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Significant spatial and temporal variation of the concentrations and chemical composition of ultrafine particulate matter over Europe

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Abstract. Ultrafine particles have attracted interest as perhaps the most dangerous fraction of atmospheric PM. This study focuses on the characterization of ultrafine particulate matter ($PM_{0.1}$) mass concentrations and their chemical composition during a summer and winter period in Europe.

Predicted levels of $PM_{0.1}$ varied substantially, both in space and in time. The average predicted $PM_{0.1}$ mass concentration was 0.6 μg m^{-3} in the summer, higher than the 0.3 μg m^{-3} predicted in the winter period. $PM_{0.1}$ chemical composition exhibited significant seasonality. In summer, $PM_{0.1}$ was mostly comprised of secondary inorganic matter (38% sulfate and 13% ammonium) and organics (9% primary and 32% secondary). During the winter, the fraction of secondary inorganic matter increased, with sulfate contributing 47% and ammonium 19%, on average. Primary organic matter contribution also increased from 9% in summer to 23% in winter, while secondary organic matter decreased significantly to 6% on average during winter.

During summertime, the model performance at 12 sites for daily average ultrafine particle volume ($PV_{0.1}$) concentrations was considered good, with normalized mean error (NME) equal to 46% and normalized mean bias (NMB) equal to 15%. For the winter period, the corresponding values for daily average levels were -27% for NMB and 64% for NME, indicating an average model performance.

Correlations between $PM_{0.1}$ and the currently regulated $PM_{2.5}$ were generally low. Better correlations were observed in cases where the primary component of $PM_{0.1}$ was significant. This suggests that there are significant differences between the dominant sources and processes of $PM_{0.1}$ and $PM_{2.5}$.

1. Introduction

UFPs dominate atmospheric particle number distribution (Seinfeld and Pandis, 2006). High concentrations of both UFP number and mass are found in urban areas and are a result of human activity, directly emitting particulates or producing them by gas-to-particle conversion processes. Atmospheric particle exposure is one of the most significant risk factors affecting human health (HEI, 2013; EPA, 2019). Ultrafine particles have attracted interest because they may be the most dangerous fraction of atmospheric particulate matter. They can reach the lung alveoli, pass into the bloodstream and from there they can move to many different organs (Schraufnagel, 2020; Sioutas et al., 2005). Their increased specific surface area with decreasing size also enhances their chemical and physical interactions, both with gaseous species outside the body and also with tissues inside the body (Kwon et al., 2020). Some epidemiological studies have noted a positive

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correlation between UFPs exposure and brain tumor incidence (Weichenthal et al., 2020). However, there are still questions about the links between ultrafine particle exposure and damage to human health (EPA, 2019).

Past studies of ultrafine particles have focused on their number concentrations (Baranizadeh et al., 2016; Merikanto et al., 2009; Patoulias et al., 2015, 2018; Wang and Penner, 2009; Yu and Luo, 2009). The comparatively scarce modelling attempts aimed at ultrafine particle mass have mostly been conducted in California and the US (Hu et al., 2014a, b, 2017; Venecek et al., 2019; Yu et al., 2019).

In the study by Hu et al. (2014a, b) for the 7-year (2000-2006) period, daily predictions of primary $PM_{0.1}$ from the UCD-P model were evaluated for California. They found good agreement of model predictions with observed $PM_{0.1}$ mass and elemental carbon (Kuwayama et al., 2013), with a Pearson correlation coefficient ($R>0.92$) during these periods. They reported model difficulties in reproducing observed values of $PM_{0.1} > 4$ μg m^{-3} or < 1 μg m^{-3}. In a subsequent study of $PM_{0.1}$, Hu et al. (2017) utilized again the UCD/CIT model. The authors reported that primary organic matter was the major component (50-90%) of $PM_{0.1}$ OA in California, with 9-year average concentrations above 2 μg m^{-3} in major urban areas. They predicted that secondary organics contribute less than 10% to $PM_{0.1}$ OA in these areas, with that contribution increasing to up to 50% in rural areas, with low organic matter content. $PM_{0.1}$ secondary organic aerosol (SOA) concentrations were predicted to be mostly biogenic (64% of SOA for the domain) and between 0.02-0.05 μg m^{-3} in the winter and 0.1-0.3 μg m^{-3} in the summer. Underprediction of secondary organic aerosol concentrations was proposed as an explanation of the $PM_{0.1}$ organic mass underprediction. Yu et al. (2019) along with Venecek et al. (2019) considered nucleation along with the rest of the major aerosol processes in a $PM_{0.1}$ study. Venecek et al. (2019) investigated $PM_{0.1}$ concentration and sources during summertime pollution events in several metropolitan areas of the US. Predicted daily average $PM_{0.1}$ levels were generally above 2 μg m^{-3}, reaching 5 μg m^{-3} in areas influenced by wildfire events. The $PM_{0.1}$ spatial gradients were much sharper than those of $PM_{2.5}$ due to the dominance of the primary $PM_{0.1}$. The dominant source of $PM_{0.1}$ was found to be natural gas combustion across all major cities in the US. Yu et al. (2019) studied UFP number as well as mass concentrations and sources in California. Xue et al. (2019) reported that meat cooking was a major source of $PM_{0.1}$ organic carbon across all California cities (13−29%), while nucleation contributed negligibly to UFP mass on an annual scale.

Experimental studies investigating ultrafine particles have focused on particle number concentrations and their spatial and temporal differences. The first detailed measurements of UFP mass have been performed in California (Bernardoni et al., 2017; Kuwayama et al., 2013; Xue et al., 2018, 2019, 2020a, b; Xue and Kleeman, 2022). In these studies, researchers collected one sample every day or used even longer averaging intervals because of the low UFP mass concentrations. Hughes et al. (1998) reported daily average mass concentrations varying from 0.8 to 1.6 μg m^{-3} in Pasadena, CA. A novel method to measure UFP mass continuously has been recently developed and tested by Argyropoulou et al. (2023, 2024), but has not been applied in field studies yet.

Major sources of $PM_{0.1}$ in the US include vehicular emissions (Bernardoni et al., 2017; Hu et al., 2014a), biomass (wood burning and meat cooking) burning (Kleeman et al., 2009) but also natural gas combustion (Xue et al., 2018) and aviation in areas close to airports (Venecek et al., 2019). Relatively little is known in areas outside the US about ultrafine particle properties other than their number concentrations and size distribution (del Águila et al., 2018; Putaud et al., 2010).

The few studies, however, using $PM_{0.1}$ as the exposure metric have shown positive correlations of ultrafine particle organic and trace metal components with negative health effects (Laurent et al., 2016; Ostro et al., 2015). For

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UFP mass, field studies as well as modelling studies have been largely restricted to California or parts of Asia, which are dominated by primary sources (Phairuang et al., 2022; Xue et al., 2019, 2020b; Zhu et al., 2002). As such, large uncertainties about their health effects still remain (Delfino et al., 2005; EPA, 2019; Ohlwein et al., 2019).

In this work, $PM_{0.1}$ mass concentrations as well as their chemical composition were studied during a typical summer (5 June - 8 July 2012) and winter period (1-30 January 2009) for several urban and rural sites in Europe using the PMCAMx-UF chemical transport model. Due to the difficulty of measuring $PM_{0.1}$ mass, $PV_{0.1}$ is used in this study to evaluate the model predictions on an hourly and daily scale.

2. Model description

PMCAMx-UF is an Eulerian regional three-dimensional chemical transport model (Jung et al., 2010) that is an extension of the PMCAMx model (Gaydos et al., 2007). The extended Dynamic Model for Aerosol Nucleation (DMANx) module is used in PMCAMx-UF for the better description of ambient ultrafine particulate matter processes (Patoulias et al., 2015). PMCAMx-UF solves the mass conservation equation for each pollutant in the gas, aqueous and particulate phases focusing especially on the aerosol number and mass size distributions and the ultrafine particles.

Processes simulated by PMCAMx-UF include transport of pollutants via advection and eddy diffusion, their chemical transformation in the gas, aerosol and aqueous (cloud) phases, their removal from the atmosphere through dry (without water involvement) and wet (with water involvement) processes, their introduction into the atmosphere by direct emission, whether from natural planetary processes or by human activity, and lastly specific physical processes for the particle phase, namely coagulation, condensation/evaporation and nucleation. PMCAMx-UF simulates the temporal variation of the complete aerosol number size distribution, beginning from particles as small as 0.8 nm and up to 10 μm. At the same time, the mass concentration of 18 major aerosol components is simulated, including inorganics (ammonium, sulfate, metals, nitrate, sodium, chloride), primary and secondary organic aerosol, elemental carbon and aerosol phase water. The secondary organic aerosol species are split into 4 volatility bins for the anthropogenic and another 4 for those of biogenic origin. An extremely low volatility secondary organic aerosol component was added by Patoulias and Pandis (2022) to simulate the extremely low volatility secondary organic compounds.

Gas phase chemistry in PMCAMx-UF is described by the extended Statewide Air Pollution Research Center (SAPRC) mechanism (ENVIRON, 2003; Patoulias and Pandis, 2022), which involves 219 thermochemical and photochemical reactions, 64 gaseous compounds, of which 11 reactivity lumped organic compounds (5 alkanes, 2 olefins, 2 aromatics, a mono- and a sesqui-terpene) and 18 free radicals. PMCAMx-UF utilizes the variable sizes resolution (VRSM) aqueous phase chemical module (Fahey and Pandis, 2001). The algorithm for horizontal advection is based on the piecewise parabolic method of Colella and Woodward (1984) and its implementation by Odman and Ingram (1996). Dry deposition is described by a first order kinetic removal rate. For gaseous pollutants, the dry deposition velocity is calculated from the series resistance to impaction model of Wesely (1989). For aerosol species, the gravitational settling velocity is in addition factored in. Its calculation follows the implementation of Slinn and Slinn (1980). Additional information about PMCAMx-UF can be found in Patoulias et al. (2018).

3. Model application

PMCAMx-UF was applied to a modelling domain spanning the European continental area, covering a 5400x5832 km^2 area, using a rotated polar stereographic domain projection. This region is divided into 36x36 km^2 cells resulting in 24300

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cells in each vertical level. In the vertical axis there are 14 levels, extending to approximately 7.2 km. The ground level, which is the main focus of this study, has a 60 m top boundary height.

The two periods examined correspond to 5 June to 8 July 2012 and 1 to 30 January 2009, during the PEGASOS and EUCAARI campaigns respectively. Inputs for this version of PMCAMx-UF and specifically for the studied periods have been described by Patoulias and Pandis (2022).

Meteorological input data for both periods were generated by the Weather Research and Forecasting (WRFv2) model (Skamarock et al., 2005). This model utilizes geospatial time-varying meteorology data as inputs that are a product of the Global Forecast System (GFSv15) of the National Oceanic and Atmospheric Administration (NOAA). WRF model grids correspond to those of the chemical transport model.

Anthropogenic particulate matter emissions have hourly space resolution and are based on the pan-European anthropogenic particle number emissions inventory and the carbonaceous aerosol inventory, both developed during the European Integrated project on Aerosol, Cloud, Climate, and Air Quality Interactions (EUCAARI) (Kulmala et al., 2011). These datasets include various anthropogenic sources such as ground transportation, shipping, industrial processes, domestic activities, etc. Anthropogenic gas-phase emissions are based on the Global and regional Earth-system Monitoring using satellite and in situ data (GEMS) inventory. Continental natural ecosystem emissions were derived using the Model of Emissions of Gases and Aerosol from Nature (MEGANv2.1) (Guenther et al., 2006). MEGAN requires the meteorological inputs described above, as well as surface area type indicators. Natural marine emissions are based on the model of O'Dowd et al. (2008). Wildfire emissions included in our simulation were taken from the Sofiev et al. (2008a, b) emission inventory. Intermediate volatility organic compound emissions were estimated based on the primary organic aerosol emission rates, with proportionality factors depending on estimated volatility (Patoulias and Pandis, 2022).

Initial and boundary conditions used in this application were constant and low to minimize their influence on model predictions. The first two days of the summer and winter simulation periods are not included in the analysis. This is a time interval which has been shown to be adequate to exclude most of the influence of initial conditions in previous PMCAMx-UF applications (Patoulias et al., 2018; Patoulias and Pandis, 2022).

3.1 Measurements

Ultrafine particle mass is difficult to measure, primarily due to its low concentration. In order to evaluate hourly model predictions of ultrafine particulate matter concentrations, we use here surface level measurements of particle number size distributions, available through the EBAS database (https://ebas-data.nilu.no), during the Pan-European-Gas-AeroSol-climate interaction Study (PEGASOS) and the European Integrated project on Aerosol, Cloud, Climate, and Air Quality Interactions (EUCAARI) (Kulmala et al., 2011) intensive measurement campaigns. The locations of the 12 measurement sites are shown in Figure 1. These include Mace Head (Ireland), Varrio, Hyytiala (Finland), Aspvreten, Vavihill (Sweden), Helsinki (Finland), Waldhof, Melpitz, Dresden, Hohenpeissenberg (Germany), Kosetice (Czech Republic) and Finokalia (Greece). Particle number distribution measurements in each site were made through mobility particle sizers, either scanning (SMPS) or differential (DMPS). The ultrafine particle volume concentrations, $PV_{0.1}$, was then calculated by integrating these distributions up to 100 nm assuming spherical particles. The $PM_{0.1}$ concentration can be calculated by multiplying with an average UFP density. However, to avoid complications $PV_{0.1}$ will be used directly for the model evaluation.

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The $PM_{0.1}$ predicted by PMCAMx-UF was converted to $PV_{0.1}$ by estimating the average ultrafine particle density, ρ_{UFP}, based on the predicted particle composition at each point at time:

$$PV_{0.1} = \frac{PM_{0.1}}{\rho_{UFP}} \quad (1)$$

$$\rho_{UFP} = \frac{\sum_{i=1}^{N} \rho_i \ PM_{0.1,i}}{PM_{0.1}} \quad (2)$$

where N is the total number of components, ρ_i is the density of component *i*, $PM_{0.1,i}$ is the $PM_{0.1}$ mass concentration of component *i*, and the total $PM_{0.1}$ the total mass concentration.

4. Results

4.1 Average spatial variation of $PM_{0.1}$

The average $PM_{0.1}$ predictions at the ground level during the summertime simulated period are shown in Figure 2. There was considerable spatial variability of $PM_{0.1}$ levels throughout Europe. The average predicted $PM_{0.1}$ in the modeling domain was 0.4 μg m^{-3}. The mean value was heavily influenced by the fact that a significant part of the domain is over the Atlantic Ocean and Northern Africa, regions with much lower concentrations of $PM_{0.1}$. Averaging without those parts of the domain increased $PM_{0.1}$ to 0.6 μg m^{-3}.

$PM_{0.1}$ was predicted to have higher values, up to 1.2 μg m^{-3}, in parts of southern and eastern Europe. High levels were also predicted for major urban areas like Paris, as well as areas with high ship traffic like the North Sea or the western Mediterranean. $PM_{0.1}$ was predicted to be, on average, 51% secondary inorganic matter (38% sulfate and 13% ammonium), 41% organic matter (9% primary and 32% secondary), with smaller contributions from elemental carbon (5%), metal oxides) (2%) and trace contributions (<1%) of nitrate, sodium and chloride. Sulfate levels were higher in the North Sea, the Mediterranean, parts of the Middle East and the Strait of Gibraltar, as well as the lower Bay of Biscay. Ammonium spatial patterns mirror those of sulfate. SOA was a major $PM_{0.1}$ contributor in most of eastern and central Europe. POA and elemental carbon contributed relatively little mass on the domain scale, with sharp spatial gradients in regions of increased human activity.

The average predicted $PM_{0.1}$ concentration and composition for the winter period are shown in Figure 3. $PM_{0.1}$ levels were on average lower across the domain, with a mean domain value of 0.18 μg m^{-3}. The average level over Europe was 0.3 μg m^{-3}.

Wintertime $PM_{0.1}$ was predicted to consist of an average of 66% secondary inorganic material (47% sulphate and 19% ammonium), 23% primary matter (9% elemental carbon, 9% organic matter and 5% metals), with small amounts of nitrate, sodium and chloride (<5%). SOA contributed 6% to the mean predicted $PM_{0.1}$, with higher contribution in northwestern Russia, northern Italy and southern Spain and Portugal. The highest SOA average concentration was 0.1 μg m^{-3} in northwestern Russia. $PM_{0.1}$ in central and western Europe, as well as in key urban areas of the Iberian Peninsula and northern Italy, was mainly composed of primary (emitted) matter. Primary matter concentration was as high as 0.9 μg m^{-3} in urban areas. Sulfate, and the associated ammonium, were the major contributors to $PM_{0.1}$ in eastern Europe according to PMCAMx-UF, however with reduced concentration relative to the summer. The $PM_{0.1}$ levels in northwestern and central Europe were lower by around 0.2 μg m^{-3} compared to the summer. In southern Italy, the concentrations were

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reduced from more than 1 μg m^{-3} to less than 0.4 μg m^{-3}. On the other hand, in many urban areas (e.g. Paris) the $PM_{0.1}$ levels were similar or even higher during the winter.

4.2 Predicted $PM_{0.1}$ chemical composition in urban areas

The average predicted chemical composition of $PM_{0.1}$ for selected sites is depicted in Figure 4 for the summer and winter period. Sulfate was a major $PM_{0.1}$ component during the summer, with its fractional mass contribution varying from 17% to 51% depending on location. Ammonium (7-16%), primary organics (4-16%), elemental carbon (2-29%) and metals (1-5%) were the remaining major contributors. SOA contributed from 2 to 10%. The mass percentage of sodium, chloride and nitrate was in most sites less than 1%. The predicted $PM_{0.1}$ summertime concentration was mostly (52% to 91%) secondary (organic or inorganic). A significant fraction of the SOA (40-73%) was predicted to be anthropogenic in all sites (Table S3).

In the urban area of Athens, the major component of $PM_{0.1}$ was sulfate (35%), followed by SOA (23%), primary organic aerosol (POA) (16%) and ammonium (13%). In Paris, elemental carbon had the highest contribution (30%) to $PM_{0.1}$. Sulfate contributed 20% and SOA 20%. At the rural site of Finokalia, $PM_{0.1}$ consisted of 51% sulfate, 27% SOA and 20% ammonium, with smaller contributions of elemental carbon (2%) and primary organic aerosol (4%).

During the winter period, primary material contributed from 22% to 61% to $PM_{0.1}$ depending on location (Fig. 4). Primary organic aerosol ranged from 10% to 23%. Elemental carbon was predicted to contribute 8% to 31%, while metals from 4% to 10% across all sites. Ammonium and sulfate remained a significant fraction of $PM_{0.1}$ (33% to 69%), especially in the urban areas in eastern Europe. The sulfate fraction ranged from 24% to 49%, with ammonium contributing from 9% to 20%. The contribution of SOA was limited, up to 9% at the sites examined. The remaining $PM_{0.1}$ components, namely nitrate, chloride and sodium, were predicted to contribute up to 1% in almost all the examined sites.

In Athens, wintertime $PM_{0.1}$ consisted of sulfate (37%), POA (23%), elemental carbon (15%) and ammonium (13%). The remaining were metals (7%) and SOA (5%). In Paris, elemental carbon was the major $PM_{0.1}$ component with a contribution of 30%. Sulfate contributed 25%, while POA 20%. Lower contributions were predicted for ammonium (10%), metals (10%) and SOA (5%). At the rural site of Finokalia, $PM_{0.1}$ mainly consisted of sulfate (49%) and ammonium (16%), with smaller contributions of primary organic aerosol (10%), elemental carbon (8%), chloride and sodium.

4.3 PMCAMx-UF evaluation

4.3.1 Summer

During the summer period, PMCAMx-UF predictions showed on average little bias with a NMB equal to 15% for hourly average concentrations (Table 1). The NME, on an hourly level, was on average 62%, a level similar to that of $PM_{2.5}$ predictions of CTMs in Europe. The model performance in this first application was clearly quite encouraging. NMB and NME hourly metrics in the various stations ranged from -29% to +109% and from +44% to +125%, respectively. The model's performance improved, as expected, for daily average concentrations (Table S1). The NME was reduced to 46%. The NMB remained at the low level of 15%. This performance was considered very good with the evaluation criteria of fine PM (Morris et al., 2005).

During the summer, for most locations, model predictions as well as measured values exhibited significant variability (Fig. 5). In most sites, the mean was larger than the median due to short-term elevated concentrations. PMCAMx-UF on average did a reasonable job reproducing the observations, with overpredictions and underpredictions

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of $PV_{0.1}$, depending on the location. Average concentrations for the full period were captured within 0.1 $\mu m^3\ cm^{-3}$ for 7 out of 12 of the examined sites, with all the predicted averages being within 0.25 $\mu m^3\ cm^{-3}$ of measurements. Focusing on the urban sites, in Dresden, mean ultrafine particle volume concentration was underpredicted by 0.17 $\mu m^3\ cm^{-3}$. For Helsinki, the mean predicted $PV_{0.1}$ was quite consistent with the measurements. The distributions of $PV_{0.1}$ were also in good agreement. In Kosetice, the model overpredicted by 0.13 $\mu m^3\ cm^{-3}$. Also, the predicted concentrations were in general higher than the measurements. Mean predicted $PV_{0.1}$ for all the sites examined was 0.34 $\mu m^3\ cm^{-3}$ and the corresponding measured value was 0.29 $\mu m^3\ cm^{-3}$. PMCAMx-UF overpredicted by 0.13 to 0.25 $\mu m^3\ cm^{-3}$ in the Vavihill, Aspvreten, Waldhof and Kosetice sites, all rural background areas in central and northern Europe.

In Dresden, the model predicted a weaker diurnal variation to that observed, but its main weakness was its underprediction of the baseline by around 0.2 $\mu m^3\ cm^{-3}$ (Fig. 6). A noticeable measured peak at 8:00 LST probably indicates traffic emissions which were not captured in the model, either through omission or due to grid resolution. The model tended overall to capture the hourly variations (Fig. S1), though it missed some high concentration periods on June the 8, 10, 16 and 24.

For Helsinki, the average measured diurnal pattern was relatively flat (Fig. 6). Measured values were reproduced well by PMCAMx-UF, with differences of around 0.05 $\mu m^3\ cm^{-3}$ throughout most of the average day. The detailed time series was also well reproduced (Fig. S1).

In Kosetice, for the first half of the day, predictions were far larger than the corresponding measurements, starting the night at +0.1 $\mu m^3\ cm^{-3}$ and peaking at 05:00-06:00 with a more than +0.2 $\mu m^3\ cm^{-3}$ difference (Fig. 6). This increase in predicted levels was due to an increase in traffic emissions. For the second half of the day, predicted and measured values were in reasonable agreement. Excluding the first two days, which were influenced by the initial conditions, the model overpredicted nighttime to early morning concentrations in several periods (June 10-12, 16-17, 24 and 26) (Fig. S1). Measured concentrations were rarely higher than those predicted, for example on July 2 and 3, when sharp peaks indicated possible nearby sources. The overprediction could indicate that emissions of UFPs in the area were overpredicted.

The average diurnal profiles of measured and predicted $PV_{0.1}$ concentrations as well as their corresponding hourly levels for the rest of the 12 sites for the summer period can be found in Figure S1 and Figure S2. PMCAMx-UF reproduced well the average diurnal profile of measured $PV_{0.1}$ in Hyytiala, with an average value of 0.25 $\mu m^3\ cm^{-3}$, while there were overpredictions during the whole day for Vavihill, Waldhof and Aspvreten.

4.3.2 Winter

PMCAMx-UF tended to underpredict the winter $PV_{0.1}$ levels with a NMB equal to -30% for hourly averaged values (Table 2). The NME for hourly predictions was higher than during the summer with a value of 72%. For daily average levels, the NMB was -27% and the NME equal to 64% (Table S2). The model overpredicted $PV_{0.1}$ by 0.03 to 0.09 $\mu m^3\ cm^{-3}$ in the sites of Vavihill, Hyytiala, Aspvreten and Varrio.

Mean predicted values in 9 out of 12 sites were within 0.1 $\mu m^3\ cm^{-3}$ of the measured mean (Fig. 7). $PV_{0.1}$ was underpredicted in 7 out of 12 sites. Despite the increased frequency of underprediction, major positive deviations between predictions and observations were found in the Varrio and Hyytiala sites, with high model error also in the Aspvreten, Vavihill, Mace Head and Dresden sites. Mean predicted $PV_{0.1}$ was 0.17 $\mu m^3\ cm^{-3}$ for all sites and mean measured $PV_{0.1}$ was 0.24 $\mu m^3\ cm^{-3}$.

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In Dresden, the ultrafine particle volume concentration was seriously underpredicted, 0.27 $\mu m^3\ cm^{-3}$ to 1.22 $\mu m^3\ cm^{-3}$ respectively. Mean ultrafine particle volume concentration for Helsinki was also underpredicted, with a predicted value of 0.18 $\mu m^3\ cm^{-3}$ and a measured value of 0.35 $\mu m^3\ cm^{-3}$. On the other hand, for the remote Hyytiala site in Finland, mean predicted total $PV_{0.1}$ was 0.16 $\mu m^3\ cm^{-3}$, compared to a measured average of 0.07 $\mu m^3\ cm^{-3}$. This suggests that the underpredictions in Helsinki were mostly due to local sources and not to regional underprediction.

In Dresden, the measured levels increased by a factor of two early in the morning while the predicted profile remained practically flat (Fig. 8). This suggests strongly the lack of one or more major local sources, probably transportation and residential heating. It could also be partially due to the coarse resolution of the model; local emissions were diluted in the large computational cell of the model covering the area of the city. The corresponding hourly concentrations are shown in Figure S4.

For Helsinki, the predicted average diurnal profile was nearly flat (variation less than 0.05 $\mu m^3\ cm^{-3}$) throughout the day, while the measurements peaked at 10:00, remaining near constant during midday and then gradually decreasing (Fig. 8). The hourly concentrations suggested that the model was rarely able to reproduce observed elevated concentration levels during specific one to two-day periods (Fig. S4). The sources of ultrafine particles during these periods need to be further examined. Errors in the meteorological inputs and especially the mixing height were also a possible explanation of these persistent errors.

In Hyytiala, the diurnal average profiles of measured and predicted values were both flat but they differed by approximately 0.1 $\mu m^3\ cm^{-3}$ (Fig. 8). This suggests that the model agreed with observations regarding the relatively low local contributions but it overpredicted the regional background. This could be partially due to the assumed boundary conditions that influenced the Nordic countries more than the rest of Europe due to the choice of modeling domain. Turning our attention to the full period hourly concentrations, substantial deviations became readily apparent (Fig. S4). For the first half of the simulated period, predicted UFP volume concentrations tended to follow measured values, with rapid increases in measured concentrations not generally predicted. These were again possibly indicative of local sources influencing the measurement site. After January 17, the model overpredicted $PV_{0.1}$. The reasons for this overprediction require future analysis. The average diurnal profiles as well as their corresponding hourly $PV_{0.1}$ concentrations for the rest of the 12 sites for this winter period can be found in Figure S3 and Figure S4.

4.4 Predicted links between $PM_{0.1}$ and $PM_{2.5}$

The correlation of predicted $PM_{2.5}$ with $PM_{0.1}$ was examined during the summer and winter period. For the summer period, the mass concentration of fine and ultrafine particles had low correlation in Zurich, Bucharest and Helsinki, with comparatively better correlations in Athens, Birmingham and Paris (Fig. 9). In Helsinki, the two values have a coefficient of determination (R^2) of 0.01. Ultrafine particle mass in Helsinki, as well as in Bucharest and Zurich was mostly secondary inorganic and organic during the summer period. In Athens, Paris and Birmingham, the correlation was significantly better, around 0.4 to 0.6. For Athens, the correlation was driven by wildfire episode (Fig. S5). If this period is excluded the correlation decreases significantly.

For the winter period, correlations were high across most major cities examined, with the notable exceptions of Bucharest and Birmingham (Fig. S6). The R^2 for Zurich, Birmingham, Bucharest and Helsinki was less than or equal to 0.4, but it was higher for Athens (0.71) and Paris (0.65).

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For most major cities, an increase in the primary component of $PM_{0.1}$, was accompanied with an increase in its correlation with $PM_{2.5}$. The exceptions were again Birmingham and Bucharest. The predicted R^2 value in both cities seems to be influenced by outliers of substantially elevated $PM_{2.5}$ values. Yu et al. (2019) reported an R^2 between predicted $PM_{2.5}$ and $PM_{0.1}$ in a year-long study in California, for all domain cells, of 0.63. In that study, $PM_{0.1}$ was mostly comprised of primary matter from combustion processes. This value is comparable to the highest observed in our study, specifically in Athens and Paris.

5. Conclusions

Predicted levels of $PM_{0.1}$ were quite variable in space and time. The average predicted total $PM_{0.1}$ for Europe was 0.6 μg m^{-3} for the summer and 0.3 μg m^{-3} for the winter period. On average, sulfate (38%), SOA (32%), ammonium (13%) and POA (8%) were the most significant $PM_{0.1}$ components during the summer. Primary and secondary inorganic matter had an increased mass fraction (16% to 23% and 51% to 66%) during the winter period. The secondary organic matter percentage contribution was quite low (6%) during the winter. The high secondary contribution to $PM_{0.1}$ is rather surprising.

$PM_{0.1}$ during the winter period correlates better (R^2=0.18-0.71) with $PM_{2.5}$ than during the summer period (R^2=0.01-0.6). However, for most major cities the correlation is low. Better correlations were observed in cases where primary sources contributed significantly to $PM_{0.1}$.

PMCAMx-UF showed little bias (15%) in reproducing the summertime ultrafine volume observations in 12 sites in Europe. During the winter, the model tended to underpredict $PM_{0.1}$ with a NMB of -30% for hourly average values. The model NME for daily average levels was 46% during the summer and 64% during the winter. Using the CTM performance criteria for $PM_{2.5}$, the model performance was considered good for the summer and average for the winter. Missing winter sources need additional investigation.

Given that this is the first effort to predict $PM_{0.1}$ in Europe with PMCAMx-UF, the model performance was quite encouraging. Potential model improvements include corrections in emissions especially during the winter, use of higher grid resolution for the major urban areas and revisiting of the boundary conditions over the northern Atlantic. Evaluation of its composition predictions is also needed.

The predicted lack of correlation between ultrafine and fine particle mass concentration suggests different sources and processes and that future emission reduction strategies will have different effects on $PM_{0.1}$ and $PM_{2.5}$.

Code and Data Availability. The model code and data used in this study are available from the authors upon request (spyros@chemeng.upatras.gr).

Author Contributions. KM carried out the simulations, the analysis, ES wrote the final manuscript with support from SNP., KM and DP, SNP supervised and coordinated the work.

Competing Interests. The authors declare no competing financial interest.

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Table 1. PMCAMx-UF hourly evaluation metrics of $PV_{0.1}$ during the period of 5 June - 8 July 2012 for the 12 measurement sites.

Station	**Mean Predicted** ($\mu m^3\ cm^{-3}$)	**Mean Observed** ($\mu m^3\ cm^{-3}$)	**NMB** (%)	**NME** (%)
Dresden	0.42	0.59	-29	45
Kosetice	0.37	0.24	54	82
Hohenpeissenberg	0.22	0.27	-19	49
Mace Head	0.05	0.06	-5	81
Finokalia	0.39	0.36	6	47
Vavihill	0.47	0.28	66	82
Helsinki	0.44	0.48	-9	44
Melpitz	0.41	0.33	21	61
Hyytiala	0.22	0.23	-3	61
Waldhof	0.50	0.31	63	81
Aspvreten	0.48	0.23	109	125
Varrio	0.10	0.10	-8	68

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Table 2. PMCAMx-UF hourly evaluation metrics of $PV_{0.1}$ during the period of 1-30 January 2009 for the 12 measurement sites.

Station	**Mean Predicted** ($\mu m^3\ cm^{-3}$)	**Mean Observed** ($\mu m^3\ cm^{-3}$)	**NMB** (%)	**NME** (%)
Dresden	0.27	1.22	-78	78
Kosetice	0.24	0.46	-47	56
Hohenpeissenberg	0.16	0.18	-16	51
Mace Head	0.02	0.11	-78	82
Finokalia	0.07	0.14	-48	65
Vavihill	0.25	0.20	27	83
Helsinki	0.18	0.35	-50	66
Melpitz	0.27	0.28	-6	52
Hyytiala	0.16	0.07	130	187
Waldhof	0.27	0.27	3	53
Aspvreten	0.11	0.08	33.5	114
Varrio	0.09	0.02	399	436

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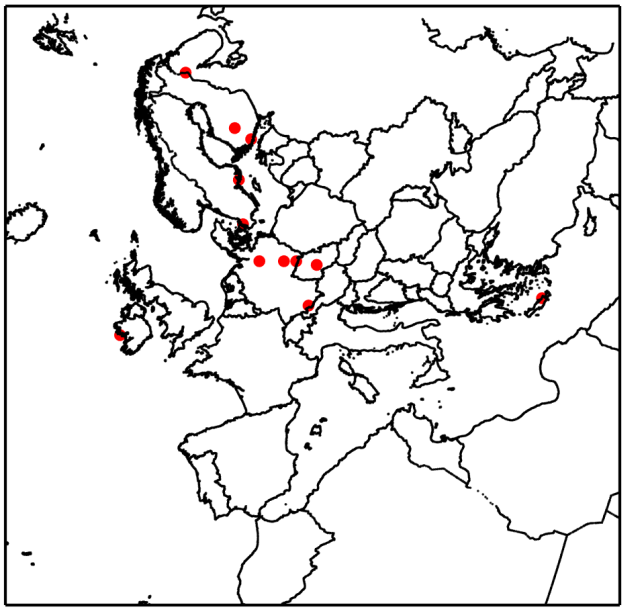

Figure 1. Map of the European modelling domain indicating (red dots) the 12 measurement sites with available particle number distribution measurements for both simulation periods.

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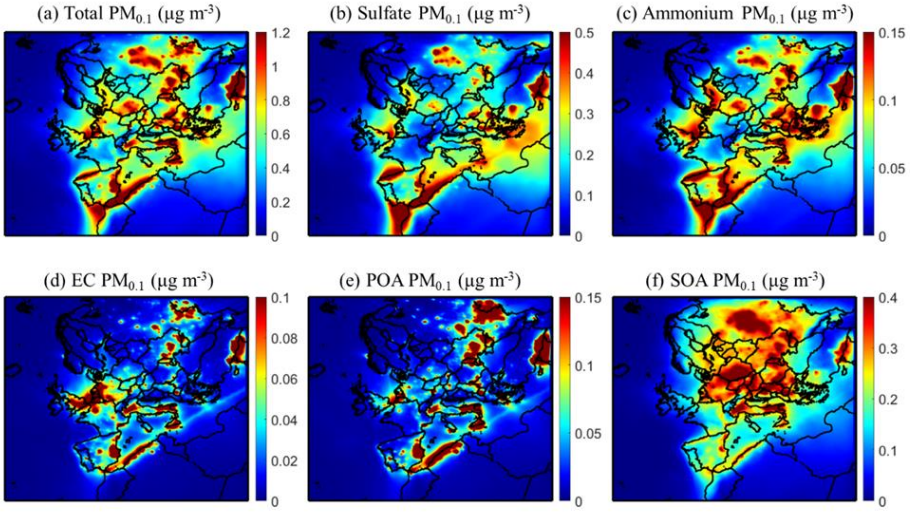

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547 **Figure 2.** Average predicted ground level $PM_{0.1}$ mass concentrations (μg m^{-3}) of (a) total $PM_{0.1}$, (b) $PM_{0.1}$ sulfate, (c)
548 $PM_{0.1}$ ammonium, (d) $PM_{0.1}$ elemental carbon, (e) $PM_{0.1}$ primary organic aerosol and (f) $PM_{0.1}$ secondary organic aerosol
549 during 5 June - 8 July 2012.
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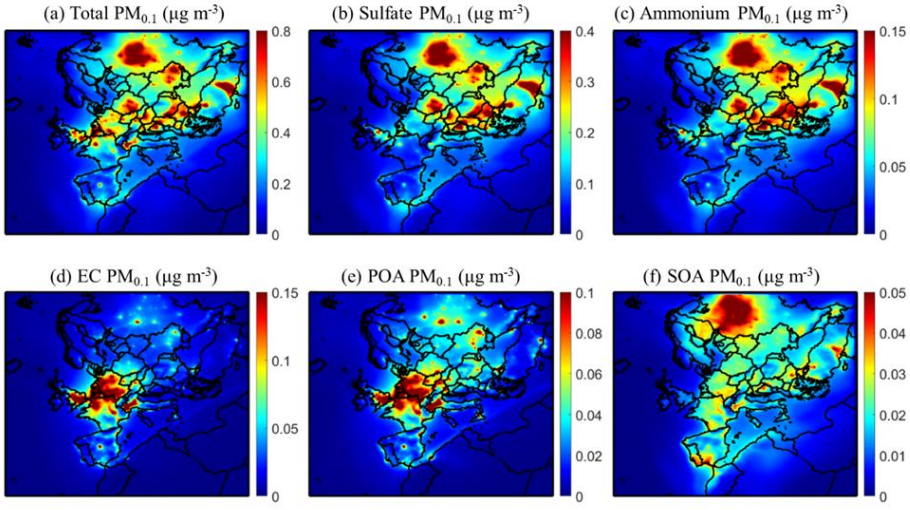

Figure 3. Average predicted ground level $PM_{0.1}$ mass concentrations (μg m^{-3}) of (a) total $PM_{0.1}$, (b) $PM_{0.1}$ sulfate, (c) $PM_{0.1}$ ammonium, (d) $PM_{0.1}$ elemental carbon, (e) $PM_{0.1}$ primary organic aerosol and (f) $PM_{0.1}$ secondary organic aerosol during 1 - 30 January 2009.

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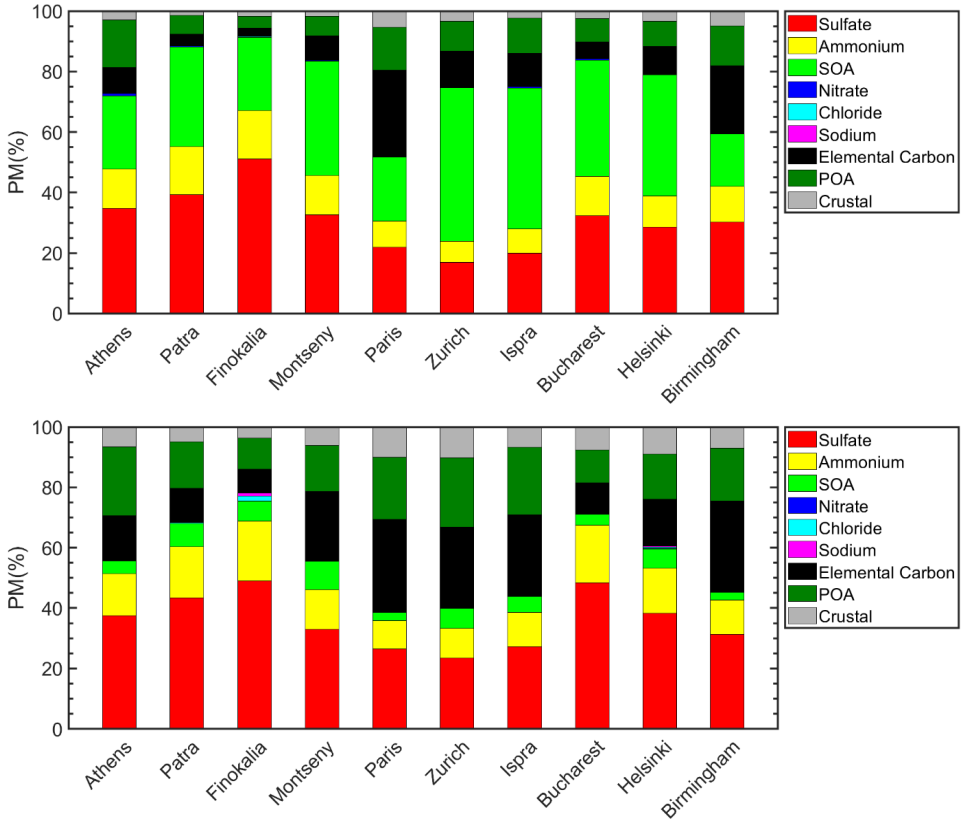

593

594 **Figure 4.** Predicted chemical composition of ultrafine particles in the areas studied during the (a) summer and (b) winter
595 period. POA (dark green) and SOA (green) stand for primary and secondary organic aerosol.

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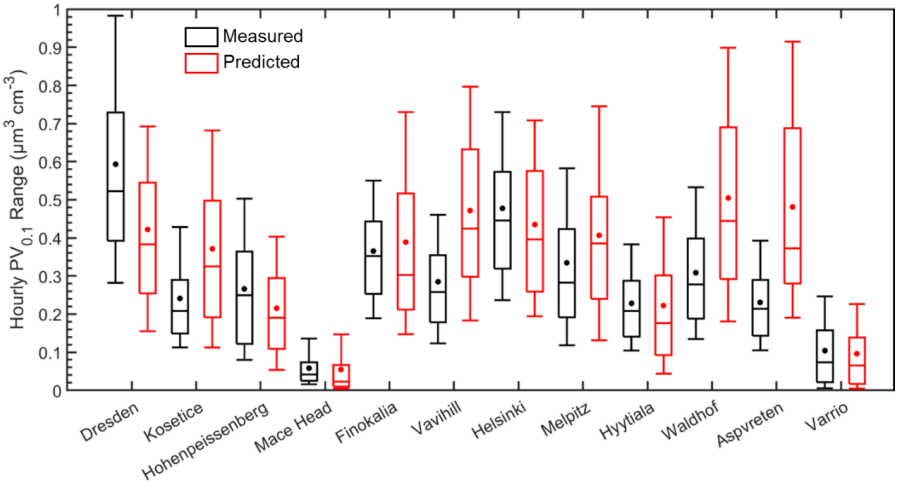

Figure 5. Distributions of predicted (red) and measured (black) hourly ground-level UFP volume (in $\mu m^3\ cm^{-3}$) during 5 June - 8 July 2012, in the 12 sites examined. Stars and lines inside each box designate the mean and the median value of the $PV_{0.1}$ distribution. Box top and bottom lines indicate the upper (75%) and lower (25%) quartiles. The upper and lower extended lines (whiskers) are for the 90^{th} and the 10^{th} UFP volume distribution percentiles.

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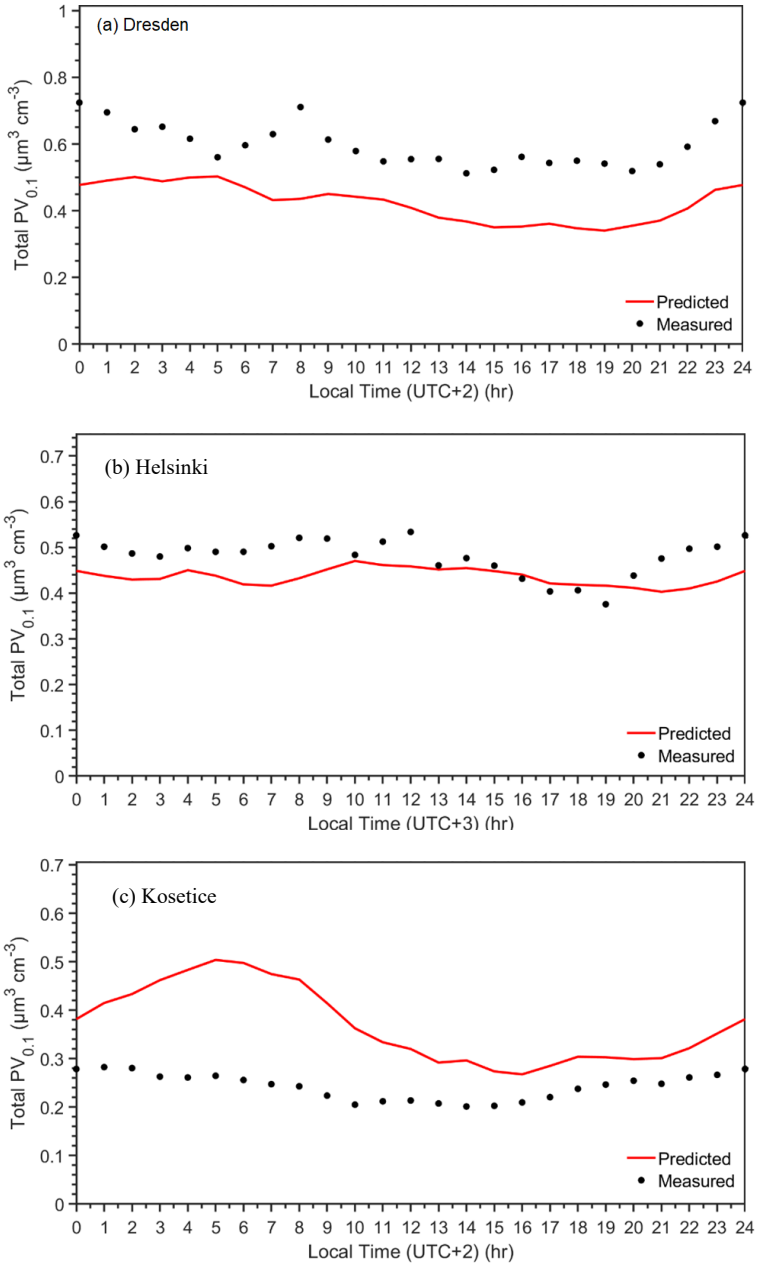

Figure 6. Average diurnal profiles of predicted and measured total volume concentrations ($\mu m^3\ cm^{-3}$) in (a) Dresden, (b) Helsinki and (c) Kosetice for the period of 5 June - 8 July 2012.

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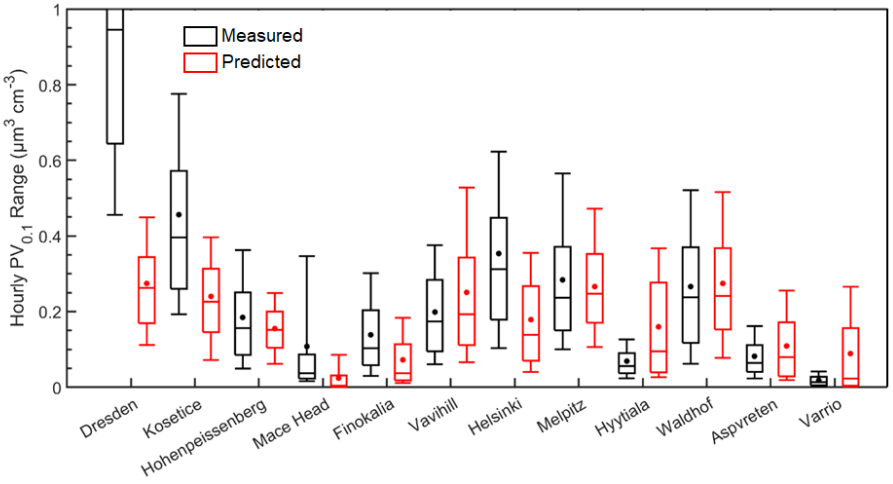

Figure 7. Distributions of predicted (red) and measured (black) ground-level UFP volume during 1-30 January 2009, in the 12 sites examined. Stars and lines inside each box designate the mean and the median value of the $PV_{0.1}$ distribution. Box top and bottom lines indicate the upper (75%) and lower (25%) quartiles. The upper and lower extended lines (whiskers) are for the 90th and the 10th UFP volume distribution percentiles.

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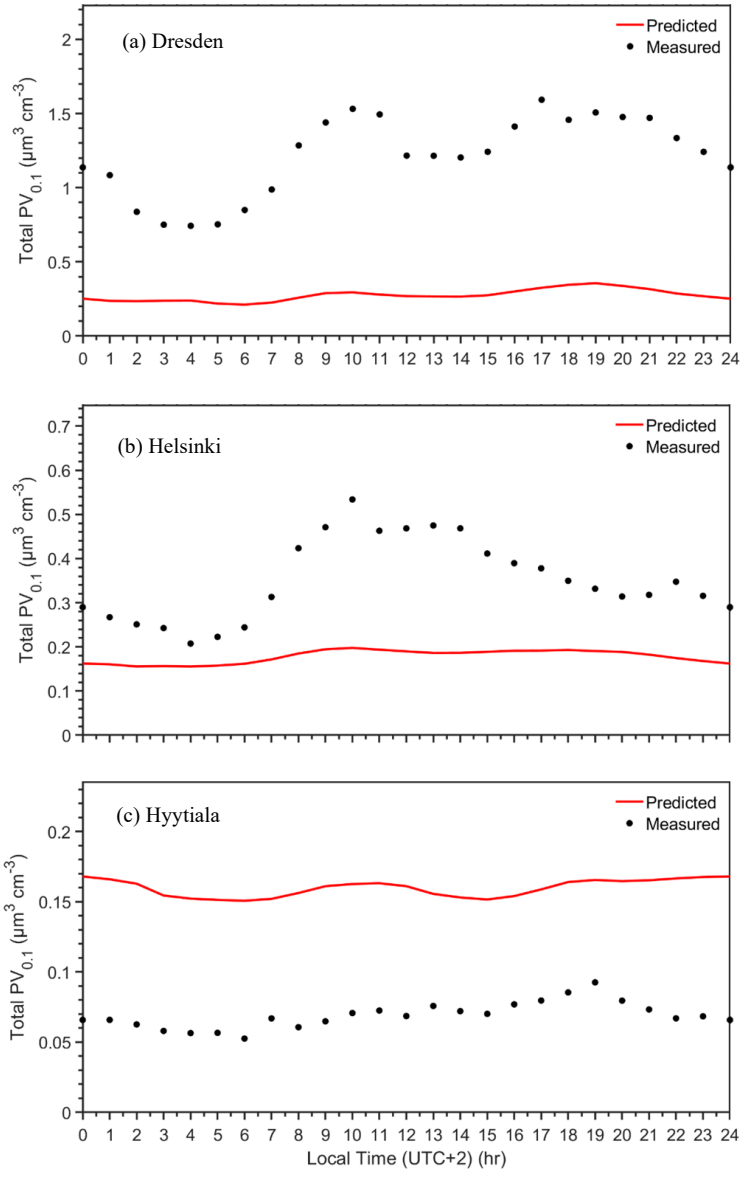

Figure 8. Average diurnal profiles of predicted and measured total volume concentrations (µm^3 cm^{-3}) in (a) Dresden, (b) Helsinki and (c) Hyytiala for the period of 1-30 January 2009.

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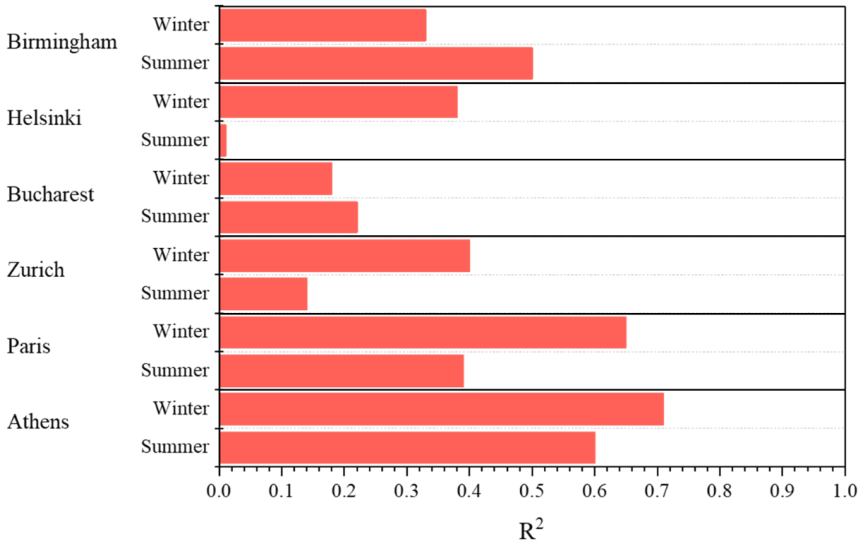

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737 **Figure 9.** R^2 values correspond to the square of the samples Pearson's correlation coefficient R for Athens, Paris, Zurich,
738 Bucharest, Helsinki and Birmingham during the summer and winter periods.

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