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HOW DOES BDE-209 ENTER THE ARCTIC AIR? BY THE MOVEMENT OF AIR OR PARTICLES?

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Introduction

It is widely believed that BDE-209 in air is almost entirely sorbed on particles due to its low vapor pressure (P_L) or high octanol-air partition coefficient (K_{OA})[1-4]. This point of view has a profound influence on projections of the environmental fate (e.g., LRAT) of this compound. It has been suggested that BDE-209 would not distribute widely through the atmosphere despite intense use in the industrialized world[1,5] and would be difficult to transport to the Arctic via LRAT[5].

Monitoring data, however, showed another story[6,7], which identified BDE-209 in atmospheric particle samples collected at various sites in North America, including some sites far away from populated and industrial centers. More importantly, BDE-209 was also found in Arctic air particulates[8] and in ice cores from Holtedahlfonna, Svalbard, Norway at concentrations many times greater than the more volatile BDE-49[5], and, most significantly, a high proportion of BDE-209 in both gas- and particle-phases was found in Arctic air[9].

These observations suggest that BDE-209 widely distributes in 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 seasons[10].

The main objectives of this work are to study G/P partitioning behavior of BDE-209 in global air and to answer the question “Is long range atmospheric transport of BDE-209 really governed by the movement of particles?”

Materials and Methods

Prediction equations

Partitioning of semi-volatile organic compounds (SVOCs) between gas- and particle-phases is usually presented by the partition quotient, K_P ($m^3 \cdot \mu g^{-1}$), given by[11]

$K_P = (C_P / TSP) / C_G$ (1)

where C_G and C_P are concentrations of gas- and particle- phases (in $pg \cdot m^{-3}$ of air), respectively, and TSP is the concentration of total suspended particle in air ($\mu g \cdot m^{-3}$).

An equation to calculate the equilibrium partition coefficient, K_{PE}, has been derived as[12]

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

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

In our previous work[13], we developed an equation under steady state by including the wet and dry deposition of particles in studying the G/P partition of PBDEs:

$\log K_{PS} = \log K_{PE} + \log \alpha = \log K_{PE} - \log (1+4.18 \times 10^{-11} f_{OM} K_{OA})$ (3)

Threshold values of log Koa

As described in Li et al[13], two threshold values of log K_{OA} (log K_{OA1} = 11.4, log K_{OA2} = 12.5) were used to describe the partitioning behavior of PBDEs. The two threshold values produce three partitioning domains: The EQ (equilibrium) domain when log K_{OA} < log K_{OA1}; the NE (non-equilibrium) domain when log $K_{OA} \geq$ log K_{OA1}; and the MP (maximum partition) domain when log $K_{OA} \geq$ log K_{OA2} (log K_{PSM} = -1.53). The G/P partition coefficients of PBDEs as functions of log K_{OA} calculated by two equations are presented in Figure 1. In contrast to prior treatments relying on equilibrium calculations, we predict that the values of log K_P reach the MP domain with log K_{PSM} = -1.53 when log $K_{OA} \geq$ log K_{OA2}, instead of linearly increasing along with log K_{OA}.

Results and Discussion

BDE-209 in global air: Prediction

The range of log K_{OA} for BDE-209 at the temperature ranged from 50 to -50°C is approximately 14~20, much larger than log K_{OA2}. Thus we make a prediction that the logarithm of partition quotient of BDE-209 is a constant (-1.53) at and any sampling site with any ambient temperature (from 50 to -50°C).

BDE-209 in global air: Monitoring data

We have collected G/P partition data for BDE-209 reported in the open literature to verify our prediction as discussed below. We define a maximum partition range (MPR) as $-1 \geq \log K_{PSM} \geq -2$ in our study, which, we expect that the values of log K_{PM} for BDE-209 should mainly be within, and would not depend on log K_{OA} and the ambient temperature.

Figures 2-5 present variation of log K_{PM} as functions of log K_{OA} for BDE-209 in Paris, France[14], Izmir Bay, Turkey[15], Zurich, Switzerland[3], and the Arctic[9], respectively, all indicating that our prediction match the monitoring data well.

The Arctic provides a particularly good location to test the steady state theory due to the low temperature which can produce high values of log K_{OA} not only for PBDEs but also for other SVOCs. Indeed, as shown in Fig. 5, the majority of logarithm of partition quotients of BDE-209 (log K_{PM}) in Arctic atmosphere are in the MPR, and do not correlate with temperature ($R^2 = 0.04$).

How does BDE-209 enter the Arctic

In this paper, we predicted the partitioning behaviour of BDE-209 in air using our steady-state equation (3) and the results matched the monitoring data well. This study clearly indicates that the proportion of BDE-209 in gas phase is much higher than those assumed or reported in the literature. Comparison of equilibrium and steady-state equations indicates that BDE-209 is under steady state but not at equilibrium under any ambient temperature conditions. In these cases, the logarithm of its partition quotient is a constant (-1.53). The BDE-209 gaseous and particulate phase fractions in air, however, are not constants, but depend on the values of TSP. The steady-state prediction is confirmed by monitoring data worldwide as reported in the literature.

According to the results provided here, 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 gas phase, especially at low TSP concentrations. From a global perspective, gaseous BDE-209 is abundant in air (87.1% when TSP = 5 $\mu g \cdot m^{-3}$ to 14.5% when TSP = 200 $\mu g \cdot m^{-3}$ from our calculation), and is the dominant congener of PBDEs 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[16,17].

Acknowledgment

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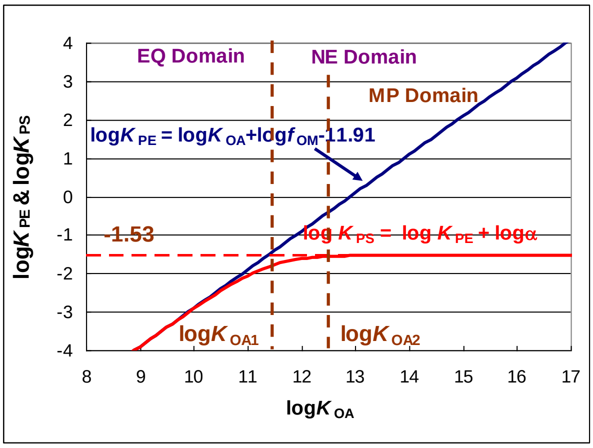
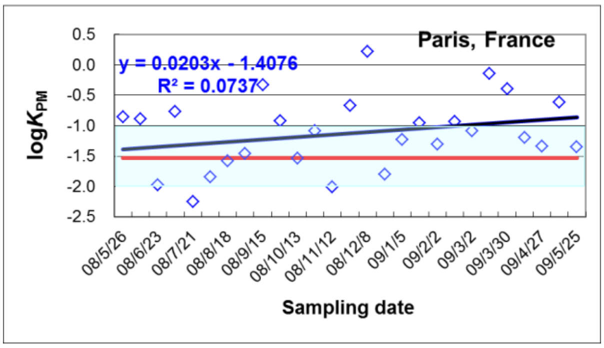


Figure 1. The G/P partition coefficients of PBDEs as functions of $\log K_{OA}$ calculated by two equations.



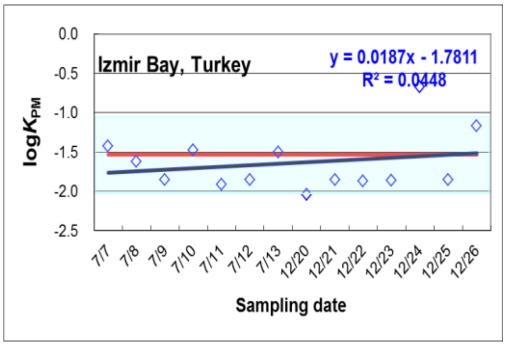
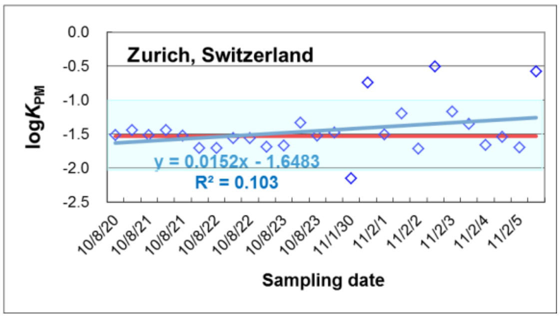


Figure 2. Variation of $\log K_{PM}$ for BDE-209 versus sampling date in downtown Paris, France. The monitoring data are[14]. Assuming that the values of *TSP* in this city were 50 μg/m^3 in summer and 100 μg/m^3 in winter

Figure 3. The values of $\log K_P$ of BDE-209 versus sampling date in Izmir Bay, Turkey in 2005[15].



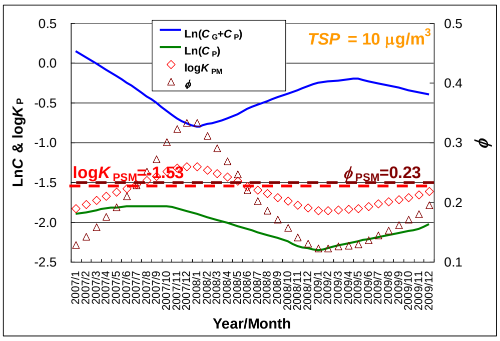


Figure 4: The values of $\log K_{PM}$ of BDE-209 versus sampling date in Zurich, Switzerland in 2010[3]. Assuming that the values of *TSP* in this city were 30 μg/m^3 in summer and 50 μg/m^3 in winter.

Figure 5: The temporal trends of concentrations of BDE-209 in the Arctic air in gas and particle phases (blue line) and in particle phase (green line) at Alert, Canada from 2007 to 2009[9]. The purple triangles and red diamonds are the values of ϕ and $\log K_P$ of BDE-209, respectively, calculated using the concentration data, and match well the values of ϕ_{PSM} (=0.23) and $\log K_{PSM}$ (-1.53).