



Multimodal Physicochemical Characterization of Tire Crumbs Used at Synthetic Turf Fields

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INTRODUCTION

- Granular recycled tire rubber (tire crumb – TC) is used as infill in synthetic turf at athletic fields, playgrounds, and physical training facilities.
- There has been some public concern regarding potential health effects from the use of TC.
- The U.S. Environmental Protection Agency (EPA), the Centers for Disease Control and Prevention/Agency for Toxic Substances and Disease Registry (ATSDR), and the U.S. Consumer Product Safety Commission (CPSC) developed a multi-agency research action plan to study key environmental human health questions related to TC use (EPA 2016).
- As part of an assessment of human exposure potential, a study to characterize the physicochemical properties of TC from 9 recycling plants and 40 synthetic turf fields is underway.
- This poster presents a multimodal approach used by EPA to characterize the trace elemental composition and size distribution of TC in these samples.

GENERAL APPROACH

- Two methods for determining concentrations of trace elements were used.
 - “Total recoverable” element concentrations were obtained by strong acid digestion and inductively coupled plasma mass spectrometry (ICPMS). Selected elements were determined in the high-resolution mode to minimize interferences.
 - X-ray fluorescence was used to estimate the total trace element concentrations in the original TC material without digestion.
- The size distribution of the TC material (particle size analysis – PSA) was determined by a sequential sieving method.
- The size distribution of the fine particles recovered in PSA was further refined using scanning electron microscopy (SEM), which also provided particle morphology.
- Electron probe microanalysis (EPMA) provided elemental composition information on individual fine particles.



EXPERIMENTAL

Sample Collection/Preparation

Details of the TC sampling strategy and procedures are available in EPA 2016. Samples were collected into cleaned 1-L polyethylene bottles using plastic implements.

Microwave Digestion and ICPMS Analysis

- A microwave-assisted digestion protocol was optimized for bulk tire crumb samples composed of particles of varying sizes. This digestion protocol used EPA method 3051A (EPA 2017) as the core digestion procedure and included necessary pre-digestion steps.
 - Subsamples of TC (250 mg) were suspended in a 3:1 mixture of nitric acid and hydrochloric acid.
 - The sealed sample vessels were gently warmed in a CEM MARS-5™ microwave system.
 - The vessels were allowed to stand overnight at room temperature, giving enough time for the acid mixture to permeate the disintegrated rubber particles.
 - Full digestion was performed at 200°C.
- Elemental analysis was performed on a Thermo Fisher Scientific Element 2™ double focusing magnetic sector field inductively coupled plasma mass spectrometer (ICPMS).
- A Multi-elemental quantitative method utilizing low, medium, and high resolution settings was chosen.
- On-line internal standard mixing, 100 µL/min PFA-ST micronebulizer and quartz cyclonic spray chamber (Elemental Scientific™, Omaha, NE) were used for sample introduction.
- Samples were gravimetrically diluted to minimize matrix effects, using a diluent of nitric acid and hydrochloric acid (2% and 1% by volume, respectively).

Particle Size Analysis and XRF

- Particle Size Analysis was done using USA Standard Test Sieves (ASTM E-11). The sizes used were numbers 10 (2.00 mm), 18 (1.00mm), 60 (0.25mm), 120 (0.125mm), 230 (0.063mm) and a bottom pan. The sieve stack was placed on a vibratory shaker and vibrated for 15 minutes. After shaking, the mass retained on each size was recorded.
- A subset of the samples received contained a uniform mineral sand component that was retained on the #60 (0.25mm) sieve. A flotation technique using sulfate or chloride solutions was used to separate the denser sand from the tire crumb material.
- XRF analysis was done on bulk samples received for metals analysis, along with samples from each fraction generated by the PSA procedure. The XRF analysis was performed with an Innov-X Alpha series field portable spectrometer™. The analysis was performed using both the standard and light element modes to give results in ppm for a suite of elements.

SEM/EPMA

- Entire fractions from the PSA retained on the #230 sieve and in the bottom pan were collected separately (nominal sizes 63 – 125 µm and < 63 µm, respectively).
- Fractions were repeatedly coned and quartered until a quantity was obtained that widely dispersed over about a 1 inch diameter circular area. Those subsamples were transferred to 1 inch diameter double-sided adhesive conductive carbon tabs mounted on SEM sample stubs.
- SEM was performed with a Zeiss Sigma VP instrument at 25 kV accelerating voltage with backscatter electron detection to provide Z-contrast between particles of similar elemental composition.
- Imaging was performed at 17 predefined locations in a radial pattern 0, 5.5, and 11 mm from the stub center. Each location was imaged at a magnification of 150x for larger particle size analysis (> 100 µm² projected area). Areas within each location with several small particles were imaged at 1200x for smaller particle size analysis (0.5 – 100 µm²).
- Particle size distributions were determined using ImageJ software.
- Selected particles were analyzed by EPMA in the single-point mode with a Bruker Quantax X-ray spectrometer.

METHODS STATUS

ICPMS and XRF

- Some of the analytes selected for the EPA tire crumb rubber study are presented in **Figure 1**.
- XRF measures total element concentration in the original sample, while ICPMS measures the concentration recoverable by digestion. This explains the lower concentration values reported by ICPMS.
- The poor precision and sensitivity of the XRF technique and the lack of a suitable standard reference material for TC limits the applicability of XRF to a screening tool in this study.
- Analytical results generated have not been finalized. However preliminary data obtained for zinc and sulfur seem consistent with concentrations used in rubber formulation.

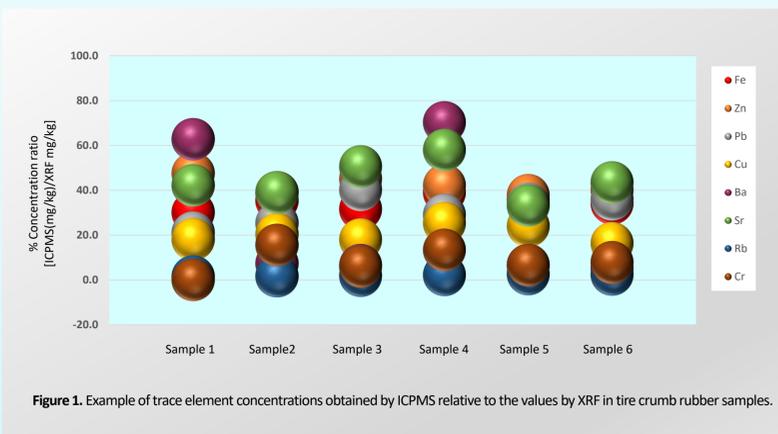


Figure 1. Example of trace element concentrations obtained by ICPMS relative to the values by XRF in tire crumb rubber samples.

PSA

- Examples of sample PSA results are shown in **Figure 2**.
- Nearly 100% of the TC mass was in the size range of 0.25 mm to 4.75 mm.
- The recovery of mass in the sieve fractions was between 99.9 and 100.2%.
- The amount of TC below 0.125 mm nominal size (the fraction submitted to SEM/EPMA analysis) averaged 0.08% by mass.

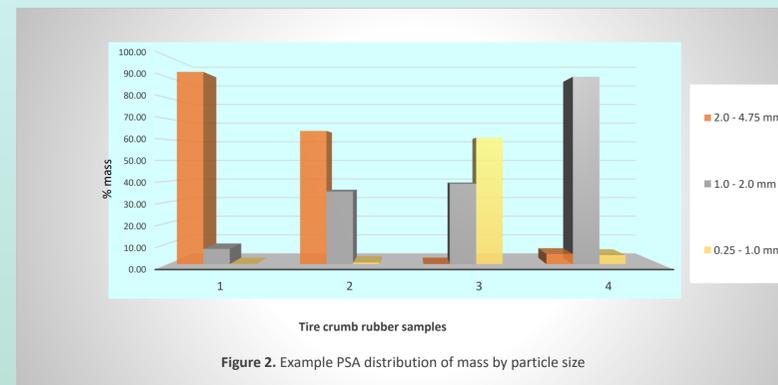


Figure 2. Example PSA distribution of mass by particle size

SEM

- The SEM images were analyzed for projected particle area manually with ImageJ (**Figure 3**). The linear scale of the image was calibrated, and the brightness threshold was set to eliminate most background noise. Areas of remaining background above the threshold were cropped from the image, and the particle projected areas were measured with the Analyze Particles function with the minimum area thresholds described in the Experimental section.
- The image analysis was dependent on a subjective setting of brightness threshold. Inter-analyst variability of the image analysis of mean projected area was evaluated and found to be approximately 3%.
- Possible particle size variation with location on the SEM stub was evaluated, because smaller particles might migrate further from the center of the subsample area during preparation. However, the mean projected area for particles 5.5 mm from the stub center was statistically indistinguishable from the mean for particles 11 mm from the center.

EPMA

- Single-point EPMA acquired an X-ray spectrum for 60 s produced by the 25 kV electron beam focused on a single particle.
- Figure 4** shows an example of an SEM image of an approximately 15 µm particle and the EPMA spectrum obtained from the point indicated by + in the image. The spectrum shows strong Fe, Cr, and Ni lines, consistent with a steel particle.
- Elemental mapping EPMA collects X-ray spectra over the entire SEM image. Acquisition time is longer than single-point EPMA (typically 10 min), and sensitivity is not as high, because data is collected for each pixel for a short time.
- Figure 5** shows an SEM image and the corresponding elemental mapping EPMA image of a TC.

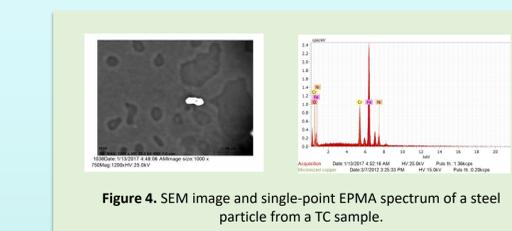


Figure 4. SEM image and single-point EPMA spectrum of a steel particle from a TC sample.

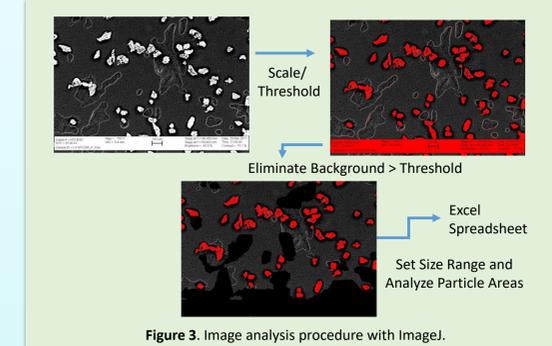


Figure 3. Image analysis procedure with ImageJ.

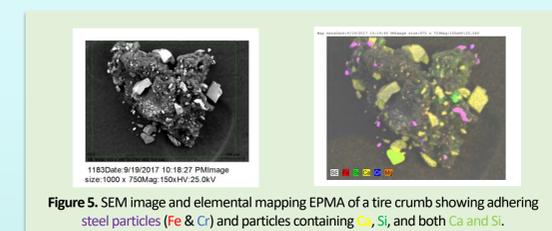


Figure 5. SEM image and elemental mapping EPMA of a tire crumb showing adhering steel particles (Fe & Cr) and particles containing Ca, Si, and both Ca and Si.

PRELIMINARY OBSERVATIONS

This multimodal characterization approach takes advantage of the complementary strengths of several techniques.

- XRF analysis provides screening estimates of total element concentrations in the solid TC material without digestion.
- Digestion followed by ICPMS determines total recoverable element concentration with high sensitivity and precision.
- PSA using sieving allows description of the gross size distribution of the TC material.
- SEM provides information on the size of fine TC particles (i.e., projected area distribution).
- EPMA is used to determine elemental composition of individual particles. In the single point mode, it provides sensitive detection of elements with X-ray emission lines up to about 10 keV (limited by the 25 keV electron beam). The elemental mapping mode allows visualization of selected elements within particles.

References:

- EPA 2016. Federal Research Action Plan on Recycled Tire Crumb Used on Playing Fields and Playgrounds Status Report. https://www.epa.gov/sites/production/files/201612/documents/federal_research_action_plan_on_recycled_tire_crumb_used_on_playing_fields_and_playgrounds_status_report.pdf. Retrieved September 12, 2017.
- EPA 2017. U.S.E.P.A. SW-846 Method 3051A. Microwave Assisted Acid Digestion of sediments, sludges, soils and oils; Revision 1, February 2007.