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Spatial Distribution, Compositional Profiles, and Potential Ecological Risks of Rubber Additives in Sediments of Lake Sihwa, South Korea: Insights into Industrial and Road-Derived Toxic Substances

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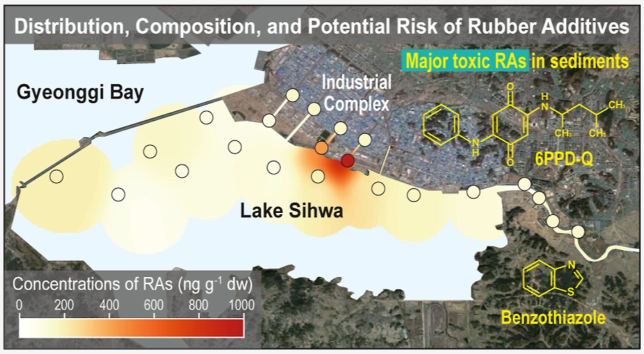

ABSTRACT: This study evaluates the distribution, composition, and potential ecological risks of rubber additives (RAs) in sediments (n = 22) and road dust (n = 2) from inland creeks and Lake Sihwa, South Korea, an area heavily influenced by industrial and vehicular emissions. A total of 20 RAs, including vulcanization accelerators, antioxidants, and coating agents, were analyzed using HPLC-MS/MS. RA concentrations ranged from 21 to 1100 ng g^{-1} dry weight (dw), with the highest levels detected near new industrial areas. Notably, benzothiazole (BT), *N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine (6PPD), and its transformation product, 6PPD-quinone (6PPD-Q), were the predominant contaminants. Road dust exhibited RA concentrations of 300 and 1270 ng g^{-1} dw, with vulcanization accelerators, such as diphenylguanidine and BT derivatives, as key constituents. Ecological risk assessments identified 6PPD-Q as a major contributor to acute toxicity, while BT posed significant chronic toxicity risks. Sites influenced by road dust deposition and industrial emissions exhibited heightened vulnerability, indicating potential threats to aquatic ecosystems. This study provides crucial baseline data on RAs contamination, underscoring the need for continuous environmental monitoring and regulatory intervention. Future research should focus on identifying additional sources, assessing ecotoxicological effects, and developing strategies to mitigate risks associated with industrial and traffic-related pollutants.

KEYWORDS: *rubber additives, benzothiazole, 6PPD-quinone, sediment, road dust, ecological risk assessment*

1. INTRODUCTION

The increasing global use of automobiles has raised significant environmental concerns regarding the release of rubber additives (RAs) from tire wear.[1,2] Recent studies have highlighted the ecological risks associated with tire wear particles (TWPs), which serve as carriers of various chemical additives.[1,3,4] Notably, *N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine (6PPD), a tire rubber-derived compound, reacts with ozone upon entering the environment, forming 6PPD-quinone (6PPD-Q). 6PPD-Q has been identified as a strong toxicant, causing acute toxicity in Coho salmon (*Oncorhynchus kisutch*) populations.[4] These findings indicate that TWPs are not merely fine particulate matter but also act as vectors for hazardous chemicals with direct implications for aquatic organisms. It also highlights the need for research on the distribution and potential toxicological effects of other toxic RAs in aquatic ecosystems.

RAs, including 6PPD, play a crucial role in the tire industry, with each compound serving a distinct function.[5] RAs are broadly classified into vulcanization accelerators, antioxidants, and coating agents.[5] Commonly used vulcanization accelerators include thiazoles [e.g., benzothiazole (BT) and 2-mercaptobenzothiazole (MBT)], thiurams (e.g., tetramethylthiuram disulfide), sulfonamides [e.g., *N*-cyclohexyl-2-benzothiazolesulfenamide (CBS)], and guanidines [e.g., 1,3-diphenylguanidine (DPG)].[6,7] These compounds facilitate the vulcanization process, enhancing the physical and mechanical properties of rubber materials.[8,9] Antioxidants, such as *p*-phenylenediamine derivatives, are incorporated to prolong the product lifespan and improve storage stability.[10] Coating agents, such as hexamethoxymethylmelamine (HMMM), are applied to enhance product quality and performance.[7]

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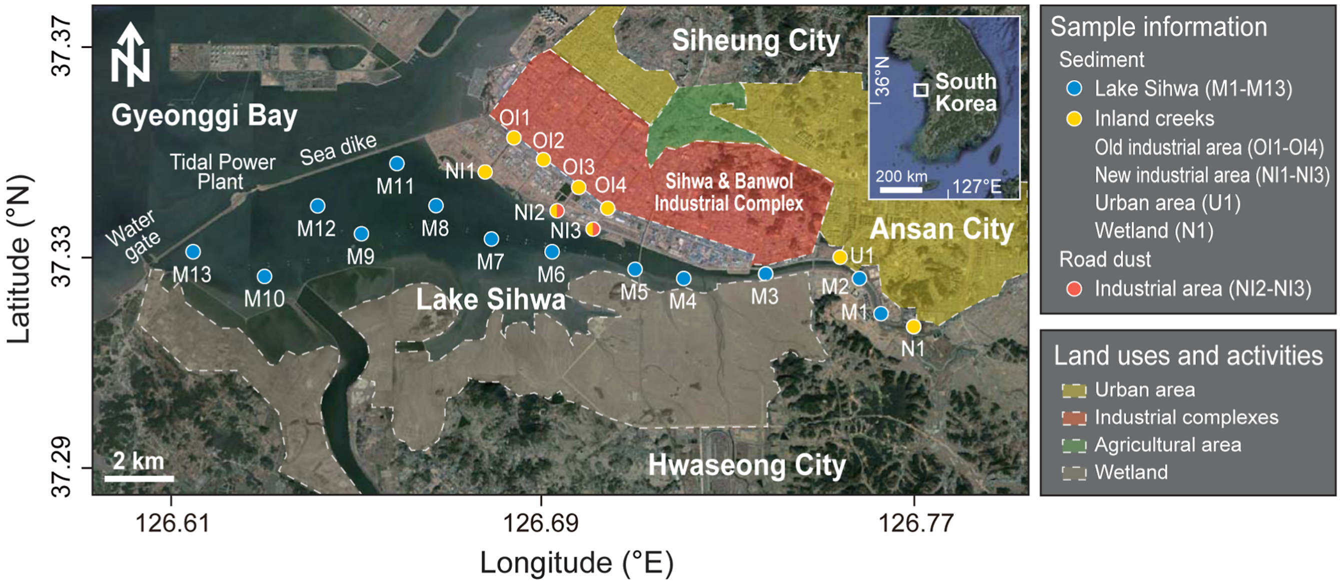

Figure 1. Map showing the sampling sites of sediments and road dust from inland creeks and Lake Sihwa, South Korea.

Due to tires and road surface friction, RAs are continuously released into the environment. TWPs generated during tire abrasion consist of fine RAs and can be directly emitted into the atmosphere or mixed with road dust.[2] Once released, TWPs remain airborne or settle on surfaces, with particularly high concentrations observed in urban areas and on roads with heavy traffic.[11] During periods of increased precipitation, accumulated TWPs and RAs on road surfaces are mobilized by rainwater and transported into aquatic environments, such as rivers and lakes, via surface runoff.[4,6] The extent and efficiency of these transport pathways are influenced by factors including precipitation frequency and intensity, road slope, and the presence or absence of drainage systems.[6] These variables are critical in determining the rate and magnitude of RA entry into aquatic ecosystems. Upon introduction, RAs are not only retained in the water column but can also undergo transformation and/or decomposition through biogeochemical processes or ultimately accumulate in sediments.[12,13]

RAs and their byproducts pose significant toxic effects on aquatic organisms. Notably, BT exhibits various toxicological properties, including mutagenicity, carcinogenicity, and endocrine-disrupting potential.[14,15] Furthermore, the metabolites of these RAs often demonstrate enhanced toxicity compared to their parent compounds, thereby exacerbating their ecological risks. A prominent example is 6PPD, which transforms 6PPD-Q upon ozone exposure, leading to acute toxicity in salmon populations.[4] Similarly, the BT derivative 2-thiocyanomethylthio-benzothiazole has been identified as a more potent carcinogen, with an increased toxicity of inducing lung and bladder cancers compared to its precursor.[16] Although RAs have been frequently detected in various aquatic environments, including surface water, wastewater, and groundwater, studies on their presence, accumulation, and ecological impacts in sediments remain limited.[6,17,18] Once released into aquatic systems, RAs can undergo biogeochemical processes and accumulate in sediments, potentially posing adverse effects on benthic organisms.[12] Thus, investigating the spatial distribution, compositional profiles, and ecological risks of RAs in sediments is essential for a more comprehensive assessment of their environmental impacts.

Lake Sihwa, an artificial lake located on the west coast of Korea, borders Siheung City, Ansan City, and Hwaseong City (Figure 1). The surrounding Sihwa and Banwol Industrial Complexes encompass diverse industrial sectors, with many factories engaged in metal processing, petrochemical production, biochemical industries, and engineering manufacturing.[19−21] Over the past two decades, industrial discharges have introduced a variety of chemicals into inland creeks, significantly contributing to the environmental deterioration of Lake Sihwa.[19−21] Due to intensive industrial activities, Lake Sihwa and surrounding inland creeks have been recognized as highly polluted with organic pollutants, including polycyclic aromatic hydrocarbons (PAHs) and styrene oligomers (SOs).[19−21] Additionally, previous studies utilizing isotopic analysis have identified anthropogenic sources, such as road dust and industrial effluents, as key contributors to contamination in the aquatic environment.[22] Thus, given the presence of numerous industrial complexes and substantial vehicular activity near Lake Sihwa, it is plausible that RAs originating from these sources accumulate in road dust, are subsequently transported to aquatic environments via nonpoint source runoff, and are ultimately deposited in sediments. Although previous studies have primarily focused on the occurrence of RAs in water and road dust, limited research has addressed their accumulation in sediments, particularly in heavily industrialized regions such as Lake Sihwa.

This study examines the distribution and composition of 20 RAs in sediments and road dust from Lake Sihwa and nearby inland creeks. In addition, ecological risks were assessed using toxicity units (TU) and Species Sensitivity Distribution−Probabilistic Risk Assessment−Inclusion-Exclusion Principle (SPI) model. The specific objectives are to (i) determine concentrations and compositions of RAs in sediments, (ii) evaluate their occurrence in road dust, (iii) assess ecological risks using TU and SPI models, and (iv) compare results with other regions. As one of the first studies to investigate RAs in sediments, this research provides novel insights into their distribution and environmental impact within an industrialized coastal region. In addition to characterizing spatial patterns and compositional profiles, the study applies sediment quality guidelines to assess ecological risks, thereby offering a comprehensive framework for monitoring of RAs in coastal sediments. The findings contribute to the development of sediment-focused pollution management strategies in urban-industrial environments.

2. MATERIALS AND METHODS

2.1. Chemicals and Reagents. This study analyzed 20 RAs, classified into three categories: vulcanization accelerators, antioxidants, and a coating agent. The vulcanization accelerators include 11 compounds: MBT, BT, 2-aminobenzothiazole (2-NH2-BT), 2-hydroxybenzothiazole (2-OH-BT), 2-methylbenzothiazole (2-Me-BT), 2-methylthiobenzothiazole (2-Me-S-BT), 2-morpholinothiobenzothiazole (MBS), CBS, 2-(*tert*-butylaminothio)benzothiazole (TBSS), tetramethylthiuram disulfide (TMTD), and DPG. The antioxidant group consists of 8 compounds: 2-mercaptobenzimidazole (MB), *N*-phenyl-1-naphthylamine (PAN(A)), *N*-phenyl-2-naphthylamine (PBN(D)), *N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine (IPPD), 6PPD-Q, 6PPD, *N*-phenyl-*p*-phenylenediamine (PPD), and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ). The coating agent group includes HMMM. The surrogate standard used in this study is 6PPD-Q-^{13}C. All compounds were purchased from LGC Standards (Teddington, UK). Detailed information on the target compounds is provided in Table S1 of the Supporting Information (SI).

2.2. Study Area and Sample Collection. A total of 22 surface sediment samples were collected from Lake Shiwa and surrounding inland creeks in July 2020 (Figure 1). Study areas were classified into five categories based on land-use types and anthropogenic activities.[22] Sediment samples were collected from the old industrial area (OI1−OI4), new industrial area (NI1−NI3), urban area (U1), wetland (N1), and Lake Sihwa (M1−M13). Additionally, road dust samples were collected from sites NI2 and NI3. All sediment and road dust samples were stored in glass bottles, placed in an icebox during transportation, and stored at −20 °C until analysis. Prior to analysis, samples were freeze-dried, sieved through a 1 mm mesh, and homogenized. Organic carbon (OC), total nitrogen (TN), and carbon and nitrogen stable isotope ratios (δ^{13}C and δ^{15}N) were analyzed, with partial results previously reported.[23]

2.3. Extraction and Purification for RAs Analysis. The analytical method for RAs was adapted from a previously established method (Figure S1).[2] For each analysis, 1.0 g of homogenized sediment or road dust sample was spiked with 2.0 ng of 6PPD-Q-^{13}C as a surrogate standard. The samples were sonicated for 30 min in 5.0 mL of a solvent mixture consisting of methanol (MeOH), acetonitrile (ACN), and deionized water (DW) (1:1:0.5, v/v/v). Following sonication, the supernatant was separated by centrifugation at 2000*g* for 10 min. This process was repeated three times, and the combined extracts were concentrated to 2.0 mL using a nitrogen concentrator.

Two types of SPE cartridges were used for purification, HLB (500 mg, 6 cc, Waters, Milford, MA) was used for the analysis of MBT, BT, 2-NH2-BT, 2-OH-BT, 2-Me-BT, and 2-Me-S-BT, and C18 (500 mg, 6 cc, Thermo Scientific) was used for the analysis of MBS, CBS, TBBS, TMTD, DPG, MB, PAN(A), PBN(D), IPPD, 6PPD-Q, 6PPD, PPD, TMQ, and HMMM. Of the extract, 1.0 mL was diluted with 10 mL of 0.1% formic acid in DW and loaded onto an HLB cartridge, preconditioned with 15 mL of MeOH:DW (1:5, v/v) and 5.0 mL of DW. The sample was then eluted twice with 5.0 mL of MeOH and concentrated to 0.5 mL. The remaining 1.0 mL of extract was processed using a C18 cartridge, preconditioned with 10 mL of MeOH and 5.0 mL of DW. The sample was eluted twice with 5.0 mL of MeOH and concentrated to 0.5 mL. Blank samples were analyzed following the same procedure to assess potential contamination during the experiment.

2.4. HPLC-MS/MS Analysis. The quantification of 20 RAs was performed using a 1290 Infinity II series HPLC (Agilent Technologies, Santa Clara, CA) coupled with a QTRAP 6500 series tandem mass spectrometer (MS/MS, AB Sciex, Concord, ON). Chromatographic separation was performed using an XBridge C18 column (2.1 × 100 mm, 3.5 μm, Waters). C18 columns have been widely used in previous studies for the analysis of RAs due to their suitability for separating moderately polar to nonpolar compounds.[24,25] The injection volume was set to 4.0 μL based on optimization for sensitivity and peak shape.[26,27] The mobile phase consisted of (A) DW with 0.1% formic acid and (B) acetonitrile (ACN) with 0.1% formic acid. The gradient program was initiated with 10% solvent B (90% solvent A) for 1 min, followed by a linear increase to 100% B over 15 min, held at 100% B for 9 min, and then decreased back to 10% B over 6 min. The flow rate was maintained at 0.4 mL min^{-1} to optimize retention times and peak separation for all target compounds. Detailed HPLC-MS/MS instrumental parameters are provided in Table S2, and the analysis conditions for the 20 RAs and surrogate standard are summarized in Table S3.

2.5. Quality Control. Calibration curves for the 20 target RAs were established across seven concentration levels (1.0, 5.0, 10, 50, 100, 200, and 500 ng mL^{-1}). The same calibration range (1.0−500 ng mL^{-1}) was applied to all RAs, and each compound showed excellent linearity, with correlation coefficients (R^2) exceeding 0.99. To assess extraction efficiency, 100 μL of a 50 ng mL^{-1} standard mixture was spiked into blank samples and processed using the extraction method described above. Recovery rates varied depending on the cartridge type, with six compounds exhibiting recoveries of 70−120% using the HLB cartridge, while 14 compounds demonstrated recoveries of 80−100% with the C18 cartridge. The detection limits of all 20 RAs ranged from 0.02 to 1.7 ng mL^{-1}. The detection limits were comparable to or lower than those reported in previous studies and were sufficiently lower than the concentrations observed in road dust and sediment samples, demonstrating the suitability of the method.[2,3,6] All procedural blanks were below the limit of detection (LOD) (Table S4). The recovery rates of the surrogate standard (6PPD-Q-$^{13}C_6$) were 100 ± 10% (mean ± standard deviation) in sediments and road dust samples, and 100 ± 5% in matrix blank samples (Table S5), indicating minimal matrix effects and supporting the reliability of the analytical method.[28]

2.6. Statistical Analysis. Principal component analysis (PCA) was conducted using SPSS 26.0 (SPSS Inc., Chicago, IL) to examine the correlation between land-use types and RAs concentrations. The suitability of the data set for PCA was confirmed by Bartlett's test of sphericity ($p < 0.001$) and the Kaiser−Meyer−Olkin (KMO) measure (KMO = 0.726). The KMO value exceeded the recommended threshold of 0.6, confirming the appropriateness of the data set for PCA.

2.7. Ecological Risk Assessment. In this study, the ecological risks of RAs in sediments and road dust were evaluated using two complementary approaches. The first method followed the United States Environmental Protection Agency (US EPA) framework, which estimates freely dissolved

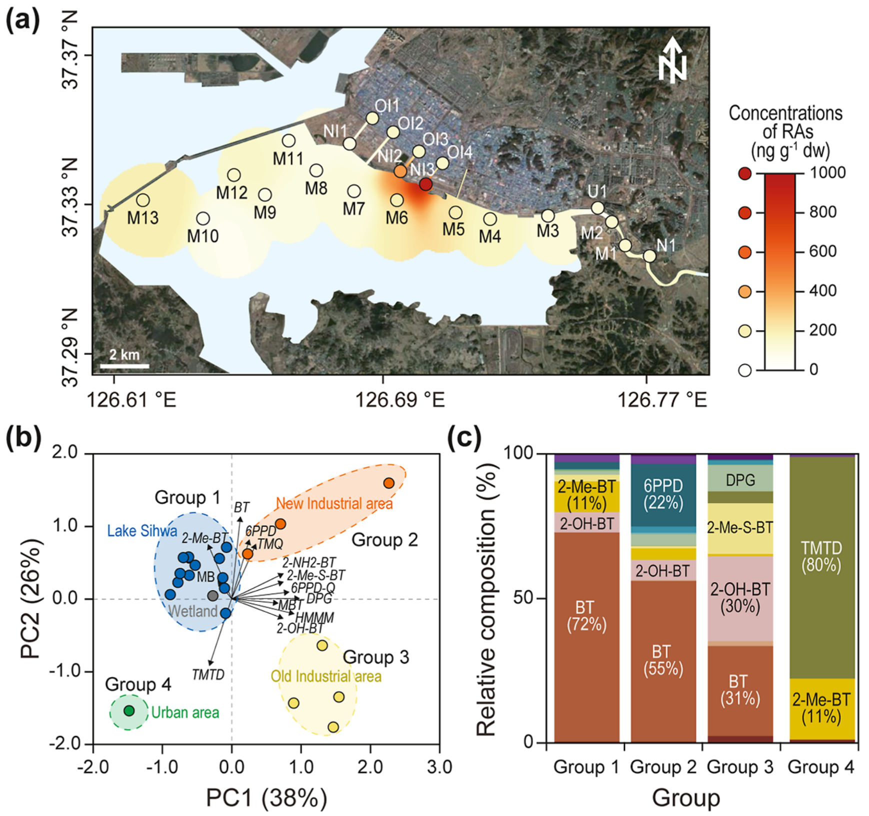

Figure 2. (a) Contour map showing the spatial distribution of 20 RAs in sediments from inland creeks and Lake Sihwa. (b) Principal component analysis (PCA) results based on the composition of RAs in sediments. (c) Dominant RAs in each group, categorized by land use types (Group 1: Lake Sihwa and wetland; Group 2: New industrial area; Group 3: Old industrial area; and Group 4: Urban area).

concentrations in porewater and calculates TU based on LC_{50} values.[3] The second approach applied the SPI model to assess probabilistic ecological risks across multiple compounds.[29] Measured concentrations were converted to porewater-equivalent concentrations using organic carbon−water partition coefficients. The potentially affected fraction (PAF) for each compound was calculated by comparing log-transformed concentrations to species-specific LC_{50} values. Cumulative mixture risks were estimated using the inclusion-exclusion principle to derive joint PAF values. The maximum individual PAF was also reported to identify the key contributors to ecological risk. Toxicity data were obtained from the EnviroTox database (v2.0.0). Detailed descriptions of the parameters and calculation formulas for both methods are provided in the SI (Supporting Methods and Tables S6 and S7).

3. RESULTS AND DISCUSSION

3.1. Organic Carbon and Total Nitrogen. The OC content in sediments ranged from 0.17 to 25%, with a mean of 2.3%, while TN contents varied from not detected (N.D.) to 22%, with a mean of 1.2%.[23] (Figure S2). The C/N ratio exhibited site-specific variations, with an overall average of 9.3 (Figure S2).[23] Sites OI2, OI4, N1, M1, M5, and M13 were predominantly influenced by terrestrial organic matter.[30,31] This influence is attributed to the inland creek locations of OI2, OI4, and N1, where substantial terrestrial organic input is assumed.[19] Among these, OI4 exhibited the highest contribution from terrestrial organic matter. The $\delta^{13}C$ values of marine organic matter typically range from −22 to −18‰, and $\delta^{15}N$ values were reported to be between 3.0 and 12‰, reflecting marine phytoplankton sources.[32,33] In contrast, terrestrial organic matter is characterized by $\delta^{13}C$ values of −33 to −25‰ and $\delta^{15}N$ values of 0.0 to 4.0‰, representing the isotopic signatures of C3 plants.[34] Consistent with the C/N ratio findings, Lake Sihwa sediments were primarily influenced by marine organic matter, whereas sediments in the old industrial complex area were predominantly of terrestrial origin (Figure S2). Overall, the results indicate that organic matter sources in Lake Sihwa vary by site, reflecting contributions from both marine and terrestrial inputs.

3.2. Distribution and Composition of RAs in Sediments. The concentration of RAs in sediments from inland creeks and Lake Sihwa ranged from 21 to 1100 ng g^{-1} dry weight (dw), with an average of 190 ng g^{-1} dw (Figure 2a and Table S8). Among the different land-use types, the highest RA concentrations were observed in the new industrial area (NI, 550 ng g^{-1} dw), followed by the wetland (N, 200 ng g^{-1} dw), old industrial area (OI, 140 ng g^{-1} dw), Lake Sihwa (M, 140 ng g^{-1} dw), and urban area (U, 21 ng g^{-1} dw). Previous studies have reported elevated levels of PAHs and SOs, in addition to RAs, in sediments from new industrial area.[19,21] These findings suggest that NI is heavily polluted, likely due to the continuous discharge of contaminants from nearby industrial facilities. Among the NI sites, NI3 exhibited the highest concentration of RAs in sediment.

In this study, the 20 RAs were categorized into vulcanization accelerators, antioxidants, and coating agents, with vulcanization accelerators being the predominant group in sediments (mean: 93%) (Table S8). Vulcanization accelerators constitute approximately 0.50−1.5% of tire mass, making them the most

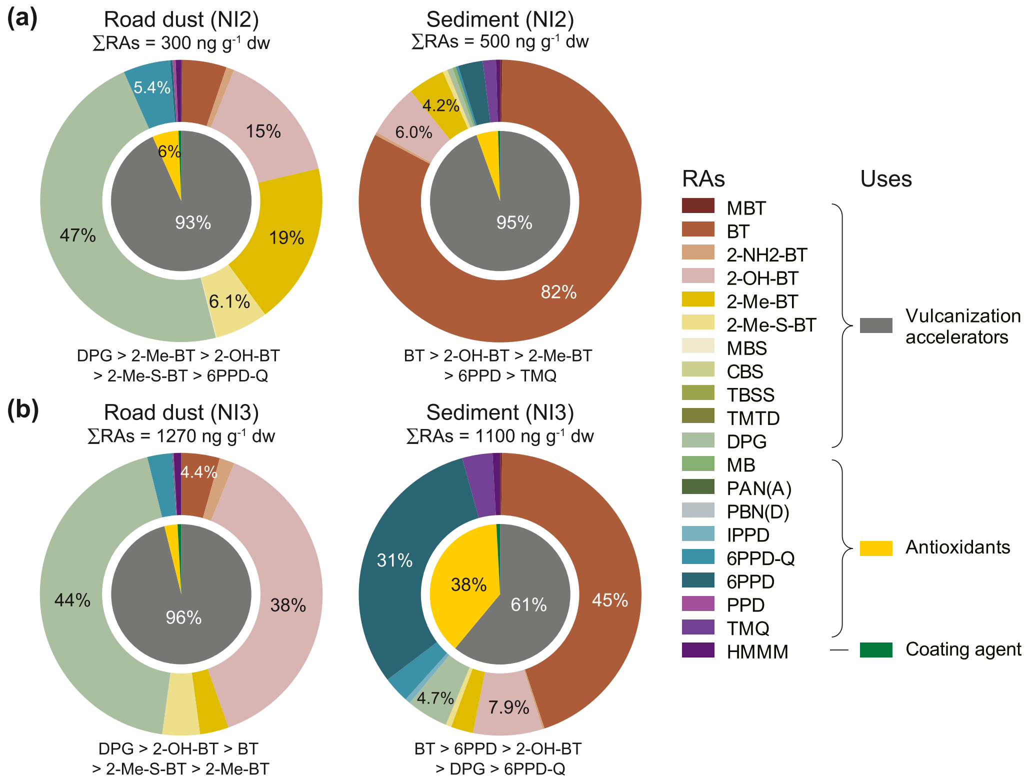

Figure 3. Relative composition of 20 RAs in sediments and road dust collected from Sites (a) NI2 and (b) NI3. The legend classifies RAs according to their industrial uses, such as vulcanization accelerators, antioxidants, and coating agents.

abundant tire additives.[35] This suggests that these compounds may accumulate in aquatic environments through the deposition of TWPs.[35] Among the vulcanization accelerators, BT exhibited the highest concentrations across most sampling sites, ranging from 16 to 490 ng g^{-1} dw (mean: 130 ng g^{-1} dw), except for OI3, OI4, and U1, indicating its role as a major pollutant in Lake Sihwa (Table S8). Since BT is used in a variety of industrial products, including antifreeze and coolant corrosion inhibitors, plastics, and leather products, the BT in the sediment samples in this study may have originated from multiple sources.[2]

The antioxidants accounted for an average of 6.6% of the total RAs concentration. Among antioxidants, 6PPD-Q and 6PPD were mainly detected, while MB, PAN(A), PBN(D), and TMQ were not detected or showed very low concentrations in the sediments. Interestingly, the concentration of 6PPD in NI3 was the highest in the study area at 340 ng g^{-1} dw, and 6PPD-Q also showed the highest concentration at 38 ng g^{-1} dw. The concentration of 6PPD was higher than that of 6PPD-Q, which may be due to the direct influx of TWPs and the higher K_{OC} value of 6PPD (11,000) than that of 6PPD-Q (2400), suggesting that it was better adsorbed to sediments (Table S6).[36] Only 15 of the 20 RAs were detected in the sediments. MBS, CBS, PAN(A), PBN(D), and PPD were not detected in the sediments. Although these five compounds were not detected in the sediments, it has been reported that the amounts of CBS and MBS used in tire rubber are increasing.[37] Thus, continuous monitoring of these RAs is also necessary.

PCA was conducted to identify land-use-specific distribution patterns of RAs in sediments. The results classified the sampling sites into four groups (Figure 2b). Group 1 included sites of Lake Sihwa and wetland, which were predominantly influenced by 2-Me-BT and BT. Group 2 consisted of new industrial areas significantly affected by BT, 6PPD, and TMQ. Group 3 encompassed the old industrial areas, characterized by elevated levels of 2-OH-BT, HMMM, and MBT (Figure 2c). Group 4 corresponded to urban areas, where TMTD was the dominant compound. These findings demonstrate that the contamination patterns of RAs in sediments are closely related to land-use types and that industrial activities significantly impact the contamination of RAs. The compositional profiles of RAs in sediments by groups revealed that BT was the dominant RA in Groups 1−3, with its relative contribution highest in Group 1 (72%), gradually decreasing to 55% in Group 2 and 31% in Group 3. BT was observed to migrate from industrial areas and persist in the lake, likely due to its relatively low K_{OC} value (48), which enhances its mobility in the water column.[38] As a result, BT exhibits lower adsorption to nearby sediments compared to other RAs and is more readily transported over long distances in its dissolved phase.

3.3. Concentration and Composition of RAs in Road Dusts.

The concentrations of 20 RAs in road dust were detected as 300 ng g^{-1} dw at NI2 and 1270 ng g^{-1} at NI3 (Figure 3). In both sediment and road dust, RA concentrations were higher at NI3 than at NI2 (Table S9). Among the three RA categories, vulcanization accelerators exhibited the highest concentrations in road dust, accounting for 93% and 96% at NI2 and NI3, respectively, a pattern similar to that observed in sediments. DPG was the predominant RA in road dust, comprising 47% and 44% of the total RAs at NI2 and NI3, respectively. The concentrations of other major RAs followed different trends at each site: at Site NI2, 2-Me-BT, 2-OH-BT, and 2-Me-S-BT were most abundant, while at Site NI3, 2-OH-BT, BT, 2-Me-S-BT, and 2-Me-BT were dominant. DPG is primarily used as a vulcanization accelerator but is also widely

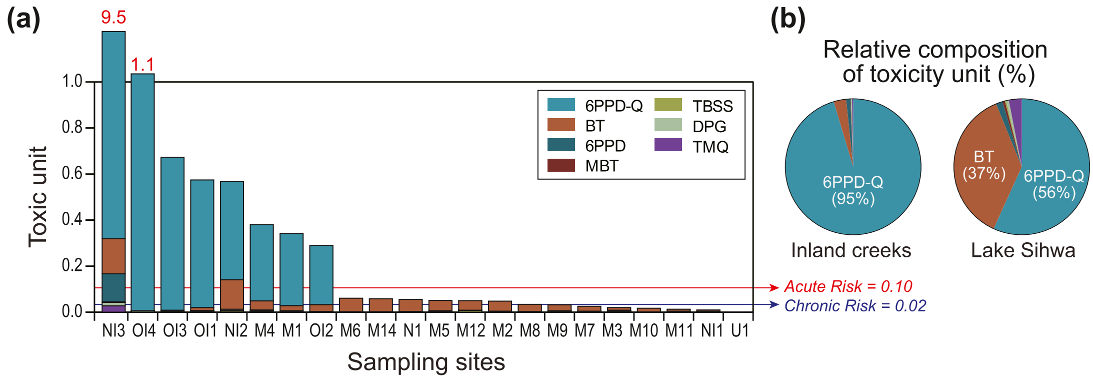

Figure 4. (a) Toxic units (TU) of RAs in sediments from inland creeks and Lake Sihwa, Korea, with threshold values indicating acute risk (TU = 0.10) and chronic risk (TU = 0.02) for fish (arrow lines). (b) Pie charts representing the relative contributions of TU for RAs in sediments of inland creeks and Lake Sihwa.

Table 1. Comparison of the Concentrations of 20 RAs in Sediments Obtained from This Study and Previous Studies [Min.−Max. (Mean)]

country		South Korea	China	China	China	China	China
regions		Lake Sihwa	Pearl River Estuary	Urban River, South China Sea	Pearl River Estuary	Coastal areas, South China Sea	Deep-sea regions, South China Sea
site number		22	26	32	21	20	12
compounds	MBT	<LOD[a]−4.9 (1.5)	−[b]	−	−	−	−
	BT	<LOD−490 (130)	21−31 (25)	−	−	−	−
	2-NH2-BT	<LOD−3.5 (2.3)	−	−	−	−	−
	2-OH-BT	<LOD−94 (44)	2.8−12 (5.5)	−	−	−	−
	2-Me-BT	<LOD−35 (16)	N.D.−33 (21)	−	−	−	−
	2-Me-S-BT	<LOD−34 (7.8)	N.D.−31 (5.0)	−	−	−	−
	MBS	N.D.[c]	−	−	−	−	−
	CBS	N.D.	−	−	−	−	−
	TBBS	<LOD−0.7 (0.3)	0.93−2.3 (1.4)	−	−	−	−
	TMTD	<LOD−16 (13)	−	−	−	−	−
	DPG	<LOD−52 (6.9)	−	−	−	−	−
	MB	<LOD−2.4 (1.5)	−	−	−	−	−
	PAN(A)	N.D.	−	−	−	−	−
	PBN(D)	N.D.	−	−	−	−	−
	IPPD	<LOD−6.8 (6.8)	−	<LOD−30 (14)	<LOD−3.4 (3.9)	<LOD−6.2 (0.14)	<LOD−0.98 (0.26)
	6PPD-Q	<LOD−33 (5.7)	−	1.87−18 (9.0)	<LOD−4.9 (2.0)	0.43−3.0 (1.3)	<LOD−3.0 (2.7)
	6PPD	<LOD−340 (19)	−	0.585−470 (14)	1.5−5.7 (3.9)	1.1−11 (1.8)	<LOD-2.7 (2.7)
	PPD	N.D.	−	−	−	−	−
	TMQ	<LOD−38 (6.4)	−	−	−	−	−
	HMMM	<LOD−9.4 (3.1)	−	−	−	−	−
references		this study	45	46	46	46	46

[a]<LOD: below limit of detection. [b]−: not analyzed. [c]N.D.: not detected.

utilized in various industries, including the production of tires, building materials, electronics, and toys.[39,40] This suggests that RAs detected in road dust may originate not only from tire rubber additives but also from nearby industrial complexes.

A previous study reported that DPG accounts for 63% of RAs in road dust, which is consistent with the findings of this study.[3] Additionally, 2-OH-BT, 2-Me-BT, and 2-Me-S-BT are known oxidation byproducts of BT, formed through friction between tires and road surfaces.[2] BT can also undergo photochemical oxidation under UV exposure as tire residues accumulate in road dust.[41] In line with prior research, 2-OH-BT was one of the most frequently detected BT derivatives in road dust, confirming its potential as a key indicator of tire-wear-related pollution.[2] Furthermore, 6PPD-Q was detected at higher concentrations than 6PPD in road dust, likely due to the ozonation of 6PPD as it accumulates in road dust.[42]

The compositions of RAs in road dust and sediments exhibited distinct differences (Figure 3). While BT was the predominant RA detected in sediments, its oxidation by-products constituted a relatively higher proportion in road dust. 2-OH-BT, 2-Me-BT, and 2-Me-S-BT are known oxidation products of BT, formed through photochemical and atmospheric oxidation processes involving UV radiation and ozone.[37] Their elevated concentrations in road dust suggest that these oxidation reactions occur more actively in atmospheric environments. Additionally, DPG was detected at high concentrations in road dust but was present at relatively lower levels in sediments. As a widely used vulcanization additive, DPG has been reported as a major RA in road dust.[3] However, studies on its distribution in sediments remain limited. While numerous studies have examined the environmental behavior and distribution of DPG in road dust, research

Table 2. Comparison of the Concentrations of 20 RAs in Road Dusts Obtained from This Study and Previous Studies [Min.–Max. (Mean)]

country		South Korea	China	China	Germany	China
regions		Lake Sihwa	Urban roads in Tianjin	55 major cities	Highway tunnel in Görlitz	Urban roads in Guangzhou
site number		2	35	55	2	10
compounds	MBT	N.D.[a]–0.38 (0.38)	–[b]	<LOD[c]–91 (44)	–	–
	BT	15–56 (36)	–	–	2700–3500 (3100)	<LOD–8600 (870)
	2-NH2-BT	2.7–22 (12)	–	0.3–3.6 (0.90)	–	–
	2-OH-BT	45–490 (270)	–	<LOD–160 (<LOD)	1300–1500 (1400)	<LOD–4000 (1800)
	2-Me-BT	42–55 (49)	–	26–110 (52)	–	–
	2-Me-S-BT	18–54 (36)	–	–	–	<LOD–3300 (780)
	MBS	0.17–0.29 (0.23)	–	–	–	–
	CBS	N.D.–0.75 (0.75)	–	<LOD–9.1 (2.5)	–	–
	TBBS	N.D.	–	<LOD–5.7 (0.51)	–	–
	TMTD	N.D.	–	–	–	–
	DPG	140–560 (350)	–	<LOD–380 (170)	29,000–34,000 (31,500)	–
	MB	N.D.	–	–	–	–
	PAN(A)	<LOD	–	–	–	–
	PBN(D)	<LOD	–	–	–	–
	IPPD	<LOD	<LOD–32 (7.1)	–	–	<LOD–250 (34)
	6PPD-Q	16–36 (26)	3.0–350 (70)	–	220,000–270,000 (245,000)	11–510 (120)
	6PPD	0.83–0.86 (0.85)	0.74–630 (61)	–	1500–1900 (1700)	15–1500 (360)
	PPD	1–1.5 (1.3)	–	–	–	–
	TMQ	N.D.	–	–	–	–
	HMMM	1.9–11 (6.5)	–	–	–	–
references		this study	2	6	47	48

[a]N.D.: not detected. [b]–: not analyzed. [c]<LOD: below limit of detection.

on its transformation processes and fate in sediments is scarce.[3,43] Thus, further investigations are required to elucidate the mechanisms by which DPG is transported into sediments, its long-term accumulation patterns, and its overall environmental behavior.

3.4. Potential Ecological Risk Assessment. The acute and chronic toxicity risk to fish due to contamination of RAs in sediments was assessed using TU_{sum} (Figure 4a). The results indicated that RA concentrations at eight sites (NI3, OI4, OI3, OI1, NI2, M4, M1, and OI2) exceeded thresholds for acute toxicity ($TU > 0.10$), highlighting the significant ecological threat posed by these compounds. In addition, nine sites (M6, M14, N1, M5, M12, M2, M8, M9, and M7) exhibited concentrations suggesting potential chronic toxicity risks to aquatic life ($TU > 0.02$).

Among the analyzed RAs, 6PPD-Q was identified as the primary contributor to acute toxicity in sediments of Lake Sihwa and inland creeks (Figure 4b). In inland creek sediments, 6PPD-Q accounted for 95% of the total TU_{sum}, while in Lake Sihwa sediments, it contributed 56%. Meanwhile, 6PPD-Q was not detected in nine sites where chronic risks were identified, with BT identified as the major causative compound. The relative contribution of BT increased from 2.9% in inland creek sediments to 37% in Lake Shiwa sediments. Notably, most sites identified as chronically at risk were located in lake environments inhabited by fish, posing a potential ecological threat. In addition to the chronic risks to fish, BT has been associated with genotoxicity, cytotoxicity, and endocrine disruption.[14] Application of the SPI model revealed that the joint PAF ranged from 0.87 to 0.99 in road dust (NI2 and NI3) and sediments (NI2, NI3, OI1, OI3, M1, and M4), indicating that 87–99% of fish species could potentially be affected, thus representing a high ecological risk. Notably, 6PPD-Q was identified as the major contributor in road dust at NI3 (0.99) and NI2 (0.94), as well as in sediment at NI3 (0.87) (Table S10).

Both models consistently identified 6PPD-Q as the major contributor to ecological risk in road dust and sediment. 6PPD-Q is an environmental transformation product formed when 6PPD, a widely used tire rubber antioxidant, reacts with atmospheric ozone. Previous studies have reported that 6PPD-Q causes acute toxicity to salmonids even at extremely low concentrations.[4] Although it is considered an environmentally significant contaminant, its toxicological mechanisms remain poorly understood. Recent research suggests that 6PPD-Q may cause direct cardiovascular damage to the heart and blood vessels of fish, along with other toxic effects, including neurotoxicity, developmental toxicity, carcinogenicity, and reproductive toxicity.[44] These findings underscore the urgent need to address the ecological risks posed by RAs, particularly 6PPD-Q and BT, in Lake Sihwa. The acute toxicity of 6PPD-Q, coupled with the chronic risks associated with BT, highlights the necessity of implementing comprehensive pollution control measures.

3.5. Comparison with Previous Studies. The concentration of RAs in Lake Sihwa sediments was higher than those reported in previous studies analyzing three or more RAs in sediments (Table 1). BT was detected at higher concentrations in Lake Sihwa sediments than in those from the Pearl River Estuary, China.[45] Additionally, the concentrations of 6PPD and 6PPD-Q in sediments from Lake Sihwa were relatively elevated compared to previously reported values.[45,46] IPPD was also detected at higher levels than in sediments from China. Interestingly, both this study and previous studies found 6PPD concentrations to be higher than those of 6PPD-Q in sediments.[45,46] In China, the 6PPD/6PPD-Q ratio in sediments decreased from 1.5 in riverine environments to 1.0 in open sea. This decline is attributed to the greater environmental stability and persistence of 6PPD-Q compared to 6PPD, which results in the progressive conversion of 6PPD to 6PPD-Q during long-distance transport.[46] The 6PPD/6PPD-Q ratio in Lake Sihwa sediments (3.3) was higher than that observed in urban river basins in China. This indicates a continuous influx of fresh 6PPD from urban runoff and road dust, with the potential for further transformation into the highly toxic 6PPD-Q within Lake Sihwa and coastal areas.

This study also compared RA concentrations in road dust with those reported in previous studies (Table 2).[2,6,47,48] The results showed that RA concentrations in road dust were lower than those in previous studies. In road dust, BT and its byproduct 2-OH-BT were detected at relatively high concentrations in all regions except the Görlitz area in Germany.[2,6,47,48] This suggests that BT undergoes oxidation during tire wear processes, leading to its presence in road dust at elevated levels. Additionally, 6PPD-Q was detected at higher concentrations than 6PPD, which is likely due to the transformation of 6PPD to 6PPD-Q through ozonation, and this conversion appears to be region-specific. While previous studies have examined a limited number of compounds to assess RA distribution in sediments and road dust, this study analyzed 20 RAs.[35] Consequently, RA concentrations in sediments were found to be higher than those reported in earlier research, and distinct differences in RA distribution between road dust and sediments were identified.

4. CONCLUSIONS

This study provides baseline data for evaluating the environmental impact of RAs originating from industrial activities and road traffic. The findings of this study indicate that high concentrations of specific RAs in sediments from new industrial areas are primarily driven by industrial activities and road dust inflows, identifying them as major sources. Among the analyzed RAs, 6PPD-Q exhibited the greatest contribution to sediment and road dust toxicity, while BT also demonstrated significant toxic potential. The concentrations of 6PPD-Q and BT in both sediments and road dust reached levels capable of inducing acute toxicity in aquatic organisms, such as fish. This presents a serious threat to marine ecosystems, emphasizing the urgent need for comprehensive monitoring and management of these contaminants. Future studies that integrate correlations with various environmental factors could clarify the source and fate of RAs and contribute to the development of effective pollution mitigation strategies. Mitigation strategies may include improved road dust management, stricter regulations on tire-derived pollutants, and enhanced monitoring of sediment contamination. Additionally, further research is needed to elucidate the toxicological mechanisms of 6PPD-Q and the long-term ecological impacts of BT.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.5c00234.

> Details on ecological risk assessment methods (Supporting methods); information on target 20 RAs (Table S1); additional details on the instrumental conditions for analyzing RAs using HPLC-MS/MS (Tables S2 and S3); result for QA/QC (Tables S4 and S5); K_{OC} and toxicity values (Table S6); PAF values (Table S7); concentrations of 20 RAs in sediments and road dust (Tables S8 and S9); Joint PAF values and major contributing compounds (Table S10); flowchart for analyzing RAs (Figure S1); and organic carbon and total nitrogen contents and their stable isotope ratios (δ^{13}C and δ^{15}N) in sediments (Figure S2) (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information for

Spatial Distribution, Compositional Profiles, and Potential Ecological Risks of Rubber Additives in Sediments of Lake Sihwa, South Korea: Insights into Industrial and Road-Derived Toxic Substances

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This PDF file includes:

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Supporting Methods

Number of Supplementary Tables: Tables S1−S10

Number of Supplementary Figures: Figures S1 and S2

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Supporting Methods

Ecological Risk Assessment using toxicity units. Toxicity values for rubber additives (RAs) were determined following the methodology outlined in a previous study.[1] In accordance with U.S. Environmental Protection Agency (US EPA) guidelines, the ecological risks of the target compounds to aquatic organisms were assessed based on the concentrations of freely dissolved chemicals in sediment porewater. The organic carbon (OC)-normalized concentration of RAs in sediments (C_{OC}) was converted to the freely dissolved concentration in water (C_{ew}) using the OC-water partition coefficient (K_{OC}), as shown in Equation 1 (Eq. 1). The toxicity unit (TU) was then calculated by dividing C_{ew} by the median lethal concentration (LC_{50}) for relevant aquatic organisms (e.g., fish), as shown in Eq. 2.

$$C_{ew} = C_{OC} / K_{OC} \qquad \text{(Eq. 1)}$$

$$TU = C_{ew} / LC_{50} \qquad \text{(Eq. 2)}$$

Toxicity data were obtained from the EnviroTox database (v2.0.0). The cumulative ecological risk of RAs in sediments was assessed by summing the TU values (TU_{sum}) for each compound, based on the principle of concentration addition. A TU_{sum} value exceeding 0.02 was considered indicative of potential chronic risk, while values exceeding 0.10 were classified as indicative of acute risk. The K_{OC} values and LC_{50} data used for these calculations are provided in Table S6.

Ecological Risk Assessment using the SPI model. To evaluate the ecological risks of RAs in sediments and road dust, this study applied the Species Sensitivity Distribution-Probabilistic Risk Assessment-Inclusion-Exclusion Principle (SPI) model, as developed in a previous study.[2] Measured concentrations of each compound in sediments and road dust (ng/g) were converted to porewater-equivalent concentrations (ng/L) using Eq. 3.

$$C_{water} = C_{sediment} / K_{OC} \times f_{OC} \qquad \text{(Eq. 3)}$$

Where $C_{sediment}$ is the measured concentration in dry sediment (ng/g), and f_{OC} is the fraction of

OC in the sample. Log-transformed exposure concentrations were then compared to species-specific LC_{50} values (µg/L) to calculate the potentially affected fraction (PAF) for each compound using Eqs. 4 and 5.

$$Z = \log (C_{water}) - \log (LC_{50}) / 42 \qquad \text{(Eq. 4)}$$

$$PAF = \Phi(Z) \qquad \text{(Eq. 5)}$$

Where $\Phi(Z)$ is the cumulative standard normal distribution function. A PAF value < 0.05 indicates low ecological risk to fish, whereas values ≥ 0.05 indicate elevated. To assess the cumulative risk posed by mixtures of RAs, joint PAF values were estimated using the inclusion-exclusion principle, as shown in Eq. 6. The joint PAF represents the probability that multiple compounds will collectively affect a given proportion of the aquatic community. This approach considers potential interactions among pollutants and reduces the risk of overestimating toxicity due to overlapping effects.

$$\text{Joint PAF}=\sum_{i-1}^{n} PAF_i - \sum_{i1<i2}^{n} PAF_{i1}PAF_{i2}\ldots + (-1)^{n+1} \sum_{i1<i2<\ldots ir}^{n} PAF_{i1}PAF_{i2}PAF_{i3} + \ldots + (-1)^{n+1}\sum_{i1<i2<\ldots ir}^{n} PAF_{i1}PAF_{i2}PAF_{i3\ldots}PAF_n \qquad \text{(Eq. 6)}$$

In addition, the maximum individual PAF (Max Individual PAF) was reported to identify the single compound contributing most significantly to the total ecological risk. Detailed parameters and calculation steps are provided in Table S7. This probabilistic method enables a more accurate assessment of mixture toxicity while minimizing the potential for overestimation.

Supplementary Tables

Table S1. Types, compounds, abbreviation, molecular formula, and molecular weight of 20 rubber additives and 1 surrogate standard.

Types	**Compounds**	**Abbreviation**	**Molecular formula**	**Molecular Weight**
Vulcanization	2-Mercaptobenzothiazole	MBT	$C_7H_5NS_2$	167.24
	Benzothiazole	BT	C_7H_5NS	135.18
	2-Aminobenzothiazole	2-NH2-BT	$C_7H_6N_2S$	150.20
	2-Hydroxybenzothiazole	2-OH-BT	C_7H_5NOS	151.18
	2-Methylbenzothiazole	2-Me-BT	C_8H_7NS	149.21
	2-Methylthiobenzothiazole	2-Me-S-BT	$C_8H_7NS_2$	181.27
	2-Morpholinothiobenzothiazole	MBS	$C_{11}H_{12}N_2OS_2$	252.35
	N-cyclohexyl-2-benzothiazolesulfenamide	CBS	$C_{13}H_{16}N_2S_2$	264.41
	2-(Tert-butylaminothio)benzothiazole	TBBS	$C_{11}H_{14}N_2S_2$	238.37
	Tetramethylthiuram disulfide	TMTD	$C_6H_{12}N_2S_4$	240.42
	1,3-Diphenylguanidine	DPG	$C_{13}H_{13}N_3$	211.27
Antioxidant	2-Mercaptobenzimidazole	MB	$C_7H_6N_2S$	150.20
	N-Phenyl-1-Naphthylamine	PAN(A)	$C_{16}H_{13}N$	219.29
	N-Phenyl-2-Naphthylamine	PBN(D)	$C_{16}H_{13}N$	219.29
	N-Isopropyl-N'-phenyl-p-phenylenediamine	IPPD	$C_{15}H_{18}N_2$	226.32
	2-Anilino-5-[(4-methyl-2-pentanyl)amino]-1,4-benzoquinone	6PPD-Q	$C_{18}H_{22}N_2O_2$	298.39
	N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine	6PPD	$C_{18}H_{24}N_2$	268.40
	N-Phenyl-p-phenylenediamine	PPD	$C_{12}H_{12}N_2$	184.24
	2,2,4-Trimethyl-1,2-dihydroquinoline	TMQ	$C_{12}H_{15}N$	173.26
Coating agent	Hexamethoxymethylmelamine	HMMM	$C_{15}H_{30}N_6O_6$	390.44
Surrogate standard	2-((4-Methylpentan-2-yl)amino)-5-((phenyl-^{13}C)amino)cyclohexa-2,5-diene-1,4-dione	6PPD-Q-^{13}C	$C_{12}{}^{13}C_6H_{22}N_2O_2$	304.34

Table S2. Instrumental conditions for analyzing rubber additives using HPLC-MS/MS.

<table>
<tr><td>Instrument</td><td colspan="3">HPLC: Agilent Infinity 1290 II, MS/MS: SCIEX Qtrap 6500</td></tr>
<tr><td>Samples</td><td colspan="3">Sediment and dust samples</td></tr>
<tr><td>Column</td><td colspan="3">XBridge C18 (2.1 mm × 100 mm i.d. × 3.5 μm film)</td></tr>
<tr><td>Column temperature</td><td colspan="3">40 ℃</td></tr>
<tr><td>Injection volume</td><td colspan="3">3 μL</td></tr>
<tr><td>Flow rate</td><td colspan="3">0.4 mL min⁻¹</td></tr>
<tr><td>Mobile phase</td><td colspan="3">A: 0.1% Formic acid in deionized water
B: 0.1% Formic acid in acetonitrile</td></tr>
<tr><td rowspan="8">Mobile phase gradient</td><td rowspan="2">Time (min)</td><td colspan="2">Solvent gradient condition</td></tr>
<tr><td>A (%)</td><td>B (%)</td></tr>
<tr><td>0</td><td>90</td><td>10</td></tr>
<tr><td>1</td><td>90</td><td>10</td></tr>
<tr><td>15</td><td>0</td><td>100</td></tr>
<tr><td>24</td><td>0</td><td>100</td></tr>
<tr><td>25</td><td>90</td><td>10</td></tr>
<tr><td>30</td><td>90</td><td>10</td></tr>
<tr><td>Ionization mode</td><td colspan="3">Electrospray ionization (ESI) Positive mode</td></tr>
<tr><td>Ion source gas</td><td colspan="3">50 psi</td></tr>
<tr><td>Curtain gas</td><td colspan="3">30 psi</td></tr>
<tr><td>Temperature</td><td colspan="3">500 °C</td></tr>
<tr><td>Ion source</td><td colspan="3">DuoSpray Ion Source</td></tr>
<tr><td>Ion spray voltage</td><td colspan="3">Positive: 5,500 V</td></tr>
</table>

Table S3. Optimization of compound-specific parameters in a tandem mass spectrometer for analyzing 20 RAs and 1 surrogate standard.

Compounds	**Molecular weight**	**Precursor ion (m/z)**	**Product ion (m/z)**	**Fragmentor (volts)**	**CE (volts)**
MBT	167.24	167.9 [M-H]$^+$	134.8	116	31
			124.0	116	27
BT	135.18	119.9 [M-H]$^+$	64.9	100	21
			92.0	100	21
2-NH2-BT	150.20	150.9 [M-H]$^+$	109.0	10	35
			124.0	10	29
2-OH-BT	151.18	151.9 [M-H]$^+$	124.1	40	9
			80.1	40	27
2-Me-BT	149.21	149.9 [M-H]$^+$	109.0	50	33
			65.0	50	43
2-Me-S-BT	181.27	181.8 [M-H]$^+$	167.0	31	33
			123.0	31	47
MBS	252.35	252.9 [M-H]$^+$	86.0	20	23
			87.0	20	25
CBS	264.41	264.9 [M-H]$^+$	165.9	11	47
			182.9	11	35
TBBS	238.37	238.9 [M-H]$^+$	183.0	81	19
			165.8	81	29
TMTD	240.42	240.8 [M-H]$^+$	88.0	20	17
			119.9	20	17
DPG	211.27	212.0 [M-H]$^+$	119.0	100	27
			94.0	100	27
MB	150.20	150.9 [M-H]$^+$	93.0	76	31
			117.9	76	37
PAN(A)	219.29	220.0 [M-H]$^+$	92.0	26	27
			128.1	26	33
PBN(D)	219.29	220.0 [M-H]$^+$	142.9	76	75
			128.1	76	35
IPPD	226.32	227.1 [M-H]$^+$	184.0	10	21
			183.6	10	45
6PPD-Q	298.39	229.0 [M-H]$^+$	240.8	130	39
			215.0	130	23
6PPD	268.40	269.0 [M-H]$^+$	184.1	56	25
			185.0	56	21
PPD	184.24	227.1 [M-H]$^+$	184.0	10	27
			183.6	10	27
TMQ	173.26	174.0 [M-H]$^+$	132.0	126	23
			144.0	126	35
HMMM	390.44	391.1 [M-H]$^+$	359.0	50	9
			283.2	50	19
6PPD-Q-^{13}C	304.34	305.0 [M-H]$^+$	221.0	10	23
			247.0	10	39

Table S4. Linear range, coefficient of determination (R^2), recovery rate of extraction efficiency, limit of detection (LOD), and procedural blank concentration for the analysis of 20 RAs using LC-MS/MS.

Compounds	Linear range (ng mL^{-1})	R^2	Recovery rate of extraction efficiency (%)		LOD (ng mL^{-1})	Procedural blank concentration (ng mL^{-1})
			HLB cartridge	C18 cartridge		
MBT	1–500	0.998	90[b]	60	0.17	<LOD[a]
BT	1–500	0.999	120	55	0.93	<LOD
2-NH2-BT	1–500	0.998	70	40	0.45	<LOD
2-OH-BT	1–500	0.995	85	80	0.52	<LOD
2-Me-BT	1–500	0.999	95	90	0.03	<LOD
2-Me-S-BT	1–500	0.998	100	55	0.02	<LOD
MBS	1–500	0.999	60	80	0.31	<LOD
CBS	1–500	0.999	65	95	0.72	<LOD
TBBS	1–500	0.995	50	85	0.16	<LOD
TMTD	1–500	0.997	53	80	0.49	<LOD
DPG	1–500	0.997	62	93	0.71	<LOD
MB	1–500	0.999	58	92	0.71	<LOD
PAN(A)	1–500	0.999	55	93	1.16	<LOD
PBN(D)	1–500	0.999	53	86	1.72	<LOD
IPPD	1–500	0.999	62	87	0.69	<LOD
6PPD-Q	1–500	0.999	60	94	0.91	<LOD
6PPD	1–500	0.998	70	95	0.47	<LOD
PPD	1–500	0.999	50	100	0.62	<LOD
TMQ	1–500	0.999	40	85	0.13	<LOD
HMMM	1–500	0.995	50	80	0.28	<LOD

[a] <LOD: Below limit of detection.

[b] The shaded compounds were purified using the corresponding cartridges and then analyzed.

Table S5. Recovery rates of surrogate standard (6PPD-Q-$^{13}C_6$) in sediments and road dust samples collected from Lake Sihwa.

Matrix	Sites	Recovery rate (%)
Sediments	OI1	100
	OI2	95
	OI3	90
	OI4	94
	NI1	98
	NI2	115
	NI3	96
	U1	110
	N1	97
	M1	110
	M2	90
	M3	90
	M4	90
	M5	90
	M6	100
	M7	110
	M8	92
	M9	93
	M10	97
	M11	95
	M12	90
	M14	98
Road dust	NI2	90
	NI3	101

Table S6. K_{OC} values and toxicity data used in the calculation of toxic units.

Compounds	**K_{OC} (L/kg)**	**Organisms**	**Effect**	**LC_{50} in Fish (mg/L)**	**Source**
MBT	178	*Oryzias latipes*	Mortality	8.4	EnviroTox
BT	49	*Pimephales promelas*	Mortality	65	EnviroTox
TBSS	200	*Oryzias latipes*	Mortality	1.4	EnviroTox
DPG	204	*Oryzias latipes*	Mortality	17	EnviroTox
6PPD-Q	2400	*Salmon*	Mortality	0.0015	EnviroTox
6PPD	11,000	*Salmon*	Mortality	0.25	EnviroTox
TMQ	209	*Oryzias latipes*	Mortality	6.7	EnviroTox

Table S7. Estimated C_{water}, Z, and PAF values for RAs in sediments and road dust.

Sample	**Site**	**Compound**	**OC (%)**	**K_{OC} (L/kg)**	**$C_{sediment}$ (ng/g dw)**	**LC50 (µg/L)**	**f_{OC}**	**C_{water} (ng/L)**	**Z**	**PAF**
Sediment	OI1	MBT	0.7	178	4.6	8400	0.007	3.7	-7.9	0.0
	OI1	BT	0.7	49	40	65000	0.007	120	-6.5	0.0
	OI1	TBSS	0.7	200	<LOD[a]	1400	0.007	–[b]	–	–
	OI1	DPG	0.7	204	15	17000	0.007	11	-7.6	0.0
	OI1	6PPD-Q	0.7	2400	1.9	1.5	0.007	0.11	-2.6	0.0041
	OI1	6PPD	0.7	11000	0.3	250	0.007	0.0038	-11	0.00
	OI1	TMQ	0.7	209	<LOD	6700	0.007	–	–	–
	OI2	MBT	3.4	178	2.7	8400	0.034	0.45	-10	0.0
	OI2	BT	3.4	49	96	65000	0.034	58	-7.2	0.0
	OI2	TBSS	3.4	200	<LOD	1400	0.034	–	–	–
	OI2	DPG	3.4	204	3.9	17000	0.034	0.56	-11	0.0
	OI2	6PPD-Q	3.4	2400	0.9	1.5	0.034	0.011	-5.0	0.0
	OI2	6PPD	3.4	11000	0.4	250	0.034	0.0011	-12	0.0
	OI2	TMQ	3.4	209	<LOD	6700	0.034	–	–	–
	OI3	MBT	4.5	178	4.9	8400	0.045	0.61	-9.8	0.0
	OI3	BT	4.5	49	1.8	65000	0.045	0.81	-12	0.0
	OI3	TBSS	4.5	200	<LOD	1400	0.045	–	–	–
	OI3	DPG	4.5	204	15	17000	0.045	1.6	-9.5	0.0
	OI3	6PPD-Q	4.5	2400	2.3	1.5	0.045	0.021	-4.4	0.00001
	OI3	6PPD	4.5	11000	0.4	250	0.045	0.00080	-13	0.0
	OI3	TMQ	4.5	209	<LOD	6700	0.045	–	–	–
	OI4	MBT	24.8	178	0.5	8400	0.248	0.011	-14	0.0
	OI4	BT	24.8	49	<LOD	65000	0.248	–	–	–
	OI4	TBSS	24.8	200	<LOD	1400	0.248	–	–	–
	OI4	DPG	24.8	204	20	17000	0.248	0.39	-11	0.0
	OI4	6PPD-Q	24.8	2400	3.8	1.5	0.248	0.0064	-5.6	0.0
	OI4	6PPD	24.8	11000	0.4	250	0.248	0.00014	-14	0.0
	OI4	TMQ	24.8	209	<LOD	6700	0.248	–	–	–
	NI1	MBT	0.4	178	1.4	8400	0.004	1.9	-8.6	0.0
	NI1	BT	0.4	49	16	65000	0.004	82	-6.8	0.0
	NI1	TBSS	0.4	200	0	1400	0.004	–	–	–
	NI1	DPG	0.4	204	11	17000	0.004	13	-7.3	0.0
	NI1	6PPD-Q	0.4	2400	<LOD	1.5	0.004	–	–	–
	NI1	6PPD	0.4	11000	2.5	250	0.004	0.057	-8.6	0.0
	NI1	TMQ	0.4	209	<LOD	6700	0.004	–	–	–
	NI2	MBT	0.5	178	1.3	8400	0.005	1.5	-8.9	0.0
	NI2	BT	0.5	49	410	65000	0.005	1700	-3.7	0.00009
	NI2	TBSS	0.5	200	0.2	1400	0.005	0.2	-9.1	0.0
	NI2	DPG	0.5	204	3.0	17000	0.005	2.9	-8.9	0.0
	NI2	6PPD-Q	0.5	2400	1.5	1.5	0.005	0.125	-2.5	0.0055
	NI2	6PPD	0.5	11000	14	250	0.005	0.25	-7.1	0.0
	NI2	TMQ	0.5	209	7.5	6700	0.005	7.2	-7.0	0.0
	NI3	MBT	0.3	178	2.5	8400	0.003	4.7	-7.7	0.0
	NI3	BT	0.3	49	490	65000	0.003	3300	-3.0	0.0012
	NI3	TBSS	0.3	200	0.2	1400	0.003	0.33	-8.5	0.0
	NI3	DPG	0.3	204	52	17000	0.003	85	-5.4	0.0
	NI3	6PPD-Q	0.3	2400	33	1.5	0.003	4.6	1.1	0.87
	NI3	6PPD	0.3	11000	340	250	0.003	10	-3.3	0.00055
	NI3	TMQ	0.3	209	38	6700	0.003	61	-4.8	0.0
	U1	MBT	0.7	178	0.2	8400	0.007	0.16	-11	0.0
	U1	BT	0.7	49	<LOD	65000	0.007	–	–	–
	U1	TBSS	0.7	200	<LOD	1400	0.007	–	–	–
	U1	DPG	0.7	204	<LOD	17000	0.007	–	–	–

U1	6PPD-Q	0.7	2400	<LOD	1.5	0.007	–	–	–
U1	6PPD	0.7	11000	<LOD	250	0.007	–	–	–
U1	TMQ	0.7	209	0.2	6700	0.007	0.14	-11	0.0
N1	MBT	3.9	178	0.7	8400	0.039	0.10	-12	0.0
N1	BT	3.9	49	170	65000	0.039	89	-6.7	0.0
N1	TBSS	3.9	200	<LOD	1400	0.039	–	–	–
N1	DPG	3.9	204	1.8	17000	0.039	0.22	-11	0.0
N1	6PPD-Q	3.9	2400	<LOD	1.5	0.039	–	–	–
N1	6PPD	3.9	11000	2.1	250	0.039	0.0049	-11	0.0
N1	TMQ	3.9	209	2.1	6700	0.039	0.26	-10	0.0
M1	MBT	1.3	178	1.9	8400	0.013	0.82	-9.5	0.0
M1	BT	1.3	49	73	65000	0.013	110	-6.5	0.0
M1	TBSS	1.3	200	0.7	1400	0.013	0.27	-8.8	0.0
M1	DPG	1.3	204	2.9	17000	0.013	1.1	-9.9	0.0
M1	6PPD-Q	1.3	2400	1.1	1.5	0.013	0.035	-3.8	0.00006
M1	6PPD	1.3	11000	6.8	250	0.013	0.048	-8.8	0.0
M1	TMQ	1.3	209	2.2	6700	0.013	0.81	-9.2	0.0
M2	MBT	0.5	178	0.2	8400	0.005	0.22	-11	0.0
M2	BT	0.5	49	140	65000	0.005	570	-4.81	0.0
M2	TBSS	0.5	200	<LOD	1400	0.005	–	–	–
M2	DPG	0.5	204	2.6	17000	0.005	2.55	-9.0	0.0
M2	6PPD-Q	0.5	2400	<LOD	1.5	0.005	–	–	–
M2	6PPD	0.5	11000	4.1	250	0.005	0.074	-8.3	0.0
M2	TMQ	0.5	209	2.2	6700	0.005	2.1	-8.3	0.0
M3	MBT	0.1	178	1.1	8400	0.001	6.2	-7.4	0.0
M3	BT	0.1	49	35	65000	0.001	710	-4.6	0.0
M3	TBSS	0.1	200	<LOD	1400	0.001	–	–	–
M3	DPG	0.1	204	3.0	17000	0.001	15	-7.2	0.0
M3	6PPD-Q	0.1	2400	<LOD	1.5	0.001	–	–	–
M3	6PPD	0.1	11000	8.7	250	0.001	0.79	-5.9	0.0
M3	TMQ	0.1	209	5.8	6700	0.001	28	-5.6	0.0
M4	MBT	0.5	178	1.5	8400	0.005	1.7	-8.7	0.0
M4	BT	0.5	49	130	65000	0.005	530	-4.9	0.0
M4	TBSS	0.5	200	0	1400	0.005	–	–	–
M4	DPG	0.5	204	4.8	17000	0.005	4.7	-8.4	0.0
M4	6PPD-Q	0.5	2400	1.2	1.5	0.005	0.1	-2.8	0.0028
M4	6PPD	0.5	11000	11	250	0.005	0.2	-7.3	0.0
M4	TMQ	0.5	209	4.3	6700	0.005	4.1	-7.6	0.0
M5	MBT	1.0	178	0.3	8400	0.01	0.17	-11	0.0
M5	BT	1.0	49	140	65000	0.01	290	-5.6	0.0
M5	TBSS	1.0	200	<LOD	1400	0.01	–	–	–
M5	DPG	1.0	204	2.5	17000	0.01	1.2	-9.8	0.0
M5	6PPD-Q	1.0	2400	<LOD	1.5	0.01	–	–	–
M5	6PPD	1.0	11000	4.9	250	0.01	0.044	-8.8	0.0
M5	TMQ	1.0	209	5.9	6700	0.01	2.8	-7.9	0.0
M6	MBT	1.0	178	0.3	8400	0.01	0.17	-11	0.0
M6	BT	1.0	49	190	65000	0.01	390	-5.2	0.0
M6	TBSS	1.0	200	0.2	1400	0.01	0.1	-9.8	0.0
M6	DPG	1.0	204	1.0	17000	0.01	0.49	-11	0.0
M6	6PPD-Q	1.0	2400	<LOD	1.5	0.01	–	–	–
M6	6PPD	1.0	11000	2.0	250	0.01	0.018	-9.8	0.0
M6	TMQ	1.0	209	<LOD	6700	0.01	–	–	–
M7	MBT	0.4	178	1.0	8400	0.004	1.4	-8.9	0.0
M7	BT	0.4	49	70	65000	0.004	360	-5.3	0.0
M7	TBSS	0.4	200	<LOD	1400	0.004	–	–	–
M7	DPG	0.4	204	0.9	17000	0.004	1.1	-9.9	0.0

	M7	6PPD-Q	0.4	2400	<LOD	1.5	0.004	–	–	–
	M7	6PPD	0.4	11000	1.8	250	0.004	0.049	-8.9	0.0
	M7	TMQ	0.4	209	4.2	6700	0.004	5.02	-7.4	0.0
	M8	MBT	0.3	178	1.4	8400	0.003	2.6	-8.3	0.0
	M8	BT	0.3	49	100	65000	0.003	680	-4.7	0.0
	M8	TBSS	0.3	200	<LOD	1400	0.003	–	–	–
	M8	DPG	0.3	204	1.0	17000	0.003	1.6	-9.5	0.0
	M8	6PPD-Q	0.3	2400	<LOD	1.5	0.003	–	–	–
	M8	6PPD	0.3	11000	2.0	250	0.003	0.061	-8.5	0.0
	M8	TMQ	0.3	209	1.6	6700	0.003	2.6	-8.1	0.0
	M9	MBT	1.0	178	1.0	8400	0.01	0.56	-9.8	0.0
	M9	BT	1.0	49	80	65000	0.01	160	-6.1	0.0
	M9	TBSS	1.0	200	0.2	1400	0.01	0.10	-9.8	0.0
	M9	DPG	1.0	204	1.1	17000	0.01	0.54	-11	0.0
	M9	6PPD-Q	1.0	2400	<LOD	1.5	0.01	–	–	–
	M9	6PPD	1.0	11000	1.8	250	0.01	0.016	-9.9	0.0
	M9	TMQ	1.0	209	5.9	6700	0.01	2.8	-7.9	0.0
	M10	MBT	0.7	178	<LOD	8400	0.007	–	–	–
	M10	BT	0.7	49	51	65000	0.007	150	-6.2	0.0
	M10	TBSS	0.7	200	<LOD	1400	0.007	–	–	–
	M10	DPG	0.7	204	1.0	17000	0.007	0.70	-10	0.0
	M10	6PPD-Q	0.7	2400	<LOD	1.5	0.007	–	–	–
	M10	6PPD	0.7	11000	1.3	250	0.007	0.017	-9.8	0.0
	M10	TMQ	0.7	209	<LOD	6700	0.007	–	–	–
	M11	MBT	1.0	178	1.2	8400	0.01	0.67	-9.7	0.0
	M11	BT	1.0	49	28	65000	0.01	57	-7.2	0.0
	M11	TBSS	1.0	200	<LOD	1400	0.01	–	–	–
	M11	DPG	1.0	204	1.0	17000	0.01	0.49	-11	0.0
	M11	6PPD-Q	1.0	2400	<LOD	1.5	0.01	–	–	–
	M11	6PPD	1.0	11000	1.7	250	0.01	0.015	-9.9	0.0
	M11	TMQ	1.0	209	3.4	6700	0.01	1.62	-8.5	0.0
	M12	MBT	0.6	178	<LOD	8400	0.006	–	–	–
	M12	BT	0.6	49	132	65000	0.006	450	-5.1	0.0
	M12	TBSS	0.6	200	<LOD	1400	0.006	–	–	–
	M12	DPG	0.6	204	0.9	17000	0.006	0.74	-10	0.0
	M12	6PPD-Q	0.6	2400	<LOD	1.5	0.006	–	–	–
	M12	6PPD	0.6	11000	1.6	250	0.006	0.024	-9.4	0.0
	M12	TMQ	0.6	209	11	6700	0.006	8.8	-6.8	0.0
	M13	MBT	1.0	178	<LOD	8400	0.01	–	–	–
	M13	BT	1.0	49	180	65000	0.01	370	-5.3	0.0
	M13	TBSS	1.0	200	<LOD	1400	0.01	–	–	–
	M13	DPG	1.0	204	1.1	17000	0.01	0.53	-11	0.0
	M13	6PPD-Q	1.0	2400	<LOD	1.5	0.01	–	–	–
	M13	6PPD	1.0	11000	1.3	250	0.01	0.012	-10	0.0
	M13	TMQ	1.0	209	2.3	6700	0.01	1.1	-8.9	0.0
Road dust	NI2	MBT	0.1	178	0.38	8400	0.001	2.1	-8.5	0.0
	NI2	BT	0.1	49	15	65000	0.001	310	-5.5	0.0
	NI2	TBSS	0.1	200	N.D.[c]	1400	0.001	–	–	–
	NI2	DPG	0.1	204	140	17000	0.001	690	-3.3	0.00051
	NI2	6PPD-Q	0.1	2400	16	1.5	0.001	6.7	1.5	0.94
	NI2	6PPD	0.1	11000	0.83	250	0.001	0.075	-8.3	0.0
	NI2	TMQ	0.1	209	N.D.	6700	0.001	–	–	–
	NI3	MBT	0.1	178	N.D.	8400	0.001	–	–	–
	NI3	BT	0.1	49	56	65000	0.001	1100	-4.1	0.00002
	NI3	TBSS	0.1	200	N.D.	1400	0.001	–	–	–
	NI3	DPG	0.1	204	560	17000	0.001	2700	-1.9	0.031

	NI3	6PPD-Q	0.1	2400	36	1.5	0.001	15	2.4	0.99
	NI3	6PPD	0.1	11000	0.86	250	0.001	0.078	-8.3	0.0
	NI3	TMQ	0.1	209	N.D.	6700	0.001	–	–	–

[a] < LOD: Below limit of detection.

[b] –: not analyzed.

[c] N.D.: Not detected.

Table S8. Concentrations of RAs in sediments from inland creeks and Lake Sihwa (ng g^{-1} dw).

Compounds	**OI1**	**OI2**	**OI3**	**OI4**	**NI1**	**NI2**	**NI3**	**U1**	**N1**	**M1**	**M2**
MBT	4.6	2.7	4.9	0.5	1.4	1.3	2.5	0.2	0.7	1.9	0.2
BT	40	96	1.8	<LOD[a]	16	410	490	<LOD	170	73	140
2-NH2-BT	2.3	1.7	2.3	3.5	<LOD	1.7	2.4	<LOD	<LOD	<LOD	<LOD
2-OH-BT	29	18	34	94	<LOD	30	87	<LOD	<LOD	<LOD	<LOD
2-ME-BT	4.2	<LOD	<LOD	<LOD	16	21	28	4.4	17	20	22
2-ME-S-BT	24	22	24	34	2.6	2.7	7.1	<LOD	4.1	4.4	3.0
MBS	N.D.[b]	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
CBS	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
TBSS	<LOD	< LOD	<LOD	<LOD	<LOD	0.2	0.2	<LOD	<LOD	0.7	<LOD
TMTD	<LOD	11	<LOD	13	<LOD	<LOD	<LOD	16	<LOD	<LOD	<LOD
DPG	15	3.9	15	20	11	3.0	52	<LOD	1.8	2.9	2.6
MB	<LOD	<LOD	<LOD	1.2	1.4	1.8	<LOD	<LOD	1.1	1.2	0.8
PAN(A)	N.D	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PBN(D)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
IPPD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	6.8	<LOD	<LOD	<LOD	<LOD
6PPD-Q	1.9	0.9	2.3	3.8	<LOD	1.5	33	<LOD	<LOD	1.1	<LOD
6PPD	0.3	0.4	0.4	0.4	2.5	14	340	<LOD	2.1	6.8	4.1
PPD	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D.	N.D.	N.D	N.D
TMQ	<LOD	<LOD	<LOD	<LOD	<LOD	7.5	38	0.2	2.1	2.2	2.2
HMMM	3.0	1.3	4.8	2.7	<LOD	2.3	9.4	<LOD	<LOD	<LOD	<LOD

[a] <LOD: Below limit of detection.

[b] N.D.: not detected

Table S8. (Continued).

Compounds	**M3**	**M4**	**M5**	**M6**	**M7**	**M8**	**M9**	**M10**	**M11**	**M12**	**M14**
MBT	1.1	1.5	0.3	0.3	1	1.4	1.0	< LOD	1.2	<LOD	<LOD
BT	35	130	140	190	70	100	80	51	28	132	180
2-NH2-BT	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2-OH-BT	35	<LOD	60	<LOD	<LOD	<LOD	13	<LOD	40	<LOD	<LOD
2-ME-BT	35	19	3.7	5.7	27	14	<LOD	21	9.5	10	18
2-ME-S-BT	3.7	4.4	1.4	2.1	3.2	2.3	2.4	3.0	4.2	3.9	6.7
MBS	N.D.	N.D.	N.D	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
CBS	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
TBSS	<LOD	<LOD	<LOD	0.2	<LOD	<LOD	0.2	<LOD	<LOD	<LOD	<LOD
TMTD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
DPG	3.0	4.8	2.5	1.0	0.9	1.0	1.1	1.0	1.0	0.9	1.1
MB	1.5	<LOD	<LOD	2.1	1.7	1.6	<LOD	<LOD	2.4	<LOD	<LOD
PAN(A)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PBN(D)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
IPPD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6PPD-Q	<LOD	1.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6PPD	8.7	11	4.9	2.0	1.8	2.0	1.8	1.3	1.7	1.6	1.3
PPD	N.D	N.D	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
TMQ	5.8	4.3	5.9	<LOD	4.2	1.6	5.9	<LOD	3.4	11	2.3
HMMM	<LOD	0.9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.4	<LOD	<LOD

[a] <LOD: Below limit of detection.

[b] N.D.: not detected

Table S9. Concentrations of RAs in road dust samples (NI2 and NI3) from Lake Sihwa.

Compounds	**NI2** (ng g^{-1} dw)	**NI3** (ng g^{-1} dw)
MBT	0.38	N.D.[a]
BT	15	56
2-NH2-BT	2.7	22
2-OH-BT	45	490
2-ME-BT	55	42
2-ME-S-BT	18	54
MBS	0.29	0.17
CBS	N.D.	0.75
TBSS	N.D.	N.D.
TMTD	N.D.	N.D.
DPG	140	560
MB	N.D.	N.D.
PAN(A)	<LOD[b]	<LOD
PBN(D)	<LOD	<LOD
IPPD	<LOD	<LOD
6PPD-Q	16	36
6PPD	0.83	0.86
PPD	1.0	1.5
TMQ	N.D.	N.D.
HMMM	1.9	11

[a] N.D.: Not detected.

[b] < LOD: Below limit of detection.

Table S10. Joint PAF values and major contributing compounds in road dust and sediments estimated using the SPI model.

Sample	Site	Joint_PAF	Top_contributor	Max_Individual_PAF
Road dust	NI3	0.99	6PPD-Q	0.99
	NI2	0.94	6PPD-Q	0.94
Sediment	NI3	0.87	6PPD-Q	0.87
	NI2	0.0055	6PPD-Q	0.0054
	OI1	0.0041	6PPD-Q	0.0041
	M4	0.0028	6PPD-Q	0.0028
	M1	0.00006	6PPD-Q	0.00006
	OI3	0.00001	6PPD-Q	0.00001

Supplementary Figures

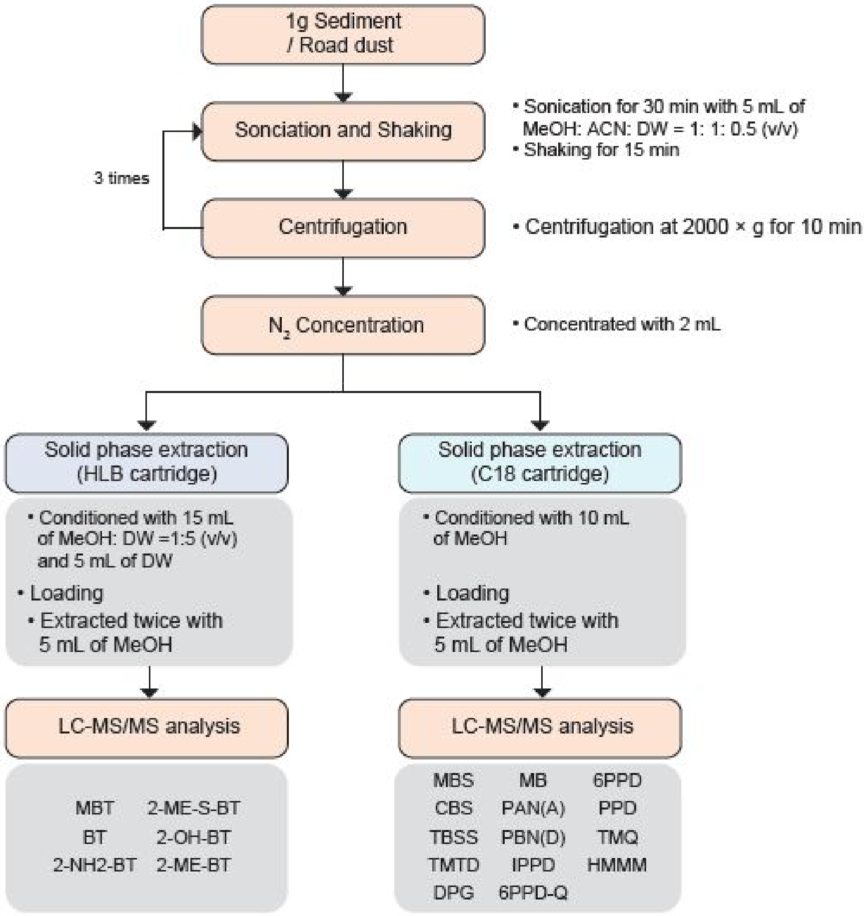

Figure S1. A flowchart illustrating the extraction and clean-up procedures for analyzing 20 rubber additives in sediment and road dust samples.

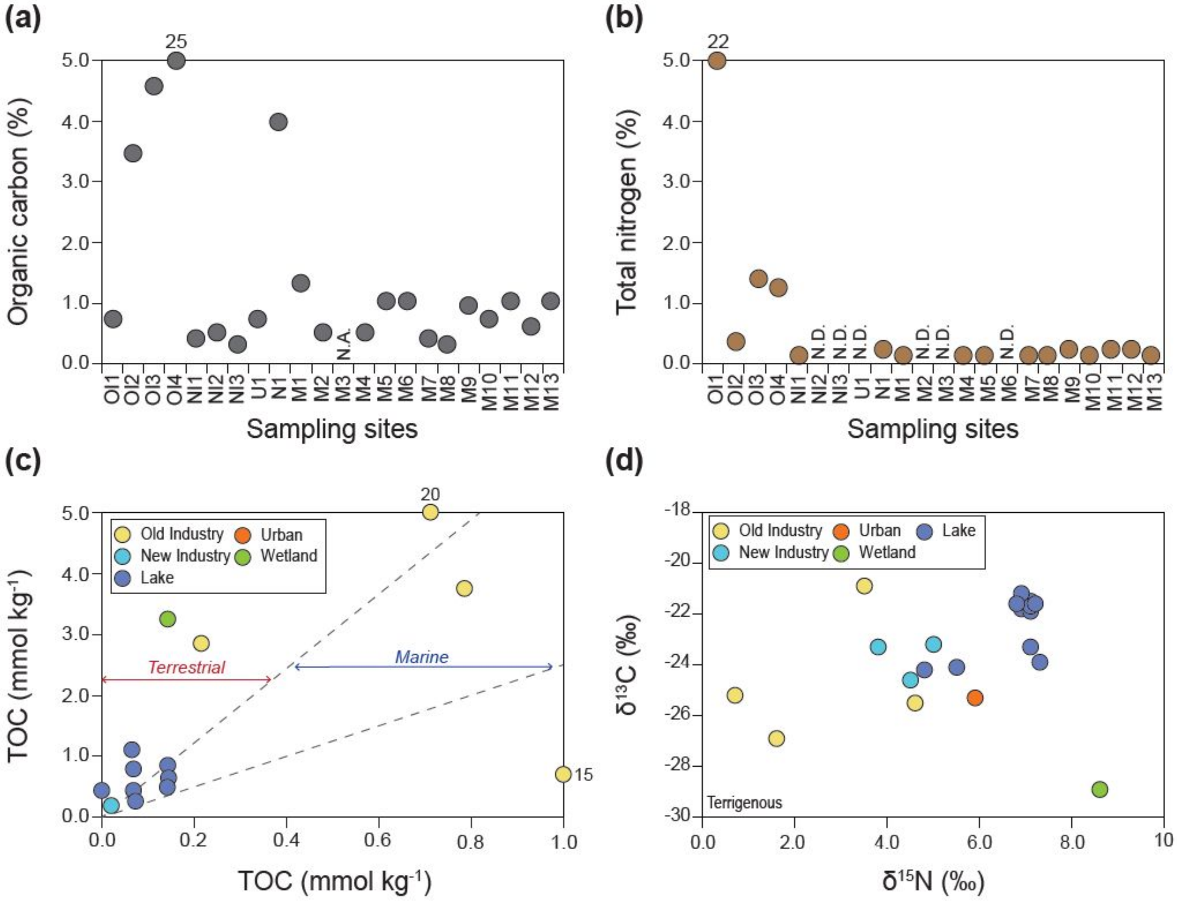

Figure S2. (a) Organic carbon content, **(b)** total nitrogen content, **(c)** C/N ratio, and **(d)** δ^{13}C and δ^{15}N values in sediments from inland creeks and Lake Sihwa, South Korea.

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