Sensitivity of Secondary Inorganic Aerosol Concentrations to Precursor Emissions and Inorganic Aerosol Modules in CAMx over Central Europe

L. Bartík, P. Huszár

Charles University, Faculty of Mathematics and Physics, Prague, Czech Republic.

O. Vlček

Czech Hydrometeorological Institute, Ambient Air Quality Department, Prague, Czech Republic.

K. Eben

Czech Academy of Sciences, Institute of Computer Science, Prague, Czech Republic.

Abstract. The Comprehensive Air Quality Model with Extensions version 6.50 (CAMx-v6.50) supports two inorganic aerosol modules (ISORROPIA and EQSAM4clim) that can be used to model partitioning of secondary inorganic aerosol (SIA) constituents between the gas and aerosol phases. In this work, we studied spatial and temporal impacts of using these two modules in CAMx-v6.50 runs on the seasonal surface concentrations of particulate ammonium (PNH4), nitrate (PNO3) and sulfate (PSO4) over Central Europe in the period between 2018–2019. Comparison between simulations showed the smallest influence on PSO4 and good agreement between PNH4 concentrations in all seasons. For PNO3, the agreement between seasonal concentrations was also good with the exception of summer when the use of EQSAM4clim has led to a significant underestimation in some regions. Based on comparison of surface concentrations obtained from the simulations to measurements, we performed other simulation (with invoked EQSAM4clim module) in which we used perturbed emissions of NH_3 and NO_x (except summer months, NH_3/NO_x emissions were decreased/increased by 50%). Comparison of outputs from this simulation to measurements showed that the used emission perturbations lead mainly to the improvement of some monthly PNH4, PNO3, NH₃ and NO₂ concentrations.

Introduction

Secondary inorganic aerosols (SIA) represent the inorganic part of total fine particulate matter (also referred to as particulate matter with aerodynamic diameter $\leq 2.5 \,\mu$ m, PM_{2.5}) in the atmosphere that is created there from their biogenic and anthropogenic gas precursors emitted from the Earth's surface. Over decades, has been well established by surface measurements that particulate ammonium (PNH4), nitrates (PNO3) and sulfates (PSO4), which refer to the content of ammonium (NH₄⁺), nitrates (NO₃⁻) and sulfates (SO₄²⁻) in SIA, belong to the most abundant constituents of SIA and that they can contribute to large fractions of the total PM_{2.5} both globally and over Europe too [e.g., *Heitzenberg*, 1989; *Zhang et al.*, 2007; *Tang et al.*, 2021]. It is also well known that the main gas precursor of PNH4, PNO3 and PSO4 are ammonia (NH₃), nitrogen oxides (NO_x) and sulfur dioxide (SO₂), respectively [e.g., *Tang et al.*, 2021].

On the other hand, chemical transport models still have difficulties capturing measured SIA concentrations which are usually attributed to uncertainties in emissions of ammonia, while the effects of uncertainties in NO_x emissions and transformations as well as uncertainties in biogenic volatile organic compounds can also not be excluded [Aksoyoglu et al., 2017, and references therein]. Except the emissions, modelled SIA concentrations gained from any kind of atmospheric model capable of including inorganic aerosol calculations are in addition to other causes also obviously dependent on numerical schemes (let us name them further as inorganic aerosol modules) that partition SIA constituents between the gas and aerosol phases.

For example, in the Comprehensive Air Quality Model with Extensions version 6.50 (CAMx-v6.50), which was used in this work, two inorganic aerosol modules (namely ISORROPIA and EQSAM4clim) are implemented [*Environ*, 2018]. While both of them represent thermodynamic equilibrium models, they ba-

sically differ in the aerosol systems, which they model: (1) ISORROPIA models the sodium–ammonium– chloride–sulfate–nitrate–water aerosol system [*Nenes et al.*, 1998, 1999]; (2) EQSAM4clim (Equilibrium Simplified Aerosol Model V4) models the potassium–calcium–magnesium–ammonium–sodium–sulfate– nitrate–chloride–water aerosol system [*Metzger et al.*, 2016] and thus more resembles to ISORROPIA II [*Fountoukis and Nenes*, 2007]. Both of them also differ conceptually: EQSAM4clim (in an effort to increase its computation efficiency) uses more analytical approaches in calculations than ISORROPIA.

Koo et al. [2020], who implemented EQSAM4clim into CAMx, have tested the influence of using ISORROPIA and EQSAM4clim in CAMx on the prediction of SIA concentrations over the continental United States of America for two month-long episodes (January and July 2011). To our knowledge, this is the only available work dealing with such a comparison in CAMx until now. Their results for concentrations predicted by CAMx using both of the inorganic aerosol modules shows that (1) PNH4 and PNO3 agree fairly well in January, (2) EQSAM4clim tends to predict lower PNO3 than ISORROPIA in July and (3) PSO4 differences are little for the both months.

Despite the importance of these results, their informative value is naturally limited by the shortness of the simulations as well as by their geographical location. Therefore, in an effort to get more robust comparisons of SIA concentrations obtained using these two inorganic aerosol modules in CAMx over the region of our interest, we decided here to perform two two-years long (2018–2019) CAMx-v6.50 simulations over Central Europe, further labelled as ISORROPIA and EQSAM simulations. Except of their mutual comparison, we also carried out the comparison between modelled and measured surface concentrations for both the SIA constituents (PNH4, PNO3 and PSO4) and some of their gas precursors (NH₃, NO₂ and SO₂). Based on this comparison, we realised one more simulation, further labelled as EQSAM_pert, with perturbed NH₃ and NO_x emissions to study impacts of such changes in the emissions on (1) the model performance of SIA and their gas precursors and (2) the potential improvement of predicted concentrations of SIA and their gas precursors with respect to their surface measurements.

Model set-up within the simulations

All simulations mentioned in the introduction (ISORROPIA, EQSAM and EQSAM_pert) were run using CAMx-v6.50 [*Environ*, 2018] on a European model domain centred over Prague, the Czech Republic (50.075° N, 14.44° E, Lambert Conic Conformal projection used) for the period between 2018–2019. The model domain was represented in horizontal layers by 172×152 grid boxes with the horizontal resolution of 9 km, in vertical direction it consisted from 20 layers from the Earth's surface up to approximately 12 km whereas the height of the lowermost layer was about 48–50 m. Driving meteorological fields (the same for all simulations) were derived using the WRFCAMx preprocessor implemented in CAMx-v6.50 from the weather forecast simulation performed using the WRF (Weather Research and Forecasting) Model Version 4.0.3., which detailed description can be found in *Ďoubalová et al.* [2020]). All needed emission inputs were prepared in the same manner as it did *Huszar et al.* [2020].

In all simulations, gas-phase chemistry was solved by Carbon Bond Version 6, Revision 4 (CB6r4) mechanism, the connection between gas-phase and aerosol chemistry was invoked using CF (coarse/fine) scheme that divides the aerosol size distribution into two static modes (coarse and fine) and organic aerosol–gas partitioning and oxidation chemistry were modelled using the semi-volatile equilibrium scheme SOAP2.1 (Secondary Organic Aerosol Processor, version 2.1) [*Environ*, 2018, and references therein]. As it was also mentioned in the introduction, while EQSAM4clim was used within EQSAM and EQSAM_pert simulations, ISORROPIA was used within ISORROPIA simulation. Further, while the same unperturbed emission inputs were used in ISORROPIA and EQSAM simulations, in EQSAM_pert simulation we used the same unperturbed emission inputs, except for NH₃ and NO_x emissions which were decreased/increased by 50%, respectively, in the winter, spring and autumn months while in the summer months, we let them unperturbed.

Results

Comparison of the simulations

To quantify spatial and temporal impacts of using the different inorganic modules in ISORROPIA and EQSAM simulations on surface PNH4, PNO3 and PSO4 concentrations, we calculated the relative percentage differences (RPDs) of the their seasonal concentrations between EQSAM and ISORROPIA simulations determined from the lowermost model layer whereas we defined them as the differences of the seasonal concentrations between EQSAM and ISORROPIA simulations divided by the appropriate



Figure 1. (a) Relative percentage differences (RPDs) of average winter (DJF, top row), spring (MAM, second row), summer (JJA, third row) and autumn (SON, bottom row) particulate sulfate (PSO4, left column), ammonium (PNH4, middle column) and nitrate (PNO3, right column) concentrations between EQSAM and ISORROPIA simulations in 2018. The relative differences of seasonal concentrations are scaled by their appropriate seasonal concentrations from ISORROPIA simulation. (b) The analogous comparisons as in panel (a) for the differences of the seasonal RPDs between the years 2019 and 2018.

seasonal concentrations from ISORROPIA simulation and expressed in percentages. Results of these calculations for the year 2018 are shown in Figure 1(a) and can be summarized as follows:

PSO4 seasonal concentrations from EQSAM simulation are, regardless of the season, only slightly higher than those from ISORROPIA simulation over the whole domain: the mean seasonal RPD over the domain during the year is in the range from 0.3% (spring) to 1.6% (winter), the maximum of seasonal RPDs over the domain reaches 6% in winter and 3% in the other seasons. Further, PNH4 seasonal concentrations from EQSAM simulation are (in contrast to those for PSO4) typically lower than ones from ISORROPIA simulation, except for some mountain and sea regions during winter and some regions in the Alps and their vicinity (e.g., in the Po Valley) during spring and autumn. However, the seasonal RPDs for PNH4 are usually not so significant: the mean seasonal RPD over the domain during the year is in the range from -10% (summer) to -0.5% (winter), the total maximum of seasonal RPDs over the domain reaches 15% in the Alps regions during winter, the maximum of seasonal RPDs underestimation over the domain exceeds -20% during summer and autumn and reaches -12% during winter and spring. Finally, PNO3 seasonal concentrations from EQSAM simulation are (similarly to those for PNH4) typically lower than ones from ISORROPIA simulation, except for the Alps regions during winter and some regions in the Alps and their vicinity (e.g., in the Po Valley) during spring and autumn. Unlike PSO4 and PNH4, their seasonal RPDs are more significant, especially during summer. While the mean seasonal RPD for PNO3 over the domain is -3% in winter and spring and -8% in autumn, it reaches -32% in summer. The main variations of RPDs in winter are connected with the mountain areas: while in the Alps they reach up to 15%, in the rest of Central European mountains they are negative and somewhere exceed -20%. Except for the southern part of the domain with some peculiar areas, RPDs do not exceed -10% and -30% in the areas with underestimation during spring and autumn, respectively. Even more of peculiar areas, where RPDs exceed over -70%, are present



Figure 2. (a) Relative percentage differences (RPDs) of average winter (DJF, top row), spring (MAM, middle row) and autumn (SON, bottom row) particulate sulfate (PSO4, left column), ammonium (PNH4, middle column) and nitrate (PNO3, right column) concentrations between EQSAM_pert and EQSAM simulations in 2018. The relative differences of seasonal concentrations are scaled by their appropriate seasonal concentrations from EQSAM simulation. (b) Average winter (DJF, top row), spring (MAM, middle row) and autumn (SON, bottom row) ammonia (NH₃, left column), nitrogen oxides (NO_x, middle column) and sulfur dioxide (SO₂, right column) concentrations from EQSAM simulations in 2018.

during summer not only near the southern boundary of the domain but also in some regions located mainly in Slovakia, Hungary, southern Austria and Slovenia.

To see if substantial differences exist in model performance between different years, we calculated the differences of the seasonal RPDs of PNH4, PNO3 and PSO4 between the years 2019 and 2018. Results of these comparisons are shown in Figure 1(b). As it is seen over Central Europe (i.e., excluding the boundary parts of the domain): (1) PSO4 shows the smallest inter-annual differences from all the studied SIA constituents that usually do not exceed the range between $\pm 1.5\%$, (2) PNH4 also manifest small inter-annual differences that typically do not exceed the range between $\pm 2\%$, except for some regions in the Alps and their vicinity where it exceed $\pm 5\%$ with positive values during winter, spring and autumn and with negative ones during summer; (3) PNO3, compared to the other two SIA constituents, shows the largest inter-annual differences that, however, typically do not exceed the ranges between $\pm 10\%$ and $\pm 5\%$ in most parts of Central Europe in summer and in the other seasons, respectively (exceptions are again connected mainly with the Alps and their neighbouring regions).

To quantify spatial and temporal impacts of using the perturbed emissions in EQSAM_pert simulation on surface PNH4, PNO3 and PSO4 concentrations, we calculated (analogously to the previous comparison) RPDs of the seasonal concentrations between EQSAM_pert and EQSAM simulation whereas in this case we defined them as the differences of the seasonal concentrations between EQSAM_pert and EQSAM simulations divided by the appropriate seasonal concentrations from EQSAM simulation and expressed in percentages. Results of these calculations for winter, spring and autumn seasons in 2018 are shown in Figure 2(a). In order to better comment on impacts of the perturbations, we present the maps of average winter, spring and autumn concentrations of NH_3 , NO_x and SO_2 from EQSAM simulation in 2018 which are shown in Figure 2(b). Impacts of the perturbations can be briefly summarized as follows:

Decrease in NH₃ emissions leads to a reduction of seasonal PSO4 concentrations over the whole domain in all studied seasons (the mean seasonal RPD over the domain equals to -31, -16 and -25%in winter, spring and autumn, respectively). However, it is also seen that responses to this decrease are in general significantly non-linear. On the other hand, simultaneous reduction of NH₃ emissions and increase in NO_x emissions leads, depending on the region, either to a reduction or, conversely, to an increase in seasonal concentrations of both PNH4 and PNO3. In winter, the seasonal concentrations of



Figure 3. (a) Comparison between station and modelled annual cycles of average (solid lines), median (dashed lines) and interpercentile range between 10th and 90th percentiles (areas) of monthly particulate ammonium (PNH4, top left), nitrate (PNO3, top right), sulfate (PSO4, bottom left) and gas ammonia (NH₃, bottom right) concentrations in 2018. Green, orange and blue lines and areas represent these statistics obtained from the combined AirBase and EMEP measurements at rural stations, ISORROPIA and EQSAM simulations, respectively. (b) The analogous comparisons as in panel (a) among the combined AirBase and EMEP measurements at rural stations in 2018 which are represented by green, red and blue lines and areas, respectively.

both PNH4 and PNO3 from EQSAM_pert simulation are underestimated over most areas of the domain (the mean winter RPD over the domain equals to -29 and -27% for PNH4 and PNO3, respectively). In spring, in contrast to winter and autumn, much more regions exist over the domain in which the seasonal concentrations of both PNH4 and PNO3 from EQSAM_pert simulation are overestimated (the mean spring RPD over the domain equals to -9 and -5% for PNH4 and PNO3, respectively). In autumn, the seasonal concentrations of PNO3 from EQSAM_pert simulation are underestimated over most areas of the domain, while those of PNO3 from EQSAM_pert simulation are underestimated over most areas of the domain, while those of PNH4 are underestimated over the whole domain (the mean autumn RPD over the domain equals to -29 and -31% for PNH4 and PNO3, respectively). In all seasons, it is seen that the regions associated with: (1) the greatest decrease and (2) the lowest decrease or increase in both PNH4 and PNO3 concentrations correlate well with the regions in which there are: (1) low and (2) high seasonal concentrations of NH₃ in EQSAM simulation.

Comparison of the simulations to surface measurements

Here, we provide a very simplified evaluation of the model predictions of the surface concentrations of PNH4, PNO3, PSO4 and some of their gas precursors (NH₃, NO₂ and SO₂) from ISORROPIA, EQSAM and EQSAM_pert simulations against their surface measurements in 2018, based on the comparison of their modelled monthly concentrations to their station equivalents. To this purpose, we used (1) available data for PNH4, PNO3, PSO4 and NH₃ from rural background stations included in the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe database (EMEP; http://ebas.nilu.no/; last access: 7 June 2021) as well as from those included in the European Environment Agency's AirBase European air quality dataset (https://www.eea.europa.eu/dataand-maps/data/aqereporting-8; last access: 7 June 2021); (2) available data for NO₂ and SO₂ from rural, suburban and urban background stations included in the AirBase European air quality dataset. Due to the horizontal resolution used in the simulations $(9 \,\mathrm{km})$, we selected only stations with an altitude not exceeding 750 meters above sea level. To calculate the modelled monthly concentrations for a given station, we used the modelled values of concentration from the grid cell in the lowermost model layer which was geographically closest to it (i.e., without using any kind of interpolation). Finally, it should be mentioned that the evaluation is mainly limited by the small number of stations measuring PNH4, PNO3, PSO4 and NH₃ (here we used data from 10, 9 and 7 stations for PNH4 and PNO3, PSO4 and NH_3 evaluation, respectively).

Table 1. Comparison of modelled data from ISORROPIA, EQSAM and EQSAM_pert simulations with measurements: evaluation of average bias (in μ g.m⁻³), root mean square error (RMSE, in μ g.m⁻³) and Pearson correlation coefficient (r) for monthly concentrations of particulate ammonium (PNH4), nitrate (PNO3) and sulfate (PSO4) for the whole year 2018 (Annual) and its winter (DJF), spring (MAM), summer (JJA) and autumn (SON) seasons.

SIA	ISORROPIA/EQSAM/EQSAM_pert				
Statistics	Annual	DJF	MAM	JJA	SON
PNH4					
bias	0.32/0.29/0.01	0.88/0.86/0.23	0.61/0.58/0.45	-0.38/-0.42/-0.42	0.17/0.12/-0.26
RMSE	0.79/0.78/0.57	1.05/1.03/0.50	0.89/0.88/0.73	0.44/0.46/0.46	0.51/0.50/0.36
r	0.77/0.77/0.76	0.86/0.86/0.89	0.96/0.97/0.98	0.15/0.13/0.13	0.77/0.80/0.78
PNO3					
bias	1.03/0.88/0.33	2.30/2.08/0.80	1.95/1.87/1.74	-0.87/-0.99/-0.99	0.75/0.56/-0.23
RMSE	2.09/2.02/1.71	2.61/2.43/1.69	2.56/2.53/2.45	0.97/1.06/1.06	1.52/1.45/0.99
r	0.75/0.75/0.69	0.75/0.76/0.78	0.95/0.95/0.98	-0.07/-0.22/-0.22	0.87/0.87/0.86
PSO4					
bias	-0.74/-0.73/-1.07	-0.15/-0.11/-0.84	-0.61/-0.61/-0.89	-1.24/-1.24/-1.24	-0.96/-0.94/-1.30
RMSE	1.07/1.07/1.18	0.82/0.82/1.06	0.88/0.88/0.98	1.25/1.25/1.25	1.17/1.17/1.33
r	0.43/0.42/0.38	0.44/0.41/0.32	0.76/0.76/0.73	0.82/0.82/0.82	0.54/0.54/0.50

For the evaluation of monthly concentrations of PNH4, PNO3 and PSO4, we calculated average bias, root mean square error (RMSE) and Pearson correlation coefficient (r) for the whole year 2018 as well as for its winter, spring, summer and autumn seasons. The values of these statistical indicators were calculated using the same formulas as in *Ďoubalová et al.* [2020] and are summarized in Table 1. Further, for all evaluated pollutants, we compared modelled and station annual cycles of average, median and interpercentile range between 10th and 90th percentiles of monthly concentrations. This comparison for PNH4, PNO3, PSO4 and NH₃ is shown in Figure 3. Before compiling the annual cycles for NO₂ and SO₂, we divided the stations on which they are measured according to the countries in which they are located. These annual cycles are shown in Figure 4. The results of the evaluation can be briefly summarized as follows:

As it is seen in Figure 3(a), modelled annual cycles of average, median and interpercentile range of monthly PNH4, PNO3, PSO4 and NH₃ concentrations from ISORROPIA and EQSAM simulations differ only slightly. For PNH4, PNO3 and PSO4, it is also confirmed by small differences between all statistical indicators from these two simulations. The same is true also for NO₂ and SO₂ (not shown here) and thus, only the modelled annual cycles from EQSAM simulation are shown in Figure 4.

For PNH4 and PNO3, the averages, medians and interpercentile ranges of their modelled monthly concentrations from both simulations are, with respect to their station equivalents, overestimated in the winter, early spring and late autumn months (the averages are overestimated by factors of 1.4–2) while in the other months, they are, in contrast, underestimated (the averages are underestimated by factors of 1.2–4.8). These conclusions are consistent with the average biases of their monthly concentrations in each season. Furthermore, the seasonal average biases and RMSEs of their monthly concentrations in each season shows that they are a little better predicted during winter, spring and autumn by EQSAM4clim module, while during summer by ISORROPIA module. Within the whole year, their monthly concentrations are thus a little better predicted by EQSAM4clim module. For PSO4, it is seen that the averages, medians and interpercentile ranges of its modelled monthly concentrations from both simulations are, with respect to their station equivalents, almost exclusively more or less underestimated, especially, however, during the late spring, summer and early autumn months (the averages are underestimated by factors of 1.7–4.3). Again, these conclusions are consistent with the average biases of its monthly concentrations. Both the seasonal and annual average biases and RMSEs of its monthly concentrations shows that they are slightly better predicted by EQSAM4clim module. For NH₃, the averages, medians and interpercentile ranges of its modelled monthly concentrations from both simulations are, with respect to their station equivalents, overestimated in February, March, April, August, September, October and November (the averages are overestimated by factors of 1.2-2.8, with the highest values occurring in February, March and April) while in the other months, they are only slightly underestimated. Based on these results, together with those for PNH4, we decreased NH_3 emissions in the winter, spring and autumn months in EQSAM_pert simulation. Comparison the averages, medians and interpercentile ranges of modelled monthly SO₂ concentrations from EQSAM simulation (remind that those from ISORROPIA simulation are very similar) to their station equivalents shows a geographical conditionality: (1) at Ger-



Figure 4. (a) Comparison between station and modelled annual cycles of average (solid lines), median (dashed lines) and interprecentile range between 10th and 90th percentiles (areas) of monthly sulfur dioxide (SO₂) concentrations at Austrian (AT, top row), German (DE, second row), Czech (CZ, third row) and Polish (PL, bottom row) rural (left column), suburban (middle column) and urban (right column) stations in 2018. Green, red and blue lines and areas represent these statistics obtained from AirBase measurements, EQSAM_pert and EQSAM simulations, respectively. (b) The analogous comparison as in panel (a) for monthly nitrogen dioxide (NO₂) concentrations in 2018.

man and Polish stations, they are usually overestimated during the winter, spring and autumn months (in summer months, they are either overestimated or underestimated depending on their positions to urban areas); (2) at Czech stations, they are typically overestimated during the winter, early spring and late autumn months (however, not to such an extent as in the previous cases) while in the rest months, they are underestimated; (3) annual cycles at Austrian stations qualitatively more resemble to those at Czech stations. Analogous comparison for NO₂ shows almost exclusively an underestimation of its modelled monthly concentrations and also a tendency of these underestimations to grow towards urban areas, regardless of the country in which the stations are located. Based on the same comparison for NO_x (not shown here), it is possible to claim qualitatively the same conclusions as for NO₂. Based on these results, we increased NO_x emissions in EQSAM_pert simulation for the same period when we reduced NH₃ emissions.

Comparison of average RMSEs of monthly PNH4 and PNO3 concentrations for the whole year as well as those for winter, spring and autumn seasons between all simulations show that the perturbed emissions used in EQSAM_pert simulation lead to some improvement of these concentrations. As it is seen in Figure 3(b), that this improvement is most evident in January, November and December. Furthermore, the perturbed emissions lead to underestimation of monthly PSO4 concentrations that is seen on all annual cycles as well as on the values of average biases from this simulation. Reduction of NH₃ emissions in EQSAM_pert simulation leads to significant improvement of its predicted monthly concentrations from February to May (the modelled averages of monthly concentrations differ from the station equivalents by factors of 1.03–1.5), however, it also leads to large underestimations from October to December and in January (the modelled averages of monthly concentrations are underestimated to station equivalents by factors of 2.0–3.6). For SO₂, the perturbed emissions cause an increase in its monthly concentrations, the rate of which is determined by the geographical location of the stations. Finally, the increase in NO_x emissions in EQSAM_pert simulation contributes to slightly improved prediction of monthly NO₂ and NO_x (not shown here) concentrations, with the exception of German rural stations.

Conclusion

In this work, we firstly studied impacts of using two different inorganic aerosol modules (ISOR-ROPIA and EQSAM4clim) implemented in CAMx-v6.50 on seasonal ammonium, sulfate and nitrate concentrations over Central Europe in the period between 2018–2019. On the one hand, the results

BARTÍK ET AL.: SENSITIVITY OF SIA CONCENTRATIONS OVER CENTRAL EUROPE

showed that both modules predicted very similar sulfate concentrations and sufficiently similar ammonium concentrations in all seasons, as well as comparable nitrate concentrations in winter, spring and autumn. On the other hand, they showed that EQSAM4clim significantly underestimated nitrate concentrations in some regions during summer. These results are qualitatively similar to those published by *Koo et al.* [2020]. Further, we tested impact of simultaneous decrease in ammonia emissions by 50% and increase in nitrogen oxides emissions by 50% during the winter, spring and autumn months on concentrations of ammonium, sulfate, nitrate, ammonia, nitrogen oxides and sulfur dioxide. Comparison of modelled monthly concentrations of these pollutants to measurement showed mainly some improvement of monthly PNH4, PNO3, NH₃ and NO₂ concentrations. The results of all simulations presented here and their more detailed analysis will help us to design further sensitivity simulations which will aim to study contribution of emissions from different sources and regions over Central Europe to the total pollution by particulate matter.

Acknowledgments. This work has been funded by the Technology Agency of the Czech Republic (TAČR) project ARAMIS (Air quality Research, Assessment and Monitoring Integrated System) No.SS02030031. We further thank the Netherlands Organisation for Applied Scientific Research (TNO) for providing the Monitoring Atmospheric Composition and Climate (MACC)-III emissions dataset, the Czech Hydrometeorological Institute for providing the Register of Emissions and Air Pollution Sources (REZZO) dataset, ATEM (Studio of ecological models; http://www.atem.cz/en, last access: 7 June 2021) for providing their traffic emissions dataset, the European Environment Agency (EEA) for providing the AirBase European air quality data and the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) for providing their air quality data.

References

- Aksoyoglu, S., G. Ciarelli, I. El-Haddad, U. Baltensperger, and A. S. H. Prévôt, Secondary inorganic aerosols in Europe: sources and the significant influence of biogenic VOC emissions, especially on ammonium nitrate, *Atmos. Chem. Phys.*, 17, 7757–7773, 2017.
- Ďoubalová, J., P. Huszár, K. Eben, N. Benešová, M. Belda, O. Vlček, J. Karlický, J. Geletič and T. Halenka, High Resolution Air Quality Forecasting over Prague within the URBI PRAGENSI Project: Model Performance during the Winter Period and the Effect of Urban Parameterization on PM, Atmosphere, 11, 625, 2020.
- Environ: CAMx User's Guide, Comprehensive Air Quality model with Extentions, version 6.50, available at: http://www.camx.com (last access: 7 June 2021), Novato, California, 2018.
- Fountoukis, C., and A. Nenes, ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+ -Ca²⁺-Mg²⁺-NH₄⁺-Na⁺-SO₄²⁻-NO₃⁻-Cl⁻-H₂O aerosols, *Atmos. Chem. Phys.*, 7, 4639-4659, 2007.
- Heitzenberg, J., Fine particles in the global troposphere, A review, *Tellus Ser. B-Chem. Phys. Meteorol.*, 41B, 149–160, 1989.
- Huszar, P., J. Karlický, J. Ďoubalová, K. Šindelářová, T. Nováková, M. Belda, T. Halenka, M. Žák, and P. Pišoft, Urban canopy meteorological forcing and its impact on ozone and PM_{2.5}: role of vertical turbulent transport, Atmos. Chem. Phys., 20, 1977–2016, 2020.
- Koo, B., S. Metzger, P. Vennam, C. Emery, G. Wilson, and G. Yarwood, Comparing the ISORROPIA and EQSAM Aerosol Thermodynamic Options in CAMx, in book: Air Pollution Modeling and its Application XXVI ed. by C. Mensink, W. Gong, and A. Hakami, Springer Proceedings in Complexity, 93–98, 2020.
- Nenes, A., S. N. Pandis, C. Pilinis, ISORROPIA: A New Thermodynamic Equilibrium Model for Multiphase Multicomponent Inorganic Aerosols, Aquat. Geochem., 4, 123–152, 1998.
- Nenes, A., S. N. Pandis, C. Pilinis, Continued development and testing of a new thermodynamic aerosol module for urban and regional air quatity models, *Atmospheric Environment*, 33, 1553–1560, 1999.
- Metzger, S., B. Steil, M. Abdelkader, K. Klingmüller, L. Xu, J. E. Penner, Ch. Fountoukis, A. Nenes, and J. Lelieveld, Aerosol water parameterisation: a single parameter framework, Atmos. Chem. Phys., 16, 7213–7237, 2016.
- Tang, Y. S., C. R. Flechard, U. Dämmgen, S. Vidic, V. Djuricic, M. Mitosinkova, et al., Pan-European rural monitoring network shows dominance of NH₃ gas and NH₄NO₃ aerosol in inorganic atmospheric pollution load, Atmos. Chem. Phys., 21, 875–914, 2021.
- Zhang, Q., et al., Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenicallyinfluenced Northern Hemisphere midlatitudes, *Geophys. Res. Lett.*, 34, L13801, 2007.