



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 MFB = -0.57 and MFE = 0.89 . Predicted PAH concentrations were highest in January with better model performance (MFB = 0.12 , MFE = 0.69 ; including all sites), and lowest in July with worse model performance (MFB = -0.90 , 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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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)).

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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. Pankov (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 Galarnau 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 (O_3). 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 O_3 (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 O_3 reaction is as important as the OH reaction. Reactions of PAHs with nitrate radical (NO_3) in the gas phase were not considered because of the much slower reaction rate under realistic atmospheric NO_3 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 + O_3 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 O_3 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):

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

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_{atm-BC} and a_{soot} are the specific surface area ($m^2 m^{-3}$) 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, $f_{OM} = m_{OM}/PMJ$, and $f_{BC} = m_{BC}/PMJ$, 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

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