Sorption and desorption of 17β-estradiol to natural sediment

H. Takigami, N. Taniguchi and Y. Shimizu

ABSTRACT

The sorption and desorption of 17β-estradiol (E2) to various natural sediment were investigated. First, the quantitative solvent–water partition indices were measured. Significant differences were found between the n-octanol–water partition coefficient ($K_{OW}$) and the n-hexane–water partition coefficient ($K_{HW}$) of E2. The value of $K_{HW}$ ($\log K_{HW} = 0.07$) is lower than those of two to four ring polyaromatic hydrocarbons (PAHs), while the value of $K_{OW}$ ($\log K_{OW} = 3.99$) and that of organic matter–water partition coefficient ($K_{OC}$) onto humic acid ($\log K_{OC} = 4.30$) were similar to those of the PAHs. Five natural sediments of various characteristics and origins were selected for sorption and desorption experiments. Linear isotherms were obtained for sorption and desorption. The equilibrium partitioning coefficients of E2 were well-correlated with their values of weight fraction of organic carbon in sediments ($f_{OC}$). Results suggest that E2 is sorbed mainly onto the organic portion of sediments and that its sorption coefficient can be estimated from $K_{OW}$ and $f_{OC}$, as in the case of non-polar PAHs. However, because of its polarity, the sorption mechanism of E2 onto sediments cannot be explained solely by the hydrophobic interaction.

Key words | 17β-estradiol, desorption, organic matter, partition coefficient, sediment, sorption

INTRODUCTION

The most effective natural estrogen, 17β-estradiol (E2), might be the strongest endocrine disruptor for water organisms in aquatic environments (Ying et al. 2002; Khanal et al. 2006; Combalbert & Hernandez-Raquet 2010). Previous reports have described findings related to sewage treatment process waters, revealing that E2, estrone (a metabolite of E2) and 17α-ethynylestradiol (synthetic estrogen) excreted from humans is the main causative substance in terms of the estrogenic activity of sewage and its treated effluents (Desbrow et al. 1998; Matsui et al. 2000; Nakada et al. 2006). In Japan, sewage treatment water has been added to urban river water increasingly with E2 concentrations on the order of nanograms per liter (Ministry of Land, Infrastructure, Transport and Tourism of Japan 2008). Thus far, not much is known about the behavior of E2 after it is released into the aquatic environment. However, several studies have been conducted to investigate the occurrence and the fate of E2 in the aquatic environment (Yu et al. 2004; Zhang & Zhou 2005; Labadie et al. 2007; Bradley et al. 2009). In this study, better understanding of E2 behavior between the natural solid and aqueous phase was especially examined. First, on a quantitative basis the solvent–water partition (e.g., n-octanol–water partition coefficient, n-hexane–water partition coefficient) was investigated experimentally. Characterization of sorption and desorption phenomena of E2 with environmental sediments were the main objectives, as investigated with laboratory experiments. To assess the equilibrium of E2 between the sediments and water, batch sorption–desorption experiments were optimized and conducted to measure the sorption and desorption isotherms. Then the relations between sorption–desorption coefficient and sediment characteristics were discussed.

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MATERIALS AND METHODS

Chemicals

Biochemical research grade E2 (purity >97%) was purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Humic acid was purchased from Aldrich Chemical Co. Inc. (Milwaukee, Wisconsin, USA). All other chemicals were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan); they were of research grade and were used without further purification.

Measurement of solvent–water partition coefficient of E2

The n-octanol–water partition coefficient ($K_{OW}$) for E2 was determined according to the OECD method (1981) with 7–57 mg l$^{-1}$ of E2 in n-octanol. After equilibrium was reached (i.e. 100 rotations in five minutes), water samples were taken and analyzed using a spectrophotometer (RF-5000; Shimadzu Corp.). Excitation and emission wavelengths were set, respectively, at 283 nm and 308 nm. $K_{OW}$ was calculated from the slope of a regression line between the two-phase equilibrium concentrations. The $n$-hexane–water partition coefficient ($K_{HW}$) was also determined in the same way as in the $K_{OW}$ experiment with 0.2–0.4 mg l$^{-1}$ of E2 in water.

Measurement of organic matter (humic acid)–water partition coefficient of E2

The partition coefficient of E2 between humic acid as natural organic matter and water was examined by using fluorescence quenching method (Gauthier et al. 1986). The procedures consisted of adding different amounts of humic acid to 50-ml Pyrex® glass centrifuge tubes with carbonate buffer (pH 7.0, pH adjusted with hydrochloric acid) to which aqueous E2 solution was added so produce a concentration of 1 mg l$^{-1}$. Then the mixtures were tumbled in a rotary shaker for 24 h at 30 rpm and 25 °C in the dark. Because of the quenching of fluorescence emitted from E2 bound to humic acid, only concentrations of free E2 in the aqueous phase were measured using a spectrophotometer in the conditions described above. The value of $K_{OC}$ onto humic acid was calculated as the ratio of equilibrium concentrations between in the aqueous phase and in the bound form to humic acid (carbon base).

Sediment samples

Five sediments of different origins and various characteristics were used for sorption–desorption experiments. Three sediments sampled, respectively, from different parts of Lake Biwa (Japan), were dried at 25 °C, ground in a mortar, mixed thoroughly, and stored in a glass bottle until use. The respective organic carbon (OC) contents of these three sediments (lake sediments A, B, C) were determined as 5.0, 1.4, and 2.4% using a TOC analyzer (TOC 5000A and SSM-5000A; Shimadzu Corp.). The other two sediments are selected from the USEPA standard samples (EPA-6, 14) whose OC contents were much lower than those of Lake Biwa sediments. Their physicochemical properties were well investigated, as presented in Table 1 (Hassett et al. 1980).

Sorption experiments

Sorption and desorption experiments were carried out based on the OECD method 106 (2000). For the sorption experiment, initial aqueous concentrations of E2 were set as 2.0–12.0 µg l$^{-1}$. Then 120 mg of the dried sediment sample was added to 12 ml of the solution (i.e. 10 g l$^{-1}$ as the solid-to-water ratio) in a glass tube (12 ml, Pyrex®) and kept airtight with the presence of sodium azide (0.2 g l$^{-1}$), which inhibits biodegradation of E2. Aqueous sediment mixtures were then tumbled in a rotary shaker for 24 h at 15 rpm and 25 °C in the dark. Equilibrium was attained within 24 h. Sediments were separated from solution by centrifugation for 10 min at 3,000 rpm. Then the concentration of E2 and pH in the supernatant were analyzed. Control tubes without sediment were prepared in the manner described above. No corrections in isotherm calculations were conducted because no system loss of E2 to control

### Table 1 | Characteristics of the EPA sediments used in this research.

<table>
<thead>
<tr>
<th>Sediment</th>
<th>pH (1:1)</th>
<th>Cation exchange capacity (meq g$^{-1}$)</th>
<th>$f_{OC}$ (%)</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA-6</td>
<td>7.83</td>
<td>0.35</td>
<td>0.0072</td>
<td>0.2</td>
<td>31.2</td>
<td>68.6</td>
</tr>
<tr>
<td>EPA-14</td>
<td>4.54</td>
<td>0.19</td>
<td>0.0048</td>
<td>2.1</td>
<td>34.4</td>
<td>63.6</td>
</tr>
<tr>
<td>Sediment</td>
<td>Amorphous metals</td>
<td>Al (wt %)</td>
<td>Si (wt %)</td>
<td>Fe (wt %)</td>
<td>Mn (µg/g)</td>
<td></td>
</tr>
<tr>
<td>EPA-6</td>
<td>0.03</td>
<td>0.44</td>
<td>0.59</td>
<td>4300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPA-14</td>
<td>0.20</td>
<td>0.10</td>
<td>1.38</td>
<td>216</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
tubes was observed. In the sorption and desorption experiments, carbonate buffer was not added to the sediment-water system, because E2 was lost from the supernatant with time possibly by the interaction of sediment contents and carbonate buffer.

Desorption experiments

After the sorption experiment, the desorption procedure was conducted by successively replacing 50% supernatant with pure water containing sodium azide (0.2 g l\(^{-1}\)). Mixing and analyses were conducted in the same manner as they were in the sorption experiment.

Analytical methods for sorption–desorption experiments

Aliquots of the final supernatant solution from adsorption–desorption experiments were sampled immediately and placed in 1-ml glass vials. Then they were analyzed using reversed-phase high pressure liquid chromatography (HPLC) (4.6 mm × 250 mm, Wakopak Wakosil 5C18-200T; Wako Pure Chemical Industries, Ltd.) equipped with a fluorescence detector (Scanning Fluorescence Detector 474; Waters Corp.). The elution was conducted in an isocratic mode with 70% acetonitrile/30% 50 mM acetate buffer (pH 4.8) at a flow rate of 1 m l\(^{-1}\) min\(^{-1}\). Concentrations of 0.5–15 µg l\(^{-1}\) could be quantified (limit of detection: 0.16 µg l\(^{-1}\), limit of quantification: 0.49 µg l\(^{-1}\)) using the fluorescence detector at 283-nm excitation wavelength and 308-nm emission spectra. External E2 standards were used to formulate calibration curves.

RESULTS AND DISCUSSION

\(K_{\text{OW}}, K_{\text{HW}}, \) and \(K_{\text{OC}}\) onto humic acid of E2

Log values of \(K_{\text{OW}}, K_{\text{HW}}, \) and \(K_{\text{OC}}\) onto humic acid of E2 were calculated and presented together with data of five polyaromatic hydrocarbons (PAHs) in Table 2 (Hassett et al. 1980; Shimizu 1990; Schwarzenbach et al. 1993; Harada 1998). Log \(K_{\text{OW}}\) of E2 is 3.99, which fits with the calculated value (3.94) reported in the program KowWin, a Log \(K_{\text{OW}}\) estimation program using an atom/fragment contribution method (Bhandari et al. 2009). Significant differences were found between the \(K_{\text{OW}}\) and \(K_{\text{HW}}\) values of E2. The value of \(K_{\text{HW}}\) is much lower than those of PAHs, which means that E2 is less soluble into \(n\)-hexane.

The E2 has a hydrophobic steroid structure, but also has 3-OH and 17-OH groups attached to the steroid, thereby imparting its polar property. The \(n\)-hexane molecules are incapable of developing polar interactions with the hydrogen bonds of E2. However, the values of \(K_{\text{OW}}\) and \(K_{\text{OC}}\) onto humic acid were nearly equal to those of PAHs. The amphiphilic (i.e. part hydrophilic and part hydrophobic) solvent \(n\)-octanol and the amphiphilic media humic acid are versatile and can accommodate rather indiscriminately a diverse group of organic solutes (Schwarzenbach et al. 1993). For PAHs, the \(K_{\text{OW}}, K_{\text{HW}}, \) and \(K_{\text{OC}}\) values of each compound are similar, which tells that PAHs molecules approach to the nonpolar ends of \(n\)-octanol solvent molecules, \(n\)-hexane solvent molecules and humic acid molecules by the common mechanism: hydrophobic reaction. However, the major factor that determines the high magnitude of \(K_{\text{OW}}\) and \(K_{\text{OC}}\) of E2 is not necessarily the hydrophobic reaction. The polar phenolic groups and non-aromatic rings of E2 molecule may be readily reactive with \(n\)-octanol and humic acid.

<table>
<thead>
<tr>
<th>Substances</th>
<th>Log (K_{\text{OW}}) [-]</th>
<th>Log (K_{\text{HW}}) [-]</th>
<th>Log (K_{\text{OC}}) [ml g(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>17(\beta)-estradiol</td>
<td>3.99</td>
<td>0.07</td>
<td>4.30</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>4.61(^a)</td>
<td>4.61(^a)</td>
<td>4.50(^a)</td>
</tr>
<tr>
<td>Fluorene</td>
<td>4.17(^a)</td>
<td>4.33(^a)</td>
<td>4.01(^a)</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>3.51(^a)</td>
<td>3.59(^a)</td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>4.54(^b)</td>
<td></td>
<td>4.46(^c)</td>
</tr>
<tr>
<td>Pyrene</td>
<td>5.13(^b)</td>
<td></td>
<td>5.40(^d)</td>
</tr>
</tbody>
</table>

\(^a\)Shimizu (1990).
\(^b\)Schwarzenbach et al. (1993).
\(^c\)Harada (1998).
\(^d\)Hassett et al. (1980).

Sorption–desorption isotherms between the sediment and water

In all cases of tested sediments, linear isotherms were obtained for sorption and desorption. The intercept of each isotherm revealed no significant difference from 0 at the 95% confidence level. Therefore, the adsorption–desorption isotherms can fit the following relation of the equation:

\[ S = K \cdot C \]  

where \(S\) (µg g\(^{-1}\)) is the E2 concentration associated with the sediment and \(C\) (µg l\(^{-1}\)) is the water-phase concentration.
Additionally, $K$ represents the linear isotherm partition coefficient.

**Figure 1** portrays sorption and desorption isotherms for Lake Biwa sediment A. No significant difference was found between the sorption and desorption isotherms at the 95% confidence level. In other words, the desorption of E2 from sediment occurred reversibly and no ‘hysteresis’ was observed. The experiments with the Lake Biwa sediment B and EPA-14 sediment yielded similar results, showing no hysteresis.

Statistically significant difference ($p < 0.05$) between the sorption and desorption isotherms were found for the Lake Biwa C and EPA-6 sediments. For Lake Biwa sediment C, desorption occurred and reached its equilibrium within 24 h, but it did not return to the level of sorption equilibrium. In the EPA-6 sediment results, desorption phenomena were not observed: sorption was irreversible (Figure 2). This sediment is unique and exceptional for the remarkable richness in amorphous manganese (4,300 µg g$^{-1}$). Despite the low organic content (0.72%), a greater quantity of PAHs than predicted is sorbed to it (Harada 1998), which is considered to be attributable to the high sorption capacity of fine manganese particles and decomposition of adsorbate oxidized by manganese.

The pH values showed no remarkable changes after each of sorption and desorption experiments without adding any buffering solution. They were influenced by the sediment characteristics. The ranges of pH after sorption and desorption experiments for respective sediments were the following: Lake Biwa sediment A 6.50–6.74; Lake sediment B 6.13–6.44; Lake sediment C 5.84–6.07; EPA-6 8.44–9.05; and EPA-14 5.12–5.56, while control showed 6.11–7.05.

**Relation between sorption coefficient and sediment characteristics**

The important role of organic solid in the overall binding of organic adsorbate is well established as demonstrated using organic carbon-normalized partition coefficients (Scheiblbaum et al. 1998). The equilibrium partitioning coefficient of E2 (i.e. the slope of isotherms, $K$) was first calculated for each sediment sample. The $K$ values are shown in **Figure 3** as a function of the organic matter content of the sediments (measured as organic carbon, $f_{OC}$). The $K$ values for sorption and desorption were well-correlated with their values of $f_{OC}$, respectively, with the exception of the EPA-6 sediment. The $K$ values of four sediments except for EPA-6 were then normalized to $f_{OC}$ as $K_{OC}$ by calculating the slopes of the two regression lines in **Figure 3**, based on the following equation.

$$K = f_{OC} \cdot K_{OC}$$  \hspace{1cm} (2)

The $K_{OC}$ values of E2 were obtained as 3.54 for sorption and 3.56 for desorption. A correlation equation between log $K_{OC}$ and log $K_{OW}$ has been proposed based on a set of
hydrophobic substances (Figure 4) (Shimizu & Terashima 1991). The $K_{OC}$ values of E2 and four PAHs are shown as a function of $K_{OW}$ in Figure 4. Linear correlation was estimated for non-polar PAHs. The $K_{OC}$ values of E2 for the sediments fit with the linear regression line for the PAHs. However, the $K_{OC}$ onto humic acid shows a higher value than the $K_{OC}$ values for the sediments, which suggests that a greater quantity of E2 is sorbed onto humic acid in the carbon base. It is considered that the polar content (hydroxy, carboxyl, carbonyl and amine groups) of humic acid affects the sorption increase of E2 to humic acid. The difference in aromaticity has also the great importance in the sorption of E2 to organic matter. Sorption and desorption equilibria of E2 were observed for an inorganic mixture solid of montmorillonite and amorphous ferric oxide (our data, data not shown). As described above, the sorption mechanism of E2 onto sediments cannot be explained solely by the hydrophobic interaction, implying that other mechanisms such as dipole–dipole interaction and hydrogen bonding between functional groups of E2 and the sediment surface might contribute to the observed sorption phenomena, at least partially. However, experimental results with sediments revealed that E2 is sorbed onto organic portion of sediments; its sorption coefficient can be estimated from the $K_{OW}$ ($n$-octanol–water partition coefficient) and $f_{OC}$, as in the case of non-polar hydrophobic organic contaminants. Therefore, it is understood that E2 is primarily sorbed onto the organic portion of sediments, although some combination of interactions might be responsible for governing sorption of E2 with natural solids. E2 also shows considerable water solubility because it has two –OH moieties that are capable of hydrogen bonding. Consequently, the desorption of E2 from contaminated soil and sediment is of importance for environmental reasons that it affects the estrogenic potential of environmental waters and the associated risk to aquatic organisms.

**CONCLUSIONS**

This study yielded experimental data related to the sediment (solvent)–water distribution of natural estrogen E2. Its sorption coefficient for environmental sediments can be estimated from $K_{OW}$ and $f_{OC}$, as in the case of non-polar hydrophobic organic contaminants. Therefore, it is understood that E2 is primarily sorbed onto the organic portion of sediments, although some combination of interactions might be responsible for governing sorption of E2 with natural solids. E2 also shows considerable water solubility because it has two –OH moieties that are capable of hydrogen bonding. Consequently, the desorption of E2 from contaminated soil and sediment is of importance for environmental reasons that it affects the estrogenic potential of environmental waters and the associated risk to aquatic organisms.

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