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

STATUS REPORT 4/2005

Transboundary particulate matter in Europe

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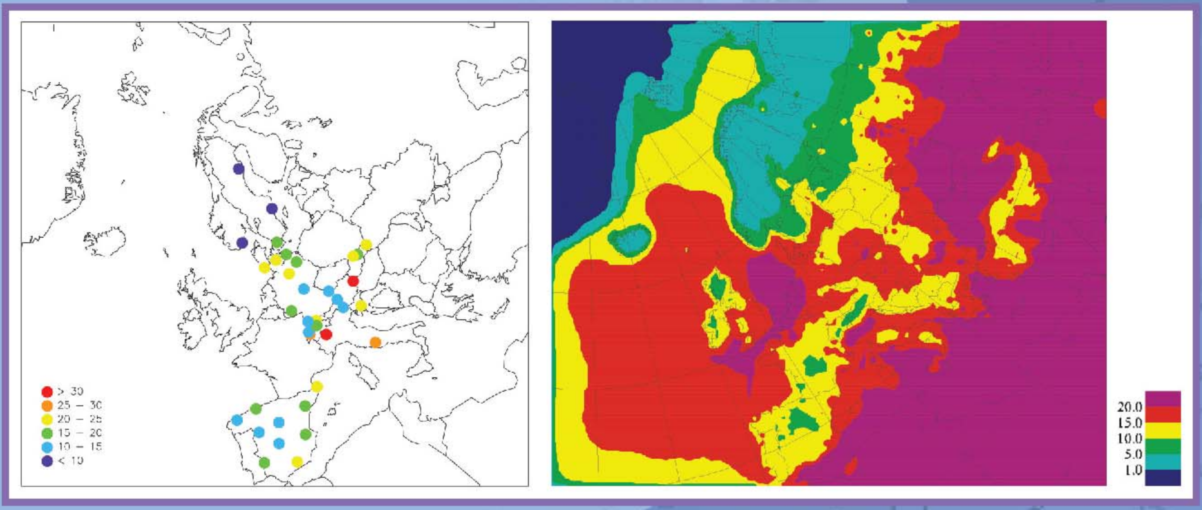

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EMEP Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe

Transboundary particulate matter in Europe
Status report 2005

Joint
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Report 2005

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Executive Summary

The objective of the present report is to provide an updated assessment of the particulate matter concentrations in 2003, made available through observations and modelling.

In 2003 measurements of PM_{10} were taken up by three more countries. Thus, ten countries currently report concentrations of PM_{10}, whereas seven of these measure $PM_{2.5}$ as well. Furthermore, two sites in Austria and Switzerland reported concentrations of PM_1 in addition to the concentrations of PM_{10} and $PM_{2.5}$. Although the number of countries and sites that reports concentrations of particulate matter increase year by year, the total number of 37 sites only covers a small part of Europe. Thus, effort should be made to increase the number of sites, and even more important, to increase the number of countries reporting concentrations of particulate matter.

None of the EMEP sites exceeded the annual limit value (40 $\mu g/m^3$) for the protection of human health, set by the EU in the first Daughter Directive as a goal for 2005. However, the limit value for daily averages of PM_{10} (50 $\mu g/m^3$) was exceeded at the Italian site IT04 on 87 days and on 49 days at the Austrian site AT02. The EU has so far set no limit value for $PM_{2.5}$ concentrations. However, five of the EMEP sites reported annual mean concentrations of $PM_{2.5}$ above the $PM_{2.5}$ standard of 15 $\mu g/m^3$ of the US EPA.

There are still only a few sites that have reported concentrations of particulate matter more than for a few years. However, based on measurements from the Austrian, the German and the Swiss sites, the concentration levels during 2003 are significantly higher compared to the past 4-5 years. This can be attributed to the extreme meteorological situation in Central Europe with high temperatures and low precipitation amounts during the summer season. The data shows that the increase in PM_{10} mainly can be attributed to the fine ($PM_{2.5}$) fraction, being consistent with the observed trends in secondary inorganics.

A chapter is included that addresses the concentration of particulate matter at the Akrotiri research station at the island of Crete (Greece). This site is situated in the Eastern Mediterranean area, which is a part of Europe currently not reporting PM to EMEP. Furthermore, the Eastern Mediterranean is situated on the outskirts of the domain area of the EMEP model, and receives a significant part of its aerosol loading from outside Europe. Thus, these measurements provide important information concerning the level, the seasonal variation, and the contributing sources of particulate matter in this area. The concentration of particulate matter was found to be higher during summer than during winter. This was attributed to the influence of Saharan dust events during summer and increased levels of precipitation during winter.

In addition to the obvious need of expanding the number of sites and countries measuring particulate matter (PM_{10}, $PM_{2.5}$ and PM_1) at sites also measuring the major chemical constituents of the particulate matter, more advanced measurements as defined by the new monitoring strategy (EB.AIR/GE.1/2004/5) are

fundamental. Through CREATE, which is a Thematic Project delivered under the 5th Framework Programme "Energy, Environment and Sustainable Development" in support of Global Monitoring for Environment and Security (GMES), advanced and otherwise unavailable European aerosol data has been made available through a database run by EMEP (www.nilu.no/projects/ccc/create/database.htm). Amongst the aerosol parameters linked to the database are: total aerosol number concentration, aerosol mass concentration ($PM_{10,}$ $PM_{2.5}$), aerosol particle size distribution, aerosol inorganic composition (nitrate, ammonium and sulphate), mass concentration of organic carbon, black carbon and total carbon and aerosol radiative data (aerosol absorption, scattering coefficient and aerosol optical depth at specified wavelengths).

The increased focus on the carbonaceous fraction of ambient aerosols, and the lack of such information motivated the EMEP EC/OC campaign, which took place from the 1st July 2002–1st July 2003. Levels of organic carbon, elemental carbon and total carbon obtained during this campaign were reported last year (EMEP Report 4/2004). In the present report, additional chemical analyses of the carbonaceous fraction of the filter samples from this campaign are presented, providing concentrations of water-soluble organic carbon (WSOC), water-insoluble organic carbon (WINSOC) and levoglucosan. These parameters provide additional information about the relative abundance of two groups of molecules with quite different chemical properties. The WSOC and WINSOC concentrations allow to investigate the residence time of aerosols in the atmosphere and forms a basis for providing more accurate estimates of the organic matter (OM) content of the aerosols. WINSOC was found to be the dominant fraction at 11 of the 13 European rural background sites investigated, ranging from 43%-83% of OC. The relative contribution of WSOC to OC ranged from 17%-57%.

Levels of the organic constituent levoglucosan, which is a source specific tracer of biomass burning, was quantified to address the spatial and seasonal variation of residential wood burning at 13 European rural background sites, and to estimate the relative contribution of wood smoke particles to the ambient level of PM_{10}. The presence of levoglucosan was demonstrated at all sites investigated. It is argued that the spatial variation reported can be attributed to population density and proximity to urban areas. Thus, the situation of the measurement site is important for the concentrations observed. Concentrations of levoglucosan was 1.3-5.9 times higher during winter compared to summer at the sites investigated, reflecting the increased impact from residential wood burning as the ambient temperature drops during winter. It is argued that wildfires contribute to the level of levoglucosan observed during summer, however, it is not known to what extent. While conversion factors from levoglucosan to organic matter concentrations are of a preliminary stage, the results indicate that on an annual basis particulate matter from residential wood burning accounts for about 2%-10% of PM_{10}.

In accordance with the work-plan for EMEP for 2005, the aerosol modelling activity at MSC-W has been focused on achieving mass closure. In addition, further investigation of the chemical composition of the particulate matter in different regions of Europe has been undertaken. There has been a particular effort in studying the contribution of particles from natural sources to the particle mass.

A preliminary parameterisation of wind blown dust has been implemented in the test version of the EMEP Unified model. To account for dust originating from the African continent, boundary conditions calculated using the global CTM model of the University of Oslo has been applied. At present monthly mean dust concentrations for 2000 are used. The first calculations performed with the model indicate that natural particles (mineral dust and sea salt) account for 5%-25% of PM_{10} in most of central Europe, in the non-coastal areas of Scandinavia and in the central and northern Russia. For the south and the south–east of Europe, the contribution of natural particles increases to 20-30%, whereas 50%-70% of PM_{10} can be attributed to natural particles in the southern parts of Spain, the southern parts of Ukraine and Russia, Caucasus and Kazakhstan.

The model performance for aerosols is continuously evaluated with observations of particulate matter. Comparison with EMEP measurements has shown that by including natural dust and water, associated with the particulate matter, the model calculations has improved with respect to both PM_{10} and $PM_{2.5}$. For PM_{10} the bias has decreased to -24%, whereas it has decreased to -15% for $PM_{2.5}$. The spatial correlation for PM_{10} is 0.73 and 0.8 for $PM_{2.5}$. By including natural dust and particle water the temporal correlation has improved for most of the sites as well. However, a proper validation concerning the models performance regarding the aerosols content of mineral dust and particle water is hampered by insufficient measurements. Thus, the calculated concentrations for dust and particle water are still rather uncertain.

According to the First Daughter Directive to the Air quality Framework Directive (Council Directive 1999/30/EC), the air quality standards for urban PM_{10} within EU are to be met by the member states by 1 January 2005. Estimates made by the EMEP model for 2000, 2002 and 2003 show that the air quality standard for urban PM_{10} within the EU is violated even in certain regional background areas, exceeding 50 $\mu g\ m^{-3}$ more than 35 days pr year. These areas in question are those close to Milan and Paris, the Po valley, the Benelux countries and the southern Spain. The EMEP model predicts that different sources, both anthropogenic and natural ones, are responsible for episodes of high PM_{10} concentrations and for exceeding the PM_{10} limit value.

1. Measurements of particulate matter

1.1 Measurements of particulate matter (PM$_{10}$, PM$_{2.5}$ and PM$_1$) in 2003

In 2003 measurements of PM$_{10}$ at EMEP sites were taken up by three more countries, namely Denmark, Sweden and Slovenia. Thus, ten countries currently report concentrations of PM$_{10}$, whereas seven of these measure PM$_{2.5}$ as well. Two more countries reported PM$_{2.5}$ for 2003, namely Italy and Sweden. Furthermore, two sites in Austria and Switzerland reported concentrations of PM$_1$ in addition to the concentrations of PM$_{10}$ and PM$_{2.5}$. From April 2003, continuous measurements of PM$_{10}$ have also been performed at Vreedepeel in The Netherlands. Although the number of countries and sites that reports concentrations of particulate matter increase year by year, the total number of 37 sites only covers a small part of Europe. Thus, effort should be made to increase the number of sites, and even more important, to increase the number of countries reporting concentrations of particulate matter. The annual averages of PM$_{10,}$ PM$_{2.5}$ and PM$_1$ are presented in Table 1.1. Maps of the annual averages for PM$_{10}$ and PM$_{2.5}$ can be seen in Figure 1.1 and Figure 1.2.

Table 1.1: Annual average of particulate matter measurements 2003

Code	PM$_{10}$	PM$_{2.5}$	PM$_1$	Code	PM$_{10}$	PM$_{2.5}$	PM$_1$
AT0002R	31.1	24.7	14.1	ES0010R	23.8	15.8	-
AT0004R	13.6	-	-	ES0011R	16.6	8.0	-
AT0005R	12.3	-	-	ES0012R	16.1	7.7	-
CH0002R	25.3	19.8	-	ES0013R	12.6	8.0	-
CH0003R	23.2	-	-	ES0014R	19.6	13.3	-
CH0004R	14.7	11.0	8.5	ES0015R	14.2	7.2	-
CH0005R	15.2	-	-	ES0016R	14.6	9.3	-
DE0002R	21.6	16.5	-	IT0001R	28.2	-	-
DE0003R	13.1	10.1	-	IT0004R	39.8	28.5	-
DE0004R	18.5	13.8	-	NO0001R	6.7	4.4	-
DE0005R	14.1	-	-	NO0099R	18.7	7.3	-
DE0007R	17.6	-	-	SE0011R	15.4	10.5	-
DE0008R	13.2	-	-	SE0012R	6.7	4.8	-
DE0009R	19.8	-	-	SE0035R	3.6	1.7	-
DE0041R	22.8	-	-	SI0008R	21.3	-	-
DK0005R	24.8	-	-	SK0004R	15.7	-	-
ES0007R	21.4	9.4	-	SK0005R	23.3	-	-
ES0008R	19.8	11.0	-	SK0006R	21.6	-	-
ES0009R	11.5	7.2	-				-

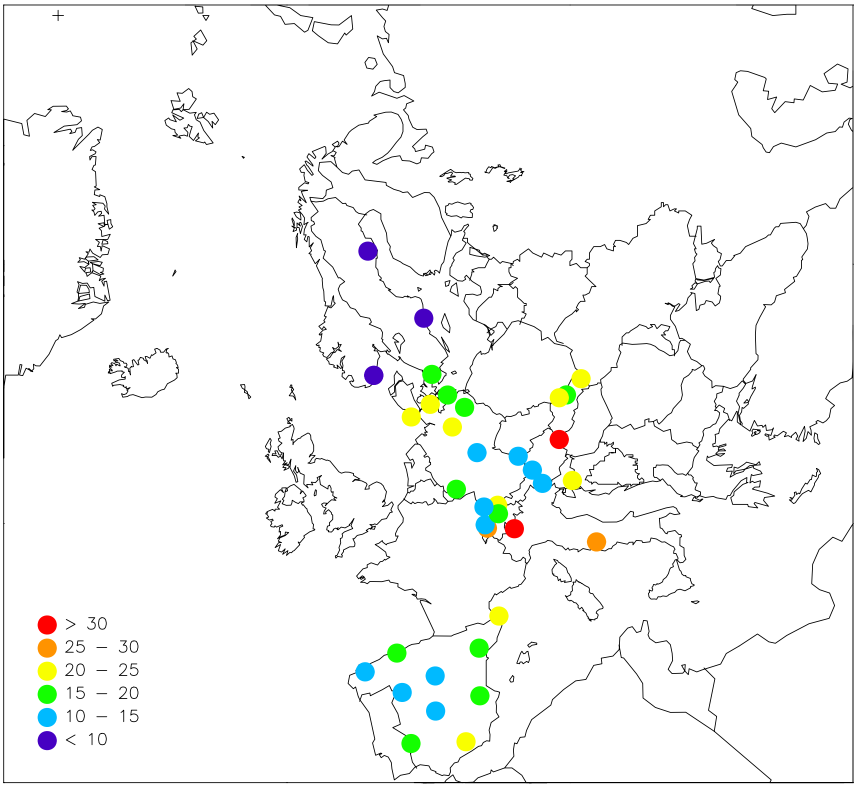


Figure 1.1: Annual 2003 averages PM_{10} mass measurements. Unit $\mu g/m^3$.

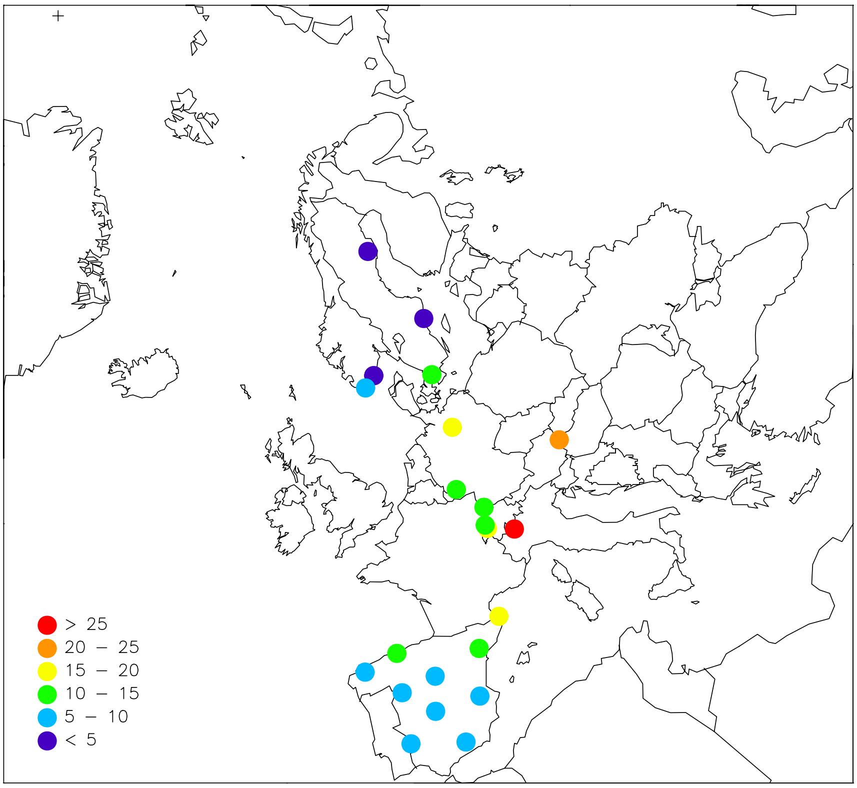


Figure 1.2: Annual 2003 averages $PM_{2.5}$ mass measurements. Unit $\mu g/m^3$.

None of the EMEP sites exceeded the annual limit value (40 µg/m^3) for the protection of human health, set by the EU in the first Daughter Directive as a goal for 2005. However, the limit value for daily averages of PM$_{10}$ (50 µg/m^3) was exceeded at the Italian site IT04 on 87 days and on 49 days at the Austrian site AT0002R. The EU has so far set no limit value for PM$_{2.5}$ concentrations. However, five of the EMEP sites reported annual mean concentrations of PM$_{2.5}$ above the PM$_{2.5}$ standard of 15 µg/m^3 of the US EPA.

At the Swiss site CH0004R, the annual mean of PM$_1$ accounts for 77% of PM$_{2.5}$, whereas the corresponding percentage for the Austrian site AT0002R is 57%. For the Austrian site, this indicates that a considerable amount of the mass of PM$_{2.5}$ actually can be found within a rather narrow size range between PM$_{2.5}$ and PM$_1$.

There are still only a few sites that have reported concentrations of particulate matter more than for a few years. However, based on measurements from the Austrian, the German and the Swiss sites, the concentration levels during 2003 are significantly higher compared to the past 4-5 years. This can be attributed to the extreme meteorological situation in Central Europe with high temperatures and low precipitation amounts during the summer season. The data shows that the increase in PM$_{10}$ mainly can be attributed to the fine (PM$_{2.5}$) fraction, being consistent with the observed trends in secondary inorganics. A more elaborate investigation of the effect climate variability on the concentrations of particulate matter is presented in EMEP Report 1/2005.

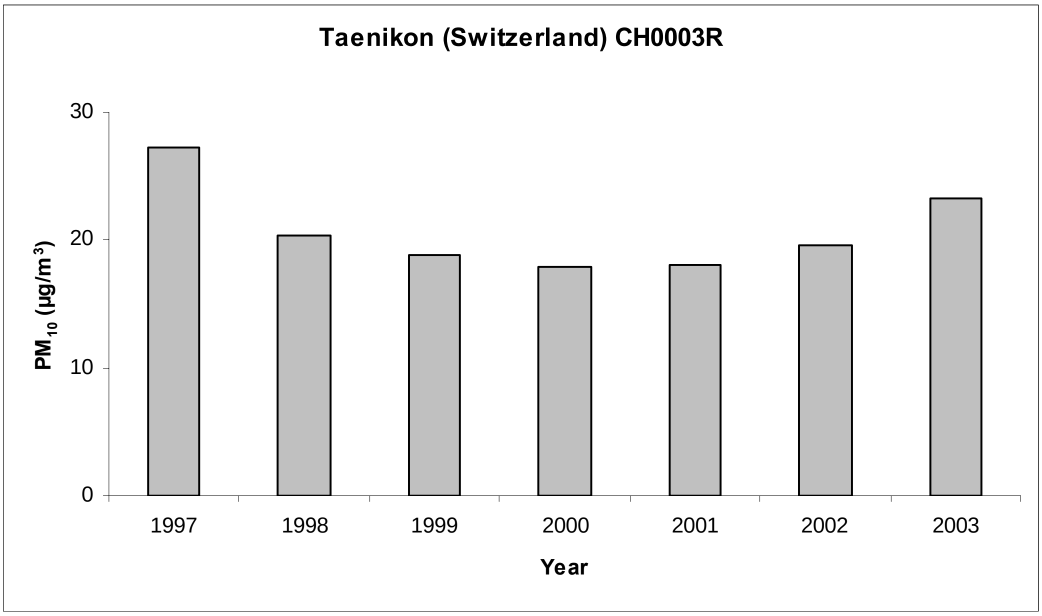


Figure 1.3: Time series of PM$_{10}$ at the Swiss site Taenikon (CH0003R).

1.2 Particulate matter measurements at the Akrotiri research station on the island of Crete, Greece

From Figure 1.1 it can be seen that the concentration of PM_{10} increases going from northern Europe to southern Europe. Furthermore, it becomes quite obvious by looking at the maps presented in Figure 1.1 and Figure 1.2 that the EMEP network does not cover a large part of Europe. Amongst the regions most poorly covered is the Eastern Mediterranean area.

In the following, data from continuous measurement of particulate matter at the Akrotiri research station at Crete (Greece), which is a rural site, is presented, providing information concerning level, seasonal variation and contributing sources of particulate matter from a part of Europe, which currently do not have EMEP sites reporting PM. Furthermore, this part of Europe is situated on the outskirts of the domain area of the EMEP model, and receives a significant part of its aerosol loading from outside Europe, thus, data on particulate matter from this area is important for the validation of the EMEP model as well. Of particular interest is the influence of Saharan dust outbreaks on the level of particulate matter in this region of Europe. In addition, it is argued that climatologically changes taking place in other parts of the world is likely to increase the particulate matter loading in the Eastern Mediterranean region, both through increased input from natural sources and from anthropogenic sources, making measurements in these areas even more important.

The mean concentration of PM_{10} during the measurement period was $35.1 \pm 17.9\ \mu g\ m^{-3}$ (Mean ± SD), whereas the mean concentration of $PM_{2.5}$ was $27.1 \pm 10.8\ \mu g\ m^{-3}$. It should be noted that the measurement period for PM_{10} (9 March 2003-10 March 2004) and $PM_{2.5}$ (10 March 2004-30 June 2005) are not overlapping. The concentrations of PM_{10} and $PM_{2.5}$ at the Akrotiri research station showed a large annual variability during the measurement period. This is illustrated for PM_{10} in Figure 1.4. The concentration of particulate matter was found to be higher during summer than during winter, which is in accordance with the majority of the rural environments in the Mediterranean region. Furthermore, the Saharan dust events are most frequent during summer, leading to elevated levels of both PM_{10} and $PM_{2.5}$. In addition, precipitation is more frequent during winter. This increases the scavenging of the particles the particles, reducing the ambient particulate matter concentration.

Throughout the year the Akrotiri site is dominated by strong north-westerly winds, which contributes significantly to the level of particulate matter, as it transports polluted air masses from the European continent. This is exemplified by elevated concentrations of PM_{10} during the period 15 November-5 December 2003, which is a period when the regional transport component dominates (Figure 1.4). However, the concentrations observed at Akrotiri during influence of north-westerly air masses are significantly lower than the concentrations observed during outbreaks of Saharan dust. In general, low concentrations of PM_{10}, and $PM_{2.5}$, is observed during winter storms and when air masses originate from the western parts of the Mediterranean Sea and the Atlantic Ocean (Figure 1.4).

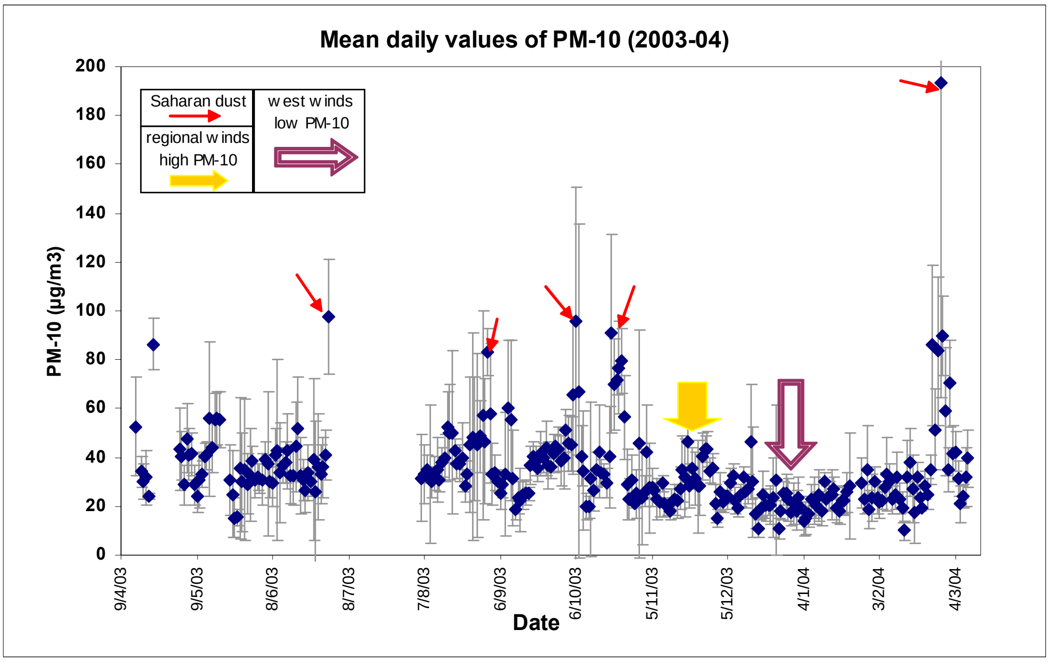


Figure 1.4: Daily mean PM$_{10}$ *concentrations at the Akrotiri research station during the period 9.04.03-04.03.04.*

The EU annual limit value for PM$_{10}$ (40 µg/m^3) to be met in 2005 was not exceeded at the Akrotiri site. However, the mean concentration reported for PM$_{2.5}$ violates the US EPA annual average PM$_{2.5}$ standard of 15 µg/m^3. Further details are found in the CCC particle report (EMEP/CCC, 2005).

1.3 CREATE – A European aerosol database

Despite the obvious need of expanding the number of sites and countries measuring particulate matter (PM$_{10}$, PM$_{2.5}$ and PM$_1$) and the major chemical constituents of the particulate matter, EMEP has to include more advanced measurements for the purpose of validation of the EMEP model as well. Previously, general recommendations have been made by EMEP/CCC (2003) to include advanced techniques providing more detailed particle properties, such as optical particle properties and particle number distributions, for a limited number of EMEP sites, as this would be of great benefit for understanding aerosol dynamics.

Through the CREATE project, more advanced and otherwise unavailable data from research groups in Europe has been made available. CREATE is a Thematic Project delivered under the 5th Framework Programme “Energy, Environment and Sustainable Development” in support of Global Monitoring for Environment and Security (GMES). GMES represents the main European contribution to the Group on Earth Observation (GEO). CREATE was established to address issues relating to measuring, modelling and monitoring of atmospheric aerosols within the priority theme: Global Atmosphere Monitoring, and the primary objective of the project has been to construct, use and deliver an European aerosol database. This database can be found at http://www.nilu.no/projects/ccc/create/database.htm and is constructed in order to make it easy both to submit and to access the data. The database is run by EMEP-CCC and is housed at NILU. Through CREATE a formal agreement has been sanctioned between NILU and JRC at Ispra, which hosts the WMO-GAW World Data Centre for Aerosols (WDCA), on establishing a coordinated dataflow in order to facilitate data submission. This means that aerosol data only needs to be submitted to the EMEP–CCC database, as the infrastructure for EMEP data flow is used to transfer submitted data to the WDCA site as well (http://ies.irc.cec.eu.int/wdca). Obviously this represents a major achievement towards harmonisation for archival of aerosol data at the European level, and it minimises the duplication of databases and for data providers and data users.

Data linked to the following aerosol parameters have been submitted to the database:

- Total aerosol number concentration
- Aerosol (PM_{10}, $PM_{2.5}$) mass concentration
- Aerosol particle size distribution
- Aerosol inorganic composition (nitrate, ammonium and sulphate)
- Mass concentration of organic carbon, black carbon and total carbon
- Aerosol radiative data (aerosol absorption, scattering coefficient and aerosol optical depth at specified wavelengths).

Table 1.2 shows the data submitted to the database by the end of March 2005. All the data can be downloaded from the Internet at http://www.nilu.no/projects/ccc/create/database.htm.

Technical information on instrumentation, techniques, meta data, references, data sources and comments for selected aerosols parameters can be found in Appendix B of the CREATE Final Report, which is accessible from the CREATE web site (http://macehead.nuigalway.ie/create).

Table 1.2: Aerosol data submitted to the database.

Station	**Component**	**Instrument**	**Time period**
CH01 Jungfraujoch	Aerosol absorption coefficient	Aethalometer	1995-2003
	Aerosol light scattering/backscattering coefficient	Nephelometer	1995-2003
	Aerosol number concentration	CPC	1995-2003
	Aerosol number distribution	SMPS	1997-1998
	Aerosol composition	Filterpack	1999-2001
DE43 Hohenpeissenberg	Particle number distribution Total particle number	DMPS	1998-2000
DE44 Melpitz	Particle number distribution Total particle number	DMPS	1996-1997 2003
	Chemical composition of PM10	High volume PM10 sampler	2000
FI50 Hyytiälä	Particle number distribution Total particle number	DMPS	1996-2003
	Particle mass	3-stage impactor	1999,2000
FI96 Pallas	Particle number distribution	DMPS	2000-2003
	Aerosol number concentration	CPC	2000-2003
	Aerosol light scattering coefficient	Nephelometer	2002
GR02 Finokalia	Aerosol number concentration	CPC	1997
	Absorption coefficient	PASP	2000
	Aerosol light scattering coefficient	Nephelometer	2002
	Suspended particulate matter	Filterpack	1998-1999
	Aerosol inorganics	Filterpack	1996-1999
IE31 Mace Head	Average attenuation coefficient	Aethalometer	1989-2002
	Particle number distribution	SMPS	2002-2004
	Aerosol numberconcentration	CPC	2000-2004
	Aerosol light scattering coefficient	Nephelometer	2000-2004
NL11 Cabauw	Nitrate mass distribution	SJAC-MOI	2002
NO01 Birkenes	Particle number distribution	DMPS	2002-2003
	EC/OC	KFG	2001-2003
	Aerosol inorganics	filterpack	1972-2003
NO42 Zeppelin	Particle number distribution	DMPS	2000-2004
	Aerosol inorganics	filterpack	1993-2003

1.4 Organic carbon concentrations

The increased focus on the carbonaceous fraction of ambient aerosols, and the lack of data concerning this parameter in Europe in general, initiated the EMEP EC/OC campaign, which took place from the 1st July 2002-1st July 2003. Levels of organic carbon, elemental carbon, total carbon and PM_{10} obtained during this campaign were reported last year (EMEP/CCC, 2004). According to the monitoring requirements for the various levels in the EMEP monitoring strategy (EB.AIR/GE.1/2004/5), providing levels of EC and OC is defined as level two activities. In the following, additional chemical analyses of the carbonaceous fraction of the filter samples from this campaign are presented, providing concentrations of water-soluble organic carbon (WSOC), water-insoluble organic carbon (WINSOC) and levoglucosan. Whereas analysis of WSOC and WINSOC is specifically listed as level three activities in the EMEP monitoring strategy, this is currently not the case for levoglucosan. Nevertheless, levels of levoglucosan, along with WINSOC and WSOC, should be regarded as more specified aerosol data providing additional information important for EMEP's work on aerosols.

1.4.1 Levels and relative contributions of WINSOC and WSOC at rural background sites in Europe

The organic carbon fraction of ambient aerosols contains a high number of individual organic compounds. Thus, a full characterization of this carbonaceous subfraction on the molecular level for the purpose of mass-closure is an insurmountable task. This great diversity has necessitated the implementation of operational definitions for bulk fractions of the carbonaceous material, such as elemental carbon (EC) and organic carbon (OC). At present, EC and OC are commonly reported in literature, although the wide range of different analytical techniques applied, and the lack of standardized sampling procedures, introduce a significant level of uncertainty to the results obtained.

The OC fraction is commonly separated according to its solubility in water. The resulting subfractions, being water-insoluble organic carbon (WINSOC) and water-soluble organic carbon (WSOC), are of interest for a number of reasons: Firstly, WSOC seems to influence the ambient aerosols ability to act as cloud condensation nuclei (CCN) (Novakov and Corrigan, 1996), and it contributes to the aqueous phase chemistry in clouds and fogs. Secondly, more detailed knowledge concerning which are the constituents of the WINSOC and the WSOC fractions, including their chemical and physical properties, will contribute to clarify if any negative health effects can be associated with these carbonaceous subfractions. Furthermore, it will add to the present knowledge of the chemical composition of the fine tropospheric aerosol and its sources. Finally, dividing OC into WSOC and WINSOC will provide more accurate estimates of the concentrations of carbonaceous matter in the atmosphere. This is particularly important, as the carbonaceous mass of ambient aerosols probably will become even more important in the future, due to the current abatement strategies.

The analytical method used to quantify EC, OC, WSOC and WINSOC only accounts for the carbon content of the organic constituents of the aerosol. Thus, a conversion factor converting levels of OC (μg C m^{-3}) to levels of organic matter (OM) (μg m^{-3}) is needed in order to account for the oxygen, hydrogen, nitrogen and sulphur associated with the molecules. This conversion step is recognized as one of the most important uncertainty factors in mass closure calculations. By segregating between WSOC and WINSOC, and by using conversion factors specific for each of these carbonaceous subfractions, more accurate concentrations of the OM can be obtained compared to using one conversion factor for OC. This can be attributed to the large difference between the conversion factors used for each of these two groups. In addition, estimates of water-soluble organic material (WSOM) and water-insoluble organic matter (WINSOM) are provided. However, it has to be recognized that the uncertainties associated with the conversion factors for WINSOC and WSOC still could bias the results.

In the present study, concentrations of WSOC and WINSOC are reported for 13 European rural background sites. Furthermore, levels of WSOM and

WINSOM are calculated. Finally, a comparison of different ways to calculate OM is reported.

The ambient aerosol content of WINSOC and WSOC was quantified using filter samples collected during the EMEP EC/OC campaign. A total of 71 samples from 13 of the 14 sites included in the campaign were analysed. An overview of the sampling sites included in the campaign, their site category and the sampling equipment used can be found in Table 1.5. For more information concerning the sampling sites and the sampling strategy the reader is referred to EMEP/CCC 3/2004.

1.4.2 Concentrations of WINSOC and WSOC and their relative contribution to organic carbon

The concentrations of WSOC and WINSOC at the sites investigated are shown in Table 1.3. The samples are not collected on the same dates. Further, there are an unequal number of samples collected during summer and winter (Table 1.3). Thus, the results reported represent a snapshot of which concentrations of WINSOC and WSOC can be encountered at the sites investigated.

The lowest mean concentration of both WINSOC (0.6 µg C m^{-3}) and WSOC (0.1 µg C m^{-3}) was reported for the Irish site. The highest concentration for WINSOC was reported for the Italian site San Pietro Capofiume (4.9 µg C m^{-3}), whereas the highest concentration of WSOC was reported for the Italian site Ispra (3.6 µg C m^{-3}).

Table 1.3: Concentrations of WSOC and WINSOC in PM$_{10}$, and relative contribution of WSOC and WINSOC to OC in PM$_{10}$.

Site	Number of samples	Samples Winter : Summer	WSOC (µg C m^{-3})	WINSOC (µg C m^{-3})	WSOC/OC (%)	WINSOC/OC (%)
AT02	n = 5	3 : 2	2.9	3.5	41	59
BE02	n = 4	2 : 2	2.2	3.2	41	59
CZ03	n = 6	6 : 0	1.2	2.5	33	67
DE02	n = 11	6 : 5	1.4	1.7	46	54
GB46	n = 5	5 : 0	0.3	0.7	31	69
IE31	n = 4	2 : 2	0.1	0.6	17	83
IT04	n = 5	3 : 2	3.0	4.9	38	62
IT08	n = 5	3 : 2	3.6	3.7	49	51
NL09	n = 3	2 : 1	1.5	1.5	49	51
NO01	n = 4	4 : 0	0.8	0.7	52	48
PT01	n = 11	6 : 5	1.5	1.1	57	43
SE12	n = 4	2 : 2	0.8	1.2	40	60
SK04	n = 4	2 : 2	1.9	4.3	30	70

WINSOC was the dominant subfraction at all sites investigated, except at the Norwegian and the Portuguese sites, ranging from 43 – 83% of OC (Table 1.3 and Figure 1.5). The highest relative contribution of WINSOC was observed at the Irish site (Mace Head), accounting for 83% of the OC. This finding is in accordance with what has been reported by Krivácsy et al. (2001), finding that

WINSOC was the major carbonaceous subfraction at Mace Head, accounting for 59% of OC. In their study, the high relative contribution of WINSOC was related to the less oxidative atmosphere over oceans. Furthermore, the higher frequency of cloud formation over oceans reduces the residence time of the water-soluble compounds in the marine environment compared to the continental environment. It has been suggested that primary biological aerosol particles contributes to the WINSOC material observed at Mace Head (Kleefeld et al., 2002).

A high relative contribution of WINSOC can also be expected at sites situated close to urban areas due to the impact of emissions from vehicle exhaust. Low WSOC/OC ratios have been reported for several sites influenced by traffic; a ratio of 12.5% (Ruellan and Cachier, 2001) and ratios between 14% and 26% (Mader et al., 2004) have been reported for curbside sites. The most likely explanation for this is low levels of polar oxygenated compounds in vehicular exhaust and the short distance from the source to the sampling site, which leaves little time for oxidation of aerosols and precursor compounds. WINSOC is quite clearly the dominant carbonaceous subfraction at the UK site (69%), the Italian site Ispra (62%), the Belgian site (59%) and the Austrian site (59%) (Table 1.3 and Figure 1.5), which all are located quite close to major urban areas. However, equally high percentages of WINSOC are reported for the Swedish site (60%), the Czech site (67%) and the Slovakian site (70%) as well, which are sites situated further away from urban areas.

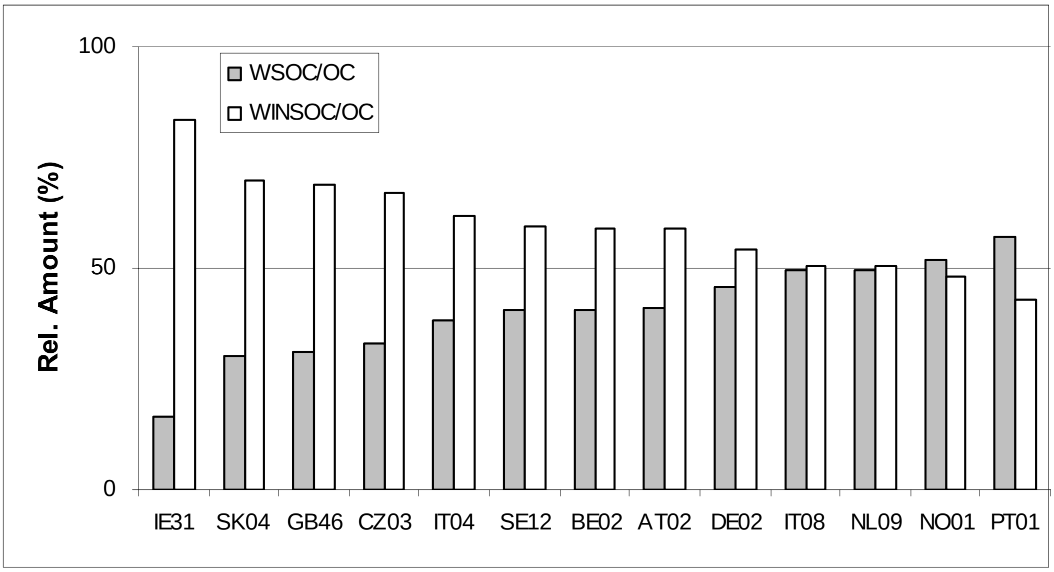


Figure 1.5: Mean WSOC/OC and WINSOC/OC percentages.

The relative contribution of WSOC to OC ranged from 17 - 57% for the sites investigated (Table 1.3 and Figure 1.5). WSOC was the dominant carbonaceous subfraction at only two of the sites, namely at the Norwegian site (52%) and at the Portuguese site (57%). The major source of particles at the Norwegian site is long-range transported particles. Thus, oxidation of particulate carbonaceous material during long-range atmospheric transport might be a possible explanation for at least a part of the WSOC concentration observed at this site.

Another important source of WSOC is wood burning. Mayol-Bracero et al. (2002) reported that 65% of OC could be attributed to WSOC when studying the chemical composition of aerosols in the Amazon region during the burning season, whereas 77% of OC could be attributed to WSOC in an area heavily influence by residential wood burning in Norway (Yttri et al., 2005). Indeed, the presence of levoglucosan, which is a tracer of particulate emissions from wood burning, has been demonstrated at all sites participating in the EMEP EC/OC campaign (see Chapter 2 in this report). Based on ambient aerosol concentrations of levoglucosan, particulate matter originating from wood burning was estimated to account for 1.7%-9.0% of the ambient PM_{10} concentration on an annual basis for the sites included in that study. Thus, the relative contribution of WSOC from wood burning to the ambient aerosol content of WSOC is suspected to be substantial. Crude estimates of how much of the ambient aerosol content of WSOC originates from wood burning can be provided combining levels of PM_{Wood} presented in Table 1.6 and emission ratios of WSOC from wood burning. Unfortunately, emission ratios of WSOC for wood burning are not readily available, although they can be deducted from studies reported in the literature, such as that of Mayol-Bracero et al. (2002) and Yttri et al. (2005). Another important source of WSOC is secondary organic aerosols (SOA). Furthermore, highly water-soluble sugars and sugar-alcohols have been associated with primary biological aerosol particles (PBAP) (Graham et al., 2003).

1.4.3 Ambient concentrations of WSOM and WINSOM and their relative contribution to organic matter

A factor of 2.1 was used to convert WSOC to WSOM, whereas a factor of 1.3 was used to convert WINSOC to WINSOM. The conversion factor used to convert WSOC to WSOM is based on the study by Kiss et al. (2002). To our knowledge their study is the only one who has provided experimentally derived conversion factors for WSOC for a European rural background site. The calculated concentrations of WINSOM and WSOM are presented in Table 1.4. As can be seen, WSOM dominates the OM fraction at the majority of the sites, ranging from 24-68%.

As previously mentioned, converting OC to OM is recognized as one of the most important factors of uncertainty in mass closure studies. In the present study we have used conversion factors for WSOC and WINSOC instead of for OC to exemplify how this uncertainty can be reduced. The benefit of this approach becomes apparent when considering how the relative contribution of WINSOC and WSOC to OC varies from site to site (Table 1.3 and Figure 1.5) and how great the difference between the conversion factors for these two subfractions are. The concentrations of OM provided by this approach, using a factor of 2.1 to convert WSOC into WSOM and a factor of 1.3 to convert WINSOC into WINSOM, is listed in Table 1.4.

Table 1.4: Concentrations of WSOM and WINSOM in PM_{10}, and relative contribution of WSOCM and WINSOM to OM in PM_{10}.

Site	WSOM (µg m^{-3})	WINSOM (µg m^{-3})	OM (µg m^{-3})	WSOM/OM (%)	WINSOM/OM (%)
AT02	6.1	4.6	10.7	57	43
BE02	4.6	4.1	8.7	53	47
CZ03	2.6	3.2	5.8	45	55
DE02	3.0	2.2	5.2	58	42
GB46	0.7	1.0	1.7	42	58
IE31	0.2	0.8	1.0	24	76
IT04	6.3	6.4	12.7	49	51
IT08	7.6	4.8	12.4	61	39
NL09	3.2	2.0	5.2	61	39
NO01	1.6	0.9	2.6	63	37
PT01	3.1	1.4	4.6	68	32
SE12	1.7	1.6	3.3	52	48
SK04	3.9	5.6	9.5	41	59

- OM is calculated by according to the following equation: OM = 2.1* WSOC + 1.3 * WINSOC

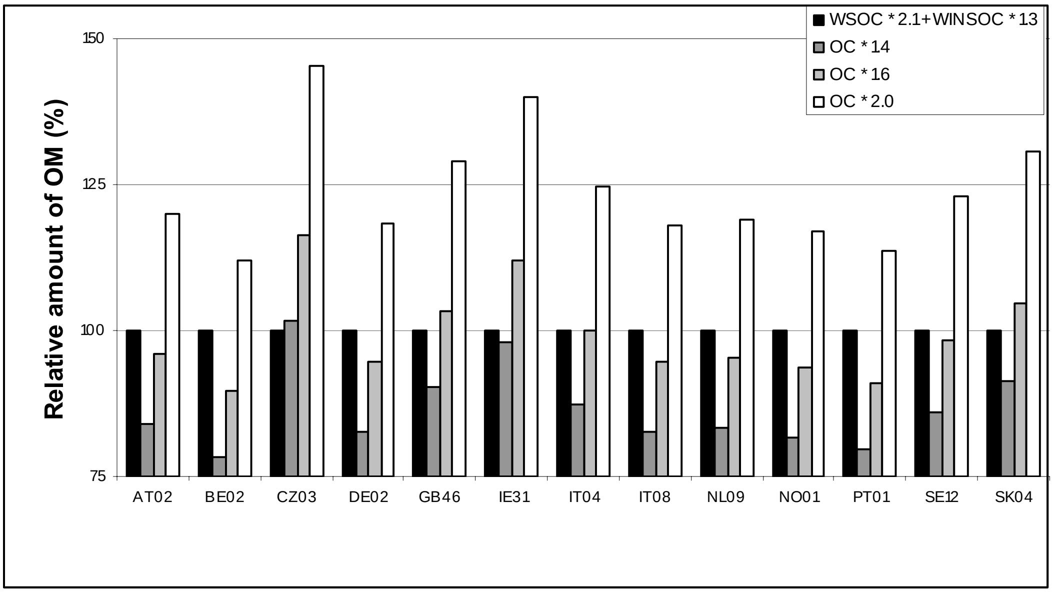


Figure 1.6: Results from calculation of OM by different approaches. The levels of OM obtained by using conversion factors for WSOC (2.1) and WINSOC (1.3) is defined as 100%.

The results presented in Figure 1.6 illustrate the difference obtained by using various approaches to calculate OM. It is assumed that applying conversion factors for subfractions of OC to calculate OM (OM = WSOC x 2.1 and WINSOC x 1.3) currently is the best approach, thus, the results obtained using this method is defined as 100%. Furthermore, OM has been calculated using conversion factors commonly cited and used in the literature, namely 1.4, 1.6 and 2.0. Using a factor of 1.4 generally underestimates the level of OM, accounting for 87% ± 7 (Mean ± SD) of the reference method for all the sites investigated. The only exception is the Czech site. Moreover, the high relative contribution of WINSOC to OC at the Czech site and at the Irish site actually favours a factor of 1.4 compared to the factors of 1.6 and 2.0. Using a factor of 1.6 both overestimates and underestimates the level of OM depending on the site addressed. Still, the results obtained using this factor comes closest (99% ± 8) to that of using conversion factors for WSOC and WINSOC. Applying a factor of 2.0 consequently overestimates the level of OM, providing estimates of 124% ± 10 compared to the reference approach. This exercise obviously illustrates the importance of a priori knowledge of which subfractions of OC prevail.

Despite the fact that this approach takes into account the relative contribution of WSOC and WINSOC to OC at the different sites, there are still uncertainties related to the conversion factors applied. Although the conversion factor for WSOC is experimentally obtained from a rural background site in Europe, it can be questioned to what extent it is applicable for a wider range of European sites, which can be influenced by other sources. Furthermore, Kiss et al. (2002) states that 2.1 is a lower estimate for the WSOC fraction. Obviously, more work is needed to provide conversion factors for a wider range of sites than what currently is the case.

1.4.4 Conclusion

The mean ambient aerosol concentration of WINSOC ranged from 0.6 µg C m^{-3} at the Irish site to 4.9 µg C m^{-3} at the Italian site Ispra. For WSOC the corresponding range was from 0.1 µg C m^{-3} at the Irish site to 3.6 µg C m^{-3} at the Italian site San Pietro Capofiume. WINSOC was the dominant subfraction at all sites investigated except at two sites, ranging from 43%-83%.

Converting WSOC to WSOM by using a conversion factor of 2.1, and WINSOC to WINSOM by using a conversion factor of 1.3, WSOM was found to dominate the OM fraction at the majority of the sites, ranging from 24%-68%.

It is argued that adding levels of WSOM and WINSOM is the best way to provide concentrations of OM in ambient aerosols. The advantage of this approach is that it accounts for the relative contribution of WSOM and WINSOM to OM, which was found to vary considerably between the 13 European background sites investigated. If concentrations of WSOM and WINSOM are not available, the next best approach to provide levels of OM was obtained by multiplying OC by a factor of 1.6, compared to using conversion factors of 1.4 and 2.0. (This conclusion is valid given that a factor of 2.1 is used to convert WSOC to WSOM and a factor of 1.3 is used to convert WINSOC to WINSOM.)

1.5 Addressing the impact of residential wood burning at rural background sites in Europe

Wood smoke can be a significant source of fine atmospheric particles. In communities where wood burning is used for residential heating, wood smoke can even dominate the fine particle burden (Fine et al., 2002a). The small size of particles originating from wood burning enables them to remain in the atmosphere for up to one week on average and to be transported over long distances. Their small size, equivalent aerodynamic diameter typically being less than 1 µm

(Kleeman et al., 1999), also makes them potentially more harmful, as they can penetrate into the alveolar region of the respiratory system. Wood smoke particles have a high content of carbonaceous material, and organic carbon is the dominating fraction, typically accounting for more than 70% of the aerosol mass ($PM_{2.5}$) (Fine et al., 2002a; Seinfeld and Pandis, 1998). Several studies have focused on wood burning because wood smoke has a high content of polycyclic aromatic hydrocarbons, which are known to be both mutagenic and carcinogenic (Hawthorne et al., 1992).

Furthermore, energy sources other than fossil fuel is gaining importance on a global scale. This is both due to increased energy prices and the fact that alternative sources of energy have to replace energy based on fossil fuel, as this production will decline significantly within the next decades. In addition, CO_2 emissions from wood burning are not included amongst the greenhouse gases such as CO_2 from fossil fuel. Thus, it can be speculated that the use of firewood as an energy source may increase.

For the reasons mentioned, a reliable tracer of particulate emissions from residential wood burning is warranted. Currently, levoglucosan is the most recognized molecular marker for tracing emissions of particulate matter from residential wood burning, as it holds certain features that make it very well suited for this purpose:

- It is emitted in high concentrations during wood burning, which makes it readily to detect in ambient aerosol samples.
- It is has a low vapour pressure due to a high molecular weight, which ensures that the compound partition to the particulate phase.
- It is associated with fine aerosols only, which makes it possible to trace emissions from wood burning on inter-continental scale.
- It does not undergo chemical reactions in the atmosphere that selectively depletes its concentration between source and receptor site.

In the present study levoglucosan is used to address the spatial and seasonal variation of residential wood burning at a number of European rural background sites, and to estimate the relative contribution of wood smoke particles to the ambient level of PM_{10}.

Table 1.5 provides an overview of the sampling sites included in the EMEP EC/OC campaign, their site category and the sampling equipment used. Further information concerning the sampling sites and the sampling strategy can be found in EMEP-CCC 3/2004.

Ten samples from each of the sites included in the campaign were analysed. Four of the samples were picked from the summer period, whereas the other six samples were picked from the winter period. The 140 samples selected for analysis were collected on the same ten dates in order to ease the comparison and to get a snapshot of the impact from residential wood burning on these days in Europe.

Table 1.5: Sampling sites in the EMEP EC/OC campaign, their site category and sampling equipment used.

Country	**Sampling site**	**Site category**	**Aerosol sampler**	**Filter size**	**Flow rate**
Austria	Illmitz (AT02)	Rural Background	Partisol	47 mm	16.7 l min^{-1}
Belgium	Ghent (BE02)	Urban Background	Gent Filter Unit	47 mm	17 l min^{-1}
The Czech Republic	Košetice (CZ03)	Rural Background	FH 95 SEQ	47 mm	38 l min^{-1}
Finland	Virolahti (FI17)	Rural Background	KFG	47 mm	38 l min^{-1}
Great Britain	Penicuik (GB46)	Rural	Partisol	47 mm	16.7 l min^{-1}
Germany	Langenbrügge (DE02)	Rural Background	Hi-Vol (Digitel)	150 mm	500 l min^{-1}
The Netherlands	Kollumerwaard (NL09)	Rural Background	KFG	47 mm	38 l min^{-1}
Ireland	Mace Head (IE31)	Rural Background	KFG	47 mm	38 l min^{-1}
Italy	Ispra (IJRC) (IT04)	Near-city	KFG	47 mm	38 l min^{-1}
Italy	San Pietro Capofiume (S.P.C) (IT08)	Urban Background	Gent Filter Unit	47 mm	17 l min^{-1}
Norway	Birkenes (NO01)	Rural Background	KFG	47 mm	38 l min^{-1}
Portugal	Braganza (PT01)	Rural Background	Hi-Vol (Sierra)	8 x 10 inch	1133 l min^{-1}
Sweden	Aspvreten (SE12)	Rural Background	Gent Filter Unit	47 mm	17 l min^{-1}
Slovakia	Stara Lesna (SK04)	Rural Background	Partisol	47 mm	16.7 l min^{-1}

1.5.1 Annual mean concentration of levoglucosan

The annual mean concentrations of levoglucosan are given in Figure 1.7 and Table 1.6. In general the lowest annual levels of levoglucosan are reported for the north-western parts of Europe (the Dutch site, the United Kingdom site, the Norwegian site and the Swedish site), whereas the highest concentrations are reported for the southern, central and eastern parts of Europe. However, care should be taken drawing general conclusions, as the situation of the various sites may be highly decisive for the concentrations observed. Notably, residential wood burning has been recognized as a significant contributor to the particulate pollution level in urban areas in Scandianvia (Ramdahl et al., 1984; Yttri et al., 2005), whereas this is not reflected when addressing the impact from this source at rural background sites in the current study.

The highest annual mean concentration of levoglucosan was observed for the Austrian site (59.4 ng m^{-3}), whereas the lowest was reported for the Dutch site (8.7 ng m^{-3}). This spatial variation might be expected, as the Austrian site is located in the densely populated Central Europe, whereas the Dutch site is situated next to the North Sea. Furthermore, the Austrian site is situated close to Bratislava, less than 20 km, and may be influenced by residential wood burning from this area. Indeed, proximity to major urban areas seems to be an important factor decisive for the concentrations observed at the various sites. It should be noted that although residential wood burning is not as common in densely populated areas as in rural areas, possibly reflecting the availability of firewood, the population density makes the urban areas the most exposed both in terms of mean and maximum concentrations. Thus, the site category, being mainly rural background sites in the present study, may be an important factor for the lower concentrations observed. Furthermore, it has been shown that the ambient

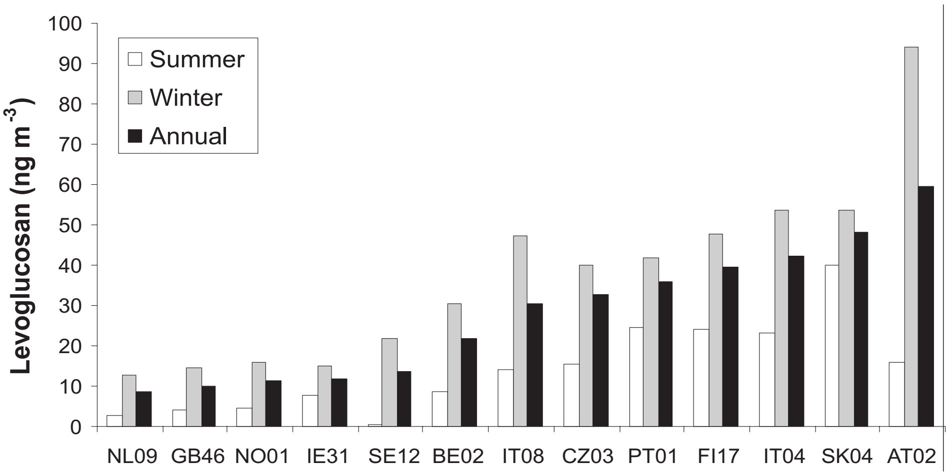


Figure 1.7: Annual and seasonal mean concentration of levoglucosan at the various sites investigated in the present study. For explanation of abbreviations, see Table 1.5.

Table 1.6: Annual and seasonal mean (min and max) concentrations of levoglucosan (ng m^{-3}) in PM_{10}, annual and winter concentrations of PM_{Wood} (µg m^{-3}) for PM_{10}, and relative contribution of PM_{Wood} to PM_{10} for the entire year and the winter season. For explanation of abbreviations, see Table 1.5.

Site	**Levoglucosan Annual (ng m^{-3})**	**Levoglucosan Winter (ng m^{-3})**	**Levoglucosan Summer (ng m^{-3})**	**PM_{Wood} Annual (µg m^{-3})**	**PM_{Wood} Winter (µg m^{-3})**	**PM_{Wood}/PM_{10} Annual (%)**	**PM_{Wood}/PM_{10} Winter (%)**
AT02	59.4 (n.d.-156)	94.2	15.9	2.47	3.92	6.6 (n.d.-15.1)	8.3
BE02	21.9 (4.5-56.1)	30.6	8.7	0.909	1.27	2.6 (0.4-6.7)	4.3
CZ03	32.9 (5.5-50.6)	39.9	15.5	1.37	1.66	3.8 (0.9-7.1)	4.6
FI17	39.7 (7.1-62.2)	47.6	24.0	1.65	1.98	10.2 (4.3-12.8)	10.3
GB46	10.0 (n.d.-18.2)	14.7	4.1	0.417	0.613	3.9 (n.d.-10.5)	5.4
IE31	12.0 (3.4-29.9)	14.8	7.7	0.498	0.616	3.3 (0.8- 10.9)	3.9
IT04	42.3 (10.2-70.5)	53.8	23.2	1.76	2.24	6.2 (3.0-54.5)	6.8
IT08	30.7 (8.0-80.0)	47.2	14.1	1.28	1.96	3.5 (1.0-7.9)	4.7
NL09	8.7 (n.d.-26.9)	12.7	2.8	0.363	0.527	1.7 (n.d.-3.8)	2.5
NO01	11.3 (n.d.-38.1)	15.8	4.6	0.472	0.658	4.9 (n.d.-61.2)	7.5
PT01	36.0 (2.3-66.9)	41.9	24.4	1.50	1.74	9.0 (0.9-28.7)	10.2
SE12	13.4 (n.d.-61.3)	22.0	0.5	0.559	0.917	4.1 (n.d.-18.2)	6.8
SK04	48.3 (10.8-94.2)	53.8	40.1	2.01	1.96	6.9 (1.3-21.8)	8.3

- Note: The mean ratio of PM_{Wood}/PM_{10} for the entire year and for the winter period is calculated according to the following equation: $(a_{mean}/b_{mean})*100$; the min and max value are calculated according to a/b * 100 (for n = i).
- When calculating PM_{Wood} from ambient levels of levoglucosan it is assumed that levoglucosan accounts for 2.4% of PM_{10} originating from wood burning.

concentration of levoglucosan increases significantly as the ambient temperature drops (Yttri et al., 2005). Thus, some of the spatial variation reported for levoglucosan can be attributed to this factor. Furthermore, meteorological conditions may prevent or promote effective dispersion of emissions from residential wood burning, being highly decisive for the concentrations observed.

1.5.2 Summer vs. winter

The concentration of levoglucosan was higher during winter than during summer at all sites investigated (Table 1.6). The highest difference was experienced for the Austrian site where it was 5.9 times higher during winter compared to the summer, whereas the smallest difference was reported for the Slovakian site, where the levoglucosan concentration was only 1.3 times higher during winter than during summer. (Although the seasonal variation for the Swedish site is greater, this is not accounted for as levoglucosan was detected in only one of the four samples picked from the summer period). This finding clearly illustrates that residential wood burning is far more common during winter than during summer, as expected. The seasonal dependence of residential wood burning is clearly illustrated in Figure 1.8A-M, showing the annual variation of levoglucosan for all sites included in the study. Typically an increase in the levoglucosan concentration is seen going from summer to fall, whereas the maximum concentrations are obtained during winter. Going from winter to spring, the concentrations decline again. It should be noted that no more than 10 days have been selected for analysis and that this low number hardly is representative for an entire year. Thus, deviation from the annual pattern described can be seen, such as the local minimum for the Slovakian site during February and March (Figure 1.8L) and the continued elevated concentrations at the Finnish site during spring (Figure 1.8J). Further, the great geographical variation of the sites most probably influences the annual variation of levoglucosan. Obviously the winter lasts longer at the sites in Scandinavia compared to those in central and southern Europe, as well as at those sites located at a certain altitude such as the Slovakian, the Czech and the Portuguese sites.

The study confirms that levoglucosan is present in a significant number of samples at the sites investigated also during summer, although in much lower concentrations than during winter. This finding indicates that residential wood burning also takes place during summer. However, wildfires can contribute to the level of levoglucosan as well. Indeed, high concentrations of fine aerosols were reported above the boundary layer in Europe during summer 2003 and suggestions were made that this could be attributed to emissions from wildfires in Siberia (Mattis et al., 2003). Furthermore, Niemi et al. (2004) showed that large-scale agricultural field burning in Eastern Europe resulted in high concentrations of fine particles in Scandinavia. Without further investigation, any attempt to distinguish between the contribution of levoglucosan from wildfires and residential wood burning during summer becomes speculative. Attempts should be made to estimate the contribution of particulate matter from wildfires in the Northern hemisphere to the fine particulate level in Europe. Currently, this source is not included in chemical transport models calculating the particulate concentrations for Europe.

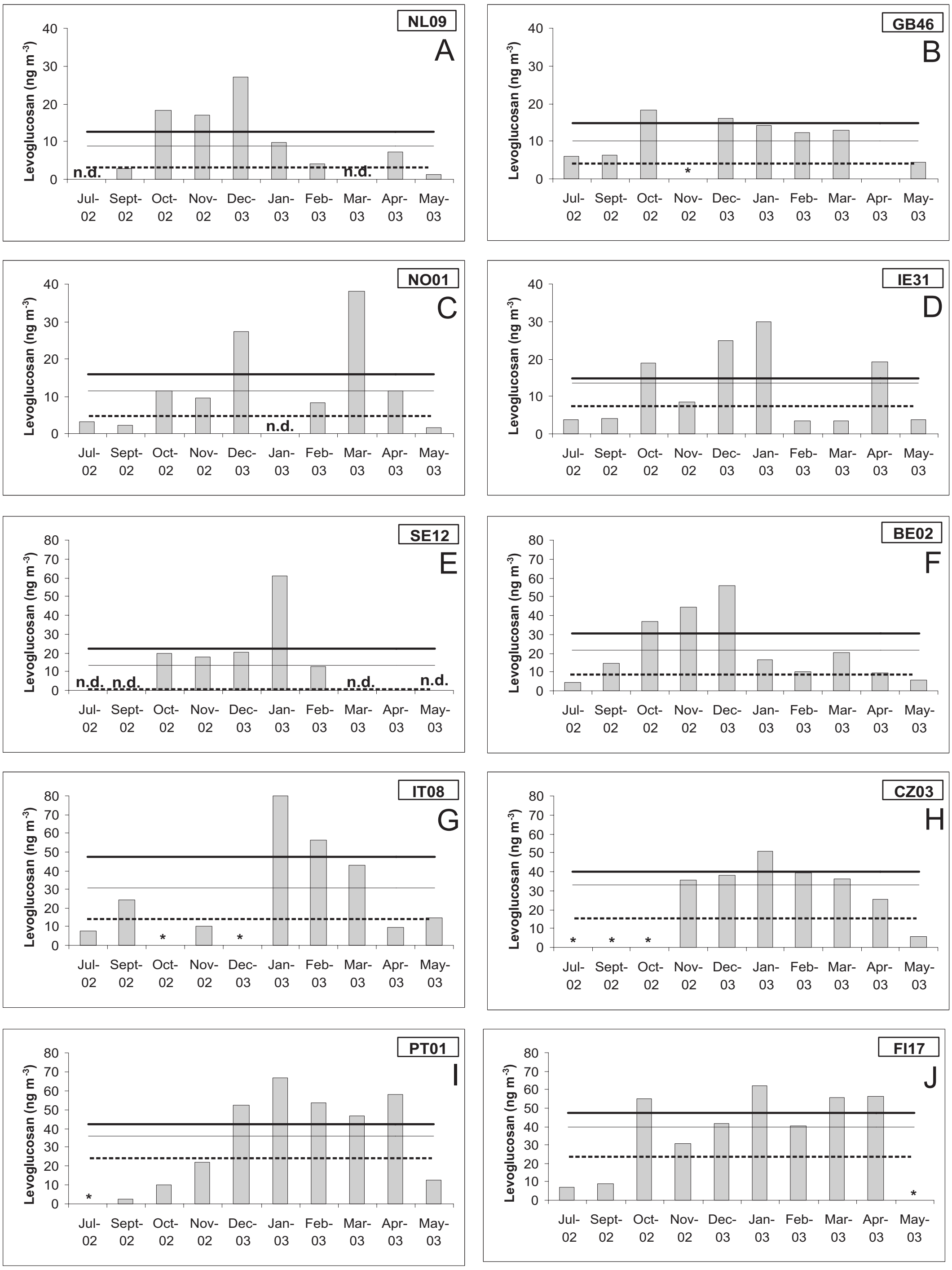


Figure 1.8: Annual variation of levoglucosan at the various sites investigated in the present study. For explanation of abbreviations, see Table 1.5. Annual mean concentration of levoglucosan (———), mean concentration of levoglucosan during winter (▬▬▬) and mean concentration of levoglucosan during summer (-------). Note that the figures do not display monthly values, but rather one day of sampling for the months listed.

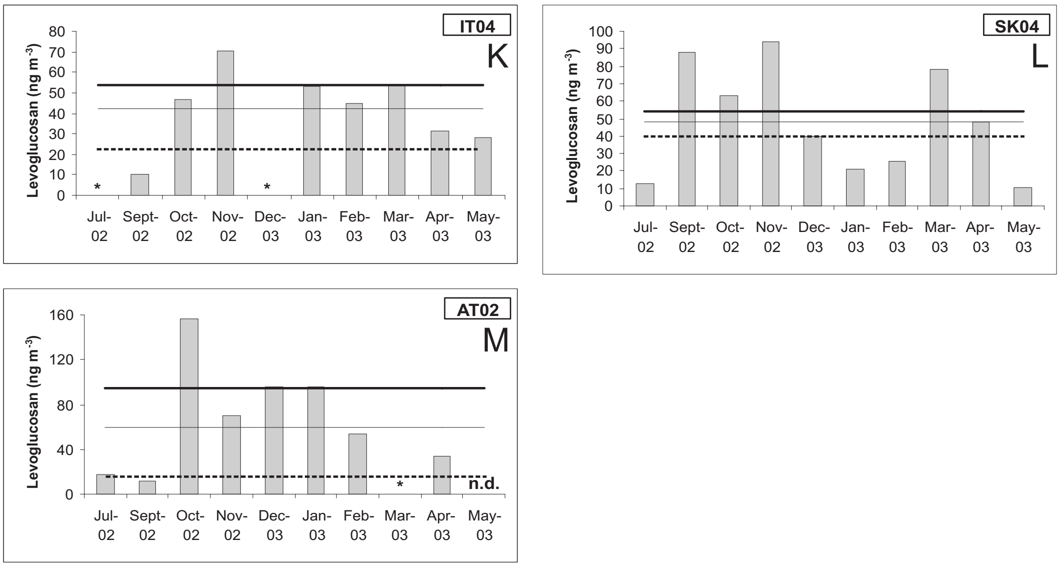


Figure 1.8, cont.

1.5.3 Relative contribution of particulate matter from wood burning to PM_{10}

By using an emission ratio of levoglucosan to PM of 2.4%, the contribution of particulate matter originating from wood burning (PM_{Wood}) has been estimated for the sites included in the study (Table 1.6). The results show that PM_{Wood} varies between 0.363 µg m^{-3} at the Dutch (NL09) site and 2.47 µg m^{-3} at the Austrian site (AT02). On an annual basis the mean relative concentrations of PM_{Wood} to PM_{10} do not vary too much between the sites investigated, ranging from 1.7% at the Dutch site to 10.2% at the Finnish site. This result indicates that residential wood burning is not a major source contributing to PM_{10} at rural background sites in Europe. Accounting for the fact that particles emitted from wood burning almost exclusively reside in the fine fraction (< $PM_{2.5}$) the relative importance of this source will be greater for $PM_{2.5}$. Typically, $PM_{2.5}$ accounts for approximately 70% of PM_{10} at rural background sites in Europe, except for some countries in the Mediterranean region where the percentage is somewhat lower. Thus, the relative contribution of particulate matter from residential wood burning is approximately 30% higher for $PM_{2.5}$ than for PM_{10}. Estimates of the relative contribution of PM_{Wood} to PM_{10} for the winter period are provided in Table 1.6. The results show that the relative contribution of PM_{Wood} to PM_{10} is higher during winter compared to the estimate provided for the entire year for all sites included, ranging from 2.5% at the Dutch site to the 10.3% at the Finnish site.

1.5.4 Conclusion

The presence of levoglucosan in ambient aerosols was demonstrated at all sites investigated. The mean annual concentration of levoglucosan varied from 8.7 ng m^{-3} at the Dutch site to 59.4 ng m^{-3} at the Austrian site. It is argued that the spatial variation reported can be attributed to population density and proximity to urban areas. Thus, the situation of the measurement site is important for the concentrations observed. Furthermore, temperature, meteorological conditions and ambient temperature will be equally important for the concentrations observed.

Concentrations of levoglucosan was higher during winter compared to summer at all sites investigated, reflecting the increased impact from residential wood burning as the ambient temperature drops during winter. The concentrations observed during winter were 1.3-5.9 times higher than reported during summer. It is argued that wildfires contribute to the level of levoglucosan observed during summer, however, it is not known to what extent.

On an annual basis particulate matter from residential wood burning accounted for 1.7% (the Dutch site) to 10.2% (the Finnish site) of PM_{10}. Providing corresponding estimates for the winter season the concentration was found to increase for all sites investigated.

Although residential wood burning has been recognized as a significant source of ambient air fine particulate pollution in several urban communities, the present study indicates that particulate emission from residential wood burning is not a major contributor to PM_{10} at rural background sites in Europe.

2. Model assessment of particulate matter in Europe in 2003

2.1 Introduction

In this chapter, we present the most recent model assessment of European particulate matter concentrations for the year 2003. The concentrations of $PM_{2.5}$, PM_{10} and individual PM components have been calculated with the EMEP Unified model.

In accordance with the work-plan for EMEP for 2005, the aerosol modelling work at MSC-W has been focused on studying the effect of natural sources of total particulate matter (PM) mass. We have also continued the investigation of PM chemical composition in different regions in Europe.

According to the First Daughter Directive to the Air Quality Framework Directive (Council Directive 1999/30/EC), the air quality standards for urban PM_{10} are to be met by member states by 1 January 2005. Our model estimates for the years 2000, 2002 and 2003 show that already regional background PM_{10} concentrations persistently exceed the limit of 50 $\mu g/m^3$ more than 35 days in a year in several locations (Milan and Po Valley, Paris, Benelux countries and the southern coast of Spain). In this chapter, we look at the relative importance of anthropogenic and natural aerosol sources during cases of elevated concentrations of PM_{10}.

Finally, we evaluate the model performance for PM_{10} and $PM_{2.5}$ and the individual components through comparing the model results with observational data from the EMEP monitoring network and national networks and measurement campaigns.

2.2 Recent model development

The recent development of the EMEP Unified model with respect to the calculation of aerosol processes has included:

1. Revision of sea-salt calculation

In the Unified model, the parameterisation of sea-salt aerosol generation is based on works by Monahan et al. (1986) and Mårtensson et al. (2003) as described in Simpson et al. (2003). The main updates to the scheme for sea-salt production affect 10 m wind velocity and sea surface temperature employed in the scheme. The revision of model calculation of the wind velocity at 10 m height, which is a key parameter in sea-salt aerosol production, has resulted in greater sea-salt aerosol emission rates. Consequently, the model now calculates higher concentrations of sea-salt (Na^+ and Cl^-), which were previously underestimated by the model. Sea surface temperature, which also affects the sea-salt particle production, is now taken directly from the HIRLAM weather prediction model.

2. Revision of particle dry deposition

The parameterisation of particle dry deposition velocity has been revised, making use of the results/suggestions in Zhang et al. (2001), Travnikov and Ilyin (2005), Rannic et al. (2003) and Garland (2001). The main result of the revision is some increase of dry deposition velocity of fine particles, especially in forested areas, which is believed to be too low previously. Also, the scheme has been further developed in order to account for particle hygroscopic growth. This allows for more sound calculation of particle sizes and thus dry deposition velocities depending on the ambient relative humidity. The overall effect is somewhat more efficient particle removal by dry deposition (especially for fine particles) and thus some decrease in particle air concentrations.

3. Implementation of natural sources of mineral dust

A test version of the Unified model has been made which accounts for wind-blown dust from semi-arid areas and agricultural soils within the EMEP domain and also for Saharan dust transported from outside. The Saharan dust is included in the model through applying boundary conditions for dust. Monthly dust concentrations from calculations performed with the global model CTM of the University of Oslo (Grini et al., 2005) have been used to derive the boundary conditions for fine and coarse dust in the EMEP Unified model.

A newly developed preliminary parameterisation of wind driven dust emissions from deserts/semi-arid areas and agricultural lands have been implemented for testing in the Unified model. Here, we give a brief description of the wind-blown dust parameterisation.

The parameterisation of soil dust production by wind erosion is based on the works of Marticorena and Bergametti (1995), Alfaro and Gomes (2001), Zender et al. (2003), Gomes et al. (2003) and others. The key parameter driving dust emissions is wind friction velocity. The horizontal particle motion, called saltation, occurs when the wind friction velocity exceeds a threshold value, which depends on the size of soil aggregates. To calculate the effective threshold friction velocity the model employs the partitioning scheme of wind shear stress between erodible and non-erodible surface elements following Marticorena and Bergametti (1995). The suppression of soil erosion by soil moisture is accounted for as suggested in Fécan et al. (1999). The general expression for threshold wind friction velocity ($u_{*,th}$) can be written as

$$u_{*,th} = \frac{u_{*,sm}}{f_{eff}} f_w$$

where $u_{*,sm}$ is the threshold friction velocity for erodible (smooth) part of surface, f_{eff} describes the partitioning of wind drag between erodible surface and non-erodible roughness elements (as in Marticorena and Bergametti, 1995), and f_w is the correction factor accounting for soil moisture as suggested in Fécan et al. (1999).

The condition for dust mobilisation by wind is $u_* \geq u_{*,th}$, where u_* is the wind friction velocity specific for different land-use categories. The horizontal (saltation) flux of loose soil particles is calculated as

$$Q_s = \frac{C\rho_{air}}{g} u_*^3 \left(1 - \frac{u_{*,th}}{u_*}\right)\left(1 + \frac{u_{*,th}}{u_*}\right)^2$$

where Q_s is the horizontal mass flux of soil particles (kg $m^{-1}s^{-1}$), ρ_{air} is the air density, g is the gravitational acceleration and C is the empirical constant of proportionality. The vertical flux of small dust particles, released by sandblasting mechanism from the large saltating particles and/or surface soil aggregates, is simulated as

$$F = A_s \cdot K \cdot \alpha \cdot Q_s$$

where F is the vertical mass flux of dust (kg m^{-2} s^{-1}), A_s is the area fraction of erodible soil in the grid cell, K is the coefficient accounting for soil erodibility, α is the sandblasting efficiency (m^{-1}). Values for K and α are taken from the field data presented in Gomes et al. (2003).

2.3 Aerosol concentration fields in 2003

In the model calculations for the year 2003 we have used 2003 meteorology calculated with the PARLAM_PS weather prediction model and emissions of SO_2, NO_x, NH_3, $PM_{2.5}$ and PM_{10} in 2003 (Vestreng et al., 2004). Grid segregation and sector allocation of the national total emissions has been done as described in EMEP Report 1/2004 (Chapter 3). The chemical speciation of primary PM emissions is based on the IIASA preliminary inventory of submicron carbonaceous particle emissions (Kupianen and Klimont, 2005). According to these estimates, the emissions of primary $PM_{2.5}$ have been divided into organic carbon (OC), elemental carbon (EC) and inorganic components, assumed to be mineral dust. Primary coarse PM has been divided into EC and mineral dust only, using a very preliminary emission estimate of coarse EC (Klimont, personal communication). Emission estimates of primary coarse OC from anthropogenic sources are not currently available. The present version of the Unified model calculates 7 individual aerosol components: SO_4^{2-}, NO_3^-, NH_4^+, OC, EC, sea-salt and mineral dust. Also, the particle water content is calculated at a temperature of 20°C and at a relative humidity of 50% (Tsyro, 2005), which are equilibrating conditions required for gravimetric PM measurements.

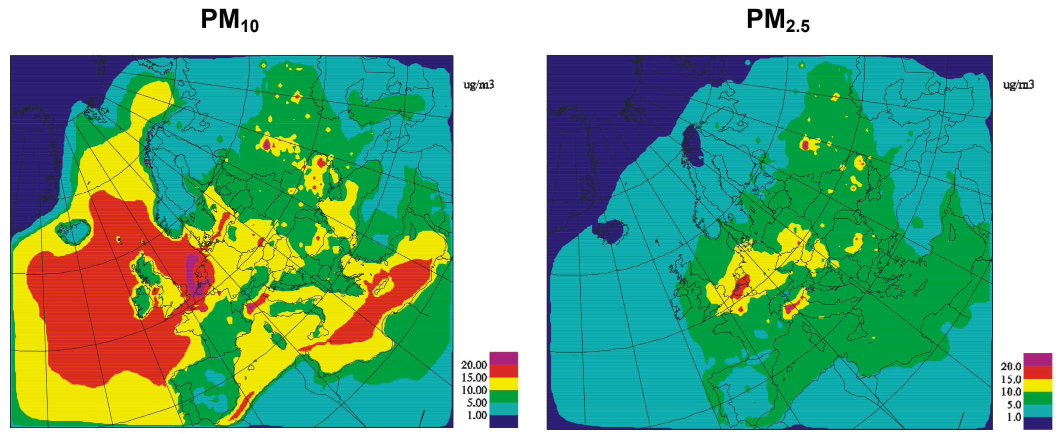
Annual mean concentration fields of PM_{10} and $PM_{2.5}$ calculated with the EMEP Unified model for the conditions of 2003 are presented in Figure 2.1. On the upper panels, the maps of dry PM_{10} and $PM_{2.5}$ concentrations, excluding natural dust are shown. These concentrations are comparable to what have been presented in previous EMEP reports. The middle panels show PM_{10} and $PM_{2.5}$ concentrations, in which wind-blown agricultural and Saharan dust are accounted for. Accounting for the contribution of natural sources of mineral dust to PM has increased $PM_{2.5}$ and PM_{10} concentrations, especially in the Mediterranean countries and the southern parts of East Europe and Russia. Finally, PM_{10} and $PM_{2.5}$ concentrations including both natural mineral dust and particle water are presented on the lower panels. Accounting for particle water increases the concentrations of $PM_{2.5}$ and PM_{10} by further 10-30%.

The concentrations of primary anthropogenic $PM_{2.5}$ and coarse PM, secondary inorganic aerosols (SIA) and PM of natural origin in 2003 are presented in Figure 2.2. SIA is the largest component in $PM_{2.5}$ and PM_{10} in most of the EMEP area. Primary anthropogenic PM becomes more important in big cities (e.g. Paris, Moscow, and Istanbul) and industrial regions with large sources of primary PM emission (e.g. north of Kola Peninsula, eastern Ukraine, and the Ural area) (Figure 2.3, left map).

Figure 2.3 shows the concentrations of the individual SIA components, SO_4^{2-}, NO_3^- and NH_4^+. Sulphate is the main SIA component in most of the regions, while nitrate dominates SIA concentrations in Benelux countries and northern Italy. Ammonium is the smallest SIA component, but its contribution to SIA in the Netherlands, Belgium, Luxemburg and northern Italy is significant.

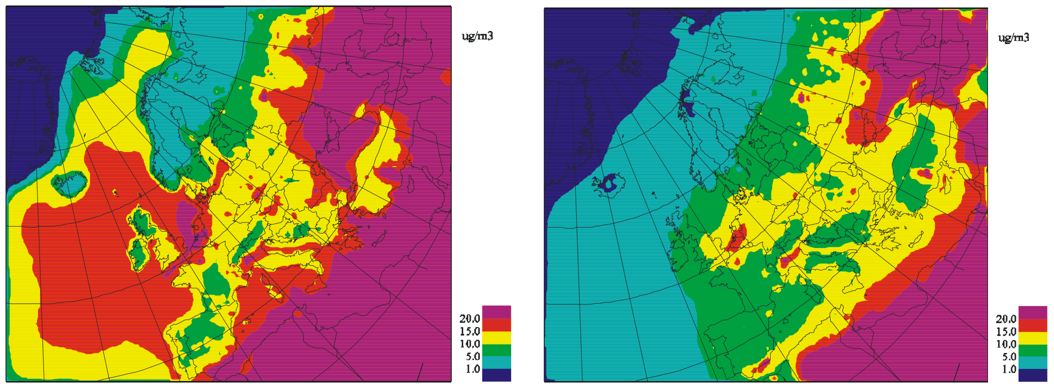
Initial model calculations show that the concentrations of aerosols from natural sources, which are sea-salt spray and soil wind erosion in the model, are 0.5-5 $\mu g/m^3$ over most of Europe (Figure 2.2, lower right map). They reach 10-20 $\mu g/m^3$ in the south and south-east of the EMEP domain due to the effect of wind-blown dust from the deserts (Sahara, Kara Kum, Kyzyl Kum) and semi-arid areas in Europe (e.g. the south-east of Spain). Figure 2.4 (middle map) shows the contribution of sea-salt and wind-blown dust to the total PM_{10} mass. The contribution of natural particles to PM_{10} is around 5-25% in central Europe, in-land parts of Scandinavia and North-Western Russia. The contribution increases to 20-30% in southern and Eastern Europe. The importance of natural aerosols increases along the sea coasts due to the contribution of sea-salt (up to 20-30% of PM_{10} mass) and in the south of Europe and southern parts of Ukraine and Russia, Caucasus and Kazakhstan due to wind-blown dust (50-70 % and more in PM_{10}).

The right map in Figure 2.4 shows that fine particles ($PM_{2.5}$) dominate PM_{10} mass practically all over Europe. The concentrations of coarse particles are mostly a factor of 2 to 4 smaller than fine PM concentrations. The concentrations of coarse particles approach that of fine particles in the areas heavily affected by sea-salt and wind-blown dust due to a considerable contribution of the natural coarse particles.



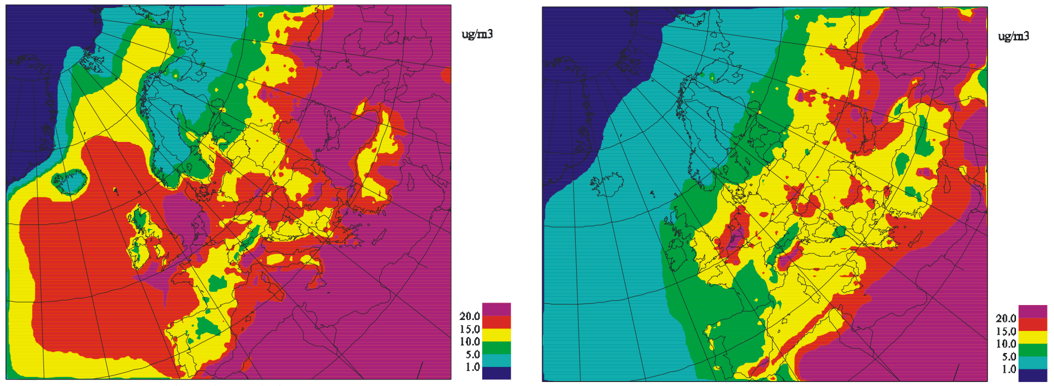
PM10(dry, w/o nat. dust), 2003

PM2.5(dry, w/o nat. dust), 2003



PM10(dry, with nat. dust), 2003

PM2.5(dry, with nat. dust), 2003



PM10(wet, with nat. dust), 2003

PM2.5(wet, with nat. dust), 2003

Figure 2.1: Model calculated PM$_{10}$ and PM$_{2.5}$ concentrations in 2003: upper panels - dry concentrations, no contribution from wind-blown dust; middle panels – dry concentrations with wind-blown dust included; lower panels – wind-blow dust and particle water (at 20°C and 50% relative humidity).

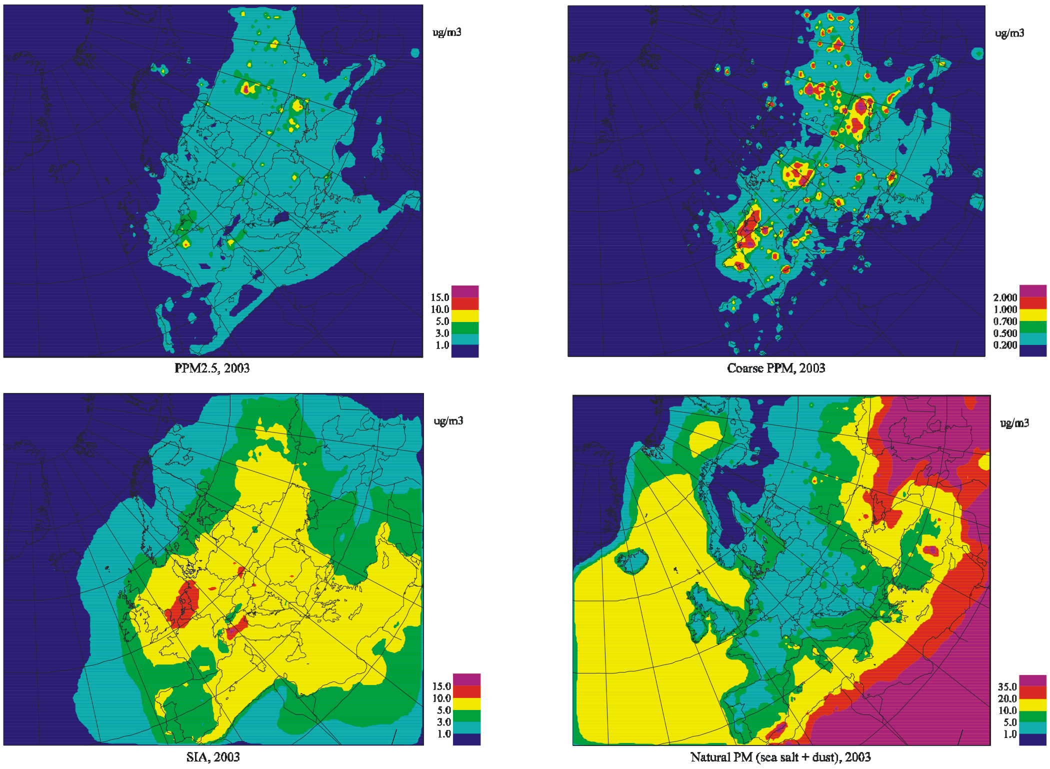


Figure 2.2: Model calculated concentrations of primary $PM_{2.5}$, primary coarse PM, SIA and natural particles (sea-salt and wind-blown mineral dust) in 2003.

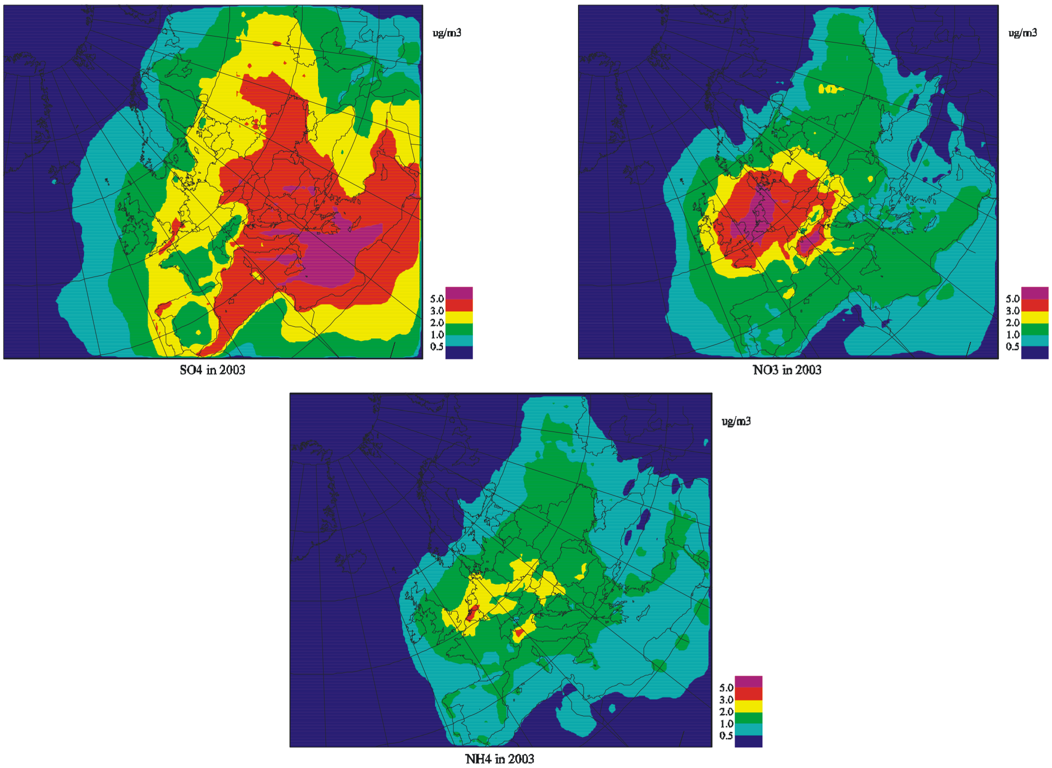


Figure 2.3: Model calculated concentrations of SO_4^{2-}, NO_3^- and NH_4^+ in 2003.

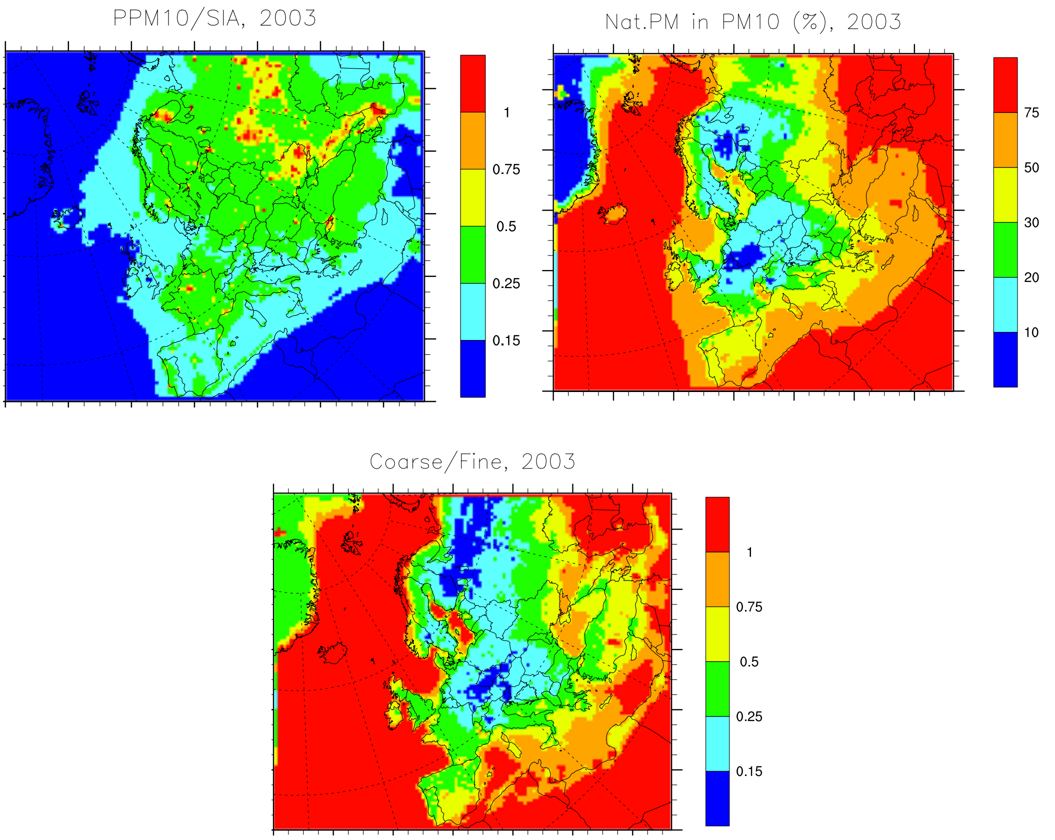


Figure 2.4: Ratios of calculated concentrations of primary PM_{10} to SIA (left panel) and coarse PM to fine PM (right panel); and the contribution of natural particles to PM_{10} (%) (middle panel) in 2003.

2.4 Calculated PM_{10} exceedances of EU limit value

The First Daughter Directive to the Air Quality Framework Directive (Council Directive 1999/30/EC) establishes air quality standards for PM_{10} to be met by Member states by 1 January 2005. The Directive requires that annual mean PM_{10} concentrations should not exceed a limit value of 40 µg/m^3 and daily PM_{10} concentrations should not exceed 50 µg/m^3 more than 35 times a calendar year. Recently WHO, based on thorough analysis of available evidences, reported that epidemiological studies on large populations was not able to identify a threshold concentration below which no effect of ambient PM is expected on human health (WHO, 2003). In the light of this, the EU limit values for PM_{10} can be used as indicators to the progress made by countries towards reducing their PM concentration levels. It is reasonable that these limit values can also be applied as a tentative progress indicator in the countries, which are not EU members.

Here, we compare model calculated PM_{10} concentrations in the years 2001, 2002 and 2003 with the PM_{10} limit values. It is important to remember that PM concentrations calculated with the EMEP model are characteristic to the regional background, whereas the EU air quality standards are established for urban PM_{10} concentrations. Consequently, the urban contribution should be added in to the long-range transported component of ambient PM concentrations calculated with the model. Notice that the model calculated PM_{10}, compared with the limit values here, includes natural wind-blown dust and particle water. Model calculations for the year 2003 show that the annual regional background concentrations of PM_{10} (see Figure 2.1) in general are below the laid down limit value of 40 $\mu g/m^3$. Exceedances of the PM_{10} limit value are observed in Azerbaijan and in the south of Kazakhstan only. This is explained by wind blown dust from desserts.

The model calculates exceedances of the 24-hour PM_{10} limit value even for regional background concentrations in some areas. The maps in Figure 2.5 show the number of days when daily PM_{10} concentrations exceeded 50 $\mu g/m^3$ for the years 2000, 2002 and 2003. As can be seen in Figure 2.5, the geographical pattern of the number of days with PM_{10} limit exceedance does not change much between the years, but the number of exceedance days shows some inter-annual variability. There are several regions (grid cells) within EU where calculated PM_{10} concentrations persistently exceed the EU limit of 50 $\mu g/m^3$ more than 35 times in all of the years. These are: Milan and Po Valley, Paris, the Benelux countries and the southern coast of Spain. The grid cell including Milan experience the highest number of daily exceedances of the PM_{10} limit value, being 90 days for 2000, 72 days for 2002 and 79 days for 2003. The most days with PM_{10} exceeding the limit value are calculated in the grid cell with Milan: 90, 72 and 79 days in respectively 2000, 2002 and 2003. The corresponding numbers for the Paris grid are 31, 45 and 45.

The inter-annual changes in the number of PM_{10} exceedance days are due to the combined effect of emission changes and meteorological variability. The increase in the number of days with PM_{10} exceedance in central Europe is because of less annual precipitation in 2002 compared to 2000. For example, in Germany, Belgium and the Netherland more days with PM_{10} exceedances are found despite smaller emissions of SO_x, NO_x and NH_3 in 2002 than in 2000. In Poland, some increase in NH_3 emissions contributed to more PM_{10} exceedance days in 2002 relative to 2000. In contrast, more annual precipitation in Southern Europe and in the Balkan countries appears to be the reason for fewer days with calculated PM_{10} exceedances in 2002 than in 2000. In Greece the effect of meteorology appears to cancel out the effect of SO_x and NH_3 emission increase on PM_{10} levels in 2002 compared to 2000.

The year 2003 was characterised by an exceptionally hot and arid summer in western, central and southern Europe. The main differences between aerosol concentration fields in 2003 and 2002 are discussed in terms of changes in emissions and in meteorological conditions in EMEP Status Report 1/2005. In particular, it was the rather small precipitation amounts which affected the PM_{10} concentrations the most in 2003 in those areas. The EMEP model calculates annual mean concentrations of $PM_{2.5}$ and PM_{10} being 5-30% (reaching 30-35%) higher in 2003 than in 2002 almost all over of the EMEP area. The largest differences in $PM_{2.5}$ and PM_{10} concentrations (around 40%) are found on the Italian-French border.

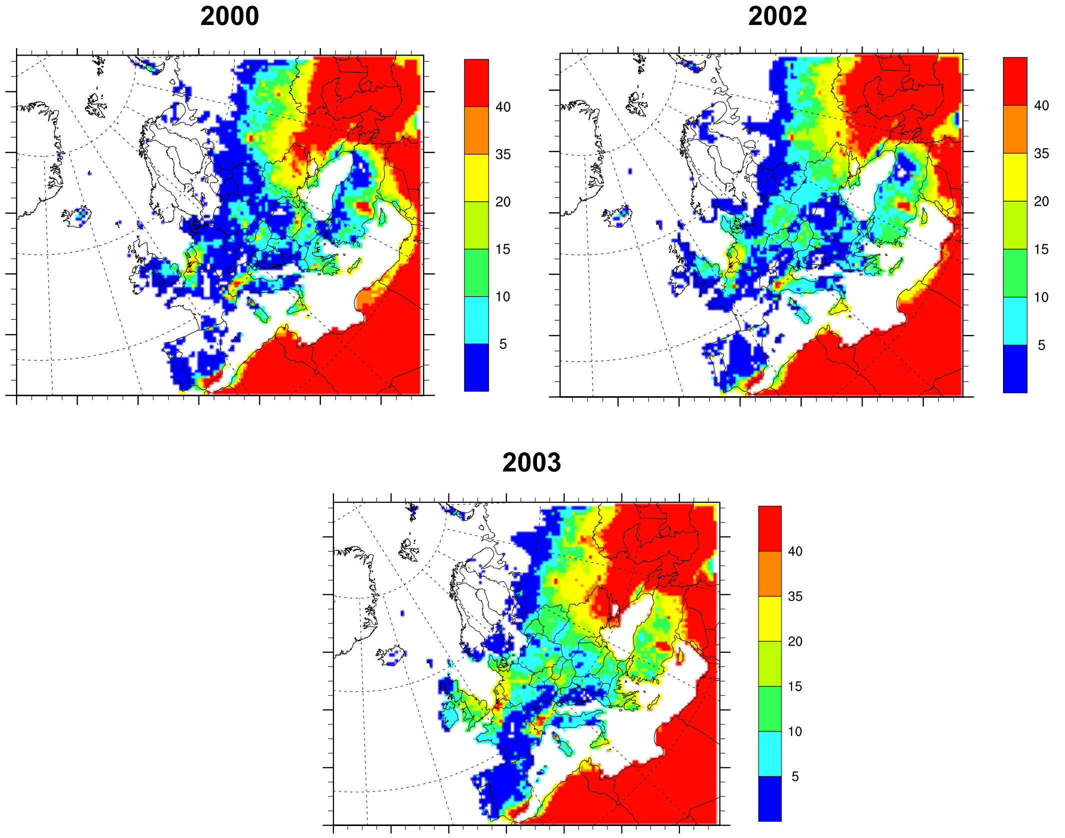


Figure 2.5: Number of days with daily regional background PM_{10} *concentrations exceeding the limit value of 50* $\mu g/m^3$ *in 2003 calculated with the EMEP model.*

Overall, the number of days with PM_{10} exceedances of the daily limit value appears to be higher in 2003 compared to the other years. The enhanced PM_{10} concentration levels and the higher number of days with PM_{10} exceedances in 2003 in Western and Central Europe is due to less precipitation and more stable atmosphere in 2003 than in 2002. In the Mediterranean countries, the increase in PM_{10} exceedance days in 2003 is due to larger impact of wind-blown dust as well. Also in Ukraine, Georgia, Armenia, Azerbaijan, the south of Russia and Kazakhstan, wind-blown dust causes more days with PM_{10} exceedances in 2003. This can be attributed to higher wind speeds (not shown here) and, thus, larger natural dust emissions in 2003.

The First Daughter Directive allows exemption for PM_{10} arising from natural episodes. Member states are not obliged to set up abatement plans if they can provide the necessary justification to demonstrate that the exceedances of PM_{10} limit value were due to the impact of natural sources, such as windblown dust from Sahara or other arid areas. Therefore, it is important that the air quality model can distinguish between anthropogenic and natural sources contributing to PM_{10} (exceedances) in different areas.

Figure 2.6 illustrates the significant differences in source contributions to PM_{10} in four grid cells where calculated PM_{10} exceeds the 24-hour limit value in more than 35 occasions in 2003. The selected grid cells are located in the following areas: Paris area, Milan area, western Belgium and southern coast of Spain (Malaga area). Both, annual mean PM_{10} compositions and PM_{10} compositions on the days with the yearly highest PM_{10} concentrations in these grid cells are shown.

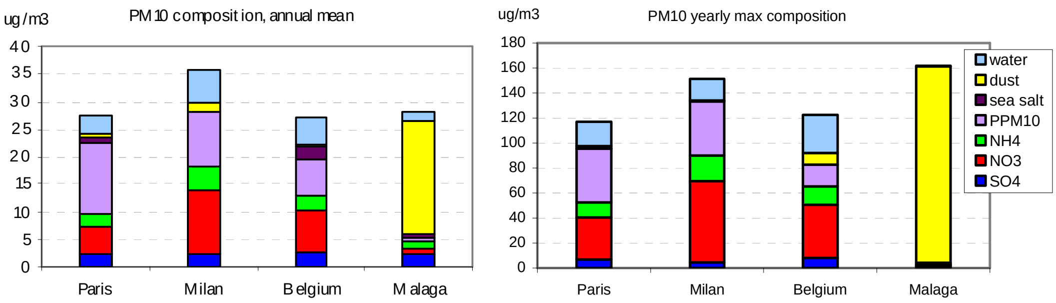


Figure 2.6: Calculated chemical composition of PM_{10} in four different grid cells with more than 35 occasions of PM_{10} daily limit exceedance: annual mean (left panel) and for the days with the yearly maximum PM_{10} (right panel) in 2003. The selected grid cells represent the Paris area, the Milan area, western Belgium and southern Spain (Malaga area).

In the Milan area, in the Po Valley, the Paris area and in Western Belgium, anthropogenic sources (SIA and PPM) are the main contributors to regional PM_{10}, while in the south of Spain (Malaga) the calculated PM_{10} exceedances are due to wind-blown dust from the desert areas there.

2.5 Comparison of model results with measurements

2.5.1 Annual mean PM and SIA

The scatter-plots of model calculated PM_{10} and $PM_{2.5}$ concentrations versus EMEP measurements in 2003 are shown in Figure 2.7. On the left panels, calculated dry PM_{10} and $PM_{2.5}$, excluding windblown dust, are compared to measurements. On the right plots, all of the calculated aerosol components, namely SIA, primary PM, sea-salt, wind-blown mineral dust and particle water, are included in the modelled PM_{10} and $PM_{2.5}$ concentrations. Note that secondary organic aerosols (SOA) are not yet included in the present model calculations of PM. Also primary biogenic organic aerosols (such as pollen, spores and fungi), which can be significant contributors to PM_{10} mass, are not accounted for in the model.

Model calculated dry PM_{10} and $PM_{2.5}$, excluding windblown dust, are 53% and 48% lower than measured values. When windblown dust and particle water are accounted for, the model underestimates observed PM_{10} and $PM_{2.5}$ concentrations only by 24% and 15%. Inclusion of windblown dust and particle water improves the spatial correlation coefficient between modelled and measured PM_{10} from 0.56 to 0.73. However, it somewhat decreases the spatial correlation coefficient for $PM_{2.5}$ from 0.84 to 0.80, which is due to uncertainties in model calculations of natural mineral dust.

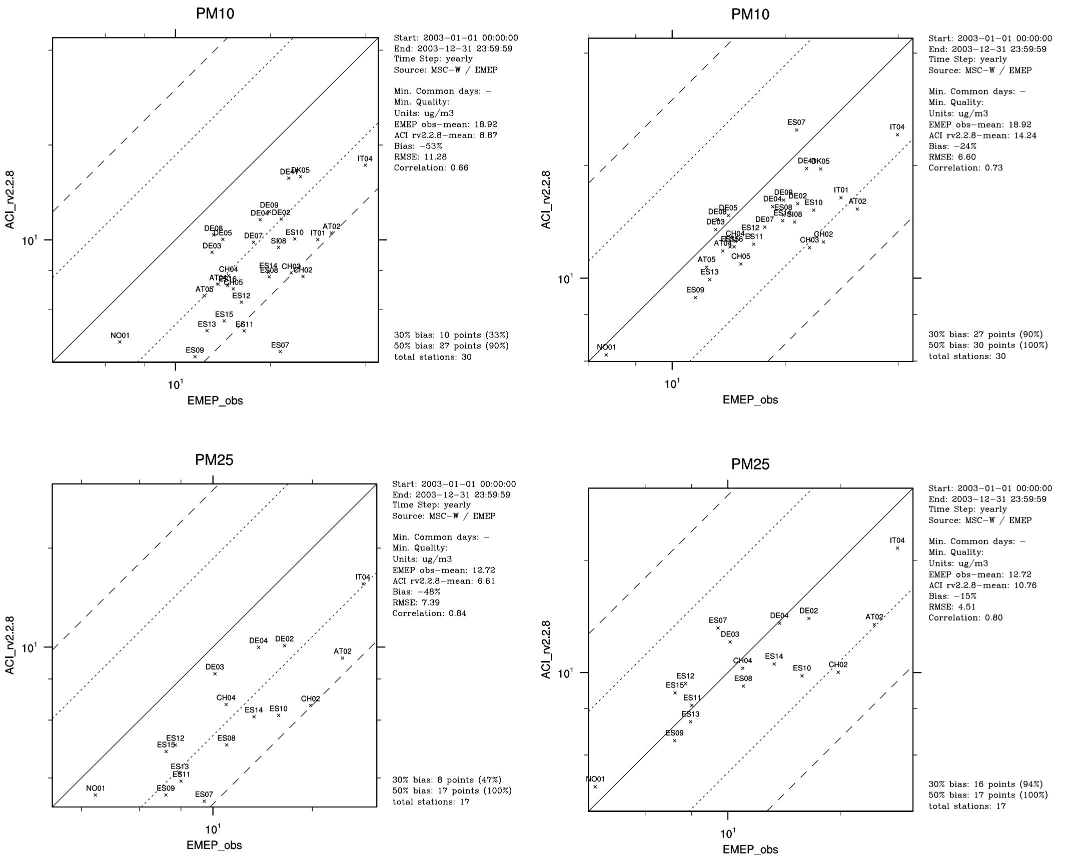


Figure 2.7: Scatter-plots of model calculated vs. measured PM_{10} and $PM_{2.5}$ in 2003. On the left panels, calculated PM is dry PM_{10} and $PM_{2.5}$ excluding windblown dust; on the right panels, PM_{10} and $PM_{2.5}$ include windblown dust and particle water.

The general improvement in model representation of regional PM concentrations is primarily due to accounting for wind-blown dust in the model. In particular, model calculated PM concentrations now agree better with observations at Spanish sites, where natural dust is an important source of PM. This improves the general model performance, as Spanish sites are over-represented among the EMEP sites measuring PM. As a result of the revised emission distribution and particle deposition calculation, the regional PM gradients in Germany are now better reproduced by the model compared to results reported in the previous years.

The following should be pointed out: The model performance substantially improves with respect to PM_{10} and $PM_{2.5}$ when wind-blown dust and particle water are accounted for. This indicates that the model gives a reasonable estimate of wind-blown dust concentrations and particle water. However, the proper validation of model results for wind-blown dust and particle water with measurements is not feasible at present because of the lack of measurements. Therefore, there are still uncertainties related to the model calculations of wind-blown mineral dust and particle water.

The scatter-plots in Figure 2.8 compare modelled versus measured concentrations of SO_4^{2-}, NO_3^- and NH_4^+ at those EMEP sites where PM_{10} and/or $PM_{2.5}$ were measured in 2003. Figure 2.8 reveals that available measurement data is insufficient to explain the underestimation of PM concentrations by the model. For example, the underestimation of SO_4^{2-} and NO_3^- is too small to explain model PM_{10} and $PM_{2.5}$ underestimation at several Spanish sites. It is not evident from Figure 2.8 why the model considerably underestimates PM_{10} and $PM_{2.5}$ at AT02, as it overestimates NO_3^- and NH_4^+ and predicts correctly SO_4^{2-} at AT02. There is no sufficient data to facilitate the understanding of the models considerable underestimation of PM at Italian (IT01 and IT04) and Swiss (CH02 and CH03) sites. At Ispra (IT04), model calculated SO_4^{2-} is only slightly smaller than observed and NO_3^- is close to what is observed. Comparison of calculated SO_4^{2-}, NO_3^- and NH_4^+ with all available EMEP observations in 2003 (Figure 2.9) shows a fairly good agreement.

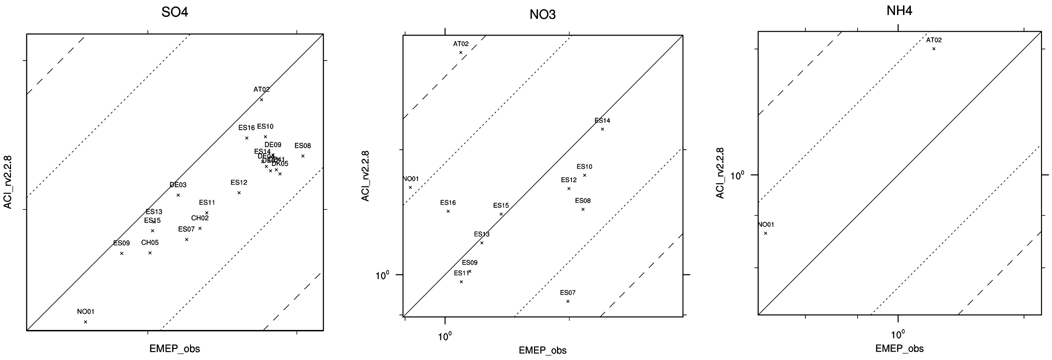


Figure 2.8: Scatter-plots of calculated vs. measured SO_4^{2-}, NO_3^- and NH_4^+ only at EMEP sites with PM_{10} measurements in 2003.

The scatter-plot for annual mean SIA (Figure 2.9) compares calculated SIA concentrations with measurements at EMEP stations where inorganic aerosols SO_4^{2-}, NO_3^- and NH_4^+ were measured concurrently in 2003. The model slightly, by 13%, overestimates measured SIA, and the correlation between modelled and observed SIA is 0.87. These results suggest that the model underestimation of PM_{10} and $PM_{2.5}$ is unlikely to be due to inaccuracies in SIA calculation.

The yearly and seasonal statistics of the model performance for PM_{10}, $PM_{2.5}$, SIA and the concentrations of individual PM components in 2003 are summarised in Appendix A.

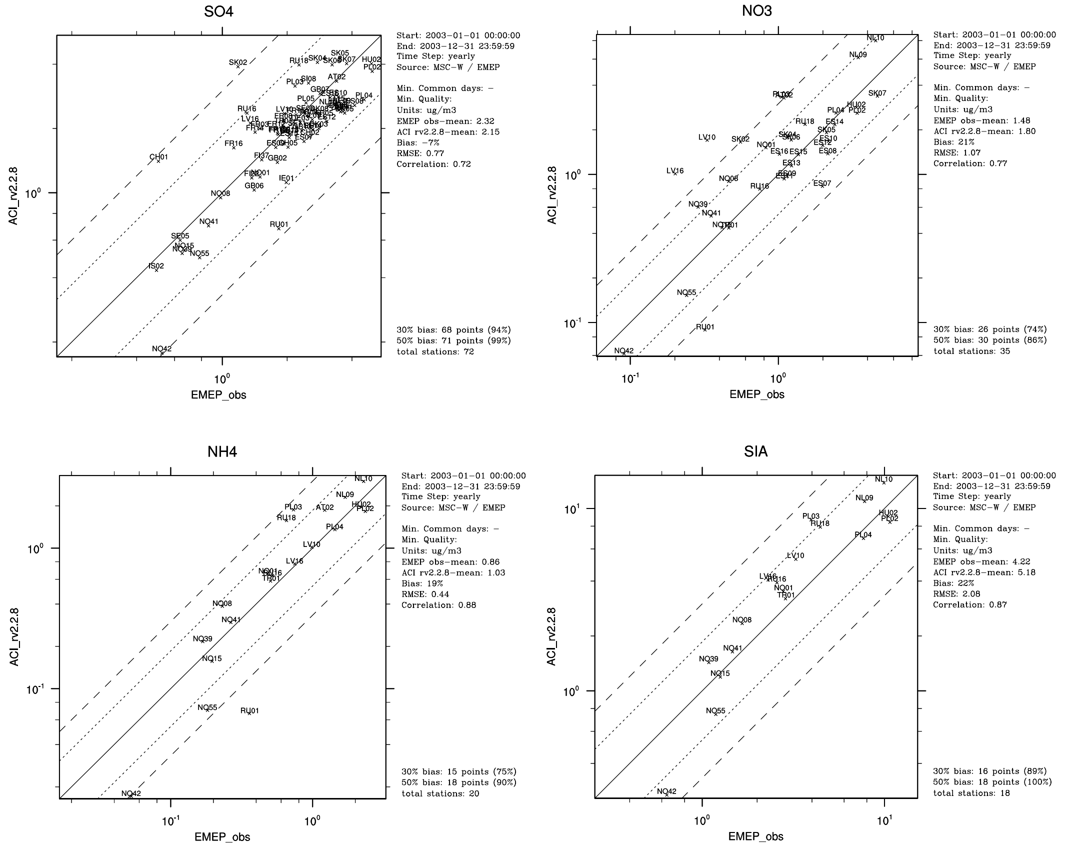


Figure 2.9: Scatter-plots of calculated vs. EMEP measured SO_4^{2-}, NO_3^-, NH_4^+ and SIA (at the stations with concurrent measurements of SO_4^{2-}, NO_3^- and NH_4^+) in 2003.

2.5.2 Monthly variations of PM and SIA

Monthly time-series of modelled and measured PM_{10} and $PM_{2.5}$ for the years from 2000 to 2003 are presented in Figure 2.10. There, three series of calculated PM concentrations represent: dry PM without wind-blown dust (magenta dots), dry PM including wind-blown dust (black curve), and PM concentrations including wind-blown dust and particle water (blue curve). In general, there is found a fair correspondence between modelled and observed PM_{10} and $PM_{2.5}$ monthly variation. The time-series show that the model tends to underestimate PM_{10} and $PM_{2.5}$ in the warm period from April to September. During the cold period, the calculated PM concentrations are closer to or overestimate measured values. The latter results from the model overestimation of SIA in the period from October to March (Figure 2.11). As a result, the model calculates a larger seasonal variability of PM_{10} and $PM_{2.5}$ compared with monitoring data. As can be seen from Figure 2.11, the model over-prediction of SIA during winter is due to too high calculated concentrations of NH_4^+, and in particular NO_3^-, in the cold period.

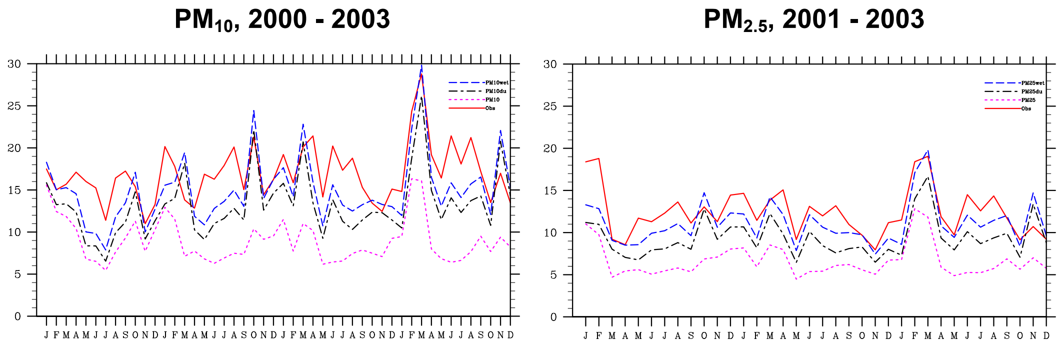


Figure 2.10: Monthly time-series from 2000/2001 to 2003 of calculated and measured PM_{10} and $PM_{2.5}$. Here, calculated PM: magenta dots - dry PM without wind-blown dust, black dot-dashed line - dry PM including wind-blown dust, and blue dashed line - PM including wind-blown dust and particle water; red solid line - measurements (the number of stations with measurements is different in different years).

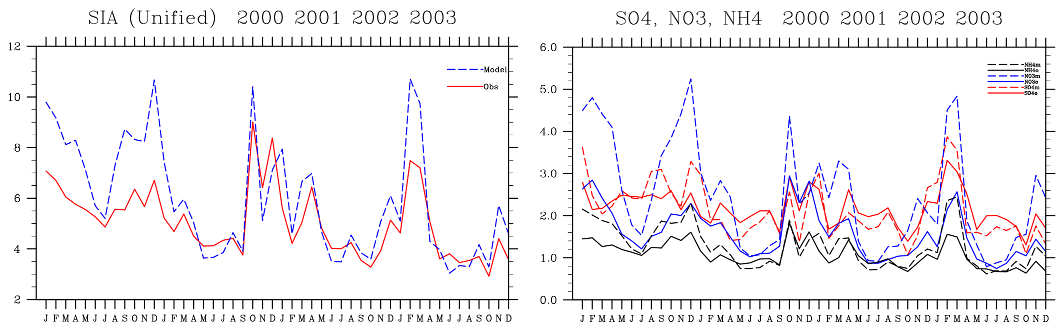


Figure 2.11: Monthly time-series from 2000 to 2003 of calculated (dashed lines) and measured (solid lines) SIA (left panel) and SO_4^{2-} (red), NO_3^- (blue) and NH_4^+ (black) (right panel).

2.5.3 Daily PM concentrations

Table 2.1 and Table 2.2 summarise the model performance with respect to PM_{10} and $PM_{2.5}$ daily concentrations against measurements at EMEP sites. The results from this comparison are presented for three different PM concentrations calculated with the EMEP model: dry PM_{10} and $PM_{2.5}$ without wind-blown dust, dry PM_{10} and $PM_{2.5}$ including wind-blown dust and PM_{10} and $PM_{2.5}$ including wind-blown dust and particle water (corresponding to the residual particle water in gravimetric PM mass). Inclusion of wind-blown dust and particle water improves the model's bias for PM_{10} and the correlation of calculated concentrations and measurements at most of the sites. Particularly significant improvement has been achieved in model PM_{10} results at Spanish sites, where wind-blow dust from Sahara and semi-arid areas in Spain makes up a significant portion of PM_{10} mass. Accounting for windblown dust has not only reduced the model underestimation of measured $PM_{10,}$ but also improved the correlation between calculated and observed PM_{10}. This improvement indicates that the first model calculations of wind-blown dust appear to give promising results.

Accounting for wind-blown dust and particle water gives somewhat mixed results for $PM_{2.5}$ compared against measurement data. The negative bias has decreased and even become positive at some Spanish sites (especially ES07). The correlation between calculated and measured $PM_{2.5}$ increased at four sites and slightly decreased at some sites. Clearly, more testing of the parameterisation for wind dust production and verification of wind blown dust calculations with measurements are needed.

Daily time-series of model calculated and measured PM_{10} and $PM_{2.5}$ concentrations at EMEP sites in 2003 are included in Appendix B.

Table 2.1: Model performance statistics for $PM_{2.5}$ (dry w/o natural dust, dry with natural dust and including natural dust and particle water) as compared with EMEP measurements in 2003

Sites		$PM_{2.5}$ obs.	Dry $PM_{10,}$ w/o dust		Dry $PM_{10,}$ with dust		Wet PM_{10} with dust	
			Bias	Corr	Bias	Corr	Bias	Corr
DE02	Langenbrügge	16.49	-35.1	0.73	-30.5	0.72	-15.2	0.75
DE03	Schauinsland	10.14	-11.8	0.33	-2.7	0.34	19.2	0.39
DE04	Deuselbach	13.76	-23.5	0.69	-19.3	0.69	-1.4	0.71
CH02	Payerne	19.76	-63.5	0.65	-57.9	0.62	-49.3	0.62
CH04	Chaumont	10.96	-33.8	0.51	-21.7	0.46	-6.3	0.51
AT02	Illmitz	24.69	-59.8	0.66	-55.6	0.62	-45.5	0.64
IT04	Ispra	28.5	-43.5	0.5	-38.9	0.46	-24.1	0.47
NO01	Birkenes	4.41	-11.7	0.52	-5.9	0.56	11.8	0.55
ES07	Viznar	9.41	-61.9	0.51	27.7	0.49	40	0.51
ES08	Niembro	11	-51.7	0.51	-31.6	0.5	-16.5	0.52
ES09	Campisabalos	7.2	-47.1	0.48	-24.8	0.4	-8.9	0.46
ES10	Cabo de Creus	15.81	-58.5	0.28	-48.7	0.25	-38	0.29
ES11	Barcarrota	8.01	-48.6	0.54	-14.3	0.55	1.9	0.59
ES12	Zarra	7.7	-31.1	0.59	1.5	0.38	21.2	0.45
ES13	Penausende	7.95	-44.7	0.57	-25.1	0.64	-7.2	0.67
ES14	Els Torms	13.32	-51.3	0.48	-35.5	0.38	-20.8	0.43
ES15	Risco Llano	7.22	-30.2	0.18	4.1	0.45	22.2	0.47
ES16	O Savinao	9.35	-39.9	0.63	-26.6	0.71	-7.3	0.69

Table 2.2: Model performance statistics for PM_{10} (dry w/o natural dust, dry with natural dust and including natural dust and particle water) as compared with EMEP measurements in 2003

Sites	PM_{10} obs.	Dry $PM_{10,}$ w/o dust		Dry $PM_{10,}$ with dust		Wet PM_{10} with dust	
		Bias	Corr	Bias	Corr	Bias	Corr
DE02 Langenbrügge	21.6	-43.2	0.66	-38.4	0.7	-26.8	0.72
DE03 Schauinsland	13.05	-24.9	0.23	-13.6	0.28	3.3	0.32
DE04 Deuselbach	18.52	-34.2	0.59	-29.4	0.62	-16.1	0.65
DE05 Brotjacklriegel	14.12	-23.7	0.3	-14.1	0.37	4.2	0.39
DE07 Neuglobsow	17.65	-41	0.75	-34.1	0.74	-22.4	0.78
DE08 Schmücke	13.21	-16.2	0.43	-8.9	0.47	8.7	0.5
DE09 Zingst	19.81	-35.4	0.76	-29.2	0.72	-18.4	0.76
DE41 Westerland/Tinnum	22.81	-29.3	0.78	-25.3	0.78	-13.8	0.81
DK05 Keldsnor	24.86	-34.1	0.76	-32.2	0.75	-21.2	0.76
CH02 Payerne	25.3	-67.4	0.61	-57.2	0.45	-50.6	0.49
CH03 Taenikon	23.23	-63.3	0.54	-55.8	0.5	-48	0.53
CH04 Chaumont	14.73	-43.6	0.49	-26.1	0.41	-14.8	0.47
CH05 Rigi	15.24	-50	0.42	-38.7	0.38	-28.4	0.4
AT02 Illmitz	31.15	-63.9	0.64	-59.1	0.63	-50.9	0.65
AT04 St. Koloman	13.64	-41.9	0.49	-24.2	0.43	-13.3	0.48
AT05 Vorhegg	12.34	-41.3	0.5	-25.4	0.45	-13.4	0.49
IT01 Montelibretti	28.18	-62.3	0.39	-49.6	0.38	-41.7	0.41
IT04 Ispra	39.84	-55.2	0.45	-49.7	0.39	-39.3	0.4
NO01 Birkenes	6.67	-23.4	0.45	-18.3	0.51	-6.5	0.5
ES07 Viznar	21.45	-78.4	0.39	10.7	0.52	16.1	0.53
ES08 Niembro	19.79	-59.9	0.39	-34.2	0.42	-25.5	0.44
ES09 Campisabalos	11.53	-60.6	0.41	-32.6	0.53	-23.1	0.56
ES10 Cabo de Creus	23.83	-56.1	0.21	-43.3	0.18	-36.2	0.2
ES11 Barcarrota	16.49	-67.4	0.42	-33.3	0.61	-25.2	0.63
ES12 Zarra	16.17	-59.1	0.43	-29	0.48	-19.5	0.5
ES13 Penausende	12.59	-56.8	0.41	-32.4	0.65	-21.3	0.67
ES14 Els Torms	19.69	-58	0.48	-37.6	0.41	-27.6	0.44
ES15 Risco Llano	14.26	-59.5	0.23	-23.7	0.62	-15	0.63
ES16 O Savinao	14.62	-49	0.5	-29.8	0.66	-17	0.66
SI08 Iskrba	21.19	-51.5	0.23	-44.6	0.34	-33.3	0.35

2.5.4 *Carbonaceous aerosols*

Carbonaceous particles include elemental carbon (EC) and organic carbon (OC). At present, the only source of EC and OC included in the model is anthropogenic primary PM emissions. Model calculated EC and OC concentrations are compared with measurements from EMEP EC/OC campaign (EMEP, 2004) during the period from July 2002 – July 2003.

Calculated EC and OC show quite good spatial correlation versus measured concentrations (Figure 2.12). For 2003, only stations of at least 8 days with measurements were included in the scatter-plots. The lower correlation coefficients in 2003 than in 2002 are due to less significant statistics available for 2003. EC is underestimated by the model by 46% in 2002 and by 23% in 2003. The model's negative bias for OC is much larger: -87 in 2002 and -80% in 2003. Note that emissions of carbonaceous particles from wild forest fires are not accounted for. Moreover, the calculated OC concentrations are much lower than measured concentrations because they do not include primary coarse OC from anthropogenic sources, secondary organic aerosols (SOA) and primary biogenic OC.

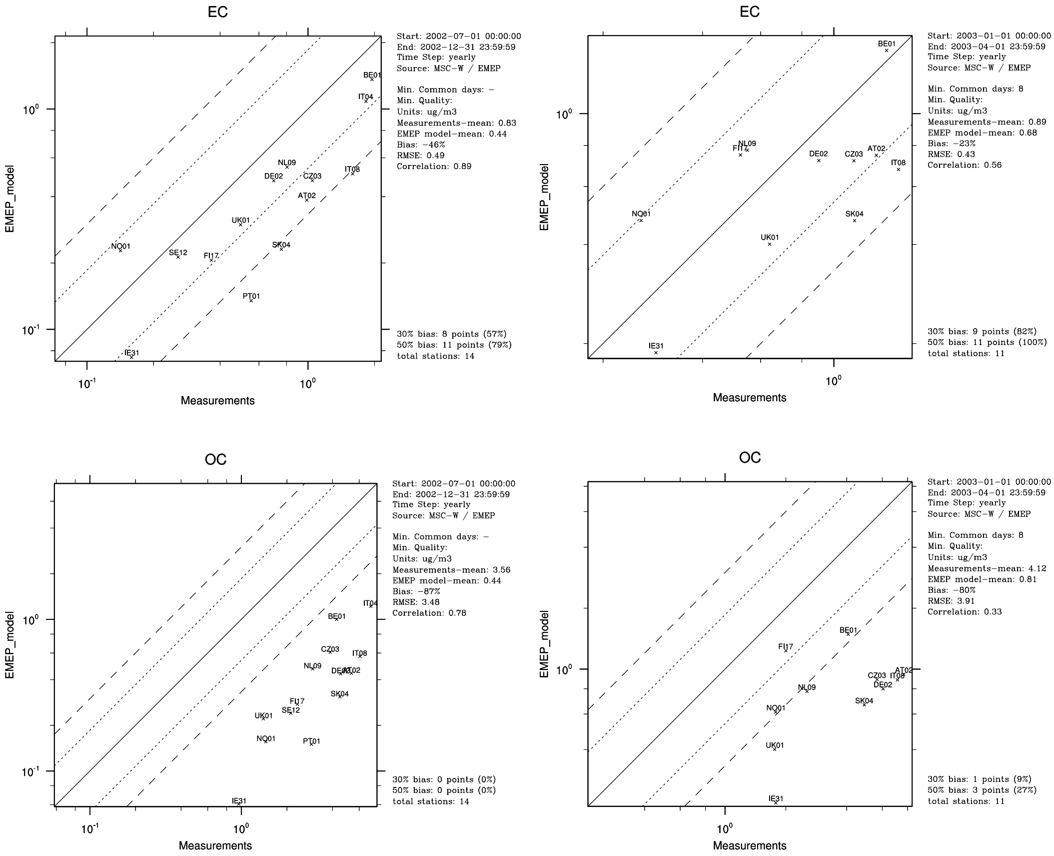


Figure 2.12: Scatter-plots of calculated vs. measured concentrations of EC and OC in July-December 2002 (left panel) and January-April 2003 (right panel). Unit: µg C/m^3.

The relative biases and temporal correlation coefficients between modelled and measured EC in 2002 and 2003 are plotted in Figure 2.13. The comparison results for EC are rather mixed. The best correspondence between calculated and measured EC, with bias within 40% and temporal correlation coefficient above 0.6, is found, for both 2002 and 2003, at NL09, NO01 and IE31. The model calculations of EC are worst compared to measurements at AT02, UK01 and SK04. The greatest model underestimation of observed EC is at PT01 (85% for 2002 and 67% for 2003), however, the correlation is quite good, 0.66 for 2002 and 0.87 for 2003.

Figure 2.14 compares daily time-series of calculated EC with EC measured in January-July 2000 in Vienna (AU01) and Streithofen (AU02), Austria (Hauck et al., 2004). At AU02, which was a rural site, model calculated EC is about a factor of 2-2.5 lower than the observations. At the urban site AU01, the model underestimation of EC is larger, approximately a factor of 3. The good temporal correlation between calculated and measure EC (0.71-0.75) indicates that the emissions of EC are probably reasonably well described in that region.

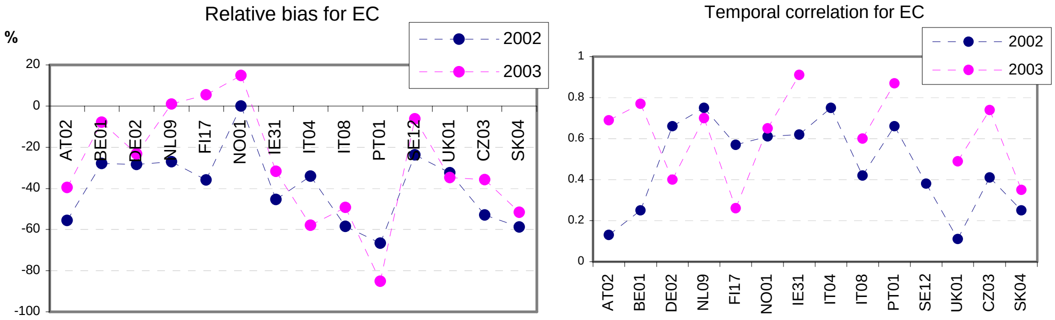


Figure 2.13: Relative biases and temporal correlation coefficients between calculated and measured EC in 2002 and 2003 (for sites with more than 8 days, i.e. 2 months, with measurements).

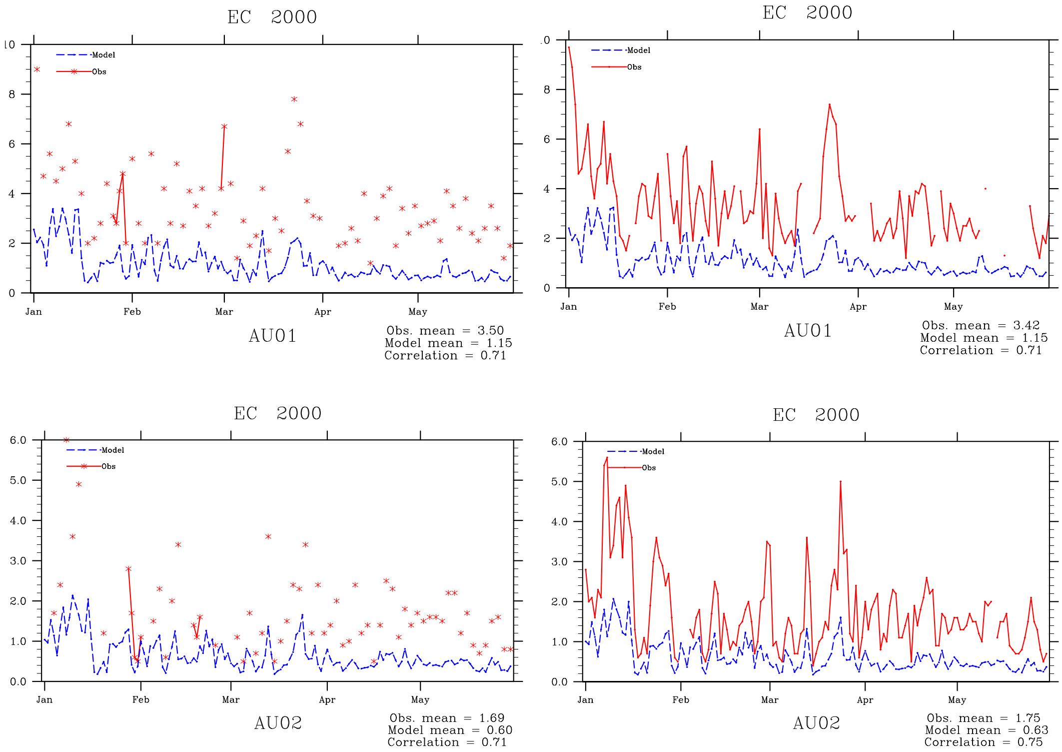


Figure 2.14: Time-series of calculated and measured daily EC concentrations in PM_{10} and $PM_{2.5}$ in January-July 2000 in Vienna (AU01) and Streithofen (AU02), Austria (Hauck et al., 2004). Unit: µg C/m^3.

2.5.5 Natural aerosols

In the EMEP model, natural aerosols are sea-salt and windblown dust from deserts and agricultural soils.

Sea-salt

Rather limited observational data for air concentrations of sodium is available from the EMEP monitoring network. The scatter-plots in Figure 2.15 compare model calculated concentrations of Na^+ (originating solely from sea-salt aerosols) with measured Na^+ concentrations for 2002 and 2003.

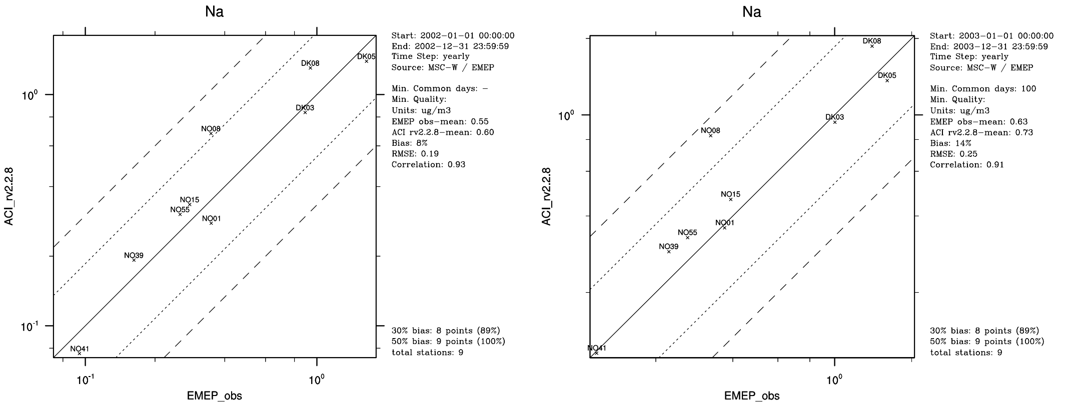


Figure 2.15: Scatter-plots of calculated vs. EMEP measured Na$^+$ for 2002 and 2003. Unit: µg/m^3.

The previous version of the EMEP model underestimated measured Na$^+$ by about a factor of 1.5-2 in 2002, as reported last year (Tsyro, 2004). The recent revisions of sea-salt calculation have improved the correspondence between model results and observations. The model slightly overestimates measured Na$^+$ by 8% in 2002 and 14% in 2003. The spatial correlation between calculated and measured Na$^+$ is very good: 0.93 in 2002 and 0.91 in 2003.

Figure 2.16 shows relative biases and temporal correlation coefficients between modelled and measured daily Na$^+$ concentrations in 2002 and 2003 at EMEP stations. The relative biases are largely within 10% and the temporal correlation coefficients vary between 0.4 and 0.8 at different sites.

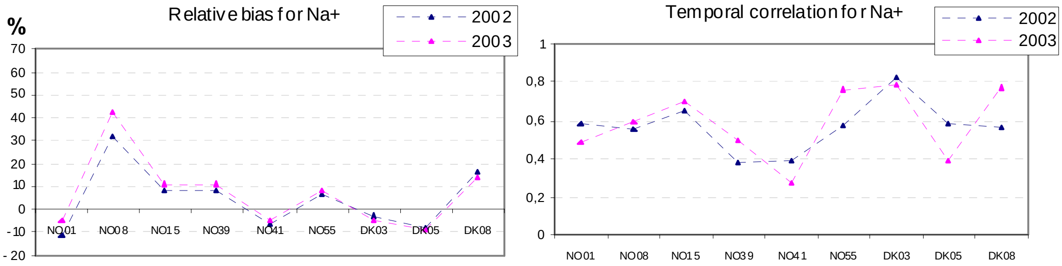


Figure 2.16: Relative biases and temporal correlation coefficients between calculated and measured Na$^+$ at EMEP sites in 2002 and 2003.

Measurements of sea-salt aerosol at Bemantes and Montseny (Spain), which is a part of the measurement campaign financed by the Spanish Ministry of Environment and the Spanish Ministery of Science and Technology, were made available to EMEP/MSC-W (Querol et al., 2004; Rodríguez S. et al., 2002). Figure 2.17 compares calculated and measured concentrations of sea-salt in PM_{10} and $PM_{2.5}$ in 2001 at Bemantes and sea-salt in PM_{10} and $PM_{2.5}$ in 2002-2003 at Montseny. Bemantes is situated at the western North-Atlantic coast of Spain, while Montseny is situated in the very north-east of Spain and affected by the Mediterranean Sea.

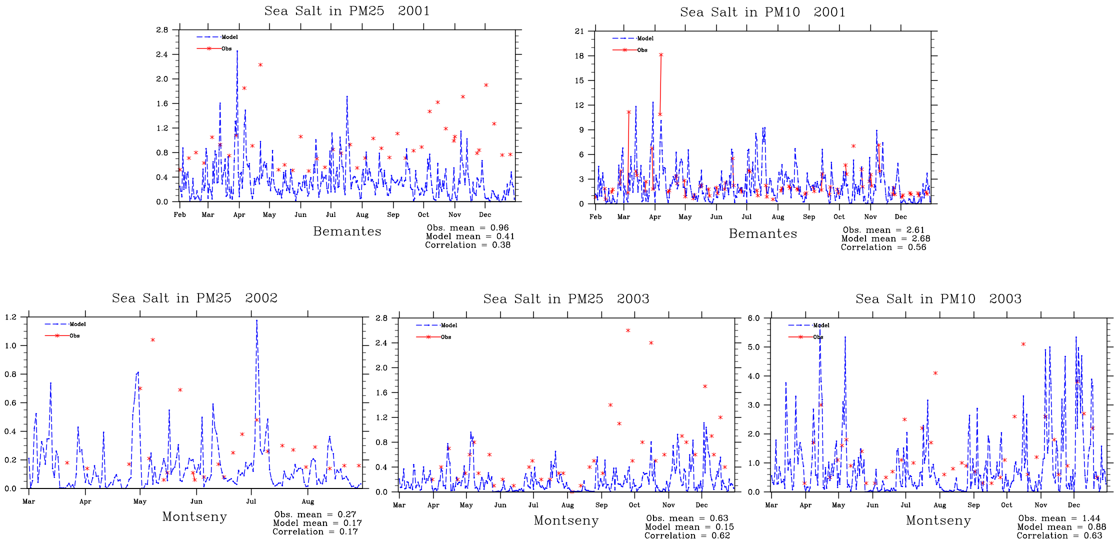


Figure 2.17: Time-series of calculated and measured daily concentrations of sea-salt in PM_{10} and $PM_{2.5}$ in 2001 at Bemantes and in 2002-2003 at Montseny. Unit: $\mu g/m^3$.

In general, the model manages to reproduce sea-salt concentrations reasonably well. At Bemantes, the calculated levels of sea-salt in PM_{10} agrees well with observations and the temporal correlation is 0.56, while fine sea-salt (in $PM_{2.5}$) is somewhat underestimated by the model and the correlation is lower (0.38). At Montseny, the model underestimates observed sea-salt concentrations. The temporal correlation between calculated and measured sea-salt is fairly good in 2003, but it is lower for fine sea-salt in 2002.

Figure 2.17 indicates that the model tends to allocate too little of sea-salt mass to the fine particles. According to the observations, about 37% and 44% of sea-salt mass are on fine particles at Bemantes and Montseny respectively, while it is only 15% and 17% in the model results. One of the possible reasons for that is that the production and size distribution of sea-salt aerosol depends on the salinity of water (Mårtensson et al., 2003). However, the constant salinity of 33 per mille, which approximately applies to most of the ocean (Mårtensson et al., 2003), is presently used in the model.

Mineral dust

Modelled mineral dust includes anthropogenic and natural components. The calculations of windblown dust presented in this section are only an initial attempt to account for this source of natural dust in PM. Because of insufficient/uncertain input information needed for windblown dust modelling (such as soil types, morphology, moisture) the calculations involve some crude assumptions. On the other hand, the anthropogenic emissions of mineral dust are still rather uncertain. Several important sources of mineral dust are still missing in the model; among those are constructions and demolition works and re-suspension.

As previously shown in this section, inclusion of windblown and Saharan dust in model calculated PM improves the bias and spatial and temporal correlation between modelled and measured PM_{10} and $PM_{2.5}$. This suggests that the model results on wind blown dust are a fairly reasonable estimate. Very limited measurements of air concentrations of mineral components for verification of model calculations are currently available. Here, we compare model calculated dust with measurements of mineral mass in PM_{10} and $PM_{2.5}$ in the years 2001, 2002 and 2003 in Spain (Figure 2.18).

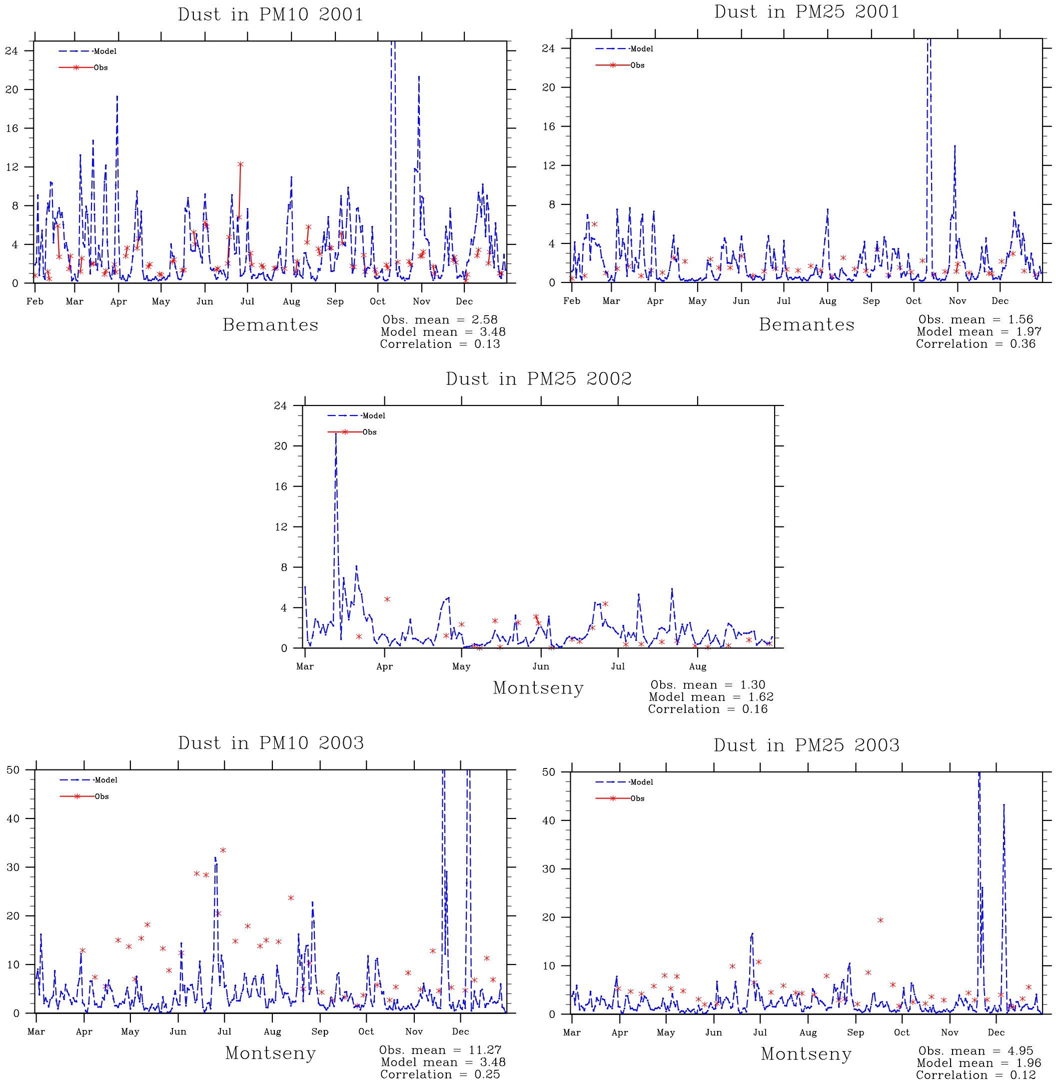


Figure 2.18: Time-series of calculated and measured daily concentrations of mineral dust in PM_{10} *and* $PM_{2.5}$ *in 2001 at Bemantes and 2002-2003 at Montseny. Unit:* $\mu g/m^3$.

At Bemantes, which is situated at the north-western coast of Spain, the model somewhat overestimates measured concentrations of both fine dust and dust in PM_{10} averaged over the days with measurements. It also slightly overestimates fine dust concentrations in 2002 at Montseny. Conversely, modelled dust concentrations are considerably lower than observed in 2003 at Montseny, especially for dust in PM_{10}. The temporal correlation between calculated and measured dust concentrations is rather low. Given the great number of uncertainties in the calculations of natural mineral dust, the first model results are considered rather encouraging. The temporal correlation is expected to improve when daily background concentrations of Saharan dust for the actual year are used in the EMEP model (monthly averages in the year 2000 is currently used). Further work on developing and testing the parameterisation schemes for windblown and re-suspended dust is envisaged for the next year.

2.5.6 PM chemical composition

The chemical composition of PM_{10} at EMEP sites calculated with the EMEP model for 2003 is presented in Figure 2.19 (left bar for each station). Also, measured PM_{10} chemical composition based on EMEP monitoring data (SO_4^{2-}, NO_3^- and NH_4^+) is shown (right bars). Here, the upper bar box (purple coloured) represents the difference between total PM_{10} concentrations and the sum of shown individual components. In model calculations, the "rest" of PM_{10} mass includes sea-salt and particle water, while in measurements it represents the not-identified components. Figure 2.19 reveals that rather limited data on concurrent measurements of PM_{10} individual components is available at the EMEP monitoring network. Most of the sites which measured PM_{10} also measured SO_4^{2-} in 2003. In addition, NO_3^- was measured at Spanish stations and NH_4^+ was measured in Ispra (IT04). Only at two EMEP sites, AT02 and NO01, all secondary inorganic components (SO_4^{2-}, NO_3^- and NH_4^+) were measured concurrently in 2003.

In general, there is quite a good correspondence between calculated and measured SO_4^{2-}, NO_3^- and NH_4^+. Figure 2.19 nicely illustrates that the discrepancies between modelled and observed concentrations of these components found at some sites (e.g. in Spain) are too small to explain the existing underestimation of total PM_{10} by the model. Thus, the model underestimation of PM_{10} must be due to PM components other than secondary inorganic particle.

In Figure 2.20, we compare calculated and measured chemical composition of PM_{10} and $PM_{2.5}$ at three Spanish sites. In contrast to the last year report (Figure 3.11 in Tsyro, 2004), the model calculations now includes mineral dust from deserts and agricultural soils. As a result, model calculated PM levels are closer to the observed concentrations. There is still a considerable underestimation of measured concentrations of total carbon by the model, which is expected to be improved when SOA is introduces in the EMEP Unified model. The upper bar boxes (purple) represent the "not determined" fraction in gravimetrically measured PM mass, which partly consists of particle water. In model results, the purple boxes represent the calculated water in PM.

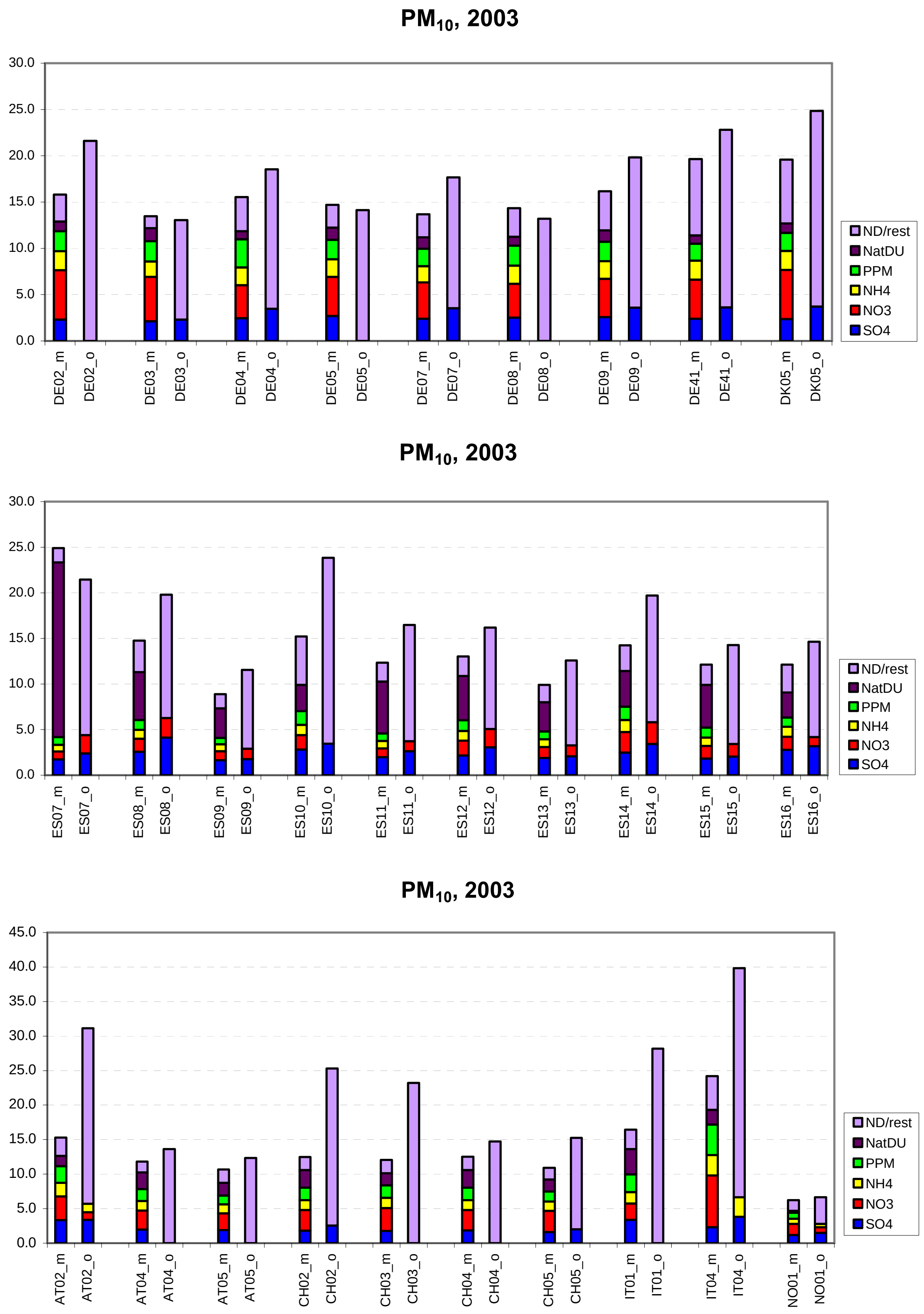


Figure 2.19: Composition of PM$_{10}$ at EMEP sites as calculated with the model ("_m") and measured ("_o") in 2003.

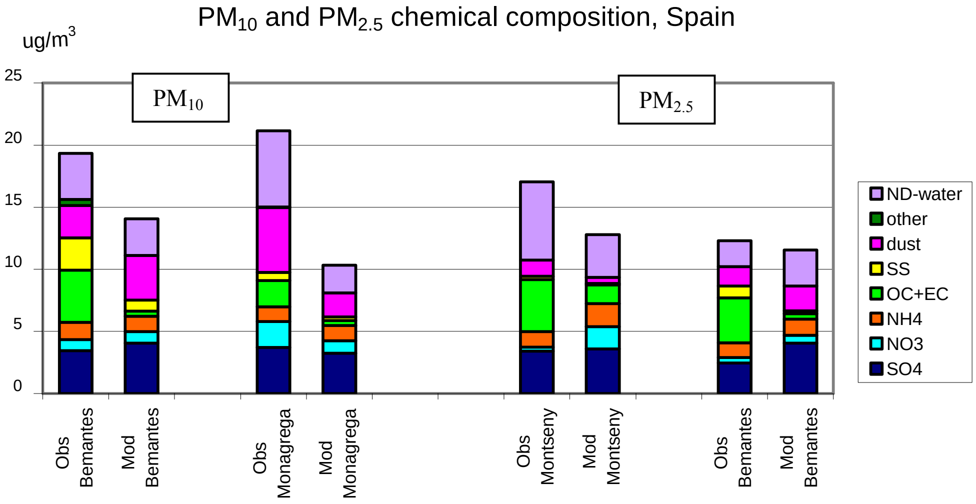


Figure 2.20: Calculated and measured chemical composition of PM_{10} *and* $PM_{2.5}$ *at Spanish sites: Monagrega in 1999-2000, Bemantes in 2001 and Montseny in 2002 (Querol et al., 2004; Rodríguez S. et al., 2002).*

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Appendix A

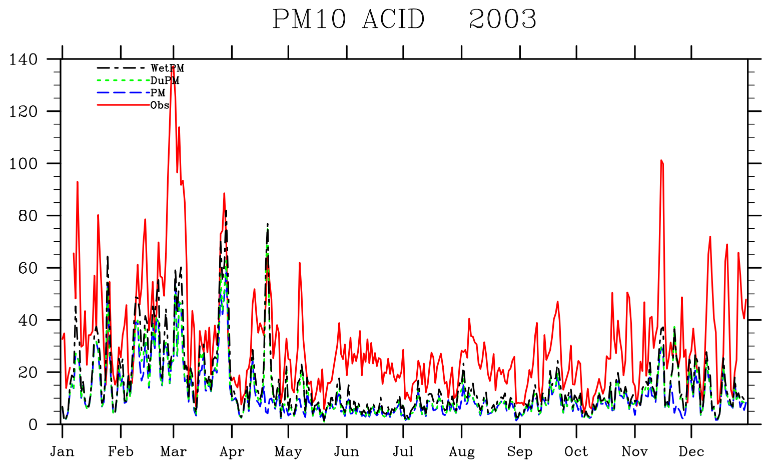
Yearly and seasonal statistics of the model performance

	Ns	pc<30%	pc<50%	Obs	Mod	Bias	RMSE	Corr
PM_{10}								
Yearly	30	-90 %	-100 %	18.92	14.24	-24	6.6	0.73*
Daily	30	-58 %	-84 %	18.89	14.26	-24	14.51	0.55
JanFeb	30	-61 %	-84 %	20.09	16.53	-17	18.22	0.57
Spring	30	-62 %	-87 %	21.51	16.24	-24	14.89	0.65
Summer	30	-45 %	-80 %	20.14	11.99	-40	13.09	0.54
Autumn	29	-65 %	-88 %	15.97	13.81	-13	13.01	0.49
$PM_{2.5}$								
Yearly	18	-94 %	-100 %	12.54	10.64	-15	4.39	0.81*
Daily	18	-62 %	-86 %	12.42	10.6	-14	10.68	0.56
JanFeb	18	-59 %	-84 %	13.67	12.28	-10	14.77	0.63
Spring	18	-68 %	-90 %	13.28	11.69	-11	10.08	0.68
Summer	18	-55 %	-84 %	13.64	9.62	-29	8.97	0.41
Autumn	18	-67 %	-88 %	10.66	10.26	-3	10.19	0.49
SIA								
Yearly	18	-89 %	-100 %	4.22	5.18	22	2.08	0.87*
Daily	18	-52 %	-76 %	4.29	5.21	21	5.48	0.67
JanFeb	17	-42 %	-66 %	5.77	8.12	40	8.41	0.58
Spring	18	-48 %	-72 %	5.08	6.2	21	6.82	0.64
Summer	18	-60 %	-85 %	3.47	3.31	-4	2.96	0.75
Autumn	18	-57 %	-81 %	3.67	4.5	22	3.74	0.78
SO_4								
Yearly	68	-94 %	-99 %	2.36	2.18	-7	0.79	0.71*
Daily	72	-56 %	-80 %	2.33	2.15	-7	2.13	0.61
JanFeb	71	-48 %	-72 %	2.68	3.02	12	3.24	0.53
Spring	72	-58 %	-81 %	2.63	2.23	-15	2.18	0.65
Summer	70	-62 %	-85 %	2.56	2.3	-10	1.87	0.62
Autumn	70	-57 %	-81 %	1.8	1.65	-8	1.5	0.61
NO_3								
Yearly	35	-71 %	-83 %	1.48	1.88	26	1.13	0.76*
Daily	35	-41 %	-65 %	1.51	1.94	28	2.72	0.61
JanFeb	34	-37 %	-58 %	1.94	3.16	62	4.24	0.49
Spring	35	-40 %	-63 %	1.9	2.39	25	3.26	0.64
Summer	35	-45 %	-71 %	1.09	0.93	-15	1.26	0.67
Autumn	35	-43 %	-67 %	1.39	1.81	30	2.28	0.63
NH_4								
Yearly	20	-70 %	-95 %	0.86	1.11	28	0.49	0.88*
Daily	20	-48 %	-71 %	0.89	1.13	27	1.27	0.66
JanFeb	19	-43 %	-65 %	1.25	1.78	42	1.92	0.6
Spring	20	-48 %	-72 %	1.08	1.43	32	1.66	0.61
Summer	20	-55 %	-77 %	0.7	0.68	-3	0.64	0.75
Autumn	20	-47 %	-70 %	0.76	0.96	26	0.84	0.78
Na								
Yearly	10	-80 %	-90 %	0.59	0.78	30	0.4	0.77*
Daily	10	-42 %	-65 %	0.6	0.78	28	0.89	0.63
JanFeb	9	-41 %	-66 %	0.63	0.89	40	1.01	0.7
Spring	10	-43 %	-66 %	0.58	0.74	26	0.79	0.63
Summer	10	-37 %	-57 %	0.56	0.62	9	0.85	0.56
Autumn	10	-44 %	-68 %	0.55	0.79	42	0.88	0.58

Here, Ns – the number of stations with measurements, pc<30% and pc<50% - the percent of data (stations) with bias less than 30% and 50%, 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 ($^{*)}$ spatial correlation for annual mean concentrations).

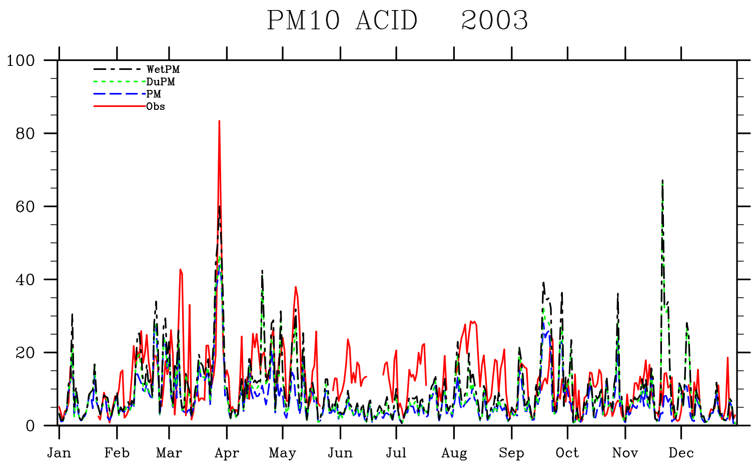
Appendix B

Daily timeseries of model calculated and measured PM_{10} and $PM_{2.5}$



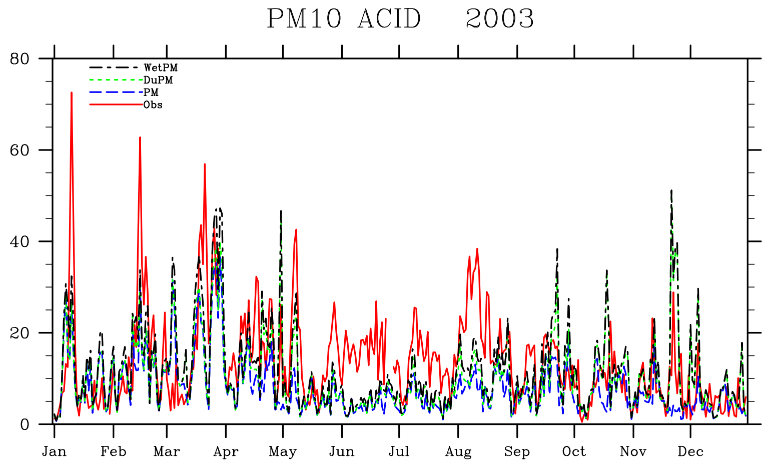
Illmitz

Obs. mean = 31.15
DryPM mean = 11.24
Corr. dryPM = 0.64
DU PM mean = 12.74
Corr. du PM = 0.63
Wet PM mean = 15.30
Corr. wet PM = 0.65



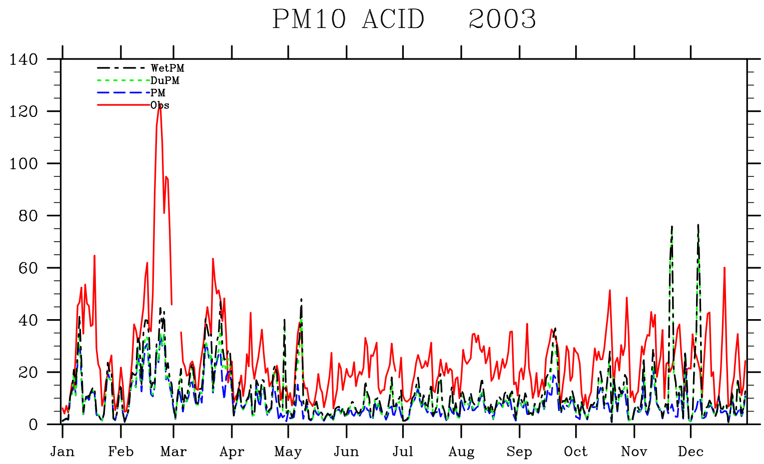
Vorhegg

Obs. mean = 12.34
DryPM mean = 7.24
Corr. dryPM = 0.50
DU PM mean = 9.21
Corr. du PM = 0.45
Wet PM mean = 10.69
Corr. wet PM = 0.49



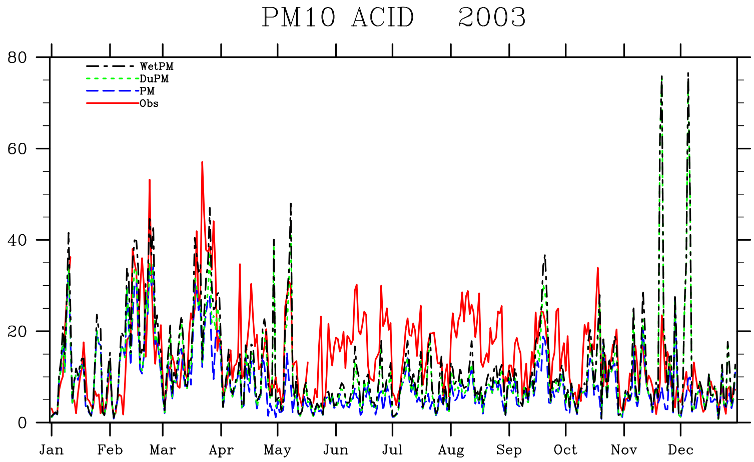
St. Koloman

Obs. mean = 13.64
DryPM mean = 7.92
Corr. dryPM = 0.49
DU PM mean = 10.34
Corr. du PM = 0.43
Wet PM mean = 11.83
Corr. wet PM = 0.48



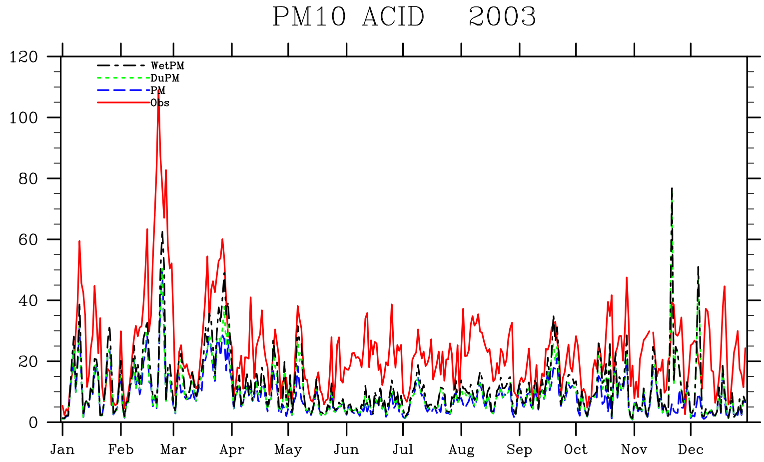
Payerne

Obs. mean = 25.30
DryPM mean = 8.26
Corr. dryPM = 0.61
DU PM mean = 10.83
Corr. du PM = 0.45
Wet PM mean = 12.50
Corr. wet PM = 0.49



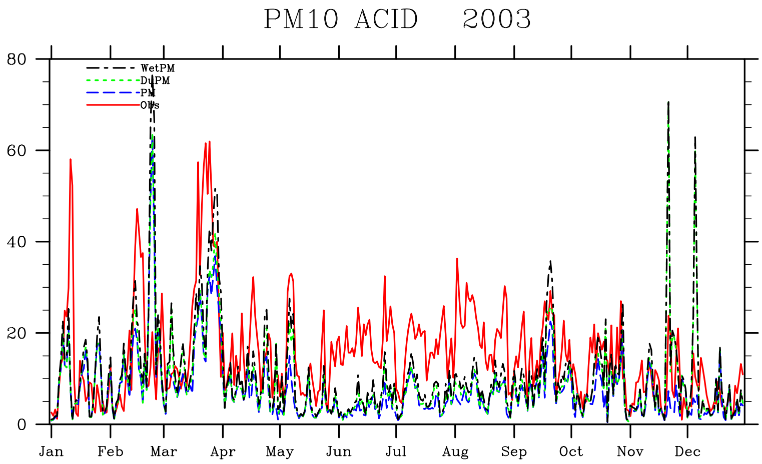
Chaumont

Obs. mean = 14.73
DryPM mean = 8.30
Corr. dryPM = 0.49
DU PM mean = 10.88
Corr. du PM = 0.41
Wet PM mean = 12.55
Corr. wet PM = 0.47



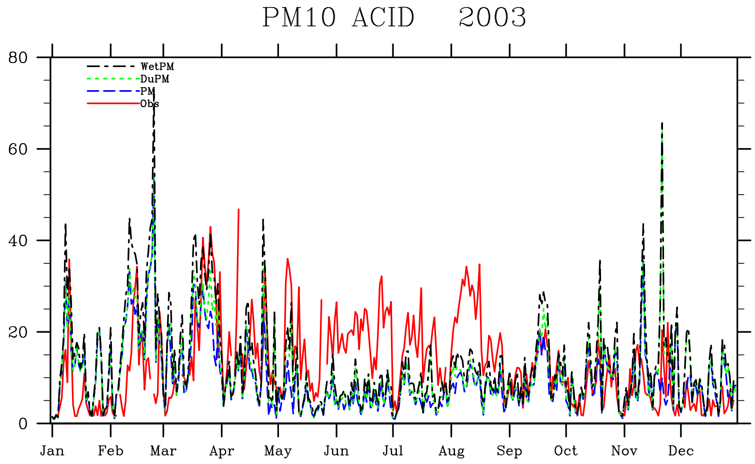
Taenikon

Obs. mean = 23.23
DryPM mean = 8.52
Corr. dryPM = 0.54
DU PM mean = 10.26
Corr. du PM = 0.50
Wet PM mean = 12.07
Corr. wet PM = 0.53



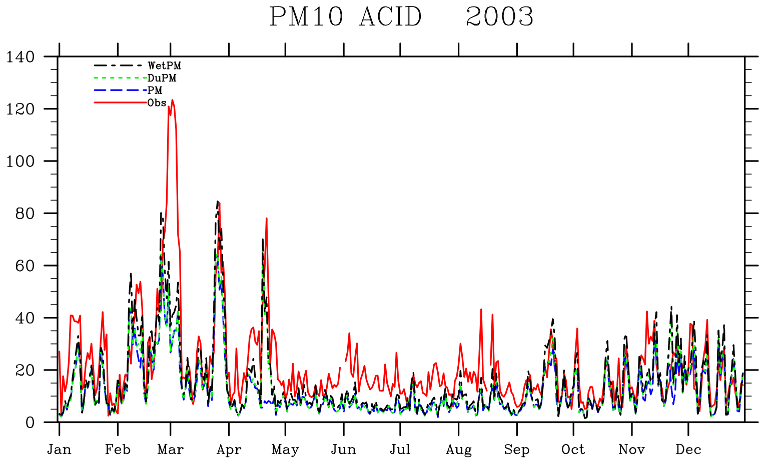
Rigi

Obs. mean = 15.24
DryPM mean = 7.62
Corr. dryPM = 0.42
DU PM mean = 9.35
Corr. du PM = 0.38
Wet PM mean = 10.91
Corr. wet PM = 0.40



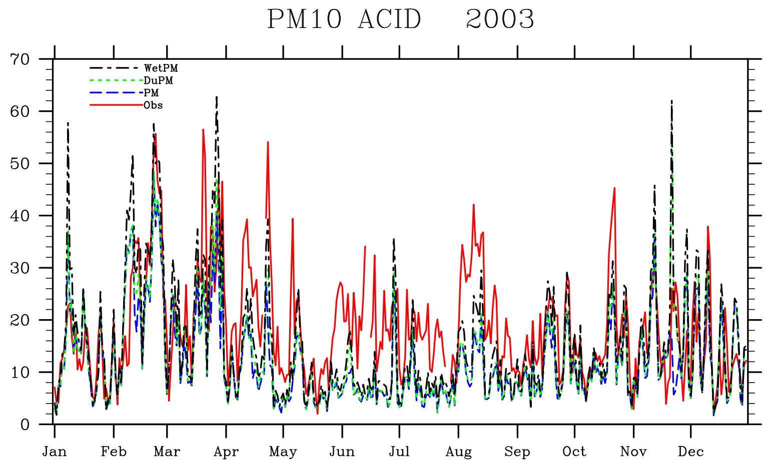
Schauinsland

Obs. mean = 13.05
DryPM mean = 9.81
Corr. dryPM = 0.23
DU PM mean = 11.27
Corr. du PM = 0.28
Wet PM mean = 13.49
Corr. wet PM = 0.32



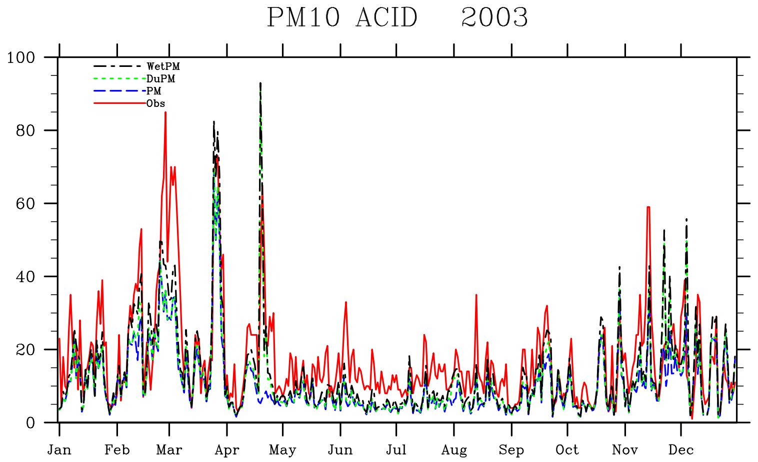
Langenbr☆gge/Waldhof

Obs. mean = 21.60
DryPM mean = 12.26
Corr. dryPM = 0.66
DU PM mean = 13.31
Corr. du PM = 0.70
Wet PM mean = 15.82
Corr. wet PM = 0.72



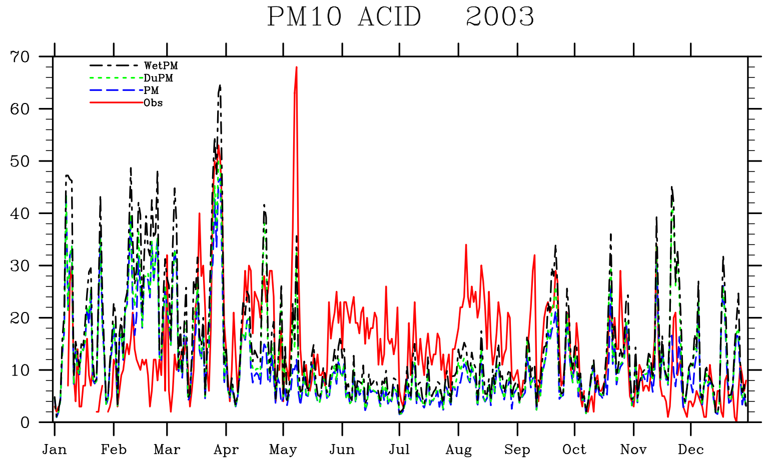
Deuselbach

Obs. mean = 18.52
DryPM mean = 12.18
Corr. dryPM = 0.59
DU PM mean = 13.07
Corr. du PM = 0.62
Wet PM mean = 15.54
Corr. wet PM = 0.65



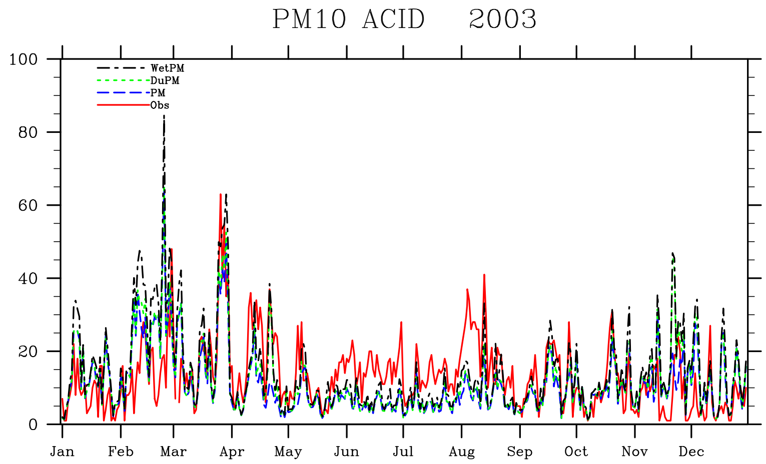
Neuglobsow

Obs. mean = 17.65
DryPM mean = 10.41
Corr. dryPM = 0.75
DU PM mean = 11.64
Corr. du PM = 0.74
Wet PM mean = 13.69
Corr. wet PM = 0.78



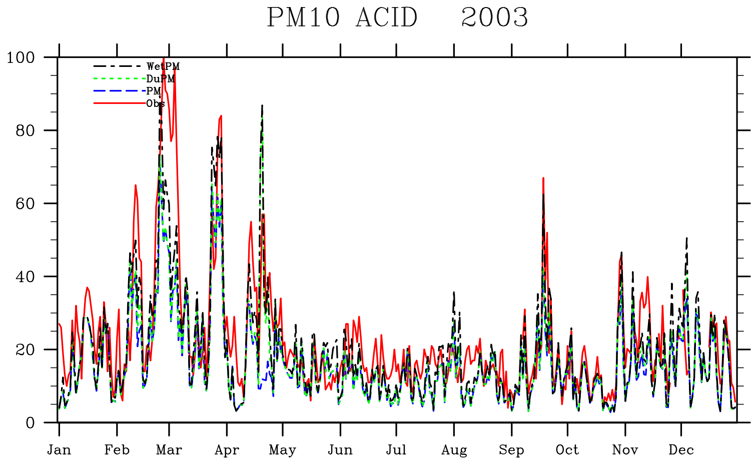
Brotjacklriegel

Obs. mean = 14.12
DryPM mean = 10.78
Corr. dryPM = 0.30
DU PM mean = 12.13
Corr. du PM = 0.37
Wet PM mean = 14.71
Corr. wet PM = 0.39



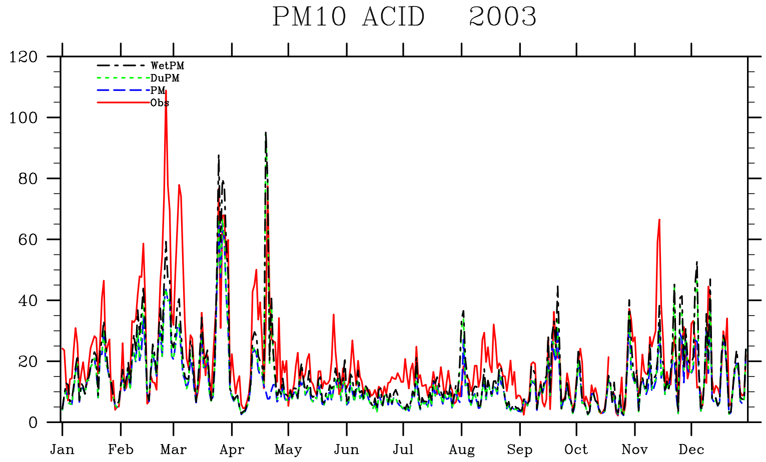
Schm☆cke

Obs. mean = 13.21
DryPM mean = 11.07
Corr. dryPM = 0.43
DU PM mean = 12.04
Corr. du PM = 0.47
Wet PM mean = 14.35
Corr. wet PM = 0.50



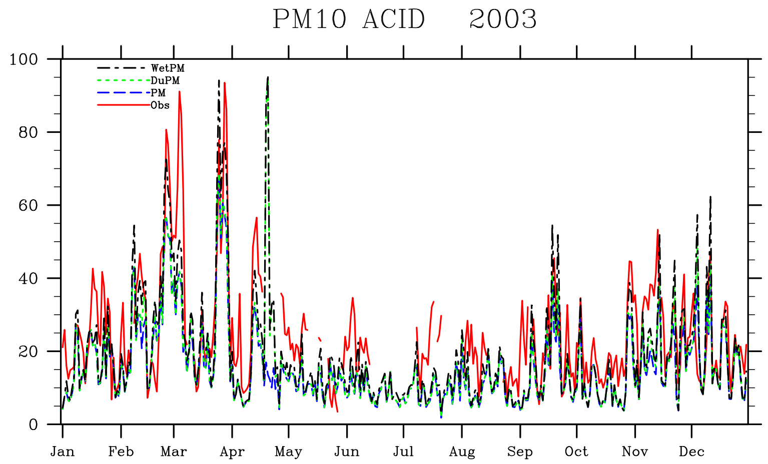
Westerland/Tinnum

Obs. mean = 22.81
DryPM mean = 16.14
Corr. dryPM = 0.78
DU PM mean = 17.03
Corr. du PM = 0.78
Wet PM mean = 19.65
Corr. wet PM = 0.81



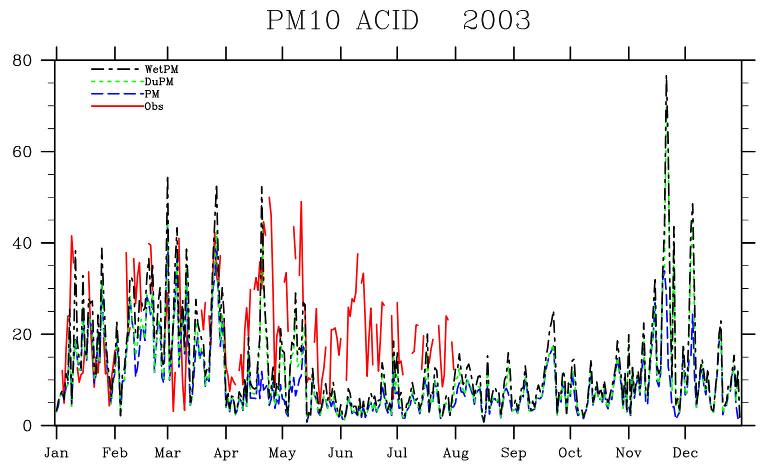
Zingst

Obs. mean = 19.81
DryPM mean = 12.80
Corr. dryPM = 0.76
DU PM mean = 14.03
Corr. du PM = 0.72
Wet PM mean = 16.17
Corr. wet PM = 0.76



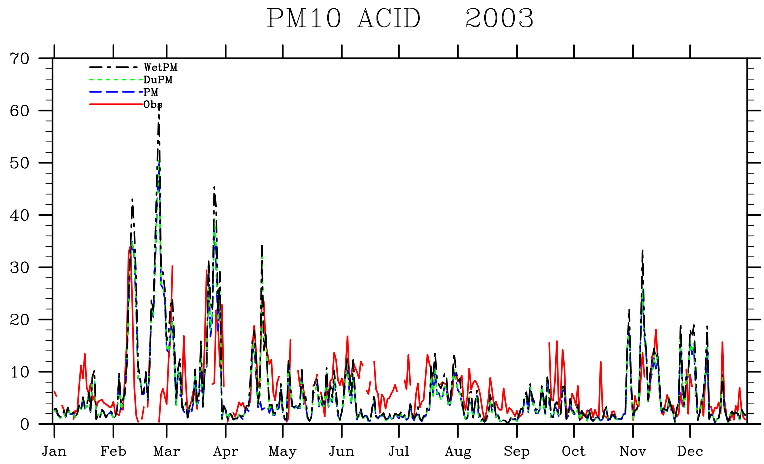
Keldsnor

Obs. mean = 24.86
DryPM mean = 16.38
Corr. dryPM = 0.76
DU PM mean = 16.86
Corr. du PM = 0.75
Wet PM mean = 19.59
Corr. wet PM = 0.76



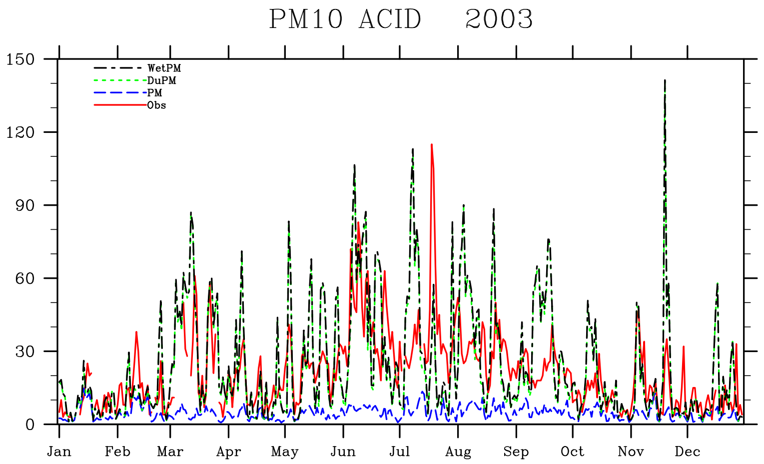
Iskrba

Obs. mean = 21.19
DryPM mean = 10.27
Corr. dryPM = 0.23
DU PM mean = 11.74
Corr. du PM = 0.34
Wet PM mean = 14.13
Corr. wet PM = 0.35



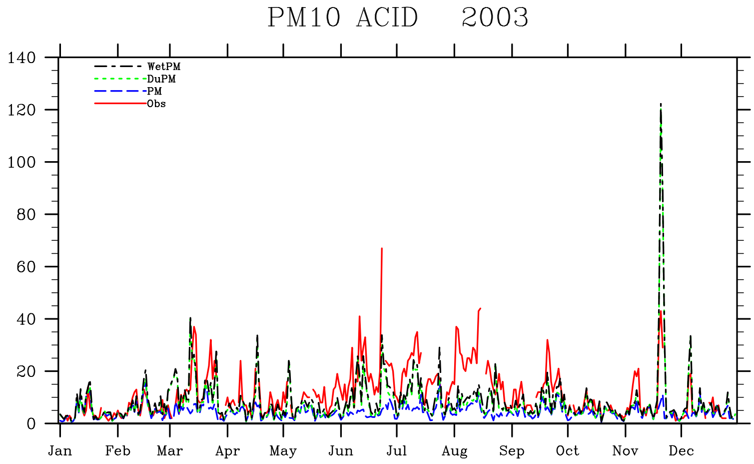
Birkenes

Obs. mean = 6.67
DryPM mean = 5.11
Corr. dryPM = 0.45
DU PM mean = 5.45
Corr. du PM = 0.51
Wet PM mean = 6.23
Corr. wet PM = 0.50



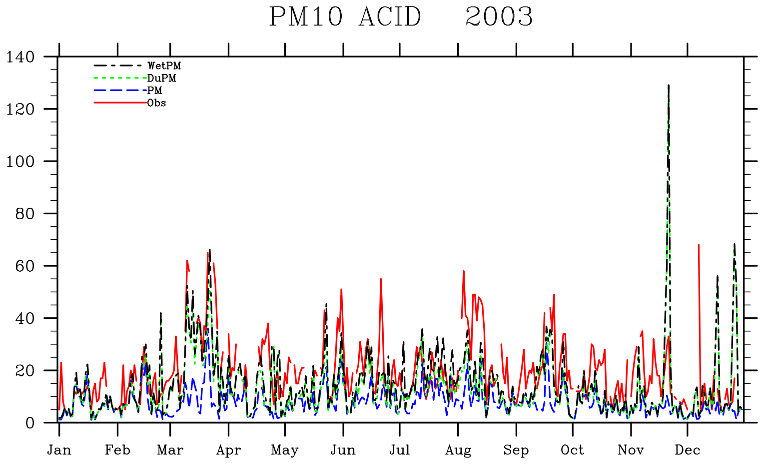
Viznar

Obs. mean = 21.45
DryPM mean = 4.63
Corr. dryPM = 0.39
DU PM mean = 23.76
Corr. du PM = 0.52
Wet PM mean = 24.91
Corr. wet PM = 0.53



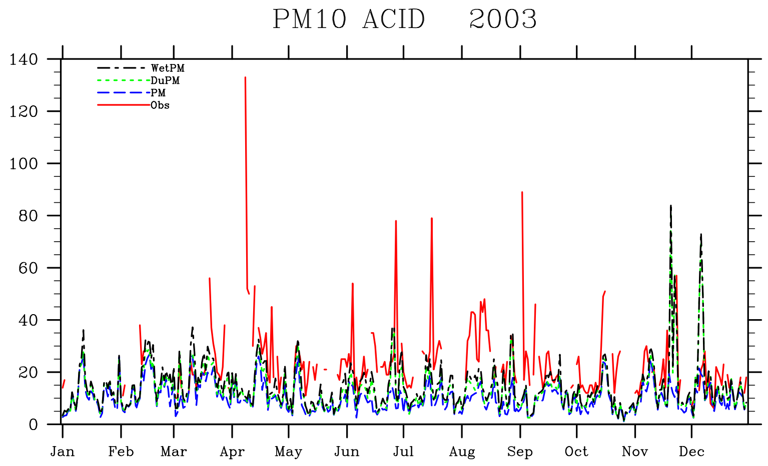
Campisabalos

Obs. mean = 11.53
DryPM mean = 4.55
Corr. dryPM = 0.41
DU PM mean = 7.77
Corr. du PM = 0.53
Wet PM mean = 8.87
Corr. wet PM = 0.56



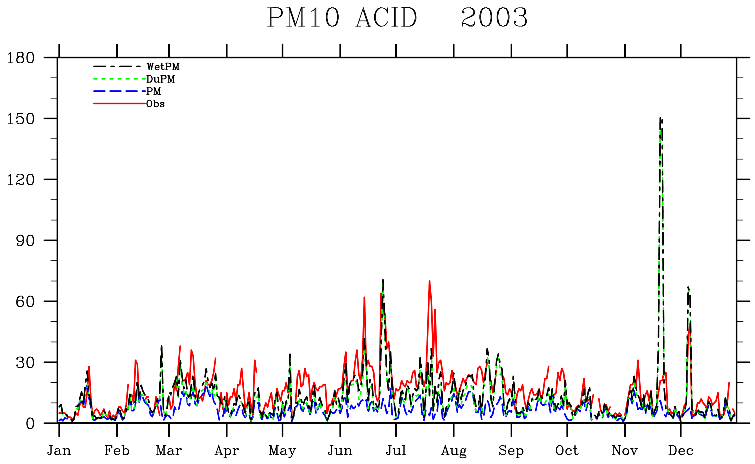
Niembro

Obs. mean = 19.79
DryPM mean = 7.94
Corr. dryPM = 0.39
DU PM mean = 13.01
Corr. du PM = 0.42
Wet PM mean = 14.75
Corr. wet PM = 0.44



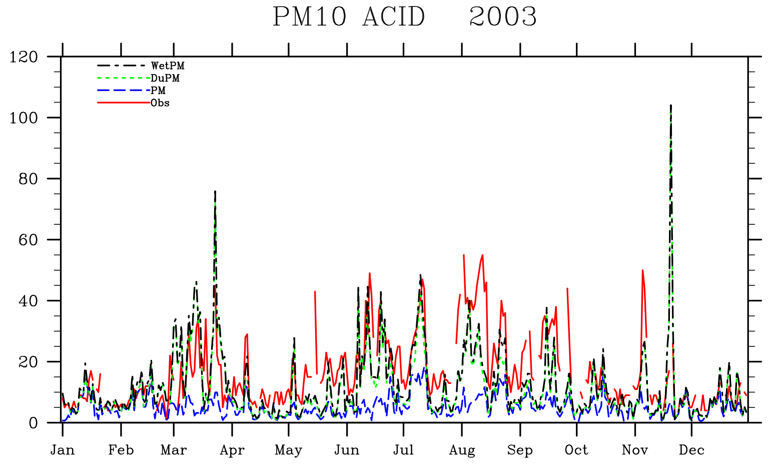
Cabo de Creus

Obs. mean = 23.83
DryPM mean = 10.46
Corr. dryPM = 0.21
DU PM mean = 13.51
Corr. du PM = 0.18
Wet PM mean = 15.20
Corr. wet PM = 0.20



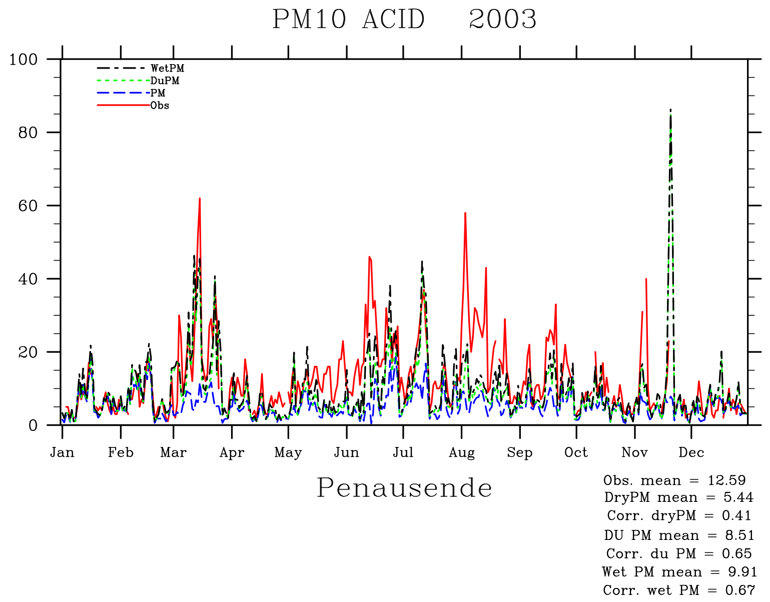
Zarra

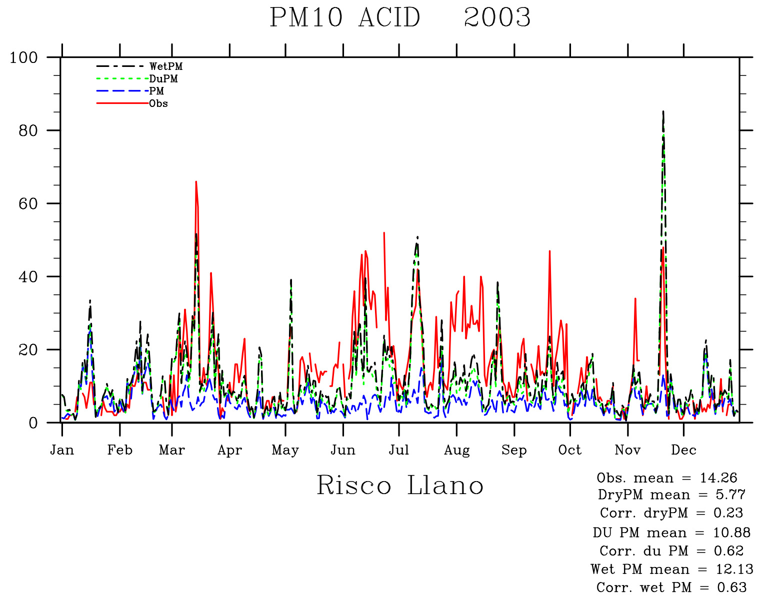
Obs. mean = 16.17
DryPM mean = 6.62
Corr. dryPM = 0.43
DU PM mean = 11.48
Corr. du PM = 0.48
Wet PM mean = 13.02
Corr. wet PM = 0.50

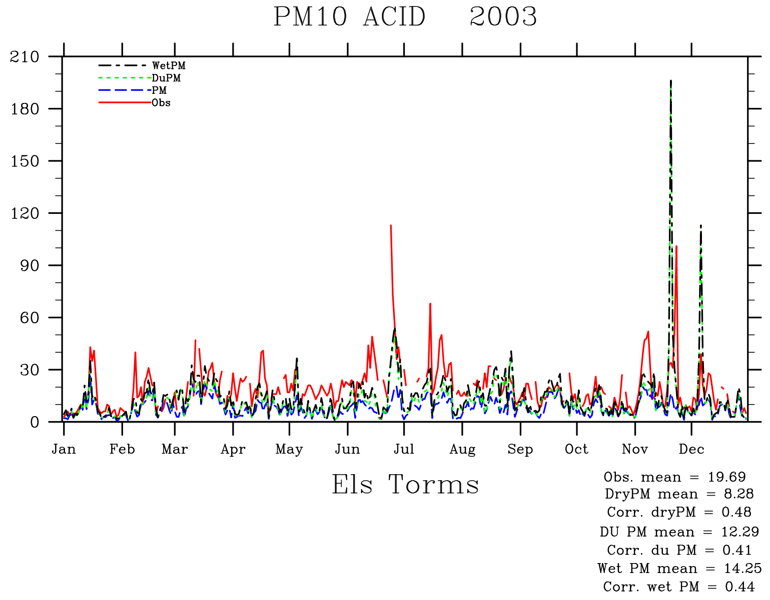


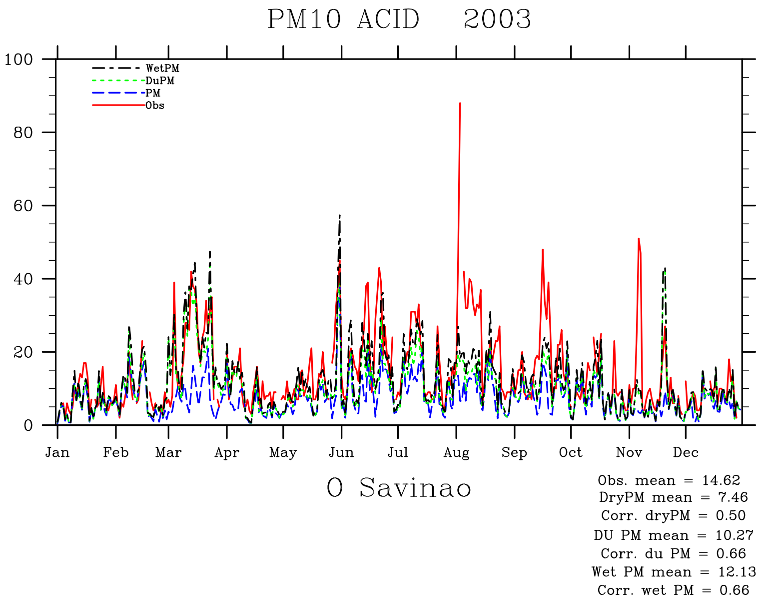
Barcarrota

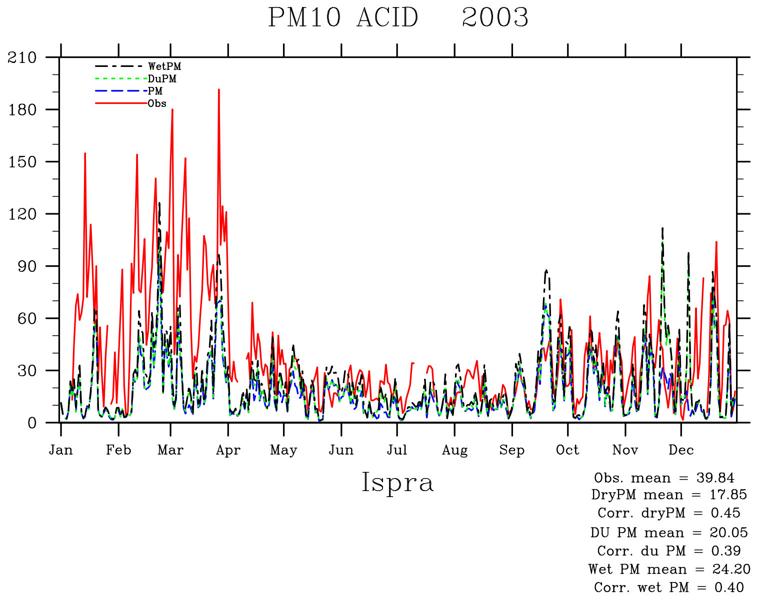
Obs. mean = 16.49
DryPM mean = 5.37
Corr. dryPM = 0.42
DU PM mean = 11.01
Corr. du PM = 0.61
Wet PM mean = 12.32
Corr. wet PM = 0.63

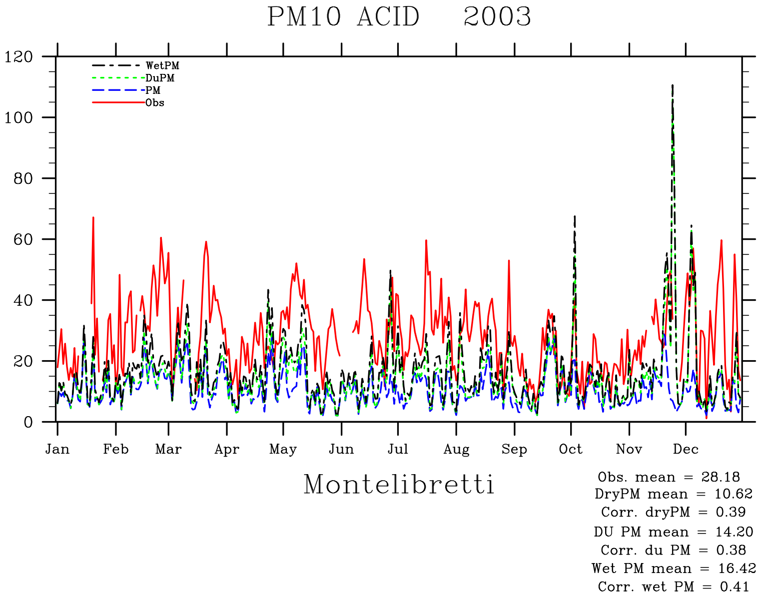

PM10 ACID 2003
WetPM
DuPM
PM
Obs
100
80
60
40
20
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Penausende
Obs. mean = 12.59
DryPM mean = 5.44
Corr. dryPM = 0.41
DU PM mean = 8.51
Corr. du PM = 0.65
Wet PM mean = 9.91
Corr. wet PM = 0.67

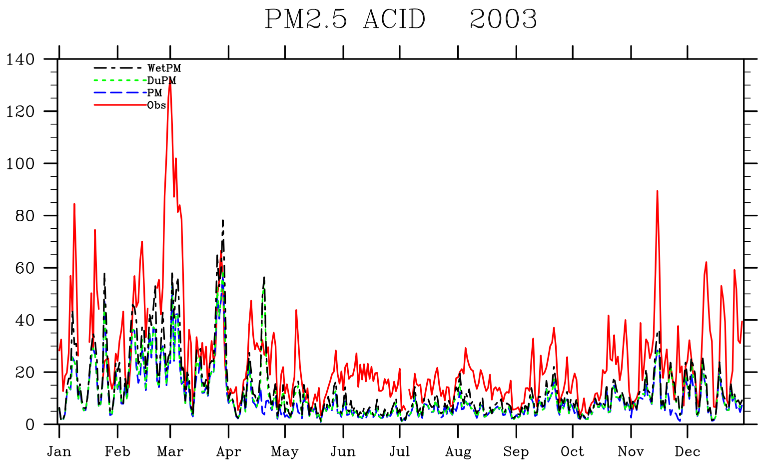

PM10 ACID 2003
WetPM
DuPM
PM
Obs
100
80
60
40
20
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Risco Llano
Obs. mean = 14.26
DryPM mean = 5.77
Corr. dryPM = 0.23
DU PM mean = 10.88
Corr. du PM = 0.62
Wet PM mean = 12.13
Corr. wet PM = 0.63


PM10 ACID 2003
WetPM
DuPM
PM
Obs
210
180
150
120
90
60
30
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Els Torms
Obs. mean = 19.69
DryPM mean = 8.28
Corr. dryPM = 0.48
DU PM mean = 12.29
Corr. du PM = 0.41
Wet PM mean = 14.25
Corr. wet PM = 0.44


PM10 ACID 2003
WetPM
DuPM
PM
Obs
0
20
40
60
80
100
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
O Savinao
Obs. mean = 14.62
DryPM mean = 7.46
Corr. dryPM = 0.50
DU PM mean = 10.27
Corr. du PM = 0.66
Wet PM mean = 12.13
Corr. wet PM = 0.66

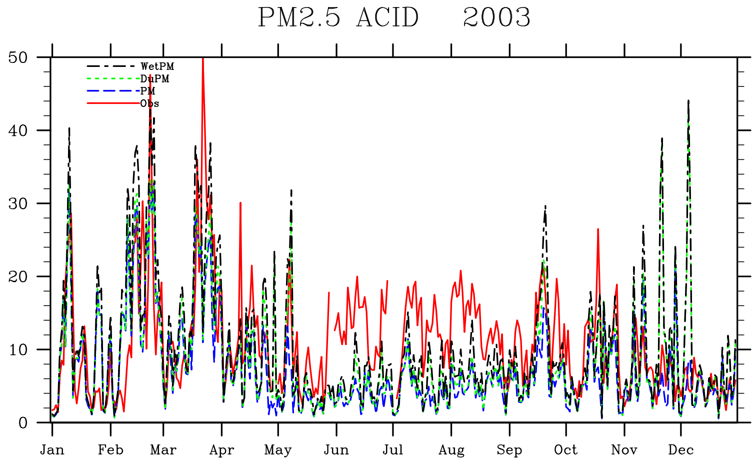

PM10 ACID 2003
WetPM
DuPM
PM
Obs
0
30
60
90
120
150
180
210
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Ispra
Obs. mean = 39.84
DryPM mean = 17.85
Corr. dryPM = 0.45
DU PM mean = 20.05
Corr. du PM = 0.39
Wet PM mean = 24.20
Corr. wet PM = 0.40


PM10 ACID 2003
WetPM
DuPM
PM
Obs
0
20
40
60
80
100
120
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Montelibretti
Obs. mean = 28.18
DryPM mean = 10.62
Corr. dryPM = 0.39
DU PM mean = 14.20
Corr. du PM = 0.38
Wet PM mean = 16.42
Corr. wet PM = 0.41



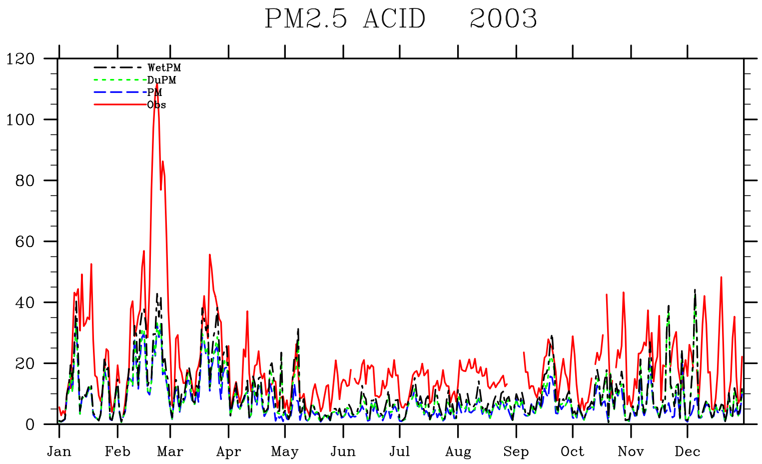
Illmitz

Obs. mean = 24.69
DryPM mean = 9.92
Corr. dryPM = 0.66
DU PM mean = 10.96
Corr. du PM = 0.62
Wet PM mean = 13.46
Corr. wet PM = 0.64



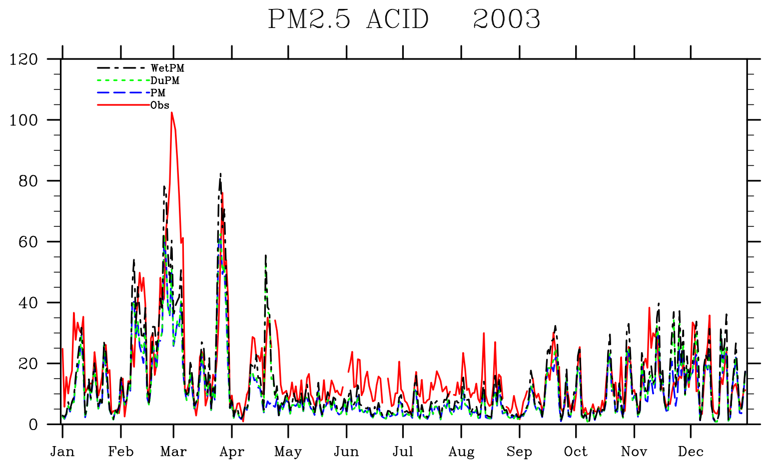
Chaumont

Obs. mean = 10.96
DryPM mean = 7.26
Corr. dryPM = 0.51
DU PM mean = 8.58
Corr. du PM = 0.46
Wet PM mean = 10.27
Corr. wet PM = 0.51



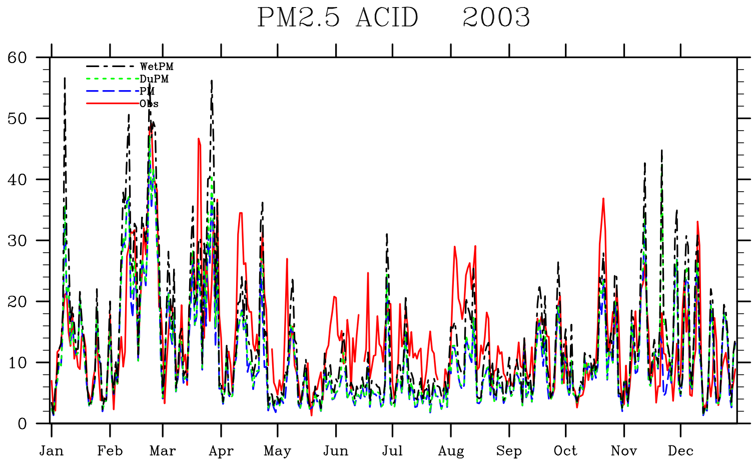
Payerne

Obs. mean = 19.76
DryPM mean = 7.20
Corr. dryPM = 0.65
DU PM mean = 8.33
Corr. du PM = 0.62
Wet PM mean = 10.02
Corr. wet PM = 0.62



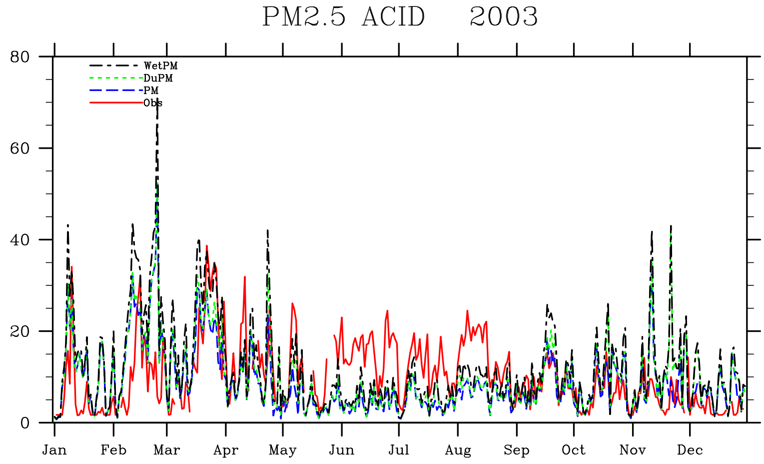
Langenbr☆gge/Waldhof

Obs. mean = 16.49
DryPM mean = 10.70
Corr. dryPM = 0.73
DU PM mean = 11.46
Corr. du PM = 0.72
Wet PM mean = 13.98
Corr. wet PM = 0.75



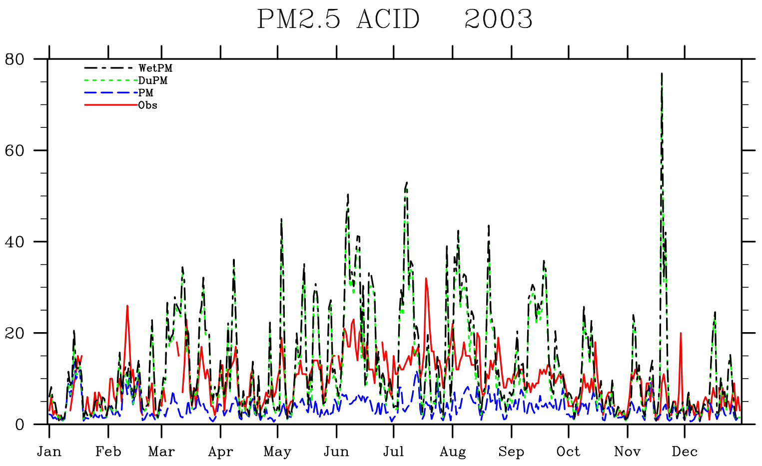
Deuselbach

Obs. mean = 13.76
DryPM mean = 10.52
Corr. dryPM = 0.69
DU PM mean = 11.10
Corr. du PM = 0.69
Wet PM mean = 13.57
Corr. wet PM = 0.71



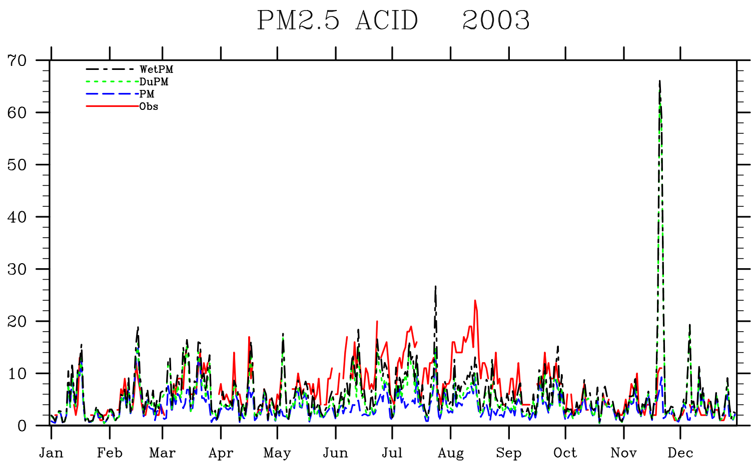
Schauinsland

Obs. mean = 10.14
DryPM mean = 8.94
Corr. dryPM = 0.33
DU PM mean = 9.86
Corr. du PM = 0.34
Wet PM mean = 12.09
Corr. wet PM = 0.39



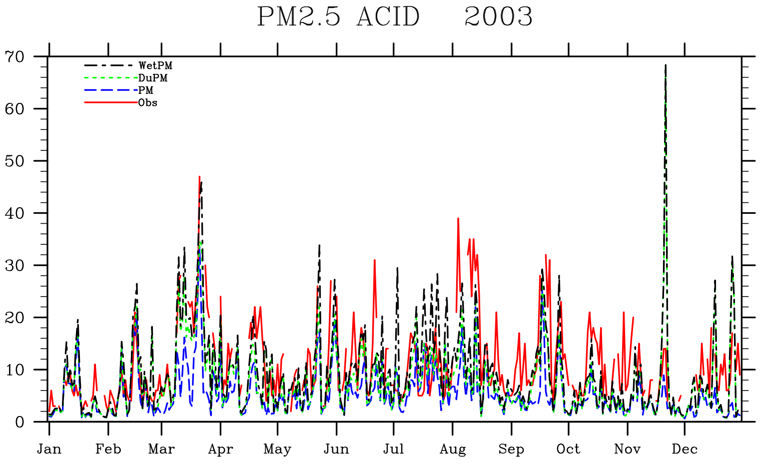
Viznar

Obs. mean = 9.41
DryPM mean = 3.59
Corr. dryPM = 0.51
DU PM mean = 12.02
Corr. du PM = 0.49
Wet PM mean = 13.18
Corr. wet PM = 0.51



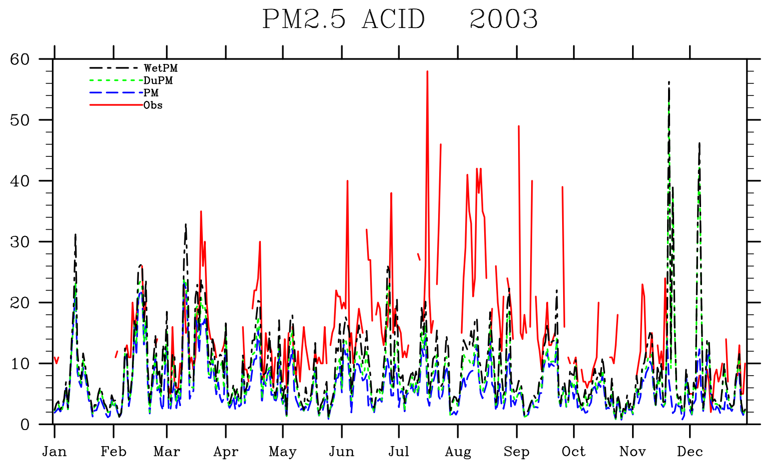
Campisabalos

Obs. mean = 7.20
DryPM mean = 3.81
Corr. dryPM = 0.48
DU PM mean = 5.42
Corr. du PM = 0.40
Wet PM mean = 6.56
Corr. wet PM = 0.46



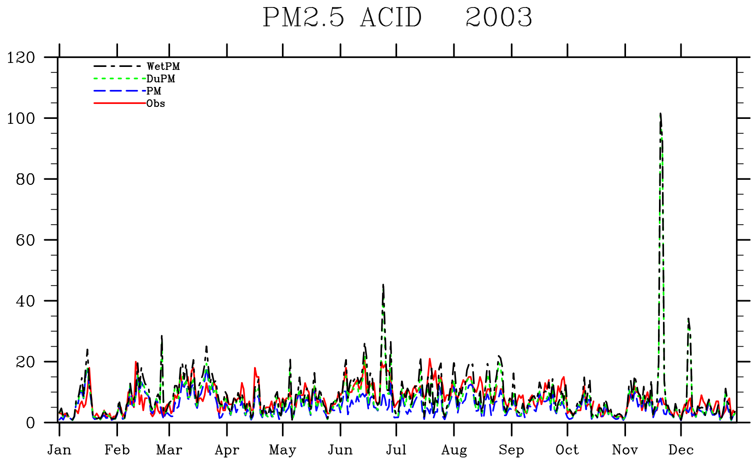
Niembro

Obs. mean = 11.00
DryPM mean = 5.31
Corr. dryPM = 0.51
DU PM mean = 7.52
Corr. du PM = 0.50
Wet PM mean = 9.19
Corr. wet PM = 0.52



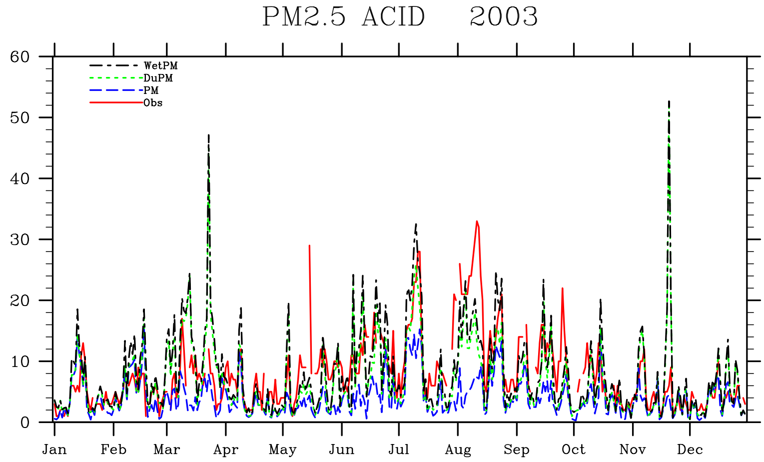
Cabo de Creus

Obs. mean = 15.81
DryPM mean = 6.56
Corr. dryPM = 0.28
DU PM mean = 8.12
Corr. du PM = 0.25
Wet PM mean = 9.80
Corr. wet PM = 0.29



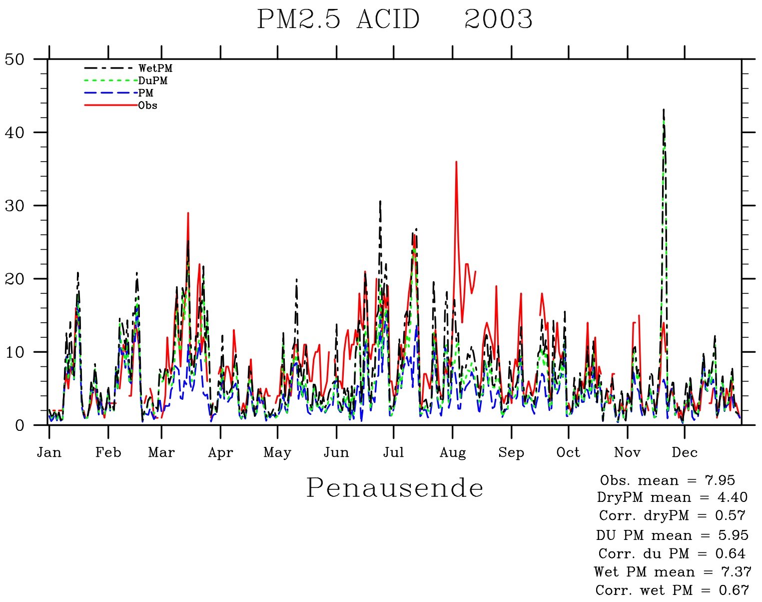
Zarra

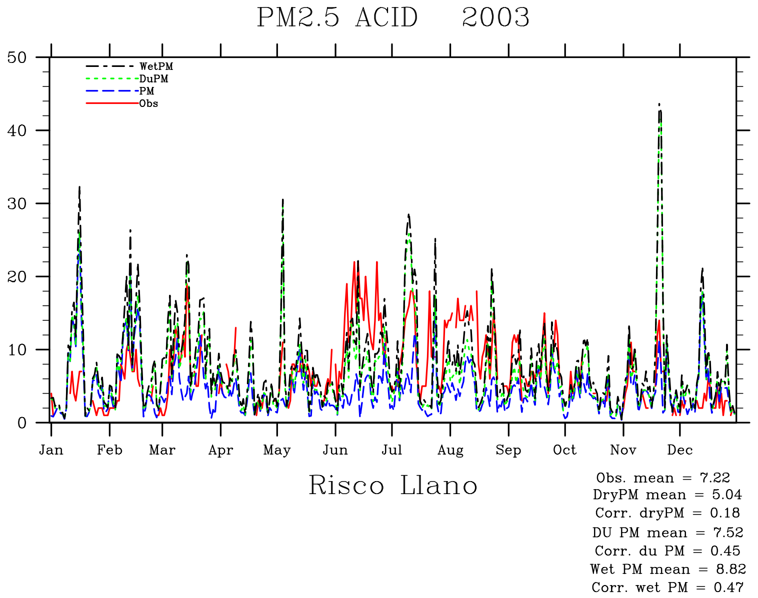
Obs. mean = 7.70
DryPM mean = 5.30
Corr. dryPM = 0.59
DU PM mean = 7.81
Corr. du PM = 0.38
Wet PM mean = 9.33
Corr. wet PM = 0.45

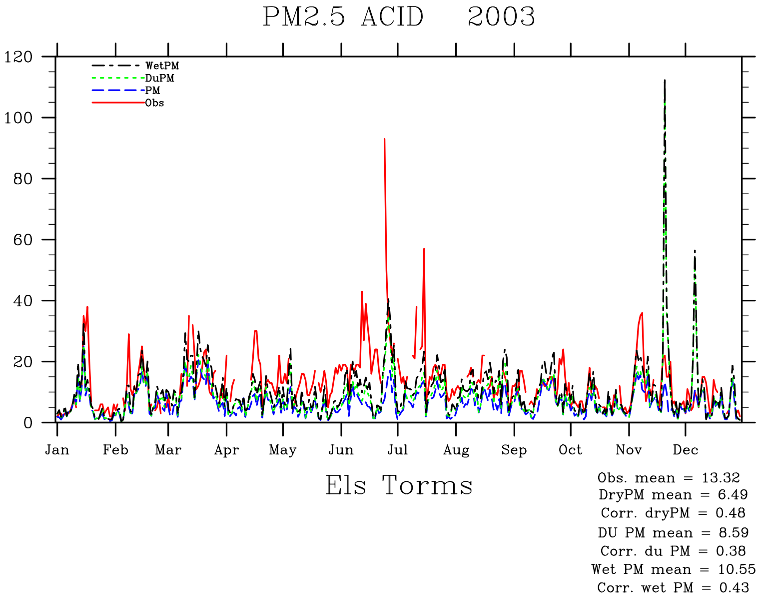


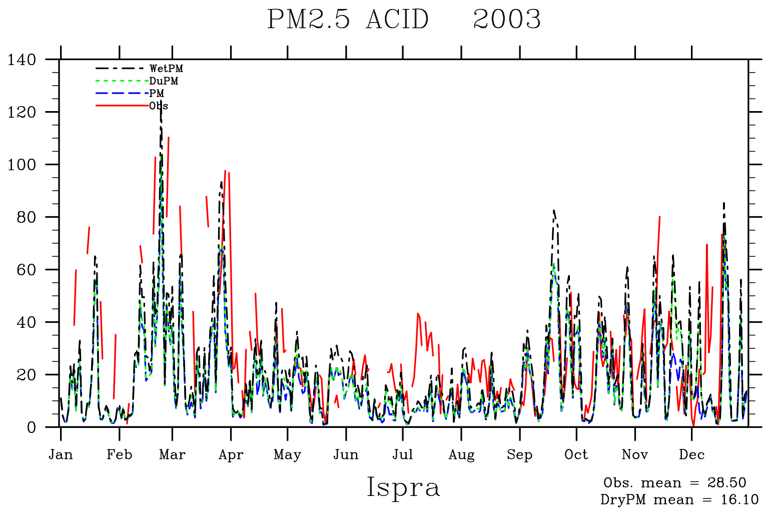
Barcarrota

Obs. mean = 8.01
DryPM mean = 4.12
Corr. dryPM = 0.54
DU PM mean = 6.86
Corr. du PM = 0.55
Wet PM mean = 8.16
Corr. wet PM = 0.59

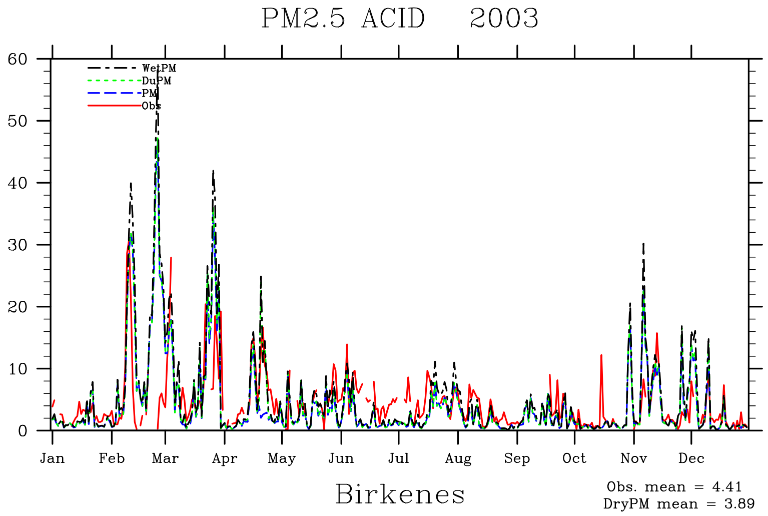

PM2.5 ACID 2003
WetPM
DuPM
PM
Obs
0
10
20
30
40
50
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Penausende
Obs. mean = 7.95
DryPM mean = 4.40
Corr. dryPM = 0.57
DU PM mean = 5.95
Corr. du PM = 0.64
Wet PM mean = 7.37
Corr. wet PM = 0.67


PM2.5 ACID 2003
WetPM
DuPM
PM
Obs
0
10
20
30
40
50
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Risco Llano
Obs. mean = 7.22
DryPM mean = 5.04
Corr. dryPM = 0.18
DU PM mean = 7.52
Corr. du PM = 0.45
Wet PM mean = 8.82
Corr. wet PM = 0.47


PM2.5 ACID 2003
WetPM
DuPM
PM
Obs
0
20
40
60
80
100
120
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Els Torms
Obs. mean = 13.32
DryPM mean = 6.49
Corr. dryPM = 0.48
DU PM mean = 8.59
Corr. du PM = 0.38
Wet PM mean = 10.55
Corr. wet PM = 0.43



Obs. mean = 28.50
DryPM mean = 16.10
Corr. dryPM = 0.50
DU PM mean = 17.42
Corr. du PM = 0.46
Wet PM mean = 21.62
Corr. wet PM = 0.47



Obs. mean = 4.41
DryPM mean = 3.89
Corr. dryPM = 0.52
DU PM mean = 4.15
Corr. du PM = 0.56
Wet PM mean = 4.93
Corr. wet PM = 0.55

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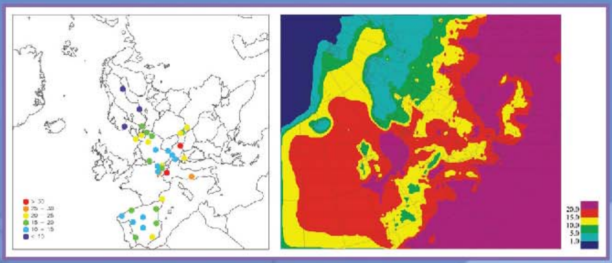

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