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Quantitative assessment of additive leachates in abiotic weathered tire cryogrinds and its application to tire wear particles in roadside soil samples

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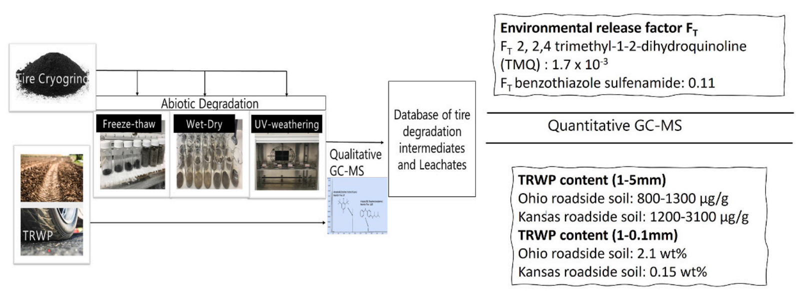
HIGHLIGHTS

- Headspace-GC-MS quantification of abiotic weathered tire cryogrinds and TRWP.
- Analysis revealed a 0.15–2.1 wt% TRWP content in Kansas and Ohio samples.
- Environmental impact assessment of additive leachates.
- Total environmental availability of 1.7 $\times$ 10^{-3} TMQ and 0.11benzothiazole.

GRAPHICAL ABSTRACT



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ABSTRACT

Tire and road wear particles (TRWP) are becoming an important research question with potential risks on ecological system. A comprehensive understanding of their detection and quantification in soils are challenged by the inherent technological inconsistencies, lack of well-set standardized methods, and generalized protocols. Reference tire cryogrinds were subjected to abiotic weathering. Next, the total environmental availability from parent elastomers and the release of additives from tire tread compounds were evaluated using mass concentration factors obtained from abiotic weathered tire cryogrinds. Headspace Gas chromatography-mass spectroscopy (HS-GC-MS) was employed as a nontargeted, suspect screening analysis technique to identify the tire related intermediates. Benzothiazole, 1,2-dihydro-2,2,4-trimethylquinoline (TMQ), aniline, phenol and benzoic acid were detected as tire tetrahydrofuran leachates. Total environmental availability of TMQ and benzothiazole were in the range of 1.7 $\times$ 10^{-3} and 0.11, respectively. Benzene and benzoic acid derivatives were identified as marker compounds for environmental samples. A TRWP content evaluation was made possible by quantifying marker concentrations and reference tire cryogrind formulation. TRWP content in the size range of 1–5 mm was between 800 and 1300 µg/g and 1200–3100 µg/g TRWP in Ohio and Kansas soil. For TRWP less than 1 mm, 0.15–2.1 wt% content was observed in Kansas and Ohio samples and were seemingly dependent on the locations and the traffic. This simple, widely applicable quantification method for TRWP analysis provides a database of tire degradation and TRWP intermediates. The TRWP content research is critical for further TRWP research development in terrestrial environment.

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1. Introduction

Tire and road wear particles (TRWP) arise from the tire wear fusing with the mineral encrustations of the road payments and are usually deposited in the soil beside the roadways (Jekel, 2019; Kreider et al., 2010). A recent study estimated that global tire debris (TRWP and larger tread pieces) was 0.2–5.5 kg/person (Baensch-Baltruschat et al., 2020). With this level, it is not surprising that TRWP are considered environmentally available and significant aqueous and atmospheric contaminants (Klöckner et al., 2020; Kreider et al., 2020; Panko et al., 2013b; Unice et al., 2013, 2019). For example (Maceira et al., 2018), detected 0.003% benzothiazole derivatives in atmospheric samples that can negatively affect the liver and kidneys and cause respiratory irritation. Further, TRWP was reported to constitute 1% of the particulate matter in the urban air (Avagyan et al., 2014; Panko et al., 2013a). Studies have detected TRWP in estuary and water bodies and cause toxicological problems on aquatic life (Marwood et al., 2011; Panko et al., 2013b). However, a recent model indicated that 50% of TWRP would be retained in the road side soils (Campanale et al., 2022). TRWP research on terrestrial soil systems has been scarce but has recently emerged as a key area (Dierkes et al., 2019; Huang et al., 2020; Hurley et al., 2018; Klöckner et al., 2021a; Piehl et al., 2018; Rogge et al., 2012; Unice et al., 2019). TRWP has been detected as a parent compound, as transformation products or as leachates of tire constituents of TRWP in soils (Marwood et al., 2011; Unice et al., 2015). Thus, there is a need to quantify TRWP present in the environment to understand its adverse effects.

Tire tread contains elastomers like natural rubber (NR) and styrene-butadiene-rubber (SBR) as the major component in combination with additives to act as curing accelerator, anti-oxidants, fillers, etc. (Rauert et al., 2021). Pyrolysis-based analytical techniques are commonly used for the quantification of TRWP in soil systems (Goβmann et al., 2021; Haydary et al., 2012; ISO/TS 21396, 2017; Nuelle et al., 2014) in addition to LC-MS (Klöckner et al., 2021a; Salas et al., 2016; Unice et al., 2015) and thermal extraction desorption gas chromatography (Klöckner et al., 2020). Using such techniques, TRWP concentrations ranging from 800 to 4500 μg/g sediment dry weight to 10,000 μg TRWP/g sediment dry weight have been reported (Marwood et al., 2011; Panko et al., 2013a; Unice et al., 2013). Non-targeted GC-MS testing has also been reported for TRWP analysis (Järlskog et al., 2021; Thomas and Irvin-barnwell, n.d.). Pyrolysis-GC-MS uses very small amount of sample and is challenging due to heterogeneous mature of road dust and soil samples. TRWP quantification markers reported include: benzothiazole (Asheim et al., 2019; Avagyan et al., 2013; Gągol et al., 2015; Pan et al., 2012; Seiwert et al., 2020; Wagner et al., 2018), para-phenylenediamines (Klöckner et al., 2021a, 2021b; Unice et al., 2015), diphenylguanidine (Challis et al., 2021; Johannessen et al., 2021; Unice et al., 2015) oleamides (Chae et al., 2021), and hexamethoxymethylmelamine (Johannessen et al., 2021). In the present work, the main objective was the TRWP analysis and quantification using non-pyrolysis method. Here, quantification was carried out by a less expensive, easily accessible, GC-MS multi-faceted approach.

2. Methods and materials

The details of the reference tire cryogrind, TRWP and the corresponding identification and quantification data sources analysis of the tire related intermediates and leachates are outlined in Supplemental Text S1. The extraction efficiency of THF for tire based additives was verified by several researchers (Ao et al., 2021; Avagyan et al., 2013; Dierkes et al., 2019).

3. Results and discussion

3.1. Qualitative HS-GC-MS results of TRWP analysis of weathered tire cryogrinds and roadside soil samples

Abiotic weathered reference tire cryogrinds exhibited several THF leachates. The most vulnerable cryogrinds were the PC-Si and T-NR. Table 1 shows the shortlisted THF leachates identified after abiotic weathering, using qualitative HS-GC-MS tests (See Supporting information S.2 for GC-MS spectra). For an exhaustive list of other impurities and compounds detected by the approach, please refer to the recently published research from Thomas et al. (2022a, 2022b).

2,2,4 trimethyl-1-2-dihydroquinoline (TMQ) and benzothiazole were the key intermediates observed after abiotic weathering. Benzothiazole was previously reported as the thermal transformation product of the benzothiazole sulfenamide (BTS) used as curing accelerator in the tire formation (Unice et al., 2015). 2,2,4 trimethyl-1-2-dihydroquinoline (TMQ), used as an anti-oxidant in the tire formulation, was detected as a THF leachate from the tire cryogrind. Wet-Dry and UV-weathering tests did not yield any pertinent THF leachates which could be used for quantification purposes. The exception was aniline which has been reported as diphenyl guanidine (DPG) thermal transformation product. Instead, transformation products including several aldehydes, ketones, and carboxylic acids (butanoic acid, propanoic acid etc.) were detected (data not shown). The low molecular weight compounds were attributed to the photo-oxidation of elastomers (Thomas et al., 2022a).

To access the combined effects of F-T, W-D and UV, cryogrinds were subjected to the abiotic tests sequentially. Intermediates detected in such combined weathering samples included phenol, benzene, and benzoic acid derivatives. It is important to note that water leaching tests (water sample post the UV + F-T + W-D tests) did not yield any intermediates. Presence of TRWP intermediates based on benzothiazole, benzoic acid, benzene derivatives via HS-GC-MS confirmed TRWP existence, as observed in the Kansas and Ohio soil samples (Table 1). These qualitative HS-GC-MS test results provided impetus to select appropriate marker compounds for the following quantification stage. Further, it also helped to analyze the results based on most aggressive tests (freeze-thaw) and most vulnerable cryogrinds (PC–Si and T-NR). The rationale behind choosing, benzoic acid, benzene derivatives as a representative of benzothiazole was due to the fact that the benzothiazole was detected in the samples when using conventional injection port GC-MS with an

Table 1
THF leachates identified in the GC-MS after Abiotic weathering tests and in soil samples.

Possible Transformation product/Leachate and Retention times	Degradation Mechanism	Samples/ Experiment	Components and Possible source
2,2,4 trimethyl-1-2-dihydroquinoline (13.360)	Leachate	Cured sheet (T-NR, T-SBR, PC-Si); Baseline cryogrind (T-SBR, PC-Si); F-T (PC–Si)	2,2,4 trimethyl-1-2-dihydroquinoline (TMQ)
Benzothiazole (10.870)	Thermal	T-NR: F-T, W-D and UV- 1.5 Year	Benzothiazole Sulfenamide (BTS) (*VANAX NS*)
Phenol	Thermal	T-SBR: F-T + W-D + UV 5 Year	Possible source: tire additives *(BTS, TMQ)*
Benzoic acid	Thermal	T-SBR: F-T + W-D + UV 5 Year and Ohio soil samples	Possible source: tire additives *(BTS, TMQ)*
Benzene	Thermal	Kansas soil samples	Possible source: tire additives *(BTS, TMQ)*

attainable GC oven temperature of 300 °C. However, only benzene and benzoic acid derivatives were detected in the very same sample when using HC-GC-MS with headspace temperature of 150 °C and an attainable GC oven temperature of 200 °C. Temperature capabilities of GC-MS system thus played a critical role in the analysis of TRWP with HC-GC-MS being the convenient method for quantification, whereas conventional GC-MS more suitable for detailed analysis of qualitative report on TRWP intermediates.

3.2. Quantification of tire reacted intermediates using HS-GC-MS and internal standards

Although tire intermediates like isoprene, styrene, vinyl cyclohexene have been reported (Chae et al., 2021; Unice et al., 2012), they were not selected as pyrolysis-GC would not be used. Based on the results of the qualitative HS-GC-MS tests on weathered cryogrinds, aniline, TMQ, and benzothiazole were selected as marker compound for cryogrind samples. Benzoic acid, benzene, and phenol were selected as marker compounds for the quantification of the TRWP intermediates in soil samples. Each sample was analyzed in duplicate to reduce sampling errors from heterogenous samples. Peak/signals of the internal standards of known concentration were first compared relative to the respective marker compound signals (marker: standard signal ratio). Next, the mass of the marker compounds was calculated and reported in duplicates (Supporting information S.3).

3.3. Assessment of environmental fate of tire tread leachates

Quantification was co-related into mass concentration factors, life cycle, and cumulative factors and a modified methodology was adopted from Unice et al. (2015) to access the environmental availability of tire leaches. However, UV weathering conditions using UV-B light and weathering tests like freeze thaw and wet-dry of tire cryogrinds are not reported elsewhere and augments our recently reported work (Thomas et al., 2022b). The mass concentrations were represented as the μg of chemical per g of cryogrind dry weight. The factors were calculated as per the quantification results and raw instrument data and are shown in the supporting information S.3. The total fraction available (F_T) was the cumulative leachate ability from water, freeze-thaw, wet-dry and UV-exposure. Standard deviations of the sample series conducted in duplicates is provided in the Supporting information S.4. Accelerated UV-weathering tests relative to terrestrial aging could not be incorporated in the factor calculation of additive leachates due to non-detection of THF leachates post UV exposure. The F_T of TMQ for PC-Si, T-SBR and T-NR were 1.43×10^{-4}, 1.71×10^{-3}, and 1.50×10^{-3}, respectively. Similarly, the F_T for benzothiazole sulfenamide for T-SBR and T-NR were 0.08 and 0.142, respectively.

3.4. Quantification of TRWP in the roadside soil samples

In general, benzene, benzoic acid, and phenol were found in the roadside soil samples using the HS-GC-MS qualitative testing and were selected as the marker compounds. The precursor for these markers can be the elastomer (SBR) in the tire formulation. However, it is more probable they were released from the additives with a benzene ring in their chemical structure which includes BTS, DPG, TMQ and PPD. This hypothesis is backed by the high leaching tendency of the additives observed by Thomas et al. (2022a). The reference tire cryogrind formulation (Vanderbilt, 2010) has the additives present in 0.6 phr (BTS) to 1.2 phr (TMQ, PPD) calculated by averaging on a total of 100 phr. Thus R_A for the additives were averaged to be 0.9/100. TRWP contents obtained in the roadside soil samples in Ohio and Kansas were 2.1% and 0.15%, respectively. TRWP contents observed in the roadside soil samples were much greater for Ohio roadside soil than in Kansas due to the increased Annual Average Daily Traffic (AADT) in the Ohio locations (see supporting information S.5). Thus, heavy traffic reported can be a major reason for higher TRWP observed in the Ohio soil samples.

Chae et al. (2021) reported a TRWP content of 1–5 wt% in the road dust whereas Youn et al. (2021) reported 0.9–2.3 wt% TRWP from industrial and residential areas. The results vary due to the difference in sampling locations and separation protocols. For the larger TRWP sizes (1–5 mm), the mass concentrations were represented as the μg of TRWP per g of roadside soil sample dry weight and yielded 800–1300 μg/g and 1200–3100 μg/g TRWP in Ohio and Kansas soil respectively. The soil based TRWP concentrations were lower than the 4500–9100 μg/g in sediments (Panko et al., 2012; Unice et al., 2013).

The dihydroquinoline derivative TMQ could also be another persistent leachate. However, since the leaching was carried out in the presence of THF solvent, it does not correlate to true environmental conditions. HS-GC-MS confirmed the TRWP presence in the samples prior to selecting markers and standards for GC-MS quantification. The main challenge that existed was the possibility of other sources for these markers, such as bitumen of asphalt road payment wear particles or any other runner components. There are no cost-effective ways to critically distinguish between the origins of TRWP in the soil samples (TRWP, bitumen and other substances) and list out the exact source for compounds like benzene, benzoic acid, and phenol. Even though recent publications by Kovochich et al. (2021) and Thomas et al. (2022a, 2022b) show the method of single particle analysis via SEM-EDX to confirm the presence of TRWP and bitumen combination, a 100% effecting mutually exclusive distinguishing criteria has not been proposed yet. However, the tire particles still remains the most prominent source for the TMQ and BTS intermediates used in for quantification stage (Asheim et al., 2019; Challis et al., 2021; Johannessen et al., 2021; McIntyre et al., 2021; Salas et al., 2016). Further, it was observed that even though HS-GC-MS is an effective and convenient method for TRWP quantification, attaining high headspace and oven temperature (≥300 °C) becomes a critical criterion when the end goal is to qualitatively identify the TRWP based degradation intermediates like in the conventional GC-MS and PY-GC-MS. Please refer to the recent publications Thomas et al. (2022a, 2022b) if readers are interested to know more about the foundational work on abiotic degradation of tire and method development of TRWP analysis from soil that resulted in this short communication on its quantification.

4. Conclusion

A simple and effective analytical method was developed utilizing BTS and TMQ based benzene and benzoic derivative markers, for the quantification of TRWP in the roadside soil samples. All the markers were initially identified and later quantified by internal standard method using HS-GC-MS. Environment release factors (F_T) of tire cryogrind leachates showed higher availability for BTS as compared to TMQ, with F_T of 0.11 and 1.7×10^{-3}, respectively. TRWP content in the size range of 1–5 mm was between 800 and 1300 μg/g and 1200–3100 μg/g TRWP in Ohio and Kansas soil. For TRWP content lesser than 1 mm, 0.15–2.1 wt% was observed in Kansas and Ohio samples and were seemingly dependent on the locations and the traffic. Correlating experimental aging on reference tire cryogrinds and the roadside soil sample TRWP is of great importance to the ongoing and future TRWP and general traditional microplastics research.

Author statement

Jomin Thomas: Formal analysis, Investigation, Writing. **Teresa J. Cutright:** Funding acquisition, Conceptualization, Project administration, Writing. **Coleen Pugh:** Funding acquisition, Conceptualization, Methodology, Writing. **Mark D. Soucek:** Resources.

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.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2022.137132.

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