



Temperature dependence of the particle/gas partition coefficient: An application to predict indoor gas-phase concentrations of semi-volatile organic compounds



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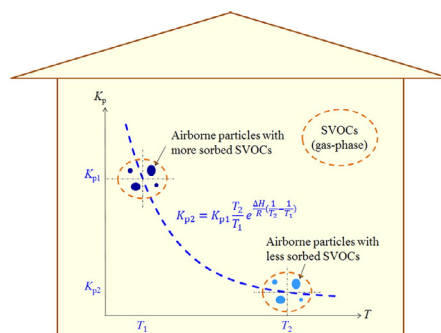
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HIGHLIGHTS

- A theoretical relationship between K_p and temperature was developed.
- The relationship was based on the SVOC absorptive mechanism.
- The temperature impact was quantified by a dimensionless analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

The indoor gas-phase concentrations of semi-volatile organic compounds (SVOCs) can be predicted from their respective concentrations in airborne particles by applying the particle/gas partitioning equilibrium. The temperature used for partitioning is often set to 25 °C. However, indoor temperatures frequently differ from this reference value. This assumption may result in errors in the predicted equilibrium gas-phase SVOC concentrations. To improve the prediction model, the temperature dependence of the particle/gas partition coefficient must be addressed. In this paper, a theoretical relationship between the particle/gas partition coefficient and temperature was developed based on the SVOC absorptive mechanism. The SVOC particle/gas partition coefficients predicted by employing the derived theoretical relationship agree well with the experimental data retrieved from the literature ($R > 0.93$). The influence of temperature on the equilibrium gas-phase SVOC concentration was quantified by a dimensionless analysis of the derived relationship between the SVOC particle/gas partition coefficient and temperature. The predicted equilibrium gas-phase SVOC concentration decreased by between 31% and 53% when the temperature was lowered by 6 °C, while it increased by up to 750% when the indoor temperature increased from 15 °C to 30 °C.

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1. Introduction

Most semi-volatile organic compounds (SVOCs), such as phthalates and polybrominated diphenyl ethers (PBDEs), have widespread consumer use and environmental occurrence, and some are suspected to be neurotoxic or endocrine-disrupting chemicals (Rudel et al., 2003; Salapasidou et al., 2011; Blanchard et al., 2014; Fournier et al., 2014; Bamai et al., 2014; Dodson et al., 2015). SVOCs in indoor environments appear in the gas-phase, on airborne particles and in dust settled on floors and other surfaces (Weschler and Nazaroff, 2008). If the gas-phase SVOC concentrations in an indoor environment have not been measured, they can be predicted from the measured concentrations in another phase. Unknown gas-phase SVOC concentrations may be predicted from the measured SVOC concentrations in airborne particles or settled dust, assuming that the partition equilibrium is reached between the different phases (Weschler et al., 2008). The partitioning of SVOCs between airborne organic particles and the gas-phase at equilibrium is characterized by the SVOC particle/gas partition coefficient, K_p , which can be estimated with the saturation vapor pressure of the pure sub-cooled liquid, p_L^0 , and the octanol/air partition coefficient, K_{OA} (Weschler et al., 2008). The K_p value is needed to predict the unknown gas-phase SVOC concentration from its measured concentration in airborne particles. K_p values can be retrieved from the literature for a limited number of SVOCs and must be calculated from the K_{OA} or p_L^0 values for the many SVOCs for which no values have been measured. Moreover K_p depends on temperature (Pankow, 1987).

Adsorption/desorption and absorption/desorption between the gas-phase and airborne particles constitute the two partitioning mechanisms for organic compounds. Previous studies show that the structure of a suspended airborne particle can be described as either a solid core covered by a SVOC liquid film or a porous material in which the pores are filled with SVOC liquid (Husar and Shu, 1975; Ancelet et al., 2011; Liu et al., 2013). Therefore, absorption/desorption may be dominant for SVOCs with low volatility.

In previous studies, the adsorptive models of the particle/gas partitioning mechanism for organic compounds have assumed physical adsorption and desorption of organic compounds between the gas-phase and airborne particles (Pankow, 1987). Thus, a theoretical linear relationship can be described between $\log_{10}K_p$ and T^{-1} (Pankow, 1987; Boethling and Mackay, 2000; Finlayson-Pitts and Pitts, 2000; Schwarzenbach et al., 2003; Seinfeld and Pandis, 2006) and between $\log_{10}K_{OA}$ and T^{-1} (T in degrees Kelvin) (Harner and Mackay, 1995) for organic compounds. Empirical relationships have also been established based on regressions of the experimental data of $\log_{10}K_p$ and T^{-1} for dioxins and furans, polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), and polycyclic aromatic hydrocarbons (PAHs) (Kaupp and McLachlan, 1999). In addition, several studies have addressed the empirical relationships between $\log_{10}K_{OA}$ and T^{-1} for some chlorobenzenes (Harner and Mackay, 1995; Shoeib and Harner, 2002; Li et al., 2006), methylsiloxanes (Xu and Kropscott, 2013), PCNs (Li et al., 2006), pesticides (Harner and Mackay, 1995; Shoeib and Harner, 2002; Li et al., 2006; Odabasi and Cetin, 2012), PAHs (Li et al., 2006; Harner and Bidleman, 1998; Odabasi et al., 2006a, 2006b; He and Balasubramanian, 2009), PCBs (Harner and Mackay, 1995; Li et al., 2006; He and Balasubramanian, 2009; Harner and Bidleman, 1996), and PBDEs (Li et al., 2006; Chen et al., 2003).

However, considering the absorption mechanism, the theoretical equations between K_p and p_L^0 or K_{OA} , which were determined by Pankow (1994) and Finizio et al. (1997), respectively, consist of temperature-independent constants and temperature-dependent parameters, e.g., K_{OA} . Thus, the temperature impact on K_p is associated with the temperature impact on K_{OA} . One limitation in the calculation of the theoretical equations is that some of the physical parameters of the equations, e.g., the activity coefficient of the absorbing SVOCs in airborne particles, have not been fully studied for most SVOCs at different temperatures and their values remain assumed in the calculation

(Harner, 1998; Weschler and Nazaroff, 2010). The empirical relationships between K_p , K_{OA} or p_L^0 in the literature, which are based on regressions of experimental data, were generally obtained at a reference temperature, e.g., 25 °C (Finizio et al., 1997; Naumova et al., 2003). No previous study has indicated whether the regression constants in the empirical equations obtained at a reference temperature can be applied to other temperature values. Because the theoretical relationship between K_p and temperature based on the absorptive mechanism has not been fully studied, the difference between the real indoor temperature and the temperature used in the literature for developing the empirical equation may lead to errors in the predicted gas-phase SVOC concentrations.

The objectives of this study were to (1) develop a theoretical relationship between the particle/gas absorptive partition coefficient and temperature for SVOCs and (2) quantitatively analyze the extent to which the indoor temperature influences the precision of the predicted SVOC concentrations in the gas-phase from the concentrations in the airborne particles.

2. Material and methods

2.1. Theoretical derivation

The equilibrium gas-phase SVOC concentration is defined by

$$C_g = \frac{F/TSP}{K_p} \quad (1)$$

where F (ng/m^3) and C_g (ng/m^3) are the equilibrium concentrations of SVOCs in the airborne particles and in the gas-phase, respectively, TSP ($\mu\text{g}/\text{m}^3$) is the total concentration of suspended airborne particles, and K_p is the particle/gas partition coefficient ($\text{m}^3/\mu\text{g}$).

According to the absorptive mechanism for SVOCs, Pankow derived the following particle/gas partition coefficient K_p ($\text{m}^3/\mu\text{g}$) (Pankow, 1994):

$$K_p = \frac{f_{om}RT}{MW_{om}\alpha p_{L,T}^0 10^6} \quad (2)$$

where f_{om} is the weight fraction of the airborne particles absorbing organic materials; R (8.314 J/(mol K)) is the gas constant; T (K) is the temperature, MW_{om} (g/mol) is the mean molecular weight of the absorbing organic material; α is the activity coefficient of the compound in the organic material phase; and $p_{L,T}^0$ (Pa) is the saturation vapor pressure of the pure sub-cooled liquid compound at a temperature T .

The phase transition of a single constituent between the liquid phase and the gas-phase can be characterized by the Clausius-Clapeyron relationship:

$$\frac{dp_{L,T}^0}{dT} = \frac{\Delta H}{T\Delta V} \quad (3)$$

where ΔH (J/mol) is the phase change enthalpy; and ΔV (m^3/mol) is the change in the volume of the constituent during the phase change. The phase change enthalpies for SVOCs can be retrieved from the literature (Acree and Chickos, 2010).

We assume that (1) the change in the SVOC volume in the liquid phase is negligible compared to the change in the gas-phase, (2) the gas-phase containing SVOCs is an ideal gas, and (3) the variation in the phase change enthalpy for SVOCs is negligible at room temperature. Thus, the change in the volume of the SVOC during the phase change can be expressed as

$$\Delta H = \frac{RT}{p_{L,T}^0} \quad (4)$$

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