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To what extent can aerosol water explain the discrepancy between model calculated and gravimetric PM_{10} and $PM_{2.5}$?

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Abstract

Inter-comparisons of European air quality models show that regional transport models, including the EMEP (Co-operative Programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe) aerosol model, tend to underestimate the observed concentrations of PM_{10} and $PM_{2.5}$. Obviously, an accurate representation of the individual aerosol constituents is a prerequisite for adequate calculation of PM concentrations. On the other hand, available measurements on the chemical characterization of ambient particles reveal that full chemical PM mass closure is rarely achieved. The fraction unaccounted for by chemical analysis can comprise as much as 30–40% of gravimetric PM_{10} or $PM_{2.5}$ mass. The unaccounted PM mass can partly be due to non-C atoms in organic aerosols and/or due to sampling and measurement artefacts. Moreover, a part of the unaccounted PM mass is likely to consist of water associated with particles. Thus, the gravimetrically measured particle mass does not necessarily represent dry PM_{10} and $PM_{2.5}$ mass. This is thought to be one of the reasons for models under-prediction of observed PM, if calculated dry PM_{10} and $PM_{2.5}$ concentrations are compared with measurements. The EMEP aerosol model has been used to study to what extent particle-bound water can explain the chemically unidentified PM mass in filter-based particle samples. Water content of $PM_{2.5}$ and PM_{10} has been estimated with the model for temperature 20°C and relative humidity 50%, which are conditions required for equilibration of dust-loaded filters according to the Reference method recommended by the European Committee for Standardization (CEN). Model calculations for Europe show that, depending on particle composition, particle-bound water constitutes 20–35% of the annual mean PM_{10} and $PM_{2.5}$ concentrations, which is consistent with existing experimental estimates. At two Austrian sites, in Vienna and Streithofen, where daily measurements of $PM_{2.5}$ mass and chemical composition are available, calculated $PM_{2.5}$ water content is found to be about 75–80% of the undetermined $PM_{2.5}$ mass and there is correlation between them. Furthermore, accounting for aerosol water has improved the agreement between modelled and measured daily $PM_{2.5}$ concentrations, whilst model calculated dry $PM_{2.5}$ concentrations appear to agree quite well with the total identified $PM_{2.5}$ mass. No information on the composition of PM measured at EMEP sites is presently available. Given that PM_{10} and $PM_{2.5}$ concentrations are measured at EMEP stations with gravimetric methods they are likely to contain water. We show that the levels of modelled PM_{10} and $PM_{2.5}$ concentrations with aerosol water included agree with measurements better than dry PM concentrations. As expected, the spatial correlation has not changed significantly, whereas the temporal correlation of daily PM_{10} and $PM_{2.5}$ with monitoring data has slightly improved at most of the EMEP sites. Our results suggest that aerosol water should be accounted for in modelled PM_{10} and $PM_{2.5}$ when compared with filter-based gravimetric measurements.

1. Introduction

The main purpose of EMEP (Co-operative Programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe) models is to support policy design for trans-boundary air pollution in Europe. Therefore, the models are required to provide reliable information on the long-range transport and the level of regional concentrations and depositions of relevant pollutants. In line with this, the EMEP aerosol model is expected to produce reliable calculations of the concentrations of particulate matter (PM) in order to facilitate the assessment of adverse health effects associated with particulate pollutants. Validation of the EMEP aerosol model involves regular comparison of calculated concentrations of policy relevant metrics $PM_{2.5}$ and PM_{10} with measurements from the EMEP monitoring network. Recently, measurement data available from EIONET (European Environment Information and Observation Network) and from national (Austrian, Spanish and Norwegian) monitoring networks and research projects have been employed for the model evaluation.

In previous studies (e.g. Tsyro, 2003), the EMEP aerosol model was found to systematically underestimate observed $PM_{2.5}$ and PM_{10} concentrations by 40–60% on average, when dry $PM_{2.5}$ and PM_{10} masses from the model were compared with measurements. The model underestimation of observed PM concentrations was partly explained by that such important aerosol components as secondary organic aerosols (SOA) and wind blown and re-suspended dust, was not yet implemented in the model. This means that the model simulations did not complete the mass closure of $PM_{2.5}$ and PM_{10}.

On the other hand, data on $PM_{2.5}$ and PM_{10} measurements supplemented with analyses of the particle chemical composition (e.g. Balasubramanian et al., 2003; Matta et al., 2003; Putaud et al., 2003; Zappoli et al. 1999; Yttri, 2003) reveal that full chemical mass closure is rarely achieved, and there is often a discrepancy between chemical and gravimetric masses. In other words, after all important aerosol components (inorganic and carbonaceous compounds, minerals and metals) are analysed a part of PM mass remains unidentified. The possible sources for the discrepancy between gravimetric PM mass and the total mass of all identified components are associated with: 1) non-C atoms, i.e. oxygen, hydrogen, nitrogen, in organic aerosol, 2) particle-bound water and 3) measurement artefacts. In this paper, we will focus on the role of particle water in PM mass. Accounting for water absorbed by collected particles on the filter tape of the Beta-gauge was discussed in Chang and Tsai (2003) and Chang et al. (2001). In the work by Neusüß et al. (2002), the mass of water associated with hygroscopic aerosol compounds, was derived from the measured particles growth factor and was estimated to be about 20–25% of PM_{10} mass at 60% relative humidity. In the same work, particle chemical mass concentrations including water were shown to correspond fairly well with the gravimetric mass concentrations.

Filter-based gravimetric methods are recommended by EMEP and EU Council for determining PM_{10} mass concentrations at monitoring sites. In accordance with the Reference Method developed by the European Committee for Standardization (CEN), the filters should be equilibrated at about 50% relative humidity and 20°C temperature before they are weighed, both prior to the sample collection and after sampling. However, equilibration of filters does not remove all particle-bound water.

The purpose of this work is to estimate with a model to what extent aerosol water can explain the unaccounted fraction of gravimetric PM mass. For this purpose, the EMEP aerosol model has been used. We also examine how accounting for particle-bound water improves the comparison of model calculated PM_{10} and $PM_{2.5}$ with observations. Firstly, a short description is given of the EMEP aerosol model. We also briefly explain the CEN Reference method recommended by EU and EMEP for measuring PM mass. Then, the main results from model verification with respect to PM_{10} and $PM_{2.5}$ are outlined and problems related to the interpretation of comparison/disagreement between calculations and measurements are identified. Further, the model estimates of water content in PM_{10} and $PM_{2.5}$ at the conditions required for filter equilibration are presented. Daily measurements of $PM_{2.5}$ concentrations and chemical composition available at two Austrian stations have been employed for more elaborate testing of model calculations of particle-bound water, dry and wet $PM_{2.5}$ mass. Finally, assuming that gravimetrically measured PM mass at EMEP sites includes particle-bound water, we compare model simulated wet (including water) PM_{10} and $PM_{2.5}$ concentrations with EMEP measurements. Summary and conclusions are given in the end.

2. The EMEP aerosol model

Below, a brief description of the EMEP aerosol model is given. Previous model versions have been described in Tsyro (2002), with a detailed model description of the latest version in Appendix A in Simpson et al. (2003).

2.1. Short model description

The EMEP aerosol model describes the emissions, chemical transformations, transport and dry and wet removal of atmospheric aerosol and calculates the size-aggregated aerosol number and mass and particle chemical composition. The particle size distribution is resolved with four monodisperse size modes, i.e. nucleation, Aitken, accumulation and coarse mode. The aerosol chemical composition is described with seven components: sulphate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), elemental (EC) and organic (OC) carbon, sea salt (NaCl) and mineral dust, which are assumed to be internally mixed. In this way, all particles in the same mode are assumed to have the same size and chemical composition. Aerosol associated water is a diagnostic parameter and calculated in the model for each size mode. The aerosol dynamics module MM32 (Pirjiola et al., 2003) is employed to calculate particle coagulation and condensational growth. The empirical parameterisation by Berndt et al., 2000 for binary nucleation rate of H_2SO_4—H_2O is currently used in the EMEP aerosol model.

The model accounts for primary and secondary aerosols. In the model, primary aerosols originate from both anthropogenic and natural sources. Primary anthropogenic emissions of PM_{10} and $PM_{2.5}$ are based on the TNO CEPMEIP inventory (TNO, 2001) scaled as far as possible with the national totals of PM emission reported to EMEP (Vestreng, 2003). As no information on the chemical and size speciation of PM emissions has been available, rather crude assumptions have been used in the model to characterise chemical composition and size distribution of PM emissions. $PM_{2.5}$ emissions have been distributed between OC, EC and mineral dust, and between the Aitken and accumulation modes, and the coarse PM emissions have been assumed to consist of mineral dust. The primary natural PM in the model includes presently sea salt aerosol, for which the formation rates are calculated following Monahan (1978) and Mårtinsson et al. (2002). Implementation in the EMEP model of natural mineral dust due to wind erosion and re-suspension is in progress, but not included in the results presented here.

Secondary aerosols in the model are formed from the anthropogenic emissions of gaseous precursors, SO_x, NO_x and NH_3, as a result of homogeneous and heterogeneous chemical transformations. Gas/aerosol partitioning of semi-volatile inorganic components is calculated with the Equilibrium Simplified Aerosol Model, EQSAM, (Metzger et al., 2002a). The EQSAM used in the EMEP model currently treats the equilibrium in SO_4^{2-}–HNO_3–NO_3^-–NH_3–NH_4^+–Na^+–Cl^- system. Several schemes to calculate the formation of secondary organic aerosols (SOA) from biogenic and anthropogenic sources have been tested (Andersson-Sköld and Simpson, 2001; Simpson and Makar, 2004), but SOA is not included presently in the aerosol model.

Aerosol water is calculated with EQSAM based on the aerosol chemical composition. At each time-step, particle diameter is calculated from the total (i.e. dry PM plus water) particle mass and the particle number concentration in each size mode. The parameterisation of particle dry deposition is based on the resistance approach, where the sub-laminar layer resistance is calculated dependent on the particle size and the type of land-use. The scheme for aerosol wet deposition employs the size dependent scavenging ratios for in-cloud and sub-cloud scavenging. In clouds, all accumulation mode particles are assumed to become activated. A rather simple approach is presently implemented in the model to account for the in-cloud activation and growth of Aitken particles (Fitzgerald, 1973; Hansson, person. commun.). The detailed model description can be found in Appendix A in Simpson et al. (2003) and on the EMEP website at http://www.emep.int.

2.2. Aerosol water in the EMEP aerosol model

The aerosol water content is calculated with the EQSAM model based on the semi-empirical so-called ZSR-relation after Zdanovski (1948) and Stokes and Robinson (1966), which assumes that the water activity of the mixed solute is equal to the water activity of all single-solute solutions. Thus, the water content associated with a mixed solution is the sum of the water content of all binary solutions. Then, the mass of aerosol liquid water content (*LWC*) is found as the sum:

$$LWC = \sum_{i}^{N} (M_i/m_i), \tag{1}$$

where *LWC* (kg/m)^3 is the liquid water content of aerosol, N is the total number of single-salt solutions, M_i (mol/m^3) is the molar concentration and m_i (mol/kg) is the molality of salt *i*. The single-solute molalities are parameterized in terms of relative humidity (detailed description can be found in Metzger et al., 2002 and Metzger, 2000).

The version of EQSAM adopted in the EMEP model assumes meta-stable aerosols, i.e. that aqueous aerosols remain in a meta-stable phase. This implies that calculated aerosol water represents the upper branch of the hysteresis curve. This is believed to be rather typical for most of the measurement conditions when the end of filter exposure is in the morning. However, in some cases when the ambient humidity is much lower than that in the conditioning room (i.e. 50%), collected particles will absorb water following the lower branch of the hysteresis curve. In such cases, the model may overestimate the water content of the particle sample. The soluble aerosol compounds in the aerosol model are SO_4^{2-}, NO_3^-, NH_4^+ and sea salt. The calculated aerosol water content will depend on the mass of soluble aerosol compounds and on the type of salt mixture in particles.

3. Measurements of PM mass

3.1. EMEP/EU guidelines for PM_{10} measurements

To establish the basis for PM_{10}-monitoring a reference method has been developed by the European Committee for Standardization (CEN). The Reference Method described in CEN standard EN 12341 “Air Quality – Field Test Procedure to Demonstrate Reference Equivalence of Sampling Methods for the PM10 fraction of particulate matter” was adopted by CEN in November 1998 (EN 12341, 1998). The method consists of a PM10 sampling inlet coupled with a filter substrate and a regulated flow device. The mass collected on the filter is determined gravimetrically by means of a microbalance under well defined environmental conditions. No European Reference Method has been established up to now for the measurements of $PM_{2.5}$. This standard is currently being developed by CEN under mandate of the European Commission (Second Position Paper, 2003).

EU Council Directive 1999/30/EC defines the reference method for the sampling and measurement of PM_{10} to be the one described in EN 12341. However, a Member State may use any other method which gives results equivalent to the reference method or displays a consistent relationship to the reference method. The EMEP manual on PM_{10} measurements (EMEP/CCC, 2001) adopted in 2002 states that the aerosol particulate mass should preferably be determined according to EN 12341 (1998), or other methods and/or instruments if proven to provide results consistent with the reference method. All of the sites currently reporting PM_{10} and $PM_{2.5}$ concentrations to EMEP use gravimetric methods, otherwise Beta-gauges (Beta Attenuation Monitors) and TEOM (Tapered Elements Oscillating Microbalance) instruments are still the most commonly used methods to monitor PM mass in European national networks.

When gravimetric methods are used for PM mass measurements, the daily samples collected on filters are transferred to the laboratory for conditioning, weighing and subsequent chemical analyses. As required by EN 12341, the filters should be equilibrated at 20°C (±1) and 50% relative humidity (±5) for 48 h. This equilibration should be performed before the filters are weighed prior to the sample collection, and after sampling, before the filter is weighed again with the collected sample. As pointed out above, filter conditioning does not remove all water associated with particles, so that the gravimetrically determined PM_{10} and $PM_{2.5}$ concentrations do not typically represent PM dry mass. On the other hand, automated instruments for PM monitoring, like TEOM or Beta-gauge, use heated inlets in order to remove moisture from the sample, so that the measured concentrations are close to dry PM concentrations.

3.2. Particle water in gravimetric PM mass

Available data on PM mass measurements, supplemented with analysis of PM chemical composition, and results of mass closure experiments presented in a number of publications, reveal that full chemical characterisation of particles is rarely achieved. There is typically a difference between the gravimetric PM mass concentration and the sum of all chemically identified components. The unaccounted part of PM mass could be as large as 25–35% of the PM_{10} and $PM_{2.5}$ mass.

It was already pointed out above, that besides sampling and analysis artefacts affecting the attainment of chemical mass balance, the unaccounted mass can partly be explained by elements associated with organic aerosols other than carbon. Moreover, a part of the unaccounted PM mass is commonly attributed to particle-bound water. Estimates based on the growth factor measurements show that for instance $(NH_4)_2SO_4$ can contain about 30% (mass) of water at 50% relative humidity (Schwela et al., 2002). Studies of the water uptake by particles on filters exposed to different humidities (Winkler and Junge, 1972) show the increase of particle mass at relative humidity of 50% to be 10–30% compared to the dry mass. Results from several studies, summarised in Schwela et al. (2002), support those findings. Further more, the amount of water in PM samples will vary for different samples and measurement sites, depending on the particle composition and the ambient relative humidity and temperature (e.g. Warneck, 2000). Depending on the ambient conditions during sampling, particles on the dust-loaded filter can either adsorb or lose water under post-equilibration. The relationship between particle mass and composition and particle water content is rather complicated due to hysteresis in the water adsorption-desorption pathways (i.e. the deliquescence and crystallization relative humidity points of the aerosol particle do not coincide). Due to the hysteresis phenomenon, the mass of water will be greater in particle samples collected at high ambient humidity and then transferred to a lower humidity environment in the laboratory, as compared to the opposite case.

4. Model calculations and comparison with measurements

4.1. Calculations of dry PM concentrations

The EMEP aerosol model, without any accounting for PM-water, was previously verified for the years 1999–2001 with data available from the EMEP monitoring network, the AIRBASE database and several national research campaigns (Tsyro, 2003; Tsyro et al., 2003). The model was found to systematically underestimate measured $PM_{2.5}$ and PM_{10} concentrations by 40–60% on average (as shown in Fig. 9, upper panels), when dry PM_{10} and $PM_{2.5}$ concentrations were compared with measurements. These discrepancies between model calculations and measurements were explained in terms of the lack of secondary organic aerosols (SOA) and wind blown and re-suspended dust. For instance, the largest underestimations of PM_{10} and $PM_{2.5}$ by the model were found at Spanish stations. This is because of the significant contribution of mineral dust to PM in Spain due to wind soil erosion and Saharan dust intrusions (Rodríguez et al., 2001; Rodríguez et al., 2002).

Particulate matter is not a single pollutant, but a complex mixture of many pollutants. Therefore, the adequate model calculation of PM_{10} and $PM_{2.5}$ depends on its accurate representation of the individual PM constituents. Unfortunately, model evaluation with respect to the individual aerosol components is presently hampered by the lack of data on particle chemical composition. Data on particle chemical characterisation, necessary for elaborating the model verification, was not available at the same EMEP and AIRBASE monitoring sites where PM_{10} and $PM_{2.5}$ concentrations were measured, except for one site in Birkenes, Norway (Table 1).

Thus, there was insufficient information for drawing conclusions on the reasons for the discrepancies between modelled and measured PM concentrations. Recently, measurements of PM_{10} and $PM_{2.5}$ chemical composition from Spanish and Austrian national networks and research campaigns (Rodrîguez et al., 2002; Querol, personal commun.; and Puxbaum et al., 2003) have been made available to us (Table 1). These data have been used for evaluating the revised model results in this work.

In Tsyro (2003), model calculated annual mean PM_{10} chemical compositions were compared with data on aerosol chemical characterization synthesized in Putaud et al. (2003). Model predictions of the annual mean concentrations of secondary inorganic aerosols (SIA), namely SO_4^{2-}, NO_3^- and NH_4^+, were generally in reasonable agreement with the measured concentrations (examples for rural stations are presented in Fig. 1). As expected, the model considerably underestimated concentrations of organic carbon (OC) as only primary anthropogenic OC was taken into account in the calculations. At some sites, especially in Spain, the model also underestimated mineral dust concentrations because wind blown and re-suspended dust was not implemented in the aerosol model. On the other hand, the uncertainties associated with anthropogenic PM emissions and, in particular, with their chemical speciation were recognised to be an important source of discrepancies between modelled and measured concentrations of carbonaceous and mineral aerosol components.

It was emphasized that improvement in the quality of PM emission data and its chemical speciation as well as the further model development to account for all important aerosol components were prerequisites for the accurate modelling of PM chemical composition. However, the question remains: would the model, providing its adequate calculation of the individual aerosol components, be able of reproducing the monitored PM_{10} and $PM_{2.5}$ concentrations? As discussed above, a part of the unidentified PM mass can probably be attributed to aerosol water. At present, particle-bound water is not measured operationally at the stations where PM is monitored. If PM mass alone is measured with filter-based gravimetric methods it appears impracticable to derive dry PM mass for appropriate model verification from the measured PM concentrations. Instead, in this work we use the model to estimate the amount of water remaining on particles after the filter conditioning and then, to account for the residual water in calculated PM_{10} and $PM_{2.5}$ concentrations when comparing them with observations.

4.2. Model calculations of particle-bound water

4.2.1. Annual mean PM water content

Water content of PM_{10} and $PM_{2.5}$ has been calculated with the model for the conditions which are required according to the Reference Method for sample equilibration, i.e. temperature of 20°C and relative humidity of 50%. Calculated in this way PM water content represents particle-bound water (henceforth also referred to as residual water) still present in gravimetric PM_{10} and $PM_{2.5}$ concentrations after the sample conditioning. Figure 2 shows the maps of model calculated annual mean mass of residual PM_{10}water and the fraction of water in "wet" PM_{10} concentrations for 2001. According to our model simulations, gravimetrically measured annual mean PM_{10} concentrations can contain between 0.5 $\mu g/m^3$ water in Scandinavia and 6.5 $\mu g/m^3$ water in the Netherlands and Belgium. The calculated annual mean mass of residual water associated with $PM_{2.5}$ varies between 0.3 and 5 $\mu g/m^3$. Particle water content is determined by the mass fraction and the type of mixture of soluble PM constituents. Thus, the geographical distribution of calculated residual aerosol water reflects the distribution of soluble aerosols, which in the model are sulphate, nitrate, ammonium and sea salt. Organic aerosols have been assumed insoluble. Because secondary inorganic components are mainly in the fine mode the water content of PM_{10} and $PM_{2.5}$ is rather similar in most inland areas. There is a noticeable increase in the mass of particle-bound water found in the coastal areas due to the contribution of sea salt particles.

According to the model estimates, the fraction of residual water varies between about 20 and 40% (largely 20–30%) in PM_{10} and between 20 and 35% in $PM_{2.5}$, depending on the fraction of soluble components. The lowest fraction of residual water in PM_{10} mass (below 20%) has been calculated for parts of Russia, where the calculated fraction of insoluble primary particles (EC, OC, mineral dust) in PM_{10} is largest (30–50%). In most of Europe, the fraction of residual water in PM_{10} is 20–30%. The calculated distribution of residual water fraction in $PM_{2.5}$ is rather similar to that in PM_{10}. The largest differences in water content of PM_{10} and $PM_{2.5}$ are calculated in coastal areas due to the contribution of water associated with coarse sea salt particles. Our calculations of PM_{10} and $PM_{2.5}$ water content at 50% relative humidity seem to be in an agreement with results from other relevant studies (e.g. Neusüß et al., 2002) and are believed to be a rather reasonable estimate of residual particle water.

Figure 3 compares the annual mean chemical composition of PM_{10} and $PM_{2.5}$ calculated with the EMEP aerosol model with measurements at stations in Spain, Austria and Norway. Here, purple colour designates both the undetermined fraction in measured PM mass (ND) and the residual particle-bound water in the model results. As expected, model calculated PM_{10} and $PM_{2.5}$ concentrations agree better with the measured values when residual water in PM is accounted for. Figure 3 indicates that the main reason for model underestimation of PM_{10} and $PM_{2.5}$ is its underestimation of the concentrations of carbonaceous particles and mineral dust in Spain.

At all considered sites, the mass of residual water calculated with the model is smaller than the unaccounted mass in measured PM_{10} and $PM_{2.5}$ (Fig. 3 and Table 2). According to the calculation results, water in PM_{10} and $PM_{2.5}$ can explain 30 to 80% of the unaccounted mass. Since aerosol water was not measured at those sites it was impracticable to validate the model calculations of residual PM_{10} and $PM_{2.5}$ water.

The calculation results in this section suggest the following:

1. The model seems to give a reasonable estimate of the mass of water in PM_{10} and $PM_{2.5}$ at 50% relative humidity. Accurate calculation of the mass of soluble components, in this case SO_4^{2-}, NO_3^- and NH_4^+, is a prerequisite for the good prediction of water content.
2. The residual particle water can explain a part of the undetermined PM mass (30–80% according our estimates), while the other, more variable part on the undetermined PM mass is probably due to other factors, e.g. non-C atoms associated with organic aerosols and/or the measurement artefacts (as discussed in Putaud et al. 2003; Yttri, 2003).

However, more measurements on PM mass and chemical composition and, in particular, measurements of particle water are needed for further testing and verification of those results.

4.2.2. Testing model results with daily data at two Austrian sites

At the sites shown in Fig. 3, the fraction of undetermined PM mass averaged over longer (6–12 months) periods is around 20–35%. However, for daily $PM_{2.5}$ and PM_{10} the unaccounted fraction varied from below 0 to 75–80% (negative values occurred in several cases were probably due to the measurement artefacts). Measurement data with a daily resolution on gravimetric $PM_{2.5}$ concentrations and $PM_{2.5}$ chemical composition was only available at two Austrian sites, Vienna and Streithofen, for the period 1 May 1999–31 May 2000. We have used these data in order to see if a correspondence can be found between daily variations of model calculated $PM_{2.5}$ water, on the one hand, and $PM_{2.5}$ unaccounted mass in observations, on the other hand. Below, we present results for 2000, while the analysis and conclusions have been based on the data from both 1999 and 2000.

Model calculated and measured chemical composition of $PM_{2.5}$ at Vienna site (AU01) and Streithofen site (AU02), averaged over the period 1 January–31 May 2000, is shown in Fig. 4.

Similar to results for PM_{10} (Fig. 3), the largest discrepancy in $PM_{2.5}$ composition between model results and measurements is found for carbonaceous particles, especially for EC, whereas model fine OC compares better with measurements than OC in PM_{10}. The larger underestimation of OC mass in PM_{10} is probably due to coarse organic particles, which are not fully represented in the model. At these sites, about 30% of measured organic carbon was found in the coarse mode and was to a certain level attributed to primary biogenic organic aerosol (Puxbaum et al., 2003), which is not included in the model.

Model calculated concentrations of the main $PM_{2.5}$ soluble components, SO_4^{2-}, NO_3^- and NH_4^+, compare reasonably well with measurements (Fig. A1 in Appendix). The temporal correlation coefficients (R) for daily concentrations in 1999 and 2000 periods vary from 0.54 to 0.56 for SO_4^{2-}, from 0.59 to 0.69 for NO_3^-, from 0.62 to 0.68 for NH_4^+ and from 0.3 to 0.62 for sea salt. The total mass of SIA is simulated correctly by the model; however there are slight discrepancies between calculated and observed contributions of the individual inorganic components. On average, the model slightly underestimates measured sulphate and ammonium concentrations in 1999 and overestimates those in 2000. Calculated average nitrate concentrations are very close to measurements in 1999 and overestimated by about 25–30% in 2000. For 1999, sea salt is under-predicted by the model, while calculations for 2000 are rather close to measurements. Based on these verification results for main hygroscopic components it can be expected that model calculations should give a reasonable estimate of water in measured $PM_{2.5}$ mass.

A rather good correspondence has been found between calculated residual aerosol water and unaccounted $PM_{2.5}$ mass in 2000 (Fig. 5), with the correlation coefficients R of 0.45 and 0.57 at Vienna and Streithofen sites respectively. On the other hand, for 1999 the corresponding correlation coefficients are 0.32 and 0.17. Notably, the correlations between unaccounted $PM_{2.5}$ mass and the measured mass of soluble $PM_{2.5}$ components (SIA and sea salt) in 2000 are much higher (0.62 at AU01 and 0.63 at AU02) than in 1999 (0.37 at AU01 and 0.35 at AU02). This may indicate that in 1999 the unaccounted PM mass was to a larger degree associated with other factors than particle water. In a number of days in 1999, the mass of undetermined $PM_{2.5}$ drops below zero, which could be attributed to the measurement/analysis uncertainties. Averaged over the whole period, the mass of model calculated residual water is smaller than the mass of $PM_{2.5}$ undetermined fraction. However, on some days the model calculated mass of $PM_{2.5}$ water exceeds the unaccounted $PM_{2.5}$ mass. The careful study of calculation results has revealed that on those days the model overestimates the concentrations of one or several soluble $PM_{2.5}$ constituents, which consequently results in overestimation of aerosol water.

As pointed out above, the contribution to organic aerosol mass from elements other than carbon (e.g. hydrogen, oxygen, nitrogen) can be one of the sources of unaccounted PM mass in measurements, if OC mass in the identified PM fraction is presented as mass of carbon. In Puxbaum et al. (2003), the factors for conversion of organic carbon mass to organic matter (OM) mass of 1.3 and 1.7 were considered appropriate for respectively urban (the Vienna site) and rural (the Streithofen site) environments. We have used those conversion factors to derive the total mass of organic aerosol (i.e. OM) in $PM_{2.5}$ and thus eliminate the unaccounted part of $PM_{2.5}$ due to non-C atoms in organic particles. Then, the unaccounted $PM_{2.5}$ mass should be largely due to particle-bound water.

In this case (Fig. 6), the model calculated mass of residual water is somewhat larger than the undetermined $PM_{2.5}$ mass and the correlation between them is slightly lowered compared to that in Fig. 5. The exceedance of unaccounted $PM_{2.5}$ mass by the model calculated mass of particle water, seen in Fig. 6, could be both due to model over-prediction of aerosol water and/or due to the rather crude assumption on conversion factors from OC to OM. As described above, the model assumes that aerosols reside in a meta-stable aqueous form what corresponds the upper branch of water adsorption-desorption curve. Therefore, the model will probably overestimate the aerosol water content in samples collected at relative humidity lower than 50%. Unfortunately, the measurement data at those sites were insufficient for more elaborate examination of the results.

The apparent association between the calculated mass of aerosol water and the unaccounted fraction of gravimetric $PM_{2.5}$ mass at those sites seems to support the suggestion that a part of the unaccounted $PM_{2.5}$ mass of can be attributed to particle-bound water. However, we recognize that these results alone do not provide the conclusive evidence that particle associated water is partly responsible for PM unaccounted mass. Instead, experimental evidences involving measurements of particle water are needed. Finally, the discrepancies found between modelled $PM_{2.5}$ water mass and $PM_{2.5}$ unaccounted mass can be due to the artefacts in particle sampling and analysis or can possibly result from different conditions of filters transportation, storage and handling. These factors can vary randomly from one day to another and are usually unknown.

4.3. Comparison of model calculated wet PM_{10} and $PM_{2.5}$ with EMEP observations

PM_{10} and $PM_{2.5}$ monitoring data from the EMEP and EIONET/AIRBASE data bases have been used in the evaluation of EMEP model performance. Within the EMEP network, gravimetric methods for determining PM mass are employed at all stations. Therefore, it is reasonable to assume that measured $PM_{2.5}$ and PM_{10} concentrations include particle-bound water. In contrast, national European monitoring stations, not included within EMEP, but reporting monitoring data to the AIRBASE information system, widely employ Beta-absorption and TEOM instruments. Those instruments use heated inlet/filters which causes additional removal of aerosol associated water (and other semi-volatile species, e.g. organic compounds, ammonium nitrate). In line with the Council Directive 1999/30/EC, at stations using any other than the Reference gravimetric method, PM concentrations are required to be corrected "by a relevant factor to produce results equivalent to those that would have been achieved by using the reference method".

To derive "wet" PM concentrations, model calculated residual particle water has been added to the dry PM mass. PM_{10} and $PM_{2.5}$ concentrations including particle water are believed to be more consistent with PM_{10} and $PM_{2.5}$ concentrations determined gravimetrically (or with the equivalent methods). Model calculated annual mean PM_{10} and $PM_{2.5}$ concentrations have been compared with EMEP and AIRBASE observations in 2000–2001. The bias in model calculated PM_{10} and $PM_{2.5}$ concentrations, both dry and including particle water, as compared with measurements is shown in Table 3.

As expected, accounting for residual water in calculated PM concentrations has decreased the model underestimation of measured PM_{10} and $PM_{2.5}$. It can be noted that the larger negative bias in 2001 compared to 2000 is due to the considerable underestimation of PM_{10} concentrations by the model at Spanish sites, which were firstly reported in 2001. As it was explained above, the model not accounting for secondary organic aerosol and natural dust is a plausible reason for PM under-prediction in Spain.

Scatter-plots of calculated versus measured PM_{10} and $PM_{2.5}$ concentrations at EMEP sites are presented in Fig. 9. The upper panels show results for modelled dry PM_{10} and $PM_{2.5}$ concentrations and the lower panels show comparisons for wet PM_{10} and $PM_{2.5}$, i.e. including aerosol water.

The scatter-plots show that calculated concentrations of PM including aerosol water agree better with the measured values, but the model still underestimates PM_{10} and $PM_{2.5}$ at most of the sites. The underestimation is expected to be further reduced when all aerosol sources are included in the model. Overestimation by the model of annual mean PM_{10} and $PM_{2.5}$ concentrations at several mountain sites (DE03, DE05, DE08, CH04 and CH05) is due to its overestimation of winter aerosol concentrations at those sites, when they are in the free troposphere. The particle water content will be overestimated as a consequence of the overestimation of PM mass. Unfortunately, no appropriate measurements of PM individual components and water were available for further checking of the results (the only relevant data was SO_4 measurements at DE03 (Schauinsland, Germany), which showed that the model overestimated sulphate for that site). As expected, the spatial correlation between modelled and measured PM_{10} and $PM_{2.5}$ has not improved.

Comparison of modelled daily PM_{10} and $PM_{2.5}$ with measurements at EMEP sites shows that accounting for particle-bound water in calculated PM mass has resulted in certain improvement of the model results (Tables A1 and A2 in Appendix). Calculated PM_{10} and $PM_{2.5}$ concentrations including aerosol water are closer to the measured values and the correlation at most of the stations is somewhat better compared to that for calculated dry PM. However at some Spanish sites, the correlation between model and measured PM_{10} and $PM_{2.5}$ becomes slightly poorer when particle water in PM is accounted for. This can feasibly result from the model's inaccurate prediction of the daily variation of PM chemical composition and hence particle water content at those sites, which was impossible to check due to the lack of necessary measurements.

Another reason for worsened correlation between calculated wet PM and observations can be that aerosol water is calculated using the same conditions (20°C and 50%) for all days and at all sites. Thus, the calculated aerosol water content is determined solely by PM chemical composition, while particle water mass on dust loaded filters will also be affected by the differences in sampling procedures or transportation, storing and weighing of filters.

As a final comment, it is important to be wary of the origin of PM measurement data when deciding on comparison of either dry or wet PM concentrations with observations. Accounting for aerosol water in calculated PM concentrations is relevant when comparing model results with PM measurements at the stations where gravimetric (or equivalent) methods are used. One should be particularly careful when comparing model results with the readings from TEOM and Beta-instruments, corrected for the losses of semi-volatile components in order to assure the comparability of those measurements with reference gravimetric method. Actually, comparison of calculated wet PM concentrations with the corrected PM mass from automated instruments is not physically justified and can give dubious results. If feasible, it is more appropriate to compare calculated dry PM concentrations with PM concentrations measured with automated instruments, in which aerosol water is removed from the filters/inlets by heating.

5. Conclusions

In this work, we have addressed the issue of particle-bound water in gravimetrically measured PM mass. Available data on PM chemical analyses show that significant fractions of $PM_{2.5}$ and PM_{10} mass remain unidentified. The EMEP aerosol model has been used to estimate to what extent particle water can explain the unaccounted PM mass. We also examine to what extend the particle water can explain discrepancies between modelled and gravimetrically measured PM_{10} and $PM_{2.5}$. For this purpose, we attempt to account for residual particle water in model calculated PM concentrations to assure their more consistent comparison with observations.

The mass of residual aerosol water in PM_{10} and $PM_{2.5}$ concentrations has been calculated with the aerosol model for filter calibration conditions required by CEN standard (i.e. 50% RH and temperature 20°C). The calculated annual mean fraction of residual aerosol water in PM_{10} and $PM_{2.5}$ varies over Europe between 20 and 35%, depending on the mass and the type of mixture of soluble PM components. At 6 stations in Austria, Norway and Spain, where data on PM_{10} or $PM_{2.5}$ chemical composition was available, the model estimates that particle water can explain between 30 and 80% of the unaccounted mass in measured PM_{10} and $PM_{2.5}$ concentrations. The inclusion of aerosol water in model calculated PM mass increases the values of calculated PM_{10} and $PM_{2.5}$

concentrations, resulting in their better agreement with the observed concentrations.

Model calculations have been tested with data at two Austrian stations in Vienna and Streithofen, where daily data on $PM_{2.5}$ chemical composition was available for the period 1 June 1999–31 May 2000. A good correspondence between calculated aerosol water and undetermined $PM_{2.5}$ mass has been found for the measurement period in 2000 (correlation coefficients R are 0.45 and 0.57). In the same period, the correlation between $PM_{2.5}$ unaccounted mass and the mass of hygroscopic $PM_{2.5}$ components is also rather high (R are 0.62 and 0.63) suggesting aerosol water to be responsible for a significant part of the unaccounted mass. On the other hand, during the measurement period in 1999, the correlation between calculated aerosol water and undetermined mass is much lower (R=0.35 and 0.17). In this period, the rather low correlation (R=0.37 and 0.35) between unaccounted mass and hygroscopic $PM_{2.5}$ mass suggests a larger contribution of other factors (tentatively related to measurement artefacts) to the unaccounted PM2.5 mass.

According to our model estimates, particle water explains up to 75–80% of undermined $PM_{2.5}$ fraction at the Austrian sites. It was also pointed out that due to the assumption that aerosols exist in a meta-stable liquid phase, the model may overestimate the aerosol water content in PM samples collected at low relative humidity conditions. However, the proper validation of the results was unfeasible as no measurements of particle water were available at those sites. Obviously, the accuracy of model predicted PM chemical composition is an essential prerequisite for the correct model calculation of aerosol water (verification results for the hygroscopic PM components is presented in Appendix). Then, providing the reasonable model prediction of PM composition, an adequate parameterisation scheme is essential for accurate calculation of aerosol water.

Furthermore, it is shown that calculated daily $PM_{2.5}$ concentrations agree better with measurements when the model accounts for aerosol residual water in PM mass. All these results suggest that a significant part of unaccounted PM mass can be attributed to particle-bound water. Given that, particle water in PM should be properly accounted for in the model. It should be pointed out that, on the other hand, the calculated dry $PM_{2.5}$ mass is found to agree rather well with the $PM_{2.5}$ identified mass measured at Austrian sites, which strengthens the trust in the general model performance.

Model calculated PM_{10} and $PM_{2.5}$ concentrations including aerosol residual water have been compared with PM measurements from EMEP and AIRBASE databases. Accounting for aerosol water in calculated PM_{10} and $PM_{2.5}$ has considerably reduced the model underestimation of measured concentrations compared with verification results for model calculated dry PM concentrations. Compared with measurements at EMEP and AIRBASE sites in 2000 and 2001, model underestimation of annual mean PM_{10} has decreased from 33–56 % to 13–42 %, and of annual mean $PM_{2.5}$ from 43 to 24 %. The spatial correlation between modelled and measured annual mean PM_{10} and $PM_{2.5}$ has not significantly changed. Comparison of model results with daily measurements at EMEP sites shows that calculated PM_{10} and $PM_{2.5}$ concentrations including particle water are closer to observed values and correlate slightly better than dry PM with measurements. The exception is Spanish sites where the effect of wind blown dust would need to be accounted for in order to improve the model PM calculations.

Summarising, the model accounting for particle water in PM_{10} and $PM_{2.5}$ is shown to improve the correspondence between calculated and measured PM concentrations. However, there are caveats to the model estimates of particle-bound water as no verification of the calculated water content is presently available due to the lack of measurement data.

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Appendix

Table A1. Validation of model calculated daily PM_{10} concentrations ($\mu g/m^3$) against measurements at EMEP stations in 2001: for dry PM_{10} and wet PM_{10}.

	Sites	Obs. Mean	Mod. mean dry PM_{10}	Corr. (R) dry PM_{10}	Mod. mean PM_{10} + water	Corr. (R) PM_{10} + water
DE01	Westerland	20.13	10.48	0.76	13.16	0.77
DE02	Langenbrügge	16.30	11.41	0.66	15.02	0.68
DE03	Schauinsland	9.92	9.88	0.23	12.89	0.27
DE04	Deuselbach	15.21	11.22	0.51	14.58	0.55
DE05	Brotjacklriegel	10.08	11.74	0.19	15.29	0.21
DE07	Neuglobsow	15.62	9.82	0.69	12.95	0.71
DE08	Schmücke	10.26	11.15	0.20	14.48	0.22
DE09	Zingst	16.86	9.99	0.77	12.96	0.81
CH02	Payerne	19.34	8.23	0.45	10.63	0.46
CH03	Taenikon	18.06	9.00	0.50	11.68	0.51
CH04	Chaumont	11.08	8.24	0.37	10.65	0.42
CH05	Rigi	11.61	7.48	0.46	9.61	0.50
AT02	Illmitz	26.21	11.05	0.59	14.30	0.59
AT04	St. Koloman	11.42	9.49	0.28	11.77	0.33
AT05	Vorhegg	10.60	7.08	0.40	8.95	0.48
IT04	Ispra	39.06	14.00	0.45	17.43	0.44
ES07	Viznar	24.17	5.44	0.41	6.76	0.35
ES08	Niembro	19.72	6.67	0.27	9.10	0.21
ES09	Campisabalos	14.20	4.85	0.15	6.67	0.17
ES10	Cabo de Creus	20.48	7.33	0.20	9.17	0.18
ES11	Barcarrota	19.15	5.67	0.42	7.65	0.36
ES12	Zarra	16.18	5.40	0.26	7.23	0.27
ES13	Penausende	14.59	5.73	0.31	7.90	0.30
ES14	Els Torms	19.48	6.45	0.39	8.66	0.41
ES15	Risco Llano	14.82	5.55	0.02	7.40	−0.01
NO01	Birkenes	6.08	3.38	0.50	4.38	0.51

Table A2. Validation of model calculated daily $PM_{2.5}$ concentrations (μg/m^3) against measurements at EMEP stations in 2001: for dry $PM_{2.5}$ and wet $PM_{2.5}$.

	Sites	Obs. Mean	Mod. mean dry $PM_{2.5}$	Corr. (R) dry $PM_{2.5}$	Mod. mean $PM_{2.5}$ + water	Corr. (R) $PM_{2.5}$ + water
AT02	Illmitz	19.54	9.61	0.56	12.57	0.56
DE02	Langenbrügge	12.46	10.69	0.68	14.25	0.69
DE03	Schauinsland	7.93	9.22	0.12	12.30	0.15
DE04	Deuselbach	11.71	10.77	0.56	14.17	0.59
CH02	Payerne	14.80	7.45	0.46	9.85	0.47
CH04	Chaumont	8.12	7.46	0.36	9.87	0.41
IT04	Ispra	32.01	12.91	0.43	16.32	0.42
ES07	Viznar	12.46	3.98	0.39	5.30	0.37
ES08	Niembro	11.16	5.82	0.41	8.18	0.34
ES09	Campisabalos	9.02	4.68	0.19	6.58	0.21
ES10	Cabo de Creus	12.09	5.93	0.33	7.78	0.29
ES11	Barcarrota	11.36	4.82	0.44	6.80	0.39
ES12	Zarra	8.89	4.97	0.38	6.82	0.40
ES13	Penausende	9.70	5.25	0.46	7.46	0.46
ES14	Els Torms	12.41	5.79	0.49	7.99	0.50
ES15	Risco Llano	8.46	4.87	0.08	6.67	0.05
NO01	Birkenes	4.04	2.59	0.55	3.39	0.55

Table 1. Overview of the stations where measurements were available of both PM mass and chemical composition.

Country	Station	Station code	Coordinates	Measurement period	Resolution
Norway	Birkenes (EMEP)	NO01	58°23′ N 8°15′ E	1 Jan.– 31 Dec. 2001	Daily SIA weekly OC/EC
Austria	Wien (urban)	AU01	48°13′ N 16°21′ E	1 June 1999– 31 May 2000	Daily
	Streithofen (rural)	AU02	48°16′ N 15°56′ E	1 June 1999– 31 May 2000	Daily
Spain	Monagrega (rural)		40°57′ N 0°17′ W	24 Mar. 1999– 29 June 2000	Daily
	Bemantes (rural)		20°15′ N 8°11′ W	8 Jan.– 27 Dec. 2001	(intermittent)
	Montseny (rural)		41°46′ N 2°21′ E	22 Mar.– 29 Aug. 2001	

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Table 2. Unaccounted mass in measured PM_{10} and mass of modelled residual aerosol water in PM_{10} ($PM_{2.5}$ at Montseny) and their fractions with respect to the mass of soluble PM (SIA+marine).

	Bemantes	Monagrega	Montseny	NO01	AU01	AU02
ND ($\mu g/m^3$)	3.5	5.86	5.97	1.68	8.43	5.9
ND/soluble PM	0.50	0.78	1.12	0.55	0.73	0.55
Mod. water ($\mu g/m^3$)	3.01	2.39	2.57	1.13	4.11	3.8
Water/soluble PM	0.47	0.41	0.41	0.39	0.39	0.41

Table 3. The annual mean bias of model calculated PM_{10} and $PM_{2.5}$, dry and including particle water (wet), as compared to EMEP and AIRBASE measurements in 2000 and 2001.

	Bias for 2000 (%)		Bias for 2001 (%)	
	Dry mass	Wet mass	Dry mass	Wet mass
PM10 (EMEP)	−33	−13	−49	−33
PM2.5 (EMEP)	–	–	−43	−24
PM10 (AIRBASE)	−43	−26	−56	−42

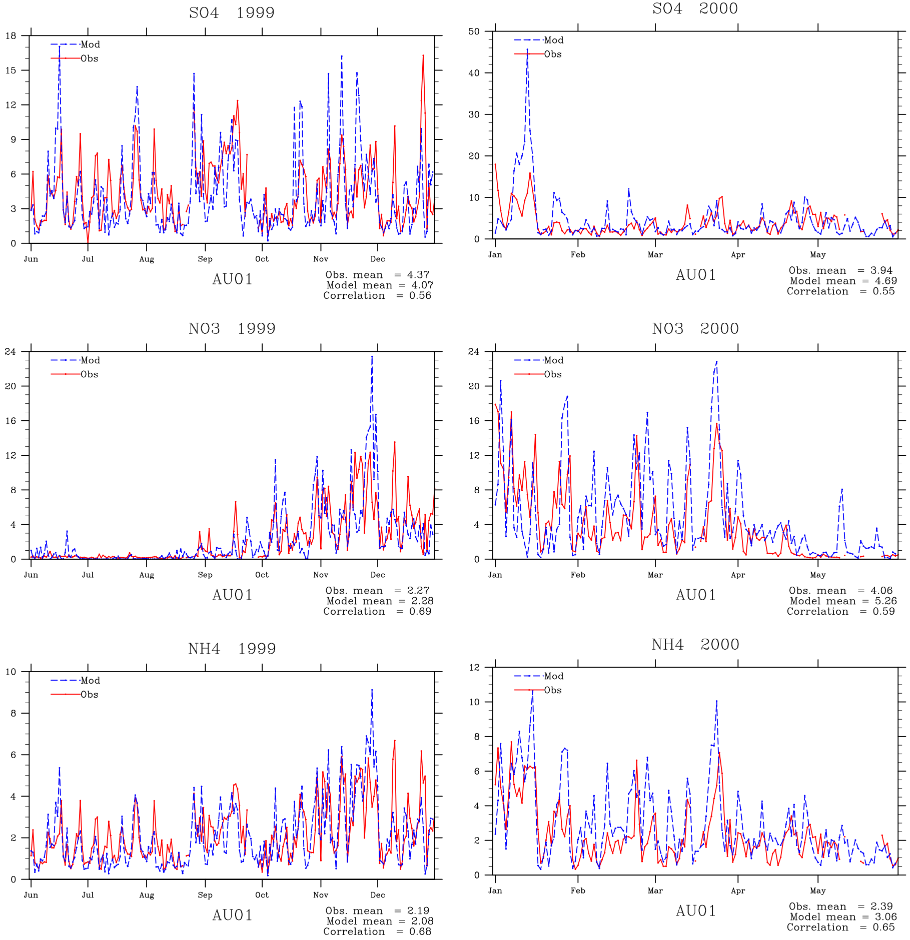

Fig. A1. Comparison of model calculated daily concentrations of secondary inorganic aerosols with observations at AU01 (Vienna) for the period 1 June 1999–31 May 2000. Units: $\mu g/m^3$.

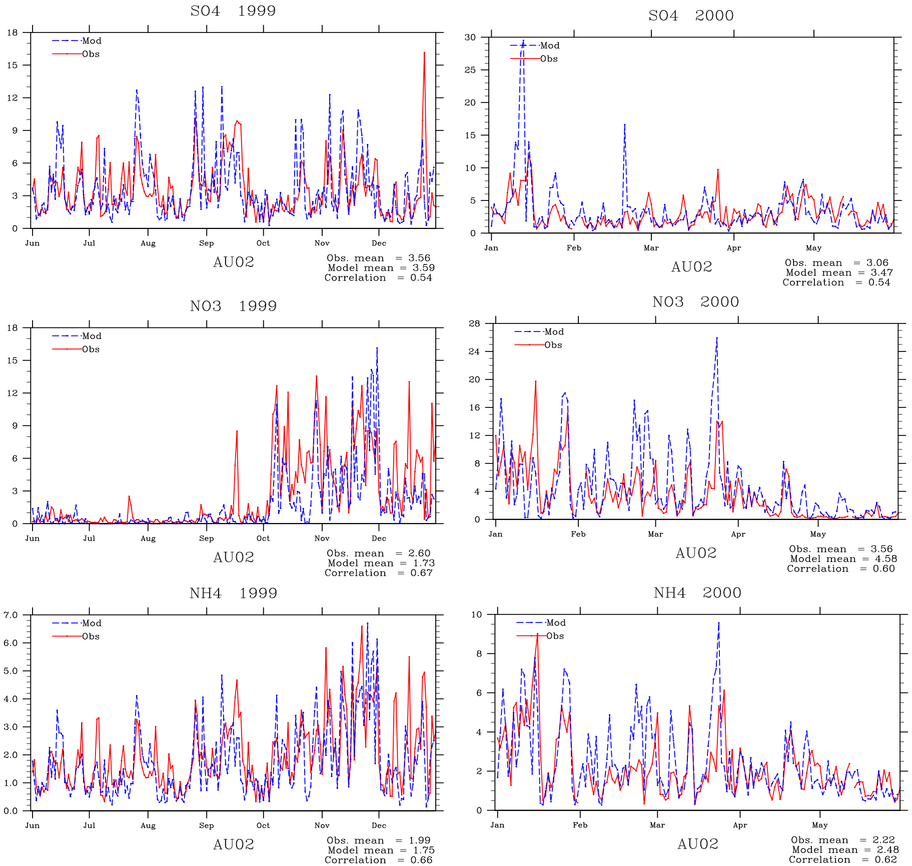

Fig. A2. Comparison of model calculated daily concentrations of secondary inorganic aerosols with observations at AU02 (Streithofen) for the period 1 June 1999–31 May 2000. Units: $\mu g/m^3$.

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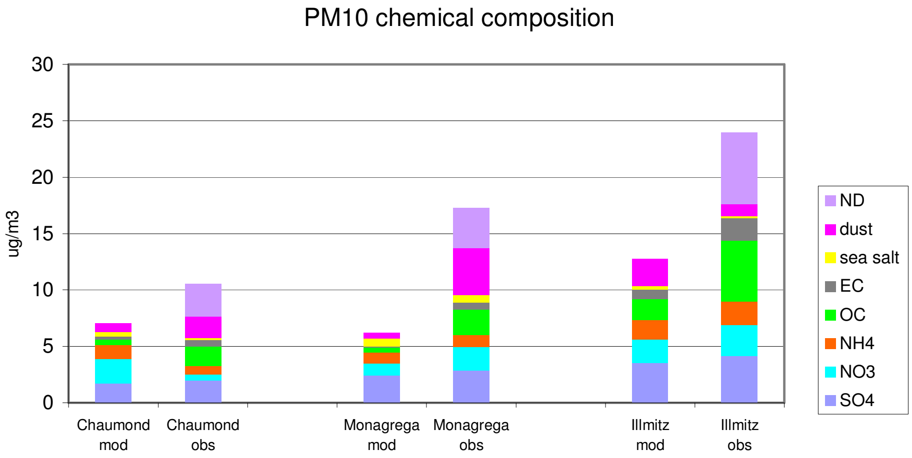

Fig. 1. Chemical composition of PM_{10} and rural stations: calculated with the EMEP aerosol model vs. measured (from Putaud et al., 2003). In the measurements, ND – denotes the unidentified PM fraction.

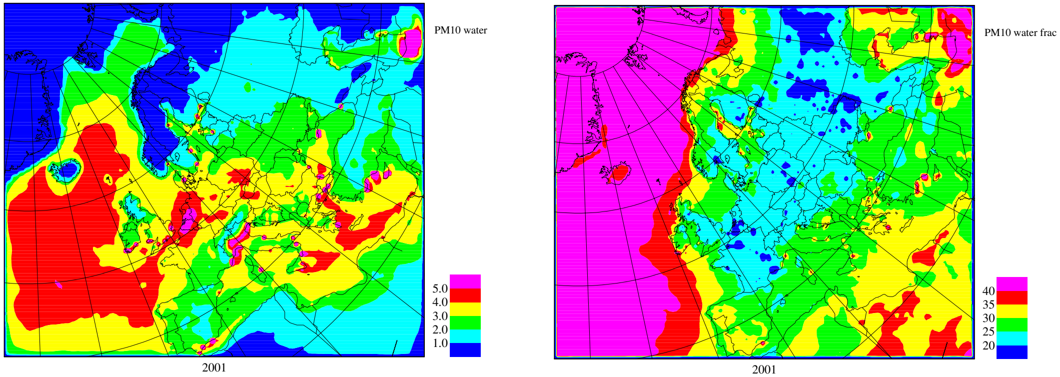

Fig. 2. Model calculated **(a)** mass (in $\mu g/m^3$) of particle water and **(b)** water fraction (%) in PM10 (water contributions calculated for 20°C and 50% RH. Year: 2001).

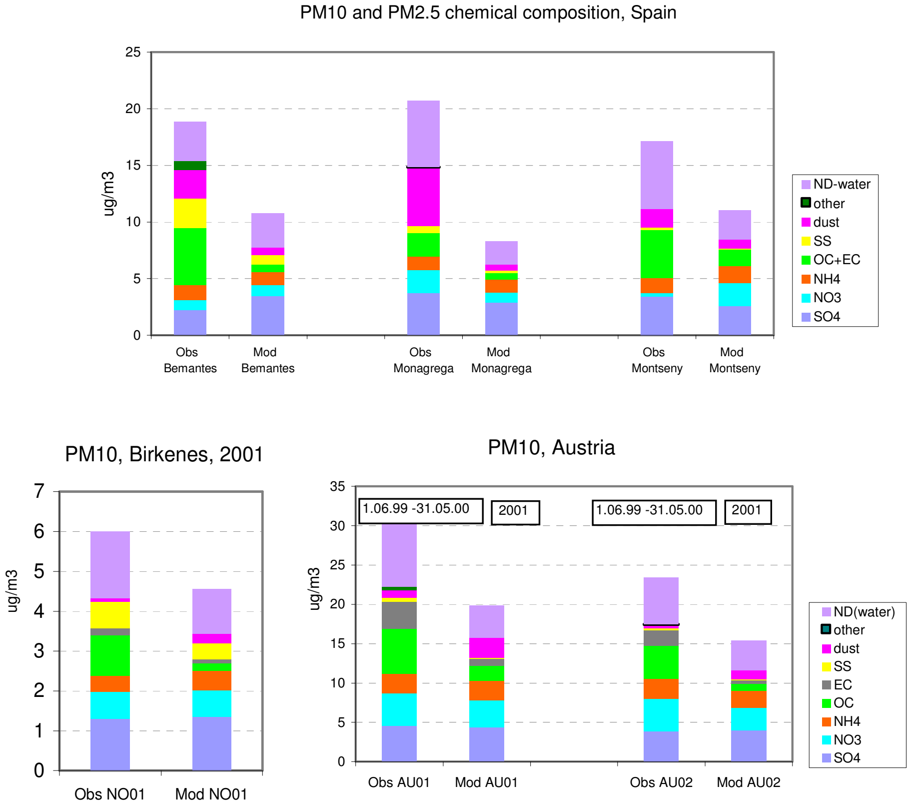

Fig. 3. Model calculated and measured chemical composition of PM_{10} ($PM_{2.5}$ at Montseny). Here, ND means "not determined PM mass" in measurements and "water" is model calculated particle water (see also explanations in the text).

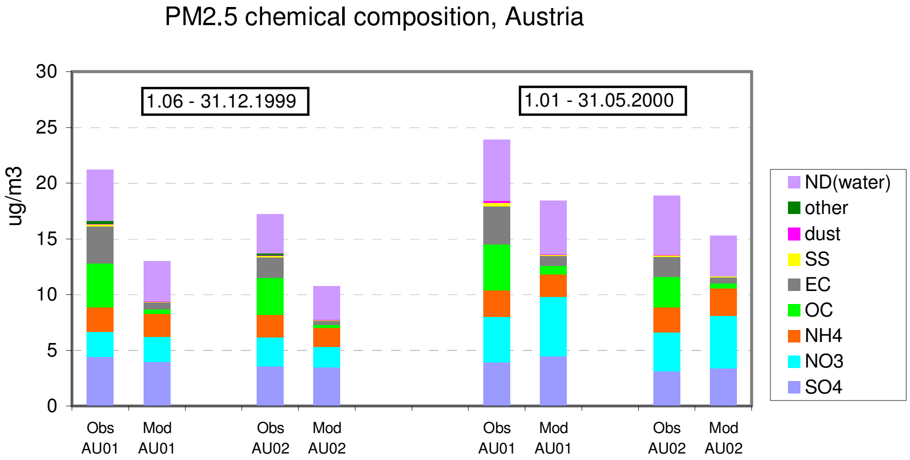

Fig. 4. Modelled and measured chemical composition of $PM_{2.5}$ at Austrian sites: AU01 (Vienna) and AU02 (Streithofen) averaged over periods 1 June–31 December 1999 and 1 January–31 May 2000.

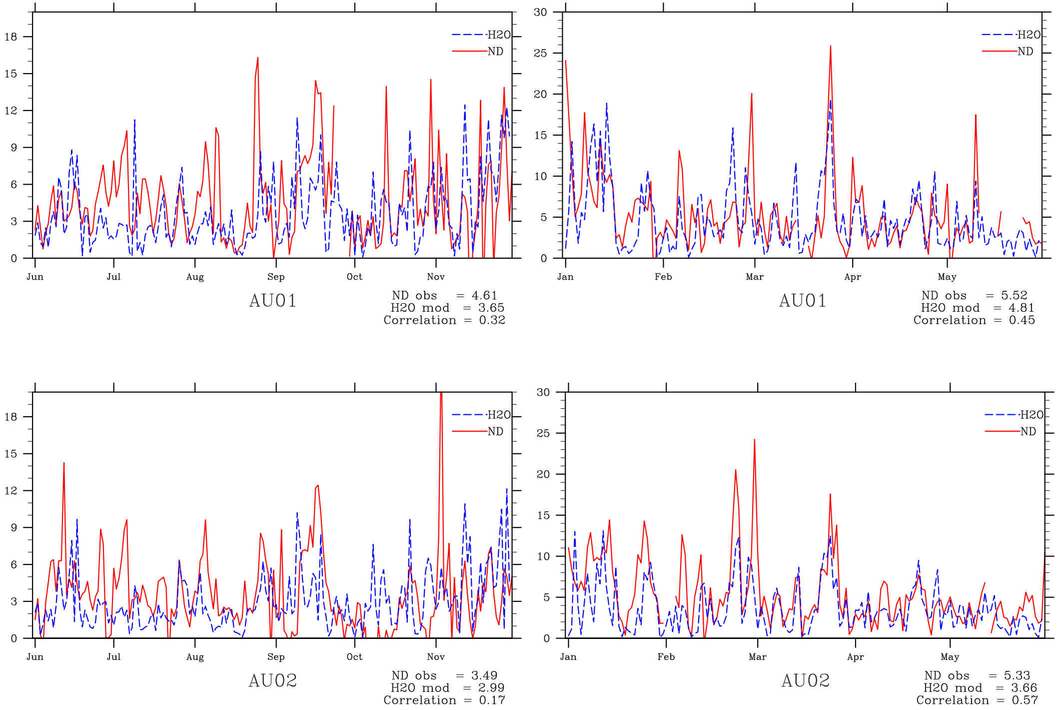

Fig. 5. Daily time-series of model calculated residual water in $PM_{2.5}$ mass (blue dashed line) and the unaccounted (*) $PM_{2.5}$ mass in measurements (red solid line) at AU01 and AU02 for the period 1 July 1999–1 June 2000. (*) Unaccounted part may include non-C atoms associated with organic aerosol.

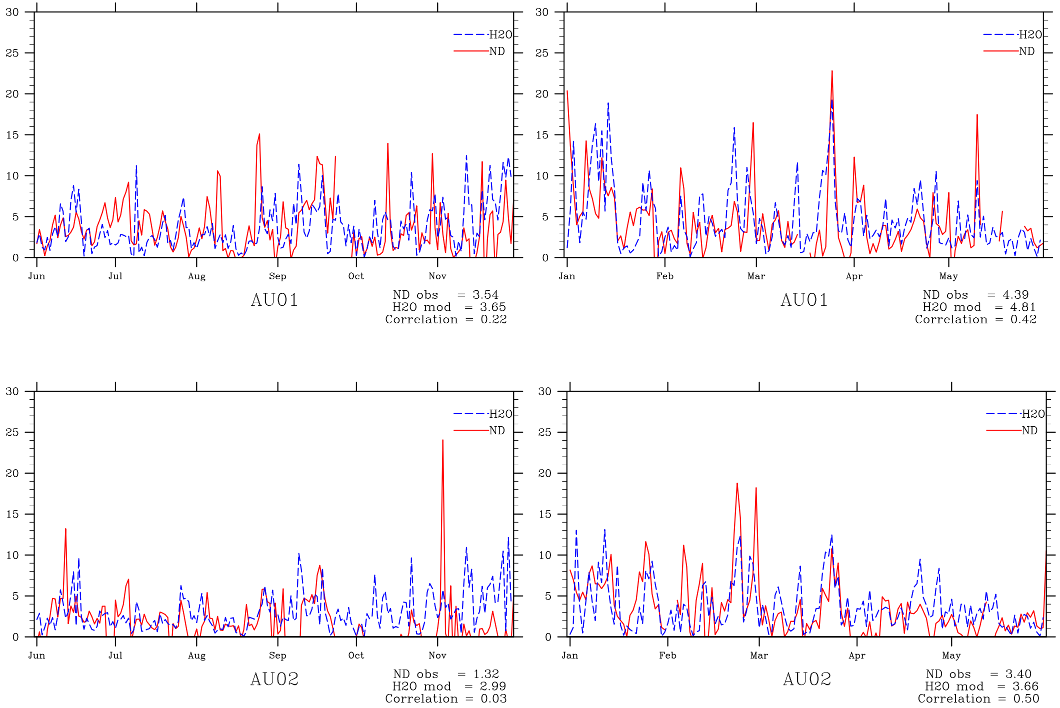

Fig. 6. Daily time-series of model calculated residual water in $PM_{2.5}$ mass (blue dashed line) and the unaccounted (*) $PM_{2.5}$ mass in measurements (red solid line) at AU01 and AU02 for the period 1 July 1999–1 June 2000. (*) OC is converted to OM and included in the identified part. Then, the unaccounted part is largely due to particle water.

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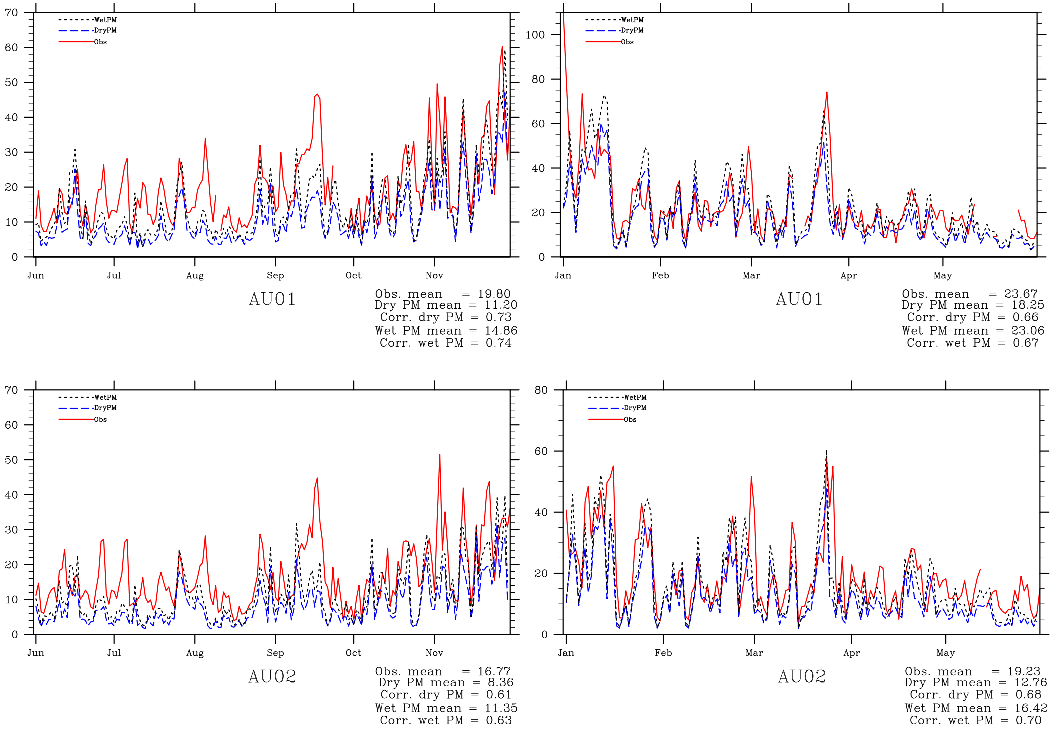

Fig. 7. Time-series of daily concentrations of model calculated dry $PM_{2.5}$ mass (blue dashed line), wet $PM_{2.5}$ (black dashed line) and measured $PM_{2.5}$ (red solid line) at AU01 and AU02 for the period 1 July 1999–1 June 2000.

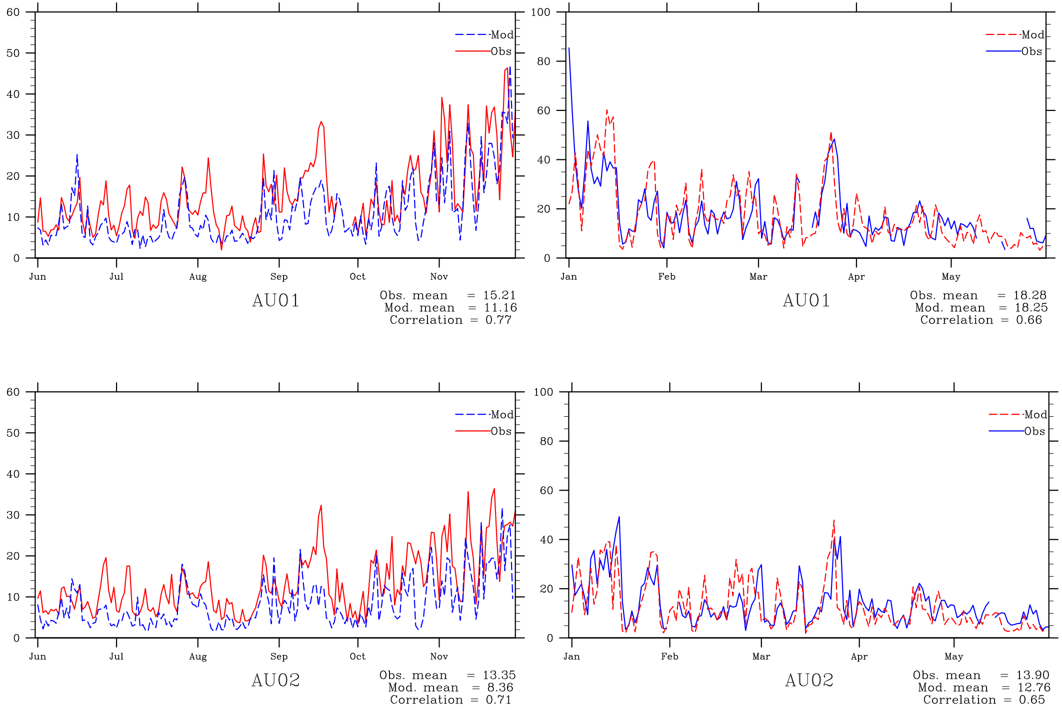

Fig. 8. Time-series of daily concentrations of model calculated dry $PM_{2.5}$ mass (blue dashed line) and the identified $PM_{2.5}$ mass in measurements (red solid line) at AU01 and AU02 for the period 1 July 1999–1 June 2000.

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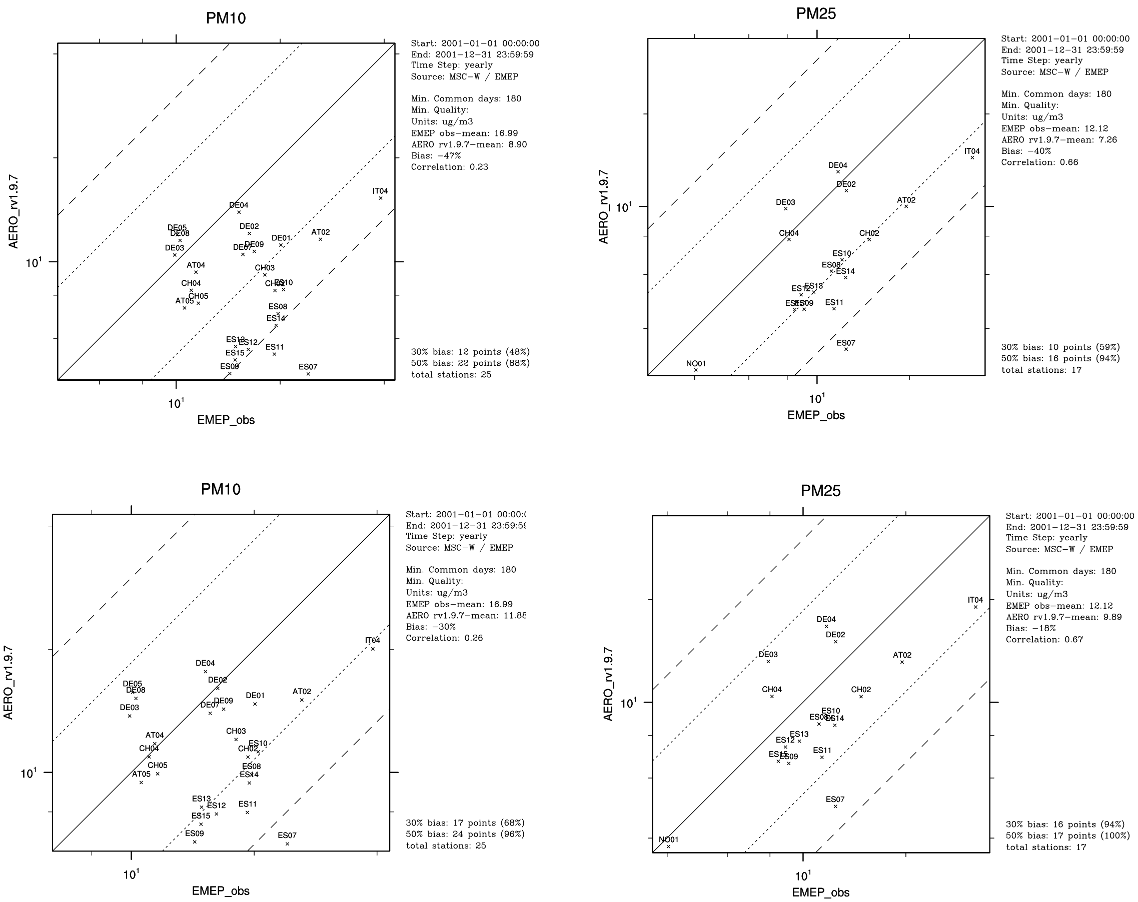

Fig. 9. Scatter-plots for PM_{10} and $PM_{2.5}$monitored at EMEP sites in 2001 versus model calculated: dry PM_{10} and $PM_{2.5}$ (upper panel) and PM_{10} and $PM_{2.5}$ with particle water accounted for (lower panel).