

Method Development for Separation and Analysis of Tire and Road Wear Particles from Roadside Soil Samples

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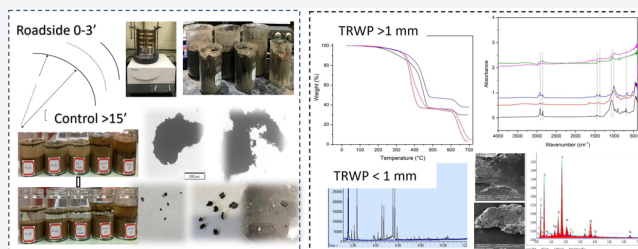
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ABSTRACT: A comprehensive understanding of tire and road wear particles (TRWPs) and their detection and quantification in soils is still challenged by the lack of well-set standardized methods, inherent technological inconsistencies, and generalized protocols. Our protocol includes soil sampling, size separation, and organic matter removal by using hydrogen peroxide followed by density separation and analysis. In this context, roadside soil samples from different sites in Kansas and Ohio, USA, were collected and analyzed. Tire cryogrinds analogous to TRWPs were used to evaluate various density separation media, and collected particles more than 1 mm in size were then subjected to infrared spectroscopy (IR), thermogravimetric analysis (TGA), and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) to confirm TRWP presence. Particles smaller than 1 mm were Soxhlet extracted, followed by gas chromatography–mass spectrometry (GC–MS) to validate the presence of tire-related intermediates. SEM-EDX validated the presence of elemental combinations (S + Zn/Na) ± (Al, Ca, Mg, K, Si) attributed to tires. Ketones, carboxylic acids, epoxies, cyclohexane, and benzothiazole sulfenamide (BTS) intermediates were the most probable tire-related intermediates observed in the roadside soil samples. Thus, this simple, widely applicable, cost-effective sample preparation protocol for TRWP analysis can assist TRWP research advancement in terrestrial environments.

KEYWORDS: method development, tire and road wear particles, soil sampling, size separation, organic matter removal



1. INTRODUCTION

The existence of microplastics in a wide variety of environments, including water, air, and soil, is of global concern.¹ However, only 3.8% of studies focus on terrestrial soils,² and all of them reported microplastic concentrations at a very high level.^{3,4} Research on tire and road wear particles (TRWPs) has increased with collaborative efforts of various academic institutions, several tire companies, and environmental agencies.^{5–8} TRWPs reportedly constitute the largest share (45%) of terrestrial microplastics.^{9,10} Although recent research has challenged the inclusion of TRWPs as a microplastic,¹¹ the local prominence of TRWPs near the roadways, influenced by heavy traffic, has been confirmed.¹² As a result of the friction of tires with the road, tire tread wears off and subsequently combines with road pavement particles to form TRWPs, leading to about 1 000 000 ton/year of TRWPs in the U.S. alone.^{13,14} Similar to the general microplastics, the effects of TRWPs on water bodies and air have been reported by many researchers^{15–20} with benzothiazole, a curing accelerator, posing a 0.003% health risk studied during three exposure scenarios and four subpopulation groups.²¹ TRWPs are also reported to cause acute toxicity of several aquatic life-forms.^{18,22} Tian et al.²³ reported that 6 PPD-quinone, an oxidant product of the common tire antioxidant, *p*-phenylenediamine (PPD), induces acute mortality in coho salmon

species. To understand their adverse effects, TRWPs must be identified and analyzed over a wide range of sequential and longitudinal scales. The dearth of suitable methods limits the TRWP analysis in the extremely complex soil matrices,²⁴ with almost no standardized or generalized techniques. Recently published ISO specifications relevant to TRWPs provide some common guidelines to follow in determining their environmental fate²⁵ and their physical and chemical characterization.²⁶

The soil matrix is composed of minerals, organic matter, and plant and animal debris, at various levels of decomposition.²⁷ The heterogeneity of soil media makes the TRWP analysis in soil very challenging. An adequate soil sampling strategy is essential in any environmental sample analysis, including TRWP analysis from soil. However, there may not be a standard sampling approach for every scenario, as several factors like site geomorphology, potential sources of TRWPs, and hypothesized analyte/TRWP distribution in the roadside

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soil complicate routine sampling.²⁸ There are several published research studies categorizing soil sampling into random sampling, systematic grid or transect sampling, hotspot or suspect sampling, and stratified sampling.^{29,30} Sampling depth also varies from the topmost 5 cm to even 30 cm.^{29,31} As with the isolation of microplastics, the first stage in extraction of TRWPs is the selection of the size range. The particle size of TRWPs is between 0.1 and 4 mm.^{12,32} However, tire wear particles obtained from road simulators are smaller and range in size between 100 and 400 μm .^{13,19} The next stage is the removal of organic matter from the soil since it can interfere with the TRWP identification.³³ Among the various digestion methods specific to the organic matter in soil, strong acids,³⁴ potassium hydroxide, enzymatic treatments, hydrogen peroxide, and Fenton's reagent are the most common.^{35,36} However, variable and heterogeneous characteristics of the organic matter in complex soil matrixes, as well as factors that could interfere with the digestion method (i.e., soil pH, moisture, conductivity) and the specific target of the study, influence the appropriate methods.³⁷ The final stage of the extraction is to isolate the particles from environmental matrixes using density separation media.³⁸ These methods include solutions of zinc chloride (1.7 g cm^{-3}), sodium chloride (1.2 g cm^{-3}), sodium iodide (1.8 g cm^{-3}), and oil media like canola and castor.^{39,40}

TRWPs have been detected in soil samples as a parent compound, as leachates, or as hydrolysis or transformation products of tire constituents.^{22,41,42} TRWPs are quantified^{19,20} by advanced sensitive analytical techniques and elastomer-specific pyrolysis markers. ISO 21396 provides a generalized method to determine TRWP mass concentration using pyrolysis-GC-MS⁴³ that has been validated by at least one study.⁴⁴ Eisentraut et al.⁴⁵ similarly used thermal extraction desorption gas chromatography (TED-GC-MS). Single particle analysis by chemical mapping of TRWPs was reported by Kovochich et al.⁴⁶ using SEM-EDX. Nontargeted GC-MS is also used to analyze TRWPs.^{7,47} However, most of the literature assessed the environmental impact of the tire particles using column leaching tests, accelerated weathering tests,^{41,48} extractions, and aerobic incubators.^{13,49} Although these studies did not separate TRWPs from soil, they do provide a database of possible transformation products.

A generalized soil sample preparation protocol for TRWP separation from roadside soil samples and its comprehensive analysis has not been reported to date. Thus, the aim of this study was to explore and validate extraction methods of TRWPs from roadside soil matrixes. Density separation techniques were tested in reference garden soil with analogous tire particles to establish the most effective extraction methodology. This study proposes a different methodology to analyze the separated TRWPs and their related intermediates found in roadside soil and their environmental accessibility.

2. METHODS

Reagent grade sodium chloride and zinc chloride, 30% hydrogen peroxide, and tetrahydrofuran were obtained from Sigma-Aldrich and used as purchased. Canola oil and olive oil were purchased from the local supermarket.

Four stages were utilized for the method development of the extraction of TRWPs from the roadside soil samples: (1) soil sampling strategies and characterization; (2) drying and

sieving; (3) purification, extraction, and subsequent filtration; and (4) TRWP identification and analysis.

2.1. Soil Sampling and Characterization. Hotspot or suspect sampling was used to identify where to collect soil samples in Kansas and Ohio. Sampling focused on roadside soil of heavily trafficked intersections, where acceleration and brake processes happened in high numbers, or a highly frequented ramp (see Table S1 for average daily car and truck traffic of sampling sites). Roadside soil sampling sites used in this paper for the investigation of TRWPs are as shown in the Table S2. Global sampling sites for the microplastics in soil were recently reported by Yang et al.⁵⁰

Clean stainless-steel trowels were used to avoid any plastic contamination. A sampling depth of 0–5 cm was chosen to reduce the risk of collecting more organic matter and associated vegetation. Control samples were taken from more than 15 in. away from the road as per sampling guidelines by the US Environmental Protection Agency and US Department of Agriculture.⁶ Where possible, control samples were collected >15 ft from the berm to minimize TRWPs. Reported soil sample quantities in microplastics study vary from 50 g⁵¹ to several kilograms.^{31,38} At each site, triplicate 1 kg samples were collected due to the discrete TRWP distribution in the roadside soil. The samples were collected in zip-lock bags with the respective location tags and stored in a refrigerator until the next stage of the analysis.

Basic soil characterization includes determination of soil texture, moisture, pH, organic matter, and conductivity, all of which may influence sample preparation protocol and analysis.^{30,52} Runoff during heavy rainfall can wash TRWPs away and transport them from roadside soils to water bodies. To increase the chance of collecting accumulated TRWPs, roadside soil samples were collected after a minimum of 5 dry weather days.

As shown in Table S3, the moisture contents of soil samples taken from locations adjacent to the berm of the road were low, which confirms the conditions were dry. Roadside soils adjacent to the roadways in sampling sites were all barren and empty of any grass or vegetation, which decreases their moisture holding capacity. The soil moisture increased with increasing distance from the berm of the roads, mainly due to increasing vegetation and grass and their higher moisture holding capacity.

2.2. Drying and Sieving. To obtain a water-free soil sample reference for the TRWP content, samples must be well dried prior to analysis. ISO 11464 suggests drying at 40 °C for 72 h,⁵³ whereas other researchers recommended drying at 70 °C for 24 h.³¹ Detailed drying conditions and procedures varying the temperature and duration can be found in the literature.⁵⁴ The main concern about using higher temperature is the possibility of degradation, melting, or change of any structural and physical properties of the polymer. Natural rubber may melt at temperatures above 30–65 °C.⁵⁵ Freeze-drying is a gentle alternative, but it poses challenges like frost wedging, dryer size constraints, time consumption, and induction of polymer brittleness.⁵⁶ In this study, soil samples were dried at room temperature for 24 h, followed by 40 °C for 72 h in an oven, adhering to the ISO standards.

Once the soil samples were dried, adequate homogenization of the samples was achieved by manual mixing. Subsamples (400 g) were sieved using a stainless-steel sieve cascade of sieve numbers 4, 16, and 140, corresponding to 5, 1, and 0.1 mm, to separate them into appropriate size fraction ranges.

Microplastics are reported to usually be between 1 and 5 mm,^{29,31,57,58} whereas tire wear particles obtained from road simulators are significantly smaller: 100–500 μm .^{13,19} TRWPs from actual environmental field samples range in size from 0.1 to 4 mm.^{12,32} This increase is presumably due to mineral encrustations from the road to the tire particles. This study analyzes two size fractions, 1–5 and 0.1–1 mm.

2.3. Purification, Extraction, and Filtration. Soil organic matter (SOM), whose density ($\sim 1.6 \text{ g/cm}^3$) is similar to that of TRWPs, should be removed prior to the extraction of TRWPs using density.⁵⁹ Alkaline and acid treatments can detrimentally affect polymers and remove relatively low SOM.^{35,38,60} Enzymatic digestion is less aggressive but has not been tested in soil samples. Further, it requires complicated sample preparation and extra filtration stages, which is time-consuming and was not cost-effective.³⁶ Although Fenton reagent in combination with hydrogen peroxide forms hydroxyl radicals capable of degrading SOM, it was ruled out as the reaction is highly exothermic and thus detrimental to the polymers.³⁵ Hydrogen peroxide (30%) is the most commonly used digestion method, with 95% SOM removal rates reported after a few hours at 70 °C.^{35,61} However, this higher temperature may degrade the polymers.⁶² Thus, in this study, the time and temperature were carefully adjusted to ensure preservation of TRWP analytes. Digestion using hydrogen peroxide (30%) was carried out at room temperature for 72 h to balance acceptable SOM digestion without degrading the rubber. SOM digestion was limited to 10 mL of hydrogen peroxide (30%) for each 100 g of sieved roadside soil sample, and the mean weight reduction of each sample was calculated after 72 h.

TRWPs ($1.2\text{--}1.4 \text{ g cm}^{-3}$)³² can be concentrated in roadside soil samples using density separation since they are more buoyant in solutions ($1.2\text{--}1.8 \text{ g cm}^{-3}$) than the soil mineral fraction (2.0 g cm^{-3}).^{63,64} Several sample containers like beakers, Erlenmeyer flasks, separation funnels, and other complex self-built setups were reported in the literature.^{35,56,61,65,66} A few preliminary experiments with a separation funnel were compared to those with the standard glass bottle. Reported sample quantities varied from 5 g to 5 kg samples with 20 mL to 10 L density solutions.^{30,67} A sample to density solution ratio was kept between 1:2 as reported in the literature.^{68,69} In the case of oil density solutions, the density gradient was built by adding 25 mL of oil followed by 150 mL of deionized water (DI) as described by Radford et al.⁷⁰ Test samples consisting of the soil (100 g) and density solutions were manually mixed in a 300 mL glass bottle, followed by 10 min of automated and controlled rolling in a tumbler mill, and were then allowed to settle for 8 h.

Zinc chloride and sodium chloride solutions were prepared by dissolving the respective salt in distilled water to achieve a final density of 1.7 and 1.2 g cm^{-3} , respectively. Multistep density separation procedures are also reported,^{30,71} with sodium heteropoly tungstate solution (SPT) (2.2 g cm^{-3})^{56,71–75} as the most promising for TRWPs. However, SPT and similar solutions are very expensive.⁷⁶ ZnCl_2 poses the disadvantages of being expensive, corrosive, toxic, and harmful to the environment and might even degrade polymers,^{2,76} whereas NaI is expensive and harmful to the environment. CaCl_2 is both expensive and is reported to cause flocculation in soil through its ion bridging.³⁸ As per the Sigma-Aldrich pricing, the costs of 100 g (as anhydrous powder, 97%) of sodium chloride, calcium chloride, zinc

chloride, and sodium iodide are \$35, \$62, \$74, and \$93, respectively. Deionized water (DI) water and sodium chloride are suitable for low-density polymers⁵² and are cheap, safe, and easily available. Further, the Na^+ conduciveness to the soil aggregate dispersion increases the extraction efficiency.³⁸

Tire tread cryogrinds and a reference garden soil were used to optimize and validate the procedure as well as determine the recovery rates of the solutions used. Cryogenic milling of tire treads has been recognized as an efficient particle size reduction method⁷⁷ for providing tire particles in TRWP reference material.⁴⁰ An industry standard test tire sample using the common constituents in a passenger car tire formulation (elastomer, vulcanizing agent, accelerating agents, antioxidants, and fillers) was formulated for this purpose. Over 98% of the cryogrind passed through the 2 mm opening. Further, soil characterization was carried out on the reference garden soil regarding the pH, moisture content, and conductivity. Although not representative of roadside soil samples, garden soil was chosen due to its absence of other impurities and organic matter debris that would otherwise interfere with the method development. Each representative 100 g of garden soil sample was spiked with 1 g of tire cryogrinds. Looking at the potential trade-off between operation effort and safety, environment impact, and reducing costs, in this study, sodium chloride was opted for subsequent roadside soil sample testing. Further, this selection also depended on the optimization and recovery efficiency study carried out using garden soil and tire cryogrinds, as discussed earlier.

The last step in this stage involved the collection and isolation of the supernatant materials for further treatment and analysis. The simplest and most cost-effective method is decanting, but particles often adhere to the surface, which increases time requirements and leads to contamination.^{52,57,78} Other reported literature also mentioned the usage of self-built apparatus³⁸ and surfactant addition.⁵⁶ This study used an overflow method wherein the supernatant was removed using continuous addition of excessive density separation solution^{61,78–80} until it spilled out into a collection dish. The TRWPs were collected in a weighing boat after they were separated out.

2.4. Identification and Analysis. The extracted samples from the lower particle size range might be too small for single particle analysis, and accurate quantification is challenged by the presence of soil debris. Therefore, two separate identification and analysis methodologies were followed: one for $>1 \text{ mm}$ and one for $<1 \text{ mm}$.

2.4.1. Particle Size Range $>1 \text{ mm}$. Particles were first visually inspected for color, texture, and feel. Black, rubbery, and flexible particles were selected for optical microscopy. Some researchers have also used a hot needle test to identify TRWPs^{10,81} in addition to FTIR and thermal methods.⁸² Optical microscopy, ATR-IR, TGA, and SEM-EDX were conducted on large-particle-size samples to verify the collection of cryogrind or TRWPs from roadside soil samples. Particles $>1 \text{ mm}$ were the big, black, rubbery, and flexible particles observed in optical microscopy and had resemblance to rubber/tires. Kovochich et al.^{46,75} have published detailed information on identification of TRWPs in soil using advanced analytical techniques, such as electron microscopy, energy dispersive spectroscopy X-ray analysis, and time-of-flight secondary ion mass-spectrometry.

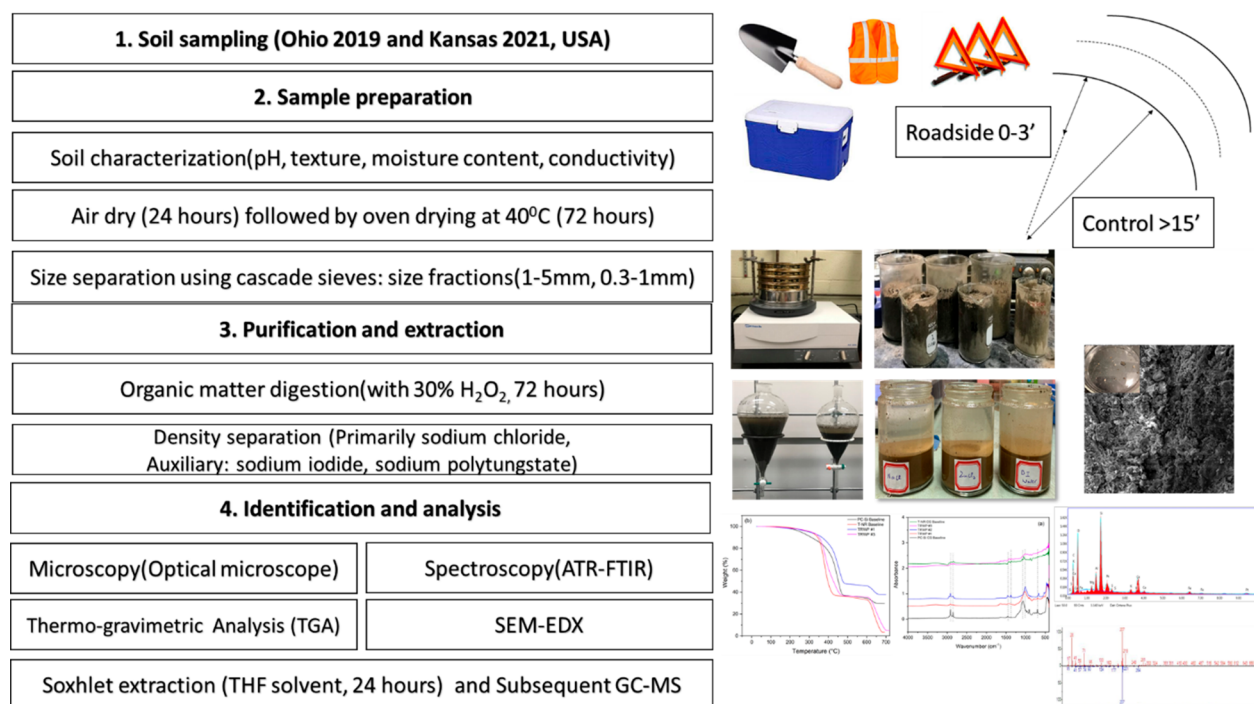


Figure 1. Generalized sampling and analysis procedures for TRWPs in soil.

A LYRA 3 TESCAN scanning electron microscope (SEM) with EDX capability was used for SEM-EDX. Cleaned TRWPs were pressed lightly against a carbon tape and were sputter coated with a platinum layer before examination using a 15 kV beam. Individual elements were resolved in the secondary electron images, except for Na/Zn due to the inability to distinguish between their close $K\alpha$ peak values.⁸³ Fourier transform infrared (FTIR) spectroscopy was performed on a Thermo Scientific Nicolet i50 instrument with attenuated total reflector attachment (ATR-IR) using a data spacing of 4 cm^{-1} and resolution with 64 scans.

The thermal stability of the thermosets was probed using TGA (TA Q500) from room temperature to $600\text{ }^{\circ}\text{C}$ under nitrogen and from 600 to $700\text{ }^{\circ}\text{C}$ under air, at a scanning rate of $20\text{ }^{\circ}\text{C}/\text{min}$ with a sample weight of about 10 mg. The spectra and thermograms were cross-referenced with those of the standard tire cryogrind supplied by the industry.

2.4.2. Particle Size Range $<1\text{ mm}$. For the particles smaller than 1 mm, individual identifications of TRWPs were challenging due to the interference caused by soil debris, dust, and biomass which are extracted out during filtration.⁸⁴ Further, it is difficult to place particles/TRWPs smaller than 1 mm onto the diamond crystal of the ATR accessory.⁸⁵ Therefore, for particles less than 1 mm, the next stage after filtration involved the Soxhlet extraction of the filtered residue using tetrahydrofuran (THF) solvent for 24 h. Several reports have also used dichloromethane, xylene, or trichlorobenzene.^{86–88} Next, the collected extract was evaporated to dryness and subsequently redissolved in THF to a concentration of 1 mg/mL . Dierkes et al.⁸⁷ used THF for extracting low concentrations of polyethylene, polypropylene, and polystyrene for their analysis of microplastics. Avagyan et al.⁸⁹ and Ao et al.⁹⁰ found that THF yielded higher extraction efficiencies of 70–90% for tire-based additives, mainly benzothiazole. A new and promising technique of extraction

of rubber intermediates using an organic solvent is thus utilized.

Pyrolysis GC–MS and nuclear magnetic resonance (NMR) have been used to evaluate the extracted intermediates.^{87,91} GC–MS was selected here as a nontargeted, suspect screening full scan analysis technique to identify all GC-amenable additive compounds in the tread and roadside soil extracts, using a GC–MS system (Agilent 7820 AGC/5975 MSD) equipped with an Agilent 19091S column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). Electron ionization mode with MS transfer line and ion source temperatures of $300\text{ }^{\circ}\text{C}$ were used with a sample injection volume of $5\text{ }\mu\text{L}$, oven temperature range of $15\text{ }^{\circ}\text{C min}^{-1}$, initial temperature of $100\text{ }^{\circ}\text{C}$, inlet temperature of $300\text{ }^{\circ}\text{C}$, hold time of 10 min, and a split flow ratio of 100:1. The chromatogram peaks were cross-referenced with the NIST database, and compounds with $>60\%$ match to the database were short-listed for further analysis.

3. RESULTS AND DISCUSSION

Figure 1 summarizes the generalized and optimized sampling and analysis protocol described in this paper. An optimization study was first carried out to finalize the density separation solution to use for the purpose of extraction of possible TRWPs from soil samples. Recovery rate efficiencies of the different density solution media used are tabulated in Table 1.

As anticipated, sodium polytungstate solution provided the highest tire cryogrind recovery efficiency ($95\% \pm 0.8$). This was followed by the sodium iodide ($89\% \pm 1.7$), zinc chloride solution ($83\% \pm 1.8$), sodium chloride solution ($74\% \pm 1.7$), and DI water ($55\% \pm 1.6$). Although $>96\%$ microplastic recovery was earlier reported using canola oil and castor oil,^{92,93} evidently because of their oleophilicity and unique densities, we were not able to separate the tire particles from the water and oil mixture in the fluvial and sticky soil matrix. Thus, we employed sodium chloride in all our subsequent testing as a balanced choice between cost, safety, and recovery.

Table 1. Recovery Rate Efficiencies of the Different Density Solution Media in the Garden Soil Performed in Triplicate

density solution	initial weight of cryogrind added (g)	final weight of cryogrind collected and dried (g)	tire cryogrind recovery (%)	mean recovery (%)
sodium polytungstate	1.12	1.07	95.54	95.44
	1.05	1.01	96.19	
	1.11	1.05	94.59	
sodium iodide	1.17	1.03	88.03	89.74
	1.02	0.92	90.20	
	1.22	1.11	90.98	
zinc chloride	1.20	1.01	84.17	83.01
	1.16	0.97	83.62	
	1.12	0.91	81.25	
sodium chloride	1.02	0.76	74.51	73.19
	1.10	0.81	73.64	
	1.05	0.75	71.43	
DI water	1.10	0.65	53.09	54.82
	1.14	0.57	54.00	
	1.12	0.62	55.36	

Simultaneously, sodium iodide and sodium polytungstate solution were also used as a subsequent density separation media for the soil samples, after the sodium chloride separation stage. The additional step was incorporated to take into consideration any high-density TRWPs ($1.4\text{--}2\text{ g cm}^{-3}$) that might have been overlooked in the density separation with NaCl. This helped improve TRWP enrichment and isolation for further characterization and chemical mapping.

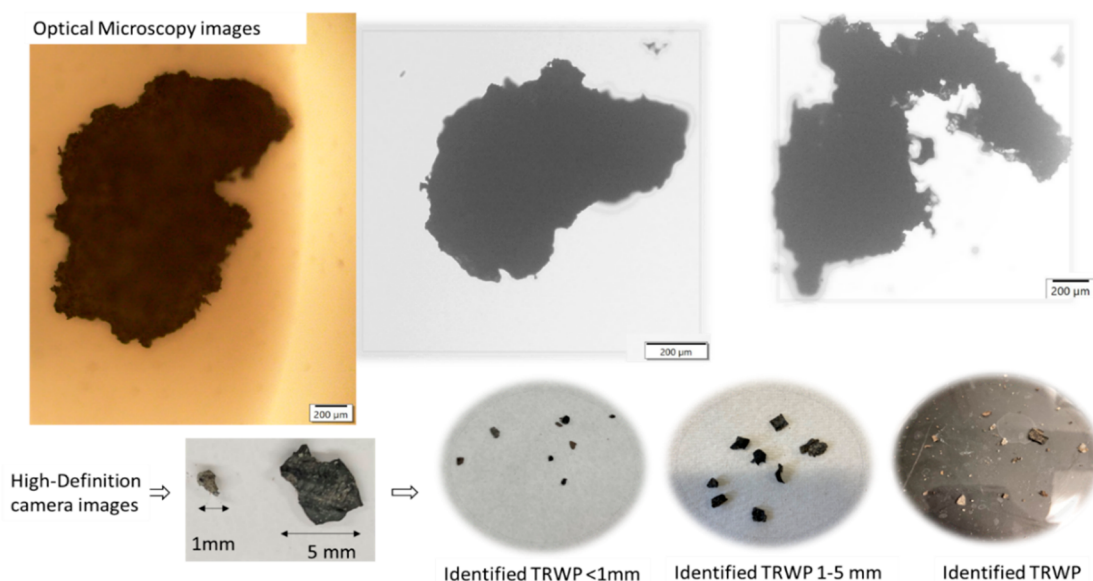
The soil sample preparation protocol was then verified using roadside soil samples. After drying, roadside soils were separated to size fractions of 1–5 and 0.1–1 mm using cascade sieving. A larger particle size range was selected in this work compared to the micrometer range reported^{12,32} widely for TRWPs, as combination with the asphalt encrustation in the road ultimately results in bigger particles. Sieving of the soil samples helped remove larger plant debris and vegetation.^{13,19}

The sieved soil samples were then purified by organic matter digestion using hydrogen peroxide. Mean weight reductions in all the samples were around 15 g, which translates to 5% weight reduction (Table S2). Density separation with sodium chloride followed by the overflow method helped to collect the possible TRWP/soil constituents from the roadside soil samples (see Table S4).

3.1. TRWP Identification and Analysis of Particle Size >1 mm. Filtered TRWPs with soil constituents were first visually inspected. Black, rubbery materials (Figure 2) were selected for the TGA and FTIR tests. Both the FTIR and TGA tests were cross-referenced to those of the reference tire tread cryogrinds (Figure 3).

As observed in Figure 3, the short-listed TRWPs are indeed tire-related particles. Their IR spectra and TGA thermograms are cross-referenced with those of the reference cryogrinds. There are several common peaks in the reference cryogrinds and TRWPs (Figure 3a). These peaks include aliphatic hydrocarbon bands (C–H stretching at 2920 and 2845 cm^{-1} and C–H bending at 1450 cm^{-1}),^{94,95} C–O–C stretching at 954 cm^{-1} , ester bands (C–O bending at 1027 cm^{-1}), and out of plane bending⁹⁶ of aromatic C–H at 700 cm^{-1} . It was evident that TRWPs 1 and 2 had similar peaks as that of the PC-Si cryogrind, whereas TRWP 3 revealed common peaks with T-NR cryogrind. However, FTIR was only employed as one of the preliminary tests due to the inherent interference (near complete absorption of IR light) of carbon-black-filled particles during spectroscopic analyses.³² These initial observations must be confirmed by other analytical techniques for single particle analysis.

The TGA thermograms of TRWPs and reference cryogrinds are shown in Figure 3b. The first 10% decomposition stage of all samples corresponds to the oils and plasticizers in the tire formulation, followed by a 50–60% elastomer degradation stage starting at around $400\text{ }^{\circ}\text{C}$. The degradation observed at $600\text{ }^{\circ}\text{C}$ corresponds to the carbon black thermal degradation of the sample in an oxygen atmosphere vs in a nitrogen atmosphere. TRWP 3 and T-NR degraded more than TRWP 1 and PC-Si in accordance with the different percentages of

**Figure 2.** Optical images and high-definition camera images of TRWP particles.

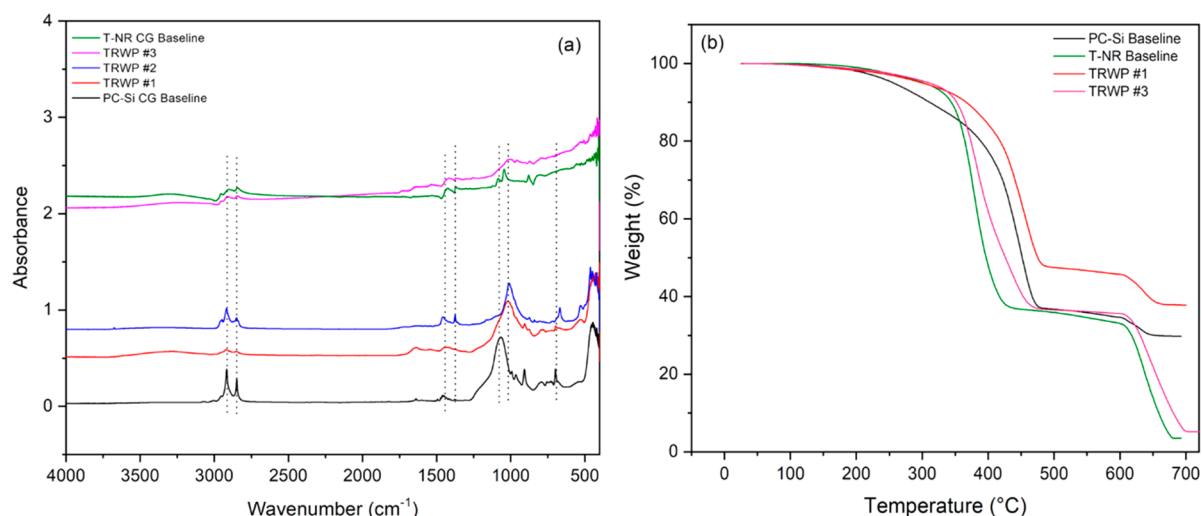


Figure 3. (a) FTIR spectra of TRWPs compared to reference cryogrinds. (b) TGA thermograms of TRWPs compared to reference cryogrinds.

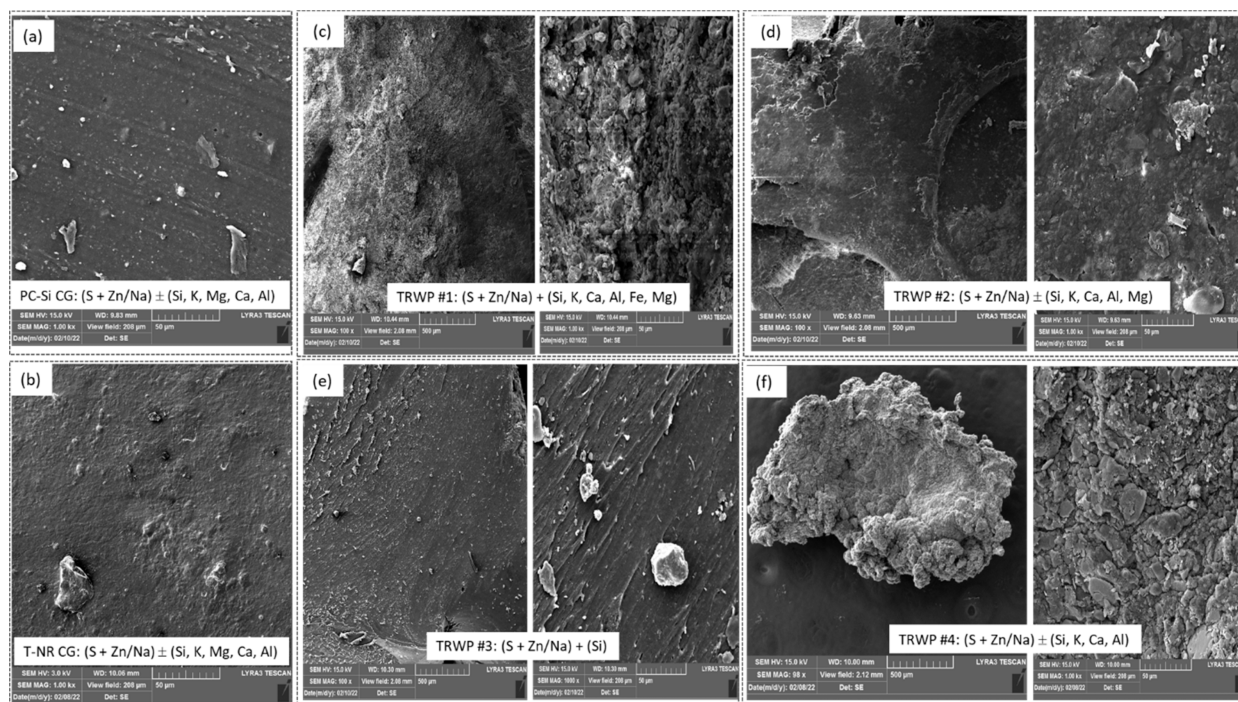


Figure 4. SEM-EDX images of the prevalent surface elements associated with TRWP 1 (c), TRWP 2 (d), TRWP 3 (e), and TRWP 4 (f), compared to reference cryogrinds PC-Si CG (a) and T-NR CG (b).

carbon black in the formulation.⁹⁷ Higher residues of 30% were observed in TRWP 1 similar to PC-Si cryogrind, whereas TRWP 3 degradation resembled the T-NR cryogrind. This corroborates the IR analyses. The higher residue is directly attributable to the silica present in the tire formulation.⁹⁸

A comparison of the SEM-EDX elemental maps of the TRWPs and the reference tire tread cryogrinds (Figure 4) confirms the IR and TGA analyses. The corresponding EDX raw data are provided in the Section S5.

Although most studies describe TRWPs as elongated particles in the size fraction 50–100 μm,⁹⁹ we observed the large-mean-particle-sized TRWPs to be rough and uneven with curvy edges that were elastic and soft to the touch. This corroborates the research by Chang et al.¹⁰⁰ who studied the characteristics of TRWPs under different tire wear mecha-

nisms. The elemental surface characteristics of the cryogrind and TRWPs shown in Figure 4 include colocalized key signatures (S + Zn/Na) with varying amounts of other elements (±Si, Mg, Ca, Al, and K). Single particle analysis has been employed to classify particles in complex environment samples.^{46,75,101,102} Kovochich et al.⁴⁶ used SEM-EDX for chemical mapping of TRWP single particles coupled with time-of-flight secondary ion mass spectroscopy (ToF-SIMS). First, SEM-EDX was performed on the two different reference tire cryogrinds representing PC-Si and T-NR (Figure 4a,b). There are varying concentrations of sulfur (S), sodium/zinc (Na/Zn), magnesium (Mg), aluminum (Al), potassium (K), and calcium (Ca) on the surface of the tire cryogrind and TRWPs particles. S and Si are generally associated with the fillers and vulcanizing agents in the tire formulation. Al, Ca, Mg, and K,

Table 2. Compounds Tentatively Identified Using GC–MS after Soil Extraction from Roadside Soil Samples: Ohio 2019 and Kansas 2021

sample no.	compound tentatively identified	retention time	possible source
1	4-hydroxybutanoic acid	2.319	thermal/photo-oxidation of elastomers in tire formulation: carboxylic acids
2	butanedial/succinic aldehyde	3.635	NR and BR elastomers: attack on allylic positions of NR and BR
3	1-hexene epoxide	4.239	thermal/photo-oxidation of elastomers in tire formulation: epoxides
4	2-methylpropanoic anhydride	4.522	thermal/photo-oxidation of elastomers in tire formulation: carboxylic acids
5	3-methoxyhexene	4.697	possible tire degradation intermediate
6	2-(benzo[4,5]thiazole[1,2,4]triazol-3-ylsulfanyl)ethyl (dimethyl) amine	4.706	thermal/photo degradation transformation product of benzothiazole sulfenamide (VANAX NS/BTS)
7	5-hexene-1-ol	4.987	thermal/photo-oxidation of elastomers in tire formulation: alcohols
8	benzoic acid, 3-(trimethylsilyloxy)-trimethylsilyl ester	5.297	possible tire degradation intermediate
9	2,4-bis(trimethylsilyloxy)benzaldehyde	5.351	possible tire degradation intermediate
10	isopropylbenzene	5.631	thermal oxidation of tire
11	oxirane-3-hydroxypropyl	5.889	thermal/photo-oxidation of elastomers in tire formulation: epoxides
12	1,4-dihydroxy-4-methylcyclohexanone	5.986	thermal/photo-oxidation of elastomers in tire formulation: ketones
13	[2-(cyclohexyl methyl)pentyl]cyclohexane	8.596	possible tire degradation intermediate
14	N-(2-acetylcyclopentylidene) cyclohexylamine	8.600	thermal/photo degradation transformation product of benzothiazole sulfenamide (VANAX NS/BTS)
15	[3-cyclohexyl 2-methyl propyl] cyclohexane	8.611	possible tire degradation intermediate
16	benzo[b]dihydropyran, 6-hydroxy-4,4,5,7,8-pentamethyl	8.997	possible tire degradation intermediate
17	2-thiazolamine, 4-(3,4-dimethoxyphenyl)-5-methyl	10.101	thermal/photo degradation transformation product of benzothiazole sulfenamide (VANAX NS/BTS)
18	3,4-bis(methoxycarbonyl)benzoic acid	10.242	possible tire degradation intermediate
19	1,2 benzisothiazol-3-amine	10.749	thermal/photo degradation transformation product of benzothiazole sulfenamide (VANAX NS/BTS)
20	N-(3 aminopropyl) hexadecane-1-sulfenamide	11.430	thermal/photo degradation transformation product of benzothiazole sulfenamide (VANAX NS/BTS)
21	diethylene glycol dibenzoate	13.680	benzo flex: plasticizer in tire and other polymer coating applications

which have also been reported in the literature,^{13,46} correspond to road wear, break wear, concrete, and soil. As with the TGA and FTIR analyses, the TRWPs can be divided into two main variants: TRWPs 1, 2, and 4 with 10% Si have similar elemental characteristics as PC-Si CG, whereas TRWP 3 with low (2%) to no Si has elemental values comparable to those of T-NR CG. Thus, the EDX mapping results are also consistent with the chemical compositions of the reference tire cryogrinds.

Sulfur, a vulcanizing agent, was present in higher concentrations in cryogrinds than in the TRWPs. However, reference tire cryogrinds are devoid of any material contribution from road or environment. Thus, even though TRWPs primarily contain tire tread compounds, cryogrinds are distinct in size, morphological differences, and mineral encrustations. Nevertheless, the tire cryogrind provides a useful reference for comparing the TRWPs. Metals and alloys like Al, Fe, K, Ca, and Mg were detected in the TRWP samples because of their interactions with the road pavement surface.^{13,44} TRWPs also contained higher amounts of elements than the reference cryogrinds, which is consistent with the earlier reported literature.¹⁰¹

3.2. TRWP Identification and Analysis of Particle Size <1 mm. TRWP particles of a size range of <1 mm from the roadside soils were extracted with THF, and the contents of the extracts were tentatively identified using GC–MS, to identify the intermediates associated with TRWPs. The short-listed intermediates and transformation products found in the TRWP analysis are tabulated in Table 2. The corresponding GC–MS spectra with the NIST database comparison are provided in Figures S6 and S7, respectively. Table S8 contains a representative chromatogram and compound summary for the control soil.

The compounds in Table 2 were short-listed based on our knowledge of the tire formulation and the many referenced reports in the literature.^{41,45,103–108} The ketones, carboxylic acids, and epoxides reported in our recent publication⁴⁸ were observed in these roadside soil samples. Several of the tentatively identified cyclohexane- and benzoic acid-related compounds can be traced back to tire components, such as styrene–butadiene–rubber (SBR). It is important to note that benzoic derivatives may be prevalent in the environment as they are often used as biocides. Among the additives present, compounds based on benzothiazole sulfenamide (BTS) were the most prominent additives in many of the soil samples.

BTs, which serve as anticorrosive additives in anti-icing fluids,¹⁰⁹ are most widely used as accelerators for rubber vulcanization and to enhance abrasion resistance and mechanical strength of tires.⁵⁰ They have acute aquatic toxicity, are hazardous to plants, and cause skin sensitization and respiratory irritation.¹¹⁰ Many plastic impurities were also tentatively identified in the soil (see Table S9).

The methodology presented in Figure 1 was successful at separating, identifying, and analyzing TRWPs in roadside soil samples. The tire-related intermediates we observed by GC–MS were confirmed using SEM-EDX, TGA, and FTIR analyses. While several transformation products of BTS were earlier reported in water and air samples,^{21,89,111–114} our results suggests that they also remain in terrestrial samples. Our data provided lab-scale validation of our analytical workflow with representative environment samples. Even though a plethora of recent publications shows the presence of TRWPs in road dust of particles less than <50 μm ,⁹⁹ our research characterized roadside soil samples with TRWP sizes ranging from 100 to 5000 μm . The results elucidated here open a new venue for identifying the tire-related compounds in

environmental samples and creating a wider TRWP database. Further, they can be used as a foundational prerequisite for all TRWP identification and quantification attempts relating to roadside soil samples.

TRWP quantification requires a specific marker selection via internal/external calibration, if evaluated by GC–MS/LC–MS techniques. The former aspect must be investigated via further studies with yet-to-be-established, clearly defined marker compounds and standards for TRWP research. We intend to publish the ongoing work on TRWP quantification soon. Our results and others' results⁹⁹ demonstrate that BT (benzothiazole) can be a good candidate for establishing quantification protocols. However, various nontire sources of BT, 2-(4-morpholinyl) benzothiazole (24 MoBT), can also be proposed as a potential indicator¹¹⁵ for TRWP contribution in roadside soil samples.

The proposed protocol has several analytical limitations in need of improvement. Recent literature suggests density separation media of 2.2 g cm⁻³ as an ideal method for complete recovery of TRWPs from soil as mineral encrustations might result in a broader particle density range.⁴⁶ This aspect needs further investigation and well-defined data sets to be established. A complete removal of soil debris in the extraction of TRWPs using this protocol has not been achieved. Also, weathering of tire particles in environmental samples poses a challenge in the identification and analysis of TRWPs, and several researchers,¹¹⁶ including our lab,⁴⁸ are working on a wider database of weathered rubber to assist in the same. SEM-EDX analysis may also identify Zn and S from road paint, brake wear, nonexhaust sources,^{117,118} and Si from concrete, soil, and road wear.¹⁰¹ However, even though these markers are not just specific to tires, the multifaceted evidence approach proposed here can aid in the identification and analysis of TRWPs. ToF-SIMS analysis described by Kovoichich et al.⁴⁶ can also be employed for mapping organic surface markers like C₆H₅⁺. Future research needs to concentrate on the interconnection of TRWPs and tire particles in the water and air and source-pathways, especially from leaching.

Extensive data on the TRWPs in soil samples are lacking in the literature, and our cognition of TRWPs in the roadside soil is still fragmented. A comprehensive study of more roadside soil samples and a corresponding protocol are necessary for more detailed insight regarding the efficacy of the protocol. Soil is considered the "storage vault" for TRWPs through which the compounds leach into water bodies. Further TRWP research is certainly imperative in fully grasping adverse effects of the microplastics as it is emerging as a hotspot of microplastics outflow. The research presented here aids in developing simple, reliable methods for TRWP detection and analysis, which can be refined and validated across different laboratories in the future for TRWP research. Further, a critical overview of the method development process was also provided for emphasizing the applicability of the protocol.

This study reported the first generalized soil sample preparation protocol for TRWP separation and analysis from roadside soil samples. A meticulous soil extraction protocol with soil sampling, purification, extraction, identification, and analysis steps was proposed. TRWP identification and analysis were primarily evaluated by comparing single particle characteristics to reference cryogrinds using TGA, FTIR, and SEM-EDX and by GC–MS. Ketones, carboxylic acids, epoxies, cyclohexane, and BTS intermediates were the most common

possible tire-related intermediates observed in the roadside soil samples. Among them, BTS intermediates could be potential markers that can be utilized in quantitative TRWP research. Thus, this paper contributes further to the current state of the art TRWP research, by testing on real terrestrial environmental soil samples, which is of great importance to the ongoing and future TRWP-related and general traditional microplastics research.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.2c03695>.

Details on average daily traffic at sampling locations; geographic locations of soil sample sites; basic soil characteristics; details on organic matter reduction; SEM-EDX data of the cryogrind samples and TRWPs; GC–MS spectra; NIST database comparison to intermediates; ion chromatogram of <1 mm soil from the secluded area; and compounds identified by GC–MS in nonseparated soils (PDF)

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Notes

The authors declare no competing financial interest.

Biography

Dr. Teresa Cutright is a Professor of Civil Engineering at the University of Akron. Dr. Cutright holds degrees in Chemical Engineering with emphasis on environmental remediation techniques. She has over 25 years of experience conducting site assessments, soil characterizations, treatability, and remediation studies for a variety of environmental contaminants. Based on her expertise, Dr. Cutright is serving on the Science Advisory Council for the State of Ohio's Attorney General.

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