



## Adsorption of diethyl phthalate ester to clay minerals

Yanhua Wu<sup>a,b</sup>, Youbin Si<sup>b</sup>, Dongmei Zhou<sup>a</sup>, Juan Gao<sup>a,\*</sup>



<sup>a</sup> Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, No. 71, East Beijing Road, Nanjing 210008, PR China

<sup>b</sup> School of Resources and Environment, Anhui Agricultural University, Hefei 230036, PR China

### HIGHLIGHTS

- Montmorillonite interlayer was important for DEP adsorption.
- Cation K<sup>+</sup> and lower temperature facilitated more adsorption of DEP.
- pH and ionic strength had limited effect on DEP adsorption to K<sup>+</sup>/Ca<sup>2+</sup> saturated montmorillonite.
- The interaction between DEP and montmorillonite was weak adsorption.

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### ABSTRACT

Phthalate esters are a group of plasticizers, which have been widely detected in China's agricultural and industrial soils. In this study, batch adsorption experiments were conducted to investigate the environmental effects on the adsorption of diethyl phthalate ester (DEP) to clay minerals. The results showed that DEP adsorption isotherms were well fitted with the Freundlich model; the interlayer spacing of K<sup>+</sup> saturated montmorillonite (K-mont) was the most important adsorption area for DEP, and di-n-butyl ester (DnBP) was limited to intercalate into the interlayer of K-mont due to the bigger molecular size; there was no significant effect of pH and ionic strength on DEP adsorption to K-mont/Ca-mont, but to Na-mont clay. The adsorption to kaolinite was very limited. Data of X-ray diffraction and FTIR spectra further proved that DEP molecules could intercalate into K-/Ca-mont interlayer, and might interact with clay through H-bonding between carbonyl groups and clay adsorbed water. Coated humic acid on clay surface would enhance DEP adsorption at low concentration, but not at high concentration (eg. C<sub>e</sub> > 0.26 mM). The calculated adsorption enthalpy ( $\Delta H_{obs}$ ) and adsorption isotherms at varied temperatures showed that DEP could be adsorbed easier as more adsorbed. This study implied that clay type, compound structure, exchangeable cation, soil organic matter and temperature played important roles in phthalate ester's transport in soil.

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### 1. Introduction

Plasticizers are a group of compounds added into plastic polymers to increase their flexibility, transparency, durability, and longevity (Sears and Darby, 1982). Phthalate esters are the most widely applied plasticizers and account for 80% of all plasticizer production (Wypych, 2004). Because there is no covalent bond between phthalate ester plasticizers and polyvinylchloride poly-

*Abbreviations:* DEP, diethyl phthalate ester; DnBP, di-n-butyl phthalate ester; HA, humic acid;  $\Delta H_{obs}$ , observed adsorption enthalpy; mont, montmorillonite; X-RD, X-ray diffraction; FTIR, Fourier transform infrared spectroscopy.

\* Corresponding author. Tel./fax: +86 25 86881318.

E-mail addresses: [860330009@qq.com](mailto:860330009@qq.com) (Y. Wu), [youbinsi@ahau.edu.cn](mailto:youbinsi@ahau.edu.cn) (Y. Si), [dmzhou@issas.ac.cn](mailto:dmzhou@issas.ac.cn) (D. Zhou), [juangao@issas.ac.cn](mailto:juangao@issas.ac.cn) (J. Gao).

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mers, these plasticizers could leach into soil (Hu et al., 2003), water (Sung et al., 2003), and air (Sun et al., 2003; Weschler et al., 2008).

After phthalate ester plasticizer reach natural environment, these chemicals have potential health risks to human, regarding to their xeno-estrogenic effects (Siddiqui and Srivastava, 1992; Nielson and Larsen, 1996), carcinogenic and mutagenic effects (Beliles et al., 1989; Schulz, 1989; Nielson and Larsen, 1996). The chemicals have been proved to influence plant growth. For example, increasing di-n-butyl phthalate (DnBP) concentration from 0.01 mg L<sup>-1</sup> to 1 mg L<sup>-1</sup> could cause chloroplasts disintegrating and disorganizing, which could damage the ultrastructures of *Arabidopsis thaliana* leaves (Wang et al., 2005). When mixed DnBP into soil at varied concentrations from 5 to 160 mg kg<sup>-1</sup>, the contents of vitamin C and capsaicin in capsicum fruit could decrease from 1.6% to 22% (Yin et al., 2003). At a low concentration (<10 mg kg<sup>-1</sup>),

phthalate ester would act as a carbon source and promote bacterial growth (Chen et al., 2004).

Although phthalate esters could be biodegraded or mineralized in soil, sludge and water, their half-lives were varied from 1 d to several months depending on their side-chain lengths and structures (Ejlertsson et al., 1997; Wang et al., 1997; Amir et al., 2005). In the previous study of Amir et al. (2005), DnBP concentration decreased during sludge composting process, and di-ethyl phthalate (DEP) and di-methyl phthalate (DMP) concentration increased, which were proposed as the biodegradation intermediates.

To assess the potential of phthalate esters leaching into ground water or bioavailability in soil, it is important to understand the interactions between the compounds and soil constituents. In the research of DEHP sorption to three soils (Murillo-Torres et al., 2012), DEHP could be sorbed rapidly by Leptosol, Phaeozem and Vertisol, and the sorption coefficients were between  $1.8 \times 10^4$  and  $4.2 \times 10^4$  L kg<sup>-1</sup>. In recent years, increasing attention has been paid to the adsorption of emerging contaminants to clay minerals (Li et al., 2004; Gao and Pedersen, 2005, 2010; Marco-Brown et al., 2014; Ugochukwu et al., 2014), especially montmorillonite clays, which belong to a group of expandable 2:1 type smectite. The  $d_{001}$  spacing of montmorillonite provides a relative hydrophobic sorption area for nonpolar compounds as compared with bulk aqueous solution. The results of Liu et al. (2013) showed that the dispersion coefficients ( $D$ ) and partition coefficients ( $K_d$ ) of phthalate esters to clay minerals increased with the side chain lengths of phthalate esters, and the clay interlayer was an important retarder for phthalate esters downward transport.

Although phthalate esters are nonpolar compounds, pH impacts were observed in some researches. The research of Yang et al. (2013a) showed that adsorptions of 17 phthalate esters to three soils increased as solution pH decreasing. However, Yang et al. (2013b) observed increasing pH and soil organic matter could slightly increase phthalate ester retaining in soil. In the study by Wang et al. (2012), the sorption of phthalate ester to carbon nano-tube was increased with increasing pH and temperature due to  $\pi$ - $\pi$  electron interaction. The differences may come from varied sorbent properties and different interactions between phthalate esters and sorbents. To date, the sorption of phthalate ester to pure soil clay minerals had not been thoroughly examined, although clay minerals were important soil constituents for the transport and transformation of organic contaminants (Nowara et al., 1997; Boyd et al., 2001; Gao and Pedersen, 2005; Gu and Karthikeyan, 2005; Gu et al., 2011).

The objectives of this study were to investigate the possible environmental factors, which would affect the interactions between phthalate ester and clay minerals, such as exchangeable cation of clay minerals, pH, ionic strength, temperature, coated humic acid (HA). The clay minerals used in this research included a smectite clay and a kaolinite clay because they were widely distributed in soil and commercially available. Besides batch experiments, X-ray diffraction spectroscopy (XRD) and Fourier transform infrared spectroscopy (FTIR) were applied to explore the interaction mechanisms. The results of this research would provide useful information of phthalate ester transport in soil environment, which would be helpful to assess the potential exposure risk of phthalate ester plasticizers in soil environment.

## 2. Materials and methods

### 2.1. Chemicals

Di-ethyl phthalate ester (DEP) and DnBP were purchased from Sigma–Aldrich Chemical (St Louis, MO), and their properties were

listed in Table 1. Sodium hydroxide (NaOH), hydrochloric acid (HCl), and methanol were obtained from National Medicines Corporation Ltd (Beijing, China); sodium chloride (NaCl), potassium chloride (KCl), calcium chloride (CaCl<sub>2</sub>) were obtained from Sino Pharm Chemical Reagent Co. Ltd. (Shanghai, China). The purities of all chemicals in this study were >99%. Ultrapure water (18.2 M $\Omega$  cm<sup>-1</sup>) from Synergy UV ultrapure water system with Millipak-40 Filter Unit (Millipore Corporation Merck KGaA, Darmstadt, Germany) was used to make solutions in the experiments.

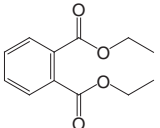
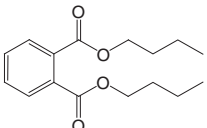
### 2.2. Clay preparation and characterization

Montmorillonite clay (mont) was purchased from Fenghong Company, Zhejiang Province, China; kaolinite clay and humic acid were purchased from Sigma–Aldrich Chemical (St Louis, MO). The procedure to prepare homoionic clay minerals followed the method of Rana et al. (2009). In brief, clays were suspended in 0.5 M NaCl for 7 h, and particles with 0.5–2.0  $\mu$ m diameters were collected by wet sedimentation; the collected particles were saturated with 0.5 M NaCl for three times; and for K-/Ca-mont clay, clay particles were further suspended to 0.5 M chloride solution with K<sup>+</sup> or Ca<sup>2+</sup> three times; then the clay particles were washed in deionized water three times to get off extra salt and Cl<sup>-</sup>; after centrifugation, the clay pellets were freeze-dried, ground to powder in an agate mortar and stored in closed containers at room temperature. Cation exchange capacity (CEC) was determined by compulsive exchange with Ba<sup>2+</sup> (Sumner and Miller, 1996); total surface areas of the clays were determined by ethylene glycol monoethyl ether (Chiou and Rutherford, 1993). The properties of clays are shown in Table 1.

### 2.3. HA coated clay preparation

Humic acid coated K-mont (HA-K-mont) complexes were prepared following the procedure of Wang and Xing (2005). Briefly, 1 g HA was dissolved in 1 L 10 mM KCl solution at pH 10 for 4 h,

**Table 1**  
Properties of sorbents and phthalate esters in this study.<sup>a</sup>

		Specific surface area m <sup>2</sup> ·g <sup>-1</sup>	CEC cmol <sub>c</sub> ·kg <sup>-1</sup>		
<i>Sorbent</i>					
Montmorillonite		324.5		73.6	
Kaolinite		29.4		5.8	
<i>Phthalate ester</i>					
Chemical	Structure	Solubility <sup>b</sup> mM	logK <sub>ow</sub> <sup>c</sup>	logK <sub>oc</sub> <sup>d</sup>	
Diethyl phthalate (DEP)	MW: 222.24 MW: 222.24 	4.86	2.31	1.55–2.08, 4.2	
Di-n-butyl phthalate (DnBP)	MW: 278.34 MW: 278.34 	0.0467	4.43	3.23–3.61, 4.11	

<sup>a</sup> Specific surface areas of clays were measured by ethylene glycol monoethyl ether (EMGE method) Chiou and Rutherford (1993); CEC, cation exchange capacity Essington (2003).

<sup>b</sup> Solubilities of DEP was at T = 20 °C and DnBP at T = 25 °C.

<sup>c</sup> Data from Yang et al. (2013a).

<sup>d</sup> Data from Yang et al. (2013a) and Thomsen et al. (1999).

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