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Widespread Occurrence and Transport of *p*-Phenylenediamines and Their Quinones in Sediments across Urban Rivers, Estuaries, Coasts, and Deep-Sea Regions

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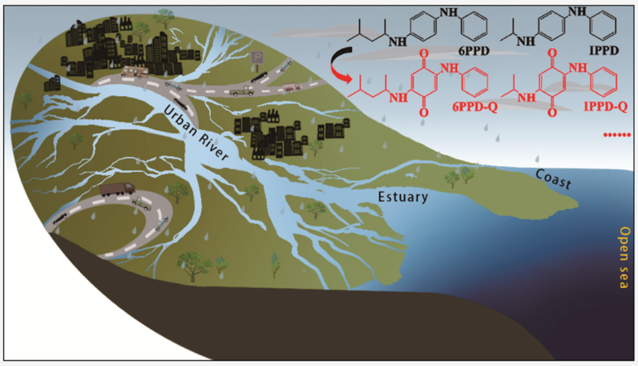

ABSTRACT: *p*-Phenylenediamines (PPDs) are widely used as antioxidants in tire rubber, and their derived quinone transformation products (PPD-Qs) may pose a threat to marine ecosystems. A compelling example is *N*-(1,3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine (6PPD)-derived quinone, called 6PPD-Q, as the causal toxicant for stormwater-linked acute mortality toward coho salmon. However, the knowledge of the co-occurrences of PPDs and PPD-Qs and their transport from freshwater to oceanic waterbodies on a large geographical scale remains unknown. Herein, we performed the first large-scale survey of these chemicals in sediments across urban rivers, estuaries, coasts, and deep-sea regions. Our results demonstrated that seven PPDs and four PPD-Qs are ubiquitously present in riverine, estuarine, and coastal sediments, and most of them also occur in deep-sea sediments. The most dominant chemicals of concern were identified as 6PPD and 6PPD-Q. Total sedimentary concentrations of PPDs and PPD-Qs presented a clear spatial trend with decreasing levels from urban rivers (medians: 39.7 and 15.2 ng/g) to estuaries (14.0 and 5.85 ng/g) and then toward coasts (9.47 and 2.97 ng/g) and deep-sea regions (5.24 and 3.96 ng/g). Interestingly, spatial variation in the ratios of 6PPD to 6PPD-Q ($R_{6PPD/6PPD\text{-}Q}$) also presented a clear decreasing trend. Our field measurements implied that riverine outflows of PPDs and PPD-Qs may be an important route to transport these tire rubber-derived chemicals to coastal and open oceans.

KEYWORDS: *p-phenylenediamines (PPDs), PPD-quinones (PPD-Qs), tire rubber-derived chemicals, riverine runoff, marine environment*

■ INTRODUCTION

p-Phenylenediamines (PPDs) are an important class of synthetic antioxidants that are used as additives in rubber-related products, mostly in rubber tires.[1,2] Among the globally used PPDs, *N*-(1,3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine (6PPD) is the most frequently used tire antioxidant and has been listed as a high production volume (HPV) chemical by the Organization for Economic Co-operation and Development (OECD).[3] In China, the current annual production of 6PPD alone is 200,000 tons, accounting for approximately 54% of the total production of all current-use rubber antioxidants.[4] Apart from China, 6PPD is also the world's most dominant PPD antioxidant, while other PPDs, including *N*-isopropyl-*N*′-phenyl-1,4-phenylenediamine (IPPD), *N*, *N*′-bis(1,4-dimethylpentyl)-*p*-phenylenediamine (77PD), and *N*, *N*′-diphenyl-*p*-phenylenediamine (DPPD), have annual productions varying from 1,000 to 15,000 tons in different countries.[5−7] The broad and massive use of PPDs in tires, as well as ubiquitous tire wear, appears to be leading to emissions of PPDs into the environment.[8−13] As a result, roadway runoff-receiving waters become the primary transport medium of these tire wear compounds around the world.[14−17] However, PPDs themselves may possess health and environmental hazards, among which 6PPD is a classic example as it can induce species-specific toxicity to aquatic organisms.[18−20]

Beyond PPDs, a recent study by Tian and colleagues[21] identified a highly toxic quinone transformation product of 6PPD, called 6PPD-quinone (6PPD-Q), as the causal toxicant responsible for acute mortality of the Pacific Northwest coho salmon when they migrate to urban freshwater streams to reproduce. This milestone discovery answered a long-standing unexplained phenomenon of "urban runoff mortality syndrome"[22] and has now triggered worldwide concern regarding the aquatic ecological risk posed by 6PPD-Q and other potentially existing PPD-derived quinones (PPD-Qs). Apart from the coho salmon,[23] 6PPD-Q was also proven to have

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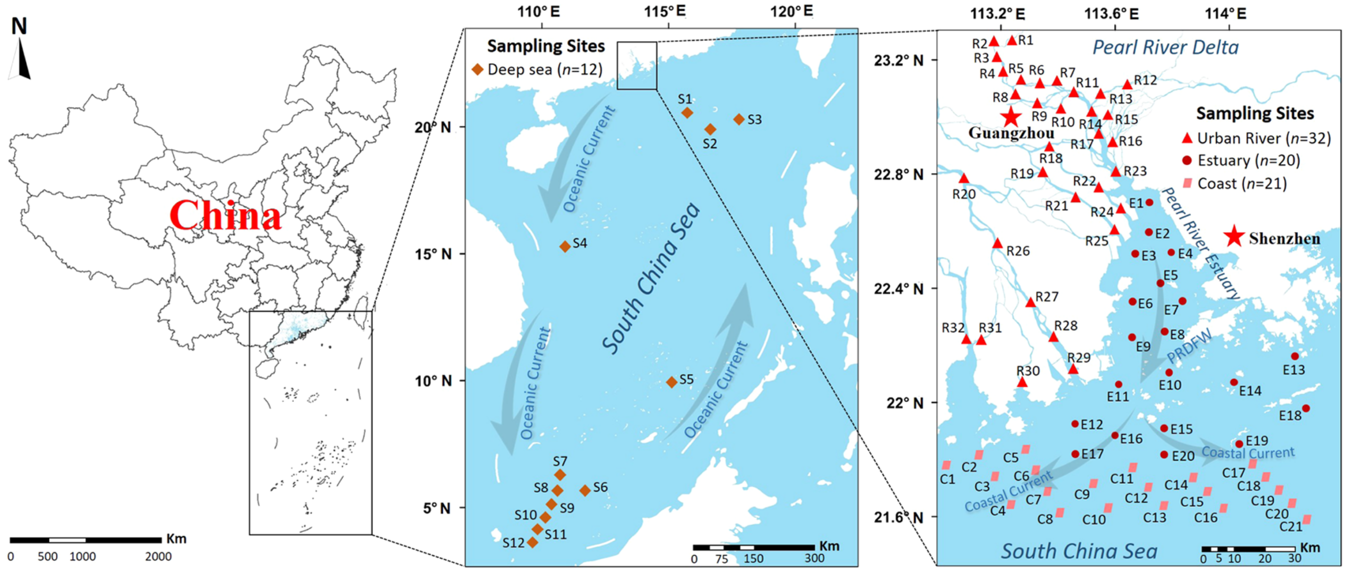

Figure 1. Map showing the sampling sites of surficial sediments in the study areas across urban rivers of the Pearl River Delta (PRD), the Pearl River Estuary (PRE), and the coasts and deep-sea regions of the South China Sea (SCS). The sampling maps depict the Pearl River diluted freshwater (PRDFW), coastal currents, and oceanic currents by large arrows based on refs 44, 45.

acute toxicity to other sensitive aquatic species.[24−26] For example, the median lethal concentrations (LC_{50}) for brook trout (24 h) and rainbow trout (72 h) were observed at 0.59 and 1.00 μg/L, respectively,[24] which are also well within the ranges of reported environmental concentrations (<0.3 to 19 μg/L) of 6PPD-Q in surface waters after stormwater runoff events,[17,21,23,27] further raising scientific concerns. Subsequent latest data discovered the pervasive occurrence of 6PPD-Q in urban runoff,[15,17] surface waters,[14,27] fine air particles ($PM_{2.5}$),[11] and dust.[28,29] In addition to 6PPD-Q, other multiple PPD-Qs, such as IPPD-quinone (IPPD-Q) and 77PD-quinone (77PD-Q), were also found in urban runoff, roadside soils, and $PM_{2.5}$.[13,30] However, to the best our knowledge, whether these emerging PPDs and PPD-Qs are more widely present in roadway runoff-receiving river waterbodies and riverine runoff-affected estuarine, coastal, and oceanic waterbodies on a large geographical scale remains unknown, hampering our understanding of their ecological risks in freshwater and marine ecosystems.

Sediment is regarded as an important sink of many organic contaminants and has a great impact on their distribution, transport, and fate in the aquatic environment.[31] Additionally, the sediment pollution level can serve as a useful indicator for the extent of water pollution and reflect ecological risks in the aquatic environment.[32] River sediment may be the major sink for PPDs and PPD-Qs because rivers are the main receptors of storm runoff and roadway runoff. Generally, sediment-bound organic contaminants can preferentially adhere to fine-grained particles such as silt and clay.[33] The fine-grained particles are readily transported through rivers in a suspended state and can be deposited on estuaries and adjacent coasts, where contaminated sediments can be further transported to open sea driven by coastal and oceanic currents.[34] Compared to river sediments, deep-sea sediments provide an ultimate sink for anthropogenic pollutants because they are considered to be devoid of human impacts.[34] Therefore, to better understand the distribution, transport, and fate of PPDs and PPD-Qs in the aquatic environment, monitoring of these emerging contaminants in sediments via a large-scale survey is of particular importance given their aquatic toxicities to sensitive aquatic species like coho salmon.[20,24−26]

The Pearl River Delta (PRD) is one of the most industrialized and urbanized regions in China and has high traffic volumes. Many urban rivers flow through the PRD and directly into the Pearl River Estuary (PRE) and adjacent South China Sea (SCS) via major riverine runoff outlets (Figure 1), carrying large amounts of municipal and industrial origin waterborne substances to estuarine, coastal, and marine environments. The PRD is located in a subtropical and East Asian monsoon zone adjacent to the SCS, with annual precipitation at 1200 to 2200 mm.[35] As a result, riverine runoff may be an important transport route for tire rubber-derived chemicals to the SCS of the western Pacific Ocean. Therefore, this large geographical region is ideal for the study of the widespread occurrence and transport of PPDs and PPD-Qs from freshwater to oceanic waterbodies.

In this study, the PRD and adjacent PRE and SCS were selected as the typical research areas for the case study and great efforts were made to comprehensively collect 85 sediment samples across rivers, estuaries, coasts, and deep-sea regions. For the first time, a large-scale survey of PPDs and PPD-Qs was conducted in different aquatic environments, with specific emphasis on elucidating their occurrence and transport from freshwater to marine sediments and the impact of their riverine outflows on the marine environment. The monitoring baseline data of such a large-scale survey of sediments are expected to greatly expand our existing knowledge of PPDs and PPD-Qs in the environment. Meanwhile, new information obtained from this study will not only advance our better understating of the environmental occurrence, distribution, and transport of these tire rubber-derived emerging chemicals but will also provide open clues and promote further investigation into their environmental fate and potential ecological risks in the future.

■ MATERIALS AND METHODS

Standards and Reagents. Seven PPDs, namely, 6PPD, IPPD, 77PD, DPPD, *N*,*N*′-di-2-butyl-*p*-phenylenediamine

(44PD), 4-(cyclohexylamino)diphenylamine (CPPD), and 1,4-bis(2-naphthylamino)benzene (DNPD), were included in this study, which are widely used as the primary PPD antioxidants in the rubber industry. Their CAS registry numbers, formulas, chemical structures, and key physicochemical properties are shown in Table S1. Authentic standards of these seven PPDs were purchased from Tokyo Chemical Industry (Tokyo, Japan), AccuStandard (New Haven, CT), and J&K Scientific (Beijing, China), with a purity of >98%. Four main PPD-derived quinones (6PPD-Q, IPPD-Q, 77PD-Q, and CPPD-Q) were included in this study based on the availability of their reference standards. Authentic standards of 6PPD-Q and IPPD-Q were bought from Dr. Ehrenstorfer (Augsburg, Germany), with a purity of 97.8%. Other PPD-Qs are not commercially available at present, while 77PD-Q and CPPD-Q can be formed via oxidation transformation of 77PD and CPPD standards under general outdoor sunlight irradiation conditions, which can be precisely identified and clearly verified (Figure S1) based on the previously reported MS^2 fragmentation spectra[13,30] and semiquantified based on their respective calibration curves of parent PPDs. Two isotope-labeled internal standards, 6PPD-d_5 and $^{13}C_6$-6PPD-Q, were purchased from Chiron (Trondheim, Norway) and Cambridge Isotope Laboratories (Andover), respectively.

Sediment Sample Collection. The sampling areas of this study cover the main rivers of the PRD, the PRE, the coasts, and deep-sea regions of the SCS and the detailed sampling sites are shown in Figure 1. The sampling plan was so designed to allow a thorough assessment of the spatial distribution and transport of PPDs and PPD-Qs in major rivers within the PRD as well as the estuarine and coastal regions and the nearby open sea. The PRD is the second largest estuarine delta in China, in which the river network is mainly comprised of the Beijiang, Zhujiang, Dongjiang, and Xijiang rivers and ultimately merges into the PRE via eight outlets.[36] The silt and clay mainly consist of suspended sediments.[37] In the PRE, the waters from the northwestern inlets tend to flow along the west coasts, owing to the effect of circulation currents and the prevailing westward wind in this region.[36] In August 2021, a sampling campaign for river sediments in the PRD was conducted. The sampling sites of river sediments covered most of the main streams of the river network in the PRD. These sample sites with intervals of 5−10 km were selected, and at each site, surface sediments (1 m away from the water−land interface) were collected from each plot. A scientific cruise covering the PRE, coasts, and deep-sea regions (water depth: 1000−2000 m) of the SCS was launched in March 2021. Estuarine sediments were collected along the PRE with site intervals of 10−20 km. Coastal sediments were collected from the northern SCS along seven transects perpendicular to the coastline with site intervals of ∼10 km. Deep-sea sediments were only collected from known mud areas (depositional zones) in the SCS along the prevailing circulation current direction, as shown in Figure 1. All sediments (top ∼10 cm) were taken onboard using a grab sampler (Van Veen grab), packed in aluminum foil, and stored in polypropylene tubes at −20 °C. At each site, three sediment samples were taken using three grab samplers and mixed as a composite sample. A total of 32, 21, 20, and 12 sediment samples were collected from the urban rivers of the PRD, the PRE, coasts, and deep-sea regions of the SCS, respectively. All samples were frozen for transport to the laboratory. Further, they were freeze-dried, weighed, sieved through a 1.0 mm mesh screen to remove coarse debris, and then stored at −80 °C until chemical analysis. The total organic carbon (TOC) content in sediment samples was determined using a Solids TOC Analyzer (O.I. Analytical) and expressed as a weight percent.

Sample Pretreatment and Instrumental Analysis. Each sieved sediment sample of 200 mg was transferred to a precleaned glass tube and spiked with the surrogate standards of 6PPD-d_5 and $^{13}C_6$−6PPD-quinone (10 ng for each). After equilibration for 30 min, 0.2 mL of 1 mmol/L glutathione solution was added as a protective agent, considering potential oxidative transformations of PPDs during sample preparation.[38] Each sample was extracted with 1.0 mL of acetonitrile by vortexing for 10 min and ultrasonication for 20 min. Following centrifugation at 3000 rpm for 10 min, the extract was transferred to another precleaned glass tube. Then, the sample was extracted a second time with the same extraction operations. The combined extract was diluted with acetonitrile to an accurate volume of 2.0 mL, and an aliquot of 1.0 mL was taken and filtered through a PTFE filter membrane (0.22 μm) for instrumental analysis.

The targets were analyzed by an ExionLC AC liquid chromatograph coupled to a Triple Quad 5500 mass spectrometer (LC−MS/MS, AB Sciex, Framingham, MA). The LC system was equipped with a C8 column (Waters XBridge BEH, 2.5 μm, 2.1 mm × 100 mm) as the optimal analytical column for chromatographic separation with an injection volume of 5 μL. The mass spectrometer was equipped with a TurboIonSpray electrospray ionization (ESI) probe in positive ion mode for determination of all targets. The mobile phase consisted of (A) 0.1% formic acid in water and (B) methanol at a flow rate of 0.3 mL/min, with the gradient as follows: 0−1.5 min, 10% B; 4−15 min, 100% B; and 15.1−20 min, 10%, B. Multiple reaction monitoring (MRM) was used to identify and quantify the analytes. All targets were quantified based on their respective calibration curves except 77PD-Q and CPPD-Q, which were semiquantified based on the calibration curves of their respective parent chemicals due to the lack of commercially available standards. Detailed MRM ion transitions and optimized parameters for all target compounds and ISs are summarized in Table S2. Extracted ion chromatograms (EICs) along with MS^2 fragmentation spectra for four PPD-Qs and EICs for seven PPDs are illustrated in Figures S1 and S2, respectively.

Quality Assurance and Quality Control (QA/QC). A series of strict QA/QC measures were adopted to guarantee accurate identification and quantification of PPDs and PPD-Qs. Two procedure blanks (using prebaked Na_2SO_4 as a substitution for dust) were included in each batch of 10 sediment samples. No PPDs and PPD-Qs were detected in any procedural blanks. To evaluate the extraction efficiency, six out of the 85 collected sediment samples that had been extracted 2 times were randomly selected for extraction a third time. No detectable target compounds were found in the third extract. Matrix spike recoveries of PPDs and PPD-Qs were evaluated by three replicate analyses of fortified sediment samples from a lake in the Tibet Plateau, which were determined to find no PPDs and PPD-Qs, at two spiked levels of 10 and 100 ng/g. The average recoveries were in the range of 81.2−93.4%, with relative standard deviations (RSDs) of less than 10%. Matrix effects were determined by comparing the response from three replicate analyses of spiked sample extracts with that of their respective standards in pure solvents, and the results were determined between 82.7 and 95.2%, indicating no significant

Table 1. Concentrations (ng/g, dw) of Seven PPDs and Four PPD-Qs Detected in Freshwater and Marine Sediment Samples (n = 85) from Urban Rivers of the Pearl River Delta (PRD), the Pearl River Estuary (PRE), and Coasts and Deep-Sea Regions of the South China Sea (SCS)

		urban rivers in the PRD (n = 32)			the PRE (n = 21)			coasts of the SCS (n = 20)			deep-sea regions of the SCS (n = 12)		
compound	MDL[a]	DF[b]	median	range	DF	median	range	DF	median	range	DF	median	range
					p-Phenylenediamine Antioxidants (PPDs)								
6PPD	0.015	100	14.4	0.585−468	100	3.92	1.49−5.71	100	1.82	1.07−11.1	83	2.66	<MDL−2.69
IPPD	0.13	97	1.61	<MDL−29.9	81	0.42	<MDL−3.42	50	0.14	<MDL−6.18	75	0.26	<MDL−0.38
44PD	0.90	50	3.02	<MDL−19.6	71	2.27	<MDL−5.67	40	<MDL	<MDL−5.05	25	<MDL	<MDL−1.70
77PD	0.040	63	5.58	<MDL−7.02	62	2.36	<MDL−3.86	85	1.77	<MDL−2.42	25	<MDL	<MDL−1.33
CPPD	0.19	91	1.38	<MDL−5.30	52	0.59	<MDL−1.59	75	0.79	<MDL−1.52	33	<MDL	<MDL−0.40
DPPD	0.74	59	2.43	<MDL−67.1	62	2.39	<MDL−4.22	20	<MDL	<MDL−1.81	25	<MDL	<MDL−1.97
DNPD	0.22	66	1.90	<MDL−12.5	33	<MDL	<MDL−4.89	55	1.03	<MDL−5.77	0	<MDL	<MDL
∑PPDs			39.7	5.11−500		14.0	5.66−17.1		9.47	4.47−19.9		5.24	3.35−6.17
					p-Phenylenediamine Quinones (PPD-Qs)								
6PPD-Q	0.043	100	9.03	1.87−18.2	95	2.00	<MDL−4.88	100	1.27	0.431−2.98	75	2.71	<MDL−3.02
IPPD-Q	0.27	100	1.24	0.434−9.91	71	1.94	<MDL−3.97	70	0.83	<MDL−1.90	58	0.66	<MDL−1.34
77PD-Q[c]		88	3.84	<MDL−17.8	57	0.92	<MDL−3.17	70	0.74	<MDL−2.31	42	<MDL	<MDL−1.11
CPPD-Q[c]		66	0.82	<MDL−3.79	29	<MDL	<MDL−0.77	25	<MDL	<MDL−1.05	8	<MDL	<MDL−0.25
∑PPD-Qs			15.2	7.20−34.5		5.85	1.92−9.96		2.97	1.06−6.61		3.96	<MDL−4.45

[a] Method detection limit (ng/g). [b] Detection frequency (%). [c] Semiquantified on the basis of their respective calibration curves of parent PPDs due to a lack of commercially available standards.

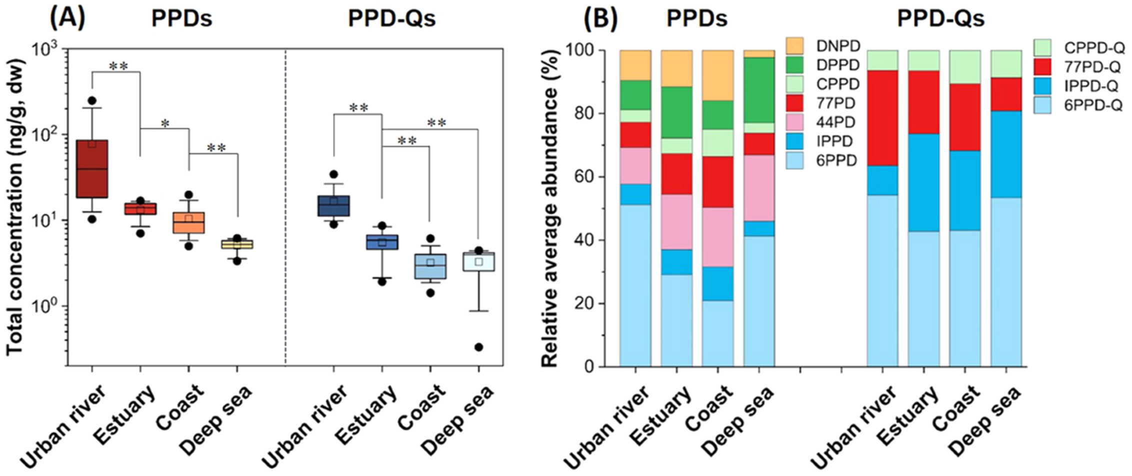

Figure 2. (A) Concentration distributions and (B) composition profiles of PPDs and PPD-Qs (percentage average mass fraction of individual compounds) in surficial sediments from freshwater to marine waterbodies along urban rivers, estuaries, coasts, and deep-sea regions in the large-scale geographical study area. The boxes represent the 25th and 75th percentiles; the black lines represent the median; the whiskers represent the 10th and 90th percentiles; and the dots represent the 5th and 95th percentiles. The one and two asterisks denote significant differences at the levels of $p < 0.05$ and 0.01, respectively.

ionization suppression or enhancement. The method detection limit (MDL) was determined by analysis of 200 mg spiked sediment samples with known concentrations of each analyte. The minimum spiked concentration at which each analyte can be reliably detected with a signal-to-noise ratio of 3 in the sample matrix and was reported as the MDL. The MDLs for individual PPDs and PPD-Qs varied from 0.015 (6PPD) to 0.90 (44PD) ng/g. Daily nine-point calibration curves within the concentration range of 0.1−100 ng/mL were prepared for quantification, with their regression coefficients (R^2) of > 0.99. All concentrations were reported on a dry weight (d.w.) basis. Detailed QA/QC results are summarized in Table S3.

Data Analysis. SPSS Statistics 23.0 software was used for statistical analysis with a significance level of $p < 0.05$. Descriptive statistics, including the detection frequency (DF), median, and range, were used to summarize measured concentrations of PPDs and PPD-Qs. The concentration below MDL was replaced by 1/2 MDL for statistical analyses. The Shapiro−Wilk test was used to determine the normality of the concentration data. Depending on the data distribution, significant differences in concentrations were examined using the *t*-test or Mann−Whitney test and correlations were determined by two-tailed Pearson or Spearman correlation analyses. Degradation half-lives in soil, water, and air, and partition coefficients between air and water ($\log K_{aw}$) and between octanol and water ($\log K_{ow}$) for PPDs and PPD-Qs were estimated by U.S. EPI Suite 4.1 software.[39] Furthermore, using these physicochemical values as input parameters, the characteristic travel distances (CTDs) and transport efficiencies (TEs) for PPDs and PPD-Qs were predicted by the OECD Pov and LRTP Screening Tool.[40]

■ RESULTS AND DISCUSSION

Sedimentary Concentrations and Spatial Distribution of PPDs from Rivers to Open Sea. Detailed concentrations of seven PPDs in sediments from the urban rivers in the PRD, PRE, coasts, and deep-sea regions of the SCS are summarized in Table 1 and provided in Table S4. All PPDs were widely detected in riverine, estuarine, and coastal sediments. More importantly, most PPDs (with the exception of DNPD) were detected in deep-sea sediments, demonstrating their widespread occurrence in various aquatic environments on a large geographical scale. Among the suite of PPDs, 6PPD was identified as the most dominant congener detected in all four types of sediment, followed by IPPD, a very similar structure congener to 6PPD. Total concentrations of all PPDs ($\sum$PPDs) presented a significant spatial gradient decreasing pattern of urban rivers > estuaries > coasts > deep-sea regions (Figures 2A and S3A). The median sedimentary concentration of $\sum$PPDs in urban rivers of the PRD was 39.7 ng/g (range of 5.11 to 500 ng/g), approximately 3 to 4 times higher than that in the PRE (14.0 ng/g) and the coasts (9.47 ng/g), but nearly one order of magnitude higher than that in the deep-sea regions of the SCS (5.24 ng/g). A halving distance of the concentrations of PPDs diluted was estimated to be approximately 26.3 km. It was reported that the PRD rivers annually deliver an amount of 5.40×10^6 to 8.04×10^6 tons of suspended sediment to the SCS.[41−43] Based on the transport amount of sediment and our measured median concentration of $\sum$PPDs, it was estimated that the riverine input mass fluxes of PPDs transported by sediment from the PRD to the SCS were 2,140 to 3,190 kg/year. This gradient spatial distribution of PPDs observed above, combined with the estimated riverine inputs of PPDs to the SCS and then their transport driven by the coastal and oceanic currents (see Figure 1),[44,45] suggested that riverine outflows might be an important pathway to transport these tire rubber-derived chemicals to the coastal and open oceans. It should be pointed out that, in addition to waterborne transport, airborne transport may be another pathway for transporting these chemicals by atmospheric deposition, but its contribution to the concentrations of PPDs in marine sediment needs further study in the future. Compared to general organic pollutants in the riverine, estuarine, and coastal sediments of this study area, the median pollutant levels of $\sum$PPDs were much lower than those of short-chain chlorinated paraffins (173 ng/g, PRD rivers)[46] and organophosphate triesters (330 ng/g, PRD rivers)[47] but were substantially higher than those of per-/polyfluoroalkyl substances (0.74−0.79 ng/g, PRD rivers and the PRE)[48,49] and polybrominated diphenyl ethers (2.98 ng/g, coasts of the SCS).[50] These findings highlighted the abundant, pervasive occurrence of PPDs across freshwater and oceanic waterbodies and implied that riverine outflows are an important route to transport tire rubber-derived chemicals to global oceans.

Of particular importance is 6PPD, exhibiting a DF of 100% in riverine, estuarine, and coastal sediments and a DF of 83% in deep-sea sediments, with its median sedimentary concentration decreasing from 14.4 ng/g in urban rivers to 1.82 ng/g at the coasts. The sedimentary levels of 6PPD in urban runoff-receiving rivers were several times higher than those in river runoff-receiving estuaries and around one order of magnitude higher than those in estuarine waters-affected coasts and even deep-sea regions. The maximum 6PPD concentration was found to be as high as 468 ng/g in roadside river sediment in Guangzhou City (the R6 in Figure 1), revealing tire rubber-related urban storm runoff and roadway runoff as the primary contributors to the high sedimentary 6PPD level. This is well consistent with recent reports of abundant, ubiquitous 6PPD detected in urban runoff[13] and receiving waters[51] and its high consumption as a global HPV chemical. Our findings also highlighted that, similar to microplastics,[52] 6PPD is becoming an extensively distributed oceanic pollutant.

Apart from 6PPD, other target PPDs used in rubber for tire manufacturing were also detected in freshwater and marine sediments. IPPD was also frequently detected with a DF of 50 to 97% in all four types of sediment but exhibited low median concentrations of 0.14 to 1.61 ng/g. IPPD has a similar chemical structure to 6PPD, and its appearance as an omnipresent pollutant should be of emerging concern. 77PD and CPPD exhibited a DF of >50% in sediment samples from at least three of the four sedimentary environments, but they showed regionally comparable or even higher median levels than that of IPPD. 44PD, DPPD, and DNPD exhibited a DF of ≥50% in two of the four types of sediment samples, while they also showed regionally similar median levels to other PPDs, except 6PPD. All PPDs showed a decreasing concentration trend from urban rivers toward offshore deep-sea regions (Figure S4).

Significant concentration correlations were observed among most of the PPDs in freshwater sediments across the PRD urban rivers, the main source region of PPDs to the PRE and SCS (Table S5). For example, 6PPD was significantly correlated with IPPD and DPPD (r = 0.462−0.768, p < 0.01) and CPPD was significantly correlated with all PPDs other than 6PPD (0.364−0.594, p < 0.01), indicating that they have common industrial applications, similar emission sources, or environmental behaviors. Comparing the composition profiles of PPDs in the four sediment types (Figure 2B), a similar distribution characterized by 6PPD as the most abundant congener was observed, but with a markedly higher abundance of sedimentary 6PPD in urban rivers (more than 50% of $\sum$PPDs) than in estuaries, coastal, and deep-sea regions. This distribution characteristic of PPDs in riverine sediments is roughly consistent with the composition pattern of PPDs previously detected in fine air particles.[13,30] No significant correlations were observed between the contents of TOC and the concentrations of PPDs (p > 0.05), suggesting that TOC was not a prevailing factor in determining the concentrations of PPDs in sediments of the studied area. The transformation of PPDs under natural environmental conditions might be a plausible factor influencing the distribution of PPDs. This is the first comprehensive, systematic, and large-scale survey of the occurrence of PPDs in freshwater and marine sediments, providing new insights into their sedimentary concentrations, profiles, transport, and spatial distributions from freshwater rivers to deep-sea regions.

First Evidence of Multiple PPD-Qs in Sediments Across the Riverine, Estuarine, Coastal, and Deep-Sea Waterbodies. Previous studies have indicated that PPDs can undergo oxidative reactions with ozone to form a series of transformation products (TPs).[12,53−56] Recently, 6PPD-Q has been demonstrated as one of the major TPs of 6PPD and gained much attention due to its high toxicity toward coho salmon[21] and other freshwater and marine fish species.[24,25] More recently, two studies have confirmed that, in addition to 6PPD, other PPDs can also undergo similar oxidative transformation to generate their corresponding PPD-Qs such

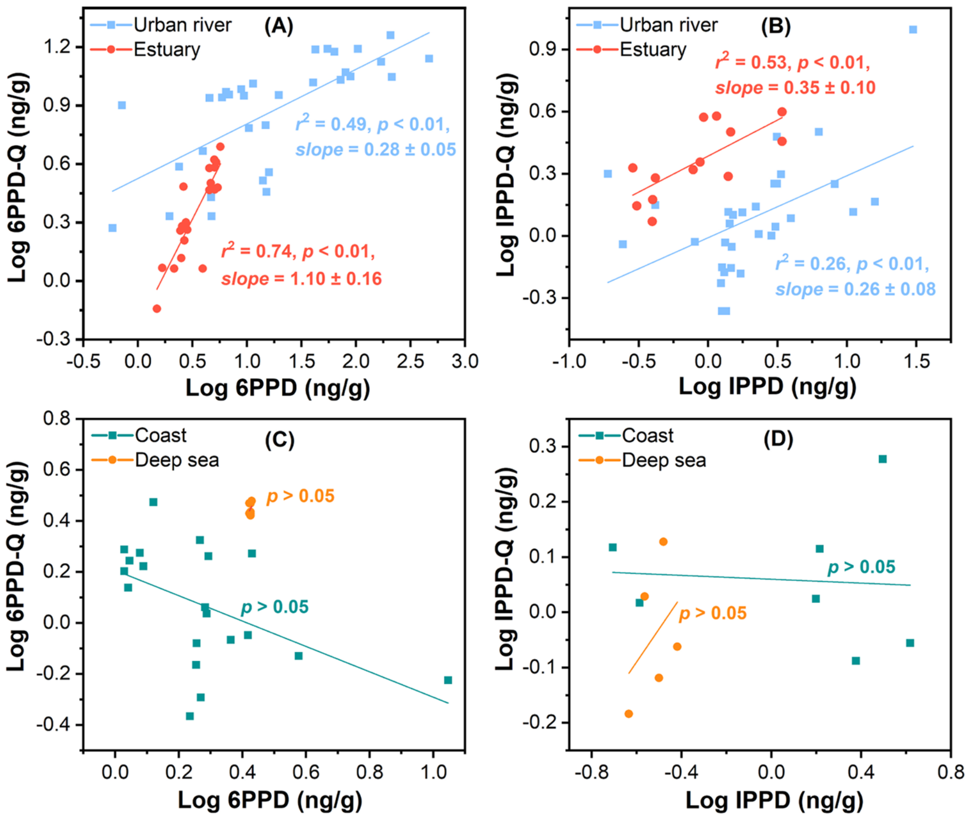

Figure 3. Correlation analysis of the log-transformed concentrations of 6PPD and 6PPD-Q in sediments from urban rivers and estuaries (A) as well as coasts and deep sea (C). Correlation analysis of the log-transformed concentrations of IPPD and IPPD-Q in sediments from urban rivers and estuaries (B) as well as coasts and deep sea (D).

as IPPD-Q, CPPD-Q, and 77PD-Q, and provided new evidence of their environmental presence in urban runoff, roadside soils, and fine air particles.[13,30] These newly discovered PPD-Qs may also possess similar aquatic toxicity similar to 6PPD-Q and thus are likely to pose a combined risk to sensitive aquatic organisms like coho salmon. Therefore, large-scale monitoring of these PPD-Qs in sediments across various aquatic environments becomes more important for a better understanding of their environmental presence and transport behavior.

As shown in Table 1, both 6PPD-Q and IPPD-Q were frequently detected in riverine, estuarine, and coastal sediments. Also, they occurred in deep-sea sediments similar to their parent PPDs, demonstrating long-range transport of these pollutants and transformation of PPDs to PPD-Qs. 6PPD-Q showed a clear spatial gradient distribution pattern, with a decreasing concentration trend of urban rivers > estuaries > coasts ≈ deep-sea regions (Figure S5). 6PPD-Q exhibited DFs of 95 to 100% in riverine, estuarine, and coastal sediments and 75% in deep-sea sediments, with median concentrations from 9.03 ng/g in urban rivers declining to 1.27 ng/g at the coasts. The highest 6PPD-Q concentration (18.2 ng/g) was also found in roadside river sediment in Guangzhou City (the R9 in Figure 1), indicating that storm runoff and roadway runoff containing tire rubber-derived chemicals and tire wear particles are the primary contributors. This is also in agreement with several recent detections of high concentrations of 6PPD-Q in storm runoff and urban runoff. The 6PPD-Q in urban rivers extending to deep-sea regions is of concern. Relative to 6PPD-Q, IPPD-Q was also frequently detected, with a DF of 100% and 58 to 71% in riverine and marine sediments, respectively; however, it exhibited substantially lower concentrations than 6PPD-Q in the same study regions. The IPPD-Q median concentrations were 1.24 ng/g in urban river sediments and 1.94 ng/g in estuarine sediments and gradually declined to 0.83 ng/g in coastal sediments and 0.66 ng/g in deep-sea sediments. Due to the similar chemical structure of IPPD-Q to 6PPD-Q, the ubiquity of IPPD-Q in sediments at a large geographical scale is of emerging concern.

In addition to 6PPD-Q and IPPD-Q, our MS analysis also revealed two peaks at m/z = 335.3 and 297.2 in 77PD and CPPD standard solutions, respectively, after general outdoor solar exposure (Figure S1), which corresponds to the $[M + H]^+$ ions of 77PD-Q and CPPD-Q as reported by Wang and Cao et al.[13,30] Moreover, the MS/MS fragmentation spectra of the two peaks (335.3 and 297.2) match well with the reported fragmentation spectra of the $[M + H]^+$ ions of 77PD-Q and CPPD-Q, respectively[13,30] (Figure S1), confirming the transformation of 77PD and CPPD to 77PD-Q and CPPD-Q under natural sunlight irradiation conditions. Further, the ion transitions for MRM analysis of 77PD-Q and CPPD-Q, which were derived from the reported MS/MS fragmentation spectra, peaked at the same retention time in broad sediment samples, demonstrating the widespread occurrences of 77PD-Q and CPPD-Q in sediments. Due to a lack of pure standards, only semiquantitative results of 77PD-Q and CPPD-Q on the basis of their respective parent calibration curves were reported here. Considering that the responses of 6PPD-Q and IPPD-Q on the MS/MS were actually 2−5 times lower than those of their respective parent chemicals, the reported concentrations of 77PD-Q and CPPD-Q may be underestimated. As shown in Table 1, semiquantification revealed DFs of 57 to 88% for

77PD-Q and 25 to 66% for CPPD-Q in riverine, estuarine, and coastal sediments, similar to the DFs of their respective parent PPDs. 77PD-Q and CPPD-Q can also be detected in deep-sea sediments, with a DF of 42 and 8%, respectively. Estimated median concentrations of 77PD-Q and CPPD-Q were 3.84 and 0.82 ng/g, respectively, in riverine sediments, much higher than their median concentrations in marine sediments. These results clearly demonstrated that, apart from 6PPD-Q, other multiple PPD-Qs also universally exist in freshwater and marine environments.

Together, the median total concentration of all detected four PPD-Qs also showed a clear spatial gradient distribution pattern similar to that of PPD-Q (Figures 2A and S3B). A halving distance of the concentrations of PPD-Qs diluted was estimated to be approximately 47.2 km. In general, all identified PPD-Qs showed lower or comparable sedimentary levels than their respective parent PPDs. Most of the significant concentration correlations observed between the main PPDs were also found between their derived PPD-Qs (Table S5), such as 6PPD-Q and IPPD-Q as well as 6PPD-Q and CPPD-Q ($r = 0.388-0.517$, $p < 0.05$), implying that they have similar environmental transformation behaviors and fates. The composition profiles of PPD-Q in surficial sediments at four sampling regions (urban rivers, estuaries, coasts, and deep sea) shared a similar distribution pattern, which was evidently characterized by 6PPD-Q as the most dominant PPD-Q (Figure 2B). This is the first report of PPD-Qs in sediments and provides the first evidence of the widespread occurrence and transport of multiple PPD-Qs across riverine, estuarine, coastal, and deep-sea waterbodies.

Correlations Analysis between PPD-Qs and PPDs and Spatial Variations of the Ratio of 6PPD/6PPD-Q. To delve into the relations between PPD-Qs and their corresponding parent PPDs, linear regressions on their log-transformed concentrations were performed. As shown in Figure 3A,B, 6PPD-Q and IPPD-Q, the most frequently detected PPD-Qs in sediments, have a high degree of convergence with their respective parent PPDs at the sampling sites in urban rives of the PRD as well as the PRE ($r^2 = 0.49-0.74$ for 6PPD-Q/6PPD and $0.26-0.53$ for IPPD-Q/IPPD, $p < 0.01$). A similar convergence was also observed in urban air particles.[30] Additionally, we found that 6PPD-Q/6PPD showed higher regression coefficients compared to IPPD-Q/IPPD in the same regions. These results suggested that the measured PPD-Qs in sediments from urban rivers and estuaries were correlated with the environmental transformation of their parent compounds. Comparatively, no convergence was observed in the coastal and deep-sea regions, as shown in Figure 3C,D. The urban rivers of the PRD and the PRE are the source and near-source regions for PPDs and PPD-Qs, while the coastal and deep-sea regions away from the source and near-source regions are considered to be less affected by direct anthropogenic inputs but more affected by oceanic conditions such as coastal and oceanic currents. The lack of significant correlations between the concentrations of PPDs and PPD-Qs in the coastal and deep-sea regions may be ascribed to multiple factors such as hydrodynamic conditions[57] as well as differential transport and deposition behaviors in the marine environment that could confound these observations. The potential transformation of PPDs to other chemicals rather than PPD-Qs under oceanic conditions might be another plausible factor. More research based on specific measurements with a larger sample size is still needed to confirm these field observations and inferential explanations. Urban runoff has been demonstrated as the primary source of tire rubber-derived PPDs and PPD-Qs, with urban runoff-receiving riverine waters and sediments naturally becoming the main transport media for these chemicals. As a result, riverine outflows may be an important route to transport these chemicals to the adjacent estuary and then to the coastal and remote deep-sea regions. Significant relationships between PPD-Qs and PPDs were observed at the source and near-source regions (urban rivers and estuaries) but not in the coastal and deep-sea regions far from terrestrial sources, which implied that long-range transport of these chemicals from land to ocean played a vital role in affecting the correlation between PPD-Qs and PPDs.

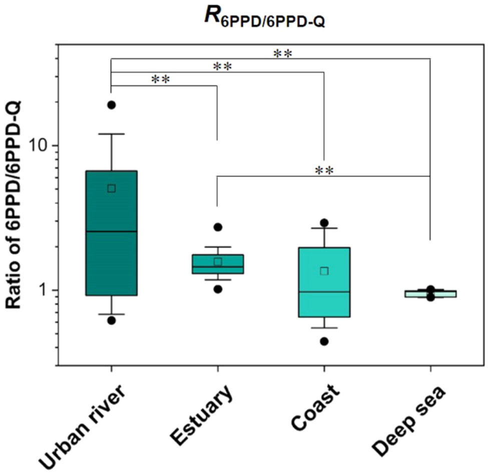

Figure 4. Variations in the ratio of 6PPD to 6PPD-Q ($R_{\text{6PPD/6PPD-Q}}$) with long-range transport from the urban rivers to the estuaries, coasts, and deep-sea regions. The boxes represent the 25th and 75th percentiles; the black lines represent the median; the whiskers represent the 10th and 90th percentiles; and the dots represent the 5th and 95th percentiles. The one and two asterisks denote significant differences at the levels of $p < 0.05$ and 0.01, respectively.

As 6PPD to 6PPD-Q are the dominant components among tire rubber-derived chemicals, to gain insights into their spatial transport, we calculated the ratios of 6PPD to 6PPD-Q ($R_{\text{6PPD/6PPD-Q}}$) in sediments across the four sampling regions. As shown in Figure 4, the values of $R_{\text{6PPD/6PPD-Q}}$ presented a clear decreasing trend from urban rivers to estuaries and then toward coastal and deep-sea regions. Significantly higher $R_{\text{6PPD/6PPD-Q}}$ values in sediments from urban rivers (median: 2.54) than from estuaries (1.45), coastal (0.97), and deep-sea regions (0.95) were identified ($p < 0.05$). A halving distance of the $R_{\text{6PPD/6PPD-Q}}$ value was estimated to be approximately 49.4 km (Figure S6). Continuous inputs of new 6PPD and 6PPD-containing tire wear particles through storm runoff and urban runoff into riverine receiving waters can well explain the high $R_{\text{6PPD/6PPD-Q}}$ values in urban rivers. Because 6PPD-Q, as the critical toxic transformation product of 6PPD, is more stable and persistent in the environment than its parent,[58] the transformation or degradation of nonpersistent 6PPD during the long-range waterborne transport may lead to decreasing $R_{\text{6PPD/6PPD-Q}}$ values in sediments corresponding to the transport distance from terrestrial sources. Here, we presented the spatial variation of $R_{\text{6PPD/6PPD-Q}}$ in sediments across urban rivers, estuaries, coasts, and deep-sea regions. The marked increasing abundance of the more toxic 6PPD-Q relative to

6PPD with long-distance transport should receive more attention. Due to the lack of existing evidence of the transformation or degradation of 6PPD and 6PPD-Q in marine environments, additional research based on field measurements is needed to confirm this phenomenon.

Implications for PPD Natural Transformation, Transport, and Risk. This study provided evidence of the ubiquitous occurrence and distribution of PPDs and their derived PPD-Qs in sediments on a large geographical scale, among which 6PPD and 6PPD-Q were the most prevalent in the aquatic environment. This discovery underlines the importance of further understanding their environmental behaviors such as transformation and transport as well as toxicity and risk, considering the broad and massive use of PPDs as the main antioxidants in vehicle tires and other rubber products. Knowledge gained from the previous example of 6PPD-Q, with its high toxicity toward coho salmon,[21] implies that other PPD-Qs, as the quinone transformation products of PPDs, may also possess higher toxicities than their parents. Thus, elucidating the natural transformation mechanism of these PPD-Qs from PPDs is particularly important. Based on the current limited knowledge, PPD-Qs were generally considered to be oxidatively formed from atmospheric ozone transformation of PPDs[12,56] but no other natural transformation pathways were confirmed. However, given the fact that PPD-Qs in waterbodies, in particular, in urban rivers, may come mainly from storm runoff, roadway runoff, and urban runoff[15,17] rather than atmospheric deposition, other natural transformation pathways of PPDs to PPD-Qs in the aquatic environment could also exist. As the ingredients (Fe^{2+} and rainwater-borne H_2O_2) for the Fenton reaction are naturally present in open waters,[59−61] we infer that natural Fenton oxidation-driven transformation may be another pathway for the formation of PPD-Qs in natural waters. Future studies are needed to test this hypothesis.

As demonstrated here, long-range transport can take place across urban rivers, estuaries, and coastal and deep-sea regions. The OECD overall persistence and long-range transport potential fugacity screening tool (Pov & LRTP tool) was applied to predict the transport potentials of PPDs and PPD-Qs.[40] The calculated characteristic travel distance (CTD) values exceeded 90 km for all PPDs and PPD-Qs (Table S1), especially for 77PD (204 km) and 77PD-Q (1,243 km), indicating a theoretically wide distribution of these new chemicals on a continental scale after point source release. In addition, as shown in Table S1, the calculated transport efficiencies (TEs) from air depositions were found to be quite low (<0.5%) for most PPDs and PPD-Qs, which might imply their restricted distribution mainly in aquatic systems.[62] Our field measurements, combined with the theoretically calculated TEs, indicated that riverine outflows of PPDs and PPD-Qs might be an important route to transport these tire rubber-derived chemicals to oceans.

The ubiquity of multiple PPD-Qs in the marine environment needs to raise special concerns regarding their ecological risks for marine organisms due to potential high aquatic toxicity, as demonstrated by the example of 6PPD-Q.[21] However, apart from 6PPD-Q, the biotoxicity of other PPD-Qs to aquatic species remains unknown, necessitating further research into this. In addition, given the coexistence of multiple PPD-Qs in aquatic environments, the combined toxic effects of these chemicals should be considered for further investigation. Additional research is urgently needed to include all existing PPD-Qs in an assessment of their overall ecological risks to the marine environment.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c07652.

> Physicochemical properties as well as overall persistence and long-range transport potential (Pov, CTD, and TE) of seven PPDs and four PPD-Qs (Table S1); optimized ESI (+)-MS/MS parameters (Table S2); summarized QA/QC results (Table S3); detailed concentration data (Table S4); Spearman's correlation analysis (Table S5); MRM chromatograms and MS^2 fragmentation patterns of four PPD-Qs (Figures S1); MRM chromatograms of seven PPDs (Figures S2); exponential regressions of the concentrations of PPDs and PPD-Qs vs the distance (Figures S3); concentration comparisons of individual PPDs and PPD-Qs at different sampling regions (Figure S4); concentration distributions of 6PPD and 6PPD-Q at different sampling regions (Figure S5); and exponential regressions of the $R_{6PPD/6PPD\text{-}Q}$ vs the distance (Figures S6) (PDF)

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Notes

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■ REFERENCES

(1) Huntink, N. M.; Datta, R. N.; Noordermeer, J. W. M. Addressing durability of rubber compounds. *Rubber Chem. Technol.* **2004**, *77*, 476−511.

(2) Hough, P.; van der Aar, N.; Qiu, Z. Compounding and Mixing Methodology for Good Performance of EPDM in Tire Sidewalls. *Tire Sci. Technol.* **2020**, *48*, 2−21.

(3) Organisation for Economic Co-operation and Development (OECD). *N-(1,3-Dimethylbutyl)-N′-phenyl-1,4-phenylenediamine*. Available at https://hpvchemicals.oecd.org/UI/handler.axd?id=5e1a446c-5969-479c-9270-7ced8726952e. (accessed October 2022).

(4) China Rubber Industry Association (CRIA). CRIA Report of Market Demand Forecast and Investment Strategy Planning on China Rubber Produsts (2021-2026). https://www.qianzhan.com/analyst/detail/220/210402-0078085b.html (in Chinese). (accessed October 2022).

(5) European Chemicals Agency (ECHA). Information from the REACH registration dossiers of 77PD. https://echa.europa.eu/information-on-chemicals. (Accessed October 2022).

(6) Organisation for Economic Co-operation and Development (OECD). *Manual for the Assessment of Chemicals*. https://www.oecd.org/env/ehs/risk-assessment/manualfortheassessmentofchemicals.htm. (Accessed October 2022).

(7) Matsumoto, M.; Yamaguchi, M.; Yoshida, Y.; Senuma, M.; Takashima, H.; Kawamura, T.; Kato, H.; Takahashi, M.; Hirata-Koizumi, M.; Ono, A.; Yokoyama, K.; Hirose, A. An antioxidant, N,N′-diphenyl-p-phenylenediamine (DPPD), affects labor and delivery in rats: A 28-day repeated dose test and reproduction/developmental toxicity test. *Food Chem. Toxicol.* **2013**, *56*, 290−296.

(8) Wu, Y.; Venier, M.; Hites, R. A. Broad Exposure of the North American Environment to Phenolic and Amino Antioxidants and to Ultraviolet Filters. *Environ. Sci. Technol.* **2020**, *54*, 9345−9355.

(9) Liu, R.; Li, Y.; Lin, Y.; Ruan, T.; Jiang, G. Emerging aromatic secondary amine contaminants and related derivatives in various dust matrices in China. *Ecotoxicol. Environ. Saf.* **2019**, *170*, 657−663.

(10) Huang, W.; Shi, Y.; Huang, J.; Deng, C.; Tang, S.; Liu, X.; Chen, D. Occurrence of Substituted p-Phenylenediamine Antioxidants in Dusts. *Environ. Sci. Technol. Lett.* **2021**, *8*, 381−385.

(11) Zhang, Y.; Xu, C.; Zhang, W.; Qi, Z.; Song, Y.; Zhu, L.; Dong, C.; Chen, J.; Cai, Z. *p*-Phenylenediamine Antioxidants in $PM_{2.5}$: The Underestimated Urban Air Pollutants. *Environ. Sci. Technol.* **2022**, *56*, 6914−6921.

(12) Seiwert, B.; Nihemaiti, M.; Troussier, M.; Weyrauch, S.; Reemtsma, T. Abiotic oxidative transformation of 6-PPD and 6-PPD quinone from tires and occurrence of their products in snow from urban roads and in municipal wastewater. *Water Res.* **2022**, *212*, No. 118122.

(13) Cao, G.; Wang, W.; Zhang, J.; Wu, P.; Zhao, X.; Yang, Z.; Hu, D.; Cai, Z. New Evidence of Rubber-Derived Quinones in Water, Air, and Soil. *Environ. Sci. Technol.* **2022**, *56*, 4142−4150.

(14) Johannessen, C.; Helm, P.; Metcalfe, C. D. Detection of selected tire wear compounds in urban receiving waters. *Environ. Pollut.* **2021**, *287*, No. 117659.

(15) Rauert, C.; Charlton, N.; Okoffo, E. D.; Stanton, R. S.; Agua, A. R.; Pirrung, M. C.; Thomas, K. V. Concentrations of Tire Additive Chemicals and Tire Road Wear Particles in an Australian Urban Tributary. *Environ. Sci. Technol.* **2022**, *56*, 2421−2431.

(16) Rauert, C.; Vardy, S.; Daniell, B.; Charlton, N.; Thomas, K. V. Tyre additive chemicals, tyre road wear particles and high production polymers in surface water at 5 urban centres in Queensland, Australia. *Sci. Total Environ.* **2022**, *852*, 158468.

(17) Challis, J. K.; Popick, H.; Prajapati, S.; Harder, P.; Giesy, J. P.; McPhedran, K.; Brinkmann, M. Occurrences of Tire Rubber-Derived Contaminants in Cold-Climate Urban Runoff. *Environ. Sci. Technol. Lett.* **2021**, *8*, 961−967.

(18) Prosser, R. S.; Parrott, J. L.; Galicia, M.; Shires, K.; Sullivan, C.; Toito, J.; Bartlett, A. J.; Milani, D.; Gillis, P. L.; Balakrishnan, V. K. Toxicity of sediment-associated substituted phenylamine antioxidants on the early life stages of *Pimephales promelas* and a characterization of effects on freshwater organisms. *Environ. Toxicol. Chem.* **2017**, *36*, 2730−2738.

(19) Prosser, R. S.; Gillis, P. L.; Holman, E. A. M.; Schissler, D.; Ikert, H.; Toito, J.; Gilroy, E.; Campbell, S.; Bartlett, A. J.; Milani, D.; Parrott, J. L.; Balakrishnan, V. K. Effect of substituted phenylamine antioxidants on three life stages of the freshwater mussel Lampsilis siliquoidea. *Environ. Pollut.* **2017**, *229*, 281−289.

(20) Peng, W.; Liu, C.; Chen, D.; Duan, X.; Zhong, L. Exposure to N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine (6PPD) affects the growth and development of zebrafish embryos/larvae. *Ecotoxicol Environ. Saf.* **2022**, *232*, No. 113221.

(21) Tian, Z.; Zhao, H.; Peter, K. T.; Gonzalez, M.; Wetzel, J.; Wu, C.; Hu, X.; Prat, J.; Mudrock, E.; Hettinger, R.; Cortina, A. E.; Biswas, R. G.; Kock, F. V. C.; Soong, R.; Jenne, A.; Du, B.; Hou, F.; He, H.; Lundeen, R.; Gilbreath, A.; Sutton, R.; Scholz, N. L.; Davis, J. W.; Dodd, M. C.; Simpson, A.; McIntyre, J. K.; Kolodziej, E. P. A ubiquitous tire rubber-derived chemical induces acute mortality in coho salmon. *Science* **2021**, *371*, 185−189.

(22) Peter, K. T.; Tian, Z.; Wu, C.; Lin, P.; White, S.; Du, B.; McIntyre, J. K.; Scholz, N. L.; Kolodziej, E. P. Using High-Resolution Mass Spectrometry to Identify Organic Contaminants Linked to Urban Stormwater Mortality Syndrome in Coho Salmon. *Environ. Sci. Technol.* **2018**, *52*, 10317−10327.

(23) Tian, Z.; Gonzalez, M.; Rideout, C. A.; Zhao, H. N.; Hu, X.; Wetzel, J.; Mudrock, E.; James, C. A.; McIntyre, J. K.; Kolodziej, E. P. 6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard. *Environ. Sci. Technol. Lett.* **2022**, *9*, 140−146.

(24) Brinkmann, M.; Montgomery, D.; Selinger, S.; Miller, J. G. P.; Stock, E.; Alcaraz, A. J.; Challis, J. K.; Weber, L.; Janz, D.; Hecker, M.; Wiseman, S. Acute Toxicity of the Tire Rubber-Derived Chemical 6PPD-quinone to Four Fishes of Commercial, Cultural, and Ecological Importance. *Environ. Sci. Technol. Lett.* **2022**, *9*, 333−338.

(25) Varshney, S.; Gora, A. H.; Siriyappagouder, P.; Kiron, V.; Olsvik, P. A. Toxicological effects of 6PPD and 6PPD quinone in zebrafish larvae. *J. Hazard. Mater.* **2022**, *424*, No. 127623.

(26) Mahoney, H.; da Silva Junior, F. C.; Roberts, C.; Schultz, M.; Ji, X.; Alcaraz, A. J.; Montgomery, D.; Selinger, S.; Challis, J. K.; Giesy, J. P.; Weber, L.; Janz, D.; Wiseman, S.; Hecker, M.; Brinkmann, M. Exposure to the Tire Rubber-Derived Contaminant 6PPD-Quinone Causes Mitochondrial Dysfunction In Vitro. *Environ. Sci. Technol. Lett.* **2022**, *9*, 765−771.

(27) Johannessen, C.; Helm, P.; Lashuk, B.; Yargeau, V.; Metcalfe, C. D. The Tire Wear Compounds 6PPD-Quinone and 1,3-

Diphenylguanidine in an Urban Watershed. *Arch. Environ. Contam. Toxicol.* **2022**, *82*, 171−179.

(28) Zhang, Y.-J.; Xu, T.-T.; Ye, D.-M.; L, Z.-Z.; Wang, F.; Guo, Y. Widespread N-(1,3-Dimethylbutyl)-N′-phenyl-*p*-phenylenediamine Quinone in Size-Fractioned Atmospheric Particles and Dust of Different Indoor Environments. *Environ. Sci. Technol. Lett.* **2022**, *9*, 420−425.

(29) Hiki, K.; Yamamoto, H. Concentration and leachability of N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine (6PPD) and its quinone transformation product (6PPD-Q) in road dust collected in Tokyo, Japan. *Environ. Pollut.* **2022**, *302*, No. 119082.

(30) Wang, W.; Cao, G.; Zhang, J.; Wu, P.; Chen, Y.; Chen, Z.; Chen, Z.; Qi, Z.; Li, R.; Dong, C.; Cai, Z. Beyond Substituted *p*-Phenylenediamine Antioxidants: Prevalence of Their Quinone Derivatives in $PM_{2.5}$. *Environ. Sci. Technol.* **2022**, *56*, 10629−10637.

(31) Ahrens, L.; Yamashita, N.; Yeung, L. W. Y.; Taniyasu, S.; Horii, Y.; Lam, P. K. S.; Ebinghaus, R. Partitioning Behavior of Per- and Polyfluoroalkyl Compounds between Pore Water and Sediment in Two Sediment Cores from Tokyo Bay, Japan. *Environ. Sci. Technol.* **2009**, *43*, 6969−6975.

(32) Peris, A.; Barbieri, M. V.; Postigo, C.; Rambla-Alegre, M.; Lopez de Alda, M.; Eljarrat, E. Pesticides in sediments of the Ebro River Delta cultivated area (NE Spain): Occurrence and risk assessment for aquatic organisms. *Environ. Pollut.* **2022**, *305*, No. 119239.

(33) Malmon, D. V.; Dunne, T.; Reneau, S. L. Predicting the fate of sediment and pollutants in river floodplains. *Environ. Sci. Technol.* **2002**, *36*, 2026−2032.

(34) Mai, B. X.; Chen, S. J.; Luo, X. J.; Chen, L. G.; Yang, Q. S.; Sheng, G. Y.; Peng, P. G.; Fu, J. M.; Zeng, E. Y. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environ. Sci. Technol.* **2005**, *39*, 3521−3527.

(35) Guan, Y.-F.; Wang, J.-Z.; Ni, H.-G.; Luo, X.-J.; Mai, B.-X.; Zeng, E. Y. Riverine inputs of polybrominated diphenyl ethers from the Pearl River Delta (China) to the coastal ocean. *Environ. Sci. Technol.* **2007**, *41*, 6007−6013.

(36) Zhang, G.; Parker, A.; House, A.; Mai, B. X.; Li, X. D.; Kang, Y. H.; Wang, Z. S. Sedimentary records of DDT and HCH in the Pearl River Delta, South China. *Environ. Sci. Technol.* **2002**, *36*, 3671−3677.

(37) Wang, S.; Zhu, G.; Peng, Y.; Jetten, M. S. M.; Yin, C. Anammox Bacterial Abundance, Activity, and Contribution in Riparian Sediments of the Pearl River Estuary. *Environ. Sci. Technol.* **2012**, *46*, 8834−8842.

(38) Du, B.; Liang, B.; Li, Y.; Shen, M.; Liu, L.-Y.; Zeng, L. First Report on the Occurrence of *N*-(1,3-Dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from South China. *Environ. Sci. Technol. Lett.* **2022**, *9*, 1056−1062.

(39) U.S. EPA. EPI Suite-Estimation Program Interface (Version 4.11). https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface (accessed April 5, 2022).

(40) Organisation for Economic Co-operation and Development (OECD). *The OECD Pov and LRTP Screening Tool (Version 2.2).* https://www.oecd.org/chemicalsafety/risk-assessment/oecdpovandlrtpscreeningtool.htm (accessed October, 2022).

(41) Liu, Y.; Gao, S.; Wang, Y. P.; Yang, Y.; Long, J.; Zhang, Y.; Wu, X. Distal mud deposits associated with the Pearl River over the northwestern continental shelf of the South China Sea. *Mar. Geol.* **2014**, *347*, 43−57.

(42) Zhang, S.; Lu, X. X.; Higgitt, D. L.; Chen, C.-T. A.; Han, J.; Sun, H. Recent changes of water discharge and sediment load in the Zhujiang (Pearl River) Basin, China. *Global Planet. Change* **2008**, *60*, 365−380.

(43) Zhang, W.; Wei, X.; Zheng, J.; Zhu, Y.; Zhang, Y. Estimating suspended sediment loads in the Pearl River Delta region using sediment rating curves. *Cont. Shelf Res.* **2012**, *38*, 35−46.

(44) Hu, J.; Li, S.; Geng, B. Modeling the mass flux budgets of water and suspended sediments for the river network and estuary in the Pearl River Delta, China. *J. Mar. Syst.* **2011**, *88*, 252−266.

(45) Wang, Q.; Wang, Y.; Sui, J.; Zhou, W.; Li, D. Effects of Weak and Strong Winter Currents on the Thermal State of the South China Sea. *J. Clim.* **2021**, *34*, 313−325.

(46) Zeng, L. X.; Lam, J. C. W.; Horii, Y.; Li, X. L.; Chen, W. F.; Qiu, J. W.; Leung, K. M. Y.; Yamazaki, E.; Yamashita, N.; Lam, P. K. S. Spatial and temporal trends of short- and medium-chain chlorinated paraffins in sediments off the urbanized coastal zones in China and Japan: A comparison study. *Environ. Pollut.* **2017**, *224*, 357−367.

(47) Liang, C.; Peng, B.; Wei, G.-L.; Gong, Y.; Liu, G.; Zeng, L.; Liu, L.-Y.; Zeng, E. Y. Organophosphate Diesters in Urban River Sediment from South China: Call for More Research on Their Occurrence and Fate in Field Environment. *ACS ES&T Water* **2021**, *1*, 871−880.

(48) Li, W.; Li, H.; Zhang, D.; Tong, Y.; Li, F.; Cheng, F.; Huang, Z.; You, J. Legacy and Emerging Per- and Polyfluoroalkyl Substances Behave Distinctly in Spatial Distribution and Multimedia Partitioning: A Case Study in the Pearl River, China. *Environ. Sci. Technol.* **2022**, *56*, 3492−3502.

(49) Gao, Y.; Fu, J.; Meng, M.; Wang, Y.; Chen, B.; Jiang, G. Spatial distribution and fate of perfluoroalkyl substances in sediments from the Pearl River Estuary, South China. *Mar. Pollut. Bull.* **2015**, *96*, 226−234.

(50) Feng, H.; Cheng, Y.; Ruan, Y.; Tsui, M. M. P.; Wang, Q.; Jin, J.; Wu, R.; Zhang, H.; Lam, P. K. S. Occurrence and spatial distribution of legacy and novel brominated flame retardants in seawater and sediment of the South China sea. *Environ. Pollut.* **2021**, *271*, No. 116324.

(51) Zhang, R.; Zhao, S.; Liu, X.; Tian, L.; Mo, Y.; Yi, X.; Liu, S.; Liu, J.; Li, J.; Zhang, G. Aquatic Environmental Fates and Risks of Benzotriazoles, Benzothiazoles, and *p*-Phenylenediamines in a Catchment Providing Water to a Megacity of China. *SSRN Electron. J.* **2022**, No. 4164982.

(52) Mai, L.; Sun, X.-F.; Xia, L.-L.; Bao, L.-J.; Liu, L.-Y.; Zeng, E. Y. Global Riverine Plastic Outflows. *Environ. Sci. Technol.* **2020**, *54*, 10049−10056.

(53) Cataldo, F. A study on the reaction between N-substituted *p*-phenylenediamines and ozone: experimental results and theoretical aspects in relation to their antiozonant activity. *Eur. Polym. J.* **2002**, *38*, 885−893.

(54) Rapta, P.; Vargova, A.; Polovkova, J.; Gatial, A.; Omelka, L.; Majzlik, P.; Breza, M. A variety of oxidation products of antioxidants based on *N, N*′-substituted *p*-phenylenediamines. *Polym. Degrad. Stab.* **2009**, *94*, 1457−1466.

(55) Lattimer, R. P.; Hooser, E. R.; Layer, R. W.; Rhee, C. K. Mechanisms of Ozonation of *N*-(1,3-Dimethylbutyl)-*N*′-Phenyl-*p*-Phenylenediamine. *Rubber Chem. Technol.* **1983**, *56*, 431−439.

(56) Hu, X.; Zhao, H. N.; Tian, Z.; Peter, K. T.; Dodd, M. C.; Kolodziej, E. P. Transformation Product Formation upon Heterogeneous Ozonation of the Tire Rubber Antioxidant 6PPD (*N*-(1,3-dimethylbutyl)-*N*′-phenyl-p-phenylenediamine). *Environ. Sci. Technol. Lett.* **2022**, *9*, 413−419.

(57) Wu, R.; Ruan, Y.; Huang, G.; Li, J.; Lao, J.-Y.; Lin, H.; Liu, Y.; Cui, Y.; Zhang, K.; Wang, Q.; Yan, M.; Wu, J.; Huang, B.; Lam, P. K. S. Source Apportionment, Hydrodynamic Influence, and Environmental Stress of Pharmaceuticals in a Microtidal Estuary with Multiple Outlets in South China. *Environ. Sci. Technol.* **2022**, *56*, 11374−11386.

(58) Klöckner, P.; Seiwert, B.; Wagner, S.; Reemtsma, T. Organic Markers of Tire and Road Wear Particles in Sediments and Soils: Transformation Products of Major Antiozonants as Promising Candidates. *Environ. Sci. Technol.* **2021**, *55*, 11723−11732.

(59) Qin, J.; Li, H.; Lin, C.; Chen, G. Can rainwater induce Fenton-driven degradation of herbicides in natural waters? *Chemosphere* **2013**, *92*, 1048−1052.

(60) Qin, J.; Li, H.; Lin, C. Fenton process-affected transformation of roxarsone in paddy rice soils: Effects on plant growth and arsenic accumulation in rice grain. *Ecotoxicol. Environ. Saf.* **2016**, *130*, 4−10.

(61) Qin, J.; Lin, C.; Cheruiyot, P.; Mkpanam, S.; Duma, N. G.-M. Potential effects of rainwater-borne hydrogen peroxide on pollutants in stagnant water environments. *Chemosphere* **2017**, *174*, 90−97.

(62) Ruan, T.; Liu, R. Z.; Fu, Q.; Wang, T.; Wang, Y. W.; Song, S. J.; Wang, P.; Teng, M.; Jiang, G. B. Concentrations and Composition Profiles of Benzotriazole UV Stabilizers in Municipal Sewage Sludge in China. *Environ. Sci. Technol.* **2012**, *46*, 2071−2079.

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