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Estimating population exposure to ambient polycyclic aromatic hydrocarbon in the United States – Part I: Model development and evaluation

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Abstract

PAHs (polycyclic aromatic hydrocarbons) in the environment are of significant concern due to their negative impact on human health. PAH measurements at the air toxics monitoring network stations alone are not sufficient to provide a complete picture of ambient PAH levels or to allow accurate assessment of public exposure in the United States. In this study, speciation profiles for PAHs were prepared using data assembled from existing emission profile data bases, and the Sparse Matrix Operator Kernel Emissions (SMOKE) model was used to generate the gridded national emissions of 16 priority PAHs in the US. The estimated emissions were applied to simulate ambient concentration of PAHs for January, April, July and October 2011, using a modified Community Multiscale Air Quality (CMAQ) model (v5.0.1) that treats the gas and particle phase partitioning of PAHs and their reactions in the gas phase and on particle surface. Predicted daily PAH concentrations at 61 air toxics monitoring sites generally agreed with observations, and averaging the predictions over a month reduced the overall error. The best model performance was obtained at rural sites, with an average mean fractional bias (MFB) of -0.03 and mean fractional error (MFE) of 0.70 . Concentrations at suburban and urban sites were underestimated with overall $\text{MFB} = -0.57$ and $\text{MFE} = 0.89$. Predicted PAH concentrations were highest in January with better model performance ($\text{MFB} = 0.12$, $\text{MFE} = 0.69$; including all sites), and lowest in July with worse model performance ($\text{MFB} = -0.90$, $\text{MFE} = 1.08$). Including heterogeneous reactions of several PAHs with O_3 on particle surface reduced the over-prediction bias in winter, although significant uncertainties were expected due to relative simple treatment of the heterogeneous reactions in the current model.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.envint.2016.12.002>.

Keywords

PAH; United States; CMAQ; SMOKE; Speciation profiles; Exposure; Model performance

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds containing multiple aromatic rings. Exposure to PAHs and their photochemical oxidation products in the ambient air has been confirmed to cause cancer in experimental animals and is suspected to cause human cancer (Boffetta et al., 1997). United States Environmental Protection Agency (US EPA) has classified 16 of the PAHs (Table S1) as priority pollutants based on their toxicity and potential of human exposures, among other factors. The US EPA has also designated seven of the PAHs (indicated in Table S1) as possible human carcinogens (Brenner, 2002). Benzo[*a*]pyrene (BaP), one of the 7-PAH species and the first chemical carcinogen discovered, is often applied as an indicator for PAHs exposure risk assessment (IARC, 2010). PAHs can be directly released into the environment from natural sources, such as volcanoes and forest fires. PAH compounds also exist in crude oil, coal, and other fossil-fuel products, and most of the PAHs are released from the high temperature combustion processes of fossil-fuel related to human commercial and industrial activities, such as power generation, petroleum production processes, and motor vehicle exhaust (Kavouras et al., 2001). While ambient concentration limits have not been included in the National Ambient Air Quality Standards (NAAQS) in the US, several other regions have already started to impose strict limits on the ambient concentrations of PAHs. For example, the European Union has set a target value of 1.0 ng m^{-3} for annual average ambient BaP (as a surrogate of total PAHs) concentrations (San Jose et al., 2013). The Ministry of the Environment (MOE) of Ontario, Canada has limited the annual average ambient concentration of BaP to a much lower value of 0.01 ng m^{-3} , and 24-h average concentration of 0.05 ng m^{-3} (see Ontario Regulation 419/05: Air Pollution – Local Air Quality (O. Reg. 419/05)).

Ambient concentrations of PAHs are influenced by emission, transport, deposition, gas-to-particle partitioning, and chemical transformation processes. In particular, several PAHs with intermediate volatility can be partitioned into the particle phase by adsorption onto the particle surface (particularly black carbon (BC)) and absorption into the amorphous particulate organic matters (OM) (Dvorska et al., 2012). The partitioning of PAHs between different phases not only depends on the properties of each species, such as subcooled liquid vapor pressure, but also the concentration of the partitioning media, such as OM and BC content. Pankow (1994) and Harner and Bidleman (1998) developed the PAH partitioning theory by relating the PAH organic-air partitioning coefficient with octanol-air partitioning coefficient. BC adsorption dominates at low semi-volatile organic compounds (SVOCs) concentration because of large surface area (Lohmann and Lammel, 2004). As the concentration of organics increases, absorption of organic matter becomes more and more important (Lohmann, 2003).

Previous modeling studies of PAHs focused on BaP ambient concentration in Europe and Asia. Aulinger et al. (2007) incorporated a PAH partitioning mechanism into the Community Multiscale Air Quality (CMAQ) model to simulate BaP concentrations. Ignoring chemical or photolytic degradation of BaP caused four times over-prediction of BaP and sensitivity analyses showed that the heterogeneous reaction of BaP with ozone had a significant impact on the prediction of ambient BaP concentration (Bieser et al., 2012). Including the appropriate seasonal and diurnal cycles in BaP emissions was important to get a better temporal and spatial resolution of BaP concentration and deposition patterns (Bewersdorff et al., 2009). Lammel et al. (2009) showed that gas-to-particle partition has great impacts on the transport and fate of PAHs, and this needs to be correctly accounted for in regional and global PAHs simulations.

In another study, Inomata et al. (2012) updated the Regional Air Quality Model (RAQM) to simulate the transport of particulate PAHs in Northeast Asia. The model predicted ambient concentrations of the PAH species in Beijing quite well. However, the predictions of PAH species in the downwind Noto monitoring site in Japan were poor and differed from observed concentrations by as much as a factor of 5. The large discrepancy of predicted and observed PAHs was also reported by Thackray et al. (2015). The conclusion was that regional emission estimation, model coefficients, and uncertainty of in-situ observations all contribute to the discrepancies.

While a large amount of PAH data has been collected at the air toxics monitoring network throughout the entire US, the coverage is still too sparse both temporally and spatially to provide a holistic understanding of the ambient concentration of the PAH species, the contributing sources and their impacts on human health. It is desirable to apply regional transport models to provide this information. For example, Zhang et al. (2009) estimated PAH population exposure and cancer risk in China using modeled regional distribution of 16 PAHs. Zhang et al. (2011) investigated long range transport of BaP from Asia to North America using a global chemical transport model. However, few prior modeling studies have quantitatively determined the concentrations of PAH species in the US utilizing regional transport models, and extensively evaluated the predicted PAH concentrations against measurements. The only study we found in the literature is by Galarneau et al. (2014), who simulated concentrations of 7 PAHs in Canada and continental US using a chemical transport model. However, the 7 PAH species modeled were not the 7 carcinogenic PAHs, and most of the data used in the evaluation were in Canada and California. The capability of the model in predicting PAHs in most areas of the US has not been tested. Thus, the objectives of this study are to (1) generate a gridded emission inventory of 16 PAH species in the US based on the most recent version of the National Emission Inventory (NEI); (2) modify the most recent version of the CMAQ model to include gas phase decay reactions, gas-to-particle partitioning and particle phase reactions to simulation ambient PAH concentrations; and (3) evaluate the model predictions with available measurement data throughout the continental US.

2. Model description

2.1. Gas phase photochemical mechanism

Reactions with oxidants in the troposphere are significant loss pathways of PAHs (Keyte et al., 2013). In this study, the gas phase SAPRC-99 photochemical mechanism (Carter, 2003) was modified to include gas phase reactions of PAH species with hydroxyl radical (OH) and ozone (O₃). The second order reaction rate coefficients ($k_{2,OH}$) for PAH-OH reactions used in this study are listed in Table 1. Except for OH reaction with naphthalene (NAPH), the temperature dependence of $k_{2,OH}$ was not considered in this study due to insufficient experimental data. Reaction rate coefficients of PAHs with O₃ (k_{2,O_3}) are typically several orders of magnitude smaller than PAH-OH reactions, however, they cannot be neglected due to high concentration of ozone in troposphere (6.9×10^{11} molecules cm⁻³, as 2011 annual average (Keyte et al., 2013)). The k_{2,O_3} values used in this study are shown in Table 2. For acenaphthylene (ACY), the reaction rate coefficient is large enough that the O₃ reaction is as important as the OH reaction. Reactions of PAHs with nitrate radical (NO₃) in the gas phase were not considered because of the much slower reaction rate under realistic atmospheric NO₃ concentrations (Finlayson-Pitts and Pitts, 1997).

Reaction products from PAH oxidation are complex and not well understood. No mechanisms have been developed to describe the products of all PAHs considered in this study in either explicit or lumped forms, and their subsequent reactions in the atmosphere. In this study, only the NAPH + OH reaction products were included, using the SAPRC-99 common intermediate products, following that of Zhang and Ying (2012). For other species, PAH + OH or PAH + O₃ reactions were treated as decay reactions without reactive reaction products. As the concentrations of the other PAHs were low (see Section 4), this simplified treatment should not significantly change the OH or O₃ budget and the atmospheric oxidation capacity in general.

2.2. Gas-to-particle partitioning of PAHs

Considering both adsorption of PAHs on BC and absorption into OM and assuming that gas-organic partitioning coefficients of PAHs are empirically related to the partitioning coefficients between octanol-air and soot-air phases, Lohmann and Lammel (2004) derived an equation to calculate the gas-particle partitioning coefficient of PAHs (K_p), as shown in Eq. (1):

$$K_p(\mu\text{g m}^{-3}) = 10^{-12} \left(f_{OM} \frac{MW_{oct} \gamma_{oct}}{MW_{OM} \gamma_{OM} \rho_{oct}} K_{oa} + f_{BC} \frac{a_{atm-BC}}{a_{soot} \rho_{BC}} K_{soot-air} \right) \quad (1)$$

where f_{OM} and f_{BC} are the fractions of OM and BC in the fine particles, respectively. K_{oa} and $K_{soot-air}$ are the octanol-air and soot-air partitioning coefficient, respectively. MW_{oct} and MW_{OM} are the molecular weight (g mol⁻¹) of octanol and organic matter, respectively. γ_{oct} and γ_{OM} are the activities of PAHs in octanol and OM, respectively. ρ_{oct} and ρ_{BC} are the density of octanol and BC, respectively (g cm⁻³). The octanol density was taken as 0.824 g cm⁻³ and ρ_{BC} was assumed to be 2.2 g cm⁻³, which is consistent with the value used in the

CMAQ model. $a_{\text{atm-BC}}$ and a_{soot} are the specific surface area (m m^{-3}) of atmospheric BC and diesel soot, respectively.

In this study, the PAHs are assumed to exist solely in the fine mode of the aerosol in the CMAQ model (i.e. the J mode). Thus, $f_{\text{OM}} = m_{\text{OM}}/\text{PMJ}$, and $f_{\text{BC}} = m_{\text{BC}}/\text{PMJ}$, where m_{OM} and m_{BC} are the mass concentration of OM and BC in the fine mode, respectively, and PMJ is the mass concentration of the fine mode aerosol. This is consistent with the treatment of other secondary organic aerosol species in the CMAQ model. A more detailed study that allows PAHs to partition into all three (ultrafine, fine and coarse) modes in the CMAQ model shows that the amount of PAHs in the ultrafine and coarse modes are several orders of magnitude lower than that in the fine mode. In addition, theoretical calculations performed by Shiraiwa and Seinfeld (2012) suggested that timescale for partitioning of semi-volatile organic compounds onto atmospheric coarse particles are on the order of hours to days. This is longer than the lifetime of the coarse particles themselves. Therefore, the current treatment is not expected to introduce significant errors in the PAH partitioning predictions (Aulinger et al., 2007). Further, a number of field studies also showed that PAHs on coarse particles only account for ~10% of the total PAHs, and most of the PAHs are in the fine aerosol model (Ladji et al., 2014). By assuming $\gamma_{\text{oct}}/\gamma_{\text{OM}}=1$, $MW_{\text{oct}}/MW_{\text{OM}}=1$, and $a_{\text{atm-BC}}/a_{\text{soot}}=1$ (Harner and Bidleman, 1998), Eq. (1) can be simplified to Eq. (2):

$$K_p = \frac{10^{-12}}{\text{PMJ}} \left(\frac{m_{\text{OM}} K_{\text{oa}}}{\rho_{\text{oct}}} + \frac{m_{\text{BC}} K_{\text{soot-air}}}{\rho_{\text{BC}}} \right) \quad (2)$$

K_{oa} is highly correlated with temperature. According to Odabasi et al. (2006), under typical atmospheric conditions, temperature dependence of $\log K_{\text{oa}}$ can be estimated with Eq. (3):

$$\log K_{\text{oa}} = A_{\text{oa}} + B_{\text{oa}}/T \quad (3)$$

where the intercept (A_{oa}) and slope (B_{oa}) are derived from linear regression of measured K_{oa} with $1/T$ under different temperatures. The values of A_{oa} and B_{oa} for 14 of the 16 PAH species (except for NAPH and pyrene (PYR)) follow the recommendations of Odabasi et al. (2006). For NAPH and PYR, K_{oa} values under different temperatures are obtained from a fragment constant method described by Li et al. (2006) to determine the A_{oa} and B_{oa} values using linear regression. A list of A_{oa} , B_{oa} and $\log K_{\text{oa}}$ values for the 16 PAH species is shown in Table 1.

As suggested by Dachs et al. (2004) and van Noort (2003), $K_{\text{soot-air}}$ can be estimated from the subcooled vapor pressure (p_L^0 , pa) and BC specific surface area (a_{BC} , $\text{m}^2 \text{g}^{-1}$), as shown in Eq. (4):

$$\log K_{\text{soot-air}} = -0.85 \log p_L^0 + 8.94 - \log(998/a_{\text{BC}}) \quad (4)$$

In this study, a_{BC} is estimated with a diesel soot specific BET surface area based on NIST standard reference material SRM 1650, which is approximately $90 \text{ m}^2 \text{ g}^{-1}$. It should be noted that a_{BC} applied in the study is more appropriate for freshly emitted particles and will decrease by approximately an order of magnitude after 2 or more days of aging. As the freshly emitted particles account for a significant fraction of BC in urban areas, using a higher a_{BC} value is appropriate but can lead to over-predictions of PAHs adsorbed onto the BC particles in remote areas.

The temperature dependent subcooled liquid vapor pressure is calculated based on van Noort (2009), as shown in Eq. (5):

$$\ln \frac{p_L^0}{p^0} = \frac{1}{R} \left(\Delta S_{vap,L} - \frac{\Delta H_{vap,L}}{T} \right) \quad (5)$$

where R is the universal gas constant, $S_{vap,L}$ and $H_{vap,L}$ are the changes of entropy and enthalpy of vaporization of the subcooled liquid, and p^0 is 101,325 pa. The $S_{vap,L}$ and $H_{vap,L}$ values for all PAHs (except for IcdP, DahA and BghiP) and their temperature dependence corrections ($d S_{vap,L}/dT$ and $d H_{vap,L}/dT$) are taken from Table S2 and S1 of van Noort (2009), respectively. For IcdP, DahA and BghiP, the regression Eq. (6) derived by van Noort (2009) is used:

$$\log p_L^0 = 7.9 + 0.79N_c - 0.00073N_c T - \frac{366N_c}{T} \quad (6)$$

where N_c is the number of carbon atoms in a PAH molecule and T is temperature in K. Table 1 shows the estimated $\log p_L^0$ as well as $\log K_{soot-air}$ at 298 K for the 16 PAH species. The gas-particle partitioning scheme described by Eqs. (2) to (6) is implemented in the CMAQ model to determine the gas-particle distribution of PAH species.

To illustrate the importance of BC in PAH partitioning, one can evaluate the ratio of $K_{soot-air}/\rho_{BC}$ to K_{oa}/ρ_{oct} (i.e. $K_{soot-air}/\rho_{BC} : K_{oa}/\rho_{oct}$). This ratio ranges from 1.67 for NAPH to 0.76 for BaP. In general, as the PAH molecules gets larger, the ratio becomes smaller. For semi-volatile PAHs, the ratio is close to unity. This indicates that on a per unit mass basis, BC is as effective in attracting PAH to the particle phase as OM. As the BC concentrations are typically lower than OM in almost all areas, OM is expected to play a more important role than BC but the contribution of BC to PAH partitioning should not be neglected.

2.3. Heterogeneous oxidation of particle-bound PAHs by ozone

It has been extensively reported that heterogeneous oxidation of PAHs on particle surface by O_3 can be an important pathway that affects the life time, and thus, the ambient concentration of PAHs in the atmosphere (Kahan et al., 2006; Kwamena et al., 2006; Kwamena et al., 2007; Kwamena et al., 2004; Miet et al., 2009; Mmereki et al., 2004; Perraudin et al., 2007). The reaction of surface adsorbed PAHs with O_3 has been analyzed

using the Langmuir-Hinshelwood mechanism, which assumes PAH and O₃ adsorbed independently and the reaction occurs between adsorbed molecules. Under realistic atmospheric O₃ concentrations, the oxidation rate of PAH can be expressed as a second order reaction using the particle bound PAH concentration and the gas phase O₃ concentration, as shown in Eq. (7):

$$\frac{d[PAH]}{dt} = -k_{2(het),O_3}[O_3][PAH] \quad (7)$$

where [O₃] is the gas phase O₃ concentration (molecules cm⁻³), [PAH] is the particle phase PAH concentration (molecules cm⁻³), and k_{2(het),O₃} is the second order reaction rate coefficient of O₃ with PAHs. Table S2 shows the k_{2(het),O₃} values used in this study, which are mostly based on Perraudin et al. (2007). Additional discussions of the uncertainty of this treatment can be found in Section 5. Reactions of particle-bound PAHs with other oxidants such as OH, NO₂ and NO₃ were not included in this study because of slower reaction rate with PAH under typical atmospheric concentrations of these species (Keyte et al., 2013).

2.4. PAH removal processes

Dry deposition of gas phase PAH species is not included in this study as the current version of CMAQ does not consider the dry deposition of the benzene and lumped aromatic compounds (ARO1 and ARO2) either. Wet deposition of PAHs is treated in the CMAQ model as other gas phase species. The Henry's Law constants needed for the scavenging calculation are taken from Sander (Sander, 1999) or estimated by the US EPA's EPI suite. PAHs in the particle phase can be removed from both dry and wet deposition along with other PM components.

2.5. Development of PAH speciation profiles

Gridded emission rates of PAHs in the gas and particle phases need to be determined for regional transport modeling. Emission inventories developed by the US EPA typically include many emission records for various sources and each record includes a source classification code (SCC). A cross reference file is used to determine the appropriate chemical speciation profile for a given SCC code, which splits the total organic gas (TOG) and PM_{2.5} emissions into emissions of individual or lumped gas and particle phase species for air quality models. The profiles used to generate these mechanism specific emissions usually do not include PAHs as they are not explicitly modeled. To generate PAH emissions, speciation profiles must be modified to include the emission factors for the 16 PAH species.

In this study, PAH speciation data for area and point source sectors were obtained from the SPECIATE database (Mobley et al., 2008) and the "Locating and Estimating air emissions from sources of Polycyclic Organic Matter" (L&E POM) document prepared by US EPA (EPA, 1998). The speciation profiles for mobile sources were extracted from the Motor Vehicle Emission Simulator (MOVES) (EPA, 2014). The SPECIATE database includes a large collection of both gas and particle phase emission profiles. Many of the detailed profiles in the SPECIATE data base already have some PAHs listed but these species are not

included explicitly when the profiles were developed for use in the Spare Matrix Operator Kernel Emission (SMOKE) model to process the NEI emissions. In this study, the profiles in the SPECIATE data base were examined and the PAH species were added back to the profiles for emission processing using SMOKE.

The L&E POM document was developed based on an extensive literature review and database search (before ~1998), and includes PAH emission factors for all major combustion sources. Since the emission factors in the L&E POM document are expressed as mass of PAHs emitted per unit mass of fuel burned, they cannot be directly incorporated into the speciation profiles used by SMOKE, which needs emission factors as PAHs emitted per unit mass of VOC or PM_{2.5} emitted. To convert the fuel-based L&E POM emission factors of PAHs ($EF_{PAH, fuel}$) to the mass-based emission factors used in SMOKE profiles ($EF_{PAH, PM_{2.5}}$), the following equation was used, assuming emissions of PAHs are in the particle phase initially:

$$EF_{PAH, PM_{2.5}} = \frac{EF_{PAH, fuel}}{EF_{PM_{2.5}, fuel}} \quad (8)$$

where $EF_{PM_{2.5}, fuel}$ is the fuel-based emission factor for PM_{2.5} (mass per unit mass of fuel burned) obtained from the “Emission Factor Listing for Criteria Pollutants” document (EPA, 2001). Gas and particles phase emissions in the L&E POM document are not separated. Since the modified CMAQ model assumes instant partitioning equilibrium, putting all emissions in the particle phase would not affect the final distribution of PAHs in gas and particle phase.

The VOC and PM_{2.5} profiles modified to include PAH emissions for use in this study are summarized in Table S3 and the detailed emission profiles with emission factors for the 16 PAH species are shown in Table S4.

3. Model application

3.1. Model domain, observation data, and meteorological and emission inputs

The PAH reactions and partitioning schemes described above were implemented in the CMAQ v5.0.1 framework to predict ambient PAH concentrations in the entire continental United States (US) in January, April, July, and October 2011. These four months were chosen to represent typical emission and meteorological conditions in winter, spring, summer and fall, respectively. The model domain used in this study was $36 \times 36 \text{ km}^2$ in horizontal resolution with 18 stretching vertical layers that reach a model top of approximately 20 km above surface. Observations of PAHs in the entire continental US were downloaded from EPA’s Air Toxics Website (<https://www3.epa.gov/ttnamti1/toxdat.html#data>). Overall, there were 61 sites observing PAH species ambient concentrations. Ten sites only have NAPH measurements, 6 sites have NAPH and BaP measurements and the rest of the sites have measurements of all PAH species. The daily average PAH concentrations are typically collected every six days. Only data above the method detection limit (MDL, approximately $1 \times 10^{-4} \mu\text{g m}^{-3}$) are retained in the analysis.

Fig. S1 shows the model domain and the locations of the monitors where PAH observations are available for 2011. Details of the monitoring sites and number of available observations at each site in each month are listed in Table S5. While several sites are reported as urban sites, they are mostly placed in the residential and commercial areas away from the major sources such as traffics. Only a few sites were in industrial settings, which could see more influences from local sources. Considering the relatively long lifetime of PAHs, the concentrations measured at the urban sites could represent the general concentrations of PAHs in the area and be used for model evaluation purposes. While it is generally true that models with relatively coarse resolution tend to under-predict the observed concentrations, the degree of under-prediction needs to be evaluated so that the amount of under-prediction in cancer risk in the urban areas using the model-predicted concentrations can be better estimated. The meteorological inputs were generated using the Weather Research and Forecasting (WRF) model version 3.6. The simulations were initialized using the North American Regional Re-analysis (NARR) data from National Oceanic and Atmospheric Administration (NOAA) (www.esrl.noaa.gov/psd/data/gridded/data.narr.html) with a 32-km horizontal resolution and 3-h time resolution, for all variables except soil moisture, which was initialized using predictions from the North American Land Data Assimilation System (NLDAS). The configuration of the physical processes and selection of algorithms were the same as those used in a previous study. Detailed evaluations of the meteorological model performance are described by Wang et al. (2017) and thus are not repeated here. In general, the WRF model performance was similar to that reported by Zhang et al. (2012).

The gridded monthly anthropogenic emissions were generated based on the 2011 NEI (US EPA, 2015) (available from: <https://www.epa.gov/air-emissions-inventories/2011-nei-technical-support-document>), using SMOKE v3.6 and the updated VOC and PM_{2.5} speciation profiles with PAH species, as described in Section 2. For Canada and Mexico emissions, VOC and PM_{2.5} for 2011 were not available and the 2005 emission estimations were used instead. Biogenic emissions were generated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006; Guenther et al., 2012). In the following section, estimated emissions of PAH species are further discussed.

3.2. Estimation of PAH emissions

Fig. 1 shows the regional distribution of the monthly emission for 16-PAH (the sum of the 16 PAHs listed in Table S1), 7-PAH (the sum of the 7 PAH species) and BaP. Elevated emissions in the upper layers due to point source emissions were combined with the surface layer emissions to calculate the total emissions. In January, a large amount of PAH emissions was from area sources in major urban areas in the US, as well as from urban areas in Canada along the US-Canada border. Residential wood combustion was the major emission source. In contrast, most emissions in July were from point sources, such as power plants and industrial emissions. Emissions from marine vessel emissions and port activities were also seen, with higher emissions in January and July. There was a high emission area located in Kansas and northern Alabama in April, which was caused by open burning activities in Flint Hill, the largest contiguous area of tallgrass prairie remaining today, where burn regimes are implemented during spring and fall (Wilgers and Horne, 2006). More

details of the source of PAH emissions are discussed in a companion paper on the source apportionment of PAHs (Zhang et al., 2016).

Total emissions of individual PAH species in the US in each month, as well as the 16-PAH and 7-PAH are listed in Table 3. Monthly emissions of 16-PAH and 7-PAH (excluding wildfire) were in the range of 2–4 Gg (10^9 g) and 80–110 Mg (10^6 g), respectively. For most of the PAH species, especially large molecular weight PAH species, emissions were typically highest in January. Fluorene (FLU) and phenanthrene (PHE) have the highest emissions in July while acenaphthylene (ACY), acenaphthene (ACE) and anthracene (ANT) emissions peak in April. NAPH accounted for 60–70% of the total PAH emissions, followed by PHE (11–17%), FLU (5–9%) and ACY (4–6%). Emissions of 7-PAH species were generally low, accounting for approximately 2% of the total PAH emissions. Among the 7-PAH species, benzo[*a*]anthracene (BaA) accounted for approximately 30% of the emissions, followed closely by BaP (~25%). Estimated annual emissions were compared with estimations by Shen et al. (2013) as well as by the US EPA (data downloaded from <https://www.epa.gov/air-emissions-inventories/2011-national-emissions-inventory-nei-data>), as shown in Fig. S2. In general, the predicted PAH emissions in this study are approximately 2–3 times higher than those estimated by Shen et al. (2013) but closer to the ones estimated by the US EPA. Similar levels of uncertainties in the PAH emission estimations have been reported by Shen et al. (2013), who compared the emissions estimation with US EPA estimations in 2002 and 2005.

4. Results

4.1. Model performance analysis

Since the measured concentrations of each species are the sum of the gas and particle phase concentrations, the CMAQ model predictions of gas and particle phase concentrations were also combined and expressed in units of $\mu\text{g m}^{-3}$ before being compared with observations. Atmospheric pressure and temperature needed for the conversion of gas phase concentrations from ppmV to $\mu\text{g m}^{-3}$ were obtained from the meteorological fields generated by the WRF model. Predicted hourly concentrations were averaged to compare with daily observations.

The mean fractional bias (MFB) and mean fractional error (MFE), as defined in Eq. (9) and (10) were used to evaluate the model performance.

$$MFB = \frac{2}{N} \sum_{i=1}^N \frac{C_{m,i} - C_{o,i}}{C_{m,i} + C_{o,i}} \quad (9)$$

$$MFE = \frac{2}{N} \sum_{i=1}^N \frac{|C_{m,i} - C_{o,i}|}{C_{m,i} + C_{o,i}} \quad (10)$$

In the above equations, N is the number of daily average concentrations at each observation station within a month. C_m and C_o are the predicted and observed daily average concentrations, respectively.

Fig. S3 shows the distribution of the MFB and MFE for each PAH species at all observation stations shown in Fig. S1. The MFB and MFE are proposed by Boylan and Russell (2006) to evaluate model performance of airborne particulate matter and its chemical components. There are no established performance criteria for predicted ambient PAH concentrations to date. Based on the results obtained in this study, and considering the wide range of the PAH concentrations and large uncertainty in emission estimations, we propose that $MFB = \pm 1.33$ and $MFE = 1.33$ be used as model performance criteria of regional daily average PAH (overall 75% of the data meets this criteria), which indicate that predicted concentrations are from 0.2 to 5 times of the observed concentrations. The performance goals can be set to $MFB = \pm 0.66$ and $MFE = 1.00$ (overall 40% of the data meets this criteria), which correspond to approximately a factor of 2 difference between the predicted and observed concentrations. Table S7 lists the percentage of data points that meet the model performance criteria and goal for each species. For most 2–3 ring PAH species, approximately 70% of the stations meet the model performance criteria, and approximately 30% meets the performance goal. The model performance for larger PAH species with 4–6 rings were generally better, with >80% and 40% of the points meeting the performance criteria and performance goals, respectively. Most of the points outside the performance criteria region were from July, with negative MFB values, indicating predictions were much lower than observations. BaA had the best model performance with 91% of the points within the performance criteria region.

Comparison of predicted vs. observed monthly average concentrations is shown in Fig. 2. The predicted monthly average concentrations were calculated using all the hourly predictions within each month. The observed concentrations at each site within a month were averaged to calculate the observed values. To reduce the bias in the monthly PAH estimation, only stations with at least four valid observations within a month were used in the model performance evaluation. The stations are color coded in the plot based on their location type (urban, suburban and rural). It can be seen clearly that concentrations of the 16 PAH species span almost three orders of magnitude (10^{-4} – $10^{-1} \mu\text{g m}^{-3}$). The predicted concentrations also span the same orders of magnitude, and are in general agreement with the observations. For all three location types, model performance was the best in January and worst in July, when predicted concentrations were significantly lower than observed concentrations at almost all stations. Most of significant under-predictions (below the 1:10 line) in July were due to smaller PAHs with 2–3 rings. It is possible that the bias was caused by missing evaporative emissions of these PAHs due to higher temperature in summer.

The MFB and MFE of the monthly average concentrations were calculated for each location type, as shown in Table 4. Model performance was worst at urban locations, with significant under-predictions as indicated by the large negative MFB value for all months except January. For the urban sites, MFE values range from 0.86 (January) to 1.23 (July), which were larger than rural and suburban sites. The poor agreement between predictions and observations was likely due to coarse spatial resolution used in this study. At urban

locations, observed concentrations were influenced by various local sources of PAHs and spatial gradients were steep near the sources. However, the predictions based on the coarse resolution domain only represent average concentrations within the grid cell. Even after all the PAH emissions within the grid cell were correctly represented, the influence of the local emissions on observed concentrations could not be accurately captured. Higher resolution modeling is needed to better capture the PAH concentrations in urban areas where local emissions lead to significant spatial gradients that cannot be well-represented by the relatively coarse resolution domain. Model performance in both MFB and MFE improved significantly for the suburban sites, which have fewer local emissions and more influenced by emissions from urban areas, although the predicted concentrations were still lower than observed concentrations. Model performance was the best at rural sites, with slight over-predictions in January and October and slight under-predictions in April and July. The MFE values for January, April, July and October were 0.68, 0.63, 0.86 and 0.61, respectively.

4.2. Spatial and temporal variation

Fig. 3 shows the regional distribution of predicted monthly average concentrations of 16-PAH, 7-PAH, and BaP. In winter, 16-PAH concentrations in the eastern US were approximately $0.2 \mu\text{g m}^{-3}$, with higher concentrations exceeding $0.4 \mu\text{g m}^{-3}$ at some large urban centers, such as New York, Boston, and Washington. The 7-PAH concentrations in the southeastern US were higher than the northeastern part, with concentrations reaching $0.02 \mu\text{g m}^{-3}$ near the coast of Louisiana. Comparatively, concentrations of 7-PAH in the northeastern were approximately $0.005 \mu\text{g m}^{-3}$. Large areas in the eastern US and several west coastal regions had high BaP concentrations in January.

PAH concentrations were lower in spring (April) and summer (July). 16-PAH concentrations in most part of the eastern US were $<0.1 \mu\text{g m}^{-3}$ and close to $0.005 \mu\text{g m}^{-3}$ for 7-PAH. For BaP, most areas in the US had concentrations lower than 1.0 ng m^{-3} , except for hot spots in big cities or wildfire locations. The high concentrations in less populated Kansas in April was due to open burning, leading to elevated concentrations of 16-PAH ($\sim 0.2 \mu\text{g m}^{-3}$), 7-PAH ($\sim 0.02 \mu\text{g m}^{-3}$), and BaP ($>1.0 \text{ ng m}^{-3}$). In fall (October), there were extremely high concentrations of PAHs near the US-Canada border in the northeastern US. 16-PAH concentration reached up to $0.2 \mu\text{g m}^{-3}$, and BaP concentrations were higher than 1.0 ng m^{-3} in big cities in the northeastern US. Concentrations in the coastal areas in Louisiana and part of Texas along the Gulf of Mexico also showed high PAH. The concentrations of 16-PAH, 7-PAH and BaP exceeded $0.6 \mu\text{g m}^{-3}$, $0.05 \mu\text{g m}^{-3}$, and 3.0 ng m^{-3} , respectively. As these areas have extensive oil-gas related activities, it was expected that contributions from industrial processes are significant.

4.3. Heterogeneous oxidation of particle-bound PAHs by ozone

Surface heterogeneous reaction rate coefficients used in this study may have significant uncertainties. To evaluate the impact of surface heterogeneous reactions of PAH with O_3 on predicted PAH concentrations, a sensitivity simulation was conducted for January and July by disabling the heterogeneous reaction pathway but retaining gas-to-particle partitioning of PAHs. Predicted concentrations from the sensitivity run are compared with the base case simulation with heterogeneous reactions.

Table S6 shows the model performance of daily PAH species for simulations with and without heterogeneous reactions with O₃. Fig. 4 shows the regional distribution of monthly averaged concentrations of ANT, PYR, BaA and BaP, the four species with fastest reaction rates, in January and July, and the increase of PAH concentrations when heterogeneous loss of PAH was turned off. As shown in Table S6, there was no obvious change in the predicted concentrations of NAPH due to heterogeneous reactions. This was expected because NAPH was entirely retained in the gas phase and the reaction rate with gas phase O₃ was slow. Most of the other 9 species showed higher concentrations when heterogeneous loss was turned off. As expected, the species with fastest O₃ reaction rates showed the most significant increase. Including heterogeneous reactions led to better model performance in both MFB and MFE for January. MFB decreased by approximately 18% on average, and MFE decreased by 7%. With heterogeneous reactions on, BaP concentration in January was predicted well with an MFB of -15%.

Although O₃ concentrations in July were higher than those in January, the predicted differences in PAH concentrations with and without heterogeneous reactions with O₃ in July were much smaller. There were almost no changes of the PYR, BaA, CHRY and BaP concentrations compared to the base case as shown in Fig. 4 (a few other PAHs that also show little change but are not shown in Fig. 5). The importance of heterogeneous reactions of PAHs with O₃ is greatly affected by temperature, as it affects the gas-particle partitioning of intermediate volatile PAH species. As shown in Fig. 5, partitioning of PYR, BaA, CHRY and BaP were strongly temperature dependent, with much higher fractions in the particle phase in January due to lower temperature. Therefore, heterogeneous reactions were less effective in reducing PAH concentrations in July for these species. The MFB and MFE values did not change significantly. Under-prediction was still persistent among many PAH species, suggesting that the under-prediction was not caused by including the heterogeneous reactions. It should be noted that the importance of the heterogeneous reactions on PAHs might be over-estimated because only PAHs on particle surface are influenced by this process.

5. Discussion and conclusions

In this study, re-volatilization of previously deposited semi-volatile PAHs from surface water or soil was not considered. This process was considered to be important by several studies using state-of-the-science multi-compartment model to invest the long range transport of 3–4 ring PAHs to remote regions as well as the global cycling and fate of PAHs (Lammel et al., 2009; Sehili and Lammel, 2007). While omitting the re-volatilization process could also lead to under-predictions of 3–4 ring PAHs in this study, it is unlikely to cause significant under-predictions in most populated regions due to significant anthropogenic emissions (see Figs. 1 and 2). The concentrations of the 3–4 ring PAHs in the remote areas far from anthropogenic emissions, such as the mountain regions, could be under-estimated. Quantitative calculations of re-volatilization need multi-year simulations and incorporate multi-compartment modules in the current regional model, which is beyond the scope of this study. To correctly account for re-volatilization, a dry deposition parameterization for PAHs such as that developed by Zhang et al. (2015) is also needed. In regions where the surface

PAH concentrations are at steady state, omitting both dry deposition and re-volatilization might lead to less overall error in the estimated PAH concentrations.

Uncertainty in the emission estimation can also lead to uncertainty in the predicted ambient PAH concentrations. Emission factors of PAHs for different source categories in this study were assembled from a small number of source profiles available in existing profile data bases. These profiles inherently have large uncertainties associated with them because they are based on very limited source testing data that could not reflect the variation in the emission factors within each source category due to differences in combustion conditions, emission control devices, fuel chemical composition, etc. In addition, uncertainty in the TOG and PM_{2.5} emission estimations and spatial and temporal allocation can also contribute to the overall uncertainty in the PAH emissions. Although model performance analyses reported in this study provides some indirect estimation of the uncertainties, quantitative estimation of the PAH emission uncertainty is out of the scope of this study. More modeling and monitoring studies are needed to better constrain the emissions.

Heterogeneous reactions of PAHs with O₃ are treated in the current study as second-order reactions with reaction rate coefficients derived from flow-tube reactor experiments. It should be noted that the specific aerosol surface area (S_A , in units of $m^2 m^{-3}$) in these studies are usually much higher than typical S_A under ambient conditions. Although the rate coefficients are generally on the order of $10^{-17} cm^6 s^{-1}$, values orders of magnitude lower have also been reported. It is unclear whether the rate coefficients derived from these studies are applicable under ambient conditions. Furthermore, these rate coefficients derived from the laboratory studies using PAH coated particles represent an upper limit of the reactivity of particle-bond PAHs because PAHs can diffuse into the bulk aerosol material or be covered by other secondary components condensing on the particle surface during atmospheric transport, leading to much longer atmospheric lifetime than anticipated from laboratory experiments (Zhou et al., 2013). Thus, this simplified treatment of heterogeneous reactions with O₃ in the model can be another source of uncertainty for the semi-volatile and non-volatile PAH species.

The performance analysis suggests the emissions of PAHs developed in this study are suitable for model simulations to capture monthly averages and represent the broad spatial distribution of PAH species in regional scales. Heterogeneous reactions of particle-bond PAHs with O₃ can lead to lower predicted concentrations of PAHs, and this process is more effective in colder winter months when several PAHs with fast heterogeneous reaction with O₃ are preferentially partitioned to the particle phase. Spatially, although total 16-PAH concentrations are higher in the northeastern US, the concentrations of 7-PAH, which are considered more harmful in terms of their carcinogenic effects, are higher in urban areas and the southeastern US. Temporally, higher PAH concentrations occur in winter and fall seasons than spring and summer, likely due to higher emissions of PAHs from areas sources such as residential wood smoke, and more often occurrence of stagnant weather conditions that lead to accumulation of pollutants in general.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. Gridded monthly emissions of 16-PAH (column A), 7-PAH (column B), and BaP (column C) for January (row 1), April (row 2), July (row 3), and October (row 4). Units are Mg/month (10^6 g/month).

Fig. 2.

Comparison of predicted and observed monthly average concentrations of individual PAH species at each monitor site. Green, blue and red symbols represent stations in urban, suburban and rural environments, respectively. Different symbol types represent the size of the PAH species, from 2 to 6 rings. Solid lines represent 1:1 ratio of the predictions vs observation, while dashed lines represent 1:10 and 10:1 ratios.

Fig. 3. Monthly average surface concentrations of 16-PAH (column A), 7-PAH (column B), and BaP (column C) for January (row 1), April (row 2), July (row 3), and October (row 4). Units are $\mu\text{g m}^{-3}$ for 16-PAH and 7-PAH, and ng m^{-3} for BaP.

Fig. 4. Winter (January) and summer (July) concentrations of four PAH species (PYR, BaA, CHRY and BaP) with large O_3 heterogeneous reaction rate coefficients. The base case is the set of simulations with heterogeneous reaction and the difference plots show increase of PAH concentrations if the heterogeneous reactions were not included. Units are ng m^{-3} .

Fig. 5. Partitioning of PAHs between the gas and particle phases in January and July, based on domain averaged gas and particle phase concentrations.

List of subcooled vapor pressure, octanol--air partitioning coefficient and second order gas phase reaction rate coefficients with hydroxyl radical (OH) for 16 PAHs.

PAHs	$\log p_L^0$ 298 K [pa]	$\log K_{\text{oct-air}}$ 298 K	A_{oa}	B_{oa}	$\log K_{\text{oa}}$ 298 K	$k_{2,\text{OH}}$ (10^{11}) [$\text{cm}^3\text{molec}^{-1}\text{s}^{-1}$]	Ref. for $k_{2,\text{OH}}$
NAPH	1.34	6.76	-7.05	3617	5.09	2.16^a	Atkinson (1986)
ACY	0.03	7.87	-1.97	2476	6.34	11.00	Atkinson and Aschmann (1987)
ACE	0.03	7.87	-2.20	2597	6.51	7.33	Note (1)
FLU	-0.62	8.42	-2.61	2833	6.90	1.40	Note (2)
PHE	-1.28	8.98	-3.37	3293	7.68	2.74	Note (3)
ANT	-1.28	8.98	-3.41	3316	7.72	13.00	Note (4)
FTH	-2.59	10.10	-4.34	3904	8.76	1.10	Brubaker and Hites (1998)
PYR	-2.59	10.10	-7.87	5010	8.94	5.00	Atkinson et al. (1987)
BaA	-3.90	11.21	-5.64	4746	10.29	12.60	EPI suite
CHRY	-3.90	11.21	-5.65	4754	10.30	5.00	EPI suite
BbF	-5.21	12.32	-6.40	5285	11.33	1.86	EPI suite
BkF	-5.21	12.32	-6.42	5301	11.37	5.36	EPI suite
BaP	-5.21	12.32	-6.50	5382	11.56	5.00	EPI suite
BghiP	-6.53	13.45	-7.03	5834	12.55	8.69	EPI suite
IcdP	-6.53	13.45	-7.00	5791	12.43	6.54	EPI suite
DahA	-6.53	13.45	-7.17	5887	12.59	5.00	EPI suite

Note (1): Average of the following: Reisen and Arey (2002), Brubaker and Hites (1998), Atkinson and Aschmann (1987), Klopffer et al. (1986), Banceu et al. (2001) and Klamt (1993).

Note (2): Average of the following: Kwok et al. (1994), Brubaker and Hites (1998) and Klopffer et al. (1986).

Note (3): Average of the following: Biermann et al. (1985), Atkinson et al. (1989), Kwok et al. (1994), Brubaker and Hites (1998) and Lee et al. (2003).

Note (4): Average of the following: Atkinson et al. (1989) and Biermann et al. (1985).

^a_{NAPH} reaction rate is temperature dependent as $k_{2,\text{OH}} = 1.07 \times 10^{-12} \exp(895/T) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.

Table 2Gas phase PAHs reaction rate coefficients with O₃.

PAHs	k_{2,O_3} (10^{19}) [$\text{cm}^3\text{molec}^{-1}\text{s}^{-1}$]	Ref.
NAPH	2.5	Atkinson and Aschmann (1986)
ACY	5500	Atkinson and Aschmann (1988)
ACE	5.0	Atkinson and Aschmann (1988)
PHE	4.0	Kwok et al. (1994)

Table 3

Monthly average emissions of PAHs (Mg) in the continental US estimated in this study.

	January	April	July	October
NAPH	2820.9	2093.2	1318.0	1538.6
ACY	206.2	144.5	79.4	99.9
ACE	51.2	45.0	39.7	40.2
FLU	95.3	74.5	53.3	57.8
PHE	245.7	193.0	139.0	156.5
ANT	52.1	40.7	29.0	32.9
FTH	90.7	79.6	55.9	69.7
PYR	95.6	87.3	72.4	78.7
BaA	34.1	32.3	27.8	30.6
CHRY	20.7	18.8	12.9	17.2
BbF	11.0	9.6	5.4	8.8
BkF	8.6	7.0	4.3	5.9
BaP	28.3	27.6	24.1	26.7
BghiP	35.0	32.4	30.1	30.7
IcdP	7.8	5.9	4.4	5.0
DahA	1.0	1.8	0.7	2.1
7-PAH	111.5	103.1	79.5	96.2
16-PAH	3804.1	2893.4	1896.3	2201.4

Table 4

Model performance statistics for monthly average PAH concentrations.

Month	Urban * (33 sites)		Suburban (14 sites)		Rural (14 sites)	
	MFB	MFE	MFB	MFE	MFB	MFE
Jan	−0.058	0.86	0.047	0.53	0.37	0.68
Apr	−0.59	0.91	−0.49	0.73	−0.11	0.63
Jul	−1.06	1.23	−0.99	1.16	−0.65	0.86
Oct	−0.82	0.96	−0.57	0.80	0.28	0.61

* See Table S5 for designation of urban, suburban and rural sites.