Introduction

Recycled tire crumb rubber (TCR) is often used as an additive material in synthetic turf playing fields as well as other playgrounds. Concerns have been raised about the safety of this material and a multi-agency Federal Research Action Plan on Recycled Tire-Related Chemicals (TCR) has been put in place to investigate key factors that could impact the environment and human health.

Here we present work done to characterize semi-volatile organic compounds (SVOCs) from the solvent extraction of TCR and atrochemical experiments.

A wide range of SVOCs (including phthalates, polycyclic aromatic hydrocarbons (PAHs) and chemicals related to rubber manufacturing) were selected for targeted analysis.

Solvent selection, extraction techniques, and instrument parameters were investigated in order to better understand the TCR material and to develop the methods and appropriate QA/QC required for sample analysis.

Sample Collection

TCR samples were collected from nine tire recycling plants and 40 synthetic turf fields across the U.S. and were divided into sub-samples for characterization experiments (Figure 1).

Emissions experiments were conducted at 25°C, 46% Relative Humidity (RH) and 1.7 L/min change (AIR) rate, and 60°C, 6.6% RH, 1.9 L/min dynamic emission micro chambers (Figure 2).

TCR and emissions samples collected for FAE (Figure 1) were extracted with 1:1 Acetone/Hexane and prepared for analysis (Figure 4).

Data were acquired for all samples using GC/MS/MS in MRM mode with a calibration range of 0.1–200 µg/L. The data were derived based on accuracy of standards compared to the calibration curve, ranged from 0.1 to 150 µg/L.

Non-targeted analysis was also performed by acquiring data by GC/MS in scan mode (15–220 m/z) and then deconvoluting and library matching the spectra to tentatively identify components.

Data obtained from these analyses will be used in conjunction with the other analyses that were conducted as part of the Federal Research Action Plan to identify key TCR chemical constituents, aid exposure assessment, and infer future studies related to TCR exposure.

Sample Preparation

Stage 1: Sample Preparation

- TCR samples were collected from nine tire recycling plants and 40 synthetic turf fields across the U.S. and were divided into sub-samples for characterization experiments (Figure 1).
- Emissions experiments were conducted at 25°C, 46% Relative Humidity (RH) and 1.7 L/min change (AIR) rate, and 60°C, 6.6% RH, 1.9 L/min dynamic emission micro chambers (Figure 2).

Stage 2: TCR and emissions samples collected for FAE (Figure 1) were extracted with 1:1 Acetone/Hexane and prepared for analysis (Figure 4).

Stage 3: Data were acquired for all samples using GC/MS/MS in MRM mode with a calibration range of 0.1–200 µg/L. The data were derived based on accuracy of standards compared to the calibration curve, ranged from 0.1 to 150 µg/L.

Stage 4: Non-targeted analysis was also performed by acquiring data by GC/MS in scan mode (15–220 m/z) and then deconvoluting and library matching the spectra to tentatively identify components.

Stage 5: Data obtained from these analyses will be used in conjunction with the other analyses that were conducted as part of the Federal Research Action Plan to identify key TCR chemical constituents, aid exposure assessment, and infer future studies related to TCR exposure.

Discussion

- Several solvent systems were evaluated and 1:1 Acetone/Hexane was selected based on its effectiveness without altering the rubber matrix.
- Targeted analysis of TCR and emissions samples was used to determine compounds to be prepared with headspace solutions to prevent solvent and sample loss. The reference standard was used in the extraction of the sample to surrogate.
- For emissions samples, matrix blanks and spiking and a recovery spike were used for QC/QC samples.
- Twenty-one organosulfur compounds were used as internal standards.
- TCR extracts were divided into 1:1 and 1:30 following sample extraction in order to stay within the analytical range of the GC/MS/MS system (0.1–150 µg/L).
- Several compounds, primarily amines and hydroxy amines, required GC/MS analysis for accurate quantification.
- Preliminary work indicated that FAE and other media need to be solvent cleaned and dried in a stainless steel septum to purge with proper grade nitrogen.
- Tire crumb rubber is a complex mixture requiring careful choices of solvents and analytical approaches.
- Targeted analysis provides valuable information on tire crumb chemical constituents and potential emissions.
- Due to the low recoveries, an extraction protocol is required to fully elucidate chemical mixtures relevant for exposure assessment.

Figure 2. TCR in Dynamic Emissions

Figure 3. PUF Plug in a Glass Cartridge

Figure 4. Sample Preparation Workflow

Figure 5. Emissions Sample Extraction

Figure 6. TCR Extraction

Figure 7. Vortex Mixing

Figure 8. PUF Plug Added to a 60 mL Jar

Figure 9. Extracts were Transferred to 250 mL Bottles

Figure 10. Micro Chambers

Figure 11. GC/MS/MS analysis (Table 1 and 2, Figure 11)

Figure 12. Representative emissions

Figure 13. Representative GC/MS/MS chromatograms of the analytical range

Figure 15. GC/MS/MS analysis (Table 3, Figure 12 and 13)