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Controllable and Scalable Engineered Soil Surrogates Utilizing Simulated Soil Organic Matter for the Study of Environmental, Ecological, and Agricultural Processes

Arjun Pandey,† Benjamin J. Haywood,† Ghada Abdalla, Stephen Smith, Balamurugan Subramanian,* David A. Spivak,*, and Robert L. Cook*

ABSTRACT: An entirely new, tunable, and scalable platform (model) approach for the detailed study of important molecular processes that take place in geomacromolecular matrices, such as soils, using block copolymer materials at inorganic interfaces has been developed and applied to gain a molecular-level understanding of environmental pollutant/soil interactions. This approach provides a scalable platform with molecular-level control of the soil organic matter (SOM) chemical composition and structure, allowing one to examine proposed SOM interactions with agricultural chemicals (ACs). Accordingly, a series of engineered soil surrogates (ESSs) utilizing simulated SOM was synthesized, in which multiblock oligomers were tethered to silica particles, creating one-, two-, and three-tiered ESSs, via controlled radical polymerization. Using norflurazon (NOR) as a model AC sorbate for batch mode sorption experiments, it was found that binding interactions with the ESSs are not just organic content-driven but are also dependent on the nature of the chemical structure of an ESS. By a stepwise increase in the polarity of the second and third tiers, it is shown that the ability of the ESS to sorb NOR decreases, pointing to a largely hydrophobic driving force for NOR adsorption to the ESSs. The ESS platform approach also allows for the investigation of other, more nuanced interactions with this study, directly showing that hydrogen bonding, electrostatic interactions, conformation, and π-stacking strongly influence NOR binding. This approach can also be applied to a range of other environmentally and agriculturally important issues, such as soil remediation, microbial community dynamics and evolution, nutrient cycling, and carbon sequestration, where soil variability between replicate samples has limited research advances.

KEYWORDS: sorption, surrogate soil, surface-initiated ATRP (SI-ATRP), norflurazon, soil organic matter (SOM), hydrology

INTRODUCTION

Despite our reliance on soils to feed the population, with approximately 99% of consumed food calories coming from terrestrial sources,¹ and the known negative impacts of agricultural chemicals (ACs) on the environment and human health, a molecular-level understanding of associated soil processes is lacking, primarily because of the complexity and heterogeneity of the natural soil matrix. Also lacking is our molecular-level understanding of a wide range of environmental and agricultural processes. For example, soil remediation, microbial community dynamics and evolution, nutrient cycling, and carbon sequestration studies, especially at the molecular level, have all been hampered because of the variability between the replicate soil samples. Stated differently, because of its complexity and heterogeneity, soil has been a mostly unknown and ill-defined matrix upon which researchers have been studying unknown processes at the molecular level.

Efforts to create ”artificial soil test” platforms were first published by the Organization for Economic Cooperation and Development (OECD)² in 1984, summarized as a combination of 70% industrial sand (fines in the range 50−200 μm), 20% kaolin clay (>30% kaolinite), and 10% organic content (sphagnum peat recommended) with pH close to 5.5−6.0. This or similar recipes have been used in a number of studies;³ however, the organic phase remains heterogeneous and ill-defined; hence, reproducibility and molecular-level information from these platforms is still elusive.⁴,⁵ This research aims at the design and synthesis of organically functionalized inorganic...
surfaces in order to develop a range of engineered soil surrogates (ESSs) utilizing simulated soil organic matter (SOM) that echo SOM. This model provides a simple, well-defined, and scalable platform to study and understand the effects of soil chemical composition and complexity at the molecular level on processes such as AC sorption.

**MATERIALS AND METHODS**

**Chemicals.** The monomers styrene, 4-vinylphenyl acetate, and methyl methacrylate were obtained from Aldrich and used after passing through an alumina column to remove the inhibitor. The compound 4-vinyl-2-methoxy phenol was obtained from Aldrich and used as a precursor to synthesize the monomer 2-methoxy-4-vinylphenyl acetate.

Trichlorohexysilane, trichlorododecysilane, and trichlorooctadecysilane were obtained from Gelest. Silica gel (Merck grade 9385, pore size 60 Å, 230–400 mesh, and surface area 550 m²/g), 10-undecen-1-ol, 2-bromoisobutyl bromide, triethyl amine, trichlorosilane, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt catalyst), copper bromide (CuBr), N,N,N′,N″,N‴-pentamethyldiethylyltrimine (PMDETA), acetic anhydride, pyridine, dimethylaninopyridine (DMAP), hydrazine hydrate, and dichloromethane (DCM) were obtained from Sigma-Aldrich. Solvents (toluene, diethyl ether, hexane, acetonitrile, ethanol, and ethyl acetate) and ethylenediaminetetraacetic acid (EDTA) disodium salt dihydrate were obtained from VWR. Norflurazon (NOR) was sourced from ChemService.

**Synthesis of 10-Undecen-1-yl 2-Bromoisobutyrate (3, Scheme S1).** The synthesis of 10-undecen-1-yl-2-bromoisobutyrate was accomplished following a procedure reported previously. To a solution of 10-undecen-1-ol (1, Scheme S1) (4.08 mL, 20.36 mmol) in 100 mL of diethyl ether in a 500 mL round-bottom flask (RBF) was added triethylamine (3.13 mL, 22.40 mmol). The flask was cooled to 0 °C, and a solution of 2-bromoisobutyl bromide (2, Scheme S1) (2.8 mL, 22.40 mmol) in dry diethyl ether (50 mL) was added dropwise through a dropping funnel under stirring for 10 min. The reaction mixture was allowed to come to room temperature and stirred for 15 h. During the reaction, triethylammonium bromide (Et₃N⁺Br⁻) precipitated out from the reaction mixture. After the completion of the reaction, 50 mL of hexanes was added, and the precipitate was removed by gravity filtration. The solvent was removed under reduced pressure to give a colorless liquid, which was purified by column chromatography using a 25:1 mixture of hexane and ethyl acetate.

**Synthesis of 11-(2-Bromo-2-methyl)propionyloxy Undecyltrichlorosilane (4, Scheme S1).** To a 100 mL RBF at 0 °C were added 10-undecen-1-yl-2-bromoisobutyrate (3, Scheme S1) (7.11 g, 22.77 mmol) and trichlorosilane (11.3 mL, 112 mmol) under a nitrogen atmosphere, followed by Karstedt’s catalyst (140 µL, 12 mmol), and stirred for 24 h. The excess reagent (HSiCl₅) was evaporated, redissolved in 50 mL hexanes, and then filtered through a plug of silica to give a colorless liquid after evaporation.

**Synthesis of 2-Methoxy-4-vinylphenyl Acetate (6, Scheme S4).** Acetic anhydride (63 mL, 666 mmol), pyridine (65 mL, 806 mmol), and DMAP (0.4 g, 3.27 mmol) were dissolved in DCM (50 mL) at 0 °C. Subsequently, 2-methoxy-4-vinyl phenol (5, Scheme S4) (10 g, 66.6 mmol) in DCM (50 mL) was added dropwise, allowed to come to room temperature, and stirred for 24 h. The reaction mixture was washed with 3 × 100 mL 10% aqueous CuSO₄ solution, 3 × 100 mL saturated aqueous NaHCO₃ solution, 3 × 100 mL aqueous NaCl solution, dried over anhydrous MgSO₄, and evaporated. Purification by column chromatography using a 1:9 ethyl acetate/hexane mixture yielded a colorless liquid.

**Surface Grafting of Tier-1 ESSs on Silica.** The SiO₂ gel (3.0 g each reaction) was heated overnight at 120 °C. After cooling, toluene (50 mL) and the trichlorosilyl-end functionalized hydrocarbon (0.216 mL C₆H₅O₃, 0.350 mL C₆H₅Br, or 0.245 mL C₆H₅Cl) was added via a syringe dropwise, and the reaction mixture was heated at 80 °C for 15 h. Afterward, toluene was decanted; the product was washed (2 × 25 mL each) using toluene, acetoneitrile, and methanol and dried overnight at 80 °C.

**Surface Grafting of Tier-1 ESS Coupled with an ATRP Initiator (SiO₂–C₁₁–Br).** Silica gel (6.0 g) was added to 50 mL of toluene under nitrogen in an oil bath at 80 °C. After 5 min, 11-(2-bromo-2-methyl) propionyloxy undecyltrichloroisilane (4, Scheme S1) (0.45 mL) was added dropwise and refluxed for 18 h, followed by cooling and washing with toluene, acetoneitrile, and ethanol (2 × 50 mL each solvent wash). The particles were then dried under nitrogen in an oven at 50 °C for 48 h.

**Surface Graft Extension for the Tier-2 Oligo(styrene), Block ESS (SiO₂–C₁₁–PS).** To a 500 mL RBF charged with 50 mL of toluene, 5.0 g of SiO₂–C₁₁–Br with 4.37% total organic fraction (TOF) (0.218 g C₁₁–Br, 0.68 mmol) was added. After 5 min, while purging with N₂, the Cu(I)Br (212 mg, 1.48 mmol) catalyst, the PMDETA ligand (0.32 mL, 1.53 mmol), and the styrene monomer (3.0 g, 28.8 mmol) were added. The RBF was fitted with a condenser, followed by purging with N₂ for 5 min, and then placed in an oil bath at 90 °C under stirring for 1 h. The reaction was cooled to room temperature, washed with (2 × 50 mL each) toluene, acetoneitrile, ethanol, half-saturated aqueous EDTA, water, and ethanol, and then dried at 50 °C for 48 h, giving a faint blue powder.

**Surface Graft Extension for the Tier-2 Oligo(4-acetoxy styrene), Block ESS (SiO₂–C₁₁–PAS).** To a 250 mL RBF, 17 mL of xylene and 2.28 g of SiO₂–C₁₁–Br with 4.52% TOF (0.10 g, 0.32 mmol C₁₁–Br) were added, followed by purging with N₂. After 5 min, the Cu(I)Br (182 mg, 1.27 × 10⁻³ mol) catalyst, the PMDETA ligand (0.32 mL, 1.53 mmol), and the monomer 4-acetoxy styrene (7.8 g, 48 mmol) were added while purging. The RBF was fitted with a condenser and purged with N₂ gas for another 5 min and then placed in an oil bath at 145 °C under stirring for 24 h. The resultant mixture was cooled to room temperature; washed with (2 × 50 mL each) toluene, acetoneitrile, ethanol, half-saturated aqueous EDTA, water, and ethanol; and then dried in an oven at 50 °C under N₂ for 48 h, giving a tan-colored powder.

**Surface Graft Extension for the Tier-2 Oligo(4-acetoxy-3-methoxystyrene), Block ESS (SiO₂–C₁₁–PAMS).** To a 250 mL RBF, 17 mL of xylene and 2.26 g of...
SiO$_2$$-$$\text{C}_{11}$$-$$\text{Br}$ with 4.42 %TOF (0.099 g, 0.31 mmol C$_{11}$$-$$\text{Br}$) were added, followed by purging with N$_2$. After 5 min, the Cu(I)Br (184 mg, 1.28 mmol) catalyst, the PMDETA ligand (0.32 mL, 1.53 mmol), and the monomer 2-methoxy-4-vinylphenyl acetate (6, Scheme S2) (10.0 g, 52 mmol) were added while purging. The RBF was fitted with a condenser, purged with N$_2$ gas for another 5 min, and then placed in an oil bath at 145 °C under stirring for 24 h. The resultant mixture was cooled down to room temperature; washed with (2 × 50 mL each) toluene, acetonitrile, ethanol, half-saturated aqueous EDTA, water, and ethanol; and then dried in an oven under N$_2$ at 50 °C for 24 h, giving a tan-colored powder.

Hydrolysis of the Acetox Group of SiO$_2$$-$$\text{C}_{11}$$-$$\text{PAS}$ and SiO$_2$$-$$\text{C}_{11}$$-$$\text{PAMS}$. Approximately, 2.0 g of polymer-grafted silica SiO$_2$$-$$\text{C}_{11}$$-$$\text{Br}$ was added to a 250 mL RBF, followed by addition of tetrahydrofuran (THF) (40 mL/g of polymer-functionalyzed silica). While stirring, hydrazine hydrate (1.165 mL/g polymer grafted silica) was added dropwise, the RBF was flushed with N$_2$ gas, and then sealed with a stopper. After stirring at room temperature for 10 h, the resulting mixture was washed with (2 × 50 mL each) THF, ethyl acetate, and ethanol and then oven-dried under N$_2$ at 50 °C for 48 h, giving a tan-colored powder.

Surface Graft Extension for the Tier-3 Oligo-(styrene)$_n$-(methylmethacrylate)$_m$ Block ESS (SiO$_2$$-$$\text{C}_{11}$$-$$\text{PS}$–$\text{PMMA}$). In a 500 mL RBF, 50 mL of toluene was added. Subsequently, 5.0 g of SiO$_2$$-$$\text{C}_{11}$$-$$\text{Br}$ with 2.87 % TOF (0.14 g, 0.45 mmol C$_{11}$$-$$\text{Br}$) were added, followed by purging with N$_2$. After 5 min, the Cu(I)Br (212 mg, 1.48 mmol) catalyst, the PMDETA ligand (0.32 mL, 1.53 mmol), and the styrene monomer (2.0 g, 19.2 mmol) were added under N$_2$. After cooling to room temperature, the solvent along with the dissolved unreacted monomer was decanted off under N$_2$, followed by addition of 50 mL of toluene and purging with N$_2$. After 5 min, the additional CuBr (212 mg, 1.48 mmol) catalyst, the PMDETA ligand (0.32 mL, 1.53 mmol), and the styrene monomer (20.0 g, 192 mmol) were added again under N$_2$. The RBF was fitted with a condenser again, and the reaction mixture was purged with N$_2$ gas for another 5 min, followed by refluxing at 90 °C under stirring for 18 h. Upon cooling to room temperature, the reaction mixture was fabricated under N$_2$.
Experimental Details). Prior to the isotherm experiments, the ESSs were washed in three repetitions by shaking with 17 mL of 18 MΩ high-pressure liquid chromatography-grade water for 24 h, followed by removal of liquid phase and oven-drying at 50 °C for 24 h.

**NOR Sorption and Desorption Isotherms.** Batch sorption and desorption isotherm experiments were carried out in accordance with the OECD method 106 [OECD (2000)]. Each experiment was performed with sets consisting of four replicates for each data point, a background solution (18 MΩ water containing 0.01 M CaCl₂, 100 ppm NaN₃, and 0.05 M MES at a pH of 5.75) with an ESS blank, and a NOR solution control (NOR concentration control). Specifically, the isotherms were performed with eight NOR concentrations of 1, 2, 4, 6, 8, 12, 16, and 20 ppm, with the mixtures horizontally being shaken in the dark at 150 rpm at 25 ± 1 °C, and then centrifuged at 3400 rpm for 10 min (more details are provided in Supporting Information SI1).

In accordance with the OECD method 106 (SI1 and SI2), prior to the NOR isotherm experiments with the ESSs, the soil-to-solution ratio and mass balance, as well as sorption–desorption kinetics equilibrium experiments, were performed to determine the appropriate solution-to-soil ratio and equilibrium time for each ESS studied, with the results being summarized in Table S1.
**RESULTS AND DISCUSSION**

**ESS Design and Synthesis.** The model soil platform assembly starts from the mineral surface with subsequent addition of alkyl, aryl, and finally polar hydrophilic domains or tiers. The choice of the alkyl inner tier is based on recent studies which show that predominantly alkyl moieties are sorbed to clay surfaces from humic substance solutions (SI3). The choice of aryl moieties as the middle tier and polar hydrophilic moieties in the outer tier (Figure 1) is based on the recent studies of sequential extractions and advanced NMR analyses of isolates and soils. The platform synthesis of tier-1 ESSs (Figure 1) consisted of hydrocarbon aliphatic chains of 6, 12, and 18 carbons immobilized on silica by heating with terminal trichlorosilyl derivatives of each hydrocarbon in toluene. For subsequent growth of the tier-2 oligomer blocks, an ATRP initiator was introduced on the free end of the aliphatic chain to give SiO\textsubscript{2}−C\textsubscript{11}−Br (Scheme S1).

The surface coverage of SiO\textsubscript{2}−C\textsubscript{11}−Br was verified by TGA, and XPS results confirmed the attachment of the C\textsubscript{11}−Br ATRP initiator on the silica particles, as indicated by the C 1s peak and a C 1s/Si 2p ratio of 6.54 for a sample with 12.0% TOF (Supporting Information, Figure S2). The C\textsubscript{11}−Br loading on SiO\textsubscript{2} was controlled by the ratio of 11-(2-bromo-2-methyl)propionylxy undecyltrichlorosilane (4, Scheme S1) to silica during the grafting process (Figure S3). SiO\textsubscript{2}−C\textsubscript{11}−Br loading of approximately 3−5% TOF was targeted to maintain the final TOF of the ESSs in the 5−25% range of typical soil models.

The platform synthesis of tier-2 (Figure 1) entails addition of aromatic monomers, providing progressively more “ligin-like” structure to the aromatic zone in the ESS. As a first lignin surrogate, oligostyrene (ESS5, ESSs are categorized by assigned number in Tables 1 and 2) was appended to the aliphatic chain using ATRP conditions modified from literature methods, which employed the Cu(I)/Br catalyst and the PMDETA ligand in toluene at 90 °C (Scheme S2). Through optimization, it was found that the 2:1 initiator (C\textsubscript{11}−Br)/Cu(I)/Br−PMDETA ratio was effective in providing the desired oligomeric aromatic block with 5−10 units. The average degree of polymerization (DP\textsubscript{avg}) was a function of the monomer/initiator ratio (Figure S4), which allowed predictive adjustment of the oligostyrene tier to target DP\textsubscript{avg} in the range of 5−10 units, as shown in Table 1.

More realistic lignin surrogates were envisioned to incorporate a phenolic group; however, the acidic phenol was anticipated not to be compatible with the ATRP conditions. Therefore, 4-acetoxy styrene and 4-acetoxy-3-methoxystyrene were used as monomers (the acetoxy group used as the protected phenol), which exhibited lower reactivity, requiring the use of refluxing xylenes to achieve polymerization at 140 °C to give ESS6 and ESS8, respectively. Monomer 4-acetoxy styrene was commercially available, while 4-acetoxy-3-methoxystyrene (6, Scheme S4) was synthesized using 2-methoxy-4-vinylphenol (5, Scheme S4) and acetic anhydride.

NaOH hydrolysis of the acetyl-protected phenols in ESS6 and ESS8 resulted in the hydrolysis of the ester linker between aliphatic and polyaryl blocks, thereby removing the oligomer from the silica particle, and the loss of silica. Hydrazine in THF provided for the selective removal of the acetyl group (Scheme S3), giving the desired phenolic oligomers in quantitative yield, as determined by TGA and verified by \textsuperscript{13}C CP-MAS NMR (SI5).

The platform synthesis of tier-3 ESSs incorporated polar groups, such as methacrylic acid, that cannot be directly polymerized by ATRP. Therefore, a block of oligoacrylates was added to the oligostyrene end of ESS5, using the same conditions as for the synthesis of second tier, which was subsequently converted to methacrylic acid (ESS11) by hydrolysis. Initial methyl methacrylate ester hydrolysis attempts using NaOH and subsequently with LiOH at 60 °C for 18 h yielded little cleavage of methacrylate ester and a significant silica hydrolysis. Following the reports of specific deprotection of methyl esters using NaCN/HMPA at 70 °C from the literature, quantitative conversion of methyl methacrylate to methacrylic acid was accomplished, as determined by \textsuperscript{13}C CP-MAS NMR. The TGA data obtained on a hydrolyzed material (ESS11) using this process showed a decreased percentage of TOF because of the loss of methyl esters and some other material, possibly hydrolysis of the ester located in between the first and second tiers.

The physical characterization of the ESS compositions posed difficulties because of the solid-phase nature of these materials. Solid-state \textsuperscript{13}C CP-MAS NMR, a semiquantitative method, provided functional group identification. The NMR spectra of ESSs (SI5) show distinct peaks in aliphatic, aromatic, and carbonyl regions corresponding to the chemical structure of the materials.

The organic content of the ESSs was further characterized by TGA, which provided a quantitative measurement of the percentage of TOF (% TOF). This was calculated by subtracting the % mass of water and volatiles including the trace solvent and then by subtracting the % TOF of the blank silica (SI7). In brief, for the %TOF calculation using TGA data, the weight loss below 180 °C is attributed to the evaporation of water and solvent residues and, above 180 °C, to the loss of the ESS organic fraction. Notably, beyond 600 °C, the mass changed imperceptibly within experimental error.

The average degree of polymerization of oligomeric blocks (DP\textsubscript{avg}) as shown in Table 1 was also calculated from TGA data using a generic equation (SI8, eq SI26). To illustrate the calculation, assume a solid substrate (such as SiO\textsubscript{2}) with mass S, grafted with an initiator-functionalized (tier-1) block of mass I, g. The initiator end of tier-1 block initiated polymerization to form a block of polymer with mass P, g. TGA data were collected after grafting of an initiator onto SiO\textsubscript{2} (tier-1) and after each polymerization step (tier-2 and further). For a tier-2 ESS, S denotes the mass of an inorganic surface obtained from a TGA measurement with the masses of the aliphatic and aromatic organic oligomers grafted onto the inorganic surface being I and P, respectively. The % TOF of tier-1 and tier-2 of an ESS (A and B, respectively) can be calculated using eqs 1 and 2, respectively. Using the % TOF values, we can calculate the average mass of the polymerized block P per oligomer chain using eq 3 and, subsequently, the DP\textsubscript{avg} of tier-2 using eq 4 (for full derivation for tier-2 and tier-3 ESSs see SI8).

\[
A = \frac{I}{1 + S} \quad (1)
\]

\[
B = \frac{I + P}{1 + P + S} \quad (2)
\]

\[
\frac{P}{\text{moles of } I} = \frac{(A - B)}{A \times (B - 1)} \times \text{MW of } I \quad (3)
\]
TOF) (eq 7) to give normalized binding of sorbate to SOM.20,25

When evaluating the ability of NOR to bind to different soil surrogates, both log $K_{OC}$ (μg kg % TOF⁻¹) and log $K_{P}$ (μg g⁻¹/μg L⁻¹) provide similar trends. For the tier-1 ESSs, there is a systematic increase in log $K_{OC}$ and log $K_{P}$ (Table 2) that correlates with the increase in % TOF. This increased sorption capacity, indicated by increased log $K_{P}$, is expected as a result of increased favorable hydrophobic–hydrophobic interactions through van der Waals (including London) forces. However, the log $K_{OC}$ values, which have been normalized for the organic content, should have remained roughly the same, pointing out that the increase in binding is not just due to increased % TOF.

A possible explanation for this is that for ESS2–ESS4, the longer chains fold over in the aqueous environment to minimize contact with water, and internal sites can form in the interstitial space of the random coil polymer chains. If the polymer is too short to “collapse” or fold, then no interstitial “internal” sites will be formed. Thus, polymer folding can introduce internal and external binding sites, with the internal sites being stronger, by the creation of a more hydrophobic domain with a higher probability of contact with a hydrophobic entity because of two hydrophobic boundaries rather than one and a highly hydrophilic boundary, in this case water, but more sterically hindered (Figure 2). This leads to a less linear NOR sorption behavior with increased chain length, as can be seen by the decreasing $N^{Mw}$ values for ESS2–ESS4 in Table 2. An $N^{Mw}$ value close to 1 indicates homogeneous binding sites that would be seen for a pure partitioning system. An $N^{Mw}$ value tending toward 0 indicates that an increase in binding heterogeneity deviates from a purely partitioning system.25,26

The addition of an oligostyrene chain with a DP of approximately 9 styrene units to the tier-1 alkyl component gave ESS5. The addition of the tier-2 oligostyrene increased the % TOF 3-fold over that of ESS4; however, the log $K_{P}$ and log $K_{OC}$ of ESS5 did actually exhibit a small decrease. This important finding again corroborates the notion that binding interactions with the surrogate soil are not just a factor of organic content. One explanation for the decrease could be that the interactions between aromatic and alkyl segments decrease the available NOR binding sites on both segments. Another possibility related to the specific chemical structure of tier-2 could be an increase in the hydration layer in the oligostyrene versus the alkyl segment, which may result in hydrophobic repulsion of NOR by the tier-2 system versus the tier-1 system (Figure 2). This is further supported by the next tier-2 derivative ESS6, which has a slight increase in %TOF versus ESS5, yet the log $K_{P}$ and log $K_{OC}$ show more than a
slight decrease. It is also possible that the acetoxy component of ESS6 sterically blocks access of the hydrophobic NOR binding site to the hydrophobic portion of the surrogate soil. Hydrolysis of the acetoxy group results in a phenolic group to give ESS8, which is capable of hydrogen bonding; however, the phenol at a buffer pH of 5.75 is still protonated and may only provide a small increase in the polarity of the aromatic region. A small increase in polarity could minimally increase hydration, causing only a small lowering of log $K_F^{sor}$ and log $K_{Nor}^{sor}$, attesting to the overriding effect of the hydrophobic driving force for NOR binding to the ESSs. This explanation is consistent with the slight lowering of log $K_F^{sor}$ and log $K_{Nor}^{sor}$ in ESS8 versus ESS6. Binding of NOR to ESS7 decreases with respect to ESS6, most likely in response to the increased polarity, which may again promote hydration of the surrogate soil, thereby repelling NOR. However, when the acetoxy group is hydrolyzed from ESS7 to give ESS9, there is a significant increase in NOR binding. At a sorption pH of 5.75, the hydrogen bonding in ESS9 (Figure 3) affords electron donation into the aromatic ring, which promotes $\pi-\pi$ interactions with the electron-deficient aromatic ring of NOR. The partially ionized aromatic ring of ESS9 is also capable of electrostatic interactions with amine groups of NOR. The greater polarity of the ESS9 would also be anticipated to increase hydration, which has a repelling effect on NOR; however, this effect appears to be overcome by the $\pi$-stacking and electrostatic interactions between NOR and ESS9, as described above. The $N_{sor}^{sor}$ values show that sorption nonlinearity is aided by binding sites within the polar part of the oligomer chains capable of noncovalent interactions with NOR described above.

Compared to the oligostyrene-functionlalized ESS5, both ESS10 and ESS11 tier-3 ESSs exhibit a significant reduction of log $K_F^{sor}$ and log $K_{Nor}^{sor}$ for NOR, which is consistent with the earlier hypothesis that polar groups create a hydration shell that inhibits the affinity toward and binding of NOR. This important observation supports the idea that interactions of NOR are directed toward the hydrophobic oligostyrene and aliphatic tiers. Hydrolysis of ESS10 to give carboxylic acids in tier-3 (ESS11) does not show a significant change in log $K_{Nor}^{sor}$ and only a small increase in log $K_{Nor}^{sor}$, indicating that the tier-3 chain only provides a hydration shell and is not participating directly in the binding of NOR. Overall, for the ESSs through ESS11 (with the exception of ESS9) series, the lower log $K_F^{sor}$ and log $K_{Nor}^{sor}$ can be explained by the hydration process causing elongation of the polymer, thereby eliminating a portion of interstitial (nonlinear) sorption sites. With these nonlinear sites eliminated, more linear adsorption isotherms are formed, and one will obtain higher $N_{sor}^{sor}$ values. Altogether, the binding analysis suggests that a combination of oligomer conformation, hydration, and noncovalent interactions plays a role in NOR sorption in soils. The lack of correlation between the O/C ratios from Table 1 and the binding trends from Table 2 clearly demonstrates the need for a more detailed understanding of how chemical structure impacts binding behavior, as afforded by the ESS platform approach utilizing appropriate ESS systems.

The ESS systems presented in this work focus on the organic matter component of a soil and, in doing so, eliminate the potential interference from other real soil components such as clays, metal oxides, carbonates, and sulfates, not to mention microbes. However, this platform also allows systematic incorporation of these additional components in a controlled manner to further extend the scope of the current study. This collection of ESS systems—and the ESS platform concept—was not conceived to address the full heterogeneity and complexity of soils or to model all the intricate and nuanced interactions that can take place in a real soil. Instead, the ESS platform should be considered as a surrogate designed to address the feasibility of interactions proposed to take place between organic pollutants, including pesticides, and organic matter within soils. This work illustrates that this new platform approach to soils allows one to directly probe proposed molecular interactions that have been challenging to study in otherwise ill-defined natural geomatrices. In particular, ESSs offer a promising tool to elucidate how pollutants interact with soils and can provide new insights into such interactions and proposed mechanisms based on such interactions. Furthermore, this work also shows the potential utility of the ESS platform approach, with appropriately formulated ESSs, in the investigations of the soil microbial community dynamics and evolution, nutrient cycling, and water cycling, advancing our molecular-level mechanistic understanding of a wide range of essential soil processes.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.0c00091.

Material and methods, soil-to-solution ratio and sorption kinetic experiments, ESS design, ESS synthesis approach, data in the form of NMR spectra and TGA thermograms, and calculations for % TOF and DP from TGA data (PDF).

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Notes

The authors declare no competing financial interest.

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■ REFERENCES


