defined protocol. Here we present some preliminary results from the intensive measurement period focusing on the carbonaceous fraction. The first model measurement intercomparison at three sites in the June campaign is also presented. The data are still being processed and analysed and a more in depth analysis will be presented next year.

Table 5.1: Measurements that has been done during the intensive periods in June 2006 and January 2007.

Sites	**Mass**		**Speciation**														**Size no. dist**	
			Daily										Intensive, hourly					
			Inorg		EC/OC		Metal		PAH		Crust		Inorg		EC/OC		Size no. dist	
	June	Jan	June	Jan	June	Jan	June	Jan	June	Jan	June	Jan	June	Jan	June	Jan	June	Jan
AT02	PM10, PM2.5 PM1	PM10, PM2.5 PM1	FP											SO4	PM2.5			
CH02	PM10 PM2.5 PM1	PM10 PM2.5 PM1	FP, PM10, PM1										PM1	PM1	PM2.5	PM2.5	X	X
CZ03	PM10 PM2.5	PM10 PM2.5			PM10	PM10	X	X										
DK41	PM10 PM2.5 PM1												NOx O3					
DE01	PM10	PM10	FP	FP						X								
DE02	PM10 PM2.5 PM1	PM10 PM2.5 PM1	FP	FP														
DE03	PM10 PM2.5	PM10 PM2.5	FP	FP						X							X	
DE07	PM10 PM2.5	PM10 PM2.5	FP	FP			X	X										
DE08	PM10	PM10	FP	FP						X								
DE09	PM10	PM10	FP	FP						X								
DE43	TSP	TSP	Berner												BC	BC	X	X
DE44	PM1 PM10	PM2.5 Berner	X	X	X	X								PM1			X	X
ES31	PM10 PM2.5 PM1	PM10 PM2.5 PM1	PM10, PM2.5		totC	totC	PM1, PM2.5				PM1, PM2.5							
FI17	PM10 PM2.5 PM1	PM10, PM2.5 PM1	X	X														
IE31	PM10, PM2.5 PM1	PM10 PM2.5 PM1	X	X	X	X							PM1	PM1			X	X
IT01	PM10, PM2.5	PM10, PM2.5	X	X	X	X	X	X			X	X					X	X
IT04	PM10, PM2.5	PM10 PM2.5	X	X	X	X							gas, PM10				X	X
NL11													gas, PM2.5, PM10					
NO01	PM10 PM2.5 PM1	PM10 PM2.5 PM1	X	X	X	X											X	X
SE12	PM2.5 PM1																	
GB36													gas, PM2.5, TSP					
GB40													gas, PM2.5, TSP					

FP = Filter pack measurements, X means chemical measurements in all the sizes, otherwise the sizes are specified.

5.2 Measurements of carbonaceous material during the EMEP intensive measurement periods in June 2006 and January 2007 – Preliminary results

A total of ten sites reported that they were going to collect ambient aerosol filter samples for subsequent analysis of the aerosols content of carbonaceous material (Table 5.2). Three sites used tandem filter set-ups (McDow and Huntzicker, 1990) operating according to the QBQ-approach (quartz-fibre filter behind quartz fibre filter) to account for the positive artefact of OC, while three used denuders. Seven of the sites used thermal optical analysis (TOA) for quantification of elemental carbon (EC), organic carbon (OC) and total carbon (TC), which is a state-of-the-art type of instrumentation that corrects for charring of OC during analysis. There are also four sites that have performed TOA analysis in two or more size fractions.

Table 5.2: Sampling site, code, size-fraction, sampling time, sampling frequency, sampling approach, correction for artefact and analytical approach for the sites measuring EC/OC/TC during the EMEP intensive measurement periods.

Site	Code	Size-fraction	Sampling time (hr)	Sampling frequency	Filter face velocity (cm s^{-1})	Sampling approach	Correction for artefact (Which/how)	Analytical approach Correction for charring? Temperature program
Illmitz	AT02	$PM_{2.5}$	1.7	Daily		Monitor	Positive artefact/Denuder1)	TOA/Yes/NIOSH 5040
Payerne	CH03	$PM_{2.5}$	1.7	Daily		Monitor	Positive artefact/Denuder1)	TOA/Yes/NIOSH 5040
Košetice	CZ03	PM_{10}	24	Daily	20	Filter	No correction	TOA/Yes/
Melpitz	DE44	PM_{10}, $PM_{2.5}$, $PM_{1.0}$ PM: 0.05/0.14/ 0.42/1.2/3.5-10	24 24	Daily Selected days	54 -	Filter Impactor3)	No correction	Thermographic 2step Method2) Thermographic 2step Method2)
Montseny	ES31	PM_{10}, $PM_{2.5}$	24	Daily	.	Filter	No correction	
K-Puszta	HU02							
Mace Head	IE31	PM_{10}, $PM_{1.0}$	50	Clean sector	Impactor	Filter	Positive/QBQ	TOA/Yes/
Mace Head	IE31	$PM_{1.0}$	3	Continuous		Monitor	No correction	R&P 5400 carbon monitor
Montelibretti	IT01	PM_{10}, $PM_{2.5}$	24	Daily	20			TOA/Yes/ NIOSH 5040
Ispra	IT04	PM_{10}, $PM_{2.5}$	24	Daily	20	Filter	Positive artefact/Denuder	TOA/Yes/EUSAAR_1
Birkenes	NO01	PM_{10}, $PM_{2.5}$, $PM_{1.0}$	24	Daily	54	Filter	Positive artefact (PM_{10})/(QBQ)	TOA/Yes (TOT)/quartz.par

1. Assuming no negative artefact at a sampling time of 1.7 hr
2. Thermographic 2 step method OC: 650 °C/N_2 and EC: 650 °C/O_2 (VDI 2465, Page 2, modification), No correction for charring
3. Berner impactor (5 stage)

By July 5, seven of the nine sites listed in Table 5.2 had reported results for the two measurement periods. Here we present some preliminary results from the two campaigns, including measured concentrations of EC, OC, and TC for the sites Illmitz (AT02) in Austria, Payerne (CH02) in Switzerland, Košetice (CZ03) in the Czech Republic, Montelibretti (IT01) and Ispra (IT04) in Italy, and Birkenes (NO01) in Norway. Common for these sites is that they all used thermal-optical analysis for quantification of EC and OC, thus the results are somewhat more comparable than those using other approaches.

The measured concentrations of EC, OC, and TC listed in Table 5.3a,b are in the same range as that reported by Yttri et al. (2007a) for 12 rural background sites in

Europe, following a one year measurement campaign within the EMEP monitoring network.

Table 5.3a: Ambient PM_{10} concentrations of carbonaceous material collected during the EMEP intensive measurement periods in June 2006 and January 2007. TC_p and OC_p indicate that the concentrations have been corrected for positive artefacts.

Site	Sampling period	n	TC	TC_p	EC	OC	OC_p	PCM	PCM/PM_{10}
NO01	Jun-06	30	1.8 ± 0.8	1.2 ± 0.6	0.12 ± 0.06	1.7 ± 0.7	1.0 ± 0.6	3.0 ± 1.3 1.9 ± 1.1	34 ± 15 21 ± 9
	Jan-07		0.5 ± 0.1		0.05 ± 0.02	0.4 ± 0.1		0.8 ± 0.2	34 ± 16
CZ03	Jun-06	23	2.7 ± 1.1		0.3 ± 0.2	2.4 ± 1.1		3.8 ± 1.3	23 ± 7
	Jan-07	29	2.4 ± 1.0		0.4 ± 0.2	2.0 ± 0.9		3.2 ± 1.3	22 ± 9
IT01	Jun-06	32	7.9 ± 2.2	5.4 ± 1.8	1.3 ± 0.6	6.6 ± 1.7	4.1 ± 1.2	11 ± 3.0 7.1 ± 2.3	39 ± 17 25 ± 11
	Jan-07	32	17 ± 7.2	12 ± 5.1	1.3 ± 0.5	15 ± 6.8	11 ± 4.7	23 ± 9.9 17 ± 7.1	62 ± 14 44 ± 10

Particulate particulate matter (PCM) was calculated using a conversion factor of 1.4 for OC for IT01, IT04 and CZ03, whereas a factor of 1.7 was used for AT02, CH02 and NO01. A conversion factor of 1.1 was used for EC.

Table 5.3b: Ambient $PM_{2.5}$ concentrations of carbonaceous material collected during the EMEP intensive measurement periods in June 2006 and January 2007. TC_p and OC_p indicate that the concentrations have been corrected for positive artefacts.

Site	Sampling period	n	TC	TC_p	EC	OC	OC_p	PCM	PCM/PM_{10}
AT02	June-06	340[1)]		2.8 ± 1.3	0.4 ± 0.2		2.3 ± 1.2	4.4 ± 2.1	30
NO01	Jun-06	30	1.6 ± 0.7	0.9 ± 0.5	0.09 ± 0.05	1.5 ± 0.6	0.8 ± 0.5	2.6 ± 1.2 1.5 ± 0.9	41 ± 14 22 ± 8
	Jan-07		0.5 ± 0.1		0.05 ± 0.02	0.5 ± 0.1		0.8 ± 0.2	53 ± 22
CH02	Jun-06	162[1)]		2.7 ± 0.8	0.4 ± 0.2		3.2 ± 0.9		
	Jan-07	261[1)]		6.8 ± 3.1	1.4 ± 0.6		5.4 ± 2.7		
IT01	Jun-06	32	7.3 ± 2.2	4.4 ± 1.7	1.1 ± 0.5	6.2 ± 1.8	3.3 ± 1.3	9.9 ± 3.0 5.8 ± 2.3	57 ± 17 33 ± 11
	Jan-07	32	18 ± 8.1	11 ± 4.9	1.1 ± 0.3	17 ± 7.9	10 ± 4.7	25 ± 11 16 ± 7.0	92 ± 22 57 ± 13
IT04	Jun-06	22		4.1 ± 1.6	0.8 ± 0.3		3.3 ± 1.3	5.3 ± 2.4	44 ± 21
	Jan-07	22		22 ± 12	4.6 ± 2.4		17 ± 9.8	29 ± 16	67 ± 13

1) Data obtained by monitor

Particulate particulate matter (PCM) was calculated using a conversion factor of 1.4 for OC for IT01, IT04 and CZ03, whereas a factor of 1.7 was used for AT02, CH02 and NO01. A conversion factor of 1.1 was used for EC.

The ambient aerosol concentration of carbonaceous material in PM_{10} and $PM_{2.5}$ increased form North to South regardless of season. The difference grew larger in winter compared to summer, as the concentrations typically were increased during winter compared to summer for all continental sites, while the opposite was observed for the Scandinavian site Birkenes. This variation in the seasonal pattern observed for Scandinavia compared to continental Europe, has previously been described by Yttri et al. (2007a). They argued that this could be attributed to a combination of increased primary and secondary biogenic emissions in summer along with reduced impact by anthropogenic sources for Scandinavian sites in summer. The increased concentrations observed in winter compared to summer for sites in continental Europe is most likely attributed to increased emissions from residential heating (coal, oil and wood) and traffic in winter and by unfavourable dispersion conditions, concentrating the particulate emissions. Further, lower temperatures will favour condensation and hence partitioning of semi-volatile organic carbon to the particulate phase.

Concurrent sampling of PM_{10} and $PM_{2.5}$ filter samples for subsequent analysis of EC and OC_p, were only performed at Birkenes (NO01) and Montelibretti (IT01) (June 2006). At both sites, coarse OC_p was found to account for approximately 10% of OC in PM_{10}, demonstrating that particulate OC mainly was associated with the fine aerosol. It has previously been shown that the concentration of coarse OC_p increases at the Birkenes site during summer and that it may account for an equal amount of OC_p in PM_{10} as fine OC_p, even on a monthly basis.

The positive artefact of OC was found to account for approximately 40% of OC in PM_{10} at those sites operating their sampler according to the QBQ-approach (IT01, NO01, and NO56) (Figure 5.1). The relative importance of the positive artefact was shown to become more important when the concentrations dropped, such as for finer particle sizes, as demonstrated in Figure 5.1. These findings underline the importance of addressing the sampling artefacts of OC when addressing the ambient concentrations of *particulate* OC. It should be noted though, that these estimates are in the upper range, as the negative sampling artefact has not been accounted for, i.e. added to OC.

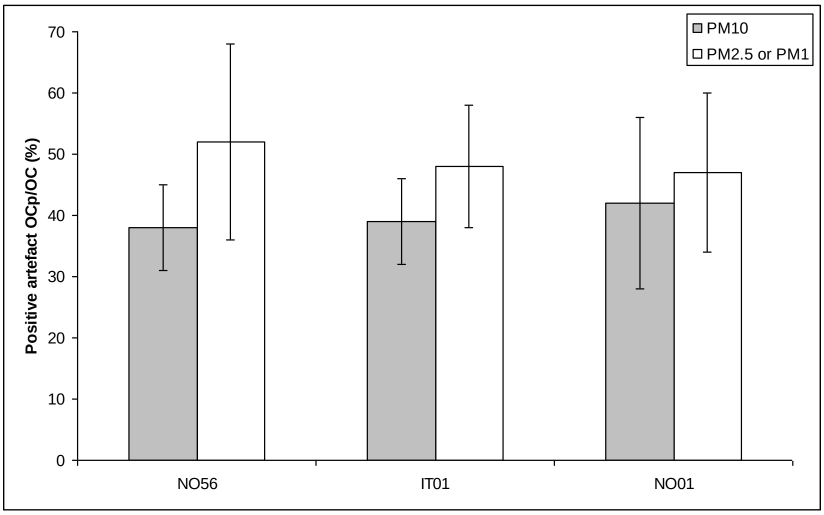


Figure 5.1: Estimates of the positive artefact of OC in PM_{10} and $PM_{2.5}/PM_1$ at the Norwegian sites Birkenes (NO01) and Hurdal (NO56), and the Italian site Montelibretti (IT01) in June 2006. For NO01 and IT01 the cut of size for fine aerosols was 2.5 µm EAD, while for NO56 it was 1 µm EAD.

To estimate the relative contribution of carbonaceous *matter* to PM, conversion factors are applied to account for elements such as Hydrogen and Oxygen that are not accounted for in thermal optical analysis. Such conversion factors are typically associated with great uncertainty. When converting OC to organic matter (OM), it is recommended to use a factor of 1.6 ± 0.2 (Turpin and Lim, 2001), while higher factors are suggested for aged aerosols and aerosols originating from wood burning. EC should be multiplied by a factor of 1.1 to account associated Hydrogen (Kiss et al., 2002). When performing such an exercise for EC and OC_p in $PM_{2.5}$, collected during the June sampling period in 2006, we found that the relative contribution of PCM (particulate carbonaceous matter = OC_p x *(1.6 ± 0.2) + EC x 1.1) ranged from 22% at the Norwegian site Birkenes to 44% at the Italian site Ispra. The estimate made for Payerne (65%) is highly uncertain as it is based on a limited number of samples and by calculating $PM_{2.5}$ based on the PM_{10} concentration and a $PM_{2.5}/PM_{10}$ ratio of 0.68 (based on the mean June $PM_{2.5}/PM_{10}$ ratio for Payerne for the period 1999-2005).

Sites that operated their samplers according to the QBQ-approach provide a conservative estimate of OC_p, as the negative artefact is not accounted for. This is also true for sites using a denuder to remove the gaseous compounds before they reach the filter. In fact, using a denuder without a backup sorbent is likely to enhance the negative artefact. The sites that provided EC/OC data by a monitor (AT02 and CH02) used a denuder to reduce the positive artefact. It is likely that the influence of the negative artefact will be reduced due to the short sampling time of the monitors, that is; the meteorological conditions are not likely to change substantially over such a short time range. Thus, the relative contribution of PCM to $PM_{2.5}$ shown in Figure 5.2, should be rather conservative.

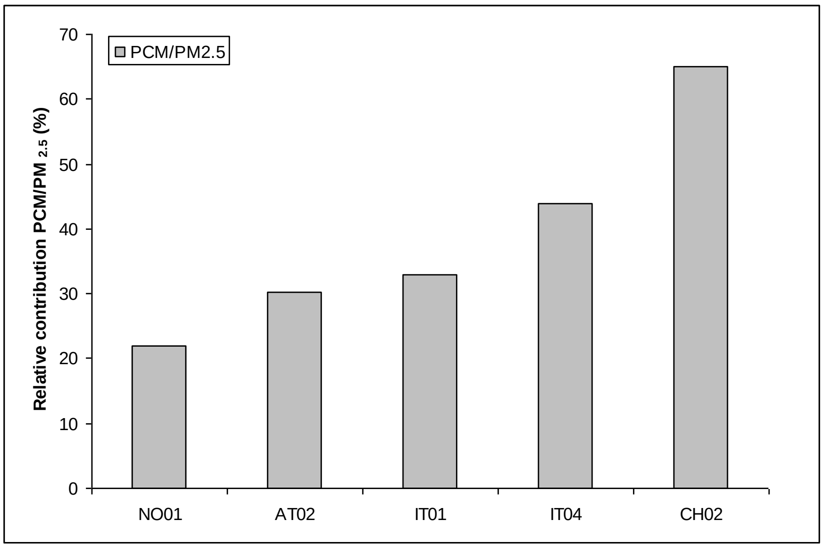


Figure 5.2: Relative contribution of PCM (Particulate Carbonaceous Matter = OCp x (1.6 ± 0.2) + EC x 1.1). The estimate made for CH02 (Payerne) is based on only a few days of measurements and the $PM_{2.5}$ *concentration is derived from the concentration of* PM_{10} *and the mean June* $PM_{2.5}/PM_{10}$ *ratio for CH02 for the period 1999-2005.*

Both the Austrian site Illmitz (AT02) and the Swiss sites Payerne (CH02) reported EC/OC data obtained by the EC/OC monitor from Sunset lab. At both sites the monitor provided 12 samples á 100 minutes pr 24 hours. By measuring EC and OC with a higher temporal resolution our current knowledge about these parameters could be greatly improved. In addition, monitors could be more economical to operate due to a reduced number of sampling site visits and an eliminated need of laboratory facilities and analysis costs. On the other hand, only a very few instruments have been tested in Europe so far, thus our experience using the EC/OC monitor is limited. The time series for EC, OC, and TC obtained at Illmitz in June 2006 is shown in Figure 5.3.

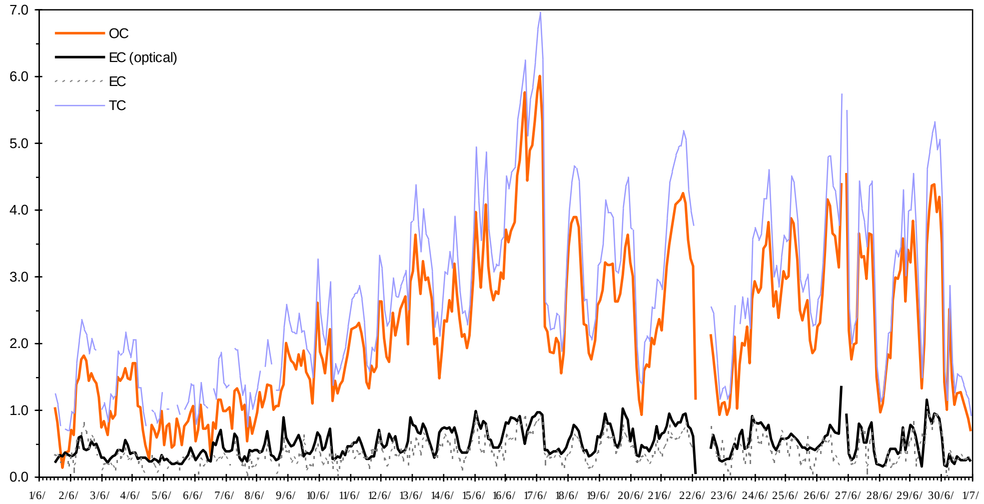


Figure 5.3: Concentrations of EC, Optical EC, OC, and TC, at the Austrian site Illmitz (AT02) during June 2006. The data was obtained by the sunset lab EC/OC monitor, which provided 12 samples á 100 minutes pr 24 hours.

From Figure 5.3 it can be seen that the concentrations of EC and OC increase steadily from the start of the month until midnight 17 of June, when the highest concentration of OC and TC during the measurement period was observed. After the peak concentration at the 17 of June the EC, OC, and TC concentrations dropped quite considerably, but then resumed again, showing quite substantial variation for the rest of the month. The EC/TC ratio decreased steadily from a maximum of nearly 0.3 at the beginning of the month to a minimum around 0.1 at the 17 of June.

To get an overview of the transport situation influencing the Illmitz site in June 2006, backward simulations were performed using the Langrangian particle dispersion model FLEXPART (Stohl et al., 2005). Figure 5.4 shows the anthropogenic emission contribution for SO_2, NO_2, and CO from the different continents arriving at Illmitz from the 1–21 of June. The anthropogenic emissions are of European origin, and there is only a slight input from North America and Africa at the start of the month and at the end of the period, respectively.

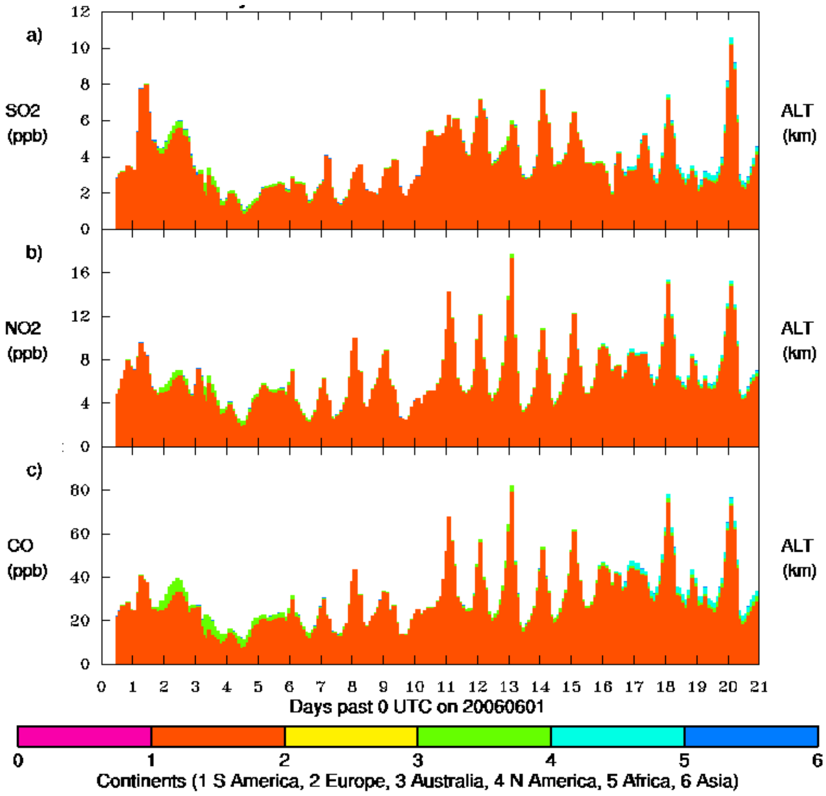


Figure 5.4: The continental emissions influencing the air masses arriving at Illmitz during the period 1 - 21 of June 2006.

Based on the backward simulations we found that there was a radical shift in the origin of the air masses on the 17 of June. Before the 17 of June, the air masses came from the north-eastern sector, whereas it shifted toward southwest after the 17 of June.

The maximum levels of OC and TC reported on the 17 of June (Figure 5.3) do not correspond to the highest peaks in the total anthropogenic emissions (Figure 5.4). The continuously decreasing EC/TC ratio, which reached its minima at this date, could indicate an increased influence by biogenic sources, but without further analysis of this remains speculative.

5.3 Preliminary comparison with model results

By the time of preparation of this report, observation data from June 2006 campaign was made available for comparison with model calculations for three stations: Birkenes (NO01), Melpitz (DE44) and Montelibretti (IT01). These sites are situated along a north-south transect and thus, are representative of different chemical and meteorological regimes in Europe. The measurements include data on mass closure for PM_{10} and $PM_{2.5}$, which is very valuable for in-deep verification of model results. The information on the chemical composition of PM_{10} and $PM_{2.5}$, provided by the intensive campaign, can help explaining the existing discrepancies between modelled and observed mass of PM_{10} and $PM_{2.5}$. It also facilitates studying the size distribution of PM components between the fine and the coarse fraction. Below, we present some preliminary results of comparison between model calculated and measured chemical composition of PM_{10} and $PM_{2.5}$ at these three sites.

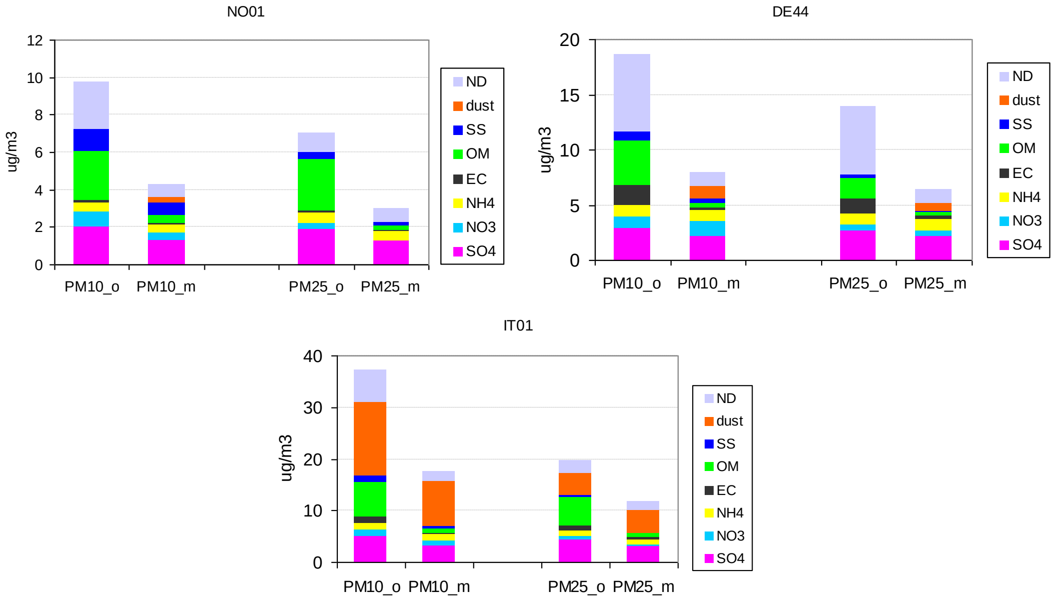


Figure 5.5: Measured and modelled chemical composition of PM_{10} and $PM_{2.5}$ in June 2006 at Birkenes, Melpitz and Montelibretti. ND means non-determined PM mass in measurements and particle water in model results. Note: OM=1.7xOC; OC measurements were corrected for artefacts at IT01, but not at NO01 and DE44.

Figure 5.5 compares average observed and modelled chemical composition of PM_{10} and $PM_{2.5}$ at Birkenes, Melpitz and Montelibretti for June 2006. Tables 3.1 and 3.2 provide statistics obtained when comparing model calculated and measured concentrations of PM_{10}, $PM_{2.5}$ and certain chemical constituents for June 2006 at Birkenes, Melpitz and Montelibretti. Note that in Figure 5.5, organic matter (OM) is plotted, where OM=1.7xOC, while OC ($\mu gC/m^3$) is used in comparison of measurements with model results in Table 5.4–Table 5.5. On average, measured PM_{10} concentrations are underestimated by the model by 54 to 60%, while $PM_{2.5}$ concentrations are underestimated by 42 to 57% at these sites in June 2006. As pointed out in the previous PM reports, the model underestimation of PM is generally greater in summer that in other seasons (see also Table 3.2). Using the data on PM mass closure, we'll try to understand the reasons for model PM underestimation for June 2006 at these sites.

5.3.1 *Analysis by components*

Practically all PM_{10} and $PM_{2.5}$ components (except for NO_3^- at DE44) are underestimated by the model at all three sites, see Table 5.4 and Figures A.1-A7.

SO_4^{2-}. The model underestimated SO_4^{2-} by approximately 35% on average. Among SIA components, underestimation of SO_4^{2-} adds to PM_{10} model underestimation the most because of its larger mass contribution: between 13% and 20% to PM_{10} and between 19% and 26% to $PM_{2.5}$.

The model does not calculate the size distribution of SO_4^{2-} as it currently does not account for coarse SO_4^{2-} formation on sea salt and dust aerosols. The observations show that only 6-8% of SO_4^{2-} was found on coarse aerosols.

NO_3^-. The average underestimation of NO_3^- in PM_{10} was only 14%, but it is as large as 54% for $PM_{2.5}$. DE44 was the only site where NO_3^- was slightly overestimated. NO_3^- accounted for only 3-8% of PM_{10} and 3-5% to $PM_{2.5}$. Thus, NO_3^- underestimation by the model contributes only insignificantly to the PM mass underestimation.

Large discrepancies were found between the measured and modelled size distribution of NO_3^-, especially for NO01 and IT01 (Figures A.1-A.4). Approximately 50% of NO_3^- measured in PM_{10} was associated with fine aerosols; whereas the model calculated that almost no NO_3^- was associated with fine aerosol at these sites (the model underestimation of fine NO_3^- was 97% for NO01 and 86% for IT01). Thus, the model appears to calculate too efficient evaporation of ammonium nitrate aerosols to gaseous nitric acid and ammonia at higher summer temperatures at NO01 and IT01. On the other hand, the model manages to reproduce well observed concentrations of fine NO_3^- at DE44. At DE44, much of NO_3^- remains in aerosol form, probably because of the higher concentrations of ammonia in that area.

NH_4^+. For PM_{10} the model underestimated NH_4^+ by 15%, whereas the corresponding percentage for $PM_{2.5}$ was 20%, which contributes respectively with 5% and 7% to PM masses.

The model does not calculate the size distribution of NH_4^+, thus it does not account for formation of coarse NH_4^+ on sea salt and dust aerosols. At NO01, 8% of measured NH_4^+ was in the coarse fraction, while at DE44 all NH_4^+ was in the fine fraction. At IT01, the average measured concentration of NH_4^+ in PM_{10} was smaller than that of NH_4^+ in $PM_{2.5}$. This could be attributed to different sampling techniques being used for two size fractions. For $PM_{2.5}$ sampling of NH_4^+ was performed by artefact free denuder measurements, while this was not the case for PM_{10}, hence the concentration was probably underestimated due to volatilisation of NH_4NO_3.

OC. For all sites, the greatest underestimation was found for organic carbon (OC). The underestimations were 82% for PM_{10} OC and 77% for $PM_{2.5}$ OC (mostly IT01 data) on average. This could partly be attributed to the fact that only primary anthropogenic OC is included in the model. Only two of the sites accounted for the positive sampling artefact of OC. Still, large underestimation of OC by the model could explain much of the model underestimation of PM_{10}, as OC is a major contributor to PM mass. When converted to organic matter (OM=1.7xOC), it accounted for 19% and 28% to PM_{10} and with about 14% and 28% to $PM_{2.5}$ at these sites.

The model currently calculates only fine OC, while measurements showed that about 10% OC were in the coarse mode.

EC. Elemental carbon is also underestimated at all sites. On average, EC concentrations are underestimated by 63% in PM_{10} and by 41% in $PM_{2.5}$. This also contributes to the model PM underestimation, but to a smaller degree as EC contribution to PM_{10} and $PM_{2.5}$ was below 10% at these sites.

The model does not manage to reproduce the size distribution of EC between the fine and the coarse modes (Figures A.1-A.7). Calculated coarse EC concentrations are by far too low at all sites (even for NO01, for which modelled fine EC compares very well with observations). This may be an indication that emissions of coarse EC are heavily underestimated. There is also a high uncertainty in the measured EC concentration. E.g. the EC level in $PM_{2.5}$ is sometimes higher than observed for PM_{10}.

Dust. The mass of crustal material was determined only at Montelibretti, where mineral dust concentrations were derived as $(1.89{\cdot}Al + 2.14{\cdot}Si + 1.4{\cdot}Ca + 1.2{\cdot}K + 1.36{\cdot}Fe) {\cdot}1.12$. Compared to observations, the model underestimated the crustal mass in PM_{10} by 39%. Since mineral dust constituted almost 40% of the measured PM_{10} mass, such underestimation also contributes significantly to the models underestimation of PM_{10} at this site. The model is doing a fairly good job reproducing the size distribution of mineral dust at IT01.

Sea salt. Concentrations of sea salt Na^+ were also significantly underestimated: by 50% for PM_{10} and 66% for $PM_{2.5}$. The relative contribution of sea salts was significant only at NO01, accounting for 10% of PM_{10} and 5% of $PM_{2.5}$). For DE44 and IT01 the relative contribution was well below 5% for both size fractions.

The model calculated reasonably well the distribution of sea salt Na^+ between the fine and the coarse modes at the three sites, although there was a tendency for a larger underestimation for fine mode compared to Na^+ in PM_{10}. Different from the other sites, there is a very low correlation between model results and observations for both fine and coarse Na^+ at IT01. It can be noted that there was almost no correlation between measured fine and coarse Na^+ (R=0.12) at this site. Therefore, it seems interesting to investigate further whether the episodes of fine and coarse sea salt really occurred at different times at IT01, as indicated by the observations.

Undetermined & particle water. Further, it should be noted that the “accumulative” model underestimation of individual components does not fully explain the PM_{10} and $PM_{2.5}$ underestimations (as seen from comparing M-O differences). As visualised in Figure 3.1, a significant part of gravimetrically measured PM concentrations remains unidentified: 28% of PM_{10} and 31% of $PM_{2.5}$ at NO01, for IT01 and DE44 the correspondent numbers are 17% and 28% and 37% and 44%, respectively. At NO01 and DE44, a part of the undetermined PM mass includes mineral dust. Also, a certain fraction of the unidentified PM mass determined by gravimetrical method consists of particle-bound water. The mass of particle associated water is calculated by the model and also shown in Figure 3.1 (in purple). It can be seen that the calculated water mass is smaller than the unidentified PM mass, especially for PM_{10} at all sites and $PM_{2.5}$ at DE44.

Summarising, model underestimations of individual PM components will contribute differently to the final PM_{10} and $PM_{2.5}$ underestimations, which depends on the relative contributions of these components to the total PM mass. In Table 5.4 and Table 5.5, PM components, causing most of PM underestimation are displayed in shaded cells.

Table 5.4: Summarised comparison statistics of modelled and measured chemical constituents of PM_{10} and $PM_{2.5}$ for Birkenes, Melpitz and Montelibretti. June 2006.

Component	Np	Obs (μg/m^3)	Mod (μg/m^3)	Bias (%)	RMSE	R
PM10	188	15.18	7.57	-50	13.13	0.77
SO4_PM10	92	3.41	2.18	-36	2.70	0.44
NO3_PM10	92	1.07	0.91	-14	1.11	0.27
NH4_PM10	91	0.99	0.85	-15	0.74	0.48
EC_PM10	188	0.60	0.22	-63	0.83	0.42
OC_PM10	188	1.99	0.35	-82	2.17	0.24
Na_PM10	92	0.36	0.18	-50	0.34	0.41
Dust_PM10	32	14.59	8.30	-43	9.19	0.85
PM25	187	9.27	5.6	-40	7.38	0.66
SO4_PM25	92	3.10	2.18	-30	2.71	0.40
NO3_PM25	92	0.47	0.22	-54	0.71	0.18
NH4_PM25	90	0.91	0.86	-7	0.67	0.46
EC_PM25	159	0.35	0.21	-41	0.46	0.51
OC_PM25	185	1.45	0.34	-77	1.60	0.30
Na_PM25	92	0.12	0.04	-66	0.11	0.37
Dust_PM25	32	4.13	4.08	-1	3.12	0.87

5.3.2 Summary by sites

The results are summarized in Table 5.5 and the figures in Appendix B.

NO01: All PM_{10} and $PM_{2.5}$ components were under predicted by the model. The under prediction of OC by 86% and 89% appears to be the main reason for the underprediction of both PM_{10} and $PM_{2.5}$. It should be noted that measured OC concentrations used here were not corrected for positive artefacts. When corrected for the positive artefact, the OC concentrations would be approximately 40% and 50% lower for PM_{10} and $PM_{2.5}$, respectively. The underestimations of SO_4^{2-} and NO_3^- (especially fine NO_3^-) accounted for a significant part of the model PM_{10} and $PM_{2.5}$ underestimation for NO01.

The temporal correlation between calculated and observed concentrations of both PM_{10} and $PM_{2.5}$ is 0.85. The correlation coefficients are also as high as 0.75-0.85 for most of the components; somewhat lower for PM_{10} NO_3^- and Na^+. The worst temporal correlation is for fine NO_3^-. As mentioned above, the largest underestimation by 97% was found for fine NO_3^-. As seen from the time-series for Birkenes (Figure A.1), there is almost no $PM_{2.5}$ NO_3^- in model results.

DE44: Also for DE44, the underestimation of OC (which is greater than 90%) contributes the most to the model PM_{10} and $PM_{2.5}$ underestimation. For this site, uncorrected for positive artefacts OC measurements have been compared with calculations. EC is also greatly underestimated by over 90% (only 3 days with observations were for $PM_{2.5}$ EC though), but the measured EC concentrations were not corrected for charring during the analysis and thus can be overestimates. The undetermined fraction is significant for PM_{10} and includes mineral dust and water. The temporal correlation between modelled and observed PM_{10} is not very good (0.37) and only slightly better for $PM_{2.5}$ (0.43). The results with respect to temporal correlation between modelled and observed concentrations of different PM components are rather mixed. The highest correlation coefficients are for Na^+ (0.88 and 0.78). Reasonable correlation is found for PM_{10} EC (R=0.66) and SO_4^{2-} (R=0.56 and 0.57) and PM_{10} OC (R=0.55), whereas for NO_3^- and NH_4^+ there is a rather poor correlation between calculations and observations.

IT01: The main reason for model PM_{10} and $PM_{2.5}$ underestimation is that the model underestimates OC concentrations by 88%. To a smaller degree, PM underestimation is due to under predictions of SO_4^{2-} and mineral dust (for PM_{10}) in model results. The undetermined PM mass is relatively small, though it exceeds model calculated mass of particle water. The temporal correlation between modelled and measured PM_{10} is as high as 0.85 and the correspondent number for $PM_{2.5}$ is 0.75. Surprisingly, among the individual components, calculated concentrations of mineral dust in PM_{10} and $PM_{2.5}$ correlate the best with observations, both correlation coefficients being equal 0.87. Very good correlations, lying between 0.62 and 0.83, are found for EC and OC; whereas all modelled SIA components correlate poorly with measured concentrations.

Correlation. Correlation coefficients for PM_{10} and all of its constituents are quite high (between 0.61 and 0.86) for NO01. For DE44, correlation is in the range of 0.21 to 0.88, being the highest for Na^+ and the lowest for NO_3^-. For IT01, a rather poor correlation is found for all SIA components (below 0.2) and even lower was correlation for sea salt. On the other hand, correlation coefficients are fairly high at for primary aerosols for IT01 (0.83 for EC and 0.75 for OC). Surprisingly high is the correlation between model and measurements obtained for mineral dust (correlation coefficient is 0.87). This is given that about 65% of calculated mineral dust being windblown dust, modelling of which is associated with high uncertainties.

In general, the situation with correlation between model and observed $PM_{2.5}$ components is similar to that for $PM_{2.5}$ components described above. As pointed out before, very low correlations for fine NO_3^- for all sites indicate that the model has a problem to reproduce this component. At present, the EMEP model uses equilibrium aerosol model EQSAM to calculate gas-aerosol partitioning for fine particles. The application of this model is envisaged to be revised in future.

Summarising, the temporal correlation between calculated and measured concentrations shows a tendency to worsen from north to south. In general, the temporal correlation is worse for $PM_{2.5}$ components compared to PM_{10} components. The spatial correlation between average calculated and observed concentrations is very good for these three sites, with just a few exceptions (e.g.

for fine Na^+). This indicates the model ability to reproduce the regional distribution of various PM components.

Table 5.5: Comparison statistics of modelled and measured PM_{10} *and* $PM_{2.5}$ *chemical composition for Birkenes (NO01), Melpitz (DE44) and Montelibretti (IT01). June 2006.* $^{*)}$ *Only 3 days with measurements. Note: OC measurements were not corrected for artefacts at NO01 and DE44 (in italic).*

		PM$_{10}$	SO$_4$	NO$_3$	NH$_4$	EC	OC	Na	dust
NO01	Obs	**10.15**	1.99	0.81	0.49	0.12	*1.66*	0.39	-
	Mod	**4.03**	1.30	0.40	0.43	0.10	*0.24*	0.24	-
	R	**0.85**	0.84	0.62	0.81	0.86	*0.69*	0.69	
	Bias %	**-60**	-35	-34	-12	-17	*-86*	-38	
	M-O	**-6.12**	-0.69	-0.41	-0.06	-0.02	*-1.42*	-0.15	
DE44	Obs	**18.91**	2.85	1.09	1.02	1.82	*2.54*	0.28	-
	Mod	**7.79**	2.14	1.41	0.97	0.25	*0.23*	0.15	-
	R	**0.37**	0.56	0.21	0.57	0.66	*0.55*	0.88	
	Bias %	**-59**	-25	29	-5	-86	*-91*	-46	
	M-O	**-11.12**	-0.71	0.32	-0.05	-1.57	*-2.31*	-0.13	
IT01	Obs	**37.74**	4.99	1.24	1.36	1.30	4.14	0.38	14.43
	Mod	**17.22**	3.19	0.98	1.19	0.36	0.48	0.15	8.81
	R	**0.85**	0.20	0.13	0.19	0.83	0.75	-0.25	0.87
	Bias %	**-54**	-36	-21	-13	-72	-88	-61	-39
	M-O	**-20.52**	-1.8	-0.26	-0.17	-0.94	-3.66	-0.23	-5.62

		PM$_{2.5}$	SO$_4$	NO$_3$	NH$_4$	EC	OC	Na	dust
NO01	Obs	**7.15**	1.87	*0.34*	0.53	0.12	*1.74*	0.12	-
	Mod	**3.06**	1.30	*0.01*	0.44	0.10	*0.16*	0.06	-
	R	**0.85**	0.87	*0.05*	0.84	0.86	*0.75*	0.41	
	Bias %	**-57**	-30	*-97*	-17	-17	*-89*	-50	
	M-O	**-4.09**	-0.57	*-0.33*	-0.09	-0.02	*-1.58*	-0.06	
DE44	Obs	**13.98**	2.67	0.56	1.02	*1.35*$^{*)}$	*1.16*	0.10	-
	Mod	**6.18**	2.14	0.59	0.97	*0.29*	*0.23*	0.04	-
	R	**0.43**	0.58	0.21	0.36	*0.96*	*0.29*	0.78	
	Bias %	**-56**	-20	5	-5	*-79*	*-80*	-60	
	M-O	**-7.8**	-0.53	0.03	-0.05	*-1.06*	*-0.93*	-0.06	
IT01	Obs	**19.8**	4.45	0.51	1.07	1.16	3.31	0.14	4.19
	Mod	**11.45**	3.19	0.07	1.19	0.35	0.48	0.03	4.33
	R	**0.75**	0.17	-0.32	0.27	0.79	0.62	0.08	0.87
	Bias %	**-42**	-28	-86	-22	-70	-85	-79	3
	M-O	**-8.35**	-1.26	-0.44	-0.34	-0.81	-2.83	-0.11	0.14

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APPENDIX A

National emissions and projections

This Appendix contains the national emission data and the different projections used throughout this report for mail pollutants and primary particle emissions. The actual gridded emission data used in the EMEP Unified model calculations will be available in autumn 2007 on http://webdab.emep.int.

Table A:1: National total emission and projections Emissions of sulphur used for modelling at the MSC-W (Gg of SO_2 per year)

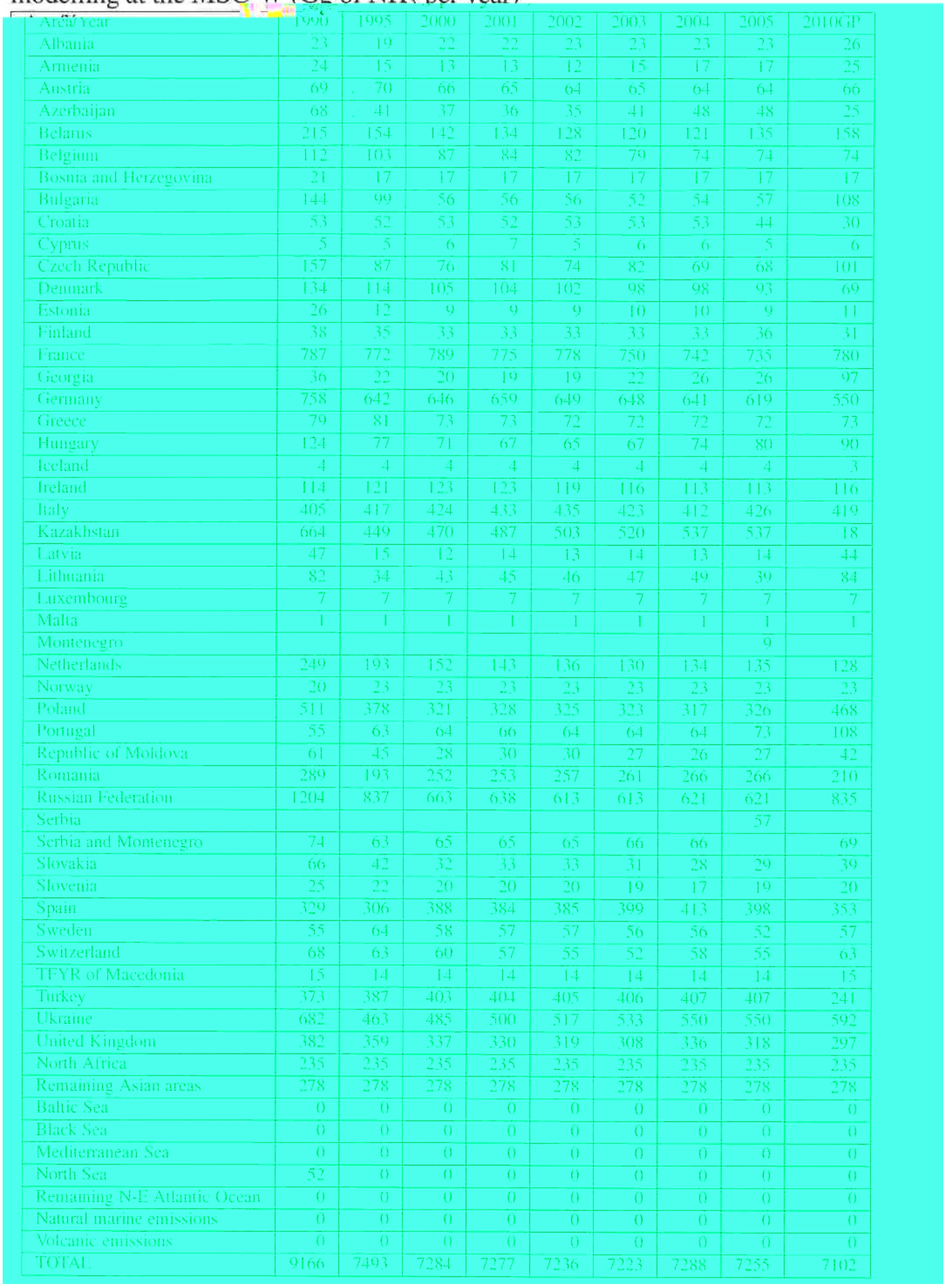
Area/Year	1990	1995	2000	2001	2002	2003	2004	2005	2010GP
Albania	74	14	32	32	32	32	32	32	30
Armenia	86	15	11	11	10	9	8	8	73
Austria	74	47	32	33	33	33	29	26	39
Azerbaijan	615	262	162	154	146	138	130	130	15
Belarus	888	344	162	126	117	107	97	103	480
Belgium	361	262	171	169	150	147	154	147	106
Bosnia and Herzegovina	484	360	420	422	423	425	427	427	411
Bulgaria	2007	1477	918	969	964	994	929	900	856
Croatia	178	70	60	63	68	75	85	60	70
Cyprus	46	41	50	47	51	45	45	42	17
Czech Republic	1876	1090	264	248	235	232	227	219	283
Denmark	176	133	27	24	24	30	23	22	55
Estonia	274	117	96	92	88	101	90	77	44
Finland	259	95	74	85	79	98	83	69	116
ance	1333	968	613	550	510	505	484	465	400
orgia	43	6	7	6	6	5	5	5	9
rmany	5289	1708	630	628	588	595	559	560	550
eece	487	536	493	502	517	554	537	537	546
ngary	1011	705	486	400	360	339	240	129	550

[redacted]

Table A:2: National total emission and projections Emissions of nitrogen oxides used for modelling at the MSC-W (Gg of NO_2 per year)

Area/Year	1990	1995	2000	2001	2002	2003	2004	2005	2010GP	
Albania	23	16	22	22	23	24	25	25	28	
Armenia	60	18	31	32	33	38	38	38	46	
Austria	212	193	204	213	220	230	227	225	107	
Azerbaijan	171	85	76	77	80	86	85	85	43	
Belarus	379	232	208	204	205	209	213	184	255	
Belgium	382	372	330	316	300	298	298	293	181	
Bosnia and Herzegovina	73	51	53	53	52	52	52	52	54	
Bulgaria	363	264	184	192	197	202	216	233	266	
Croatia	88	66	77	70	69	69	70	69	87	
Cyprus	19	20	25	19	23	22	19	17	21	
Czech Republic	742	413	398	332	316	324	328	278	286	
Denmark	266	253	188	184	181	189	171	186	127	
Estonia	74	38	37	38	40	39	37	32	28	
Finland	299	258	235	220	208	218	205	177	170	
France	1829	1643	1390	1335	1282	1243	1218	1207	860	
Georgia	64	13	30	30	31	32	32	32	30	
Germany	2878	2131	1855	1763	1674	1605	1554	1443	1081	
ece	299	320	328	343	318	343	317	317	344	Gre
ıgary	276	193	194	192	196	192	190	203	198	Hur
and	9	8	9	9	9	11	11	11	30	Icel
ınd	119	120	129	132	122	117	116	116	65	Irel
/	1945	1808	1377	1366	1275	1259	1244	1173	1000	Italy
akhstan	179	162	119	127	135	151	151	151	50	Kaz
/ia	69	41	34	38	37	38	39	41	84	Lat
ıuania	158	65	49	47	51	53	55	58	110	Lith
embourg	20	32	33	32	31	30	29	29	11	Lux
ta	14	13	12	12	11	12	12	12	6	Mal
ıtenegro								21		Mo
herlands	549	464	389	381	368	367	360	344	266	Netl
way	224	221	224	220	212	215	215	197	156	Nor
ınd	1581	1121	838	848	796	808	804	811	879	Pola
ugal	243	274	285	286	294	271	271	275	260	Port
ublic of Moldova	131	79	27	23	25	30	38	31	90	Rep
ıania	527	400	331	335	338	342	346	346	437	Ron
sian Federation	3600	2570	2457	2582	2698	3105	3093	3093	2758	Rus
ɔia								128		Serl
ɔia and Montenegro	165	133	137	140	141	146	149		168	Serl
/akia	215	174	109	109	101	98	98	97	130	Slov
/enia	63	66	60	59	58	56	57	58	45	Slov
in	1247	1351	1477	1459	1522	1519	1519	1405	847	Spa
:den	306	271	217	211	206	203	197	205	148	Swe
tzerland	156	119	101	97	92	88	87	86	79	Swi
'R of Macedonia	46	35	39	41	42	43	42	30	41	TFY
key	691	789	942	940	937	934	932	932	852	Turl
aine	1753	1245	861	886	911	936	960	960	1222	Ukr
	2932	2355	1857	1799	1693	1685	1621	1627	1181	United Kingdom
	96	96	96	96	96	96	96	96	96	North Africa
	169	169	169	169	169	169	169	169	79	Remaining Asian areas
	236	268	303	311	318	327	335	343	361	Baltic Sea
	62	70	80	82	84	86	88	90	94	Black Sea
	1234	1402	1593	1634	1677	1720	1765	1810	1914	Mediterranean Sea
	508	575	652	668	685	703	721	739	777	North Sea
Ocean	565	639	724	742	760	779	799	819	863	Remaining N-E Atlantic
s	0	0	0	0	0	0	0	0	0	Natural marine emission:
	0	0	0	0	0	0	0	0	0	Volcanic emissions
	28310	23715	21593	21515	21343	21809	21713	21399	19310	TOTAL

Table A:3: National total emission and projections Emissions of ammonia used for modelling at the MSC-W (Gg of NH_3 per year)



Area/Year	1990	1995	2000	2001	2002	2003	2004	2005	2010GP
Albania	23	19	22	22	23	23	23	23	26
Armenia	24	15	13	13	12	15	17	17	25
Austria	69	70	66	65	64	65	64	64	66
Azerbaijan	68	41	37	36	35	41	48	48	25
Belarus	215	154	142	134	128	120	121	135	158
Belgium	112	103	87	84	82	79	74	74	74
Bosnia and Herzegovina	21	17	17	17	17	17	17	17	17
Bulgaria	144	99	56	56	56	52	54	57	108
Croatia	53	52	53	52	53	53	53	44	30
Cyprus	5	5	6	7	5	6	6	5	6
Czech Republic	157	87	76	81	74	82	69	68	101
Denmark	134	114	105	104	102	98	98	93	69
Estonia	26	12	9	9	9	10	10	9	11
Finland	38	35	33	33	33	33	33	36	31
France	787	772	789	775	778	750	742	735	780
Georgia	36	22	20	19	19	22	26	26	97
Germany	758	642	646	659	649	648	641	619	550
Greece	79	81	73	73	72	72	72	72	73
Hungary	124	77	71	67	65	67	74	80	90
Iceland	4	4	4	4	4	4	4	4	3
Ireland	114	121	123	123	119	116	113	113	116
Italy	405	417	424	433	435	423	412	426	419
Kazakhstan	664	449	470	487	503	520	537	537	18
Latvia	47	15	12	14	13	14	13	14	44
Lithuania	82	34	43	45	46	47	49	39	84
Luxembourg	7	7	7	7	7	7	7	7	7
Malta	1	1	1	1	1	1	1	1	1
Montenegro								9	
Netherlands	249	193	152	143	136	130	134	135	128
Norway	20	23	23	23	23	23	23	23	23
Poland	511	378	321	328	325	323	317	326	468
Portugal	55	63	64	66	64	64	64	73	108
Republic of Moldova	61	45	28	30	30	27	26	27	42
Romania	289	193	252	253	257	261	266	266	210
Russian Federation	1204	837	663	638	613	613	621	621	835
Serbia								57	
Serbia and Montenegro	74	63	65	65	65	66	66		69
Slovakia	66	42	32	33	33	31	28	29	39
Slovenia	25	22	20	20	20	19	17	19	20
Spain	329	306	388	384	385	399	413	398	353
Sweden	55	64	58	57	57	56	56	52	57
Switzerland	68	63	60	57	55	52	58	55	63
TFYR of Macedonia	15	14	14	14	14	14	14	14	15
Turkey	373	387	403	404	405	406	407	407	241
Ukraine	682	463	485	500	517	533	550	550	592
United Kingdom	382	359	337	330	319	308	336	318	297
North Africa	235	235	235	235	235	235	235	235	235
Remaining Asian areas	278	278	278	278	278	278	278	278	278
Baltic Sea	0	0	0	0	0	0	0	0	0
Black Sea	0	0	0	0	0	0	0	0	0
Mediterranean Sea	0	0	0	0	0	0	0	0	0
North Sea	52	0	0	0	0	0	0	0	0
Remaining N-E Atlantic Ocean	0	0	0	0	0	0	0	0	0
Natural marine emissions	0	0	0	0	0	0	0	0	0
Volcanic emissions	0	0	0	0	0	0	0	0	0
TOTAL	9166	7493	7284	7277	7236	7223	7288	7255	7102

Table A:4: National total emission and projections Emissions of non-methane volatile organic compounds used for modelling at the MSC-W (Gg of NMVOC per year)

Area/Year	1990	1995	2000	2001	2002	2003	2004	2005	2010GP
Albania	30	31	29	30	31	31	32	32	36
Armenia	95	37	47	47	48	49	49	49	81
Austria	284	221	179	182	176	175	172	154	159
Azerbaijan	376	202	233	233	233	234	234	234	9
Belarus	497	378	340	320	301	314	326	326	309
Belgium	305	255	201	194	181	173	165	155	144
Bosnia and Herzegovina	48	35	40	40	41	41	42	42	46
Bulgaria	214	192	123	128	123	121	132	147	185
Croatia	105	74	80	83	91	104	122	92	90
Cyprus	16	16	16	16	16	16	12	9	6
Czech Republic	374	281	266	257	238	238	240	218	220
Denmark	166	152	127	122	118	116	116	118	85
Estonia	71	47	38	34	39	41	41	36	30
Finland	221	187	154	157	151	145	142	131	130
France	2414	2032	1658	1587	1476	1411	1367	1439	1100
Georgia	151	53	110	110	109	108	107	107	19
Germany	3584	2100	1569	1476	1381	1272	1268	1253	995
Greece	281	302	295	289	261	278	262	262	261
Hungary	252	191	187	179	176	171	172	177	137
Iceland	12	12	9	10	10	11	11	11	7
Ireland	111	105	90	87	81	78	63	62	55
Italy	2023	2022	1538	1453	1344	1307	1273	1261	1159
Kazakhstan	214	122	140	143	145	147	150	150	50
Latvia	73	62	58	58	59	60	64	63	136
Lithuania	136	71	78	71	72	75	67	84	92
Luxembourg	16	22	13	12	11	11	10	10	9
Malta	8	8	8	8	8	8	7	5	2
Montenegro								21	
Netherlands	491	364	267	242	236	222	216	176	191
Norway	295	367	379	389	343	297	265	222	195
Poland	832	771	606	607	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]

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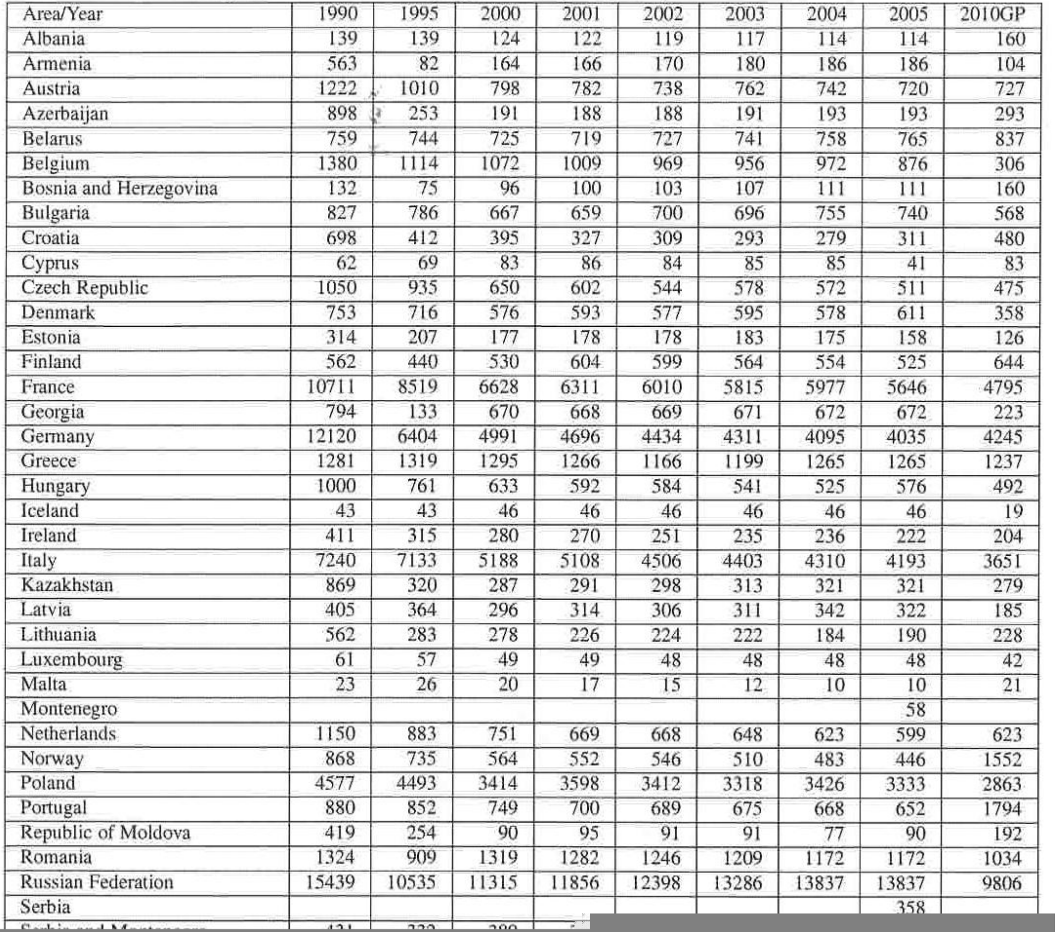
Table A:5: National total emission and projections Emissions of carbon monoxide used for modelling at the MSC-W (Gg of CO per year)



Area/Year	1990	1995	2000	2001	2002	2003	2004	2005	2010GP
Albania	139	139	124	122	119	117	114	114	160
Armenia	563	82	164	166	170	180	186	186	104
Austria	1222	1010	798	782	738	762	742	720	727
Azerbaijan	898	253	191	188	188	191	193	193	293
Belarus	759	744	725	719	727	741	758	765	837
Belgium	1380	1114	1072	1009	969	956	972	876	306
Bosnia and Herzegovina	132	75	96	100	103	107	111	111	160
Bulgaria	827	786	667	659	700	696	755	740	568
Croatia	698	412	395	327	309	293	279	311	480
Cyprus	62	69	83	86	84	85	85	41	83
Czech Republic	1050	935	650	602	544	578	572	511	475
Denmark	753	716	576	593	577	595	578	611	358
Estonia	314	207	177	178	178	183	175	158	126
Finland	562	440	530	604	599	564	554	525	644
France	10711	8519	6628	6311	6010	5815	5977	5646	4795
Georgia	794	133	670	668	669	671	672	672	223
Germany	12120	6404	4991	4696	4434	4311	4095	4035	4245
Greece	1281	1319	1295	1266	1166	1199	1265	1265	1237
Hungary	1000	761	633	592	584	541	525	576	492
Iceland	43	43	46	46	46	46	46	46	19
Ireland	411	315	280	270	251	235	236	222	204
Italy	7240	7133	5188	5108	4506	4403	4310	4193	3651
Kazakhstan	869	320	287	291	298	313	321	321	279
Latvia	405	364	296	314	306	311	342	322	185
Lithuania	562	283	278	226	224	222	184	190	228
Luxembourg	61	57	49	49	48	48	48	48	42
Malta	23	26	20	17	15	12	10	10	21
Montenegro								58	
Netherlands	1150	883	751	669	668	648	623	599	623
Norway	868	735	564	552	546	510	483	446	1552
Poland	4577	4493	3414	3598	3412	3318	3426	3333	2863
Portugal	880	852	749	700	689	675	668	652	1794
Republic of Moldova	419	254	90	95	91	91	77	90	192
Romania	1324	909	1319	1282	1246	1209	1172	1172	1034
Russian Federation	15439	10535	11315	11856	12398	13286	13837	13837	9806
Serbia								358	

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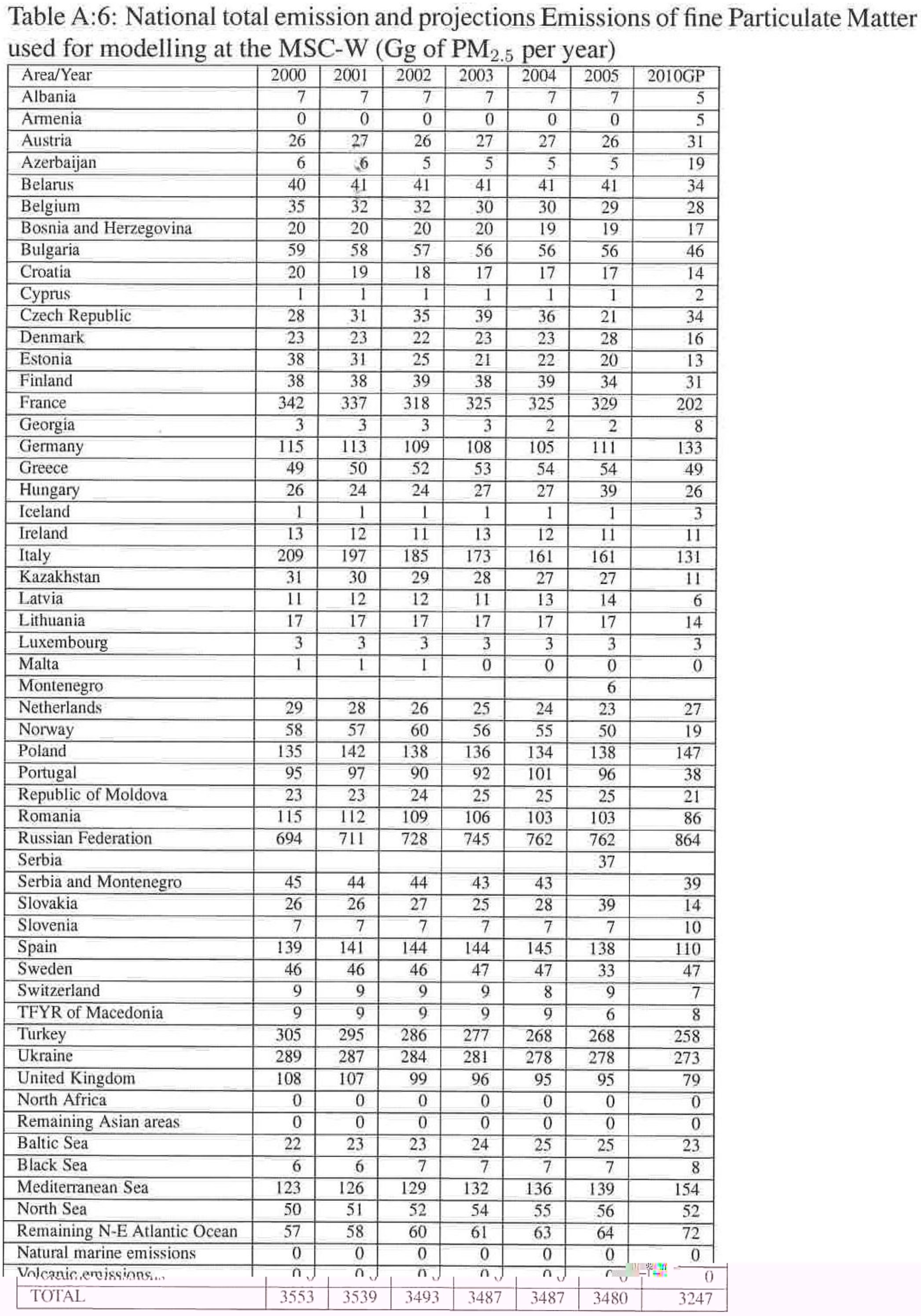


Table A:6: National total emission and projections Emissions of fine Particulate Matter used for modelling at the MSC-W (Gg of $PM_{2.5}$ per year)

Area/Year	2000	2001	2002	2003	2004	2005	2010GP
Albania	7	7	7	7	7	7	5
Armenia	0	0	0	0	0	0	5
Austria	26	27	26	27	27	26	31
Azerbaijan	6	6	5	5	5	5	19
Belarus	40	41	41	41	41	41	34
Belgium	35	32	32	30	30	29	28
Bosnia and Herzegovina	20	20	20	20	19	19	17
Bulgaria	59	58	57	56	56	56	46
Croatia	20	19	18	17	17	17	14
Cyprus	1	1	1	1	1	1	2
Czech Republic	28	31	35	39	36	21	34
Denmark	23	23	22	23	23	28	16
Estonia	38	31	25	21	22	20	13
Finland	38	38	39	38	39	34	31
France	342	337	318	325	325	329	202
Georgia	3	3	3	3	2	2	8
Germany	115	113	109	108	105	111	133
Greece	49	50	52	53	54	54	49
Hungary	26	24	24	27	27	39	26
Iceland	1	1	1	1	1	1	3
Ireland	13	12	11	13	12	11	11
Italy	209	197	185	173	161	161	131
Kazakhstan	31	30	29	28	27	27	11
Latvia	11	12	12	11	13	14	6
Lithuania	17	17	17	17	17	17	14
Luxembourg	3	3	3	3	3	3	3
Malta	1	1	1	0	0	0	0
Montenegro						6	
Netherlands	29	28	26	25	24	23	27
Norway	58	57	60	56	55	50	19
Poland	135	142	138	136	134	138	147
Portugal	95	97	90	92	101	96	38
Republic of Moldova	23	23	24	25	25	25	21
Romania	115	112	109	106	103	103	86
Russian Federation	694	711	728	745	762	762	864
Serbia						37	
Serbia and Montenegro	45	44	44	43	43		39
Slovakia	26	26	27	25	28	39	14
Slovenia	7	7	7	7	7	7	10
Spain	139	141	144	144	145	138	110
Sweden	46	46	46	47	47	33	47
Switzerland	9	9	9	9	8	9	7
TFYR of Macedonia	9	9	9	9	9	6	8
Turkey	305	295	286	277	268	268	258
Ukraine	289	287	284	281	278	278	273
United Kingdom	108	107	99	96	95	95	79
North Africa	0	0	0	0	0	0	0
Remaining Asian areas	0	0	0	0	0	0	0
Baltic Sea	22	23	23	24	25	25	23
Black Sea	6	6	7	7	7	7	8
Mediterranean Sea	123	126	129	132	136	139	154
North Sea	50	51	52	54	55	56	52
Remaining N-E Atlantic Ocean	57	58	60	61	63	64	72
Natural marine emissions	0	0	0	0	0	0	0
Volcanic emissions	0	0	0	0	0	0	0
TOTAL	3553	3539	3493	3487	3487	3480	3247

Table A:7: National total emission and projections Emissions of Particulate Matter used for modelling at the MSC-W (Gg of PM_{10} per year)

Area/Year	2000	2001	2002	2003	2004	2005	2010GP
Albania	9	9	9	9	9	10	7
Armenia	1	1	1	0	0	0	7
Austria	44	46	46	46	47	45	43
Azerbaijan	7	6	6	6	5	6	30
Belarus	56	56	57	57	57	57	49
Belgium	66	64	63	61	62	43	48
Bosnia and Herzegovina	48	47	46	46	45	45	37
Bulgaria	94	94	93	92	92	92	80
Croatia	30	28	27	26	24	24	20
Cyprus	1	1	1	1	1	1	3
Czech Republic	44	47	50	56	52	34	52
Denmark	30	31	30	31	31	38	26
Estonia	51	42	35	30	30	26	18
Finland	54	54	55	55	58	53	37
France	549	541	519	531	532	508	281
Georgia	4	3	3	3	3	2	12
Germany	193	187	184	184	173	194	219
Greece	75	78	80	82	84	85	67
Hungary	60	57	56	61	60	64	37
Iceland	1	1	1	1	1	1	3
Ireland	20	19	18	18	18	15	18
Italy	273	258	243	229	214	213	182
Kazakhstan	56	53	51	48	45	45	22
Latvia	14	15	14	14	16	16	8
Lithuania	21	21	21	21	20	21	18
Luxembourg	4	4	4	4	4	4	4
Malta	1	1	1	1	1	0	1
Montenegro						12	
Netherlands	48	47	45	41	41	40	50
Norway	64	64	66	62	61	57	24
Poland	279	300	291	286	280	289	206
Portugal	119	127	117	118	128	124	48
Republic of Moldova	41	42	43	45	46	46	38
Romania	171	167	162	157	152	151	135
Russian Federation	1161	1220	1268	1336	1366	1366	1388
Serbia						74	
Serbia and Montenegro	93	91	89	88	86		76
Slovakia	45	46	41	38	41	50	22
Slovenia	9	9	9	9	9	9	14
Spain	208	209	215	214	213	178	160
Sweden	68	68	68	70	69	53	58
Switzerland	20	19	19	19	18	19	13
TFYR of Macedonia	21	21	20	20	19	19	16
Turkey	436	421	405	390	374	375	365
Ukraine	473	469	466	462	458	458	457
United Kingdom	180	176	160	155	154	150	130
North Africa	0	0	0	0	0	0	0
Remaining Asian areas	0	0	0	0	0	0	0
Baltic Sea	23	24	25	25	26	26	24
Black Sea	7	7	7	7	7	7	8
Mediterranean Sea	129	133	136	140	143	147	162
North Sea	52	54	55	57	58	59	55
Remaining N-E Atlantic Ocean	60	62	63	65	66	68	76
Natural marine emissions	0	0	0	0	0	0	0
Volcanic emissions	0	0	0	0	0	0	0
TOTAL	5519	5538	5484	5513	5501	5418	4852

APPENDIX B

Figures to Chapter 5

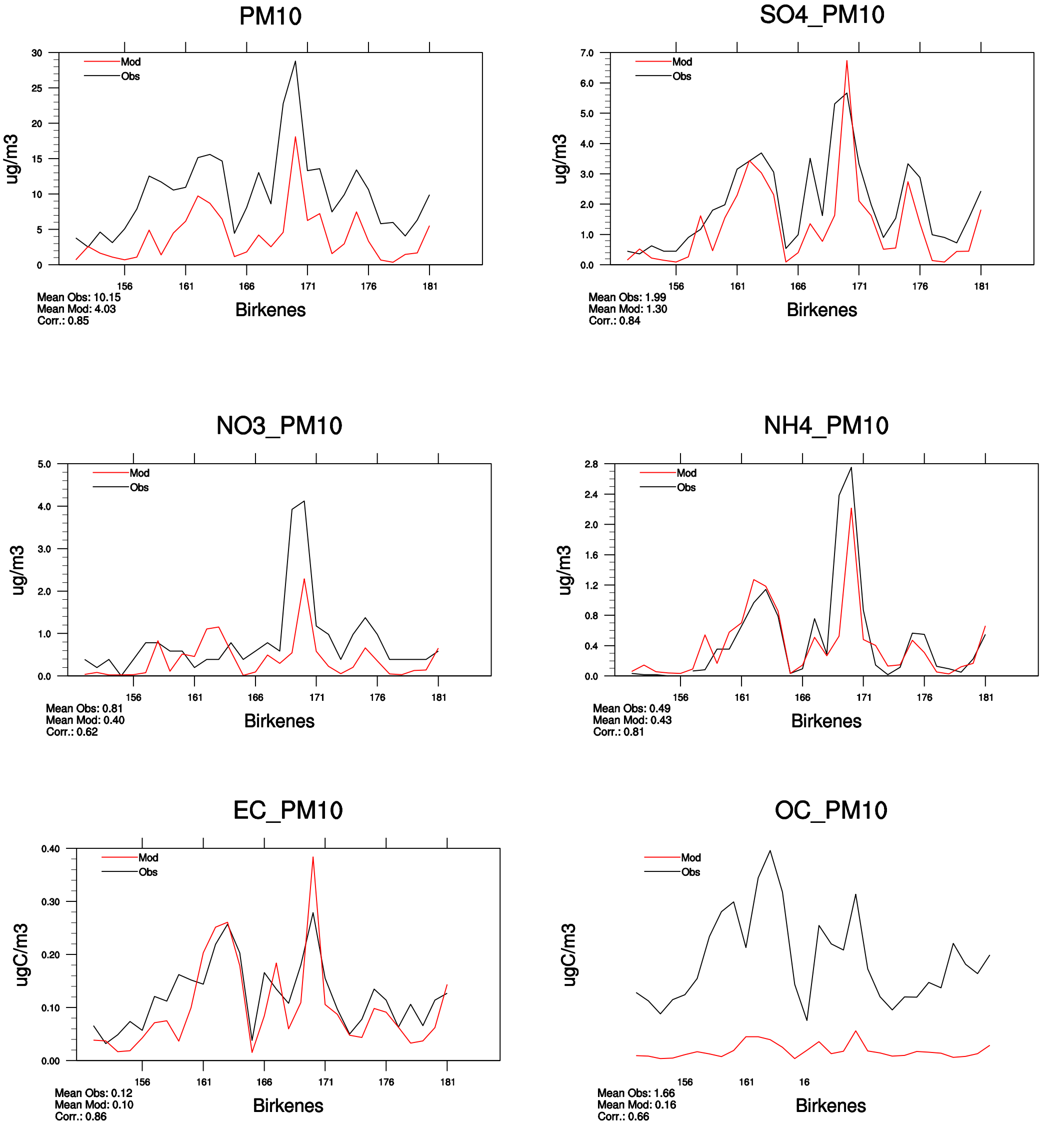
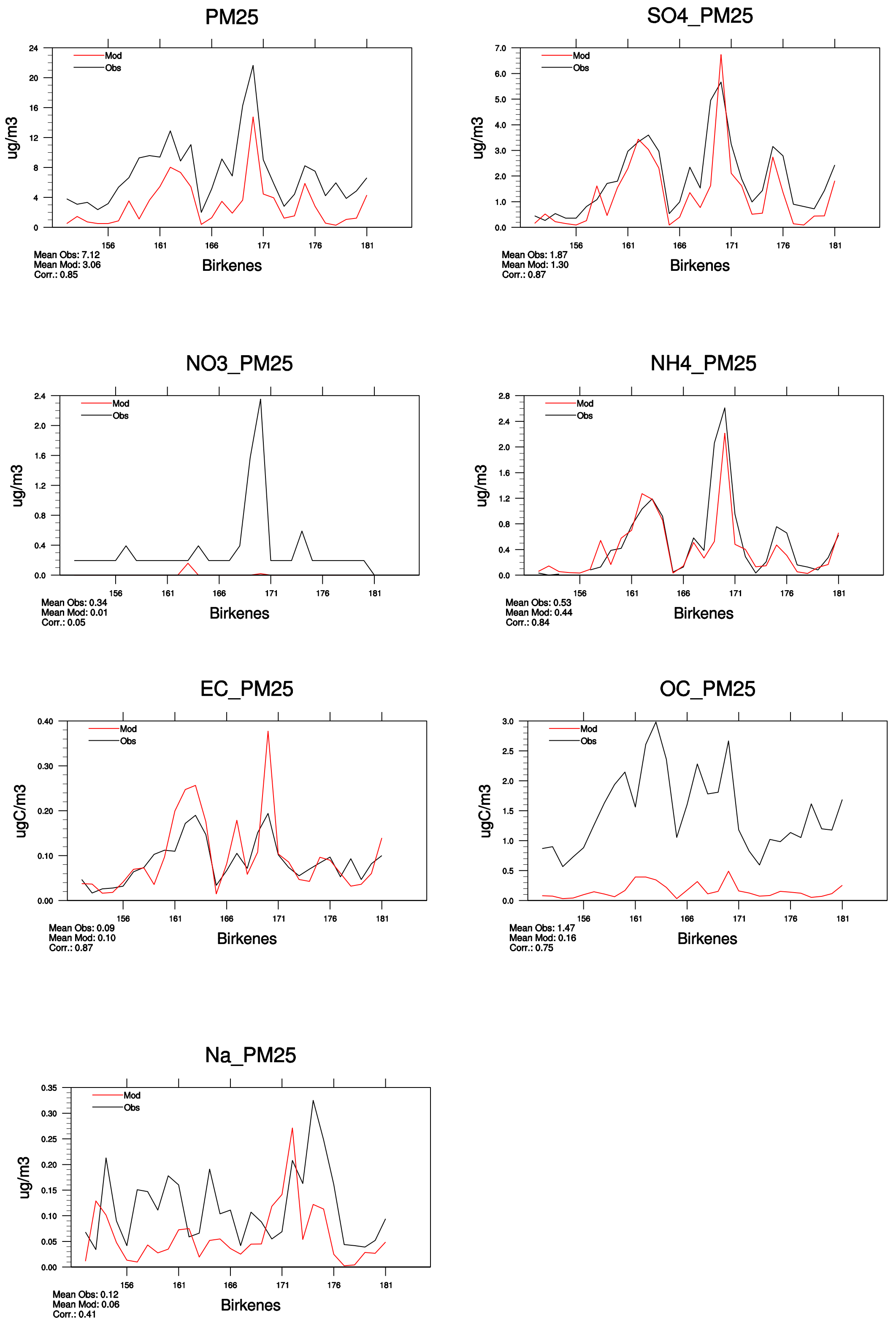


Figure A.1: Time-series of measured and modelled PM_{10} and its constituents for Birkenes, Norway (NO01). June, 2006.


PM25

Mean Obs: 7.12
Mean Mod: 3.06
Corr.: 0.85

SO4_PM25

Mean Obs: 1.87
Mean Mod: 1.30
Corr.: 0.87

NO3_PM25

Mean Obs: 0.34
Mean Mod: 0.01
Corr.: 0.05

NH4_PM25

Mean Obs: 0.53
Mean Mod: 0.44
Corr.: 0.84

EC_PM25

Mean Obs: 0.09
Mean Mod: 0.10
Corr.: 0.87

OC_PM25

Mean Obs: 1.47
Mean Mod: 0.16
Corr.: 0.75

Na_PM25

Mean Obs: 0.12
Mean Mod: 0.06
Corr.: 0.41

Figure A.2: Time-series of measured and modelled PM$_{2.5}$ and its constituents for Birkenes, Norway (NO01). June, 2006.

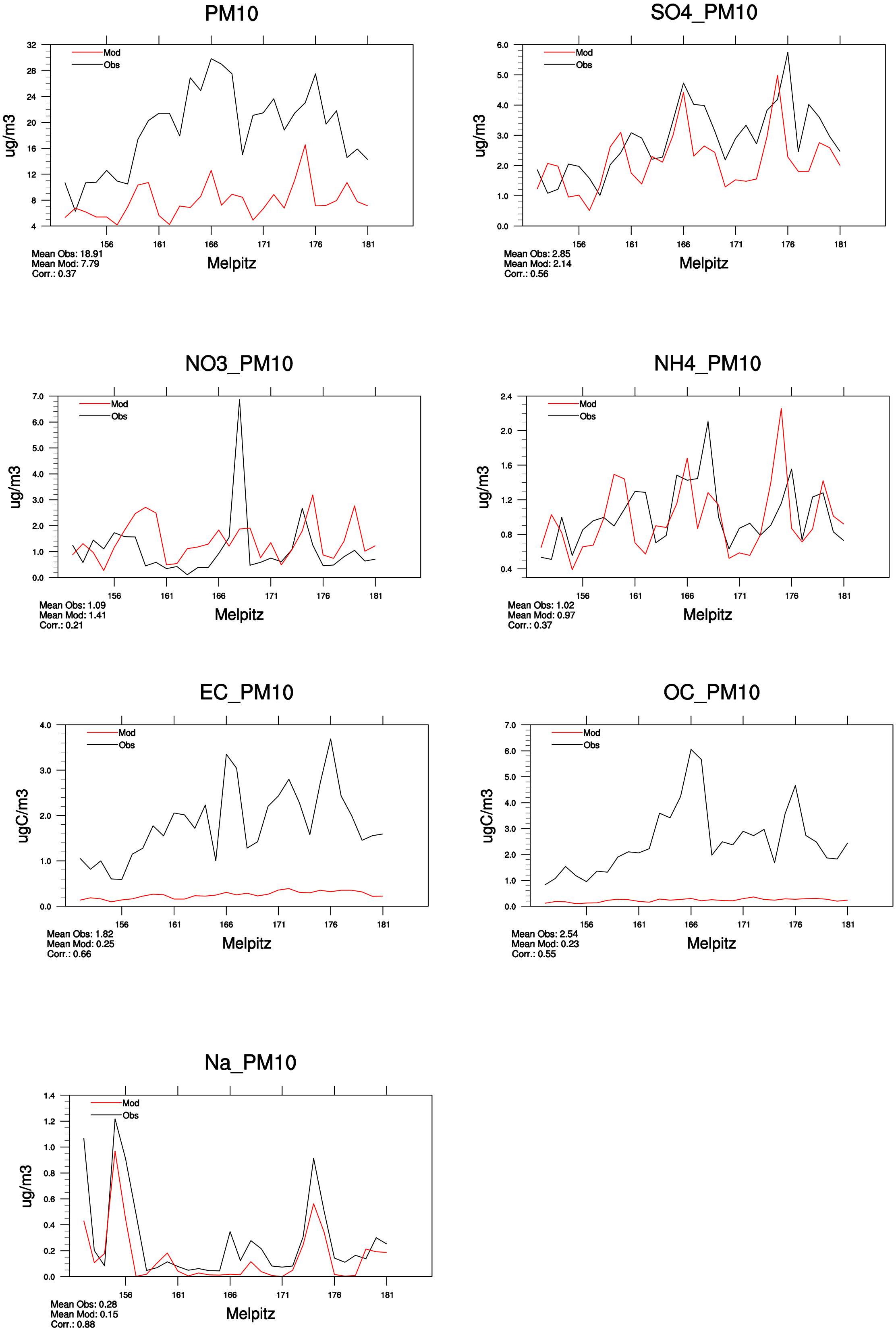


Figure A.3: Time-series of measured and modelled PM$_{10}$ *and its constituents for Melpitz, Germany (DE44). June, 2006.*

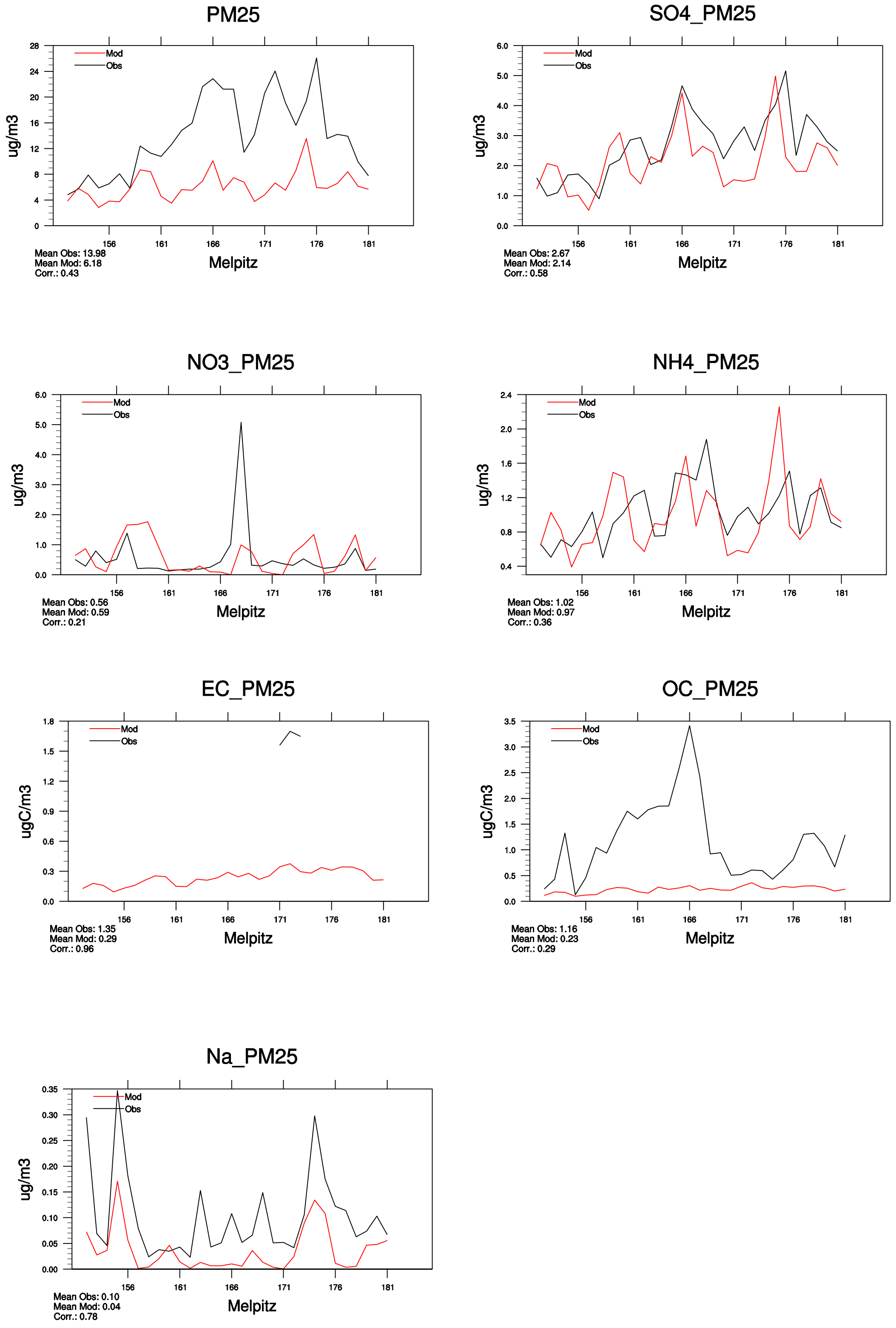


Figure A.4: Time-series of measured and modelled PM$_{2.5}$ and its constituents for Melpitz, Germany (DE44). June, 2006.

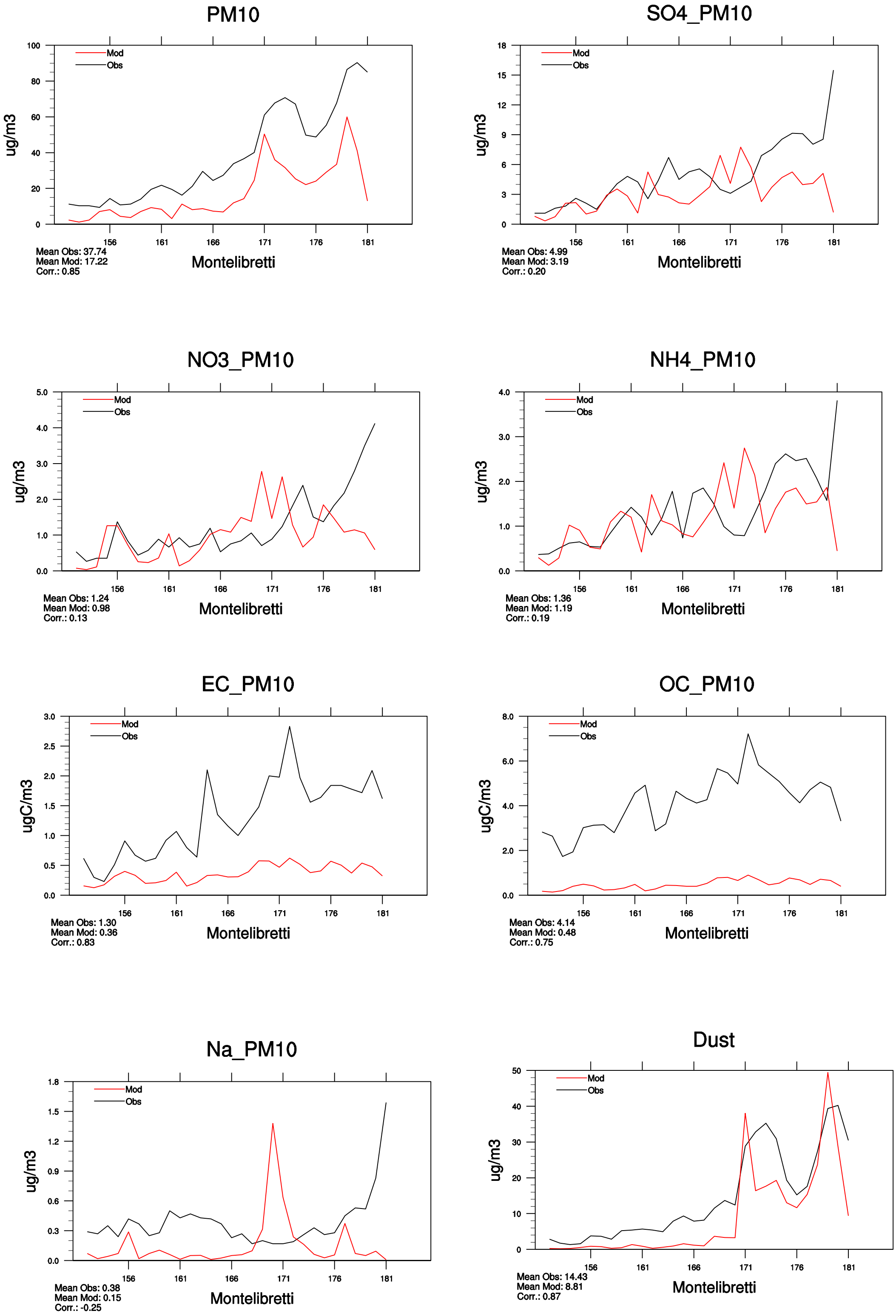


Figure A.5: Time-series of measured and modelled PM_{10} and its constituents for Montelibretti, Italy (IT01). June, 2006.

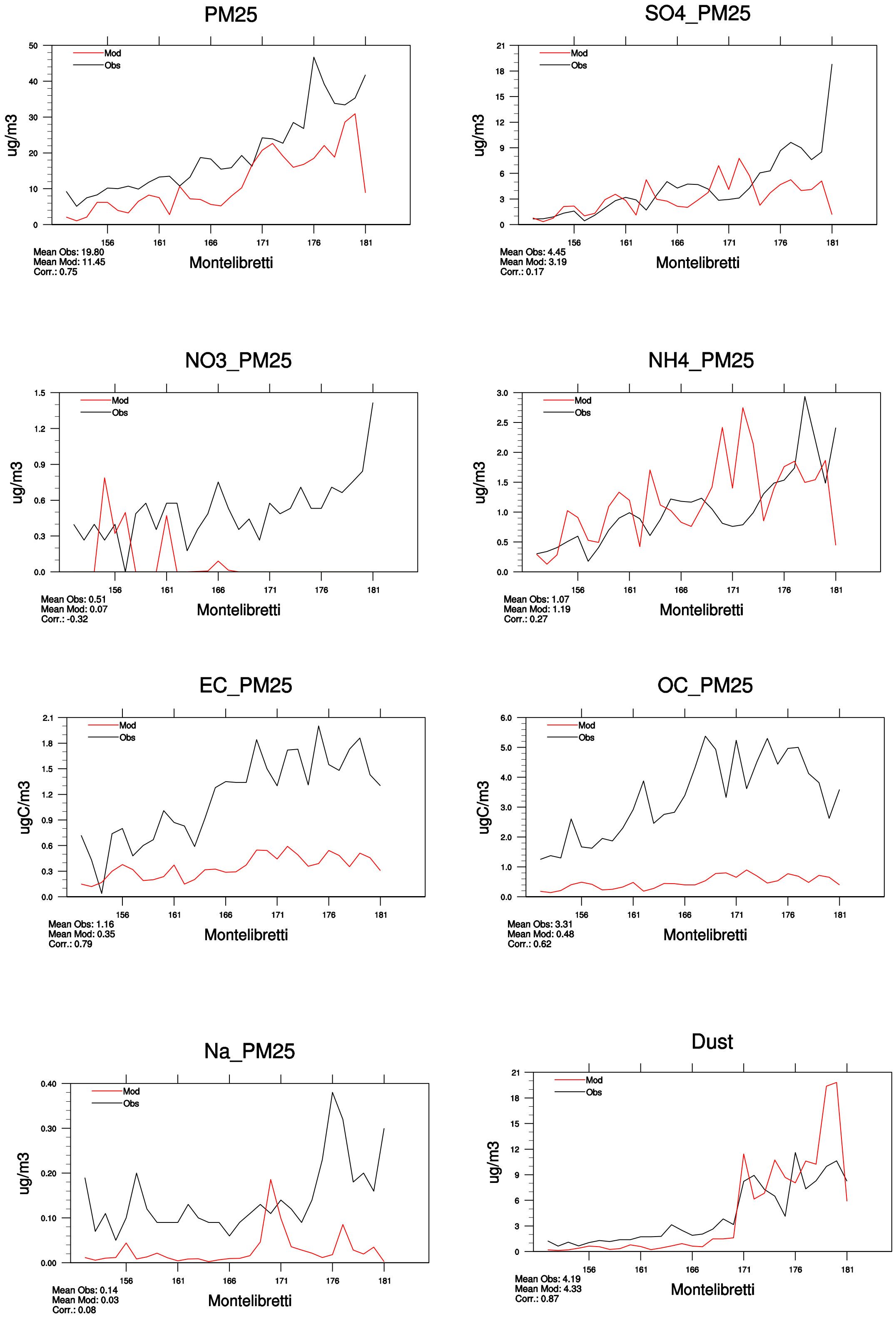


Figure A.6: Time-series of measured and modelled $PM_{2.5}$ and its constituents for Montelibretti, Italy (IT01). June, 2006.

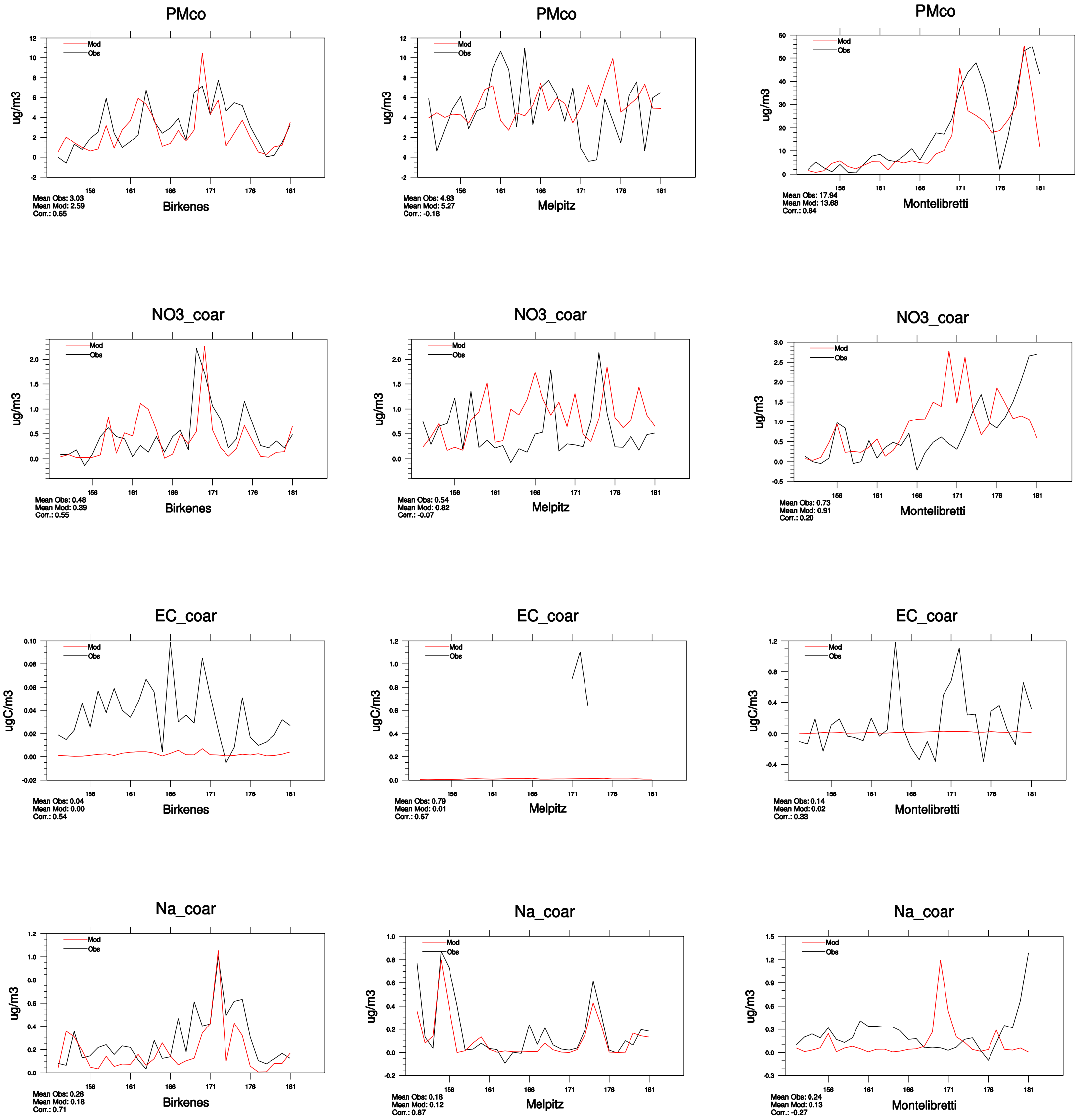


Figure A.7: Time-series of measured and modelled coarse PM and some of its constituents for Birkenes, Melpitz and Montelibretti. June, 2006.

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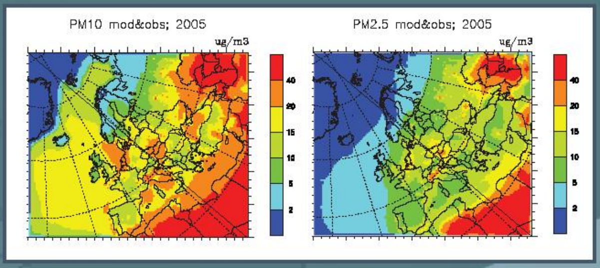

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