Steady-State Mass Balance Model for Predicting Particle–Gas Concentration Ratios of PBDEs

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ABSTRACT: Assuming equilibrium partitioning between the gas and particle phases has been shown to overestimate the fraction of low-volatility chemicals in the particle phase. Here, we present a new steady-state mass balance model that includes separate compartments for fine and coarse aerosols and the gas phase and study its sensitivity to the input parameters. We apply the new model to investigate deviations from equilibrium partitioning by exploring model scenarios for seven generic aerosol scenarios representing different environments and different distributions of emissions as the gas phase, fine aerosol, and coarse aerosol. With 100% of emissions as the particle phase, the particle–gas concentration ratio in our model is similar to the equilibrium model, while differences are up to a factor of 10^6 with 100% of emissions as the gas phase. The particle–gas concentration ratios also depend on the particle size distributions and aerosol loadings in the different environmental scenarios. The new mass balance model can predict the particle–gas concentration ratio with more fidelity to measurements than equilibrium models. However, further laboratory-based evaluations and calibrations of the standard sampling techniques, field investigations with preferably size-resolved measurements of aerosol particle composition, together with the appropriate process modeling for low-volatility chemicals are warranted.

INTRODUCTION

Transport in the atmosphere can spread chemicals from source areas to remote regions such as the Arctic and Antarctic. The distribution of organic chemicals between the gas phase and aerosol particles plays an important role in atmospheric transport because it affects the extent of wet and dry deposition of chemicals, and the availability of chemicals for degradation in the gas phase. Usually, gas–particle partitioning has been modeled using single-parameter linear free energy relationships (spLFERs), which relate the gas–particle partition ratio ($K_P$) to the subcooled vapor pressure ($P_v$) or octanol–air partition ratio ($K_{OA}$). These spLFER models assume equilibrium between the gas phase and aerosols in the atmosphere. They perform well in describing gas–particle partitioning of volatile, and many semivolatile, organic chemicals in laboratory and field studies. However, spLFER models overestimate the fraction of some semivolatile chemicals associated with the aerosol phase, and for low-volatility organic chemicals such as decabromodiphenyl ether (BDE-209), the modeled partitioning to aerosols can be several orders too high when compared with field measurements.

Kinetic models demonstrate that low-volatility chemicals need longer times to reach the equilibrium state between gas and particle phases as compared with more volatile chemicals, providing one potential explanation for the discrepancy between the spLFER models and observations. Already in 2003, a mass balance model that included kinetically limited exchange between aerosol particles and the gas phase was used to demonstrate that disequilibrium could arise, when the time scale for chemicals sorbed to aerosol particles to be removed from the atmosphere by deposition is shorter than the time scale required for diffusive chemical exchange between the gas and particle phases to bring the system to equilibrium. In addition to volatility, the time scale for equilibration between the gas and particle phases varies with other factors such as particle diameter, volume fraction of particles in air, and mass accommodation coefficients assumed for the condensing chemicals, while the time scale for chemicals to be removed from the atmosphere by particle deposition varies with rainfall rate, dry deposition velocity, organic matter content of particles, volume fraction of particles in air, rain scavenging ratio, and time scales of atmospheric deposition during dry and wet periods.

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Table 1. Seven Generic Aerosol Scenarios Representing Different Environments\(^a\)

| Scenario           | Partitioning | \(t_{dp}\) (h) | \(t_{est}\) (h) | \(d^{sc}\) (μm) | \(U_1\) (m/h) | \(f_{OM}\) | \(V_p/V_A\) |
|--------------------|--------------|----------------|----------------|----------------|---------------|------------|------------|
| urban fine         | 9.70 × 10\(^{-9}\) | 120            | 12             | 0.3            | 3.6           | 0.84\(^*\) | 3.64 × 10\(^{-11}\) |
| coarse fine        | 9.70 × 10\(^{-9}\) | 120            | 12             | 15             | 20            | 0.23\(^*\) | 4.82 × 10\(^{-11}\) |
| marine fine        | 9.70 × 10\(^{-9}\) | 120            | 12             | 0.56           | 3.6           | 0.12\(^*\) | 2.04 × 10\(^{-12}\) |
| coarse fine        | 9.70 × 10\(^{-9}\) | 120            | 12             | 7              | 10            | 0.05\(^*\) | 1.39 × 10\(^{-11}\) |
| rural fine         | 9.70 × 10\(^{-9}\) | 120            | 12             | 0.3            | 3.6           | 0.84\(^*\) | 4.53 × 10\(^{-12}\) |
| coarse fine        | 9.70 × 10\(^{-9}\) | 120            | 12             | 8              | 20            | 0.23\(^*\) | 1.73 × 10\(^{-11}\) |
| remote fine        | 9.70 × 10\(^{-9}\) | 120            | 12             | 0.2            | 3.6           | 0.84\(^*\) | 7.31 × 10\(^{-12}\) |
| free troposphere   | 1 × 10\(^{-9}\)  | 8760\(^b\)     | 12\(^b\)       | 0.9            | 0.001         | 0.2\(^*\)  | 6.07 × 10\(^{-14}\) |
| Polar (clean)      | 9.70 × 10\(^{-9}\) | 360\(^b\)      | 12\(^b\)       | 0.35           | 3.6           | 0.3\(^*\)  | 1.4 × 10\(^{-13}\)  |
| coarse             | 9.70 × 10\(^{-9}\) | 360\(^b\)      | 12\(^b\)       | 3              | 20            | 0.1\(^*\)  | 8.89 × 10\(^{-13}\) |
| desert coarse      | 9.70 × 10\(^{-9}\) | 720            | 12             | 20             | 20            | 0.05\(^*\) | 1.77 × 10\(^{-9}\)  |

\(^a\)\(t_{dp}\) and \(t_{est}\) are the time scales of atmospheric deposition during dry and wet periods, respectively. \(d\) and \(U_1\) are the diameter and deposition velocity of aerosols, respectively. \(f_{OM}\) is the fraction of organic matter in aerosol particles. \(V_p/V_A\) is the volume fraction of aerosol particles in air.

\(^b\)Data are estimated.

Recently, Qiao et al.\(^{19}\) systematically studied the particle–gas concentration ratio by comparing eight models. The eight models include five equilibrium models, two empirical models based on monitoring data, and a steady-state model. The steady-state model called the Li–Ma–Yang model showed the best performance with highest conformity to the measurements for selected polybrominated diphenyl ethers (PBDEs). However, further investigation of the features and applicability of the Li–Ma–Yang model is warranted. First, it is well-known that values of annual rainfall rate and fraction of organic matter are varied with environmental scenarios and types of aerosols, while the Li–Ma–Yang model assumes them to be constant.\(^{20}\) Second, the value of a parameter (\(C = S\)) was introduced without reference, and the value has to be changed in different environmental scenarios in order to describe measurements well, being essentially a fitting parameter.\(^{20}\) Third, the Li–Ma–Yang model does not explicitly specify the fraction of the chemical emitted in the gas and aerosol phases. However, the phase distribution of the emissions from various sources is not well constrained.\(^{20}\)

In this work, we present a new steady-state mass balance model that includes separate compartments for fine and coarse aerosols and the gas phase and does not assume equilibrium partitioning. In addition, three phases of emissions as fine and coarse aerosols and gas phases are considered. Using polybrominated diphenyl ethers (PBDEs) that have a range of volatilities as a case, we apply the model to systematically study (1) the differences of particle–gas concentration ratios of chemicals in seven generic environmental scenarios (urban, marine, rural, remote, free troposphere, Polar, and desert) as compared with the equilibrium approach; (2) the influence of the initial phase of the emissions on the particle–gas concentration ratios in various source regions; and (3) the model sensitivity to input variables and uncertainties in environmental variables and the organic aerosol phase. Finally, we compare the model scenarios against field measurements of the particle–gas concentration ratios of PBDEs. Based on the comparison, we discuss the key driving factors that determine the distribution of PBDEs between the gas phase and aerosol particles, potential reasons for disagreements between observations and model predictions, and key steps forward to improve the mechanistic understanding of gas–particle partitioning of PBDEs.

**METHODS**

**Equilibrium Model.** As a baseline for comparison to our steady-state mass balance model, we selected a \(K_{OA}\)-based splLFER equation as a representative equilibrium model. For low-polarity organic chemicals, \(K_{OA}\)-based models and models based on \(P_1\)\(^*\) have been shown to perform equally well\(^9,\(^{21}\) and can be used interchangeably.\(^{22}\) The equilibrium model equation is as follows\(^{23}\)

\[
K_p = f_{OM} \frac{10^{-9} M O A f} {\rho O M_0 \gamma_{OM}}
\]

where \(K_p\) (m\(^3\) air/μg), \(f_{OM}\) (kg/m\(^3\)), \(M\), and \(\gamma\) are the particle–gas partition ratio, fraction of organic matter in aerosols, density of octanol, molar mass, and activity coefficient, respectively. The subscripts \(O\) and \(OM\) represent octanol and organic matter, respectively. Here, we assume \(\rho O = 840\) (kg/m\(^3\)\(^2\))\(^{22}\) \(M_{OA}/M_{OM} = 0.6\)\(^{24}\) \(\gamma_O/\gamma_{OM} = 1\)\(^{22}\) and that \(f_{OM}\) varies in our different environmental scenarios as shown in Table 1.

**New Steady-State Mass Balance Model and the Investigated Cases.** The new steady-state multimedia mass balance model is formulated using fugacity theory.\(^{25}\) It is embedded within a regional contaminant fate model that consists of five compartments: gas phase, fine aerosol particles, coarse aerosol particles, water, and soil (Figure S1). Details of the model parametrization and the equations used to describe transport processes in the atmosphere and from the atmosphere to the surface are shown in Tables S1–S4. Fine and coarse particles are represented with separate compartments that are linked by diffusive chemical exchange to the gas phase compartment, which allows us to study the effect of the different diameters of particles, deposition rates, organic matter contents, and concentrations on the predicted particle–gas concentration ratio.

Instead of assuming equilibrium partitioning of chemicals between the gas and particle phases, the new steady-state mass balance model includes the diffusion process between the gas and aerosol particle compartments. The fugacity rate coefficients (\(D_{GF}\)) of the diffusion process are calculated using the approach described by Cahill and Mackay,\(^{10}\) and have the following form:
where $d_p$ is the diameter of the aerosol particles (m), $B$ is the chemical's molecular diffusivity in air (m$^2$/s), $\lambda$ is the mean free path in air (m), $\alpha$ is the accommodation coefficient, $V_A$ is the volume of bulk air in the modeled region, $Q_F$ is the number concentration of aerosol particles (particles/m$^3$), and $Z_{pa}$ is the fugacity capacity of the gas phase. $Z_{pa} = 1/RT$, where $R$ (m$^3$ Pa/(K mol)) is the gas constant, and $T$ (K) is the temperature.

To study differences in particle–gas concentration ratio in different environmental scenarios, we have adopted seven generic environmental scenarios.\textsuperscript{26} These seven generic scenarios are urban, marine, rural, remote, free troposphere, Polar, and desert and were previously adopted by Götz et al.\textsuperscript{7} to compare equilibrium models based on spLFRs (see Table 1). We selected the urban scenario as a base case, for which more detailed investigations of model sensitivity are presented.

**Physicochemical Properties of PBDEs and the Aerosol Constituents.** Polybrominated diphenyl ethers (PBDEs) have served as model chemicals in this field of research since PBDE congeners have a large range of volatility (log $K_{OA}$ from 8 to 20).\textsuperscript{27,28} The physicochemical properties assumed for the PBDEs and the organic aerosol phase that they are assumed to partition into are given for the base case in Table S1. For simplicity, we assumed the molecular properties and degradation rates of each congener of PBDEs to be the same, with half-lives in the gas phase, water, and soil of 7 632 (h),\textsuperscript{19} 37 992 (h),\textsuperscript{29} and 75 960 (h),\textsuperscript{29} respectively. The degradation half-lives of particle-associated organic chemicals are highly uncertain and are the subject of current experimental investigations. Given the uncertainties, we assumed the degradation half-lives of PBDEs associated with fine and coarse aerosols to be the same as degradation half-lives in the gas phase.\textsuperscript{3} The assumed degradation half-lives of PBDEs in the gas phase and on aerosols are long relative to the half-times for other processes and thus have very little influence on the modeled particle–gas concentration ratio.

**Emissions.** Our model requires the initial phase of the emissions to be specified. Gas-phase emissions represent releases of chemicals via volatilization (as a result of, e.g., combustion) whereas emissions as the aerosol phase could occur, for example, from physical abrasion.\textsuperscript{30–32} The model includes compartments for two size fractions of aerosols with different deposition rates and properties, so we further divided aerosol-bound emissions into emissions as the fine (diameter $< 1 \mu m$) and coarse aerosol (1 $\mu$m < diameter $< 20 \mu$m) phases.\textsuperscript{26} Since our focus is on studying the distribution of chemicals between the gas and aerosol phases rather than absolute concentrations, all model scenarios were run assuming arbitrary generic emission rates of 1 kg of chemical per hour. We assumed 100% of the emissions as the gas phase in many model experiments since the largest deviation from equilibrium occurs in this case, but the sensitivity of the model results to this assumption is demonstrated.

**New Steady-State Particle–Gas Concentration Ratio.** The new steady-state particle–gas concentration ratio of chemicals calculated by our model is\textsuperscript{22}

$$K_p^* = \frac{C_p^{*}/\text{TSP}}{C_G}$$

where $C_p$ (μg/m$^3$ air) and $C_G$ (μg/m$^3$ air) are the chemical concentrations in fine (or coarse) aerosols and gas phase, respectively, and TSP (μg/m$^3$ air) is the total suspended fine (or coarse) aerosol concentration in air.

In field work on organic contaminants such as PBDEs, fine and coarse aerosols are usually not separated. Generally, experiments only report the total particle–gas concentration ratio and/or particle-associated fraction of the chemicals of interest. Our model distinguishes between fine and coarse aerosol fractions, but we also calculate steady-state total particle–gas concentration ratios. The new steady-state total particle–gas concentration ratio is

$$K_p^* = \frac{K_p^{*}/\text{TSP}_F + K_p^{*}/\text{TSP}_C}{\text{TSP}_F + \text{TSP}_C}$$

where the subscripts F and C refer to the fine and coarse fractions of total aerosols, respectively.

**Sensitivity Analysis.** To quantify the response of the ratios of concentrations in gas phase and particle phases predicted by our model to variability and uncertainties in the key input parameters, we performed Monte Carlo analysis\textsuperscript{13} using the commercial software package Oracle Crystal Ball. The investigated parameters and their respective confidence factors are presented in Table S5. Input variables shown in Table S5 were varied log normally according to their prescribed confidence factors. Monte Carlo uncertainty analysis was performed using 15 000 trials, and total particle–gas concentration ratios were monitored. We also calculated contributions of each individual input parameter to total variance in output variables by squaring, summing, and normalizing to 100% of the rank correlation coefficients.

**Measurement Data.** Particle–gas concentration ratios of PBDEs measured in the field were collected from the literature to evaluate the performance of the equilibrium and steady-state mass balance models. For publications that do not report an explicit particle–gas concentration ratio but have separate concentrations of chemicals in gas phase and aerosol particles, we used eq 4 with an assumed value of TSP taken from Table 1 to calculate $K_{OA}^*$. log $K_{OA}$ of the PBDEs are calculated based on the equation log $K_{OA} = A + B/(T + 273.15)$, where $T$ is the temperature in each sampling site, and parameters $A$ and $B$ are from the reference.\textsuperscript{27} For publications that used a different and explicitly specified value of log $K_{OA}$, we still use the above equation to calculate the log $K_{OA}$ to make our data set internally consistent. We selected measurement data in urban (Japan,\textsuperscript{33} Turkey,\textsuperscript{11} and China\textsuperscript{35}), rural (China\textsuperscript{36} and North American Great Lakes\textsuperscript{37}), and Polar (European Arctic,\textsuperscript{38} Alert,\textsuperscript{39} and Toolik Lake\textsuperscript{40}) areas to compare to our model in different generic aerosol scenarios. Also, we selected measurement data in two industrial areas (Izmir\textsuperscript{41} and Italy\textsuperscript{42}) and one of the world’s largest e-waste recycling sites (Guiyu, China\textsuperscript{42}) to evaluate the model in regions with strong local sources.

## RESULTS AND DISCUSSION

**Comparison of Particle–Gas Concentration Ratios in the Equilibrium and Steady-State Mass Balance Models.** Figure 1 illustrates the predicted particle–gas concentration ratios in the new steady-state model as compared with the standard equilibrium approach. log $K_{OA}^*$ calculated with the equilibrium model increases linearly with log $K_{OA}$ (red lines in Figure 1a). At small log $K_{OA}$, the log $K_{OA}^*$ calculated with the new steady-state mass balance model is
very similar to the equilibrium model but plateaus below the equilibrium value at log $K_{OA}$ larger than about 14 (black dotline in Figure 1a). The fine particles dominate the total particle signal due to the majority of the PBDEs binding to fine aerosols, consistent with experimental studies.45−47 The two regimes present in the log $K_P^*$ vs log $K_{OA}$ plot, namely, the regime corresponding to the equilibrium value and the plateau at higher log $K_{OA}$, are determined by the length of the equilibration time scale13,17,18 as compared with the atmospheric residence time of the particulate matter. If the time to reach equilibrium is 10−20 times longer than the time for deposition, the rate of wet and dry deposition of aerosols determines log $K_P^*$, and the particle−gas concentration ratio reaches a nearly constant value independent of the volatility of the species (see Figure S2 and mechanism study in the Supporting Information for further details).

The degree to which log $K_P^*$ deviates from the equilibrium value depends strongly on the assumption of the phase of the emissions (Figure 1b): while the assumption of 100% gas phase emission corresponds to the lower limit of the log $K_P^*$ values (black curve in Figure 1b), assuming all of the emitted material to reside in the particle phase results in log $K_P^*$ that is indistinguishable from the equilibrium case (blue line in Figure 1b). For chemicals with log $K_{OA}$ smaller than 13, the predicted log $K_P^*$ in the new steady-state model is the same with the standard equilibrium approach, regardless of the assumption of the phases of emissions. This result is due to the time scale for chemical exchange between the gas and particle phases being longer than the deposition removal time scale of the sorbed chemicals. However, the predicted log $K_P^*$ of chemicals with log $K_{OA}$ larger than 13 in our model depends strongly on the assumption of the phases of emissions, because the time scale of transfer from the gas phase to the particle phase is longer than the time scale of transfer from the particle phase to gas phase. The case where the emissions are assumed to be 50/50 divided between the gas and particle phases (green curve in Figure 1b) resembles the case with entirely gas-phase emissions. The new steady-state particle−gas concentration ratio of very low-volatility chemicals is thus largely determined by the phase of emissions (see Figure S3 for further information). This sensitivity also suggests the potential of the new steady-state mass balance model to estimate the phase of given emissions by comparing the model output to reliable measurements of the particle−gas concentration ratios.

Figure 1. Particle−gas concentration ratios as a function of log $K_{OA}$ in the urban base case scenario. (a) Comparison of steady-state mass balance models (black lines) and equilibrium (red lines), when 100% are gas phase emissions. log $K_{P^f}$, log $K_{Pc}$, and log $K_{PT}$ represent gas−fine particle, gas−coarse particle, and total particle−gas concentrations ratios, respectively. (b) Sensitivity of the predicted total particle−gas concentration ratios to the assumed phase of emissions. Different colors represent different ratios of emissions as gas, fine, and coarse particle phases (expressed as gas: fine: coarse in the legend).

Figure 2. Comparison of steady-state mass balance (black lines) and equilibrium (red lines) models in six generic aerosol scenarios, when 100% are gas phase emissions in the new steady-state model. (a) Marine; (b) rural; (c) remote; (d) free troposphere; (e) Polar; and (f) desert (see Table 1 for the assumed environmental characteristics).
The predicted steady-state particle–gas concentration ratios behave qualitatively similarly in all the studied environments (Figure 2), showing agreement with the equilibrium case at low log $K_{OA}$ and plateauing to a constant log $K_{P}^{*}$ at higher values of log $K_{OA}$. The exact value of the maximum log $K_{P}^{*}$ varies slightly with the environment, depending on the volume fraction of particles in air, assumed diameter of the particle population, rainfall rate, and deposition velocity (see Table 1), described by the following equations (see mechanism study in the Supporting Information for derivation)

$$K_{PF}^{*} = \frac{12BaH}{10} \left( MTC_{QdF} + S_{P}MTC_{rain} \right) \left( 2r + ad_{PF} \right)d_{PF}$$  

(5a)

$$K_{PC}^{*} = \frac{12BaH}{10} \left( MTC_{QdC} + S_{C}MTC_{rain} \right) \left( 2r + ad_{PC} \right)d_{PC}$$  

(5b)

$$K_{P}^{*} = \frac{K_{PF}^{*}V_{PF} + K_{PC}^{*}V_{PC}}{V_{PF} + V_{PC}}$$  

(5c)

where $H$ is the height of the air compartment, $\rho_{Q}$ the density of the aerosol particles, $MTC_{rain}$ the rain fall rate, $MTC_{QdF}$ the fine aerosol deposition velocity, and $MTC_{QdC}$ the coarse aerosol deposition velocity. $V$, $d$, and $S$ are the volume fraction of particles in air, diameter of the particle population, and rain scavenging ratio of the dominant aerosol population, respectively; the subscripts $P$ and $C$ refer to the fine and coarse particles (see Tables S1–S4). $K_{PF}^{*}$ increases with decreasing aerosol deposition velocity ($MTC_{QdF}$), decreasing rain fall rate ($MTC_{rain}$), decreasing rain scavenging ratio ($S_{P}$), decreasing diameter of particle population ($d_{PF}$), and diffusivity of chemicals in air (B) (eq 5a). This result is understandable in light of $MTC_{QdF}$, $MTC_{rain}$, and $S_{P}$ that have negative relationships with the time scale for chemicals to be removed from the atmosphere by deposition, while $B$ has a negative and $d_{PF}$ a positive relationship with the time scale for chemical exchange between the gas and particle phases.

Among urban, marine, rural, remote, free troposphere, Polar, and desert scenarios, the fine particle diameter and deposition rate of particles are relatively large in the marine case, resulting in the lowest fine particle–gas concentration ratio (log $K_{PF}^{*}$ = 1.22). The lowest rainfall rate in free troposphere leads to the largest fine particle–gas concentration ratio (log $K_{PF}^{*}$ = 2.74). The coarse particle diameter and rainfall rate are relatively large in the remote region, leading to the lowest coarse particle–gas concentration ratio (log $K_{PC}^{*}$ = −2.61).

The log $K_{P}^{*}$ calculated with our steady-state mass balance model in each generic aerosol scenario has a similar dependence on log $K_{OA}$ as the Li–Ma–Yang equation. However, our model allows an analysis of the dependence of log $K_{P}^{*}$ on aerosol properties in different generic scenarios. In addition, the log $K_{P}^{*}$ calculated with our steady-state mass balance model depends strongly on the assumption of the phases of the emissions, while the Li–Ma–Yang equation does not explicitly specify the fraction of the chemical emitted as the gas and aerosol phases.

Sensitivity and Uncertainty Analysis. The predicted steady-state concentration ratios for very low-volatility chemicals (log $K_{OA} = 20$) have a large uncertainty due to the uncertainty and variability of input variables (see Table S5). Figure 3 illustrates this sensitivity of the total particle–gas concentration ratio for the urban base case with 100% gas phase emission. For this case, the mean value of the new steady-state concentration ratio is −0.25 with the corresponding standard deviation of 2.47 (Figure 3a). The main drivers of the variability of the new steady-state concentration ratio are variations in the (effective) accommodation coefficient (as an indicator of, e.g., diffusion limitations within the particle phase), the diameter of the fine particles (as an indicator of the surface area available for vapor uptake), and the gas-phase diffusivity of the chemical investigated—although it should be noted that the confidence intervals for these properties are conservative estimates in terms of the uncertainties. The overall volume concentrations of the fine and coarse particles as well as their removal rates are also important, but to a lesser degree (Figure 3b).

The single-parameter sensitivities of the new steady-state concentration ratios as a function of log $K_{OA}$ for the eight input parameters with the largest contribution to the overall uncertainty are illustrated in Figure 4. These results highlight the need to know the kinetic properties of the chemicals being transported in the context of their uptake to the organic aerosol phase (see also eqs 5a–5c), in particular the potential particle phase diffusion limitations manifested in the effective mass accommodation coefficient. Furthermore, and unsurprisingly, knowing the properties of the aerosol size distribution present in the environment in question is essential. Finally, these results highlight the need for accurate and quantitative constraints on aerosol removal by deposition in various environments. Overall, however, the sensitivity to the chemical, aerosol, and environmental properties is smaller than the importance of knowing the phase of the emissions (Figure 1b).

Comparison of Modeled Particle–Gas Concentration Ratio with Measurements. Comparisons of the predicted steady-state concentration ratios assuming 100% gas-phase emission to observations at six urban, two rural, and three Polar sites are presented in Figure 5. The calculated steady-state concentration ratios agree reasonably well with observations at log $K_{OA}$ values smaller than about 14 but still generally tend to overpredict the particle-bound fraction as compared to the reported observations at the larger log $K_{OA}$ values corresponding to the lower-volatility chemicals. Interestingly, however, the model agrees remarkably well with the observations for the urban site near an e-waste handling plant at Guiyu, China. These results, together with
the model uncertainty and sensitivity demonstrated in Figures 3 and 4, suggest that, to resolve the difference between the modeled log $K_{op}^*$ and the reported observations, some combination of improved description of particulate-phase transport, accurate knowledge on the phase of the emission, together with observations of aerosol size distributions and overall mass loadings would be needed. Besides uncertainties stemming from the model such as the inclusion of particle phase diffusion limitations, also measurement uncertainties can contribute to the discrepancy for the low-volatility chemicals. While detailed discussion of the sampling and analysis methods is outside of the scope of this paper, it is well-known that accurate and simultaneous measurements of gas and particle concentrations of low-volatility chemicals are notoriously challenging over the relevant atmospheric time scales.$^{50-53}$

The sensitivity studies and model evaluation presented in this paper illustrate the value of explicit modeling at the process level for understanding transportation and transformation of chemicals in the environment. Besides the properties of the chemicals, our results highlight the importance of knowing the phase distribution of the PBDEs upon emission (Figure 1b), but also the particle size distributions and loadings on the various environments (Figures 3 and 4), and ideally size-resolved and simultaneous measurement of gas and particle phase concentrations of PBDEs. The latter is undoubtedly difficult, but perhaps achievable through studies utilizing and further developing emerging techniques currently applied in atmospheric aerosol science (e.g., Thornton et al., 2020$^{53}$). The new steady-state mass balance model can also be applied to other chemical groups that have measured or estimated values for chemical properties listed in Table S1. Our new steady-state mass balance model can be incorporated into existing chemical fate and transport models to enable process-based modeling of
long-range transport potential of low-volatility organic chemicals whose log $K_{eq}^*$ is not well-described by equilibrium models. However, based on the model–measurement inter-comparison, further laboratory-based evaluations and calibrations of the standard sampling techniques for low-volatility chemicals are warranted.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c04368.

Additional information on model structure of the new steady-state mass balance model; model parametrization; input confidence factors; comparison of particle–gas concentration ratios in the new steady-state mass balance model and ratio of time scales; the impact of the phases of emissions on steady-state log $K_{eq}^*$ under urban scenario; and mechanism study (PDF).

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**Notes**
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