

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

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4 Yi-Fan Li^{1,2,3}, Wan-Li Ma¹, Meng Yang²

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6 ¹International Joint Research Center for Persistent Toxic Substances (IJRC-PTS), State Key
7 Laboratory of Urban Water Resource and Environment/School of Municipal and
8 Environmental Engineering, Harbin Institute of Technology, Harbin 150090, P. R. China

9 ²IJRC-PTS, Dalian Maritime University, Dalian, 116026, P. R. China

10 ³IJRC-PTS-NA, Toronto, Ontario, M2N 6X9, Canada

11

12 Correspondence and requests for materials should be addressed to YFL (email:
13 ijrc_pts_paper@yahoo.com)

14 **Abstract**

15 Gas/particle (G/P) partitioning for semivolatile organic compounds (SVOCs) is an
16 important process that primarily governs their atmospheric fate, long-range atmospheric
17 transport, and their routes to enter human body. All previous studies on this issue have
18 hypothetically based on equilibrium condition, the results of which do not predict results
19 from monitoring studies well in most cases. In this study, a *steady-state* model instead of an
20 equilibrium-state model for the investigation of the G/P partitioning behavior for
21 polybrominated diphenyl ethers (PBDEs) was established, and an equation for calculating the
22 partition coefficients under *steady state* (K_{PS}) for PBDEs ($\log K_{PS} = \log K_{PE} + \log a$) was
23 developed, in which an equilibrium term ($\log K_{PE} = \log K_{OA} + \log f_{OM} - 11.91$, where f_{OM} is
24 organic matter content of the particles) and a nonequilibrium term ($\log a$, caused by dry and
25 wet depositions of particles), both being functions of $\log K_{OA}$ (octanol-air partition coefficient),
26 are included. It was found that the equilibrium is a special case of *steady state* when the
27 nonequilibrium term equals to zero. A criterion to classify the equilibrium and
28 nonequilibrium status for PBDEs was also established using two threshold values of $\log K_{OA}$,
29 $\log K_{OA1}$ and $\log K_{OA2}$, which divide the range of $\log K_{OA}$ into 3 domains: equilibrium,
30 nonequilibrium, and maximum partition domain; and accordingly, two threshold values of
31 temperature t , t_{TH1} when $\log K_{OA} = \log K_{OA1}$ and t_{TH2} when $\log K_{OA} = \log K_{OA2}$, were identified,
32 which divide the range of temperature also into the same 3 domains for each PBDE congener.
33 We predicted the existence of the maximum partition domain (the values of $\log K_{PS}$ reach a
34 maximum constant of -1.53) that every PBDE congener can reach when $\log K_{OA} \geq \log K_{OA2}$, or
35 $t \leq t_{TH2}$. The novel equation developed in this study was applied to predict the G/P partition
36 coefficients of PBDEs for our China-SAMP-II program in China and other monitoring
37 programs worldwide, including Asia, Europe, North America, and the Arctic, and the results
38 matched well with all the monitoring data, except those obtained at e-waste sites due to the

39 unpredictable PBDE emissions at these sites. This study provided evidence that, the newly
40 developed *steady-state*-based equation is superior to the equilibrium-state-based equation that
41 has been used in describing the G/P partitioning behavior in decades. We suggest that, the
42 investigation on G/P partitioning behavior for PBDEs should be based on *steady state*, not
43 equilibrium state, and equilibrium is just a special case of *steady state* when nonequilibrium
44 factors can be ignored. We also believe that our new equation provides a useful tool for
45 environmental scientists in both monitoring and modeling research on G/P partitioning for
46 PBDEs and can be extended to predict G/P partitioning behavior for other SVOCs as well.

47

48

49 **1 Introduction**

50 Atmospheric transport is a major mechanism to move semivolatile organic
51 compounds (SVOCs), including persistent organic pollutants (POPs), from
52 source regions to other remote places, including Arctic and Antarctic, where these
53 chemicals have never been produced and used (Barrie et al. 1992; Macdonald et al.
54 2000; Li et al.1998; Li and Bidleman, 2003; Eckhardt and Manø, 2007). The gas/particle
55 (also called aerosol) (G/P) partitioning for SVOCs is a very important process that
56 primarily governs their atmospheric fate (Lohmann et al., 2000), since wet and dry
57 depositions and other processes act differently on gaseous and particulate SVOCs, thus
58 affecting the efficiency and scope of their long-range atmospheric transport and fate
59 (Bidleman, 1988). In addition, SVOCs are an important class of indoor pollutants that are
60 of great health concern to humans (Weschler and Nazaroff, 2008). The gaseous and
61 particulate SVOCs have different routes to enter human body, and therefore the G/P
62 partitioning for SVOCs has a significant influence on human exposure (Weschler, 2003).

63 The G/P partitioning behavior of SVOCs, K_P , is commonly defined as (Yamasaki et al.
64 1982, Pankow 1991, Pankow and Bidleman 1991)

$$65 \quad K_P = (C_P/TSP)/C_G \quad (1)$$

66 where C_G and C_P are concentrations of SVOCs in gas- and particle-phases (both in $\text{pg}\cdot\text{m}^{-3}$ of
67 air), respectively, and TSP is the concentration of total suspended particle in air ($\mu\text{g}\cdot\text{m}^{-3}$).
68 Thus K_P has a unit of $\text{m}^3\cdot\mu\text{g}^{-1}$. In this study, the term of *partition quotient* instead of
69 *partition coefficient*, is used for K_P , because *partition coefficient* is used for equilibrium
70 condition only, and Eq. (1) was not defined under equilibrium condition.

71 The value of K_P , calculated by Eq. (1) using the monitoring data TSP , C_P , and C_G , is
72 denoted as K_{PM} (subscript “M” in K_{PM} means measurement). It has been shown that there is a
73 linear relationship between $\log K_{PM}$ and $\log K_{OA}$ (K_{OA} is octanol-air partition coefficient)

74 (Finizio et al. 1997, Harner and Bidleman, 1998, Pankow, 1998) and between $\log K_{\text{PM}}$ and
75 $\log P_{\text{L}}$ (P_{L} is sub-cooled liquid vapor pressure) (Pankow, 1987; Bidleman and Foreman, 1987;
76 Pankow and Bidleman, 1991, 1992). The $\log K_{\text{OA}}$ -based model given by

$$77 \quad \log K_{\text{PR}} = m_{\text{O}} \log K_{\text{OA}} + b_{\text{O}} \quad (2)$$

78 has been widely used in describing the partitioning behavior for SVOCs, where slope m_{O} and
79 intercept b_{O} are fitting constants obtained using regression of $\log K_{\text{PM}}$ (from Eq. (1)) against
80 $\log K_{\text{OA}}$. The subscript “R” in K_{PR} indicates regression.

81 Unfortunately, Eq. (2) is not very useful to environmental modelers, since this equation can
82 only be used when the monitoring data of SVOCs concentrations in both gas- and
83 particle-phases are known, while the modelers need the equations to predict environmental
84 behavior, including their concentrations in air with both gas- and particle-phases, based on
85 physicochemical properties of SVOCs, their emissions, climate and meteorological
86 conditions.

87 Under the conditions of the equilibrium ($m_{\text{O}}=1$), the dominant absorption processes
88 between gas- and particle-phases, and equivalence of octanol to the sorbing organic matter in
89 particle, Harner and Bidleman (1998) derived the following equation,

$$90 \quad \log K_{\text{PE}} = \log K_{\text{OA}} + \log f_{\text{OM}} - 11.91 \quad (3)$$

91 where f_{OM} is organic matter content of the particle. The subscript “E” in K_{PE} indicates
92 equilibrium. In comparison to Eq. (2), Eq. (3) has an advantage to predict K_{PE} from the values
93 of K_{OA} and f_{OM} without the need of real monitoring data.

94 However, as discussed in the previous publications (Finizio et al., 1997; Cetin and
95 Odabasi, 2007; Tian et al., 2011; Yang et al., 2013; Li and Jia, 2014), Eq. (3) cannot describe
96 accurately the relationship between gas- and particle-phases polybrominated diphenyl ethers
97 (PBDEs). It is evident that Eq. (3) can be applied only in a few cases, such as for less
98 brominated PBDE congeners (such as BDE-17 and -28) or at high temperatures, and becomes

99 inaccurate in most cases, especially for highly brominated PBDE congeners, such as BDE-66,
100 -85, -99, -100, -153, -154, and -183, or at low temperatures (Yang et al., 2013; Li and Jia,
101 2014). This has been blamed by the artifacts and nonequilibrium factors (Finizio et al., 1997;
102 Cetin and Odabasi, 2007; Tian et al., 2011; Su et al., 2006).

103 Based on a large dataset of more than 700 pairs of air samples in both gas- and
104 particle-phases with a wide ambient temperature range of 60 °C from -22 to +38 °C obtained
105 from our Chinese POPs Soil and Air Monitoring Program, Phase 2 (China-SAMP-II), we
106 investigated G/P partitioning behavior of PBDEs in Chinese air (Yang et al., 2013; Li and Jia,
107 2014). We derived for the first time empirical equations to predict the values of slopes and
108 intercepts for both K_{OA} -based and P_L -based models as functions of temperature, and thus
109 predicted partition quotient (K_P) without assuming an equilibrium status and free of artifacts
110 (Li and Jia, 2014). The slope m_O and the intercept b_O were given as functions of temperature
111 (in °C),

$$112 \quad m_O(t) = 0.011t + 0.263 \quad (4)$$

$$113 \quad b_O(t) = -(0.135t + 5.006) \quad (5)$$

114 The temperature t in Eqs. (4) and (5) is usually a mean value of temperature for a series of
115 sampling events, such as annual or monthly mean temperature at each sampling site. After the
116 values of m_O and b_O are calculated using Eqs. (4) and (5), we can use Eq. (2) to calculate the
117 values of $\log K_P$. Since this method can be used to predict the values of $\log K_P$, we use K_{PP} (the
118 second “P” in the subscript K_{PP} indicates “Prediction”) instead of K_{PR} in Eq. (2), and rewrite
119 them as

$$120 \quad \log K_{PP} = m_O(t) \log K_{OA} + b_O(t) \quad (6)$$

121 where $m_O(t)$ and $b_O(t)$ are given by Eqs. (4) and (5), respectively.

122 It is noteworthy that $\log K_{PP}$ in Eq. (6) depends on two parameters, temperature t and K_{OA} ,
123 which is also a function of temperature, and given by an empirical equation (Harner and

124 Shoeib, 2002)

$$125 \quad \log K_{OA} = A + B / (t + 273.15) \quad (7)$$

126 where t (in °C) is the temperature for each sampling event, and the parameters A and B are
127 given in **Table S1** in the Supplement for several PBDE congeners. It should be borne in mind
128 that temperature t in Eqs. (4) and (5) can be also the temperature for each sampling event,
129 and thus using Eq. (7), we can express $\log K_{PP}$ in Equation (6) as a function of a single
130 independent variable of $\log K_{OA}$ as (Li and Jia, 2014)

$$131 \quad \log K_{PP} (K_{OA}) = 0.011B(\log K_{OA} - 12.27) / (\log K_{OA} - A) - 2.74\log K_{OA} + 31.85 \quad (8)$$

132 These two Eqs. (6) and (8) have been successfully applied to predict the values of K_P for
133 PBDEs as functions of $\log K_{OA}$ in air of China and other countries in the north temperate zone
134 and also at an Arctic site in East Greenland (Li and Jia, 2014), and our results matched the
135 monitoring data well at background, rural, urban, and suburban sites, but not at e-waste sites
136 due to the unpredictable PBDE emissions at these sites, and the results indicated that our new
137 equations have a better performance than Eq. (3) in describing G/P partitioning behavior of
138 PBDEs in air as functions of $\log K_{OA}$. We also found for the first time that the G/P partitioning
139 of PBDE congeners can reach a maximum value if the ambient temperature is low enough. A
140 criterion to classify the equilibrium and nonequilibrium status for PBDEs was also
141 established using $\log K_{OA}$ (Li and Jia, 2014).

142 These equations, however, suffer from two drawbacks. First, these equations derived at the
143 temperature range from -22 to +38 °C, thus cannot be used at temperatures beyond this range;
144 secondly, these equations were obtained empirically, and do not have a strong theoretical
145 foundation. Therefore, in this paper, we study the G/P partitioning behavior of PBDEs in
146 global air in a theoretical way. The objectives of this study are to establish a partitioning
147 model between gaseous and particulate phases for PBDEs, which can reveal the real
148 partitioning mechanism of PBDEs between these two phases and to predict the partition

149 quotients defined in Eq. (1) accurately for PBDEs in air, thus to achieve a capability to
150 address a series of G/P partitioning issues for these chemicals, such as those presented
151 previously (Yang et al., 2013; Li and Jia, 2014).

152

153 **2 Theory**

154 **2.1 Equilibrium state and steady state**

155 To develop a new model in simulating G/P partitioning behavior, we need to understand the
156 equilibrium state and steady state for SVOCs in environment. The steady state is a state in
157 which no change occurs with time, or all time derivatives are equal to zero. “*Equilibrium*
158 implies that phases have concentrations such that they experience no tendency for net
159 transfer of mass” (Mackay 2001). These two terms have been frequently mistaken with each
160 other. In his book (Mackay 2001), Mackay gave examples to explain the difference between
161 these two states, indicating a chemical is in equilibrium between two media (phases) as long
162 as its fugacities in the two media (phases) are equal no matter the system is steady or
163 unsteady.

164 We also noticed that, although equilibrium is actually an ideal event since such a system
165 cannot exist in real environment; this state has been successfully applied in some cases.
166 Good examples are to treat air-water exchange for gaseous pesticide
167 α -hexachlorocyclohexane (α -HCH) (Jantunen and Bidleman, 1996; 1997; Li et al. 2004) and
168 air-soil exchange for gaseous polychlorinated biphenyls (PCBs) (Li et al. 2010). In these two
169 examples, the factors other than the diffusion due to random molecular movement were
170 negligible, and the systems can be treated as equilibrium, thus the net flux of
171 gaseous α -HCH between air and water, and gaseous PCBs between air and soil are zero. We
172 realized, however, that the exchange of SVOCs between the gas- and particle-phases is
173 different since the advection processes, such as dry and wet depositions, caused by an

174 external force (gravity) on the particles, cannot be ignored in studying the partitioning
175 behavior of SVOCs between these two phases. Therefore, we suggest that the steady state,
176 not equilibrium state, should be applied here.

177 **2.2 G/P partitioning model under steady state**

178 **2.2.1 Basic equation**

179 A model to describe G/P partitioning under steady state for PBDEs is

$$180 \quad N_{G-P} = N_{P-G} + N_{P-S} \quad (9)$$

181 where N_{G-P} is flux of PBDEs from gas phase to particle phase, N_{P-G} is flux of PBDEs from
182 particle phase to gas phase, and N_{P-S} the net flux of particle-bound PBDEs between air and
183 earth surface, such as water body or surface soil. For the sake of simplicity, we only consider
184 dry and wet depositions in N_{P-S} , which is given by (Mackay 2001)

$$185 \quad N_{P-S} = f_P(D_D + D_W) \quad (10)$$

186 where f_P is fugacity of particle in air, given by Eq. (S1) in the Supplement with subscript
187 “T” being “P”, and D_D is D value of dry deposition of particle-phase PBDEs described by
188 (Mackay 2001)

$$189 \quad D_D = U_D v_P A Z_P \quad (11)$$

190 where U_D is dry deposition velocity, a typical value being 10 m/h, A is the area between air
191 and earth (water or soil), and Z_P is Z value of aerosol, given by Eq. (S3) in the Supplement,
192 and v_P is the volume fraction of aerosol, given by

$$193 \quad v_P = 10^{-9} TSP / \rho \quad (12)$$

194 where TSP is the concentration of total suspended particles in air ($\mu\text{g}\cdot\text{m}^{-3}$) and ρ is the density
195 of the particle ($\text{kg}\cdot\text{m}^{-3}$).

196 D_W is D value of wet deposition given by (Mackay 2001)

$$197 \quad D_W = U_R Q v_P A Z_P \quad (13)$$

198 where U_R is rain rate, a typical value being 0.5 ($\text{m}\cdot\text{year}^{-1}$). Q is a scavenging ratio

199 representing the volume of air efficiently scavenged by rain of its particle content, per unit
 200 volume of rain. A typical value for Q of 200,000 may be used. Substituting the above 2
 201 Equations in Eq. (10) leads to

$$202 \quad N_{P-S} = f_P (U_D + U_R Q) v_P A Z_P \quad (14)$$

203 **2.2.2 Gas/particle exchange of PBDEs**

204 One of the most important issues for investigating the G/P partitioning behavior is the
 205 exchange of PBDE between air and particle. We treat each particle as a ball with a mean
 206 diameter of d , a volume of $v = \pi d^3 / 6$, surface area $a = \pi d^2$, and a mass $m = \rho v$, where ρ is the
 207 density of the particle. The number of particles in 1 m^3 of air, $n = TSP/m$. In air with volume
 208 of Ah (h is the height of atmosphere), the total area of the particles is

$$209 \quad A_P = 6TSP(\text{g} \cdot \text{m}^{-3}) \times A(\text{m}^2)h(\text{m}) / (\rho(\text{g} \cdot \text{m}^{-3})d(\text{m})) \quad (15)$$

210 Assuming $\rho = 1.5 \times 10^6 \text{ g} \cdot \text{m}^{-3}$, $d = 1.0 \times 10^{-7} \text{ m}$ (Rissler et al. 2006), $h = 1.0 \times 10^3 \text{ m}$, the above
 211 equation becomes

$$212 \quad A_P = 0.04A \times TSP \quad (16)$$

213 To be simplified, we treat the particles as a film, called the *particle film*, with a thickness of d ,
 214 a surface area of A_P , as shown in **Fig. S1** in the Supplement. The ratio between A_P and A is

$$215 \quad R_P = A_P / A = 0.04 TSP \quad (17)$$

216 which is a linear function of TSP .

217 In order to study the movement of SVOCs between air and particle, we adapted the method
 218 used for the air-soil interface introduced by Mackay (2001). For diffusion, the two-resistance
 219 approach is used, and the overall D values is given by

$$220 \quad 1/D_V = 1/D_E + 1/(D_A + D_H) \quad (18)$$

221 where D_E is air boundary layer D value, D_A and D_H are diffusion D values of chemical in air
 222 and water sub-phases in particle film, respectively. D_E is deduced as the product of the
 223 surface area of the particle film, $A_P (\text{m}^2)$, a mass transfer coefficient $k_V (\text{m} \cdot \text{h}^{-1})$, and the Z

224 value of air Z_G , given by:

$$225 \quad D_E = A_P k_V Z_G \quad (19)$$

226 Here,

$$227 \quad k_V = B_a / l_a \quad (20)$$

228 where B_a is the chemical's molecular diffusivity in air ($0.018 \text{ m}^2 \cdot \text{h}^{-1}$ was assumed), and l_a is
229 an air boundary layer thickness (0.00475 m was assumed) (Mackay 2001).

230 In comparison to the soil surface in air-soil exchange, the particle-film that we suggested
231 in our model keeps moving within the atmosphere and thus has much more chances to
232 intersect with the chemical in gas phase. Therefore, the mass transfer coefficient will be
233 larger than that given by Eq. (20), and accordingly, a parameter C is introduced in Eq. (20),
234 leading to

$$235 \quad k_V = C B_a / l_a \quad (21)$$

236 Thus the term $C B_a$ is the chemical's molecular diffusivity for the particle film in air, and its
237 value will be determined later.

238 Since most of the SVOCs (including PBDEs) are associated with the organic matter of the
239 particles, again for the sake of simplicity, the 2 terms, D_A and D_H , in Eq. (18) are neglected,
240 which becomes

$$241 \quad D_V = D_E = A_P k_V Z_G \quad (22)$$

242 The flux of PBDEs from gas phase to particle phase, N_{G-P} , becomes

$$243 \quad N_{G-P} = f_G D_E \quad (23)$$

244 and the flux from particle phase to gas phase, N_{P-G} , is

$$245 \quad N_{P-G} = f_P D_E \quad (24)$$

246 If the term N_{P-S} is dropped from Eq. (9), i.e., the net flux of particle-bound PBDEs
247 between air and surface is neglected, we will have

$$248 \quad N_{G-P} = N_{P-G} \quad (25)$$

249 From Eqs. (23) and (24), the fugacities of a chemical in gas phase (f_G) and in particle phase
 250 (f_P) are equal, and thus the steady state becomes equilibrium. Therefore, it is concluded that
 251 equilibrium is just a special case of steady state when N_{P-S} is ignored.

252 **2.3 G/P equations under steady state**

253 **2.3.1 G/P partition coefficient under steady state**

254 We use Eqs. (10), (23), and (24) into Eq. (9), leading to

$$255 \quad f_p(D_E + D_D + D_W) = f_G D_E \quad (26)$$

256 By using Eqs. (S6) and (S7) in the Supplement, the above equation leads to

$$257 \quad C'_p / C_G = (Z_P / Z_G) (D_E / (D_E + D_D + D_W)) = K_{PG} (1 / [1 + (D_D + D_W) / D_E])$$

258 where C'_p (pg/m³ of *particle*) and C_G (pg/m³ of *air*) are concentrations of SVOCs in particle-
 259 and gas-phases, respectively, and K_{PG} is dimensionless *G/P partition coefficient* under
 260 equilibrium (= Z_P / Z_G). Setting a parameter **a** as

$$261 \quad \mathbf{a} = 1 / [1 + (D_D + D_W) / D_E] \quad (27)$$

262 and the above equation becomes

$$263 \quad C'_p / C_G = \mathbf{a} K_{PG} \quad (\text{at steady state}) \quad (28)$$

264 By using Eqs. (S10) and (S11), C'_p and K_{PG} are replaced by C_p and K_{PE} , respectively, Eq. (28)
 265 becomes

$$266 \quad (C_p / TSP) / C_G = \mathbf{a} K_{PE} \quad (29)$$

267 Defining a *G/P partition coefficient under steady state*,

$$268 \quad K_{PS} = (C_p / TSP) / C_G \quad (\text{at steady state}) \quad (30)$$

269 where C_G and C_p are concentrations of PBDEs in gas- and particle-phases (both in pg·m⁻³ of
 270 air), respectively, *at steady state*, and the subscript “S” in K_{PS} indicates steady state. Although
 271 Eq. (30) seems the same as Eq. (1) (for K_P) and Eq. (S8) (for K_{PE}), they are different since Eq.
 272 (30) is defined under steady state, Eq. (S8) is under equilibrium, and Eq. (1) was defined at
 273 neither steady nor equilibrium state. Thus Eq. (29) becomes

274
$$\log K_{PS} = \log K_{PE} + \log a \quad (31)$$

275 In the above equation, $\log K_{PE}$ is designated the *equilibrium term*, given by Eq. (3), and
 276 $\log a$ is the *nonequilibrium term*. Therefore, we have two predicted partition coefficients:
 277 partition coefficient K_{PS} under steady state when the system is at steady state, or partition
 278 coefficient K_{PE} under equilibrium when the system is at equilibrium. Eq. (31) indicates that
 279 the equilibrium is just a special case of the steady state when $\log a = 0$.

280 2.3.2 Nonequilibrium term $\log a$

281 In Eq. (27), setting

282
$$G = C (D_D + D_W) / D_E \quad (32)$$

283 Eq. (27) becomes

284
$$a = 1 / (1 + G/C) \quad (33a)$$

285 or

286
$$\log a = -\log (1 + G/C) \quad (33b)$$

287 Substituting Eqs. (11), (13) and (19) in Eq. (32), which leads after some manipulations,

288
$$G = 2.09 \times 10^{-10} f_{OM} K_{OA} \quad (34)$$

289 Thus, as K_{PE} , $\log a$ is also a function of f_{OM} and K_{OA} .

290 2.4 $\log a$ as functions of $\log K_{OA}$ and temperature

291 **Fig. S2** in the Supplement depicts variation of $\log a$ as functions of $\log K_{OA}$ and temperature t
 292 with $C=5$. As shown in **Fig. S2A**, the function of $\log a$ versus $\log K_{OA}$ is a curve shared by all
 293 PBDE congeners, showing that when $\log K_{OA} < \sim 10.4$, $\log a = 0$, the state is equilibrium. In
 294 contrast with the function of $\log a$ versus $\log K_{OA}$, the functions of $\log a$ versus t are different
 295 for different PBDE congeners, as shown in **Fig. S2B** in the Supplement. This figure explains
 296 why light PBDE congeners, such as BDE-17 and -28, can reach equilibrium state much more
 297 easily than heavy PBDE congeners. It is obvious from **Fig. S2B** that the curves of BDE-17

298 and -28 deviate significantly from zero at a low temperature ($\sim -10^{\circ}\text{C}$), indicating that the
 299 values of $\log a$ are equal or close to 0 at a wide range of environmental temperature ($t > -10^{\circ}\text{C}$).
 300 For highly brominated congeners, BDE-153 for example, the values of $\log a$ deviates
 301 significantly from zero even when $t < +40^{\circ}\text{C}$, causing the equilibrium state at a much
 302 narrower ambient temperature range for this chemical ($t > +40^{\circ}\text{C}$) than BDE-17 and -28.

303 **2.5 Threshold values of $\log K_{\text{OA}}$ and temperature**

304 Since all the equations to calculate the parameter K_{PE} and K_{PS} link only the PBDE parameter
 305 $\log K_{\text{OA}}$, it may be advantageous to explore partitioning behavior according to $\log K_{\text{OA}}$, rather
 306 than individual PBDE congeners or homolog groups. Under this consideration, we drew
 307 $\log K_{\text{PS}} - \log K_{\text{OA}}$ and $\log K_{\text{PE}} - \log K_{\text{OA}}$ graphs, for all PBDE congeners/homologues at an
 308 environmental temperature range of -50 to $+50^{\circ}\text{C}$, as shown in **Fig. 1**. The straight line (thick
 309 blue) for $\log K_{\text{PE}}$ and the curve (red) for $\log K_{\text{PS}}$ can be used for all PBDE
 310 congeners/homologues as long as their ranges of $\log K_{\text{OA}}$ are known. Of course, it should be
 311 mentioned that the different PBDE congeners have different ranges of $\log K_{\text{OA}}$ at the same
 312 temperature span, thus are represented by different portions of the curves in the **Fig. 1**,
 313 accordingly showing different G/P partitioning behaviors.

314 There are three cases for G in Eq. (33b).

315 (1) $G \ll C$ ($D_{\text{D}} + D_{\text{W}} \ll D_{\text{E}}$)

316 In this case, Eq. (33b) becomes

$$317 \log a = -\log(1 + G/C) \approx 0 \quad (35)$$

318 which is equilibrium state.

319 (2) $G=C$ ($D_{\text{D}} + D_{\text{W}} = D_{\text{E}}$)

320 In this case, Eq. (33b) becomes

$$321 \log a = -\log 2 \quad (36)$$

322 If we assume that $f_{OM} = 0.1$ and $C = 5$, then we have the *first threshold value* from Eqs. (33b)
 323 and (34),

$$324 \quad \log K_{OA1} = 11.4 \quad (37)$$

325 which is very close to the threshold value of $\log K_{OA} = 11.5$ suggested by Li and Jia (2014). The
 326 physical meaning of $\log K_{OA1}$ is, at this threshold, the data of $\log K_{PS}$ deviates from $\log K_{PE}$ by
 327 an amount of $\log 2$.

328 (3) $G \gg C$ ($D_D + D_W \gg D_E$)

329 In this case, Eq. (33b) becomes

$$330 \quad \log a \approx -\log(G/C) = \log C - \log K_{PE} - 2.23 \quad (38)$$

331 thus $\log K_{PS}$ in Eq. (31) reaches its maximum value,

$$332 \quad \log K_{PSM} = -1.53 \quad \text{or} \quad K_{PSM} = 0.03 \quad (39)$$

333 when $G \gg C$. This is very close to the maximum value of -1.5 suggested by Li and Jia (2014).
 334 The maximum value of $\log K_{PS}$ is clearly shown in **Fig. 1** (the thin blue horizontal line), and
 335 we define the *second threshold value* as

$$336 \quad \log K_{OA2} = 12.5 \quad (40)$$

337 As shown in **Fig. 1**, the first threshold value of $\log K_{OA}$ divides the whole range of $\log K_{OA}$
 338 into *equilibrium* (EQ) and *nonequilibrium* (NE) domains. The second threshold indicates the
 339 start of the *maximum partition* (MP) domain, in which the values of $\log K_{PS}$ reach a maximum
 340 value of $\log K_{PSM}$, which is independent of the values of f_{OM} and K_{OA} .

341 In brief, as shown in **Fig. 1**, the curve of $\log K_{PS}$, originally coinciding with the straight line
 342 of $\log K_{PE}$, increases along with increase of $\log K_{OA}$, and separates visibly (by a mount of $\log 2$)
 343 from the straight line of $\log K_{PE}$ at the first threshold value of $\log K_{OA1}$, entering the NE
 344 domain from the EQ domain. After the second threshold value of $\log K_{OA2}$, the curve of
 345 $\log K_{PS}$ enters the MP domain and becomes a horizontal straight line of $\log K_{PS} = -1.53$.

346 The values of $\log K_{OA}$ depend on each PBDE congener and the ambient temperature, as
 347 discussed previously (Harner and Shoeib, 2002). Accordingly, we defined two threshold
 348 values for temperature, the *threshold temperatures* t_{TH1} and t_{TH2} , which are the temperatures
 349 when $\log K_{OA}$ of PBDE congeners equals to the threshold values $\log K_{OA1}$ and $\log K_{OA2}$,
 350 respectively. As presented in **Fig. 2**, while the threshold values of $\log K_{OA1}$ and $\log K_{OA2}$ are
 351 constants for all congeners, the threshold values for t_{TH1} and t_{TH2} are different for different
 352 PBDE congeners. These two threshold temperature values divided the temperature space also
 353 into the same 3 domains; the EQ domain when $t > t_{TH1}$, the NE domain when $t \leq t_{TH1}$, and the
 354 MP domain when $t \leq t_{TH2}$. Taking BDE-47 as an example, with its $t_{TH1} = +11^\circ\text{C}$ and $t_{TH2} = -6^\circ\text{C}$,
 355 BDE-47 is in EQ domain when $t > +11^\circ\text{C}$; in NE domain when $t \leq +11^\circ\text{C}$; and in MP domain at
 356 $t \leq -6^\circ\text{C}$.

357 **2.6 Particle phase fraction**

358 Another important parameter, the fraction of chemical on the particle phase, f ($=$
 359 $C_P/(C_G+C_P)$), can be calculated from K_P as

$$360 \quad f_{PX} = K_{PX} TSP / (1 + K_{PX} TSP) \quad (41)$$

361 where the subscript “PX” can be one of “PS”, “PE”, and “PR”. Thus the maximum value of
 362 particle phase fraction can be obtained from Eqs. (39) and (41) as

$$363 \quad f_{PSM} = 0.03 TSP / (1 + 0.03 TSP) \quad (42)$$

364 which indicates that, while the maximum partition coefficient $\log K_{PSM}$ is a constant for all
 365 PBDE congeners, it's corresponding maximum value of particle phase fraction is not, but
 366 depends on TSP . The variation of f_{PSM} as a function of TSP is depicted in **Fig. S3** in the
 367 Supplement.

368

369 **3. Application of the equations**

370 **3.1 G/P partitioning of PBDEs in Chinese Air from China-SAMP-II**

371 In the previous section, we derived an Eq. (31) to predict the values of *partition coefficient*
372 *under steady state* K_{PS} . In this subsection, we used these equations to predict K_P for air
373 samples collected at 15 sites across China under our PBDE monitoring program,
374 China-SAMP-II (Yang et al., 2013, Li and Jia, 2014), and the results will be compared with
375 the predicted values of *partition coefficient under equilibrium state* K_{PE} , obtained using Eq.
376 (3); and the values of *partition quotient*, K_{PR} , obtained using Eq. (2) with the help of K_{PM} ,
377 calculated from Eq. (1) using the monitoring data C_P and C_G . Among the three modeled
378 values (K_{PS} , K_{PE} , and K_{PR}), K_{PR} values are the ones most close to the values of K_{PM} since
379 $\log K_{PR}$ values are obtained directly from $\log K_{PM}$ by least squares regression against $\log K_{OA}$,
380 and the accuracy of the equations of K_{PS} and K_{PE} depends on how their results close to those
381 given by K_{PR} .

382 **Figs. S4 and S5** in the Supplement depict the variations of $\log K_{PS}$, $\log K_{PE}$, and $\log K_{PR}$ as
383 functions of $\log K_{OA}$ for the 15 sampling sites and 10 PBDE congeners, respectively, both
384 showing the curve of $\log K_{PS}$ is closer to the regression line of $\log K_{PR}$ than $\log K_{PE}$. It is
385 worthwhile to point out that, for the best match between the results of $\log K_{PS}$ and $\log K_{PR}$ for
386 PBDEs, $C = 5$ was used in Eq. (5) to calculate $\log K_{PS}$ in air at all the sampling sites with an
387 exception of the site of Waliguan, where $C = 50$ was used. The reason why much higher value
388 of C was used at this site will be explained later. **Fig. S5** also shows that, from the light
389 PBDE congeners to the heavy ones, the ranges of $\log K_{OA}$ for each PBDE congeners (at
390 temperature range of $-22\text{ }^{\circ}\text{C} - +38\text{ }^{\circ}\text{C}$) move from left to right, from smaller than $\log K_{OA1}$ for
391 BDE-17 to larger than $\log K_{OA1}$ for BDE-183, or the states that these congeners reside in
392 change from EQ domain to the NE domain, and finally reach the MP domain.

393 The 10 regression lines ($\log K_{PR}$) for the 10 PBDE congeners shown in **Fig. S5** are all

394 presented in **Fig. S6** in the Supplement along with the curves of $\log K_{PE}$ and $\log K_{PS}$, indicating
395 evidently that these 10 lines of $\log K_{PR}$ change their slopes m_O along the curve of $\log K_{PS}$, not
396 the straight line of $\log K_{PE}$, and accordingly, the curve of $\log K_{PS}$ matches the monitored G/P
397 partitioning data very well for all the 10 PBDE congeners in Chinese air.

398 We understand that, modelers are most interested in K_P values as a function of temperature
399 for each PBDE congener. **Fig. S7** in the Supplement presents variations of $\log K_{PS}$, $\log K_{PE}$,
400 and $\log K_{PR}$ as functions of temperature for the 10 PBDE congeners, indicating that, the curve
401 of $\log K_{PS}$ matches the line of $\log K_{PR}$ for each PBDE congener, the highly brominated
402 congeners in particular, dramatically well. It is interesting to note that the two threshold
403 temperatures, t_{TH1} and t_{TH2} , designed by two vertical dashed lines, increase from the less
404 brominated to highly brominated PBDEs. For example, the value of t_{TH1} of BDE-17 equals to
405 $-16.5\text{ }^\circ\text{C}$, meaning that this compound is in the EQ domain in the most ambient temperature
406 range of $\geq -16.5\text{ }^\circ\text{C}$, while for BDE-183, $t_{TH1}=36.5\text{ }^\circ\text{C}$ and $t_{TH2}=15\text{ }^\circ\text{C}$, meaning that this
407 compound is in the EQ domain only when $t > 36.5\text{ }^\circ\text{C}$, in the NE domain when $t \leq 36.5\text{ }^\circ\text{C}$, and
408 in the MP domain when $t \leq 15.0\text{ }^\circ\text{C}$. We also calculated the modeled values of $\log K_{PS}$ for 5
409 typical PBDE congeners as functions of temperature from -50 to $+50\text{ }^\circ\text{C}$, and the results are
410 given in **Fig. S8** in the Supplement, showing that, along with decrease of temperature, the
411 values of $\log K_{PS}$ for PBDE congeners increase to a maximum partition value; the more highly
412 brominated the congener is, the higher is its value of the first threshold temperature (t_{TH1} , data
413 are not shown) and the second threshold temperature (t_{TH2}), and thus the higher temperatures
414 at which the congener reaches the NE and MP domains.

415 As shown in **Fig. 1**, the partitioning behavior of PBDEs depends on ambient temperature
416 of sampling events. There are three squares presented in **Fig. 1** indicating the three regions
417 with different temperature ranges, $0 - +50\text{ }^\circ\text{C}$ (the orange one), $-30 - +30\text{ }^\circ\text{C}$ (the green one),
418 and $-50 - 0\text{ }^\circ\text{C}$ (the blue one). Here, we take the two sampling sites from China-SAMP-II

419 (Yang et al., 2013; Li and Jia, 2014), one is Harbin in the northeast of China, with a sampling
420 temperature range of $-22 - +28$ °C, within the green square, and the other is Guangzhou in the
421 south of China, with a range of $+8 - +38$ °C, within the orange square, as examples to show
422 how the threshold values can be used in study the G/P partitioning behavior of PBDEs.

423 We determined the ranges of $\log K_{OA}$ for the 10 PBDEs at the site of Harbin (vertical bars)
424 based on the ambient temperature range of $-22 - +28$ °C at the site, and the results are
425 presented in **Fig. 3**. The two threshold values of $\log K_{OA}$, $\log K_{OA1}$ and $\log K_{OA2}$ (the horizontal
426 light blue dashed lines), divide the space of $\log K_{OA}$ (the left axis) into three domains, the EQ,
427 the NE, and the MP domains, and accordingly, the 10 PBDEs in Harbin air can be segregated
428 into 3 groups; BDE-17 and 28 (3-Br homologue) as equilibrium EQ-group, BDE-47 and 66
429 (4-Br homologue) as semiequilibrium SE-group, and others (>4 -Br homologues) as
430 nonequilibrium NE-group. The dominant portions of $\log K_{OA}$ for the EQ-group (purple lines)
431 are under the line of $\log K_{OA1}$, i.e., these congeners are mainly in the EQ domain, while the
432 dominant or whole portions of the NE-group (blue lines) are above the line of $\log K_{OA1}$,
433 indicating that these congeners are in the NE and the MP domains. The SE-group (green lines)
434 is in both the EQ and the NE domains. It is noteworthy that, the major portions of $\log K_{OA}$ for
435 the PBDE congeners in the NE-group were in the MP domain. These three domains can also
436 be identified in the temperature space. In **Fig. 3**, the two threshold temperatures, t_{TH1} (the red
437 diamonds) and t_{TH2} (the red square), are also shown (the right axis), which is similar to **Fig. 2**.
438 In the real ambient temperature range, formed by the two red dashed lines (-22 °C and $+28$ °C)
439 at the Harbin site, the major temperature portions of PBDEs in the EQ-group were in the EQ
440 domain ($t < t_{TH1}$), those of the NE-group in the NE and MP domains ($t \geq t_{TH1}$), and those of the
441 SE-group in both the EQ and NE domains.

442 **Fig. 4** presents the $\log K_P - \log K_{OA}$ graph for the 10 PBDEs in Harbin, which is almost
443 identical to the one contained in the green square of **Fig. 1**. The ranges of $\log K_{OA}$ for the three

444 groups and their corresponding $\log K_P - \log K_{OA}$ diagram are also shown. For example, the
445 $\log K_P - \log K_{OA}$ diagram for the EQ-group (3-Br homologue), bound by the 2 purple dashed
446 lines, is mainly in the EQ domain, with a small portion in the NE domain; the $\log K_P - \log K_{OA}$
447 diagram for the SE group (4-Br homologue), contained by 2 green dashed lines, is mainly in
448 the NE domain, with a small portion in the MP domain; and the $\log K_P - \log K_{OA}$ diagram for
449 the NE-group (>4-Br homologue), formed by the 2 blue dashed lines, is mainly in the NE and
450 MP domains.

451 Similar analysis was carried out for the 10 PBDEs at the site of Guangzhou at an ambient
452 temperature range of +8– +38 °C at the site (Yang et al., 2013), and the results are presented
453 in **Figs. S9 and S10** in the Supplement. The 10 PBDEs at Guangzhou air can also be
454 segregated into 3 groups, BDE-17, -28, and -47 as EQ-group, BDE-66, 99, and 100 as
455 SE-group, and the others, BDE-85, -99, -100, and -183 as NE-group, which are quite
456 different from those for Harbin, caused by the different ambient temperature ranges at the two
457 sites.

458 We concluded that the PBDEs in Chinese air at 15 sampling sites across China were in the
459 steady state instead of equilibrium state, in realizing that, for less brominated PBDE
460 congeners, BDE-17 and -28, this steady state can be treated as equilibrium state since their
461 nonequilibrium term ($\log a$) can be ignored in comparison to the equilibrium term ($\log K_{PE}$) in
462 the temperature range of -22 °C to +38 °C (see **Fig. S2B**).

463 **3.2 G/P partitioning of PBDEs in air from other sources**

464 There are only a few data available in the literature that we can compare to our prediction
465 data.

466 We predicted the partitioning behavior of gaseous and particle-bound PBDEs in the
467 atmosphere at an e-waste site and a rural site in southern China during 2007-2008 using the
468 information given by Tian et al. (2011). We calculated the values of $\log K_{PS}$, $\log K_{PE}$, and

469 $\log K_{PR}$ as functions of $\log K_{OA}$, and the results are presented in **Fig. S11**. It is noticeable that
470 our predicted results are obviously better than those obtained by the equilibrium model at the
471 rural site, but not at the e-waste site, where the data from equilibrium model matched the
472 monitoring data better than those predicted using our equation. This seemed unexpected but
473 could possibly be explained by the fact that the emissions of PBDEs from the e-waste site
474 compensated the flux of PBDEs due to dry and wet deposition, leading a situation that
475 seemed to be at equilibrium. We cannot, however, accept the point of view that the PBDEs in
476 air at the rural area cannot reach equilibrium, but those in air at the e-waste sites can.

477 The G/P partitioning behavior was studied for 7 PBDEs (BDE-28, -47, -99, -100, -153,
478 -154 and -209) at four sites (1 suburban, 2 urban, and 1 industrial) in Izmir, Turkey, in
479 summer and winter in 2004-2005 with a temperature range of 1.8 - 22.4 °C (Cetin and
480 Odabasi, 2007). We calculated the particle phase PBDEs fractions f_{PS} and f_{PE} , using Eq. (41)
481 and compared them with the monitoring data, and the results are depicted in **Fig. S12**. It was
482 noted by the authors that their monitoring data were much lower than the predicted values by
483 the equilibrium equation (f_{PE}) (Cetin and Odabasi, 2007), but it is obvious that their results
484 matched our predicted data (f_{PS}) very well, among which, the best agreement was observed
485 for BDE-209, the most highly brominated congener of PBDEs.

486 We calculated the G/P partition coefficients for PBDEs in atmosphere of Kyoto, Japan,
487 which were measured in August 2000, and January and September 2001 (Hayakawa et al.,
488 2004), and the variations of $\log K_{PE}$ and $\log K_{PS}$ as functions of $\log K_{OA}$ are presented in **Fig.**
489 **S13**, indicating obviously that the values of $\log K_{PS}$ was in a better agreement with the
490 monitoring data than $\log K_{PE}$.

491 Air samples were collected from 1 urban, 2 rural, and 1 remote sites near the Great Lakes
492 in 1997-1999 as part of the Integrated Atmospheric Deposition Network (IADN), among
493 which, those taken when the ambient atmospheric temperatures were 20 ± 3 °C were

494 analyzed for the G/P partitioning behavior of PBDEs, and the log-log relation of K_P and their
495 subcooled liquid vapor pressures (P_L) for BDE-47, -99, -100, -153, and -154 were calculated
496 (Strandberg et al. 2001). By using these data, we calculated both $\log K_P$ and f_P as functions of
497 $\log K_{OA}$ for the same 5 PBDE congeners, using the values of $f_{OM} = 0.2$ and $TSP = 25 \mu\text{g m}^{-3}$
498 suggested by Harner and Shoeib (2002), which are presented in **Fig. S14**, along with the
499 predicted results under equilibrium state and steady state. Again the results indicated that the
500 prediction by our new equation is more accurate than those by the equilibrium equation.

501 **3.3 G/P partitioning of PBDEs in the Arctic air**

502 As discussed in the previous sections, each PBDE congener will reach the maximum partition
503 domain when $\log K_{OA} \geq \log K_{OA2}$ or $t \leq t_{TH2}$. The value of t_{TH2} of BDE-183 is 15°C , meaning
504 that BDE-183 in air will be in MP domain when $t < 15^\circ\text{C}$. The value of t_{TH2} for BDE-209
505 should be higher ($\log K_{OA}=14.98$ for BDE-209 was estimated at 25°C by Cetin and Odabasi
506 (2007) in comparison to $\log K_{OA}=11.97$ for BDE-183 at the same temperature). Accordingly,
507 BDE-209 in arctic air should be in the MP domain, with a constant of $\log K_{PSM} (= -1.53)$ and
508 the corresponding $f_{PSM} (=0.23$ if $TSP = 10 \text{ mg m}^{-3}$ is assumed). This prediction was
509 remarkably in agreement with monitoring data for BDE-209 measured in arctic air at Alert,
510 Canada from 2007 to 2009 with a temperature range between 10 and -50°C (NCP 2013),
511 lower than the value of t_{TH2} for BDE-209 (see **Fig. 5**). The comparisons between the
512 predicted values and the monitoring data at Alert for other values of $TSP (= 5$ and $2 \text{ mg m}^{-3})$
513 given in **Fig. S15** also showed great consistence. It should be stressed from the figure that the
514 values of $\log K_{PE}$ of BDE-209 are from 3.06 at 10°C to 8.36 at -50°C calculated by Eq. (3),
515 which means that the values of K_{PE} are from more than 5 orders at 10°C to 10 orders at -50
516 $^\circ\text{C}$ of magnitude higher than the monitoring data, a huge error that cannot be tolerated. The
517 corresponding values of f_{PE} are 1, indicating that BDE-209 are all in particle phase in the
518 Arctic air predicted by the equilibrium equation, which was not the case given by the

519 monitoring data. In other words, the maximum value 0.23 of f_{PSM} indicates that, from our
520 prediction, more than half BDE-209 (~ 0.77) is in gas phase in arctic air, which was confirmed
521 by the monitoring data shown in **Fig. 5**.

522 We also studied the G/P partition for the 10 PBDEs (BDE-28, -47, -66, -85, -99, -100, -153,
523 -154, -183, and -209) in the Arctic atmosphere in East Greenland Sea in August and
524 September 2009 with a temperature range between $-0.5\text{ }^{\circ}\text{C}$ and $+6.5\text{ }^{\circ}\text{C}$ (Möller et al., 2011).
525 We calculated the values of $\log K_{\text{PS}}$, $\log K_{\text{PE}}$, and $\log K_{\text{PR}}$ as functions of $\log K_{\text{OA}}$, and the
526 results are shown in **Fig. S16**. Once again, the equation of $\log K_{\text{PS}}$ had a better performance
527 than the equation of $\log K_{\text{PE}}$, especially for those congeners in the NE domain with $\log K_{\text{OA}} \geq$
528 $\log K_{\text{OA1}}$.

529

530 **4. Conclusions and Discussion**

531 **4.1 G/P partitioning of PBDEs in global air**

532 **Figure At a Glance** in the Supplement presents G/P partition coefficients of PBDEs ($\log K_{\text{PS}}$
533 and $\log K_{\text{PE}}$) as functions of $\log K_{\text{OA}}$ at ambient temperature ranging from -50 to $+50\text{ }^{\circ}\text{C}$, which
534 can be applied at any sites worldwide (the top middle panel, similar to **Fig. 1**). The three
535 squares in the panel designate the $\log K_{\text{P}}\text{-}\log K_{\text{OA}}$ graphs with three different temperature
536 ranges: $0 - +50\text{ }^{\circ}\text{C}$, $-30 - +30\text{ }^{\circ}\text{C}$, and $-50 - 0\text{ }^{\circ}\text{C}$, representing the tropical and subtropical
537 climate zones, warm temperate climate zone, and boreal and tundra climate zones,
538 respectively. Monitoring data ($\log K_{\text{PM}}$), their regression data ($\log K_{\text{PR}}$), and the predicted
539 results $\log K_{\text{PS}}$ and $\log K_{\text{PE}}$ in the three different temperature zones are presented in the figure;
540 the site Guangzhou, China, within the subtropical climate zone, shown in the top-left panel,
541 the site Harbin, China, within the warm temperate climate zone, shown in the bottom panel,
542 and in the site Alert, Canada, within tundra climate zone, shown in the top-right panel, all
543 introduced in the previous sections. The data at these three sampling sites all indicated that

544 the curve of our new equation ($\log K_{PS}$) are superior to the equilibrium equation ($\log K_{PE}$) in
545 G/P prediction of partitioning behavior for PBDEs in global air, at the sites in warm
546 temperate, boreal, and tundra climate zones.

547 **4.2 Equilibrium state vs steady state**

548 Harner and Bidleman (1998) developed in 1998 the Eq. (3), which can predict for the first
549 time the partition coefficients of selected SVOCs in air under the condition of equilibrium
550 between gas- and particle-phases. Four years later, Harner and Shoeib (2002) used this
551 equation to predict the partitioning behavior for 11 PBDE congeners at 25 °C and 0 °C, the
552 results of which, along with the results from our new equation under steady state, are given in
553 **Fig. S17** in the Supplement. As shown in the figure, the equilibrium Eq. (3) predicted that, at
554 0 °C, the particle fraction of PBDE congeners can reach as high as ~1, which means that
555 PBDE congeners can completely sorbed to the particles. According to our new Eq. (31) under
556 steady state, however, the maximum particle fraction of PBDE congeners was about 0.42
557 when $\log K_{OA} \geq \log K_{OA2}$, which was less than half of the highest values predicted by Eq. (3).
558 In other words, we predict that the maximum particle fraction of PBDE congeners in air
559 cannot be more than 50% under steady state if $TSP < 30 \text{ mg/m}^3$ (See **Fig. S3** in the
560 Supplement). In order to support their prediction results, Harner and Shoeib (2002) used the
561 monitoring data of gaseous and particle-bound PBDEs in the Great Lakes air at $20 \pm 3 \text{ }^\circ\text{C}$
562 (Strandberg et al. 2001). However, as demonstrated in **Fig. S14**, the prediction by our new
563 equation is much accurate than those by the equilibrium equation. This suggests that PBDEs
564 in the Great Lakes atmosphere were in the steady state, not in the equilibrium state.

565 In brief, we cannot treat the gas- and particle-phases as a closed system for studying G/P
566 partitioning behavior of PBDEs, since the third compartment, the surface of the earth has to
567 be considered. If the nonequilibrium term, $\log a$, in Eq. (31) cannot be ignored, then the
568 fugacities of PBDEs in gas- and particle-phases are not equal, indicating that the system is

569 not at equilibrium but at steady state. For some less brominated PBDEs (such as BDE-17 and
570 -28) at certain temperature, the values of $\log a$ is small enough in comparison to the value of
571 $\log K_{PE}$ in Eq. (31), which is considered as a small perturbation, the system can be considered
572 as equilibrium.

573 **4.3 The maximum partition coefficient**

574 In our previous study (Li and Jia, 2014), we predicted for the first time by an empirical
575 approach the existence of a maximum partition coefficient that every PBDE congener can
576 reach, and was wrongly termed as “saturation state”. This prediction was confirmed in this
577 study by a theoretical approach. As shown in **Fig. 1**, the logarithm of the maximum partition
578 coefficient $\log K_{PSM}$ is equal to -1.53 (or $K_{PSM} = 0.03$) when $\log K_{OA} \geq \log K_{OA2}$ ($=12.5$ for all
579 PBDE congeners), or equally when the ambient temperature is smaller than or equal to t_{TH2} ,
580 which is from -34.5 °C for BDE-17 to 15 °C for BDE-183, and cannot increase linearly along
581 with increase of $\log K_{OA}$ as predicted by the straight line of $\log K_{PE}$. The difference of
582 prediction data between these two equations can be very great. For example, as shown in **Fig.**
583 **1**, the difference can reach as high as ~ 5.5 order of magnitude when $\log K_{OA} = 17$. Obviously,
584 the state in the MP domain is a steady state, but not an equilibrium state since the fugacities
585 of PBDEs in gas- and particle-phases are not equal.

586 The best example is the case for BDE-209 in the Canadian Arctic site Alert predicted by
587 our new steady equation discussed previously (**Fig. 5**). In fact, this is true for any PBDE
588 congener, not for BDE-209 only. As shown in **Fig. 1**, the blue square with a temperature
589 range of $-50 - 0$ °C could most likely be the situation for the Arctic atmosphere. **Fig. 2** shows
590 that, for the 7 PBDE congeners (BDE-66, -85, -99, -100, 153, -154, and -183), $t_{TH2} > 0$ °C.
591 Thus we predict that, as the G/P partitioning behavior is considered, these 7 PBDE congeners
592 do not behave differently in the Arctic air, and are all have the same partition coefficient,
593 $\log K_{PSM} = -1.53$. Unfortunately, there are no data for the PBDE congeners other than

594 BDE-209 available for confirmation of this prediction in the Arctic air.

595 **4.4 Comparison to the empirical equations**

596 The two empirical Eqs. (6) and (8) have been successfully applied to predict the values of K_P
597 for PBDEs in air of China and other countries in the north temperate zone and also at an
598 Arctic site in East Greenland (Li and Jia, 2014). The Eq. (31) for $\log K_{PS}$ derived in this study
599 is superior to these empirical equations $\log K_{PP}$ and $\log K_{PP}(K_{OA})$ in two ways. First, the
600 steady-state Eq. (31) was derived theoretically, and secondly, this steady-state equation can be
601 used at any ambient temperature, from equator to polar regions, while the empirical equations
602 can only be used at a temperature range of $-22\text{ }^\circ\text{C}$ to $+38\text{ }^\circ\text{C}$.

603 Comparison between steady-state Eq. (31) for $\log K_{PS}$ and empirical equations $\log K_{PP}$ given
604 by Eq. (6) and $\log K_{PP}(K_{OA})$ given by Eq. (8) in Harbin air at a temperature range of -22 to
605 $+28\text{ }^\circ\text{C}$ are presented in **Fig. 6**, and the equilibrium equation $\log K_{PE}$, given by Eq. (3), is also
606 included for comparison. It is evident from **Fig. 6** that, the straight line $\log K_{PP}$ deviates
607 apparently from the straight line $\log K_{PE}$ at $\log K_{OA} = \log K_{OA1}$, and increases linearly with
608 $\log K_{OA}$. Different lines of $\log K_{PP}(K_{OA})$ for different PBDE congeners are able to predict the
609 G/P partitioning behavior of PBDE more accurately than the straight line $\log K_{PP}$. It is
610 interesting to note that, the different lines of $\log K_{PP}(K_{OA})$ for different PBDE congeners
611 change their trends along with the single line of steady-state equation $\log K_{PS}$, which is the
612 best equation that can be used to predict the G/P partitioning behavior for all PBDE
613 congeners and at all ranges of ambient temperature.

614 **4.5 The limitation of applications**

615 In order to derive Eq. (31), several assumptions were made, which include that, the G/P
616 partitioning reached steady state, the annual rainfall was 0.5 m yr^{-1} , $f_{OM} = 0.1$, $C = 5$, and
617 some others. This equation, however, has been successfully applied in all situations that we
618 discussed in this study, in which some of the assumptions were not satisfied. We should be

619 aware, however, that the situations in which some abnormal conditions exist, such as heavy
620 wind, heavy rains, or the sampling sites close to e-waste or PBDE manufactures, should be
621 best treated separately. For example, as described in the previous section, the constant C
622 should be changed from 5 to 50 in Eq. (5) for Site Waliguan. The reason why much higher
623 value of C was used at this site is possibly due to the high wind speed there. At Waliguan,
624 where annual average wind speed reaches 4.6 m/s, and the northwest wind with speed > 10
625 m/s being quite often in the winter and spring seasons
626 (<http://gaw.empa.ch/gawsis/reports.asp?StationID=12>), much higher than the other sites; and
627 the air sampler was installed at the top of the mountain (see Supplementary Fig. S18),
628 suffering from the highest wind speed without any blocks in the area, causing the higher
629 value of C than those at the other 14 sites. An analytic equation may exist to relate the
630 parameter C and the wind speed (and possibly other factors too), but this equation is not
631 available at present and planned for future study. The case for the Chinese e-waste site is also
632 worth to mention. Our equation cannot be used at the e-waste sites and most likely at the
633 PBDE manufacturers as well since the emissions of PBDEs at these sites could be too large
634 and also variable with time so that the steady state cannot be reached or maintained

635 It should be borne in mind that the steady state discussed here is still an idealized scenario
636 since only dry and wet depositions were discussed in the study, other factors, such as
637 humidity and artifacts, will also play roles to a certain extent to affect the G/P partitioning. As
638 anticipated, results obtained from this study do not perfectly fit monitoring data. However,
639 this study revealed the major internal factors governing the gas-particle partitioning processes
640 for PBDEs, and explicated how these processes can be more correctly treated as being in
641 steady state rather than in equilibrium state. At least, the steady-state model, not the
642 equilibrium-state model, should be applied to analyze the gas-particle relationship of SVOCs,
643 such as PBDEs. Further study for other SVOCs, like PCBs and PAHs, is on the way.

644

645 **The Supplement related to this article is available online at**

646

647 **Author contribution:**

648 Y.F.L. designed the research on the new theory of G/P partitioning of PBDE in air under
649 steady state; Y.F.L., W.L.M., and M.Y. performed the research; Y.F.L., W.L.M, and M.Y.
650 analyzed data; and Y.F.L. wrote the paper, with input from W.L.M., and M.Y.

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652

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780

781 **Figure captions**

782 **Figure 1.** Variation of $\log K_{PE}$ and $\log K_{PS}$ as functions of $\log K_{OA}$ with a temperature range of
783 $-50 - +50$ °C. Two threshold values of $\log K_{OA}$ ($\log K_{OA1}$ and $\log K_{OA2}$) are also shown,
784 which divide the space of $\log K_{OA}$ into three domains: the equilibrium (EQ), the
785 nonequilibrium (NE), and the maximum partition (MP) domains. The three squares
786 designate the $\log K_P$ - $\log K_{OA}$ graphs with three different temperature ranges: $0 - +50$ °C,
787 $-30 - +30$ °C, an $-50 - 0$ °C, representing the tropical and subtropical climate zones,
788 warm temperate climate zone, and boreal and tundra climate zones, respectively.

789 **Figure 2.** The first and second threshold temperatures, t_{TH1} and t_{TH2} for 10 PBDE congeners,
790 which divide the temperature space into the same 3 domains (EQ, NE, and MP).

791 **Figure 3.** The range of $\log K_{OA}$ (the left axis) and the threshold temperatures (the right axis)
792 for 10 PBDE congeners in Harbin air at a temperature range of -22 to $+28$ °C. The
793 ranges of $\log K_{OA}$ for the 10 PBDE congeners are given by the vertical bars. The 2
794 horizontal light blue dashed lines give the 2 threshold values of $\log K_{OA1}$ and $\log K_{OA2}$,
795 and the red diamonds and red squares present respectively the two corresponding
796 threshold temperatures, t_{TH1} and t_{TH2} . The former divides the space of $\log K_{OA}$ (the left
797 axis) and the later divides the temperature space (the right axis) into three domains: the
798 EQ domain, the NE domain, and the MP domain. Thus the PBDE congeners
799 (homologues) in Harbin air can be segregated into 3 groups; BDE-17 and -28 (3-Br
800 homologue) as equilibrium EQ-group, BDE-47 and -66 (4-Br homologue) as
801 semiequilibrium SE-group, and others (>4-Br homologues) as nonequilibrium
802 NE-group.

803 **Figure 4.** The $\log K_P$ - $\log K_{OA}$ diagram for the 10 PBDE congeners in Harbin air at a
804 temperature range of -22 to $+28$ °C. The EQ Group includes BDE-17 and -28, the SE
805 Group contains BDE-47 and -66, and the rests belong to NQ Group. The range of

806 $\log K_{OA}$ for each group and their corresponding $\log K_P - \log K_{OA}$ diagram are also shown.
807 The $\log K_P - \log K_{OA}$ diagram for the EQ Group, boned by 2 purple dashed lines, is
808 mainly in the EQ domain, with a small portion in NE domain; the $\log K_P - \log K_{OA}$
809 diagram for the SE Group, contained by 2 green dashed lines, is mainly in the NE
810 domain, with a small portion in MP domain; and the $\log K_P - \log K_{OA}$ diagram for the NE
811 Group, formed by the 2 blue dashed lines, is mainly in the NE and MP domains.

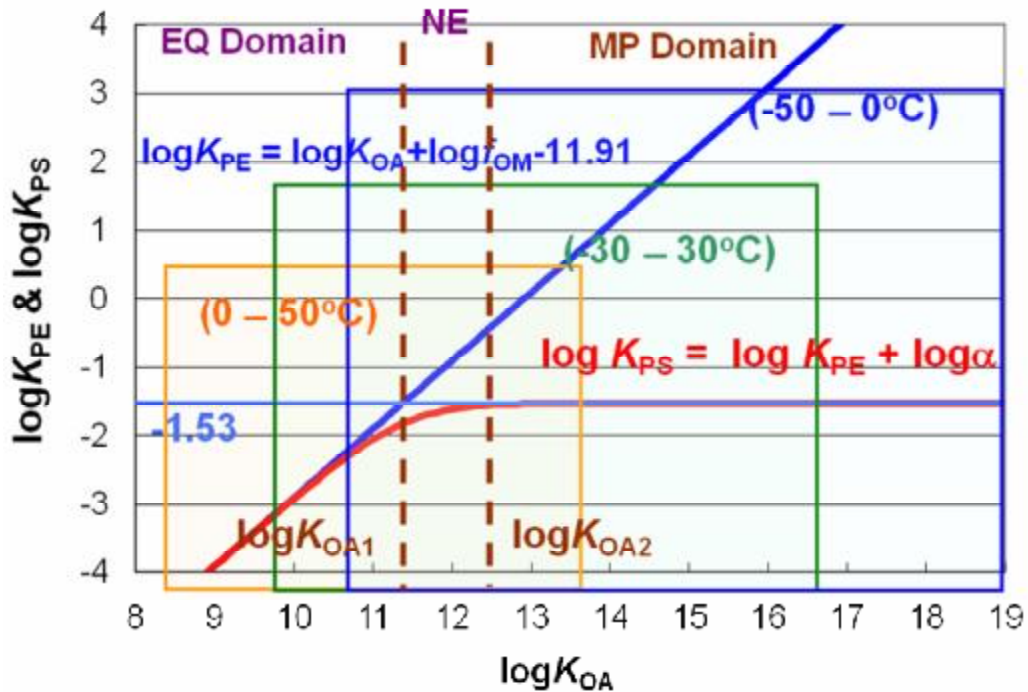
812 **Figure 5.** The temporal trends of concentrations of BDE-209 in the Arctic air in gas + particle
813 phase (blue line) and in particle phase (green line) at Alert, Canada from 2007 to 2009
814 (NCP 2013). The purple triangles and red diamonds are the values of f and $\log K_P$ of
815 BDE-209, respectively, calculated using the concentration data, and match well the
816 values of f_{PSM} (=0.23) and $\log K_{PSM}$ (-1.53), respectively ($TSP = 10 \text{ } \mu\text{g m}^{-3}$ was
817 assumed).

818 **Figure 6.** Variation of $\log K_{PS}$ (the thick red line, given by Eq. (31)), $\log K_{PE}$ (the thick dark
819 green line, given by Eq. (3)), and $\log K_{PP}$ (the thick pink line, given by Eq. (6)) as
820 functions of $\log K_{OA}$. The functions of $\log K_{PP}(K_{OA})$ (the thin lines, given by Eq. (8))
821 versus $\log K_{OA}$ for the 10 PBDE congeners in Harbin air at a temperature range of -22 to
822 +28 °C are also included.

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825 **Figures**

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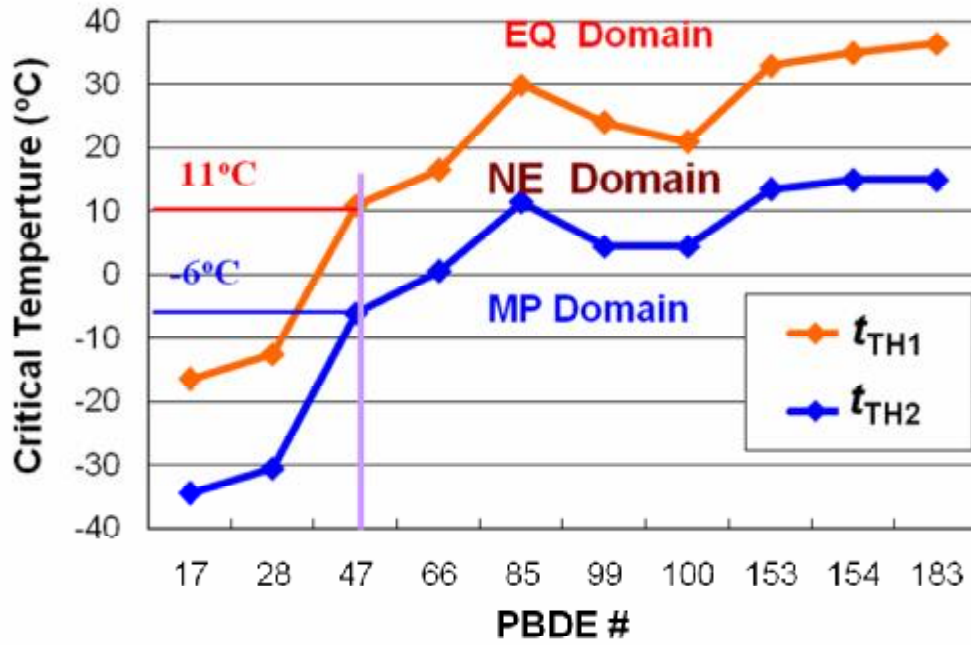


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 829 $-50 - +50$ °C. Two threshold values of $\log K_{OA}$ ($\log K_{OA1}$ and $\log K_{OA2}$) are also shown, which
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 831 (NE), and the maximum partition (MP) domains. The three squares designate the
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 834 zone, and boreal and tundra climate zones, respectively.

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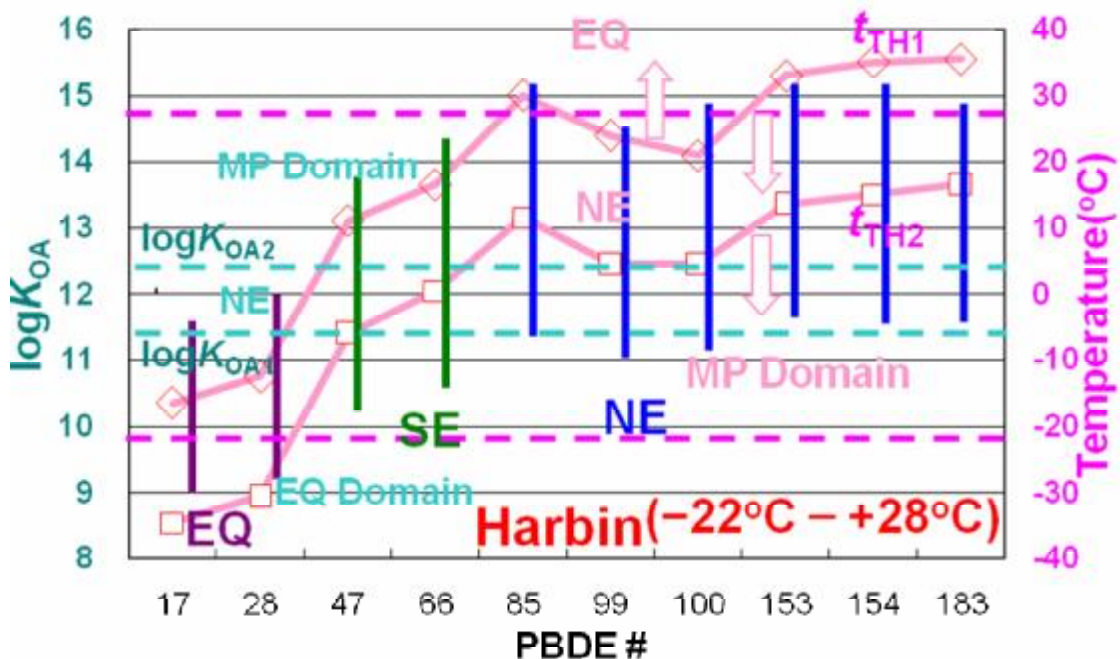
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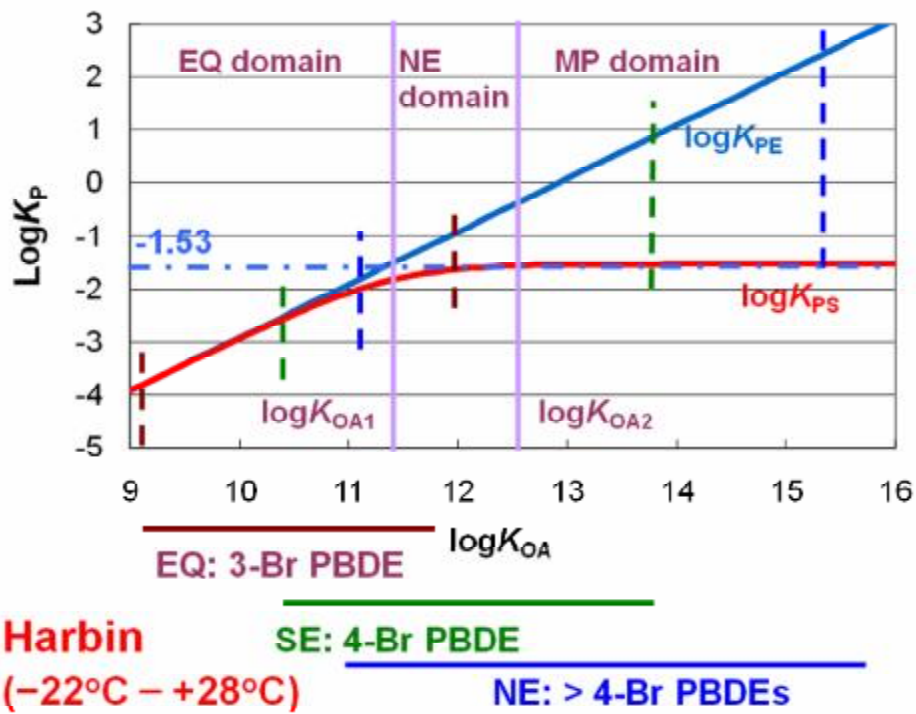
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 849 space (the right axis) into three domains: the EQ domain, the NE domain, and the MP domain.
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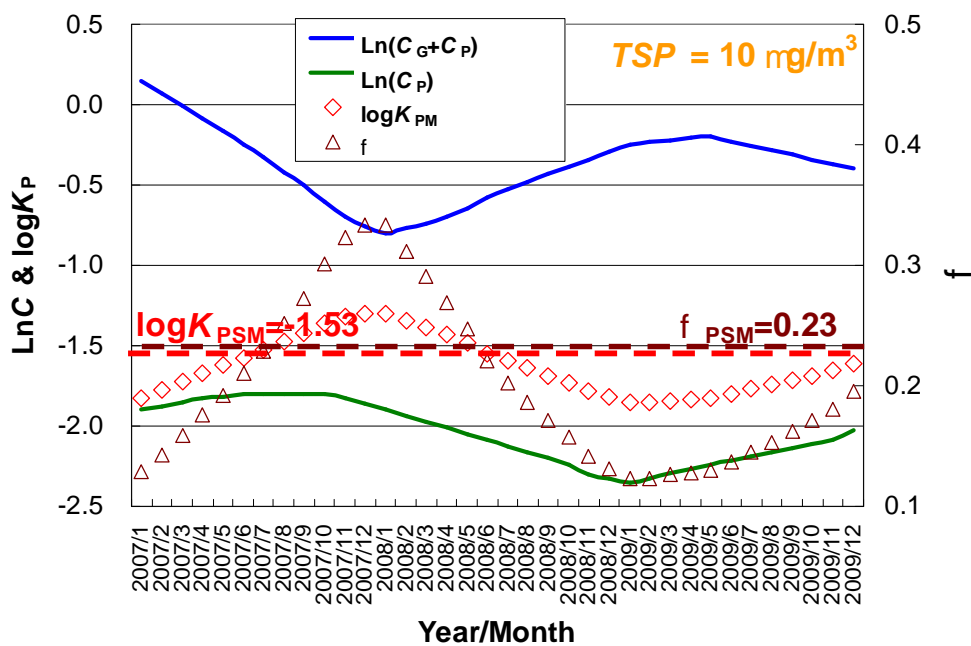
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864 green dashed lines, is mainly in the NE domain, with a small portion in MP domain; and the
865 $\log K_P - \log K_{OA}$ diagram for the NE Group, formed by the 2 blue dashed lines, is mainly in the
866 NE and MP domains.

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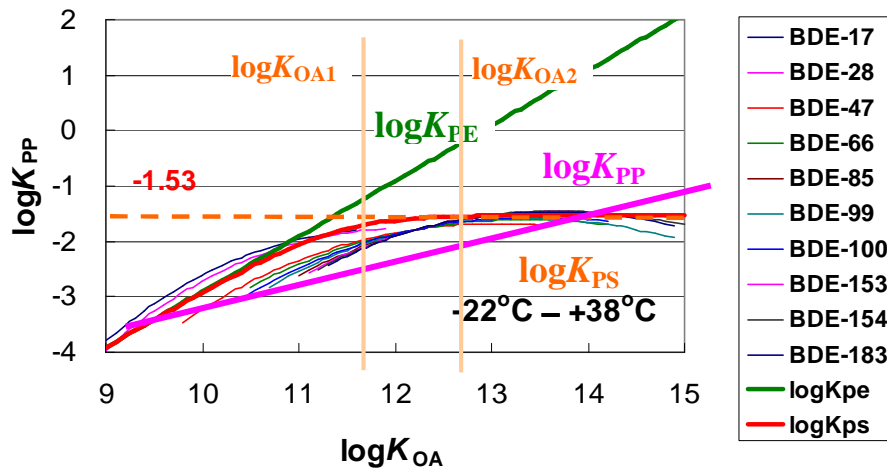
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 884 PBDE congeners in Harbin air at a temperature range of -22 to $+28$ °C are also included.

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