



# Experimental investigation on the soil sorption properties and hydrophobicity of polymethoxylated, polyhydroxylated diphenyl ethers and methoxylated-, hydroxylated-polychlorinated diphenyl ethers



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## HIGHLIGHTS

- Fifty-nine DEs were synthesized and their  $\log K_{ow}$  and  $\log K_{oc}$  were determined.
- Sorption behaviors of five DEs on soil were well fitted the Freundlich model.
- The number of substituents significant influenced the  $\log K_{ow}$  and  $\log K_{oc}$  of DEs.
- Linear relationships were observed for the  $\log K_{ow}$  and  $\log K_{oc}$  of all studied DEs.

## ARTICLE INFO

### Article history:

Received 7 April 2014

Received in revised form 2 April 2015

Accepted 7 April 2015

Handling Editor: I. Cousins

### Keywords:

Soil sorption

Hydrophobicity

PMeODEs

PHODEs

MeO- and HO-PCDEs

## ABSTRACT

In the present study, twenty-six types of polymethoxylated diphenyl ethers (PMeODEs), twenty types of polyhydroxylated diphenyl ethers (PHODEs), seven types of methoxylated-polychlorinated diphenyl ethers (MeO-PCDEs) and seven types of hydroxylated-polychlorinated diphenyl ethers (HO-PCDEs) were synthesized. The  $\log K_{ow}$  and  $\log K_{oc}$  values of all of the synthesized compounds were then determined using HPLC. The soil sorption properties of five types of selected substituted diphenyl ethers (DEs) were investigated. Sorption behavior studies suggested that rapid sorption played a primary role in the sorption process of the selected DEs and their sorption isotherms were fitted the Freundlich logarithmic model. For PMeODEs and PHODEs, with the increase in the number of substituents, both  $\log K_{ow}$  and  $\log K_{oc}$  values exhibited linearly decreasing trends. Unlike PMeODEs and PHODEs, both  $\log K_{ow}$  and  $\log K_{oc}$  values of MeO/HO-PCDEs were decreased linearly with the increasing number of chlorine atoms. The reason maybe that both methoxy and hydroxyl are hydrophilic groups, whereas the chlorine atom is hydrophobic group. Linear relationships were observed for the  $\log K_{ow}$  and  $\log K_{oc}$  of all studied DEs. Moreover, the  $\log K_{ow}$  of PMeODEs, PHODEs, MeO- and HO-PCDEs and their corresponding PCDEs showed good linearity.

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## 1. Introduction

Diphenyl ethers (DEs) are important organic compounds that play significant roles in the chemical industries and medicine chemistry (Nicolaou et al., 1999; Sawyer, 2000). These compounds are widely used in many industries, including material products

and commercial dyes (Nicolaou et al., 1998). Due to their wide application, DEs and their derivatives are released into the environment and may lead to environmental risks. There may be various substituents in the benzene rings of DEs, such as bromine atoms, chlorine atoms, and hydroxyl and methoxyl groups, and these substituents can significantly influence the physicochemical properties and toxicities of DEs (Bonz and Schmidt, 1997).

Polychlorinated diphenyl ethers (PCDEs), a series of typical diphenyl ether derivatives, have wide environmental distributions and various adverse effects on the environment and organisms

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(Rahman et al., 2001; Domingo, 2006). Polymethoxylated diphenyl ethers and polyhydroxylated diphenyl ethers are structurally similar to PCDEs and are termed PMeODEs and PHODEs, respectively (Fig. 1). To date, studies on the two series of compounds mainly focused on their synthetic methods and toxic effects (Martina et al., 2002; Strieter et al., 2005; Zhang et al., 2014a,b).

Similar to PBDEs, PCDEs congeners in the environment may experience various metabolic processes (e.g., dechlorination, hydroxylation and methoxylation), and the corresponding methoxylated and hydroxylated metabolites of PCDEs (i.e., MeO-PCDEs and HO-PCDEs) are produced as a result (Komsta et al., 1988; Cheng et al., 2012). Therefore, for the assessment of the environmental risks of PCDEs, investigations of their metabolites (MeO-PCDEs and HO-PCDEs) are needed.

The *n*-octanol/water partition coefficient ( $\log K_{ow}$ ) and the soil sorption coefficient normalized to organic carbon ( $\log K_{oc}$ ) are important physicochemical properties of persistent organic pollutants (POPs) and play significant roles in the environmental fate of POPs (Zhang et al., 2005; Kholod et al., 2009; Yang et al., 2013a,b). However, to date, information on the two properties of PMeODEs, PHODEs, MeO-PCDEs and HO-PCDEs is still lacking, which could limit further investigations on their environmental behaviors and scientific assessments on their potential environmental risks.

The objective of this study was to investigate the soil sorption property and hydrophobicity of DEs through experimental method. In the present study, 26 congeners of PMeODEs, 20 congeners of PHODEs, 7 types of MeO-PCDEs and 7 types of HO-PCDEs were synthesized and their  $\log K_{ow}$  and  $\log K_{oc}$  values were determined in RP-HPLC system. The soil sorption behaviors of five selected typical DEs were investigated. The relationships between substituted number and  $\log K_{ow}/\log K_{oc}$  were discussed. Comparative studies of the relationship of the  $\log K_{ow}$  and  $\log K_{oc}$  values of all studied DEs were also carried out. Furthermore, the relationship of the  $\log K_{ow}$  values among PMeODEs, PHODEs, MeO-PCDEs and HO-PCDEs and PCDEs was discussed. The obtained experimental data of those compounds could support future in-depth studies on their environmental behaviors.

## 2. Materials and methods

### 2.1. Materials

The raw materials (including substituted methoxy phenols and iodo or bromo methoxybenzene, purity  $\geq 99\%$ ) were purchased from Energy Chemical (Shanghai, China). Cuprous iodide (CuI), tetramethylethylenediamine, caesium carbonate, hydrobromic acid, and anhydrous magnesium sulfate were bought from J&K Scientific Ltd (Shanghai, China). Ethyl acetate, and petroleum ether was provided by Nanjing Chemical Reagent Co, Ltd. (Nanjing, China). Other reagents of analytical grade were obtained domestically. Methanol, *n*-hexane and acetic acid of chromatographic grade were purchased from Merck (Darmstadt, Germany).

The  $^1\text{H}$  NMR spectra were determined at room temperature using Bruker Avance-500 MHz NMR spectrometer with TMS as an internal standard in  $\text{CDCl}_3$  (PMeODEs and MeO-PCDEs) or  $\text{DMSO}-d_6$  (PHODEs and HO-PCDEs). Agilent 1200 HPLC was used to determine the purity of synthesized compounds and measure  $\log K_{ow}$  and  $\log K_{oc}$  of the synthesized compounds (chromatographic column: Agilent ZORBAX SB-C18, 5  $\mu\text{m}$ , 4.6  $\times$  150 mm).

### 2.2. Experimental methods

#### 2.2.1. Synthesis of DEs

PMeODEs were synthesized through the method described in our former study (Zhang et al., 2013). The synthesized PMeODEs

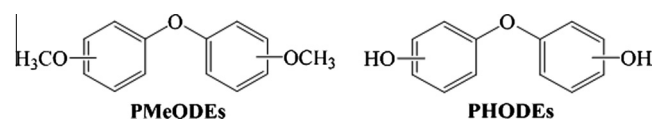


Fig. 1. The structural formulas of PMeODEs and PHODEs.

were then used to produce PHODEs via a demethylation process (Liu et al., 2013). The structures of all of the products were characterized by their  $^1\text{H}$  NMR spectra (See Supplementary Data for detailed descriptions). The purities of all of the products were determined to be greater than 98% through HPLC. Twenty-six types of PMeODEs and 20 types of PHODEs were synthesized in this study (Table 1). Similar to the synthesis of PMeODEs, seven types of MeO-PCDEs were synthesized with chloriodobenzenes and methoxyphenols as substrates. In addition, the corresponding HO-PCDEs were then obtained via the demethylation of MeO-PCDEs (Table 1). All of the reactions gave the target products at moderate to good yields (48–91%).

#### 2.2.2. Determination of $\log K_{ow}$

The  $\log K_{ow}$  values of the synthesized compounds were determined through the slow-stirring method, which followed the Organization for Economic Co-operation and Development (OECD) guideline for chemicals tests (OECD, 2006). Analytical-grade *n*-octanol saturated with distilled water was used as the organic phase, and distilled water saturated with *n*-octanol was used as the aqueous phase. The chemicals were dissolved in water-saturated *n*-octanol. The concentrations of the tested compounds in water-saturated *n*-octanol were 0.8 mM and 0.08 mM. All of the chemicals were completely dissolved in water-saturated *n*-octanol at the two experimental concentrations. *n*-octanol-saturated water (500 mL) and the test substance in water-saturated *n*-octanol solution (50 mL) were equilibrated for 24–96 h with a thermostated magnetic stirrer. During this process, glass flasks were covered with tin foil to avoid light irradiation and maintain the temperature at  $25.0 \pm 0.5$  °C. The exchange between the phases was accelerated by stirring with a 5-cm cylindrical PTFE magnetic bar (the maximum vortex depth was 0.5 cm). Due to the rather low concentrations of the test substances in the water phase, extraction of the water phase with *n*-hexane and pre-concentration of the extract using a rotation evaporator were employed if necessary. The concentrations of the test substances in the two phases were determined by HPLC. The  $\log K_{ow}$  value was calculated using the following formula:

$$\log K_{ow} = \log(C_o/C_w) \quad (1)$$

where  $C_o$  and  $C_w$  is the equilibrium concentration ( $\text{mg L}^{-1}$ ) of the test substance in water-saturated *n*-octanol and *n*-octanol-saturated water respectively.

#### 2.2.3. Soil sorption behaviors of five selected DEs

In the present study, soil (yellow brown soil) was obtained from Xianlin (32.104°N, 118.947°W), Qixia District, Nanjing, Jiangsu, China. Before sorption experiments, the soil organic carbon, cation exchange capacity (CEC) and total nitrogen of soil were determined following the methods that reported in previous studies (Nelson and Sommers, 1996; Ciesielski and Sterckeman, 1997; Marco et al., 2002). In addition, pH, texture and moisture content were also measured (Table 2). The organic compound residues in the tested soil were examined prior to the sorption experiments, and the results demonstrated that the residues were negligible.

Batch equilibrium experiments were conducted to study the sorption kinetics and isotherms of DE, 4,4'-di-MeODE, 4,4'-di-HODE, 2-MeO-2',4,4'-tri-CDE and 2-OH-2',4,4'-tri-CDE (triclosan).

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