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# Effects of Physical−Chemical Characteristics on the Sorption of Selected Endocrine Disruptors by Dissolved Organic Matter Surrogates

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Sorption coefficients ($K_{oc}$ values) of selected endocrine disruptors for a wide variety of dissolved organic matter (DOM) were measured using fluorescence quenching and solubility enhancement. 17$\beta$-Estradiol, estriol, 17$\alpha$-ethynylestradiol, *p*-nonylphenol, *p-tert*-octylphenol, and dibutylphthalate were selected as endocrine disruptors. Aldrich humic acid, Suwannee River humic and fulvic acids, Nordic fulvic acid, alginic acid, dextran, and tannic acid were selected as DOM surrogates. The resulting sorption coefficients (log $K_{oc}$) were independent of octanol−water partitioning coefficients (log $K_{ow}$) of the selected endocrine disruptors, indicating the hydrophobic interaction is not the predominant sorption mechanism. Moreover, the $K_{oc}$ values for the selected endocrine disruptors, especially the steroid estrogens, correlated much better with UV absorptivity at 272 nm ($A_{272}$) and phenolic group concentration of the DOM than with either the H/O or the (O+N)/C atomic ratio of the DOM. This suggests that the sorption mechanism is closely related to the interaction between $\pi$-electrons and the hydrogen bonds, i.e., the affinity between phenolic groups of the steroid estrogens and DOM is suggested to provide a relatively large contribution to the overall sorption and yield the $K_{oc}$ values of the steroid estrogens as high as those of the alkylphenols and dibutylphthalate, which are suggested to be dominated by nonspecific hydrophobic interaction.

## Introduction

It is widely recognized that the sorption of hydrophobic organic compounds onto dissolved natural organic matter may significantly increase their aqueous solubility (*1*−*6*). This solubility enhancement affects the fate of these chemical species in an aqueous environment (*7*−*9*) and water treatment processes (*10, 11*). Furthermore, increases in dissolved organic matter (DOM) concentration results in decreases in the bioavailability and the bioaccumulation of these chemicals (*12*−*14*) while attenuating their toxicity (*15*−*17*). Consequently, trends in sorption of hydrophobic chemical compounds by DOM are of critical importance for the understanding of the solubility, fate, and impact of these compounds in the environment.

Steroid estrogens and endocrine-disrupting phenolic compounds (e.g., alkylphenols and bisphenol A) are one class of hydrophobic organics ubiquitous in the environment whose fates are important. They have been linked to recent reproductive health problems reported in humans and wild animals (e.g., ref *18*). In wastewater treatment plant effluents and surface waters, concentrations of steroid estrogens have been found as high as 200 ng/L (*19*−*26*), while those for alkylphenols and phthalates have been reported as high as 40 $\mu$g/L (*20, 23, 25*−*27*). Given the difficulties in quantifying these trace chemicals and DOM, little is known about how their interactions influence the fate of endocrine-disrupting compounds.

Consequently, the sorption of endocrine disruptors including steroid estrogens by DOM is of critical importance for the understanding of the fate of these compounds in the environment. Although the sorption of highly hydrophobic compounds such as PAHs, PCBs, and pesticides by DOM have been extensively studied over the last three decades (*1*−*6, 28*−*53*), little is known about the sorption of moderately hydrophobic compounds such as steroid estrogens and alkylphenols by organic matter except for some recent studies on the sorption of steroid estrogens by sediments (*54, 55*) and the sorption of nonylphenol by terrestrial soil (*56*). Hence the sorption of three steroid estrogens, 17$\beta$-estradiol, estriol, and 17$\alpha$-ethynylestradiol, and three endocrine-disrupting chemicals, *p*-nonylphenol, *p-tert*-octylphenol, and dibutylphthalate, by a wide variety of DOM surrogates are investigated using fluorescence quenching and solubility enhancement. The correlation between the measured sorption coefficients (log $K_{oc}$ value) and the octanol−water partitioning coefficients (log $K_{ow}$) for these species are evaluated and compared with other reported results. Moreover, the relationships between log $K_{oc}$ and physical−chemical characteristics (e.g., absorptivity, H/O atomic ratio, and the concentration of phenolic group) of the DOM surrogates are also investigated to better understand the sorption mechanisms.

## Experimental Section

17$\beta$-Estradiol was selected as one of the most common steroid estrogens, one often used as a positive control for the screening tests for estrogenic compounds. Additional steroid estrogens selected were estriol (E3), an important pregnancy estrogen as well as a metabolite of 17$\beta$-estradiol (E2), and 17$\alpha$-ethynylestradiol (EE2), the main component of contraceptive pills. *p*-Nonylphenol (NP), *p-tert*-octylphenol (OP), and dibutylphthalate (DBP) were selected as synthetic estrogenic compounds because of their high production and release to the environment as well as their ability to fluoresce. The chemical structure and physical−chemical properties of the selected compounds are shown in Table 1. 17$\alpha$-Ethynylestradiol (98%, HPLC grade) and dibutylphthalate (98%) were purchased from Sigma Chemical Co. (St. Louis, MO), while 17$\beta$-estradiol (Minimum 97%), estriol (98%), *p*-nonylphenol (tech grade), and *p-tert*-octylphenol (97%) were purchased from Aldrich Chemical Co. (Milwaukee, WI).

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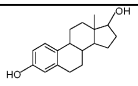
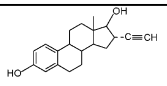
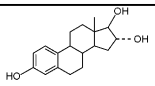
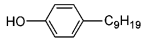
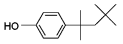
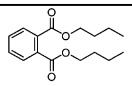
**TABLE 1. Structure and Physicochemical Properties of Selected Endocrine Disruptors**

| Name | 17β-estradiol (E2) | 17α-ethynyl-estradiol (EE2) | estriol (E3) | *p*-nonylphenol (NP) | *p-tert*-octyl-phenol (OP) | dibutylphthalate (DBP) |
|---|---|---|---|---|---|---|
| Chemical Structure |  |  |  |  |  |  |
| Chemical Formula | $C_{18}H_{24}O_2$ | $C_{20}H_{24}O_2$ | $C_{18}H_{24}O_3$ | $C_{15}H_{24}O$ | $C_{14}H_{22}O$ | $C_{16}H_{22}O_4$ |
| Aqueous Solubility | 3.85 mg/L[a] | 19.1 mg/L[a] | 30.2 mg/L[a] | 1.66 mg/L[b] | 4.52 mg/L[b] | 9.43 mg/L[c] |
| Reported Log $K_{ow}$[d] | 4.01[e] (3.94) | 3.67[e] (4.12) | 2.45[e] (2.81) | 5.76[e] (5.99) | 5.85[f] (5.28) | 4.57[e] (4.61) |
| pKa | 10.23[f] | 10.21[f] | 10.05[f] | 10.25[f] | 10.24[f] | - |

[a] From ref *67*. [b] From ref *68*. [c] From ref *69*. [d] Values inside parentheses are estimated using KowWin Log P software (*70*). [e] From ref *71*. Estimated from phenol using the fragment method (*72*). [f] Estimated from Hammet and Taft Equations (*73*).

The selected DOM surrogates included Aldrich humic acid, Suwannee River humic acid, Suwannee River fulvic acid, and Nordic fulvic acid. Humic acid and fulvic acid account for 6−8% and 54−72%, respectively, of the total organic carbon (TOC) in DOM extracted from typical rivers and streams (*57*). Suwannee River humic and fulvic acids and Nordic fulvic acid were purchased from the international humic substance society (IHSS) (St. Paul, MN) and were used without any additional pretreatment. Prior to any batch experiments, the peat based Aldrich humic acid purchased from Aldrich Chemical Co. was dialyzed using dialysis membrane made of regenerated cellulose (Por 7, MWCO 10 000, purchased from Spectrum Co.) to remove the higher molecular weight fraction, which is considered as the cause of its higher sorption compared with aquatic humic substances (*43, 58*). Alginic acid and dextran were selected as representative of polysaccharides, which account for 6−12% of total organic carbon in the typical river and streams (*57*). Alginic acid (purchased as its sodium salt from Aldrich Chemical Co.) is reported as a negatively charged polyelectrolyte, possesses extended random coils, and has molecular weight of approximately 210 000 (*59*). Dextran is reported a neutral polysaccharide with a dense coil structure and has molecular weight of 3000 to 200 000 (*60*), and the dextran purchased from Sigma Chemical Co. has an average molecular weight of 65 282 according to the manufacturer. Another DOM surrogate tannic acid was selected from the group of plant polyphenols, as a model of plant residues. Also called gallotannin, tannic acid consists of a D-glucose core and five galloyls. Each galloyl possesses at least three phenolic groups (for a total of 15 or more), and gallotannin has molecular weight of approximately 950. ACS reagent grade tannic acid was purchased from Sigma Chemical Co.

Sorption coefficients of selected steroid estrogens and estrogenic compounds by the selected DOM surrogates were determined using the fluorescence quenching technique (*32*) and solubility enhancement technique (*5, 43*). For fluorescent compounds, the fluorescence quenching technique has significant advantages in time, cost, and simplicity over the other sorption characterization methods. The fluorescence quenching technique, however, requires several assumptions (*32*) and has been criticized by many researchers (*42, 44, 50, 52*) because of some limitations such as the interferences by quenchers other than the DOM surrogates (e.g., dissolved oxygen) (*42*). In this study, preliminary experiments were conducted to evaluate all the assumptions required for fluorescence quenching. If the assumptions were not satisfied for any DOM surrogate, the more reliable technique, the solubility enhancement technique, was used instead. A few additional experiments were also conducted using the solubility enhancement technique even for DOM surrogates that are suggested to satisfy the assumptions for the fluorescence quenching technique for Supporting Information and comparison.

Stock concentrations of DOM, steroid estrogens, and estrogenic compounds were prepared. Appropriate volumes of each and MilliQ water were then added to Pyrex 13 mL centrifuge tubes to reach the desired total concentrations. The tubes were sealed with Teflon stoppers. The use of plastics was avoided, and all the apparatus used in the experiments were washed carefully to prevent possible contamination by plastic additives. Initial concentration of the selected endocrine disruptors was set at approximately 700 $\mu$g/L, well below aqueous solubility limit of those compounds. The concentration range used for each DOM surrogate was approximately between 2 and 10 mg C/L, which is a realistic TOC level in the environment (*57*). Headspace was minimized to prevent possible volatilization. Phosphate buffer was used to adjust the pH to 7 and sodium chloride was used to adjust the ionic strength to 0.02 M, as the standard conditions. The centrifuge tubes were mixed with a tumbler in the dark at 22 °C room temperature until equilibrium was attained. Preliminary studies showed 24 h was sufficient for the equilibration. After 24 h, total fluorescence was measured using a Perkin-Elmer LS-5 fluorescence spectrophotometer. The fluorescence of each DOM surrogate was measured and subtracted from the total fluorescence. The excitation and emission wavelengths used were 276 and 310 nm, respectively, for all the selected compounds except for dibutylphthalate, for which 230 and 368 nm were used instead. Absorbances at the excitation and emission wavelengths were measured using an Agilent 8453E UV−visible spectrophotometer, and inner filter corrections (*39*) were conducted for each sample. The inner filter correction factors were relatively small within the range of the DOM concentration in this study. Background fluorescence was relatively low for all the DOM:endocrine disruptor combinations except for the combination of DBP and Aldrich humic acid. The concentration of each DOM surrogate was measured using a Tekmar Dormann Apollo 9000 TOC analyzer. Six or more samples with four different DOM surrogate concentrations and duplicate samples without DOM were prepared for each combination of endocrine disruptor and DOM surrogate. The fluorescence without DOM surrogates ($F_o$) was divided by the corrected total fluorescence ($F$), and this ratio ($F_o/F$) was plotted against DOM surrogate concentration in the form of a Stern−Volmer plot (*32*). The sorption coefficient ($K_{oc}$ with units of L/kg C of DOM surrogate) was determined as the slope of the best fit line of the form:

$$F_o/F = 1 + K_{oc}\,[\text{DOM (kg C/L)}] \qquad (1)$$

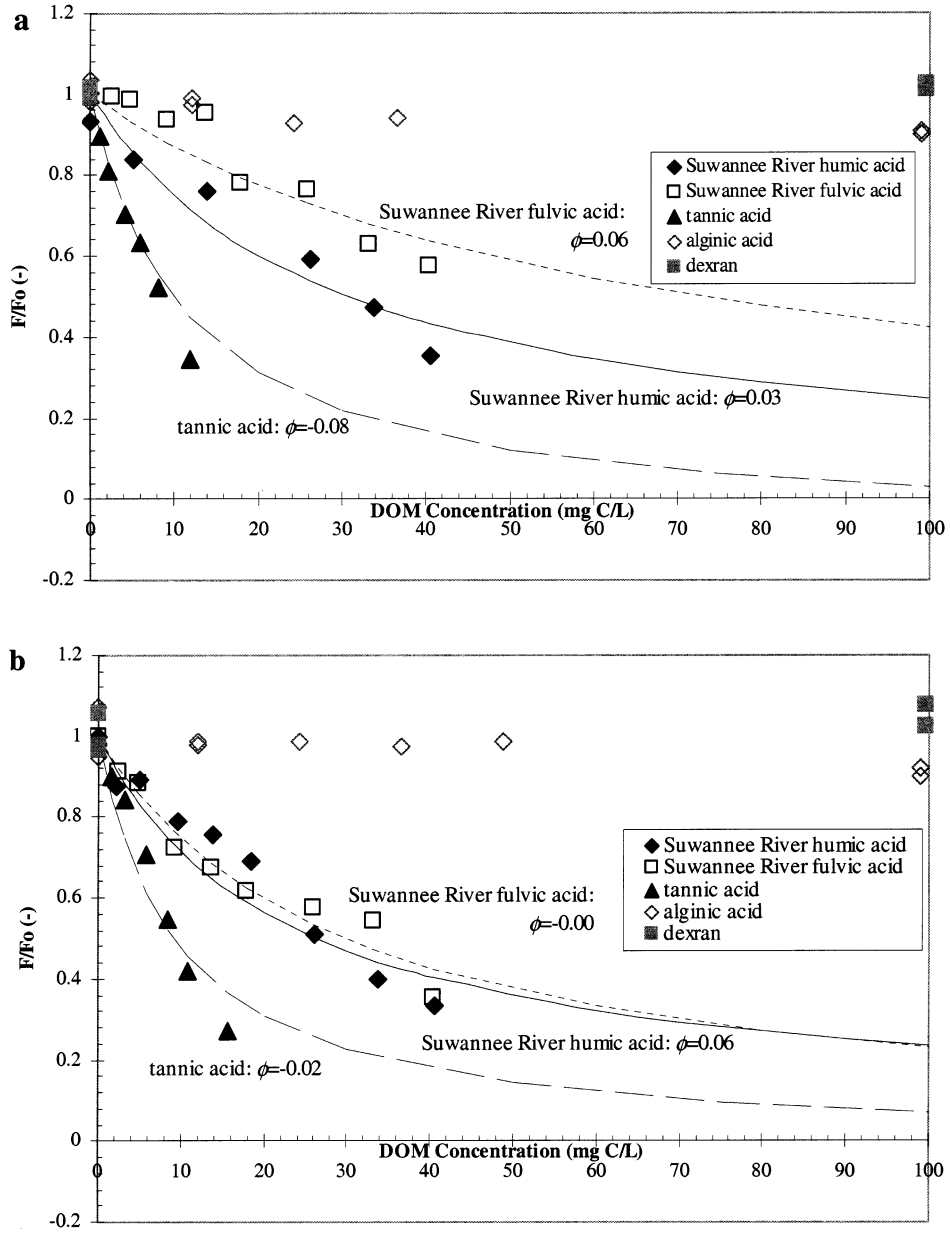



**FIGURE 1. Determination of quantum yield of the fraction of (a) 17$\beta$-estradiol (E2) and (b) *p*-nonylphenol (NP) bound to model DOM surrogates.**

As an alternative technique, the solubility enhancement technique, which is the most frequently used by other researchers (*1*−*6*, *42*, *43*, *45*, *48*), was used. The procedure developed by Chiou and co-workers (*5*) was modified by the authors and used in this study. Briefly, the endocrine disrupter solution in volatile organic solvent (dichloromethane) was plated on the Pyrex 13 mL centrifuge tube with nitrogen gas. Appropriate amount of DOM stock solution (ranged from 2 to 200 mg C/L) and phosphate buffer solution was added. As with the fluorescence quenching technique, the centrifuge tubes were mixed with a tumbler in the dark at 22 °C room temperature for 24 h. After the mixing, the tubes were centrifuged (3000 rpm, 10 min) to remove the insoluble residue. The concentration of the selected endocrine disruptor in the supernatant was measured using the HPLC (Shimadzu, SIL-10A) equipped with ODS column (Shim-Pack, VP-ODS) and PDA detector (Shimadzu, SPD-M10AVP). Mixture of acetonitrile and water (40:60 for steroid estrogens and 70:30 for NP and DBP) was used as mobile phase at flow rate of 1 mL/min. UV wavelength at 280 nm was used for the detection of steroid estrogens, 278 nm was used for NP, and 274 nm was used for DBP.

The molecular weight distribution of the selected DOM surrogate was determined using a Waters 510 gel permeation chromatograph equipped with Ultra Hyfrogel Linear Column and the differential refractometer (HP Series 1050). Sodium nitrate (0.1 N) was used as mobile phase at flow rate of 0.1 mL/min. The analyzer was calibrated using dextran standard solutions of known average molecular weight between 1000 and 635 000. The absorptivity of each DOM surrogate at 272 nm was calculated by dividing the absorbance at 272 measured using the UV−visible spectrophotometer in 1 cm quartz cell by the TOC level of the solution.

## Results and Discussion

**Validation of the Fluorescence Quenching Technique for the Determination of Sorption Coefficients.** As presented above, the fluorescence quenching method has been extensively used for the determination of the sorption coefficient of highly hydrophobic and nonpolar organic chemicals

**TABLE 2. Comparison of Sorption Coefficients Obtained Using Fluorescence Quenching and Solubility Enhancement for Model DOM**

| model endocrine disruptor | model DOM surrogate | sorption coefficient[a] (L/kg C) | |
|---|---|---|---|
| | | fluorescence quenching | solubility enhancement |
| 17$\beta$-estradiol | Suwannee River humic acid | 8.38 ($\pm$ 1.03) $\times$ $10^4$ | 3.65 ($\pm$ 0.46) $\times$ $10^4$ |
| | tannic acid | 19.01 ($\pm$ 0.79) $\times$ $10^4$ | 8.65 ($\pm$ 1.30) $\times$ $10^4$ |
| *p*-nonylphenol | Suwannee River humic acid | 9.05 ($\pm$ 1.23) $\times$ $10^4$ | 6.46 ($\pm$ 1.62) $\times$ $10^4$ |
| | tannic acid | 13.26 ($\pm$ 2.27) $\times$ $10^4$ | 5.33 ($\pm$ 0.46) $\times$ $10^4$ |

[a] Inside the parentheses ($\pm$ standard deviation).

**TABLE 3. Sorption Coefficients (Log $K_{oc}$ Values)[a,b] onto DOM Surrogates and Octanol–Water Partition Coefficients (Log $K_{ow}$ Values) of the Selected Endocrine Disruptors**

| | 17$\beta$-estradiol (E2) | 17$\alpha$-ethynylestradiol (EE2) | estriol (E3) | *p*-nonylphenol (NP) | *p-tert*-octylphenol (OP) | dibutylphthalate (DBP) |
|---|---|---|---|---|---|---|
| Aldrich humic acid | 4.94 ($\pm$ 0.03) | 4.78 ($\pm$ 0.02) | 4.99 ($\pm$ 0.03) | 4.83 ($\pm$ 0.10) | 4.84 ($\pm$ 0.17) | 4.95 ($\pm$ 0.02)[e] |
| Suwannee River humic acid | 4.92 ($\pm$ 0.05) | 4.80 ($\pm$ 0.02) | 4.96 ($\pm$ 0.03) | 4.96 ($\pm$ 0.06) | 4.94 ($\pm$ 0.06) | 4.80 ($\pm$ 0.04) |
| Suwannee River fulvic acid | 4.57 ($\pm$ 0.02) | 4.55 ($\pm$ 0.05) | 4.64 ($\pm$ 0.03) | 4.70 ($\pm$ 0.04) | 4.63 ($\pm$ 0.08) | 4.65 ($\pm$ 0.07) |
| Nordic fulvic acid | 4.61 ($\pm$ 0.06) | 4.63 ($\pm$ 0.08) | NA[d] | 4.71 ($\pm$ 0.05) | NA[d] | 4.75 ($\pm$ 0.05) |
| alginic acid | 3.75 ($\pm$ 0.08) | 3.23 ($\pm$ 0.06) | NA[d] | 4.84 ($\pm$ 0.04) | NA[d] | 4.11 ($\pm$ 0.07) |
| dextran | 2.76 ($\pm$ 0.29) | 3.04 ($\pm$ 0.19) | NA[d] | ND[c] | NA[d] | ND[c] |
| tannic acid | 5.28 ($\pm$ 0.02) | 5.22 ($\pm$ 0.03) | 5.32 ($\pm$ 0.01) | 5.12 ($\pm$ 0.07) | 5.16 ($\pm$ 0.03) | 4.84 ($\pm$ 0.05) |
| log $K_{ow}$ | 4.01 | 3.67 | 2.45 | 5.76 | 5.85 | 4.57 |

[a] Unit of $K_{oc}$ (L/kg C). [b] Inside the parentheses ($\pm$ standard deviation). [c] Not detected ($R^2 < 0.5$ and 95% confidence level of $K_{oc}$ overlaps zero). [d] Not available. [e] Significant fluorescence signal was detected for DOM, and the results might be questionable.

**TABLE 4. Physical–Chemical Characteristics of the Selected DOM Surrogates Possibly Affecting the Sorption Mechanism**

| | weight standard molecular weight average ($Mw_w$) | (O+N)/C atomic ratio | H/O atomic ratio | absorptivity at 272 nm ($A_{272}$) (L/kg C cm) | carboxylic (mol/kg C) | phenolic (mol/kg C) |
|---|---|---|---|---|---|---|
| Aldrich humic acid | 4637 (8373[a]) | (0.43[a,b]) | (2.03[a,b]) | 58600 | NA[c] | NA[c] |
| Suwannee River humic acid | 6544 | 0.63[d] | 1.66[d] | 50700 | 16.03[d] | 7.21[d] |
| Suwannee River fulvic acid | 4012 | 0.64[d] | 1.60[d] | 31400 | 21.15[d] | 5.45[d] |
| Nordic fulvic acid | 5398 | 0.66[d] | 1.42[d] | 40900 | 19.27[d] | 5.43[d] |
| tannic acid | 950[e] | 0.63[e] | 1.62[e] | 115600 | none | 29.74[e] |
| alginic acid | 744451 | 1.00[f] | 1.67[f] | 389 | 13.91[f] | none |
| dextran | 71141 | 0.83[f] | 2.00[f] | 4.4 | none | none |

[a] Before dialysis pretreatment. [b] From ref *58*. [c] Not available. [d] From manufacturer. [e] Assuming that tannic acid has the structure of pentagalloyl-D-glucose. [f] From the proposed chemical structure (*57*).

by DOM (*9*, *32*, *34*, *39*, *41*, *44*, *47*). However, several assumptions, such as insignificant static quenching compared with dynamic quenching (*32*) and full quenching rather than partial quenching (*40*), were required for the reliable measurement of sorption coefficients. These assumptions were suggested for some pairs of DOM and nonpolar PAH (*9*, *32*, *34*, *39*, *41*, *44*, *47*), but few reports were available (*62*, *63*) for polar chemical compounds such as the selected endocrine disruptors. Even for nonpolar compounds, limitations of the fluorescence quenching technique to determine the sorption coefficients for aliphatic poly(acrylic acid) ester were suggested (*51*, *52*). Therefore, some preliminary experiments were conducted to show the validity of those assumptions necessary for the fluorescence quenching of the selected DOM:endocrine disruptor pairs.

First, the efficiency of static quenching of the selected endocrine disruptors by DOM surrogates was checked using some representing a DOM:endocrine disruptor pair. According to Backhus and Gschwend (*9*), total fluorescence $F$ with addition of DOM can be expressed as

$$F = F_o\{(\text{freely dissolved fraction}) + (\text{sorbed fraction})\ \phi\} \quad (2)$$

where $F_o$ is the fluorescence without DOM and $\phi$ is the fluorescence quantum yield of the DOM-bound endocrine disruptor. This equation can be rearranged as

$$F/F_o = \{1 + \phi\, K_{oc}\,[\text{DOM (kg C/L)}]\}/\{1 + K_{oc}\,[\text{DOM (kg C/L)}]\} \quad (3)$$

Only if $\phi$ is zero, the DOM surrogate can be suggested as a full quencher, and the Stern–Volmer equation (eq 1) can be derived from eq 3. Fluorescence quenching of two representing endocrine disruptors, 17$\beta$-estradiol and *p*-nonylphenol, by representing humic substances (Suwannee River humic and fulvic acids), tannic acid, algnic acid, and dextran was examined in this study. $\phi$ values of nearly zero were obtained for Suwannee River humic and fulvic acids and tannic acid for 17$\beta$-estradiol and *p*-nonylphenol (Figure 1). These results suggest full quenching and the acceptable reliability of the fluorescence quenching method for the selected humic substances and tannic acid. In contrast, alginic acid and dextran did not significantly quench the fluorescence of 17$\beta$-estradiol and *p*-nonylphenol under 100 mg C/L and were suggested as either partial quenchers or nonquenchers. Additionally, the effects of other quenchers such as dissolved oxygen are also the significant concern for the use of the fluorescence quenching technique. Thus, effects of oxygen on the fluorescence measurement were examined, and no significant difference was found for 17$\beta$-estradiol and *p*-nonylphenol.

Finally, $K_{oc}$ values obtained using fluorescence quenching and solubility enhancement were compared with each other for E2 and NP with Suwannee River humic acid and tannic acid. As shown in Table 2, $K_{oc}$ values measured using the fluorescence quenching technique were approximately twice as high as those measured using the solubility enhancement technique for all the four combinations. This trend, however, agrees with the $K_{oc}$ values of PAHs for Suwannee River humic substances and Aldrich humic acid obtained by these two different techniques (*42*, *44*). Thus, the fluorescence quenching technique could slightly overestimate $K_{oc}$ values but can be suggested to much more easily provide the acceptable estimate of $K_{oc}$ values of endocrine disruptors for humic substances and tannic acid. In this study, the fluorescence quenching technique was used for to determine $K_{oc}$ values of endocrine disruptors for humic substances and tannic acid although slight overestimate and artifacts by this technique should be taken into consideration. For two polysaccharides, algnic acid and dextran, solubility enhancement technique was used for more reliable measurement of the sorption coefficient.

**Relationship between Sorption Coefficients and Octanol−Water Partitioning Coefficients.** The sorption coefficients, obtained by the fluorescence quenching for humic substances and tannic acid and by the solubility enhancement for alginic acid and dextran, are presented as log $K_{oc}$ in Table 3 with reported log octanol−water partition coefficients (log $K_{ow}$) of the selected endocrine disrupters. In Figure 2, relationships between log $K_{oc}$ and log $K_{ow}$ values are indicated for the Aldrich humic acid and Suwannee River humic and fulvic acids. $K_{oc}$ values reported for PAHs, PCBs, and other hydrophobic organic compounds with these humic substances are included for comparison.

As in Figure 2(a), the log $K_{oc}$ values measured in this study were independent of the log $K_{ow}$ values of the endocrine disruptors although a slight overestimate of $K_{oc}$ values is possible due to the use of the fluorescence quenching technique. Furthermore, the log $K_{oc}$ values for all the selected endocrine disruptors with dialyzed Aldrich humic acid narrowly ranged from 4.78 to 4.99 (Table 3) and are between those reported for PAHs with three and four aromatic rings (anthracene and fluoranthene, "$PAH_3$", and pyrene and phenanthrene, "$PAH_4$", in Figure 1a, respectively). The two alkylphenols and dibutylphthalate are below or close to the regression line for literature results, while the three steroid estrogens are above or close to the regression line. The lack of significant correlation between log $K_{ow}$ and log $K_{oc}$ suggests that sorption mechanisms other than the nonspecific hydrophobic interaction should be a more important role in the sorption of these selected endocrine disruptors. Additionally, the lack of the effects of ionic strength on the sorption coefficients (*61*) also suggested the relatively weak contribution of hydrophobic interaction for the sorption. Thus, the ability to predict $K_{oc}$ values of endocrine disruptors by DOM based on linear free energy relationships (LFER) using solely log $K_{ow}$ values is suggested to be limited. In this study, removal of the higher molecular weight fraction over 10 000 by the pretreatment of Aldrich humic acid was suggested as a result of pretreatment using dialysis membrane of molecular weight cut off of 10 000. This pretreatment possibly resulted in a decrease in the hydrophobicity and aromaticity of the treated Aldrich humic acid as well as a smaller hydrophobic interaction between the selected endocrine disruptors and the dialyzed Aldrich humic acid, as compared with the untreated Aldrich humic acid used by other researchers. In contrast, log $K_{oc}$ values determined by other researchers for untreated Aldrich humic acid showed a fairly good linear correlation ($R^2 = 0.844$) with log $K_{ow}$ using mainly PAHs, PCBs, and DDT. Additionally, for soil organic matter, a relatively strong linear relationship between log

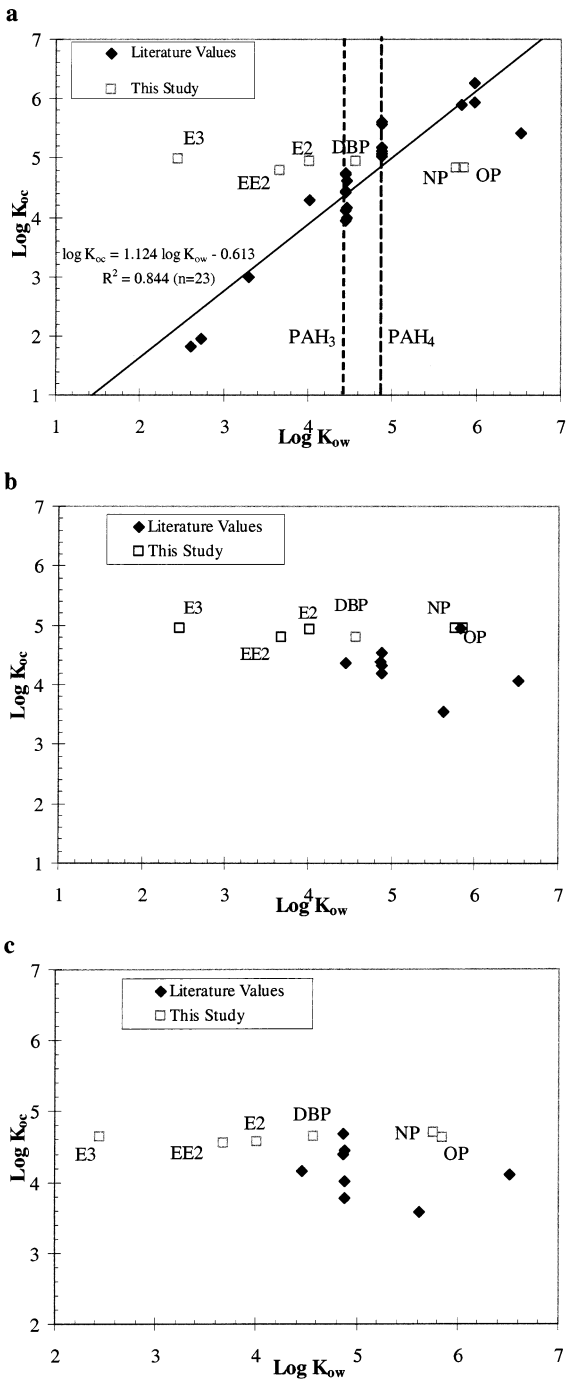



**FIGURE 2. Relationship between sorption coefficients and octanol−water partition coefficients of selected endocrine disruptors and comparison with the conventional studies (*5, 6, 9, 28−30, 32, 33, 37, 39−44*) for (a) Aldrich humic acid, (b) Suwannee River humic acid, and (c) Suwannee River fulvic acid.**

$K_{ow}$ values of highly hydrophobic organic compounds and log $K_{oc}$ values was repeatedly reported by several researchers (e.g., refs *64* and *65*). For steroid estrogens, contrarily, the linear relationship between log $K_{ow}$ values and log $K_{oc}$ values was suggested to be poor for sediment organic matter (*54*, *55*), and this trend agrees with the results obtained in this study. Since the number of endocrine disruptors selected is limited and due to the possible difficulties in fluorescence quenching, further investigation is necessary using an even wider variety of endocrine disruptors and using the technique other than the fluorescence quenching.

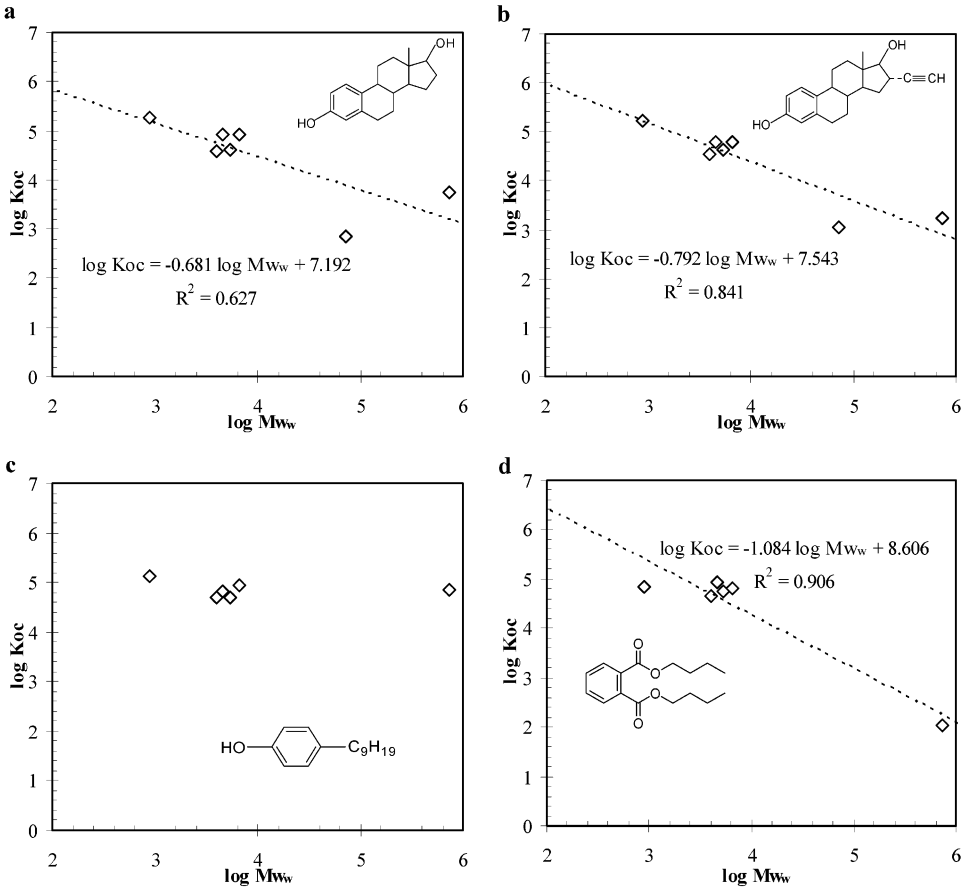



**FIGURE 3. Relationship between sorption coefficients and weight standard molecular weight of the selected DOM surrogates for (a) 17$\beta$-estradiol (E2), (b) 17$\alpha$-ethynylestradiol (EE2), (c) *p*-nonylphenol (NP), and (d) dibutylphthalate (DBP).**

As shown in Figure 2(b),(c), the log $K_{oc}$ values measured for Suwannee River humic and fulvic acids were also independent of the log $K_{ow}$ values of the endocrine disruptors as with the Aldrich humic acid. Moreover, the log $K_{oc}$ values for all the selected endocrine disruptors with Suwannee River humic and fulvic acid narrowly ranged from 4.80 to 4.96 and from 4.55 to 4.70, respectively (Table 3). Again, the lack of significant correlation between log $K_{ow}$ and log $K_{oc}$ suggests that sorption mechanisms other than the nonspecific hydrophobic interaction should be more important role in the sorption of these selected endocrine disruptors by Suwannee River humic substances especially for less hydrophobic steroid estrogens. In addition, the log $K_{oc}$ values measured for nonylphenol and octylphenol with Suwannee River humic acid were similar to that reported for perylene (log $K_{ow}$ = 5.82), and those obtained in this research for the steroid estrogens and dibutylphthlate were similar to or slightly higher than those reported for PAHs with four rings (pyrene or phenanthrene). Less data have been reported for Suwannee River humic and fulvic acids than for Aldrich humic acid, as indicated in Figure 2(b),(c). As with the Aldrich humic acid, further investigation is necessary using an even wider variety of endocrine disruptors and using the technique other than the fluorescence quenching because the number of endocrine disruptors selected is limited and the possible difficulties in fluorescence quenching. Since some of the selected compounds (e.g., 17$\beta$-estradiol and estriol) are biodegradable, the use of nonsterile humic and fulvic acids could cause the diminishing of these compounds and also result in the overestimate of the sorption coefficients.

As far as Nordic fulvic acid is concerned, the trend was similar to that of Suwannee River fulvic acid. Again, the narrow range of the log $K_{oc}$ values (Table 3) suggest the relatively less contribution of hydrophobic interaction between the selected endocrine disruptors and Nordic fulvic acid as with Suwannee River fulvic acid.

As in Table 3, tannic acid had the highest $K_{oc}$ values among the DOM surrogates for all the endocrine disruptors tested, except for dibutylphthalate. Whereas the log $K_{oc}$ values ranged from 4.84 to 5.32 and the range was wider than the selected humic substances, slightly higher sorption coefficients were found for steroid estrogens than for the selected alkylphenols and dibutylphthalate. As with the selected humic substances, log $K_{oc}$ values were independent of reported log $K_{ow}$ values and sorption mechanisms other than the hydrophobic interaction should be more important role in the sorption of these selected endocrine disruptors by tannic acid.

As presented in the previous section, sorption coefficients of four representing endocrine disruptors, 17$\beta$-estradiol, 17$\alpha$-ethynylestradiol, *p*-nonylphenol, and dibutylphthalate by two polysaccharides, algnic acid and dextran, were determined using the solubility enhancement technique. As shown in Table 3, a moderate linear relationship between log $K_{oc}$ values and reported log $K_{ow}$ values was suggested for alginic acid ,while no significant sorption or relatively small log $K_{oc}$ values were detected for detran. Unlike humic substances and tannic acid, the nonspecific hydrophobic interaction is suggested to play a relatively important role in the sorption of the selected endocrine disruptors by alginic acid. For dextran, no significant sorption was detected, and the relationship between log $K_{oc}$ values and reported log $K_{ow}$ values was uncertain.

Overall, log $K_{oc}$ values were independent of the reported log $K_{ow}$ values of the selected endocrine disruptors for tannic acid and the selected humic substances. A moderate linear correlation was suggested for alginic acid, while no significant

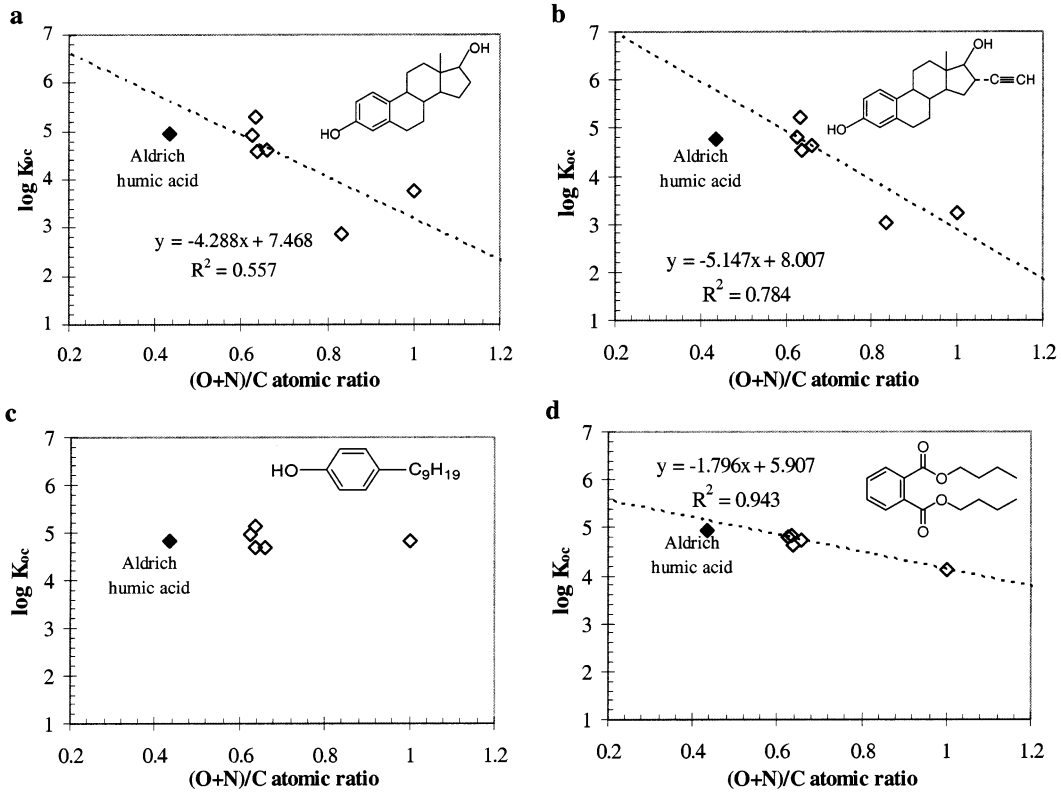



**FIGURE 4. Relationship between sorption coefficients and (O+N)/C atomic ratios of the selected DOM surrogates for (a) 17$\beta$-estradiol (E2), (b) 17$\alpha$-ethynylestradiol (EE2), (c) *p*-nonylphenol (NP), and (d) dibutylphthalate (DBP).**

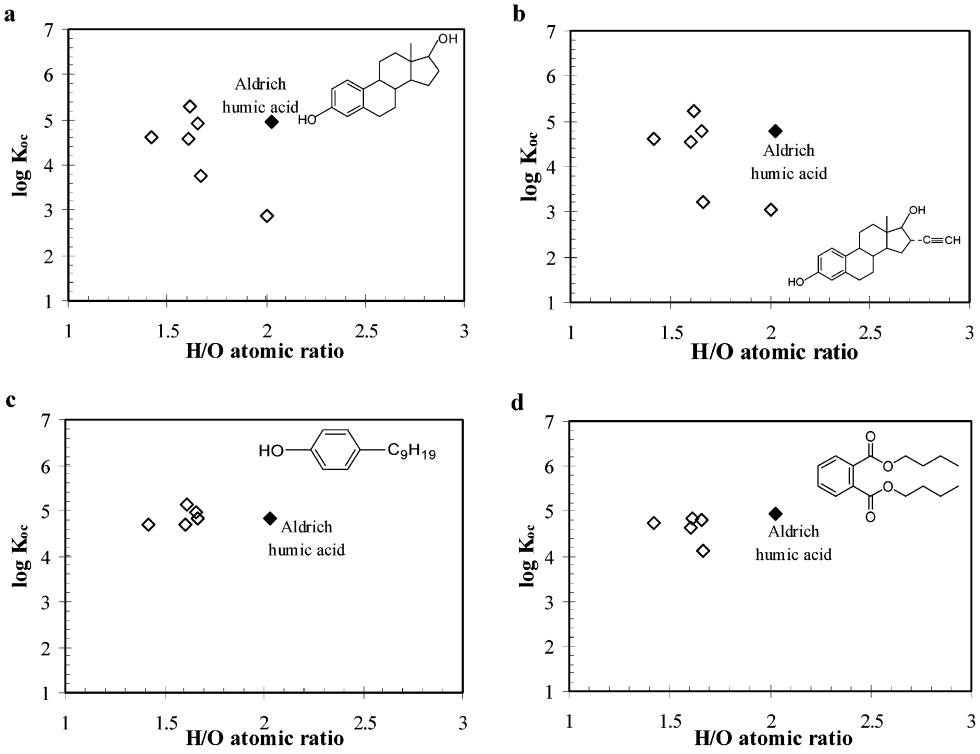



**FIGURE 5. Relationship between sorption coefficients and H/O atomic ratios of the selected DOM surrogates for (a) 17$\beta$-estradiol (E2), (b) 17$\alpha$-ethynylestradiol (EE2), (c) *p*-nonylphenol (NP), and (d) dibutylphthalate (DBP).**

sorption was detected for detran. Next, similarities and differences in $K_{oc}$ values for DOM compounds are briefly discussed as follows.

First, the measured results of this study agree well with those available from conventional studies, which reported $K_{oc}$ values for Suwannee River humic acid slightly higher, by a factor of 1.5−2, than those for Suwannee River fulvic acid for the same PAHs (e.g., refs *28* and *42*). The humics' and fulvics' log $K_{oc}$ values were slightly lower than or similar to those for tannic acid, while the $K_{oc}$ values for the polysaccharides, alginic acid and dextran, were 1−2 orders of magnitude lower than those for the humic substances and

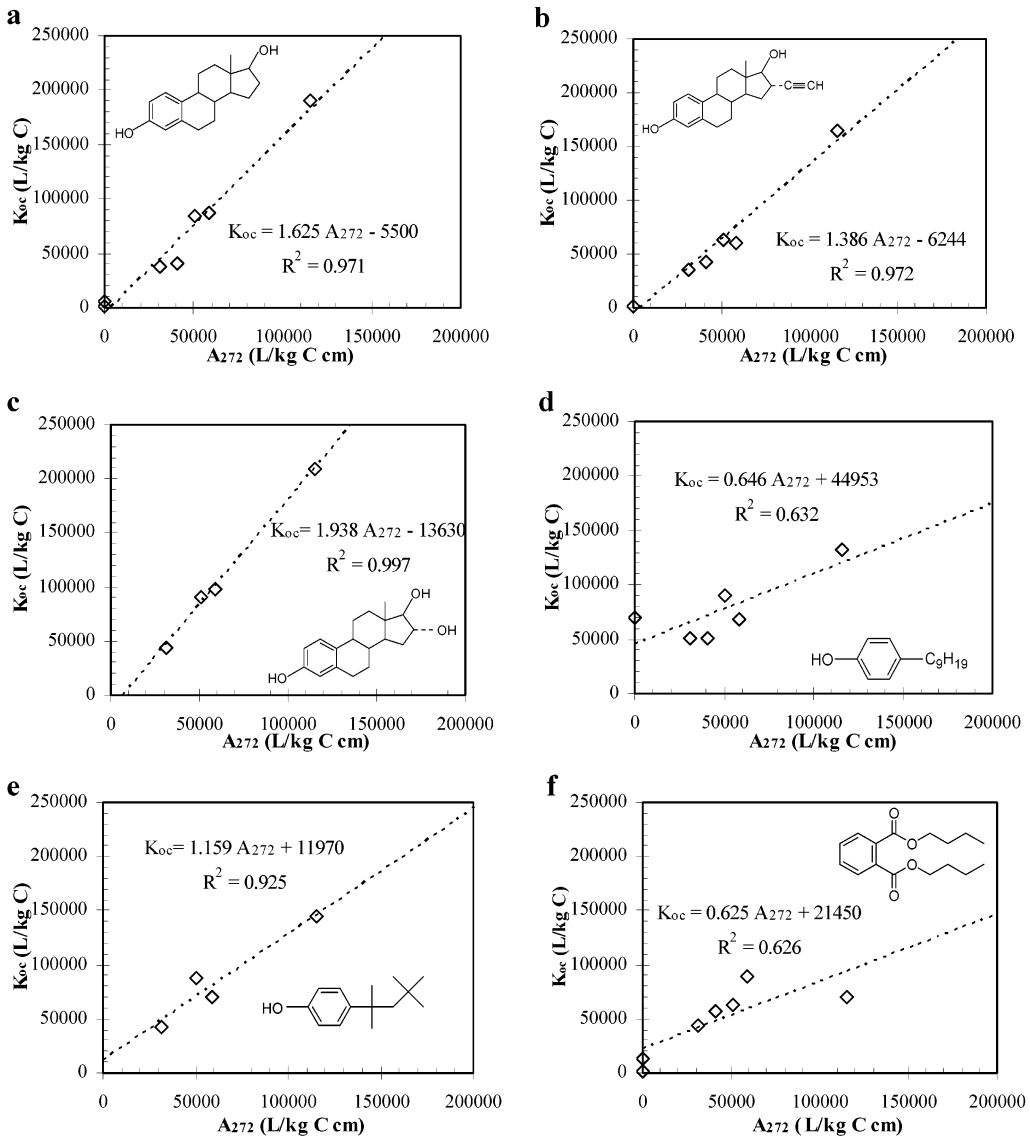



**FIGURE 6. Relationship between sorption coefficients and absorptivity of the selected DOM surrogates at 272 nm ($A_{272}$) for (a) 17$\beta$-estradiol (E2), (b) 17$\alpha$-ethynylestradiol (EE2), (c) estriol (E3), (d) *p*-nonylphenol (NP), (e) *p-tert*-octylphenol (OP), and (f) dibutylphthalate (DBP).**

tannic acid. Similar log $K_{oc}$ values were found for Suwannee River fulvic acid and Nordic fulvic acid, and no significant difference in log $K_{oc}$ values due to the source of fulvic acid was suggested. The similar log $K_{oc}$ values for dialyzed Aldrich humic acid and Suwannee River humic acid obtained in this study is in contrast to the reported significantly higher log $K_{oc}$ values of hydrophobic organic chemicals, such as PAHs, PCBs, and DDT, for untreated Aldrich humic acid than for Suwannee River humic acid (e.g., refs *6* and *43*). In this study, the average molecular weight of Aldrich humic acid was significantly decreased from 8373 to 4637 by the dialysis (Table 4). This dialysis pretreatment resulting in a lower molecular weight fraction could contribute to the smaller $K_{oc}$ values than those reported for *p*-nonylphenol and *p-tert*-octylphenol with untreated Aldrich humic acid and similar $K_{oc}$ values to those for Suwannee River humic acid. The similarity of the sorption coefficients of dialyzed Aldrich humic acid of this study and Suwannee River humic acid also implies the possibility of the using a less expensive soil humic acid such as Aldrich humic acid after the dialysis pretreatment to model aquatic humic acids although further investigation is necessary.

Less is known about sorption to tannic acid and polysaccharide species compared with humic substances. Enfield et al. (*36*) investigated the sorption coefficient of hexachlorobenzene (HCB, log $K_{ow} = 5.73$) and pyrene (log $K_{ow} = 4.88$) on dextran using the column method and found 2 orders of magnitude lower log $K_{oc}$ values (3.08 for HCB and 3.15 for pyrene) than those on soil humic acid (5.98 for HCB and 4.88 for pyrene). Similarly in this study, $K_{oc}$ values for dextran were lower, by 2−3 orders of magnitude, than those for the humic acids for 17$\beta$-estradiol and 17$\alpha$-ethynyestradiol. Differences in the experimental setup and materials (dextran) may account for the lower $K_{oc}$ values for observed for dextran in this study. Garbarini and Lion (*33*) found that tannic acid had smaller $K_{oc}$ values than Aldrich humic acid using toluene (log $K_{ow} = 2.73$) and trichloroethene (log $K_{ow} = 2.61$) as the testing compounds. In this study, $K_{oc}$ values were significantly higher for tannic acid than those for dialyzed Aldrich humic acid except for dibutylphthalate, the only species lacking a phenolic group used in this study. The relationships between the physical−chemical characteristics such as the concentration phenolic groups of DOM compounds and the sorption coefficients are further investigated in the next section. Given the significant differences of the testing compounds (i.e., sources of tannic acid and pretreatment of Aldrich humic acid), the results are not directly comparable. Similarly, no comparable data are currently available for alginic acid.

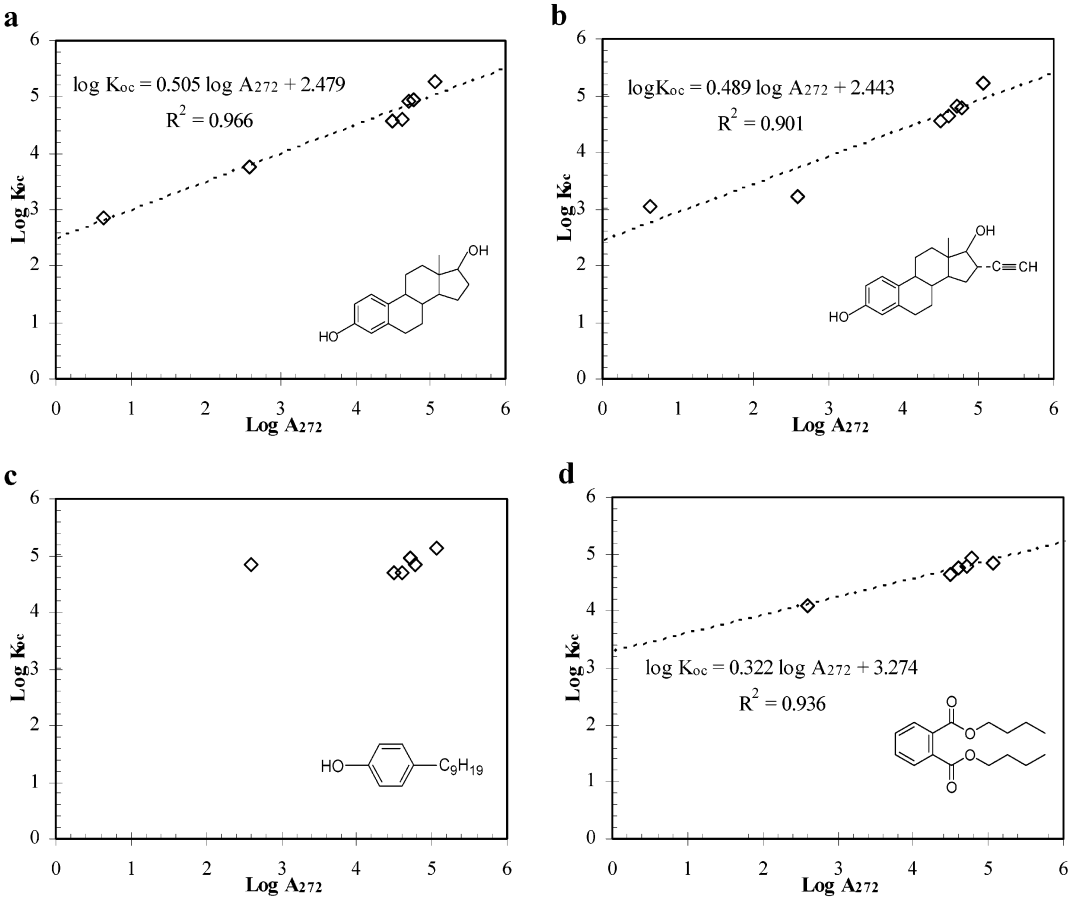



**FIGURE 7. Relationship between sorption coefficients and logarithm of the absorptivity of the selected DOM surrogates at 272 nm (log $A_{272}$) for (a) 17$\beta$-estradiol (E2), (b) 17$\alpha$-ethynylestradiol (EE2), (c) *p*-nonylphenol (NP), and (d) dibutylphthalate (DBP).**

**Relationships between the Physical−Chemical Characteristics of the Selected DOM Surrogates and $K_{oc}$ Values.** The $K_{oc}$ values vary considerably among the DOM surrogates and are highly dependent on the physical−chemical properties of the sorbents. Some of the characteristics that can influence sorption are presented in Table 4. For Aldrich humic acid, no data were available about the atomic ratios, and the data for the untreated are highlighted and shown instead. The relationship between the log $K_{oc}$ value of each selected endocrine disrupter and weight standard average molecular weight of each DOM is shown in Figure 3. In Figures 4 and 5, the log $K_{oc}$ values for each of the selected endocrine disrupters are plotted against the (O+N)/C atomic ratio and the H/O atomic ratio, respectively, of each DOM surrogate. UV absorptivity at 272 nm ($A_{272}$) (alternatively, 270 or 280 nm have been used) has been proposed to be related with the aromaticity of the DOM compounds. Therefore, $K_{oc}$ versus $A_{272}$ is plotted on a linear scale in Figure 6 and on a log−log scale for all the DOM surrogates in Figure 7. Finally, the $K_{oc}$ values are plotted against the fraction of the carboxylic group and the phenolic group in the DOM surrogate in Figures 8 and 9, respectively.

As in Figure 3, the logarithm of the weight standard average showed a relatively weak negative linear correlation with the $K_{oc}$ values for the DOM except for *p*-nonylphenol. Conversely, *p*-nonylphenol showed no linear relationship between $K_{oc}$ values and the molecular weight. Dextran was far below the regression line as shown in Figure 3(a) for 17$\beta$-estradiol. $R^2$ was as high as 0.906 for dibutylphthalate without the data for dextran and was as low as 0.627 for 17$\beta$-estradiol with the data for dextran. These weak negative correlations oppose the positive correlation obtained by Chin et al. (*66*) for the aquatic humic and fulvic acids. For this study, all four humic substances, including the pretreated AHA, showed relatively similar molecular weight averages, and log $K_{oc}$ values did not show any correlation with log $Mw_w$ within these humic substances. Since the number of samples other than humic substances is only 2 or 3 for this study and dextran is far from the regression line, the negative correlation obtained in this research remained questionable, and further investigation is necessary.

As shown in Figure 4, the sorption coefficient has a weak negative linear relationship with the (O+N)/C atomic ratios except for *p*-nonylphenol, if dextran is excluded for 17$\beta$-estradiol and 17$\alpha$-ethynylestradiol. These negative relationships agree with that proposed by De Paolis and Kukkonen (*45*). However, the relationship is questionable, as a result of the exception of dextran, the absence of atomic ratio data for treated Aldrich humic acid, and given that the (O+N)/C ratios of the three aquatic humic and fulvic substances and tannic acid were so similar, that there were only three values of the independent variable to determine any trend. In contrast, no linear correlation was evident for *p*-nonylphenol.

As indicated in Figure 5, no correlation was evident between log $K_{oc}$ and H/O atomic ratios. The lack of correlation does not agree with the observation of Grathwohl (*38*), who found a positive linear relationship between the log $K_{oc}$ and the H/O atomic ratio using TCE with a wide variety of DOM surrogates including soil humic substances, aquatic humic substances, and tannic acid.

In Figure 6, $K_{oc}$ shows a relatively strong positive correlation ($R^2$ values higher than 0.97) with absorptivity at 272 nm ($A_{272}$) for three steroid estrogens. These relatively strong correlations for steroid estrogens agree with the report by

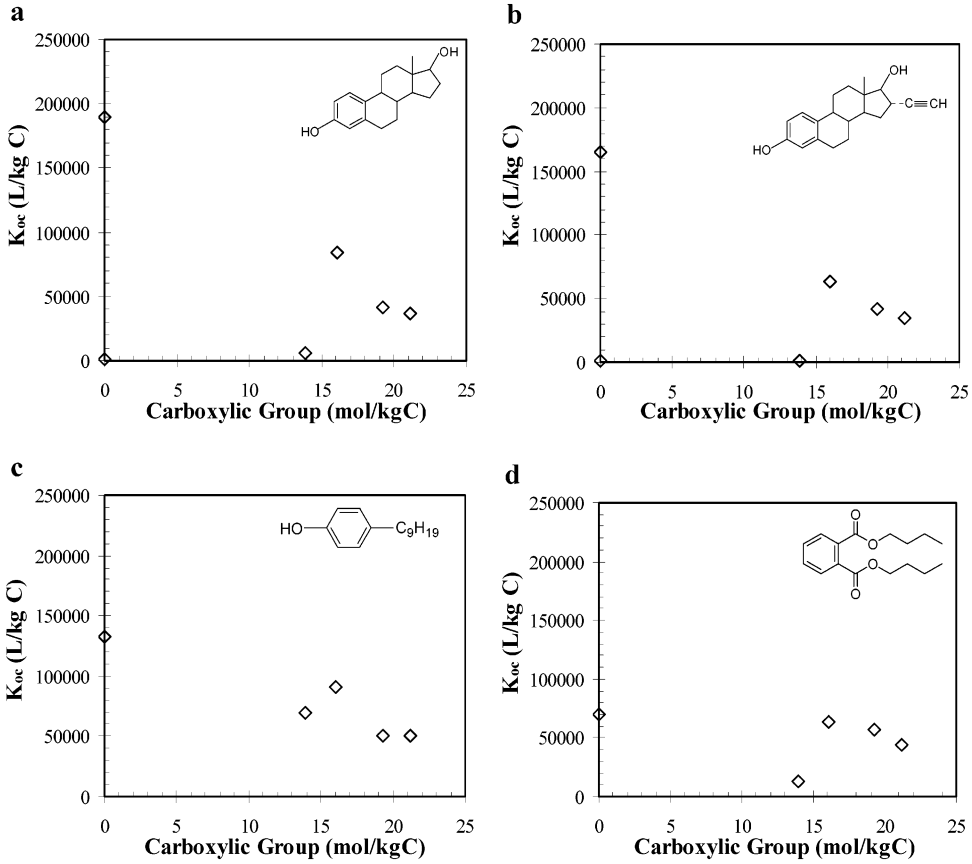



**FIGURE 8. Relationship between $K_{oc}$ values and carboxylic group contents of the selected DOM surrogates for (a) 17$\beta$-estradiol (E2), (b) 17$\alpha$-ethynylestradiol (EE2), (c) *p*-nonylphenol (NP), and (d) dibutylphthalate (DBP).**

Gauthier et al. (*34*) using pyrene with marine and terrestrial humic acids and by Kukkonen and Oikari (*14*) using B(a)P with lake DOM. The later study used absorptivity at 270 nm instead of 272 nm, but absorbance in the UV between 254 and 280 nm is closely related to the aromaticity of the DOM (*66*). The abundance of aromatic rings in the DOM structure is suggested to have critical importance in the sorption mechanism of the selected steroid estrogens, which possess one aromatic and four cyclic nonaromatic rings, by the selected DOM compounds. Hence, the interaction between $\pi$-electrons of steroid estrogens and DOM is a probable and could be a major contribution to the overall sorption in this study. In contrast, *p*-nonylphenol and dibutylphthalate showed moderate or weak linear relationships with $R^2$ values slightly over 0.6. For *p-tert*-octylphenol, the $R^2$ value is as high as 0.92 but $K_{oc}$ was measured for neither alginic acid nor dextran and the strong linear correlation is questionable. Additionally, the intercepts of the regression lines are far above the origin for these three compounds, while the intercept is nearly the origin for three steroid estrogens. *p*-Nonylphenol dibutylphthalate and *p-tert*-octylphenol have significantly higher $K_{ow}$ values than three steroidal estrogens and also have aliphatic structure in their molecule. Their nonring structure and higher hydrophobicity are suggested to cause relatively higher contribution of nonspecific hydrophobic interactions with nonaromatic part of DOM (*34*). Furthermore, the relatively small contribution of the interaction between $\pi$-electrons of nonsteroidal estrogenic compounds and DOM was suggested.

In Figure 7, the applicability of the relationship between $A_{272}$ and $K_{oc}$ for the polysaccharides alginic acid and dextran is emphasized by plotting the same data from Figure 6 on a log−log scale. As shown, log $K_{oc}$ strongly correlates with log $A_{272}$ (i.e., $R^2$ values were above 0.90) for 17$\beta$-estradiol, 17$\alpha$-ethynylestradiol, and dibutylphthalate. Thus, $A_{272}$ appears to be a useful index to estimate the $K_{oc}$ values of steroid estrogens containing aromatic groups for a wide variety of DOM including humic substances, tannic acid, and polysaccharides, although further investigation is needed to test the range of applicability due to the significantly low log $K_{ow}$ values for dibutylphthalate. On the contrary, the linear relationship between log $K_{oc}$ and log $A_{272}$ was not evident for *p*-nonylphenol. Again, the contribution of nonspecific hydrophobic interaction is suggested to be higher for *p*-nonylphenol than the steroid estrogens.

As indicated in Figure 8, no correlation was evident between the $K_{oc}$ values and the concentration of carboxylic groups in the DOM for the endocrine disruptors selected in this study. Most of the carboxylic groups are negatively charged at the neutral pH and thus can significantly contribute to the sorption of cations, especially transition metals. However, the selected endocrine disruptors with p$K_a$s above 10, as shown in Table 1, are predominantly nonionic at the neutral pH investigated, and charge contributions to the overall sorption are small.

Conversely as shown in Figure 9, $K_{oc}$ correlated with the concentration of the phenolic group on the DOM strongly for 17$\beta$-estradiol and 17$\alpha$-ethynylestradiol, moderately for *p*-nonylphenol, and weakly for dibutylphthalate. In addition, a relatively steep slope and the intercept of nearly zero were found for the two steroid estrogens, while a moderate slope and the intercept significantly above zero were found for *p*-nonylphenol and dibutylphthalate. Relatively higher contributions of the interaction between $\pi$-electrons of DOM and steroid estrogens and hydrogen bonds are suggested for the overall sorption of 17$\beta$-estradiol and 17$\alpha$-ethynylestradiol by the DOM surrogates. The poor correlation for dibutylphthalate was possibly attributed to the absence of a

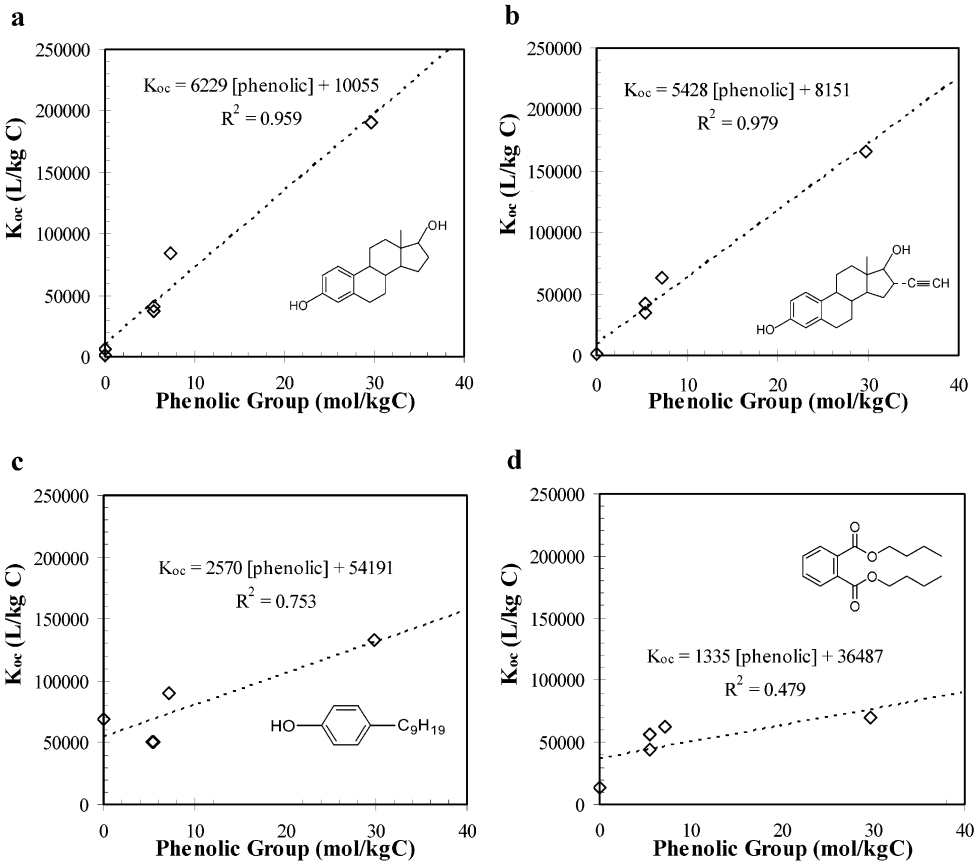



**FIGURE 9. Relationship between $K_{oc}$ values and phenolic group contents of the selected DOM surrogates for (a) 17$\beta$-estradiol (E2), (b) 17$\alpha$-ethynylestradiol (EE2), (c) *p*-nonylphenol (NP), and (d) dibutylphthalate (DBP).**

phenolic group in its structure. Its ester groups have lower H-donor and polarizability contributions to sorption than phenolic groups and thus possibly lower affinity with the DOM with the large number of phenolic groups. Both *p*-nonylphenol and the estrogens have a phenolic group, but the relatively weaker correlation for *p*-nonylphenol may result from that larger dispersive van der Waals contribution of nonpolar nonyl group to its sorption as compared with the additional H-donor and polarizability contributions of the secondary alcohol groups on the cyclic rings of the estrogens.

The highest $K_{oc}$ values were found for tannic acid compared with other DOM compounds, as presented in Table 2. The higher affinity results from the abundance of phenolic groups in the structure of tannic acid interacting with the phenolic group in the steroid estrogens and alkylphenols. Hence, the interaction between phenolic groups of endocrine disruptors, especially steroid estrogens, and DOM increases the importance of H-donor, H-acceptor, and polarizability contributions relative to the simple hydrophobic interactions in the sorption mechanisms.

Log $K_{oc}$ values ranged narrowly and looked independent of log $K_{ow}$ values of selected endocrine disruptors in Figure 2 for Aldrich humic acid and Suwannee River humic and fulvic acids. The relatively strong linear correlation of $K_{oc}$ values with $A_{272}$ and phenolic group concentration was found for the steroid estrogens. The higher contribution of the interaction between $\pi$-electrons and hydrogen bonds suggested from the strong correlation possible resulted in $K_{oc}$ values of the steroid estrogens as high as those of alkylphenols and dibutylphthalate, which are much more hydrophobic and close to the results obtained by other researchers (Figure 2). Since the fluorescence quenching technique itself is significantly sensitive and could result in some difficulties to determine the $K_{oc}$ values as presented above, further investigation using the other technique such as solid-phase microextraction method is obviously necessary.

## Supporting Information Available

Time profile of the fluorescence signal of E2 solution (Figure S.1) and Tables S1−S13. This material is available free of charge via the Internet at http://pubs.acs.org.

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