Role of dissolved humic substances surrogates on phthalate esters migration from sewage sludge

Z. Zheng, P. J. He, H. Zhang and L. M. Shao

ABSTRACT

The facilitated transport of dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP), the priority endocrine disrupting chemicals in sludge, by dissolved humic substances (HS) was evaluated by batch extraction. The DBP, much less hydrophobic than DEHP, was inclined to migrate from sludge matrix into humic substances solutions, while the DEHP could not migrate facilitated by most humic and fulvic acids solutions, except the humic acid surrogate of high humification. This result revealed that the affinity of DEHP in sludge matrix exceeded DBP and was not susceptible by weak HS. The hydrophobic property controlled the association of phthalic acid esters on sludge residual phases. Migration rate of DBP was positively correlated to the weight-average molecular weight of HS surrogates and the aromatic extents of HA. Some functional groups in HS molecules benefited to the facilitated transport of DBP.

Key words | dissolved organic matter, humic substance, mobility, phthalic acid esters, sewage sludge

INTRODUCTION

Phthalic acid esters (PAEs), typical endocrine disrupting chemicals (EDCs), were widely used as plasticizers in the manufacture of many household commodities. PAEs can be mineralized or sorbed onto sewage sludge particles during biological treatment of wastewater (Marttinen et al. 2003; Roslev et al. 1998). It has been found that significant part of di(2-ethylhexyl) phthalate (DEHP), a kind of PAEs with long ester chains, in sludge-amended soils may escape mineralization for more than 1 year (Madsen et al. 1999). The potential of PAEs releasing into soil or aquatic environments in land-application of sludge has attracted considerable research interest (Gledhill et al. 1980; Gron et al. 2000).

The PAEs in sludge could interact with several compositions in sludge-amended soils (Majumdar & Singh 2007). The passive sorption on the envelopes of cell and intracellular accumulation retards PAEs movement through soil while extracellular interactions and complexation with removable substances may facilitate their transport in aquifer. de Jonge et al. (2002) revealed that 3.4% of DEHP were leached out from a sandy loam soil column amended by homogeneous sludge, and the dissolved organic matter (DOM) derived from the sludge-amended soil played a main role in the mobility of DEHP (de Jonge et al. 2002). Similar result was obtained in experiments on napropamid (Williams et al. 2002).

The characteristics of DOM as well as the contaminants are crucial in their association. The humic substances (HS) in DOM are recognized to contribute greatly to the facilitated transport of organic contaminants. Humification of DOM was correlative to its ability to absorb organic contamination (Cox et al. 2000). Yamamoto et al. (2003) further examined the relationship between physical-chemical characteristics of HS surrogates and their sorption of selected endocrine disruptors (including dibutyl phthalate, DBP).

Most of the previous work focused on the interaction between sludge DOM (or bacterial extracellular polymers) and contaminants in amended soil (de Jonge et al. 2002; Zhou et al. 2004). However, the influence of dissolved HS

from soil or other sources on mobility of contaminants in sludge is less considered. The purpose of the present work is to evaluate the mobile potential of DBP and DEHP when dissolved HS interfered with sewage sludge. The role of HS characteristics and PAEs hydrophobicity in the PAEs leaching risk was studied. The three-dimensional excitation emission matrix (EEM) fluorescence spectroscopy, ultraviolet absorbance, and molecular weight (MW) distribution of DOM were used to measure the characteristics of sludge-derived DOM.

MATERIALS AND METHODS

Materials

All solvents were ABSOLV pure grade purchased from Tedia (Fairfield, OH). All glassware was sequentially rinsed with acetone, hexane, dichloromethane, and then dried at 400 °C before use. The mixed DBP and DEHP standard was purchased from Sigma-Aldrich (St. Louis, MO) for calibration and dissolved in dichloromethane. The XAD-2 resin (Supelco, Bellefonte, PA) was cleaned for 24 h by Soxhlet extraction using methanol, dichloromethane, and methanol sequentially, and was soaked in distilled water before use.

Environmental samples

The dewatered sewage sludge was collected from a municipal wastewater treatment plant in Shanghai, China, which adopts a typical activated sludge process following anaerobic digestion. The dewatered sludge had a water content of 84.0% w w−1 and an organic matter of 77.4% w w−1 by dry weight (dw). The background of extractable DBP and DEHP in the sewage sludge was 22.8 μg g−1 dw and 1110 μg g−1 dw, respectively.

The selected dissolved humic acid (HA) and fulvic acid (FA) surrogates were extracted from landfill leachates, named H1-H5 and F1-F3, respectively. The extractions were performed using a procedure described by He et al. (2006). These HA and FA surrogates had different characteristics. All the surrogates were filtered by 0.45 μm PTFE filters (Mosu Scientific Equipment Co., Shanghai, China) before batch experiments to remove particles.

Batch experiment for PAEs mobility

To evaluate the effect of dissolved HS on PAEs mobility in sludge, 70 g of dewatered sludge (approximately 10 g by dry weight) was weighed into 500 ml dark glass bottles, and 200 ml of double distilled water or HS surrogate solution was added. The sludge extraction by double distilled water was considered as the native DOM fraction of sludge. In order to reduce the influence of HS mass on PAEs mobility, all the HS surrogates solutions were diluted to the same concentration (dissolved organic carbon (DOC) was 50 mg l−1). The mixtures were rotated for 24 h at 25 °C and filtered by a membrane with 0.45 μm pore size. The filtrates were termed as the DOM fraction of sludge or HS surrogates. The mobility of PAEs, expressed as “transfer ratio”, was defined as the PAEs concentration in filtrate divided by that in original sludge.

Analytical methods

DOC from the HS surrogates was determined using a TOC/TN analyzer (multi N/C 3000, Analytik Jena AG, Germany). A spectrophotometer (752, Precision & Scientific instrument Co., Shanghai, China) assessed the UV absorbance for the humic substance surrogates. The specific UV absorbance at wavelength 254 nm (SUVA254) was defined as the UV absorbance at 254 nm divided by the measured DOC.

Fluorescence Excitation Emission Matrix (EEM) spectra were recorded using a fluorescence spectrophotometer (F-4500, Hitachi, Tokyo, Japan) with a xenon lamp as the excitation source. Excitation and emission slit widths of 10 nm were used. The EEM spectra were excited at an excitation wavelength ranging from 200 to 450 nm at 4 nm increments and collected spectra from 250 to 700 nm at 5 nm intervals.

The weight-average molecular weight (Mw) of DOM was assessed by gel permeation chromatography (LC-10A, Shimadzu, Kyoto, Japan) using a refraction index detector and a gel column (TSK G4000PWXL, TOSOH, Tokyo, Japan) at flow rate of 0.5 ml min−1 and temperature 40 °C.

DBP and DEHP measurement

The background concentrations of DBP and DEHP in sludge sample were measured by extracting the freeze-dried
samples over 24 h using dichloromethane. The extract was evaporated and reconstituted in 2-ml hexane with ultrasound assistance and cleaned with Florisil column (EPA method 3535) before GC analysis. DBP and DEHP in DOM samples (including HS filtrates before and after batch experiments) were concentrated by Amberlite XAD-2 (Supelco, Bellefonte, PA) and the extract was cleaned in a Florisil column before GC analysis. Each test was performed in triplicate to check data reproducibility.

A GC-FID system (Focus GC, Thermo Electron, Waltham, MA) was used to quantify DBP and DEHP using capillary column DM-5 (30 m × 0.32 mm diameter × 0.25μm film thickness, Dikma, USA). The gas chromatograph temperature was increased from 70 to 220 °C at 20 °C min⁻¹ with an initial holding time of 1 min, and then further heated to 270 °C at 5 °C min⁻¹ with carrier gas flow of 1.5 ml min⁻¹. The FID temperature was set at 270 °C.

RESULTS AND DISCUSSION

Characteristics of sludge DOM and HS surrogates

Table 1 listed the characteristics of sludge DOM and HS surrogates. Figure 1 showed the fluorescence EEM spectra of sludge DOM and HS surrogates.

The Mw of sludge DOM was similar to that of HS surrogates while SUVA₂₅₄, which was correlated with the aromatic extent of samples, of the former was lower than that of latter. The selected dissolved HS surrogates had different characteristics in content. H₁ and F₁ were not as condensed as the others. The SUVA₂₅₄ of F₁ was similar to H₁ while its Mw was much lower than the latter.

In EEM plot of sludge DOM (Figure 1 (g)), two characteristic peaks presented at excitation/emission (Ex/Em) of 280–284/315–370 nm (peak C) and of 220–230/325–390 nm (peak D). These peaks were correlated with those for soluble microbial byproduct-like materials and simple aromatic proteins (Chen et al. 2003b). Another two characteristic peaks appeared at 313–348/430–450 nm (peak A) and 248–260/450–465 nm (peak B) (Figure 1, (a)–(f)) for FA and some HA samples. These characteristic peaks were correlated with those for humic and fulvic materials (Coble et al. 1990; Coble 1996). Due to the low humification of H₁ and H₂, no peak appeared in their EEM plot. Different compositions were contained in sludge DOM and HS surrogates. Compared to F₁, peak A and B of F₂ and F₃ shifted to longer wavelength in both emission and excitation wavelength (wavelengths of F₃ were also longer than that of F₂), resulting from an increased content of high molecular weight materials (Chen et al. 2003a) and increased humification (Ohno 2002).

Compared with Her et al. (2003), the SUVA₂₅₄ of some HS surrogates reached to the value of surface water sample and second effluent of wastewater treatment plant, but much lower than that of ground water sample. The excitation and emission wavelength in EEM plots of F₁ and F₂ was close to natural samples and wastewater samples, and the emission wavelength was shorter than that of Suwannee River humic substance that has been used in some references as humic surrogates (Yamamoto et al. 2003).

Distributions of PAEs in filtrate and sludges residuals

The concentrations of DBP and DEHP in filtrate and sludge residual after batch extraction were shown in Table 2. The DEHP concentration of original sludge sample exceeded the limit of 100 μg g⁻¹ dw, the limit suggested by the European Union’s “working document on sludge” for agricultural uses (EU 2000). About 2.63% of DBP and 0.73% of DEHP from the original sludge were distributed on sludge DOM. Most DBP and DEHP were remained in the solid residual fraction following water extraction.

Table 1 | Characteristics of humic substance surrogates and sludge DOM

<table>
<thead>
<tr>
<th>Parameters</th>
<th>H₁</th>
<th>H₂</th>
<th>H₃</th>
<th>F₁</th>
<th>F₂</th>
<th>F₃</th>
<th>Sludge DOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUVA₂₅₄ (l mg⁻¹ m⁻¹)</td>
<td>0.49</td>
<td>1.07</td>
<td>1.54</td>
<td>0.41</td>
<td>1.96</td>
<td>1.27</td>
<td>0.21</td>
</tr>
<tr>
<td>Mw (× 10⁴ Da)</td>
<td>1417</td>
<td>13097</td>
<td>16856</td>
<td>78</td>
<td>1576</td>
<td>1692</td>
<td>1599</td>
</tr>
</tbody>
</table>
This result was consistent with the observation of de Jonge et al. (2002).

During the batch experiments with HS surrogates, the DBP concentrations of filtrates increased by 15% to 322%. More than 80% of the DBP was still reserved in sludge residual fraction. Facilitated by humic substances solutions, DBP was more inclined to transfer from sludge matrix into filtrate compared to the sludge DOM. For the DEHP, only in F3 and H3, the concentrations of DEHP increased during the batch experiment. Except H1 and H3, DEHP concentrations in HS filtrates were no more than that in sludge native DOM. Even some DEHP associated with several HA surrogates transferred to sludge matrix in the batch experiments. The affinity of DEHP in sludge matrix exceeded DBP and was insusceptible by weak HS. It was revealed that the association between organic contaminants and sludge residual phases,

![Figure 1](https://iwaponline.com/wst/article-pdf/57/4/607/438697/607.pdf)

**Table 2** | Concentration of PAEs in sludge and its extraction

<table>
<thead>
<tr>
<th></th>
<th>DBP concentration (μg·g⁻¹ dw)</th>
<th>DEHP concentration (μg·g⁻¹ dw)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original sludge</td>
<td>Sludge DOM</td>
</tr>
<tr>
<td>F1</td>
<td>1.2</td>
<td>1.6</td>
</tr>
<tr>
<td>F2</td>
<td>2.6</td>
<td>3.6</td>
</tr>
<tr>
<td>F3</td>
<td>22.8</td>
<td>0.6</td>
</tr>
<tr>
<td>H1</td>
<td>2.1</td>
<td>2.5</td>
</tr>
<tr>
<td>H2</td>
<td>3.3</td>
<td>3.8</td>
</tr>
<tr>
<td>H3</td>
<td>1.8</td>
<td>4.5</td>
</tr>
</tbody>
</table>
involving sorption on the envelopes of cell and intracellular accumulation, was correlative to hydrophobicity of organic contaminants.

Relationship between characteristics of selected HS surrogates and PAEs mobility

The relationship between the transfer ratio of PAEs and $M_w$ of HS surrogate was shown in Figure 2. In Figure 3, the transfer ratio was plotted against the SUVA$_{254}$ of each HS surrogate. Solid lines were the linear fitting for all HS surrogates. Dashed lines were the linear fitting for HA surrogates and dotted lines were for FA surrogates.

As shown in Figure 2, the $M_w$ was positively correlated with the transfer ratio of DBP ($R^2 = 0.899$, $P = 0.014$). What’s more, this relationship could be more prominent in FA or HA separately ($R^2 = 0.993$ and 0.951). For DEHP, the correlation coefficient of linear equation ($R^2$) was only 0.688 and there was no significant correlation in FA or HA separately. During the humification process of DOM, lower molecular weight organic compounds were converted into condensed, higher molecular weight polymers (Ohno 2002). Our finding suggested that some typical functional groups in HS molecules benefited to the facilitated transport of DBP. Due to the strong affinity of DEHP in sludge, the functional groups had less effect on these DEHP.

As shown in Figure 3, both the transfer ratio of DBP and DEHP were not significantly correlated with SUVA$_{254}$ (no more than 0.8) of all HS surrogates. Based on the SUVA$_{254}$ of HA surrogates, transfer ratio of DBP was positively correlated to the aromatic extents of HA ($R^2 = 0.994$), which suggested that the denseness of HA phenyl structure might be related to its association with DBP.

The structures of DBP and DEHP differ in the length of aliphatic chains; hence the interactions between these two PAEs and HS surrogates should be similar except for the magnitudes of nonaromatic hydrophobic interactions. However, our data indicated that these two PAEs had discrepant aromatic interactions with HA. So, it should be the strong interaction between DEHP and sludge matrix interfered the aromatic interactions of DEHP and HA.
CONCLUSION

In this study, the correlation between PAEs mobility from sewage sludge and the characteristics of dissolved humic substances was determined using batch equilibration experiments. The dewatered activated sludge was sampled from sewage treatment plant treating domestic wastewater. Three humic acid (HA) and three fulvic acid (FA) samples extracted from different landfill leachates were selected as humic substances surrogates.

The results showed that the dibutyl phthalate (DBP), much less hydrophobic than di(2-ethylhexyl) phthalate (DEHP), was inclined to migrate from sludge matrix into humic substances solutions, while the DEHP could not be facilitated-transported by most humic and fulvic acids solutions, except the HA surrogate of high humification. The hydrophobic property influenced the association of PAEs on solutions, except the HA surrogate of high humification. Both the characteristics of PAEs and the dissolved humic substances controlled the PAEs partition between sludge and solution.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support given by Hi-Tech Research and Development Program of China (863 Program) (2006AA06Z384) and the General Programs of the National Natural Science Foundation of China (NSFC) (50578115).

REFERENCES


