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Article

Concentrations of Tire Additive Chemicals and Tire Road Wear Particles in an Australian Urban Tributary

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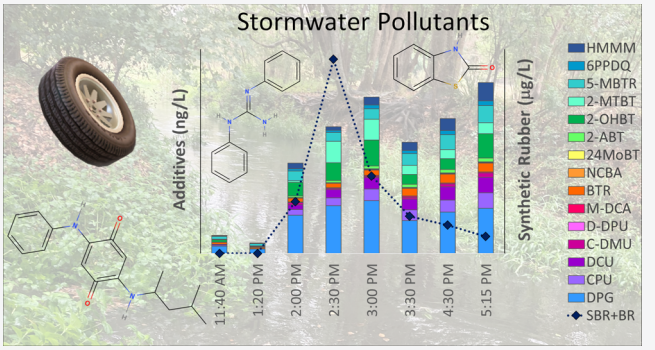
ABSTRACT: Tire road wear particles (TRWPs) are one of the largest sources of microplastics to the urban environment with recent concerns as they also provide a pathway for additive chemicals to leach into the environment. Stormwater is a major source of TRWPs and associated additives to urban surface water, with additives including the antioxidant derivative *N*-(1,3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine-quinone (6PPD-quinone) demonstrating links to aquatic toxicity at environmentally relevant concentrations. The present study used complementary analysis methods to quantify both TRWPs and a suite of known tire additive chemicals (including 6PPD-quinone) to an urban tributary in Australia during severe storm events. Concentrations of additives increased more than 40 times during storms, with a maximum concentration of 2760 ng/L for $\sum_{15}$additives, 88 ng/L for 6PPD-quinone, and a similar profile observed in each storm. TRWPs were detected during storm peaks with a maximum concentration between 6.4 and 18 mg/L, and concentrations of TRWPs and all additives were highly correlated. Contaminant mass loads to this catchment were estimated as up to 100 g/storm for $\sum_{15}$additives, 3 g/storm for 6PPD-quinone, and between 252 and 730 kg of TRWPs/storm. While 6PPD-quinone concentrations in this catchment were lower than previous studies, elevated concentrations post storm suggest prolonged aquatic exposure.



KEYWORDS: *TRWP, tire additives, 6PPD-quinone, Australian environment, mass loads*

INTRODUCTION

Tire road wear particles (TRWPs) are estimated to be one of the largest sources of microplastics to the urban environment,[1] and as a result, the number of studies investigating the environmental occurrence of TRWPs has rapidly increased. TRWPs are formed by the abrasion of tire tread on road surfaces through normal use and are generated in a range of sizes.[2] Smaller particles can be airborne with up to 3−7% of $PM_{2.5}$ suggested to be tire wear.[3] The larger particles collect on or near roads and can be a significant pollution source to urban surface water during storm events.[4−7]

Tires are comprised of a range of materials including synthetic and natural rubbers, fillers, and a wide range of additive chemicals. The additive chemicals are included during production for a range of functions and include vulcanization agents (typically sulfur or various organic chemicals) and vulcanization accelerators or activators (e.g., zinc oxide, magnesium oxide, various amines and amine soaps, benzothiazoles) that reduce the amount of vulcanization agent needed or provide a delayed action acceleration of the vulcanization process.[8] Antioxidants are added to extend the life of the product, catalytic plasticizers reduce the viscosity of the rubber, and carbon black is used extensively as a filler.[8]

While the final tire formulations are generally not disclosed, common organic chemicals that are known to be used in tire manufacturing include hexa(methoxymethyl) melamine (HMMM), used extensively as a tire bonding agent,[8,9] and a range of vulcanization accelerators including 1,3-diphenylguanidine (DPG), 2-(4-morpholinyl)benzothiazole (24MoBT), and *N*-cyclohexyl-2-benzothiazolamine (NCBA).[8,10] A range of *N*′-disubstituted *p*-phenylenediamines also have had widespread growth as antioxidants in tire applications.[8]

These chemical additives are of high concern as acute toxicity to TRWP leachate has been demonstrated for a range of aquatic species including fish, daphnids, and copepods,[11] with toxic effects linked to leaching of zinc, benzothiazoles, phthalates, and resin acids.[11] More recently, a quinone derivative of the antioxidant *N*-(1,3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine (6PPD), commonly known as 6PPD-

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quinone, has raised attention due to demonstrated toxicity toward coho salmon (*Oncorhynchus kisutch*) at environmentally relevant concentrations.[12,13] There are a few studies reporting tire additives in the Australian environment, with HMMM and a range of cyclic amines reported in the surface waters of South East Queensland,[14] but to date, 6PPD-quinone has not been reported in the Australian environment.

Generally, there are fewer studies reporting TRWP concentrations in surface water than studies reporting the additives, as quantification methods present a range of analytical challenges.[10] The black color can impede the identification of TRWPs by microscopic techniques, and additives easily leach into the surrounding environment or can have multiple sources and so cannot be reliably used as a proxy for calculating TRWP mass. Thermal techniques that calculate TRWP concentrations based on the quantification of synthetic or natural rubber content, such as pyrolysis gas chromatography mass spectrometry (Pyr-GCMS) or thermal extraction and desorption GCMS (TED-GCMS), are limited when % rubber contents vary extensively between tire brands/models and the extent of this variation is not known.[15] To date, TRWPs have been identified in only a few studies in the Australian environment.[16,17] These studies used Fourier transform infrared spectroscopy (FTIR) to report the concentration as a particle count, rather than a mass-based concentration, with a size limitation of detection of particles >25 μm in diameter.

The aim of the current study was to utilize complimentary analysis methods of liquid chromatography tandem mass spectrometry (LC-MS/MS) and Pyr-GCMS to determine concentrations of both a range of chemicals commonly used as tire additives (including 6PPD-quinone) and synthetic rubber (as a proxy for TRWP concentration) in an Australian urban surface water catchment. The temporal trends of additives and TRWP concentrations throughout consecutive severe storms were determined and the corresponding mass loads of the pollutants to this urban creek were estimated.

MATERIALS AND METHODS

Chemicals. The term tire additive chemical has been used in this study as a way of grouping the target analytes with their common use, but it is recognized that there are additional uses of many of these chemicals that cannot be dismissed as sources. The target tire additive chemicals (n = 15) were chosen based on previously reported links with TRWPs and their reported presence in stormwater.[4,10,12,18] Additives included 6PPD-quinone, HMMM, a range of benzothiazoles and benzotriazoles (known vulcanizing accelerators and corrosion inhibitors), and a range of aromatic amines reported to co-occur with HMMM[4] and are thermal degradation products from tire manufacturing processes.[8] Specific chemical details are listed in Table S1a of the Supporting Information (SI), and a synthesized standard of 6PPD-quinone was obtained from the University of California,[19] with a summary of the synthesis included as Text S1 in the SI.

Polymer standards including styrene butadiene rubber copolymer (SBR 1500), isoprene, and d_6-polybutadiene (d_6-PB) were purchased from Polymer Source Inc. (Dorval, Canada) with specific polymer details (molecular weight, % isomer content) listed in Table S1b. Analysis-grade acetone, methanol, and dichloromethane were purchased from Merck Pty Ltd. (Victoria, Australia), and ultrapure water was purified with a MilliQ system (Millipore, Bedford).

Sample Collection. Samples were collected from a southwestern tributary of the Brisbane River (27°31′01″S, 152°57′25″E), known as Cubberla Creek, with the collection site 160 m downstream of a major motorway in Brisbane (M5, Western Freeway) and 1.8 km downstream of a second major highway (Moggill Road) (Figure S1). The Cubberla Creek catchment covers 10.5 km^2, and the sampling site is at the beginning of a wide open grassed floodplain.[20] The land use of this catchment is characterized as low-density residential, environmental conservation areas, recreation, and open space areas, with no industrial or wastewater inputs.[20] Upstream of the Western Freeway is another floodplain incorporating grassland sporting fields with no artificial turf application.[20]

Surface water (grab) samples were collected during major storm events on 9th, 10th, and 14th June and 21st, 22nd, 24−27th October 2020 in 600 mL polypropylene jars (Plasdene Glass-Pak Pty Ltd., Milperra, NSW), prerinsed with acetone and methanol. A total volume of 1 L was collected at each sampling time point, and samples were immediately sealed until transportation back to the laboratory where they were frozen (−20 °C) until analysis. Sample details are listed in Table S2. The area had not received rain for 18 days prior to collection in the June sampling campaign. Prior to the October sampling campaign, the area received 3 mm on 19th October but otherwise had not received rain for ∼30 days. Rainfall at the site was recorded with a Holman rain gauge (Bunnings, Rosalie, QLD), installed on the creek bank of ∼5 m from the sampling site, with volumes cross-referenced against recorded values from the closest meteorological monitoring station (Archerfield), operated by the Australian Government Bureau of Meteorology.[21]

Traffic data for the M5 motorway was not available for 2020 but was provided for 2019.[22] Brisbane city suffered a relatively short SaRS-COV-2 lockdown in 2020, with lockdown restrictions easing in May and the state borders reopening in July. Therefore, while traffic may have been slightly lower than previous years in the June sample period, it was back to normal conditions for the October sampling period, and we have used the 2019 traffic data as an estimate of 2020 traffic volumes. On average, 48 000 vehicles per day crossed the motorway near the sampling location on weekdays and 39 000 on weekends. The provided traffic data does not distinguish between passenger (car) and heavy (truck) vehicles.

Sample Extraction. Collected samples (1 L total volume) were spiked with 20 ng of d_6-5-methylbenzotriazole (d_6-5-MBTR) and d_5-atrazine (Table S1a) as internal standards. The samples were filtered sequentially through Whatman 1 and 0.7 μm glass fiber filters (GFFs) to collect particulates (47 mm, GF/A and GF/F, Rowe Scientific, Wacol, Australia). GFFs were wrapped in aluminum foil (precleaned with acetone), dried in an Orbital incubator at 50 °C (Thermoline Scientific, Wetherill Park, Australia), weighed, and analyzed for TRWPs with Pyr-GCMS.

The filtrate was extracted for tire additives with solid-phase extraction (SPE) following the previously published method.[14] Briefly, samples were loaded onto precleaned 6 mL Oasis HLB cartridges (150 mg, Waters, Rydalmere, Australia) and eluted with 10 mL of methanol. The eluant final volume was reduced to 0.2 mL and then made to a final volume of 1 mL in MilliQ water. $^{13}C_3$-caffeine (20 ng) was added as an injection standard prior to analysis with LC-MS/MS to calculate internal standard recoveries.

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Environ. Sci. Technol. 2022, 56, 2421−2431

LC-MS/MS Analysis. Samples were analyzed for tire additives on a SCIEX Triple Quad 6500+ LC-MS/MS (AB Sciex, Ontario, Canada), following the previously reported methodology.[14] Analytes were separated with an ExionLC AD high-performance liquid chromatograph with 10 μL of sample injected onto a Kinetex biphenyl 100 Å analytical column (2.6 μm, 50 mm × 2.1 mm) from Phenomenex (Lane Cove, Australia) heated at 45 °C. Mobile phases consisted of 0.1% formic acid in MilliQ water and 0.1% formic acid in methanol as mobile phases A and B, respectively. The gradient program started at 5% B as initial conditions, linearly increased to 10% B at 0.5 min, linearly increased to 100% B at 5.2 min, held at 100% B until 9.5 min, before returning to initial conditions and held for a further 3 min, with a constant flow rate of 0.3 mL/min throughout the program. The MS/MS was equipped with an electrospray ionization (ESI) source, operated in a positive ion mode, and multiple reaction monitoring (MRM) mode was used for detection. Monitored MRM transitions and optimized MS/MS conditions are listed in Table S3. Target analytes were quantified using internal standard correction, and calibration curves ranged from 0.01 to 1000 μg/L, with a linear curve over this range for all analytes.

Pyr-GCMS Analysis. The residues collected on the GFFs were analyzed for synthetic rubber on a multishot micro-furnace pyrolyzer (EGA/PY-3030D) coupled with a GC2030 GCMS (Shimadzu Corporation, Japan), following the previously reported methodology.[15] The filter paper was cut into 1/8th sections, with one section rolled and inserted into an 80 μL pyrolysis sample cup. The sample cup was then spiked with 50 μg of d_6-polybutadiene (d_6-PB) and 1 μg of d_{12}-triphenylene (d_{12}-TriPH) as internal standards. Samples were pyrolyzed using a double shot method, and data was collected in a full scan mode over a mass range of 40−600 m/z.

The synthetic rubber content of commercial tires is composed of a range of different formulations and % contents of styrene butadiene rubber (SBR) and butadiene rubber (BR). As such, a range of common pyrolysis products of both SBR + BR were analyzed to quantify the total SBR + BR concentrations in the sample and then calculate the concentration of TRWPs. Details on monitored pyrolysis products and thermal desorption and pyrolysis methods are listed in Table S4.

The final reported concentration of SBR + BR was calculated using the 4-vinylcyclohexene (4-VCH) pyrolysis product due to its sensitivity and a more realistic calculated % synthetic rubber content in tread than the styrene butadiene dimer or trimer.[15] The SBR + BR concentration was converted to an estimated concentration of tire tread in the sample using eq 1

$$M_T = \frac{M_{SBR} \times 0.9}{\%SBR + BR \times 100} \quad (1)$$

where M_T is the mass of tire tread (μg) and M_{SBR} is the mass of SBR + BR in the sample (μg), as calculated from 4-VCH. A correction factor of 0.9 is applied to correct for the difference in the styrene content between the SBR 1500 standard used in the calibration curve (23.5%) and the suggested SBR formulation used in the tire industry (15%).[23] The %SBR + BR is the % synthetic rubber content of tire tread. Due to the previously demonstrated variability of the SBR + BR content in tire formulations[15] and lack of available information on formulations in use on Australian roads, the %SBR + BR content is reported as a probability range. As the %SBR + BR content of n = 8 Australian commercially available tires was previously determined to range from 0.25 to 17.5%,[15] the 95% confidence interval of these values (4.5−13%) was used to estimate the probability range of the concentration of tire tread in the environmental samples.

Finally, previous studies have converted tire tread to a TRWP concentration by assuming TRWPs are 50% tread and 50% other particles such as minerals, soil, dust, and organic matter.[23] For comparability with previous studies, this factor has also been applied to report the final TRWP concentrations.

QA/QC. 6PPD (the precursor of 6PPD-quinone) was initially included in the analysis; however, it was found to degrade substantially over 1 month in calibration standards, which are prepared in 20% MeOH and 80% MilliQ water. Stability tests of 6PPD in samples have not yet been conducted; therefore, 6PPD is not included further in this study.

Duplicate 1 L samples were collected for 30% of the time points (n = 10), and tire additive chemicals were in good agreement between duplicates with reported concentrations having a relative percent difference (RPD) ≤ 20% when concentrations were greater than 10 times the limit of reporting (method detection limit; Table S5).[24] More variation was seen during the storm peak on the 27th October, where 12 RSDs were between 30 and 50% for HMMM, DPG, BTR, and 2-MTBT, which may indicate a variability and limitation with collecting consecutive grab samples during a high-volume, high-flow event. Reported concentrations are the average of replicate analyses. The calculated SBR + BR mass in the filtered residue had a greater variability between duplicates (RPD ranging from 8 to 95% for n = 8 duplicates) and also between 1/8th replicates from the same GFF (54% with RPD < 50%, n = 26 repeats), demonstrating the heterogeneity within the collected particulate samples. This was not unexpected as the total mass of residue collected from the samples was also highly variable between duplicates, with the RPD ranging from 23 to 157% for n = 10 duplicates. The final reported concentration of SBR + BR is an average of all analyses from that time point (duplicates and replicate analyses of 1/8th GFF sections).

Field blanks (1 per 10 samples) were prepared by filling a sampling jar with MilliQ water, transporting to the site, and returning to the laboratory for processing with samples. Twelve of the tire additives were detected in field blanks (Table S5), and method detection limits (MDLs) were calculated from concentrations in field blanks as the mean concentration + 3 × standard deviation. Where tire additives were not detected, MDLs were calculated as the concentration of a peak with a signal-to-noise ratio of 10:1. The only SBR + BR pyrolysis product detected in field blanks was benzene and was not included in further analysis. MDLs of the other pyrolysis products were calculated as the concentration of a peak with a signal-to-noise ratio of 10:1.

Internal standard recoveries (calculated from $^{13}C_3$-caffeine injection standard) averaged 78 ± 26% and 75 ± 27% for d_6-5-MBTR and d_5-atrazine, respectively. SPE recovery tests were conducted for the new tire additives not previously reported in Rauert et al.[14] by spiking 500 mL of MilliQ water with 50 ng of all analytes and internal standards and extracting following the above SPE protocol. Suitable recoveries for all targets were obtained with a mean of 98 ± 11%, except for 2-MTBT, which had average recoveries of 36 ± 8%. Reported concentrations of 2-MTBT were thus corrected, assuming an extraction recovery

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Environ. Sci. Technol. 2022, 56, 2421−2431

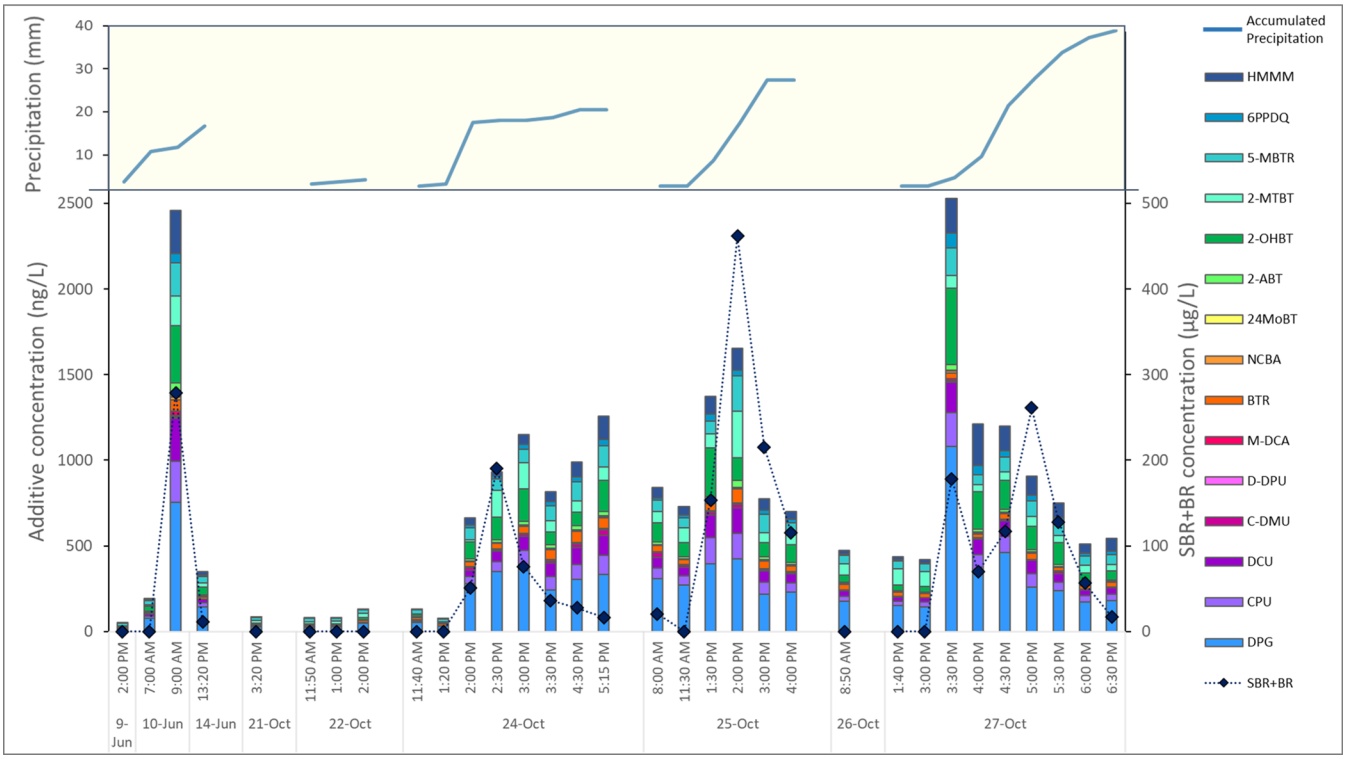

Figure 1. Concentrations of tire additives (bar graphs, ng/L) and synthetic rubber (diamonds and dotted line, SBR + BR µg/L) in Cubberla Creek, Brisbane, from grab samples. Accumulated precipitation over each storm event is represented in the top panel.

of 40%. Method spikes (n = 3) consisting of 500 mL of MilliQ, spiked with 20 ng of each target tire additive, were included in the analysis batches to assess the recovery of the whole sample processing method, with average recoveries of 100 ± 9% for all analytes except 2-MTBT with average recoveries again of 43 ± 8% (Table S6).

QC samples (n = 6) were prepared for Pyr-GCMS analysis by spiking a pyrolysis cup with 10 µg of SBR 1500 and 50 µg of d_6-PB internal standard. QCs were run every 10 samples as an instrument performance check with acceptable recoveries (110 ± 20%). Statistical analyses, including regression analysis (95% confidence level), were performed with Microsoft Excel for Microsoft 365.

Leachate Experiments. Leachates of six Australian tires (Table S7) were prepared for the comparison of additive profiles, with 50 mg of ground tire tread added to 200 mL of MilliQ water and gently stirred for 48 h. The ground tread was prepared from tire tread slivers collected using a scalpel precleaned with acetone. The tread was ground to fine particle size using a polymer prepper (Frontier Laboratories Ltd., Japan). A subsection of the ground particles from the Dunlop tire was further characterized (morphology, size) by an Olympus SZ-CTV microscope coupled with a Motic Images Plus (Software Version 3.0) camera. Four milligrams of ground tire tread was weighed onto a 0.7 µm GFF, and a representative 1/10th of the sample was imaged. Dimensions of 100 particles were captured, with the majority of the sizes distributed between 50 and 350 µm for the longest length and 50−100 µm in width (Figure S2) and all particles were a long-stretched rubber shape (Figure S3). It is recognized that this microscopy method has a size limitation of ∼30 µm, and smaller particles may be present that are not captured with this imaging technique.

Generated leachates were spiked with internal standards, filtered through 1 µm GFFs, and extracted with SPE following the same protocol as the samples. Extracts were analyzed for tire additives with LC-MS/MS.

Load Calculations. The mass load of additive chemicals and TRWPs to the sampling site were estimated using a numeric integration model[25] as in eq 2

$$\text{load} = \sum_{i=1}^{n} c_i q_i t_i \tag{2}$$

where c is the analyte concentration (ng/L), q is the corresponding flow (L/h), and t is the time interval (h) of the ith sample. Flow data was not available during the storm events, and gauges are not installed within the Cubberla Creek catchment;[20] however, the flow rate was manually measured at baseflow conditions on the 24th October as 0.009 m^3/s (flow of 20 m/s × creek width of 3 m × height of 6 cm). The peak discharge from the Western Freeway during flood events has previously been estimated as 79.4 m^3/s.[20] with a creek height of 10 m. In the current study, the maximum creek height reached up to 1 m, and therefore, the estimated maximum flow rate was taken as 7.94 m^3/s. Flow rates at each sampling time point during the 24th, 25th, and 27th October storms were estimated by assuming a linearly increasing gradient from baseflow conditions (prestorm collected sample) to the maximum flow rate when the creek reached maximum height. The flow was assumed to stay elevated at 7.94 m^3/s for the remainder of the sampling periods during that storm. Using these calculated flows and measured concentrations, the additive chemical mass load was calculated for each storm as g/storm and the TRWP mass load probability range as kg/storm.

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Environ. Sci. Technol. 2022, 56, 2421−2431

Table 1. Concentrations of Tire Additive Chemicals (ng/L), Synthetic Rubber (SBR + BR, μg/L), and Calculated Probability Range of TRWPs (μg/L) in Samples

		concentration (ng/L)															concentration (μg/L)	
		HMMM	DPG	CPU	DCU	C−DMU	D-DPU	M-DCA	6PPD-Q	BTR	NCBA	24MoBT	2-ABT	2-OHBT	2-MTBT	5-MBTR	SBR + BR	TRWP
9th Jun	02:00pm	<0.5	13	0.74	<8	<15	<0.06	2.3	0.39	5.5	<0.4	<0.7	4.6	2.2	5.2	13	<0.1	<MDL
10th Jun	07:00am	7.2	78	13	10	<15	<0.06	0.32	4.0	9.2	0.70	0.61	7.5	28	9.6	25	<0.1	<MDL
	09:00am	248	752	239	253	10	6.9	26	58	64	16	6.4	77	333	176	191	279	3860 −11,150
14th Jun	01:20pm	23	144	23	20	<15	<0.06	3.2	7.5	12	1.1	0.87	8.8	44	25	38	11	155−448
21st Oct	03:20pm	0.37	30	<0.01	<8	<15	<0.06	0.89	0.51	7.5	<0.4	<0.7	2.1	7.3	16	16	<0.1	<MDL
22nd Oct	11:50am	<0.5	24	<0.01	<8	<15	<0.06	0.61	0.43	7.9	<0.4	<0.7	1.8	7.9	16	17	<0.1	<MDL
	01:00pm	<0.5	27	<0.01	<8	<15	<0.06	0.84	0.38	8.0	<0.4	<0.7	1.9	6.1	16	17	<0.1	<MDL
	02:00pm	2.1	49	3.9	<8	<15	<0.06	1.1	0.83	10	<0.4	0.43	2.9	13	26	20	<0.1	<MDL
24th Oct	11:40am	5.3	52	7.9	6.2	<15	0.09	0.63	0.64	14	0.40	<0.7	3.0	14	5.3	22	<0.1	<MDL
	01:20pm	2.5	32	1.3	<8	<15	0.08	0.34	0.86	11	0.53	0.60	1.3	4.4	4.5	17	<0.1	<MDL
	02:00pm	42	280	42	37	16	0.19	3.9	16	28	4.0	1.8	10	101	12	70	51	700−2040
	02:30pm	26	351	57	61	10	0.11	3.6	14	33	2.9	1.5	17	129	158	64	190	2640−7610
	03:00pm	58	389	85	84	10	<0.06	5.4	24	42	4.1	3.2	22	191	153	77	76	1050−3030
	03:30pm	59	242	79	78	15	<0.06	8.3	25	57	4.1	2.8	22	74	66	86	36	504−1450
	04:30pm	88	303	89	97	20	<0.06	8.4	29	65	4.4	3.6	25	80	68	109	28	384−1110
	05:15pm	134	333	113	114	32	<0.06	7.8	36	65	5.1	4.8	26	180	80	126	17	231−667
25th Oct	08:00am	60	308	61	61	31	<0.06	5.0	14	36	2.7	2.3	14	111	67	65	21	284−821
	11:30am	51	273	54	50	9.7	<0.06	4.7	14	28	2.2	2.0	13	82	88	58	<0.1	<MDL
	01:30pm	100	395	152	131	18	0.08	8.3	41	40	6.2	4.8	31	287	82	74	153	2124−6137
	02:00pm	128	422	149	149	20	0.08	11	32	81	4.1	6.2	41	131	274	207	462	6390−18,470
	03:00pm	67	219	69	65	9.2	<0.06	4.0	26	47	3.3	4.4	15	83	58	104	215	2980−8620
	04:00pm	47	231	54	52	9.7	0.07	4.1	19	34	2.9	1.8	13	105	60	69	115	1590−4600
26th Oct	08:50am	22	177	30	33	<15	<0.06	4.9	7.4	33	1.6	1.4	9.7	38	69	48	<0.1	<MDL
27th Oct	01:45pm	19	151	27	24	<15	<0.06	3.2	5.4	24	1.0	0.78	7.9	33	97	45	<0.1	<MDL
	03:00pm	18	145	28	24	<15	<0.06	3.0	5.7	23	0.97	0.84	7.5	31	89	45	<0.1	<MDL
	03:30pm	201	1079	198	179	8.4	<0.06	12	88	35	10	6.6	30	449	72	160	178	2470−7140
	04:00pm	241	351	99	90	<15	<0.06	6.4	57	22	7.1	4.5	17	219	43	55	70	965−2780
	04:30pm	143	459	98	90	<15	0.10	6.3	40	35	4.9	3.9	17	167	49	86	117	1620−4680
	05:00pm	113	258	80	78	<15	<0.06	4.6	32	38	3.9	3.5	14	134	55	93	261	3620−10,440
	05:30pm	88	240	48	50	12	<0.06	3.5	25	21	3.1	2.3	9.4	129	42	78	128	1770−5120
	06:00pm	53	172	36	35	<15	<0.06	3.2	19	21	2.2	1.9	8.4	59	46	54	57	783−2260
	06:30pm	73	180	38	38	<15	<0.06	2.9	21	29	2.2	2.2	7.6	57	36	57	17	239−691

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Environ. Sci. Technol. 2022, 56, 2421−2431

RESULTS AND DISCUSSION

Tire additives were detected in all samples, with a clear trend of increasing concentrations of all additives during storm events. SBR + BR was detected in residue samples during the peak of the storm events and concentrations of the sum of tire additives and SBR + BR were correlated ($p < 0.001$; Figure S4). The correlation was influenced by two samples with higher concentrations; however, the correlation was still significant with these outliers removed ($p = 0.001$). Individual additives were also correlated with SBR + BR ($p < 0.01$; Table S8), suggesting that there may be common sources. However, there are additional commercial and domestic uses for many of the included target chemicals, such as in coatings and plastics (HMMM)[26] or as corrosion inhibitors (benzotriazoles and benzothiazoles),[27] and these additional sources cannot be ruled out.

SBR + BR pyrolysis products were below detection limits on the 0.7 μm GFFs, suggesting that the majority of TRWPs in the grab samples are >1 μm in size. It has been reported that under laboratory conditions the majority of TRWPs are generated in the range of 10−200 μm^2, and in tunnel dust, TRWPs have recently been reported to primarily occur in the 20−50 μm size range.[28] Figure 1 graphs concentrations of tire additives (ng/L) and of SBR + BR (μg/L) from each collection time point, with the accumulative precipitation over these storm events. All data is also listed in Table 1.

The June pilot study determined the feasibility of detecting both tire additives and TRWPs at this urban site and provided the first snapshot of the chemical profile of these additives to the sampling site. The prestorm collection on 9th June provided baseflow (or background) concentrations, with only eight of the tire additives detected, and at low concentrations ($\sum_8$additives = 63 ng/L). Concentrations increased on 10th June following storm activity overnight, with some of the highest concentrations of the study detected at 9 am ($\sum_{15}$additives = 2760 ng/L), indicating that the "urban flush"[29] had reached the sampling site. SBR + BR was also detected in this elevated sample, with an estimated TRWP concentration between 3.9 and 11 mg/L at this time point.

Following this pilot study, a more regular sampling protocol was set up for storm events in October to determine trends throughout the storm and to provide further information on profiles or traffic-related influences to the sampling site. Sampling on 21st October again provided baseflow levels, with a similar profile and concentrations to that detected on 9th June ($\sum_9$additives = 80 ng/L). The storm on 22nd October was relatively minor, with only ∼2 mm of precipitation, and as can be seen in Figure 1, there was little increase in concentrations at this site. However, the storms on the 24th, 25th, and 27th October were more significant, with a total daily precipitation of 18, 25, and 37 mm, respectively, and elevated additive and TRWP concentrations were detected as the storms progressed. Concentration trends of additives and TRWPs were similar with peaks at the beginning of or during the storm event. TRWP concentrations decreased to below detection levels toward the end of the storm, while additive concentrations remained elevated above baseflow concentrations. One sample was also collected on 26th October (between storms), and while the water depth had reduced back to baseflow levels, the concentrations of additives were still elevated. This may indicate the transport of TRWP/additive chemicals from additional sources upstream of the Western Freeway, such as Moggill Road interchange or the presence of settled TRWPs continuing to leach tire additives into this urban creek post storm activity.

The individual storms showed complex trends with concentration peaks post storm in June and concentration peaks at the beginning or middle of the storm in October. These trends are influenced by several different factors. The June storms saw prolonged rainfall, with the total daily precipitation of 10 mm falling over a period of about 15 h. The October storms meanwhile saw a high volume of precipitation fall in a much shorter time period (2−3 h). During the October storm events, the level of the creek increased between 40−60 cm on 24th and 25th and more than 100 cm on 27th October, where the creek entered the surrounding floodplains, and a dilution effect on the concentrations is seen in this storm. The 2017 Brisbane City Council Cubberla Creek Flood Study[20] notes the complex hydraulics of the floodplains surrounding the sampling site due to the major hydraulic structures on Moggill Road and the Western Freeway. The Western Freeway is comprised of a bridge crossing with numerous overflow obstructions on the freeway such as crash barriers, concrete impact barriers, and noise barriers that create blockages and storage of floodwaters within the road corridor, all impacting the discharge from this freeway into the creek.[20] Soil saturation was also observed following the October 24th storm, leading to increased surface runoff following storms.

Influence of Tire Additive Chemicals on a Brisbane Urban Tributary. Throughout all storm events, a similar profile for the tire additives was observed, with DPG, HMMM, 2-hydroxybenzothiazole (2-OHBT), a byproduct of the vulcanization accelerator 2-mercaptobenzothiazole,[30] and the cyclic amines 1-cyclohexyl-3-phenylurea (CPU) and 1,3-dicyclohexylurea (DCU) dominating the profiles. 6PPD-quinone was detected in every sample (0.4−88 ng/L), and this is the first time it has been reported in the Australian environment. Concentrations of 6PPD-quinone in this Brisbane creek were at least an order of magnitude lower than previously reported in surface water from the United States (<300−3500 ng/L)[12] and Canada (210−760 ng/L)[31] and an order of magnitude lower than the concentrations reported, with demonstrated toxicity to Coho Salmon (800 ± 160 ng/L);[12] however, these LC_{50} estimates have been refined recently to 95 ng/L for coho salmon[32] and the maximum concentration in this study is approaching these revised LC_{50} levels.

HMMM and the cyclic amines have been reported previously by the authors in the Australian surface water at 40 catchments in South East Queensland, with concentrations ranging <5−46 ng/L for HMMM and <MDL to 280 ng/L for the cyclic amines.[14] These concentrations were in line with baseflow conditions at this creek (<0.5−5.3 and <MDL to 7.9 ng/L for HMMM and the cyclic amines, respectively) but at least an order of magnitude lower than stormwater-influenced samples. However, the maximum HMMM concentrations in this Australian site (250 ng/L) were generally toward the lower end of surface water concentrations from the United States (1−200 ng/L),[4,29] Canada (55−2100 ng/L),[6,31] and Germany (10−800 ng/L)[26,33−35] and surface water with industrial inputs from Germany (210−6160 ng/L)[36] and China (1−6880 ng/L).[37] HMMM concentrations in the current study were well below the calculated predicted no effect concentration (PNEC) of 54 μg/L from a recent surface water risk assessment.[38]

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Environ. Sci. Technol. 2022, 56, 2421−2431

DPG had the highest concentrations of the tire additives in this study (13−1079 ng/L), and concentrations were in line with concentrations from surface water in the United States (5−540 ng/L),[39] Canada (160−760 ng/L),[31] Germany (10−65 ng/L),[40] and 14 further European sites (up to 100 ng/L).[41] Meanwhile, for the benzotriazoles and benzothiazoles, concentrations of 2-methylthiobenzothiazole (2-MTBT), 2-OHBT, and 5-methyl-1*H*-benzotriazole (5-MBTR) in this Brisbane creek (2−450 ng/L) were in line with surface water concentrations reported from China (30−680 ng/L),[27,42] Germany (180−320 ng/L),[43,44] and Spain (8−270 ng/L).[45] Benzotriazole (BTR), however, was lower at this site (6−81 ng/L) than reported in these previous studies (23−1470 ng/L), which may indicate additional sources (e.g., industrial or domestic use as anticorrosives) to the previous studies. All concentrations detected in this urban environment were well below the reported lowest observed effect concentrations (LOECs) and EC_{50} values for various aquatic species.[46] Interestingly, the additive profile observed in this study was similar to that reported in an urban creek in the United States,[29] where DPG, HMMM, DCU, 2-OHBT, BTR, and 5-MBTR tended to dominate the profile from a range of surveyed contaminants covering six analyte classes.

The additive concentration mass loads during the storms on October 24th, 25th, and 27th were calculated from the grab sample concentrations and estimated flow rates at each time point. The $\sum_{15}$additive mass loads ranged 104, 87, and 83 g/storm, and the 6PPD-quinone mass load ranged 2.7, 2.3, and 2.9 g/storm, for the October 24th, 25th, and 27th storms, respectively (Table S9). Considering an excess volume of water entered the floodplains on the 27th October and that concentrations remained elevated post storm, this is likely an underestimate of the total mass load but indicates the capacity for large quantities of these chemicals to be transported by urban runoff, as demonstrated in previous studies.[29]

Influence of TRWPs on a Brisbane Urban Tributary. The concentration of SBR + BR in the samples ranged from <0.1 to 387 μg/L, with a calculated probability range of TRWP concentrations in the highest sample of between 6.4 and 18 mg/L (Table 1). It is noted that there is still much uncertainty over the most appropriate method for determining the mass of TRWPs in environmental samples. As reported in Rauert et al.,[15] tires can contain a wide range of synthetic rubber contents and different synthesized polymer backbones, resulting in variable concentrations calculated from different pyrolysis products in the same sample. For the purposes of the current study, 4-VCH was chosen for quantification due to its analytical sensitivity, and TRWP concentrations are reported as an estimated probability range calculated from the knowledge currently available of the SBR + BR content in tires used on Australian roads.

Previous studies have reported tire wear in surface water and road runoff using leached tire additives as markers to calculate the concentration of TRWP or TWP, including NCBA, 24MoBT, 2-OHBT, and BTR. These previously reported concentrations were generally in line or within an order of magnitude of TRWP concentrations measured in the present study, with <MDL to 0.8 mg/L reported in China,[47] 1.6−92 mg/L in the United States,[11] 97 mg/L in Germany,[11] and 2.2−179 mg/L in Japan.[11,48] Eisentraut et al.,[49] meanwhile, used the thermogravimetric method TED-GCMS to report TRWP concentrations of 35−70 mg/g dry weight in road runoff in Germany, an order of magnitude higher than concentrations in the present study (<MDL to 4 mg/g). It is noted that comparisons between studies that use different analysis methods are difficult due to the challenges with each method, as previously discussed.

Peter et al.[29] also calculated TWPs in the U.S. surface water from the ratio of concentrations of HMMM, DPG, and DCU to TWPs in laboratory-prepared leachates. Assuming that the same ratio of additives to tire wear occurs in both environments, the previous estimate of additive concentration in tire tread (23 μg HMMM/g TWP, 16−101 μg DPG/g TWP, and 18 μg DCU/g TWP[4]) is generally within the same range as average concentrations in the present study of 33 μg HMMM/g TWP, 107 μg DPG/g TWP, and 27 μg DCU/g TWP, where values from the present study have been converted from TRWP to TWP by dividing by a factor of 2. However, these comparisons are treated with caution as there are many factors influencing the concentrations of tire additives in the water column. As discussed previously, the additive profiles in tire tread are highly variable, while concentrations in surface water may also be collected from road surfaces themselves, without the collection of the TRWPs, and the laboratory-prepared TWPs may differ (size, shape) from the environmental TWPs. Also, the grab samples in the current study sampled at the top of the water column and TRWP with a density of 1.3−1.7 g/cm^3[28] are expected to settle or travel lower in the water column or closer to the creek bed, leading to a potential underestimation of TRWP concentrations in the present study.

Toxicity data on TRWPs in aquatic environments is limited but the concentrations in the present study are lower than the reported EC_{50} toward *Daphnia magna*, which ranged from 290 to 32 000 mg/L when exposed to 12 different TRWP leachates.[50] The reported concentrations are in line with or higher than the PNEC concentration of 3.9 mg/L reported from long-term studies with *Ceriodaphnia dubia* and *Pseudokirchneriella subcapitata*.[11]

The TRWP mass load was also estimated from the TRWP concentration range as between 81−234, 252−730, and 136−392 kg/storm on October 24th, 25th, and 27th, respectively (Table S9). There are noted uncertainties with these calculations, including the estimation of the flow rate and the conversion from synthetic rubber to TRWP concentration, as discussed above. These calculations also assume that TRWPs are uniformly distributed throughout the water column, which will not be the case as dynamics in the creek will rely on the size and density of the particles. Despite the above uncertainties, this first estimate of mass load to this urban creek during severe storm events demonstrates the potential for large masses to enter local surface water, major rivers, and potentially marine environments.

Assessing the Variability of TRWP Sources. Considering the wide range of formulations that are used in commercial tires, the similarity in additive profiles in every storm event was not necessarily expected. To investigate further, laboratory-prepared leachates from six common tires used in Australia were analyzed for the suite of tire additives. Highly variable profiles were observed (Figure S6, Table S10), and while 2-OHBT generally dominated the profiles, DPG, HMMM, CPU, and DCU, which dominated this urban surface water profile, were not present in all leachate samples, further demonstrating the variability of tire formulations. The highly reproducible profiles in the urban surface water, however, suggest a commonality of sources of the additives and TRWPs during

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Environ. Sci. Technol. 2022, 56, 2421−2431

each storm. It is noted that many of these additives have additional uses such as in coatings and plastics (HMMM)[26] or as corrosion inhibitors (benzotriazoles and benzothiazoles),[27] so additional sources to this catchment may be possible from the residential areas. The correlation between additives and TRWPs does suggest a commonality of the primary source of both sets of pollutants to this catchment (e.g., road surfaces). This may be in the form of TRWPs themselves or TRWPs with the addition of additives on the road surface that are not attached to TRWPs.

To provide more information on the association of additives with particulates entering this creek, the thermal desorption analysis (first shot of the Pyr-GCMS run) of the residue samples was analyzed for the tire additives. Individual standards of additives were run to confirm spectra and retention times; however, concentrations were not quantified as calibration curves of SVOCs could not be prepared with this analysis method. As such, additives were investigated in a qualitative manner, and 10 of the tire additives were detected. Additives were only detected in samples where SBR + BR was also detected, with HMMM, DPG, CPU, 2-OHBT, NCBA, 2-ABT, and 2-MTBT dominating (Table S11), further suggesting that particulates (likely from roadway surfaces) are a key source of the additives to this site.

To investigate the unexpected uniformity of profiles at this site further, the ratio of the different TRWP pyrolysis products was compared as this has shown to be highly variable in previous analyses of different tire treads and influenced by other styrene-containing polymers.[15] The ratio of 4-VCH/α-methyl styrene was lower in samples (0.27−0.85) than in standards and QCs (5.6 ± 1.5). This may indicate another more dominant polymer/rubber source to the site such as styrene butadiene styrene copolymer, which is commonly used in the polymer-modified bitumen applied on pavements and in SBS-modified asphalt[51] and has a lower ratio of 4-VCH/α-methyl styrene than SBR.[52] To provide more insight, the previous analysis of n = 39 commercial tires[15] was reanalyzed to assess ratios of these pyrolysis products in individual tire samples. The 4-VCH/α-methyl styrene ratios were highly variable in the tire tread, ranging from 0.14 to 26 (mean 3.1), and the lower ratio in environmental samples is more likely due to the highly variable nature of tire formulations entering the environment, rather than another polymer source dominating this sampling site.

The natural rubber (NR) content of the tires was also monitored qualitatively through the dipentene (DP) pyrolysis product.[15] It has previously been suggested that the total rubber content of tires (natural and synthetic rubbers) is 50%, with truck tires primarily consisting of NR.[23] This has been demonstrated to not be the case,[15] and the % content of NR can be just as variable as SBR + BR,[15] with a DP/4-VCH ratio ranging from 0.06 to 13 (mean 3.0) in commercial tires. However, in the samples from this creek, the DP/4-VCH ratio had a smaller range (0.41−4.74, mean 1.55), with normalized peak areas of DP and 4-VCH highly correlated (p < 0.001) (Figure S5).

The smaller variability of the 4-VCH/α-methyl styrene and DP/4-VCH ratios in the environmental samples, as compared to commercially available tires, suggests a dominance and well mixing on the roads of only a few tires/brands contributing TRWPs. The Australian tire market is dominated by four companies: Bridgestone, Goodyear, Yokohama, and Kumho tires, accounting for 70% of the total tire market,[53] with Bridgestone and Goodyear accounting for nearly 40% of the market.[54] Therefore, it is reasonable that there are a few popular passenger car tire models that cover the majority of use in Brisbane and contribute a similar TRWP signature to this site at all time points. Investigating profiles at other surface water sites in Brisbane and nationally would provide more insight into this in future studies.

Implications for the Australian Environment. Surface water concentrations of tire additives, including 6PPD-quinone and HMMM, and calculated concentrations of TRWPs in this study were toward the lower end of previously reported concentrations from the United States, Canada, and Germany.

One contributing factor may be higher-estimated TRWP emission rates for the United States of 1 524 740 tonnes/year, as compared to those for Australia of 20 000 tonnes/year.[3,55] Australian vehicles also use all-season tires that are formulated to last longer than summer and winter tires[56] that are commonly used in northern Europe and northern United States, further reducing the TRWP emissions in Australia as compared to these countries. It was noted that similar daily traffic counts are estimated for the Western Freeway and Highway 509 in Washington (the closest highway to the Miller Creek sampling site where coho salmon mortality was observed), with 62 000 vehicles per day in 2015.[57] The population densities vary between the different regions, with Brisbane being a sprawling city with a population density of 1500 people/km^2 in the catchment area. Metropolitan Seattle (United States) and Toronto (Canada), meanwhile, have population densities of ∼3390 and 5900 people/km^2, respectively, so TRWP emissions are expected to be greater in these catchment areas. However, after normalizing the previously reported 6PPD-quinone concentrations for population density, concentrations in this study are still 2−15 times lower than those reported in surface water from Toronto and Seattle.

Information on the length of the Western Freeway that drains into the catchment is unavailable, although a 1.5 km stretch of the Western Freeway runs parallel to Tributary C, which joins Cubberla Creek upstream of the sampling site. Using the emission rate for an average Australian tire of 0.03 g/km,[55] this 1.5 km stretch of freeway generates a total of 8.64 kg/day of tire wear on weekdays and 7.02 kg/day on weekends or 57 kg/week. A much higher estimate of TRWP mass load/storm was calculated from the TRWP concentrations during storm events, suggesting that a larger freeway area may be washed in the catchment, as well as transport from additional sources upstream such as the Moggill Road interchange or a resuspension of TRWP in settled sediment in these high-energy storms.

The current study reports concentrations and tends of both tire additives and TRWPs to an urban surface water in Brisbane, Australia. The contamination profile of these tire additives to this microenvironment is defined, and the influence of storm events is clearly demonstrated, with concentrations of tire additives increasing by more than 40 times during storm peaks. Concentrations of 6PPD-quinone are reported in the Australian environment for the first time, demonstrating its ubiquity in the global environment.

There are several key areas for further research highlighted by this study, such as a need for standardized methodologies for quantifying TRWPs. In particular, the ability to confidently quantify TRWPs in environmental samples is impeded by the lack of information on the wide range of tire formulations in

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Environ. Sci. Technol. 2022, 56, 2421−2431

use (including rubber content and additive chemical content). Knowledge on formulations of key tire brands/models primarily used on Australian roads would assist with refining TRWP concentration calculations and the relationship between TRWPs and tire additive concentrations in environmental samples.

Furthermore, the elevated concentrations of tire additives remaining in this Brisbane creek post storm suggest prolonged exposure of these chemicals to aquatic organisms. Further investigation of the fate of TRWPs and additive chemicals in Australian surface water is needed, including the time scale for elevated concentrations to flush from these systems and the extent that TRWPs will travel this creek before settling. The high mass load of TRWPs and additive chemical pollution in this one Australian site demonstrates the impact of stormwater runoff on these ecosystems and the need for improved understanding in terms of fate-exposure-effects-risk in catchments across Australia.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c07451.

> Target analyte and analysis method details, validation data, map of sampling site, ground tire tread details, statistical analyses, mass load calculations, and tire leachate profiles and text describing the synthesis of 6PPD-quinone (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

HMMM	hexa(methoxymethyl) melamine
DPG	1,3-diphenylguanidine
CPU	1-cyclohexyl-3-phenylurea
DCU	1,3-dicyclohexylurea
C-DMU	3-cyclohexyl-1,1-dimethylurea
D-DPU	1,3-diethyl-1,3-diphenylurea
M-DCA	*N*,*N*-dicyclohexylmethylamine
6PPD	*N*-(1,3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine
6PPD-Q	6PPD-quinone
BTR	1*H*-benzotriazole
NCBA	*N*-cyclohexyl-1,3-benzothiazol-2-amine
24MoBT	2-morpholin-4-yl-benzothiazole
2-ABT	2-aminobenzothiazole
2-OHBT	2-hydroxybenzothiazole
2-MTBT	2-(methylthio)benzothiazole
5-MBTR	5-methyl-1*H*-benzotriazole
SBR + BR	total synthetic rubber (styrene butadiene rubber + butadiene rubber)
TWRPs	tire road wear particles

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Environ. Sci. Technol. 2022, 56, 2421−2431