Supporting Information for:

Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber-Derived Toxicant 6PPD-quinone

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Text S1. Aqueous 6PPD-quinone (6PPDQ) solution preparation

Pure aqueous phase 6PPDQ solutions were prepared for solubility, sorption assessment and stability experiments. Different volumes of ethanolic 6PPDQ stock solutions were transferred into amber glass bottles with Hamilton syringes, the solutions were applied to the bottom and side of the bottles as even as possible and dried thoroughly with high purity nitrogen (>99 %) at ~5 L/min flow rate for 150 s and placed within a fume hood for an additional 30 s to let excess organic solvent vapor evacuate. After drying, different volumes of ultrapure water were added into the bottles to reconstitute the aqueous 6PPDQ solution, the bottles were sonicated for 60 minutes and transferred onto a shaker (70 rpm/min) for mixing overnight (>12hr) before use. The mass recovery for the aqueous 6PPDQ solution at 5 μg/L concentration (100 μL of 100 mg/L) was measured in the preliminary studies at 85 ± 6 %.

Given the tendency of 6PPDQ sorption to different materials, during all experiments the aqueous 6PPDQ solutions were stored in glass bottles and transferred with glass Pasteur pipets.

Text S2. Tire tread wear particle preparation and extraction

Tire tread wear particles (TWP) were made by physical abrasion of the treads of nine tires (brand, vehicle type, and use history in **Table S3**) using an angle grinder with a steel carbide disk (Parkes MCM90; Miller Tire, Wauseon, OH, U.S.A.) and mixed in equal weights. The TWPs were stored in a zip-lock bag to be isolated from ambient air prior to experiments.

Text S3. TWP physical property measurement

The sizes of TWPs were measured (N=27 replicates) by a particle analyzer (Horiba) using refractive index at 1.5249.[2] Water was used as chamber fluid and 0.5 g of TWP sample was mixed and measured; detailed measurement results are shown in **Figure S5A**.

The specific surface areas of the TWPs were measured by an Automated 3-station BET analyzer. Approximately 0.1 g samples were loaded into the pre-weighed BET cell, and the cell was weighed after the analysis with samples loaded to measure exact sample masses. Prior to BET analyses, samples were in-situ degassed for 12 hours at 60 ℃; nitrogen was used as analyzing gas. A typical measurement curve is shown in **Figure S5B**.

Text S4. Analytical instrument methods and data processing

6PPDQ quantification was conducted with an Agilent 1290 Infinity ultrahigh performance liquid chromatography (UHPLC) system coupled to a triple-quadrupole mass spectrometer (Agilent G6460A) with electrospray ionization (ESI+ mode). The chromatographic separation of samples (10 μL) used a reversed-phase analytical column (Eclipse Plus C18, 2.1 mm × 100 mm, 1.8 μm particle size; Agilent, USA) with a Zorbax Eclipse XDB-C18 Guard Column (2.1 mm × 12.5 mm, 5 μm particle size; Agilent, USA) held at 25 °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: started at 5% B, held at 5% B to 1 min, 50% B at 4 min, 100% B from 17-20 min, then 5% B from 20–24 min for re-equilibration. For the aqueous stability test sample analyses, the initial 5 minutes and the last 2 minutes of LC eluent were directed to waste to avoid high-concentration salt contamination of the system. Nitrogen was used as nebulizing and dessolvation gas (350 °C, 10 L/min) and capillary voltages

were 3500 V. The 6PPDQ was analyzed in multiple reaction monitoring (MRM) mode using two individual ion transitions (299 → 187 and 299 → 215). The ion with higher peak area response was used for quantification (299 → 187) and the other ion for qualification and identity confirmation (maximum tolerance of ± 20% for quantifier-to-qualifier ion ratios). For quality assurance and quality control (QA/QC), 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). A typical 6PPDQ calibration curve is shown in **Figure S2**. TWP leaching data were fitted to the model described in the main text using scipy package on Python. Confidence intervals of regressions were calculated from covariance matrices.[3]

Text S5. 6PPDQ release potential calculation

Based on the estimation by Kole et al.[4] of annual TRWP release for the US (1,250,000-1,800,000 metric tons TRWP/year), the mass distribution of TRWPs proposed by Wagner et al.[5] (45-77% of total TWP will be retained on the roadside), the assumption that TRWPs consist of 50% TWP, and the leaching potential of 6PPDQ derived from the current study (7.14±1.3 for water leaching and 15.6±1.3 for solvent extraction in μg 6PPDQ per gram TWP), an environmental release potential of 6PPDQ can be calculated as follows:

Low-emission scenario:

Annual total 6PPDQ available in mass:

$$1250000\frac{\text{metric ton TWP}}{\text{year}} \times 45\% \times 50\% \times 7.14\frac{\mu g\ \ 6PPDQ}{\text{g TWP}} = 2008\ \frac{\text{kg } 6PPDQ}{\text{year}}$$

High-emission scenario:

Annual total 6PPDQ available in mass:

$$1800000\frac{\text{metric ton TWP}}{\text{year}} \times 77\% \times 15.6\frac{\mu g\ \ 6PPDQ}{\text{g TWP}} = 10811\ \frac{\text{kg } 6PPDQ}{\text{year}}$$

The total highway lane length is 14,200,000 km; with lane width of 3.7 m,[6] the total highway area is:

$$14200000 \times 3.7 = 52592\ km^2 = 5.25 \times 10^{10} m^2$$

The annual average roadway runoff can be predicted as:

$$0.769(m/year) \times 0.85 \times 5.25 \times 10^{10} m^2 = 3.44 \times 10^{10}(m^3/year) = 3.43 \times 10^{13}(L/year)$$

Consequently, 6PPDQ concentration in roadway runoffs can be predicted for the low-emission scenario as:

$$2008\ \frac{\text{kg } 6PPDQ}{\text{year}} \div (3.44 \times 10^{13}\frac{\text{L}}{\text{year}}) = 58.4\frac{ng}{L}$$

or for the high-emission scenario as:

$$10811\ \frac{\text{kg } 6PPDQ}{\text{year}} \div (3.44 \times 10^{13}\frac{\text{L}}{\text{year}}) = 314.3\frac{ng}{L}$$

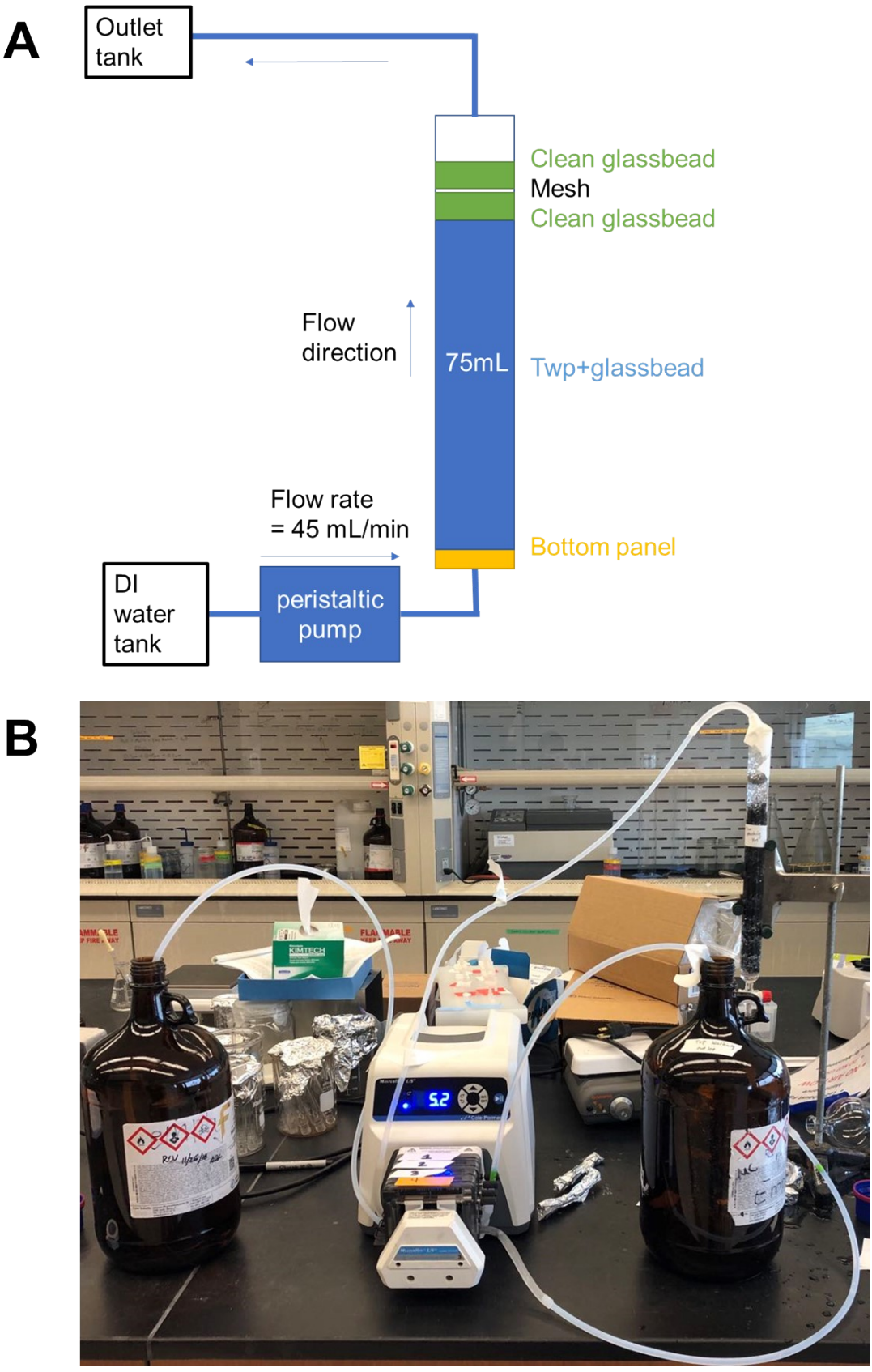

Figure S1. The flow-through leaching system setup. (A) Schematic diagram of the setup; and (B) photo of the leaching system setup in the lab.

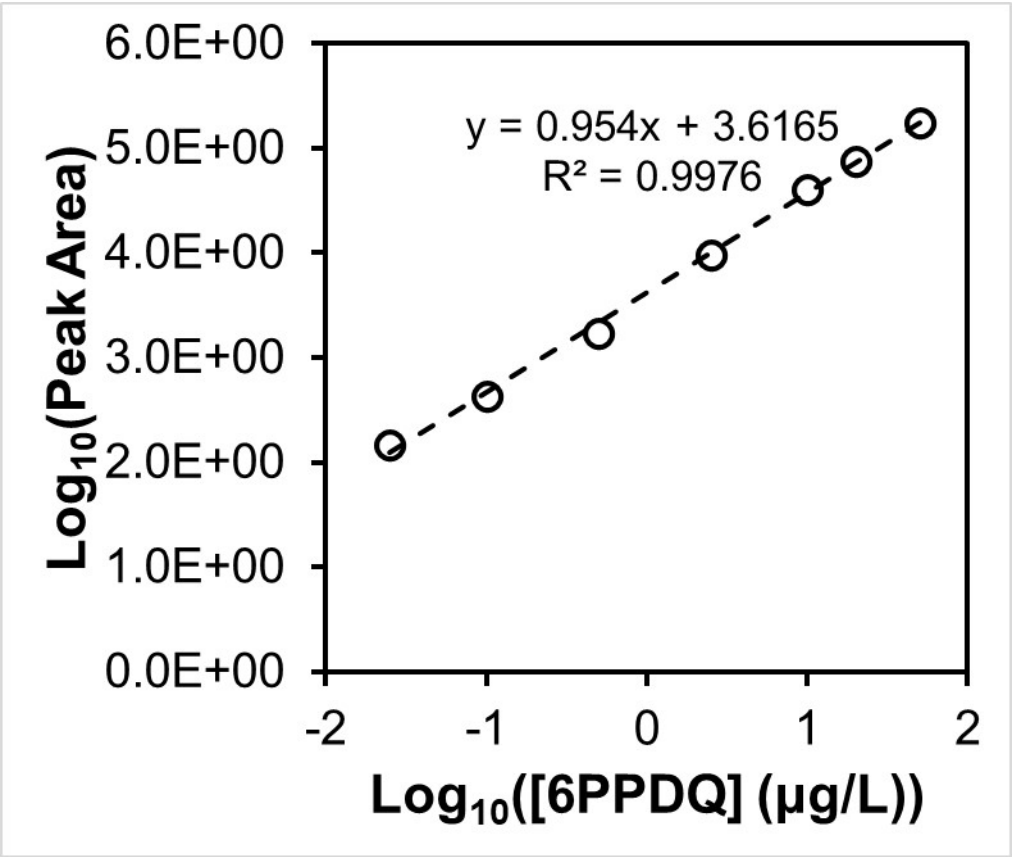

Figure S2. Typical calibration curve (log scale) for 6PPDQ on LC-MS/MS system. The peak areas were adjusted with 6PPDQ-d5 ISTD peak area response.

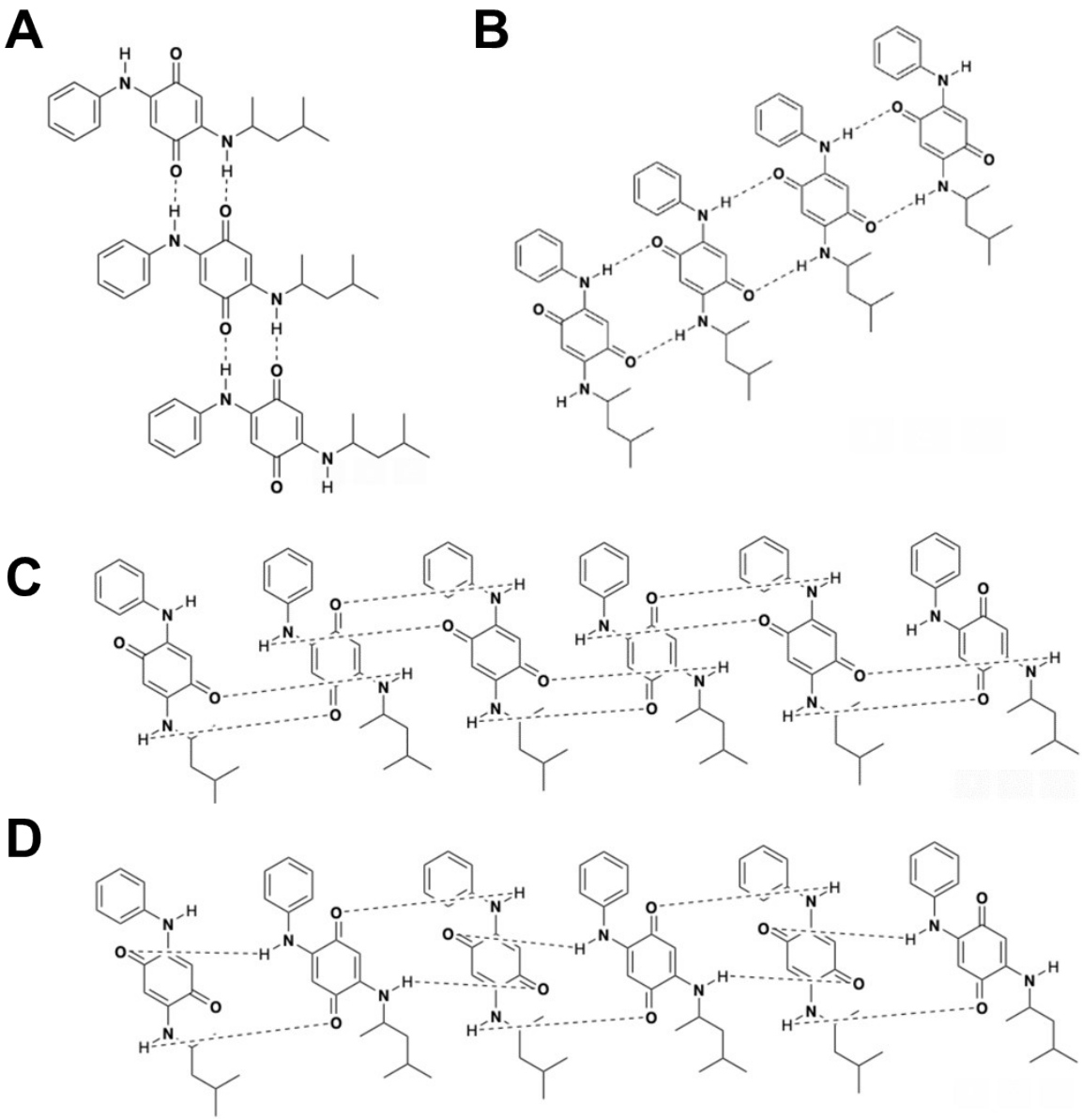

Figure S3. Examples of possible H-bonding structures of 6PPDQ contributing to strong solute-solute interactions for 6PPDQ solid phases.

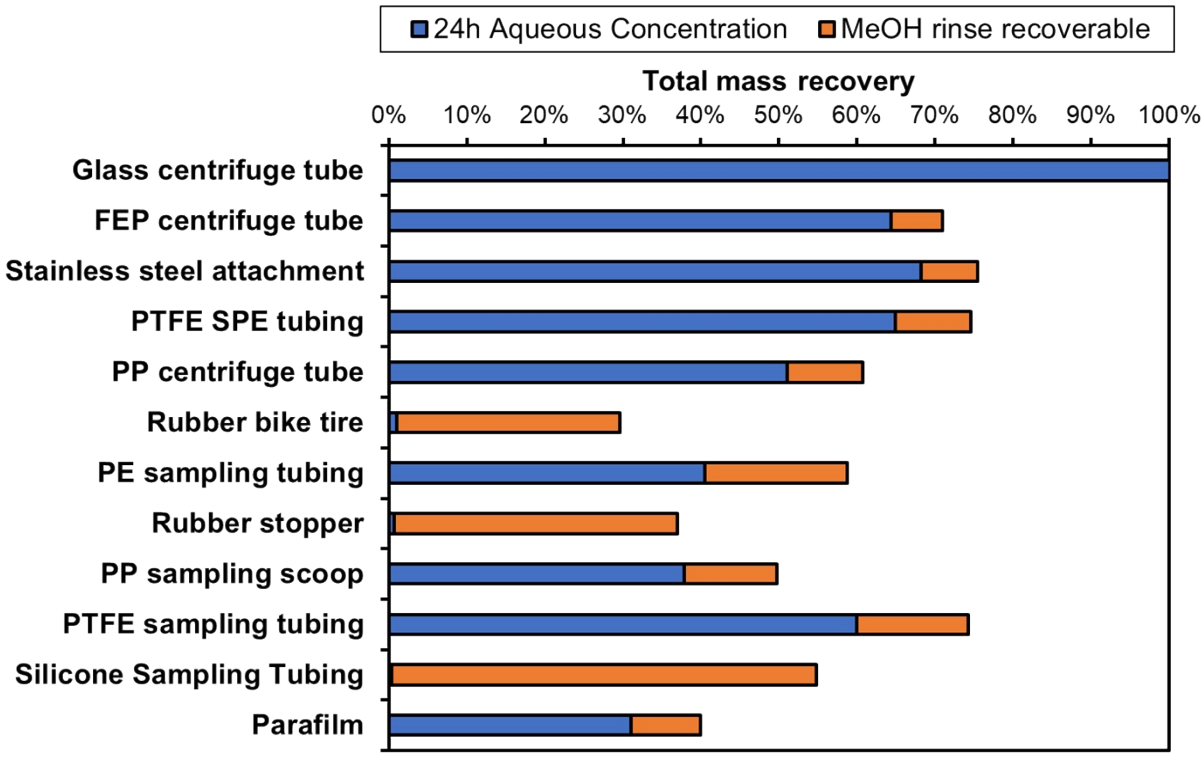

Figure S4. Total solvent-recoverable mass of 6PPDQ from containers and test materials after 24 h sorption test. Values represent averages from experimental triplicates.

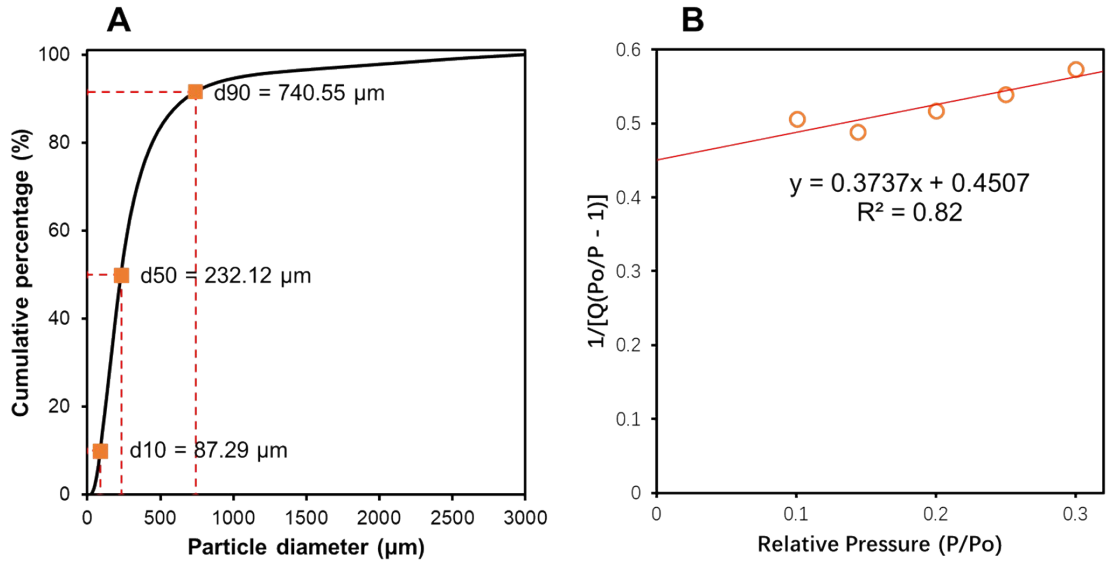

Figure S5. Physical characterization of TWPs used for these laboratory studies, including: (A) cumulative percentage of particle diameters measured using particle analyzer; and (B) typical BET surface area plot for the TWPs.

Table S1. Aqueous 6PPDQ solution preparation conditions

Nominal Concentration (µg/L)	Spike Volume (µL)	Spiked Concentration (mg/L)	Final Volume (mL)	Actual Concentration (µg/L)*	Observed / Nominal Concentration (%)	Replicates
5	50	10	100	4.3 ± 0.3	85 ± 6	3
10	50	20	100	7.3 ± 0.2	73 ± 2	3
25	50	50	100	15.7 ± 0.3	63 ± 1	3
50	50	100	100	26.3 ± 1.9	53 ± 4	3
100	40	100	40	38.5 ± 2.1	39 ± 2	3
200	80	100	40	44.8 ± 0.8	22 ± 0	3
300	120	100	40	71.5 ± 16.5	24 ± 6	9

*The actual concentration of 6PPDQ stock solution is the same as the pre-centrifuge concentration of 6PPDQ in the **Figure 1** for each concentration group.

Table S2. Summary of materials used for sorption potential measurements.

	Testing material	Material Shape	6PPDQ stock volume added
Common Materials	Green stopper (GS)	Fragment pieces	10 mL
	Bike tire rubber (BTR)	Fragment pieces	10 mL
	Sampling Tube PE housing (ST-PE)	Coupon	10 mL
	Sampling Tube PTFE liner (ST-PTFE)	Coupon	10 mL
	Sampling Tube Silicone (ST-Silic)	Coupon	10 mL
	PTFE tubing for SPE (SPE-PTFE)	Coupon	10 mL
	Parafilm (PF)	Coupon	10 mL
Centrifuge Tubes	PP centrifuge tube (CT-PP)	Original container	10 mL
	FEP centrifuge tube (CT-FEP)	Original container	10 mL
	Glass centrifuge tube (CT-G)	Original container	10 mL
Containers	Stainless Steel (SS)	Cylinder shaped attachment	30 mL
	PP Sampling Scoop (SS-PP)	Original container	30 mL

Table S3. Information about the nine tires used to produce tire tread wear particles (TWPs), also reported in detail elsewhere.[1] The TWP mixture used for these studies was an equal-weight mixture of the nine tire types listed below.

Tire ID	Manufacturer	Season	New/Used	Vehicle Type	Tire code
1	A	All-season	Used	Car	205/55R16 91H
2	B	All-season	Used	Car	195/70R14 91H
3	C	All-season	Used	Car	P185/65R15 86T
4	D	Winter	Used	Car	175/65R14 82S
5	E	All-season	Used	Car	P185/85R15 86S
6	E	All-season	Used	Light Truck	LT235/85R16 120R
7	F	All-season	New	Car	P205/60R15 90T
8	G	All-season	New	Car	P205/60R16 92H
9	H	All-season	Used	Car	P225/60R17 98T

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