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Assessing the influence of secondary organic versus primary carbonaceous aerosols on long-range atmospheric PAH transport

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Abstract

We use the chemical transport model GEOS-Chem to evaluate the hypothesis that atmospheric polycyclic aromatic hydrocarbons (PAHs) are trapped in secondary organic aerosol (SOA) as it forms. We test the ability of three different partitioning configurations within the model to reproduce observed total concentrations in the mid-latitudes and the Arctic as well as mid-latitude gas-particle phase distributions. The configurations tested are: (1) the GEOS-Chem default configuration, which uses instantaneous equilibrium partitioning to divide PAHs between the gas phase, a primary organic matter (OM) phase (absorptive), and a black carbon (BC) phase (adsorptive); (2) an SOA configuration, in which PAHs are trapped in SOA when emitted and slowly evaporate from SOA thereafter, and (3) a configuration in which PAHs are trapped in primary OM/BC upon emission and subsequently slowly evaporate. We also test the influence of changing the fraction of PAH available for particle-phase oxidation. Trapping PAHs in SOA particles upon formation and protecting against particle-phase oxidation (2) better simulates observed remote concentrations compared to our default configuration (1). However, simulating adsorptive partitioning to BC is required to reproduce the magnitude and seasonal pattern of gas-particle phase distributions. Thus, the last configuration (3) results in the best agreement between observed and simulated concentration/phase distribution data. The importance of BC rather than SOA to PAH transport is consistent with strong observational evidence that PAH and BC are co-emitted.
Introduction

Polycyclic aromatic hydrocarbons (PAHs) are toxic semi-volatile organic compounds (SVOCs) that partition between gas and aerosol phases and travel long distances in the atmosphere.\textsuperscript{1,2} The chemical and physical processes influencing transport of PAHs from areas of high emissions to remote regions are still largely unknown. In particular, the influence of atmospheric aerosols (i.e., particles) on PAH long-range transport (LRT) is highly uncertain. A number of schemes have been proposed to estimate gas-particle distribution of PAHs, with each predicting different PAH LRT potential. Additionally, there is debate within the atmospheric chemistry literature regarding aerosol formation and evolution over time, and how best to simulate these processes. Here, we conduct simulations of atmospheric PAH transport using the chemical transport model GEOS-Chem with different assumptions about (1) gas-particle partitioning and (2) physicochemical characteristics of different aerosol types to test how these variables affect PAH LRT efficiency.

PAHs have been extensively measured in both gas and particle phases. Schemes for estimating measured phase distributions have evolved over time, as recently reviewed by Lohmann and Lammel\textsuperscript{3} and Keyte et al.\textsuperscript{4} To summarize, PAH gas-particle partitioning has been described with four different schemes, each assuming instantaneous equilibrium partitioning (EqP): (1) the Junge-Pankow adsorption scheme,\textsuperscript{5-8} in which PAH adsorption to total suspended particles depends on the PAH sub-cooled liquid vapor pressure; (2) the Finizio scheme\textsuperscript{9}, which partitions PAHs to particles based on a gas-particle equilibrium partition coefficient ($K_P=[\text{PAH}]_{\text{particle}}/[\text{PAH}]_{\text{gas}}$) that is empirically related to the octanol-air partition coefficient ($K_{OA}=([\text{PAH}]_{\text{octanol}}/[\text{PAH}]_{\text{air}}$); (3) the Harner-Bidleman scheme,\textsuperscript{10} which augments the Finizio scheme by accounting for the fraction of organic material (OM, used here interchangeably with “organic aerosol”, or OA) within a particle; and finally, (4) the Dachs and Eisenreich (“D&E”) scheme,\textsuperscript{11} which considers both absorption into OM and adsorption to black/elemental carbon (BC) within the particle.

In general, the Junge-Pankow, Finizio, and Harner-Bidleman schemes underestimate particulate fractions and particle phase concentrations (i.e., they underpredict $K_P$), both when compared directly to observations\textsuperscript{3,12,13} and when employed in atmospheric transport models.\textsuperscript{14,15} Schemes considering absorption into OM generally perform better than the
Junge-Pankow, however. The D&E scheme better represents observed PAH concentrations and phase distributions in various comparisons,\textsuperscript{3, 12-16} especially in remote regions. This is consistent with knowledge about PAH partitioning in the marine environment, where sorption to sedimentary BC limits aquatic PAH concentrations, and thus, availability and toxicity to marine organisms.\textsuperscript{17-20} However, the D&E scheme cannot explain the observed lack of correlation between particle and gas phases,\textsuperscript{21} and can overpredict observed $K_P$ values.\textsuperscript{11} Collectively, the inability of these partitioning schemes to accurately estimate PAH phase distribution suggests the assumption of instantaneous equilibrium is inaccurate.

It has recently been suggested, based on laboratory studies, that PAHs become trapped in secondary organic aerosol (SOA) during SOA formation, preventing them from evaporating to the gas phase and protecting them from degradation via oxidation.\textsuperscript{22} This process could explain the observed lack of gas-particle correlation and generally low estimated $K_P$ values compared to measurements. Unlike primary organic aerosol (POA), which is directly emitted to the atmosphere, SOA forms within the atmosphere. Thus, total atmospheric organic aerosol (OA or OM) contains both POA and SOA. SOA has traditionally been considered aerosol formed from the oxidation and condensation of gas-phase precursors, including SVOCs such as PAHs. Recently, however, oxidation of gas-phase compounds that have evaporated from POA has been recognized as another source of SOA.\textsuperscript{23} SOA is estimated to comprise over 30% of total atmospheric OM,\textsuperscript{24} though this fraction may be much greater if current estimates are missing key sources. The contribution of PAHs to SOA formation could be significant in anthropogenically influenced locations. One study estimated that PAHs account for >10% of SOA in Houston, TX (USA),\textsuperscript{25} and another showed that alkanes and PAHs combined may account for 20-30% of ground-level anthropogenic SOA in the U.S.\textsuperscript{26}

While PAH modeling studies use various schemes for representing gas-particle partitioning, none explicitly consider the role of SOA on PAH LRT. Evaluating the impact of SOA on PAHs is important from two different perspectives. First, if PAHs are trapped in SOA during SOA formation, they may be shielded from oxidative degradation and prevented from exchanging with the gas phase. This could explain why PAH $K_P$ values are generally underpredicted by EqP schemes. Second, OA models, including the GEOS-Chem model used in the present study, tend to underestimate observed OA concentrations, implying potential
missing SOA sources. Incorporation of PAHs during SOA formation has been found to significantly decrease SOA evaporation rates, potentially increasing SOA atmospheric lifetimes and simulated OA concentrations, though we do not evaluate this.

Here, we use a global model to test the importance of SOA to PAH LRT, with the hypothesis that incorporating SOA into the model will better reproduce observed gas-particle distributions compared to a model that uses primary carbonaceous aerosols for partitioning. We modify the previously developed and evaluated GEOS-Chem PAH model to include SOA partitioning, and compare results from the SOA-inclusive simulation to those from the default simulation, which employs the D&E OM/BC absorption/adsorption EqP scheme. We conduct additional sensitivity simulations to determine the importance of different PAH-aerosol assumptions besides partitioning: aerosol deposition efficiencies; concentrations of primary aerosols (OM/BC) versus SOA; and constant versus spatiotemporally varying oxidant concentrations. We conduct all simulations for pyrene, given its semivolatility (i.e., substantial mass is found in both the gas and particle phases) and because its physicochemical relationship with SOA has been evaluated extensively compared to other PAHs.

Methods

GEOS-Chem PAH model: default configuration

The development and evaluation of the GEOS-Chem PAH model (v8-03-02) has been described in full elsewhere. To summarize, the model includes: oxidation of gas phase PAHs by hydroxyl radical (OH; scaled for diurnal variation); oxidation of particle-phase PAHs by ozone ($O_3$); wet and dry deposition of both gas and particle phase PAHs; and temperature-dependent partitioning between the gas phase and two particle phases (hydrophobic primary OM and BC) following the D&E scheme. The particle phases used in the default model are primary hydrophobic carbonaceous aerosols only; i.e., “primary OM” refers to OM that does not include SOA. $K_{\text{OAS}}$ are used to describe absorptive partitioning between the gas and primary OM phases, and BC-air equilibrium partition coefficients ($K_{\text{BC}}=[\text{PAH}]_{\text{BC}}/[\text{PAH}]_{\text{gas}}$) describe adsorptive partitioning between gas and BC. A separate NO$_x$-Ox-hydrocarbon-aerosol version of GEOS-Chem (v9-01-02) is used to generate monthly mean concentrations of OH, $O_3$, hydrophobic organic carbon (OC), and hydrophobic BC,
which are archived and read into the PAH model as input. Sensitivity simulations with daily versus monthly oxidant and aerosol inputs suggest monthly averaging results in, at most, a 2% change in PAH concentrations. 

OC concentrations are multiplied by 1.8 to represent primary OM. OM and BC particles with which PAHs are associated convert from hydrophobic to hydrophilic species with a lifetime of 1.2 days, increasing the efficiency of wet scavenging over time with no change in PAH chemistry. PAHs partition between the gas phase and hydrophobic aerosols only; once particles become hydrophilic, PAHs remain associated with the particle until depositing. In the default model, BC plays a much larger role than primary OM in sequestering PAHs within the particle phase: 98% of particulate PAHs are associated with BC rather than OM. A land-atmosphere exchange module was developed and employed recently to evaluate the effect of climate on PAH transport; to reduce variables in the present study, however, we neglect land-atmosphere exchange, which results in minor (~1%) decreases to simulated concentrations with no effect on partitioning. We use a global PAH primary emissions inventory from 2004 compiled on a country-by-country basis, spatially allocated on a 1°x1° grid, and assimilated meteorology from the NASA Goddard Earth Observing System’s GEOS5 dataset degraded to 6 hours temporally, 4°x5° horizontally, and 47 levels vertically. All physicochemical constants used are shown in Table S1. We refer to our standard PAH model using the D&E partitioning scheme as the “default” configuration.

**Default configuration updates and modifications**

The version of the model used here includes several updates relative to previously published work. We include particle-phase oxidation by NO₃ (in addition to O₃) following recently-published data. We use monthly mean NO₃ concentrations archived from NOₓ-Ox-hydrocarbon-aerosol GEOS-Chem simulations, scaled for diurnal variation, and reaction rates provided by Liu et al. (Table S1). We also use improved Leaf Area Indices (LAI) for calculating dry deposition fluxes. We evaluate the influence of including these processes on simulated PAH concentrations relative to previous model versions in the SI (Figures S1 and S2); in general, these updates improve model-measurement comparisons.

**SOA-PAH configuration**
We develop a separate configuration of the GEOS-Chem PAH model to address SOA partitioning (the “SOA-PAH” configuration). We first generate global SOA concentrations with the GEOS-Chem NO$_x$-Ox-hydrocarbon-aerosol model (v9-01-02). GEOS-Chem assumes sources of 23.4 Tg yr$^{-1}$ biogenic and 3.1 Tg yr$^{-1}$ anthropogenic SOA, which combined is on the low end of SOA estimates. This does not include a ~100 Tg yr$^{-1}$ source of “anthropogenically-enhanced” SOA that has been recommended for inclusion in models based on reduced mean error between simulated SOA concentrations and measurements, and we discuss uncertainties associated with this below. We archive monthly mean concentrations of total SOA (mean of 2006-2008) for input to the PAH model. Simulated SOA surface concentrations are generally several times greater than primary hydrophobic OM and BC (Figure S3). For the SOA-PAH configuration, we simulate PAHs in two phases: a gas phase, and a particle phase consisting solely of SOA-bound PAH (ignoring partitioning to primary OM and BC). Gas-phase PAHs oxidize and deposit as described above and in our previous PAH model studies. SOA-bound PAH is scavenged in convective updrafts, rainout, and washout with an efficiency of 80% following Chung and Seinfeld, consistent with SOA behavior in GEOS-Chem. This differs from primary OM- and BC-bound PAHs in the default simulation, which are wet scavenged at 0% efficiency while hydrophobic and 100% efficiency after becoming hydrophilic. Dry deposition is treated similar to the default simulation, following a resistance-in-series scheme with no size dependence.

Simulations to evaluate partitioning

We use the default and SOA-PAH configurations described above to run individual simulations comparing the effect of these different partitioning schemes on PAH LRT. Table 1 lists these simulations under #1, with additional sensitivity simulations (discussed below) under #2. Simulations employing the SOA-PAH configuration are divided into two emissions scenarios based on uncertainties in phase distribution upon emission. In the default configuration, PAHs are emitted as total mass (gas plus particle) and distributed instantaneously between the gas and primary OM/BC phases according to $K_{OA}$, $K_{BC}$, and ambient OM/BC concentrations within the boundary layer. This is a known source of uncertainty, as in-situ measurements of the phase upon emission are limited or vary substantially for most major PAH sources. Similarly, few data exist to suggest a suitable
approach for distributing emissions between gas and SOA phases. Thus, we construct two
emissions scenarios within the SOA-PAH configuration to capture a range of potential phase
distributions upon emission: (a) 100% of PAHs are trapped in SOA upon emission (denoted
“100% in SOA”), and (b) the fraction of PAH emissions trapped is determined by partitioning
between SOA and gas phases according to $K_{OA}$ and boundary layer SOA concentrations
(“SOA/gas”). Both scenarios assume PAHs can only become trapped in SOA within the 4°x5°
grid box into which PAHs are emitted. Though both scenarios may neglect entrapment after
LRT, the lifetimes of SOA precursors are short enough that SOA formation relevant to PAH
entrapment likely happens before substantial LRT has taken place; i.e., we assume the effect
is small.

After initial partitioning as described above, simulations employing the SOA-PAH
configuration use a chemistry and partitioning scheme following the experimental results of
Zelenyuk et al.\textsuperscript{22} In contrast to the instantaneous EqP scheme of the default configuration,
PAHs in SOA-PAH simulations slowly evaporate from SOA after their initial entrapment.
According to Zelenyuk et al., \textasciitilde50-80% of PAH trapped in SOA during SOA formation
remains associated with the particle after 24 hours, with 80% likely the more realistic estimate
given differences between laboratory and atmospheric conditions. We model this evaporation
process using an exponential decay function:

$$m(t) = m(0) \times e^{-kt} \quad (1)$$

where $m(t)$ is the mass of SOA-bound PAH at time $t$, $m(0)$ is the initial mass of SOA-bound
PAH, and $k$ is the evaporation rate, which is set to correspond to 80% PAH remaining after 24
hours (unless otherwise noted). Zelenyuk et al. also estimated that only 10% of PAH
associated with SOA is on or near the particle surface. We thus assume for SOA-PAH
simulations that only 10% of SOA-associated PAHs are susceptible to heterogeneous particle-
phase oxidation, in contrast to the default configuration where 100% of primary OM and BC-
associated PAHs undergo oxidation. For both the default and SOA-PAH configurations, we
conduct simulations with and without particle-phase oxidation, and SOA-PAH simulations
are conducted under both emission scenarios (simulations 1a-1f under \#1 in Table 1).

We note that there are several uncertainties associated with the Zelenyuk scheme that
have implications for results from SOA-PAH simulations, including the degree to which SOA
exists as a viscous, semi-solid substance in the atmosphere, which namely depends on temperature and relative humidity\(^3\) (Zelenyuk et al. conducted their experiments under dry conditions). These uncertainties could modify the degree of PAH trapping and oxidation, and lead to variations in resulting gas-particle ratios. We address this by running simulations with an evaporation rate corresponding to 50% PAH remaining trapped after 24 hours, the lower limit of the range mentioned above.

**Simulations to evaluate sensitivity to other model parameters**

We conduct three additional sensitivity simulations with the SOA-PAH configuration to test the influence of parameters not directly related to partitioning scheme (simulations 2a-2c, Table 1). These are: differences in wet deposition efficiency between primary OM/BC and SOA; the influence of OH concentration; and the concentration/spatiotemporal difference between OM/BC and SOA. To test the effect of differences in wet deposition efficiency, which could affect particulate PAH lifetimes relevant to LRT, we replace the deposition efficiency of SOA with that of hydrophobic OM/BC (simulation 2a, Table 1). OH concentrations influence gas-phase degradation lifetimes. Some previous PAH modeling exercises have assumed constant OH concentrations,\(^2\) while others have found that seasonal variations in OH can cause marked differences in PAH concentrations.\(^3\) To diagnose the influence of these assumptions we replace spatially- and temporally-varying OH concentrations with a blanket OH concentration of \(10^6\) molecules/cm\(^3\) (simulation 2b). Spatial and temporal variability in aerosols could also affect transport pathways by changing particle availability for partitioning, and thus, PAH gas-particle distribution. To assess differences in the spatial and temporal distribution of hydrophobic primary aerosols versus SOA, we use monthly mean archived concentrations of primary OM/BC in place of SOA concentrations (simulation 2c).

The “100% in SOA” emission scenario is more sensitive than the “SOA/gas” scenario to the effect of wet deposition, since it allocates a greater fraction of PAH (100%) to the particulate phase, while the SOA/gas emission scenario has greater sensitivity to spatial and temporal distribution of aerosol. The latter is because when PAHs are divided between gas and particulate phases by \(K_{OA}\), the fraction of particulate PAH is calculated according to the
volume ratio between air and particles; hence, particle concentrations need to be known. This is in contrast to the 100% in SOA emissions scenario, where there is no dependence on particle concentration because the PAH particulate fraction is assumed to be independent of air-particle volume ratios. Finally, the SOA/gas emission scenario is more sensitive to changes in OH, because a greater fraction of PAH exists in the gas phase. We thus use the 100% in SOA scenario for our wet deposition sensitivity simulations, and the SOA-gas partitioning emission scenario for spatial and temporal distribution and OH sensitivity simulations. Partitioning in the latter two sensitivity scenarios follows the SOA/gas emissions scenario, using the $K_{OA}$ alone to partition PAHs upon emission, even when primary OM/BC is substituted for SOA (i.e., the $K_{BC}$ is not used, so we can isolate the effect of aerosol concentration/deposition versus difference in partitioning strength).

Simulations to assess the role of instantaneous equilibrium partitioning versus aerosol type: OM/BC-evap configuration

In a final set of simulations (Table 1, #3), we evaluate the possibility that PAHs are trapped in primary carbonaceous species (OM/BC) rather than SOA, with subsequent slow evaporation following Eq. 1 as in the SOA-PAH configuration. In this configuration, termed “OM/BC-evap”, PAHs partition to ambient primary OM/BC when emitted following both the $K_{OA}$ and $K_{BC}$, and 80% of PAH remains in the particle after 24 hours. The OM/BC-evap configuration isolates the effect of SOA versus BC (i.e., aerosol type) from the effect of EqP because (1) the trapping scenario is used instead of EqP, and (2) in all simulations where primary OM and BC represent the particle phase, BC-bound PAH accounts for 98% of the particle phase budget; primary OM plays only a minor role in sequestering pyrene. We conduct simulations with this “OM/BC-evap” configuration with and without particle-phase oxidation (simulations 3a and 3b Table 1).
Model evaluation

To evaluate how well each simulation captures observed concentrations, we conduct paired t-tests for differences between simulated and observed three-year (2006-2008) mean total (gas+particulate) concentrations at northern hemisphere stations reporting at least monthly measurements (see Table S2 for station information). We compare annual means only at stations distant from sources (i.e., non-urban mid-latitude and Arctic sites). We also compare simulated and observed monthly mean total concentrations from sites in Table S2 to assess how well simulations capture seasonal variability at non-urban mid-latitude and Arctic sites. Finally, we compare simulated and observed monthly mean particulate fractions (i.e., $[\text{PAH}]_{\text{particulate}}/ [\text{PAH}]_{\text{total}}$). We make this comparison only at stations operated by the Integrated Atmospheric Deposition Network (over the U.S. and Canadian Great Lakes), where phase-resolved measurements are prioritized and considered reliable for model evaluation.

Results

Statistical comparison of annual means

Scatter plots of simulated versus observed mean concentrations are shown in Fig. S4, while linear best-fit equations, correlation coefficients ($r=0.65-0.70$), and log mean biases (LMB=$-0.08-0.21$) are shown in Table S3. Our default configuration is able to capture annual mean PAH concentrations: for default simulations (1a and 1b, Table 1), there is no significant difference ($\alpha=0.05$) between simulated and observed annual means, both with and without particle-phase oxidation turned on (p=0.97 and 0.07, respectively). Annual means from SOA-PAH simulations using the SOA/gas emissions scenario (1e and 1f) also are not statistically different from observed means (p=0.27 and 0.26 for with and without particle-phase oxidation, respectively). In contrast, comparison of simulated and observed annual means shows that simulating 100% PAH entrapment in SOA upon emission does not match observations of LRT (1c and 1d). Annual means are significantly higher than observations for SOA-PAH simulations when 100% of emissions are allocated to SOA: simulated concentrations are 4.4x higher than observed with particle-phase oxidation (p=0.01) and 7.4x higher without (p<0.01). These results confirm that if PAHs are indeed trapped in SOA upon emission, it is unlikely that 100% of PAH becomes associated with SOA.
SOA-PAH simulations using an evaporation rate corresponding to 50% of particulate PAH remaining after 24 hours (rather than the default of 80%) resulted in, at most, a 15% decrease in simulated annual mean concentrations (data not shown). Though this is a relatively minor change, we note that the 50-80% evaporation rate range used here was obtained under dry conditions, which are unlikely in the atmosphere. Thus, true atmospheric evaporation rates probably have even greater variability and could have stronger influence on PAH concentrations.

Monthly mean concentrations

We compare monthly mean observed and simulated total concentrations and particulate fractions to further assess simulations using different partitioning schemes (under #1 in Table 1). Fig. 1A and 1B show simulated vs. observed monthly means at nonurban mid-latitude and Arctic stations, respectively, while Fig. 1C compares simulated and observed particulate fractions at IADN sites in the U.S./Canadian Great Lakes. Results from simulations to evaluate partitioning (Table 1, 1a-1f; green, blue, and red lines in Fig. 1) are compared to observations (black lines) in this section; simulations to evaluate the effect of PAH trapping by BC (Table 1, 3a and 3b; purple lines in Fig. 1) are discussed later.

Comparison of simulated and observed monthly mid-latitude concentrations (Fig. 1A) shows that phase distribution upon emission has more influence on PAH LRT than partitioning behavior during transport. All simulations capture the inter-monthly trend in mid-latitude concentrations (more in winter, less in summer). Simulations in which PAHs are partitioned between gas and particle phases upon emission (1a, 1b, 1e, and 1f, Table 1; green and red lines, Fig. 1A) result in concentrations that fall within +/- one standard deviation of monthly means, regardless of whether they are partitioned to primary OM/BC or SOA, and whether they following the default EqP scheme or the SOA-PAH scheme. Consistent with the annual mean comparison, SOA-PAH simulations following the 100% in SOA emissions scenario (1c and 1d, Table 1; blue lines, Fig. 1A) overestimate measured values. Including particle-phase oxidation (dotted lines) does not substantially change results.

In contrast to mid-latitude concentrations, comparisons to monthly mean Arctic concentrations (Fig. 1B) show that when larger fractions of PAH are distributed to the particle
phase upon emission and protected from oxidation there is a better match to observations. All simulations generally capture concentrations during colder months within +/- one standard deviation of measured means, but underestimate summer concentrations by up to ~100x. Summer underestimates are likely partially due to the influence of local sources not included in model emissions (e.g., camp or wildfires). Simulated concentrations are generally higher, and closer to Arctic measured values, when a greater fraction of PAH is allocated to the particle phase when emitted and protected from oxidation. Thus, in contrast to annual mean and mid-latitude monthly comparisons, the SOA-PAH 100% in SOA scenario performs best, consistent with the hypothesis that trapping of PAHs in SOA may account for high particulate fractions in remote areas. Similar to the mid-latitudes, however, simulated transport to the Arctic is more strongly influenced by distribution upon emission than partitioning scheme subsequent to emission; e.g., simulations 1a and 1e, the green and red solid lines in Fig. 1, which partition PAH upon emission to primary OM/BC and SOA, respectively, show nearly identical results, despite different partitioning behavior during transport.

Comparison with particulate fractions shows that the SOA-PAH configurations under- and overestimate particulate fraction while the default configuration performs best (Fig. 1C). Default simulations (1a and 1b, Table 1) predict particulate fractions closest to measured values and capture the inter-monthly trend of higher particulate fractions in winter versus summer most accurately (green lines, Fig. 1C). The particulate fraction is highly overestimated by SOA-PAH simulations with 100% of emissions in SOA, even when particle-phase oxidation is turned on (1c and 1d, Table 1, and solid and dotted blue lines, Fig. 1C, respectively). The SOA-PAH 100% entrapment scenario also fails to capture seasonal variation in particulate fraction, predicting higher fractions in summer versus winter, whereas observed particulate fraction is lowest in summer. In contrast, particulate fractions are severely underestimated in the SOA/gas scenario (simulation 1e; red solid line, Fig. 1C), especially when oxidation is implemented (simulation 1f; red dotted line, Fig. 1C; >10x lower than mean measured values).

Although concentration and phase distribution results suggest allocating more PAH to the particulate phase during emission increases LRT, they also imply the two have a complex relationship. This can be observed by comparing 100% in SOA simulations with and without particle phase oxidation (1c and 1d, Table 1). Implementing particle phase oxidation does not
affect the extreme overestimates of particulate fraction (blue lines, Fig. 1C), but causes
table decreases in concentrations (blue lines, Fig. 1A and 1B). That is, nearly identical
particle phase fractions exhibit different LRT results. Another example is seen when default
simulations are compared to SOA/gas emissions scenario simulations (1a and 1b to 1e and 1f,
respectively). Simulated particulate fractions vary dramatically between these two
configurations (green and red lines, Fig. 1C), but predicted total concentrations are very
similar (green and red lines, Fig. 1A and 1B). Thus, different particle phase fractions result in
similar total LRT. This complex relationship between phase distribution and total PAH
transport has been noted in other PAH modeling studies comparing different partitioning
parameterizations.\textsuperscript{16} Thus, our results suggest the amount of PAH partitioning to particles
cannot alone be used to predict LRT potential.

Arctic particulate fractions from different simulations (Fig. S5) have distinctly
different seasonal patterns. We do not compare these to observations, however, as Arctic
sampling requires high airflow rates and long sampling periods, which can cause phase
resolution artifacts. Similar to mid-latitude results, 100% in SOA simulations (1d and 1e)
produce the highest particulate fractions (blue lines, Fig. S5), though overall particulate
fraction is smaller in the Arctic than at mid-latitudes. The particulate fraction for SOA-PAH
simulations (blue and red lines) are maximum in summer, while default simulations (green
lines) are minimum in summer. While data to constrain seasonal variations in Arctic
particulate fraction have methodological limitations, as noted above, Sofowote et al.\textsuperscript{40} found
that pyrene Arctic particulate fraction was maximum in summer and minimum in winter,
opposite of that found in the mid-latitudes. Sofowote et al. attributed the summer-time
maximum to a shift to local emissions sources (not included in our model emissions).
However, this nevertheless suggests SOA-PAH simulations capture the seasonal trend in
Arctic particulate fraction better than default simulations.

**Effect of factors other than partitioning**

Sensitivity simulations suggest interaction with primary aerosols rather than SOA is
more important than the influence of wet deposition efficiency or spatiotemporal variation in
OH concentrations for matching observed phase distributions. Fig. 2 shows the results of this
sensitivity simulation (simulation 2c, Table 1) compared with observations. Also shown for comparison are default and SOA/gas results for simulations without particle-phase oxidation (i.e., simulations 1a and 1e from Table 1; solid green and red lines from Fig. 1). Results of the other two sensitivity simulations are shown (Fig. S6) and discussed in the SI.

Substituting primary OM/BC concentrations for SOA (red line with circles) causes very little change in total concentration (<1% increase in both the mid-latitudes and Arctic; Fig. 2A and 2B), but there is an average increase (17%) in particulate fraction (Fig. 2C), which better matches observations. More important, the seasonal pattern of particulate fraction in the primary OM/BC concentration sensitivity simulation better matches observations. This is consistent with seasonal trends for aerosols: SOA tends to be higher in summer because emissions correlate with temperature, while primary carbonaceous aerosols often peak in winter because of burning for heat. This suggests interaction with primary aerosols rather than SOA is what drives the better match to observed phase distributions in the default simulation. We note that the addition of greater sources of anthropogenically controlled SOA to OA models has been recommended in the past, and it is possible that anthropogenically controlled SOA could exert similar controls on PAH LRT as primary aerosols. We discuss the potential influence of including these sources below.

Assessing the role of instantaneous equilibrium partitioning versus aerosol type

The OM/BC-evap simulation with no particle-phase oxidation, (3a, Table 1; purple lines, Fig. 1) agrees better than the default configuration (green lines, Fig. 1) with observed phase distribution (Fig. 1C) and Arctic concentrations (Fig. 1B). Mid-latitude results (Fig. 1A) are biased high, however, and there is a significant difference between annual simulated and observed means (p=0.03; Fig. S4). Turning on particle-phase oxidation (simulation 3b) improves mid-latitude seasonal (Fig. 1A) and annual concentrations, such that there is no longer a significant difference between annual means (p=0.07; Fig. S4), but the match to remote observations degrades, as does the match to phase distribution (Fig. 1B and 1C).

The OM/BC-evap configuration substantially increases Arctic particulate fractions compared to the default configuration (e.g., from an annual mean of 0.02 for simulation 1a to 0.4 for simulation 3a), and reverses the seasonal pattern (Fig. S5). The OM/BC-evap
configuration produces an Arctic particle phase maximum in summer consistent with what Sofowote et al.\textsuperscript{40} observed for pyrene. Thus, the OM/BC-evap configuration captures mid-latitude and remote concentrations and phase distributions simultaneously with the most skill.

**Discussion**

**The role of black carbon**

Our results demonstrate that trapping PAHs in carbonaceous aerosols upon emission improves agreement between measured and simulated PAH concentrations in remote regions and particle phase distributions, compared to a scheme that uses EqP. Simulations employing SOA as the sole particle phase to which PAHs partition result in PAH particulate fractions that are either too high or too low compared to observations, however, and with the opposite seasonal pattern. In contrast, default simulations with EqP between the gas phase and primary hydrophobic carbonaceous aerosols (OM/BC) closely capture particulate fraction magnitude and seasonal variation as well as mid-latitude total concentrations, but underestimate remote concentrations. Thus, we created a configuration (“OM/BC-evap”) that explicitly considers adsorption to BC (i.e., with the $K_{BC}$) to test whether the strong sorption to BC versus SOA was the main reason for better particulate phase model-observation agreement with the default configuration (versus EqP). Indeed, simulating entrapment of PAHs by BC and limiting exchange with the gas phase provides the best match to all observations, especially with respect to magnitude and seasonality of phase distribution. Exchange with the gas phase during transport has only a small influence on ability to reproduce measurements. Collectively, our results suggest two considerations of primary importance in determining PAH LRT, with a particular emphasis on the role of BC: 1) physicochemical behavior governing initial PAH association with particles (i.e., magnitude of partition coefficients and a particle’s ability to sequester/trap PAHs during emission), and 2) particle concentrations close to or within emission sources.

Evidence of BC’s importance to PAH LRT can be found in the similarity between simulations distributing PAH between the gas and aerosol phases upon emission. Default (1a and 1b) and SOA-gas emission scenarios (1e and 1f) predict remarkably similar concentration results, both in the mid-latitudes and Arctic, compared with simulations trapping 100% of
PAH in SOA upon emission (1c and 1d). This suggests that PAH gas-particle distribution upon emission is a key process determining how PAHs transport, and PAHs are much more likely associated with BC versus SOA when emitted. Activities producing the greatest PAH emissions globally are also those producing large quantities of BC,\(^{31,41}\) namely combustion of bio- and fossil fuels. Indeed, there is a large amount of literature demonstrating pyrogenic PAHs and BC (or soot) are co-emitted, with strong evidence that PAHs are molecular intermediates in the process of BC formation and growth during combustion.\(^{42}\) While PAHs also have petrogenic and biogenic sources, globally these are minor compared to pyrogenic.\(^{31}\)

An important role for atmospheric BC is consistent with PAH behavior in aquatic/sediment environments, and also with results of other studies of PAH partitioning in the air beyond the D&E study. For example, Arp et al.\(^{43}\) investigated over 500 measured \(K_P\) values for a wide range of SVOCs, including PAHs. Their results indicated that for most neutral SVOCs, the water-insoluble OM fraction of aerosol was a good predictor of \(K_P\). PAHs, however, exhibited anomalous behavior in that measured \(K_P\)s were up to \(~100\times\) higher than predicted, which was attributed to a non-exchangeable fraction associated with BC. Indeed, PAHs were the only SVOCs studied that are co-emitted with BC.

**Uncertainties**

The interpretation of our results is subject to a number of uncertainties. First, we do not account for particle size, relative humidity, or particle heterogeneity. PAHs associated with different particle sizes can deposit differently,\(^{44}\) while humidity can impact oxidation rates\(^{45,46}\) and diffusion of PAHs to particle surfaces.\(^{38}\) Within the GEOS-Chem PAH model, primary carbonaceous aerosols consist solely of hydrophobic OM and BC, when in reality aerosols are only partially comprised of these components and can contain a number of other phases, such as minerals and salts.\(^{42,47}\) Furthermore, the mixing of OM and BC within a single particle from aging could affect PAH partitioning substantially. For example, OM coatings that develop during transport could either diminish PAH adsorption to BC during transport or trap PAHs already associated with BC. Concentrations of primary carbonaceous aerosols, SOA, and oxidants in the PAH model are subject to the uncertainties of the GEOS-Chem NO\(_x\)-Ox-hydrocarbon-aerosol model\(^{24,30,48}\) with which they were generated.
We extend observations of SOA trapping of pyrene, determined via experiments with SOA generated from α-pinene, to BC in our final OM/BC-evap simulations. Given differences between the formation of SOA and BC, it is likely that pyrene-BC interactions differ considerably from pyrene-α-pinene interactions. The process of SOA formation itself is largely unknown, with ongoing debate as to whether SOA is a semi-solid or liquid and whether it is formed primarily from the oxidation of gas-phase precursors or from previously emitted particles. The degree to which PAHs take part in SOA formation is still largely unknown as well, and extending observations of PAH entrapment in SOA to BC adds yet another layer of uncertainty. We acknowledge that our OM/BC-evap configuration may represent a process for which there is little physical evidence in the atmosphere, but nonetheless the simulations provide valuable information regarding agreement between observations in mid-latitude and remote regions.

Additionally, it is possible that introducing greater sources of “anthropogenically enhanced” SOA into the model could produce a PAH phase distribution similar to what we observe with BC. Spracklen et al. recommended adding a ~100 Tg/yr of anthropogenically-controlled SOA to model sources to minimize SOA observation-model discrepancies. Heald et al. did just that with the GEOS-Chem SOA model, using simulated aromatic SOA as a proxy for anthropogenically controlled SOA, and found dramatically better measurement-model agreement near sources, but overestimates aloft and in remote regions. We note that anthropogenically derived SOA and BC sources are likely correlated, and thus, the improved phase distribution model-measurement agreement seen when PAHs partition primarily to BC might also be observed if simulations were conducted with additional anthropogenically controlled SOA instead.

There are uncertainties in pyrene oxidation rates in both the gas and particle phases beyond the impact of humidity. For example, the gas phase OH reaction rate constant we use for pyrene has been deduced from ionization potential rather than empirically determined, and particle phase oxidation rate constants have been measured for PAHs associated with model substrates such as decanol, graphite, or diesel, rather than ambient particulate matter. These uncertainties could cause considerable variation in the loss of both the gas and particle phases.
Finally, there are uncertainties in emissions, both in magnitude and spatial/temporal distribution, which could lead to deviations in simulation performance. Sensitivity simulations conducted with +/-20% of baseline emissions, however, demonstrate no notable change in phase distribution. This suggests gas-particle distributions depend more strongly on PAH and particle physicochemical behavior and phase distribution when emitted than emissions magnitude.

**Supporting Information Available**

The supporting information includes physicochemical constants, measurement station data, model and measurement correlation data, and comparison of previous model version results to those presented here. This information is available free of charge via the Internet at http://pubs.acs.org/.

**Acknowledgments**

This work was supported by the MIT Leading Technology and Policy Initiative and the U.S. National Science Foundation Atmospheric Chemistry (Grant #1053658) and Arctic Natural Sciences Programs (Grant #1203526).
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15. Sehili, A. M.; Lammel, G. Global fate and distribution of polycyclic aromatic


28. Friedman, C. L.; Selin, N. E. Climate change and emissions impacts on atmospheric


44. Kaupp, H.; McLachlan, M. S. Atmospheric particle size distributions of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polycyclic aromatic hydrocarbons (PAHs) and their implications for wet and dry deposition. *Atmos. Environ.* **1998**, *33*, 85-95.


### Table 1. Summary of simulations conducted in this study. *Simulation results presented in the Supporting Information.*

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Model configuration</th>
<th>Emission scenario</th>
<th>Instantaneous EqP?</th>
<th>% of PAH available for particle-phase oxidation</th>
<th>Additional details</th>
<th>Color in figures</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Default</td>
<td>OM, BC, and gas</td>
<td>Yes</td>
<td>0%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>Default</td>
<td>OM, BC, and gas</td>
<td>Yes</td>
<td>100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>SOA-PAH</td>
<td>100% in SOA</td>
<td>No</td>
<td>0%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td>SOA-PAH</td>
<td>100% in SOA</td>
<td>No</td>
<td>10%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1e</td>
<td>SOA-PAH</td>
<td>SOA/gas</td>
<td>No</td>
<td>0%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1f</td>
<td>SOA-PAH</td>
<td>SOA/gas</td>
<td>No</td>
<td>10%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2a*</td>
<td>SOA-PAH</td>
<td>100% in SOA</td>
<td>No</td>
<td>0%</td>
<td>OM/BC wet deposition efficiency substituted for SOA</td>
<td></td>
</tr>
<tr>
<td>2b*</td>
<td>SOA-PAH</td>
<td>SOA/gas</td>
<td>No</td>
<td>0%</td>
<td>Constant OH concentration</td>
<td></td>
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<tr>
<td>2c</td>
<td>SOA-PAH</td>
<td>SOA/gas</td>
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<td>0%</td>
<td>Sum of OM/BC concentrations in place of SOA concentrations</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>OM/BC-evap</td>
<td>OM, BC, and gas</td>
<td>No</td>
<td>0%</td>
<td>Default model without equilibrium partitioning</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>OM/BC-evap</td>
<td>OM, BC, and gas</td>
<td>No</td>
<td>10%</td>
<td>Default model without equilibrium partitioning</td>
<td></td>
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</table>
Figure 1. A) Monthly geometric mean nonurban mid-latitude total concentrations; B) monthly geometric mean Arctic total concentrations; and, C) monthly mean particulate fractions. Results shown are from simulations listed under #1 and #3 of Table 1. Results for simulations without particle phase oxidation (solid lines) and with (dotted lines) are shown. Measured data are for sites in Table S2 for 2006-2008. Error bars are ± 1 standard deviation of monthly means across sites. Numbers/letters in parentheses correspond to simulation labels from Table 1.
Figure 2. A) Monthly geometric mean nonurban mid-latitude total concentrations; B) monthly geometric mean Arctic total concentrations; and, C) monthly mean particulate fractions for sensitivity simulations. Simulations did not include particle-phase oxidation, and SOA-PAH model simulations were conducted with 20% evaporation by 24 hours. Numbers/letters in parentheses correspond to simulation labels from Table 1.
Assessing the influence of secondary organic aerosols on long-range atmospheric PAH transport – Supporting Information

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<td></td>
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</tr>
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<td>Parameter</td>
<td>Description</td>
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<td>-----------</td>
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<td>log $K_{BC}$</td>
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<td>log $K_{AW}$</td>
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<td>Enthalpy of phase transfer from gas phase to OC</td>
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<td>$\Delta_{BC}H$ (kJ/mol)</td>
<td>Enthalpy of phase transfer from gas phase to BC</td>
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<td>$\Delta_{AW}H$ (kJ/mol)</td>
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<td>$B$ (molec/cm$^3$)</td>
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<td>$\rho_{BC}$ (kg/m$^3$)</td>
<td>Density of BC</td>
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<td>$\tau_{OCBC}$ (d)</td>
<td>Lifetime of hydrophobic OC and BC before converting to hydrophilic</td>
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<td>$k_{NO3}$ (cm$^3$/molec/s)</td>
<td>Reaction rate constant for particle phase oxidation by NO$_3$</td>
<td>6.4e-12</td>
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**Table S1.** Pyrene physicochemical constants used in the model. References: (a) Ma et al., 2010$^1$; (b) Lohmann and Lammel, 2004$^2$; (c) Schwarzenbach et al., 2003$^3$; (d) U.S. EPA Episuite software$^4$; (e) Kahan et al., 2006$^5$; (f) Park et al., 2003$^6$; (g) deduced from Zelenyuk et al., 2012$^7$; (h) Liu et al., 2012$^8$. 
<table>
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<th>Station</th>
<th>Observation years</th>
<th>Ref</th>
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<td>2006-2008</td>
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<td>80</td>
<td>12</td>
<td>Spitsbergen/Zeppelinfjell, Norway</td>
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<td>68</td>
<td>24</td>
<td>Pallas/Matorova, Finland</td>
<td>2006-2007</td>
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<td>60</td>
<td>17</td>
<td>Aspvreten, Sweden</td>
<td>2006-2008</td>
<td>2</td>
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<td>58</td>
<td>8</td>
<td>Birkenes, Norway</td>
<td>2006, 2008</td>
<td>2</td>
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<td>Rao, Sweden</td>
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<td>55</td>
<td>8</td>
<td>Westerland, Germany</td>
<td>2006-2008</td>
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<td>54</td>
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<td>Zingst, Germany</td>
<td>2006-2008</td>
<td>2</td>
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<td>54</td>
<td>-1</td>
<td>High Muffles, Great Britain</td>
<td>2006-2007</td>
<td>2</td>
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<td>51</td>
<td>11</td>
<td>Schmuucke, Germany</td>
<td>2006-2008</td>
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<td>2006-2008</td>
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<td>48</td>
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<td>2006-2007</td>
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<td>Sleeping Bear Dunes, MI, USA†</td>
<td>2006-2007</td>
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<td>2006-2007</td>
<td>3</td>
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</table>

Table S2. Northern hemisphere measurement stations used to evaluate simulated pyrene concentrations against observed. †Gas-particle ratios provided by reference and used to evaluate simulated gas-particle ratios. §Site considered urban and/or highly impacted by local sources and not used to evaluate background concentrations. Sites > 66°N are considered Arctic. Observations formatted similarly (e.g., bold or italics) occurred within the same GEOS-Chem grid box and were averaged. References: (1) Northern Contaminants Program and Environment Canada; (2) Cooperative Programme for Monitoring and Evaluation of Long-range Transmissions of Air Pollutants (EMEP); (3) Integrated Atmospheric Deposition Network (IADN). Data from reference 3 was provided prior to a routine QA/QC procedure.
<table>
<thead>
<tr>
<th>Simulation</th>
<th>Particle Phase Oxidation?</th>
<th>Slope of Best Linear Fit</th>
<th>Intercept of Best Linear Fit</th>
<th>Correlation Coefficient (r)</th>
<th>Log Mean Bias</th>
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<tr>
<td>1a: Default</td>
<td>No</td>
<td>1.05</td>
<td>0.14</td>
<td>0.68</td>
<td>0.16</td>
</tr>
<tr>
<td>1b: Default</td>
<td>Yes</td>
<td>0.65</td>
<td>0.10</td>
<td>0.65</td>
<td>-0.08</td>
</tr>
<tr>
<td>1c: SOA-PAH, 100% in SOA</td>
<td>No</td>
<td>1.91</td>
<td>0.29</td>
<td>0.70</td>
<td>0.42</td>
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<tr>
<td>1d: SOA-PAH, 100% in SOA</td>
<td>Yes</td>
<td>1.45</td>
<td>0.18</td>
<td>0.69</td>
<td>0.23</td>
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<tr>
<td>1e: SOA-PAH, SOA/gas</td>
<td>No</td>
<td>0.79</td>
<td>0.13</td>
<td>0.66</td>
<td>0.09</td>
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<td>1f: SOA-PAH, SOA/gas</td>
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<td>0.79</td>
<td>0.13</td>
<td>0.66</td>
<td>0.09</td>
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<tr>
<td>3a: OM/BC-evap</td>
<td>No</td>
<td>1.23</td>
<td>0.16</td>
<td>0.69</td>
<td>0.21</td>
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<tr>
<td>3b: OM/BC-evap</td>
<td>Yes</td>
<td>1.10</td>
<td>0.14</td>
<td>0.68</td>
<td>0.14</td>
</tr>
</tbody>
</table>

**Table S3.** Linear best-fit slopes, intercepts, and correlation coefficients for mean annual model-observation comparisons shown in Figure S4. The log mean bias (LMB) is also presented, and is given as

\[
LMB = \frac{\sum (\log_{10}(S_i) - \log_{10}(O_i))}{N}
\]

where \(S_i\) and \(O_i\) are simulated and observed pyrene concentrations at each observation location, i, and \(N\) is the number of observation locations.
Figure S1. Comparison of pyrene concentrations (mean of 2006-2008) simulated with a previously published version of the model to the version in the present study, which uses two new processes. First, the present Leaf Area Index (LAI) dataset is derived from the Moderate Resolution Imaging Spectroradiometer (MODIS) of NASA’s Terra satellite, versus the NOAA Advanced Very High Resolution Radiometer (AVHRR) satellite as was done previously. This is because the MODIS LAI dataset has greater global coverage, includes data specific to model years used here, and is the default dataset for the NOx-Ox-hydrocarbon-aerosol GEOS-Chem model used for generating all particle and oxidant fields. Second, we include particle-phase oxidation by NO3 in the present model, compared to particle-phase oxidation only by O3 in the previous version.
Figure S2. Same figure as S1 but showing the sum of wet and dry pyrene deposition rather than concentration (mean of 2006-2008). Wet and dry deposition are evaluated only for stations routinely reporting it (those from Sweden and Finland listed in Table S2).
**Figure S3.** Surface concentrations (µg m⁻³) of (A) SOA, (B) primary hydrophobic OM, and (C) primary hydrophobic BC, as simulated by GEOS-Chem (mean of 2006-2008). Also shown is the difference between SOA and primary aerosol concentrations (D).
Figure S4. Simulated (2006-2008) versus observed annual mean total pyrene concentrations from sites in Table S2. Numbers/letters in parantheses are simulation labels from Table 1 in the main text.
Figure S5. Simulated pyrene particulate fraction in the Arctic. Simulated values are means from GEOS-Chem grid boxes corresponding to Arctic observation stations (see Table S2). Numbers/letters in parentheses correspond to simulation labels in Table 1 in the main text.
Figure S6. A) Monthly geometric mean nonurban mid-latitude total concentrations; B) monthly geometric mean Arctic total concentrations; and, C) monthly mean particulate fractions for sensitivity simulations. Simulations did not include particle-phase oxidation,
and SOA-PAH model simulations were conducted with 20% evaporation by 24 hours. Numbers/letters in parentheses correspond to simulation labels from Table 1.

Figure S4 shows results of our three sensitivity simulations to test the influence of wet deposition efficiency, OH concentrations, and spatiotemporal aerosol distribution, respectively (simulations 2a-2c, Table 1) compared with observations (mid-latitude means in A, Arctic means in B, and particulate fraction in C). Also shown for comparison are default and SOA-PAH configuration results for simulations without particle-phase oxidation (i.e., simulations 1a, 1c, and 1e; solid green, blue, and red lines from Fig. 1).

Wet deposition efficiency changes have little impact on overall results (blue line with triangles). Replacing SOA wet deposition efficiency with that of primary OM/BC increases the high bias in simulated concentrations. Mid-latitude concentrations increase by 13% (Fig. S4A) and Arctic concentrations increase by 2.3x (Fig. S4B). Phase distribution does not change (Fig. S4C); particle fractions are still considerably overestimated.

Applying a constant OH concentration (red lines with triangles) increases gas-phase oxidation (+11% increase in the annual budget), leading to 1.7x lower total mid-latitude concentrations (Fig. S4A), 8.9x lower Arctic concentrations (Fig. S4B), and 1.9x higher particulate fractions (Fig. S4C). Though this generally improves model-measurement agreement in the mid-latitudes, the particle phase is still largely underestimated compared to observations, as are Arctic concentrations.

Results for substituting primary OM/BC concentrations for SOA (red line with circles) are discussed in the main text.
Literature Cited


