



Integrated assessment of tire and rubber wear-derived compounds in wastewater treatment systems and receiving environments

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ABSTRACT

Tire and rubber wear-derived compounds (TRDCs) are emerging contaminants released through tire abrasion and transferred mainly by urban runoff, with environmental relevance concern. Since wastewater treatment plants (WWTPs) act as point sources by treating combined urban runoff and wastewater, this study assessed 25 TRDCs across an integrated water cycle, including wastewater, sewage sludge and surface water from one of Europe's longest river basins. Widespread occurrence was observed, highlighting the impact of urban and industrial activities on aquatic ecosystem. Benzothiazoles (BTHs) and benzotriazoles (BTRs) dominated the pollution profile, while the highly toxic 6PPD-quinone (6PPD-Q) was frequently detected at lower concentrations. Surface water (346 ng/L, median; 1.68–1510 ng/L, min-max) showed significant lower ($p < 0.01$) levels than wastewater (3923 ng/L, 422–23422 ng/L), while sludge accumulated notably high TRDC concentrations (424 ng/g, 184–2257 ng/g), acting as a reservoir and potential source for agricultural soils. Although some compounds (2-OH-BTH, MBTH, 6PPD-Q) showed high removal efficiencies ($>75\%$), conventional WWTPs were not fully effective. Surface water concentrations were significantly higher ($p < 0.01$) in urban and high-traffic areas, confirming road runoff as a key source. Ecotoxicological assessment indicated substantial acute risks in aquatic ecosystem associated with PPDs, particularly 6PPD-Q, and moderate chronic risks under cumulative exposure scenarios. Potential risks for soil organisms were also observed considering annual sludge amendments (from 1 to 100 years) to agricultural soil at agronomic conditions. These findings underscore the need for continuous monitoring, mitigation strategies, and regulatory consideration, adopting a One Health approach within the European Water Framework Directive.

1. Introduction

Tire and rubber wear-derived compounds (TRDCs) constitute a family of emerging contaminants whose environmental relevance has increased markedly in recent years. These compounds are continuously released into the environment as a result of friction between the tire tread and the road surface during driving (Baensch-Baltrusch et al., 2020; Zhang et al., 2023; Abudumutailifu et al., 2025). Tires are composed of 40–60% polymers, including both natural and synthetic rubber, as well as a wide variety of chemical additives designed to improve durability and performance. These additives include antioxidants (p-phenylenediamines, PPDs), vulcanization accelerators (i.e., guanidines and benzothiazoles), plasticizers, fillers, and cross-linking

agents (hexamethoxymethylmelamine, HMMM) (Baensch-Baltrusch et al., 2020; Zhang et al., 2023; Han et al., 2026). Most of them are not covalently bound to the rubber matrix. That facilitates their release through mechanical abrasion and leaching and their subsequent entry into ecological systems (Johannessen et al., 2021; Cao et al., 2022; Xie et al., 2024; Han et al., 2026). Many other rubber-derived products were also potential sources of TRDCs, such as recreational facilities, sporting equipment, clothes, rubber pipes, wires and cables (Chen et al., 2023). TRDCs represent a critical threat to public health due to the inevitable exposure through various routes, including ingestion, inhalation, and direct contact (Wang et al., 2016; Li et al., 2024; Wan et al., 2024; Abudumutailifu et al., 2025). In addition, these emerging pollutants affect the ecological biodiversity because of their environmental

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mobility and ubiquity (Been et al., 2021) as well as their bioavailability and toxicity (Zeng et al., 2016; Zhang et al., 2022; Han et al., 2026).

One of the greatest concerns is closely linked to their impact on water quality and potential adverse effects on freshwater life. Surface waters are highly vulnerable to TRDC contamination due to effluents and urban runoff. Following rainfall, concentrations of the transformation product 6PPD-quinone (6PPD-Q) have been found in the $\mu\text{g/L}$ range, far exceeding acute toxicity thresholds (Tian et al., 2021; Chen et al., 2023). Other TRDCs, such as 1,3-diphenylguanidine (DPG), reach hundreds of $\mu\text{g/L}$ in urban runoff, while persistent compounds such as benzothiazoles and benzotriazoles are pervasively detected in surface waters (Herrero et al., 2013; Challis et al., 2021). Research on traffic-influenced or urban rivers and sanitation infrastructure evidence their dissemination worldwide (i.e., Europe, North America, China, and Australia; Van Leerdam et al., 2009; Rauert et al., 2020; Challis et al., 2021; Johannessen et al., 2021; Chen et al., 2023; Xie et al., 2024; Xu et al., 2024; Escobar-Arnanz et al., 2026). Within the European regulatory framework, the presence of contaminants in surface waters is assessed under the Water Framework Directive (2000/60/EC). Directive 2013/39/EU of the European Parliament and of the Council introduced the watch list as a tool for monitoring emerging contaminants prior to the establishment of environmental quality standards (Directive 2013/39/EU). The recent inclusion of 6PPD and 6PPD-Q on this list (European Commission, 2025) highlights the urgent need to generate robust and comparable data on their presence, distribution, and fate in aquatic systems. Important toxicological impact has been reported derived from these pollutants. The most concerning TRDC is 6PPD-Q, formed by the ozonation of the antioxidant 6PPD. This compound is the primary cause of coho salmon (*Oncorhynchus kisutch*) mass mortality, with median lethal concentration (LC50) near 95 ng/L, a level frequently exceeded in surface waters following storm events (Tian et al., 2022). In addition, other TRDCs have shown sublethal effects in aquatic organisms, including developmental alterations, changes in locomotor behavior, and oxidative stress, denoting a potential risk associated with chronic exposure (Alhelou et al., 2019; Chen et al., 2023).

Wastewater treatment plants (WWTPs) are potential TRDC dissemination pathways due to the combined treatment of urban runoff and wastewater (Alhelou et al., 2019; Seiwert et al., 2022; Xu et al., 2024) and represent important complex sources of chemical mixtures entering the water cycle. In addition, recycling WWTP sludge (biosolids) on agricultural soil is internationally recognized as the most sustainable option for its management, improving the soil structure properties and reducing dependence on chemical fertilizers, an approach aligned with the European Commission's Farm to Fork strategy (European Commission, 2020). Particularly, 86% of the sludge produced in Spain in 2022 was applied to agriculture (Eurostat, 2026). Therefore, this disposal practice might facilitate the subsequent redistribution of pollutants among environmental compartments and its entry pathway into the food chain (Navarro et al., 2018; Sherman et al., 2024).

Despite the emerging and growing concern on TRDCs, significant knowledge gaps remain. Most research has focused on individual matrices or a limited number of compounds, primarily 6PPD-Q, while other relevant TRDCs, such as guanidines, benzothiazoles, and cross-linking agents, have received less attention. Likewise, few studies have evaluated the translocation of TRDCs between different compartments in an integrated approach, hindering realistic ecological risk assessments, specifically under scenarios of chronic exposure and complex mixtures. This lack is particularly evident in southern European regions, where climatic and hydrological conditions differ from those under which most of the available evidence has been generated.

In this context, the present work provides new insights based on a holistic, multi-compartment study, considering surface waters, wastewater, and sewage sludge with the aim of improving more broadly the understanding of environmental behavior, transfer and fate of 25 TRDCs in the water cycle. Ecotoxicological implications premised on aquatic and terrestrial risk assessments were also explored, thereby providing

relevant information for future environmental risk evaluations and development of management strategies.

2. Material and methods

2.1. Reagents and chemicals

A total of 25 TRDCs, including parent additives and transformation products, were analyzed: N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine (6PPD), 2-((4-methylpentan-2-yl)amino)-5-(phenylamino)cyclohexa-2,5-diene-1,4-dione (6PPD-Q), Benzothiazole (BTH), N-cyclohexylbenzothiazole-2-sulfenamide (CBS), 1,3-dimethylbutylamine (DMBA), 1,3-diphenylguanidine (DPG), N, N'-diphenyl-1,4-phenylenediamine (DPPD), 1,3-di-o-tolylguanidine (DTG), Hexamethoxymethylmelamine (HMMM), 4-isopropylaminodiphenylamine (IPPD), N-Isopropyl-N'-phenyl-p-phenylenediamine quinone (IPPD-Q), N,N'-Bis(methylphenyl)-1,4-benzenediamine (DTPD), 2-mercaptobenzothiazole (MBTH), Dicyclohexylurea (DCU), N-cyclohexyl-2-benzothiazol-amine (DCMA), N,N-dicyclohexylmethylamine (DCA), 1-cyclohexyl-3-phenylurea (CPU), 2-aminobenzothiazole (2-ABTH), 2-hydroxybenzothiazole (2-OH-BTH), 2-(methylthio)benzothiazole (2-MeS-BTH), 1H-Benzotriazole (BTR), 5-Methyl-1H-benzotriazole (Me-BTR), 4-hydroxydiphenylamine (4-HDPA), Dibenzylamine (DBZA), and Tributylamine (TBA) (Table S1, Excel). The isotopically labeled analogues used comprised: i) surrogate standards (6PPD-Q-d5, DPG-d10, 5-Me-BTR-d6, DPA-d10, BTH-d4, BTR-d4, and IPPD-Q-d5) and ii) injection standards (clothianidin-d3).

2.2. Sampling design

The Tagus River is the longest in the Iberian Peninsula (1007 km), draining one of its largest and most anthropized basins. Due to its geographic position, the watershed is an important area for transport and trade, which results in a considerable human impact on the environment.

Two wastewater treatment plants (WWTP 1 and WWTP 2), both representative of the Tagus River basin, were selected as they receive wastewater from densely populated areas. WWTP 1 treated around 9000 m³/day from a mixed urban-industrial area, whereas WWTP 2 processed approximately 18,000 m³/day of predominantly urban input. Both facilities have a primary treatment to remove suspended solids followed by a secondary process based on biological digestion with activated sludge (Royano et al., 2024). Grab samples of wastewater (n = 16; influent and effluent) and sewage sludge (n = 16; before and after digestion) were collected quarterly during 2022. Additionally, 51 grab surface water samples were collected quarterly in 2022 across 13 locations (Fig. 1). Polypropylene and amber glass bottles pre-rinsed with methanol were used for water and sludge, respectively. Upon arrival at the laboratory, all samples were stored at -20 °C until analysis. The strategic position of both WWTPs with no other major discharges in between, enables the assessment of how treatment processes and effluent releases influence TRDC pollution in the riverine system. Further details related to study area and sampling collection can be found in previous works (Royano et al., 2023, 2024). Although sampling was conducted independently of precipitation events, the monthly average rainfall in the Tagus River during 2022 was recorded to assess seasonality (Fig. S1).

2.3. Extraction

Filtered water samples (1 L) were spiked with 50 ng of labeled surrogate standards and extracted using Oasis HLB SPE (6 mL, 500 mg). Cartridges were conditioned with 10 mL of dichloromethane, 10 mL of methanol, and 10 mL of Milli-Q water and, after sample loading, were dried under vacuum for 1 h. Subsequently, analytes were eluted with 10 mL of methanol and 10 mL of dichloromethane, and extracts were

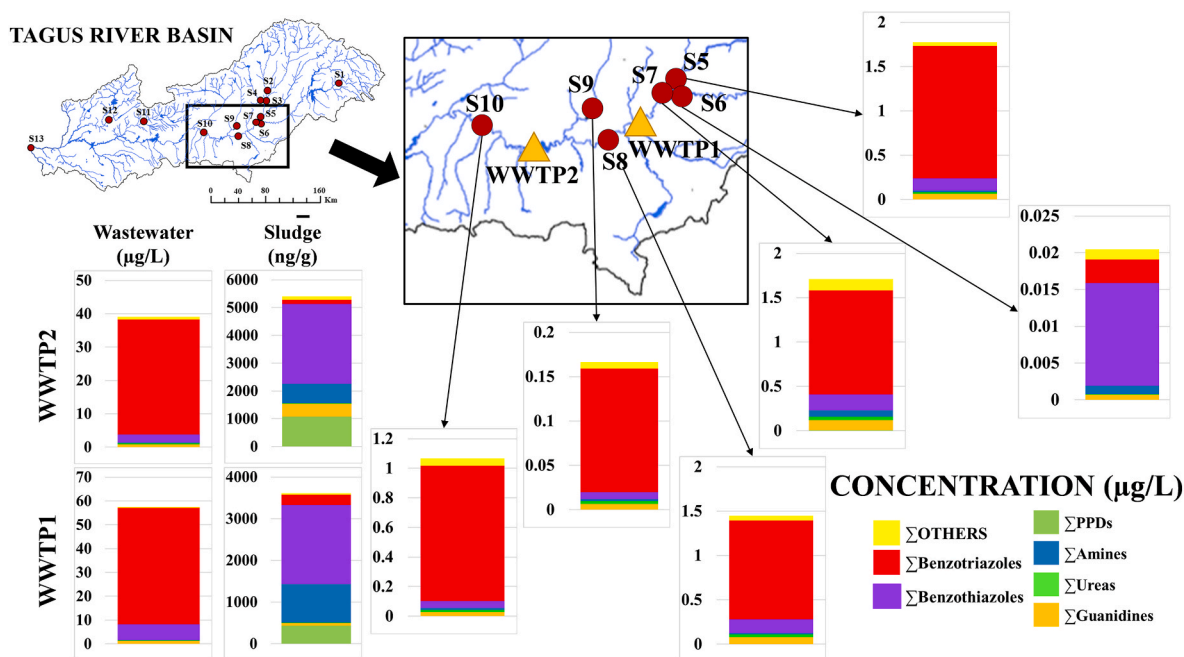


Fig. 1. Details of study design in the Tagus River basin. TRDC concentration ($\mu\text{g/L}$) in the water cycle related to WWTPs.

concentrated to 300 μL under a gentle nitrogen stream. Sewage sludge samples (1 g) also spiked with 50 ng of labeled surrogate standards were treated with 5 mL of acetonitrile and sonicated for 15 min (two cycles). Then, a second extraction was performed using 5 mL of a 1:1 acetone/hexane (v/v) mixture under the same sonication conditions. Extracts were centrifuged at 3000 rpm ($1900\times g$) for 5 min, and the combined supernatants were concentrated to 100 μL , dissolved in 0.4 mL of methanol, and finally filtered. Prior to instrumental analysis, all extracts were spiked with 100 ng of clothianidin-d3 as injection standard.

2.4. Instrumental determination

The analysis of TRDCs was conducted using an ExionLC ultra-high performance liquid chromatography (UHPLC) system coupled to a Triple QuadTM 3500 MS/MS spectrometer (SCIEX, MA, USA). Separation was achieved on a Luna[®] Omega C18 100 Å column (100×2.1 mm i. d., 1.6 μm , Phenomenex) with 0.1% formic acid and 5 mM ammonium formate in Milli-Q water (A) and 0.1% formic acid in methanol (B). The gradient program began with 5% B for 1 min, followed by a linear increase to 20% B over 15 min, ramping to 100% B between 15 and 17 min, and returning to the initial conditions. Target compounds were determined in positive or negative electrospray ionization mode with a temperature set at 550 $^{\circ}\text{C}$, curtain gas pressure at 25 psi and ion spray voltage at 5500 V, using multiple reaction monitoring (MRM) technique. MS/MS parameters are described in more detail in the Supplementary material (Table S2).

2.5. QA/QC and statistical analysis

The analytical methods were validated according to the performance criteria established in SANTE/2020/12830 and SANTE/11312/2021. Validation was performed at three fortification levels: 1, 5, and 50 ng/L for water samples and 1, 5, and 50 ng/g dried weight (d.w.) for sludge samples. The limits of quantification (LOQs) were defined as the lowest validated level for each analyte with recoveries between 70 and 120% and RSDs below 20%. In total, 64% of the analytes achieved LOQs of 1 ng/L or 1 ng/g d. w., while the remainder reached 5 ng/L or 5 ng/g d. w., with the exception of BTH (Tables S3 and S4). Limits of detection (LODs) were calculated from the lowest validated concentration, based on a

signal/noise of 3:1. LODs ranged between 0.01 ng/L (DPG) and 0.64 ng/L (BTH) in water (Table S3), and 0.01 ng/g d. w. (HMMM) and 1.26 ng/g d. w. (4-HDPA) in sludge (Table S4). Recoveries of surrogate standards ranged between 77 and 90%. Field, procedural and instrumental blanks were analyzed in each batch to verify the absence of contamination or carry over effects in the HPLC-MS/MS system. No analytes were detected above the LOD in any blank samples.

2.6. Calculation of mass flow rates, partition coefficients and removal efficiencies

WWTP mass flow rates were calculated from TRDC wastewater and sludge concentrations and the inlet and outlet flows from the facilities. On the other hand, river mass flow rates of individual compounds were also estimated considering TRDC concentration in surface water and the mean daily flow measured at the sampling time (Royano et al., 2023; Table S5). The water–sludge partition coefficient (K_d) was estimated by relating the median concentrations detected in sewage sludge (before and after digester) to those measured in the wastewater (influent and effluent) (Navarro et al., 2025). Besides, removal efficiencies (RE, %) in the WWTPs were calculated using the median concentrations of each analyte on positive ($>\text{LOD}$) wastewater (influent/effluent) and sludge (before/after digester) samples (Royano et al., 2024). WWTP characteristics used in the RE calculations are detailed in the Supplementary material (Table S6).

2.7. Environmental risk assessment calculations

2.7.1. Risk assessment in aquatic ecosystem

The potential ecological risk of TRDCs was evaluated in the aquatic ecosystem by combining the concentration addition (CA, RQ_{mix}) and independent action (IA, RQ_{STU}) approaches (Backhaus and Faust, 2012), providing complementary perspectives on environmental hazard. Both chronic and acute exposure scenarios for aquatic organisms were considered. Chronic risk (RQ_{water}) was estimated using the measured concentrations (MEC_{50} , median and MEC_{max} , maximum) in surface water samples in each sampling point (S1–S13) and $\text{PNEC}_{\text{water}}$ (Predicted No-Effect concentration for aquatic organisms) (European Commission, 2003; Navarro et al., 2025). Risk quotients for mixtures

(RQ_{mix}) of TRDCs were also calculated. Acute risk (RQ_{STU}) was further assessed by calculating toxic units (TUs) for three representative trophic levels (algae, invertebrates and fish), using median and maximum concentrations for the sum of TRDCs, and the ecotoxicological endpoints. The total toxicity of the mixture (RQ_{STU}) was based on the sum of toxic units (STU) for the most sensitive trophic level applying an assessment factor of 1000 (Casillas et al., 2022).

2.7.2. Risk assessment in terrestrial ecosystem

The environmental risk in the terrestrial compartment (RQ_{soil}) was estimated covering direct exposure of soil organisms, at local scenario, simulating the application of WWTP sludge to agricultural soil. RQ_{soil} was obtained as the quotient between Predicted Environmental Concentrations (PEC_{soil} ; Equation (1)) and $PNEC_{soil}$ (Predicted No-Effect Concentration for the soil compartment) (European Commission, 2003; ECHA, 2008, 2016a, 2016b; Navarro et al., 2018; Royano et al., 2024).

$$PEC_{soil}(n) = C_{soil}(0) \times \left[1 + \sum_{n=1}^{n-1} Facc^n \right] \quad \text{Equation (1)}$$

where $PEC_{soil}(n)$ is the initial concentration in soil after n sludge applications, $C_{soil}(0)$, derived from the measured sludge concentrations, is the initial concentration after the first application (Equation (2)) and $Facc$ is the accumulation fraction of pollutant in one year (Equation (3)).

$$C_{soil}(0) = \frac{C_{sludge} \left(\frac{mg}{kg} \right) \times APPL \left(\frac{kg}{m^2} \right)}{DEPTH(m) \times RHO_{soil} \left(\frac{kg}{m^3} \right)} \quad \text{Equation (2)}$$

$$Facc = e^{-365k} \quad \text{Equation (3)}$$

C_{sludge} is the TRDC concentration measured in sludge, $APPL$ represents the dry sludge application rate, and $DEPTH$ and RHO_{soil} are theoretical parameters related to depth of the soil-sludge mixture and the bulk density of soil, respectively (ECHA, 2016a). The k parameter is a removal rate constant, derived from physico-chemical properties of each TRDC, which encompasses volatilization, leaching and biodegradation (ECHA, 2016a).

2.8. Prioritization of hazardous tire-derived compounds

To prioritize the most relevant TRDCs with environmental implications in the ecosystem studied, a methodology based on two main criteria (risk quotient and frequency of occurrence) was applied. Then, a selection of the top three TRDCs of concern for aquatic and terrestrial organisms was established based on a score value calculated by multiplying the risk quotient (RQ_{water} and RQ_{soil}) by the detection frequency of each analyte (Abrantes et al., 2024).

2.9. Statistical calculations

Data analysis was conducted using SPSS (version 14.0) and Statgraphics Centurion XVIII. Differences among groups were evaluated using the Kruskal–Wallis test and Mann–Whitney U test. Relationships among detected compounds were examined using Spearman's rank correlation analysis. To further explore TRDC distribution, a principal component analysis (PCA) was performed, where concentrations below the LOD were substituted with $LOD/\sqrt{2}$ (De la Torre et al., 2020).

3. Results and discussion

3.1. Occurrence of TRDCs in WWTPs

3.1.1. Wastewater samples

All TRDCs, except IPPD and CBS, were detected in the wastewater

samples with detection frequencies (Df) above 75% for 58% of the compounds (Table S7). Although a variable distribution was found (Fig. 2), their widespread presence denoted substantially high total concentrations ($\sum$ TRDCs) ranging from 422 to 23422 ng/L and a median value of 3923 ng/L (Table S7).

Benzotriazoles and benzothiazoles clearly dominated the chemical profile, showing significantly higher levels than other TRDC families (Table S8). Me-BTR (2154 ng/L, median) and BTR (995 ng/L, median) were detected in 100% of the samples, followed by benzothiazoles such as BTH (151 ng/L), 2-OH-BTH (103 ng/L), and 2-MeS-BTH (90.8 ng/L). In addition to their use in car tire rubber, this prevalence probably corresponds to multiple indoor applications such as textiles, pigments or detergents (Xie et al., 2024). Strong correlations among these compounds suggested common sources and similar behaviour during wastewater transport and treatment (Table S9). BTR has been classified by the German Environment Agency as very persistent and very mobile (vPvM), while BTH and DPG have been also identified as potentially persistent, mobile and toxic (PMT) pollutant (Fuchte et al., 2022). DPG and HMMM were also frequently detected (94% and 100%, Df, respectively) with median concentrations of 97.5 ng/L and 50.4 ng/L. Their consistent presence across seasons and treatment plants supports a continuous release into wastewater associated with urban activities. DPG and together with its transformation product phenylguanidine, have been proposed as chemical indicators in stormwater (Peter et al., 2022).

Statistical analysis of the 25 target compounds indicated that significant relationships occurred mainly within specific chemical groups (Table S8). Tire-related compounds such as PPDs and benzothiazoles were strongly associated, suggesting common sources or similar environmental behavior. Clear links were also observed between parent compounds and their transformation products, indicating co-occurrence in wastewaters. Consistent with observations in other environmental matrices, 6PPD-Q was detected more frequently (94%, Df; 1.90, median; 0.16–7.09, min-max) than its parent compound 6PPD (13%, Df; 1.20, median; 0.30–2.11, min-max), supporting the rapid transformation of 6PPD under oxic conditions during wastewater transport and treatment (Zhang et al., 2023; Lane et al., 2024).

Influent and effluent profiles from both WWTPs remained remarkably consistent across seasons, although higher input was observed mainly in summer (Fig. S2). Seasonal trends for specific compounds have been reported, such as increased 6PPD-Q concentrations in late spring due to enhanced atmospheric oxidation (Chen et al., 2023), higher BTH concentrations during dry periods because of reduced

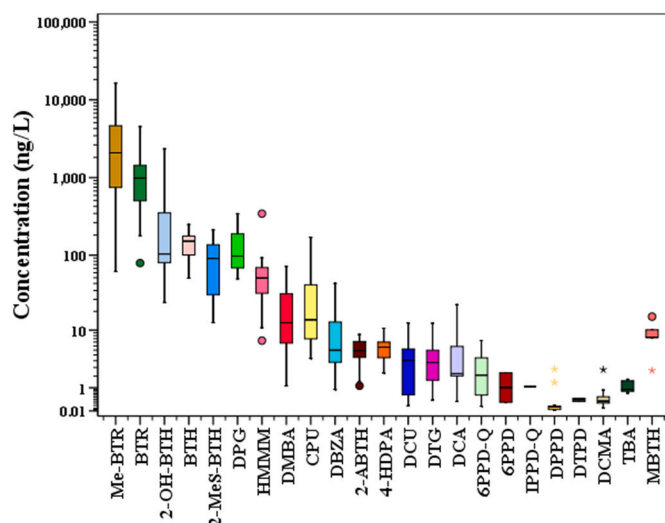


Fig. 2. Concentrations (ng/L, logarithmic scale) of all compounds analyzed in wastewater.

dilution (Zhang et al., 2023), or rainfall-driven mobilisation of additives such as DPG in surface waters (Escobar-Armanz et al., 2026). Besides, other studies have highlighted the role of rain events in the transport of TRDCs and their transformation products, particularly via stormwater runoff in summer and snowmelt in spring, which can result in short but intense increases in contaminant loads entering WWTPs (Challis et al., 2021; Seiwert et al., 2022). In general, no statistically significant differences were observed between influent and effluent samples, nor between wastewater treatment plants. Mass flow rates showed significantly higher ($p < 0.05$) TRDC discharge in water line at WWTP1 (52.6 g/d) than WWTP2 (25.8 g/d; Table S10). Some compounds (e.g. 2-OH-BTH, MBTH, 6PPD-Q) showed high removal efficiencies ($>75\%$; Table S10) in accordance with other studies (Maurer et al., 2023) or moderate (i.e. BTR, $>40\%$), but in general rates mostly underscored that conventional wastewater treatment processes are not fully effective at removing these pollutants. While the use of grab samples could represent a limitation for precise mass-balance, the observed patterns were consistent with previously reported composite-sample data (Maurer et al., 2023). Complex mixtures of TRDCs in influents can inhibit nitrification and denitrification, reduce the abundance of key functional genes, and damage microbial biomass through oxidative stress, potentially compromising treatment efficiency (Han et al., 2026). In addition, continuous inputs from urban runoff, vehicle washing, and industrial discharges may further contribute to their persistence within wastewater treatment systems (Janna et al., 2011). Interestingly, a 2.5–4.5 fold increase was observed for HMMM in the water and sludge line treatments (Table S10). Despite the aerobic biodegradation of HMMM has been evidenced, the concentration rise in the wastewater treatment by a factor of 2–4 has been also reported (Alhelou et al., 2019). This trend suggest that further HMMM might generate from precursors present in the untreated wastewater through a formation process faster than the HMMM transformation. HMMM precursors may be by-products or reaction products that are formed during use of HMMM as a cross-linker (Bauer, 1982). The occurrence of HMMM precursors has been previously corroborated in wastewater (Alhelou et al., 2019).

3.1.2. Sewage sludge samples

TRDCs were highly detected in sewage sludge (Fig. 3), showing detection frequencies above 75% for 68% of the analytes; concretely, almost half of the compounds (48%) were found in all samples. Σ TRDC concentrations ranged from 184 to 2257 ng/g d. w., with a median value of 424 ng/g d. w. (Table S11). MBTH (179 ng/g d. w., median), 2-OH-BTH (34.8 ng/g d. w.), DBZA (19.1 ng/g d. w.), DPG (13.9 ng/g d. w.), DMBA (12.1 ng/g d. w.) and 2-MeS-BTH (9.31 ng/g d. w.) were the

most abundant compounds, reflecting significantly higher levels ($p < 0.05$, Table S12). Benzothiazoles clearly dominated both pre- and post-digestion sludge (Fig. S3), and DPG was also prevalent (100%, Df; 13.9 ng/g d. w., median, 1.70–187 ng/g d. w.). Its occurrence in suspended solids from WWTPs (Xie et al., 2024), urban runoff (Kang et al., 2024) and surface waters (Zahn et al., 2018; Yoganandham et al., 2024), highlights its environmental relevance. Both 6PPD and 6PPD-Q were frequently detected (88% and 100%, respectively), and although data on these compounds in sludge remain limited, levels obtained (3.61 ng/g and 2.64 ng/g, median, respectively) were in accordance to others previously reported (5.50 ng/g 6PPD and 6.40 ng/g 6PPD-Q, Cao et al., 2023; 31.5 ng/g 6PPD and 6.62 ng/g, 6PPD-Q, Xu et al., 2024).

Significant associations among several compounds were observed in sewage sludge samples (Table S13). Compounds belonging to the same chemical groups, particularly benzothiazoles, guanidines and PPDs, showed strong positive correlations, suggesting common sources and similar partitioning behavior. Previous studies indicate that TRDCs in sludge and suspended solids exhibit correlation patterns driven by compound origin and chemical affinity. For instance, Xie et al. (2024) reported strong co-occurrence among guanidines, PPDs and 6PPD-Q in influent suspended solids, whereas benzotriazoles correlated weakly with PPDs, indicating additional sources. Besides, PPDs loads in sludge have been positively correlated with local Gross Domestic Product (GDP), suggesting that vehicular and anthropogenic activity might govern contamination levels (Xu et al., 2024). Partitioning towards the solid phase is especially relevant for hydrophobic compounds such as 6PPD, whose load is predominantly particulate (90–99%) (Seiwert et al., 2022; Xie et al., 2024). In this study, distribution coefficients (K_d) calculated from wastewater and sludge concentrations are detailed in Table S14. The highest values were observed for 6PPD (66.9 L/kg, median), MBTH (12.6 L/kg) and DPPD (9.07 L/kg), confirming their strong affinity for sludge.

MBTH was the dominant compound in sludge from both WWTPs, accounting for 46% of total concentration in WWTP1 and 40% in WWTP2 (Fig. S3), followed by DMBA (9–10%), 6PPD (8–10%), 2-OH-BTH (6–10%) and DBZA (5–6%). No significant differences between WWTP1 and WWTP2 were observed for most compounds, except DPG ($p < 0.05$), likely related to differences in land use, sewer systems and wastewater sources (Sun et al., 2019).

Overall, the combined evaluation of wastewater and sludge supports the hypothesis that inefficient removal processes (Table S10) facilitate the transfer of tire-derived compounds to agricultural soils via sludge application and to aquatic environments through effluent discharge (Jachimowicz et al., 2023).

3.2. Occurrence of TRDC in river surface water

A total of 21 out of the 25 target compounds were found in surface waters collected along the Tagus River and its tributaries (Fig. 4). Σ TRDC concentrations (346 ng/L, 1.68–1510 ng/L; median, min-max, Table S15) were substantially lower ($p < 0.01$) than those observed in wastewaters. The five TRDCs with the highest concentrations were Me-BTR (141 ng/L, median), BTR (134 ng/L), 2-OH-BTH (13.9 ng/L), DPG (7.77 ng/L) and HMMM (6.92 ng/L), all exhibited high Df (86%–98%).

Similar to wastewaters, benzotriazoles and benzothiazoles were the dominant chemical groups in surface waters ($p < 0.05$, Table S16), characterized by high water solubility and resistance to biodegradation, promoting their mobility throughout the water cycle (Van Leerdam et al., 2009). This behavior is consistent with the low K_d values obtained (0.01–0.24; Table S14), indicating low affinity for solid phases (Struk-Sokołowska et al., 2022). BTR, Me-BTR, DBZA and 2-OH-BTH were the main contributors (36%, 34%, 10% and 6%, respectively) across all seasons (Fig. S4), suggesting continuous inputs from domestic and industrial sources, rather than being solely dependent on rainfall-driven tire wear runoff (Herrero et al., 2013; Struk-Sokołowska et al., 2022; Wang et al., 2023). Average precipitation in the Tagus basin

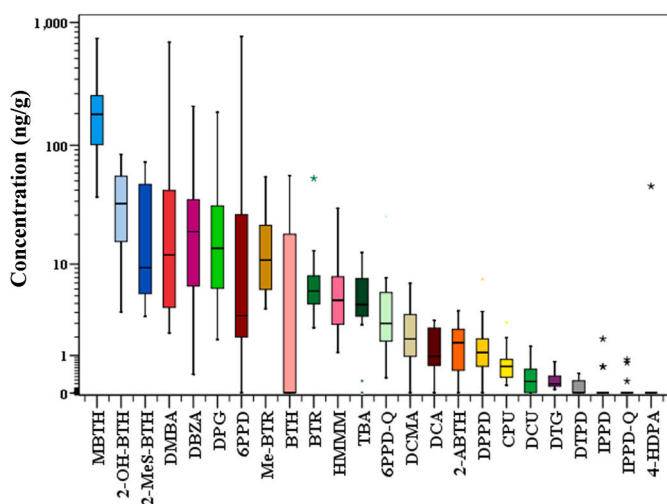


Fig. 3. Concentrations (ng/g, logarithmic scale) of all compounds analyzed in sewage sludge.

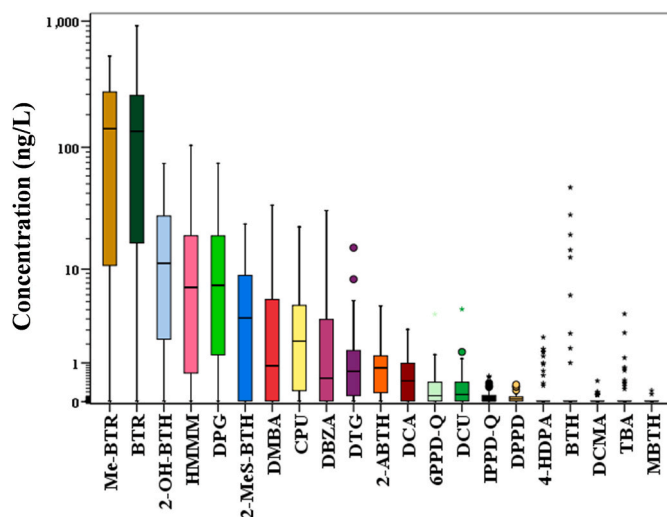


Fig. 4. Concentrations (ng/L, logarithmic scale) of all compounds analyzed across river surface water.

(Fig. S1) reached maximum values in March–April and October–December, although its influence was not denoted in TRDC concentrations (Fig. S4). DPG (7.77 ng/L, median; 0.02–74.4 ng/L, min–max) and HMMM (6.92 ng/L, 0.01–103 ng/L) were the following most abundant compounds in surface waters. Both are used as tire additives to enhance performance and durability, and ecotoxicological studies have reported adverse effects on aquatic organisms (Baensch-Baltrusch et al., 2020). Results obtained in surface waters are consistent with previous reports (Johannessen & Parnis, 2021; Cao et al., 2022; Anquetin et al., 2025). Strong correlations were observed among several TRDCs (Table S17), underscoring a common origin. Remarkably, no relationships between BTH and its derivatives were found. Benzothiazole may also stem from other sources, e.g., from the fungicide thiocyanomethylthiobenzothiazole (Seiwert et al., 2020). Surprisingly, although 6PPD was not detected in surface waters, its transformation product 6PPD-Q was frequently found (51% Df, 0.41 ng/L, median; 0.10–3.86 ng/L, min–max). Surface runoff has been identified as its main source, with reported concentrations reaching up to 890 ng/L (Johannessen et al., 2021; Rauert et al., 2022; Chen et al., 2023; Zhao et al., 2024). However, its detection frequency was lower than in wastewater (94%) due to a possible dilution effect and its dispersion along the river, denoting higher values (88%, median) in the most anthropically impacted areas (Table S5).

Spatial distribution of TRDCs varied among sampling sites. Those characterized by anthropogenic influence and high traffic intensity revealed higher concentrations (Table S18), highlighting S4, S3, S2 and S5 ($\sum$ TRDC, 4491, 3062, 2626 and 2343 ng/L, respectively). In contrast, the lowest levels ($p < 0.01$) were associated with low traffic and anthropogenic density areas (S1, S6, S11 and S13). These results suggest that both road traffic and human activity constitute relevant sources of TRDC pollution in the aquatic ecosystem. Mass flow rates of TRDCs in the Tagus watershed ranged between 0.34 and 905 kg/y (Table S19). Similarly to the tendency related to concentrations, urban locations (i.e. S3>S7>S4>S8>S10) presented higher TRDC discharge ($p < 0.01$). Interestingly, the PCA (Fig. S5) revealed different behaviour for $\sum$ Benzotriazoles, underscoring their widespread use in industrial and domestic applications. Besides, the probable influence of a near WWTP effluent discharge at S4, denoted higher levels of this chemical group (4107 ng/L; Table S18; Fig. S5a).

3.3. Dynamics of TRDCs in the water cycle

TRDCs were found across the different environmental compartments

explored, highlighting the ubiquity previously described in other studies (Table S19, Excel). These compounds tend to accumulate in solids, such as sludge, and persist in surface waters, demonstrating mobility throughout the water cycle. Remarkably, WWTPs may act as an important point source due to the combined treatment of urban runoff and wastewater (Xu et al., 2024); in fact, WWTP samples showed higher detection frequencies, which underscores their anthropogenic pollution load and their diffusion potential to other environmental systems.

TRDC composition differed among the environmental compartments assessed due to their specific physico-chemical properties (Fig. 5), however, 21 out of 25 compounds (84% of the total analytes) were simultaneously detected in the three matrices. As expected, highly soluble compounds with low organic carbon-water partition coefficients, such as Me-BTR (1769 mg/L, solubility; 1.71, Log Koc) or BTR (5957 mg/L; 1.17) (Table S1), remained preferably in the aqueous matrices. Interestingly, similar profile was observed in wastewater and surface water, denoting WWTP effluents as a substantial source of TRDC emissions into river ecosystem. In contrast, other compounds with lower water solubility (e.g. DMBA, 2-MeS-BTH, 6PPD) or higher affinity for organic matter (MBTH) showed strong sorption in sludge. Previous studies evidenced that 6PPD and 6PPD-Q are preferably present in the particulate phase (Seiwert et al., 2022).

As previously mentioned, similar TRDC pattern was observed in wastewater and surface water, predominating $\sum$ Benzotriazoles and $\sum$ Benzothiazoles (Fig. 1), and denoting possible influence due to the discharge of WWTP effluents into the Tagus basin. The annual TRDC loads were substantially higher in urban areas (such as S3, S7, S4 and S8, Table S20). Particularly, S8 (1241 ng/L, $\sum$ TRDCs, located downstream WWTP1, Fig. 1) and S10 (1299 ng/L, $\sum$ TRDCs; downstream WWTP2) showed comparable levels but lower than other sites located in highly populated cities (S3, 3062 ng/L; S4, 4491 ng/L). Although traffic density may also be one of the main emission pathways of TRDC contamination in the freshwater environment, WWTP discharges cannot be neglected.

3.4. Ecotoxicological risk in different environmental compartments

3.4.1. Risk assessment in the aquatic ecosystem

In general, low chronic risk ($RQ < 0.1$) for aquatic organisms under both median and maximum exposure scenarios was estimated for individual compounds (Table S21). A negligible risk ($RQ < 0.01$) was observed for 6PPD-Q in all cases, while DPG, 2-MeS-BTH, BTR and HMMM showed low ($0.01 < RQ < 0.1$) or moderate ($0.1 < RQ < 1$) risk. Interestingly, the cumulative approach revealed a medium risk ($0.1 < RQ < 1$) at sampling points S3, S4 and S9. Notably, S3 and S4 were

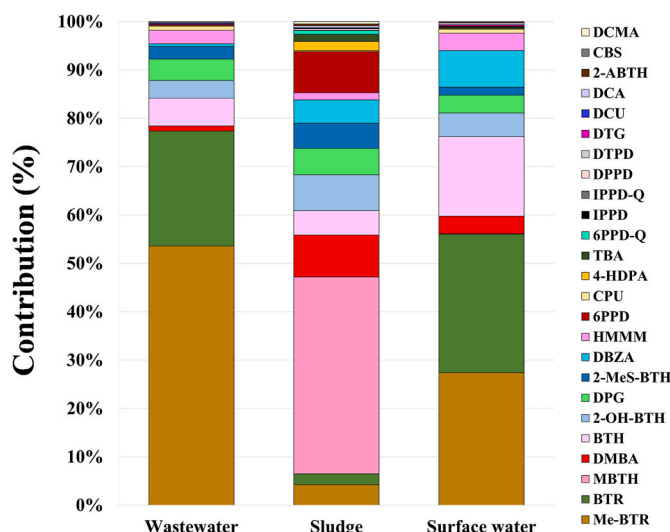


Fig. 5. Contribution (%) of the TRDCs in the water cycle.

located in areas with high anthropogenic pressure and intense traffic, highlighting their potential pollution impact. On the other hand, high acute risk ($RQ_{STU} > 1$) associated with the PPDs family (mainly due to the contribution of 6PPD-Q and to a lesser extent DPPD), and total TRDC concentrations was obtained at most of locations (Table S22). Consistent with these findings, previous studies have demonstrated that TRDCs pose significant ecotoxicological risks, manifested through both acute toxicity and chronic sublethal effects (Baensch-Baltruschat et al., 2020; Zhang et al., 2023). 6PPD-Q has been directly linked to mass mortality events of coho salmon (*Oncorhynchus kisutch*) in the Pacific Northwest, exhibiting an extremely low median lethal concentration (LC_{50}) of only 95 ng/L (Tian et al., 2022). Beyond coho salmon, other fish species such as rainbow trout (*Oncorhynchus mykiss*) and brook trout (*Salvelinus fontinalis*) have also shown high sensitivity to 6PPD-Q (Maurer et al., 2023; Jiao et al., 2023). It is also noteworthy that 6PPD and 6PPD-Q have been recently included in the 5th Watch List of the EU Water Framework Directive (European Commission, 2025), revealing their probable concerning impact in the aquatic environment. Although low risk was denoted for DPG and benzothiazoles, adverse effects such as behaviour alteration, oxidative stress, neurotoxicity and endocrine disruption have been evidenced in fish and aquatic invertebrates (Wang et al., 2016; Chen et al., 2023).

3.4.2. Risk assessment in the terrestrial ecosystem

Risk for soil organisms due to the exposure to several TRDCs was observed, considering one sludge application (1st year) and successive amendments (from 1st to 100th year) at agronomic conditions (Table S23). High risk ($RQ > 1$) was observed for 14 out of 22 compounds since the first amendment (1st year). The highest risk values were estimated for 6PPD, MBTH, 2-MeS-BTH and BTR. These findings highlight the long-term potential impact of these compounds in soils amended with contaminated sludge. Particularly, 6PPD-Q evidenced medium to high risk in sludge-amended soils (Xu et al., 2024). Sludge application represents a significant pathway for TRDCs to enter soils, from where they may migrate to crops, groundwater, and soil organisms such as earthworms (Montemurro et al., 2021). While some TRDCs degrade within roughly one year, repeated applications can lead to the accumulation of more persistent compounds, maintaining sustained risks over time (Walters et al., 2010).

3.5. Prioritization of hazardous tire-derived compounds

The TRDC widespread use, ubiquity and persistence can lead their common occurrence as contaminants in the ecosystems. The environmental risk assessments performed in section 3.4 were derived from pollutant concentrations found, but it is also important to consider the frequency of occurrence to rate the potential exposure on organisms in the scenarios studied. Therefore, a TRDC ranking was established based on a relevant TRDC mixture with higher impact on aquatic organisms (defined per sampling site), and terrestrial organisms (derived from sludge amendment in agricultural soil). In total, five TRDCs were identified as compounds of concern in the aquatic environment studied (Table S24) and seven in the terrestrial ecosystem (Table S25). HMMM emerged as the most representative compound of concern for freshwater organisms, followed by DPG, BTR, and 2-MeS-BTH. In contrast, the terrestrial priority list showed greater heterogeneity, with MBTH being the most frequent concerning compound. Overall, these results evidenced the presence of hazardous TRDC mixtures in both compartments, driven by differences in emission sources, environmental behavior, and persistence.

4. Conclusions

This study provides a comprehensive assessment of 25 TRDCs in wastewater, sewage sludge and surface waters from the Tagus River basin. TRDCs were detected in all matrices, confirming their widespread

occurrence, persistence, and mobility in urban-influenced aquatic systems. Benzothiazoles and benzotriazoles dominated the TRDC profile in the water cycle studied, while transformation products, such as 6PPD-Q, were frequently detected, highlighting the environmental relevance of tire antioxidant degradation. WWTPs exhibited limited removal efficiency, both in the wastewater and sludge lines, with hydrophobic compounds preferentially partitioning into sludge. Surface water concentrations were elevated in areas with intense traffic and urban activity, demonstrating that road runoff is a major source of these contaminants.

Ecotoxicological assessment denoted low chronic risk for aquatic organisms for individual compounds, but cumulative exposure at high-anthropogenic pressure sites reached moderate risk. Acute toxicity was primarily associated with PPD derivatives, particularly 6PPD-Q, posing significant risk to aquatic organisms. In terrestrial systems, several TRDCs presented long-term risks due to sludge application, underscoring persistence, bioaccumulation potential, and impact on soil health.

These findings evidence the urgent need for continuous monitoring, improved wastewater treatment strategies, and regulatory consideration of TRDCs, particularly 6PPD-Q, as emerging contaminants. Adopting a One Health approach is essential, recognizing the interconnected risks of TRDCs to human, animal, and environmental health. Management and mitigation strategies should be implemented under the Water Framework Directive to reduce the ecological and public health impacts of these pollutants and ensure the protection of aquatic and terrestrial ecosystems.

CRedit authorship contribution statement

Melanie Alejandra Rojas: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Irene Navarro:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Silvia Royano:** Writing – review & editing, Validation, Methodology, Investigation. **Juan Escobar-Arnanz:** Writing – review & editing, Validation, Methodology, Investigation. **Adrián de la Torre:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization. **María Ángeles Martínez:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2026.128865>.

Data availability

Data will be made available on request.

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