Testing Artificial Turf Materials: Options and Lessons Learned



TURI Report #2021-002 April 2021

Acknowledgments

This report was prepared by Rachel Massey and Lindsey Pollard, with input from Liz Harriman and Greg Morose (TURI), Molly Jacobs (Lowell Center for Sustainable Production), and Jeff Gearhart (Ecology Center). The work presented in this report was supported by funding from the Heinz Endowments.



UMASS LOWELL

Toxics Use Reduction Institute University of Massachusetts Lowell The Offices at Boott Mills West 126 John St., Suite 14 (2nd floor) Lowell, MA 01852-1152 (978) 934-3275 • www.turi.org

Contents

Introduction	5
How to use this report	5
Goals of testing	5
Overview: Choosing chemicals to examine	6
Challenges related to standardization	6
Resources from federal agencies	7
TURI's experience with laboratory testing of turf materials	
Benzothiazole (testing conducted at ATS)	10
Flame retardants (testing conducted at the Stapleton Lab at Duke University)	11
PAHs (testing conducted at Mt. Sinai School of Medicine and ATS)	12
Mt. Sinai School of Medicine	12
ATS	
Phenols (testing conducted at AIRL, Inc.)	13
Phthalate esters (testing conducted at AIRL, Inc.)	
Volatile organic compounds (VOCs) (testing conducted at AIRL, Inc., and ATS)	14
AIRL, Inc	
ATS	
Incidental findings	15
Appendix A: Considerations related to metals	
Appendix B: Considerations related to polyaromatic hydrocarbons (PAHs)	
Appendix C: Testing play surfacing: suggestions and resources for communities	
References	23

List of Tables

Table 1: Artificial turf materials tested	9
Table 2: Summary of tests	10
Table 3: Benzothiazole measurements in four synthetic infill types	11
Table 4: Flame retardants examined at Stapleton Lab, Duke University	11
Table 5: Phenols measured in seven infills and a sample of artificial turf carpet	13
Table 6: Off-gassed volatile organic compounds measured in infill materials (ppb [µg/kg])	15
Table 7: AIRL: Incidental findings	16
Table 8: Categories of toy materials under EN 71-3	18
Table 9: EPA priority PAHs and EU-8 PAHs	20

(this page intentionally left blank)

Introduction

The Toxics Use Reduction Institute (TURI) has received many queries about options for testing artificial turf materials, including infill, carpet backing, and carpet fibers (artificial grass fibers). TURI has contracted with outside laboratories to conduct selected tests, and has reviewed literature on testing.

This report provides a record of the laboratory tests that TURI has ordered from both academic and private sector laboratories. In addition to providing information on the methods used and results obtained, the report notes lessons learned and factors that should be considered when planning tests. The report includes information on difficulties that can be encountered when testing play surfacing materials, as well as background information on certain chemical categories. This information may be useful for other organizations working to test artificial turf materials or materials used in playground surfacing.

Appendices A and B provide information on considerations related to testing of metals and of polyaromatic hydrocarbons (PAHs). PAHs are a broad category of chemicals that have been a particular source of concern in tire crumb. Finally, Appendix C provides pointers for organizations interested in conducting testing projects of their own.

How to use this report

This report is designed to be a companion to other TURI publications, and it should be used in combination with those other publications, depending on the reader's needs. The main findings of TURI's literature reviews and selected laboratory tests are presented in a 2018 report, *Athletic Playing Fields: Choosing Safer Options for Health and the Environment*,¹ and in a 2020 article, *Artificial Turf Infill: A Comparative Assessment of Chemical Contents*.² Most readers may wish to review the 2018 report and the 2020 article first, and then consult this report for more details if they plan to do additional testing of their own. In addition, readers should consult TURI's extended fact sheet, "Per- and Polyfluoroalkyl Substances (PFAS) in Artificial Turf," if they wish to conduct testing for PFAS.³

Goals of testing

Testing may be organized around several possible goals.

Testing for specific chemicals of concern. Testing may be designed to determine the presence, absence, or level of one or more specific chemicals of particular concern. For example, tests are frequently conducted to determine whether lead or other toxic metals are present in a material, and if so, at what level.

Material characterization. Testing may be designed to fully determine and describe a material's composition. This can include identifying all the chemicals present in the material and determining the percentages at which they are present. It can also include gathering information about other characteristics of the material, such as the range of particle sizes or the shape of those particles. Material characterization is more challenging than testing for individual chemicals.

Leaching tests. Some studies may use a variety of methods to assess leaching of chemicals from polymers. It is worth noting that leaching tests may not take account of the full range of environmental conditions to which a polymer may be exposed, including UV light, temperature extremes and mechanical abrasion.

Exposure assessment. Some tests are designed to help predict levels of human or environmental exposure to chemicals found in a material. For example, researchers may use in vitro bioaccessibility studies to estimate human exposures that could occur. These studies may use artificial fluids to simulate fluids in the human body (such as fluid in the lungs, in the digestive tract, or on the skin).

It is worth noting that exposure assessment research adds an additional level of complication to an already complex task. In addition to determining which chemicals to evaluate and what methods to use for detecting those chemicals, it is necessary to determine how best to simulate the human body's exposure conditions. Additional assumptions and modeling are necessary in order to draw even tentative conclusions from such testing. In this report we have not addressed exposure-related testing, and TURI has not been involved in any testing of this kind for play surfacing materials.

Overview: Choosing chemicals to examine

In deciding what chemicals to test for, it may be useful to consider both types of chemical and the functions performed by chemicals.

Chemical categories. Chemical categories of interest can include metals, volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), polyaromatic hydrocarbons (PAHs), thiazoles, amines, per-and polyfluoroalkyl substances (PFAS) and phenols.

Chemical categories may overlap with one another depending how they are defined by a particular laboratory. For example, a subset of PAHs may be included in a standard panel of SVOCs. In addition, any one of these categories can be defined in a variety of ways. For example, a test for metals can focus on just one or two metals of particularly high health or environmental concern, or can test for dozens of metals. Similarly, a PAH test can consider just a handful of PAHs or can encompass dozens or even hundreds of chemicals in this category.

Functional categories. Functional categories of interest can include vulcanization compounds, antimicrobials, and UV protectants.

Challenges related to standardization

Testing tire crumb presents a number of challenges related to standardization of test methods. Challenges include choosing what chemicals to test for, choosing what methods to use in those tests, and ensuring there is a method for checking the validity and repeatability of those methods and tests. Testing multiple infill materials adds additional challenges, as methods that are practical for testing tire crumb will not necessarily be usable in the same manner for other materials (for example, if those materials melt at high temperatures).

Some of these challenges have been described by the U.S. Environmental Protection Agency (EPA). An abstract for a 2017 presentation on analyses conducted by EPA and the Consumer Product Safety Commission (CPSC)

noted that "recycled crumb rubber is a complex and potentially variable matrix with many metal, VOC, and SVOC constituents, presenting challenges for characterization and exposure assessment. The material may also weather differently over time on fields, potentially increasing the variability in its chemical and physical properties." EPA also noted that "lack of reference materials and differences in methods and performance between laboratories may present some concerns for data comparability and exposure assessment."⁴ In their presentation poster, the researchers also noted that challenges for characterizing tire crumb included a lack of "suitable reference materials" for quality assurance and control, and that "differences in methods across studies may affect comparability."⁴ They also noted that "further non-targeted assessment" would be necessary in order to better understand the chemicals present in the material.

Researchers have also noted that due to the heterogeneity of crumb rubber, it is important to use a sampling method that includes adequate numbers of samples to characterize the homogeneity.

EPA's presentation focused solely on the analysis of tire crumb, but similar challenges can apply to other materials. For these reasons, it is important to understand the limits and challenges of testing, and to set realistic goals for any testing project.

Resources from federal agencies

Over the period 2016–2020, the US Environmental Protection Agency (US EPA), the Centers for Disease Control/Agency for Toxic Substances and Disease Registry (ATSDR), and the Consumer Product Safety Commission (CPSC) worked together to conduct research on tire crumb, the material used most widely as infill in artificial turf. This effort also included research on playgrounds. In the process of conducting this work, the agencies developed and refined methods for characterizing and testing tire crumb. The agencies did not focus on other infill materials. As part of this effort, the National Toxicology Program (NTP) carried out a series of studies on tire crumb as well.

The work of these federal agencies had not yet been completed at the time TURI undertook some of its efforts related to laboratory testing. Now that these federal agencies have completed their work, communities interested in gathering test data should begin any project by reviewing the relevant methods used by these agencies. Communities may wish to go beyond the tests conducted by the federal agencies, or may wish to use different methods, but it is useful to take account of those methods as a starting point.

At the same time, it is important to understand that the methods used by the federal agencies may not be usable for materials other than waste tire material. For example, the temperature used for off-gassing tests may not be appropriate for materials that behave differently at high temperatures, such as thermoplastic elastomers (TPE). Similarly, a solvent extraction method that works well for characterizing chemicals present in waste tire material may not function equally well for characterizing another material. Nonetheless, in the absence of other standardized methodologies, the methods developed by the federal agencies for testing waste tire materials can serve as a useful starting point.

EPA's Standard Operating Procedures (SOPs). EPA has published a set of standard operating procedures (SOPs) for materials characterization research on tire crumb.⁵ These SOPs include procedures for both sample collection and laboratory analysis. The laboratory SOPs include procedures for analyzing formaldehyde, VOCs, SVOCs, and metals. EPA notes that its SOPs were developed for research purposes, and "are not official EPA"

methods. They are made available as a reference for anyone interested in pursuing additional research, and/or modifying or implementing some of the procedures."

In its material characterization research, EPA conducted targeted analyses of 21 metals, 49 SVOCs, and 31 VOCs, as well as examining other factors such as particle sizes and indicators of the presence of bacteria.⁶ EPA focused solely on tire crumb and did not analyze other components of the artificial turf system or any other infill materials.⁶

NTP. A 2019 National Toxicology Program (NTP) report provides an overview of work conducted by NTP to characterize a set of tire crumb samples using a variety of techniques.⁷ NTP's methods included microscopy to determine the range of particle sizes; thermogravimetric analysis to determine fraction by weight of volatile organic compounds (VOCs) and inorganic compounds; elemental analysis to determine the presence of certain metals; and analysis of VOCs using gas chromatography and mass spectrometry.

The choice of solvent can affect which chemicals are identified in a material. NTP conducted extractions using a variety of solvents and determined what portion of the material could be extracted from tire crumb using six possible solvents: water, ethanol, ethyl acetate, hexane, methylene chloride, or carbon disulfide.

NTP's publications can serve as a useful reference for reviewing methods. Equipment, materials and methods are described in detail for each type of analysis. A community or institution wishing to contract with a commercial or academic laboratory to study any of the parameters covered by NTP could ask the laboratory to follow the exact methods used by NTP, in order to achieve comparable results. It is important to bear in mind, however, that these methods were developed for characterizing tire crumb; they could be useful for other materials as well, but have not been validated for other materials.

TURI's experience with laboratory testing of turf materials

In 2018–2019, TURI undertook a project of testing selected artificial turf materials for a subset of the chemicals of concern that could be present in these materials. The goal of the project was to help fill gaps in publicly available information about chemical contents of infill other than tire crumb (alternative infills). In addition, the project sought to identify lessons that could be learned through the testing experience. Standardized testing protocols for artificial turf materials were not available at the time when these tests were conducted. Since these tests were conducted, some standardized procedures have been published by federal agencies for research on tire crumb, as described above; however, there are still open questions about best practices for testing other play surfacing materials. TURI's experience may be helpful to others attempting to test artificial turf materials or working to understand the range of test results that are already available.

More extensive information on methods used to analyze chemicals in tire crumb can be found in recent publications from US EPA and the NTP, as described above. In addition, methods for tire crumb analysis can be found in many individual studies conducted by academic or government researchers. It is important to note that the vast majority of these studies have focused only on tire crumb, and have not compared tire crumb with the other rubber, plastic or plant- and mineral-based materials that are marketed as alternatives for tire crumb in artificial turf applications. Methods that are validated for use in analyzing tire crumb may be useful for these other materials as well, but this question needs to be examined in each case before proceeding with testing. *Materials tested*. TURI contracted with laboratories for limited testing on five synthetic infill materials, two plant-based infill materials, and one sample of artificial turf carpet (grass fibers and backing). Some tests were conducted on all the materials, and some were conducted on a subset. These materials are summarized in Table 1.

Material	Use
Tire crumb	Infill
Ethylene propylene diene terpolymer (EPDM)	Infill
Thermoplastic elastomer (TPE)	Infill
Acrylic-coated sand	Infill
Waste athletic shoe material	Infill
Plant-based - made from walnut shells	Infill
Plant-based - made from a coconut-cork mix	Infill
Artificial turf carpet	Carpet

Table 1: Artificial turf materials tested

Chemicals included in the tests. These tests were conducted to determine presence and concentration of phthalates, phenols, volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons (PAHs) in all the infill materials. For the artificial turf carpet, the tests examined phthalates, phenols, and VOCs. TURI also sent three synthetic infill materials to an academic laboratory for flame retardant testing.

Metals were not included in TURI's test effort. Information on metals is important, but TURI did not prioritize metals because knowledge in this area was already well developed. Information on presence and concentration of metals is provided routinely by vendors, and can be repeated by communities as needed. In contrast, vendors do not necessarily make information readily available for other chemical categories, and communities may lack a clear starting point for investigating these other categories. Considerations related to interpreting vendor information on metal testing can be found in Appendix A.

Laboratories. TURI's work to test artificial turf materials was carried out with two academic laboratories and two commercial laboratories. The academic laboratories were at the Icahn School of Medicine at Mt. Sinai (Dr. Homero Harari) and at Duke University (Dr. Heather Stapleton). The commercial laboratories were AIRL, Inc., in Cleveland, TN, and Applied Technical Services (ATS) in Atlanta, GA. TURI does not endorse any individual laboratory.

Limits of detection. In the discussion below, information is provided on the sample detection limit and the calibration detection limit for certain tests. The sample detection limit refers to the lowest level of the chemical that the laboratory equipment can detect. The calibration detection limit refers to the level to which the equipment was calibrated for the individual test. In some cases, these are the same.

Table 2 provides an overview of the tests that were carried out in this project.

Table 2: Summary of tests

Chemicals	Laboratories	Summary
Benzothiazole	AIRL, Inc.	 Initially identified through incidental findings; identified as a priority for follow-up tests. Detected in 3 out of 4 infill materials tested.
Flame retardants (selected)	Duke University	 3 infill materials screened for 9 flame retardants; none detected.
PAHs	Mt. Sinai; ATS	 Mt. Sinai (7 infill materials tested): PAHs detected in all samples, varying levels. ATS (4 infill materials tested): PAHs not detected in any samples (likely due to a problem with methods).
Phenols	AIRL, Inc.	 7 infill materials and 1 carpet sample tested. Of 7 chemicals examined, 1 was detected in tire crumb. No chemicals in this category were detected in the other materials.
Phthalates	AIRL, Inc.	 7 infill materials and 1 carpet sample tested. No phthalates detected.
VOCs	AIRL, Inc.; ATS	 AIRL – no VOCs detected. ATS – some VOCs detected in all four samples.
OTHER – Incidental findings	AIRL, Inc.	 AIRL reported several incidental findings; these findings led to chemical-specific testing for benzothiazole.

Benzothiazole (testing conducted at ATS)

Background information. Benzothiazole, which is used as a vulcanization agent, has been identified as a concern in tire crumb. Health hazards of benzothiazole include respiratory irritation and dermal sensitization, and laboratory testing suggests the potential for carcinogenic effects. A structural analogue,

2-mercatobenzothiazole, which has been more extensively tested, "is a rodent carcinogen with rubber industry data supporting an association with human bladder cancer."⁸

In incidental findings provided to TURI by AIRL, benzothiazole appeared in EPDM. For these incidental findings, the laboratory was only able to provide information on presence/absence of a chemical, not on concentration. Thus, TURI decided to have ATS test all four samples of synthetic infill specifically for benzothiazole in order to understand whether levels in alternative infills were similar to those in tire crumb.

Approach. ATS conducted the benzothiazole testing using EPA Method 3545A: Pressurized Fluid Extraction (PFE) and EPA Method 8270D: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS).

Results. As shown in Table 3, benzothiazole concentration levels were highest in tire crumb. Waste athletic shoe material was an order of magnitude lower than tire crumb, and EPDM was two orders of magnitude lower than waste athletic shoes. Benzothiazole was not detected in TPE. This finding is consistent with the use of benzothiazole as a vulcanizing agent; tire crumb, shoe material, and EPDM are vulcanized materials, whereas TPE is not.

Comments. This finding adds to existing knowledge about the comparison among infill types. If these samples are representative, alternative infills may be expected to have lower levels of benzothiazole compared with tire crumb, even if vulcanized materials are used.

Material	Benzothiazole (ppb, μg/kg)
Tire crumb	45,000
Shoe material	1,980
EPDM	34
TPE	n.d. (<25)*

Table 3: Benzothiazole measurements in four synthetic infill types

*n.d. indicates no detection of substance.

Flame retardants (testing conducted at the Stapleton Lab at Duke University)

Approach. The laboratory screened three infill samples (tire crumb, EPDM, and TPE) for the presence of nine flame retardants (individual chemicals and mixtures). The detection limit for these measurements was 0.1% by weight. The flame retardants included in the screening are listed in Table 4. These flame retardants are commonly found in furniture, and have been the focus of the furniture foam testing project led by Heather Stapleton at Duke University.⁹

Results. None of these particular flame retardants were measured above this detection limit for any of the three infill samples.

Comments. This screening test provided preliminary information on three commonly used infills, indicating that they are unlikely to contain the nine flame retardants tested. The test did not provide information on other turf materials, including carpet fibers and backing, on other infills, or on other flame retardants.

Pentabromodiphenyl ether (PentaBDE) Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) Tris(1-chloro-2-propyl)phosphate (TCPP)
Tris(1-chloro-2-propyl)phosphate (TCPP)
Tris-isobutylated triphenyl phosphate (TBPP)
Isopropyl triphenyl phosphate (ITP Mix)
Methyl phenyl phosphate (MPP Mix)
2,2-bis(chloromethyl)propane-1,3-diyltetrakis(2-chloroethyl) bisphosphate (V6)
e Firemaster [®] 550 (FM 550)
Firemaster [®] 600 (FM 600)

Table 4: Flame retardants examined at Stapleton Lab, Duke University

Information drawn from: Duke University Superfund Research Center. "Flame Retardant Chemicals Commonly Found in Furniture." Durham, NC. Retrieved from

http://foam.pratt.duke.edu/sites/foam.pratt.duke.edu/files/images/Common Flame Retardants 92718.pdf

PAHs (testing conducted at Mt. Sinai School of Medicine and ATS)

Background information. TURI contracted with two laboratories to test for PAHs in infill materials. For more information on considerations related to testing PAHs, see Appendix B.

Mt. Sinai School of Medicine

Approach. The laboratory examined the 16 PAHs on EPA's priority list using a novel method for solvent extraction.

Results. All the PAHs on the EPA priority list were detected in the tire crumb samples. In addition, certain PAHs were detected some of the alternative infill samples. The tire crumb sample contained the largest total PAH level. Waste athletic shoe material and EPDM had the next largest total PAHs, although they were both an order of magnitude lower than tire crumb.

Looking at just the subset of PAHs on the list that have been classified in the International Agency for Research on Cancer (IARC) Groups 1, 2A, or 2B, tire crumb had the highest levels, followed by EPDM and waste athletic shoe material.

ATS

Approach. TURI provided a separate set of four samples (tire crumb, EPDM, TPE and waste shoe material) to ATS laboratories to have them tested for a larger group of 21 PAHs.^a

We also inquired about the possibility of testing for specific PAHs that have been found in tire crumb in recent studies such as that by Donald et al. (as discussed in Appendix B). For example, we hoped to test for dibenzo[def,p]chrysene and benzo[c]fluorene. However, ATS did not have the capacity to test for these PAHs.

ATS used the EPA Method 3545A: *Pressurized Fluid Extraction (PFE)* and EPA Method 8270D: *Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GCIMS)*. ATS used a low detection limit of 200 parts per billion (ppb, or µg/kg).

Results. ATS did not detect PAHs in any of the materials.

Comments. In general, ATS uses three solvents for PAH testing: toluene, methylene chloride, and iso-octane. The first two were not compatible with the samples, so the laboratory chose to use iso-octane in this case. Because of this solvent choice, the results have limited value. Other studies have clearly demonstrated the presence of PAHs in tire crumb. Since ATS did not detect PAHs in tire crumb, their results are also not likely to be useful for the other materials tested.

^a Specifically, ATS tested for the following PAHs: Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[e]pyrene, benz[e]acephenanthrylene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene.

For comparison, one published study (Menichini et al. 2011) used methylene chloride followed by n-hexane as extraction solvents for studying PAHs in tire crumb.¹⁰

Phenols (testing conducted at AIRL, Inc.)

Approach. The laboratory used a solvent extraction method, ASTM D 7065: *Standard Test Method for* Determination of Nonylphenol, Bisphenol A, p-tert-Octylphenol, Nonylphenol Monoethoxylate and Nonylphenol Diethoxylate in Environmental Waters by Gas Chromatography Mass Spectrometry, to measure seven phenols, including bisphenol A, nonylphenols, and octylphenols. The laboratory applied these methods to both infill and carpet samples. The lowest calibration level varied depending on the chemical, as shown in Table 5.

The laboratory also considered an alternative testing option, EPA method 625/8270C. This method measures a longer list of phenols, but excludes bisphenol A. Based on existing literature and community queries, TURI was primarily interested in the nonylphenols, octylphenols, and bisphenol A; therefore, this alternative method was not chosen.

Results. 4-tert-octylphenol was measured at 9.035 ppm in tire crumb. No other phenols were detected above the lowest calibration level in any of the infill and carpet materials.

Comments. The presence of 4-tert-octylphenol in the tire crumb sample is consistent with other studies of tire crumb.¹¹ The results suggest that the alternative materials could either be free of, or have lower levels of, this particular chemical of concern.

It is important to note that the ASTM method used in this test has not been validated for solid materials. EPA's SOP includes testing of 4-tert-octylphenol in tire crumb, so this may be a useful resource for design of future tests.⁵

0.32	n.d.
0.32	9.035 in tire crumb
1.6	n.d.
0.32	n.d.
0.32	n.d.
6.4	n.d.
3.2	n.d.
	0.32 1.6 0.32 0.32 6.4

Table 5: Phenols measured in seven infills and a sample of artificial turf carpet

* Results for all materials have been combined in one column. n.d. indicates no detection of the substance in any sample.

Phthalate esters (testing conducted at AIRL, Inc.)

Approach. TURI provided AIRL with samples of the seven infill types listed above in Table 1, and a sample of artificial turf carpet. The laboratory used method CPSC-CH-C1001-09.4: *Determination of Phthalates, January 17, 2018.* The lowest calibration level and sample detection level were 0.01% by weight for all the phthalates. AIRL tested for the presence of six phthalates: bis(2-ethylhexyl)phthalate, butyl benzyl phthalate, diisodecyl phthalate, di-n-butylphthalate, and di-n-octylphthalate.

Results. No phthalates were detected in any of the materials.

Comments. Other studies have detected phthalate esters in several synthetic infill materials.²

Volatile organic compounds (VOCs) (testing conducted at AIRL, Inc., and ATS)

TURI contracted with two commercial laboratories for testing of VOCs using both solvent extraction (to determine material composition) and off-gassing (to determine releases from the material).

AIRL, Inc.

Approach - Solvent Extraction. AIRL used method EPA 8260B: *Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry* to extract and measure 22 VOCs, shown in the table below. The lowest calibration level and sample detection limit was 25 ppb (or µg/kg) for all chemicals.

Results. The lab was not able to detect VOCs above the lowest calibration level (25 ppb) in any of the materials.

Comments. The lab used water as the extracting solvent. Water was an inappropriate solvent to extract VOCs, except for a study intended specifically to test for leaching into water. This result is noted here as a caution related to clarifying the extraction solvent to be used by the laboratory and ensuring it is appropriate for the purpose.

ATS

Approach - Off-gassing. ATS tested off-gassing of VOCs in four infill materials: tire crumb, EPDM, TPE, and waste athletic shoe material. ATS heated samples to 120 degrees Celsius and used method ASTM D4526-12: *Standard Practice for Determination of Volatiles in Polymers by Static Headspace Gas Chromatography* to measure 22 VOCs.

Results. The lab detected nine VOCs in tire crumb, ten in EPDM, two in TPE, and seven in the shoe material, as shown in Table 6.

Substance	Tire crumb	EPDM	Shoe material	TPE
1,2-Ethanediol	n.d.	223	n.d.	n.d.
2,2'-Oxybis-ethanol	n.d.	362	n.d.	n.d.
2-Butanone	n.d.	274	n.d.	n.d.
2-Ethyl-1-hexanol	n.d.	n.d.	n.d.	613
2-Methoxy-ethanol	n.d.	19,800	n.d.	n.d.
2-Methyl-2-propanamine	395	n.d.	n.d.	n.d.
2-Methyl-2-propanol	n.d.	3,050	289	n.d.
2-Methylfuran	256	n.d.	n.d.	n.d.
Acetaldehyde	n.d.	1,540	n.d.	n.d.
Acetic acid	196	n.d.	n.d.	n.d.
Acetone	583	1,250	252	n.d.
Alpha-cumyl alcohol	n.d.	n.d.	191	n.d.
Benzothiazole	262	n.d.	n.d.	n.d.
Butylated hydroxytoluene	n.d.	n.d.	1,180	n.d.
Carbon disulfide	n.d.	n.d.	211	n.d.
Cyclohexanone	254	n.d.	n.d.	n.d.
Ethanol	1,180	194	2,150	n.d.
Glycerin	n.d.	n.d.	n.d.	1,140
Isopropyl alcohol	n.d.	n.d.	364	n.d.
Methyl alcohol	n.d.	1,000	n.d.	n.d.
Methyl isobutyl ketone	3,600	n.d.	n.d.	n.d.
Poor match (i.e., unknown compound)	229	n.d.	n.d.	n.d.
Propanal	n.d.	207	n.d.	n.d.

Table 6: Off-gassed volatile organic compounds measured in infill materials (ppb [µg/kg])

Incidental findings

Approach. AIRL also provided TURI with information on certain chemicals that were incidentally detected in the materials while testing for the chemicals we had requested. These are chemicals for which peaks were visible; they are not necessarily the highest-quality results or the most significant additional chemicals in these materials.

Results. Table 7 shows these incidental findings.

Comments. Of the chemicals listed, one interesting finding was the presence of benzothiazole in the EPDM sample. Benzothiazole had been flagged as a concern in tire crumb,¹² so TURI was interested in understanding whether it was present in other materials as well. This finding led to follow up testing, in which the laboratory tested concentrations of benzothiazole. The finding of a diisocyanate in the grass carpet material is not likely to be meaningful or accurate, as this chemical is too reactive to remain in the material.

Table 7: AIRL: Incidental findings

Material	Substance	CAS #
Tire crumb	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl	793-24-8
Waste shoe material	Phenol, 2,4,6-tris(1-methylethyl)-	2440-22-4
FPDM	Toluene-4-sulfonic acid, 2,7-dioxatricyclo[4.3.1.0(3,8)]dec-10-yl ester	n/a
EPDM	Benzothiazole	95-16-9
TPE	Drometrizole	2440-22-4
Plant based: coconut & cork	2-sec-Butyl-4,6-dinitrophenyl 3-methylcrotonate (binapacryl)	485-31-4
Carpet	Benzene, 1,1'-methylenebis[4-isocyanato-	101-68-8

Appendix A: Considerations related to metals

(Note: information presented in this appendix originally appeared in TURI's 2017 document, "Chemicals in Artificial Turf: Overview"¹³)

As noted above, TURI did not focus on testing for metals because information on metals is more readily available than information on the other compounds discussed here. However, many communities may wish to focus on metals before considering other chemical categories.

A number of tests have been designed to examine infill in relation to the European Standard EN 71-3: *Safety of Toys Part 3: Migration of certain elements.* EN 71-3 "specifies requirements and test methods" for migration of 19 metals or categories of metal compounds from "toy materials and from parts of toys."¹⁴

Since this test is cited frequently, it may be useful to understand its structure. As shown in Table 2, below, the standard divides toy materials into three categories: Category I ("dry, brittle, powder like or pliable materials"), Category II ("liquid or sticky materials"), and Category III ("scraped-off materials").

For each category, certain assumptions have been made about the amount a child may ingest in the course of play. For Category II, the standard is based on an assumption that a child may ingest 400 mg per day of the material. For Category III, the standard is based on an assumption of a much lower level of ingestion of the material, at 8 mg per day. Category I makes an intermediate assumption that a child may ingest 100 mg per day.

Corresponding to these assumptions about ingestion, Category III has the highest values for each metal (i.e., it is the easiest standard for a material to meet) and Category II provides the lowest values (i.e., it is the most difficult standard for a material to meet). For example, for lead, Category III allows the presence of up to 160 mg/kg of lead in the material, while Category II allows up to 3.4 mg/kg.

A number of manufacturers have compared the results of their infill tests against the Category III values. For purposes of TURI's analysis, we have checked those same results against the somewhat more stringent Category I values. Regardless of the category used, it is important to note that the EN 71-3 standard was designed for toys, and may have limited applicability to synthetic turf infill.

ASTM standard. In 2016, ASTM International issued a standard for testing infill for certain metals, measuring the amount to which players could be exposed in case of accidental ingestion of the infill. A number of industry groups announced that they would voluntarily adopt the standard, ASTM F3188-16.¹⁵

	Category 1	Category II	Category III
Category description	"Dry, brittle, powder like or pliable materials"	"Liquid or sticky materials"	"Scraped-off materials"
Additional information	"[I]ncludes solid <i>toy</i> <i>material</i> from which powder- like material is released during play. The material can be ingested. Contamination of the hands with powder contributes to enhanced oral exposure."	"[I]ncludes fluid or viscous <i>toy material</i> which can be ingested and/or to which dermal exposure occurs during playing."	"[I]ncludes solid <i>toy</i> <i>material</i> with or without a <i>coating</i> which can be ingested as a result of biting, tooth <i>scraping</i> , sucking or licking. This category includes those materials which are not covered by category I and II."
Categorization of "common toy materials": Examples	 "Compressed paint tablets, materials intended to leave a trace (e.g. the cores of colouring pencils, chalk, crayons)" "Pliable modelling materials, including modelling clays" 	"Liquid paints""Glue sticks"	 "Coatings of paints" "Polymeric and similar materials, including laminates" "Paper and board" "Textiles" "Glass, ceramic, metallic materials," "Other materials (e.g. wood, fibre board)"
Assumed ingestion (mg/day)	100	400	8
Sample value: Lead (mg/kg)**	13.5	3.4	160

Table 8: Categories of toy materials under EN 71-3

Source: European Standard EN 71-3:2013+A1. October 2014. ICS 97.200.50. *Safety of Toys – Part 3: Migration of Certain Elements*. Available at <u>https://law.resource.org/pub/eu/toys/en.71.3.2015.html</u>. Information shown here is drawn from Table 1 (Cross-reference table for determining category), Table 2 (Migration limits from toy materials), and Annex H (Rationale).

Appendix B: Considerations related to polyaromatic hydrocarbons (PAHs)

Polyaromatic hydrocarbons (PAHs) are a group of chemicals that can be manufactured intentionally, or can be formed incidentally through incomplete burning of organic substances. A number of PAHs have been identified as known or suspected human carcinogens by the International Agency for Research on Cancer.¹⁶

People can be exposed to PAHs through a variety of routes, such as cigarette smoke and ambient air pollution. In addition, PAHs have been identified as a particular source of concern in tire crumb. Highly aromatic oils used in tire manufacturing are an important source of PAHs in the material.¹⁷

Given these concerns, communities often have questions about PAH levels in both tire crumb and alternative infills. Some communities may request information on PAHs from vendors, while others may wish to conduct their own testing. In this context, it is useful to understand some background information related to the lists of PAHs that may be used in designing laboratory tests.

EPA's PAH Priority Pollutants. There are hundreds of PAHs. However, many PAH testing efforts – whether for tire crumb, for soil, or for other environmental media – use a list of 16 PAHs that are designated by EPA as Priority Pollutants under the Clean Water Act. This list of 16 PAHs was created in the 1970s, and it has been used consistently across many research projects and over many years. The list of 16 PAH Priority Pollutants has been useful in many ways. It provides comparability and consistency across many projects. Use of this list has made it possible to refine and standardize testing methods, and to track trends in a consistent representative sample of PAHs over time. However, the list of 16 PAH Priority Pollutants does not include all PAHs of concern, and researchers have expressed concern that focusing on this list alone can lead to important toxicity information being missed.¹⁸

Researchers including Andersen and Achten (2015) have proposed creation of an expanded list that could be used as a standard resource for researchers. Such a list would include the chemicals on EPA's original list as well as a number of additional PAHs that are of equal or greater concern for human health and the environment.¹⁸

EU-8. In the European Union, a regulatory proposal has been made to limit the levels of eight PAHs in sports turf infills and in materials used in loose form on playgrounds.¹⁹ These eight PAHs are regulated as carcinogens under the European Union's Registration, Evaluation and Authorization of Chemicals (REACH) regulation.

The list of eight PAHs regulated as carcinogens under REACH (referred to in some publications as EU-8), overlaps with, but is not an exact subset of, the EPA priority list of 16. Six of the EU 8 PAHs are on the EPA priority list, while two are not, as shown in Table 9.

Additional PAHs of interest. The EPA priority list and the EU8 list may be useful as preliminary indicators of PAH content, but they omit many chemicals of possible importance. In fact, PAHs that are not on these lists may be more important from a health standpoint than PAHs that are on the lists. Certain PAHs are much more carcinogenic than those that are traditionally measured in the standard EPA priority list, so it is important to understand whether they are present in infill materials.²⁰

Donald et al. (2019) expanded the information available on PAH exposures associated with tire crumb infill by using silicone wrist bands to study PAHs released to air from artificial turf fields.²¹ This study identified a number of PAHs that had not been addressed in prior studies. Some of these PAHs may pose greater carcinogenicity concerns than those that are studied more routinely.^{2, 21} For example, Donald et al. highlighted benzo[c]fluorene as a concern; this PAH has "an estimated carcinogenic potency 20 times greater than benzo[a]pyrene," and has been identified in other areas of research as "a large contributor to the atmospheric carcinogenic risk of PAHs."^{21, 22} Donald et al. also identified a number of oxygenated PAHs and other chemicals that had not been captured in EPA's literature review and that could be worthy of further attention.

Expanding the list of PAHs of interest can present some additional complications related to methods and standards. For example, laboratories may not have standards readily available for testing infills for some of the PAHs that have not been a focus to date.

Carcinogenicity information. All but one of the EPA priority PAHs have been evaluated by the International Agency for Research on Cancer (IARC) with regard to carcinogenicity. Group 1, the highest level of concern, consists of chemicals that are known human carcinogens. Groups 2A and 2B, respectively, refer to chemicals that are "probably" and "possibly" carcinogenic to humans. A chemical categorized in Group 3 is "not classifiable as to its carcinogenicity in humans." As shown in Table 9, of the PAHs on the EPA priority list, one is classified in IARC Group 1 (carcinogenic to humans); one is in Group 2A (probably carcinogenic to humans); and seven are in Group 2B (probably carcinogenic to humans).

Table 9 shows the PAHs included on the EPA priority list; those on the EU-8 list; and the IARC classifications for each.²³

Chemical name	EPA Priority list of PAHs	EU-8 list of PAHs	IARC group
Acenaphthene	Х		3
Acenaphthylene	Х		n/a
Anthracene	Х		3
Benzo[a]anthracene	Х	Х	2B
Benzo[a]pyrene	Х	Х	1
Benzo[e]pyrene		Х	3
Benzo[b]fluoranthene	Х	Х	2B
Benzo[g,h,i]perylene	Х		3
Benzo[j]fluoranthene (BjFA)		Х	2B
Benzo[k]fluoranthene	Х	Х	2B
Chrysene	Х	Х	2B
Dibenzo[a,h]anthracene	Х	Х	2A
Fluoranthene	Х		3
Fluorene	Х		3
Indeno[1,2,3-cd]pyrene	Х		2B
Naphthalene	Х		2B
Phenanthrene	Х		3
Pyrene	Х		3

Table 9: EPA priority PAHs and EU-8 PAHs

Appendix C: Testing play surfacing: suggestions and resources for communities

Before starting a testing project, be sure to clarify the purpose of your project. If you are working to make a decision about a potential future installation, you may wish to focus on obtaining test results from the vendor(s) with which you are communicating, and seeking expertise as needed for interpreting the information provided by the vendor. On the other hand, if you are concerned about a material that has already been installed, you may wish to collect your own samples and send them to a laboratory, preferably with assistance from an organization that has expertise in planning and understanding laboratory testing.

There are several challenges associated with conducting laboratory testing for consumer products, including artificial turf. Testing for metals is the most straightforward option, but provides only a limited set of information. When testing for other compounds, it is necessary both to define what compounds are of interest, and what methods will be used to test for them.

The following tips may be useful when planning a testing project.

1. Ask the vendor for all available information

Before conducting your own tests, contact the vendor and request information on all the chemicals of interest. In addition to metals, this should include benzothiazole and other vulcanization compounds; PAHs; phthalate esters; VOCs; semivolatile organic compounds; phenols; and per- or polyfluorinated alkyl substances. Some of these categories may overlap with one another.

In addition, within these categories, the vendor should make clear how many individual chemicals have been tested. For example, if the vendor provides information on PAHs, check to see how many PAHs the vendor has tested for.

2. Gather information on past testing

Find out whether other organizations have already tested play surfacing materials for the chemical(s) you are concerned about. Check to see if the answers to your questions are available in published literature. If you are interested in testing tire crumb, which has been studied extensively already, be sure to find out if the chemical in question has already been examined in prior studies. EPA's 2016 literature review is a good starting point, as it comprehensively covers everything that was examined prior to that date.¹¹ Clarify what new information will be added if you conduct your own tests.

In addition, check whether there are published methods for examining the chemical(s) you are interested. Start by checking the methods used by NTP and EPA, while bearing in mind these methods were developed for tire crumb, not for other materials.

3. Understand the purpose of the tests

If you are testing for a subset of all the chemicals that may be present, define your goals up front. For example, is the goal to determine presence/absence of lead and other toxic metals? What will be the implications of any test results obtained?

Understand the difference between testing for chemical contents of the material and testing for exposure.

4. Ensure that methods are clearly defined

When working with a commercial laboratory, gather information about the methods the laboratory will be using. For example, for a solvent extraction test, it is important to determine what extraction solvent will be used and to ensure that the solvent is an appropriate choice for the materials being studied. For an off-gassing test, it is important to verify the temperature at which off-gassing will be measured. If the laboratory will be testing a material that can melt at high temperatures, check that the methods selected will function correctly at the desired temperature.

If the laboratory is planning to use an EPA standard, check whether it is a method that has been used for infill materials in the past. Similarly, if the laboratory is following the methods from a published study, ensure the laboratory will use the same methods for sample preparation and analysis that were used in that study. Finally, check what approaches the laboratory has in place for quality assurance and quality control (QA/QC).

5. Resources – nonprofit organizations with lab testing expertise

It may be helpful to partner with a nonprofit organization that has expertise in testing. For example, the Ecology Center in Ann Arbor, MI, has a program that tests a range of consumer products for chemicals of concern. The Ecology Center has conducted tests of both artificial turf and playground surfacing materials. The Center for Environmental Health (CEH) in Oakland, CA, also has expertise in testing consumer products.

6. Resources - lead testing

For lead testing, EPA provides a list of laboratories that have been accredited to conduct testing of paint chips, dust or soil samples.²⁴ These laboratories are generally able to test artificial turf materials as well. For the list of laboratories, see: <u>www.epa.gov/lead/national-lead-laboratory-accreditation-program-nllap.</u>

Running a single lead test is simple and low-cost (around \$50 per sample). For example, one community member contacted TURI for advice about how to test lead in pour-in-place playground surfacing material at a school. The community member chose to send the sample to Con-Test in East Longmeadow, MA. The laboratory sent a cooler and a jar for submitting the sample, and the results were returned within three weeks.

Another option in some cases is to use a hand-held X-ray fluorescence (XRF) meter to check lead levels. Some organizations have used this approach for testing playground surfacing.

References

- 1. Toxics Use Reduction Institute (TURI). 2018. *Athletic Playing Fields: Choosing Safer Options for Health and the Environment. TURI Report #2018-002*. Retrieved from www.turi.org/artificialturfreport
- 2. Massey, R., Pollard, L., Jacobs, M., Onasch, J., & Harari, H. 2020. Artificial turf infill: a comparative assessment of chemical contents. *New Solutions*, *30*(1), 10–26.
- Toxics Use Reduction Institute (TURI). 2020. Per- and Poly-fluoroalkyl Substances (PFAS) in Artificial Turf Carpet. Retrieved from https://www.turi.org/TURI_Publications/TURI_Chemical_Fact_Sheets/PFAS_in_Artificial_Turf_Carpet?fbc lid=IwAR0DfBbF5E-f_ZwcdH7YGkhleugP_gMxPBuS6cxnABvWQpngF9SuQoJdN04,
- Thomas, K., & Irvin-barnwell, E. (n.d.). Chemical and Physical Analysis Methods for Characterizing Tire Crumb Rubber Used in Synthetic Turf Fields (p. 2). Retrieved from https://cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryId=338350&Lab=NERL
- U.S. Environmental Protection Agency Office of Research and Development. 2018. *Tire Crumb Characterization Study: Field Collection and Laboratory Standard Operating Procedures (SOPs). EPA/600/R-18/238.* Washington, DC. Retrieved from https://www.epa.gov/sites/production/files/2019-07/documents/tire_crumb_characterization_study_field_collection_and_laboratory_standard_operating _procedures_sops.pdf
- 6. U.S. Environmental Protection Agency. (n.d.). EPA Tools and Resources Webinar: Final Report Part 1: Tire Crumb Characterization. U.S. Federal Research Action Plan (FRAP) on Recycled Tire Crumb Used on Synthetic Turf Playing Fields and Playgrounds. August 6, 2019. Retrieved from https://www.epa.gov/sites/production/files/2019-08/documents/tc_public_webinar_-_august_6_2019.pdf
- National Toxicology Program (NTP). 2019. The Chemical and Physical Characterization of Recycled Tire Crumb Rubber; NTP RR-11. Retrieved from https://ntp.niehs.nih.gov/ntp/results/pubs/rr/reports/rr11_508.pdf
- 8. Ginsberg, G., Toal, B., & Kurland, T. 2011. Benzothiazole Toxicity Assessment in Support of Synthetic Turf Field Human Health Risk Assessment. *Journal of Toxicology and Environmental Health, Part A*, 74(17), 1175–1183.
- Duke University Superfund Research Center. (n.d.). Flame Retardant Chemicals Commonly Found in Furniture. Durham, NC. Retrieved from http://foam.pratt.duke.edu/sites/foam.pratt.duke.edu/files/images/Common Flame Retardants_92718.pdf
- Menichini, E., Abate, V., Attias, L., De Luca, S., di Domenico, A., Fochi, I., Forte, G., Iacovella, N., Iamiceli, A. L., Izzo, P., Merli, F., & Bocca, B. 2011. Artificial-turf playing fields: Contents of metals, PAHs, PCBs, PCDDs and PCDFs, inhalation exposure to PAHs and related preliminary risk assessment. *Science of The Total Environment*, 409(23), 4950–4957.
- 11. U.S. Environmental Protection Agency (US EPA). 2016. *Literature Review and Data Gap Analysis Spreadsheet*. Retrieved from https://www.epa.gov/chemical-research/december-2016-status-report-federal-research-action-plan-recycled-tire-crumb
- 12. Ginsberg, G., Toal, B., Simcox, N., Bracker, A., Golembiewski, B., Kurland, T., & Hedman, C. 2011. Human Health Risk Assessment of Synthetic Turf Fields Based Upon Investigation of Five Fields in Connecticut. *Journal of Toxicology and Environmental Health, Part A*, 74(17), 1150–1174.
- 13. Massey, R., & Onasch, J. 2017. Sports Turf Alternatives Assessment: Preliminary Results: Chemicals in

Artificial Turf Infill: Overview. Lowell, MA. Retrieved from https://www.turi.org/content/download/10747/177072/file/Infills Artificial Turf. February 2017.pdf

- 14. European Committee for Standardization. EN 71-3:2013+A1: Safety of toys Part 3: Migration of certain elements (2014). Retrieved from https://law.resource.org/pub/eu/toys/en.71.3.2015.html
- 15. ASTM International. 2017. New Standard Helps Test Safety of Synthetic Turf Infill. *ASTM Standardization News, January-Fe*. Retrieved from https://www.astm.org/standardization-news/?q=update/new-standard-helps-test-safety-synthetic-turf-infill
- 16. International Agency for Research on Cancer (IARC). 2018. Agents classified by the IARC monographs, Volumes 1-123. Retrieved from https://monographs.iarc.fr/agents-classified-by-the-iarc/
- 17. National Institute for Public Health and the Environment (RIVM) Bureau REACH. 2018. *Annex XV Restriction Report: PAHs in Synthetic Turf Infill Granules and Mulches*. Bilthoven, Netherlands.
- 18. Andersson, J. T., & Achten, C. 2015. Time to Say Goodbye to the 16 EPA PAHs? Toward an Up-to-Date Use of PACs for Environmental Purposes. *Polycyclic aromatic compounds*, *35*(2–4), 330–354.
- 19. European Chemicals Agency (ECHA). 2018. Lower concentration limit proposed for PAHs found in granules and mulches. Retrieved November 2, 2018, from https://echa.europa.eu/-/lower-concentration-limit-proposed-for-pahs-found-in-granules-and-mulches. Also archived at https://web.archive.org.
- Dybing, E., Schwartze, P. E., Nafstad, P., Victorin, K., & Penning, T. M. (n.d.). Chapter 7: Polycyclic Aromatic Hydrocarbons in Ambient Air and Cancer. In International Agency for Research on Cancer (IARC) (Ed.), *IARC Scientific Publication 161* (pp. 75–94). Retrieved from https://www.iarc.fr/wpcontent/uploads/2018/07/161-Chapter7.pdf
- 21. Donald, C. E., Scott, R. P., Wilson, G., Hoffman, P. D., & Anderson, K. A. 2019. Artificial turf: chemical flux and development of silicone wristband partitioning coefficients. *Air Quality, Atmosphere and Health*, *12*(5), 597–611.
- 22. Massey, R. I. 2020. *Use of Tire Crumb in Recreational Settings: Science and Policy Implications*. University of Massachusetts Lowell.
- 23. International Agency for Research on Cancer (IARC). 2019. Agents Classified by the IARC Monographs, Volumes 1 125. Retrieved from https://monographs.iarc.fr/list-of-classifications/
- 24. US Environmental Protection Agency (US EPA). (n.d.). The National Lead Laboratory Accreditation Program (NLLAP). Retrieved from https://www.epa.gov/lead/national-lead-laboratory-accreditationprogram-nllap

(this page intentionally left blank)

About the Toxics Use Reduction Institute

The Toxics Use Reduction Institute (TURI) at the University of Massachusetts Lowell provides resources and tools to help Massachusetts businesses and communities make the Commonwealth a safer and more sustainable place to live and work. Established by the state's Toxics Use Reduction Act of 1989, TURI provides research, training, technical support, laboratory services and grant programs to reduce the use of toxic chemicals while enhancing the economic competitiveness of Massachusetts businesses. Learn more at www.turi.org.



Toxics Use Reduction Institute University of Massachusetts Lowell The Offices at Boott Mills West 126 John Street, Suite 14 (2nd Floor) Lowell, MA 01852-1152 (978) 934-3275 • www.turi.org