



Comparison of prediction methods for octanol-air partition coefficients of diverse organic compounds



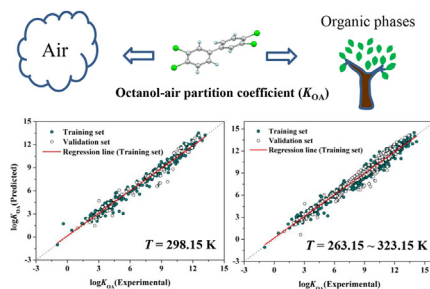
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HIGHLIGHTS

- 939 K_{OA} data for 379 compounds at 263.15–323.15 K are collected from literature.
- Three methods are systematically developed and evaluated for K_{OA} prediction.
- An optimal QSAR model is recommended for predicting K_{OA} at various temperatures.
- It is the first time to use the ab initio SM8AD solvation model for K_{OA} prediction.

GRAPHICAL ABSTRACT



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ABSTRACT

The octanol-air partition coefficient (K_{OA}) is needed for assessing multimedia transport and bio-accumulability of organic chemicals in the environment. As experimental determination of K_{OA} for various chemicals is costly and laborious, development of K_{OA} estimation methods is necessary. We investigated three methods for K_{OA} prediction, conventional quantitative structure–activity relationship (QSAR) models based on molecular structural descriptors, group contribution models based on atom-centered fragments, and a novel model that predicts K_{OA} via solvation free energy from air to octanol phase (ΔG_{O}^0), with a collection of 939 experimental K_{OA} values for 379 compounds at different temperatures (263.15–323.15 K) as validation or training sets. The developed models were evaluated with the OECD guidelines on QSAR models validation and applicability domain (AD) description. Results showed that although the ΔG_{O}^0 model is theoretically sound and has a broad AD, the prediction accuracy of the model is the poorest. The QSAR models perform better than the group contribution models, and have similar predictability and accuracy with the conventional method that estimates K_{OA} from the octanol–water partition coefficient and Henry's law constant. One QSAR model, which can predict K_{OA} at different temperatures, was recommended for application as to assess the long-range transport potential of chemicals.

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1. Introduction

The octanol-air partition coefficient (K_{OA}), defined as the equilibrium partitioning of a chemical between the octanol and air phase (Harner and Mackay, 1995), is used as surrogate for the

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partition of chemicals between air and environmental organic phases (Harner and Bidleman, 1996, 1998; Harner and Shoeib, 2002; Prevedouros et al., 2004a, 2004b; Kelly, 2007; Thuens et al., 2008; Dreyer et al., 2009; Lamon et al., 2009). K_{OA} is needed for assessing bioaccumulation of organic chemicals in marine mammalian, terrestrial mammalian and human food chain (Kelly, 2007). The establishment of multimedia environmental models (Prevedouros et al., 2004a, 2004b; Lamon et al., 2009), and especially the models that evaluate the global distribution, transport and fate of persistent organic pollutants (POPs), requires the K_{OA} data (Prevedouros et al., 2004b).

K_{OA} values for chemicals of several classes have been determined by the methods of generator column (Harner and Mackay, 1995; Harner and Bidleman, 1996, 1998; Harner et al., 2000; Harner and Shoeib, 2002; Shoeib and Harner, 2002; Thuens et al., 2008; Dreyer et al., 2009), fugacity meter (Komp and McLachlan, 1997), solid-phase microextraction (SPME) (Treves et al., 2001), head-space gas-chromatographic (HS-GC) (Abraham et al., 2001) and GC retention index (Gruber et al., 1997; Zhang et al., 1999; Su et al., 2002; Wania et al., 2002; Lei et al., 2004; Odabasi et al., 2006; Zhao et al., 2009, 2010). However, to the best of our knowledge, all together 939 K_{OA} values for 379 chemicals have been experimentally determined, in contrast to the >140 000 chemicals that have been pre-registered by the REACH regulation. The strong temperature dependence of K_{OA} and the variability of ambient temperature further increase the data requirement of K_{OA} (Harner and Bidleman, 1996). As experimental determination of K_{OA} is costly (requirement of special equipment and authentic chemical standards) and laborious, efforts have been devoted to develop K_{OA} prediction methods for the needs of screening the large and ever-increasing number of synthesized chemicals (Binetti et al., 2008).

The methods for K_{OA} prediction include the straight forward estimation with the octanol–water partition coefficient (K_{OW}) and Henry's law constant K_H (K_{OW} – K_H method) (Meylan and Howard, 2005), the quantitative structure–activity relationship (QSAR) methods (Chen et al., 2002a, 2002b, 2003a, 2003b, 2003c; Staikova et al., 2004; Zhao et al., 2005; Li et al., 2006), and the linear free energy relationship (LFER) models (Abraham, 1993; Abraham et al., 2001). Among the QSAR models, some are group contribution models that summarizes the contributions from atom-centered fragments (Li et al., 2006), and some are conventional QSAR models (Chen et al., 2002a, 2002b, 2003a, 2003b, 2003c; Zhao et al., 2005) based on theoretical molecular structural descriptors.

In 2007, the OECD issued a guidance document on QSAR model development and validation (OECD, 2007). Generally, many previous QSAR models for K_{OA} prediction do not fully comply with the OECD guidelines: some lack validation of the models (Zhao et al., 2005), and some lack definition of the applicability domain (AD) (Chen et al., 2002a, 2003a, 2003b). In addition, many models lack the ability of predicting K_{OA} at different environmental temperatures (T) (Chen et al., 2002b, 2003c; Zhao et al., 2005), which limits the practical application of the models as the strong temperature dependence of K_{OA} makes the parameter very important for assessing the long-range transport potency of POPs (Halsall et al., 2001). Thus, it became necessary to develop new K_{OA} prediction models that satisfy the OECD guidelines.

The LFER approach by Abraham et al. is reliable for predicting equilibrium partitioning in any solvent phase, whereas the experimental descriptors for each solute have to be pre-determined accurately based on other partition coefficients. For many environment relevant compounds, e.g., dioxins, brominated diphenyl ethers as well as fluorinated compounds, the availability of such descriptors is currently limited (Endo and Goss, 2014). The QSAR methodology is attractive as QSAR models generate results with molecular structures and are applicable for regulatory purposes

(2007). However, the utility of QSARs is constrained as they strongly rely on experimental databases, and are only valid for compounds within the AD. Theoretically, K_{OA} can otherwise be calculated directly from the solvation free energy of a chemical from air to octanol phase (ΔG_O^0), and this method is inherently applicable to all chemicals by definition. Under standard thermodynamic conditions,

$$\Delta G_O^0 = -RT \ln K_{OA}, \text{ or } \log K_{OA} = -\frac{\Delta G_O^0}{2.303RT} \quad (1)$$

where R ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) is the gas constant, and T is absolute temperature (K).

In recent years, the calculation methods on solvation free energy (ΔG_O^0) (Tomasi et al., 2005) have been gradually improving, including some popular approaches as the SMx model developed by Truhlar et al. (Thompson et al., 2004), the COSMO-RS model by Klamet et al. (Klamt, 1995), and the polarizable continuum model (PCM) by Tomasi et al. (Miertus et al., 1981). For example, the SM8 model (Marenich et al., 2007) was developed recently and applied to compute ΔG_O^0 and it outperformed the former SMx series models as well as the PCM model due to inclusion of solvation free energies of ions in nonaqueous solvent in the parametrization (Marenich et al., 2007). One important distinction of the solvation model method from QSARs is that this method is able to estimate K_{OA} ab initio, namely, relying only on the molecular structures (Marenich et al., 2007). Thus, we hypothesized that ΔG_O^0 can be accurately calculated by the latest solvation model, and can be employed to predict K_{OA} for non-ionizable organic chemicals.

It was the purpose of this study (a) to verify a new K_{OA} prediction method based on the quantum mechanics calculated ΔG_O^0 values; (b) to develop new QSAR and group contribution models; and (c) to compare the different K_{OA} prediction methods (including the K_{OW} – K_H method) according to the OECD guidelines so as to recommend an appropriate method for practical application. The currently available experimental K_{OA} values for diverse organic compounds were collected, and employed for model establishment and validation.

2. Materials and methods

2.1. Data compilation

939 K_{OA} values determined at different temperatures (263.15–323.15 K) for 379 compounds were collected from well-documented literature (Harner and Mackay, 1995; Harner and Bidleman, 1996; Gruber et al., 1997; Komp and McLachlan, 1997; Harner and Bidleman, 1998; Zhang et al., 1999; Harner et al., 2000; Abraham et al., 2001; Treves et al., 2001; Harner and Shoeib, 2002; Shoeib and Harner, 2002; Su et al., 2002; Wania et al., 2002; Lei et al., 2004; Odabasi et al., 2006; Thuens et al., 2008; Dreyer et al., 2009; Zhao et al., 2009, 2010). The data set covers compounds of various categories, e.g., about 52 polychlorinated naphthalenes (PCNs), 33 polychlorinated biphenyls (PCBs), 32 polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs), 59 polybrominated diphenyl ethers and their hydroxylated/methoxylated analogues (OH/CH₃O-PBDEs), 16 polycyclic aromatic hydrocarbons (PAHs), 18 organochlorine pesticides (OCPs), 17 fluorinated compounds, 41 alkanes/alkenes, 25 alcohols/ethers, 13 ketones/aldehydes, 18 acids/esters. All the $\log K_{OA}$ values together with their experimental determination methods are listed in Table S1 of the Supporting Information (SI). The $\log K_{OA}$ values at 298.15 K range from –0.95 for tetrafluoromethane to 13.18 for 6-hydroxy-2,3,3',4,4',5'-hexabromodiphenyl ether. It should be noted that these experimental $\log K_{OA}$ values are prone to different levels of

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