

1 *Supporting Information for*

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5 **Investigation of 6PPD-quinone in rubberized asphalt concrete mixtures**

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33 *Text SI Analysis Methods*

34 *Chemical Analysis of 6PPD-quinone (6PPD-Q)*

35 High-performance liquid chromatography (HPLC) coupled with a diode-array detector (DAD) for
36 ultraviolet (UV) analysis (Agilent Technologies 1260, Folsom, CA, USA) was used for analysis of 6PPD-
37 quinone (6PPD-Q) in the sorption experiments. For the HPLC-UV analysis, a reversed-phase C18 column
38 (Agilent Eclipse plus, 5 μm , 4.6 \times 150 mm) was used; the mobile phase (1 mL/min) consisted of 0.1% formic
39 acid in DDI (35%) and methanol (65%). The calibration curve was established for 6PPD-Q in the
40 concentration range of 10–1000 $\mu\text{g/L}$ using calibration points of 10, 20, 30, 40, 50, 100, 200, 400, 600, 800,
41 and 1000 $\mu\text{g/L}$ with UV absorbance at 287 nm. (**Supporting Information (SI), Figure S6**). HPLC-UV
42 analysis was used to study the sorption of 6PPD-Q by asphalt particles and columns, and partial samples were
43 verified using HPLC coupled with time of flight mass spectrometry (HPLC-TOF-MS) analysis. HPLC-TOF-
44 MS was conducted with an instrument (G6230A, Agilent Technologies, Folsom, CA, USA): C18 column
45 (Agilent Eclipse plus, 5 μm , 4.6 \times 150 mm, Agilent Technologies, Folsom, CA, USA) was used; mobile phase
46 (1 mL/min) consisted of 0.1% formic acid in each of water (A) and acetonitrile (B) using a gradient: 15% B
47 at 0 – 1 min, 100% B at 30 min, 100% B at 30–35 min, 15% B at 35–40 min and 15% B at 40–45 min. For
48 the TOF-MS, the analytical condition was as follows: The drying gas was controlled at 5 mL/min at 325°C,
49 the nebulizer pressure was set at 20 psi, and the capillary was maintained at 3500 V. Ions were captured in
50 positive mode. The integrated peak area for the selected ion with $m/z = 299.176$ at the retention time of 22.1
51 \pm 0.03 min was used for the calibration curve (**SI, Figure S7**). An analytical calibration curve was established
52 for 6PPD-Q in the range of 10–1000 $\mu\text{g/L}$ using calibration points of 10, 25, 50, 250, 500, and 1000 $\mu\text{g/L}$.
53 (**SI, Figure S8**). The detection limit was quantified by following the U.S. Environmental Protection Agency
54 (EPA) guideline: 5 replicates of the background were analyzed. The detection limit was estimated based on
55 the average value of background and S/N of 3. Standard solutions with a spiked concentration of the estimated
56 detection limit were measured 7 times. The detection limit was calculated based on a 99% confidence level
57 using the determined standard deviation.

58

59 *SPE-HPLC-TOF-MS analysis for 6PPD-Q*

60 For solution samples in the desorption and rainfall simulation experiment, the samples were analyzed with
61 HPLC-TOF-MS upon concentration through a solid phase extraction (SPE), conducted with the equipment
62 AutoTrace 280 automated SPE (Thermo Fisher, Sunnyvale, CA). For the SPE process, the samples were
63 loaded onto the C18 SPE cartridge with a flow rate of 1 mL/min, and then the analytes were eluted out
64 using 30 mL methanol. The eluent was concentrated to 1 mL in acetonitrile and blown with N₂ gas (purity
65 of > 98.5%, Praxair, Danbury, CT, USA) to 100 μL before analysis for 6PPD-Q with HPLC-TOF-MS. DDI
66 water was run through the process to determine the process background. Thereafter, DDI water was spiked

67 with 1 µg/L 6PPD-Q and analyzed with the same procedure to determine the recovery of 6PPD-Q through
68 the analysis.

69

70 *Analysis of 6PPD-Q in solid particles*

71 To determine the content of 6PPD-Q in rubberized asphalt mixtures: crushed loose (loose particles, ~5 mm)
72 rubberized asphalt mixtures were frozen in liquid nitrogen and ground into powders (50 mesh) (**SI, Figure**
73 **S4**). The samples were extracted with 25 mL of acetonitrile for 12 hours on a horizontal shaker (100 rpm)
74 at room temperature. Extracts were purified through a silica gel column (10 g, packed in methanol). 6PPD-
75 Q was eluted with 30 mL of 2:1 hexane: dichloromethane (DCM) solvent. Before HPLC-TOF-MS analysis,
76 the purified extract was concentrated to 1 mL in acetonitrile. Solvent blanks were run through the process
77 for the background analysis. Non-rubberized asphalt mixture spiked with 6PPD-Q was analyzed with the
78 same protocol to determine the process recovery.

79

80 *Sorption Analysis*

81 Freundlich equation given below was used to fit the sorption isotherm.

$$82 \quad C_s = K_f \cdot (C_w)^n$$

83 Where:

84 C_s = amount of solute in the solid phase (µg/kg)

85 C_w = amount of solute in the aqueous phase (µg/L)

86 K_f = Freundlich constant (µg/kg)(L/µg)ⁿ

87 n = Freundlich exponent or non-linearity index, which represents the intensity of adsorption.

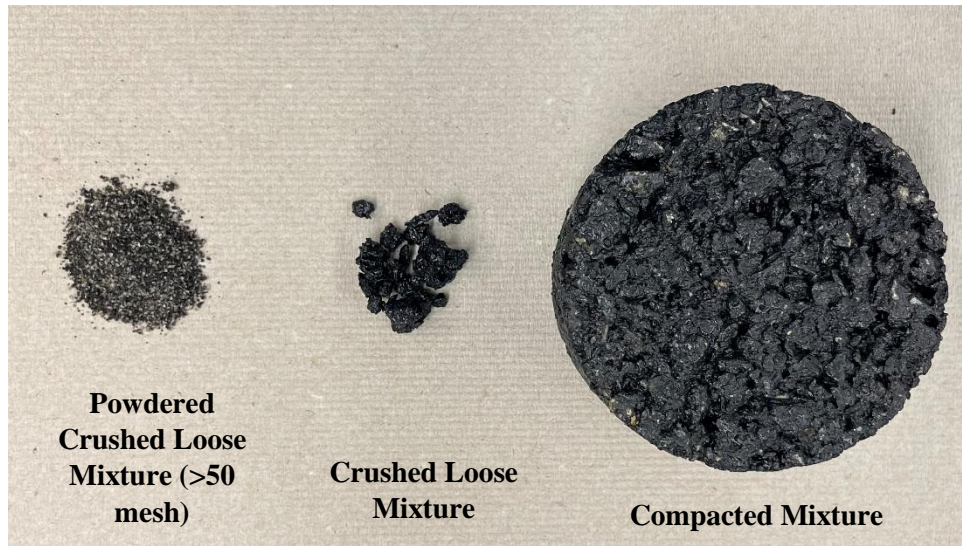
88 Sorption Coefficient = C_s/C_w

89

90 The non-linearity index (n) in the Freundlich equation characterizes the deviation from linearity in the sorption
91 process. It indicates the degree of non-ideality or heterogeneity in the system. A value of n greater than 1
92 suggests a favorable and non-linear adsorption behavior, while a value less than 1 indicates linear or less
93 favorable adsorption.

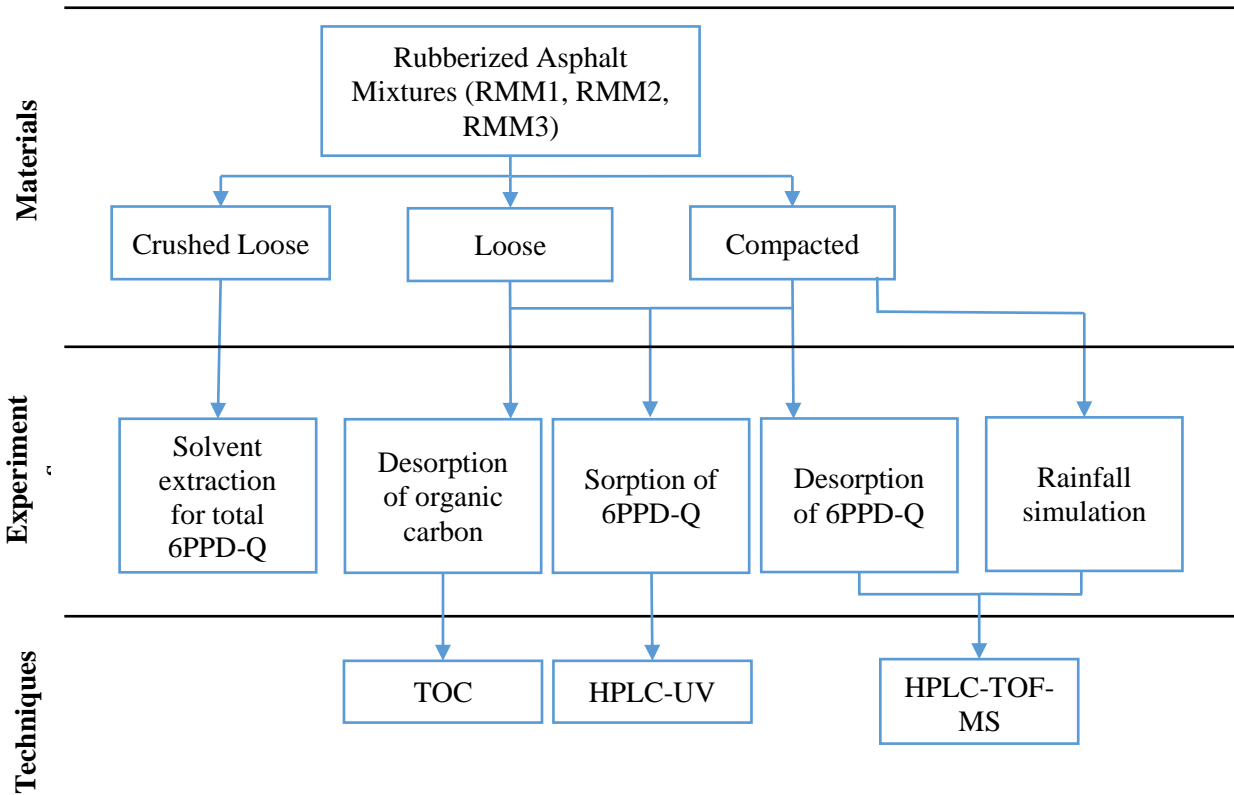
94 The sorption coefficient is the ratio of C_s/C_a . It represents the sorption capacity or ability of the sorbent to
95 adsorb solute from the solution. A higher sorption coefficient indicates a greater affinity of the sorbent for the
96 solute, implying a higher adsorption capacity.

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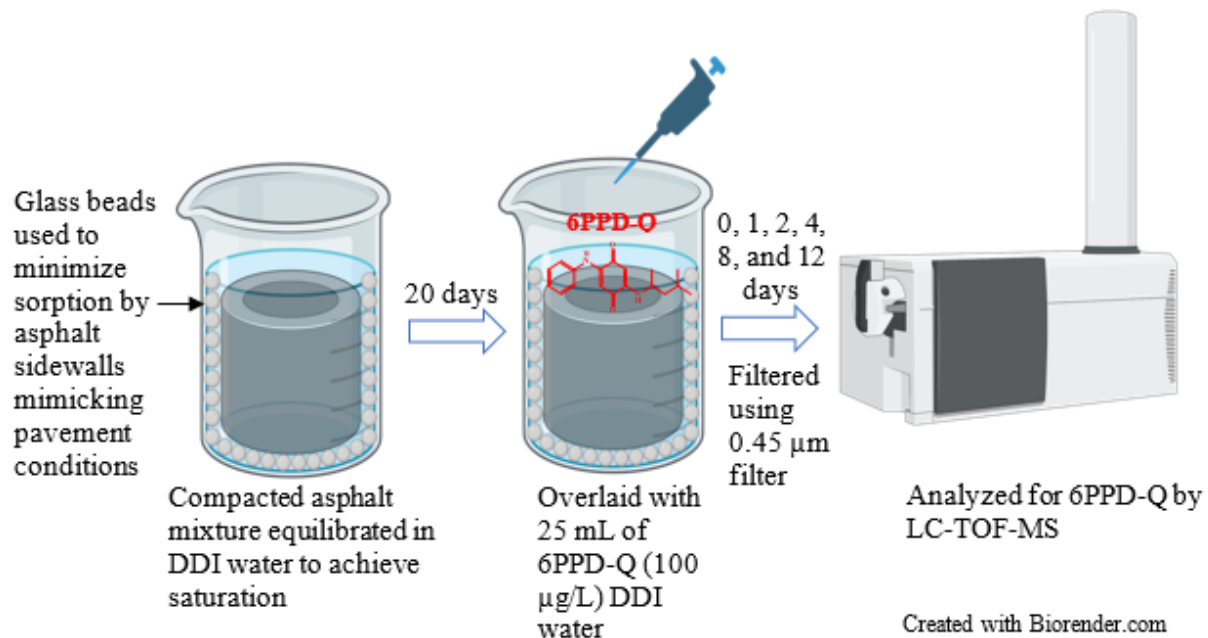
99 **Figure S1.** Types of samples used for the sorption, desorption, and rainfall simulation.



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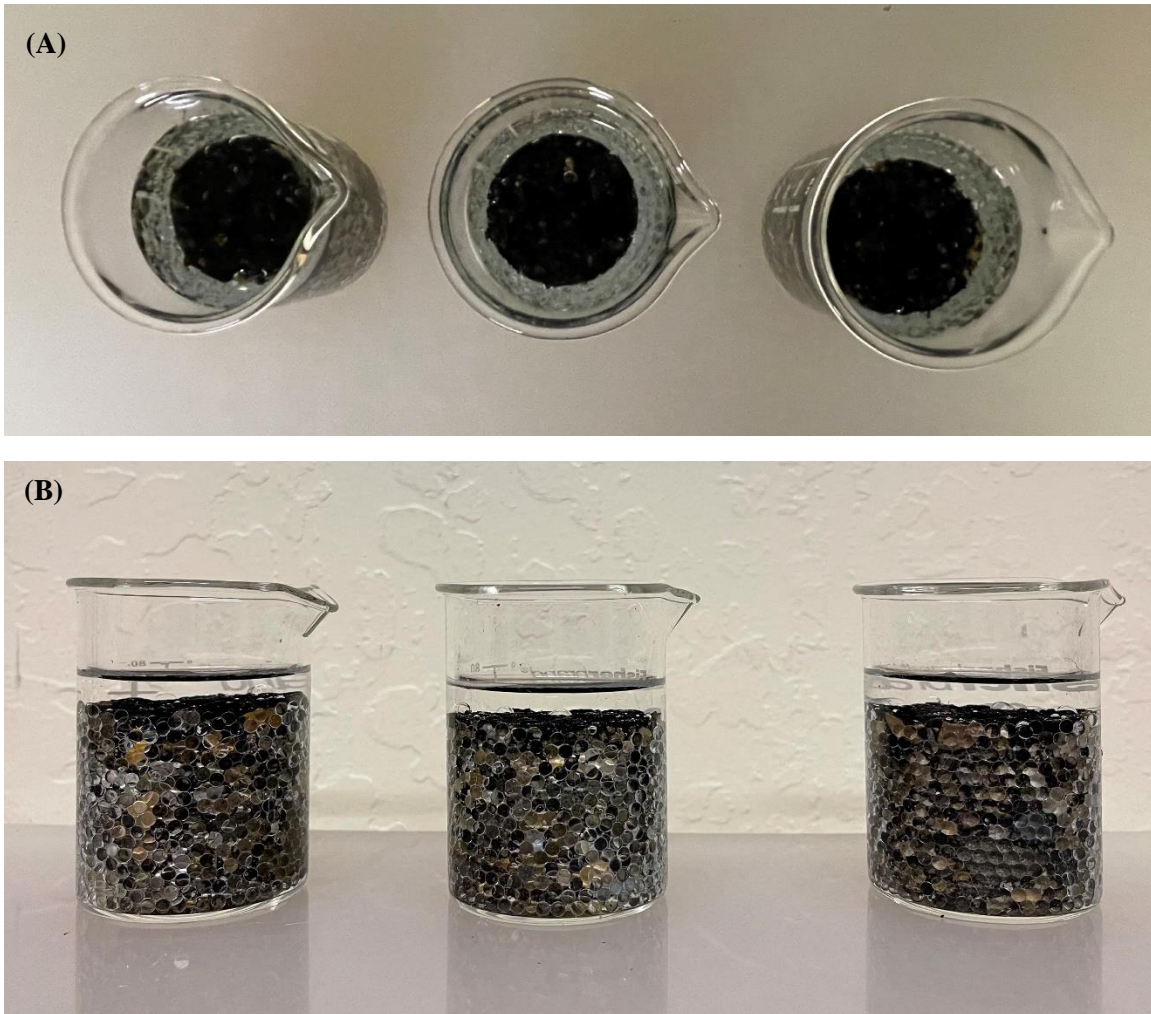
102 **Figure S2:** Flowchart indicating the different materials used, experiments conducted, and the techniques
 103 used for the chemical analysis.

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106 **Figure S3:** Schematic of the sorption kinetics experiment using compacted asphalt mixtures.



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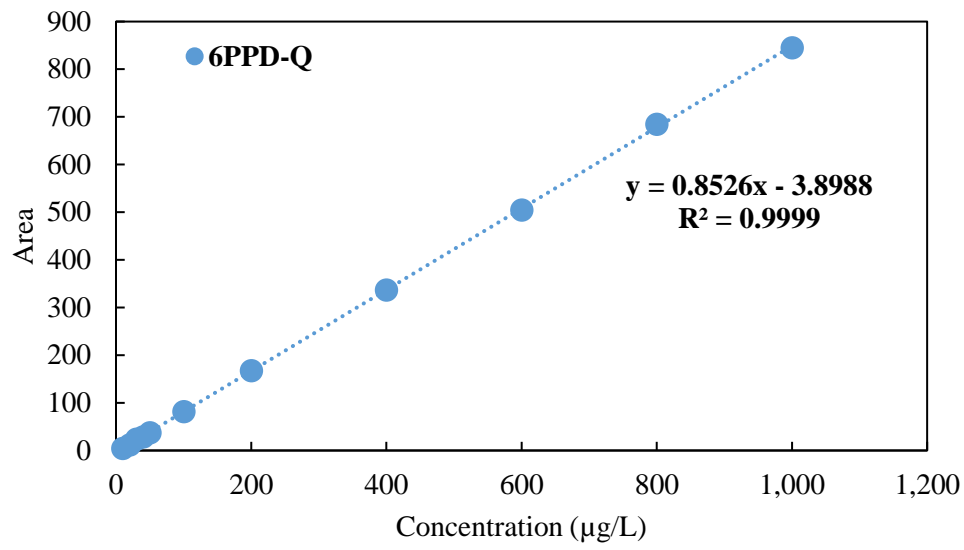
108 **Figure S4.** (A) Top and (B) side view of the sorption setup using compacted rubberized RMM2 asphalt
109 mixtures. Glass beads (5 mm diameter) were filled in the side space along the walls of the compacted
110 mixtures to minimize the sorption through the sides.



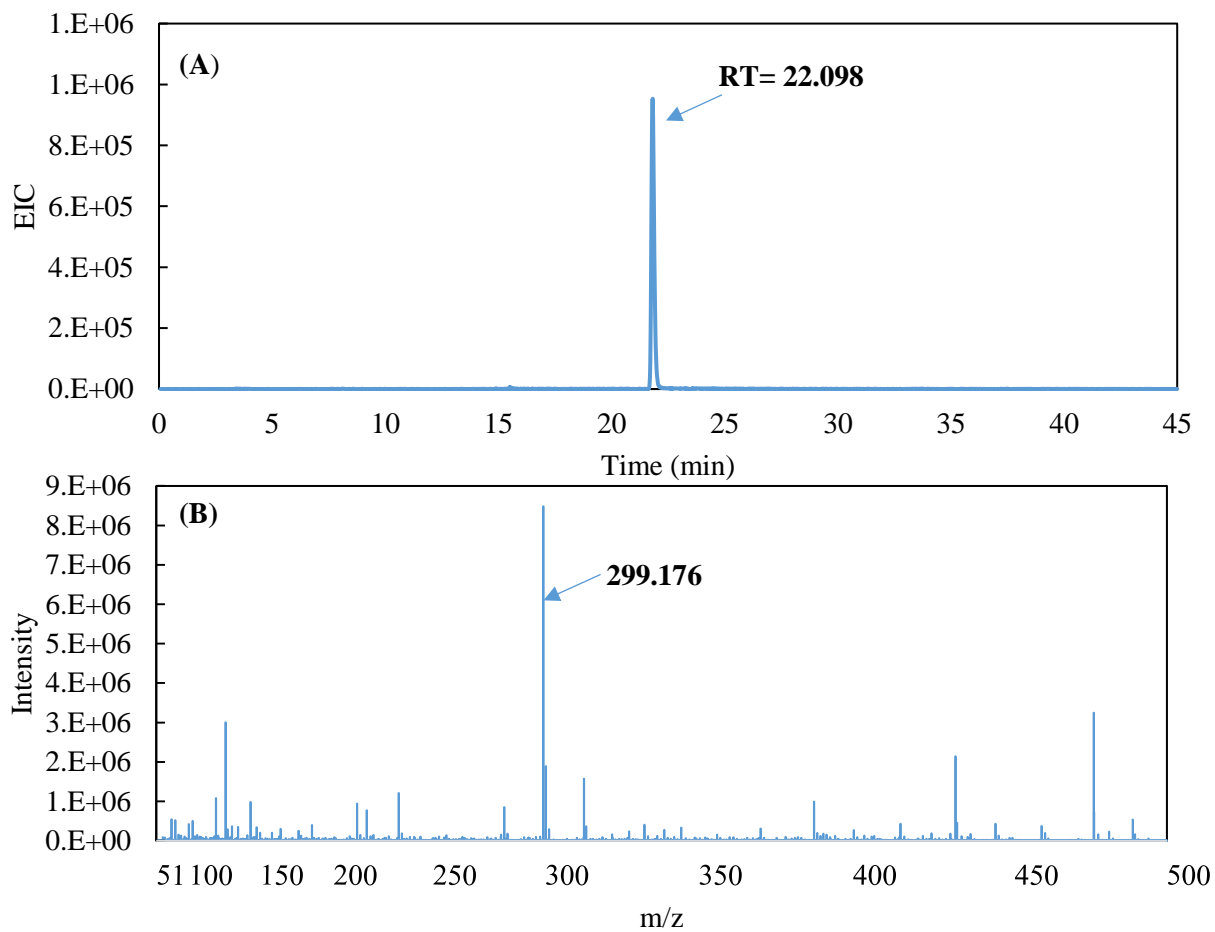
111

112 **Figure S5.** 3D-printed rainfall simulator with the top part of a funnel with a size of 76 mm height and
113 101.6 mm diameter and 462 pores of 0.508 mm diameter; the holder of the pavement column with the
114 size of 63.5 mm height and 101.6 mm diameter and a trapezoid extension for water collection.

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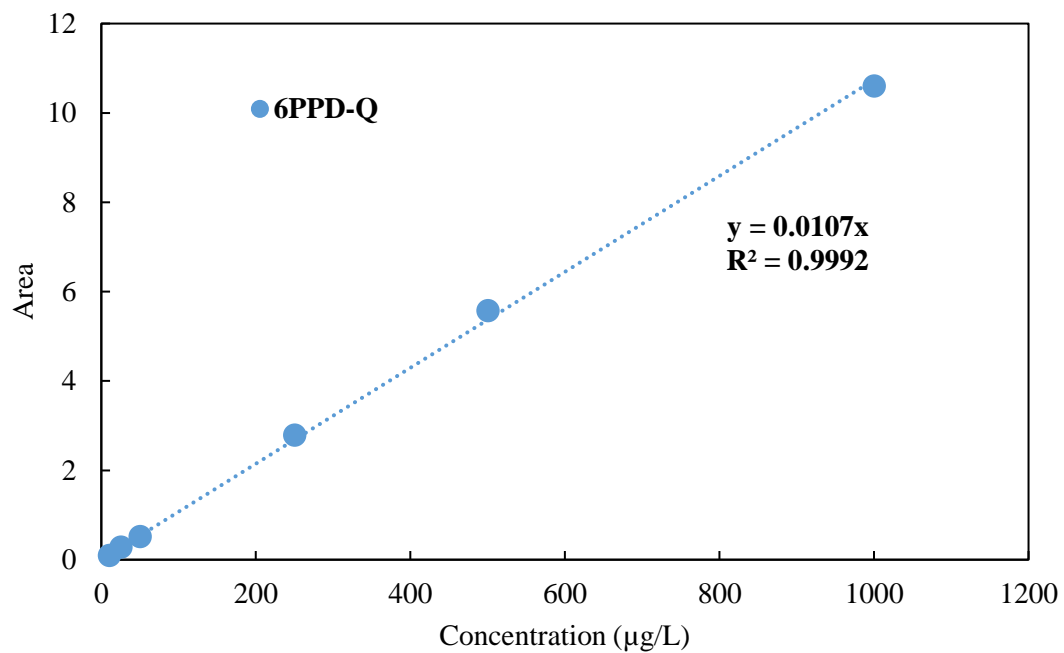


117 **Figure S6.** High-performance liquid chromatography (HPLC) calibration curve for N-(1,3-dimethylbutyl)-
118 N'-phenyl-p-phenylenediamine (6PPD)-quinone (6PPD-Q) with UV analysis at 287 nm.

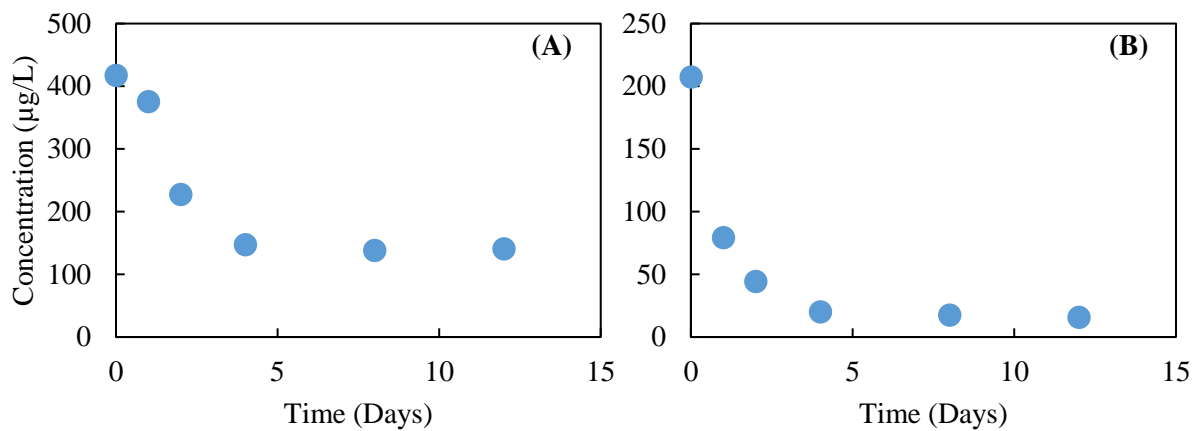


119 **Figure S7.** (A) Extracted ion chromatogram of 500 µg/L 6PPD-Q at the retention time of 22.098 min; (B)

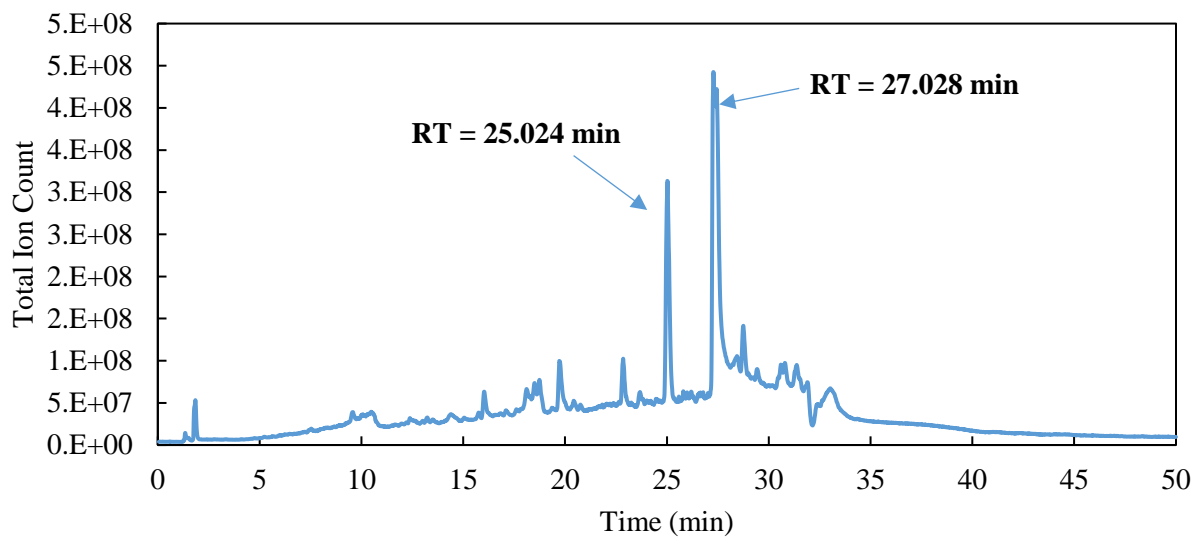
120 The associated mass spectra for the 22.098 min retention time.



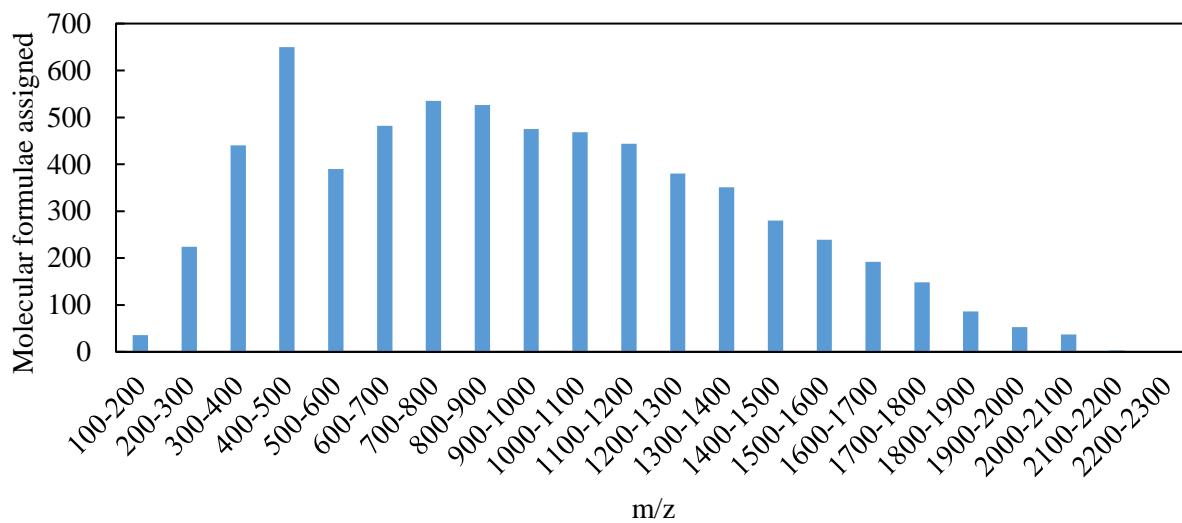
121 **Figure S8.** HPLC coupled with time of flight mass spectrometry (HPLC-TOF-MS) calibration curve for
122 6PPQ-Q.



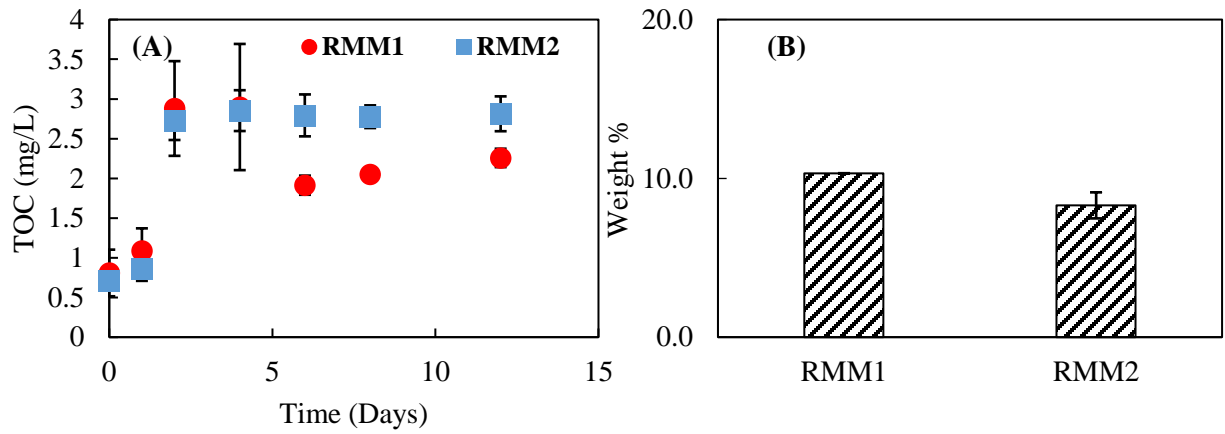
123 **Figure S9.** Kinetics for the adsorption of 6PPD-Q onto RMM2 compacted asphalt columns with a starting
124 concentration of 6PPD-Q equal to (A) 400 µg/L and (B) 200 µg/L. Error bars represent standard deviation
125 derived from duplicate experiments, which is too small to be visualized for most data points.



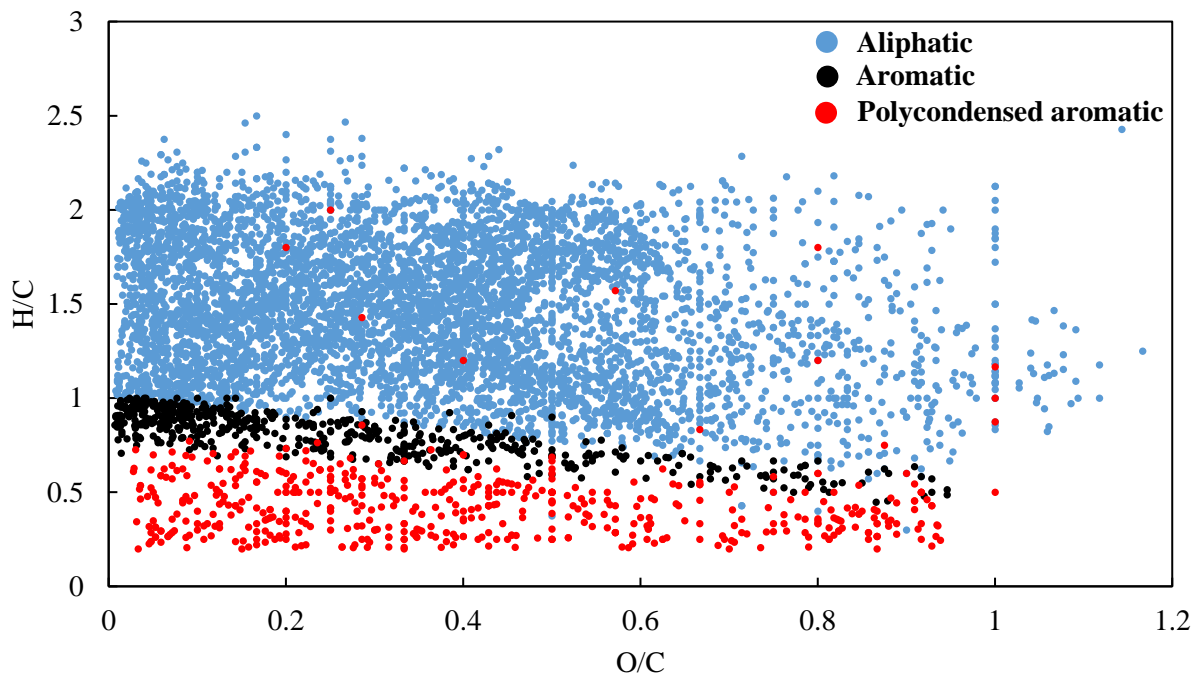
126 **Figure S10.** HPLC-TOF-MS chromatogram for the compounds released from RMM1 crushed loose
127 rubberized asphalt mixtures (12 days). In brief, 20 g of sample was suspended in DDI water for 12 days,
128 concentrated, and analyzed through the SPE-LC-TOF-MS analysis workflow.



129 **Figure S11.** The number for the compounds with molecular formula assigned for the desorption from RMM1
 130 crushed loose rubberized asphalt mixtures (12 days). Formula assignment was done using formularity
 131 software. Formulae were assigned as $C_xH_yO_z$. Error ppm for formula assignment was fixed to less than 5 ppm.



132 **Figure S12. (A)** Kinetics of total organic carbon released into the aqueous phase from loose rubberized
 133 asphalt mixtures (20 g) into 1L DDI water. **(B)** Total carbon as weight percent contained in the loose
 134 asphalt mixtures. Error bars represent standard deviation derived from triplicate experiments, which is too
 135 small to be visualized for some data points.



136
137 **Figure S13.** Van Krevelen diagram showing the captured compounds for RMM1 rubberized asphalt
138 mixtures with 1 L of DDI water during the rainfall simulation. The different colors indicate the aliphatic,
139 aromatic, and polycondensed aromatics based on AI_{mod} . Formulae assignments were done as $C_xH_yO_z$, and
140 the error ppm was set to 5 ppm.

141 **Table S1.** Major characteristics of synthesized stormwater.

NaCl	100 mg/L
CaCl ₂	80 mg/L
NaOAc	1.3 mg/L as C
ZnCl ₂	0.5 mg/L as Zn
CuCl ₂	0.06 mg/L as Cu
NaHSO ₃	2.2 mg/L
pH	5 and 7
Total Precipitation	1 L, 2 L

142

143 **Table S2.** Fitting parameters for the sorption isotherm of 6PPD-quinone on crushed loose asphalt mixtures
144 using the Freundlich equation

Freundlich Parameters	RMM1	RMM2	RMM3
K (ug/kg)(ug/L) ⁻ⁿ	170.8	219.6	163.1
n	1.26	1.027	1.134
r^2	0.9	0.96	0.95

145

146 **Table S3.** Fitting parameters for the sorption isotherm of 6PPD-quinone on compacted asphalt mixtures
147 using the Freundlich equation

Freundlich Parameters	RMM1	RMM2	RMM3
K (ug/kg)(ug/L) ⁻ⁿ	151.6	241.4	257.5
n	0.893	1.008	1.011
r^2	0.87	0.88	0.90

148