



Cite this: *Environ. Sci.: Processes Impacts*, 2025, 27, 3498

## Environmental aging of tire and road wear particles and tire additives: a long-term field study

Steffen Weyrauch, <sup>a</sup> Bettina Seiwert, <sup>a</sup> Milena Voll <sup>a</sup>  
and Thorsten Reemtsma \*<sup>ab</sup>

The long-term fate of tire and road wear particles (TRWP) significantly governs the distribution of tire-related chemicals. In addition to previous lab experiments a field study is performed, exposing TRWP and cryo-milled tire tread (CMTT) to sunlight for 20 months and to microorganisms in water in a sedimentation pond for 17 months. No indications of physical disintegration were obtained over all experimental times and conditions. The extractable concentration of 27 polar and moderately polar compounds was analyzed by liquid-chromatography-mass spectrometry (LC-MS), among them tire additives such as *para*-phenylenediamines, phenylguanidines, benzothiazoles and known transformation products. Total quantified extractables (TQE) decreased for about 62–92% within the first sampling period of 8–10 months. However, even after 17–20 months concentrations of 100–200  $\mu\text{g g}^{-1}$  of TQE remained in TRWP, mainly benzothiazolesulfonic acid (BTSA) and hydroxy-benzothiazole after sunlight exposure and *N*-(1,3-dimethylbutyl)-*N'*-phenyl-1,4-phenylenediamine (6-PPD) after exposure in the sedimentation pond. For the sunlight exposure the results of this long-term field study are well comparable to the results of a previous lab study. A laboratory study on (bio) degradation in water with optimized conditions appears to overestimate both leaching and (bio) degradation occurring in the sedimentation pond. Despite these differences, this field study confirms the previous conclusion that, while a substantial part of the polar and moderately polar chemicals is rapidly released, tire particles can be a long-term source of tire-related chemicals. Preventing TRWP from entering aqueous environments would substantially reduce the load of polar and moderately polar compounds transported with them.

Received 6th June 2025  
Accepted 2nd September 2025

DOI: 10.1039/d5em00444f

rsc.li/espi

### Environmental significance

Tire and road wear particles are released in large quantity into the environment but their environmental fate is not well known, yet. TRWP and cryo-milled tire tread (CMTT) were exposed for almost 2-years to sunlight and to surface water. No significant physical alteration of the particles was recorded. Extractable chemicals decreased drastically in total amount (by 60–90% in less than 8–10 months) and changed in composition (from parent compounds to transformation products). Even after 17–20 months TRWP still contained considerable concentrations of extractables. Retaining TRWP after run-off from roads for a certain period of time would reduce the burden of polar and moderately polar tire-chemicals transported into the aqueous environment; some of it will remain for >2 years.

## 1. Introduction

Tire and road wear particles (TRWP) are emitted from driving tires in very high amounts,  $6 \times 10^9$  kg per year globally.<sup>1–3</sup> The major environmental transport pathway of TRWP is expected to be washing off by precipitation events, transport by surface water and settling into sediments as their final fate.<sup>4</sup> During this transport the particles are assumed to become physically altered and to release chemicals.<sup>4</sup> These aging processes of tire

particles are often studied in laboratory experiments. This has the advantage that experiments can be performed easily, aging conditions can be well controlled and the effect of single factors (sunlight, temperature, *etc.*) can be studied separately.<sup>5–8</sup>

Quantitative data from laboratory experiments are useful for predicting the environmental fate of TRWP. However, it requires experimental verification to which extent lab results can be quantitatively extrapolated to the real environment. While lab aging studies usually involve optimized or at least stable conditions, environmental conditions are more variable and not necessarily optimal for degradation processes to take place. Another limitation of most lab studies is their relatively short duration of a few weeks,<sup>9–13</sup> which is very short compared to the anticipated long residence time of TRWP in the environment.<sup>5,6</sup>

<sup>a</sup>Helmholtz-Centre for Environmental Research – UFZ, Department of Environmental Analytical Chemistry, Permoserstrasse 15, 04318 Leipzig, Germany. E-mail: thorsten.reemtsma@ufz.de

<sup>b</sup>University of Leipzig, Institute of Analytical Chemistry, Linnéstrasse 3, 04103 Leipzig, Germany



As a test material, cryo-milled tire tread (CMTT) is used in most cases.<sup>9–12</sup> This material is relatively cheap and easy to obtain in sufficient quantities and by reproducible conditions. However, recent studies show significant differences between CMTT and TRWP in terms of their physical appearance and their chemical content and leaching potential as well.<sup>5,6</sup> TRWP can be generated and collected in driving test facilities. Abraded tire tread changes essential properties in terms of physical appearance, chemical composition and incorporation of further particulates, which makes lab generated TRWP much more representative for real world TRWP than CMTT.<sup>5,6</sup>

For the reasons given above, this field study explores the effects of long-term exposure of TRWP and CMTT to sunlight on a rooftop and to water and microorganisms in a sedimentation pond for highway runoff. These environments should reflect processes to which TRWP are exposed after generation, directly on roads (sunlight exposure) or after being washed away with road-runoff (sedimentation ponds).

This study is based on previous studies with the same materials on effects of abiotic and biotic aging in the laboratory.<sup>5,6</sup> The major questions to answer in this study were: (i) what is the effect of long-term (>1 year) exposure to natural sunlight and in an aqueous system on the physical properties and the chemical composition of CMTT and TRWP? (ii) to which extent do these effects correspond to those found in the laboratory in earlier studies.<sup>5,6</sup>

## 2. Materials and methods

### 2.1. CMTT and TRWP

As test materials two types of tire particles have been used, both provided by Cardno ChemRisk (now Stantec). The materials – CMTT and TRWP – consist of blends derived from the same three tire models, though differing in their storage histories. CMTT was prepared by cutting tire tread, followed by cryogenic milling. TRWP was generated in accordance with ISO/TS 22638:2018<sup>14</sup> using a laboratory-scale rotating drum apparatus. Detailed single-particle characterization of TRWP has been previously reported.<sup>5,6,15</sup>

Due to the production method, the TRWP sample contained approximately 45% loose stone dust, as determined through density fractionation. For all subsequent analyses, only the TRWP particle fraction was considered. Both CMTT and TRWP were characterized in terms of particle size distribution, inorganic content, and mean density (Table S1). These materials have been previously employed and comparatively assessed in an earlier study.<sup>5</sup>

### 2.2. Environmental aging experiments

**2.2.1 Sunlight exposure on the rooftop.** In sunlight-transparent quartz-containers (outer diameter: 120 mm, height: 20 mm, glass thickness: 1.25 mm) particles were exposed to natural light-radiation. The radiation-intensity was measured on the same rooftop nearby. 1.5 grams of CMTT and 3 grams of TRWP are deposited per sample to perform analysis after 8, 13 and 20 months exposure time.

CMTT and TRWP were exposed to sunlight for up to 20 months in quartz containers avoiding contact with rain or dust. Particles were mixed regularly to ensure homogeneous light exposure of all particles in the containers. For more information, see SI Section S1.

Solar irradiance was constantly measured and logged every 30 minutes on the rooftop. The yearly total irradiance at this location was  $1119 \pm 75 \text{ kWh m}^{-2}$  during the time of exposure in 2021 and 2022.

### 2.3. Floating in sedimentation pond

In customized sieve cages TRWP were exposed in a sedimentation pond next to a highway nearby Leipzig, Germany (51.27463, 12.49187). The mesh size of the used sieves was  $9.5 \mu\text{m}$  to prevent loss of TRWP. The exposure conditions in the sedimentation pond were variable with respect to sunlight, wind and temperature. Exposure started in June and August of 2021. Data on mean daily air temperature can be found in the SI Fig. S3. A highway area of roughly  $690\,000 \text{ m}^2$  is discharging into this pond. Six cages with a volume of around 100 mL each were used, three filled with 3 g of CMTT and three with 5 g of TRWP. One of each was recovered after 10, 10 and 17 months exposure time. The data of the two 10 months samples are mean values from both duplicates (06/2021–04/2022 and 08/2021–06/2022). The values of the duplicates show a mean deviation of 15% (SI Section S3). The containers were held in place  $\sim 50 \text{ cm}$  under the surface by a floater and in the middle area of the pond by an anchor. The concentration of dissolved organic carbon (DOC) of the pond water was analyzed once (14 February 2022) and was in the range of surface water ( $5.2 \text{ mg L}^{-1}$ ). Concentrations of tire chemicals in the water of the sedimentation pond were analyzed once, in a sample taken on 17 January 2023 (Table S5). All values are very low if not <LOQ. For more detailed information, see SI Section S1.

### 2.4. Analysis of physical parameters

Particle size distributions by number were measured using laser obscuration, ranging from 10 to  $3600 \mu\text{m}$ , with the Eyetechnic instrument (lens B100; Ambivalu bv, The Netherlands). The aspect ratio and circularity of the particles were also assessed using the Eyetechnic, operating in dynamic image analysis mode, which allows for the characterization of particles within the size range of 20 to  $3600 \mu\text{m}$ . Electron microscopy images were obtained at all sampling intervals using a Zeiss Merlin VP Compact field emission scanning electron microscope (SEM; Carl Zeiss Microscopy, Germany).

### 2.5. Analysis of organic compounds

The selection of the 27 organic analytes for quantitative analysis was based on their mass concentrations in tire tread, widespread use in tire manufacturing, functional roles within the tread formulation, leaching behavior, and detectability by liquid chromatography-mass spectrometry (LC-MS) (Table S2).

**2.5.1 Sample preparation for extraction of organic additives.** Approximately 20 mg of freeze-dried TRWP or CMTT were extracted with 5 mL of methanol (MeOH; Biosolve,



Valkenswaard, Netherlands) using an ultrasonic bath (Sonorex Digitec DT 255 H, Bandelin Instruments, Berlin, Germany) for 60 minutes. A 1 mL aliquot of the extract was transferred to a 1.5 mL Eppendorf tube and centrifuged for 10 minutes at 1000 rpm (Rotanta 460, RCF = 217 g; Andreas Hettich, Tuttingen, Germany). Subsequently, a volume of 500  $\mu$ L of the clear supernatant was transferred to a 2 mL screw-cap vial (ND8, Labsolute, Th. Geyer, Renningen, Germany), diluted with 500  $\mu$ L of ultrapure water (Milli-Q), and analyzed immediately. The sum of all quantified extractable analytes is referred to as the total quantified extractables (TQE).

**2.5.2 Sample preparation for analysis of leachables.** Triplicate samples of approximately 12 mg each were weighed into amber glass vials (15 mL, screw top, solid cap with PTFE liner; Supelco, Bellefonte, USA) and supplemented with 12 mL of ultrapure water. The vials were placed on a laboratory shaker (IKA HS 501 digital; IKA, Germany) and shaken for 72 hours. Following equilibration, the supernatant was withdrawn using a 2 mL syringe (Injekt Solo, B. Braun, Melsungen, Germany) and filtered through a 0.45  $\mu$ m regenerated cellulose syringe filter (Minisart RC 4; Sartorius, Stonehouse, UK) into 2 mL screw-cap vials (ND8, Labsolute, Th. Geyer, Renningen, Germany). Samples were analyzed within 4 hours of filtration. This procedure has been evaluated and reported elsewhere.<sup>5</sup>

**2.5.3 UPLC-HRMS analysis.** Extracts were analyzed using an ACQUITY UPLC system coupled to a XEVO G2-S quadrupole time-of-flight mass spectrometer (qTOF-MS; Waters GmbH, Eschborn, Germany). Additional analytical details are provided in the SI (Section S1).

### 3. Results and discussion

This study investigates the environmental aging of tire particles under real-world conditions using two test specimens: Tire and Road Wear Particles (TRWP), which are more representative of actual environmental particles but generated in a test facility, and Cryogenically Milled Tire Tread (CMTT), which is less realistic but widely used in research. The study involves two scenarios: (i) exposure to sunlight for up to 20 months in quartz containers (on a roof top) under dry conditions, and (ii) exposure in water in a sedimentation pond for highway runoff for up to 17 months. The effects on particle size, shape, extractable and leachable chemicals were analyzed at defined intervals.

#### 3.1. Physical properties

No sign of change in particle size distribution or morphology of CMTT and TRWP could be observed in the long-term environmental exposure in this study (see SI for detailed information). For CMTT, a slight increase in particle size was observed, suggesting minor agglomeration, but no surface alterations were detected through SEM imaging. TRWP showed no significant changes in particle size distribution or shape, though some larger aggregates were visible. These findings suggest that long-term sunlight exposure and exposure in the sedimentation pond have minimal impact on the size distribution and

morphology of tire particles, aligning with prior laboratory studies.<sup>5,6</sup>

#### 3.2. Sunlight exposure

A total of 27 tire-related chemicals and transformation products were quantified in CMTT and TRWP (Table S2) before, during and after sunlight exposure. The total quantified extractables (TQE) decreased by 92% in CMTT and 62% in TRWP until the first sampling after 8 months (Fig. 1a and b). Afterwards no significant further decrease was observed until month 20 in both materials. Rooftop exposure allows for the photolytic transformation of chemicals but other loss processes (evaporation, leaching) were reduced to a minimum. When photolytic processes were completed, no further transformation took place. Unlike in experiments under wet conditions, polar transformation products were not lost from the particles by leaching.

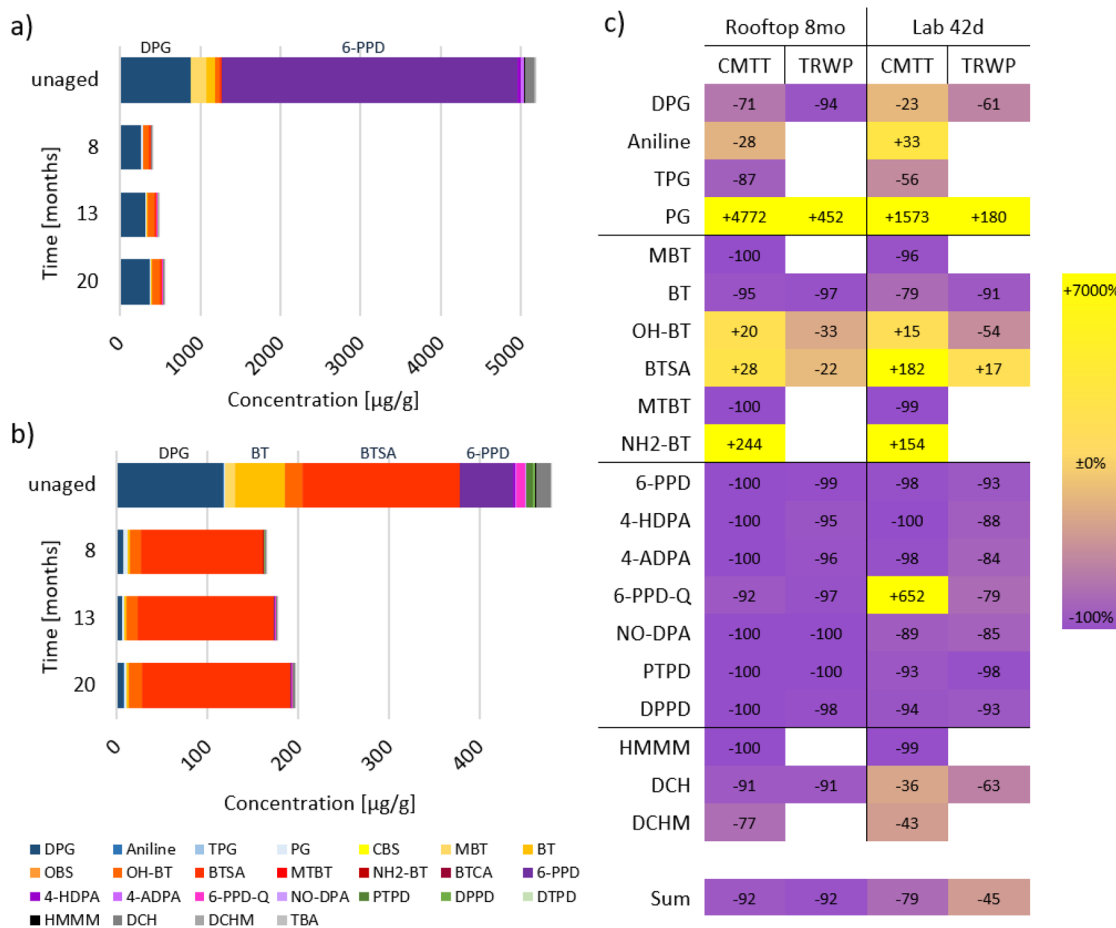
The starting composition of the TQE in TRWP was significantly lower than in CMTT, and it was more diverse with a higher share of transformation products. CMTT is dominated by parent chemicals such as DPG and 6-PPD (Fig. 1a), while BT and BTSA are much more prominent in TRWP (Fig. 1b). The dominance of reactive parent compounds in CMTT also explains why the decrease in TQE was more pronounced for this material than for TRWP.

The difference in the chemical composition of the two materials appears to outcompete the differences in particle size: from that TRWP, with the smaller particle size (mean diameter 73  $\mu$ m) and the larger specific surface area would have been expected to show stronger effects than CMTT (mean diameter 183  $\mu$ m; Table S1).

Also after sunlight exposure, the composition of the two materials differs markedly, with DPG still dominating the TQE of CMTT, and BTSA dominating in TRWP. Despite these differences in the initial and in the final composition of CMTT and TRWP, some common trends were visible for chemicals extracted from both materials upon sunlight exposure. DPG is reduced by 70–90%, with a higher relative removal in TRWP, the material with the lower start concentration (Fig. 1b and c). The content of PG increased strongly as it is a photodegradation product of DPG.<sup>16</sup>

Apart from the increasing PG (+4800%), other transformation products increase as well: OH-BT (+20%), BTSA (+28%) and NH<sub>2</sub>-BT (+244%) in CMTT, whereas in TRWP the increase is visible only after prolonged exposure times beyond 8 months onwards (BT, OHBT; Fig. 1b). The more pronounced and faster increase of some TPs in CMTT as compared to TRWP is a consequence of the higher concentration of the respective parent chemicals in this material; this speeds up TP formation. The photodegradation of mercaptobenzothiazole (MBT), a main additive in tire, can yield different products depending on the availability of oxygen and radical scavengers.<sup>17</sup> The principal photoproduct in absence of oxygen is BT<sup>18</sup> while in oxygenated environment BTSA is primarily formed.<sup>17,18</sup> BT itself may be further transformed in presence of oxygen to OH-BT. Formation of OH-BT and BTSA by photooxidation has already been





**Fig. 1** Concentration of the 27 analytes extracted from (a) CMTT and (b) TRWP after 0, 8, 13 and 20 months of sunlight exposure on a rooftop. (c) Relative changes in the concentration of selected analytes during environmental exposure and in a previous laboratory study.<sup>5</sup> The horizontal lines tie the chemicals to groups (DPG-related compounds, benzothiazoles, PPDs and others (from top to bottom)). Empty fields for TRWP indicate that start and end values were too close to LOQ ( $<20 \times$  LOQ) to reliably conclude a tendency. Full names of the chemicals and their LOQs are given in Table S2.

observed in other studies using dissolved BT or tire particles.<sup>5,19,20</sup> In TRWP, BTSA and OH-BT were quite prominent already in the start material (40% of TQE). In the following environmental sunlight exposure, both are fairly stable (Fig. 1c) which leads to the dominance of BTSA with over 90% of TQE of TRWP at all later sampling times.

6-PPD, the major extractable of CMTT (Fig. 1a), has almost completely disappeared from the extractables of both particles ( $-100\%$  in CMTT and  $-99\%$  in TRWP) during the first 8 months, just as its transformation products (4-HDPA, 4-ADPA, 6-PPDQ, NO-DPA) (Fig. 1c). The same is true for other PPDs such as the BENPAT isomers (DTPD, DPPD, PTPD). Previous studies on the oxidative transformation (including OH radicals, indirect photodegradation and ozone) of 6-PPD and 6-PPDQ have shown that a large number of TPs are being formed.<sup>21</sup> Those TPs of 6-PPD included in this quantitative analysis are all TPs that are formed in early stages of the transformation pathways.<sup>22</sup> This may explain why these TPs are not increasing in concentration while 6-PPD is decreasing so markedly (Fig. 1c).

Trends visible for sunlight exposure on the rooftop compare well to those obtained in a previous study for lab photodegradation (after 42 days).<sup>5</sup> While the particles at the rooftop received around  $670 \text{ kWh m}^{-2}$  (Table S3), the particles in the lab experiment received  $500 \text{ kWh m}^{-2}$ ,<sup>5</sup> 75% of the rooftop exposure. Correspondingly, the loss of TQE in the lab experiment reached 86% for CMTT and 73% for TRWP of the loss observed on the rooftop. This suggests a high level of agreement between these two studies.

Also concerning individual chemicals, there is generally good agreement between rooftop and lab exposure to sunlight (Fig. 1c). However, larger differences do occur for some chemicals: 6-PPDQ increases strongly in the lab experiment with CMTT while it decreased during exposure on the rooftop; the relative loss of its precursor 6-PPD was comparable in both cases. Obviously, formation of 6-PPDQ was faster than its further photolytic transformation in the lab experiment than at the rooftop. Other factors than light intensity affect the kinetics of transformation, such as temperature and humidity; these may contribute the differences between these field and lab



results. However, an earlier lab study has shown that exposure to sunlight has a much more pronounced effect on chemicals in tire particles compared to the sole exposure to elevated temperature.<sup>5</sup>

Also, for BTSA a much stronger increase was noted during CMTT exposure in the lab (+180%) compared to the rooftop (+28%) (Fig. 1c). As mentioned above BT and BTSA are both photoproducts of MBT, with BTSA being favoured in oxygenated environment.<sup>17</sup> The more pronounced increase of BTSA in the lab compared to the field experiment may be due to this effect.

For DPG the decrease was weaker in the lab than at the rooftop (Fig. 1c); the reason for this remains unclear. But, generally speaking sunlight exposure of tire particles in the laboratory simulated the processes occurring outdoor (rooftop) quite well.

Sunlight exposure of tire particles occur on roads and other impervious surfaces in their proximity. Rainfall may wash the particles away and allows for leaching of tire chemicals and their transformation products.<sup>4</sup>

This leaching was studied with CMTT and TRWP subjected to sunlight photolysis for different periods of time. The results outline that polar compounds are leached effectively (Fig. S14). This applies to polar tire-chemicals that were still present in the tire particles, such as DPG (from CMTT) as well as to polar transformation products formed by sunlight photolysis, such as PG (from CMTT), OH-BT and BTSA (from TRWP) (Fig. S14, Tables S12 and S13). These data for the effect of leaching after sunlight exposure of tire particles agree well with previous laboratory studies.<sup>5</sup>

### 3.3. (Bio-) degradation in water in a sedimentation pond

As a second environmental aging process (bio-) degradation in the water column of a sedimentation pond was studied. Over the whole experimental period of 17 months, the concentration of the TQE decreased in CMTT by 68% and in TRWP by 77% (Fig. 2a and b). While a progressive decrease of the chemicals occurs in CMTT over the 17 months, the decrease from TRWP almost came to a halt within 10 months.

The major processes that are expected to affect the chemicals in CMTT and TRWP during this exposure inside a floating container in the sedimentation pond are leaching and (bio-) degradation. Both processes are expected to proceed throughout the whole experimental time. However, when the reservoir of a chemical in the particles progressively decreases, also leaching slows down. This may be the reason why no further decrease was measurable for most of the chemicals in TRWP between 10 and 17 months of exposure in the pond. Also the smaller particle size of the TRWP (Table S1) would favor a faster leaching compared to CMTT. No sub-samples were taken at each sampling time but individual batches were deployed for the 10 months and the 17 months sampling. This leads to additional experimental uncertainty that can mask small changes in concentration between month 10 and 17. Other processes like photodegradation did not play a relevant role as the cages in which the particles were exposed had grids only at the vertical sides.

For CMTT, with the almost 10-fold higher initial TQE concentration, these aspects do not play a major role and TQE decrease throughout the whole experimental period of 17 months (Fig. 2a). Interestingly, TQEs relative composition remained rather unchanged during that time (Fig. 2a). The parent compounds DPG (20–30% of TQE) and 6-PPD (65–75% of TQE) dominate the composition of TQE at all experimental times and transformation products do not increase notably (Fig. 2a). For TRWP the composition of TQE changes more strongly; namely polar TPs such as BTSA and BT and DCH were higher in relative concentration from begin on and are markedly decreasing during exposure in the water (Fig. 2b and c).

This general trend is explainable by the fact that transformation of tire chemicals preferentially occurs at the particles surface (or in solution) so that a loss of parent compounds is not reflected in an increase of the respective TPs inside the particles.

In both materials, 6-PPD was the dominant extractable remaining after 17 months of exposure, with concentrations of around 1000  $\mu\text{g g}^{-1}$  (CMTT) and around 50  $\mu\text{g g}^{-1}$  (TRWP). This is in strong contrast to the sunlight exposure, under which 6-PPD was transformed completely from both materials (Fig. 1c). The sedimentation pond is a far less oxidative environment, slowing down the oxidative transformation of 6-PPD. Owing to the hydrophobicity of 6-PPD, leaching is a slow process, too.

When comparing these results with a previous lab experiment on (bio-) degradation in water,<sup>6</sup> the decline of TQE from CMTT and TRWP was weaker after the sampling points of 10 months of exposure in the sedimentation pond (–50%, –77%) than during 4 months of biodegradation in aqueous medium in the lab (–91%, –80%) (Fig. 2c).<sup>6</sup> This suggests that the extent of leaching (and transformation) for the particles exposed in the sedimentation pond was lower than in the lab experiment. One possible reason for this is less particle movement of the water in the cages in which they were exposed in the sedimentation pond compared to the constantly stirred lab experiment.<sup>6</sup> As a consequence, a more pronounced boundary layer will develop around the particles in the cage, slowing down the kinetics of the leaching process. Correspondingly, the loss of chemicals was clearly lower in the sedimentation basin compared to the lab experiment. Most prominent examples are 6-PPD and DPG, which contribute much to the TQE, namely of CMTT (Fig. 2a and b).

However, benzothiazoles (MBT, BT, OH-BT, BTSA, MTBT,  $\text{NH}_2$ -BT) and the amines HMMM and DCH show a quite similar behavior in the field and the lab experiment (Fig. 2c). For TPG in CMTT larger differences are seen with a 60% removal in the pond compared to an almost constant concentration in the lab experiment (Fig. 2c); its concentration was low, however, in all cases.

An indication that biodegradation took place is the increase in concentration of 2-(methylthio)benzothiazole (MTBT) in CMTT; methylation of MBT to MTBT has previously been shown to be a microbial process.<sup>23</sup> The stronger increase of MTBT in the lab (+7000%; Fig. 2c) may indicate that microbial activity was higher under optimized conditions in the lab experiment than in the field (+400%). For TRWP such an increase was not





Fig. 2 Concentration of the 27 analytes extracted from (a) CMTT and (b) TRWP after 0, 10 and 20 months of exposure in a sedimentation pond. (c) Relative changes in the concentration of selected analytes during environmental exposure and in a previous laboratory study.<sup>6</sup> The horizontal lines tie the chemicals to groups (DPG-related compounds, benzothiazoles, PPDs and others (from top to bottom)). Empty fields for TRWP indicate that start and end values have been too close to LOQ ( $<20 \times \text{LOQ}$ ) to reliably conclude a tendency. Full names of the chemicals and their LOQs are given in Table S2.

visible, likely because of the lower start concentration of the parent compound MBT (Tables S12 and S13).

In general, the trends of the long-term field and lab study on (bio-) degradation in water agree well for the extractable chemicals. However, many of the processes leading to decreasing concentrations in CMTT and TRWP were slower in the field experiment. This suggests that laboratory biodegradation tests with their optimized conditions can overestimate environmental degradation processes affecting TRWP under real world. No data on extractables of TRWP and CMTT after environmental aging could be found in literature, neither for long nor for short exposure periods. Therefore, the results obtained in this study cannot be compared with other field studies.

## 4. Conclusions

This study investigated the time-resolved effects of long-term exposure (17–20 months) of both CMTT and TRWP to sunlight and in a sedimentation pond. Most of the loss of the 27

polar and moderately polar compounds included in this study from TRWP upon exposure to sunlight (rooftop) and to water and microorganisms (sedimentation pond) occurred within the first sampling period of 8–10 months. Preventing TRWP from reaching rivers and creeks for such a period would substantially reduce the amount of tire-related chemicals reaching aqueous environments with TRWP. However, even after 17–20 months TRWP still contain measurable concentrations of TQE ( $100\text{--}200 \mu\text{g g}^{-1}$ ). This outlines the preservative effect that chemicals experience in the rubber matrix of tires; this effect should allow these chemicals to be transported over long distances with TRWP in aqueous environments. Learning more about TRWP transport in surface water will, thus, help to better assess the transport of tire-related chemicals.

Extrapolation from laboratory to field appears straightforward for sunlight exposure of CMTT and TRWP, also in quantitative terms. With respect to biodegradation in water the situation is more complex as leaching as well as (bio-) degradation conditions may differ more strongly. Optimized lab conditions may indeed overestimate the loss of tire-related



chemicals from TRWP in the environment. It is reasonable to assume that these processes are slowed down even further if TRWP are buried in sediments.

## Author contributions

Weyrauch: investigation, data processing, writing – original draft, writing – review & editing, visualization. Seiwert: analyses, data processing and exploitation, supervision; manuscript writing. Voll: formal analysis, investigation, visualization. Reemtsma: conceptualization, methodology, validation, data exploitation, resources, writing – original draft, writing – review & editing, supervision, project administration, funding acquisition.

## Conflicts of interest

There are no conflicts of interest to declare.

## Data availability

The data supporting this article have been included as part of the SI. The SI provides additional information on the CMTT and TRWP test materials and the analytes of this study, on experimental and measurement protocols, on the effects on phys-chem properties and extractables and the concentration data of analytes in the extracts and leachates of TRWP and CMTT. See DOI: <https://doi.org/10.1039/d5em00444f>.

## Acknowledgements

We are grateful for the support of Petra Keil, Daniel Kolb, Madlen Zieseniß, Niels Wollschläger, Matthias Schmidt and our workshop team (all UFZ) in field and lab work. We thank the ProVIS Centre for Chemical Microscopy which is supported by European Regional Development Funds (EFRE) and the Helmholtz Association for scanning electron microscopy. Furthermore, we would like to thank the staff of the Autobahnmeisterei Leipzig (Die Autobahn GmbH) for supporting the field experiment. Funding by the Tire Industry Project (TIP) is gratefully acknowledged. The TIP is an international consortium of 10 tire manufacturers collaborating to identify and address the human health and environmental impact of tires, under the oversight of the World Business Council for Sustainable Development (WBCSD, Geneva, Switzerland). The study design, execution, interpretation and manuscript preparation were conducted solely by the authors.

## References

- B. Baensch-Baltruschat, B. Kocher, F. Stock and G. Reifferscheid, Tyre and Road Wear Particles (TRWP) – A Review of Generation, Properties, Emissions, Human Health Risk, Ecotoxicity, and Fate in the Environment, *Sci. Total Environ.*, 2020, **733**, 137823, DOI: [10.1016/j.scitotenv.2020.137823](https://doi.org/10.1016/j.scitotenv.2020.137823).
- P. J. Kole, A. J. Löhr, F. Van Belleghem and A. Ragas, Wear and Tear of Tyres: A Stealthy Source of Microplastics in the Environment, *Int. J. Environ. Res. Public Health*, 2017, **14**(10), 1265, DOI: [10.3390/ijerph14101265](https://doi.org/10.3390/ijerph14101265).
- Z. Luo, X. Zhou, Y. Su, H. Wang, R. Yu, S. Zhou, E. G. Xu and B. Xing, Environmental Occurrence, Fate, Impact, and Potential Solution of Tire Microplastics: Similarities and Differences with Tire Wear Particles, *Sci. Total Environ.*, 2021, **795**, 148902, DOI: [10.1016/j.scitotenv.2021.148902](https://doi.org/10.1016/j.scitotenv.2021.148902).
- S. Wagner, P. Klöckner and T. Reemtsma, Aging of Tire and Road Wear Particles in Terrestrial and Freshwater Environments – A Review on Processes, Testing, Analysis and Impact, *Chemosphere*, 2022, **288**, 132467, DOI: [10.1016/j.chemosphere.2021.132467](https://doi.org/10.1016/j.chemosphere.2021.132467).
- S. Weyrauch, B. Seiwert, M. Voll, S. Wagner and T. Reemtsma, Accelerated Aging of Tire and Road Wear Particles by Elevated Temperature, Artificial Sunlight and Mechanical Stress – A Laboratory Study on Particle Properties, Extractables and Leachables, *Sci. Total Environ.*, 2023, **904**, 166679, DOI: [10.1016/j.scitotenv.2023.166679](https://doi.org/10.1016/j.scitotenv.2023.166679).
- S. Weyrauch, B. Seiwert, M. Voll and T. Reemtsma, Long Term Biodegradation Study on Tire and Road Wear Particles and Chemicals Thereof, *Sci. Total Environ.*, 2025, **975**, 179240, DOI: [10.1016/j.scitotenv.2025.179240](https://doi.org/10.1016/j.scitotenv.2025.179240).
- L. Fohet, J.-M. Andanson, T. Charbouillot, L. Malosse, M. Lereboure, F. Delor-Jestin and V. Verney, Time-Concentration Profiles of Tire Particle Additives and Transformation Products under Natural and Artificial Aging, *Sci. Total Environ.*, 2023, **859**, 160150, DOI: [10.1016/j.scitotenv.2022.160150](https://doi.org/10.1016/j.scitotenv.2022.160150).
- J. Thomas, S. K. Moosavian, T. Cutright, C. Pugh and M. D. Soucek, Investigation of Abiotic Degradation of Tire Cryogrinds, *Polym. Degrad. Stab.*, 2022, **195**, 109814, DOI: [10.1016/j.polymdegradstab.2021.109814](https://doi.org/10.1016/j.polymdegradstab.2021.109814).
- B. Klun, U. Rozman and G. Kalčíková, Environmental Aging and Biodegradation of Tire Wear Microplastics in the Aquatic Environment, *J. Environ. Chem. Eng.*, 2023, **11**(5), 110604, DOI: [10.1016/j.jece.2023.110604](https://doi.org/10.1016/j.jece.2023.110604).
- K. Kobetičová, J. Fořt and R. Černý, Toxic and Biodegradation Potential of Waste Tires for Microorganisms Based on Two Experimental Designs, *Appl. Sci.*, 2023, **13**(8), 4871, DOI: [10.3390/app13084871](https://doi.org/10.3390/app13084871).
- A.-L. Altenhoff, J. de Witt, R. Andler and A. Steinbüchel, Impact of Additives of Commercial Rubber Compounds on the Microbial and Enzymatic Degradation of Poly(Cis-1,4-Isoprene), *Biodegradation*, 2019, **30**(1), 13–26, DOI: [10.1007/s10532-018-9858-5](https://doi.org/10.1007/s10532-018-9858-5).
- M. Christiansson, B. Stenberg and O. Holt, Toxic Additives – A Problem for Microbial Waste Rubber Desulphurisation, *Resour. Environ. Biotechnol.*, 2000, **3**, 11–21, [https://hero.epa.gov/hero/index.cfm/reference/details/reference\\_id/5740838](https://hero.epa.gov/hero/index.cfm/reference/details/reference_id/5740838), (accessed 2024-03-13).
- L. Calarnou, M. Traïkia, M. Lereboure, L. Malosse, S. Dronet, A.-M. Delort, P. Besse-Hoggan and B. Eyheraguibel, Assessing Biodegradation of Roadway Particles via Complementary Mass Spectrometry and NMR



- Analyses, *Sci. Total Environ.*, 2023, **900**, 165698, DOI: [10.1016/j.scitotenv.2023.165698](https://doi.org/10.1016/j.scitotenv.2023.165698).
- 14 International Organization for Standardization, *ISO/TS 22638:2018 - Rubber — Generation and Collection of Tyre and Road Wear Particles (TRWP) — Road Simulator Laboratory Method*, 2018.
- 15 M. Kovichich, M. Liang, J. A. Parker, S. C. Oh, J. P. Lee, L. Xi, M. L. Kreider and K. M. Unice, Chemical Mapping of Tire and Road Wear Particles for Single Particle Analysis, *Sci. Total Environ.*, 2021, 757, 144085, DOI: [10.1016/j.scitotenv.2020.144085](https://doi.org/10.1016/j.scitotenv.2020.144085).
- 16 J. Chen, T. Tang, Y. Li, R. Wang, X. Chen, D. Song, X. Du, X. Tao, J. Zhou, Z. Dang and G. Lu, Non-Targeted Screening and Photolysis Transformation of Tire-Related Compounds in Roadway Runoff, *Sci. Total Environ.*, 2024, **924**, 171622, DOI: [10.1016/j.scitotenv.2024.171622](https://doi.org/10.1016/j.scitotenv.2024.171622).
- 17 Z. Zajíčková and C. Párkányi, Photodegradation of 2-Mercaptobenzothiazole Disulfide and Related Benzothiazoles, *J. Heterocycl. Chem.*, 2008, **45**(2), 303–306, DOI: [10.1002/jhet.5570450201](https://doi.org/10.1002/jhet.5570450201).
- 18 M. Serdechnova, V. L. Ivanov, M. R. M. Domingues, D. V. Evtugin, M. G. S. Ferreira and M. L. Zheludkevich, M. Photodegradation of 2-Mercaptobenzothiazole and 1,2,3-Benzotriazole Corrosion Inhibitors in Aqueous Solutions and Organic Solvents, *Phys. Chem. Chem. Phys.*, 2014, **16**(45), 25152–25160, DOI: [10.1039/C4CP03867C](https://doi.org/10.1039/C4CP03867C).
- 19 A. Kloepfer, M. Jekel and T. Reemtsma, Occurrence, Sources, and Fate of Benzothiazoles in Municipal Wastewater Treatment Plants, *Environ. Sci. Technol.*, 2005, **39**(10), 3792–3798, DOI: [10.1021/es048141e](https://doi.org/10.1021/es048141e).
- 20 H. E. Fuchte, N. Beck, E. Bieg, V. J. Bayer, C. Achten, M. Krauss, A. Schäffer and K. E. C. Smith, A Look down the Drain: Identification of Dissolved and Particle Bound Organic Pollutants in Urban Runoff Waters and Sediments, *Environ. Pollut.*, 2022, **302**, 119047, DOI: [10.1016/j.envpol.2022.119047](https://doi.org/10.1016/j.envpol.2022.119047).
- 21 X. Yan, J. Xiao, C. Kiki, Y. Zhang, H. P. Manzi, G. Zhao, S. Wang and Q. Sun, Unraveling the Fate of 6PPD-Q in Aquatic Environment: Insights into Formation, Dissipation, and Transformation under Natural Conditions, *Environ. Int.*, 2024, **191**, 109004, DOI: [10.1016/j.envint.2024.109004](https://doi.org/10.1016/j.envint.2024.109004).
- 22 B. Seiwert, M. Nihemaiti, M. Troussier, S. Weyrauch and T. Reemtsma, Abiotic Oxidative Transformation of 6-PPD and 6-PPD Quinone from Tires and Occurrence of Their Products in Snow from Urban Roads and in Municipal Wastewater, *Water Res.*, 2022, **212**, 118122, DOI: [10.1016/j.watres.2022.118122](https://doi.org/10.1016/j.watres.2022.118122).
- 23 A. Foscari, B. Seiwert, D. Zahn, M. Schmidt and T. Reemtsma, Leaching of Tire Particles and Simultaneous Biodegradation of Leachables, *Water Res.*, 2024, **253**, 121322, DOI: [10.1016/j.watres.2024.121322](https://doi.org/10.1016/j.watres.2024.121322).

