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Screening *p*-Phenylenediamine Antioxidants, Their Transformation Products, and Industrial Chemical Additives in Crumb Rubber and Elastomeric Consumer Products

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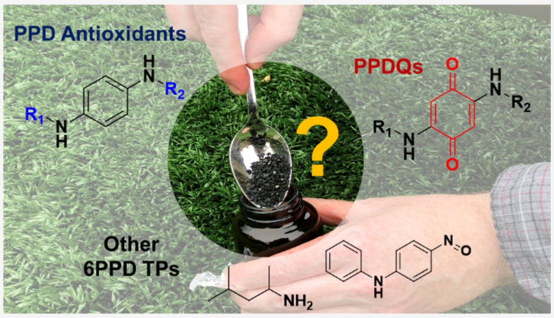
ABSTRACT: Recently, roadway releases of *N*,*N*′-substituted *p*-phenylenediamine (PPD) antioxidants and their transformation products (TPs) received significant attention due to the highly toxic 6PPD-quinone. However, the occurrence of PPDs and TPs in recycled tire rubber products remains uncharacterized. Here, we analyzed tire wear particles (TWPs), recycled rubber doormats, and turf-field crumb rubbers for seven PPD antioxidants, five PPD-quinones (PPDQs), and five other 6PPD TPs using liquid chromatography-tandem mass spectrometry. PPD antioxidants, PPDQs, and other TPs were present in all samples with chemical profiles dominated by 6PPD, DTPD, DPPD, and their corresponding PPDQs. Interestingly, the individual [PPDQ]/[PPD] and [TP]/[PPD] ratios significantly increased as total concentrations of the PPD-derived chemical decreased, indicating that TPs (including PPDQs) dominated the PPD-derived compounds with increased environmental weathering. Furthermore, we quantified 15 other industrial rubber additives (including bonding agents, vulcanization accelerators, benzotriazole and benzothiazole derivatives, and diphenylamine antioxidants), observing that PPD-derived chemical concentrations were 0.5−6 times higher than these often-studied additives. We also screened various other elastomeric consumer products, consistently detecting PPD-derived compounds in lab stoppers, sneaker soles, and rubber garden hose samples. These data emphasize that PPD antioxidants, PPDQs, and related TPs are important, previously overlooked contaminant classes in tire rubbers and elastomeric consumer products.



KEYWORDS: *PPD antioxidants, PPD-quinones, crumb rubber, elastomeric consumer products, environmental contaminants, weathering*

■ INTRODUCTION

N,*N*′-Substituted *p*-phenylenediamines (PPDs) are widely used as antioxidants in the rubber industry.[1,2] Various PPDs, including 6PPD (*N*-(1,3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine), IPPD (*N*-isopropyl-*N*′-phenyl-1,4-phenylenediamine), 7PPD (*N*-(1,4-dimethylpentyl)-*N*′-phenyl-*p*-phenylenediamine), 77PD (*N*,*N*′-bis(1,4-dimethylpentyl)-*p*-phenylenediamine), DPPD (*N*,*N*′-diphenyl-*p*-phenylenediamine), and DTPD (*N*,*N*′-ditolyl-*p*-phenylenediamine), are almost all high production volume chemicals.[3−5] Global production of 6PPD, ubiquitously used in tire rubbers, was estimated at 130,000 tons in 2001,[6] while China alone produced 200,000 tons in 2020.[7] IPPD production was 10,000−15,000 tons in 2001,[8] with no availability of more recent production data for other PPDs to the best of our knowledge. The ecological risks of 6PPD have now attracted considerable attention because its ozonation transformation product (TP) 6PPD-quinone (6PPDQ) is so highly toxic (coho salmon *Oncorhynchus kisutch*, 24-h LC_{50} of 0.095 μg/L; brook trout *Salvelinus fontinalis*, 24-h LC_{50} of 0.59 μg/L; rainbow trout *Oncorhynchus mykiss*, 72-h LC_{50} of 1.0 μg/L) at environmentally relevant concentrations.[9−13] 6PPD also showed quite low 96-h LC_{50} (28 μg/L for *Oryzias latipes*,[6] 160−200 μg/L for *Gobiocypris rarus*[13]) and sublethal effects (zebrafish (*Danio rerio*) larval behavior change at 10 μg/L exposures to embryos[14]) for aquatic species. IPPD showed 14-d LC_{50} of 90 μg/L for fathead minnow (*Pimephales promelas*),[8] although the stability of reactive PPD antioxidants throughout these longer term exposures remains unclear. Global reports now document PPD antioxidants and TPs, including the toxic 6PPDQ and quinones generated from other PPDs (PPDQs), ubiquitously in roadway-impacted air,[15−18] dust,[19−21] soil, and water,[17,22−25] with growing concern for the

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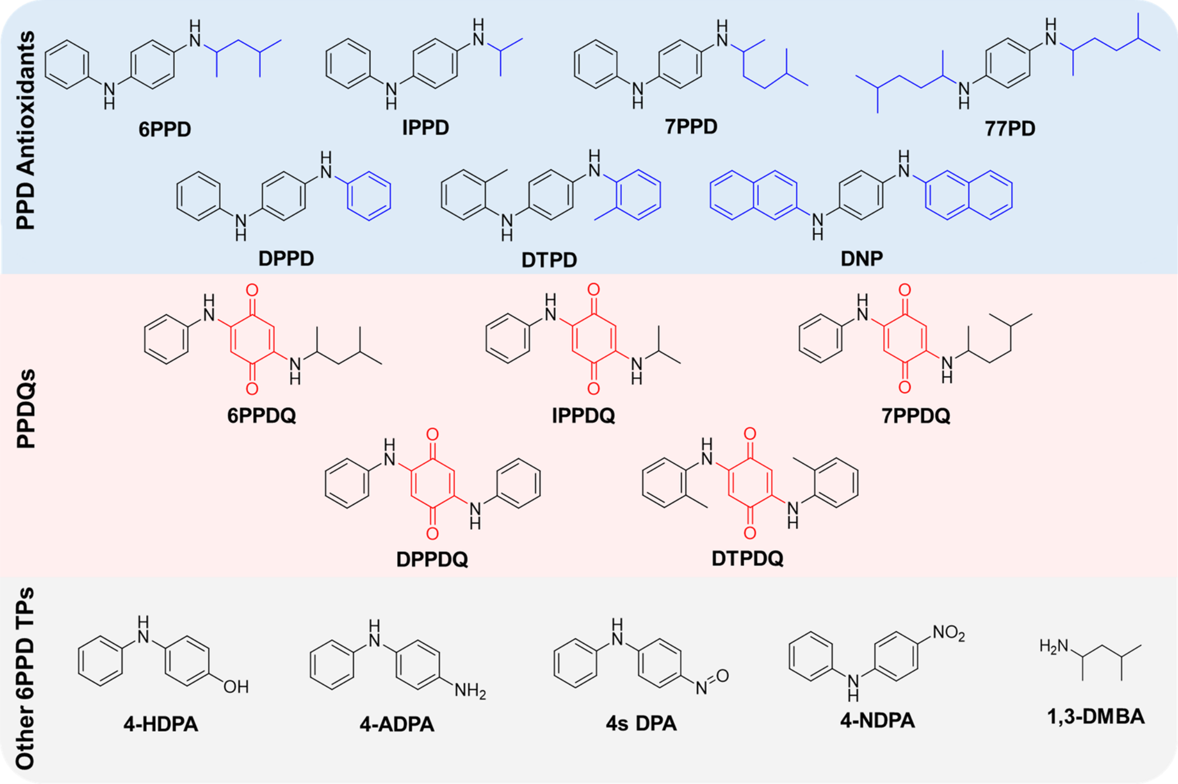

Figure 1. Structures of the targeted *p*-phenylenediamine (PPD) antioxidants, PPD-quinones (PPDQs), and 6PPD transformation products (TPs), with color highlights for key structural attributes. Full names of the analytes are presented in Table S1.

environmental dispersal, fate, and exposure implications of tire tread wear particles (TWPs) and associated chemicals.[26]

Notably, dispersed TWPs only represent a small portion of total tire rubber mass: after initial product use and replacement, most tire mass exists as "waste tires" (~10^9 generated globally annually) and is converted to various "recycled" rubber products (e.g., crumb rubber used in artificial turf fields or playgrounds, gym mats, building materials).[27,28] These rubber products are subject to weathering and various modes of environmental release (e.g., 1500−2500 kg crumb rubber annually lost from each full-size playing field)[28−30] that represent additional discharge pathways of PPD antioxidants and TPs. PPD antioxidants are additionally used in other rubber and elastomeric products, including pipes, belts, hoses, and footwear.[6,20,31,32] Both virgin and recycled rubber consumer products are often human proximate, raising concerns over human exposures to PPD antioxidants and toxic TPs, such as 6PPDQ. For example, PPD antioxidants and PPDQs were recently reported in wastewater,[25] house dusts,[20] e-waste dusts,[21] and human urine.[33] 6PPD and 6PPDQ in crumb rubbers were recently shown to be orally bioaccessible using synthetic body fluids.[34,35] IPPD has been linked to contact dermatitis in tire rubber workers[36] and people wearing rubber boots.[37] DPPD exposure induced prolonged gestation in female rats at 50 mg/kg bw/day and dystocia outcomes at 300 mg/kg bw/day.[38] Despite the human and environmental exposure risks, little information is yet available on the occurrence of multiple PPD antioxidants and the newly identified TPs in crumb rubber and other types of elastomeric consumer products.

To address this data gap, we first analyzed crumb rubbers from artificial turf fields and recycled rubber doormats for PPD antioxidants, PPDQs, and five other ozonation or aqueous reaction TPs of 6PPD[6,25,39] (Figure 1) using liquid chromatography-tandem mass spectrometry (LC-MS/MS). For comparison, we quantified these analytes in TWPs, and screened for 15 other industrial additives, including tire bonding agents (e.g., hexa(methoxymethyl) melamine, HMMM), vulcanization accelerators (e.g., 1,3-diphenylguanidine, DPG; N-cyclohexyl-2-benzothiazolamine, NCBA), corrosion inhibitors (e.g., benzotriazole (BTR) and benzothiazole (BTH) derivatives), and diphenylamine antioxidants (DPAs). Lastly, we screened a few samples of garden hose, liquid rubber sealant, baby bottle nipple, sneaker sole, rubber band, toy tire, mouse pad, rubber boots, car mat, resistance band, and lab stoppers for PPD family compounds to represent consumer products not directly related to tire rubbers.

■ MATERIALS AND METHODS

Chemicals. Chemical standards of 7PPDQ, IPPDQ, and DTPDQ were synthesized in-house (Table S1 for full names and acronyms; Text S1, Figure S1−S8 for synthetic details). Standards of seven PPD antioxidants, 6PPDQ, DPPDQ, other 6PPD TPs (5 compounds), other additives (15 tire-related chemicals, corrosion inhibitors, or DPAs), and corresponding internal standards (ISTDs) were purchased commercially (Table S1). OPTIMA grade methanol (MeOH), water, formic acid (FA), and ammonium acetate (NH_4Ac) were purchased from Fisher Scientific (Pittsburgh, PA, USA).

Sample Collection and Extraction. Crumb rubbers were collected in dry weather (date: 5/17/21 and 5/21/21, >48 h antecedent dry period) from public park (*n* = 3) or school (*n* = 6) artificial turf fields in Pierce, King, and Snohomish counties (WA, USA). Samples for each field were composited from >20 locations evenly distributed on the field, collected with methanol-cleaned stainless steel spatulas into 120 mL amber glass bottles, and stored in ambient conditions until analysis (∼20 days storage time). A few samples of consumer products containing virgin or recycled rubbers that are commonly encountered, including doormats (containing recycled tire rubber per vendor website; number of individual products (n) = 2), rubber garden hose (n = 1; black), liquid rubber sealant (n = 1, black), and baby bottle nipples (n = 2; yellow, natural rubber), were purchased. Used sneaker soles (n = 3; 2 blue, 1 black rubber), rubber bands (n = 3; multicolor), toy tires (n = 2, black), mouse pads (n = 2, black), rubber boots (n = 2, black), car floor mats (n = 2, black) and a resistance band (n = 1, blue) were donated by lab members. Used rubber laboratory stoppers (n = 3; 2 black, 1 green) were originally purchased from Fisher Scientific (Pittsburgh, PA, USA). All consumer products were claimed to be "rubber" based on physical or website descriptions of the products, except the rubber bands, mouse pad, rubber boots, and car mats for which unequivocal brands/manufacturers were unavailable. All consumer products appeared to be elastomeric and abrasion resistant, which met the empirical definition of rubber materials. More crumb rubber samples (n = 9) were collected compared with the consumer products ($n \leq 3$ for each type) because of the diverse environmental aging conditions in turf fields. TWP samples (n = 1) were equal weight mixtures of rubber tread particles from nine used and new tires (generated by physical abrasion), described previously.[9]

Identifiable debris (e.g., artificial grass, pebbles, soil) in crumb rubbers was manually removed. Crumb rubbers had diameters <3 mm and were extracted without further processing. Consumer products were cut into similarly sized small particles (length <5 mm) with methanol-cleaned stainless-steel blades. Crumb rubber, consumer product, or TWP samples (∼50 mg) were weighed into a glass centrifuge tube and spiked with 50 μL of 1 mg/L mixed procedure ISTDs in methanol (Table S1). Samples were loosely covered with aluminum foil and stored overnight under ambient conditions to evaporate solvent. Preliminary data for crumb rubber showed similar 6PPDQ concentrations (11% relative standard deviation) using methanol, acetone, ethyl acetate, or hexane extraction. Therefore, methanol was selected for extraction to simplify solvent exchange. Samples were extracted twice with methanol (5 mL × 2) by vortexing (∼1 min), shaking (rotary shaker, ∼10 min, 60 rpm), and sonicating (∼20 min), and the supernatants collected after centrifugation (2500 rpm, 20 min). Extracts were concentrated to ∼0.8 mL under nitrogen, gravimetrically brought to 1 mL, and cooled at −20 °C overnight. Extracts were then filtered while still cold with 0.2 μm PTFE syringe filters and diluted 10-fold with methanol for LC-MS/MS analysis. The concentration−redilution steps helped to facilitate consistency and compact extract storage. All samples were extracted in triplicate. Method blanks (n = 3, empty centrifuge tubes without rubber samples) were included for each batch of sample extraction (three extraction batches, n = 9 method blanks total) and processed identically.

LC-MS/MS Analysis. Analyte quantification used an Agilent 1290 Infinity HPLC coupled to 6430 triple quadrupole MS/MS (LC-MS/MS). Agilent Poroshell HPH-C18 column (2.1 × 100 mm, 2.7 μm) was employed with a C18 guard column (2.0 × 4 mm, Phenomenex, Torrance, California) at 40 °C. Three LC-MS/MS methods were employed: (1) For DPPD, DTPD, DNP, and 1,3-DMBA, LC mobile phases were 4 mM NH_4Ac in both water (A) and MeOH (B) with the following gradient: 0 min, 5% B; 1 min, 5% B; 4 min, 50% B; 17 min, 100% B, 20 min, 100% B, 20.1 min, 5% B, 24.5 min, 5% B. MS/MS employed ESI+ mode, with 350 °C gas temperature, 5 L/min gas flow, 400 °C sheath gas temperature, 11 L/min sheath gas flows, 3.0 kV capillary voltage, 0.5 kV nozzle voltage, 45 psi nebulizer pressure, and 110 V fragmentor voltage. Quantification was achieved in dynamic multiple reaction monitoring mode (dMRM) and 2−3 ion transitions were developed for each analyte (Table S2). (2) For other PPD antioxidants and TPs, 0.1% FA in both water (A) and MeOH (B) were used as the mobile phase, with identical gradient and source parameters as above (dMRM transitions in Table S2). (3) For all other additives, methods of Hou et al. were followed.[40] Methods (1) and (2) were needed for optimal chromatography and sensitivity for all target analytes because DPPD, DTPD, DNP, and 1,3-DMBA showed front-tailing peak shapes under 0.1% FA mobile phases, while 6PPD, IPPD, 7PPD, 4-ADPA, and 4-HDPA showed poor peak area responses under 4 mM NH_4Ac mobile phases (Figure S9).

Analytes were quantified with 7-point calibration curves (0.1, 0.5, 2.5, 10, 20, 50, 100 μg/L with 5 μg/L ISTDs, $R^2 > 0.995$) on log-scales based on the peak area ratios of the target analytes to the ISTDs. 6PPDQ-d_5 was used as the procedure ISTD for all PPD antioxidants, PPDQs, and other 6PPD TPs; four additional isotope labeled standards were used for the 15 industrial additive chemicals based on structural similarity (Table S1). Calibration curves for PPD antioxidants were newly prepared from solid standards (stored at 4 °C in airtight bags) for each analytical batch to mitigate their inherent reactivity and instability. Calibration curves for other analytes were prepared once, and used across sample batches (−20 °C storage for ∼3 months). Notably, concentrations of 6PPD, DTPD, and DPPD exceeded calibration ranges in some TWPs, doormats, and crumb rubber samples, so these extracts were diluted 10- and 50-fold and reanalyzed to overcome detector saturation (relative mass of analyte/ISTD did not change but peak area ratios may change). Calculated concentrations were similar (<10% difference) in the 10- and 50-fold dilutions (Table S4); therefore, concentrations in the 50-fold diluted samples were reported but marked as semiquantitative (Table S5). We note that such analytical uncertainties were nearly unavoidable because of the lower boundary of weight measurement accuracy (the amount of material extracted cannot be too low) and the preservation of ISTD response (hard to spike procedure ISTD at amount matching the target analytes without prior knowledge).

Triplicate method blanks were analyzed for each sample extraction batch and, if detected, average blank concentrations were subtracted from detected analyte concentrations. Limits of detection (LODs) and quantification (LOQs) were defined as the average plus 3- and 10-fold standard deviation of method blank levels, or analyte concentrations with signal-to-noise ratios of 3 and 10, whichever was higher. Twelve of the 32 analytes were detected at low levels in the method blanks (PPD antioxidants, 0.048−0.11 μg/g; PPDQs, < LOD; other 6PPD TPs, < LOD-0.30 μg/g; industrial additives, < LOD-0.56 μg/g). The LODs were 0.018−0.18 μg/g for PPD antioxidants, 0.031−0.92 μg/g for PPDQs (<0.05 μg/g for all PPDQ except for DPPDQ), 0.009−0.96 μg/g for other 6PPD TPs, and 0.002−2.9 μg/g for the industrial additives. LOQs for the analytes were 0.010−8.2 μg/g (Table S3). Values < LOD were assigned as zero in statistical analyses.

To evaluate method recovery, all analytes (except 77PD and the DPAs for which concentrations of the purchased stock solutions were too low for spikes) were spiked in triplicate into the CRS6 crumb rubber samples at three levels (1, 2, 10 μg/g) and extracted as above. Recovery was defined as the detected concentrations in spiked samples, corrected for detection in unspiked samples, over nominal spike concentrations. For PPD antioxidants, recoveries were 34−52% for 1−2 μg/g spikes and 83−130% at 10 μg/g (Table S3). We speculate that some spiked mass irreversibly sorbed or reacted (e.g., during overnight solvent evaporation) on crumb rubber surfaces, but cannot confidently account for the mass loss in lower spikes. Here, we consider the measurements of PPD antioxidants specifically semiquantitative throughout and caution that some low bias may exist, but we still report and discuss the concentrations for these reactive antioxidants. Confident PPD quantification methods remain needed for research studies. For PPDQs, recoveries were 89−140% across the three spike levels except for DPPDQ (36−68%). Recoveries for other 6PPD TPs were 40−120% across the three spike levels, and were 52−130% for the industrial additives except for 2-OH-BTH (34−84%; Table S3).

To evaluate storage stability for the PPD-derived chemicals (PPD antioxidants and TPs), spike recovery extracts were reanalyzed after three months of storage at −20 °C (reflecting actual storage times), with new calibration curves prepared from solid standards by a different technician. The storage stability was defined as the ratio of the recovery measured after three months over the original measurement. For PPD antioxidants, storage stabilities were 61−180% at 1−2 μg/g and 60−120% at 10 μg/g. Storage stabilities were 86−120% and 60−150% for PPDQs and other 6PPD TPs across the spiked concentrations, respectively (Table S3). Stability was not evaluated for the industrial additives because similar experiments were reported previously.[40] The standard deviations of the measured spike recoveries were <31% across all analytes and spike concentrations (Table S3).

RESULTS AND DISCUSSION

Crumb Rubber. Guided by principles of waste minimization and the development of a circular economy, crumb rubber production is a major outcome for waste tires globally.[41,42] However, the presence of residual hazardous chemicals in waste rubbers poses substantial environmental and human exposure risks.[43] Here, concentrations of PPD antioxidants and associated TPs were measured in crumb rubber from artificial turf fields (n = 3 for public parks, n = 6 for schools) and compared to TWPs (n = 1) and recycled-tire rubber doormats (n = 2).

PPD Antioxidants. 6PPD, DPPD, and DTPD were detected ubiquitously in the TWP, doormat, and crumb rubber samples (12/12), while IPPD (8/12), 7PPD (8/12), DNP (2/12), and 77PD (0/12) had lower detection frequencies (Table S5). The co-occurrence of multiple PPDs is consistent with "mixed PPDs" compositions in industrial rubber formulations and technical mixtures. For example, 6PPD and 7PPD are commonly used as 1:2 blends.[44] 6PPD and IPPD (N-alkyl-N'-aryl PPD) are often combined with DTPD or DPPD (N,N'-diaryl PPD) because alkyl-aryl PPDs provide short-term protection while the larger diaryl PPDs have slower diffusion rates through rubber materials and therefore provide longer-term protection.[45,46] Other undocumented performance, cost, and manufacturing considerations also likely influence PPD antioxidant choice in consumer products.

Semiquantitatively, parent PPD antioxidants were detected at higher concentrations in TWPs (∑PPDs, 2600 μg/g) and doormats (∑PPDs, 800−900 μg/g) than crumb rubbers (∑PPDs, 0.36−280 μg/g, median 22 μg/g; Table 1, Figure 2a). While several concurrent processes govern PPD fate, higher PPD concentrations in TWPs and doormats likely resulted from reduced weathering and leaching relative to the field-applied crumb rubbers. Notably, the ∑PPDs exhibited 3 orders of magnitude variation across the crumb rubber samples (Figure 2a). These differences plausibly reflect different aging periods or recent replacements for some crumb rubber fields ("new" crumb rubbers should have higher PPD concentrations), but may also indicate different source rubbers or manufacturing methods (e.g., ambient grinding vs cryogenic processing). 6PPD, DTPD, and DPPD dominated ∑PPD compositions among the PPDs here analyzed (Figure 2b). 6PPD had higher concentrations than DTPD and DPPD in TWPs and doormats, while DTPD dominated crumb rubber samples where 6PPD and DPPD were similar (Figure 2b). This is consistent with the slow migration of diaryl PPDs and the presumptive "older" crumb rubber as discussed above. Consistent with our study, 6PPD and DTPD were previously detected with high peak intensities in TWPs by high-resolution mass spectrometry (HRMS) analysis.[47] 6PPD and DPPD were identified in HRMS analysis of crumb rubbers by the United States Environmental Protection Agency (US EPA).[48] In road dust samples from China, 6PPD, DPPD, IPPD, and CPPD (N-phenyl-N'-cyclohexyl-p-phenylenediamine) were major contributors to the total PPD profiles (DNP and 77PD were minor; 7PPD and DTPD were not analyzed),[20] consistent with detection of 6PPD and DPPD in our TWPs and crumb rubber products. In contrast, 77PD was the single dominant species in atmospheric particulate matter and house dusts from China.[15,20] The lack of 77PD detection in TWPs and crumb rubber products in this study indicated diverse industrial formulations of PPD antioxidants and correspondingly diverse PPD sources from different products within environmental compartments.

PPDQs and Other 6PPD TPs. Beyond the parent PPD antioxidants, all five PPDQs were detected in all (6PPDQ, DTPDQ) or some (DPPDQ, 7PPDQ, IPPDQ) TWPs and recycled rubber products (Table 1, Figure 2b). Noting that the TWP sample included new and used tires, and was stored under ambient conditions for ∼1 year in airtight bags (polyethylene plastic), so detected chemical compositions inherently reflect both industrial and environmental TPs generation during this product history. The ∑PPDQs was similar across TWP (19 μg/g) and doormat (11−30 μg/g) compositions but unlike the more variable parent PPD antioxidants, ∑PPDQs in crumb rubbers exhibited reduced variation (1.2−30 μg/g) and the median concentration (12 μg/g) were close to those in TWPs and doormats. While some initial compositional uncertainty exists, this may indicate that PPDQ TPs were more stable with longer lifetimes in crumb rubber relative to parent PPDs. 6PPDQ was the most abundant PPDQ in TWPs (12 μg/g), doormats (2/2 detection, 11−26 μg/g), and crumb rubbers (9/9, 0.3−25 μg/g, median 9.8 μg/g). DPPDQ was second with concentrations ∼2−10-fold lower than 6PPDQ (Figure 2b). DTPDQ was ∼3-fold lower than DPPDQ, followed by 7PPDQ and IPPDQ (Table 1, Figure 2b). 6PPDQ and DPPDQ abundances were generally consistent with parent 6PPD and DPPD compositions. However, DTPDQ concentrations were 1−2 orders of magnitude lower despite similar levels of parent 6PPD and DTPD, potentially due to higher instability or lower yields of DTPDQ during exposure to ozone, or more leaching of 6PPD during environmental weathering of crumb rubber. Consistent with these results, 6PPDQ and DPPDQ were identified as the dominant PPDQ species in roadside soils and

Table 1. Median Concentrations (μg/g) of Detected PPD Antioxidants, Transformation Products, and Other Rubber Additives in TWPs, Crumb Rubbers, and Elastomeric Consumer Products[a]

	TWP (*n* = 1)	Crumb rubber (*n* = 9)	Doormat (*n* = 2)	Sneaker Sole (*n* = 3)	Laboratory stopper (*n* = 3)	Garden hose (*n* = 1)	Mousepad (*n* = 2)	Rubber band (*n* = 3)	Rubber boot (*n* = 2)	Bottle nipple (*n* = 2)	Resistance band (*n* = 1)	Rubber sealant (*n* = 1)	Car mat (*n* = 2)	Toy tire (*n* = 2)
p-phenylenediamine (PPD) antioxidants														
6PPD[b]	2300	1.2 (0.047−95)	630 (500−770)	0.14 (0.051−0.41)	0.71 (<LOD-3.7)	0.071	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
IPPD[b]	0.89	0.011 (<LOD-0.12)	0.24 (0.16−0.32)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
7PPD[b]	13	0.022 (<LOD-0.56)	0.55 (0.2−0.9)	<LOD	0.026 (<LOD-0.034)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
77PD[b]	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
DPPD[b]	30	1.1 (0.12−18)	26 (3.9−49)	<LOD (<LOD-0.08)	0.34 (<LOD-1.7)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
DTPD[b]	300	20 (0.2−160)	190 (20−360)	0.19 (<LOD-0.69)	5 (<LOD-16)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
DNP[b]	<LOD	<LOD (<LOD-0.03)	1.5 (<LOD-3)	0.27 (<LOD-1.1)	<LOD	0.074	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PPD transformation products														
6PPDQ	12	9.8 (0.3−25)	18 (11−26)	0.48 (0.37−0.75)	0.47 (<LOD-1.7)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
1,3-DMBA	86	2.8 (0.27−7.1)	4.3 (2.5−6)	<LOD	<LOD (<LOD-0.59)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4-HDPA	16	0.23 (0.089−2.2)	4.3 (1.9−6.8)	<LOD	0.14 (<LOD-0.23)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4-ADPA	11	0.22 (<LOD-6.4)	1.9 (1.1−2.8)	<LOD	<LOD	<LOD	<LOD	<LOD	1.4 (<LOD-2.7)	<LOD	<LOD	<LOD	<LOD	<LOD
4s DPA	0.47	<LOD (<LOD-1.4)	1.6 (0.54−2.7)	<LOD	<LOD (<LOD-0.044)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4-NDPA	1.2	0.35 (<LOD-1.1)	0.7 (0.027−1.4)	<LOD (<LOD-0.01)	<LOD (<LOD-0.069)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
IPPDQ	<LOD	0.062 (<LOD-0.093)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
7PPDQ	0.1	0.077 (<LOD-0.23)	0.02 (<LOD-0.04)	<LOD	<LOD (<LOD-0.015)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
DPPDQ	5.7	1.6	1.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Table 1. continued

	TWP (*n* = 1)	Crumb rubber (*n* = 9)	Doormat (*n* = 2)	Sneaker Sole (*n* = 3)	Laboratory stopper (*n* = 3)	Garden hose (*n* = 1)	Mousepad (*n* = 2)	Rubber band (*n* = 3)	Rubber boot (*n* = 2)	Bottle nipple (*n* = 2)	Resistance band (*n* = 1)	Rubber sealant (*n* = 1)	Car mat (*n* = 2)	Toy tire (*n* = 2)
PPD transformation products														
		(0.8–4)	(<LOD-3.1)		(<LOD-0.84)									
DTPDQ	1.6	0.37 (0.099–1.2)	0.43 (0.066–0.79)	0.03 (0.027–0.048)	<LOD (<LOD-0.075)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
vehicle-related chemicals														
DPG	290	2 (<LOD-21)	0.74 (0.64–0.84)	0.3 (0.26–0.38)	<LOD (<LOD-0.35)	<LOD	0.26 (0.25–0.26)	<LOD (<LOD-1.1)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
HMMM	47	<LOD (<LOD-3.1)	8.3 (0.26–16)	<LOD (<LOD-0.2)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
NCBA	130	1.9 (<LOD-8.2)	9.1 (4.4–14)	<LOD (<LOD-2.5)	0.45 (<LOD-2.5)	<LOD	<LOD	<LOD	<LOD	0.069 (<LOD-0.14)	<LOD	<LOD	<LOD	<LOD
DCU	19	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.29 (<LOD-0.58)	<LOD	<LOD	<LOD	<LOD
benzotriazoles and benzothiazoles														
1-H-BTR	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
5-Me-1-H-BTR	<LOD	<LOD	<LOD	0.29 (<LOD-0.38)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
UV-234	<LOD	<LOD	0.035 (<LOD-0.07)	2 (0.054–43)	0.024 (<LOD-0.085)	<LOD	0.007 (<LOD-0.01)	<LOD (<LOD-0.006)	<LOD	<LOD	<LOD	<LOD	0.055 (<LOD-0.11)	<LOD
UV-326	<LOD	<LOD	<LOD	11 (0.87–95)	<LOD (<LOD-0.53)	<LOD	1.6 (1.1–2.1)	<LOD	1.2 (1.1–1.4)	0.38 (0.36–0.39)	0.22	4.2	180 (5–350)	510 (340–680)
2-NH2-BTH	4.6	0.072 (<LOD-0.76)	0.8 (0.19–1.4)	0.08 (0.023–3.4)	<LOD	<LOD	4 (3.7–4.4)	0.19 (0.14–1.3)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2-OH-BTH	380	1.5 (<LOD-26)	110 (72–140)	63 (25–65)	38 (<LOD-58)	15	380 (120–640)	72 (68–74)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2-Mo-BTH	20	0.18 (<LOD-0.82)	3.8 (1.1–6.6)	0.17 (0.13–0.27)	0.18 (0.09–1.3)	7.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.028 (0.014–0.042)	<LOD

runoff waters in China, with ~4−10 fold more 6PPDQ than DPPDQ.[17]

Beyond 6PPDQ, other TPs of 6PPD (three ozone-derived TPs and two aqueous reaction TP; Table S1) were detected. Their concentrations were lower than 6PPDQ except in TWPs where 1,3-DMBA was ~8-fold higher than 6PPDQ (Figure 2c). Sum concentrations of the other 6PPD TPs (excluding 6PPDQ) was also highest in TWPs (∑otherTPs, 120 μg/g), followed by doormats (6.0−20 μg/g) and crumb rubbers (0.4−15 μg/g; Figure 2a), with variance in crumb rubber similar to ∑PPDQs and 1 order of magnitude lower than the variance of ∑PPDs. 1,3-DMBA was the highest TP detected (Figure 2c). Notably, although 1,3-DMBA was included in this study as a 6PPD TP, it is a powerful, unauthorized stimulant sometimes used in dietary supplements that became more widely used after another similar amine (dimethyl amylamine) was phased out due to severe health risks (strokes, heart failure, sudden death).[49,50] The CompTox Chemicals Dashboard also reports possible androgenic activity for 1,3-DMBA.[4] 4s DPA, a TP of 6PPD with a nitroso group and therefore potentially carcinogenic,[51−53] was detected in the doormat and crumb rubber samples. Careful consideration of the ecological and human health concerns surrounding the occurrence of several 6PPD TPs may therefore be merited. As a small aliphatic amine, we would also note the potential for multiple structural and usage sources for 1,3-DMBA beyond environmental transformations of 6PPD. It also was possible that 1,3-DMBA was poorly separated from its isomers in C18-LC (retention time of 3.9 min over a 24.5 min gradient). For example, the similar *n*-hexylamine (linear chain) is used as a corrosion inhibitor in rubber materials. However, standard spikes, isocratic LC separations, and HRMS/MS retention times and spectra using the commercial standard (Figure S10) did confirm the 1,3-DMBA identification, although we cannot conclusively exclude the presence of similar coeluting compounds. To the best of our knowledge, this is the first report of these 6PPD TPs and other PPDQs in TWPs, crumb rubbers, and elastomeric consumer products.

Notably, the individual [TP]/[PPD] ratio in TWPs, doormats, and crumb rubbers ($n = 12$) was significantly negatively correlated with the ∑(PPDs+TPs) concentrations ($p < 0.05$, $R^2 > 0.75$; Figures 2b, 2c and S11). Simply, although absolute concentrations were sometimes low, PPDQs and TPs are dominating the chemical profiles as residual mass of PPD and related known TPs decreases. For example, [6PPDQ]/[6PPD] ratio was 0.005 in TWPs and 0.01−0.05 in doormats; it shifted to 0.3−1.3 in four crumb rubber samples with high ∑PPDs (CRS1-CRS4) and was as high as 6.4−18 for the remaining crumb rubber samples with low ∑PPDs (CRS5, CRS6, CRP1-CRP3). Similarly, [DPPDQ]/[DPPD] increased from 0.19 in TWPs to 6.8 in the low PPD mass crumb rubbers, [DTPDQ]/[DTPD] increased from 0.005 to 0.50, and [1,3-DMBA]/[6PPD] was 0.04 in TWPs and was as high as 6.6 in the crumb rubbers (Figures 2b, 2c and S11). We were able to determine the installation dates for 4 out of the 9 turf fields to estimate the crumb rubber age. Indeed, crumb rubbers with higher [TP]/[PPD] ratios were generally from turf fields installed earlier while those with lower [TP]/[PPD] ratios were generally "younger" (Figure S11). These data further support that environmental weathering time scales determined the different ∑(PPDs+TPs) and [TP]/[PPD] ratios in crumb rubbers, although more work, such as time series analysis of the same crumb rubber, is certainly needed to confirm this conclusion. Higher PPDQ and TP proportions in "older" crumb rubbers

Table 1. continued

	TWP (n = 1)	Crumb rubber (n = 9)	Doormat (n = 2)	Sneaker Sole (n = 3)	Laboratory stopper (n = 3)	Garden hose (n = 1)	Mousepad (n = 2)	Rubber band (n = 3)	Rubber boot (n = 2)	Bottle nipple (n = 2)	Resistance band (n = 1)	Rubber sealant (n = 1)	Car mat (n = 2)	Toy tire (n = 2)
						substituted diphenylamine (DPA) antioxidants								
SDPA-diAMS	<LOD	1.5	0.38	2.1	0.12	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
		(0.3−48)	(0.3−0.47)	(0.97−69)	(0.11−3.5)									
SDPA-C4C8	0.88	1.3	2.5	19	0.19	<LOD	<LOD	<LOD	<LOD	<LOD	0.051	<LOD	<LOD	<LOD
		(<LOD-8.6)	(2−3.1)	(1.6−19)	(0.17−0.24)			(<LOD-0.093)						
SDPA-C8C8	1.5	5	13	28	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.054	<LOD	<LOD	<LOD
		(<LOD-21)	(4.1−22)	(14−53)	(<LOD-21)									
SDPA-C9C9	1.2	1	4.6	1.7	0.64	0.45	<LOD	0.55	0.45	<LOD	<LOD	<LOD	<LOD	0.21
		(<LOD-3)	(2.6−6.6)	(0.78−15)	(0.63−0.8)			(<LOD-0.75)	(0.43−0.48)					(<LOD-0.42)

[a] All samples below were analyzed in triplicate; n values reflect the discrete number of samples analyzed. Concentration ranges are shown in parentheses. [b] Concentrations for PPD antioxidants are considered semiquantitative because of <50% spike recoveries at low (1 μg/g) and middle (2 μg/g) spiking levels.

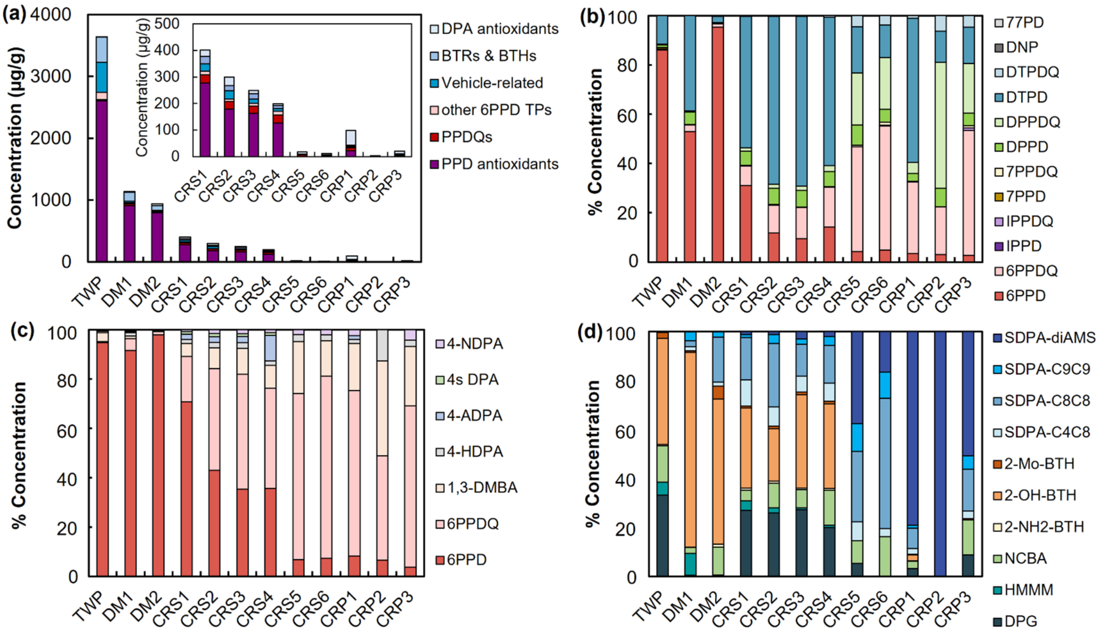

Figure 2. Concentrations of targeted additive chemicals in tire wear particles (TWPs), doormats (DM), and crumb rubbers (CRS, school turf; CRP, public park turf). (a) Total detected concentrations of *p*-phenylenediamine (PPD) antioxidants, PPD-quinones (PPDQs), other 6PPD transformation products (TPs), and other rubber additives (vehicle-related chemicals, benzotriazoles and benzothiazoles (BTRs & BTHs), diphenylamine (DPA) antioxidants). Crumb rubber samples were additionally showed in an inset figure with lower *y*-axis values. (b) Profiles of individual PPDs and PPDQs, by normalizing concentration of each chemical to the total concentration in each sample. (c) Profiles of 6PPD and individual TPs (including 6PPDQ). (d) Profiles of other additives. DCU, 1-H-BTR, 5-Me-1-H-BTR, UV-234, and UV-326 were not included because they were not detected or detected in only one sample (1/12). Values < LODs were estimated as 0.

likely resulted from (1) more PPD oxidation/reaction than PPD TP as crumb rubbers aged (e.g., in natural aging of cryomilled tire tread particles, 6PPD showed decay half-lives of a few days, while 6PPDQ concentrations increased within ∼1 month then decayed with half-lives of ∼20 days[54]); (2) higher leaching potentials of parent PPDs relative to PPDQs and other TPs (e.g., measured solubility: 560 ± 200 μg/L for 6PPD, 67 ± 5 μg/L for 6PPDQ; measured logK_{oc}: 2.5−2.6 for 6PPD, 3.2−3.5 for 6PPDQ).[19,55] In roadside soil from China, Cao et al. observed [6PPDQ]/[6PPD], [DPPDQ]/[DPPD], and [DTPDQ]/[DTPD] values of 0.76, 5, and 1.6, respectively. These ratios were ∼2 order of magnitude higher than the [PPDQ]/[PPD] ratios observed in our TWPs (suggesting aging of TWP-derived PPDs and TPs in those soils) and generally aligned with values for the crumb rubbers.[17] Overall, these data indicate that with more weathering, TPs, including PPDQs, were relatively more stable and environmentally persistent PPD-related compounds, at least across the structurally identified compounds. Concerning absolute concentrations, declines paralleled expected aging, suggesting that attenuation processes are decreasing total PPD-derived compounds, including PPDQs, over time.

Other Additives. Chemical contaminants often co-occur within mixture compositions that are defined by common originating sources (e.g., vehicles, wastewater, agriculture). To compare occurrence of PPD-derived contaminants with more widely studied industrial additives, we concurrently measured the concentrations of 4 vehicle-related chemicals (DPG, HMMM, NCBA, DCU; see Table S1), 7 BTRs and BTHs derivatives (vulcanization accelerators, corrosion inhibitors, or UV stabilizers), and 4 DPAs (Table S1). DCU, 1-H-BTR, 5-Me-1-H-BTR, UV-234, and UV-326 were not detected or detected in only one of the TWPs, doormats, or crumb rubber samples (total *n* = 12). The other additive chemicals were detected in 7 or more samples.

Consistent with PPD-derived compounds, concentrations of the vehicle-related chemicals (DPG, HMMM, NCBA, DCU) and BTRs and BTHs were ∼2 orders of magnitude higher in TWPs (∑vehicle-chemicals, 490 μg/g; ∑(BTR+BTH), 410 μg/g) and doormats (∑vehicle-chemicals, 15−22 μg/g; ∑(BTR+BTH), 80−150 μg/g) versus crumb rubbers (∑vehicle-chemicals, < LOD-31 μg/g; ∑(BTR+BTH), < LOD-27 μg/g; Figure 2a). In contrast, DPA in TWPs was not as high (3.6 μg/g) compared with those in doormats (14−27 μg/g) and crumb rubbers (0.3−55 μg/g in crumb rubbers), potentially indicating less use of DPA in this TWPs sample. DPG (vulcanization accelerator) was the dominant species for the vehicle-chemicals, and 2-OH-BTH (an impurity and photochemical TP of another vulcanization accelerator 2-mercaptobenzothiazole[24,56,57]) was the largest among the BTRs and BTHs (Figure 2d). For SDPA, SDPA-C8C8 dominated compositions in doormat and CRS1-CRS6, while in the remaining crumb rubber samples (CSP1-CSP3) SDPA-diAMS contributed the most (Figure 2d).

Overall, despite the wide reports of the vehicle-related chemicals, BTRs, BTHs, and DPAs in receiving waters,[23,24,58,59] concentrations of PPD-related compounds (∑(PPDs + PPDQs + otherTPs)) were 0.5−6 times higher than these industrial additives in the TWPs, doormats, and crumb rubbers (Figure 2a), again suggesting PPD-related compounds as an abundant yet previously overlooked contaminant class. These data emphasize the need to characterize relative leaching rates of these compounds while also including PPD antioxidants and related TPs in environmental and human exposure studies.

Elastomeric Products. A few additional consumer products were screened to initially characterize elastomeric chemical compositions beyond directly tire-related sample types. Among these consumer products, PPD family compounds (parent PPDs, PPDQs, and other 6PPD TPs) were consistently detected in sneaker soles and laboratory stoppers. PPDs only occurred at trace levels in the garden hose ($\sum$PPDs 0.14 μg/g) and were not detected in the other product samples, except for occasional detections of 4-ADPA in rubber boots (Figure 3). PPD compound detections in sneakers were consistent with reported 6PPD use in footwear.[20,31] Interestingly, for the laboratory stoppers, PPD compounds were detected in two black rubber stoppers but not in the green rubber stopper, consistent with the dark coloration of 6PPD oxidation products and related PPD discoloration concerns for light colored rubbers.[46,60,61] 6PPD and related compounds were not detected in the two rubber boot samples, but 6PPD was previously reported in boots.[20,31] For example, Ikarashi et al. (2000) detected 6PPD and IPPD in 5 of 8 rubber boots at concentrations (130−1800 μg/g) as high as the TWPs we measured here.[32] More samples may have been needed.

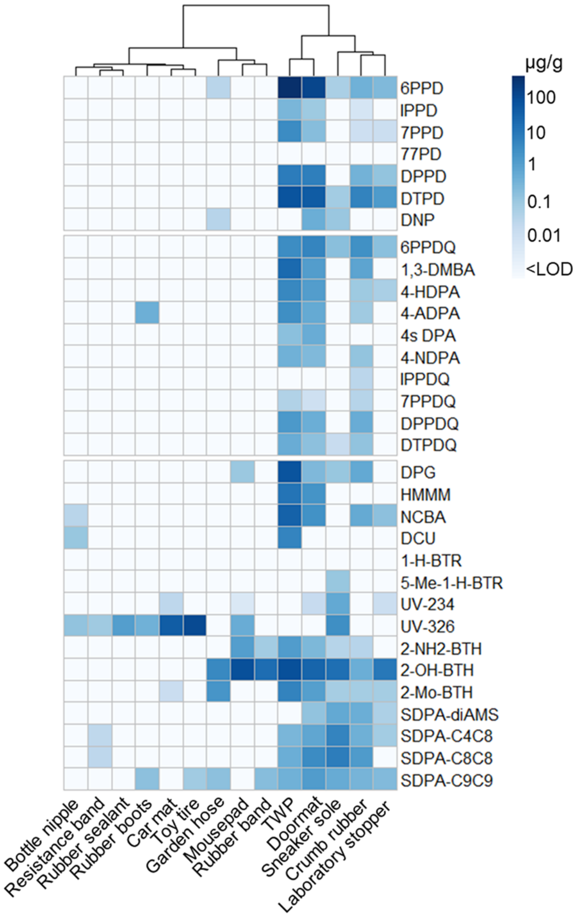

Figure 3. Heatmap communicating relative concentrations of *p*-phenylenediamine (PPD) antioxidants, their transformation products, and other rubber additives in TWPs, crumb rubbers, and various consumer products. Median concentrations in each product category are presented. Cluster analysis was performed with the Ward's minimum variance method (ward.D2) in R programming language using the *pheatmap* package (version 1.0.12). Values < LODs were estimated as 0.

Compared with TWPs, PPD family concentrations in laboratory stoppers (2/3, $\sum$PPDs, 6.1−21 μg/g; $\sum$PPDQs, 0.54−2.6 μg/g; $\sum$otherTPs, 0.14−0.94 μg/g) were 1−2 orders of magnitude lower, likely reflecting differing material needs for antioxidants and antidegradants. Concentrations in sneaker soles (3/3, $\sum$PPDs, 0.69−1.1 μg/g; $\sum$PPDQs, 0.40−0.80 μg/g; $\sum$otherTPs, < LOD) were similar to or slightly lower than laboratory stoppers (Table 1). Despite small sample sizes ($n = 3$ lab stoppers, $n = 3$ sneaker soles, $n = 1$ garden hose), these products had more diverse PPD compositions than TWPs and tire-based products. For example, DNP dominated two sneaker samples (0.27−1.1 μg/g) and the garden hose (0.07 μg/g), while other products (two stoppers, one sneaker) were more similar to TWPs with abundant DTPD (stopper, 5.0−16 μg/g; sneaker, 0.69 μg/g) and 6PPD (stopper, 0.71−3.7 μg/g; sneaker, 0.41 μg/g; Table S5). For TPs, 6PPDQ was the dominant in these products followed by DTPDQ (Figure 3). Additional studies with more samples across more rubber types are merited to better define relationships between consumer product and PPD-family chemical composition. We note that the 6PPDQ detection, and other additives described below, in lab rubber stoppers highlights the importance of materials screening to avoid background interferences during laboratory and toxicological analyses. To the best of our knowledge, this is the first observation of 6PPDQ and DTPDQ in consumer products beyond tire rubbers and related recycled rubber products.

Like PPD family compounds, the "vehicle-related" chemicals (DPG, HMMM, NCBA, DCU) were only detected in lab stoppers (2/3 detection, $\sum$vehicle-chemicals, 0.80−2.5 μg/g; dominated by NCBA) and sneaker soles (3/3 detection, $\sum$vehicle-chemicals, 0.30−2.8 μg/g; dominated by NCBA and DPG), except a trace detection (<LOQs) of DPG in mouse pads, and NCBA and DCU detected in the bottle nipple sample (0.14−0.58 μg/g; Figure 3, Table 1). The $\sum$vehicle-chemicals in these consumer products were 2 orders of magnitude lower than those in TWPs (490 μg/g), indicating the ubiquity, and disparate compositions, of antioxidant and additive chemicals in tire rubbers and elastomeric products. In contrast to the PPD family and vehicle-related additives, benzotriazole and benzothiazole derivatives were widely present in diverse product types ($\sum$(BTRs + BTHs), 0.2−680 μg/g, median 24 μg/g), including products not dominated by PPD antioxidants (Figure 3). Similar to the BTRs and BTHs profiles in TWPs, doormats, and crumb rubbers, 2-OH-BTH dominated in lab stopper, sneaker sole, garden hose, rubber band, and mousepad samples, with concentrations up to 640 μg/g (in mousepad). In contrast, the compositions of toy tire, car mat, rubber boots, rubber sealant, resistance band, and bottle nipple samples were dominated by UV-326, a high molecular weight hydroxyphenyl benzotriazole UV stabilizer, with concentrations up to 510 μg/g in toy tires. The four DPAs had lower concentrations, with $\sum$DPAs < LOD-116 μg/g (Figure 3).

To investigate compositional relationships, we categorized the TWPs, crumb rubbers, and consumer products with hierarchical cluster analysis based on the targeted chemicals. This analysis discriminated two main clusters and four subclusters among the products (Figure 3). Not surprisingly, doormat, sneaker sole, crumb rubber, lab stoppers, and TWP comprised one main cluster. This cluster was best characterized by the frequent and unique occurrence of PPDs and vehicle-related chemicals. Within this cluster, doormat rubber and TWPs formed a subcluster, observationally linked to high 6PPD, DTPD, DPPD, and 6PPDQ detections. Somewhat surprisingly, crumb rubber formed another subcluster with lab stopper and sneaker sole, potentially due to similar (and lower) concentrations of additives. The remaining elastomeric products comprised the second main cluster, best characterized by abundant benzotriazole and benzothiazole derivatives. The garden hose, mousepad, and rubber band formed a subcluster, observationally linked to 2-OH-BTH detections. Finally, the toy tire, car mat, rubber boots, rubber sealant, resistance band, and bottle nipple also comprised a subcluster, observationally linked to UV-326. Previous studies have proposed NCBA, 2-OH-BTH, 2-Mo-BTH, and 1-H-BTR as chemical tracers of environmental TWPs.[24,62−64] Based on these data, NCBA and 2-Mo-BTH seem to be more specific and more abundant in tire-related products. 2-OH-BTH also was present in many consumer products, and 1-H-BTR was unexpectedly not detected in TWPs or any elastomeric products we screened. These data also suggest that PPD-related compounds, especially 6PPDQ, are good chemical tracers for TWPs and tire-related products. However, the medium-term stability of many PPD TPs, including 6PPDQ, also remains unclear and is a current research need for most compounds described here. Although the parent 6PPD, DPPD, and DPTD antioxidants are abundant, their instability[6,65] does limit their utility as chemical tracers. Alternatively, their negative correlations with PPD TPs may represent tracers of environmental weathering of rubber products, although more research is needed to validate such applications and identify stable end-members.

Environmental Implications. These data indicated the presence of PPD-derived compounds in multiple rubber consumer products at concentrations that are often similar or higher than the more well-known HMMM, DPG, benzothiazoles, and benzotriazoles. In addition, the total concentrations of PPDs and related TPs in crumb rubbers detected here (1.9−320 μg/g, median 37 μg/g) were similar or even up to 10-fold higher than reports of polycyclic aromatic hydrocarbons ($\sum$PAHs, 0.81−230 μg/g), $\sum$phenols (2.3−6.3 μg/g), or $\sum$phthalates (1.1−9500 μg/g) in crumb rubbers, compounds commonly studied and prioritized in the regulations or watch lists from the European Chemicals Agency and US EPA on crumb rubber chemicals.[28,42,66] We also observed that the [TP]/[PPD] ratios in TWPs and weathered crumb rubbers were inversely correlated with the total mass of PPD-derived compounds and the decrease in [TP]/[PPD] paralleled decreased age of the crumb rubbers, indicating that TPs were relatively more stable and environmentally persistent PPD-related compounds and likely dominate fate and exposure outcomes for PPD-derived chemicals. Notably, in addition to the commonly detected 6PPDQ, four other environmental PPDQs were frequently detected in these rubber products, especially the detections of DPPDQ and DTPDQ in crumb rubber at similar concentrations to 6PPDQ. These PPDQ detections again indicate that quinone TP formation may occur for many PPD antioxidants, producing PPDQs with as-yet unknown toxicity characteristics.[17,18,21] In addition to the quinone products, other interesting TPs of 6PPD were detected, including the bioactive stimulant 1,3-DMBA and the potentially carcinogenic nitroso-compound 4s DPA.

Limitations do exist for the current study. First, confident quantification of PPD antioxidants and related TPs remains challenging. At the time of this study, 6PPDQ-d_5 was the only isotope-labeled standard commercially available for PPD antioxidants and PPDQs and was employed as the procedure ISTD for all PPD-related molecules. Spike recoveries for highly reactive PPD antioxidants were sometimes low especially at the 1−2 μg/g spiking levels, likely due to irreversible sorption or surface reaction. While noting these limitations, we do provide concentration estimates of PPDs and related compounds in these rubber products. Second, diverse types of consumer products were sampled but with few replicates for each sample type. No detections in this study do not necessarily reflect no use of PPD antioxidants in the product type, but may be artifacts of the low sample numbers (e.g., no detection in rubber boots despite previous reports). We note that additional replicates and sample numbers would help establish representative chemical concentrations for each product category. Here, we performed a broad screening for PPD-related chemicals in diverse rubbery products without attempting to benchmark chemical concentrations in all of these consumer products.

Tire tread wear particles (i.e., tire microplastics), residual rubber-derived chemicals, and their associated toxicological effects are receiving growing attention.[62] While this interest is well-merited, observations of aquatic toxicity for crumb rubber and rubber materials used in aquaculture[66] support growing needs to broadly define chemical compositions and toxicological effects of rubber-based products. While there are good reasons to maintain focus on traditional and well-known contaminant classes like metals, PAHs, or phthalates, or potentially include a few well-known antioxidants and additives such as benzothiazoles or phenolic compounds,[42,66−69] substantial chemical complexity exists beyond these constituents. Unfortunately, despite their substantial environmental dispersal and human exposure potentials, tire rubbers and elastomeric consumer products lack publicly accessible insights into their chemical composition because chemical ingredients are typically protected as proprietary and confidential business information. Absent regulatory requirements to release such information into the public domain, environmental and human health risk assessment will remain challenging, uncertain, and subject to underestimation. Although the data in this study are limited, many elastomeric consumer products clearly contain PPD antioxidants, their related TPs, and other industrial additives and, therefore, are significant sources of rubber-derived contaminants. Especially for indoor environments not directly tire-related (e.g., house dusts,[20] e-waste dusts[21]), consumer products likely contribute to or explain the observed presence of PPD-derived chemicals. Beyond existing literature reports, we also identified 6PPDQ in public mass spectrometry data files of surface swab samples of office, research, or teaching buildings, as well as marine waters from San Diego County, CA, USA, by searching the MS/MS spectra of 6PPDQ against all public mass spectrometry data in the MassIVE repository (GNPS job link: https://gnps.ucsd.edu/ProteoSAFe/status.jsp?task=0e2a60e7c6e9481abed6e635975dc260).[70−72] The presence of PPD-derived chemicals in such sample types have direct human exposure implications. Addressing the many data gaps around the human and environmental occurrence, fate, transport, and exposure risks of these classes of industrial chemicals and related TPs would seem quite useful.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c07014.

Supplementary texts on synthesis of PPD-quinone standards (Text S1); HRMS sample analysis (Text S2) and principal component analysis (Text S3); Supplementary tables on the names, abbreviation, and sources of the target analytes (Table S1); LC-MS/MS method parameters (Table S2); quality assurance and quality control data (Table S3); dilution analysis of 6PPD, DPPD, and DTPD (Table S4); Supplementary figures on the spectral data for synthetic PPDQs (Figure S1−S8); chromatograms of PPD chemicals under different mobile phase additives (Figure S9); LC-HRMS/MS confirmation of 1,3-DMBA (Figure S10); the correlations between [TP]/[PPD] and total PPD-related chemical concentrations in TWPs and crumb rubber products (Figure S11); principle component analysis of the elastomeric/rubber products using HRMS features (Figure S12). (PDF)

Concentration details of the analytes in each sample (Table S5) (XLSX)

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Notes

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