Response to co-Editor

Comments to the Author:
Thank you for the revised version of the manuscript. While some effort has been made to address the original reviewer comments, unfortunately the most critical concerns have not been satisfactorily addressed in the revised manuscript. Specifically, I am referring to 1) the redundancy of the partitioning schemes (raised by original Referee #1) and 2) the validity of the scheme by Lohmann and Lammel (2004) which has been challenged in the literature, and has been raised by all three reviewers. Furthermore, the new Referee #3 also raises concerns about the novelty of the work as compared with what has already been done.

For a revised manuscript to be reconsidered, the authors need to do a better job in convincingly arguing for and describing the approaches they have used and the novelty of their work. Regarding the first point, indeed it seems redundant to use both saturation vapor pressures and partitioning coefficients in an additive manner as pointed out by Referee #1. If the authors disagree, convincing arguments on the grounds should be provided. Regarding the second point, it is not enough to state that an approach is "accepted and suitable" but instead provide a thorough argumentation on why the arguments made by Goss (Environ. Sci. Technol. 2004) are invalid or can be neglected, along with (if indeed the approach is best available) a thorough discussion on the uncertainties associated with the chosen approach as suggested by the original Referee #2. Furthermore, the novelty of the work needs to be clearly justified and the previous work on the topic needs to be adequately discussed (see comments by Referee #3).

Besides these critical concerns, the new Referee #3 also provides some useful suggestions on potential improvements on the paper, which I recommend you consider if you wish to submit a revised manuscript, along with a ensuring the presentation of the manuscript to be as clear and transparent as possible.

If you think that you can sufficiently address these concerns, a revised manuscript can be reconsidered, but a further review will be necessary. Due to the significant time this would likely require, I also fully understand if you choose to submit the manuscript elsewhere.

I am sorry I cannot be more positive at this point,

best regards,

Ilona Riipinen

We would like to thank the Co-Editor for the valuable remarks and suggestions to further clarify the concerns raised by the referees. In order to satisfactory address those points, a revised manuscript has been submitted. With respect to the first point, a more elaborate justification is presented as a response to Referee #1. Regarding the second point, we would like bring to the co-editor's attention that the validity of the Lohmann and Lammel scheme (Environ. Sci. Technol. 2004) has not been raised by all three reviewers. Moreover, neither the Dachs-Eisenreich scheme nor the Lohmann and Lammel scheme have ever been criticized (instead the scheme suggested by Lohmann & Lammel represents the state of the art for PAH partitioning, has been widely used, and the paper has been cited some 170 times). What has been criticized is, the derivation of one of the parameters used in the scheme, K_{SA}, i.e., namely its derivation from K_{ow} (Goss, Environ. Sci. Technol. 2004) as done in the originally submitted version. This criticism was not published after Lohmann and Lammel (2004), but at the same time. As has been pointed out (in our subsequent reply to the first reviews), an alternative exists (K_{SA} derived as a function of the BC specific surface area; suggested by Dachs et al., Environ. Sci. Technol. 2004, and van Noort, Environ. Toxicol. Chem. 2003), which is not subject to a principle weakness. We have included this additional parameterisation in the revised version. With respect to the novelty of this work, we feel it adequately serves as a foundation model that currently undergoes further development with respect to PAH/POP modelling (i.e. further species for which aerosol processes and cycling between air and ground compartments are essential). Moreover, as we note in our comments to Referee #3, the very specific novelty and focus of this work (i.e first study that evaluates a wide range of gas/particle partitioning schemes in CMAQ) have been pointed out by Referee #1 and #2, as well as in the most recent publication in the field by Galarneau et al. (Atmos. Chem. Phys., 2014, p. 4075), where the relevance of a similarly titled manuscript was highlighted (Galarneau, E.: Evaluation of particle/gas partitioning in a regional air quality model (AURAMS-PAH), in preparation, 2014).

Despite the time and (computational) resource constraints, we have performed additional model simulations and the results are included in the revised version.

Anonymous Referee #1

After reviewing the author's response to earlier comments from myself and another reviewer, I recommend rejecting the paper for final publication.

The novel contribution of the paper is the incorporation of gas/particle partitioning schemes into CMAQ. However, the authors have made a mess of the job by 1) implementing redundant schemes (the JP and Koa models implemented additively) and 2) a scheme that has been convincingly argued in the literature to be conceptually flawed (Lohmann & Lammel 2004).

These two criticisms are basically the same as I offered in my first review of the paper. The arguments and small changes to the paper the authors offered in response are not satisfying to me.

With regard to point 1: The sub-cooled liquid vapor pressure of the PAHs is essentially directly proportional to their Koa. Thus there is no mathematical difference between schemes based on vapor pressure and Koa except constants in the equations and the conceptual interpretation of the meaning of those constants. Adding these two schemes together does not provide insight about the relative contributions of adsorption versus absorption processes for the PAHs. The author's arguments about other chemicals used in fitting the JP relationship do not seem relevant to me.

Reply: We disagree, as:

(a) Proportionality of sub-cooled liquid vapor pressure and K_{oa} can mean, but does not necessarily mean that each pair of single-parameter linear free energy relationships (spLFERs), one using p_L, the other K_{oa} are 'mathematically redundant'. This depends on the data sets regressions have been fitted on.

(b) Proportionality of sub-cooled liquid vapor pressure and K_{oa} is expected for substances which gas-particle partitioning is determined by absorption into OM (Pankow, Atmos. Environ. 1998; Xiao and Wania, Atmos. Environ. 2003). Accordingly, for substance classes which gas-particle partitioning is in fact dominated by absorption into OM i.e., chlorobenzenes, PCBs, PCNs, PCDD/Fs, PBDEs (Finizio et al., Atmos. Environ. 1997; Harner and Bidleman, Environ. Sci. Technol. 1998, besides others), Xiao and Wania (2003) find the descriptors p_L and K_{oa} 'very highly correlated' (see the abstract), not for PAHs. Proportionality of sub-cooled liquid vapor pressure and K_{oa} is furthermore expected for substances which gas-particle partitioning is less determined by absorption into OM, because of the uncertainties of the experimental data (related to sampling artefacts biasing the observed phase distribution, to temperature variation during sample collection), the uncertainties of the substance properties (quality and consistency e.g., experimentally inaccessible sub-cooled liquid vapor pressure) (as both pointed out by Xiao and Wania, 2003), and the temperature sensitivity of other types of molecular interaction of these substances with PM than sorption into OM. In other words, a correlation for apolar molecules such as PAHs is not a surprise, but does not necessarily indicate that their gas-particle partitioning is determined by absorption into OM.

(c) For PAHs it has been shown (Lohmann and Lammel, 2004) that assuming solely absorption to explain gas-particle partitioning (K_{oa} model e.g., Finizio et al., 1997) is deficient, while a dual model which considers also adsorption to soot (Dachs and Eisenreich, 2000) is superior i.e., better predicting observed partitioning at a large variety of sites. This parameterisation (Lohmann and Lammel, 2004) has been representing the state of the art, which is reflected in numerous (>> 50) applications for PAH gas-particle partitioning in the literature, including applications testing various models (Lammel et al., Chemosphere 2009; Wang et al., Atmos. Environ. 2013; Wang et al., Environ. Sci. Pollut. Res. 2013; Friedman et al., Environ. Sci. Technol. 2014; Galarneau et al., Atmos. Chem. Phys. 2014; Sangiorgi et al., Environ. Sci. Pollut. Res 2014; Liu et al., Chemosphere 2015; Li et al., Atmos. Environ. 2016; besides others).

(d) Adsorptive contributions to the overall sorption process (such as being described by the Junge-Pankow model) and absorptive contributions (such as into a liquid or semi-solid organic phase being described by the so-called K_{oa} model) are indeed expected to behave almost additive, as these single parameter linear free energy relationships go with the assumption that the one parameter describes the dominant of all possible types of molecular interactions of an organic molecule with the matrix (see e.g. Schwarzenbach et al., Env. Organic Chem. 2nd ed, Wiley 2003, ch. 11.2; Goss and Schwarzenbach, Environ. Sci. Technol. 2001, 35, 1-9), while other interactions are negligible and not captured. There is a small 'redundancy' when combining the Junge-Pankow with a K_{oa} model (scenarios 3-5), which has been detailed in the reply to the first round of reviews, repeated here: We agree, the parameter c_J (high for strong sorption, low for weak sorption) in the Junge-Pankow (JP) model may not be totally free from absorptive contributions. Therefore, adding θ of JP and K_{oa} may eventually lead to overpredictions, but these should be very low (negligible), as the absorptive contribution within JP is very low. It is very low, as the fitting was done for all possible vapors, and many of these were inorganic and polar (almost not soluble in octanol). Unfortunately, no c_J for BAP based on measurements has ever been published. However, we found recently in background aerosol of Central Europe (Kosetice 2012-13, n=162 aerosol samples, c_J derived from experimental S/V data; Shahpoury et al., to be published in Environ. Sci. Technol. 2016, following minor revision) that c_J for BaP is very low, namely 0.01-5.46 Pa cm (median = 0.44 Pa cm; and also low for all other PAHs, with one exception, anthracene for which c_J>17.2 Pa cm is found). This finding is not representative for all types of aerosol in the simulation, but for the European background aerosol. It supports the perception that a possible implicit absorptive contribution to PAHs' c_J must be very low i.e., negligible. Therefore, the combined partitioning according to both the JP and a K_{oa} model is justified (note that the Harner-Bidleman version of the K_{oa} model is present only in scenario 3 – Table was modified to avoid confusion).

Finally, we should also stress that so far in literature, all regional-scale air pollution modelling studies that utilize the aerosol module AERO of CMAQ and employ both adsorptive (JP scheme) and absorptive contributions (K_{oa} variants) to the overall sorption process, did so in an additive manner (see Table S1 – i.e Aulinger et al., 2007, Matthias et al., 2009, Bieser et al., 2012, Silibello et al., 2012). When bringing empirical models into a mechanistic modelling framework it is important to understand both the limitations of the empirical schemes (i.e. dependency on the data sets regressions have been fitted on, addressed in previous paragraphs), as well as the limitations posed by the predefined modelling framework where they are brought to interact (i.e., CMAQ's aerosol module AERO). While CMAQ has one of the most advanced aerosol modules among regional air quality models, certain simplifications in the treatment of coarse PM and OM (e.g., CMAQ does not include organic materials in coarse PM; however measurements show that organics constitute a significant component, see Binkowski, J. Geophys. Res. 2003; Li et al., Atmos. Chem. Phys., 2013) are posing limitations to fully exploit the advanced empirical gas-particle partitioning models (K_{oa}, Dachs-Eisenreich) in this specific mode. Furthermore, the large discrepancies in the OM and BC emission inventories (i.e. 2000-2001 SMOKE-EU totals were found to be a factor of 5 lower over Europe compared to previous estimates for the year 1995; Kupiainen and Klimont, Atmos. Environ. 2007; Matthias et al., Atmos. Chem. Phys. 2008) along with limited availability of observations have a considerable impact on the performance of these advanced schemes. An implicit overlap of the JP model with the K_{oa} (or another absorption) model causes a small inconsistency, much smaller than existing uncertainties of output aerosol parameters propagating from emission estimates and from the current design and state of development of the CMAQ aerosol module (AERO). Although the importance of organic aerosol has been noted in the CMAQ literature (Mathur et al., J. Geophys. Res. 2008; Matthias et al., Atmos. Chem. Phys. 2008), measurements in Europe are still sparse and a detailed assessment could not be done in this study. A future more sophisticated and consistent CMAQ aerosol module will expectedly allow to identify and better quantify remaining inconsistencies of gas-particle partitioning.

New text in the revised section of the conclusions (after line 8, page 14) reads: "In addition, certain simplifications in the treatment of coarse PM and OM within the aerosol module of CMAQ (Binkowski, 2003; Mathur et al., 2008) are posing limitations to fully exploit the advanced empirical gas-particle partitioning models (K_{oa}, Dachs-Eisenreich) in this specific mode. An implicit overlap of the empiric adsorption model (JP) with the K_{oa} (or another absorption) model (see section 2.1.1) may cause a small inconsistency, which is considered to be negligible compared to existing uncertainties of output aerosol parameters propagating from emission estimates and from the current design and state of development of the CMAQ aerosol module (AERO)."

With regard to point 2: I do not agree that a model that is "commonly accepted" but that has been shown to be conceptually flawed should continue to be applied and propagated in the literature.

Reply: We disagree. This is probably a misunderstanding by the reviewer: The Dachs-Eisenreich scheme or Lohmann and Lammel scheme (have to our) knowledge never been criticized in the literature. Their common acceptance is documented by >>50 applications in the literature including a number of comparative usage against other schemes (Lammel et al., Chemosphere 2009; Wang et al. Atmos Environ 2013; Wang et al. Environ Sci Pollut Res 2013; Friedman et al Environ Sci Technol 2014; Galarneau et al., Atmos Chem Phys 2014; Sangiorgi et al., Environ Sci Pollut Res 2014; Liu et al., Chemosphere 2015; Li et al., Atmos Environ 2016; besides others). What has in fact been criticized is the derivation of one of the parameters used in the scheme, K_{SA}, i.e., namely its derivation from K_{ow} (Goss Env Sci Technol 2004), as was done in the originally submitted version (see also reply to comments of the editor, above). However, the results achieved with this conceptually flawed method, were found to be similarly good, than those derived using the alternative method (Dachs et al. Environ Sci Technol 2004, 38, pp 1624–1625). In the revised version we use another, not conceptually flawed method to derive $K_{soot/air}$ (see above).

Anonymous Referee #3

This paper describes the application of the CMAQ model to simulate benoz[a]pyrene (BaP), one of the more toxic polycyclic aromatic hydrocarbons (PAHs). Several different parameterizations of gas-particle partitioning are implemented in the existing aerosol module and evaluated against one another. While this study represents a contribution to scientific progress with the new capability for modeling BaP within CMAQ, much of what is presented in terms of the gas-particle partitioning scheme comparisons has already been shown in other modeling studies, both at regional and global scales. The paper is also lacking detail, both in the description of the model construction and specifics about the results shown, but also in the form of little discussion of previous work and how these results compare. I recommend a resubmission after major revision. Specifically, my concerns are:

The novelty is the implementation of BaP behavior in CMAQ, but not to a regional model (first paragraph, page 3; Galarneau et al., ACP 2014, already cited within, compared these schemes within a regional model).

We would like to thank the referee for the constructive comments. In fact, BaP had first been modelled using CMAQ by Aulinger et al. (2007). Instead, the novelty of our study lies precisely in a more extensive evaluation of gas-particle partitioning schemes currently available for BaP within an air quality model such as CMAQ. Furthermore, Galarneau et al., (ACPD 2014) as erroneously mentioned, have not compared the full spectrum of the GPP schemes presented here (less than half), nor did all other studies (see Table S1). The novelty of the present study was indeed inspired by the research gap pointed in Galarneau et al., 2014, where the relevance of a similarly titled manuscript was highlighted (Galarneau, E.: Evaluation of particle/gas partitioning in a regional air quality model (AURAMS-PAH), in preparation, 2014; - not yet published, to our best knowledge).

The authors characterize the work as an extension of CMAQ to POPs, but “POPs” covers a very large set of chemicals and the model is tested for only one compound. I recommend at a minimum that “PAHs” is substituted for “POPs”, even though only one PAH is tested.

Reply: POPs indeed cover a large number of chemicals with varying properties, however the rest of the sentence makes it clear that the focus is on “an adaptable framework that accounts for gaseous chemistry, heterogeneous reactions, and gas-particle partitioning (GPP)”. The modelling framework and routines implemented within CMAQ are largely the same, and only these property-specific algorithms need to be (and have been) modified for other POPs. In addition, the introductory paragraphs explain and reference that some PAHs - and its most well studied representative (BaP) - are considered POPs.

There is at least one mischaracterization of previous work within the literature review and I recommend the authors check for others: Friedman and Selin 2012 (line 28, page 2) presented a meteorologically driven PAH model, not a general circulation model.

Reply: The work by Friedman and Selin, 2012, is based on GEOS-Chem, a global 3-D chemical transport model which has also been adapted to run with climate data from the NASA/GISS general circulation model. In order to take into account the suggestion, the term general circulation model was replaced by chemical transport model for clarity.

Recent work has suggested that the equilibrium gas-particle partitioning schemes tested here, which were first presented over a decade ago (Lohmann and Lammel, 2004), may not be representative of partitioning during long-range transport (see DOI: 10.1021/es302743z and DOI: 10.1021/es405219r). There is no discussion related to the hypothesis that SOA may facilitate PAH transport and I think there needs to be (even if brief).

Reply: We agree, SOA play an important role in long-range transport of POPs and a brief mention of the so-called “burial effect” was already mentioned in section 2.2. Additional discussion is provided at the end of the manuscript that now reads (after line 25, page 14): “Following modelling studies should focus on quantifying the long-range transport potential and examining the hypothesis that secondary organic aerosol (SOA) may facilitate PAH transport by utilising more sophisticated aerosol and heterogeneous chemistry parameterisations or submodels (i.e. accounting also for the burial effect - cf. Sect. 2.2). More specifically, recent evidence suggests that in cold and dry air accessibility of PAHs in OM is reduced (due to low diffusivity), which might explain the apparent inconsistency of high LRT potential (BaP levels in the Arctic) on one hand side and relative high heterogeneous reactivity measured in the laboratory (Friedman et al., 2014; Zelenyuk et al., 2012; Zhou et al., 2012; 2013). As understanding of PAHs' atmospheric lifetimes, PAHs' interaction with SOA, and chemical composition of ambient OM progresses, a new need for additional studies quantifying GPP and LRT potential under a wide range of atmospheric conditions is emerging. In view of such findings, the WRF-CMAQ-BaP modelling system should be extended to study a wide range of additional organic pollutants and processes (i.e. multicompartmental cycling, biodegradation, heterogeneous chemistry)."

The manuscript is quite brief and lacks context. Is this model an improvement over other European PAH models? I found no comparison to results from other modeling studies from the same region, and no justification or motivation for choosing the particular model domain. There also could be a much greater discussion of how these results, particularly for the gas-particle partitioning schemes and the heterogeneous O3 reactions, compare to results of other modeling studies; there is indeed a number of modeling studies already published that examine the same partitioning schemes and employ the same O3 reaction rates.

Reply: The goal of this study was not to provide with a comparison against previous work on the field, but rather with a more complete approach in treating gas-particle partitioning. Even if some of the studies performed over Europe using a regional air quality model, it was with different model or aerosol module, GPP schemes, and emissions. The domain is within the area covered by the UNECE-CLRTAP (and its POP protocol, covering PAHs) and was specifically chosen such as to exploit recently prepared high-resolution emission data of one of the authors (Bieser et al., Geosci Model Dev 2012) and make use of the only monitoring network in the region (EMEP). BaP heterogeneous chemistry, even with ozone, let alone other oxidants, is incompletely studied (few model aerosol materials, limited temperature and humidity ranges, phase states and particle morphologies). Therefore, the test of a number of scenarios of reactivity, in line with present lab and field knowledge would be a study of its own. Such modelling is under way, but not subject of the present study. Of course, a model performance comparison would be of great value and could be pursued in the future and could be feasible under the auspices of a larger intercomparison study such as AQMEII (http://aqmeii-eu.wikidot.com/).
New text in the revised version reads (after line 27, page 8) : "The domain is within the area covered by the UNECE-CLRTAP (and its POP protocol, covering PAHs) and was specifically chosen such as to exploit recently prepared high-resolution emission data (Bieser et al., 2011) and make use of the only monitoring network in the region (EMEP, see below)"

There is no quantitative discussion of the uncertainties contributed by physicochemical properties or emissions.

Reply: Regarding the quantitative discussion of the uncertainties introduced by the BaP emission inventory, this has been the direct topic of a study that has already been published by one of the co-authors (as pointed out previously to Referee #2). With respect to the physicochemical properties, an additional scenario and simulation was performed to investigate uncertainties contributed by different methodologies to calculate K_{oa}. In addition, the revised version of the manuscript now includes another simulation which has been performed to address uncertainties contributed by different methods in calculating K_{SA}.

New text in the revised version reads (after line 27, page 6): “As a step to address uncertainties contributed by different methods in calculating K_{SA}, a thermodynamic estimation model suggested by van Noort (2003) was also tested:

$$\log K_{SA} = -0.85 \log p_L^{\circ} + 8.94 - \log(998/a_{soot}) \qquad (12)$$

The soot specific surface area was set to 18.21 m^2 g^{-1}, derived as the geometric mean of surface areas for traffic, wood, coal, and diesel soot (i.e. 59.4, 3.6, 8.2, and 62.7 m^2 g^{-1}, respectively) (Jonker and Koelmans, 2002). Additionally, in order to estimate uncertainties arising from K_{oa} and its temperature dependence, two different parameterisations were tested, the first based on the work of Beyer et al. (2002) and the second following the temperature-dependent parameterisation suggested by Odabasi et al. (2006).”

(after line 23, page 12): “In addition, simulations that address the uncertainties contributed by the method of estimating K_{SA} were performed for the winter period of 2006 using the DE scheme. Figure S6 reveals similar results with BaP levels slightly higher in cells with strong emissions sources. However, with the exception of Moscow, the average difference BaP concentration in urban cells did not exceed 0.02 ng m^3 when K_{SA} was calculated based on the thermodynamic estimation model suggested by van Noort (2003). Similarly to K_{oa}, results suggest that the partitioning based on each K_{SA} approach is sufficiently similar.”

Table 2 is unclear. It seems to imply that a given scenario can include both the Junge-Pankow scheme and the Harner-Bidleman or the Dachs-Eisenreich scheme. This would be redundant; they are different approaches for modeling the same phenomenon.

Reply: minor/negligible ‘redundance’, see response to the Referee #1 above;

Something that would significantly enhance the contribution of this study to the current science is to apply the presented gas-particle partitioning schemes (once fully evaluated against measurements) to air-surface exchange (it is unclear if surface-air exchange is considered in the model presently). The authors mention that a) air-surface exchange is an area of POPs transport with considerable uncertainty and b) their framework could be extended to simulate mass exchange between different environmental compartments – to do so here would demonstrate the utility of the POPs modeling capability in CMAQ and add more novelty to the manuscript.

Reply: We agree, but an air-surface model is of little relevance when applied to BaP. As this is an extreme task to undertake in this very same publication (new species, compartments, air-surface exchange module with inputs and parameterisations), we are reserved to present and evaluate it in a subsequent manuscript once the foundation model in its current form has been fully evaluated.

The definition of an abbreviation is not always given on first use (e.g., WRF).

Reply: Definition of the abbreviation for WRF was misplaced later in the text. Corrected for the first instance.

It is not clear, but it seems that all of the concentration comparisons are conducted for total (gaseous and particulate) BaP concentrations. There is no comparison of simulated gas-particle speciation to observations of fraction in the particle versus gas phase. This data is available for Europe and should be included to fully evaluate the accuracy of the different schemes (a comparison between schemes has little use without any ground-truthing).

Reply: This is because there simply is no data available for the gas phase BaP for Europe (the striking majority of observations < LOQ, EMEP reports total gas+aerosol, no other data available). BaP is expected to rapidly move from gas to particulate phase close to combustion sources, or even be mostly emitted in particulate phase.This has been also confirmed by preliminary calculations of particulate mass fraction, θ, for the simulations presented in this work, which indeed show very low gas-phase BaP (even in tests treating it as non-reactive gas, similar to Aulinger et al., 2007).

Anonymous Referee #1

This manuscript presents an evaluation of alternative gas-particle partitioning schemes in a modified version of the WRF-CMAQ model run for Benzo-a-pyrene (BaP). The authors compare modeled BaP concentrations within a European model domain under 5 different gas-particle partitioning schemes and also compare model results to measurement data from EMEP monitoring sites.
The novel aspect of this work seems to be announcing that the different gas-particle partitioning schemes have been incorporated into CMAQ. The more complicated schemes apparently provide the best model performance relative to measurement data, but the authors state that the disagreements between measurements and the model are likely mostly attributable to uncertainties in emission estimates. Therefore it is difficult to draw conclusions about which partitioning scheme is best based just on results reported in this paper.

We appreciate the thoughtful review and the recognition of the novelty of the approach in 3D air quality systems such as CMAQ, despite the limited spatiotemporal coverage of the EMEP network.

I have two scientific concerns about the paper. I think both are significant, but possibly #1 arises from unclear presentation in the paper.
1) I understand Table 2 and the text to say that Scenarios 3, 4 and 5 include both the Junge-Pankow adsorption model *and* the Harner-Bidleman Koa absorption model. Is that correct? If so, I think the model is perhaps adding two redundant descriptions of gas-particle partitioning.
It has been a while since I looked at the JP model, but my recollection is that it includes a fitting parameter that was derived from empirical data under the assumption that all partitioning was by adsorption to aerosol surfaces. But, the assumption that adsorption dominates could not be confirmed.

Xiao and Wania (http://www.sciencedirect.com/science/article/pii/S1352231003002139) later showed that vapor pressure and Koa both describe sorption to organic matter equally well. Therefore, I think partitioning schemes that include both vapor pressure and Koa as chemical parameters are likely including redundant information, and could easily be over-fitted.

Reply: We agree, the parameter c_J (high for strong sorption, low for weak sorption) in the JP model may not be totally free from absorptive contributions. Therefore, adding θ of JP and K_{oa} may eventually lead to overpredictions, but these should be very low (negligible), as the absorptive contribution within JP is very low. It is very low, as the fitting was done for all possible vapors, and many of these were inorganic (almost not soluble in octanol). Unfortunately, no c_J for BAP based on measurements has ever been published. However, we found recently in background aerosol of Central Europe (Kosetice 2012-13, n=162 aerosol samples, c_J derived from experimental S/V data; Shahpoury et al., 2016) that c_J for BaP is very low, namely 0.01-5.46 Pa cm (median = 0.44 Pa cm; and also low for all other PAHs, with one exception, anthracene for which c_J>17.2 Pa cm is found). This finding is not representative for all types of aerosol in the simulation, but for the European background aerosol. It supports the perception that a possible implicit absorptive contribution to PAHs' c_J must be very low i.e., negligible. Therefore, the combined partitioning according to both the JP and a K_{oa} model is justified (note that the Harner-Bidleman version of the K_{oa} model is present only in scenario 3 – Table was modified to avoid confusion).
New text in the revised version reads (after line 13, page 5): "The empiric JP model, despite assuming adsorption to be the only relevant partitioning process, may eventually not be free from absorptive contributions (to c_J), but these should be very low. The fitting in the empiric parameterisation was done for all possible vapours, many of these not soluble in octanol. No c_J for BAP derived from ambient measurements has ever been published. However, we found recently in background aerosol of Central Europe (Kosetice 2012-13, n=162 aerosol samples, c_J derived from experimental S/V data; Shahpoury et al., 2016) that c_J for BAP is very low, namely 0.01-5.46 Pa cm (median 0.44 Pa cm), supporting the perception that a possible implicit absorptive contribution to c_J must be very low."

Shahpoury P., Lammel G., Albinet A., Sofuoglu A., Domanoğlu Y., Sofuoglu C.S., Wagner Z., Zdimal V.: Evaluation of a conceptual model for gas-particle partitioning of polycyclic aromatic hydrocarbons using poly-parameter linear free energy relationships, Environ. Sci. Technol., under review 2016.

2) The authors state that soot-air partition coefficients were calculated as the ratio of soot-water adsorption constants (Ksw) and the Henry's Law constant. Kai Goss has pointed out that applying a thermodynamic triangle for a solid interface in contact with water and the same solid interface in contact with an adjacent gaseous phase is a conceptual mistake that can lead to very large errors (http://pubs.acs.org/doi/abs/10.1021/es0301370).
I actually do not see a good option for the authors to overcome this problem, since the Lohmann & Lammel (2004) and the Dachs & Eisenreich (2000) papers that are the basis for the gas-particle partitioning scheme applied in this paper are both based on thermodynamic triangles that Goss argues (convincingly!) are invalid.

Reply: We thank the reviewer for pointing this out. We agree that the method applied is imperfect, but it is the best available and, hence, commonly accepted in atmospheric modelling (as cited by the referee, Galarneau et al., 2014, Wang et al. Atmos Environ 2013; Wang et al. Environ Sci Pollut Res 2013; Friedman et al Environ Sci Technol 2014; Galarneau et al. Atmos Chem Phys 2014; Sangiorgi et al. Environ Sci Pollut Res 2014; Liu et al.. Chemosphere 2015; Li et al Atmos Environ 2016, and others). The only other option available (suggested by Dachs et al., 2004, and van Noort, 2003) parameterises $K_{soot\text{-}air}$ as a function of the BC specific surface area, which is basically unknown and certainly transient while aging (typically changing by at least one order of magnitude within one day following emission from combustion sources). Dachs concludes that prediction of K_{sa} by either method provide reasonably similar results.
New text in the revised version reads (after line 24, page 6): "This method is subject to uncertainties (Goss, 2004), but is accepted and suitable (Dachs et al., 2004; besides others)."

van Noort, P.: A thermodynamics-based estimation model for adsorption of organic compounds by carbonaceous materials in environmental sorbents, Environ. Toxicol. Chem., 22(6), 1179–1188, doi:10.1002/etc.5620220601, 2003.
Dachs, J., Ribes, S., van Drooge, B., Grimalt, J., Eisenreich, S. J. and Gustafsson, Ö.: Response to the comment on "Influence of soot carbon on the soil−air partitioning of polycyclic aromatic hydrocarbons," Environ. Sci. Technol., 38(5), 1624–1625, doi:10.1021/es0307118, 2004.
Goss, K.-U.: Comment on "Influence of soot carbon on the soil−air partitioning of polycyclic aromatic hydrocarbon," Environ. Sci. Technol., 38(5), 1622–1623, doi:10.1021/es0301370, 2004.

Anonymous Referee #2

General comments

The manuscript describes the application of community air quality model CMAQ to study atmospheric transport of B(a)P and effects of gas-particle partitioning and degra- dation. Several gas-particle partitioning models were implemented in the CMAQ model extending its capabilities with respect to modeling of PAHs. Though the subject of the study is of importance with regard to existing air quality problems in Europe, description of this study suffers from obscurity and thus requires substantial revisions.

First of all, I would mention not clear enough description of parameters applied in the equations 10 and 11, related to gas-particle partitioning (e.g. KOA, KSA). Secondly, evaluation of the effects of several GPP mechanisms through their incremental testing (incremental testing is defined in section 3.2 and Table 2) is not quite clearly described with regard to sensitivity of CMAQ model output to particular partitioning mechanisms in model simulation scenarios. In some cases abbreviations, defined for GPP models and scenarios and used throughout the analysis, are mixed like e.g. DE model and DE scenario. This leads to problems with understanding what is presented, for example, in the second column of tables 4 and S8 called 'Model'. There are both abbreviations for scenarios and models (for example, JP-W and DE, HB, etc.). Finally, the underestimation of observed B(a)P concentrations in air is explained by low emissions. At the same time, there is no discussion of potential problems of emission data used, no comparison of total annual emissions with other studies, for example, with similar studies e.g. Aulinger et al. (2007) and others.

Reply: We appreciate the very thorough and detailed review along with the recognition of the potential relevance of the presented study. The first two points of concern have been addressed in a revised manuscript. Regarding the last area of concern, we feel that the manuscript adequately discusses the limitations of emission data used, which have been the major topic of work published by the authors (Bieser et al., 2012).

Specific comments

Page 3, line 12-13: "CMAQ contains modules representing advection, eddy diffusion, in-cloud, and precipitation processes". It would be better to use 'in cloud and below- cloud scavenging with precipitation'.

Reply: Corrected

Page 3, line 26: 'gas phase reactions' instead of 'gas reactions'.

Reply: Corrected

Page 4, line 23: Though the equation 2 follows the publication of Aulinger et al. (2007), it is not clear how the particulate fractions in each mode i, fi, are obtained, because in the cited work (Cooter and Hutzell, 2002) similar equation is written for the sum of partition coefficients, but not for fractions of a compound in particulate phase.

Reply: According to equations 1-4 in Cooter and Hutzell (2002), particulate fractions are defined for each mode i of CMAQ aerosol.

Page 5, equation 7: fOM is used without index i. Does it mean that the fraction of organic matter in aerosol particles is the same in each of three modes?

Reply: Corrected throughout the text

Page 6, line 3: assumptions used here for ratio of activity coefficients and ratio of mean molar weights of organic matter of the particles and octanol (that they are equal unity) need to be discussed with regard to their uncertainties as it was shown in e.g. (doi: 10.5194/acpd-14-21341-2014).

Reply: More explanations will be added. The new text reads (after line 7, page 6): "Assuming that octanol imitates organic matter in PM, Harner and Bidleman (1998) suggested that the ratio of γ_{oct}/γ_{OM} and M_{oct}/M_{OM} can be assumed to be 1. However, it was later suggested that M_{OM} could be much higher, particularly in secondary organic aerosols containing polymeric structures (Kalberer et al., 2004); a mean value of 500 g mol^{-1} was later suggested by Götz et al. (2007), which results in M_{oct}/M_{OM} of 0.26."

Götz, C. W., Scheringer, M., MacLeod, M., Roth, C. M. and Hungerbühler, K.: Alternative approaches for modeling gas−particle partitioning of semivolatile organic chemicals: model development and comparison, Environ. Sci. Technol., 41(4), 1272–1278, doi:10.1021/es060583y, 2007.
Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A. S. H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R. and Baltensperger, U.: Identification of polymers as major components of atmospheric organic aerosols, Science, 303(5664), 1659–1662, doi:10.1126/science.1092185, 2004.

Page 6, line 14-15: Soot-air partition coefficients were calculated as the ratio of soot water adsorption constants KSW and the inverse Henry's Law constant (HC), with KSA values adopted from Bärring et al. (2002). Concerning the way of deriving the KSA it would be important to provide estimates of uncertainties that would be introduced by this assumption. Moreover, it is unclear how this adopting was performed for B(a)P since the publication of Bärring et al. (2002) was focused on experimental determination of the soot–water distribution coefficients for PCDDs, PCDFs, and PBDEs.

Reply: K_{sa} was calculated based on K_{sw} (typo fixed) following the approach described in the footnotes of Table 1 in Lohmann and Lammel (2004). Despite the publication title not mentioning PAHs, this value is also referenced in Table 4 of Bärring et al. (2002). This information will be included in Table 1 for clarity. We agree that the method applied is imperfect, but it is the best available and, hence, commonly accepted in atmospheric modelling (as cited by the referee, Galarneau et al., 2014, Wang et al. Atmos Environ 2013; Wang et al. Environ Sci Pollut Res 2013; Friedman et al Environ Sci Technol 2014; Galarneau et al. Atmos Chem Phys 2014; Sangiorgi et al. Environ Sci Pollut Res 2014; Liu et al.. Chemosphere 2015; Li et al Atmos Environ 2016, and others). The only other option available (suggested by Dachs et al., 2004, and van Noort, 2003) parameterises $K_{soot\text{-}air}$ as a function of the BC specific surface area, which is basically unknown and certainly transient while aging (typically changing by at least one order of magnitude within one day following emission from combustion sources). Dachs concludes that prediction of K_{sa} by either method provide reasonably similar results.

New text in the revised version (following a suggestion of the other reviewer) reads (after line 24, page 6):
"This method is subject to uncertainties (Goss, 2004), but is accepted and suitable (Dachs et al., 2004; besides others)."

van Noort, P.: A thermodynamics-based estimation model for adsorption of organic compounds by carbonaceous materials in environmental sorbents, Environ. Toxicol. Chem., 22(6), 1179–1188, doi:10.1002/etc.5620220601, 2003.
Dachs, J., Ribes, S., van Drooge, B., Grimalt, J., Eisenreich, S. J. and Gustafsson, Ö.: Response to the comment on "Influence of soot carbon on the soil−air partitioning of polycyclic aromatic hydrocarbons," Environ. Sci. Technol., 38(5), 1624–1625, doi:10.1021/es0307118, 2004.

Goss, K.-U.: Comment on "Influence of soot carbon on the soil−air partitioning of polycyclic aromatic hydrocarbon," Environ. Sci. Technol., 38(5), 1622–1623, doi:10.1021/es0301370, 2004.

Page 6, line 16: There would be a need to describe more clearly these two parameterizations for K_{oa} (e.g. to give equations, to show difference).

Reply: The two K_{oa} parameterisations are described in the cited publications. Previous modelling studies of BaP followed either Beyer et al. (Aulinger, 2007) or Odabasi et al. (Galarneau, 2014). The relevant text was amended to explicitly state that Odabasi et al. determine K_{oa} as a function of temperature.

Page 10, line 6: It would be better to provide the difference (relative or absolute) between the maps in Figures 2a and 2b instead of direct comparison.

Reply: The goal of Figure 2 is to provide an illustration of BaP distributions and gradients across Europe. For better clarity we selected logarithmic scale. The difference is in fact provided in Figure 3 that provides the absolute difference comparison plot, discussed in the following paragraph.

Page 21, Table 1: it is not shown from where the values for $K_{soot\text{-}water}$, $K_{soot\text{-}air}$, and OH reaction rate were taken.

Reply: Corrected

Page 22, table 2: Table 2 does not correspond to its description in section 3.2 for 4th and 5th scenarios.

Reply: Corrected

Page 27, figure 3: Please, correct the abbreviations JB-W and DL, as they were not defined earlier. The same for figure S5. Concerning the maps, it would better to show the difference between them in relative units.

Reply: Corrected the abbreviations uniformly throughout the text. However, no visual benefit when moving from absolute to relative units was noticeable in the figures, therefore omitted.

Table 4 and Table S8 do not present mean modeled and observed B(a)P concentrations. In the column 'Model' both abbreviations for scenarios and for GPP models are used (for example, JP-W and DE, HB, etc.). Please, provide equations or references for IOA etc.

Reply: Corrected the abbreviations throughout the text and according to previous comment. The metrics of performance have been calculated based on the openair R package (Carslaw and Ropkins, 2012) as noted in section 3.2 (equations/references can be found therein).

Evaluation of gas-particle partitioning in a regional air quality model for organic pollutants

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Abstract. Persistent organic pollutants (POPs) are of considerable concern due to their well-recognised toxicity and their potential to bioaccumulate and engage in long-range transport. These compounds are semi-volatile and therefore partition between vapour and condensed phases in the atmosphere, while both phases can undergo chemical reactions. This work describes the extension of the Community Multi-scale Air Quality (CMAQ) modelling system to POPs with a focus on establishing an adaptable framework that accounts for gaseous chemistry, heterogeneous reactions, and gas-particle partitioning (GPP). The effect of GPP is assessed by implementing a set of independent parameterisations within the CMAQ aerosol module, including the Junge-Pankow (JP) adsorption model, the Harner-Bidleman (HB) organic matter (OM) absorption model, and the dual Dachs-Eisenreich (DE) black carbon (BC) adsorption and OM absorption model. Use of these descriptors in a modified version of CMAQ for benzo[a]pyrene (BaP), results in different fate and transport patterns as demonstrated by regional scale simulations performed for a European domain during 2006. The dual DE model predicted 24.1% higher average domain concentrations compared to the HB model, which was in turn predicting 119.2% higher levels compared to the baseline JP model. Evaluation against measurements from the European Monitoring and Evaluation Programme (EMEP) reveal the capability of the more extensive DE model to better capture the ambient levels and seasonal behaviour of BaP. It is found that the heterogeneous reaction of BaP with O_3 may decrease its atmospheric lifetime by 25.2% (domain and annual average) and near-ground concentrations by 18.8%. Marginally better model performance was found for one of the six EMEP stations (Košetice) when heterogeneous BaP reactivity was included. Further analysis shows that for the rest of the EMEP locations the model continues to underestimate BaP levels, an observation that can be attributed to low emission estimates for such remote areas. These findings suggest that, when modelling the fate and transport of organic pollutants on large spatiotemporal scales, the selection and parameterisation of GPP can be as important as degradation (reactivity).

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of lipophilic organic compounds with demonstrated carcinogenicity and potential to bioaccumulate (Diamond and Hodge, 2007; Finlayson-Pitts and Pitts, 1999; Pedersen et al., 2004; 2005; WHO, 2003). Typically emitted to the atmosphere as a mixture of semi- to low-volatile congeners with variable carcinogenic potency, their fate and transport in the environment is difficult to assess. Current limitations involve inadequate knowledge of photochemistry (Keyte et al., 2013), air-surface exchange (Galarneau et al., 2014; Keyte et al., 2013; Lammel et al., 2009), and combustion sources (Bieser et al., 2012; Lammel et al., 2013). In addition, aluminium and steel production along with petrogenic sources are significant in some environments (Wenborn et al., 1999). This relationship to anthropogenic activity and population density raised awareness on their potential as health stressors, with hot spots identified in urban industrial settings around the world (Šrám et al., 2013; Zhu et al., 2015). On the other hand, observations of PAHs at remote sites and global circulation model studies indicate long-range transport (Keyte et al., 2013; Sehili and Lammel, 2007). Therefore, and due to resistance to degradation, PAHs are classified as persistent organic pollutants (POPs) by the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (CLRTAP) and are listed in the Protection of the Marine Environment of the North-East Atlantic (OSPAR).

Much of the scientific literature is focussed on the 16 U.S. EPA priority PAHs i.e., acenaphthene (Ace), acenaphthylene (Acy), fluorene (Fln), naphthalene (Nap), anthracene (Ant), fluoranthene (Flt), phenanthrene (Phe), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), chrysene (Chr), pyrene (Pyr), benzo[ghi]perylene (BgP), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DBahA), and indeno[1,2,3-cd]-pyrene (IPy), albeit not well justified (Andersson and Achten, 2015). Used as a biomarker for the carcinogenic risk of PAHs, BaP is a criteria pollutant in many countries, sometimes together with a few other bioaccumulative members. While in North America no federal guidelines are currently in effect, the European Union indicative limit value is set at 1 ng m^{-3} of BaP (EC, 2004), and certain countries have established stricter air quality standards (i.e. 0.25 ng m^{-3} of BaP in the United Kingdom) (DETR, 2009).

A number of studies, which aimed at exploring the atmospheric fate and transport of POPs on various scales, have been presented in the last two decades. These include relatively simple mass balance models developed under the Lagrangian framework, some of which have been extended to multi-media applications for studying the accumulation and exchange of POPs between various compartments (Halsall et al., 2001; Lang et al., 2008; 2007; Liu et al., 2007; Prevedouros et al., 2004; 2008; Van Jaarsveld et al., 1997). Eulerian grid models add yet another level of complexity regarding process detail that is accompanied by additional computational demands. Global scale chemical transport models (Friedman and Selin, 2012; Lammel et al., 2009; Sehili and Lammel, 2007), as well as hemispheric models (Gusev et al., 2005; Hansen et al., 2006; Shatalov et al., 2005) have been applied to study the long-range transport of POPs. Moreover, coupled meteorological and air quality modelling frameworks have presented efforts to further investigate the treatment of physical and chemical atmospheric processes related to POPs in higher resolution (Aulinger et al., 2007; Bieser et al., 2012; Cooter and Hutzell, 2002; Galarneau et al., 2014; Inomata et al., 2012; Matthias et al., 2009; Meng et al., 2007; San José et al., 2013; Silibello et

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al., 2012; Zhang et al., 2009). Table S1 provides a summary of the most relevant processes covered in the respective regional model implementations and subsequent evolution tracked by author. While such studies represent the initial efforts to accurately model POPs on regional scale, important processes such as gas-particle partitioning, heterogeneous reactivity, and a multi-compartment approach for the relevant compounds are not always studied. The Weather Research Forecast along with the Community Multi-scale Air Quality for BaP (WRF-CMAQ-BaP) model presented in this article is considered to be the first effort to examine the full spectrum of gas-particle partitioning models relevant to POPs in the same regional-scale modelling application. The model attempts to capture POPs' aerosol chemistry and dynamics within the CMAQ framework and can be extended to account for mass exchange between adjacent compartments for compounds that such processes are deemed critical (i.e soil volatilization).

2 Model development

The model development framework is based on the CMAQ version 4.7.1 modelling system (Byun and Schere, 2006; Byun and Ching, 1999) with the CB05 gas phase chemistry mechanism (Yarwood et al., 2005) and the AERO4 version of aerosol module (Binkowski, 2003). In addition, CMAQ contains modules representing advection, eddy diffusion, in-cloud and below-cloud scavenging with precipitation. Advection and diffusion satisfy mass conservation and include removal by dry deposition, while in-cloud and precipitation processes simulate aqueous chemistry and wet deposition by cloud droplets (Byun, 1999a; 1999b). The aerosol module (Binkowski, 2003) determines concentrations of trimodal size distributed particulate material of diameter less than 10 μm. According to this model, each mode can be described as an internal mixture of several compounds; mixing state on the single particle level is not addressed, but is considered equivalent to internal mixing. Aitken and accumulation modes include particles of diameter ~2.5 μm or less (PM2.5), which are either emitted or produced by gas-to-particle conversion processes. A thermodynamic mechanism, based on temperature and relative humidity, determines air concentrations of water, sulfate, ammonium, and nitrate aerosols in the fine modes (Nenes et al., 1998; Zhang et al., 2000). Organic and elemental carbon species are also included in these modes. The third mode represents coarse material having diameters between 2.5 and 10 μm and includes dry inorganic material emitted by natural and anthropogenic sources. Other processes like coagulation, particle growth, aerosol-cloud interactions, and new particle formation are included in the treatment.

CMAQ adaptations are required to fully address the behaviour of semi-volatile organic compounds (SOCs) in the atmosphere and include additional homogeneous gas phase reactions, a modular algorithm to describe the mass exchange of SOCs between the gas and particulate phases, and a description of deposition for each phase state of the compound of interest. For the case of benzo(a)pyrene (BaP), one gas-phase species and three particulate-sorbed species, one for each aerosol mode, are introduced. It is assumed that only the gaseous molecule undergoes chemical degradation through a reaction with the hydroxyl (OH) radical, leading to an unspecified product that does not undergo further chemical reaction. A summary of the physico-chemical data used in this study is presented in Table 1. Furthermore, a module that accounts for heterogeneous chemistry was included for compounds that such reactions represent a significant loss according to experimental studies (e.g. BaP reaction with O_3).

2.1 Modular implementation of gas-particle partitioning (GPP) in CMAQ

The distribution of POPs between the gas and the particulate phases is widely recognised as the most important parameter in describing their fate and transport in the atmosphere. PAHs like benzo(a)pyrene can be adsorbed to mineral surfaces or elemental carbon, absorbed by organic aerosol, or absorbed by aerosol water (Lohmann and Lammel, 2004). Therefore, the aerosol module of CMAQ was enhanced with an array of models that assume different processes as determining gas-particle partitioning, i.e. an adsorption model (Junge-Pankow (Junge, 1977; Pankow, 1987)), an organic matter (OM) absorption model (K_{oa} (Harner and Bidleman, 1998)), and a dual OM absorption and elemental or black carbon (EC/BC) adsorption model (Dachs and Eisenreich, 2000; Lohmann and Lammel, 2004). In addition, a method for calculating the absorption in particulate phase water was included in the module, employed for all aerosol modes in a manner similar to the GPP processes (Aulinger et al., 2007; Cooter and Hutzell, 2002).

The new GPP algorithm for CMAQ brings together existing implementations for pesticides (Cooter and Hutzell, 2002), PAHs (Aulinger et al., 2007; San José et al., 2013), polychlorinated biphenyls (PCBs) (Meng et al., 2007), dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Zhang et al., 2009) in a unified module that allows for flexible GPP model combinations, making it applicable to a wide range of SOCs. The following assumptions were taken into consideration: instantaneous relaxation to phase equilibrium (no mass transport kinetic limitations), the compound does not irreversibly transform in the particulate phase, and sorption processes do not interact. By extending the gas-phase and modal aerosol treatments in CMAQ for SOCs, these assumptions allow the use of simple ratios to determine the concentration of each form following

$$a_i = \phi_i(a_i + g) \qquad (1)$$

where a_i is the particulate concentration in each mode (i=1=Aitken, 2=accumulation, 3=coarse), g is the gaseous concentration and ϕ_i is the particulate fraction of the compound in mode, with a general formulation (Aulinger et al., 2007; Cooter and Hutzell, 2002)

$$\phi_i = \phi_i^{ad} + \phi_i^{ab} + \phi_i^{aq} \qquad (2)$$

This way, all partitioning processes: adsorption (ϕ_i^{ad}), absorption in OM (ϕ_i^{ab}), and absorption (solution) in aerosol water (ϕ_i^{aq}) are simultaneously treated. Following the rule of mass conservation for the compound in both phases, the total concentration c_{tot} can be introduced

$$g = c_{tot} - a_1 - a_2 - a_3 \qquad (3)$$

leading to a system of three linear equations

$$\begin{bmatrix} 1 & \phi_1 & \phi_1 \\ \phi_2 & 1 & \phi_2 \\ \phi_3 & \phi_3 & 1 \end{bmatrix} \cdot \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} = c_{tot} \times \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \end{bmatrix} \qquad (4)$$

that yields the particulate concentrations a_i in each mode. Subsequently, using the previous equation, the gaseous concentration g can be calculated.

2.1.1 Junge – Pankow adsorption model

The first GPP scheme is based on the model of exchangeable SOC adsorption to aerosols presented by Junge (1977) and later critically reviewed by Pankow (1987)

$$\phi_i^{ad} = c_J S_i / \left(p_L^\circ + c_J S_i\right) \tag{5}$$

The equation above relates the mass fraction of chemical adsorbed to particles in each mode i (ϕ_i^{ad}) to the subcooled liquid vapor pressure of the compound (p_L°, Pa) and the aerosol surface density (S_i, m^2 of particles' surface per m^3 of air). The parameter c_J (unit, Pa m) depends on the chemical nature of both the adsorbant and the adsorbate, and cannot be expected to be a constant, as confirmed by field experiments (Lammel et al., 2010). Nevertheless, a value of c_J = 0.172 Pa m has been suggested (Pankow, 1987) and is often used in modelling applications. The surface area parameter, S_i, which is a characteristic of the aerosol required for the Junge-Pankow model, is calculated at each time step for each mode within the aerosol module of CMAQ (Binkowski, 2003).

The empiric JP model, despite assuming adsorption to be the only relevant partitioning process, may eventually not be free from absorptive contributions (to c_J), but these should be very low. The fitting in the empiric parameterisation was done for all possible vapors, many of these not soluble in octanol. No c_J for BAP derived from ambient measurements has ever been published. However, we found recently in background aerosol of Central Europe (Kosetice 2012-13, n=162 aerosol samples, c_J derived from experimental S/V data; Shahpoury et al., 2016) that c_J for BAP is very low, namely 0.01-5.46 Pa cm (median 0.44 Pa cm), supporting the perception that a possible implicit absorptive contribution to c_J must be very low.

2.1.2 K_{oa} absorption model

The second GPP scheme follows the work of Pankow (1994; 2007), with refinements from Harner and Bidleman (1998) that described how the particulate fraction of a compound could be derived from the aerosol-air partitioning coefficient Kp. Following this approach for each mode i, the predicted particulate fraction ϕ_i^{ab} is linked to the total mass concentration of suspended particles c_{TSP_i} with the following equation

$$\phi_i^{ab} = K_{p,i}^{OM} c_{TSP_i} / \left(K_{p,i}^{OM} TSP_i + 1\right) \tag{6}$$

Pankow (1987; 1998) demonstrated that the gas-particle partitioning coefficient, Kp, and the use of p_L° as its descriptor are valid both for adsorption and absorption of SOCs. In the case of absorptive partitioning, Pankow (1998) derived

$$K_{p,i}^{OM}(m^3 \mu g^{-1}) = \frac{f_{OM_i} 760 RT}{10^6 M_{OM} \gamma_{OM} p_L^\circ} \tag{7}$$

where f_{OM_i} is the mass fraction of OM in the particle that can absorb gaseous SOCs, R is the ideal gas constant (= 8.314 Pa m^3 $mol^{-1}K^{-1}$), T (K) is absolute temperature, M_{OM} (g mol^{-1}) is the mean molecular weight of the OM phase, γ_{OM} is the activity coefficient of the selected SOC in the OM on a mole fraction basis, and p_L° (Pa) is the vapour pressure of the pure SOC (subcooled liquid in the case of solids). Partitioning coefficients normalized to the OM content were introduced to further support the absorption hypothesis (Finizio et al., 1997). Pankow (2007), and Harner and Bidleman (1998) replaced p_L° by the octanol-air partitioning coefficient, K_{oa}

$$K_{p,i}^{OM} = 10^{-12} \frac{f_{OM_i} M_{oct} \gamma_{oct} K_{oa}}{M_{OM} \gamma_{OM} \rho_{oct}} \tag{8}$$

where M_{oct}, M_{OM} ($g\ mol^{-1}$) are the molecular weights of octanol (= $130\ g\ mol^{-1}$) and the OM phase, γ_{oct}, γ_{OM} are the activity coefficients of the SOC in octanol and OM, respectively, and ρ_{oct} is the density of octanol (0.82 kg L^{-1}). Assuming that octanol imitates organic matter in PM, Harner and Bidleman (1998) suggested that the ratio of γ_{oct}/γ_{OM} and M_{oct}/M_{OM} can be assumed to be 1. However, it was later suggested that M_{OM} could be much higher, particularly in secondary organic aerosols containing polymeric structures (Kalberer et al., 2004); a mean value of 500 g mol-1 was later suggested by Götz et al. (2007), which results in M_{oct}/M_{OM} of 0.26. Under the assumptions that γ_{oct}/γ_{OM} and $MW_{oct}/MW_{OM} = 1$, the equation above can be simplified to the following

$$log\, K_{p,i}^{OM} = log\, K_{oa} + log\, f_{OM} - 11.91 \tag{9}$$

2.1.3 Dual OM absorption and black carbon adsorption model

Finally, the third GPP scheme extends the previous OM absorption model to include adsorption onto particulate soot, according to evidence showing the measured K_p to be exceeding the predicted K_p based solely on absorption in OM (Dachs and Eisenreich, 2000; Fernandez et al., 2002; Lohmann and Lammel, 2004; Ngabe and Poissant, 2003). Considering the contribution of those two additive processes a modified partition coefficient can be employed

$$K_{p,i}^{dual} = 10^{-12} \left(\frac{f_{OM_i} M_{oct} \gamma_{oct} K_{oa}}{M_{OM} \gamma_{OM} \rho_{oct}} + \frac{f_{BC_i} a_{atm-BC} K_{SA}}{a_{soot} \rho_{BC}} \right) \tag{10}$$

where f_{BC_i} is the fraction of black carbon in the particulate matter, a_{atm-BC} and a_{soot} are the available surfaces of atmospheric black carbon (BC) and diesel soot, respectively, K_{SA} is the partitioning coefficient between diesel soot and air. A density value of 1 kg L^{-1} has often been assumed for BC, however values in the range of 1.7-1.9 kg L^{-1} have been measured and recommended by Bond and Bergstrom (2006). Thus, the equation can be simplified

$$K_{p,i}^{dual} = 10^{-12} (0.32 \times f_{OM_i} K_{oa} + 0.55 \times f_{BC_i} K_{SA}) \tag{11}$$

This method is subject to uncertainties (Goss, 2004), but is accepted and suitable (Dachs et al., 2004; besides others). Soot-air partition coefficients (K_{SA}) were calculated as the ratio of soot-water adsorption constants K_{SW} and the inverse Henry's Law constant (H'), with K_{SW} values adopted from Bärring et al. (2002). As a step to address uncertainties contributed by different methods in calculating K_{SA}, a thermodynamic estimation model suggested by van Noort (2003) was also tested:

$$logK_{SA} = -0.85\, log\, p_L^\circ + 8.94 - log(998/a_{soot}) \tag{12}$$

The soot specific surface area was set to 18.21 m^2 g^{-1}, derived as the geometric mean of surface areas for traffic, wood, coal, and diesel soot (i.e. 59.4, 3.6, 8.2, and 62.7 m^2 g^{-1}, respectively) (Jonker and Koelmans, 2002). Additionally, in order to estimate uncertainties arising from K_{oa} and its temperature dependence, two different parameterisations were tested, the first based on the work of Beyer et al. (Beyer et al., 2000) and the second following the temperature-dependent parameterisation suggested by Odabasi et al. (2006).

2.2 Dissolution into aerosol water

An assumption of the CMAQ aerosol module is that organics influence neither the water content nor the ionic strength of the system. While this assumption may not be valid for many atmospheric aerosols, sufficient basic data are not available to treat the system in a more complete way. In a similar manner, the dissolution of PAHs in the aqueous electrolyte was calculated using the inverse Henry's Law constant (Aulinger et al., 2007; Cooter and Hutzell, 2002; Lohmann and Lammel, 2004). Lohmann and Lammel (2004) derived the partitioning coefficient $K_{p,i}^{aq}$, although they conclude that as long as a solid-air interface exists, the contribution of dissolved PAHs to the gas-particle partitioning will always be negligible. To account for this, a "wet aerosol" switch was introduced and associated with the relevant partitioning coefficient

$$\log K_{p,i}^{aq} = \log K_{wa} + \log f_{wa,i} - 12.0 \qquad (13)$$

where $f_{wa,i}$ is the mass fraction of aerosol water in each mode i and K_{wa} is the water-air partitioning coefficient, which is equal to H′. The aerosol water content is computed in CMAQ based on a variation of the ZSR method (Byun and Ching, 1999; Kim et al., 1993). As suggested by Aulinger et al. (2007) for CMAQ, only if the ratio of ammonium sulfate to aerosol water drops below the solubility of ammonium sulfate, the aerosol is treated as wet and absorption into aerosol water takes effect, while adsorption to inorganic material is switched off.

2.3 Gas-phase and heterogeneous reactions

Reactions with the hydroxyl radical (OH), ozone (O_3), and the nitrate radical (NO_3) may determine the atmospheric fate and long-range transport potential of SOCs. Gas-phase reactions with OH are believed to be the dominant loss pathway for semi-volatile PAHs (3-4 rings), like anthracene and pyrene (Atkinson and Arey, 1994; Finlayson-Pitts and Pitts, 1999; Keyte et al., 2013). On the other hand, in the case of non-volatile PAHs (5 and more rings, like BaP), loss due to heterogeneous reaction with ozone is believed to dominate (Finlayson-Pitts and Pitts, 1999). Experimental studies of the kinetics of PAHs sorbed to particles indicate strong influences of mixing state (single particle anisotropy), morphology, and phase state of the particles (Kwamena et al., 2004; Perraudin et al., 2007; Pöschl et al., 2001; Shiraiwa et al., 2009; Zhou et al., 2012). Yet, detailed heterogeneous chemistry models would require corresponding additional parameters and a more sophisticated surface layer model (Kaiser et al., 2011; Shiraiwa et al., 2010; Springmann et al., 2009). However, in the studies by Kahan et al. (2006) and Kwamena et al. (2004; 2007), the reactivity could be well described by a Langmuir – Hinshelwood

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mechanism (i.e. one species [BaP] is adsorbed to the surface while the second species, ozone, is in phase equilibrium). This approach is followed in the CMAQ aerosol module by introducing the degradation rate coefficient k in the following form

$$k = \frac{k_{max}K_{O_3}c_{O_3}}{1 + K_{O_3}c_{O_3}} \qquad (14)$$

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where k_{max} is the maximum rate coefficient (0.060 ± 0.018 s^{-1}), K_{O_3} is the ozone gas to surface equilibrium constant (0.028 ± 0.014×10^{-13} cm^3), and c_{O_3} the concentration of ozone (molecules/cm^3). As this reaction neglects the substance fraction not accessible for gaseous O_3 molecules (so-called burial effect; Zhou et al., 2012), an upper estimate for BaP reactivity is simulated.

2.4 Dry and wet deposition

SOCs and their degradation products are removed from the atmosphere through dry and wet deposition. Dry deposition is modelled in CMAQ as a one-way flux out of the lowest layer of the atmosphere. Particulate forms have dry deposition velocities determined by Brownian diffusion, turbulence, and sedimentation. Mass and diameter of the mode are used to estimate the sedimentation velocity (Binkowski, 2003; Byun and Ching, 1999). The deposition velocity of gaseous molecules is based on an electrical resistance analogue that includes aerodynamic (R_a), quasi-laminar boundary layer (R_b), and surface canopy (R_c) resistance (Pleim et al., 1999). R_a is computed using similarity theory with heat flux. R_b depends on landuse specific friction velocity and molecular characteristics of gases. R_c is consisted of several components, including bulk stomatal, dry cuticle, wet cuticle, ground, and in-canopy aerodynamic resistance (Pleim et al., 1999). Cuticle and ground resistances are based on ozone and sulphur dioxide observations and neglect absorption into organic plant or soil material. Values for time-dependent R_c parameters are determined via landuse and mesoscale meteorological models, which provide fractional vegetation cover, leaf area index, fractional leaf area wetness, and leaf stress associated with radiation, root zone soil moisture, temperature, and humidity (Pleim and Xiu, 1995).

Wet deposition of gaseous molecules occurs through in-cloud and below-cloud scavenging. Both processes are assumed to have the same scavenging efficiency and dependency on Henry's Law, water content of the cloud, and precipitation rate (Chang et al., 1986). Wet scavenging parameterization of the particulate phase molecules follows the method of Roselle and Binkowski (Byun and Ching, 1999) and depends on the aerosol mode (size) and time required to remove all liquid water from a cloud volume. No ice phase scavenging is included in the 4th version of the aerosol module in CMAQ.

3 Model implementation and study design

The model domain included entire Europe and neighbouring countries as shown in Figure 1. The domain is within the area covered by the UNECE-CLRTAP (and its POP protocol, covering PAHs) and was specifically chosen such as to exploit recently prepared high-resolution emission data (Bieser et al., 2011) and make use of the only monitoring network in the region (EMEP, see below). Computational simulations were performed on a 36 × 36 km Lambert Conformal Conic grid

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using offline hourly meteorological fields, generated by the Weather Research Forecasting (WRF) model version 3.4.1 using GFS meteorological reanalysis data (spatial resolution 0.5° × 0.5°) as input. The parameterization of WRF included the following schemes: Milbrandt-Yau Double-Moment 7-class microphysics (Milbrandt and Yau, 2005a; 2005b), Rapid radiative transfer model (RRTMG) longwave and shortwave scheme (Iacono et al., 2008), asymmetric convective model of PBL (Pleim, 2007), Pleim-Xiu surface layer model (Pleim and Xiu, 2003; Xiu and Pleim, 2001), and the improved version of Grell-Devenyi (Grell, 1993; Grell and Devenyi, 2002) ensemble scheme for cumulus parameterization. On the vertical dimension, the domain was resolved in 36 layers, following the eta coordinate system. Subsequently, CMAQ-ready meteorological input fields for 2006 were prepared using the Meteorology-Chemistry Interface Processor (MCIP) (Otte and Pleim, 2010). Computational simulations were performed in a distributed computing infrastructure operated and managed by the Czech National Grid Organization MetaCentrum NGI.

3.1 Emissions

Capturing the spatiotemporal pattern of emissions is of crucial importance to determine the fate and transport of PAHs. Several attempts have been carried out during the past decades, with varying spatial and temporal resolutions in historical, current, and future projection terms for Europe (Bieser et al., 2012; Pacyna et al., 2003). Currently, 4 database sources with gridded BaP emissions exist for Europe and Russia: the TNO database (Denier van der Gon et al., 2006), the EMEP one (Mantseva et al., 2004), a dataset for POPCYCLING-Baltic project (Pacyna et al., 2003), and a global emission inventory for the year 2008. The SMOKE for Europe (SMOKE-EU) model (Bieser et al., 2011) output used in this study, follows a methodology that is based on the TNO database and has been evaluated in a number of subsequent CMAQ applications (Aulinger et al., 2011; Bewersdorff et al., 2009; Matthias et al., 2008). In order to spatially disaggregate BaP emissions in a more realistic way, SMOKE-EU improves on using a linear dependency on the population density as surrogate factor, by introducing different relevant relationships based on source classification and meteorological parameters. For example, the relationship to wood availability and the level of urban agglomeration have been introduced as an effort to include the effect of burning biomass. The resulting spatial distribution and annual average emission flux of BaP for our domain during the year 2006 is shown in Figure 1. In addition, BaP emissions are shaped temporally using diurnal and weekly functions. As residential combustion is associated with the majority of BaP emissions, a strong dependence on the season and spatial variability is expected. To account for this dependence, heating degree days have been introduced as a proxy (Aulinger et al., 2011). A major strength of the SMOKE-EU inventory is provision of CMAQ-ready emissions for all species involved in the desired chemical mechanism (e.g. CB5) and aerosol module (e.g. aero4). Following the trimodal representation of aerosol in CMAQ, 0.1% of the emissions of BaP was allocated to the Aitken mode, while the rest was emitted in the accumulation mode, as this is the default treatment with all primary organic aerosol species in the model.

3.2 Evaluation data and sensitivity simulations

The spatiotemporal coverage of BaP in air and deposition in Europe and Russia is limited, in many regions sporadic or not available at all. For 2006, concentration in air is available from eight stations (n=173), while deposition information is available from six stations of the EMEP monitoring network (Aas and Breivik, 2012). An overview of the data, including site codes, geographical information, and the sampling strategies is provided in Table S2. It is evident that during 2006, only four of the total of ten sites provide information on concentration and deposition simultaneously. Additionally, the sampling strategy varies widely among the stations, leading to a non-homogeneous pool of data. For example, on the Košetice (CZ0003R) and Niembro (ES0008R) stations, BaP is measured for 24 hours once a week, while in Aspvreten (SE0012R) and in Pallas (FI0036R) samples cover one week and are taken once every month. On the other hand, the Latvian sites (LV0010R, LV0016R) are sampled on a monthly basis, while for the High Muffles location (GB0014R) a three-month sample is obtained four times in 2006. Finally, the sites located in Germany (DE0001R, DE0009R) provided information only in terms of wet deposition and on a monthly basis during 2006.

Based on the set of GPP mechanisms described before, the effect of each parameterization was evaluated against the EMEP measurements by incremental testing of the models involved, while keeping the same meteorological and emission inputs. Table 2 summarizes the 5 annual scenarios that were developed for 2006 (1: Junge-Pankow, 2: Scenario 1 with water dissolution, 3: Scenario 2 with the Harner-Bidleman (HB) K_{oa} absorption model, 4: Scenario 2 with dual OM absorption and black carbon adsorption model Dachs-Eisenreich (DE) scheme, 5: Scenario 4 supplemented by a heterogeneous reactivity module). A spin-up time of 7 days was allowed for each simulation in order to maintain a low influence of the initial conditions. Comparisons against measurements of BaP in ambient air were produced using the statistical computing framework of the R language, and the model performance was evaluated building on a wide range of statistics calculated using the Models-3 and the openair packages (Carslaw and Ropkins, 2012).

4 Results and discussion

4.1 Spatiotemporal distributions of BaP over Europe

The pattern of normalized annual mean BaP concentrations over the domain using the baseline scenario 1 (JP) is presented in Figure 2a. Elevated levels were found in regions with strong emission sources in Central Europe (Po Valley, Rhine-Ruhr, Poland and Ukraine areas), as well as in the vicinity of large cities (among others Moscow, Paris, Vienna, Madrid, and Istanbul). In addition, annual mean BaP concentrations according to the fully expanded scenario 5 (KW) are depicted in Figure 2b. Comparing the output from the aforementioned simulations revealed higher BaP levels with scenario 5, which can be associated with the geographic distribution of emissions. This is the first indication that the chosen partitioning approach has a significant impact on the model results for total BaP concentrations. However, it is also evident that in southern Europe and the Mediterranean region the BaP losses associated with the addition of an upper estimate of heterogeneous reactivity with O_3 (Scenario 5 – Figure 2b) may have a limiting effect on BaP long-range transport (LRT) potential. This can be supported by the prominent BaP gradients calculated over the Mediterranean Sea, acting as a sink that is driven by low BaP emissions and elevated O_3 levels. The overall model patterns show a good agreement with recent regression methods mapping BaP levels that provide with a partial coverage of our EU domain. Discrepancies over Eastern Europe indicate that a more elaborate emissions inventory (i.e. domestic heating adjustments) would be beneficial.

4.1.1 Effect of GPP parameterizations and heterogeneous reactivity with O_3

Figure 3 and Table 3 illustrate the differences resulting from the incrementally tested scenarios (Table 2), expressed as annual mean BaP concentrations over the entire domain of interest and the individual EU-28 member states. As expected, the effect of dissolution into aerosol water (Figure 3a) is limited throughout most of the domain, with coastal urban areas being the most influenced (i.e. Istanbul, North Sea). BaP dissolution in aerosol liquid water according to scenario 2 led to less than 0.36% reduction of ground level BaP in Europe as compared to the baseline JP scheme (Table 3). Introducing the HB absorption scheme (scenario 3) resulted in ~119.2% higher average BaP concentrations (Figure 3b) with extremes observed in areas associated with emission sources in Central Europe (i.e. Po Valley) and large cities (i.e. Moscow, Paris, Vienna, and Istanbul). Expressed in terms of domain-wide atmospheric lifetimes (defined as $\tau = b_{tot}/F_{em}$, where b_{tot} denotes the total atmospheric burden and F_{em} the total emissions), scenario 3 leads to a 210% increase for BaP over scenario 2. Similarly, shifting to the DE scheme (scenario 4) appears to have an additive effect on near-ground BaP concentrations with total lifetimes reaching a domain-average increase of 13%. Compared to the scenario 3, scenario 4 affects a larger area of the domain (Figure 3c), even though the magnitude of the effect is less pronounced due to its association with the availability of black carbon. The domain mean of modelled elemental carbon is 0.0212 μg m^{-3} and the spatial distribution is matching its emission pattern (Figure S3). These levels are significantly lower compared to field studies in the urban air of south-west Europe (EEA, 2013; Milford et al., 2016), and may subsequently lead to hindered performance of the DE scheme.

Finally, the introduction of heterogeneous chemistry (scenario 5) had, as expected, a substantially negative effect on the BaP concentrations within our domain culminating in major conurbations (i.e. Po Valley, Moscow, and Istanbul; cf. Figure 3d). Heterogeneous degradation due to the reaction with O_3 accounts for an approximate 18.8% reduction of the mean ground level BaP and a 25% reduction of its atmospheric lifetime in the European domain (Table 3). As mentioned in Sect. 4.1, the BaP concentration gradients reveal a strong spatial link with emission sources in the south, as well as high O_3 concentrations typically found across the coasts of the Mediterranean Sea (Figure S4). CMAQ calculates ozone patterns that are in accordance to the findings of recent analyses, exhibiting similar performance compared against measurements at the European level (de Smet et al., 2009).

4.1.2 Seasonality and relevant parameters affecting BaP fate and transport

Seasonally disaggregated distributions of BaP, as simulated scenario 4 are presented in Figure 4. Strong emissions during wintertime and fall have an apparent effect on the average ground level concentrations. In addition, a normalized effect of long-range transport for BaP can be observed in the vicinity of Istanbul and other coastal metropolitan areas, over parts of the large water bodies of the Mediterranean and the Black Sea. This scenario, however, does not include the treatment of the heterogeneous reaction with ozone, and therefore provides an upper bound estimate of the LRT potential of BaP. On the other hand, Figure 5 demonstrates the seasonal effect of the heterogeneous reaction of BaP with ground-level ozone on BaP concentrations. Distributions of BaP concentration differences reveal a stronger reduction during winter that is influenced by central and southern European emission sources and mid-latitude ozone availability. Interestingly, the differences between winter and summertime appear to be comparable in terms of magnitude, despite the substantially weaker sources during summer that shift the process to the south.

An important factor for the performance of the BaP model is the mass concentration and composition of the aerosols in the three different modes and their relationship with the temperature of the ambient air. Figure 6 illustrates the aerosol distributions as simulated at model cells representing three different settings (Urban: City of Vienna, Suburban: CZ0003R, Remote: FI0036R) during a typical winter and summer day. As we move further away from the vicinity of the sources, we notice not only a decrease of the overall BaP levels but also a change in the distribution influenced by each individual simulated scenario. While the basic Junge-Pankow implementation results in higher coarse mode BaP concentrations, the HB and DE schemes accentuate the strength of the accumulation mode where most of the BaP aerosol mass is emitted. The disproportionately higher coarse BaP fractions calculated at the remote grid cells during the summertime can be explained by conditions favouring long-range transport.

Regarding the parameterizations of the HB and DE schemes, the calculation of the parameter K_{oa} has a direct effect on the relevant model results (Scenarios 3 and 4). Use of the regression parameters for the semi-logarithmic temperature-dependent form proposed by Odabasi et al., (2006), results in a mixed effect over its predecessor scheme that is seasonally disaggregated and presented in Figure S5. These figures suggest that the partitioning based on each K_{oa} approach is sufficiently similar for most of the domain during the winter. However, differences between the two expressions with respect to simulating summertime BaP concentrations over Central Europe were noted. In addition, simulations that address the uncertainties contributed by the method of estimating K_{SA} were performed for the winter period of 2006 using the DE scheme. Figure S6 reveals similar results with BaP levels slightly higher in cells with strong emissions sources. However, with the exception of Moscow, the average difference BaP concentration in urban cells did not exceed 0.02 ng m^3 when K_{SA} was calculated based on the thermodynamic estimation model suggested by van Noort (2003). Similarly to K_{oa}, results suggest that the partitioning based on each K_{SA} approach is sufficiently similar.

4.2 Model evaluation against EMEP measurements

The EMEP network database and model output from all 5 scenarios were imported in the R language framework to create measurement-model pairs for further analysis. Figure 7 illustrates the resulting timeseries plots for selected EMEP sites against CMAQ output extracted from scenario 4. This figure also demonstrates differences in terms of sampling protocols among individual sites, with the extreme of the High Muffles station (4 samples/year – Table S2). Aggregate temporal

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profiles of the modelled and measured BaP concentrations across all sites depicted in Figure 8 reveal a strong seasonal pattern that is captured well by the model. However, BaP concentrations appear to be underestimated during the colder months. This effect can be attributed to the strength of emissions, which is probably related to inadequate coverage of residential heating in current inventories (wood/biofuel burning). Figure S7 illustrates this by comparing annual average BaP emission fluxes between model cells enclosing EMEP monitoring site locations, and selected metropolitan areas of Europe during 2006. While known deficiency of PAH inventories, it may limit the usefulness of background measurements (such as those in the EMEP network) in assessing the overall model performance under different GPP scenarios.

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It is evident from the metrics obtained across all sites (Table 4 and Taylor diagram summary Figure S8) that the increased complexity in GPP formulation results in better agreement with the EMEP measurements. For reasons mentioned in Sect. 2.2-2.3 and 4.1.1, deviations from this observation are the simulated scenarios that introduce the dissolution to aerosol water (scenario 2) and degradation due to the heterogeneous reaction with ozone (scenario 5). Overall, the dual model (DE) employed in scenario 4 showed the best agreement with the measurements. The DE parameterisation also performed best when compared with the JP and HB schemes on global scale applications (Lammel et al., 2009). However, when looking at site-specific performance metrics (Table S9), the Košetice location (CZ0003R) reveals a better agreement with the fully expanded scenario 5 that treats degradation by ozone. The Košetice site is the closest to conurbations among the EMEP sites available during 2006. This could indicate that the heterogeneous chemistry, which is implemented as an upper estimate in this model, tends to underestimate BaP levels further away from the sources. The best model performance was observed at the Pallas station (FI0036R), where scenario 4 was capable of matching 50% of the measurements within a factor of 2. For the remaining remote sites in Finland, the simulation under scenario 5 calculated underestimated BaP levels. Based on the Index Of Agreement (IOA) metric, a ranking of the overall model performance similar to the Pallas site was observed for the rest of the monitoring sites. Finally a qualitative analysis of the deposition measurements for the few stations that measured BaP showed that CMAQ calculated plausible patterns of dry and wet deposition (cf. Figure S10).

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5 Conclusions

This study presented the development of a new modelling system for investigating the dynamics of transport and gas-particle partitioning schemes for POPs at the regional scale over Europe. The implementation of this model is based on the WRF-CMAQ model framework with additional algorithms for GPP schemes and a module that accounts for heterogeneous reactivity of BaP with ozone. Predictions from the WRF-CMAQ-BaP model were compared against measurements obtained from the EMEP monitoring network. Model evaluation has revealed satisfactory agreement to the measurements and performance metrics similar to those of previous studies with significantly higher measurement availability. The results presented in this work suggest that the new expanded model is able to simulate fairly well the ambient levels of BaP. It is found that BaP distributions in Europe are very sensitive to the choice of GPP models. While this statement has been also indicated at the global scale (Lammel et al., 2009), GPP has not been adequately explored by previous regional scale studies (cf. Table S1 and references therein). We conclude that the dual OM absorption and black carbon adsorption (DE) parameterisation (scenario 4-5) offer a better performance, as BaP predictions tend to be closer to the measurements. Introducing an independent upper estimate of heterogeneous BaP reactivity is found to significantly reduce BaP levels throughout the domain, with a reduction pattern that follows the spatial distribution of ozone and emission sources. Despite the limited BaP monitoring network, a partly better agreement was found when complementing WRF-CMAQ-BaP with the upper estimate for heterogeneous reactivity (scenario 5). Uncertainties and limitations of the current emission inventory estimates of BaP, OM, and BC along with insufficient laboratory data are of major concern, hampering the efforts to fully evaluate the long-range transport potential and the effect of photochemistry and interactions of such compounds. In addition, certain simplifications in the treatment of coarse PM and OM within the aerosol module of CMAQ (Binkowski, 2003; Mathur et al., 2008) are posing limitations to fully exploit the advanced empirical gas-particle partitioning models (K_{oa}, Dachs-Eisenreich) in this specific mode. An implicit overlap of the empiric adsorption model (JP) with the K_{oa} (or another absorption) model (see section 2.1.1) may cause a small inconsistency, which is considered negligible compared to existing uncertainties of output aerosol parameters propagating from emission estimates and from the current design and state of development of the CMAQ aerosol module (AERO).

The modelling approach presented here allows simultaneous estimation of organic pollutants, including semivolatiles (such as most POPs) within the CMAQ framework, and can be used as a supplementary component of a population exposure modelling system. Although similar systems are currently explored, they rely heavily on observation data while using a very basic air quality model structure (Guerreiro et al., 2016). At this time, annual exposure estimates are more useful due to the low accuracy accompanying highly time-resolved models. As previous efforts to evaluate the use of mesoscale models for BaP dispersion studies also conclude, changes in emission patterns and their strength is of particular importance. While there is undeniable effort to shift from fossil fuels to renewables which has led to updated emission inventories, domestic heating across Europe has also a complex relationship to economic factors and human activities that varies tremendously between countries and fuel types (Lohmann et al., 2006; Saffari et al., 2013). Besides the need of updated emission inventories for the Eastern Europe, extended simulations are suggested during years with higher measurement availability and density. Following modelling studies should focus on quantifying the long-range transport potential and examining the hypothesis that secondary organic aerosol (SOA) may facilitate PAH transport by utilising more sophisticated aerosol and heterogeneous chemistry parameterisations or submodels (i.e. accounting also for the burial effect - cf. Sect. 2.2). More specifically, recent evidence suggests that in cold and dry air accessibility of PAHs in OM is reduced (due to low diffusivity), which might explain the apparent inconsistency of high LRT potential (BaP levels in the Arctic) on one hand side and relative high heterogeneous reactivity measured in the laboratory (Friedman et al., 2014; Zelenyuk et al., 2012; Zhou et al., 2012; 2013). As understanding of PAHs' atmospheric lifetimes, PAHs' interaction with SOA, and chemical composition of ambient OM progresses, a new need for additional studies quantifying GPP and LRT potential under a wide range of atmospheric conditions is emerging. In view of such findings, the WRF-CMAQ-BaP modelling system should be

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extended to study a wide range of additional organic pollutants and processes (i.e. multicompartmental cycling, biodegradation, heterogeneous chemistry).

Acknowledgements

The authors thank Frank Binkowski, Sarav Arunachalam, and Zac Adelman at the University of North Carolina (UNC) for their guidance and support during the onset of this project. EMEP is acknowledged for the monitoring data. Access to computing and storage facilities owned by parties and projects contributing to the National Grid Infrastructure MetaCentrum provided under the programme "Projects of Large Infrastructure for Research, Development, and Innovations" (LM2010005) is also greatly appreciated. This research was supported by the Granting Agency of the Czech Republic (project No. 312334), the National Sustainability Programme of the Czech Ministry of Education, Youth and Sports (LO1214), and the RECETOX research infrastructure (LM2015051).

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Table 1. Physicochemical parameters and reaction rate coefficients used in the WRF-CMAQ-BaP model.

Inverse Henry's Law Constant[1]	log H′	-4.7
Subcooled liquid vapour pressure[1,2]	log p_L	-5.2 (Pa)
Octanol-Water partition coefficient[1]	log K_{ow}	5.9
Octanol-Air partition coefficient[1,3]	log $K_{oa(dry)}$	11.1[1] (b=12.04, m=5382)[3]
Water saturated octanol-Air partition coefficient[1]	log $K_{oa(wet)}$	10.6
Diesel Soot-Water partition coefficient[4]	log $K_{soot\text{-}water}$	8.4
Diesel Soot-Air partition coefficient[4,8]	log $K_{soot\text{-}air}$	13.0[4], 11.59[8]
Gas-phase OH reaction rate constant	k_{OH}	50×10^{-12} (cm^3 $molec^{-1}$ s^{-1})
Ozone gas-surface equilibrium constant[6]	K_{O3}	0.028×10^{-13} (cm^3)
Maximum rate coefficient[6]	k_{max}	0.060 (s^{-1})

[1](Beyer et al., 2000); [2](de Maagd et al., 1998; Offenberg and Baker, 1999); [3](Odabasi et al., 2006), $\log K_{OA} = m/T(K) + b$; [4](Bärring et al., 2002), $\log K_{soot\text{-}water} = 1.39 \log K_{ow} + 0.1$; [5]($\log K_{soot\text{-}air} = \log K_{soot\text{-}water} - \log H'$); [6]Estimated values (EPIWIN;USEPA); [7](Kwamena et al., 2004), [8](van Noort, 2003)

[1]

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Table 2. Summary of the simulated scenarios designed to test gas-particle partitioning and heterogeneous reactivity of BaP.

	Scenario				
Description and references	1	2	3	4*	5
Gas phase reaction with OH	Yes	Yes	Yes	Yes	Yes
Adsorption model (JP) [1]	JP	JP	JP	JP	JP
Aerosol water dissolution (W)	-	W	W	W	W
Absorption to OM (HB) [2]	-	-	HB	-	-
Absorption to EC/BC (DE) [3]	-	-	-	DE	DE
Heterogeneous reaction with O_3 (KW) [4]	-	-	-	-	KW

[1] Junge, 1977 and Pankow, 1987; [2] Harner and Bidleman, 1998; [3] Dachs and Eisenreich, 2000; [4] Kwamena et al., 2004; *Additional simulations with temperature-dependent octanol-air partition coefficient calculated based on Odabasi et al., 2006 and a thermodynamic estimation model suggested by van Noort (van Noort, 2003).

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Table 3. Average ground level BaP concentrations, c_{BaP} (pg/m^3) over the entire domain and in individual EU-28 member states for all simulated scenarios, and concentration changes Δc_{BaP} (%) between subsequent scenarios.

	1	2		3		4		5	
	c_{BaP} pg/m^3	c_{BaP} pg/m^3	Δc_{BaP} %	c_{BaP} pg/m^3	Δc_{BaP} %	c_{BaP} pg/m^3	Δc_{BaP} %	c_{BaP} pg/m^3	Δc_{BaP} %
Domain average	10.4	10.4	-0.4	22.8	119.2	28.3	24.1	23.0	-18.8
Austria	58.4	58.4	0.0	89.0	52.4	103.4	16.1	86.5	-16.3
Belgium	36.2	36.1	-0.1	65.8	82.1	75.8	15.2	62.5	-17.6
Bulgaria	14.7	14.7	-0.1	28.9	97.1	37.7	30.4	26.7	-29.3
Croatia	15.2	15.2	-0.1	35.1	131.0	45.5	29.9	32.2	-29.4
Cyprus	11.2	11.2	0.0	13.2	17.8	24.7	87.2	10.1	-59.1
Czech Republic	38.6	38.6	0.0	70.1	81.5	83.5	19.1	67.9	-18.7
Denmark	7.3	7.2	-1.3	22.4	213.0	26.0	16.0	24.5	-5.7
Estonia	9.5	9.5	-0.9	28.9	205.3	34.6	19.7	32.0	-7.4
Finland	6.0	5.8	-2.9	16.1	176.0	21.9	36.2	17.7	-19.5
France	27.1	27.1	0.0	48.0	76.9	56.6	18.0	44.7	-21.0
Germany	30.3	30.3	-0.1	57.6	90.2	69.2	20.2	55.6	-19.6
Greece	7.4	7.4	-0.1	14.7	97.7	22.3	52.2	12.4	-44.6
Hungary	29.3	29.3	-0.1	61.3	109.5	75.1	22.5	59.7	-20.5
Ireland	3.8	3.8	-0.1	6.8	80.0	8.7	27.5	6.0	-31.7
Italy	36.9	36.9	0.0	62.8	70.1	76.3	21.6	57.9	-24.1
Lithuania	10.0	10.0	-0.5	32.7	228.4	38.4	17.5	36.3	-5.5
Luxemburg	37.1	37.1	0.0	62.0	67.2	71.7	15.8	57.9	-19.3
Latvia	6.0	5.9	-1.3	25.7	335.0	30.2	17.7	29.8	-1.4
Malta	0.5	0.4	-0.5	0.5	20.6	0.7	37.1	0.5	-36.6
Netherlands	24.0	23.9	-0.3	52.5	119.5	63.1	20.2	51.5	-18.4
Poland	25.6	25.6	-0.2	56.7	121.7	67.4	18.8	57.4	-14.8
Portugal	15.0	15.0	0.0	20.9	39.1	28.4	36.3	18.1	-36.5
Romania	12.7	12.7	0.0	27.4	115.8	36.0	31.4	25.7	-28.6
Spain	8.4	8.4	0.0	11.9	41.8	16.8	41.4	9.3	-44.8
Sweden	3.7	3.6	-2.4	11.3	211.7	14.3	26.7	13.2	-7.7
Slovakia	27.0	27.0	-0.1	53.5	98.1	65.2	21.9	52.5	-19.5
Slovenia	28.5	28.5	0.0	60.3	111.3	71.3	18.3	57.0	-20.1

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United Kingdom	3.3	3.3	-0.4	8.9	170.6	11.4	28.4	8.2	-27.6

Table 4. Comparison between modelled and measured BaP concentrations for the entire 2006 EMEP dataset (n=173) along with performance metrics and ranking across all sites.

Rank	Scenario	FAC2	MB	MGE	NMB	NMGE	RMSE	r	COE	IOA
1	4	0.29480	-0.05622	0.07145	-0.65264	0.82950	0.14729	0.35193	0.22443	0.61222
2	3	0.25434	-0.06279	0.07280	-0.72889	0.84516	0.15081	0.33423	0.20979	0.60490
3	5	0.21387	-0.07021	0.07345	-0.81511	0.85272	0.15179	0.47598	0.20273	0.60136
4	1	0.18497	-0.07640	0.07887	-0.88699	0.91559	0.16069	0.31088	0.14395	0.57197
5	2	0.17919	-0.07649	0.07894	-0.88798	0.91642	0.16076	0.30793	0.14317	0.57158

FAC: Fraction of predictions within a factor of two, MB: Mean bias, MGE: Mean Gross Error, NMB: Normalised mean bias, NMGE: Normalised mean gross error, RMSE: Root mean squared error, r: Correlation coefficient, COE: Coefficient of Efficiency, IOA: Index of Agreement.

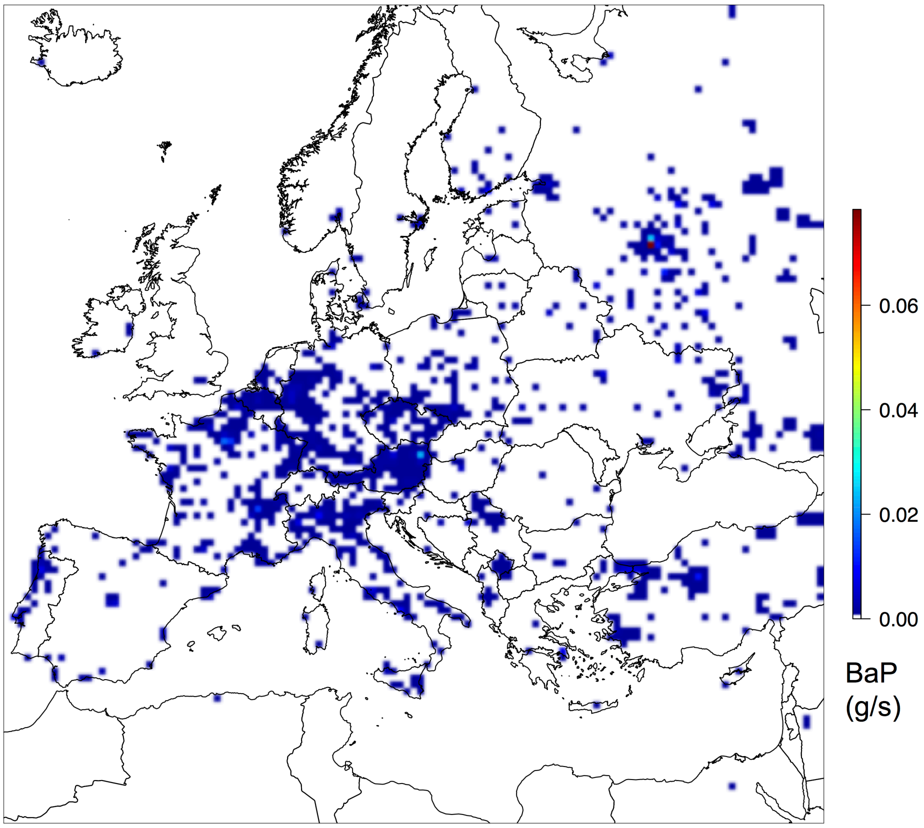

Figure 1. Study domain and 2006 annual grid cell-mean BaP emission flux (g s^{-1}) at the surface.

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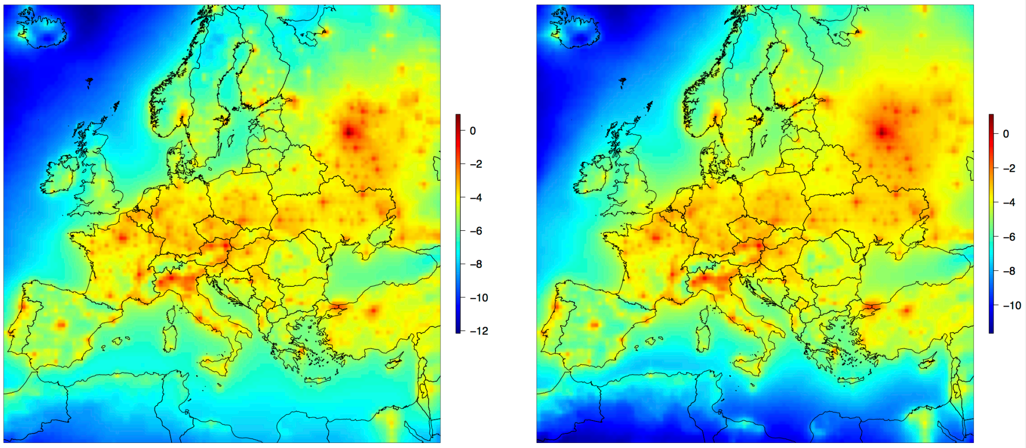
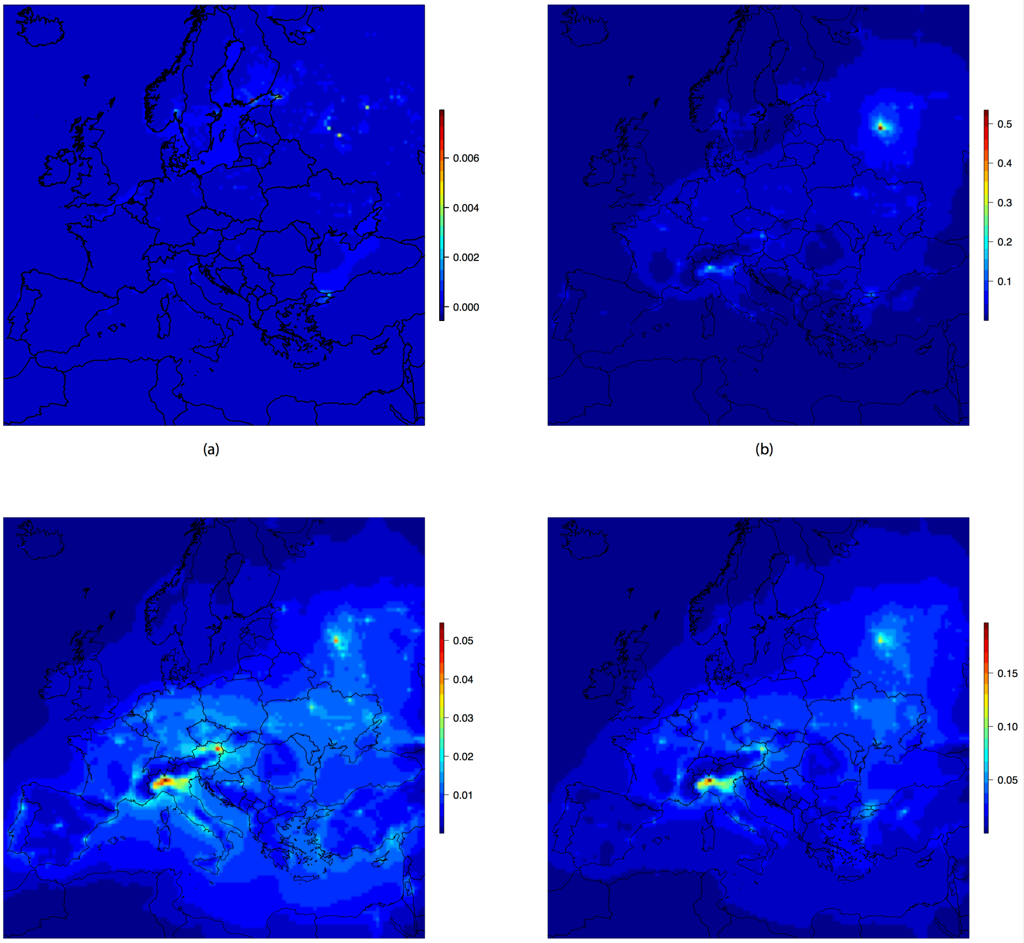


(a)

(b)

Figure 2. Annual average surface-level BaP concentrations [log c_{BaP} (ng m^{-3})] during 2006 plotted in logarithmic scale for (a) the Junge-Pankow (JP) scenario 1 and (b) for the fully expanded GPP scenario 5 that includes a heterogeneous reaction with ozone.



(a) (b) (c) (d)

Figure 3. Differences in annual average surface-level BaP concentrations (ng m^{-3}) during 2006 plotted for (a) water dissolution effect: scenario 1 – scenario 2, (b) K_{oa} effect: scenario 3 – scenario 2, (c) dual model effect: scenario 4 – scenario 3, and (d) O_3 degradation effect: scenario 4 – scenario 5.

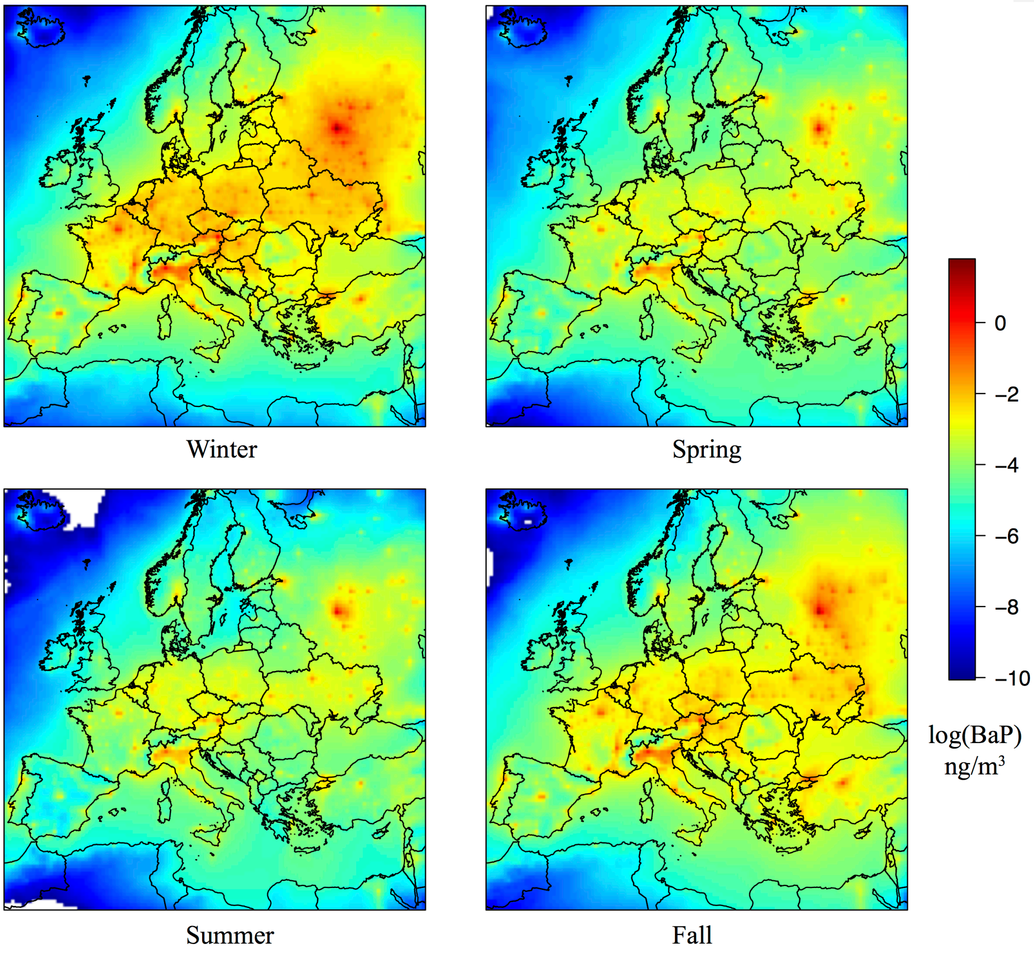
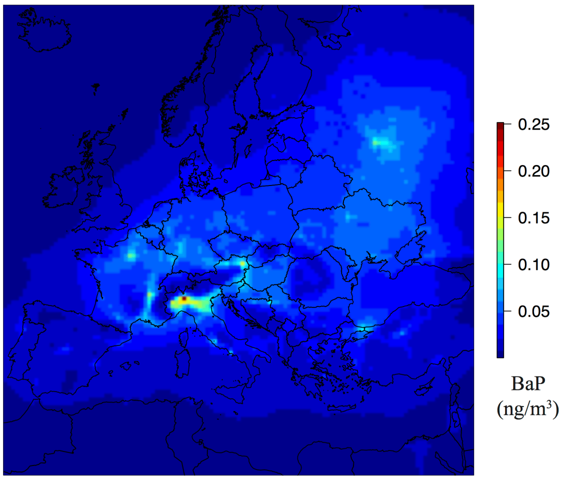
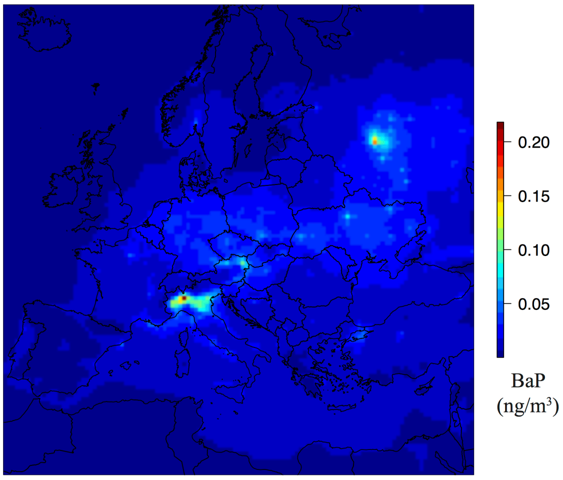


Figure 4. Seasonally disaggregated average surface-level BaP concentration [log c_{BaP} (ng m^{-3})] maps predicted by scenario 4 during 2006.



Winter



Summer

Figure 5. Average difference of surface-level BaP concentrations (ng m^{-3}) between scenario 4 and the fully expanded GPP scenario 5 that includes the heterogeneous reaction with ozone during the winter and summer months of 2006 (scenario 4 – scenario 5).

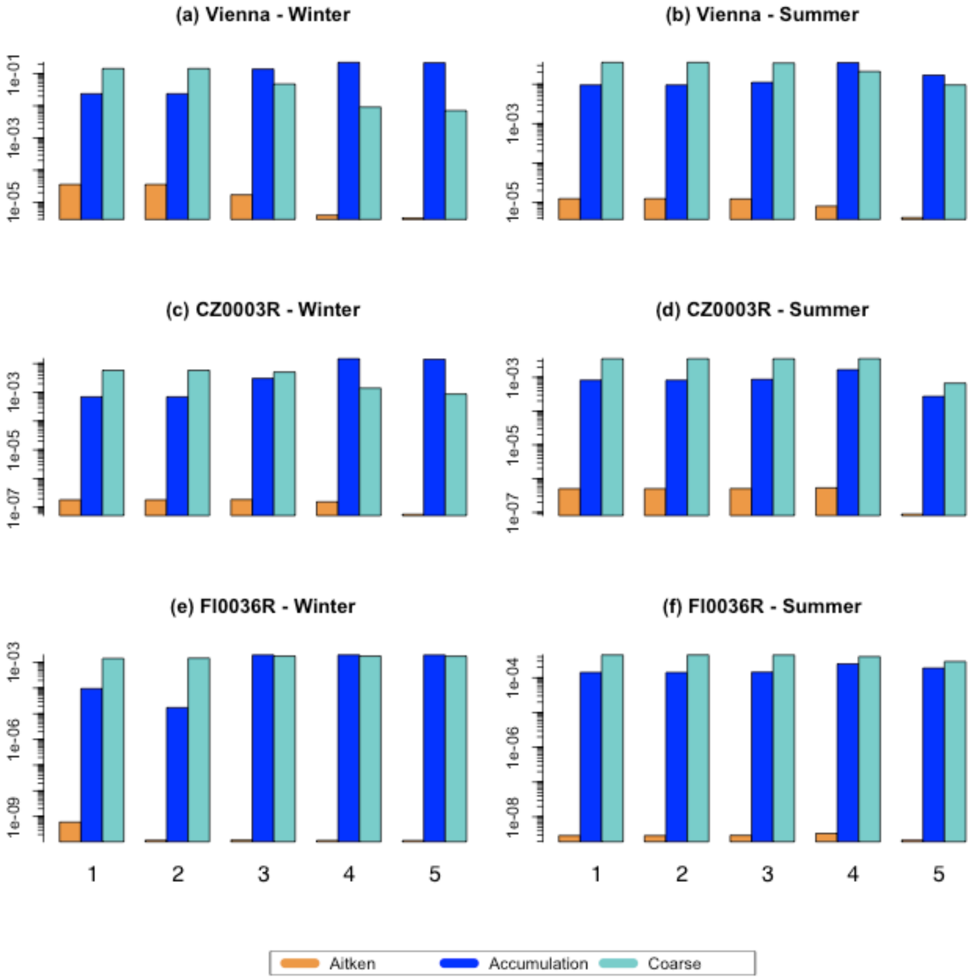


Figure 6. Distribution of BaP mass [log c_{BaP} (ng m^{-3})] in aerosols of three different modes in 3 different cells [Urban (Vienna), suburban (CZ0003R), and remote (FI0036R)] for each scenario as calculated during a winter (January 20) and a summer (July 20) day.

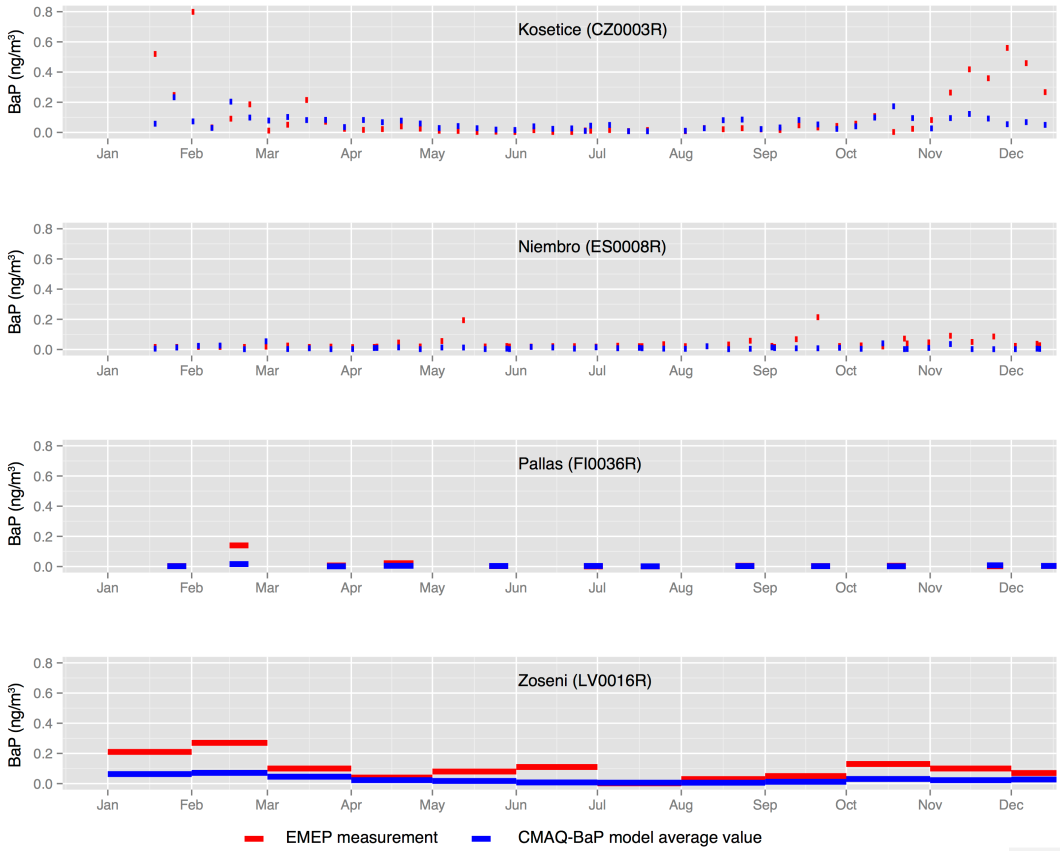


Figure 7. Model predicted and observed concentration (ng m^{-3}) timeseries at selected EMEP monitoring sites during 2006 for the dual GPP model scenario 4.

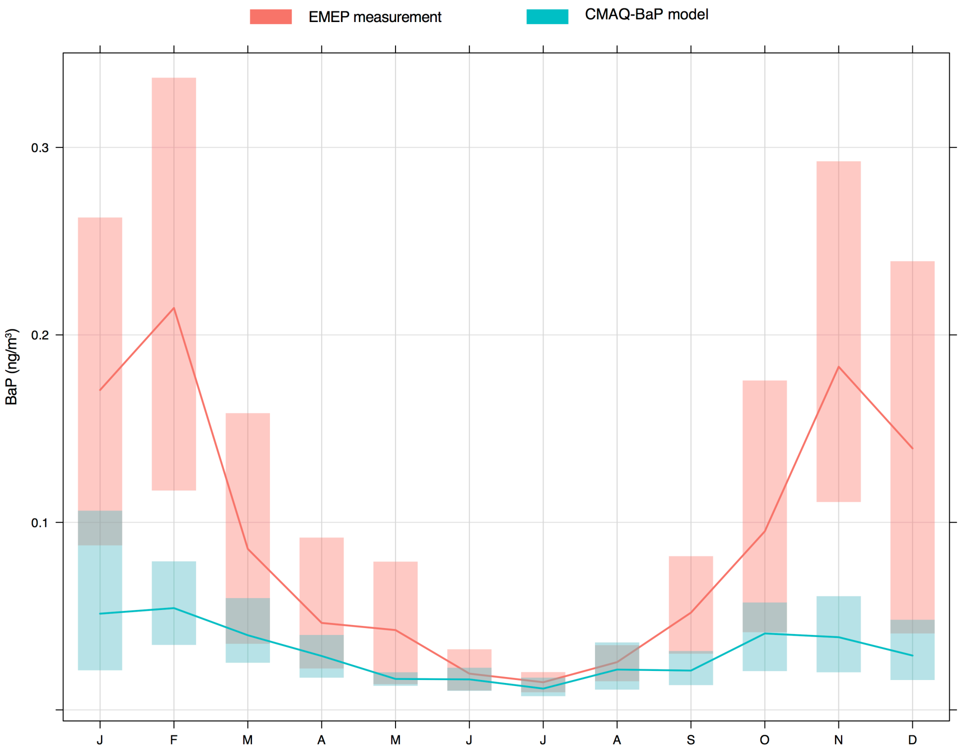


Figure 8. Model predicted and observed monthly BaP concentrations (ng m^{-3}) across all EMEP sites in 2006 for the dual GPP model scenario 4.