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DEPARTMENT OF HEALTH & HUMAN SERVICES·USA

CDC CENTERS FOR DISEASE CONTROL AND PREVENTION

Synthetic Turf Field Recycled Tire Crumb Rubber Research Under the Federal Research Action Plan

FINAL REPORT PART 1– TIRE CRUMB RUBBER CHARACTERIZATION VOLUME 1

National Exposure Research Laboratory
Office of Research and Development

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Synthetic Turf Field Recycled Tire Crumb Rubber Research Under the Federal Research Action Plan

Final Report Part 1 –
Tire Crumb Rubber Characterization

Volume 1

July 25, 2019

By

U.S. Environmental Protection Agency / Office of Research and Development (EPA/ORD)

Centers for Disease Control and Prevention / Agency for Toxic Substances and Disease Registry (CDC/ATSDR)

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Foreword

The U.S. Environmental Protection Agency (EPA) Office of Research and Development (ORD) and the Centers for Disease Control and Prevention (CDC) Agency for Toxic Substances and Disease Registry (ATSDR) have worked collaboratively to complete the research activities on synthetic turf playing fields under the "Federal Research Action Plan on Recycled Tire Crumb Used on Playing Fields and Playgrounds." The Agencies plan to release the research activities' results in two parts. This report (Part 1) summarizes the research effort to characterize tire crumb rubber, which includes characterizing the components of, and emissions from, recycled tire crumb rubber. The exposure characterization report (Part 2) will summarize the potential exposures that may be experienced by users of synthetic turf playing fields with recycled tire crumb rubber infill, such as how people come in contact with the materials, how often and for how long. Part 2 will be released at a later date, along with results from a planned biomonitoring study conducted by CDC/ATSDR.

The study is not a risk assessment; however, the results of the research described in this and future reports will advance our understanding of exposure to inform the risk assessment process. We anticipate that the results from this multi-agency research effort will be useful to the public and interested stakeholders to understand the potential for human exposure to chemicals found in recycled tire crumb rubber used on synthetic turf fields.

This report has been prepared to communicate to the public the research objectives, methods, results and findings for the tire crumb rubber characterization research conducted as part of the Federal Action Research Plan. The report has undergone independent, external peer review in accordance with EPA and CDC policies. A summary of key reviewer recommendations and relevant responses on this part of the research is provided with this report. A response-to-peer review comments document will be released with Part 2.

The mission of the EPA is to protect human health and the environment so that future generations inherit a cleaner, healthier environment that supports a thriving economy. Science at EPA provides the foundation for credible decision-making to safeguard human health and ecosystems from environmental pollutants. ORD is the scientific research arm of EPA, whose leading-edge research helps provide the solid underpinning of science and technology for the Agency. ORD supports six research programs that identify the most pressing environmental health research needs with input from EPA offices, partners and stakeholders.

CDC works 24/7 to protect America from health, safety and security threats, both foreign and in the United States. ATSDR is a non-regulatory, environmental public health agency that was established by Congress under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980. ATSDR protects communities from harmful health effects related to exposure to natural and man-made hazardous substances by responding to environmental health emergencies; investigating emerging environmental health threats; conducting research on the health impacts of hazardous waste sites; and building capabilities of and providing actionable guidance to state and local health partners.

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Acronyms and Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
ACH	Air change per hour
AIC	Akaike information criterion
ANOVA	Analysis of variance
APHC	U.S. Army Public Health Center
API	Analytical profile index
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BLP	Bacteria-like particles
BSD	Backscattered electron detector
BTEX	Benzene, toluene, ethylbenzene, xylenes
°C	Degrees Celsius
CalEPA	California Environmental Protection Agency
CalOSHA	California Division of Occupational Safety and Health
CAS	Chemical Abstracts Service
CDC	Centers for Disease Control and Prevention
CFU	Colony forming units
CICAD	Concise International Chemical Assessment Documents
cm	Centimeter
COC	Chain of custody
CP	Carcinogenic potency
CPSC	Consumer Product Safety Commission
CVAA	Cold vapor atomic absorption
DAD	Diode array detector
DBA + ICDP	Sum of Dibenz[a,h]anthracene and Indeno(1,2,3-cd)pyrene
ddPCR	Droplet digital polymerase chain reaction
DNA	Deoxyribonucleic acid
DNPH	Dinitrophenyl hydrazine
dNTP	Deoxyribonucleotide triphosphate
dsDNA	Double-stranded DNA
DSSTox	EPA's Distributed Structure-Searchable Toxicity Database
EI	Electron impact
EOHSI	Environmental and Occupational Health Sciences Institute
EPA	U.S. Environmental Protection Agency
EPMA	Electron probe microanalysis
ESI	Electrospray ionization
eV	Electronvolt
FLM	Fence line monitor
FRAP	Federal Research Action Plan on Recycled Tire Crumb Used on Playing Fields and Playgrounds
g	Gram
GC/MS	Gas chromatography/mass spectrometry

GC/TOFMS	Gas chromatography/time-of-flight mass spectrometry
GS/MS/MS	Gas chromatography/tandem mass spectrometry
h	Hour
HDPE	High density polyethylene
HEAST	Health Effects Assessment Summary Table
HPLC	High performance liquid chromatography
HR-ICPMS	High resolution magnetic sector inductively coupled plasma mass spectrometer
HS	High-sensitivity
Hz	Hertz
IAC	Internal amplification control
IARC	International Agency for Research on Cancer
ICP/AES	Inductively coupled plasma-atomic emission spectrometry
ICP/MS	Inductively coupled plasma/mass spectrometry
ICR	Information Collection Request
in	Inch
IOAA	Immediate Office of the Assistant Administrator
IPCS	WHO International Programme on Chemical Safety
IRB	Institutional Review Board
IRIS	U.S. EPA Integrated Risk Information System
IS	Internal standard
ISO	International Standards Organization
IUR	Inhalation unit risk
JTI	Jacobs Technology, Inc.
kg	Kilogram
kV	Kilovolt
L	Liter
LC/MS	Liquid chromatography/mass spectrometry
LC/TOFMS	Liquid chromatography/time-of-flight mass spectrometry
LOD	Limit of detection
LOQ	Limit of quantitation
lpm	Liters per minute
LRGA	Literature Review and Data Gaps Analysis
mg	Milligram
m/z	Mass-to-charge ratio
MADL	Maximum allowable dose levels
Max	Maximum
mecA	Gene for methicillin resistance
MFE	Molecular feature extraction
min	Minute
Min	Minimum
mL	Milliliter
mm	Millimeter
mM	Millimolar
Mohm	Megaohm
mol	Mole
MQL	Method quantifiable limit

MRL	Minimum risk level
MRM	Multiple reaction monitoring
MRSA	Methicillin-resistant *Staphylococcus aureus*
MSD	Mass selective detector
N/A	Not applicable/Not available
NAM	New approach methods
NCCT	U.S. EPA National Center for Computational Toxicology
NCEA	U.S. EPA National Center for Environmental Assessment
NERL	U.S. EPA National Exposure Research Laboratory
ng	Nanogram
NHEERL	U.S. EPA National Health and Environmental Effects Research Laboratory
NIEHS	National Institutes of Environmental Health Sciences
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
nM	Nanomolar
NR	Not reported
NRMRL	U.S. EPA National Risk Management Research Laboratory
NSRL	No significant risk level
ns	Nanosecond
NTP	National Toxicology Program
OCHP	U.S. EPA Office of Children's Health Protection
OEM	Original equipment manufacturer
OEHHA	California Office of Environmental Health Hazard Assessment
OLEM	U.S. EPA Office of Land and Emergency Management
OMB	U.S. Office of Management and Budget
ORAU	Oak Ridge Associated Universities
ORCR	U.S. EPA Office of Resource Conservation and Recovery
ORD	U.S. EPA Office of Research and Development
ORISE	Oak Ridge Institute for Science and Education
OSF	Oral slope factor
OSHA	Occupational Safety and Health Administration
OSP	U.S. EPA Office of Science Policy
OTU	Operational taxonomic unit
PAH	Polyaromatic hydrocarbon
PCDL	Personal compound database list
PCR	Polymerase chain reaction
PEL	Permissible exposure limit
pM	Picomolar
ppbv	Parts per billion by volume
ppm	Parts per million
PPRTV	Provisional peer-reviewed toxicity value
PSA	Particle size analysis
psi	Pounds per square inch
PUF	Polyurethane foam
QA	Quality assurance
QC	Quality control
REL	Recommended exposure limit/Reference exposure levels

RF	Radio frequency
RfC	Reference concentration
RfD	Reference dose
RH	Relative humidity
RIVM	Netherlands National Institute for Public Health and the Environment
RNA	Ribonucleic acid
RPM	Revolutions per minute
rRNA	Ribosomal ribonucleic acid
%RSD	Percent relative standard deviation
s	Second
SBR	Styrene-butadiene rubber
SD	Standard deviation
SEE	Senior Environmental Employee
SEM	Scanning electron microscopy
SF	Slope factor
SOP	Standard operating procedure
SSC	Student Services Contractor
STEL	Short term exposure limit
Sum15PAH	Sum of 15 of the 16 EPA ‘priority’ PAHs
SumBTEX	Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene
SVOC	Semi-volatile organic compound
S-W	Shapiro-Wilk
TCR	Tire crumb rubber
TD	Thermal desorption
TIC	Total ion current
TIFF	Tagged image file format
TLV	Threshold limit value
TOFMS	Time-of-flight mass spectrometry
TPE	Thermoplastic elastomers
TSA	Technical systems audit
TSP	Total suspended solids
TWA	Time weighted average
µm	Micrometer
µL	Microliter
UR	Unit risk
U.S.	United States of America
U.S. EPA	United States Environmental Protection Agency
UV	Ultraviolet spectrometry
VID	Video identification number
V	Volt
VOC	Volatile organic compound
W	Watt
WHO	World Health Organization
XRF	X-ray fluorescence spectrometry

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Executive Summary

The goal of the research under the Federal Research Action Plan on Recycled Tire Crumb Used on Playing Fields and Playgrounds (FRAP) is to characterize potential human exposures to the substances associated with recycled tire crumb rubber used on synthetic turf fields. Results of the effort are being reported in two parts. Part 1 (this document) communicates the research objectives, methods, results and findings for the tire crumb rubber characterization research (i.e., what is in the material). Part 2, to be released at a later date, will characterize potential human exposures to the chemicals found in the tire crumb rubber material while using synthetic turf fields. Neither Part 1 nor Part 2 of this study, separately or combined, will constitute an assessment of the risks associated with playing on synthetic turf fields with recycled tire crumb rubber infill. The results of the research described in both Part 1 and Part 2 of the final report can be used to inform future risk assessments.

Key Research Activities Discussed in Part 1

- **Collect tire crumb rubber samples from tire recycling facilities and tire crumb rubber infill samples from synthetic turf playing fields.**
- **Collect information on synthetic turf field use and maintenance.**
- **Characterize the chemical, physical, and microbiological makeup of recycled tire crumb rubber.**
- **Characterize organic chemical emissions and bioaccessibility of metals associated with tire crumb rubber.**
- **Collate toxicological reference information on chemical constituents associated with tire crumb rubber.**

In the United States, synthetic turf fields are used at municipal and county parks; schools, colleges, and universities; professional sports stadiums and practice fields; and military installations and are designed to simulate the experience of practicing and playing on grass fields.[1] First introduced in the 1960s, synthetic turf fields have evolved over time from first-generation systems made of tightly curled nylon fibers to third-generation systems typically made of polyethylene yarn fibers. These third-generation systems typically use small pieces of recycled tires, referred to as "recycled tire crumb rubber" (or simply "tire crumb rubber"), to fill the space between the polyethylene yarn fibers. The recycled tire crumb rubber (sometimes mixed with sand or other raw materials) is added for ballast, support for the synthetic grass blades, and as cushioning for field users. Third-generation synthetic turf field systems are widely used today. There are between 12,000 and 13,000 synthetic turf fields in the United States, with 1,200 – 1,500 new installations each year. It is estimated that millions of people use and/or work at these fields.

Recently, parents, athletes, schools and communities have raised concerns about the use of recycled tire crumb rubber on synthetic turf fields. To help address these concerns, the Centers for Disease Control and Prevention/Agency for Toxic Substances and Disease Registry (CDC/ATSDR) and the U.S. Environmental Protection Agency (EPA), in collaboration with the Consumer Product Safety Commission (CPSC), launched a multi-agency research effort in February 2016.

[1] More information on the intended uses of synthetic turf can be found at: https://www.syntheticturfcouncil.org/page/About_Synthetic_Turf.

This multi-agency research effort, known as the Federal Research Action Plan on Recycled Tire Crumb Used on Playing Fields and Playgrounds (FRAP)[2], is focused on assessing potential human exposure, which includes conducting research activities to characterize the chemicals associated with recycled tire crumb rubber and to identify the ways in which people may be exposed to those chemicals based on their activities on synthetic turf fields. Also, the FRAP includes characterizing emissions and bioaccessibility to differentiate what is present in the recycled tire crumb rubber from what people may actually be exposed to from recycled tire crumb rubber.

The research laid out in the FRAP is not intended to be a risk assessment. Like other studies, this research has limitations, and risks cannot be inferred from the information and conclusions found in this study. Prior to initiating the FRAP, most studies examining these potential risks have been considered inconclusive or otherwise incomplete. Based upon available literature, this research effort represents the largest tire crumb rubber study conducted in the United States. The information and results from the effort will fill specific data gaps about the potential for human exposure to chemical constituents associated with recycled tire crumb rubber used in synthetic turf fields.

A status report was previously released describing FRAP activities as of December 2016 (EPA/600/R-16/364, available at: http://www.epa.gov/TireCrumb). The status report included a summary of stakeholder outreach, an overview of the tire crumb rubber manufacturing industry, progress on the research activities, and the final peer-reviewed literature review/gaps analysis (LRGA) white paper. The results of the research activities under the FRAP are being documented in two parts. Part 1 documents the tire crumb characterization activities and results. Part 2 will document the results from the exposure characterization research and will be released along with a planned biomonitoring study to be conducted by CDC/ATSDR. Part 2 will also include a discussion of potential follow-up activities that could provide additional insights into potential exposures to recycled tire crumb rubber used on synthetic turf fields.

Literature Review/Gaps Analysis (LRGA)

- **Summary of the available literature on tire crumb rubber and its associated exposure information.**
- **Multiple types of information on constituents, releases, environmental presence, and exposures were identified, along with important data gaps.**
- **Information was collated, and a final white paper was made available (Appendix C of this part of the report).**

[2] The multi-agency research effort, called the *Federal Research Action Plan on Recycled Tire Crumb Used on Playing Fields and Playgrounds* (FRAP), was launched in February 2016. Prior to initiating the study, federal researchers developed a research protocol, *Collections Related to Synthetic Turf Fields with Crumb Rubber Infill*, which describes the study's objectives, research design, methods, data analysis techniques and quality assurance/quality control (QA/QC) measures. These documents are available at: http://www.epa.gov/TireCrumb. CPSC is conducting the work on playgrounds and results from that effort will be reported separately. While artificial turf is also used at residences, that turf does not typically include tire crumb rubber; as a result, the use of artificial turf at residences is not part of the FRAP study.

This Executive Summary provides a review of the tire crumb rubber research (Part 1 of the study). Section 1 of this report provides introductory information; Section 2 provides a more complete technical summary of these activities and the study's key findings; Sections 3 and 4 describe the methods and contain detailed results for the tire crumb rubber characterization activities, with result tables focusing on select chemicals of interest; and Section 5 provides information on the availability of toxicity reference information for the chemicals associated with tire crumb rubber. Complete result tables are provided in the Appendices (Volume 2).

Tire Crumb Rubber Characterization

Tire crumb rubber samples were collected from nine tire recycling facilities, and tire crumb rubber infill material was collected from 40 synthetic turf fields located across the United States. The fields included a range of field types (indoor versus outdoor), field ages and geographic locations. Laboratory analyses were conducted to measure the physical, chemical and microbiological characteristics of the tire crumb rubber material (Figure ES-1). Results of these analyses provided information about the number and types of chemicals associated with recycled tire crumb rubber, the amount of chemicals released into the air and into simulated biological fluids, and the range and variability of these parameters. As expected, the research team found a range of metals, semivolatile organic compounds (SVOCs), volatile organic compounds (VOCs) and bacteria in and on tire crumb rubber infill material. Many of the chemicals measured in this study have been identified as present in recycled tire crumb rubber in previous studies. Other VOC and SVOC chemicals have been tentatively identified in this study but have not been confirmed. Additional detail on these analyses can be found in Section 4.12 of this document.

Recycled Tire Crumb Rubber Characterization

- **As expected, a range of metals, semivolatile organic compounds (SVOCs), volatile organic compounds (VOCs) and bacteria were measured in and on recycled tire crumb rubber infill.**
- **Many chemicals were found at similar concentrations in other studies of recycled tire crumb rubber, where comparable data are available.**

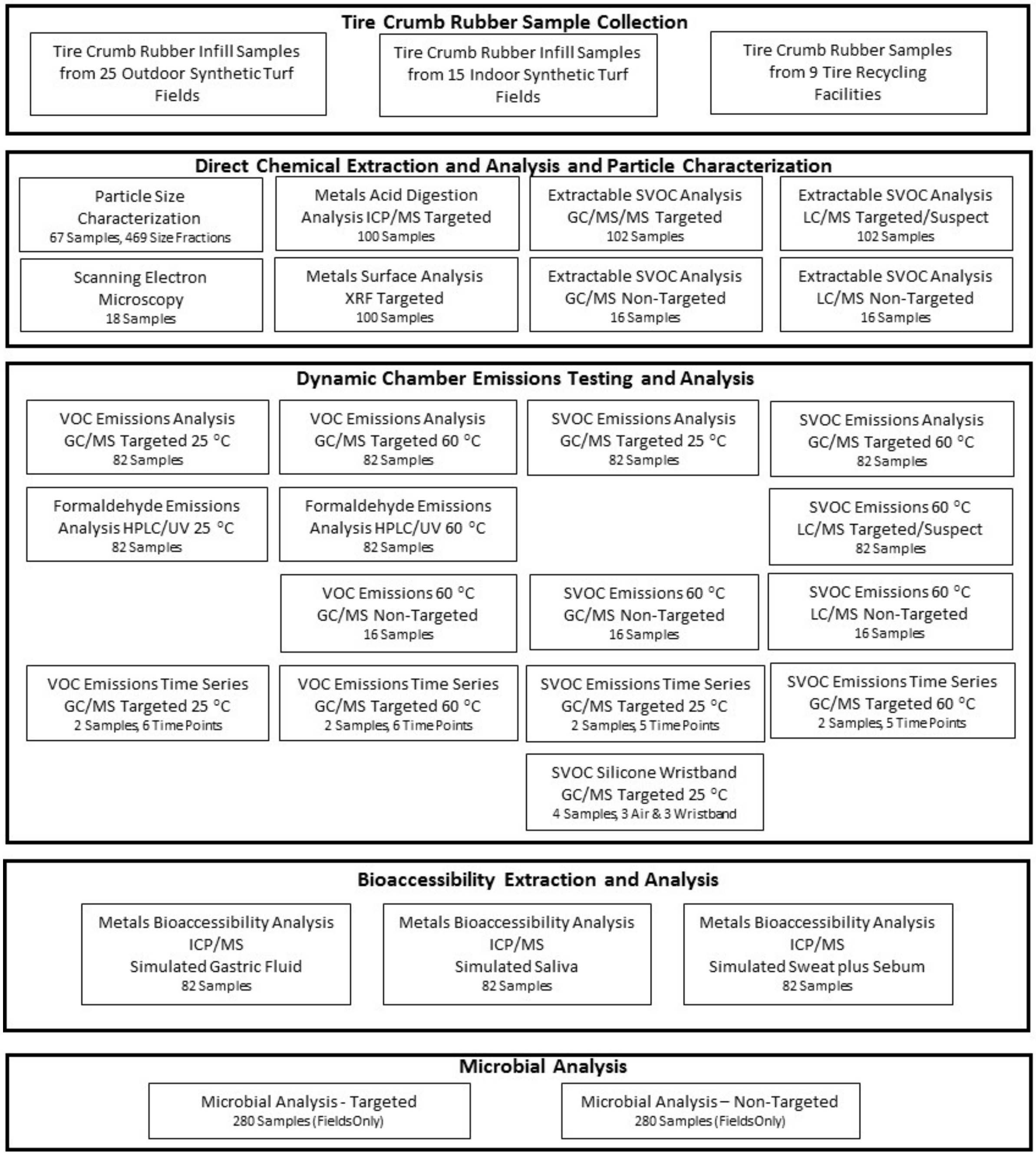

Figure ES-1. Tire crumb rubber characterization research schematic overview.

Chemicals specifically targeted for analysis in the tire crumb characterization research included 21 metals, 49 SVOCs and 31 VOCs. Most of the targeted metals and SVOCs, and several of the VOCs were found to be associated with recycled tire crumb rubber infill collected at fields across the United States. Average concentrations for the target analytes varied widely, by up to four orders of magnitudes for metals and three orders of magnitudes for polycyclic aromatic hydrocarbons (PAHs). Additional SVOCs including phthalates, thiazoles and other compounds associated with tire rubber were identified in infill samples as well. In general, where comparable data are available, most target analyte concentrations measured in this study were similar to concentrations found in previous studies of recycled tire crumb rubber. For the microbial analysis, all tire crumb rubber samples collected from the 40 synthetic turf fields tested positive for a universal bacterial gene (16s rRNA). This is not surprising, as bacteria are present in soil and on surfaces in indoor environments. The research team observed higher concentrations of total bacteria in outdoor fields relative to indoor fields, but a gene commonly associated with the human skin microbiome (i.e., *Staphylococcus aureus*) was detected more often in indoor fields than outdoor fields.

Differences Among Recycled Tire Crumb Rubber Samples from Recycling Plants and Synthetic Turf Fields

- **When comparing tire crumb rubber from recycling plants and synthetic turf fields:**
  - **Concentrations of most metals were comparable between fields and recycling plants.**
  - **Many organic chemical concentrations and emissions were higher with tire crumb obtained directly from a recycling plant.**
  - **A few chemicals had higher average concentrations in materials from fields.**
- **Levels of many organic chemicals were higher for indoor fields compared to outdoor fields, suggesting potential exposures may be greater at indoor fields.**
- **Levels of organic chemicals were often lower in older outdoor fields.**

The presence of a substance does not directly equate with human exposure. While there are many chemicals associated with recycled tire crumb rubber, our laboratory experiments suggest that the amount of chemicals available for exposure through release into the air and simulated biological fluids is relatively low. Air emissions tests were performed at both 25 °C (77 °F) and 60 °C (140 °F), temperatures chosen to represent moderate and high-end field temperature conditions, respectively. For most VOC and SVOC target chemicals, air emissions were low at 25 °C and in many cases, not measurable above the detection limit or above background levels. At 60 °C, higher emissions were measured for some, but not all, VOCs and SVOCs. Overall, methyl isobutyl ketone and benzothiazole had the highest emission factors among the target analytes in this study.

Bioaccessibility tests of 19 metals were conducted on the tire crumb rubber samples using three types of simulated biological fluids (gastric fluid, saliva and sweat plus sebum[3]). Only small fractions of metals were released into simulated biological fluids. For all metals, the mean bioaccessibility values averaged about 3% in gastric fluid and less than 1% in saliva and sweat plus sebum. These results fill important knowledge gaps about potential bioavailability of chemicals associated with recycled tire crumb rubber. Based on these results, a default to 100% bioaccessibility should not be used when assessing potential exposures to most metals in tire crumb rubber.

[3] Sebum is the oil-like substance produced by the sebaceous glands in the skin.

Results from this tire crumb rubber characterization research also suggest that concentrations of many organic chemicals found in tire crumb rubber infill material vary with synthetic turf field age and type (i.e., indoor versus outdoor). In general, concentrations of many organic chemicals appeared to decrease with increasing field age. These results suggest that vaporization, weathering and/or other removal mechanisms may lead to lower concentrations of many organic chemicals over time, particularly for outdoor fields. However, since longitudinal measurements at individual fields were outside the scope of the current activities, it cannot be ruled out that some differences in chemical concentrations across fields of different ages are a result of differences in the initial chemical composition of the tire crumb rubber. Levels of many organic chemicals also tended to be higher for indoor fields compared to outdoor fields, suggesting that exposures may be greater at indoor synthetic turf fields. Additional research is needed to determine whether indoor field users experience higher exposures than those using outdoor fields as a result of these differences. Univariate statistical analysis did not, in general, show significant differences for fields across the four U.S. census regions, but multivariate analysis results suggest that differences across regions cannot be completely ruled out.

Organic Chemical Emissions and Metals Bioaccessibility

- **Emissions of most SVOCs and many VOCs were low when tested at 25 °C, while emissions were higher for some, but not all at 60 °C.**
- **The amount of metals released into simulated biological fluids was low, on average about 3% in gastric fluid and less than 1% in saliva and sweat plus sebum.**
- **The emissions and bioaccessibility measurements suggest that exposures to most chemicals may be relatively low but exposure measurements are being conducted to confirm these results.**

The same target analytes were measured in tire crumb rubber collected at tire recycling plants and synthetic turf fields. The concentrations of most metals in both materials were comparable. Many organic chemicals had higher concentrations in, and emissions from, tire crumb rubber collected at recycling plants compared to tire crumb rubber infill collected at synthetic turf fields. A few chemicals [e.g., lead and bis(2-ethylhexyl) phthalate] had higher average concentrations in infill samples from synthetic turf fields than in tire crumb rubber samples collected at recycling plants. Additional research may be needed to better understand whether there are contributions of some chemicals at fields from sources other than the recycled tire crumb rubber. Emission measurements suggested that several VOCs, such as benzene and toluene, may be present primarily at the surface of the rubber particles; other VOCs, such as methyl isobutyl ketone and benzothiazole, appear more likely to be intrinsic to the tire crumb rubber material.

Toxicity Reference Information

Toxicological reference information was compiled for potential tire crumb rubber chemical constituents. One or more toxicity reference values was identified for 167 (about 47%) of the 355 chemical compounds potentially associated with recycled tire crumb rubber as reported in the LRGA. When narrowing this down from the LRGA's list of 355 to its subset of target analytes in this study (95), one or more toxicity reference values is available for 78 of those analytes (about 82%). It is important to recognize that some of these target analytes were not found, or were not consistently found, in tire crumb rubber in this study.

Toxicity Reference Information on Constituents of Recycled Tire Crumb Rubber

- **Toxicity reference values are available for some of the potential chemicals associated with tire crumb rubber and for most of those in the target analyte list of this study.**
- **Not all target analytes were consistently found in the samples.**

Conclusions

This part of the report communicates the research objectives, methods, results and findings for the tire crumb rubber characterization (what is in the material) and fills specific data gaps about what chemicals are found in recycled tire crumb rubber used on synthetic turf fields.

As expected, a range of chemicals was found in the recycled tire crumb rubber, including metals and organic chemicals. Where comparative data are available concentrations of most metal and organic chemicals found in tire crumb rubber were found to be similar when comparing this study to previous studies. Further, the emissions of many organic chemicals into air were typically found to be below detection limits or test chamber background, and releases of metals into simulated biological fluids were very low (mean bioaccessibility values averaged about 3% in gastric fluid and less than 1% in saliva and sweat plus sebum). Together, these findings support the premise that while many chemicals are present in the recycled tire crumb rubber, exposure may be limited based on what is released into air or biological fluids.

What We Learned

- **As expected, a range of metals, organic chemicals, and bacteria was found to be associated with recycled tire crumb rubber.**
- **Results are comparable to other studies characterizing tire crumb where available.**
- **While many chemicals are present in the recycled tire crumb rubber, exposure may be limited based on what is released into air or biological fluids.**

Toxicity reference information was available for most of the target analytes. This information will contribute to the public's understanding of the potential hazards that may exist from chemicals associated with recycled tire crumb rubber.

Risk is a function of both hazard (toxicity) and exposure; therefore, understanding what is present in the material (Part 1) and how individuals are potentially exposed (Part 2 to be released at a future date) is critical to understanding potential risk. It is important to note that the study activities completed as part of this multi-agency research effort were not designed, and are not sufficient by themselves, to directly answer questions about potential health risks. Other studies may aid in this regard.[4] Overall, we anticipate that the results from this multi-agency research effort will be useful to the public and interested stakeholders for understanding the potential for human exposure to chemicals associated with recycled tire crumb rubber infill material used on synthetic turf fields.

[4] Other research studies in the United States and Europe will also provide data to better understand whether there are human health risks from playing on synthetic turf fields containing recycled tire crumb rubber. For example, the California Office of Environmental Health Hazard Assessment (OEHHA) will provide tire crumb rubber characterization data for additional fields in California. They will also characterize additional synthetic turf field component materials and particles in the air above the synthetic fields as a result of simulated activities and measure the bioaccessibility of inorganic and organic chemicals from tire crumb rubber. The National Toxicology Program (NTP) is conducting short-term toxicity studies on the recycled tire crumb rubber material itself, not specific chemical constituents found in the material.

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1.0 Introduction

1.1 Background

Synthetic turf systems have been installed in the United States since the 1960s. Currently, there are between 12,000 and 13,000 synthetic turf sports fields in the United States, with approximately 1,200 to 1,500 new installations each year (Synthetic Turf Council et al., 2016). These fields, which are designed to simulate the experience of practicing and playing on grass fields, are installed at a variety of venues, including parks, schools, colleges, stadiums and practice fields, and are used by a wide variety of people, such as professional, college and youth athletes; coaches; referees; and recreational users of all ages. It is estimated that 95% of synthetic turf fields utilize recycled rubber infill exclusively or in mixture with sand or alternative infills (Synthetic Turf Council et al., 2016). Infill is added for ballast, support for the synthetic grass blades and as cushioning for field users. The recycled rubber infill material used on these fields is produced from waste automobile and truck tires, which are reprocessed using either an ambient or cryogenic method to create "crumb"-sized material, with reported approximate diameters ranging from 1 to 6 mm (Lim & Walker, 2009). In addition to its use in synthetic turf, recycled tire material is increasingly being used for playground surfaces in the Unites States.

Some in the public have raised concerns about the potential for human exposure to chemicals associated with the tire crumb rubber used on synthetic turf fields and playgrounds. To date, most studies examining these potential risks have been considered inconclusive or otherwise incomplete. In most studies of potential tire crumb rubber-related chemicals only a limited number of chemicals were measured, and there are gaps in exposure information and measurement data for dermal and ingestion pathways. In addition, no single study has evaluated large numbers of fields or people to comprehensively characterize potential exposures to tire crumb rubber infill material. Three recent studies examined potential relationships between synthetic turf fields and cancer; none reported evidence supporting such a relationship (WDOH, 2017; RIVM, 2017; Bleyer & Keegan, 2018).

Tires are manufactured with a range of materials, including rubber and elastomers; reinforcement filler material; curatives including vulcanizing agents, activators and accelerators; antioxidants and antiozonants; inhibitors and retarders; extender oils and softeners; phenolic resins, plasticizers; metal wire; polyester or nylon fabrics; and bonding agents (NHTSA, 2006; Chem Risk Inc. & DIK Inc., 2008; Cheng et al., 2014; Dick & Rader, 2014). Chemicals of concern range from polycyclic aromatic hydrocarbons (PAHs) in carbon black to zinc oxide (ZnO), which is used as a vulcanizing agent and may contain trace amounts of lead and cadmium. Chemicals in many other classes may be used in tires as well, including sulphenamides, guanidines, thiazoles, thiurams, dithiocarbamates, sulfur donors, phenolics, phenylenediamines, and other chemicals (Chem Risk Inc. & DIK Inc., 2008). There is limited information available to assess whether some of these chemicals may carry impurities or byproducts or whether they may undergo chemical transformation over time. In addition to chemicals used in their production, tires may also pick up and absorb chemicals over their lifetime of use, and once installed on a field, tire crumb rubber may serve as a sorbent for chemicals in the air and in dust that falls onto the field. For example, one laboratory reported irreversible adsorption of volatile organic compound (VOC) and semivolatile organic compound (SVOC) analytes spiked onto tire crumb rubber (Lim & Walker, 2009). Alternatively, the tire crumb rubber may also emit VOC and SVOC species into the air, especially at higher outdoor temperatures (Marsili et al., 2014; CAES, 2010).

Users of synthetic turf fields with tire crumb rubber infill can potentially be exposed to these chemicals in a variety of ways, including while breathing (i.e., inhalation exposure), when contacting the material with their skin (i.e., dermal exposure), and/or by ingesting the material (i.e., ingestion exposure).

Concerns have been raised about the potential adverse health effects of these exposures. In addition to the potential for chemical exposures, concerns have been raised about the potential for exposure to microbial pathogens at synthetic turf fields. For example, methicillin-resistant *Staphylococcus aureus* (MRSA) has caused outbreaks among athletic teams, and artificial turf has been implicated as a fomite in transmission of MRSA among college athletes (Begier et al., 2004). In general, very few studies have been conducted regarding the potential for microbial pathogen exposures at synthetic turf fields, and few potential pathogens have been investigated.

1.2 The Federal Research Action Plan

In light of the data gaps and concerns raised about the safety of recycled tire crumb rubber used in playing field and playground surfaces in the United States, the U.S. Environmental Protection Agency (EPA), Centers for Disease Control and Prevention/Agency for Toxic Substances and Disease Registry (CDC/ATSDR), and Consumer Product Safety Commission (CPSC) released a *Federal Research Action Plan on Recycled Tire Crumb Used on Playing Fields and Playgrounds* in February 2016 (U.S. EPA, CDC/ATSDR, & CPSC, 2016a). This coordinated federal research action plan (FRAP) includes outreach to key stakeholders, among its many activities, and has these high-level research objectives:

- Determine key knowledge gaps related to chemical characterization, exposure, human health hazards.
- Identify and characterize chemical compounds found in tire crumb used in artificial turf fields and playgrounds.
- Characterize exposures, or how people are exposed to these chemical compounds based on their activities on the fields.
- Identify follow-up activities that could be conducted to provide additional insights about potential risks.

The overall purpose of this multi-agency research action plan is to study the potential for human exposure resulting from the use of tire crumb rubber in playing fields and playgrounds, and in doing so, provide important information needed for any follow-up evaluation of risk that might be performed.

1.3 Scope and Objectives of EPA, CDC/ATSDR and CPSC Activities

The FRAP defines the scope and agency leads for each of the research efforts, including:

- Stakeholder Outreach (EPA, CDC/ATSDR and CPSC),
- Literature Review/Gaps Analysis (EPA, CDC/ATSDR and CPSC),
- Tire Crumb Characterization Research – Synthetic Turf Fields (EPA and CDC/ATSDR),
- Exposure Characterization Research – Synthetic Turf Fields (EPA and CDC/ATSDR), and
- Playgrounds Study (CPSC).

To support elements of the FRAP, the Agencies developed a research protocol titled, *Collections Related to Synthetic Turf Fields with Crumb Rubber Infill* (U.S. EPA & CDC/ATSDR, 2016), which describes the literature review and gaps analysis and details the research design for characterizing tire crumb rubber and human exposure associated with synthetic turf fields. The research protocol does not include tire crumb rubber characterization and exposure characterization research performed for playgrounds; the CPSC is independently developing and implementing research plans for playgrounds. The research protocol received independent external peer review, and the information collection components of the protocol received review and public comment through the Office of Management and Budget (OMB) Information Collection Request (ICR) process, as well as review and approval by the CDC Institutional Review Board (IRB).

This report summarizes research results from EPA and CDC/ATSDR efforts to characterize tire crumb rubber. It also includes a summary of stakeholder outreach and the literature review and knowledge gaps assessment conducted by all three agencies. The CPSC efforts to characterize exposures associated with playgrounds (CPSC 2018a; CPSC 2018b) are not described in this report. Research results from the exposure characterization research activities will be reported separately.

1.3.1 Outreach to Key Stakeholders

The stakeholder outreach efforts conducted as part of the FRAP had two main objectives: (1) gather and share information that may be used to inform research efforts, and (2) inform the public, researchers and research organizations, industry, government organizations and non-profit organizations about the FRAP, including research progress updates and results.

1.3.1.1 Gather and Share Information

EPA, CDC/ATSDR and CPSC gathered relevant information from stakeholders and shared information as the activities under the FRAP progressed. The information was gathered and shared by convening discussions and requesting feedback on components of the research. Information gathering and sharing activities included:

- Field users providing first-hand perspectives on potential exposures;
- Government agencies regularly meeting to discuss the federal research, share relevant information from state-level and international studies, request support, and identify current best practices for minimizing exposures;
- Industry representatives sharing information to help researchers better understand the manufacturing process and use parameters for recycled tire crumb used in synthetic turf fields and for recycled tire-derived playground surface materials; and
- The public providing comment on the information collection components of the FRAP, including the plans for collecting tire crumb samples from fields and manufacturing facilities, and the exposure characterization study.

Agency researchers gathered information from industry, non-governmental organizations, and others to inform the design and implementation of the research on synthetic turf fields containing tire crumb rubber infill. This included collecting information on how tires and tire crumb rubber are manufactured and how synthetic turf fields are constructed, installed, and maintained. From February to September 2016, the study team held meetings with five industry trade associations, three synthetic turf field companies, two synthetic turf field maintenance professionals, one academic institution, and five non-profit organizations. EPA, CDC/ATSDR and CPSC scientists toured a total of five tire recycling facilities in the south, west, and northeast regions of the United States, where they observed different types of tire crumb rubber processing technologies. Varying degrees of mechanized technologies to process the tires were observed at the facilities. The tire crumb rubber infilling process was observed on two field installations. Through these meetings, tours, and observed field installations, the team gathered information on the following topics:

- The current state of tire manufacturing and scrap-tire collection and recycling;
- The nature and varieties of processes and machinery used in the processing of scrap tires into tire crumb rubber;
- Tire manufacturing standards;
- Tire recycling process standards and tire crumb rubber product standards;
- Tire crumb rubber infill product types;
- Storage, packaging and transportation of tire crumb rubber to fields;
- The number and types of synthetic turf fields; and
- Synthetic turf field construction, installation and maintenance practices.

This information was originally summarized in section I.V.A. "Industry Overview" of the *Federal Research Action Plan on Recycled Tire Crumb Used on Playing Fields and Playgrounds: Status Report* released in December 2016 (U.S. EPA, CDC/ATSDR, & CPSC, 2016b) and is included as Appendix A of this report for completeness.

1.3.1.2 Informing Stakeholders

EPA, CDC/ATSDR and CPSC informed stakeholder groups about the FRAP when it was released, provided status updates as the research progressed, and will continue to share research findings. Following the release of the FRAP, the Agencies established a FRAP website (www.epa.gov/tirecrumb) and hosted a public webinar to provide an overview of the FRAP.

The Agencies provided updates to stakeholders as the research progressed through a number of outreach activities:

- Regularly updating the FRAP website with links to the FRAP and the Research Protocol, Tire Crumb Questions and Answers, government websites that provide recommendations for recreation on fields with tire crumb, and other information.
- Distributing study updates to an e-mail list of about 800 stakeholders.
- Releasing the Status Report in December 2016 summarizing research progress.
- Communicating with other federal, state, and international government organizations involved in planning or conducting tire crumb research, including California's Office of Environmental Health Hazard Assessment, the Washington State Department of Health, the National Toxicology Program at the National Institute of Environmental Health Sciences, the European Chemicals Agency, and the Netherlands National Institute for Public Health and the Environment.
- Presenting about the FRAP at conferences and annual meetings which allowed for interactions with researchers and the academic community, including the International Society of Exposure Science Annual Meeting, Society of Environmental Toxicology and Chemistry Annual Meeting, California Tire Conference, and Recycled Rubber Products Technology Conference, and the American Public Health Association Annual Meeting.
- Responding to public, media and Congressional inquiries about the FRAP.

The agencies will update the FRAP website and continue outreach efforts to share and discuss research findings from this and future reports. The Agencies also expect to host webinars to provide the public an overview of research findings as they are released. In addition, the findings will be presented at conferences, and the three agencies implementing the FRAP, along with other state and international governmental organizations with an interest in tire crumb research, expect to continue to convene to exchange information.

Stakeholder outreach information was originally summarized in the *Federal Research Action Plan on Recycled Tire Crumb Used on Playing Fields and Playgrounds: Status Report* released in December 2016 (U.S. EPA, CDC/ATSDR, & CPSC, 2016b) and is included as Appendix B of this report for completeness.

1.3.2 Data and Knowledge Gap Analysis

EPA, CDC/ATSDR, and CPSC conducted a Literature Review/Gaps Analysis (LRGA) to provide a summary of the available literature on tire crumb rubber and to identify data gaps characterized in the literature. The overall goals of the LRGA were to inform the interagency research study and to identify potential areas for future research. The LRGA did not include critical reviews of the strengths and weaknesses of each study, but did provide the authors' conclusions regarding their research, where applicable. The LRGA also did not make any conclusions or recommendations regarding the safety of recycled tire crumb rubber used in synthetic turf fields and playgrounds.

The LRGA identified 88 references from bibliographic databases, including PubMed, Medline (Ovid®), Embase (Ovid®), Scopus, Primo (Stephen B. Thacker CDC Library), ProQuest Environmental Science Collection, Web of Science, ScienceDirect and Google Scholar. Each reviewed reference was categorized according to 20 general information categories (e.g., study topic, geographic location, sample type, conditions, populations studied, etc.) and more than 100 subcategories (e.g., for study topic: site characterization, production process, leaching, off-gassing, microbial analysis, human risk, etc.). The peer-reviewed white paper summarizing the LRGA results, *State-of-Science Literature Review/Gaps Analysis, White Paper Summary of Results,* was originally published in the FRAP Status Report (U.S. EPA, CDC/ATSDR, & CPSC, 2016b); it is included in its entirety in Appendix C of this report for completeness.

Several organizations have published important information on this topic since the FRAP LRGA was completed and published in December 2016. Brief summaries of some of these research efforts and publications have been included in the introductory information of Appendix C. For example, one important study was conducted by the Netherlands National Institute for Public Health and the Environment (RIVM 2017). The RIVM research effort collected tire crumb rubber samples from 100 fields in the Netherlands, measured a select group of chemicals in all or a subset of fields, assessed the release of select chemicals, estimated exposures, and evaluated potential risks based on exposures to PAHs in the tire crumb. Federal researchers have had frequent contact with RIVM researchers, and with the European Chemicals Agency (ECHA), to share information and to better understand the research studies.

The data and knowledge gaps identified in the LRGA are summarized in Table 1 of Appendix C. The FRAP research was designed to address many of these gaps, particularly with respect to tire crumb rubber characterization and exposure characterization. Some of these data gaps are also being addressed by other research organizations. However, the U.S. federal study is providing information that cannot be replaced by state and international organizations, and has unique research elements to provide data not being produced by other research efforts. Important data gaps that the federal study is addressing are summarized below.

While a number of research studies have examined tire crumb rubber constituents, most U.S. studies have been relatively small, restricted to a few fields or material sources, and measured a limited number of constituents. Few studies have assessed tire crumb rubber directly from recycling plants for comparison to infill at synthetic turf fields to assess potential changes due to weathering or the potential for increases in some chemical constituents from external sources. Few studies have compared infill and exposures at indoor fields to those at outdoor fields; it may be important to understand potential differences for exposure assessment. Many of the U.S. studies have examined metal constituents and a modest number have measured VOCs, PAHs and benzothiazole, but relatively few studies have tried to systematically measure or look for the presence or absence of many other organic chemicals potentially associated with tire materials across a large range of samples from around the U.S. Also, most of the synthetic field measurements from the studies conducted to date have been for particles, metals or organics in air; only a few studies measured chemicals present on field surfaces or in field dust.

A few small studies have investigated bacterial loads and the occurrence of select pathogens in synthetic turf athletic fields. The investigations that have been conducted did not focus directly on tire crumb rubber infill material; rather, the samples were collected from the fields and few potential pathogens were investigated. Furthermore, all studies reported to date have used traditional culture methods to detect and quantify total bacteria and pathogen densities. These methods can underestimate densities because culture media cannot support the growth of all bacteria and pathogens. Furthermore, bacteria can enter a viable, but nonculturable state in some environments (Oliver, 2005), which prohibits their detection by culture methods. The use of molecular methods, like polymerase chain reaction (PCR) and high throughput sequencing, are not hindered by these limitations and can provide a more thorough and robust analysis of bacteria and pathogens in tire crumb rubber infill.

While research efforts have tended to focus on characterizing tire crumb rubber constituents and environmental concentrations of related chemicals, less research has been performed to examine human exposures and potential risks to people using synthetic turf fields and playgrounds, especially for children. With respect to exposure characterization, human exposure measurement data for synthetic turf field users are limited. There are significant data gaps in human activity parameters for various synthetic turf field activities, and this information is essential for estimating exposures and evaluating risks from contact with tire crumb rubber constituents. While the potential for inhalation exposures has been characterized for some constituents, there is far less information for characterizing dermal and ingestion exposures. Improved exposure factor information is needed to estimate and model exposures from the inhalation, dermal, and ingestion pathways. There are also significant limitations in the methods that have been developed and used to characterize human exposure from activities on synthetic turf fields. These include challenges collecting relevant surface, dust, and personal air samples; limited measurements of dermal exposures; and limited collection of urine or blood samples, which could be used for measuring biomarkers of exposure to chemicals in crumb rubber infill.

Some elements of the research design outlined in the Research Protocol (U.S. EPA & CDC/ATSDR, 2016) were intended to fill these knowledge gaps and address the limitations of prior studies. There are two on-going studies in the United States that are providing information complementary to that under the FRAP. California's Office of Environmental Health Hazard Assessment (OEHHA, 2019) began a study in 2015 under contract with CalRecycle to examine synthetic turf and potential human health impacts. OEHHA researchers are also conducting research aimed at reducing data gaps for tire crumb rubber constituents and human exposures. The federal research team regularly consults with OEHHA scientists to discuss how the two studies can be mutually informative. The federal and state researchers have attempted to identify and implement methods and approaches that will, where feasible, produce comparable data. This could effectively expand the overall U.S. research sample size and will provide additional insight into potential exposure variability. There are also important differences between the federal and OEHHA studies that will provide complementary data addressing different data gaps. The complementary approaches conserve resources for each study and will expand our knowledge for improved exposure assessment. Additionally, the National Toxicology Program (NTP) of the National Institutes of Environmental Health Sciences (NIEHS) has performed recent research to characterize chemicals in 'fresh' tire crumb rubber from two recycling plants, assessed methods for conducting toxicity testing of the material, and performed short-term in-vivo and in-vitro toxicity testing (Cristy, 2018; Gwinn, 2018; Richey, 2018; Roberts, 2018).

The results of the FRAP research will complement research efforts by providing information not being produced by other organizations. FRAP research is characterizing tire crumb rubber collected from recycling plants, indoor fields and outdoor fields across the United States; assessing releases of chemicals into the air and into simulated biological fluids; performing exposure measurements to better understand the potential exposures from inhalation, dermal and ingestion pathways; and conducting biomonitoring studies for children and adults using synthetic turf fields. Results from the FRAP, along with research results from other organizations, will fill multiple data gaps and will be essential for improving exposure and risk assessment.

1.3.3 Tire Crumb Rubber Characterization

The tire crumb rubber characterization portion of the study was a pilot-scale effort that involved collecting tire crumb rubber material from nine tire recycling plants and 40 synthetic turf fields around the United States, with laboratory analysis for a wide range of metals (21 target analytes), VOCs (31 target analytes), SVOCs (49 target analytes) and microbes. As defined in the research protocol (U.S. EPA & CDC/ATSDR, 2016), there were three primary aims or objectives for the tire crumb characterization research:

> **Aim 1:** Characterize a wide range of chemical, physical and microbiological constituents and properties for tire crumb rubber infill material collected from tire recycling plants and synthetic turf fields around the United States;
>
> **Aim 2:** Collect information from facilities around the United States to better understand how synthetic turf fields with tire crumb rubber infill are operated, maintained, and used with regard to characteristics potentially impacting human exposure to tire crumb rubber constituents; and,
>
> **Aim 3:** Identify and collate existing toxicity reference information for selected chemical constituents identified through the tire crumb rubber characterization measurements.

To meet the first research objective, the Agencies collected and tested different types of tire crumb rubber to better understand the constituents that are present and might be emitted from the material, as well as constituents that can be transferred from tire crumb when a person comes into contact with it (e.g., when tire crumb comes in contact with sweat on the skin or is accidentally ingested by athletes playing on synthetic turf fields). Tire crumb rubber samples were collected directly from tire recycling plants to provide information on constituents in unused material, while samples from outdoor and indoor synthetic turf fields were collected to provide a better understanding of constituents potentially available for exposure in different weathering conditions and facility types. Characterization utilized multiple analytical methods, including direct extraction and analysis of metals and SVOC constituents of tire crumb rubber, dynamic emission chamber measurements of VOC and SVOC emissions and emission rates from tire crumb rubber, and bioaccessibility testing of metals. The emissions and bioaccessibility experiments provided important information about the types and amounts of chemical constituents in the tire crumb rubber material available for human exposure through inhalation, dermal, and ingestion pathways. A combination of targeted quantitative analysis, suspect screening, and non-targeted approaches was applied for VOCs and SVOCs to ascertain whether there may be potential chemicals of interest that have not been identified or reported in previous research. Physical characteristics, such as particle size, sand content and moisture content, were also examined to better understand potential exposures, and analyses were employed to address gaps in knowledge regarding microbial pathogens associated with tire crumb rubber on synthetic turf fields.

To meet the second objective, questionnaires were administered to facility owners and managers to obtain information about potential factors that may affect exposures, including source materials, material age, tire crumb rubber addition or replacement frequencies, maintenance procedures, facility operations, and facility use.

To meet the third objective, toxicity reference information was identified and collated from existing on-line databases and literature sources for select chemical constituents. The selection of chemicals to include in toxicity reference information gathering was based on a combination of factors, such as presence/absence, frequency of detection, relative concentration magnitude, and other information identified in the LRGA.

The data collection components of the tire crumb rubber characterization study went through the OMB Information Collection Request review process. On August 5, 2016, EPA and CDC/ATSDR received final approval to begin the research.

1.4 Report Organization

This report is organized into two volumes – Volume 1 contains the body of the report; Volume 2 contains the appendices. Volume 1 consists of seven sections:

- **Section 1** provides background and an introduction to the federal research action plan and its objectives.
- **Section 2** provides a summary of the research results and main conclusions from the tire crumb rubber characterization study, along with important limitations.
- **Section 3** provides detailed methods for the tire crumb rubber characterization research.
- **Section 4** provides detailed results for the tire crumb rubber characterization, with result tables and figures focusing on select chemicals of interest.
- **Section 5** summarizes toxicity reference information for tire crumb rubber chemicals.
- **Section 6** contains the references.
- **Section 7** contains a listing of appendices.

Volume 2 of this report consists of 22 appendices:

- **Appendices A-C** are included from the FRAP Status Report (U.S. EPA, CDC/ATSDR & CPSC, 2016b) for completeness.
- **Appendix D** contains a list of standard operating procedures (SOPs) used for the tire crumb rubber characterization study.
- **Appendix E** contains the Quality Assurance/Quality Control section.
- **Appendix F** contains the study questionnaire for the tire crumb characterization research effort.
- **Appendices G-U** include more complete reporting of results from the tire crumb characterization research activities.
- **Appendix V** contains a summary of external peer review comments.

2.0 Summary of Results and Findings

This section is divided into several parts: 1) an overview and 2) detailed summary of the results of individual components of this part of the research study, specifically focusing on the tire crumb rubber characterization and toxicity reference information and the associated findings based on those results; and, a discussion of 3) research limitations; 4) recommendations for next steps; and 5) major conclusions.

Technical details of the methods and detailed research results are provided in subsequent sections (3–5) and their associated appendices. A list of research standard operating procedures (SOPs) is provided in Appendix D, and the SOPs will be published in a separate report. Quality assurance and quality control results can be found in Appendix E.

2.1 Overview of Research Activities

The federal research described in this report provides new and additional data needed for more complete tire crumb rubber characterization that will be useful for improving exposure estimation for individuals using synthetic turf fields with recycled tire crumb rubber infill. The study is not a risk assessment; however, the results of the research described in this and future reports should advance the understanding of exposure to inform the risk assessment process. Specific activities undertaken and described in this report are summarized in Table 2-1.

Table 2-1. Topic Areas and Specific Activities Described in This Report

Topic Area	Activities
Recycling Plant and Synthetic Turf Field Recruitment and Sampling	Recruiting and collecting samples at multiple tire recycling facilities producing tire crumb rubber and multiple synthetic turf fields with tire crumb rubber infill across the United States
Synthetic Turf Field Operations and Maintenance	Collecting information from synthetic turf field owners/managers to better understand field operations, types and numbers of field users, field maintenance practices and the use of chemical or other product treatments on the fields
Tire Crumb Rubber Chemical, Physical and Microbiological Characterization	Preparing the samples collected from tire recycling plants and synthetic turf fields for several types of characterizations and analyses Measuring particle size ranges and other particle characteristics of ‘fresh’ tire crumb rubber from tire recycling plants and tire crumb rubber infill from synthetic turf fields across the United States, with further exploration of particle size and morphology using scanning electron microscopy Completing quantitative characterization of the inorganic and organic chemical substances found in the sampled tire crumb rubber from tire recycling plants and tire crumb rubber infill from synthetic turf fields Providing insight on differences between chemical substances associated with ‘fresh’ tire crumb rubber produced at recycling plants and what is found in tire crumb rubber infill on synthetic turf fields Examining emissions of organic chemicals from tire crumb rubber material at two temperatures for improved understanding of the potential for inhalation exposures Assessing variability of chemicals associated with tire crumb rubber within and between recycling plants, as well as within and between fields

Table 2-1 Continued

Topic Area	Activities
Tire Crumb Rubber Chemical, Physical and Microbiological Characterization (Continued)	Examining the range of chemical concentrations found in tire crumb rubber infill from fields across the United States and some of the important characteristics associated with those differences across fields, including indoor vs. outdoor fields, fields with a wide range of installation dates and fields in different U.S. regions Using suspect screening and non-targeted analysis approaches to elucidate the potentially larger range of chemicals for which additional information may be needed to better understand exposures and risks Measuring the bioaccessibility of metals from tire crumb rubber as an important characteristic for improving understanding of potential exposure Performing targeted and non-targeted microbial assessments to elucidate microbiological populations associated with tire crumb rubber infill at synthetic turf fields and characteristics associated with differences across a range of fields in the United States
Toxicity Reference Information	Identifying and collating toxicity reference information on potential chemical constituents of tire crumb rubber from existing on-line databases and literature sources

2.2 Tire Crumb Rubber Characterization: Overview of Research Approach, Results and Key Findings

2.2.1 Research Approach

The tire crumb rubber characterization part of the FRAP's study involved the collection of crumb rubber material from tire recycling plants and synthetic turf fields across the United States, with laboratory analysis for a wide range of metals/metalloids, volatile organic compounds (VOCs), and semivolatile organic compounds (SVOCs).[5] Analyses of physical characteristics were performed to measure tire crumb particle size fractions, particle characteristics, moisture content, and sand content. Laboratory analyses included direct quantitative analysis of select target metals, following acid digestion, and SVOCs, following solvent extraction. Chamber tests were performed to estimate the amounts of VOCs and SVOCs released into the air (emission factors) under different temperature conditions. Bioaccessibility tests were performed to measure the amounts of metals released from tire crumb rubber using three simulated biological fluids (i.e., gastric fluid, saliva, and sweat plus sebum). The emissions and bioaccessibility experiments were designed to provide information about the types and amounts of chemicals in the recycled tire crumb rubber material available for human exposure through inhalation, dermal, and ingestion pathways. In addition to quantitative target chemical analyses, additional analysis methods (suspect screening and non-targeted analysis) were used to determine whether there may be other VOCs and SVOCs that have not been identified or reported in previous research. The tire crumb characterization research effort also included collecting recycled tire crumb rubber infill from synthetic turf fields to assess microbial populations.

[5] Among the target analytes, arsenic and antimony are commonly considered metalloids, while selenium is sometimes considered a metalloid; these elements are included in the 'metals' category in this report for simplicity.

2.2.2 Overview of Results and Key Findings

Synthetic turf field recycled tire crumb rubber infill particles were found in sizes predominantly ranging from 0.25 to 4 mm in diameter, with a great deal of variability within this range. While the proportion of small particles in synthetic turf field infill (sizes ≤ 0.063 mm) was relatively low (mean = 0.63 g/kg; median = 0.1 g/kg), their presence was consistently found at synthetic turf fields. These smaller particles may be important for inhalation exposures and for exposure through dermal contact and ingestion.

Particle Size

Particles ≤ 0.063 mm in size were consistently found in synthetic turf field infill. Although the proportion of these particles was relatively low, small particles like these may be important for potential exposures.

Most of the target analytes among the 21 metals and 49 SVOCs, and several of the 31 target VOCs were found in tire crumb rubber infill collected at fields across the United States. Average concentrations ranged from <1 mg/kg for several metals and extractable SVOCs up to 15,000 mg/kg for zinc. Examples of these measurement results are highlighted in Figure 2-1 for metal target analytes and in Figure 2-2 for select polycyclic aromatic hydrocarbon (PAH) analytes. In addition, suspect screening and non-targeted analyses demonstrated that other VOCs and SVOCs may be associated with the material. Several SVOCs tentatively identified through suspect screening analysis included chemicals reported to be used as accelerators, anti-oxidants or anti-ozonants in rubber manufacture; however, more work would be needed to confirm chemical identities.

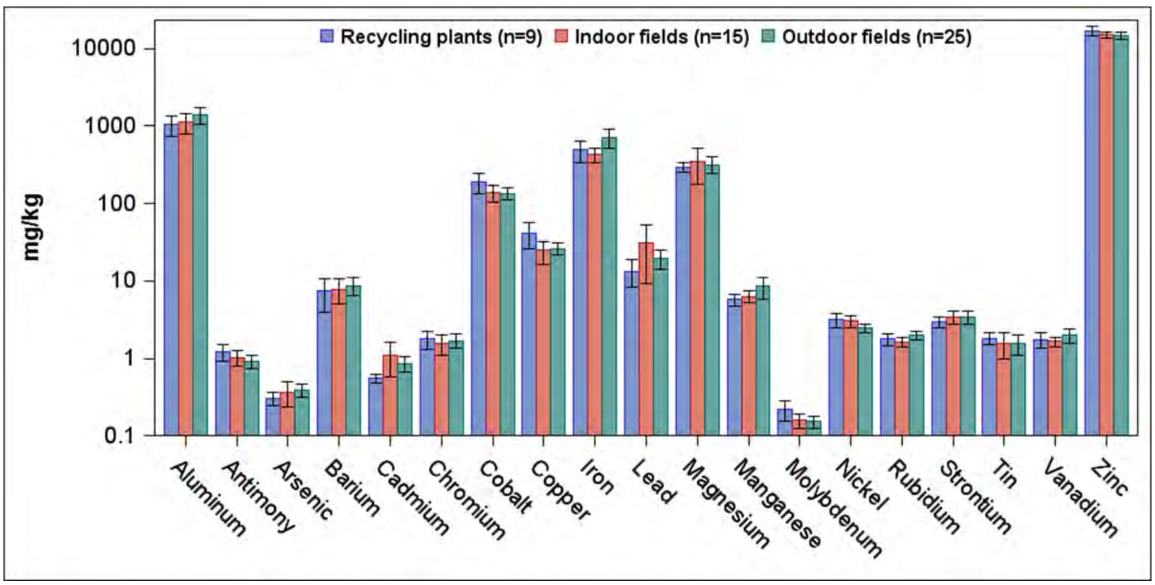

Figure 2-1. Average measurement results for metals in tire crumb rubber samples collected from tire recycling plants and indoor and outdoor synthetic turf fields with tire crumb rubber infill.

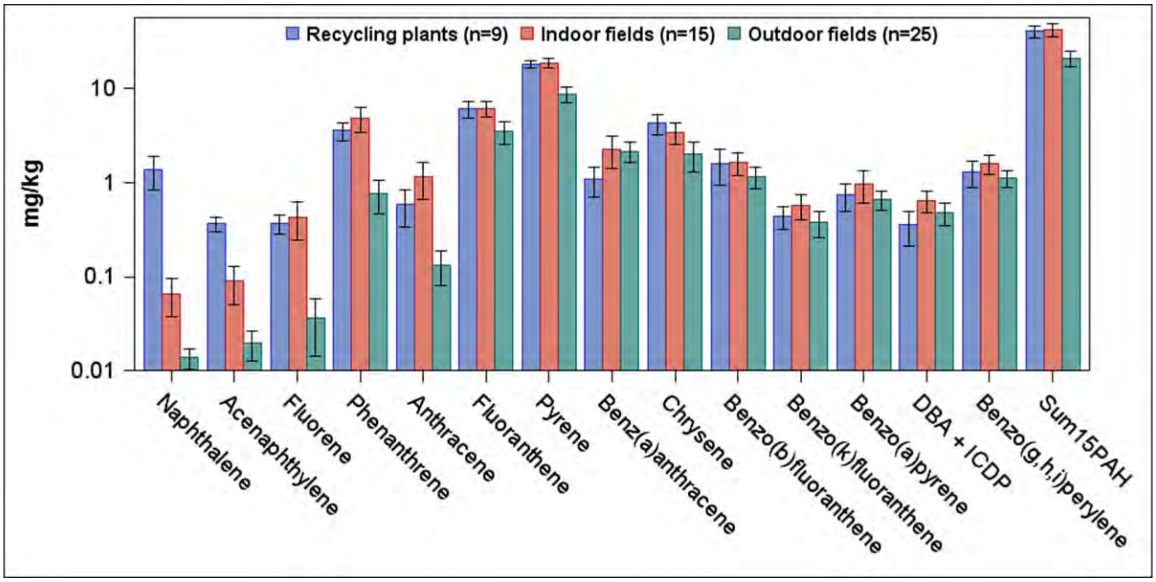

Figure 2-2. Average measurement results for selected extractable polyaromatic hydrocarbons in tire crumb rubber samples. [DBA + ICDP = Sum of Dibenz[a,h]anthracene and Indeno(1,2,3-cd)pyrene; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

Comparison of chemical measurements from 'fresh' tire crumb rubber samples produced at recycling plants (i.e., tire crumb rubber not yet installed at a field) to tire crumb rubber infill from synthetic turf fields showed that most of the chemicals found in synthetic turf infill were also present in the 'fresh' tire crumb rubber from recycling plants. Many of the SVOCs and VOCs were found at average higher levels in tire crumb rubber from recycling plants. Additional research involving longitudinal studies at individual fields would be needed to confirm that vaporization, weathering, and/or other mechanisms may lead to lower concentrations of these chemicals over time when installed on playing fields. A few chemicals, including lead and bis(2-ethylhexyl) phthalate, had higher average levels in tire crumb rubber infill from synthetic turf fields compared to tire crumb rubber from recycling plants. Similarly, additional research would be needed to determine if external sources may contribute to the levels of some chemicals found in the tire crumb rubber infill at synthetic turf fields.

One synthetic turf field had a substantially higher measured concentration of lead (160 mg/kg) in its composite tire crumb rubber infill sample than other fields, while another field had similar levels in two of seven individual location samples. These results suggest sources of lead other than tire crumb rubber may be present at some locations.

Chemical Constituents

- **Most metals and many semivolatile organic compounds (SVOCs) found in previous tire crumb rubber studies were found at similar concentrations in the infill of synthetic turf fields.**
- **Some SVOCs and VOCs not widely reported in previous studies have been tentatively identified but not confirmed.**

'Fresh' Tire Crumb vs. Tire Crumb Rubber Infill

- **Most tire crumb rubber metals were present in synthetic turf field infill at levels similar to those in 'fresh' tire crumb rubber from recycling plants.**
- **Many organic chemicals were present in synthetic turf field infill at levels lower than those in 'fresh' tire crumb rubber from recycling plants.**
- **A few chemicals, including lead and bis(2-ethylhexyl) phthalate, were present, on average, at higher levels in the infill of synthetic turf fields compared to 'fresh' tire crumb rubber.**

This study afforded the largest sample size to date in the United States to examine variability in chemicals associated with tire crumb rubber infill at synthetic turf fields and field characteristics related to those differences. In general, the variability in chemical concentrations between fields was much greater than the variability within fields for most organic chemicals (VOCs and SVOCs), with more mixed results found for metals. Most organic chemicals were found at higher levels at indoor fields compared to outdoor fields. Many organic chemicals, particularly those in the more volatile ranges, showed a pattern of decreasing concentration with increasing field installation age at outdoor fields.

Variability in Organic Chemical Concentrations

- **Most organic compounds were found at higher levels at indoor fields compared to outdoor fields.**
- **At outdoor fields, lower levels of organic chemicals, particularly VOCs and the more volatile SVOCs, were found with increased age of the synthetic turf field.**
- **For most organic chemicals there was more variability in levels between different fields than at different locations within a field.**

Measurement results in this study for metal and extractable SVOC target analytes were compared to those reported in other studies. Table 2-2 shows select metal concentration results obtained in this study compared to results in several previous studies. In general, concentrations measured in this study were consistent with, and within the range of, concentrations found in previous studies. Table 2-3 shows select extractable SVOC concentrations measured in this and other studies. In general, concentrations measured for outdoor fields in this study were within the range of measurements from other studies for most analytes where comparable data are available. Benzothiazole and bis(2-ethylhexyl) phthalate measurements in this study were higher than results obtained in two recent studies. There were relatively few measurements available for comparisons with recycling plant and indoor field samples from previous studies.

Table 2-2. Comparison of Select Tire Crumb Rubber Metal Analysis Results Across Multiple Studies[a]

Chemical	This Study 2019 – Recycling Plants (n=9)	Cristy 2018 – Recycling Plants (n=2)	Marsili 2014 – New Unused (n=5)	This Study 2019 – Indoor Fields (n=15)	This Study 2019 – Outdoor Fields (n=25)	Celeiro 2018 – Outdoor Fields (n=2)	Marsili 2014 – Outdoor Fields (n=4)	Ruffino 2013 Outdoor Fields (n=4)	Kim 2012 – Outdoor Fields (n=50)	Menichini 2011 – Outdoor Fields (n=4)	U.S. EPA 2009 – Outdoor Fields (n=4 fields; n=26 samples)	Bocca 2009 – Outdoor Fields (n=32)	Zhang 2008 – Outdoor Fields (n=2 fields; n=4 samples)
Arsenic	0.30	0.81	N/A	0.37	0.39	0.71	N/A	N/A	N/A	0.19	0.24	0.24	1.4
Cadmium	0.55	0.65	1.8	1.1	0.86	0.84	1.5	N/A	0.46	1.3	0.70	0.37	0.30
Chromium	1.8	N/A	7.0	1.5	1.7	1.4	3.5	N/A	11	2.5	0.56	6.2	1.0
Cobalt	190	145	N/A	139	135	184	N/A	112	N/A	28	N/A	15	N/A
Lead	13	13	21	31	20	21	26	96 (26)[b]	39	21	28	22	17
Zinc	17000	16800	6437	15000	15000	14150	4809	13125	3752	13514	8749	10229	7849

[a] All results are mean values with exception of median values reported in Bocca 2009; All results are in mg/kg; N/A = not applicable

[b] Tire crumb rubber at one field had a lead concentration of 308 mg/kg. The average is 26 mg/kg without that field included.

Table 2-3. Comparison of Selected Tire Crumb Rubber Extractable SVOC Analysis Results Across Multiple Studies[a]

Chemical	This Study 2019 – Recycling Plants (n=9)	Marsili 2014 – New Unused (n=5)	Gomes 2010 – Recycling Plant (n=1)	This Study 2019 – Indoor Fields (n=15)	Salonen[b] 2015 – Indoor Fields (n=4)	This Study 2019 – Outdoor Fields (n=25)	Celeiro[c] 2018 – Outdoor Fields (n=15)	RIVM[d] 2017 – Outdoor Fields (n=91 fields or n=7 fields)	Marsili 2014 – Outdoor Fields (n=4)	Ruffino 2013 – Outdoor Fields (n=4)	Menichini 2011 – Outdoor Fields (n=5)	Zhang[e] 2008 –Outdoor Fields (n=4 fields, n=7 samples)
Phenanthrene	3.6	0.74	1.4	4.8	6.0	0.76	0.75	<0.6	0.34	N/A	N/A	1.2
Fluoranthene	6.1	2.4	4.5	6.2	9.9	3.5	3.5	3.4	1.4	N/A	N/A	4.9
Pyrene	18	5.2	14	19	26	8.8	8.0	7.5	4.0	22	6.6	6.3
Benzo[a]pyrene	0.74	0.25	1.2	0.98	1.4	0.66	1.0	<1.1	0.26	0.96	3.6	2.0
Benzo[ghi]perylene	1.3	0.55	<0.08	1.6	5.0	1.1	3.3	4.1	0.40	2.5	N/A	2.3
Benzothiazole	79	N/A	N/A	19	N/A	5.6	1.9	2.7	N/A	N/A	N/A	N/A
4-tert-octylphenol	30	N/A	N/A	20	N/A	3.5	N/A	4.5	N/A	N/A	N/A	N/A
Diisobutyl phthalate	0.50	N/A	N/A	2.7	N/A	0.36	2.5	<0.5	N/A	N/A	N/A	N/A
Bis(2-ethylhexyl) phthalate	12	N/A	N/A	65	N/A	29	8.7	7.6	N/A	N/A	N/A	N/A

[a] All results are mean values with exception of a single measurement in Gomes 2010 and median values reported in RIVM 2017; All results are in mg/kg; N/A = not applicable

[b] For the several values that were below the limit of detection, one-half the limit of detection was substituted for calculating a mean result.

[c] Mean values reported in Celeiro et al. (2018) Table 2 were based only on reported (non-missing) values. It was assumed that the missing values were non-detects. A substitution of one-half the lowest reported value was made for missing results to calculate overall means for this table. Mean results in this table differ from means in Celeiro et al., as a result.

[d] This study included 546 samples from 91 fields for many PAHs and two phthalates [bis(2-ethylhexyl) phthalate and diisobutyl phthalate]; 43 samples from 7 fields for the remaining phthalates; and 7 samples from 7 fields for several PAHs, phenols, and thiazoles.

[e] Substituted detection limits for non-detects.

Measurement of emissions of organic chemicals from tire crumb rubber infill was conducted to improve our understanding of the potential for human exposures through the inhalation pathway. This study generated emission test results for VOCs and SVOCs using dynamic emissions testing chambers in the laboratory. Tests were performed at 25 °C and 60 °C. For most VOC and SVOC target analytes, emissions were low at 25 °C and in many cases, not measurable above the method limit of detection or above chamber background levels. At 60°C, higher emissions were measured for some, but not all, VOCs and SVOCs. The less volatile SVOCs had very low or non-measurable emissions, with the 5- and 6-ring PAHs generally not measurable above the limit of detection at either 25 °C or 60 °C.

Emissions for most VOCs and SVOCs were higher for tire crumb rubber from recycling plants compared to tire crumb rubber infill from synthetic turf fields. Higher emissions were observed for most chemicals from infill collected at indoor fields compared to outdoor fields, and several of the VOC and SVOC target analytes showed a pattern of decreasing emissions with increasing field installation age at outdoor fields.

The amount of chemicals released from tire crumb rubber and solubilized into body fluids (bioaccessibility) characterizes the potential exposure of a receptor to the chemical, which in turn determines what is available for absorption (bioavailability). The bioaccessibility of metals in the tire crumb rubber and tire crumb rubber infill samples collected in this study was measured using three artificial biological fluids, specifically gastric fluid, saliva, and sweat plus sebum. For metals, only small fractions were released into simulated biological fluids (e.g., the average bioaccessibility values for lead from tire crumb rubber infill were approximately 3% for gastric fluid and less than 0.1% for saliva and sweat plus sebum). For all metals, the mean bioaccessibility values averaged approximately 3% in gastric fluid, and less than 1% in saliva and sweat plus sebum. These results fill important knowledge gaps about potential bioavailability of recycled tire crumb rubber. While it is recognized that presence of a chemical in a material does not mean that the chemical is available for absorption, exposure and risk assessments often default to using 100% of the chemical being bioaccessible and/or bioavailable in the absence of medium-specific information (U.S. EPA, 2007). Findings from this study support the premise that while many chemicals are present in the recycled tire crumb rubber, exposure may be limited based on what is released into air or biological fluids. A default to 100% bioaccessibility should not be used when assessing potential exposures to most metals in tire crumb rubber.

Organic Chemical Emissions

- **Measuring emissions of organic chemicals is important for understanding the potential for inhalation exposures associated with tire crumb rubber.**
- **Emissions tests were performed at 25 °C and 60 °C to reflect moderate and high-end field temperature conditions.**
- **At 25 °C, emissions of most organic chemicals were low, and in many cases, not measurable above the detection limit or background level.**
- **At 60 °C, emissions increased for some organic chemicals; some chemical emissions remained very low or non-measurable even at higher temperatures.**
- **Among the chemicals examined, methyl isobutyl ketone and benzothiazole had the highest emission factors.**
- **Higher emissions were observed for most chemicals at indoor fields compared to outdoor fields.**
- **At outdoor fields, lower emissions of several organic chemicals were found with increased age of the synthetic turf field.**
- **People may also inhale small particles of tire crumb rubber at fields; this type of exposure was not assessed in the chamber emission testing.**

Tire crumb rubber infill samples collected from synthetic turf fields were analyzed for select targeted microbe genes; non-targeted analysis was also performed to assess the wider microbial community. All samples tested from the 40 fields were positive for bacteria genes, showing widespread microbial presence at synthetic turf fields. Synthetic turf fields contain diverse bacterial communities, as 1,424 unique bacterial taxa were detected across the fields examined. Fields that were in outdoor settings tended to have higher concentrations of bacteria than indoor fields. However, indoor fields showed a higher occurrence of methicillin resistance genes than outdoor fields. Likewise, a gene for *Staphylococcus aureus*, a common member of the human skin microbiome and potential carrier of methicillin resistance genes, was detected more frequently in indoor fields than outdoor fields. Although methicillin resistance genes were detected in the community of bacteria in synthetic turf fields, it is uncertain if these genes were carried by potential human pathogens.

There were no directly-comparable genetic studies found for either synthetic turf or grass playing fields. Small studies that cultured bacteria have found more colony forming units (CFU) for some bacteria at grass fields compared to synthetic turf fields (McNitt et al., 2007; Vidair, 2010), and two independent studies showed that the addition of rubber to soil significantly reduced concentrations of culturable bacteria and the metabolic activity of the natural microbial community (Goswami et al., 2017; Pochron et al., 2017). The presence of a bacterial community in synthetic turf fields is not surprising, however. Bacteria have been reported at similar concentrations in environments that humans encounter, such as indoor air (5.6 $\log_{10}$ bacteria-like particles [BLP]/m^3), outdoor air (8.4 $\log_{10}$ BLP/m^3; Prussin, et al. 2015) and common household items, including mobile phones (4.2 $\log_{10}$ gene copies of 16S ribosomal ribonucleic acid (rRNA) genes per phone; Koljalg et al., 2017) and kitchen hand towels (7.2 $\log_{10}$ CFU per towel; Gerba et al. 2014). It should also be noted that the human body harbors an estimated 13.6 $\log_{10}$ bacteria (Sender et al., 2016). In another study (Vidair, 2010), researchers cultured *Staphylococcus* and methicillin-resistant *Staphylococcus aureus* (MRSA) from samples collected at five synthetic turf field and two grass fields. In that study, 2 of the 30 samples collected from synthetic turf were positive for a species of *Staphylococcus* compared to 6 of 12 samples collected from natural turf. No MRSA was detected on synthetic turf, while a single sample of blades from natural turf was positive for MRSA. Vidair (2010) concluded that their data indicated that the new generation of synthetic turf containing crumb rubber infill harbors fewer bacteria than natural turf, including *Staphylococcus* and MRSA.

Bioaccessibility of Metals

- **Bioaccessibility of metals for absorption by the human body was tested by measuring the amount of metals released from tire crumb rubber and able to be solubilised in three artificial body fluids (gastric fluid, saliva, and sweat plus sebum).**
- **For all metals, the mean bioaccessibility values averaged approximately 3% in gastric fluid, and less than 1% in saliva and sweat plus sebum.**
- **Average bioaccessibility values for lead from tire crumb rubber infill were approximately 3% for gastric fluid and less than 0.1% for saliva and sweat plus sebum.**

Microbes and Bacteria

- **All synthetic turf field samples tested positive for bacteria, but this is not surprising given that bacteria have been reported at similar concentrations in indoor air, outdoor air and on common household items.**
- **The bacterial community present in synthetic turf fields is diverse - over 1,424 unique bacteria were found in the samples tested.**
- **Outdoor fields tended to have higher overall levels of bacteria compared to indoor fields; however higher levels of two specific bacteria genes were found at indoor fields.**

2.2.3 Tire Crumb Rubber Characterization Synopsis

Based upon available literature, this research represents the largest and most robust study of synthetic turf fields and tire crumb rubber to date in the United States. Tire crumb rubber samples were collected from nine tire recycling facilities, and tire crumb rubber infill was collected from 40 synthetic turf fields across the United States. The fields represented a range of field types, field ages and geographic locations and included both indoor and outdoor fields. Multiple analytical techniques were applied to measure physical, chemical and microbiological attributes of the various groups of samples. Tire crumb rubber characterization results from this portion of the research provide insight into the number and types of chemicals associated with the material, the amount of chemicals released into the air and biological fluids, and the range and variability of these parameters.

- As expected, because of the complexity of the material, many chemicals were found to be associated with tire crumb rubber collected from tire recycling plants and tire crumb rubber infill collected from fields across the United States, including a range of metals, PAHs, phthalates and other tire rubber related chemicals. Suspect screening and non-targeted analyses showed an additional number of organic chemicals, many of which had not been characterized in previous studies, however, further work would be needed to confirm identities of these chemicals. In general, concentrations of chemicals measured in outdoor synthetic turf field infill were similar to those measured in other studies where comparable data are available.
- Concentrations of many organic chemicals appeared to decrease with increasing field age. These results support the idea that vaporization, weathering (including leaching from rainfall or irrigation) and/or other mechanisms for removal lead to lower concentrations of many organic chemicals over time, particularly for outdoor fields. While an alternative explanation that there may have been different concentrations of chemicals in recycled tires over time cannot be ruled out, the patterns seen across vapor pressure and water solubility, and differences between indoor and outdoor fields of similar ages appear to favor a weathering explanation for the differences. Additional research, including longitudinal studies at individual fields, would be needed to confirm this.
- Organic chemical concentrations were generally higher at indoor fields, which have reduced weathering effects. When combined with the lower ventilation rates for indoor facilities compared to outdoor fields, these results suggest that exposures to organic chemicals associated with tire crumb rubber may be higher for people using indoor fields. Additional research would be needed to confirm this. Results from two sets of indoor air measurements in other studies support this finding (Norwegian Institute of Public Health and the Radium Hospital, 2006; Simcox et al., 2010), however, relatively few indoor fields have been studied.
- VOC and SVOC laboratory chamber emission experiments provided information about the potential for chemicals associated with tire crumb rubber to be released into the air and to become available for inhalation exposure. Most of the target organic chemicals had relatively low or non-measurable emissions at 25 °C. Some, but not all, had higher emissions at 60 °C. Methyl isobutyl ketone and benzothiazole had among the highest emission factors and have also been measured in the air at synthetic turf fields in other studies, above ambient background levels. In the few studies taking measurements at indoor field facilities, chemicals associated with tire crumb rubber have been shown to have higher concentrations in indoor air compared to the air at outdoor fields. Releases and exposures are also likely to be higher for some organic chemicals as the field temperature increases. Emissions data from this and other studies as well as field measurement data could be further developed in modeling approaches to estimate air

concentrations and inhalation exposures under different conditions for both vapor- and particle-phase chemicals associated with tire crumb rubber.

- While the characterization measurements demonstrate that there are many chemicals detected in tire crumb rubber, the in vitro bioaccessibility measurements of the metals in three simulated biological fluids indicate that the amounts that can be released from the material for absorption are relatively low when compared to a default assumption of 100% bioaccessibility. For all metals, the mean bioaccessible fractions averaged approximately 3% in artificial gastric fluid, and less than 1% in saliva and in sweat plus sebum. Although bioaccessibility of organic chemicals, such as PAHs, was not measured in this study, other studies suggest they too are bioaccessible at low percentages – < 10% of PAHs into simulated gastrointestinal tract and < 0.1% into simulated sweat in two studies (RIVM, 2017; Pronk et al., 2018) and below the detection limits in another study (Pavilonis et al., 2014).
- The presence of many chemicals in combination with low bioaccessibility suggest the complexity and challenge to accurately assess cumulative exposures for synthetic turf field users that can occur through different exposure pathways.

2.3 Toxicity Reference Information: Overview of Research Approach, Results and Key Findings

Extant toxicological reference information was compiled for potential tire crumb rubber chemical constituents identified in the tire crumb rubber Literature Review and Gap Analysis (LRGA; released December 30, 2016 and included as Appendix C in this report). Eleven sources of toxicity reference information were searched. At least one source of extant toxicity reference information was available for 167 (47%) of the 355 potential constituents examined. When narrowing this down from the LRGA's list of 355 to its subset of target chemicals in this study (95), toxicity reference information is available from at least one source for 78 of those (about 82%).

In summary, some toxicity reference information is available for almost half of the list of potential chemicals associated with tire crumb rubber and for most of those in the target analyte list of this study. It is important to recognize that some of these target analytes were not found, or were not consistently found, in tire crumb rubber in this portion of the study. Some potential toxicity-related information beyond the sources reviewed may be available in the literature but was not evaluated here. In addition to the target chemicals measured in this study, the presence of many other organic chemicals was found through non-targeted assessment. Further work would be needed to positively identify chemicals and their amounts, and to determine the availability of toxicity information for these chemicals.

Toxicity of Recycled Tire Crumb Rubber

- **Toxicity reference information was identified for 167 of 355 potential tire crumb rubber constituents.**
- **When narrowing this down from the LRGA's list of 355 to its subset of target constituents in this study (95), toxicity reference information is available for most (78) of those (about 82%).**

Toxicity testing of the whole material vs. individual constituents (being performed by the National Toxicity Program) is a reasonable approach for assessing cumulative toxicity for a complicated multi-chemical material such as tire crumb rubber. While the National Toxicology Program has recently presented short-term toxicity results for the recycled tire crumb rubber material itself using in vivo and in vitro testing (Gwinn et al., 2018; Richey et al., 2018; Roberts et al., 2018), more comprehensive data may be needed for both cumulative toxicity and risk assessments.

2.4 Detailed Summaries of Research Results

2.4.1 Recycling Plant and Synthetic Turf Field Recruitment and Sampling

Organizations across the United States were recruited to allow for collection of tire crumb rubber samples for analysis. These included tire recycling facilities producing "fresh" tire crumb rubber for use on synthetic turf fields and owners of synthetic turf fields with tire crumb rubber infill.

- CDC/ATSDR and EPA reached sample collection agreements with six tire recycling companies that manufacture recycled tire crumb rubber infill at nine tire recycling facilities where tire crumb rubber samples were collected.
- The nine tire recycling facilities from which samples were collected used two different processes to manufacture the recycled tire crumb rubber – three used a cryogenic process and six used an ambient process.
- A total of 40 synthetic turf fields with tire crumb rubber infill were recruited for sample collection, including 21 community fields and 19 synthetic turf fields at U.S. Army military installations.
- The distribution of the 40 synthetic turf fields included 25 outdoor synthetic turf fields and 15 indoor fields across the four U.S. census regions, with nine fields in the Northeast, 13 in the South, eight in the Midwest, and 10 in the West.
- The synthetic turf fields sampled included a variety of ages, with 11 fields installed between 2004 and 2008, 18 fields installed from 2009 to 2012, and 11 fields installed from 2013 to 2016.

2.4.2 Synthetic Turf Field Operations and Maintenance

A total of 40 questionnaires were administered over the phone to field owners or managers of the 40 synthetic turf fields recruited in this study to obtain information on field use and field maintenance practices. A majority of the interviewed facility persons reported they were managers of the synthetic turf fields (87.5%).

- Replacing all tire crumb rubber infill on the fields was not commonly reported. Only one indoor field and one outdoor field reported replacing all tire crumb rubber infill.
- Interviewees for indoor fields were more likely to report refreshing or adding tire crumb rubber (60%) than outdoor fields (46%).
- Interviewees for indoor fields were more likely to report treatment with cleaning agents, anti-static agents, or with biocides than outdoor fields (50% and 17%, respectively).
- Brushing and leveling were commonly-reported infill maintenance practices for both indoor fields (60% and 40%, respectively) and outdoor fields (56% and 52%, /respectively).
- A large majority of the fields (85%) reported they did not have standard practices in place to reduce exposure to tire crumb rubber.

2.4.3 Tire Crumb Rubber Physical, Chemical and Microbiological Characterization

2.4.3.1 Particle Size and Characteristics

Particle size analysis was performed for three tire crumb rubber samples collected from each of the nine tire recycling plants and from composite tire crumb rubber infill samples collected at each of the 40 synthetic turf fields. A sieving method was used to generate seven particle size fractions for each sample, ranging from ≤ 0.063 to > 4.75 mm, for weighing.

- For 'fresh' tire crumb rubber samples from recycling plants, on average, a majority of the tire crumb was found in the > 1- to 2-mm size fraction (780 g/kg), with smaller amounts in the > 0.25- to 1-mm (140 g/kg) and the > 2- to 4.75-mm (86 g/kg) size fractions. On average, 1.2 g/kg was measured in the > 0.125- to 0.25-mm fraction, 0.35 g/kg was measured in the > 0.063- to 0.125-mm fraction, 0.089 g/kg in the > 4.75-mm fraction and 0.037 g/kg in the ≤ 0.063-mm fraction.
- For synthetic turf field tire crumb rubber infill samples, on average, the majority of the tire crumb was also found in the > 1- to 2-mm size fraction (580 g/kg), with smaller amounts in the > 2- to 4.75-mm (250 g/kg) and the > 0.25- to 1-mm (170 g/kg) size fractions. On average, 0.75 g/kg was measured in the > 0.125- to 0.25-mm fraction, 0.63 g/kg in the ≤ 0.063-mm fraction, 0.47 g/kg was measured in the > 0.063- to 0.125-mm fraction and 0.18 g/kg in the > 4.75-mm fraction.
- While a majority of the tire crumb rubber was found in the > 1- to 2-mm size fraction, there was substantial variability across the amounts measured in the > 0.25- to 1-mm, > 1- to 2-mm, and > 2- to 4.75-mm size fractions for infill collected at synthetic turf fields.
- On average, there were higher amounts of the smallest particle size fraction on fields as compared to 'fresh' tire crumb rubber from recycling plants. It could not be directly determined if the higher amounts of these smaller particles present at the synthetic turf fields was a result of the breakdown of larger tire rubber particles. Particles from crustal, atmospheric deposition and biogenic sources are also likely to be present at the fields, but the relative amounts of non-rubber particles were not measured.
- Examples of the different size ranges of tire crumb rubber infill collected at synthetic turf fields are shown in Figure 2-3.

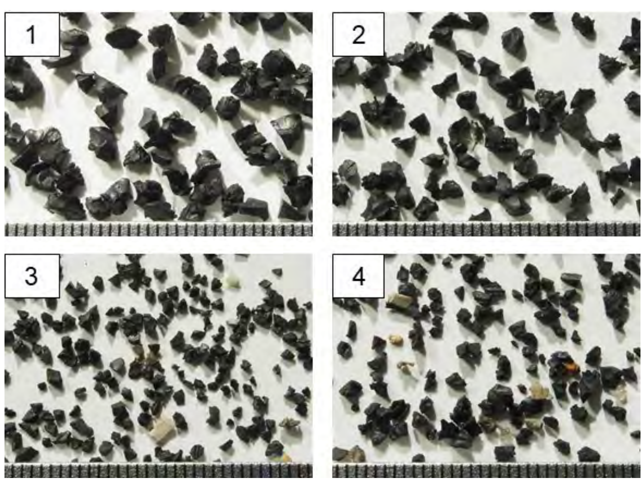

Figure 2-3. Example close-up photos of tire crumb rubber infill collected at four synthetic turf fields showing a range of particle sizes. Scale gradations are 1 mm.

- With one exception, there were no statistically-significant differences in size fractions of tire crumb rubber infill samples grouped by field characteristics, including indoor vs. outdoor, installation age, and geographic region. For the > 2- to 4.75-mm size fraction, mean values ranged from 100 to 390 g/kg at fields across the four U.S. census regions, and the differences among regions was statistically significant at the $\alpha = 0.05$ level ($p = 0.0168$).
- The average moisture content in tire crumb rubber samples from recycling plants was 0.81% (range 0.52 to 0.99%). In tire crumb rubber infill from synthetic turf fields, the average moisture content was 1.0% (range 0.40 to 6.2%). All chemical analysis measurement results were adjusted for moisture and reported as amount per dry tire crumb rubber material.
- Sixteen fields (40%) had sand in the tire crumb rubber infill samples. The average sand content among the infill samples collected from the surface of those sixteen fields was 19% by weight (range 0.33 to 53%). Chemical analysis measurement results in this report have not been adjusted for sand fraction in the synthetic turf field infill.

2.4.3.2 Metals

Tire crumb rubber from recycling plants and tire crumb rubber infill from synthetic turf fields was quantitatively analyzed for 21 metals by acid extraction and inductively coupled plasma/mass spectrometry (ICP/MS) analysis, with 20 of those metals measurable above the detection limit in most samples. Selenium was not measured above the method detection limit in any sample. (Mercury was analyzed only in the bioaccessibility samples and is not reported here).

- Examples of average metal measurement results for samples collected at recycling plants vs. synthetic turf fields include chromium (1.8 vs. 1.6 mg/kg), lead (13 vs. 24 mg/kg), cobalt (190 vs. 140 mg/kg) and zinc (17,000 vs. 15,000 mg/kg).
- Maximum values of these four metals in synthetic turf field samples were 3.7, 160, 290 and 22,000 mg/kg for chromium, lead, cobalt, and zinc, respectively.
- Examples of the measurement results and comparisons between recycling plant samples and synthetic turf field samples are shown in Figure 2-4 for lead and zinc.

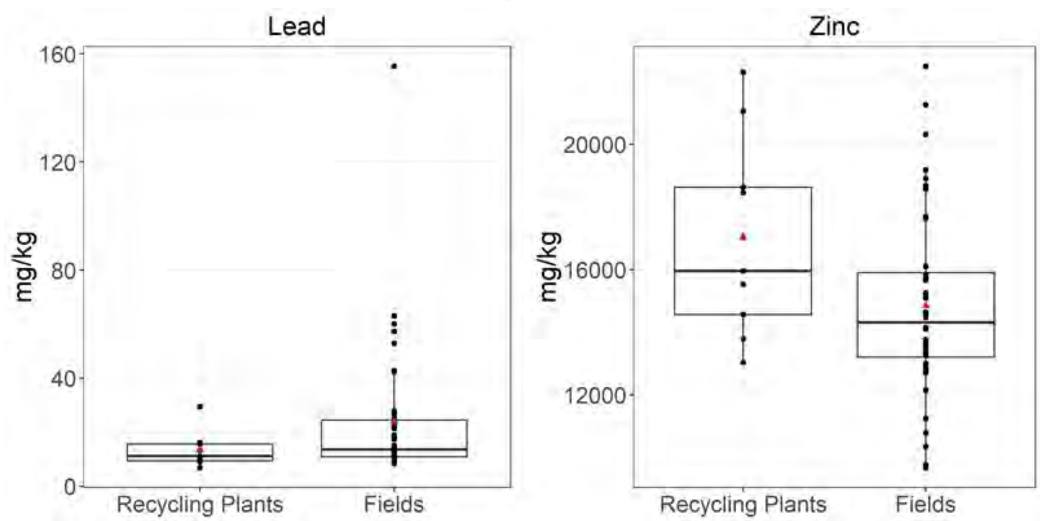

Figure 2-4. ICP/MS metal analysis results (mg/kg) for tire crumb rubber collected from tire recycling plants and tire crumb rubber infill composite samples from synthetic turf fields for lead and zinc.

- Lead was found, on average, at statistically significant higher levels (p-value = 0.0060) on synthetic turf fields compared to 'fresh' material coming from recycling plants (24 vs. 13 mg/kg, respectively). Additional research would be needed to confirm this trend at individual fields; if confirmed, possible explanations include atmospheric deposition or transport from nearby soils, track-in by field users, and/or presence in and release from other synthetic turf field materials. It is also possible that tires recycled in years prior to 2016 had higher levels of lead than tires being recycled now, but no evidence of this was found in the literature.
- Zinc was found, on average at statistically significant lower levels (p-value = 0.0063) on synthetic turf fields compared to 'fresh' material coming from recycling plants (15,000 vs. 17,000 mg/kg, respectively). Zinc has been shown to leach from tire crumb rubber in water. If additional research confirmed this trend at individual fields, rainfall and/or irrigation could be one possible explanation for the lower levels found at fields. In this study, however, there was no statistically significant difference in levels of zinc found in crumb rubber collected at outdoor and indoor fields, both had average concentrations of 15,000 mg/kg.
- Table 2-4 shows a comparison of average metal measurement results in this study to measurements obtained in other studies. The comparison studies were restricted to those analyzing uncoated tire crumb rubber from synthetic turf fields or recycling plants. In general, measurements in this study were within or near to the range of measurements from other studies. There were fewer comparable studies with results for indoor fields or recycling plants. No directly comparable data were found for some of this study's target analytes, and some other studies provided results for analytes that were not quantitatively analyzed in this study.

Table 2-4. Comparison of Tire Crumb Rubber Metal Analysis Results Across Multiple Studies[a]

Chemical	This Study 2019 – Recycling Plants Mean (n=9)	Cristy 2018 – Recycling Plants Mean (n=2)	Marsili 2014 – New Unused Mean (n=5)	This Study 2019 – Indoor Fields Mean (n=15)	This Study 2019 – Outdoor Fields Mean (n=25)	Celeiro 2018 – Outdoor Fields Mean (n=2)	Marsili 2014 – Outdoor Fields Mean (n=4)	Ruffino 2013 – Outdoor Fields Mean (n=4)	Kim 2012 – Outdoor Fields Mean (n=50)	Menichini 2011 – Outdoor Fields Mean (n=4)	U.S. EPA 2009 – Outdoor Fields Mean (n=4 fields, n=26 samples)	Bocca 2009 – Outdoor Fields Median (n=32)	Zhang 2008 – Outdoor Fields Mean (n=2 fields, n=4 samples
Aluminum	1000	1060	N/A	1100	1400	512	N/A	828	N/A	407	321	755	N/A
Antimony	1.2	N/A	N/A	1.0	0.91	N/A	N/A	N/A	N/A	0.65	N/A	1.1	N/A
Arsenic	0.30	0.81	N/A	0.37	0.39	0.71	N/A	N/A	N/A	0.19	0.24	0.24	1.4
Barium	7.4	5.2	N/A	7.8	8.6	5.1	N/A	819	N/A	8.9	38	22	N/A
Beryllium	0.015	N/A	N/A	0.0035	0.011	N/A	N/A	N/A	N/A	0.018	N/A	0.040	N/A
Cadmium	0.55	0.65	1.8	1.1	0.86	0.84	1.5	N/A	0.46	1.3	0.70	0.37	0.30
Chromium	1.8	N/A	7.0	1.5	1.7	1.4	3.5	N/A	11	2.5	0.56	6.2	1.0
Cobalt	190	145	N/A	140	140	184	N/A	112	N/A	28	N/A	15	N/A
Copper	42	45	37	25	26	37.5	28	42	N/A	17	9.7	12	N/A
Iron	490	432	1778	430	710	509	682	723	N/A	354	271	305	N/A
Lead	13	13	21	31	20	21	26	96 (26)[b]	39	21	28	22	17
Magnesium	290	344	N/A	340	320	426	N/A	435	N/A	408	N/A	456	N/A
Manganese	5.7	5.9	N/A	6.3	8.5	5.2	N/A	2.4	N/A	3.7	4.6	5.2	N/A
Molybdenum	0.22	N/A	N/A	0.16	0.15	N/A	N/A	N/A	N/A	0.19	N/A	0.20	N/A
Nickel	3.2	5.9	11	3.1	2.5	N/A	5.1	N/A	N/A	1.9	2.6	2.0	N/A
Rubidium	1.8	N/A	N/A	1.6	2.0	N/A	N/A	N/A	N/A	1.6	N/A	1.7	N/A
Strontium	2.9	N/A	N/A	3.4	3.4	N/A	N/A	N/A	N/A	4.6	N/A	1.2	N/A
Tin	1.8	2.0	N/A	1.6	1.6	N/A	N/A	268	N/A	1.5	N/A	12	N/A
Vanadium	1.7	N/A	N/A	1.7	2.0	N/A	N/A	N/A	N/A	2.1	N/A	2.2	N/A
Zinc	17000	16800	6437	15000	15000	14150	4809	13125	3752	13514	8749	10229	7849

[a] All results in mg/kg; N/A = not applicable

[b] Tire crumb rubber at one field had a lead concentration of 308 mg/kg. The average is 26 mg/kg without that field included.

2.4.3.3 SVOCs

Tire crumb rubber from recycling plants and tire crumb rubber infill from synthetic turf fields was quantitatively analyzed for 39 target SVOCs by solvent extraction and gas chromatography/tandem mass spectrometry (GC/MS/MS) analysis. An additional 10 target SVOCs were analyzed non-quantitatively by liquid chromatography/time-of-flight mass spectrometry (LC/TOFMS). Target analytes included PAHs, phthalates, other tire rubber chemicals or degradates, and several chemicals previously reported in other studies. Most extractable target SVOC analytes were measurable above the detection limit in all samples.

- Average extractable SVOC measurement results for samples collected at recycling plants vs. synthetic turf fields and analyzed by GC/MS/MS include pyrene (18 vs. 12 mg/kg), benzo[a]pyrene (0.74 vs. 0.78 mg/kg), benzothiazole (79 vs. 11 mg/kg), 4-tert-octylphenol (30 vs. 9.8 mg/kg) and bis(2-ethylhexyl) phthalate (12 vs. 43 mg/kg).
- Average measurement results are shown in Figure 2-5 for select phthalates and in Figure 2-6 for benzothiazole, 4-tert-octylphenol, aniline, and n-hexadecane. Non-quantitative results are reported for two thiazoles and three cyclohexylamines in Figure 2-7.

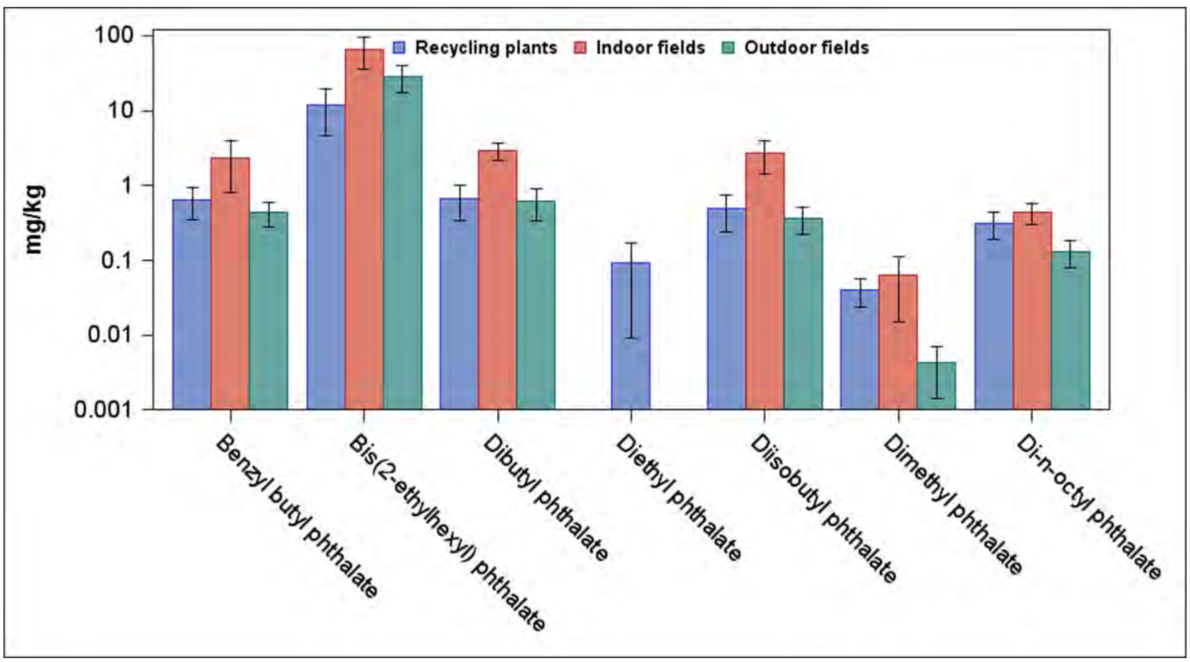

Figure 2-5. Average measurement results for phthalates in solvent extraction samples from tire crumb rubber collected at tire recycling plants (n=9), indoor synthetic turf fields (n=15), and outdoor synthetic turf fields (n=25).

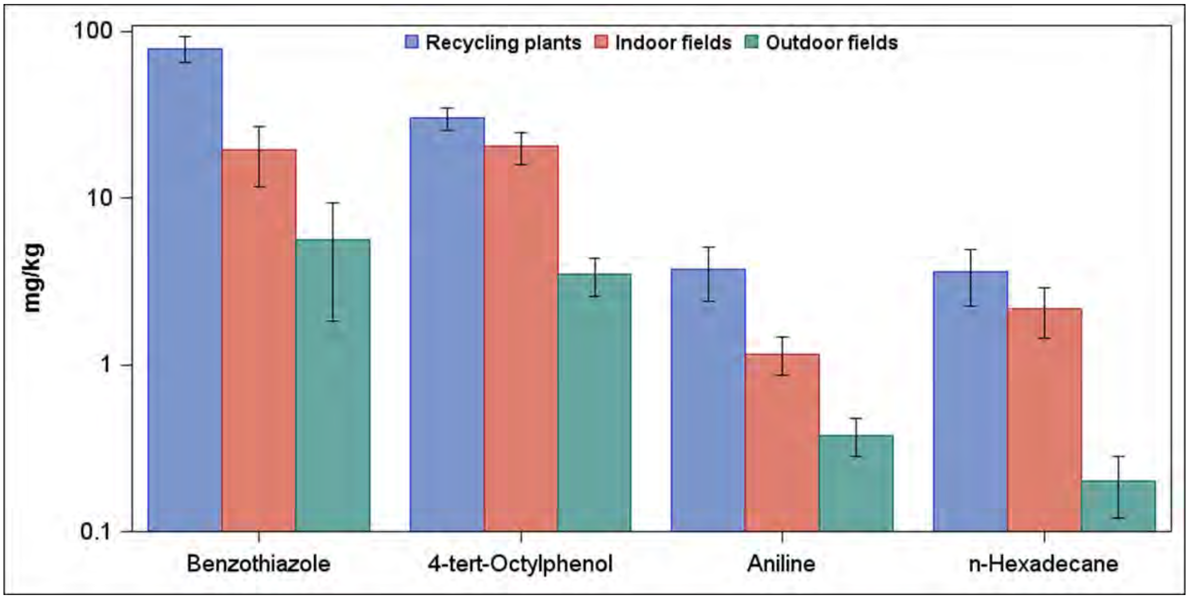

Figure 2-6. Average measurement results for select semivolatile organic compounds in solvent extraction samples from tire crumb rubber collected at tire recycling plants (n=9), indoor synthetic turf fields (n=15), and outdoor synthetic turf fields (n=25).

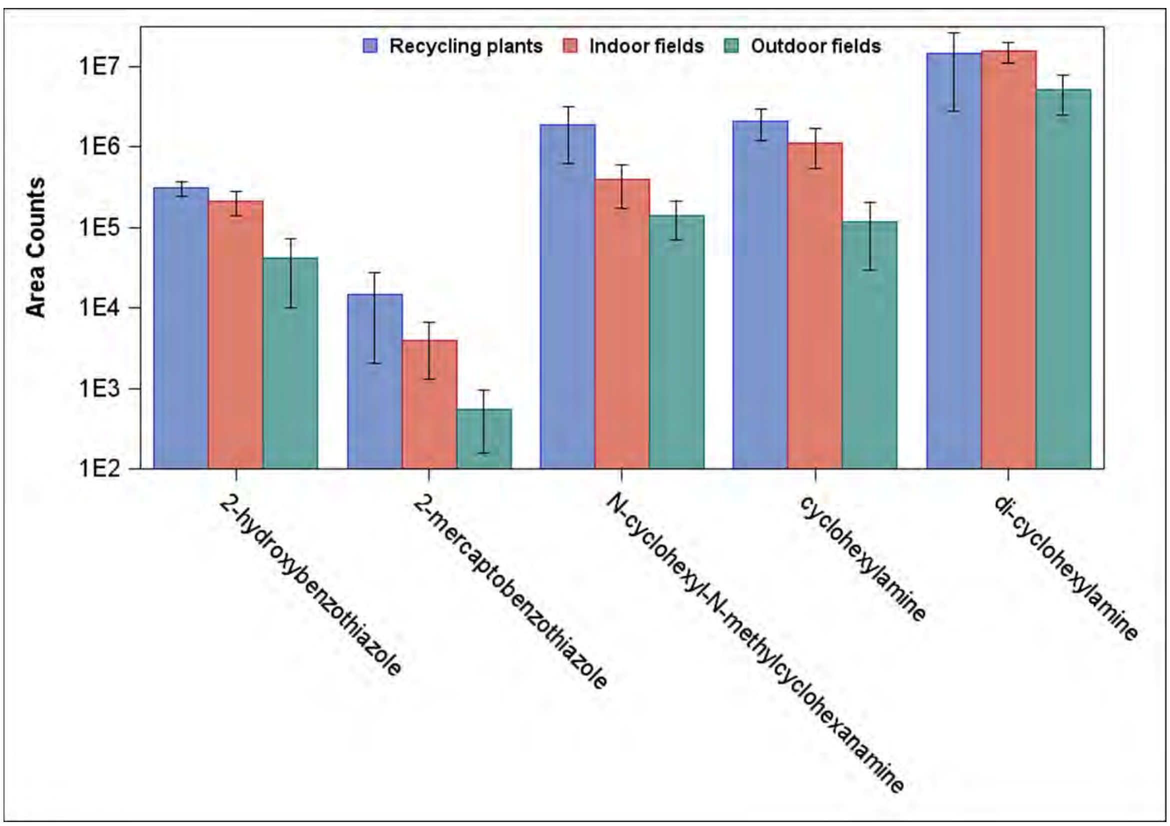

Figure 2-7. Average relative chromatographic peak area count results for select semivolatile organic compounds in solvent extraction samples from tire crumb rubber collected at tire recycling plants (n=9), indoor synthetic turf fields (n=15), and outdoor synthetic turf fields (n=25). These results are not quantitative, but compound identities were confirmed.

- Maximum values for pyrene, benzo[a]pyrene, benzothiazole, 4-tert-octylphenol, and bis(2-ethylhexyl) phthalate in synthetic turf field samples were 25, 3.0, 54, 33, and 170 mg/kg, respectively.
- Many analytes on the more volatile end of the SVOC spectrum were found at higher levels in 'fresh' material from tire recycling plants than found in synthetic turf field infill samples. If additional research confirmed this trend through longitudinal assessments at individual fields, a possible explanation for the lower levels found at synthetic turf fields could include volatilization from the rubber on the fields over time and, possibly, rain- or irrigation-driven leaching.
- Many of the less volatile SVOC analytes, including the five- and six-ring PAH chemicals, showed little to no difference between average concentrations in tire recycling plant samples and average concentrations in synthetic turf field samples.
- Several phthalate chemicals were found, on average, at higher levels in samples from synthetic turf fields than in 'fresh' material coming from tire recycling plants. If additional research confirmed this trend of higher levels of phthalates at individual fields, possible explanations could be: atmospheric deposition; track-in by field users or releases from shoes, clothing or other personal products; presence in and release from other synthetic turf field materials; or from chemical treatments applied to fields.
- Examples of measurement results and comparisons between tire recycling plant samples and synthetic turf field samples are shown in Figure 2-8 for pyrene and benzothiazole.

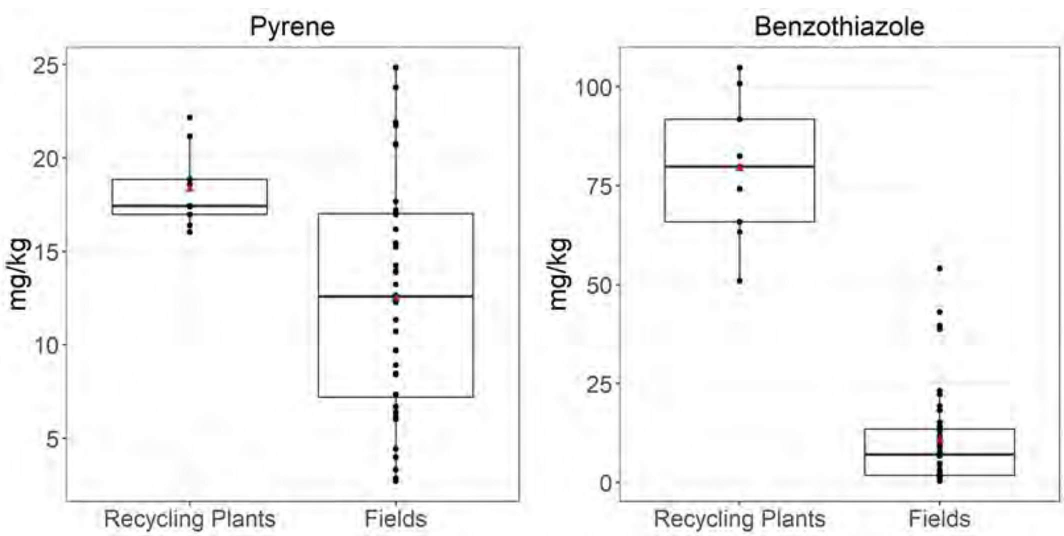

Figure 2-8. Example comparison of GC/MS/MS extract SVOC analysis results (mg/kg) between tire rubber collected from tire recycling plants and tire crumb rubber infill composite samples from synthetic turf fields for pyrene and benzothiazole.

- Table 2-5 shows a comparison of selected average extractable SVOC measurement results in this study compared to measurements obtained in other studies. The comparison studies were restricted to those analyzing uncoated tire crumb rubber from synthetic turf fields or recycling plants. In some cases, assumptions were made in other studies' results to allow a comparison of values, for example substitution of values below detection limit results to calculate study averages.

Table 2-5. Comparison of Tire Crumb Rubber Extractable SVOC Analysis Results Across Multiple Studies[a]

Chemical	This Study 2019 – Recycling Plants Mean (n=9)	Marsili 2014 – New Unused Mean (n=5)	Gomes 2010 – Recycling Plant Result (n=1)	This Study 2019 – Indoor Fields Mean (n=15)	Salonen[b] 2015 – Indoor Fields Mean (n=4)	This Study 2019 – Outdoor Fields Mean (n=25)	Celeiro[c] 2018 – Outdoor Fields Mean (n=15)	RIVM[d] 2017 – Outdoor Median (n=91fields or n=7 fields)	Marsili 2014 – Outdoor Fields Mean (n=4)	Ruffino 2013 – Outdoor Fields Mean (n=4)	Menichini 2011 – Outdoor Fields Mean (n=5)	Zhang[e] 2008 – Outdoor Fields Mean (n=4 fields, n=7 samples)
Phenanthrene	3.6	0.74	1.4	4.8	6.0	0.76	0.75	<0.6	0.34	N/A	N/A	1.2
Fluoranthene	6.1	2.4	4.5	6.2	9.9	3.5	3.5	3.4	1.4	N/A	N/A	4.9
Pyrene	18	5.2	14	19	26	8.8	8.0	7.5	4.0	22	6.6	6.3
Benzo[a]pyrene	0.74	0.25	1.2	0.98	1.4	0.66	1.0	<1.1	0.26	0.96	3.6	2.0
Benzo[ghi]perylene	1.3	0.55	<0.08	1.6	5.0	1.1	3.3	4.1	0.40	2.5	N/A	2.3
Benzothiazole	79	N/A	N/A	19	N/A	5.6	1.9	2.7	N/A	N/A	N/A	N/A
Dibutyl phthalate	0.68	N/A	N/A	2.9	N/A	0.63	1.6	N/A	N/A	N/A	N/A	N/A
Bis(2-ethylhexyl) phthalate	12	N/A	N/A	65	N/A	29	8.7	7.6	N/A	N/A	N/A	N/A
Aniline	3.8	N/A	N/A	1.2	N/A	0.38	N/A	N/A	N/A	N/A	N/A	N/A
4-tert-octylphenol	30	N/A	N/A	20	N/A	3.5	N/A	4.5	N/A	N/A	N/A	N/A
n-Hexadecane	3.6	N/A	N/A	2.2	N/A	0.20	N/A	N/A	N/A	N/A	N/A	N/A
Naphthalene	1.4	0.88	0.16	0.067	0.28	0.014	0.038	N/A	0.50	N/A	N/A	0.20
1-Methylnaphthalene	1.6	N/A	N/A	0.12	N/A	0.0085	N/A	N/A	N/A	N/A	N/A	N/A
2-Methylnaphthalene	1.8	N/A	N/A	0.20	N/A	0.016	N/A	N/A	N/A	N/A	N/A	N/A
Acenaphthylene	0.37	N/A	N/A	0.090	0.70	0.020	0.15	N/A	N/A	N/A	N/A	N/A
Fluorene	0.37	5.6	0.12	0.43	0.54	0.036	0.029	N/A	2.6	N/A	N/A	0.35
Anthracene	0.59	0.12	0.13	1.2	0.64	0.13	0.13	<0.5	0.075	N/A	N/A	0.037
1-Methylphenanthrene	1.4	N/A	N/A	2.8	N/A	0.87	N/A	N/A	N/A	N/A	N/A	N/A
2-Methylphenanthrene	1.4	N/A	N/A	5.9	N/A	1.2	N/A	N/A	N/A	N/A	N/A	N/A
3-Methylphenanthrene	2.1	N/A	N/A	4.2	N/A	1.2	N/A	N/A	N/A	N/A	N/A	N/A
Benz(a)anthracene	1.1	0.72	1.3	2.3	1.3	2.2	1.0	<0.9	0.14	10	0.37	0.59
Chrysene	4.3	1.9	2.8	3.4	4.5	2.0	1.2	1.3	0.68	2.6	2.1	2.4
Benzo(b)fluoranthene	1.6	6.8	<0.08	1.6	1.3	1.2	1.3	N/A	3.7	3.8	N/A	1.1
Benzo(k)fluoranthene	0.44	0.56	<0.08	0.58	0.37	0.38	0.42	<0.5	1.1	1.9	N/A	1.5
Benzo(e)pyrene	1.7	N/A	N/A	2.4	N/A	1.6	N/A	2.8	N/A	N/A	N/A	N/A
Coronene	0.82	N/A	N/A	0.69	N/A	0.45	N/A	N/A	N/A	N/A	N/A	N/A
Dibenzothiophene	0.42	N/A	N/A	0.66	N/A	0.096	N/A	N/A	N/A	N/A	N/A	N/A

Table 2-5 Continued

Chemical	This Study 2019 – Recycling Plants Mean (n=9)	Marsili 2014 – New Unused Mean (n=5)	Gomes 2010 – Recycling Plant Result (n=1)	This Study 2019 – Indoor Fields Mean (n=15)	Salonen[b] 2015 – Indoor Fields Mean (n=4)	This Study 2019 – Outdoor Fields Mean (n=25)	Celeiro[c] 2018 – Outdoor Fields Mean (n=15)	RIVM[d] 2017 – Outdoor Median (n=91fields or n=7 fields)	Marsili 2014 – Outdoor Fields Mean (n=4)	Ruffino 2013 – Outdoor Fields Mean (n=4)	Menichini 2011 – Outdoor Fields Mean (n=5)	Zhang[e] 2008 – Outdoor Fields Mean (n=4 fields, n=7 samples)
Dimethyl phthalate	0.04	N/A	N/A	065	N/A	0.004	N/A	N/A	N/A	N/A	N/A	N/A
Diethyl phthalate	0.091	N/A	N/A	1.5	N/A	0	2.2	N/A	N/A	N/A	N/A	N/A
Diisobutyl phthalate	0.50	N/A	N/A	2.7	N/A	0.36	2.5	<0.5	N/A	N/A	N/A	N/A
Benzyl butyl phthalate	0.64	N/A	N/A	2.4	N/A	0.44	0.07	N/A	N/A	N/A	N/A	N/A
Di-n-octyl phthalate	0.32	N/A	N/A	0.44	N/A	0.13	N/A	N/A	N/A	N/A	N/A	N/A

[a] All results in mg/kg; N/A = not applicable

[b] For the several values that were below the limit of detection, one-half the limit of detection was substituted for calculating a mean result.

[c] Mean values reported in Celeiro et al. (2018) Table 2 were based only on the reported (non-missing) values. It was assumed that the missing values were non-detects. A substitution of one-half the lowest reported value was made for missing results to calculate overall means for this table. Mean results in this table differ from means in Celeiro et al., as a result of the substitutions.

[d] This study included 546 samples from 91 fields for many PAHs and two phthalates [bis(2-ethylhexyl) phthalate and diisobutyl phthalate]; 43 samples from 7 fields for the remaining phthalates; and 7 samples from 7 fields for several PAHs, phenols, and thiazoles.

[e] Substituted detection limits for non-detects.

- In general, most measurements for outdoor fields in this study were within or near to a range of measurements from other studies. Benzothiazole and bis(2-ethylhexyl) phthalate were found at higher levels in this study compared to two recent studies. There were fewer comparable studies with results for indoor fields or recycling plants. No directly comparable data were found for some of this study's target analytes, and some studies reported results for SVOC analytes that were not quantitatively analyzed in this study.
- Ten additional target SVOCs were analyzed non-quantitatively by liquid chromatography/time-of-flight mass spectrometry (LC/TOFMS) following solvent exchange from the extracts used for GC/MS/MS analyses. These analyses showed the presence of 2-mercaptobenzothiazole, 2-hydroxybenzothiazole, and three cyclohexylamine compounds in 100% of the recycling plant samples and >70% of the synthetic turf field samples.

2.4.3.4 Field Characteristics and Differences in Chemical Substance Levels

In addition to examining differences in chemical measurements from tire crumb rubber samples taken at tire recycling plants and synthetic turf fields, the research design allowed exploratory analysis of potential differences in chemical measurements at synthetic turf fields and their association with other synthetic turf field characteristics, including:

- outdoor versus indoor field locations,
- the age of fields (installation year age groups 2004 – 2008, 2009 – 2012, 2013 – 2016), and
- across the four U.S. census regions (Northeast, South, Midwest, West).

Outdoor vs. Indoor Fields - Twenty-five study fields were outdoor synthetic turf fields, and 15 fields were indoor fields.

- No statistically significant differences in metal concentrations were observed in tire crumb rubber infill from outdoor fields versus indoor fields.
- Most extractable SVOCs were found at statistically significant higher levels (p-values < 0.05; often < 0.0001) in tire crumb rubber infill from indoor fields than outdoor fields. Average SVOC levels were 1.5 to 10 times higher in tire crumb rubber infill from indoor fields than outdoor fields.
- The more volatile SVOCs had higher indoor/outdoor concentration ratios than less volatile SVOCs. A likely contribution to these differences is increased weathering at outdoor locations, including sunshine, ventilation rates and rainfall.
- Figure 2-9 shows examples of the observed differences in select metal and SVOC measurements in tire crumb rubber infill from outdoor and indoor synthetic turf fields.

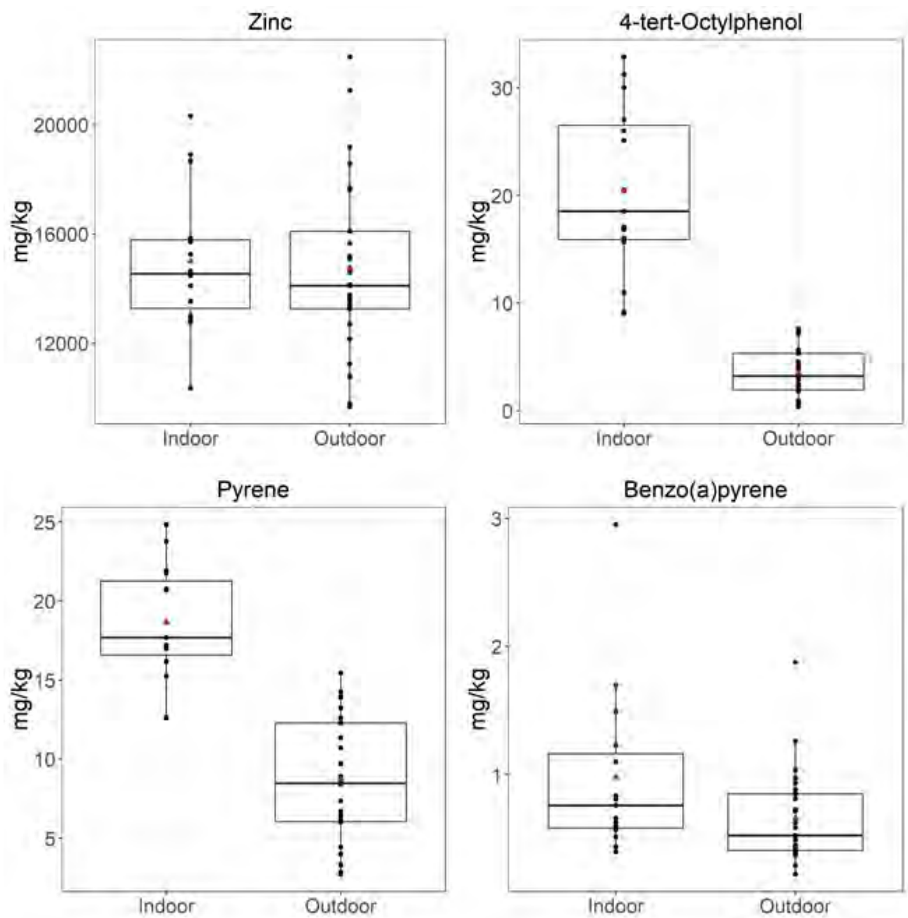

Figure 2-9. Comparison of analysis results (mg/kg) between tire crumb rubber infill composite samples from indoor and outdoor synthetic turf fields for zinc, 4-tert-octylphenol, pyrene and benzo[a]pyrene.

Field Age – An assessment of differences in chemical substance concentrations was performed for all fields across the installation age groups: 2004 – 2008 (n=11), 2009 – 2012 (n=18), and 2013 – 2016 (n=11).

- Some differences were observed for metals, but generally not in a monotonically decreasing or increasing direction.
- Assessing differences in extractable SVOC concentrations among the three age groups was complicated, because most indoor fields were in the two older age groups, and the indoor/outdoor differences were relatively large.
- When analyses were restricted to outdoor fields only, many SVOCs had statistically significant different (p-values < 0.05) concentrations among age groups, with an inverse relationship of decreasing average SVOC levels with increasing field installation age group. These results provide supporting evidence for the contribution weathering might be expected to play in changes to concentrations of some SVOCs in tire crumb rubber used on fields.
- Figure 2-10 shows examples of the observed differences in select metal and SVOC measurements in tire crumb rubber from recycling plants versus synthetic turf fields, outdoor versus indoor fields, and field installation age groups.

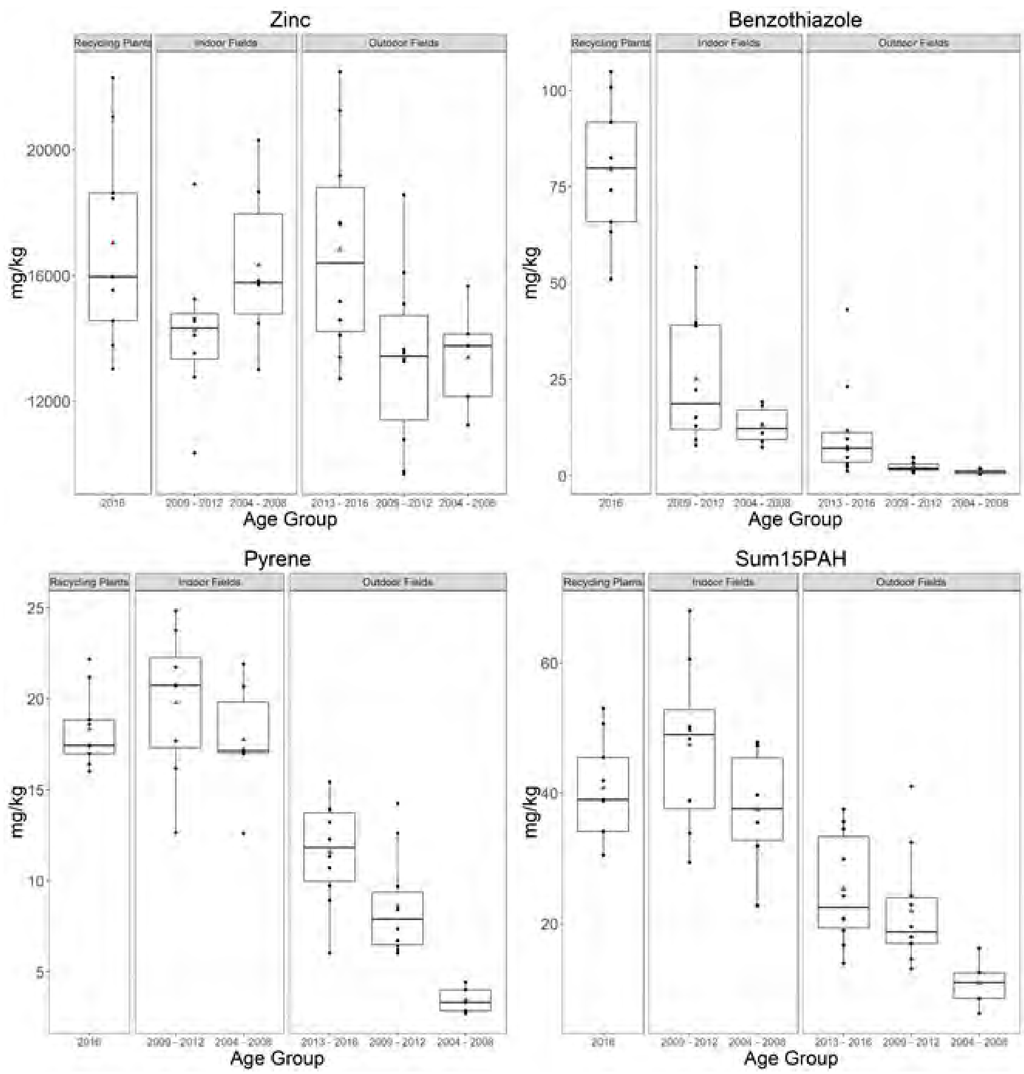

Figure 2-10. Analysis results (mg/kg) for tire crumb rubber from tire recycling plants and tire crumb rubber infill composite samples from synthetic turf fields with different characteristics by age group. [Sum15PAH = Sum of 15 of the 16 EPA ‘priority’ PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

Field Region – Synthetic turf fields were recruited across the four U.S. census regions, including the Northeast (n = 9 fields), South (n = 13 fields), Midwest (n = 8 fields) and West (n = 10 fields).

- Few consistent differences were observed for metals or extractable SVOCs in tire crumb rubber infill samples collected from fields across the four U.S. census regions.
- Analysis by field region was complicated, because there was a much higher percentage of indoor fields in the Midwest region, and a lower percentage of indoor fields in the South region. It was also limited by the relatively small numbers of fields in each region.
- Multivariate analyses (statistical analyses that consider field type, age, and location together) showed statistically significant interactions (p-values < 0.05) among field characteristics, including field region, for some chemicals associated with tire crumb rubber, suggesting that differences between regions cannot be ruled out.

2.4.3.5 Chemical Variability Within and Between Recycling Plants and Fields

The research was designed to provide information for assessing the variability of chemicals associated with tire crumb rubber within and between recycling plants and within and between synthetic turf fields. Three samples were collected at each recycling plant. For five synthetic turf fields, seven samples collected at different locations on the field were analyzed to assess variability within fields.

- Variability of metals in tire crumb rubber collected at tire recycling plants differed by metal. For example, zinc and chromium had greater between-plant variability than within-plant variability. On the other hand, arsenic, cadmium, cobalt and lead exhibited greater within-plant variability.
- For metals in synthetic turf field infill, higher between-field variability was measured for cobalt and zinc, while arsenic, cadmium, chromium, and lead had higher within-field variability.
- Variability of extractable SVOCs in tire crumb rubber collected at tire recycling plants differed by SVOC. For example, pyrene, benzothiazole, and 4-tert-octylphenol had greater between-plant variability than within-plant variability, while benzo[a]pyrene and bis(2-ethylhexyl) phthalate exhibited greater within-plant variability.
- For SVOCs in synthetic turf field infill, there was uniformly higher between-field variability than within-field variability, with the amount of total variance accounted for by between-field differences typically greater than 75%.
- The variability in measurements of zinc, pyrene, and benzothiazole in samples from tire recycling plants and synthetic turf fields are shown as examples in Figure 2-11.

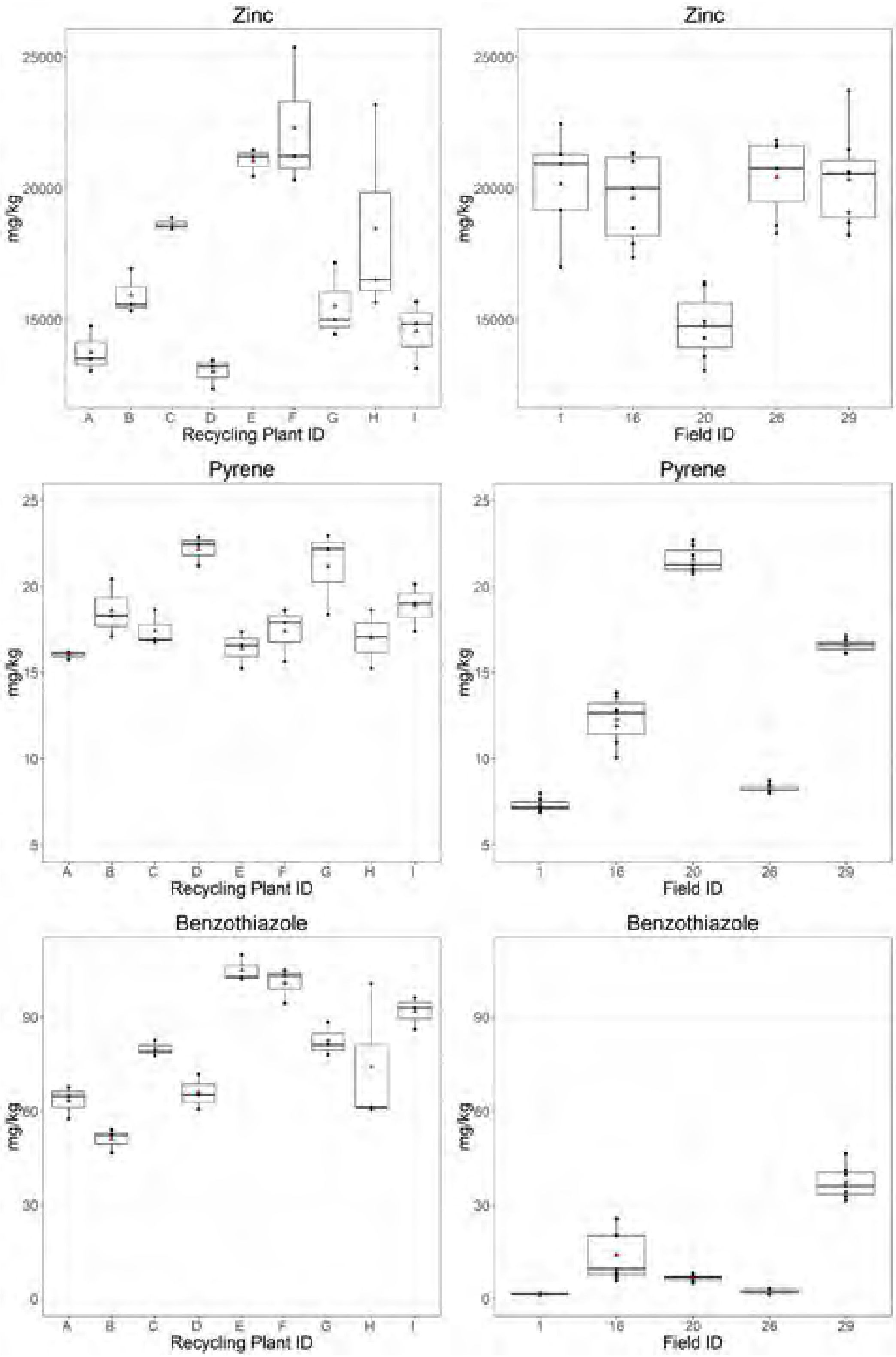

Figure 2-11. Within-plant and within-field variability of zinc, pyrene and benzothiazole measurements at each of the nine tire recycling plants (left side) and each of the five synthetic turf fields (right side). Within-plant variability shows the variability in the three samples taken at each tire recycling plant and within-field variability shows the variability in the seven individual samples taken at each of the five synthetic turf fields.

2.4.3.6 SVOC Suspect Screening and Non-Targeted Chemical Analysis

In addition to targeted chemical analyses of extractable SVOCs in tire crumb rubber, suspect screening and non-targeted analyses were applied to help elucidate the potentially-wider range of organic chemicals associated with tire crumb rubber material.

Through a review of published literature and reports, 89 chemicals were selected a-priori for suspect screening; these chemicals were reported in previous tire crumb rubber studies or were potentially an ingredient, component, or degradate in tire rubber. Suspect screening analyses were performed by LC/TOFMS in both positive and negative ionization modes for solvent extracts from tire crumb rubber samples from recycling plants and tire crumb rubber infill samples from synthetic turf fields.

- Recycling plant samples had, on average, 12 suspect screening chemical matches; outdoor fields had, on average, 10 matches; and indoor fields had, on average, 11 suspect matches.
- Several of the tentatively-identified chemicals are potential tire rubber ingredients or degradates. Examples of chemicals tentatively identified through suspect screening include 2,2,4-Trimethyl-1,2-dihydroquinoline (TMQ, a tire rubber antioxidant) and other potential tire rubber chemicals that may be used as rubber vulcanization accelerators, rubber antioxidants or rubber antiozonants, such as:
    - N,N'-Diphenyl-p-phenylenediamine (DPPD),
    - N,N'-Ditolyl-p-phenylenediamine (DTPD),
    - N,N-Dicyclohexyl-2-benzothiazolesulfenamide (DCBS),
    - N-tert-Butyl-2-benzothiazolesulfenamide (TBBS), and
    - N-Isopropyl-N'-phenyl-p-phenylenediamine (IPPD).
- It is important to emphasize that the suspect screening results are tentative and require further confirmation through analysis of chemical standards.

Non-targeted assessment was performed for a subset of recycling plant tire crumb rubber samples and synthetic turf field tire crumb rubber infill samples. Both GC/MS and LC/TOFMS methods were applied to solvent extracts and emission samples for SVOCs, and GC/TOFMS methods were applied to emission samples for VOCs. This approach yielded only highly-tentative and non-quantitative chemical identifications and should be considered only the first step of a multi-step process that would ideally be used to confirm chemical identities and, eventually, lead to quantitative analyses.

- GC/MS analysis of SVOC solvent extracts from tire recycling plant samples yielded 49 tentative chemical matches with unique names. Outdoor field samples had 53 tentative chemical matches with unique names, and indoor field samples had 54 tentative chemical matches with unique names.
- LC/TOFMS analysis of SVOC solvent extracts from tire recycling plant samples had 295 tentative chemical matches in positive ionization mode and 86 in negative ionization mode. Outdoor field samples had 228 tentative chemical matches in positive ionization mode and 101 matches in negative ionization mode; and indoor field samples had 293 tentative chemical matches in positive ionization mode and 91 matches in negative ionization mode.
- GC/TOFMS analysis of VOCs in 60 °C emission tests of recycling plant samples had 151 tentative chemical matches with unique names. Outdoor field samples had 115 tentative chemical matches with unique names and indoor field samples had 136 tentative chemical matches with unique names.

- It is important to emphasize that the non-targeted analysis results, while illustrating the presence of numerous organic chemicals that were not target analytes, are highly tentative and require further confirmation through analysis of chemical standards. Due to the tentative nature of the results, no attempts were made to try to identify toxicity reference information for these chemicals.

2.4.3.7 Microbiological

Tire crumb rubber infill samples collected from synthetic turf fields were analyzed for select targeted microbial genes, and non-targeted analysis was performed to characterize a wider microbial community.

- Targeted analysis was performed to determine concentrations of the 16S rRNA gene (an indicator of total bacteria), a protein gene for the *Staphylococcus aureus* bacteria, and a gene for methicillin resistance in bacteria (*mecA* methicillin resistance gene).
- Every sample from the 40 fields was positive for 16S rRNA genes. A total of 17 fields (42%) had at least one sample with quantifiable *Staphylococcus aureus* genes, while 28 fields (70%) had a least one positive sample for the methicillin resistance gene.
- Outdoor fields had statistically significant higher (p-value < 0.0001) quantities of 16S rRNA genes than indoor fields, while indoor fields had statistically significant higher (p-values < 0.0001) quantities of *Staphylococcus aureus* and methicillin resistance genes than outdoor fields.
- When considering samples from outdoor fields only, older fields had statistically significant increased (p-value < 0.0001) concentrations of 16S rRNA genes than younger fields, but field age was not associated with concentrations of *Staphylococcus aureus* or methicillin resistance genes.
- For non-targeted microbial analysis, 1,424 different bacterial types were found across the 40 fields.
- At this time, there are no analogous non-targeted bacterial assessment studies available for grass fields for comparison. Small studies have previously found more colony forming units for some bacteria at grass fields compared to synthetic turf fields.

2.4.4 Tire Crumb Rubber Exposure-Related Availability Characterization

2.4.4.1 VOC Emissions

The release of chemicals associated with tire crumb rubber into the air is, potentially, an important mechanism leading to human exposure. Dynamic small-chamber emissions testing was performed to measure emission factors for 31 VOC target analytes in tire crumb rubber from recycling plants and tire crumb rubber infill from synthetic turf fields. All samples were tested at both 25 °C and 60 °C, after a 24-hour equilibration period.

- For tests conducted at 25 °C, more VOCs were measurable above limits of detection for tire crumb rubber from recycling plants than for tire crumb rubber infill from synthetic turf fields.
- Analytes with ≥ 60% of the measurements above the limit of detection in 25 °C emissions tests of recycling plant samples included methyl isobutyl ketone, benzothiazole, toluene, styrene, m/p-xylenes, and o-xylene. For synthetic turf field samples, analytes with ≥ 60% of the measurements above the limit of detection included benzothiazole and o-xylene.

- Median 25 °C emission factors from synthetic turf field infill samples included 15 ng/g/h for benzothiazole, 0.87 ng/g/h for methyl isobutyl ketone, and 0.044 ng/g/h for the sum of BTEX compounds (benzene, toluene, ethylbenzene, m/p-xylenes, and o-xylene).
- VOC emission factors at 25 °C were higher in tire recycling plant samples than synthetic turf field samples. For example, mean benzothiazole emission factors were 6 times higher in recycling plants, and the emission factors for the sum of BTEX compounds were 5.5 times higher.
- For tests conducted at 60 °C, more VOCs were measurable above limits of detection than at 25°C.
- Examples of median 60 °C emission factors from synthetic turf field infill samples included 68 ng/g/h for benzothiazole, 34 ng/g/h for methyl isobutyl ketone, 15 ng/g/h for formaldehyde, and 0.40 ng/g/h for styrene.
- VOC emission factors at 60 °C were higher in tire recycling plant samples than synthetic turf field samples. For example, mean methyl isobutyl ketone emission factors were 3.3 time higher in recycling plant samples, benzothiazole emission factors were 3.9 times higher, formaldehyde emission factors were 2.5 times higher, and styrene emission factors were 2.4 times higher. Examples of the differences in VOC emission factors between recycling plant and synthetic turf field samples are shown in Figure 2-12 for formaldehyde and methyl isobutyl ketone.

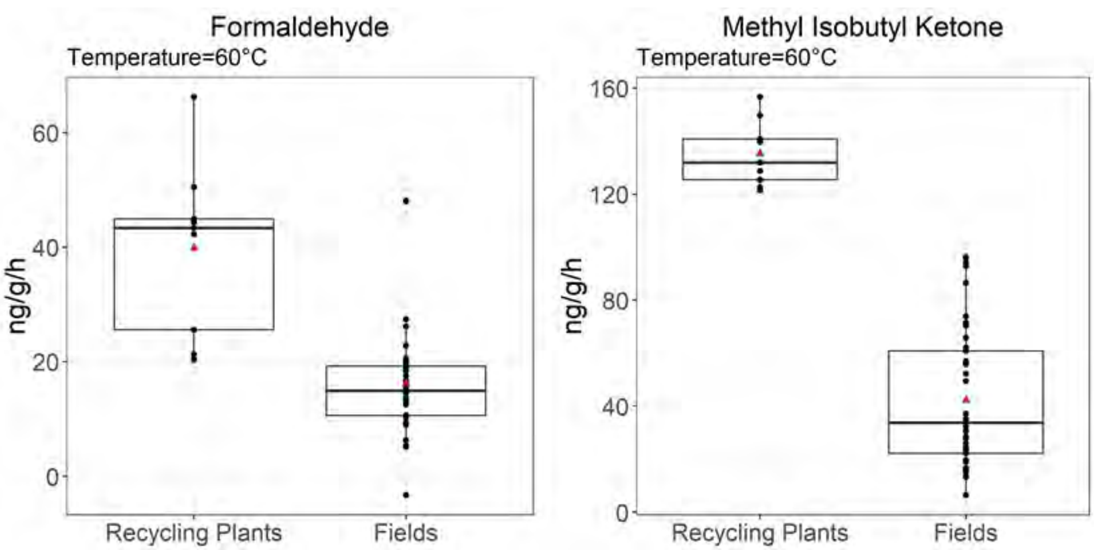

Figure 2-12. Comparison of volatile organic compound 60 °C emission factor results (ng/g/h) between tire rubber collected from tire recycling plants and tire crumb rubber infill composite samples from synthetic turf fields for formaldehyde and methyl isobutyl ketone.

- Many target VOC compounds had higher emission factors in emission experiments performed at 60 °C than 25 °C. Examples of these differences are shown for benzothiazole and styrene in Figure 2-13.

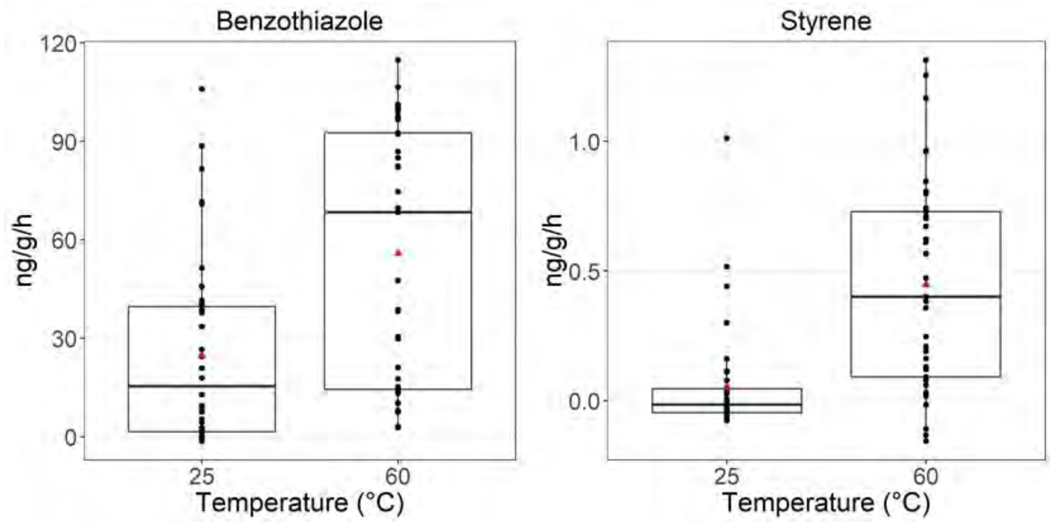

Figure 2-13. Comparison of volatile organic compound 25 °C and 60 °C emission factor results (ng/g/h) for tire crumb rubber infill collected from synthetic turf fields for benzothiazole and styrene.

- Several compounds did not show appreciable differences in emissions at the two temperatures, including several of the BTEX chemicals. It appeared that some VOCs were driven off the tire crumb during the 24-hour equilibration period in the test chamber at 60 °C, prior to sample collection (i.e., there was also some evidence to support this in the small number of emissions time series tests performed). This may have implications for understanding whether some chemicals may be found at the surface of tire crumb rubber particles, perhaps from atmospheric absorption, versus chemicals intrinsic to the rubber material. More experimental work would be needed to better understand these dynamics.
- Most VOC chemicals followed patterns similar to the SVOC extract samples with regard to differences associated with different field characteristics. Emission factors were higher for indoor fields versus outdoor fields. Several VOCs also showed an inverse association of decreasing emission factors with increasing field installation age, when the analysis was limited to outdoor fields.

2.4.4.2 SVOC Emissions

Dynamic micro-chamber emissions testing was performed to measure emission factors for 39 SVOC target analytes in tire crumb rubber from tire recycling plants and tire crumb rubber infill from synthetic turf fields. All samples were tested at both 25 °C and 60 °C after a 24-hour equilibration period with analysis by GC/MS/MS. An additional 10 SVOC analytes were analyzed non-quantitatively by LC/TOFMS in the 60 °C samples only.

- For tests conducted at 25 °C, approximately 50% of the target GC/MS/MS SVOCs were measurable above limits of detection in at least 60% of the samples. Rates of detection were higher for the more volatile SVOCs and lower for the less volatile SVOCs.
- Emission factors for SVOCs at 25 °C in synthetic field tire crumb rubber infill were low. Examples of median 25 °C emission factors included 1.8 ng/g/h for benzothiazole, 0.16 ng/g/h for aniline, and 0.082 ng/g/h for 4-tert-octylphenol.
- Emission factors at 25 °C were higher for 10 of the 18 SVOCs that had ≥ 60% of the samples above the detection limits in recycling plant samples versus synthetic turf fields. For example,

mean benzothiazole emission factors were 9.8 times higher in recycling plant samples and aniline emission factors were 10 times higher.

- For tests conducted at 60 °C, approximately 70% of the target SVOCs were measurable above limits of detection in at least 60% of the samples. Rates of detection remained higher for the more volatile SVOCs and lower for the less volatile SVOCs. The 5- and 6-ring PAH compounds, for example, were rarely measured above the detection limits.
- Examples of median 60 °C emission factors from synthetic turf field infill samples included 18 ng/g/h for benzothiazole, 0.81 ng/g/h for aniline, 5.1 ng/g/h for 4-tert-octylphenol, and 0.22 ng/g/h for pyrene.
- Emission factors at 60 °C were higher for most SVOCs in tire recycling plant samples versus synthetic turf fields. For example, mean benzothiazole emission factors were 15 times higher in recycling plant samples, aniline emission factors were 6.6 times higher and 4-tert-octylphenol factors were 3.4 times higher. Examples of the differences between recycling plant and synthetic turf field emission factors are shown in Figure 2-14 for the sum of 15 PAH analytes and 4-tert-octylphenol.

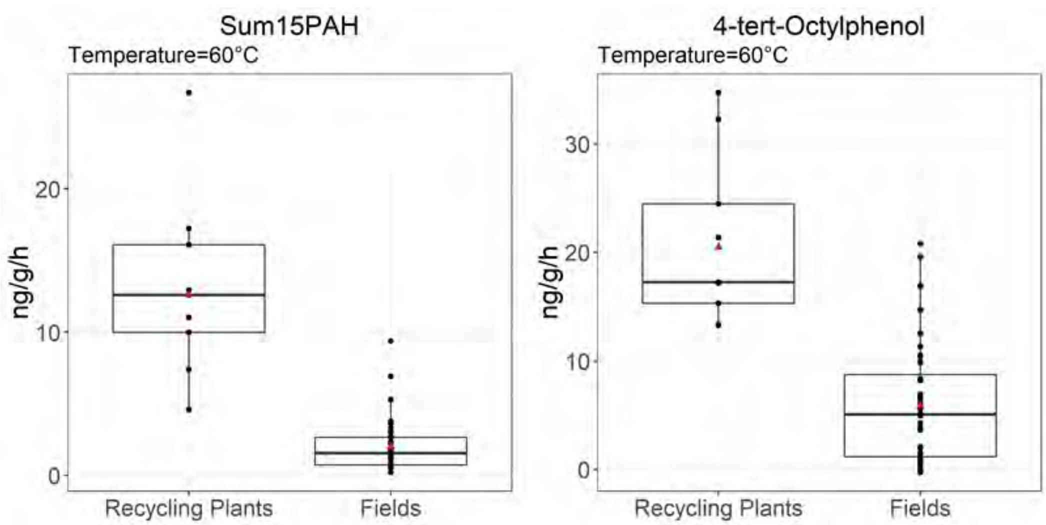

Figure 2-14. Comparison of semivolatile organic compound (SVOC) 60 °C emission factor results (ng/g/h) between tire rubber collected from tire recycling plants and tire crumb rubber infill composite samples from synthetic turf fields for Sum15PAH and 4-tert-octylphenol. [Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

- Most target SVOCs had higher emission factors in emission experiments performed at 60 °C than at 25 °C. Examples are shown for the sum of 15 PAH analytes and 4-tert-octylphenol in Figure 2-15.

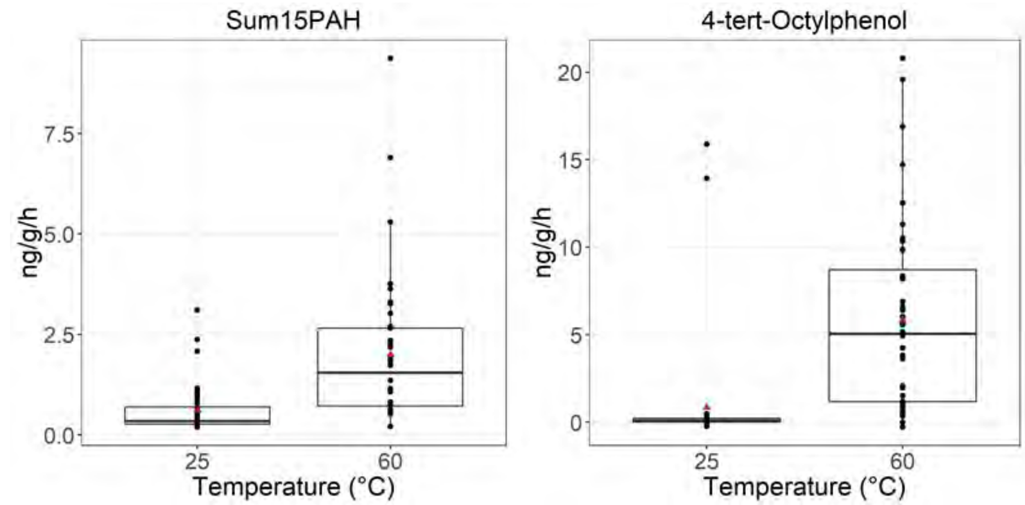

Figure 2-15. Comparison of semivolatile organic compound (SVOC) 25 °C and 60 °C emission factor results (ng/g/h) for tire rubber infill collected from synthetic turf fields for Sum15PAH and 4-tert-octylphenol.[Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

- Most SVOC emission factors were higher for indoor fields versus outdoor fields. Many SVOCs also showed an inverse association with increasing field installation age group, when the analysis was limited to outdoor fields.
- Benzothiazole was analyzed in both VOC and SVOC emissions testing. Higher maximum levels were observed in the SVOC testing than in the VOC testing. The VOC upper benzothiazole emission rates may be underestimated due to approaching upper calibration limits during analysis. Other differences may be the result of testing in two different chamber systems with different characteristics (including chamber wall surface area).

2.4.4.3 Metals Bioaccessibility

Bioaccessibility testing was performed for 20 metal target analytes in 27 tire crumb rubber samples from recycling plants and tire crumb rubber infill samples from synthetic turf fields using three artificial fluids (gastric, sweat with sebum, and saliva). The amount of each metal released in each artificial fluid was determined, and the percentage of the total amount of metal in the tire crumb rubber that was released was calculated (i.e., % *in vitro* bioaccessibility) for 19 metals.[6]

- For metals in tire crumb samples, *in vitro* bioaccessibility was the highest in artificial gastric fluid followed by sweat with sebum, while metals' bioaccessibility in artificial saliva was near zero, based on both bioaccessible metal concentrations in artificial fluid extracts and calculated percent *in vitro* bioaccessibility.
- Among the metals tested for bioaccessibility, zinc had the highest median concentrations in all three artificial biofluid extracts, at 129, 11, and 0.72 mg/kg in artificial gastric fluid, sweat with sebum, and saliva, respectively.

[6] Mercury was not measured by ICP/MS in the tire crumb samples; therefore, percent bioaccessibility could not be calculated for mercury.

- Manganese had the highest median percent *in vitro* bioaccessibility values in artificial gastric fluid (12%) and sweat with sebum (1.5%). In saliva, magnesium had the highest median percent *in vitro* bioaccessibility at 0.2%.
- For lead in tire crumb samples, the median (range) bioaccessible concentrations were 0.29 mg/kg (0.056–2.8 mg/kg), 0 mg/kg (0–0.19 mg/kg), and 0 mg/kg (0–0.048 mg/kg) in artificial gastric fluid, sweat with sebum, and saliva, respectively. Median (range) percent bioaccessibility values for lead were 1.9% (0.2–13.5%), 0% (0–1.9%), and 0% (0–0.5%) in artificial gastric fluid, sweat with sebum, and saliva, respectively.
- For lead, average gastric fluid bioaccessible concentrations and % bioaccessibility were significantly higher (p-values < 0.001) in synthetic turf field infill samples compared to tire crumb rubber from recycling plants (0.54 vs. 0.18 mg/kg; 3.2% vs. 1.8%). The observed higher lead concentrations in artificial gastric fluid from field samples could in part be driven by the higher lead concentrations in the field samples, as reported earlier in the section. Another possible explanation for the observed higher bioaccessibility from field samples is that some of the lead in synthetic turf field infill could come from external sources and be available on the surface of the infill rubber.
- Based on the findings, metals in tire crumb samples had low bioaccessibility in artificial gastric fluid, saliva, and sweat with sebum when compared to a default assumption of 100% bioaccessibility.
- Based upon available literature, this is the largest study on *in vitro* bioaccessibility of metals in tire crumb samples, in terms of number of samples tested and number of metals evaluated.
- Our results are generally consistent with a previous scoping study conducted by EPA for lead (U.S. EPA, 2009) and a 2017 report by the Netherlands National Institute for Public Health and the Environment (cadmium, cobalt, lead; RIVM, 2017). However, caution should be taken while interpreting and comparing bioaccessibility results across studies.

2.4.5 Toxicity Reference Information

One objective of the effort to characterize tire crumb rubber materials was to identify and collate existing toxicity reference information for select chemical constituents. To achieve this goal, a list of chemical constituents was developed as part of the Literature Review/Gaps Analysis (LRGA), based on chemicals identified in the various studies reviewed and supplemented by additional chemicals measured in this study. Searches were performed for a total of 355 chemicals in 11 different toxicity reference data sources.

- The percentage of chemicals with toxicity reference information available in the 11 extant reference data sources ranged from 7% to 28%.
- A total of 101 chemicals were found in EPA's Integrated Risk Information System (IRIS), 96 chemicals were found in the International Agency for Research on Cancer (IARC) references, 89 in California Occupational Safety and Health (CalOSHA) sources, 78 in sources from the National Institute for Occupational Safety and Health (NIOSH), 83 from the American Council of Government Industrial Hygienists, and 81 in OSHA sources.
- More information was available when narrowing to a subset of constituents in the target analyte list. For 95 constituents on the target list that were examined, toxicity reference information was available for 78 of them.

- Not all of the chemicals included in the toxicity reference information search had large or even measurable concentration results in tire crumb rubber analyses portion of this study.

2.5 Research Limitations

2.5.1 Research Design Constraints

A representative sampling design was considered, but the time required to develop and implement a study based on a national sampling frame of synthetic turf fields was beyond the scope of the research effort. Another design constraint was a decision to focus characterization research on the recycled tire crumb rubber infill and not to include other synthetic turf field materials (e.g., synthetic grass blades and backing material) due to the expanded scope that would be needed for a high-quality characterization of all these materials.

2.5.2 Planned Work Not Completed in this Part of the Study

Not all research goals for this portion of the study were completely met. Bioaccessibility measurements were planned for SVOCs using three simulated biological fluids. However, there were no validated methods for SVOCs; therefore, this work could not be done at the time of the sample analysis. Quantitative analyses of approximately 10 extractable SVOC chemicals were planned for the liquid chromatography/time-of-flight mass spectrometry (LC/TOFMS) analyses, but only non-quantitative analyses were completed. The results from these non-quantitative analyses were still informative as to the presence of select SVOCs and relative amounts and differences between recycling plants and fields, and among fields with different characteristics.

2.5.3 Other Limitations

The research described in this report was exclusively aimed at synthetic turf fields with recycled tire crumb rubber infill. While it may be desirable for reasons noted below to include other types of fields, it was beyond the scope of this study to investigate other types of fields (e.g., natural grass, synthetic fields with natural product infill, or synthetic fields with ethylene propylene diene terpolymer [EPDM] or thermoplastic elastomer [TPE] infill). It was also beyond the scope of this part of the study to evaluate the use of recycled tire crumb rubber as a soil amendment or natural grass top dressing. While there is concern about chemical exposures resulting from the use of recycled tire and other materials in synthetic fields, it is important to recognize that some of the chemicals are likely to be present in other types of fields, including natural grass fields. For example, metals (including lead) and PAHs (including benzo[a]pyrene) of potential concern at synthetic turf fields with tire crumb rubber infill are also often found in surface soil in the United States and may be present at natural grass playing fields. Insecticides and herbicides may be used on some natural grass fields, leading to exposures that may not be experienced by synthetic turf field users. Because many recreational and sports field users spend time on both natural grass and synthetic fields (either concurrently or during different life stages), characterization of chemical and microbiological agents at all relevant field types and an understanding of relative exposures across the different field types might be needed for risk assessment and epidemiological investigations.

There are several potential limitations affecting the ability to interpret the laboratory chamber emission test results. First, we selected 60 °C as an upper-bound temperature condition, but this selection was based on sparse and incomplete information. In a report based on a field in Connecticut at a measured air temperature of approximately 36 °C, the maximum field surface temperature for the grass fibers was

69 °C, but the maximum crumb rubber temperature at a 1-inch depth was 44 °C (Milone & MacBroom, 2008). It is not clear which temperature is most relevant for emissions from the crumb rubber. Information compiled from several studies and summarized in the Toronto Health Impact Assessment showed field surface temperatures ranging from 47 to 78 ºC for artificial turf with black infill on warm to hot days in direct sunlight (Toronto Public Health, 2015). However, temperature measurements in the infill itself were not reported. (The on-going California Office of Environmental Health Hazard Assessment (Cal-OEHHA, 2017) study has performed a set of high-quality field and air temperature measurements at multiple depths and heights above the field for up to 35 synthetic turf fields; these data should be informative regarding potential temperature profiles potentially affecting emissions and exposures. Second, we have highlighted later in the report some findings that may affect interpretation of the laboratory chamber emissions test results. Several findings related to the emissions testing suggest a better understanding of the dynamics of chemical emissions from tire crumb rubber is needed. Relating the laboratory chamber results to actual field conditions is challenging. We noted that for some VOCs, such as the benzene, toluene, ethylbenzene and xylene (BTEX) compounds, it appears that the chemicals might be primarily surface absorbed from the atmosphere rather than intrinsic to the rubber in substantial amounts; these VOCs were largely depleted during the 24-hour equilibration period in the test chamber at 60 °C prior to air sample collection whereas, for example, the intrinsic VOC chemical methyl isobutyl ketone was not. The chamber emission experiments may also be producing measurements that overestimate long-term emissions occurring at fields, particularly for the SVOCs; longer duration tests might improve our understanding of emissions as they occur at the fields. In general, though, we believe the chamber experiments provided important information regarding differences in emissions between 'fresh' material from recycling plants and tire crumb rubber infill at synthetic turf fields, show the decreases in emission rates over time at outdoor fields, and highlight important differences in emission rates at indoor versus outdoor fields.

Finally, data were not collected to directly address the potential for ecological exposure and risks beyond performing chemical characterization of the tire crumb rubber material.

2.6 Future Research Recommendations

While this part of the study added considerable new information for better understanding tire crumb rubber to inform exposure assessment for chemical substances and microbes at synthetic turf fields, ongoing exposure research is being conducted and additional research could be performed to further inform and improve future exposure and risk assessments.

- Given the complex nature of tire crumb, it is not unexpected that many chemicals were observed during characterization testing. The ability to resolve which, if any, of those that were tentatively identified are relevant for further evaluation is further complicated by the limitations on toxicity information that may be available for many chemicals. Approaches for whole material toxicity testing, such as those used by the National Toxicology Program, could be further developed and applied for assessing potential effects of the material.

Recommended Follow-up Activities

- **Approaches for whole material toxicity testing, such as those used by the National Toxicology Program, could be further developed and applied for assessing potential effects of the material**
- **Further research to understand the increased potential for exposure to chemicals associated with tire crumb rubber at indoor synthetic turf fields**

- Results in this study and other studies suggest that organic chemicals associated with recycled tire crumb rubber infill can be higher at indoor synthetic turf fields as compared to outdoor fields. Higher concentrations in, and emissions from tire crumb rubber, when combined with the reduced ventilation rates at indoor fields, suggest that indoor field users may experience higher exposures to some chemicals. Future studies might be directed at collection of more air and exposure measurements at indoor facilities to assess the potential differences in exposures between indoor and outdoor field users.

2.7 Conclusions

- Based upon available literature, this research effort represents the largest tire crumb rubber study conducted in the United States, and the information and results from the effort will fill specific data gaps about the potential chemical constituents found to be associated with recycled tire crumb rubber infill material.
- This report provides new and additional data on tire crumb rubber characterization of samples collected from 40 synthetic turf fields and 9 recycling plants located across the United States. Extensive physical, chemical and microbiological characteristics of the tire crumb rubber material obtained in this research will be useful for improving exposure estimation for individuals using synthetic turf fields with recycled tire crumb rubber infill.
- As expected, a range of metals, organic chemicals, and bacteria was found to be associated with recycled tire crumb rubber.
- These results are generally comparable to other studies characterizing tire crumb where available.
- While many chemicals are present in the recycled tire crumb rubber, exposure may be limited based on what is released into air or biological fluids.
- The study is not a risk assessment; however, the results of the research described in this and future reports should advance the understanding of exposure to inform the risk assessment process. The study activities completed as part of this multi-agency research effort were not designed, and are not sufficient by themselves, to directly answer questions about potential health risks.
- Risk is a function of both hazard and exposure; therefore, improved understanding through this research regarding what is present in the material and how individuals are exposed is critical to understanding the risk. Ongoing exposure characterization research being performed under the FRAP will further extend and improve our ability to apply the tire crumb rubber characterization results included in this report in an exposure context.

Overall, we anticipate that the results from this multi-agency federal research effort, along with studies being performed by other organizations, will be useful to the public and interested stakeholders for understanding the potential for human exposure to chemicals of potential interest and concern found in recycled tire crumb rubber infill material used on synthetic turf fields.

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3.0 Tire Crumb Rubber Characterization Methods

3.1 Research Design Summary

As described in the Federal Research Action Plan (U.S. EPA, CDC/ATSDR, and CPSC, 2016a) and in the research protocol, *Collections Related to Synthetic Turf Fields with Crumb Rubber Infill* (U.S. EPA and CDC/ATSDR, 2016), this portion of the research was aimed at providing information and data for characterizing tire crumb rubber used at synthetic turf fields. The tire crumb rubber characterization study was designed to collect tire crumb rubber material from tire recycling plants and synthetic turf fields around the United States and analyze the material in the laboratory for a wide range of metals, volatile organic compounds (VOCs), and semi-volatile organic compounds (SVOCs), as well as particle and microbial characterizations. A schematic outline of the tire crumb rubber characterization research, as implemented, is shown in Figure 3-1.

The research design included recruiting up to nine tire recycling plants that produce tire crumb rubber for use on synthetic turf fields to provide tire crumb rubber material samples. The samples from the tire recycling plants represents 'fresh' tire crumb rubber material newly manufactured from used tires that has not undergone weathering and was collected for comparison with tire crumb rubber material from synthetic turf fields, which had undergone weathering and active play. Tire recycling plants that use both ambient production processes and cryogenic production processes were recruited for collection of the tire crumb rubber samples. Samples were collected from three different flexible intermediate bulk containers at each plant. These containers typically held one ton of tire crumb rubber for storage and transport and were closed at the top to prevent rainwater intrusion. In most cases, the bulk containers sampled were outdoors at the recycling plant. No researcher efforts were implemented to assess whether storage conditions might affect the presence or concentrations of chemicals or microbes prior to installation at synthetic turf fields.

The research design included recruiting up to 40 facilities with synthetic turf fields with tire crumb rubber infill across the continental United States. Fields were recruited from across the four U.S. census regions (Figure 3-2). The geographic extent of the recruitment was intended to provide a range of material weathering conditions for outdoor fields and potentially, differences in tire crumb rubber source material. Consideration of facility type (indoor vs. outdoor fields) was also integrated in the study design at the facility identification and recruitment stage. Higher air concentrations of organic chemicals potentially associated with tire crumb rubber have been measured in some studies of indoor facilities compared to levels measured at outdoor fields. Stratification of tire crumb rubber characterization by facility type could help determine whether the potential exposures vary by facility type and if so, whether the variation is due to differential weathering and its effect on the amounts and types of chemicals available for exposure or is a function of ventilation rates at indoor facilities. Although not an explicit stratification characteristic, fields were also recruited across a range of synthetic turf ages to allow potential differences in chemical content and particle size distribution to be assessed with age. Samples were collected from seven set locations at each field to allow for analysis of between-field and within-field variation. Questionnaires were also administered to facility owners and field managers to obtain information on types and numbers of field users, maintenance practices, and any uses of cleaning or other treatment products on the field.

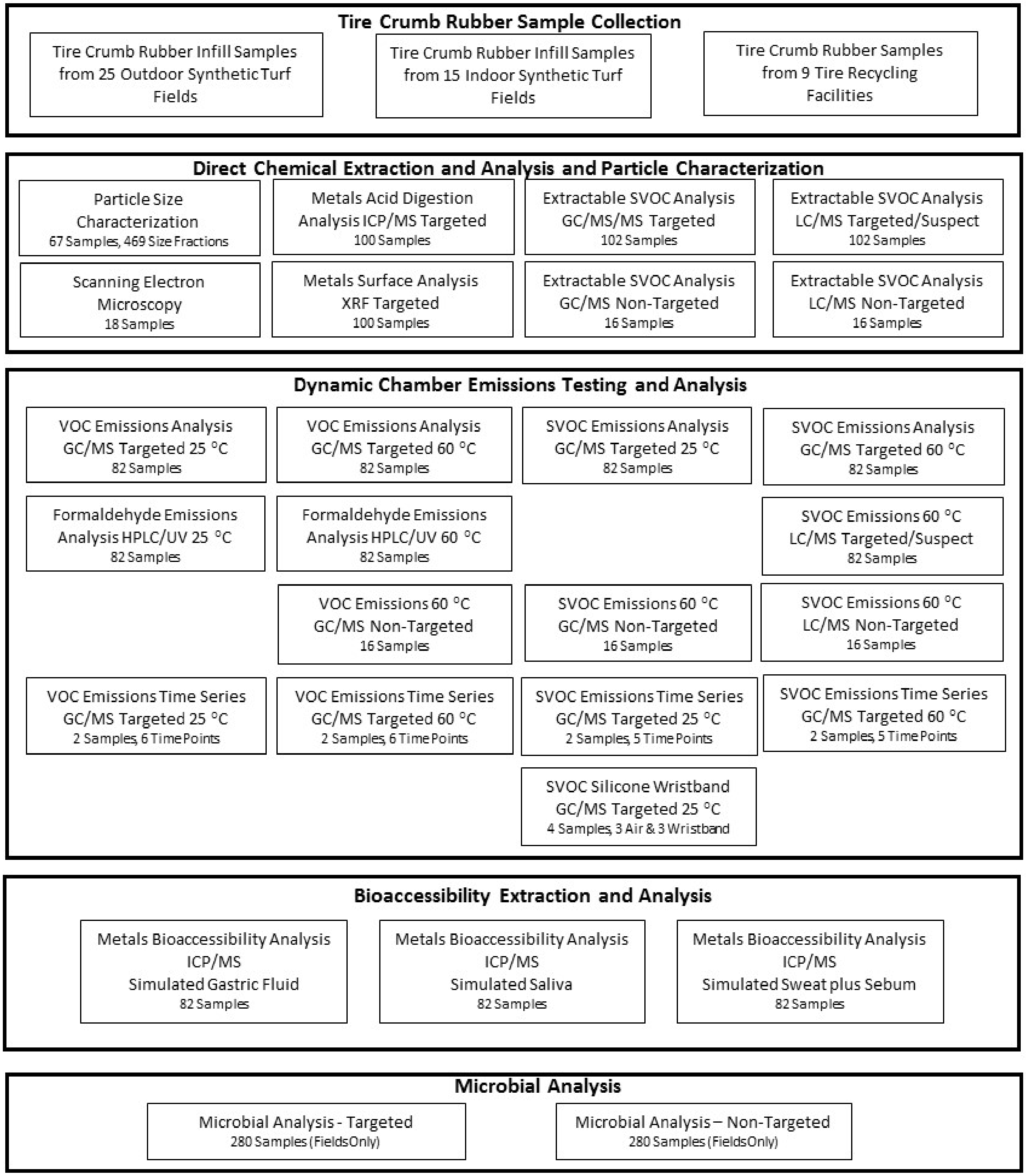

Figure 3-1. Tire crumb rubber characterization research schematic overview.

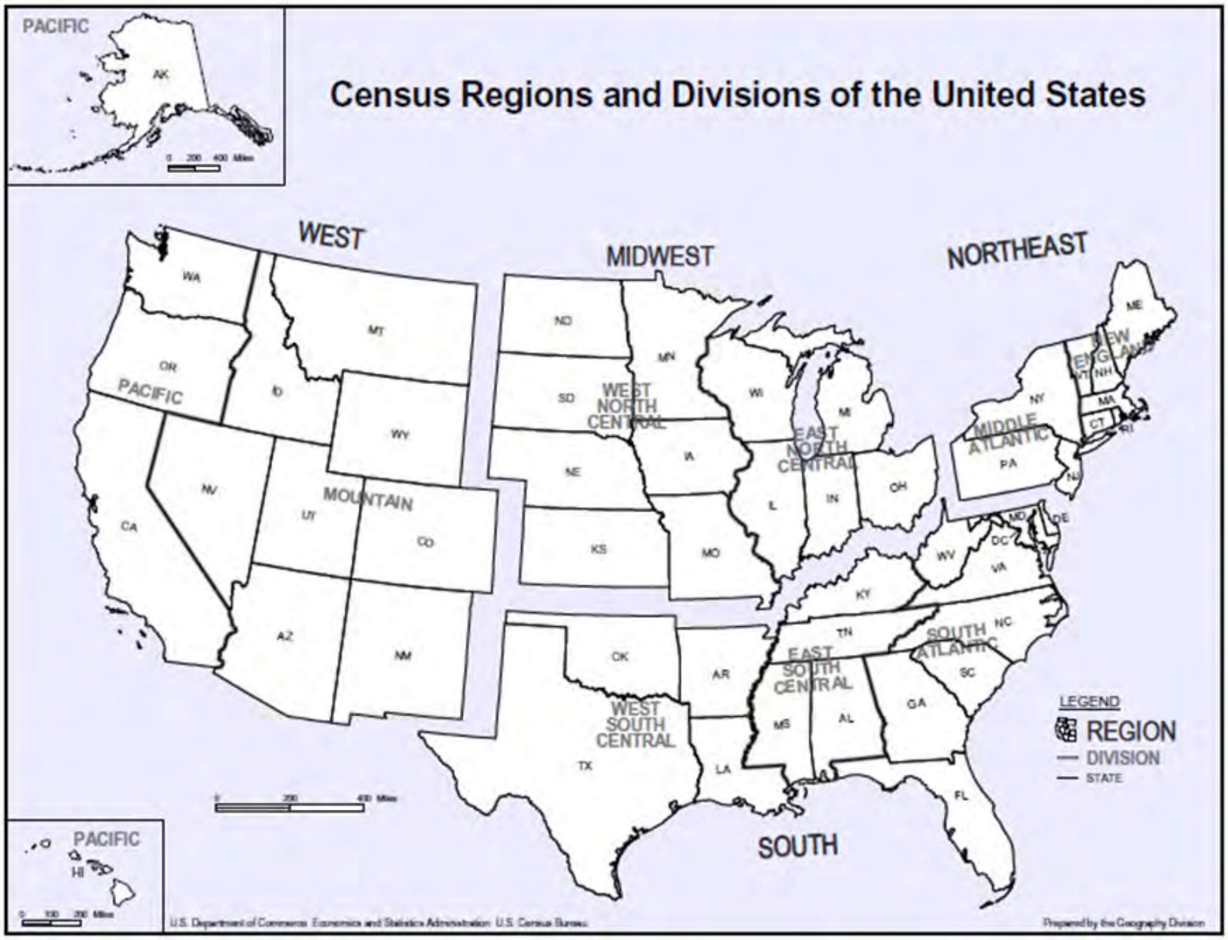

Figure 3-2. United States census regions.

The wide range of chemical, physical and microbiological analyses conducted on the tire crumb rubber collected at the tire recycling plants and synthetic turf fields for this study are summarized in Figure 3-3. Laboratory analyses included:

- characterization for particle size, sand content (synthetic turf field samples only) and moisture content;
- direct extraction and analysis of metals and SVOCs in tire crumb rubber;
- dynamic emission chamber measurements for formaldehyde, VOCs and SVOCs under two temperature conditions – 25 and 60 degrees Celsius (°C);
- bioaccessibility measurements for metals using synthetic sweat, saliva, and gastric fluids; and
- for synthetic turf field samples, targeted and non-targeted characterization of microbes.

The emissions and bioaccessibility experiments were conducted to provide important information about the types and amounts of chemical constituents in the tire crumb rubber material available for human exposure through inhalation, dermal, and ingestion pathways. In addition to quantitative target chemical analyses, suspect screening and non-targeted analysis methods were applied for VOCs and SVOCs to identify whether there may be potential chemicals of interest that have not been identified or reported in previous research. Chemical constituents from indoor and outdoor synthetic turf field samples were compared with the samples of 'fresh' tire crumb rubber from recycling plants to better understand the impact of weathering and facility use on the types and amounts of constituents available for human exposure. The tire crumb rubber infill from synthetic turf fields was also analyzed to assess microbial populations using targeted and non-targeted analyses. A final piece of this research activity was to identify and collate extant toxicity reference data for selected chemical constituents and contaminants identified through the laboratory analyses.

Constituents

Solvent Extraction
SVOCs – GC/MS/MS
SVOCs – LC/TOFMS

Acid Digestion
Metals – ICP/MS

Spectrometry
Metals – XRF

Particle Characterization
Particle Size – Gravimetric
Moisture Content
Rubber/Sand Content
Particle Size/Morphology – SEM/EPMA

Microbial Characterization
Targeted Species – ddPCR
Non-Targeted Species – PCR

Exposure-Related

Small Chamber Emissions
Formaldehyde – HPLC/UV
VOCs –GC/TOFMS

Micro Chamber Emissions
SVOCs – GC/MS/MS
SVOCs – LC/TOFMS

Bioaccessibility
Metals – Sweat - ICP/MS
Metals – Saliva – ICP/MS
Metals – Gastric – ICP/MS

Figure 3-3. Summary of chemical, physical and microbial analyses performed for tire crumb rubber characterization. Microbial characterization and analysis of rubber/sand content was only performed for samples from synthetic turf fields. [ddPCR = Droplet digital polymerase chain reaction; EPMA = Electron probe microanalysis; GC/MS/MS = Gas chromatography/tandem mass spectrometry; GC/TOFMS = Gas chromatography/time-of-flight mass spectrometry; HPLC/UV = High performance liquid chromatography/ultraviolet spectrometry; ICP/MS = Inductively coupled plasma/mass spectrometry; LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry; PCR = Polymerase chain reaction; SEM = Scanning electron microscopy; SVOC = Semivolatile organic compound; VOC = Volatile organic compound; XRF = X-ray fluorescence]

3.1.1 Target Chemicals

An important goal of this research was to apply a range of sensitive and specific analytical methods that were likely to provide quantitative measurement or presence/absence data for a wide range of chemicals potentially associated with tire crumb rubber. Proposed metal, VOC and SVOC target analytes are shown in Tables 3-1 through 3-5. Target analyte selection was based on a combination of information from previous tire crumb rubber research studies, information on potential tire manufacturing chemical ingredients, and analytical laboratory and method capabilities. The Literature Review/Gaps Analysis (Appendix C) identified several hundred chemicals that have been reported in the literature based on analysis of tire crumb rubber or playground surface rubber, rubber leachate, headspace analysis or environmental measurements. In some cases, the literature reported only presence of chemical constituents, without quantitative measurements. Some chemicals were included in the analysis because they were reported through the literature or other sources to be potential tire manufacturing components, process chemicals or degradates. Many of the VOC secondary analytes were included because the existing standards were available and included in mixtures typically analyzed in the laboratory.

Chemical lists are divided into primary and secondary analytes for reporting efficiency in this report. Results for the primary analytes are included in the body of this report. Results for both primary and secondary analytes are included in report appendices. The primary analytes highlighted in the body of the report were selected from the larger list of chemicals based on their reported potential association with tire crumb rubber in this study or other studies, and in part because of their potential interest as well-known chemicals. Many SVOC chemicals were proposed for suspect screening LC/TOFMS analysis based on previous reports that they may be associated with tire crumb rubber and where mass spectra may be available to identify the presence of the chemical with some degree of confidence (Table 3-5). A subset of VOC and SVOC samples was also analyzed using non-targeted approaches, which generated characteristic mass spectra that were explored to tentatively identify or propose chemical presence for further investigation.

Table 3-1. Target Metal Analytes in Tire Crumb Rubber Samples Analyzed by ICP/MS and XRF[a]

Metal	Analyte Category	CAS Number[b]	ICP/MS	XRF	Literature Review/Gaps Analysis Reference ID (see Appendix C)
Arsenic	Primary	7440-38-2	Yes	Yes	6, 7, 17, 36, 45, 49, 51, 60, 63, 66, 71, 79
Cadmium	Primary	7440-43-9	Yes	Yes	6, 7, 17, 28, 34, 45, 47, 49, 51, 60, 63, 66, 71, 79, 89
Chromium	Primary	7440-47-3	Yes	Yes	6, 7, 17, 28, 32, 36, 45, 47, 49, 51, 57, 60, 63, 66, 71, 76, 78, 79, 89
Cobalt	Primary	7440-48-4	Yes	Yes	6, 7, 49, 63
Lead	Primary	7439-92-1	Yes	Yes	6, 7, 16, 17, 20, 28, 32, 34, 36, 45, 47, 49, 51, 57, 60, 63, 66, 71, 78, 79, 89
Zinc	Primary	7440-66-6	Yes	Yes	6, 7, 17, 28, 32, 34, 36, 47, 49, 51, 54, 57, 61, 63, 66, 71, 72, 79, 89
Aluminum	Secondary	7429-90-5	Yes	No	6, 7, 36, 49, 63, 66, 71
Antimony	Secondary	7440-36-0	Yes	Yes	6, 7, 49
Barium	Secondary	7440-39-3	Yes	Yes	6, 7, 17, 36, 49, 51, 57, 63, 71, 78
Beryllium	Secondary	7440-41-7	Yes	No	6, 45, 49, 60
Copper	Secondary	7440-50-8	Yes	Yes	6, 7, 17, 36, 45, 47, 49, 51, 57, 60, 63, 66, 71
Iron	Secondary	7439-89-6	Yes	Yes	6, 7, 36, 47, 49, 57, 63, 66, 71
Magnesium	Secondary	7439-95-4	Yes	No	6, 7, 36, 45, 49, 60, 66
Manganese	Secondary	7439-96-5	Yes	Yes	6, 17, 36, 49, 57, 63, 66, 71
Mercury[c]	Secondary	7439-97-6	No	No	6, 7, 28, 49, 51, 71, 78, 89
Molybdenum	Secondary	7439-98-7	Yes	Yes	6, 7, 49, 66
Nickel	Secondary	7440-02-0	Yes	Yes	6, 7, 17, 47, 49, 51, 57, 63, 66, 71
Rubidium[d]	Secondary	7440-17-7	Yes	Yes	6, 36, 49
Selenium	Secondary	7782-49-2	Yes	Yes	6, 7, 34, 45, 49, 51, 60, 66, 71
Strontium	Secondary	7440-24-6	Yes	Yes	6, 36, 49
Tin	Secondary	7440-31-5	Yes	Yes	6, 28, 49, 63, 71, 89
Vanadium	Secondary	7440-62-2	Yes	No	6, 7, 45, 49, 60

[a] ICP/MS = Inductively coupled plasma/mass spectrometry; XRF = X-ray fluorescence spectrometry

[b] Unique numerical identifier assigned by the Chemical Abstracts Service (CAS)

[c] Mercury was a target analyte only in the bioaccessibility measurements

[d] Not analyzed in bioaccessibility analyses

Table 3-2. Target VOC Analytes in Tire Crumb Rubber Emission Samples Analyzed by GC/TOFMS[a]

VOC	Analyte Category	CAS Number[b]	Literature Review/Gaps Analysis Reference ID (see Appendix C)
Formaldehyde[c]	Primary	50-00-0	55, 94
Methyl isobutyl ketone	Primary	108-10-1	15, 16, 32, 54, 55, 57, 71
Benzothiazole	Primary	95-16-9	7, 12, 15, 16, 17, 34, 36, 46, 51, 54, 55, 57, 71, 82
1,3-Butadiene	Primary	106-99-0	N/A
Styrene	Primary	100-42-5	11, 12, 15, 16, 55
Benzene	Primary	71-43-2	2, 10, 11, 12, 15, 16, 32, 55, 57, 63, 65, 71
Toluene	Primary	108-88-3	8, 10, 11, 12, 15, 16, 32, 55, 57, 61, 63, 65, 71, 76, 78
Ethylbenzene	Primary	100-41-4	10, 11, 15, 16, 57, 61
m/p-Xylene	Primary	108-38-3, 106-42-3	8, 10, 11, 12, 15, 16, 32, 55, 57, 61, 63, 65
o-Xylene	Primary	95-47-6	16, 55, 57, 61
SumBTEX[d]	Primary	N/A	N/A
trans-2-Butene	Secondary	624-64-6	N/A
cis-2-Butene	Secondary	590-18-1	N/A
4-Ethyltoluene	Secondary	622-96-8	8, 16
1,3,5-Trimethylbenzene	Secondary	108-67-8	16, 61
1,1-Dichloroethene	Secondary	75-35-4	N/A
1,1-Dichloroethane	Secondary	75-34-3	N/A
cis-1,2-Dichloroethene	Secondary	156-59-2	61
1,2-Dichloroethane	Secondary	107-06-2	16
1,1,1-Trichloroethane	Secondary	71-55-6	12
Carbon tetrachloride	Secondary	56-23-5	16, 32, 57
1,2-Dichloropropane	Secondary	78-87-5	16
Trichloroethylene	Secondary	79-01-6	16
Tetrachloroethylene	Secondary	127-18-4	16, 57
Chlorobenzene	Secondary	108-90-7	16
m-Dichlorobenzene	Secondary	541-73-1	N/A
p-Dichlorobenzene	Secondary	106-46-7	57
o-Dichlorobenzene	Secondary	95-50-1	N/A
Trichlorofluoromethane (Freon™ 11)	Secondary	75-69-4	16, 32, 57
Dichlorodifluoromethane (Freon™ 12)	Secondary	75-71-8	16, 32, 57
1,1,2-Trichlorotrifluoroethane (Freon™ 113)	Secondary	76-13-1	16

[a] VOC = Volatile organic compound; GC/TOFMS = Gas chromatography/time-of-flight mass spectrometry; N/A = Not applicable

[b] Unique numerical identifier assigned by the Chemical Abstracts Service (CAS)

[c] Formaldehyde was analyzed by HPLC/UV

[d] SumBTEX = Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene

Table 3-3. Target SVOC Analytes for Tire Crumb Rubber Extraction and Emission Samples Analyzed by GC/MS/MS[a]

SVOC	Analyte Category	CAS Number[b]	Literature Review/Gaps Analysis Reference ID (see Appendix C)
Phenanthrene	Primary	85-01-8	7, 10, 12, 15, 17, 23, 28, 45, 46, 47, 61, 65, 72, 79, 82, 89
Fluoranthene	Primary	206-44-0	7, 10, 12, 15, 17, 23, 28, 45, 46, 47, 61, 65, 72, 79, 82, 89
Pyrene	Primary	129-00-0	7, 10, 12, 15, 17, 23, 28, 45, 46, 47, 49, 61, 63, 65, 72, 79, 82, 89
Benzo[a]pyrene	Primary	50-32-8	12, 15, 23, 28, 45, 46, 47, 49, 63, 65, 79, 82, 89
Benzo[ghi]perylene	Primary	191-24-2	12, 15, 23, 28, 46, 47, 49, 63, 65, 79, 89
Sum15PAH[c]	Primary	N/A	N/A
Benzothiazole	Primary	95-16-9	7, 12, 15, 16, 17, 34, 3646, 51, 54, 55, 57, 71, 82
Dibutyl phthalate	Primary	84-74-2	23, 46, 54, 57, 61, 72, 82
Bis(2-ethylhexyl) phthalate	Primary	117-81-7	23, 36, 46, 54, 57, 61, 72, 82
Aniline	Primary	62-53-3	7, 36, 54, 57
4-tert-octylphenol	Primary	140-66-9	16, 17, 34, 51, 61, 72
Hexadecane	Primary	544-76-3	17, 34
Naphthalene	Secondary	91-20-3	7, 10, 12, 15, 17, 23, 28, 45, 46, 47, 57, 61, 72, 79, 82, 89
1-Methylnaphthalene	Secondary	90-12-0	15, 17, 23
2-Methylnaphthalene	Secondary	91-57-6	15, 17, 23
Acenaphthylene	Secondary	208-96-8	12, 15, 23, 28, 45, 46, 61, 82, 89
Fluorene	Secondary	86-73-7	7, 15, 23, 28, 45, 46, 47, 61, 72, 79, 82, 89
Anthracene	Secondary	120-12-7	12, 23, 28, 45, 46, 47, 61, 72, 79, 82, 82, 89
1-Methylphenanthrene	Secondary	832-69-9	23
2-Methylphenanthrene	Secondary	2531-84-2	23
3-Methylphenanthrene	Secondary	832-71-3	23
Benz[a]anthracene	Secondary	56-55-3	12, 15, 23, 28, 45, 46, 47, 49, 63, 65, 79, 82, 89
Chrysene	Secondary	218-01-9	7, 12, 15, 23, 28, 45, 46, 47, 49, 63, 65, 79, 82, 89
Benzo(b)fluoranthene	Secondary	205-99-2	7, 12, 15, 28, 45, 46, 47, 49, 63, 65, 79, 82, 89
Benzo(k)fluoranthene	Secondary	207-08-9	12, 15, 28, 45, 46, 47, 63, 79, 82, 89
Benzo(e)pyrene	Secondary	192-97-2	12, 15, 23
DBA + ICDP[d]	Secondary	53-70-3; 193-39-5	12, 23, 28, 45, 46, 47, 49, 63, 65, 79, 82, 89
Coronene	Secondary	191-07-1	12, 23
Dibenzothiophene	Secondary	132-65-0	12, 23, 46
2-Bromomethylnaphthalene	Secondary	939-26-4	36
n-Butylbenzene	Secondary	104-51-8	55, 61
Dimethyl phthalate	Secondary	131-11-3	23, 46, 61, 72
Diethyl phthalate	Secondary	84-66-2	23, 46, 54, 57, 61, 72, 82
Diisobutyl phthalate	Secondary	84-69-5	46, 54, 82
Benzyl butyl phthalate	Secondary	85-68-7	23, 46, 54, 61, 72, 82
Di-n-octyl phthalate	Secondary	117-84-0	23, 61, 72, 82

Table 3-3 Continued

SVOC	Analyte Category	CAS Number[b]	Literature Review/Gaps Analysis Reference ID (see Appendix C)
2,6-Di-tert-butyl-p-cresol (BHT)	Secondary	128-37-0	15, 16, 17, 34, 46, 54, 82, 94
Bis-(2,2,6,6-tetramethyl-4-piperidinyl) sebacate	Secondary	52829-07-9	54
Cyclohexyl isothiocyanate	Secondary	1122-82-3	54, 57

[a] GC/MS/MS = Gas chromatography/tandem mass spectrometry; N/A = Not applicable

[b] Unique numerical identifier assigned by the Chemical Abstracts Service (CAS)

[c] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

[d] DBA + ICDP = Sum of Dibenz[a,h]anthracene and Indeno(1,2,3-cd)pyrene

Table 3-4. Target SVOC Analytes for Tire Crumb Rubber Extraction and Emission Samples Analyzed by LC/TOFMS[a]

SVOC	CAS Number[b]	Literature Review/Gaps Analysis Reference ID (see Appendix C)
Di(2-ethylhexyl) adipate	103-23-1	7, 46, 82
Diisononyl phthalate	28553-12-0	23, 46, 61, 72
Diisodecyl phthalate	26761-40-0	23, 46, 72
2-Mercaptobenzothiazole (MBT)	149-30-4	46, 57, 71, 94
2-hydroxybenzothiazole	934-34-9	7, 36, 54, 57, 71
Dicyclohexylamine	101-83-7	7, 54
Cyclohexanamine	108-91-8	54
N-cyclohexyl-N-methylcyclohexanamine	7560-83-0	54, 57
Phthalimide	85-41-6	7, 57
Resorcinol	108-46-3	71, 94

[a] SVOC = Semivolatile organic compound; LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry

[b] Unique numerical identifier assigned by the Chemical Abstracts Service (CAS)

Table 3-5. Target SVOC Analytes for Suspect Screening Analysis of Tire Crumb Rubber and Emissions Samples by LC/TOFMS[a]

SVOC	CAS Number[b]	Literature Review/Gaps Analysis Reference ID (see Appendix C)
1,3-Dicyclohexylurea	2387-23-7	54
N,N'-diphenyl-1,4-Benzenediamine	74-31-7	36, 94
Dehydroabietic acid	1740-19-8	36
2-(1-phenylethyl)-phenol	26857-99-8	54
2-(Methylthio)benzothiazole	615-22-5	54
2-(4-morpholinothio)benzothiazole (MBS)	102-77-2	2, 71, 94
2,2,4-Trimethyl-1,2-dihydroquinoline (TMQ)	147-47-7	94
2,2'-Methylene-bis-(4-methyl-6-tert-butylphenol) (BPH)	119-47-1	94
2,4-Dimethylphenol	105-67-9	57

Table 3-5 Continued

SVOC	CAS Number[b]	Literature Review/Gaps Analysis Reference ID (see Appendix C)
2,6-Di-tert-butyl-4-methylphenol (BHT)	128-37-0	15, 16, 17, 34, 46, 54, 82, 94
2,2’-Dithiobis(benzothiazole) (MBTS)	120-78-5	94
2-Ethylanthracene-9,10-dione	84-51-5	36
2-Morpholinodithiobenzothiazole (MBSS)	95-32-9	94
2-Phenylbenzimidazole	716-79-0	36
2-Phenylbenzothiazole	883-93-2	36
3,5-Di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	54
4-Nonylphenol	104-40-5	54, 61, 72
4-tert-Butylphenol	98-54-4	46
5-Methyl-2-hexanone	110-12-3	54
Acetophenone	98-86-2	54, 57
Isocyanatobenzene	103-71-9	54
Benzoic acid	65-85-0	55, 57
Benzyl alcohol	100-51-6	54, 57
Biphenyl	92-52-4	23, 55
Butylated hydroxyanisole (isomeric mixture)	25013-16-5	17
Caprolactam disulfide (CLD)	23847-08-7	94
Carbazole	86-74-8	45, 57
p-Cresol	106-44-5	57
o-Cresol	95-48-7	57
Isocyanatocyclohexane	3173-53-3	54
Cyclohexanone	108-94-1	7, 54
Cyclohexylthiophthalimide (CTP)	17796-82-6	N/A
Di-(2-ethyl)hexylphosphorylpolysulfide (SDT)	Not Found	94
Dibenzofuran	132-64-9	23
Dicyclohexylamine	101-83-7	7, 54
Dimethyldiphenylthiuram disulfide (MPTD)	53880-86-7	94
Di-ortho-tolylguanidine (DOTG)	97-39-2	94
Dipentamethylenethiuram tetrasulfide (DPTT)	120-54-7	94
Diphenylamine	122-39-4	2, 36
Dithiodimorpholine (DTDM)	103-34-4	94
Docosanoic acid	112-85-6	36
Dodecanoic acid	143-07-7	54
Dotriacontane	544-85-4	36
Drometrizol	2440-22-4	54
Eicosane	112-95-8	36
Erucylamide	112-84-5	54
1-(2-Butoxyethoxy)ethanol	54446-78-5	54
2-Butoxyethanol	111-76-2	54
Ethanone, 1,1'-(1,3-phenylene)bis-	6781-42-6	54
Ethanone, 1,1'-(1,4-phenylene)bis-	1009-61-6	54
1-[4-(1-methylethenyl)phenyl]ethanone	5359-04-6	54

Table 3-5 Continued

SVOC	CAS Number[b]	Literature Review/Gaps Analysis Reference ID (see Appendix C)
Ethylenethiourea (ETU)	96-45-7	94
N-Cyclohexylformamide	766-93-8	54
Heptadecane	629-78-7	36
Hexa(methoxymethyl)melamine	3089-11-0	54
Hexacosane	630-01-3	36
2-Ethylhexanoic acid	149-57-5	54
Isononylphenol	11066-49-2	61, 72
Isophorone	78-59-1	57
N,N'-Bis(1,4-dimethylpentyl)-p-phenylenediamine (7PPD)	3081-14-9	94
N,N-Dicyclohexyl-2-benzothiazolesulfenamide (DCBS)	4979-32-2	94
N,N'-Diethylthiourea (DETU)	105-55-5	94
N,N'-Diphenylguanidine (DPG)	102-06-7	94
N,N'-Diphenyl-p-phenylenediamine (DPPD)	74-31-7	36, 94
N,N'-Ditolyl-p-phenylenediamine (DTPD)	27417-40-9	94
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD)	793-24-8	94
N-Cyclohexyl-2-benzothiazolesulfenamide (CBS)	95-33-0	94
N-Isopropyl-N'-phenyl-p-phenylenediamine (IPPD)	101-72-4	54, 71, 94
N-Methyl-2-pyrrolidone	872-50-4	54
N-Nitrosodiphenylamine	86-30-6	57
Nonadecane	629-92-5	36
N-Oxydiethylenedithiocarbamyl-N`-oxydiethylenesulfenamide (OTOS)	13752-51-7	94
N-tert-Butyl-2-benzothiazolesulfenamide (TBBS)	95-31-8	94
Octadecane	593-45-3	N/A
Methyl stearate	112-61-8	36
o-Cyanobenzoic acid	3839-22-3	7, 36
Pentacosane	629-99-2	36
2,4-Bis(1,1-dimethylethyl)phenol	96-76-4	54
2,4-Bis(1-methyl-1-phenylethyl)phenol	2772-45-4	36, 54
m-tert-butylphenol	585-34-2	54
p-Phenylenediamine (PPD)	106-50-3	71
Pyrazole	288-13-1	36
Pyrimidine, 2-(4-pentylphenyl)-5-propyl-	94320-32-8	36
Tetrabenzylthiuram disulfide (TBZTD)	10591-85-2	71, 94
Tetrabutylthiuram disulfide (TBTD)	1634-02-2	71, 94
Tetracosane	646-31-1	36
Tetramethylthiuram disulfide (TMTD)	137-26-8	94
Tetramethylthiuram monosulfide (TMTM)	97-74-5	94
Tricosane	638-67-5	36

[a] SVOC = Semivolatile organic compound; LC/TOFMS = Liquid chromatography/time-of-flight spectrometry; N/A = Not applicable

[b] Unique numerical identifier assigned by the Chemical Abstracts Service (CAS)

3.2 Recruiting Recycling Plants and Synthetic Turf Fields

3.2.1 Recycling Plant Recruitment and Selection

Researchers aimed to recruit and seek consent from nine tire recycling plants producing tire crumb rubber for use as synthetic turf infill – five plants using an ambient production process and four plants using a cryogenic production process. Another goal was to recruit tire recycling plants across the four U.S. census regions. CDC/ATSDR and EPA participated in the recruitment effort and contacted seven companies operating tire recycling plants that produce tire crumb rubber for synthetic turf infill. Sample collection agreements were reached with six of those companies, resulting in successful sample collection at nine tire recycling plants operated by those six companies. The nine recycling plants were located across all four U.S. census regions. Six recycling plants used ambient processing and three used cryogenic processing.

3.2.2 Synthetic Turf Field Recruitment and Selection

Researchers aimed to recruit and seek consent from 40 synthetic turf fields with recycled tire crumb rubber infill – 10 fields in each of the four U.S. census regions. However, if the study team could not obtain the maximum sample size in a specific U.S. census region by the end of the recruitment period, researchers consented and sampled field(s) in alternate census regions. There were no restrictions on field age, "grass blade" composition or color, or field type (i.e., soccer, baseball, or softball). Researchers requested field size information, but that was not a specific exclusion criterion. The study team did exclude synthetic turf fields with encapsulated, colored or painted tire crumb rubber and limited participation to two outdoor fields per facility. To include two fields at one facility, the fields had to meet one of two criteria: the fields must be of different ages or the fields must be installed by different manufacturers. Researchers did allow two fields from the same facility of the same age if one was an indoor field and the other was an outdoor field.

CDC/ATSDR used a convenience sampling approach to recruit community facilities with synthetic turf fields. Researchers found prospective facilities using online search engines and the following key search terms: "recreational fields," "sports training facilities," "sports training," "sport fields," "sporting fields," "soccer fields," "baseball fields," "football fields," and "parks and recreation." The researchers used these key search terms combined with the state or area of focus. Additionally, potential facilities and fields were allowed to self-identify if interested in participating.

Between August and November 2016, CDC/ATSDR researchers initiated contact with a total of 306 community facility and field owners. Potential facilities and fields were classified into one of six categories based on the initial contact: (1) no answer (a voicemail was left, if applicable); (2) incorrect contact person (correct contact information was requested); (3) immediate declination; (4) requested additional information; (5) non-eligible (i.e., did not have a synthetic turf field); and (6) verbal consent. Contact with facilities in categories 1 and 2 was limited to five times. For those immediately declining participation in the study, researchers requested information regarding the declination. In general, those declining to participate gave reasons that were limited to three main issues:

- Liability: Contacted field owners and managers expressed concern about the potential liability associated with sampling their fields.
- Confidentiality: As expressed in the agreement forms, individual facility names and locations would not be released in the public reports, although the number of fields sampled per U.S.

census region would be noted. CDC/ATSDR and EPA could not, however, assure the facility of complete anonymity or confidentiality.

- Not at this time: Although many field owners and managers were interested in the study, they declined participation in the current study.

For those facility or field owners/managers requesting additional information, CDC/ATSDR researchers sent a fact sheet describing the study and the facility agreement form via email. For those agreeing to participate, researchers administered the eligibility screening and sent the agreement form to those facilities deemed eligible. The researchers categorized eligible fields as indoor or outdoor and by age (2008 or older, 2009 to 2012, and 2013 to 2016). The researchers contacted the facilities that verbally agreed to participate weekly until (1) obtaining written agreement, (2) attaining the maximum number of facilities consented for the census region, or (3) reaching the project recruitment period end, which was in early November 2018.

For inclusion in the study, facility owners or managers had to provide written agreement to recycled tire crumb rubber sample collection at their facility and answering a questionnaire on field maintenance procedures and field use. CDC/ATSDR researchers obtained participation agreements from 21 community fields, including 9 outdoor fields and 12 indoor fields. Researchers also collaborated with the U.S. Army Public Health Center (APHC) to identify 19 synthetic turf fields at Army installations across the United States for participation in the study, including 16 outdoor fields and 3 indoor fields.

3.3 Tire Crumb Rubber Sample Collection Method Summaries

Standard operating procedures (SOPs) were developed for all tire crumb rubber sample collection and processing methods. A list of SOPs is provided in Appendix D. Brief method summaries are provided below.

3.3.1 Recycling Plant Sample Collection

Researchers collected recycled tire crumb rubber samples of the size category used in synthetic turf fields (typically 10 to 20 mesh or 0.84 to 2 mm) from nine tire recycling plants around the United States. The samples were collected from three different storage containers (typically flexible intermediate bulk containers) at each plant. The samples collected from each sack were placed into pre-cleaned 1-liter (L) glass or high-density polyethylene (HDPE) wide-mouth jars (see Figure 3-4). From each storage container, researchers filled two 1-L HDPE jars for metals analysis, two 1-L amber glass jars with Teflon™-lined lids for organic chemical analysis, and one 1-L HDPE jar for particle characterization. At most plants, the study team used pre-cleaned stainless-steel scoops to gather tire crumb rubber for organics analysis and pre-cleaned plastic scoops to gather tire crumb rubber for metals analysis and particle characterization. At one plant, researchers collected samples from storage containers using the plant's established equipment and protocol; samples were collected using a stainless-steel sampling spike designed to include material from multiple levels of the storage container in the vertical and horizontal dimensions.

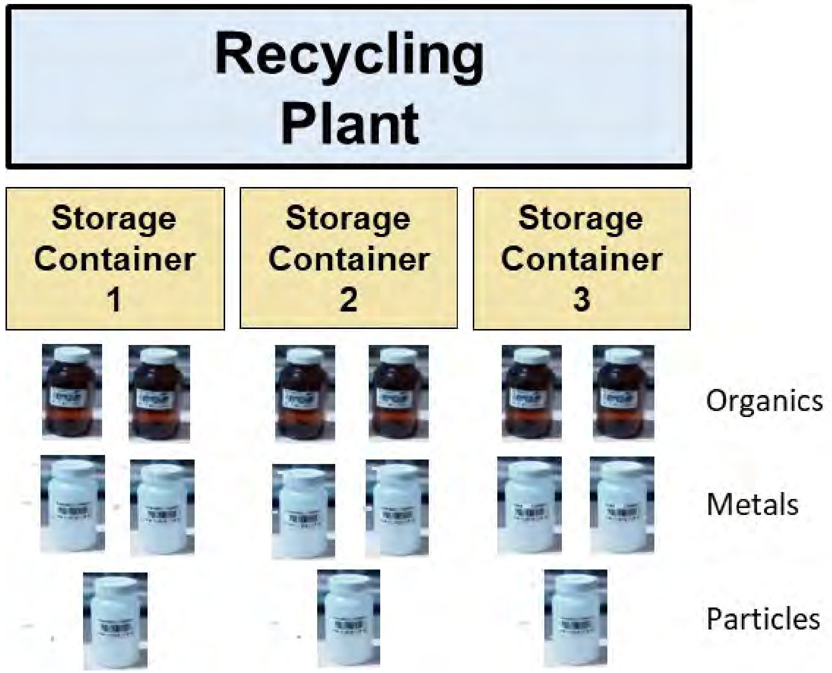

Figure 3-4. Schematic representation of tire crumb rubber sample collection at tire recycling plants. All collections made into 1-L pre-cleaned glass or high-density polyethylene (HDPE) jars.

3.3.2 Synthetic Turf Field Sample Collection

Researchers collected tire crumb rubber samples from 40 synthetic turf fields to support characterization of chemical constituents and to examine microbial species. Substantial variability in tire crumb rubber chemical concentrations have been reported; therefore, researchers used a composite sample collection approach at synthetic turf fields. Researchers used specified sampling locations for rectangular fields, such as soccer and football fields (Figures 3-5) and for baseball and softball fields (Figure 3-6).

Figure 3-5. Sample collection locations for rectangular synthetic turf fields, including soccer, football and other rectangular fields.

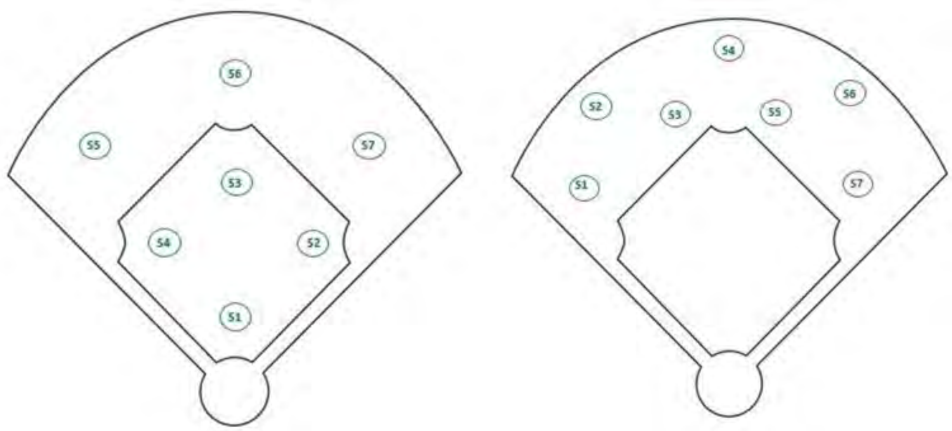

Figure 3-6. Sample collection locations for baseball and softball synthetic turf fields with A) turf in the infield and B) no turf in the infield.

Researchers collected samples from each of the seven locations at each field for organic chemical (VOC and SVOC), metal, microbial, and particle characterization analyses (Figure 3-7). At each location, researchers filled one 250-milliliter (mL) HDPE jar for metals analysis, one 250-mL amber glass jar with a Teflon™-lined lid for organic chemical analysis, one 250-mL HDPE jar for particle characterization, and one sterile 50-mL tube for microbial analysis.

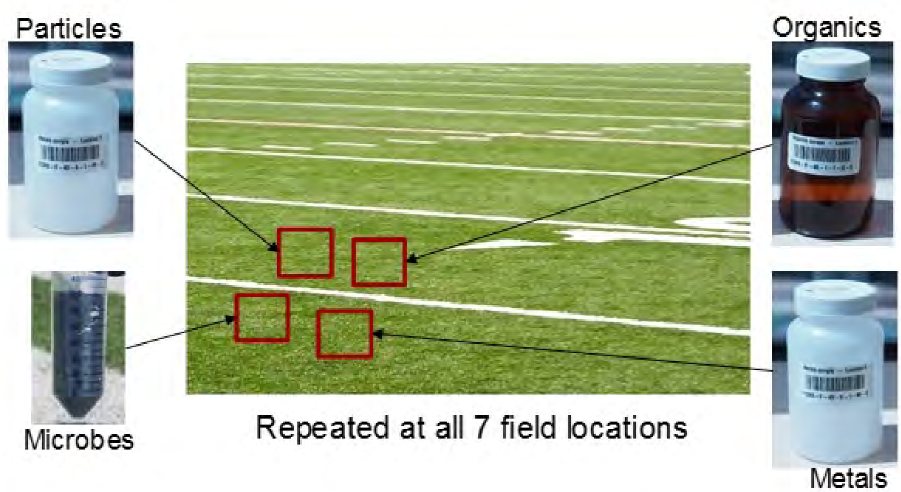

Figure 3-7. Schematic representation of the four samples that were collected at each of the seven locations on each field. Samples for chemical and particle characterization were collected into 250-mL pre-cleaned amber glass or high-density polyethylene (HDPE) jars. Microbial samples were collected into sterile 50-mL tubes.

Synthetic turf fields were recruited for sample collection from across the continental United States, which precluded being able to drive directly from a central location to the various fields. And often, the fields were only available for sample collection for short time periods during the scheduled sampling day. In addition, samples collected for microbial analysis had to be shipped cold, as soon as possible after collection, for arrival at the laboratory the following morning. Due to these constraints, the study team developed self-contained sampling kits – one for tire crumb rubber sample collection for metals, organics and particle analyses (Figure 3-8) and one for tire crumb rubber sample collection for microbial analysis (Figure 3-9). These kits could be rapidly shipped to sampling locations, contained all required sampling materials, and provided for rapid overnight return shipment using the same packaging materials. With these sampling kits, sample collection could usually be completed in 1.5 to 2.0 hours. Field sampling most often occurred in the morning, allowing samples to be transported to a delivery service office for overnight shipment to the appropriate laboratories, and sampling was only scheduled Monday through Thursday to allow overnight shipment and laboratory receipt Tuesday through Friday.

Figure 3-8. Sample collection kit for metal, organic and particle sample collection at synthetic turf fields.[COC = Chain of custody; HDPE = High-density polyethylene]

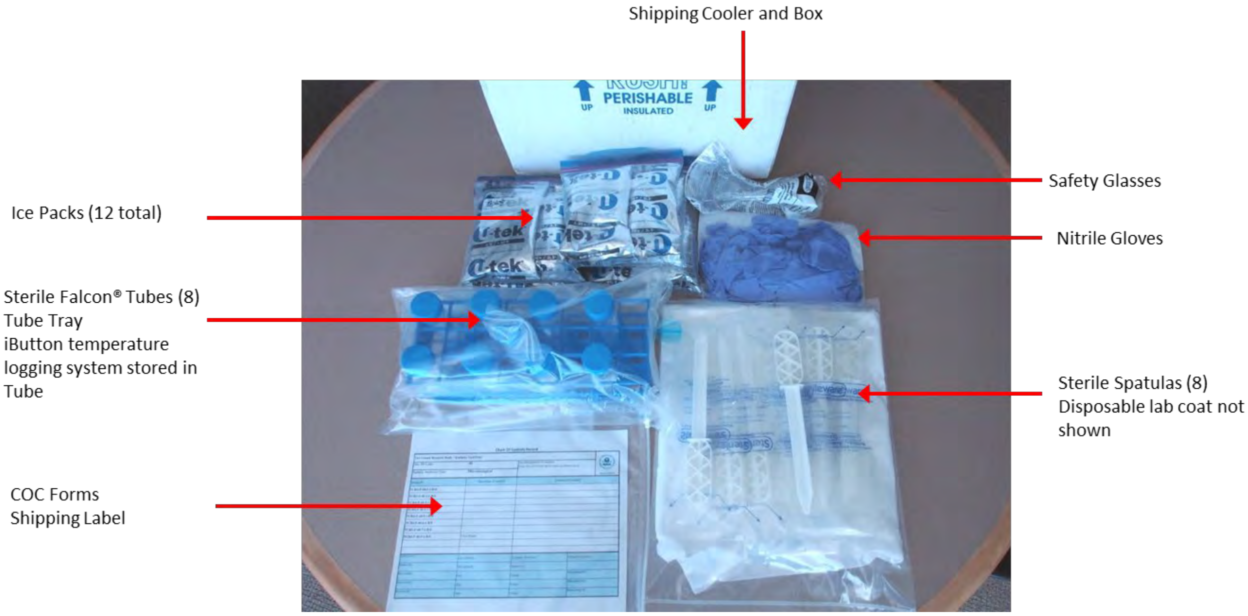

Figure 3-9. Sample collection kit for microbial sample collection at synthetic turf fields.
[COC = Chain of custody]

Researchers collected tire crumb rubber samples for organic chemical, metal, and particle analyses by removing tire crumb rubber from about the top 3 centimeters (cm) of the synthetic turf field surface, using either a comb or spatula (Figure 3-10). The 3-cm depth was selected because it is likely that most exposures occur to tire crumb rubber infill available near the surface of the field. Researchers collected samples for organics (SVOC and VOC) analysis, using a small handheld metal comb or spatula to pull tire crumb rubber from the field at each location, and placed the collected tire crumb rubber into certified pre-cleaned 250-mL amber glass wide-mouth containers with Teflon™-lined lids. For metals analysis, researchers used a small handheld plastic comb or spatula to pull tire crumb rubber from the field at each location and placed the collected tire crumb rubber into certified pre-cleaned 250-mL HDPE wide-mouth jars. For samples to be used for particle characterization, researchers used a small handheld plastic comb or spatula to pull tire crumb rubber from the field at each location and placed collected tire crumb rubber into certified pre-cleaned 250-mL HDPE wide-mouth jars. At some fields (e.g., older fields with greater wear and higher blade and rubber compression), samples that were to be collected by comb, had to alternatively be collected by spatula.

Researchers also collected individual samples for microbe analysis from each of the seven locations at each field. Researchers employed aseptic techniques when collecting tire crumb rubber samples for microbial analysis by wearing a new disposable lab coat, wearing clean nitrile gloves at all times, and donning new gloves at each location on the field. A new, sterile polypropylene spatula was used at each of the seven locations to collect the sample for microbial analysis. At each of the seven locations, researchers inserted the sterile spatula into the synthetic turf field surface to a maximum depth of about 3 cm from the surface, moved it forward to collect tire crumb material, and placed the tire crumb rubber into a new, sterile 50-mL polypropylene tube with volumetric lines (Figure 3-10). The tubes were filled with tire crumb rubber material to the 25-mL line. Once samples were collected, the researchers immediately placed them into a cooler with ice packs and shipped the samples the same day they were collected, in a container with ice packs, to the appropriate laboratory by overnight shipment.

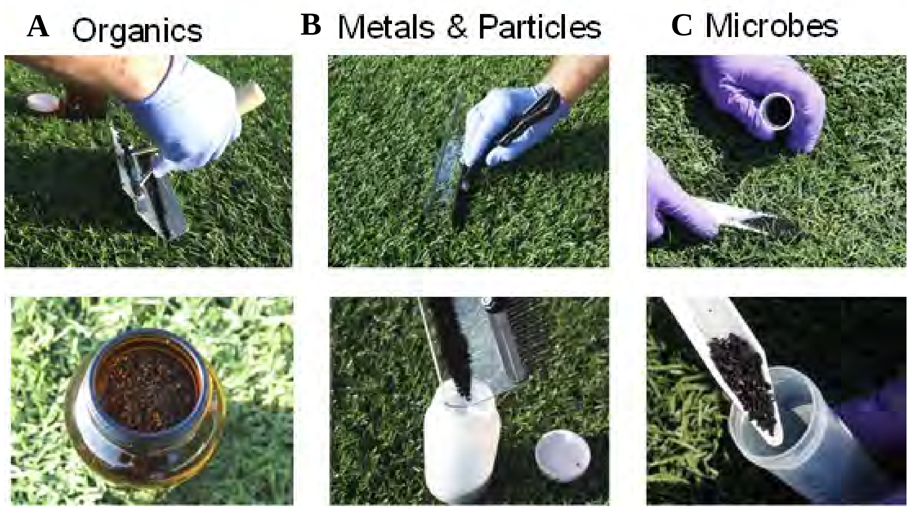

Figure 3-10. Sample collection methods using A, B) combs and C) spatulas to remove tire crumb rubber from about the top 3 cm of the synthetic turf field surface.

3.4 Synthetic Field Use and Maintenance Questionnaire Administration

A copy of the questionnaire was provided to each field owner/manager prior to questionnaire administration as some of the questions required time in advance to find specific answers. The interview was conducted via phone, lasted approximately 30 minutes, and included questions on the type of synthetic turf field, how the facility was used, and the standard operating procedures (SOPs) for maintenance of the field. The interviewer entered the answers to these questions directly into an Epi Info™ Version 7.2 database (CDC, 2017). After completion of the questionnaire, the field owner/manager was given contact information for any further questions. The questionnaire is provided in Appendix F.

3.5 Tire Crumb Rubber Sample Processing Method Summaries

3.5.1 Recycling Plant Sample Processing

As described in section 3.3.1, researchers collected tire crumb rubber samples from three different storage containers at each plant. The three samples collected from each recycling plant were kept as individual samples and a portion of each sample was prepared for metals, organics, and particle analysis (Table 3-6). Tire crumb rubber from recycling plants was not analyzed for microbes.

Table 3-6. Sample Preparation and Analysis of Tire Crumb Rubber Samples Collected at Tire Recycling Plants

Sample Analyses[a]	Type of Analysis	Sample Preparation
SVOC Extraction	Organics	All samples
Metals Digestion - ICP/MS	Metals	All samples
Metals – XRF	Metals	All samples
VOC Emissions	Organics	All samples
SVOC Emissions	Organics	All samples
Particle Size - Gravimetric	Particle	All samples
Metal Bioaccessibility	Metals	All samples
Moisture Content	Particle	All samples

Table 3-6 Continued

Sample Analyses[a]	Type of Analysis	Sample Preparation
SVOC Extraction Non-Targeted	Organics	Subset of samples
VOC Emission Non-Targeted	Organics	Subset of samples
SVOC Emission Non-Targeted	Organics	Subset of samples
Particle Characterization - SEM	Particle	Subset of samples
Particle Characterization - EPMA	Particle	Subset of samples
VOC Emission Time Series	Organics	Subset of samples
SVOC Emission Time Series	Organics	Subset of samples
SVOC Chamber Wristband Tests	Organics	Subset of samples

[a] SVOC = Semivolatile organic compound; ICP/MS = Inductively coupled plasma/mass spectrometry; XRF = X-ray fluorescence spectrometry; VOC = volatile organic compound; SEM = scanning electron microscopy; EPMA = electron probe microanalysis

3.5.2 Synthetic Turf Field Sample Processing

As described in section 3.3.2, researchers collected individual tire crumb rubber samples from seven locations at each field for organics (VOC and SVOC), metals, microbial and particle characterization analyses. For microbial analyses, all seven individual location samples from each field were scheduled for separate analysis (Figure 3-11). The microbial samples were shipped cold, as soon as possible after collection, to the laboratory for analysis; all other samples were sent to a central processing laboratory, where they were processed for individual or composite analysis. Figure 3-11 shows the approach for preparation and analysis of composite and individual tire crumb rubber samples collected from synthetic turf fields.

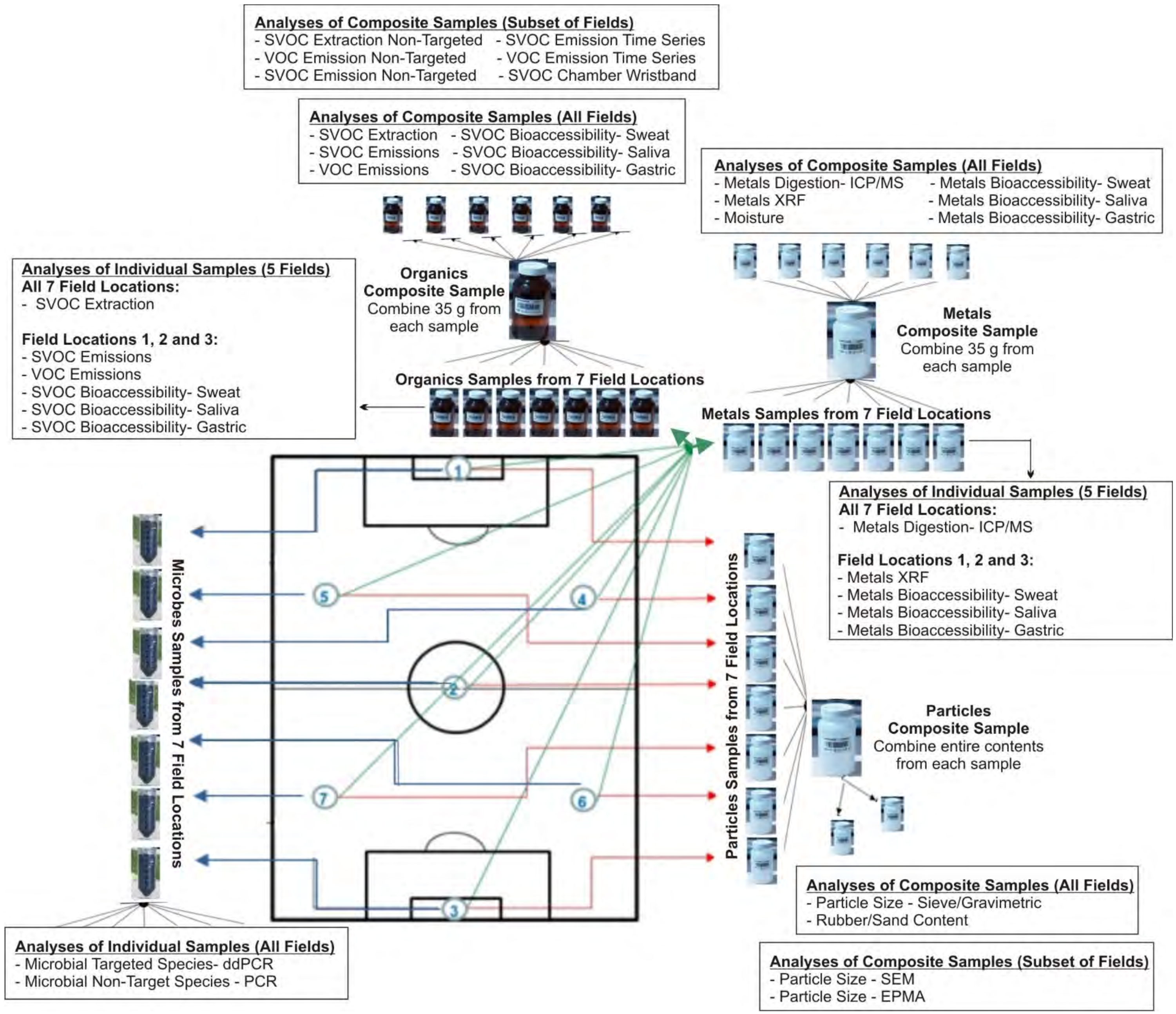

Figure 3-11. Schematic showing composite and individual location sample preparation and analysis for samples collected at synthetic turf fields.

To support between-field assessments of chemical constituents in a cost- and time-effective manner, the researchers took portions of the seven individual samples collected from each field for metals and organics analysis and created a single metals composite sample and organics composite sample for each field. For organics analyses, researchers added 35 grams (g) of the tire crumb rubber material from each of the seven individual organics samples to a single certified pre-cleaned 500-mL amber wide-mouth glass container with Teflon™-lined lid and mixed the composite sample thoroughly. Researchers then removed sub-samples of the composite sample and added them to smaller, pre-cleaned and certified amber glass containers to distribute to the analysis laboratories (Figure 3-11). Researchers used the same procedure to prepare composite samples and sub-samples for metals analysis from the seven individual metals samples, using certified pre-cleaned HDPE containers (Figure 3-11). Sub-samples prepared for moisture analysis also came from the metals composite samples. To support a within-field variability assessment of chemical constituents, researchers also prepared sub-samples of three to seven of the individual location samples from a subset of five fields for separate metals and organics analyses (Figure 3-11). For particle characterization analysis, the researchers combined the entire contents of the seven 250-mL individual location samples collected from each field for particle analysis and mixed to form a single particles composite sample for each field (Figure 3-11). Researchers retained the remaining composite and individual samples in their sealed containers and stored all samples in a freezer at -20 °C.

3.6 Tire Crumb Rubber Sample Analysis Method Summaries

Standard operating procedures (SOPs) were developed for all tire crumb rubber sample analyses. A list of SOPs is provided in Appendix D. Brief method summaries are provided below.

3.6.1 Moisture Analysis

A portion of each of the three tire crumb rubber samples collected from the recycling plants and a portion of the synthetic turf field composite tire crumb rubber sample for metals analysis were analyzed for moisture content. This analysis was performed so that chemical analysis results could be reported consistently in terms of the amount of chemical per the amount of dry tire crumb rubber.

Moisture analysis was performed using a HE53 halogen moisture analyzer (Mettler Toledo, Columbus, OH, USA). To determine the moisture content, the tire crumb rubber sample was removed from the freezer and allowed to reach room temperature while the moisture analyzer was set up. Prior to measurement, the balance calibration was verified using certified check weights. When the sample had equilibrated to room temperature, the moisture analysis process was started. A disposable sample pan was placed onto the moisture analyzer and tared. Tire crumb sample (2 g) was then spread in a thin, even layer across the total surface of the pan and the weight was recorded on a moisture analysis form. The moisture analysis was then started, with the analyzer heating the sample to 110 ºC, and continued until the mass loss was less than 1 milligram (mg)/30 seconds (s). The percent moisture content displayed on the HE53 halogen moisture analyzer was then recorded on the form. All moisture analyses were performed on duplicate samples (a second portion of tire crumb rubber from the same bottle) and the average of the two measurements was used.

3.6.2 Sand/Rubber Fraction Analysis

Infill used on synthetic turf fields is sometimes installed as a mixture of tire crumb rubber and sand, and sand may also be used as a base layer in some synthetic turf field installations. A number of the synthetic turf field samples had a visible sand component, so an analysis was conducted to determine the sand/rubber fraction of all synthetic turf field samples. Measurement of the sand fraction was performed to allow calculation of analysis results as either the amount of chemical analyte (metal or organic analyte) per kilogram of infill (rubber plus sand) or amount of chemical analyte per kilogram of tire crumb rubber in the infill.

One sample had a small fine gravel/coarse sand component that was retained on Number (No.) 4 and No. 10 (4.75- to 2.00-millimeter [mm]) sieves. This material was separated by hand and weighed. In 15 samples, the sand was confined to the infill material (rubber plus sand) retained on a No. 60 (0.25-mm) sieve. To separate the sand fraction from these samples, a floatation technique was employed. A salt solution of either a sulfate or calcium chloride was mixed to create a solution that had a density higher than the tire crumb, but lower than the mineral sand. The tire crumb material floated to the top of the solution and was removed. The tire crumb and sand fractions were then rinsed, dried and weighed. The percentage of sand and tire crumb in the No. 60 sieve fraction was then calculated, along with the percentage of sand and tire crumb in the total sample.

Unless otherwise noted, the synthetic turf field tire crumb rubber infill samples prepared for physical, chemical and microbial analyses included the sand fraction, when it was present, as part of the infill material collected.

3.6.3 Gravimetric Particle Size Analysis

Tire crumb rubber from recycling plants and synthetic turf fields was analyzed for particle size analysis (PSA). The total weight of the composited particles samples from each synthetic turf field ranged from 800 to 1100 g. The three samples collected from the recycling plants for particle analysis each weighed between 400 and 525 g and were analyzed individually. All samples were air dried for at least 24 hours in a fume hood before analysis. After drying, blades of synthetic turf in the field samples were removed by hand.

The PSA was done using a stack of Hogentogler & Co, Inc. (Columbia, MD, USA) No. 10 (2.00-mm), 18 (1.00-mm), 60 (0.25-mm), 120 (0.125-mm), and 230 (0.63-mm) U.S. Standard Series test sieves conforming to American Society for Testing and Materials (ASTM) Standard E11 (ASTM International, 2017) specifications. For larger field samples, a No. 4 (4.75-mm) sieve was added on top of the stack because the sample volume was too great to fit in the top (No. 10) sieve before analysis. The sieve stack was placed on a vibratory sieve shaker (CSC Scientific, Inc., Fairfax, VA, USA), and the shaker was set on intensity 5 and run for 15 minutes. After shaking, the mass of tire crumb retained on each sieve was recorded and the percentage of each fraction was calculated. In synthetic turf field samples that contained sand as part of the infill material, the rubber and sand were not separated as part of this particle size assessment.

3.6.4 SEM and EPMA Particle Characterization

3.6.4.1 Background

The surface area-to-mass ratio of particles is inversely proportional to particle size; therefore, the size distribution and elemental composition of the smallest sample size fractions separated by gravimetric PSA could be useful data in assessing exposure potential to the chemical constituents of the tire crumb rubber. Particles retained on the No. 230 sieve (0.63- to 0.125-mm nominal sieve opening) and the particles collected in the pan in the PSA (< 0.63 mm) were analyzed by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) to characterize size distribution and qualitative elemental composition, respectively. Because of the complexity and time-intensiveness of these analyses, a subset of nine recycling plant and nine synthetic turf field samples were analyzed by SEM and EPMA.

3.6.4.2 Sample Preparation

The entire contents of either the No. 230 sieve or the collection pan were transferred to a 76.2-mm (3-in) diameter aluminum pan. The sample size was reduced by a cone and quarter method (U.S. EPA, 1993). The process was repeated until the remaining material appeared to be sufficient for a loosely-spaced layer over about a 38.1-mm (1.5-in) diameter area. This material was transferred to the center of a second 3-in diameter aluminum pan, and the pan was gently tapped and tilted until such a layer was formed. A 25.4-mm (1-in) diameter double-sided adhesive carbon PELCO tab™ on an aluminum SEM stub (Ted Pella, Inc., Redding, CA, USA) was pressed onto the center of the layer to collect the subsample to be analyzed.

3.6.4.3 SEM Imaging and Particle Size Distribution Analysis

Pre-determined locations in a 17-point double-cross pattern (i.e., on four bisecting lines) covering the entire 25.4-mm (1-in) diameter sample were imaged at 25-kilovolt (kV) accelerating voltage. Photographs were recorded at 150x and 1200x magnification, with a Sigma VP SEM backscattered electron detector (BSD; Carl Zeiss AG, Oberkochen, Germany). The BSD provided qualitative differentiation of particles according to the atomic number of the major constituent element (i.e., particles composed primarily of heavier elements appeared brighter). The tagged image file format (TIFF) photographs from the BSD were processed using ImageJ freeware (ImageJ/Fiji, version 1.46r, National Institutes of Health, Bethesda, MD; Ferreira and Rasband, 2012). The images were scaled using the Set Scale function and adjusted with the Threshold function to minimize noise without losing significant particle area. Areas with obvious substrate features and the metadata banner were cleared, and the remaining area was processed with the Analyze Particles function for particle projected area in square micrometer (μm^2). A minimum area corresponding to 9 pixels was set to eliminate most remaining noise. The projected particle area values from the 17 imaged locations were combined in a Microsoft Excel spreadsheet. Histograms of particle projected area in two ranges – about 400 to 25,000 μm^2 and 1 to 400 μm^2 (corresponding to spherical particles about 20- to 173-µm and 1- to 20-µm diameter in size, respectively) – were constructed, and the median and mean projected areas were calculated.

3.6.4.4 Electron Probe Microanalysis

A Quantax energy dispersive EPMA system (Bruker Corporation, Billerica, MA, USA) on the SEM was used for electron probe microanalysis. The 25-kV accelerating voltage of the SEM allowed elements through about the first transition element series to be detected. A few particles from each imaged location were selected for point analysis (i.e., stationary electron beam on a single point in the image). The particles were selected to include a range of brightness, and therefore, presumably, a range of elemental compositions. The X-ray spectrum of each particle was integrated over 30 s, and the peaks were identified using the spectrometer software.

3.6.5 Microwave-Assisted Acid Extraction and ICP/MS Metals Analysis

A microwave-assisted extraction protocol was optimized to handle tire crumb rubber samples composed of particles of varying sizes. This extraction protocol used EPA Method 3051A (U.S. EPA 2017a) as the core digestion procedure and included a pre-digestion step. Optima™ grade concentrated hydrochloric acid (HCl), 70% nitric acid (HNO_3), and 30% hydrogen peroxide (H_2O_2) in water (Fisher Scientific

International, Inc., Hampton, NH, USA) were used as reagents in the extraction, and a custom multi-element standard solution (SCP Science, Quebec, Canada; Catalogue No. AQ0-008-122) was used as a matrix spike standard. Tire crumb rubber from recycling plants and synthetic turf fields was dried and weighed (250 mg) into a 100-mL XP-1500 Plus microwave digestion vessel with TFM® liner (CEM Corporation, Matthews, NC, USA). A handheld static neutralizer gun (Quantum Instruments, Inc., Hauppauge, NY, USA) was used to reduce static charges within or on the surface of the rubber particles and release particles clinging to the vessel's surface. Nitric acid and hydrochloric acid, 3:1 by volume, was added to each sample. A total of 24 samples, including quality control (QC) samples, were prepared at a time. The mixture of tire crumb and acids was allowed to react at room temperature for at least 30 minutes (min). The TFM® vessels were then sealed and placed in a MARS-5™ microwave digestion unit fitted with a ESP-1500 Plus pressure sensor and RTP-300 Plus fiber optic temperature sensor (temperature range -40 to 250 ºC; CEM Corporation, Matthews, NC, USA), where the samples were gently warmed to 120 °C within 30 min and kept at this temperature for an additional 20 min. This pre-digestion step allowed enough time for the larger rubber particles to disintegrate rather than exploding in the vessel. The microwaved samples were stored at room temperature overnight, giving additional time for the acid mixture to permeate the rubber particles. After venting the vessels to release excess pressure and replacing the safety membranes, the sample slurries were subjected to the full microwave digestion regiment at 200 °C. Hydrogen peroxide (750 microliters [µL]) was added to each cooled sample, which was then diluted to 50 g with 18.2 megaohm (Mohm) deionized water and transferred into acid-cleaned polyethylene bottles to await high resolution magnetic sector inductively coupled plasma mass spectrometer (HR-ICPMS) analysis.

3.6.5.1 ICP/MS Analysis

Quantitative elemental concentration measurements of tire crumb rubber samples were carried out using an Element 2™ HR-ICPMS (Thermo Finnigan, Bremen, Germany). The sample introduction system consisted of a PFA micro nebulizer, cyclonic quartz spray chamber, and platinum sampler and skimmer cones. All sample handling and analysis was performed in an ISO Class 5 Clean Room (ISO, 2015).

Tire crumb rubber sample acid digests (described above) were received as 18% HNO_3, 6% HCl, and 1.5% H_2O_2 volume to volume (v/v) and gravimetrically diluted with 2% HNO_3 and 0.5% HCl (v/v). External calibrations were performed with multi-element standards (High-Purity Standards, Charleston, SC, USA), and prepared with 2% HNO_3, 0.5% HCl, and 1% ethanol (v/v). An internal standard (IS) solution (2 parts per billion [ppb] indium) was prepared at the matrix acid levels and introduced in-line along with samples to account for analytical signal drift. National Institute of Standards and Technology (NIST)-certified standard reference materials (SRM® 1640a and SRM® 1643f; NIST, Gaithersburg, MD, USA) were used to verify instrument performance and analytical accuracy. Two instrument methods were used based on the elements of interest, the instrument resolutions, and the sample dilution factor. Instrument settings and method parameters are listed in Table 3-7. Although more isotope data was collected, only the reported elements are listed in Table 3-7.

Table 3-7. HR-ICPMS Method Settings and Parameters[a]

Instrument Setting	**Value**		
Radio frequency (RF) power	1200–1260 watts (W)		
Gas flow rate – Cool	17 liters per minute (lpm)		
Gas flow rate – Auxiliary	0.9 – 1.2 lpm		
Gas flow rate – Sample	0.9 – 1.20 lpm		
Sample update rate	~100 µL/min		
Sampler cone (Pt)	1.1-mm orifice diameter		
Skimmer cone (Pt)	0.8-mm orifice diameter		
Nebulizer	100-µL Teflon microneb		
Spray chamber	Cyclonic quartz		
Detector dead time	30 nanoseconds (ns)		
Internal standard solution	2.0 ppb solution of Indium115 and Iridium193		
Instrument Resolution	**Reported Isotopes[b]**		
Low resolution (LR)	Be9, Rb85, Sr88, Mo95, Cd111, Sb121, Ba137, Pb206, Pb207, Pb208, (In115, Ir193)		
Medium resolution (MR)	Mg24, Al27, V51, Cr52, Fe57, Co59, Ni60, Cu63, Zn66, Sn118, (In115, Ir193)		
High resolution (HR)	As75, Se77, Se78, Sn118, (In115, Ir193)		
Acquisition Parameter	**Low Resolution**	**Medium Resolution**	**High Resolution**
Mass task window, %	100	125	150
Samples/peak	30	20	15–20
Sample time/ns	10	20–50	100–500
Scan type	E Scan	E Scan	E Scan
Detector mode (analog/counting)	Both	Both	Both
No. replicates (runs)	3	3	3
No. scans per replicate (pass)	2	2	2
Evaluation Parameters	**Low Resolution**	**Medium Resolution**	**High Resolution**
Search task window, %	100	100	80–100
Integration task window, %	40	60	60–70
Integration type	Avg	Avg	Avg
Calibration type	Weighted	Weighted	Linear
Internal standard (Indium/Iridium)	Indium	Indium	Indium

[a] High resolution magnetic sensor inductively coupled plasma mass spectrometry (HR-ICPMS) was conducted using an Element 2™ HR-ICPMS.

[b] Al = Aluminum; As = Arsenic; Ba = Barium; Be = Beryllium; Cd = Cadmium; Co = Cobalt; Cr = Chromium; Cu = Copper; Fe = Iron; In = Indium; Ir = Iridium; Mg = Magnesium; Mo = Molybdenum; Ni = Nickel; Pb = Lead; Rb = Rubidium; Sb = Antimony; Se = Selenium; Sn = Tin; Sr = Strontium; V = Vanadium; Zn = Zinc

3.6.6 XRF Metals Analysis

Tire crumb rubber from recycling plants and synthetic turf fields was analyzed for X-ray fluorescence (XRF). Tire crumb rubber samples from recycling plants were received as three 10-g samples, and samples from synthetic turf fields were received as either 10-g composites prepared from all field sampling locations or as 5-g samples from individual locations. All 5- or 10-g samples received for XRF analysis were split into two samples using a soil splitter and placed into HDPE analysis cups covered with a Mylar membrane.

Samples analyzed for particle size (gravimetric PSA) were also prepared for XRF analysis. For all particle size fractions where enough material was retained on a sieve, two samples were taken from the size fraction and placed into HDPE analysis cups covered with a Mylar membrane.

The XRF analysis was performed using an Innov-X Alpha Series™ X-Ray Fluorescence Spectrometer (Innov-X Systems, Woburn, MA, USA). This unit is a portable analyzer with a mode for testing soil media. The Innov-X XRF spectrometer was used in a test stand, with the sample cups placed Mylar side down on the analysis window for testing. The XRF spectrometer was set to analyze for 300 seconds in standard mode for heavy metals and 300 seconds for light element analysis. The analyzer then combined the data from the two modes to give concentration data (in parts per million [ppm]) for a range of elements. The data was downloaded from the analyzer and the target element results were reported for each sample.

3.6.7 Solvent Extraction and Semivolatile Organic Compound (SVOC) Analysis

3.6.7.1 Tire Crumb Rubber Extraction

Prior to beginning extractions of tire crumb rubber for SVOC analysis, several solvents and solvent combinations were tested as potential extraction fluids for the tire crumb rubber material. A 1:1 mixture of acetone and hexane appeared to provide extracts with the greatest number/intensity of chromatographic features, while not dissolving the tire rubber material, which was observed when methylene chloride was used as the extraction solvent.

The solvent extraction method used in this study is not likely to completely extract all of the target chemicals contained in the tire crumb rubber particles. While this method is not a total extraction method, it is likely relevant with regard to the potential for human exposure. When combined with ceramic homogenizers, the vortex extraction method was fairly aggressive and very efficient in terms of throughput, which was very important given our tight timeline for completing the laboratory work. Prior to using this method, multiple sequential extractions were evaluated using this technique and it was determined that the majority of extractable organics were removed in the first extraction cycle. This method was also evaluated for linearity across tire crumb mass, as well as precision of replicates and was found to perform well across the range of semivolatile organics we were measuring. This method has an advantage compared to more aggressive extraction techniques in that it minimizes the potential for analyte losses due to no heating, solvent evaporation, or extensive sample handling. The use of solvents or methods that would approach total SVOC extraction would result in residues that could rapidly impair analytical systems, likely require more extensive time and effort in sample clean-up and result in greater potential for analyte losses. (It is also important to note that the results of this study are in general agreement with extractable SVOC measurement results from several other studies [shown in tables in section 2] that used different extraction methods).

Tire crumb rubber samples were stored in a freezer at -20 ºC after receipt at the EPA laboratory. Prior to extraction, the samples were allowed to warm to room temperature. The samples were homogenized inside of their storage jars by shaking to cycle the contents from the bottom of the jar to the top of the jar. Two separate 1-g aliquots were removed from each sample, shaking the sample jar between each aliquot. Each 1-g aliquot was transferred to a clean 50-mL polypropylene centrifuge tube. An internal standard solution (100 µL) was added to each tube along with a ceramic homogenizer. A 10-mL volume of 1:1 acetone:hexane was then added to each sample tube. The tubes were capped and vortex-mixed for 1 min, allowed to sit for 2 min, then vortex-mixed for an additional 1 min. The tubes were then centrifuged at 4,000 revolutions per minute (RPM) for 5 min. The solvent was removed and transferred to a 15-mL vial. A 1-mL aliquot of the extract was transferred to an autosampler vial for gas chromatography tandem mass spectrometry (GC/MS/MS) analysis. The remaining extract was stored in a freezer at -20 ºC.

3.6.7.2 GC/MS/MS Analysis for Target SVOCs

SVOC extraction samples were analyzed using an Agilent Model 7890 gas chromatograph equipped with a VF-5ms column (30 m × 0.25 mm, 0.25 µm) and a Model 7010 triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). The GC/MS/MS parameters in Table 3-8 were used for data acquisition. The instrument was standardized using High Sensitivity Electron Impact (EI) Autotune and was calibrated for target analytes in the range of 0.1 nanograms (ng)/mL to 500 ng/mL. Calibration checks were run using a mid-level standard between every 10 samples. Quantitation was performed using linear regression curves generated from the responses and nominal concentrations of calibration standard solutions.

Table 3-8. GC/MS/MS Parameters for Target SVOC Analysis[a]

System Component	Parameter	Value
Gas Chromatograph	Injector Mode	Capillary injector in splitless mode
Gas Chromatograph	Injector Split Ratio	Pulsed splitless at 25 pounds per square inch (psi) for 0.5 min, then split at 50 mL/min at 1 min
Gas Chromatograph	Injector Temperature	250 ºC
Gas Chromatograph	Injector Liner	Single gooseneck glass, deactivated
Gas Chromatograph	Injection Volume	1 µL
Gas Chromatograph	Column Flow	1.2 mL/min
Gas Chromatograph	Temperature Program	50 ºC for 2 min to 325 ºC at 10 ºC/min, hold 5 min
Mass Spectrometer	Detector Mode	Electron Impact (EI) operating in Multiple Reaction Monitoring (MRM)/Scan mode
Mass Spectrometer	Detector Tuning	Electron Multiplier Voltage by Gain Curve
Mass Spectrometer	Detector Transfer Line Temperature	300 ºC

[a] Gas chromatography tandem mass spectrometry (GC/MS/MS) was conducted using an Agilent 7890 gas chromatograph with a VF-5ms column and an Agilent 7010 Triple Quadrupole mass spectrometer. SVOC = semivolatile organic compound

3.6.7.3 GC/MS Analysis for Non-Target SVOCs

A subset of the tire crumb extraction samples was subsequently submitted for non-targeted analysis using an Agilent Model 6890 gas chromatograph equipped with a VF-5Sil ms column (60 m × 0.25 mm, 0.25 µm) and Model 5973 mass selective detector (MSD; Agilent Technologies, Santa Clara, CA, USA). The instrument was standardized using EI Standard Spectrum Tune and was operated using the parameters listed in Table 3-9. The mass spectral data were analyzed by deconvolution and spectral matching to the NIST (2011) Mass Spectral Database using Agilent MassHunter Workstation Quantitative Analysis (Version B.07.01, Agilent Technologies, Santa Clara, CA, USA) Unknowns Analysis.

Table 3-9. GC/MS Parameters for Non-target SVOC Analysis[a]

System Component	Parameter	Value
Gas Chromatograph	Injector Mode	Capillary injector in splitless mode
Gas Chromatograph	Injector Split Ratio	Splitless, then split at 50 mL/min at 0.75 min.
Gas Chromatograph	Injector Temperature	250 ºC
Gas Chromatograph	Injector Liner	Single gooseneck glass, deactivated
Gas Chromatograph	Injection Volume	1 µL
Gas Chromatograph	Column Flow	1.2 mL/min
Gas Chromatograph	Temperature Program	40º C for 2 min to 340º C at 5º C/min, hold 5 min.
Mass Selective Detector	Detector Mode	Electron Impact (EI) operating in Scan mode
Mass Selective Detector	Detector Scan Parameters	Mass Range: 50-550 m/z (mass-to-charge ratio), Scan Rate: 1.52 scans/s, Threshold: 1000
Mass Selective Detector	Detector Tuning	Electron Multiplier Voltage = Tune + 400
Mass Selective Detector	Detector Transfer Line Temperature	300 ºC

[a] Gas chromatography mass spectrometry (GC/MS) was conducted using an Agilent Model 6890 gas chromatograph with a VF-5Sil ms column and an Agilent Model 5973 mass selective detector. SVOC = semivolatile organic compound

3.6.7.4 LC/TOFMS Analysis for Target SVOCs

Liquid chromatography/time-of-flight mass spectrometry (LC/TOFMS) analysis was performed to focus on target SVOCs that were difficult to analyze by GC/MS/MS. A 1-mL aliquot of each of the 1:1 acetone:hexane sample extracts prepared for GC/MS/MS analysis was transferred to a vial and used for LC/TOFMS analysis. A solvent exchange was used to prepare the sample extracts for analysis. The extracts were first placed in a hood, and the solvent was allowed to evaporate at room temperature. This was done to avoid the target analyte loss that can occur at temperatures greater than 60 ºC. After evaporation was complete, 1 mL of methanol was added to each vial to reconstitute the extract for LC/TOFMS analysis.

A portion of the sample extract was added to a propylene autosampler vial containing 2-millimolar (mM) ammonium acetate buffer to match the starting conditions (75% water:25% methanol) of the mobile phase gradient used. Each vial was capped and vortexed to ensure mixing of the organic sample with the aqueous buffer. The bottom of each vial was checked for air bubbles and if present, bubbles were removed by tapping on the vial. After making sure that there were no air bubbles, the samples were placed in the high-performance liquid chromatography (HPLC) autosampler and analyzed.

The LC/TOFMS analysis was performed using an Agilent 1100 HPLC equipped with an Eclipse Plus C18 HPLC column (2.1 mm × 50 mm, 3.5 µm) with an injection volume loop of 40 µL and interfaced with an Agilent Model G1969A LC/MSD TOF System (Agilent Technologies, Santa Clara, CA, USA). A 45-min gradient HPLC run was used with mobile phase components of methanol and 2-mM formate or acetate buffer, at a flow rate of 300 µL/min (Table 3-10). Electrospray ionization was used in the mass spectrometer source, which was maintained at 325 ºC. Molecular weights for the 10 LC/TOFMS target analytes are shown in Table 3-11.

Table 3-10. HPLC Gradient Program Used for Characterization of Tire Crumb Rubber Samples[a]

Time (min)	Flow Rate (mL/min)	%A[b]	%B[c]
0	0.2	75	25
25	0.2	20	80
40	0.2	0	100
45	0.2	0	100
Post time (4 mins)	0.2	75	25

[a] High-performance liquid chromatography (HPLC) analysis was conducted using and Agilent 1100 HPLC System.

[b] Mobile phase component A consisted of 2-mM ammonium formate or acetate in deionized water

[c] Mobile phase component B consisted of methanol; acetonitrile was used for additional assay, if needed

Table 3-11. List of Target SVOC Analytes for LC/TOFMS Analysis[a]

Target SVOC Analytes[b]	CAS Number[c]	Molecular Weight grams/mole (g/mol)
Resorcinol	108-46-3	110.11
Phthalimide	85-41-6	147.13
1-Hydroxypyrene	5315-79-7	218.26
Cyclohexylamine	108-91-8	99.18
Dicyclohexylamine	101-83-7	181.32
N-cyclohexyl-N-methylcyclohexanamine	7560-83-0	195.35
2-Mercaptobenzothiazole	149-30-4	167.25
2-Hydroxybenzothiazole	934-34-9	151.19
Diisononyl phthalate	28553-12-0	418.62
Diisodecyl phthalate	26761-40-0	446.67

[a] Liquid chromatography/time-of-flight mass spectrometry (LC/TOFMS) was conducted using an Agilent 1100 HPLC equipped with an Eclipse Plus C18 HPLC column (2.1 mm × 50 mm, 3.5 µm) and an Agilent Model G1969A LC/MSD TOF System

[b] SVOC = semivolatile organic compound

[c] Unique numerical identifier assigned by the Chemical Abstracts Service (CAS)

3.6.7.5 LC/TOFMS Suspect Screening and Analysis of Non-target SVOCs

Suspect screening and non-targeted screening of tire crumb rubber sample extracts were performed using an Agilent 1100 HPLC equipped with an Eclipse Plus C18 HPLC column (2.1 mm × 50 mm, 3.5 µm) with an injection volume loop of 40 µL and interfaced with an Agilent Model G1969A LC/MSD TOF (Agilent Technologies, Santa Clara, CA, USA). The same solvent exchange procedure and chromatographic procedure used for target SVOC analysis was applied to all the extracts. A portion of the reconstituted sample extract was added to a propylene auto-sampler vial containing 2-mM ammonium acetate buffer to match the starting conditions (75% water:25% methanol) of the mobile phase gradient used. Each vial was capped and vortexed to ensure mixing of the organic sample with the aqueous buffer. The bottom of each vial was checked for air bubbles and if present, bubbles were removed by tapping on the vial. After making sure that there were no air bubbles, the samples were placed in the HPLC autosampler and analyzed. A 45-min gradient HPLC run was used with mobile phase components of methanol and 2-mM formate or acetate buffer at a flow rate of 300 µL/min. Electrospray ionization was used in the mass spectrometer source, which was maintained at 325 ºC.

Non-targeted analysis (NTA) and suspect screening do not use traditional calibration standards. However, a series of known calibration compounds in an original equipment manufacturer (OEM) solution can be used to mass calibrate the instrument daily before its use and to auto-tune the TOFMS instrument. Agilent ESI-L Low Concentration Tuning Mix (Agilent Part No. G1969-85000, Agilent Technologies, Santa Clara, CA, USA) was used to assure the mass accuracy of the instrument on a regular basis. In addition, solutions with a second set of known compounds (called reference compounds) were continually infused into the TOFMS for real-time mass correction. These reference compounds and their source solutions were:

- purine [exact mass = 120.043596]:
  5-mM purine in acetonitrile:water (Agilent Part No. 18720242, Agilent Technologies, Santa Clara, CA, USA),
- HP0921 hexakis (1H,1H,3H-tetrafluoropropoxy) phosphazene [exact mass = 921.002522]:
  2.5-mM HP0921 in acetonitrile:water (Agilent Part No. 18720241, Agilent Technologies, Santa Clara, CA, USA), and
- tetrahydroperfluorononanoic acid (THPNA) [exact mass = 391.0009]:
  1000 ng/µL THPNA (not Agilent reference solution)

Reference solutions were created for both the positive and negative analytical modes of the analysis using these reference compounds:

- Reference Solution for Positive Mode Dual Electrospray Ionization (ESI) Analysis
  - 500 mL of Acetonitrile:deionized water (90:10)
  - 1.5 mL of Agilent 5-mM purine solution
  - 750 µL Agilent 2.5-mM HP0921solution

- Reference Solution for Negative Mode Dual ESI Analysis
  - 1000 mL of Acetonitrile:deionized water (90:10)
  - 300 µL of Agilent 5-mM purine solution
  - 150 µL Agilent 2.5-mM HP0921solution
  - 100 µL of 1000 ng/µL solution of THPFNA

In addition, any known compound that was not expected to be present in the samples and had an exact mass could be added. Depending on the polarity of the instrument and the mobile phase modifiers used, different reference masses were seen. Refer to Table 3-12 for additional references masses and forms used in this analysis.

Table 3-12. Reference Masses for Real-time Mass Correction in TOFMS Analysis[a]

Species	Positive Ion m/z	Negative Ion m/z
CF_3 (trifluoro acetic acid [TFA] fragment)	N/A	68.995758
TFA anion	N/A	112.985587
purine	121.050873	119.036320
HP0921	922.009798	N/A
HP0921 (formate adduct)	N/A	966.000725
HP0921 (acetate adduct)	N/A	980.016375
HP0921 (TFA adduct)	N/A	1033.988109
THPFNA	N/A	391.0009

[a] TOFMS= Time-of-flight mass spectrometry; m/z = Mass-to-charge ratio; CF_3 = Trifluoromethyl; N/A = Not applicable; TFA = Trifluoro acetic acid; THPFNA = Tetrahydroperfluorononanoic acid

All method and matrix blanks, quality control samples, calibration standards, replicates, and unknown samples were subjected to the same sample preparation and analysis. The samples were analyzed in both positive and negative modes and subjected to a molecular feature extraction (MFE) algorithm to identify peaks for further exploration. Features identified for suspect screening purposes were compared to EPA's Distributed Structure-Searchable Toxicity (DSSTox) Database of approximately 750,000 chemicals (https://www.epa.gov/chemical-research/distributed-structure-searchable-toxicity-dsstox-database). Chemicals matching within 5 ppm of the suspect chemical according to accurate mass and scoring >80% were deemed as a provisional match. Features not matching were subjected to a non-targeted screening workflow where the features were prioritized based on occurrence and abundance into discrete data packets. Features were also compared with a personal compound database list (PCDL) that included previously reported SVOCs in the literature related to tire crumb.

3.6.8 Dynamic Chamber Emissions Testing

3.6.8.1 Tire Crumb Material Preparation for Emission Chamber Tests

Tire crumb rubber samples from tire recycling plants and synthetic turf fields were received in amber glass bottles with chain of custody records. The samples were then stored in the freezer at ≤ -15 °C until several hours before testing, at which time they were removed from the freezer and allowed to warm to room temperature before being placed in the testing chambers.

3.6.8.2 Selection of Test Chambers and Conditions

Constituents such as VOCs and SVOCs can be released to the environment from tire crumb rubber under different environmental conditions. Laboratory chamber dynamic emission tests were performed to characterize the emissions of VOCs and SVOCs from tire crumb rubber and tire crumb rubber infill under two different chamber conditions (i.e., 25 °C and 50% relative humidity [RH]; and 60 °C and approximately 7% RH) and defined air change rates. The selection of appropriate testing chambers and test conditions is an important part of the testing. For VOCs, the small (53-L) chamber tests were selected to be consistent with methods described in the ASTM Standard Guide D5116-10 (ASTM, 2010). A chamber air exchange rate of one air change per hour, an equilibration period of 24 h, and a 15-g sample size were selected both for consistency with the ASTM method and through initial testing to determine the best conditions for obtaining usable analysis results. Selecting appropriate chamber systems and conditions for measuring SVOC emissions is more challenging. SVOC adsorption to chamber walls limits the use of chambers with large relative surface areas (such as the 53-L chamber) to experiments requiring long equilibration durations (many days to weeks). Therefore, micro-chambers were selected, having volumes of 44 or 114 mL, minimizing chamber to sample surface area ratios. Chamber air exchange rates of 28 – 32 air changes per hour, an equilibration period of 24 h, and a 10-g sample size were selected through initial testing for determining the best conditions for obtaining usable analysis results in reasonable time periods.

3.6.8.3 Small Chamber Emission Tests

Small Chamber Emission Test Method for VOCs

VOC and formaldehyde source emission tests were conducted in 53-L electro-polished stainless-steel chambers in Model SCN4-52 temperature-controlled incubators (So-Low Environmental Equipment Co., Inc., Cincinnati, OH, USA; Figure 3-12A). An OPTO 22 Data Acquisition System (OPTO 22, Temecula, CA, USA) was used for continuous recording of the outputs of the mass flow controllers, temperature, and relative humidity (RH) probes in the chambers. Emissions of VOCs and formaldehyde were measured under two different chamber environmental conditions: 1 h^{-1} air change per hour (ACH), 25 °C, and 45% RH; and 1 h^{-1} ACH, 60 °C and 7% RH.

Chamber background samples were collected prior to the test material being loaded into the chambers. During tests, clean VOC-free air was supplied to the chambers. For each test, 15 g of tire crumb rubber material was placed in the center of the small chamber floor on an aluminum weighing pan (Figure 3-12B, C). After the test material had been in the chamber for 24 hours, air samples were collected at the chamber exhaust glass manifold using Carbopack™ X Fence Line Monitor (FLM) tubes (Sigma-Aldrich, Saint Louis, MO, USA) at 100 mL/min for 60 minutes and 2, 4-dinitrophenylhydrazine (DNPH) cartridges (Waters Corporation, Milford, MA, USA) at 400 mL/min for 90 minutes (Figure 3-12D). Field blank and duplicate samples were collected, and 12 duplicate tests were conducted. After sampling, Carbopack™ X samples were capped and placed individually into glass culture tubes in the refrigerator at ≤ 4 °C until analysis.

Tests with two tire crumb materials (one recycling plant sample and one synthetic turf field sample) were also conducted using these same small chamber environmental conditions and air sample collection procedures to determine VOC and formaldehyde emission profiles. Carbopack™ X and DNPH samples were collected at 1, 2, 4, 8, 24, and 48 hours after materials were placed inside the chamber.

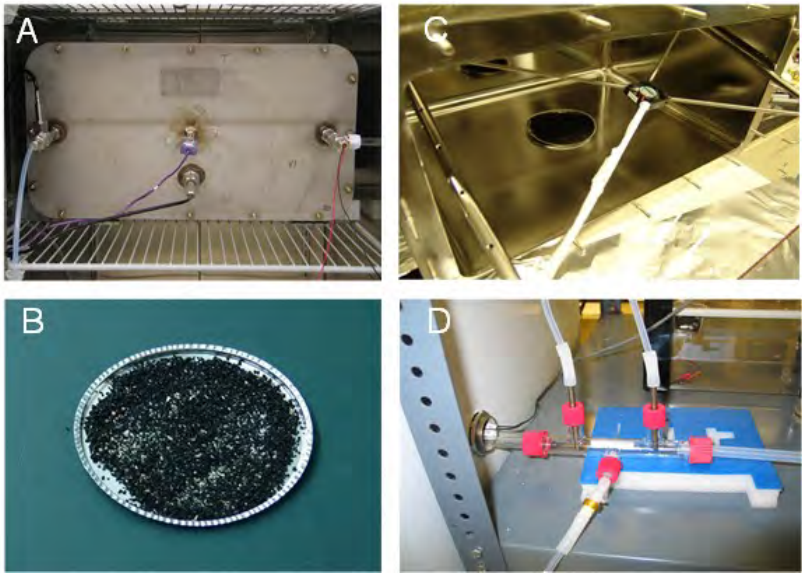

Figure 3-12. Small emission chamber set-up, including A) sealed 53-L chamber in incubator cabinet; B) 15 g tire crumb rubber infill sample prepared for testing; C) chamber interior with sample in place and mixing fan pulled out; D) external manifold for air sample collection.

Silicone wristbands are increasingly being used as personal exposure samplers. They operate by passively absorbing organic chemicals from a person's environment while they are worn. To understand how silicone wristbands might be used in future exposure measurement studies of synthetic field users, a separate set of wristband tests were conducted in the small chambers with four different tire crumb rubber materials (one recycling plant sample and three synthetic turf field samples) at 25 °C, 1 h^{-1} ACH, and 45% RH. For each test, 60 g of tire crumb material was used to cover a wristband in an aluminum foil tray with an internal diameter of 9 cm. The tray was then placed in the center of the chamber floor. Another two wristbands were suspended over the tray. SVOC air samples were collected on ORBO™ 1000 pre-cleaned small polyurethane foam (PUF) cartridges (Sigma-Aldrich, Saint Louis, MO, USA) after the chamber was sealed. Air sample collections began at 0, 48, and 112 hours, and the sampling durations for the three PUF sample collections were 48, 64, and 48 hours at 100 mL/min. Wristbands were moved out of the chamber to tightly sealed glass jars after the test and stored in the freezer until solvent extraction.

<u>HPLC/UV Analysis of Chamber Emission Samples for Formaldehyde</u>

Air samples collected on DNPH cartridges were extracted with 5 mL acetonitrile within 7 days after sampling and analyzed using an Agilent 1200 HPLC equipped with an Eclipse XDB-C18 column (4.6 m × 150 mm, 5µm) and a diode array detector (DAD; Agilent Technologies, Santa Clara, CA, USA). The HPLC was calibrated using an external standard method with formaldehyde-DNPH in the range of 0.03 to 15 µg/mL. Formaldehyde-DNPH detection in selected samples was confirmed by LC/TOFMS.

<u>TD/GC/TOFMS Analysis of Chamber Emission Samples for VOCs (Targeted and Non-Targeted Analysis)</u>

Carbopack™ X Fence Line Monitor (FLM) sorbent tube samples transferred to the VOC laboratory by the Chamber Emissions Testing staff were removed from the refrigerator (where they were stored at 6 ºC) and were allowed to come to room temperature prior to analysis. Samples were analyzed using a

Unity 2™ Ultra 50:50™ thermal desorption (TD) system (Markes International, Inc., Gold River, CA, USA) interfaced to an Agilent 7890B gas chromatograph equipped with an Rxi-ms column (60 m × 0.32 mm, 1 µm; Agilent Technologies, Santa Clara, CA, USA) and a Markes International BenchTOF™ Select MSD System (Markes International, Inc., Gold River, CA, USA). The instrument was tuned using the AutoOpt function and was calibrated using an internal standard method with concentrations of target compounds in the nominal range of 0 to 50 parts per billion by volume (ppbv) per compound. Internal standards were manually loaded onto all tubes analyzed, including calibration tubes, QC samples, and field samples. The actual mass loading (in ng/tube) depends on the molecular weight of the individual compound and the loaded volume of gaseous calibration standard. For example, mass loadings in the nominal range of 0 to 160 ng/tube benzene and 0 to 260 ng/tube benzothiazole were observed for the calibration curve. Calibration checks were run using a low-level standard between every 11 samples. The TD/GC/TOFMS instrument operating parameters are shown in Table 3-13.

MSD ChemStation Enhanced Data Analysis Software (Version E.02.02.1431, Agilent Technologies, Santa Clara, CA, USA) was used for peak identification/integration and combination of individual files into a database. The database was exported to Microsoft® Excel (Office 365, Microsoft Corporation, Redmond, WA, USA) for final data reduction. Quantitation was performed using quadratic curves generated from the relative response ratios and concentration ratios of internal standards and calibration standards. Inherent artifacts of target compounds found on Carbopack™ X sorbent (e.g., benzene) were addressed through the use of blank corrected calibration curves. VOC results were reported as ng/tube. The volume of chamber air pulled through the Carbopack™ X FLM sorbent tube was used to calculate the analyte concentration (ng/L).

Table 3-13. TD/GC/TOFMS Parameters for VOC Chamber Emission Sample Analysis[a]

System Component	Parameter	Value
Thermal Desorption System	Trap	TO-15/TO-17 air toxics focusing trap
Thermal Desorption System	Split Flows	Inlet split – none; Outlet split – 25:1
Gas Chromatograph	Column Flow	1.5 mL/min
Gas Chromatograph	Temperature Program	Initial: Set point 30 ºC, hold for 10 min Ramp 1: Rate 5 ºC/min to set point 130 ºC, hold 0 min Ramp 2: Rate 20 ºC/min to set point 200 ºC, hold 5.5 min Ramp 3: Rate 20 ºC/min to set point 220 ºC, hold 7.5 min
Mass Selective Detector	Mass Range	Mass range: 35-350 mass to charge ratio (m/z)
Mass Selective Detector	Data Rate	3 Hertz (Hz)
Mass Selective Detector	Transfer Line Temperature	250 ºC;
Mass Selective Detector	Ion Source Temperature	280 ºC
Mass Selective Detector	Voltage	Ionization Voltage = 70 electronvolt (eV); Filament voltage = 1.6 volt (V)
Mass Selective Detector	Filament Drops	10.40 to 11.67 min: 1.53 V 22.33 to 23.25 min: 1.53 V 38.10 to 38.49 min: 1.53 V

[a] Thermal desorption/liquid chromatography/time-of-flight mass spectrometry (TD/LC/TOFMS) was conducted using a Unity 2™ Ultra 50:50™ Thermal Desorption (TD) system interfaced to an Agilent 7890B gas chromatograph equipped with a Rxi-ms column (60 m × 0.32 mm, 1 µm) and Markes International BenchTOF™ Select Mass Selective Detector System. VOC = Volatile organic compound

3.6.8.4 Micro-Chamber Emissions Tests

Micro-Chamber Emission Test Method for SVOCs

Emissions testing for SVOCs was not performed using the same small chambers used for VOCs because the relatively large chamber wall surface area, and SVOC adsorption to those walls would result in prohibitively long times to reach steady-state conditions. To minimize chamber wall surface effects and to speed emissions testing, SVOC source emission tests were conducted using two micro-chamber systems – the Model µ-CTE™ and M-CTE250™ Micro-Chamber/Thermal Extractor™ (Markes International, Inc., Gold River, CA, USA). The Model M-CTE250™ system consists of four 114-mL micro chambers, and the Model µ-CTE™ system (Figure 3-13A) consists of six 44-mL micro chambers that allow up to six sample materials to be tested simultaneously at the same temperature and flow rate (Figure 3-13C). During tests, clean air flow from the same clean air system used in the small chamber was supplied to the micro chambers. The micro chambers were operated at a flow rate of 60 mL/min, resulting in an air exchange rate of 82 ACH at 25 °C or 72 ACH at 60 °C for the µ-CTE™ system and 32 ACH at 25 °C or 28 ACH at 60 °C for the M-CTE250™ system. Both systems have temperature and humidity control, which allowed the tests to be conducted at 45% RH at 25 °C or 7% RH at 60 °C. Temperature, RH, and air flow measurements were manually recorded. Prior to each test, the micro chambers were cleaned.

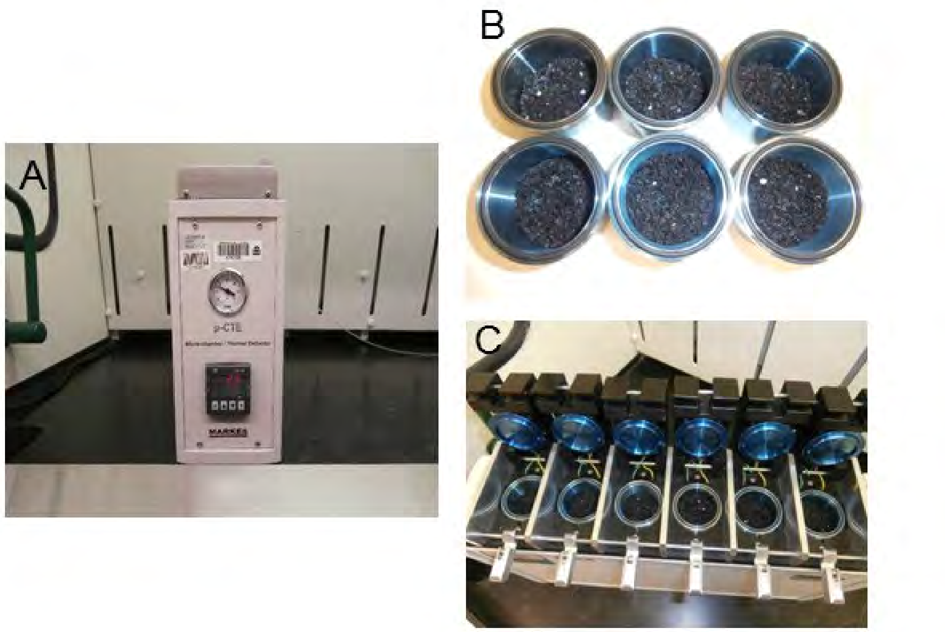

Figure 3-13. Micro chamber set-up, including A) µ-CTE™ system; B) 10 g tire crumb rubber infill samples in micro-chamber cups; C) samples placed in micro chamber for testing.

For each of the emission tests, 10 g of tire crumb rubber sample material was placed in a micro chamber (Figure 3-13B). After the test material had been in the chamber for 24 hours, one SVOC air sample was collected on a PUF cartridge at the exhaust port of each micro chamber at 60 mL/min for 180 minutes. Chamber background and field blank samples were collected. Twelve duplicate tire crumb rubber sample tests were also conducted. After sampling, PUF samples were capped, wrapped in clean aluminum foil in pre-labeled plastic bags, and stored in the refrigerator at ≤ 4°C until transfer to the analysis laboratory.

Tests with two tire crumb materials (one recycling plant sample and one synthetic turf field sample) were also conducted using the same micro chamber environmental conditions and air sample collection procedures to determine SVOC emission profiles. PUF samples were collected at 1.5, 5.5, 9, 24, and 48 hours.

GC/MS/MS Targeted Analysis of Chamber Emission Samples for SVOCs

Micro chamber emissions samples for SVOC analysis were collected on 22-mm × 7.6-cm PUF plugs. After collection, the glass sample tubes containing the PUF plugs were wrapped in foil and were placed into individual zip-top bags. The samples were stored in a freezer at approximately -20 º C until removed for extraction. For each sample, a 250-mL narrow-mouth glass collection bottle was labelled and fitted with a glass funnel. After the samples had warmed to room temperature, they were removed from the bag and foil and the PUF plug was transferred to an appropriately-labelled, clean 60-mL glass sample jar, using stainless steel forceps. The glass tube that contained the PUF plug was rinsed into the corresponding collection bottle with approximately 5 mL of 1:1 acetone:hexane. Each sample jar was filled with 50 mL of 1:1 acetone:hexane and sealed with a polytetrafluoroethylene (PTFE)-lined cap. The jars were placed in an ultrasonic cleaner with water level well below the level of the jar cap. The ultrasonic cleaner was then turned on for 15 minutes. Sample jars were removed from the cleaner and the extracts were transferred through funnels into the corresponding collection bottles. The funnels were rinsed with 1:1 acetone:hexane from a wash bottle after the extracts were added. The solvent addition, extraction and transfer was repeated two more times. The combined extracts in the collection bottles were then evaporated to 2–5 mL using a parallel evaporator (Buchi Multivapor model P-6, Flawil, Switzerland). The concentrated extracts were transferred to a 15-mL graduated glass tube, along with two 2-mL 1:1 acetone:hexane rinses of the collection bottle, prior to being concentrated to a final volume of 1 mL under nitrogen. The extracts were then transferred to autosampler vials (Agilent Technologies, model 5182-0716, Santa Clara, CA, USA) for analysis.

Emissions sample extracts were analyzed using an Agilent Model 7890 gas chromatograph equipped with a VF-5ms column (30 m × 0.25 mm, 0.25 µm) and a Model 7010 triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). The same parameters previously described in Table 3-8 were used for data acquisition. The instrument was standardized using High Sensitivity EI Autotune and was calibrated for target analytes in the range of 0.1 ng/mL to 500 ng/mL. Calibration checks were run using a mid-level standard between every 10 samples. Quantitation was performed using linear regression curves generated from the responses and nominal concentrations of calibration standard solutions. Data were processed using Agilent MassHunter Workstation Quantitative Analysis (Version B.07.01), Agilent Technologies, Santa Clara, CA, USA) and exported to Microsoft Excel (Office 365) for further data reduction.

GC/MS Non-Targeted Analysis of Chamber Emission Samples for SVOCs

A subset of the emissions sample extracts was subsequently submitted for non-targeted analysis using an Agilent Model 6890 gas chromatograph equipped with a VF-5Sil ms column (60 m × 0.25 mm, 0.25 µm) and Model 5973 mass selective detector (MSD; Agilent Technologies, Santa Clara, CA, USA). The instrument was standardized using EI Standard Spectrum Tune and was operated using the same parameters previously listed in Table 3-9. The mass spectral data were analyzed by deconvolution and spectral matching to the NIST (2011) Mass Spectral Database using Agilent MassHunter Workstation Quantitative Analysis (Version B.07.01, Agilent Technologies, Santa Clara, CA, USA) Unknowns Analysis.

LC/TOFMS Targeted Analysis of Chamber Emission Samples for SVOCs

A subset of the emissions samples generated for SVOC analyses was analyzed by LC/TOFMS to explore whether significant emissions of chemicals amenable to LC/MS analysis could be observed. All samples collected under the 60 °C emission test condition and a smaller number of the samples collected under the 25 °C emission test condition were analyzed by LC/TOFMS. The solvent exchange procedure and the analyses procedures described in section 3.6.7 for LC/TOFMS analysis of target SVOCs were also used for LC/TOFMS analysis of the SVOC emission sample extracts.

3.6.9 Bioaccessibility Testing

All *in vitro* bioaccessibility testing was conducted at CDC's National Institute of Occupational Safety and Health (NIOSH). Validated *in vitro* bioaccessibility methods did not exist for metals in tire crumb rubber samples when this study was conducted. Therefore, the methods used in this study were based on modifications of existing *in vitro* bioaccessibility methods for other solid materials, such as EPA Method 1340, "*In Vitro* Bioaccessibility Assay for Lead in Soil" (U.S. EPA, 2017c).

3.6.9.1 Preparation of Artificial Biofluids

In vitro bioaccessibility testing was conducted to assess bioaccessibility of 20 metals in three artificial biofluids (i.e., gastric fluid, saliva and sweat plus sebum). The artificial biofluids used in the *in vitro* accessibility testing were prepared based on previously published formulations, after removing ingredients that contained metals of interest. Artificial gastric fluid was prepared using an existing formulation by Stefaniak et al. (2010a), after removing copper (II) chloride dihydrate and cobalamine concentrate. Artificial sweat was prepared using an existing formulation by Harvey et al. (2010), after removing cadmium chloride anhydrous, copper (II) chloride dehydrate, iron sulfate heptahydrate, manganese (II) chloride, and lead, nickel and zinc reference solutions. Artificial saliva and sebum were prepared using previously published formulations by Simoneau and Rijk (2001) and Stefaniak et al. (2010b), respectively, without any modification.

For artificial gastric fluid, saliva and sweat, 5 L of each artificial biofluid was prepared, aliquoted into 500-mL bottles, and stored at -20 °C until usage. For artificial sebum, 500 mL was prepared and stored at 4 °C until usage.

3.6.9.2 Extraction of Tire Crumb Rubber Constituents in Artificial Biofluids

Eighty-two tire crumb rubber samples (27 individual recycling plant samples and 55 individual or composite synthetic turf field samples) were placed in the artificial biofluids for bioaccessibility testing. All experiments were performed at a typical body temperature of 37 °C. Extraction of tire crumb rubber constituents in artificial saliva and gastric fluid was conducted using a protocol modified after EPA Method 1340 (U.S. EPA, 2017b). A 2±0.005 g portion of each of the tire crumb rubber samples identified for bioaccessibility testing was weighed on a calibrated Mettler B303 balance (Mettler-Toledo, LLC, Columbus, OH, USA) and put in a 15-mL polypropylene conical centrifuge tube (BD Biosciences, San Jose, CA, USA). Artificial biofluids (8 mL at 37 °C) were dispensed into each tube and rotated (220±2 rpm, 25.4-mm (1-in) stroke) at 37 °C for one hour, using a New Brunswick Innova® 40 shaking incubator (Eppendorf, Hauppauge, NY, USA). The sample mixture was then centrifuged using a Sorvall™ Super T21 (ThermoFisher Scientific, Waltham, MA, USA) at 1500 x g relative centrifugal force (RCF) for 30 min, after which 5-6 mL of the artificial biofluid extract was decanted to a clean conical centrifuge tube, capped, and refrigerated at 4 °C until analyses for metals.

Tire crumb rubber samples were also extracted in artificial sweat and sebum with compositions that closely approximated human sweat. First, 0.5 mL of artificial sebum was used to coat each centrifuge tube, and the coated tube was allowed to dry for 1 hour. The tubes were then inverted and allowed to drip dry for an additional 30 minutes. The extraction of tire crumb rubber constituents in artificial sweat was conducted in the sebum-coated tubes following the same protocol used to extract the tire crumb rubber constituents in artificial saliva and gastric fluid.

3.6.9.3 Analytical Methods for Measuring Metals in Biofluids Extracts

Measurements of 20 metals (shown in Table 3-14) were carried out in the artificial biofluid extracts by Maxxam Laboratories (Novi, MI, USA) following established EPA methods.

Table 3-14. Methods for Measuring Metals in Biofluid Extract

Analyte	Method[a]
Aluminum	ICP/AES
Antimony	ICP/MS
Arsenic	ICP/MS
Barium	ICP/MS
Beryllium	ICP/MS
Cadmium	ICP/MS
Chromium	ICP/MS
Cobalt	ICP/MS
Copper	ICP/MS
Iron	ICP/AES
Lead	ICP/MS
Magnesium	ICP/AES
Manganese	ICP/MS
Mercury	Cold vapor atomic absorption
Molybdenum	ICP/MS
Nickel	ICP/MS
Selenium	ICP/MS
Strontium	ICP/MS
Tin	ICP/AES
Zinc	ICP/AES

[a] ICP/AES = inductively coupled plasma/atomic emission spectrometry;
ICP/MS = inductively coupled plasma/mass spectrometry

For metals analysis (with exception of mercury), artificial biofluid extracts were first subjected to acid digestion following the EPA Method 3010 (U.S. EPA, 1992). All samples were then analyzed using both inductively coupled plasma-atomic emission spectrometry (ICP/AES) following EPA Method 6010D (U.S. EPA, 2014a) and inductively coupled plasma-mass spectrometry (ICP/MS) following EPA Method 6020B (U.S. EPA, 2014b). For these analyses, 2.0 mL of the sample aliquot was combined with 1.5 mL of 15.6-M nitric acid and 2.5 mL of 12.1-M hydrochloric acid and heated for 30 min at 95 °C. After cooling to room temperature, the digestates were brought up to a final volume of 20 mL (1:10 dilution) and analyzed using both an Agilent 7900 ICP-MS (Agilent Technologies, Inc., Santa Clara, CA, USA) and a Dual-view Optima™ 5300DV ICP-OES (PerkinElmer Inc., Waltham, MA, USA).

For mercury analysis, artificial biofluid extracts were digested and analyzed using a cold vapor atomic absorption procedure following the EPA Method 7470 (U.S. EPA, 1994). A 2.0-mL portion of the sample aliquot was combined with 0.63 mL of 15.6-M nitric acid, 1.3 mL of sulfuric acid, and 3.75 mL of 5% potassium permanganate ($KMnO_4$), diluted to 20 mL (1:10 dilution) with deionized water, and heated for two hours at 95 °C. After cooling to room temperature, the digestates were brought up to a final volume of 30 mL and analyzed using a QuickTrace® M-7600 Cold Vapor Atomic Absorption (CVAA) Mercury Analyzer (Teledyne Leeman Labs, Hudson, NH, USA).

3.6.9.4 Calculation of *In vitro* Bioaccessibility

The amount of target analyte in the *in vitro* bioaccessibility extraction was calculated by multiplying the analyte concentration in extract with the volume of the biofluid extract and dividing by the weight of the tire crumb rubber sample used. The *in vitro* percent bioaccessibility value was determined by dividing the amount of analyte extracted in the *in vitro* extraction by the concentration of the corresponding analyte in the tire crumb rubber sample and multiplying by 100.

In vitro percent bioaccessibility was calculated for 19 of the 20 measured metals. Mercury was not measured in the tire crumb constituent analyses, and therefore, *in vitro* percent bioaccessibility of mercury could not be calculated.

In vitro bioaccessibility testing was not completed for SVOCs in the tire crumb rubber due to the large number of target SVOC analytes, insufficient knowledge of SVOC levels in the tire crumb rubber samples, lack of an existing validated method for *in vitro* bioaccessibility test of SVOCs in other solid materials, and insufficient time and capacity for method development and optimization.

3.6.10 Microbial Analysis

3.6.10.1 Isolation of Microbes and Microbial Genomic DNA

Upon receipt, the individual location samples for microbe analysis were held at 4 °C. All samples were processed the day they were received. From each sample, 5 g of tire crumb rubber was transferred to a sterile, 50-mL polypropylene conical tube. To collect microbes from the tire crumb rubber, 20 mL of a filter-sterilized solution composed of 0.005% weight-to-volume (w/v) sodium polyphosphate, 0.005% (v/v) Tween®-80, and 0.0005% (v/v) Antifoam Y-30 Emulsion (all manufactured by Sigma-Aldrich Corporation, St. Louis, MO, USA) was added to the tube. The tube was then vortexed at max speed for 2 min using a Vortex-Genie (Scientific Industries, Inc., Bohemia, NY, USA). The supernatant was then filtered through a 0.45-µm nitrocellulose membrane filter (Pall Corporation, Port Washington, NY, USA), and the filter apparatus was washed twice with 15 mL of sterile 1X Dulbecco's Phosphate Buffer Saline (Sigma-Aldrich Corporation, St. Louis, MO, USA). The membrane filters were then aseptically transferred to a bead tube from the PowerWater® DNA Isolation Kit (MoBio Laboratories, Inc., Carlsbad, CA, USA) and stored at -20 °C. The genomic deoxyribonucleic acid (DNA) of the microbes recovered from the tire crumb rubber was extracted using the PowerWater® DNA Isolation Kit, per the manufacturer's instructions. Genomic DNA was eluted in 100 µL of elution buffer, and the total DNA yield was determined immediately using the Qubit™ Double-stranded DNA (dsDNA) High-Sensitivity (HS) Assay Kit (ThermoFisher Scientific, Waltham, MA, USA), per the manufacturer's instructions. DNA extracts were stored at -80 °C. Positive and negative controls were implemented for elution from tire crumb rubber and extraction of genomic DNA (all quality control results are reported in Appendix E).

3.6.10.2 Quantification of Targeted Microbial Genes

The QX200™ AutoDG™ Droplet Digital™ PCR System (BioRad Laboratories, Inc., Hercules, CA, USA) was used to determine the quantities of 16S ribosomal ribonucleic acid (rRNA) genes (an indicator of total bacteria), the *Staphylococcus aureus* SA0140 protein gene, and the gene for methicillin resistance (*mecA*) in the tire crumb rubber samples. For each sample, duplicate 25-µL droplet digital PCR (ddPCR™) reactions were prepared that contained 1X ddPCR Supermix for Probes (No dUTP, BioRad Laboratories, Inc., Hercules, CA, USA), 5 µL of extracted sample, 900 nanomolar (nM) each of forward and reverse primer, and 250 nM probe. When necessary, dilutions of extracted DNA were made with 10-mM Tris-HCl at pH 8.5. The BACT2 primer-probe assay described by Suzuki et al. (2000) was used to quantify the 16S rRNA gene. The *S. aureus* and *mecA* genes were quantified using the primer-probe assays from Kelley et al. (2013). An internal amplification control (IAC) was implemented for each sample to monitor potential PCR inhibition. A synthetic custom minigene (Integrated DNA Technologies, Inc., Coralville, IA, USA) containing the sequence to the IAC described in EPA Method 1615 was obtained and detected with the primer and probe assay described in EPA Method 1615 (Fout et al., 2016). Droplets were made in the QX200™ AutoDG™ Droplet Digital™ PCR, which was operated at 95 °C for 5 min, followed by 50 cycles of 95 °C for 30 sec and 60 °C (55 °C for *mecA*) for 1 min, and a final incubation at 98 °C for 10 min. PCR amplification was determined with the QX200™ Droplet Reader. An IAC was implemented for each sample to monitor potential PCR inhibition. To determine gene concentrations in each ddPCR™ reaction, thresholds were set manually at the amplitude mean + 10 times the standard deviation (SD) of the droplets in the negative control reactions. Quantities of the microbial genes per gram were determined after accounting for 1/20th of the genomic DNA extract used in the ddPCR™ reaction and considering that the total volume of the genomic DNA extract was from 5 g of tire crumb rubber. Results were reported as targeted molecules per gram of tire crumb rubber. Non-parametric t-test and one-way analysis of variance (ANOVA) were performed in SigmaPlot™ (Version 13.0, Systat Software, Inc., San Jose, CA, USA).

3.6.10.3 Non-targeted Microbial Gene Analysis

Variable regions 1, 2 and 3 of the 16S rRNA gene were amplified using the 27F and 534 primers described by Bradley et al. (2016) and barcoded with dual indices outlined by Kozich et al. (2013). PCR reactions were carried out in triplicate with the Roche FastStart™ High Fidelity PCR System (Sigma-Aldrich Corporation, St. Louis, MO, USA). The 50-µL reactions were comprised of 5 µL of 10X Reaction Buffer, 1 µL of dimethyl sulfoxide (DMSO), 1 µL of 10-mM deoxyribonucleotide triphosphate (dNTPs), 2 µL each of 10-µM forward and reverse primers, 0.5 µL of Enzyme Blend, and 1 ng total DNA. The PCR was operated at 95 °C for 2 min, followed by 25 cycles of 95 °C for 30 sec, 55 °C for 30 sec, and 72 °C for 1 min, and final extension at 72 °C for 10 min. The replicate reactions were pooled, and amplicons were purified and normalized using the SequalPrep™ Normalization Plate Kit (ThermoFisher Scientific, Waltham, MA, USA) per the manufacturer's instructions and exercising the option of using two wells per sample. Samples were then pooled by volume and the concentration of libraries was assessed using KAPA Library Quantification Kit (Kapa Biosystems, Inc., Wilmington, MA, USA) and the Agilent High Sensitivity DNA Kit (Agilent Technologies, Inc., Santa Clara, CA, USA). For amplicon sequencing, the library was diluted to 5.6 picomolar (pM) and mixed with PhiX Control v3 (Illumina Inc., San Diego, CA, USA). Sequencing was carried out with the MiSeq system (Illumina, Inc., San Diego, CA, USA) using the 600-cycle MiSeq Reagent Kit V3 (Illumina Inc., San Diego, CA, USA) as prescribed by the manufacturer. Quality controls for PCR reactions were run with every 30 tire crumb rubber samples and were subsequently sequenced to determine sequencing. Positive controls were a 10-member microbiome, containing a mixture of equal concentrations of genomic DNA of *Streptococcus pneumoniae, Staphylococcus aureus, Porphyromonas gingivalis, Neisseria* *meningitidis, Listeria monocytogenes, Lactobacillus gasseri, Deinococcus radiodurans, Acinetobacter baumannii, Bacillus cereus, and Rhodobacter sphaeroides* (American Type Culture Collection, Manassas, VA, USA). Negative controls contained a volume of 10-mM Tris-HCl at pH 8.5, the same solution used to dilute genomic DNA for ddPCR analysis. The sequence reads generated by the MiSeq system were processed using mothur (Version 1.39.5, Schloss et al., 2009). Quality processing of the reads included filtering to accept those with a Phred quality score of Q30, and maximum lengths of 544 nucleotides, while excluding those with any ambiguous base calls and more than eight homopolymers. Chimeric sequences were detected and removed with the VSEARCH algorithm of the USEARCH software (Edgar, 2010). Reads were classified using the Ribosomal Database Project Classifier and training set 16, using a minimum bootstrap of 80% (Wang et al., 2007).

3.7 Data Processing and Data Analysis for Select Data

This section describes the data processing and data analysis procedures undertaken for the particle size fraction data, ICP/MS and XRF tire crumb metals data, SVOC extraction data, and the VOC and SVOC emissions data. Data analyses performed for scanning electron microscopy results (sections 3.6.4 and 4.5.4), bioaccessibility measurements (sections 3.6.9 and 4.13), and microbial measurements (3.6.10 and 4.14) are described in their respective method and/or results sections.

3.7.1 Data Processing

Following secondary data review by an independent expert, the particle size fraction data, ICP/MS and XRF tire crumb metals data, SVOC extraction data, and the VOC and SVOC emissions data sets were submitted to the project's data manager. The data manager uploaded data sets using SAS/STAT® 13.1 (SAS Institute Inc., Cary, NC, USA) and performed a series of organizational, review, cleaning, and output steps. Following initial intake and organization, the data manger provided data reports to the analyst and project manager to review for potential data issues or labeling problems and to determine whether any additional cleaning or organization was required. Following resolution, final draft data files were created for further data processing operations. The analysts and data manager then consulted with the project manager to interpret the quality control results for each analysis (shown in Appendix E) and make decisions on required adjustments (if any) and calculation requirements to bring measurement data into the correct final result. Analytical data file processing was undertaken for several of the analyses in this study:

- For ICP/MS metals analysis data files, the digestion and analytical files were combined to generate final amounts of metals measured per kilogram of tire crumb rubber. Samples had been dried prior to analysis, so no moisture content adjustment was performed. Results were adjusted by subtracting the method blank values from the samples measurement results on a batch-specific basis.
- For SVOC extraction with GC/MS/MS analysis, the measurement results were calculated amounts of SVOC analyte per kilogram of crumb rubber. Concentrations were adjusted for tire crumb rubber moisture content and adjusted further by subtracting the average method blank values from the sample measurement results. Due to apparent differences in response across batches of sample analyses, batch-specific recovery corrections were performed by multiplying the measurement result by the average reagent spike result across all batches and dividing that batch's reagent spike result.
- For LC/TOFMS analysis of SVOCs extracted from tire crumb rubber, the non-quantitative results were reported as chromatographic area counts. Results were adjusted by subtracting the average method blank area count values from the sample measurement results.

- For GC/TOFMS analysis of VOCs in chamber emission samples, the measurement results were calculated as emission factors by incorporation of chamber ventilation conditions, sampling rates and times, and amounts of tire crumb rubber placed in the chamber. Concentrations were adjusted for tire crumb rubber moisture content. Results were further adjusted by subtracting the average chamber background measurement result for each chamber experiment batch from the sample measurement result for samples in that chamber experiment batch. Each chamber experiment batch was conducted at either 25 °C or 60 °C, so the chamber background adjustments were effectively on a temperature-specific basis.
- For GC/MS/MS analysis of SVOCs chamber emission samples, the measurement results were calculated as emission factors by incorporation of chamber ventilation conditions, sampling rates and times, and amounts of tire crumb rubber placed in the chamber. Concentrations were adjusted for tire crumb rubber moisture content. Results were further adjusted by subtracting the average chamber background measurement result for each chamber experiment batch from the sample measurement results for samples in that chamber experiment batch. Each chamber experiment batch was at either 25 °C or 60 °C, so the chamber background adjustments were effectively on a temperature-specific basis.
- For HPLC/UV analysis of formaldehyde in chamber emission samples, the measurement results were calculated as emission factors by incorporation of chamber ventilation conditions, sampling rates and times, and amounts of tire crumb rubber placed in the chamber. Concentrations were adjusted for tire crumb rubber moisture content. Results were adjusted by subtracting the average chamber background measurement across all batches, separately for 25 °C and 60 °C experiments.
- For LC/TOFMS analysis of SVOCs in chamber emission samples, the non-quantitative results were reported as chromatographic area counts. Results were adjusted by subtracting the average chamber background area count result for each chamber experiment batch from the sample measurement area count for samples in that chamber experiment batch. Each chamber experiment batch was conducted at either 25 °C or 60 °C, so the chamber background adjustments were effectively on a temperature-specific basis.

The final processed measurement data were then placed into data analysis files. Separate data analysis files were prepared for recycling plants, synthetic turf field composite samples, and synthetic turf field individual location samples. A file was also created with the various types of duplicate measurement and replicate analysis measurement data. Some chemical measurement results did not meet quality control requirements and were flagged as “not acceptable”. These data were retained in the processed data files, but not included in the final data analysis files. Finally, other types of information needed for data analysis were added to the final data analysis files (e.g., recycling plant and synthetic turf field information, chamber experiment temperatures, chemical names and reporting orders, and analysis grouping variables).

3.7.2 Data Analysis

Chemical concentration, emission, and particle size measurement values and their summary statistics were presented in tables generated using SAS/STAT® 13.1 (SAS Institute Inc., Cary, NC, USA; SAS Institute Inc., 2013a) and in graphics, with data reported at two significant figures. Boxplots, scatterplots and bar charts were prepared in the R package *ggplot2* (Wickham, 2009) scatterplots, while modeled curves and bar charts were prepared in the SAS/GRAPH® 9.3 procedure SGPLOT (SAS Institute Inc., 2016).

For chemical concentration value, emission factor, and particle size tables, tests for equality of group means were performed in log-scale by 1-way ANOVA models fitted in the SAS MIXED procedure (SAS/STAT® 13.1). The logarithmic transformations for these tests of group means were based on the Shapiro-Wilk test for normality, which showed for a majority of the analytes the hypothesis of a normal distribution was not rejected following log transformation. Results of Shapiro-Wilk testing for untransformed and transformed data are shown in Appendix G. A conservative approach was taken to suppress reporting p-values when any chemical-specific or particle size data values represented in a table was zero or negative, since log-transformation could not be performed, and the result was a less than complete data set.

Tables for selected (primary) chemicals are given in the report body (Volume 1); full tables (with primary and secondary analytes) are given in Appendices I through Q (Volume 2). Chemical concentration and emission factor tables present and summarize results for a combination of sample sources (e.g., recycling plant and synthetic turf field samples) and, when applicable (e.g. for emission factors), also present temperature data. Summary statistics tables cover all chemicals and give the number of samples, percent of samples where the chemical was detected above the quantifiable limit, mean and standard deviation of the sample values, percent relative standard deviation (i.e., coefficient of variation), and selected percentiles. Other concentration and emission factor tables are restricted to chemicals with at least 60 percent detection above the quantifiable limit; these tables compare group means (e.g., recycling plants versus synthetic turf fields; indoor versus outdoor synthetic fields; synthetic fields in three installation age categories; and synthetic fields across four census regions). Additional analyses explore variance components, such as within- and between-field variations (estimated by random effects models fitted in the SAS MIXED procedure, with group as the random effect), synthetic turf field composite and individual sample values, recycling plant individual sample values, and duplicate/replicate data. Other tables present and summarize recycling plant and synthetic turf field particle size distributions and differences among fields with different characteristics. All laboratory-reported values were used in data analyses, even when below the quantifiable limit (in-lieu of using substitution or other censored data approaches). Some results appear as negative values due to subtraction of blank or background measurements; these negative values were retained in tables, figures, and calculations and were not arbitrarily set to zero.

Boxplots and scatterplots present chemical-specific exposure factor or concentration sample values and summary statistics by selected categorical variables, including synthetic turf field and recycling plant sites, and for synthetic turf fields, installation year groups, indoor/outdoor status, and census regions. An example boxplot annotated with descriptive statistics and individual sample values is given in Figure 3-14.

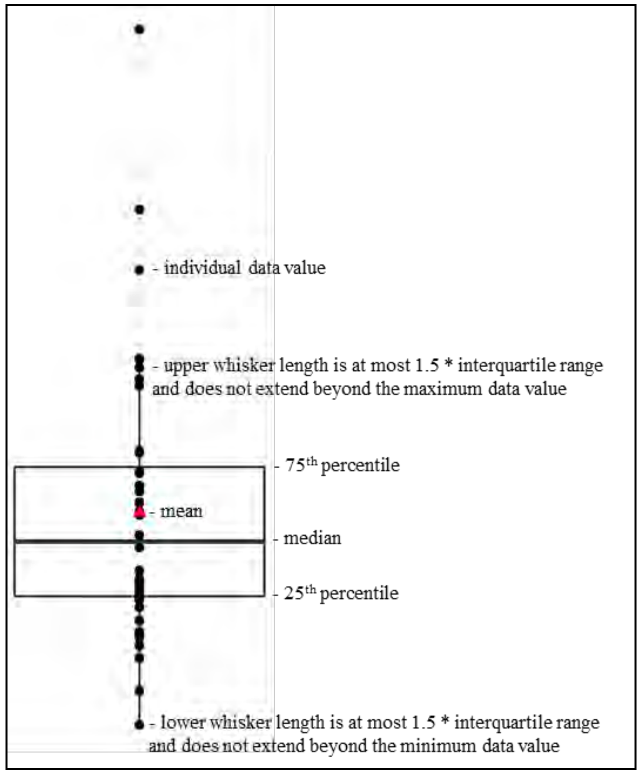

Figure 3-14. Example boxplot annotated with descriptive statistics and sample values.

3.7.3 SVOC Decay Time Half-Live Analysis

Outdoor synthetic turf field composite mean and recycling plant mean extractable SVOC concentrations were analyzed using generalized linear models with the categorical fixed effect of field/recycling plant installation year. These composite concentration models were fitted using the SAS GLIMMIX procedure (SAS Institute Inc., 2013b), where the exponential distribution was specified for the composite concentrations with (default) log link function. Chemical substance half-life estimates (years since field installation) were calculated based on model-predicted composite concentrations using recycling plant model predictions as initial values for the exponential decay constants; recycling plant year was approximated as mid-2016 (Stewart, 1991). Chemical substance half-life estimates were also calculated omitting recycling plants using model predictions for fields installed in 2016 as initial values for the exponential decay constants.

3.7.4 Field Characteristics Modeling Analysis

Fifteen chemical analyte concentrations and/or emission factors for composite infill samples collected from synthetic turf fields were selected for analysis using a linear model with categorical fixed effects of age group, indoor vs. outdoor field, and census region. These 15 concentration or emission factor models were fitted using the SAS MIXED procedure in backward elimination, starting with the full factorial model and stopping with the final reduced model for each of the chemical substances considered. Model selection was based on main effect and interaction term p-values using α=0.05, the Akaike information criterion (AIC) statistic, and model residuals. Model residuals were assessed graphically in SAS MIXED and tested for normality using the Shapiro-Wilk statistic in the SAS UNIVARIATE procedure (SAS/STAT® 13.1). Models for log-transformed composite concentrations were fitted as indicated by the residuals analysis.

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4.0 Tire Crumb Rubber Characterization Results

4.1 Overview

The tire crumb rubber characterization results are reported in this section for specific research areas and research activities as summarized in Table 4-1.

Table 4-1. Research Area and Research Activity Results Reported in This Section

Research Area	Research Activities
Recycling Plant and Synthetic Turf Field Recruitment and Sampling	Recruiting and collecting samples at multiple tire recycling facilities producing tire crumb rubber and multiple synthetic turf fields with tire crumb rubber infill across the United States
Synthetic Turf Field Operations and Maintenance	Collecting information from synthetic turf field owners/managers to better understand field operations, types and numbers of field users, field maintenance practices, and the use of chemical or other product treatments on the fields
Tire Crumb Rubber Chemical, Physical, and Microbiological Characterization	Preparing the samples collected from tire recycling plants and synthetic turf fields for several types of characterizations and analyses Measuring particle size ranges and other particle characteristics of tire crumb rubber from tire recycling plants and tire crumb rubber infill from synthetic turf fields across the United States, with further exploration of particle size and morphology using scanning electron microscopy Completing quantitative characterization of the inorganic and organic chemical substances found in the sampled tire crumb rubber from tire recycling plants and tire crumb rubber infill from synthetic turf fields Providing insight on differences between chemical substances associated with ‘fresh’ tire crumb rubber produced at recycling plants and what is found in tire crumb rubber infill on synthetic turf fields Examining emissions of organic chemicals from tire crumb rubber material at two temperatures for improved understanding of the potential for inhalation exposures Assessing variability of chemicals associated with tire crumb rubber within and between recycling plants, as well as within and between fields Examining the range of chemical concentrations found in tire crumb rubber infill from fields across the United States and some of the important characteristics associated with those differences across fields, including indoor vs. outdoor fields, fields with a wide range of installation dates, and fields in different U.S. regions Using suspect screening and non-targeted analysis approaches to elucidate the potentially larger range of chemicals for which additional information may be needed to better understand exposures and risks Measuring the bioaccessibility of metals from tire crumb rubber as an important characteristic for improving understanding of potential exposure Performing targeted and non-targeted microbial assessments to elucidate microbiological populations associated with tire crumb rubber infill at synthetic turf fields and characteristics associated with differences across a range of fields in the United States

4.2 Recycling Plant and Synthetic Turf Field Recruitment

4.2.1 Recycling Plant Selection and Recruitment

CDC/ATSDR and EPA contacted seven companies operating tire recycling plants that produce tire crumb rubber for synthetic turf infill. CDC/ATSDR and EPA reached agreements with six companies to collect samples at nine recycling plants operated by those companies across the United States. Six recycling plants used the ambient process, and three used the cryogenic process (see Appendix A for more information on these processes). The nine recycling plants were located across all four U.S. census regions.

4.2.2 Synthetic Turf Field Selection and Recruitment

Between August and November 2016, CDC/ATSDR researchers contacted a total of 306 community field owners (Table 4-2). The majority of those owners did not respond to the recruitment attempts, some owners declined participation for the reasons discussed in section 3.2.2 (i.e., liability, confidentiality or timing), and some fields were not eligible to participate in the study. The researchers obtained participation agreements to sample at 21 community fields with synthetic turf. Researchers also collaborated with the U.S. Army Public Health Center (APHC) to identify synthetic turf fields at military installations across the U.S. This recruitment effort resulted in the inclusion of 19 additional U.S. Army fields for sampling, bringing the recruited fields to 40 total (Table 4-2). Characteristics of the recruited fields are enumerated in Tables 4-3 through 4-5.

Table 4-2. Synthetic Turf Field Recruitment Efforts, by U.S. Census Region

Region	Number of Community Fields Contacted[a]	Number of Community Fields Ineligible	Number of Community Fields Declined[b]	Number of Community Fields Recruited	Number of U.S. Army Fields Recruited
Northeast	118	22	20	4	5
Midwest	96	10	9	8	0
South	40	11	13	5	8
West	52	8	9	4	6
Total	**306**	**51**	**51**	**21**	**19**

[a] Facilities with more than one field were only counted as n=1.

[b] Facilities that did not return phone calls or other attempts (i.e., email) at recruiting are not included in the number of fields declining; the majority of community fields contacted failed to respond to recruitment attempts.

Table 4-3. Synthetic Turf Fields Recruited, by Field Type (Outdoor and Indoor) and U.S. Census Region

Region	Number of Outdoor Fields	Number of Indoor Fields	Total Number of Fields
Northeast	5	4	9
Midwest	2	6	8
South	11	2	13
West	7	3	10
Total	**25**	**15**	**40**

Table 4-4. Synthetic Turf Fields Recruited, by Installation Year Group and U.S. Census Region

Region	Number of Fields Installed 2004 - 2008	Number of Fields Installed 2009 - 2012	Number of Fields Installed 2013 - 2016
Northeast	3	5	1
Midwest	2	5	1
South	2	5	6
West	4	3	3
Total	**11**	**18**	**11**

Table 4-5. Synthetic Turf Fields Recruited, by Field Type (Outdoor and Indoor) and Installation Year Group

Field Installation Year	Number of Outdoor Fields	Number of Indoor Fields	Total Number of Fields
2004 - 2008	5	6	11
2009 - 2012	10	8	18
2013 - 2016	10	1	11
Total	**25**	**15**	**40**

4.3 Synthetic Field Use and Maintenance Questionnaires

The questionnaire responses received from owners and/or managers of the recruited synthetic turf fields are summarized in this section for several topics, including tire crumb refreshment/replacement, field maintenance, treatment of fields with chemical products, and field uses and users. Most of the interviewed facility personnel (87.5%) reported they were managers of the synthetic turf fields (Table 4-6).

Table 4-6. Relationship of Questionnaire Interviewee to Facility

Position at Synthetic Turf Field/Facility	Number of Interviewees	Percent of Interviewees
Manager	35	87.5%
Owner	3	7.5%
Other	2	5.0%
Total	**40**	**100%**

Tire crumb maintenance (i.e., replacing or refreshing the tire crumb rubber infill) varied among the synthetic turf fields. Replacing all the tire crumb rubber was not commonly reported; only one indoor field (6.7%) and one outdoor field (4.2%) had tire crumb rubber infill completely replaced. Refreshing or adding tire crumb rubber was more common, with 60% of indoor fields and 48.5% of outdoor fields having had the tire crumb infill refreshed, but the majority of outdoor fields never had tire crumb rubber refreshed or replaced (Table 4-7). The frequency in which the tire crumb rubber was refreshed or replaced at these fields varied from every six months to rarely (Table 4-8).

Table 4-7. Tire Crumb Rubber Maintenance (Refreshment by Partial Addition or Replacement) at Recruited Synthetic Turf Fields[a]

Tire Crumb Maintenance	Number of Indoor Fields	Percent of Indoor Fields	Number of Outdoor Fields	Percent of Outdoor Fields
Refresh Tire Crumb	9	60%	11	45.8%
Replace Tire Crumb	1	6.67%	1	4.2%
Did Not Refresh or Replace Tire Crumb	5	33.3%	12	50.0%

[a] Missing responses from one outdoor field; Indoor fields (n=15) and outdoor fields (n=24).

Table 4-8. Frequency of Tire Crumb Rubber Maintenance at Recruited Synthetic Turf Field(s) Having Experienced Tire Crumb Refresh or Replacement[a]

Frequency of Tire Crumb Maintenance	Number of Indoor Fields with Tire Crumb Refreshed	Number of Indoor Fields with Tire Crumb Replaced	Number of Outdoor Fields with Tire Crumb Refreshed	Outdoor Fields with Tire Crumb Replaced
Every 6 months	2	0	2	0
Yearly	1	0	3	0
Every 2-3 years	2	0	0	0
Every 3-5 years	0	0	1	0
Every 5-7 years	1	0	0	0
Never/Rarely	3	1	2	1
Don’t know	0	0	2	0
Missing	0	0	1	0

[a] Includes only those indoor fields (n=10) and outdoor fields (n=12) for which tire crumb rubber replacement or refreshment was performed.

Field owners or managers were asked whether their fields had ever been treated with biocides, herbicides, insecticides, fungicides, or other agents. More indoor fields than outdoor fields were reported to have been treated (50% to 16.7% respectively; Table 4-9); however, one response was missing from each type of field, indoor and outdoor. No insecticide or herbicide treatments were reported at any field. Other agents were reported to have been used at two of the indoor fields and two outdoor fields; an unknown biocide was also reported to have been used at two indoor fields (Table 4-10). Common chemicals reported to be used in field treatment include PureGreen24 disinfectant fungicide (Pure Green, LLC, Nashville, TN, USA), Simple Green® (Sunshine Makers, Inc., Huntington Beach, CA), hydrogen peroxide, Waxie 710 multi-purpose disinfectant cleaner (WAXIE Sanitary Supply, San Diego, CA, USA), and fabric softener (Table 4-10).

Table 4-9. Synthetic Turf Field Treatment with Cleaners, Biocides, Herbicides, Insecticides, Fungicides, or Other Agents[a,b]

Field Treatment	Number of Indoor Fields	Percent of Indoor Fields	Number of Outdoor Fields	Percent of Outdoor Fields
Yes	7	50.0%	4	16.7%
No	5	35.7%	19	79.2%
Don't Know	1	7.1%	1	4.2%
Refused	1	7.1%	0	0%
Total	**14**	**100%**	**24**	**100%**

[a] Missing responses from one indoor and one outdoor field; indoor field responses (n=14) and outdoor field responses (n=24); N/A = Not applicable.

[b] No herbicide or insecticide treatments were reported at any field.

Table 4-10. Products Used to Treat Synthetic Turf Fields and Frequency of Treatment[a]

Field Type	Product Used to Treat Field	Frequency of Treatment
Indoor	PureGreen24 disinfectant fungicide	2 times a month
Indoor	Disinfectant/sterilant made by Pioneer	Yearly
Indoor	Hydrogen peroxide, fabric softener	2 times a year
Indoor	Fabric softener	Not reported
Indoor	Waxie 710 multipurpose disinfectant cleaner	1 time a month
Indoor	Unknown Biocide	2 times a month
Indoor	Unknown Biocide	Not reported
Outdoor	Simple Green® and water	4 times a year
Outdoor	Simple Green® and water	4 times a year
Outdoor	Fabric softener and a disinfectant	Not reported
Outdoor	Fabric softener	Yearly

[a] Includes only those fields for which treatment with cleaners, biocides, herbicides, insecticides, fungicides, or other agents was reported.

The most commonly reported field maintenance activities were brushing and leveling for both indoor and outdoor fields (Table 4-11). Magnet sweep (32%), aerating fields (28%), and other field maintenance activities were more commonly performed at outdoor fields than indoor fields; the frequency at which this field maintenance was conducted is shown in Table 4-12. For field maintenance procedures, a common response included in the other category was sanitization with ultraviolet (UV) light.

Table 4-11. Synthetic Turf Field Maintenance Activities[a]

Maintenance Activity	Number of Indoor Fields	Percent of Indoor Fields	Number of Outdoor Fields	Percent of Outdoor Fields
Brushing	9	60%	14	56%
Leveling	6	40%	13	52%
Deep Cleaning	5	33.3%	5	20%
Magnet Sweep	4	27%	8	32%
Aerating	2	13%	7	28%
Other	2	13%	5	20%

[a] Indoor fields (n=15); Outdoor fields (n=25).

Table 4-12. Frequency of Synthetic Turf Field Maintenance Activities[a]

Field Maintenance	Number of Fields Performing Maintenance Weekly or Less	Number of Fields Performing Maintenance Monthly	Number of Fields Performing Maintenance Yearly	Number of Fields Missing Response Regarding Frequency
Indoor Fields – Brushing	1	3	4	1
Outdoor Fields – Brushing	3	6	4	1
Indoor Fields – Leveling	1	1	3	1
Outdoor Fields – Leveling	4	5	4	0
Indoor Fields – Deep Cleaning	0	2	3	0
Outdoor Fields – Deep Cleaning	0	1	4	0
Indoor Fields – Magnet Sweep	0	2	2	0
Outdoor Fields – Magnet Sweep	0	6	2	0
Indoor Fields – Aerating	0	0	2	0
Outdoor Fields – Aerating	0	4	3	0
Indoor Fields – Other	0	1	1	0
Outdoor Fields – Other	0	4	1	0

Over half of the synthetic turf fields were reported as not open to the public (52.5%), with a majority of use limited to organizational or membership use (67.5%; Tables 4-13 and 4-14). Additionally, only 32.5% of both indoor and outdoor fields were reported to offer open or free-play (Table 4-15), with outdoor fields more likely to have open or free-play (48%) than indoor fields (6.7%).

Table 4-13. Synthetic Turf Fields Open to the Public

Field Open to Public	Number of Fields	Percent of Fields
Yes	17	42.5%
No	21	52.5%
Refused	2	5.0%
Total	**40**	**100%**

Table 4-14. Synthetic Turf Field Use Limited to Organization or Membership

Field Use Limited to Organization/Membership	Number of Fields	Percent of Fields
Yes	27	67.5%
No	11	27.5%
Refused	2	5.0%
Total	**40**	**100%**

Table 4-15. Open or Free-Play at the Facility

Open or Free-Play Offered	Number of Indoor Fields	Percent of Indoor Fields	Number of Outdoor Fields	Percent of Outdoor Fields	Total Number of Fields	Percent of Total Fields
Yes	1	6.7%	12	48.0%	13	32.5%
No	13	86.7%	12	48.0%	25	62.5%
Refused	1	6.7%	1	4.0%	2	5.0%
Total	**15**	**100%**	**25**	**100%**	**40**	**100%**

The synthetic turf fields were most commonly reported to be open an average 7 days per week for all seasons (Table 4-16). The average number of hours per day the fields were used per season varied (Table 4-17). These two survey questions were not answered for all fields.

Table 4-16. Days per Week Synthetic Turf Fields Open During Each Season

Days per Week Field Open	Number of Fields in Fall	Number of Fields in Winter	Number of Fields in Spring	Number of Fields in Summer
0	0	2	0	1
3	1	1	2	3
5	4	4	5	5
6	3	1	2	2
7	30	29	29	27
Total	**38**	**37**	**38**	**38**

Table 4-17. Average Hours per Day Synthetic Turf Fields Used per Season

Hours per Day Field Used	Number of Fields in Fall	Number of Fields in Winter	Number of Fields in Spring	Number of Fields in Summer
0	0	3	0	1
2	0	1	0	0
3	2	0	2	4
4	1	1	2	2
5	5	3	5	3
6	1	2	3	4
7	3	2	1	1
8	7	6	6	3
9	1	1	1	0
10	3	4	3	3
11	1	1	1	3
12	3	5	1	1
14	6	4	8	7
15	2	2	2	2
16	0	0	0	1
20	1	0	1	1
Total	**36**	**35**	**36**	**36**

The highest average number of daily field users for indoor fields occurs in winter, while spring and summer have the highest averages for outdoor fields sampled (Table 4-18). The maximum number of daily users for indoors fields was 300 field users less than the outdoor fields – 900 and 1200 people, respectively. For almost all seasons, the most commonly reported frequency of people per day was the under 200 people category for both the indoor and outdoor fields (Table 4-19).

Table 4-18. Number of People per Day Using Synthetic Turf Fields per Season

Statistic	Indoor Fields - Fall	Indoor Fields - Spring	Indoor Fields - Summer	Indoor Fields - Winter	Outdoor Fields - Fall	Outdoor Fields - Spring	Outdoor Fields - Summer	Outdoor Fields - Winter
Average	223	191	149	284	303	305	305	252
Minimum	25	25	0	0	20	27.5	27.5	0
Median	135	120	110	200	175	200	200	160
Maximum	700	900	500	900	1200	1200	1200	1000

Table 4-19. Frequencies of Average Number of People per Day Using Synthetic Turf Fields per Season

Daily Field Users	Indoor Fields - Fall	Indoor Fields - Spring	Indoor Fields - Summer	Indoor Fields - Winter	Outdoor Fields - Fall	Outdoor Fields - Spring	Outdoor Fields - Summer	Outdoor Fields - Winter
< 200	8	10	9	5	11	10	10	11
200 – 399	2	1	2	5	5	6	6	5
400 – 599	0	0	1	0	2	2	2	2
600 – 799	2	0	0	1	0	0	1	1
800 – 999	0	1	0	1	1	1	0	0
1000+	0	0	0	0	2	2	2	2

The most commonly reported types of sports or other activities played on synthetic turf fields include soccer (80%), physical training (67.5%), and football (55%). Other sports reported but not listed on the questionnaire include lacrosse, track and field, and flag football (Table 4-20). Furthermore, a large majority (85%) of the fields did not state they had standard practices in place to reduce tire crumb exposure (Table 4-21).

Table 4-20. Types of Sports Played on Synthetic Turf Fields

Sport	Frequency	Percentage
Soccer	32	80%
Physical Training	27	67.5%
Football	22	55%
Softball	14	35%
Ultimate Frisbee	12	30%
Baseball	11	27.5%
Rugby	11	27.5%
Other[a]	20	50%

[a] Facilities reported other types of sports frequently played on the fields that were not already listed in the questionnaire.

Table 4-21. Standard Practices in Place to Reduce Tire Crumb Exposure to People Using the Synthetic Fields

Practices in Place to Reduce Tire Crumb Exposure	Number of Fields	Percent of Fields
Yes	6	15%
No	34	85%
Total	**40**	**100%**

4.4 Tire Crumb Rubber Sample Collection and Sub-Sample Preparation

4.4.1 Recycling Plant Sample Collection

Researchers collected recycled tire crumb rubber samples from nine tire recycling plants around the United States. These plants produced tire crumb rubber of the size category used as infill for synthetic turf fields (typically 10 to 20 mesh). Three of the plants used a cryogenic process for creating tire crumb rubber, whereas the remaining six plants used an ambient process. Researchers generated a total of 27 samples for organic chemical analysis (including extraction, emissions testing, and bioaccessibility analysis), 27 samples for metals analysis (including digestion, spectroscopy, and bioaccessibility analysis), and 27 samples for particle characterization.

4.4.2 Synthetic Turf Field Sample Collection

Researchers collected tire crumb rubber infill samples from 40 synthetic turf fields to support characterization of chemical constituents, particle characterization, and examination of microbial species. Following training by EPA and CDC/ATSDR researchers, APHC personnel collected the samples at the 19 synthetic turf fields located at Army installations across the United States –16 outdoor fields and 3 indoor fields. Trained CDC/ATSDR and EPA staff collected samples at the 21 community fields. The total numbers of fields included in sample collection are shown in Table 4-22.

Researchers collected tire crumb rubber infill from the top 3 centimeters (cm) of the synthetic turf field surface for chemical and particle characterization and microbial analysis. Chemical characterization included analysis of SVOC and metal analytes, metals bioaccessibility analysis, and emissions testing of VOCs and SVOCs; and particle characterization included analysis of moisture content, sand content, particle size, and SEM for a subset of samples. Microbial analysis included isolation and quantification of microbial genes.

Information about the numbers of samples collected from synthetic turf fields in the four U.S. census regions for each type of analysis is shown in Table 4-22. Between 8 and 13 fields in each census region were sampled. Sampling took place at 25 outdoor fields and 15 indoor fields – one field was a baseball/softball field, three were Army physical training fields, and the remainder were soccer/football-type playing fields (Table 4-23). Field installation dates ranged from 2004 to 2016 (Table 4-23). The characteristics for each individual synthetic turf field where tire crumb rubber infill samples were collected are described in Table 4-23. This table provides a reference for figures and tables later in this section that show results for individual fields.

Table 4-22. Samples Collected for Analyses at Synthetic Turf Fields[a]

Region	Number of Fields	Number of Individual Location Samples for Organics Analysis	Number of Individual Location Samples for Metals Analysis	Number of Individual Location Samples for Particle Characterization	Number of Individual Location Samples for Microbial Analysis	Total Composite Samples Prepared[b]
Northeast	9	63	63	63	63	27
Midwest	8	56	56	56	56	24
South	13	91	91	91	91	39
West	10	70	70	69[c]	70	30
Total	**40**	**280**	**280**	**279**	**280**	**120**

[a] At each of the 40 fields, samples were collected from seven individual locations.

[b] For each synthetic turf field, one composite sample was prepared in the laboratory from the seven individual location samples for organic chemical analyses, one composite sample was prepared for metals analyses, and one composite sample was prepared for particle size fraction analysis.

[c] The cap came off one sample collection container during transport, resulting in an unusable sample.

Table 4-23. Individual Field Characteristics

Field ID	Outdoor or Indoor Field	Installation Age Category	U.S. Census Region Location
1	Outdoor	2009 – 2012	South
2	Outdoor	2013 – 2016	South
3	Outdoor	2004 – 2008	Northeast
4	Indoor	2009 – 2012	Northeast
5	Outdoor	2013 – 2016	Northeast
6	Indoor	2009 – 2012	Northeast
7	Indoor	2009 – 2012	Northeast
8	Outdoor	2013 – 2016	West
9	Outdoor	2004 – 2008	West
10	Outdoor	2009 – 2012	West
11	Outdoor	2013 – 2016	South
12	Outdoor	2009 – 2012	South
13	Outdoor	2009 – 2012	West
14	Outdoor	2013 – 2016	West
15	Outdoor	2013 – 2016	South
16	Outdoor	2013 – 2016	South
17	Outdoor	2009 – 2012	South
18	Outdoor	2013 – 2016	South
19	Outdoor	2009 – 2012	West
20	Indoor	2004 – 2008	South
21	Outdoor	2013 – 2016	South
22	Indoor	2009 – 2012	South
23	Outdoor	2004 – 2008	West
24	Indoor	2009 – 2012	Midwest
25	Indoor	2009 – 2012	Midwest

Table 4-23 Continued

Field ID	Outdoor or Indoor Field	Installation Age Category	U.S. Census Region Location
26	Outdoor	2013 – 2016	Midwest
27	Indoor	2013 – 2016	West
28	Indoor	2009 – 2012	Midwest
29	Indoor	2009 – 2012	Midwest
30	Indoor	2004 – 2008	Midwest
31	Outdoor	2009 – 2012	Northeast
32	Outdoor	2004 – 2008	Northeast
33	Indoor	2004 – 2008	Northeast
34	Outdoor	2009 – 2012	Northeast
35	Outdoor	2009 – 2012	Midwest
36	Indoor	2004 – 2008	Midwest
37	Indoor	2004 – 2008	West
38	Indoor	2004 – 2008	West
39	Outdoor	2004 – 2008	South
40	Outdoor	2009 – 2012	South

4.4.3 Preparation and Scheduled Analysis for Tire Crumb Rubber Samples and Sub-Samples

Table 4-24 shows the total number of samples and subsamples prepared for the range of analyses to be applied. This table includes the totals from both tire recycling plants and synthetic turf fields but does not include quality control samples and analyses. The numbers and types of sample analyses scheduled for tire crumb rubber characterization analysis are further described in Table 4-25. Tire crumb rubber material was analyzed by laboratories for a wide range of volatile and semi-volatile organic (VOC and SVOC) and metals constituents. Quantitative analyses were performed for some target analyte chemicals (Tables 3-1 through 3-4). Metals analyses were performed using both ICP/MS and XRF, and SVOC analyses were performed using both GC/MS/MS and LC/TOFMS methods to capture a wide potential range of chemicals with differing chemical and physical properties. Suspect screening analyses for additional SVOCs was performed by LC/TOFMS, and non-targeted analysis methods were applied to a subset of VOC and SVOC samples.

Table 4-24. Number of Recycling Plant and Synthetic Turf Field Tire Crumb Rubber Samples Prepared for Analyses[a,b,c]

Analyses	Sample Type	Number of Composite Samples	Number of Individual Samples	Total Number of Samples
Particle Characterization	Particle size characteristics	40	27	67
Particle Characterization	SEM and EPMA analysis	9	9	18
Particle Characterization	Moisture content	40	9	49
Particle Characterization	Sand/Rubber fraction analysis	40	0	40
Direct Chemical Constituent	Metals constituent ICP/MS analyses	40	60	100
Direct Chemical Constituent	Metals constituent XRF analyses	40	60	100
Direct Chemical Constituent	Targeted SVOC constituent GC/MS/MS analyses[d]	40	62	102
Direct Chemical Constituent	Targeted SVOC constituent LC/TOFMS analyses[d]	40	62	102

Table 4-24 Continued

Analyses	Sample Type	Number of Composite Samples	Number of Individual Samples	Total Number of Samples
Dynamic Chamber Emissions Experiments	Chamber experiments for VOCs at 25 °C	40	42	82
Dynamic Chamber Emissions Experiments	Chamber experiments for VOCs at 60 °C	40	42	82
Dynamic Chamber Emissions Experiments	Chamber experiments for SVOCs at 25 °C	40	42	82
Dynamic Chamber Emissions Experiments	Chamber experiments for SVOCs at 60 °C	40	42	82
Emissions Sample	Targeted VOC emissions GC/TOFMS analyses[d]	80	84	164
Emissions Sample	Formaldehyde emissions analyses	80	84	164
Emissions Sample	Targeted SVOC emissions LC/TOFMS analyses[d]	80	84	164
Emissions Sample	Targeted SVOC emissions GC/MS/MS analyses[d]	80	84	164
Bioaccessibility	Metals bioaccessibility – simulated saliva	40	42	82
Bioaccessibility	Metals bioaccessibility – simulated gastric fluid	40	42	82
Bioaccessibility	Metals bioaccessibility – simulated sweat	40	42	82
Microbial	Microbial analyses – targeted	0	280	280
Microbial	Microbial analyses – non-targeted	0	280	280

[a] Does not include quality control/quality assurance samples or analyses; does not include chamber background samples.

[b] The total numbers of samples are based on 40 synthetic turf field composite samples, 15 to 35 synthetic turf field individual location samples, and 27 individual recycling plant samples from 9 recycling plants; except for microbial analysis where all 280 individual synthetic turf field location samples are scheduled for analysis.

[c] EPMA = Electron probe microanalysis; GC/MS/MS = Gas chromatography/tandem mass spectrometry; GC/TOFMS = Gas chromatography/time-of-flight mass spectrometry; ICP/MS = Inductively coupled plasma/mass spectrometry; LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry; PCR = Polymerase chain reaction; SEM = Scanning electron microscopy; SVOC = Semivolatile organic compound; VOC = volatile organic compound; XRF = X-ray fluorescence

[d] In addition to analysis for target analytes, 16 of the samples will be selected for non-targeted analysis.

Table 4-25. Scheduled Numbers of Sample Analyses for Tire Crumb Rubber Characterization[a]

Analyses	Sample Type	Number of Analyses[b]	Additional Information
Particle Characterization	Moisture analysis	49	Field composite and plant samples
Particle Characterization	Sand fraction analysis	40	Field composite samples
Particle Characterization	Particle size analysis	469	7 size fractions for 67 samples
Particle Characterization	SEM and EPMA analysis	18	9 plant and 9 field composite samples
Direct Constituent	Metals ICP/MS analyses	102[c]	N/A
Direct Constituent	Metals XRF analyses	102[c]	N/A
Direct Constituent	Targeted SVOC GC/MS/MS analyses	102[c]	N/A
Direct Constituent	Non-targeted SVOC GC/MS analyses	16	Subset of plant and field samples
Direct Constituent	Target and suspect screening SVOC LC/TOFMS analyses	204	Both positive and negative modes
Direct Constituent	Non-targeted SVOC LC/TOFMS analyses	32	Subset of plant and field samples

Table 4-25 Continued

Analyses	Sample Type	Number of Analyses[b]	Additional Information
Dynamic Chamber Emissions Experiments	Chamber experiments for VOCs[e]	328	82[d] experiments at 25 °C and 60 °C
Dynamic Chamber Emissions Experiments	Chamber experiments for SVOCs[e]	328	82[d] experiments at 25 °C and 60 °C
Dynamic Chamber Emissions Experiments	Chamber time series experiments for VOCs[f]	8	4 experiments at 25 °C and 60 °C
Dynamic Chamber Emissions Experiments	Chamber time series experiments for SVOCs[f]	8	4 experiments at 25 °C and 60 °C
Dynamic Chamber Emissions Experiments	Wristband experiments for SVOCs[g]	4	25 °C only
Emissions	Samples for formaldehyde analyses	328	N/A
Emissions	Samples for targeted VOC GC/TOFMS analyses	376	N/A
Emissions	Samples for non-targeted VOC GC/TOFMS analyses	16	Subset of plant and field samples
Emissions	Samples for targeted SVOC GC/MS/MS analyses	376	N/A
Emissions	Wristband samples for SVOC GC/MS/MS analyses	24	N/A
Emissions	Samples for non-targeted SVOC GC/MS analyses	16	Subset of plant and field samples
Emissions	Samples for SVOC LC/TOFMS analyses	376[h]	Both positive and negative modes
Emissions	Samples for non-targeted SVOC LC/TOFMS analyses	32	Subset of plant and field samples
Bioaccessibility	Metals bioaccessibility ICP/MS analyses	246	82[d] samples; 3 simulated fluids
Microbial	Microbial targeted analyses	280	N/A
Microbial	Microbial non-targeted analyses	280	N/A

[a] EPMA = Electron probe microanalysis; GC/MS = Gas chromatography/mass spectrometry; GC/MS/MS = Gas chromatography/tandem mass spectrometry; GC/TOFMS = Gas chromatography/time-of-flight mass spectrometry; ICP/MS = Inductively coupled plasma/mass spectrometry; LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry; N/A = Not applicable; PCR = Polymerase chain reaction; SEM = Scanning electron microscopy; SVOC = Semivolatile organic compound; VOC = Volatile organic compound; XRF = X-ray fluorescence

[b] Does not include quality control/quality assurance samples or analyses.

[c] The total of 102 samples is based on 40 synthetic field composite samples, 35 synthetic field individual samples, and 27 individual recycling plant samples.

[d] The total of 82 samples is based on 40 synthetic field composite samples, 15 synthetic field individual samples, and 27 individual recycling plant samples.

[e] Each emission experiment included a chamber background sample followed by a tire crumb emission sample.

[f] Each time series experiment generated 6 samples.

[g] Each wristband experiment generated 6 samples.

[h] Only a subset of the SVOC emission samples were analyzed by LC/TOFMS.

4.5 Tire Crumb Rubber Particle Characterization Results

4.5.1 Tire Crumb Rubber Moisture

Moisture content was measured in tire crumb rubber collected at nine recycling plants and in tire crumb rubber infill collected at 40 synthetic turf fields (Table 4-26). Moisture measurements were made in one of the three samples collected at recycling plants for metals analysis, and in the metals composite sample prepared for each synthetic turf field. All moisture measurements were made in duplicate. Average percent moisture results are shown in Figures 4-1 and 4-2.

Moisture content in all recycling plant tire crumb rubber samples was < 1%, with a median value of 0.87%. Moisture content in tire crumb rubber infill collected at synthetic turf fields ranged from 0.4% to 6.2%, with a median value of 0.81%. Samples collected from several synthetic turf fields had visible moisture, which was reflected in the measurements, as six fields had > 3% moisture content. The visible moisture may have been a result of slight precipitation or heavy dew present at the time of sample collection.

In order to provide more comparable results, when measurements were based on a weighed amount of tire crumb rubber used for analysis, many of the chemical analysis results were adjusted for moisture content prior to data analysis. The adjustment was not performed for metals ICP/MS or XRF analyses because these samples were dried prior to analysis.

Table 4-26. Moisture Content in Tire Crumb Rubber from Recycling Plants and Infill from Synthetic Turf Fields

Tire Crumb Rubber Sampling Location	N	Mean % Moisture	Standard Deviation (%)	Median % Moisture	Minimum % Moisture	Maximum % Moisture
Recycling Plants	9	0.81	0.17	0.87	0.52	0.99
Synthetic Turf Fields	40	1.39	1.38	0.81	0.40	6.22

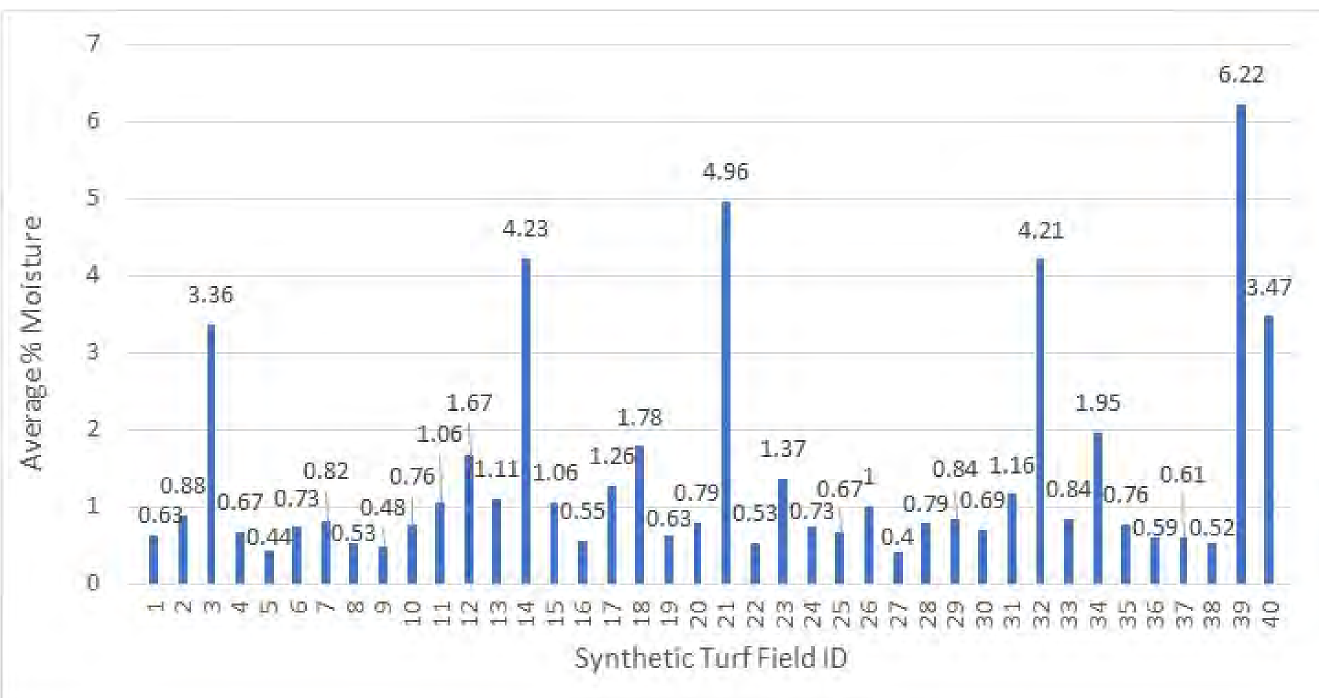

Figure 4-1. Average % moisture in tire crumb rubber infill from synthetic turf fields, by field ID.

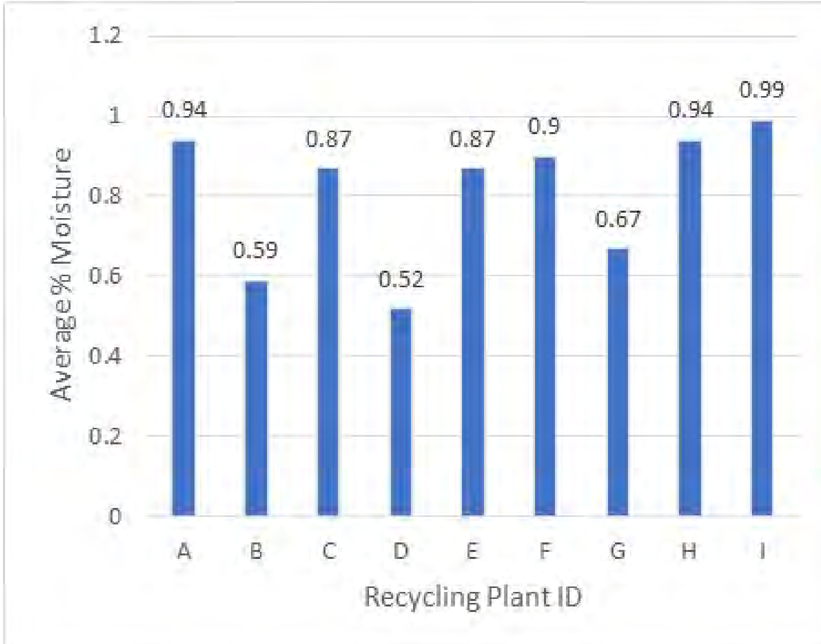

Figure 4-2. Average % moisture in tire crumb rubber from recycling plants, by plant ID.

4.5.2 Infill Sand/Rubber Fractions

Sand is sometimes added as an infill component in a mixture with tire crumb rubber and in other cases, it is used as a base layer prior to tire crumb rubber deposition. There may also be some cases where windblown or tracked-in sand is present on fields. Synthetic turf field tire crumb rubber infill collected from the upper 3 cm of the infill at 40 fields was analyzed for sand content and results are shown in Table 4-27 and Figure 4-3. There were 24 fields with no measured sand content and 16 fields with sand content in the collected infill ranging from 0.33% to 53.3%. Of those with sand content, six fields had sand content values of < 10%, while ten fields had sand content values between 10% and 39%. No sand was observed in tire crumb rubber samples collected at tire recycling plants, so analyses were not performed, and the material was assumed to be 100% tire crumb rubber. Examples of infill material with and without sand are shown in Figure 4-4.

Most of the chemical characterization analyses were performed using weighed portions of synthetic turf field tire crumb rubber infill. Results from these analyses can be considered in two ways – a) as the amount of chemical per the amount of synthetic turf infill, or b) the amount of chemical per the amount of tire crumb rubber in the infill. It may be of interest to consider both of these metrics, the first as perhaps being most relevant for exposure assessment, and the second perhaps being most relevant for more direct comparisons of tire crumb rubber constituents. Where applicable, measurement results were calculated both with and without adjustment for % sand content, allowing for both data assessments to be performed. Except where otherwise noted, results in this report are shown using measurement results that have not been adjusted for % sand content. An assessment of the potential differences in chemical measurement results resulting from correcting and not correcting for sand content is presented in section 4.6.3.

Table 4-27. Sand Fraction in Tire Crumb Rubber Infill Collected at Synthetic Turf Fields

Sand Fraction Measure	Synthetic Turf Fields Value[a]
Mean % Sand	7.7
Standard Deviation (%)	13.1
Minimum % Sand	0
Median % Sand	0
Maximum %Sand	53.3
Number of Fields 0% Sand	24
Number of Fields 1 – 9% Sand	6
Number of Fields 10 – 19% Sand	3
Number of Fields 20 – 29% Sand	3
Number of Fields 30 – 39% Sand	3
Number of Fields 40 – 49% Sand	0
Number of Fields 50 – 59% Sand	1
Number of Fields > 59% Sand	0

[a] Synthetic Turf Fields (n = 40)

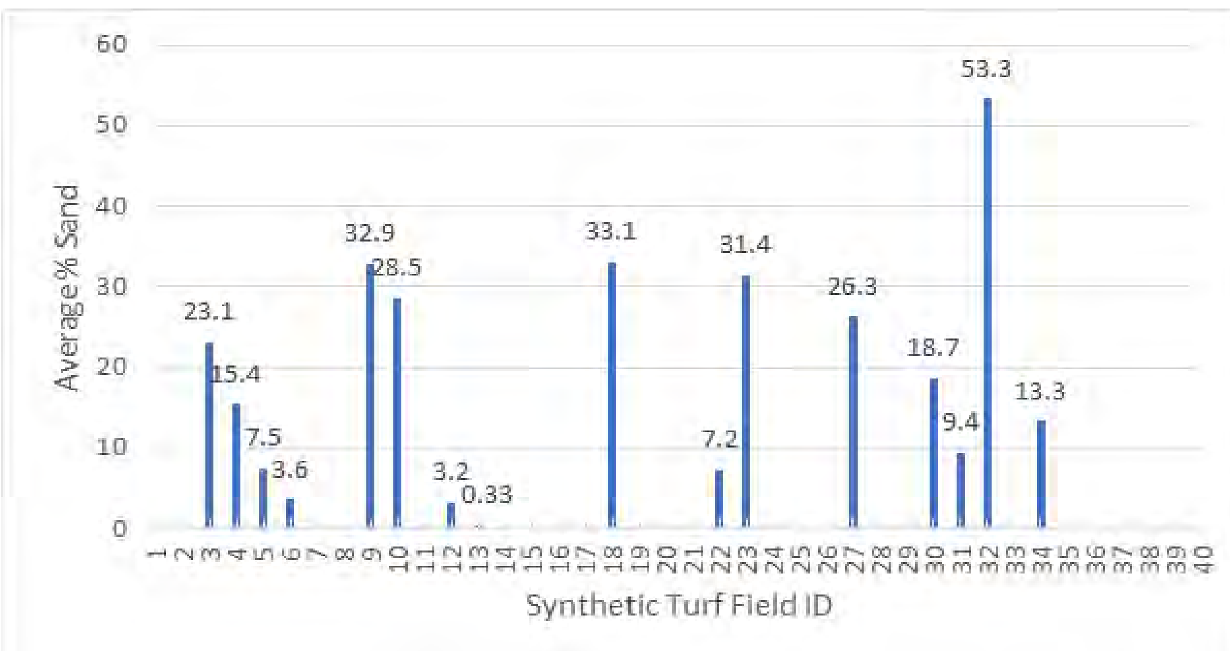

Figure 4-3. Percent sand in tire crumb rubber infill, by synthetic turf field ID. If % sand value is not shown, there was no sand in the infill from that field.

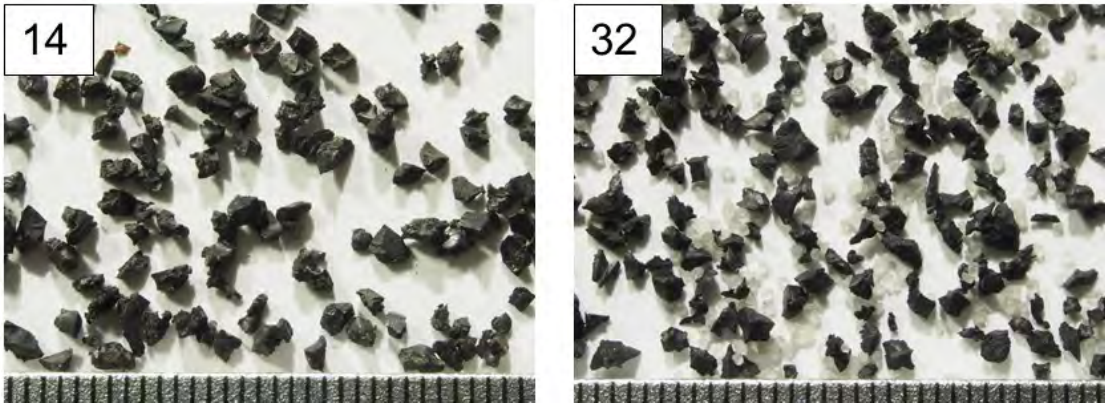

Figure 4-4. Example synthetic turf field infill material without sand (Field 14) and with sand (Field 32). Scale gradations are 1 mm.

4.5.3 Particle Size Distributions for Recycling Plants and Fields

Particle size analysis was performed for three tire crumb rubber samples collected from each of nine tire recycling plants and from composite tire crumb rubber infill samples collected at each of the 40 synthetic turf fields. A sieving and gravimetric method was used to generate seven particle size fractions, ranging from ≤ 0.063 to > 4.75 mm. A summary of size fraction results for recycling plants and synthetic turf fields is reported in Table 4-28.

Table 4-28. Particle Size Fraction Summary Statistics for Tire Crumb Rubber Collected at Tire Recycling Plants and Tire Crumb Rubber Infill Collected at Synthetic Turf Fields[a,b]

Particle Size Fraction (mm)	Recycling Plants Mean (g/kg)	Recycling Plants Standard Deviation (g/kg)	Recycling Plants Minimum (g/kg)	Recycling Plants Median (g/kg)	Recycling Plants Maximum (g/kg)	Synthetic Turf Fields Mean (g/kg)	Synthetic Turf Fields Standard Deviation (g/kg)	Synthetic Turf Fields Minimum (g/kg)	Synthetic Turf Fields Median (g/kg)	Synthetic Turf Fields Maximum (g/kg)
> 4.75	0.089	0.37	0	0	1.9	0.18	0.53	0	0	2.8
> 2 – 4.75	86	70	0.1	80	270	250	290	0.4	75	930
> 1 – 2	780	120	380	810	930	580	240	73	550	990
> 0.25 – 1	140	130	0.5	110	620	170	200	0.5	61	640
> 0.125 – 0.25	1.2	1.6	0	0.6	5.9	0.75	1.3	0	0.3	5.7
> 0.063 – 0.125	0.35	0.42	0	0.1	1.3	0.47	1.1	0	0.1	5
≤ 0.063	0.037	0.069	0	0	0.2	0.63	2.1	0	0.1	13

[a] Results are reported in grams of rubber in a size fraction per kilogram of total rubber collected. This is effectively a proportion of the amount of rubber falling within each size fraction.

[b] Recycling plants (n=27); Synthetic turf fields (n=40)

Results for each recycling plant and each field are reported in Appendix H. For recycling plant tire crumb rubber samples, on average, a majority of the tire crumb was found in the > 1- to 2-mm fraction (780 g/kg), with smaller amounts in the > 2- to 4.75-mm (86 g/kg) and the > 0.25- to 1-mm (140 g/kg) size fractions. On average, 0.35 g/kg was measured in the > 0.063- to 0.125-mm fraction and 0.037 g/kg in the ≤ 0.063-mm fraction. Size distribution measurements may have been impacted to some extent by collecting samples only from the top of 1-ton storage bags at eight of nine recycling plants.

For synthetic turf field tire crumb rubber infill samples, on average, a majority of the tire crumb was found in the > 1- to 2-mm fraction (580 g/kg), with smaller amounts in the > 2- to 4.75-mm (250 g/kg) and the > 0.25- to 1-mm (170 g/kg) size fractions. On average, 0.47 g/kg was measured in the > 0.063- to 0.125-mm fraction and 0.63 g/kg in the ≤ 0.063-mm fraction. Sixty-five percent of the fields had ≤ 0.1 g/kg in the ≤ 0.063-mm fraction, while the maximum amount measured in that size fraction was 13 g/kg.

The distribution of particle size fraction proportions is shown in Figure 4-5 for recycling plants and Figure 4-6 for synthetic turf fields. Examples of tire crumb rubber infill collected at synthetic turf fields with different size ranges are shown in Figures 4-7 and 4-8. Photos of tire crumb rubber collected from each recycling plant and each field are shown in Appendix H.

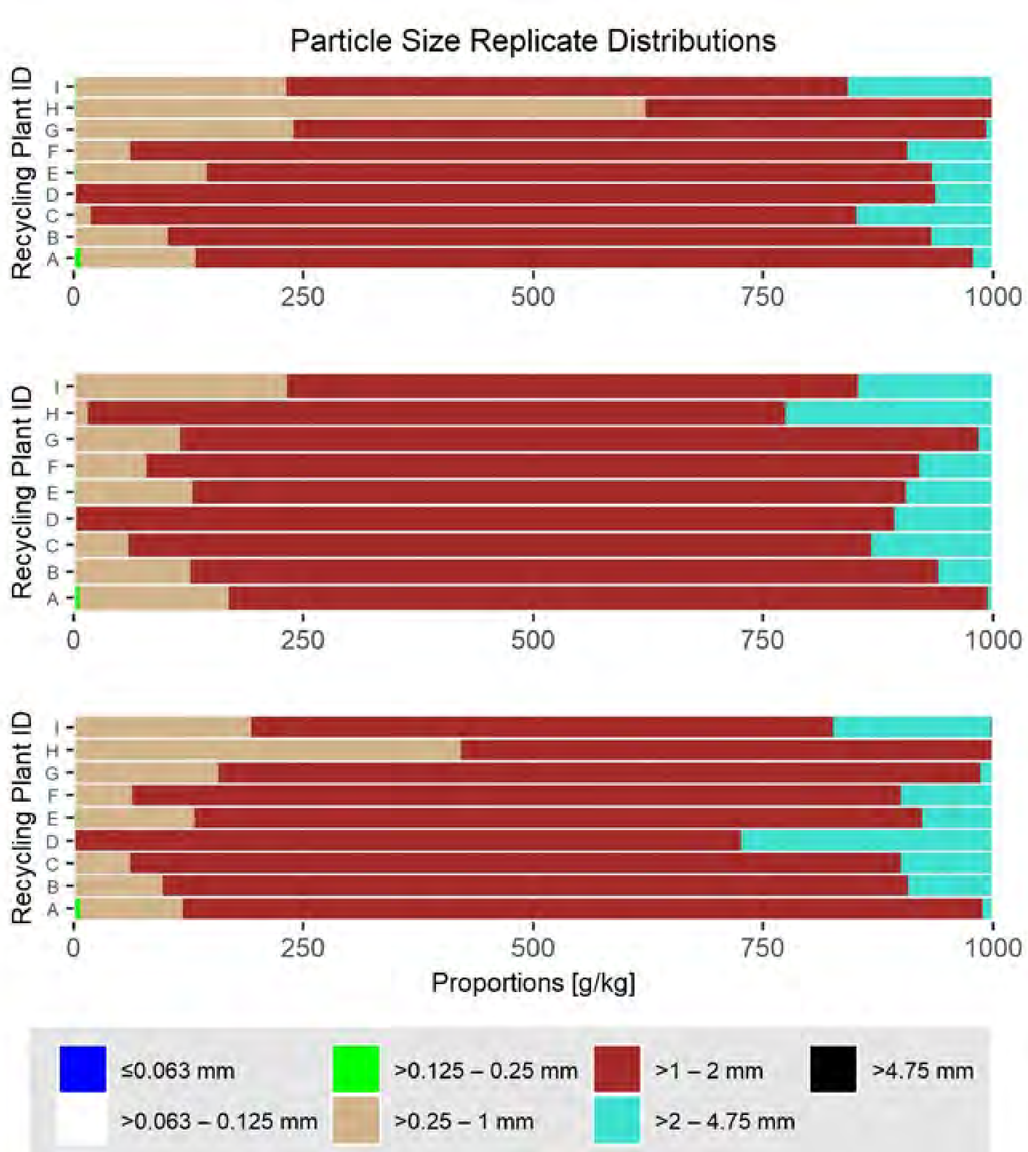

Figure 4-5. Tire crumb rubber particle size distributions for nine recycling plants (three samples from each plant).

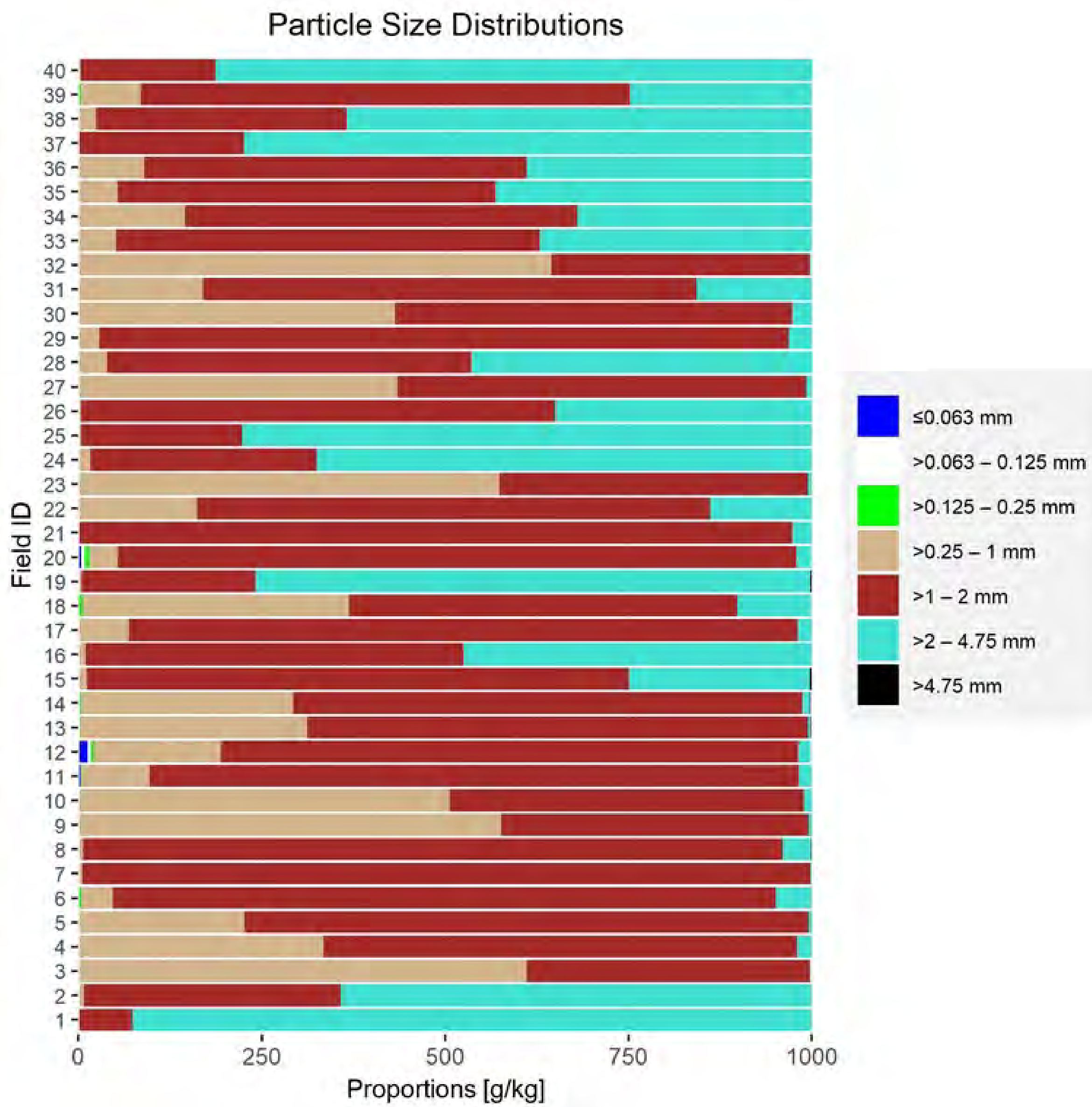

Figure 4-6. Tire crumb rubber infill particle size distributions for 40 synthetic turf fields.

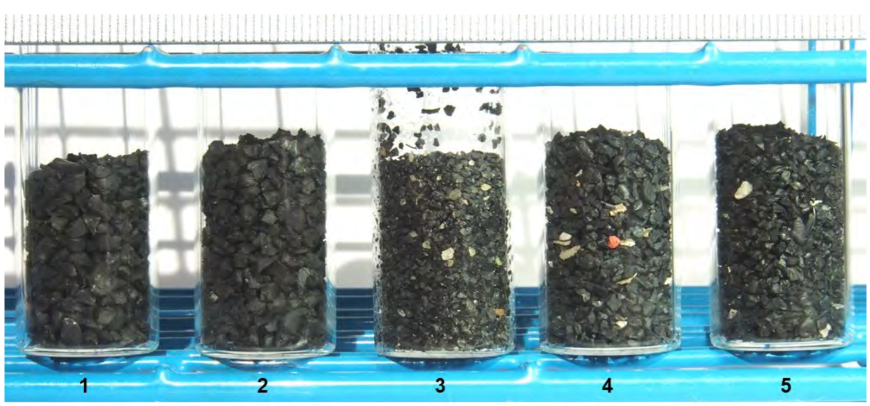

Figure 4-7. Example photos of tire crumb rubber infill collected from five synthetic turf fields. Scale gradations are 1 mm.

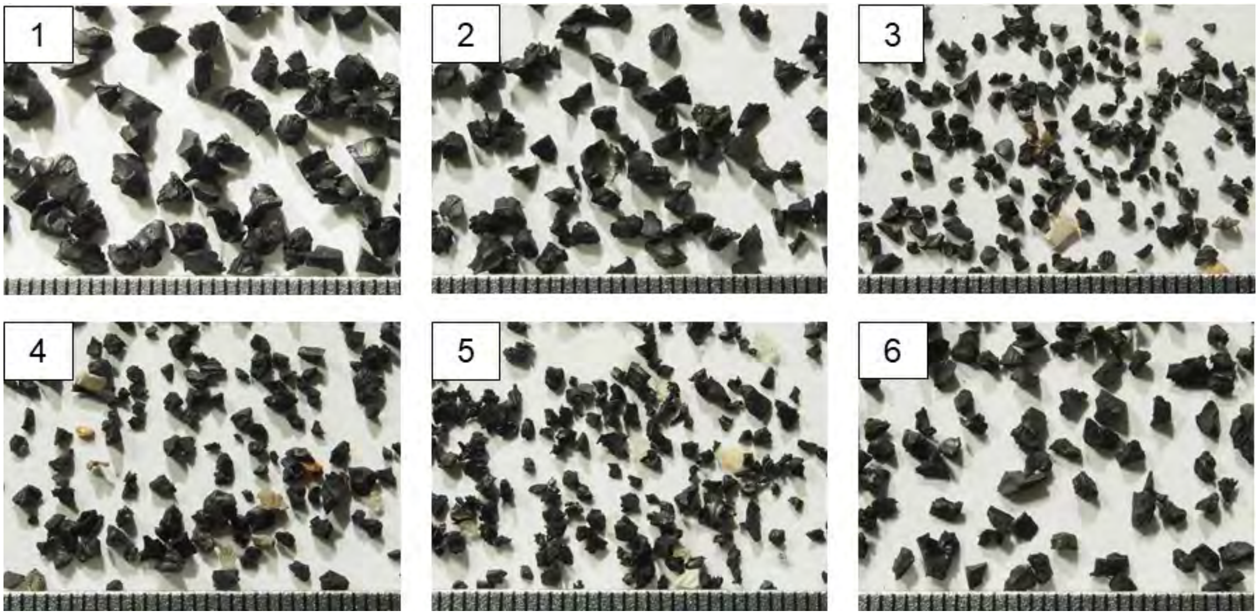

Figure 4-8. Example close-up photos of tire crumb rubber infill collected at six synthetic turf fields. Scale gradations are 1 mm.

There was substantial variability across the amounts measured in the > 0.25- to 1-mm, > 1- to 2-mm, and > 2- to 4.75-mm size fractions for infill collected at synthetic turf fields. Particle size fractions were further examined for differences among the three primary field characteristic categories, including indoor vs. outdoor, installation age groups, and the four geographic regions. Results for these comparisons are shown in Tables 4-29, 4-30, and 4-31. The only statistically significant result was for differences among the four geographic regions, where a smaller average proportion in the >2 – 4.75 mm size fraction was found in samples from Northeast fields and higher mean fractions in Midwest fields. There were some other non-significant differences, including lower proportions of >1 – 2 mm and greater proportions of >0.25 – 1 mm size fractions for fields in the oldest installation age group compared the two newer installation age groups.

Table 4-29. Comparison of Particle Size Fractions for Tire Crumb Rubber Infill at Outdoor and Indoor Synthetic Turf Fields [a,b]

Particle Size Fractions (mm)	Outdoor Fields Mean (g/kg)	Outdoor Fields Standard Deviation (g/kg)	Indoor Fields Mean (g/kg)	Indoor Fields Standard Deviation (g/kg)	F-test p-value[c]
> 4.75	0.28	0.65	0.02	0.077	NR
> 2 – 4.75	230	290	290	310	0.3152
> 1 – 2	570	240	590	260	0.7769
> 0.25 – 1	200	220	110	150	0.6600
> 0.125 – 0.25	0.72	1.1	0.80	1.5	NR
> 0.063 – 0.125	0.44	1.0	0.52	1.2	NR
≤ 0.063	0.78	2.6	0.38	0.98	NR

[a] Results are reported in grams of rubber in a size fraction per kilogram of total rubber collected. This is effectively a proportion of the amount of rubber falling within each size fraction.

[b] Outdoor fields (n=25); Indoor fields (n=15)

[c] NR = Not Reported; one or more measurement results were 0, precluding natural log-transformed testing for the complete data set.

Table 4-30. Comparison of Particle Size Fractions for Tire Crumb Rubber Infill at Synthetic Turf Fields in Three Field Installation Age Groups[a,b]

Particle Size Fractions (mm)	Fields Installed 2004 – 2008 Mean (g/kg)	Fields Installed 2004 – 2008 Standard Deviation (g/kg)	Fields Installed 2009 – 2012 Mean (g/kg)	Fields Installed 2009 – 2012 Standard Deviation (g/kg)	Fields Installed 2013 – 2016 Mean (g/kg)	Fields Installed 2013 – 2016 Standard Deviation (g/kg)	F-test p-value[c]
> 4.75	0.027	0.090	0.14	0.40	0.39	0.86	NR
> 2 – 4.75	220	280	310	340	170	220	0.4893
> 1 – 2	490	190	570	280	690	200	0.1811
> 0.25 – 1	280	280	110	140	130	170	0.2592
> 0.125 – 0.25	1.2	1.6	0.56	0.88	0.65	1.4	NR
> 0.063 – 0.125	0.62	1.4	0.49	1.2	0.29	0.49	NR
≤ 0.063	0.45	1.1	0.87	3.0	0.43	0.97	NR

[a] Results are reported in grams of rubber in a size fraction per kilogram of total rubber collected. This is effectively a proportion of the amount of rubber falling within each size fraction.

[b] Fields installed between 2004 and 2008 (n=11); between 2009 and 2012 (n=18); and between 2013 and 2016 (n=11).

[c] NR = Not Reported; one or more measurement results were 0, precluding natural log-transformed testing for the complete data set.

Table 4-31. Comparison of Particle Size Fractions for Tire Crumb Rubber Infill at Synthetic Turf Fields in Four Geographic Regions[a,b]

Particle Size Fractions (mm)	Northeast Mean (g/kg)	Northeast Standard Deviation (g/kg)	South Mean (g/kg)	South Standard Deviation (g/kg)	Midwest Mean (g/kg)	Midwest Standard Deviation (g/kg)	West Mean (g/kg)	West Standard Deviation (g/kg)	F-test p-value[c]
> 4.75	0	0	0.22	0.78	0	0	0.44	0.52	NR
> 2 – 4.75	100	150	280	320	390	270	220	340	0.0168
> 1 – 2	650	220	630	290	520	220	500	230	0.6418
> 0.25 – 1	250	240	78	100	83	140	270	250	0.1452
> 0.125 – 0.25	0.56	0.68	1.3	2.0	0.33	0.42	0.59	0.70	NR
> 0.063 – 0.125	0.26	0.28	0.96	1.8	0.15	0.15	0.28	0.47	NR
≤ 0.063	0.17	0.14	1.6	3.6	0.088	0.11	0.22	0.39	NR

[a] Results are reported in grams of rubber in a size fraction per kilogram of total rubber collected. This is effectively a proportion of the amount of rubber falling within each size fraction.

[b] Northeast (n=9); South (n=13); Midwest (n=8); West (n=10)

[c] NR = Not Reported; one or more measurement results were 0, precluding natural log-transformed testing for the complete data set.

4.5.4 Scanning Electron Microscopy

4.5.4.1 Scanning Electron Microscopy Results

A typical electron micrograph of sieved small particles from a recycling plant sample is shown in Figure 4-9. Bright sampled particles appear against the gray background of the adhesive-coated carbon SEM tab (Ted Pella, Inc., Redding, CA, USA). Micrographs also invariably contained artifacts that appear as holes and tears on the adhesive surface. Field samples and recycling plant samples presented similar electron micrographs. Particles were very polydisperse – generally, several large particles (50-100 µm) were present along with many smaller particles. In the case of the sieve No. 230 samples, the particles were often smaller than the 63-µm sieve openings. These could have been adsorbed on or aggregated with larger particles during sieving and subsequently been released during storage. Bottom pan particle distributions were also polydisperse (see example in Figure 4-10), with most particles having projected areas less than 700 µm^2 per particle. These areas correspond to nominal diameters of less than about 30 µm, assuming spherical particle shape.

Particle area analyses were conducted on the 16 images obtained from each sample, using Image J software (ImageJ/Fiji, version 1.46r, National Institutes of Health, Bethesda, MD, USA; Ferreira and Rasband, 2012). Given the background noise from the SEM tabs, a lower limit of 30 µm^2 projected area was set for particle analysis. Summary results for the 9 field samples and 9 recycling plant samples are shown in Table 4-32 (one bottom pan fraction had insufficient sample to analyze). Using a two-tailed t-test with a significance level of 0.05, the null hypothesis that the means of the field and recycling plant mean areas are the same can be rejected for the Sieve 230 fraction, but it cannot be rejected for the bottom pan (nominally < 63 µm) fraction.

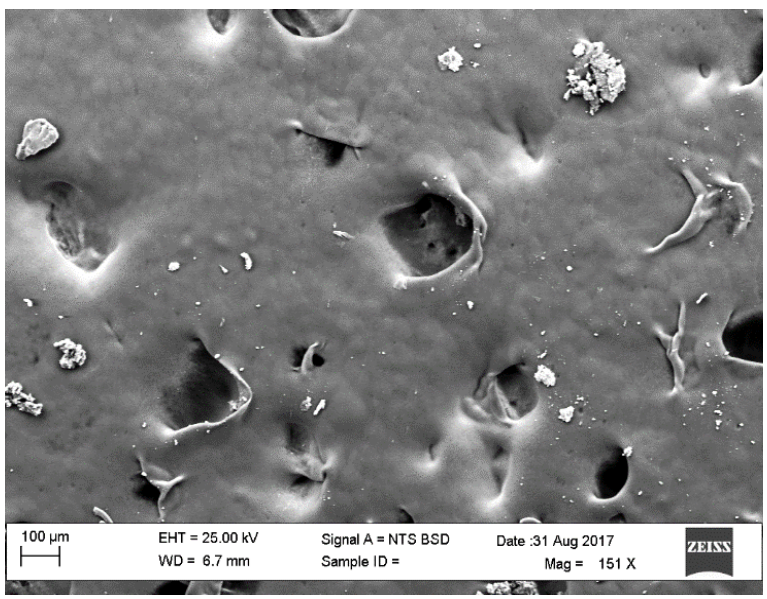

Figure 4-9. Representative electron micrograph of small particles seived from a recycling plant tire crumb rubber sample.

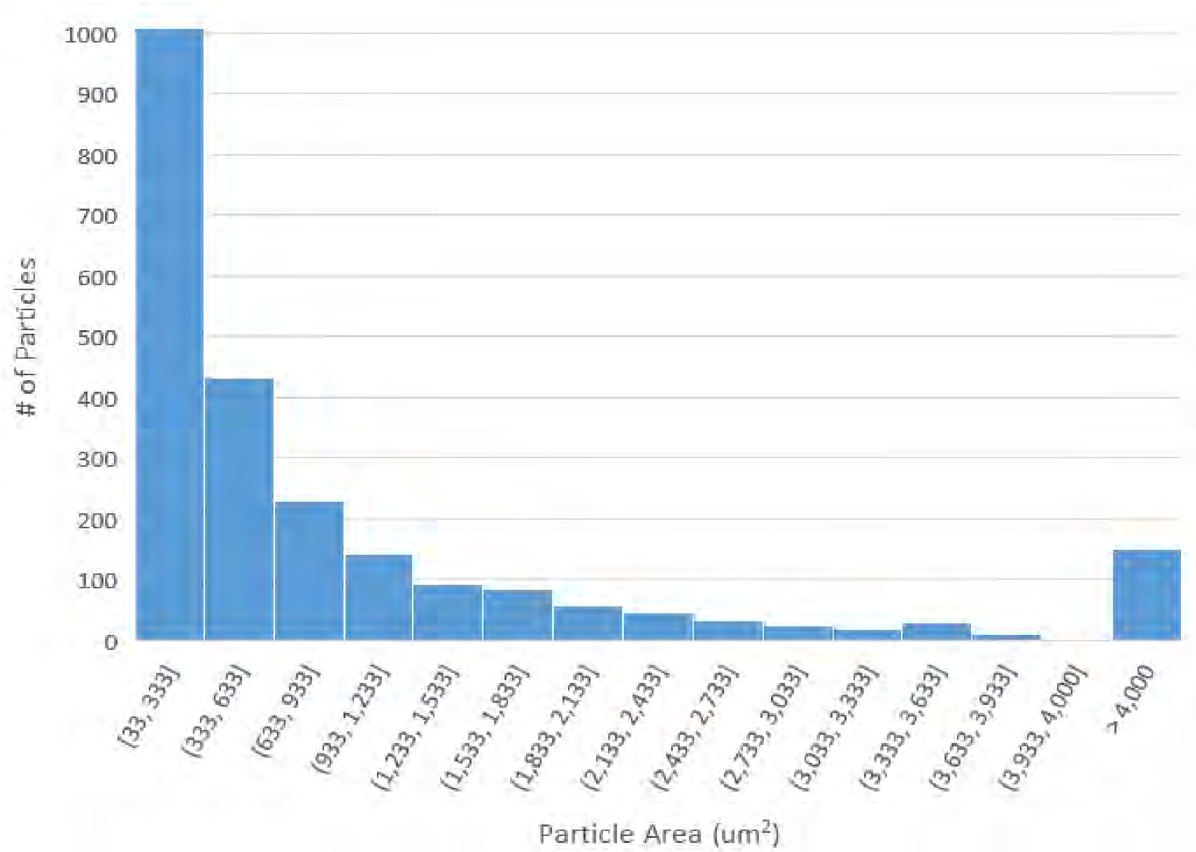

Figure 4-10. Representative histogram of the frequency of individual particle areas observed in the bottom pan sample. µm = micrograms

Table 4-32. Particle Areas for Tire Crumb Rubber at Recycling Plants and Synthetic Turf Fields

Particle Size Fraction	Recycling Plants n	Recycling Plants Mean (μm^2)	Recycling Plants Standard Deviation (μm^2)	Synthetic Turf Fields n	Synthetic Turf Fields Mean (μm^2)	Synthetic Turf Fields Standard. Deviation (μm^2)
Sieve 230 fraction (0.063- to 0.125-mm)	9	1000	300	9	2400	1200
Bottom pan fraction (< 0.063 mm)	8	1000	420	9	1300	630

A more detailed inspection of the bottom pan results was conducted by dividing the particles into area ranges of 30 – 314 µm², > 314 – 962 µm², > 962 – 1963 µm², > 1963 – 3318 µm², and > 3318 µm². These ranges correspond to nominal diameters (assuming spherical particles) of about 5 – 20 µm, > 20 – 35 µm, > 35 – 50 µm, > 50 – 65 µm, and > 65 µm. Quartiles were then calculated for the field samples and recycling plant samples separately. The results are presented in Table 4-33. While the smallest fraction (≤ 20-µm nominal diameter) ranged from 12% to 57% of the total particle number for field samples, it always accounted for at least 34%, and up to 76%, of the particles from recycling plant samples. The reason for the more uniformly fine particles in the plant samples is not clear but given that particles in the ≤ 20-µm range are probably more relevant to inhalation exposure, this property may be important.

Table 4-33. Quartile Analyses of Recycling Plant and Synthetic Turf Field Particle Numbers in the Bottom Sieve Pan (< 0.063 mm) Samples

Tire Crumb Rubber Sampling Location	Quartile Bounds	% Bottom Pan Particles 30 – 314 μm²	% Bottom Pan Particles > 314 – 962 μm²	% Bottom Pan Particles > 962 – 1963 μm²	% Bottom Pan Particles > 1963 – 3318 μm²	% Bottom Pan Particles > 3318 μm²
Recycling Plants	Minimum	34%	11%	6.9%	3.2%	2.0%
Recycling Plants	Quartile 1	52%	12%	7.9%	4.6%	3.5%
Recycling Plants	Quartile 2	57%	15%	14%	9.3%	5.7%
Recycling Plants	Quartile 3	67%	17%	15%	11%	9.1%
Recycling Plants	Max	76%	19%	23%	14%	11%
Synthetic Turf Fields	Minimum	12%	4.1%	10%	5.5%	2.3%
Synthetic Turf Fields	Quartile 1	28%	12%	15%	7.2%	2.8%
Synthetic Turf Fields	Quartile 2	34%	23%	22%	12%	10%
Synthetic Turf Fields	Quartile 3	47%	26%	26%	15%	13%
Synthetic Turf Fields	Maximum	57%	31%	28%	33%	23%

4.5.4.2 Electron Probe Microanalysis Results

Electron probe microanalysis (EPMA) was performed on selected particles to evaluate its utility for determination of particle composition. Two EPMA modes were used. In the first, the electron beam was maintained at one location for the entirety of the X-ray acquisition. This single-point mode maximizes the signal-to-noise ratio and allows the elemental composition of very small particles to be determined. In Figure 4-11A, EPMA results are shown for two particles. The large particle in the center of the electron micrograph has X-ray peaks for sulfur (S) and zinc (Zn; Figure 4-11B), which is consistent with a rubber particle. However, the small particle above the large central particle has prominant aluminum (Al), silicon (Si), potassium (K), and iron (Fe) peaks, along with a little sulfur (S), which is definitely not rubber and could be an alumina silicate dust or soil particle.

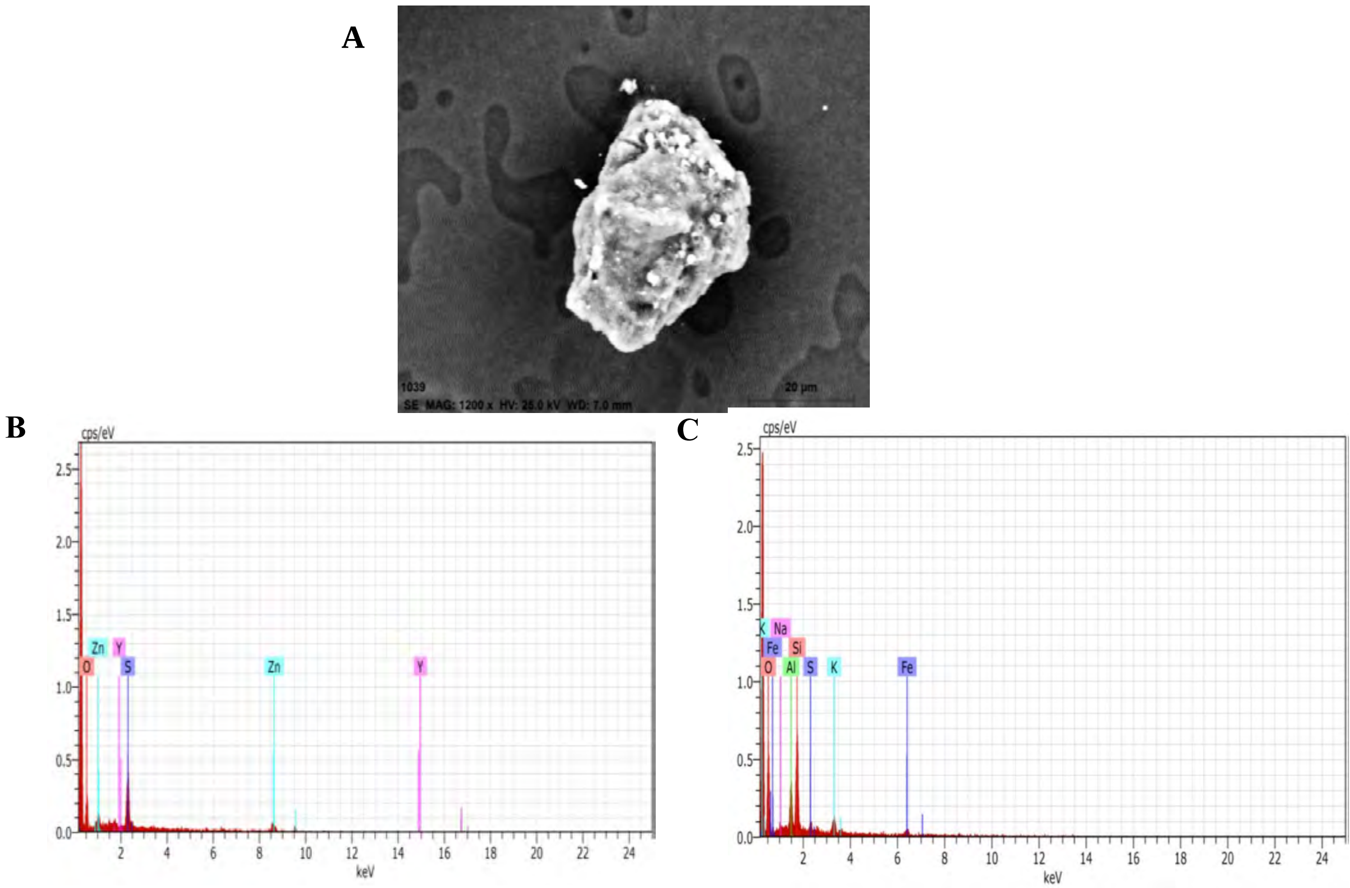

Figure 4-11. A) Electron micrograph of small particle cluster from a field sample; B) EPMA spectrum of the center of the large center particle; C) Spectrum of smaller particle above the central particle. [EPMA = Electron probe microanalysis; Al = Aluminum; Fe = Iron; K = Potassium; Na = Sodium; O = Oxygen; S = Sulfur; Si = Silicon; Y = Yttrium; Zn = Zinc]

EPMA was also performed in the elemental-mapping mode, in which X-ray spectra are obtained for every point in the electron micrograph as the electron beam rasters. This mode is much less sensitive than the single-point mode, but it allows visualization of the distribution of the major elemental components of a particle. In Figure 4-12A, the sulfur distribution in the particle indicates that the main body is consistent with rubber. The multi-element maps (Figure 4-12B and C) show the distribution of several elements in separate smaller particles on the surface of the large particle. Note the co-occurrence of iron (Fe) and chromium (Cr) in Figure 4-12B, possibly indicating steel particles.

In future studies, elemental mapping could also give a rough estimate of the fraction of rubber versus non-rubber particles. Figure 4-13 shows a backscatter electron micrograph of a recycling plant sample, as well as an elemental mapping of sulfur, silicon, and calcium (Ca). Assuming that only particles with high sulfur content are tire crumb rubber (an upper estimate, given that there could be, for example, inorganic sulfate particles as well), it appears that there are a number of rubber particles in this area of the SEM tab. There are also several particles of high Si or Ca content, possibly crustal in origin. Also, note that particles with high calcium are easily distinguished from Si- or S- bearing particles even in the backscatter electron micrograph, due to the greater primary electron scatter of the higher atomic number Ca.

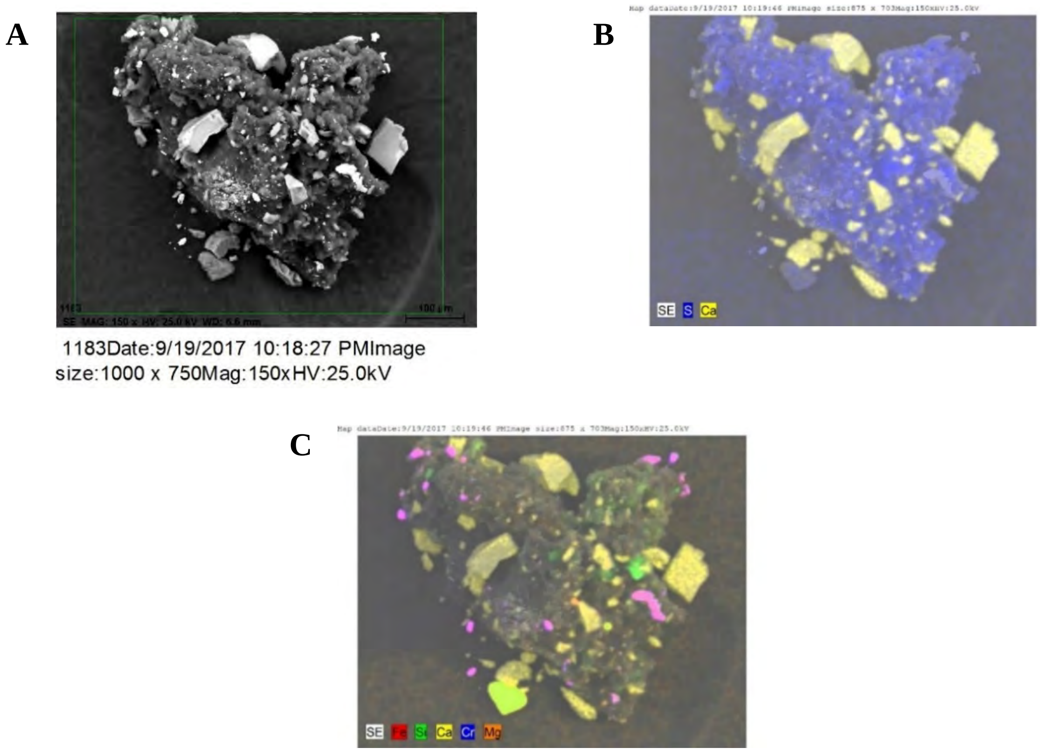

Figure 4-12. Three EPMA element mapping images. A) Original electron micrograph; B) Sulfur map indicating primary rubber particle; and C) multielement map showing inclusions probably steel (Fe+Cr) and possibly soil (Si, Ca). [EPMA = Electron probe microanalysis; Ca = Calcium; Cr = Chromium; Fe = Iron; Mg = Magnesium; S = Sulfur; Si = Silicon]

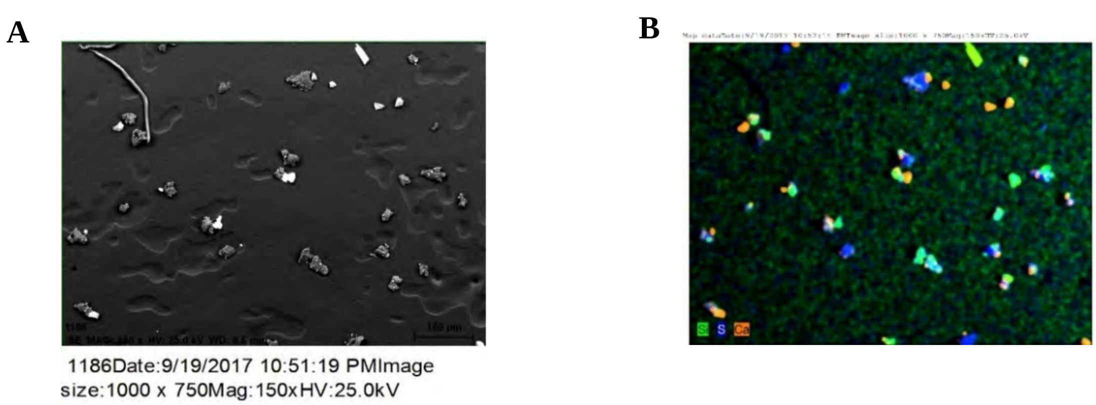

Figure 4-13. A) Backscatter electron micrograph of a recycling plant sample, and B) elemental mapping of sulfur, silicon, and calcium. [Ca = Calcium; S = Sulfur; Si = Silicon]

4.5.4.3 Summary of SEM/EPMA Studies

The SEM analysis of bottom pan and sieve No. 230 samples demonstrated that these size fractions are generally very polydisperse, although it appears that the bottom pan fractions from recycling plants have a higher fraction of very small particles than do those from field samples. The minimum size analyzed in this study was approximately 5-µm nominal diameter, limited by the image analysis noise caused by the adhesive-coated sample tabs. The analysis approach did not allow study of potential tire crumb rubber particles < 5-µm nominal diameter, which limits current understanding about the presence of, and potential for exposures to, fine particles and nanoparticles. Before future SEM studies are conducted to determine particle size distributions and particle morphology, alternative means of sampling using smoother SEM stub substrates, as well as the use of optical microscopy, should be investigated. Nanoparticle analysis is probably outside the scope of SEM analysis until very different sampling procedures are developed.

The selected EPMA analyses were conducted as a proof-of-concept study and demonstrated high elemental sensitivity on small particles in the single-point mode. The elemental-mapping mode could possibly be used to selectively analyze rubber particles, as well as investigate adsorption of metals on rubber particles.

4.6 Chemical Measurement Summary Statistics

4.6.1 Direct Tire Crumb Rubber Chemical Substance Measurements

Several types of quantitative analyses of target analytes were performed to measure chemical substances potentially associated with tire crumb rubber from recycling plants and tire crumb rubber infill from synthetic turf fields. Summary statistics were generated from the 27 samples collected from nine recycling plants and from 40 composite samples collected from synthetic turf fields. Summary statistic results are reported here for a subset of the chemical substances selected for highlighting, with complete results for all target analytes shown in Appendix I. Results for the following analysis types are included in this summary statistics reporting subsection for tire crumb rubber sampled from recycling plants and synthetic turf fields:

- Metals analyzed by ICP/MS
- Metals analyzed by XRF
- SVOCs analyzed in solvent extracts by GC/MS/MS
- SVOCs non-quantitative analysis of solvent extracts by LC/TOFMS
- VOC emission factors from analysis by GC/TOFMS
- SVOC emission factors from analysis by GC/MS/MS
- SVOC non-quantitative emission results from analysis by LC/TOFMS

More direct comparisons of results between recycling plants and synthetic turf fields are described in section 4.7, so much of the narrative in this section focuses on results from synthetic turf fields.

4.6.1.1 Metals by ICP/MS Analysis

Tire crumb rubber from recycling plants and tire crumb rubber infill from synthetic turf fields was quantitatively analyzed for 21 metals by acid extraction and ICP/MS analysis, with 19 of those metals measurable above the method detection limit in 100% of the samples. Selenium was not measured above the method detection limit in any sample. Compounds of two metals, zinc and cobalt, are used in tire manufacturing, and several other target analyte metals may be present if steel belts and cords are not fully excluded in the tire recycling process.

Summary statistics are reported in Table 4-34. Average values for metal concentrations in tire crumb rubber from synthetic turf fields ranged from 0.38 mg/kg for arsenic up to 15000 mg/kg for zinc. Average concentrations of cobalt and lead were 140 mg/kg and 24 mg/kg, respectively. Maximum values for synthetic turf field samples were 160 mg/kg, 22,000 mg/kg, 290 mg/kg, and 3.7 mg/kg for lead, zinc, cobalt, and chromium, respectively. Examples of the measurement results across the 40 synthetic turf fields are shown in Figure 4-14 for chromium, cobalt, lead, and zinc.

Table 4-34. Summary Statistics for Select Metals Analyzed by ICP/MS in Tire Crumb Rubber Samples Collected from Tire Recycling Plants and Tire Crumb Rubber Collected from Synthetic Turf Fields[a]

Tire Crumb Rubber Sampling Location	Chemical	n	% > LOD	Mean (mg/kg)	Standard Deviation (mg/kg)	% Relative Standard Deviation	10th Percentile (mg/kg)	25th Percentile (mg/kg)	50th Percentile (mg/kg)	75th Percentile (mg/kg)	90th Percentile (mg/kg)	Maximum (mg/kg)
Recycling Plants	Arsenic	27	100	0.30	0.088	29	0.20	0.24	0.28	0.37	0.45	0.51
Recycling Plants	Cadmium	27	100	0.55	0.13	23	0.40	0.45	0.55	0.63	0.73	0.93
Recycling Plants	Chromium	27	100	1.8	0.70	39	1.0	1.2	1.7	2.0	2.4	3.6
Recycling Plants	Cobalt	27	100	190	87	46	96	120	180	250	280	440
Recycling Plants	Lead	27	100	13	10	78	7.7	9.4	10	14	22	61
Recycling Plants	Zinc	27	100	17000	3500	20	13000	14000	16000	20000	21000	25000
Synthetic Turf Fields	Arsenic	40	100	0.38	0.20	52	0.19	0.26	0.34	0.45	0.60	1.1
Synthetic Turf Fields	Cadmium	40	100	0.95	0.68	72	0.49	0.57	0.70	1.1	1.7	4.2
Synthetic Turf Fields	Chromium	40	100	1.6	0.84	51	0.97	1.2	1.6	1.9	2.7	3.7
Synthetic Turf Fields	Cobalt	40	100	140	60	44	68	85	120	180	220	290
Synthetic Turf Fields	Lead	40	100	24	26	110	9.3	11	14	25	55	160
Synthetic Turf Fields	Zinc	40	100	15000	3000	20	11000	13000	14000	16000	19000	22000

[a] ICP/MS = Inductively coupled plasma/mass spectrometry; LOD = Limit of detection

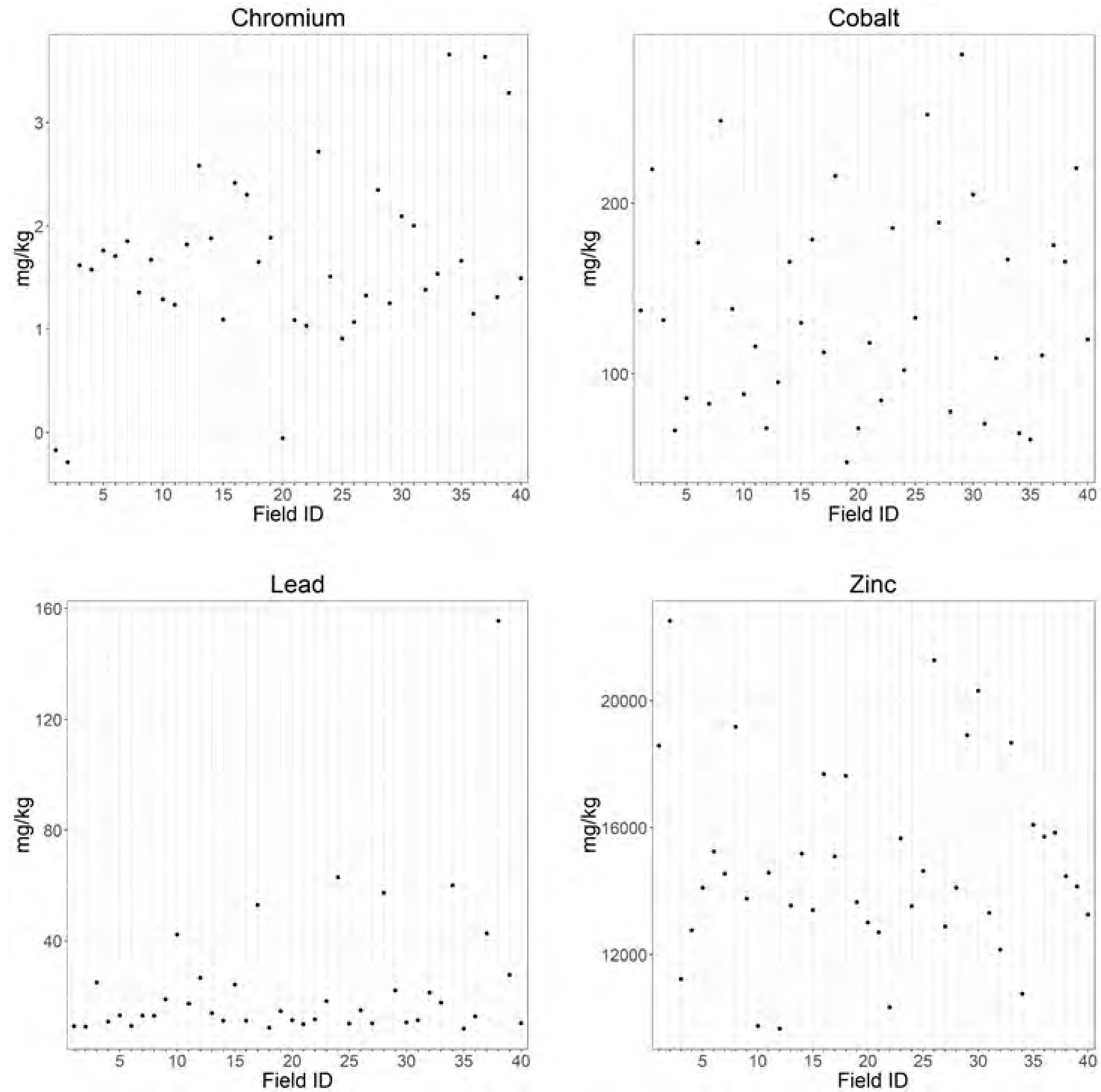

Figure 4-14. ICP/MS metal analysis results (mg/kg) for chromium, cobalt, lead, and zinc from tire crumb rubber infill composite samples collected from each synthetic turf field.
[ICP/MS = Inductively coupled plasma/mass spectrometry]

4.6.1.2 Metals by XRF Analysis

Tire crumb rubber from recycling plants and tire crumb rubber infill from synthetic turf fields was quantitatively analyzed for 17 metals by x-ray fluorescence spectroscopy analysis, with 10 of those metals (chromium, cobalt, lead, zinc, barium, copper, iron, molybdenum, rubidium, and strontium) measurable above the method detection limit in 100% of the samples and seven metals below 10% measurable above the method detection limit (arsenic, cadmium, antimony, manganese, nickel, selenium, and tin).

Summary statistics are reported in Table 4-35. Average values for metal concentrations in synthetic turf fields ranged from 14 mg/kg for chromium up to 33,000 mg/kg for zinc. Average concentrations of cobalt and lead were 39 mg/kg and 36 mg/kg, respectively. Maximum values for synthetic turf field samples were 110 mg/kg, 47,000 mg/kg, 69 mg/kg, and 20 mg/kg for lead, zinc, cobalt, and chromium, respectively.

Table 4-35. Summary Statistics for Selected Metals Analyzed by XRF in Tire Crumb Rubber Samples Collected from Tire Recycling Plants and Tire Crumb Rubber Infill collected from Synthetic Turf Fields[a]

Tire Crumb Rubber Sampling Location	Chemical	n	% > LOD	Mean (mg/kg)	Standard Deviation (mg/kg)	% Relative Standard Deviation	10th Percentile (mg/kg)	25th Percentile (mg/kg)	50th Percentile (mg/kg)	75th Percentile (mg/kg)	90th Percentile (mg/kg)	Maximum (mg/kg)
Recycling Plants	Arsenic	27	0	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Recycling Plants	Cadmium	27	0	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Recycling Plants	Chromium	27	100	15	4	26	10	12	15	18	21	25
Recycling Plants	Cobalt	27	100	58	35	61	24	31	52	72	130	150
Recycling Plants	Lead	27	100	35	8.6	25	23	29	37	41	47	54
Recycling Plants	Zinc	27	100	39000	8800	22	30000	32000	36000	48000	54000	58000
Synthetic Turf Fields	Arsenic	40	3	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	12
Synthetic Turf Fields	Cadmium	40	8	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	27
Synthetic Turf Fields	Chromium	40	100	14	2.9	21	10	12	13	16	17	20
Synthetic Turf Fields	Cobalt	40	100	39	17	44	15	22	43	52	61	69
Synthetic Turf Fields	Lead	40	100	36	22	61	15	22	33	44	54	110
Synthetic Turf Fields	Zinc	40	100	33000	7100	22	26000	29000	31000	37000	45000	47000

[a] XRF = X-ray fluorescence; LOD = Limit of detection

*Values reported only when % >LOD is ≥ 60%.

Average XRF measurement results were substantially higher than ICP/MS measurements for arsenic, cadmium, chromium, lead and zinc, and substantially lower for cobalt. The ICP/MS approach was based on known analyte concentration calibration solutions, while the XRF method did not have an exact analog to the tire crumb rubber for calibration assessment. Given some of the substantial differences in measurement results between XRF and ICP/MS, it appears more work may be needed before applying XRF as a field measurement method for obtaining accurate measurements.

4.6.1.3 SVOCs by GC/MS/MS Analysis

Tire crumb rubber from recycling plants and tire crumb rubber infill from synthetic turf fields was quantitatively analyzed for 39 target SVOCs by acetone/hexane solvent extraction and GC/MS/MS analysis. Target analytes included PAHs, phthalates, other tire rubber chemicals or degradates, and several chemicals previously reported in other studies. Most analytes were measurable above the method detection limit in 100% of the samples.

Summary statistics are reported in Table 4-36 for SVOCs analyzed by GC/MS/MS. Average values for SVOC concentrations in tire crumb rubber infill collected from synthetic turf fields ranged from 0.67 mg/kg for aniline to 43 mg/kg for bis(2-ethylhexyl) phthalate. The average value for pyrene, the most abundant of the quantified PAHs, was 12 mg/kg, while the average result for the sum of 15 PAH compounds was 29 mg/kg. Examples of average measurement results for samples collected at recycling plants vs. synthetic turf fields include pyrene (18 vs. 12 mg/kg), benzo[a]pyrene (0.74 vs. 0.78 mg/kg), benzothiazole (79 vs. 11 mg/kg), 4-tert-octylpheol (30 vs. 9.8 mg/kg) and bis(2-ethylhexyl) phthalate (12 vs. 43 mg/kg). Maximum values for SVOCs in synthetic turf field samples were 25 mg/kg, 3.0 mg/kg, 54 mg/kg, 33 mg/kg, and 170 mg/kg, respectively, for pyrene, benzo[a]pyrene, benzothiazole, 4-tert-octylphenol, and bis(2-ethylhexyl) phthalate.

Examples of the measurement results across the 40 synthetic turf fields are shown in the Figure 4-15 and 4-16 scattergraphs for eight SVOC analytes. For some SVOCs, the majority of the measurements at the 40 fields were below a certain concentration (e.g., majority of samples below 5 mg/kg for phenanthrene, below 1 mg/kg for benzo[a]pyrene, below 20 mg/kg for benzothiazole, below 10 mg/kg for 4-tert-octylphenol, below 50 mg/kg for bis(2-ethylhexyl) phthalate, and below 2 mg/kg for n-hexadecane); while other showed different patterns.

Table 4-36. Summary Statistics for Selected SVOCs Analyzed by GC/MS/MS in Solvent Extracts for Tire Crumb Rubber Samples Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Collected from Synthetic Turf Fields[a]

Tire Crumb Rubber Sampling Location	Chemical[b]	n	% > LOD	Mean (mg/kg)	Standard Deviation (mg/kg)	% Relative Standard Deviation	10th Percentile (mg/kg)	25th Percentile (mg/kg)	50th Percentile (mg/kg)	75th Percentile (mg/kg)	90th Percentile (mg/kg)	Maximum (mg/kg)
Recycling Plants	Phenanthrene	27	100	3.6	1.3	35	1.8	2.6	3.6	4.5	5.8	5.9
Recycling Plants	Fluoranthene	27	100	6.1	1.7	27	4.3	4.8	5.8	6.7	8.6	10
Recycling Plants	Pyrene	27	100	18	2.4	13	16	17	18	20	22	23
Recycling Plants	Benzo[a]pyrene	27	100	0.74	0.39	52	0.39	0.47	0.64	0.95	1.4	1.9
Recycling Plants	Benzo[ghi]perylene	27	100	1.3	0.59	45	0.82	0.97	1.1	1.3	2.0	3.4
Recycling Plants	Sum15PAH	27	100	41	8.9	22	31	34	39	49	53	62
Recycling Plants	Benzothiazole	27	100	79	19	24	54	61	79	96	100	110
Recycling Plants	Dibutyl phthalate	27	100	0.68	0.44	65	0.27	0.31	0.44	0.85	1.5	1.7
Recycling Plants	Bis(2-ethylhexyl) phthalate	27	100	12	14	120	2.9	3.5	6.1	15	34	58
Recycling Plants	Aniline	27	100	3.8	1.8	47	2.3	2.3	2.6	5.5	6.3	7.2
Recycling Plants	4-tert-octylphenol	27	100	30	6.2	21	23	25	30	34	40	46
Recycling Plants	n-Hexadecane	27	100	3.6	1.8	51	1.8	2.1	2.7	5.5	6.5	6.6
Synthetic Turf Fields	Phenanthrene	40	100	2.3	2.6	110	0.26	0.44	1.1	3.3	6.1	10
Synthetic Turf Fields	Fluoranthene	40	100	4.5	2.6	57	2.0	2.4	3.9	6.5	8.1	10
Synthetic Turf Fields	Pyrene	40	100	12	6.2	49	4.2	7.0	13	17	21	25
Synthetic Turf Fields	Benzo[a]pyrene	40	100	0.78	0.52	66	0.38	0.43	0.62	0.91	1.4	3.0
Synthetic Turf Fields	Benzo[ghi]perylene	40	100	1.3	0.64	49	0.47	0.64	1.4	1.8	2.0	2.8
Synthetic Turf Fields	Sum15PAH	40	100	29	15	51	13	17	27	38	49	68
Synthetic Turf Fields	Benzothiazole	40	100	11	13	120	1.1	1.8	7.0	14	31	54
Synthetic Turf Fields	Dibutyl phthalate	40	100	1.5	1.5	100	0.054	0.26	0.97	2.3	3.5	6.6
Synthetic Turf Fields	Bis(2-ethylhexyl) phthalate	40	100	43	42	100	4.9	7.8	28	58	100	170
Synthetic Turf Fields	Aniline	40	100	0.67	0.53	79	0.16	0.27	0.57	0.96	1.2	2.4
Synthetic Turf Fields	4-tert-octylphenol	40	100	9.8	9.7	99	0.90	2.5	5.6	16	27	33
Synthetic Turf Fields	n-Hexadecane	40	100	0.94	1.3	130	0.079	0.10	0.26	1.3	2.6	5.4

[a] SVOC = Semivolatile organic compound; GC/MS/MS = Gas chromatography/tandem mass spectrometry; LOD = Limit of Detection

[b] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

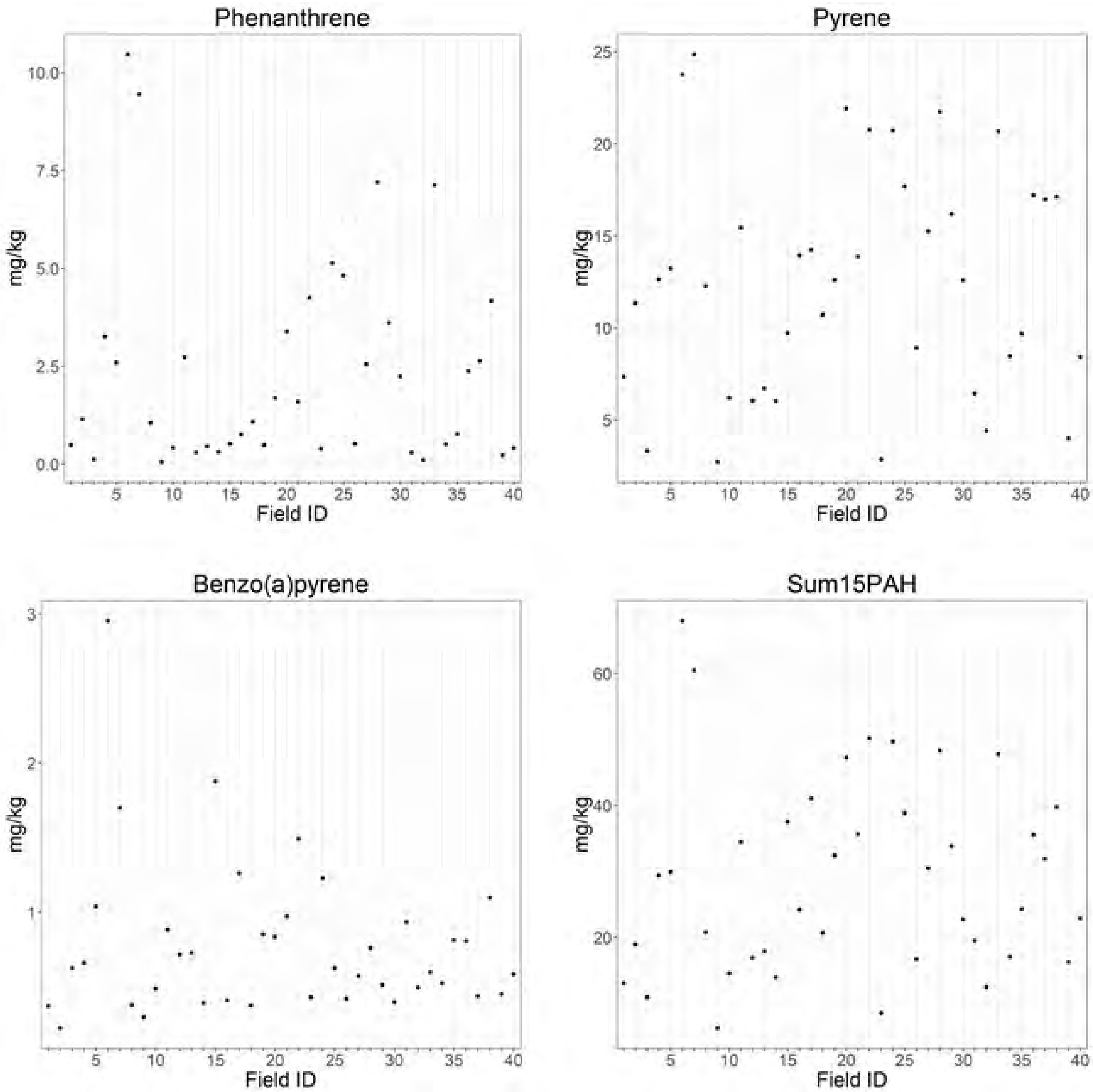

Figure 4-15. GC/MS/MS extract analysis results (mg/kg) for phenanthrene, pyrene, benzo[a]pyrene, and the sum of 15 PAH from tire crumb rubber infill composite samples collected from each synthetic turf field. [GC/MS/MS = Gas chromatography/tandem mass spectrometry; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

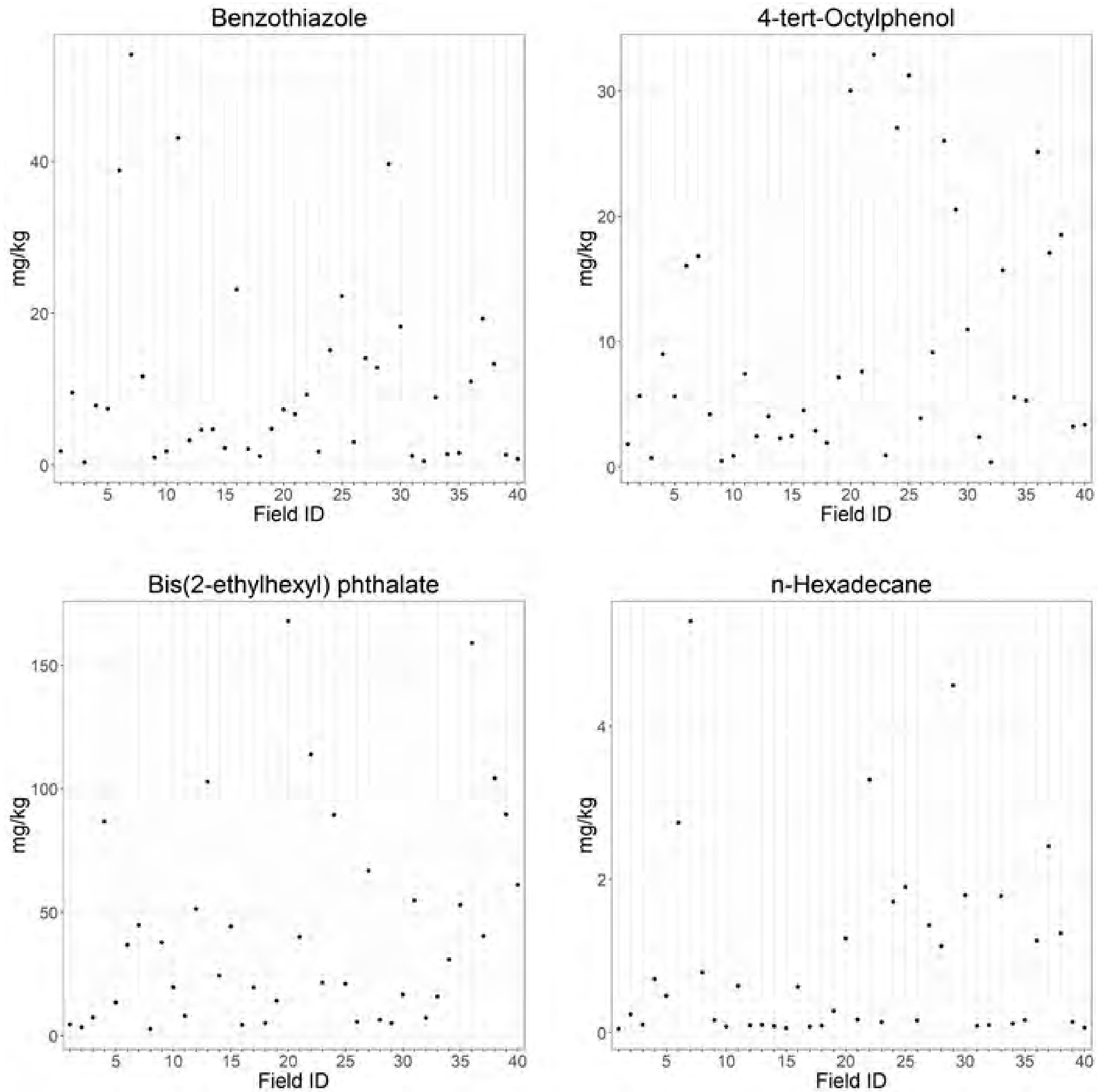

Figure 4-16. GC/MS/MS extract analysis results (mg/kg) for benzothiazole, 4-tert-octylphenol, bis(2-ethylhexyl) phthalate, and n-hexadecane from tire crumb rubber infill composite samples collected from each synthetic turf field. [GC/MS/MS = Gas chromatography/tandem mass spectrometry]

4.6.1.4 SVOCs by LC/TOFMS Analysis

Summary statistics are reported in Table 4-37 for SVOCs analyzed by LC/TOFMS. This analysis was not quantitative based on analysis of target analyte calibration solutions. However, known chemical standards were used to confirm retention times and spectra for these analytes. Results are shown for chromatographic peak area counts to gauge the relative amounts of chemicals present. The analytes 2-hydroxybenzothiazole, cyclohexylamine, di-cyclohexylamine, N-cyclohexyl-N-methylcyclohexanamine, and diisononylphthalate were measured in 100% of the tire crumb rubber infill samples collected at synthetic turf fields. The analytes 2-mercaptobenzothiazole and diisodecylphthalate were measured above the method detection limit in at least 73% of the samples.

Table 4-37. Summary Statistics for Selected SVOCs Analyzed Non-quantitatively by LC/TOFMS in Solvent Extracts for Tire Crumb Rubber Samples Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Collected from Synthetic Turf Fields[a,b,c]

Tire Crumb Rubber Sampling Location	Chemical	n	% > LOD	Mean Area Counts	Area Counts Standard Deviation	% Relative Standard Deviation	10th Percentile Area Counts	25th Percentile Area Counts	50th Percentile Area Counts	75th Percentile Area Counts	90th Percentile Area Counts	Maximum Area Counts
Recycling Plants	2-mercaptobenzothiazole	27	100	1.5E+04	1.8E+04	130	1.1E+03	1.9E+03	4.1E+03	2.8E+04	4.9E+04	5.3E+04
Recycling Plants	2-hydroxybenzothiazole	27	100	3.1E+05	1.1E+05	37	2.0E+05	2.6E+05	3.1E+05	3.7E+05	4.8E+05	5.5E+05
Recycling Plants	cyclohexylamine	27	100	2.1E+06	1.4E+06	70	3.3E+05	6.0E+05	2.2E+06	3.3E+06	3.7E+06	5.6E+06
Recycling Plants	di-cyclohexylamine	27	100	1.4E+07	1.8E+07	130	9.0E+05	1.2E+06	4.3E+06	2.9E+07	4.3E+07	5.8E+07
Recycling Plants	N-cyclohexyl-N-methylcyclohexanamine	27	100	1.9E+06	1.7E+06	94	2.6E+05	5.5E+05	1.0E+06	2.5E+06	4.5E+06	6.6E+06
Recycling Plants	diisononylphthalate	27	96	7.9E+04	1.6E+05	200	-1.3E+04	-1.3E+04	-1.2E+04	1.7E+05	3.2E+05	5.6E+05
Recycling Plants	diisodecylphthalate	27	93	5.5E+03	6.2E+03	110	7.2E+02	1.7E+03	3.1E+03	5.6E+03	1.7E+04	1.9E+04
Synthetic Turf Fields	2-mercaptobenzothiazole	40	73	1.9E+03	3.4E+03	190	< LOD	< LOD	3.1E+02	1.8E+03	6.6E+03	1.5E+04
Synthetic Turf Fields	2-hydroxybenzothiazole	40	100	1.0E+05	1.2E+05	120	1.7E+03	6.9E+03	3.2E+04	1.8E+05	3.1E+05	4.2E+05
Synthetic Turf Fields	cyclohexylamine	40	100	4.9E+05	7.9E+05	160	8.9E+03	2.2E+04	1.2E+05	4.1E+05	2.0E+06	2.7E+06
Synthetic Turf Fields	di-cyclohexylamine	40	100	9.0E+06	8.5E+06	95	4.6E+05	1.4E+06	8.1E+06	1.3E+07	2.2E+07	3.2E+07
Synthetic Turf Fields	N-cyclohexyl-N-methylcyclohexanamine	40	100	2.3E+05	3.0E+05	130	8.1E+03	4.2E+04	1.3E+05	3.7E+05	5.0E+05	1.7E+06
Synthetic Turf Fields	diisononylphthalate	40	100	2.8E+04	9.4E+04	330	-1.1E+04	-9.8E+03	-7.4E+03	8.6E+02	1.8E+05	4.2E+05
Synthetic Turf Fields	diisodecylphthalate	40	85	4.8E+04	2.7E+05	560	< LOD	2.1E+03	4.3E+03	7.5E+03	1.7E+04	1.7E+06

[a] SVOC = Semivolatile organic compound; LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry; LOD = Limit of detection

[b] No quantitative analysis was performed. Chromatographic area counts were reported. Chemical identities and retention times confirmed with purchased chemical standards.

[c] Several results are reported as negative values. This is a result of the subtraction of blank values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.

4.6.2 Chemical Emissions from Tire Crumb Rubber

4.6.2.1 VOC Emission Factors Analysis

Tire crumb rubber from recycling plants and tire crumb rubber infill from synthetic turf fields was quantitatively analyzed for 31 target VOCs by chamber emission testing at 25 °C and at 60 °C with HPLC/UV analysis for formaldehyde and GC/TOFMS analysis for the remainder of the VOC analytes. Emission factor results are reported in units of ng/g/h, which is nanograms of analyte emitted per gram of tire crumb rubber per hour. Some emission factor statistics are reported as negative values; this is because some measurements were below the average chamber background measurements, resulting in slightly negative results following chamber background subtraction.

The target analytes included methyl isobutyl ketone and benzothiazole, which have been previously reported in tire crumb rubber headspace analysis and samples in the air above synthetic turf fields. Other analytes include the BTEX chemicals benzene, toluene, ethylbenzene, the co-eluting m/p-xylenes, and o-xylene. Styrene and 1,3-butadiene were measured as potential chemicals of interest as well, because tires are often constructed with styrene-butadiene rubber (SBR). There is minimal information from previous studies regarding the presence and emissions of styrene and 1,3-butadiene from tire crumb rubber, and it is important to understand the extent that these two elastomer-building monomers might remain present and available for exposure. Formaldehyde was also included since it was previously reported in emissions testing of tire-derived flooring and is reportedly used in tire manufacturing. Many of the other analytes, including chlorinated VOCs and Freon™ chemicals were included on the list as typical chemicals for ambient air monitoring, with some having been reported in previous tire crumb rubber studies.

VOC Emissions at 25 °C –The complete VOC 25 °C emission factor measurement dataset is reported in Appendix I, Table I-9. Nine (9) of the 31 analytes from synthetic turf field tire crumb rubber infill samples were not measured above the method detection limit, with the remainder having between 3 and 100% measurable. Benzothiazole, o-xylene, the sum of BTEX chemicals, trichlorofluoromethane (Freon 11), and dichlorofluoromethane (Freon 12) were the only analytes with > 60% of measurements above the method detection limits. Their average emission factors were 25 ng/g/h, 0.032 ng/g/h, 0.31 ng/g/h, 0.034 ng/g/h, and -0.022 ng/g/h, respectively. Their maximum emission factors were 110 ng/g/h, 0.34 ng/g/h, 2.9 ng/g/h, 1.1 ng/g/h, and 0.056 ng/g/h, respectively. Notably, all formaldehyde measurements were below quantifiable limits for synthetic field tire crumb rubber infill, while 1,3-butadiene and styrene measurements were above quantifiable limits in only a few samples and the emission factors were low for these few samples (≤1.0 ng/g/h). Overall, VOC emission factors were low for most of the target analytes, often below the method detection limit and/or the chamber background levels. Summary statistics are reported in Table 4-38 for 25 °C VOC emission factor measurement results for select analytes.

Table 4-38. Summary Statistics for Selected VOC 25 °C Emission Factors for Tire Crumb Rubber Samples Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Collected from Synthetic Turf Fields[a,b]

Tire Crumb Rubber Sampling Location	Chemical[c]	N	% > LOD	Mean (ng/g/h)	Standard Deviation (ng/g/h)	% Relative Standard Deviation	10th Percentile (ng/g/h)	25th Percentile (ng/g/h)	50th Percentile (ng/g/h)	75th Percentile (ng/g/h)	90th Percentile (ng/g/h)	Maximum (ng/g/h)
Recycling Plants	Formaldehyde	26	11	*	*	*	< LOD	< LOD	< LOD	< LOD	8.8	25
Recycling Plants	Methyl isobutyl ketone	27	96	24	16	65	5.7	14	21	31	48	72
Recycling Plants	Benzothiazole	27	96	150	41	28	93	130	150	180	180	180
Recycling Plants	1,3-Butadiene	27	0	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Recycling Plants	Styrene	27	85	0.31	0.21	69	< LOD	0.16	0.23	0.41	0.70	0.87
Recycling Plants	Benzene	27	44	*	*	*	< LOD	< LOD	< LOD	0.33	0.76	1.4
Recycling Plants	Toluene	27	93	0.39	0.35	91	0.027	0.095	0.24	0.61	0.99	1.3
Recycling Plants	Ethylbenzene	27	41	*	*	*	< LOD	< LOD	< LOD	0.086	0.17	0.27
Recycling Plants	m/p-Xylene	27	96	0.86	0.81	95	0.13	0.32	0.63	1.2	1.6	3.7
Recycling Plants	o-Xylene	27	93	0.21	0.20	93	0.0077	0.095	0.16	0.32	0.45	0.89
Recycling Plants	SumBTEX	27	100	1.7	1.3	77	0.10	0.86	1.5	2.7	3.4	5.4
Synthetic Turf Fields	Formaldehyde	38	0	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Synthetic Turf Fields	Methyl isobutyl ketone	38	58	*	*	*	< LOD	< LOD	0.87	1.4	4.5	20
Synthetic Turf Fields	Benzothiazole	38	63	25	28	110	< LOD	< LOD	15	40	72	110
Synthetic Turf Fields	1,3-Butadiene	38	13	*	*	*	< LOD	< LOD	< LOD	< LOD	0.094	0.23
Synthetic Turf Fields	Styrene	38	21	*	*	*	< LOD	< LOD	< LOD	< LOD	0.30	1.0
Synthetic Turf Fields	Benzene	38	18	*	*	*	< LOD	< LOD	< LOD	< LOD	0.74	2.2
Synthetic Turf Fields	Toluene	38	26	*	*	*	< LOD	< LOD	< LOD	0.081	0.27	0.77
Synthetic Turf Fields	Ethylbenzene	38	26	*	*	*	< LOD	< LOD	< LOD	0.032	0.089	0.48
Synthetic Turf Fields	m/p-Xylene	38	50	*	*	*	< LOD	< LOD	0.0082	0.13	0.21	0.70
Synthetic Turf Fields	o-Xylene	38	76	0.032	0.09	290	< LOD	-0.028	0.0088	0.077	0.14	0.34
Synthetic Turf Fields	SumBTEX	38	89	0.31	0.84	270	< LOD	-0.23	0.044	0.54	1.3	2.9

[a] VOC = Volatile organic compound; LOD = Limit of detection

[b] Several results are reported as negative values. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.

[c] SumBTEX = Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene results.

*Values reported only when % > LOD is ≥ 60%.

VOC Emissions at 60 °C – The complete VOC 60 °C emission factor measurement dataset is reported in Appendix I, Table I-10. Seven (7) of the 31 analytes from synthetic turf field tire crumb rubber infill samples were not measured above the method detection limit, with the remainder having between 3 and 100% measurable. Benzothiazole, methyl isobutyl ketone and formaldehyde had average emission factors of 56 ng/g/h, 42 ng/g/h, and 16 ng/g/h, respectively. Their maximum emission factors were 110 ng/g/h, 96 ng/g/h, and 48 ng/g/h, respectively. Interestingly, the BTEX chemical emission factors were not higher than those in the 25 °C emissions tests and were often below the average chamber background levels. For 1,3-butadiene, measurements were above quantifiable limits in only a few samples, and for both 1,3-butadiene and styrene the emission factors were low (≤ 1.3 ng/g/h). Examples of the emission factor measurement results across the 40 synthetic turf fields are shown in Figure 4-17 for benzothiazole, methyl isobutyl ketone, styrene, and formaldehyde. Summary statistics are reported in Table 4-39 for 60 °C VOC emission factor measurement results for select analytes.

Further comparisons of VOC emission results at the two chamber test temperatures are illustrated and discussed in section 4.8.1.

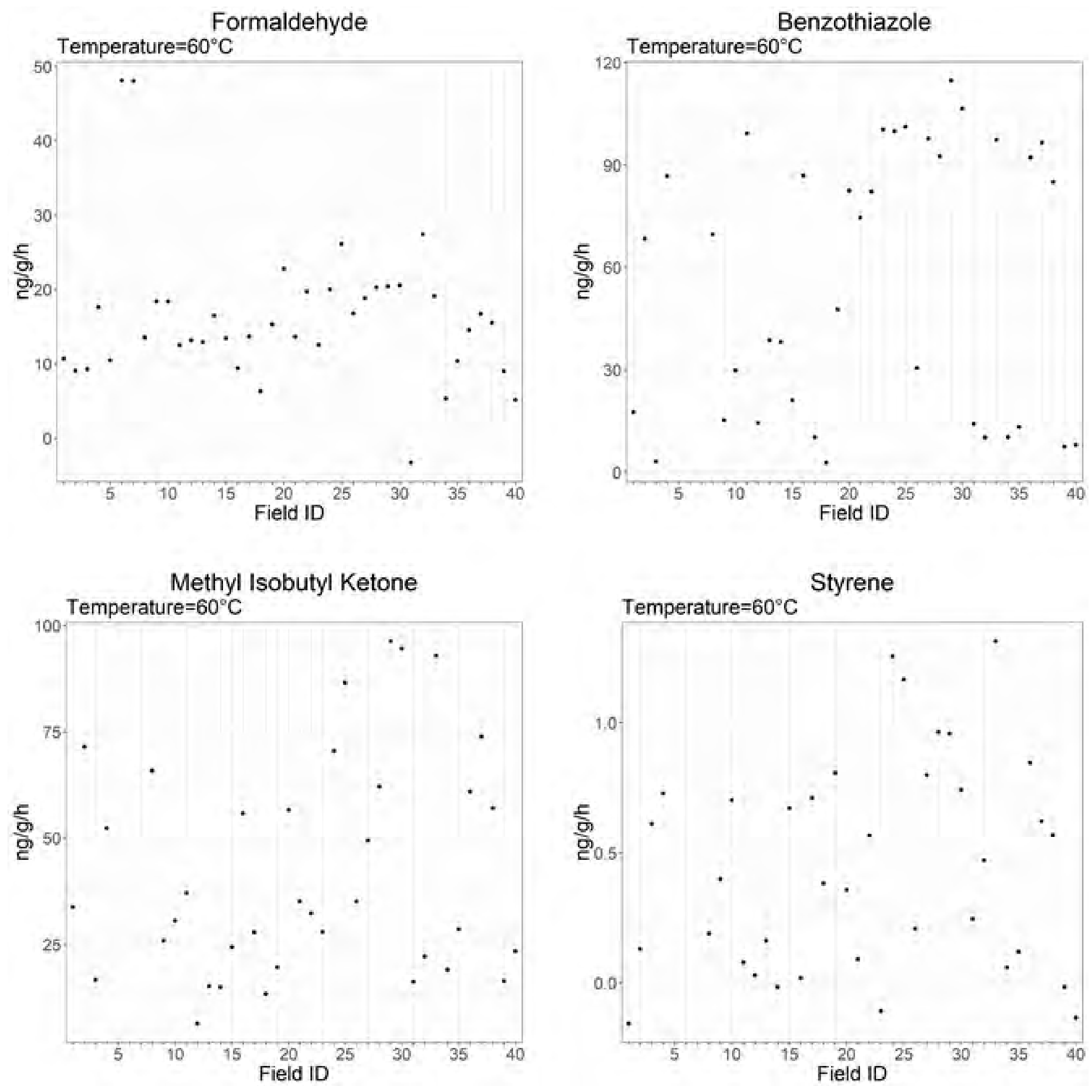

Figure 4-17. VOC 60 °C emission factor results (ng/g/h) for formaldehyde, benzothiazole, methyl isobutyl ketone, and styrene from tire crumb rubber infill composite samples collected from each synthetic turf field. [VOC = Volatile organic compound]

Table 4-39. Summary Statistics for Selected VOC 60 °C Emission Factors for Tire Crumb Rubber Samples Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Collected from Synthetic Turf Fields[a,b]

Tire Crumb Rubber Sampling Location	Chemical[c]	n	% > LOD	Mean (ng/g/h)	Standard Deviation (ng/g/h)	% Relative Standard Deviation	10th Percentile (ng/g/h)	25th Percentile (ng/g/h)	50th Percentile (ng/g/h)	75th Percentile (ng/g/h)	90th Percentile (ng/g/h)	Maximum (ng/g/h)
Recycling Plants	Formaldehyde	27	96	40	16	40	20	24	40	49	62	73
Recycling Plants	Methyl isobutyl ketone	27	100	140	15	11	110	130	130	150	160	160
Recycling Plants	Benzothiazole	27	100	220	8.3	3.7	210	220	220	230	230	240
Recycling Plants	1,3-Butadiene	27	0	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Recycling Plants	Styrene	27	100	1.1	0.58	53	0.33	0.55	1.0	1.6	1.9	2.1
Recycling Plants	Benzene	27	89	0.21	0.45	220	< LOD	-0.098	0.027	0.64	0.92	1.2
Recycling Plants	Toluene	27	100	1.1	0.95	85	0.20	0.30	0.64	1.7	2.6	3.2
Recycling Plants	Ethylbenzene	27	100	-0.0055	0.26	-4800	-0.22	-0.18	-0.13	0.092	0.52	0.68
Recycling Plants	m/p-Xylene	27	100	1.2	0.71	57	0.36	0.60	1.1	1.6	2.1	2.9
Recycling Plants	o-Xylene	27	100	-0.40	0.43	-110	-0.80	-0.73	-0.49	-0.28	0.23	0.79
Recycling Plants	SumBTEX	27	100	2.1	2.2	100	-0.57	0.36	1.9	3.4	5.7	7.7
Synthetic Turf Fields	Formaldehyde	40	75	16	9.5	58	< LOD	11	15	19	24	48
Synthetic Turf Fields	Methyl isobutyl ketone	37	100	42	26	61	15	22	34	61	87	96
Synthetic Turf Fields	Benzothiazole	37	95	56	39	70	8.0	14	68	93	100	110
Synthetic Turf Fields	1,3-Butadiene	37	11	*	*	*	< LOD	< LOD	< LOD	< LOD	0.12	0.81
Synthetic Turf Fields	Styrene	37	100	0.45	0.41	91	-0.016	0.092	0.40	0.73	0.96	1.3
Synthetic Turf Fields	Benzene	37	49	*	*	*	< LOD	< LOD	< LOD	0.21	0.55	0.73
Synthetic Turf Fields	Toluene	37	100	0.15	0.31	200	-0.15	-0.048	0.07	0.22	0.72	0.91
Synthetic Turf Fields	Ethylbenzene	37	100	-0.082	0.22	-270	-0.33	-0.27	-0.16	0.14	0.28	0.40
Synthetic Turf Fields	m/p-Xylene	37	100	0.24	1.0	410	-0.96	-0.58	0.16	0.73	1.7	2.5
Synthetic Turf Fields	o-Xylene	37	100	-0.35	0.66	-190	-0.99	-0.88	-0.44	-0.024	0.61	1.5
Synthetic Turf Fields	SumBTEX	37	100	-0.085	2.2	-2600	-2.5	-2.3	-0.40	0.94	3.3	4.6

[a] VOC = Volatile organic compound; LOD = Limit of detection

[b] Several results are reported as negative values. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.

[c] SumBTEX = Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene results.

*Values reported only when % >LOD is ≥ 60%.

4.6.2.2 SVOC Emission Factors Analysis

Tire crumb rubber from recycling plants and tire crumb rubber infill from synthetic turf fields was quantitatively analyzed for 39 target SVOCs by chamber emission testing at 25 °C and at 60 °C with GC/MS/MS analysis, and non-quantitatively for 10 target SVOCs at 60 °C with LC/TOFMS analysis. Emission factor results are reported in units of ng/g/h, which is nanograms of analyte per gram of tire crumb rubber per hour. Some emission factor statistics are reported as negative values; this is because some measurements were below the average chamber background measurements, resulting in slightly negative results following chamber background subtraction.

SVOC Emissions at 25 °C – The complete SVOC 25 °C emission factor measurement dataset is reported in Appendix I, Table I-13. Six of the 39 analytes from synthetic turf field tire crumb rubber infill samples were not measured above the method detection limit, with the remainder having between 3 and 100% measurable. Eighteen of the analytes had > 60% of measurements above the method detection limits. Average emission factors for benzothiazole, 4-tert-octylphenol and the sum of 15 PAH compounds were 4.2 ng/g/h, 0.85 ng/g/h, and 0.62 ng/g/h, respectively. Their maximum emission factors were 19 ng/g/h, 16 ng/g/h, and 3.1 ng/g/h, respectively. Overall, SVOC emission factors were low for most of the target analytes, often below the method detection limit and/or the chamber background levels. Summary statistics are reported in Table 4-40 for 25 °C SVOC emission factor measurement results for selected analytes measured by GC/MS/MS.

SVOC Emissions at 60 °C – The complete SVOC 60 °C emission factor measurement dataset is reported in Appendix I, Table I-14. Seven of the 39 analytes from synthetic turf field tire crumb rubber infill samples were not measured above the method detection limit, with the remainder having between 3 and 100% measurable. Twenty-five of the analytes had > 60% of measurements above the method detection limits. Average emission factors for benzothiazole, 4-tert-octylphenol, pyrene, and the sum of 15 PAH compounds were 34, 5.8, 0.29 and 2.0 ng/g/h, respectively. Their maximum emission factors were 220, 21, 0.89 and 9.4 ng/g/h, respectively. Emission factors for the five- and six-ring PAH compounds (e.g., benzo[a]pyrene, benzo(a)pyrene, benzo(k)fluoranthene, coronene) were rarely above the method detection limits. Summary statistics are reported in Table 4-41 for 60 °C SVOC emission factor measurement results measured by GC/MS/MS for select analytes. Examples of the emission factor measurement results across the 40 synthetic turf fields are shown in Figure 4-18 for pyrene, the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol.

Table 4-40. Summary Statistics for Select SVOC 25 °C Emission Factors for Tire Crumb Rubber Samples Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Collected at Synthetic Turf Fields[a,b]

Tire Crumb Rubber Sampling Location	Chemical[c]	n	% > LOD	Mean (ng/g/h)	Standard Deviation (ng/g/h)	% Relative Standard Deviation	10th Percentile (ng/g/h)	25th Percentile (ng/g/h)	50th Percentile (ng/g/h)	75th Percentile (ng/g/h)	90th Percentile (ng/g/h)	Maximum (ng/g/h)
Recycling Plants	Phenanthrene	27	100	-0.0071	0.07	-980	-0.12	-0.02	0.014	0.037	0.051	0.087
Recycling Plants	Fluoranthene	27	22	*	*	*	< LOD	< LOD	< LOD	< LOD	0.0074	0.024
Recycling Plants	Pyrene	27	22	*	*	*	< LOD	< LOD	< LOD	< LOD	0.01	0.034
Recycling Plants	Benzo[a]pyrene	27	0	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Recycling Plants	Benzo[ghi]perylene	27	0	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Recycling Plants	Sum15PAH	27	100	2.3	1.1	46	0.84	1.2	2.3	3.2	3.7	4.2
Recycling Plants	Benzothiazole	27	100	41	26	65	16	20	38	52	65	140
Recycling Plants	Dibutyl phthalate	27	100	-0.021	0.67	-3200	-0.50	-0.36	-0.067	0.14	0.44	2.9
Recycling Plants	Aniline	27	100	3.5	2.0	58	0.42	2.0	4.1	4.7	6.4	6.9
Recycling Plants	4-tert-octylphenol	27	100	0.47	0.25	52	0.21	0.31	0.42	0.63	0.80	1.3
Synthetic Turf Fields	Phenanthrene	40	100	0.025	0.049	200	-0.015	-0.00032	0.018	0.043	0.093	0.15
Synthetic Turf Fields	Fluoranthene	40	28	*	*	*	< LOD	< LOD	< LOD	0.0034	0.0085	0.016
Synthetic Turf Fields	Pyrene	40	20	*	*	*	< LOD	< LOD	< LOD	< LOD	0.011	0.04
Synthetic Turf Fields	Benzo[a]pyrene	40	0	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Synthetic Turf Fields	Benzo[ghi]perylene	40	3	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	0.02
Synthetic Turf Fields	Sum15PAH	40	100	0.62	0.63	100	0.23	0.27	0.34	0.72	1.2	3.1
Synthetic Turf Fields	Benzothiazole	40	100	4.2	5.2	120	0.043	0.49	1.8	5.3	12	19
Synthetic Turf Fields	Dibutyl phthalate	40	100	-0.011	0.38	-3500	-0.50	-0.20	-0.044	0.20	0.54	0.83
Synthetic Turf Fields	Aniline	40	88	0.34	0.45	130	< LOD	-0.0026	0.16	0.53	1.1	1.5
Synthetic Turf Fields	4-tert-octylphenol	40	85	0.85	3.3	390	< LOD	-0.00074	0.082	0.23	0.43	16

[a] SVOC = Semivolatile organic compound; LOD = Limit of detection
[b] Several results are reported as negative values. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.
[c] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene.

*Values reported only when % >LOD is ≥ 60%.

Table 4-41. Summary Statistics for Select SVOC 60 °C Emission Factors for Tire Crumb Rubber Samples Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Collected from Synthetic Turf Fields[a,b]

Tire Crumb Rubber Sampling Location	Chemical[c]	n	% > LOD	Mean (ng/g/h)	Standard Deviation (ng/g/h)	% Relative Standard Deviation	10th Percentile (ng/g/h)	25th Percentile (ng/g/h)	50th Percentile (ng/g/h)	75th Percentile (ng/g/h)	90th Percentile (ng/g/h)	Maximum (ng/g/h)
Recycling Plants	Phenanthrene	26	100	0.83	0.34	41	0.4	0.63	0.76	1.0	1.3	1.6
Recycling Plants	Fluoranthene	26	100	0.16	0.054	33	0.11	0.12	0.15	0.20	0.25	0.27
Recycling Plants	Pyrene	26	100	0.34	0.072	22	0.23	0.28	0.34	0.40	0.44	0.45
Recycling Plants	Benzo[a]pyrene	26	0	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Recycling Plants	Benzo[ghi]perylene	26	4	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	0.013
Recycling Plants	Sum15PAH	26	100	13	7	56	4.8	7.6	13	16	18	38
Recycling Plants	Benzothiazole	26	100	520	340	66	220	290	400	690	950	1500
Recycling Plants	Dibutyl phthalate	26	100	0.21	0.72	350	-0.49	0.014	0.085	0.34	0.95	3
Recycling Plants	Aniline	26	100	23	7.2	31	18	19	21	25	34	46
Recycling Plants	4-tert-octylphenol	26	100	20	8.8	43	14	15	18	23	35	47
Synthetic Turf Fields	Phenanthrene	40	100	0.58	0.71	120	0.035	0.069	0.29	0.89	1.4	3.1
Synthetic Turf Fields	Fluoranthene	40	98	0.16	0.11	73	0.046	0.068	0.12	0.23	0.33	0.46
Synthetic Turf Fields	Pyrene	40	98	0.29	0.21	73	0.083	0.15	0.22	0.40	0.62	0.89
Synthetic Turf Fields	Benzo[a]pyrene	40	0	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Synthetic Turf Fields	Benzo[ghi]perylene	40	0	*	*	*	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Synthetic Turf Fields	Sum15PAH	40	100	2.0	1.9	93	0.55	0.70	1.5	2.7	3.7	9.4
Synthetic Turf Fields	Benzothiazole	40	100	34	50	150	1.9	3.1	18	34	120	220
Synthetic Turf Fields	Dibutyl phthalate	40	100	0.14	0.41	290	-0.3	-0.15	0.073	0.38	0.63	1.5
Synthetic Turf Fields	Aniline	40	100	3.5	5.1	150	0.12	0.26	0.81	3.8	11	22
Synthetic Turf Fields	4-tert-octylphenol	40	98	5.8	5.5	94	0.50	1.2	5.1	9.1	14	21

[a] SVOC = Semivolatile organic compound; LOD = Limit of detection

[b] Several results are reported as negative values. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.

[c] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene.

*Values reported only when % >LOD is ≥ 60%.

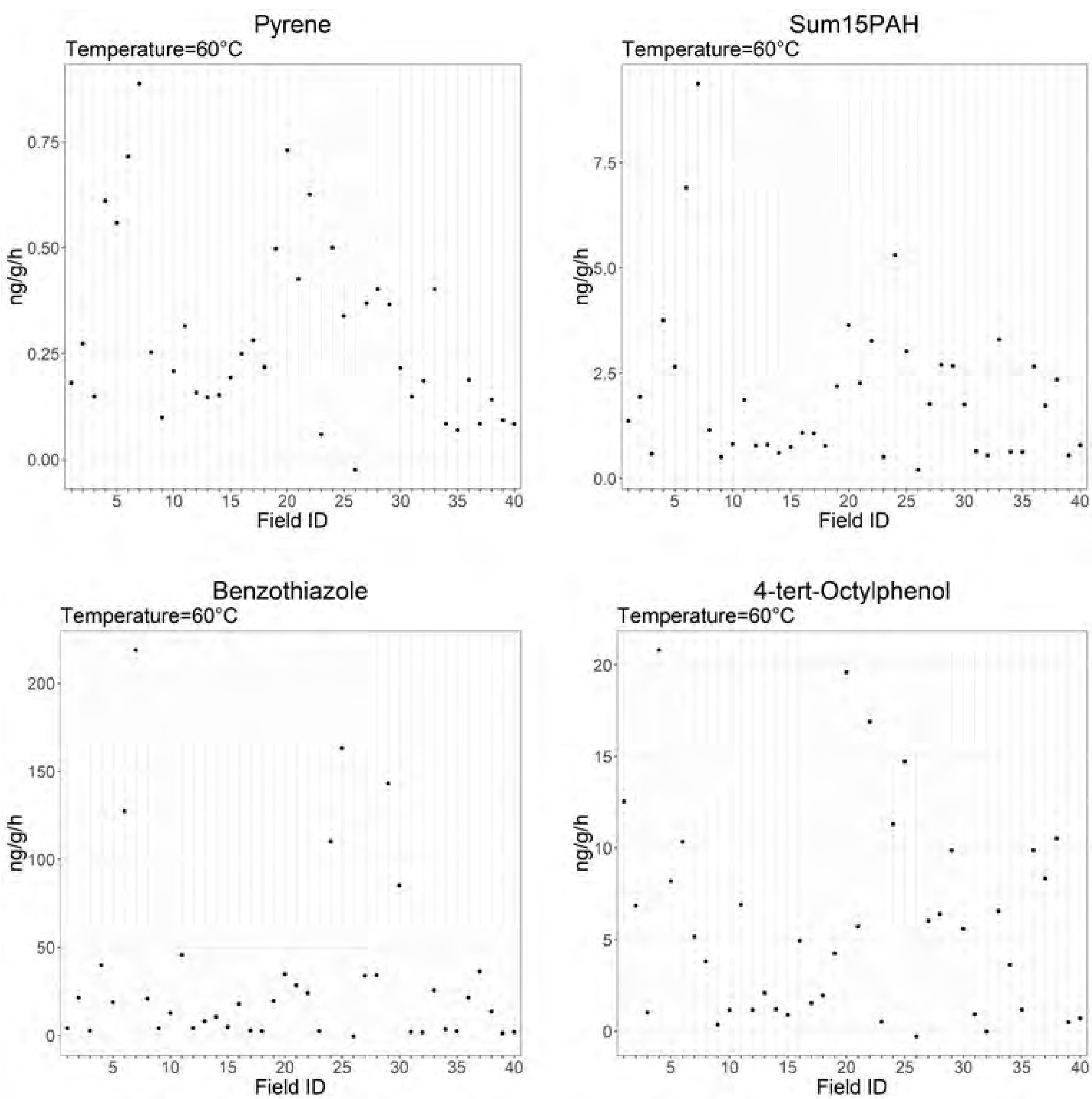

Figure 4-18. SVOC 60 °C emission factor results (ng/g/h) for pyrene, the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol from tire crumb rubber infill composite samples collected from each synthetic turf field. [SVOC = Semivolatile organic compound; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

Summary statistics are reported in Table 4-42 for 60 °C SVOC emission factor measurement results for selected analytes measured by LC/TOFMS. These analyses were non-quantitative and are based on chromatographic area counts. Six analytes were not reported; 2-mercaptobenzothiazole because it was not measured in the emission samples, and diisononyl phthalate, diisodecyl phthalate, di(2-ethyhexyl) adipate, phthalimide, and resorcinol because they were not distinguishable from chamber background levels. Two remaining analytes, 2-hydroxybenzothiazole and N-cyclohexyl-N-methylcyclohexanamine, were measurable in fewer than 60% of the samples. Cyclohexylamine and di-cyclohexylamine were measurable in 100% and 93% of the samples, respectively.

Benzothiazole was analyzed in both VOC and SVOC emissions testing. Higher maximum levels were observed for the SVOC testing than for the VOC testing. The VOC upper benzothiazole emission rates may be underestimated due to approaching the upper calibration limits during analysis. Differences may also be a result of testing in two different chamber systems with different characteristics. The small chambers used for VOC testing had greater chamber wall surface area than did the microchambers used for SVOC testing, possibly resulting in wall adsorption effects in the VOC chamber tests.

Further comparisons of SVOC emission results at the two temperatures are illustrated and discussed in section 4.8.2.

Table 4-42. Summary Statistics for Select SVOC 60 °C Emission Samples Analyzed Non-quantitatively by LC/TOFMS for Tire Crumb Rubber Samples Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Collected from Synthetic Turf Fields[a,b,c]

Tire Crumb Rubber Sampling Location	Chemical	n	% > LOD	Mean Area Counts	Area Counts Standard Deviation	% Relative Standard Deviation	10th Percentile Area Counts	25th Percentile Area Counts	50th Percentile Area Counts	75th Percentile Area Counts	90th Percentile Area Counts	Maximum Area Counts
Recycling Plants	N-cyclohexyl-N-methylcyclohexanamine	27	96	1.9E+04	4.6E+04	250	-2.7E+01	2.5E+00	5.0E+02	1.1E+04	5.7E+04	1.9E+05
Recycling Plants	2-hydroxybenzothiazole	27	78	5.0E+02	8.5E+02	170	< LOD	2.0E+02	2.4E+02	5.8E+02	1.2E+03	4.4E+03
Recycling Plants	Cyclohexylamine	27	100	3.4E+05	2.8E+05	83	5.1E+04	1.5E+05	2.6E+05	4.4E+05	6.8E+05	1.2E+06
Recycling Plants	Di-cyclohexylamine	27	100	7.3E+05	1.3E+06	180	6.8E+04	1.2E+05	2.3E+05	5.5E+05	3.7E+06	4.8E+06
Synthetic Turf Fields	N-cyclohexyl-N-methylcyclohexanamine	40	55	*	*	*	< LOD	< LOD	0.0E+00	6.2E+01	4.5E+02	3.2E+03
Synthetic Turf Fields	2-hydroxybenzothiazole	40	40	*	*	*	< LOD	< LOD	< LOD	3.0E+02	7.9E+02	1.3E+03
Synthetic Turf Fields	Cyclohexylamine	40	100	2.4E+04	6.3E+04	260	-8.4E+03	-5.6E+03	6.2E+02	2.5E+04	6.8E+04	3.3E+05
Synthetic Turf Fields	Di-cyclohexylamine	40	93	1.2E+05	2.3E+05	180	-7.1E+02	-3.0E+02	7.6E+02	1.1E+05	4.8E+05	9.2E+05

[a] SVOC = Semivolatile organic compound; LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry; LOD = Limit of detection

[b] No quantitative analysis was performed. Chromatographic area counts were reported. Chemical identities and retention times confirmed with purchased chemical standards.

[c] Several results are reported as negative values. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.

*Values reported only when % >LOD is ≥ 60%.

4.6.3 Comparison of Total Infill vs. Sand Corrected Results

Sand is sometimes used as a base layer or as a mixture with tire crumb rubber in synthetic turf fields. Sand and other crustal materials may also be present at fields from windborne deposition and track-in by field users. As stated previously, 16 of the 40 fields in this study had sand in the tire crumb rubber infill samples. The average sand content among the infill samples collected from the surface of those sixteen fields was 19.2% by weight (range 0.33 to 53.3%; Figure 4-3).

Chemical analysis measurement results included in this report have not been adjusted for sand fraction in the synthetic turf field infill. This decision was based on two factors – a) the results not corrected for sand are likely to be a better metric for exposure assessment, and b) the report would become unreasonably lengthy if both uncorrected and corrected results were presented.

It is, however, useful to provide examples showing the potential differences between using results that are not corrected for sand content versus results that are corrected for sand content. Results corrected for sand content reflect the amount of target analyte per amount of tire crumb rubber in the infill. Table 4-43 shows summary statistic results for select metals using measurements not corrected and corrected for infill sand content. Overall, the results for the mean and median statistics are similar, with differences typically < 15%. The maximum sand corrected result for zinc was 26,000 mg/kg as compared to the uncorrected result of 22,000 mg/kg. Figure 4-19 presents the uncorrected and corrected distribution of results graphically for chromium, cobalt, lead, and zinc.

Table 4-43. Summary Statistics for Select Metals Analyzed by ICP/MS in Tire Crumb Rubber Infill Samples Collected from Synthetic Turf Fields, With and Without Correction for Infill Sand Content[a]

Correction Type	Chemical	n	% > LOD	Mean (mg/kg)	Standard Deviation (mg/kg)	% Relative Standard Deviation	10th Percentile (mg/kg)	25th Percentile (mg/kg)	50th Percentile (mg/kg)	75th Percentile (mg/kg)	90th Percentile (mg/kg)	Maximum (mg/kg)
Without sand correction	Arsenic	40	100	0.38	0.20	52	0.19	0.26	0.34	0.45	0.60	1.1
Without sand correction	Cadmium	40	100	0.95	0.68	72	0.49	0.57	0.70	1.1	1.7	4.2
Without sand correction	Chromium	40	100	1.6	0.84	51	0.97	1.2	1.6	1.9	2.7	3.7
Without sand correction	Cobalt	40	100	140	60	44	68	85	120	180	220	290
Without sand correction	Lead	40	100	24	26	110	9.3	11	14	25	55	160
Without sand correction	Zinc	40	100	15000	3000	20	11000	13000	14000	16000	19000	22000
With sand correction	Arsenic	40	100	0.43	0.25	59	0.19	0.28	0.34	0.60	0.76	1.3
With sand correction	Cadmium	40	100	1.1	0.74	71	0.53	0.61	0.78	1.3	1.9	4.2
With sand correction	Chromium	40	100	1.8	0.98	53	0.99	1.2	1.8	2.4	3.1	4.2
With sand correction	Cobalt	40	100	150	73	48	73	92	130	210	250	320
With sand correction	Lead	40	100	26	27	100	9.9	12	14	28	59	160
With sand correction	Zinc	40	100	16000	4000	24	13000	14000	15000	19000	23000	26000

[a] ICP/MS = Inductively coupled plasma/mass spectrometry; LOD = Limit of detection

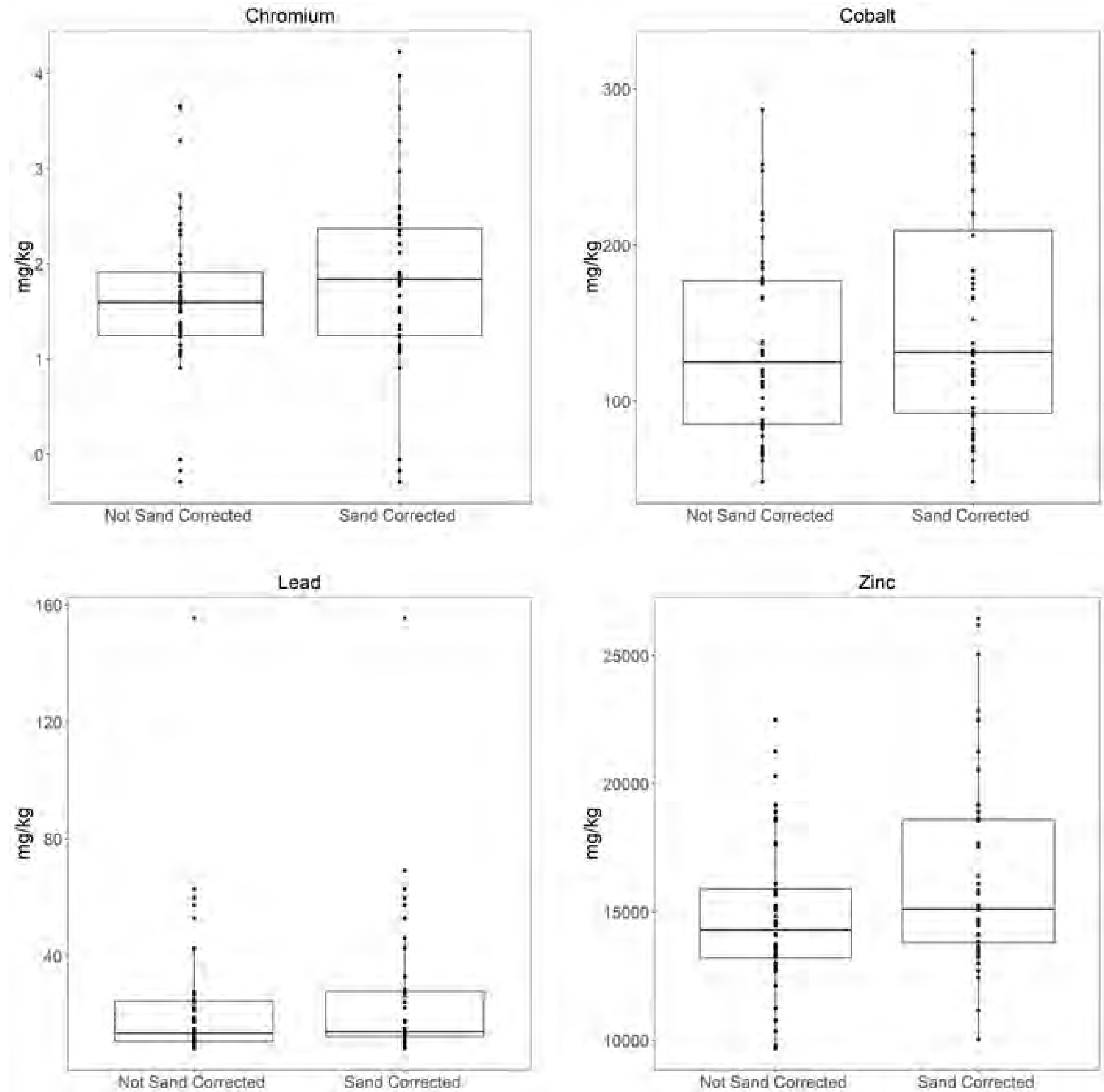

Figure 4-19. Distributions of select metals analyzed by ICP/MS in tire crumb rubber infill samples collected from synthetic turf fields, with and without correction for infill sand content. [ICP/MS = Inductively coupled plasma/mass spectrometry]

Table 4-44 shows summary statistic results for select SVOCs from solvent extract GC/MS/MS analysis using measurements not corrected and corrected for infill sand content. Overall, the results for the mean values are typically < 10% different and the median values are typically < 20% different. The maximum sand corrected result for the sum of 15 PAHs was 71 mg/kg as compared to the uncorrected result of 68 mg/kg. Figure 4-20 presents the uncorrected and corrected distribution of results graphically for pyrene, benzothiazole, the sum of 15 PAHs, and 4-tert-octylphenol.

Differences between not corrected and corrected results are relatively small for the overall statistics in this study because only 40% of the fields had sand in the infill and because the average sand fraction was only 19%. However, for the field that had a sand fraction of 53%, the sand fraction corrected results would be approximately 50% higher than the not corrected results. The impact in other studies that might have more combined rubber + sand infill samples or higher fractions of sand in the infill could be larger than the relatively modest impact for this study.

Table 4-44. Summary Statistics for Select SVOCs Analyzed by GC/MS/MS in Solvent Extracts for Tire Crumb Rubber Infill Samples, With and Without Correction for Infill Sand Content[a]

Correction Type	Chemical[b]	n	% > LOD	Mean (mg/kg)	Standard Deviation (mg/kg)	% Relative Standard Deviation	10th Percentile (mg/kg)	25th Percentile (mg/kg)	50th Percentile (mg/kg)	75th Percentile (mg/kg)	90th Percentile (mg/kg)	Maximum (mg/kg)
Without sand correction	Phenanthrene	40	100	2.3	2.6	110	0.26	0.44	1.1	3.3	6.1	10
Without sand correction	Fluoranthene	40	100	4.5	2.6	57	2.0	2.4	3.9	6.5	8.1	10
Without sand correction	Pyrene	40	100	12	6.2	49	4.2	7.0	13	17	21	25
Without sand correction	Benzo[a]pyrene	40	100	0.78	0.52	66	0.38	0.43	0.62	0.91	1.4	3.0
Without sand correction	Benzo[ghi]perylene	40	100	1.3	0.64	49	0.47	0.64	1.4	1.8	2.0	2.8
Without sand correction	Sum15PAH	40	100	29	15	51	13	17	27	38	49	68
Without sand correction	Benzothiazole	40	100	11	13	120	1.1	1.8	7.0	14	31	54
Without sand correction	Dibutyl phthalate	40	100	1.5	1.5	100	0.054	0.26	0.97	2.3	3.5	6.6
Without sand correction	Bis(2-ethylhexyl) phthalate	40	100	43	42	100	4.9	7.8	28	58	100	170
Without sand correction	Aniline	40	100	0.67	0.53	79	0.16	0.27	0.57	0.96	1.2	2.4
Without sand correction	4-tert-octylphenol	40	100	9.8	9.7	99	0.90	2.5	5.6	16	27	33
Without sand correction	n-Hexadecane	40	100	0.94	1.3	130	0.079	0.10	0.26	1.3	2.6	5.4
With sand correction	Phenanthrene	40	100	2.4	2.6	110	0.27	0.51	1.1	3.5	6.1	11
With sand correction	Fluoranthene	40	100	4.8	2.5	52	2.0	2.7	4.6	6.6	8.3	10
With sand correction	Pyrene	40	100	13	6.0	45	5.2	8.6	14	17	22	25
With sand correction	Benzo[a]pyrene	40	100	0.84	0.52	62	0.40	0.50	0.75	1.0	1.4	3.1

Table 4-44 Continued

Correction Type	Chemical[b]	n	% > LOD	Mean (mg/kg)	Standard Deviation (mg/kg)	% Relative Standard Deviation	10th Percentile (mg/kg)	25th Percentile (mg/kg)	50th Percentile (mg/kg)	75th Percentile (mg/kg)	90th Percentile (mg/kg)	Maximum (mg/kg)
With sand correction	Benzo[ghi]perylene	40	100	1.4	0.64	46	0.51	0.87	1.6	1.9	2.1	2.8
With sand correction	Sum15PAH	40	100	31	14	46	14	19	31	39	49	71
With sand correction	Benzothiazole	40	100	11	13	120	1.3	2.0	7.0	14	31	54
With sand correction	Dibutyl phthalate	40	100	1.6	1.6	100	0.061	0.29	1.0	2.4	3.9	6.6
With sand correction	Bis(2-ethylhexyl) phthalate	40	100	45	43	95	4.9	12	33	61	100	170
With sand correction	Aniline	40	100	0.71	0.54	75	0.2	0.28	0.61	0.98	1.3	2.4
With sand correction	4-tert-octylphenol	40	100	10	9.8	96	1.3	2.8	5.9	17	27	35
With sand correction	n-Hexadecane	40	100	0.99	1.3	130	0.084	0.14	0.26	1.5	2.6	5.4

[a] SVOC = Semivolatile organic compound; GC/MS/MS = Gas chromatography/tandem mass spectrometry; LOD = Limit of detection

[b] Sum15PAH = Sum of 15 of the 16 EPA ‘priority’ PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

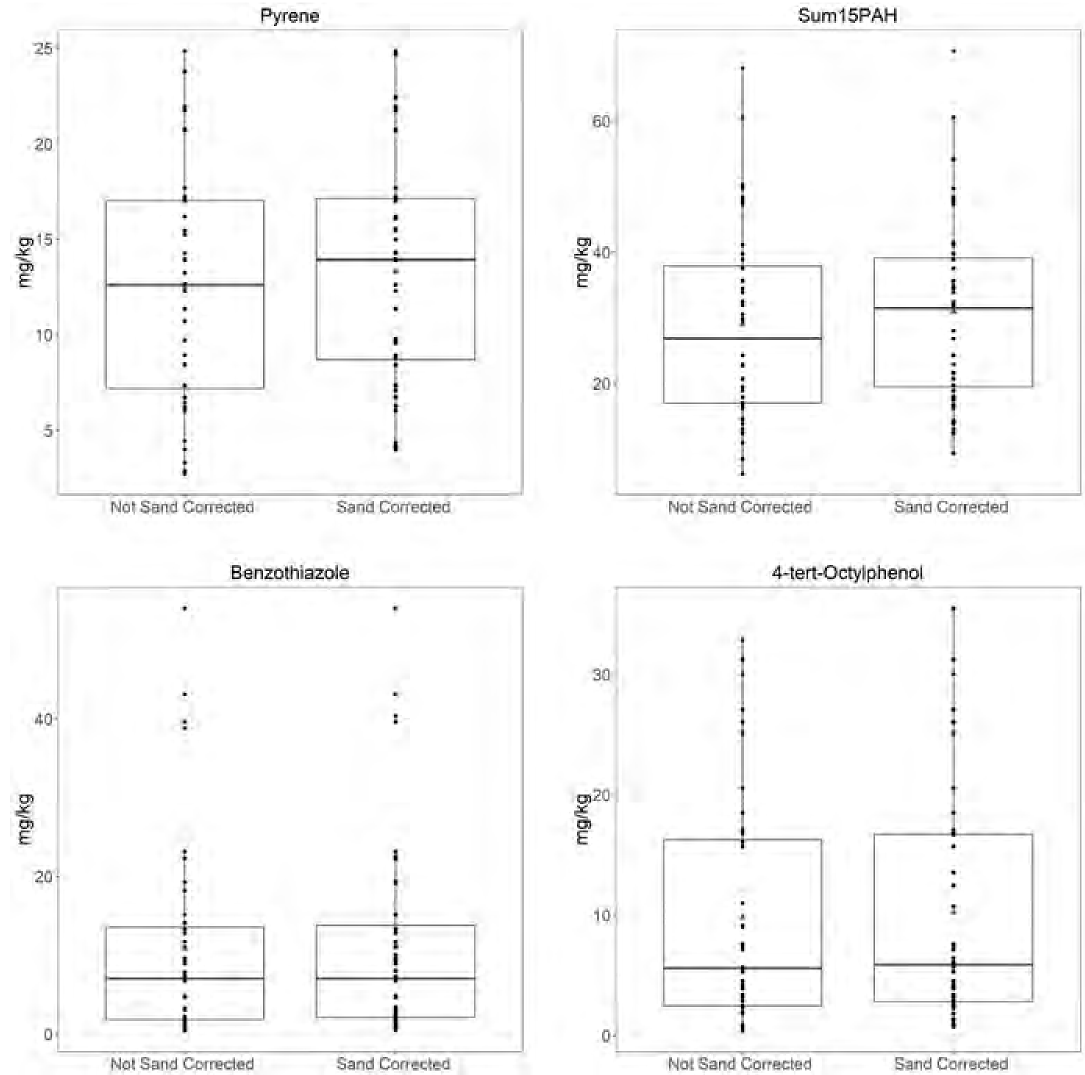

Figure 4-20. Distributions of select SVOCs in solvent extracts analyzed by GC/MS/MS from tire crumb rubber infill samples collected from synthetic turf fields, with and without correction for infill sand content. [SVOC = Semivolatile organic compound; GC/MS/MS = Gas chromatography/tandem mass spectrometry; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

4.7 Comparison of Recycling Plants and Synthetic Turf Fields

Comparisons were performed of chemical measurements in tire crumb rubber samples from recycling plants and tire crumb rubber infill collected from synthetic turf fields. These comparisons are designed to provide information about differences in the presence and amounts of specific chemicals in 'fresh' tire crumb material from recycling plants and the chemicals found in the synthetic turf field infill to help determine:

- Whether there are chemicals appearing in synthetic turf field infill that may have sources other than the tire rubber material, and
- Whether there are differences in chemical concentrations that may be attributable to losses or removal of chemicals over time following installation at the fields.

Comparison results are reported here for a subset of the chemical substances selected for highlighting, with complete results for all target analytes shown in Appendix K. Results for the following analysis types are included in this reporting sub-section:

- Metals analyzed by ICP/MS
- Metals analyzed by XRF
- SVOCs analyzed in solvent extracts by GC/MS/MS
- SVOCs non-quantitative analysis of solvent extracts by LC/TOFMS
- VOC emission factors from analysis by GC/TOFMS
- SVOC emission factors from analysis by GC/MS/MS
- SVOC non-quantitative emission results from analysis by LC/TOFMS

4.7.1 Direct Tire Crumb Rubber Measurements

4.7.1.1 Metals by ICP/MS and XRF

Table 4-45 shows results for mean concentrations of selected target metal analytes for recycling plants and synthetic turf fields. Results are shown for both the ICP/MS analysis and the XRF analysis. Examples of the measurement results and comparisons between recycling plant samples and synthetic turf field samples are shown in Figure 4-21 for chromium, cobalt, lead, and zinc.

Examples of average measurement results for samples collected at recycling plants vs. synthetic turf fields include lead (13 vs. 24 mg/kg), zinc (17,000 vs. 15,000 mg/kg), cobalt (190 vs. 140 mg/kg), and chromium (1.8 vs. 1.6 mg/kg).

Table 4-45. Comparison of Selected Metal Analysis Results Between Tire Rubber Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Composite Samples from Synthetic Turf Fields[a]

Analysis[b]	Analyte	Recycling Plants Mean (mg/kg)	Recycling Plants Standard Deviation (mg/kg)	Synthetic Turf Fields Mean (mg/kg)	Synthetic Turf Fields Standard Deviation (mg/kg)	t-test p-value[c]
ICP/MS Analysis	Arsenic	0.30	0.088	0.38	0.20	0.2261
ICP/MS Analysis	Cadmium	0.55	0.13	0.95	0.68	0.0002
ICP/MS Analysis	Chromium	1.8	0.70	1.6	0.84	NR[d]
ICP/MS Analysis	Cobalt	190	87	140	60	0.0056
ICP/MS Analysis	Lead	13	10	24	26	0.0060
ICP/MS Analysis	Zinc	17000	3500	15000	3000	0.0063
XRF Analysis	Chromium	15	4.0	14	2.9	0.0702
XRF Analysis	Cobalt	58	35	39	17	0.0208
XRF Analysis	Lead	35	8.6	36	22	0.4630
XRF Analysis	Zinc	39000	8800	33000	7100	0.0019

[a] Recycling Plants (n=27); Synthetic Turf Fields (n=40)

[b] ICP/MS = Inductively coupled plasma/mass spectrometry; XRF = X-ray fluorescence spectrometry

[c] Statistical tests performed using ln-transformed measurement values.

[b] NR = Not Reported; one or more measurement results were ≤0, precluding ln-transformed testing for the complete data set.

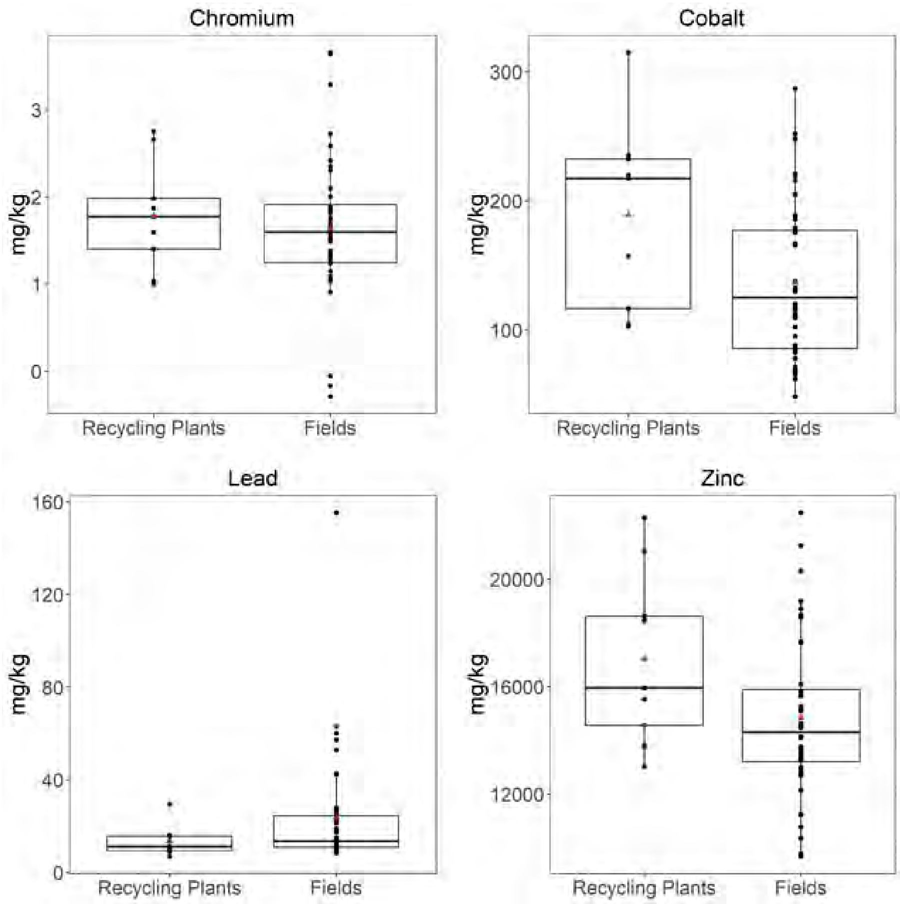

Figure 4-21. Comparison of ICP/MS metal analysis results (mg/kg) between tire crumb rubber collected from tire recycling plants and tire crumb rubber infill composite samples from synthetic turf fields for chromium, cobalt, lead, and zinc. [ICP/MS = Inductively coupled plasma/mass spectrometry]

The reason that lead was found, on average, at higher levels on fields compared to ‘fresh’ material coming from recycling plants is not certain. Possible explanations include higher levels of lead in tires in earlier years compared to tires being recycled in 2016 (although no literature citations could be identified to support this), atmospheric deposition or transport from nearby soils, track-in by field users, presence in and release from other synthetic turf field materials, or from trace contamination of chemical treatments applied to the synthetic fields.

When considering these comparisons, it is important to recognize that recycling plant samples were 100% tire crumb rubber while, on average, the synthetic turf field infill contained 19% sand in this study. As noted in section 4.6.3, the results for sand corrected synthetic turf field infill measurements (perhaps a more direct comparison of tire crumb rubber) would have been about modestly higher (≤ 15%) on average.

4.7.1.2 SVOCs by GC/MS/MS

Table 4-46 shows results for mean concentrations of select target SVOCs analyzed by GC/MS/MS in solvent extracts of samples collected from recycling plants and synthetic turf fields. Examples of mean measurement results for samples collected at recycling plants versus synthetic turf fields include pyrene (18 vs. 12 mg/kg), benzo[a]pyrene (0.74 vs. 0.78 mg/kg), benzothiazole (79 vs. 11 mg/kg), 4-tert-octylphenol (30 vs. 9.8 mg/kg) and bis(2-ethylhexyl) phthalate (12 vs. 43 mg/kg).

Many analytes on the more volatile end of the SVOC spectrum (e.g. aniline, hexadecane, benzothiazole, phenanthrene) were found at higher levels, on average, in ‘fresh’ material from recycling plants compared to levels found in synthetic turf fields. The likely explanation for the differences includes volatilization from the rubber on the fields over time and, possibly, rain- or irrigation-driven leaching for compounds with a higher degree of water solubility (e.g. aniline, benzothiazole, 4-tert-octylpheonol). Water-based leaching has been demonstrated in the laboratory for several tire crumb rubber-associated analytes, including some metals and several more water-soluble organic, but with less evidence for PAH analytes (see *Literature Review/Gaps Analysis* report in Appendix C). Many of the less volatile SVOC analytes, including the five and six-ring PAH chemicals, showed little to no difference between average concentrations in recycling plant samples compared to synthetic turf field samples. However, it is also possible that differences in concentrations between recycling plant and field infill samples could be a result of differences in the original concentrations of chemicals in tires at different times. Longitudinal studies at individual fields would be needed to confirm that weathering effects are primarily responsible for these differences.

Examples of the measurement results and comparisons between recycling plant samples and synthetic turf field samples are shown in Figures 4-22 through 4-23 for eight select SVOCs analyzed by GC/MS/MS.

When considering these comparisons, it is important to recognize that recycling plant samples were 100% tire crumb rubber while, on average, the synthetic turf field infill contained 19% sand in this study. As noted in section 4.6.3, the results for sand corrected synthetic turf field infill measurements (perhaps a more direct comparison of tire crumb rubber) would have been modestly higher (≤ 10%) on average.

Table 4-46. Comparison of Select SVOC GC/MS/MS Analysis Results Between Tire Rubber Solvent Extracts for Samples Collected from Tire Recycling Plants and Synthetic Turf Fields[a,b]

Analyte[c]	Recycling Plants Mean (mg/kg)	Recycling Plants Standard Deviation (mg/kg)	Synthetic Turf Fields Mean (mg/kg)	Synthetic Turf Fields Standard Deviation (mg/kg)	t-test p-value[d]
Phenanthrene	3.6	1.3	2.3	2.6	< 0.0001
Fluoranthene	6.1	1.7	4.5	2.6	0.001
Pyrene	18	2.4	12	6.2	< 0.0001
Benzo[a]pyrene	0.74	0.39	0.78	0.52	0.9556
Benzo[ghi]perylene	1.3	0.59	1.3	0.64	0.5983
Sum15PAH	41	8.9	29	15	< 0.0001
Benzothiazole	79	19	11	13	< 0.0001
Dibutyl phthalate	0.68	0.44	1.5	1.5	0.6508
Bis(2-ethylhexyl) phthalate	12	14	43	42	< 0.0001
Aniline	3.8	1.8	0.67	0.53	< 0.0001
4-tert-octylphenol	30	6.2	9.8	9.7	< 0.0001
n-Hexadecane	3.6	1.8	0.94	1.3	< 0.0001

[a] SVOC = Semivolatile organic compound; GC/MS/MS = Gas chromatography/tandem mass spectrometry

[b] Recycling Plants (n=27); Synthetic Turf Fields (n=40)

[c] Sum15PAH = Sum of 15 of the 16 EPA ‘priority’ PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

[d] Statistical tests performed using ln-transformed measurement values.

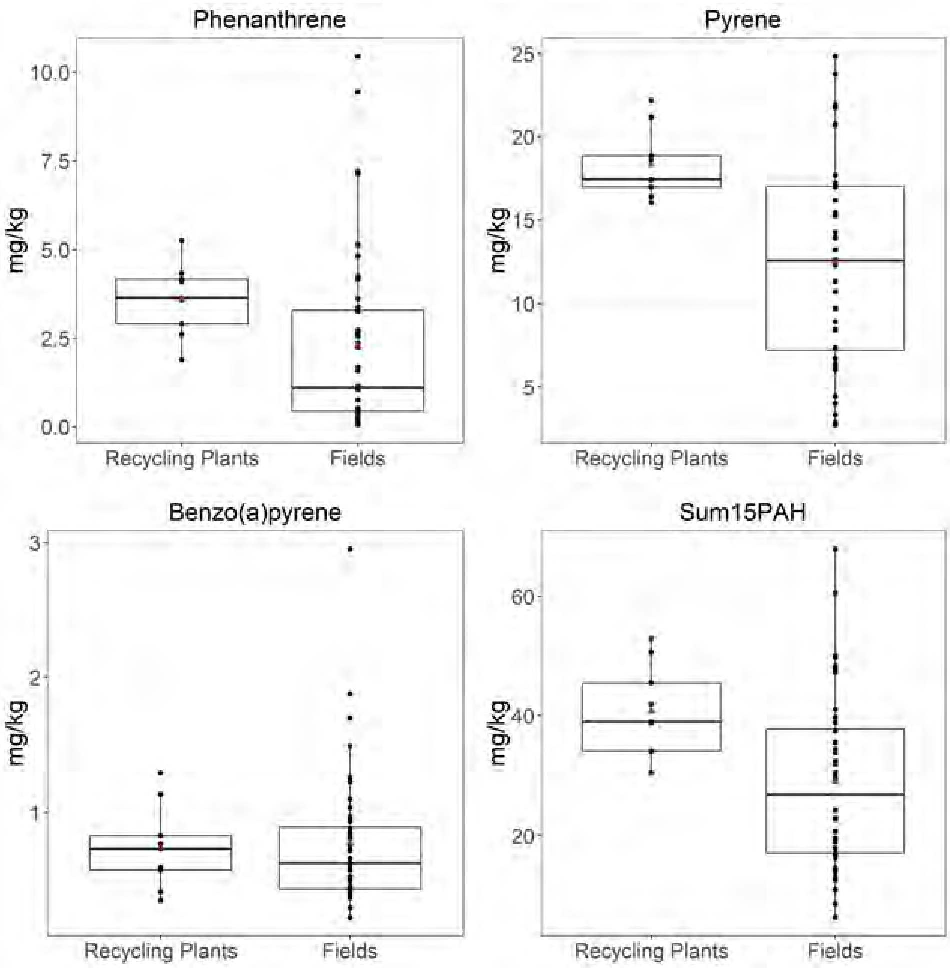

Figure 4-22. Comparison of GC/MS/MS extract SVOC analysis results (mg/kg) between tire crumb rubber collected from tire recycling plants and tire crumb rubber infill composite samples from synthetic turf fields for phenanthrene, pyrene, benzo[a]pyrene, and the sum of 15 PAHs. [SVOC = Semivolatile organic compound; GC/MS/MS = Gas chromatography/ tandem mass spectrometry; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

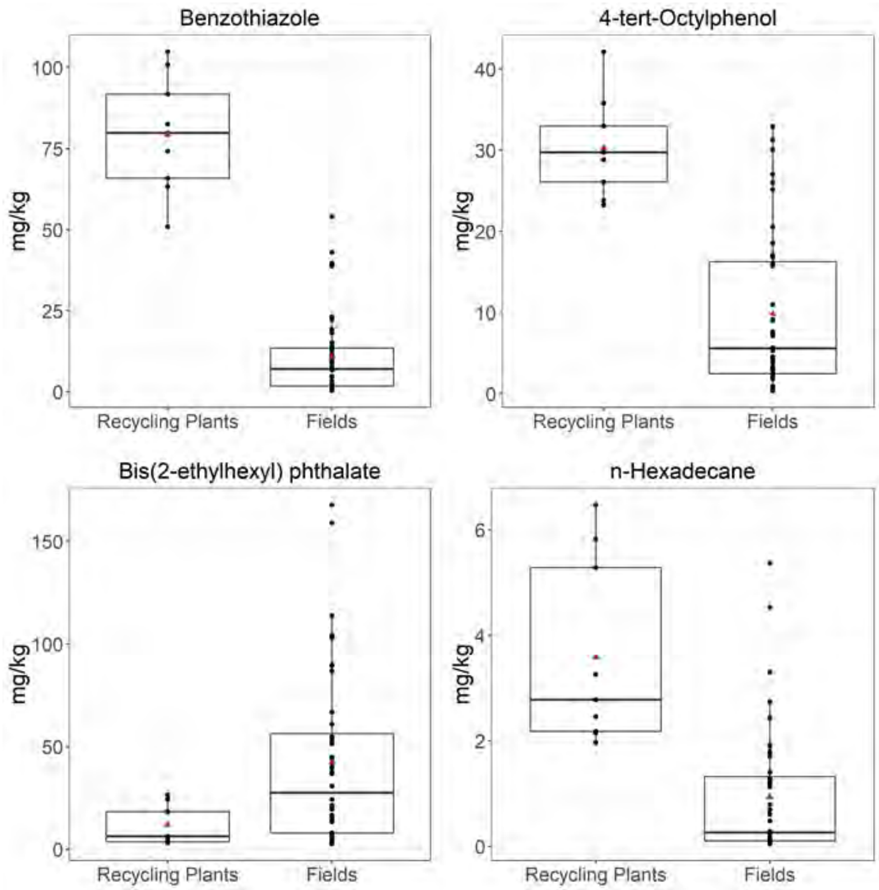

Figure 4-23. Comparison of GC/MS/MS extract SVOC analysis results (mg/kg) between tire crumb rubber collected from tire recycling plants and tire crumb rubber infill composite samples from synthetic turf fields for benzothiazole, 4-tert-octylphenol, bis(2-ethylhexyl) phthalate, and n-hexadecane. [SVOC = Semivolatile organic compound; GC/MS/MS = Gas chromatography/tandem mass spectrometry]

Several phthalate chemicals were found, on average, at higher levels on fields compared to 'fresh' material coming from recycling plants. Benz(a)anthracene and the unresolved mixture of indeno[1,2,3-cd]pyrene and dibenzo[a,h]anthracene (DBA + ICDP) were also found at higher average levels in synthetic field samples compared to recycling plant samples (Appendix K, Table K-3). Higher levels of phthalates at fields could result from atmospheric deposition; track-in by field users or releases from shoes, clothing or other personal products; presence in and release from other synthetic turf field materials; or from chemical treatments applied to fields.

4.7.1.3 SVOCs by LC/TOFMS

Seven additional target SVOCs were analyzed by LC/TOFMS following solvent exchange from the extracts used for GC/MS/MS analyses. While these analyses were not performed quantitatively, valuable non-quantitative results based on chromatographic peak areas were obtained. The three cyclohexylamine compounds, 2-mercaptobenzothiazole, and 2-hydroxybenzothiazole followed the pattern of having higher amounts in recycling plant tire crumb rubber versus synthetic field tire crumb rubber infill (Table 4-47). Diisononyl phthalate was present at somewhat higher levels in recycling plant samples compared to synthetic turf field samples, while the reverse was true for diisodecyl phthalate. Table 4-47 shows non-quantitative results for target SVOCs in solvent extracts analyzed by LC/TOFMS and Figure 4-24 provides examples of the measurement results and comparisons between recycling plant samples and synthetic turf field samples for four select SVOCs.

Table 4-47. Comparison of Select SVOC LC/TOFMS Non-quantitative Analysis Results Between Tire Rubber Solvent Extracts for Samples Collected from Tire Recycling Plants and Synthetic Turf Fields[a,b]

Analyte[c]	Recycling Plants Mean Area Counts	Recycling Plants Area Counts Standard Deviation	Synthetic Turf Fields Mean Area Counts	Synthetic Turf Fields Area Counts Standard Deviation	t-test p-value[d]
2-mercaptobenzothiazole	1.5E+04	1.8E+04	1.9E+03	3.4E+03	NR
2-hydroxybenzothiazole	3.1E+05	1.1E+05	1.0E+05	1.2E+05	NR
Cyclohexylamine	2.1E+06	1.4E+06	4.9E+05	7.9E+05	NR
Di-cyclohexylamine	1.4E+07	1.8E+07	9.0E+06	8.5E+06	0.5898
N-cyclohexyl-N-methylcyclohexanamine	1.9E+06	1.7E+06	2.3E+05	3.0E+05	< 0.0001
Diisononylphthalate	7.9E+04	1.6E+05	2.8E+04	9.4E+04	NR
Diisodecylphthalate	5.5E+03	6.2E+03	4.8E+04	2.7E+05	NR

[a] SVOC = Semivolatile organic compound; LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry

[b] Recycling Plants (n=27); Synthetic Turf Fields (n=40)

[c] Statistical tests performed using ln-transformed measurement values.

[d] NR = Not Reported; one or more measurement results were ≤0, precluding ln-transformed testing for the complete data set.

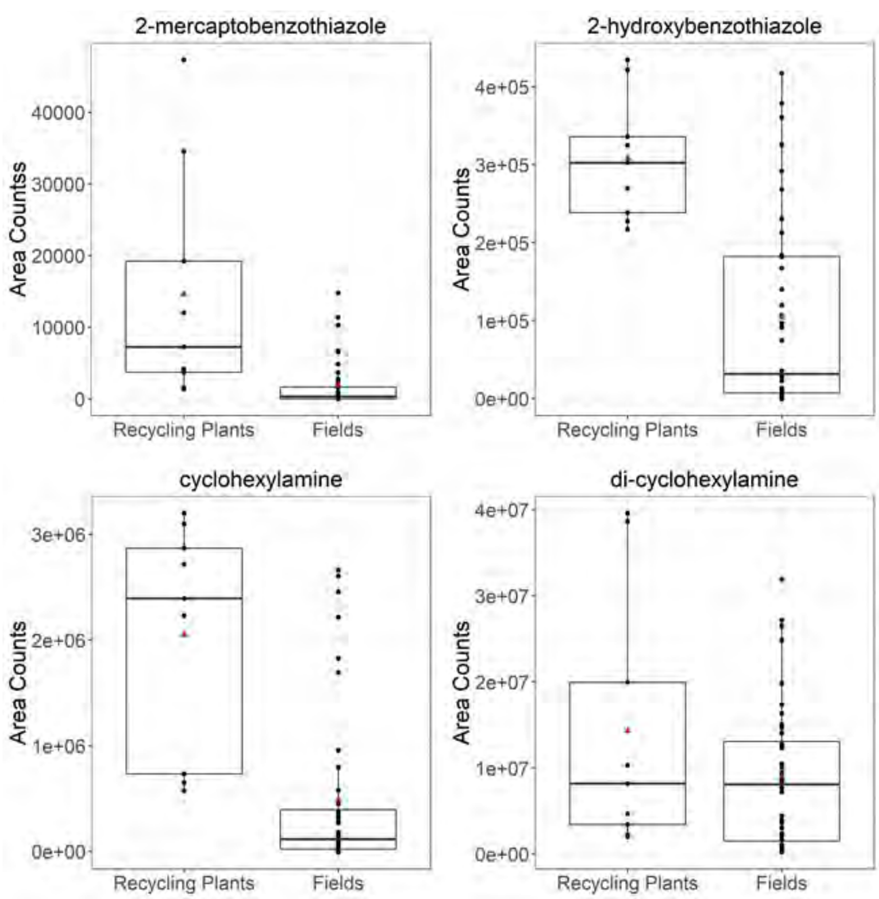

Figure 4-24. Comparison of LC/TOFMS positive ionization extract SVOC non-quantitative analysis results (chromatographic area counts) between tire crumb rubber collected from tire recycling plants and tire crumb rubber infill composite samples from synthetic turf fields for 2-mercaptobenzothiazole, 2-hydroxybenzothiazole, cyclohexylamine, and di-cyclohexylamine. [SVOC = Semivolatile organic compound; LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry]

4.7.2 *Chemical Emissions from Tire Crumb Rubber*

4.7.2.1 VOCs Emission Factors

Table 4-48 shows select target VOC mean emission factors at 25 °C and 60 °C for samples collected from recycling plants and synthetic turf fields. Emission factors at 25 °C were higher for VOCs in recycling plant samples versus synthetic turf fields. For example, mean benzothiazole emission factors were 6 times higher, and the sum of BTEX compounds 5.5 times higher. Emission factors at 60 °C were higher for VOCs in recycling plant samples versus synthetic turf fields. For example, mean methyl isobutyl ketone emission factors were 3.3 time higher, benzothiazole 3.9 times higher, formaldehyde 2.5 times higher, and styrene 2.4 times higher. Examples of the measurement results and comparisons between recycling plant samples and synthetic turf field samples are shown in Figure 4-25 for methyl isobutyl ketone, benzothiazole, styrene, and formaldehyde for the 60 °C emissions results.

Many VOC analytes showed higher emission factors, on average, in ‘fresh’ material from recycling plants compared to levels found in synthetic turf fields. The likely explanation for the difference is the volatilization from the rubber on the fields over time; however, longitudinal studies at individual fields would be needed to confirm this.

Table 4-48. Comparison of Select VOC Emission Factor Results Between Tire Rubber Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Composite Samples from Synthetic Turf Fields[a,b,c]

Emissions Test	Analyte[d]	Recycling Plants Mean (ng/g/h)	Recycling Plants Standard Deviation (ng/g/h)	Synthetic Turf Fields Mean (ng/g/h)	Synthetic Turf Fields Standard Deviation (ng/g/h)	t-test p-value[e,f]
Emission Factors at 25 °C	Benzothiazole	150	41	25	28	NR
Emission Factors at 25 °C	o-Xylene	0.21	0.20	0.032	0.090	NR
Emission Factors at 25 °C	SumBTEX	1.7	1.3	0.31	0.84	NR
Emission Factors at 60 °C	Formaldehyde	40	16	16	9.5	NR
Emission Factors at 60 °C	Methyl isobutyl ketone	140	15	42	26	< 0.0001
Emission Factors at 60 °C	Benzothiazole	220	8.3	56	39	< 0.0001
Emission Factors at 60 °C	Styrene	1.1	0.58	0.45	0.41	NR
Emission Factors at 60 °C	Toluene	1.1	0.95	0.15	0.31	NR
Emission Factors at 60 °C	Ethylbenzene	-0.0055	0.26	-0.082	0.22	NR
Emission Factors at 60 °C	m/p-Xylene	1.2	0.71	0.24	1.0	NR
Emission Factors at 60 °C	o-Xylene	-0.40	0.43	-0.35	0.66	NR
Emission Factors at 60 °C	SumBTEX	2.1	2.2	-0.085	2.2	NR

[a] VOC = Volatile organic compound

[b] Recycling Plants (n=27); Synthetic Turf Fields (n=38 for emissions tests at 25 °C; n=37 for emissions tests at 60 °C, with exception of formaldehyde at n=40)

[c] Several results are reported as negative values. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results

[d] SumBTEX = Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene results.

[e] Statistical tests performed using ln-transformed measurement values.

[f] NR = Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

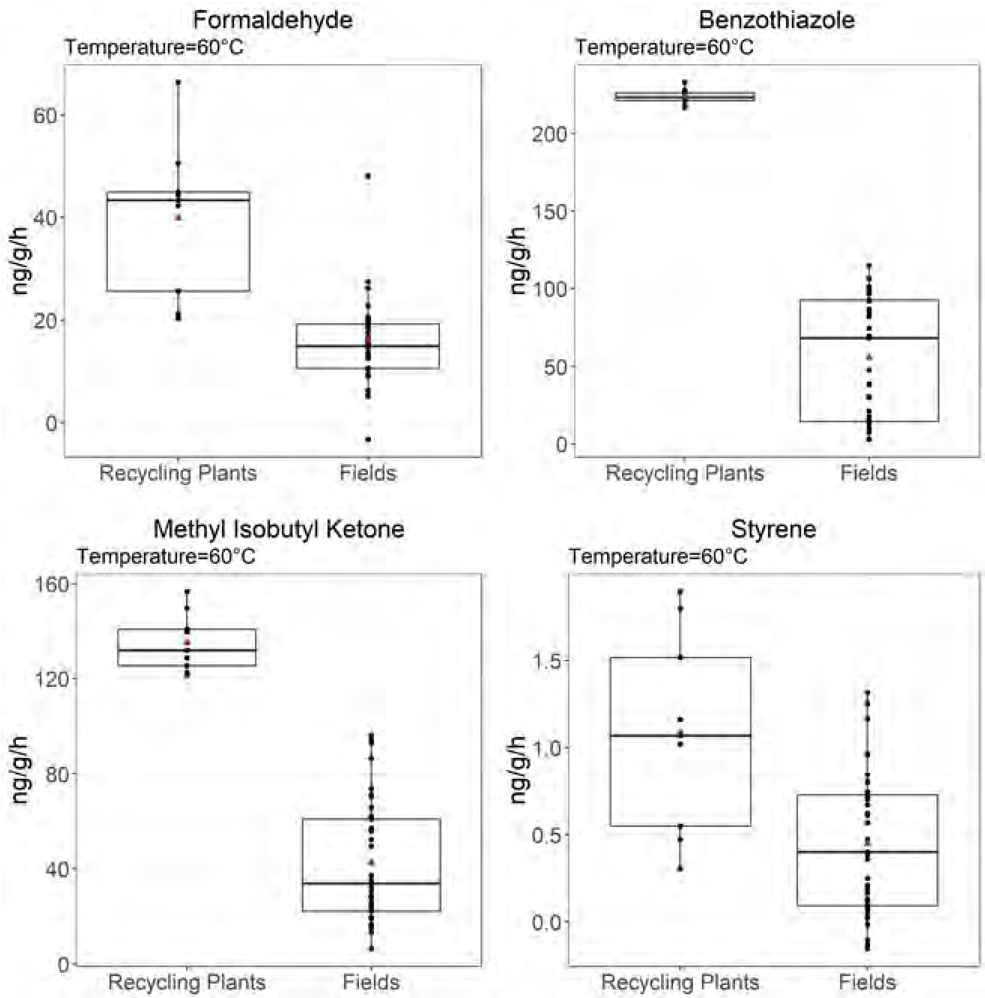

Figure 4-25. Comparison of VOC 60 °C emission factor results (ng/g/h) between tire crumb rubber collected from tire recycling plants and tire crumb rubber infill composite samples from synthetic turf fields for formaldehyde, benzothiazole, methyl isobutyl ketone, and styrene. [VOC = Volatile organic compound]

4.7.2.2 SVOC Emission Factors

Table 4-49 shows select target SVOC mean emission factors at 25 °C and 60 °C for samples collected from recycling plants and synthetic turf fields. Emission factors at 25 °C were higher for some SVOCs in recycling plant samples versus synthetic turf fields. For example, mean benzothiazole emission factors were 9.8 times higher and aniline was 10 times higher. Emission factors at 60 °C were higher for most SVOCs in recycling plant samples versus synthetic turf fields. For example, mean benzothiazole emission factors were 15 time higher, aniline was 6.6 times higher, and 4-tert-octylphenol was 3.4 times higher.

Examples of the 60 °C emission measurement results and comparisons between recycling plant samples and synthetic turf field samples are shown in Figure 4-26 for pyrene, the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol.

Table 4-49. Comparison of Select SVOC Emission Factor Results Between Tire Rubber Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Composite Samples from Synthetic Turf Fields[a,b,c]

Emissions Test	Analyte[d]	Recycling Plants Mean (ng/g/h)	Recycling Plants Standard Deviation (ng/g/h)	Synthetic Turf Fields Mean (ng/g/h)	Synthetic Turf Fields Standard Deviation (ng/g/h)	t-test p-value[e,f]
Emission Factors at 25 °C	Phenanthrene	-0.0071	0.07	0.025	0.049	NR
Emission Factors at 25 °C	Sum15PAH	2.3	1.1	0.62	0.63	< 0.0001
Emission Factors at 25 °C	Benzothiazole	41	26	4.2	5.2	NR
Emission Factors at 25 °C	Dibutyl phthalate	-0.021	0.67	-0.011	0.38	NR
Emission Factors at 25 °C	Aniline	3.5	2.0	0.34	0.45	NR
Emission Factors at 25 °C	4-tert-octylphenol	0.47	0.25	0.85	3.3	NR
Emission Factors at 60 °C	Phenanthrene	0.83	0.34	0.58	0.71	NR
Emission Factors at 60 °C	Fluoranthene	0.16	0.054	0.16	0.11	NR
Emission Factors at 60 °C	Pyrene	0.34	0.072	0.29	0.21	NR
Emission Factors at 60 °C	Sum15PAH	13	7.0	2.0	1.9	< 0.0001
Emission Factors at 60 °C	Benzothiazole	520	340	34	50	NR
Emission Factors at 60 °C	Dibutyl phthalate	0.21	0.72	0.14	0.41	NR
Emission Factors at 60 °C	Aniline	23	7.2	3.5	5.1	NR
Emission Factors at 60 °C	4-tert-octylphenol	20	8.8	5.8	5.5	NR

[a] SVOC = Semivolatile organic compound

[b] Recycling Plants (n=27 for emissions tests at 25 °C; n=26 for emissions tests at 60 °C); Synthetic Turf Fields (n=40)

[c] Several results are reported as negative values. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.

[d] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

[e] Statistical tests performed using ln-transformed measurement values.

[f] NR = Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

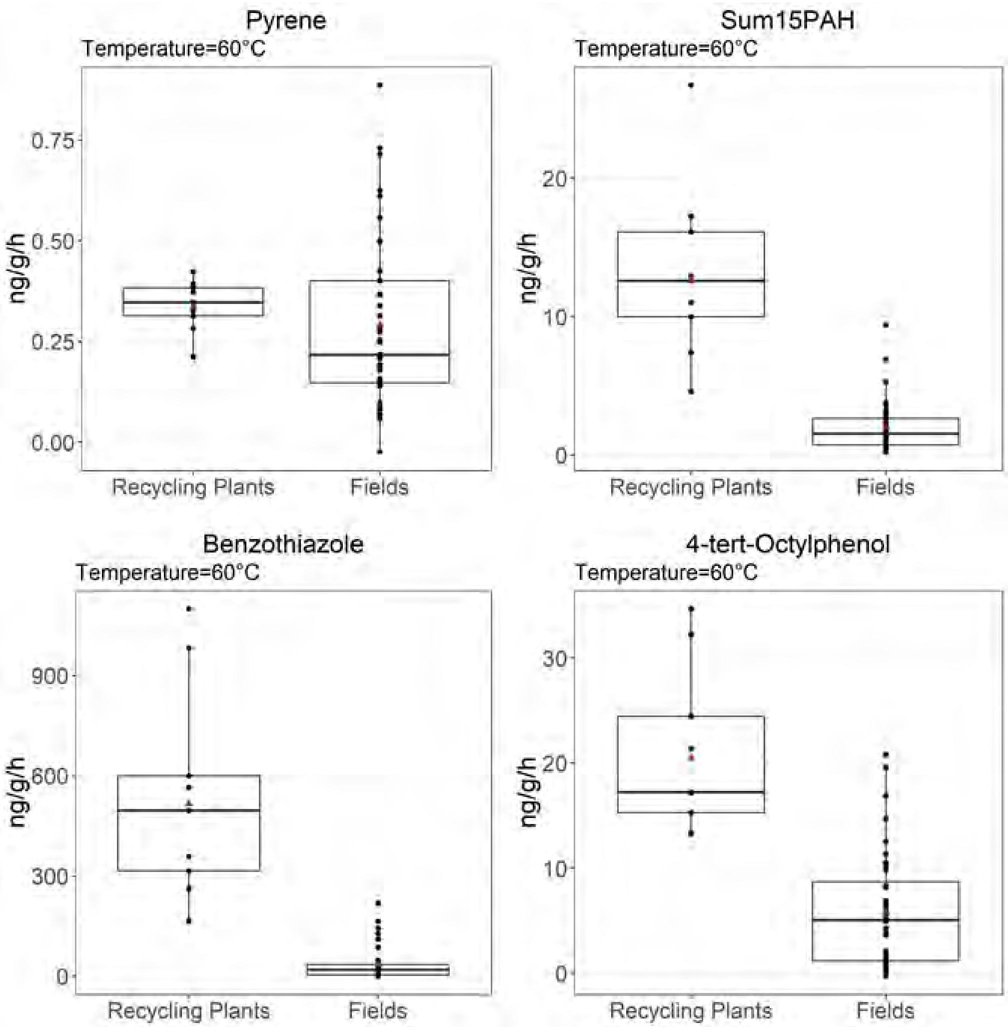

Figure 4-26. Comparison of SVOC 60 °C emission factor results (ng/g/h) between tire crumb rubber collected from tire recycling plants and tire crumb rubber infill composite samples from synthetic turf fields for pyrene, the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol. [SVOC = Semivolatile organic compound; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

4.8 Comparison of Emission Factors at 25 °C and 60 °C

Comparisons were performed for chemical emission measurements obtained at two different temperatures for tire crumb rubber samples from recycling plants and tire crumb rubber infill collected from synthetic turf fields. These comparisons are designed to provide information about differences in emission factors that may be temperature dependent.

The 25 °C and 60 °C measurement results were previously reported as part of the summary statistics sub-section (section 4.6.2). Temperature comparison results are reported here using graphical representations to illustrate important differences. Results for the following analysis types are included in this reporting subsection:

- VOC 25 °C and 60 °C emission factors from analysis by GC/TOFMS
- SVOC 25 °C and 60 °C emission factors from analysis by GC/MS/MS

4.8.1 VOC Emission Factors

Differences in 25 °C and 60 °C emission factor distributions for formaldehyde, benzothiazole, methyl isobutyl ketone, and styrene are shown in Figures 4-27 and 4-28 for tire crumb rubber samples collected at tire recycling plants and tire crumb rubber infill samples collected at synthetic turf fields, respectively. These target VOC analytes showed higher emission factors in emission experiments performed at 60 °C than at 25 °C. The differences between the 60 °C and 25 °C emission factors were somewhat larger for recycling plant samples than the differences for synthetic turf field samples. Except for benzothiazole, a majority of the measurements at 25 °C were below the method detection limit or chamber background levels. At 60 °C, a majority of measurements for the chemicals shown in Figures 4-27 and 4-28 were above the method detection limit, but this was not the case for many of the other VOC target analytes.

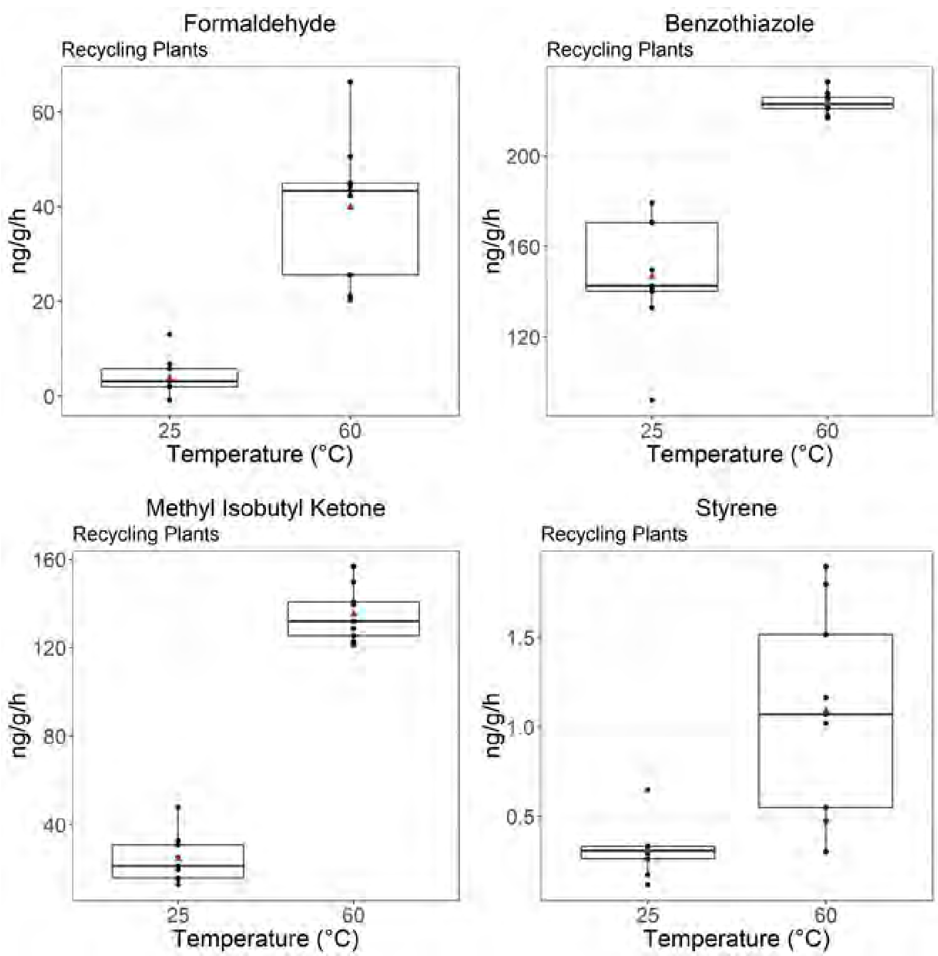

Figure 4-27. Comparison of VOC 25 °C and 60 °C emission factor results (ng/g/h) for formaldehyde, benzothiazole, methyl isobutyl ketone, and styrene from tire crime rubber collected from recycling plants. [VOC = Volatile organic compound]

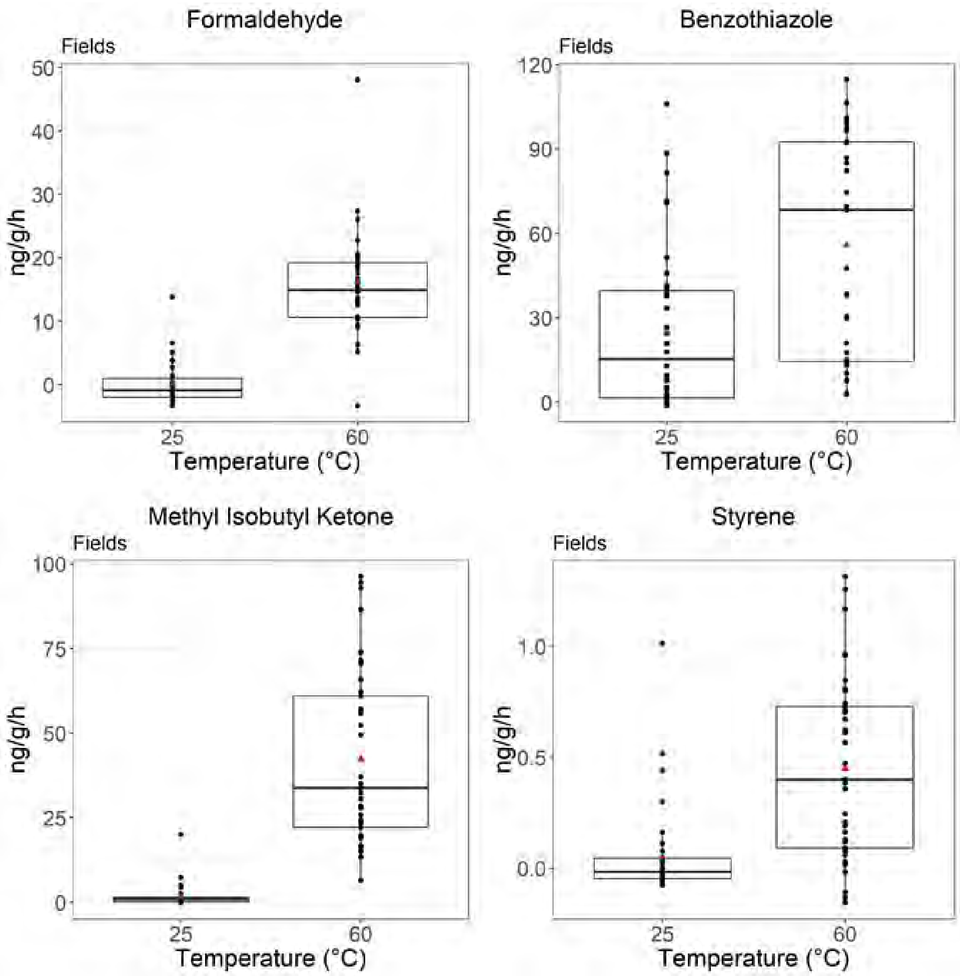

Figure 4-28. Comparison of VOC 25 °C and 60 °C emission factor results (ng/g/h) for formaldehyde, benzothiazole, methyl isobutyl ketone, and styrene from tire crumb rubber infill collected from synthetic turf fields. [VOC = Volatile organic compound]

Several compounds did not show appreciable differences in emissions for the two temperatures, including most of the BTEX chemicals (benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene). Distributions for SumBTEX 25 °C and 60 °C emission factors are shown in Figure 4-29 for recycling plants and synthetic turf fields. The overall results are lower in the 60 °C tests as compared to the 25 °C tests. In fact, a majority of the synthetic turf field measurements at 60 °C were below the average chamber background measurements, resulting in slightly negative results following background subtraction. It appeared that some VOCs were driven off the tire crumb during the 24-hour equilibration period in the test chamber at 60 °C prior to chamber air sample collection. This may have implications for understanding whether some chemicals may be found at the surface of tire crumb rubber particles, perhaps from atmospheric absorption, versus chemicals intrinsic to the rubber material that would continue to replenish what is lost at the particle surface. Based on the experimental results, it would appear that chemicals like benzothiazole, methyl isobutyl ketone, and styrene are intrinsic to the tire crumb rubber, while the BTEX chemicals are not, or at least not at substantial concentrations. More experimental work is needed to better understand these emission dynamics.

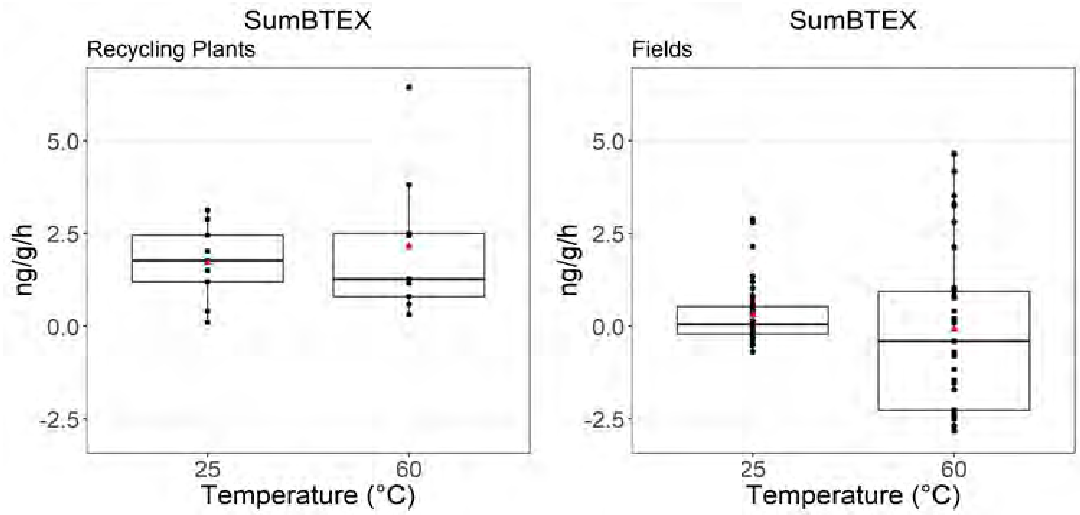

Figure 4-29. Comparison of VOC 25 °C and 60 °C emission factor results (ng/g/h) for SumBTEX from tire crumb rubber collected from recycling plants and tire crumb rubber infill collected from synthetic turf fields. [VOC = Volatile organic compound; SumBTEX = Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene results]

While the emissions testing performed in this study provides valuable information to help understand the types and ranges of chemical emissions from tire crumb rubber, it is not clear how well the test methods apply to the wide range of conditions at synthetic turf fields and whether the results can be successfully applied to estimating real-world emissions to inform exposure assessment. Conditions such as short-term changes in temperature (e.g., daily diurnal cycle), infill depth, effective ventilation rates at indoor and outdoor fields, or other factors may affect emissions variability and net emissions at fields. More directed experimental work at fields and in the laboratory would improve our understanding about how well laboratory emissions testing can be used to model or predict exposures under different situations.

4.8.2 SVOC Emission Factors

Differences in 25 °C and 60 °C emission factor distributions for pyrene, the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol are shown in Figures 4-30 and 4-31 for tire crumb rubber samples collected at tire recycling plants and tire crumb rubber infill samples collected at synthetic turf fields, respectively. These target SVOC analytes showed higher emission factors in emission experiments performed at 60 °C than at 25 °C. The differences between the 60 °C and 25 °C emission factors were somewhat larger for recycling plant samples than the differences for synthetic turf field samples. Many of the emission factor measurements performed at 25 °C were below the method detection limit and/or the chamber background. Most of the more volatile SVOCs showed similar results, with emission factors at 60 °C exceeding those at 25 °C; however, the five- and six-ring PAH compounds were generally below the method detection limits in both 60 °C and 25 °C emissions tests, consistent with their very low vapor pressures.

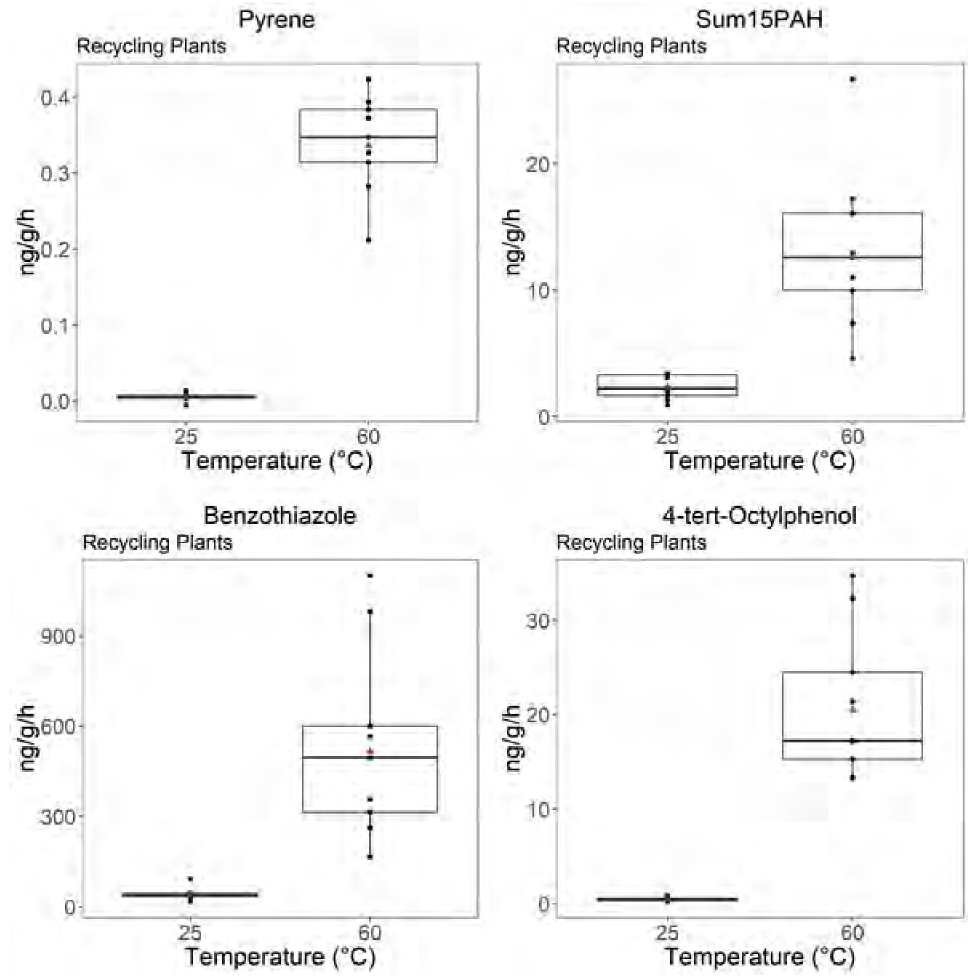

Figure 4-30. Comparison of SVOC 25 °C and 60 °C emission factor results (ng/g/h) for pyrene, the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol from tire crumb rubber collected from tire recycling plants. [SVOC = Semivolatile organic compound; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

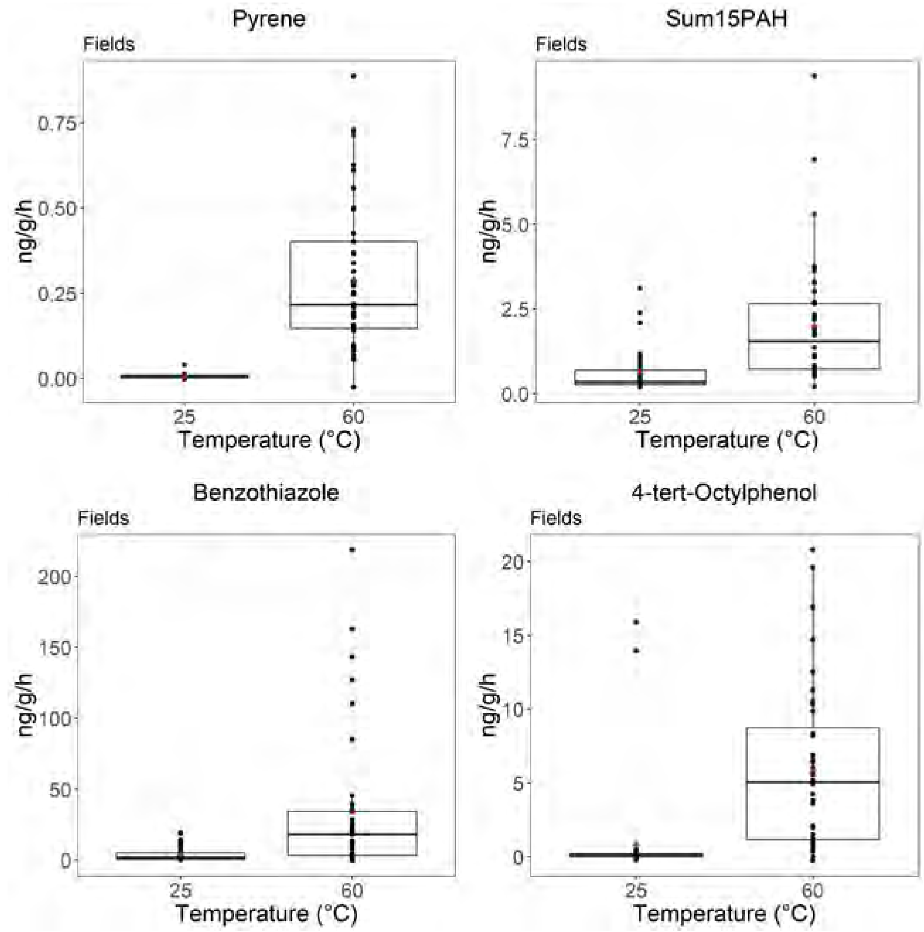

Figure 4-31. Comparison of SVOC 25 °C and 60 °C emission factor results (ng/g/h) for pyrene, the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol from tire crumb rubber infill collected from synthetic turf fields. [SVOC = Semivolatile organic compound; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

4.9 Heterogeneity/Homogeneity Assessments

An important gap exists for information about the variability of chemicals associated with tire crumb rubber, both within synthetic turf fields and between fields in different locations. This is important for several reasons. First, there are few U.S. studies with data available for assessing the range of tire crumb rubber chemical concentrations across the country, and thus, the potential range of exposures people may experience. Likewise, there are few data to assess differences in chemicals associated with tire crumb rubber within a field. Within-field differences are important for understanding whether there might be different exposure potentials across a given field and how best to collect samples to provide representative results for a field.

This federal research study was designed to help fill gaps in knowledge about within-field and between-field variability in chemicals associated with tire crumb rubber infill. Measurements were performed at several different scales to assess measurement precision, homogeneity, and variability. The following types of precision, homogeneity, and variability assessments have been performed and are reported in this section. These assessments build in scale from analytical precision up to between-field variability:

- For metal digestion and SVOC solvent extraction analyses, replicate injections of the digestate or extract were performed to assess analytical precision.
- For VOC chamber emission experiments, duplicate samples were collected during a subset of chamber experiments to assess emissions measurement precision.
- For metals digestion and SVOC extraction, duplicate portions of tire crumb rubber from the same sample bottle were digested or extracted to assess homogeneity and variability of chemicals associated with tire crumb rubber at a very small spatial scale.
- For SVOC and VOC chamber emissions experiments, duplicate portions of tire crumb rubber from the same sample bottle were used in two entirely separate emissions experiments to assess homogeneity and variability of chemicals associated with tire crumb rubber at a very small spatial scale.
- For all analyses, tire crumb rubber infill samples collected at a subset of five fields, at different locations on the field, were analyzed separately. This was done to assess within-field variability of chemicals associated with tire crumb rubber at the spatial scale of a single field. This was also accomplished for tire recycling plants through analysis of samples collected from three different storage sacks at each plant.
- For all analyses, samples collected from multiple fields were used to examine between-field differences in chemicals associated with tire crumb rubber infill. This was first done for the subset of five fields that also had measurements for individual field locations, so that within- and between-field relative variances could be calculated. In later sections, differences between composite samples prepared from tire crumb rubber infill collected at 40 fields were examined for several field characteristics (indoor vs. outdoor, field installation age, and U.S. census region). Samples collected from tire recycling plants were also assessed for between- and within-plant variability.

4.9.1 Measurement Precision and Sample Variability

Precision and variability measurement results were only reported if both members of the paired measurements had measurement values exceeding zero. Measurement results near the method detection limit were retained, but the precision of measurements near detection limits is often relatively poor and may influence the overall results.

Table 4-50 reports both the analytical precision for replicate analyses of select metals in sample digestates (replicate sample digest analysis) and homogeneity of those metals through analysis of duplicate portions of tire crumb rubber sample removed from the same sample jar (duplicate tire crumb sample analysis). A very high level of analytical precision was obtained, with average percent relative standard deviations (%RSDs) for paired measurements < 2%. For duplicate portions of tire crumb rubber from the same jar, average %RSDs for the paired measurements ranged from 4.8 to 32%. Relatively high variability in lead levels from samples in the same collection bottle have been previously reported; in this study, the lead %RSD was 25% for portions of tire crumb from the same jar, compared to an analytical precision %RSD of 1.3%. Cobalt and zinc, two other metals associated with tire crumb rubber, had %RSDs of 13% and 4.8%, respectively, in duplicate portions of tire crumb rubber from the same sample jar.

Table 4-50. Precision and Variability of Tire Crumb Rubber Sample Digestion Metals Measurements by ICP/MS[a,b,c]

Chemical	Replicate Sample Digest Analysis %RSD – n	Replicate Sample Digest Analysis %RSD – Mean	Replicate Sample Digest Analysis %RSD – Minimum	Replicate Sample Digest Analysis %RSD – Maximum	Duplicate Tire Crumb Sample Analysis %RSD – n	Duplicate Tire Crumb Sample Analysis %RSD – Mean	Duplicate Tire Crumb Sample Analysis %RSD – Minimum	Duplicate Tire Crumb Sample Analysis %RSD – Maximum
Arsenic	10	1.3	0.33	3.6	10	32	7.1	58
Cadmium	10	0.47	< 0.1	1.4	10	20	4.4	37
Chromium	11	1.5	< 0.1	5.8	8	15	1.5	33
Cobalt	11	0.72	0.12	2.3	9	13	2.4	29
Lead	10	1.3	0.32	3.1	10	25	0.20	96
Zinc	11	0.81	0.17	2.6	9	4.8	1.0	8.7

[a] ICP/MS = Inductively coupled plasma/mass spectrometry

[b] Replicate Sample Digest Analysis = replicate analyses of the same digest from a sample; %RSD is the percent relative standard deviation between pairs of measurements.

[c] Duplicate Tire Crumb Sample Analysis = Two different portions of tire crumb rubber samples from the same bottle extracted and analyzed separately; %RSD is the percent relative standard deviation between pairs of measurements.

Table 4-51 reports both the analytical precision for replicate analyses of select SVOCs in sample extracts (replicate sample extract analysis) and homogeneity of those SVOCs through analysis of duplicate portions of tire crumb rubber sample removed from the same sample jar (duplicate tire crumb sample analysis). Modest levels of analytical precision were obtained, with average percent relative standard deviations (%RSDs) for paired measurements ranging from 11% to 34% for most analytes and 63% for 4-terty-octylphenol. These results may have been affected by a large maximum value, which in turn may have been affected by results near the detection limit. For duplicate portions of tire crumb rubber from the same jar, average %RSDs for the paired measurements ranged from 4.8 to 20%. All tire crumb rubber samples produced for SVOC extraction analysis had duplicate measurements, so this represents a robust assessment of small spatial scale homogeneity of SVOC chemicals associated with tire crumb rubber.

Table 4-51. Precision and Variability of Tire Crumb Rubber Sample Solvent Extract SVOC Measurements by GC/MS/MS[a,b,c]

Chemical	Replicate Sample Extract Analysis %RSD – n	Replicate Sample Extract Analysis %RSD – Mean	Replicate Sample Extract Analysis %RSD – Minimum	Replicate Sample Extract Analysis %RSD – Maximum	Duplicate Tire Crumb Sample Analysis %RSD – n	Duplicate Tire Crumb Sample Analysis %RSD – Mean	Duplicate Tire Crumb Sample Analysis %RSD – Minimum	Duplicate Tire Crumb Sample Analysis %RSD – Maximum
Phenanthrene	7	13	3.3	25	101	4.8	0.12	40
Fluoranthene	7	15	0.96	49	101	4.9	< -0.1	50
Pyrene	7	32	4.3	120	101	5.1	< 0.1	52
Benzo[a]pyrene	7	34	< 0.1	63	101	20	0.35	64
Benzo[ghi]perylene	7	34	16	47	100	17	0.18	130
Sum15PAH	7	21	0.8	110	101	5.1	< 0.1	49
Benzothiazole	7	29	0.28	72	101	8.9	0.19	78
Dibutyl phthalate	7	13	< 0.1	71	101	11	< 0.1	71

Table 4-51 Continued

Chemical	Replicate Sample Extract Analysis %RSD – n	Replicate Sample Extract Analysis %RSD – Mean	Replicate Sample Extract Analysis %RSD – Minimum	Replicate Sample Extract Analysis %RSD – Maximum	Duplicate Tire Crumb Sample Analysis %RSD – n	Duplicate Tire Crumb Sample Analysis %RSD – Mean	Duplicate Tire Crumb Sample Analysis %RSD – Minimum	Duplicate Tire Crumb Sample Analysis %RSD – Maximum
Bis(2-ethylhexyl) phthalate	7	31	0.62	82	100	14	< 0.1	130
Aniline	7	11	< 0.1	27	101	7.8	0.13	37
4-tert-octylphenol	7	63	37	110	101	8.3	< 0.1	41
n-Hexadecane	7	12	< 0.1	51	96	10	<0.1	130

[a] SVOC = Semivolatile organic compound; GC/MS/MS = Gas chromatography/tandem mass spectrometry

[b] Replicate Sample Extract Analysis = Replicate analyses of the same extract from a sample; %RSD is the percent relative standard deviation between pairs of measurements.

[c] Duplicate Tire Crumb Sample Analysis = Two different portions of tire crumb rubber samples from the same bottle extracted and analyzed separately; %RSD is the percent relative standard deviation between pairs of measurements.

The analytical precision for SVOC emission chamber testing is shown in Table 4-52. This table shows the results for replicate injections of the extracts from PUF samples used to collect chamber air samples during the emissions experiments. Average %RSDs ranged from < 0.1% to 31%.

Table 4-52. Precision of Replicate Extracts Analyses for Chamber Emission SVOC Measurements by GC/MS/MS[a,b]

Chemical[c]	n	Replicate Emission Sample Extract Analysis %RSD – Mean	Replicate Emission Sample Extract Analysis %RSD – Minimum	Replicate Emission Sample Extract Analysis %RSD – Maximum
Phenanthrene	3	0.43	0.013	1.2
Fluoranthene	2	0.12	< 0.1	0.14
Pyrene	3	31	< 0.1	94
Benzo[a]pyrene	1	1.3	1.3	1.3
Benzo[ghi]perylene	2	8.2	5.9	10
Sum15PAH	4	0.91	< 0.1	3.4
Benzothiazole	4	14	< 0.1	42
Dibutyl phthalate	2	23	0.30	46
Aniline	4	2.7	< 0.1	11
4-tert-octylphenol	3	< 0.1	< 0.1	0.25

[a] SVOC = Semivolatile organic compound; GC/MS/MS = Gas chromatography/tandem mass spectrometry

[b] Replicate Emission Sample Extract Analysis = Replicate analyses of the same extract from an emission sample; %RSD is the percent relative standard deviation between pairs of measurements.

[c] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

The variability in SVOC chamber emissions measurement results is shown in Table 4-53 for six repeated tests performed at 25 °C and six repeated tests performed at 60 °C tests. At 25 °C, average %RSDs ranged from 28% to 130%. The relatively high variability at 25 °C may be a result, in part, of the very low levels measured for most of the analytes. At 60 °C, average %RSDs ranged from 8.4% to 37%. The lower variability at 60 °C is likely a result of the higher levels measured for many of the analytes.

Table 4-53. Variability of 25°C and 60°C Chamber Emission SVOC Measurements by GC/MS/MS[a,b]

Chemical[c]	25 °C Repeated Chamber Emission Experiment %RSD – n	25 °C Repeated Chamber Emission Experiment %RSD – Mean	25 °C Repeated Chamber Emission Experiment %RSD – Minimum	25 °C Repeated Chamber Emission Experiment %RSD – Maximum	60 °C Repeated Chamber Emission Experiment %RSD – n	60 °C Repeated Chamber Emission Experiment %RSD – Mean	60 °C Repeated Chamber Emission Experiment %RSD – Minimum	60 °C Repeated Chamber Emission Experiment %RSD – Maximum
Phenanthrene	3	50	18	76	5	8.4	0.23	16
Fluoranthene	4	29	22	42	5	21	7.4	35
Pyrene	3	30	8.7	54	5	18	8.0	30
Sum15PAH	6	35	1.4	84	6	30	9.7	72
Benzothiazole	5	28	10	48	5	37	15	65
Dibutyl phthalate	2	130	130	130	0	NR	NR	NR
Aniline	5	30	6.4	56	5	35	17	59
4-tert-octylphenol	5	74	24	130	5	18	11	27

[a] SVOC = Semivolatile organic compound; GC/MS/MS = Gas chromatography/tandem mass spectrometry; NR = Not reported

[b] Two completely different chamber experiments using different portions of tire crumb rubber samples from the same bottle; %RSD is the percent relative standard deviation between pairs of measurements.

[c] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

It was possible to collect duplicate samples using the small chambers during the VOC emissions experiments, but that was not possible for the micro-chambers used for the SVOC emissions tests. Table 4-54 shows measurement precision results for duplicate sample collection of VOC emission samples and variability results for the six repeated experiments performed at 25 °C. Average %RSD values ranged from 17% to 67% for duplicate samples. Most of these measurements were at low concentrations; benzothiazole was found at the highest concentrations and it had the lowest %RSD (17%). Average %RSD values ranged from 6.6% to 140% for repeated emission experiments at 25 °C. As noted previously, most of the selected analytes had measurements at low concentrations near the method detection limits.

Table 4-54. Precision and Variability of 25°C Chamber Emission VOC Measurements by GC/TOFMS[a,b,c]

Chemical[d]	Duplicate Chamber Sample %RSD – n	Duplicate Chamber Sample %RSD – Mean	Duplicate Chamber Sample %RSD – Minimum	Duplicate Chamber Sample %RSD – Maximum	Repeated Chamber Emission Experiment %RSD – n	Repeated Chamber Emission Experiment %RSD – Mean	Repeated Chamber Emission Experiment %RSD – Minimum	Repeated Chamber Emission Experiment %RSD – Maximum
Formaldehyde	6	51	13	91	2	7.8	5.6	10
Methyl isobutyl ketone	17	45	1.1	130	4	10	2.1	21
Benzothiazole	18	17	0.79	91	4	6.8	1.4	18
1,3-Butadiene	1	65	65	65	1	82	82	82
Styrene	6	56	3.8	110	2	46	16	77
Benzene	6	67	22	86	1	140	140	140
Toluene	7	45	0.26	110	2	6.6	2.7	10
Ethylbenzene	8	59	0.10	140	2	67	36	98
m/p-Xylene	12	40	0.12	130	3	63	1.2	110
o-Xylene	12	28	0.22	110	3	68	12	110
SumBTEX	10	59	2.4	140	3	57	12	100

[a] VOC = Volatile organic compound; GC/TOFMS = Gas chromatography/time-of-flight mass spectrometry

[b] Duplicate Chamber Sample = Two samples collected from the chamber air at the same time during the same chamber experiment; %RSD is the percent relative standard deviation between pairs of measurements.

[c] Repeated Chamber Emission Experiment = Two completely different chamber experiments using different portions of tire crumb rubber samples from the same bottle; %RSD is the percent relative standard deviation between pairs of measurements.

[d] SumBTEX = Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene results

Table 4-55 shows measurement precision results for duplicate sample collection of VOC emission samples and variability results for the six repeated experiments performed at 60 °C. Average %RSD values ranged from 8.8% to 100% for duplicate samples. The precision improved for most of the analytes found to be most strongly associated with tire crumb rubber in the 60 °C emission testing, including benzothiazole, methyl isobutyl ketone, formaldehyde, and styrene. Most of the other measurements were at low concentrations. Average %RSD values ranged from 3.4% to 65% for repeated emission experiments at 60 °C. As noted previously, most of the selected analytes had measurements at low concentrations near the method detection limits except for benzothiazole, methyl isobutyl ketone, formaldehyde, and styrene. It is difficult to discern from these results how much of the variability is due to measurement imprecision and how much is due to variability in the chemicals associated with tire crumb rubber.

Table 4-55. Precision and Variability of 60°C Chamber Emission VOC Measurements by GC/TOFMS[a,b,c]

Chemical[d]	Duplicate Chamber Sample %RSD – n	Duplicate Chamber Sample %RSD – Mean	Duplicate Chamber Sample %RSD – Minimum	Duplicate Chamber Sample %RSD – Maximum	Repeated Chamber Emission Experiment %RSD – n	Repeated Chamber Emission Experiment %RSD – Mean	Repeated Chamber Emission Experiment %RSD – Minimum	Repeated Chamber Emission Experiment %RSD – Maximum
Formaldehyde	10	11	0.34	31	5	9.7	1.2	30
Methyl isobutyl ketone	17	17	0.55	85	4	29	7.1	87
Benzothiazole	17	8.8	0.47	43	4	3.4	2.0	7.4
1,3-Butadiene	3	100	76	130	1	11	11	11
Styrene	14	14	1.7	43	4	46	11	130
Benzene	8	60	1.4	130	1	11	11	11
Toluene	11	40	4.1	120	2	50	45	55
Ethylbenzene	4	51	33	89	0	NR	NR	NR
m/p-Xylene	9	16	0.58	30	2	65	55	75
o-Xylene	3	45	6.9	69	0	NR	NR	NR
SumBTEX	6	36	9.4	83	1	29	29	29

[a] VOC = Volatile organic compound; GC/TOFMS = Gas chromatography/time-of-flight mass spectrometry; NR = Not reported

[b] Duplicate Chamber Samples = Two samples collected from the chamber air at the same time during the same chamber experiment; %RSD is the percent relative standard deviation between pairs of measurements.

[c] Repeated Chamber Emission Experiment = Two completely different chamber experiments using different portions of tire crumb rubber samples from the same bottle; %RSD is the percent relative standard deviation between pairs of measurements.

[d] SumBTEX = Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene results

4.9.2 Variability Within and Between Recycling Plants or Synthetic Turf Fields

Within-field, between-field, within-recycling plant, and between-recycling plant assessments were performed to further examine variability in chemicals associated with tire crumb rubber at larger spatial scales. Tire crumb rubber infill samples collected at a subset of five fields, at different locations on the field, were analyzed separately. This was done to assess within-field variability of chemicals associated with tire crumb rubber at the spatial scale of a single field. This was also accomplished for tire recycling plants through analysis of samples collected from three different storage sacks at each plant. Variance analyses were performed to further assess within- and between-field differences for the five fields that had individual location sample analyses performed. The same type of analysis was also performed for the recycling plants. It is important to recognize that these assessments were based on modest sample sizes.

4.9.2.1 Metals by ICP/MS Analysis

Table 4-56 shows average and individual measurement results for cobalt, lead, and zinc for tire crumb rubber samples collected from three storage bags at nine tire recycling plants. %RSD values ranged from 9.1% to 56% for cobalt, 6.2% to 94% for lead, and 1.2% to 22% for zinc. The greatest variability was consistently observed for Plant ID H, where the particle size analysis showed that there were substantially different particle size fractions across the storage sacks that were sampled. Also, different types of tires were reported for Sample 1 versus Samples 2 and 3 for Plant ID H.

Table 4-56. Select ICP/MS Measurement Results for Individual Tire Crumb Rubber Samples Collected at Nine Recycling Plants for Assessing Within-Plant Variability[a,b,c]

Chemical	Plant ID	Mean (mg/kg)	Standard Deviation (mg/kg)	% Relative Standard Deviation	Individual Sample 1 Results (mg/kg)	Individual Sample 2 Results (mg/kg)	Individual Sample 3 Results (mg/kg)
Cobalt	A	113	12	10	120	100	120
Cobalt	B	157	21	13	140	180	150
Cobalt	C	217	55	25	160	270	220
Cobalt	D	105	13	13	120	98	96
Cobalt	E	233	29	12	200	250	250
Cobalt	F	313	113	36	280	440	220
Cobalt	G	103	50	48	160	76	72
Cobalt	H	220	125	57	360	120	180
Cobalt	I	233	38	16	260	250	190
Lead	A	16	7.0	44	13	11	24
Lead	B	14	3.7	27	9.7	14	17
Lead	C	11	1.8	17	13	9.7	10
Lead	D	9.5	1.4	15	8.2	11	9.4
Lead	E	8.9	0.55	6.2	8.4	8.9	9.5
Lead	F	6.9	1.4	20	7.7	7.7	5.3
Lead	G	15	6.1	40	22	10	14
Lead	H	30	28	93	9.7	61	18
Lead	I	10	0.23	2.3	9.6	10	10
Zinc	A	14000	1000	7.1	15000	13000	14000
Zinc	B	16000	1000	6.3	15000	17000	16000
Zinc	C	18667	577	.3.1	18000	19000	19000
Zinc	D	12667	577	4.6	12000	13000	13000
Zinc	E	20667	577	2.8	20000	21000	21000
Zinc	F	22000	2646	12	20000	25000	21000
Zinc	G	15333	1528	10	17000	15000	14000
Zinc	H	18667	3786	20	23000	16000	17000
Zinc	I	14667	1528	10	15000	16000	13000

[a] ICP/MS = Inductively coupled plasma/mass spectrometry

[b] Each sample collected from a different storage bag at the recycling plants.

[c] Statistics were calculated using original unrounded measurement results; all results in this table have been rounded to two significant figures.

Table 4-57 shows average and individual measurement results for cobalt, lead, and zinc for tire crumb rubber samples collected from up to seven locations at five synthetic turf fields. %RSD values ranged from 12% to 41% for cobalt, 14% to 110% for lead, and 7.2% to 11% for zinc. The average concentrations from individual location samples for cobalt and zinc were similar to those from the composite sample that was prepared from the seven individual location samples. For lead, the average results from the seven individual locations were substantially different than the composite sample measurement for two fields (Field ID #20 and #29). There was substantial variability at individual locations for lead at Field ID #20, and as noted earlier, and there was substantial within-sample bottle variability for lead. The variability in measurement results for individual samples collected at tire recycling plants and synthetic turf fields is shown graphically in Figure 4-32.

Table 4-57. Select ICP/MS Measurement Results for Individual Location Tire Crumb Rubber Infill Samples Collected at Five Synthetic Turf Fields for Assessing Within-Field Variability[a,b,c]

Chemical	Field ID	Composite Sample[d] (mg/kg)	Individual Location Mean (mg/kg)	Individual Location % Relative Standard Deviation	Individual Field Sample Location 1 Results (mg/kg)	Individual Field Sample Location 2 Results (mg/kg)	Individual Field Sample Location 3 Results (mg/kg)	Individual Field Sample Location 4 Results (mg/kg)	Individual Field Sample Location 5 Results (mg/kg)	Individual Field Sample Location 6 Results (mg/kg)	Individual Field Sample Location 7 Results (mg/kg)
Cobalt	1	140	180	33	250	230	160	160	99	N/A	N/A
Cobalt	16	180	220	12	200	210	230	270	190	240	200
Cobalt	20	68	99	41	100	170	100	120	63	60	71
Cobalt	26	250	250	16	220	260	260	170	270	280	260
Cobalt	29	290	250	14	270	220	260	230	240	330	230
Lead	1	9.3	8.6	28	7.6	12	9.7	8.4	5.4	N/A	N/A
Lead	16	11	14	33	11	18	10	16	8.2	12	21
Lead	20	11	81	68	28	150	94	150	12	56	76
Lead	26	15	15	110	10	54	6.5	8.5	7.7	11	7.9
Lead	29	22	11	14	12	11	9.3	13	9.3	12	13
Zinc	1	19000	20000	11	21000	22000	21000	19000	17000	N/A	N/A
Zinc	16	18000	20000	8.6	17000	18000	18000	21000	21000	21000	20000
Zinc	20	13000	15000	8.6	14000	14000	13000	16000	15000	15000	16000
Zinc	26	21000	20000	7.2	22000	22000	22000	21000	19000	20000	18000
Zinc	29	19000	20000	9.3	21000	21000	24000	19000	18000	21000	19000

[a] ICP/MS = Inductively coupled plasma/mass spectrometry; N/A = The individual samples were depleted, no analysis performed.

[b] Refer to Figure 3-5 for a schematic representation of positions for samples collected from locations 1 – 7.

[c] Statistics were calculated using original unrounded measurement results; all results in this table have been rounded to two significant figures.

[d] This is the measurement result for the analysis of the composite sample that was prepared from portions of tire crumb rubber infill from the seven locations on the synthetic turf field.

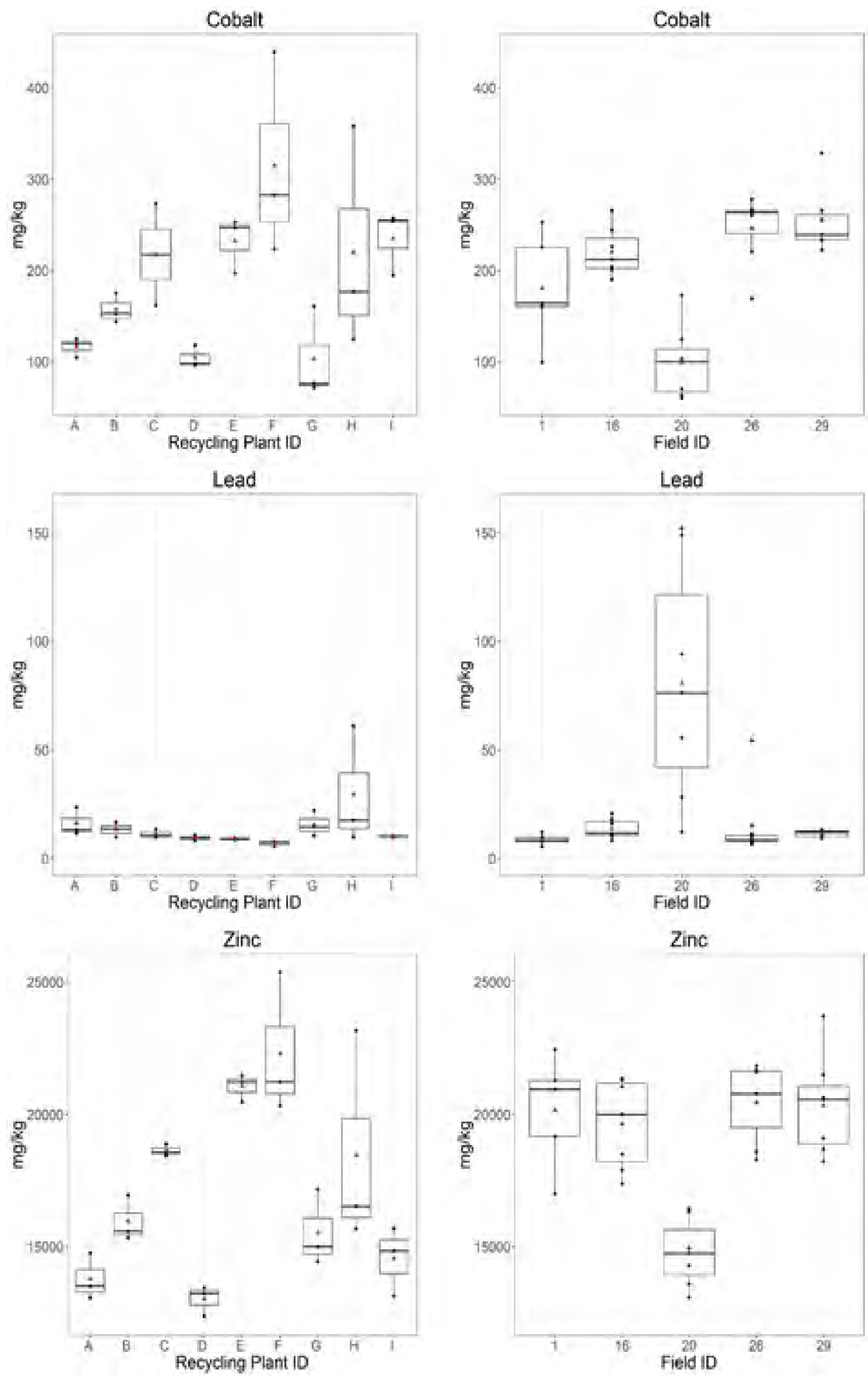

Figure 4-32. Within-tire recycling plant variability (left side) and within-synthetic turf field variability (right side) for ICP/MS metal analysis results (mg/kg) in tire crumb rubber for cobalt, lead, and zinc. [ICP/MS = Inductively coupled plasma/mass spectrometry]

The percent of total variance explained by within-recycling plant and between-recycling variances is shown in Table 4-58 for select metals. For chromium and zinc, there is greater between-plant variability than within-plant variability. For cobalt, the within- and between-plant variability is similar, and for arsenic, cadmium, and lead, there is greater within-plant variance. The percent of total variance explained by within-field and between-field variances is also shown in Table 4-58 for select metals. For cobalt and zinc, there is greater between-field variability than within-field variability. For lead, the within- and between-field variability is similar, and for arsenic, cadmium, and chromium, there is greater within-field variance.

Table 4-58. Within- and Between-recycling Plant or Field Variability for Select Metal ICP/MS Analysis for Tire Crumb Rubber Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Collected from Synthetic Turf Fields [a]

Tire Crumb Rubber Sampling Location	Analyte	Number of Plants or Fields	Number of Samples per Plant or Field	Between-Plant or Field % Variance	Within-Plant or Field % Variance
Recycling Plants	Arsenic	9	3	38	62
Recycling Plants	Cadmium	9	3	27	73
Recycling Plants	Chromium	9	3	61	39
Recycling Plants	Cobalt	9	3	46	54
Recycling Plants	Lead	9	3	8	92
Recycling Plants	Zinc	9	3	71	29
Synthetic Turf Fields	Arsenic	5	5	5	95
Synthetic Turf Fields	Cadmium	5	5	6	94
Synthetic Turf Fields	Chromium	5	5	13	87
Synthetic Turf Fields	Cobalt	5	5	65	35
Synthetic Turf Fields	Lead	5	5	48	52
Synthetic Turf Fields	Zinc	5	5	60	40

[a] ICP/MS = Inductively coupled plasma/mass spectrometry

4.9.2.2 SVOC Extracts by GC/MS/MS Analysis

Table 4-59 shows average and individual measurement results for pyrene, benzothiazole, and 4-tert-octylphenol for tire crumb rubber samples collected from three storage bags at nine tire recycling plants. %RSD values ranged from 1.5% to 12% for pyrene, 3.3% to 31% for benzothiazole, and 1.3% to 18% for 4-tert-octylphenol, reflecting generally similar concentrations within recycling plants. The greatest variability was consistently observed for Plant ID H, where the particle size analysis showed that there were substantially different particle size fractions across the storage sacks that were sampled. Also, different types of tires were reported for Sample 1 versus Samples 2 and 3 for Plant ID H.

Table 4-59. Select SVOC Extraction GC/MS/MS Measurement Results for Individual Tire Crumb Rubber Samples Collected at Nine Recycling Plants for Assessing Within-Plant Variability[a,b,c]

Chemical	Plant ID	Mean (mg/kg)	Standard Deviation (mg/kg)	% Relative Standard Deviation	Individual Sample 1 Results (mg/kg)	Individual Sample 2 Results (mg/kg)	Individual Sample 3 Results (mg/kg)
Pyrene	A	16	0.23	1.5	16	16	16
Pyrene	B	19	1.7	9.1	20	18	17
Pyrene	C	17	1.0	5.9	19	17	17
Pyrene	D	22	0.86	3.9	21	22	23
Pyrene	E	16	1.1	6.5	15	17	17
Pyrene	F	17	1.6	9.0	19	18	16
Pyrene	G	21	2.5	12	23	18	22
Pyrene	H	17	1.7	10	15	17	19
Pyrene	I	19	1.4	7.2	20	19	17
Benzothiazole	A	63	5.1	8.1	58	65	67
Benzothiazole	B	51	3.8	7.4	52	47	54
Benzothiazole	C	80	2.6	3.3	83	79	78
Benzothiazole	D	66	5.7	8.6	61	72	65
Benzothiazole	E	100	4.4	4.2	100	110	100
Benzothiazole	F	100	5.6	3.5	100	100	94
Benzothiazole	G	82	5.3	6.5	88	81	78
Benzothiazole	H	74	23	31	100	61	60
Benzothiazole	I	92	5.3	5.7	86	96	93
4-tert-octylphenol	A	30	0.38	1.3	30	29	30
4-tert-octylphenol	B	30	1.5	4.9	30	29	32
4-tert-octylphenol	C	26	1.2	4.5	27	27	25
4-tert-octylphenol	D	36	4.1	11	40	33	34
4-tert-octylphenol	E	24	0.45	1.9	23	24	24
4-tert-octylphenol	F	23	0.95	4.1	24	23	22
4-tert-octylphenol	G	29	2.0	6.9	27	30	30
4-tert-octylphenol	H	33	5.8	18	27	35	38
4-tert-octylphenol	I	42	3.0	7.0	46	40	41

[a] SVOC = Semivolatile organic compound; GC/MS/MS = Gas chromatography/tandem mass spectrometry

[b] Each sample collected from a different storage bag at the recycling plants.

[c] Statistics were calculated using original unrounded measurement results; all results in this table have been rounded to two significant figures.

Table 4-60 shows average and individual measurement results for pyrene, benzo[a]pyrene, benzothiazole, and 4-tert-octylphenol for tire crumb rubber samples collected from seven locations at five synthetic turf fields. %RSD values ranged from 2.3% to 11% for pyrene, 16% to 31% for benzo[a]pyrene, 12 to 57% for benzothiazole, and 13% to 39% for 4-tert-octylphenol. The average concentrations from individual location samples for most analytes and most fields were similar to those from the composite sample that was prepared from the seven individual location samples. The variability in measurement results for individual samples collected at tire recycling plants and synthetic turf fields is shown graphically for select chemicals in Figures 4-33 and 4-34.

Table 4-60. Select SVOC Extraction GC/MS/MS Measurement Results for Individual Location Tire Crumb Rubber Infill Samples Collected at Five Synthetic Turf Fields for Assessing Within-Field Variability[a,b,c]

Chemical	Field ID	Composite Sample[d] (mg/kg)	Individual Location Mean (mg/kg)	Individual Location % Relative Standard Deviation	Individual Field Sample Location 1 Results (mg/kg)	Individual Field Sample Location 2 Results (mg/kg)	Individual Field Sample Location 3 Results (mg/kg)	Individual Field Sample Location 4 Results (mg/kg)	Individual Field Sample Location 5 Results (mg/kg)	Individual Field Sample Location 6 Results (mg/kg)	Individual Field Sample Location 7 Results (mg/kg)
Pyrene	1	7.3	7.3	5.3	8.0	7.0	7.2	7.7	7.4	6.9	7.2
Pyrene	16	14	12	11	14	14	13	12	10	13	11
Pyrene	20	22	22	3.5	22	21	21	23	21	21	22
Pyrene	26	8.9	8.3	3.0	8.3	8.2	8.5	8.7	8.1	8.0	8.2
Pyrene	29	16	17	2.3	17	17	16	17	17	17	16
Benzo[a]pyrene	1	0.37	0.34	31	0.44	0.22	0.41	0.49	0.27	0.27	0.28
Benzo[a]pyrene	16	0.41	0.49	18	0.46	0.55	0.51	0.46	0.32	0.58	0.57
Benzo[a]pyrene	20	0.83	1.0	17	0.97	0.75	0.93	0.90	1.3	1.1	1.1
Benzo[a]pyrene	26	0.42	0.48	16	0.52	0.42	0.50	0.59	0.53	0.36	0.44
Benzo[a]pyrene	29	0.51	0.68	21	0.89	0.60	0.84	0.55	0.74	0.61	0.52
Benzothiazole	1	1.8	1.5	12	1.6	1.6	1.7	1.3	1.4	1.2	1.5
Benzothiazole	16	23	14	57	26	20	20	9.6	6.0	8.4	7.1
Benzothiazole	20	7.3	6.5	16	8.1	7.1	7.1	5.0	6.1	5.5	6.7
Benzothiazole	26	3.0	2.3	30	3.2	2.0	1.4	2.9	2.9	1.8	1.9
Benzothiazole	29	40	37	14	31	40	33	41	46	36	34
4-tert-octylphenol	1	1.8	2.3	24	1.9	1.5	2.3	3.1	2.5	2.4	2.3
4-tert-octylphenol	16	4.5	6.3	39	6.6	5.5	3.6	9.7	4.2	9.3	4.9
4-tert-octylphenol	20	30	27	15	34	30	29	24	24	24	25
4-tert-octylphenol	26	3.9	4.3	13	5.3	4.1	4.6	4.0	4.4	3.9	3.6
4-tert-octylphenol	29	21	15	27	14	14	13	8.4	16	19	21

[a] SVOC = Semivolatile organic compound; GC/MS/MS = Gas chromatography/tandem mass spectrometry

[b] Refer to Figure 3-5 for a schematic representation of positions for samples collected from locations 1 – 7.

[c] Statistics were calculated using original unrounded measurement results; all results in this table have been rounded to two significant figures.

[d] This is the measurement result for the analysis of the composite sample that was prepared from portions of tire crumb rubber infill from the seven locations on the synthetic turf field.

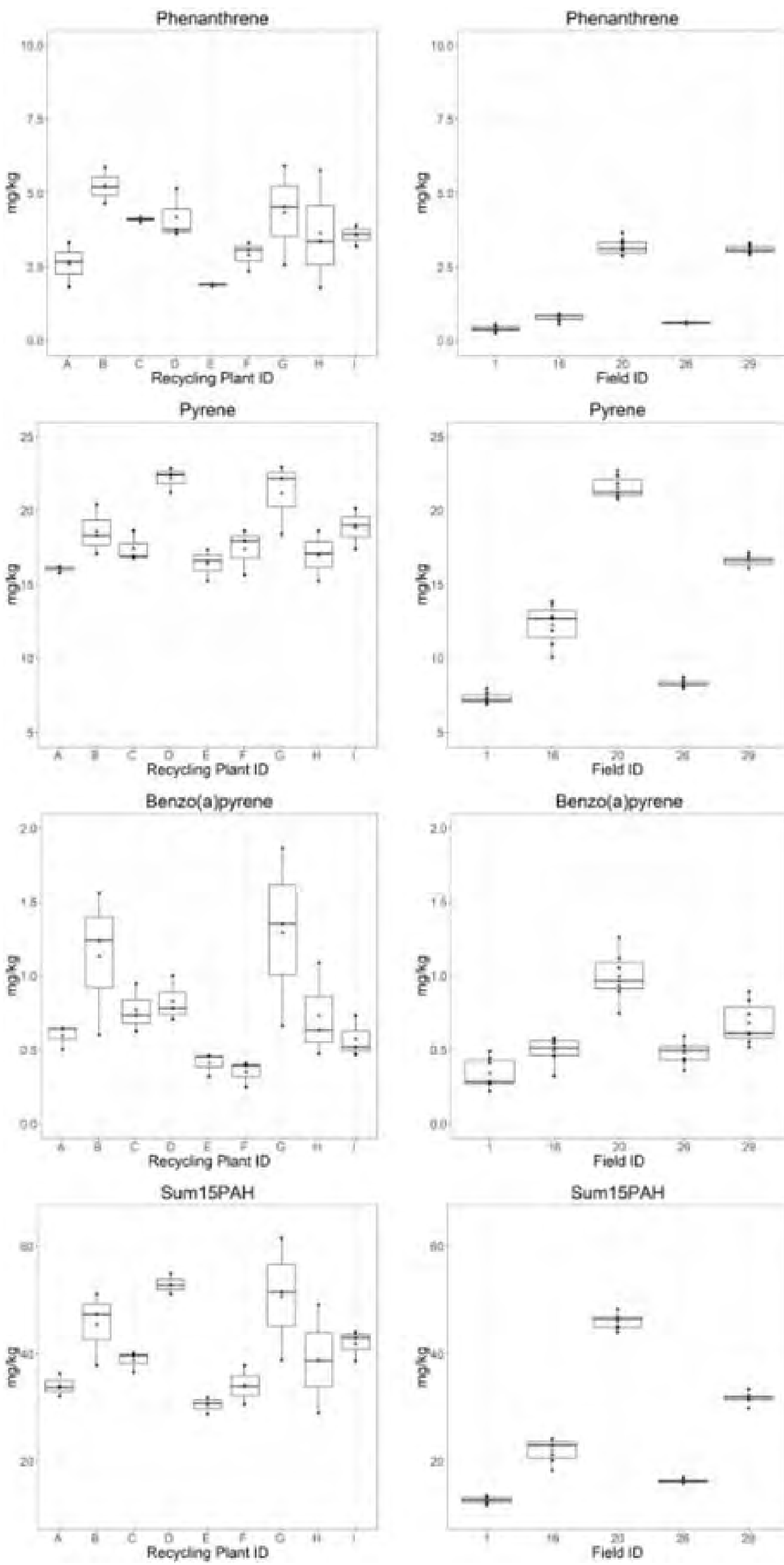

Figure 4-33. Within-tire recycling plant variability (left side) and within-synthetic turf field variability (right side) for GC/MS/MS extract SVOC analysis results (mg/kg) in tire crumb rubber for phenanthrene, pyrene, benzo[a]pyrene, and the sum of 15 PAHs. [GC/MS/MS = Gas chromatography/ tandem mass spectrometry; SVOC = Semivolatile organic compound; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

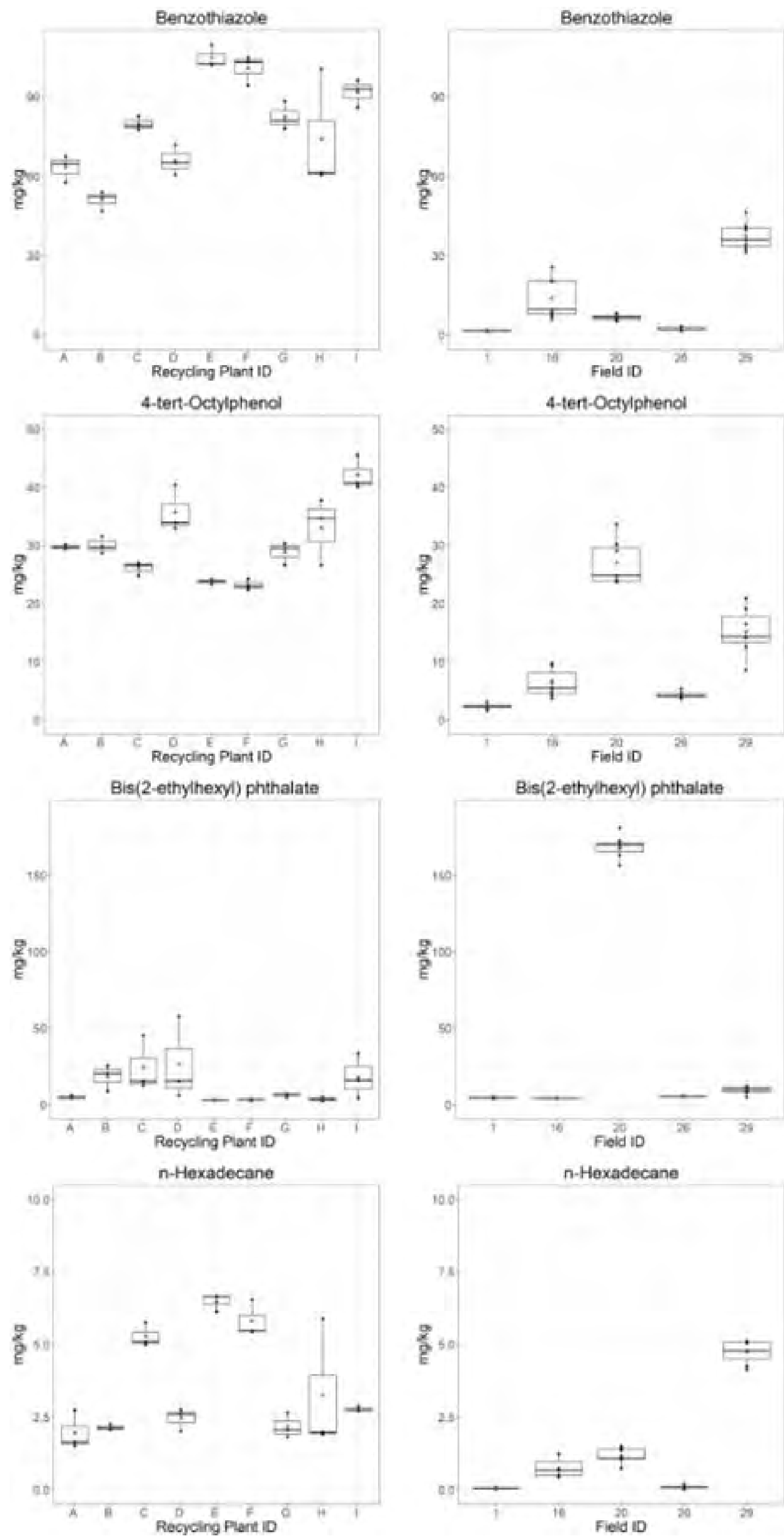

Figure 4-34. Within-tire recycling plant variability (left side) and within-synthetic turf field variability (right side) for GC/MS/MS extract SVOC analysis results (mg/kg) in tire crumb rubber for benzothiazole, 4-tert-octylphenol, bis(2-ethylhexyl) phthalate, and n-hexadecane.
[GC/MS/MS = Gas chromatography/tandem mass spectrometry; SVOC = Semivolatile organic compound]

The percent of total variance explained by within-recycling plant and between-recycling plant variances is shown in Table 4-61 for select SVOCs. Most of the chemicals had greater between-plant variability than within-plant variability except for phenanthrene, benzo[a]pyrene, and bis(2-ethylhexyl) phthalate. The percent of total variance explained by within-field and between-field variances is also shown in Table 4-61 for select SVOCs. The amount of variability explained by between-field differences was much greater than the amount explained by within-field differences for all SVOC chemicals.

Table 4-61. Within- and Between-recycling Plant or Field Variability for Select SVOC Extraction GC/MS/MS Analysis Results for Tire Crumb Rubber Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Collected from Synthetic Turf Fields[a]

Tire Crumb Rubber Sampling Location	Analyte[b]	Number of Plants or Fields	Number of Samples per Plant or Field	Between Plant or Field % Variance	Within Plant or Field % Variance
Recycling Plants	Phenanthrene	9	3	37	63
Recycling Plants	Fluoranthene	9	3	64	36
Recycling Plants	Pyrene	9	3	60	40
Recycling Plants	Benzo[a]pyrene	9	3	39	61
Recycling Plants	Benzo[ghi]perylene	9	3	59	41
Recycling Plants	Sum15PAH	9	3	54	46
Recycling Plants	Benzothiazole	9	3	76	24
Recycling Plants	Dibutyl phthalate	9	3	91	9
Recycling Plants	Bis(2-ethylhexyl) phthalate	9	3	17	83
Recycling Plants	Aniline	9	3	84	16
Recycling Plants	4-tert-octylphenol	9	3	80	20
Recycling Plants	n-Hexadecane	9	3	77	23
Synthetic Turf Fields	Phenanthrene	5	7	98	2
Synthetic Turf Fields	Fluoranthene	5	7	95	5
Synthetic Turf Fields	Pyrene	5	7	98	2
Synthetic Turf Fields	Benzo[a]pyrene	5	7	77	23
Synthetic Turf Fields	Benzo[ghi]perylene	5	7	83	17
Synthetic Turf Fields	Sum15PAH	5	7	99	1
Synthetic Turf Fields	Benzothiazole	5	7	90	10
Synthetic Turf Fields	Dibutyl phthalate	5	7	88	12
Synthetic Turf Fields	Bis(2-ethylhexyl) phthalate	5	7	100	0
Synthetic Turf Fields	Aniline	5	7	82	18
Synthetic Turf Fields	4-tert-octylphenol	5	7	91	9
Synthetic Turf Fields	n-Hexadecane	5	7	98	2

[a] GC/MS/MS = Gas chromatography/ tandem mass spectrometry; SVOC = Semivolatile organic compound
[b] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

4.9.2.3 VOC Emission Factors Analysis

Table 4-62 shows average and individual VOC 25 °C emission measurement results for methyl isobutyl ketone, benzothiazole, and styrene for tire crumb rubber samples collected from three storage bags at nine tire recycling plants. %RSD values ranged from 2.8% to 87% for benzothiazole. Methyl isobutyl ketone and styrene emission factors were low at this temperature, and there was considerable variability, as evidenced by the high %RSD. The results for the second individual sample at Plant ID D were very low compared to other measurements. It is not clear whether this represents a true difference, or a measurement error for that sample.

Table 4-62. Select VOC 25 °C Emission Factor Measurement Results for Individual Tire Crumb Rubber Samples Collected at Nine Recycling Plants for Assessing Within-Plant Variability[a,b]

Chemical	Plant ID	Mean (ng/g/h)	Standard Deviation (ng/g/h)	% Relative Standard Deviation	Individual Sample 1 Results (ng/g/h)	Individual Sample 2 Results (ng/g/h)	Individual Sample 3 Results (ng/g/h)
Methyl isobutyl ketone	A	21	11	51	17	13	33
Methyl isobutyl ketone	B	25	5.0	20	31	24	21
Methyl isobutyl ketone	C	13	7.4	58	20	12	5.7
Methyl isobutyl ketone	D	15	13	88	26	0.28	19
Methyl isobutyl ketone	E	48	29	61	56	72	15
Methyl isobutyl ketone	F	33	18	54	36	13	48
Methyl isobutyl ketone	G	19	4.6	24	21	14	23
Methyl isobutyl ketone	H	16	9.4	60	24	5.6	18
Methyl isobutyl ketone	I	31	11	35	22	43	28
Benzothiazole	A	140	37	26	99	170	160
Benzothiazole	B	140	3.9	2.8	140	140	140
Benzothiazole	C	150	54	36	180	180	87
Benzothiazole	D	92	80	87	130	0.045	150
Benzothiazole	E	170	17	9.9	180	180	150
Benzothiazole	F	170	5.1	3.0	170	170	160
Benzothiazole	G	130	9.3	7.0	130	120	140
Benzothiazole	H	140	46	32	180	150	93
Benzothiazole	I	180	2.1	1.2	180	180	180
Styrene	A	0.26	0.14	55	0.41	0.12	0.26
Styrene	B	0.12	0.081	70	0.21	0.068	0.071
Styrene	C	0.33	0.26	79	0.16	0.20	0.63
Styrene	D	0.32	0.33	100	0.70	0.067	0.20
Styrene	E	0.29	0.17	59	0.23	0.16	0.49
Styrene	F	0.31	0.14	44	0.17	0.31	0.44
Styrene	G	0.65	0.27	41	0.87	0.72	0.35
Styrene	H	0.17	0.032	19	0.13	0.19	0.19
Styrene	I	0.33	0.036	11	0.35	0.29	0.36

[a] VOC = Volatile organic compound

[b] Each sample collected from a different storage bag at the recycling plants.

Table 4-63 shows average and individual VOC 25 °C emission measurement results for benzothiazole for tire crumb rubber infill samples collected from three locations at five synthetic turf fields. %RSD values ranged from 3% to 51%. No other chemicals are reported in this table because most other chemicals had one or more results that were not greater than the chamber background.

Table 4-63. Select VOC 25 °C Emission Factor Measurement Results for Individual Location Tire Crumb Rubber Infill Samples Collected at Five Synthetic Turf Fields for Assessing Within-Field Variability[a,b]

Chemical	Field ID	Composite Sample[c] (ng/g/h)	Mean (ng/g/h)	% Relative Standard Deviation	Individual Field Sample Location 1 Results (ng/g/h)	Individual Field Sample Location 2 Results (ng/g/h)	Individual Field Sample Location 3 Results (ng/g/h)
Benzothiazole	1	1.9	1.5	51	1.5	2.2	0.7
Benzothiazole	16	33	22	21	17	26	24
Benzothiazole	20	25	19	37	11	22	24
Benzothiazole	26	1.2	3.5	40	4.5	1.9	4.1
Benzothiazole	29	110	86	3.0	85	84	89

[a] VOC = Volatile organic compound

[b] Refer to Figure 3-5 for a schematic representation of positions for samples collected from locations 1 – 3.

[c] This is the measurement result for the analysis of the composite sample that was prepared from portions of tire crumb rubber infill from seven locations on the synthetic turf field.

Table 4-64 shows average and individual VOC 60 °C emission measurement results for formaldehyde, methyl isobutyl ketone, and benzothiazole for tire crumb rubber samples collected from three storage bags at nine tire recycling plants. %RSD values ranged from 5.2 to 30% for formaldehyde, 1.5% to 18% for methyl isobutyl ketone, and 1.2% to 6.2% for benzothiazole.

Table 4-64. Select VOC 60 °C Emission Factor Measurement Results for Individual Tire Crumb Rubber Samples Collected at Nine Recycling Plants for Assessing Within-plant Variability[a,b]

Chemical	Plant ID	Mean (ng/g/h)	Standard Deviation (ng/g/h)	% Relative Standard Deviation	Individual Sample 1 Results (ng/g/h)	Individual Sample 2 Results (ng/g/h)	Individual Sample 3 Results (ng/g/h)
Formaldehyde	A	44	7.3	16	49	36	48
Formaldehyde	B	42	6.1	14	49	40	37
Formaldehyde	C	21	1.1	5.2	23	20	21
Formaldehyde	D	43	2.4	5.6	46	44	41
Formaldehyde	E	20	4.0	19	16	24	20
Formaldehyde	F	26	5.1	20	31	21	24
Formaldehyde	G	45	8.4	19	44	54	37
Formaldehyde	H	51	15	30	62	33	56
Formaldehyde	I	66	8.9	13	56	69	73
Methyl isobutyl ketone	A	130	13	11	140	110	130
Methyl isobutyl ketone	B	140	8.4	6.0	150	130	150
Methyl isobutyl ketone	C	130	7.3	5.7	140	120	130

Table 4-64 Continued

Chemical	Plant ID	Mean (ng/g/h)	Standard Deviation (ng/g/h)	% Relative Standard Deviation	Individual Sample 1 Results (ng/g/h)	Individual Sample 2 Results (ng/g/h)	Individual Sample 3 Results (ng/g/h)
Methyl isobutyl ketone	D	120	11	8.9	130	110	120
Methyl isobutyl ketone	E	160	3.0	1.9	150	160	160
Methyl isobutyl ketone	F	150	11	7.2	160	140	150
Methyl isobutyl ketone	G	130	2.0	1.5	130	130	130
Methyl isobutyl ketone	H	120	22	18	150	100	120
Methyl isobutyl ketone	I	140	6.4	4.6	130	150	140
Benzothiazole	A	230	14	6.2	240	220	240
Benzothiazole	B	220	7.0	3.2	220	220	230
Benzothiazole	C	220	5.2	2.4	230	220	220
Benzothiazole	D	220	5.3	2.4	220	220	210
Benzothiazole	E	220	11	4.7	210	220	230
Benzothiazole	F	230	2.7	1.2	230	220	230
Benzothiazole	G	230	5.6	2.5	230	230	220
Benzothiazole	H	220	10	4.8	230	210	210
Benzothiazole	I	220	4.1	1.8	230	220	230

[a] VOC = Volatile organic compound

[b] Each sample collected from a different storage bag at the recycling plants.

Table 4-65 shows average and individual VOC 60 °C emission measurement results for formaldehyde, methyl isobutyl ketone, and benzothiazole for tire crumb rubber infill samples collected from three locations at five synthetic turf fields. %RSD values ranged from 2 to 67% for formaldehyde, 4.8% to 16% for methyl isobutyl ketone, and 5.7% to 21% for benzothiazole. These results suggest low to modest variability for these chemicals in emissions at 60 °C for samples collected at multiple locations on a synthetic turf field.

Table 4-65. Select VOC 60 °C Emission Factor Measurement Results for Individual Location Tire Crumb Rubber Infill Samples Collected at Five Synthetic Turf Fields for Assessing Within-field Variability[a,b]

Chemical	Field ID	Composite Sample[c] (ng/g/h)	Mean (ng/g/h)	% Relative Standard Deviation	Individual Field Sample Location 1 Results (ng/g/h)	Individual Field Sample Location 2 Results (ng/g/h)	Individual Field Sample Location 3 Results (ng/g/h)
Formaldehyde	1	11	12	12	13	10	13
Formaldehyde	16	9.4	11	17	13	9.0	12
Formaldehyde	20	23	21	2.0	22	21	21
Formaldehyde	26	17	8.7	10	7.9	9.7	8.6
Formaldehyde	29	20	15	67	3.4	22	20
Methyl isobutyl ketone	1	34	32	14	32	27	36
Methyl isobutyl ketone	16	56	64	16	75	61	55
Methyl isobutyl ketone	20	57	61	7.9	65	56	62
Methyl isobutyl ketone	26	35	33	4.8	34	31	34
Methyl isobutyl ketone	29	96	89	9.7	87	99	82

Table 4-65 Continued

Chemical	Field ID	Composite Samplec (ng/g/h)	Mean (ng/g/h)	% Relative Standard Deviation	Individual Field Sample Location 1 Results (ng/g/h)	Individual Field Sample Location 2 Results (ng/g/h)	Individual Field Sample Location 3 Results (ng/g/h)
Benzothiazole	1	18	19	21	19	16	24
Benzothiazole	16	87	86	5.7	92	83	84
Benzothiazole	20	82	87	5.7	91	82	89
Benzothiazole	26	30	32	16	37	27	33
Benzothiazole	29	110	110	1.4	110	110	110

[a] VOC = Volatile organic compound

[b] Refer to Figure 3-5 for a schematic representation of positions for samples collected from locations 1 – 3.

[c] This is the measurement result for the analysis of the composite sample that was prepared from portions of tire crumb rubber infill from the seven locations on the synthetic turf field.

The variability in 60 °C emission measurement results for individual samples collected at tire recycling plants and synthetic turf fields is shown graphically for selected chemicals in Figure 4-35.

The percent of total variance explained by within-recycling plant and between-recycling plant variances is shown in Table 4-66 for select VOC 25 °C emission factor measurements. All chemicals had greater within-plant variability than between-plant variability. The percent of total variance explained by within-field and between-field variances is also shown in Table 4-66 for select VOC 25 °C emission factor measurements. The amount of variability explained by between-field differences was much greater than the amount explained by within-field differences for benzothiazole. The reverse was observed for o-xylene and the sum of BTEX compounds.

The percent of total variance explained by within-recycling plant and between-recycling plant variances is shown in Table 4-67 for select VOC 60 °C emission factor measurements. Some chemicals had greater within-plant variability than between-plant variability, while the reverse was observed for other chemicals. The percent of total variance explained by within-field and between-field variances is also shown in Table 4-67 for select VOC 60 °C emission factor measurements. The amount of variability explained by between-field differences was much greater than the amount explained by within-field differences for all chemicals except formaldehyde and toluene.

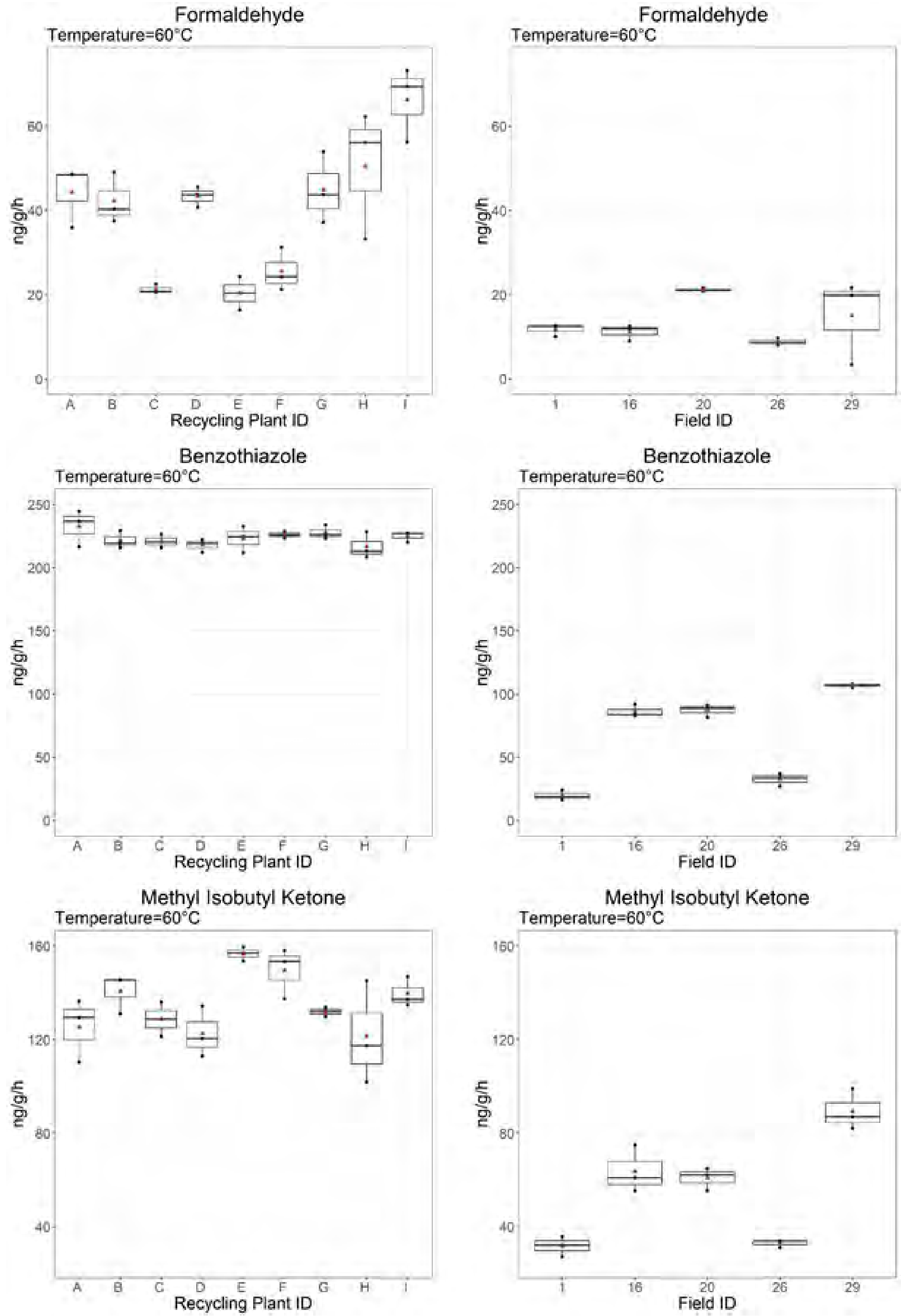

Figure 4-35. Within-tire recycling plant variability (left side) and within-synthetic turf field variability (right side) variability for VOC emission factor 60 °C analysis results (ng/g/h) in tire crumb rubber for formaldehyde, benzothiazole, and methyl isobutyl ketone. [VOC = Volatile organic compound]

Table 4-66. Within- and Between-recycling Plant or Field Variability for Select VOC 25 °C Emission Factor Analysis Results for Tire Crumb Rubber Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Collected from Synthetic Turf Fields

Tire Crumb Rubber Sampling Location	Analyte[a]	Number of Plants or Fields	Number of Samples per Plant or Field	Between Plant or Field % Variance	Within Plant or Field % Variance
Recycling Plants	Methyl isobutyl ketone	9	3	19	81
Recycling Plants	Benzothiazole	9	3	8	92
Recycling Plants	Styrene	9	3	16	84
Recycling Plants	Toluene	9	3	43	57
Recycling Plants	m/p-Xylene	9	3	29	71
Recycling Plants	o-Xylene	9	3	26	74
Recycling Plants	SumBTEX	9	3	36	64
Synthetic Turf Fields	Benzothiazole	5	3	98	2
Synthetic Turf Fields	o-Xylene	5	3	24	76
Synthetic Turf Fields	SumBTEX	5	3	30	70

[a] SumBTEX = Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene

Table 4-67. Within- and Between-recycling Plant or Field Variability for Select VOC 60 °C Emission Factor Analysis Results for Tire Crumb Rubber Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Collected from Synthetic Turf Fields

Tire Crumb Rubber Sampling Location	Analyte[a]	Number of Plants or Fields	Number of Samples per Plant or Field	Between Plant or Field % Variance	Within Plant or Field % Variance
Recycling Plants	Formaldehyde	9	3	76	24
Recycling Plants	Methyl isobutyl ketone	9	3	45	55
Recycling Plants	Benzothiazole	9	3	0	100
Recycling Plants	Styrene	9	3	88	12
Recycling Plants	Benzene	9	3	63	37
Recycling Plants	Toluene	9	3	62	38
Recycling Plants	Ethylbenzene	9	3	47	53
Recycling Plants	m/p-Xylene	9	3	16	84
Recycling Plants	o-Xylene	9	3	44	56
Recycling Plants	SumBTEX	9	3	60	40
Synthetic Turf Fields	Formaldehyde	5	3	34	66
Synthetic Turf Fields	Methyl isobutyl ketone	5	3	91	9
Synthetic Turf Fields	Benzothiazole	5	3	98	2
Synthetic Turf Fields	Styrene	5	3	95	5
Synthetic Turf Fields	Toluene	5	3	26	74
Synthetic Turf Fields	Ethylbenzene	5	3	82	18
Synthetic Turf Fields	m/p-Xylene	5	3	85	15
Synthetic Turf Fields	o-Xylene	5	3	72	28
Synthetic Turf Fields	SumBTEX	5	3	86	14

[a] SumBTEX = Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene

4.9.2.4 SVOC Emission Factors Analysis

Table 4-68 shows average and individual SVOC 25 °C emission measurement results for the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol for tire crumb rubber samples collected from three storage bags at nine tire recycling plants. %RSD values ranged from 2% to 64% for Sum15PAH, 8.2% to 63% for benzothiazole, and 3.5% to 51% for 4-tert-octylphenol.

Table 4-68. Select SVOC 25 °C Emission Factor Measurement Results for Individual Tire Crumb Rubber Samples Collected at Nine Recycling Plants for Assessing Within-Plant Variability[a,b]

Chemical[c]	Plant ID	Mean (ng/g/h)	Standard Deviation (ng/g/h)	% Relative Standard Deviation	Individual Sample 1 Results (ng/g/h)	Individual Sample 2 Results (ng/g/h)	Individual Sample 3 Results (ng/g/h)
Sum15PAH	A	3.4	0.31	9.3	3.7	3.2	3.2
Sum15PAH	B	3.0	0.31	10	2.9	2.8	3.4
Sum15PAH	C	0.87	0.31	36	0.66	0.72	1.2
Sum15PAH	D	3.3	0.84	25	3.9	2.4	3.7
Sum15PAH	E	1.3	0.20	16	1.5	1.1	1.3
Sum15PAH	F	1.6	1.0	64	0.84	1.2	2.8
Sum15PAH	G	2.2	0.044	2.0	2.2	2.2	2.3
Sum15PAH	H	2.0	0.8	41	1.1	2.6	2.2
Sum15PAH	I	3.4	1.1	31	4.2	2.2	3.7
Benzothiazole	A	18	3.8	22	13	19	20
Benzothiazole	B	17	2.6	15	16	15	20
Benzothiazole	C	36	11	31	34	27	48
Benzothiazole	D	45	18	41	65	40	29
Benzothiazole	E	91	46	50	140	78	56
Benzothiazole	F	41	9.3	23	34	52	38
Benzothiazole	G	45	6.2	14	41	42	53
Benzothiazole	H	34	21	63	58	27	16
Benzothiazole	I	37	3.1	8.2	39	39	34
4-tert-octylphenol	A	0.22	0.017	7.6	0.22	0.21	0.24
4-tert-octylphenol	B	0.23	0.075	33	0.19	0.18	0.32
4-tert-octylphenol	C	0.32	0.099	31	0.22	0.31	0.42
4-tert-octylphenol	D	0.54	0.14	26	0.41	0.51	0.69
4-tert-octylphenol	E	0.41	0.049	12	0.46	0.39	0.37
4-tert-octylphenol	F	0.51	0.26	51	0.34	0.39	0.81
4-tert-octylphenol	G	0.45	0.016	3.5	0.44	0.46	0.44
4-tert-octylphenol	H	0.88	0.35	40	0.63	0.71	1.3
4-tert-octylphenol	I	0.71	0.12	17	0.57	0.75	0.80

[a] Each sample collected from a different storage bag at the recycling plants.

[b] Statistics were calculated using original unrounded measurement results; all results in this table have been rounded to two significant figures.

[c] Sum15PAH = Sum of 15 of the 16 EPA ‘priority’ PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

Table 4-69 shows average and individual SVOC 25 °C emission measurement results for the sum of 15 PAHs and benzothiazole for tire crumb rubber infill samples collected from three locations at five synthetic turf fields. %RSD values ranged from 3.6% to 36% for the sum of 15 PAHs and 11% to 67% for benzothiazole. No other chemicals are reported in this table because most other chemicals had one or more results below chamber background levels.

Table 4-69. Select SVOC 25 °C Emission Factor Measurement Results for Individual Location Tire Crumb Rubber Infill Samples Collected at Five Synthetic Turf Fields for Assessing Within-Field Variability[a,b]

Chemical [c]	Field ID	Composite Sample[d] (ng/g/h)	Mean (ng/g/h)	% Relative Standard Deviation	Individual Field Sample Location 1 Results (ng/g/h)	Individual Field Sample Location 2 Results (ng/g/h)	Individual Field Sample Location 3 Results (ng/g/h)
Sum15PAH	1	2.4	2.7	3.6	2.6	2.8	2.7
Sum15PAH	16	0.78	0.52	33	0.43	0.41	0.71
Sum15PAH	20	3.1	1.5	36	1.4	1.1	2.1
Sum15PAH	26	0.19	0.53	36	0.40	0.74	0.43
Sum15PAH	29	0.33	0.42	16	0.37	0.49	0.39
Benzothiazole	1	0.37	0.21	67	0.28	0.31	0.048
Benzothiazole	16	5.6	4.9	32	6.7	3.9	4.1
Benzothiazole	20	4.9	5.2	19	6.3	4.3	5.1
Benzothiazole	26	0.57	0.59	49	0.91	0.42	0.42
Benzothiazole	29	19	16	11	15	18	16

[a] Refer to Figure 3-5 for a schematic representation of positions for samples collected from locations 1 – 3 at synthetic turf fields.

[b] Statistics were calculated using original unrounded measurement results; all results in this table have been rounded to two significant figures.

[c] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

[d] This is the measurement result from the analysis of the composite sample that was prepared from portions of tire crumb rubber infill from the seven individual sample locations on the synthetic turf field.

Table 4-70 shows average and individual SVOC 60 °C emission measurement results for pyrene, benzothiazole, and 4-tert-octylphenol for tire crumb rubber samples collected from three storage bags at nine tire recycling plants. %RSD values ranged from 1.9% to 27% for pyrene, 8.4% to 53% for benzothiazole, and 7.9% to 56% for 4-tert-octylphenol.

Table 4-70. Select SVOC 60 °C Emission Factor Measurement Results for Individual Tire Crumb Rubber Samples Collected at Nine Recycling Plants for Assessing Within-Plant Variability[a,b]

Chemical	Plant ID	Mean (ng/g/h)	Standard Deviation (ng/g/h)	% Relative Standard Deviation	Individual Sample 1 Results (ng/g/h)	Individual Sample 2 Results (ng/g/h)	Individual Sample 3 Results (ng/g/h)[c]
Pyrene	A	0.39	0.0091	2.3	0.40	0.39	0.39
Pyrene	B	0.37	0.044	12	0.34	0.35	0.42
Pyrene	C	0.31	0.039	12	0.28	0.30	0.36
Pyrene	D	0.42	0.035	8.2	0.40	0.45	N/A
Pyrene	E	0.33	0.030	9.3	0.33	0.30	0.36
Pyrene	F	0.28	0.0055	1.9	0.28	0.28	0.29
Pyrene	G	0.38	0.07	18	0.44	0.30	0.41
Pyrene	H	0.35	0.094	27	0.27	0.33	0.45
Pyrene	I	0.21	0.013	6.4	0.20	0.23	0.21
Benzothiazole	A	310	26	8.4	340	310	290
Benzothiazole	B	160	61	37	140	120	230
Benzothiazole	C	600	320	53	530	320	950
Benzothiazole	D	1100	530	48	720	1500	N/A
Benzothiazole	E	980	320	33	780	1300	820
Benzothiazole	F	570	180	32	360	650	690
Benzothiazole	G	500	54	11	530	430	520
Benzothiazole	H	30	58	22	240	220	330
Benzothiazole	I	360	74	21	400	400	270
4-tert-octylphenol	A	17	1.6	9.3	18	18	15
4-tert-octylphenol	B	13	7.5	56	4.6	17	18
4-tert-octylphenol	C	15	2.1	14	18	14	14
4-tert-octylphenol	D	35	17	50	23	47	N/A
4-tert-octylphenol	E	21	3.2	15	25	19	20
4-tert-octylphenol	F	13	1.1	7.9	12	14	14
4-tert-octylphenol	G	17	1.7	10	17	19	15
4-tert-octylphenol	H	24	9.0	37	20	18	35
4-tert-octylphenol	I	32	3.1	9.6	32	35	29

[a] Each sample collected from a different storage bag at the recycling plants.

[b] Statistics were calculated using original unrounded measurement results; all results in this table have been rounded to two significant figures.

[c] N/A – SVOC measurement results not usable for Plant ID 85.

Table 4-71 shows average and individual SVOC 60 °C emission measurement results for pyrene, the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol for tire crumb rubber infill samples collected from three locations at five synthetic turf fields. %RSD values ranged from 1.8% to 9.0% for pyrene, 4.6% to 21% for Sum15PAH, 11% to 27% for benzothiazole, and 1.7% to 39% for 4-tert-octylphenol. These results suggest low to modest variability in emissions at 60 °C for samples collected at multiple locations on a synthetic turf field for these chemicals. The composite measurement results for Field ID #26 were very low compared to other measurements, appearing as negative results due to chamber background subtraction; it is not clear whether this represents a true difference, or a measurement error for that sample. The variability in 60 °C emission measurement results for individual samples collected at tire recycling plants and synthetic turf fields is shown graphically for selected SVOC chemicals in Figure 4-36.

Table 4-71. Select SVOC 60 °C Emission Factor Measurement Results for Individual Location Tire Crumb Rubber Infill Samples Collected at Five Synthetic Turf Fields for Assessing Within-Field Variability[a,b,c]

Chemical[d]	Field ID	Composite Sample[e] (ng/g/h)	Mean (ng/g/h)	% Relative Standard Deviation	Individual Field Sample Location 1 Results (ng/g/h)	Individual Field Sample Location 2 Results (ng/g/h)	Individual Field Sample Location 3 Results (ng/g/h)
Pyrene	1	0.18	0.19	9.0	0.21	0.18	0.19
Pyrene	16	0.25	0.23	4.5	0.22	0.23	0.24
Pyrene	20	0.73	0.68	3.4	0.68	0.7	0.66
Pyrene	26	-0.025	0.15	8.0	0.14	0.15	0.17
Pyrene	29	0.37	0.31	1.8	0.31	0.31	0.32
Sum15PAH	1	1.4	1.8	8.5	1.9	1.7	1.6
Sum15PAH	16	1.1	1.2	21	1.1	1.5	0.97
Sum15PAH	20	3.6	3.8	4.6	3.9	3.9	3.6
Sum15PAH	26	0.21	0.7	9.9	0.75	0.62	0.72
Sum15PAH	29	2.7	2.4	7.8	2.6	2.3	2.3
Benzothiazole	1	4.0	4.7	11	4.2	5.3	4.7
Benzothiazole	16	18	17	27	22	17	13
Benzothiazole	20	35	38	15	43	39	32
Benzothiazole	26	-0.53	5.3	25	6.9	4.5	4.6
Benzothiazole	29	140	110	20	110	130	90
4-tert-octylphenol	1	13	2.2	39	1.8	1.7	3.2
4-tert-octylphenol	16	4.9	4.2	24	5.3	3.8	3.4
4-tert-octylphenol	20	20	20	1.7	20	20	20
4-tert-octylphenol	26	-0.27	2.2	26	2.1	1.7	2.9
4-tert-octylphenol	29	9.9	12	24	11	15	9.6

[a] Several results are reported as negative values. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.

[b] Statistics were calculated using original unrounded measurement results; all results in this table have been rounded to two significant figures.

[c] Refer to Figure 3-5 for a schematic representation of positions for samples collected from locations 1 – 3.

[d] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

[e] This is the measurement result for the analysis of the composite sample that was prepared from portions of tire crumb rubber infill from the seven locations on the synthetic turf field.

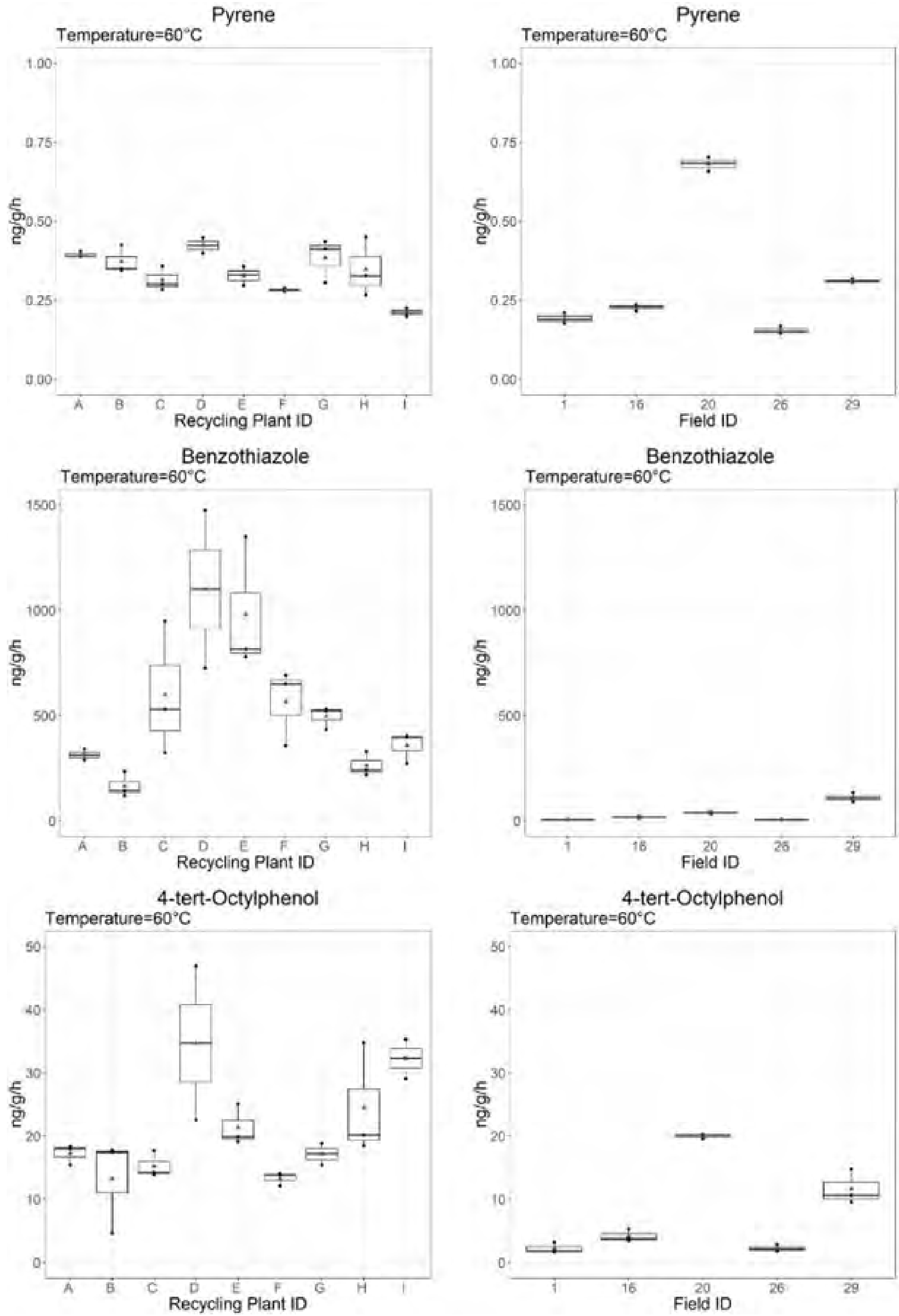

Figure 4-36. Within-tire recycling plant variability (left side) and within-synthetic turf field variability (right side) variability for SVOC emission factor 60 °C analysis results (ng/g/h) in tire crumb rubber for pyrene, benzothiazole, 4-tert-octylphenol. [SVOC = Semivolatile organic compound]

The percent of total variance explained by within-recycling plant and between-recycling plant variances is shown in Table 4-72 for select SVOC 25 °C emission factor measurements. Some chemicals had greater within-plant variability than between-plant variability, while the reverse was observed for other chemicals. The percent of total variance explained by within-field and between-field variances is also shown in Table 4-72 for select SVOC 25 °C emission factor measurements. The amount of variability explained by between-field differences was greater than the amount explained by within-field differences for four chemicals. The reverse was observed for phenanthrene and dibutyl phthalate; however, these results may have been affected by low measured emission factors.

Table 4-72. Within- and Between-Recycling Plant or Field Variability for Select SVOC 25 °C Emission Factor Analysis Results for Tire Crumb Rubber Collected from Tire Recycling Plants and Tire Crumb Rubber Infill Collected from Synthetic Turf Fields[a]

Tire Crumb Rubber Sampling Location	Analyte	Number of Plants or Fields	Number of Samples per Plant or Field	Between Plant or Field % Variance	Within Plant or Field % Variance
Recycling Plants	Phenanthrene	9	3	90	10
Recycling Plants	Sum15PAH	9	3	61	39
Recycling Plants	Benzothiazole	9	3	47	53
Recycling Plants	Dibutyl phthalate	9	3	14	86
Recycling Plants	Aniline	9	3	84	16
Recycling Plants	4-tert-octylphenol	9	3	54	46
Synthetic Turf Fields	Phenanthrene	5	3	10	90
Synthetic Turf Fields	Sum15PAH	5	3	91	9
Synthetic Turf Fields	Benzothiazole	5	3	96	4
Synthetic Turf Fields	Dibutyl phthalate	5	3	0	100
Synthetic Turf Fields	Aniline	5	3	94	6
Synthetic Turf Fields	4-tert-octylphenol	5	3	70	30

[a] SVOC = Semivolatile organic compound; Sum15PAH = Sum of 15 of the 16 EPA ‘priority’ PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

The percent of total variance explained by within-recycling plant and between-recycling plant variances is shown in Table 4-73 for select SVOC 60 °C emission factor measurements. Some chemicals had greater within-plant variability than between-plant variability, while the reverse was observed for other chemicals. The percent of total variance explained by within-field and between-field variances is also shown in Table 4-73 for select SVOC 60 °C emission factor measurements. The amount of variability explained by between-field differences was greater than the amount explained by within-field differences for all chemicals. This matches the results observed for SVOCs that were solvent extracted from tire crumb rubber infill collected at synthetic turf fields.

Table 4-73. Within- and Between-Recycling Plant or Field Variability for Select SVOC 60 °C Emission Factor Analysis Results for Tire Crumb Rubber Collected from Tire Recycling Plants

Tire Crumb Rubber Sampling Location	Analyte[a]	Number of Plants or Fields	Number of Samples per Plant or Field	Between Plant or Field % Variance	Within Plant or Field % Variance
Recycling Plants	Phenanthrene	9	2	15	85
Recycling Plants	Fluoranthene	9	2	54	46
Recycling Plants	Pyrene	9	2	56	44
Recycling Plants	Sum15PAH	9	2	47	53
Recycling Plants	Benzothiazole	9	2	60	40
Recycling Plants	Dibutyl phthalate	9	2	25	75
Recycling Plants	Aniline	9	2	55	45
Recycling Plants	4-tert-octylphenol	9	2	51	49
Synthetic Turf Fields	Phenanthrene	5	3	92	8
Synthetic Turf Fields	Fluoranthene	5	3	97	3
Synthetic Turf Fields	Pyrene	5	3	99	1
Synthetic Turf Fields	Sum15PAH	5	3	97	3
Synthetic Turf Fields	Benzothiazole	5	3	94	6
Synthetic Turf Fields	Dibutyl phthalate	5	3	80	20
Synthetic Turf Fields	Aniline	5	3	99	1
Synthetic Turf Fields	4-tert-octylphenol	5	3	96	4

[a] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

4.10 Assessment of Characteristics Potentially Associated with Differences Among Synthetic Turf Fields

In addition to examining tire crumb rubber chemical substance differences between recycling plants and synthetic turf fields, the research design allowed for exploration and analysis of potential differences in the chemicals associated with tire crumb rubber infill among synthetic turf fields with different characteristics including:

- Outdoor versus indoor field locations;
- The age of fields (installation year age groups 2004 – 2008, 2009 – 2012, 2013 – 2016); and
- Across the four U.S. census regions (Northeast, South, Midwest, West).

The numbers of fields with each of these characteristics was previously described. Comparison results are reported here for a subset of chemical substances selected for highlighting observed differences, with complete results for all target analytes shown in Appendices O through Q. Results for the following analysis types are included in this reporting sub-section:

- Metals analyzed by ICP/MS
- Metals analyzed by XRF
- SVOCs analyzed in solvent extracts by GC/MS/MS

- SVOCs non-quantitative analysis of solvent extracts by LC/TOFMS
- VOC emission factors from analysis by GC/TOFMS
- SVOC emission factors from analysis by GC/MS/MS.

4.10.1 Outdoor versus Indoor Synthetic Turf Fields

Tire crumb rubber infill mean chemical measurement results were compared for the group of outdoor fields versus the group of indoor fields. For statistical analysis results, p-values are reported for between-group differences in the cases where all measurement results were >0 (because the statistical testing was performed on the log-transformed measurement results).

4.10.1.1 Metals by ICP/MS and XRF Analysis

Table 4-74 shows results for differences in mean concentrations of select metals analyzed in acid digests by ICP/MS and in XRF analyses of tire crumb rubber infill collected at outdoor and indoor fields. No statistically significant outdoor versus indoor differences were observed for metal concentrations in tire crumb rubber infill. Average lead concentrations were approximately 50% higher in indoor fields compared to outdoor fields, but the variability in lead concentrations, particularly for indoor fields, was large; the variability was driven to a large extent by one higher lead measurement at an indoor field. Figure 4-37 illustrates the distributions in ICP/MS measurement results for outdoor and indoor fields for chromium, cobalt, lead, and zinc.

Table 4-74. Comparison of Select Metals Analyzed in Tire Crumb Rubber Infill Collected at Outdoor and Indoor Synthetic Turf Fields[a]

Analysis[b]	Analyte	Outdoor Fields Mean (mg/kg)	Outdoor Fields Standard Deviation (mg/kg)	Indoor Fields Mean (mg/kg)	Indoor Fields Standard Deviation (mg/kg)	F-test p-value[c]
ICP/MS Analysis	Arsenic	0.39	0.18	0.37	0.23	0.488
ICP/MS Analysis	Cadmium	0.86	0.45	1.1	0.96	0.3997
ICP/MS Analysis	Chromium	1.7	0.88	1.5	0.80	NR[d]
ICP/MS Analysis	Cobalt	140	60	140	63	0.8128
ICP/MS Analysis	Lead	20	14	31	39	0.4709
ICP/MS Analysis	Zinc	15000	3300	15000	2600	0.6996
XRF Analysis	Chromium	14	3.0	14	2.9	0.9667
XRF Analysis	Cobalt	40	17	36	17	0.4099
XRF Analysis	Lead	31	13	45	31	0.1433
XRF Analysis	Zinc	33000	7900	34000	5800	0.458

[a] Outdoor Fields (n=25); Indoor Fields (n=15)

[b] ICP/MS = Inductively coupled plasma/mass spectrometry; XRF = X-ray fluorescence spectrometry

[c] Statistical tests performed using ln-transformed measurement values.

[d] NR = Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

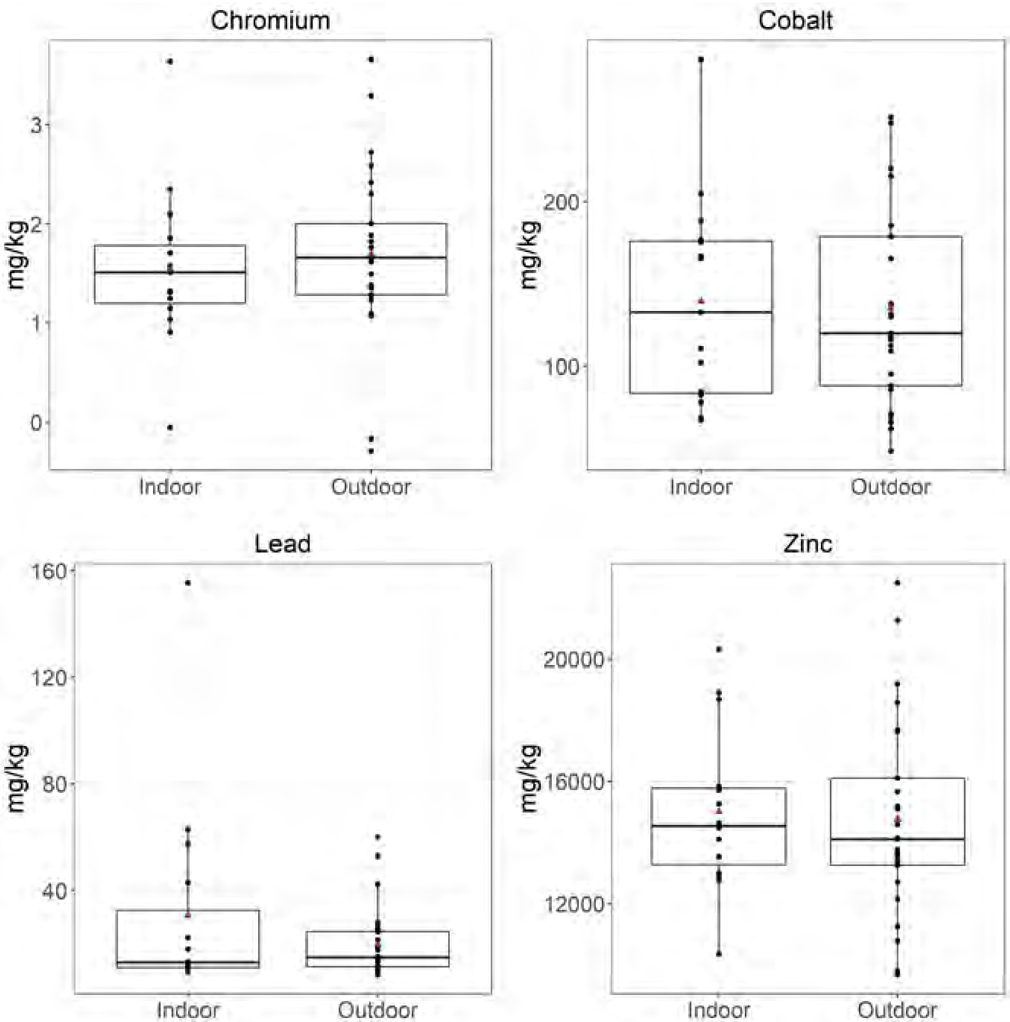

Figure 4-37. Comparison of ICP/MS metal analysis results (mg/kg) between tire crumb rubber infill composite samples from indoor and outdoor synthetic turf fields for chromium, cobalt, lead, and zinc. [ICP/MS = Inductively coupled plasma/mass spectrometry]

4.10.1.2 SVOC Extracts by GC/MS/MS and LC/TOFMS Analysis

Table 4-75 shows results for differences in mean concentrations of select SVOCs in solvent extracts analyzed by GC/MS/MS for tire crumb rubber infill collected at outdoor and indoor fields. Table 4-76 shows results for differences in mean chromatographic peak areas of select SVOCs in solvent extracts analyzed by LC/TOFMS. Most of the SVOCs had statistically significant higher average measurements in indoor versus outdoor field tire crumb rubber infill. Average indoor levels ranged from 1.5 to 10 times higher than outdoor levels for most SVOCs. The more volatile SVOCs had higher indoor/outdoor ratios than less volatile SVOCs. A likely contribution to these differences is increased weathering at outdoor locations, including heat, sunshine, ventilation rates, and rainfall. Figures 4-38 through 4-40 illustrate distributions in measurement results for outdoor and indoor fields for twelve SVOC analytes.

Table 4-75. Comparison of Select SVOC Extracts Analyzed by GC/MS/MS for Tire Crumb Rubber Infill Collected at Outdoor and Indoor Synthetic Turf Fields[a]

Analyte[b]	Outdoor Fields Mean (mg/kg)	Outdoor Fields Standard Deviation (mg/kg)	Indoor Fields Mean (mg/kg)	Indoor Fields Standard Deviation (mg/kg)	F-test p-value[c]
Phenanthrene	0.76	0.71	4.8	2.6	<.0001
Fluoranthene	3.5	2.3	6.2	2.2	0.0004
Pyrene	8.8	3.9	19	3.7	<.0001
Benzo[a]pyrene	0.66	0.37	0.98	0.67	0.0375
Benzo[ghi]perylene	1.1	0.54	1.6	0.68	0.0315
Sum15PAH	21	9.4	42	12	<.0001
Benzothiazole	5.6	9.2	19	14	<.0001
Dibutyl phthalate	0.63	0.70	2.9	1.4	<.0001
Bis(2-ethylhexyl) phthalate	29	27	65	53	0.0185
Aniline	0.38	0.24	1.2	0.54	<.0001
4-tert-octylphenol	3.5	2.2	20	7.9	<.0001
n-Hexadecane	0.20	0.20	2.2	1.3	<.0001

[a] Outdoor Fields (n=25); Indoor Fields (n=15)

[b] Sum15PAH = Sum of 15 of the 16 EPA ‘priority’ PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

[c] Statistical tests performed using ln-transformed measurement values.

Table 4-76. Comparison of Select SVOC Extracts Non-quantitative Analysis Results by LC/TOFMS for Tire Crumb Rubber Infill Collected at Outdoor and Indoor Synthetic Turf Fields[a]

Analyte	Outdoor Fields Mean Area Counts	Outdoor Fields Area Counts Standard Deviation	Indoor Fields Mean Area Counts	Indoor Fields Area Counts Standard Deviation	F-test p-value[b,c]
2-mercaptobenzothiazole	5.5E+02	9.5E+02	4.0E+03	4.9E+03	NR
2-hydroxybenzothiazole	4.2E+04	7.7E+04	2.1E+05	1.2E+05	NR
cyclohexylamine	1.2E+05	2.1E+05	1.1E+06	1.0E+06	NR
di-cyclohexylamine	5.1E+06	6.4E+06	1.5E+07	7.8E+06	<.0001
N-cyclohexyl-N-methylcyclohexanamine	1.4E+05	1.7E+05	3.9E+05	3.9E+05	0.0026
diisononylphthalate	2.8E+03	4.7E+04	7.1E+04	1.3E+05	NR
diisodecylphthalate	6.3E+03	8.8E+03	1.2E+05	4.4E+05	NR

[a] Outdoor Fields (n=25); Indoor Fields (n=15)

[b] Statistical tests performed using ln-transformed measurement values.

[c] NR=Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

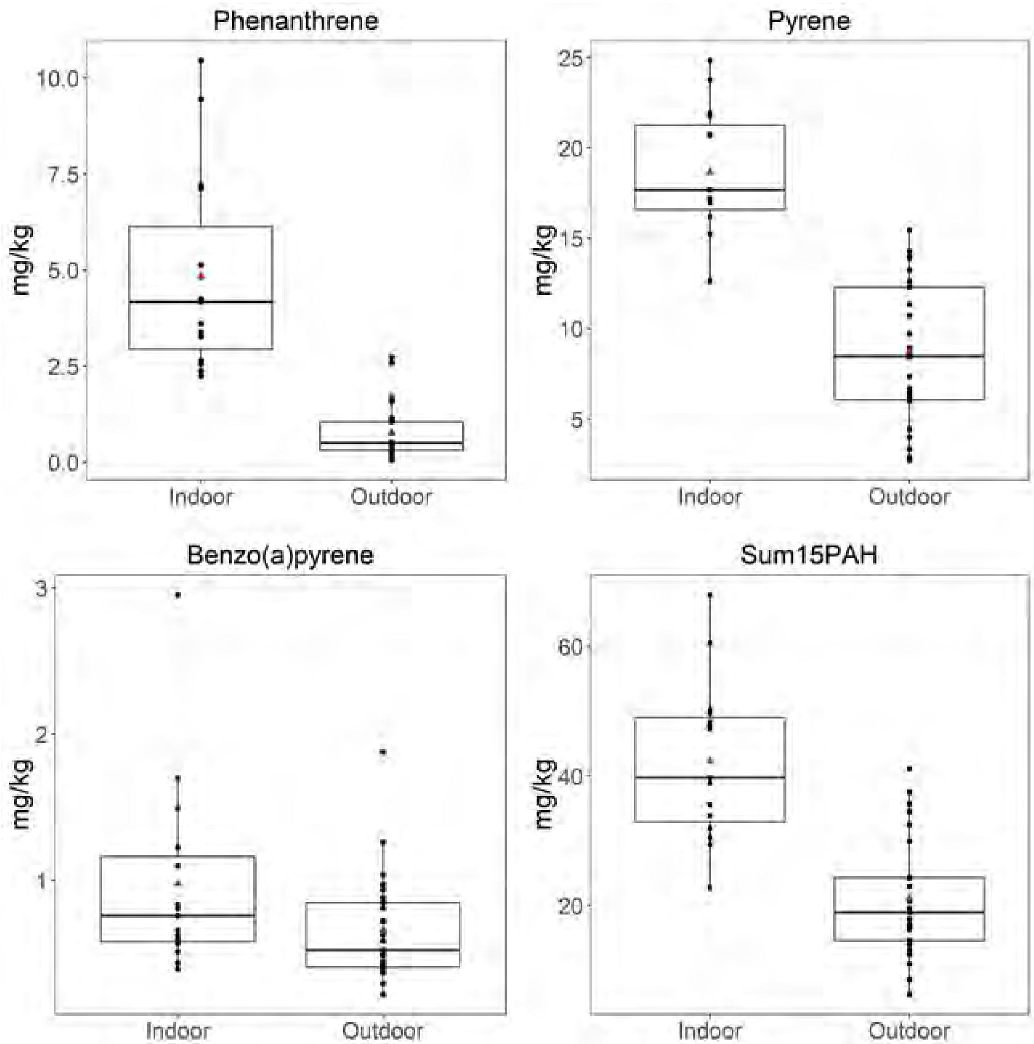

Figure 4-38. Comparison of GC/MS/MS extract SVOC analysis results (mg/kg) between tire crumb rubber infill composite samples from indoor and outdoor synthetic turf fields for phenanthrene, pyrene, benzo[a]pyrene, and the sum of 15 PAHs. [GC/MS/MS = Gas chromatography/tandem mass spectrometry; SVOC = Semivolatile organic compound; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

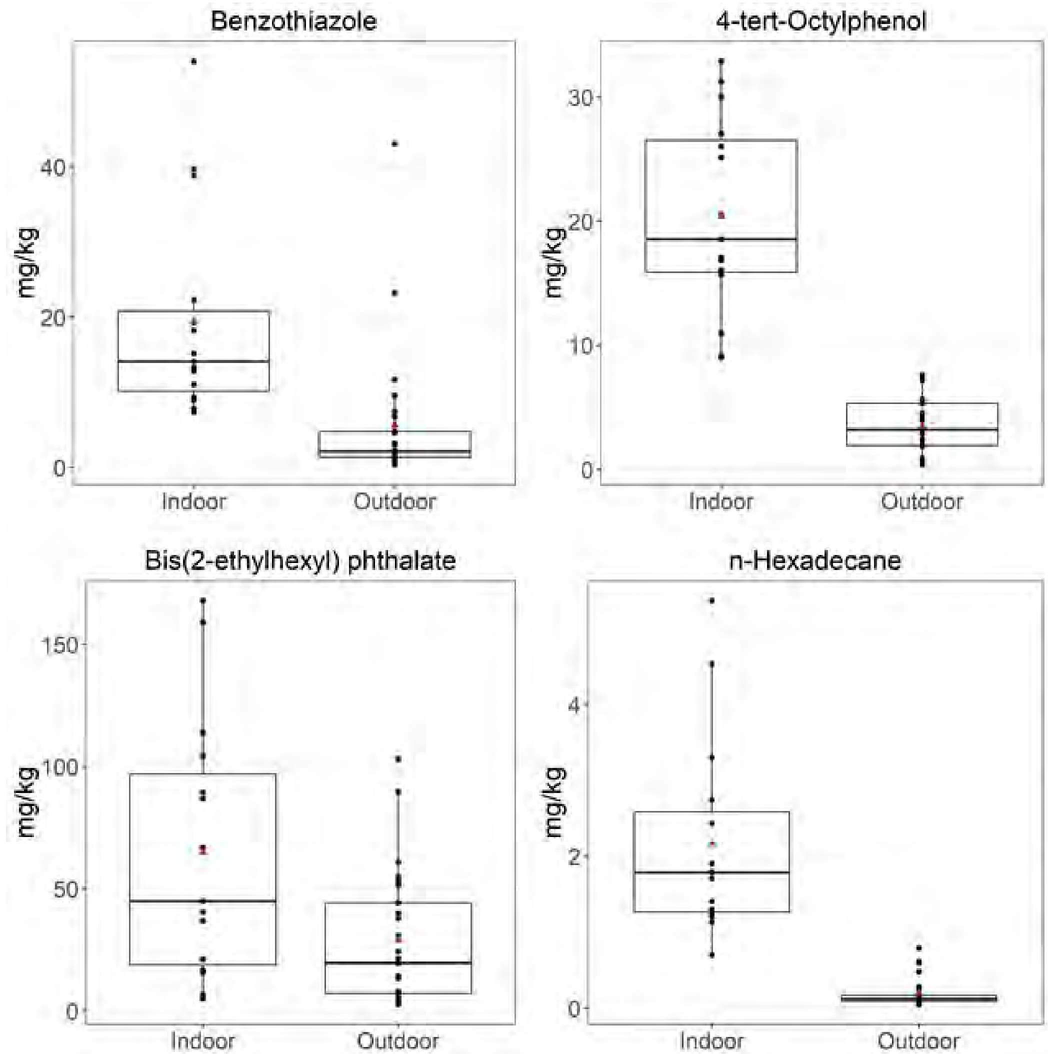

Figure 4-39. Comparison of GC/MS/MS extract SVOC analysis results (mg/kg) between tire crumb rubber infill composite samples from indoor and outdoor synthetic turf fields for benzothiazole, 4-tert-octylphenol, bis(2-ethylhexyl) phthalate, and n-hexadecane. [GC/MS/MS = Gas chromatography/tandem mass spectrometry; SVOC = Semivolatile organic compound]

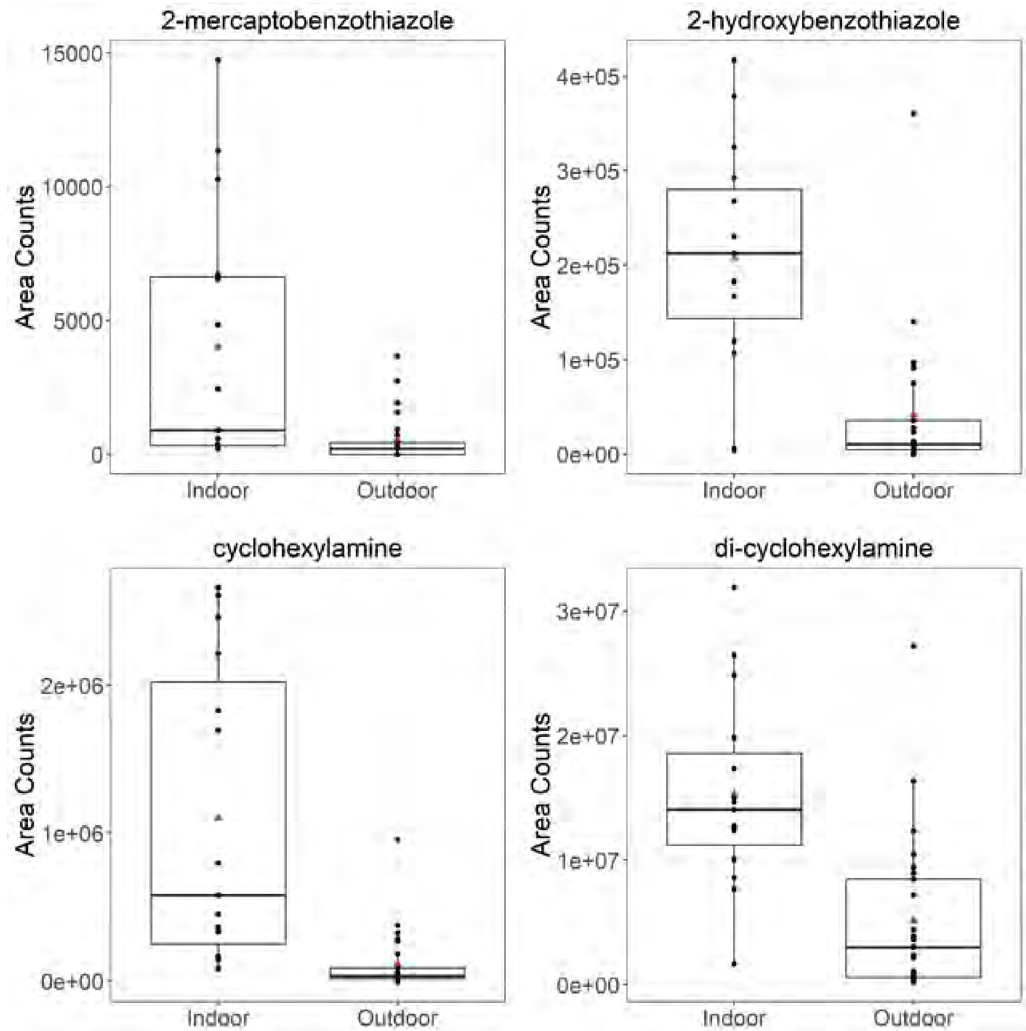

Figure 4-40. Comparison of LC/TOFMS extract SVOC non-quantitative positive ionization analysis results between tire crumb rubber infill composite samples from indoor and outdoor synthetic turf fields for 2-mercatpobenzothiazole, 2-hydroxybenzothiazole, cyclohexylamine, di-cyclohexylamine. [LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry; SVOC = Semivolatile organic compound]

4.10.1.3 VOC Emission Factors

Table 4-77 shows results for differences in mean 25 °C and 60 °C emission factors for select VOCs analyzed by GC/TOFMS for tire crumb rubber infill collected at outdoor and indoor fields. Most of the VOCs had higher emission factors for indoor versus outdoor fields, with the two chemicals with all measurements > 0 showing statistically significant differences. Average indoor field emission factors ranged from 2 to 34 times higher than outdoor field levels. A likely contribution to these differences is increased weathering at outdoor locations, including heat, sunshine, ventilation rates, and rainfall. Figure 4-41 illustrates distributions in 60 °C emission factor measurement results for outdoor and indoor fields for formaldehyde, benzothiazole, methyl isobutyl ketone, and styrene.

Table 4-77. Comparison of Select VOC Emission Factors for Tire Crumb Rubber Infill Collected at Outdoor and Indoor Synthetic Turf Fields[a,b]

Emission Test	Analyte[c]	Outdoor Fields Mean (ng/g/h)	Outdoor Fields Standard Deviation (ng/g/h)	Indoor Fields Mean (ng/g/h)	Indoor Fields Standard Deviation (ng/g/h)	F-test p-value[d,e]
Emissions at 25 °C	Benzothiazole	9.4	16	51	26	NR
Emissions at 25 °C	o-Xylene	0.0024	0.068	0.081	0.10	NR
Emissions at 25 °C	SumBTEX	0.22	0.98	0.46	0.51	NR
Emissions at 60 °C	Formaldehyde	12	5.7	23	10	NR
Emissions at 60 °C	Methyl isobutyl ketone	28	16	68	20	<.0001
Emissions at 60 °C	Benzothiazole	35	31	95	9.6	<.0001
Emissions at 60 °C	Styrene	0.24	0.29	0.84	0.29	NR
Emissions at 60 °C	Toluene	0.11	0.33	0.24	0.24	NR
Emissions at 60 °C	Ethylbenzene	-0.12	0.20	-0.0059	0.26	NR
Emissions at 60 °C	m/p-Xylene	0.043	0.97	0.61	0.97	NR
Emissions at 60 °C	o-Xylene	-0.39	0.7	-0.27	0.60	NR
Emissions at 60 °C	SumBTEX	-0.44	2.2	0.58	2.1	NR

[a] Several results are reported as negative values. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.

[b] Outdoor Fields (n=24 – 25); Indoor Fields (n=13 – 15)

[c] SumBTEX = Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene

[d] Statistical tests performed using ln-transformed measurement values.

[e] Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

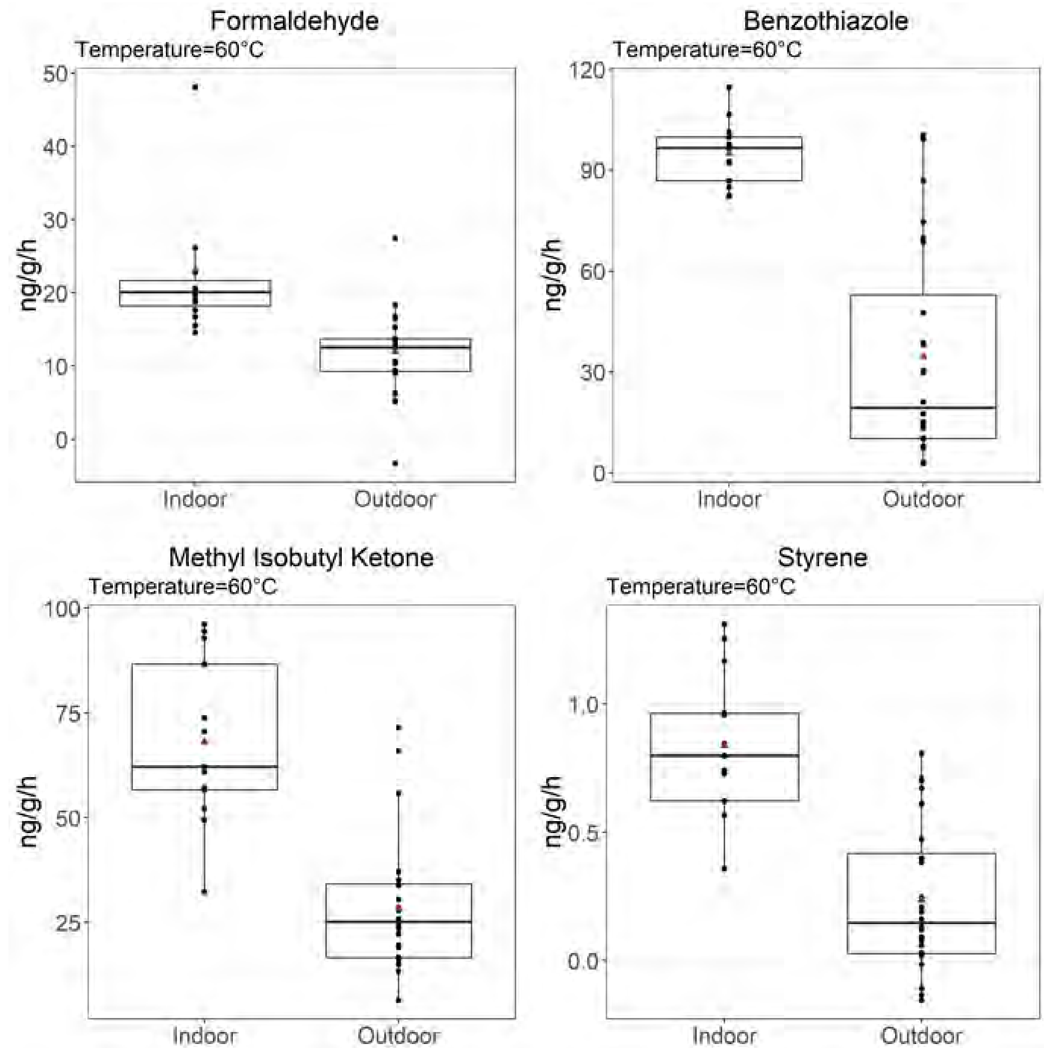

Figure 4-41. Comparison of VOC 60 °C emission factor results (ng/g/h) between tire crumb rubber infill composite samples from indoor and outdoor synthetic turf fields for formaldehyde, benzothiazole, methyl isobutyl ketone, and styrene.
[VOC = Volatile organic compound]

4.10.1.4 SVOC Emission Factors

Table 4-78 shows results for differences in mean 25 °C and 60 °C emission factors for select SVOCs analyzed by GC/MS/MS for tire crumb rubber infill collected at outdoor and indoor fields. Most of the SVOCs had higher emission factors for indoor versus outdoor fields, particularly at the 60 °C test temperature. At 25 °C, many of the emissions measurement results were below the method detection limit and/or below chamber background measurements. At 60 °C, average indoor field emission factors ranged from approximately 2 to 8 times higher than outdoor field emission factors. A likely contribution to these differences is increased weathering at outdoor locations, including heat, sunshine, ventilation rates, and rainfall. Figure 4-42 illustrates distributions in 60 °C emission factor measurement results for outdoor and indoor fields for pyrene, the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol.

Table 4-78. Comparison of Select SVOC Emission Factors for Tire Crumb Rubber Infill Collected at Outdoor and Indoor Synthetic Turf Fields[a,b]

Emission Test	Analyte[c]	Outdoor Fields Mean (ng/g/h)	Outdoor Fields Standard Deviation (ng/g/h)	Indoor Fields Mean (ng/g/h)	Indoor Fields Standard Deviation (ng/g/h)	F-test p-value[d,e]
Emissions at 25 °C	Phenanthrene	0.017	0.050	0.038	0.045	NR
Emissions at 25 °C	Sum15PAH	0.56	0.56	0.72	0.74	0.323
Emissions at 25 °C	Benzothiazole	1.5	2.6	8.7	5.3	NR
Emissions at 25 °C	Dibutyl phthalate	0.088	0.36	-0.18	0.36	NR
Emissions at 25 °C	Aniline	0.088	0.20	0.77	0.42	NR
Emissions at 25 °C	4-tert-octylphenol	0.65	3.2	1.2	3.5	NR
Emissions at 60 °C	Phenanthrene	0.17	0.22	1.2	0.75	NR[b]
Emissions at 60 °C	Fluoranthene	0.11	0.085	0.23	0.11	NR
Emissions at 60 °C	Pyrene	0.20	0.14	0.44	0.24	NR
Emissions at 60 °C	Sum15PAH	1.0	0.65	3.6	2.1	<0.0001
Emissions at 60 °C	Benzothiazole	9.7	11	74	64	NR
Emissions at 60 °C	Dibutyl phthalate	0.11	0.43	0.20	0.39	NR
Emissions at 60 °C	Aniline	0.79	1.0	8.0	6.1	NR
Emissions at 60 °C	4-tert-octylphenol	2.9	3.1	11	5.0	NR

[a] One result is reported as a negative value. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.

[b] Outdoor Fields (n=25); Indoor Fields (n=15)

[c] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

[d] Statistical tests performed using ln-transformed measurement values.

[e] NR = Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

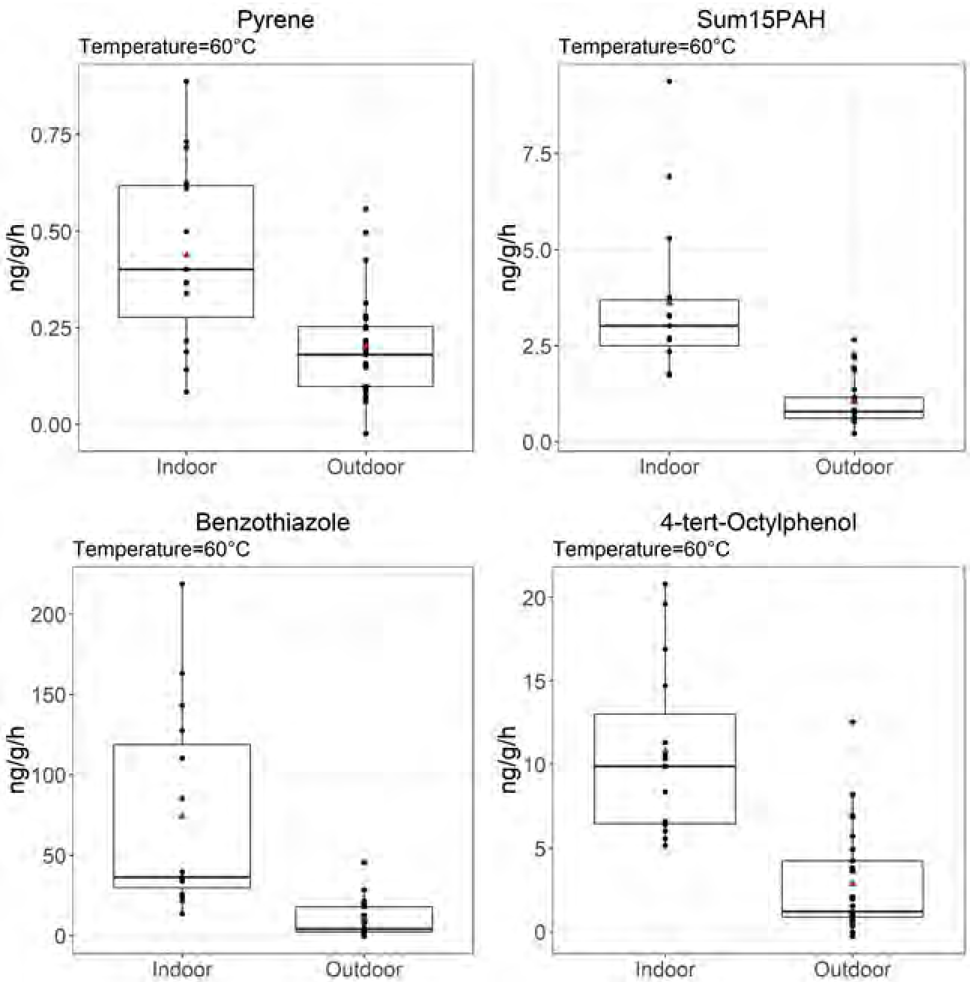

Figure 4-42. Comparison of SVOC 60 °C emission factor results (ng/g/h) between tire crumb rubber infill composite samples from indoor and outdoor synthetic turf fields for pyrene, the sum of 15 PAHs, benzothiazole, 4-tert-octylphenol. [SVOC = Semivolatile organic compound; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

4.10.2 Synthetic Field Installation Age

Tire crumb rubber infill mean chemical measurement results were compared for synthetic turf fields organized into three groups, based on year of installation, as a measure of field age. For the statistical analysis results, p-values are reported for between-group differences in the cases where all measurement results were > 0 (because the statistical testing was performed on the log-transformed measurement results). It is important to recognize that 50% of the field owners/managers reported the addition of new tire crumb rubber material to the fields and two reported replacement of tire crumb rubber infill. Because the timing and frequency of refreshment varied considerably across the fields, and some timing information was not reported, no attempts at adjustment or further analyses by age were performed based on this information. When viewing these results, it is also important to remember that substantial differences were observed for outdoor versus indoor fields for the organic chemicals. In this section, there is no differentiation between indoor and outdoor fields in each age category. In a later section, this analysis is repeated but is restricted to outdoor fields only.

4.10.2.1 Metals by ICP/MS and XRF Analysis

Figure 4-43 illustrates the distributions in measurement results across the three field installation age groups for chromium, cobalt, lead, and zinc. Differences in mean concentrations of select metals analyzed in acid digests by ICP/MS and in XRF analyses are shown in Table 4-79 for tire crumb rubber infill collected at fields in three different installation age groups. Average cobalt measurements had statistically significant differences among the age group categories, but the differences were not monotonic by field installation age. Results for zinc reached near-significance, but again, there was no monotonic trend by field installation age. Lead ICP/MS average measurements showed a pattern of increasing concentration with older installation age category; however, the increase was not statistically significant. It is not clear whether this result for lead is an indicator of increasing external source deposition over time, differences in lead concentrations in tires over time, or a chance result. The average lead value for the oldest installation age group is highly influenced by one relatively high measurement result.

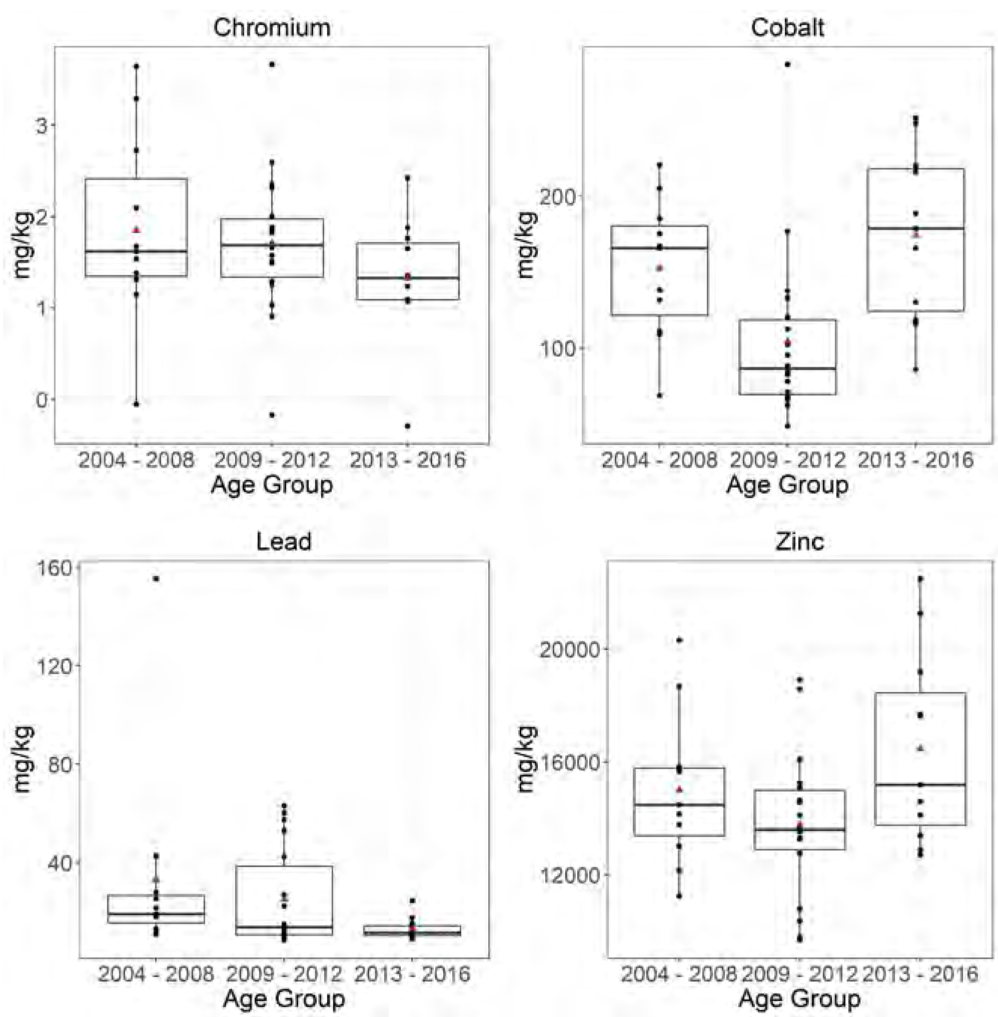

Figure 4-43. Comparison of ICP/MS metal analysis results (mg/kg) between tire crumb rubber infill composite samples from synthetic turf fields in three installation age groups for chromium, cobalt, lead, and zinc.

Table 4-79. Comparison of Selected Metals in Tire Crumb Rubber Infill Collected from Synthetic Turf Fields in Three Field Installation Age Groups

Analysis[b]	Analyte	Fields Installed 2004 – 2008 Mean (mg/kg)	Fields Installed 2004 – 2008 Standard Deviation (mg/kg)	Fields Installed 2009 – 2012 Mean (mg/kg)	Fields Installed 2009 – 2012 Standard Deviation (mg/kg)	Fields Installed 2013 – 2016 Mean (mg/kg)	Fields Installed 2013 – 2016 Standard Deviation (mg/kg)	F-test p-value[c,d]
ICP/MS Analysis	Arsenic	0.39	0.15	0.42	0.25	0.30	0.1	0.4723
ICP/MS Analysis	Cadmium	0.97	0.45	1.1	0.91	0.72	0.37	0.3463
ICP/MS Analysis	Chromium	1.8	1.0	1.7	0.79	1.3	0.68	NR[b]
ICP/MS Analysis	Cobalt	150	46	100	56	170	56	0.0006
ICP/MS Analysis	Lead	33	42	25	20	13	4.6	0.079
ICP/MS Analysis	Zinc	15000	2700	14000	2600	16000	3400	0.0501
XRF Analysis	Chromium	14	2.7	13	3.2	15	2.3	0.1121
XRF Analysis	Cobalt	39	16	32	16	49	17	0.0629
XRF Analysis	Lead	38	26	41	24	27	12	0.2297
XRF Analysis	Zinc	33000	7200	31000	6300	37000	7500	0.1074

[a] Fields installed 2004 – 2008 (n=11); 2009 – 2012 (n=18); 2013 – 2016 (n=11)

[b] ICP/MS = Inductively coupled plasma/mass spectrometry; XRF = X-ray fluorescence spectrometry

[c] Statistical tests performed using ln-transformed measurement values.

[d] NR=Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set

4.10.2.2 SVOC Extracts by GC/MS/MS and LC/TOFMS Analysis

Table 4-80 shows results for differences in mean concentrations of select SVOCs analyzed in solvent extracts by GC/MS/MS for tire crumb rubber infill collected at fields in three different installation age groups. Benzo[a]pyrene, benzo[ghi]perylene and bis(2-ethylhexyl) phthalate showed statistically significant differences among the age group categories. Only bis(2-ethylhexyl) phthalate showed a monotonic trend of increasing average concentration with older field age category. It is not clear whether this result is an indicator of increasing external source deposition over time, differences in concentrations in tires over time, or a chance result. Table 4-81 shows results for differences in mean chromatographic peak areas of select SVOCs analyzed in solvent extracts by LC/TOFMS for tire crumb rubber infill collected at fields in three different installation age groups. None of the LC/TOFMS analytes showed any statistically significant differences across age groups or any apparent trends with field installation age categories. Figures 4-44 through 4-46 illustrates the distributions in measurement results across the three field installation age groups for twelve SVOC analytes.

Table 4-80. Comparison of Select SVOC Extracts Analyzed by GC/MS/MS for Tire Crumb Rubber Infill Collected from Synthetic Turf Fields in Three Field Installation Age Groups[a]

Analyte[b]	Fields Installed 2004 – 2008 Mean (mg/kg)	Fields Installed 2004 – 2008 Standard Deviation (mg/kg)	Fields Installed 2009 – 2012 Mean (mg/kg)	Fields Installed 2009 – 2012 Standard Deviation (mg/kg)	Fields Installed 2013 – 2016 Mean (mg/kg)	Fields Installed 2013 – 2016 Standard Deviation (mg/kg)	F-test p-value[c]
Phenanthrene	2.1	2.2	3.0	3.3	1.3	0.93	0.389
Fluoranthene	3.6	2.6	5.1	2.9	4.5	1.7	0.1098
Pyrene	11	7.8	14	6.6	12	2.9	0.2171
Benzo[a]pyrene	0.59	0.24	0.95	0.62	0.68	0.48	0.0531
Benzo[ghi]perylene	1.4	0.70	1.5	0.59	0.88	0.47	0.0232
Sum15PAH	25	16	33	17	26	8.2	0.2033
Benzothiazole	7.5	7.2	12	16	12	12	0.4355
Dibutyl phthalate	1.9	2.1	1.5	1.4	1.1	0.84	0.8196
Bis(2-ethylhexyl) phthalate	61	60	45	34	20	21	0.0215
Aniline	0.55	0.37	0.81	0.71	0.58	0.25	0.563
4-tert-octylphenol	11	11	12	11	5.0	2.4	0.4372
n-Hexadecane	0.95	0.85	1.3	1.7	0.43	0.41	0.5861

[a] Fields installed 2004 – 2008 (n=11); 2009 – 2012 (n=18); 2013 – 2016 (n=11)

[b] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

[c] Statistical tests performed using ln-transformed measurement values.

Table 4-81. Comparison of Select SVOC Extracts with Non-quantitative LC/TOFMS Analysis for Tire Crumb Rubber Infill Collected from Synthetic Turf Fields in Three Field Installation Age Groups[a,b]

Analyte	Fields Installed 2004 – 2008 Mean Area Counts	Fields Installed 2004 – 2008 Area Counts Standard Deviation	Fields Installed 2009 – 2012 Mean Area Counts	Fields Installed 2009 – 2012 Area Counts Standard Deviation	Fields Installed 2013 – 2016 Mean Area Counts	Fields Installed 2013 – 2016 Area Counts Standard Deviation	F-test p-value[c,d]
2-mercaptobenzothiazole	1.4E+03	2.2E+03	2.7E+03	4.7E+03	8.7E+02	1.1E+03	NR
2-hydrozybenzothiazole	1.1E+05	1.4E+05	1.1E+05	1.3E+05	8.9E+04	1.1E+05	NR
cyclohexylamine	5.8E+05	8.9E+05	6.0E+05	9.2E+05	2.0E+05	2.8E+05	NR
di-cyclohexylamine	8.6E+06	9.7E+06	8.5E+06	8.6E+06	1.0E+07	7.7E+06	0.4479
N-cyclohexyl-N-methylcyclohexanamine	1.8E+05	1.8E+05	2.6E+05	4.0E+05	2.4E+05	2.0E+05	0.2555
diisononylphthalate	1.5E+04	5.5E+04	4.5E+04	1.2E+05	1.5E+04	7.0E+04	NR
diisodecylphthalate	1.6E+05	5.1E+05	8.0E+03	1.0E+04	2.4E+03	2.0E+03	NR

[a] Fields installed 2004 – 2008 (n=11); 2009 – 2012 (n=18); 2013 – 2016 (n=11)

[b] Statistical tests performed using ln-transformed measurement values.

[c] NR = Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

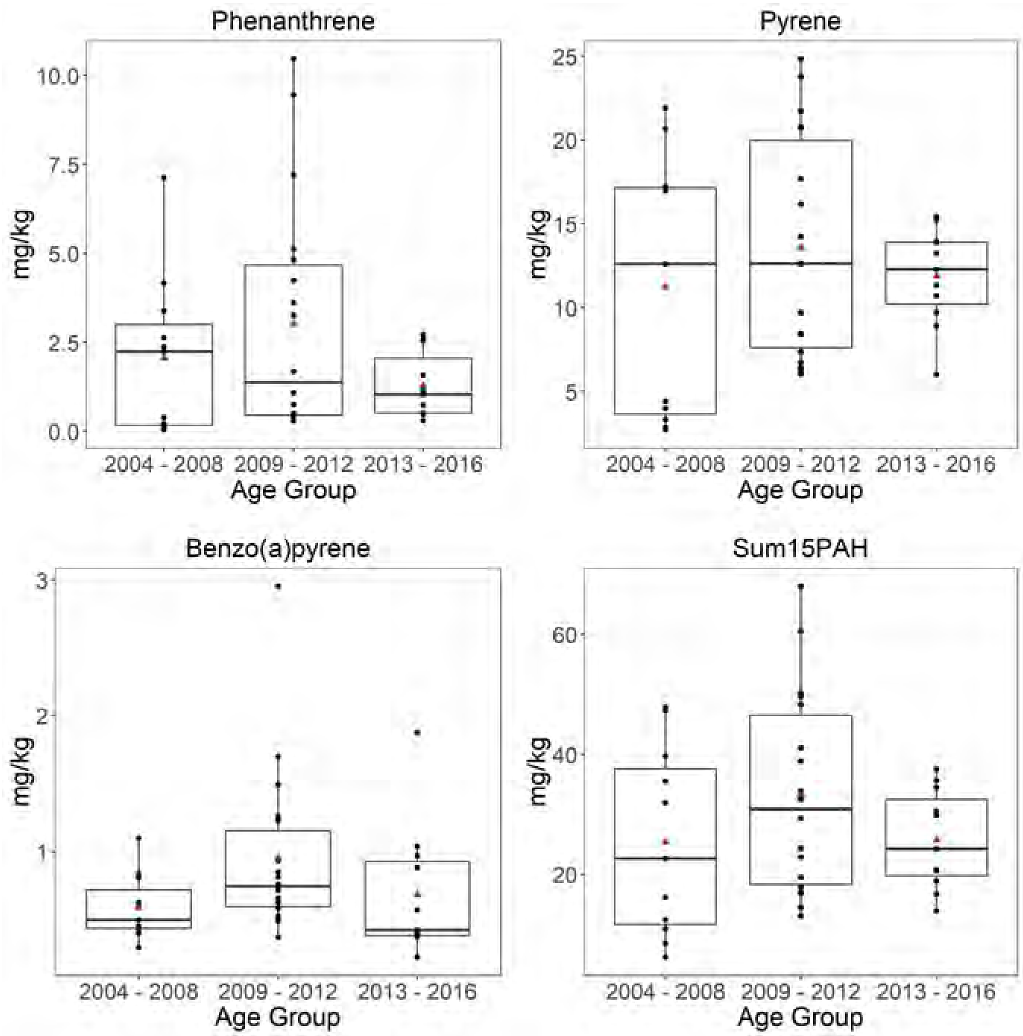

Figure 4-44. Comparison of GC/MS/MS extract SVOC analysis results (mg/kg) between tire crumb rubber infill composite samples from synthetic turf fields in three installation age groups for phenanthrene, pyrene, benzo[a]pyrene, and the sum of 15 PAHs.
[GC/MS/MS = Gas chromatography/tandem mass spectrometry; SVOC = Semivolatile organic compound; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

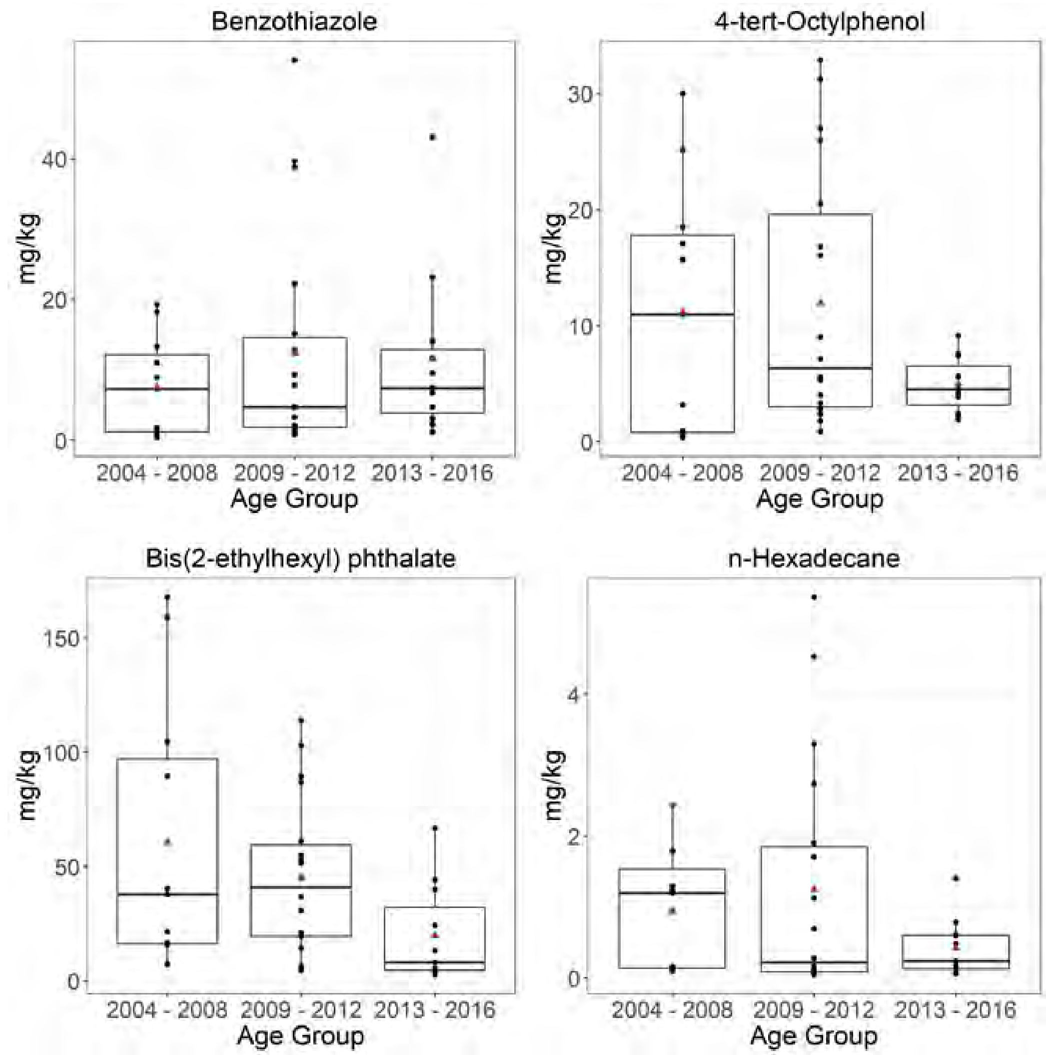

Figure 4-45. Comparison of GC/MS/MS extract SVOC analysis results (mg/kg) between tire crumb rubber infill composite samples from synthetic turf fields in three installation age groups for benzothiazole, 4-tert-octylphenol, bis(2-ethylhexyl) phthalate, and n-hexadecane. [GC/MS/MS = Gas chromatography/tandem mass spectrometry; SVOC = Semivolatile organic compound]

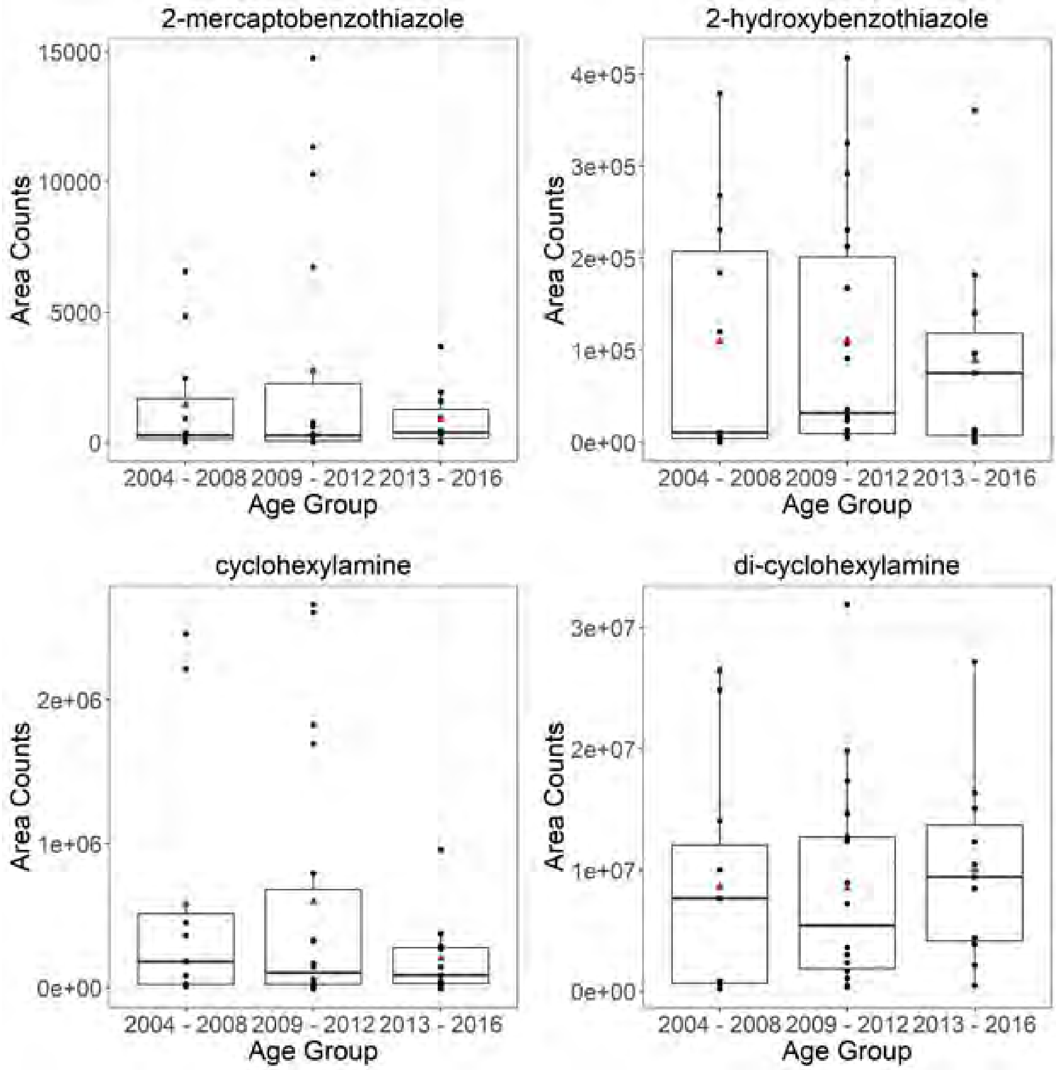

Figure 4-46. Comparison of LC/TOFMS extract SVOC non-quantitative positive ionization analysis results between tire crumb rubber infill composite samples from synthetic turf fields in three installation age groups for 2-mercaptobenzothiazole, 2-hydroxybenzothiazole, cyclohexylamine, and di-cyclohexylamine. [LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry; SVOC = Semivolatile organic compound]

4.10.2.3 VOC Emission Factors

Table 4-82 shows results for differences in mean 25 °C and 60 °C emission factors for select VOCs analyzed by GC/TOFMS for tire crumb rubber infill collected at fields in three different installation age groups. There were no statistically significant differences across the age groups, although most analytes had some results that were < 0. Only toluene showed an apparent monotonic trend of increasing average concentration with newer field age category. Figure 4-47 illustrates the distributions in 60 °C emission factor measurement results across the three field installation age groups for formaldehyde, benzothiazole, methyl isobutyl ketone, and styrene.

Table 4-82. Comparison of Select VOC Emission Factors in Tire Crumb Rubber Infill Collected from Synthetic Turf Fields in Three Field Installation Age Groups[a,b]

Emissions Test	Analyte[c]	Fields Installed 2004 – 2008 Mean (ng/g/h)	Fields Installed 2004 – 2008 Standard Deviation (ng/g/h)	Fields Installed 2009 – 2012 Mean (ng/g/h)	Fields Installed 2009 – 2012 Standard Deviation (ng/g/h)	Fields Installed 2013 – 2016 Mean (ng/g/h)	Fields Installed 2013 – 2016 Standard Deviation (ng/g/h)	F-test p-value[d,e]
Emissions at 25 °C	Benzothiazole	25	26	26	34	22	22	NR
Emissions at 25 °C	o-Xylene	0.054	0.083	0.042	0.11	-0.012	0.053	NR
Emissions at 25 °C	SumBTEX	0.25	0.91	0.39	0.72	0.22	1.0	NR
Emissions at 60 °C	Formaldehyde	17	5.6	18	13	13	3.7	NR
Emissions at 60 °C	Methyl isobutyl ketone	50	29	39	27	40	20	0.5356
Emissions at 60 °C	Benzothiazole	63	44	49	40	59	34	0.8176
Emissions at 60 °C	Styrene	0.53	0.39	0.51	0.46	0.26	0.28	NR
Emissions at 60 °C	Toluene	0.092	0.16	0.14	0.31	0.25	0.42	NR
Emissions at 60 °C	Ethylbenzene	-0.11	0.22	-0.067	0.24	-0.071	0.23	NR
Emissions at 60 °C	m/p-Xylene	0.29	1.1	0.33	1.1	0.059	0.82	NR
Emissions at 60 °C	o-Xylene	-0.3	0.75	-0.28	0.7	-0.52	0.51	NR
Emissions at 60 °C	SumBTEX	-0.26	2.0	0.055	2.5	-0.11	2.0	NR

[a] Several results are reported as negative values. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.

[b] Fields installed 2004 – 2008 (n=11); 2009 – 2012 (n=16 – 18); 2013 – 2016 (n=10 – 11)

[c] SumBTEX = Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene

[d] Statistical tests performed using ln-transformed measurement values.

[e] NR = Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

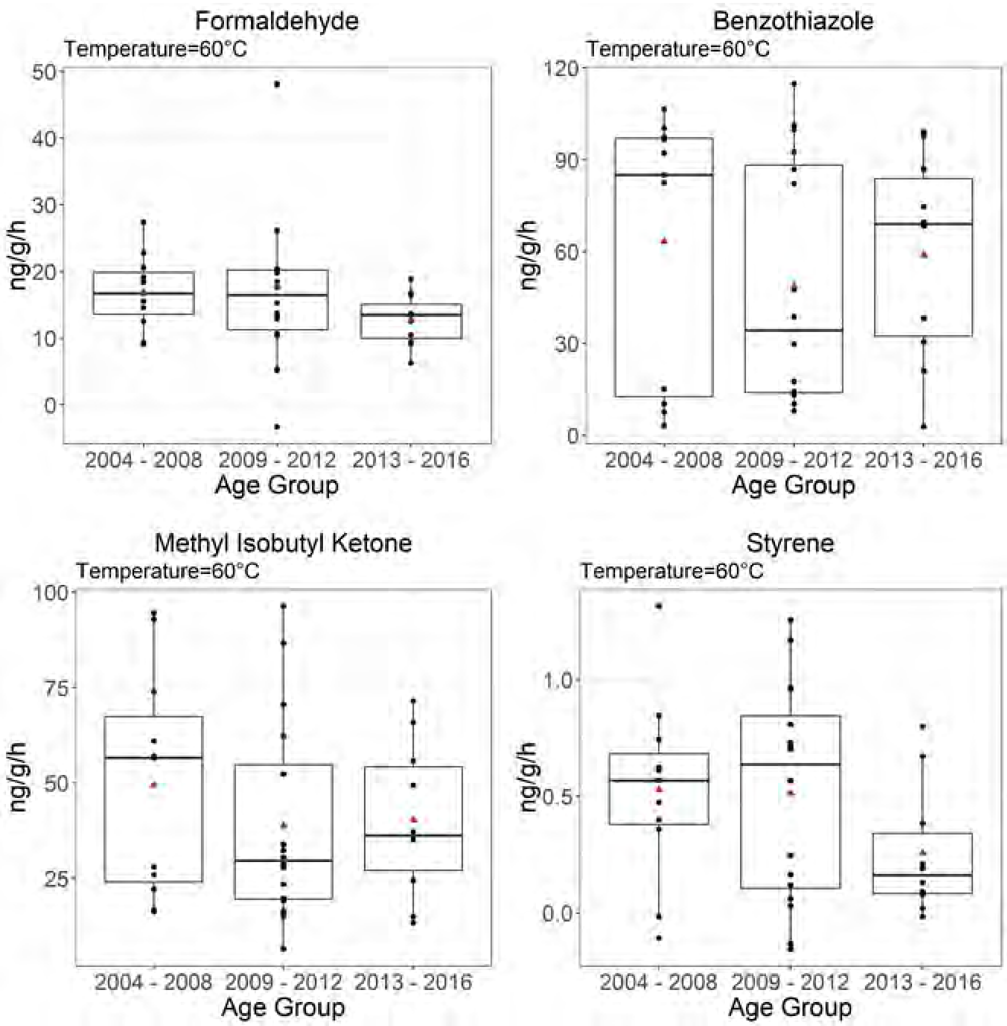

Figure 4-47. Comparison of VOC 60 °C emission factor results (ng/g/h) between tire crumb rubber infill composite samples from synthetic turf fields in three installation age groups for formaldehyde, benzothiazole, methyl isobutyl ketone, and styrene. [VOC = Volatile organic compound]

4.10.2.4 SVOC Emission Factors

Table 4-83 shows results for differences in mean 25 °C and 60 °C emission factors for select SVOCs analyzed by GC/MS/MS for tire crumb rubber infill collected at fields in three different installation age groups. There were no statistically significant differences across the age groups, although most analytes had some results that were < 0 due to subtraction of chamber background levels. In emissions testing at 25 °C, 4-tert-octylphenol showed an apparent monotonic trend of increasing average concentration with newer installation age group and aniline showed an apparent monotonic trend of decreasing average concentration with newer installation age group. However, neither trend was apparent in 60 °C emission test results. Figure 4-48 illustrates the distributions in 60 °C emission factor measurement results across the three field installation age groups for pyrene, the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol.

Table 4-83. Comparison of Select SVOC Emission Factors in Tire Crumb Rubber Infill Collected from Synthetic Turf Fields in Three Field Installation Age Groups[a,b]

Emissions Test	Analyte[c]	Fields Installed 2004 – 2008 Mean (ng/g/h)	Fields Installed 2004 – 2008 Standard Deviation (ng/g/h)	Fields Installed 2009 – 2012 Mean (ng/g/h)	Fields Installed 2009 – 2012 Standard Deviation (ng/g/h)	Fields Installed 2013 – 2016 Mean (ng/g/h)	Fields Installed 2013 – 2016 Standard Deviation (ng/g/h)	F-test p-value[d,e]
Emissions at 25 °C	Phenanthrene	0.027	0.035	0.032	0.045	0.012	0.066	NR
Emissions at 25 °C	Sum15PAH	0.73	0.83	0.58	0.55	0.58	0.56	0.7377
Emissions at 25 °C	Benzothiazole	3.7	4.5	5.2	6.3	3.2	3.5	NR
Emissions at 25 °C	Dibutyl phthalate	-0.031	0.25	0.029	0.42	-0.056	0.43	NR
Emissions at 25 °C	Aniline	0.46	0.53	0.34	0.48	0.24	0.26	NR
Emissions at 25 °C	4-tert-octylphenol	0.12	0.15	0.90	3.3	1.5	4.8	NR
Emissions at 60 °C	Phenanthrene	0.46	0.51	0.81	0.93	0.31	0.27	NR
Emissions at 60 °C	Fluoranthene	0.13	0.10	0.19	0.13	0.13	0.088	NR
Emissions at 60 °C	Pyrene	0.21	0.20	0.35	0.24	0.27	0.15	NR
Emissions at 60 °C	Sum15PAH	1.6	1.2	2.6	2.5	1.4	0.77	0.2777
Emissions at 60 °C	Benzothiazole	21	25	51	69	18	14	NR
Emissions at 60 °C	Dibutyl phthalate	0.048	0.21	0.19	0.52	0.17	0.39	NR
Emissions at 60 °C	Aniline	3.0	3.7	5.0	6.8	1.5	1.4	NR
Emissions at 60 °C	4-tert-octylphenol	5.7	6.2	6.9	6.3	4.2	2.9	NR

[a] Two results are reported as negative values. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.

[b] Fields installed 2004 – 2008 (n=11); 2009 – 2012 (n=16 – 18); 2013 – 2016 (n=10 – 11)

[c] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

[d] Statistical tests performed using ln-transformed measurement values.

[e] Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

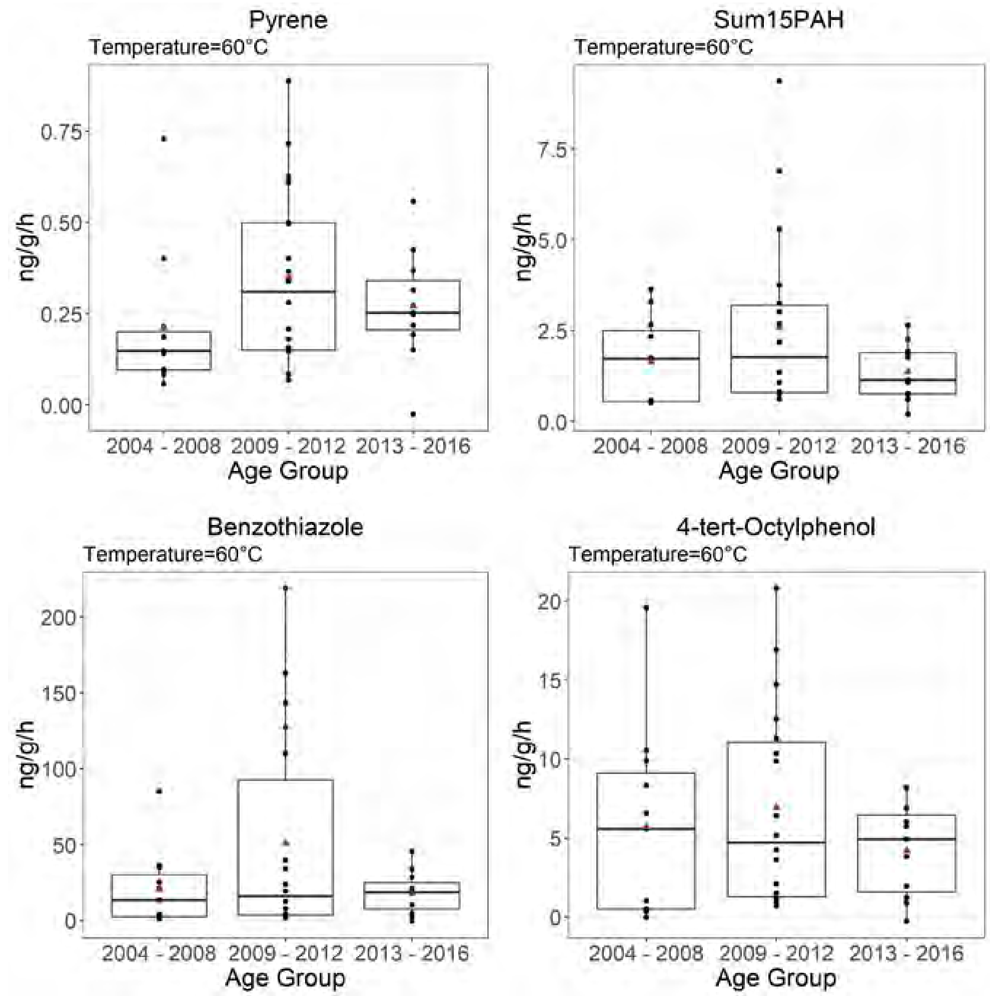

Figure 4-48. Comparison of SVOC 60 °C emission factor results (ng/g/h) between tire crumb rubber infill composite samples from synthetic turf fields in three installation age groups for pyrene, the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol. [SVOC = Semivolatile organic compound; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

4.10.3 Synthetic Field Installation Age Restricted to Outdoor Fields

In order to help distinguish whether differences in chemicals associated with tire crumb rubber infill may be related to field age, the field installation age group analyses were re-run, this time restricted to outdoor fields only. This was done to remove the contributions of the indoor versus outdoor differences that were previously observed, particularly for the organic chemicals. The sample sizes were reduced through the restriction to outdoor fields only. Analyses were not performed separately for indoor fields because of the small group sample sizes, and because all but one indoor field were in the two older field installation age categories.

4.10.3.1 Metals by ICP/MS and XRF Analysis

Figure 4-49 illustrates the distributions in measurement results for recycling plants and across both the indoor/outdoor and installation age groups for select metals analyzed by ICP/MS. Differences in mean concentrations of select metals analyzed in acid digests by ICP/MS and in XRF analyses are shown in Table 4-84 for tire crumb rubber infill collected at outdoor fields in three different installation age groups. Average cobalt measurements had statistically significant differences among the age group categories, but the differences were not monotonic by field installation age group. Results for zinc reached significance, with the highest average concentrations found in the newest installation age category. While the analysis measurement results, with statistical test results, reported in tables in this sub-section are restricted to outdoor fields only, figures have been prepared to expand on comparisons, with the recycling plant results shown alongside the results for both indoor and outdoor fields in different age groups.

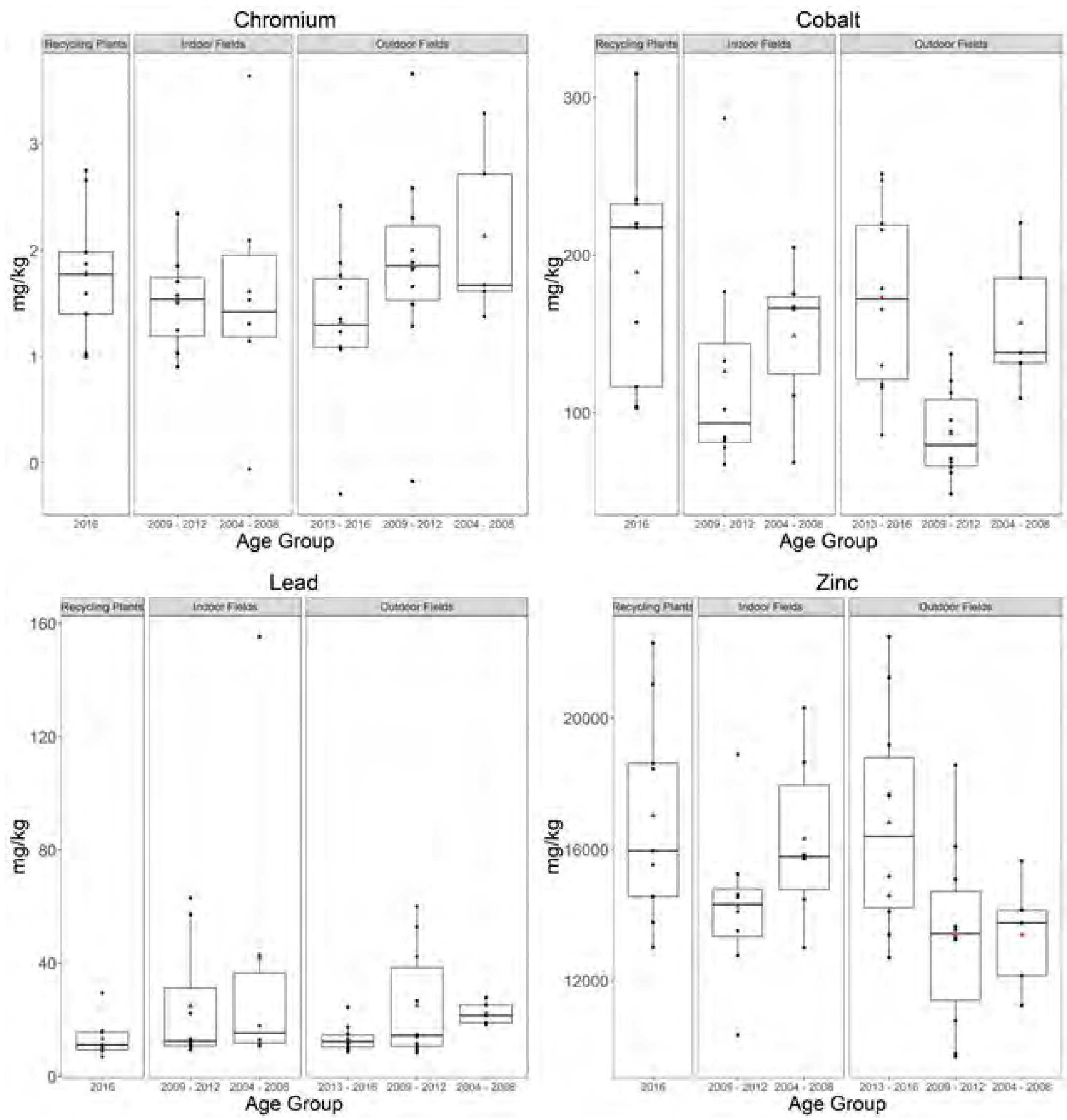

Figure 4-49. Comparison of ICP/MS metal analysis results (mg/kg) between tire crumb rubber from recycling plants and tire crumb rubber infill composite samples from synthetic turf fields by age group for chromium, cobalt, lead, and zinc. [ICP/MS = Inductively coupled plasma/mass spectrometry]

Table 4-84. Comparison of Select Metals in Tire Crumb Rubber Infill Collected from Outdoor Synthetic Turf Fields in Three Field Installation Age Groups[a]

Analysis[b]	Analyte	Fields Installed 2004 – 2008 Mean (mg/kg)	Fields Installed 2004 – 2008 Standard Deviation (mg/kg)	Fields Installed 2009 – 2012 Mean (mg/kg)	Fields Installed 2009 – 2012 Standard Deviation (mg/kg)	Fields Installed 2013 – 2016 Mean (mg/kg)	Fields Installed 2013 – 2016 Standard Deviation (mg/kg)	F-test p-value[c]
ICP/MS Analysis	Arsenic	0.43	0.12	0.46	0.22	0.29	0.094	0.0618
ICP/MS Analysis	Cadmium	0.96	0.30	0.94	0.56	0.73	0.39	0.3877
ICP/MS Analysis	Chromium	2.1	0.83	1.9	0.98	1.3	0.71	NR[d]
ICP/MS Analysis	Cobalt	160	45	87	29	170	59	0.0002
ICP/MS Analysis	Lead	22	4.1	25	20	13	4.7	0.09
ICP/MS Analysis	Zinc	13000	1700	13000	2800	17000	3400	0.02
XRF Analysis	Chromium	14	1.7	13	3.9	14	2.4	0.2588
XRF Analysis	Cobalt	38	14	33	16	49	18	0.1183
XRF Analysis	Lead	29	13	38	14	26	12	0.1714
XRF Analysis	Zinc	29000	7400	30000	6800	37000	7900	0.0534

[a] Fields installed 2004 – 2008 (n=5); 2009 – 2012 (n=10); 2013 – 2016 (n=10)

[b] ICP/MS = Inductively coupled plasma/mass spectrometry; XRF = X-ray fluorescence spectrometry

[c] Statistical tests performed using ln-transformed measurement values.

[d] NR = Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set

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4.10.3.2 SVOC Extracts by GC/MS/MS and LC/TOFMS

Table 4-85 shows results for differences in mean concentrations of selected SVOCs analyzed in solvent extracts by GC/MS/MS for tire crumb rubber infill collected at outdoor fields in three different installation age groups. Most of the analytes show statistically significant differences across the age groups. In many, but not all cases, there is a monotonic trend of decreasing average concentrations with older field installation age group. Table 4-86 shows results for differences in mean chromatographic peak areas of selected SVOCs analyzed in solvent extracts by LC/TOFMS for tire crumb rubber infill collected at outdoor fields in three different installation age groups. Monotonic trends of decreasing average concentrations with older field installation age group were observed for the four chemicals reported in that table, as well.

When analyses were restricted to outdoor fields only, many SVOCs had statistically significant different concentrations among age groups, with decreasing average levels with older field installation age. These results support the likely importance of weathering for changes in SVOC concentrations in tire crumb rubber infill used on outdoor fields over time. However, because no longitudinal measurements were performed at individual fields, it cannot be entirely ruled out that some results represent differences in the chemical composition of the recycled tires of different ages. The differences in concentrations in indoor field infill versus outdoor field infill for the same installation age groups supports a weathering effect explanation for most chemicals.

Figures 4-50 through 4-52 illustrate the distributions in measurement results for recycling plants and across both the indoor/outdoor and installation age groups to provide a more global illustration of differences among characteristics categories for chemicals in tire crumb rubber and tire crumb rubber infill. For most of the SVOC target analytes shown in these figures, recycling plant average concentrations are similar to or higher than those for the indoor fields, which in turn are generally higher than those the outdoor fields. The pattern was less clear for benzo[a]pyrene, which, as a five-ring PAH, has a very low vapor pressure. Bis(2-ethylhexyl) phthalate did not follow this pattern; instead, concentrations were generally higher in the synthetic turf field samples as compared to recycling plant samples, and indoor levels were generally higher than outdoor levels.

Table 4-85. Comparison of Select SVOC Extracts Analyzed by GC/MS/MS for Tire Crumb Rubber Infill Collected from Outdoor Synthetic Turf Fields in Three Field Installation Age Groups[a,b]

Analyte[c]	Fields Installed 2004 – 2008 Mean (mg/kg)	Fields Installed 2004 – 2008 Standard Deviation (mg/kg)	Fields Installed 2009 – 2012 Mean (mg/kg)	Fields Installed 2009 – 2012 Standard Deviation (mg/kg)	Fields Installed 2013 – 2016 Mean (mg/kg)	Fields Installed 2013 – 2016 Standard Deviation (mg/kg)	F-test p-value[d]
Fluoranthene	1.4	0.71	3.5	2.5	4.6	1.8	0.0002
Pyrene	3.5	0.74	8.6	2.8	12	2.8	<.0001
Benzo[a]pyrene	0.46	0.12	0.73	0.26	0.70	0.51	0.2415
Benzo[ghi]perylene	1.1	0.41	1.4	0.54	0.84	0.48	0.0700
Sum15PAH	11	3.8	22	8.7	25	8.5	0.0004
Benzothiazole	1.0	0.58	2.3	1.4	11	13	0.0002
Dibutyl phthalate	0.074	0.043	0.58	0.7	0.95	0.72	0.0034
Bis(2-ethylhexyl) phthalate	33	34	41	29	15	16	0.029
Aniline	0.18	0.10	0.31	0.18	0.54	0.23	0.0005
4-tert-octylphenol	1.1	1.2	3.6	1.9	4.6	2.0	0.0001
n-Hexadecane	0.13	0.027	0.11	0.067	0.33	0.27	0.0212

[a] SVOC = Semivolatile organic compound; GC/MS/MS = Gas chromatography/tandem mass spectrometry

[b] Fields installed 2004 – 2008 (n=5); 2009 – 2012 (n=10); 2013 – 2016 (n=10)

[c] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

[d] Statistical tests performed using ln-transformed measurement values.

Table 4-86. Comparison of Select SVOC Extracts with Non-quantitative LC/TOFMS Analysis for Tire Crumb Rubber Infill Collected from Outdoor Synthetic Turf Fields in Three Field Installation Age Groups[a,b]

Analyte	Fields Installed 2004 – 2008 Mean Area Counts	Fields Installed 2004 – 2008 Area Counts Standard Deviation	Fields Installed 2009 – 2012 Mean Area Counts	Fields Installed 2009 – 2012 Area Counts Standard Deviation	Fields Installed 2013 – 2016 Mean Area Counts	Fields Installed 2013 – 2016 Area Counts Standard Deviation	F-test p-value[c,d]
2-mercaptobenzothiazole	9.5E+01	1.3E+02	4.2E+02	8.5E+02	9.2E+02	1.2E+03	NR
2-hydroxybenzothiazole	4.1E+03	4.7E+03	2.3E+04	2.6E+04	8.0E+04	1.1E+05	NR
cyclohexylamine	5.1E+04	7.3E+04	5.5E+04	9.7E+04	2.1E+05	3.0E+05	NR
di-cyclohexylamine	5.9E+05	2.4E+05	3.0E+06	3.0E+06	9.5E+06	7.9E+06	0.0009

[a] SVOC = Semivolatile organic compound; LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry

[b] Fields installed 2004 – 2008 (n=5); 2009 – 2012 (n=10); 2013 – 2016 (n=10)

[c] Statistical tests performed using ln-transformed measurement values.

[d] NR = Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

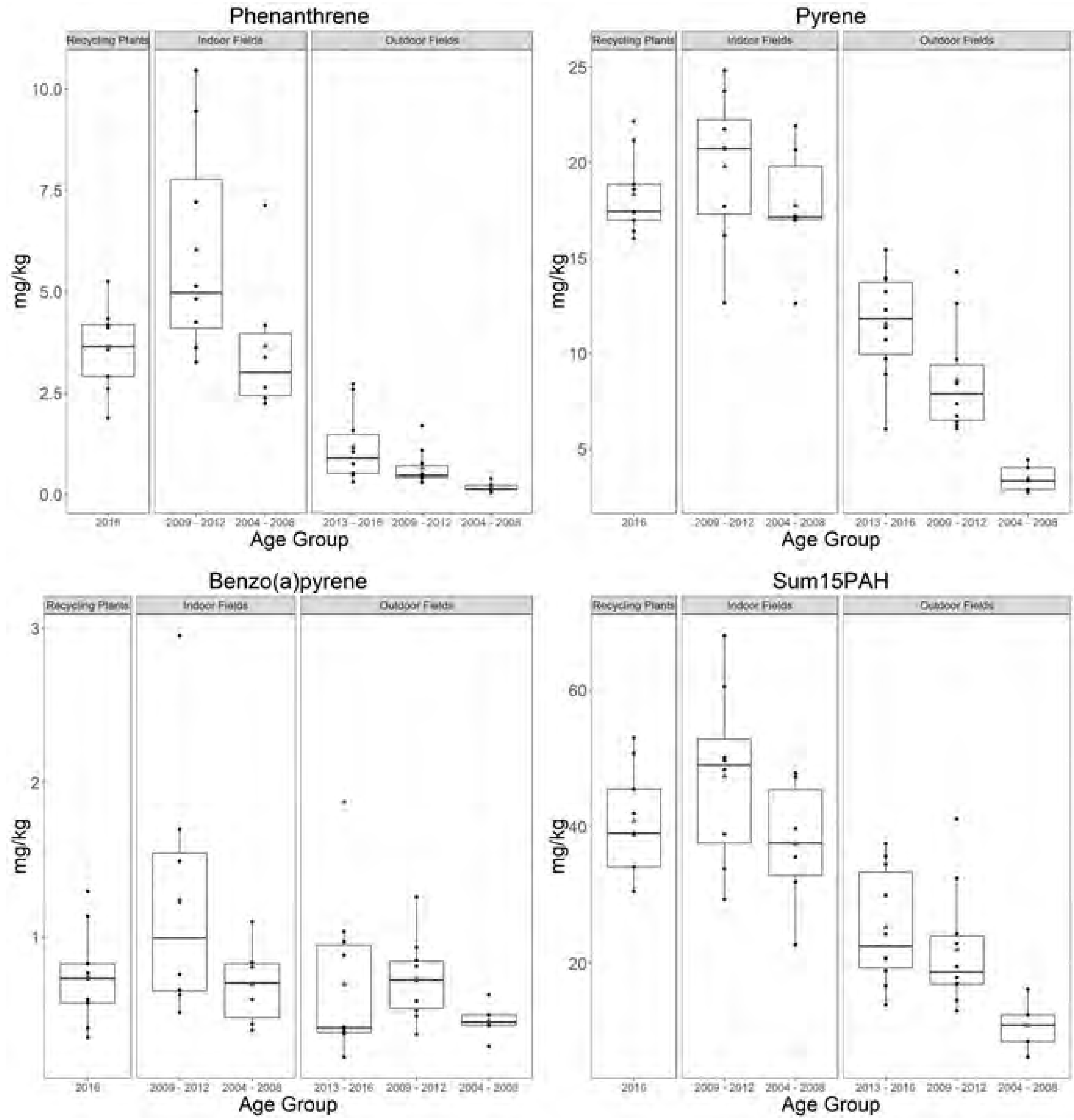

Figure 4-50. Comparison of GC/MS/MS extract SVOC analysis results (mg/kg) between tire crumb rubber from recycling plants and tire crumb rubber infill composite samples from synthetic turf fields by age group for phenanthrene, pyrene, benzo(a)pyrene, and the sum of 15 PAHs. [GC/MS/MS = Gas chromatography/tandem mass spectrometry; SVOC = Semivolatile organic compound]

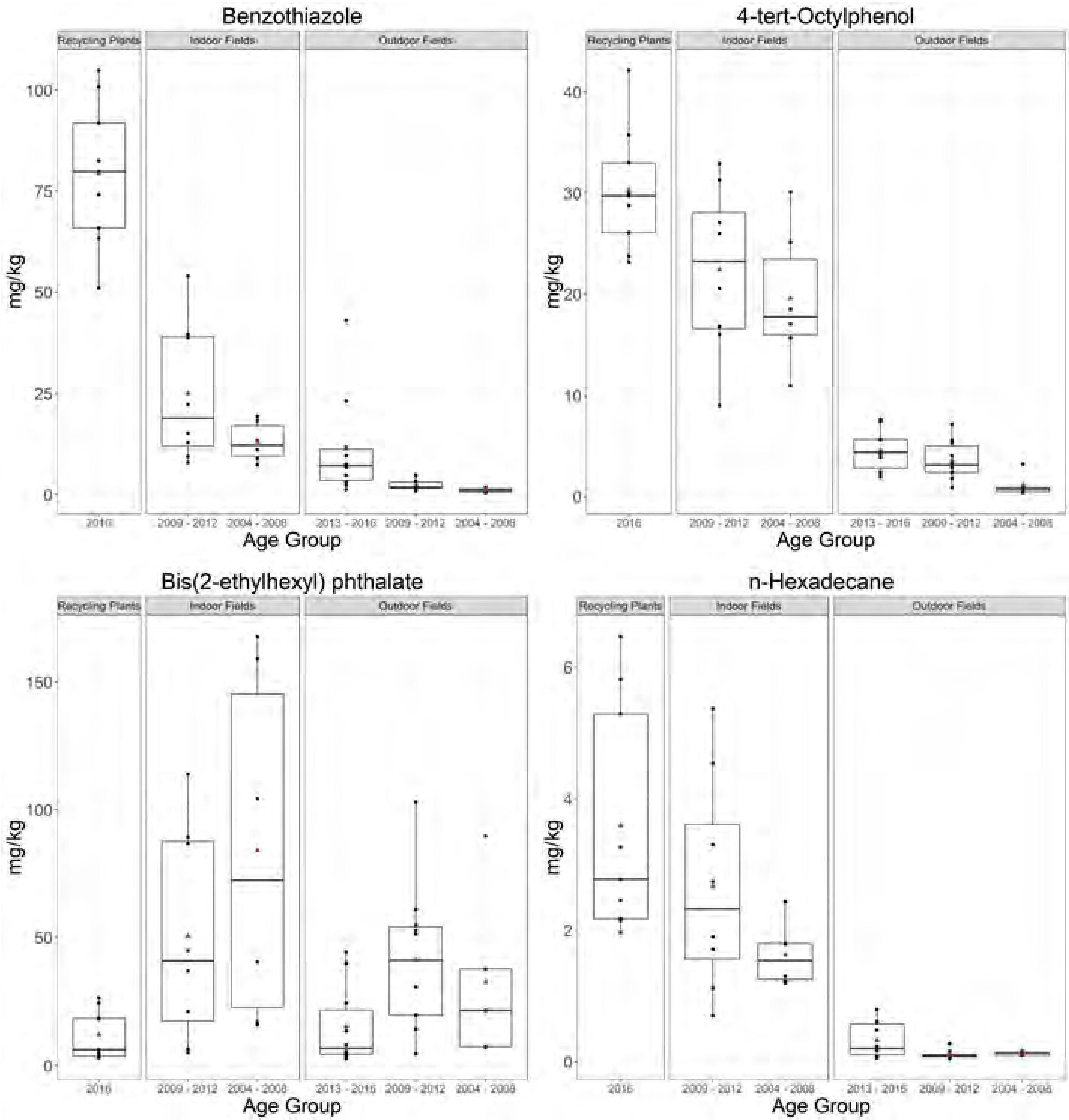

Figure 4-51. Comparison of GC/MS/MS extract SVOC analysis results (mg/kg) between tire crumb rubber from recycling plants and tire crumb rubber infill composite samples from synthetic turf fields by age group for benzothiazole, 4-tert-octylphenol, bis(2-ethylhexyl) phalate, and n-hexadecane.
[GC/MS/MS = Gas chromatography/tandem mass spectrometry; SVOC = Semivolatile organic compound]

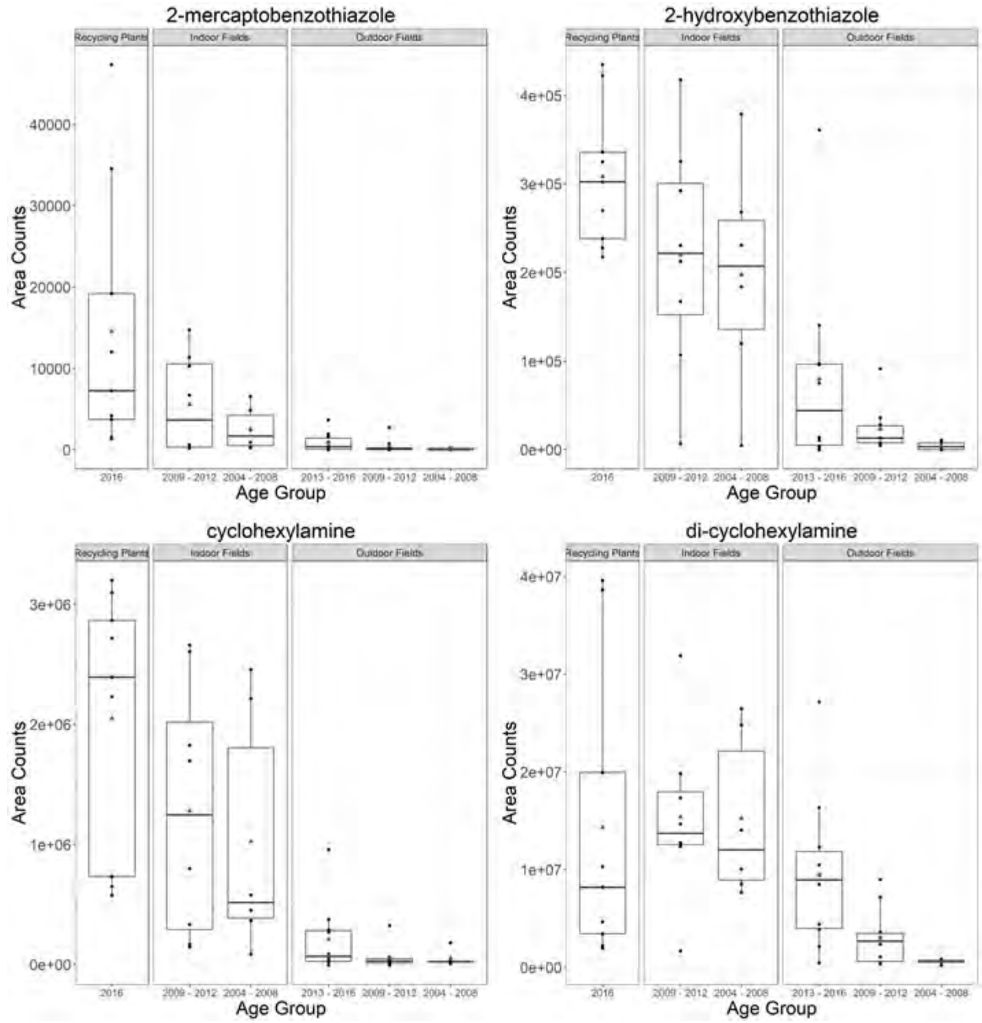

Figure 4-52. Comparison of LC/TOFMS extract SVOC non-quantitative positive ionization analysis results between tire crumb rubber from recycling plants and tire crumb rubber infill composite samples from synthetic turf fields by age group. Results for fields are shown separately for indoor and outdoor fields in two or three installation age groups for 2-mercaptobenzothiazole, 2-hydroxybenzothiazole, cyclohexylamine, di-cyclohexylamine. [LC/TOFMS = Liquid chromatography/ time-of-flight mass spectrometry; SVOC = Semivolatile organic compound]

4.10.3.3 VOC Emission Factors

Table 4-87 shows results for differences in mean 25 °C and 60 °C emission factors for select VOCs analyzed by GC/TOFMS for tire crumb rubber infill collected at outdoor fields in three different installation age groups. There were no statistically significant differences across the age groups, although most analytes had some results that were not > 0. Benzothiazole and methyl isobutyl ketone results approached statistical significance for their 60 °C emission factors. There were no apparent monotonic trends of decreasing average concentration with older field installation group. For benzothiazole and methyl isobutyl ketone, the two target analytes with the greatest emission factors at 60 °C, the highest emission factors were measured from fields in the newest field installation age category.

Table 4-87. Comparison of Select VOC Emission Factors in Tire Crumb Rubber Infill Collected from Outdoor Synthetic Turf Fields in Three Field Installation Age Groups[a,b]

Emissions Test	Analyte[c]	Fields Installed 2004 – 2008 Mean (ng/g/h)	Fields Installed 2004 – 2008 Standard Deviation (ng/g/h)	Fields Installed 2009 – 2012 Mean (ng/g/h)	Fields Installed 2009 – 2012 Standard Deviation (ng/g/h)	Fields Installed 2013 – 2016 Mean (ng/g/h)	Fields Installed 2013 – 2016 Standard Deviation (ng/g/h)	F-test p-value[d,e]
Emissions at 25 °C	Benzothiazole	2.6	6.0	3.5	4.0	20	23	NR
Emissions at 25 °C	o-Xylene	0.073	0.1	-0.012	0.041	-0.021	0.047	NR
Emissions at 25 °C	SumBTEX	0.47	1.4	0.11	0.77	0.19	1.1	NR
Emissions at 60 °C	Formaldehyde	15	7.7	10	6.3	12	3.3	NR
Emissions at 60 °C	Methyl isobutyl ketone	22	5.3	22	8.4	39	21	0.061
Emissions at 60 °C	Benzothiazole	27	41	20	14	55	33	0.0709
Emissions at 60 °C	Styrene	0.27	0.32	0.26	0.36	0.20	0.21	NR
Emissions at 60 °C	Toluene	0.073	0.21	-0.013	0.24	0.27	0.44	NR
Emissions at 60 °C	Ethylbenzene	-0.14	0.19	-0.13	0.22	-0.11	0.21	NR
Emissions at 60 °C	m/p-Xylene	0.14	1.3	0.11	1.1	-0.089	0.71	NR
Emissions at 60 °C	o-Xylene	-0.18	1.0	-0.30	0.74	-0.62	0.44	NR
Emissions at 60 °C	SumBTEX	-0.45	2.4	-0.51	2.5	-0.36	1.9	NR

[a] Several results are reported as negative values. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.

[b] Fields installed 2004 – 2008 (n=5); 2009 – 2012 (n=10); 2013 – 2016 (n=9)

[c] SumBTEX = Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene

[d] Statistical tests performed using ln-transformed measurement values.

[e] NR= Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

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Figure 4-53 illustrates the distributions in 60 °C emission factor measurement results for recycling plants and across both the indoor/outdoor and installation age groups to provide a more global illustration of differences among characteristic categories for chemicals in tire crumb rubber and tire crumb rubber infill. Average recycling plant emission factors are generally higher than those for the indoor fields, which in turn are generally higher than those the outdoor fields.

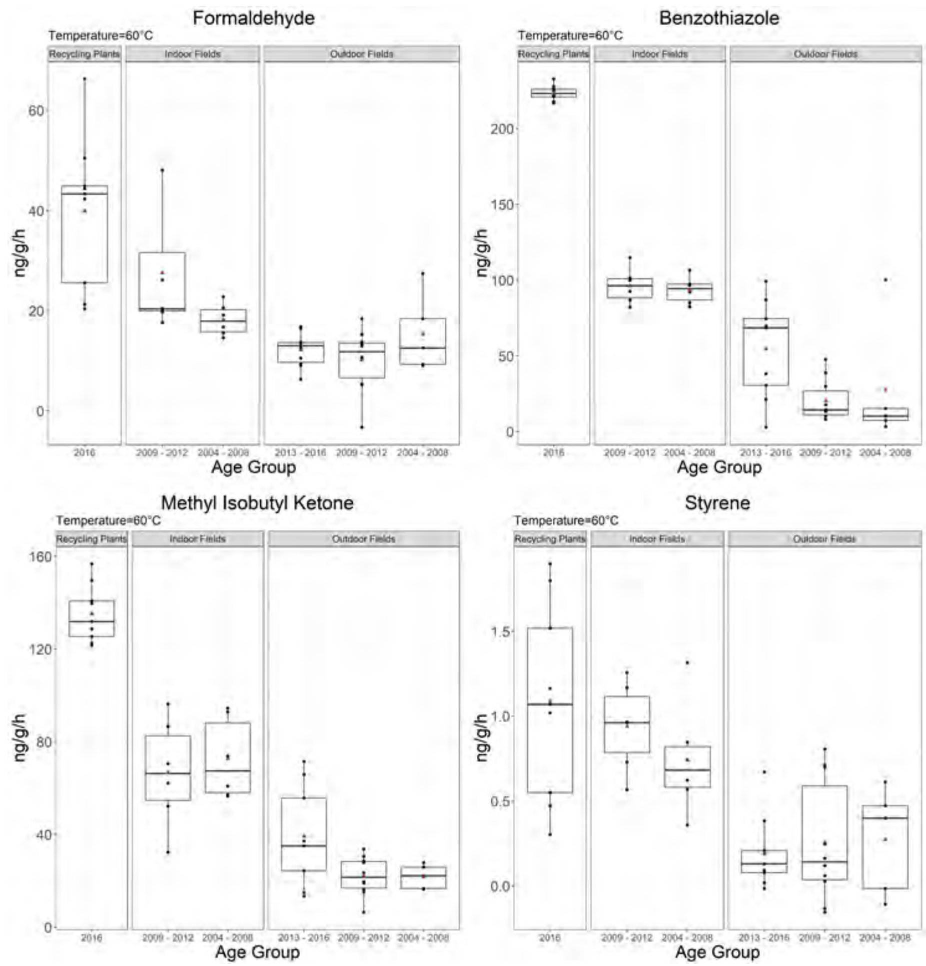

Figure 4-53. Comparison of VOC 60 °C emission factor results (ng/g/h) between tire crumb rubber from recycling plants and tire crumb rubber infill composite samples from synthetic turf fields by age group for formaldehyde, benzothiazole, methyl isobutyl ketone, and styrene. [VOC = Volatile organic compound]

4.10.3.4 SVOC Emission Factors

Table 4-88 shows results for differences in mean 25 °C and 60 °C emission factors for select SVOCs analyzed by GC/MS/MS for tire crumb rubber infill collected at outdoor fields in three different installation age groups. At 60 °C there was an apparent trend of decreasing emission factors with older field installation age group.

Table 4-88. Comparison of Select SVOC Emission Factors in Tire Crumb Rubber Infill Collected from Outdoor Synthetic Turf Fields in Three Field Installation Age Groups[a]

Emissions Test	Analyte	Fields Installed 2004 – 2008 Mean (ng/g/h)	Fields Installed 2004 – 2008 Standard Deviation (ng/g/h)	Fields Installed 2009 – 2012 Mean (ng/g/h)	Fields Installed 2009 – 2012 Standard Deviation (ng/g/h)	Fields Installed 2013 – 2016 Mean (ng/g/h)	Fields Installed 2013 – 2016 Standard Deviation (ng/g/h)	F-test p-value[b,c]
Emissions at 25 °C	Phenanthrene	0.0064	0.023	0.027	0.038	0.013	0.070	NR
Emissions at 25 °C	Sum15PAH	0.63	0.29	0.49	0.67	0.61	0.58	0.3117
Emissions at 25 °C	Benzothiazole	0.065	0.14	0.70	0.46	3.1	3.7	NR
Emissions at 25 °C	Dibutyl phthalate	0.076	0.34	0.16	0.38	0.021	0.37	NR
Emissions at 25 °C	Aniline	0.011	0.065	0.00092	0.084	0.21	0.26	NR
Emissions at 25 °C	4-tert-Octylphenol	0.010	0.044	0.0012	0.12	1.6	5.0	NR
Emissions at 60 °C	Phenanthrene	0.0023	0.095	0.15	0.17	0.28	0.27	NR
Emissions at 60 °C	Fluoranthene	0.059	0.037	0.11	0.091	0.13	0.092	NR
Emissions at 60 °C	Pyrene	0.12	0.05	0.19	0.13	0.26	0.16	NR
Emissions at 60 °C	Sum15PAH	0.54	0.029	0.97	0.48	1.3	0.8	0.0774
Emissions at 60 °C	Benzothiazole	2.4	1.1	6.0	5.8	17	14	NR
Emissions at 60 °C	Dibutyl phthalate	-0.14	0.11	0.21	0.53	0.14	0.40	NR
Emissions at 60 °C	Aniline	0.17	0.096	0.48	0.43	1.4	1.4	NR
Emissions at 60 °C	4-tert-Octylphenol	0.47	0.37	2.9	3.6	4.0	2.9	NR

[a] Fields installed 2004 – 2008 (n=5); 2009 – 2012 (n=10); 2013 – 2016 (n=10)

[b] Statistical tests performed using ln-transformed measurement values.

[c] NR = Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

Figure 4-54 illustrates the distributions in 60 °C emission factor measurement results for recycling plants and across both the indoor/outdoor and installation age groups to provide a more global illustration of differences among characteristic categories for chemicals in tire crumb rubber and tire crumb rubber infill. Average recycling plant emission factors are generally higher than those for the indoor fields, which in turn are generally higher than those the outdoor fields.

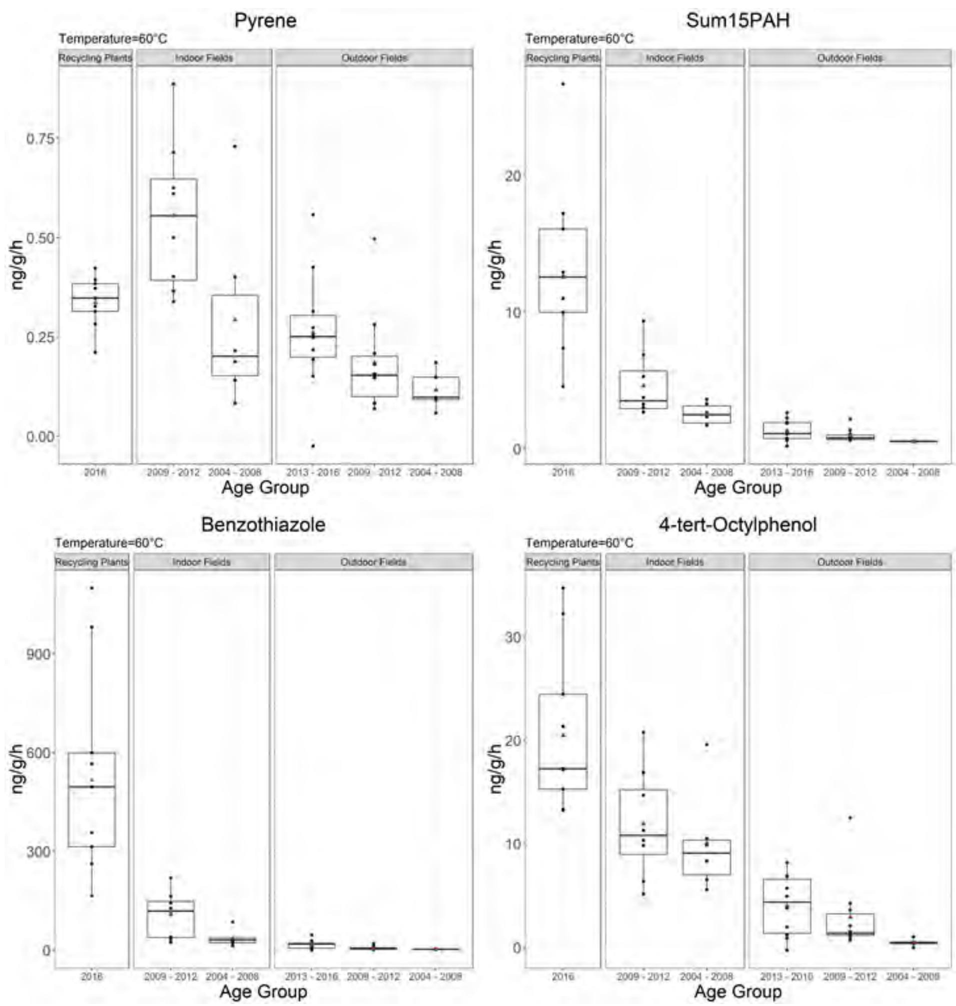

Figure 4-54. Comparison of SVOC 60 °C emission factor results (ng/g/h) between tire crumb rubber from recycling plants and tire crumb rubber infill composite samples from synthetic turf fields by age group. Results for fields are shown separately for indoor and outdoor fields in two or three installation age groups for pyrene, the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol. [SVOC = Semivolatile organic compound; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene]

4.10.4 Decay Rates of SVOCs Over Time at Outdoor Fields

Data collected in this study afforded further opportunity to explore relationships between field age and the concentration of chemicals associated with tire crumb rubber infill at outdoor fields. Samples were collected at 25 outdoor fields with installation dates ranging from 2004 through 2016, giving a 12-year range of field ages to examine changes in extractable SVOC concentrations over time. Modeled relationships between six extractable PAH concentrations, assumed to be exponentially distributed, and years since installation are shown graphically as curves in Figure 4-55. The PAH concentrations in outdoor field composite samples and average concentration of the chemicals in recycling plant samples are shown plotted against years in the figure. Concentrations and modeled relationships for three phthalates and three other rubber-associated chemicals are similarly shown in Figure 4-56. For all chemicals except bis(2-ethylhexyl) phthalate, there was an apparent trend of decreasing chemical concentration with increasing years since field installation.

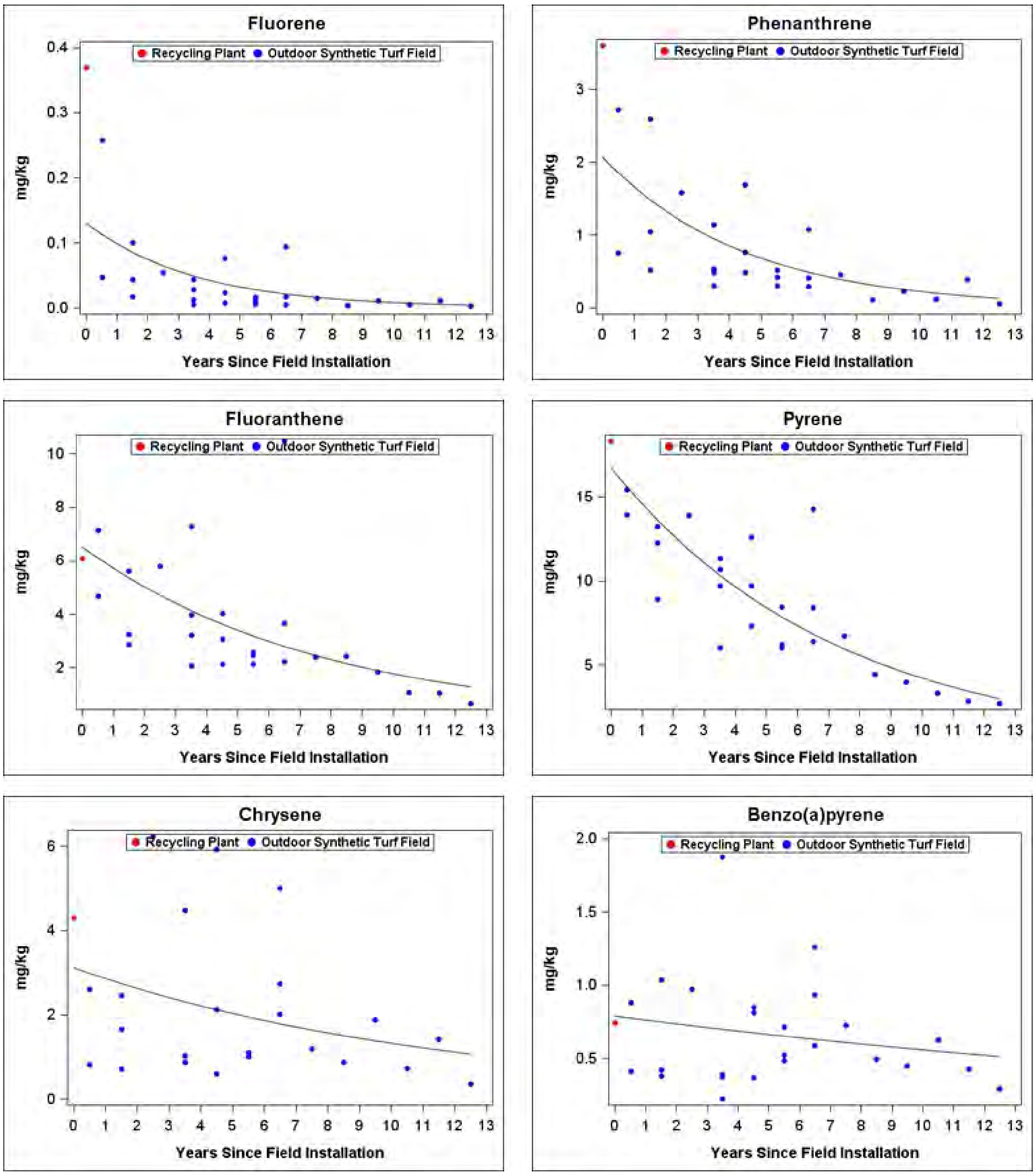

Figure 4-55. Concentrations of select extractable PAHs in outdoor field composite tire crumb rubber infill samples versus years since field installation. The average concentration for the recycling plant tire crumb rubber is also shown on each graph as a zero point for time. The modeled relationships between the concentrations and years are shown as curves. [PAH = Polycyclic aromatic hydrocarbons]

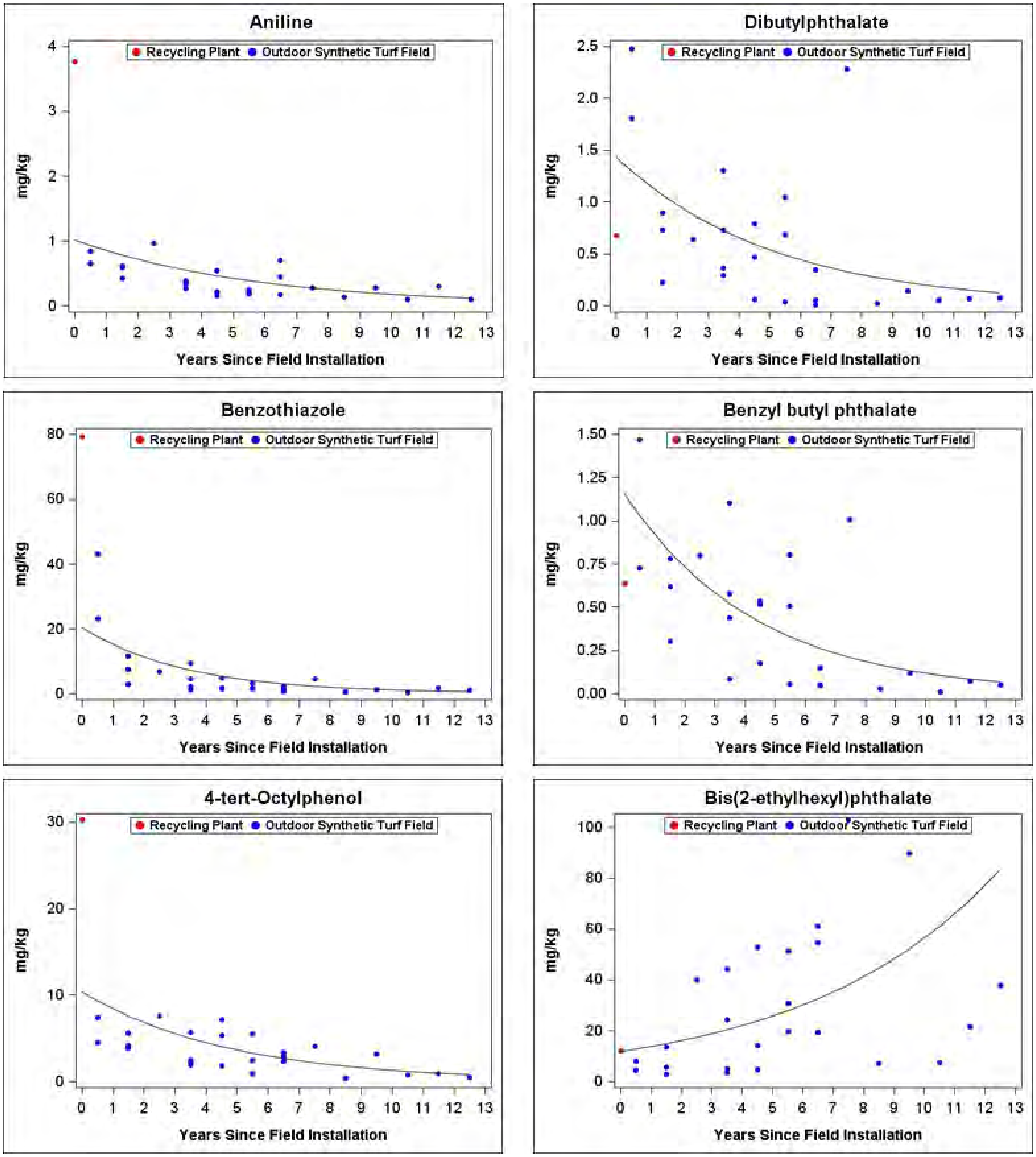

Figure 4-56. Concentrations of select extractable phthalates and other SVOCs in outdoor field composite tire crumb rubber infill samples versus years since field installation. The average concentration for the recycling plant tire crumb rubber is also shown on each graph as a zero point for time. The modeled relationships between the concentrations and years are shown as curves. [SVOC = Semivolatile organic compound]

The shapes of the curves vary appreciably across the chemicals shown in Figures 4-55 and 4-56. Some chemicals such as benzothiazole, aniline, 4-tert-octylphenol, and fluorene show an apparent very rapid initial decrease in concentrations, compared to average concentrations measured in recycling plant samples, with a more gradual decrease at longer time periods. Other chemicals such as fluoroanthene and pyrene show a more gradual initial decline and an apparent exponential decay function that is often observed for chemical emissions from materials. Benzo[a]pyrene, on the other hand, appears to have a nearly linear decrease in concentration over time. Finally, the concentrations of bis(2-ethylhexyl) phthalate have considerable variability but, in general, appear to increase in concentrations over time. This could be a result of sources of bis(2-ethylhexyl) phthalate other than the tire crumb rubber infill contributing chemical to the rubber over time.

Decay half-lives were estimated for these chemicals based on an assumed exponential decay function. Estimated half-lives are shown in Table 4-89 with and without the average tire recycling plant concentration included as a ‘zero’ time point. Estimated decay half-lives ranged from 2.3 years for benzothiazole to 20 years for benzo[a]pyrene with the average recycling plant concentration included. Information for several chemical properties are also included in Table 4-89 because factors such as vapor pressure, water solubility, and octanol:water partition coefficients may help explain differences in the changes in concentration over time. In general, the lighter and more volatile SVOCs had shorter decay half-lives and more rapid initial decreases in concentrations when compared to average concentrations for tire crumb rubber collected at recycling plants. There could also be a water solubility relationship for chemicals like aniline, benzothiazole, and 4-tert-octylphenol having very rapid initial decreases in concentrations at outdoor fields. There may be an initial extraction effect of rainwater and/or irrigation water contributing to the rapid reduction of concentrations of the more water-soluble chemicals at the rubber particle surfaces. Benzo[a]pyrene, with its very low vapor pressure and water solubility and relatively high octanol:water partition coefficient, exhibited the longest decay half-life.

There are several limitations to these decay half-life estimates, including relatively small sample sizes. There is considerable variability for some chemicals that may be related to factors such as differences in initial concentrations, weather and climate effects for heat and rain or irrigation, field maintenance practices (including possible degradation of organic analytes with oxidative disinfectants), activity levels and types, and refreshment with new tire crumb rubber infill material. The data set is too small to support further assessment of these factors. The decay half-life estimation also relies on an assumed exponential decay function. While an exponential function fit most chemical patterns reasonably well, the very rapid initial decrease for some chemicals suggests the possibility of different chemical/physical processes at early and later times that may have different underlying time distributions. Finally, it is also important to acknowledge that differences in concentrations in synthetic field infill samples could be a result of differences in the original concentrations of chemicals in tires at different times. Longitudinal studies at individual fields would be needed to confirm that weathering effects are primarily responsible for these differences.

Table 4-89. Estimated Time Decay Half-lives and Chemical Properties for Selected Extractable SVOCs in Tire Crumb Rubber Infill Samples Collected at Outdoor Fields with a Range of Ages [a,b]

Analyte	Estimated Half-Life (years), including average recycling plant	Estimated Half-Life (years), not including average recycling plant	Molecular Weight (g/mol)	Boiling Point (° C)	Vapor Pressure (mm Hg)	Solubility in Water (mol/L)	LogP: Octanol-Water
Fluorene	2.4	2.8	166	295	6.0E-04	1.1E-05	4.2
Phenanthrene	3.1	3.3	178	339	1.2E-04	6.4E-06	4.5
Fluoranthene	5.3	5.2	202	380	9.2E-06	1.1E-06	5.2
Pyrene	5.0	5.1	202	399	4.5E-06	6.7E-07	4.9
Chrysene	8.1	9.1	228	448	6.2E-09	8.8E-09	5.8
Benzo[a]pyrene	20	19	252	495	5.5E-09	6.4E-09	6.1
Aniline	3.9	5.7	93	184	4.9E-01	3.9E-01	0.9
Benzothiazole	2.3	2.7	135	230	4.7E-02[c]	3.2E-02	2.0
4-tert-octylphenol	3.3	4.2	206	280	4.8E-04	3.1E-04	4.8
Dibutyl phthalate	3.5	3.3	278	340[c]	2.0E-05	4.0E-05[c]	4.5
Benzyl butyl phthalate	3.0	2.9	312	370	8.2E-06	8.6E-06	4.7
Bis(2-ethylhexyl) phthalate	-4.4[d]	-4.4[d]	391	308	1.4E-07	1.1E-07	7.6

[a] Field ages ranged from 0.5 to 12 years based on reported year of field installation.

[b] Chemical properties from EPA Chemical Dashboard; average experimental values shown unless otherwise noted.

[c] No experimental value reported; predicted average value used.

[d] Average concentrations were higher in field samples than recycling plant samples and appeared to increase at fields over time.

These results, along with the chamber emission factor temperature differences (section 4.7.2) and chamber time series tests (Appendix J), may provide some insight on the dynamic processes for releases of organic chemicals from the tire crumb rubber. There appears to be a difference between chemicals at the surface of the rubber material and chemicals found in deeper rubber particle layers. It may be possible that the production of the tire crumb rubber at the recycling plant opens fresh new surfaces where chemicals become available for relatively rapid emission into the air and extraction – whether by rainwater at the fields or by solvent in laboratory experiments. Effective surface depletion rates may be slowed at first by emitted chemicals being rapidly absorbed again on the surfaces of neighboring, tightly bunched particles in the storage sacks (or in sample collection bottles). Once on the field, the exchange between neighboring particle surfaces may continue for the layer of infill applied to the field, with some emitted chemicals entering the air above the field being permanently lost. Shortly after deployment on the field, rain events or irrigation may rapidly extract the more water-soluble chemicals at the particle surface throughout the infill layer. A more rapid phase of initial emission dynamics may be governed predominantly at first by the solid:air partition coefficient. Once the surface layer is sufficiently depleted of the chemical, a slower emission rate may be observed as the surface needs to be replenished with chemical from deeper layers in the rubber particle. At that time, the chemical solid mass diffusion coefficient may become the more dominant dynamic rate limiting step, as more chemical has to diffuse to the particle surface before it becomes available for emission or extraction. The dynamics for each chemical will depend on its surface:air partition coefficient, mass diffusion coefficient, vapor pressure, and water solubility, along with the conditions at the field and surface to volume particle ratios. Additional laboratory work would be required to better understand these dynamics across chemicals, and how these dynamics may affect the amounts of chemicals available for exposure under different time and condition scenarios.

The insight on dynamic processes for organic chemical in tire crumb rubber also helps inform interpretation of results in this report. For example, based on the concentration derived from the solvent extract and the emission factors measured for the more volatile organics such as benzothiazole, one might estimate that the chemical would be fully depleted from the material in less than a year. However, complete depletion is clearly not occurring over that time scale. First, it is likely that the solvent extraction is only removing chemicals from near the surface of the rubber particles and not from deeper layers. While this is probably a good measure for understanding the potential for exposures at a given time point, it likely underestimates the total amount of chemical associated with the rubber on a mg/kg basis and available for release over many years. Second, the emission factors measured at 24-hour time points in the chamber tests likely reflect the more rapid period of release from the rubber particle surface layer and not the slower dynamics that would likely take over at later times when the mass diffusion of the chemical from deeper particle layers may become the dominant dynamic driver, especially for material from the recycling plants and newer fields. It may also help explain why the BTEX chemicals were not generally measured with higher emission factors in 60 °C tests as compared to the 25 °C tests. If the source of the BTEX chemicals is from atmospheric absorption onto the rubber particle surface, it is likely that these volatile chemicals will be rapidly emitted over short time periods at high temperatures. If there are not BTEX compounds deeper in the rubber (or if they are at very low concentrations in the rubber) then there may be no further emissions (or lower emissions) over time after they are emitted from the surface. The chamber time series tests reported in Appendix J support this dynamic scenario.

4.10.5 Geographic Region

Tire crumb rubber infill mean chemical measurement results were compared for synthetic turf fields organized into four groups, based on U.S. census region. For the statistical test results, p-values are reported for between-group differences in the cases where all measurement results were > 0 (because the statistical testing was performed on the log-transformed measurement results). When viewing these results, it is also important to remember that substantial differences were observed for outdoor versus indoor fields, and for organic chemicals, modest differences were observed in average concentrations across age groups. In this section, there is no differentiation between indoor and outdoor fields or field installation age group, within each geographical region category. Results for linear multivariate modeling of all three field characteristics are reported in the next sub-section (section 4.10.6).

4.10.5.1 Metals by ICP/MS and XRF

Table 4-90 shows results for differences in mean concentrations of select metals analyzed in acid digests by ICP/MS and in XRF analyses of tire crumb rubber infill collected at fields in four different U.S. census regions. There were no statistically significant differences among the groups for any analytes. Figure 4-57 illustrates the distributions in measurement results across the four geographic region groups for chromium, cobalt, lead, and zinc.

Table 4-90. Comparison of Select Metals in Tire Crumb Rubber Infill Collected at Synthetic Turf Fields in Four U.S. Census Regions[a]

Analysis[b]	Analytes	Northeast Mean (mg/kg)	Northeast Standard Deviation (mg/kg)	South Mean (mg/kg)	South Standard Deviation (mg/kg)	Midwest Mean (mg/kg)	Midwest Standard Deviation (mg/kg)	West Mean (mg/kg)	West Standard Deviation (mg/kg)	F-test p-value[c]
ICP/MS Analysis	Arsenic	0.36	0.13	0.33	0.23	0.43	0.29	0.42	0.11	0.2021
ICP/MS Analysis	Cadmium	1.1	0.49	0.75	0.41	1.3	1.2	0.78	0.38	0.1562
ICP/MS Analysis	Chromium	1.9	0.68	1.3	1.1	1.5	0.51	2.0	0.78	NR[d]
ICP/MS Analysis	Cobalt	110	43	140	55	150	84	150	59	0.3609
ICP/MS Analysis	Lead	20	16	18	13	25	22	34	44	0.5454
ICP/MS Analysis	Zinc	14000	2400	15000	3500	17000	3000	14000	2400	0.1387
XRF Analysis	Chromium	14	2.3	14	2.8	14	3.3	13	3.4	0.419
XRF Analysis	Cobalt	29	16	42	16	42	17	40	18	0.2355
XRF Analysis	Lead	38	28	35	20	36	11	37	28	0.94
XRF Analysis	Zinc	29000	6700	34000	7400	37000	6400	33000	6700	0.0767

[a] Northeast (n=9); South (n=13); Midwest (n=8); West (n=10)

[b] ICP/MS = Inductively coupled plasma/mass spectrometry; XRF = X-ray fluorescence spectrometry

[c] Statistical tests performed using ln-transformed measurement values.

[d] NR = Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

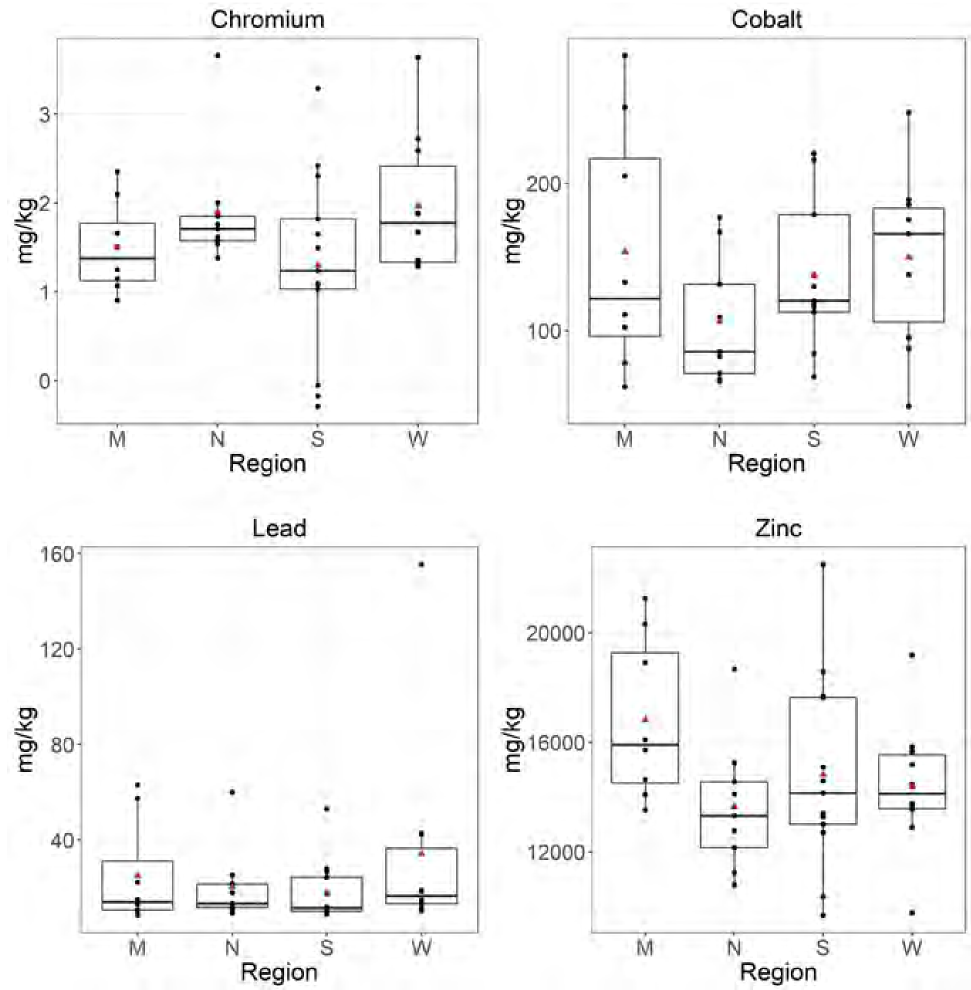

Figure 4-57. Comparison of ICP/MS metal analysis results (mg/kg) between tire crumb rubber infill composite samples from synthetic turf fields in four U.S. census regions for chromium, cobalt, lead, and zinc. [ICP/MS = Inductively coupled plasma/mass spectrometry; M = Midwest; N = Northeast; S = South; W = West]

4.10.5.2 SVOC Extracts by GC/MS/MS and LC/TOFMS

Table 4-91 shows results for differences in mean concentrations of select SVOCs analyzed in solvent extracts by GC/MS/MS for tire crumb rubber infill collected at fields in four different U.S. census regions. Fluoranthene and 4-tert-octylphenol showed statistically significant differences across region groups. In both cases, the average concentration for the West region were lower than the other regions. For 4-tert-octylphenol, the average concentration in the Midwest region was substantially higher than those in the other regions. It is important to note that the Midwest region had the largest number of indoor fields, and higher levels of SVOCs were consistently found for indoor fields versus outdoor fields. Table 4-92 shows results for differences in mean chromatographic peak area counts of select SVOCs analyzed in solvent extracts by LC/TOFMS. Figures 4-58 through 4-60 illustrate the distributions in measurement results across the four geographic region groups for twelve SVOC analytes.

Table 4-91. Comparison of Select SVOC Extracts Analyzed by GC/MS/MS for Tire Crumb Rubber Infill Collected at Synthetic Turf Fields in Four U.S. Census Regions[a,b]

Analytes[c]	Northeast Mean (mg/kg)	Northeast Standard Deviation (mg/kg)	South Mean (mg/kg)	South Standard Deviation (mg/kg)	Midwest Mean (mg/kg)	Midwest Standard Deviation (mg/kg)	West Mean (mg/kg)	West Standard Deviation (mg/kg)	F-test p-value[d]
Fluoranthene	5.1	3.4	5.2	2.6	4.9	1.9	2.8	1.3	0.0494
Pyrene	13	8.3	12	5.3	16	4.8	9.9	5.6	0.1743
Benzo[a]pyrene	1.1	0.80	0.80	0.49	0.69	0.27	0.57	0.25	0.1887
Benzo[ghi]perylene	1.5	0.37	1.4	0.83	1.1	0.63	1.2	0.57	0.4213
Sum15PAH	33	21	29	12	34	12	22	11	0.1567
Benzothiazole	13	19	8.6	12	15	12	7.7	6.4	0.3539
Dibutyl phthalate	2.0	2.5	1.0	1.1	1.8	1.1	1.4	1.2	0.3835
Bis(2-ethylhexyl) phthalate	33	26	47	51	45	55	43	36	0.9489
Aniline	0.75	0.75	0.57	0.33	0.98	0.68	0.50	0.31	0.2898
4-tert-octylphenol	8.0	6.7	8.2	11	19	11	6.5	6.6	0.0392
n-Hexadecane	1.3	1.8	0.52	0.90	1.6	1.4	0.68	0.80	0.0665

[a] SVOC = Semivolatile organic compound; GC/MS/MS = Gas chromatography/tandem mass spectrometry

[b] Northeast (n=9); South (n=13); Midwest (n=8); West (n=10)

[c] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

[d] Statistical tests performed using ln-transformed measurement values.

Table 4-92. Comparison of Select SVOC Extracts with Non-quantitative LC/TOFMS Analysis for Tire Crumb Rubber Infill Collected at Synthetic Turf Fields in Four U.S. Census Regions[a,b]

Analyte	Northeast Mean Area Counts	Northeast Area Counts Standard Deviation	South Mean Area Counts	South Area Counts Standard Deviation	Midwest Mean Area Counts	Midwest Area Counts Standard Deviation	West Mean Area Counts	West Area Counts Standard Deviation	F-test p-value[c,d]
2-mercaptobenzothiazole	3.5E+03	4.0E+03	4.4E+02	5.2E+02	3.7E+03	5.6E+03	7.3E+02	1.5E+03	NR
2-hydroxybenzothiazole	1.0E+05	1.2E+05	6.9E+04	1.1E+05	2.3E+05	1.5E+05	5.1E+04	6.1E+04	NR
cyclohexylamine	9.5E+05	1.1E+06	1.1E+05	1.3E+05	1.0E+06	1.0E+06	1.2E+05	2.0E+05	NR
di-cyclohexylamine	7.0E+06	7.3E+06	8.1E+06	7.9E+06	1.3E+07	1.1E+07	8.9E+06	8.5E+06	0.6126
N-cyclohexyl-N-methylcyclohexanamine	4.1E+05	5.1E+05	2.0E+05	1.9E+05	2.0E+05	1.9E+05	1.6E+05	1.7E+05	0.591
diisononylphthalate	6.6E+04	1.2E+05	4.6E+04	1.3E+05	3.7E+03	1.6E+04	-8.1E+03	2.4E+03	NR
diisodecylphthalate	1.9E+05	5.7E+05	3.7E+03	2.8E+03	5.8E+03	6.7E+03	9.1E+03	1.3E+04	NR

[a] SVOC = Semivolatile organic compound; LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry

[b] Northeast (n=9); South (n=13); Midwest (n=8); West (n=10)

[c] Statistical tests performed using ln-transformed measurement values.

[d] NR = Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

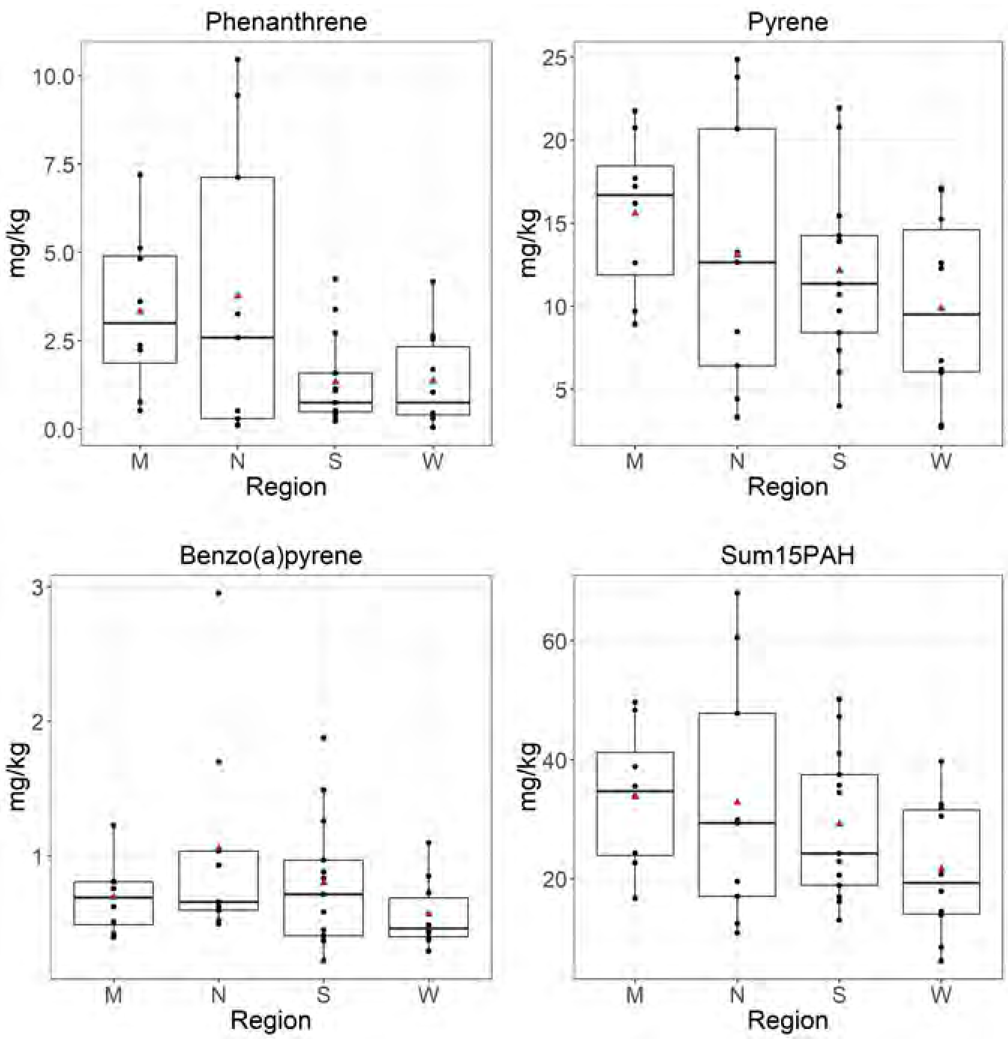

Figure 4-58. Comparison of GC/MS/MS extract SVOC analysis results (mg/kg) between tire crumb rubber infill composite samples from synthetic turf fields in four U.S. census regions for phenanthrene, pyrene, benzo[a]pyrene, and the sum of 15 PAHs. [GC/MS/MS = Gas chromatography/tandem mass spectrometry; SVOC = Semivolatile organic compound; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene; M = Midwest; N = Northeast; S = South; W = West]

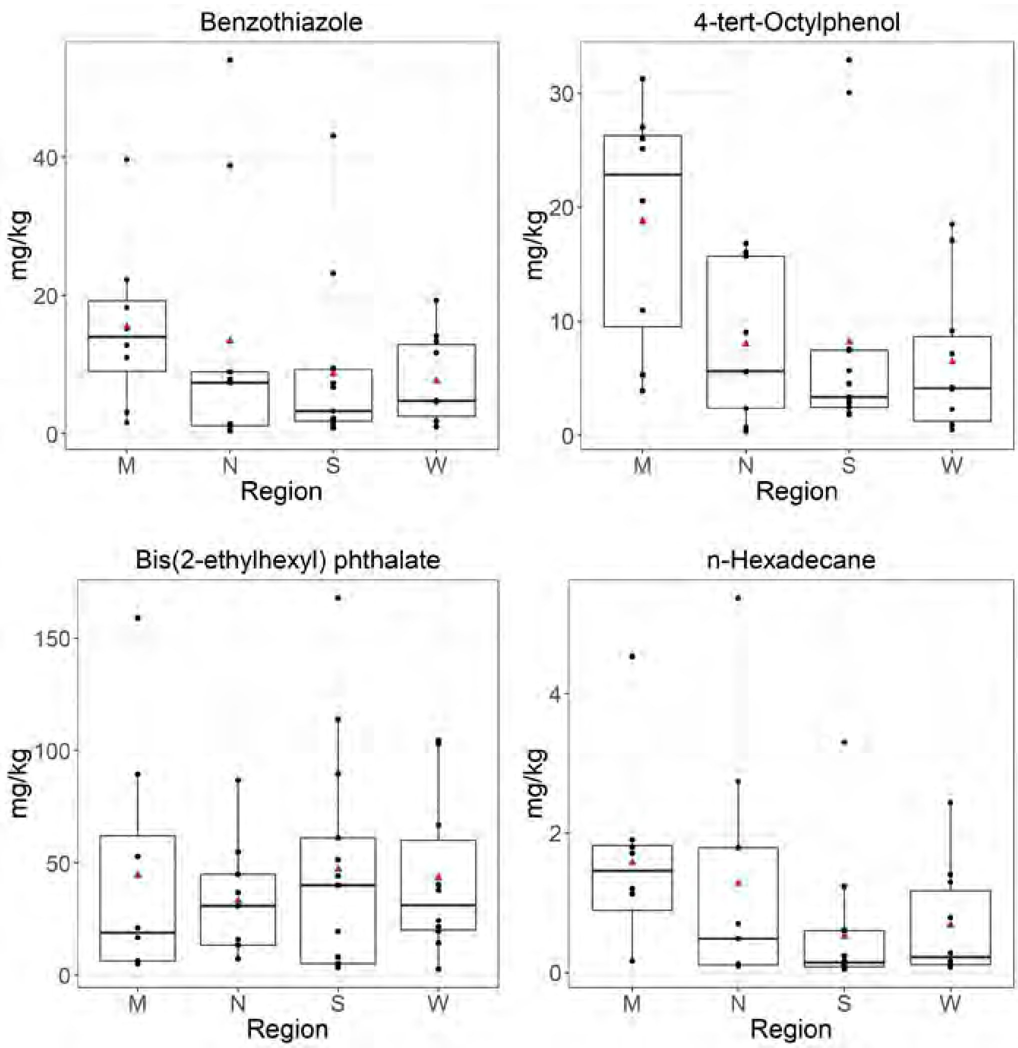

Figure 4-59. Comparison of GC/MS/MS extract SVOC analysis results (mg/kg) between tire crumb rubber infill composite samples from synthetic turf fields in four U.S. census regions for benzothiazole, 4-tert-octylphenol, bis(2-ethylhexyl) phthalate, and n-hexadecane. [GC/MS/MS = Gas chromatography/tandem mass spectrometry; SVOC = Semivolatile organic compound; M = Midwest; N = Northeast; S = South; W = West]

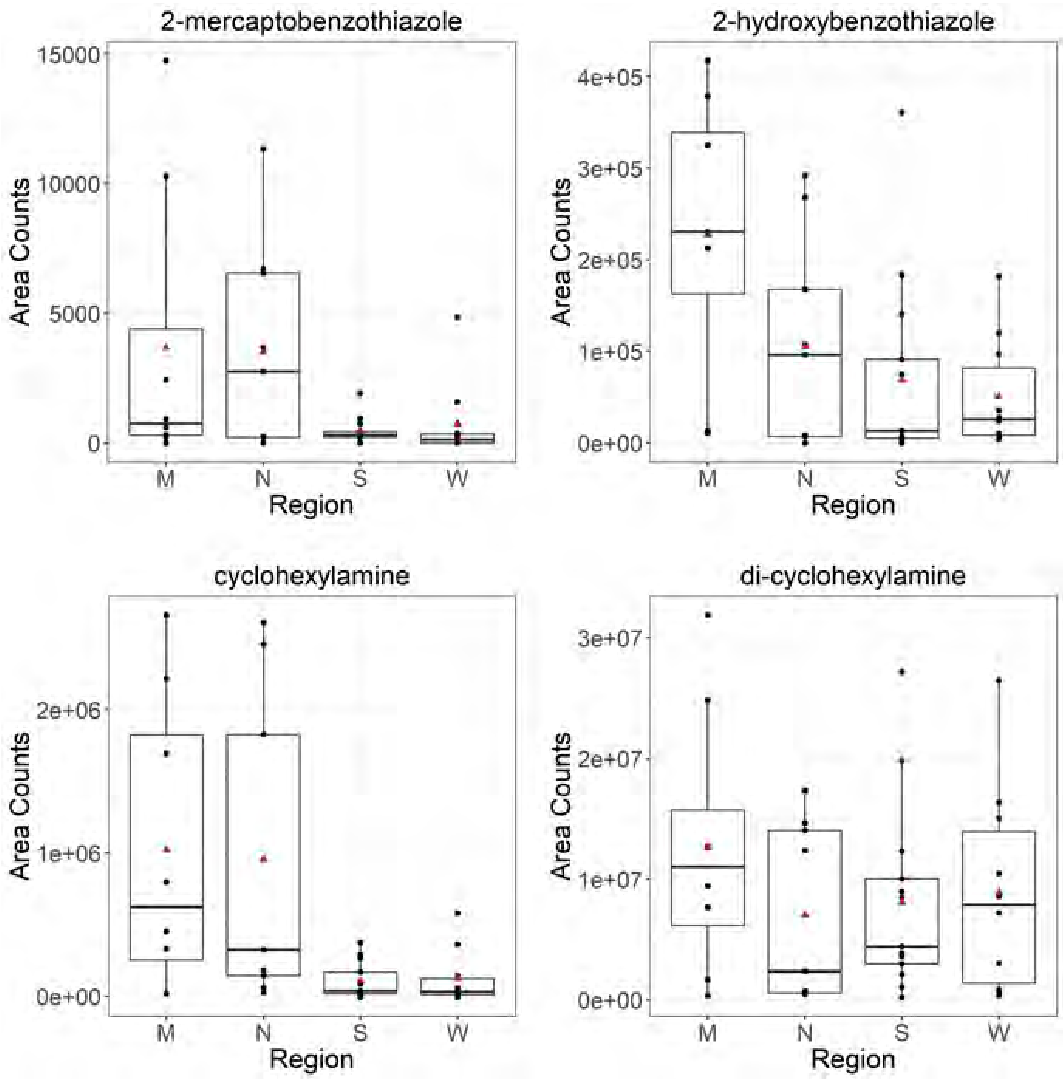

Figure 4-60. Comparison of LC/TOFMS extract SVOC non-quantitative positive ionization analysis results between tire crumb rubber infill composite samples from synthetic turf fields in four U.S. census regions for 2-mercaptobenzothiazole, 2-hydroxybenzothiazole, cyclohexylamine, di-cyclohexylamine. [LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry; SVOC = Semivolatile organic compound; M = Midwest; N = Northeast; S = South; W = West]

Overall, it is difficult to distinguish regional patterns in the SVOC analysis results. This may be due in part to uneven distributions of indoor fields across regions and distributions of outdoor field age. Ideally, the outdoor fields might be placed into climatic zones for assessing the relevance of heat, sun and rainfall. However, the number of outdoor fields is too small to support a regional analysis based on multiple climatic zones. There might also be regional differences in the types of tires that are recycled to produce infill material, but the number of recycling plants in each region was too small to support a regional difference analysis. These results do suggest that regional differences are unlikely to be the most important characteristic underlying differences in SVOC levels in tire crumb rubber infill at synthetic turf fields.

4.10.5.3 VOC Emission Factors

Figure 4-61 illustrates the distributions in 60 °C emission factor results across the four geographic region groups for formaldehyde, benzothiazole, methyl isobutyl ketone, and styrene. Differences in mean 25 °C and 60 °C emission factors for select VOCs analyzed by GC/TOFMS are shown in Table 4-93 for tire crumb rubber infill collected at fields in four different U.S. census regions. Methyl isobutyl ketone and benzothiazole showed statistically significant differences in 60 °C emission factors by U.S. census region. In both cases, the average concentration for the Midwest region were higher than other groups. It should be noted that there was a higher proportion of indoor fields in the Midwest region and that higher emission factors were observed for indoor fields than for outdoor fields. Many of the emission factor measurement results, particularly for the 25 °C tests, were not above the method detection limit or chamber background levels.

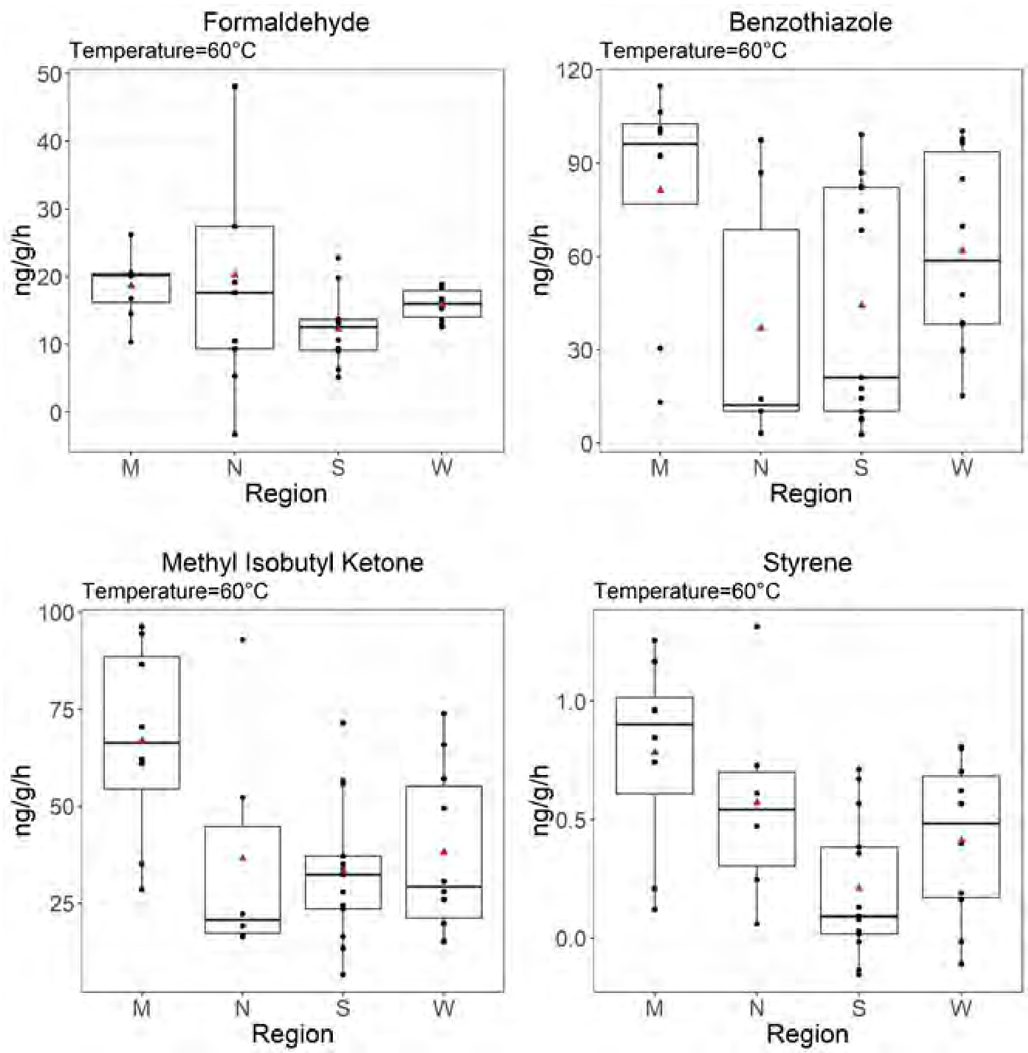

Figure 4-61. Comparison of VOC 60 °C emission factor results (ng/g/h) between tire crumb rubber infill composite samples from synthetic turf fields in four U.S. census regions for formaldehyde, benzothiazole, methyl isobutyl ketone, and styrene.
[VOC = Volatile organic compound; M = Midwest; N = Northeast; S = South; W = West]

Table 4-93. Comparison of Select VOC Emission Factors for Tire Crumb Rubber Infill Collected at Synthetic Turf Fields in Four U.S. Census Regions[a,b]

Emissions Test	Analytes[c]	Northeast Mean (ng/g/h)	Northeast Standard Deviation (ng/g/h)	South Mean (ng/g/h)	South Standard Deviation (ng/g/h)	Midwest Mean (ng/g/h)	Midwest Standard Deviation (ng/g/h)	West Mean (ng/g/h)	West Standard Deviation (ng/g/h)	F-test p-value[d,e]
Emissions at 25 °C	Benzothiazole	23	31	15	22	46	38	21	18	NR
Emissions at 25 °C	o-Xylene	0.068	0.12	0.005	0.081	0.040	0.097	0.030	0.068	NR
Emissions at 25 °C	SumBTEX	0.17	0.53	0.12	0.89	0.37	0.61	0.63	1.1	NR
Emissions at 60 °C	Formaldehyde	20	18	12	4.9	19	4.7	16	2.3	NR
Emissions at 60 °C	Methyl isobutyl ketone	37	31	33	19	67	26	38	22	0.0267
Emissions at 60 °C	Benzothiazole	37	43	44	38	81	38	62	32	0.0393
Emissions at 60 °C	Styrene	0.57	0.44	0.21	0.30	0.78	0.42	0.41	0.34	NR
Emissions at 60 °C	Toluene	0.032	0.18	0.074	0.35	0.29	0.30	0.22	0.29	NR
Emissions at 60 °C	Ethylbenzene	-0.074	0.24	-0.20	0.17	0.038	0.20	-0.023	0.25	NR
Emissions at 60 °C	m/p-Xylene	0.20	0.83	-0.34	0.66	0.78	0.97	0.60	1.2	NR
Emissions at 60 °C	o-Xylene	-0.31	0.46	-0.72	0.47	-0.19	0.56	-0.024	0.87	NR
Emissions at 60 °C	SumBTEX	-0.31	1.8	-1.2	1.7	1.0	2.0	0.67	2.5	NR

[a] Several results are reported as negative values. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.

[b] Northeast (n=6-9); South (n=13); Midwest (n=8); West (n=9-10)

[c] SumBTEX = Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene

[d] Statistical tests performed using ln-transformed measurement values.

[e] NR = Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

4.10.5.4 SVOC Emission Factors

Figure 4-62 illustrates the distributions in 60 °C emission factor results across the four U.S. census regions for pyrene, the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol. Differences in mean 25 °C and 60 °C emission factors for select SVOCs analyzed by GC/MS/MS are shown in Table 4-94 for tire crumb rubber infill collected at fields in four different U.S. census regions. The sum of 15 PAHs showed statistically significant different 25 °C emission factors, with the highest average concentration in the South and lowest average concentration in the West. However, this relationship was not observed for the 60 °C sum of 15 PAH emission factors. Many of the emission factor measurement results, particularly for the 25 °C tests, were not above the method detection limit or chamber background levels.

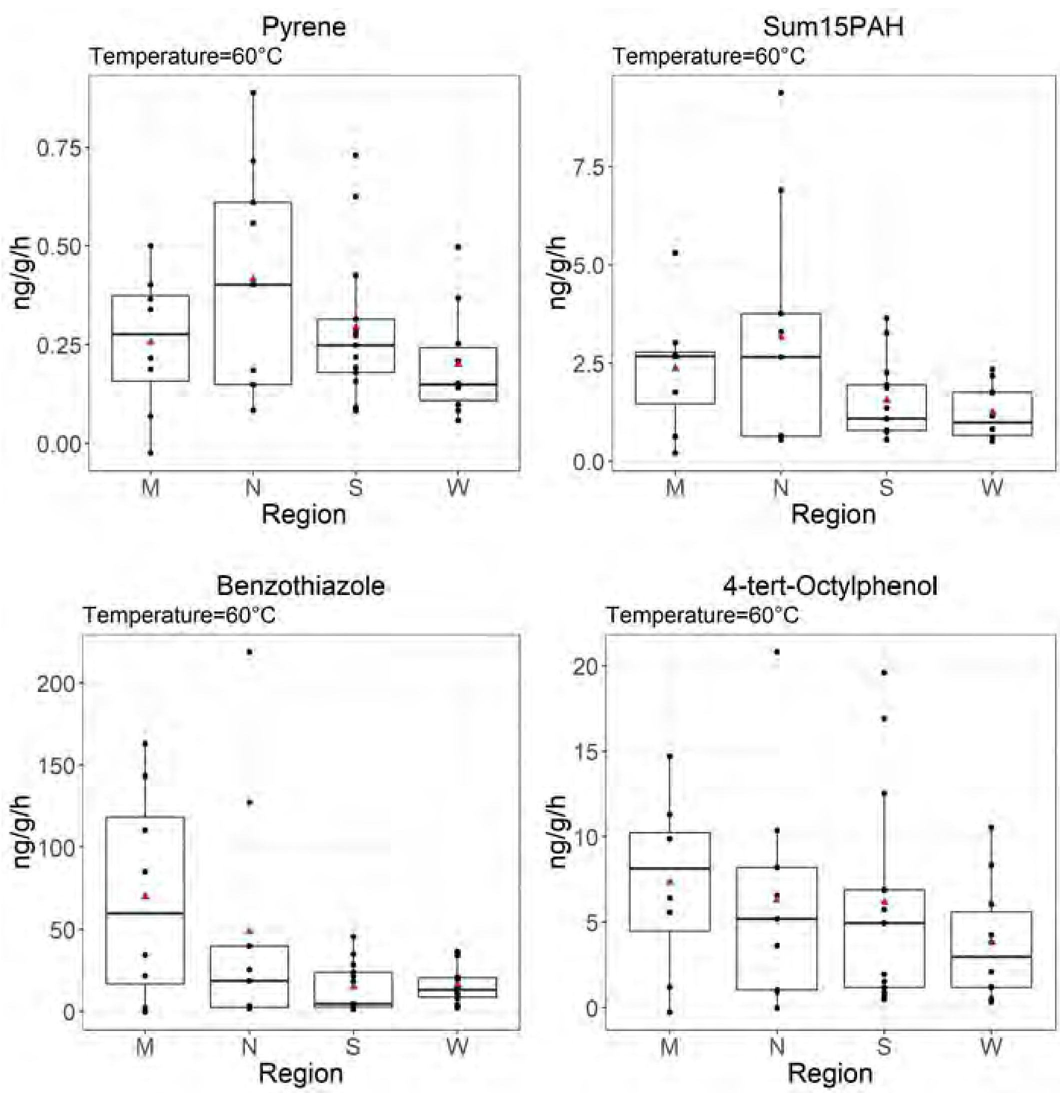

Figure 4-62. Comparison of SVOC 60 °C emission factor results (ng/g/h) between tire crumb rubber infill composite samples from synthetic turf fields in four U.S. census regions for pyrene, the sum of 15 PAHs, benzothiazole, and 4-tert-octylphenol.
[SVOC = Semivolatile organic compound; Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene; M = Midwest; N = Northeast; S = South; W = West]

Table 4-94. Comparison of Select SVOC Emission Factors for Tire Crumb Rubber Infill Collected at Synthetic Turf Fields in Four U.S. Census Regions[a,b]

Emissions Test	Analytes[c]	Northeast Mean (ng/g/h)	Northeast Standard Deviation (ng/g/h)	South Mean (ng/g/h)	South Standard Deviation (ng/g/h)	Midwest Mean (ng/g/h)	Midwest Standard Deviation (ng/g/h)	West Mean (ng/g/h)	West Standard Deviation (ng/g/h)	F-test p-value[d,e]
Emissions at 25 °C	Phenanthrene	0.021	0.074	0.040	0.055	0.028	0.025	0.0056	0.011	NR
Emissions at 25 °C	Sum15PAH	0.71	0.37	0.92	0.97	0.37	0.23	0.35	0.15	0.0403
Emissions at 25 °C	Benzothiazole	4.8	6.5	2.8	3.6	7.9	6.7	2.5	2.9	NR
Emissions at 25 °C	Dibutyl phthalate	0.095	0.41	0.15	0.37	-0.27	0.27	-0.11	0.33	NR
Emissions at 25 °C	Aniline	0.25	0.38	0.19	0.28	0.82	0.57	0.24	0.36	NR
Emissions at 25 °C	4-tert-octylphenol	1.7	4.6	1.3	4.4	0.23	0.16	0.061	0.082	NR
Emissions at 60 °C	Phenanthrene	1.0	1.2	0.35	0.44	0.71	0.57	0.35	0.36	NR
Emissions at 60 °C	Fluoranthene	0.23	0.15	0.16	0.1	0.13	0.081	0.11	0.093	NR
Emissions at 60 °C	Pyrene	0.42	0.29	0.29	0.19	0.26	0.18	0.20	0.14	NR
Emissions at 60 °C	Sum15PAH	3.2	3.2	1.5	1.0	2.4	1.6	1.2	0.7	0.4212
Emissions at 60 °C	Benzothiazole	49	75	15	15	70	64	16	12	NR
Emissions at 60 °C	Dibutyl phthalate	0.14	0.34	0.27	0.31	-0.037	0.45	0.13	0.55	NR
Emissions at 60 °C	Aniline	6.2	8.1	1.0	1.2	6.5	5.3	1.9	2.2	NR
Emissions at 60 °C	4-tert-octylphenol	6.3	6.5	6.2	6.4	7.3	5.1	3.8	3.5	NR

[a] Several results are reported as negative values. This is a result of the subtraction of chamber background values from the sample measurement results. Although this does not represent a physical reality, the negative results are retained as part of the distribution of corrected results.

[b] Northeast (n=9); South (n=13); Midwest (n=8); West (n=10)

[c] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene

[d] Statistical tests performed using ln-transformed measurement values.

[e] NR = Not Reported; one or more measurement results were ≤ 0, precluding ln-transformed testing for the complete data set.

4.10.6 Linear Model Analysis for Field Characteristics

Linear models were fitted to further examine relationships and interactions for selected chemical measurement results for three primary synthetic turf field characteristics examined in this study – outdoor vs. indoor facility type; field installation age group, and U.S. census region field location. Table 4-95 gives p-values for all main effect and interaction terms included in the final model for each of the chemical substances and the p-value for the corresponding Shapiro-Wilk test for normality. For example, the final model for log-transformed lead found statistically significant associations for the main effect of age group and the sole interaction term of indoor/outdoor and region, indicating a differential effect of indoor/outdoor by region.

Interpretation of the relationships illustrated by the models given in Table 4-95 focuses only on the fields included in this study, an important caveat. The study design for the 40 fields sampled is not a probability-based sample, potentially resulting in selection bias and lack of representativeness for the target population (Lohr, 2009). The 40 fields sampled also were not balanced across age group, indoor/outdoor, and Census region categories; this lack of balance results in sparsity for some combinations of the categorical data. These features limit generalizability of the model results.

For the 40 fields studied, over half of the chemical substance composite concentration relationships examined in this analysis are characterized by statistically significant combinations (interactions) of the categorical model terms:

- Seven (7) of the 15 models with interaction terms include an interaction with indoor/outdoor. A total of 14 models includes the indoor/outdoor category in a model term.
- Six (6) of the 15 models with interaction terms include an interaction with age group. A total of 12 models includes the age group category in a model term.
- Ten (10) of the 15 final models include interaction terms, and all but 1 of these 10 models includes an interaction with region. Of the remaining 6 models, 4 include the main effect of region. A total of 13 models includes the region category in a model term.

Consequently, only six of the final models are limited to 1 or more main effect model terms. For a majority of the chemical substances analyzed using linear models, their relationships with the categories of age group, indoor/outdoor, and Census region are best characterized using combinations. The generalizability of these relationships is highly uncertain, but for the fields sampled in this study, all three primary field characteristics apparently contributed to the overall variability in chemicals associated with the tire crumb rubber infill.

Table 4-95. P-values for Final Linear Models of Select Measurement Results for Three Synthetic Turf Field Characteristics – Outdoor vs. Indoor Field, Field Installation Age Category, and U.S. Census Region Field Location[a]

Analysis[b]	Analyte[c]	Main Effect Term – Age Group	Main Effect Term – Indoor/ Outdoor	Main Effect Term – Region	Interaction Term – Age Group by Indoor/ Outdoor	Interaction Term – Age Group by Region	Interaction Term – Indoor/ Outdoor by Region	Interaction Term – Age Group by Indoor/ Outdoor by Region	Shapiro-Wilk p-value
ICP/MS Acid Digestion	Cobalt	0.0003	0.565	0.2303	N/A	N/A	0.0627	N/A	0.5093*
ICP/MS Acid Digestion	Lead	0.0375	0.9629	0.0757	N/A	N/A	0.0205	N/A	0.2312*
ICP/MS Acid Digestion	Zinc	0.0041	0.6605	0.0064	N/A	N/A	0.0252	N/A	0.4851
GC-MS Solvent Extraction	Pyrene	0.0077	<.0001	N/A	0.0135	N/A	N/A	N/A	0.7059
GC-MS Solvent Extraction	Sum15PAH	0.0119	<.0001	0.0341	N/A	N/A	N/A	N/A	0.9571
GC-MS Solvent Extraction	Benzothiazole	0.0001	<.0001	N/A	N/A	N/A	N/A	N/A	0.9774*
GC-MS Solvent Extraction	4-tert-octylphenol	0.0027	<.0001	0.0591	0.0018	0.1670	0.7340	0.0141	0.3479*
GC-MS Solvent Extraction	Bis(2-ethylhexyl) phthalate	0.0920	0.0131	0.0378	N/A	0.0520	N/A	N/A	0.3710
Chamber SVOC Emission Factors at 60°C	Pyrene	<.0001	<.0001	<.0001	0.2486	0.0018	0.0010	0.0020	0.1752
Chamber SVOC Emission Factors at 60°C	Sum15PAH	0.0019	<.0001	0.0001	N/A	0.0024	N/A	N/A	0.3735*
Chamber SVOC Emission Factors at 60°C	Benzothiazole	<.0001	<.0001	0.7447	N/A	N/A	0.0188	N/A	0.4736*
Chamber SVOC Emission Factors at 60°C	4-tert-octylphenol	N/A	<.0001	0.0486	N/A	N/A	N/A	N/A	0.2104
Chamber VOC Emission Factors at 60°C	Benzothiazole	N/A	<.0001	N/A	N/A	N/A	N/A	N/A	0.1261*
Chamber VOC Emission Factors at 60°C	Methyl isobutyl ketone	N/A	N/A	0.0111	N/A	N/A	N/A	N/A	0.1788

Table 4-95 Continued

Analysis[b]	Analyte[c]	Main Effect Term – Age Group	Main Effect Term – Indoor/ Outdoor	Main Effect Term – Region	Interaction Term – Age Group by Indoor/ Outdoor	Interaction Term – Age Group by Region	Interaction Term – Indoor/ Outdoor by Region	Interaction Term – Age Group by Indoor/ Outdoor by Region	Shapiro-Wilk p-value
Chamber VOC Emission Factors at 60°C	Styrene	0.3634	<.0001	0.0496	N/A	0.0037	N/A	N/A	0.1360
Chamber VOC Emission Factors at 60°C	SumBTEX	N/A	N/A	0.0434	N/A	N/A	N/A	N/A	0.2097

[a] P-values for all main effect and interaction terms included in final model for each analyte and corresponding Shapiro-Wilk (S-W) test for normality; model fitting used backward elimination starting with the full factorial model and selection based on p-values (α=0.05), Akaike information criterion (AIC) statistic, and model residuals.

[b] ICP/MS = Inductively coupled plasma/mass spectrometry; GC/MS = Gas chromatography/mass spectrometry; SVOC = Semivolatile organic compound; VOC = Volatile organic compound; N/A = Not applicable; main effect or interaction term not included in final model

[c] Sum15PAH = Sum of 15 of the 16 EPA 'priority' PAHs, including Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo(b)fluoranthene, Benzo[ghi]perylene, Benzo(k)fluoranthene, Chrysene, Dibenz[a,h]anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene; SumBTEX = Sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene

*Model fitted for log-transformed concentration as indicated by Shapiro-Wilk test statistic; otherwise concentration not transformed.

4.11 Suspect Screening Chemical Analysis

Suspect screening is a technique used to tentatively identify chemicals using mass spectrometry methods when there is prior information about the potential for those chemicals to be present in a medium of interest. Many SVOC chemicals (Table 3-5) were proposed for suspect screening by LC/TOFMS analysis based on previous reports (compiled in the Literature Review and Data Gaps Analysis, Appendix C) that they were observed in tire crumb rubber analysis studies or because they were identified as potentially being used (or are transformation products or degradates of chemicals being used) in tire manufacturing. Chemicals were selected where mass spectra were available to identify the presence of the chemical.

The samples were analyzed in both positive and negative ionization modes and subjected to a molecular feature extraction (MFE) algorithm to identify peaks for further exploration. Features identified were compared to a personal compound database list (PCDL) created using spectra for the suspect screening chemicals in the U.S. EPA's Distributed Structure-Searchable Toxicity (DSSTox) database. Chemicals matching within 5 ppm of the suspect chemical according to accurate mass and scoring >80% in spectra match comparisons were deemed as a provisional match.

In some cases, the same chemical identity was reported multiple times in the same sample. This was due in part because chemical isomers have the same accurate mass and may generate the same or very similar spectra that are matched to a single library reference spectrum. In many cases, it was observed that the same chemical match was reported for spectra produced at different chromatographic retention times, making the presence of isomers more likely. And, of course, some repeated chemical matches may be the result of incorrect matching identifications. In order to be reported, average area counts within at least one of the three sample types (recycling plant, indoor field, or outdoor field) had to be more than three times greater than the average area counts in the method blanks for a tentatively-identified chemical.

Suspect screening chemicals tentatively identified in tire crumb rubber solvent extract samples from recycling plants and tire crumb rubber infill solvent extract samples from synthetic turf fields are shown in Table 4-96 for positive ionization mode analysis and Table 4-97 for negative ionization mode. Chemicals previously reported in targeted analyses were not included in these tables.

Fifteen unique chemicals were tentatively identified in the positive ionization analysis. Multiple instances of 2,2,4-Trimethyl-1,2-dihydroquinoline (TMQ), a tire rubber antioxidant chemical, were observed in recycling plant and field samples. Other potential tire rubber chemicals, such as N,N'-Diphenyl-p-phenylenediamine (DPPD), N,N'-Ditolyl-p-phenylenediamine (DTPD), N-tert-Butyl-2-benzothiazolesulfenamide (TBBS,) and n-Isopropyl-n'-phenylparaphenylenediamine (IPPD), with reported uses as accelerators, antioxidants, or antiozonants, were observed widely in recycling plant samples and occasionally to often in the synthetic turf field samples. The chemical 1,3-Dicyclohexylurea may be used in anti-exposure cracking (antiozonant) formulations and was observed in all sample types. Hexa(methoxymethyl)melamine has been reported as an adhesion promotor for rubber compounds and was observed in all sample types.

Eight chemicals were tentatively identified in the negative ionization analysis. Six of these chemicals were observed in many of the recycling plant samples and at lower frequencies in synthetic turf field samples. The chemical 2,2'-Methylene-bis-(4-methyl-6-tert-butylphenol) may be used as an antioxidant, while dehydroabietic acid and fatty acids are reported as used in tire manufacturing. The compound 3,5-di-tert-butyl-4-hydroxybenzaldehyde was observed in many samples and may be present as a transformation product of the antioxidant butylated hydroxytoluene (BHT).

Table 4-96. Tentative Suspect Screening Chemical Identifications Through Positive Ionization LC/TOFMS Analysis of Tire Crumb Rubber Solvent Extracts[a,b]

Tentative Chemical Name	CAS Number[c]	Recycling Plants Frequency[d]	Recycling Plants Mean Area	Indoor Fields Frequency[d]	Indoor Fields Mean Area	Outdoor Fields Frequency[d]	Outdoor Fields Mean Area	Blanks Frequency[d]
1,3-Dicyclohexylurea	2387-23-7	13	3.23E+06	20	4.08E+06	5	5.17E+05	0
Dehydroabietic acid	1740-19-8	24	3.06E+05	19	5.31E+05	30	3.74E+05	0
2,2,4-Trimethyl-1,2-dihydroquinoline (TMQ)	147-47-7	101	2.18E+07	112	1.60E+07	163	6.35E+06	0
2-Phenylbenzothiazole	883-93-2	5	1.14E+06	7	9.12E+05	1	7.85E+05	0
3,5-Di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	0	N/A	4	3.19E+05	0	N/A	0
Diphenylamine	122-39-4	11	6.34E+05	0	N/A	0	N/A	0
Hexa(methoxymethyl)melamine	3089-11-0	23	2.52E+07	21	1.73E+07	7	9.10E+05	0
N,N'-Diphenyl-p-phenylenediamine (DPPD)	74-31-7	37	2.61E+06	13	1.64E+06	8	5.30E+05	0
N,N'-Diphenylguanidine (DPG)	102-06-7	0	N/A	0	N/A	4	5.88E+06	0
N,N'-Ditolyl-p-phenylenediamine (DTPD)	27417-40-9	25	2.72E+06	11	1.19E+06	1	7.56E+05	0
N,N-Dicyclohexyl-2-benzo thiazolesulfenamide (DCBS)	4979-32-2	7	4.48E+05	13	4.98E+05	4	5.65E+05	0
N-tert-Butyl-2-benzothiazolesulfenamide (TBBS)	95-31-8	11	1.10E+06	0	N/A	0	N/A	0
Pyrimidine, 2-(4-pentylphenyl)-5-propyl-	94320-32-8	17	3.88E+07	20	8.44E+06	10	5.05E+06	0
n-Isopropyl-n'-phenylparaphenyl enediamine (IPPD)	101-72-4	11	3.00E+06	7	7.86E+05	0	N/A	0
n-Nitrosodiphenylamine	86-30-6	2	5.09E+05	0	N/A	0	N/A	0

[a] LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry; N/A = Not applicable

[b] Recycling Plants (N = 27 samples); Indoor Fields (N=29 samples); Outdoor Fields (N=46 samples); Blanks (N = 9)

[c] Unique numerical identifier assigned by the Chemical Abstracts Service (CAS)

[d] Frequency of observation. Sometimes the frequency exceeds the number of samples analyzed; this may be a result of the presence of same formula isomers or incorrect chemical identity matching.

Table 4-97. Tentative Suspect Screening Chemical Identifications Through Negative Ionization LC/TOFMS Analysis of Tire Crumb Rubber Solvent Extracts[a,b]

Tentative Chemical Name	CAS Number[c]	Recycling Plants Frequency[d]	Recycling Plants Mean Area	Indoor Fields Frequency[d]	Indoor Fields Mean Area	Outdoor Fields Frequency[d]	Outdoor Fields Mean Area	Blanks Frequency[d]
Dehydroabietic acid	1740-19-8	19	3.22E+06	8	3.66E+06	3	2.93E+06	0
1H-isoindole-1,3 (2H)-dione	85-41-6	2	7.43E+04	0	N/A	0	N/A	0
2,2'-Methylene-bis-(4-methyl-6-tert-butylphenol)	119-47-1	26	1.45E+06	2	2.59E+05	0	N/A	0
3,5-Di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	19	8.34E+05	9	6.81E+05	2	8.18E+04	0
Benzoic acid	65-85-0	0	N/A	1	7.00E+04	0	N/A	0
Docosanoic acid	112-85-6	7	2.96E+04	9	4.19E+04	3	1.02E+05	0
Dodecanoic acid	143-07-7	24	2.03E+05	10	1.67E+05	2	1.08E+05	0
Octadecanoic acid, methyl ester	112-61-8	10	1.46E+05	9	9.58E+04	3	7.47E+04	0

[a] LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry

[b] Recycling Plants (N = 27 samples); Indoor Fields (N=29 samples); Outdoor Fields (N=46 samples); Blanks (N = 9)

[c] Unique numerical identifier assigned by the Chemical Abstracts Service (CAS)

[d] Frequency of observation. Sometimes the frequency exceeds the number of samples analyzed; this may be a result of the presence of same formula isomers or incorrect chemical identity matching.

Suspect screening analyses were also performed by LC/TOFMS for chamber emission samples collected during experiments performed at 60°C. No suspect screening chemicals were observed that met the requirement of having average area counts for a tentatively identified chemical within at least one of the three sample types that was more than three times greater than the average area counts in the chamber background samples.

These suspect screening analysis results show 23 chemicals tentatively identified in tire crumb rubber samples from recycling plants or synthetic turf fields that had either been reported in earlier research studies or were reported to be tire manufacturing chemicals or transformation products. Some chemicals found in ‘fresh’ tire crumb rubber from recycling plants were not observed in samples from the fields. And in some cases, the chemicals were observed in field samples, but at lower frequencies or lower average intensities. This may reflect patterns seen for the target organic analytes in this study, where many organic chemicals had lower levels in field infill as compared to recycling plant tire crumb rubber, and higher levels in indoor fields as compared to outdoor fields.

There are several limitations to these suspect screening analysis results. First, the chemical identities generated in this research must be considered tentative and would need further analysis of known chemical standards for confirmation. Second, chemicals present in the tire crumb rubber or tire crumb rubber infill may not have been present in the extract or emission samples because of the solvents or conditions used; other methods may have resulted in additional or different sets of chemicals. It is also important to note that different instruments and methods can produce somewhat different mass spectra for the same chemicals, making translation across methods and platforms somewhat difficult.

4.12 Non-Targeted Chemical Analysis

In addition to the target chemical and suspect screening analyses, non-targeted analyses were performed to begin to further elucidate a wider range of organic chemicals associated with tire crumb rubber. Targeted analysis begins with a known chemical and/or standard and methods are directed toward identification or quantification. In contrast, non-targeted analysis begins with a survey of a sample and builds a body of evidence to support an identification for each chemical that can be detected, but not necessarily assigned. Tire crumb samples were analyzed in non-targeted mode and vendor software was used to identify chemical features, which are unidentified chemicals with masses, retention times, and mass spectral data measured from the sample. It is important to emphasize that the non-targeted chemical identification results included in this report should be considered highly tentative and only the first step of what would be a multi-step process to confirm chemical identities and the amounts of chemicals present. Many of the highly-tentative chemical identities included in this report are likely to be incorrect. Given this uncertain outcome, it is important to explain why this work was done:

- Many chromatographic peaks and mass spectral features other than the target chemical analytes were observed in tire crumb rubber solvent extracts and emission samples analyzed in this study.
- Assessment of exposures to a limited set of target chemical analytes may not provide a full picture of the cumulative exposures encountered by synthetic turf field users.
- This initial step in non-targeted analysis provides insight about the scope and nature of the non-targeted chemicals that may be associated with tire crumb rubber.
- The results from this set of non-targeted analyses provides researchers with information useful for future investigations that could be undertaken for confirming chemical identities, measuring the amounts of chemicals associated with the tire crumb rubber, and assessing the potential for exposure to these chemicals. For example, this information has been shared with OEHHA (under

CalEPA/USEPA MCRADA #996-17) to aid their efforts in prioritizing and performing confirmatory analyses for some SVOCs.

The multi-chemical nature of tire crumb rubber material is illustrated in Figures 4-63 and 4-64, where example chromatographs from GC/MS SVOC solvent extract analysis and GC/TOFMS VOC emission analyses show many chromatographic features across a range of intensities. For the SVOCs in Figure 4-63, there are a number of chromatographic peaks that have higher intensities than benzothiazole, which was the most abundant target analyte in the analysis. For the VOCs in Figure 4-64, the target analytes methyl isobutyl ketone and benzothiazole had higher intensities than the other chromatographic peaks. The non-targeted analysis performed as part of this research is a first step in understanding the nature of those unidentified chromatographic peaks in terms of identity and abundance, and the potential relevance for human exposures.

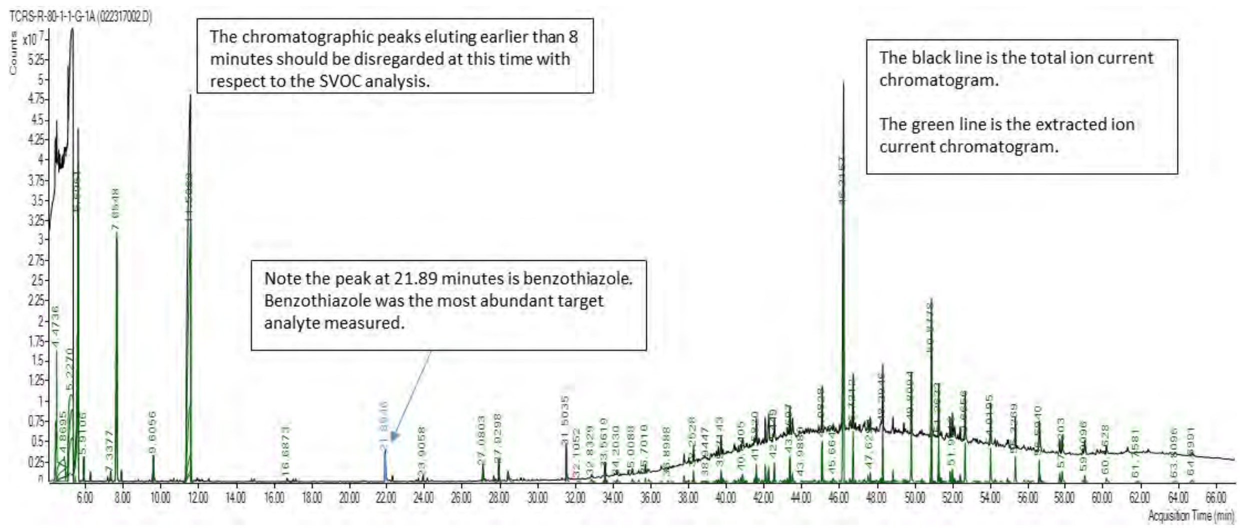

Figure 4-63. Example GC/MS SVOC solvent extraction sample analysis showing total ion current and extracted ion current chromatograms for a recycling plant sample. [GC/MS = Gas chromatography/mass spectrometry; SVOC = Semivolatile organic compound]

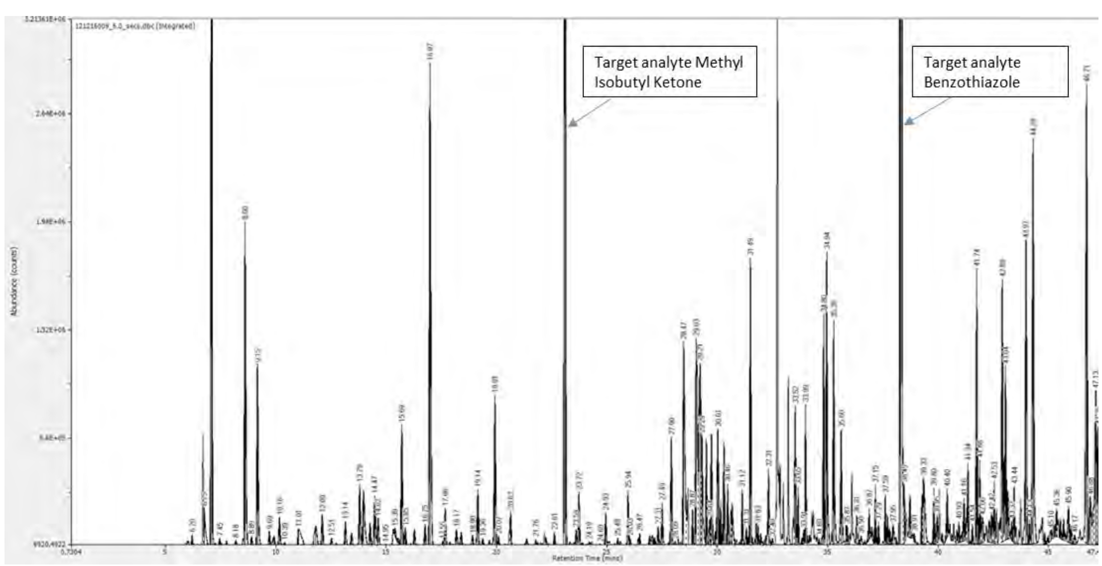

Figure 4-64. Example GC/TOFMS VOC 60 °C chamber emission sample analysis total ion current chromatogram for a synthetic turf field. [GC/TOFMS = Gas chromatography/time-of-flight mass spectrometry; VOC = Volatile organic compound]

In this study, we selected a subset of tire crumb rubber samples from recycling plants and a subset of tire crumb rubber infill samples from indoor and outdoor synthetic turf fields for non-targeted analysis. This strategy allowed for assessment of chemicals potentially associated with 'fresh' recycled tire material and to see whether those chemicals were also observed in the infill collected at synthetic turf fields. The strategy also allowed for the reverse assessment – chemicals found in synthetic turf field infill samples that were not observed in the recycling plant samples – to better assess the extent that chemicals from sources other than the tire crumb rubber material are appearing in the infill.

Six tire recycling plant samples, five outdoor field infill samples, and five indoor field infill samples were selected for non-targeted analyses. Non-targeted analyses were performed for solvent extract samples by both GC/MS and LC/TOFMS. Non-targeted analyses were also performed for chamber emission test samples generated at 60° C using GC/MS and LC/TOFMS methods for SVOCs and by GC/TOFMS for VOCs.

Each of the three analytical methods (GC/MS SVOC, LC/TOFMS SVOC, and GC/TOFMS VOC) produced different types of data and applied different approaches for tentative chemical identification. The methods were previously described in section 3.6. Briefly, the GC/MS SVOC method produced characteristic mass spectra that were matched to the National Institute of Standards and Technology (NIST) spectral library (U.S. Department of Commerce, Gaithersburg, MD, USA) using Unknowns Analysis software (Agilent Technologies, Santa Clara, CA, USA) and the total ion current (TIC) Analysis approach. The deconvolution approach was not used because an excessive number of both false positives and negatives were observed. TIC analysis is more accurate for this data set, but is not as sensitive, so only chemicals with relatively-high concentrations were tentatively identified. A 50% matching score cut-off was applied. In addition, chemicals with retention times below that of nonane were excluded due to the uncertainty associated with the elution of the extraction solvents. The instrument and methods available for GC/MS in this study were not ideal for non-targeted analysis, and results may reflect limitations.

The high-resolution LC/TOFMS SVOC method produced accurate chemical mass values that were used to provide exact chemical formulas. The formulas were referenced against the DSSTox chemical database with over 750,000 chemical references. A chemical formula for each compound was predicted by matching against the EPA Chemistry Dashboard (https://comptox.epa.gov/dashboard), which returns possible chemical formulas, along with a score indicating certainty of the assignment. Formulas below a score of 80 were ignored and the chemicals were excluded from the report. Further analysis and/or expansion of the database may, in the future, allow identification of these compounds. Formula assignments with scores above 80 were assigned a single compound identity from the database, and the number of possible alternates was noted. The assigned chemical was the most likely chemical based on consumer/commercial prevalence (see McEachran et al., 2017), as measured by frequency of literature data sources. Where multiple chemical features with the same formula exist, the features were flagged indicating the chemical formula is accurate, but the chemical assignment is one of many that are possible.

The GC/TOFMS VOC method produced characteristic mass spectra that were matched to the NIST spectral library, applied to chromatographic peaks above a minimum area count, and combined with a forward and reverse spectral match score. Forward and reverse matches determined for each compound had to both meet a minimum score of 75% for the compound to be included in the listing.

Additional acceptance criteria were also applied following spectral matching and selection. A minimum frequency of at least three occurrences was required in at least one of the sample types (recycling plant, indoor field, outdoor field) before a tentative chemical was included in the compilation. Also, average area counts for a tentatively-identified chemical had to be more than three times greater within at least one of the three sample types (recycling plant, indoor field, outdoor field) than the average area counts in the blank or chamber background samples.

The full tables for the five sets of non-targeted highly tentative chemical identification results are provided in Appendix R. Summaries of the frequencies of chemicals tentatively identified in recycling plant, outdoor field, and indoor field samples are shown in Table 4-98. In some cases, the same chemical identity was reported multiple time in the same sample. This was due in part because chemical isomers may generate the same or very similar spectra that are matched to a single library reference spectrum. For example, a C19 saturated alkane can have numerous branched isomers in addition to its unbranched form. In many cases, it was observed that the same chemical match was reported for spectra produced at different chromatographic retention times, making the presence of isomers more likely. In some types of mass spectral analyses, some chemicals may produce very similar mass spectra that are incorrectly matched to library spectra. The high-resolution LC/TOFMS avoids this problem by matching to exact chemical formulas but is limited in further chemical elucidation because it lacks chemical fragmentation spectra. And some repeated chemical matches may simply be the result of incorrect matching identifications.

The results in Table 4-98 show that several hundred organic chemicals may be associated with tire crumb rubber and tire crumb rubber infill. Many, but not all, target chemicals were observed in the non-targeted analyses. Several of the chemicals tentatively identified were included on the suspect screening analysis list but were not observed in the LC/TOFMS suspect screening analysis. An example of this is N-1,3-(dimethyl-butyl)-N'-phenyl-p-phenylenediamine (6PPD), an antiozonant/antioxidant compound, which was observed in non-targeted GC/MS analysis in recycling plant and synthetic turf field samples with relatively high response area counts.

However, many of the chemicals that were tentatively identified were not target analytes or suspect screening analytes in this study. Some of these chemicals may have been original tire chemical ingredients, or they may be transformation products or degradates of those ingredients. Some of the chemicals may have been absorbed by the tire material over the life course of the tire. Some chemicals found in ‘new’ tire crumb rubber from recycling plants were not observed in samples from the fields. And in some cases, the chemicals were observed in field samples, but at lower frequencies or lower average intensities, which may reflect patterns seen for the target organic analytes in this study (where many organic chemicals had lower levels in field infill as compared to recycling plant tire crumb rubber and higher levels in indoor fields as compared to outdoor fields). The results also show that there were chemicals present in tire crumb rubber infill from synthetic turf fields that were not observed in the ‘new’ tire crumb rubber from recycling plants. This suggests that some chemicals in synthetic turf field infill have sources other than the recycled tire material.

It is important to note that many other chromatographic and mass spectral features observed in these analyses did not match to library reference spectra and were not included in the compilation of highly-tentative chemical IDs in this report. This was particularly true for the solvent extraction LC/TOFMS analysis. Therefore, the numbers of potential tire crumb associated chemicals in this report may be underestimated.

Emphasizing that these non-targeted analysis chemical identifications are highly tentative, it is not recommended that these results be used for cumulative exposure assessment, toxicity information collation, or risk assessment at this time. Additional work is needed to build upon these results to ascertain chemical identity confirmations and determination or estimations of relative amounts.

Table 4-98. Non-targeted Analysis Frequency Summaries for Highly Tentative Chemical Identifications[a,b,c]

Facility Type	GC/MS SVOC Solvent Extract Analysis – n	GC/MS SVOC Solvent Extract Analysis – *Average frequency of unique chemicals*	LC/TOFMS SVOC Solvent Extract Analysis – n	LC/TOFMS SVOC Solvent Extract Analysis – *Positive ionization mode frequency unique chemicals*	LC/TOFMS SVOC Solvent Extract Analysis – *Negative ionization mode frequency unique chemicals*	GC/TOFMS VOC 60 °C Emission Sample Analysis – n	GC/TOFMS VOC 60 °C Emission Sample Analysis – *Average frequency of unique chemicals identified*	GC/MS SVOC 60 °C Emission Sample Analysis – n	GC/MS SVOC 60 °C Emission Sample Analysis – *Average frequency of unique chemicals*	LC/TOFMS SVOC 60 °C Emission Sample Analysis – n	LC/TOFMS SVOC 60 °C Emission Sample Analysis – *Positive ionization mode frequency unique chemicals*	LC/TOFMS SVOC 60 °C Emission Sample Analysis – *Negative ionization mode frequency unique chemicals*
Recycling Plants	6	49	6	295	86	6	151	6	18	6	32	4
Indoor Synthetic Turf Fields	5	54	5	293	91	4	136	5	13	5	32	4
Outdoor Synthetic Turf Fields	4	53	5	228	101	5	115	5	20	5	26	4

[a] GC/MS = Gas chromatography/mass spectrometry; LC/TOFMS = Liquid chromatography/time-of-flight mass spectrometry; SVOC = Semivolatile organic compound; VOC = Volatile organic compound

[b] The highly tentative chemical identities for each sample type can be found in Appendix R.

[c] Many chemicals were identified more than once in a sample; this may be because multiple isomers were present or as a result of incorrect mass spectral matching

There are several limitations to these non-targeted analysis results. First, as previously noted, the chemical identities generated in this research must be considered highly tentative and considerable future research is needed to confirm identifications. Second, the methods did not attempt to identify chromatographic peaks with very low intensities. While it was important to try to identify the major components, some chemicals with potential toxicological significance at lower levels in tire rubber (e.g., dibenzopyrenes, see Sadiktsis et al., 2012) may have been missed. Third, tentative identities for mass spectra that did not meet specified matching scores were not reported, but that does not mean that a chemical was not present at that chromatographic retention time. It may mean that tire crumb rubber-associated chemical or chemical degradate spectra were not available for matching. Finally, chemicals present in the material may not have been present in the extract or emission sample because of the solvents or conditions used; other methods may have resulted in additional or different sets of chemicals. It is also important to note that different instruments and methods can produce somewhat different mass spectra for the same chemicals, making translation across methods and platforms somewhat difficult.

4.13 Bioaccessibility Testing for Metals

Bioaccessibility testing was performed for tire crumb rubber samples collected from recycling plants and tire crumb rubber infill collected from synthetic turf fields using three simulated biofluids. All bioaccessibility testing's metal measurement concentrations (i.e., μg of analyte/mL biofluid extract) were blank-subtracted before any calculations and analyses. If the blank-corrected concentrations were below zero, the results were set to zero. All biofluid extract analysis results were labeled with one of the three detection categories – 1) above the analytical limit of quantitation (LOQ), 2) below the LOQ and above the LOD, or 3) below the LOD. For metal results that were below the LOD, we used the reported metal concentrations in biofluid extracts and did not conduct imputation (i.e., replace the concentration below LOD with a value). Table 4-99 gives the percent detection rates (%) in the three artificial biofluid extracts of the tire crumb sample, stratified by the detection categories. Overall, artificial gastric fluid extracts contained the most detectable metals (13 metals with 50% or higher results over the LOD), followed by artificial sweat plus sebum extracts (7 metals with 50% or higher results over the LOD), while artificial saliva extracts contained the least detectable metals (3 metals with 50% or higher results over the LOD). The detection rate (i.e., result > LOD) for lead was 100%, 22%, and 12% in artificial gastric fluid, saliva, and sweat plus sebum, respectively.

Table 4-99. Detection Rates (%) of 19 Metals in Tire Crumb Sample Extracts (Stratified by Artificial Biofluid)[a]

Artificial Biofluid	Analyte	Method[b]	< LOD (%)	> LOD and < LOQ (%)	> LOQ (%)
Gastric fluid	Aluminum	ICP/AES	1	13	86
Gastric fluid	Antimony	ICP/MS	54	13	33
Gastric fluid	Arsenic	ICP/MS	61	35	4
Gastric fluid	Barium	ICP/MS	0	0	100
Gastric fluid	Beryllium	ICP/MS	67	28	5
Gastric fluid	Cadmium	ICP/MS	34	23	43
Gastric fluid	Chromium	ICP/MS	40	33	28
Gastric fluid	Cobalt	ICP/MS	0	0	100
Gastric fluid	Copper	ICP/MS	0	0	100
Gastric fluid	Iron	ICP/AES	0	8	92
Gastric fluid	Lead	ICP/MS	0	0	100

Table 4-99 Continued

Artificial Biofluid	Analyte	Method[b]	< LOD (%)	> LOD and < LOQ (%)	> LOQ (%)
Gastric fluid	Magnesium	ICP/AES	1	3	97
Gastric fluid	Manganese	ICP/MS	8	4	88
Gastric fluid	Mercury	CVAA	90	10	0
Gastric fluid	Molybdenum	ICP/MS	82	17	2
Gastric fluid	Nickel	ICP/MS	33	25	43
Gastric fluid	Selenium	ICP/MS	96	4	0
Gastric fluid	Strontium	ICP/MS	8	21	72
Gastric fluid	Tin	ICP/AES	98	2	0
Gastric fluid	Zinc	ICP/AES	0	0	100
Saliva	Aluminum	ICP/AES	87	8	5
Saliva	Antimony	ICP/MS	65	22	13
Saliva	Arsenic	ICP/MS	94	6	0
Saliva	Barium	ICP/MS	56	29	16
Saliva	Beryllium	ICP/MS	93	7	0
Saliva	Cadmium	ICP/MS	90	9	1
Saliva	Chromium	ICP/MS	93	5	3
Saliva	Cobalt	ICP/MS	11	24	65
Saliva	Copper	ICP/MS	62	5	33
Saliva	Iron	ICP/AES	88	10	2
Saliva	Lead	ICP/MS	78	13	9
Saliva	Magnesium	ICP/AES	20	28	52
Saliva	Manganese	ICP/MS	63	23	14
Saliva	Mercury	CVAA	99	0	1
Saliva	Molybdenum	ICP/MS	97	2	1
Saliva	Nickel	ICP/MS	92	6	3
Saliva	Selenium	ICP/MS	94	6	0
Saliva	Strontium	ICP/MS	74	22	4
Saliva	Tin	ICP/AES	100	0	0
Saliva	Zinc	ICP/AES	7	24	69
Sweat plus sebum	Aluminum	ICP/AES	70	13	17
Sweat plus sebum	Antimony	ICP/MS	78	14	8
Sweat plus sebum	Arsenic	ICP/MS	93	8	0
Sweat plus sebum	Barium	ICP/MS	20	5	75
Sweat plus sebum	Beryllium	ICP/MS	91	3	6
Sweat plus sebum	Cadmium	ICP/MS	78	14	8
Sweat plus sebum	Chromium	ICP/MS	68	23	9
Sweat plus sebum	Cobalt	ICP/MS	0	0	100
Sweat plus sebum	Copper	ICP/MS	26	16	58
Sweat plus sebum	Iron	ICP/AES	73	16	12
Sweat plus sebum	Lead	ICP/MS	88	4	8
Sweat plus sebum	Magnesium	ICP/AES	7	12	82

Table 4-99 Continued

Artificial Biofluid	Analyte	Method[b]	< LOD (%)	> LOD and < LOQ (%)	> LOQ (%)
Sweat plus sebum	Manganese	ICP/MS	33	18	49
Sweat plus sebum	Mercury	CVAA	98	2	0
Sweat plus sebum	Molybdenum	ICP/MS	96	3	2
Sweat plus sebum	Nickel	ICP/MS	59	19	22
Sweat plus sebum	Selenium	ICP/MS	80	20	0
Sweat plus sebum	Strontium	ICP/MS	36	42	23
Sweat plus sebum	Tin	ICP/AES	100	0	0
Sweat plus sebum	Zinc	ICP/AES	1	3	97

[a] LOD = Limit of detection; LOQ = Limit of quantitation

[b] ICP/MS = Inductively coupled plasma/mass spectrometry; ICP/AES = inductively coupled plasma-atomic emission spectrometry; CVAA = Cold vapor atomic absorption

Among the 82 tire crumb samples tested for bioaccessibility using each artificial biofluid, repeated bioaccessibility tests were performed for a subset of samples for each artificial biofluid. Thirty-four (34) samples had repeated bioaccessibility tests for artificial gastric fluid, 24 samples for saliva, and 34 samples for sweat plus sebum (see Appendix E for detailed information on repeated measurements). The arithmetic means of the repeated test results were used in the final percent bioaccessibility calculation. Table 4-100 presents the summary statistics of measured metal concentrations bioaccessible in the biofluid extracts (in mg analyte/kg tire crumb rubber, or mg/kg TCR).

Overall, artificial gastric fluid extracts contained the highest levels of metals, followed by artificial sweat plus sebum extracts; artificial saliva contained the lowest levels of metals. The concentrations of 19 metals in each artificial biofluid were highly variable, spanning several orders of magnitude. Zinc had the highest median (i.e., 50th percentile) concentrations in all three artificial biofluids. The three most abundant metals (based on median concentrations) were zinc, iron and magnesium for artificial gastric fluid extracts; zinc, magnesium and cobalt for artificial saliva; and zinc, magnesium and copper for artificial sweat plus sebum (Table 4-100).

Table 4-100. Summary Statistics of Measured Metal Levels in Artificial Biofluid Extracts of Tire Crumb Samples, Stratified by Artificial Biofluid[a]

Artificial Biofluid	Analyte	Mean (mg/kg TCR)	Standard Deviation (mg/kg TCR)	Minimum (mg/kg TCR)	25th Percentile (mg/kg TCR)	50th Percentile (mg/kg TCR)	75th Percentile (mg/kg TCR)	Maximum (mg/kg TCR)
Gastric fluid	Aluminum	6.2	5.4	0	2.0	5.0	8.8	24
Gastric fluid	Antimony	0.060	0.39	*0*	*0*	*0.0036*	0.034	3.6
Gastric fluid	Arsenic	0.0039	0.0054	*0*	*0*	*0*	0.0078	0.019
Gastric fluid	Barium	0.45	0.35	0.073	0.24	0.37	0.52	1.8
Gastric fluid	Beryllium	0.00048	0.00090	*0*	*0*	*0*	0.00074	0.0052
Gastric fluid	Cadmium	0.0043	0.0080	*0*	*0*	0.0023	0.0050	0.064
Gastric fluid	Chromium	0.067	0.10	*0*	*0.012*	0.045	0.092	0.71
Gastric fluid	Cobalt	0.37	0.23	0.072	0.20	0.31	0.52	1.0
Gastric fluid	Copper	3.1	3.3	0.25	1.0	2.02	3.6	20

Table 4-100 Continued

Artificial Biofluid	Analyte	Mean (mg/kg TCR)	Standard Deviation (mg/kg TCR)	Minimum (mg/kg TCR)	25th Percentile (mg/kg TCR)	50th Percentile (mg/kg TCR)	75th Percentile (mg/kg TCR)	Maximum (mg/kg TCR)
Gastric fluid	Iron	31	22	5.6	17	25.6	39	143
Gastric fluid	Lead	0.42	0.40	0.056	0.17	0.29	0.56	2.8
Gastric fluid	Magnesium	10	10	0.12	3.4	6.7	15	66
Gastric fluid	Manganese	0.82	0.62	0	0.40	0.67	1.1	3.2
Gastric fluid	Mercury	0.00024	0.00067	*0*	*0*	*0*	*0*	0.0026
Gastric fluid	Molybdenum	0.0041	0.0094	*0*	*0*	*0*	*0.0027*	0.048
Gastric fluid	Nickel	0.060	0.10	*0*	*0.015*	0.039	0.069	0.68
Gastric fluid	Selenium	0.00040	0.0016	*0*	*0*	*0*	*0*	0.011
Gastric fluid	Strontium	0.24	0.39	0	0.051	0.11	0.25	2.5
Gastric fluid	Tin	0.0032	0.023	*0*	*0*	*0*	*0*	0.19
Gastric fluid	Zinc	138	63	34	94	129	164	358
Saliva	Aluminum	0.059	0.32	*0*	*0*	*0*	*0*	2.9
Saliva	Antimony	0.0072	0.025	*0*	*0*	*0*	0.010	0.22
Saliva	Arsenic	0.00060	0.0021	*0*	*0*	*0*	*0*	0.012
Saliva	Barium	0.0081	0.017	*0*	*0*	*0.0010*	0.0088	0.12
Saliva	Beryllium	0.000091	0.00040	*0*	*0*	*0*	*0*	0.0032
Saliva	Cadmium	0.00023	0.00067	*0*	*0*	*0*	*0*	0.0031
Saliva	Chromium	0.0067	0.029	*0*	*0*	*0*	*0*	0.21
Saliva	Cobalt	0.048	0.055	0	0.0068	0.024	0.069	0.22
Saliva	Copper	0.057	0.11	*0*	*0*	*0*	0.084	0.55
Saliva	Iron	0.12	0.43	*0*	*0*	*0*	*0*	2.9
Saliva	Lead	0.0	0.0061	0	0	0	0.0017	0.048
Saliva	Magnesium	1.2	2.1	0	0.23	0.63	1.3	16
Saliva	Manganese	0.089	0.44	*0*	*0*	*0*	0.047	3.9
Saliva	Mercury	0.00011	0.0010	*0*	*0*	*0*	*0*	0.009
Saliva	Molybdenum	0.00052	0.0031	*0*	*0*	*0*	*0*	0.024
Saliva	Nickel	0.0047	0.016	*0*	*0*	*0*	*0*	0.084
Saliva	Selenium	0.00031	0.0012	*0*	*0*	*0*	*0*	0.0068
Saliva	Strontium	0.0098	0.028	*0*	*0*	*0*	0.0096	0.22
Saliva	Tin	0	0	*0*	*0*	*0*	*0*	*0*
Saliva	Zinc	1.1	1.4	0	0.44	0.72	1.3	10
Sweat plus sebum	Aluminum	0.20	0.84	*0*	*0*	*0*	0.20	7.4
Sweat plus sebum	Antimony	0.0028	0.0061	*0*	*0*	*0*	*0.0042*	0.037
Sweat plus sebum	Arsenic	0.0012	0.0026	*0*	*0*	*0*	*0*	0.0089
Sweat plus sebum	Barium	0.052	0.066	0	0.015	0.038	0.058	0.40
Sweat plus sebum	Beryllium	0.00044	0.0014	*0*	*0*	*0*	*0*	0.0084
Sweat plus sebum	Cadmium	0.00064	0.0013	*0*	*0*	*0*	*0.00088*	0.0068
Sweat plus sebum	Chromium	0.012	0.020	*0*	*0*	*0*	0.021	0.084

Table 4-100 Continued

Artificial Biofluid	Analyte	Mean (mg/kg TCR)	Standard Deviation (mg/kg TCR)	Minimum (mg/kg TCR)	25th Percentile (mg/kg TCR)	50th Percentile (mg/kg TCR)	75th Percentile (mg/kg TCR)	Maximum (mg/kg TCR)
Sweat plus sebum	Cobalt	0.15	0.10	0.017	0.065	0.12	0.23	0.50
Sweat plus sebum	Copper	0.17	0.16	*0*	*0.040*	0.14	0.24	0.78
Sweat plus sebum	Iron	0.31	0.58	*0*	*0*	*0*	0.33	2.7
Sweat plus sebum	Lead	0.0036	0.021	*0*	*0*	*0*	*0.00080*	0.19
Sweat plus sebum	Magnesium	2.2	2.7	0	0.74	1.2	2.9	18
Sweat plus sebum	Manganese	0.12	0.13	*0*	*0.015*	0.092	0.16	0.67
Sweat plus sebum	Mercury	0.00003	0.00023	*0*	*0*	*0*	*0*	0.002
Sweat plus sebum	Molybdenum	0.0016	0.012	*0*	*0*	*0*	*0*	0.10
Sweat plus sebum	Nickel	0.014	0.030	*0*	*0*	*0.0031*	0.016	0.22
Sweat plus sebum	Selenium	0.0010	0.0016	*0*	*0*	*0*	*0.0024*	0.0051
Sweat plus sebum	Strontium	0.061	0.11	*0*	*0.011*	0.023	0.056	0.68
Sweat plus sebum	Tin	0	0	*0*	*0*	*0*	*0*	*0*
Sweat plus sebum	Zinc	13	9.5	0.39	4.8	11	18	40

[a] Tire crumb samples (n=82); mg/kg TCR = milligrams analyte/kilogram tire crumb rubber

* Percentiles in italics are less than limit of detection

Among the 82 tire crumb samples tested for bioaccessibility, 27 were collected at recycling plants and 55 were collected from synthetic turf fields (including 40 composite samples and 15 individual location samples). Table 4-101 presents the mean and standard deviation of measured metal concentrations in the biofluid extracts, stratified by recycling plant vs. synthetic turf field samples. We sought to compare the metal concentrations in biofluid extracts between the tire crumb samples collected at recycling plants and synthetic turf fields for analytes/biofluid extracts with 50% or higher detection rate. Because the assumptions of parametric tests were not met (such as normality), we chose to use the rank-based nonparametric Kruskal Wallis test, in which the null hypothesis was that the distributions were identical, and the alternative was that they differ (with one of the distributions yielding larger observations than the other). The p-values from the Kruskal Wallis test are given in Table 4-101. Among the 13 metals with 50% or higher detection rate in artificial gastric fluid extracts, aluminum ($p < 0.001$), cobalt ($p = 0.02$), lead ($p < 0.001$) and nickel ($p = 0.02$) were present at statistically significant higher levels in the extracts of synthetic turf field samples than those of recycling plant samples, while copper ($p < 0.001$) and iron ($p < 0.001$) were lower in field sample extracts than recycling plant sample extracts. The rest of the detectable metals were all present at non-statistically significant higher levels in field sample extracts than in recycling plant sample extracts ($p = 0.06 – 0.98$). In artificial saliva extracts, none of the three metals with 50% or higher detection rate had statistically significant differences between the plant and field samples ($p = 0.15 – 0.48$). In artificial sweat plus sebum extracts, magnesium ($p < 0.001$) and strontium ($p < 0.001$) were present at statistically significant higher levels in the extracts of synthetic turf field samples than those of the recycling plant samples.

Table 4-101. Measured Metal Levels in Artificial Biofluid Extracts of Tire Crumb Samples, Stratified by Recycling Plant vs. Synthetic Turf Field Samples[a]

Artificial Biofluid	Analyte	Recycling Plant – Mean (mg/kg TCR)	Recycling Plant – Standard Deviation (mg/kg TCR)	Synthetic Turf Field – Mean (mg/kg TCR)	Synthetic Turf Field – Standard Deviation (mg/kg TCR)	Kruskal Wallis p-value[b,c]
Gastric fluid	Aluminum	1.8	0.6	8.4	5.3	*< 0.001*
Gastric fluid	Antimony	0.031	0.025	0.074	0.48	N/A
Gastric fluid	Arsenic	0.0037	0.0048	0.0039	0.0056	N/A
Gastric fluid	Barium	0.35	0.12	0.5	0.41	0.38
Gastric fluid	Beryllium	0.00025	0.00076	0.00059	0.00095	N/A
Gastric fluid	Cadmium	0.0029	0.0016	0.0051	0.0096	0.38
Gastric fluid	Chromium	0.057	0.064	0.071	0.12	0.98
Gastric fluid	Cobalt	0.29	0.18	0.41	0.24	*0.02*
Gastric fluid	Copper	6.0	4.3	1.7	1.2	*< 0.001*
Gastric fluid	Iron	48	27	23	13	*< 0.001*
Gastric fluid	Lead	0.18	0.12	0.54	0.43	*< 0.001*
Gastric fluid	Magnesium	6.1	3.7	12	12	0.06
Gastric fluid	Manganese	0.79	0.50	0.83	0.67	0.75
Gastric fluid	Mercury	0.00056	0.00092	0.00008	0.00043	N/A
Gastric fluid	Molybdenum	0.0076	0.0096	0.0024	0.009	N/A
Gastric fluid	Nickel	0.032	0.028	0.074	0.12	*0.02*
Gastric fluid	Selenium	0.00041	0.0022	0.0004	0.0014	N/A
Gastric fluid	Strontium	0.098	0.059	0.31	0.46	0.08
Gastric fluid	Tin	0.0071	0.037	0.0013	0.0097	N/A
Gastric fluid	Zinc	120	41	150	70	0.07
Saliva	Aluminum	0.034	0.065	0.071	0.39	N/A
Saliva	Antimony	0.0044	0.0059	0.0086	0.03	N/A
Saliva	Arsenic	0	0	0.00089	0.0025	N/A
Saliva	Barium	0.0034	0.0077	0.01	0.02	N/A
Saliva	Beryllium	0.00004	0.00013	0.00012	0.00048	N/A
Saliva	Cadmium	0.00005	0.0001	0.00032	0.0008	N/A
Saliva	Chromium	0.003	0.0092	0.0085	0.034	N/A
Saliva	Cobalt	0.036	0.044	0.055	0.059	0.32
Saliva	Copper	0.02	0.091	0.075	0.11	N/A
Saliva	Iron	0.18	0.35	0.095	0.46	N/A
Saliva	Lead	0.002	0.0093	0.0017	0.0037	N/A
Saliva	Magnesium	0.59	0.49	1.5	2.5	0.15
Saliva	Manganese	0.036	0.04	0.12	0.54	N/A
Saliva	Mercury	0	0	0.00016	0.0012	N/A
Saliva	Molybdenum	0	0	0.00077	0.0037	N/A

Table 4-101 Continued

Artificial Biofluid	Analyte	Recycling Plant – Mean (mg/kg TCR)	Recycling Plant – Standard Deviation (mg/kg TCR)	Synthetic Turf Field – Mean (mg/kg TCR)	Synthetic Turf Field – Standard Deviation (mg/kg TCR)	Kruskal Wallis p-value[b,c]
Saliva	Nickel	0.0012	0.006	0.0064	0.019	N/A
Saliva	Selenium	0	0	0.00046	0.0015	N/A
Saliva	Strontium	0.0057	0.0085	0.012	0.033	N/A
Saliva	Tin	0	0	0	0	N/A
Saliva	Zinc	1.1	1.9	1.1	1	0.48
Sweat plus sebum	Aluminum	0.14	0.13	0.23	1	N/A
Sweat plus sebum	Antimony	0.0045	0.0054	0.002	0.0063	N/A
Sweat plus sebum	Arsenic	0.00019	0.00096	0.0018	0.003	N/A
Sweat plus sebum	Barium	0.046	0.033	0.055	0.077	0.46
Sweat plus sebum	Beryllium	0.0013	0.0022	0.00003	0.0002	N/A
Sweat plus sebum	Cadmium	0.0012	0.0019	0.00038	0.00076	N/A
Sweat plus sebum	Chromium	0.01	0.02	0.013	0.02	N/A
Sweat plus sebum	Cobalt	0.13	0.1	0.15	0.11	0.42
Sweat plus sebum	Copper	0.16	0.15	0.17	0.17	0.78
Sweat plus sebum	Iron	0.62	0.75	0.15	0.41	N/A
Sweat plus sebum	Lead	0.00062	0.0014	0.0051	0.026	N/A
Sweat plus sebum	Magnesium	1.1	0.55	2.7	3.1	*< 0.001*
Sweat plus sebum	Manganese	0.14	0.14	0.11	0.12	N/A
Sweat plus sebum	Mercury	0.00007	0.00038	0.00001	0.0001	N/A
Sweat plus sebum	Molybdenum	0.0039	0.02	0.00056	0.0022	N/A
Sweat plus sebum	Nickel	0.007	0.0098	0.018	0.036	N/A
Sweat plus sebum	Selenium	0	0	0.0015	0.0017	N/A
Sweat plus sebum	Strontium	0.016	0.014	0.082	0.12	*< 0.001*
Sweat plus sebum	Tin	0	0	0	0	N/A
Sweat plus sebum	Zinc	13	8.8	12	9.9	0.66

[a] Recycling Plant (n=27); Synthetic Turf Field (n=55); mg/kg TCR = milligrams analyte/kilogram tire crumb rubber

[b] p-values for Kruskal Wallis test between the recycling plant samples and synthetic turf field samples

[c] N/A = not available for analytes/artificial fluids with less than 50% detection rate

Percent *in vitro* bioaccessibility was calculated by dividing the blank-subtracted metal concentration in the biofluid extract with the corresponding metal's blank-subtracted concentration measured by ICP/MS in that tire crumb sample. Mercury was not measured by ICP/MS in the tire crumb samples; therefore, percent bioaccessibility could not be calculated for mercury. Percent *in vitro* bioaccessibility was calculated only when the blank-subtracted concentration in tire crumb constituent (i.e., denominator of the % bioaccessibility calculation) was above 3 times the corresponding reporting limit. Two calculated % *in vitro* bioaccessibility values were above 100% (i.e., antimony in one synthetic turf field sample and molybdenum in another). In both cases, the analyte concentrations in tire crumb constituent were very low – at 10th percentile and less than 5th percentile for these two samples/analytes, respectively. Additionally, given the large heterogeneity of many metals in tire crumb samples even within the same sample containers (see section 4.9.1 in this report; U.S. EPA, 2009; Pavilonis et al., 2014), the calculated above-100% bioaccessibility values in these two samples/analytes were most likely due to the low concentrations in tire crumb samples and the heterogeneity of the tire crumb samples, and therefore, were excluded in subsequent data analyses.

Table 4-102 gives the summary descriptive statistics of the percent *in vitro* bioaccessibility results for metals in the 82 tire crumb samples in three artificial biofluids (i.e., the portion of the analyte in tire crumb samples that were extractable, or in other words, bioaccessible, in the artificial biofluids). Overall, metals in the 82 tire crumb samples had the highest percent *in vitro* bioaccessibility in artificial gastric fluid (median 0 – 12%) for the 19 metals, followed by artificial sweat plus sebum (median 0 – 1.5%); the metals *in vitro* bioaccessibility values in artificial saliva were predominantly near 0%. The same pattern was also observed on mean percent bioaccessibility values that averaged 3.4% in gastric fluid, 0.7% in sweat plus sebum, and 0.3% in saliva among all metals. In artificial gastric fluid, four metals' median percent *in vitro* bioaccessibility values were above 5%, including manganese (12%), copper (7.3%), iron (6.4%), and barium (6.0%). In artificial sweat plus sebum, three metals' median percent bioaccessibility values were above 0.5%, including manganese (1.5%), strontium (0.9%), and barium (0.6%). For lead, the median *in vitro* bioaccessibility was 1.9% (range: 0.2 – 13.5%), 0% (range: 0 – 0.5%), and 0% (0 – 1.9%) in artificial gastric fluid, saliva, and sweat plus sebum, respectively.

Table 4-103 presents the *in vitro* percent bioaccessibility results (mean and standard deviation) in three artificial biofluids, stratified by recycling plant vs. synthetic turf field samples. The nonparametric Kruskal Wallis test was used to compare the percent *in vitro* bioaccessibility between the tire crumb samples collected at recycling plants and synthetic turf fields for analytes/biofluid extracts with 50% or more detection rate. The *p*-values from the Kruskal Wallis test are given in Table 4-103. Among the 13 metals with 50% or higher detection rates in artificial gastric fluid extracts, 7 metals (aluminum, cadmium, cobalt, lead, magnesium, nickel and zinc) had statistically significant higher percent bioaccessibility in synthetic turf field samples than recycling plant samples, while copper and iron had lower bioaccessibility in field samples than recycling plant samples ($p < 0.001$). For artificial sweat plus sebum and saliva, the percent *in vitro* bioaccessibility did not have statistically significant differences between the plant and field samples for all detectable metals, except for strontium in artificial sweat plus sebum, which exhibited higher *in vitro* bioaccessibility for synthetic turf field samples than plant samples ($p = 0.001$).

Several previous studies (Pronk et al., 2018; RIVM, 2017; U.S. EPA, 2009; Pavilonis et al., 2014; Zhang et al., 2008) have investigated *in vitro* bioaccessibility of metals in tire crumb samples and reported either metal concentrations in artificial biofluid extracts (Tables 4-104 and 4-105), or percent *in vitro* bioaccessibility (Table 4-106) in artificial biofluids, or both. Most previous studies had a much smaller sample size and fewer number of metal analytes, which makes this study the largest study that we know of on *in vitro* bioaccessibility testing of metals in tire crumb samples.

It should be noted that the bioaccessibility testing (numerator for percent bioaccessibility calculation) used the tire crumb samples as is without drying, while the constituent concentrations (denominator) were based on moisture-free contents. As described in Section 4.5.1, the median (with range) moisture levels in the field samples (n=40) and recycling facilities (n=9) are 0.81% (0.40%-6.22%) and 0.87% (0.52%-0.99%), respectively. Therefore, the moisture contents lead to a slight overestimate (about a factor of 0.01) of the calculated percent bioaccessibility results.

Table 4-102. Summary Descriptive Statistics of Calculated *In Vitro* Percent Bioaccessibility Results for Metals in Tire Crumb Samples that are Bioaccessible in Three Artificial Biofluids

Artificial Biofluid	Analyte	N[a]	*In Vitro* % Bioaccessibility Mean (%)	*In Vitro* % Bioaccessibility Standard Deviation (%)	*In Vitro* % Bioaccessibility Minimum (%)	*In Vitro* % Bioaccessibility 25th Percentile (%)	*In Vitro* % Bioaccessibility Median, 50th Percentile (%)	*In Vitro* % Bioaccessibility 75th Percentile (%)	*In Vitro* % Bioaccessibility Maximum (%)
Gastric fluid	Aluminum	82	0.6	0.5	0.0	0.2	0.6	0.8	2.6
Gastric fluid	Antimony	81	1.4	1.8	0.0	0.0	0.4	2.8	7.6
Gastric fluid	Arsenic	82	1.1	1.7	0.0	0.0	0.0	2.4	8.4
Gastric fluid	Barium	82	6.9	4.8	0.2	4.5	6.0	9.1	29.7
Gastric fluid	Beryllium	55	3.1	6.7	0.0	0.0	0.0	4.6	38.3
Gastric fluid	Cadmium	82	0.5	0.6	0.0	0.0	0.4	0.7	3.4
Gastric fluid	Chromium	76	4.1	7.3	0.0	0.8	2.6	5.0	55.1
Gastric fluid	Cobalt	82	0.3	0.2	0.0	0.1	0.2	0.3	1.2
Gastric fluid	Copper	82	8.5	4.9	1.6	4.4	7.3	11.4	20.5
Gastric fluid	Iron	82	6.9	4.0	0.1	3.4	6.4	9.5	17.0
Gastric fluid	Lead	82	2.8	2.3	0.2	1.3	1.9	3.3	13.5
Gastric fluid	Magnesium	82	3.5	3.2	0.1	1.3	2.2	4.6	20.4
Gastric fluid	Manganese	82	12.9	8.1	0.0	8.7	12.0	15.8	35.0
Gastric fluid	Molybdenum	81	1.7	3.9	0.0	0.0	0.0	1.0	24.1
Gastric fluid	Nickel	82	2.5	4.5	0.0	0.3	1.4	2.8	32.6
Gastric fluid	Selenium	9	0.6	1.8	0.0	0.0	0.0	0.0	5.4
Gastric fluid	Strontium	82	6.5	7.6	0.0	1.8	3.6	8.7	42.4
Gastric fluid	Tin	80	0.2	1.1	0.0	0.0	0.0	0.0	7.3
Gastric fluid	Zinc	82	0.9	0.5	0.2	0.6	0.8	1.1	2.5
Saliva	Aluminum	82	0.0	0.0	0.0	0.0	0.0	0.0	0.3
Saliva	Antimony	82	0.7	1.8	0.0	0.0	0.0	0.7	14.9
Saliva	Arsenic	82	0.2	0.7	0.0	0.0	0.0	0.0	4.5
Saliva	Barium	82	0.1	0.2	0.0	0.0	0.0	0.1	1.4
Saliva	Beryllium	55	0.5	2.3	0.0	0.0	0.0	0.0	15.9
Saliva	Cadmium	82	0.0	0.1	0.0	0.0	0.0	0.0	0.5
Saliva	Chromium	76	0.3	1.1	0.0	0.0	0.0	0.0	8.7
Saliva	Cobalt	82	0.0	0.1	0.0	0.0	0.0	0.0	0.2
Saliva	Copper	82	0.2	0.6	0.0	0.0	0.0	0.3	4.3
Saliva	Iron	82	0.0	0.1	0.0	0.0	0.0	0.0	0.6

Table 4-102 Continued

Artificial Biofluid	Analyte	N[a]	In Vitro % Bioaccessibility Mean (%)	In Vitro % Bioaccessibility Standard Deviation (%)	In Vitro % Bioaccessibility Minimum (%)	In Vitro % Bioaccessibility 25th Percentile (%)	In Vitro % Bioaccessibility Median, 50th Percentile (%)	In Vitro % Bioaccessibility 75th Percentile (%)	In Vitro % Bioaccessibility Maximum (%)
Saliva	Lead	82	0.0	0.1	0.0	0.0	0.0	0.0	0.5
Saliva	Magnesium	82	0.4	0.7	0.0	0.1	0.2	0.5	5.0
Saliva	Manganese	82	1.1	4.1	0.0	0.0	0.0	0.8	32.2
Saliva	Molybdenum	82	0.8	6.4	0.0	0.0	0.0	0.0	57.6
Saliva	Nickel	82	0.2	0.8	0.0	0.0	0.0	0.0	5.0
Saliva	Selenium	9	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Saliva	Strontium	82	0.3	0.5	0.0	0.0	0.0	0.3	3.1
Saliva	Tin	80	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Saliva	Zinc	82	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Sweat plus sebum	Aluminum	82	0.0	0.1	0.0	0.0	0.0	0.0	0.3
Sweat plus sebum	Antimony	82	0.2	0.6	0.0	0.0	0.0	0.3	3.9
Sweat plus sebum	Arsenic	82	0.4	0.9	0.0	0.0	0.0	0.0	4.4
Sweat plus sebum	Barium	82	0.8	0.9	0.0	0.2	0.6	1.0	4.8
Sweat plus sebum	Beryllium	55	4.7	12.2	0.0	0.0	0.0	0.0	61.7
Sweat plus sebum	Cadmium	82	0.1	0.2	0.0	0.0	0.0	0.1	1.6
Sweat plus sebum	Chromium	76	0.8	1.4	0.0	0.0	0.0	1.2	6.8
Sweat plus sebum	Cobalt	82	0.1	0.1	0.0	0.0	0.1	0.1	0.5
Sweat plus sebum	Copper	82	0.6	0.6	0.0	0.1	0.4	0.9	3.2
Sweat plus sebum	Iron	82	0.1	0.1	0.0	0.0	0.0	0.1	0.9
Sweat plus sebum	Lead	82	0.0	0.2	0.0	0.0	0.0	0.0	1.9
Sweat plus sebum	Magnesium	82	0.8	1.0	0.0	0.2	0.4	1.0	5.5
Sweat plus sebum	Manganese	82	1.9	1.8	0.0	0.3	1.5	3.0	7.6
Sweat plus sebum	Molybdenum	82	1.1	6.5	0.0	0.0	0.0	0.0	53.9
Sweat plus sebum	Nickel	82	0.5	1.0	0.0	0.0	0.2	0.7	6.5
Sweat plus sebum	Selenium	9	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sweat plus sebum	Strontium	82	1.7	2.3	0.0	0.4	0.9	1.9	9.6
Sweat plus sebum	Tin	80	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sweat plus sebum	Zinc	82	0.1	0.1	0.0	0.0	0.1	0.1	0.3

[a] *In vitro* percent bioaccessibility was not calculated when analyte concentration in ICP/MS tire crumb constituent analysis (i.e., denominator of the % bioaccessibility calculation) was less than 3 times of the corresponding reporting limit.

Table 4-103. *In Vitro* Percent Bioaccessibility Results in Three Artificial Biofluids, Stratified by Recycling Plant vs. Synthetic Turf Field Samples

Artificial Biofluid	Analyte	Recycling Plants *In Vitro* % Bioaccessibility – N[a]	Recycling Plants *In Vitro* % Bioaccessibility – Mean±Standard Deviation (%)	Recycling Plants *In Vitro* % Bioaccessibility – Median (Min-Max) (%)	Synthetic Turf Fields *In Vitro* % Bioaccessibility – N[a]	Synthetic Turf Fields *In Vitro* % Bioaccessibility – Mean±Standard Deviation (%)	Synthetic Turf Fields *In Vitro* % Bioaccessibility – Median (Min-Max) (%)	p-value[b,c]
Gastric fluid	Aluminum	27	0.2±0.2	0.2 (0-0.8)	55	0.8±0.5	0.7 (0.1-2.6)	*< 0.0001*
Gastric fluid	Antimony	27	2.4±1.8	2.7 (0-6.1)	54	0.9±1.6	0 (0-7.6)	N/A
Gastric fluid	Arsenic	27	1.2±1.6	0 (0-5.3)	55	1.1±1.7	0 (0-8.4)	N/A
Gastric fluid	Barium	27	6.5±3.2	5.8 (0.9-13.1)	55	7.2±5.4	6.1 (0.2-29.8)	0.92
Gastric fluid	Beryllium	24	1.4±4	0 (0-16.3)	31	4.4±8	0 (0-38.3)	N/A
Gastric fluid	Cadmium	27	0.5±0.3	0.6 (0.1-1.6)	55	0.5±0.7	0.3 (0-3.5)	*0.049*
Gastric fluid	Chromium	27	3.1±2.5	2.5 (0-8.4)	49	4.6±9	3 (0-55.1)	0.99
Gastric fluid	Cobalt	27	0.2±0.1	0.2 (0.1-0.3)	55	0.3±0.3	0.3 (0-1.2)	*0.001*
Gastric fluid	Copper	27	13.7±4.1	13.2 (5.8-20.5)	55	5.9±2.8	5.6 (1.6-15.2)	*< 0.0001*
Gastric fluid	Iron	27	9.8±3	9.6 (4.9-17)	55	5.5±3.6	5.3 (0.1-14.3)	*< 0.0001*
Gastric fluid	Lead	27	1.8±2.4	1.3 (0.3-13.5)	55	3.2±2.1	2.9 (0.2-9.6)	*< 0.0001*
Gastric fluid	Magnesium	27	2.2±1.4	1.8 (1-7.5)	55	4.1±3.7	3.8 (0.1-20.5)	*0.036*
Gastric fluid	Manganese	27	13.6±5.4	12.1 (3.5-27.1)	55	12.5±9.1	11.3 (0-35)	0.32
Gastric fluid	Molybdenum	27	3.2±4.2	0 (0-16.7)	54	0.9±3.5	0 (0-24.1)	N/A
Gastric fluid	Nickel	27	1.2±1.1	0.9 (0-3.5)	55	3.1±5.4	1.8 (0-32.6)	*0.016*
Gastric fluid	Selenium	6	0.9±2.2	0 (0-5.5)	3	0±0.1	0 (0-0.1)	N/A
Gastric fluid	Strontium	27	3.3±1.9	3 (0-8.7)	55	8.1±8.7	6.3 (0-42.4)	0.055
Gastric fluid	Tin	27	0.3±1.4	0 (0-7.3)	53	0.1±0.9	0 (0-6.8)	N/A
Gastric fluid	Zinc	27	0.7±0.2	0.7 (0.3-1.1)	55	1±0.6	0.9 (0.2-2.5)	*0.02*
Saliva	Aluminum	27	0±0	0 (0-0)	55	0±0.1	0 (0-0.3)	N/A
Saliva	Antimony	27	0.3±0.5	0 (0-2)	55	0.8±2.2	0 (0-14.9)	N/A
Saliva	Arsenic	27	0±0	0 (0-0)	55	0.3±0.9	0 (0-4.5)	N/A
Saliva	Barium	27	0.1±0.2	0 (0-1)	55	0.2±0.3	0.1 (0-1.4)	N/A
Saliva	Beryllium	24	0.3±1.1	0 (0-5.1)	31	0.7±2.9	0 (0-15.9)	N/A
Saliva	Cadmium	27	0±0	0 (0-0.1)	55	0±0.1	0 (0-0.5)	N/A
Saliva	Chromium	27	0.2±0.5	0 (0-2.2)	49	0.3±1.3	0 (0-8.7)	N/A

Table 4-103 Continued

Artificial Biofluid	Analyte	Recycling Plants In Vitro % Bioaccessibility – N[a]	Recycling Plants In Vitro % Bioaccessibility – Mean±Standard Deviation (%)	Recycling Plants In Vitro % Bioaccessibility – Median (Min-Max) (%)	Synthetic Turf Fields In Vitro % Bioaccessibility – N[a]	Synthetic Turf Fields In Vitro % Bioaccessibility – Mean±Standard Deviation (%)	Synthetic Turf Fields In Vitro % Bioaccessibility – Median (Min-Max) (%)	p-value[b,c]
Saliva	Cobalt	27	0±0	0 (0-0.1)	55	0±0.1	0 (0-0.2)	0.11
Saliva	Copper	27	0±0.1	0 (0-0.6)	55	0.4±0.7	0.1 (0-4.3)	N/A
Saliva	Iron	27	0.1±0.1	0 (0-0.6)	55	0±0.1	0 (0-0.6)	N/A
Saliva	Lead	27	0±0.1	0 (0-0.5)	55	0±0	0 (0-0.1)	N/A
Saliva	Magnesium	27	0.2±0.2	0.2 (0-0.7)	55	0.5±0.8	0.3 (0-5)	0.18
Saliva	Manganese	27	0.6±0.5	0.7 (0-1.9)	55	1.4±5	0 (0-32.2)	N/A
Saliva	Molybdenum	27	0±0	0 (0-0)	55	1.2±7.8	0 (0-57.6)	N/A
Saliva	Nickel	27	0.1±0.3	0 (0-1.4)	55	0.3±0.9	0 (0-5)	N/A
Saliva	Selenium	6	0±0	0 (0-0)	3	0±0	0 (0-0)	N/A
Saliva	Strontium	27	0.2±0.3	0 (0-0.8)	55	0.3±0.6	0 (0-3.1)	N/A
Saliva	Tin	27	0±0	0 (0-0)	53	0±0	0 (0-0)	N/A
Saliva	Zinc	27	0±0	0 (0-0.1)	55	0±0	0 (0-0)	0.30
Sweat plus sebum	Aluminum	27	0±0	0 (0-0.1)	55	0±0.1	0 (0-0.3)	N/A
Sweat plus sebum	Antimony	27	0.3±0.4	0.2 (0-1.4)	55	0.2±0.6	0 (0-3.9)	N/A
Sweat plus sebum	Arsenic	27	0.1±0.5	0 (0-2.4)	55	0.5±1	0 (0-4.4)	N/A
Sweat plus sebum	Barium	27	0.9±0.8	0.8 (0-4.4)	55	0.8±1	0.6 (0-4.8)	0.21
Sweat plus sebum	Beryllium	24	10.5±16.8	0 (0-61.7)	31	0.2±1.3	0 (0-7.1)	N/A
Sweat plus sebum	Cadmium	27	0.2±0.4	0 (0-1.6)	55	0±0.1	0 (0-0.4)	N/A
Sweat plus sebum	Chromium	27	0.7±1.4	0 (0-6.8)	49	0.9±1.3	0 (0-4.7)	N/A
Sweat plus sebum	Cobalt	27	0.1±0	0.1 (0-0.2)	55	0.1±0.1	0.1 (0-0.5)	0.08
Sweat plus sebum	Copper	27	0.4±0.4	0.2 (0-1.7)	55	0.7±0.7	0.6 (0-3.2)	0.09
Sweat plus sebum	Iron	27	0.1±0.2	0.1 (0-0.9)	55	0±0.1	0 (0-0.6)	N/A
Sweat plus sebum	Lead	27	0±0	0 (0-0.1)	55	0±0.3	0 (0-1.9)	N/A
Sweat plus sebum	Magnesium	27	0.4±0.2	0.4 (0.1-1)	55	1±1.1	0.5 (0-5.6)	0.11
Sweat plus sebum	Manganese	27	2.2±1.6	2 (0.3-5.7)	55	1.7±1.8	1.4 (0-7.6)	0.08
Sweat plus sebum	Molybdenum	27	2±10.4	0 (0-53.9)	55	0.7±3.3	0 (0-22.1)	N/A

Table 4-103 Continued

Artificial Biofluid	Analyte	Recycling Plants In Vitro % Bioaccessibility – N[a]	Recycling Plants In Vitro % Bioaccessibility – Mean±Standard Deviation (%)	Recycling Plants In Vitro % Bioaccessibility – Median (Min-Max) (%)	Synthetic Turf Fields In Vitro % Bioaccessibility – N[a]	Synthetic Turf Fields In Vitro % Bioaccessibility – Mean±Standard Deviation (%)	Synthetic Turf Fields In Vitro % Bioaccessibility – Median (Min-Max) (%)	P-value[b,c]
Sweat plus sebum	Nickel	27	0.3±0.4	0 (0-1.3)	55	0.7±1.2	0.2 (0-6.5)	N/A
Sweat plus sebum	Selenium	6	0±0	0 (0-0)	3	0±0	0 (0-0)	N/A
Sweat plus sebum	Strontium	27	0.6±0.5	0.5 (0-1.6)	55	2.3±2.7	1.1 (0-9.6)	*0.001*
Sweat plus sebum	Tin	27	0±0	0 (0-0)	53	0±0	0 (0-0)	N/A
Sweat plus sebum	Zinc	27	0.1±0.1	0.1 (0-0.3)	55	0.1±0.1	0.1 (0-0.3)	0.74

[a] *In vitro* percent bioaccessibility was not calculated when analyte concentration in tire crumb constituent analysis (i.e., denominator of the % bioaccessibility calculation) was less than 3 times the corresponding reporting limit.

[b] p-values for Kruskal Wallis test between the recycling plant samples and synthetic turf field samples

[c] N/A = Not available for analytes/artificial fluids with less than 50% detection rate

Table 4-104. Reported *In Vitro* Bioaccessible Metal Concentrations in Artificial Biofluid Extracts for Tire Crumb Samples Collected on Synthetic Turf Fields[a]

Artificial Biofluids[b,c]	Analyte	This study – N	This study – > Limit of Detection (%)	This study – *In Vitro* Bioaccessible Concentration Range (mg/kg TCR)	Literature – N	Literature – > Limit of Detection (%)	Literature – *In Vitro* Bioaccessible Concentration Range (mg/kg TCR)	Literature – Reference
Gastric fluid or Digestive fluids	Antimony	55	38	0 – 3.6	2	0	Max: < LOD	Pronk et al., 2018
Gastric fluid or Digestive fluids	Arsenic	55	29	0 – 0.019	2	0	Max: < LOD	Pronk et al., 2018
Gastric fluid or Digestive fluids	Arsenic	55	29	0 – 0.019	7	0	< 3.0	Pavilonis et al., 2014
Gastric fluid or Digestive fluids	Barium	55	100	0.073 – 1.8	2	N/A	Max: 6	Pronk et al., 2018
Gastric fluid or Digestive fluids	Beryllium	55	31	0 – 0.0052	7	0	< 0.40	Pavilonis et al., 2014
Gastric fluid or Digestive fluids	Cadmium	55	55	0 – 0.064	2	0	Max: < LOD	Pronk et al., 2018

Table 4-104 Continued

Artificial Biofluids[b,c]	Analyte	This study – N	This study – > Limit of Detection (%)	This study – In Vitro Bioaccessible Concentration Range (mg/kg TCR)	Literature – N	Literature – > Limit of Detection (%)	Literature – In Vitro Bioaccessible Concentration Range (mg/kg TCR)	Literature – Reference
Gastric fluid or Digestive fluids	Cadmium	55	55	0 – 0.064	7	100	2.5 – 11	Pavilonis et al., 2014
Gastric fluid or Digestive fluids	Cadmium	55	55	0 – 0.064	5	N/A	Max: < LOD	RIVM, 2017
Gastric fluid or Digestive fluids	Chromium	55	64	0 – 0.71	2	N/A	Max: 1	Pronk et al., 2018
Gastric fluid or Digestive fluids	Chromium	55	64	0 – 0.71	7	0	< 6.0	Pavilonis et al., 2014
Gastric fluid or Digestive fluids	Cobalt	55	100	0.072 – 1	2	N/A	Max: 2	Pronk et al., 2018
Gastric fluid or Digestive fluids	Cobalt	55	100	0.072 – 1	5	N/A	Max: 2	RIVM 2017
Gastric fluid or Digestive fluids	Copper	55	100	0.25 – 5.2	2	N/A	Max: 78	Pronk et al., 2018
Gastric fluid or Digestive fluids	Copper	55	100	0.25 – 5.2	7	0	< 20	Pavilonis et al., 2014
Gastric fluid or Digestive fluids	Lead	55	100	0.16 – 2.8	2	N/A	Max: 9	Pronk et al., 2018
Gastric fluid or Digestive fluids	Lead	55	100	0.16 – 2.8	7	100	2.5 – 260	Pavilonis et al., 2014
Gastric fluid or Digestive fluids	Lead	55	100	0.16 – 2.8	5	N/A	Max: 9	RIVM, 2017
Gastric fluid or Digestive fluids	Lead	55	100	0.16 – 2.8	26	100	10.7 – 61.2	U.S. EPA, 2009
Gastric fluid or Digestive fluids	Magnesium	55	98	0.12 – 66	7	0	< 900	Pavilonis et al., 2014
Gastric fluid or Digestive fluids	Molybdenum	55	7	0 – 0.048	2	0	Max: <LOD	Pronk et al., 2018
Gastric fluid or Digestive fluids	Nickel	55	64	0 – 0.68	2	N/A	Max: 2	Pronk et al., 2018

Table 4-104 Continued

Artificial Biofluids[b,c]	Analyte	This study – N	This study – > Limit of Detection (%)	This study – In Vitro Bioaccessible Concentration Range (mg/kg TCR)	Literature – N	Literature – > Limit of Detection (%)	Literature – In Vitro Bioaccessible Concentration Range (mg/kg TCR)	Literature – Reference
Gastric fluid or Digestive fluids	Selenium	55	4	0 – 0.0084	2	N/A	Max: 1	Pronk et al., 2018
Gastric fluid or Digestive fluids	Selenium	55	4	0 – 0.0084	7	0	< 2.0	Pavilonis et al., 2014
Gastric fluid or Digestive fluids	Tin	55	0	0 – <LOD	2	0	Max: <LOD	Pronk et al., 2018
Gastric fluid or Digestive fluids	Zinc	55	100	34 – 360	2	N/A	Max: 419	Pronk et al., 2018
Sweat or Sweat plus sebum[c]	Arsenic	55	13	0 – 0.0089	7	86	1.4 – 1.7	Pavilonis et al., 2014
Sweat or Sweat plus sebum	Beryllium	55	2	0 – 0.0015	7	0	< 0.20	Pavilonis et al., 2014
Sweat or Sweat plus sebum	Cadmium	55	16	0 – 0.0032	7	100	Max: 0.02	Pronk et al., 2018
Sweat or Sweat plus sebum	Cadmium	55	16	0 – 0.0032	7	0	< 0.20	Pavilonis et al., 2014
Sweat or Sweat plus sebum	Cadmium	55	16	0 – 0.0032	7	N/A	Max: 0.02	RIVM, 2017
Sweat or Sweat plus sebum	Chromium	55	36	0 – 0.069	7	86	2.1 – 2.7	Pavilonis et al., 2014
Sweat or Sweat plus sebum	Cobalt	55	100	0.025 – 0.35	7	N/A	Max: 0.48	RIVM, 2017
Sweat or Sweat plus sebum	Cobalt	55	100	0.025 – 0.35	7	100	Max: 0.48	Pronk et al., 2018
Sweat or Sweat plus sebum	Copper	55	73	0 – 0.78	7	86	1.8 – 2.2	Pavilonis et al., 2014
Sweat or Sweat plus sebum	Lead	55	18	0 – 0.19	7	86	< 0.20 – 1.5	Pavilonis et al., 2014
Sweat or Sweat plus sebum	Lead	55	18	0 – 0.19	7	100	Max: 0.07	Pronk et al., 2018

Table 4-104 Continued

Artificial Biofluids[b,c]	Analyte	This study – N	This study – > Limit of Detection (%)	This study – In Vitro Bioaccessible Concentration Range (mg/kg TCR)	Literature – N	Literature – > Limit of Detection (%)	Literature – In Vitro Bioaccessible Concentration Range (mg/kg TCR)	Literature – Reference
Sweat or Sweat plus sebum	Lead	55	18	0 – 0.19	7	N/A	Max: 0.07	RIVM, 2017
Sweat or Sweat plus sebum	Magnesium	55	95	0 – 18	7	0	< 10	Pavilonis et al., 2014
Sweat or Sweat plus sebum	Selenium	55	35	0 – 0.0051	7	0	< 0.70	Pavilonis et al., 2014

[a] mg/kg TCR = milligrams analyte/kilogram tire crumb rubber; LOD = Limit of detection; N/A= not available

[b] Pavilonis et al. 2014 tested bioaccessibility in artificial digestive fluids, which included a mixture of artificial saliva, gastric fluid, and intestinal fluid. Pronk et al. 2018 tested bioaccessibility in artificial gastric/intestinal juices.

[c] This study tested bioaccessibility in artificial sweat in tubes coated with artificial sebum, while all other studies assessed bioaccessibility in artificial sweat and did not use artificial sebum.

Table 4-105. Reported *In Vitro* Bioaccessible Metal Concentrations in Artificial Biofluid Extracts for New/Unused Tire Crumb Samples [a,b,c]

Artificial Biofluid	Analyte	This study – N	This study – > Limit of Detection (%)	This study – *In Vitro* Bioaccessible Concentration Range (mg/kg TCR)	Pavilonis et al. 2014 – N	Pavilonis et al. 2014 – > Limit of Detection (%)	Pavilonis et al. 2014 – *In Vitro* Bioaccessible Concentration Range (mg/kg TCR)
Gastric fluid or Digestive fluid	Arsenic	27	37	0 – 0.012	6	50	< 0.10 – 0.48
Gastric fluid or Digestive fluid	Beryllium	27	15	0 – 0.0036	6	0	< 0.40
Gastric fluid or Digestive fluid	Cadmium	27	100	0.00059 – 0.007	6	0	< 4.0
Gastric fluid or Digestive fluid	Chromium	27	74	0 – 0.3	6	0	< 7.0
Gastric fluid or Digestive fluid	Copper	27	100	1.1 – 20	6	67	< 20 – 32
Gastric fluid or Digestive fluid	Lead	27	100	0.056 – 0.72	6	100	5.3 – 66

Table 4-105 Continued

Artificial Biofluid	Analyte	This study – N	This study – > Limit of Detection (%)	This study – In Vitro Bioaccessible Concentration Range (mg/kg TCR)	Pavilonis et al. 2014 – N	Pavilonis et al. 2014 – > Limit of Detection (%)	Pavilonis et al. 2014 – In Vitro Bioaccessible Concentration Range (mg/kg TCR)
Gastric fluid or Digestive fluid	Magnesium	27	100	2.2 – 18	6	17	< 1000 – 4600
Gastric fluid or Digestive fluid	Selenium	27	4	0 – 0.011	6	17	< 0.90 – 1.5
Sweat or Sweat plus sebum	Arsenic	27	0	0 – 0.005	9	0	< 0.50
Sweat or Sweat plus sebum	Beryllium	27	37	0 – 0.0084	9	0	< 0.20
Sweat or Sweat plus sebum	Cadmium	27	41	0 – 0.0068	9	11	< 0.090 – 0.11
Sweat or Sweat plus sebum	Chromium	27	30	0 – 0.084	9	100	0.70 – 1.2
Sweat or Sweat plus sebum	Copper	27	85	0 – 0.59	9	44	< 0.080 – 0.54
Sweat or Sweat plus sebum	Lead	27	0	0 – 0.0068	9	100	0.090 – 1.6
Sweat or Sweat plus sebum	Magnesium	27	100	0.32 – 3.1	9	78	< 7.0 – 980
Sweat or Sweat plus sebum	Selenium	27	0	0 – 0	9	0	< 1.9

[a] mg/kg TCR = milligrams analyte/kilogram tire crumb rubber

[b] This study tested bioaccessibility in artificial gastric fluid and artificial sweat in tubes coated with artificial sebum for unused recycling plant tire crumb rubber samples.

[c] Pavilonis et al. 2014 tested bioaccessibility in artificial digestive fluids (which included a mixture of artificial saliva, gastric fluid, and intestinal fluid) and artificial sweat for new tire crumb rubber infill samples. These samples were unused recycled tire crumb rubber from an architectural firm specializing in synthetic turf installation.

Table 4-106. Reported *In Vitro* Percent Bioaccessibility of Metals in Artificial Biofluids, Stratified by Synthetic Turf Field Samples from this Study vs. the Literature [a]

Artificial Biofluids	Analyte	This study – N	This study – In Vitro % Bioaccessibility Range (%)	Literature – N	Literature – In Vitro % Bioaccessibility Range (%)	Reference
Gastric fluid	Arsenic	55	0 – 8.4	2	< LOD	Zhang et al., 2008
Gastric fluid	Cadmium	55	0 – 3.4	2	< LOD	Zhang et al., 2008
Gastric fluid	Chromium	49	0 – 55.1	2	0 – 23.3	Zhang et al., 2008
Gastric fluid	Lead	55	0.2 – 9.6	2	24.7 – 44.2	Zhang et al., 2008
Gastric fluid	Lead	55	0.2 – 9.6	26	1.6 – 10.1	U.S. EPA, 2009
Saliva	Arsenic	55	0 – 4.5	1	< LOD	Zhang et al., 2008
Saliva	Cadmium	55	0 – 0.5	1	< LOD	Zhang et al., 2008
Saliva	Chromium	49	0 – 8.7	1	0	Zhang et al., 2008
Saliva	Lead	55	0 – 0.13	1	0	Zhang et al., 2008

[a] LOD = Limit of detection

Results from this study are generally consistent with a previous scoping study conducted by the U.S. EPA (2009), as well as a recent report and publication by the Dutch National Institute for Public Health and the Environment (Pronk et al., 2018; RIVM, 2017). Lead's percent *in vitro* bioaccessibility in artificial gastric fluid was 0.2 – 9.6% (mean: 3.2±2.1%) among the 55 field samples in this study. In comparison, the scoping study (U.S. EPA, 2009) found that the *in vitro* bioaccessibility for lead in artificial gastric fluid ranged from 1.6 – 10.1% (mean: 4.7±2.3%) in 26 field samples. RIVM (2017) tested five or seven field tire crumb samples and reported the maximum bioaccessible concentrations (mg/kg TCR) for cadmium, cobalt and lead in artificial gastric fluid and sweat. Pronk et al. (2018) reported maximum bioaccessible concentrations from 2 samples in artificial gastric/intestinal juices (16 metals) and 7 samples in artificial sweat (3 metals). Our findings on maximum bioaccessible concentrations are consistent or lower than those reported by RIVM (Pronk et al., 2018; RIVM, 2017), except for maximum lead concentration in artificial sweat (this study: 0.19 mg/kg TCR vs. RIVM: 0.07 mg/kg TCR).

Pavilonis et al. (2014) reported *in vitro* bioaccessible concentrations of eight metals in artificial digestive biofluids (a mixture of artificial saliva, gastric and intestinal fluids), sweat, and lung biofluids in six or nine new infills (from an architectural firm) and seven field tire crumb samples. The LODs in the Pavilonis et al. (2014) study appear to be several orders of magnitude higher than this study. Further, lead and cadmium results in the digestive biofluid extracts were higher than those from acid digestion of tire crumb samples (i.e., percent *in vitro* bioaccessibility, if calculated, would be higher than 100%). These factors made it difficult to compare the results between the Pavilonis et al. (2014) study and this study.

Zhang et al. (2008) measured percent *in vitro* bioaccessibility of four metals in two field tire crumb samples – one sample was extracted by artificial saliva and gastric fluid and another was extracted by artificial gastric fluid and intestinal fluid. Arsenic and cadmium were not detected in any artificial fluid extracts of samples, while chromium was detected in the gastric fluid extract of one sample. Lead was detected in the artificial gastric fluid extract of both samples, with a calculated percent *in vitro* bioaccessibility of 24.7 and 44.2%, respectively.

It should be noted that *in vitro* bioaccessibility test results can be affected by many factors, including the formulation of various artificial biofluids, methods for dissolution of materials in artificial biofluids, analytical methods for measuring analytes in artificial biofluid extracts, analytical method for measuring analytes in tire crumb samples, and the heterogeneity of the tire crumb material. As a result, caution should be taken while interpreting and comparing bioaccessibility results across studies.

4.14 Microbiological Analysis

4.14.1 Targeted Microbial Analysis

Each of the 7 samples collected from the 40 synthetic turf fields were analyzed to determine concentrations of the 16S ribosomal ribonucleic acid (rRNA) gene, *S. aureus* SA0140 protein gene and the methicillin resistance gene (*mecA*). A complete list of the number of targeted molecules per gram of tire crumb rubber in each sample are shown in Appendix S. An evaluation of the internal amplification controls showed that 4 of the 280 samples indicated polymerase chain reaction (PCR) inhibition and were removed from analysis. A summary of the targeted microbial gene concentrations from samples collected at all fields is shown in Table 4-107. The mean concentration of 16S rRNA, *S. aureus* and *mecA* gene molecules per gram of tire crumb rubber were 1.1 x 10^7, 19.9 and 109.5, respectively. The variation in the number of targeted gene molecules measured from replicate samples of each field is summarized in Table 4-108, with full results shown in Appendix S. Every sample from the 40 fields was positive for 16S rRNA genes and the percent relative standard deviation ranged from 26.9 – 190.4% across the fields. However, *S. aureus* SA0140 protein and *mecA* genes were detected less frequently. A total of 17 (42.5%) fields had at least 1 sample with quantifiable *S. aureus* genes, while 28 (70%) fields had a least 1 positive sample for the *mecA* gene.

The factors of facility (outdoor/indoor), geographical region and field age had statistically significant impacts for the targeted gene quantities observed in the synthetic turf field samples. As shown in Table 4-109 and Figure 4-65, outdoor fields had statistically significant higher quantities of 16S rRNA genes than indoor fields, while indoor fields had statistically significant higher quantities of *S. aureus* SA0140 and *mecA* genes than outdoor fields.

Table 4-107. Summary of the Concentrations of the Targeted Microbial Genes Measured in Samples from Synthetic Turf Fields[a,b]

Gene Target	N	% > Limit of Detection	Mean (molecules/ g TCR	Standard Deviation (molecules/ g TCR)	% Relative Standard Deviation	10th Percentile (molecules/ g TCR)	25th Percentile (molecules/ g TCR)	50th Percentile (molecules/ g TCR)	75th Percentile (molecules/ g TCR)	90th Percentile (molecules/ g TCR)	Maximum (molecules/ g TCR)
16S rRNA gene	276	100	1.08E+07	1.45E+07	135	3.40E+05	9.19E+05	3.93E+06	1.51E+07	2.82E+07	8.70E+07
S. aureus SA0140 protein	276	25.4	1.99E+01	8.06E+01	405	0	0	0	9.60E+00	4.79E+01	8.90E+02
mecA methicillin resistance gene	276	51.1	1.10E+02	2.18E+02	200	0	0	4.70E+00	1.12E+02	3.86E+02	1.28E+03

[a] molecules/g TCR = molecules/gram of tire crumb rubber; rRNA = Ribosomal ribonucleic acid

Table 4-108. Summary of the Variability in Targeted Microbial Gene Quantities Measured in Replicate Samples from Each Field

Gene Target[a]	Number of Fields	% Relative Standard Deviation Mean	% Relative Standard Deviation Standard Deviation
16S rRNA gene	40	63.9	34.1
S. aureus SA0140 protein	17	154	79.2
mecA methicillin resistance gene	28	116	78.1

[a] rRNA = Ribosomal ribonucleic acid

Table 4-109. Mean Quantities of Targeted Microbial Genes in Outdoor and Indoor Synthetic Turf Fields[a,b]

Gene Target	Outdoor Fields Mean ($\log_{10}$ molecules/ g TCR)	Outdoor Fields Standard Deviation ($\log_{10}$ molecules/ g TCR)	Indoor Fields Mean ($\log_{10}$ molecules/ g TCR)	Indoor Fields Standard Deviation ($\log_{10}$ molecules/ g TCR)	Mann-Whitney T-test p-value
16S rRNA gene	6.9	0.6	5.9	0.6	< 0.001
S. aureus SA0140 protein	0	0.3	1.0	0.8	< 0.001
mecA methicillin resistance gene	0.2	0.5	2.2	0.5	< 0.001

[a] Outdoor fields (N=172); Indoor fields (N=104)

[b] $\log_{10}$ molecules/g TCR = $\log_{10}$ molecules/gram of tire crumb rubber; rRNA = Ribosomal ribonucleic acid

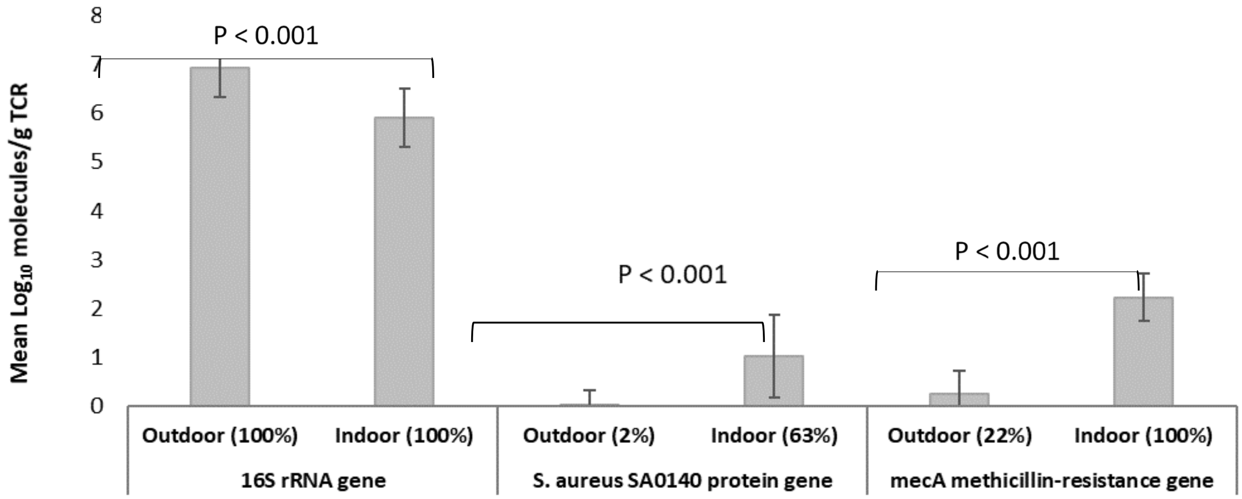

Figure 4-65. Mean log10 concentrations of 16S rRNA genes, S. aureus SA0140 protein gene and mecA methicillin-resistance genes in samples collected from outdoor (n=172) and indoor (n=104) artificial turf fields. Numbers in parentheses specify the percentage of positive samples. Error bars represent standard deviation. P-values indicate results of Mann-Whitney Rank Sum Test. [rRNA = Ribosomal ribonucleic acid; mecA = methicillin-resistance gene; TCR = Tire crumb rubber]

The fields in the oldest age category (2004–2008) tended to have higher quantities of the targeted microbial genes than fields in the youngest age category (Table 4-110). An ANOVA on Ranks shows that statistically significant different gene quantities exist across the three field age categories. The geographical region in which the sampled synthetic turf fields is located also influences quantities of the targeted microbial genes based on ANOVA on Ranks (Table 4-111). It is important to note, however, that the influence of outdoor vs. indoor fields may be impacting results for field age (where there was only one indoor field in the 2013-2016 age group) and census region (where there were higher proportions of indoor fields in the Midwest and Northeast regions than in the south and west regions). When considering samples from outdoor fields only, older fields had statistically significant increased concentrations of 16S rRNA genes than younger fields, but field age did not impact concentrations of *S. aureus* or *mecA* genes (Table 4-110), likely due to a large number of samples with non-detectable values. Likewise, geographical region did not affect concentrations of *S. aureus* genes, but statistically significant different concentrations were observed across the regions for 16S rRNA and *mecA* genes in the outdoor field samples analyzed; highest concentrations were measured in the Midwest and lowest concentrations were detected in the West (Table 4-111). An examination of samples from indoor fields revealed that field age did have a statistically significant impact on indoor fields, as youngest fields showed the highest concentrations and intermediate-aged fields had the lowest concentration of all targeted microbial genes (Table 4-110). Similarly, geographical region had a statistically significant impact for concentrations of the targeted microbial genes in indoor field samples, but the trends varied. Highest concentrations of 16S rRNA genes were measured in the Midwest, while highest concentrations of *S. aureus* and *mecA* were detected in the West (Table 4-111).

Some fields were disinfected with biocides. In total, biocides were applied to 11 fields (4 outdoor and 7 indoor fields), while 5 fields (2 outdoor and 3 indoor) had missing information about biocide usage. An ANOVA of biocide usage on indoor and outdoor fields showed that biocides had a statistically significant association with reduced quantities of 16S rRNA genes in outdoor fields (Table 4-112). However, biocide usage had no impact on concentrations of 16S rRNA genes in indoor fields or the other microbial gene markers in either indoor or outdoor fields.

Table 4-110. Mean Quantities of Targeted Microbial Genes in Synthetic Turf Field Samples, by Installation Age Group[a]

Gene Target	Synthetic Turf Field Data Set	Fields Installed 2004 – 2008 N	Fields Installed 2004 – 2008 Mean (log_{10} molecules/ g TCR)	Fields Installed 2004 – 2008 Standard Deviation (log_{10} molecules/ g TCR)	Fields Installed 2009 – 2012 N	Fields Installed 2009 – 2012 Mean (log_{10} molecules/ g TCR)	Fields Installed 2009 – 2012 Standard Deviation (log_{10} molecules/ g TCR)	Fields Installed 2013 – 2016 N	Fields Installed 2013 – 2016 Mean (log_{10} molecules/ g TCR)	Fields Installed 2013 – 2016 (log_{10} molecules/ g TCR)	ANOVA On Ranks ρ-value
16S rRNA gene	All	76	6.7	0.8	124	6.4	0.8	76	6.6	0.7	0.034
16S rRNA gene	Outdoor	34	7.3	0.3	69	7.0	0.5	69	6.7	0.7	< 0.001
16S rRNA gene	Indoor	42	6.1	0.6	55	5.7	0.5	7	6.2	0.1	< 0.001
S. aureus SA0140 protein	All	76	0.6	0.8	124	0.4	0.8	76	0.2	0.5	< 0.001
S. aureus SA0140 protein	Outdoor	34	0	0	69	0.1	0.5	69	0	0	0.047
S. aureus SA0140 protein	Indoor	42	1.2	0.8	55	0.9	0.9	7	1.7	0.2	0.013
mecA methicillin resistance gene	All	76	1.4	1.2	124	1.1	1.1	76	0.4	0.8	< 0.001
mecA methicillin resistance gene	Outdoor	34	0.2	0.5	69	0.3	0.6	69	0.2	0.4	0.953
mecA methicillin resistance gene	Indoor	42	2.3	0.5	55	2.1	0.4	7	2.6	0.1	0.007

[a] log_{10} molecules/g TCR = log_{10} molecules/gram of tire crumb rubber; ANOVA = Analysis of variance; rRNA = Ribosomal ribonucleic acid

Table 4-111. Mean Quantities of Targeted Microbial Genes in Synthetic Turf Field Samples, by U.S. Geographical Regions[a]

Gene Target	Synthetic Turf Field Data Set	Northeast Region – N	Northeast Region – Mean (log_{10} molecules /g TCR)	Northeast Region – Standard Deviation (log_{10} molecules /g TCR)	South Region – N	South Region – Mean (log_{10} molecules /g TCR)	South Region – Standard Deviation (log_{10} molecules /g TCR)	Midwest Region – N	Midwest Region – Mean (log_{10} molecules /g TCR)	Midwest Region – Standard Deviation (log_{10} molecules /g TCR)	West Region – N	West Region – Mean (log_{10} molecules /g TCR)	West Region – Standard Deviation (log_{10} molecules /g TCR)	ANOVA On Ranks ρ-value
16S rRNA gene	All	63	6.6	0.9	91	6.8	0.7	55	6.1	0.8	67	6.5	0.5	< 0.001
16S rRNA gene	Outdoor	35	7.2	0.4	77	6.9	0.7	14	7.3	0.2	46	6.6	0.4	< 0.001
16S rRNA gene	Indoor	28	5.8	0.8	14	6.1	0.3	41	6.8	0.5	21	6.2	0.5	0.002
S. aureus SA0140 protein	All	63	0.6	0.8	91	0.2	0.6	55	0.5	0.8	67	0.5	0.8	0.010
S. aureus SA0140 protein	Outdoor	35	0.03	0.2	77	0	0	14	0	0	46	0.1	0.5	0.131
S. aureus SA0140 protein	Indoor	28	1.2	0.9	14	1.3	0.8	41	0.7	0.8	21	1.4	0.6	0.006
mecA methicillin resistance gene	All	63	1.1	1.1	91	0.7	0.9	55	1.7	0.9	67	0.8	1.1	< 0.001
mecA methicillin resistance gene	Outdoor	35	0.26	0.6	77	0.1	0.5	14	0.5	0.6	46	0.07	0.3	0.005
mecA methicillin resistance gene	Indoor	28	2.1	0.5	14	1.4	0.6	41	2.1	0.5	21	2.4	0.3	0.008

[a] log_{10} molecules/g TCR = log_{10} molecules/gram of tire crumb rubber; ANOVA = Analysis of variance; rRNA = Ribosomal ribonucleic acid

Table 4-112. Mean Quantities of Targeted Microbial Genes in Synthetic Turf Fields, with and without Biocide Application[a,b]

Gene Target	Synthetic Turf Field Data Set	With Biocide Application – N	With Biocide Application – Mean (log_{10} molecules/ g TCR)	With Biocide Application – Standard Deviation (log_{10} molecules/ g TCR)	Without Biocide Application – N	Without Biocide Application – Mean (log_{10} molecules/ g TCR)	Without Biocide Application – Standard Deviation (log_{10} molecules/ g TCR)	ANOVA ρ-value
16S rRNA gene	Outdoor	26	6.74	0.49	132	6.90	0.63	0.024
16S rRNA gene	Indoor	49	5.93	0.51	34	6.06	0.60	0.402
S. aureus SA0140 protein	Outdoor	26	0.05	0.23	132	0.05	0.33	0.691
S. aureus SA0140 protein	Indoor	49	1.03	0.79	34	1.00	0.91	0.993
mecA methicillin resistance gene	Outdoor	26	0.19	0.57	132	0.22	0.45	0.329
mecA methicillin resistance gene	Indoor	49	2.26	0.45	34	2.30	0.48	0.763

[a] log_{10} molecules/g TCR = log_{10} molecules/gram of tire crumb rubber; ANOVA = Analysis of variance; rRNA = Ribosomal ribonucleic acid

[b] Biocides were applied to 11 fields (4 outdoor and 7 indoor fields), while 5 fields (2 outdoor and 3 indoor) had missing information about biocide usage

Few studies have investigated the microbiological composition of synthetic turf fields with tire crumb rubber infill. McNitt et al. (2007) reported average total bacterial counts of 4.2 $\log_{10}$ colony forming units (CFU) per gram of tire crumb rubber from 20 infilled synthetic turf systems in Pennsylvania using non-selective culture media. Outdoor fields tended to have more total bacteria than indoor fields, although only three indoor fields were examined. Presence of *S. aureus* was investigated using selective media but was not detected, and presence of the *mecA* methicillin resistance gene was not investigated. Vidair (2010) sampled tire crumb rubber from five soccer fields in the San Francisco Bay Area. The maximum concentration of total bacteria reported in these fields was 4.7 $\log_{10}$ CFU per gram of tire crumb rubber infill. While two species of *Staphylococcus* (*S. warneri* and *S. hominis*) were identified in tire crumb rubber, *S. aureus* was not detected. Additionally, methicillin-resistant *Staphylococcus aureus* was not detected. Finally, Bass & Hintze (2013) examined two synthetic turf fields in Utah. One field was in use for a year, while the other field had been in use for 7 years. Total bacteria concentrations averaged 8.0 $\log_{10}$ CFU per gram of tire crumb rubber on the old field and 5.4 $\log_{10}$ CFU per gram of tire crumb rubber on the new field. *Staphylococcus spp.* concentrations of 2.4 $\log_{10}$ CFU per gram of tire crumb rubber were reported on the new turf and 3.8 log10 CFU per gram of tire crumb rubber on older turf, but presence of *S. aureus* was not confirmed, and presence of methicillin resistance was not investigated.

Although the methodologies differ between previous work described above and the results described here, some similar trends were observed. The mean concentration of rRNA genes observed across 40 indoor and outdoor fields was 7.0 $1og_{10}$ molecules per gram of tire crumb rubber, which equates roughly to 6.4 $1og_{10}$ bacterial cells per gram of tire crumb rubber (bacterial cells have an average of 4.2 copies of 16S rRNA genes; Větrovský & Baldrian, 2013) and is within the range of concentrations (4.2–8.0 $\log_{10}$ CFU per gram of tire crumb rubber) reported previously. Similar to previous reports, we observed higher concentrations of total bacteria in outdoor fields compared to indoor fields and in older outdoor fields compared to newer outdoor fields. None of the previous studies detected *S. aureus* or methicillin-resistant *S. aureus* using culture methods in tire crumb rubber samples. We observed the presence of genes corresponding to *S. aureus* and methicillin resistance in bacterial populations isolated from 42% and 70% of artificial turf field samples, respectively. This may be due to the increased sensitivity of the PCR-based methods used here compared to the culture-based methods employed in the previous studies.

4.14.2 Non-targeted Microbial Analysis

A total of 280 samples collected from 40 synthetic turf fields were examined to characterize the microbial community by analysis of the 16S rRNA gene. Of the 280 synthetic turf field samples, one was excluded during quality filtering of 16S rRNA sequence reads, 28 were removed due to failures of quality controls during processing, and 8 were omitted since they contained less than 1000 16S rRNA sequence reads (i.e., the quality control threshold). A summary of the total number of 16S rRNA sequence reads obtained per sample from all fields is listed in Table 4-113. Collectively, these samples contained 1424 operational taxonomic units (OTUs) or unique bacterial taxa. Classification of these unique taxa was performed using the Ribosomal Database Project Classifier (Michigan State University, Lansing, MI, USA) to the lowest taxonomic level possible. The OTUs that contribute 90% of the total 16S rRNA gene sequence reads and their count for each synthetic turf field sample, along with their taxonomic classification, is listed in a database that is available online at the study's website (see https://www.epa.gov/tirecrumb).

Table 4-113. Summary of Total 16S rRNA Sequence Read Counts Obtained from the Non-targeted Microbial Community Analysis of Synthetic Turf Fields

Gene Target	Mean	Standard Deviation	% Relative Standard Deviation	10th Percentile	25th Percentile	50th Percentile	75th Percentile	90th Percentile	Maximum
16S rRNA sequence read counts per sample[a]	1.24E+04	6.79E+03	55	3.87E+03	6.70E+03	1.13E+04	1.80E+04	2.11E+04	2.89E+04

[a] rRNA= ribosomal ribonucleic acid; N=243 samples; % > Limit of Detection = 100%

Vidair (2010) profiled the bacterial community in tire crumb rubber collected from five fields. This census was conducted by selecting the three most prominent types of bacteria isolated on culture plates. Identification was performed using the analytical profile index (API®) System of biochemical tests and can provide species-level resolution. A total of 20 unique taxa were identified, of which 18 species were identified to species and 2 taxa were identified to genus. Using a genetic-based technique, we identified 1424 unique taxa in the bacterial communities of tire crumb rubber collected from 36 artificial turf fields. Although the genetic methods allow more thorough profile of community composition, taxonomic classification is limited to genus-level. A comparison of community members at the genus-level shows that the 20 genera identified in the Vidair (2010) study are present in tire crumb rubber bacterial communities observed in this study.

4.15 Initial Testing of Silicone Wristbands

Collecting samples to measure personal exposures to chemicals is very challenging for people engaged in sport activities on synthetic turf fields and for athletic and physical training activities in general. Personal sampling devices must be relatively small, must not restrict research participant activities, and must be safe to wear, even during vigorous activities. Due to the relatively short activity periods and relatively low concentrations of chemicals, personal sampling devices must also overcome the challenge of collecting sufficient chemical amounts for accurate measurements.

The use of silicone wristbands as a tool for personal and area chemical sample collection in exposure assessment research has increased in popularity. Silicone wristbands can serve as passive samplers for many types of organic chemicals and are especially effective for chemicals present in air. With no power requirements, minimal participant burden and interaction requirements and their ease of use, these silicone wristbands may be useful for personal sample collection during sport activities. There is interest in how silicone wristbands might be used in future exposure measurement studies for synthetic field users, where bulky air sampling equipment can’t be worn safely during intense athletic activity. A critical question regarding their suitability for synthetic turf field personal sampling is whether, and at what rate, they collect chemicals of interest associated with tire crumb rubber or other field materials.

4.15.1 Dynamic Chamber Testing of Wristbands

As a first step towards determining feasibility, it is important to understand how to measure the relevant chemicals in wristbands and to assess the sorption of chemicals when exposed to tire crumb rubber materials. Exploratory tests were designed to provide an initial assessment and demonstration. The results are intended to inform evaluation of the potential utility for personal monitoring and/or field air monitoring in future synthetic turf field research studies. A small set of screening-level experiments were performed in controlled dynamic emission chambers. The tests were designed to measure the amount of selected tire crumb rubber SVOCs absorbed to wristbands when covered with tire crumb rubber, and the amount absorbed in wristbands suspended in the air above tire crumb rubber under controlled conditions of temperature, humidity, and ventilation. The experimental approach and full results for these initial silicone wristband tests are reported in Appendix T.

The wristbands that were covered with tire crumb rubber absorbed targeted SVOC chemicals associated with tire crumb rubber over a 6-day experiment. The amounts of chemicals absorbed were somewhat proportional to their concentrations in the tire crumb rubber but appeared to be highly related to chemical vapor pressures. The wristbands that were suspended in the chamber air above the tire crumb rubber also absorbed measurable levels of most of the target SVOCs that had been emitted into the chamber air during the 6-day experiment. Again, the amounts of chemicals absorbed were somewhat proportional to their concentrations in the tire crumb rubber but appeared to be highly related to chemical vapor pressures. For example, the 5- and 6-ring PAHs were emitted at very low or non-measurable amounts into the chamber air, and likewise, were often near or below measurable levels for wristband extracts. The controlled chamber conditions allowed estimation of effective sampling rates for each SVOC that could be measured in the wristbands. These effective sampling rates allow estimations of how long silicone wristbands might have to be deployed at synthetic turf fields to be able to measure tire crumb rubber associated chemicals.

While the initial tests show that the wristbands have some promise as field area samplers, more field testing is needed to confirm that measurable amounts of chemicals of interest can be measured in reasonable time frames at both outdoor and indoor fields. It is likely that use of silicone wristbands as personal samplers will require that participants wear the wristbands during multiple practice and/or game days, with storage in a clean airtight container between uses. This intermittent sampling will likely be needed to collect sufficient amounts of target chemicals for analysis. Pilot testing with athletes, coaches, and/or referees would help provide more information regarding the suitability of silicone wristbands as a personal sampling device for synthetic turf field users.

5.0 Toxicity Reference Information

5.1 Background

The objective of the effort to characterize tire crumb rubber material was to identify and collate toxicity reference information on potential chemical constituents of tire crumb rubber from existing on-line databases and literature sources. To achieve this goal, a list of potential chemical constituents was developed as part of the Literature Review/Gaps Analysis (LRGA), based on chemicals identified in the various studies reviewed. More than 350 distinct chemical compounds potentially associated with recycled tire crumb rubber were reported in the appendix of the peer-reviewed white paper summarizing the LRGA results, *State-of-Science Literature Review/Gaps Analysis, White Paper Summary of Results*. The white paper and constituents list have been reproduced in Appendix C. The Summary Spreadsheet of the Literature Review/Gaps Analysis includes the name of these chemicals, Chemical Abstracts Service (CAS) numbers, synonyms, and concentrations reported in the literature. Some major classes of constituents identified in the literature include inorganics and VOCs/SVOCs. Frequently studied inorganics include lead, zinc, cadmium and chromium, and frequently studied VOCs/SVOCs include benzothiazole and PAHs. Less frequently studied constituents include microbials and a variety of complex organic compounds.

5.2 Approach

Extant toxicity reference information was compiled for the potential tire crumb rubber chemical constituents identified in the LRGA. Data gaps were identified, including chemicals for which toxicity reference data were unavailable. The information sources used to gather the toxicity reference information are shown in Table 5-1.

Table 5-1. Information Sources Used to Compile Reference Toxicity Information

Information Source	URL	Description
EPA Integrated Risk Information System (IRIS)	https://cfpub.epa.gov/ncea/iris2/atoz.cfm	Provides toxicity values for health effects resulting from chronic exposure to chemicals, including cancer and noncancer hazard characterization and oral reference doses (RfDs), inhalation reference concentrations (RfCs), oral slope factors (OSFs), and inhalation unit risks (IURs). [a]
EPA Provisional Peer-reviewed Toxicity Value (PPRTV)	https://hhpprtv.ornl.gov/quickview/pprtv.php	PPRTVs have been developed for EPA's Superfund program and can also include provisional RfDs and RfCs for non-cancer effects and provisional OSFs and IURs for cancer.
EPA Health Effects Assessment Summary Table (HEAST)	https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=2877	Provides oral and inhalation toxicity values developed for EPA's Superfund program.
Agency for Toxic Substances and Disease Registry (ATSDR) Minimal Risk Levels (MRLs)	http://www.atsdr.cdc.gov/mrls/pdfs/atsdr_mrls.pdf	Like RfDs, ATSDR oral and inhalation MRLs represent estimates of the daily human exposure to a hazardous substance that is likely to be without appreciable adverse non-cancer health effects over a specified duration of exposure.

Table 5-1 Continued

Information Source	URL	Description
World Health Organization (WHO) International Programme on Chemical Safety (IPCS) Concise International Chemical Assessment Documents (CICAD)	http://www.who.int/ipcs/publications/cicad/cicads_alphabetical/en/	Provides summaries of potential health effects of chemicals on human health and the environment.
International Agency for Research on Cancer (IARC) Monographs	http://monographs.iarc.fr/ENG/Classification/latest_classif.php	Provides summary information on chemicals that can increase the risk of human cancer.
California Environmental Protection Agency (CalEPA) Toxicity Criteria Database	http://oehha.ca.gov/prop65/pdf/P65safeharborlevels040116.pdf http://www.oehha.ca.gov/air/allrels.html https://oehha.ca.gov/media/CPFs042909.pdf	Provides No Significant Risk Levels (NSRLs) for carcinogens, Maximum Allowable Dose Levels (MADLs) for chemicals causing reproductive toxicity, and Reference Exposure Levels (RELs) which represent air concentrations at or below which no adverse health effects are anticipated to occur in human populations, including sensitive subgroups.
Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs) [b]	https://www.osha.gov/dsg/annotated-pels/	Provides regulatory limits on the amount or concentration of a substance in the air to protect workers against the health effects of exposure to hazardous substances. They may also contain a skin designation. PELs are enforceable. OSHA PELs are based on an 8-hour time weighted average (TWA) exposure.
California Division of Occupational Safety and Health (CalOSHA) Permissible Exposure Limits (PELs) for Chemical Contaminants [b]	http://www.dir.ca.gov/title8/ac1.pdf	Provides an extensive list of PELs that are enforced in workplaces under the jurisdiction of CalOSHA. Although not enforceable outside of CalOSHA's jurisdiction, the PELs can provide information on acceptable levels of chemicals in the workplace. CalOSHA PELs are based on an 8-hour TWA exposure.
National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limits (RELs) [b]	https://www.osha.gov/dsg/annotated-pels/ https://www.cdc.gov/niosh/npg/npgsyn-a.html	RELs are authoritative Federal agency recommendations established to limit exposure to hazardous substances in workplace air to protect worker health. NIOSH RELs are based on a 10-hour TWA exposure.
American Conference of Governmental Industrial Hygienists (ACGIH®) Threshold Limit Values (TLVs®) [b]	https://www.osha.gov/dsg/annotated-pels/	TLVs® are health-based values. TLVs® represent airborne concentrations of chemicals under which it is believed that nearly all workers may be repeatedly exposed, day after day, over a working lifetime, without adverse effects.

[a] An RfD is an estimate (with uncertainty spanning an order of magnitude perhaps) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime, while RfCs similarly represent an estimate of a daily inhalation exposure. An OSF is an upper-bound estimate, approximating a 95% confidence limit, of the increased cancer risk from a lifetime oral exposure to an agent. This estimate, usually expressed in terms of the proportion (of a population) affected per mg/kg-day, is generally reserved for use in the low-dose region of the dose-response relationship (i.e., for exposures corresponding to risks less than 1 in 100). IURs are similarly an estimate of the increased cancer risk from a lifetime inhalation exposure. OSFs and IURs can be multiplied by estimated lifetime exposures to estimate the lifetime cancer risk.

[b] While not directly applicable to all populations that may be exposed to tire crumb rubber, occupational limits developed by OSHA, CalOSHA, NIOSH, and ACGIH® were also reviewed for tire crumb rubber constituents. Typically, these values represent recommended levels of chemicals in workplace air that should not be exceeded over an 8- or 10-hour workday.

5.3 Results

A database (Excel spreadsheet) was developed that cross-references chemicals in the tire crumb list of potential constituents with toxicity data from the sources described above. The database is available online through the U.S. EPA's study website (see http://www.epa.gov/tirecrumb), and will be useful for informing future screening-level health risk assessments and for identifying data gaps. This information is also available in Appendix U. Table 5-2 provides a summary of the number and percent of LRGA chemical constituents with toxicity data in the various information sources used to gather toxicity reference information.

Table 5-2. Summary of LRGA Chemical Constituents[a] with Available Toxicity Data

Sources[b]	Number of Chemicals with Available Data[c]	Percent of Chemicals with Available Data
IRIS	101	28%
PPRTV	51	14%
HEAST	75	21%
ATSDR	58	16%
CICAD	24	7%
IARC	95	27%
CalEPA	776	22%
OSHA	81	23%
CalOSHA	89	25%
NIOSH	84	24%
ACGIH®	83	23%

[a] Total number of chemicals evaluated was 355; data were available from at least one source for 167 chemicals (47%). LRGA = Literature Review/Gaps Analysis

[b] IRIS = EPA Integrated Risk Information System; PPRTV = EPA Provisional Peer-reviewed Toxicity Value; HEAST = EPA Health Effects Assessment Summary Table; ATSDR = Agency for Toxic Substances and Disease Registry; CICAD = WHO Concise International Chemical Assessment Documents; IARC = International Agency for Research on Cancer; CalEPA = California Environmental Protection Agency; OSHA = Occupational Health and Safety Administration; CalOSHA = California Division of Occupational Safety and Health; NIOSH = National Institute for Occupational Safety and Health; ACGIH® = American Conference of Governmental Industrial Hygienists;

[c] Some chemicals have data from more than one source.

The larger list of over 350 chemicals was narrowed down to its subset of chemicals that are also included on the targeted analyte list (Tables 3-1 thru 3-4). Of the 95 identified,[7] toxicity reference information was available for 78 (82%) of these. It is important to recognize that some of these target analytes were not found, or were not consistently found, in tire crumb rubber in this study. Table 5-3 provides a summary of the number and percent of these target analyte chemical constituents with toxicity data in the various information sources used to gather toxicity reference information.

[7]From Table 3-1, mercury was included. Benzothiazole appears on both Table 3-2 and Table 3-3 but was only counted once. DBA and ICDP from Table 3-3 were counted independently. The following VOCs from Table 3-2 were not included: SumBTEX (sum of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene); trans-2-butene; cis-2-butene; 1,1-dichloroethene; 1,1-dichloroethane; m-dichlorobenzene; and o-dichlorobenzene.

Table 5-3. Summary of Target Chemical Constituents with Available Toxicity Data[a]

Sources[b]	Number of Chemicals with Available Data[c]	Percent of Chemicals with Available Data
IRIS	59	62%
PPRTV	25	26%
HEAST	40	42%
ATSDR	41	43%
CICAD	12	13%
IARC	49	52%
CalEPA	40	42%
OSHA	44	46%
CalOSHA	48	51%
NIOSH	42	44%
ACGIH®	46	48%

[a] Total number of chemicals evaluated was 95; data were available from at least one source for 78 chemicals (82%).

[b] IRIS = EPA Integrated Risk Information System; PPRTV = EPA Provisional Peer-reviewed Toxicity Value; HEAST = EPA Health Effects Assessment Summary Table; ATSDR = Agency for Toxic Substances and Disease Registry; CICAD = WHO Concise International Chemical Assessment Documents; IARC = International Agency for Research on Cancer; CalEPA = California Environmental Protection Agency; OSHA = Occupational Health and Safety Administration; CalOSHA = California Division of Occupational Safety and Health; NIOSH = National Institute for Occupational Safety and Health; ACGIH® = American Conference of Governmental Industrial Hygienists

[c] Some chemicals have data from more than one source.

Table 5-4 provides toxicity data for a selection of metals and Table 5-5 provides toxicity data for a selection of VOCs and SVOCs from the LRGA list of potential constituents. The chemicals included in Tables 5-4 and 5-5 were selected from the larger list of over 350 chemicals for highlighting based on their reported potential association with tire crumb rubber in this study or other studies and in part because of their potential interest as well-known chemicals.

Table 5-4. Chemical-specific Toxicity Data for Select Metals [a]

Note: Acronyms and units are defined in the footnote for each information source

Chemical	IRIS[b]	PPRTV[c]	HEAST[d]	ATSDR[e]	CICAD[f]	IARC[g]	CalEPA[h]	OSHA[i]	CalOSHA[j]	NIOSH[k]	ACGIH®[l]
Arsenic	RfD=3e-4 OSF=1.5 Class A Dr. Water UR=5e-5 Inhal. UR=4.3e-3	N/A	Subchronic RfD=3e-4	Oral Acute MRL=0.005 Oral Interm. MRL=3e-4	N/A	Group 1	NSRL= 0.06 (inhal.) NSRL= 10 except (inhal.) Oral Chronic REL=0.0035 Inhal. Acute REL=0.2 Inhal. Chronic REL=0.015 OSF=1.5 Inhal. SF=12 Inhal. UR=3.3e-3	PEL=0.5	8-hour TWA PEL=0.2	Ceiling =0.002	N/A
Cadmium	RfD=5e-4 (water) RfD=1e-3 (food) Class B1 Inhal. UR=1.8e-03	N/A	N/A	Oral Interm. MRL=0.0005 Oral Chronic MRL=0.0001 Inhal. Acute MRL=0.00003	N/A	Group 1	NSRL= 0.05 (inhal.) MADL= 4.1 (oral) Oral Chronic REL=0.5 Inhal. Chronic REL=0.02 OSF=15 Inhal. UR=4.2e-3	8-hour TWA PEL=0.1 (fume) 8-hour TWA PEL=0.2 (dust) Ceiling=0.3 (fume) Ceiling=0.6 (dust)	8-hour TWA PEL=0.005	N/A	8-hour TWA TLV=0.01 (total) 8-hour TWA TLV=0.002 (resp.)

Table 5-4 Continued

Chemical	IRIS[b]	PPRTV[c]	HEAST[d]	ATSDR[e]	CICAD[f]	IARC[g]	CalEPA[h]	OSHA[i]	CalOSHA[j]	NIOSH[k]	ACGIH®[l]
Chromium	RfD=1.5 (CrIII) RfD=3e-3 (CrVI) RfC=8e-6 (CrVI mists) RfC=1e-4 (CrVI partic.) Class D (CrIII) Class A (CrVI-inhal) Class D (CrVI-oral) Inhal. UR= 1.2e-2 (CrVI)	N/A	Subchronic RfD=1.0 (CrIII) Subchronic RfD=2e-2 (CrVI) Inhal. SF= 40 (CrVI)	Oral Interm. MRL=0.005 (CrVI) Oral Chronic MRL= 0.0009 (CrVI) Inhal. Interm. MRL=1e-4 (CrIII sol. partic.) Inhal. Interm. MRL=0.005 (CrIII insol. partic.) Inhal. Interm. MRL=5E-6 (CrVI mists) Inhal. Interm. MRL=3e-4 (CrVI partic.) Inhal. Chronic MRL=5e-6 (CrVI mists)	Tolerable Intake= 9e-4 (CrVI non-canc.)	Group 3	NSRL=0.001 (CrVI inhal.) MADL= 8.2 (oral) Oral Chronic REL=20 (CrVI) Inhal. Chronic REL=0.2 (CrVI) OSF=0.42 (CrVI) Inhal. SF=510 (CrVI) Inhal. UR=0.15 (CrVI)	PEL=0.5(CrIII cmpds) PEL=1 (metal, insol salts)	8-hour TWA PEL=0.5 (CrIII) 8-hour TWA PEL=0.005 (CrVI) Ceiling= 0.1 (CrVI)	10-hr TWA REL=0.5	8-hour TWA TLV=0.5 (CrIII) 8-hour TWA TLV=0.05 (CrVI sol.) 8-hour TWA TLV= 0.01 (CrVI insol.)
Cobalt	N/A	Chronic RfD=3.0e-4 Chronic RfC=6.0e-6 Subchronic RfD=3.0e-3 Subchronic RfC=2.0e-5 Inhal. UR=9.0	N/A	Oral Interm. MRL=0.01 Inhal. Chronic MRL= 0.0001	Tolerable Conc=1.0e-1	Group 2B	N/A	PEL=0.1	8-hour TWA PEL=0.02	10-hr TWA REL=0.05	8-hour TWA TLV=0.02
Lead	Class B2	N/A	N/A	N/A	N/A	Group 2B	NSRL= 15 (oral) MADL= 0.5 (oral) OSF=8.50e-3 Inhal. SF=4.20e-2 Inhal. UR=1.20e-5	N/A	8-hour TWA PEL=0.05	10-hr TWA REL=0.05	8-hour TWA TLV=0.02

Table 5-4 Continued

Chemical	IRIS[b]	PPRTV[c]	HEAST[d]	ATSDR[e]	CICAD[f]	IARC[g]	CalEPA[h]	OSHA[i]	CalOSHA[j]	NIOSH[k]	ACGIH®[l]
Zinc	RfD=3.0e-1 Class D	N/A	Subchronic RfD=3.0e-1	Oral Interm. MRL=0.3 Oral Chronic MRL=0.3	N/A	N/A	N/A	N/A	N/A	N/A	N/A

[a] See online spreadsheet (https://www.epa.gov/chemical-research/recycled-tire-crumb-non-targeted-microbial-analysis-results-and-constituent-list) or Appendix W for additional chemicals. N/A = no information was provided.

[b] IRIS = EPA Integrated Risk Information System; RfD = Reference dose (mg/kg-d); OSF = Oral slope factor $(mg/kg\text{-}d)^{-1}$; RfC = Reference concentration (mg/m^3); Cancer classes: Class A=human carcinogen, Class B1=probable human carcinogen - based on limited evidence of carcinogenicity in humans, Class B2=probable human carcinogen - based on sufficient evidence of carcinogenicity in animals, Class C=possible human carcinogen; Class D=not classifiable as to human carcinogenicity, Class E=evidence of non-carcinogenicity in humans; Dr. Water UR=Drinking water unit risk $(\mu g/l)^{-1}$; Inhal. UR=Inhalation unit risk $(\mu g/m^3)^{-1}$.

[c] PPRTV = EPA Provisional Peer-reviewed Toxicity Value; Chronic RfD = Chronic reference dose (mg/kg-d); Chronic RfC = Chronic reference concentration (mg/m^3); Subchronic RfD = Subchronic reference dose (mg/m^3); Subchronic RfC = Subchronic reference concentration (mg/m^3); Inhal. UR = Inhalation unit risk (mg/m^{3-1}).

[d] HEAST = EPA Health Effects Assessment Summary Table; Chronic RfD = Chronic reference dose (mg/kg-d); Subchronic RfD = Subchronic reference dose (mg/m^3); Subchronic RfC = Subchronic reference concentration (mg/m^3); Inhal. SF = Inhalation slope factor ($mg/kg\text{-}day^{-1}$.

[e] ATSDR = Agency for Toxic Substances and Disease Registry; MRL = Minimum Risk Level – Acute, Interm. = Intermediate, or Chronic; Oral in mg/kg-day, Inhalation in mg/m^3 unless otherwise stated).

[f] CICAD = WHO Concise International Chemical Assessment Documents; Tolerable Intake (mg/kg-d unless otherwise stated); Tolerable Conc. = Tolerable Concentration ($\mu g/m^3$); Est. CP = Estimated carcinogenic potency (mg/m^3), which is the concentration associated with a 1% increase in mortality due to leukemia); Berk Ov Cancer (mice) = Benchmark value for ovarian cancer in mice.

[g] IARC = International Agency for Research on Cancer; IARC cancer classifications: Group 1=carcinogenic to humans; Group 2A=probably carcinogenic to humans; Group 2B=possibly carcinogenic to humans; Group 3= not classifiable as to its carcinogenicity in humans; Group 4=probably not carcinogenic to humans.

[h] CalEPA = California Environmental Protection Agency; NSRL = No Significant Risk Level (µg/day), Oral or Inhal. = Inhalation; MADL = Maximum Allowable Dose Level (µg/day), Oral or Inhal. = Inhalation; Oral Chronic REL = Chronic Oral recommended exposure limit (µg/kg-d); Inhal. Acute REL = inhalation acute recommended exposure limit ($\mu g/m^3$); Inhal. 8-hr REL = inhalation 8-hr recommended exposure limit ($\mu g/m^3$); Inhal. Chronic REL = inhalation chronic recommended exposure limit ($\mu g/m^3$); OSF=Oral slope factor $(mg/kg\text{-}d)^{-1}$; Inhal. SF=Inhalation slope factor $(mg/kg\text{-}d)^{-1}$; Inhal. UR=Inhalation unit risk $(\mu g/m^3)^{-1}$.

[i] OSHA = Occupational Health and Safety Administration; PEL=permissible exposure limit (in mg/m^3 unless otherwise stated); 8-hr TWA = 8-hour time weighted average (in mg/m^3 unless otherwise stated); Ceiling = permissible exposure limit ceiling (mg/m^3 unless otherwise stated).

[j] CalOSHA = California Division of Occupational Safety and Health; 8-hr TWA PEL = 8-hour time weighted average permissible exposure limit (in mg/m^3 unless otherwise stated); STEL = Short term exposure limit (in mg/m^3 unless otherwise stated); Ceiling = permissible exposure limit ceiling (mg/m^3 unless otherwise stated).

[k] NIOSH = National Institute for Occupational Safety and Health; 10-hr TWA REL=10-hour time weighted average recommended exposure limit (in mg/m^3 unless otherwise stated); STEL=Short term exposure limit (in mg/m^3 unless otherwise stated); Ceiling = recommended exposure limit ceiling (in mg/m^3 unless otherwise stated).

[l] ACGIH® = American Conference of Governmental Industrial Hygienists; 8-hr TWA TLV = 8-hour time weighted average threshold limit value (in mg/m^3 unless otherwise stated); STEL TLV = Short term exposure limit threshold limit value (in ppm); Ceiling = threshold limit value ceiling (in ppm).

Table 5-5. Chemical-specific Toxicity Data for Select VOCs and SVOCs [a]

Note: Acronyms and units are defined in the footnote for each information source

Chemical	IRIS[b]	PPRTV[c]	HEAST[d]	ATSDR[e]	CICAD[f]	IARC[g]	CalEPA[h]	OSHA[i]	CalOSHA[j]	NIOSH[k]	ACGIH®[l]
Aniline	RfC=1.0e-3 OSF=5.7e-3 Class B2 Dr. Water UR=1.6e-7	Chronic RfD=7.0e-3	Subchronic RfC=1.0e-2	N/A	N/A	Group 3	NSRL=100 OSF=5.70E-3 Inhal. UR=1.60e-6	PEL=19	8-hour TWA PEL=7.6	N/A	8-hr TWA TLV=2
Benzene	RfD=4.0e-3 RfC=3.0e-2 Class A OSF=1.5e-02 to 5.5e-02 Dr. Water UR=4.4e-07 to 1.6e-06 Inhal. UR= 2.2e-06 to 7.8e-05	Subchronic RfD=1.0e-2 Subchronic RfC=8.0e-2	Inhal. SF=2.9e-2	Oral Chronic MRL=5e-3 Inhal. Acute MRL=9e-3 Inhal. Interm. MRL=6e-3 Inhal. Chronic MRL=0.003	N/A	Group 1	NSRL=6.4 (oral) NSRL=13 (inhalation) MADL=24 (oral) MADL=49 (inhalation) Inhal. Acute REL=27 Inhal. 8-hr REL=3 Inhal. Chronic REL=3 OSF=1.00e-1 Inhal. UR=2.90e-5	8-hr TWA=10 Ceiling=25 ppm	8-hr TWA PEL=1 ppm STEL=5 ppm	10-hr TWA REL=0.1 STEL=1 ppm	8-hr TWA TLV=0.5 STELTLV= 2.5
Benzo(a)pyrene	Class B2 Oral OSF= 7.3 Dr. Water UR=2.1e-4	N/A	N/A	N/A	N/A	Group 1	NSRL=0.06 OSF=12 Inhal. SF=3.6 Inhal. UR= 1.10e-3	PEL=0.2 (coal tar pitch volatiles)	8-hr TWA PEL=0.2 (coal tar pitch volatiles)	10-hr TWA REL=0.1 (cyclohexane extractable fraction)	8-hr TWA TLV=0.2 (coal tar pitch volatiles)
Benzo(ghi) perylene	Class D	N/A	N/A	N/A	N/A	Group 3	N/A	N/A	N/A	N/A	N/A
Benzothiazole	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
2-hydroxybenzo thiazole	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Bis(2-ethylhexyl) phthalate	RfD=2.0e-2 Class B2 OSF=1.4e-2 Dr. Water UR=4.0e-7	N/A	N/A	Oral Interm. MRL=0.1 Oral Chronic MRL=0.06	N/A	Group 2B	NSRL=310 MADL=410 (adult oral) OSF=8.40e-3 Inhal. UR= 2.40e-6	PEL=5	N/A	10-hr TWA REL=5 STEL=10	8-hr TWA TLV=5

Table 5-5 Continued

Chemical	IRIS[b]	PPRTV[c]	HEAST[d]	ATSDR[e]	CICAD[f]	IARC[g]	CalEPA[h]	OSHA[i]	CalOSHA[j]	NIOSH[k]	ACGIH®[l]
1,3-Butadiene	RfC=2.0e-3 Class A Inhal. UR= 3.0e-5	N/A	N/A	N/A	Est. CP= 1.7 Berk. Ov. Cancer (mice)=0.57	Group 1	Inhal. acute REL=660 Inhal. 8-hr REL=9 Inhal. Chronic REL=2 OSF=6.00e-1 Inhal. SF= 6.00e-1 Inhal. UR=1.70e-4	PEL=1ppm	8-hr TWA PEL=1 ppm 8-hr TWA PEL=2.2 STEL=5 ppm STEL=11	N/A	8-hr TWA TLV=2 ppm
Cyclohexylamine	RfD=2.0e-1	N/A	Subchronic RfD=3.0e-1	N/A	N/A	N/A	N/A	N/A	8-hr TWA PEL=10 ppm 8-hr TWA PEL=40	10-hr TWA REL=10 ppm 10-hr TWA REL=40	N/A
Di-cyclohexylamine	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Cyclohexanamine, N-cyclohexyl-N-methyl-	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Dibutyl phthalate	RfD=1.0e-1 Class D	N/A	Subchronic RfD=1	Oral Acute MRL=0.5	N/A	N/A	MADL=8.7	PEL=5	8-hr TWA PEL=5	10-hr TWA REL=5	8-hr TWA TLV=5
Ethyl benzene	RfD=1.0e-1 RfC=1 Class D	Subchronic RfD= 5.0e-2 Subchronic RfC=9		Oral Interm. MRL=0.4 Inhal. Acute MRL=5ppm Inhal. Interm. MRL=2ppm Inhal. Chronic MRL=0.06	N/A	Group 2B	NSRL= 41 (oral) NSRL= 54 (inhalation) Inhal. Chronic REL=2000 OSF=1,10e-2 Inhal. SF= 8.70e-3 Inhal. UR=2.50e-6	PEL=100 ppm PEL=435	8-hr TWA PEL=5 ppm 8-hr TWA PEL=22 STEL=30 ppm STEL=130	10-hr TWA REL=100 ppm 10-hr TWA REL=435 STEL REL=125 ppm STEL REL=545	8-hr TWA TLV=20 ppm
Fluoranthene	RfD=4.0e-2 Class D	Subchronic RfD=1.0e-1	Subchronic RfD=4.0e-1	Oral Interm. MRL=0.4	N/A	Group 3	N/A	N/A	N/A	N/A	N/A

Table 5-5 Continued

Chemical	IRIS[b]	PPRTV[c]	HEAST[d]	ATSDR[e]	CICAD[f]	IARC[g]	CalEPA[h]	OSHA[i]	CalOSHA[j]	NIOSH[k]	ACGIH®[l]
Formaldehyde	RfD=2.0e-1 Class B1	N/A	Subchronic RfD=2.0e-1	Oral Interm. MRL=0.3 Oral Chronic MRL=0.2 Inhal. Acute MRL=0.04 Inhal. Interm. MRL=0.03 Inhal. Chronic MRL=0.008	Tolerable Intake=2600 µg/L	Group 1	NSRL=40 Inhal. Acute REL=55 Inhal. 8-hr REL=9 Inhal. Chronic REL=9 OSF=2.10e-2 Inhal. UR=6.00e-6	N/A	8-hr TWA PEL=0.75 STEL=0.2	10-hr TWA REL=0.016 Ceiling =0.1ppm	Ceiling=0.3
Hexadecane	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
2-Mercaptobenzo thiazole	N/A	N/A	N/A	N/A	N/A	Group 2A	N/A	N/A	N/A	N/A	N/A
Methyl isobutyl ketone	RfC=3	N/A	Subchronic RfD=8.0e-1	N/A	N/A	Group 2B	N/A	PEL=100 ppm PEL=410	8-hr TWA PEL=50 ppm 8-hr TWA PEL=205 STEL=75 ppm STEL=300	10-hr TWA REL=50 ppm 10-hr TWA REL=205 STEL=75 ppm STEL=300	8-hr TWA TLV=20 STEL TLV=75
4-tert-octylphenol	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Phenanthrene	Class D	N/A	N/A	N/A	N/A	Group 3	N/A	PEL=0.2 (coal tar pitch volatiles)	8-hr TWA PEL=0.2 (coal tar pitch volatiles)	10-hr TWA REL=0.1 (cyclohexane extractable fraction)	8-hr TWA TLV=0.2 (coal tar pitch volatiles)
Pyrene	RfD=3.0e-2 Class D	Subchronic RfD=3.0e-1	Subchronic RfD=3.0e-1	N/A	N/A	Group 3	N/A	PEL=0.2 (coal tar pitch volatiles)	8-hr TWA PEL=0.2 (coal tar pitch volatiles)	10-hr TWA REL=0.1 (cyclohexane extractable fraction)	8-hr TWA TLV=0.2 (coal tar pitch volatiles)

Table 5-5 Continued

Chemical	IRIS[b]	PPRTV[c]	HEAST[d]	ATSDR[e]	CICAD[f]	IARC[g]	CalEPA[h]	OSHA[i]	CalOSHA[j]	NIOSH[k]	ACGIH®[l]
Styrene	RfD=2.0e-1 RfC=1	N/A	Subchronic RfC=3	Inhal. Acute MRL=5 Inhal. Chronic MRL=0.2	N/A	Group 2B	Inhal. Acute REL=21000 Inhal. Chronic REL=900	8-hr TWA=100 Ceiling=200 ppm	8-hr TWA PEL=50 ppm 8-hr TWA PEL=215 STEL=100 ppm STEL=425 Ceiling=500 ppm	10-hr TWA REL=50 ppm 10-hr TWA REL=215 STEL=100 ppm STEL=425	8-hr TWA TLV=20 STEL TLV=40
Toluene	RfD=8.0e-2 Class D	Subchronic RfD= 8.0e-1 Subchronic RfC=5	Subchronic RfC=2	Oral Interm. MRL=0.2 Inhal. Acute MRL= 0.2 Inhal Chronic MRL=1	N/A	Group 3	MADL=7000 Inhal. Acute REL=37000 Inhal. Chronic REL=900	8-hr TWA=200 Ceiling=300 ppm	8-hr TWA PEL=10 ppm 8-hr TWA PEL=37 STEL=150 ppm STEL=560 Ceiling=500 ppm	10-hr TWA REL=100 ppm 10-hr TWA REL=375 STEL=150 ppm STEL=560	8-hr TWA TLV=20
o-Xylene	N/A	N/A	Chronic RfD=2	N/A	N/A		Inhal. Acute REL=22000 Inhal. Chronic REL=700	PEL=100ppm PEL=435	N/A	10-hr TWA REL=100 ppm 10-hr TWA REL=435 STEL=150 ppm STEL=655	8-hr TWA TLV=100 STEL TLV=150
Xylenes (m-, p-, o-)	RfD=2.0e-1 RfC=1.0e-1	Subchronic RfD= 4.0e-1 Subchronic RfC=4.0e-1	N/A	Oral Interm. MRL=0.4 Oral Chronic MRL=0.2 Inhal. Acute MRL=2 Inhal. Interm. =0.6 Inhal. Chronic MRL=0.05	N/A	Group 3	Inhal. Acute REL=22000 Inhal. Chronic REL=700	PEL=100ppm PEL=435	8-hr TWA PEL=100 ppm 8-hr TWA PEL=435 STEL=150 ppm STEL=655 Ceiling=300 ppm	N/A	8-hr TWA TLV=100 STEL TLV=150

[a] See online spreadsheet (https://www.epa.gov/chemical-research/recycled-tire-crumb-non-targeted-microbial-analysis-results-and-constituent-list) or Appendix W for additional chemicals. VOCs = volatile organic compounds; SVOCs = semivolatile organic compounds; N/A = no information was provided.

[b] IRIS = EPA Integrated Risk Information System; RfD = Reference dose (mg/kg-d); OSF = Oral slope factor (mg/kg-d)$^{-1}$; RfC = Reference concentration (mg/m^3); Cancer classes: Class A=human carcinogen, Class B1=probable human carcinogen - based on limited evidence of carcinogenicity in humans, Class B2=probable human carcinogen - based on sufficient evidence of carcinogenicity in animals, Class C=possible human carcinogen; Class D=not classifiable as to human carcinogenicity, Class E=evidence of non-carcinogenicity in humans; Dr. Water UR=Drinking water unit risk (µg/l)$^{-1}$; Inhal. UR=Inhalation unit risk (µg/m^3)$^{-1}$.

[c] PPRTV = EPA Provisional Peer-reviewed Toxicity Value; Chronic RfD = Chronic reference dose (mg/kg-d); Chronic RfC = Chronic reference concentration (mg/m^3); Subchronic RfD = Subchronic reference dose (mg/m^3); Subchronic RfC = Subchronic reference concentration (mg/m^3); Inhal. UR = Inhalation unit risk (mg/m$^{3-1}$).

[d] HEAST = EPA Health Effects Assessment Summary Table; Chronic RfD = Chronic reference dose (mg/kg-d); Subchronic RfD = Subchronic reference dose (mg/m^3); Subchronic RfC = Subchronic reference concentration (mg/m^3); Inhal. SF = Inhalation slope factor (mg/kg-day^{-1}.

[e] ATSDR = Agency for Toxic Substances and Disease Registry; MRL = Minimum Risk Level – Acute, Interm. = Intermediate, or Chronic; Oral in mg/kg-day, Inhalation in mg/m^3 unless otherwise stated).

[f] CICAD = WHO Concise International Chemical Assessment Documents; Tolerable Intake (mg/kg-d unless otherwise stated); Tolerable Conc. = Tolerable Concentration (µg/m^3); Est. CP = Estimated carcinogenic potency (mg/m^3), which is the concentration associated with a 1% increase in mortality due to leukemia); Berk Ov Cancer (mice) = Benchmark value for ovarian cancer in mice.

[g] IARC = International Agency for Research on Cancer; IARC cancer classifications: Group 1=carcinogenic to humans; Group 2A=probably carcinogenic to humans; Group 2B=possibly carcinogenic to humans; Group 3= not classifiable as to its carcinogenicity in humans; Group 4=probably not carcinogenic to humans.

[h] CalEPA = California Environmental Protection Agency; NSRL = No Significant Risk Level (µg/day), Oral or Inhal.= Inhalation; MADL = Maximum Allowable Dose Level (µg/day), Oral or Inhal. = Inhalation; Oral Chronic REL = Chronic Oral recommended exposure limit (µg/kg-d); Inhal. Acute REL = inhalation acute recommended exposure limit (µg/m^3); Inhal. 8-hr REL = inhalation 8-hr recommended exposure limit (µg/m^3); Inhal. Chronic REL = inhalation chronic recommended exposure limit (µg/m^3); OSF=Oral slope factor (mg/kg-d)$^{-1}$; Inhal. SF=Inhalation slope factor (mg/kg-d)$^{-1}$; Inhal. UR=Inhalation unit risk (µg/m^3)$^{-1}$.

[i] OSHA = Occupational Health and Safety Administration; PEL=permissible exposure limit (in mg/m^3 unless otherwise stated); 8-hr TWA = 8-hour time weighted average (in mg/m^3 unless otherwise stated); Ceiling = permissible exposure limit ceiling (mg/m^3 unless otherwise stated).

[j] CalOSHA = California Division of Occupational Safety and Health; 8-hr TWA PEL = 8-hour time weighted average permissible exposure limit (in mg/m^3 unless otherwise stated); STEL = Short term exposure limit (in mg/m^3 unless otherwise stated); Ceiling = permissible exposure limit ceiling (mg/m^3 unless otherwise stated).

[k] NIOSH = National Institute for Occupational Safety and Health; 10-hr TWA REL=10-hour time weighted average recommended exposure limit (in mg/m^3 unless otherwise stated); STEL=Short term exposure limit (in mg/m^3 unless otherwise stated); Ceiling = recommended exposure limit ceiling (in mg/m^3 unless otherwise stated).

[l] ACGIH® = American Conference of Governmental Industrial Hygienists; 8-hr TWA TLV = 8-hour time weighted average threshold limit value (in mg/m^3 unless otherwise stated); STEL TLV = Short term exposure limit threshold limit value (in ppm); Ceiling = threshold limit value ceiling (in ppm).

5.4 Conclusions

Of the 355 constituents examined, extant toxicity reference information was limited, with information available for only 167 (47%) of the chemicals. The greatest sources of information were IRIS values (available for 28% of the constituents), IARC cancer classifications (27% of the constituents), CalOSHA 8-hr time-weighted average (TWA) PEL values (available for 25% of the constituents), and NIOSH 10-hr TWA REL values (available for 24% of the constituents).

However, when narrowing to a subset of 95 constituents on the target analyte list, extant toxicity information was available for 78 of them (82%). Similarly, for the 31 constituents of interest in Tables 5-4 and 5-5, extant toxicity information was available for 25 of them (81%). The greatest sources of information for the chemicals of interest were IRIS values (available for 71% of Table 5-4 and 5-5 constituents), IARC cancer classifications (available for 68% of Table 5-4 and 5-5 constituents), CalOSHA 8-hr TWA PEL values (available for 65% of Table 5-4 and 5-5 constituents), and ACGIH values (61% of Table 5-4 and 5-5 constituents). No toxicity reference information was found in the information sources examined for six of the Table 5-5 constituents: benzothiazole, 2-hydroxybenzothiazole, N-cyclohexyl-cyclohexanamine, N-cyclohexyl-N-methylcyclohexanamine, hexadecane, or 4-tert-octylphenol. In addition to the target chemicals measured in this portion of the study, the presence of many other organic chemicals was found through non-targeted assessment. Further work would be needed to positively identify chemicals and their amounts, and to cross-reference with the availability of toxicity information for these chemicals.

While toxicity reference information was available for a higher proportion of the target analyte constituents and the constituents of interest than for the chemicals in the full list of potential constituents identified from the LRGA, data gaps remain for both sets of constituents. Potential toxicity-related information beyond the sources reviewed here may be available in the literature for some of these chemicals, but additional, significant effort would be required to identify and review such information for use in future human health risk assessments of tire crumb rubber.

The U.S. Department of Health and Human Services' National Toxicology Program has been exploring the feasibility of in vitro studies to assess bioaccessibility and cytotoxicity of the crumb rubber material (Gwinn et al., 2018), and in vivo studies to examine the short-term toxicity effects from various routes of exposure (Richey et al., 2018; Roberts et al., 2018). These 'bulk toxicity' approaches may provide avenues to develop more comprehensive data that would be needed for conducting human health risk assessments that address the cumulative risk of multiple chemical exposures. Overall, the large number of chemical constituents identified in recycled tire crumb rubber combined with the varying degree of availability of toxicity reference information for many of these chemicals presents challenges for understanding the potential human health risks from exposure to these chemicals.

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7.0 Appendices

The following Appendices can be found in Volume 2 of this report:

A Industry Overview

B Stakeholder Outreach

C State-of-Science Literature Review/Gaps Analysis

D Standard Operating Procedure (SOP) Lists for Tire Crumb Rubber Characterization Research

E Quality Assurance and Quality Control

F Synthetic Turf Field Facility Owner/Manager Questionnaire

G Shapiro-Wilk Test Results for Selected Tire Crumb Rubber Characterization Measurement Distributions

H Tire Crumb Rubber Particle Size Characterization Results and Sample Photos

I Tire Crumb Rubber Measurement Results – Summary Statistics

J Dynamic Chamber Emissions Measurements Time Series Test Results

K Tire Crumb Rubber Measurement Results – Differences Between Recycling Plants and Synthetic Turf Fields

L Tire Crumb Rubber Measurement Results – Replicate and Duplicate Analysis Precision and Homogeneity

M Tire Crumb Rubber Measurement Results – Within and Between Recycling Plant Variability

N Tire Crumb Rubber Measurement Results – Within and Between Synthetic Turf Field Variability

O Tire Crumb Rubber Measurement Results – Differences Between Outdoor and Indoor Synthetic Turf Fields

P Tire Crumb Rubber Measurement Results – Differences Among Synthetic Turf Fields with Different Installation Ages

Q Tire Crumb Rubber Measurement Results – Differences Among Synthetic Turf Fields in Different U.S. Census Regions

R Non-Targeted Screening Analysis Results for SVOCs and VOCs

S Targeted Microbiological Analysis Results for Tire Crumb Rubber Infill Samples Collected at Synthetic Turf Fields

T Dynamic Chamber Silicone Wristband Experiments

U Toxicity Reference Information

V Summary of External Peer Review Comments

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