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

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ABSTRACT

We here report chemical characteristics relevant to the fate and transport of the recently discovered environmental toxicant 6PPD-quinone (2-((4-Methylpentan-2-yl)amino)-5-(phenylamino)cyclohexa-2,5-diene-1,4-dione, or “6PPDQ”). 6PPDQ is a transformation product of the tire rubber antioxidant 6PPD that is ubiquitous in roadway environments, including atmospheric particulate matter, soils, runoff, and receiving waters, after dispersal from tire rubber use and wear on roadways. The aqueous solubility and octanol-water partitioning coefficient (i.e. $\log K_{OW}$) were measured for 6PPDQ as 38±10 μg/L and 4.30±0.02, respectively. Within a context of analytical measurement and laboratory processing, sorption to various laboratory materials was evaluated, indicating that glass was largely inert but loss of 6PPDQ to other materials was common. Aqueous leaching simulations from tire tread wear particles (TWPs) indicated short term release of ~5.2 μg 6PPDQ per gram TWP over 6 h under flow-through conditions. Aqueous stability tests observed slight-to-moderate loss of 6PPDQ over 47 days (26±3% loss) for pH 5, 7 and 9. These measured physicochemical properties suggest 6PPDQ is generally poorly soluble but fairly stable over short time periods in simple aqueous systems. 6PPDQ also can leach readily from TWPs for subsequent environmental transport, posing high potential for adverse effects in local aquatic environments.

Environmental Significance Statement. This work investigated 6PPDQ chemical properties to evaluate the chemical characteristics and stabilities of this potent environmental toxicant. These data help to better understand and predict the analysis, fate, and transport of 6PPDQ in laboratory and environmental systems.

INTRODUCTION

Complementing decades of investigation of conventional water pollutants such as nutrients, salts, and trace heavy metals,(1–7) various synthetic organic contaminants are now receiving more research attention in roadway systems.(8–15) Recently, 6PPD-quinone (2-((4-methylpentan-2-yl)amino)-5-(phenylamino)cyclohexa-2,5-diene-1,4-dione) or "6PPDQ", a tire rubber derived compound that can induce acute toxicity to coho salmon (*Oncorhynchus kisutch*), was reported globally in atmospheric particulate matter, dusts, soils, runoff, surface waters and even human urine.(16–23) 6PPDQ is a transformation product of the common antioxidant 6PPD (*N*-(1,3-dimethylbutyl)-*N′*-phenyl-*p*-phenylenediamine) that is ubiquitously used in tire rubber products (0.4-2% by mass).(24) The parent compound 6PPD converts into 6PPDQ via oxidative reactions, especially those involving reactions with atmospheric ozone, during the tire service life; 6PPDQ is therefore introduced into roadway environments by tire rubber use and wear.(11,13,16,18,25,26) In addition to atmospheric pathways, both dissolved 6PPDQ and tire tread wear particles (TWP) containing 6PPDQ are transported in runoff from roadways during storm events where they can induce adverse ecological effects in sensitive aquatic species upon release.

Currently, there exists limited information concerning the chemical properties, environmental fate, and transport of 6PPDQ.(16,17,19) To the best of our knowledge, the chemical properties and characteristics needed to inform the environmental risks of 6PPDQ have not been fully reported.(26–29) To address this data gap, this study measured the aqueous solubility, logK_{OW}, sorption potential, leaching, and stability of 6PPDQ in environments typical of the laboratory and simple aqueous systems. Specifically, we measured or estimated: (1) basic physicochemical properties (logK_{OW} and solubility); (2) sorption potentials to different conventional materials; (3) leaching dynamics and timescales from representative TWP; (4) stability within simple aqueous solutions; and (5) potential for environmental occurrence via mass balance calculations. These data will inform procedures for laboratory handling and analysis while guiding environmental fate and management strategies for 6PPDQ.

MATERIALS AND METHODS

Chemicals and Reagents. 6PPDQ (98.8%) and 6PPDQ-d_5 (98%) were purchased from HPC Standards Inc. (Atlanta, GA, USA). Sodium phosphate dibasic anhydrous, sodium phosphate monobasic anhydrous and sodium hydroxide solution (10N) were purchased from Fisher Scientific (Waltham, MA, USA). Methanol, acetone, formic acid, (all Optima LC/MS grade, ≥99%), absolute ethanol (200 Proof, ~99.5%), 1-octanol (ACS spectrophotometric grade, ≥99%) were purchased from Fisher Scientific (Waltham, MA, USA) and Sigma-Aldrich (St. Louis, MO, USA). Ultrapure deionized (DI) water was obtained using a water purification system (Thermo Barnstead Nanopure Diamond UV, Dubuque, IA, USA) or Milli-Q® Advantage A10 purification system (Millipore, Burlington, MA, USA). Glass Pasteur pipets were used for all the subsampling process for aqueous samples contains 6PPDQ to reduce the possible sorption loss of 6PPDQ. Alternative measurements including using PTFE lined tubing (e.g., during SPE process) or reduced contact time (e.g., <10s while pipetting 6PPDQ solution) were taken to handle 6PPDQ water solution when glass material is not available.

Aqueous Solubility and Octanol–Water Partition Coefficient. Solubility assessment of 6PPDQ followed the centrifugation method described in the OECD protocol for aquatic toxicity testing with modification.(30) Aqueous 6PPDQ solutions were prepared at different nominal concentrations (**Table S1**; 5-300 μg/L nominal) prior to experiments as described in **Text S1**; these solutions were mixed on a shaker for >12 hours before experiments. Experiments were conducted in triplicate for each concentration. After equilibration, 10 mL aliquots from 6PPDQ aqueous stocks at different nominal concentrations (**Text S1; Table S1**) were transferred into 15 mL high strength glass centrifuge tubes with rubber sleeves (DWK Life Sciences, Vineland, NJ, USA) and adapters (Thermo Scientific, Waltham, MA, USA). 500 μL aliquots were sampled from each tube before centrifugation. Then, centrifugation separations were performed with a Sorvall X1 centrifuge (equipped with a Fiberlite F15-8x50cy Fixed Angle Rotor) at 10,200 g for 30 min, with temperature control at 20 ℃. After centrifugation, 500 μL of supernatant was sampled from each tube. Samples were diluted with 450 μL methanol and spiked with 50 μL 6PPDQ-d_5 ISTD (5μg/L) for instrumental analysis **(Text S4).**

Octanol-water partition coefficient ($\log K_{OW}$) measurements followed EPA guidelines with minor modification;(31) experiments were conducted in triplicate. A 6PPDQ stock solution in ethanol (10 mg/L; 0.5 mL) was dried under gentle nitrogen flow (<1 L/min) within 15 mL glass centrifuge tubes, reconstituted with 1 mL octanol (precleaned with NaOH and ultrapure water to remove impurities) and 5 mL of ultrapure water, then sonicated (15 min). These mixtures were centrifuged (30 min, 2,500 rpm, 20 °C) until complete separation of aqueous and organic phases. Octanol aliquots were withdrawn by glass pipet while remaining octanol phase was removed and discarded prior to aqueous phase sampling. Octanol subsamples were diluted with methanol 1000-fold while aqueous phases were analyzed directly, given their low 6PPDQ concentration (~2 µg/L; well below the aqueous solubility limit). For instrumental analysis, 950 µL aliquots (both diluted octanol and aqueous phases) were spiked with 50 µL 6PPDQ-d5 ISTD.

Sorption to materials. An aqueous 6PPDQ stock solution (at 5 µg/L nominal concentration) was prepared as for solubility studies (**Text S1**). All materials or containers were 6PPDQ free and pre-cleaned prior to experiments. The selected materials (sampling tube, polyethylene housing [ST-PE]; sampling tubing, polytetrafluoroethylene liner [ST-PTFE]; silicone sampling tubing [ST-Sil]; polytetrafluoroethylene SPE tubing [SPE-PTFE]; parafilm [PF]; rubber stopper [RS]; and bike tire rubber [BTR]) were cut into flat pieces (0.5 g) and placed within amber glass bottles. Centrifuge tubes (15 mL polypropylene centrifuge tube [CT-PP], 10 mL fluorinated ethylene propylene centrifuge tube [CT-FEP], and 15 mL glass centrifuge tube [CT-G]) and lab equipment (1L polypropylene sampling scoop [SS-PP] and stainless-steel attachment [SS]) were tested directly without further treatment. All sorption tests were conducted in triplicate for each material. Aliquots of 6PPDQ solution (10 mL for common materials and centrifuge tubes; 30 mL for tested containers) were transferred via glass pipets into the amber glass bottles containing material samples or the original testing containers (see **Table S2**). Tested vessels were mixed on the shaker (70 rpm) and 500 µL aliquots sampled with glass Pasteur pipets after 5 min, 30 min, and 24 h. These subsamples were diluted with 450 µL methanol and spiked with 50 µL 6PPDQ-d5 ISTD for instrumental analysis. To measure the total recoverable adsorbed 6PPDQ mass, after 24 hours mixing, aqueous 6PPDQ solution was removed from all the tested containers and 10 mL methanol was added into the tubes. These were shaken and sonicated (30 min), then 950 µL aliquots were sampled and spiked with 50 µL 6PPDQ-d5 for analysis.

Leaching dynamic of 6PPDQ from TWP. Preparation of TWP (focused on passenger car and light truck tires) for leaching studies was described elsewhere(16) (**Text S2)**. The particle size distribution and surface area of TWP were characterized with surface analyzer and BET surface analysis (**Text S3**). For leaching studies, 0.25 g of TWP were dispersed into 75 mL of pre-cleaned glass beads (0.3 cm diameter) in a glass beaker (100 mL). The mixture was transferred into a glass chromatography column (300 mm × 20 mm ID, fused mesh base); any residual TWP in the mixing beaker was transferred into the column as a slurry in 5 mL DI water (with transfer time limited to <30s to minimize pre-leaching contact time between water and TWPs). The column was then topped with two layers of clean glass beads and a stainless-steel mesh (**Figure S1**), ultrapure DI water was pumped through the column by a peristaltic pump at 45 mL/min using a single pass (i.e., effluent sent to waste) upflow design. Leachates were collected at 0.25, 0.5, 1, 1.5, 2, 3, 4, 5, and 6 h, **Figure S1**. Preliminary tests (15, 45, and 90 mL/min) determined optimal flow rates without apparent advective limitations. These tests were conducted in triplicate with identical TWP mass and leaching time. At each time point, 200 mL of TWP leachate was collected, stored at 4 °C and extracted within 24 h.(16,32)

Leachates were extracted using preconditioned (10 mL methanol, 25mL water) SPE cartridges (Oasis HLB) at 5-10 mL/min. SPE cartridges were then rinsed with 10 mL DI water, air-dried (30 min), then eluted with methanol (2 × 5 mL). Eluates were concentrated under nitrogen to 1 mL for instrumental analysis. At the time this experiment was conducted, 6PPDQ-d_5 isotopic internal standard (ISTD) was not commercially available, so ISTD was not spiked into these extracts for recovery correction. Here, the method spiking recovery (i.e., 6PPDQ spiked leachate at t = 0, prior to leaching experiment) for 6PPDQ was measured as 69±7%, largely reflecting potential 6PPDQ loss during sample processing (e.g., SPE and evaporation concentration);(16) concentration data were not normalized to observed recoveries for later calculations.

Aqueous stability. A 6PPDQ aqueous solution (20 μg/L) for aqueous stability tests was made using protocols described in **Text S1**. Aqueous stability measurements followed the methods of Su et al. with slight modification.(33) Phosphate buffer (mixture of monopotassium and dipotassium phosphate) solutions (10 mM) were prepared and adjusted to pH 5, 7 and 9 (100 mL for each pH) using 0.1M sodium hydroxide. Twenty mL of 6PPDQ aqueous solution was then diluted with 80 mL buffer and separated into 20 mL triplicate aliquots in 100 mL amber glass bottles for stability tests, the bottles were capped with PTFE lined caps during the test. The remaining 40 mL pH adjusted 6PPDQ solution was retained identically and used for pH measurements at 0, 7, 14 and 47 days using a pH meter (Thermo Scientific, Waltham, MA, USA). All bottles were mixed on a shaker under room temperature (20-22℃). The pH was generally stable (±0.05 for pH 5 and 7 groups, decreased to 8.7 for pH 9 solutions due to absorption of atmospheric carbon dioxide) throughout the experimental period. At each time point (0, 0.25, 1, 3, 7, 14, and 47 d), 500 µL of the solution was sampled with Pasteur glass pipet, diluted with 450 µL of methanol, spiked with 50 µL 6PPDQ-d5 ISTD (100 ug/L) and stored at -20 °C until instrument analysis.

Instrumental analysis. Physical properties of TWP were measured by a particle analyzer and a BET analyzer (**Text S3**). For 6PPDQ quantification, a liquid chromatography-tandem mass spectrometry system (Agilent 1290-6460 systems, described previously) was used in ESI+ mode.(19) The data was processed by Agilent MassHunter Quantitative Analysis; a calibration curve for 6PPDQ is shown in **Figure S2**. The collected data were processed through a Python-based platform with scipy package (version 1.6.3) for leaching kinetics modeling. Detailed analytical and data processing methods are described in **Text S4**.

RESULTS AND DISCUSSION

Solubility and octanol–water partitioning. Prior to aqueous solubility experiments, 6PPDQ solubility in the stock solvent (ethanol) was tested in a preliminary study (>100 mg/L in ethanol at 20 °C). Solubility tests in water were conducted across a range of concentrations (**Table S1**) via a centrifugation method(30); resulting aqueous solutions were equilibrated >12 hrs at room temperature prior to centrifugation. For 6PPDQ solutions at higher nominal concentrations (>50 µg/L), light-pink solids accumulated within centrifuge tubes after centrifugation, which implied that excess solid precipitates existed within the solution. 6PPDQ solubility was estimated by comparison of samples before and after centrifugation. Notably, in contrast to the predicted solubility estimates derived from software (i.e., 2.4 – 140,000 mg/L from EPI-suite(34), Marvin(35) and SPARC(36)), the experimental results indicated a surprisingly low 6PPDQ solubility of 38±10 µg/L (**Figure 1**). This measurement aligned well with the solubility estimate of Hiki et al. (67±5 µg/L)(29) and highlights the potential large inaccuracies of estimates obtained from software predictions. It is an open, and important, question as to why software predictions so diverged from observation for 6PPDQ.

Comparing measured versus nominal concentration of 6PPDQ yielded observations of 99±5% during preliminary screening studies conducted in various organic solvents (acetonitrile, ethyl acetate, and ethanol), indicating that no obvious chemical reactions interfered with solubility observations for 6PPDQ within organic solvents. Note that similar to methods reported by Hiki et al.,(29) our preparation process involved drying of an initial ethanolic stock. We speculate that under the tested conditions, solute-solute intermolecular forces may be especially important for 6PPDQ solid dissolution, given that hydrogen bonding between 6PPDQ and water should be fairly typical of solvent-solute interactions for similarly polar, similarly structured and sized compounds and serve to promote dissolution. Instead, solute-solute intermolecular forces in the 6PPDQ solid phase (e.g. **Figure S3**) may hinder dissolution and even contribute to strong "protective film" formation and stability, an outcome much emphasized in the industrial chemistry literature describing rubber protection by oxidation products of PPD antiozonants(28). Similarly, the strength of such solute-solute interactions would be expected to favor precipitation of 6PPDQ solids from the aqueous phase even at very low dissolved 6PPDQ concentrations, and could therefore also explain the extremely low observed aqueous solubility of 6PPDQ molecules present under equilibrium conditions in solution. This is supported by the negative linear relationship between the measured and the nominal concentration of the reconstituted 6PPDQ aqueous solutions (**Table S1**). One potential (albeit speculative) explanation for such low solubility could derive from a mechanism of complementary H-bonding and van der Waals interactions that promote stacked crystalline and other intermolecular interactions amongst molecules of 6PPDQ (and potentially other similar structured compounds) (37–40) (**Figure S3**), whether one is considering 6PPDQ dissolution from the solid phase or its precipitation from the aqueous phase.

Although aqueous solubility is low, 6PPDQ solubility easily exceeds exposure concentrations where coho salmon mortality occurs (LC_{50} = 95 ng/L) and aligns with observations of mortality and transport during storms.(16,19) Given limited solubility and reported 6PPDQ TWP concentrations,(41) there should exist other environmental transport pathways for 6PPDQ aside from dissolution and transport in water. Most reports of 6PPDQ environmental occurrence derive from surface water or airborne particulate matter samples(16,18,20,22), so further investigation of partitioning of 6PPDQ into other environmental medias (e.g., soil, sediments, DOMs) to fully elucidate environmental fate is merited. We also emphasize the importance of understanding solubility limitations in any experimental designs involving 6PPDQ aqueous solutions (e.g., toxicity assessment, photolysis studies) and note that co-solvent effects might be particularly important for higher concentrations of 6PPDQ or behavior in complex solutions.

The logK_{OW} of 6PPDQ was measured at 4.30±0.02, slightly lower than the reported 4.84

for the parent 6PPD.(26) The measured results were similar to the numbers discussed by Cao et al (3.98 for 6PPDQ and 4.47 for 6PPD).(42) This “moderate-high” logK_{OW} value indicated that some fraction of 6PPDQ mass would be expected to partition to soil, sediments, rubber or plastic materials in aqueous systems. Notably, chemicals with logK_{OW} values within the range of 3-7 have optimal uptake efficiency through gill tissues,(43) an important bioavailability consideration for the highly toxic 6PPDQ, as chemicals with low logK_{OW} values tend to be insoluble in lipids, while high logK_{OW} chemicals bind to lipid membranes and prevent further uptake.(43) Further investigation of the bioavailability and uptake of 6PPDQ and other tire rubber-derived roadway contaminants to fish, especially within the context of relative toxicity outcomes,(29) is merited.

Sorption to materials. To assess potential sorption losses during sampling and laboratory processes, sorption to 12 materials was evaluated, including 10 common labware materials (ST-PE, ST-PTFE, ST-Sil, SPE-PTFE, PF, CT-PP, CT-FEP, CT-G, RS, and SS-PP) and 2 conventional materials (BTR and SS). The rubber materials (RS and BTR) were analyzed and confirmed 6PPDQ-free before the experiment; no 6PPDQ (<0.025 ug/L) was detected. For short (5 min) exposures that simulated contact times for transfer between containers or rapid contact with sampling equipment or tubing materials, most materials showed low to moderate sorption (>75% residual 6PPDQ concentrations detected; **Figure 2**). Unsurprisingly, for longer 30-minute contact periods, which simulated temporary storage or sample processing, more extensive sorptive losses occurred. Glass, stainless steel and plastics (PTFE, FEP, PE and PP) had zero to moderate sorption tendency (>60% residual 6PPDQ concentrations vs t_0), while rubber (BTR: 35±8.6%; RS: 8.7±3.2%) and silicone (ST-Sil 25±0.1%) promoted substantial concentration reductions. With longer (24 h) contact, even more loss to rubber (BTR: 0.97±0.13%; RS: 0.7±0.21%) and silicone (ST-Sil: 0.34±0.22%) occurred.

Similar to outcomes for 6PPD(26,28), the hydrophobicity ($\log K_{OW}$ = 4.3; aqueous solubility = 38±10 μg/L) of 6PPDQ should promote high sorption losses of 6PPDQ from aqueous solution to rubber, silicone, and plastic materials. For instance, although it is highly variable and depends upon material type and sizes, the surface area of rubbers are typically high (e.g., the surface area of crumb rubbers are measured at hundreds to thousands of cm^2/g(44–46)). The high specific surface area indicates a porous structure which can retain inaccessible or kinetically limited 6PPDQ mass during equilibration(47–49) compared to smooth surface materials (e.g., glass). Stainless steel and plastics designed to be more chemically inert (e.g., FEP, PTFE) showed moderate sorption potentials, with higher residual 6PPDQ concentrations after 24-hour contact. Substantial 6PPDQ mass was sorbed by PP (residual 6PPDQ mass; CT-PP: 51±1.4%; SS-PP: 38±1.5%) and parafilm (residual 6PPDQ mass; PF: 31±2.3%). Note that for all contact times, no significant 6PPDQ sorption (t-test; p-value=0.59, 0.32 and 0.12 at 5 min, 30 min and 24 hr vs t_0, respectively) occurred for glass (101±0.3%, 100±1.3% and 100±0.3% residual concentrations at 5 min, 30 min, and 24 hr vs t_0, respectively), suggesting glass as the preferred material for labware and processing.

After 24 h contact periods, aqueous phases were removed and all containers and materials were methanol extracted (30 min sonication) to evaluate recovery of sorbed mass. Mass balances indicated that all materials except glass retained ~25-70% of initial 6PPDQ mass that was not recoverable with methanol (**Figure S4**). The rubber materials (6PPDQ total mass loss: BTR: 70±1.6%; RS: 63±2.1%) exhibited substantially higher mass loss than other materials, indicating 6PPDQ has higher and stronger sorption potentials to these materials. The methanol non-recoverable mass loss may result from strong hydrophobic interactions, material microporosities, slow mass transfer, or chemical reactions. During the contact period and subsequent methanol extraction, rubber and silicone materials were especially prone to initial mass loss (>95%) from aqueous phases over 24 h equilibration, but substantial proportions of the sorbed 6PPDQ were recoverable (30 min methanol extraction with respect to total 6PPDQ mass; BTR: 29±1.5%; RS: 36±1.9%; ST-Sil: 54±2.6%) with methanol, indicating most of the total mass was partitioned onto/into the materials. Seiwert et al.(18) recently reported that most 6PPDQ mass remained in TWP particles (distribution ratio or water to particle = 0.001) after environmental deposition, consistent with the 6PPDQ sorption data of rubber materials. In contrast, plastic materials were less sorptive during the 24 h tests (~30-60% 6PPDQ mass loss during 24 h equilibration) while much less sorbed 6PPDQ mass was methanol recoverable (30 min methanol extraction: CT-FEP: 6.6±0.99%; SS: 7.3±2.5%; SPE-PTFE: 9.7±0.64%; CT-PP: 9.6±1.6%; ST-PE: 18±5.4%; SS-PP: 12±1.5%; ST-PTFE: 14±2.1%; PF: 8.9±0.85%). These plastic materials also showed a high total recoverable mass (24 h contact solution mass + methanol recoverable mass; ~40-75%), suggesting 6PPDQ has less tendency to sorb to or react with them. This comparison indicates that rubber and silicone materials have much higher sorption capacities, likely resulting from a combination of more porosity and more surface area, in addition to hydrophobic and electrostatic interactions between 6PPDQ and material surfaces, or compounds present on the surfaces of these materials, that affect sorbent capacities.(50)

These results provide a general guideline for material selection for aqueous phase samples containing 6PPDQ in lab studies and field sampling events. For short-term contact events, glass, stainless steel and PTFE labware and containers are preferred options. For long-term storage or sample transport, glass would be the best material to handle 6PPDQ aqueous solutions in the lab operations and sampling processes, with solvent rinsing becoming especially important for other materials. We also note a consistent inability (at least by us) to fully recover all spiked 6PPDQ mass in these example systems with various types of materials (e.g., all the tested materials except glass; including plastic, rubber, silicone and stainless steel) following preliminary extraction (30 min methanol sonication extraction). The potential for strong surface interactions or chemical instability, leading to low bias in dissolved concentrations, seems to exist for some experimental conditions and remains a data gap. The results also indicate that suspended particles in the environment, especially various microplastic particles (e.g., plastic debris or waste) may sorb, accumulate, and transport 6PPDQ in the environment.(51)

Leaching dynamics. Physical properties of the TWP used here were measured via BET, yielding a specific surface area of 5.88±0.66 m^2/g, median particle diameter (d_{50}) of 232 μm and a uniformity coefficient (d_{60}/d_{10}) of 3.21 (**Figure S5**). Note that these measurements are substantially dependent on the tire material, TWP preparation method, TWP shape, size and morphology, and therefore might be subject to large variance for different tested TWP. Nevertheless, Fan et al reported a 0.3-16.65 m^2/g BET-specific surface area measured on TWP during UV aging processes, aligned with current measurements(46). The BET-specific surface area indicated that the tire rubber materials were porous,(52) and measured particle sizes of this laboratory generated were slightly larger than reports for tire-road wear particles (TRWP; 20-100 μm for most particles) that were agglomerations of tire rubber particles and roadway materials.(11,13) The 6 h flow-through leaching system employed here simulated short-term leaching of TWP; for example, the timescale of a rainstorm event on a roadway surface. Over the 6 hours of leaching 250 mg of TWP, 6PPDQ leachate concentrations decreased 50% (6PPDQ concentration in collected leachates: 125±20 ng/L at 15 min decreasing to 60±9 ng/L at 6 hr, **Figure 3A**). Given the complex surface characteristics of the TWP and high flow rate, one dimensional leaching dynamics were assumed and the data was fit to an empirical first-order kinetic model with the following assumptions: a) 6PPDQ dissolution is the dominant surface reaction during leaching; b) the column is an ideal, well mixed reactor with no dispersion; and c) TWP surface-associated 6PPDQ instantaneously equilibrates with the leachate.

Based on these assumptions, leachate concentrations would be calculated:

$$V\frac{dC_{leachate}}{dt} = k_{diss}C_{TWP}A_{TWP} - QC_{leachate} \qquad \text{(Eq. 1)}$$

where V is the reactor volume (mL), Q is leachate flow rate (mL/min), $C_{leachate}$ is the leachate 6PPDQ concentration (ng/mL; assuming column concentration equals outlet concentration), t is the leaching time (min), C_{TWP} is the surface area normalized 6PPDQ concentration (ng/cm^2) and A_{TWP} is the surface area of TWP (cm^2); k_{diss} is the empirical first-order kinetic rate constant (min^{-1}). Integrating and solving Equation 1 yields:

$$M_{leachate} = M_{TWP} * (1 - exp\,(k_{diss}t)) \qquad \text{(Eq. 2)}$$

where M is surface area normalized mass of 6PPDQ (ng/cm^2), $M_{leachate}$ and M_{TWP} are the cumulative mass leached and total surficial mass available on TWP for leaching (converted from 6PPDQ leachate concentration using BET surface area); k_{diss} is the empirical first-order kinetic rate constant (min^{-1}) and t is leaching time (min).

A regression of the cumulative 6PPDQ mass data was fitted to Equation 2 and the confidence interval of the coefficients was calculated from the covariance matrix **(Text S4)**.(53) The measured cumulative leached mass was 0.086±0.005 ng/cm^2 6PPDQ (equivalent to 5.15±0.3 ug 6PPDQ per g TWP) over 6 hours of leaching.(54) There was good agreement between observed and modeled data, with no statistically significant differences between them (t-test; p-value>0.05; **Figure 3B**), indicating the leaching process under tested conditions was dominated by kinetics of 6PPDQ dissolution from the TWP surface. The 6PPDQ leaching dynamics under the studied conditions can be therefore described by Equation 3:

$$M_{Cumulative} = 0.135 * (1 - \exp\,(0.0027t)) \qquad \text{(Eq. 3)}$$

The predicted first-order dissolution rate constant is 0.0027±0.0005 min^{-1}. Based on the regression model and assuming unlimited time for leaching, the total surficial 6PPDQ mass available for leaching is predicted at 0.135±0.021 ng/cm^2 (7.14±1.3 µg 6PPDQ per gram TWP). In comparison, solvent extraction with methanol of this TWP yielded 15.6±1.3 µg 6PPDQ per gram TWP, which translates to 0.295±0.025 ng/cm^2 (**Text S2**). The solvent extractable 6PPDQ measured here aligned well with reports of Masset et al. (14 µg 6PPDQ per gram cryogenically milled tire tread)(55). These data indicate ~46% of the total surficial 6PPDQ mass was water leachable over 6 hours. Note here that these estimates do not consider formation of additional 6PPDQ upon continued 6PPD reaction with ozone or long-term TMP dynamics. Therefore, the total leachable 6PPDQ of TWP over its service life would be much higher than above estimates considering the substantial amount of 6PPD used in tires and expectations for slow diffusion rates (1.39×10^{-8} - 8.56×10^{-8} cm^2/s) reported for 6PPD through rubber phases.(28) Such processes will ultimately regenerate 6PPDQ via oxidative reactions on tire rubber surfaces to act as a continuing environmental source of 6PPDQ.(26)

6PPDQ concentrations in tire leachate over time fit first-order kinetics (k_{diss}=0.0027±0.0005 min^{-1}) without any obvious lag period. Similar rapid leaching dynamics seem likely for storm events where 6PPDQ dissolution into runoff happens quickly (<15min) and concentrations are maintained above effective toxic levels throughout the storm event (a few hours up to a day) by continued leaching. Complementing roadway runoff sources, TWP may themselves transport through the environment and act as a diffuse and continuing source of contaminants.

Aqueous stability and pH. After 6PPDQ is leached, it is expected to transport into surface waters via roadway runoff and presumably minor pathways such as deposition of atmospheric particulates. The stability of 6PPDQ in aqueous solutions such as roadway runoff and surface waters is consequently important to the potential for adverse environmental effects.(16) Here, noting the rapid, pH-dependent transformation in aqueous solution reported for the parent 6PPD(26), the aqueous stability of 6PPDQ in deionized water was tested over 47 days at pH 5, 7 and 9 at 20-22 °C (**Figure 4**). Over 3 days, no significant loss was observed for any pH condition (two-tailed t-test; *p*-value = 0.84 for pH 5, 0.19 for pH 7 and 0.31 for pH 9). At 14 days, 6PPDQ was generally stable, with no obvious change in concentration in pH 5 and pH 9 (p-value = 0.11 for pH 5; 0.06 for pH 9). The pH 7 group significantly decreased (p-value = 0.03) with 15% concentration reduction. At 47 days, 6PPDQ concentrations exhibited a 26±10% decrease on average (p-values >0.05 for all groups). In general, 6PPDQ appears to be stable in simple aqueous systems, although Hiki et al., reported a much shorter 33 hr half-life for 6PPDQ at 23 °C in dechlorinated tap water.(29) Fohet et al.(56) also reported concentration evolutions of 6PPDQ in tire and road wear particles under different conditions (photoaging τ_{photo}=9.6days, natural aging $\tau_{outdoor}$=9.6days and no thermoaging decrease were observed), suggesting moderate environmental stability of 6PPDQ. Obviously, as solution complexity increases (e.g., co-contaminants, natural organic matter, microbiota, redox active constituents and solid phases), the potential for reactive loss would increase substantially. Solution factors promoting instability remain important research needs for 6PPDQ and other similar roadway contaminants.

6PPDQ roadway mass balances. Kole et al.(57) estimated 1,250,000-1,800,000 metric tons TRWP/year release in the U.S. Using the mass distribution of TRWP of Wagner et al.(11), 45-77% of total TRWP will be retained on the roadside. If roadway residual TRWP consists of 50% tire rubber, 280,000-690,000 metric tons TWP/year is deposited to the road and available for localized leaching. Using measurements from this study, 7.14±1.3 (by aqueous leaching model) to 15.6±1.3 (by solvent extraction) µg of surficial 6PPDQ is available per gram TWP, yielding a minimum of 2000 to 10800 kg surficial 6PPDQ/year. According to the 2020 Department of Transportation statistics(58), total road lane length of the U.S highways is

14,200,000 km; with lane width of 3.7 meters (12 feet), the estimated total highway area for the US is 52,600 km^2. At average precipitation rate of 769 mm/year(59) and assuming a runoff coefficient of 0.85,(60) we estimate an average roadway runoff volume of 3.44×10^{13} L/year on U.S. roadways. Using these estimates, average 6PPDQ concentrations in roadway runoff would range from 60-310 ng/L. We note that the above calculation only considers TRWP as a source of TWP-derived contaminants; contributions from whole tire surfaces on vehicles and other sources would increase these values. We also note this estimate does not consider regeneration of 6PPDQ (as 6PPD continues to react with ozone), does not consider possible differences in surface area available for leaching mass across tires, TWP, and TRWP, does not account for non-roadway TRWP, and does not consider any attenuation (**Text S5**). The prediction is of the same magnitude as our previous observations.(19) Although such models and assumptions still require substantial further refinement and data collection to address the many data gaps existing for the 6PPDQ environmental mass balance, it is clear that risk thresholds to sensitive species are easily attainable, especially for areas with substantial traffic and roadway runoff impact.(19,29,61,62)

Environmental implications. This study investigated basic chemical properties (logK_{OW} and solubility), leaching, and aqueous stabilities of 6PPDQ. Agreeing reasonably well with software predictions, we observed a moderately high logK_{OW} (4.30±0.02) for 6PPDQ, but far lower aqueous solubility (38.4 μg/L) than expected by software prediction. Nevertheless, the aqueous solubility of 6PPDQ easily exceeds the reported LC_{50} value for coho salmon(19). Stability experiments suggested relatively high stability of 6PPDQ over 14 d but some

(26±10%) loss over 47 d in simple deionized water systems.

6PPDQ sorption studies provided a guideline for materials selection during sampling and sample processing. Specifically, glass is recommended for lab operations and storage if possible. For short-term contact, such as transport or field sampling, chemically inert plastics (PTFE and FEP) are likely acceptable as tubing materials or containers (<10% sorption observed during 5 min contact time), although solvent rinsing for recovery of sorbed 6PPDQ may be needed as contact times grow. Extra caution may be needed for rubbers and silicon materials in contact with 6PPDQ (e.g., rubber stoppers, silicone fittings), as these materials can strongly sorb 6PPDQ from aqueous solution (up to 92% 6PPDQ sorption during 30 min) with substantial unrecoverable mass, even using standard methanol rinsing procedures.

During 6 hr leaching tests, a cumulative leached mass of 0.086±0.005 ng/cm^2 6PPDQ (5.15±0.3 ug 6PPDQ per g TWP; k_{diss}=0.0027±0.0005 min^{-1}) was observed, indicating expected reasonably rapid discharge of 6PPDQ into roadway runoff during storms. Extending these data to estimates of TRWP on roadways yielded predictions of 60-310 ng/L of TRWP-derived 6PPDQ in roadway runoff, although there currently exist very few confident and well-validated estimates of TWP, TRWP and tire rubber phases on roadways and none reflecting whole tire sources to the best of our knowledge.(13,15,57)

While the measured attributes above are helpful, there still exist many substantial data gaps around characteristics, environmental fate and transport of 6PPDQ, including the partitioning behavior of 6PPDQ into sediments and soil, biological availability of 6PPDQ to aquatic organisms and human exposure risks of 6PPDQ. Further investigations are merited to understand the roles of dissolved organic matter and other solution components in modulating 6PPDQ dissolution and partitioning behavior as examined in current studies. Investigation of TWP surface chemistry dynamics during leaching, related sorption processes, and 6PPDQ transformation mechanisms in more complex aqueous solutions (with natural organic matter, co-constituents, and biota) will also provide critical information needed to evaluate 6PPDQ environmental fate and risks. These data will all help to guide field measurements and improved characterization of TWP, roadway runoff, and receiving waters to understand locations and time periods of maximum discharge that will enable the short-term management of environmental risks arising from the occurrence of highly toxic, and ubiquitous, 6PPDQ in roadway runoff.

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Supporting Information Statement. Supporting Information 1: Additional experimental details, instrument methods, data processing methods and 6PPDQ mass balance calculations (DOC).

REFERENCES

1. Ahamad A, Madhav S, Singh AK, Kumar A, Singh P. Types of Water Pollutants: Conventional and Emerging. In: Pooja D, Kumar P, Singh P, Patil S, editors. Sensors in Water Pollutants Monitoring: Role of Material [Internet]. Singapore: Springer; 2020 [cited 2021 Jun 24]. p. 21–41. (Advanced Functional Materials and Sensors). Available from: https://doi.org/10.1007/978-981-15-0671-0_3
2. Kroiss H, Rechberger H, Egle L. Phosphorus in Water Quality and Waste Management [Internet]. Integrated Waste Management - Volume II. IntechOpen; 2011 [cited 2021 Jul 2]. Available from: https://www.intechopen.com/books/integrated-waste-management-volume-ii/phosphorus-in-water-quality-and-waste-management
3. Puckett LJ. Identifying the major sources of nutrient water pollution. 1995;7.
4. Corsi SR, Graczyk DJ, Geis SW, Booth NL, Richards KD. A Fresh Look at Road Salt: Aquatic Toxicity and Water-Quality Impacts on Local, Regional, and National Scales. Environ Sci Technol. 2010 Oct 1;44(19):7376–82.
5. Braukmann U, Böhme D. Salt pollution of the middle and lower sections of the river Werra (Germany) and its impact on benthic macroinvertebrates. Limnologica. 2011 May 1;41(2):113–24.
6. Zhou Q, Yang N, Li Y, Ren B, Ding X, Bian H, et al. Total concentrations and sources of heavy metal pollution in global river and lake water bodies from 1972 to 2017. Glob Ecol Conserv. 2020 Jun 1;22:e00925.
7. Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ. Heavy Metals Toxicity and the Environment. EXS. 2012;101:133–64.
8. Peter KT, Hou F, Tian Z, Wu C, Goehring M, Liu F, et al. More Than a First Flush: Urban Creek Storm Hydrographs Demonstrate Broad Contaminant Pollutographs. Environ Sci Technol. 2020 May 19;54(10):6152–65.
9. Peter KT, Tian Z, Wu C, Lin P, White S, Du B, et al. Using High-Resolution Mass Spectrometry to Identify Organic Contaminants Linked to Urban Stormwater Mortality Syndrome in Coho Salmon. Environ Sci Technol. 2018 Sep 18;52(18):10317–27.
10. Hou F, Tian Z, Peter KT, Wu C, Gipe AD, Zhao H, et al. Quantification of organic contaminants in urban stormwater by isotope dilution and liquid chromatography-tandem mass spectrometry. Anal Bioanal Chem. 2019 Nov;411(29):7791–806.
11. Wagner S, Hüffer T, Klöckner P, Wehrhahn M, Hofmann T, Reemtsma T. Tire wear particles in the aquatic environment - A review on generation, analysis, occurrence, fate and effects. Water Res. 2018 Aug 1;139:83–100.
12. Alhelou R, Seiwert B, Reemtsma T. Hexamethoxymethylmelamine – A precursor of persistent and mobile contaminants in municipal wastewater and the water cycle. Water Res. 2019 Nov;165:114973.
13. Klöckner P, Seiwert B, Weyrauch S, Escher BI, Reemtsma T, Wagner S. Comprehensive characterization of tire and road wear particles in highway tunnel road dust by use of size and density fractionation. Chemosphere. 2021 Sep 1;279:130530.
14. Kumata H, Yamada J, Masuda K, Takada H, Sato Y, Sakurai T, et al. Benzothiazolamines

as Tire-Derived Molecular Markers: Sorptive Behavior in Street Runoff and Application to Source Apportioning. Environ Sci Technol. 2002 Feb 1;36(4):702–8.

15. Unice KM, Bare JL, Kreider ML, Panko JM. Experimental methodology for assessing the environmental fate of organic chemicals in polymer matrices using column leaching studies and OECD 308 water/sediment systems: Application to tire and road wear particles. Sci Total Environ. 2015 Nov 15;533:476–87.
16. Tian Z, Zhao H, Peter KT, Gonzalez M, Wetzel J, Wu C, et al. A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon. Science. 2021 Jan 8;371(6525):185–9.
17. Klöckner P, Seiwert B, Wagner S, Reemtsma T. Organic Markers of Tire and Road Wear Particles in Sediments and Soils: Transformation Products of Major Antiozonants as Promising Candidates. Environ Sci Technol [Internet]. 2021 Aug 17 [cited 2021 Aug 25]; Available from: https://doi.org/10.1021/acs.est.1c02723
18. Seiwert B, Nihemaiti M, Troussier M, Weyrauch S, Reemtsma T. Abiotic oxidative transformation of 6-PPD and 6-PPD quinone from tires and occurrence of their products in snow from urban roads and in municipal wastewater. Water Res. 2022 Apr 1;212:118122.
19. Tian Z, Gonzalez M, Rideout C, Zhao H, Hu X, Wetzel J, et al. 6PPD-Quinone: Revised Toxicity Assessment and Quantification Method Development with a Commercial Standard. Environ Sci Technol Lett. 2021 Oct 27;
20. Zhang Y, Xu C, Zhang W, Qi Z, Song Y, Zhu L, et al. p-Phenylenediamine Antioxidants in PM2.5: The Underestimated Urban Air Pollutants. Environ Sci Technol [Internet]. 2021 Sep 22 [cited 2021 Nov 1]; Available from: https://doi.org/10.1021/acs.est.1c04500
21. Wang W, Cao G, Zhang J, Wu P, Chen Y, Chen Z, et al. Beyond Substituted p-Phenylenediamine Antioxidants: Prevalence of Their Quinone Derivatives in PM2.5. Environ Sci Technol. 2022 Aug 2;56(15):10629–37.
22. Huang W, Shi Y, Huang J, Deng C, Tang S, Liu X, et al. Occurrence of Substituted p-Phenylenediamine Antioxidants in Dusts. Environ Sci Technol Lett [Internet]. 2021 Apr 6 [cited 2021 May 25]; Available from: https://pubs.acs.org/doi/pdf/10.1021/acs.estlett.1c00148
23. Du B, Liang B, Li Y, Shen M, Liu LY, Zeng L. First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China. Environ Sci Technol Lett [Internet]. 2022 Nov 21 [cited 2022 Dec 23]; Available from: https://pubs.acs.org/doi/pdf/10.1021/acs.estlett.2c00821
24. Sheridan M. The Vanderbilt Rubber Handbook. Norwalk, CT: R.T. Vanderbilt Company, Inc.; 2010. (14th edition).
25. Councell TB, Duckenfield KU, Landa ER, Callender E. Tire-Wear Particles as a Source of Zinc to the Environment. Environ Sci Technol. 2004 Aug 1;38(15):4206–14.
26. OSPAR Commission. OSPAR background document on 4-(dimethylbutylamino)diphenylamine (6PPD). 2006c.
27. Drzyzga O. Diphenylamine and derivatives in the environment: a review. Chemosphere. 2003 Dec;53(8):809–18.

28. Huntink NM. Durability of rubber products: Development of new antidegradants for long-term protection. 2003 Nov 7 [cited 2021 May 25]; Available from: https://research.utwente.nl/en/publications/durability-of-rubber-products-development-of-new-antidegradants-f

29. Hiki K, Asahina K, Kato K, Yamagishi T, Omagari R, Iwasaki Y, et al. Acute Toxicity of a Tire Rubber-Derived Chemical, 6PPD Quinone, to Freshwater Fish and Crustacean Species. Environ Sci Technol Lett [Internet]. 2021 Aug 10 [cited 2021 Aug 25]; Available from: https://doi.org/10.1021/acs.estlett.1c00453

30. OECD. Guidance Document on Aquatic Toxicity Testing of Difficult Substances and Mixtures [Internet]. Paris: Organisation for Economic Co-operation and Development; 2019 [cited 2022 Jan 24]. Available from: https://www.oecd-ilibrary.org/environment/guidance-document-on-aquatic-toxicity-testing-of-difficult-substances-and-mixtures_0ed2f88e-en

31. USEPA. DETERMINATION OF OCTANOL/WATER DISTRIBUTION COEFFICIENTS, WATER SOLUBILITIES, AND SEDIMENT/WATER PARTITION COEFFICIENTS FOR HYDROPHOBIC ORGANIC POLLUTANTS [Internet]. 1979 [cited 2022 Jan 24]. Available from: https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NERL&dirEntryId=45876&fed_org_id=770&SIType=PR&TIMSType=&showCriteria=0&address=nerl&view=citation&keyword=Water&sortBy=pubDateYear&count=100&dateBeginPublishedPresented=

32. Quantification of organic contaminants in urban stormwater by isotope dilution and liquid chromatography-tandem mass spectrometry | SpringerLink [Internet]. [cited 2021 May 21]. Available from: https://link.springer.com/article/10.1007/s00216-019-02177-3

33. Su G, Letcher RJ, Yu H. Organophosphate Flame Retardants and Plasticizers in Aqueous Solution: pH-Dependent Hydrolysis, Kinetics, and Pathways. Environ Sci Technol. 2016 Aug 2;50(15):8103–11.

34. Seung Lim J. EPI Suite: A Fascinate Predictive Tool for Estimating the Fates of Organic Contaminants | OMICS International [Internet]. 2016 [cited 2021 Aug 25]. Available from: https://www.omicsonline.org/open-access/epi-suite-a-fascinate-predictive-tool-for-estimating-the-fates-of-organiccontaminants-2155-6199-1000e171.php?aid=70728

35. ChemAxon - Software Solutions and Services for Chemistry & Biology [Internet]. [cited 2021 Aug 25]. Available from: https://chemaxon.com/

36. HILAL, S. H. Estimation of Physical Properties and Chemical Reactivity Parameters of Organic Compounds for Environmental Modeling by SPARC [Internet]. [cited 2022 Feb 26]. Available from: https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NERL&dirEntryId=203108

37. Kuhn B, Mohr P, Stahl M. Intramolecular Hydrogen Bonding in Medicinal Chemistry. J Med Chem. 2010 Mar 25;53(6):2601–11.

38. Burke J. Solubility Parameters: Theory and Application [Internet]. The Book and Paper Group of the American Institute for Conservation; 1984 [cited 2022 Nov 22]. Available from: https://cool.culturalheritage.org/coolaic/sg/bpg/annual/v03/bp03-04.html

39. Tuttle MR, Davis ST, Zhang S. Synergistic Effect of Hydrogen Bonding and π–π Stacking Enables Long Cycle Life in Organic Electrode Materials. ACS Energy Lett. 2021 Feb

12;6(2):643–9.

40. Sieuw L, Jouhara A, Quarez É, Auger C, Gohy JF, Poizot P, et al. A H-bond stabilized quinone electrode material for Li–organic batteries: the strength of weak bonds. Chem Sci. 2019 Jan 2;10(2):418–26.
41. Hu X, Zhao HN, Tian Z, Peter KT, Dodd MC, Kolodziej EP. Transformation Product Formation upon Heterogeneous Ozonation of the Tire Rubber Antioxidant 6PPD (N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine). Environ Sci Technol Lett. 2022 May 10;9(5):413–9.
42. Cao G, Wang W, Zhang J, Wu P, Zhao X, Yang Z, et al. New Evidence of Rubber-Derived Quinones in Water, Air, and Soil. Environ Sci Technol. 2022 Apr 5;56(7):4142–50.
43. McKim J, Schmieder P, Veith G. Absorption dynamics of organic chemical transport across trout gills as related to octanol-water partition coefficient. Toxicol Appl Pharmacol. 1985 Jan 1;77(1):1–10.
44. Shen J, Amirkhanian S, Xiao F, Tang B. Influence of surface area and size of crumb rubber on high temperature properties of crumb rubber modified binders. Constr Build Mater. 2009 Jan 1;23(1):304–10.
45. Zhang Y, Liu Z, Peng J. Silane Modification of Crumb Rubber on the Rheological Properties of Rubberized Asphalt. Appl Sci. 2019 Jan;9(22):4831.
46. Fan X, Ma Z, Zou Y, Liu J, Hou J. Investigation on the adsorption and desorption behaviors of heavy metals by tire wear particles with or without UV ageing processes. Environ Res. 2021 Apr 1;195:110858.
47. Kasner AI, Meinecke EA. Porosity in Rubber, a Review. Rubber Chem Technol. 1996 Jul 1;69(3):424–43.
48. Angelin AF, Lintz RCC, Gachet-Barbosa LA, Osório WR. The effects of porosity on mechanical behavior and water absorption of an environmentally friendly cement mortar with recycled rubber. Constr Build Mater. 2017 Oct 1;151:534–45.
49. Rostami-Tapeh-Esmaeil E, Vahidifar A, Esmizadeh E, Rodrigue D. Chemistry, Processing, Properties, and Applications of Rubber Foams. Polymers. 2021 May 13;13(10):1565.
50. Joo SH, Liang Y, Kim M, Byun J, Choi H. Microplastics with adsorbed contaminants: Mechanisms and Treatment. Environ Chall. 2021 Apr 1;3:100042.
51. Müller A, Kocher B, Altmann K, Braun U. Determination of tire wear markers in soil samples and their distribution in a roadside soil. Chemosphere. 2022 May 1;294:133653.
52. Milani M, Pucillo FP, Ballerini M, Camatini M, Gualtieri M, Martino S. First evidence of tyre debris characterization at the nanoscale by focused ion beam. Mater Charact. 2004 Jul 1;52(4):283–8.
53. Cai TT, Liang T, Zhou HH. Law of log determinant of sample covariance matrix and optimal estimation of differential entropy for high-dimensional Gaussian distributions. J Multivar Anal. 2015 May 1;137:161–72.
54. Monaghan J, Jaeger A, Agua AR, Stanton RS, Pirrung M, Gill CG, et al. A Direct Mass Spectrometry Method for the Rapid Analysis of Ubiquitous Tire-Derived Toxin N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine Quinone (6-PPDQ). Environ Sci Technol Lett. 2021 Dec 14;8(12):1051–6.

55. Masset T, Ferrari BJD, Dudefoi W, Schirmer K, Bergmann A, Vermeirssen E, et al. Bioaccessibility of Organic Compounds Associated with Tire Particles Using a Fish In Vitro Digestive Model: Solubilization Kinetics and Effects of Food Coingestion. Environ Sci Technol. 2022 Nov 15;56(22):15607–16.
56. Fohet L, Andanson JM, Charbouillot T, Malosse L, Leremboure M, Delor-Jestin F, et al. Time-concentration profiles of tire particle additives and transformation products under natural and artificial aging. Sci Total Environ. 2023 Feb 10;859:160150.
57. Kole PJ, Löhr AJ, Van Belleghem FGAJ, Ragas AMJ. Wear and Tear of Tyres: A Stealthy Source of Microplastics in the Environment. Int J Environ Res Public Health. 2017 Oct 20;14(10).
58. Highway Statistics 2020 - Policy | Federal Highway Administration [Internet]. [cited 2022 Dec 14]. Available from: https://www.fhwa.dot.gov/policyinformation/statistics/2020/
59. Annual 2020 National Climate Report | National Centers for Environmental Information (NCEI) [Internet]. [cited 2022 Dec 28]. Available from: https://www.ncdc.noaa.gov/sotc/national/202013
60. Stormwater Design Manual | NC DEQ [Internet]. [cited 2022 Dec 28]. Available from: https://deq.nc.gov/about/divisions/energy-mineral-and-land-resources/stormwater/stormwater-program/stormwater-design
61. Feist BE, Buhle ER, Baldwin DH, Spromberg JA, Damm SE, Davis JW, et al. Roads to ruin: conservation threats to a sentinel species across an urban gradient. Ecol Appl. 2017;27(8):2382–96.
62. Brinkmann M, Montgomery D, Selinger S, Miller JGP, Stock E, Alcaraz AJ, et al. Acute Toxicity of the Tire Rubber-Derived Chemical 6PPD-quinone to Four Fishes of Commercial, Cultural, and Ecological Importance. Environ Sci Technol Lett. 2022 Apr 12;9(4):333–8.

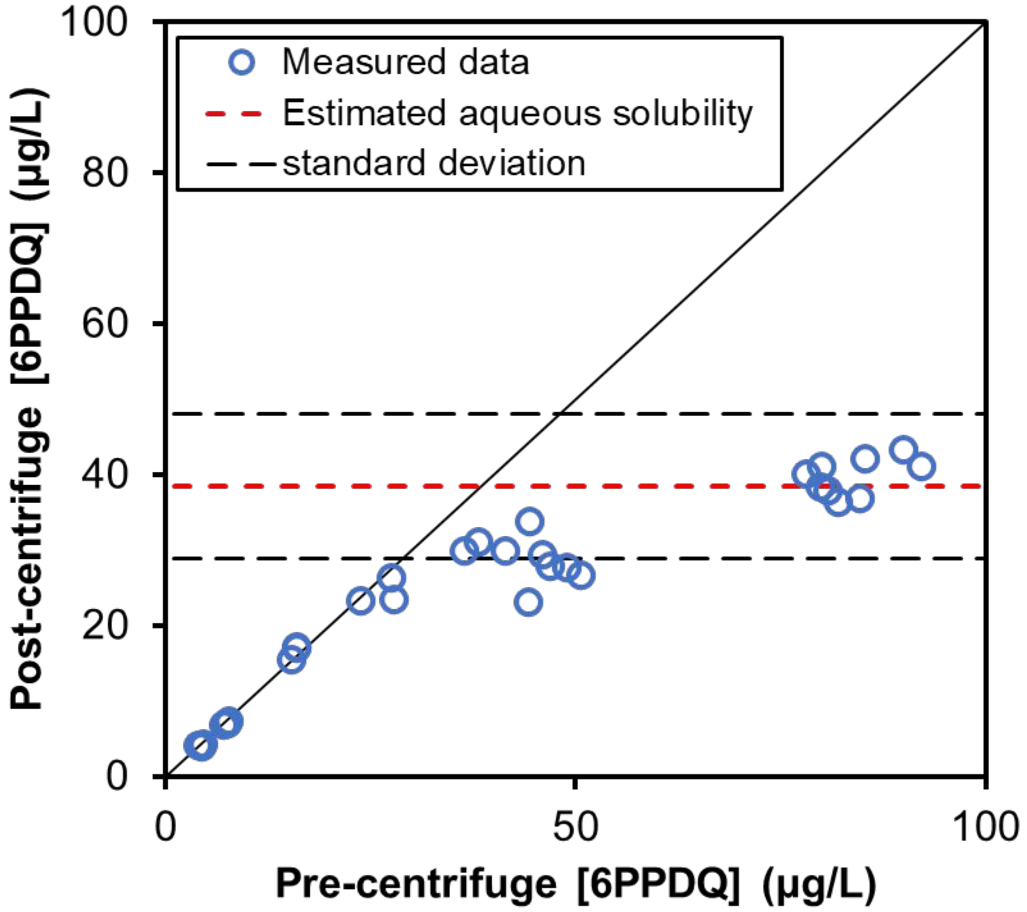


Figure 1. 6PPDQ aqueous solubility measurements after overnight (>12 hrs) mixing and sonication (30 min). Each datapoint corresponds to 6PPDQ measurements for an individual sample before and after centrifugation. The diagonal line represents a complete dissolution scenario (1:1 pre- versus post-centrifugation 6PPDQ concentrations). The red dashed line represents the average estimate of 6PPDQ aqueous solubility (38.4 µg/L). The black dashed lines represent one standard deviation above and below the estimated aqueous solubility.

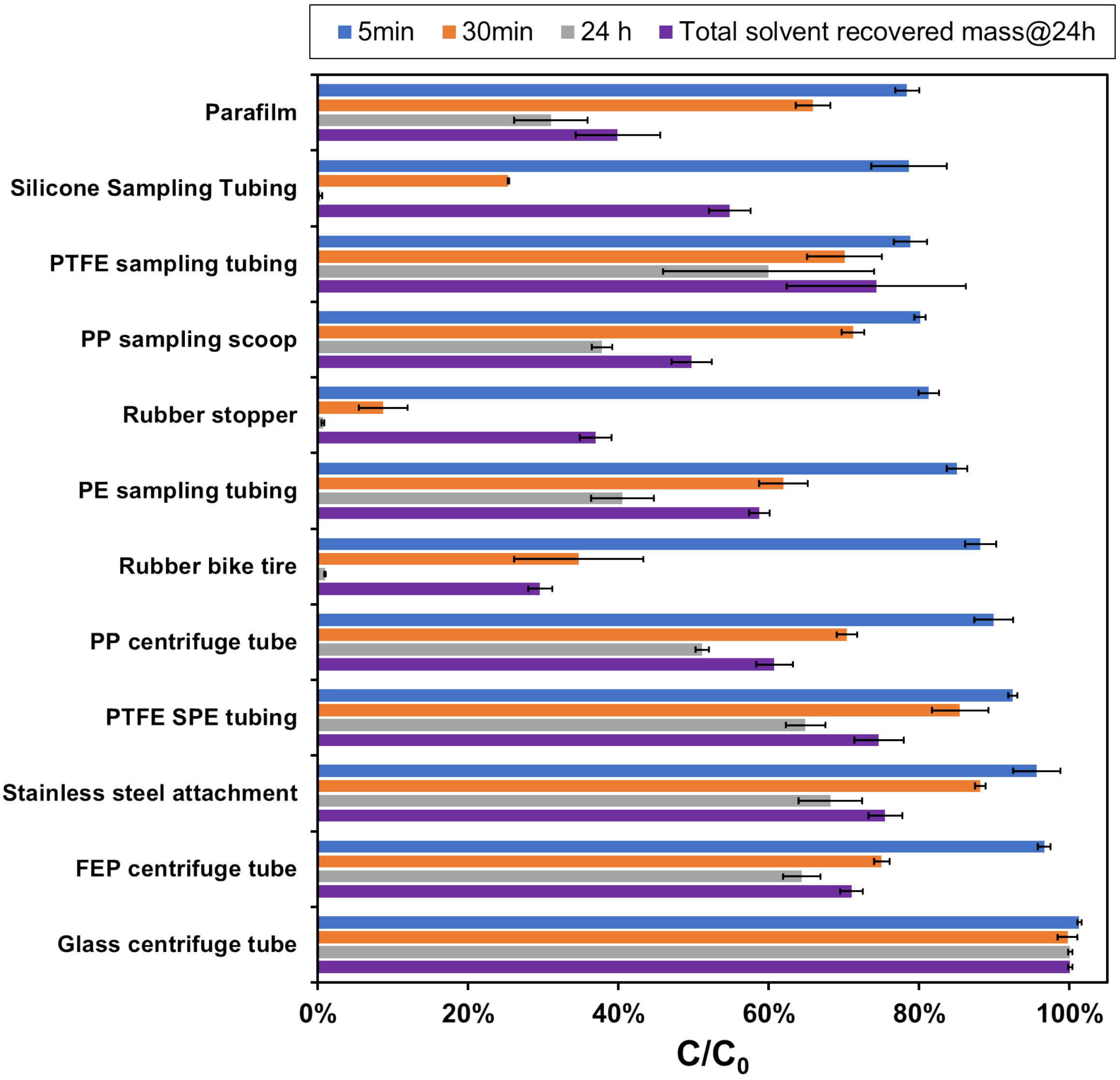
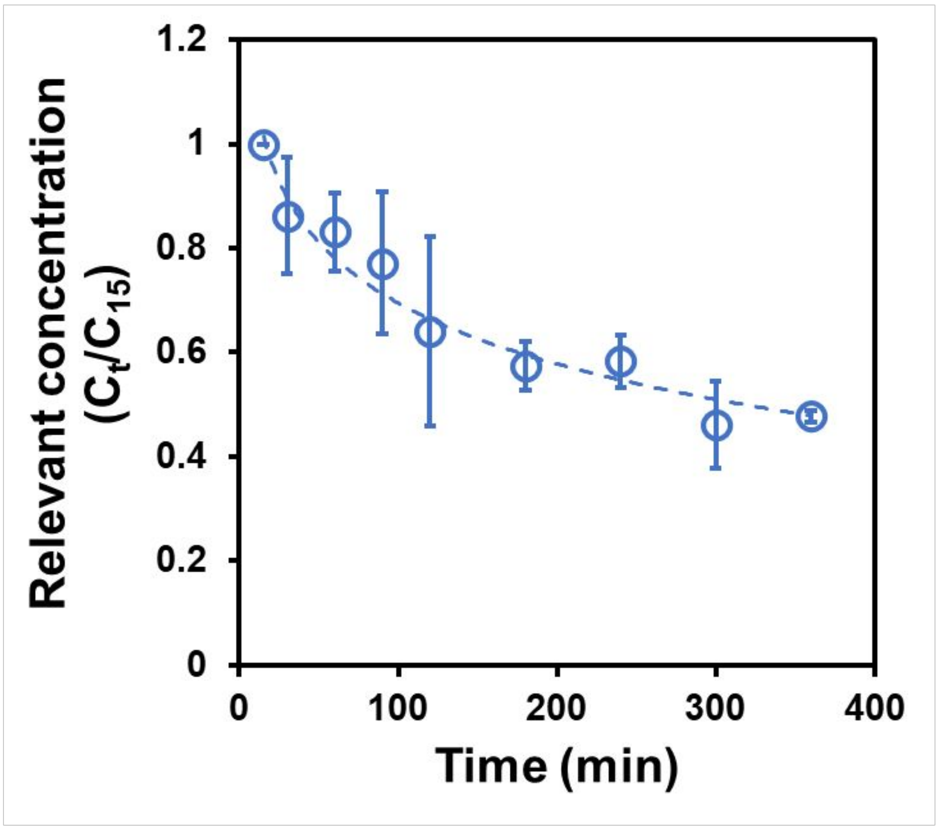


Figure 2. Sorption losses of 6PPDQ to different materials over 24 hours. Relative concentrations (C/C$_o$) were derived by comparing residual aqueous 6PPDQ concentrations to initial 6PPDQ concentrations in the aqueous stock (5 µg/L) used for the tests. Error bars correspond to standard deviations about the mean from three replicate samples.

A


1.2
1
0.8
0.6
0.4
0.2
0
Relevant concentration (C_t/C_{15})
0
100
200
300
400
Time (min)

B

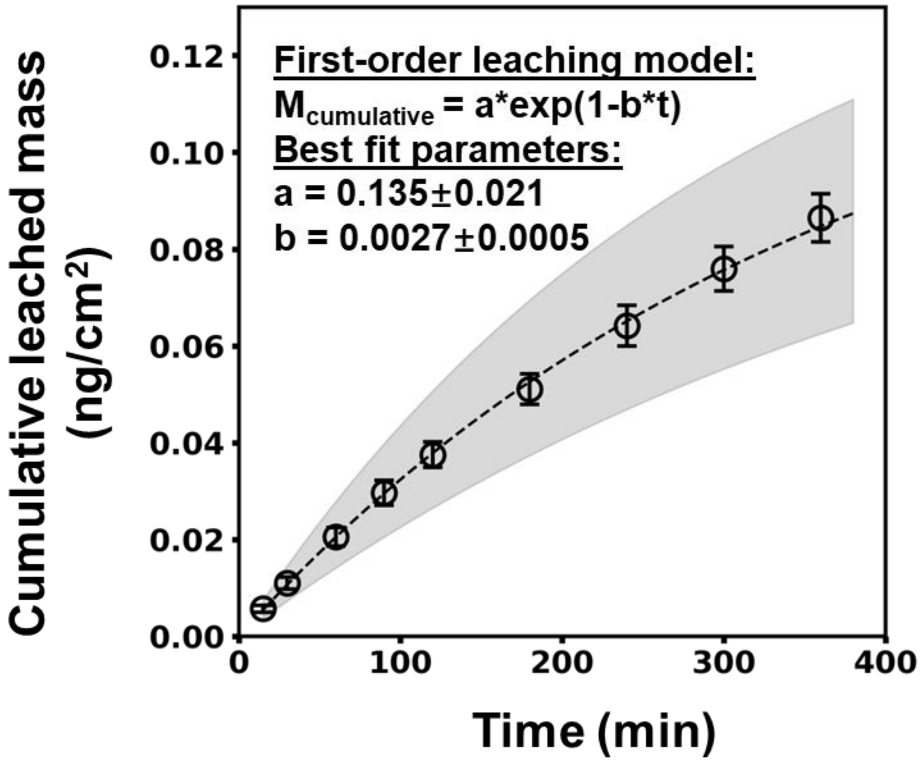

First-order leaching model:
$M_{cumulative}$ = a*exp(1-b*t)
Best fit parameters:
a = 0.135±0.021
b = 0.0027±0.0005
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Cumulative leached mass (ng/cm^2)
0
100
200
300
400
Time (min)

Figure 3. 6PPDQ aqueous leaching kinetics from TWPs over 6 hours in a flow through column system (flow rate = 45 mL/min). (A) 6PPDQ aqueous concentration vs time, normalized to the observed "initial" concentration measured at 15 minutes. (B) Cumulative surface area normalized mass of 6PPDQ leached into aqueous solution over time. Error bars represent standard deviation about the mean from three replicate samples; dashed lines in both figures represent regression fit of the data points; shaded boundaries represent 95% confidence intervals.

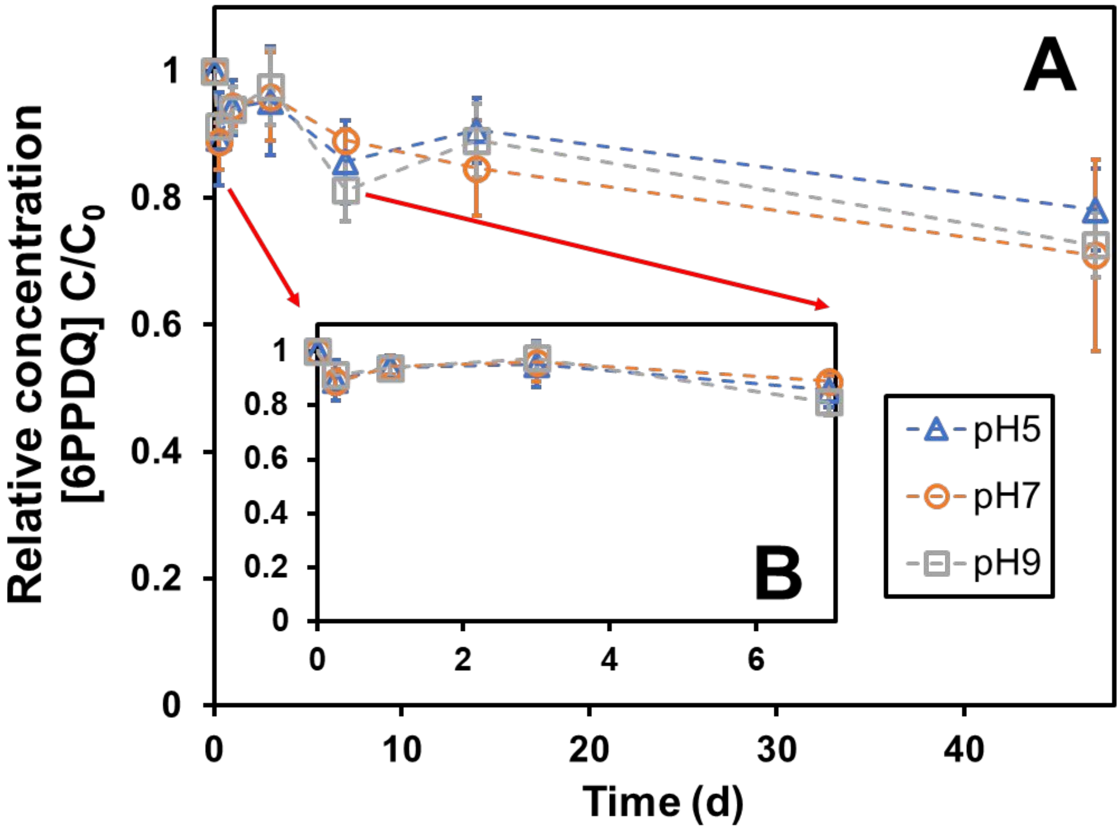


Figure 4. 6PPDQ stability in 10 mM aqueous phosphate buffer at pH 5, 7 and 9. (A) Long-term 6PPDQ stability over 47 d (t-test t_0 vs. t_{47}: p-value=0.023, 0.045 and 0.001 for pH 5, 7 and 9, respectively), and (B) short-term 6PPDQ stability over 7 d (t-test t_0 vs. t_7: p-value=0.097, 0.002 and 0.005 for pH 5, 7 and 9, respectively). Error bars represent standard deviations about the mean from triplicate samples.