Evaluation of 6PPD-Quinone Sorption to Treatment Media and Engineered Soil Mixtures

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Project Objectives

The goal of this project was to evaluate the sorption of 6PPD-quinone (or "6PPDQ") to soils in Washington and sorbent media types typical of stormwater treatment systems. The overall project objective was to assess the likely effects of these medias on the partitioning and treatment of 6PPDQ using laboratory scale sorbent-water systems. This study utilized targeted liquid chromatography tandem mass spectrometry (LC/MS-MS) for quantitative detection of 6PPDQ in lab samples and systems.

The main objectives of this research project were to:

- 1. Purchase and install an accelerated solvent extraction (ASE) system, then use it to develop ASE analytical methods to extract 6PPDQ from representative soils and treatment media;
- 2. Evaluate the partitioning (sorption and desorption, kinetics, partitioning coefficients) of 6PPDQ from natural or engineered soils representative of environments that meet soil suitability criteria or are used for road embankments; and
- 3. Evaluate the partitioning (sorption and desorption, kinetics, partitioning coefficients) of 6PPDQ from engineered geomedia and sorbents typically used in stormwater treatment systems.

The first objective was accomplished by acquiring and installing an ASE system. The ASE system was used to run a series of method development experiments, with screening level analysis of 6PPDQ by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). The

second and third objectives were accomplished by obtaining and/or generating representative or engineered soils and sorbent media types, then performing a series of laboratory partitioning and sorption studies to determine partitioning constants and relative media capacities (as possible) and then quantifying 6PPDQ by LC-MS/MS. This report is the data summary deliverable per contract C2300072.

Introduction and Background

For over 20 years in the Puget Sound region, researchers have documented urban runoff mortality syndrome (URMS), a phenomenon in which urban stormwater exposure causes widespread acute mortality in 100s-1000s of adult coho salmon (*Oncorhynchus kisutch*) annually (Scholz et al., 2011). This phenomenon occurs throughout urbanized areas of the Salish Sea, including the greater Seattle region and the Vancouver BC area, with anecdotal observations elsewhere. Urban stormwater, specifically roadway runoff from multilane roadways, has subsequently been shown to be lethally toxic to juvenile coho salmon (Chow et al., 2019). Coho salmon have tremendous cultural, ecological, and economic value in Washington State, and they also are a widely accepted sentinel/indicator species for habitat quality across the western coastal U.S. In the southern parts of their range, some populations of coho salmon are federally listed as threatened or endangered species, meriting special legal and regulatory protections. In addition to substantial value in regional recreational fisheries, which may exceed commercial fisheries value by over 10-fold, Washington State commercial fisheries averaged \$4.3M/year for coho from 2000-2014 (\$30.2M/year across all of the US) (NOAA, 2016).

URMS is caused by polluted urban stormwater derived from roadway runoff (Feist et al., 2017; McIntyre et al., 2018) and has more specifically been linked to chemicals derived from tire rubber (McIntyre et al., 2021; Peter et al., 2018). Recently, the primary causal toxicant for URMS was identified as 6PPD-quinone (6PPDQ), a previously unknown ozonation transformation product of the common tire rubber antiozonant 6PPD (Tian et al., 2021). This compound was discovered after it was observed that tire leachate was lethally toxic to juvenile coho salmon, spurring a series of separation and identification studies that determined the links between 6PPD and coho salmon mortality.

To the best of our knowledge, 6PPD, the common antiozonant and the parent compound of 6PPDQ, is ubiquitously used in passenger and commercial vehicle tires (0.4-2% by mass) (Babbit, 1978). 6PPD is designed to diffuse through the rubber matrix to the surface, where it preferentially reacts with ozone and other oxidants, forming transformation products such as 6PPDQ (Lattimer et al., 1983; Hu et al., 2022). Industrial literature indicates that 6PPD is prone to form protective surface films during ozonation by oxidative polymerization and/or radical interactions (Huntink, 2003; Lattimer et al., 1983; OSPAR Commission, 2006). These processes may impact availability/release of 6PPD and 6PPDQ from whole tires on vehicles and tire wear particles, with differences across new and used rubbers expected (Wagner et al., 2022). We also know that the solubility of 6PPDQ (38-100 ug/L) is far lower than expected based upon expectations from computational modeling based on structure alone, potentially reflecting a high propensity for intermolecular hydrogen bonding or other molecular interactions (Hiki et al 2022; Hu et al. 2023). Observationally, 6PPDQ is also easy to precipitate and very slow to dissolve, indicating that we might expect an interesting and atypical variety of sorption interactions to occur for this particular chemical structure.

Currently, given that 6PPDQ was recently discovered, there exist many data needs and uncertainties regarding its presence and management in the environment. 6PPDQ is acutely toxic to juvenile coho salmon at concentrations near or below 100 ng/L, with sensitive individuals perishing at concentrations as low as 20 ng/L. Driven by its widespread use in tire rubbers and ubiquitous presence in roadway runoff (at concentrations up to 100s-1000s ng/L for busy roads), we expect this toxic chemical to occur in all receiving waters downstream of busy roadways (Tian et al., 2021, 2022; Klöckner et al., 2021a), likely at lethal concentrations during some storm events. It would be expected that adverse sublethal impacts (endpoints currently under investigation by several research groups) might be occurring at even lower exposure concentrations, for example, in fish that survive the short-term acute exposures, but are still biochemically affected by the 6PPDQ exposure. These low ng/L concentrations are far lower than current global observations for expected concentrations in roadway runoff and stormwater-impacted receiving waters, indicating that highly effective source management or runoff treatment strategies will be needed for 6PPDQ. Absent current regulations, such concentrations provide quantitative goals for treatment and water quality management efforts.

Although they are not as sensitive, 6PPDQ is also lethal to brook trout and rainbow trout among other salmonids, and thus these results also apply to systems where protecting other sensitive salmonids, or ecological health more generally, is of interest. Coho salmon return from the ocean to spawn in freshwater streams in the fall, and the offspring rear in the same streams for up to a year after hatching. Both adults and juveniles are reported to be adversely impacted by 6PPDQ exposure and seem to have similar sensitivities and exposure time scales.

Much of the work to understand URMS was done in the Puget Sound area, the second largest estuary in the United States. Therefore, it is of importance to investigate sorption and desorption to natural soils representative of the Puget Sound region. The creeks used by coho salmon throughout the region have been impacted by human development and increasing urbanization, with resulting degradation of both physical and chemical habitat quality. In particular, non-point sources of pollution such as urban runoff are increasingly recognized as a growing threat to water quality (Walsh et al., 2005). Notably, population modeling predicts localized extinction of coho in urbanized watersheds due to the acute toxicity of roadway runoff to coho salmon (Spromberg and Scholz, 2011). Projected increases in human population (Quinn, 2010) are anticipated to increase development, transportation infrastructure, and corresponding contaminant loads in urbanizing watersheds.

6PPDQ was recently identified as the primary coho salmon toxicant in roadway runoff and urban stormwater (Tian et al., 2021). Since discovery of 6PPDQ, several other researchers have confirmed its environmental ubiquity, with detections in urban surface waters, roadside dust, roadside soils, PM2.5, and human urine (Challis et al., 2021; Huang et al., 2021; Johannessen et al., 2021b, 2021a; Klöckner et al., 2021a, 2021b). Such detections imply relevance across several

key environmental compartments beyond roadway runoff and surface water and increase the need for focused 6PPDQ management. Although a few studies have examined leaching of 6PPD and other rubber additives (e.g., 1,3-diphenylguanidine) from tire rubbers (Müller et al., 2022; Peter et al., 2020; Seiwert et al., 2020; Unice et al., 2015), there are currently no studies that examine sorption outcomes for these compounds with various soil types and sorbent treatment media materials.

Notably, 6PPDQ is a transformation product; it is generated from the reaction of an antioxidant 'parent' chemical 6PPD that is added to all vehicle tires. Both 6PPD and 6PPDQ are high risk aquatic toxicants (OSPAR Commission, 2006; Tian et al., 2021). While this newly discovered chemical and its suspected provenance have been identified and verified in the scientific literature, considerable research is needed to characterize its environmental transport and fate, its removal in treatment systems, and conditions promoting treatment to reduce toxicity that it induces in coho salmon and other species relevant to Washington State waters.

Following discovery of the environmental relevance of the tire additive 6PPD and the oxidized byproduct 6PPDQ, WA Ecology and partners have reviewed and prioritized a list of data gaps. One research priority is to evaluate and optimize the performance of natural soils and stormwater treatment media regarding 6PPDQ. Because 6PPDQ is expected to occur widely wherever tires are used, there will be a variety of settings where stormwater runoff management tools for this parameter may be needed. Stormwater management is typically done through best management practices (BMPs). BMPs designed for treatment of runoff often use sorbent medias designed to sorb pollutants as part of the engineering design.

Study Approach. This research effort was undertaken to improve the basic understanding of the chemical properties and aspects of 6PPDQ treatment with natural or engineered soils and engineered sorbent media types commonly used in BPMs. The research described here was conducted in a laboratory setting but is relevant throughout similar soil or media-based treatment systems that employ sequestration or partitioning steps for 6PPDQ removal.

This study examined the sorption potential of 6PPDQ, a transformation product of the antiozonant 6PPD that is used in tire tread and sidewalls, as well as in various other rubber seals and materials (Babbit, 1978; OSPAR Commission, 2006). In these studies, chemical contaminant analysis was performed at the UWT (University of Washington) CUW (Center for Urban Waters) laboratory facility utilizing already developed liquid chromatography separation coupled to tandem mass spectrometry (LC/MS/MS) detection techniques. The methodology, including stocks and standards preparation, sample, preparation, and analytical approach, is documented in the CUW SOP entitled "Extraction and Analysis of 6PPD-Quinone in Water" (Appendix A).

6PPDQ Method Accreditation

The CUW team applied for accreditation for analysis of 6PPDQ by a LC/MS/MS method in July 2021, and after several rounds of editing and feedback, method accreditation was denied in May 2023 due to undefined terms in CUW SOPs. Data acquisition for this study (Ecology contract 2300072) has proceeded under an Ecology approved waiver process; a method renewal package

(submitted in February 2023) and updated data/documents were re-submitted for accreditation in May 2023. Materials remain under review by the Ecology Laboratory Accreditation Unit as of December 2023.

Materials and Methods

Chemicals. Commercial standards of 6PPDQ (10 mg, 98.8% purity, solid) and D5-6PPDQ (solution in acetonitrile, 100 mg/L) were purchased from HPC (Atlanta, GA). Methanol (MeOH, LCMS grade), ethanol (absolute, 200 proof), formic acid (HPLC grade), monopotassium phosphate, monohydrate and dipotassium phosphate, and heptahydrate were obtained from Fisher Scientific (Fair Lawn, NJ, USA). A Thermo Barnstead Nanopure Diamond UV water purification system (Dubuque, IA, USA) was used to provide 18 M Ω water.

Sorbent Media. Various engineered and natural materials were collected for the study. Full descriptions of these materials and their suppliers are provided in **Table 1** and **Table 2**. The project intended to gather multiple natural soils from across Washington state but given time constraints only one sample was collected and analyzed. To help fill this data gap, artificial soils were created by mixing compost and sand volumetrically to create 10%, 5%, and 1% mixtures.

Sample Collection and Storage. Some commercial engineered materials (biochars, GACs, zeolite, perlite, and Ottawa sand) arrived dry and ready to use. Other materials (composts, sands, bark mulch, etc.) contained moisture from outdoor storage. These materials were collected from cites in amber jars and air dried at room temperature. The natural prairie soil was collected from Rochester, WA (46.8235000, -123.0980000) and was filtered through a 2 mm mesh sieve then air dried at room temperature. All sorbent materials were stored in amber jar at room temperature after processing.

Table 1. Description and suppliers of treatment media materials acquired; all were used for initial sorption studies. Only a select representative subset was used for kinetic studies. Each material was labeled with a sample code, which will be used as shorthand throughout the report to refer to the specific material. These sample codes are provided in the right most column.

Name	Supplier	Specs	Capacity ¹	Code
Organic Compost	Dirt Exchange	• Recycled garden prunings and trimmings, no food waste	Low	A1
Pacific Garden Mulch	Pacific Topsoil	 Made from composted yard and garden waste Processed to ½" and smaller, but up to 5% of wood material larger than ½" may be let through 	Low	B2
<u>Compost</u> (Medium)	Cedar Grove Composting	• Made from locally recycled garden prunings, food products, and vegetable trimmings	Low	C2
Rain Garden/ Bioretention	Dirt Exchange	• 65% sand, 35% compost	Low	A2
<u>60/40 Lawn Mix</u>	Cedar Grove Composting	• 60% sand, 40% compost	Low	C3
VIS Sand Blend	Cedar Grove Composting	 Custom Bioretention Compost/Sand Mix Designed with large gravel type sand that allows for high drainage 	Low	C4
Construction Sand	Cedar Grove Composting	• Sand for area filling	Low	S3
VIS Sand	Cedar Grove Composting	• Large gravel-like sand for a custom blend to facilitate drainage	Low	S4
Ottawa Sand	Spectrum Chemical	 Sand, Ottawa, Standard, 20-30 Mesh CAS# 14808-60-7 	Low	S5
<u>Arborist Chips</u>	Dirt Exchange	Locally sourced ground trees and branches	Low	A13
Arbor Mulch	Cedar Grove Composting	 Medium fine bark for weed control Does not add nutrients From locally sourced ground arborist cuttings 	Low	С7

Fine Dark Bark	Dirt Exchange	• Not dyed, not treated, aged fir + hemlock mix	Low	A6
Fine Orange Bark	Dirt Exchange	• Not dyed, not treated, fir + hemlock mix	Low	A7
<u>Filtrasorb 300</u>	Calgon Carbon	 Approx. 8-30 mesh Effective Size: 0.8-1.0 mm Granular activated carbon used in liquid phase applications for the removal of dissolved organic compounds CAS# 7440-44-0 	High	A5
<u>Filtrasorb 400</u>	Calgon Carbon	 Approx 12-40 mesh Effective Size: 0.55-0.75 mm Granular activated carbon used in liquid phase applications for the removal of dissolved organic compounds CAS# 7440-44-0 	High	A8
Mountain Crest Biochar	GroPro	 Initial shipment contained a large range of sizes We sized materials to 30-50 mesh Produced in a downdraft gasifier (1400 C) The biochar is the 1% waste material from the gasifier The feedstock is mixed with softwood-probably mostly ponderosa pine Subject to reduction-surface is highly reduced 	High	A10
<u>OLC 12x30</u>	Calgon Carbon	 Coconut granular activated carbon (biochar) Approx 12-30 mesh Used in water, wastewater, and process liquid applications for the removal of dissolved organic compounds CAS# 7440-44-0 	High	A12
Clinoptilolite Zeolite 14 x 40 (mesh)	Ida Ore	 14 x 40 mesh (<u>specs</u>) Usually used for <u>turf infill</u> 	Low	E2
Natural Clinoptilolite Zeolite 14 x 40 (mesh)	Bear River Zeolite	 Generally used for drinking water treatment and artificial grass infill 14 x 40 mesh (1.410-0.400 mm) <u>Size chart</u> <u>Application by size</u> <u>Material Information</u> 	Low	E3

<u>Fine Horticultural</u> <u>Grade</u>	Supreme Perlite	 Total porosity (% vol): 61% Water space (% vol): 45% For <u>horticulture</u> <u>Size chart</u> 	Low	D1
<u>Medium Horticultural</u> <u>Grade</u> <u>(Also Media Filter</u> <u>Drain Grade)</u>	Supreme Perlite	 Meets or exceeds the requirements for Horticultural Grade Perlite as described in the WSDOT Highway Runoff Manual M 31-16.04 Used in approved DOT Media Filter Drain Mixes Approx 4-18 mesh Approx ½" - 3/16" Bulk density 4.5-6.5 lb/cu ft Total porosity (% vol): 60% Water space (% vol): 20% For <u>horticulture</u> For <u>water quality management</u> <u>Size chart</u> 	Low	D2
Natural Prairie Soil	Thurston County Water Planning	 Rochester, WA (46.8235000, -123.0980000) Collected April 4th, 2023 	Low	N1
Artificial Soil	Mix of Cedar Grove Materials	• 99% sand (S3) and 1% compost (C2) by volume	Low	M1
Artificial Soil	Mix of Cedar Grove Materials	• 95% sand (S3) and 5% compost (C2) by volume	Low	M2
Artificial Soil	Mix of Cedar Grove Materials	• 90% sand (S3) and 10% compost (C2) by volume	Low	M3

¹The capacity column describes the expected ability of the sorbent to uptake organic contaminants. Literature reporting high-capacity sorption of organic contaminants for that material (i.e. biochar and GAC) and inability to detect 6PPDQ in the aqueous phase under the initial conditions are the two criteria used for classifying a high-capacity sorbent. Initial conditions were deemed low-capacity conditions because they worked for lower capacity sorbents and the modified conditions were labeled as high-capacity conditions because they were needed for the high-capacity sorbent studies.

Material Type(s)	Supplier	Contact	Location
GACs Biochar	Calgon Carbon	Mark Boardman <u>Mark.Boardman@kuraray.com</u>	Pittsburgh, PA
Compost BSM Wood chips Mulch	Cedar Grove Composting	Chris Cunningham <u>chris.cunningham@cgcompost.com</u>	Seattle, WA (Western Washington)
Compost BSM Wood chips Mulch	Pacific Topsoils	Tad Forman <u>sales@pacifictopsoils.com</u> <u>tforman@pacifictopsoils.com</u>	Seattle, WA (Western Washington)
Compost BSM Wood chips Mulch	<u>Dirt Exchange</u>	206-599-3478 1521 NW 50th ST Seattle 98107 info@dirtexchange.com	Seattle, WA
Perlite	Supreme Perlite	Alan <u>alan@supremeperlite.com</u> (503) 286 4333	Portland, OR
Biochar	GroPro	Sherri (530) 467-5211	СА
Zeolite	<u>Ida Ore</u>	Matt 208-807-0166 <u>matt@ida-ore.com</u>	Nampa, ID
Zeolite	Bear River Zeolite	Gretchen <u>brzsales@atcnet.net</u> (208) 589-3696	Preston, ID
Natural Soil	Thurston County Water Planning	Kevin Hansen <u>hansenk@co.thurston.wa.us</u> (360) 867-2075	Rochester, WA

Table 2. Summary of contacts and suppliers for media and materials.

Sorbent Surface Characterization. The "high" capacity sorbent media (see **Table 1**) were characterized for surface area using BET-N₂ analysis provided by the University of Washington Clean Energy Testbeds laboratory. Only sorbent media easily characterized by BET-N₂ analysis with known literature methods were analyzed due to time constraints and the need for further method optimization. BET-N₂ analysis uses nitrogen gas to measure surface area. BET-N₂ works by contacting the degassed material with nitrogen gas, which allows a nitrogen gas monolayer to build up on the surface of the material, and then measuring the amount of nitrogen lost from the gas phase once equilibrium is reached to determine the exact surface area. The specific surface areas of the sorbent media were measured by an Automated 3-station BET analyzer. Approximately 0.1 g samples were loaded into a tared BET cell, analysis cells were then

weighed after the BET analysis to determine the exact sample mass that was analyzed. Prior to BET analyses, samples were in-situ degassed for 12 hours at 300 °C (250 °C for zeolite samples). The surface adsorption data was inconclusive for the perlite samples and one of the zeolite samples.

Inconclusive BET data indicates that adsorptive equilibrium could not be reached during the analysis, which is common for mesoporous materials, organic rich materials, or those with poorly defined surfaces. Due to the time sensitive nature of this study inconclusive samples were not rerun although repeating measurements would likely yield results for BRZ 14x40 data because a published method that worked for other zeolite materials was used in this study (Galarneau et al., 2018). However, it would take time to optimize BET conditions for perlite surface area measurements. Few published studies have yet measured the surface areas of perlites. Of these studies limited information about BET parameters is reported (Björklund et al. 2016). Additionally, the surface areas of the soil, compost, wood chips, mulches, etc. were not measured as literature indicated that these were difficult and time consuming to measure, the fractal nature of such materials typically limits attainment of equilibrium (Feller et al. 1992). Thus, these measurements exceed the scope of the current short-term study and were not conducted.

Sorption experiments. Phosphate buffers (pH 7; 10 mM) were prepared prior to the experiment and stored at 4 °C until use. All the sorption experiments (5-day sorption and timeseries kinetics measurements) were conducted within shaken batch reactors (120 mL amber glass jars) under room temperature (20-26°C). Initial trials tested different conditions and sorbents were grouped according to the conditions that yielded the highest percent recovery of 6PPDQ in preliminary trials. The sorbent conditions that yielded the best recovery seemed to correlate to their surface area, so sorbents were grouped as high-capacity or low-capacity based on their estimated (or measured) surface area. Sorbent classification is noted in Table 1. Specific experimental conditions are noted in Table 3. All low-capacity sorbents were run under Condition 1 unless otherwise noted. It was unclear if perlite and zeolite would be low- or high-capacity sorbents, so they were run under multiple conditions (Conditions 1, 3, and 4). All high-capacity sorbents were run under Condition 4 unless otherwise noted. Conditions 5-8 were attempted for the high-capacity sorbents to increase the final aqueous concentration on day five to try to align with OECD 106 protocol (OECD, 2000). Other variations in spiked 6PPDQ mass among conditions (i.e. Condition 2) resulted from initial testing to optimize parameters. Finally, after review of the data and writing the initial draft report, Condition 9 was developed with a lower spike mass to better match the low solubility of 6PPDQ. The highest aqueous concentration measured in a no-sorbent control was 38 µg/L, so the target concentration was adjusted to this concentration for future trials.

Triplicate batch reactors were prepared in 120 mL amber glass jars using either 50 mL or 100 mL of phosphate buffer (pH 7; 10 mM) and a given mass of sorbent within the range of 10 to 100 mg. 6PPDQ methanolic stock solution was prepared at 50 mg/L and 100 mg/L. Using the reverse pipette method and a disposable plastic pipette tip, 50 uL of the 6PPDQ methanolic stock solution was spiked into each reactor. (Note: for Condition 9, only 38 uL of the 50 mg/L solution was spiked into each reactor). 6PPDQ methanolic stock solutions were spiked to maintain a solvent to water ratio of < 0.1% (v:v) in accordance with OECD 106 (OECD, 2000). Buffer volumes,

sorbent mass, and 6PPDQ spike concentration are listed in **Table 3**. After spiking, the bottles were shaken (185 rpm) while isolated from light.

For 5-day sorption experiments, both water and solid phase samples were collected at the end of day 5. Aqueous samples were filtered through a 0.22 um glass fiber syringe filter into a clean glass centrifuge tube. After filtration, 500 uL of the aqueous phase was sampled with a plastic pipette tip and diluted with 450 uL of LCMS grade methanol and 50 uL of d₅-6PPDQ ISTD (internal standard). Residual aqueous phase was removed from the batch reactors with a longtipped glass Pasteur pipette, taking care not to remove solid phase. After the aqueous phase was removed, a solid phase extraction step was completed. OECD Test No. 106 (2000), recommends use of aqueous phase measurements and solid extractions with an appropriate solvent in cases when the sorbent cannot be accurately determined due to instability of the test substance or adsorption of the test substance on the surfaces of the test vessels. Both conditions were true for 6PPDQ based on the controls. Methanol was chosen as the solvent based on previous solvent extraction methods for rubber materials reported in the literature (Zhao et al., 2023). For the solid phase extraction, 10 mL of LCMS grade methanol was added to each batch reactor, contacted with the inside of the jar and all sorbent, then shaken (185 rpm) for 1 hour. These samples were sonicated (30 min) and again shaken (30 min). Methanol extracts were filtered through a 0.22 um glass fiber syringe filter into a clean centrifuge tube, then 950 uL of the methanol extract was pipetted into a clean HPLC vial and spiked with 50 uL of d₅-6PPDQ ISTD. All samples were vortexed (~10 s) prior to LC/MS/MS analysis.

For the time-series kinetic experiments, water phase samples were collected at 0, 1, 3, 6, 24, 48 and 120 hours (i.e. 5 days) and solid phase samples collected at 120 h only. At each sampling point for the aqueous phase, 500 µL of the aqueous phase was sampled with plastic pipette tips into 1mL HPLC vials, diluted with 450 µL methanol and 50 µL d₅-6PPDO ISTD. The vial is then vortexed for ~10s, pipetted into a 1 mL plastic syringe, and filtered through a 0.22 µm glass fiber syringe filter prior to the instrumental analysis. Prior to the solid phase extraction, all aqueous phase was removed using a long-tipped glass Pasteur pipette taking care to exclude the solid phase. Samples processed this way had a slightly lower standard deviation for sorbent small particles (less than 40 mesh), but the results were consistent with manual removal of the aqueous phase. After the aqueous phase was removed, 10 mL of LCMS grade methanol was added and contacted with the solids and the inside of the jar, then shaken (185 rpm, 1 hr), sonicated (30 min) and shaken (30 min). The solvent extract was then filtered through a 0.22 um glass fiber syringe filter and 950 uL of the methanol extract was pipetted into a clean HPLC vial. The methanol samples were spiked with 50 uL of d₅-6PPDQ ISTD, sonicated for ~10 seconds, and sent for LC/MS/MS analysis. Most solvent extractions were completed immediately after aqueous phase samples were processed. However, if timing did not permit subsequent extraction, the solid samples were stored at 4 °C overnight. No significant difference was noted between samples processed directly after or those stored.

Condition	Sorbent Capacity	Solid:Solution	Sorbent	6PPDQ	Aqueous	Nominal
	(Table 1)	Ratio	Mass	Mass	Volume	Concentration
		[w:w]	[mg]	[ng]	[mL]	[ng/mL]
Condition 1	Low	1:500	100	2500	50	50
Condition 2	Low	1:500	100	500	50	10
Condition 3	Medium	1:1000	50	2500	50	50
Condition 4	High	1:2500	20	2500	50	50
Condition 5	High	1:2500	10	5000	50	100
Condition 6	High	1:5000	10	2500	50	100
Condition 7	High	1:5000	20	5000	100	50
Condition 8	High	1: 10000	10	5000	100	50
Condition 9	Low	1:500	100	1900	50	38

Table 3. Summary of batch reactor conditions for 6PPDQ sorption and kinetic studies.

Desorption Experiments. Triplicate batch reactors were set up using 120 mL amber jars with 100 mg of sorbent and 50 mL of phosphate buffer (pH 7; 10 mM). 6PPDQ (50 uL of 50 mg/L) was spiked into each reactor, then a time-series kinetic study was conducted. Kinetic studies sampled 500 uL at time 0, 0.5, 1, 3, 6, 24, 48, and 120 hours and processed these aqueous samples as described above. Immediately upon conclusion of the kinetic studies, desorption studies were conducted to evaluate reversible solid-liquid partitioning by removing the excess water from each batch reactor and leaving all sorbents behind. Fresh phosphate buffer (50 mL, pH 7; 10 mM) was added, mixed, and initial samples collected immediately (time 0 hr). Jars were shaken in the dark at 185 rpm and 500 uL samples collected at time 0.5, 1, 3, 6, 24, 48, 120, and 168 hours. Next, 450 uL of LCMS grade methanol and 50 uL of d₅-6PPDQ ISTD, were added, vortexed (~10 s), and filtered (0.22 um glass fiber syringe filter) prior to LC-MS/MS analysis.

Instrumental Analysis. 6PPDQ quantification was conducted with an Agilent 1290 Infinity ultrahigh performance liquid chromatography (UHPLC) system coupled to a triplequadrupole mass spectrometer (Agilent G6460A) with electrospray ionization (ESI+ mode). The chromatographic separation of samples (5 μ L) used a reversed-phase analytical column (Agilent Poroshell HPH-C18 2.1 × 100 mm, 2.7 mm particle size) and C18 guard column at 45 °C. Binary mobile phases (0.2 mL/min flow rate) consisting of DI water (A) and methanol (B), both with 0.1% formic acid, were used. The gradient program was set as follows: 50% B 0-0.5 min, 100% B at 10.5-12 min, 50% B at 13-16 min (0.2 mL/min flow rate). Nitrogen was used as nebulizing and dessolvation gas (350 °C, 10 L/min) and capillary voltages were 3000 V. The 6PPDQ and d5-6PPDQ ISTD was analyzed in multiple reaction monitoring (MRM) mode using two individual ion transitions (see **Table 4** for instrument parameters). For quality assurance and quality control (QA/QC) assessment, samples were run in the following order: calibration curve samples were run at beginning, experimental replicates were analyzed sequentially with a methanol blank frequently run in the middle to check for carryover (no carryover observed), and a QC sample from the calibration curve set was reanalyzed at the end of the sequence (<5% variation of peak area was observed). The instrumental data was processed with Agilent Masshunter Quantitative software and Excel. Calibration curve ranges, the isotope-labeled internal standard used for quantification, minimum detection limit (MDL) and minimum quantitation limit (MQL) are summarized in **Table 5**. MDL and MQL were determined as the lowest concentrations giving signal to noise (S:N) ratios of 3 and 10, respectively. Calibration curve determination coefficients (R^2) were >0.99.

Table 4. Critical LC/MS/MS dMRM parameters for 6PPDQ analysis including retention time (RT), precursor ion (m/z), quantifier and qualifier ions (m/z); collision energy included in parentheses, eV), and fragmentor voltage.

Analyte	RT [min]	Precursor ion	Quantifier ion	Qualifier ion	Fragmentor voltage [V]
6PPDQ	7.5	299.2	187.1 (23)	215.1 (14)	110
6PPDQ-d5	7.5	304.2	220.1 (14)	192.1 (26)	110

Table 5. Calibration range, ISTD, method detection limit (MDLs) and method quantification limit (MQLs, ng/L) for 6PPDQ analysis via LC/MS/MS.

Target Analyte	Calibration range [µg/L]	ISTD	ISTD Concentration in final extract [µg/L]	MDL [ng/L]	MQL [ng/L]
6PPDQ	0.025-100	d₅-6PPD-Q	5	2.5	5.1

Quality Assurance and Quality Control. Method blanks were identically prepared with DI water in triplicate and processed identically; results are summarized in **Table 6**. For 5-day sorption tests, aqueous method blanks were collected on day 5 (120 hours). For kinetic studies, aqueous method blank samples were collected at time 0, 0.5, 1, 3, 6, 24, 48, and 120 hr (**Figure 1**). Solid phase method blank samples were taken on day 5 (120 hours) for both 5-day sorption tests and kinetic studies; samples were processed as described above.

Initial method blank results (**Table 6**, for both the aqueous and solid phase) demonstrated detection of 6PPDQ. The method blank samples were collected in triplicate and the 6PPDQ concentration was consistent across triplicate samples. These results were used to identify and isolate a cross-contamination issue associated with the ISTD syringe washing procedure; ISTD spikes were subsequently added via reverse pipetting which reduced method blank detections to below method detection limits (MDL) consistently for all triplicate samples. For the sample sets where 6PPDQ was detected in method blanks, sample concentrations were adjusted with the method blank values. Specifically, the average value of the aqueous method blank concentrations (reported in **Table 6**) was subtracted from the aqueous sample concentrations for the entire batch processed on the same date. Likewise, the average value of the solid method blank concentrations

(reported in **Table 6**) was subtracted from the solid sample concentrations for the entire batch processed on the same date. However, for subsequent sample sets with method blanks below the MDL, for these batches the sample concentrations were not adjusted because no 6PPDQ was detected in the blanks.

Table 6. Summary of QA/QC data for 5-day sorption and time series tests. The reported values are the average and standard deviation of the triplicate method blanks from the aqueous sample processing and the solid phase sample processing.

8	OA/OC Type		Aqueous phase	Solvent extract	Solvent extract
Date Run		Aqueous phase blanks average [µg/L]	blanks standard deviation	blanks average [µg/L]	blanks standard deviation
5/02/2022*		0.25	[µg/L]	0.007	[µg/L]
5/03/2023*	Method Blank	0.35	0.029	0.096	0.018
6/17/2023*	Method Blank	0.0054	0.0038	0.79	1.1
6/23/2023	Method Blank	<mdl< td=""><td><mdl< td=""><td>0.13</td><td>0.19</td></mdl<></td></mdl<>	<mdl< td=""><td>0.13</td><td>0.19</td></mdl<>	0.13	0.19
7/12/2023	Method Blank	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
7/31/2023	Method Blank	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
8/1/2023*	Method Blank	0.023	0.020	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
12/04/2023	Method Blank	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
12/20/2023	Method Blank	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
5/03/2023	No-Sorbent Control (120 hours)	5.1	1.2	44	11
6/17/2023	No-Sorbent Control (0 hours)	34	0.45	NA	NA ²
6/17/2023	No-Sorbent Control (120 hours)	23	1.7	66	2.2
6/23/2023	No-Sorbent Control (0 hours)	40	1.1	NA	NA ²
6/23/2023	No-Sorbent Control (120 hours)	16	0.55	67	10
7/12/2023	No-Sorbent Control (0 hours)	35	6.3	NA	NA ²
7/12/2023	No-Sorbent Control (120 hours)	16	3.0	84	6.0

7/31/2023	No-Sorbent	6.3	3.0	130	28
	Control				
	(120 hours)				
8/1/2023	No-Sorbent	4.4	0.36	130	2.0
	Control				
	(120 hours)				
12/04/202331	No-Sorbent	2.9	0.13	74	7.6
	Control				
	(120 hours)				
12/20/20231	No-Sorbent	29	0.28	NA	NA ²
	Control				
	(0 hours)				
12/20/2023 ¹	No-Sorbent	8.8	0.66	50.	5.5
	Control				
	(120 hours)				

¹The total 6PPDQ mass spiked for these trials was 1900 ng (Condition 9) as opposed to 2500 ng (Conditions 1 and 4) to match the measured aqueous solubility of 6PPDQ.

²No solvent extractions were done after zero hours. Solvent extractions only occurred after the 120-hour (5-day) sorption test was complete.

^{*}Trials where 6PPDQ was detected in the method blanks. The value of the method blank detect was subtracted from all calculated sample concentrations for that batch.

No-sorbent controls were prepared in triplicate by spiking 50 uL (or 38 uL) of 50 mg/L 6PPDQ methanolic stocks into 50 mL of buffered DI water (pH 7; 10 mM phosphate buffer) in 120 mL amber jars, spikes were processed as described above. For the 5-day sorption test, the aqueous phase sample was taken just on day 5 (120 hour). For kinetic studies, aqueous phase samples were taken at the same time points (0, 0,5, 1, 3, 6, 24, 48, 120 hours) as the laboratory samples and processed using the same procedure. For both the 5-day sorption test and kinetic studies, solid phase extractions were only done on day 5 (120 hours).

Spike and recovery results for total mass recovered from water phase and solvent are summarized in **Table 6** for 5-day sorption tests and time series kinetic tests. The use of method blanks and spike and recovery experiments that were conducted concurrent with extractions for sampling events, throughout these experiments are summarized in **Table S1**.

Data Analysis

Sorption Coefficients. The solid-aqueous partition coefficient (K_d) is the ratio of the mass of the adsorbate sorbed to the mass of the adsorbate in solution. The sorption reaction can be modeled as follows:

$$A + C_{ag}^{ads} \rightarrow C_s^{ads}$$

Equation 1

The mass action for expression for K_d is:

$$K_d = \frac{\text{mass of adsorbate sorbed}}{\text{mass of adsorbate in solution}} = \frac{C_s^{ads}(eq)}{C_{aq}^{ads}(eq)}$$
 Equation 2

Where A is the free unoccupied sorption sites, $C_s^{ads}(eq)$ is the concentration of adsorbate on the solid at equilibrium, and $C_{aq}^{ads}(eq)$ is the concentration of adsorbate in aqueous phase at equilibrium.

The assumption of the sorption reaction model used in **Equation 1** assumes that the unoccupied sorption cites (A) are in excess compared to the concentration of the adsorbate in solution at equilibrium ($C_{aq}^{ads}(eq)$) and that the activity of the adsorbate sorbed to the solid ($C_s^{ads}(eq)$) is equal to 1.

In line with OECD 106 data processing, the sorption coefficient K_d was estimated from the collected data as follows (OECD, 2000):

$$K_d = \frac{C_s^{ads}(eq)}{C_{aq}^{ads}(eq)} = \frac{m_s^{ads}(eq)}{m_{aq}^{ads}(eq)} \frac{V_0}{m_{soil}} (cm^3 g^{-1})$$
 Equation 3

Where $C_s^{ads}(eq)$ and $C_{aq}^{ads}(eq)$ represents the 6PPDQ concentration retained in the soil phase ($\mu g^{-1*}g$) and aqueous phase ($\mu g^* cm^{-3}$) at adsorption equilibrium, respectively. $m_s^{ads}(eq)$ and $m_{aq}^{ads}(eq)$ represents 6PPDQ mass retained in the soil phase (μg) and aqueous phase (μg) at adsorption equilibrium, respectively. m_{soil} represents the quantity of the soil phase, expressed in dry mass of soil (g) and V_0 represents the initial volume of the aqueous phase in contact with the soil (cm³). K_d is typically reported in units of mL/g or L/kg.

Sorption Kinetics. Consistent with literature approaches, kinetics were evaluated via the pseudo first order, pseudo second order, and intraparticle diffusion kinetic models (Fu, et al. 2016) as follows:

$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 * t$	Equation 4: Pseudo-first order
$\frac{t}{Q_t} = \frac{1}{k_2 * Q_e^2} + \frac{t}{Q_e}$	Equation 5: Pseudo-second order
$Q_t = k_i * t^{0.5} + C$	Equation 6: Intraparticle diffusion

Where Q_e and Q_t (ug/g) represent the mass of 6PPDQ sorbed to solids at equilibrium and time t (hr), respectively. Parameters k_1 (hr⁻¹), k_2 (g*ug^{-1*}hr⁻¹), and k_i (ug*g^{-1*}hr^{-0.5}) are the rate constants derived from the pseudo first order, pseudo second order, and intraparticle diffusion equations, respectively. C (ug/g), is the intercept of the intraparticle diffusion model.

Results and Discussion

Sorbent Characteristics. Twelve of the sorbents were characterized for surface area using BET analysis (**Table 7**). BET surface analysis was inconclusive for all sorbent media containing perlite as well as the Zeolite 14 x 40 (BRZ) material. Across the materials that generated data, the zeolites exhibited the lowest measured surface areas in the range of 36-49 m²/g. Biochars (710-

800 m²/g) and coal-based GAC products ("Filtrasorb XXX products"; 680-870 m²/g) had relatively similar measured surface areas, about 15-20-fold higher than those for the zeolites. Notably, the MCG biochar had a high surface area value near that of many commercial GAC products, indicating a possible propensity for effective and high-capacity sorption of organic pollutants because adsorptive processes scale with media surface area. Across the data and materials, there was no easily observable relationship between grain size or material and measured surface area, although the relatively low sample numbers and material types/sizes preclude confident assessment of trends in surface area. Measured GAC surface areas were relatively similar (slightly lower) to manufacturer reported values for these materials, when available.

Material	Туре	BET Surface Area [m²/g]
Filtrasorb 300	GAC	779
Filtrasorb 400	GAC	865
Filtrasorb 600	GAC	679
OLC 12x30	Biochar	713
MCG Biochar (30-50 mesh)	Biochar	801
Zeolite 14 x 40 (IdaOre)	Zeolite	49.0
Zeolite 14 x 40 (BRZ)	Zeolite	Inconclusive
Zeolite 4 x 6 (IdaOre)	Zeolite	35.6
Zeolite 4 x 8 (BRZ)	Zeolite	48.0
Perlite, Construction Grade	Perlite	Inconclusive
Perlite, Medium Horticulture	Perlite	Inconclusive
Perlite, Enviroperl TM Adsorbent Grade	Perlite	Inconclusive

Table 7. Observed BET surface area measurements for high-capacity sorbents.

6PPDQ characteristics and stability. The characteristics and stability of 6PPDQ are important considerations when evaluating 6PPDQ fate in partitioning studies. As a reactive quinone, 6PPDQ is a redox active compound and potentially unstable analyte in complex solid-water systems, especially those with redox active constituents that might be capable of redox reactions. The scientific literature indicates some solid and mineral phases are capable of electron transfer, along with NOM and other dissolved organic constituents. While some data exists for this recently discovered compound (e.g., Hu et al. 2023), the likely existence of unknown or partially evaluated chemical characteristics (e.g. volatility, environmental stability) do have substantial bearing on the interpretation of control and sorbent data outcomes. As one example, Hu et al., 2023

reported 38 µg/L solubility for 6PPDQ in deionized water; Hiki et al., 2022 reported 50-60 µg/L for 6PPDQ solubility limits. These values place relatively low upper bounds on working concentration ranges for experimental systems, although in more complex systems, natural organic matter and co-solvent effects would be expected to slightly increase these solubility limits. Notably, in our experience, 6PPDQ also is slow to dissolve or partition between the solid and dissolved phase, potentially due to relatively strong intermolecular interactions such as hydrogen bonding (Hu et al. 2023). We also observed evidence for oxidative polymerization and other complex processes for this compound. These characteristics of 6PPDQ may imply slower than expected partitioning equilibrium, or enhanced propensity for removal and sorption to solid phases, or reduced propensity for desorption, or increased mass loss in solution.

Hu et al. 2023 reported that 6PPDQ is prone to efficiently sorb to many plastic and rubber materials, including those commonly used in laboratory situations, and there was limited ability to recover sorbed 6PPDQ mass with polar solvent washes. Irreversible, or reactive sorption (e.g. covalent bond formation) to some materials or compounds may be an especially likely outcome for 6PPDQ; this attribute would be highly beneficial for efficient treatment but complicates data interpretation for these research studies. Similarly, quinones are redox-active compounds that tend to display system specific stability depending on the presence of co-occurring metals, redox-active chemicals, or other reactive impurities. For example, we have sometimes observed long term (many months) stability for 6PPDQ in complex systems, yet other similar systems seem to exhibit rapid (hours) partial loss of 6PPDQ followed by longer term (i.e. months) stability. The potential volatility of 6PPDQ and its sensitivity to atmospheric gases, oxidants, or light (direct or indirect photo reactivity) are being investigated in the scientific community, but have not been determined or reported experimentally, we therefore cannot exclude the potential for such complicating factors to affect data quality. We do not yet understand the mechanistic basis or validity of all these observations, but instead report them to communicate caution and care when interpreting experimental data for 6PPDQ in any complex system. Such factors may complicate any efforts to conduct laboratory studies or accurately interpret study data, making use of proper control studies and apples to apples comparisons especially important for 6PPDQ at the current time.

Differences in experimental set up. For this study, small-scale batch reactor systems were set up. Two experimental systems were used: i) <u>5-day sorption tests</u> and ii) <u>time series (kinetic)</u> <u>tests</u>. The specifics of the experimental set-ups can be found in the methods section. The key differences are that the 5-day sorption tests were left to shake with sampling only on day 5, whereas the time series tests were sampled at pre-selected intervals from day 0 and day 5. The 5-day sorption test data is used to calculate the solid aqueous partition coefficient (K_d) and the time series tests are used to calculate the kinetic constants: the pseudo-second-rate constant (k₂) and the equilibrium sorption capacity (q_e). Undisturbed batch reactors used for solid-aqueous partitioning calculations will be called <u>5-day sorption tests</u>, and the time sampled batch reactors used for solid-aqueous partitioning forward. Tabulated mass balances for the 5-day sorption test values are in **Table 8**, and tabulated mass balances for the time series tests) are in **Table 9**.

Mass Balances. Even in the simplest systems, not all 6PPDQ mass was recovered, indicating that 6PPDQ loss or irreversible or unrecoverable sorption processes were occurring. Sand-water systems and no-sorbent controls exhibited recoveries in the 51-75% range. The first no-sorbent control had a total recovery of 29%, lower than those observed for similar systems in the past (see Table 8). We evaluated our processes and concluded that 6PPDQ needed more time for mass transfer, so the solid phase extraction procedure was updated to increase contact time between solvent, glassware, and sorbent. After additional time and contact with the solvent recoveries consistently were exhibited in the 51-75% range for all no-sorbent controls for both the 5-day sorption tests (Table 8) and time series tests (Table 9). When the 6PPDQ spiked mass was reduced to 1900 ng, the recovery in the no-sorbent controls dropped to 47%, likely due to a higher percentage of the mass being lost to the same unrecoverable loss mechanisms with less of a buffer or sorbed solution for collection. The recovery results are slightly low, but broadly consistent with our laboratory results over the past three years where most complex, multi-phase experimental systems like soil-water, sorbent water, or 6PPDQ-exposed fish tanks, have exhibited mass loss across comparisons of spiked or nominal mass to measured mass (often 60-75% recovery after equilibration). Additional testing of the system components and 6PPDQ stability testing could clarify loss pathways that may help to close the mass balance.

Notably, a substantial amount of 6PPDQ mass was adsorbed to the glass and recovered by solvent washing the empty bottles. We also think bottle caps may serve as a large net mass sink in these systems. For all no-sorbent control samples in the 5-day sorption experiments the mass recovered from solvent washes accounted for 83-86% of the recovered mass (see **Table 8**). The high percentage of undissolved mass could be due to solubility challenges at spiked concentrations. However, this phenomenon occurred at spiked concentrations within literature reported solubility limits (38 - 50 ug/L), indicating that 6PPDQ may still favor some partitioning to glassware near reported solubility limits. Furthermore, initial measured masses in all systems tended to be about 80% of nominal, likely due to low solubility and/or slow dissolution kinetics of 6PPDQ into the aqueous phase after spiking.

Material Type	#	Date Run	Solid: Solution	Spiked Mass (ng)	Aqueous Mass (ng)	Solvent Extract Mass (ng)	Total Recovered Mass (ng)	Recovery (%)
No-Sorbent Control	SPK	5/3/2023	NA	2500	270	445	715	29
No-Sorbent Control	SPK	7/31/2023	NA	2500	316	1310	1630	65
No-Sorbent Control	SPK	8/1/2023	NA	2500	219	1300	1520	61
No-Sorbent Control	SPK	12/4/2023	NA	1900	147	745	892	47
Sand	S3	4/26/2023	1:500	2500	308	787	1090	44

Table 8. Summary of system mass balances and percent recoveries for 5-day sorption experiments; data was evaluated at the end of 5-days.

Sand	S3	7/31/2023	1:500	2500	258	1400	1660	66
Sand	S3	12/4/2023	1:500	1900	220	490	710	37
Sand	S4	4/26/2023	1:500	2500	322	1020	1340	54
Sand	S5	4/26/2023	1:500	2500	316	1060	1370	55
Sand	S5	7/31/2023	1:500	2500	250	1530	1780	71
Compost	A1	4/19/2023	1:500	2500	57.2	1600	1650	66
GAC	A5	3/29/2023	1:2500	2500	16.6	516	532	21
Bark mulch	A6	3/10/2023	1:500	1000	27.5	666	693	69
Bark mulch	A7	3/10/2023	1:500	1000	46.9	629	676	68
GAC	A8	3/10/2023	1:2500	2500	30.0	569	599	24
Biochar	A10	3/10/2023	1:2500	2500	5.03	204	209	8.4
Biochar	A12	8/1/2023	1:2500	2500	20.6	19.1	40	0.016
Compost	B2	4/19/2023	1:500	2500	88.0	1660	1750	70
Compost	C2	4/19/2023	1:500	2500	25.2	1860	1890	76
Compost	C2	7/31/2023	1:500	2500	29.8	2100	2130	85
Compost	C2	12/4/2023	1:500	1900	28	1240	1270	67
Bioretention	C3	4/19/2023	1:500	2500	222	1270	1490	60
Bioretention	C3	7/31/2023	1:500	2500	242	1500	1740	70
Bioretention	C3	12/4/2023	1:500	1900	174	713	887	47
Bioretention	C4	4/26/2023	1:500	2500	191	1230	1420	57
Bioretention	C4	7/31/2023	1:500	2500	404	1140	1550	62
Compost	C6	4/26/2023	1:500	2500	55.8	1560	1620	65
Wood chips	C7	4/26/2023	1:500	2500	152	1590	1750	70
Wood chips	C7	7/31/2023	1:500	2500	212	1780	1990	80
Perlite	D1	5/3/2023	1:2500	2500	401	676	1080	43
Perlite	D2	5/3/2023	1:2500	2500	406	586	992	40
Perlite	D2	8/1/2023	1:500	2500	412	1100	1510	61
Zeolite	E2	5/3/2023	1:2500	2500	369	570	939	38
Zeolite	E2	8/1/2023	1:500	2500	314	1020	1330	53
Zeolite	E3	5/3/2023	1:2500	2500	449	648	1100	44

Artificial soil	M1	12/4/2023	1:500	1900	361	323	684	36
Artificial soil	M2	12/4/2023	1:500	1900	364	360	724	38
Artificial soil	M3	12/4/2023	1:500	1900	313	355	668	35
Natural Soil	N1	5/3/2023	1:500	2500	303	696	999	40
Natural Soil	N1	8/1/2023	1:500	2500	390	918	1310	52

Table 9. Net system recovery of 6PPDQ from solid-water systems for time series studies (kinetic experiments); data was evaluated at the end of 5-days.

Material Type	#	Date	Solid: Solution	Mass Added (ng)	Aqueous Mass (ng)	Solid Extract Mass (ng)	Total Mass (ng)	Percent Recovery (%)
No-Sorbent Control	SPK	6/5/2023	N/A	5000	947	2590	3540	71
No-Sorbent Control	SPK	6/17/2023	N/A	2500	1160	648	1810	72
No-Sorbent Control	SPK	6/23/2023	N/A	2500	870	669	1540	62
No-Sorbent Control	SPK	7/12/2023	N/A	2500	844	843	1690	67
No-Sorbent Control	SPK	12/15/2023	N/A	1900	438	498	940	51
Sand	S3	6/23/2023	1:500	2500	961	711	1680	67
Sand	S3	12/15/2023	1:500	1900	459	483	940	52
Sand	S5	6/23/2023	1:500	2500	863	664	1530	61
Compost	A1	6/5/2023	1:500	5000	378	3420	3800	76
Bioretention Mix	A2	6/5/2023	1:5000	5000	1160	1830	2990	60
GAC	A5	6/5/2023	1:10000	5000	316	883	1200	24
Bark Mulch	A7	7/10/2023	1:500	2500	432	1640	2070	83
GAC	A8	7/10/2023	1:5000	2500	111	434	545	22
Biochar	A10	7/10/2023	1:10000	2500	87.7	577	665	13
Biochar	A10P	6/5/2023	1:10000	5000	156	654	809	16
Compost	C2	6/17/2023	1:500	2500	238	1940	2180	87
Compost	C2	12/15/2023	1:500	1900	129	1180	1310	71
Bioretention Mix	C3	12/15/2023	1:500	1900	509	1060	1570	85
Wood Chips	C7	7/12/2023	1:500	2500	703	1480	2180	87
Perlite	D2	7/12/2023	1:1000	2500	1480	407	1890	75
Zeolite	E2	7/12/2023	1:1000	2500	1050	541	1590	64

Artificial soil	M1	12/15/2023	1:500	1900	764	197	960	52
Artificial soil	M2	12/15/2023	1:500	1900	830	252	1080	58
Artificial soil	M3	12/15/2023	1:500	1900	870	360	1230	66
Natural Soil	N1	6/17/2023	1:500	2500	1480	843	2320	93

System losses of 6PPDQ occurred over time even in the no-sorbent controls, likely representing sorption to glass jars or a reactive process (Figure 1). Silica sand-water system results were similar to no-sorbent controls in both mass balance results (Table 8 and Table 9) and in loss of 6PPDQ concentration over time (Figure 1 and Figure 2). This indicates that silica sand had little impact on 6PPDQ partitioning or stability and limited treatment potential. Both silica sand and natural soils losses were indistinguishable from no-sorbent controls. The sand-water results are broadly similar to past observations (e.g. Tian et al. 2021) where sand treatment and sand filtration exhibited little to no effect on removing either bulk stormwater toxicity, or 6PPDQ specifically, during laboratory studies.



Figure 1. Relative concentration (C/C_0) of 6PPDQ versus time for select sorbents over a 120hour time series. The results show relative loss compared to the initial spiked mass of 2500 ng. Sorbents include: no sorbent control (SPK), sand (S3), compost (C2), natural soil (N1), and biochar (A10). Error bars reflect standard deviations of triplicate studies.

Softwood biochars, commercially available biochars, and GACs are generally considered highly effective, high capacity sorbents for sequestrative treatment of organic pollutants in the literature. As expected, **Figure 1** showed the overall system mass loss from the aqueous phase was

highest in the high capacity biochar systems. Compost had the second highest mass loss, likely due to its high organic carbon (OC) content. Sand had little effect on the system, following the same loss trends as the no-sorbent control. The natural soil tested had the lowest total system losses in Figure 1. The initial decrease in 6PPDQ concentration in the natural soil sample over the first hour may indicate sorption, however, the longer term (5 day) stability of 6PPDQ concentration compared to the no-sorbent control likely indicate stabilization of 6PPDQ via colloidal interactions. Similar results were seen in replicated time series and in time series tests conducted with artificial soils (M1, M2, M3) comprised of sand-compost mixtures. Results for all three sandcompost mixture compositions were nearly identical. These artificial soils all resulted in lower mass losses, and apparent mass stabilization, relative to sand and no-sorbent controls, and with little net irreversible or reactive removal of 6PPDQ from the aqueous phase (see Figure 2). These data are highly consistent with colloidal effects that act to stabilize 6PPD in solution by maintaining 6PPDQ mass in the dissolved phase. Washing and pre-processing the compost to removal colloidal material and small particles may have been necessary, leaving behind the larger stable solids that could act to better sequester and removal 6PPDQ from solution. It is possible these results would have changed substantially with such compost pre-processing. We also are evaluating the possible loss, and unexpectedly effective sorbent capacity, of the bottle caps used in these systems as a possible source of mass loss in the cleaner no-sorbent and sand systems.



Figure 2. Relative concentration (C/C_0) of 6PPDQ versus time for select sorbents over a 120hour time series. The results show the loss compared to the initial spiked mass of 1900 ng. Sorbents include: no sorbent control (SPK), artificial soil (99/1 sand/compost) (M1), artificial soil (95/5 sand/compost) (M2), artificial soil (90/10 sand/compost) (M3), and sand (S3). Error bars reflect standard deviations of triplicate studies.

OECD-recommended aqueous concentrations at equilibrium are 20-80% of initial aqueous concentration. Due to the low solubility of 6PPDQ and the high removal capacity of biochar (A10) and GACs (the high-capacity sorbents) >95% of 6PPDQ aqueous mass was removed from the system, resulting in less than 5% of initial aqueous concentration. However, with the small batch reactors (50 mL aqueous volume in a 120 mL jar) it was not possible to adjust the reactor to retain >20% initial 6PPDQ mass in the aqueous phase at equilibrium for this sorbent given the low solubility of 6PPDQ and the high sorption capacity for the high-capacity sorbents. Because aqueous phase concentrations were so low, and OECD study guidelines could not be achieved, there is more variability in calculated K_d values and kinetic parameters are potentially biased low. Large capacity systems would be required to evaluate such effects for slightly soluble analytes like 6PPDQ.

Batch reactors using 5-day sorption tests to determine partition coefficients (K_d) were run first, these preliminary studies yielded systems variability and unacceptable losses of 6PPDQ within the experimental systems. As experimental procedures were optimized based upon QA/QC results and redesign, significantly higher 6PPDQ recoveries were evident for later time series sorption studies as compared to the initial 5-day sorption tests. However, when the lower concentration spike (1900 ng) studies were run to minimize solubility and mass transfer effects, the recoveries for all sorbents and controls were consistently lower, likely due to fixed capacities within the system for sorptive removal.

Like the controls and sand system, most other sorbents demonstrated system recoveries in the 60-75% range, although the natural soil, bark mulch and wood chips sometimes exhibited recoveries in the 80-94% range. Notably, the lowest overall system recoveries (0.01-24%) were observed for GAC and biochar due to low measured aqueous concentrations and low recoverable mass via solvent extractions. This outcome is highly consistent with the common outcomes using these sorbents for treatment of organic pollutants, where the high surface area and reactive surface sites result in effective and irreversible sorption of organic contaminants despite extraction with strong organic solvents.

Partition Coefficients. For any specific compound, the solid-aqueous partition coefficient (K_d) reflects the ratio of the concentration sorbed to the solid to the concentration of the aqueous phase when the system is at equilibrium (**Equation 2**; United States Environmental Protection Agency, 1999). K_d is commonly used to describe the extent a given contaminant is sorbed to solids, which is correlated to its potential for treatment by sequestration processes. K_d can be used to help predict fate and transport in environmental models as well as estimate the treatment efficacy of various sorbents for contaminant removal. Here, K_d was estimated using the batch laboratory method. It is rapid and amenable to efficiently testing multiple sorbents; given the recent discovery of 6PPDQ and the lack of information about its physio-chemical parameters batch testing is useful and reasonable at this point to estimate relative ranges of sorption possible under controlled conditions. On the other hand, the batch laboratory method has some significant uncertainties,

including: 1) the batch method is not able to fully reproduce environmental conditions more typical of continuous flow systems, which may overestimate K_d values relative to natural systems; and 2) K_d values are frequently used under the assumption that adsorption and desorption reactions are reversible. Most experimental observations show hysteresis, with much slower or different desorption characteristics, which is contrary to this assumption. Thus, the calculated K_d values from batch reactors may overestimate contaminant remobilization (United States Environmental Protection Agency, 1999). To address the first uncertainty, our results will be interpreted conservatively, assuming the K_d values determined from batch studies may overestimate environmentally relevant sorption and 6PPDQ may be more mobile in the environment. To address the second uncertainty, we investigated the desorption of sorbed mass after sorption equilibrium to assess potential contaminant remobilization from solids as opposed to assuming that adsorption and desorption reactions are reversible.

As a study that generated a significant amount of data on a wide range of sorbents at two different laboratory locations, we first assessed data quality across trials, varied sorbents, and conditions. Study data was consistent across work location, material type, and trial number. While we report data collected under standardized conditions whenever possible, often, data from slightly different conditions (i.e. different 6PPDQ spike between Conditions 1 and 2) yielded results within experimental standard deviations. Further, for repeat measurements of sorbent types (e.g. compost, zeolite, etc.) we see similar K_d values even from materials acquired from a different manufacturer (e.g. see **Figure 3, Table 10**). These outcomes indicate that sorbent type, rather than other factors, was the biggest contributor to quantitative sorption outcomes.

All batch reactors were run in triplicate and standard deviations were calculated for K_d values. Some materials had very little variation between triplicates while others had larger variations evident. Factors that influenced observed variation were: 1) procedures to remove the aqueous phase; 2) uniformity of tested sorbents that were not very consistent in size or shape; and 3) aqueous concentration at equilibrium. First, the batch method required removal of the aqueous phase in a way that was consistent between samples. Some of the sorbents were smaller in diameter than others, making aqueous phase separation from sorbents more difficult (e.g. biochar sized to 30-50 mesh). Second, sorbents that were variable in composition were more difficult to create small, representative, and consistent samples to test. For example, 100 mg representative samples of wood chips were difficult to achieve because many individual woodchips were >100 mg. Additionally, bioretention soil mixes contained slightly different compost to sand ratios depending on the sample collection. More uniform sorbents like sand, sieved natural soil, and sized perlite were easier to create representative samples from and thus resulted in closer standard deviations between triplicate batches.

Multiple conditions were used for the batch reactor tests because of the low aqueous solubility of 6PPDQ and the wide range of sorbents that had vastly different sorption capacities. The low aqueous solubility, coupled with the large variation in sorbent capacity required the use of disparate conditions. For example, our attempts to achieve OECD-recommended aqueous concentrations at equilibrium that are 20-80% of initial concentration were not achievable because of the low aqueous solubility of 6PPDQ in conjunction with the high sorption capacity of biochars

and GACs. To attain OECD guidelines, bottle sizes of many liters would have been needed for small sorbent masses, these experiments could not be practically conducted in our labs (e.g. how do you shake >10L bottles?). Highly carbonaceous materials with high sorption capacities (biochar and GAC) usually adsorbed 6PPDQ to below method detection limits, so high-capacity conditions were developed around a smaller initial sorbent mass with all other conditions the same (Condition 4). Alternative conditions (Conditions 5-7) with higher spiked mass or larger buffer volumes did not significantly increase the equilibrium aqueous concentration and made the results less comparable to low-capacity sorbent conditions. Therefore, Condition 4 was considered most appropriate for this study. The equilibrium aqueous concentrations in biochar or GAC systems were \sim 2-3% of the initial sorbate concentration after optimization.

Estimated solid-aqueous partition (distribution) coefficient (K_d) values are reported in **Table 10** and presented in **Figure 3** for high capacity and low-capacity sorbents. The high-capacity conditions likely underestimate the partition coefficient (K_d) due to the inability of the solvent extraction to recover 6PPDQ mass from the high-capacity sorbents. As mentioned before, it appears that much of the sorbed mass is irreversible for the high-capacity sorbents tested. Due to the high affinity 6PPDQ sorption that the tested biochars and GACs exhibited, OECD 106 protocol requires use of a solid extraction to find the K_d values along. However, solid phase extractions resulted in low recoveries for high-capacity sorbents, resulting in underestimated K_d values. Therefore, the full capacities for these sorbents were not fully explored by this study.



Figure 3. Estimated solid-water partitioning coefficient K_d for (a) low-capacity sorbents run under condition 1, and (b) high-capacity sorbents run under condition 4. K_d values are reported as an average of the triplicate data and associated standard deviations are shown as error bars.

No-sorbent control reactors were run in triplicate and silica sand sorbents were run as an additional control to define baseline partition coefficient (K_d) values for these systems. Because no-sorbent controls and the sand systems have similar trends over time (**Figure 1** and **Figure 2**), the resulting K_d values from sand likely reflect 6PPDQ reaction or loss rather than sorption to solid media. Sand trials resulted in K_d values of 1.4 ± 0.0047 L/kg, 2.8 ± 0.80 L/kg, and 1.2 ± 0.60 L/kg for construction sand, 1.7 ± 0.29 for VIS sand, and 1.8 ± 0.42 L/kg and 3.1 ± 0.14 L/kg for Ottawa sand (clean, sized lab grade sand). The natural soil resulted in a K_d value of 1.3 ± 0.55

L/kg and 1.2 ± 0.11 L/kg. Because the range of the K_d value reported for natural soil overlaps with the reported K_d value of sands, the natural soil evaluated here likely had very little excess sorption capacity. Also, the mass recovered from natural soil (28-34%) via solvent extraction was indistinguishable to mass recovery from no sorbent controls (25-52%) and silica sand (25-62%; see **Table 8** and **Table 9**). Therefore, for this particular soil tested, little to no sorption is expected. As discussed earlier, the time series concentration losses for 6PPDQ in the natural soil and artificial soils tested followed a different trend than the sand and no-sorbent controls, indicating there may be some sorption and/or interactions in the aqueous matrix that allow for 6PPDQ stabilization in the presence of natural and artificial soils. Thus, testing of other soils and soil characteristics is necessary to understand 6PPDQ interactions with soils generally.

To complement additional natural soils, artificial soils typical of engineered geomedia in treatment systems were tested. Artificial soils were created by mixing sand (for permeability and flow) with low volumes of compost (1-10% by volume) to achieve realistic organic carbon ranges realistic of engineered soils. The resulting values of the sand compost mixture as well as the parent components (sand and compost) are shown in **Figure 4** and listed in **Table 10**. Overall, the artificial soils resulted in lower measured K_d values compared to all measured sorbents including sand (S3). This would indicate that there are less net aqueous losses of 6PPDQ (which is backed up by the high measured aqueous concentrations in **Table 10**) in the system relative to the control (sand), which made up the bulk of the solution. Therefore, the presence of small amounts of compost repeatably and consistently increased 6PPDQ stability in the aqueous solution. One potential explanation for this is that colloidal interactions between dissolved organic carbon help to stabilize 6PPDQ in solution, as discussed earlier. Further investigation of colloidal effects and small particle generation or stabilization is needed. It also is possible that the composts generated dissolved organic matter that competed with 6PPDQ for system reactive sites or provided some sort of stabilization capacity for 6PPDQ in system. These effects are not currently understood.

Among the sand/compost mixtures, the K_d values increased as the mass of compost (and thereby the organic carbon content) increased. The 1% compost by volume mixture (M1) resulted in a K_d value of 0.45 ± 0.093 L/kg; the 5% compost by volume mixture (M2) resulted in a K_d value of 0.49 ± 0.1 L/kg; and the 10% compost by volume mixture (M3) resulted in a K_d value of 0.57 ± 0.05 L/kg. This would indicate that increasing amounts of compost (or organic carbon content) may have increased the sorption capacity of natural and artificial soils, although these differences would not be statistically significant. The K_d value of the bioretention mix (60/40 sand/compost mixture) (C3) was measured as 2.1 ± 0.35 L/kg, indicating that somewhere between 10% compost by volume and 40% compost by volume, sand/compost mixtures begin to have sorption effects that are greater than background losses.



Figure 4. Estimated solid-water partitioning coefficient K_d for low-capacity sorbents of varying sand/compost mixtures run under condition 9. Sorbents include: sand (S3), 99/1 sand/compost mixture (M1), 95/5 sand/compost mixture (M2), 90/10 sand/compost mixture (M3), BRM = bioretention mix (60/40 sand/compost mixture) (C3), and compost (C2). K_d values are reported as an average of the triplicate data and error bars reflect standard deviations of triplicate studies.

Composts yielded K_d values of 45 ± 29 L/kg, 23 ± 6.1 L/kg, 12 ± 1.2 L/kg, 18 ± 6.1 L/kg, and 20 ± 0.18 L/kg. High variation among compost triplicates is likely due to the breakdown of compost during sonification step of the solvent extraction and the subsequent filtration. The resulting solid-aqueous partition coefficients for compost were the largest for the carbonaceous sorbents. The bioretention mixes (compost/sand mixtures) yielded K_d values of 3.1 ± 0.066 L/kg, 4.3 ± 2.5 L/kg, and 2.1 ± 0.35 L/kg, which is in between the calculated K_d values for sand and compost and similar to expected theoretical values calculated from their components. For example, a 40% compost 60% sand mixture should yield a K_d value as follows:

$$K_d = 0.6 * 1.3 \frac{L}{kg} + 0.4 * 12 \frac{L}{kg} = 5.58 \frac{L}{kg}$$

Bark mulch yielded K_d values of 12 ± 2.1 L/kg and 6.8 ± 1.0 L/kg. Wood chips yielded K_d values of 6.7 ± 2.9 L/kg and 4.6 ± 1.9 L/kg. The values for the organic sorbents (compost, bioretention mixes, bark mulch, wood chips) indicate that they are more effective sorbents for 6PPDQ relative to perlite and zeolite (inorganic materials). These K_d values of the organic sorbents demonstrate higher capacities for sorption for high organic content, high organic carbon material types that are expected to be very amenable to hydrophobic partitioning for compounds like 6PPDQ.

Inorganic materials like perlite and zeolite, resulted in low measured K_d values. For low-capacity conditions (Condition 1) zeolite had K_d values of 1.5 ± 6.2 L/kg, 1.6 ± 0.25 L/kg, and 0.75 ± 8.4 L/kg. For low-capacity condition (Condition 1) perlite had K_d values of 0.54 ± 9.5 L/kg, 0.57 ± 0.24 L/kg, and 1.4 ± 0.47 L/kg.

Finally, the high-capacity sorbents had very high sorption capacities 100 ± 41 (softwood biochar), 82 ± 48 L/kg (GAC: Filtrasorb 300), and 51 ± 19 L/kg (GAC: Filtrasorb 400), respectively. However, a coconut derived biochar resulted in low Kd values of 3.0 ± 2.0 L/kg even though the aqueous concentration indicated >90% removal. These values are estimates because the final aqueous concentration at equilibrium fell outside the range recommended by the OECD 106 protocol due to high affinity for the sorbate and low aqueous solubility of the sorbate. Further, the solid extraction masses were low and variable across these studies, resulting in high standard deviation and potential low bias to K_d values. However, these estimates (and observed removal from aqueous systems) are well aligned with other literature values showing high sorption capacity for biochar and GAC for similar trace organic constituents. We would expect high performance of 6PPDQ removal by softwood biochar and GAC, however, the removal mechanisms for these sorbents are notably unselective and may result in less sorption under environmentally relevant conditions where competition for sorption sites with other organic contaminants is expected.

Table 10. Summary of solid-liquid partitioning coefficient (Kd) data from 5-day sorption trials. Table includes sorbent media, sorbent type, solid to solution ratio, experimental condition, Kd value, standard deviation, and percent recovery.

Sorbent	Sorbent Type	#	Soil:Soln Ratio [w:w]	Experimental Conditions	Kd [L/kg]	Standard Deviation [L/kg]	Recovery [%]
Construction Stand (Cedar Grove)	Sand	S3	1:500	Condition 1	1.4	0.047	44
Construction Stand (Cedar Grove)	Sand	S3	1:500	Condition 1	2.8	0.80	66
Construction Stand (Cedar Grove)	Sand	S3	1:500	Condition 9	1.2	0.60	37
VIS Sand (Cedar Grove)	Sand	S4	1:500	Condition 1	1.7	0.29	54
Ottawa Sand	Sand (Control)	S5	1:500	Condition 1	1.8	0.42	55
Ottawa Sand	Sand (Control)	S5	1:500	Condition 1	3.1	0.14	71
Organic Compost (Dirt Exchange)	Compost	A1	1:500	Condition 1	18	6.1	66
Filtrasorb 300	GAC	A5	1:2500	Condition 4	82	48*	21
Dark Bark Mulch (Dirt Exchange)	Bark mulch	A6	1:500	Condition 2	12	2.1	69
Fine Orange Bark (Dirt Exchange)	Bark mulch	A7	1:500	Condition 2	6.8	1.0	68
Flitrasorb 400	GAC	A8	1:2500	Condition 4	51	19	24
MCG Biochar (30-50 mesh)	Biochar	A10	1:2500	Condition 4	100	41	8.4
Coconut Biochar	Biochar	A12	1:2500	Condition 4	3.0	2.0	1.6
Compost (Pacific Topsoil)	Compost	B2	1:500	Condition 1	12	1.2	70

					r	r	r
Medium Compost (Cedar Grove)	Compost	C2	1:500	Condition 1	45	29	85
Medium Compost (Cedar Grove)	Compost	C2	1:500	Condition 9	23	6.1	67
60/40 mix (Cedar Grove)	Bioretention Mix	C3	1:500	Condition 1	3.1	0.066	60
60/40 mix (Cedar Grove)	Bioretention Mix	C3	1:500	Condition 1	3.3	1.2	70
60/40 mix (Cedar Grove)	Bioretention Mix	C3	1:500	Condition 9	2.1	0.35	47
VIS Blend (Cedar Grove)	Bioretention Mix	C4	1:500	Condition 1	4.3	2.5	57
VIS Blend (Cedar Grove)	Bioretention Mix	C4	1:500	Condition 1	1.5	0.61	62
Landscape Mulch (Cedar Grove)	Compost/Mulch	C6	1:500	Condition 1	20	0.81	65
Arborist Chips (Cedar Grove)	Wood chips	C7	1:500	Condition 1	6.7	2.9	70
Arborist Chips (Cedar Grove)	Wood chips	C7	1:500	Condition 1	4.6	1.9	80
Perlite, Fine Horticultural (Supreme Perlite)	Perlite	D1	1:500	Condition 1	0.57	0.24	47
Perlite, Medium Horticulture (Supreme Perlite)	Perlite	D2	1:500	Condition 1	0.54	9.5*	41
Perlite, Medium Horticulture (Supreme Perlite)	Perlite	D2	1:500	Condition 1	1.4	0.47	61
Perlite, Fine Horticultural (Supreme Perlite)	Perlite	D1	1:2500	Condition 4	4.4	0.23	43
Perlite, Medium Horticulture (Supreme Perlite)	Perlite	D2	1:2500	Condition 4	3.8	0.15	40
Zeolite 14 x 40 (IdaOre)	Zeolite	E2	1:500	Condition 1	1.5	6.2*	39
Zeolite 14 x 40 (IdaOre)	Zeolite	E2	1:500	Condition 1	1.6	0.25	54

Zeolite 14 x 40 (BRZ)	Zeolite	E3	1:500	Condition 1	0.75	8.4	39
Zeolite 14 x 40 (IdaOre)	Zeolite	E2	1:2500	Condition 4	4.0	0.56	38
Zeolite 14 x 40 (BRZ)	Zeolite	E3	1:2500	Condition 4	3.8	0.56	44
Artificial Soil	Sand/Compost Mix	M1	1:500	Condition 9	0.45	0.093	36
Artificial Soil	Sand/Compost Mix	M2	1:500	Condition 9	0.49	0.10	38
Artificial Soil	Sand/Compost Mix	M3	1:500	Condition 9	0.57	0.050	35
Prairie Soil	Natural Soil	N1	1:500	Condition 1	1.3	0.55	40
Prairie Soil	Natural Soil	N1	1:500	Condition 1	1.2	0.11	52

*Additional 5-day sorption tests were run to replicate results, reduce standard deviation between triplicates, and reduce 6PPDQ concentration in method blanks after trouble shooting study designs and procedures.

Sorption Kinetics. Understanding partitioning kinetics helps to better understand the timescales needed for 6PPDQ mass transfer in environmental and treatment systems. To evaluate kinetics, studies were run over 5-day periods with 6PPDQ aqueous phase sampling throughout. Kinetic models were fit to the experimental data to determine which model best represented the sorption behavior of 6PPDQ, including pseudo-first order, pseudo-second order, and intraparticle diffusion models (Björklund et al. 2016, Fu et al., 2016). Figures 5-11 show the outcomes of these sorption models, with all kinetic models for all data presented in Figures S1-S21. Kinetic samples also were run in triplicate; generally speaking, the observed variation in standard deviations seemed to be specific to sorbent type. Samples with more uniform materials (those with mesh sizes and fines removed) had less variation in triplicate measurements (e.g. biochar). Samples such as bioretention media and wood chips, with greater material variation (e.g. size, shape, composition) generally had higher standard deviations. Throughout the sorbent selection process, care was taken to create representative samples, but the small-scale studies using 10-100 mg of sample made representative samples difficult. Larger systems that include larger masses of heterogeneous materials and much more liquid volume would help to mitigate these effects. Similar to batch studies described above, high-capacity and low-capacity conditions were essential to collect data on a low-solubility sorbate over a wide range of varied sorbents.

The first order linear fit is shown only for a representative set of materials because too many materials were evaluated to fit on the same graph and data was consistent across material types (Figure 4). The fit to the pseudo-first order linearization was poor, with substantial data bias, non-linear trends, and correlation coefficients of 0.64 - 0.98. Pseudo-first order fits are found in the appendix Figures S1-S21 for all materials tested. Similar poor outcomes also were observed when the intraparticle diffusion model was fit to the data (e.g. representative sorbents in Figure 6). Like the pseudo-first order linearization, the data points were biased and not randomly distributed with correlation coefficients of 0.57-0.95. Because of their poor fits, these models were not used for subsequent quantitative analysis.



Figure 5. Pseudo-first order linearization of sorption kinetic data for 6PPDQ partitioning to seven media types, including compost (C2), GAC (A5), biochar (A10), BRM = bioretention mix (C3), wood chips = arborist chips (C7), zeolite (E2), and soil (N1).



Figure 6. Linearization of sorption kinetic data fit to the intraparticle diffusion model for 6PPDQ partitioning to seven media types including compost (C2), GAC (A5), biochar (A10), BRM = bioretention mix (C3), wood chips = arborist chips (C7), zeolite (E2), and soil (N1). (a) all seven media types including the high-capacity sorbents (biochar and GAC). (b) zoomed in version of the five low-capacity media types excluding high-capacity sorbents (biochar and GAC).

The pseudo-second order linearization for the representative set of materials yielded generally better outcomes, with correlation coefficients ranging from 0.9684 to 1 and most correlation coefficients >0.99 (**Figure 7**). Natural soil (N1) exhibited the most variability across models and poorest fit to the pseudo-second order model (correlation coefficient of 0.9684), but the pseudo-second order fit was consistently better than outcomes for both the pseudo-first order and intraparticle diffusion models (**Figure 9a and Figure S13**). Some of the difficulty fitting the natural soil (N1) sorption data could be due to data accuracy and potentially complex interactions in the experimental system, slow sorption processes, or additional pathways of 6PPDQ loss. Similar outcomes were seen for the sand-water control systems. Besides the samples with low K_d values and high aqueous equilibrium concentrations (natural soil, sand, and perlite), all other sorbents were well fit to the pseudo-second order linearization over the whole range of sorption conditions evaluated here (representative sorbents in **Figure 8, 9**).



Figure 7. Pseudo-second order linearization of sorption kinetic data for 6PPDQ partitioning to seven media types, including compost (C2), GAC (A5), biochar (A10), BRM = bioretention mix (C3), wood chips = arborist chips (C7), zeolite (E2), and soil (N1).



Figure 8. Pseudo-second order kinetics modeling for 7 representative samples, including compost (C2), GAC (A5), biochar (A10), BRM = bioretention mix (C3), wood chips/arborist chips (C7), zeolite (E2), and soil (N1).



Figure 9. Pseudo-second order kinetics modeling outcomes for five representative low-capacity sorbents (a) compost (C2), BRM = bioretention mix (C3), wood chips/arborist chips (C7), zeolite (E2), soil (N1); and two high-capacity sorbents (b) GAC (A5) and biochar (A10).

Additional time series were run after data analysis with a lower system 6PPDQ mass (Condition 9). The resulting kinetic models indicated pseudo-second kinetics were favored over pseudo-first order kinetics or intraparticle diffusion. The resulting linearization of the pseudo-second order kinetics resulted in significantly improved correlation constants and consistently better fits. Correlation coefficients for the new batch ranged from 0.9969-0.9997 (**Figure 10**). The improved kinetic fit (**Figure 11**) based on the decreased spiked mass, indicated that likely the sorbents with low K_d values were undergoing complex interactions and potential losses

within the system for 6PPDQ. Decreasing the spiked mass consistently improved the kinetic models for all sorbents, including sand.



Figure 10. Pseudo-second order linearization of sorption kinetic data for 6PPDQ partitioning to sand/compost mixtures, including sand (S3), 99/1 sand/compost mixture (M1), 95/5 sand/compost mixture (M2), 90/10 sand/compost mixture (M3), BRM = bioretention mix (C3), and compost (C2). The time series was run under Condition 9.



Figure 11. Pseudo-second order kinetics modeling for sand/compost mixtures, including sand (S3), 99/1 sand/compost mixture (M1), 95/5 sand/compost mixture (M2), 90/10 sand/compost mixture (M3), BRM = bioretention mix (C3), and compost (C2). The time series was run under Condition 9. Error bars reflect standard deviation of triplicate measurements.

The pseudo-second-order kinetic model assumes that changes to the initial bulk concentration during the experiment are small enough that they do not affect the kinetic relationship and that the rate limiting step to the solid-water partitioning process is chemical sorption (chemisorption). Chemisorption includes hydrophobic interactions, hydrogen bonding, ionic bonding, and covalent bonding. Chemisorption is generally stronger than physical adsorption, which relies on weaker Van der Waals forces. In chemisorption, the adsorbate typically needs to contact the adsorbent surface for sorption interactions to occur. After modification of conditions, all sorbents seem to fit the pseudo-second order model well. The kinetic data also indicates that sorption is initially rapid and reached an equilibrium sorption capacity, indicating that surface sites were present and can be filled, which is consistent with a single-layer adsorption process. Additionally, the unrecoverable 6PPDQ mass under strong solvent extraction conditions indicates that stronger, irreversible interactions associated with chemical sorption have likely occurred.

Substantial differences in estimated equilibrium sorption capacities (q_e) for the different sorbents were evident in the kinetic data (e.g. see relative data plateaus in **Figures 8**, **9**, **11**). Because the pseudo-second-order kinetic model predicted the behavior well over the whole range of sorption, this model was used to calculate the equilibrium adsorption capacity (q_e) and related parameters (**Figure 12**, **Table 11**) and the pseudo-second order rate constant (k₂; see **Figure 13** and **Table 11**). The control data indicated that in these systems, other losses had occurred beyond sorption to the sorbent. To evaluate such systemic bias effects, these studies used the silica sandwater systems as a control because sand batch reactors had nearly identical mass losses and dynamics as the no-sorbent control systems (see earlier discussions and **Figure 1** and **Figure 2**). Silica sand had estimated equilibrium sorption capacities of 14.5, 15.9, and 16.8 ug of 6PPDQ per gram sorbent that likely reflect systemic losses to glassware or other competing mechanisms such as reactions. These values should likely be considered the reference point, reflecting systemic losses in kinetic studies.

Estimated parameters also were dependent on the concentration of solids in the aqueous solution C_s (g/L). Lower masses of the high-capacity sorbents were added to batch reactors resulting in lower C_s values of 0.1 g/L and higher masses of the low-capacity sorbents were added to batch reactors, resulting in higher C_s values of 2 g/L. These two conditions are not directly comparable but can help to estimate relative kinetic parameters and visualize sorption differences.

Table 11. Calculated second order rate constants (k_2) for 6PPDQ sorption to treatment media and engineered soil. Calculated sorption equilibrium capacity (q_e) (ug 6PPDQ / g of solid). The concentration of solids in the aqueous batch reactors are denoted as C_s (g/L). A C_s of 0.1 g/L was used for high-capacity sorbents and a C_s of 2 g/L was used for low-capacity sorbents.

Media Type	#	k2 [g/ug*min]	qe [ug/g]	Cs [g/L]
GAC (Filtrasorb 300)	A5	0.0334*	469	0.1
MCG Biochar (30-50 mesh)	A10	0.116*	994	0.1
MCG Biochar (20-30 mesh)	A10P	0.0977*	488	0.1
Compost (A1)	A1	1.54	46.0	2

Bark Mulch (A7)	A7	4.93	20.8	2
Compost (C2)	C2	3.86	17.8	2
Bioretention Soil Mix (C3)	C3	2.42	13.7	2
Bioretention Soil Mix (C3)	C3	1.74	13.9	2
Arbor Chips (C7)	C7	1.17	18.7	2
Artificial Soil (M1)	M1	2.83	11.3	2
Artificial Soil (M2)	M2	5.62	10.8	2
Artificial Soil (M3)	M3	5.34	10.4	2
Soil (N1)	N1	1.12	11.9	2
Sand (S3)	S3	0.506	15.9	2
Sand (S3)	S3	2.88	14.5	2
Sand (S5)	S5	0.526	16.8	2

^{*}The second order rate constant (k_2) for these sorbents is likely biased low. The mass of 6PPDQ in the system was not high enough to have sufficient aqueous concentration of 6PPDQ in the system. A consistent mass of sorbate is necessary for the most precise pseudo-second order calculations. Due to the high-capacity sorption the concentration of 6PPDQ in water quickly dwindled to less than 5% of the starting mass, and resulted in diffusion limited kinetics, slowing the net reaction rate. Experimental parameters used here were limited by 6PPDQ mass solubility and experimental reactor size, as well as minimum amount of measurable sorbent mass.



Figure 12. (a) Estimated equilibrium sorption coefficient, q_{e_1} (ug/g) for low-capacity sorbents derived from the pseudo second order model. Low-capacity sorbents were run under Condition 1 except sorbents noted with an * were run under Condition 9. (b) Estimated equilibrium sorption coefficient, q_{e_1} (ug/g) for high-capacity sorbents.

Overall, trends in equilibrium sorption capacity (q_e) followed trends noted for K_d values although these results were derived from different experimental data. This outcome indicated consistency across trials of the time series kinetic studies and the 5-day sorption studies. With respect to the data, the natural soil (N1) had a lower equilibrium sorption capacity than the silica sand control but was indistinguishable from controls values and indicated little evidence of excess 6PPDQ sorption. This data indicated that this particular natural soil would provide little to no expected sorption or treatment capacity for 6PPDQ or that other mechanisms may be at play that make it difficult to distinguish sorption effects. Further studies need to be completed with other representative soil samples in Washington that would help to better understand if this trend is seen in samples from multiple locations or how different soils vary with respect to their treatment potentials. Given their widespread role in incidental treatment, additional assessment of the treatment capacity of natural soils is merited, as we would expect at least some treatment capacity for 6PPDQ in many natural systems.

Artificial soils (M1, M2, M3) were tested to help elucidate findings for the natural soil (N1). The artificial soils had somewhat unexpected results for us, while noting that replicates and outcomes were consistent. Equilibrium sorption capacities for the 1% compost mixture (M1) was 11.3 ug 6PPDQ/g sorbent, for the 5% compost mixture (M2) was 10.8 ug 6PPDQ/g sorbent, and for the 10% compost mixture was 10.4 ug 6PPDQ/g sorbent. This consistent outcome across an order of magnitude variation in organic content may indicate that other mechanisms dominated the batch system and resulted in more 6PPDQ stability in aqueous solution, As explained earlier, this effect is potentially due to colloidal interactions or other competition from dissolved organic matter for sorption or reaction sites. This observation may also account for the lower than expected equilibrium sorption capacity observed for natural soil compared to sand, system interactions seemed to stabilize 6PPDQ and maintain an aqueous concentration. Additional studies that investigate the effect of dissolved organic carbon and colloids on 6PPDQ stability in aqueous solutions may be needed to more fully understand these outcomes.

The most effective sorbent tested under time series was the MCG biochar (30-50 mesh) which absorbed 990 ug 6PPDQ/g of biochar. Of the materials tested under low-capacity conditions, compost performed the best with an equilibrium capacity of 46 ug 6PPDQ/g of compost. Other notable potential treatment methods were bark mulch, and wood chips with equilibrium absorption capacities of 21 and 19 ug 6PPDQ/g of sorbent, respectively.



Figure 13. Bar plots with the pseudo second order rate constants k_2 (g*ug⁻¹*min⁻¹) for: (a) the low-capacity sorbent experiments and (b) the high-capacity sorbents. Low-capacity sorbents were run under Condition 1 except sorbents noted with an * were run under Condition 9.

The pseudo-second order model also allowed us to estimate pseudo-second order rate constants (k_2). Artificial soils, compost, and bark mulch had the highest rate constants. Artificial soils had rate constants of 5.62, 5.34, and 2.83 g/ug*min. Bark mulch had a rate constant of 4.93 g/ug*min. Compost (C2) had a rate constant of 3.86 g/ug*min. These calculated rate constants indicated rapid uptake and equilibrium for these systems. However, the slow sorption observed for

the sand controls (0.506 - 0.526 g/ug*min), indicated slow loss mechanisms (e.g. transformation) or slow sorption to the glassware. Natural soil (N1) had a higher rate constant (1.12 g/ug*min), which indicated that there may be a limited amount of sorption that proceeds moderately before the plateau at the equilibrium sorption capacity. The high pseudo-second order rate constants for the artificial soils (M1, M2, M3) may indicate a similar phenomenon of moderate to high speed sorption of limited capacity to these media. For the high-capacity sorbents, GAC and biochar, results yielded very small pseudo-second-order rate constants. These results are probable underestimates because the aqueous 6PPDQ concentration became too low to effectively evaluate kinetically driven sorption outcomes, where mass limitations dominated kinetic rate limitations.

Desorption. Due to time constraints, one limited series of desorption experiments were conducted over 5-7 days for compost and natural soil sorbents (**Figure 14a**). For both sorbents, there was high standard deviation and high variation among sampling points that made it difficult to determine equilibrium values from this data, but there was some evidence of desorbed mass over these time scales. In the natural soil, aqueous concentrations of desorbed 6PPDQ stabilized at 24-48 hours and indicated that a 5-day period would be sufficient for desorption trials. The data from compost system was more complex and complicated by high standard deviation in the 4-hour and 6-hour triplicates, with initial rapid desorption over the first 6 hours and then declining concentrations over later periods. We would like to repeat these studies in the future.

The natural soil desorption tests consistently resulted in higher 6PPDQ mass recovery relative to the compost (**Table 12, Figure 14b**). To calculate aqueous concentrations from the desorption trials the aqueous concentrations from 24 to 120 hours were averaged to represent an equilibrium concentration. The total mass desorbed (ng) was then calculated from this concentration and compared to the total mass (ng) that was solvent extracted (with methanol) in the corresponding 5-day adsorption study. The values of C/C_0 were very low because the low overall 6PPDQ concentration that desorbed was compared to the high initial starting concentration (50 ug/L). Despite this distinction, some 6PPDQ mass was re-entering the dissolved phase over time. Some of the desorbed mass likely arose from interactions with the glass reactors or bottle caps (noting ~50% decrease in no sorbent controls). This experimental design did not move sorbents to new, clean glassware, so the "desorbed" 6PPDQ mass represented here does include mass from other sources including residual aqueous phase left in the jar or 6PPDQ mass sorbed to the glassware. Given the possible reversible interactions of 6PPDQ with glassware, further desorption trials should include studies where sorbent is dried and removed from the jars and added to a clean jar. After sorbent removal, the original glassware can act as a control.

Material	Mass of Solid Extract [ng]	Equilibrium Desorption [ng]	Standard Deviation of Desorption [ng]	Percent Desorption [%]	Standard Deviation [%]
Compost (C2)	1940	196	24.5	10.1	1.3
Natural Soil (N1)	843	475	59.8	56.3	7.1

Table 12. Mass balance and observed desorption outcomes for compost (C2) and natural soil (N1) from initial desorption trials.



Figure 14. (a) Desorption of 6PPDQ from compost (C2) and natural soil (N1) over seven days. **(b)** Observed desorption outcomes for compost (C2) and natural soil (N1).

Implications for 6PPDQ Treatment

These studies assessed the solid-water partitioning and kinetics of sorption of the toxic tirederived pollutant 6PPDQ to various potential treatment media, a natural soil, and artificial soils. Scientific and observational data indicates the clear need for mitigation and treatment strategies for 6PPDQ and roadway runoff more generally, largely driven by the fact that maximum 6PPDQ concentrations in roadway runoff greatly exceed published toxicological thresholds. It is likely that protective thresholds for biological organisms will require removal of 6PPDQ down to nodetect levels. To address these needs, the main goals of this study were to: 1) understand how 6PPDQ may interact with unamended soils in the environment, and 2) identify treatment media that are effective at sequestering or removing 6PPDQ for further investigation or potentially for short-term treatment. The initial method development and optimization processes consistently demonstrated slow and mass limited partitioning processes for 6PPDQ, even to "more favorable" solvents or surfaces. As experimental procedures were validated and improved, steps such as additional cleaning procedures and longer contact/equilibrium times were needed to ensure reproducible outcomes and quantitative mass transfer of 6PPDQ in these types of experimental systems. Most effective were the biochars and GACs. One of the biochars, derived from softwoods, was found to be an effective engineered sorbent for treatment, with similar performance to the more expensive and engineered GAC media. This biochar (A10) had a K_d value of 100 L/kg and an equilibrium sorption capacity of 994 ug/g for 6PPDQ. As common for GAC and biochar studies, the uptake to 6PPDQ to this biochar was so effective that the concentration remaining in solution was too low for confident kinetic studies without further experimental optimization. Of the other organic sorbent materials, bark mulch performed best with a higher uptake rate than the other sorbents. Bark mulch (A7) had a partition coefficient of 6.8 L/kg and an equilibrium sorption capacity paired with the high rate of uptake would indicate bark mulch may be an effective sorbent for treatment. Other bark mulch tested had comparable K_d values (see **Table** 7). Additionally, bark mulch has a high capacity for infiltration, which could help facilitate high surface area contact of stormwater runoff.

Other notable sorbents with treatment capacity included wood chips, bioretention mixes, and compost, although their partitioning values and constants tended to be lower than those reported for the biochar and bark mulch. Limited or no sorption of 6PPDQ was observed for silica sand, perlite, or zeolite. The natural soil sample and the engineered soil samples evaluated here indicated complex, and somewhat surprising, interactions that require additional testing to understand. Contrary to expectations, the presence of compost in the sand/compost mixture lowered the K_d values and equilibrium sorption capacity compared to sand, and actually resulted in a faster equilibrium. These results indicate that the natural soil and artificial soils may have trace elements or colloidal interactions that are allowing for 6PPDQ stability, or reducing other system interactions, in these systems.

Generally, 6PPDQ sorbs to materials due to specific interactions with surface sites or hydrophobic partitioning to organic matter phases. Like other organic contaminants, 6PPDQ tended to prefer sorption to organic carbonaceous materials (e.g. compost, bark mulch) with complex organic compositions and characteristics over inorganic materials relying upon interactions with specific and homogeneous surface sites (e.g. perlite and zeolite). Additionally, the batch reactor sorption studies indicated relatively high fractions of unrecoverable 6PPDQ mass from these systems at the end of 5 days, indicating the probable irreversible binding or transformation of 6PPDQ to or within these sorbent materials. Despite this promising data, these data did indicate systematic losses of 6PPDQ mass through the sorption trials that were not fully explained by the collected control data. Further detailed investigation of these systems, including strong extractions and analysis of 6PPDQ transformation products is needed to help close the mass balance for more confident data interpretation.

The one representative natural soil tested demonstrated little excess sorption capacity compared to other materials tested. Likewise, the artificial soils tested indicated little sorption capacity, but sorption capacity may be difficult to fully understand given that the experimental matrix for soil, water, 6PPDQ systems are more complex than controls. While additional natural soils need to be evaluated to fully define their treatment potential, it is far more likely that many

natural soils may sometimes offer limited treatment for 6PPDQ. Any potential treatment capacity of natural soil would be further reduced if the soil is tightly packed and allows for little infiltration.

Based on these initial findings, the use of bioretention mixes (sand/compost mixtures) in roadside bioretention systems as advised by the Puget Sound Action Team, Washington State Department of Ecology, and Washington State University Pierce County Extension Program (2006) would likely help to sequester 6PPDQ during treatment. The use of some types of biochar and GAC type media to enhance 6PPDQ removal from stormwater is clearly merited by this data, the softwood biochar tested in this study was one of the most effective sorbents and seemed coeffective to the "gold standard" GAC sorbent material. Other biochars known to effectively sorb organic contaminants of a similar size may also be good treatment media, but additional testing is required to understand effectiveness of other types of biochar. Where 6PPDO is of particular concern in runoff, media such as GAC, biochar, or bark mulch would be great treatment amendments. Bioretention soil mix (60/40 sand/compost) may also offer additional treatment. Treatment practices also include a discussion of filters implemented for specific contaminant removal. Use of biochar or GAC filters indicates potential for high removal efficiency, but use of materials like zeolite or perlite may be unlikely to result in substantial 6PPDQ treatment without further development of multi-barrier processes better suited for control of trace organic pollutants. Furthermore, sand filters that are used for other purposes are unlikely to have any significant treatment efficacy of 6PPDQ beyond physical removal of 6PPDQ-bearing rubber microplastics.

Conclusions

6PPDQ is a highly toxic and recently reported environmental pollutant whose management will require basic data collection, including its stability, reactivity, environmental transport, and leaching capacity, etc. before treatment and other management methods are fully understood. The adsorption coefficients and the sorption capacities derived from these benchtop studies indicate that many of the common organic sorbents (compost, bioretention mixes, bark mulch, etc.) would be effective initial treatments in bioretention systems and other roadside amendments. The addition of more bioretention systems or addition of mulch as amendments to existing systems would be advised in the short term until 6PPDQ is phased out of tires or more selective adsorbents specific to the structural characteristics of 6PPDQ are developed. The use of filter systems with softwood biochar (A10) or GAC (or even the incorporation of softwood biochar (A10) into bioretention systems) would likely reduce the concentrations of 6PPDQ (as well as other vehicle- and tirederived organic contaminants) in stormwater runoff, especially relative to the performance expected for zeolite or perlite materials. Further studies are required to determine if 6PPDQ can be reduced to sub-lethal levels via organic material additions to bioretention systems due to the extremely low LC₅₀ (40-95 ng/L) values of 6PPDQ to coho salmon or whether the systems will need engineered high surface area/high-capacity sorbents like biochar and GAC to ensure full performance over the long term. Longer term studies, including both column studies and pilot systems in the field, also are needed to better understand long term treatment system capacity and maintenance processes.

We note that the benchtop kinetic studies in this report were completed at room temperature in the warmer spring and summer months. The pseudo-second order kinetic models indicate that hydraulic resident times of 24-48 hours should be sufficient for sorption of 6PPDQ to near equilibrium sorption capacity at these temperatures. However, the conditions of interest causing the urban runoff mortality syndrome in coho salmon occurs do happen in the rainy season when average temperatures are often below the ambient temperatures these data were collected. For example, the average temperatures in Seattle in October are highs of 59 °F and lows of 50 °F and in November are highs of 51 °F and lows of 43 °F, indicating sorption may be slower and hydraulic residence times of the selected BMP may need to be somewhat lengthened (48 hours+) at lower temperatures to optimize effectiveness during key times of year that are most important to ecological water quality. Temperature effects were not specifically addressed during these studies.

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Appendix

Media tested	Method blank	No-sorbent control	Туре
A1, C2, C3, B2	N/A	N/A	5-day sorption
C4, C6, C7, S3, S4, S5	N/A	N/A	5-day sorption
N1, A12, D1, D2, E2, E3	n=3	6PPDQ = 2500 ng (n=3)	5-day sorption
A1, A2, A3, A4, A5	N/A	N/A	5-day sorption
A6, A7, A8, A9, A10	N/A	N/A	5-day sorption
A1, A2, A5	N/A	N/A	5-day sorption
D1, D2, A10P	N/A	N/A	5-day sorption
A8, A10, A10P	N/A	N/A	5-day sorption
A7, A8, A10	N/A	n=3	Time series
A1, A2, A5, A10P	N/A	6PPDQ=5000 ng (n=3)	Time series
C2, N1	n=2	6PPDQ=2500 ng (n=3)	Time series
C2, N1, S3, S5	n=3	6PPDQ=2500 ng (n=3)	Time series
C3, C7, D2, E2, N1	n=3	6PPDQ=2500 ng (n=3)	Time series
C2, C3, C6, C7, S3, S5	n=3	6PPDQ=2500 ng (n=3)	5-day sorption
N1, A12, D2, E2	n=3	6PPDQ=2500 ng (n=3)	5-day sorption
S3, S5, C2, C3, C4, C7	n=3	6PPDQ=2500 ng (n=3)	5-day sorption
A12, D2, E2, N1	n=3	6PPDQ=2500 ng (n=3)	5-day sorption
S3, M1, M2, M3, C2, C3	n=3	6PPDQ=1900 ng (n=3)	5-day sorption
S3, M1, M2, M3, C2, C3	n=3	6PPDQ=1900 ng (n=3)	Time Series

Table S1. Summary of media tested, and QA/QC results for each sample batch.



Figure S1. Sorption kinetics modeling for compost sample A1. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S2. Sorption kinetics modeling for bioretention mix sample A2. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S3. Sorption kinetics modeling for granular activated carbon (GAC) sample A5. Pseudosecond order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S4. Sorption kinetics modeling for bark mulch sample A7. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S5. Sorption kinetics modeling for granular activated carbon (GAC) sample A8. Pseudosecond order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S6. Sorption kinetics modeling for biochar sample A10. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S7. Sorption kinetics modeling for biochar sample A10P. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S8. Sorption kinetics modeling for compost sample C2. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S9. Sorption kinetics modeling for bioretention media C3. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S10. Sorption kinetics modeling for wood chips sample C7. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S11. Sorption kinetics modeling for perlite sample D2. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S12. Sorption kinetics modeling for zeolite sample E2. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S13. Sorption kinetics modeling for natural soil sample N1. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S14. Sorption kinetics modeling for sand sample S3. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S15. Sorption kinetics modeling for sand sample S5. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S16. Sorption kinetics modeling for sand sample S3 under Condition 9. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S17. Sorption kinetics modeling for artificial soil sample M1 under Condition 9. Pseudosecond order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S18. Sorption kinetics modeling for artificial soil sample M2 under Condition 9. Pseudosecond order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S19. Sorption kinetics modeling for artificial soil sample M3 under Condition 9. Pseudosecond order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S20. Sorption kinetics modeling for compost sample C2 under Condition 9. Pseudosecond order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.



Figure S21. Sorption kinetics modeling for bioretention mix sample C3 under Condition 9. Pseudo-second order, pseudo-first order, and intraparticle diffusion models were evaluated for potential fit.