# Characterization of Semi-Volatile Organic Chemicals from Tire Crumb Rubber

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## INTRODUCTION

- Recycled tire crumb rubber (TCR) is often used as infill material in synthetic turf playing fields as well as some playgrounds.
- Concerns have been raised about the safety of this material and a multi-agency Federal Research Action Plan on Recycled Tire Crumb Used on Playing Fields and Playgrounds was developed 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 direct solvent extraction of TCR and airborne emissions experiments.
- A wide range of SVOCs (including PAHs, phthalates, 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 QAQC required for sample analysis.

## GENERAL APPROACH

- TCR samples were collected from nine tire recycling plants and 40 synthetic turf fields across the U.S. and were divided into subsamples for characterization experiments (Figure 1).
- Emissions experiments were conducted at 25ºC, 46 % Relative Humidity (RH) and 1 $h^{-1}$ air change (ACH) rate, and 60ºC, 6.6 % RH, 1 $h^{-1}$ ACH in dynamic emission micro chambers (Figure 2)
- TCR and emissions samples collected on PUF (Figure 3) 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 0.1-500 pg/µL. MQLs, which were derived based on accuracy of standards compared to the calibration curves, ranged from 0.1-10 pg/µL.
- Non-targeted analysis was also performed by acquiring data by GCMS in scan mode (50-550 m/z) and then deconvoluting and library matching the spectra to tentatively identify components.
- Data obtained from the SVOC 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 inform future studies related to TCR exposure.

## SAMPLE COLLECTION

Figure 1. Subsample Preparation

Figure 2. TCR in Dynamic Emissions Micro Chambers

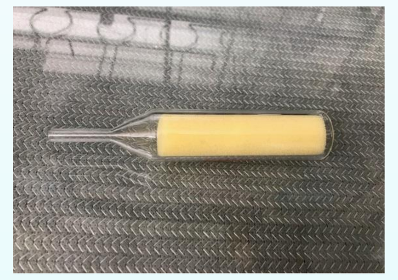

Figure 3. PUF Plug in a Glass Cartridge

## SAMPLE PREPARATION

Figure 4. Sample Preparation Workflow

**TCR Extraction**

1. 1 g of TCR sample weighed into a 50 mL tube (Figure 5)
2. Add IS solution, a ceramic homogenizer and 10 mL of 1:1 Acetone:Hexane (Figure 6)
3. Vortex for 1 minute (Figure 7)
4. Let sit for 2 minutes
5. Vortex for an additional minute
6. Centrifuge at 4000 RPM for 5 minutes
7. Transfer the extract into a 15 mL amber vial with a PTFE-lined cap.
8. Transfer 1 mL to an autosampler vial for GC/MS/MS Analysis

**Emissions Sample Extraction**

1. PUF Plug is transferred to a 60 mL amber jar (Figure 8)
2. Collection tube is rinsed with 1:1 Acetone Hexane into the jar
3. Add IS Solution and 50 mL of 1:1 Acetone Hexane
4. Sonicate for 15 minutes
5. Transfer extract to a 250 mL bottle (Figure 9)
6. Add solvent, sonicate and transfer two more times
7. Concentrate the extract to 2-5 mL with a parallel evaporator (Figure 10)
8. Transfer the concentrated extract to a 15 mL graduated tube
9. Evaporate to a final volume of 1 mL under nitrogen
10. Transfer to an autosampler vial for GC/MS/MS analysis (Table 1 and 2, Figure 11)
11. Perform Non-targeted Analysis by GC/MS (Table 3, Figure 12 and 13)

Figure 5. TCR was Weighed into a 50 mL Tube

Figure 8. PUF Plug Added to a 60 mL Jar

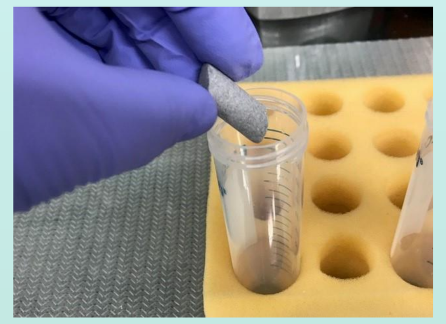

Figure 6. Adding a Ceramic Homogenizer

Figure 9. Extracts were Transferred to 250 mL Bottles

Figure 7. Vortex Mixing

Figure 10. Extracts Concentrated with a Parallel Evaporator

## SAMPLE ANALYSIS PARAMETERS

| Parameter | Value |
|---|---|
| GC System | Agilent 7890 Gas chromatograph |
| Injector | Capillary injector in splitless mode<br>Pulsed splitless at 25 psi for 0.5 min, then split at 50 mL/min at 1 min.<br>Temperature: 250ºC<br>Liner: Single gooseneck glass, deactivated<br>Injection volume: 1 µL |
| Column | Agilent VF-5ms, 30 M x 0.25 mm x 0.25 µm,<br>Column flow: 1.2 mL/min |
| Temperature Program | 50º C for 2 min to 325º C at 10º C/min, hold 5 min. |
| Detector | Agilent 7010 Triple Quadrupole<br>Mode: Electron Impact (EI) operating in MRM/Scan mode<br>Electron Multiplier Voltage by Gain Curve<br>Transfer Line: 300º |

Table 1. GC/MS/MS Conditions

| Parameter | Value |
|---|---|
| GC System | Agilent 6890 Gas chromatograph |
| Injector | Capillary injector in splitless mode, Split at 50 mL/min at 0.75 min.<br>Temperature: 250ºC<br>Liner: Single gooseneck glass, deactivated<br>Injection volume: 1 µL |
| Column | Restek RTX-5 Sil MS, 60 M x 0.25 mm x 0.25 µm,<br>Column flow: 1.0 mL/min |
| Temperature Program | 40º C for 2 min to 340º C at 5º C/min, hold 5 min. |
| Detector | Agilent 5973 MSD, Transfer Line: 300º<br>Mode: Electron Impact (EI) operating in Scan mode<br>Scan Range – 50-550 m/z<br>Threshold = 1000<br>Scan rate – 1.52 Scans/s<br>Electron Multiplier - Tune + 400V |

Table 3. GC/MS Conditions for Non-Targeted Analysis

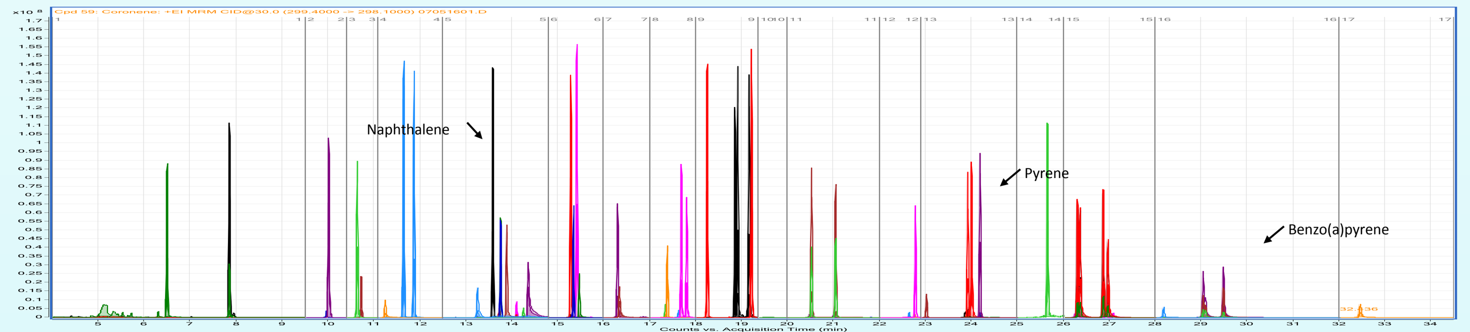


Figure 11. Representative MRM Chromatogram

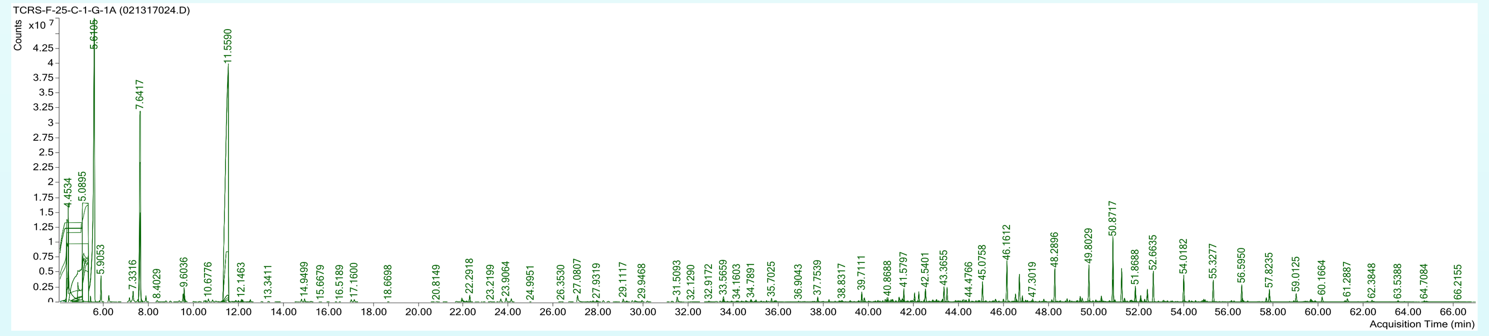


Figure 12. Representative Deconvoluted Chromatogram for TCR Collected from a Field

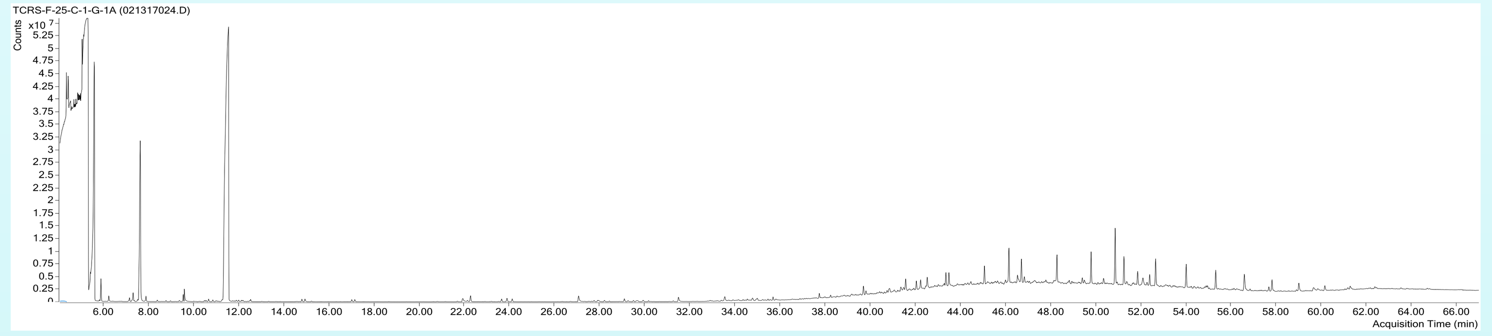


Figure 13. Representative Total Ion Chromatogram for TCR Collected from a Field

| Time Segment | Compound | Class | RT | Pre1 | Prod 1 | Prod1 CE | Pre2 | Prod 2 | Prod2 CE | Pre3 | Prod 3 | Prod3 CE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Cyclohexaneamine | TCR | 4.471 | 69.8 | 43.1 | 15 | 99.8 | 56 | 10 | | | |
| 1 | Analine | TCR | 6.521 | 92.7 | 66.1 | 15 | 65 | 39.1 | 15 | | | |
| 1 | n-Butylbenzene | TCR | 7.858 | 90.5 | 65.1 | 20 | 134 | 91.2 | 25 | | | |
| 2 | Naphthalene d8 | PAH | 9.956 | 136 | 108.1 | 10 | 136 | 84.1 | 30 | | | |
| 2 | Naphthalene | PAH | 10.003 | 127.9 | 102.1 | 20 | 127.9 | 78.1 | 20 | | | |
| 3 | Benzothiazole | TCR | 10.62 | 135 | 82.1 | 30 | 135 | 108 | 20 | | | |
| 3 | Cyclohexylisothiocyanate | TCR | 10.713 | 81.9 | 67 | 10 | 140.6 | 55.1 | 25 | | | |
| 4 | Resorcinol | TCR | 11.241 | 109.8 | 82.1 | 15 | 109.8 | 69 | 20 | | | |
| 4 | 2-Methylnaphthalene | PAH | 11.638 | 142.3 | 141.2 | 20 | 142.3 | 115.1 | 45 | 114.7 | 89.1 | 20 |
| 4 | 1-Methylnaphthalene | PAH | 11.863 | 142.3 | 141.2 | 20 | 142.3 | 115.1 | 45 | 114.7 | 89.1 | 20 |
| 5 | Dicyclohexamine | TCR | 13.229 | 137.5 | 56.1 | 10 | 137.5 | 83.1 | 15 | | | |
| 5 | Dimethyl phthalate | Phthalate | 13.584 | 163 | 77 | 30 | 163 | 135 | 15 | | | |
| 5 | Acenaphthalene d8 | PAH | 13.712 | 159.9 | 158.1 | 20 | 159.9 | 132.1 | 20 | | | |
| 5 | Acenaphthalene | PAH | 13.743 | 151.9 | 126.1 | 30 | 151.9 | 102.1 | 30 | | | |
| 5 | Phthalimide | TCR | 13.889 | 146.8 | 103.1 | 10 | 146.8 | 76.1 | 35 | | | |
| 5 | Acenaphthene d10 | PAH | 14.092 | 164.1 | 162.1 | 30 | 162.1 | 160.1 | 15 | | | |
| 5 | Acenaphthene | PAH | 14.169 | 152.1 | 126.1 | 30 | 152.1 | 102.1 | 30 | | | |
| 5 | 2,6-Di-tert-butyl-p-cresol | TCR | 14.241 | 144.5 | 105.1 | 15 | 144.5 | 129.1 | 20 | | | |
| 5 | N,N-Dicyclohexylmethylamine | TCR | 14.33 | 151.5 | 70.1 | 10 | 151.5 | 55.1 | 25 | | | |
| 6 | Diethyl phthalate d4 | Phthalate | 15.252 | 153 | 69.1 | 50 | 153 | 97.1 | 30 | | | |
| 6 | Diethyl phthalate | Phthalate | 15.278 | 149 | 65 | 30 | 149 | 93 | 20 | | | |
| 6 | n-Hexadecane | TCR | 15.322 | 85.1 | 43.1 | 10 | 98.9 | 57.1 | 10 | | | |
| 6 | Fluorene d10 | PAH | 15.33 | 176 | 174.2 | 20 | 175 | 172.1 | 50 | | | |
| 6 | Fluorene | PAH | 15.401 | 166.1 | 165.1 | 15 | 165.1 | 164.1 | 15 | | | |
| 6 | 4-tert-Octylphenol | TCR | 15.453 | 106.8 | 77.1 | 20 | 134.3 | 107.1 | 15 | | | |
| 7 | 2-Bromomethylnaphthalene | PAH | 16.29 | 140.6 | 115.1 | 20 | 219.8 | 141.1 | 10 | | | |
| 7 | 2-Hydroxybenzothiazole | BT | 16.396 | 150.7 | 96.1 | 25 | 150.7 | 123.1 | 20 | | | |
| 8 | Dibenzothiophene d8 | BT | 17.34 | 191.5 | 146.1 | 50 | 191.5 | 160.1 | 30 | | | |
| 8 | Dibenzothiophene | BT | 17.385 | 183.4 | 139.1 | 25 | 183.4 | 152.1 | 50 | | | |
| 8 | Phenanthrene d10 | PAH | 17.622 | 188.3 | 160.2 | 40 | 188.3 | 186.3 | 30 | | | |
| 8 | Phenanthrene | PAH | 17.678 | 177.9 | 152.1 | 25 | 176.1 | 150.1 | 25 | | | |
| 8 | Anthracene | PAH | 17.8 | 177.9 | 152.1 | 25 | 176.1 | 150.1 | 25 | | | |
| 9 | Diisobutyl phthalate | Phthalate | 18.249 | 149 | 65 | 25 | 149 | 93 | 15 | | | |
| 9 | 3-Methylphenanthrene | PAH | 18.843 | 192.2 | 191.2 | 20 | 188.7 | 163.1 | 40 | 192.2 | 165.1 | 45 |
| 9 | 2-Methylphenanthrene | PAH | 18.906 | 188.7 | 163.1 | 40 | 192.2 | 191.2 | 20 | 192.2 | 165.1 | 45 |
| 9 | 1-Methylphenanthrene | PAH | 19.153 | 188.7 | 163.1 | 40 | 192.2 | 191.2 | 20 | 192.2 | 165.1 | 45 |
| 9 | Dibutyl phthalate | Phthalate | 19.212 | 149 | 65 | 30 | 149 | 93 | 20 | | | |
| 10 | 2-Mercaptobenzothiazole | TCR | 19.45 | 166.5 | 123 | 10 | 166.5 | 109 | 30 | | | |
| 11 | Fluoranthene d10 | PAH | 20.467 | 211.9 | 210.2 | 20 | 211.9 | 208.1 | 20 | | | |
| 11 | Fluoranthene | PAH | 20.51 | 202.1 | 200.1 | 30 | 202.1 | 152.1 | 30 | | | |
| 11 | Pyrene d10 | PAH | 20.994 | 211.9 | 210.2 | 20 | 211.9 | 208.1 | 20 | | | |
| 11 | Pyrene | PAH | 21.036 | 201.1 | 200.1 | 15 | 200.1 | 174.1 | 30 | | | |
| 12 | Di-N-hexylphthalate (2)13C2 | Phthalate | 22.647 | 153 | 66 | 25 | 153 | 95.1 | 20 | | | |
| 12 | Benzyl butyl phthalate d4 | Phthalate | 22.756 | 153 | 69.1 | 25 | 153 | 97.1 | 5 | | | |
| 12 | Benzyl butyl phthalate | Phthalate | 22.77 | 149 | 65 | 25 | 91 | 65 | 15 | | | |
| 13 | bis(2-Ethylhexyl) adipate | Phthalate | 23.017 | 147 | 55.1 | 25 | 111 | 55.1 | 15 | | | |
| 13 | Benz(a)anthracene d12 | PAH | 23.858 | 240.2 | 236.2 | 50 | 118.1 | 116.1 | 15 | | | |
| 13 | Benz(a)anthracene | PAH | 23.911 | 228.1 | 226.2 | 30 | 114 | 101.1 | 10 | | | |
| 13 | Chrysene d12 | PAH | 23.929 | 240.2 | 236.2 | 50 | 118.1 | 116.1 | 15 | | | |
| 13 | Chrysene | PAH | 23.989 | 228.1 | 226.2 | 30 | 114 | 101.1 | 10 | | | |
| 13 | Bis-2-ethylhexyl phthalate d4 | Phthalate | 24.165 | 153 | 69.1 | 25 | 153 | 97.1 | 20 | | | |
| 13 | Bis-2-ethylhexyl phthalate | Phthalate | 24.184 | 149 | 65 | 30 | 149 | 93 | 20 | | | |
| 13 | 1-Hydroxypyrene | PAH | 24.195 | 217.5 | 189.1 | 40 | 188.5 | 163.1 | 40 | | | |
| 14 | Di-n-octyl phthalate | Phthalate | 25.65 | 149 | 65 | 30 | 149 | 93 | 20 | | | |
| 15 | Benzo(b)fluoranthene d12 | PAH | 26.243 | 263.9 | 260.2 | 50 | 132.2 | 118.1 | 10 | | | |
| 15 | Benzo(b)fluoranthene | PAH | 26.297 | 126.1 | 113.1 | 10 | 252.1 | 250.2 | 35 | | | |
| 15 | Benzo(k)fluoranthene d12 | PAH | 26.311 | 263.9 | 260.2 | 50 | 132.2 | 118.1 | 10 | | | |
| 15 | Benzo(k)fluoranthene | PAH | 26.355 | 252.1 | 250.2 | 35 | 126.1 | 113.1 | 10 | | | |
| 15 | Benzo(e)pyrene d12 | PAH | 26.84 | 264 | 260.2 | 40 | 132.2 | 118.1 | 15 | | | |
| 15 | Benzo(e)pyrene | PAH | 26.86 | 252 | 250.2 | 50 | 125 | 112 | 20 | | | |
| 15 | Benzo(a)pyrene d12 | PAH | 26.907 | 264 | 260.2 | 40 | 132.2 | 118.1 | 15 | | | |
| 15 | Benzo(a)pyrene | PAH | 26.959 | 252.1 | 250.1 | 35 | 125 | 124.2 | 10 | | | |
| 15 | Perylene d12 | PAH | 27.08 | 264 | 260.1 | 40 | 130.1 | 116.1 | 15 | | | |
| 16 | Bis(2,2,6,6-tetramethyl-4piperidyl) sebecate | TCR | 28.153 | 123.6 | 107.1 | 10 | 97.6 | 42.1 | 20 | | | |
| 16 | Indeno[1,2,3-cd]pyrene d12 | PAH | 28.988 | 288 | 284.2 | 50 | 288 | 286.2 | 40 | | | |
| 16 | Dibenz(a,h)anthracene d14 | PAH | 29.022 | 288 | 284.2 | 50 | 288 | 286.2 | 40 | | | |
| 16 | Indeno(1,2,3-cd)pyrene | PAH | 29.03 | 138.1 | 137.2 | 10 | 137 | 136.1 | 15 | | | |
| 16 | Dibenz(a,h)anthracene | PAH | 29.075 | 138.1 | 137.2 | 10 | 125 | 124.2 | 10 | | | |
| 16 | Benzo(g,h,i)perylene d12 | PAH | 29.43 | 288 | 284.2 | 50 | 288 | 286.2 | 20 | | | |
| 16 | Benzo(g,h,i)perylene | PAH | 29.473 | 276.1 | 274.1 | 45 | 138 | 125.1 | 15 | | | |
| 17 | Coronene | PAH | 32.449 | 299.4 | 298.1 | 30 | 299.4 | 298.1 | 30 | | | |

Table 2. Target Analytes and Transitions Monitored

## DISCUSSION

- Several solvent systems were evaluated and 1:1 Acetone Hexane was selected based on it's effectiveness without solvating the rubber itself.
- For TCR extraction, a composite TCR sample was prepared and was used as a reference sample to be prepared with all sample batches along with reagent blanks and spikes. The reference sample was used due to the lack of a suitable TCR surrogate.
- For Emissions samples, matrix blanks and spikes and a recovery spike were used for QAQC samples.
- Twenty-one isotopically labelled analogs were used as internal and surrogate standards.
- TCR extracts were diluted 1/10 and 1/100 following sample extraction in order to stay within the analytical range of the GC/MS/MS system (0.1-500 ng/mL)
- Several compounds, primarily amines and hydroxy PAHs, required LC/MS analysis for accurate quantification.
- Preliminary work indicated that PUF and other media need to be solvent cleaned and dried in a stainless steel vessel by purging with carrier grade nitrogen.
- Tire crumb rubber is a complex matrix requiring careful choices of solvents and analytical approaches
- Extractions result in a complex mixture of SVOCs requiring substantial data processing
- Targeted analyte provide valuable information on tire crumb chemical constituents and potential emissions
- Further non-targeted assessment is required to fully elucidate chemical mixtures relevant for exposure assessment