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Evaluation of a three-dimensional chemical transport model (PMCAMx) in the European domain during the EUCAARI May 2008 campaign

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Abstract

PMCAMx-2008, a detailed three dimensional chemical transport model (CTM), was applied to Europe to simulate the mass concentration and chemical composition of particulate matter (PM) during May 2008. The model includes a state-of-the-art organic aerosol module which is based on the volatility basis set framework treating both primary and secondary organic components to be semivolatile and photochemically reactive. The model performance is evaluated against high time resolution aerosol mass spectrometer (AMS) ground and airborne measurements. Overall, organic aerosol is predicted to account for 32% of total PM_1 at ground level during May 2008, followed by sulfate (30%), crustal material and sea-salt (14%), ammonium (13%), nitrate (7%), and elemental carbon (4%). The model predicts that fresh primary OA (POA) is a small contributor to organic PM concentrations in Europe during late spring, and that oxygenated species (oxidized primary and biogenic secondary) dominate the ambient OA. The Mediterranean region is the only area in Europe where sulfate concentrations are predicted to be much higher than the OA, while organic matter is predicted to be the dominant PM_1 species in Central and Northern Europe. The comparison of the model predictions with the ground measurements in four measurement stations is encouraging. The model reproduces more than 94% of the daily averaged data and more than 87% of the hourly data within a factor of 2 for PM_1 OA. The model tends to predict relatively flat diurnal profiles for PM_1 OA in many areas, both rural and urban, in agreement with the available measurements. The model performance against the high time resolution airborne measurements at multiple altitudes and locations is as good as its performance against the ground level hourly measurements. There is no evidence of missing sources of OA aloft over Europe during this period.

1 Introduction

Fine particulate matter is a prime contributor to various air quality problems such as visibility reduction (Seinfeld and Pandis, 2006), public health (Pope et al., 2002), formation of acid rain (Burtraw et al., 2007) and climate change (Schwartz, 1996). Sulfate and organics are the major components of sub-micrometer particles (PM_1) in most locations throughout the world. Organic particulate matter, originating from many different natural and anthropogenic sources and processes, is the least understood component of atmospheric aerosols. More than 50% of the atmospheric fine aerosol mass can be comprised of organic compounds at continental mid-latitudes and as high as 90% in tropical forested areas (Andreae and Crutzen, 1997; Roberts et al., 2001; Kanakidou et al., 2005).

Organic aerosol (OA) is generally categorized into two types; primary organic aerosol (POA) which is injected into the atmosphere in the particulate phase and secondary organic aerosol (SOA) which is emitted as volatile organic compounds (VOCs) in the gas phase and then reacts and condenses in the particulate phase. In order to gain more insight into sources and processes of organic aerosol, quantification, characterization and speciation of organic aerosol is needed which was until recently hindered by analytical difficulties (Turpin et al., 2000; Kanakidou et al., 2005). For instance, conventional techniques (e.g. GC-MS) can only be used for the speciation of a small fraction of the OA mass. Within the last decade, several new methods have emerged that can analyze and quantify the different types of OA present in ambient aerosol. Among several measurement techniques, the Aerosol Mass Spectrometer (AMS) is the most commonly used to measure the size-resolved mass concentration and corresponding total mass spectrum of organic aerosols with a time resolution of minutes (Jayne et al., 2000; Jimenez et al., 2003; Zhang et al., 2005a; Takegawa et al., 2005). Information about processes or sources contributing to the OA levels can be provided from the Positive Matrix Factorization (PMF) method (Paatero and Tapper, 1994; Paatero, 1997; Lanz et al., 2007, 2009; Ng et al., 2009) or the principal component analysis (Zhang et al., 2005b) of the AMS measurements. These methods allow a classification of the OA into two different types based on their different temporal and mass spectral signatures; the hydrocarbon-like organic aerosol (HOA) and the oxygenated organic aerosol (OOA) which together usually account for most of the OA mass measured by the AMS (Zhang et al., 2005b). HOA correlates with fossil fuel fresh POA in urban areas while OOA correlates with secondary OA.

In order to better understand the role of organic aerosol, regional and global air quality and climate models need to be able to correctly predict the concentrations of these different types of OA. Chemical transport models have traditionally treated POA as non-volatile and non-reactive and SOA as semi-volatile products of VOCs' oxidation (Kanakidou et al., 2005). However, several recent studies have shown that POA is semi-volatile (Lipsky and Robinson, 2006; Robinson et al., 2007; Huffman et al., 2009a, 2009b) while SOA can be seriously underpredicted by models that use traditional SOA precursors and do not take into account further oxidation of these compounds (Baltensperger et al., 2005; Ng et al., 2006; Hildebrandt et al., 2009; Dzepina et al., 2009). Lane et al. (2008) implemented the volatility basis set framework (Donahue et al., 2006; Stanier et al., 2008) in PMCAMx for the SOA components using four surrogate species with saturation concentrations of 1, 10, 100, and 1000 $\mu g\,m^{-3}$ at 298 K, and employed a chemical aging mechanism which shifts mass down by one volatility bin during gas-phase reactions of the corresponding surrogate species with OH. Shrivastava et al. (2008), using the chemical transport model PMCAMx, reassigned the nonvolatile POA to volatility bins and incorporated the chemical aging of the gas-phase POA by assuming reaction with the hydroxyl radical OH, thus treating POA as semi-volatile and reactive. The above two approaches for POA and SOA were combined in a single CTM (PMCAMx-2008) (Murphy and Pandis, 2009; Tsimpidi et al., 2010; Karydis et al., 2010). Tsimpidi et al. (2010) applied PMCAMx-2008 to the polluted area of Mexico City during April 2003 and March 2006. The model reproduced well the AMS measurements of HOA and OOA. Murphy and Pandis (2009) applied PMCAMx-2008 in the Eastern United States and evaluated the new modeling framework against daily ambient measurements from the EPA STN (Speciated Trends Network) and the IMPROVE (Interagency Monitoring of Protected Visual Environments) data as well as hourly data from PAQS (Pittsburgh Air Quality Study). Unfortunately, AMS data were not available for the evaluation of the predictions of the model.

In this work PMCAMx-2008 is applied for the first time in the European domain to simulate the chemical composition and mass of the major PM_1 components during the month of May 2008 during which an intensive campaign of measurements was performed in Europe as part of the European Aerosol Cloud Climate and Air Quality Interactions project (Kulmala et al., 2009). The model performance is evaluated against hourly averaged AMS ground measurements as well as airborne measurements from an aircraft field campaign over Europe (Morgan et al., 2010b).

2 PMCAMx-2008 description

PMCAMx-2008 (Murphy and Pandis, 2009; Tsimpidi et al., 2010; Karydis et al., 2010) uses the framework of the CAMx air quality model (Environ, 2003) describing the processes of horizontal and vertical advection, horizontal and vertical dispersion, wet and dry deposition, and gas-phase chemistry. For the aerosol processes, three detailed aerosol modules are used. The approach of Fahey and Pandis (2001) is used for the simulation of aqueous-phase chemistry. The inorganic aerosol growth is described in Gaydos et al. (2003) and Koo et al. (2003), and the secondary organic aerosol (SOA) formation and growth in Koo et al. (2003). These aerosol modules use a sectional approach to dynamically track the size evolution of the aerosol mass across 10 size sections spanning from 40 nm to 40 µm. The aerosol species modeled include sulfate, nitrate, ammonium, sodium, chloride, potassium, calcium, magnesium, elemental carbon, primary and secondary organics. The chemical mechanism used in the gas-phase chemistry is based on the SAPRC99 mechanism (Carter, 2000; Environ, 2003). The version of SAPRC99 used here includes 211 reactions of 56 gases and 18 radicals and has five lumped alkanes, two olefins, two aromatics, isoprene, a lumped monoterpene species, and a lumped sesquiterpene species.

Three options are available in PMCAMx-2008 for the simulation of inorganic aerosol growth. The most computationally efficient approach is the bulk equilibrium approach, which assumes equilibrium between the bulk inorganic aerosol and gas phase. At a given time step the amount of each species transferred between the gas and aerosol phases is determined by applying the aerosol thermodynamic equilibrium model ISORROPIA (Nenes et al., 1998) and is then distributed over the aerosol size sections by using weighting factors for each size section based on their surface area (Pandis et al., 1993). The second approach (hybrid approach) assumes equilibrium for the fine particles (<1 µm) and solves the mass transfer differential equations for the coarse particles (Capaldo et al., 2000). The most accurate but computationally demanding method is the dynamic approach where mass transfer is simulated explicitly for all particles (Pilinis et al., 2000). In this work we use the bulk equilibrium approach since we are focusing on the model's performance for fine particles.

Based on the approach of Shrivastava et al. (2008), primary organic aerosol in PMCAMx-2008 is assumed to be semivolatile. Nine surrogate POA species are used, with effective saturation concentrations at 298 K ranging from 10^{-2} to $10^{6}\,\mu\mathrm{g\,m^{-3}}$. POA is simulated in the model in three types, "fresh" (unoxidized) POA, oxidized POA (OPOA) and any aged organic aerosol transported into the domain from the boundary conditions. SOA consists of organic aerosol of anthropogenic (aSOA) and biogenic (bSOA) origin. The SOA volatility basis-set approach (Lane et al., 2008) used in the current version of the model includes four SOA species for each VOC with 4 volatility bins (1, 10, 100, 1000 $\mu\mathrm{g\,m^{-3}}$). Laboratory results from recent smog-chamber experiments (Ng et al., 2006; Hildebrandt et al., 2009) have been used to update the SOA module in PMCAMx in order to include anthropogenic aerosol yields. The SOA module incorporates $\mathrm{NO_x}$-dependent SOA yields (Lane et al., 2008b) which are based on an assumed density of $1.5\,\mathrm{g\,cm^{-3}}$. The model treats all organic species (primary and secondary) as chemically reactive. Chemical aging through gas-phase oxidation of OA vapors is modeled using a gas-phase OH reaction with a rate constant of

$k = 1 \times 10^{-11}$ cm^3 molec^{-1} s^{-1} for anthropogenic SOA and $k = 4 \times 10^{-11}$ cm^3 molec^{-1} s^{-1} for the primary OA (Atkinson and Arey, 2003). The base-case simulation does not age biogenic SOA (Ng et al., 2006; Presto et al., 2006; Lane et al., 2008b). Each reaction is assumed to decrease the volatility of the vapor material by a factor of 10.

3 Model application

During May 2008 an intensive campaign of measurements was performed in Europe as part of the European Aerosol Cloud Climate and Air Quality Interactions (EUCAARI) project (Kulmala et al., 2009). The campaign included both ground measurements at various European measurement stations as well as airborne measurements in North-Western Europe. The PMCAMx-2008 modeling domain covers a 5400 × 5832 km^2 region in Europe with 36 × 36 km grid resolution and 14 vertical layers covering approximately 6 km (Fig. 1). PMCAMx-2008 was set to perform simulations on a rotated polar stereographic map projection. The first two days of each simulation were excluded from the analysis to limit the effect of the initial conditions on the results. Concentrations of the major PM$_1$ species at the boundaries of the domain are shown in Table 1, representing background concentrations. The boundary condition organic aerosol (BC-OA) is expected to consist of both SOA and oxidized POA. Here we assume that the BC-OA is all oxidized and half of it is biogenic OA and the other half oxidized primary OA (Kanakidou et al., 2005; Farina et al., 2010). All concentrations reported here are under ambient temperature and pressure conditions.

The necessary inputs to the model include horizontal wind components, vertical diffusivity, temperature, pressure, water vapor, clouds and rainfall. The meteorological model WRF (Weather Research and Forecasting) (Skamarock et al., 2005) was used to create the above inputs. WRF was driven by static geographical data and dynamic meteorological data (near real-time and historical data generated by the Global Forecast System (1 × 1°)). 27 sigma-p layers up to 0.1 bars were used in the vertical dimension. Each layer of PMCAMx-2008 is aligned with the layers used in WRF. The WRF

May 2008 run was periodically re-initialized (every 3 days) to ensure accuracy in the corresponding fields that are used as inputs in PMCAMx-2008.

Anthropogenic and biogenic hourly emission gridded fields were developed for the European domain for gases and primary particulate matter. Volatile organic compounds are split based on the SAPRC 99 chemical mechanism. Anthropogenic gas emissions that were used to develop the gridded fields include land emissions from the GEMS dataset (Visschedijk et al., 2007) as well as international shipping emissions. Anthropogenic particulate matter mass emissions of organic and elemental carbon are based on the Pan-European Carbonaceous Aerosol Inventory that has been developed as part of the EUCAARI activities (Kulmala et al., 2009). A variety of emission sources are identified in the two inventories, including industrial, domestic, agricultural and traffic. Three different datasets are combined in order to produce the biogenic gridded emissions for the model. Emissions from ecosystems are produced by MEGAN (Model of Emissions of Gases and Aerosols from Nature) (Guenther et al., 2006). MEGAN inputs include the leaf area index, the plant functional type and the emission factors while the weather data needed for MEGAN are provided from the WRF model. The sesquiterpene emissions have been set to 30% of the monoterpene emissions (Helmig et al., 2006) and the oxidation of the species is modeled based on the results of Griffin et al. (1999). Since sea surface covers a considerable portion of the domain, the marine aerosol emission model developed by O'Dowd et al. (2008) has been used to estimate mass fluxes for both accumulation and coarse mode including the organic aerosol fraction. Wind speed data from WRF and chlorophyll-a concentrations are the inputs needed for the marine aerosol model. Wildfire emissions from May 2008 were also included (Sofiev et al., 2008a; 2008b). Table 2 shows a summary of the PM_{10} emission rates from the different sources for the European domain during May 2008. The OA emissions in PMCAMx-2008 were distributed by volatility using the volatility distributions of Tsimpidi et al. (2010).

The model results are compared against hourly mean values from four measurement ground sites in Cabauw (the Netherlands), Finokalia (Greece), Mace Head (Ireland)

and Melpitz (Germany). All observation sites are representative of regional atmospheric conditions.

The Cabauw site is located at a rural area in the western part of the Netherlands (51.971° N, 4.927° E). The nearby region is agricultural while the North Sea is more than 50 km away to the WNW. During May 2008, aerosol mass spectrometric measurements were performed at the Cabauw station with an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS; Morgan et al., 2010a).

The Finokalia sampling station (35.33° N, 25.67° E) is located at a remote area in the Eastern Mediterranean, in the northern coast of Crete (Greece). The nearest largest urban center (with 150 000 inhabitants) is located 70 km west of Finokalia while no human activities can be found at a distance shorter than 15 km. Located 50 m from the shore and 230 m above sea level, the site is a "crossroad" of aged aerosol coming from Europe, the marine boundary layer, the African continent or the biomass burning sources (Mihalopoulos et al., 1997; Koulouri et al., 2008; Bougiatioti et al., 2009). As part of the EUCAARI intensive May 2008 campaign, the Finokalia Aerosol Measurement Experiment 2008 (FAME-08) was conducted from May 4 to 8 June 2008 in order to characterize the physical and chemical properties of aged aerosol (Pikridas et al., 2010). A Quadrupole Aerosol Mass Spectrometer (Q-AMS) was employed to measure the size-resolved chemical composition of non-refractory submicron aerosol (NR-PM_1) as well as to estimate the extent of oxidation of the organic aerosol (Hildebrandt et al., 2010).

Melpitz is an atmospheric research station in Eastern Germany, 40 km northeast of Leipzig (12.93° E, 51.54° N). The station is mainly surrounded by agricultural pastures and forests. Atmospheric aerosol observations at the Melpitz site can be regarded as representative of the regional central European aerosol, confirmed on the basis of a multiple site comparison within the German Ultrafine Aerosol Network (Birmili et al., 2009). A basic overview of the physical and chemical characterization methods can be gathered, for instance, from Birmili et al. (2008). Most generally, the air masses occurring at Melpitz tend to partition into Atlantic (westerly) air masses with lower particle mass concentrations, and continental (easterly) air masses with higher particle mass concentrations (Engler et al., 2007; Spindler et al., 2010). A HR-ToF-AMS instrument was deployed in May and June 2008 to characterise the size-resolved mass concentrations of the non-refractory sub-µm aerosol.

The Mace Head site (53.32° N, 9.88° W) is located on the west coast of Ireland on a hilly area (height around 35 m) surrounded by a number of small lakes and is exposed to the North Atlantic ocean. It is 88 km west of Galway (population approximately 60 000) which is the nearest major city. A HR-ToF-AMS was used to measure mass concentrations of the non-refractory aerosol components from mid-May to mid-June 2008 (Dall'Osto et al., 2009).

As part of the EUCAARI project, the LONG Range EXperiment (LONGREX; http://www.pa.op.dlr.de/aerosol/eucaari2008/), an aircraft field campaign that took place from 6 to 23 May 2008, aimed at characterizing the distribution of aerosol over Europe via utilisation of airborne in-situ and remote sensing measurements. An Aerodyne Time-of-Flight Aerosol Mass Spectrometer was used to measure the size-resolved chemical composition of non-refractory particulate matter of widely varying volatility with high time resolution (Morgan et al., 2010a, b). Based at Oberpfaffenhofen (Germany), the aircraft performed flights mainly in West-East and North-South transects across Europe. The LONGREX campaign involved among others an extensively equipped research aircraft, the UK Facility for Airborne Atmospheric Measurements (FAAM) BAe-146 research aircraft, and included a total of 15 flights (approximately 50 flight hours in total).

3.1 Predicted aerosol concentrations

Figures 2 and 3 show the PMCAMx-2008 average ground-level concentrations over the entire period of simulation (1–29 May 2008) for PM_1 total mass, sulfate, nitrate, ammonium, elemental carbon (EC), OA and its components. Overall, OA is predicted to account for 32% of total PM_1 at ground level averaged over the entire domain, followed by sulfate (30%), ammonium (13%), nitrate (7%), and finally EC (4%). The remaining 14% is crustal material, sea-salt and metal oxides. The highest predicted concentrations for fine sulfate are over the Eastern Mediterranean region while nitrate concentrations are the highest over a wide area from west of England to Denmark with a predicted maximum of 6.5 µg m^{-3} at the north coast of France. PM$_1$ nitrate concentrations in the rest of the domain are generally low, less than 1 µg m^{-3} in most areas. Ammonium concentrations show a similar pattern with nitrate in the domain. Elevated ammonium concentrations show strong association with nitrate, evidence of NH_4NO_3 formation in the specific area.

The average ground concentrations of "fresh" POA, oxidized POA, anthropogenic SOA, biogenic SOA, EC and total OA predicted by PMCAMx-2008 are shown in Fig. 3. Fresh POA concentrations are relatively high (up to 7 µg m^{-3}) in various urban and suburban areas mainly in central and Northern Europe and drop dramatically (less than 0.5 µg m^{-3}) in the rest of the domain (Fig. 3a). Less than 7% of total PM$_1$ OA is predicted to consist of fresh POA on average over the entire domain with a maximum of 70% in the area of St. Petersburg, northwest of Russia. OPOA concentrations are predicted to be higher than the fresh POA in the modeling domain with an average of 52% contribution to total OA. The model indicates that much of the traditionally thought as particulate primary OA emissions are actually evaporating to produce low-volatility organic vapors which are the source (through photochemical aging) of a substantial amount of oxygenated OA that is distributed not only in urban and suburban areas but rural regions as well. Oxidized POA is predicted to be the dominant OA component during this period contributing 56% to the total oxygenated OA (sum of OPOA, SOA and BC-OA) in the modeling domain. Biogenic SOA comprises on average almost one third of the total predicted OA over the domain while almost 35% of the total oxygenated OA consists of bSOA. The highest absolute concentrations are predicted over Germany with a peak value of 1.2 µg m^{-3}. However, biogenic SOA is the dominant OA component over a large area covering NE of Serbia, Romania and West of Ukraine where the contribution of bSOA to total OA ranges from 40 to 50%. Anthropogenic

SOA concentrations are predicted to be generally low in the modeling domain (less than 0.5 µg m^{-3} in most areas). Elevated aSOA concentrations are predicted in the area covering England, North of France, Belgium, the Netherlands and west of Germany. The model predicts an almost uniform distribution of aged organic aerosol transported into the domain from the boundaries (~0.5 µg m^{-3}). An average of 0.2 µg m^{-3} is predicted for PM$_1$ EC concentrations in the domain, although much higher values are predicted locally (up to 4 µg m^{-3}) in urban areas.

Organic matter is predicted to be the dominant PM$_1$ component in central and Northern Europe with a peak value of 10.1 µg m^{-3} (in northwestern Russia). The average monthly contribution of OA to total PM$_1$ mass ranges from 35 to 50% in central and Northern Europe and drops to 15–30% at the rest of the domain (Fig. 4a). The Mediterranean region is the only area in Europe where sulfate concentrations are predicted to be much higher than the OA values among the PM$_1$ species (Fig. 4b). Unlike the rest of Europe, sulfate levels over the Mediterranean are almost 2 times larger than the OA levels. In central and Northern Europe, PMCAMx-2008 predicts the opposite with an average OA to sulfate mass ratio of 2.5.

4 Model evaluation

The prediction skill of PMCAMx-2008 is quantified in terms of the normalized mean bias (NMB), the normalized mean error (NME), the mean bias (MB), the mean absolute gross error (MAGE), the fractional bias (FBIAS), and the fractional error (FERROR),

$$\mathrm{NMB} = \sum_{i=1}^{n} (P_i - O_i) \Big/ \sum_{i=1}^{n} O_i$$

$$\mathrm{NME} = \sum_{i=1}^{n} |P_i - O_i| \Big/ \sum_{i=1}^{n} O_i$$

$$\mathrm{MB} = {}^{1}\!/_{n} \sum_{i=1}^{n} (P_i - O_i)$$

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$$\mathrm{MAGE} = {}^{1}/_{n} \sum_{i=1}^{n} |P_i - O_i|$$

$$\mathrm{FBIAS} = {}^{2}/_{n} \sum_{i=1}^{n} {}^{(P_i - O_i)}/_{(P_i + O_i)}$$

$$\mathrm{FERROR} = {}^{2}/_{n} \sum_{i=1}^{n} {}^{|P_i - O_i|}/_{(P_i + O_i)}$$

where P_i represents the model predicted value for data point i, O_i is the corresponding observed value and n is the total number of data points. The prediction skill metrics of PMCAMx-2008 against AMS hourly ground measurements from 4 stations are summarized in Table 3.

PMCAMx-2008 predictions agree reasonably well with the AMS measurements at Cabauw for all species. The measured monthly average concentrations for OA, nitrate, sulfate and ammonium were 4.1, 2.5, 1.5 and 1.7 µg m^{-3} respectively compared to the predicted average of 4.0, 3.2, 2.2 and 1.9 µg m^{-3}. The model reproduces more than 89% of the hourly PM$_1$ OA data within a factor of 2. In agreement with the AMS measurements, the model predicts that OA makes up the largest portion of the PM$_1$ total mass in Cabauw, followed by nitrate, sulfate and ammonium. OA is predicted to be mostly dominated by oxygenated OA components (77% contribution) characteristic of rural areas in the Northern Hemisphere (Zhang et al., 2007). Oxidized POA makes up most (60%) of the oxygenated OA aerosol in Cabauw with a monthly average predicted value of 1.8 µg m^{-3}.

Figure 5 shows the predicted and measured timeseries of PM$_1$ OA, sulfate, and ammonium concentrations at Finokalia during the EUCAARI May 2008 campaign. The average predicted concentration is 2.1 µg m^{-3} for total OA, 4.7 µg m^{-3} for sulfate, 1.3 µg m^{-3} for ammonium and 0.09 µg m^{-3} for nitrate compared to the observed average of 2.5 µg m^{-3}, 5.2 µg m^{-3}, 1.5 µg m^{-3} and 0.08 µg m^{-3}, respectively. In agreement with observations, PM$_1$ nitrate (not shown) is predicted to be low (less than 0.1 µg m^{-3}) throughout the month. Contrary to the Cabauw site, the dominant PM$_1$ species at the Finokalia station is sulfate as shown both from the measurements and the model predictions. The model predicts oxidized POA to be the dominant species among OOA components with 60% contribution, followed by bSOA (23%) and aSOA (17%). Compared to a positive matrix factorization analysis of the organic aerosol AMS data at Finokalia (Hildebrandt et al., 2010), PMCAMx-2008 correctly predicts negligible HOA concentrations at Finokalia (~0.02 µg m^{-3}) a result of no strong local sources and rapid conversion of POA to OPOA. On average, both AMS and PMCAMx-2008 give high (more than 98% of total OA) oxygenated organic aerosol concentrations. A more detailed analysis of the comparison between model predicted concentrations of OA components and the PMF analysis of AMS data from various European sites will be presented in a forthcoming paper.

At Mace Head, the model predicts reasonably well both PM$_1$ OA and sulfate, reproducing 79% and 74% of the hourly data within a factor of 2. However, much larger errors are seen for PM$_1$ nitrate and ammonium. This is because of the bulk equilibrium assumption and the fact that a significant amount of nitrate in Mace Head is associated with sea-salt which shifts nitrate and ammonium to the coarse mode. This was also seen in the high-dust concentration area of Mexico City (Karydis et al., 2010) where the bulk equilibrium approach of PMCAMx-2008 was unable to capture this effect, thus significantly underpredicting concentrations of nitrate and ammonium in the coarse mode and overpredicting in the fine mode.

Encouraging agreement with the AMS data is also seen in Melpitz although measurements from only the last week of May were available. Among the 4 stations, the OA concentrations in Melpitz are the highest as shown both from measurements and model predictions. The model reproduces more than 81% of the hourly PM$_1$ OA data within a factor of 2.

The diurnal profiles of OA and sulfate concentrations from 2 major cities and 2 rural areas are shown in Fig. 6. The model predicts relatively flat average diurnal profiles in both the rural and urban cites. At the two rural areas, the predicted diurnal profile of both sulfate and total OA do not vary significantly, in agreement with the observations. At Cabauw, the highest average value for PM$_1$ OA was observed and predicted to be 4.7 and 4.3 µg m^{-3}respectively, both at the same time (07:00 a.m.). At Finokalia, the model underpredicts the observed OA by roughly 20% while it succeeds in reproducing the high degree of oxidation in the eastern Mediterranean. It captures the small increase of the observed OA concentrations in the afternoon which suggests a slow but significant atmospheric photo-oxidation. The relatively flat diurnal profiles that the model tends to predict in many areas, are rather surprising considering the expected diurnal variations due to emissions, photochemical activity and temperature changes. Previous modeling efforts suggested strong diurnal OA variation that is in most cases inconsistent with observations (Pun et al., 2003).

Overall, the model agreement with the AMS ground measurements is encouraging. A scatter plot of the comparison for PM_1 sulfate and OA is shown in Fig. 7. More than 87% of the (hourly) data points for PM_1 OA and 70% for sulfate lay within the error. Model predictions for sulfate were subject to significant scatter (NME = 47%, mean error = 1.3 $\mu g\,m^{-3}$) while the discrepancy between predicted and observed values for organic matter is partly explained as a systematic bias (NMB= −11%). Possible errors in the emission rates could be responsible for the bias considering the importance of anthropogenic sources in the overall OA budget. Larger errors are seen for aerosol nitrate and ammonium which could be partly attributed to the use of bulk equilibrium approach for the simulation of the inorganic aerosol growth. The model significantly overpredicts both nitrate and ammonium especially in Mace Head. If the data points from Mace Head are excluded from the statistical analysis, the NMB is reduced from 67 to 29% for PM_1 nitrate and from 24 to 2% for PM_1 ammonium while significantly reducing the mean bias to 0.4 and 0.03 $\mu g\,m^{-3}$, respectively. Compared to the daily averaged measurement values, the model performs well reproducing more than 94% and 82% of the hourly data within a factor of 2 for OA and sulfate, respectively.

The capability of the model to reproduce the vertical distribution of sub-micron aerosol chemical composition is evaluated by comparing its predictions with the airborne AMS data. Figure 8 shows predicted and observed vertical concentration profiles of the aerosol chemical species calculated for 500 m altitude bins averaged over the entire EUCAARI-LONGREX campaign. The overall agreement of PMCAMx-2008

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predictions with the LONGREX airborne data is encouraging. Contrary to previous studies (Heald et al., 2005) that found high concentrations of SOA in the free troposphere over the NW Pacific during the ACE-Asia campaign, both PMCAMx-2008 and the observations reveal low OA concentrations in the 2–6 km altitude range over Europe during May 2008. Table 4 shows statistical metrics of the comparison between the airborne AMS data and PMCAMx-2008 predictions. Compared to the ground measurements, the scatter in this comparison is larger yet expected since the model predicted values are compared against each one of the AMS measurements (total of ~7000 points) instead of comparing hourly averages. The model can correctly predict both the OA and sulfate concentrations to within a factor of 2 of the observations for the majority of the data points (>66% and >62% respectively). When the observed concentrations for OA and sulfate are higher than 1.0 $\mu g\,m^{-3}$ the model reproduces more than 75% and 77% of the data within a factor of 2 for both species respectively. The ability of the model to reproduce the high time resolution airborne measurements at multiple altitudes and locations is quite similar to its ability to capture the ground level (hourly) observations.

5 Conclusions

A detailed three dimensional chemical transport model, PMCAMx-2008, was applied to the European domain for the first time, in order to simulate the chemical composition and mass of the major PM_1 components during the month of May 2008 during which an intensive campaign of measurements was performed in Europe as part of the European Aerosol Cloud Climate and Air Quality Interactions project. PMCAMx-2008 assumes both primary and secondary organic aerosol to be semivolatile and photochemically reactive. On a domain-average basis, the model predicts organics to account for 32% of total PM_1 at ground level during May 2008, followed by sulfate (30%), ammonium (13%), nitrate (7%), and finally elemental carbon (4%). The model performance is evaluated against ground measurements taken at 4 European measurement stations as well as airborne measurements from an aircraft field campaign over Europe. The comparison of the model predictions with hourly average Aerosol Mass Spectrometry (AMS) ground measurements is encouraging. The model reproduces more than 87% of the hourly data and more than 94% of the daily averaged data within a factor of 2, for PM_1 OA. The model performs well in reproducing the high degree of oxidation as well as the average diurnal profile of the organic concentrations observed in the Eastern Mediterranean region. The capability of the model to reproduce the vertical distribution of sub-micron aerosol chemical composition was evaluated by comparing its predictions with the airborne AMS data from 15 flights. The model performance against the high time resolution airborne measurements of OA and sulfate at multiple altitudes and locations is quite similar to its performance against the ground level hourly measurements.

The model shows that the Mediterranean region is the only area in Europe where PM_1 sulfate concentrations are predicted to be much higher than the PM_1 OA during late spring, while organic matter is predicted to be the dominant PM_1 species over a large part of the continental Europe. The model predicts low levels of fresh POA and a ubiquity of oxygenated species in organic aerosol, which is predicted to be predominantly composed of oxidized primary OA (55–60%) and biogenic SOA (30–35%). Much of the traditionally thought as particulate primary OA emissions is actually evaporating to produce low-volatility organic vapors which are the source (through photochemical aging) of a substantial amount of oxygenated OA that is distributed not only in urban and suburban areas but rural regions as well. PMCAMx-2008 tends to predict relatively flat diurnal profiles for PM_1 OA in many areas, both rural and urban. Finally, the model predicts no significant OA concentrations in the free troposphere over Europe.

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Table 1. Aerosol concentrations (in µg m^{-3}) at the boundaries of the domain.

	Boundaries			
Species	North	South	West	East
OA	1	0.5	0.5	1
Sulfate	1	1	1	1
Ammonium	0.37	0.37	0.37	0.37
Nitrate	0.1	0.02	0.01	0.1
Sodium	0.001	0.005	0.09	0.03
Chloride	0.002	0.01	0.1	0.05

Table 2. Emission mass totals (in ktons month^{-1}) for the European domain during May 2008.

Species	CO	NO_x	SO_2	NH_3	NMVOC	NO_3^-	Sulfate	NH_4^+	EC	OC	Na^+	Cl^-
Anthropogenic	3682	1461	1675	501	1291	–	–	–	59	82	–	–
Biogenic (MEGAN)	439	24	–	–	2879	–	–	–	–	–	–	–
Biogenic (Sea salt)	–	–	–	–	–	–	1294	–	–	43	4951	8900
Biogenic (Fires)	768	22	3	11	11	7	15	1	16	50	–	–

Table 3. Prediction skill metrics of PMCAMx-2008 against AMS hourly ground measurements from 4 stations (Cabauw, Finokalia, Mace Head, Melpitz) during the EUCAARI campaign in May 2008*.

PM_1	Mean Observed ($\mu g\,m^{-3}$)	Mean Predicted ($\mu g\,m^{-3}$)	MB ($\mu g\,m^{-3}$)	MAGE ($\mu g\,m^{-3}$)	NMB (%)	NME (%)	FBIAS	FERROR	Percent within a factor of 2
Cabauw									
OA	4.1	4.0	−0.1	1.1	−3	27	0.005	0.3	89
Sulfate	1.5	2.2	0.7	1.1	49	72	0.3	0.5	60
Nitrate	2.5	3.2	0.8	1.7	33	71	0.3	0.7	53
Ammonium	1.7	1.9	0.2	0.7	15	42	0.1	0.4	76
Finokalia									
OA	2.5	2.1	−0.4	0.7	−16	30	−0.1	0.3	92
Sulfate	5.2	4.7	−0.5	2.0	−9	38	−0.005	0.4	83
Nitrate	0.08	0.09	0.02	0.1	–	–	–	–	–
Ammonium	1.5	1.3	−0.2	0.5	−16	38	−0.1	0.4	83
MaceHead									
OA	2.3	2.0	−0.4	0.8	−18	35	−0.2	0.4	79
Sulfate	1.8	1.7	−0.1	0.7	−7	40	−0.1	0.4	74
Nitrate	0.8	3.2	2.4	2.6	298	320	1.1	1.2	16
Ammonium	1.0	2.5	1.5	1.6	158	165	0.8	0.9	23
Melpitz									
OA	5.1	3.7	−1.4	1.6	−29	32	−0.3	0.3	81
Sulfate	2.3	2.1	−0.2	1.1	−10	49	−0.1	0.4	65
Nitrate	0.7	0.5	−0.1	0.4	−25	58	−0.6	0.8	43
Ammonium	1.0	0.9	−0.01	0.4	−1	47	−0.02	0.4	70
Overall									
OA	3.3	3.0	−0.4	1.0	−11	30	−0.1	0.3	87
Sulfate	2.8	2.9	0.1	1.3	3	47	0.1	0.4	70
Nitrate	1.7	2.8	1.1	1.8	67	105	0.4	0.8	28
Ammonium	1.5	1.7	0.3	0.8	23	58	0.2	0.5	67

[*] Number of datapoints; Cabauw: 640, Finokalia: 490, Mace Head: 330, Melpitz: 160.

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Table 4. Prediction skill metrics of PMCAMx-2008 against AMS airborne measurements during the EUCAARI-LONGREX campaign in May 2008*.

	Mean Observed (µg m^{-3})	Mean Predicted (µg m^{-3})	MB (µg m^{-3})	MAGE (µg m^{-3})	NMB (%)	NME (%)	FBIAS	FERROR	Percent within a factor of 2
OA	2.6	2.2	−0.4	1.1	−15	42	−0.2	0.6	66
Sulfate	1.6	1.6	−0.1	0.8	−3	51	0.2	0.6	62
Nitrate	1.6	1.4	−0.2	1.1	−14	69	−0.3	1.0	38
Ammonium	1.2	1.3	0.01	0.7	1	57	−0.08	0.7	53

[*] 7010 data points.

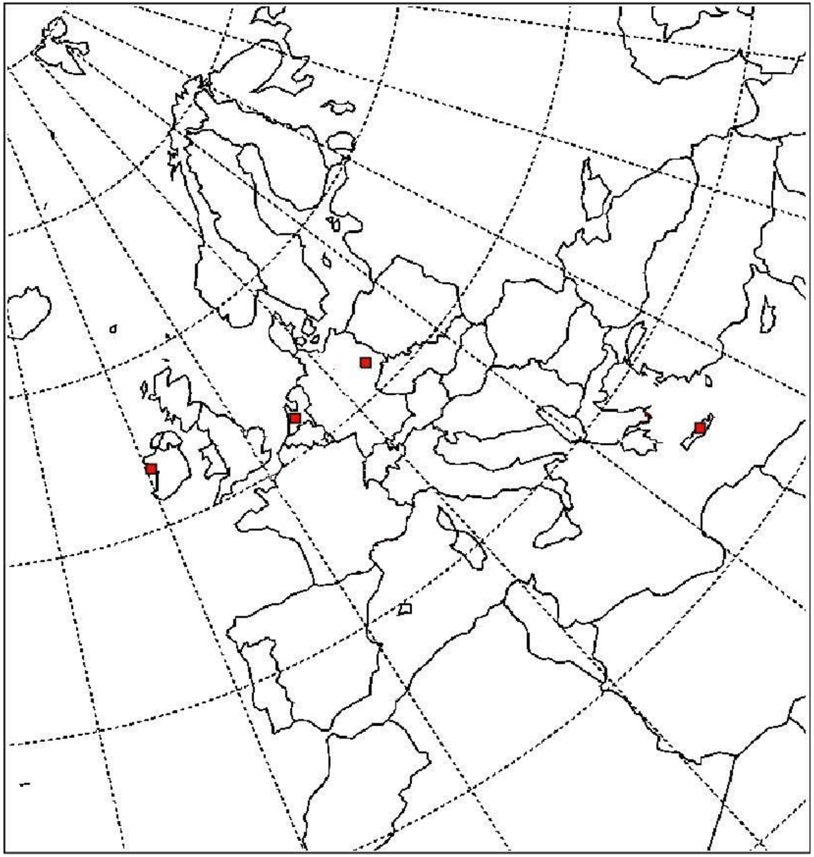

Fig. 1. Modeling domain of PMCAMx-2008 for Europe. Red squares show the measurement stations.

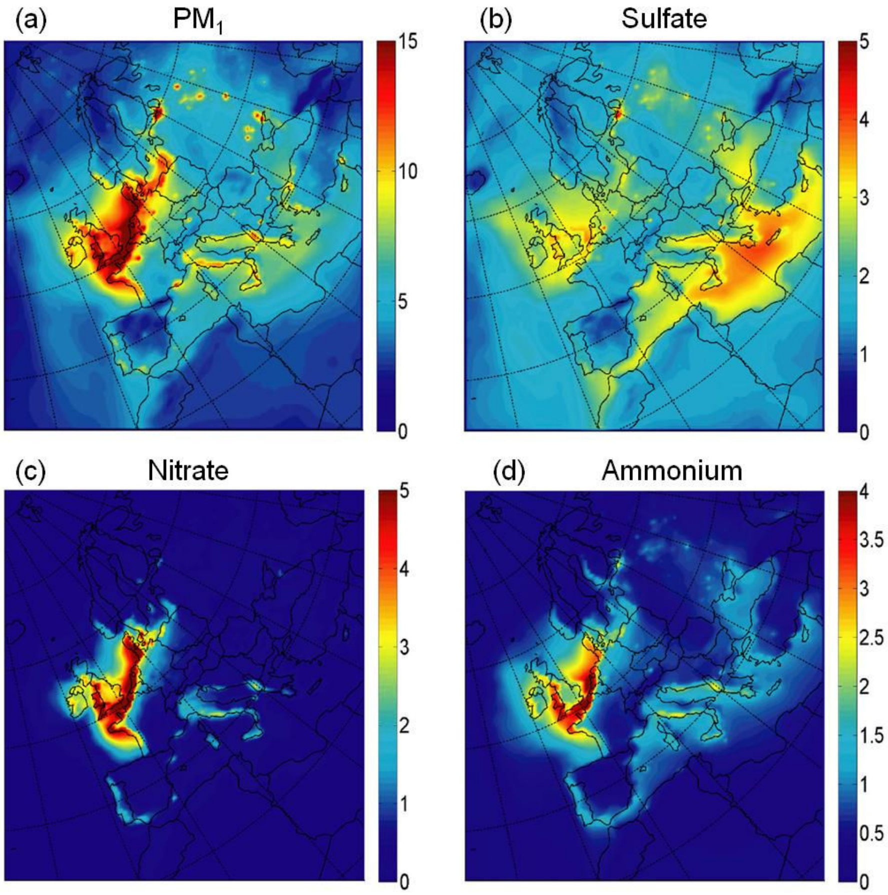

Fig. 2. Ground-level concentration predictions averaged over the entire simulation period (1–29 May 2008) for PM$_1$ **(a)** total aerosol mass, **(b)** sulfate, **(c)** nitrate and **(d)** ammonium (in µg m^{-3}). Different scales are used.

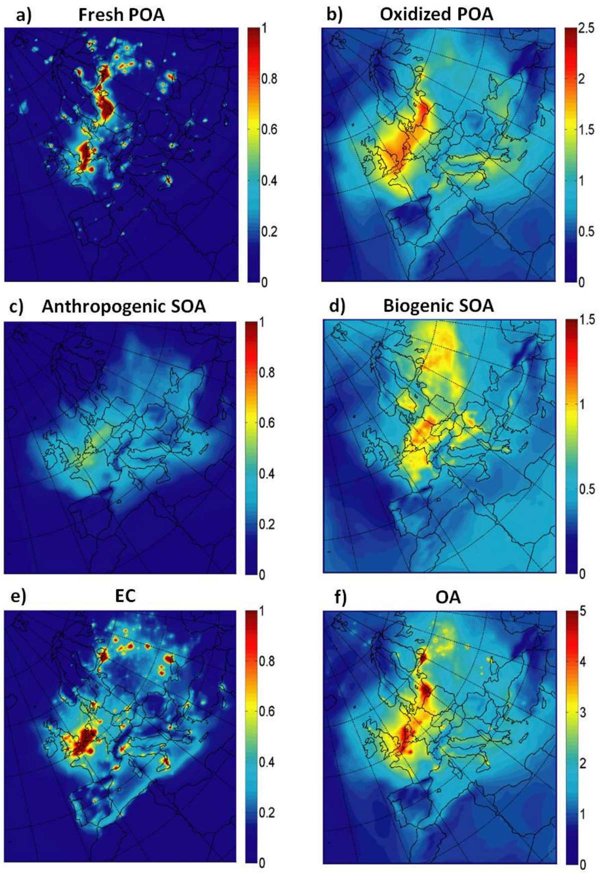

Fig. 3. Ground-level concentration predictions averaged over the entire simulation period (1–29 May 2008) for PM$_1$ **(a)** "fresh" POA, **(b)** oxidized POA, **(c)** anthropogenic SOA, **(d)** biogenic SOA, **(e)** elemental carbon and **(f)** total organic aerosol (in μg m^{-3}). Different scales are used.

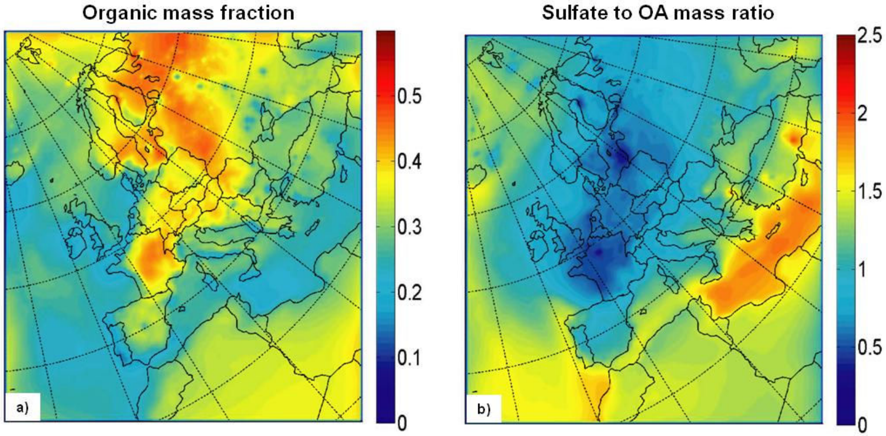

Fig. 4. **(a)** Contribution of organic aerosol to total PM_1 mass and, **(b)** PM_1 sulfate to OA mass ratio averaged over the entire simulation period (1–29 May 2008).

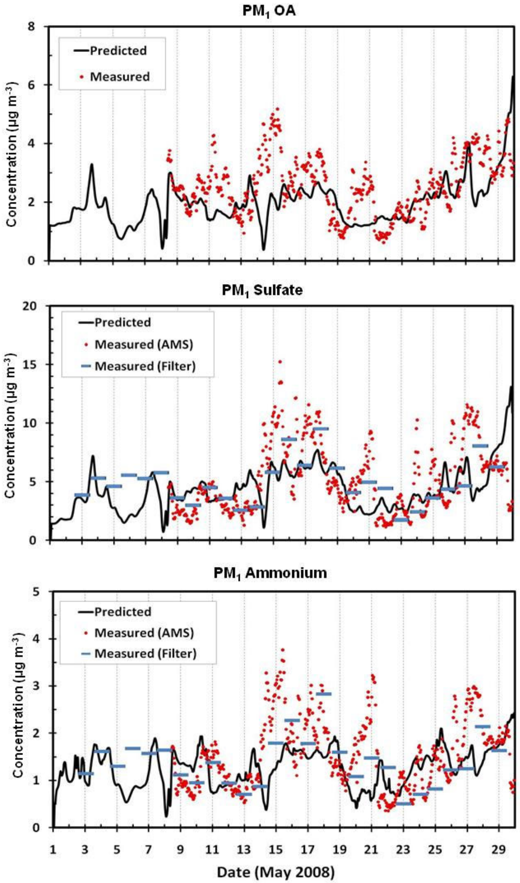

Fig. 5. Comparison of model predictions with measurements of PM$_1$ OA, sulfate, and ammonium (in µg m^{-3}) taken at Finokalia during the EUCAARI May 2008 campaign.

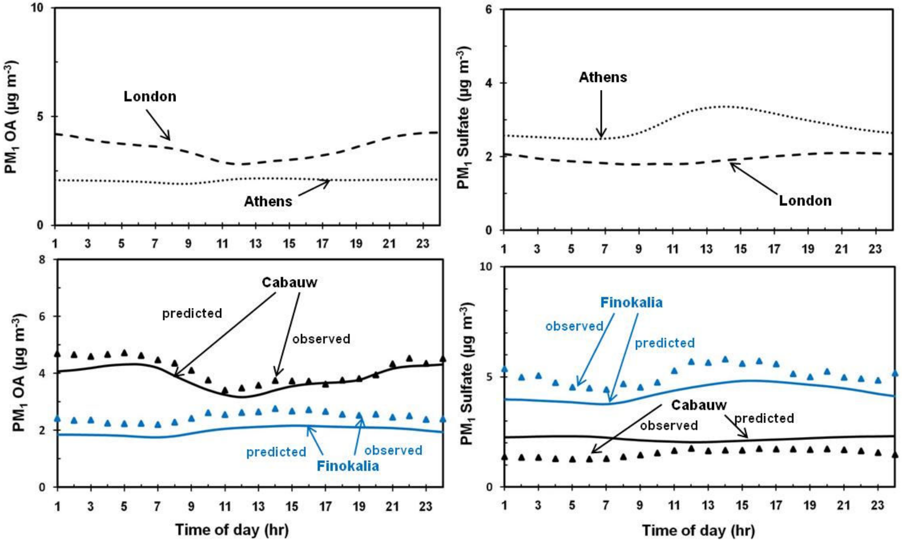

Fig. 6. Average diurnal profiles of PM_1 OA and sulfate at 2 urban and 2 rural sites during the EUCAARI May 2008 campaign.

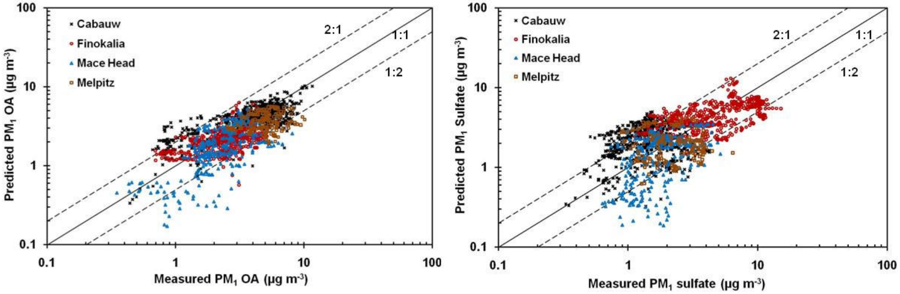

Fig. 7. Comparison of predicted vs. observed PM$_1$ organic matter and sulfate concentrations (μg m^{-3}) from 4 measurement stations during the EUCAARI May 2008 campaign. Each point corresponds to a 1-h average value. Also shown the 1:1, 2:1 and 1:2 lines. Observed data represent AMS measurements.

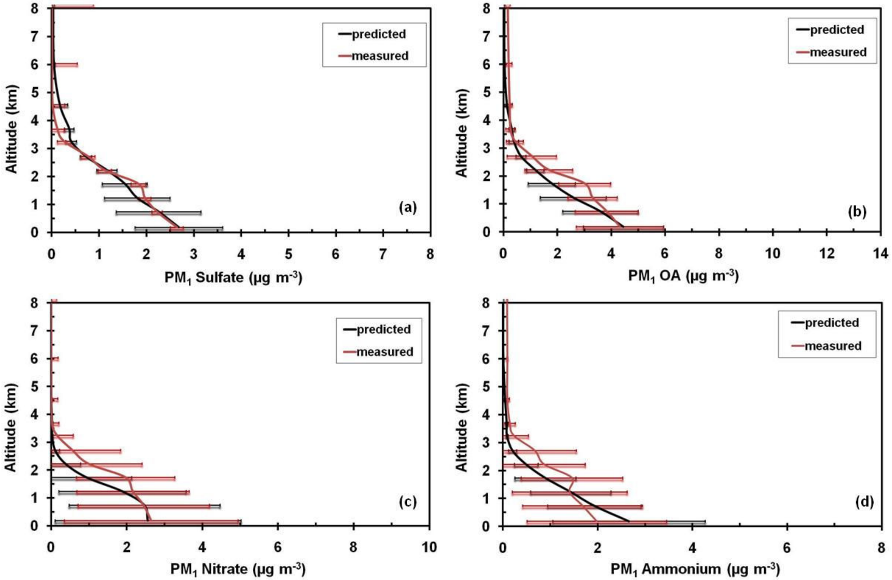

Fig. 8. Comparison of predicted (PMCAMx-2008) vs. observed (AMS) vertical profiles of aerosol chemical composition averaged over the entire EUCAARI-LONGREX campaign for PM$_1$ **(a)** sulfate, **(b)** organics, **(c)** nitrate and **(d)** ammonium. The horizontal bars indicate one standard deviation for each 500 m altitude bin mean value.