ELSEVIER

Chemosphere 62 (2006) 1817–1828

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Prediction of environmental partition coefficients and the Henry's law constants for 135 congeners of chlorodibenzothiophene

Tomasz Puzyn, Paweł Rostkowski, Artur Świeczkowski, Aneta Jędrusiak, Jerzy Falandysz *

Department of Environmental Chemistry and Ecotoxicology, University of Gdańsk, 18 Sobieskiego Street, PL 80-952 Gdańsk, Poland

Received 2 September 2004; received in revised form 31 May 2005; accepted 9 July 2005
Available online 7 October 2005

Abstract

Polychlorinated dibenzothiophenes (PCDTs) could be classified as persistent organic pollutants (POPs) in the environment and are particularly interesting due to their structural resemblance to highly toxic dioxins. We show here some basic environmental properties such as *n*-octanol water (K_{OW}), *n*-octanol/air (K_{OA}) and air/water (K_{AW}) partition coefficients as well as Henry's law constants (K_H) for all 135 congeners of chlorodibenzothiophene. Predictions were made by regression of principal components (PCR) and with aid of a set of standard chemicals, for which physical–chemical properties are well featured. Computed K_{OW}, K_{OA}, K_{AW} and K_H values for mono-CDTs ranged, respectively, between 4.66 and 4.71, 7.48 and 7.55, −2.84 and −2.82, 3.56 and 3.74; for di-CDTs between 5.02 and 5.28, 8.03 and 8.29, −3.01 and −2.95, 2.42 and 2.75; for tri-CDTs between 5.53 and 5.70, 8.65 and 8.87, −3.2 and −3.11, 1.58 and 1.92; for tetra-CDTs between 5.95 and 6.13, 9.27 and 9.50, −3.39 and −3.27, 1.02 and 1.33; for penta-CDTs between 6.38 and 6.51, 9.88 and 10.05, −3.54 and −3.45, 0.72 and 0.88; for hexa-CDTs between 6.83 and 6.97, 10.54 and 10.66, −3.72 and −3.64, 0.47 and 0.56; for hepta-CDTs between 7.28 and 7.35, 11.12 and 11.20, −3.81 and −3.87, 0.33 and 0.38; for octa-CDT 7.74, 11.78, −4.04 and 0.23. An estimated value of the three types of partition coefficient and Henry's law constants suggest that polychlorinated dibenzothiophenes are lipophilic and semi-volatile persistent organic pollutants. Their mobility in the environment seems to be very similar to that of some well-known POPs such as polychlorinated dibenzofurans, -dibenzo-*p*-dioxins, and -biphenyls or organochlorine pesticides.

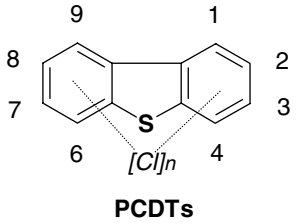
Keywords: Chlorodibenzothiophene; Polychlorinated dibenzothiophenes; PCDTs; Dioxin-like compounds; Physical–chemical properties; Environmental chemistry; QSPR

1. Introduction

2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) and its 2,3,7,8-substituted analogues of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), but also planar polychlorinated

* Corresponding author. Tel.: +48 58 3450372; Fax: +48 58 3450472.
E-mail address: jfalandy@chem.univ.gda.pl (J. Falandysz).

0045-6535/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2005.07.055



PCDTs

Fig. 1. Structure of PCDTs and numbering of carbon atoms.

biphenyls (pPCBs) as well as polychlorinated naphthalenes (PCNs) are key organohalogenated contaminants extensively studied in recent decades of years, while a much less studied are other possible dioxin analogues including substances such as polychlorinated pyrenes (PCPYs) or dibenzothiophenes (PCDTs) (Fig. 1) (Falandysz, 1998, 2003; Falandysz et al., 2000; Paasivirta, 2000; Puzyn and Falandysz, 2003, 2005; Yamashita et al., 2003; Falandysz and Puzyn, 2004; Noma et al., 2004a,b,c, 2005a,b). PCDTs derived from dibenzofurans are considered as proof for presence of sulphur-analogues of PCDD/Fs (Sinkkonen, 1997, 1998; Sielex and Andersson, 1998).

The molecular weight of 135 congeners of chlorodibenzothiophene is between 218.71 and 459.83 g mol^{-1}. The major identified sources of PCDTs in the environment are high temperature processes related to municipal and hazardous waste incineration, fossil fuels combustion, metallurgy and metal reclamation. Another possible source is automobile exhaust, wood combustion, manufacture of PCBs, trichlorobenzene sulphonates and sewage sludge (Sinkkonen et al., 1994; Takasuga et al., 1994; Sinkkonen, 1997, 1998; Sinkkonen et al., 2001; Ishaq et al., 2003). 2,4,6,8-teCDT has been found in contaminated sediment at concentration up to 3680 ng/kg, while soil at the site contaminated with waste after incineration of PCBs contained PCDTs at concentration up to 67 μg/kg (Sinkkonen, 1998). These compounds have been detected also in invertebrates, fish and marine mammals (Irwin, 1997).

The current knowledge on sulphur analogues to PCDD/Fs is limited and including their toxicological relevance as well as environmental mobility (Irwin, 1997; Sinkkonen, 1997, 1998). The goal of presented study was to generate environmental partition coefficients describing mobility potential and Henry's law constants for 135 congeners of chlorodibenzothiophene.

2. Materials and methods

The study is based on the fundamental QSPR (quantitative structure–property relationships) approach, that structural differences also determinate variations in

Table 1
The full list of structural descriptors used in the study

Descriptor	Description	Reference
CI_0	Zeroth-order (atomic) molecular connectivity index Chi 0 for the chemical sample	Kier and Hall (1986)
CI_1	First-order (bond) molecular connectivity index Chi 1 for the chemical sample	Kier and Hall (1986)
CI_2	Second-order (path) molecular connectivity index Chi 2 for the chemical sample	Kier and Hall (1986)
HOMO	Energy of the highest occupied molecular orbital	Stewart (1990, 2002)
LUMO	Energy of the lowest unoccupied molecular orbital	Stewart (1990, 2002)
SAS	Solvent accessible surface area of the molecule in water	Tomasi and Persico (1994)
K_1	The shape index of order 1 (kappa 1)	Hall and Kier (1991)
K_2	The shape index of order 2 (kappa 2)	Hall and Kier (1991)
K_3	The shape index of order 3 (kappa 3)	Hall and Kier (1991)
HOF	Heat of formation of the molecule	Stewart (1990, 2002)
VCI_0	Zeroth-order (atomic) valence molecular connectivity index Chi 0V	Kier and Hall (1986)
VCI_1	First-order (bond) valence molecular connectivity index Chi 1V	Kier and Hall (1986)
VCI_2	Second-order (path) valence molecular connectivity index Chi 2V	Kier and Hall (1986)
MOL_REF	Molar refractivity calculated using the scheme of Ghose and Crippen	Ghose et al. (1988)
DIPOLE	Dipole moment	Stewart (1990, 2002)
DV_X	Dipole vector **X**	Stewart (1990, 2002)
DV_Y	Dipole vector **Y**	Stewart (1990, 2002)
DV_Z	Dipole vector **Z**	Stewart (1990, 2002)
w	Wienner index	Wiener (1947)
X0sol	Solvation connectivity index Chi 0	Hall and Kier (1991)
X1sol	Solvation connectivity index Chi 1	Hall and Kier (1991)
X2sol	Solvation connectivity index Chi 2	Hall and Kier (1991)
X3sol	Solvation connectivity index Chi 3	Hall and Kier (1991)
X4sol	Solvation connectivity index Chi 4	Hall and Kier (1991)
X5sol	Solvation connectivity index Chi 5	Hall and Kier (1991)
*Q*max−	Maximal value of negative partial charge	Stewart (1990, 2002)
*Q*max+	Maximal value of positive partial charge	Stewart (1990, 2002)