

Steady-state theory of particle/gas partitioning for SVOCs in the atmosphere and its applications

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Introduction:

Atmospheric transport is a major mechanism of moving semi-volatile organic compounds (SVOCs), including persistent organic pollutants (POPs), from source regions to other remote places, including the Arctic and Antarctic, where these chemicals have never been produced and used. The particle/gas (P/G) partitioning of SVOCs is a very important process that primarily governs their atmospheric fate, since wet and dry depositions and other processes act differently on gaseous and particulate SVOCs, thus affecting the efficiency and scope of their long-range atmospheric transport and fate. Equilibrium theory of P/G partitioning for SVOCs in the atmosphere has been applied for several decades, whereas the steady-state theory of P/G partitioning has been established since 2015¹, which has been applied in many areas in the research for SVOCs. The objectives of this presentation are 1) to introduce both the equilibrium and steady-state P/G partition theories, and 2) to describe the applications of this theory.

Materials and Methods:

1. Equilibrium and steady-state P/G partition theories

The P/G *partition quotient* K_P ($\text{m}^3/\mu\text{g}$) is defined as

$$K_P(\text{m}^3/\mu\text{g}) = C_P(\text{pg}/\text{m}^3\text{air})/TSP(\mu\text{g}/\text{m}^3\text{air})/C_G(\text{pg}/\text{m}^3\text{air}) \quad (1)$$

where C_G and C_P are the concentrations of SVOCs in atmospheric gas and particle phases, respectively, and TSP is the concentration of total suspended particles in air. The above definition is constrained neither to equilibrium nor to steady state. At equilibrium, K_P in Eq. (1) becomes the partition coefficient at equilibrium (K_{PE}) and at steady state, K_P becomes the partition coefficient at steady state (K_{PS}).

K_P of a SVOC in environment can be estimated from other physicochemical properties of the substance.

There have been many equilibrium models developed, among which the most widely used one is the Harner-Bidleman model

$$\log K_{PE} = \log K_{OA} + \log f_{OM} - 11.91 \quad (2)$$

where f_{OM} is organic matter content of the particles. The conclusions from the equilibrium theory are

- (1) VOCs in the atmosphere are in equilibrium between gas- and particle-phases;
- (2) The relationship between $\log K_{PE}$ and $\log K_{OA}$ ($\log P_L$, P_L is subcooled liquid vapor pressure) is linear with its slope equal to 1 (-1); and
- (3) The deviations of slopes from 1 ($\log K_{PE} - \log K_{OA}$) or -1 ($\log K_{PE} - \log P_L$) are caused by all kinds of artifacts.

A steady-state P/G model was published in 2015 by Li and co-workers¹, given by

$$\log K_{PS} = \log K_{PE} + \log \alpha \quad \log K_{P-LMY} = \log K_{P-EQ} + \log \alpha \quad (3)$$

In the above equation, the *equilibrium term*, $\log K_{PE}$, is given by Eq. (2), and $\log \alpha$ is the *non-equilibrium term*, given by

$$\log \alpha = -\log(1 + 4.18 \times 10^{-11} f_{OM} K_{OA}) \quad (4)$$

Results:

1. Steady-state P/G partition theories

The conclusions from the steady-state theory are (only K_{OA} is discussed here, but the conclusions derived here are also valid for P_L).

- (1) VOCs in the atmosphere are in steady-state between gas- and particle-phases, and equilibrium is an approximation when $\log \alpha$ can be neglected;
- (2) the relationship between $\log K_{PS}$ and $\log K_{OA}$ for SVOCs is not linear as indicated by Eq. (3) but can be treat as a linear relationship for monitoring data with its slope of $\log K_{PE} - \log K_{OA}$ from 0 to 1; ^{2,3}
- (3) the deviations of slopes from 1 for $\log K_{PE} - \log K_{OA}$ are not mainly caused by artifacts, but depend on their physicochemical property K_{OA} ; and
- (4) according to the above equations, two threshold values of $\log K_{OA}$ may be identified. As shown in **Fig. 1**, the first threshold value of $\log K_{OA}$ (=11.4) divides the whole range of $\log K_{OA}$ into *equilibrium* (EQ) and *nonequilibrium* (NE) domains. The second threshold (=12.5) indicates the start of the *maximum*

partition (MP) domain, in which the values of $\log K_{PS}$ reach a maximum value of $\log K_{PSM}$ (-1.53), which is independent of K_{OA} .

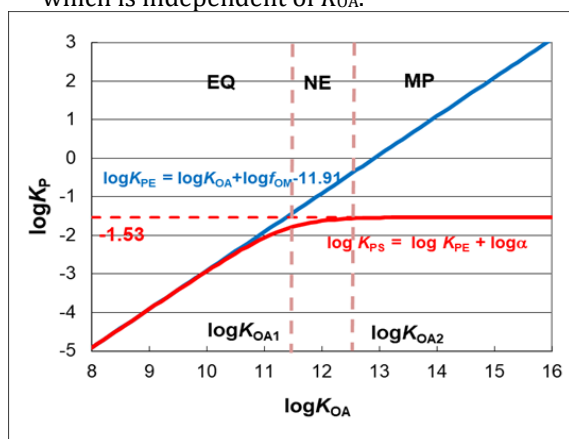


Fig. 1. Variation of $\log K_{PE}$ and $\log K_{PS}$ as functions of $\log K_{OA}$. Two threshold values of $\log K_{OA}$ ($\log K_{OA1}$ and $\log K_{OA2}$) are also shown, which divide the $\log K_{OA}$ into three domains: the equilibrium (EQ), the non-equilibrium (NE), and the maximum partition (MP) domains.¹

2. Application of the steady-state P/G partition theory

(1) Projection of the values of $\log K_P$ for SVCOs

The eight models used to predict $\log K_P$ comprise three groups: five equilibrium-based models, two empirical models, and one steady-state-based model.⁴

A comparison of the predicted results from the eight models with monitoring data published by several research groups worldwide leads to the following conclusions: 1) In the EQ domain, all 8 models perform well in predicting the P/G partitioning of polybrominated diphenyl ethers (PBDEs) in the atmosphere, and 2) in the EQ and MP domains, the MP domain in particular, the Li-Ma-Yang model¹ shows the best performance with highest conformity to the measurements for selected PBDEs ($94.4 \pm 1.6\%$ data points within ± 1 log unit). Overall, the Li-Ma-Yang model appears to capture the most important factors that affect the partitioning of PBDEs between gaseous and particulate phases in the atmosphere.⁴

(2) Long-rang transport of BDE-209

BDE-209 has been considered as a nonvolatile BFR. According to the P/G equilibrium theory, BDE-209 is sorbed almost entirely to the particles in the atmosphere based on its very high octanol-air partition coefficient or low vapor pressure. This point of view has a profound influence on projections of the environmental fate (e.g., LRAT) of this compound. As a particulate, it has been suggested that BDE-209 would not distribute widely through the atmosphere despite intense use in the industrialized world, and would be difficult to transport to the Arctic via LRAT. Monitoring data, however, show another story. BDE-209 has been identified in air at various sites in North America, which included some sites far away from populated and industrial centers and in Arctic air. These observations suggest that BDE-209 widely distributes through the atmosphere and enters the Arctic through LRAT. This puzzling phenomenon was explained by the proposal that LRAT must occur for BDE-209 by the movement of particles, not air, and this particle transport could travel great distances, especially during the Arctic haze season.

According to the steady-state theory, particulate transport is not actually required for BDE-209 to enter the Arctic. Even though it has high $\log K_{OA}$ properties, a significant proportion of BDE-209 remains in the gas phase, especially at low TSP concentrations (**Fig. 2**). From a global perspective, gaseous BDE-209 is abundant in air (87.1% when $TSP = 5 \mu\text{g}\cdot\text{m}^{-3}$ to 14.5% when $TSP = 200 \mu\text{g}\cdot\text{m}^{-3}$ from our estimation), and is the dominant congener presented in gas phase in many populated areas. Similar to other SVOCs, gas phase BDE-209 is subject to LRAT with the result that there is a general migration from warmer to colder areas leading to eventual accumulation in Polar Regions. Furthermore, without further evaluation, it is risky to assume that other toxic chemicals with high K_{OAs} are entirely constrained to the atmospheric particulate phase.⁵

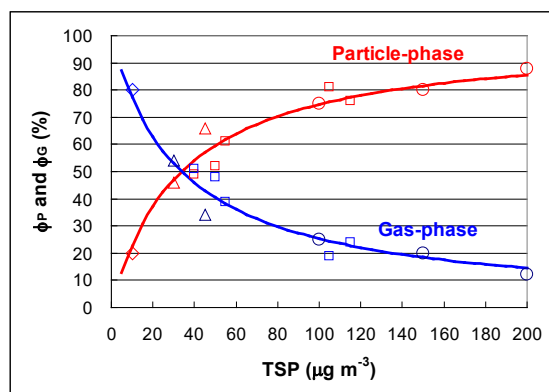


Fig. 2. The gas and particle phase fractions of BDE-209 in air as a function of *TSP*. The solid lines are values predicted by Equation (2), and the open symbols are monitoring data. Diamonds: Arctic (average for 6-year data); Triangles: Izmir Bay and Izmir City; Squares: Zurich; Circles: China. Detailed information see Li et al.⁵

(3) Size-resolved gas-particle partitioning quotients

P/G partition quotients of SVOCs for bulk air have been widely discussed in experimental and theoretical contexts, but research on size-resolved P/G partition quotients (K_{Pi}) are scarce and limited in scope. To investigate P/G partition behavior of PBDEs for size-segregated particles in the atmosphere, 396 individual size-segregated particulate samples and 108 pairs of concurrent gaseous and bulk particulate samples were collected in Harbin, China. The levels of PBDEs⁶ and eight NBFR congeners⁷ were measured, and their values of $\log K_{Pi}$ were calculated. Based on these data, size-resolved gas-particle partitioning quotients were derived.

$$\log K_{Pi} = \log K_{Ps} + \Delta \log K_{Pi} \quad (5)$$

where $\Delta \log K_{Pi}$ is the deviation of $\log K_{Pi}$ from the bulk $\log K_{Ps}$ as a function of $\log f_{OMi}$ (the organic matter contents of size-segregated particles), given by

$$\Delta \log K_{Pi} = 0.52 \log f_{OMi} + 0.56 \quad (6a)$$

or as a function of $\log d_i$, (the diameter of the particles) given by

$$\Delta \log K_{Pi} = 0.35 \log d_i + 0.41 \quad (6b)$$

This equation can well predict K_{Pi} with knowledge of the bulk partition quotient (K_{Ps}), ambient temperature, and f_{OMi} or d_i . Eqs. (5) – (6) can predict $\log K_{Pi}$ well, and results of which are in a good agreement with monitoring data in Harbin and other published data collected in Shanghai and Guangzhou of China and Thessaloniki of Greece (detail information see Reference^{6,7}).

(4) Treatment of P/G partitioning in fugacity models

Fugacity models can be run under steady- and unsteady-state conditions, and can be categorized as level I, II, III, or IV reflecting an increasing complexity in the mass balance equations. The level III fugacity models have been more widely used as they are more realistic than levels I and II models and simpler than level IV models. Currently used Level III fugacity models consider the entire system as a steady state. However, within that steady state, chemicals are assumed to be in equilibrium between gaseous and particulate phases in the bulk air compartment, and between liquid and suspended particulate matters (SPMs) in the bulk water compartment. This treatment in the models raises two questions. (1) What are real states for chemicals partitioning between gaseous and particulate phases in the atmosphere and between liquid and SPMs in aquatic systems? (2) If steady state between gas and particles or between liquid and SPMs differs from equilibrium, then can level III model results be considered a true representation of steady state for the entire system? Answering these two questions is crucial to determining whether or not the currently used level III models actually reflect the true conditions of a steady state system.

This issue has been discussed by Li et al.⁸⁻¹⁰, who developed two level III fugacity models for a six-compartment environmental system (air, aerosols, liquid, SPMs, soil, sediments) as a “unit world” for PBDEs. The first model assumed equilibrium between air and aerosols in the atmosphere and between liquid and SPMs in the water, thus requiring only four fugacities (**E4F Model**); the second model removed all equilibrium conditions, thus requiring six fugacities (**S6F Model**). It was found that PBDEs are in both steady state and equilibrium between liquid and SPMs, whereas chemicals are in steady state, not equilibrium, between air and aerosols, or the fugacities of air and aerosols are not equal. Later, a method was developed wherein the fugacity of a chemical in the particle-phase is set equal to that in the gaseous phase (a pseudo equilibrium) but still maintains steady state of the chemical between air and aerosols in the atmosphere. Using this approach, a condition of steady state between air and aerosols is developed and applied in a level III six-compartment six-fugacity model, which becomes a steady-state level III six-compartment four-fugacity model (**S4F Model**). This model has been successfully applied to real-world monitoring data.

The crucial question is, which model among these three should be selected for modeling the transport and transfer of chemicals in multimedia? Here, we propose three criteria to inform that selection: (1) The model must produce an internally consistent system in which a SVOC is mass balanced in each compartment;

(2) the SVOC in air predicted by the model cannot attain 100% particle phase; and (3) the results should be verified by comparison to monitoring data. The comparison among the three models, the E4F, S6F, and S4F models, is listed in **Table 1**. Presently, only the **S4F Model** meets all the three criteria, and thus is suitable to use as a Level-III model for transport and transfer of SVOCs in multimedia.

Table 1. The differences among the three models¹⁰.

	E4F Model	S6F Model	S4F Model
Produces an internally consistent system?	No. The system is internally inconsistent with chemicals not in steady state for air and aerosols.	Yes only for all gaseous emission. The system becomes internally inconsistent when particle fraction in emission increases.	Yes. The system is internally consistent with chemicals in steady state in all six compartments.
Predicts chemical in 100% particle phase?	Yes, when $\log K_{OA} > 14$	Yes, when emission has particle-phase portion	Never
Matches well the air monitoring data?	No	Yes	Yes

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