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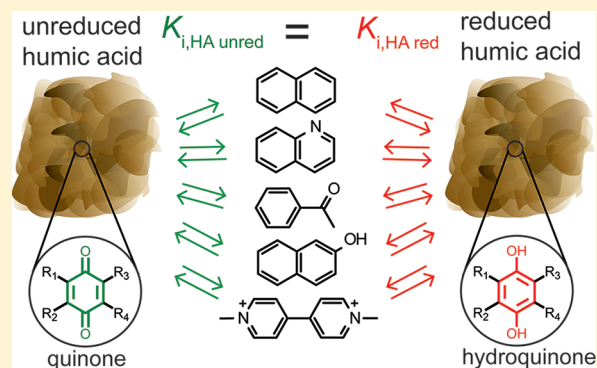
Assessing the Effect of Humic Acid Redox State on Organic Pollutant Sorption by Combined Electrochemical Reduction and Sorption Experiments

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S Supporting Information

ABSTRACT: Natural Organic Matter (NOM) is a major sorbent for organic pollutants in soils and sediments. While sorption under oxic conditions has been well investigated, possible changes in the sorption capacity of a given NOM induced by reduction have not yet been studied. Reduction of quinones to hydroquinones, the major redox active moieties in NOM, increases the number of H-donor moieties and thus may affect sorption. This work compares the sorption of four nonionic organic pollutants of different polarities (naphthalene, acetophenone, quinoline, and 2-naphthol), and of the organocation paraquat to unreduced and electrochemically reduced Leonardite Humic Acid (LHA). The redox states of reduced and unreduced LHA in all sorption experiments were stable, as demonstrated by a spectrophotometric 2,6-dichlorophenol indophenol reduction assay. The sorption isotherms of the nonionic pollutants were highly linear, while paraquat sorption was strongly concentration dependent. LHA reduction did not result in significant changes in the sorption of all tested compounds, not even of the cationic paraquat at pH 7, 9, and 11. This work provides the first evidence that changes in NOM redox state do not largely affect organic pollutant sorption, suggesting that current sorption models are applicable both to unreduced and to reduced soil and sediment NOM.



INTRODUCTION

Natural Organic Matter (NOM) is a major environmental sorbent for organic pollutants. The sorption of organic pollutants to NOM is well investigated and understood at the molecular level.^{1–11} While all organic pollutants interact with NOM by nonspecific van der Waals (vdW) interactions, monopolar (i.e., either H-donor or -acceptor) and bipolar (i.e., H-donor and -acceptor) compounds additionally undergo specific H-donor–acceptor (HDA) interactions with polar functional moieties in NOM. Furthermore, organocations may exhibit high affinities to NOM due to strong electrostatic attraction to carboxylate and phenolate moieties.¹² The sorption of polar and cationic organic pollutants therefore depends on the numbers of H-donor and H-acceptor moieties, and of anionic sites in NOM, respectively.¹³ In addition, sorption of any organic pollutant depends on NOM cohesive energy, which itself is expected to increase with increasing HDA interactions between polar moieties within the NOM.

The abundance of polar and anionic moieties varies between different types of NOM.^{14,15} The abundance of such moieties may, however, also change for a given NOM when it undergoes chemical reactions. Reduction and oxidation reactions of NOM are of particular interest, because many contaminated soils, sediments, and aquifers may undergo spatial and temporal changes in redox conditions. For humic acids (HA) and fulvic acids, two major components of NOM, electron-accepting

capacities of up to 2 mmol of electrons per gram have been reported.^{16–18} It has been shown that quinone/hydroquinone pairs are major redox-active moieties in NOM that may reversibly undergo reduction and oxidation.^{19–22} Reduction of quinones to hydroquinones increases the number of H-donor moieties, and the deprotonation of the hydroquinones at high pH results in the formation of mono- and diphenolate anions^{23,24} (Table 1; top). The increase in the number of H-donor moieties upon reduction may, on the one hand, enhance the sorption of monopolar H-acceptor and of bipolar organic pollutants. On the other hand, it may render sorption of all organic pollutants energetically less favorable by increasing intra-NOM HDA interactions and hence the cohesive energy of the NOM. Increases in the number of anionic sites upon reduction at high pH may lead to increased organocation sorption. Finally, reduction may also affect sorption by altering the conformational structure of NOM aggregates.^{25–27}

The few studies that addressed possible effects of NOM reduction state on the sorption of organic pollutants have exclusively used apolar model compounds. The majority of these studies reported altered organic pollutant sorption upon

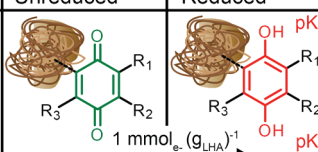
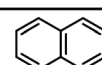
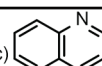
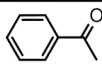
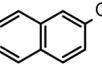
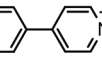
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Table 1. (Top) Some Important Chemical Characteristics of Unreduced and Partially Reduced Leonardite Humic Acid (LHA);^a (Bottom) Chemical Structures of the Probe Compounds and Their Respective Interactions with Quinone and Hydroquinone Moieties

Leonardite Humic Acid					Unreduced	Reduced
Structural properties:						
Element	C	H	O	N		
mmol (g _{LHA}) ⁻¹	53.1	36.6	19.5	0.9		
	Aromatic		Aliphatic			
[%]	58		14			
Phenolic moieties [mmol (g _{LHA}) ⁻¹]:					~1.4	~2.4 (+ 71%)
Carboxylic moieties [mmol (g _{LHA}) ⁻¹]:					~4.6	~4.6
Probe compounds					Interactions with quinones	Interactions with hydroquinones
naphthalene 'apolar'					vdW	vdW (+ HDA) (weak H-bond acceptor)
quinoline monopolar (& ionic)					vdW	vdW + HDA (+ ES, pK _{a,quin} = 4.9)
acetophenone monopolar					vdW	vdW + HDA
2-naphthol bipolar					vdW + HDA	vdW + HDA
paraquat monopolar & ionic					vdW (+ ES*)	vdW + HDA + ES

* quinones substituted with acidic functional groups (e.g. carboxyl- and hydroxyl groups)

^aThe elemental composition, the aliphaticity and aromaticity values, and the acidic functional group content of the unreduced LHA were taken from refs. 14, 15, and 33. The increase in the content of phenolic moieties upon LHA reduction was calculated assuming that all electrons were transferred to quinone moieties. vdW, van der Waals interactions; HDA, H-donor–acceptor interactions; ES, electrostatic interactions.

changes in the redox states of contaminated soils and sediments (e.g., reaeration of reduced samples).^{27–32} The complexity of the investigated systems, however, impaired assessing whether changes in NOM redox state contributed to altered sorption. Coates et al. reported decreased naphthalene sorption to microbially reduced Aldrich HA as compared to the unreduced HA.²⁷ This finding may have reflected an increase in the cohesive energy of the HA upon reduction. None of the previous studies, however, included polar and cationic organic compounds to more selectively probe for changes in the H-donor and acceptor properties and the number of anionic moieties in NOM upon its reduction.

The goal of this work was to assess whether NOM reduction affects its properties as sorbent for organic pollutants. To this end, sorption of five model organic pollutants (Table 1, bottom) was studied to both unreduced and electrochemically reduced Leonardite Humic Acid (LHA). The pollutants included the weak H-acceptor naphthalene (referred to as “apolar” in the following), the monopolar, H-acceptor acetophenone and quinoline, the bipolar H-donor and -acceptor 2-naphthol, and the organocation paraquat (Table 1). LHA, a kerogen-derived HA, was chosen because it has

been used in previous sorption studies,^{1,2,12} and it is well-characterized^{14–16} (Tables 1 and S1). Furthermore, due to its high aromaticity and C/O ratio, LHA represents a humin-like end-member among the HAs and hence is considered as a model for both HA and humin. Finally, the EAC of LHA is about 1.7 mmol e[−] (g_{LHA})^{−1}, which is among the highest reported values for HA.¹⁶ With quinones as the major reducible moieties in LHA,^{16,23} even partial reduction of LHA results in a significant increase in the number of phenolic H-donor sites (see below). LHA was reduced by direct electrochemical reduction.¹⁶ In contrast to previous methods that relied on the use of chemical reductants, the electrochemical reduction allows for a selective electron transfer to reducible moieties to yield reduced HA with well-defined reduction states and devoid of chemical reductants. The electrochemically reduced HA can be directly used in subsequent experiments. Both before and after the sorption experiments, the redox states of unreduced and reduced LHA were quantified by their reductive decolorization of the added redox dye 2,6-dichlorophenol indophenol.¹⁶

MATERIALS AND METHODS

Chemicals. All chemicals were of analytical grade and were used as received. 2,6-Dichlorophenol indophenol sodium salt hydrate (DCPIP), 2-naphthol, acetophenone, hydrochloric acid (32%), and sodium hydroxide solutions (32%) were from Fluka, quinoline, naphthalene, and methylviologen dichloride monohydrate (paraquat) were from Sigma Aldrich, sodium dihydrogen phosphate monohydrate, potassium dihydrogen phosphate, sodium hydrogen carbonate, boric acid, and potassium chloride were from Merck AG, and methanol was from Scharlau. All aqueous solutions were prepared with NanoPure water.

Anoxic Experiments. Electrochemical reductions and all sorption experiments were conducted in an anoxic glovebox (N₂ atmosphere at 25 ± 1 °C, O₂ < 0.1 ppm; M. Braun Ltd., Germany). Aqueous solutions were made anoxic by purging with argon for 2 h on a stir plate heated to 150 °C and for 1 h at room temperature. Methanol was made anoxic by purging with argon for 1 h without heating.

Sorbent. Leonardite Humic Acid (LHA) standard was purchased from the International Humic Substances Society (St. Paul, MN) and was used as received. Selected physicochemical properties of LHA are given in Tables 1 and S1, Supporting Information. LHA solutions (125 mL, 2 g_{LHA} L^{−1}) were prepared in the glovebox by dissolving LHA in aqueous solutions containing 0.1 M phosphate (pH 7), borate (pH 9), or carbonate (pH 11) as pH buffers and 0.1 M KCl as electrolyte for accurate potential control during electrochemical reduction. The pH was adjusted to ±0.02 pH units by addition of anoxic NaOH (32%). A total of eight batches (I–VIII) of LHA solutions were prepared and stored in light-protected flasks. An aliquot of each batch was withdrawn and used as unreduced LHA in the sorption experiments. Another aliquot was reduced electrochemically and then used as reduced LHA in the sorption experiments.

Direct Electrochemical Reduction. LHA was reduced in a bulk electrolysis cell according to Aeschbacher et al.¹⁶ Briefly, 65 mL of the LHA solution from each batch was transferred into an electrochemical cell containing a glassy carbon working electrode (Sigradur G, HTW, Germany), an Ag/AgCl reference electrode, and a coiled platinum wire auxiliary electrode (both from Bioanalytical Systems Inc., West Lafayette, IN). To

minimize reoxidation of reduced LHA at the auxiliary electrode, the anodic compartment was separated from the cathodic compartment by a porous glass frit. A model 630C potentiostat (CHInstruments, U.S.) was used to measure the current, I , and to control the potential, E_h , at the working electrode. LHA solutions were reduced under stirring for 60 h at an $E_h = -0.59$ V (vs standard hydrogen electrode), and the number of electrons, n_e , transferred per mass of LHA was obtained by integration of the reductive current over time.

Sorption Experiments. Sorption experiments were carried out in custom-made dialysis cells.¹² Each cell consisted of two approximately 4 mL compartments separated by a dialysis membrane that was impermeable to LHA but permeable to the organic pollutants. Prior to use, the dialysis membranes were immersed in water and made anoxic by purging with argon for 2 h. A 500 Da molecular weight cutoff (MWCO) Spectra/Por cellulose ester membrane (Spectrum Laboratories, U.S.) was used for all sorption experiments with nonionic pollutants. Control experiments showed that paraquat diffused very slowly across the 500 Da MWCO membrane. To facilitate attainment of diffusive equilibrium, a 2000 Da MWCO cellulose membrane (Roth, Germany) was employed for the paraquat experiments instead. Prior to the paraquat sorption experiments, the LHA solutions were pre-dialyzed against pH-buffered solutions to remove low molecular weight LHA constituents that passed through the 2000 Da MWCO membrane. Pre-dialysis was carried out for 7 days in the same dialysis cells which were subsequently used for the sorption experiments. The dialysate was replaced after 2, 4, and 7 days.

All sorption experiments were carried out in triplicates. The experiments with the nonionic pollutants were run at pH 7 and for quinoline also at pH 9. For each pollutant and at each pH, the sorption experiments were conducted at four different initial pollutant concentrations $C_{i, \text{aq}}^0$ in the LHA free dialysis cell (see Table S2, Supporting Information). Sorption of paraquat was studied at two C_{aq}^0 values at pH 7, 9, and 11. Sorption was initiated by filling one of the two compartments of each dialysis cell with 4 mL solutions containing reduced or unreduced LHA (2 g L⁻¹ for the nonionic pollutants and 0.2 g L⁻¹ for paraquat) and by filling the second compartment of each cell with solutions containing the organic pollutant. Cells were shaken horizontally for 7 and 8 days in the dark to attain sorption equilibrium of the nonionic pollutants and paraquat, respectively (see Table S3, Supporting Information). Three 1 mL aliquots were withdrawn from the LHA-free half-cells and analyzed to determine the aqueous pollutant concentration. For the nonionic pollutants, 3 mL aliquots were withdrawn from the LHA-containing solutions, extracted with 3 mL of ethyl acetate, and the pollutant concentration was quantified in the extract. Control experiments demonstrated quantitative extraction by ethyl acetate (see Table S4, Supporting Information). Concentrations of the nonionic organic pollutants were quantified by HPLC-UV (Dionex PDA-100). The cationic paraquat could not be extracted from LHA-containing half-cells with organic solvents. Paraquat was therefore only quantified in the LHA-free half-cells by derivative spectrophotometry at $\lambda = 241$ nm³⁴ to eliminate artifacts resulting from weak UV absorbance of small amounts of LHA that had diffused across the membrane during the sorption experiment. Further details on the quantification of the organic pollutants are provided in Table S5 in the Supporting Information.

The sorbed concentrations of the nonionic pollutants and of paraquat, $C_{i, \text{LHA}}$ [mol (g_{LHA})⁻¹], were calculated according to eqs 1 and 2, respectively.

$$C_{i, \text{LHA}} = \frac{C_{i, \text{LHA cell}} \cdot V_{\text{LHA cell}} - C_{i, \text{aq}} \cdot V_{\text{buffer cell}}}{m_{\text{LHA}}} \quad (1)$$

$$C_{i, \text{LHA}} = \frac{(C_{i, \text{aq}}^0 - 2 \cdot C_{i, \text{aq}}) \cdot V_{\text{buffer cell}}}{m_{\text{LHA}}} \quad (2)$$

where $C_{i, \text{aq}}$ [mol L⁻¹] is the aqueous pollutant concentration, $C_{i, \text{aq}}^0$ [mol L⁻¹] is the initial aqueous pollutant concentration in the LHA-free solution, $V_{\text{LHA cell}}$ and $V_{\text{buffer cell}}$ with $V_{\text{LHA cell}} \approx V_{\text{buffer cell}}$ [L] are the volumes of the LHA-containing and LHA-free solutions, respectively, and m_{LHA} [g] is the mass of LHA in each dialysis cell.

While only small fractions of quinoline, acetophenone, and paraquat sorbed to the membrane, approximately 30% of the total mass of naphthalene and 2-naphthol sorbed to the membranes, as shown by membrane extraction. When accounting for sorption to the membrane, overall high recoveries were found for all compounds (Table S4, Supporting Information).

The sorption isotherms for the nonionic pollutants were plotted as $\log_{10}(C_{i, \text{LHA}})$ versus $\log_{10}(C_{i, \text{aq}})$ and fitted by the logarithmized Freundlich equation (eq 3) to determine Freundlich affinity coefficients, $K_{i, \text{F}}$ [mol^{1-N} L^N (g_{LHA})⁻¹], and the Freundlich exponents, N_i :

$$\log_{10}(C_{i, \text{LHA}}) = \log_{10}(K_{i, \text{F}}) + N_i \cdot \log_{10}(C_{i, \text{aq}}) \quad (3)$$

The apparent organic carbon normalized distribution coefficient, $K_{i, \text{OC}}$ [L (kg_C)⁻¹], was calculated according to eq 4. For the nonionic compounds $K_{i, \text{OC}}$ was calculated at $C_{i, \text{aq}} = 50$ and 100 μM , and $C_{i, \text{LHA}}$ was extrapolated from eq 3. For paraquat, K_{OC} was calculated for the experimental concentrations.

$$K_{i, \text{OC}} = \frac{C_{i, \text{LHA}}}{f_{\text{OC}} \cdot C_{i, \text{aq}}} \quad (4)$$

where $f_{\text{OC}} = 6.22 \times 10^{-4}$ [kg_C (g_{HA})⁻¹] is the ash-corrected organic carbon content of LHA.¹⁵

Sorption of the nonionic compounds to unreduced and reduced LHA was compared based on the 95% confidence intervals of the fitted isotherm parameters, $\log_{10}(K_{i, \text{F}})$ and N_i , and based on the prediction intervals for $K_{i, \text{OC}}$ obtained at given $C_{i, \text{aq}}$ from the fitted isotherm parameters. Paraquat sorption to unreduced and reduced LHA was compared on the basis of the 95% confidence intervals of the concentration-dependent K_{OC} values.

Spectrophotometric Redox Assay. The redox states of unreduced and reduced LHA were analyzed before and after the sorption experiments by a spectrophotometric assay based on the reductive decolorization of the blue redox dye DCPIP ($\epsilon = 20.6$ mM⁻¹ cm⁻¹ at $\lambda = 603$ nm).^{16,35} Aliquots of unreduced and reduced LHA solutions were withdrawn from the respective LHA solutions prior to filling of the dialysis cells and from all half-cells containing LHA solutions after termination of the sorption experiment. Three different volumes of the LHA aliquots were transferred to plastic cuvettes (Brand GMBH, Germany) with solutions containing DCPIP in excess amounts relative to n_e . A fourth cuvette containing DCPIP was not amended with LHA solutions. The

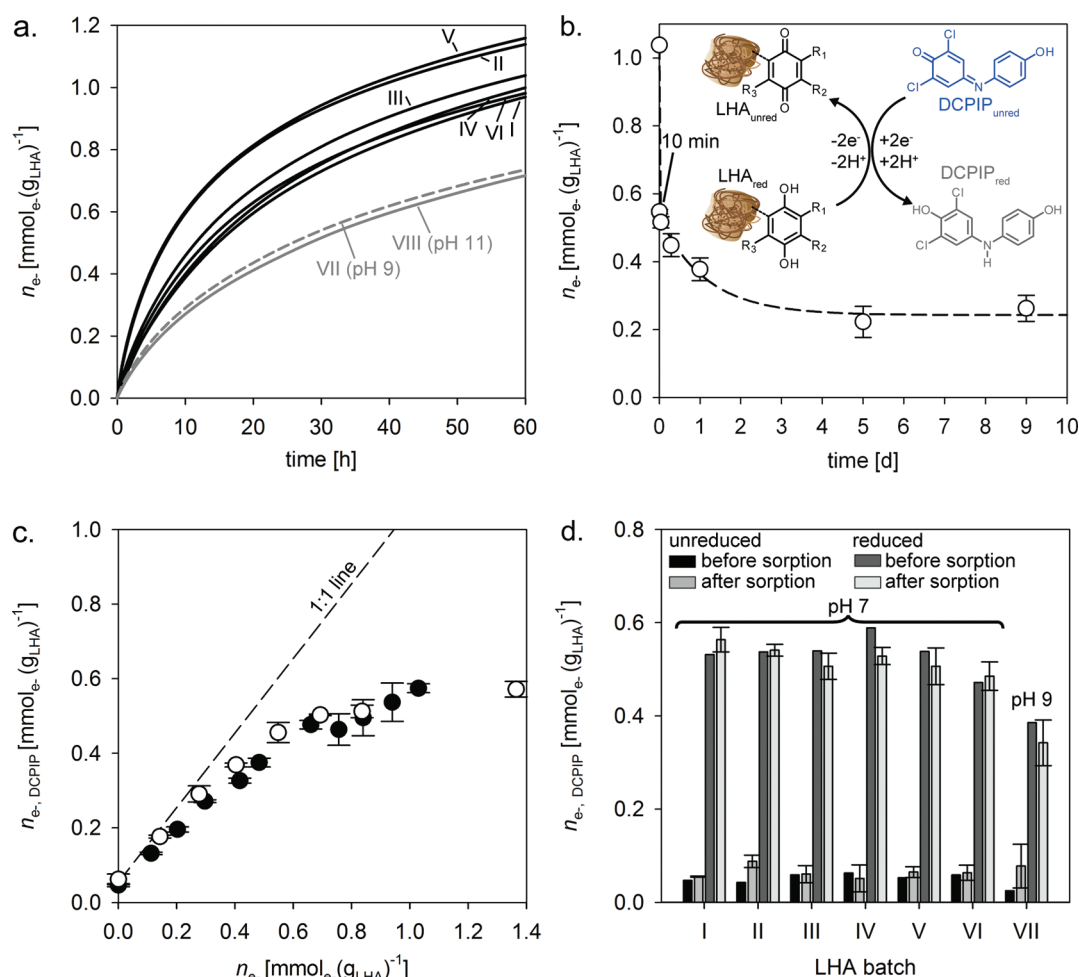


Figure 1. (a) The number of electrons, n_{e-} , transferred per mass of Leonardite Humic Acid (LHA) during electrochemical bulk reduction of batches I–VI (pH 7), batch VII (pH 9), and batch VIII (pH 11). (b) Reoxidation kinetics of reduced LHA by 2,6-dichlorophenol indophenol (DCPIP) at pH 7. The initial value of $n_{e-} = 1.04 \text{ mmol}_{e-} \text{ g}_{\text{LHA}}^{-1}$ corresponds to the number of electrons transferred to LHA during the direct electrochemical reduction. The other values were calculated by subtracting the number of electrons transferred to DCPIP, $n_{e-,\text{DCPIP}}$, from the initial n_{e-} value. (c) Number of electrons recovered from reduced LHA by DCPIP (reaction time of 10 min), $n_{e-,\text{DCPIP}}$, versus the moles of electrons transferred to LHA withdrawn from the electrochemical cell in aliquots at different times during direct electrochemical reduction, n_{e-} (duplicate experiments; the error bars represent standard errors). (d) Number of electrons transferred to DCPIP, $n_{e-,\text{DCPIP}}$, from unreduced and reduced LHA for all batches. $n_{e-,\text{DCPIP}}$ values were quantified prior to and after each sorption experiment. The bars represent averages and the error bars represent standard deviations of $n_{e-,\text{DCPIP}}$ for LHA solutions of the respective batch taken from dialysis cells after termination of the sorption experiment.

cuvettes were sealed, mixed, and transferred out of the glovebox. The absorbance spectra of DCPIP were measured (400–800 nm) after a reaction time of approximately 10 min on a Cary100 spectrophotometer (Varian Instruments, U.S.). The number of electrons transferred from LHA to DCPIP, $n_{e-,\text{DCPIP}}$, was calculated from the decrease in DCPIP absorbance at $\lambda = 603 \text{ nm}$ with increasing LHA concentration and served to quantify the redox state of the LHA samples. Further details are provided in the Supporting Information and in Aeschbacher et al.¹⁶ The kinetics of electron transfer from reduced LHA to DCPIP and the dependence of the detected $n_{e-,\text{DCPIP}}$ on the electrochemically transferred n_{e-} were analyzed separately.

RESULTS AND DISCUSSION

Electrochemical LHA Reduction. The data in Figure 1a show the number of electrons, n_{e-} , transferred per mass of LHA during bulk electrolysis of the eight batches of LHA with batches I–VI at pH 7, batch VII at pH 9, and batch VIII at pH 11. As shown previously,¹⁶ LHA-containing solutions showed

much higher reductive currents and therefore higher n_{e-} than LHA-free solutions (data not shown), demonstrating negligible reduction of H^+ to H_2 at the glassy carbon working electrode at the given pH and applied potential. The rate of electron transfer from the working electrode to LHA gradually decreased over the 60 h reduction periods. The number of electrons transferred in 60 h decreased with increasing pH from $1.05 \pm 0.08 \text{ mmol}_{e-} \text{ g}_{\text{LHA}}^{-1}$ at pH 7 (average \pm standard deviation of batches I–IV), to $0.76 \text{ mmol}_{e-} \text{ g}_{\text{LHA}}^{-1}$ at pH 9 and pH 11. The n_{e-} at pH 7 agreed well with a previously published value obtained under the same reduction conditions,¹⁶ demonstrating the high reproducibility of direct electrochemical reduction. The slight variations in n_{e-} between the different batches at pH 7 reflect different kinetics of electron transfer from the electrode to LHA, possibly due to differences in the extent of adsorption of LHA to the electrodes and/or in the cell geometries. Slower reductions and lower final n_{e-} at pH 9 and pH 11 as compared to pH 7 are consistent with the decrease in the reduction potentials of the quinone moieties in LHA with increasing pH.²³

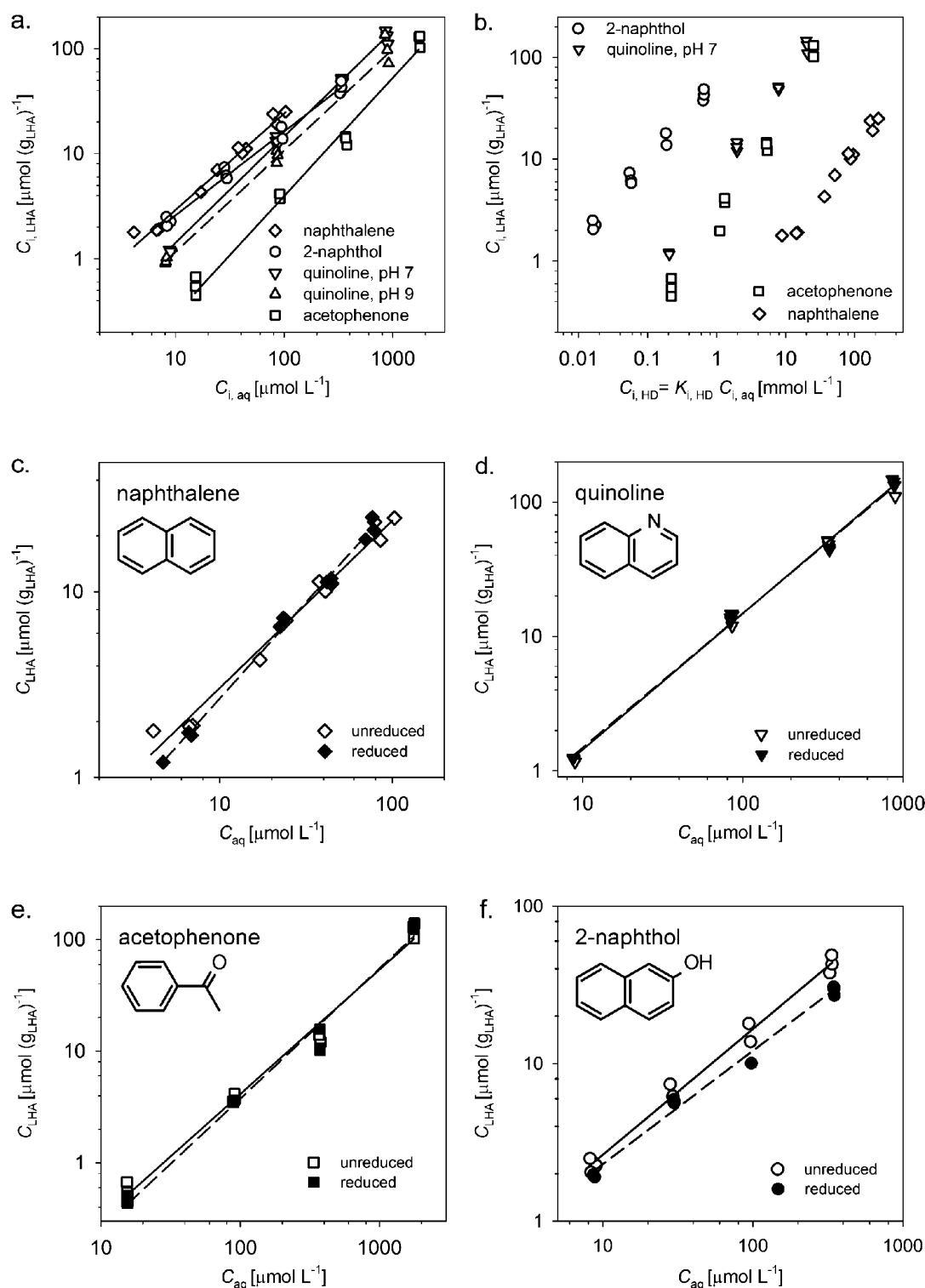


Figure 2. (a) Sorption isotherms of naphthalene, acetophenone, and 2-naphthol at pH 7 and of quinoline at pH 7 and 9, to unreduced Leonardite Humic Acid (LHA). $C_{i,aq}$ and $C_{i,LHA}$ are the equilibrium molar aqueous and sorbed concentrations, respectively. The lines represent fits of the Freundlich model. (b) Sorption isotherms of naphthalene, acetophenone, quinoline, and 2-naphthol to unreduced LHA at pH 7 replotted from panel (a) as $C_{i,LHA}$ versus the calculated dissolved concentrations of the tested compounds in *n*-hexadecane, $C_{i,HD}$, in equilibrium with $C_{i,aq}$. (c)–(f) Sorption isotherms of naphthalene (panel c), quinoline (panel d), acetophenone (panel e), and 2-naphthol (panel f) to unreduced LHA (open symbols) and reduced LHA (closed symbols). The solid and dashed lines represent the respective Freundlich model fits.

Direct electrochemical reduction provided reduced LHA samples with known redox states. In contrast to previous reduction methods that rely on the use of chemical reductants (e.g., refs 17,36,37), the electrochemical reduction selectively

alters the redox state of LHA, which can be used without purification in follow-up experiments. Given that electrons are primarily transferred to quinones in LHA,^{16,23} the electrochemical reduction resulted in the formation of approximately

Table 2. Freundlich Affinity Coefficients, $\log_{10}(K_{i,F})$ [$\log_{10}(\text{mol}^{1-N} \text{L}^N (\text{g}_{\text{LHA}})^{-1})$], and the Freundlich Exponent N_i (each with $\pm 1/2$ of the 95% Confidence Intervals) and the Organic Carbon Normalized Distribution Coefficients, $\log_{10}(K_{i,OC})$, for the Sorption of Naphthalene, 2-Naphthol, Acetophenone, and Quinoline to Unreduced and Reduced Leonardite Humic Acids (LHA)^a

compound	redox state	pH	$\log_{10}(K_{i,F})$	N_i	R^2	n	$\log_{10}(K_{i,OC})$ 50 μM $C_{i,aq} =$	$\log_{10}(K_{i,OC})$ 100 μM $C_{i,aq} =$	$\log_{10}(K_{i,OC})$ literature
naphthalene	unreduced	7	-0.42 ± 0.14	0.90 ± 0.10	0.98	11	2.62 ± 0.15	2.59 ± 0.16	$2.87 \pm 0.15,^b 2.71,^d 2.53^e$
	reduced	7	-0.61 ± 0.08	1.04 ± 0.06	0.99	12	2.66 ± 0.08	2.67 ± 0.09	
2-naphthol	unreduced	7	-0.37 ± 0.11	0.80 ± 0.06	0.99	11	2.49 ± 0.13	2.43 ± 0.13	$2.04,^d 2.09^e$
	reduced	7	-0.35 ± 0.11	0.72 ± 0.06	0.99	10	2.37 ± 0.12	2.29 ± 0.13	
acetophenone	unreduced	7	-1.61 ± 0.21	1.12 ± 0.09	0.99	11	1.79 ± 0.25	1.82 ± 0.24	$1.55 \pm 0.13,^b 1.44,^d 1.07^e$
	reduced	7	-1.76 ± 0.21	1.17 ± 0.10	0.99	12	1.73 ± 0.28	1.78 ± 0.28	
quinoline 7	unreduced	7	-0.86 ± 0.11	1.01 ± 0.05	1.00	12	2.37 ± 0.11	2.38 ± 0.11	$3.05,^c 1.59,^d 1.47^e$
	reduced	7	-0.83 ± 0.08	1.00 ± 0.04	1.00	13	2.38 ± 0.10	2.38 ± 0.10	
quinoline 9	unreduced	9	-0.93 ± 0.18	0.99 ± 0.09	0.99	9	2.26 ± 0.22	2.26 ± 0.22	
	reduced	9	-0.86 ± 0.14	0.94 ± 0.07	0.99	9	2.23 ± 0.18	2.22 ± 0.18	
compound	redox state	pH	C_{aq}	$\log_{10}(K_{OC})$		n	C_{aq}	$\log_{10}(K_{OC})$	n
paraquat	unreduced	7	56 ± 2	4.12 ± 0.03		3	673 ± 3	3.27 ± 0.02	2
	reduced	7	51 ± 3	4.21 ± 0.05		3	676 ± 18	3.24 ± 0.14	3
	unreduced	9	29 ± 3	4.62 ± 0.06		3	656 ± 3	3.37 ± 0.02	2
	reduced	9	27 ± 4	4.66 ± 0.10		3	640 ± 6	3.44 ± 0.03	3
	unreduced	11	27 ± 1	4.65 ± 0.03		3	628 ± 22	3.49 ± 0.10	3
	reduced	11	27 ± 1	4.65 ± 0.03		3	617 ± 24	3.54 ± 0.11	3

^aThe $\log_{10}(K_{i,OC})$ values were evaluated at aqueous concentrations of $C_{i,aq} = 50$ and $100 \mu\text{mol L}^{-1}$ for the apolar and polar compounds (each with $\pm 1/2$ of the 95% prediction interval) and of $C_{aq} \approx 25, 50$, and $600 \mu\text{mol L}^{-1}$ for paraquat. n is the number of replicates. The experimental $\log_{10}(K_{i,OC})$ values are compared to literature values. ^bAverage $K_{i,OC}$ values for different soils and sediments, compiled in ref 11. ^cFor Aldrich HA from ref 42. ^dExtrapolated from polyparameter linear free energy relationships (ppLFERs) with LHA descriptors from ref 2 and compound descriptors from refs 44,45. ^eExtrapolated from ppLFER for Pahokee Peat.⁴

0.5 mmol of hydroquinones per gram LHA at pH 7. The reduction therefore significantly altered the chemical structure of LHA as it affected more than 5% of all oxygen atoms and more than 10% of all noncarboxylic oxygen atoms in LHA, and it resulted in a 71% increase in the concentration of phenol moieties (see Table 1).^{14,15}

Stability of the LHA Reduction State. All sorption experiments were conducted in an anoxic glovebox because oxygen rapidly and extensively reoxidizes reduced HA.^{16,38} To confirm that reduced LHA solutions were not reoxidized over the course of the sorption experiments, the redox states of reduced and unreduced LHA were reanalyzed prior to and after the sorption experiments using the recently developed spectrophotometric DCPIP assay.¹⁶ This assay allows for a high sample throughput and thus allowed analyzing LHA samples from all (>100) dialysis cells.

The reoxidation of electrochemically reduced LHA over time after addition of DCPIP is shown in Figure 1b. The LHA reoxidation kinetics were clearly biphasic: about 55% of the electrons transferred to LHA during electrochemical reduction were transferred to DCPIP within 10 min, while the transfer of the remaining electrons occurred at a much slower rate. After 9 days, DCPIP recovered close to 80% of the electrons transferred to LHA during reduction. The reoxidation data demonstrate that the reduced moieties in LHA exhibited different electron transfer rates to DCPIP and that about 20% of the reduced moieties were not readily reoxidized by DCPIP over 9 days. Similar biphasic kinetics and incomplete oxidation were reported for reduced LHA by O_2 ¹⁶ and of reduced Pahokee Peat HA by Fe^{3+} complexes.³⁹ It is reasonable to assume that those moieties in LHA that rapidly transfer electrons to DCPIP also rapidly transfer electrons to O_2 .

The number of electrons transferred from reduced LHA to DCPIP, $n_{e-,DCPIP}$, within 10 min of reaction increased with the moles of electrons transferred to LHA during electrochemical reduction, n_{e-} (Figure 1c), demonstrating that the DCPIP assay was highly sensitive to changes in the LHA redox state. Furthermore, the assay yielded reproducible results, as shown by the good agreement between the duplicate experiments. Consequently, the assay was used to assess whether changes occurred in the redox state of LHA during the sorption experiments.

The data in Figure 1d show the number of electrons transferred from unreduced and reduced LHA to DCPIP, $n_{e-,DCPIP}$, quantified both prior to and after the sorption experiments. As expected, $n_{e-,DCPIP}$ was much larger for the reduced than for the unreduced LHA samples. Comparable $n_{e-,DCPIP}$ values obtained for reduced LHA at pH 7 (batches I–VI) were consistent with the comparable n_{e-} transferred to these samples during electrochemical reduction (Figure 1a). The lower $n_{e-,DCPIP}$ values of reduced LHA at pH 9 (batch VII) reflected the lower n_{e-} transferred to the LHA at this pH (Figure 1a). More importantly, there were no significant differences in the $n_{e-,DCPIP}$ of samples collected from a given batch prior to and after the sorption experiments (Figure 1d). This finding implies that there were no detectable changes in the reduction states of both the unreduced and reduced LHA during the sorption experiments, which excludes reoxidation of reduced LHA, for instance, by traces of O_2 in the glovebox.

Sorption Isotherms. The data in Figure 2a show the sorption isotherms of naphthalene, acetophenone, and 2-naphthol at pH 7 and of quinoline at pH 7 and pH 9 to unreduced LHA and the Freundlich isotherm fits to the sorption data. The corresponding Freundlich affinity coefficients, $K_{i,F}$, and the Freundlich exponents, N_i , are provided in

Table 2. Sorption of apolar naphthalene, and the H-acceptors acetophenone and quinoline at pH 7, were concentration independent, as is evident from linear sorption isotherms (i.e., $N_i \approx 1$). Conversely, the sorption of bipolar 2-naphthol was slightly concentration dependent ($N_i \approx 0.80$). These observations suggest that the interaction energies between 2-naphthol molecules and sorption sites in LHA decreased with increasing sorbed concentrations, C_{LHA} . The high affinity sorption sites that were preferentially occupied at low C_{LHA} may have involved H-acceptor moieties, given that nonlinearity was observed only for bipolar 2-naphthol but not for the apolar and monopolar, H-accepting model compounds. On the basis of the Freundlich model parameters, the organic carbon normalized partition coefficients, $K_{i,OC}$, of the nonionic pollutants were calculated for solution concentrations of $C_{i,aq}$ equal to 50 and 100 μM (Table 2). The $K_{i,OC}$ values of naphthalene agreed well with literature values. The $K_{i,OC}$ values of the polar compounds were, however, between 0.3 and 0.9 log units higher than the corresponding $K_{i,OC}$ values calculated from pp-LFERs (Table 2). The differences between measured and calculated $K_{i,OC}$ values likely resulted from the use of different types of organic matter as sorbents and/or different experimental setups (i.e., sorption from the gas phase at 100% relative humidity versus sorption from water).

At pH 7, about 1% of the quinoline in solution was cationic ($\text{p}K_{a,\text{quinoline}} = 4.9^{40}$). Electrostatic attraction of organocations to anionic sites in HA may result in high affinity sorption.⁴¹ For example, sorption of the sulfonamide antibiotic sulfathiazole to LHA is dominated by the cationic species up to 3 pH units above the $\text{p}K_a$ value of the aniline moiety in sulfathiazole.¹² To assess the contribution of the quinoline cation to quinoline sorption at pH 7, sorption experiments were also carried out at pH 9 at which less than 0.01% of the quinoline was cationic. Comparable sorption at pH 7 and pH 9 (Figure 2a, Table 2) demonstrates that the neutral quinoline species dominated sorption at pH 7. These findings are in agreement with previous work by Nielsen and co-workers⁴² who reported constant K_{OC} values for quinoline to Aldrich humic acid between pH 7 and pH 12.

The contributions of HDA interactions of the compounds with polar moieties in LHA to overall sorption cannot be directly assessed by comparing the isotherms of $C_{i,LHA}$ versus $C_{i,aq}$ (Figure 2a). Water, and hence $C_{i,aq}$, is not a suitable reference phase for such a comparison as the tested compounds experience large differences in HDA interactions with water molecules. To assess the contribution of HDA interactions of the compounds with polar LHA moieties to total sorption, $C_{i,LHA}$ values instead need to be compared on the basis of dissolved concentrations in an apolar phase, in which only vdW interactions occur. *n*-Hexadecane (HD) has previously been used as such a reference phase.^{6,43} Partition coefficients between HD and water, $K_{i,HD-water}$, are reported for numerous organic pollutants.⁴⁴

In Figure 2b, $C_{i,LHA}$ values from panel a are replotted versus the pollutant concentration in *n*-hexadecane, $C_{i,HD}$, in equilibrium with $C_{i,aq}$. The $C_{i,HD}$ values were calculated by multiplying the experimental $C_{i,aq}$ of each compound, i , with the respective $K_{i,HD-water}$ value.⁴⁴ At the same $C_{i,HD}$, $C_{i,LHA}$ values of the bipolar 2-naphthol were about 1 order of magnitude larger than those of the monopolar compounds, which again were about an order of magnitude larger than the C_{LHA} of naphthalene. Specific HDA interactions with polar moieties in LHA therefore decreased from naphthol, to acetophenone and

quinoline, to naphthalene. The same trend was evident when plotting $K_{i,OC}$ versus $K_{i,HD-water}$ of the tested compounds (Figure S1, Supporting Information). The findings of pronounced HDA interactions between polar moieties in LHA and the polar compounds demonstrate that these compounds were suitable probes to assess whether LHA reduction altered the sorption of polar compounds by increasing the number of H-donor moieties. Naphthalene, which may only form relatively weak HDA interactions with LHA, may selectively probe for changes in the cohesive energy of LHA upon its reduction.

The results of paraquat sorption to LHA at two different concentrations and at pH 7, 9, and 11 are shown in Table 2. The K_{OC} values of paraquat were highly concentration dependent and increased from pH 7 to pH 9 and 11. The concentration and pH-dependencies support electrostatic attraction between cationic paraquat and anionic sites in LHA as dominant sorption mechanism. Sorption increased with increasing pH due to an increase in the number of anionic sites that resulted from deprotonation of phenolic moieties (Table S1, Supporting Information).

Effect of LHA Reduction on Sorption. The sorption isotherms of naphthalene, 2-naphthol, acetophenone, and quinoline to unreduced LHA (open symbols) and reduced LHA (closed symbols) are compared in Figure 2c–f, respectively. The isotherms show that LHA reduction had little, if any, effect on the sorption of the four nonionic pollutants. The same conclusion can be drawn on the basis of the overlapping confidence intervals of the fitted $K_{i,F}$ and N_i values for sorption to unreduced and reduced LHA (Table 2).

In Figure 3, the $\log_{10}(K_{i,OC})$ values for the sorption of all compounds to reduced LHA are plotted versus the corresponding $K_{i,OC}$ values for the sorption to unreduced LHA. For the nonionic compounds, $K_{i,OC}$ values were calculated at $C_{i,aq}$ equal to 50 and 100 μM from the fitted

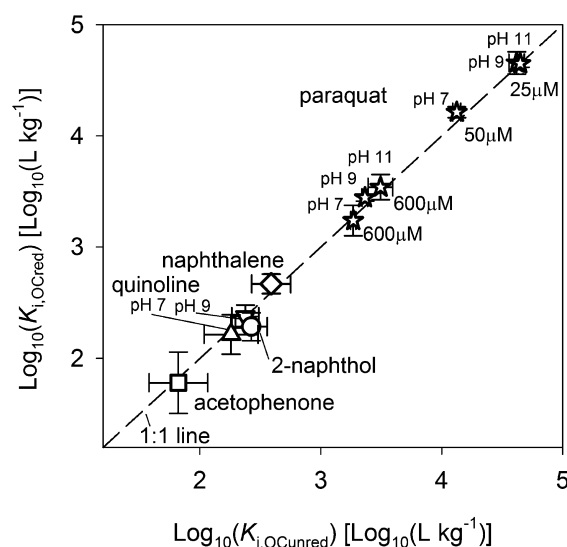


Figure 3. Logarithms of the organic-carbon normalized distribution coefficients of naphthalene, acetophenone, 2-naphthol, quinoline, and paraquat to reduced Leonardite Humic Acid (LHA), $\log_{10}(K_{i,OCred})$, versus the corresponding values to unreduced LHA, $\log_{10}(K_{i,OCunred})$. The $K_{i,OC}$ values were calculated for an aqueous concentration of $C_{i,aq} = 100 \mu\text{M}$ for the apolar and polar compounds and at the specified C_{aq} for paraquat.

Freundlich parameters (Table 2). The apparent K_{OC} values for paraquat were calculated directly from the experimentally determined C_{aq} and C_{LHA} values according to eq 4. As for the nonionic pollutants, sorption of paraquat was not significantly affected by LHA reduction: the confidence intervals of the K_{OC} values for sorption to the oxidized and reduced LHA overlapped, except for sorption of paraquat at the lowest tested concentration at pH 7 (Table 2).

The experimental results show that extensive reduction of LHA did not significantly affect the sorption coefficients of the apolar, monopolar, and cationic probe compounds. Several possible explanations for the absence of an observable effect of the LHA redox state on organic pollutant sorption are possible. First, it is possible that the redox active moieties in the HS are situated in microenvironments that were not readily accessible by the organic pollutants. However, this seems unlikely given that these moieties were directly reduced at the working electrode and that the reduced moieties can transfer electrons to DCPIP (this work) and to organic pollutants such as nitroaromatic compounds and chlorinated hydrocarbons.^{19,46} Second, it is conceivable that the increase in the number of H-donor sites by reduction of quinones to hydroquinones was masked by the preferential sorption of water molecules to these sites. Water molecules are expected to strongly compete with the polar and bipolar pollutants for H-donor and -acceptor moieties. Yet, enhanced sorption of the polar and bipolar compounds over naphthalene (Figure 2b) clearly demonstrated that HDA interactions were important for sorption of organic pollutants to LHA in water. Comparable sorption of naphthalene to unreduced and reduced LHA shows that changes in the cohesive energy of LHA upon reduction, if they occurred, did not significantly affect organic pollutant sorption. Third, and the most likely explanation, reduction did not increase the number of H-donor sites and cohesive energy of LHA to an extent detectable by the sorption of the organic probe compounds. Reduction also did not result in a detectable increase in the anionic binding sites for paraquat. Comparable sorption of paraquat to unreduced and reduced LHA at pH 7 may be rationalized considering that reduced moieties formed during the reduction of LHA and other HA deprotonate at pH > 7.^{16,24,47} At pH 9 and pH 11, however, the hydroquinones in LHA are expected to deprotonate,¹⁴ but apparently this deprotonation did not result in a noticeable increase in paraquat sorption. It is possible that unreduced LHA contains a significant number of deprotonated hydroxy-substituted quinones, which, upon reduction, would not result in a strong increase in the overall phenolate concentrations, even at high pH. The presence of such moieties in LHA has recently been suggested.²³ Finally, if reduction resulted in changes of conformational structure of the LHA aggregates, these did not affect sorption of the probe compounds.

ENVIRONMENTAL IMPLICATIONS

This work on the effect of HA redox state on organic pollutant sorption has several implications. From a methodological perspective, this work demonstrates that direct electrochemical reduction of HA at glassy carbon electrodes in bulk electrolysis cells is a suitable method to generate large amounts of “clean” reduced HA samples with well-defined redox states that can be directly used in follow-up experiments, such as sorption studies, as shown herein. Furthermore, this work demonstrates that the redox states of HA samples can be readily quantified by a spectrophotometric assay based on the reductive decolorization

of the redox dye DCPIP. The assay is highly reproducible, simple, and allows for a high sample throughput. Reduction of DCPIP is directly quantified spectrophotometrically. This is an advantage over the Fe^{3+} -citrate assay commonly used to quantify HA redox states in which the formed Fe^{2+} needs to be complexed prior to spectrophotometric detection.

In the context of environmental fate and risk assessment, this work suggests that changes in the chemistry and the conformational structure of HA upon reduction do not significantly alter its properties as a sorbent for organic pollutants. Because LHA has one of the highest electron-accepting capacities among the previously analyzed humic substances,¹⁶ it is unlikely that reduction of other humic substances with similar or smaller electron-accepting capacities than LHA significantly affects their sorbent properties. Changes in redox conditions in natural systems may alter organic pollutant sorption to NOM indirectly by affecting solution pH, microbial activity, and aqueous concentrations of metals. This work provides first evidence that organic pollutant sorption is not affected by redox-dependent interconversion of quinone and hydroquinone moieties in NOM. As a consequence, fate and transport models can employ redox-independent organic carbon partition coefficients for organic pollutants.

ASSOCIATED CONTENT

Supporting Information

Additional material on the sorption experiments and the spectrophotometric redox assay. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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