Estimation of dust emissions and their effects on atmospheric pollution over Europe

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by
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Also I would like to thank all the members of LAQS for the pleasant working conditions and especially Dr. Ksakousti Skyllakou.

Last but not least, I dedicate this thesis to my family, Katerina, Apostolis and Dimitris who always supported and encouraged me during my studies.
To my parents, Katerina and Apostolis,

and my brother, Dimitris
Abstract

Simulation of the concentration of dust and its interactions with other inorganic components of particulate matter (nitrate, ammonium, sulfate) remains a major modeling challenge due to the lack of accurate dust emission inventories. In this study the chemical transport model PMCAMx is applied over Europe during the period of May 2008 (EUCAARI campaign). First, the existing EUCAARI emission inventory is used and the model predictions are compared with available measurements of PM$_{10}$ from 43 stations in Europe. Periods of Saharan dust transport are excluded. The predicted dust levels are too low compared to measurements especially in the urban areas (fractional bias for PM$_{10}$ equal to $-67\%$). We test the hypothesis that the error is related to underestimation of road transport dust emissions. The fractional bias decreases after the increase of dust emissions related with on-road transportation by a factor of ten. There is significant improvement of the model performance for PM$_{10}$ in both southern and northern Europe, but also in urban and rural and remote areas. In the second part of the work the hybrid version of PMCAMx is used with the improved dust emissions, in order to study mineral dust interactions with the rest of the pollutants. The average predicted PM$_{1-10}$ (particles with diameter between 1 and 10 $\mu$m) calcium, magnesium, and potassium concentrations are 0.02, 0.006, and 0.01 $\mu$g m$^{-3}$ respectively over Europe. Average PM$_1$ (particles with diameters less than 1 $\mu$m) concentrations of nitrate, ammonium, and sulfate decrease 0.04, 0.06, 0.16 $\mu$g m$^{-3}$, while PM$_{1-10}$ concentrations increase 0.06, 0.03, 0.03 $\mu$g m$^{-3}$ respectively over Europe due to mineral dust. These results are sensitive to the assumed composition of dust.
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Chapter 1

Introduction

Atmospheric particulate matter from anthropogenic and natural sources has adverse impacts on human health and contributes to the Earth’s climate change. Dust is a significant component of atmospheric coarse particulate matter (particles with diameter from 1 to 10 μm) in urban areas, it is also emitted by transportation through re-suspension (Amato et al., 2009, 2011; Karanasiou et al., 2011; Pant et al., 2013; Querol et al., 2004; Viana et al., 2007). Road dust accounts for 15-40% of the total PM$_{10}$ concentrations in urban areas (Athanasopoulou et al., 2010). Agricultural operations such as plowing, disking, harrowing, and harvesting emit significant amounts of dust in rural areas (Winiwarter et al., 2009). Natural sources, such as wildfires also emit dust through re-suspension due to the intense turbulence that they generate. It is estimated that soil dust accounts for 10% of PM$_{10}$ emissions during early fire stages (Kavouras et al., 2012). Dust transport from deserts such as Sahara is another major natural source. In this study we will focus on periods during which Europe is not affected by transport of dust from the Sahara.

Dust is mainly inert, but also includes small amounts of Ca$^{2+}$, Mg$^{2+}$, K$^+$, etc. These are chemically active and can participate in heterogeneous reactions, for example forming nitrate or sulfate salts after reactions with HNO$_3$ or H$_2$SO$_4$ vapors (Karydis et al., 2010, 2011). These reactions can also affect indirectly the fine particulate matter by changing the fine nitrate and sulfate levels (Wang et al., 2012; Karydis et al., 2011).

Previous studies have shown that the simulation of these dust effects with the proper emissions can considerably improve model predictions (Dentener et al., 1996; Jacobson, 1999; Song and Carmichael, 2001; Moya et al., 2002; Bian and Zender, 2003; Laskin et al., 2005; Hodzic et al., 2006; Astitha and Kallos, 2009; Athanasopoulou et al., 2010; Fountoukis et al., 2009; Karydis et al., 2010, 2011, 2016; Wang et al., 2012; Trump et al., 2015). However, a small number of those
studies is focused on Europe and urban emissions are often neglected. Comparing predicted dust concentrations to measurements is an effective way to evaluate emissions (Winiwarter et al., 2009). In atmospheric chemical transport models, the particulate and gas phases are often assumed to be in equilibrium. This assumption may lead to errors since the coarse particles may need hours to reach equilibrium (Meng and Seinfeld, 1996; Karydis et al., 2011). Dynamic models simulate explicitly the mass transfer between the gas phase and each particle group minimizing the error.

The aim of the present study is to estimate dust emissions over Europe and to quantify their effects on fine and coarse particulate matter concentration and composition.
Chapter 2

Model description and application

PMCAMx-2008 is a three dimensional chemical transport model (CTM) and the research version of the publicity available CAMx model (Environ, 2003). It simulates horizontal and vertical advection, horizontal and vertical dispersion, dry and wet deposition and gas-aqueous and aerosol chemistry (Appendix A). The gas-phase chemical mechanism used includes 211 reactions of 18 radicals and 56 gases and is based on the SAPRC mechanism (Carter, 2000; Environ, 2003). Furthermore, aqueous-phase chemistry (Fahey and Pandis, 2001), inorganic aerosol formation (Gaydos et al., 2003; Koo et al., 2003) and secondary organic aerosol formation (Lane et al., 2008), are simulated. The aerosol size and composition distribution is described using 10 size bins with diameters from 40 nm to 40 μm. The aerosol species simulated are primary and secondary organics, elemental carbon, crustal species, sodium, chloride, sulfate, nitrate, ammonium, and water. The formation of inorganic aerosol can be simulated either with the bulk equilibrium approach or the hybrid approach.

The bulk equilibrium approach is based on the assumption that the bulk aerosol and gas phases are always in equilibrium. The amount of each species transferred between the aerosol and gas phases is determined by the thermodynamic equilibrium model ISORROPIA (Nenes et al., 1998) which treats the thermodynamics of NH$_4^+$-Na$^+$-SO$_4^{2−}$-NO$_3^−$-Cl$^−$-H$_2$O aerosol systems.

In the hybrid approach fine particles (diameter less than 1 μm) are simulated assuming bulk equilibrium while for the coarse particles (diameter from 1 to 10 μm) the mass transfer between the gas and particle phases is simulated dynamically (Capaldo et al., 2000) by using the MADM model of Pilinis et al. (2000) as extended by Gaydos et al. (2003). The thermodynamic equilibrium model ISORROPIA-II (Fountoukis and Nenes 2007), which treats the thermodynamics of Ca$^{2+}$ -K$^+$ -Mg$^{2+}$ -NH$_4^+$ -Na$^+$ -SO$_4^{2−}$ -NO$_3^−$ -Cl$^−$ -H$_2$O aerosol systems, is used the calculation of the equilibrium vapor pressures of HNO$_3$, NH$_3$, HCl, and also the aerosol water concentration.
2.1 Model application

The simulation period is May of 2008. This is the EUCAARI project summer intensive measurement period. The modeling domain is a region of $5400 \times 5832$ km$^2$, including all of Europe with $36 \times 36$ km grid resolution and 14 vertical layers with total height 6 km above ground level (Figure 2.1). Dust PM$_{10}$ concentrations at the boundaries of the domain are considered constant with typical small values (Table 2.1). Inputs to the model such as vertical diffusivity, horizontal wind components, pressure, temperature, water vapor, clouds and rainfall are provided by the Weather Research and Forecasting (WRF) meteorological model (Skamarock et al., 2008).

The dust emissions used are based on the EUCAARI Pan European inventory (Kulmala et al., 2011), derived from the IIASA’s GAINS inventory (Klimont et al., 2002; Kupiainen and Klimont, 2004). Details of the rest of the aerosol and gas emissions are described in Fountoukis et al. (2011). More details about the initial EUCAARI emissions are available in Visschedijk et al. (2007) and Kulmala et al. (2011). In the initial Pan European emission inventory the dust emissions were not separated from other sources and the size distribution of dust particles was problematic. The above errors were corrected by Kakavas (2017).

In the corrected EUCAARI emission inventory the size distribution of dust is based on Bessagnet et al. (2008). This corrected inventory includes dust emissions mainly from agricultural operations, non-exhaust road transport, and wildfires. Agricultural dust emissions in PM$_1$ are assumed to represent 23% of the total PM$_1$ emissions by this source (Trippetta et al., 2016). Wildfires emissions are taken from IS4FIRES (Sofiev et al., 2009) and the size and composition distribution of PM$_{10}$ is based on Andreae and Merlet (2001). The PM$_{2.5-10}$ fraction accounts for about 25% of the emissions by wildfires. Non-exhaust PM$_1$ road transport dust emissions account for about 3% of total PM$_1$ emissions by this source (Amato et al., 2009). The spatial distribution is shown in Figure 2.1c. Table 2.2 shows a summary of the corrected EUCAARI inventory PM$_{10}$ dust emission rates for the major sources of dust.

| Table 2.1: PM$_{10}$ dust concentrations (in μg m$^{-3}$) at the boundaries of the domain |
|-----------------------------------|-----|-----|-----|-----|
| Species                           | North | South | East | West |
| Dust                              | 0.3   | 1.0   | 1.0   | 0.3  |
Figure 2.1: Spatial distribution of PM$_{10}$ dust emissions in the corrected EUCAARI inventory (a) agricultural, (b) wildfires, (c) road transport and, (d) total (kg d$^{-1}$ km$^{-2}$).

Calcium, magnesium, potassium and sodium emissions, initial and boundary conditions are estimated as a constant fraction of mineral dust ones, 2.4% for Ca$^{2+}$, 1.5% for K$^+$, 1.2% for Na$^+$ and, 0.9% for Mg$^{2+}$, based on Sposito (1989) and Karydis et al. (2016).

Table 2.2: Domain PM$_{10}$ dust emissions in the corrected EUCAARI inventory (tons d$^{-1}$)

<table>
<thead>
<tr>
<th>Source type</th>
<th>PM$_{10}$ dust emissions (tons d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Road transport</td>
<td>1509</td>
</tr>
<tr>
<td>Wildfires</td>
<td>493</td>
</tr>
<tr>
<td>Agriculture</td>
<td>3185</td>
</tr>
</tbody>
</table>
Figure 2.2: Spatial distribution of PM$_{10}$ dust emissions in the increased road transport inventory (a) road transport and, (b) total (kg d$^{-1}$ km$^{-2}$).

As a sensitivity test, road transport dust emissions are increased by a factor of ten. The spatial distribution of PM$_{10}$ dust emissions in the increased road transport inventory is shown in Figure 2.2. Table 2.3 shows a summary of the increased road transport inventory PM$_{10}$ dust emission rates.

**Table 2.3:** Domain increased road transport PM$_{10}$ dust emissions (tons d$^{-1}$)

<table>
<thead>
<tr>
<th>Source type</th>
<th>PM$_{10}$ dust emissions (tons d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increased road transport</td>
<td>15090</td>
</tr>
<tr>
<td>Total</td>
<td>18795</td>
</tr>
</tbody>
</table>
Figure 2.3: Spatial distribution of emissions (a) NH₃, and (b) improved agricultural dust (kg d⁻¹ km⁻²).

In the EUCAARI inventory agricultural dust emissions in Spain, Italy, Greece, Romania and Czech Republic were set equal to zero because the corresponding values were not reported. We use the mean dust emission rate of agricultural areas in these countries and the spatial distribution of ammonia emissions for these countries. (Figure 2.3a) However, these agricultural dust emissions are rough guesses and clearly require further investigation.

Table 2.4: Domain improved agricultural PM₁₀ dust emissions (tons d⁻¹)

<table>
<thead>
<tr>
<th>Source type</th>
<th>PM₁₀ dust emissions (tons d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Added agricultural</td>
<td>332</td>
</tr>
<tr>
<td>Total</td>
<td>19127</td>
</tr>
</tbody>
</table>
2.2 Measurements for model evaluation

Measurements of PM$_{10}$ concentrations with daily temporal resolution are used for the PMCAMx evaluation for the May 2008. The location and the main characteristics of the stations are shown in Figure 2.4 and Table 2.5 respectively. Fine aerosol mode PMCAMx results have been already evaluated in previous work (Fountoukis et al., 2011; 2014).

Figure 2.4: Location of the selected for the study monitoring sites measuring daily PM$_{10}$ concentrations (red dots).
Table 2.5: Main characteristics of the selected background monitoring sites

<table>
<thead>
<tr>
<th>Location (Country)</th>
<th>Type of area</th>
<th>Region</th>
<th>Latitude</th>
<th>Longitude</th>
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<tbody>
<tr>
<td>Montelibretti (Italy)</td>
<td>suburban</td>
<td>south</td>
<td>42.1</td>
<td>12.6</td>
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<td>Paris (France)</td>
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<td>north</td>
<td>48.8</td>
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<td>37.9</td>
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<td>44.4</td>
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<td>Patras (Greece)</td>
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<td>Finokalia (Greece)</td>
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</tr>
<tr>
<td>Rucava (Latvia)</td>
<td>rural</td>
<td>north</td>
<td>56.1</td>
<td>21.1</td>
</tr>
<tr>
<td>Zoseni (Latvia)</td>
<td>rural</td>
<td>north</td>
<td>57.1</td>
<td>25.9</td>
</tr>
<tr>
<td>Citignano casa stabbi (Italy)</td>
<td>rural</td>
<td>south</td>
<td>43.6</td>
<td>11.9</td>
</tr>
<tr>
<td>Fontechiari (Italy)</td>
<td>rural</td>
<td>south</td>
<td>41.6</td>
<td>13.6</td>
</tr>
</tbody>
</table>
Chapter 3

Model results

3.1 PM$_{10}$ Dust concentrations

The predicted average concentrations of PM$_{10}$ dust during the simulation period with the corrected EUCAARI emission inventory are shown in Figure 3.1a. Predicted PM$_{10}$ dust concentrations are generally low, with concentrations varying from 0.5 to 1 μg m$^{-3}$ over most of Europe except in Netherlands and Belgium where the concentrations exceed 4 μg m$^{-3}$ due to high agricultural emissions. Total PM$_{10}$ concentrations are higher over the Mediterranean Sea and over parts of the Atlantic due to high sea salt levels.

The predicted average concentrations of PM$_{10}$ dust levels after increasing road transport emissions by a factor of ten are shown in Figures 3.1c. Predicted PM$_{10}$ dust concentrations are increased in entire Europe. Dust concentrations in United Kingdom, Italy, France and Germany are influenced more and now exceed 4 μg m$^{-3}$. Total PM$_{10}$ concentrations also increased as expected, mainly in urban areas of Europe, such as Paris, Madrid, London, etc.
Figure 3.1: Predicted average concentrations of (a) PM$_{10}$ dust, (b) total PM$_{10}$ (in μg m$^{-3}$) with the corrected EUCAARI emission inventory, and (c) PM$_{10}$ dust, (d) total PM$_{10}$ (in μg m$^{-3}$) after increasing road transport emissions by a factor of ten during May 2008.

The predicted average concentration change of PM$_{10}$ dust and total PM$_{10}$ over the period of May 2008 after adding agricultural emissions in Spain, Italy, Greece, Romania and Czech Republic is shown in Figure 3.2. Both PM$_{10}$ dust and total PM$_{10}$ mean concentrations slightly increased by 0.1-0.2 μg m$^{-3}$.

Figure 3.2: Predicted average concentration increase of PM$_{10}$ (in μg m$^{-3}$) after adding agricultural emissions in Spain, Italy, Greece, Romania, and Czech Republic during May 2008.
3.2 Evaluation of PMCAMx

The fractional bias and fractional error of the model predictions are calculated:

\[
\text{Fractional bias} = \frac{2}{N} \sum_{i=1}^{N} \frac{P_i - O_i}{P_i + O_i}
\]

\[
\text{Fractional error} = \frac{2}{N} \sum_{i=1}^{N} \frac{|P_i - O_i|}{P_i + O_i}
\]

where \(P_i\) is the predicted concentration, \(O_i\) is the observed concentration at the same time, and \(N\) is the total number of the observed values used for the evaluation. Morris et al. (2005), proposed four model performance levels: “excellent” (absolute fractional bias \(\leq 15\%\) and fractional error \(\leq 35\%\)), “good” (absolute fractional bias \(\leq 30\%\) and fractional error \(\leq 50\%\)), “average” (absolute fractional bias \(\leq 60\%\) and fractional error \(\leq 75\%\)), and “problematic” (absolute fractional bias \(\geq 60\%\) and fractional error \(\geq 75\%\)).

The comparison between bulk equilibrium PMCAMx predicted daily PM\(_{10}\) concentrations and measurements is depicted in Figure 3.3. The fractional bias of the model after the EUCAARI emissions correction is \(-0.41\), showing a tendency towards underprediction, and the fractional error is 0.57 (Table 3.1) making the model performance average. After increasing road transport emissions by a factor of ten, the fractional bias of the model is \(-0.29\) and the fractional error is 0.52 (Table 3.1).

![Figure 3.3: Predicted daily PM\(_{10}\) values versus observed ones (in \(\mu g m^{-3}\)) from the 43 monitoring stations: (a) after the EUCAARI emissions correction and, (b) after the increase of road transport emissions by a factor of ten.](image-url)
Both, fractional bias and error decreased and the model performance improved (Figure 3.6a).

**Remote areas:** The relatively low PM$_{10}$ concentrations are reproduced well by PMCAMx on both simulations (Figure 3.4). The fractional bias of the model with the corrected EUCAARI emissions is −0.32, and the fractional error is 0.50 (Table 3.1). Dust PM$_{10}$ represents only 5% of total PM$_{10}$ mass concentration for these sites when the EUCAARI inventory is used. After increasing road transport emissions by a factor of ten, the fractional bias of the model is −0.24 and the fractional error is 0.48 (Table 3.1). Both, fractional bias and error decreased and the model performance improved from average to good (Figure 3.6b). In this case, dust PM$_{10}$ is predicted to account for about 14% of total PM$_{10}$ mass concentration.

**Rural areas:** The fractional bias of the model for the EUCAARI corrected emissions is −0.34, and the fractional error is 0.55. Dust PM$_{10}$ constitutes only 6% of PM$_{10}$ mass concentration. After increasing road transport emissions by a factor of ten, the fractional bias of the model decreased to −0.25 and the fractional error to 0.51 (Table 3.1) improving the model performance (Figure 3.6b). In this case, dust PM$_{10}$ accounts for about 15% of total PM$_{10}$ mass concentration.

**Urban areas:** Daily PM$_{10}$ concentrations for the EUCAARI corrected emissions are seriously underestimated (Figure 3.4) and the model performance is problematic (fractional bias is −0.67 and fractional error is 0.72). Dust PM$_{10}$ also constitutes only 7% of total PM$_{10}$. After increasing road transport emissions by a factor of ten, the model performance improved to average (Figure 3.6b), suggesting that dust emissions in urban areas are seriously underestimated by almost an order of magnitude in the initial EUCAARI emission inventory. The fractional bias decreased to −0.44 and the fr-
Figure 3.4: Predicted daily PM$_{10}$ values versus observed ones (in $\mu g m^{-3}$) for remote, rural, and urban areas: (a) after EUCAARI emissions correction and, (b) after the increase of road transport emissions by a factor of ten.

actional error to 0.59 (Table 3.1). In this case, dust PM$_{10}$ accounts for about 30% of total according PMCAMx.

The comparison between PMCAMx predicted daily PM$_{10}$ concentrations and measurements for northern and southern regions of Europe is shown in Figure 3.5.

**Northern Europe:** The fractional bias is $-0.32$ and the fractional error is 0.53 (Table 3.1) for the corrected EUCAARI emissions and the model performance is average. After increasing road transport emissions by a factor of ten, the fractional bias of the model decreased to $-0.19$ and the fractional error to 0.49 (Table 3.1) improving the model performance to good (Figure 3.6c).

**Southern Europe:** After increasing road transport emissions by a factor of ten, there was significant improvement in model predictions. The fractional bias decreased from $-0.56$ to $-0.45$ and the fractional error from 0.63 to 0.57 (Table 3.1), but for both cases the model performance is average (Figure 3.6c).
Figure 3.5: Predicted daily PM$_{10}$ values versus observed ones (in μg m$^{-3}$) for northern and southern region of Europe: (a) after the EUCAARI emissions correction and, (b) after the increase of road transport emissions by a factor of ten.
Figure 3.6: Fractional error versus fractional bias after the EUCAARI emissions correction (blue), and after increasing road transport emissions by a factor of ten (red) for: (a) overall evaluation, (b) area type evaluation, and (c) regional evaluation. The symbols used: for urban areas (u), for remote areas (re), for rural areas (ru), for northern region (n), and for southern region (s).

To evaluate the effect of our increased agricultural emissions, the PMCAMx predicted daily PM$_{10}$ concentrations were compared with measurements for Spain, Italy, Greece, Romania, and Czech Republic (SIGRC) is done (Figure 3.7). The EUCAARI emissions resulted in significant underprediction (fractional bias is $-0.61$ and fractional error is 0.67). After increasing road transport emissions by a factor of t-

Table 3.1: Error metrics for the evaluation of PMCAMx against daily PM$_{10}$ measurements

<table>
<thead>
<tr>
<th>Area</th>
<th>Number of measurements</th>
<th>Fractional bias</th>
<th>Fractional error</th>
<th>Fractional bias</th>
<th>Fractional error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Domain</td>
<td>1136</td>
<td>-0.41</td>
<td>0.57</td>
<td>-0.29</td>
<td>0.52</td>
</tr>
<tr>
<td>Remote</td>
<td>364</td>
<td>-0.32</td>
<td>0.50</td>
<td>-0.24</td>
<td>0.48</td>
</tr>
<tr>
<td>Rural</td>
<td>505</td>
<td>-0.34</td>
<td>0.55</td>
<td>-0.25</td>
<td>0.51</td>
</tr>
<tr>
<td>Urban</td>
<td>267</td>
<td>-0.67</td>
<td>0.72</td>
<td>-0.44</td>
<td>0.59</td>
</tr>
<tr>
<td>Northern Europe</td>
<td>694</td>
<td>-0.32</td>
<td>0.53</td>
<td>-0.19</td>
<td>0.49</td>
</tr>
<tr>
<td>Southern Europe</td>
<td>442</td>
<td>-0.56</td>
<td>0.63</td>
<td>-0.45</td>
<td>0.57</td>
</tr>
<tr>
<td>SIGRC</td>
<td>411</td>
<td>-0.61</td>
<td>0.67</td>
<td>-0.48</td>
<td>0.60</td>
</tr>
</tbody>
</table>
Figure 3.7: Predicted daily PM$_{10}$ values are shown versus observed ones (in μg m$^{-3}$) for SIGRC: (a) after the EUCAARI emissions correction and, (b) after the increase of road transport emissions by a factor of ten and adding agricultural dust emissions.

Even the fractional bias of the model decreased to −0.48 and the fractional error to 0.60 improving the model performance to average. Added agricultural dust emissions slightly decreased fractional bias and fractional error to −0.47 and 0.59 respectively (Figure 3.8). So the improvement suggests missing sources of dust in these countries.

Figure 3.8: Fractional error versus fractional bias after the EUCAARI emissions correction (blue), after increasing road transport emissions by a factor of ten (red), and after adding agricultural emissions (green) for Spain, Italy, Greece, Romania, and Czech Republic (SIGRC).
3.3 Effect of residual particle water content during PM$_{10}$ measurements

The PM$_{10}$ measurements are performed at 50% relative humidity, so some of the measured PM$_{10}$ is water. This biases the measurements highly and could be responsible for part of the model underprediction of PM$_{10}$. The evaluation of the model was repeated, this time after estimating the PM$_{10}$ water content at 50% and 60% relative humidity, and adding it to the PMCAMx predictions of PM$_{10}$. The results of the comparison between PM$_{10}$ predictions and measurements are shown in Figure 3.9.

50% RH: The mean PM$_{10}$ water content concentration is 0.63 μg m$^{-3}$. For the increased road transport emissions, the fractional bias decreased from −0.29 to −0.25 and the fractional error from 0.52 to 0.51 (Table 3.2).

60% RH: The mean PM$_{10}$ water content concentration increased to 3.3 μg m$^{-3}$. As a result, the fractional bias of the model decreased to −0.10 and the fractional error is slightly decreased to 0.48 (Table 3.2).

**Figure 3.9:** Predicted daily PM$_{10}$ values, including particle water content, versus observed ones (in μg m$^{-3}$) after increasing road transport emissions by a factor of ten: (a) for 50% RH, (b) for 60% RH.
Table 3.2: Error metrics for the overall evaluation of PMCAMx against daily PM$_{10}$ measurements with particle water content in predictions

<table>
<thead>
<tr>
<th>RH</th>
<th>Mean PM$_{10}$ water content (μg m$^{-3}$)</th>
<th>Fractional bias</th>
<th>Fractional error</th>
</tr>
</thead>
<tbody>
<tr>
<td>50%</td>
<td>0.63</td>
<td>-0.25</td>
<td>0.51</td>
</tr>
<tr>
<td>60%</td>
<td>3.31</td>
<td>-0.10</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Figure 3.10: Fractional error versus fractional bias after increasing road transport emissions by a factor of ten (red), without particle water content (NPW), including water with 50% RH, and 60% RH.
3.4 Effects on other PM components

The hybrid PMCAMx model is used with the increased road transport dust emissions and the added agricultural ones, in order to simulate the concentrations of calcium potassium, magnesium, and sodium and study their interactions with the rest

Figure 3.11: Predicted hybrid PMCAMx average concentrations of PM$_1$ (a) nitrate, (b) sulfate, (c) ammonium, (d) chloride, and (e) sodium (in μg m$^{-3}$) during May 2008.
of the inorganic aerosol components. The predicted average concentrations of PM$_1$ nitrate, sulfate, ammonium, chloride, and sodium over May 2008 are shown in Figure 3.11. The highest predicted nitrate concentrations are over Netherlands, Belgium and North France (over 4 $\mu$g m$^{-3}$). Lower concentrations are predicted in the rest of Europe. The highest sulfate concentrations are over the Mediterranean and neighboring countries such as Italy and Greece (over 4 $\mu$g m$^{-3}$) Ammonium is enhanced significantly in the areas with high nitrate levels (up to 2 $\mu$g m$^{-3}$) and it exists mainly as ammonium nitrate and ammonium sulfate. Fine chloride and sodium concentrations are low in most of Europe (less than 0.5 $\mu$g m$^{-3}$) with higher levels over water.

The predicted average concentrations of coarse (PM$_{1-10}$) nitrate, sulfate, ammonium, sodium, chloride, calcium, potassium, and magnesium are shown in Figure 3.12. The spatial distribution of calcium, potassium, and magnesium is similar to that of dust due to their common origin. Potassium, and magnesium average concentrations are generally lower (up to 0.4, 0.1 $\mu$g m$^{-3}$ respectively), than calcium (up to 0.5 $\mu$g m$^{-3}$). The concentrations of these cations are comparable with measured values (Yin et al., 2008; Terzi et al., 2010), suggesting that the mineral dust composition used in this study was of the correct order of magnitude.
Figure 3.12: Predicted hybrid PMCAMx average concentrations of PM$_{1-10}$ (a) nitrate, (b) sulfate, (c) ammonium, (d) sodium, (e) chloride, (f) calcium, (g) potassium, and (h) magnesium (in μg m$^{-3}$) during May 2008.
To quantify the effects of mineral dust components (Na\(^+\), Ca\(^{2+}\), K\(^+\), Mg\(^{2+}\)) on the rest of the inorganic aerosol components, we performed an additional simulation turning off the dust aerosol chemistry. The predicted average concentrations change of fine and coarse sulfate, nitrate, and ammonium due to dust components interactions is shown in Figures 3.13, 3.14 respectively. Nitrate PM\(_1\) decreases due to dust aerosol chemistry, by approximately over 0.5 \(\mu g\) m\(^{-3}\) (around 20 \%) in the United Kingdom, Netherlands, North France and Belgium, while in the rest of Europe smaller decreases up to 0.2 \(\mu g\) m\(^{-3}\) are observed. Fine ammonium decreases up to 0.3 \(\mu g\) m\(^{-3}\) (~14 \%) in the same areas as nitrate does, and less than 0.1 \(\mu g\) m\(^{-3}\) (less than 10 \%) in the rest of Europe. Sulfate PM\(_1\) decreases slightly (less than 5 \%).

Figure 3.13: Concentrations change (\(\mu g\) m\(^{-3}\)) of PM\(_1\) (a) nitrate, (b) sulfate, and (c) ammonium due to dust aerosol chemistry. A negative change corresponds to a decrease.
Figure 3.14: Concentrations change (μg m\(^{-3}\)) of PM\(_{1-10}\) (a) nitrate, (b) sulfate, and (c) ammonium due to dust aerosol chemistry. A positive change corresponds to an increase.

Coarse (PM\(_{1-10}\)) nitrate ground level concentrations are increased over 1 μg m\(^{-3}\) (more than 90 %) in Paris, Netherlands and Belgium due to dust. In the rest of Europe smaller increases are observed (up to 0.6 μg m\(^{-3}\)). Coarse sulfate concentrations slightly increase but the change is less than 5 %. Coarse ammonium increases mainly in the marine areas.
Chapter 4

Sensitivity to dust composition

A sensitivity test has performed, in which mass fraction of Ca$^{2+}$, K$^+$, Mg$^{2+}$, Na$^+$ in the emitted dust was increased by a factor of two, Calcium, potassium, and magnesium average concentrations are increased by up to 0.4, 0.3, and 0.1 $\mu$g m$^{-3}$ respectively compared with the base case simulation as shown in Figure 4.1.

![Figure 4.1](image)

**Figure 4.1:** Concentrations increase (μg m$^{-3}$) of PM$_{1-10}$ (a) calcium, (b) potassium, and (c) magnesium assuming higher abundance in dust.
Figure 4.2: Concentrations change (μg m⁻³) of PM₁ (a) nitrate, (b) sulfate, and (c) ammonium assuming higher abundance in dust. A negative change corresponds to a decrease.

Fine (PM₁) inorganic aerosols concentrations change is shown in Figure 4.2. Fine nitrate, sulfate, and ammonium are further decreased by up to 0.5, 0.01, 0.2 μg m⁻³ respectively over Europe. Coarse nitrate, sulfate, and ammonium average concentrations are further increased by 0.5, 0.03, 0.007 μg m⁻³ respectively after increasing Ca²⁺, K⁺, Mg²⁺, and Na⁺ mass fraction in the emitted dust by a factor of two (Figure 4.3).
Calcium, potassium, and magnesium concentrations almost doubled and nitrate concentrations affected the most compared with sulfate and ammonium after increasing Ca$^{2+}$, K$^+$, Mg$^{2+}$, and Na$^+$ mass fraction in the emitted dust by a factor of two.

**Figure 4.3:** Concentrations change (μg m$^{-3}$) of PM$_{1-10}$ (a) nitrate, (b) sulfate, and (c) ammonium due to sensitivity test.
Chapter 5

Conclusions

In the present study we combine the three dimensional chemical transport model PMCAMx with improved emissions and PM$_{10}$ measurements in order to better quantify the European sources of dust and their effects on fine and coarse PM. Periods during which Europe was affected by Saharan dust are excluded in an effort to focus on the European dust sources. We use two emission inventories, the corrected version of the default EUCAARI emission inventory, and one in which dust emissions related with on road transportation are increased by a factor of ten.

Use of the corrected EUCAARI inventory leads to a significant underprediction of PM$_{10}$ levels, with a fractional bias of $-41\%$ and a fractional error of $57\%$. After increasing road transport emissions by a factor of ten the fractional bias is reduced to $-29\%$ and the fractional error to $52\%$. Accounting for residual water in the measured PM$_{10}$ assuming $50\%$ RH, the fractional bias is reduced to $-25\%$ and the fractional error to $51\%$. Assuming a $60\%$ RH during the PM$_{10}$ measurements, the fractional bias and error are reduced to $-10\%$ and $48\%$ respectively, pointing out the importance of this in using PM$_{10}$ measurements.

The PMCAMx performance improved in northern Europe, southern Europe, remote, rural and mainly in urban areas after increasing non-exhaust road transport dust emissions by a factor of ten. These results suggest that dust emissions related with on road transportation or other urban dust sources like construction are underestimated approximately by an order of magnitude in the initial EUCAARI emission inventory.

The average predicted PM$_{1-10}$ calcium, magnesium, and potassium concentrations are $0.02$, $0.006$, and $0.01$ $\mu$g $m^{-3}$ respectively over Europe. Average PM$_1$ concentrations of nitrate are decreased $0.04$ $\mu$g $m^{-3}$ due to dust aerosol chemistry, while average fine ammonium and sulfate are decreased $0.06$, $0.16$ $\mu$g $m^{-3}$ respectively over Europe. Average PM$_{1-10}$ concentrations increased $0.06$, $0.03$, $0.03$ $\mu$g $m^{-3}$ for nitrate, sulfate, and ammonium respectively over Europe. Sensitivity test
indicates that calcium, potassium, and magnesium concentrations almost doubled and nitrate concentrations affected the most after increasing $\text{Ca}^{2+}$, $\text{K}^+$, $\text{Mg}^{2+}$, and $\text{Na}^+$ mass fraction in the emitted dust by a factor of two.
References


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Appendix A

Additional information for PMCAMx

The three-dimensional chemical transport model PMCAMx (Particulate Matter Computational Air Quality Model with extensions) solves the following general equation that describes the change in concentration of a chemical pollutant as a function of time:

$$\frac{\partial c_i}{\partial t} = \left( \frac{\partial c_i}{\partial t} \right)_{\text{adv}} + \left( \frac{\partial c_i}{\partial t} \right)_{\text{diff}} + \left( \frac{\partial c_i}{\partial t} \right)_{\text{cloud}} + \left( \frac{\partial c_i}{\partial t} \right)_{\text{dry}} + \left( \frac{\partial c_i}{\partial t} \right)_{\text{aerosol}} + R_{gi} + E_i \quad \text{(A.1)}$$

where the various terms denote the rates of change of the pollutant concentration $C_i$ due to advection, diffusion, cloud processes (aqueous-phase reactions, cloud scavenging, wet deposition, etc.), dry deposition, and aerosol processes (transport between aerosol and gas phases, aerosol dynamics, etc.) respectively; $R_{gi}$ is the net production from gas-phase reactions; and $E_i$ is the emission rate (Seinfeld and Pandis, 2006).

The simulation of each process in the model is done separately in each time step using operator splitting. The splitting method separates the original partial differential equation into multiple parts over a time step, each corresponding to a physical or chemical process. This allows the use of different numerical methods for simulation of processes like advection, dispersion, chemistry, removal, aerosol dynamics, etc. The results are then combined to form a solution to the original equation. The master simulation time step varies usually ranges from 5 to 15 minutes, while smaller time steps are used to simulate each process in order to maintain the accuracy of the solution. The simulation order of the processes in the operating splitting scheme used in PMCAMx is: emissions, horizontal advection, vertical advection, vertical diffusion, horizontal diffusion, wet deposition, gas-phase chemistry, the aerosol processes: nucleation, coagulation, condensation, secondary organic aerosol growth, and finally aqueous phase-chemistry. Each process is described in brief below.
**Horizontal advection**: Horizontal transport is described by:

\[
\frac{\partial c_i}{\partial t} \bigg|_{\text{x-advection}} = - \frac{\partial uc_i}{\partial x}
\]

\[
\frac{\partial c_i}{\partial t} \bigg|_{\text{y-advection}} = - \frac{\partial vc_i}{\partial y}
\]

where \( u \) is the velocity of the wind in the \( x \) direction and \( v \) is the velocity in the \( y \) direction. The order of the horizontal transport directions \( x \) and \( y \) is alternated so as to avoid any numerical biases when this order is constant.

**Vertical advection**: The change of concentration due to the vertical transport of pollutants is described by:

\[
\frac{\partial c_i}{\partial t} \bigg|_{\text{z-advection}} = - \frac{\partial wc_i}{\partial z}
\]

where \( w \) is the velocity of the wind in the \( z \) direction.

**Vertical dispersion**: Concentration can change due to horizontal dispersion described by:

\[
\frac{\partial c_i}{\partial t} \bigg|_{\text{diffusion}} = \frac{\partial}{\partial z} \left[ \rho K_v \frac{\partial (\xi_i)}{\partial z} \right]
\]

where \( K_v \) is the vertical dispersion coefficient and is provided as a meteorological input and \( \rho \) is the atmospheric density.

**Horizontal dispersion**: Concentration change due to horizontal dispersion is described by the following equation:

\[
\frac{\partial c_i}{\partial t} \bigg|_{\text{XY-diffusion}} = \frac{\partial}{\partial x} \left[ \rho K_x \frac{\partial (\xi_i)}{\partial x} \right] + \frac{\partial}{\partial y} \left[ \rho K_y \frac{\partial (\xi_i)}{\partial y} \right]
\]

where \( K_x \) and \( K_y \) are the horizontal dispersion coefficients.
Gas-phase chemistry: The gas-phase chemistry reactions are numerically integrated using the Chemical Mechanism Compiler (CMC) solver (Environ, 2003). The CMC uses the steady-state approximation for the fast reacting species (radicals), while the slower reacting (state) species are separated into two groups. The differential equations for the fast state species (with chemical lifetimes of seconds to a few minutes) are solved using a second order implicit Runge-Kutta method, while those for the slow state species (with longer chemical lifetimes) are solved explicitly. This mechanism includes 211 reactions between 56 gases and 18 free radicals.

Wet deposition: The change in concentration within or below a cloud that produces rain can be parameterized using a scavenging coefficient, $\Lambda$:

$$ \frac{\partial c_i}{\partial t} = -\Lambda c_i \quad (A.7) $$

The scavenging coefficient is different for gases and particles and is calculated separately, based on Seinfeld and Pandis (2006). The mass transfer coefficient below the clouds depends on the rain droplet diameter and its falling speed. Within a cloud, the partitioning of the total concentration of a species between the aqueous and gas phases is calculated using the Henry’s law. Below the cloud layer, the collection efficiency depends on the particle diameter (Seinfeld and Pandis, 2006).

Dry Deposition: For gases, the deposition velocity, $v_d$ is calculated by:

$$ v_d = \frac{1}{r_a + r_b + r_c} \quad (A.8) $$

where $r_a$ is the aerodynamic resistance, $r_s$ surface resistance, and $r_c$ canopy resistance. For aerosol particles, the deposition velocity of particles is given by:

$$ v_d = v_{sed} + \frac{1}{r_a + r_b + r_a r_b v_{sed}} \quad (A.9) $$

where $v_{sed}$ is the gravitational settling velocity.
Aqueous phase chemistry: To simulate cloud chemistry, the VSRM model of Fahey et al. (2001) is used. The model is based on the chemical mechanism of Pandis and Seinfeld (1989) with the addition of Ca$^{2+}$ to the list of particle components as well as H$_2$SO$_4$ in the gas phase (Fahey and Pandis, 2001). When the liquid water ratio is more than 0.05 g m$^{-3}$, the suspended particles that are larger than the 0.7 μm activation diameter (Strader et al., 1998) are assumed to instantly form cloud droplets. The model selects in which cases it will use the general approach or the 2-droplet group approach (divided by 2.5 μm) for each cell using the decision algorithm of Fahey and Pandis (2001).

Size distribution of dust emissions: The size distribution used for dust is shown in Figure A.1:

![Figure A.1](image.png)

**Figure A.1:** Dust emissions size distribution used in order to correct the EUCAARI emission inventory based on Bessagnet et al. (2008).
Appendix B

Additional PMCAMx results

B.1: The PM$_{10}$ dust emissions from domestic heating and mining are shown in Figure B.1.

![Spatial distribution of dust emissions](image)

**Figure B.1**: Spatial distribution of dust emissions (a) domestic heating (b) mining, (tons day$^{-1}$ km$^{-2}$).

B.2: Additional bulk equilibrium PMCAMx results

![Additional bulk equilibrium](image)
Figure B.2: Predicted bulk equilibrium PMCAMx average concentrations of PM$_1$ (a) chloride, (b) sodium, (c) ammonium, (d) nitrate, and (e) sulfate (in $\mu g m^{-3}$) during May 2008.
Figure B.3: Predicted bulk equilibrium PMCAMx average concentrations of PM$_{1-10}$ (a) chloride, (b) sodium, (c) ammonium, (d) nitrate, and (e) sulfate (in μg m$^{-3}$) during May 2008.

B.3: Additional hybrid PMCAMx results (dust chemically inactive)
Figure B.4: Predicted hybrid PMCAMx (dust chemically inactive) average concentrations of PM$_1$ (a) chloride, (b) sodium, (c) ammonium, (d) nitrate, and (e) sulfate (in μg m$^{-3}$) during May 2008.
Figure B.5: Predicted hybrid PMCAMx (dust chemically inactive) average concentrations of PM$_{1-10}$ (a) chloride, (b) sodium, (c) ammonium, (d) nitrate, and (e) sulfate (in μg m$^{-3}$) during May 2008.
B.4: Additional hybrid PMCAMx results (percentile ground level concentration change) for base case simulation with dust chemically active

Figure B.6: Percentile concentrations change of PM$_1$ (a) nitrate, (b) sulfate, (c) ammonium, (d) chloride, and (e) sodium due to dust aerosol chemistry. A negative change corresponds to a decrease.
Figure B.7: Percentile concentrations change of PM$_{1-10}$ (a) nitrate, (b) sulfate, (c) ammonium, (d) chloride, and (e) sodium due to dust aerosol chemistry.
Figure B.8: Predicted hybrid PMCAMx average concentrations of PM$_1$ (a) sodium, (b) chloride, (c) ammonium, (d) nitrate, and (e) sulfate (in μg m$^{-3}$) after increasing dust components composition by a factor of two during May 2008.
Figure B.9: Predicted hybrid PMCAMx average concentrations of PM$_{1-10}$ (a) sodium, (b) chloride, (c) ammonium, (d) nitrate, (e) sulfate, (f) calcium, (g) potassium, and (h) magnesium (in μg m$^{-3}$) after increasing dust components composition by a factor of two during May 2008.