Fairbanks North Star Borough $PM_{2.5}$ Non-Attainment Area CMAQ Modeling

Final Report Phase II

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1. Background

The Community Multiscale Air Quality (CMAQ) model version 4.7.1 was adapted to simulate the $PM_{2.5}$-concentrations in Fairbanks, Interior Alaska in phase I [*Mölders and Leelasakultum*, 2011]. The adapted CMAQ was applied to a two-week episode in January/February, 2008 and November, 2008 each for investigations on and understanding of the $PM_{2.5}$-situation in the Fairbanks nonattainment area.

According to the final report of phase I [*Mölders and Leelasakultum*, 2011], the CMAQ model was configured to use the global mass-conserving Yamartino advection scheme, the eddy vertical diffusion module, the Carbon Bond Five (CB05) lumped gas phase chemistry mechanism, which uses the Euler Backward Iterative (EBI) as solver, the AERO5 aerosol mechanism, the photolysis inline module, and the Asymmetric Convective Method (ACM) cloud processor to compute convective mixing (cloud_acm_ae5). As described in the final report of phase I, we had made several changes to the CMAQ code to improve the prediction of $PM_{2.5}$-concentrations and to represent the conditions in the Fairbanks domain. Those changes were the development of Alaska specific initial and boundary conditions, modification of the dry deposition code, reducing of the minimum mixing height, replacing the minimal stomata resistances, decreasing the lowest and highest eddy diffusivity coefficients by half and scaling them according to the fraction of land-use, and reducing the wind-speed by half in valleys within the domain. The latter step has been abandoned in the further studies. This step was only done only for investigation of the magnitude of the impact of the overestimated wind-speeds obtained from the Alaska adapted WRF (see *Gaudet and Staufer* [2012] for details on this WRF version). This means all results reported in the current report use the original simulated wind-speed as obtained from WRF.

Based on the CMAQ's output in phase I, Sierra Research Inc. had improved the emission input data generated by using the Sparse Matrix Operator Kernel Emission (SMOKE). Penn State [*Gaudet and Staufer*, 2012] had updated the meteorological input data generated for the Alaska adapted CMAQ model (called adapted CMAQ hereafter) by using the Weather Research and Forecasting (WRF; *Skamarock et al*. [2009]) in its version adapted for Fairbanks by *Gaudet and Staufer* [2011]. Hereafter, we refer to the January/February episode data before and after the update as January v1 and January v2, respectively. Without the reducing wind-speed in the valleys by half, the new version of the emission inventory data and the meteorological input data brought an increase in the simulated $PM_{2.5}$-concentrations at the grid-cell holding the State Office Building site. Here CMAQ underestimated the $PM_{2.5}$-concentrations previously. Therefore, the reduction of the wind-speeds in the valleys by half is not required for the January v2 and November episode.

2. Activities

Building upon the Alaska adapted CMAQ described in the final report of phase I and the results of phase I, we incorporated the final Penn State WRF output files and the first complete emissions inventory from SMOKE which accounts for Fairbanks specific temporal and spatial variations that we obtained from Sierra Research Inc.. We prepared an assessment of the CMAQ performance, which includes using metrics established by *Boylan and Russell* [2006] and running CMAQ Process Analysis (PA). In the following sections, we describe and assess the results of these activities.

2.1 Configuration of CMAQ for the November 2008 Episode

The November episode covers November 2 to November 16, 2008. The emissions developed for the November episode were updated by Sierra Research Inc. for the emissions from mobile sources. They also included the emissions from airports. The temporal evolutions of 24h-average of simulated $PM_{2.5}$-concentrations show that the model overestimates the 24h-average $PM_{2.5}$-concentrations at the State Office Building site at the beginning of the episode (November 2-4); the adapted model failed to capture the peaks on November 6, 9 and 16, and shows a nonexistent temporal minimum on November 7 (Fig. 1).

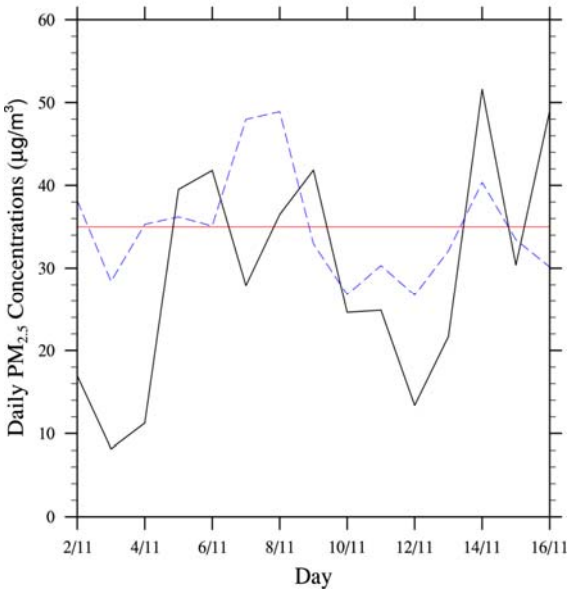


Fig. 1 Time series of simulated (blue dashed line) and observed (black solid line) 24h-average $PM_{2.5}$-concentrations as obtained with the adapted CMAQ simulation that used the revised WRF and SMOKE input for the November episode at the State Office Building site.

The 24h-average $PM_{2.5}$-concentrations obtained from the adapted CMAQ simulations with the observations have a correlation coefficient of 0.31. The scatter between simulated and observed 24h-average $PM_{2.5}$-concentrations is shown in Figure 2. We also found that allowing for a time lag of one between the simulation results and the observations increases the correlation

coefficient from 0.31 to 0.37. According to the observations, there are nine days in the November episode that have $PM_{2.5}$-concentrations below the National Ambient Air Quality Standard (NAAQS) of 35 µg/m^3, and there are six days with $PM_{2.5}$-concentrations above the NAAQS. For most of the days of the episode, the simulated and observed 24h-average $PM_{2.5}$-concentrations agree well; there are two days with false alarm, two days of missed events and three pairs of data outside the factor of two agreement (Fig. 2).

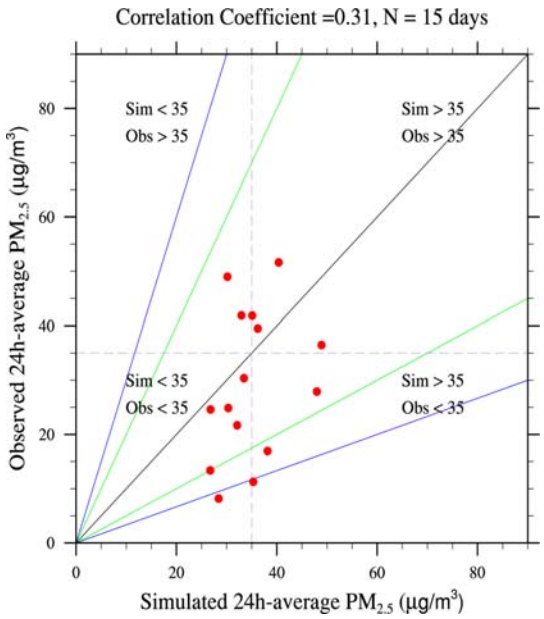


Fig.2 Scatter plot of 24h-average $PM_{2.5}$-concentrations as obtained from the adapted CMAQ simulation that used the revised WRF and SMOKE input for the November episode and the observations at the State Office Building site. The green line indicates the factor of two and the blue line indicates the factor of three agreement.

The bugle plots and soccer plots show that the adapted CMAQ simulation has five days outside the performance criteria (Fig. 3, a-c). Three of five days are the days in the beginning of the episode, which are probably due to spin-up effects in the CMAQ model itself. Moreover, all of those five days have very low (below NAAQS) 24h-average $PM_{2.5}$-concentrations.

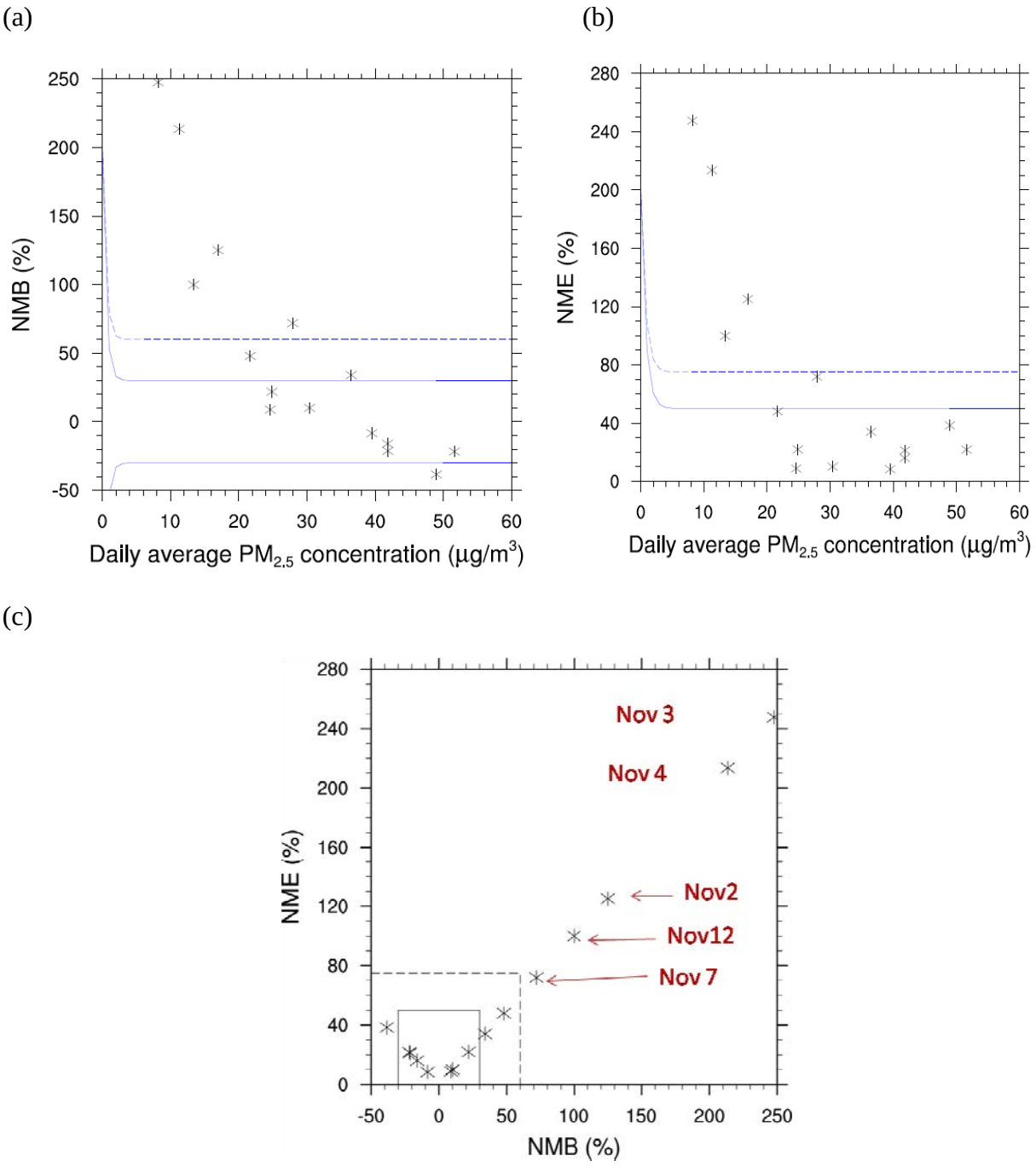


Fig. 3 Bugle plots of (a) normalized mean biases, (b) normalized mean errors, and soccer plots of (c) normalized mean errors and biases of simulated 24h-average $PM_{2.5}$-concentrations as obtained from the adapted CMAQ simulations that used the revised WRF and SMOKE input for the November episode at the State Office Building site.

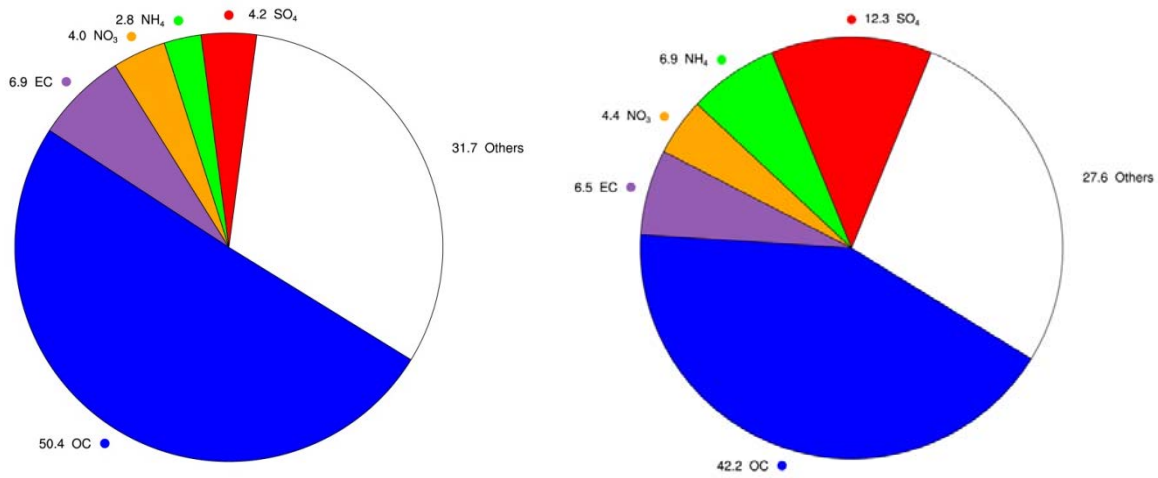


Fig. 4 Composition of simulated 24h-average total $PM_{2.5}$ as obtained by the CMAQ with modifications on average over the November episode (left), and as observed on average over the 3 days, for which data was available during that episode, at the State Office Building site. In the observations, the category "others" includes Al, Br, Ca, Na, Cl, Cu, Fe, Pb, Ni, K, Se, Si, S, Sn, Ti, V, Zn. In the simulations, the category "others" refers to unspecified anthropogenic mass (A25i+A25j), Na and Cl.

Comparing the simulated and observed composition of 24h-average $PM_{2.5}$ aerosol showed that the adapted CMAQ overestimated the percentage of organic carbon, but underestimated the percentage of sulfate and ammonium (Fig. 4).

Data of observed $PM_{2.5}$-composition data are available on a 1-in-3 day basis. The 24h-average $PM_{2.5}$-composition as simulated by the Alaska adapted CMAQ for the November episode were compared for each day that had observations (Fig. 5). On November 8 and 14 (with respect to Alaska Standard Time; AST), which have observed $PM_{2.5}$-composition data, there are small contributions from transport from outside the domain into the area [*Mölders and Leelasakultum*, 2012]. Note that typically advection from outside Alaska does not increase $PM_{2.5}$-concentrations by more than 2 $\mu g/m^3$ [e.g. *Cahill*, 2003; *Tran* et al., 2011; *Mölders* et al., 2012]. For details, see discussion later in this report. The simulations are not able to capture the peak on November 14 well.

Simulated sulfate and ammonium are underestimated on all three days (Fig. 5). Sodium and chloride are both underestimated. A possible reason for the underestimation of sodium (Na) and chloride (Cl) is that no sea-salt is emitted into the domain as there is no ocean and that some sodium and chlorine might be advected during the episode. However, this shortcoming has no big impact on the concentrations of total $PM_{2.5}$ as Na and Cl make up only a small amount of $PM_{2.5}$-composition (<1%). Simulated organic, nitrate and elemental carbon are almost in the same order of magnitude as observed.

We also conducted a process analysis. Process analysis is a technique that provides information about the impacts of individual processes on the change in a species' concentration. In the following, we refer to horizontal transport as the sum of horizontal advection and diffusion, and to vertical transport as the sum of vertical advection and diffusion. In our discussion, the term aerosol processes represents the net effects of aerosol thermodynamics, new particle formation, condensation of sulfuric acid and organic carbon on preexisting particles, and the coagulation within and between the Aitken and accumulation modes of particulate matter. Cloud processes represent the net effects of cloud attenuation of photolytic rates, aqueous-phase chemistry, below-and in-cloud mixing with chemical species, cloud scavenging and wet deposition [*Liu et al.*, 2010].

According to the process analysis, emissions were the dominant contributor to the $PM_{2.5}$ and SO_4 concentrations, and the horizontal transport contributed to and removed $PM_{2.5}$ and SO_4 at the grid-cell holding the State Office Building site (Fig. 6a-b). The aerosol processes played a small role here. This means $PM_{2.5}$ is mainly composed of primary PM and SO_4 at this site. $PM_{2.5}$ and SO_4 were mainly vented out through vertical transport. Dry deposition played a small role in the removal of $PM_{2.5}$ and cloud process did not play any role here. Note that cloud processes are irrelevant when there are not clouds as these processes then do not occur.

Different from the findings for sulfate, the aerosol processes played the main role for nitrate formation. At the grid-cell holding the State Office Building site, horizontal transport contributed strongly to nitrate. Note that the nitrate concentrations also show an offset like found for $PM_{2.5}$ (see discussion above). The major removal process was vertical transport, i.e. vertical mixing. Note that various studies performed with WRF for Alaska indicated that WRF has difficulties to simulate the strength of inversions with temperature gradients greater than 8K/100m and that WRF tends to overestimate vertical mixing [e.g. *Mölders et al.*, 2011, 2012, *Tran*, 2012]. An overestimation of the vertical transport of pollutants may lead to diluted concentrations and underestimation of the concentrations as particles are too quickly removed from the breathing level. The process analysis also revealed that dry deposition caused a small loss to nitrate. Cloud processes neither produced nor removed nitrate in this grid-cell (Fig. 6c).

For ammonium, the aerosol processes are the dominant contributor at the grid-cell of the State Office Building site. Horizontal transport contributed to ammonium on some days. The major removal process was vertical transport, and dry deposition caused only a small loss to ammonium. Cloud processes did not play a role here similar to what was found for both sulfate and nitrate (Fig. 6d).

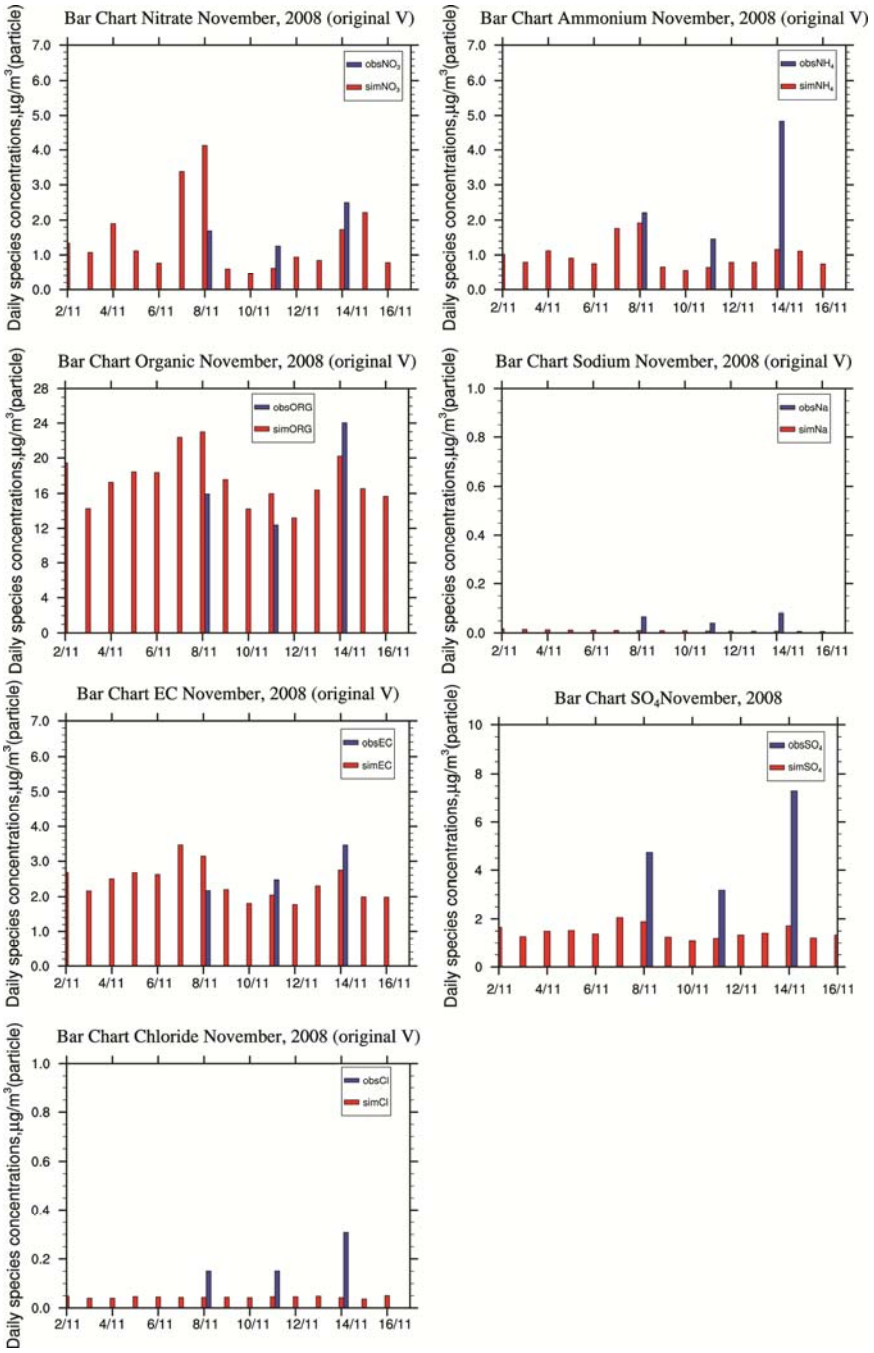


Fig. 5 Bar charts of simulated (red) and observed (blue) 24h-average $PM_{2.5}$-composition for NO_3, NH_4, EC, OC, Na, Cl, SO_4 as obtained for the November episode at the State Office Building site.

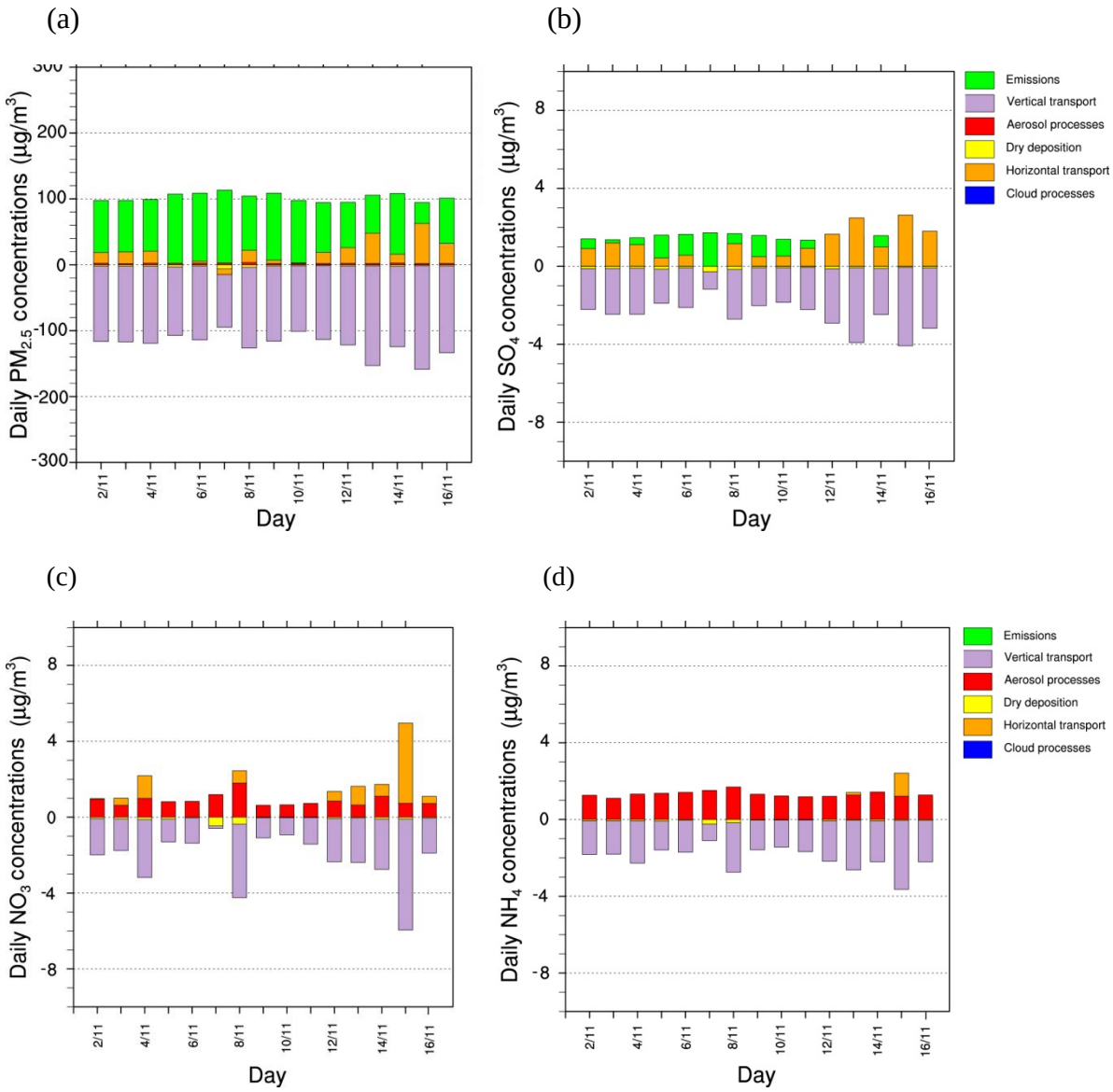


Fig. 6 Daily mean hourly contributions of individual processes to the (a) $PM_{2.5}$-concentrations, (b) SO_4-concentrations, (c) NO_3-concentrations and (d) NH_4-concentrations as obtained from the process analysis at the State Office Building site for the November episode. Simulations were performed using the revised WRF and SMOKE input.

2.2 Configuration of CMAQ for the January/February 2008 Episode (January v2)

The January episode covers January 23 to February 9, 2008. The temporal evolutions of 24h-average simulated $PM_{2.5}$-concentrations show that the model mostly overestimates the 24h-average $PM_{2.5}$-concentrations at the State Office Building site; the model fails to capture the peak on February 8 (Fig. 7). The model predicts a non-existing temporal minimum on February 2 (Fig. 7). The CMAQ model seems to be ahead in predicting 24h-average $PM_{2.5}$-concentrations by about 24 hours.

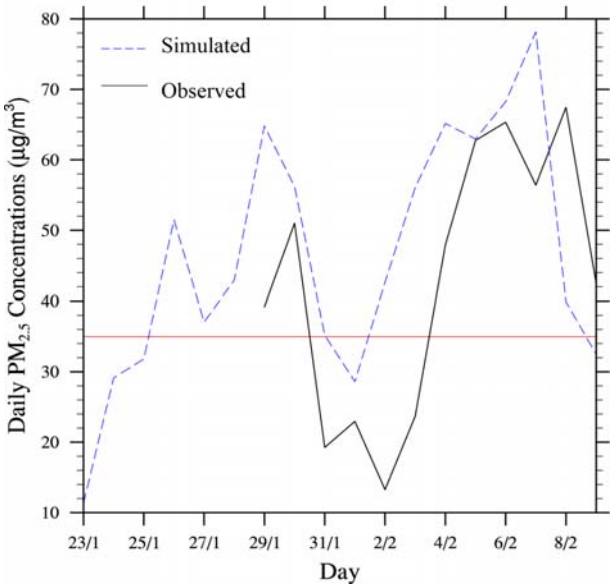


Fig. 7 Timeseries of simulated (blue dashed line) and observed (black solid line) 24h-average $PM_{2.5}$-concentrations at the State Office Building site as obtained from the adapted CMAQ simulation that used the revised WRF and SMOKE input for the January episode.

The 24h-average $PM_{2.5}$-concentrations obtained from the adapted CMAQ simulations correlate with the observations with a correlation coefficient of 0.52. Figure 7 shows the scatter of the simulated and observed values. To examine the reasons for the relatively low correlation we examined the timeseries. The temporal evolutions of simulated and observed hourly and 24h-average $PM_{2.5}$-concentrations suggested an offset. To quantify the offset we calculated the correlation with various time lags. We found that allowing for a time lag for one day increases the correlation coefficient from 0.52 to 0.84 [*Mölders and Leelasakultum*, 2012]. Allowing a 24h-time lag can increase the correlation coefficients of the hourly average $PM_{2.5}$-concentrations at the State Office Building site from 0.23 to 0.50, and the correlation increases even more to 0.59 when we allow a time lag of 26 hours. This means that some of the low correlation is caused by a temporal offset between simulated and observed 24h-average $PM_{2.5}$-concentrations.

It also means that if this shift in timing would not exist, the adapted CMAQ would perform better.

According to the observations, there are four days in the January episode that have $PM_{2.5}$-concentrations below the NAAQS, and there are eight days with $PM_{2.5}$-concentrations above this standard. On most of the days of the January episode, the simulated and the observed 24h-average $PM_{2.5}$-concentrations agree well; there are two days with false alarm, one day of a missed event, and two pairs of data outside the factor of two agreement (Fig. 8).

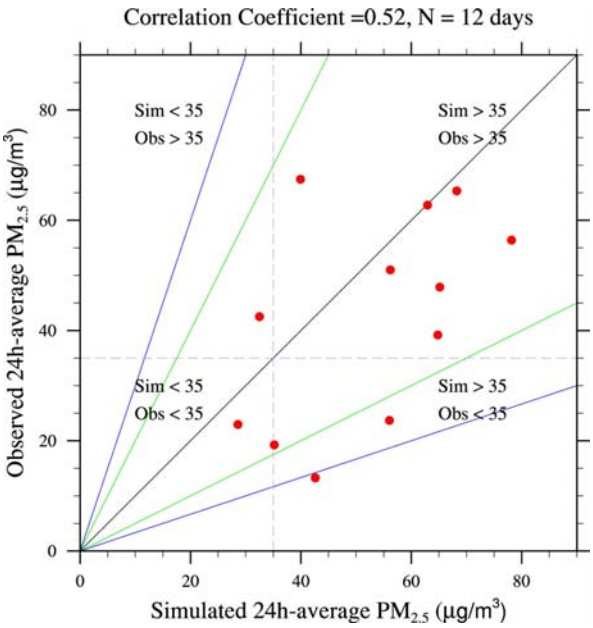
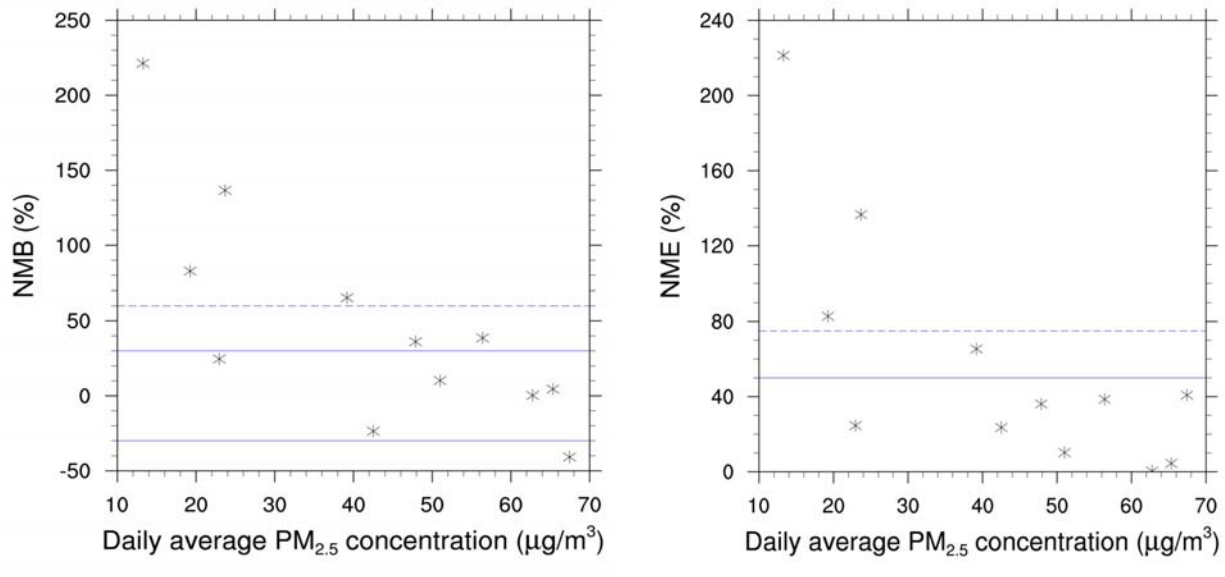


Fig.8 Scatter plots of 24h-average $PM_{2.5}$-concentrations as obtained from the adapted CMAQ simulation that used the revised WRF and SMOKE input during the January episode at the State Office Building site. The green line indicates the factor of two and the blue line indicates the factor of three agreement.

(a) (b)



(c)

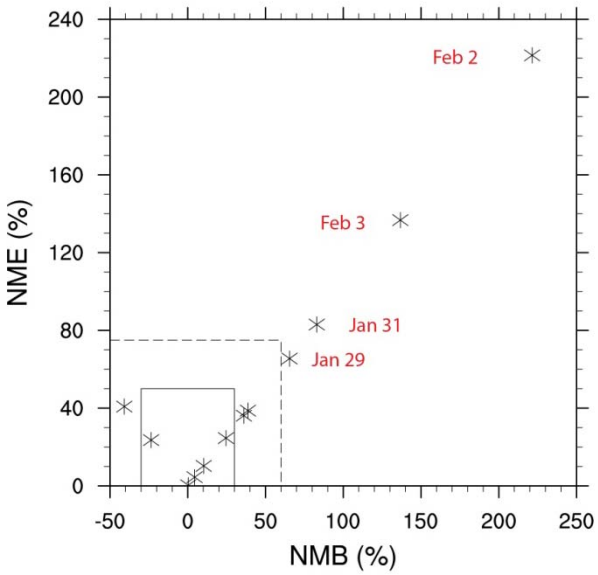


Fig. 9 Bugle plots of (a) normalized mean biases (NMB), and (b) normalized mean errors (NME) and soccer plot of normalized mean errors and biases of 24h-average $PM_{2.5}$-concentrations at the State Office Building site as obtained from the adapted CMAQ simulations that used the revised WRF and SMOKE input for the January episode.

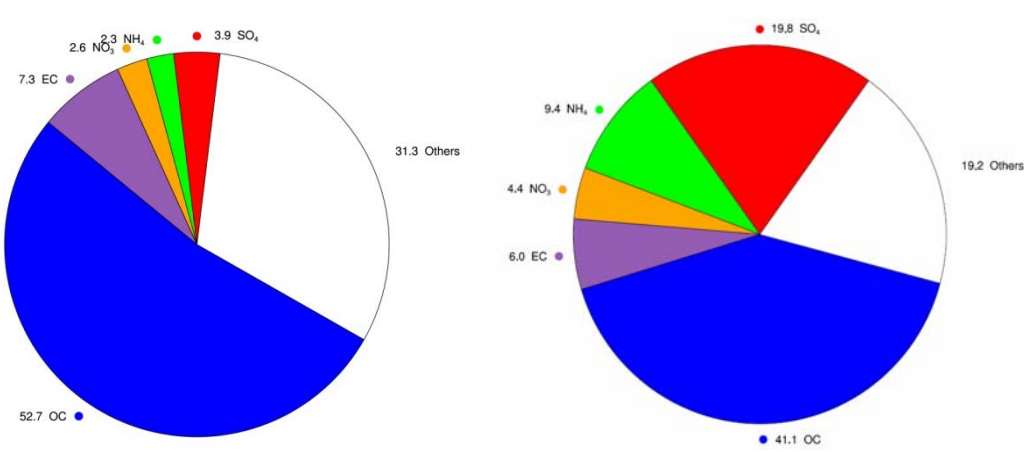


Fig. 10 Composition of simulated 24h-average total $PM_{2.5}$ as obtained by CMAQ with the modifications on average over the January episode (left), and as observed on average over the six days, for which data was available at the State Office Building site. In the observations, the category "others" includes Al, Br, Ca, Na, Cl, Cu, Fe, Pb, Ni, K, Se, Si, S, Sn, Ti, V, Zn. In the simulations, the category "others" refers to unspecified anthropogenic mass (A25i+A25j), Na and Cl.

The bugle plots and soccer plots show that on four days the adapted CMAQ simulation provides results outside the performance criteria (Fig. 3, a-c). Three of these four days are days, on which the 24h-average $PM_{2.5}$-concentrations are below the NAAQS. Therefore, we conclude that the adapted CMAQ model has difficulties to capture extremely low $PM_{2.5}$-concentrations well. Note that it is harder to predict very low than high concentrations correctly. Thus, this behavior is typical in air-quality modeling [e.g. *Boylan and Russell*, 2006].

Comparison of the simulated and observed composition of 24h-average $PM_{2.5}$ aerosol showed that the adapted CMAQ overestimated the percentage of organic carbon, but underestimated the percentage of sulfate, ammonium, nitrate and elemental carbon at the State Office Building site for the January episode (Fig. 10).

The 24h-average $PM_{2.5}$-composition as simulated by the Alaska adapted CMAQ for the January episode was compared for each day that had observed data (Fig. 11). During February 5-10, there was higher sulfur content, and on February 6 and 9 (AST), there were small contributions from long-range transport [*Mölders and Leelasakultum*, 2012]. Simulated sulfate (SO_4) and Ammonium (NH_4) are underestimated on all six days (Fig. 11). Sodium and chloride are both underestimated (see earlier discussion for reasons). Simulated organic, nitrate (NO_3) and elemental carbon (EC) concentrations are almost of the same order of magnitude as the observations and well follow the temporal evolution of the observations.

Similar to the findings of the November episode, in the January episode, emissions were the dominant contributor to the $PM_{2.5}$- and SO_4-concentrations at the grid-cell holding the State

Office Building (Fig. 12a-b). Horizontal transport contributed to and removed $PM_{2.5}$ and SO_4 at this site. The aerosol processes played a small role here. This fact indicates that $PM_{2.5}$ is composed mainly of primary PM and SO_4 at this site. $PM_{2.5}$ and SO_4 were mainly vented out through vertical transport. Dry deposition played a small role in the removal of $PM_{2.5}$ and cloud process did not play any role here. Note that if there are no clouds cloud processes cannot contribute to/affect the concentrations.

Like for the November episode, the findings obtained for nitrate differed from those for sulfate. The aerosol processes played the main role for nitrate formation. High contributions of nitrate also came from horizontal transport, i.e. neighbored grid-cells, but could not capture the conditions on February 9. The major removal process was vertical transport, and dry deposition caused a small loss to nitrate. Cloud processes neither produced nor removed nitrate in this grid-cell (Fig. 12c).

For ammonium, the aerosol processes are the dominant contributor at this site. Horizontal transport form neighbored grid-cells contributed to the ammonium concentrations on some days. The major removal process was vertical transport, and dry deposition caused only a small loss to ammonium. Cloud processes did not play a role here similar to what was found for both sulfate and nitrate (Fig. 12d).

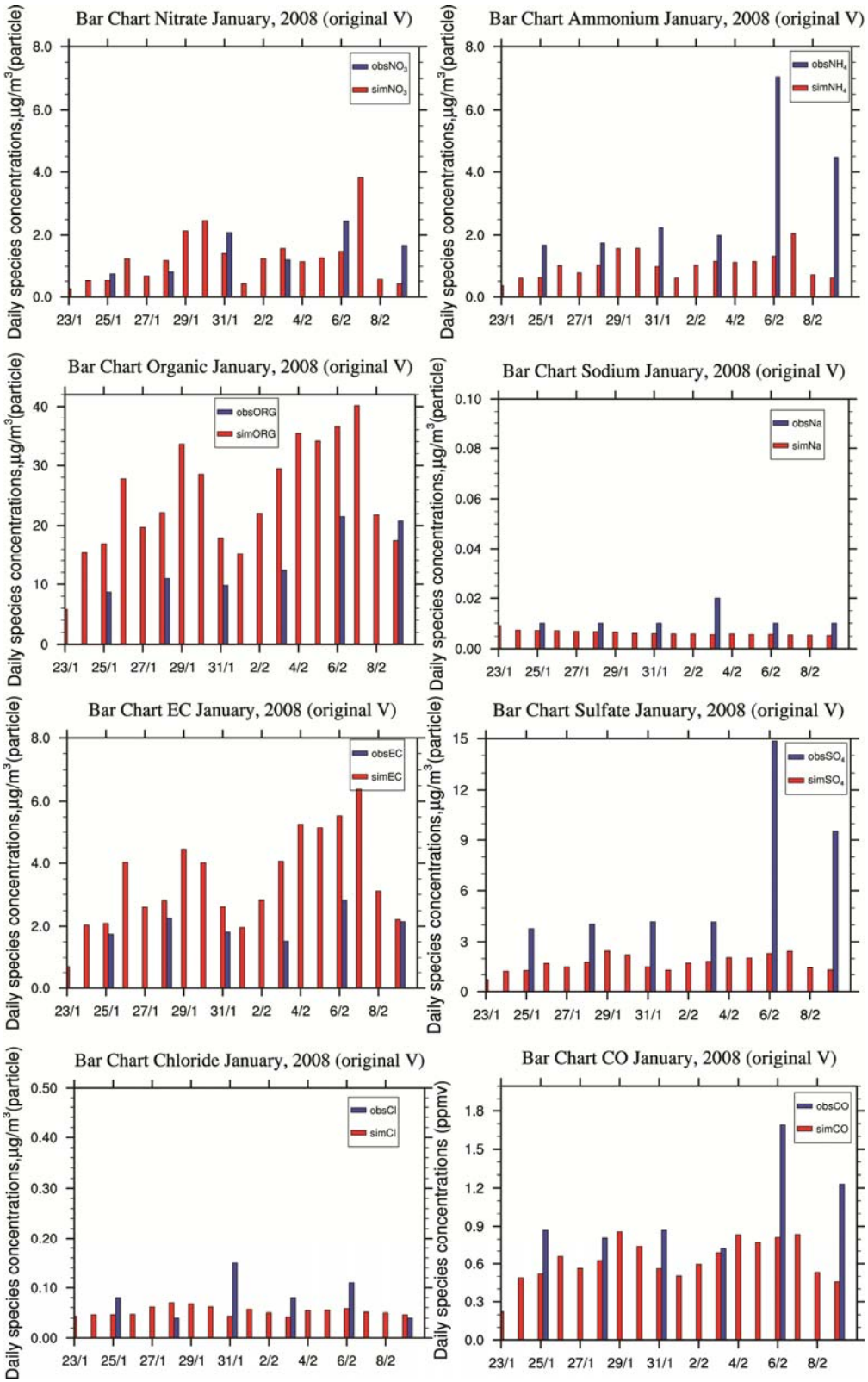


Fig. 11 Bar charts of simulated (red) and observed (blue) 24h-average $PM_{2.5}$-composition for NO_3, NH_4, EC, OC, Na, Cl, SO_4 as obtained at the State Office Building for the January episode.

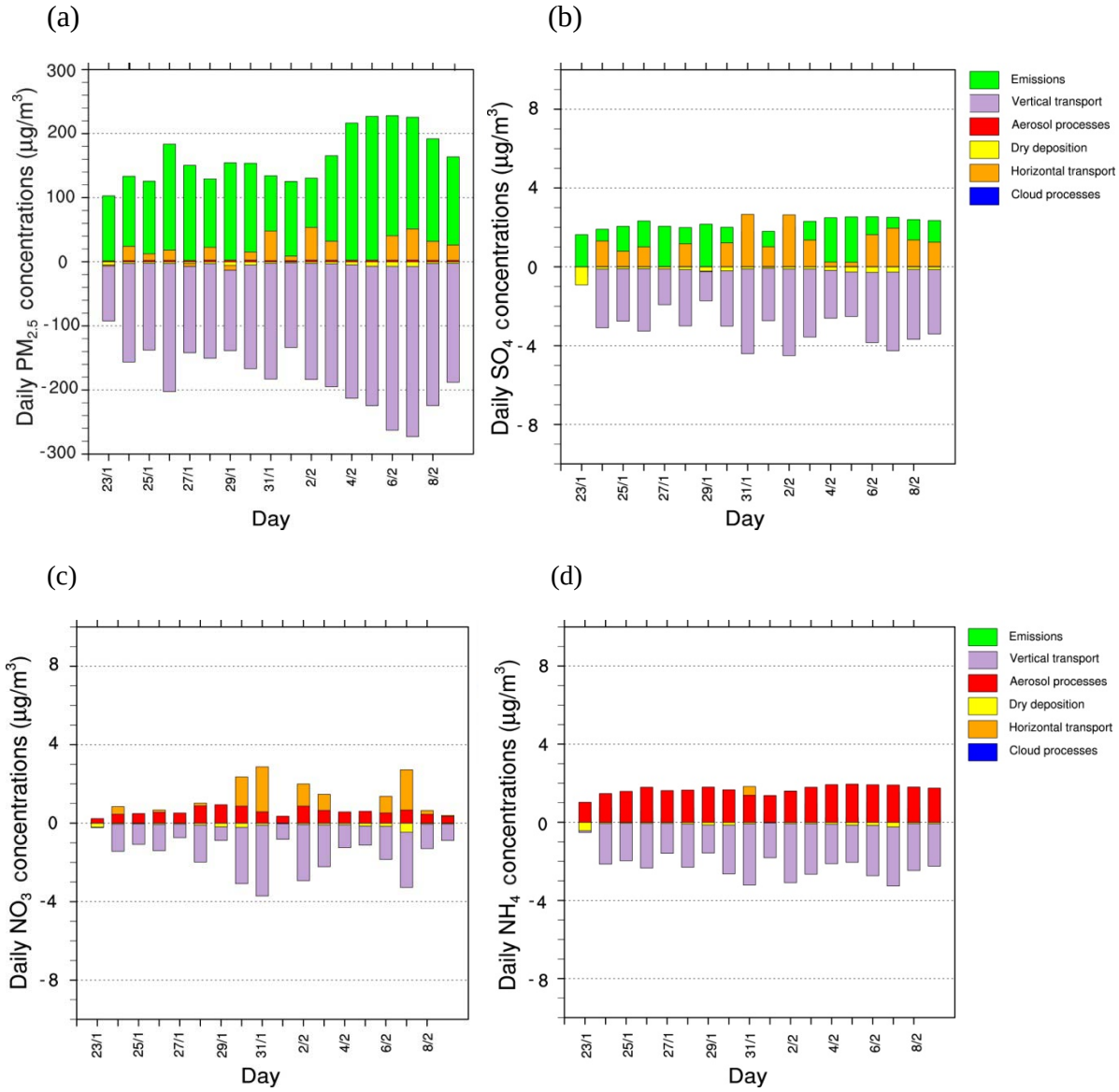


Fig. 12 Daily mean hourly contributions of individual processes to the (a) $PM_{2.5}$-concentrations, (b) SO_4-concentrations, (c) NO_3-concentrations, and (d) NH_4-concentrations as obtained at the State Office Building site from the adapted CMAQ simulation that used the revised WRF and SMOKE input for the January episode.

2.3 Documentation of Changes in CMAQ and Performance Improvements Made during Phase II

The simulations of the Alaska adapted CMAQ model underestimated sulfate (SO_4). Sulfate is the second major component in the composition of $PM_{2.5}$ in the Fairbanks nonattainment area. The simulations of the Alaska adapted CMAQ model also showed a time lag of ~24 hours in comparison with the observations at the State Office Building site for both the January and November episodes.

2.3.1 Improvements Implemented to Reduce the Sulfate-Underestimation

The performance of CMAQ in predicting fine particulate matter ($PM_{2.5}$) and its species has been evaluated in many studies [e.g. *Appel et al.*, 2008; *Eder and Yu*, 2006; *Mathur et al.*, 2008]. Obviously, according to these studies, CMAQ's performance tends to be lower in winter than summer for $PM_{2.5}$ and most species. CMAQ is also likely to underpredict sulfate during winter [*Appel et al.*, 2008; *Eder and Yu*, 2006; *Mathur et al.*, 2008].

The statistical performance skills for sulfate are poorer for the Fairbanks domain than for other US states (Table 1). Slightly lower performance skills were also found for Alaska than the Lower 48 for WRF/Chem simulations [*Mölders et al.*, 2012]. Thus, based on the literature, we may conclude that air-quality models may generally have difficulty with relatively lower temperature conditions. Thus, the extremely low temperature during the winter in Fairbanks might be a reason of the sulfate underestimation. This conclusion is backed by the evaluation studies for the Lower 48 that report weaker performance for $PM_{2.5}$-prediction winter than summer episodes [e.g. *Appel et al.*, 2008]. Therefore, we made several changes to the code of CMAQv4.7.1 to improve the sulfate simulation.

We performed various studies to examine the reasons for and to reduce the underestimation of sulfate and $PM_{2.5}$. In the following, first, the changes are described and later their impact will be discussed.

1) Increase of the Default Values for Fe and Mn in AQ_PAEAMS.EXT

In aerosol and aqueous chemistry, iron and manganese can play important roles for sulfate formation. Therefore, we updated the background values of Fe (III) and Mn (II) from $0.010\mu g/m^3$ to $0.040\mu g/m^3$ and decreased Mn (II) from $0.005\mu g/m^3$ to $0.001\mu g/m^3$following the measurement made in Fairbanks during winter 2011-2012 by *Peltier* [2012].

2) Increase of Sulfate and SO_2-concentrations for the Initial and Background concentrations (IC/BC)

The concentrations of sulfate and SO_2 of the previous initial and background concentrations were suspected to be too low. We now use the concentrations from the Clean Air Status and Trends Network (CASTNet) at the Denali site of winter 2008/09 (October–February). Thus, at the near-surface level the new SO_2-concentration is now 3.50×10^{-4} ppm. This value is closer to the default values that are used in the Eastern US. Modifying the near-surface concentration lead to ~1.7 increased near-surface SO_4-concentrations as compared to the total SO_4-concentrations obtained with the old values. The vertical profiles of SO_2 and sulfate are still based on *Jaeschke et al.* [1999] as no other vertical profile data is available to our best knowledge.

3) Change the dry deposition code back to the CMAQ v.4.7.1 original code

The modifications introduced for the dry deposition of SO_2 in phase I (deposition onto tundra, which was switched off in the original CMAQ, revised vegetation parameters for Alaska, formulations for dry deposition onto snow; see *Mölders and Leelasakultum* [2012]) led to increased removal of sulfate as compared to the original CMAQ. Therefore, we changed the parameterization of the SO_2 dry deposition processes back to their original version as it was in CMAQv.4.7.1 except that we kept the dry deposition on tundra. Note that if we would change this back to the original code it would mean that no deposition would be considered over most of the domain. Note that tundra covers most of the domain. In the original version of CMAQ, the code run over all vegetation types except for tundra to save computational time. This procedure is justifiable and makes sense for regions without tundra vegetation. However, in regions where tundra occurs, it would mean that no deposition is calculated over these tundra areas.

We want to point out that the changes that we originally made in phase I, are valid from a scientific point of view. The dry deposition over snow is quite different than over snow-free surfaces and should be dealt with similar as described in *Zhang et al.* [2003], i.e. likea we introduced it into CMAQ during phase I. The change back to the original formulation was only made to come closer to the observations and because of the philosophy to stay with the original code when changes do not lead to improvement for Alaska.

4) Reduction of the liquid-water threshold for resolvable scale clouds

Mueller et al. [2006] found that CMAQ underestimated sulfate because of a problem in the diagnosis of cloud cover. They found that reducing the liquid-water threshold values by 50% can decrease the cloud bias and lead to better results for sulfate predictions. Therefore, we decreased these threshold values by 50% in “rescld.F” of CMAQ model. The response will be discussed later.

5) Improved parameterization for the sulfuric acid – water nucleation rates

In CMAQ, the parameterization of the homogeneous nucleation rate of sulfuric acid and water is based on *Kulmala et al.* [1998]. *Vehkamaki et al.* [2002] published an extension of the formulation by *Kulmala et al.* [1998] to lower temperatures and a wider relative humidity range. CMAQ model v4.7.1 had not yet been updated to include this extension. Its formulas hold for temperatures between -43^{o}C and 32^{o}C, relative humidity between 0.01% and 100%, nucleation rates between 10^{-7} and 10^{10}cm^{-3}s^{-1}, and sulfuric acid concentrations of 10^{4} to 10^{11}cm^{3}. We coded and implemented this extended parameterization for the calculation of the nucleation rates based on *Vehkamaki et al.* [2002] and presented the results in the secondary quaterly report phase II. Later on, we updated the calculation based on personal communication with *Vehkamak* [2012]. This updated calculation is basically similar to what we have done, but the numbers include more digits. Furthermore, there are more conditions considered [*Vehkamaki*, 2012; pers. comm.]. The fortran code can be found at

http://www.atm.helsinki.fi/~hvehkama/publica/vehkamaki_hi_t_binapara.f90.

2.3.2 Response to the Improvements Made to Reduce the Sulfate-Underestimation

The introduction of the above improvements led to an increase in the percentage sulfate concentrations of total $PM_{2.5}$ at the grid-cell of the State Office Building site. The percentage of sulfate increased from 4.2 to 5.3% and from 3.9 to 5.0% for the November and January episode, respectively (Fig. 13). The increase in the percentage of SO_4 affected the partitioning of other species. This means concurrently the percentage of NH_4 increased, while the percentage of NO_3 and organic compounds decreased. These shifts in percentage may be explained as follows. The enhancement of sulfur dioxide and sulfate affected the thermodynamic equilibrium of the aerosol system. The sulfate-related aerosol acidity may be further neutralized by NH_3 to form ammonium sulfate aerosol ($(NH_4)_2SO_4$) [*Lovejoy*, 1996; *Seinfeld*, 2006]. The rest of ammonia can also neutralize nitric acid (HNO_3), and forms ammonium nitrate aerosol (NH_4NO_3).

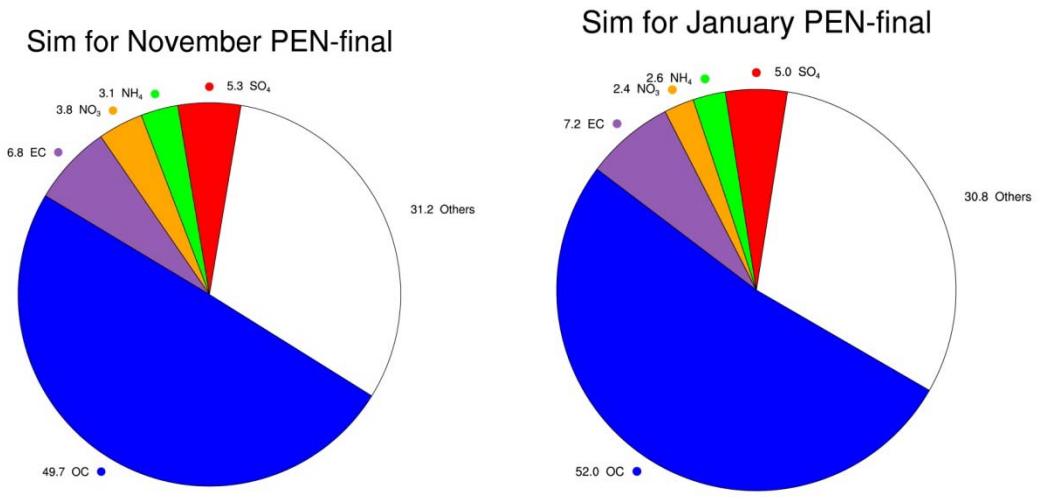


Fig. 13 Composition of simulated 24h-average total $PM_{2.5}$ as obtained by the CMAQ simulations with the final modifications and using the PennState provided meteorology (PEN-final) on average over the November episode (left), and the January episode (right) at the grid-cell of the State Office Building site. In the simulations, the category "others" refers to unspecified anthropogenic mass (A25i+A25j), Na and Cl. In the observations, the category "others" includes Al, Br, Ca, Na, Cl, Cu, Fe, Pb, Ni, K, Se, Si, S, Sn, Ti, V, Zn.

The comparison of the absolute differences between the simulations before and after the improvements shows increases in sulfate, and ammonium and decreases in nitrate on every simulated day for both episodes (Figs. 14, 15). On average, the absolute increase of sulfate is 0.4 $\mu g/m^3$ or 28-29% for both episodes. The improvements did not bring a change in the organic concentrations (Figs. 14, 15); the decreased percentage of organic compounds is due to the increase of the percentage of SO_4 and NH_4. Note that the final modifications did not change the

temporal evolutions of sulfate and $PM_{2.5}$-concentrations, and the final version of Alaska adapted CMAQ still underpredicts sulfate aerosol.

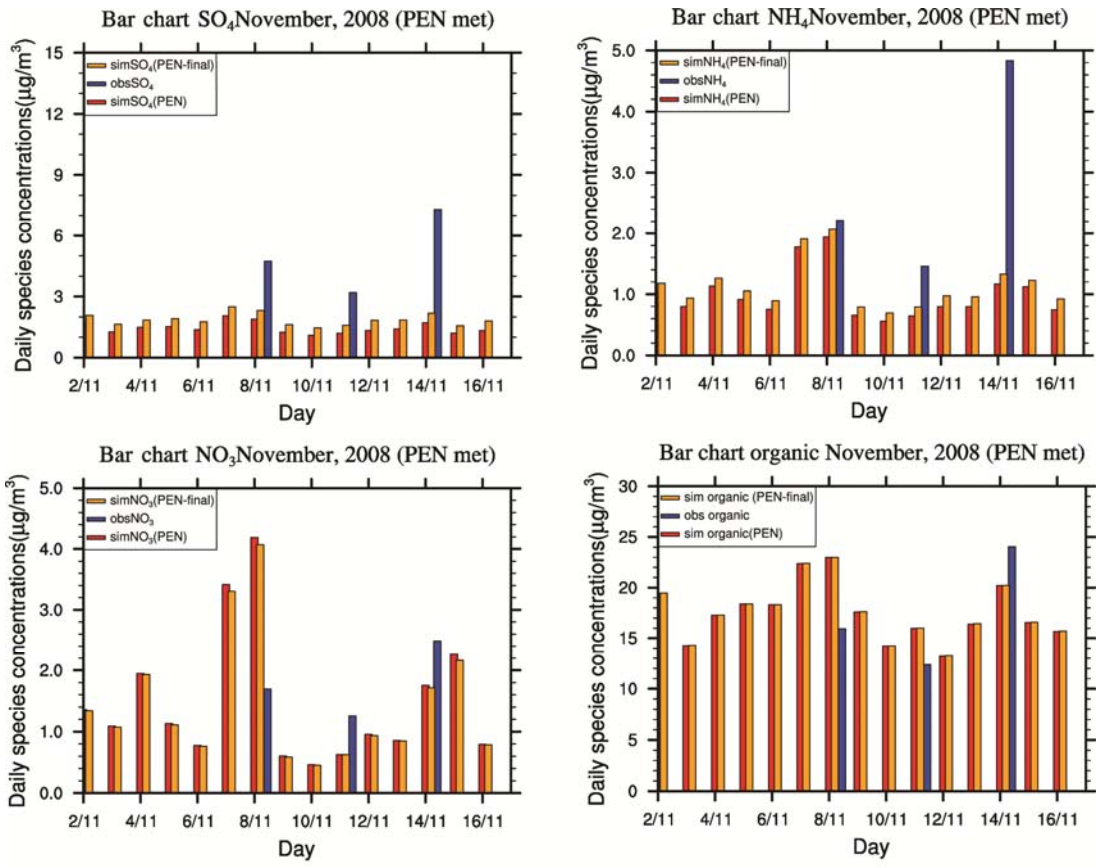


Fig. 14 Bar charts of simulated species as obtained from the previous CMAQ modification described in the final report of phase I (red), and as obtained from the final CMAQ modification described above (orange) and observed species (blue) of the 24h-average $PM_{2.5}$-composition for SO_4, NH_4, NO_3, and organic carbon for the November episode.

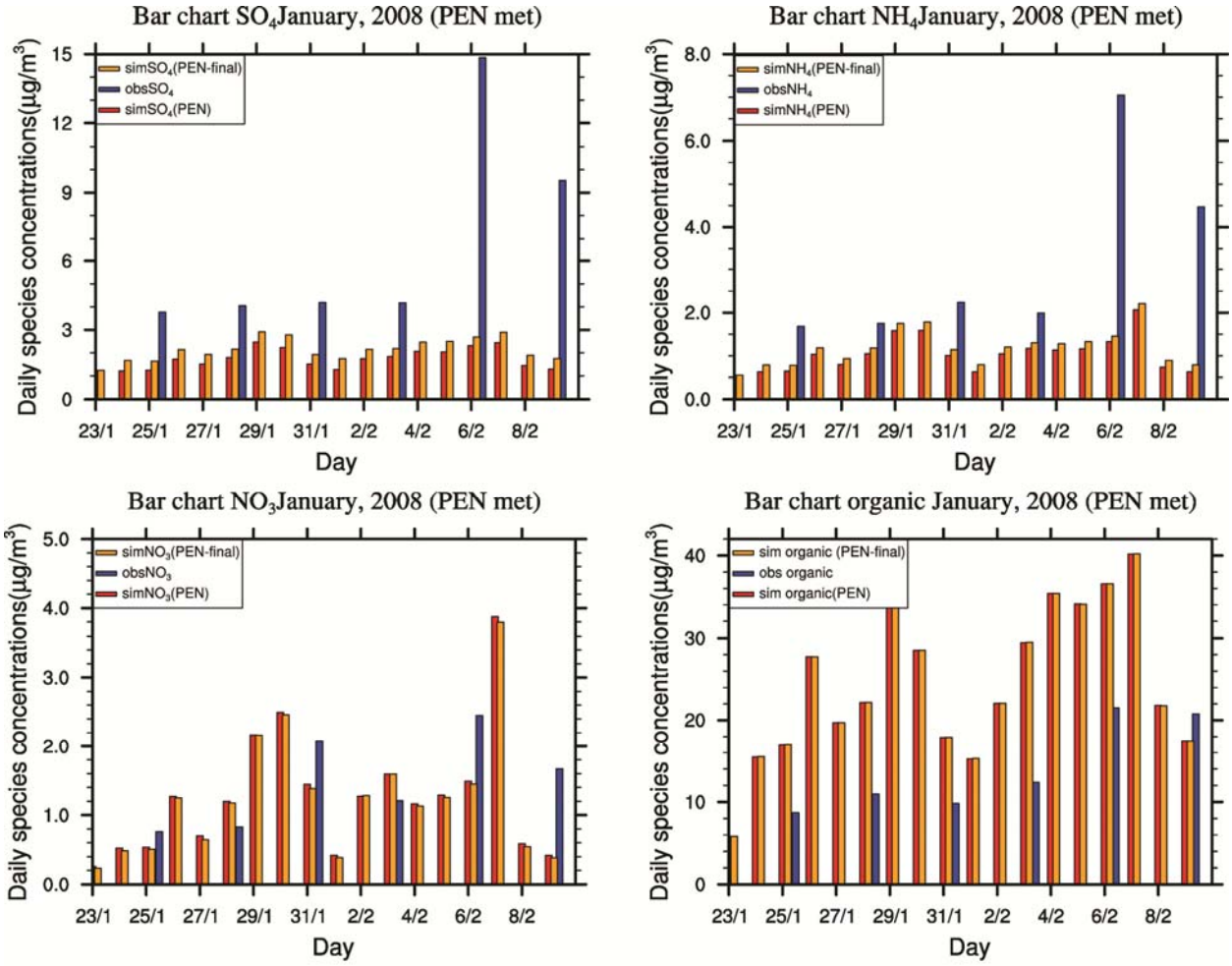


Fig. 15 Bar charts of simulated species as obtained from the previous CMAQ modification described in the final report of phase I (red), and as obtained from the final CMAQ modification described above (orange) and observed species (blue) of the 24h-average $PM_{2.5}$-composition for SO_4, NH_4, NO_3, and organic carbon for the January episode.

The process analysis of sulfate concentrations at the grid-cell of the State Office Building site shows that the final modifications caused changes in the horizontal and vertical transport (Fig. 16). This means that the modifications led to changes in neighbored grid-cells. These changes then led to advection of slightly modified (composition wise) air. On average in the November episode, the final CMAQ modification increased the contribution of sulfate from horizontal transport, cloud and aerosol processes by 0.39, 8.4×10^{-7} and 4.8×10^{-4}µg/m^3, respectively. The contributions to sulfate from removal by dry deposition and vertical transport decreased by -0.02 and 0.28µg/m^3. There was no change in the emissions as we used the same emission inventory.

On average over the January episode, the final CMAQ modification led to increased contributions of sulfate from horizontal transport, cloud and aerosol processes by 0.30, 1.1×10^{-6} and 5.6×10^{-4} µg/m^3, respectively. In the runs with the modifications, the removal of sulfate by

dry deposition and by vertical transport decreased by -0.02 and 0.37μg/m^3, respectively, as compared to the run without the modifications.

Table 1. Performance statistics for sulfate species simulated by the CMAQ model that did not employ the revised WRF and SMOKE input (January v1 episode), the CMAQ model with the previous modification (January v2 episode, PEN-WRF) described in the final report of phase I, and with the CMAQ model version with the final modification (PEN-WRFfinal) for the January and November episode on the days. Statistics are based on the observed sulfate data was available at the Fairbanks State Office Building site. The statistics of the annual simulations of sulfate in other states in US as reported by *Eder and Yu* [2006] are included for comparison. Here "No." stands for the number of days with observations. Furthermore, r, MB, RMSE, NMB and NME are the correlation skill score, mean bias, root-mean-square error, normalized mean bias, and normalized mean error.

Sulfate	**No.**	**Mean model**	**Mean observed**	**r**	**MB**	**RMSE**	**NMB (%)**	**NME (%)**
	January v1 episode							
PEN-WRF	6	1.3	6.8	0.36	-5.4	6.8	-80.3	80.3
	January v2 episode							
PEN-WRF	6	1.7	6.8	0.56	-5.1	6.4	-75.4	75.4
PEN-WRFfinal	6	2.1	6.8	0.61	-4.7	6.1	-69.6	69.6
	November episode							
PEN-WRF	3	1.6	5.1	0.61	-3.5	3.8	-68.5	68.5
PEN-WRFfinal	3	2.0	5.1	0.66	-3.1	3.4	-60.0	60.0
Eder and Yu, 2006	6970	3.33	3.40	0. 77	-0.77	2.25	-2.0	42.0

The statistical performance of the Alaska adapted CMAQ version that did not employ the revised WRF and SMOKE input (January v1), the CMAQ with the modifications that employs the revised WRF and SMOKE (January v2), and from the final CMAQ modification in simulating sulfate are compared in Table 1. Introducing the changes in the parameterizations increased the mean sulfate concentrations on the days, which had observed sulfate concentrations at the State Office Building site, in the range of 1.7 to 2.1μg/m^3 and 1.6 to 2.2μg/m^3 for the January and November episode, respectively. The mean biases (MB) were -4.7 and -3.1 μg/m^3 for the latest changes in the parameterization for the January and November episode, respectively. The

normalized mean bias (NMB) and normalized mean error (NME) from all simulations are high (exceed 50%) in comparison with the annual NMBs in the study by *Eder and Yu* [2006]. The examination the NMB and NME for the two episodes reveals better performance in simulating sulfate with the latest modifications. Our analysis of the performance also revealed that the correlation coefficients between the observed and simulated sulfate data increase as the concentrations of sulfate increase (Table 1).

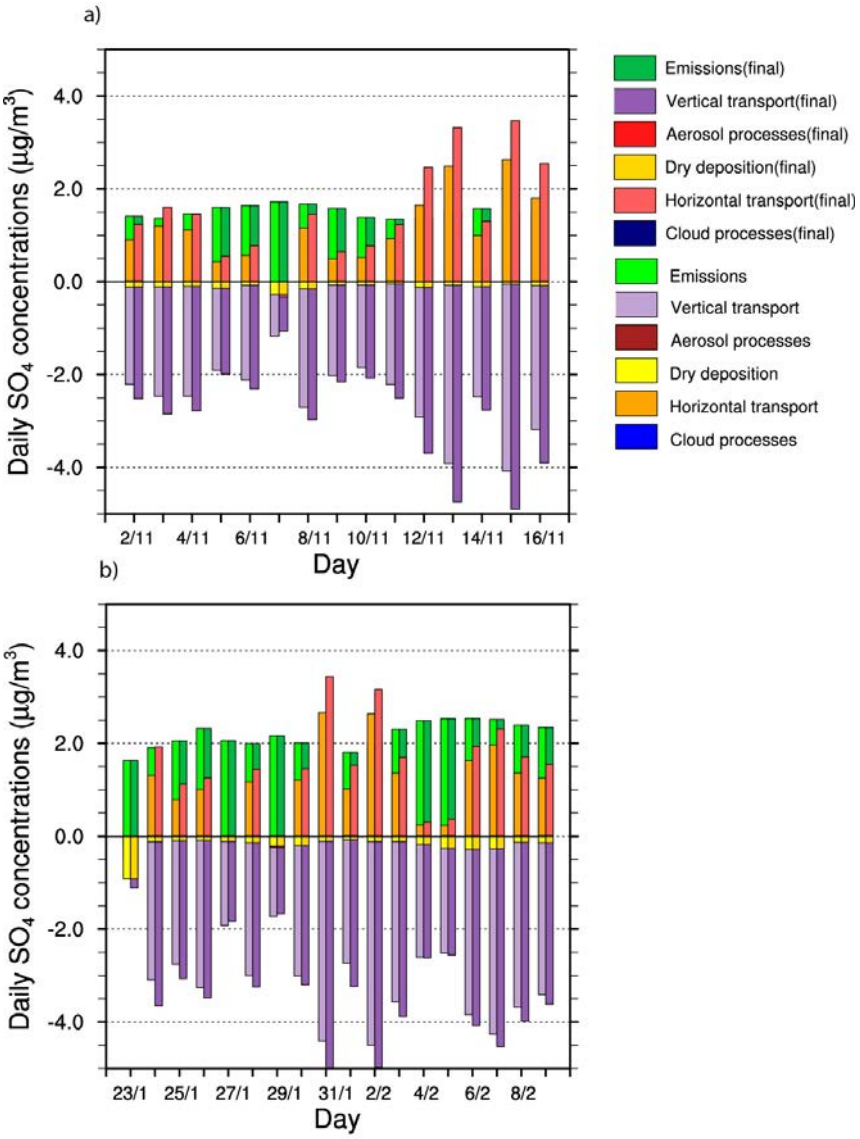


Fig. 16 Comparison of the daily contributions of individual processes to the SO_4-concentrations as obtained by CMAQ with the previous modifications and with CMAQ with the modifications described in this report at the grid-cell of the State Office Building site for the (a) November and (b) January episode.

Table 2. Performance statistics for the 24h-average $PM_{2.5}$-concentrations as obtained from the Alaska adapted CMAQ with the previous modifications and the CMAQ with the final modifications at the grid-cell of the State Office Building site for the January v1, January v2 and November episodes. The small differences as compared to the 1st quarterly report of phase II are due to the use of the SMVGEAR solver instead of the EBI solver that is needed for the process analysis.

24h-average $PM_{2.5}$-concentrations	**January v1**	**January v2**	**November**	**Final modifications**	
				January	**November**
Number of pairs used in the calculation of the statistics	12	12	15	12	15
Mean simulated($\mu g/m^3$)	35.0	52.6	34.9	53.1	35.5
Mean observed ($\mu g/m^3$)	42.6	42.6	29.3	42.6	29.3
Mean bias ($\mu g/m^3$)	-3.0	6.6	5.6	7.0	6.2
Mean fractional bias (%)	-1	17	26	18	31
Mean error ($\mu g/m^3$)	9.2	10.8	12.1	11.0	15.7
Mean fractional error (%)	24	26	42	27	54
Average difference (sim-obs)	-4.5	9.9	5.6	10.5	6.2
Simulated min| max ($\mu g/m^3$)	26.6 | 49.7	28.6 | 78.2	26.8 | 49.0	29.3 | 78.8	27.3 |49.4
Observed min|max ($\mu g/m^3$)	13.3 | 67.4	13.3 | 67.4	8.2 | 51.6	13.3 | 67.4	8.2 | 51.6
Number of simulated exceedance days	7	10	7	10	7
Number of observed exceedance days	8	8	6	8	6
STDEV of simulation ($\mu g/m^3$)	7.3	16.2	6.8	16.2	6.7
STDEV of observation ($\mu g/m^3$)	19.0	19.0	13.7	19.0	13.7
Variance of simulation$(\mu g/m^3)^2$	52.8	262.2	46.0	262.0	45.5
Variance of observation$(\mu g/m^3)^2$	362.8	362.8	188.3	362.8	188.3
Correlation coefficient	0.38	0.52	0.31	0.52	0.31

The Alaska adapted CMAQ with the final modifications given in this report is still not able to simulate sulfate concentrations as high as the observations suggest. As the process analysis indicated that the emission process is the main source of sulfate at the grid-cell of the State

Office Building site, we performed simulations with the same CMAQ configuration, but used an earlier version of the emission inventory. The comparison showed that the model showed better performance in simulating sulfate at the State Office Building site with the earlier version of the emission inventory. Therefore, we compared the emission inventories to examine what changes in the emissions led to these differences in model performance. Our investigations showed that in the latest version of the emission inventory there was a decrease of sulfate from 7% to 2-3% in the partitioning of the $PM_{2.5}$-emissions in comparison with the earlier version of the emission inventory (see also discussion in *Mölders and Leelasakultum* [2012]). Therefore, the decrease of sulfate in the partitioning of the $PM_{2.5}$-emissions is probably the main cause of underestimation of sulfate concentrations. The main differences we see in these WRF-CMAQ runs that only differ by the emission inventory used, show us the sensitivity of the model to the emissions and their partitioning. However, the latest version of the emission inventory reflects the latest inventory accuracy with new woodstove changeout, census and mobile numbers. Therefore, the latest emission inventory has to be considered superior over the earlier versions from a from a research standpoint.

Finally, we compared the performance statistics of the 24h-average $PM_{2.5}$-concentrations from Alaska adapted CMAQ version that did not employ the revised WRF and SMOKE input, the CMAQ modification that employed the revised WRF and SMOKE, and the CMAQ with the final modifications (Table 2). The final modifications did not increase the correlation coefficient or change the temporal evolution. The results of soccer plot and bugle plot are similar as prior to introducing the latest changes. As the differences are not statistically relevant, they are not shown here.

2.3.3 Investigation of the Causes for the Temporal Offset

As discussed above, the time-lag effect caused the model to fail to capture the temporal evolution of $PM_{2.5}$-concentrations well. Consequently, the correlation coefficients between the simulated and observed $PM_{2.5}$-concentrations for both episodes are lower than they should be. We run a hierarchy of simulations to test the causes for the temporal offset found at the grid-cell of the State Office Building site.

In the earlier simulations, the time-steps for the operator splitting were set as follows: maximum sync time-step = 12 min, minimum sync time-step=1.5 minute, and up to sigma = 0.9. We hypothesized that the CMAQ model might be too slow in updating the chemistry, which consequently could lead to the temporal offset at the grid-cell of the State Office Building site. Therefore, we reduced the time step for the operator splitting to be as follows: maximum sync time-step = 6 min, minimum sync time-step=1minute, and up to sigma =0.7. The temporal evolution of $PM_{2.5}$-concentrations for the longer time-step (PEN-WRF) and the shorter time-step (PEN-WRFfinal) were compared. The comparison showed no difference in the temporal evolutions for both the January and November episode (Figs. 17, 18). The differences in concentrations might be due to the improvement of parameterizations in the PEN-final version.

Additionally, we also run the simulations by using the emission of the next day (PEN-Eshift), i.e. we shifted the emissions by one day. The temporal evolutions of simulated $PM_{2.5}$-concentrations showed only marginal differences from those simulations that used the emissions in sync with the meteorological data (Fig. 17).

Another reason for the temporal offset between simulated and observed $PM_{2.5}$-concentrations was hypothesized to be an offset in the simulated meteorology. Therefore, we ran WRF for the two episodes in a different configuration than the PennSate WRF. In the following, we refer to these simulations as "UAF-WRF". Our WRF-simulations differ in the model configuration from the WRF-simulations performed and provided by PennState. Note that the simulations provided by PennState are called "PEN-WRF", hereafter. The new WRF simulations served to examine whether an offset in meteorology is the cause for the time lag in the $PM_{2.5}$-concentrations.

The domains for the simulations with the UAF-WRF are based on the domains used in the PEN-WRF for easy comparison. Our model configuration like theirs used three one-way nested horizontal grids with horizontal grid spacing of 12km, 4km and 1.3km, respectively. Domain 3 that has a 1.3km grid increment was used to provide the meteorological input data to simulate the chemical transport and transformation of species with the CMAQ model. For the UAF-WRF simulations, the initial meteorological conditions were downscaled from the $1^o \times 1^o$, 6h-resolution National Centers for Environmental Prediction global final analyses. The simulations were performed in forecast mode (turning off nudging) for January 23, 2008 0000UTC to February 12, 2008 0000UTC and November 02, 2008 0000UTC to November 18, 2008 0000UTC. The selection of options in the first simulations of the UAF-WRF (UAF-WRFv1) bases on long-year experience of the PI and her research group with meteorological simulations for Alaska [e.g. *Mölders and Olson*, 2004; *Mölders and Walsh*, 2004; *Mölders and Kramm*, 2007; 2010; *Chigullapalli and Mölders*, 2008; *Yarker et al.*, 2010; *Mölders et al.*, 2011; 2012]. The selection of options in the second set of simulations with the UAF-WRF (UAF-WRFv2) for domain 3 is the same as those in the PEN-WRF except that we turned off the OBS nudging. The meteorological fields were initialized every day. The model configurations for both the PEN-WRF and UAF-WRFv1 and UAF-WRFv2 are compared in Table 3.

Nudging to observations (OBS nudging) is a technique that adds artificial forcing functions to a model's prognostic equations to nudge the solutions toward the observations. Those individual observations are spread in space and time. In domain 3, there is a limited number of radiosonde sounding sites [*Mölders et al.*, 2011]. Thus, OBS nudging might cause a temporal offset, as obviously the WRF model was unable to capture the temperature inversion at the right time and place. Therefore, we turned off the OBS nudging for a sensitivity study for both UAF-WRFv1 and UAF-WRFv2. Note that in Fairbanks, many inversions are locally forced when the right synoptic conditions exist [*Mayfield*, 2012].

The comparison of the temporal evolutions of the $PM_{2.5}$-concentrations as obtained by CMAQ with the UAF-WRFv1 and UAF-WRFv2 with those obtained with the PEN-WRF indicates that

the meteorological input data led to changes in the temporal evolutions of $PM_{2.5}$-concentrations. However, none of the obtained changes in $PM_{2.5}$-concentrations led a perfect fit with the observed $PM_{2.5}$-concentrations (Figs.17, 18). The UAF-WRFv1 simulations with the *Lin et al.*'s [1983] microphysics scheme seem to provide the highest $PM_{2.5}$-concentration peaks in the beginning of the November episode and the lowest dip in the $PM_{2.5}$-concentrations on November 11 as compared with the other simulations (Fig. 17). For the January episode, the simulation with the *Lin et al.* [1983] microphysics scheme showed the smallest temporal shift as compared to the PEN-WRF, but still showed the offset (Fig. 18). The simulations with the Morrison 2-moment [*Morrison et al.*, 2005] scheme tend to smooth the peak and dip. As a result, the simulations with the UAF-WRFv2 clearly brought the 24h-average $PM_{2.5}$-concentrations down.

Table 3. WRF-model configurations of the PennState University (PEN-WRF) and University of Alaska Fairbanks simulations for domain 3 version 1 (UAF-WRFv1) and version 2 (UAF-WRFv2). The main differences of model configurations are indicated in bold letters.

Model Configurations	PEN-WRF	UAF-WRFv1	**UAF-WRFv2**
Cumulus Parameterization	None	Grell G3	None
Microphysics	Morrison 2-moment	Lin et al.	Morrison 2-moment
Longwave radiation	RRTMG	RRTM	RRTMG
Shortwave radiation	RRTMG	Goddard	RRTMG
PBL scheme	Mellor-Yamada-Janjic (Eta)	Mellor-Yamada-Janjic (Eta)	Mellor-Yamada-Janjic (Eta)
Surface Layer scheme	Monin-Obukhov (Janjic Eta)	Monin-Obukhov (Janjic Eta)	Monin-Obukhov (Janjic Eta)
Land-surface scheme	RUC Land-Surface Model	RUC Land-Surface Model	RUC Land-Surface Model
Urban model	No urban physics	No urban physics	No urban physics
Land use classification	USGS	USGS	USGS
3D analysis nudging	OFF	OFF	OFF
SFC analysis nudging	OFF	OFF	OFF
OBS nudging	**ON**	**OFF**	**ON**

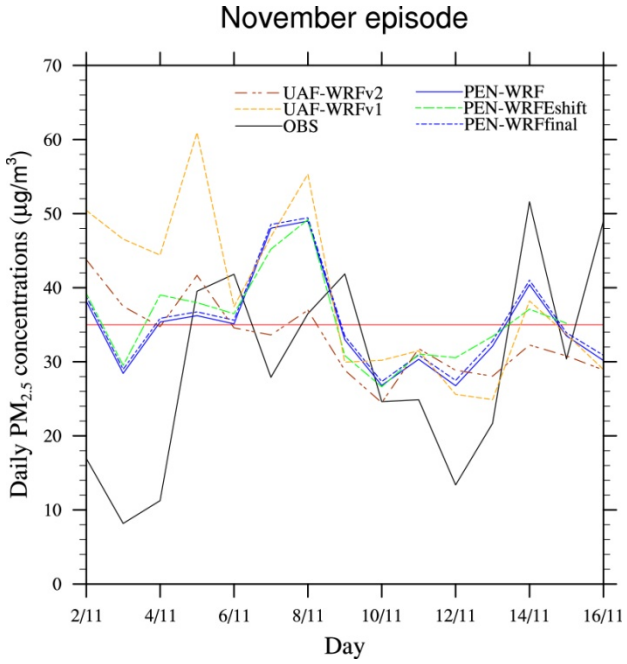


Fig. 17 Temporal evolutions of 24h-average $PM_{2.5}$-concentrations as simulated at the grid-cell of the State Office Building site by the Alaska adapted CMAQ that uses a longer time-step (PEN-WRF) and the shorter time-step (PEN-final), emission on the next day, with the UAF-WRF version 1 (UAF-WRFv1) and version 2 (UAF-WRFv2) and as observed (OBS) at the State Office Building for the November episode.

The correlation coefficients between the simulated $PM_{2.5}$-concentrations obtained with CMAQ using the PEN-WRF, PEN-WRFEshift, PEN-WRFfinal, UAF-WRFv1 and UAF-WRFv2 and the observations are 0.31, 0.26, 0.31, -0.01 and -0.12, respectively for the November episode. For the January episode, the correlation coefficients were all 0.52 no matter whether CMAQ used the PEN-WRF, PEN-WRFfinal and UAF-WRFv1 meteorology. It can be clearly seen that the PEN-WRF is providing the best correlation coefficient of simulated and observed $PM_{2.5}$-concentrations. However, the temporal offset of the model still exists even when we run the WRF with the OBS nudging turned off, but otherwise with the same options as used by PennState. Therefore, we recommend to do more tests and find a WRF-setup that better represents the temporal evolution of 24h-average $PM_{2.5}$-concentrations at the State Office Building site.

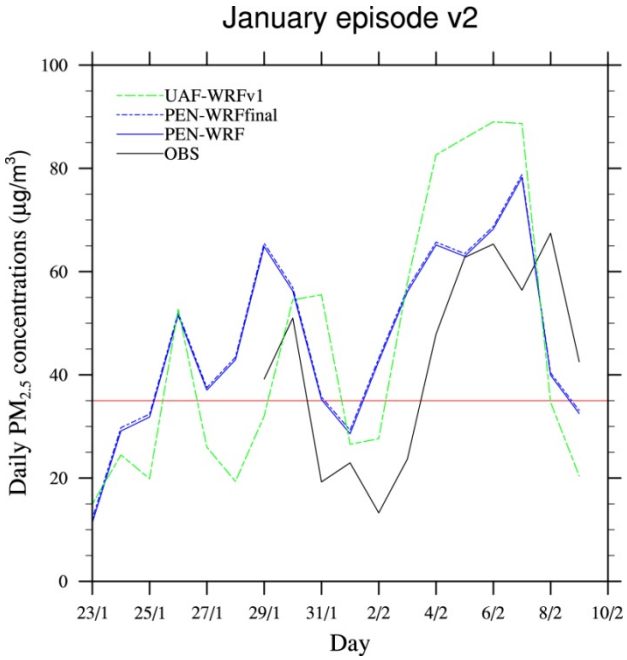


Fig. 18 Temporal evolutions of 24h-average $PM_{2.5}$-concentrations as simulated by the Alaska adapted CMAQ that uses a longer time-step (PEN), a shorter time-step (PEN-final), emission of the next day, with the UAF-WRF version 1 (UAF-WRFv1) and version 2 (UAF-WRFv2) and observed at the State Office Building site (OBS) for the January episode.

2.4 Investigation on the Boundary and Initial Conditions

To create the boundary conditions (BC) for domain 3, we would have had to run CMAQ on domain 2 at least. However, emission data for domain 1 and 2 were never created as various studies with WRF/Chem [*Tran et al.*, 2011; *Mölders et al.*, 2012] and observational analysis [*Cahill*, 2003] showed that the contribution by transport of $PM_{2.5}$ towards Alaska are more than an order of magnitude smaller than the concentration of the NAAQS. This means that there were no issues related to the BC. Consequently, the Alaska Department of Environmental Conservation did not request Sierra Research Inc. to create an emission inventory for Alaska and did not ask us to perform CMAQ simulations on domain 2. Note that typically, the chemical fields predicted on domain 2 at the boundaries of domain 3 would serve as the BC for domain 3. For these reasons, we could not investigate the impact of the BC on the concentrations in domain 3 directly. Nevertheless, we performed a work intensive series of tests to investigate the impact of the BC on the concentrations simulated in domain 3 indirectly. These tests as their results are discussed in the following.

In the final report of phase I [*Mölders and Leelasakultum*, 2012], we already reported on potential impacts of BC when comparing the results at the boundaries of the smaller 66×66 domain with concentrations at these places in simulations on a 199×199 domain. The interested reader is referred to this document for further reading on BC impacts.

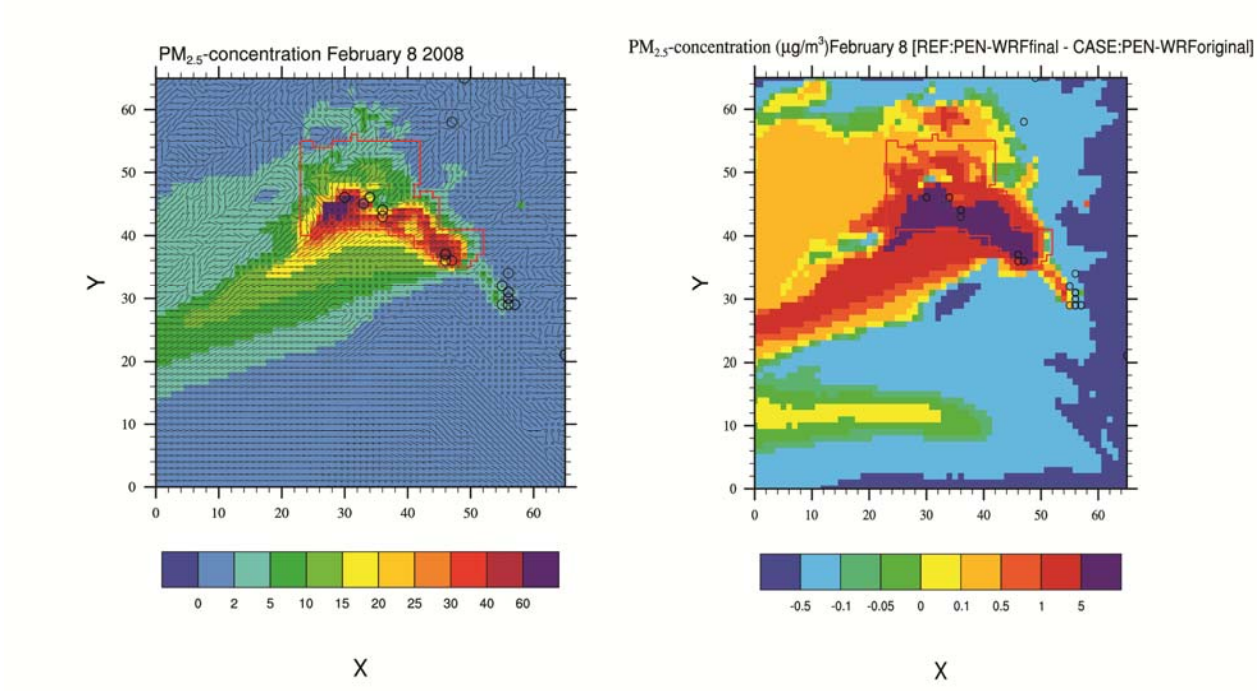


Fig. 19 Exemplary plot of (a) 24h-average $PM_{2.5}$-concentrations as simulated by CMAQ with the PEN-WRF meteorology (PEN-WRFfinal) with the wind barbs and (b) 24h-average $PM_{2.5}$-concentration differences at breathing level between the simulations with the final CMAQ and the PEN-WRF meteorology that uses the cleaner IC/BC conditions (see text for details) and the original CMAQ with that uses the default initial and boundary condition and PEN-WRF meteorology (PEN-WRForiginal). Differences are PEN-WRFfinal-PEN-WRForiginal.

To determine the impact of the initial conditions (IC) and BC, we compared the results from the final Alaska adapted CMAQ simulation that was generated with the PennState meteorological data (PEN-WRFfinal) with the results from the original CMAQ version with the default initial and boundary conditions that represent the background concentrations in the eastern United States. We assumed that the initial and boundary conditions developed for Alaska are "clean" background conditions. The boundary-condition impacts on the 24h-average $PM_{2.5}$-concentrations make a difference of less than 0.5µg/m^3 outside the nonattainment area (Fig. 19). For the January episode, the maximum difference due to the boundary conditions amounts 1.4 µg/m^3. However, on some days, effects of the boundary conditions can be found inside the nonattainment area in the range of 0.1 to 0.5µg/m^3. The magnitude of the BC impacts depends on wind-speed and direction.

For example on February 8, the northeast wind blows the $PM_{2.5}$ to the southwest. This consequently results in an impact of the boundary condition on the concentrations inside the nonattainment area (Fig. 19). The difference between the clean background condition and the default BC also shows in a difference in the 24h-average $PM_{2.5}$-concentrations about 0.1-0.5

$\mu g/m^3$. The results for the impact of recirculation pattern on the $PM_{2.5}$-concentrations in the domain are shown in the Appendix.

Using IMPROVE network observations of winter 2008/09 combined with HYSPLIT [*Draxler et al.*, 2009] backward meteorological trajectories simulations at 0000 UTC on days with high $PM_{2.5}$-concentrations ($>2\mu g/m^3$) at the Denali IMPROVE site and heights of 1000m to 8500m in steps of 500m above ground showed transport of particles from Asia to Denali Park at several levels. However, at the Denali IMPROVE site the $PM_{2.5}$-concentrations are still far away from the NAAQS and typically below $3\mu g/m^3$. This means long-range transport may contribute to the $PM_{2.5}$-concentrations in the nonattainment area by a couple of $\mu g/m^3$, but is not the reason for the exceedances. In winter, the advected amount of $PM_{2.5}$ is too small to cause an exceedance unless the $PM_{2.5}$-concentrations are already close to the NAAQS.

Photochemical modeling with WRF/Chem, for which various emission datasets were available, showed that the region receives only minor amounts of pollution from long-range transport [*Tran et al.*, 2011; *Mölders et al.*, 2012]. The major sources of primary particulate matter are within the nonattainment area. Typically, $PM_{2.5}$-exceedances occur during strong temperature-inversions on calm-wind days when the inversion traps local emissions from heating and vehicles near the surface [*Tran and Mölders*, 2011; *Mölders et al.*, 2012]. On these days, wind-speeds are low and advection from outside the nonattainment area is marginal.

2.5 Assessment of CMAQ Sensitivity to Secondary Chemistry

We investigated the sensitivity of the Alaska adapted CMAQ model version to chemistry before the final improvements were made for the January v1 and November episode. In the nonattainment area, the overall and average concentrations of sulfate, nitrate and organic for turning on and turning off chemistry were compared (Table 4).

The comparison of the sulfate, nitrate and organic concentrations of the two episodes shows that the concentrations of all three species are higher in the January than November episode. Turning off the chemistry decreases the sulfate concentrations by 9% and 3% for the January and November episode, respectively. Doing so, decreases the organic compound concentrations by 1% and less than 1%, and decreases the nitrate concentrations by 90% and 95% for the January and November episode, respectively (Table 4). The nitrate-aerosol production is related to the neutralization of HNO_3 vapor, which is a by-product of photochemical reactions. In the November episode, there is more sunlight than January episode. Thus, gas-phase and aerosol chemistry of nitrate play a greater role than in the January episode. For sulfate and organic compounds, the lower temperatures and dry conditions of the January episode support more gas-to-particle conversion than in the November episode. Consequently, those aqueous vapors tend to convert into particles and increase the mass of sulfate and organic particulate matter.

Table 4. Overall mass and average mass of sulfate, nitrate and organic compounds in the nonattainment area for the case of turning off the chemistry (chem_noop and aero_noop in CMAQ), turning off the gas chemistry (chem_noop), turning off the aerosol chemistry (aero_noop), and turning on the chemistry.

Nonattainment area	**Sulfate (μg/m^3)**	**Nitrate(μg/m^3)**	**Organic(μg/m^3)**
Overall mass			
January			
Turn on chemistry	152,490	103,508	713,109
Turn off gas-chemistry	148,521 (-3%)	40,787(-61%)	712,325(N)
Turn off aero-chemistry	139,856(-8%)	10,764(-90%)	708,086(-1%)
Turn off chem.	139,317(-9%)	10,161(-90%)	707,934(-1%)
November			
Turn on	125,201	189,067	1,354,795
Turn off gas-chemistry	125,413(N)	30,136(-84%)	1,354,053(N)
Turn off aero-chemistry	121,161(-3%)	10,489(-94%)	1,351,743(N)
Turn off chemistry	122,050(-3%)	10,069(-95%)	1,351,745(N)
Average mass			
January			
Turn on	0.85	0.57	3.96
Turn off gas-chemistry	0.82(-3%)	0.23(-61%)	3.95(N)
Turn off aero-chemistry	0.78(-8%)	0.06(-90%)	3.93(-1%)
Turn off chemistry	0.77(-9%)	0.06(-90%)	3.93(-1%)
November			
Turn on	0.88	1.33	9.53
Turn off gas-chemistry	0.88(N)	0.21(-84%)	9.52(N)
Turn off aero-chemistry	0.85(-3%)	0.07(-94%)	9.51(N)
Turn off chemistry	0.86(-3%)	0.07(-95%)	9.51(N)

At the grid-cell of the State Office Building site, the ratios of simulated to observed sulfate, nitrate and organic carbon and of precursors to concentrations were also investigated. On average over the January episode, the ratios of modeled SO_2/modeled aerosol sulfate are 189.0 and 154.1 for the Alaska adapted CMAQ model before and after the improvements, respectively. For the November episode, the average ratios of modeled SO_2/modeled aerosol sulfate are 184.8 and 147.5 for the Alaska adapted CMAQ model before and after the improvements, respectively. These findings mean that introducing the improvements led to more conversion of SO_2 to sulfate at the grid-cell of the State Office Building site. The ratios of emitted SO_2/emitted sulfate are 248.6 and 227.8 for the January episode v2 and for the November episode, respectively. The ratios of modeled SO_2/modeled aerosol sulfate divided by emitted SO_2/emitted sulfate are 0.62 and 0.65 for the final improvements of CMAQ for the January v2 and November episode, respectively. Note that there is no observed SO_2 data for the two episodes.

Furthermore, for the simulations that did not employ the revised WRF and SMOKE inputs, the ratio of modeled SO_2/modeled aerosol sulfate divided by emitted SO_2/emitted sulfate are very close (0.63 and 0.62). However, the ratio of emitted SO_2/emitted sulfate for the January v1 is 380.1, which is higher than for the January v2 case. The ratio of modeled SO_2/modeled aerosol sulfate divided by emitted SO_2/emitted sulfate is close to one. This finding indicates that the concentrations of SO_2 and sulfate at the grid-cell of the State Office Building site are mainly from emissions.

For organic carbon, the averaged ratios of modeled VOC/modeled organic carbon are 0.20 for both the Alaska adapted CMAQ model before and after the improvements for the January v2 episode. For the November episode, the average ratio of modeled VOC/modeled organic carbon is 0.18 for the Alaska adapted CMAQ model both before and after the improvements, i.e. it stayed the same. The introduction of the improvements does not lead to a difference in the organic carbon concentrations at the gri-d-cell of the State Office Building site. The ratios of emitted VOC/emitted organic carbon are 72.2 and 94.4 for the January episode v2 and for the November episode, respectively. The ratios of modeled VOC/modeled organic carbon divided by emitted VOC/emitted organic carbon are 0.19 and 0.18 for the final improvements of CMAQ for the January v2 and November episode, respectively. The simulations that did not employ the revised WRF and SMOKE inputs, have a ratio of modeled VOC/modeled organic carbon divided by emitted VOC/emitted organic carbon of 0.66. For the January v1 episode, the ratio of emitted VOC/emitted organic carbon is 30.1, which is lower than for the January v2 case. The low ratio of modeled VOC/modeled organic carbon divided by emitted VOC/emitted organic carbon indicates that there is higher gas-to-particle conversion of VOC to organic carbon than sulfate at the grid-cell of the State Office Building site.

For nitrate, the averaged ratios of modeled NO_2/modeled aerosol sulfate are 175.4 and 179.2 for the January v2 episode before and after implementation of the improved parameterizations. For the November episode, the averaged ratios are 137.8 and 140.7 before and after implementation of the improved parameterizations. The increase of sulfate concentrations after the improvement

brought about a decrease of the modeled nitrate aerosol concentrations. The averaged ratios of modeled NO_2/modeled aerosol sulfate for the January v1 episode is 180.7.

The temporal evolutions the ratios of modeled SO_2/modeled aerosol sulfate divided by emitted SO_2/emitted sulfate agree with the temporal evolutions of the meteorological variables such as 2m-temperatures and 2m-water mixing ratios clearly in both episodes (Fig. 20). Lower temperature and lower water mixing ratio conditions lead to more gas-to-particle conversion. We found that on the first day of the simulations, the ratios are very low. These low ratios might be the effect of the spin-up of the chemistry in CMAQ.

a)

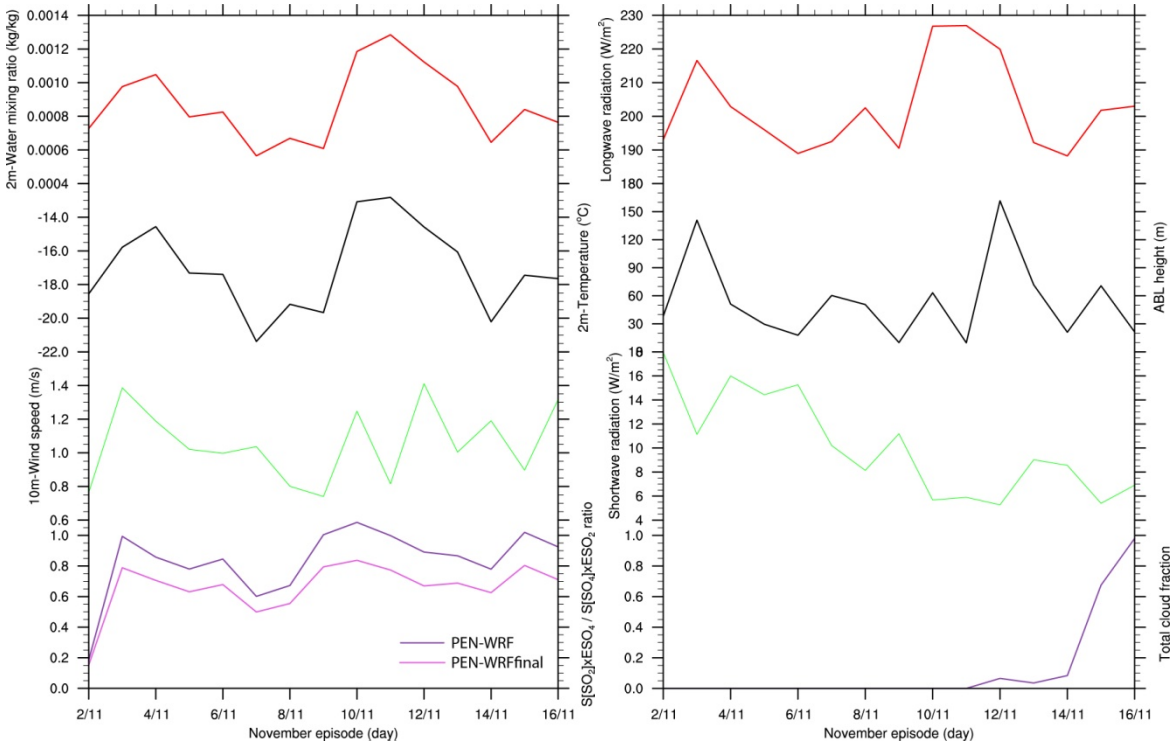


Fig. 20 continued

b)

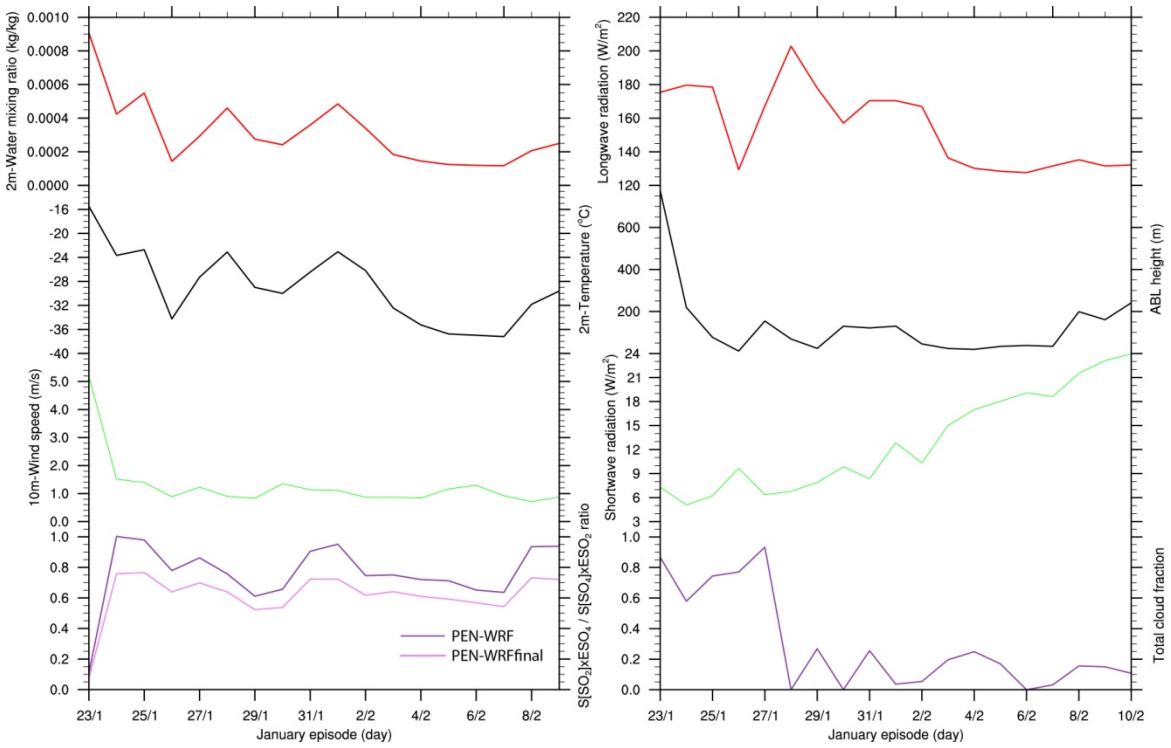


Fig. 20 Temporal evolutions of ratios of modeled SO_2/modeled aerosol sulfate divided by emitted SO_2/emitted sulfate as obtained from the CMAQ simulations prior to the improvements (PEN-WRF) and after the CMAQ improvements (PEN-WRFfinal) described in this report and the temporal evolutions of the meteorological variables generated by MCIP for the CMAQ model, which include 2m-water mixing ratio, 2m-temperature, 10m-windspeed, long-wave radiation, atmospheric boundary layer (ABL) height, shortwave radiation and total cloud fraction as obtained at the grid-cell of the State Office Building site for the (a) January and (b) November episode.

3. Conclusions and Recommendations

With the final improvements of the parameterizations and parameters made within the framework of this contract, the Alaska adapted CMAQ model showed an increase in the simulated sulfate concentrations at the grid-cell of the State Office Building site. Despite this success, the adapted CMAQ model still underpredicts the sulfate concentrations at the grid-cell of the State Office Building site. The normalized mean errors are 60% and 70% for the November and January episode, respectively.

We made various sensitivity simulations and tests to examine the reasons for the underestimation. These investigations and the process analysis provide strong evidence that most likely the partitioning of the emitted $PM_{2.5}$ is part of the reason for the underestimation of sulfate at the grid-cell of the State Office Building site. However, we have to use the emissions as they

partitioned in the newest version of the emission inventory as it is based on the most current insights on the emission situation in Fairbanks. Therefore, we strongly recommend further assessing and/or improving the percent partitioning of total particulate matter emissions into sulfate and other species.

Our results support the findings from other authors [e.g. *Appel et al.,* 2008] for winter cases in the Lower 48 that CMAQ underpredicts sulfate compared to observations. At UAF, currently further research is performed within the framework of a dissertation why CMAQ underestimates sulfate at low temperatures. Thus, it has to be expected that possible changes to CMAQ will become available in the future to better capture the sulfate concentrations for subarctic conditions.

Another reason for the underestimation that we cannot exclude is that in the subarctic there may be physical/chemical processes in the sulfate chemistry that are of relevance at low temperatures, low water vapor mixing ratios or both. These conditions rarely exist in the Lower 48. Thus, if such processes exit in the subarctic they may have been overlooked in studies for mid-latitudes. It is obvious that when a relevant process has not yet been found/identified, it, of course, is not considered in the code. Thus, the model cannot simulate the process and its impact on sulfate concentrations. The detection of missing processes would require long laboratory studies. Eventually, it would require long test series to derive parameterizations of the processes from the data and to implement and test the parameterizations in the model.

Our investigations and sensitivity studies also showed that the input meteorology and temporal offsets therein strongly determine the temporal evolutions of simulated 24h-average $PM_{2.5}$-concentrations. Therefore, we recommend further tests for the best options in the WRF setup for producing meteorological data with less temporal offset.

Our investigations suggest that the CMAQ for these episodes needs about three days to spin up the chemical fields. Therefore, we recommend to discard the first three days of simulations as spin up time and to not consider them in any assessment for the State Implementation Plan development. We further recommend that the simulation results of the first three days should be discarded from any evaluation as the chemical fields still spin-up.

We recommend that the final Alaska adapted CMAQ version presented here is tested for other episodes that have more observational data that the January and November episodes. The low data density does not permit assessment whether the occasional weak performance is related to model, emission and/or observational errors. Furthermore, with data available at just one site it is impossible to assess whether CMAQ captures the spatial distribution right. Some of the discrepancies might be just spatial offsets due to the overestimation of wind-speed. Low data availability always bears the risk to adapt a model in the wrong direction, as one can be easily right for the wrong reason at one place. This risk decreases when the amount of data increases.

A revised version of the emission inventory just became available [*Hixson*, 2012; pers. comm.]. It has to be examined how much the updated emissions will impact the simulated $PM_{2.5}$-concentrations and affect the simulated sulfate concentrations.

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Appendix 1

The following pages show an hourly sequence of plots illustrating how polluted Fairbanks air that left the nonattainment area enters the nonattainment area as aged polluted air. The wind barbs indicate wind direction. Circles mean zero wind speed and hence no wind direction. The color gives the $PM_{2.5}$-concentrations as indicated in the legend.