

Author's response on Interactive comment on “On the long term impact of emissions from central European cities on regional air-quality”  
by P. Huszar et al.

The authors would like to thank for the detailed review of the manuscript including valuable comments and corrections. Our responses follow one-by-one:

### **Reviewer #1**

Reviewer's comment:

*My impression is that is too much work for one paper. I am convinced about findings concerning goal 2 (the sensitivities part), but several questions remain on goal 1 (the evaluation part, which I would primarily see as an evaluation of the modeling system per se, followed by the estimation of the contribution of the impact of emissions on air quality).*

*Ideally, I would first expect to see a pure evaluation paper, investigating thoroughly the basic weaknesses of the modelling system (e.g. poor temporal correlation and large biases) by looking into emissions and the way they are disaggregated, the impact of Boundary Conditions and the biases of key-meteorological variables on chemistry. If this work, which is forced by reanalysis meteorological fields produces average (occasionally below average) metrics, it cannot be expected to perform better, when coupled to a regional climate model to study for example the impact of future emissions/climate on air quality.*

*The importance of this works lies in using an on-line modeling system as a tool for the investigation of the impact of emissions controls on air quality. The online regional meteorology-chemistry models are an emerging community, which establishes fast in the field of air quality modeling studies. Before replacing the widely used offline meteorology-air quality models, it is important to evaluate the performance of the new-generation online models, and gain some valuable insight into the nature of the complex and not so well understood interactions of meteorology and chemistry.*

*This work, includes a considerable amount of work on the impact of emissions on central European air quality and the some impact metrics (e.g. AOT40), however I missed some information on the added value of this work, compared to similar previous literature using offline models. What is the incentive to use an online model in this specific study instead of an offline? What will be the added value for having a computational expensive system to investigate emission/air quality issues? And more importantly: Is this model capable to reproduce accurately the state of the atmosphere? Or we simply use a more sophisticated but less understood modeling system, undermining the quality of final results? Can you compare the evaluation performance of this modeling system with the offline system and support the use of the online?*

Authors' response:

The reviewed manuscript presents results within a wider scientific scope: to quantify and qualify the present and future impact of urban emissions on both air-quality (tropospheric chemistry in general) and climate (see the acknowledgement for the related project). We chosen an integrated assessment developing and applying an online coupled modeling system. This is a step forward, as using an offline coupled system could produce valuable information on the impact of emissions on atmospheric chemistry, however, the climate feedbacks trough radiation (e.g. on temperature) would remain unknown. This work thus involved large number of online simulations were the climate and chemistry were calculated simultaneously.

Regarding the presentation of all the concerning work, we have chosen the following approach. 1) first

we intended to present a paper that evaluates the “chemical” part of the results, leading to this paper. 2) the results concerning the climate impact of the chemical perturbations due to city emissions (ozone and aerosols) are planned for a follow-up paper currently being in preparation.

In accordance with the above, we decided to include the description of the modelling system in the first paper (this one), and, as this manuscript focuses on 'chemical' results, we also included the validation of the air-quality related output with surface measurements; unlike the meteorological model outputs, which will undergo evaluation in the follow-up paper mentioned before. We, however, admit that a better concept would have been to organize this two papers in a companion paper (Part II) with this manuscript as Part I.

The description of the modeling system and the validation is done in light of the performance of previous version of the coupled system RegCM3CAMx, which was detailed and thoroughly validated in our earlier study, Huszar et al. (2012). Many of the model discrepancies, especially regarding ozone, are found to be similar as in this earlier study, however, some improvements are also identified that can be attributed to better (1hour) time resolution of data exchange between the participating models (RegCM + CAMx). One major deficiency of this earlier work was the relatively large ozone bias which we tried to eliminate by using a larger domain for developing more realistic chemical boundary conditions for the inner (10 km x 10 km) domain. However, we admit that even choosing so, many of the ozone biases remained (although a bit smaller) and in future, time and space varying chemical boundary conditions have to be definitely used.

In Huszar et al. (2012), considering online coupled ozone and aerosols led to 1) a slight (but statistically significant) improvement in model performance regarding temperature 2) or to not significant improvement at all. We have earlier applied the model RegCM in many other studies at a same or similar set-up as here. Although these studies did not include online coupled chemistry and two-way interactions (as in this study), we can make an assumption that the climate impact of perturbed air-chemistry (mainly on radiation temperature) is small changing the RegCM's performance only a little (as seen in Huszar et al. 2012).

So, answering the reviewer's questions:

*What is the incentive to use an online model in this specific study instead of an offline?*

The goal which gave us an incentive to use an online coupled model was to quantify not only the chemical impact of urban emissions but also the simultaneous radiative feedbacks triggered by these chemical perturbations. This goal requires an integrated online coupled climate-chemistry model approach, chosen in this study.

*What will be the added value for having a computational expensive system to investigate emission/air quality issues? And more importantly: Is this model capable to reproduce accurately the state of the atmosphere?*

The added value is the possibility to calculate radiative feedbacks and impacts on temperature (and climate in general). We also assume, based on previous validation studies involving RegCM and CAMx that the capability of these models reproducing the state of the atmosphere (both meteorology and climate) is will not change significantly if coupling them online w.r.t case when they are coupled offline.

*Or we simply use a more sophisticated but less understood modeling system, undermining the quality of final results?*

Choosing an online coupled system was a requirement rather than an option, given what was mentioned above.

*Can you compare the evaluation performance of this modeling system with the offline system and support the use of the online?*

The performance of was compared to the previous version of the RegCM-CAMx coupled system published in Huszar et al. (2012) and a slight improvement is noted, which is attributed the improvements made in the upgraded version of RegCM-CAMx couple used in this study. We can further assume, that the calculated species concentrations in an offline couple would be very similar (at least in a climate sense) as, between an online and offline realization of the same run, only the meteorological driving conditions are different, but these are considered small in a 10 year average.

Technical comments:

*Reviewer's comment: Introduction is rather lengthy, could be shortened to reflect a literature overview on issues relevant to European emission/air quality.*

Authors' response: We shortened the introduction where it was possible (e.g. in the listing of studies from different cities).

*Reviewer's comment: Sections 4.1.1 to 4.1.4: These sections are very short and there is no attempt to explain the current findings. On the other hand, Section 5 "Discussion and conclusions" is a very lengthy one. My suggestion is to move parts of the S5 discussion into S4.1.1-S4.1.4 and try to provide some connections, between the findings that can be related (e.g. O3 biases with NOx biases).*

Authors' response: The reason, sections 4.1.1 to 4.1.4. (the validation) does not contain any explanation of the current findings is, that these sections are only presenting the results and all the related discussion/explanation is included in the Discussion and Conclusion section, which also connect findings concerning NOx and ozone biases. To make a paper more readable, we split the last section into pure Discussion (that contains all the explanation of the results and discussion of the findings) and the main conclusions are included into the Conclusion section.

*Reviewer's comment: My major concern is the poor O3 correlation. Eventually the invariant boundaries could be the problem? Authors can refer to literature and cite previous work reporting improvement of temporal correlations with the use of space/time variant BCs, and also explain, to which extent they believe that improving the BCs in their mother domain, could improve results in the nested central European domain. I think it should also be a priority for the modeling group to update the BCs in future versions.*

Authors' response: Indeed, we believe the time/space invariant BC conditions for large mother domain are the major source for ozone biases and low correlation. Recently, Akritidis et al. (2013) were investigating the impact of BC on the simulated ozone concentrations using the same two models as in our study (an offline couple of models RegCM and CAMx). They found a clear improvement in the correlation coefficient when using global chemistry model (ECHAM5/MOZART) based BC (which are thus time and space variant). Their correlation of monthly ozone values using time/space invariant BCs is 0.74 that compares very well to our value (0.77). Introducing the MOZART BCs, the correlations increased by often more than 0.1.

As a conclusion, we will focus on improving the BCs (taken from global model) in future simulations with the presented couple. We also included the comparison with this study in the Discussion section to provide additional explanation for ozone biases.

*Reviewer's comment: Also in the evaluation plan of the modeling system I think authors could include*

*some key meteorological parameters like temperature, radiation which strongly affect chemistry and emissions. May be it will be too much too add for the current manuscript that is already very lengthy, but I think is an important action, which need to be considered as a future action.*

Authors' response: As mentioned above, we would like to separate the presentation of chemistry (air-quality) and meteorology related results of the conducted experiments. We rely on previous validation experiments done by RegCM which showed that this model is capable of reproducing the mean state and variability of the atmosphere. However, the follow-up manuscript being in preparation will definitely contain a validation of the meteorological parameters, especially those related to radiation (radiative fluxes, temperature etc.).

*Reviewer's comment: Discussion and conclusions could be separated. Conclusions could be a short paragraph summarizing the most basic findings of this work and eventually future steps to improve the methodology followed.*

Authors' response: We separated the last section into a Discussion section which now only discusses and explains the results (also in the light of previous studies). The Conclusion section then contains the main conclusions of the study with future steps to improve the methodology used.

Reviewer's corrections were included in the revised manuscript.

#### References:

Akritidis D., P. Zanis, E. Katragkou, M. Schultz, I. Tegoulas, A. Poupkou, K. Markakis I. Pytharoulis, Th. Karacostas, Evaluating the impact of chemical boundary conditions on near surface ozone in regional climate–air quality simulations over Europe, *Atmospheric Research*, 134, 116–130, 2013.

Huszar, P., Miksovsky, J., Pisoft, P., Belda, M. and Halenka, T.: Interactive coupling of a regional climate model and a chemistry transport model: Evaluation and preliminary results on ozone and aerosol feedback, *Clim. Res.*, 51:59-88, 2012. doi: 10.3354/cr01054

#### **Reviewer #2**

*Reviewer's comment: The paper is well written, although a bit lengthy in the introduction and conclusions. I would recommend to move some of the discussion to the results section and reduce section 5 only to the main conclusions of the study and therefore gain some more space for the validation part to include maybe meteorology as an online-coupled model is used.*

Authors' response: As already responded to reviewer #1, the choice of online-coupled modelling system was required as we were interested not only on the emission impact on air-quality (or chemistry in general) but also in the simultaneous radiative feedbacks and impact on temperature (or climate in general). In this paper, we presented the 'chemical' part of the results, including a 'chemical' validation. In a follow-up paper, the focus will be on climate impact, i.e. the meteorological feedbacks (through radiation) will be presented and that manuscript will contains also a detailed validation of the meteorological fields, like temperature, radiation, precipitation etc. Our manuscript is lengthy and would become even more if meteorological output would be validated as well. We rely on previous performances of RegCM used in our studies showing satisfactory reproduction of the mean state and variability of the atmosphere.

*Reviewer's comment: One important technical comment is that the figure legends and axes would look much better and more readable if larger fonts are used.*

Authors' response: We enlarged the legends and the numbers describing the colorbars which were too

small in the original manuscript. The figures are now more readable, and if not, by zooming, more details appear, as they are saved and included in the manuscript in a high dpi (dots-per-inch).

Changes to the original manuscript: apart from minor corrections made following the reviewers comments, the most important changes include 1) The introduction was shortened a bit, 2) splitting the last section into two separated: Discussion, and, Conclusions. 3) additional explanation of the biases encountered in case of ozone, and its connection to NO<sub>2</sub> biases, included in the Discussion part. 4) enlarging fonts in the figures were it was necessary.

# On the long term impact of emissions from central European cities on regional air-quality

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**Abstract.** For the purpose of qualifying and quantifying the impact of urban emission from Central European cities on the present-day regional air-quality, the regional climate model RegCM4.2 was coupled with the chemistry transport model CAMx, including two-way interactions. A series of simulations was carried out for the 2001–2010 period either with all urban emissions included (base case) or without considering urban emissions. Further, the sensitivity of ozone production to urban emissions was examined by performing reduction experiments with  $-20\%$  emission perturbation of  $\text{NO}_x$  and/or non-methane volatile organic compounds (NMVOC).

The modeling system's air-quality related outputs were evaluated using AirBase and EMEP surface measurements showed reasonable reproduction of the monthly variation for ozone ( $\text{O}_3$ ), but the annual cycle of nitrogen dioxide ( $\text{NO}_2$ ) and sulfur dioxide ( $\text{SO}_2$ ) is more biased. In terms of hourly correlations, values achieved for ozone and  $\text{NO}_2$  are 0.5–0.8 and 0.4–0.6, but  $\text{SO}_2$  is poorly or not correlated at all with measurements ( $r$  around 0.2–0.5). The modeled fine particulates ( $\text{PM}_{2.5}$ ) are usually underestimated, especially in winter, mainly due to underestimation of nitrates and carbonaceous aerosols.

European air-quality measures were chosen as metrics describing the cities emission impact on regional air pollution. Due to urban emissions, significant ozone titration occurs over cities while over rural areas remote from cities, ozone production is modeled, mainly in terms of number of exceedances and accumulated exceedances over the threshold of 40 ppbv. Urban  $\text{NO}_x$ ,  $\text{SO}_2$  and  $\text{PM}_{2.5}$  emissions also significantly contribute to concentrations in the cities themselves (up to 50–70 % for  $\text{NO}_x$  and  $\text{SO}_2$ , and up to 60 % for  $\text{PM}_{2.5}$ ), but the contribution is large over rural areas as well (10–20 %). Although air pollution over cities is largely determined by the local urban emissions, considerable (often a few tens of %) fraction of the concentration is attributable

to other sources from rural areas and minor cities. For the case of Prague (Czech Republic capital), it is further shown that the inter-urban interference between large cities does not play an important role which means that the impact on a chosen city of emissions from all other large cities is very small. At last, is shown that to achieve significant ozone reduction over cities in central Europe, the emission control strategies have to focus on the reduction of NMVOC, as reducing  $\text{NO}_x$  (due to suppressed titration) leads often to increased  $\text{O}_3$ . The influence over rural areas is however always in favor of improved air-quality, i.e. both  $\text{NO}_x$  and/or NMVOC reduction ends up in decreased ozone pollution, mainly in terms of exceedances.

## 1 Introduction

Cities have significant environmental impact that follows primarily two pathways. They emit large amount of gaseous species and aerosols into air, having direct impact on the composition and chemistry of the atmosphere (Timothy and Lawrence, 2009) and harmful effect on the their population (Gurjar et al., 2010). Secondly, having specific mechanical, radiative, thermal, and hydraulic properties, urban surfaces affect meteorological conditions and therefore the climate (Lee et al., 2011; Huszar et al., 2014).

The first pathway has an indirect impact on the meteorology and climate as well. Certain gases and aerosols interact with radiation in the atmosphere, modifying the radiative and consequently the thermal balance resulting in temperature changes. Aerosols further interact with the clouds, changing their micro-physical and optical properties (Seinfeld and Pandis, 1998).

Emission from cities encompass the oxides of nitrogen ( $\text{NO}_x$ ), that are produced mainly during fossil fuel combus-

tion in road transportation and energy production. Carbon monoxide (CO) is a product of incomplete combustion and is dominantly emitted in African and Asian cities reflecting the older-than-average technologies used (Streets and Waldhoff, 2000). Non-methane volatile organic compounds (NMVOCs) are products of road transport and solvents use in North American and European cities; however in Africa and Asia, they originate mainly from domestic combustion (Denier van der Gon et al., 2010). SO<sub>2</sub> emissions are released mainly due to energy production and industry and they are relatively low in European cities.

Emissions of NO<sub>x</sub> and VOC are predominantly affecting photochemistry and depending on their ratio, the photochemical regime in and around cities is either NO<sub>x</sub>-controlled or VOC-controlled (Xue et al., 2014). When the concentrations of NO<sub>x</sub> are much higher than of VOCs (NO<sub>x</sub>-saturated case), the ozone (O<sub>3</sub>) formation is controlled by the changes of VOCs: ozone increases with increasing VOCs while if NO<sub>x</sub> increases, ozone decreases by titration. This regime is called VOC-controlled. On the other hand when VOCs/NO<sub>x</sub> ratio is high, ozone production depends on the change of nitrogen oxides: with increasing NO<sub>x</sub> concentration ozone increases as well and a NO<sub>x</sub>-controlled regime occurs (Sillman, 1999). The ratio NO<sub>x</sub>/VOC is usually high in North-American agglomerations, many eastern Asian cities and in European agglomerations like Athens, Paris, Milan or Berlin as well and ozone is usually titrated over these cities (Beekmann and Vautard, 2010). However, according to actual meteorological conditions, pollution from cities can be transported over large distances where the aged plume from the city mixes with additional VOC sources and can become NO<sub>x</sub> sensitive leading to ozone production (Beekmann and Derognat, 2003). The overall effect of city emissions on ozone production/destruction can further depend on model's resolution. Thunis et al. (2007), analyzing Berlin, Milan, Paris and Prague found that while models with large spatial step usually predict ozone production due to emissions from cities, high resolution modeling studies attribute VOC-controlled regime to cities that leads to ozone destruction.

...part of the introduction deleted here!!!!...

Emissions of gaseous pollutants from cities can further perturb the aerosol burden. Sulfur dioxide, nitrogen (di)oxide and ammonia emissions lead, in presence of water vapor, to formation of secondary inorganic aerosols: ammonium-sulfate-nitrate particles (Martin et al., 2004). The primary precursor for sulfate aerosol (PSO<sub>4</sub>) formation is sulfur dioxide. Barth and Church (1999) investigated the sulfate formation due to SO<sub>2</sub> originating from Mexico City and cities from southeastern China, still the largest SO<sub>2</sub> emitter regions nowadays. They found significant perturbation of the global sulfate aerosol burden due to these two regions and cities located therein. NO<sub>x</sub> emissions do not affect only photochemistry (and the consequent ozone formation/destruction) but also the formation of nitrate aerosol (PNO<sub>3</sub>). If the meteorological conditions are favorable, nitrate oxide emissions

from cities can enhance background nitrate aerosol levels significantly (Lin et al., 2010). Emissions of ammonia (NH<sub>3</sub>) from cities are an efficient contributor to formation of sulfate and nitrate aerosol (by forming ammonium-sulfates and ammonium-nitrates) and its importance in connection with cities emissions are studied recently by many (Behera and Sharma, 2010, and references therein). Generally, the thermodynamic system of ammonium-sulfate-nitrate-water solution is rather complicated and its equilibrium state is highly dependent on the initial ratio of SO<sub>2</sub>-NO<sub>x</sub>-NH<sub>3</sub> given by their emissions, and the governing meteorological conditions (Martin et al., 2004), thus the contribution of different cities to these particles can be very variable.

Finally, organic gaseous material (volatile, intermediate- and semi-volatile VOC) released from cities can contribute to formation of secondary organic aerosols and significantly enhance the total aerosol burden in urban, as well as the downwind environment, as showed by Paredes-Miranda et al. (2009), Hodzic et al. (2010) and Zhang et al. (2015).

Numerous studies were dealing with the impact of emissions from cities on air-quality over local, regional and even global scale. Many of them were based on measurements within and outside of the urban plumes from particular cities (Freney et al., 2014; Lin et al., 1996; Gaffney et al., 1999; Molina et al., 2010; Kuhn et al., 2010; Wang et al., 2006). There has been also model based effort to estimate the cities fingerprint on the atmospheric chemistry across multiple scales: on global scale, Lawrence et al. (2007), Butler and Lawrence (2009), Folberth et al. (2010) and Stock et al. (2013) gave estimates on the city emissions impact on the surrounding environment. On regional scales, many studies focused on European urban centers, especially those in the Mediterranean region (e.g. Im et al., 2011a, b; Escudero et al., 2014; Finardi et al., 2014), but also covering London and the Ruhr area (Hodneborg et al., 2011), or Paris (Skylakou et al., 2014; Markakis et al., 2015). The importance of multi-model modelling approach for investigating the megacities impact on air-quality and climate was analyzed in detail by Baklanov et al. (2010) in the framework of the European FP7 project MEGAPOLI. Within another European project, FP7 project CITYZEN, Im and Kanakidou (2012) investigated the impact of emissions from eastern Mediterranean megacities, Athens and Istanbul.

Here we present a study that is inspired by a wider effort to describe quantitatively the urban/climate/air-quality interactions over the target area of central Europe. Previously, Huszar et al. (2014) presented the impact of urban landsurface forcing on climate. Here, we link to this study and look at a further aspect of the urban impact on environment: we aim to provide a chemistry transport model based estimate of the long term impact of emissions from cities in central Europe on the regional air-quality. The study brings four novelties: (1) the above listed studies over Europe focused either on the region of Mediterranean, which encounters dry warm climate, and/or on large megacities only (London, Paris, Is-

tanbul, Athens). In contrary, our target region is central Europe with different climate (temperate maritime to continental) and without any megacity. (2) Previously, model based estimates of urban emission impact over Europe considered relatively short time periods (1–2 months) often separately for winter and summer seasons (e.g. Im et al., 2011a; Im and Kanakidou, 2012; Finardi et al., 2014). These periods are however short to eliminate the potential influence of specific meteorological conditions during those time periods. Therefore, we have proposed to conduct continuous, 10 yr long simulations which decreases the uncertainty originating in the driving meteorological conditions. This choice was preferred also by Katragkou et al. (2010) and Zanis et al. (2011) or Markakis et al. (2015) (3) Most of the above listed regional studies focused on only one or two megacities (and their impact). Here we consider all large city within the region in focus. This is an important step, as the combined impact of emissions from all cities may, due to chemical nonlinearities, significantly differ from the cumulative impact evaluated separately for each city. (4) Our study evaluates the impact on policy relevant metrics that include also exceedances above a threshold, instead of evaluating simply seasonal averages that often lack information on extreme pollution.

The study has two main goals: (1) to evaluate the present-day contribution of city emissions to the regional air pollution over central Europe. (2) To calculate the potential impact of mitigation strategies by testing the regional fingerprint of urban emissions reductions. The possible climate impact of the presented urban-induced chemical perturbation of the atmosphere will be addressed as well in future paper. Within the first goal, the study tries to answer two questions: (a) what is the contribution of urban emissions to the air-quality over rural areas further from cities, (b) to what extent is the urban air-quality influenced by non-urban emissions. Regarding the second goal, the question asked is which urban emission reductions are the most effective in controlling regional scale ozone pollution.

The impact will be evaluated in terms of surface concentrations and exceedances of key gaseous pollutants ( $O_3$ ,  $NO_2$ ,  $SO_2$ ) and fine aerosol (size  $< 2.5 \mu m$ ,  $PM_{2.5}$ ).

## 2 Emissions

Emissions used in the study are the TNO emissions prepared for year 2005 in the framework of the FP 7 MEGAPOLI project (Kuenen et al., 2010). This high resolution ( $1/8^\circ$  longitude  $\times$   $1/16^\circ$  latitude, roughly  $7 km \times 7 km$ ) European emission database provides annual emissions estimates for  $NO_x$ ,  $SO_2$ , NMVOC,  $CH_4$ ,  $NH_3$ , CO and primary  $PM_{10}$  and  $PM_{2.5}$  in 10 source sectors.

For the purpose of calculating the impact of urban emissions, emission mask had to be built for selected cities. These were built according to the administrative borders of the particular city in combination with the subgrid urban land-

surface data used in Huszar et al. (2014), originally extracted from the Corine2006 database (EEA, 2012). The selection of certain cities, in general, comprises cities considered to be large within the particular region. As such we chose the threshold of 500 000 inhabitants representing a “large” city. This threshold was reduced to 200 000 inhabitants over selected regions (Czech Republic, Slovakia, Hungary, Romania, partly Poland, Austria, Italy). Figure 1 presents the distribution of the annual emissions over selected cities for the main pollutants: CO, NMVOC,  $NO_x$ ,  $NH_3$ ,  $SO_2$  and  $PM_{2.5}$ . It clearly reveals the emission density differences between the urban centers and suburban areas and that the emissions are mostly comprised of CO,  $NO_x$  and NMVOC, which can reach 500, 100 and  $100 Mg km^{-2} yr^{-1}$ , respectively, especially in urban centers.

Figure 2 plots the absolute annual emissions for the whole domain, for all the cities and for six selected cities (namely, Vienna, Budapest, Berlin, Prague, Munich, Warsaw). The plot shows that in most of the sectors, urban emissions form roughly 10 % of all emissions, while they cover slightly more than 3.5 % of the area of the focused region. The sector to which they contribute less is the agriculture where they emit less than 0.5 % of all emissions.

In general, road transportation is the sector contributing most to urban emissions, followed by non-industrial combustion in Central Europe. However, large differences are identified between cities. While emissions from sector SNAP 8 that include ship and airport traffic are generally small, in selected cities with major international airports or intense vessel traffic (on rivers), these can be of comparable magnitude with the road transportation (e.g. Munich), or even exceed road traffic (Vienna).

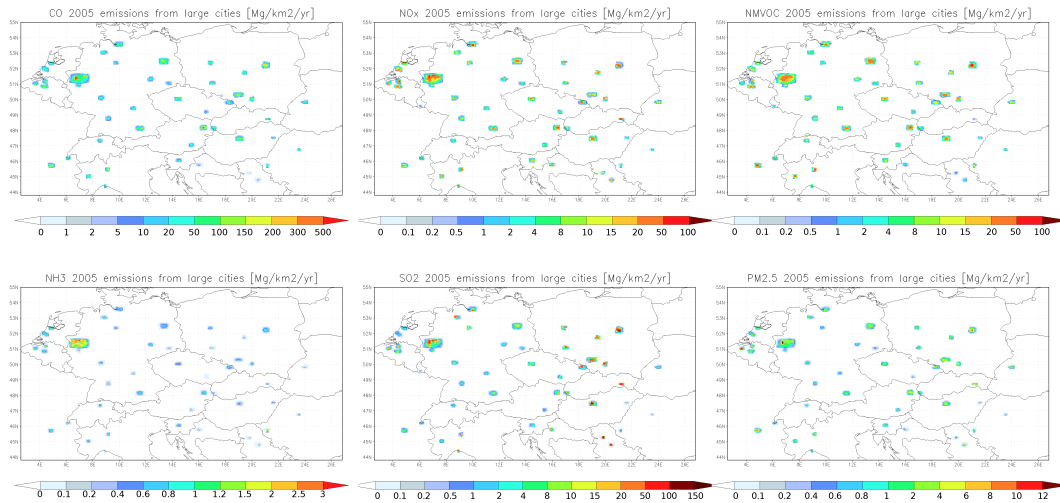
The most contributing substance to city emissions is carbon monoxide with an approximately 56 % contribution (in mass units) in average, followed by  $NO_x$  and NMVOC both with around 14 %.  $SO_2$  makes 12 % of all the city emissions in average, being somewhat higher in eastern European urban centers (almost 20 % in Budapest, and 18 % in Warsaw).

## 3 Models and experimental design

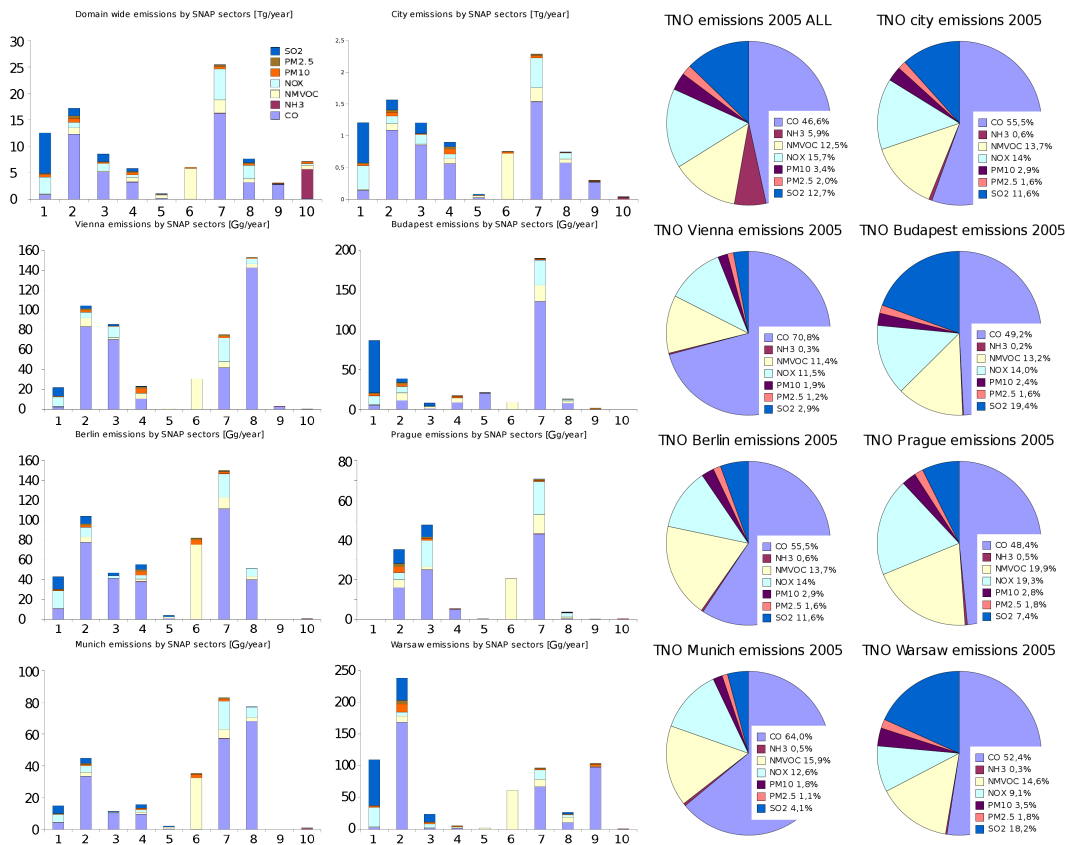
### 3.1 The regional climate model RegCM4.2

As a meteorological driver, we used the regional climate model RegCM version 4.2 (hereafter referred to as RegCM4.2) developed by The International Centre for Theoretical Physics. Although the up-to-date version of RegCM is 4.5 (June 2015), the development of the modeling tools for this study started earlier when the newest version was 4.2. RegCM4.2 and its evolution from RegCM3 is fully described by Giorgi et al. (2012). Its dynamical core is based on the hydrostatic version of the NCAR-PSU Mesoscale Model version 5 (MM5) (Grell et al., 1994). The radiation is solved





**Figure 1.** Annual emissions from the cities considered in the study based on the TNO MEGAPOLI 2005 emissions as  $\text{Mg km}^{-2} \text{yr}^{-1}$  for CO, NO<sub>x</sub>, NMVOC, NH<sub>3</sub>, SO<sub>2</sub> and PM<sub>2.5</sub>.



**Figure 2.** First two columns: annual emissions (2005) per sector for the entire domain in  $\text{Tg yr}^{-1}$ , for all the cities in  $\text{Tg yr}^{-1}$  and for six selected cities from the domain in  $\text{Gg yr}^{-1}$ . Right two columns: the same as the first two one, but for the relative contribution of individual pollutants in %.

within the Community Climate Model version 3 (CCM3) (Kiehl et al., 1996). The large-scale precipitation and cloud processes are calculated following Pal et al. (2000) and for convection parameterization we use the Grell scheme (Grell, 1993) using the Fritsch and Chappell (1980) closure assumption in this study. RegCM4.2 includes two land-surface models: Biosphere–Atmosphere Transfer Scheme (BATS) originally developed by Dickinson et al. (1993) and the CLM3.5 model (Oleson et al., 2008). In this study, the BATS scheme is activated. The single layer urban canopy model coupled to RegCM4.2 introduced by Huszar et al. (2014) was not applied assuming that the urban-meteorological influence on the emissions impact will be minor and further, to meet the computational demand of long climate simulations.

### 3.2 The chemistry transport model CAMx

The chemistry simulations were carried out with the chemistry transport model CAMx (version 5.4). CAMx is an Eulerian photochemical dispersion model developed by ENVIRON Int. Corp. (<http://www.camx.com>). CAMx includes the options of two-way grid nesting, multiple gas phase chemistry mechanism options (CB-IV, CBV, CBVI, SAPRC99), evolving multi-sectional or static two mode particle size treatments, wet deposition of gases and particles, plume-in-grid (PiG) module for sub-grid treatment of selected point sources, Ozone and Particulate Source Apportionment Technology, mass conservative and consistent transport numerics, parallel processing. The ISORROPIA thermodynamic equilibrium model (Nenes and Pandis, 1998) is implemented in CAMx to calculate the composition and phase state of an ammonia-sulfate-nitrate-chloride-sodium-water inorganic aerosol system in equilibrium with gas phase precursors. A detailed description of the model (the version used here) can be found at [http://www.camx.com/files/camxusersguide\\_v5-40.pdf](http://www.camx.com/files/camxusersguide_v5-40.pdf).

### 3.3 The coupled model RegCMCAMx4

To achieve the goals of the study, a coupled system was designed consisting of RegCM4.2 and CAMx (denoted RegCMCAMx4) following the technique of online access coupling defined by Baklanov (2010). It represents an interactive two-way coupled modeling framework where chemistry is driven by the climate model and the calculated concentrations of the radiatively active gases and aerosols are fed back to the climate model's radiation code.

RegCMCAMx4 is more advanced version of the original RegCMCAMx couple described by Huszar et al. (2012). The update interval for the meteorology from RegCM remained 1 h which is sufficient (Grell and Baklanov, 2011). However, the original update interval for the species in the radiation code of 6 h was too coarse for describing the diurnal species evolution, therefore it has been reduced to 1 h as well. The original RegCMCAMx considered only the direct effect

of sulfates and primary organic and black carbon. RegCM-CAMx4 introduces the indirect effect of secondary inorganic aerosols (both sulfates and nitrates). For sulfates, it follows the work of Giorgi and Qian (2003) where the cloud droplet concentration and effective droplet radius is modified according to the aerosol concentration. For nitrates both direct and indirect radiative effects are computed with the same method as for sulfates but with slightly modified optical properties following the works of McMeeking et al. (2005) and Wang et al. (2010).

RegCMCAMx4 further replaces the O'Brien (1970) method for calculating the coefficients of vertical turbulent diffusion (which is required by CAMx) with the newer Byun (1999) scheme (as used in CMAQ model), which provides better agreement of model results with measurements, as shown by Eben et al. (2005) in a CAMx application over the same region and at similar horizontal resolution like in this study.

### 3.4 Experimental set-up

The period of 2001–2010 was chosen to analyze the present day impact of urban emissions on the air-quality over central Europe. Calculation with RegCMCAMx4 were carried out on 10 km × 10 km horizontal resolution domain centered over Prague, Czech republic of 160 × 120 × 24 (in  $x$ ,  $y$ , and  $z$  direction) gridboxes for the climate model up to 50 hPa, while the chemistry model was integrated only on the lowest 16 levels (approximately up to 300 hPa or 9000 m). The integration time step for the climate model was 30 s and 10 min for the chemistry model.

The ERA Interim reanalysis (Simmons et al., 2010) was chosen as driving meteorological conditions while for the chemical model, chemical boundary conditions (CBC) were taken from a similar 10 year run performed by RegCM-CAMx4 over a larger, 30 km × 30 km domain covering whole Europe.

As already mentioned, the TNO 2005 emissions were chosen to cover the studied period. Over the focused region, their resolution is about 7 km × 7 km, so sufficient for a 10 km × 10 km computational grid. TNO are sector based annual emission data were first regridded into the model grid. Then for each sector, specific temporal disaggregation factors and NMVOC speciation profiles were used to decompose the annual sums into hourly emissions following the inventory (Winiwarter and Zueger, 1996). The temporal profiles they provide were compiled to describe typical central European human activity profiles regarding transport, combustion, production etc. Biogenic emission of isoprene and monoterpenes were calculated following Guenther et al. (1993).

A number of experiments was carried out to examine the effect of city emissions on the regional air quality. These are summarized in Table 1. The total impact of all city emissions is evaluated as the difference between experiments 05BASE and 05ZERO (the "05" means that the 2005 emis-

**Table 1.** Summary of the conducted experiments including the experiment name, the time period, the emissions considered and whether radiative feedbacks on meteorology are considered.

Experiment	Period	Emissions	Radiative feedbacks
05ZERO	2001–2010	All except cities	yes
05BASE	2001–2010	All	yes
05ZEROPRAGUE	2001–2010	Urban emission only from Prague	yes
0580NO <sub>x</sub>	2005–2009	80 % urban NO <sub>x</sub> emissions	no
0580NMVOC	2005–2009	80 % urban NMVOC emissions	no
0580N80 V	2005–2009	80 % urban NO <sub>x</sub> and NMVOC emissions	no

sion were used). We were also interested in the impact the emissions from all other cities have on a selected city. To achieve this goal, we performed a run where all city emissions are removed except those from Prague. Apart from the total impact, it is also of interest to see how the individual species emitted contribute to the overall impact. We therefore evaluate also the partial impact of major gaseous pollutants, namely NO<sub>x</sub>, NMVOC. As the interest of policy makers is to estimate the consequences of possible emission reduction in present day cities, we propose to evaluate this partial impact in a framework of a sensitivity test where the emissions of the above mentioned pollutants will be reduced by 20 %. For the sensitivity runs, no radiative feedbacks were calculated and the same meteorological conditions were thus used as a driver for these simulations. **The assumption here made was that the main driver for the air-quality changes are emissions, as the meteorological impact of the online coupled ozone and aerosols are expected to be small.**

## 4 Results

### 4.1 Model validation

In order to justify the model's applicability for the presented goal, a detailed quantitative validation is provided for surface concentrations of O<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub> and PM<sub>2.5</sub>. The validation of the meteorological results is planned in a follow-up study, which intends to present the meteorological feedbacks of the presented chemical perturbation induced by urban emissions. For the chemical validation, the AirBase version 8 data (<http://www.eea.europa.eu/data-and-maps/data/airbase-the-european-air-quality-database-8>) provided by the European Environmental Agency, is used. We selected only rural background stations which are more consistent with the model provided value that represents a 10 km × 10 km average. Further the stations are filtered to exclude high elevation stations (above 2000 m). In the end, 328 stations for O<sub>3</sub>, 280 for NO<sub>2</sub>, 200 for SO<sub>2</sub> and 53 for PM<sub>2.5</sub> were selected for comparison with model results. For the gaseous pollutants, hourly, daily and monthly averages are considered while for aerosols only daily and monthly data. The validation is done separately for winter (DJF), summer (JJA) months and for the whole year. The

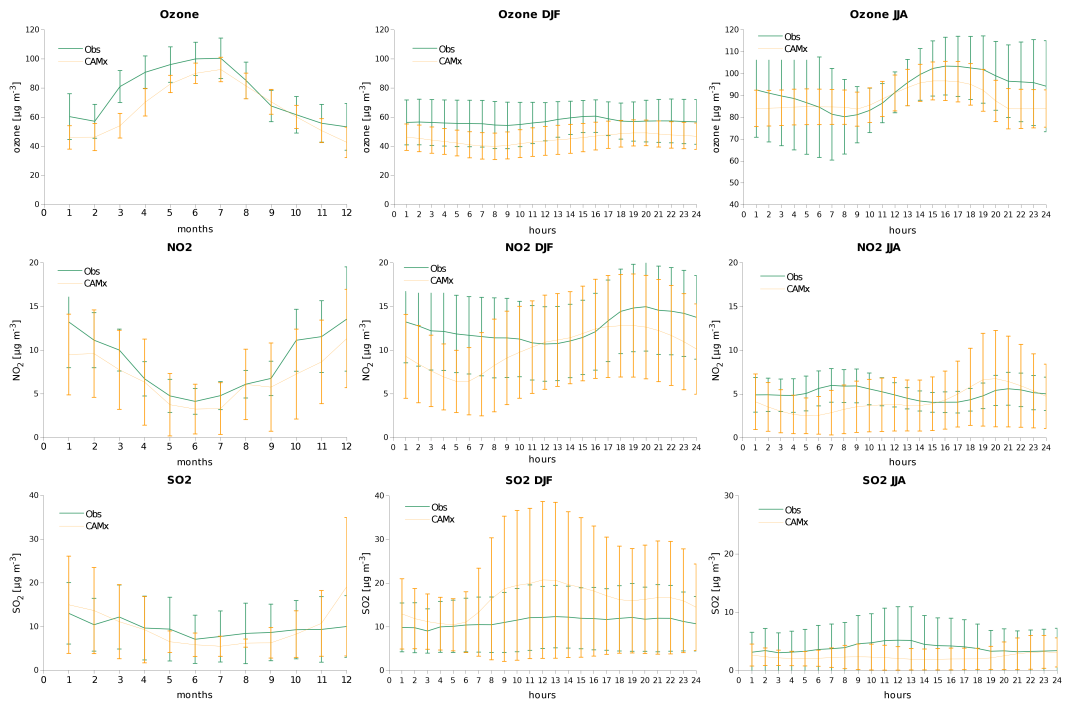
statistical measures evaluated were the correlation coefficient ( $r$ ), root mean square error (RMSE), normalized mean square error (NMSE), the ratio of standard deviations ( $\sigma_r$ , calculated as  $\sigma_{\text{observation}}$  divided by  $\sigma_{\text{model}}$ ) and fractional bias (FB), as defined by Borrego et al. (2008) and adopted by Juda-Rezler et al. (2012). They identified these metrics as the most important in assessing air-quality model accuracy. Choosing these metrics further ease the comparison of the RegCMCAMx4 model performance with its former version presented in Huszar et al. (2012) who applied the same metrics. The experiment 05BASE gave the base for the validation.

The above mentioned statistical measures are collected in Table 2 for O<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub> and PM<sub>2.5</sub>. 3-3-3 columns are dedicated for hourly, daily and monthly data averaged over the whole year, DJF and JJA, respectively.

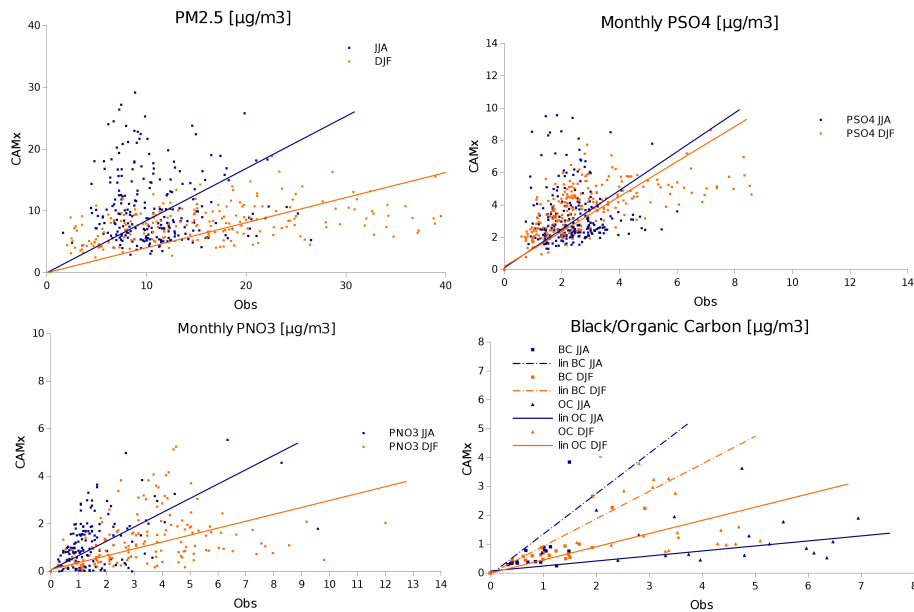
The average monthly and hourly cycles for DJF and JJA were selected, which provide measure of the model's ability to capture the basic chemical climatology of key-species concentrations. Figure 3 plots the average monthly variation (left column) of the gaseous species O<sub>3</sub>, NO<sub>2</sub> and SO<sub>2</sub>. The middle and right column provide the average diurnal cycle of these species for DJF and JJA, respectively.

Further, the monthly mean values of PM<sub>2.5</sub> and its major components were compared to observations (Fig. 4) distinguishing between DJF and JJA. For PSO<sub>4</sub> and PNO<sub>3</sub>, measurements from the already mentioned AirBase database were used. For carbonaceous aerosol, the monthly data from the BC/OC measurement campaign data described by Yttri et al. (2007) covering July 2002–June 2003 were used with the assumption that the basic climatology of these data is similar to the 2001–2010 average. These measurements considered BC/OC from PM<sub>10</sub> aerosol (size < 10 μm), our model (CAMx) that uses a two bin approach (fine and coarse particles), calculates them as fine particles (size < 2.5 μm). We applied the factor of 0.8 to the measured values to estimate the PM<sub>2.5</sub> fraction. This value is compiled from Chen et al. (1997), Offenberg and Baker (2000) and Samara et al. (2014) as an average of different seasons and character of the measurement site (cold vs. warm season and urban vs. rural).

We assessed the model bias further for urban stations as well, although it is well accepted that these stations are not suitable for standard chemistry transport model evaluation



**Figure 3.** Left column: comparison of the 2001–2010 mean monthly variation of O<sub>3</sub>, NO<sub>2</sub> and SO<sub>2</sub> averaged over all stations with vertical error bars indicating the standard deviation of the average. Middle column: comparison of the 2001–2010 DJF mean diurnal variation for the same species with error bars indicating the standard deviation of the average. Right column: same as middle column but for summer months (JJA).



**Figure 4.** Comparison of monthly values of PM<sub>2.5</sub> and its major components (sulfate-, nitrate aerosol, black and organic carbon) for DJF (orange) and JJA (dark blue) months. For carbonaceous aerosol, square stands for BC and triangle for OC. Linear trend lines are also shown.

**Table 2.** Comparison of model data with measurements: evaluation of the correlation coefficient ( $r$ ), root mean square error (RMSE; in  $\mu\text{g m}^{-3}$ ), normalized mean square error (NMSE), the ratio of standard deviations ( $\sigma_r$ ) and fractional bias (FB; in %) for hourly, daily and monthly averages for winter (DJF) and summer (JJA) months and for the whole year (“annual”) for pollutants O<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub> and PM<sub>2.5</sub>. For PM<sub>2.5</sub>, no hourly data were available.

Ozone									
	Annual	hourly DJF	JJA	Annual	daily DJF	JJA	Annual	monthly DJF	JJA
$r$	0.569	0.408	0.533	0.671	0.485	0.621	0.770	0.610	0.700
RMSE	32.073	28.880	33.903	25.207	24.586	24.245	18.411	17.253	16.392
NMSE	0.301	0.510	0.196	0.185	0.369	0.100	0.097	0.182	0.045
$\sigma_r$	1.174	1.167	1.303	1.063	1.184	1.067	1.072	1.327	1.095
FB	-4.3	-16.4	-2.3	-4.3	-16.3	-2.3	-4.4	-16.1	-2.1
NO <sub>2</sub>									
	Annual	hourly DJF	JJA	Annual	daily DJF	JJA	Annual	monthly DJF	JJA
$r$	0.451	0.409	0.342	0.547	0.466	0.464	0.683	0.590	0.618
RMSE	15.940	19.073	13.190	12.745	15.871	10.042	8.906	10.746	7.245
NMSE	1.282	1.005	1.925	0.816	0.697	1.116	0.403	0.320	0.592
$\sigma_r$	0.839	1.004	0.639	0.854	1.039	0.612	0.870	1.053	0.633
FB	-14.8	-23.7	-10.5	-14.8	-23.5	-10.4	-14.4	-21.3	-10.4
SO <sub>2</sub>									
	Annual	hourly DJF	JJA	Annual	daily DJF	JJA	Annual	monthly DJF	JJA
$r$	0.305	0.292	0.255	0.397	0.361	0.363	0.579	0.532	0.492
RMSE	15.086	27.155	9.730	11.346	21.694	7.648	12.409	14.950	5.787
NMSE	6.436	6.683	8.531	2.822	2.102	5.244	7.065	7.515	2.956
$\sigma_r$	0.670	0.749	2.517	0.645	0.747	2.406	0.641	0.721	2.362
FB	20.0	51.1	-36.1	19.0	50.9	-35.9	19.7	49.9	-35.7
PM <sub>2.5</sub>									
	Annual	hourly DJF	JJA	Annual	daily DJF	JJA	Annual	monthly DJF	JJA
$r$	-	-	-	0.374	0.409	0.313	0.419	0.458	0.376
RMSE	-	-	-	21.209	30.675	15.488	15.871	22.805	9.891
NMSE	-	-	-	2.825	4.948	1.695	1.578	2.836	0.725
$\sigma_r$	-	-	-	1.886	3.396	0.447	1.783	3.690	0.492
FB	-	-	-	-52.5	-92.6	18.3	-49.0	-90.2	16.2

(at such resolution as in this study). We selected 10 urban background stations for Berlin, Budapest, Frankfurt, Katowice, Ljubljana, Milan, München, Prague, Vienna and Warsaw. The same statistical metrics were chosen as above but only for hourly (daily) averages for gases (particle matter). The results are collected in Table 3.

#### 4.1.1 Ozone

The correlations of modeled ozone data with measurements are highest for the monthly means reaching 0.77 when considering the whole period. It is generally lower in DJF than during JJA and decreases for shorter averaging periods. For the hourly means, it is about 0.57 for the whole period, and about 0.41 and 0.53 for DJF and JJA. Relatively high RMSE and NMSE values are modeled for the hourly values and get smaller for longer averaging period (around  $17 \mu\text{g m}^{-3}$  for the monthly means). The ratios of standard deviation are slightly higher than 1 indicating that the measured ozone values have higher variability than the modeled ones. In terms of fractional bias, the model underestimates ozone for both DJF

and JJA (FB being around  $-16$  and  $-2\%$ ) giving an overall underestimation of  $\text{FB} = -4.3\%$  for the whole period.

The negative ozone bias is clearly seen in terms of the monthly means and is highest during early spring ( $-20 \mu\text{g m}^{-3}$ ) and reaching almost zero during August, September and October. On an hourly basis, the model is always negatively biased in DJF (by  $10\text{--}15 \mu\text{g m}^{-3}$ ) showing minimum diurnal variations (in accordance with the measurements). During JJA, the model reasonably captures the timing of the ozone daily maximum values but underestimates the daily amplitude by giving smaller daytime peak values by almost  $20 \mu\text{g m}^{-3}$ .

The correlations for individual cities are lower in general but the RMSE are of similar value. FBs indicate a slight overestimation in JJA, in contrary with the rural station values. The DJF negative bias is stronger for urban stations than for their rural counterparts.

#### 4.1.2 Nitrogen dioxide

The modeled NO<sub>2</sub> values are less correlated with the measured ones than in case of ozone. Again, they are highest for

**Table 3.** Comparison of model data with measurements: city based evaluation of the correlation coefficient ( $r$ ), root mean square error (RMSE; in  $\mu\text{g m}^{-3}$ ), normalized mean square error (NMSE), the ratio of standard deviations ( $\sigma_r$ ) and fractional bias (FB; in %) for hourly (for gases) and daily (for  $\text{PM}_{2.5}$ ) averages for winter (DJF) and summer (JJA) months and for the whole year (“annual”) for pollutants  $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{SO}_2$  and  $\text{PM}_{2.5}$ .

	Ozone				$\text{NO}_2$				$\text{SO}_2$				$\text{PM}_{2.5}$							
	$r$	RMSE	NMSE	$\sigma_r$	FB	$r$	RMSE	NMSE	$\sigma_r$	FB	$r$	RMSE	NMSE	$\sigma_r$	FB	$r$	RMSE	NMSE	$\sigma_r$	FB
Vienna																				
Annual	0.55	35.04	0.64	1.17	-22	0.28	26.76	0.66	0.98	0	0.14	15.21	6.58	0.31	110	0.12	17.64	1.21	1.93	-49
DJF	0.22	28.09	1.10	1.16	-31	0.30	25.05	0.54	1.34	13	0.03	22.12	5.98	0.35	116	0.18	26.26	1.91	3.07	-82
JJA	0.38	37.53	0.34	1.24	9	0.19	28.14	0.95	0.79	8	0.07	3.78	1.89	0.62	52	-0.03	10.07	0.64	0.63	-2
Prague																				
Annual	0.57	33.89	0.73	1.19	-26	0.25	24.37	0.65	1.02	0	0.26	20.12	4.32	0.34	111	0.04	19.97	1.81	1.73	-58
DJF	0.23	26.31	1.32	1.05	-37	0.30	22.93	0.46	1.31	-6	0.14	29.47	4.11	0.40	116	0.28	27.36	2.79	4.26	-90
JJA	0.48	35.49	0.35	1.26	12	0.13	24.55	1.07	0.85	-34	0.14	6.62	1.70	0.54	71	-0.04	14.76	1.13	0.47	-2
Frankfurt																				
Annual	0.70	28.22	0.31	1.25	-3	0.38	12.54	0.85	1.13	-29	0.23	10.42	2.97	0.41	66	0.05	23.51	2.58	2.21	-86
DJF	0.44	21.59	0.46	1.00	-13	0.34	14.25	0.58	1.05	-12	0.14	16.09	3.17	0.48	89	0.28	34.03	4.52	5.54	-113
JJA	0.60	29.79	0.18	1.45	4	0.12	10.51	1.37	1.37	-41	0.07	2.47	0.78	0.64	29	0.02	13.09	0.95	0.47	-19
Berlin																				
Annual	0.61	32.89	0.50	1.21	-12	0.33	17.30	0.93	0.86	-24	0.21	11.63	4.86	0.40	79	0.07	21.51	1.45	1.12	-45
DJF	0.44	24.95	0.76	1.08	-32	0.34	17.74	0.62	1.03	-19	0.17	17.10	4.48	0.39	95	0.15	26.15	1.69	2.02	-71
JJA	0.56	34.00	0.29	1.34	2	0.11	15.73	1.52	0.65	-34	0.06	3.79	2.62	0.93	10	0.12	14.15	1.54	0.74	-21
Münich																				
Annual	0.54	34.77	0.59	1.09	-20	0.20	32.94	1.09	1.25	-53	0.23	7.30	1.55	0.61	39	-0.03	16.41	1.07	0.91	-39
DJF	0.44	29.70	1.00	0.89	-37	0.27	38.81	1.38	1.58	-76	0.24	8.73	1.10	0.64	21	0.46	19.72	1.17	2.37	-79
JJA	0.50	36.98	0.33	1.09	16	0.16	27.51	0.94	0.98	-30	-0.04	4.71	0.94	0.45	23	-0.11	17.81	1.14	0.19	-26
Budapest																				
Annual	0.60	37.42	0.69	1.32	-6	0.22	30.26	1.09	1.47	-20	0.21	50.20	17.83	0.09	152	0.17	16.90	1.98	2.63	-72
DJF	0.30	26.90	1.43	1.32	-19	0.22	31.00	0.89	1.93	-23	0.05	82.63	18.06	0.08	164	0.07	25.35	2.57	4.08	-99
JJA	0.45	41.21	0.36	1.52	1	0.16	28.37	1.28	1.19	-14	-0.01	12.44	5.85	0.14	115	0.06	7.53	0.77	0.58	-11
Milan																				
Annual	0.62	41.15	1.09	1.21	-10	0.14	42.20	0.71	1.05	-6	0.45	41.17	5.76	0.26	132	0.15	38.93	2.08	3.10	-78
DJF	0.17	22.68	2.38	0.58	-29	0.22	41.84	0.50	1.55	-25	0.21	59.04	3.73	0.27	121	0.03	63.83	2.86	3.92	-115
JJA	0.39	51.86	0.51	1.28	9	0.22	47.44	1.52	0.64	-38	-0.08	16.38	4.91	0.34	130	0.05	11.96	0.62	0.61	-1
Katowice																				
Annual	0.62	34.30	0.85	1.22	-17	0.31	24.54	0.63	1.03	-8	0.31	69.92	3.65	0.37	105	-0.16	20.07	0.89	1.12	-25
DJF	0.32	23.37	2.03	1.15	-42	0.34	25.85	0.49	1.12	-3	0.14	94.40	2.73	0.44	97	0.00	18.97	0.51	2.24	-13
JJA	0.52	37.14	0.37	1.50	2	0.17	26.49	1.13	1.25	-24	0.09	28.17	2.95	0.39	100	-0.08	15.99	0.80	0.43	19
Warsaw																				
Annual	0.58	31.92	0.66	1.14	-11	0.28	23.79	0.76	1.14	-14	0.20	61.58	6.59	0.31	121	0.12	20.39	0.88	1.86	-43
DJF	0.35	24.70	1.17	1.11	-44	0.27	20.64	0.47	1.09	-2	0.05	86.24	5.10	0.36	118	0.13	26.03	1.25	2.83	-45
JJA	0.46	32.69	0.31	1.34	11	0.16	24.86	1.38	1.29	-36	0.04	22.29	4.86	0.35	105	-0.19	18.73	0.85	1.21	-57
Ljubljana																				
Annual	0.64	40.08	0.61	1.36	-33	0.36	21.94	0.94	1.44	-45	0.26	8.80	3.04	0.63	63	0.05	23.29	3.02	3.53	-104
DJF	0.11	31.75	1.29	1.22	-51	0.25	27.41	0.88	1.53	-49	0.12	12.70	1.99	0.65	54	0.02	37.13	4.42	6.10	-130
JJA	0.52	46.27	0.39	1.80	-31	0.21	17.14	1.05	1.30	-41	0.00	2.94	2.31	1.23	38	0.15	9.81	0.99	1.17	-68

the monthly means (0.68, 0.59 and 0.62 for the whole pe-  
 510 riod, for DJF and JJA months, respectively). The RMSE val-  
 ues are lower than for  $\text{O}_3$ , being highest for DJF and for the  
 515 hourly means (around  $19 \mu\text{g m}^{-3}$ ). The observation-model  
 agreement is in general best for JJA. However, during JJA,  
 the model exhibits much larger standard deviation than the  
 measured values, while during DJF, the ratio of standard de-  
 viations is close to 1. In general, the model tends to underes-  
 520 timate both DJF and JJA  $\text{NO}_2$  values with FB values around  
 -14.8, -23.7 and -10.5 % for all the months, for DJF and  
 JJA, respectively. This is also well described by the average  
 525 monthly and diurnal variation plots (Fig. 3, middle row): the  
 DJF  $\text{NO}_2$  values are underestimated by up to  $5 \mu\text{g m}^{-3}$  but  
 a fair agreement is modeled during late spring to early au-  
 530 tumn months with only a slight underestimation around 1–  
 2  $\mu\text{g m}^{-3}$ .

The diurnal course for DJF is captured in the model  
 as well, but it peaks around 18:00 UTC compared to  
 525 20:00 UTC in observations. The diurnal amplitude is of com-  
 parable magnitude due to both maximum and minimum val-  
 ues lower in model than in observations. Especially the night-  
 530 time  $\text{NO}_2$  values are underestimated during DJF (by more  
 than  $5 \mu\text{g m}^{-3}$ ). In JJA, the observations reveal two peaks,  
 in the morning and early evening hours, but the model re-  
 produces (although poorly) only the evening peak with an  
 535 overestimation around  $2 \mu\text{g m}^{-3}$ .

Similarly to ozone, the observation-model correlation for  
 individual cities is much smaller, or there is no correlation  
 at all. The model remains negatively biased but it is highest  
 for JJA. The variability in urban stations is much underesti-  
 mated, in opposite to the rural stations above.

### 4.1.3 Sulfur dioxide

The model results of  $\text{SO}_2$  are, in general, characterized  
 540 by a low correlation with measurements, especially for  
 the hourly averages. Highest correlations are achieved for  
 monthly values (over  $r = 0.5$ ). The RMSE values are high-  
 est for the hourly values and lowest for the monthly ones  
 indicating a better model-observation agreement in terms of  
 545 monthly means. The standard deviation of the modeled val-  
 ues is overestimated in DJF, however in JJA, the observed  
 standard deviations are more than two times higher than the  
 modeled ones. The FB values indicates that the DJF  $\text{SO}_2$  val-  
 ues are overestimated in DJF and underestimated in JJA (-50  
 and 55 %, respectively).

The overestimation of  $\text{SO}_2$  in DJF is apparent from the  
 average monthly and diurnal cycle in DJF (Fig. 3, bottom  
 left). The model predicts much larger concentrations than the  
 observed ones especially in December, and, in terms of the  
 hourly variation, during mid-day. During JJA,  $\text{SO}_2$  is under-  
 550 estimated by 2–3  $\mu\text{g m}^{-3}$ , especially during noon hours.

From an urban station perspective, the model is very poorly correlated with measurements (correlations not exceeding 0.4) and the values are strongly overestimated (often by more than 100 % in terms of FB) in both JJA and DJF, in contrary to model performance evaluated for rural stations.

#### 4.1.4 PM<sub>2.5</sub> and components

The modeled PM<sub>2.5</sub> values are low correlated with measurements, higher for monthly values and for DJF (up to  $r = 0.45$ ). In terms of RMSE and NMSE, the model performs better during JJA, especially for the monthly means. In DJF, the standard deviation of the observed values is largely underestimated by the model, while in JJA, only half of the observed variability is predicted. PM<sub>2.5</sub> is largely underestimated in DJF (with around -90 % fractional bias) and slightly overestimated in JJA (FB = 17 %). This is further well seen on the monthly scatter plot in Fig. 4 (upper row, left). The DJF values (orange) do not exceed  $20 \mu\text{g m}^{-3}$  in DJF in the model, while they often reach  $40 \mu\text{g m}^{-3}$  in observations. In JJA, the range of values is similar, but the correlations are low, as already seen in Table 2.

The monthly scatter plots of individual components of the PM<sub>2.5</sub> aerosol are plotted in Fig. 4 as well. A relatively good agreement is achieved for PSO<sub>4</sub> during DJF with values ranging in both measurements and model up to  $8 \mu\text{g m}^{-3}$ . However, sulfates are often over-predicted by the model in JJA. A different situation occurs for PNO<sub>3</sub>, where the model exhibits a negative bias, especially for DJF, when values often above  $6 \mu\text{g m}^{-3}$  are measured, in contrary with the modeled monthly values. The modeled BC and OC fractions of PM<sub>2.5</sub> are usually underestimated with a few exceptions. In case of OC, a slightly better agreement is achieved for DJF. In JJA, however, the model is unable to reproduce values over  $5 \mu\text{g m}^{-3}$ , often seen in measured data.

Over urban station, the model is very low correlated with measurements and tends to underestimate the fine particulate matter concentrations in JJA, in contrary to the rural stations. In terms of other metrics, the model performs similarly than over rural stations.

#### 4.2 Impact of city emissions on air-quality

The impact of urban emissions from large cities on the regional air quality is evaluated in terms of selected air quality measures. For quantifying the exposure of the ecosystems, particularly crops, to elevated ozone levels, a widely used measure, the accumulated exposure over the threshold (AOT), introduced by Fuhrer et al. (1997), can be used. In this study, we evaluated the present AOT for the threshold of 40 ppbv for crops and forests (AOT40crop/forest) where the integration is done from May to July and from April to September, respectively. Further, the number of exceedances above a certain threshold is evaluated for daily maximum 8 h running ozone mean, the hourly NO<sub>2</sub> and SO<sub>2</sub> and the

**Table 4.** The EC air-quality standards and AOT40 (in  $\mu\text{g m}^{-3}$  and ppbv h, respectively) for different averaging interval. (+): the average concentration is evaluated instead of the number of the exceedances. (-): no threshold value defined.

Averaging interval	O <sub>3</sub>	NO <sub>2</sub>	SO <sub>2</sub>	PM <sub>2.5</sub>
Hourly	-	200	350	-
Daily	120 (8 h max)	-	125	-
Annual	-	+	+	+
DJF	-	-	+	+
JJA	+	-	-	-
AOT (crop/forest) JJA	+	-	-	-

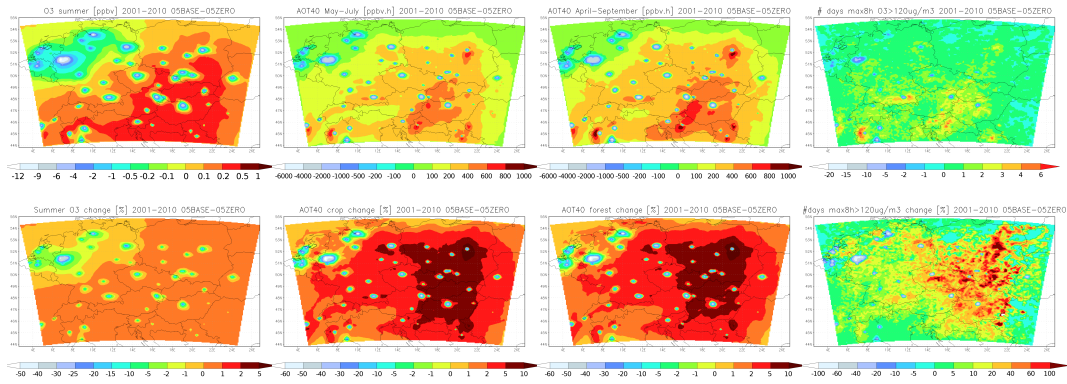
daily SO<sub>2</sub> values. Finally, the mean JJA O<sub>3</sub>, mean DJF and annual SO<sub>2</sub> and the mean annual PM<sub>2.5</sub> surface concentrations are considered. These measures are established in the EC Directive on ambient air quality and cleaner air for Europe (2008/50/EC) and are implemented also in the Czech legislation. These are summarized in Table 4.

In further, we will present the spatial distributions of the (1) absolute change of the chosen metrics by the introduction of city emissions (calculated as experiment 05BASE minus 05ZERO) and the (2) relative change which is calculated differently for ozone and for other pollutants. In case of ozone, which (as we will see in further) both increases and decreases, the change is shown relative to the no-urban emission case (05ZERO). For all other species, the change is shown relative to the all-emission case (05BASE), i.e. we are interested in the relative contribution. We also calculated the all-city-average of the maximum impact which coincide with the location of the cities themselves, summarized in Table 5.

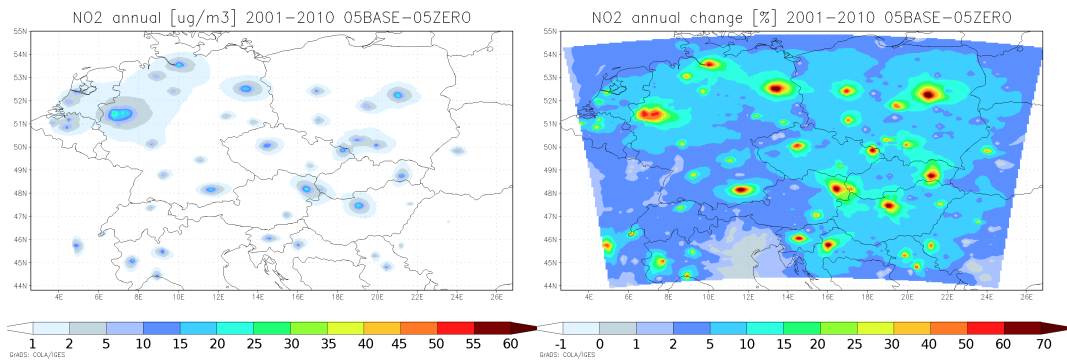
##### 4.2.1 Ozone

The impact of urban emissions on the average JJA surface ozone concentration (Fig. 5) is characterized by a clear reduction peaking over city centers from -4 ppbv over smaller cities up to -12 ppbv over western Germany urban agglomerations (e.g. Rhur area). This corresponds to more than 30 % ozone decrease. Further inland or over the southern part of the domain, the influence of city emissions is smaller in relative sense with change around -20 % while the city influence peaks around -4 to -6 ppbv. Over rural regions, JJA ozone tends to decrease slightly for the western part of the domain. However, over southern and eastern part of the domain, the mean JJA ozone concentrations increase due to city emissions by up to 0.5 ppbv, representing an 1 % increase. The average decrease over cities is  $-5.1(\pm 3.3)$  ppbv, or  $-34.1(\pm 18.3)$  %.

The impact on AOT40 values are, similarly to the JJA average ozone, characterized by a significant decrease over and around cities up to -4000 ppbv h (for both impact on crops and forests) or -40 to -60 % in relative sense. An opposite impact is modeled over areas neighboring or even



**Figure 5.** Impact of city emissions on ozone related air-quality measures listed in Table 4. Upper row presents the absolute change averaged over 2001–2010. The lower row corresponds to the change relative to the zero urban emission case (05ZERO).



**Figure 6.** Impact of city emissions on the annual  $\text{NO}_2$  concentration. Left figure presents the absolute change averaged over 2001–2010, while the relative contribution due to city emissions is shown on the right.

further from cities. City emissions increase AOT40 values up to 600 ppbv h over many regions, meaning an 5–10 %. In the vicinity of many cities (Milan, Zagreb, Warsaw), the both AOT40s increase by up to 1000 ppbv h while the above mentioned decrease occurs just a few 10 kms towards the city center. The averaged decrease over cities is  $-1800(\pm 1300)$  ppbv h or  $-29.1(\pm 18.3)$  % for crops and  $-2460(\pm 1800)$  or  $-30.7(\pm 18)$  for forests, respectively.

A similar picture to previous ones is obtained when evaluating the number of days with maximum 8 h ozone greater than  $120 \mu\text{g m}^{-3}$ . City emissions clearly decrease this number over and near cities (by up to  $-15 \text{ days yr}^{-1}$ ), but further from them, the increase of extreme ozone days is evident (up to  $6 \text{ days yr}^{-1}$ ). This corresponds to from 10 % increase over many parts of western Europe up to more than 40 % enhancement in central Europe with selected regions encountering even higher, up to 100 % increase. The all-city-average decrease of the number of exceedances was calculated to  $-2.9(\pm 4.0)$  or  $-28.7(\pm 39.8)$  %.

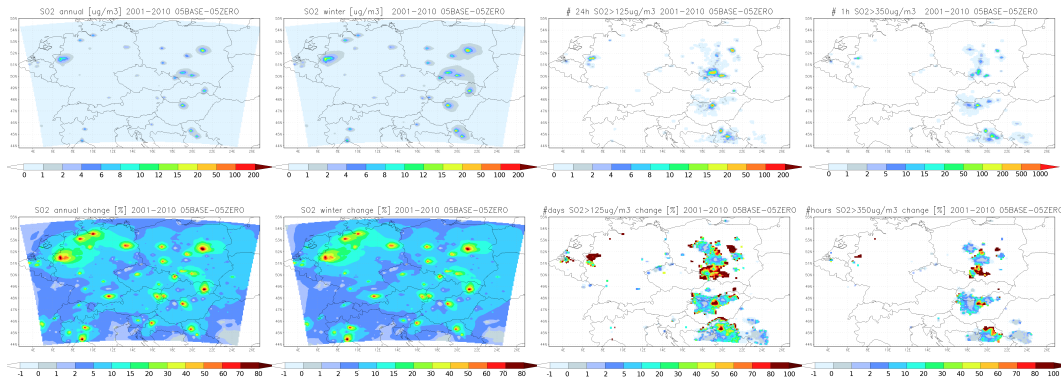
#### 4.2.2 Nitrogen oxides

Due to systematic negative bias the model was unable to predict exceedances over  $200 \mu\text{g m}^{-3}$ , therefore only the impact of city emissions on the annual  $\text{NO}_2$  concentration is shown (Fig. 6). The annual mean change can be as high as  $30 \mu\text{g m}^{-3}$  over the cities themselves, making around 50 % contribution to the absolute values over the western part of the domain, while over Central European cities (e.g. Berlin, Warsaw, Vienna, Budapest) it can reach 70 %. Over areas further from cities, the contribution quickly decreases making less than 10 % of the absolute  $\text{NO}_2$  values but remaining above 5 % over much of the domain. Comparing the absolute  $\text{NO}_2$  change over cities and the JJA ozone decrease in previous figure it is clear that larger urban  $\text{NO}_2$  perturbation the more pronounced is the ozone suppression. Indeed, linear fit between these two quantities (the plot not shown here) has a coefficient of determination  $R^2 = 0.86$  indicating a strong link. The averaged urban induced  $\text{NO}_2$  increase over cities is  $12.8(\pm 6.8) \mu\text{g m}^{-3}$ , corresponding to  $42.7(\pm 18.3)$  % contribution to the total value.



**Table 5.** The averaged maximal impact of urban emission on air-quality (in terms of the quantities from Tab. 4) over cities. The 2nd and the 5th column stands for the absolute impact, the 3rd and the 6th column for the relative impact (for ozone related quantities) and contribution (for other species). The standard deviation of the all-city-average is included as well.

measure	absolute change	relative change [%]	measure	absolute change	relative change [%]
O <sub>3</sub> JJA [ppbv]	-5.1(± 3.3)	-34.1(± 18.3)	SO <sub>2</sub> annual [ $\mu\text{g}\cdot\text{m}^{-3}$ ]	14.6(± 16.7)	41.4(± 24.4)
AOT40crop [ppbv.h]	-1800(± 1300)	-29.1(± 18.3)	SO <sub>2</sub> winter [ $\mu\text{g}\cdot\text{m}^{-3}$ ]	21.8(± 26.0)	38.6(± 23.8)
AOT40forest [ppbv.h]	-2460(± 1800)	-30.7(± 18)	SO <sub>2</sub> over 125 $\mu\text{g}\cdot\text{m}^{-3}$	8.6(± 18.9)	40.1(± 44.8)
O <sub>3</sub> over 120 $\mu\text{g}\cdot\text{m}^{-3}$	-2.9(± 4.0)	-28.7(± 39.8)	SO <sub>2</sub> over 350 $\mu\text{g}\cdot\text{m}^{-3}$	15.1(± 43.0)	23.8(± 40.0)
NO <sub>2</sub> annual [ $\mu\text{g}\cdot\text{m}^{-3}$ ]	12.8(± 6.8)	42.7(± 18.3)	PM <sub>2.5</sub> [ $\mu\text{g}\cdot\text{m}^{-3}$ ]	4.2(± 3.7)	24.3(± 12.8)



**Figure 7.** Impact of city emissions on SO<sub>2</sub> related air-quality measures listed in Table 4: upper row shows the absolute change, the lower row the relative contribution from the urban emissions.

### 4.2.3 Sulfur dioxide

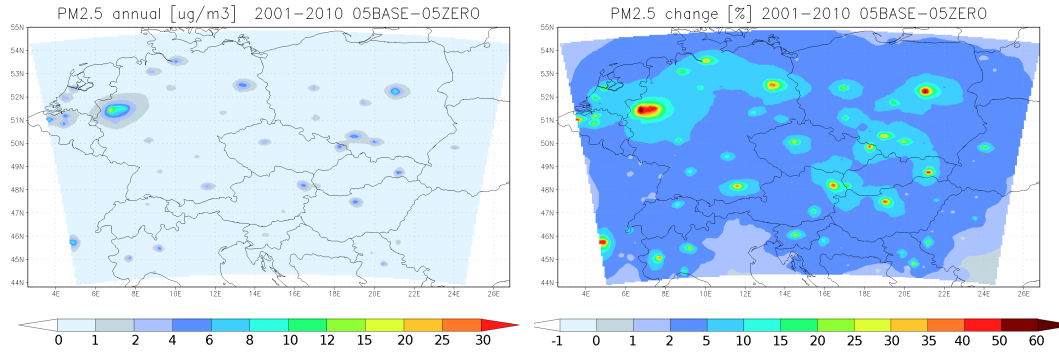
Figure 7 shows the impact on SO<sub>2</sub>. The annual mean increase due to city emissions reaches 50  $\mu\text{g}\cdot\text{m}^{-3}$  over Eastern European cities and can be as high as 12  $\mu\text{g}\cdot\text{m}^{-3}$  over Western European cities (e.g. the Ruhr area). In relative manner, the contribution peaks at 80 % and is above 70 % over many cities all over the domain. However, it can stay higher even further from the cities: over large parts of northern Germany, the contribution to the annual SO<sub>2</sub> values is between 10 and 20 %. A similar picture is revealed when looking at the DJF SO<sub>2</sub> impact with up to 20  $\mu\text{g}\cdot\text{m}^{-3}$  increase over the cities themselves giving relative contribution of similar magnitude as in case of the annual means (up to 80 % in cities). The all-city-average increases of annual and winter values are 5.5(±6.3) and 8.2(±9.8)  $\mu\text{g}\cdot\text{m}^{-3}$ , or, 41.4(±24.4) and 38.6(±23.8) % as contributions, respectively.

The urban emissions contribution to the daily SO<sub>2</sub> exceedances over the 125  $\mu\text{g}\cdot\text{m}^{-3}$  threshold is again highest over cities making more than 20 days yr<sup>-1</sup> contribution. Over Eastern Europe, larger regions are affected with city emissions increasing the number of exceedances by 1–2 days. In relative sense, larger areas around cities are affected by higher daily SO<sub>2</sub> values often reaching 90–100 % meaning that vast majority of the high SO<sub>2</sub> occurrences are due to emissions from cities. Even further from cities, especially over Eastern Europe, up to 10 % of all the elevated daily SO<sub>2</sub> values are due to city emissions. The impact on

hourly SO<sub>2</sub> exceedances is again highest over cities (so in line with the emissions) with up to 100 h yr<sup>-1</sup> contribution to the absolute number of exceedances and, in general, Central and Eastern Europe is affected the most. Increases in hourly exceedances due to urban emissions are modeled at even larger distances from cities (similarly to daily exceedances) up to 1–2 h yr<sup>-1</sup>. In relative numbers, the contribution is around 80–90 % over cities, but quickly reduces below 20 % further from them. The averaged increases in exceedances over cities are very variable: 8.6(±18.9) and 15.1(±43.0) for the daily and hourly averaging period, giving 40.1(±44.8) % and 23.8(±40.0) % relative contribution.

### 4.2.4 PM<sub>2.5</sub>

According to Fig. 8, urban emissions increase annual PM<sub>2.5</sub> levels by 4–8  $\mu\text{g}\cdot\text{m}^{-3}$  over cities with the highest impact over the Ruhr area and Warsaw (up to 15  $\mu\text{g}\cdot\text{m}^{-3}$ ). These correspond to about 20–60 % contribution to the total PM<sub>2.5</sub> levels. Above rural areas further from cities, the impact goes rapidly below 1  $\mu\text{g}\cdot\text{m}^{-3}$ . However, in a relative manner, it remains around 5–10 %, e.g. over Northern Germany or Central Europe. The averaged urban induced PM<sub>2.5</sub> increase over cities is 4.2(±3.7)  $\mu\text{g}\cdot\text{m}^{-3}$ , corresponding to 24.3(±12.8) % contribution to the total value.



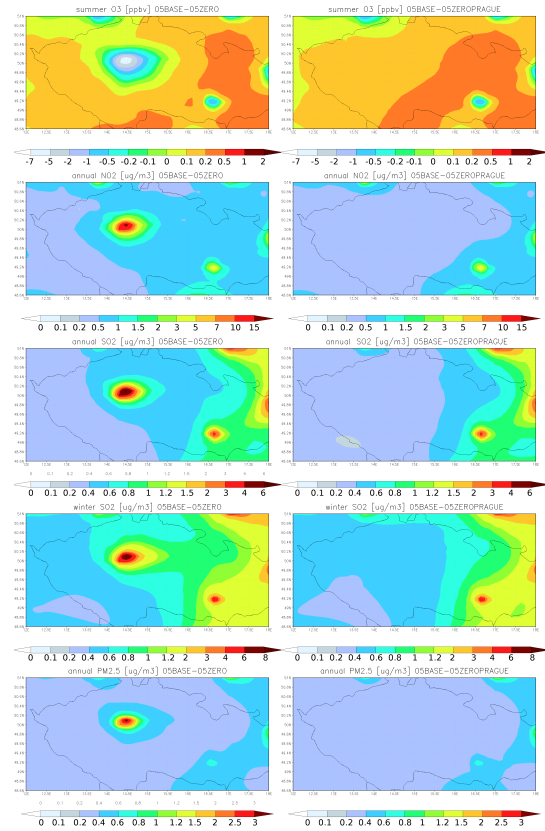
**Figure 8.** Impact of city emissions on the annual  $PM_{2.5}$  concentration. Left figure presents the absolute change averaged over 2001–2010, while the relative contribution due to city emissions is shown on the right.

### 4.2.5 Impact on a particular city

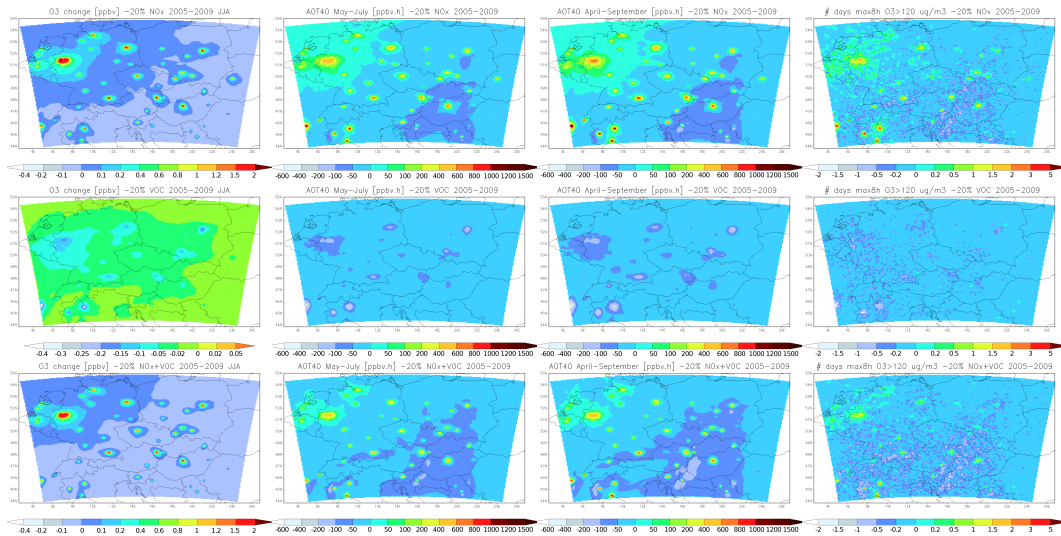
It was seen in Figs. 5–8 that urban emissions impact air-quality mainly over the cities themselves and the influence on rural air is much smaller. The question is how the emissions from other cities contribute to the impact over a particular city, or in other words, what fraction of the total impact (due to all cities) is attributable to the impact of the local emissions. To examine this, we selected the city of Prague lying in the center of the domain and representing a middle sized city from the domain. Figure 9 presents the total impact (i.e. from all urban emissions; left column) and the impact of emissions from the rest of the cities not considering the emissions from Prague (right column). We evaluated this in terms of the average quantities from Table 4 (annual, DJF and JJA means), showing only the relevant part of the domain. The total impact (right column) actually corresponds to a detail of the impact presented in Figs. 5–8. and gives  $-7$  ppbv, 15, 6, 8, 3  $\mu g m^{-3}$  as the maximum change over Prague due to all urban emissions for JJA  $O_3$ , annual  $NO_2$ , annual and DJF  $SO_2$  and annual  $PM_{2.5}$ . The same quantities from the right column give, for Prague, approximately 0.2 ppbv, 0.5, 0.4, 0.6, 0.5  $\mu g m^{-3}$ . This represents about 3, 3, 7, 7, 16 % of the impact due to all urban emissions.

### 4.2.6 Sensitivity experiments

The response to possible urban emission reductions of selected ozone related measures presented in Table 4 is evaluated here. The results are presented in Fig. 10. Reducing city  $NO_x$  emissions by 20%, due to limited reaction with NO, JJA ozone concentrations are enhanced by around 1.5–2 ppbv over city centres but  $O_3$  increases over larger areas as well, although by much smaller magnitude (0.1–0.2 ppbv increase over Western Germany). The AOT40s responded in similar manner: due to reduced ozone titration, elevated AOT40s are modeled over and around cities (by up to 500–1500 ppbv h). However, over Central and Southern Europe, AOT40s tend to slightly decrease (by up to  $-200$  ppbv h)



**Figure 9.** Impact of city emissions on average  $O_3$  (ppbv; summer),  $NO_2$  ( $\mu g m^{-3}$ ; annual),  $SO_2$  ( $\mu g m^{-3}$ ; annual and DJF) and  $PM_{2.5}$  ( $\mu g m^{-3}$ ; annual). Left column: impact of all cities, right column: impact off all cities except Prague.



**Figure 10.** Impact of 20 % reduction of  $\text{NO}_x$  (upper row), 20 % reduction of NMVOC (middle row) and 20 % reduction of both  $\text{NO}_x$  and NMVOC (bottom row) on ozone related air-quality measures: average JJA ozone, AOT40 for crops and forest, and, the average number of days with maximum 8 h ozone running mean greater than  $120 \mu\text{g m}^{-3}$ .

with decreasing urban  $\text{NO}_x$  emissions. The reduced titra- 800  
tion is evident on the change in the number of ozone ex-  
ceedances which increases over cities often by more than 2–  
3 days  $\text{yr}^{-1}$ . Further from urban centers, however, less  $\text{NO}_x$   
emitted tend to decrease ozone exceedances (especially over  
Central Europe, by up to  $-1.5$  days  $\text{yr}^{-1}$  in average).

While  $\text{NO}_x$  reduction increased ozone over cities, and  
caused small decreases elsewhere, especially in terms of 805  
occurrences of higher values, reduced NMVOC emissions  
cause ozone decrease all over the domain. In terms of JJA  
average  $\text{O}_3$ , it is highest over cities, up to  $-0.3$  ppbv. De-  
creases are modeled for AOT40s (up to  $-400$  ppbv h) and  
for the number of exceedances (up to  $-1-2$  days  $\text{yr}^{-1}$ ) as 810  
well.

The simultaneous reduction of both  $\text{NO}_x$  and NMVOC  
leads to similar changes in JJA ozone means values: only  
the peak changes over cities – caused by decreased titration,  
are smaller, up to  $1.5$  ppbv. In terms of AOT40crop/forest, 815  
reduction of urban  $\text{NO}_x + \text{NMVOC}$  emissions leads to in-  
creases over cities, but again by a smaller magnitude than  
in case of purely  $\text{NO}_x$  reduction. On the other hand, over  
rural areas, AOT40s decreased more than due to  $\text{NO}_x$  re-  
duction alone. The increases of 8 h ozone exceedances due to 820  
decreased  $\text{NO}_x + \text{NMVOC}$  go up to  $2-3$  days  $\text{yr}^{-1}$ , which is  
again less than for  $\text{NO}_x$  reduction. On the other hand, again,  
the decrease in the number of exceedances over rural areas  
is slightly larger in case of simultaneous  $\text{NO}_x + \text{NMVOC}$  re-  
duction than due to  $\text{NO}_x$  emission reduction only. 825

## 5 Discussion

### The validation of the modeling system

The validation showed that the modeling system captures  
the observed annual cycle of ozone with negative bias en-  
countered in each months except late summer and autumn.  
The chemical boundary conditions used by our model were  
taken from a 10 yr simulation from a larger domain, which  
however was forced with time invariant, spatially constant  
boundary conditions ( $40$  ppbv) and this artificial constraint  
could propagate to the inner domain. Katragkou et al. (2010)  
showed that the final ozone levels greatly depend on the im-  
posed boundary conditions. This constant constrain is also  
evident in the underestimation of the standard deviation for  
each averaging period, especially for DJF. **The diurnal cycle underlines the monthly model bias, giving lower hourly values in DJF and better agreement in JJA, but with an underestimation of the JJA daily maximum values. The lower afternoon values of ozone in JJA can be attributed also by higher afternoon and evening  $\text{NO}_2$  values, as a result of the  $\text{NO} + \text{O}_3$  reaction. A very similar result is provided by Huszar et al. (2012) both in terms of monthly and hourly variation.**

Recently, Akritidis et al. (2013) were investigating the im-  
pact of CBC on the simulated ozone concentrations using the  
same two models as in our study (an offline couple of mod-  
els RegCM and CAMx). They found a clear improvement  
in the correlation coefficient when using global chemistry  
model (ECHAM5/MOZART) based CBC. Their correlation  
of monthly ozone values using time/space invariant CBCs is  
 $0.74$  that compares very well to our value ( $0.77$ ). Introduc-  
ing the MOZART based CBCs, the correlations increased by  
often more than  $0.1$ . 830

Compared to Huszar et al. (2012), our modeling system performs better in terms of correlation, with  $r = 0.6$  and  $r = 0.67$  for hourly and daily values against 0.51 and 0.53 in the later study who used an earlier version of the RegCM-CAMx coupled system. This improvement probably lies in the duration of the data of comparison: in a 10 year time-frame, the main drivers of the variability are the diurnal and monthly variations which contribute to overall correlation in a significant way (Hogrefe et al., 2001). Zanis et al. (2011), who used the same models in offline couple for also a 10 yr experiment over Europe, achieved similar values of correlations. In general, our model performs for ozone better during JJA, when photochemistry is more intensive. This is true also for RMSE, NMSE and FB. Katragkou et al. (2010) and Zanis et al. (2011) came to the same conclusion.

Very low correlations are achieved in case of  $\text{NO}_2$ , especially for the hourly values. In general, it is difficult to achieve higher degree of agreement in case of precursor species for at least two reasons. The driving meteorology, which greatly influences the hour-to-hour evolution of the  $\text{NO}_2$  concentrations, is a result of a 10 yr climate model run. The climate model does not need to accurately reproduce the hour-to-hour, day-to-day weather pattern; however it has to reconstruct the climate close to reality in terms of averaged quantities and capability to capture extremes (Halenka et al., 2006). Further, the emission decomposition into hourly values is based on numerous assumptions about the typical temporal evolution of a certain activity sector and the actual emissions may differ for a particular hour. At last, ozone precursor species are modeled always with higher degree of uncertainty with great differences between models and set-ups (including chemistry mechanism) while they give very similar results in terms of final ozone concentrations (Kuhn et al., 1998).

Another striking feature is the underestimation of the modeled  $\text{NO}_2$  values. Huszar et al. (2012), who encountered a similar negative model bias, concluded that one reason lies in the overall underestimation of emissions and in the suppressed  $\text{NO}$  to  $\text{NO}_2$  conversion due to volatile organic compounds in CB-IV mechanism. Our configuration invoked the CB-V chemistry mechanism which was to remove this erroneous feature in the earlier version of the CB mechanism (Sarwar et al., 2008). However, the negative bias persists in our simulations, which in consequence could mean that the emissions are probably underestimated for the region modeled. Further, seen in the hourly plots, the underestimation mainly occurs during night-time similarly as in Huszar et al. (2012). Many other studies argued that chemistry in air-quality models performs less biased during daylight (Zanis et al., 2011). At last, biomass burning emission were not accounted for in our simulations while it is an important contributor to  $\text{NO}_2$  burdens, especially for southern stations (Baldasano et al., 2011).

The strong DJF overestimation of the  $\text{SO}_2$  levels in Huszar et al. (2012) was attributed to inadequate treatment of emis-

sions in considering them as only area sources. An important improvement in the RegCMCAMx4 model against its earlier version was the treatment of part of  $\text{SO}_2$  emissions as elevated source which better compiles with the reality. However, our results suggest minor improvement in DJF and the positive bias, although smaller, remained. On the other hand, summer encounters a clear negative bias. This could indicate that both the incorrect monthly disaggregation of the annual  $\text{SO}_2$  emissions and the overestimated conversion to sulfate aerosol (in JJA) play role here as well. Reduced deposition can contribute to  $\text{SO}_2$  overestimation (Baker and Scheff, 2007) as well, as concluded by Huszar et al. (2012) who applied the same deposition scheme as in this study.

To understand the model performance concerning the  $\text{PM}_{2.5}$  levels, we have to look at the comparison of the main fine particle matter components. In DJF,  $\text{PM}_{2.5}$  is largely underestimated: the main contributors to this bias is the underestimation of nitrate aerosol and both black and organic carbon. The DJF sulfate aerosol is in acceptable agreement with the observations, which, given that  $\text{SO}_2$  is overestimated, means that the  $\text{SO}_2$  to  $\text{SO}_4$  conversion is underestimated, leading to fair observation-model agreement. During JJA on the other hand, probably too strong  $\text{SO}_2$  to  $\text{SO}_4$  transition occurs, resulting in (1)  $\text{SO}_2$  concentrations even more negatively biased and an (2) overestimated sulfate aerosol. Huszar et al. (2012) achieved better agreement for  $\text{PSO}_4$  than for  $\text{SO}_2$  arguing that, again, precursor species are often simulated with lower accuracy than secondarily formed pollutants. Baker and Scheff (2007), who used CAMx with the same chemistry mechanism and aerosol module (ISORROPIA) arrived to the same conclusion. This is however not true for nitrate aerosol in our experiments, which shows a reasonable agreement (at least in terms of range of simulated values) with observations for JJA, but DJF model values are greatly underestimated. Bessagnet et al. (2004) encountered the opposite situation, they had larger difficulties to capture JJA values than those during DJF. In our case, the DJF underestimation is probably connected with the less  $\text{NO}_2$  simulated during this season. Similar underestimation occurs in the study of Myhre et al. (2006), especially for high concentrations. In general, the secondary inorganic aerosol model biases can be attributed to overall difficulties in simulating heterogeneous and aqueous phase processes (Bessagnet et al., 2004).

Black carbon is usually underestimated in both DJF and JJA, in a similar extent than in Huszar et al. (2012). Schiap et al. (2004) obtained comparable values as well and attributed this negative model bias to deficiencies in describing coating processes which are burdened by large uncertainties and directly determine the BC lifetime (BC has to become hydrophilic to get washed out by the wet deposition). Even more striking underestimation occurs for the organic carbon, although this bias is reduced compared to Huszar et al. (2012). This is probably due to different emission data used here for primary OC. However, the largest source for low

modeled OC values probably lies in: (1) in modeling the gas-to-particle partitioning that is affected with uncertainty with large number of tunable parameters (Simpson et al., 2007), (2) disregarding biomass burning aerosol that occurred in 2003 in eastern Europe affecting the measurements of Yttri et al. (2007).

As expected, for selected urban stations, our modeling system is, in general, less accurate, especially in terms of correlations. Urban stations are often influenced by local or nearby emissions sources, far below the models spatial resolution. The relatively coarse input emissions data cannot resolve the variability of these sources leading to much worse observation-model agreement compared to rural background stations. In case of ozone, the model over urban stations is positively biased in summer, which can be explained by the instant dilution of concentrated urban emission into the 10 km model grid which tends to ozone production overestimation (Hodneborg et al., 2011). The opposite holds for the modeled  $\text{NO}_2$  concentrations which, due to instant dilution, are negatively biased in the model within urban environment. The model performance for  $\text{SO}_2$  and  $\text{PM}_{2.5}$  is worse as well over urban stations compared to rural ones, probably for the same reasons as for ozone and  $\text{NO}_2$ .

### The urban emissions impact on air-quality

Generally, the impact of city emissions on ozone is characterized by two main features: over cities, all examined metrics decreased. Enhancements are encountered further from urban centers and are of lower magnitude than the decreases. Im et al. (2011a, b) performed regional chemistry simulations over Istanbul and Athens and arrived to similar results: decrease of  $\text{O}_3$  over urban areas due to reaction with  $\text{NO}$  and, as a consequence of NMVOC transport, a smaller production of  $\text{O}_3$  at downwind areas due to increasing NMVOC/ $\text{NO}_x$  ratio. Previously, Poupkou et al. (2008) showed that regional transport plays an important role in carrying urban pollution to larger distances leading to  $\text{O}_3$  formation downwind from cities. Im and Kanakidou (2012) focused on both Istanbul and Athens and found up to 27 and 5 ppbv decreases of ozone due to urban emissions from these cities. Although they are not covered by our domain and are characterized by warmer climate, the changes are consistent with our JJA mean changes, especially in case of Athens, which is affected by higher background pollution (Kanakidou et al., 2011) as typical for cities over our domain as well.

Our results further suggest, that while the enhancement of average ozone further from cities (as a result of downwind transport) is relatively small (up to 0.5 ppbv), however, much larger increase is detected when considering metrics describing accumulated and extreme ozone values. In conclusion, the importance of cities' impact on ozone levels lies in higher potential for extreme ozone pollution over downwind areas during favorable meteorological conditions rather than in increase of average levels. This is seen especially in changes in

the number of exceedances, but the AOT40 levels show often large enhancement around cities as well.

The impact on  $\text{NO}_2$  levels is important only over cities themselves indicating that in urban plume further from urban areas, the  $\text{NO}_x$  ages to  $\text{HNO}_3$  decreasing the contribution to the total  $\text{NO}_2$  levels. The contribution in cities goes up to 50 to 70 % indicating that large part (i.e. 30–50 %) of the urban  $\text{NO}_2$  pollution is of non-urban origin. This supports region or country wide emission control strategies as their emissions undergo regional transport. Im and Kanakidou (2012) found for Athens and Istanbul even larger contribution around 95–96 % over these cities. Earlier, Guttikunda et al. (2005) calculated the eastern Asia megacities contribution to  $\text{NO}_z$  levels and found values around 10–30 % over cities, however  $\text{NO}_z$  contains species produced during plume aging further from city centers causing this lower contribution.

In terms of average quantities (annual and DJF mean), the urban sulfur dioxide contribution is similar to  $\text{NO}_2$  contribution. Urban  $\text{SO}_2$  emissions are responsible for up to 70–80 % of pollution in over urban areas themselves. In other words, 20–30 % of urban  $\text{SO}_2$  pollution comes from other areas (rural and minor cities, villages) giving importance on the regional emission transport. Guttikunda et al. (2003) found over 50 to 75 % contribution near megacities of eastern Asia and 10–30 % over large areas in eastern China far from megacities. Similar values are obtained in our simulations (around 10–20 %) over large parts of the domain. They argue that large contribution within the cities indicate that the industry is concentrated within urban areas. This is often the case for eastern European cities where we obtained the highest urban  $\text{SO}_2$  contributions. The urban contribution to  $\text{SO}_2$  daily and (mainly) hourly exceedances is slightly higher than the contribution to average values and much more resembles the emission pattern indicating the enhanced importance of local urban emission in high air pollution episodes (when these exceedances occur) compared to the inter-urban pollution transport.

The annual average  $\text{PM}_{2.5}$  impact calculated in our simulations (up to  $10\text{--}15\ \mu\text{g m}^{-3}$ ) are in line with values obtained for Istanbul and Athens from Im and Kanakidou (2012): 18 and  $12\ \mu\text{g m}^{-3}$ , respectively. However, their relative contribution is higher due to probably lower background pollution (around 62 and 55 %, respectively) compared to ours (30–60 % contribution over cities).

The emission reduction sensitivity test showed that in cities, the chemical regime is  $\text{NO}_x$ -saturated meaning it is dominated by the reaction of  $\text{NO}$  with  $\text{O}_3$ . This causes that  $\text{NO}_x$ -oriented emission reduction actually worsen the ozone levels above cities and its close environment. This holds for the AOT40s and exceedance change as well, where decreases are modeled only far from cities, where the urban plumes undergoes photochemical aging. The response to 20 % NMVOC emission reduction is less dominant and in terms of all metrics it leads to reduction of ozone. Im et al. (2011b) tested the ozone response to 30 % reduced  $\text{NO}_x$

or NMVOC emissions and found the ozone concentrations more sensitive to  $\text{NO}_x$  emissions than to VOC emission. They also showed that above and around cities, reduced (increased)  $\text{NO}_x$  emissions led to enhanced (suppressed) ozone by up to 8–10 % (in both direction), which is similar to the percentage change extracted from our simulations giving about 5–8 % ozone increase due to 20 %  $\text{NO}_x$  emission reduction. The smaller numbers can be partly due to the lower emission reduction scenario. In case of NMVOC emission reduction, our numbers (up to –2 %) are only half of the relative ozone reduction achieved in their study (up to –4 %). The small ozone decreases due to  $\text{NO}_x$  reduction in terms of AOT40s and exceedances further from cities in our simulations are probably caused by less  $\text{NO}_x$  available in urban plumes when it mixes with biogenic NMVOC emissions over downwind areas (Im et al., 2011a, b; Finardi et al., 2014).

Interestingly, the simultaneous  $\text{NO}_x$  + NMVOC reduction scenario led to very similar ozone response than the  $\text{NO}_x$  reduction alone. This can be explained by the dominating effect of ozone titration due to  $\text{NO}_x$  emissions. Indeed, the NMVOC reduction caused only minor ozone changes. Consequently, the effective ozone reduction strategy depend on the targeted area. Urban emission reduction of  $\text{NO}_x$  and NMVOC improves the air-pollution over rural areas, however over the cities themselves, this usually leads to worsening of the ozone levels. According to our simulations, the only effective emission reduction strategy to decrease ozone levels is to reduce NMVOC emissions significantly while changing the  $\text{NO}_x$  emissions only slightly or not at all.

Compared to the impact of all (100 %) emissions, the 20 %  $\text{NO}_x$  + VOC emission change approximately equals to the 1/5th of the total impact (mainly for JJA ozone and AOT40s). This justifies the 100 % emission perturbation approach instead of a smaller perturbation introduced to maintain linearity. A similar approach was used recently for aviation emission impact (Huszar et al., 2013).

## 6 Conclusions

### Conclusions separately ...

Answering the questions raised in the introduction, the air quality over cities is largely determined by the urban emissions but considerable (often a few tens of %) fraction of the surface concentration is attributable to other sources from rural areas, minor cities (which we did not consider here) or transported from distant areas (via the boundary conditions). On the other hand, the contribution of urban emission to surface pollution over rural areas is in general lower, around 5–10 %. It is further a question, how one city impacts the air pollution of other cities or, in other words, how is the air pollution in a certain city impacted by other cities. Huszar et al. (2014), who examined the urban land-surface forcing on regional climate (mainly temperature) using very similar modeling framework on the same domain as here, show that the

urban impact on temperature is localized, meaning that there is only a minor influence of neighboring cities on a certain city (Prague, in their case). Here, for the impact of emissions on chemistry, it is shown for the case of Prague that the impact from “all-except-Prague” urban emissions on Prague is rather small (a few %, to over 10 % in case of  $\text{PM}_{2.5}$ ) meaning that the air pollution over Prague is determined mainly by local urban sources rather than urban emissions from other cities. The inter-urban influence is largest for fine aerosol which has, in general, longer lifetime giving more importance to long range transport.

In summary, we showed that air-pollution over urban areas is a combination of the local urban emissions and those from rural areas without large cities with this later having often more than 50 % contribution. This implies that to meet the air-quality standards over cities, emission from the surrounding rural areas and long range transport have to be considered as well. Further it is shown, that the inter urban air-pollution is minor meaning that emissions from large cities do not influence each other in a significant way, at least as a long-term average.

It has to be emphasized that the long-term impact was evaluated here. Depending on the meteorological conditions (wind direction, temperature, boundary layer state), the impact of urban emissions represented by the urban-plume can be much larger than showed here, corresponding to the averaged impact.

Finally, numerous caveats of the modeling system were identified that has to be taken into account in future developments. The most important ones are: inclusion of time/space variant chemical boundary conditions that highly affected ozone performance, improvement in the representation of the annual cycle of emissions, considering biomass burning emissions, inclusion of dust emissions and their radiative effects as well as those of secondary organic aerosol.

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## References

- Akritidis, D., Zanis, P., Katragkou, E., Schultz, M., Tegoulas, I., Poupkou, A., Markakis, K., Pytharoulis, I., and Karacostas, T.: Evaluating the impact of chemical boundary conditions on near surface ozone in regional climate–air quality simulations over Europe, *Atmos Res*, 134, 116–130, doi:, 2013.
- Baker, K. and Scheff, P.: Photochemical model performance for  $\text{PM}_{2.5}$  sulfate, nitrate, ammonium, and precursor species  $\text{SO}_2$ ,  $\text{HNO}_3$ , and  $\text{NH}_3$  at background monitor locations in the central and eastern United States, *Atmos. Environ.*, 41, 6185–6195, 2007.

- Baklanov, A.: Chemical weather forecasting: a new concept of integrated modelling, *Adv. Sci. Res.*, 4, 23–27, doi:10.5194/asr-4-23-2010, 2010.
- 1155 Baklanov, A., Lawrence, M., Pandis, S., Mahura, A., Finardi, S., Moussiopoulos, N., Beekmann, M., Laj, P., Gomes, L., Jafrezo, J.-L., Borbon, A., Coll, I., Gros, V., Sciare, J., Kukkonen, J., Galmarini, S., Giorgi, F., Grimmond, S., Esau, I., Stohl, A., Denby, B., Wagner, T., Butler, T., Baltensperger, U., 1160 Buitjes, P., van den Hout, D., van der Gon, H. D., Collins, B., Schluenzen, H., Kulmala, M., Zilitinkevich, S., Sokhi, R., Friedrich, R., Theloke, J., Kummer, U., Jalkinen, L., Halenka, T., Wiedensholer, A., Pyle, J., and Rossow, W. B.: MEGAPOLI: concept of multi-scale modelling of megacity impact on air quality and climate, *Adv. Sci. Res.*, 4, 115–120, doi:10.5194/asr-4-115-2010, 2010. 1225
- Baldasano, J. M., Pay, M. T., Jorba, O., Gasso, S., and Jimenez-Guerrero, P.: An annual assessment of air quality with the CALIOPE modeling system over Spain, *Sci. Total Environ.*, 409, 2163–2178, doi:10.1016/j.scitotenv.2011.01.041, 2011.
- 1170 Barth, M. C. and Church, A. T.: Regional and global distributions and lifetimes of sulfate aerosols from Mexico City and southeast China, *J. Geophys. Res.*, 104, 30231–30239, 1999.
- Beekmann, M. and Derognat, C.: Monte Carlo uncertainty analysis of a regional-scale transport chemistry model constrained by measurements from the Atmospheric Pollution Over the Paris Area (ESQUIF) campaign, *J. Geophys. Res.*, 108, 8559, doi:10.1029/2003JD003391, 2003.
- 1175 Beekmann, M. and Vautard, R.: A modelling study of photochemical regimes over Europe: robustness and variability, *Atmos. Chem. Phys.*, 10, 10067–10084, doi:10.5194/acp-10-10067-2010, 2010. 1245
- Behera, N. S. and Sharma, M.: Investigating the potential role of ammonia in ion chemistry of fine particulate matter formation for an urban environment, *Sci. Total Environ.*, 408, 3569–3575, 2010.
- Bessagnet, B., Hodzic, A., Vautard, R., Beekmann, M., Cheinet, S., Honoré, C., Lioussé, C., and Rouil, L.: Aerosol modeling with CHIMERE—preliminary evaluation at the continental scale, *Atmos. Environ.*, 38, 2803–2817, doi:10.1016/j.atmosenv.2004.02.034, 2004. 1250
- 1190 Borrego, C., Monteiro, A., Ferreira, J., Miranda, A. I., Costa, A. M., Carvalho, A. C., and Lopes, M.: Procedures for estimation of modelling uncertainty in air quality assessment, *Environ. Int.*, 34, 613–620, doi:10.1016/j.envint.2007.12.005, 2008.
- Butler, T. M. and Lawrence, M. G.: The influence of megacities on global atmospheric chemistry: a modelling study, *Environ. Chem.*, 6, 219–225, doi:10.1071/EN08110, 2009.
- Byun, D. W.: Dynamically consistent formulations in meteorological and air quality models for multiscale atmospheric studies. Part I: Governing equations in a generalized coordinate system, *J. Atmos. Sci.*, 56, 3789–3807, 1999.
- 1200 Chen, S. J., Liao, S. H., Jian, W. J., and Lin, C. C.: Particle size distribution of aerosol carbons in ambient air, *Environ. Int.*, 23, 475–488, 1997. 1205
- Denier van der Gon, H. A. C., Kuenen, J., and Butle, T.: A Base Year (2005) MEGAPOLI Global Gridded Emission Inventory (1st Version), Deliverable D1.1, MEGAPOLI Scientific Report 10-13, MEGAPOLI-16-REP-2010-06, TNO Built Environment and Geosciences, Utrecht, the Netherlands, 2010.
- Dickinson, R. E., Henderson-Sellers, A., and Kennedy, P.: Biosphere–atmosphere transfer scheme (BATS) version 1 as coupled to the NCAR community climate model, Tech Rep, National Center for Atmospheric Research Tech Note NCAR.TN387 + STR, NCAR, Boulder, CO, 1993.
- Eben, K., Jurus, P., Resler, J., Belda, M., Pelikán, E., Krüger, B. C., and Keder, J.: An ensemble Kalman filter for short-term forecasting of tropospheric ozone concentrations, *Q. J. Roy. Meteorol. Soc.*, 131, 3313–3322, doi:10.1256/qj.05.110, 2005.
- EEA: Corine Land Cover 2006 technical guidelines, EEA (European Environment Agency), OPOCE (Office for Official Publications of the European Communities), blackboxPlease provide place of publication., 2012.
- Escudero, M., Lozano, A., Hierro, J., del Valle, J., and Mantilla, E.: Urban influence on increasing ozone concentrations in a characteristic Mediterranean agglomeration, *Atmos. Environ.*, 99, 322–332, doi:10.1016/j.atmosenv.2014.09.061, 2014.
- Finardi, S., Silibello, C., D’Allura, A., and Radice, P.: Analysis of pollutants exchange between the Po Valley and the surrounding European region, *Urban Climate*, 10, 682–702, doi:10.1016/j.uclim.2014.02.002, 2014.
- Folberth, G. A., Rumbold, S., Collins, W. J., and Butler, T.: Determination of Radiative Forcing from Megacity Emissions on the Global Scale, MEGAPOLI Project Scientific Report 10e08, UK MetOffice Hadley Center, Exeter, UK, 2010.
- Freney, E. J., Sellegri, K., Canonaco, F., Colomb, A., Borbon, A., Michoud, V., Doussin, J.-F., Crumeyrolle, S., Amarouche, N., Pichon, J.-M., Bourianne, T., Gomes, L., Prevot, A. S. H., Beekmann, M., and Schwarzenböck, A.: Characterizing the impact of urban emissions on regional aerosol particles: airborne measurements during the MEGAPOLI experiment, *Atmos. Chem. Phys.*, 14, 1397–1412, doi:10.5194/acp-14-1397-2014, 2014.
- Fritsch, J. M. and Chappell, C. F.: Numerical prediction of convectively driven mesoscale pressure systems, Part I: Convective parameterization, *J. Atmos. Sci.*, 37, 1722–1733, 1980.
- Fuhrer, J., Skärby, L., and Ashmore, M. R.: Critical levels for ozone effects on vegetation in Europe, *Environ. Pollut.*, 97, 91–106, 1997.
- Gaffney, J. S., Marley, N. A., Cunningham, M. M., and Doskey, P. C.: Measurements of peroxyacyl nitrates (PANS) in Mexico City: implications for megacity air quality impacts on regional scales, *Atmos. Environ.*, 33, 5003–5012, 1999.
- Giorgi, F., Bi, X., and Qian, Y.: Indirect versus direct effects of anthropogenic sulfate on the climate of east Asia as simulated with a regional coupled climate-chemistry/aerosol model, *Climatic Change*, 58, 345–376, 2003.
- Giorgi, F., Coppola, E., Solmon, F., Mariotti, L., Sylla, M., Bi, X., Elguindi, N., Diro, G. T., Nair, V., Giuliani, G., Cozzini, S., Guetter, I., O’Brien, T. A., Tawfi, A. B., Shalaby, A., Zakey, A., Steiner, A., Stordal, F., Sloan, L., and Brankovic, C.: RegCM4: model description and preliminary tests over multiple CORDEX domains, *Clim. Res.*, 52, 7–29, 2012.
- 1205 Grell, G.: Prognostic evaluation of assumptions used by cumulus parameterizations, *Mon. Weather Rev.*, 121, 764–787, 1993.
- Grell, G. and Baklanov, A.: Integrated modeling for forecasting weather and air quality: a call for fully coupled approaches, *Atmos. Environ.*, 45, 6845–6851, 2011.
- Grell, G., Dudhia, J., and Stauffer, D. R.: A description of the fifth generation Penn State/NCAR Mesoscale Model (MM5), Na-

- tional Center for Atmospheric Research Tech Note NCAR/TN-398 + STR, NCAR, Boulder, CO, 1994. <sup>1330</sup>
- Guenther, A. B., Zimmermann, P. C., Harley, R., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses, *J. Geophys. Res.*, **98**, 12609–12617, 1993. <sup>1275</sup>
- Gurjar, B. R., Jain, A., Sharma, A., Agarwal, A., Gupta, P., Nagpure, A. S., and Lelieveld, J.: Human health risks in megacities due to air pollution, *Atmos. Environ.*, **44**, 4606–4613, doi:10.1016/j.atmosenv.2010.08.011, 2010. <sup>1335</sup>
- Guttikunda, K. S., Carmichael, G. R., Calori, G., Eck, C., and Woo, J.-H.: The contribution of megacities to regional sulfur pollution in Asia, *Atmos. Environ.*, **37**, 11–22, doi:10.1016/S1352-2310(02)00821-X, 2003. <sup>1280</sup>
- Guttikunda, S. K., Tang, Y., Carmichael, G. R., Kurata, G., Pan, L., Streets, D. G., Woo, J.-H., Thongboonchoo, N., and Fried, A.: Impacts of Asian megacity emissions on regional air quality during spring 2001, *J. Geophys. Res.*, **110**, D20301, doi:10.1029/2004JD004921, 2005. <sup>1285</sup>
- Halenka, T., Kalvova, J., Chladova, Z., Demeterova, A., Zemanekova, K., and Belda, M.: On the capability of RegCM to capture extremes in long term regional climate simulation – comparison with the observations for Czech Republic, *Theor. Appl. Climatol.*, **86**, 125–145, doi:10.1007/S00704-005-0205-5, 2006. <sup>1290</sup>
- Hodnebrog, Ö., Stordal, F., and Berntsen, T. K.: Does the resolution of megacity emissions impact large scale ozone?, *Atmos. Environ.*, **45**, 6852–6862, 2011. <sup>1295</sup>
- Hodzic, A., Jimenez, J. L., Madronich, S., Canagaratna, M. R., Decarlo, P. F., Kleinman, L., and Fast, J.: Modeling organic aerosols in a megacity: potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary organic aerosol formation, *Atmos. Chem. Phys.*, **10**, 5491–5514, doi:10.5194/acp-10-5491-2010, 2010. <sup>1300</sup>
- Hogrefe, C., Rao, S. T., Kasibhatla, P., Hao, W., Sistla, G., Mathur, R., and McHenry, J.: Evaluating the performance of regional-scale photochemical modeling systems: Part II – ozone predictions, *Atmos. Environ.*, **35**, 4175–4188, doi:10.1016/S1352-2310(01)00183-2, 2001. <sup>1305</sup>
- Huszar, P., Miksovsky, J., Pisoft, P., Belda, M., and Halenka, T.: Interactive coupling of a regional climate model and a chemistry transport model: evaluation and preliminary results on ozone and aerosol feedback, *Clim. Res.*, **51**, 59–88, doi:10.3354/cr01054, 2012. <sup>1310</sup>
- Huszar, P., Teyssède, H., Michou, M., Voldoire, A., Olivie, D. J. L., Saint-Martin, D., Cariolle, D., Senesi, S., Salas Y Melia, D., Alias, A., Karcher, F., Ricaud, P., and Halenka, T.: Modeling the present and future impact of aviation on climate: an AOGCM approach with online coupled chemistry, *Atmos. Chem. Phys.*, **13**, 10027–10048, doi:10.5194/acp-13-10027-2013, 2013. <sup>1315</sup>
- Huszar, P., Halenka, T., Belda, M., Zak, M., Sindelarova, K., and Miksovsky, J.: Regional climate model assessment of the urban land-surface forcing over central Europe, *Atmos. Chem. Phys.*, **14**, 12393–12413, doi:10.5194/acp-14-12393-2014, 2014. <sup>1320</sup>
- Im, U. and Kanakidou, M.: Impacts of East Mediterranean megacity emissions on air quality, *Atmos. Chem. Phys.*, **12**, 6335–6355, doi:10.5194/acp-12-6335-2012, 2012. <sup>1325</sup>
- Im, U., Poupkou, A., Incecik, S., Markakis, K., Kindap, T., Unal, A., Melas, D., Yenigun, O., Topcu, O., Odman, M. T., Tayanc, M., and Guler, M.: The impact of anthropogenic and biogenic emissions on surface ozone concentrations in Istanbul, *Sci. Total Environ.*, **409**, 1255–1265, doi:10.1016/j.scitotenv.2010.12.026, 2011a.
- Im, U., Markakis, K., Poupkou, A., Melas, D., Unal, A., Gerasopoulos, E., Daskalakis, N., Kindap, T., and Kanakidou, M.: The impact of temperature changes on summer time ozone and its precursors in the Eastern Mediterranean, *Atmos. Chem. Phys.*, **11**, 3847–3864, doi:10.5194/acp-11-3847-2011, 2011b.
- Juda-Rezler, K., Reizer, M., Huszar, P., Krueger, B., Zanis, P., Syrakov, D., Katragkou, E., Trapp, W., Melas, D., Chervenkov, H., Tegoulis, I., and Halenka, T.: Modelling the effects of climate change on air quality over central and Eastern Europe: concept, evaluation and projections, *Clim. Res.*, **53**, 179–203, doi:10.3354/cr01072, 2012.
- Kanakidou, M., Mihalopoulos, N., Kindap, T., Im, U., Vrekoussis, M., Gerasopoulos, E., Dermitzaki, E., Unal, A., Kocak, M., Markakis, K., Melas, D., Kouvarakis, G., Youssef, A. F., Richter, A., Hatzianastassiou, N., Hilboll, A., Ebojje, F., von Savigny, C., Ladstaetter-Weissenmayer, A., Burrows, J., and Moubasher, H.: Megacities as hot spots of air pollution in the East Mediterranean, *Atmos. Environ.*, **45**, 1223–1235, 2011.
- Katragkou, E., Zanis, P., Tegoulis, I., Melas, D., Kioutsioukis, I., Krüger, B. C., Huszar, P., Halenka, T., and Rauscher, S.: Decadal regional air quality simulations over Europe in present climate: near surface ozone sensitivity to external meteorological forcing, *Atmos. Chem. Phys.*, **10**, 11805–11821, doi:10.5194/acp-10-11805-2010, 2010.
- Kiehl, J., Hack, J., Bonan, G., Boville, B., Breigleb, B., Williamson, D., and Rasch, P.: Description of the NCAR Community Climate Model (CCM3), National Center for Atmospheric Research Tech Note NCAR/TN-420 + STR, NCAR, Boulder, CO, 1996.
- Kuenen, J., Denier van der Gon, H., Visschedijk, A., van der Brugh, H., Finardi, S., Radice, P., d'Allura, A., Beevers, S., Theloke, J., Uzbasich, M., Honor, C., and Perrussel, O.: A Base Year (2005) MEGAPOLI European Gridded Emission Inventory (Final Version), Deliverable D1.6, MEGAPOLI Scientific Report 10-17, MEGAPOLI-20-REP-2010-10, TNO Built Environment and Geosciences, Utrecht, the Netherlands, p. 39, 2010.
- Kuhn, M., Bultjes, P. J. H., Poppe, D., Simpson, D., Stockwell, W. R., Andersson-Skold, Y., Baart, A., Das, M., Fiedler, F., Hov, Kirchner, F., Makar, P. A., Milford, J. B., Roemer, M. G. M., Ruhnke, R., Strand, A., Vogel, B., and Vogel, H.: Intercomparison of the gas-phase chemistry in several chemistry and transport models, *Atmos. Environ.*, **32**, 693–709, 1998.
- Kuhn, U., Ganzeveld, L., Thielmann, A., Dindorf, T., Schebeske, G., Welling, M., Sciare, J., Roberts, G., Meixner, F. X., Kesselmeier, J., Lelieveld, J., Kolle, O., Ciccioli, P., Lloyd, J., Trentmann, J., Artaxo, P., and Andreae, M. O.: Impact of Manaus City on the Amazon Green Ocean atmosphere: ozone production, precursor sensitivity and aerosol load, *Atmos. Chem. Phys.*, **10**, 9251–9282, doi:10.5194/acp-10-9251-2010, 2010.
- Lawrence, M. G., Butler, T. M., Steinkamp, J., Gurjar, B. R., and Lelieveld, J.: Regional pollution potentials of megacities and other major population centers, *Atmos. Chem. Phys.*, **7**, 3969–3987, doi:10.5194/acp-7-3969-2007, 2007.
- Lee, S.-H., Kim, S.-W., Angevine, W. M., Bianco, L., McKeen, S. A., Senff, C. J., Trainer, M., Tucker, S. C., and



- Zamora, R. J.: Evaluation of urban surface parameterizations in the WRF model using measurements during the Texas Air Quality Study 2006 field campaign, *Atmos. Chem. Phys.*, 11, 2127–2143, doi:10.5194/acp-11-2127-2011, 2011. <sup>1450</sup>
- Lin, X., Roussel, P. B., Laszlo, S., Taylor, R., Melo, O. T., Shepson, P. B., Hastie, D. R., and Niki, H.: Impact of Toronto urban emissions on ozone levels downwind, *Atmos. Environ.*, 30, 2177–2193, 1996. <sup>1390</sup>
- Lin, Y.-C., Cheng, M.-T., Lin, W.-H., Lan, Y.-Y., and Tsuang, B.-J.: Causes of the elevated nitrate aerosol levels during episodic days in Taichung urban area, Taiwan, *Atmos. Environ.*, 44, 1632–1640, doi:10.1016/j.atmosenv.2010.01.039, 2010. <sup>1395</sup>
- Markakis, K., Valari, M., Perrussel, O., Sanchez, O., and Honore, C.: Climate-forced air-quality modeling at the urban scale: sensitivity to model resolution, emissions and meteorology, *Atmos. Chem. Phys.*, 15, 7703–7723, doi:10.5194/acp-15-7703-2015, 2015. <sup>1400</sup>
- Martin, S. T., Hung, H.-M., Park, R. J., Jacob, D. J., Spurr, R. J. D., Chance, K. V., and Chin, M.: Effects of the physical state of tropospheric ammonium-sulfate-nitrate particles on global aerosol direct radiative forcing, *Atmos. Chem. Phys.*, 4, 183–214, doi:10.5194/acp-4-183-2004, 2004. <sup>1405</sup>
- McMeeking, G. R., Kreidenweis, S. M., Carrico, C., Lee, T., Collett Jr., J. L., and Malm, W. C.: Observations of smoke-influenced aerosol during the Yosemite Aerosol Characterization Study: size distributions and chemical composition, *J. Geophys. Res.*, 110, D09206, doi:10.1029/2004JD005389, 2005. <sup>1410</sup>
- Molina, L. T., Madronich, S., Gaffney, J. S., Apel, E., de Foy, B., Fast, J., Ferrare, R., Herndon, S., Jimenez, J. L., Lamb, B., Osornio-Vargas, A. R., Russell, P., Schauer, J. J., Stevens, P. S., Volkamer, R., and Zavala, M.: An overview of the MILAGRO 2006 Campaign: Mexico City emissions and their transport and transformation, *Atmos. Chem. Phys.*, 10, 8697–8760, doi:10.5194/acp-10-8697-2010, 2010. <sup>1415</sup>
- Myhre, G., Grini, A., and Metzger, S.: Modelling of nitrate and ammonium-containing aerosols in presence of sea salt, *Atmos. Chem. Phys.*, 6, 4809–4821, doi:10.5194/acp-6-4809-2006, 2006. <sup>1420</sup>
- Nenes, A., Pandis, S. N., and Pilinis, C.: ISORROPIA: a new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols, *Aquat. Geochem.*, 4, 123–152, 1998. <sup>1425</sup>
- O'Brien, J. J.: A note on the vertical structure of the eddy exchange coefficient in the planetary boundary layer, *J. Atmos. Sci.*, 27, 1213–1215, 1970. <sup>1430</sup>
- Offenberg, J. H. and Baker, J. E.: Aerosol size distributions of elemental and organic carbon in urban and over-water atmospheres, *Atmos. Environ.*, 34, 1509–1517, doi:10.1016/S1352-2310(99)00412-4, 2000. <sup>1435</sup>
- Oleson, K. W., Bonan, J. B., Feddema, J., Vertenstein, M., and Grimmond, C. S. B.: An urban parameterization for a global climate model, Part I: Formulation and evaluation of two cities, *J. Appl. Meteorol. Clim.*, 47, 1038–1060, 2008. <sup>1440</sup>
- Pal, J. S., Small, E. E., and Eltahir, E. A. B.: Simulation of regional scale water and energy budgets: representation of subgrid cloud and precipitation processes within RegCM, *J. Geophys. Res.-Atmos.*, 105, 29579–29594, 2000. <sup>1445</sup>
- Paredes-Miranda, G., Arnott, W. P., Jimenez, J. L., Aiken, A. C., Gaffney, J. S., and Marley, N. A.: Primary and secondary contributions to aerosol light scattering and absorption in Mexico City during the MILAGRO 2006 campaign, *Atmos. Chem. Phys.*, 9, 3721–3730, doi:10.5194/acp-9-3721-2009, 2009. <sup>1450</sup>
- Poupkou, A., Symeonidis, P., Lisaridis, I., Melas, D., Ziomas, I., Yay, O. D., and Balis, D.: Effects of anthropogenic emission sources on maximum ozone concentrations over Greece, *Atmos. Res.*, 89, 374–381, 2008.
- Samara, C., Voutsas, D., Kouras, A., Eleftheriadis, K., Maggos, T., Saraga, D., and Petrakakis, M.: Organic and elemental carbon associated to PM<sub>10</sub> and PM<sub>2.5</sub> at urban sites of northern Greece, *Environ. Sci. Pollut. R.*, 21, 1769–1785, 2014.
- Sarwar, G., Luecken, D., Yarwood, G., Whitten, G. Z., and Carter, W. P. L.: Impact of an updated carbon bond mechanism on predictions from the CMAQ modeling system: preliminary assessment, *J. Appl. Meteorol. Clim.*, 47, 3–14, 2008.
- Schaap, M., van Loon, M., ten Brink, H. M., Dentener, F. J., and Builtjes, P. J. H.: Secondary inorganic aerosol simulations for Europe with special attention to nitrate, *Atmos. Chem. Phys.*, 4, 857–874, doi:10.5194/acp-4-857-2004, 2004.
- Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, J. Wiley, New York, 1998.
- Sillman, S.: The relation between ozone, NO<sub>x</sub> and hydrocarbons in urban and polluted rural environments, *Millennial Review series*, *Atmos. Environ.*, 33, 1821–1845, 1999.
- Simmons, A. J., Willett, K. M., Jones, P. D., Thorne, P. W., and Dee, D. P.: Low-frequency variations in surface atmospheric humidity, temperature and precipitation: inferences from reanalyses and monthly gridded observational datasets, *J. Geophys. Res.*, 115, D01110, doi:10.1029/2009JD012442, 2010.
- Simpson, D., Yttri, K. E., Klimont, Z., Kupiainen, K., Caseiro, A., Gelencser, A., Pio, C., Puxbaum, H., and Legrand, M.: Modeling carbonaceous aerosol over Europe: analysis of the CARBOSOL and EMEP EC/OC campaigns, *J. Geophys. Res.*, 112, D23S14, doi:10.1029/2006JD008158, 2007.
- Skyllakou, K., Murphy, B. N., Megaritis, A. G., Fountoukis, C., and Pandis, S. N.: Contributions of local and regional sources to fine PM in the megacity of Paris, *Atmos. Chem. Phys.*, 14, 2343–2352, doi:10.5194/acp-14-2343-2014, 2014.
- Streets, D. G. and Waldhoff, S. T.: Present and future emissions of air pollutants in China: SO<sub>2</sub>, NO<sub>x</sub>, and CO, *Atmos. Environ.*, 34, 363–374, 2000.
- Stock, Z. S., Russo, M. R., Butler, T. M., Archibald, A. T., Lawrence, M. G., Telford, P. J., Abraham, N. L., and Pyle, J. A.: Modelling the impact of megacities on local, regional and global tropospheric ozone and the deposition of nitrogen species, *Atmos. Chem. Phys.*, 13, 12215–12231, doi:10.5194/acp-13-12215-2013, 2013.
- Thunis, P., Rouil, L., Cuvelier, C., Stern, R., Kerschbaumer, A., Bessagnet, B., Schaap, M., Builtjes, P., Tarrason, L., Douros, J., Moussiopoulos, N., Pirovano, G., and Bedogni, M.: Analysis of model responses to emission-reduction scenarios within the CityDelta project, *Atmos. Environ.*, 41, 208–220, doi:10.1016/j.atmosenv.2006.09.001, 2007.
- Timothy, M. and Lawrence, M. G.: The influence of megacities on global atmospheric chemistry: a modeling study, *Environ. Chem.*, 6, 219–225, doi:10.1071/EN08110, 2009.
- Wang, T., Ding, A., Gao, J., and Wu, W. S.: Strong ozone production in urban plumes from Beijing, China, *Geophys. Res. Lett.*, 33, L21806, doi:10.1029/2006GL027689, 2006. <sup>1505</sup>

- 1510 Wang, T., Li, S., Shen, Y., Deng, J., and Xie, M.: Investigations on direct and indirect effect of nitrate on temperature and precipitation in China using a regional climate chemistry modeling system, *J. Geophys. Res.*, 115, D00K26, doi:10.1029/2009JD013264, 2010.
- Wayne, R. P.: *Chemistry of Atmospheres*, 3rd Edn., Oxford University Press, 2000.
- 1515 Winiwarter, W. and Zueger, J.: Pannonisches Ozonprojekt, Teilprojekt Emissionen, Endbericht, Report OEFZS-A-3817, Austrian Research Center, Seibersdorf, 1996.
- Xue, L. K., Wang, T., Gao, J., Ding, A. J., Zhou, X. H., Blake, D. R., Wang, X. F., Saunders, S. M., Fan, S. J., Zuo, H. C., Zhang, Q. Z., and Wang, W. X.: Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes, *Atmos. Chem. Phys.*, 14, 13175–13188, doi:10.5194/acp-14-13175-2014, 2014.
- 1520 Yttri, K. E., Aas, W., Bjerke, A., Cape, J. N., Cavalli, F., Ceburnis, D., Dye, C., Emblico, L., Facchini, M. C., Forster, C., Hanssen, J. E., Hansson, H. C., Jennings, S. G., Maenhaut, W., Putaud, J. P., and Tørseth, K.: Elemental and organic carbon in PM<sub>10</sub>: a one year measurement campaign within the European Monitoring and Evaluation Programme EMEP, *Atmos. Chem. Phys.*, 7, 5711–5725, doi:10.5194/acp-7-5711-2007, 2007.
- 1530 Zanis, P., Katragkou, E., Tegoulas, I., Poupkou, A., Melas, D., Huszar, P., and Giorgi, F.: Evaluation of near surface ozone in air quality simulations forced by a regional climate model over Europe for the period 1991–2000, *Atmos. Environ.*, 45, 6489–6500, doi:10.1016/j.atmosenv.2011.09.001, 2011.
- 1535 Zhang, Q. J., Beekmann, M., Frenay, E., Sellegri, K., Pichon, J. M., Schwarzenboeck, A., Colomb, A., Bourriane, T., Michoud, V., and Borbon, A.: Formation of secondary organic aerosol in the Paris pollution plume and its impact on surrounding regions, *Atmos. Chem. Phys. Discuss.*, 15, 8073–8111, doi:10.5194/acpd-15-8073-2015, 2015.