http://www.atmos-chem-phys.net/15/1669/2015/
doi:10.5194/acp-15-1669-2015-supplement
© Author(s) 2015. CC Attribution 3.0 License.

Supplement of

Prediction of gas/particle partitioning of polybrominated diphenyl ethers (PBDEs) in global air: A theoretical study

Y.-F. Li et al.

Correspondence to: Y.-F. Li (ijrc_pts_paper@yahoo.com)
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>At a Glance</td>
<td>1</td>
</tr>
<tr>
<td>Supplementary Methods</td>
<td>3</td>
</tr>
<tr>
<td>S1. Fugacities and fugacity capacities</td>
<td>3</td>
</tr>
<tr>
<td>S2. Gas-particle partition equations at equilibrium state</td>
<td>3</td>
</tr>
<tr>
<td>Supplementary Figures</td>
<td>5</td>
</tr>
<tr>
<td>Supplementary Table</td>
<td>26</td>
</tr>
<tr>
<td>References</td>
<td>27</td>
</tr>
</tbody>
</table>
At a Glance

Log K

Guangzhou (+8.0 – +38.0°C)

log K OA

log K OA1 log K OA2

-1.53

log K PM

log K PE

log K PS

log K PR

Harbin (-22.0 – +28.0°C)

log K OA

log K OA1 log K OA2

(-22.0 – +28.0°C)

log K PM

log K PE

log K PS

log K PR

Alert, Canada (-50 – 10°C)

log K PM

log K PE

log K PS

log K PR

EQ Domain

NE Domain

MP Domain

log K PS = log K PE + log a (-30 – 30°C)

log K OA1 log K OA2

(0 – 50°C)

log K OA

log K PE & log K PS

log K PE = log K OA + log f... (-50 – 0°C)
G/P Partition coefficients of PBDEs in global air:
The top middle panel depicts the G/P partition coefficients of PBDEs as functions of log$K_{OA}$ at environmental ambient temperature ranging from -50 to +50°C, calculated by two equations. First one is G/P partition equation at equilibrium (Eq. (3)), presented by the dark blue straight line, and the second one is our newly developed G/P partition equation at steady state (Eq. (31)), presented by the red curve in the figure. Two threshold values of log$K_{OA}$ ($logK_{OA1}$ and $logK_{OA2}$, represented by two vertical pink dashed lines) divide the space of log$K_{OA}$ into three domains: the equilibrium (EQ) domain, the nonequilibrium (NE) domain, and the maximum partition (MP) domain. Obvious difference in G/P partition coefficients between log$K_{PS}$ and log$K_{PE}$ can be observed when log$K_{OA} \geq logK_{OA1}$, and becomes larger when the values of log$K_{OA}$ increases. One appealing result is that, our new equation leads to a conclusion that the G/P partition coefficients reach a maximum value of log$K_{PS}$ ($logK_{PSM} = -1.53$, represented by the horizontal light blue line) when log$K_{OA} \geq logK_{OA2}$ maximum partition. The three squares in the panel designate the log$K_{P}$-log$K_{OA}$ graphs with three different temperature zones: 0 – +50°C, -30 – +30°C, and -50 – 0°C, representing the tropical and subtropical climate zones, warm temperate climate zone, and boreal and tundra climate zones, respectively. Monitoring data (log$K_{PM}$), their regression data (log$K_{PR}$), and the predicted results log$K_{PS}$ and log$K_{PE}$ in Guangzhou, China (Yang et al. 2013), within the subtropical climate zone, shown in the top-left panel, and those in Harbin, China (Yang et al. 2013), within the warm temperate climate zone, shown in the bottom panel indicating that the curve of our new equation (log$K_{PS}$) is closer to the line of log$K_{PR}$ than log$K_{PE}$. The top-right panel gives the predicted results log$K_{PSM}$ and log$K_{PE}$ of BDE-209 in Alert, Canada, which is an Arctic sampling site in tundra climate zone. The monitoring data of BDE-209 (log$K_{PM}$) for three years from 2007 to 2009 by Environment Canada (NCP 2013), denoted by the diamond, square, and triangle marks, match our predicted data (log$K_{PSM} = -1.53$) extremely well (assuming $TSP = 10 \, \mu g \, m^{-3}$). All these indicate that the steady equation (log$K_{PS}$) is superior than the equilibrium equation (log$K_{PE}$) in G/P prediction of partitioning behavior for PBDEs in air.
S1. Fugacities and fugacity capacities (Mackay 2001)

The fugacity \( f \) is a measure of a SVOC (a PBDE congener, for example) escaping tendency from a particular medium; and SVOCs tend to move from medium where it has higher fugacity to medium where it has lower fugacity. Fugacity is proportional to concentration in the medium and given by

\[
f_I = \frac{C_I}{Z_I}
\]  

where the subscript “I” indicates the medium I, and \( C_I \) is the concentration (in \( \text{mol/m}^3 \) of medium I) of a SVOC. The fugacity capacity \( Z_I \) (\( Z \)-value, \( \text{mol m}^{-3} \text{Pa}^{-1} \)) describes the potential of a medium I to retain a SVOC.

The \( Z \)-value for air is given by

\[
Z_G = \frac{1}{RT}
\]  

where \( R \) is the gas constant (8.314 \( \text{Pa m}^3 \text{mol}^{-1} \text{K}^{-1} \)), and \( T \) is air temperature in K.

The fugacity capacity for particles is given by

\[
Z_P = K_{PG} Z_G
\]  

\[
Z_P = \frac{K_{PG} Z_G}{RT}
\]

where \( K_{PG} \) is dimensionless partition coefficient of a SVOC between gas- and particle-phases at equilibrium.

S2. Gas-particle partition equations at equilibrium state

At equilibrium, the fugacities of a chemical in gas-phase \( (f_G) \) and in particle-phase \( (f_P) \) are equal,

\[
f_G = f_P
\]  

where,

\[
f_G = \frac{C_G}{Z_G}
\]  

\[
f_P = \frac{C'_P}{Z_P}
\]

In the above equations, \( Z_G \) and \( Z_P \) are given by Eqs. (S2) and (S4), respectively, and \( C_G \) is the concentration of the comical in gas phase (\( \text{mol} \cdot \text{m}^{-3} \) of air), while \( C'_P \) is concentration in particle phase (\( \text{mol} \cdot \text{m}^{-3} \) of particles). Equations (S7) gives the relationship between \( C_G \) and \( C'_P \) at equilibrium.
\[ \frac{C'}{P} / C_G = Z_P / Z_G = K_{PG} \quad \text{(at equilibrium)} \quad \text{(S7)} \]

The G/P partition coefficient of SVOCs has another more commonly used form, \( K_{PE} \), defined as

\[ K_{PE} = \frac{(C_P/TSP)}{C_G} \quad \text{(at equilibrium)} \quad \text{(S8)} \]

where \( C_G \) and \( C_P \) are concentration of SVOCs in gas- and particle-phases (both in mol·m\(^{-3}\) of air), respectively, \textit{at equilibrium}, and \( TSP \) is the concentration of total suspended particle in air (\( \mug \cdot m^{-3} \)). Thus \( K_{PE} \) has a unit of \( m^3 \mug^{-1} \), the reciprocal unit of \( TSP \). Harner and Bidleman (1998) derived the following equation to calculate \( K_{PE} \),

\[ \log K_{PE} = \log K_{OA} + \log f_{OM} - 11.91 \quad \text{(S9)} \]

where \( f_{OM} \) is organic matter content of the particles.

The relationship between \( K_{PG} \) and \( K_{PE} \) is given by

\[ K_{PG} = 10^9 \rho (\text{kg} \cdot \text{m}^{-3}) K_{PE} (\text{m}^3 \mug) \quad \text{(S10)} \]

where \( \rho \) is density of particles in the unit of kg·m\(^{-3}\). The relationship between \( C'_{P} \) and \( C_{P} \) is given by

\[ C'_{P} (\text{pg} \cdot \text{m}^{-3} \text{ of particle}) = 10^9 \rho (\text{kg} \cdot \text{m}^{-3}) C_{P} (\text{pg} \cdot \text{m}^{-3} \text{ of air}) / TSP (\mug \cdot \text{m}^{-3}) \quad \text{(S11)} \]
**Figure S1**: Particles are treated as a “particle film”.

Particle film with thickness $A_p = 0.1 \mu m$ and height $h = 1000 m$.
Figure S2: Variation of loga as functions of (A) log\(K_{OA}\) and (B) temperature for 10 PBDE congeners (C=5).
**Figure S3**: The maximum particle phase fraction as a function of TSP. While $\log K_{PSM} = -1.53$ is a constant, $\phi_{PSM}$ is a function of TSP.
Figure S4: Variations of $\log K_{PS}$, $\log K_{PE}$, and $\log K_{PR}$ as functions of $\log K_{OA}$ for 15 sampling sites. Red lines are for $\log K_{PS}$ from Equation (31) under steady state; blue lines for $\log K_{PE}$ from Equation (3) under equilibrium state. ($C = 5$ at all sampling sites but Waliguan, where $C = 50$) (Data for $\log K_{PR}$: Yang et al., 2013).
**Figure S5:** Comparisons among the predicted $K_{PS}$ values using Equation (31), predicted $K_{PE}$ values using Equation (3), and the regression $K_{PR}$ values using Equation (2) as functions of $\log K_{OA}$ for the 10 PBDE congeners (Data for $\log K_{PR}$: Yang et al., 2013).
Figure S6: The regression curves (log$K_{PR}$) for the 10 PBDE congeners from Figure S5 along with the curves of log$K_{PE}$ and log$K_{PS}$, indicating that these 10 lines of log$K_{PR}$ change their slopes $m_O$ along the curve of log$K_{PS}$, not the straight line of log$K_{PE}$. 
**Figure S7**: Variations of log$K_{PS}$, log$K_{PE}$, and log$K_{PR}$ as functions of temperature for 10 PBDE congeners. Red lines are for log$K_{PS}$ from Equation (31) under steady state; blue lines for log$K_{PE}$ from Equation (3) under equilibrium state; and green lines are for log$K_{PR}$ from Equation (2). These figures indicate that, the curve of log$K_{PS}$ matches the line of log$K_{PR}$ for each PBDE congener, the high brominated congeners in particular, dramatically well (Data for log$K_{PR}$ were from Yang et al., 2013).
**Figure S8:** The modeled values of log$K_{PS}$ for typical 5 PBDE congeners as functions of temperature. Along with decrease of temperature, the values of log$K_{PS}$ for each PBDE congener increases to the maximum partition value (-1.53). The second threshold temperatures ($t_{TH2}$), are also show.
Figure S9: The range of log\(K_{OA}\) for 10 PBDE congeners (vertical bars) in Guangzhou air with a temperature range from +8 to +38 °C and the 2 light blue horizontal dashed lines give the 2 threshold values of log\(K_{OA1}\) and log\(K_{OA2}\), which divide the space of log\(K_{OA}\) (the left axis) into three domains: the equilibrium (EQ), the nonequilibrium (NE), and the maximum partition (MP) domains. The minimum and the maximum temperatures (+8°C and +38°C) in Guangzhou (the red dashed lines) and the two threshold temperatures, \(t_{TH1}\) (the red diamonds) and \(t_{TH2}\) (the red squares) for the 10 PBDE congeners (the right axis) are also presented in the figure. The lines of \(t_{TH1}\) and \(t_{TH2}\) also divide the temperature space (the right axis) into the same 3 domains. The PBDE congeners in Guangzhou air can be segregated into 3 groups; BDE-17, -28, and -47 as equilibrium EQ-group, BDE-66, -99, and -100 as semiequilibrium SE-group, and the others as nonequilibrium NE-group.
Figure S10. The log\(K_P\) - log\(K_{OA}\) diagram for PBDEs in Guangzhou air. The range of log\(K_{OA}\) for each group and their corresponding log\(K_P\) - log\(K_{OA}\) diagram are also shown. The log\(K_P\) - log\(K_{OA}\) diagram for the EQ Group, boned by 2 purple dashed lines, is mainly in the EQ domain; the log\(K_P\) - log\(K_{OA}\) diagram for the SE Group, contained by 2 green dashed lines, is mainly in the NE domain; and the log\(K_P\) - log\(K_{OA}\) diagram for the NE Group, formed by the 2 blue dashed lines, is mainly in the NE and MP domains.
Figure S11: Variation of log$K_{PE}$, log$K_{PS}$, log$K_{PR}$, and log$K_{PM}$ as functions of log$K_{OA}$ at (A) an e-waste site and (B) a rural site. Two threshold values of log$K_{OA}$ are also shown. (Monitoring data were from Tian et al. 2011).
**Figure S12**: Variation of particle fractions as functions of log\(K_{OA}\) for 7 PBDE congeners (BDE-28, -47, -99, -100, -153, -154 and -209) at four sites (1 suburban, 2 urban, and 1 industrial) in Izmir, Turkey in summer and winter in 2004-2005 with a temperature range between 1.8°C and 22.4°C. The monitoring data are from (Cetin and Odabasi, 2007). The four different colors design 4 different site types. The solid lines are for \(\phi_{PS}\) and the dashed lines for \(\phi_{PE}\). Two threshold values of log\(K_{OA}\) and the maximum values of particle fractions \(\phi_{PSM}\) are also shown. The modeled particle fractions \(\phi_{PS}\) and \(\phi_{PE}\) are compared with the monitoring data. Different from the figure by (Cetin and Odabasi, 2007), there are four lines of \(\phi_{PE}\) in this figure caused by different values of TSP. It is obvious that the results of our steady model (\(\phi_{PS}\)) can make a better prediction on the particle fractions than equilibrium model (\(\phi_{PE}\)). It is noticed that although the maximum values of log\(K_{PSM}\) are same at the 4 sites, all equal to -1.53, the maximum values of \(\phi_{PSM}\) are different due to different concentration of TSP for the 4 sampling sites. The concentration of TSP in the four sites were (in \(\mu g/m^3\)), suburban: 50.5; urban-1: 114; urban-2: 53.5; and industrial: 99.5. The value of 0.55 was used for \(f_{OM}\) at the four sites. It is interesting to note that the best agreement was observed for BDE-209. The monitoring data of PBDEs were corrected to 25°C by Cetin and Odabasi, (2007).
Figure S13: Variation of log\(K_{PE}\), log\(K_{PS}\), and log\(K_{PM}\) as functions of log\(K_{OA}\) for PBDEs in atmosphere of Kyoto, Japan, measured in August 2000, January and September 2001 (The monitoring data are from Hayakawa et al. (2004)). The two threshold values of log\(K_{OA}\) are also shown.
**Figure S14:** Partition coefficients (A) and particle fraction (B) of 5 PBDE congeners (BDE-47, -99, -100, -153, and -154) in air of the Great Lakes from Strandberg et al. (2001) along with predicted data using Eqs. (3) and (41) for equilibrium and Eqs. (31) and (41) for steady state at 20°C as functions of log$K_{OA}$. The values of log$K_{OA}$ for the 5 PBDE congeners were calculated by using Eq. (7) with $t=20°C$. The typical values of $f_{OM} = 0.2$ and $TSP = 25 \mu g/ m^3$ suggested by Harner and Shoeib (2002) were used for calculation.
**Figure S15:** The results of log\(K_{\text{PSM}}\) and log\(K_{\text{PE}}\) of BDE-209 at an Arctic sampling site, Alert, Canada as functions of temperature. The monitoring data of BDE-209 (log\(K_{\text{PM}}\)) for three years from 2007, 2008, and 2009 by Environment Canada (NCP 2013), denoted by the diamond, square, and triangle marks, respectively, matched our predicted data (log\(K_{\text{PSM}} = -1.53\)) well. (A) \(TSP = 5 \mu g \text{ m}^{-3}\), (B) \(TSP = 2 \mu g \text{ m}^{-3}\). In order to calculate log\(K_{\text{PE}}\) for BDE-209, we used the value of 14.98 at 25 °C by Cetin and Odabasi (2007), and assumed that the variation of log\(K_{\text{OA}}\) for BDE-209 is the same as BDE-183.
Figure S16: The values of log\(K_{PS}\), log\(K_{PE}\), and log\(K_{PR}\) as functions of log\(K_{OA}\). The two threshold values of log\(K_{OA}\) are also shown. It is clearly shown that the data of log\(K_{PS}\) (the red line) matched the data of both log\(K_{PM}\) (the blue diamonds) and log\(K_{PR}\) (the green line) better than the equation of log\(K_{PE}\) (the blue line), especially for those congeners in the nonequilibrium domain with log\(K_{OA}\) > log\(K_{OA1}\). The monitoring data are from Möller et al (2011).
**Figure S17:** (A) Partition coefficients of 11 PBDE congeners (BDE-17, -28, -66, -77, -99, -100, -126, -153, -154, -156, and -183) at 25 °C and 0 °C calculated using Eq. (3) for equilibrium and Eq. (31) for steady state (Assuming $f_{OM} = 0.2$). (B) Particle fraction of the 11 PBDE congeners at 25 °C and 0 °C calculated using Eq. (41) from the data shown in (A) (Assuming $TSP = 25$ μg/m$^3$). The source for the results under equilibrium: Harner and Shoeb (2002). The values of $\log K_{OA}$ for the 11 PBDE congeners were calculated by using Eq. (7).
Figure S18: Sampling site Waliguan. Our air sampler was installed on the top of the building (Photo was taken by Yi-Fan Li).
**Supplementary Tables**

**Table S1:** Parameters $A$ and $B$ for PBDEs, used to calculate $\log K_{OA}$ ($\log K_{OA} = A + B/(t+273.15)$) (Harner and Shoeib, 2002).

<table>
<thead>
<tr>
<th>PBDE Congener</th>
<th>$A$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-17</td>
<td>-3.45</td>
<td>3803</td>
</tr>
<tr>
<td>BDE-28</td>
<td>-3.54</td>
<td>3889</td>
</tr>
<tr>
<td>BDE-47</td>
<td>-6.47</td>
<td>5068</td>
</tr>
<tr>
<td>BDE-66</td>
<td>-7.88</td>
<td>5576</td>
</tr>
<tr>
<td>BDE-77</td>
<td>-5.69</td>
<td>4936</td>
</tr>
<tr>
<td>BDE-85</td>
<td>-6.22</td>
<td>5331</td>
</tr>
<tr>
<td>BDE-99</td>
<td>-4.64</td>
<td>4757</td>
</tr>
<tr>
<td>BDE-100</td>
<td>-7.18</td>
<td>5459</td>
</tr>
<tr>
<td>BDE-126</td>
<td>-8.41</td>
<td>6077</td>
</tr>
<tr>
<td>BDE-153</td>
<td>-5.39</td>
<td>5131</td>
</tr>
<tr>
<td>BDE-154</td>
<td>-4.62</td>
<td>4931</td>
</tr>
<tr>
<td>BDE-156</td>
<td>-5.8</td>
<td>5298</td>
</tr>
<tr>
<td>BDE-183</td>
<td>-3.71</td>
<td>4672</td>
</tr>
</tbody>
</table>
References


