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Review

Predictability of physicochemical properties of polychlorinated dibenzo-*p*-dioxins (PCDDs) based on single-molecular descriptor models☆

Minhee Kim [a], Loretta Y. Li [a, *], John R. Grace [b]

[a] Department of Civil Engineering, University of British Columbia, 6250 Applied Science Lane, Vancouver, BC, V6T 1Z4 Canada
[b] Department of Chemical and Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, BC, V6T 1Z3 Canada

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins (PCDDs) are of global concern due to their persistence, bioaccumulation and toxicity. Although the fate of PCDDs in the environment is determined by their physical-chemical properties, such as aqueous solubility, vapor pressure, octanol/water-, air/water-, and octanol/water-partition coefficients, experimental property data on the entire set of 75 PCDD congeners are limited. The quantitative structure-property relationship (QSPR) approach is applied to predict the properties of all PCDD congeners. Experimental property data available from the literature are correlated against 16 molecular descriptors of five types. Reported and newly developed QSPR models for PCDDs are presented and reviewed. The values calculated by the best QSPRs are further adjusted to satisfy fundamental thermodynamic relationships. Although the single-descriptor models with chlorine number, molar volume, solvent accessible surface area and polarizability are based on good statistical results, these models cannot distinguish among PCDDs having the same chlorine number. The QSPR model based on the hyper-Wiener index of quantum-chemical descriptor gives useful statistical results and is able to distinguish among congeners with the same chlorine number, as well as satisfying thermodynamic relationships. The resulting consistent properties of the 75 PCDD congeners can be used for environmental modeling.

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1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) are unintentional by-products from thermal and metallurgical processes, such as municipal waste incinerators, metal scrap smelters, sintering plants of the iron and steel industry, facilities of the nonferrous metal industry, cement kilns, and power plants (Fiedler, 1999; Gotoh et al., 1999; Li et al., 2004; Olie et al., 1977; Rappe and Buser, 1988). Kim et al. (2005) found that the concentration of PCDDs in an industrial waste incinerator of South Korea were 6.43 ng Nm^{-3} in the stack gas, 127 ng g^{-1} on fly ash, 27.4 ng g^{-1} on dust, and 0.432 ng g^{-1} on bottom ash. Abad et al. (2006) and Shi et al. (2008) also reported that PCDDs emissions from municipal solid waste incinerators in Spain and China disperse nearly 0.656 and 42.8 ng Nm^{-3} refuse into the atmosphere, respectively. However, due to their very high lipophilicity and chemical stability, their half-life in the environment reaches on average 30–100 years (Wiater-Protas, 2005). PCDDs tend to bioaccumulate in humans (554 pg g^{-1} lipids, Kim et al., 2005), pine needles (144 pg g^{-1} wet weight, Kim et al., 2005) and fish (5.38 pg g^{-1} wet weight, Hasegawa et al., 2007), and to adsorb onto soil (71,900 pg g^{-1} dry weight, Kiguchi et al., 2007) and sediment (12,300 pg g^{-1} dry weight, Sakai et al., 2008). According to Safe (1986), PCDD bioaccumulation in animal and human adipose tissues causes a wide variety of toxic responses that include immune toxicity, carcinogenicity and adverse effects on reproduction, development and endocrine functions. To combat the threat posed by PCDDs to human health and the environment, PCDDs were listed in the Annex C of the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2001, requiring parties to take measures to reduce unintentional releases (UNEP (United Nations Environment Programme), 2001).

Although considerable research in the most recent three decades has focused on PCDDs in the environment, the transport,

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* Corresponding author.
E-mail address: lli@civil.ubc.ca (L.Y. Li).

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accumulation and reactions of PCDDs in air, water, soils, sediments and biota are not fully elucidated. Czuczwa and Hites (1986) and Brubaker and Hites (1997) found noticeable differences in PCDDs homologue profiles between sources and sinks. Brzuzy and Hites (1996) and Baker and Hites (2000) found discrepancies in global PCDDs estimates for emission and deposition. Although uncertainties about the behavior and fate of PCDD in environmental paths from source to sink have been revealed, physical-chemical properties controlling partition between various media, and thus dictating accumulation, are unknown or inaccurate for some PCDD congeners. Experimental determination of PCDD properties is not only expensive, but can also be environmentally unfriendly because of the use of other toxic chemicals and solvents (Harner et al., 2000; Rordorf et al., 1986; Shiu et al., 1988). Also, experimental errors can be introduced, especially, for solubility and K_{OW} of PCDD congeners which are difficult to separate and identify by chromatography (Yang et al., 2007). Hence, establishing respective properties can be difficult.

Due to the experimental limitations resulting in a lack of physical-chemical property data for PCDDs, there is a growing need for the quantitative structure-property relationship (QSPR) method to estimate the physical-chemical properties of PCDDs. Several attempts have been made to utilize the QSPR model based on limited experimental data and descriptive parameters (molecular descriptors) related to the structure of PCDD congeners. For example, Shiu et al. (1988) estimated water solubilities, vapor pressures, octanol/water partition coefficients and Henry's law constants of 15 PCDDs as a function of chlorine number and molar volume. Zhao et al. (2005) developed a quantitative relationship between the octanol/air coefficients and molecular connectivity indexes of ten PCDDs. Yang et al. (2007) analyzed single-descriptor QSPR models based on only quantum-chemical descriptors to predict the solubility and octanol/water partition coefficients of 12 PCDDs. Liang and Gallagher (1997) correlated solvent accessible surface area with the aqueous solubility of 14 PCDDs. Åberg et al. (2008) reported regression results between molecular weight and internally consistent final adjusted solubilities, vapor pressures, Henry's law constants, and octanol/water and octanol/air partitioning coefficients of 15 PCDDs. However, these previous QSPR models are limited for several reasons: (i) Although there are 75 PCDD congeners, physicochemical properties for most of these congeners are still missing. (ii) The main molecular descriptors are generally distinguished with constitutional, topological, geometric, electrostatic and quantum-chemical descriptors (Devillers and Balaban, 1999). However, previous QSPR models for PCDDs have been limited to only one or two of these molecular descriptors. (iii) Few experimental physical-chemical property data have been reported for PCDD congeners. (iv) When QSPR models for an array of physical-chemical properties have been reported for PCDDs, these have not been tested for internal consistency.

In this study, we (i) review existing experimental physicochemical property data (i.e., solubility, vapor pressure, octanol/water partition coefficient, air/water partition coefficient and octanol/air partition coefficient) for PCDD congeners; (ii) review previous QSPR models for PCDDs in the literature; (iii) develop QSPR models for key physical-chemical properties of all 75 PCDD congeners based on constitutional, topological, geometric, electrostatic and quantum-chemical descriptors, including structural information; (iv) compare QSPR models developed in this study with previous QSPR models reported in the literature and select the best QSPR models for all 75 congeners; (v) provide a complete set of reliable physicochemical property data for all 75 congeners after requiring internal consistency based on fundamental thermodynamic relationships.

2. Methodology

2.1. Collection of experimental property data

In this study, similar criteria as in Yue and Li (2013) and Kim et al. (2015) have been applied to gather available data from the literature, with the selection based on the following criteria: (i) The physical-chemical property data must be from direct measurements using the best available, or a generally acceptable, experimental method. Calculated and estimated values are excluded. (ii) The values must have been measured at standard conditions (298 K and 760 mm Hg). (iii) Where multiple data are available from the same research group, the most recent values are chosen. (iv) If data are available from different research groups and it is unclear which are more reliable, the values are averaged and converted to a log scale for modeling. (v) Obviously dubious values are excluded.

For each of the properties of interest, half of the data points, chosen randomly, constituted the training set and the other half the validation set. The training set values were then used to perform least squares fitting, and the validation set to test the validity of the correlations.

2.1.1. Aqueous solubility (S_L)

The aqueous solubility, S_L, is a key parameter in determining the mobility and controlling the distribution of chemicals between different phases (air- and sediment-water partitioning) (Oleszek-Kudlak et al., 2007). The generator-column method employing high-performance liquid chromatography (HPLC) is widely accepted for accurate determination of the aqueous solubilities of highly hydrophobic compounds (Friesen and Webster, 1990). Webster et al. (1983), Friesen et al. (1985), Shiu et al. (1988) and Mackay et al. (1992b) used HPLC generator columns to measure the water solubilities of a series of chlorinated dioxins, including dioxin-like congeners. These experimental solubility values measured by HPLC were collected to predict the aqueous solubility of all 75 PCDD congeners in this study. Collected solubility data (hereafter labelled Ext-log S_L, with S_L in mol L^{-1}) are presented in Supplementary Information, Table S1.

2.1.2. Vapor pressure (P_L)

The vapor pressure, P_L, describes air-surface exchange of PCDD, related to volatility (Xiao and Wania, 2003). Rordorf (1985a, b), Rordorf (1986) and Rordorf et al. (1986) used a gas saturation method to estimate the solid-phase vapor pressures of some PCDDs (mainly low-chlorinated dioxins). Mackay et al. (1992a) also reported PCDD experimental vapor pressures measured by Rordorf (1987, 1989) using a gas-flow method in a saturation oven. Schroy et al. (1985) and Podoll et al. (1986) determined vapor pressure for 2,3,7,8-TCDD using ^{14}C-labeled 2,3,7,8-TCDD and a gas saturation technique. Vapor pressures reported by Schroy et al. (1985) were chosen by SRC (Syracuse Research Corporation, 1991) as definitive values. The gas saturation and gas chromatography methods were successfully employed for reference compounds. In this study, experimental vapor pressures (Ext-log P_L, with pressure in Pa) were collected from measured data based on these two methods (Supplementary Information, Table S1). The resulting data sets are used for QSPR analysis of PCDD properties.

To eliminate the congener-specific effect of melting point, aqueous solubilities (S_S, in mol L^{-1}) and vapor pressures (P_S, in Pa) for solid substances were converted into sub-cooled liquid values (subscript L) using the equation proposed by Mackay et al. (1980),

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