Appendix D

OEHHA Synthetic Turf Study

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Appendix D. Standard Operation Procedures for Sample Collection, Preparation, and Analysis

D.1. Sample Collection and Preparation

Following this Field Sampling Protocol, OEHHA and Lawrence Berkeley National Laboratory (LBNL) performed the Phase 3 Field Work to collect crumb rubber and environmental samples (samples of chemical vapors and fine particles in the air) at 35 selected synthetic turf fields in California for chemical characterization study of the OEHHA Synthetic Turf Study (the Study).

D.1.1. Environmental Survey

D.1.1.1. Pre-Visit Online Survey

Before the field visit, the OEHHA field lead conducted a pre-visit environmental survey (Section D.1.7.1) using field information available online. The internet search included these activities:

1. A review of the field surroundings within a 1-mile radius using Google maps (e.g., satellite maps)
2. Documentation of the presence and location of nearby freeways, industrial facilities, and other potential sources of chemical emissions that may impact the field samples
3. Documentation of local precipitation history for the week prior to the field visit
4. A check of the weather forecast for the day before and day of sampling, considering the prior week's precipitation history to determine if the sampling schedule needed to be adjusted or rescheduled.

D.1.1.2. On-site Survey

On the day of field sampling, OEHHA staff conducted an on-site survey (Section D.1.7.2) before and during field sample collection to gather information on the weather at the time of sampling (e.g., temperature, field surface temperature, and precipitation), surrounding environment of the field (e.g., confirm locations of nearby freeway and industrial facilities identified in the Pre-Visit Environmental Survey), and visible conditions on the field (e.g., standing water from sprinklers, previous rain, or overnight condensation). The staff also noted the level of automobile traffic, and any other relevant information that may affect potential chemical emissions or exposure.

The OEHHA field lead visually inspected the field and documented (photographed, if possible) the dampness of the crumb rubber and turf blades at the time of collection. Crumb rubber samples were not collected when either the turf blades or crumb rubber on the fields were perceptibly moist or wet. Shaded areas on the field were also noted on the environmental survey especially in areas near or at the proposed sampling

locations. If there was an unforeseen field condition, the OEHHA field lead immediately called the OEHHA project lead and discussed if field sampling activity needed to be adjusted or rescheduled.

D.1.1.3. Post-Visit Survey

After the field visit, the OEHHA field lead conducted a post-visit survey (Section D.1.7.3) using the internet to document the local temperature, relative humidity, wind speed, and wind direction at the time of sample collection.

D.1.2. Sample Collection

D.1.2.1. Sampling Map (Field Diagram)

Before the field sampling day, the OEHHA and LBNL field leads worked together to develop a field-specific sampling diagram (Section D.1.7.4) illustrating field shape and orientation (compass showing the North direction) and sampling details (including preliminary sampling locations, types and number of samples collected at each location). Section D.1.7.4 shows template of on-site pre-selected sampling locations for each type of field (e.g., soccer, football) to be sampled. The diagram was used during the field sampling to guide the sample collection. The OEHHA field lead documented any deviations from the plan on the sampling map and in the field sampling diary (Section D.1.7.5).

D.1.2.2. Crumb Rubber Collection

At a location outside the field, the OEHHA and LBNL field leads set up a staging area to set up all the sampling supplies and a trash bag, and then briefed the OEHHA and LBNL field staff (sampling team) on the sampling activity of the day and assigned members of the sampling team with specific sampling tasks. The leads distributed all sampling tools and the sampling map. The OEHHA field staff collected crumb rubber samples at the pre-selected locations detailed on the sampling map. At each sampling location, the OEHHA field staff used commercially available pre-cleaned metal or plastic sampling scoops provided by LBNL to collect crumb rubber from the field surface. The protocol for crumb rubber collection was as follows:

1. Identified and marked each on-field sample location using area indicator (a measured rope) to identify approximately a 1 square meter surface area (the sample collection area) to collect the sample from.
2. Put on a pair of fresh nitrile gloves.
3. Identified the 120 mL wide-mouth amber glass and 120 mL polyethylene (PE) bottle with the affixed label corresponding to the first sampling location.
4. Carried supplies from the staging area to the sample location and placed them on the ground within the marked area.

5. Pressed the side of the sampling scoop (metal scoop to be used with glass bottle, plastic scoop to be used with PE bottle) down onto the turf at an approximately 45 degree angle and moved back and forth on the turf surface to collect crumb rubber within the sample collection area.
6. Scooped the crumb rubber into the sampling bottle.
7. Repeated the sample collection as needed at the same location or moved to a different location within the designated sample collection area until both the glass and plastic bottles were full.
8. When bottles were full, insured that lids were tightly sealed, gathered supplies and returned to the staging area.
9. Recorded the date, time, and initials of sample collectors on sampling bottle label and into Chain-of-Custody, COC, form (Section D.1.7.6).
10. Placed each sample in ice chest chilled with blue ice.
11. Before going to next sample location, changed to a new pair of nitrile gloves, got a set of clean scoops and clean sampling bottles.
12. Repeated steps 3 to 11 until all samples were collected.
13. When done with all sample locations, returned all field tools to the staging area. Ensured that nothing was left on the field.

D.1.2.3. Environmental Sample Collection

During the Phase 2 and 3 Studies, at each field tested, environmental samples were collected at an on-field location with and without activity to evaluate exposures and an off-field location for background comparison.

D.1.2.4. Pre-Sampling Preparation

Field information, along with availability and location of power supply on a field were collected during a field visit with the owner. Prior to arrival at the field, satellite images and weather apps were reviewed to determine the field orientation and weather forecast on the day of testing (e.g., wind direction and speed). This information was used to identify the pre-arrival on- and off-field sample locations and orientation relative to the field.

The sampling packages were setup on four carts (three on-field and one off-field locations) and one stratification tower (on-field, various elevations) as detailed in Table D-1 prior to transport to the field. The on-field sampling locations were selected to maximize cross field airflow upstream of the monitoring area. The monitoring area was defined as the area bordered by and in front of a regulation soccer goal (7.3 meters wide by approximately 10 meters deep) with individual sample locations to each side and behind (downwind) the goal. The off-field sample location was typically selected to include different ground cover material (e.g., soil, natural grass turf, or concrete) and to

provide a location that was not directly influenced by airflow across the field.

D.1.2.5. Setup and Sampling Activity

Upon arrival at the field, and after any required check-in procedures were completed, the field lead for environmental sample collection reviewed the initial selection of monitoring locations and made final adjustments to account for access to power supply, as well as current field and meteorological conditions. The rationale for the final selection of sampling location and instrument orientation was documented in the field log.

Before entering the field, the OEHHA and LBNL field leads briefed the sampling team on the sampling activity of the day and assigned staff with specific setup and sampling tasks. If the field had a movable and regular size soccer goal, the goal would be used for the study and placed at the sample location with the goal opening facing into the predominant wind. The three on-field monitoring carts with sampling packages were installed to the left and right of the goal frame and behind the net. In addition, the stratification tower (tripod with samplers at various elevations) was installed near the center behind the net.

The sample carts and tower orientation on-field and measuring devices on each cart or tower were the same at each field as noted in Table D-1. The devices were launched and logged continuously to a dedicated computer on each cart. Integrated samples including volatile organic chemicals (VOCs), semi-volatile organic chemicals (SVOCs) and particulate matters (PM) collected on filters were run on a combination of pre-programmed pumps that were calibrated before and after each use and manual on/off pumps with continuous flow control.

The fields were tested during static (no activity) and active (similar to soccer game or practice) conditions. Following the LBNL Institutional Review Board approved protocol, human subjects were recruited to create the active conditions. They performed vigorous soccer drills in the monitoring area to agitate field surface and simulate the active field conditions. The pace of soccer activity was dictated by a soccer ball kicking machine that launched a ball into the goal area on a 10-second cycle. Typically, the ball kicking machine was set up approximately 25 meters from the face of the goal net and adjusted to bounce the balls in front of the net where the human subjects would interact with the ball (catch, dribble, kick etc.) before kicking the ball back for reloading the machine.

Table D-1. Field Instrument Package

Target Metric	Instrument, Method, or Device	Sample Type	Cart Position[a]
Wind speed and direction	3-D anemometer logged to onboard laptop	Continuous	S, B & O
Surface	Infrared surface temperature probe	Continuous	S, B & O

Target Metric	Instrument, Method, or Device	Sample Type	Cart Position[a]
temperature	logged to onboard laptop		
Ambient temperature and relative humidity	HOBO U10 or equivalent shielded and logged internally	Continuous	S, B & O
Temperature profile	Thermocouples below surface and stratified ambient above surface logged to HOBO UX120 four channel logger	Continuous	B
VOCs	Hourly samples collected on thermal desorption sorbent tubes	Integrated	S & O
Stratified VOCs	One-hour sample collected at 4 levels above field on thermal desorption sorbent tubes	Integrated	B
ALDs	USEPA method TO11 or equivalent using DNPH cartridge	Integrated	S
PAHs and SVOCs	EPA method TO13 or equivalent using $PM_{2.5}$ cyclone onto glass fiber filter followed by polyurethane foam + XAD™-2 sample train	Integrated	S & O
$PM_{2.5}$	Particle mass collected using PEM with 2.5 µm size cut on Teflon filters collocated with SVOC sample heads	Integrated	S & O
$PM_{2.5}$	DustTrak II 8530 particle mass analyzer fit with $PM_{2.5}$ impactor logged internally	Continuous	S, B & O
PM_{10}	DustTrak II 8530 particle mass analyzer fit with PM_{10} impactor logged internally	Continuous	S, B & O (subset of fields)
$PM_{2.5}$	MetOne BT 645 continuous laser optical sensor with $PM_{2.5}$ cyclone logged to onboard computer	Continuous	B (subset of fields)
$PM_{2.5}$	MetOne ES 642 forward scatter laser nephelometer with $PM_{2.5}$ cyclone logged to onboard computer	Continuous	O (subset of fields)
Size resolved particle number concentration	MetOne 637 five size fractions at three elevations above field logged to onboard computer	Continuous	S & B
Size resolved particle number concentration	TSI 3321 aerodynamic particle sizer resolved from ~ 300 nm (0.3 µm) to 20 µm placed near surface and logged	Continuous	B

Target Metric	Instrument, Method, or Device	Sample Type	Cart Position[a]
	internally		
Ozone	2B Technologies model 202 logged continuously to onboard computer	Continuous	B, O

[a]S: left and right of the goal; B: back of net; and O: off field

ALDs: aldehydes and ketones, DNPH: 2,4-dinitrophenylhydrazine; PAHs: polyaromatic hydrocarbons; $PM_{2.5}$: particulate matter that is 2.5 µm or smaller; PEM: personal environmental monitor; PM_{10}: particulate matter that is 10 µm or smaller; SVOCs: semi-volatile organic chemicals; VOCs: volatile organic chemicals; and XAD™: XAD is a registered trademark of The Dow Chemical Company or an affiliated company of Dow

The basic environmental field sampling sequence were: 1) a one to two hours of instrument setup and device launching period; 2) an hour of sampling under static field conditions; 3) three hours of active condition sampling; and 4) a final hour of static condition sampling. After the five-hour sampling, instrument was taken down in reverse order of the setup and data from real-time devices were backed up prior to leaving the field. An example of the detailed playbook showing the order of activities during a field testing event is shown in Section D.1.7.7. The field protocol for environmental sample collection was as follows:

1. A one to two hours of instrument setup and device launching period:
    a Confirm location on field for sampling area.
    b If available on the field, move goal net frame into place with the opening of the net facing into the predominant wind. If no net is available, build soccer net and place with the opening of the net facing into the predominant wind.
    c Starting from back of net, uncoil main power cable with three-way plug at the net end stretching away from the sampling area.
    d If no power is available at the field, place generator at end of power cable, and install fume exhaust system with ducting running away from the sampling area. Set up any caution flags/cones and end of duct anchor in place. Start the generator.
2. An hour of sampling under static field conditions:
    a Move three carts into position with all carts placed side-by-side at back of net and plug in power supply for carts. Move fourth cart to “off field” location.
    b Install and orient the 3-D anemometers and align the infrared probe pointing to the general area near the sampling area.
    c Place pre-programmed semi-volatile organic compound (SVOC) pump on ground behind the cart and connect vacuum line to SVOC sample head (at height of 1 meter above field surface).

d Place pre-programmed volatile organic compound/aldehyde and ketone (VOC/ALD) sample pumps on the carts.

e Place soccer ball kicking machine to the front of the net 18 to 20 yards from the front of the goal and install battery pack.

f Load VOC tube sand ALD cartridges in preprogrammed sampling boxes (at a height of 1 meter above field surface) and launch all devices.

g Prior to start of SVOC sample collection, assemble sample train with sorbent cartridges and filters (this is only for the three hours active sampling period at the Pilot#1).

h After sampling period begins, record all sample airflows (VOC, ALD and SVOC) at least once per hour.

3. Three hours of active condition sampling:

   a To start the active phase of testing, move two carts from back of net to sides of net.

   b Start and continue to run ball kicking machine with voluntary participants conducting soccer drills inside the net taking 20-minute turns for each person with two people receiving and running machine assisted/supervised by LBNL and/or OEHHA staff.

   c Collect samples at the pre-determined locations for 3 hours.

4. A final hour of static condition sampling:

   a Collect samples for another hour with no field activity.

   b At the end of the sampling period, all digital data were saved on the device or laptop associated with the specific sampling cart and the data was backed up on an external hard drive specific to the project.

   c All integrated samples were removed from the sampling boxes, labeled, and returned to shipping/handling containers for transport back to lab.

D.1.3. Sample Handling and Shipping

Environmental samples and crumb samples were packaged and transported/shipped in separate containers. The sample handling, transportation, and/or shipping followed the COC and quality assurance/quality control (QA/QC) protocol specified in the sampling plan (Section D.1.6). A sample COC form is provided in Section D.1.7.6. Details specific to the crumb samples and environmental samples are provided below.

D.1.3.1. Crumb Rubber Samples

Once a bottle is filled, the date and time of collection, and initials of the sample collector were clearly entered onto the label of each sampling bottle. The OEHHA field lead

accounted for all the sampling bottles after the completion of field sampling. Each sampling bottle was placed into an individual Ziploc bag, sealed, wrapped, and placed into an insulated container (Styrofoam box or cooler) containing blue ice (4 °C). Each box of samples contained the COC for the specific samples within the box. The boxes were shipped via FedEx overnight or delivered on the same day to LBNL.

D.1.3.2. Environmental Samples

Environmental samples included both digital information logged on instruments or devices and physical samples collected on sampling media to be processed within a laboratory setting.

All digital data files were assigned a unique descriptive name, saved on the instrument/device/computer associated with the sample and backed up on an external project specific hard drive as part of the shutdown procedure each day (or at each location if more than one location is tested on a given day).

D.1.4. Deviations from the Sampling Protocol

The OEHHA field lead immediately contacted (by phone or text) and sought approval from the OEHHA project lead for deviations from the sampling protocol that were deemed to be necessary due to variances in the field conditions. The OEHHA field lead documented all the deviations in the COC records (Section D.1.6.4) and the field sampling diary (Section D.1.6.5).

D.1.5. Health and Safety

At least a day before the field visit, the OEHHA lead identified and printed out the contact information and full address of the nearest local emergency facility or hospital.

Before entering the field, the LBNL and OEHHA field leads held a tailgate meeting to go over the safety protocol. OEHHA field lead presented the emergency facility information and discussed potential physical (e.g., trip, fall, and slip hazards; heat exhaustion and heat stress; dehydration; proper lifting techniques; use of personal protective equipment including eye protection; potential exposure hazards from chemicals applied to or that are on the turf; hygiene techniques; and first aids) and biological hazards (e.g., insect bites). The LBNL field lead described detailed procedure on proper handling of mechanical, electrical, and electronic equipment. OEHHA and LBNL staff were to immediately report to the LBNL or OEHHA lead the following health and safety concerns:

- Changes in field/weather conditions that may impact the health safety of the team or individuals
- Signs of heat stress noticed on individuals
- Safety concerns observed on the field or individuals

The OEHHA and LBNL field leads were to assess the conditions, report immediately to the OEHHA and LBNL project leads, contact OEHHA's industrial hygienist, and seek further assistance from the appropriate authorities (e.g., contact the local hospital), if warranted.

D.1.6. Quality Assurance and Quality Control (QA/QC)

D.1.6.1. QA/QC Procedures

The QA/QC procedures were employed at the field and in the laboratory. The QA/QC samples collected in the field sampling events included field blanks and trip blanks. Field QA/QC procedures were implemented at the fields and consist of the following measures:

1. A COC form accompanied all samples collected from a particular field during transportation. They were used to ensure the integrity of the samples collected.
2. A field sample log was kept by OEHHA to record type and total number of samples collected from a particular field. It also included sampling details, crumb rubber field locations, field ID, sampling date and times (begin and end), and sample identification numbers. Pages were numbered, dated, and signed by the OEHHA and LBNL field staff performing sampling and data logging.
3. A field sampling diary was maintained to document all deviations from the sampling protocol and justifications for the changes. Communications between the OEHHA and LBNL field staff and the OEHHA and LBNL project leads for approval of protocol modifications on-site were also summarized.
4. One field QA/QC sample and one trip blank of each sampling bottle type was collected at each synthetic turf field (i.e., a total of four blanks per field) and submitted for analysis along with the crumb rubber field samples.

D.1.6.2. Field Blanks Preparation

A field blank is a quality control measure used to identify potential contamination that may have occurred during crumb rubber sampling at the field and during the sample shipment to the analytical laboratory. A field blank is prepared by opening and closing a sample container at the field. OEHHA prepared two field blanks (one for plastic bottle and for glass bottle) for each field. The field blanks were preserved, packaged, and sealed in the same manner described for crumb rubber samples. For identification, a unique sample number was assigned to each field blank.

D.1.6.3. Trip Blanks Preparation

A trip blank is a quality control measure used to evaluate any potential contamination (e.g., migration of volatile organic chemicals, VOCs) as a result of shipping and handling of samples. A trip blank was prepared by taking a sealed, clean sampling container and carrying it to the field. The blank container was not opened and

accompanied the sampling containers during the sampling and in the shipment to the laboratory. OEHHA prepared a glass bottle and a plastic bottle trip blank for each field. The trip blanks were handled under the same protocol for the crumb rubber samples, as described in this sampling plan. The trip blanks were preserved, packaged, and sealed in the same manner described for crumb rubber samples. For identification, a unique sample number was assigned to each trip blank.

D.1.6.4. Chain-of-Custody Records (COC)

COC records were used to document sample collection and accompanied all sample shipments to the laboratory. The COC record identified the contents of each shipment and maintained the custodial integrity of the samples. COC forms were completed and signed by sample collectors and sample handlers and sent with the samples for each shipment. If multiple coolers were sent to a single laboratory on a single day, COC forms will be completed and sent with the samples for each cooler. Generally, a sample is considered in a person's custody, if it is either in the person's physical possession, in the person's view, locked up, or kept in a secured area that is restricted to authorized personnel. Until receipt by the laboratory, the custody of the samples was the responsibility of OEHHA staff.

D.1.6.5. Field Sampling Diary

The field sampling diary included the location of sample collection, the name of the lead and the names of field staff who participated in the sample collection at each field. All deviations from the sampling protocol described in Sections D.1.2.2 and D.1.2.3 were noted including the reason for deviation and its justification. The OEHHA field lead immediately contacted (by phone or text), discussed options with, and sought approval from the OEHHA project lead for the need to deviate from the sample protocol before acting. The discussion and approval were summarized in the field sampling diary.

Attachments (Section D.1.7): Seven surveys, maps, template, form, and playbook

D.1.7. Attachments

D.1.7.1. Pre-Visit Environmental Survey

Field ID: _____

Sampling Date: _____

No. Samples Taken: _____

Sampling Time: Start: _____ End: _____

Weather Forecast for day of field sampling:

Precipitation: _____

Temperature (High): _____

Nearest Weather Station

(Weather Underground)*: _____

Nearby and surrounding areas (within 1 miles):

□ Freeway/Highway: _____

□ Industrial facilities: _____

□ Athletic fields: _____

□ Airport: _____

□ Other potential sources of chemical emissions:

_____

Traffic intensity: □ Light □ Moderate □ Heavy

Precipitation History (previous week):

Date	Precipitation

Pictures:

Picture #	Description

Other comments:

Name and Signature of Surveyor: _____

Date: _____

Google Maps image of synthetic turf field (1-mile radius)

D.1.7.2. On-site Environmental Survey

Field ID: _____

Sampling Date: _____

No. Samples Taken: _____

Sampling Time: Start:_____ End:_____

Meteorological Data Collected on the Field:

Precipitation: _____

	At Start	At End
Field Surface Temperature:		

Nearby and surrounding areas (within 1 miles):

□ Freeway/Highway: _____

□ Industrial facilities: _____

□ Athletic fields: _____

□ Airport: _____

□ Other potential sources of chemical emissions:

_____

Traffic intensity: □ Light □ Moderate □ Heavy

Precipitation History (previous week):

Date	Precipitation

Pictures:

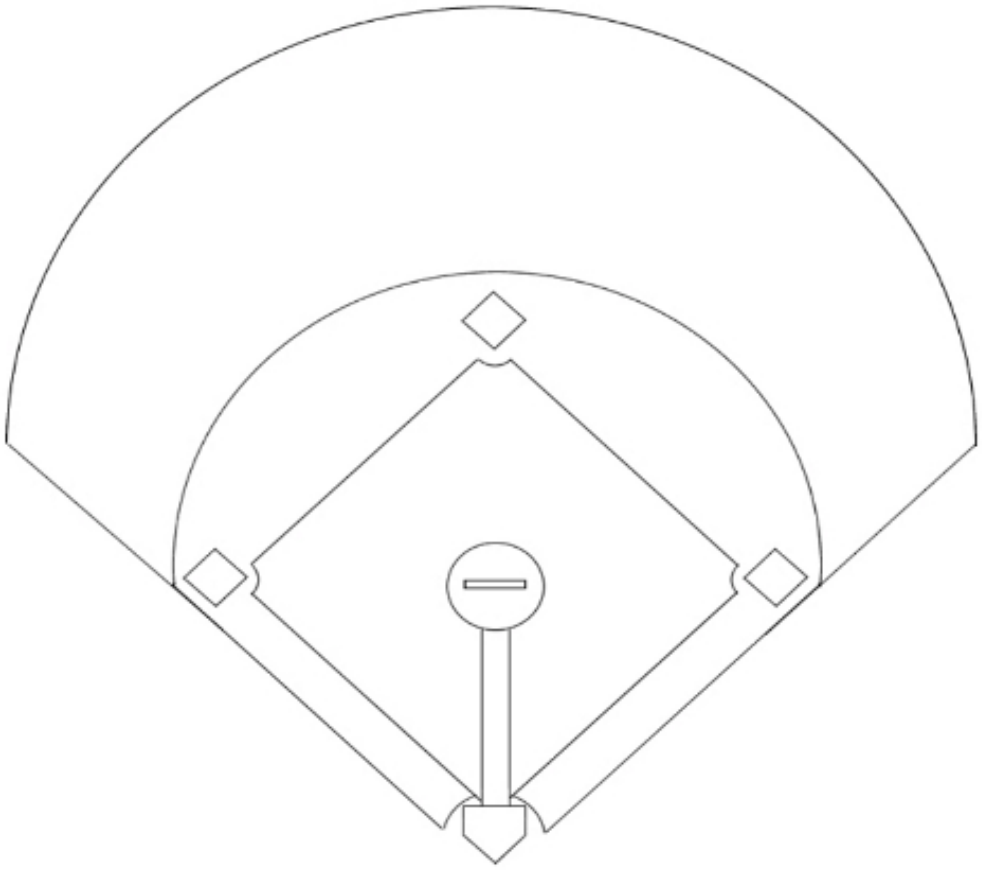
Picture #	Description

Other comments:

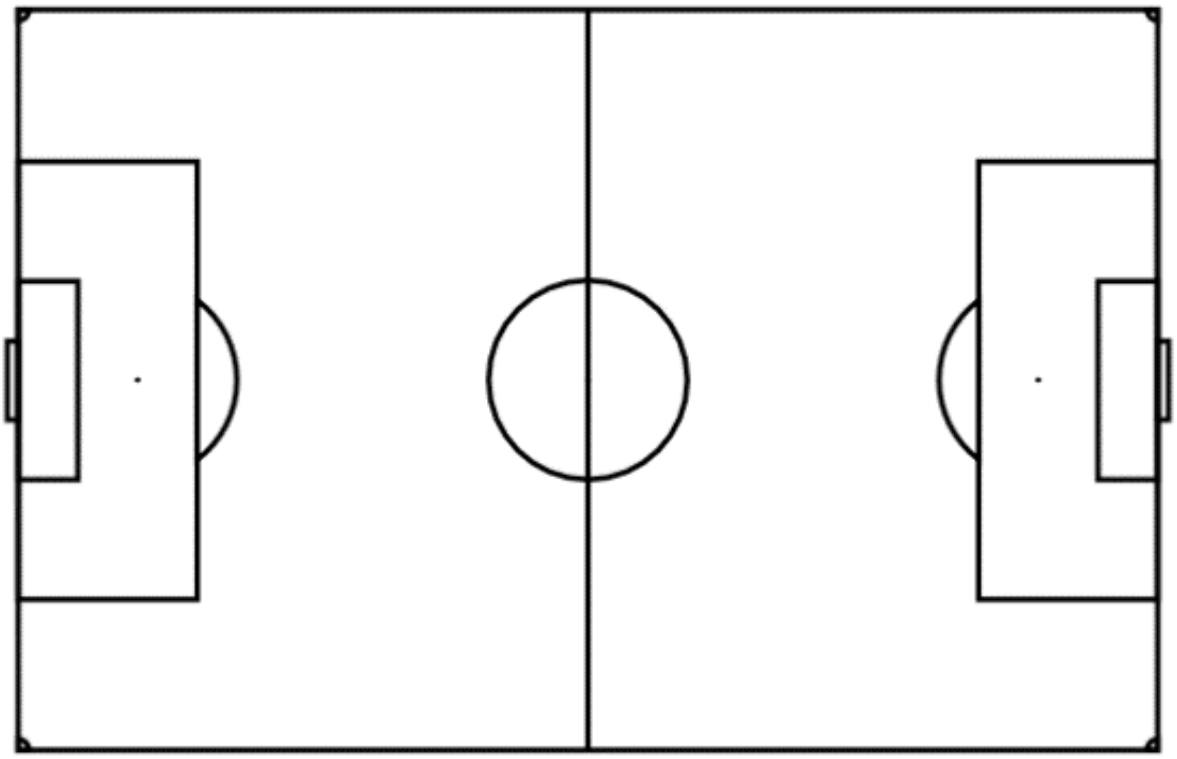
Name and Signature of Surveyor: _____

Date: _____

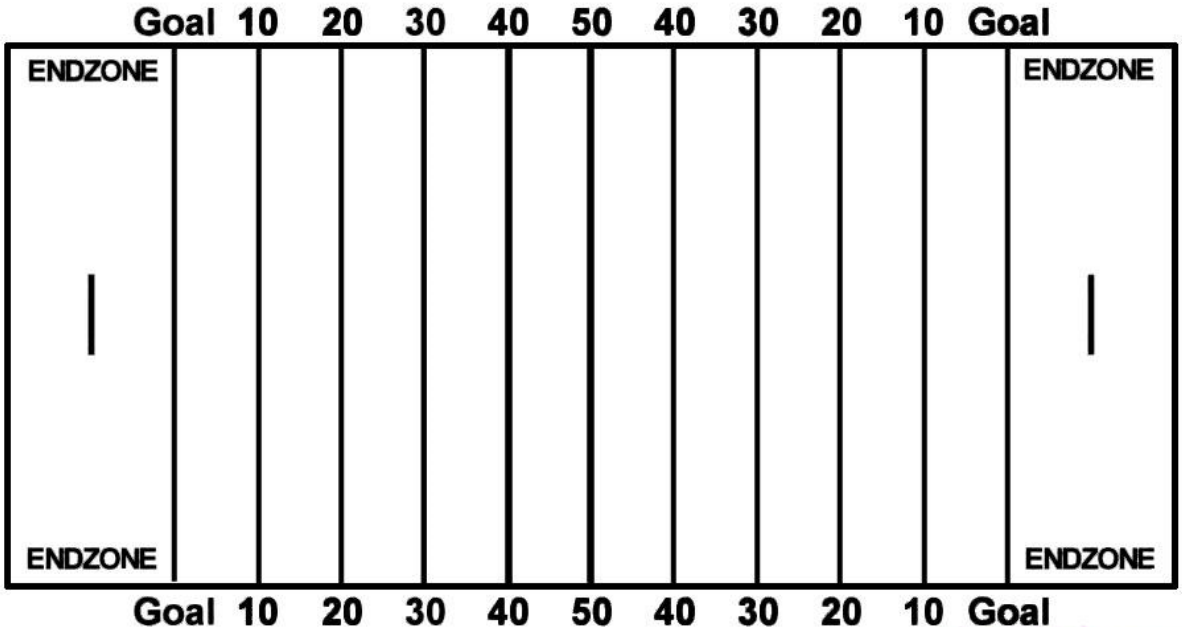
Field Diagram (Sketch field characteristics including trees, shaded areas, indicate synthetic turf, sand, gravel, grass, asphalt, concrete, etc.):



Field Diagram (Sketch field characteristics including trees, shaded areas, indicate synthetic turf, sand, gravel, grass, asphalt, concrete, etc.):



Field Diagram (Sketch field characteristics including trees, shaded areas, indicate synthetic turf, sand, gravel, grass, asphalt, concrete, etc.):



D.1.7.3. Post-Visit Environmental Survey

Field ID: _____

Sampling Date: _____

No. Samples Taken: _____

Sampling Time: Start:_____ End:_____

Weather Record for the day of field sampling:

Precipitation: _____

Temperature High: _____

Nearest Weather Station
(Weather Underground):_____

	At Start	At End
Air Temperature		
Relative Humidity		
Wind Speed and Direction		

Nearby and surrounding areas (within 1 miles):

□ Freeway or Highway: _____

□ Industrial facilities: _____

□ Athletic fields: _____

□ Airport: _____

□ Other potential sources of chemical emissions:

_____

Traffic intensity: □ Light □ Moderate □ Heavy

Precipitation History (previous week):

Date	Precipitation

Pictures:

Picture #	Description

Other comments:

Name and Signature of Surveyor: _____

Date: _____

D.1.7.4. Template On-Site Sampling Maps (Field Diagrams)

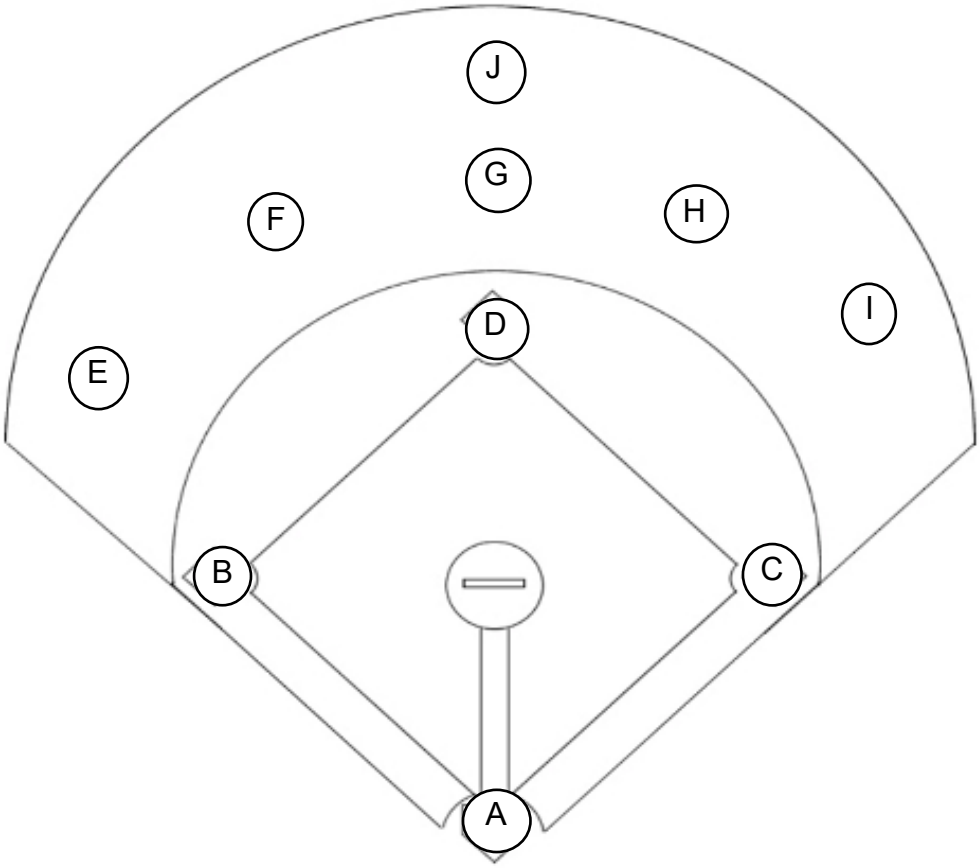


Figure D-1. A template on-site sampling map to indicate the ten pre-selected sampling locations on a baseball field identified by the circles on the map.

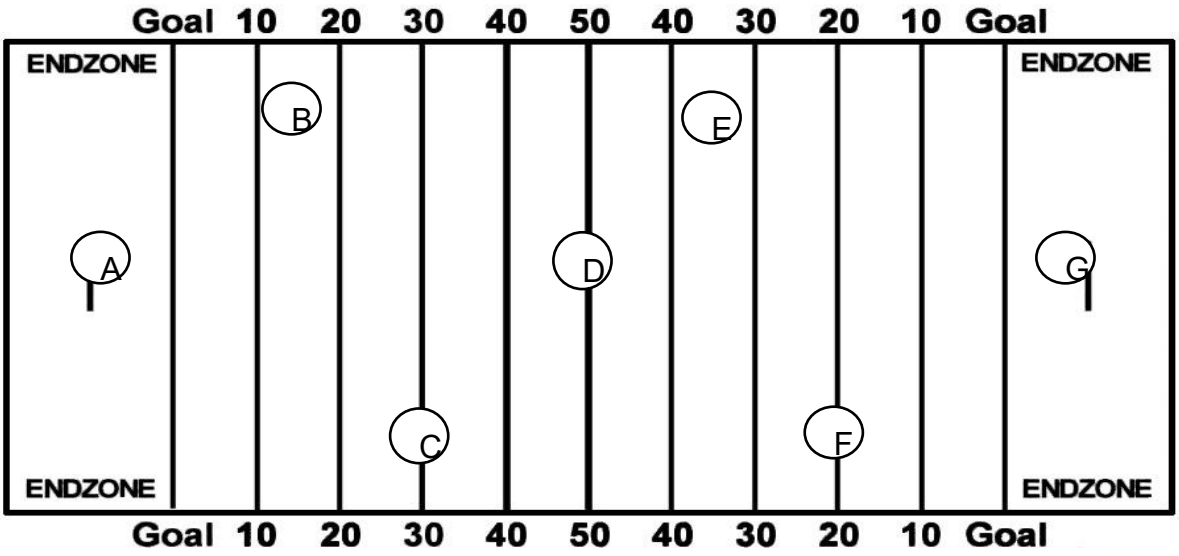


Figure D-2. A template on-site sampling map to indicate the seven pre-selected sampling locations on a football field at identified by the circles on the map.

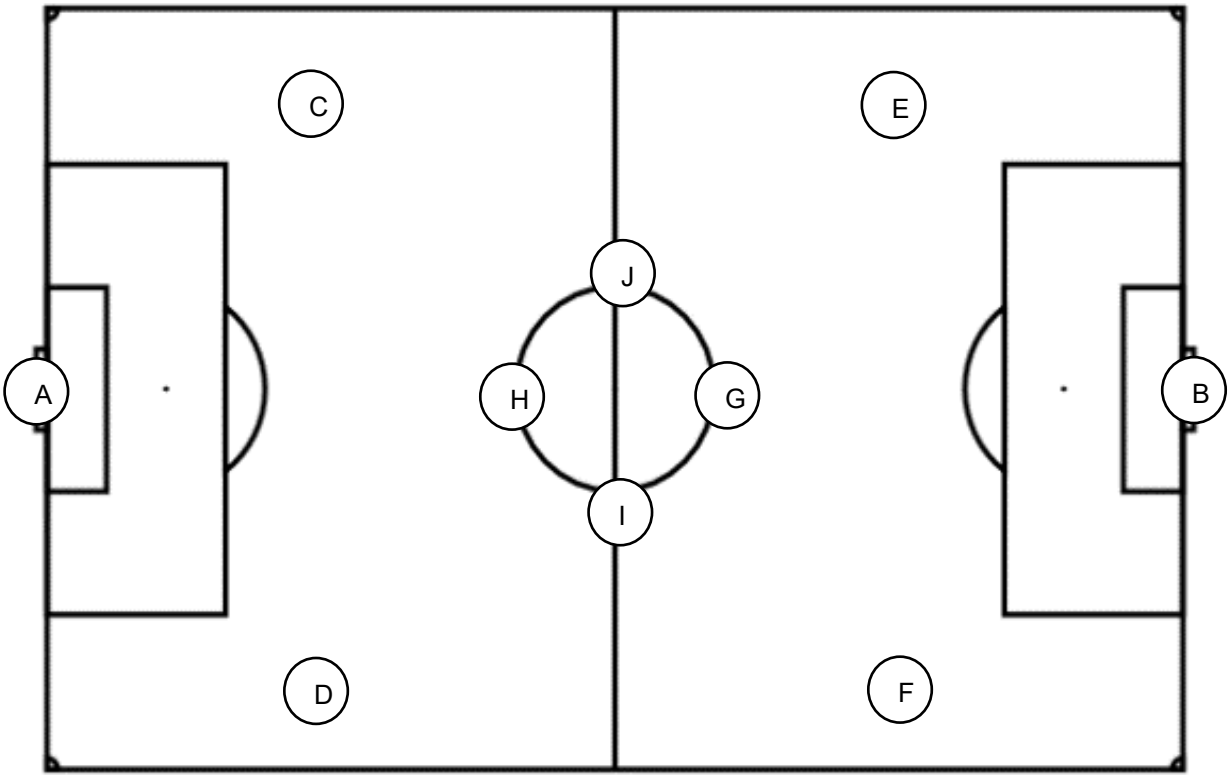


Figure D-3. A template on-site sampling map to indicate the ten pre-selected sampling locations on a soccer field identified by the circles on the map.

D.1.7.5. Field Sampling Diary Template

Sampling Date: _____ Log Completed By: _____

Field ID: _____

Field Name: _____

Field Location: _____

Field Contact: _____

Collection Time: _____

Samples Collected (indicate # of samples, the amount, type, and sample IDs):

_____

_____

_____

Sample Collector's Initials: _____

Observations:

Comments:

D.1.7.6. Chain of Custody Form

Field ID: _____

Recorder Signature: _____ Date: _____

Table D-1. Chain-of-Custody (COC) Record

Sample ID	Collection Date	Collection Time	Collector Initials	Date Relinquished	Relinquished to	Receiver by and Initials*

*Please write your name and initial to maintain COC record

D.1.7.7. Example of Field Sampling Playbook

1. Before Scheduled Test Day
    a Confirm player recruits availability and provide detailed instructions on when, where and what to expect
    b Confirm sufficient water (with ice) and sun screen for player recruits
    c Charge all sample pumps and ball kicking machine battery
    d Complete any special requirements for field access if necessary
    e Identify access point for getting equipment on field and travel time to field (Plan to arrive at field 2 hours before scheduled start time)
    f Program start times into SVOC and VOC sample boxes and data loggers used for temperature and humidity (can be done on-site during setup)
    g Load all supplies and equipment in box van (or check loaded fan for previous trip) except sample media
    h Receive (if traveling) or pickup (if leaving from lab) clean/loaded/labeled SVOC cartridges, conditioned VOC tube and fresh ALD cartridges in cooler with fresh blue ice and field specific tracking sheets
    i Load and label pre-weighed PEM filters and cleaned glass fiber filters in filter housings with field specific tracking sheets
2. Day of Testing
    a 2 hours (prior to schedule start time) – Arrive at field
        i lead walks field to confirm
    b initial field orientation
    c on- and off-field access points
    d availability of power supply
    e availability of movable soccer goal
    f on- and off-field sprinklers (if present, confirm that sprinklers disabled)
    g possible sources of shade on-field

    h 1.5 hours (prior to schedule start time) – Setup and prepare for sampling
        i Unload box van and setup staging area with table and chairs as needed
        ii Install main power cord from on/near field location extending onto field (end of cord dictates location for on-field test)
            - If power supply is not available then place generator with exhaust hood “downwind” of monitoring location and extend cord onto field
        iii Move on-site goal to monitoring location on field (repair or replace damaged

net if necessary) or setup portable goal with net and adjust orientation with front of net facing into expected wind

iv Move sampling carts into location

- Cart 2 back center of net
- Carts 1 and 3 to left and right of net (from back)
- Cart 4 at off field location

v Connect extension cords to main power line (or source for off-field location) and place power supply/battery backup near each monitoring location

vi Set orientation of 3-D anemometers on all carts to magnetic north

vii Place SVOC boxes and PEM pumps near Carts 1, 3 and 4

viii Launch all devices that aren't already preprogrammed to start and confirm onboard data logging

ix Load VOC tubes in VOC boxes at staging table and set internal clock and install pre-programmed SD-cards in VOC boxes then move VOC boxes into position on Carts 1, 3 and 4

x Set internal clock on SVOC boxes and load pre-programmed SD-cards

xi Setup ball kicking machine (25 meters from front of goal) with solar charger and canopy

xii Setup VOC/temperature "stratification tower" to one side of Cart 2 and install air temperature sensors at marked heights on tower with T/RH sensor at top of tower and temperature probes inserted into crumb surface

xiii Adjust all surface temperature sensors (Carts 1, 3 4 and tower) to point at sunny location throughout the day

xiv Check pre-sampling flow on all portable pumps (used for ALD samples on Carts 1 and 3 and for VOC samples on stratification tower) and program portable pumps to launch and run at appropriate times

i *0 hours (Start) – 1 hour (elapsed time)*

i Confirm all devices running and data logging

ii Collect first VOC sample (1 hour integrated samples) on Carts 1, 3 and 4

iii Check and record flows on all VOC samplers at least once per hour

iv Install SVOC cartridges, Filters and $PM_{2.5}$ cyclone on Carts 1, 3 and 4

v Install PEMs with 10 LPM pumps on Carts 1, 3 and 4

vi Install ALD samplers on Carts 1 and 3

vii Recruited players arrive, get orientation and sign consent forms

j *1 hour – 2 hour (elapsed time)*

i Start and run ball kicking machine with participants taking turns conducting soccer drills in goal area to maintain continuous activity in the monitoring area during active period

ii Monitor players and continue to load and run ball kicking machine

iii Start and run SVOC samples on Carts 1, 3 and 4 (3 hour samples)

iv Start and run PEM filters on Carts 1,3 and 4 (3 hours samples)

v Check flows on PEM and SVOC pumps at least once per hour during sampling

vi Start ALD samples on Carts 1 and 3 (3 hour samples)

vii Start 2nd VOC samples collected on Carts 1, 3 and 4

k *2 hour – 3 hour (elapsed time)*

i Continue ball kicking activity

ii Load tubes on VOC tower with pre-programmed sampling pumps

iii Start 3rd VOC samples collected on Carts 1, 3 and 4

iv Record field layout and monitoring area orientation using range finder from known points and compass

l *3 hour – 4 hour (elapsed time)*

i Continue ball kicking activity

ii Continue to check sampler pump flows and device data logging

iii Start VOC stratification tower samples

iv Start 4th VOC samples collected on Carts 1, 3 and 4

v At end of period, stop kicking machine and dismiss recruited players

m *4 hour – 5 hour (elapsed time)*

i Start 5th VOC samples collected on Carts 1, 3 and 4

ii Harvest ALD cartridges and pumps

iii Harvest VOC tubes and pumps from stratification tower

iv Check and record post sampling flows on ALD and VOC pumps

v Collect SVOC cartridges, GFFs and PEMs and return to cooler

vi Move net away from monitoring area and breakdown net

vii Breakdown ball kicking machine, canopy and cleanup area where players gathered and move equipment back to staging area near truck

n *5 hour – 6 hour End of test period*

i All stop at elapsed time = 5 hours

ii Confirm all data downloaded to on-board laptops at each cart

iii Backup all data to external hard drive

iv Harvest VOC tubes and return samples to cooler

v Move all equipment and cords back to staging area near truck

vi Load truck

vii Collect all signs and barriers

viii Lead walks field to confirm cleaned up and good to go

ix Checkout from field as needed and depart field

3. After Completion of Testing

a Complete chain of custody forms

b Package sample media (VOCs, ALDs, SVOCs) with fresh blue ice and ship media overnight to lab

c Unload GF filters and PEM filters from holders and package filter samples (store on-site and ship to lab as needed)

d Return pumps and equipment to chargers

e Make any necessary repairs and replenish supplies

D.1.8. Preparation of Composite Samples for Chemical Analyses

D.1.8.1. Composite Field Samples for Metal and Metalloid Analyses

Two composite crumb rubber samples will be prepared for each field including one representing the “high impact” (HI, e.g., goal areas on a soccer field and end zones on a football field) area and one representing the “rest of field” (RoF, areas excluding HI). The composite sample will be prepared as follows:

1. Most fields have two HI samples and eight RoF samples.
    a. There were three exceptions for the HI samples including one field each with zero, one and four HI area samples.
    b. The RoF per field ranges from five to nine but most include eight samples.
    c. All samples from a given field are stored at room temperature in individual file boxes in a chemical cabinet.
2. Prepare composite sample in a solvent cleaned and labeled polyethylene bottle with Teflon lined cap (Qorpak, GLC-02190 or GLC-02118) by transferring the same mass from each location sample using roughly the same number of scoops. This provides a representative composite sample assuming that each location specific sample represents the same total surface area of the HI or RoF portion of the field.
    a. In each case, only fill composite bottles to a little over half the volume to allow room for the samples to be tumbled and mixed.
    b. The composite HI sample should target ~75 mL (~ 36 gram) of crumb in a 120 mL bottle.
    c. The composite RoF sample should target ~ 150 mL (~75 gram) of crumb in a 240 mL bottle.
3. All location specific sample bottles for a field will be removed from the cabinet.
4. Each location specific sample bottle will be thoroughly mixed by angled rotation for ≥ 30 minute prior to pulling a sub-sample (using Enviro-Genie Shaker, model SI-1200, with the rotating platform installed).
    a. Make sure lid is tightly closed on the sample bottle.
    b. Insert up to two bottles into each magnetic screen basket and secure with a rubber band.
    c. Attach up to two baskets to each side of the magnetic rocking/rolling platform at a ~45 degree angle and centered on the surface. Slide the basket on the magnetic surface slightly until a good magnetic grip is obtained. This orientation provides a figure-eight mixing pattern.
    d. Turn on mixer and make sure the screen baskets remain in place during the tumbling.

5. While samples are mixing, measure and record the tare weight of the pre-labeled composite collection bottles on the tracking sheet and calculate the target mass per location sample for addition.
6. Select a clean (detergent washed, hot water rinsed, 2x deionized water rinsed, air dried) plastic measuring spoon using 1 teaspoon (5 mL) for the HI samples and ½ teaspoon (2.5 mL) for the RoF samples.
7. Transfer material from the location specific sample to the composite bottle.
    a Place the tared bottle on the balance with the lid removed but also on the balance.
    b Sequentially take four scoops from each location specific sample bottle by scooping deep into the mixed jar and pulling scoop through the infill material at different angles to collect material then gently tap the measuring spoon to achieve a level scoop desired then transfer to the composite container. Rotate the bottle in between scoops.
    c Monitor the total mass, as compared to the target mass, as crumb is added to the composite bottle. After the 4th scoop (typical), grab additional scoop(s) and slowly drop into the composite until the target mass is reached.
    d If crumb was spilled on the balance during the transfers, cap the composite bottle, remove from the balance and blow off the balance with DustOff (canned air) to clean the balance. Return the composite bottle and cap to the balance for the final reading of the mass.
    e Record the final total mass of the bottle and mass of crumb added on the tracking sheet.
    f Calculate the next target mass and repeat until all location specific samples from each field are added.
8. The measuring spoon should be detergent washed, rinsed thoroughly with deionized (DI) water and then air dry. A clean measuring spoon (detergent washed) should be used for each field and area (i.e., 1 spoon for HI and 1 spoon for RoF).
9. Once all material is transferred to the composite bottle, close the bottle tightly and thoroughly mix by angled rotation for ≥ 5 minutes (see step H-1.4 above). Place the bottle in a ziplock bag, labeled with the field ID, and store in the cabinet at room temperature.
10. Once the preparation of the composite sample of a field is completed, place a dot on the original field storage box. The remainder of individual location specific samples will be retained in their original sealed containers in the chemical cabinet.

D.1.8.2. Composite Field Samples for Bioaccesibility Tests

Two composite crumb rubber samples will be prepared for each field including one representing the “high impact” (HI) area and one representing the “rest of field” (RoF). The composite sample will be prepared as follows:

1. Most fields have two HI samples and eight RoF samples.
    a There were three exceptions for the HI samples including one field each with zero, one and four HI area samples.
    b The RoF per field ranges from five to nine but most include eight samples.
    c All samples from a given field are stored in individual file boxes in the freezer.
2. Prepare composite sample in a solvent cleaned and labeled amber glass bottle with Teflon lined cap (Qorpak, GLC-02190 or GLC-02118) by transferring the same mass from each location sample using roughly the same number of scoops. This provides a representative composite sample assuming that each location specific sample represents the same total surface area of the HI portion of the field.
    a In each case, only fill composite bottles to a little over half the volume to allow room for the samples to be tumbled and mixed.
    b The composite HI sample should target ~75 mL (~ 36 gram) of crumb in a 120 mL bottle.
    c The composite RoF sample should target ~ 150 mL (~75 gram) of crumb in a 240 mL bottle.
3. All location specific sample bottles for a field will be removed from the freezer and allowed to come to room temperature with all condensation dried or wiped off prior to mixing and opening. This takes about one hour.
4. Each location specific sample bottle will be thoroughly mixed by angled rotation for ≥ 30 minute prior to pulling a sub-sample (using Enviro-Genie Shaker, model SI-1200, with the rotating platform installed).
    a Make sure lid is tightly closed on the sample bottle.
    b Insert up to two bottles into each magnetic screen basket and secure with a rubber band.
    c Attach up to two baskets to each side of the magnetic rocking/rolling platform at a ~45 degree angle and centered on the surface. Slide the basket on the magnetic surface slightly until a good magnetic grip is obtained. This orientation provides a figure-eight mixing pattern.
    d Turn on mixer and make sure the screen baskets remain in place during the tumbling.
5. While samples are mixing, measure and record the tare weight of the pre-labeled composite collection bottles on the tracking sheet and calculate the target mass per

location sample for addition.

6. Select a clean (detergent washed and 2x acetone rinsed) stainless steel measuring spoon using 1 teaspoon (5 mL) for the HI samples and ½ teaspoon (2.5 mL) for the RoF samples.
7. Transfer material from the location specific sample to the composite bottle.
   a Place the tared bottle on the balance with the lid removed but also on the balance.
   b Sequentially take four scoops from each location specific sample bottle by scooping deep into the mixed jar and pulling scoop through the infill material at different angles to collect material then gently tap the measuring spoon to achieve a level scoop desired then transfer to the composite container. Rotate the bottle in between scoops.
   c Monitor the total mass, as compared to the target mass, as crumb is added to the composite bottle. After the 4th scoop (typical), grab additional scoop(s) and slowly drop into the composite until the target mass is reached.
   d If crumb was spilled on the balance during the transfers, cap the composite bottle, remove from the balance and blow off the balance with DustOff (canned air) to clean the balance. Return the composite bottle and cap to the balance for the final reading of the mass.
   e Record the final total mass of the bottle and mass of crumb added on the tracking sheet.
   f Calculate the next target mass and repeat until all location specific samples from each field are added.
8. The measuring spoon should be detergent washed, rinsed thoroughly with DI water and then dried in the oven for 20 minutes. After cooling, they are then rinsed two times with acetone and then air dried in the fume hood. A clean measuring spoon (detergent washed and acetone rinsed) should be used for each field and area (i.e., 1 spoon for HI and 1 spoon for RoF).
9. Once all material is transferred to the composite bottle, close the bottle tightly and thoroughly mix by angled rotation for ≥ 5 minutes (see step H-2.4 above). Place the bottle in a ziplock bag, labeled with the field ID, and store in the freezer.
10. Once the preparation of the composite sample of a field is completed, place a dot on the original field storage box. The remainder of individual location specific samples will be retained in their original sealed containers in the large freezer in Room 103.

D.2. Instrument Descriptions and Procedures for Chemical Analyses of Samples Collected from the Air at the Fields and Extracts of Crumb Rubber Samples Collected from the Fields

D.2.1. Analysis of Volatile Organic Chemicals (VOCs) by Thermal Desorption Coupled with Gas Chromatography Mass Spectrometry (TD-GC-MS)

VOCs were collected onto multibed glass thermal desorption tubes (Supelco, P/N 28286-U) custom packed with primary bed of Carbopack B© sorbent (4 mm) and backed with a 2 mm section of Carbopack X©. Prior to use, the sorbent tubes were conditioned at 345 °C for 30 minutes with a helium purge (30 c.c. per minute) then sealed in Teflon capped TDS3 storage containers (Sigma P/N 25045-U). VOC samples were collected using a calibrated vacuum pump to pull air through the sample tubes at nominal flow rate of 100 c.c. per minute. Approximately 6 L of sample was collected. Flows were verified using a calibrated flow meter prior to and during sampling. Exposed sorbent tubes were sealed with Teflon lined caps after use and stored on ice for transport to the laboratory for analysis.

Before analysis, a gas-phase internal standard (120 ng of 1-bromo-4-fluorobenzene) was injected into each sorbent tube with a helium purge (30 c.c. per minute) at room temperature for 4 minutes. Once prepared, the sorbent tubes were analyzed by thermal desorption coupled gas chromatography mass spectrometry (GC-MS) using the following thermal desorption injection system: a ThermoDesorption Autosampler (Model TDSA2; Gerstel), a thermal desorption oven (Model TDS3, Gerstel) and a cryogenically cooled injection system (Model CIS4; Gerstel). The cooled injection system contained a Tenax-TA©-packed glass injection liner (P/N 013247- 005-00; Gerstel). The samples were desorbed at 50 c.c. per minute (splitless) using the following temperature profile: 25 °C (0.5 minute delay) followed by a 60 °C per minute ramp to 330 °C with a 1 minute hold time. The cooled inlet was held at 1 °C and then heated after 0.1 minutes to 300 °C at a rate of 12 °C per second, followed by a 2 minute hold time. The gas chromatograph (GC) was operated in the solvent vent mode with a splitless injection. Compounds were resolved on a GC (Series 6890 Plus; Agilent Technologies) equipped with a 30 m by 0.25-mm-diameter Restek Rxi-624Sil MS capillary column (P/N 13868) with 1.4 micron film thickness. The initial oven temperature was 1 °C, held for 2 minutes, then increased to 100 °C at 5 °C per minute (hold 2 minutes), increase to 140 °C at 3 °C per minute, then to 300 °C at 10 °C per minute and held for 10 minutes. The helium flow through the column was held constant at 1.2 mL per minute (initial pressure 47 kPa, 39 cm per second). The resolved analytes were detected using electron impact MS (5973; Agilent Technologies) operated in total ion current (TIC) mode with target and qualifier ions specified for each targeted compound. The mass spectrometry (MS) temperature settings were 240 °C, 230 °C, and 150 °C for the transfer line, MS source, and MS quad, respectively. The MS was operated in scan mode with a range of 34 mass to charge ratio (m/z) to 450 m/z. Multipoint calibrations were prepared from pure

standards for all targeted VOCs. The response for each analyte was normalized to the internal standard response.

D.2.2. Analysis of Low Molecular Weight Carbonyls by High Performance Liquid Chromatography (HPLC)

Targeted aldehydes and ketones with low molecular weight (i.e., formaldehyde, acetaldehyde, and acetone) were actively sampled onto silica gel cartridges coated with 2,4-dinitrophenylhydrazine (DNPH, XPoSure Aldehyde Sampler P/N WAT047205; Waters corporation) with ozone scrubbers installed upstream (P/N WAT054420; Waters). An SKC pump was used to draw the air through the sampling media with a target sampling flow rate of approximately 1000 mL per minute. Before the start of sampling, the airflow rates through each sampling line were measured using a BIOS flow meter (S/N 118925) and adjusted to the target flow rate. Actual airflow rates were recorded on a sampling record sheet once at the start and once towards the end of each sampling period. Sampling was carried out for 180 minutes at two locations on field.

The DNPH-coated cartridges were analyzed for the targeted aldehydes by high-performance liquid chromatography (HPLC). Each cartridge was eluted with 2 mL of high purity acetonitrile (P/N 018-4, Burdick & Jackson) and analyzed by HPLC (1200 Series; Agilent Technologies). Targeted analytes were resolved on a 200 mm by 3.2 mm Allure AK column (P/N 9159523-700; Restek) and run with 60:40 acetonitrile in water mobile phase at 0.5 mL per minute with UV detection at 360 nm. Multipoint calibration curves were prepared from certified standard hydrazone derivatives of the targeted analytes (CRM47651: Sigma-Aldrich).

D.2.3. Analysis of Volatile Sulfur Compounds (VSCs) by Thermal Desorption coupled with Gas Chromatography Sulfur Chemiluminescence Detection (TD-GC-CD)

Volatile sulfur chemicals (VSCs) were collected using the same protocol for VOCs. They were collected onto multibed glass thermal desorption tubes (Supelco, P/N 28286-U) custom packed with primary bed of Carbopack B© sorbent (4 mm) and backed with a 2 mm section of Carbopack X©. Prior to use, the sorbent tubes were conditioned at 345 °C for 30 minutes with a helium purge (30 c.c. per minute) then sealed in Teflon capped TDS3 storage containers (Sigma P/N 25045-U). VSC samples were collected using a calibrated vacuum pump to pull air through the sample tubes at nominal flow rate of 100 c.c. per minute. Approximately 6 L of sample was collected. Flows were verified using a calibrated flow meter prior to and during sampling. Exposed sorbent tubes were sealed with Teflon lined caps after use and stored on ice for transport to the laboratory for analysis.

The sorbent tubes were analyzed by thermal desorption coupled gas chromatography

and a sulfur chemiluminescence detector (TD-GC-SCD). Samples were introduced into the system using the following thermal desorption injection system: a ThermoDesorption Autosampler (Model TDSA2; Gerstel), a thermal desorption oven (Model TDS3, Gerstel) and a cryogenically cooled injection system (Model CIS4; Gerstel). The cooled injection system contained a deactivated glass bead liner (P/N 011714-005-00; Gerstel). The samples were desorbed at 50 c.c. per minute (splitless) using the following temperature profile: 20 °C (0.5 minute delay) followed by a 60 °C per minute ramp to 280 °C with a 2.3 minute hold time. The cooled inlet was held at -120 °C and then heated after 0.1 minutes to 280 °C at a rate of 12 °C per second, followed by a 2 minute hold time. The GC was operated in the solvent vent mode with a splitless injection. Compounds were resolved on a GC (Series 7890 Plus; Agilent Technologies) equipped with a 30 m by 0.32-mm-diameter DB-1 capillary column (P/N 123-1033;Agilent) with 1.0 mm film thickness. The initial oven temperature was 10 °C, held for 1 minute, then increased to 120 °C at 8 °C per minute, hold for 2 minutes then to 280 °C at 16 °C per minute and held for 10 minutes. The helium flow through the column was held constant at 3.5 mL per minute. The resolved analytes were detected by Sulfur Chemiluminescence (8355; Agilent Technologies) with a burner temperature of 800 °C and base temperature of 250 °C.

D.2.4. Analysis of Semi-Volatile Organic Compounds (SVOCs) by High Efficiency Source Gas Chromatography Mass Spectrometry (HES-GC-MS)

Before analysis extracts of SVOC sample trains, deuterated internal standards (100 ng of deuterated polyaromatic hydrocarbon, d-PAH, Table D-39) and recovery standards (100 ng of d-PAH and p-terphenyl-d14, Table D-39) were added to each sample according to details described in Section D.4.2.2.1.

For analysis of SVOCs in crumb rubber, a deuterated internals standard (100 pg of p-terphenyl-d14) was added to each sample before the analysis. Once prepared, 1 µL of sample was injected into a GC (Series 7890 Plus; Agilent Technologies) fitted with a programmable temperature vaporizer inlet (Model CIS4; Gerstel) with a septumless sampling head. The injection system contained a deactivated glass wool injection liner (P/N 23432; Restek). The samples were introduced into the system via a splitless injection at a pressure of 45 kPa using the following temperature profile: 40 °C (0.1 minute delay) followed by a 20 °C per minute ramp to 275 °C with a 5 minute hold time. Compounds were resolved on a 30 m by 0.25-mm diameter DB-UI8270D column (Agilent, P/N 122-9732) with 2.5 micron film thickness. The initial oven temperature was 40 °C, held for 2 minutes, then increased to 320 °C at 20 °C per minute (hold 5 minutes). The helium flow through the column was held constant at 1.2 mL per minute. The resolved analytes were detected on a high efficiency source MS detector (HES-MS, 5977B; Agilent Technologies) via electron impact. The MS temperature settings were 300 °C, 200 °C, and 150 °C for the transfer line, MS source, and MS quad, respectively. The MS was operated in scan mode with a range of 34 m/z to 1000 m/z. Multipoint

calibrations were prepared from pure standards for all targeted SVOCs. The response for each analyte was normalized to the internal standard response.

D.2.5. Analysis of Semi-Volatile Organic Compounds (SVOCs) by High Efficiency Source Gas Chromatography Mass Spectrometry (HES-GC-MS) with Synchronous Scan and Selected Ion Monitoring (SIM)

D.2.5.1. Pure Standards

Multipoint calibration standards were prepared from pure chemicals for all targeted analytes. Compounds were diluted in dichloromethane (DCM) to produce 11 calibration levels ranging from 30 ng per µL to 1 pg per µL. Each standard also contained 100 pg per µL of each of 18 d-PAH surrogates (P/N ES-2528, Cambridge Isotope Laboratories) which serve as an internal standard (Table D-3), plus 100 pg per µL of a recovery standard mix (used to normalize instrument response). The recovery standard mix contained three d-PAHs purchased from Cambridge Isotope Laboratories: 2-methylnaphthalene-d10 (P/N DLM-1322-S), p-terphenyl-d14 (P/N DLM-382-S), and perylene-d12 (P/N DLM-366-S). Before analysis, recovery standard was added to each sample to a final concentration of 100 pg per µL.

Table D-1. List of Deuterium Labeled PAHs (d-PAHs) Used as Internal Standards

Internal Standard	Chemical Abstracts Service Registry Number
Naphthalene-d8	1146-65-2
Acenaphthylene-d8	93951-97-4
Acenaphthene-d10	15067-26-2
Fluorene-d10	81103-79-9
Phenanthrene-d10	1517-22-2
Anthracene-d10	1719-06-8
Fluoranthene-d10	93951-69-0
Pyrene-d10	1718-52-1
Benz[a]anthracene-d12	1718-53-2
Chrysene-d12	1719-03-5
Benzo[b]fluoranthene-d12	93951-98-5
Benzo[k]fluoranthene-d12	93952-01-3
Benzo[a]pyrene-d12	63466-71-7
Indeno[1,2,3-c]pyrene-d12	203578-33-0
Dibenz[a,h]anthracene-d14	13250-98-1
Benzo[g,h,i]perylene-d12	93951-66-7

D.2.5.2. Instrument Parameters

Once prepared, 2 µL of standard or sample was introduced into an Agilent model 7890A gas chromatograph using a septumless sampling head (Gerstel, model SLH) fitted with a deactivated baffled injection liner (P/N 6492-U, Gerstel). The injection liner was held

at 40 °C for 0.1 minute for the manual injection, then heated to 275 °C at 12 °C per minute with a 3-minute hold. The GC was operated in the solvent vent mode with a splitless injection. An Agilent DB-UI8270D column (30 m x 0.25 mm x 0.25 µm) was heated at 40 °C for 1 minute then ramped to 320 °C at 20 °C per minute and held for 5.5 minutes under a constant helium flow of 1.0 mL per minute. The resolved analytes were detected using an HES-MS (5977B MSD; Agilent Technologies) operated in synchronous scan/selected ion monitoring (SIM) mode using trace ion detection and a gain factor of 0.5. The MS temperature settings were 300 °C, 300 °C, and 150 °C for the transfer line, MS source, and MS quad, respectively. Target and qualifier ions specified for each analyte, surrogate and internal standard compound listed in Table D-4 were programmed into the detector settings.

Table D-1. Parameters for Selected Ion Monitoring (SIM) Measurement of Semi-Volatile Organic Chemicals (SVOCs)

Targeted Chemical	RT Time (min)	SIM Group	SIM Start Time (min)	M/Z ion	Q1 Signal	Q2 Signal	Dwell Time (ms)
Cyclohexylamine	5.40	1	5.000	56.10	99.00	NA	40
2,5-Hexanedione	5.73	1	5.000	99.00	71.00	NA	40
n-Caproic acid vinyl ester	6.04	2	5.890	99.10	71.10	NA	30
Aniline	6.14	2	5.890	93.00	66.00	NA	30
Limonene	6.54	3	6.370	68.10	93.10	NA	30
Benzene, n-butyl-	6.72	3	6.370	91.10	134.10	NA	30
Naphthalene-d8	7.72	4	7.300	136.10	134.10	NA	30
Naphthalene	7.74	4	7.300	128.00	127.00	NA	30
Benzothiazole	8.08	5	7.950	135.00	108.00	NA	20
Cyclohexyl isothiocyanate	8.12	5	7.950	55.10	83.10	NA	20
Resorcinol	8.40	5	7.950	110.00	82.00	NA	20
2-Methylnaphthalene-d10	8.75	6	8.640	152.10	150.10	NA	30
Naphthalene, 2-methyl	8.81	6	8.640	142.00	141.00	NA	30
Naphthalene, 1-methyl-	8.99	6	8.640	142.00	141.00	NA	30
5,9-Undecadien-2-one, 6,10-dimethyl-	10.36	7	9.900	69.10	151.10	NA	25
Cyclohexanamine, N-cyclohexyl-	10.37	7	9.900	138.10	181.10	NA	25

Targeted Chemical	RT Time (min)	SIM Group	SIM Start Time (min)	M/Z ion	Q1 Signal	Q2 Signal	Dwell Time (ms)
Naphthalene, 1,6-dimethyl-	10.52	7	9.900	156.10	141.00	NA	25
Dimethyl phthalate	10.70	8	10.595	163.00		NA	15
Naphthalene, 1-5-dimethyl-	10.77	8	10.595	156.10	141.00	NA	15
Naphthalene, 2,3-dimethyl-*	10.78	8	10.595	156.10	141.00	NA	15
Acenaphthylene-d8	10.94	8	10.595	160.10	158.10	NA	15
Acenaphthylene	10.98	8	10.595	152.00	151.00	NA	15
Naphthalene, 1,2-dimethyl-	11.02	8	10.595	141.00	156.10	NA	15
Phthalimide	11.04	8	10.595	147.00	76.00	NA	15
2,5-di-tert-Butyl-1,4-benzoquinone*	11.15	8	10.595	163.00	205.10	NA	15
Acenaphthene-d10	11.45	9	11.320	162.10	164.10	NA	25
Butylated Hydroxytoluene	11.73	9	11.320	205.20	220.10	NA	25
N,N-Dicyclohexylmethylamine	11.87	9	11.320	152.05	70.10	NA	25
Pyridine, 2-(4-methylphenyl)-	13.30	10	12.600	169.10	168.00	NA	15
Diethyl Phthalate	13.40	10	12.600	149.00		NA	15
Fluorene-d10	13.43	10	12.600	174.10	176.10	NA	15
Fluorene	13.55	10	12.600	166.00	165.00	NA	15
Hexadecane	13.72	10	12.600	57.10	71.10	NA	15
4-tert-Octylphenol	13.75	10	12.600	135.10	107.00	NA	15
Naphthalene, 2-(bromomethyl)-	15.26	11	14.600	141.00	139.00	NA	30
2-Benzothiazolone	15.33	11	14.600	150.90	95.90	NA	30
Dibenzothiophene	17.63	12	17.000	184.00	139.00	NA	30
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	17.65	12	17.000	219.10	191.00	NA	30
Phenanthrene-d10	18.24	13	18.000	188.10	184.10	NA	15
Phenanthrene	18.36	13	18.000	178.00	176.00	NA	15
Anthracene-d10	18.56	13	18.000	188.10	184.10	NA	15
1,4-Benzenediol, 2,5-bis(1,1-dimethylethyl)-	18.61	13	18.000	222.20	207.10	NA	15
Anthracene	18.67	13	18.000	178.10	176.00	NA	15

Targeted Chemical	RT Time (min)	SIM Group	SIM Start Time (min)	M/Z ion	Q1 Signal	Q2 Signal	Dwell Time (ms)
1-Octadecene	18.75	13	18.000	97.10	83.10	NA	15
Phenol, 4-(1-phenylethyl)-	18.82	13	18.000	183.00	198.10	NA	15
Diisobutyl Phthalate	20.47	14	19.600	149.00		NA	100
Phenanthrene, 2-methyl-	21.47	15	21.000	192.10	191.00	189.00	40
Phenanthrene, 3-methyl	21.62	15	21.000	192.10	191.10	189.00	40
Anthracene, 2-methyl-	21.92	15	21.000	192.10	191.10	189.00	40
Phenanthrene, 1-methyl	22.27	15	21.000	192.10	191.10	189.00	40
N-Phenylbenzamide	23.14	16	22.500	105.00	77.00	NA	25
Dibutyl phthalate	23.20	16	22.500	149.00		NA	25
Benzothiazole, 2-phenyl-	23.76	16	22.500	211.00	108.00	NA	25
Fluoranthene-d10	25.94	17	25.000	212.10	210.00	NA	25
Fluoranthene	26.03	17	25.000	202.00	200.00	NA	25
Pyrene-d10	27.19	17	25.000	212.10	210.00	NA	25
Pyrene	27.27	17	25.000	202.00	200.00	NA	25
Anthracene, 9,10-dimethyl	27.63	18	27.490	206.10	191.00	NA	30
Methyl stearate	27.88	18	27.490	74.00	87.00	NA	30
p-Terphenyl-d14	28.76	19	28.300	244.10	243.10	NA	30
7H-Benzo[c]fluorene	29.52	19	28.300	216.10	215.10	NA	30
Benzyl butyl phthalate	31.31	20	30.500	149.00	91.00	NA	30
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	31.41	20	30.500	211.10	268.10	NA	30
Bis(2-Ethylhexyl)adipate	32.04	21	31.750	129.00	70.10	NA	30
Anthracene, 9-phenyl	32.27	21	31.750	254.10	252.10	NA	30
Cyclopenta[cd]pyrene	32.66	22	32.480	226.00	224.00	NA	25
Benz[a]anthracene-d12	32.70	22	32.480	240.10	236.10	NA	25
Benz[a]anthracene	32.78	22	32.480	228.10	226.00	NA	25
Chrysene-d12	32.81	22	32.480	240.10	236.10	NA	25
Chrysene	32.91	22	32.480	228.10	226.00	NA	25
1-Hydroxypyrene	33.33	23	33.250	218.00	189.00	NA	20
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	33.36	23	33.250	315.20	237.10	NA	20
Demecolcine	33.36	23	33.250	207.00	315.20	NA	20
Diisooctylphthalate	33.96	23	33.250	149.00	167.00	NA	20

Targeted Chemical	RT Time (min)	SIM Group	SIM Start Time (min)	M/Z ion	Q1 Signal	Q2 Signal	Dwell Time (ms)
1,4-Benzenediamine, N,N'-diphenyl-	36.07	24	35.200	260.10	183.00	NA	40
Di-n-octyl phthalate	36.90	24	35.200	149.00		NA	40
Benzo[b]fluoranthene-d12	37.32	25	37.100	264.10	260.00	NA	30
Benzo[b]fluoranthene	37.43	25	37.100	252.10	250.00	NA	30
Benzo[k]fluoranthene-d12	37.47	25	37.100	264.10	260.00	NA	30
Benzo[k]fluoranthene	37.56	25	37.100	252.10	250.00	NA	30
Benzo[e]pyrene	38.61	25	37.100	252.10	250.00	NA	30
Benzo[a]pyrene-d12	38.74	25	37.100	264.10	260.00	NA	30
Benzo[a]pyrene	38.84	25	37.100	252.10	250.00	NA	30
Perylene-d12	39.13	25	37.100	264.10	260.00	NA	30
Anthracene, 9,10-diphenyl-	41.80	26	41.000	330.10	252.10	NA	50
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	43.14	27	42.500	124.10	341.90	NA	50
Indeno[1,2,3-c]pyrene-d12	43.92	28	43.500	288.10	284.10	NA	20
Indeno[1,2,3-c]pyrene	44.03	28	43.500	276.00	274.00	NA	20
Dibenz[a,h]anthracene-d14	44.13	28	43.500	292.10	288.10	NA	20
Dibenz[a,h]anthracene	44.28	28	43.500	278.10	276.00	NA	20
Benzo[g,h,i]perylene-d12	45.02	29	44.630	288.10	284.10	NA	30
Benzo[g,h,i]perylene	45.14	29	44.630	276.00	274.00	NA	30
17-Pentatriacontene	49.95	30	47.000	57.00	97.00	NA	30
Coronene	51.77	30	47.000	300.00	150.00	NA	30

M/Z: mass to charge; NA: not available Q1: first quadrupole mass filter; and Q2: second quadrupole mass filter; RT: retention time; SIM: selected ion monitoring.

D.2.6. Analysis of Polar Organic Chemicals in Extract of Crumb Rubber by High Resolution Accurate Mass LC-MS (HRAM LC-MS) – Instrumental Settings

Samples of crumb rubber extracts were analyzed using a 1200 series liquid chromatography (LC) system (Agilent Technologies, Santa Clara, CA) that was connected in line with an (linear ion trap) LTQ-Orbitrap-XL mass spectrometer equipped with an electrospray ionization (ESI) source (ThermoFisher Scientific, W). The LC

system contained the following modules: G1322A solvent degasse, G1311A quaternary pump, G1316A thermostatted column compartment, and G1329A autosampler (Agilent Technologies). The LC column compartment was equipped with an Atlantis T3 column (length: 150 mm, inner diameter: 1.0 mm, particle size: 3 µm, part number: 186003714, Waters). Water purified to a resistivity of 18.2 MΩ·cm (at 25 °C) using a Milli-Q Gradient ultrapure water purification system (Millipore) and methanol (Optima LC-MS grade, 99.9 percent, Fisher) were used to prepare the mobile phase solvents, A and B, respectively. The elution program consisted of isocratic flow at 5 percent (volume to volume ratio) B for 2 minutes, a linear gradient to 30 percent B over 0.5 minutes, a linear gradient to 95 percent B over 32 minutes, isocratic flow at 95 percent B for 5 minutes, a linear gradient to 5 percent B over 0.5 minutes, and isocratic flow at 5 percent B for 20 minutes, at a flow rate of 100 µL per minute. The column compartment was maintained at 40 °C and the sample injection volume was 25 µL. Full-scan mass spectra were acquired over the range of m/z = 50 to 1800 using the Orbitrap mass analyzer, in profile format, with a mass resolution setting of 60,000 (at m/z = 400, measured at full width at half-maximum peak height, FWHM). In the data-dependent mode, the six most intense ions exceeding an intensity threshold of 10,000 raw ion counts were selected from each full-scan mass spectrum for tandem mass spectrometry (MS/MS) analysis using collision-induced dissociation (CID). MS/MS spectra were acquired using the linear ion trap, in centroid format, with the following parameters: isolation width 5 m/z units, normalized collision energy 35%, default charge state 1, activation Q 0.25, and activation time 30 millisecond. Real-time charge state screening was enabled to exclude unassigned charge states and charge states ≥4 from MS/MS analysis. To avoid the occurrence of redundant MS/MS measurements, real-time dynamic exclusion was enabled to preclude re-selection of previously analyzed precursor ions, with the following parameters: repeat count 3, repeat duration 30 second, exclusion list size 500, exclusion duration 180 second, and exclusion mass width ± 20 parts-per-million. Measurements were acquired using the positive ion mode and the negative ion mode. Data acquisition was controlled using Xcalibur software (version 2.0.7, Thermo Fisher Scientific).

D.2.7. Analysis of Metals and Metalloids in Extract of Crumb Rubber by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Before sample analysis, check instrument performance daily, run calibrations for each metal and metalloid, run QC check standard, and run blanks. During and after sample analysis, run QC check standard and blanks.

Approximately 0.2 grams (g) aliquots from a sub-set of 40 individual samples were weighted with a precision better than 0.1 milligrams (mg) and used for an assessment of in-field variability and method reproducibility, as described below.

Based on the results of the variability analysis, two composite crumb rubber samples, corresponding to high impact (HI) and rest of field (RoF) areas, were prepared for each

field (see Section D.1.8.1). For the composite samples, approximately 15-20 g of the tire crumb rubber material collected from each individual location was added to a single clean polyethylene (PE) bottle. A 120 mL bottle was used for the HI areas (using between 1 and 4 samples), and a 1 L bottle was used for the RoF areas (between 6 and 9 samples). The composite samples were thoroughly mixed through rotation and shaking. The remainder of the individual samples were retained in their original containers.

Samples were analyzed for 30 metals and metalloids by an inductively couple plasma coupled with a mass spectrometry, ICP-MS (ELAN DRC II, Perkin Elmer). Two analytical methods were used to assess the inorganic composition of the samples:

a) USEPA 3051A method (USEPA, 2007c) - This method uses microwave extraction and concentrated acids to achieve a comprehensive multi-element dissolution prior to analysis. It was developed for the digestion of sediments, sludges, soils and oils. Approximately 0.2 g aliquots of individual samples were weighted with a precision better than 0.1 mg in a fluoropolymer microwave vessel, extracted with a mixture of concentrated nitric acid (HNO_3, 9 mL) and concentrated hydrochloric acid (HCl, 3 mL) using a microwave system (Multiwave 3000, Anton Paar). The sealed vessel was heated by increasing the temperature to 175 °C over 5.5 minutes, and remaining at that temperature for an additional 10 minutes digestion period. The contents were allowed to cool overnight and filtered with 0.45 µm polyvinylidene fluoride (PVDF) membrane (Acrodisc LC 13 mm syringe filter, PALL Life Sciences). The filtrate was analyzed by ICP-MS. Two filtrate aliquots from each sample were diluted with HNO_3 with dilution factors of 20 (for the analysis of most metals and metalloids, except zinc) and 5,000 (for the analysis of zinc).

b) ASTM F3188-16 method (ASTM International, 2016)- This method was developed specifically to quantify extractable metals and metalloids in synthetic turf infill materials following ingestion. Samples were extracted under conditions (time, temperature and pH) that are similar to those experienced in the stomach during the digestive process. Approximately 0.2 g aliquots of individual samples were weighted with a microbalance (precision <0.1 mg) in 15 mL screw capped conical base tubes. A 10 mL 0.08 M hydrochloric acid (HCl) solution (prepared from ultrapure HCl) was added to each tube and the tube was wrapped with aluminum foil to protect from the light. After shaking the tube for 1 minute at 37 °C in an incubator, the pH of the extracts was measured. If the pH was higher than 1.5, additional 2 M HCl was added dropwise to bring the pH to between 1 and 1.5. The tube was shaken for 1 hour at 37 °C in an incubator, and allowed to stand for another hour at the same temperature. The supernatant was filtered using a 0.45 µm PVDF membrane (Acrodisc LC 13 mm syringe filter, PALL Life Sciences). The filtrate was analyzed by ICP-MS. Nitric acid (2 percent) was added to the filtrate, resulting to a dilution factor of 10.

Mercury analysis (PerkinElmer Inc, 2011) was carried out on separate aliquots for both methods because addition of gold to the filtrate was required to prevent the loss of mercury from the extracts. Gold (in the form of $AuCl_3$) was added (200 parts per billion, ppb) to all samples (mercury samples, standard solutions and blanks) and the ICP-MS rinse solutions.

To measure the background concentration of metals and metalloids in the extraction solution, a blank solution was prepared for each batch of sample preparation with no crumb rubber added to the tube. Batch specific background concentration of a metal or metalloid was subtracted from the detected concentrations of metal or metalloid in the filtrates to obtain the extractable concentrations of metal or metalloid from the crumb rubber.

The filtrates were analyzed simultaneously for 30 metals and metalloids by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer ELAN DRC II). Sample analysis was repeated for mercury using the sample instrument. Mercury analysis was conducted following the PerkinElmer ICP-MS application note (PerkinElmer Inc, 2011), while simultaneous analysis of all other metals and metalloids was conducted following the PerkinElmer user manual (PerkinElmer Inc, 2004).

D.3. Identification of Chemicals for Targeted Analyses of Field Samples and Validation of Chemical Analytical Data from

D.3.1. Environmental Chamber and Emissions Testing of Crumb Rubber

D.3.1.1. Material Preparation

New (un-installed) samples of artificial “grass” blades and crumb rubber samples were stored at room temperature and in the dark. Crumb rubber samples were stored in amber glass jars and the grass blade samples were wrapped in aluminum foil and sealed in plastic bags. Samples were coded with identification numbers only and scientists at LBNL were blinded as to the source of the material. In preparation for testing, a section of turf field was created in a 6 inch x 6 inch x 2 inch stainless steel box. A sample of artificial blades was removed from its individual sealed bag and a 6-inch (15.25 cm) square was cut from the piece using a straight edge and razor knife. The sample was placed into the stainless steel box then filled with 300 g of crumb rubber to create a reconstructed section of turf field (Figure D-4). The turf sections were reconstructed based on previous report from the Norwegian Institute for Air Research (NILU, 2017) on amounts of crumb rubber used in soccer field applications.

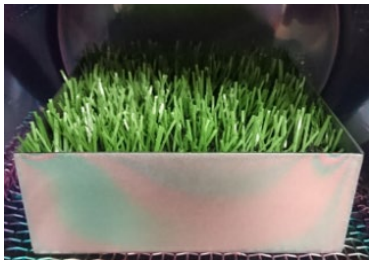


Figure D-1. Example of a 6 x 6 x 2 inch reconstructed turf field sample for emission testing

D.3.1.2. Material Testing

Emission testing generally followed the protocols in the American Society for Testing and Materials (ASTM) Standard Guide D-5116-97 (ASTM International, 2017) and California Specification 01350 using small emission chambers (CDPH, 2010). The emission testing apparatus consisted of four 10.75-liter stainless steel chambers (Figure D-5) that were treated with Sulfinert® coating (http://www.silcotek.com/) to minimize wall interaction for active compounds. The test materials were placed on a Sulfinert® treated screen resting slightly below the center of the test chambers and the chambers were sealed with clamp-on lids. The chambers were mounted inside a controlled environment incubator (Forma Scientific, Model 3919) that was used to provide a constant temperature.

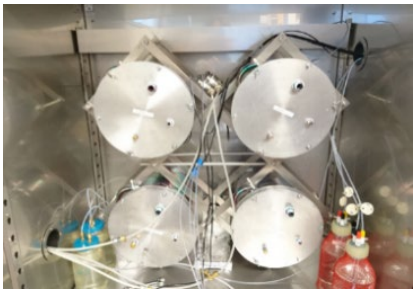


Figure D-1. Four emission chambers

All four chambers were maintained at a nominal standard temperature and humidity (25 °C and 50 percent relative humidity, RH). HOBO data loggers (Onset Model U12-011) were used to record temperature and RH. Preconditioned air was supplied to each chamber continuously at 1 liter per minute (LPM). Dry house air was passed through an activated carbon filter followed by a high efficiency particulate air (HEPA) filter and then a portion of the air stream was passed through a bubbler containing deionized water. A small amount of activated carbon was placed in the bubbler reservoir. The wet and dry air streams were mixed to produce the desired relative humidity and the humidified air was delivered (at 1 LPM) to each chamber using flow control valves and taper-tube flow meters (Figure D-6). The ventilation rate in the chambers was approximately 5.6 air changes per hour (ACH). Reconstructed turf field samples were sealed into a chamber typically 24 hours before sampling to allow time for the conditions to stabilize.

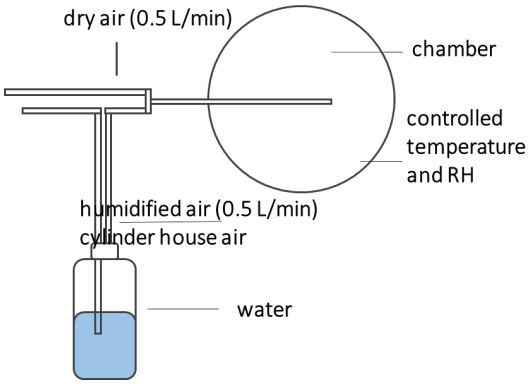


Figure D-2. Flow of conditioned air to emission chamber

D.3.1.3. Air Sampling and Analysis for Volatile Organic Chemicals (VOCs) and Low Molecular Weight Carbonyls

The samples were drawn directly from the chamber through a port in the lid of the chamber. The sampling rate was maintained at less than 80 percent of the total flow through the chamber to prevent backflow of air into the test chamber. VOC samples were collected onto multibed custom sorbent tubes containing a primary bed of Carbopack B® with a backup bed of Carbopack X® (Supelco). Prior to use, the sorbent tubes were conditioned by helium purge (25 c.c. per minute) at 345 °C for 30 minutes and sealed in Teflon capped tubes. A variable speed peristaltic pump (MasterFlex, Cole-Parmer) was used to pull air through the sample tubes at a sampling rate of 100 c.c. per minute. Flows were checked using a DryCal gas flow meter (BIOS, 500 c.c. per minute) at least twice during each sampling period. Approximately 3 liters of air were collected from the emission chambers. After sample collection, the sorbent tubes were sealed with Teflon lined caps and transferred to a freezer until analysis by GC-MS (see Section D.2.1).

Samples of low molecular weight carbonyl compounds were collected and analyzed following ASTM Test Method D 5197-92 (ASTM International, 1997). The air samples were drawn directly from the small emission chamber at steady state. Samples were collected on commercially available silica gel cartridges coated with 2,4-dinitrophenyl-hydrazine (DNPH, XPoSure Aldehyde Sampler P/N WAT047025; Waters corporation). Chamber air was drawn through the sample cartridge at 850 c.c. per minute using a peristaltic pump (MaterFlex, Cole-Parmer). Sample cartridges were capped and stored in the freezer until extraction and analyzed by high performance liquid chromatography, HPLC (see Section D.2.2).

D.3.2. Direct Thermal Desorption Measurements of Crumb Rubber

Pre-installed crumb rubber samples were directly desorbed into the GC-MS to provide information on mid-range VOCs in the crumb rubber with a high confidence that the chemicals were from crumb rubber samples. A small amount (10 mg) of pre-installed crumb rubber was placed into a clean thermal desorption tube. The tube was heated at 150 °C under a flow of helium and directly injected into the GC-MS following details in Section D.2.1.

D.3.3. Crumb Rubber Extraction for Gas Chromatography Mass Spectrometry (GC-MS) Non-Targeted Chemical Analysis

SAFETY: This procedure uses flammable solvents and a high pressure extraction system located in B70-217 at LBNL. Workers need to have WPC approval (EA-0002) for work on this system. All work is to be performed in the fume hood while wearing nitrile gloves, safety glasses and lab coat.

D.3.3.1. Extracting Crumb Rubber Samples for Gas Chromatography Mass Spectrometry (GC-MS) Non-targeted Analysis

Crumb rubber samples are extracted with 50:50 acetone: hexanes using the Accelerated Solvent Extraction (ASE).

Table D-1. Equipment and Supplies

Accelerated solvent extraction system (Dionex, ASE 200)	Amber bottle, 1 L
Micro balance	40 ml amber volatile organic analysis (VOA) vials (Ichem)
Muffle furnace	Caps for 40 ml vials
Crumb samples	Septa, (P/N 288-7222; Thermo)
N_2 cylinder	Glass drying dish
Hexanes, pesticide residue grade	Weigh boat, Aluminum foil
Dichloromethane, pesticide residue grade	Spatula
Acetone, pesticide residue grade	ASE glass fiber filter, solvent clean
Diatomaceous earth	Kimwipes™
Small ASE cells, 11 ml	Bench paper
Caps for ASE cells	Nitrile gloves
Funnel, aluminum	Timer
Not applicable	Labeling tape

D.3.3.2. Procedure

1. Preparation of Diatomaceous Earth (D.E.)
   a Solvent clean 1 L amber bottle and lid, air dry.
   b Solvent clean glass Pyrex drying dish.
   c Place about 500 mL of D.E. in drying dish.
   d Bake in muffle furnace for 4 hours at 400 °C.
   e Cool overnight and store tightly sealed in 1 L bottle.
2. Crump Rubber Preparation
   a Solvent rinse ASE cell and caps with DCM followed by acetone then air dry.
   b Clean spatula, funnel, and foil weigh boat with DCM followed by acetone.
   c Record the number on ASE 11 mL cell. Assemble bottom cap and insert a cleaned filter.
   d Weigh 0.45 g of crumb rubber and record weight.
   e Weigh 1.85 g D.E.
   f Add D.E. to crumb sample in the weigh boat.

g Mix thoroughly so crumb particles are dispersed into the D.E.

h Transfer prepared sample to the prepared ASE cell using the funnel.

i Cap cell tightly.

j Clean the forceps and use a new clean weigh boat for each sample.

k Label one 40 mL VOA vial for each sample and place in ASE carousel.

l Run ASE Method 17 for each ASE cell. (50 percent acetone and 50 percent hexanes).

Table D-1. ASE Program: Method 17/Schedule 17

Oven temp: 75 °C	Pressure: 1500 psi
Preheat: 0 minutes	Static: 5 minutes
Heat: 5 minutes	Solvent: 50 percent Acetone and 50 percent Hexanes
Cycles: 1	Purge: 120 seconds
Flush: 50 percent	Elapsed time: 30 minutes

3. When finished, replace vial cap with a closed top cap.

4. Store sample extracts in the fridge until analysis.

D.3.3.3. Analysis of Extract by GC-MS

Before analysis, the crumb rubber extracts were brought to room temperature. Samples were directly injected without any concentration. Once prepared, 1 µL of sample was injected into a gas chromatograph (GC, Series 7890 Plus; Agilent Technologies) fitted with a programmable temperature vaporizer (PTV) inlet (Model CIS4; Gerstel) with a septumless sampling head. The injection system contained a deactivated glass wool injection liner (P/N 23432; Restek). The samples were introduced into the system via a splitless injection at a pressure of 45kPa using the following temperature profile: 40 °C (0.1 minute delay) followed by a 20 °C per minute ramp to 275 °C with a 5 minute hold time. Compounds were resolved on a 30 meter by 0.25-mm diameter DB-UI8270D column (Agilent, P/N 122-9732) with 2.5 micron film thickness. The initial oven temperature was 40 °C, held for 2 minutes, then increased to 320 °C at 20 °C per minute (hold 5 minutes). The helium flow through the column was held constant at 1.2 mL per minute. The resolved analytes were detected on a high efficiency source mass spectrometry (HES-MS) detector (5977B; Agilent Technologies) via electron impact. The MS temperature settings were 300 °C, 200 °C, and 150 °C for the transfer line, MS source, and MS quad, respectively. The MS was operated in scan mode with a range of 34 m/z to 1000 m/z.

D.3.3.4. Non-Targeted Analysis of GC-MS Data

The GC-MS data were analyzed using two different computer algorithms:

- Enhanced ChemStation (version F.01.03.2357 Agilent Technologies, Inc., Santa Clara, CA)(Agilent Technologies, 2009): a GC-MS integration software for data acquisition and evaluation,

- Automatic Mass Spectral Deconvolution and Identification System (AMDIS, NIST Standard Reference Data Program, Gaithersburg, MD)(NIST, 2019): a deconvolution software for extracting the spectrum of each component in a mixture.

Suspect screening analysis is performed by comparing the MS fragmentation patterns (acquired by GC-MS) with reference spectra in the National Institute of Standards and Technology 14 (NIST 14) spectral library (NIST, 2020). Matched suspects with a quality score of at least 80 percent are labeled as tentative chemicals in the crumb rubber extracts. Tentative chemicals are being prioritized based on toxicity information obtained from the USEPA CompTox Chemicals Dashboard (USEPA, 2023) and availability of reference standards. Reference standards are used to confirm the identity of the tentative chemicals by matching the chromatographic (GC retention time) and spectral (MS fragmentation pattern) data.

D.3.4. Crumb Rubber Extraction for Liquid Chromatography Mass Spectrometry (LC-MS) Non-Targeted Chemical Analysis

SAFETY: This procedure uses flammable solvents and a high pressure extraction system located in B70-217 at LBNL. Workers need to have WPC approval for work on this system. All work is to be performed in the fume hood while wearing nitrile gloves, safety glasses and lab coat.

D.3.4.1. Extracting Crumb Rubber Samples for Liquid Chromatography Mass Spectrometry (LC-MS) Analysis

Crumb rubber samples are extracted with 90:10 water: methanol using the Accelerated Solvent Extractor (ASE).

Table D-1. Equipment and Supplies

Accelerated solvent extraction system (Dionex, ASE 200)	Amber bottle, 1 L
Micro balance	40 ml amber volatile organic analysis (VOA) vials (Ichem)
Muffle furnace	Caps for 40 ml vials
Crumb samples	Septa, (P/N 288-7222; Thermo)
N_2 cylinder	Weigh boat
Water, HPLC grade	Spatula
Methanol, HPLC grade	ASE glass fiber filter, solvent clean
Dichloromethane	Kimwipes™
Diatomaceous earth (D.E.)	Bench paper
Small ASE cells, 11 mL	Nitrile gloves
Caps for ASE cells	Timer
Not applicable	Labeling tape

D.3.4.2. Procedure

1. Preparation of Diatomaceous Earth (D.E.)
   a Solvent clean 1 L amber bottle and lid, air dry.
   b Solvent clean glass Pyrex drying dish.
   c Place about 500 mL of D.E. in drying dish.
   d Bake in muffle furnace for 4 hours at 400 °C.
   e Cool overnight and store tightly sealed in 1 L bottle.
2. Crump Rubber Preparation
   a. Solvent rinse ASE cell and caps with DCM followed by acetone, then air dry.
   b. Clean spatula, funnel, and foil weigh boat with DCM followed by acetone.
   c. Record the number on ASE 11 mL cell. Assemble bottom cap and insert a cleaned filter.
   d. Weigh desired amount of crumb and record weight.
   e. Add D.E. to crumb sample in the weigh boat.
   f. Mix thoroughly so crumb particles are dispersed into the D.E.
   g. Transfer prepared sample to the ASE cell.
   h. Cap cell tightly.
   i. Label one 40 mL VOA vial for each sample and place in ASE carousel.
   j. Run ASE Method 16 (Table D-8) for each ASE cell. (90 percent water and 10 percent methanol).

Table D-1. ASE Program: Method 16. CRUMB Extraction

Oven temp: 75v°C	Pressure: 1500 psi
Preheat: 0 minute	Static: 5 minutes
Heat: 5 minutes	Solvent: 90 percent Water in 10 percent Methanol
Cycles: 1	Purge: 120 seconds
Flush: 50 percent	Elapsed time: 30 minutes

3. When finished, replace vial cap with a closed top cap.
4. Store sample extracts in the fridge until analysis.
5. Enter sample information into a tracking sheet (see example in Table D-9).

Table D-2. Example Tracking sheet: Sample IDs and Weights (Uninstalled Crumb Rubber, CR, Sample XX Was Used)

Sample ID	Crumb Rubber, Percent by Weight	Cell ID	ASE position	Weight of CR, g	Diatomaceous Earth Weight, g
CRBXX-100	100	K14609	1	4.5000	0
CRBXX-75	75	K11994	2	3.3842	0.5053
CRBXX-50	50	K14538	3	2.2445	0.9965
CRBXX-25	25	K12039	4	1.1200	1.5054
CRBXX-10	10	K15122	5	0.4500	1.8079
CRBXX-00	0	K14480	6	0	2.00

D.3.4.3. Analysis of Extract by High Resolution Accurate-Mass Liquid Chromatography Mass Spectrometry (HRAM LC-MS)

Samples of uninstalled or field composite crumb rubber extracts were analyzed using a 1200 series liquid chromatography (LC) system (Agilent Technologies, Santa Clara, CA) that was connected in line with an (linear ion trap) LTQ-Orbitrap-XL mass spectrometer equipped with an electrospray ionization (ESI) source (ThermoFisher Scientific, W) (see Section D.2.6 for detailed instrumental setup). MS/MS spectra were acquired using the linear ion trap, in centroid format, with the following parameters: isolation width 5 m/z units, normalized collision energy 35 percent, default charge state 1, activation Q 0.25, and activation time 30 millisecond. Real-time charge state screening was enabled to exclude unassigned charge states and charge states ≥4 from MS/MS analysis. Measurements were acquired using the positive ion mode and the negative ion mode. Data acquisition was controlled using Xcalibur software (version 2.0.7, Thermo Fisher Scientific).

D.3.4.4. Non-Targeted Analysis of LC-MS Data: Two-Tiered Non-Targeted Analysis Approach to Identify Tentative Extractable Polar Chemicals in Crumb Rubber:

D.3.4.4.1. Tier 1. Suspect Screening Analysis of Polar Organic Chemicals in Crumb Rubber Extracts Using Established Chemical Databases

1. Match Mass of Molecular Ions (MS1) with Established Tire-Related Chemical Lists

   a Tire-Related Chemical Lists:

      i *OEHHA Tire-Related Chemical List* (OEHHA, 2016) - tire-related chemicals (confirmed or unconfirmed) reported in literature and chemicals used in tire manufacturing processes (information provided by the Rubber Manufacturers Association (USTMA, https://www.ustires.org/whats-tire-0) and International Carbon Black Association (ICBA, 2016), along with chemicals advertised for use tire or rubber manufacturing).

      ii *Chemical Information from the Federal Tire Studies* – chemicals identified (confirmed or unconfirmed) in tire studies conducted by federal agencies.

   b Download Monoisotopic Masses of Chemicals in the Established Tire-Related Chemical List:

i Import Chemical Abstracts Service Registry Numbers (CASRN) of chemicals on the Tire-Related Chemical Lists into the US EPA DSSTox Database and batch search for monoisotopic mass of the chemicals.

ii Incorporate monoisotopic masses into the Tire-Related Chemical Lists.

c Match Molecular Ion Peaks on LC-MS (MS1) with Chemicals on the Tire-Related Chemical List.

i Use Compound Discoverer software (version 3.0, ThermoFisher Scientific, Waltham, MA) to derive molecular mass of molecular ions on MS1 spectra of the crumb rubber extracts and truncate molecular masses to the 100th decimal place.

ii Truncate monoisotopic mass of listed chemicals to the 100th decimal place.

iii Make tentative chemical identifications through matching the monoisotopic masses on the Tire-Related Chemical Lists with the molecular masses obtained from the LC-MS analysis of crumb rubber extracts.

iv Enter the matched chemicals to the Tentatively Identified Chemicals List for crumb rubber.

d Use the USEPA DSSTox Database Search to Further Enrich the Tentatively Identified Chemical List:

i Import the exact neutral mass of molecular ions from Compound Discoverer (LC-MS analysis of field sample extracts) into the USEPA DSSTox Database (USEPA, 2024)for batch search of parent chemicals that generate fragment(s) with monoisotopic mass matching the mass of the unknown molecular ions, within (±) 5 ppm.

ii Export CASRN of matched parent chemicals.

iii Make tentative chemical identifications by matching the CASRN of the exported parent chemicals with the Tire-Related Chemical Suspect Lists.

iv Enter the matched chemicals to the Tentatively Identified Chemical List for crumb rubber.

2. Identify Tentatively Identified Chemical Using Only the USEPA DSSTox Database – Search Molecular Masses Derived from Mass of Molecular Ions on the USEPA DSSTox Database:

a Import the exact neutral mass of molecular ions from Compound Discoverer (LC-MS analysis of field sample extracts) into the USEPA DSSTox Database for batch search of parent chemicals that generate fragment(s) with monoisotopic mass matching the mass of the molecular ions, within (±) 5 ppm.

b Export the chemicals and enter into the Tentative Chemical List of crumb rubber.

3. Prioritize and Confirm Tentatively Identified Chemicals according to the priority

scheme show in Figure D-7.

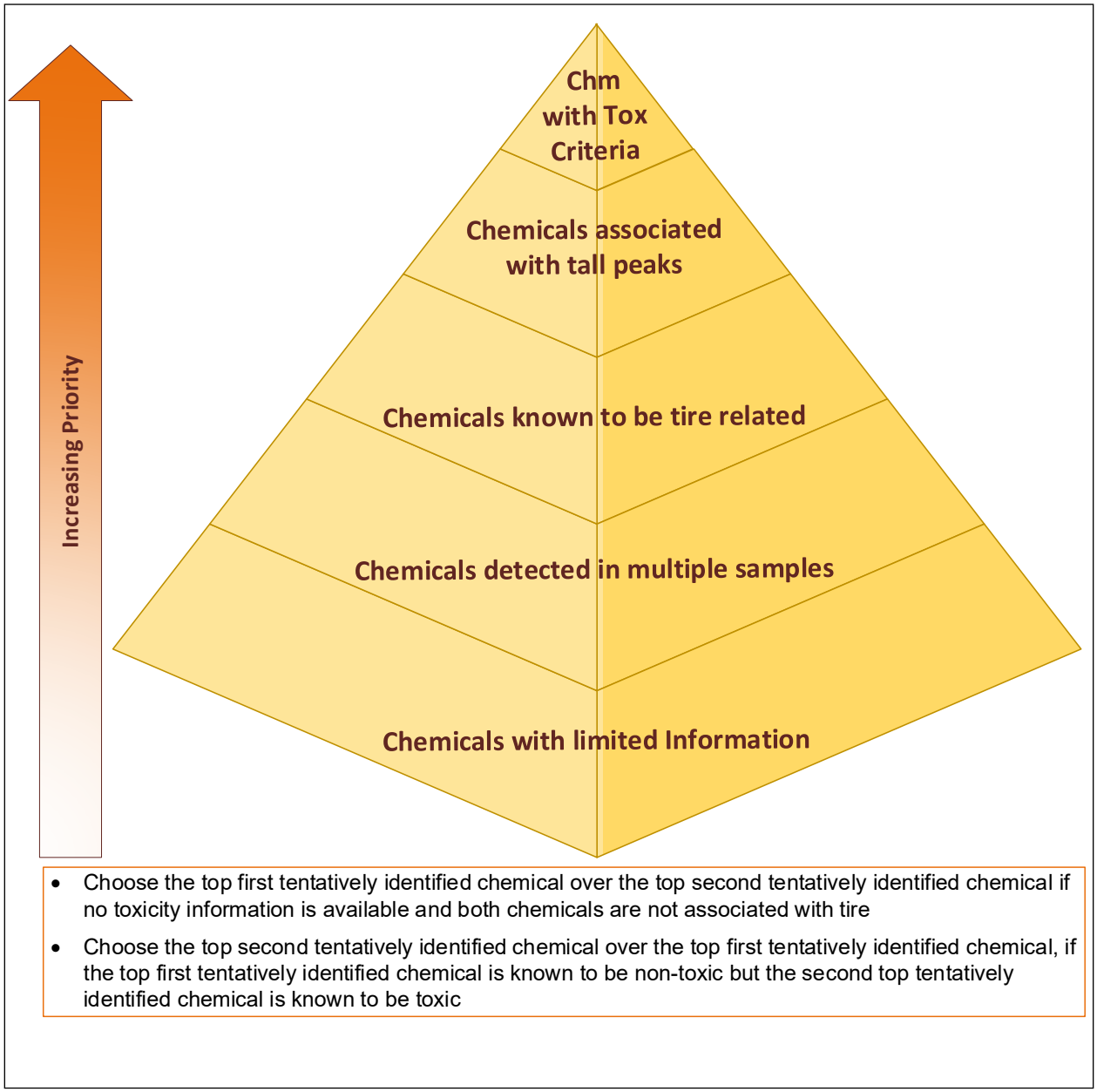


Figure D-1. Prioritization Scheme of Tentatively Identified Chemicals in Crumb Rubber Extracts

4. Use reference standards to confirm the identity of the tentatively identified chemicals by comparing their LC retention time and spectral data (MS1 and MS2).
5. Add the confirmed chemicals to the Chemical Target List, which will be used to guide the bioaccessibility measurements.

D.3.4.4.2. Tier 2. Non-Targeted Chemical Analysis of Polar Chemicals in Crumb Rubber Extracts with the Aid of Cheminformatics Tools

Tentative chemicals are identified through matching unknown spectral data (from the HRAM- LC-MS analysis of crumb rubber extracts) with spectral library using Compound Discoverer (version 3.0.0.294, ThermoFisher Scientific, Waltham, MA). The algorithm built into Compound Discoverer allow it to search its spectral library, which is compiled with in silico mass spectra and experimental spectral data collected from various databases. Below are the steps of the analysis:

1. Use Compound Discoverer to process the raw data obtained from the HRAM-LC/MS instrument using the following customized workflow:

[Select Spectra (1)]
-->Align Retention Times (37)

[Align Retention Times (37)]
-->Detect Compounds (24)

[Detect Compounds (24)]
-->Group Compounds (25)
-->Merge Features (14)

[Group Compounds (25)]
-->Search mzCloud (27)
-->Assign Compound Annotations (30)
-->Fill Gaps (41)
-->Search ChemSpider (22)
-->Predict Compositions (40)
-->Search mzVault (46)

[Fill Gaps (41)]
-->Mark Background Compounds (39)

[Search ChemSpider (22)]
-->Apply mzLogic (42)

[Search mzCloud (27)]
[Assign Compound Annotations (30)]
[Mark Background Compounds (39)]
[Apply mzLogic (42)]
[Predict Compositions (40)]
[Search mzVault (46)]
[Merge Features (14)]
[Differential Analysis (31)]
[Descriptive Statistics (45)]

Processing node 1: Select Spectra
---
1. General Settings:
- Precursor Selection: Use MS(n - 1) Precursor
- Use Isotope Pattern in Precursor Reevaluation: True
- Provide Profile Spectra: Automatic
- Store Chromatograms: False

2. Spectrum Properties Filter:
- Lower RT Limit: 0
- Upper RT Limit: 60
- First Scan: 0
- Last Scan: 0
- Ignore Specified Scans: (not specified)
- Lowest Charge State: 0
- Highest Charge State: 0
- Min. Precursor Mass: 100 Da
- Max. Precursor Mass: 5000 Da
- Total Intensity Threshold: 0
- Minimum Peak Count: 1

3. Scan Event Filters:
- Mass Analyzer: Any
- MS Order: Any
- Activation Type: Any
- Min. Collision Energy: 0
- Max. Collision Energy: 1000
- Scan Type: Is Full
- Polarity Mode: Is - *(or + depending on data being analyzed)*

4. Peak Filters:
- S/N Threshold (FT-only): 1.5

5. Replacements for Unrecognized Properties:
- Unrecognized Charge Replacements: 1
- Unrecognized Mass Analyzer Replacements: ITMS
- Unrecognized MS Order Replacements: MS2
- Unrecognized Activation Type Replacements: CID
- Unrecognized Polarity Replacements: - *(or + depending on data being analyzed)*
- Unrecognized MS Resolution@200 Replacements: 60000
- Unrecognized MSn Resolution@200 Replacements: 30000

Processing node 37: Align Retention Times
---
1. General Settings:
- Alignment Model: Adaptive curve

- Alignment Fallback: Use Linear Model
- Maximum Shift [min]: 2
- Shift Reference File: True
- Mass Tolerance: 5 ppm
- Remove Outlier: True

Processing node 24: Detect Compounds
---
1. General Settings:
- Mass Tolerance [ppm]: 2 ppm
- Intensity Tolerance [%]: 30
- S/N Threshold: 3
- Min. Peak Intensity: 62500
- Ions: [M-H]-1
- Base Ions: [M-H]-1
- Min. Element Counts: C H
- Max. Element Counts: C90 H190 Br3 Cl4 F6 K2 N10 Na2 O18 P3 S5

2. Peak Detection:
- Filter Peaks: True
- Max. Peak Width [min]: 0.8
- Remove Singlets: False
- Min. # Scans per Peak: 3
- Min. # Isotopes: 1

Processing node 25: Group Compounds
---
1. Compound Consolidation:
- Mass Tolerance: 2 ppm
- RT Tolerance [min]: 0.1

2. Fragment Data Selection:
- Preferred Ions: [M-H]-1

Processing node 27: Search mzCloud
---
1. Search Settings:
- Compound Classes: All
- Match Ion Activation Type: True
- Match Ion Activation Energy: Match with Tolerance
- Ion Activation Energy Tolerance: 20
- Apply Intensity Threshold: True
- Precursor Mass Tolerance: 5 ppm
- FT Fragment Mass Tolerance: 10 ppm
- IT Fragment Mass Tolerance: 10 ppm
- Identity Search: Cosine

- Similarity Search: Similarity Forward
- Library: Reference
- Post Processing: Recalibrated
- Match Factor Threshold: 50
- Max. # Results: 20

Processing node 30: Assign Compound Annotations
---
1. General Settings:
- Mass Tolerance: 5 ppm

2. Data Sources:
- Data Source #1: mzCloud Search
- Data Source #2: Predicted Compositions
- Data Source #3: mzVault Search
- Data Source #4: ChemSpider Search
- Data Source #5: (not specified)

Processing node 41: Fill Gaps
---
1. General Settings:
- Mass Tolerance: 2 ppm
- S/N Threshold: 1.5
- Use Real Peak Detection: True

Processing node 39: Mark Background Compounds
---
1. General Settings:
- Max. Sample/Blank: 5
- Max. Blank/Sample: 0
- Hide Background: True

Processing node 22: Search ChemSpider
---
1. Search Settings:
- Database(s):
    ACToR: Aggregated Computational Toxicology Resource
    DrugBank
    EAWAG Biocatalysis/Biodegradation Database
    EPA DSSTox
    EPA Toxcast
    FDA UNII - NLM
    KEGG
    MassBank
    NIST

NIST Chemistry WebBook
NIST Spectra
PubMed
- Search Mode: By Formula or Mass
- Mass Tolerance: 2 ppm
- Max. # of results per compound: 2000
- Max. # of Predicted Compositions to be searched per Compound: 3
- Result Order (for Max. # of results per compound): Order By Reference Count (DESC)

2. Predicted Composition Annotation:
- Check All Predicted Compositions: True

Processing node 42: Apply mzLogic
---
1. Search Settings:
- FT Fragment Mass Tolerance: 10 ppm
- IT Fragment Mass Tolerance: 0.4 Da
- Max. # Compounds: 0
- Max. # mzCloud Similarity Results to consider per Compound: 10
- Match Factor Threshold: 30

Processing node 40: Predict Compositions
---
1. Prediction Settings:
- Mass Tolerance: 2 ppm
- Min. Element Counts: C H
- Max. Element Counts: C90 H190 Br3 Cl8 F18 N10 O18 P3 S5
- Min. RDBE: 0
- Max. RDBE: 40
- Min. H/C: 0.1
- Max. H/C: 3.5
- Max. # Candidates: 10
- Max. # Internal Candidates: 500

2. Pattern Matching:
- Intensity Tolerance [%]: 30
- Intensity Threshold [%]: 0.1
- S/N Threshold: 3
- Min. Spectral Fit [%]: 30
- Min. Pattern Cov. [%]: 80
- Use Dynamic Recalibration: True

3. Fragments Matching:
- Use Fragments Matching: True
- Mass Tolerance: 5 ppm
- S/N Threshold: 3

Processing node 46: Search mzVault
---
1. Search Settings:
- mzVault Library: MoNA.db
- Max. # Results: 10
- Match Factor Threshold: 50
- Search Algorithm: HighChem HighRes
- Match Analyzer Type: True
- IT Fragment Mass Tolerance: 0.4 Da
- FT Fragment Mass Tolerance: 10 ppm
- Use Retention Time: False
- Precursor Mass Tolerance: 10 ppm
- Apply Intensity Threshold: False
- Match Ionization Method: True
- Ion Activation Energy Tolerance: 20
- Match Ion Activation Energy: Match with Tolerance
- Match Ion Activation Type: False
- Compound Classes: All
- Remove Precursor Ion: True
- RT Tolerance [min]: 2

Processing node 14: Merge Features
---
1. Peak Consolidation:
- Mass Tolerance: 2 ppm
- RT Tolerance [min]: 0.1

Processing node 31: Differential Analysis
---
1. General Settings:
- Log10 Transform Values: True

Processing node 45: Descriptive Statistics
---

2. Designate the top candidates, with the Fragment Ion Search (FISh) scoring algorithm, as tentative chemicals for the corresponding molecular ion peak.
3. Prioritize and Confirm Tentatively Identified Chemicals according to the priority scheme show in Figure D-7.
4. Use reference standards to confirm the tentative chemical identifications by comparing their LC retention time and spectral data (MS1 and MS2).
5. Add the confirmed chemicals to the Chemical Target List, which will used to guide

the bioaccessibility measurements.

D.3.5. Results of Non-Targeted Chemical Analyses and Chemicals Identified from Literature Review

D.3.5.1. Lists of Organic Chemicals Targeted in the Analyses of Samples Collected from Air On- or Off-Fields are summarized in Table D-10 and Table D-11.

Table D-1. List of Volatile Organic Chemicals (VOCs, Including Low Molecular Weight Carbonyls) Targeted in the Analyses of Vapor Sampled from the 35 Selected Synthetic Turf Fields during the Phase 3 Field Work

Targeted Chemical	CASRN	Analyzed in Sample
2-Butanone	78-93-3	ALD
Acetaldehyde	75-07-0	ALD
Acetone	67-64-1	ALD
Acrolein	107-02-8	ALD
Crotonaldehyde	123-73-9	ALD
Formaldehyde	50-00-0	ALD
m-Tolualdehyde	620-23-5	ALD
Propionaldehyde	123-38-6	ALD
Valeraldehyde	110-62-3	ALD
Benzaldehyde	100-52-7	ALD and VOC
Butanal	123-72-8	ALD and VOC
Hexanal	66-25-1	ALD and VOC
Methacrolein	78-85-3	ALD and VOC
1-Hexanol, 2-ethyl-	104-76-7	VOC
2-Butoxyethanol	111-76-2	VOC
2-Hexanone, 5-methyl	110-12-3	VOC
3-Carene	13466-78-9	VOC
a-Pinene	7785-70-8	VOC
a-Terpineol	98-55-5	VOC
Azulene	275-51-4	VOC
Benzene	71-43-2	VOC
Benzene, 1,2,3-trimethyl-	526-73-8	VOC
Benzene, 1,2,4,5-tetramethyl-	95-93-2	VOC
Benzene, 1,2,4-trimethyl-	95-63-6	VOC
Benzene, 1,4-dichloro	106-46-7	VOC
Benzene, 1-chloro-4-(trifluoromethyl)-	98-56-6	VOC
Benzene, 1-ethyl-2,4-dimethyl-	874-41-9	VOC
Benzene, 2-ethyl-1,4-dimethyl-	1758-88-9	VOC

Targeted Chemical	CASRN	Analyzed in Sample
Benzene, n-butyl-	104-51-8	VOC
Benzothiazole	95-16-9	VOC
Benzothiazole, 2-methylthio-	615-22-5	VOC
Biphenyl	92-52-4	VOC
Butylated Hydroxytoluene	128-37-0	VOC
Cyclohexanone	108-94-1	VOC
Cyclopentasiloxane, decamethyl-	541-02-6	VOC
Cyclotetrasiloxane, octamethyl-	556-67-2	VOC
Cyclotrisiloxane, hexamethyl-	541-05-9	VOC
Decanal	112-31-2	VOC
Decane	124-18-5	VOC
D-Limonene	5989-27-5	VOC
Dodecane	112-40-3	VOC
Ethylbenzene	100-41-4	VOC
Formamide, N-(1,1-dimethylethyl)-	2425-74-3	VOC
Furan, 2-methyl	534-22-5	VOC
g-Terpinene	99-85-4	VOC
Heptanal	111-71-7	VOC
Heptane	142-82-5	VOC
Hexane	110-54-3	VOC
Indan	496-11-7	VOC
m/p-Xylene	106-42-3	VOC
Mesitylene	108-67-8	VOC
Methyl Isobutyl Ketone	108-10-1	VOC
Naphthalene	91-20-3	VOC
Nonanal	124-19-6	VOC
Octanal	124-13-0	VOC
Octane	111-65-9	VOC
o-Xylene	95-47-6	VOC
p-Cymene	99-87-6	VOC
Phenol	108-95-2	VOC
Styrene	100-42-5	VOC
Tetrachloroethylene	127-18-4	VOC
Tetradecane	629-59-4	VOC
Texanol, TXIB (mono-isomer)	25265-77-4	VOC
Toluene	108-88-3	VOC
Trichloroethylene	79-01-6	VOC
Trichloromethane	67-66-3	VOC

Targeted Chemical	CASRN	Analyzed in Sample
TXIB "Kodaflex"	6846-50-0	VOC
Undecane	1120-21-4	VOC

ALD: carbonyl vapor samples collected with 2,4-dinitrophenylhydrazine coated silica gel cartridges and analyzed by high performance liquid chromatography; CASRN: Chemical Abstracts Service Registry Number; and VOC: volatile organic chemical vapor samples collected with sorbent tubes and analyzed by gas chromatography mass spectrometry.

Table D-2. List of Semi-Volatile Organic Chemicals (SVOCs) Targeted in the Analyses of Semi-Volatile Sample Trains Collected from the 35 Selected Synthetic Turf Fields during the Phase 3 Field Work

Targeted Chemical	CASRN	Analyzed in Sample
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	793-24-8	SVOC
1,4-Benzenediamine, N,N'-diphenyl-	74-31-7	SVOC
1,4-Benzenediol, 2,5-bis(1,1-dimethylethyl)-	88-58-4	SVOC
17-Pentatriacontene	6971-40-0	SVOC
1-Hydroxypyrene	5315-79-7	SVOC
1-Octadecene	112-88-9	SVOC
2,5-di-tert-Butyl-1,4-benzoquinone	2460-77-7	SVOC
2,5-Hexanedione	110-13-4	SVOC
2-Benzothiazolone	934-34-9	SVOC
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	SVOC
4-tert-Octylphenol	140-66-9	SVOC
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	SVOC
7H-Benzo[c]fluorene	205-12-9	SVOC
Acenaphthylene	208-96-8	SVOC
Aniline	62-53-3	SVOC
Anthracene	120-12-7	SVOC
Anthracene, 2-methyl-	613-12-7	SVOC
Anthracene, 9,10-dimethyl	781-43-1	SVOC
Anthracene, 9,10-diphenyl-	1499-10-1	SVOC
Anthracene, 9-phenyl	602-55-1	SVOC
Benz[a]anthracene	56-55-3	SVOC
Benzo[a]pyrene	50-32-8	SVOC
Benzo[b]fluoranthene	205-99-2	SVOC
Benzo[e]pyrene	192-97-2	SVOC
Benzo[g,h,i]perylene	191-24-2	SVOC
Benzo[k]fluoranthene	207-08-9	SVOC
Benzothiazole, 2-phenyl-	883-93-2	SVOC

Targeted Chemical	CASRN	Analyzed in Sample
Benzyl butyl phthalate	85-68-7	SVOC
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	52829-07-9	SVOC
Bis(2-ethylhexyl)adipate	103-23-1	SVOC
Chrysene	218-01-9	SVOC
Coronene	191-07-1	SVOC
Cyclohexanamine, N-cyclohexyl-	101-83-7	SVOC
Cyclohexyl isothiocyanate[a]	1122-82-3	SVOC
Cyclohexylamine	108-91-8	SVOC
Cyclopenta[cd]pyrene	27208-37-3	SVOC
Demecolcine	477-30-5	SVOC
Dibenz[a,h]anthracene	53-70-3	SVOC
Dibenzothiophene	132-65-0	SVOC
Dibutyl phthalate	84-74-2	SVOC
Diethyl Phthalate	84-66-2	SVOC
Diisobutyl Phthalate	84-69-5	SVOC
Diisooctylphthalate	27554-26-3	SVOC
Dimethyl phthalate	131-11-3	SVOC
Di-n-octyl phthalate	117-84-0	SVOC
Fluoranthene	206-44-0	SVOC
Fluorene	86-73-7	SVOC
Hexadecane	544-76-3	SVOC
Indeno[1,2,3-cd]pyrene	193-39-5	SVOC
Limonene	138-86-3	SVOC
Methyl stearate	112-61-8	SVOC
N,N-Dicyclohexylmethylamine	7560-83-0	SVOC
Naphthalene, 1,2-dimethyl-	573-98-8	SVOC
Naphthalene, 1,6-dimethyl-	575-43-9	SVOC
Naphthalene, 1-methyl-	90-12-0	SVOC
Naphthalene, 2-(bromomethyl)-	939-26-4	SVOC
Naphthalene, 2,3-dimethyl-	581-40-8	SVOC
Naphthalene, 2-methyl	91-57-6	SVOC
n-Caproic acid vinyl ester	3050-69-9	SVOC
N-Phenylbenzamide	93-98-1	SVOC
Phenanthrene	85-01-8	SVOC
Phenanthrene, 1-methyl	832-69-9	SVOC
Phenanthrene, 2-methyl-	2531-84-2	SVOC
Phenanthrene, 3-methyl	832-71-3	SVOC

Targeted Chemical	CASRN	Analyzed in Sample
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	2772-45-4	SVOC
Phenol, 4-(1-phenylethyl)-	1988-89-2	SVOC
Phthalimide[a]	85-41-6	SVOC
Pyrene	129-00-0	SVOC
Pyridine, 2-(4-methylphenyl)-	4467-06-5	SVOC
Resorcinol	108-46-3	SVOC

[a] Two chemicals failed calibration and were not quantified in the analysis of the SVOC sample trains: cyclohexyl isothiocyanate and phthalimide due to the maximum calibration levels were below the limit of quantification and the method detection limit, respectively (see Section D.3.6.3 for discussion of quality control analysis of chemical data). Chemicals failed calibration and were not quantified in the analysis of the SVOC samples.
CASRN: Chemical Abstracts Service Registry Number; and SVOC: semi-volatile organic chemical samples collected with SVOC sample trains for SVOC vapor and airborne fine particulate matters with diameter 2.5 µm and below from the air.

D.3.5.2. Lists of Chemicals Targeted in the Bioaccessibility Analyses of Crumb Rubber Samples are Table D-12 and Table D-13.

Table D-1. List of Targeted Organic Chemicals for Gastrointestinal and Dermal Bioassessibility Measurements of Crumb Rubber Sampled from the 35 Synthetic Turf Fields

Targeted Chemical	CASRN	Analysis
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	793-24-8	GC
1,4-Benzenediol, 2,5-bis(1,1-dimethylethyl)-	88-58-4	GC
17-Pentatriacontene	6971-40-0	GC
1-Hydroxypyrene	5315-79-7	GC
1-Octadecene	112-88-9	GC
2,5-di-tert-Butyl-1,4-benzoquinone	2460-77-7	GC
2,5-Hexanedione	110-13-4	GC
4-tert-Octylphenol	140-66-9	GC
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	GC
7H-Benzo[c]fluorene	205-12-9	GC
Acenaphthylene	208-96-8	GC
Aniline	62-53-3	GC
Anthracene	120-12-7	GC
Anthracene, 2-methyl-	613-12-7	GC
Anthracene, 9,10-dimethyl	781-43-1	GC
Anthracene, 9,10-diphenyl-	1499-10-1	GC
Anthracene, 9-phenyl	602-55-1	GC

Targeted Chemical	CASRN	Analysis
Benz[a]anthracene	56-55-3	GC
Benzene, n-butyl-	104-51-8	GC
Benzo[a]pyrene	50-32-8	GC
Benzo[b]fluoranthene	205-99-2	GC
Benzo[e]pyrene	192-97-2	GC
Benzo[g,h,i]perylene	191-24-2	GC
Benzo[k]fluoranthene	207-08-9	GC
Benzothiazole, 2-phenyl-	883-93-2	GC
Benzyl butyl phthalate	85-68-7	GC
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	52829-07-9	GC
Bis(2-Ethylhexyl)adipate	103-23-1	GC
Butylated Hydroxytoluene	128-37-0	GC
Chrysene	218-01-9	GC
Coronene	191-07-1	GC
Cyclohexyl isothiocyanate	1122-82-3	GC
Cyclohexylamine	108-91-8	GC
Cyclopenta[cd]pyrene	27208-37-3	GC
Demecolcine	477-30-5	GC
Dibenz[a,h]anthracene	53-70-3	GC
Dibenzothiophene	132-65-0	GC
Dibutyl phthalate	84-74-2	GC
Diethyl Phthalate	84-66-2	GC
Diisobutyl Phthalate	84-69-5	GC
Diisooctylphthalate	27554-26-3	GC
Dimethyl phthalate	131-11-3	GC
Di-n-octyl phthalate	117-84-0	GC
Fluoranthene	206-44-0	GC
Fluorene	86-73-7	GC
Hexadecane	544-76-3	GC
Hexanoic Acid, 2-ethyl	149-57-5	GC
Indeno[1,2,3-cd]pyrene	193-39-5	GC
Limonene	138-86-3	GC
Methyl stearate	112-61-8	GC
Naphthalene	91-20-3	GC
Naphthalene, 1,2-dimethyl-	573-98-8	GC
Naphthalene, 1,6-dimethyl-	575-43-9	GC
Naphthalene, 1-methyl-	90-12-0	GC
Naphthalene, 2-(bromomethyl)-	939-26-4	GC
Naphthalene, 2,3-dimethyl-	581-40-8	GC
Naphthalene, 2-methyl	91-57-6	GC

Targeted Chemical	CASRN	Analysis
n-Caproic acid vinyl ester	3050-69-9	GC
N-Phenylbenzamide	93-98-1	GC
Phenanthrene	85-01-8	GC
Phenanthrene, 1-methyl	832-69-9	GC
Phenanthrene, 2-methyl-	2531-84-2	GC
Phenanthrene, 3-methyl	832-71-3	GC
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	2772-45-4	GC
Phenol, 4-(1-phenylethyl)-	1988-89-2	GC
Phthalimide	85-41-6	GC
Pyrene	129-00-0	GC
Pyridine, 2-(4-methylphenyl)-	4467-06-5	GC
Resorcinol	108-46-3	GC
1,4-Benzenediamine, N,N'-diphenyl-	74-31-7	GC and LC
2-Benzothiazolone	934-34-9	GC and LC
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	GC and LC
Benzothiazole	95-16-9	GC and LC
Cyclohexanamine, N-cyclohexyl-	101-83-7	GC and LC
N,N-Dicyclohexylmethylamine	7560-83-0	GC and LC
1,3-Benzothiazole-2-thiol	149-30-4	LC
1,3-Diphenylguanidine	102-06-7	LC
2-(Methylthio)benzothiazole	615-22-5	LC
2-Azacyclotridecanone	947-04-6	LC
Diphenylurea	102-07-8	LC
Linoleic acid	60-33-3	LC
N,N'-Dicyclohexylurea	2387-23-7	LC
Oleic acid	112-80-1	LC
Phenoxazine	135-67-1	LC
Ricinoleic acid	141-22-0	LC
Triethylene glycol monobutyl ether	143-22-6	LC

CASRN: Chemical Abstracts Service Registry Number; GC: gas chromatography; and LC: liquid chromatography.

Table D-2. List of Targeted Metals and Metalloids for Gastrointestinal Bioassessibility Measurements of Crumb Rubber Sampled from the 35 Synthetic Turf Fields

Targeted Metal or Metalloid	Symbol	Atomic Number	Analysis
Aluminum	Al	13	IPC-MS
Antimony	Sb	51	IPC-MS
Arsenic	As	33	IPC-MS
Barium	Ba	56	IPC-MS
Beryllium	Be	4	IPC-MS

Targeted Metal or Metalloid	Symbol	Atomic Number	Analysis
Boron	B	5	IPC-MS
Cadmium	Cd	48	IPC-MS
Calcium	Ca	20	IPC-MS
Chromium	Cr	24	IPC-MS
Cobalt	Co	27	IPC-MS
Copper	Cu	29	IPC-MS
Iron	Fe	26	IPC-MS
Lead	Pb	82	IPC-MS
Lithium	Li	3	IPC-MS
Magnesium	Mg	12	IPC-MS
Manganese	Mn	25	IPC-MS
Molybdenum	Mo	42	IPC-MS
Nickel	Ni	28	IPC-MS
Potassium	K	19	IPC-MS
Rubidium	Rb	37	IPC-MS
Selenium	Se	34	IPC-MS
Silicon	Si	14	IPC-MS
Silver	Ag	47	IPC-MS
Sodium	Na	11	IPC-MS
Strontium	Sr	38	IPC-MS
Thallium	Tl	81	IPC-MS
Tin	Sn	50	IPC-MS
Titanium	Ti	22	IPC-MS
Vanadium	V	23	IPC-MS
Zinc	Zn	30	IPC-MS

ICP-MS: Inductively Coupled Plasma Mass Spectrometry

D.3.6. Determination of the Method Detection Limits (MDLs) and Limits of Quantification (LOQs) for Validation of Analytical Chemical Data of Field Samples

D.3.6.1. Definition and procedure for the determination of the MDL:

The USEPA (USEPA, 2016) defines the method detection limit (MDL) as: “the minimum measured concentration of a substance that can be reported with 99 percent confidence that the measured concentration is distinguishable from method blank results.” The procedures outlined in the USEPA document 40 CFR 136 for determining the initial MDL can be summarized as following:

1. Select a spiking level, typically 2 to 10 times the estimated MDL.
2. Process a minimum of seven spiked samples and seven method blank samples through all steps of the method. The samples used for the MDL must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates.

3. Compute the MDLs (the MDL based on spiked samples) as follows:

$$MDL_s = t_{(n-1,1-\infty=0.99)}S_S \quad \text{Equation D-1}$$

where:

MDL_s = the method detection limit based on spiked samples

$t_{(n-1,1-\infty=0.99)}$ = the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom.

S_s = sample standard deviation of the replicate spiked sample analyses.

4. Compute the MDL_b (the MDL based on method blanks) as follows:

$$MDL_b = X + t_{(n-1,1-\infty=0.99)}S_b \quad \text{Equation D-2}$$

where:

MDL_b = the MDL based on method blanks

X = mean of the method blank results (use zero in place of the mean if the mean is negative)

$t_{(n-1,1-\infty=0.99)}$ = the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom.

S_b = sample standard deviation of the replicate method blank sample analyses

5. Select the greater of MDL_s or MDL_b as the initial MDL.

The following sections briefly describe the procedures for determining the values of MDL for analyses of organic chemicals, metals, and metalloids by various instruments. Standard operating procedures (SOPs) of the instrumental analyses are detailed in Section D.2 Prior to the analysis of blank and spike samples, LBNL optimized the instrumentation and made sure it passed daily performance checks. They conducted the calibration with eight calibration standards and found excellent quality control (QC) agreement.

Based on the MDL determined for each targeted chemicals (including metals and metalloids), OEHHA derived the limit of quantification (LOQ) for the instrumental analysis of each chemical. We applied the values of MDL and LOQ of each targeted chemical to perform QC on the analytical data of samples collected from the 35 synthetic turf fields. This Appendix includes a discussion the SOP for QC of analytical data (Section D.3.6.3)

D.3.6.1.1. Determination of MDL by Thermal Desorption Coupled with Gas Chromatography Mass Spectrometry (TD-GC-MS) for the Analysis of Sorbent Tube Volatile Organic Chemical (VOC) Samples

Table D-14 provides the values of method detection limits for each VOC targeted in the analysis of the sorbent tube samples collected from the air. LBNL determined the values of MDL using the blanks and the spiked samples by following the steps below:

1. Preparation of Spiked Samples: A gas-phase internal standard (120 ng of 1-bromo-4-fluorobenzene) was injected into each sorbent tube with a helium purge (30 c.c. per min) at room temperature for 4 minutes. The tubes were also spiked with VOCs with the same amounts as the lowest calibration standards. To determine the MDL_s the lowest calibration standard (including the internal standard) for each target chemical was injected 29 times and analyzed by GC-MS following the SOP in Section D.2.1.
2. Preparation of Blank Samples: Thirty-one travel blanks collected on synthetic turf fields and playgrounds were spiked with internal standard and analyzed with the same procedure as the spiked samples.

Table D-1. Method Detection Limit (MDL) for the Thermal Desorption Coupled with Gas Chromatography Mass Spectrometry Analysis of Volatile Organic Chemicals (VOCs) in the Sorbent Tube Samples Collected from the Air

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (ng per Liter)	MDL_b (ng per Liter)	Selected MDL (ng per Liter)[b]	Selected MDL (ng per m^3)[b]
1,4-Benzenediamine, N,N'-diphenyl-	74-31-7	2.79	0.245	not detected	0.245	245
1-Hexanol, 2-ethyl-	104-76-7	2.97	0.0715	0.121	0.121	121
2-Butoxyethanol	111-76-2	3.18	0.089	0.323	0.323	323
2-Hexanone, 5-methyl	110-12-3	3.14	0.362	not detected	0.362	362
3-Carene	13466-78-9	3.01	0.108	not detected	0.108	108
Aniline	62-53-3	3.05	0.268	0.0395	0.268	268
a-Pinene	7785-70-8	3.06	0.0996	not detected	0.0996	99.6
a-Terpineol	98-55-5	3.03	0.126	not detected	0.126	126
Azulene	275-51-4	2.97	0.0968	not detected	0.0968	96.8
Benzaldehyde	100-52-7	3.12	0.129	0.0264	0.129	129
Benzene	71-43-2	3.69	0.18	0.111	0.18	180

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (ng per Liter)	MDL_b (ng per Liter)	Selected MDL (ng per Liter)[b]	Selected MDL (ng per m^3)[b]
Benzene, 1,2,3-trimethyl-	526-73-8	3.14	0.101	not detected	0.101	101
Benzene, 1,2,4,5-tetramethyl-	95-93-2	2.91	0.0269	not detected	0.0269	26.9
Benzene, 1,2,4-trimethyl-	95-63-6	3.14	0.133	0.00922	0.133	133
Benzene, 1,4-dichloro	106-46-7	3.45	0.0789	not detected	0.0789	78.9
Benzene, 1-chloro-4-(trifluoromethyl)-	98-56-6	3.17	0.0334	not detected	0.0334	33.4
Benzene, 1-ethyl-2,4-dimethyl-	874-41-9	3.01	0.025	not detected	0.025	25
Benzene, 2-ethyl-1,4-dimethyl-	1758-88-9	3.10	0.0165	not detected	0.0165	16.5
Benzene, butyl-	104-51-8	3.07	0.0734	not detected	0.0734	73.4
Benzothiazole	95-16-9	3.24	0.0821	0.00922	0.0821	82.1
Benzothiazole, 2-mercapto	149-30-4	2.91	0.256	not detected	0.256	256
Benzothiazole, 2-methylthio-	615-22-5	2.91	0.0381	not detected	0.0381	38.1
Biphenyl	92-52-4	3.42	0.0619	not detected	0.0619	61.9
Butanal	123-72-8	3.37	0.321	0.0474	0.321	321
Butylated Hydroxytoluene	128-37-0	2.45	0.248	not detected	0.248	248
Cyclohexanone	108-94-1	3.38	0.25	not detected	0.25	250
Cyclo-pentasiloxane, decamethyl-	541-02-6	3.07	0.0805	0.0988	0.0988	98.8
Cyclotetrasiloxane, octamethyl-	556-67-2	3.09	0.0377	0.101	0.101	101
Cyclotrisiloxane, hexamethyl-	541-05-9	3.12	0.225	1.05	1.05	1050
Decanal	112-31-2	3.18	0.0596	0.171	0.171	171
Decane	124-18-5	3.22	0.108	not detected	0.108	108
Dibutyl phthalate	84-74-2	3.07	0.0728	0.00922	0.0728	72.8
Diethyl phthalate	84-66-2	3.01	0.128	0.0145	0.128	128

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (ng per Liter)	MDL_b (ng per Liter)	Selected MDL (ng per Liter)[b]	Selected MDL (ng per m^3)[b]
Dimethyl phthalate	131-11-3	3.15	0.0574	not detected	0.0574	57.4
D-Limonene	5989-27-5	2.99	0.134	0.0329	0.134	134
Dodecane	112-40-3	3.09	0.118	not detected	0.118	118
Ethylbenzene	100-41-4	3.63	0.236	0.00659	0.236	236
Formamide, N-(1,1-dimethylethyl)-	2425-74-3	3.19	0.121	not detected	0.121	121
Furan, 2-methyl	534-22-5	3.24	0.0297	0.0211	0.0297	29.7
g-Terpinene	99-85-4	2.96	0.14	not detected	0.14	140
Heptanal	111-71-7	3.03	0.129	not detected	0.129	129
Heptane	142-82-5	3.52	0.177	not detected	0.177	177
Hexadecane	544-76-3	2.98	0.385	not detected	0.385	385
Hexanal	66-25-1	3.38	0.238	0.245	0.245	245
Hexane	110-54-3	3.45	0.0849	0.267	0.267	267
Indan	496-11-7	2.53	0.0259	not detected	0.0259	25.9
m/p-Xylene	106-42-3	3.63	0.235	0.00922	0.235	235
Mesitylene	108-67-8	3.05	0.0255	not detected	0.0255	25.5
methacrolein	78-85-3	4.13	0.103	not detected	0.103	103
Methyl isobutyl ketone	108-10-1	3.09	0.243	not detected	0.243	243
Naphthalene	91-20-3	3.03	0.0865	0.00659	0.0865	86.5
Naphthalene, 1-methyl-	90-12-0	2.92	0.035	not detected	0.035	35
Naphthalene, 2-methyl-	91-57-6	3.06	0.0416	not detected	0.0416	41.6
Nonanal	124-19-6	3.06	0.544	0.149	0.544	544
Octanal	124-13-0	3.17	0.0346	0.0553	0.0553	55.3
Octane	111-65-9	3.68	0.233	0.0171	0.233	233
o-Xylene	95-47-6	3.60	0.267	not detected	0.267	267

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (ng per Liter)	MDL_b (ng per Liter)	Selected MDL (ng per Liter)[b]	Selected MDL (ng per m^3)[b]
p-Cymene	99-87-6	3.02	0.0317	not detected	0.0317	31.7
Phenol	108-95-2	3.30	0.109	0.138	0.138	138
Styrene	100-42-5	3.23	0.0910	0.025	0.091	91
Tetrachloro-ethylene	127-18-4	4.25	0.278	not detected	0.278	278
Tetradecane	629-59-4	3.17	0.142	not detected	0.142	142
Texanol TXIB (mono-isomer)	25265-77-4	3.10	0.0438	not detected	0.0438	43.8
Toluene	108-88-3	3.66	0.200	0.0382	0.2	200
Trichloro-ethylene	79-01-6	3.49	0.0186	not detected	0.0186	18.6
Trichloro-methane	67-66-3	3.91	0.156	0.0105	0.156	156
TXIB "Kodaflex"	6846-50-0	3.16	0.138	not detected	0.138	138
Undecane	1120-21-4	3.08	0.101	not detected	0.101	101

[a]Spiked samples have the same concentrations as the lowest detected calibration standards.
[b]MDL: method detection limit; selected the greater of MDL_s or MDL_b as the MDL. MDL_b were not determined for chemicals that were not detected in the blank samples and MDL_s were selected as the MDL for those chemicals. Average volume of air flow through the sorbent tubes were 7.59 liter among all the VOC samples. MDL (ng per Liter) = MDL (ng) ÷ 7.59 Liter. MDL (ng per m^3) = MDL (ng per Liter) x 1000 (Liter per m^3).
CASRN: Chemical Abstracts Service Registry Number; MDL_b: MDL based on method blanks, calculated using Equation D-2; and MDL_s: MDL based on spiked samples, calculated using Equation D-1.
All values shown are rounded to three significant figures.

D.3.6.1.2. Determination of MDL by High Efficiency Source Coupled with Gas Chromatography Mass Spectrometry (HES-GC-MS) for the Analysis of SVOCs Extracted from the SVOC Sample Trains

Table D-15 provides the values of method detection limits for the HES-GC-MS analysis of each targeted SVOC in the extracts of SVOC sample trains collected from the air. Similar to the determination of MDL for sorbent tube VOC samples, LBNL determined the values of MDL for the SVOCs using the blanks and the spiked samples by following the steps below:

1. Preparation of Blank Samples: Thirteen trip blank SVOC sample trains (polyurethane/XAD™ [1] media/glass fiber filter) from synthetic turf fields or playgrounds were extracted as described in Section D.4.2.1. The extracts were spiked with internal standards and then concentrated as described in the Section D.4.2.2. The extracts were analyzed by HES-GC-MS, following to SOPs described in Section D.2.5, to determine the MDL_b.
2. Preparation of Spiked Samples: To determine the MDL_s, the lowest calibration standard (including the internal standard) for each target chemical was injected seven times and analyzed by HES-GC-MS following the SOPs described in Section D.2.5.

Table D-1. Method Detection Limits for the High Efficiency Source Coupled with Gas Chromatography Mass Spectrometry Analysis of Semi-Volatile Organic Chemicals (SVOCs) in Extracts of the SVOC Sample Trains Collected from the Air

Targeted Chemical	CASRN	MDL_s (pg per µL)	Average. Background (pg per µL)[a]	MDL_b (pg per µL)	Background Subtracted MDL_b (pg per µL)[b]	Selected MDL (pg per µL)[b]	MDL (ng per m^3)[b]
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	793-24-8	0.846	not detected	not detected	not detected	0.846	0.0522
1,4-Benzenediamine, N,N'-diphenyl-	74-31-7	38.4	0.636	4.91	4.28	4.28	0.264
1,4-Benzenediol, 2,5-bis(1,1-dimethylethyl)-	88-58-4	800	not detected	not detected	not detected	800	49.4
17-Pentatriacontene	6971-40-0	60.6	82.9	262	179	179	11
1-Hydroxypyrene	5315-79-7	167	not detected	not detected	not detected	167	10.3
1-Octadecene	112-88-9	0.986	29.8	71.5	41.7	41.7	2.57
2,5-di-tert-Butyl-1,4-benzoquinone*	2460-77-7	1.49	not detected	not detected	not detected	1.49	0.0919
2,5-Hexanedione	110-13-4	0.397	1650	4500	2840	2840	176
2-Benzothiazolone	934-34-9	167	456	939	483	483	29.8
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	0.234	357	1270	914	914	56.4
4-tert-Octylphenol	140-66-9	1.04	2.57	16.9	14.3	14.3	0.884
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	0.711	35.5	102	66.8	66.8	4.12

[1]XAD is a sorbent material registered by the Dow Chemical Company or an affiliated company of Dow.

Targeted Chemical	CASRN	MDL_s (pg per µL)	Average. Background (pg per µL)[a]	MDL_b (pg per µL)	Background Subtracted MDL_b (pg per µL)[b]	Selected MDL (pg per µL)[b]	MDL (ng per m^3)[b]
7H-Benzo[c]fluorene	205-12-9	0.178	0.681	2.2	1.52	1.52	0.0936
Acenaphthylene	208-96-8	0.092	15.4	43.2	27.8	27.8	1.72
Aniline	62-53-3	1.74	106	378	272	272	16.8
Anthracene	120-12-7	0.201	4.98	14.7	9.71	9.71	0.599
Anthracene, 2-methyl-	613-12-7	0.197	0.464	1.19	0.724	0.724	0.0447
Anthracene, 9,10-dimethyl	781-43-1	0.567	0.287	1.76	1.47	1.47	0.0909
Anthracene, 9,10-diphenyl-	1499-10-1	0.96	0.571	3.82	3.25	3.25	0.201
Anthracene, 9-phenyl	602-55-1	0.291	1.64	8.26	6.63	6.63	0.409
Benz[a]anthracene	56-55-3	0.474	1.43	5.05	3.62	3.62	0.223
Benzene, n-butyl-	104-51-8	0.928	85.9	308	222	222	13.7
Benzo[a]pyrene	50-32-8	0.566	0.0938	0.965	0.871	0.871	0.0537
Benzo[b]fluoranthene	205-99-2	0.628	2.28	6.8	4.52	4.52	0.279
Benzo[e]pyrene	192-39-5	0.792	0.535	1.91	1.37	1.37	0.0848
Benzo[g,h,i]perylene	191-24-2	0.839	0.243	1.32	1.08	1.08	0.0664
Benzo[k]fluoranthene	207-08-9	1.16	1.75	5.5	3.75	3.75	0.231
Benzothiazole	95-16-9	5.18	29400	98000	68600	68600	4230
Benzothiazole, 2-phenyl-	883-93-2	0.272	0.948	7.24	6.3	6.3	0.389
Benzyl butyl phthalate	85-68-7	0.485	153	405	252	252	15.5
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	52829-07-9	67.1	555	1920	1360	1360	84.1
Bis(2-Ethylhexyl)adipate	103-23-1	0.501	1880	4920	3040	3040	188
Butylated Hydroxytoluene	128-37-0	0.706	20100	74400	54300	54300	3350
Chrysene	218-01-9	0.861	1.64	6.2	4.56	4.56	0.282
Coronene	191-07-1	2.1	0.71	3.46	2.75	2.75	0.17
Cyclohexanamine, N-cyclohexyl-	101-83-7	0.491	2.41	7.39	4.99	4.99	0.308
Cyclohexyl isothiocyanate	1122-82-3	2.38	3830	10600	6810	6810	420
Cyclohexylamine	108-91-8	334	not detected	not detected	not detected	334	20.6

Targeted Chemical	CASRN	MDL_s (pg per µL)	Average. Background (pg per µL)[a]	MDL_b (pg per µL)	Background Subtracted MDL_b (pg per µL)[b]	Selected MDL (pg per µL)[b]	MDL (ng per m^3)[b]
Cyclopenta[cd]pyrene	27208-37-3	0.302	0.0427	0.335	0.293	0.293	0.0181
Demecolcine	477-30-5	69.3	not detected	not detected	not detected	69.3	4.28
Dibenz[a,h]anthracene	53-70-3	1.2	0.102	0.869	0.768	0.768	0.0474
Dibenzothiophene	132-65-0	0.109	13.7	35.9	22.2	22.2	1.37
Dibutyl phthalate	84-74-2	2.15	4490	13500	8980	8980	554
Diethyl Phthalate	84-66-2	2.09	592	2520	1930	1930	119
Diisobutyl Phthalate	84-69-5	0.722	93	222	129	129	7.97
Diisooctylphthalate*	27554-26-3	2.14	383	1260	876	876	54.1
Dimethyl phthalate	131-11-3	1.34	83.2	346	263	263	16.2
Di-n-octyl phthalate	117-84-0	0.355	7.01	18.8	11.8	11.8	0.727
Fluoranthene	206-44-0	0.137	9.81	24.4	14.6	14.6	0.903
Fluorene	86-73-7	0.185	51.7	126	74	74	4.57
Hexadecane	544-76-3	0.479	471	1160	685	685	42.3
Indeno[1,2,3-c]pyrene	193-39-5	1.15	4.38	17.5	13.2	13.2	0.812
Limonene	138-86-3	1.97	172	697	525	525	32.4
Methyl stearate	112-61-8	0.153	45.1	158	113	113	7
N,N-Dicyclohexylmethylamine	7560-83-0	0.234	0.773	6.2	5.42	5.42	0.335
Naphthalene	91-20-3	4	966	2640	1670	1670	103
Naphthalene, 1,2-dimethyl-	573-98-8	0.0809	27.8	66.7	38.9	38.9	2.4
Naphthalene, 1,6-dimethyl-	575-43-9	0.089	35.5	86.3	50.8	50.8	3.13
Naphthalene, 1-methyl-	90-12-0	0.305	141	369	228	228	14.1
Naphthalene, 2-(bromomethyl)-	939-26-4	0.879	17.2	44.2	27.1	27.1	1.67
Naphthalene, 2,3-dimethyl-*	581-40-8	0.575	27.3	67.3	40	40	2.47
Naphthalene, 2-methyl	91-57-6	1.57	267	672	405	405	25
n-Caproic acid vinyl ester	3050-69-9	1.03	345	1100	753	753	46.5
N-Phenylbenzamide	93-98-1	0.284	359	957	598	598	36.9
Phenanthrene	85-01-8	0.176	97.4	248	150	150	9.27

Targeted Chemical	CASRN	MDL_s (pg per µL)	Average. Background (pg per µL)[a]	MDL_b (pg per µL)	Background Subtracted MDL_b (pg per µL)[b]	Selected MDL (pg per µL)[b]	MDL (ng per m^3)[b]
Phenanthrene, 1-methyl	832-69-9	0.311	5.05	13	7.99	7.99	0.493
Phenanthrene, 2-methyl-	2531-84-2	0.0917	7.3	18.2	10.9	10.9	0.673
Phenanthrene, 3-methyl	832-71-3	0.165	7.59	21.4	13.9	13.9	0.855
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	2772-45-4	1.15	2.03	8.55	6.52	6.52	0.402
Phenol, 4-(1-phenylethyl)-	1988-89-2	11.7	not detected	not detected	not detected	11.7	0.72
Phthalimide	85-41-6	70	1880	6400	4520	4520	279
Pyrene	129-00-0	0.16	7.13	17.6	10.5	10.5	0.649
Pyridine, 2-(4-methylphenyl)-	4467-06-5	0.707	0.279	2.2	1.92	1.92	0.118
Resorcinol	108-46-3	164	not detected	not detected	not detected	164	10.1

[a]Average background levels detected in 13 trip blank samples.

[b]MDL: method detected limit; selected the greater of MDL_s or background subtracted MDL_b as the MDL. MDL_b were not determined for chemicals not detected in the blank samples. MDL_s were selected as the MDL for those chemicals. Due to the high background levels of some chemicals in the extracts of SVOC sample train media, the background subtracted MDL_b were used in the determination of MDL for each chemical. The average background levels were also subtracted from the analytical results of the field samples before applying the MDL for data validation. Average volume of air flow through the field SVOC sample trains was 16.2 m^3 and average volume of extracts was 1.00 mL. MDL (ng per m^3) = MDL (pg per µL) × 1 (mL) × 1000 (µL per mL) ÷ 16.2 m^3 ÷ 1000 (ng per pg).

CASRN: Chemical Abstracts Service Registry Number; MDL_b: MDL based on method blanks, calculated using Equation D-2; and MDL_s: MDL based on spiked samples, calculated using Equation D-1. Spiked samples have the same concentrations as the lowest detected calibration standards. Lower limits of the calibration were used in calculating the MDL_s. MDL_s were not determined for chemicals that were not detected at the low calibration standards.

D.3.6.1.3. Determination of MDL by High Performance Liquid Chromatography (HPLC) for the Analysis of Carbonyls Extracted from the 2,4-Dinitrophenylhydrazine (DNPH) Coated Silica Gel Cartridge Samples

Table D-16 provides the values of method detection limits for each targeted carbonyl in the HPLC analysis of the extracts of DNPH-coated cartridge samples collected from the air. LBNL determined the values of MDL for HPLC analysis of the targeted low molecular weight carbonyls in the extracts of DNPH-coated cartridge samples using the blank and the spiked samples with following the steps below:

1. Preparation of Blank Samples: Fourteen XPoSure DNPH Sep-Pack Cartridge (Waters category number 047205) that were used as trip blanks from synthetic turf fields or playgrounds were extracted and analyzed as described in Section

D.2.2. These results were used to determine the MDL_b.

2. Preparation of Spiked Samples: The MDLs was determined by analyzing 10 injections of the lowest calibration standard detectable for each targeted carbonyl by HPLC.

Table D-1. Method Detection Limit for the High Performance Liquid Chromatography Analysis of Carbonyls in Extracts of the 2,4-Dinitrophenylhydrazine Coated Silica Gel Cartridge Samples Collected from the Air

Targeted Chemical	CASRN	Spiked Amount (ng per µL)[a]	MDL_s (ng per µL)	MDL_b (ng per µL)[b]	Selected MDL (ng per µL)[b]	MDL (µg per m^3)[b]
Formaldehyde	50-00-0	1.31E-02	2.62E-03	2.00E-02	2.62E-03	2.91E-02
Acetaldehyde	75-07-0	1.32E-02	5.43E-03	3.00E-02	5.43E-03	6.04E-02
Acrolein	107-02-8	1.31E-02	4.85E-03	Not detected	4.85E-03	5.39E-02
Acetone	67-64-1	1.31E-02	4.29E-03	8.00E-02	4.29E-03	4.76E-02
Propionaldehyde	123-38-6	1.31E-02	4.51E-03	Not detected	4.51E-03	5.01E-02
Crotonaldehyde	123-73-9	1.32E-02	6.04E-03	1.00E-02	6.04E-03	6.71E-02
Methacrolein	78-85-3	1.31E-02	6.34E-03	Not detected	6.34E-03	7.04E-02
Butyraldehyde	123-72-8	1.31E-02	6.65E-03	Not detected	6.65E-03	7.39E-02
2-Butanone	78-93-3	1.32E-02	3.47E-03	1.00E-02	3.47E-03	3.86E-02
Benzaldehyde	100-52-7	1.32E-02	4.25E-03	Not detected	4.25E-03	4.72E-02
Valeraldehyde	110-62-3	1.32E-02	4.26E-03	2.00E-02	4.26E-03	4.73E-02
m-Tolualdehyde	620-23-5	1.32E-02	6.21E-03	3.00E-02	6.21E-03	6.90E-02
Hexaldehyde	66-25-1	1.31E-02	8.37E-03	Not detected	8.37E-03	9.30E-02

[a]Spiked samples have the same concentrations as the lowest detected calibration standards.
[b]MDL: method detection limit. Blanks were intermittently positive, so the maximum trip blank value was used as the MDL_b. and MDLs was selected as the MDL. Average volume of air flow through the cartridge samples was 180 Liters and average volume of extracts was 2000 µL. MDL (µg per m^3) = MDL (ng per µL) × 2000 (µL) × 1000 (µL per m^3) ÷ 180 (L) ÷ 1000 (ng per µg).
CASRN: Chemical Abstracts Service Registry Number; MDL_b: MDL based on method blanks, calculated using Equation D-2. MDL_b were not determined for chemicals that were not detected in the blank samples; and MDL_s: MDL based on spiked samples, calculated using Equation D-1.
All values shown are rounded to three significant figures.

D.3.6.1.4. Determination of MDL for the Organic Chemicals Targeted in the Analyses of Samples Collected from the Air During the Phase 3 Field Work

As shown in Table D-14, Table D-15, and Table D-16 several organic chemicals

(including carbonyls) were detected in more than one types of samples collected from the air (sorbent tubes, SVOC sample trains, and/or DNHP-coated cartridge samples) at the 35 selected synthetic turf fields. In order to estimate the exposure to each chemical via an inhalation pathway, the Study needed to determine a concentration of each chemical in air that best represent the environmental conditions at each field. OEHHA, therefore, chose the analytical data from the most suitable sample type for each chemical based on the following criteria:

- volatility of a chemical
- adhesion of a chemical to an environmental matrix (airborne fine particulate matters)
- stability of a chemical in a sampling matrix
- sensitivity of a chemical in an instrumental analysis (e.g., value of MDL)
- response of a chemical in the instrument (e.g., peak resolution observed on the chromatograms)

Table D-17 shows the selected values of MDL and limit of quantification (LOQ) of each organic chemical targeted in the analyses of samples collected from the air during the Phase 3 Field Work. The table also lists the type of sample selected (source of MDL), for each targeted chemical, to determine the chemical concentrations in the air.

Table D-1. Method Detection Limits (MDL, mg per cubic m) and Limit of Quantification (LOQ, ng per cubic m) of Chemicals Targeted in the Analyses of Samples Collected from the Air at the 35 Selected Synthetic Turf Fields during the Phase 3 Field Work

Targeted Chemical	CASRN	MDL[a]	LOQ[b]	Source of MDL[c]	Quantifiable in Sample Type[d]	Note
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	793-24-8	5.22E-02	1.57E-01	SVOC	SVOC	NA
1,4-Benzenediamine, N,N'-diphenyl-	74-31-7	2.64E-01	7.92E-01	SVOC	SVOC and VOC	Higher analytical sensitivity in HES-GC-MS analysis of extracts from SVOC samples than TD-GC-MS analysis of VOC samples
1,4-Benzenediol, 2,5-bis(1,1-dimethylethyl)-	88-58-4	4.94E+01	1.48E+02	SVOC	SVOC	NA
17-Pentatriacontene	6971-40-0	1.10E+01	3.31E+01	SVOC	SVOC	NA
1-Hexanol, 2-ethyl-	104-76-7	1.21E+02	3.64E+02	VOC	VOC	NA
1-Hydroxypyrene	5315-79-7	1.03E+01	3.10E+01	SVOC	SVOC	NA
1-Octadecene	112-88-9	2.57E+00	7.72E+00	SVOC	SVOC	NA
2,5-di-tert-Butyl-1,4-benzoquinone	2460-77-7	9.19E-02	2.76E-01	SVOC	SVOC	NA

Targeted Chemical	CASRN	MDL[a]	LOQ[b]	Source of MDL[c]	Quantifiable in Sample Type[d]	Note
2,5-Hexanedione	110-13-4	1.76E+02	5.27E+02	SVOC	SVOC	NA
2-Benzothiazolone	934-34-9	2.98E+01	8.95E+01	SVOC	SVOC	NA
2-Butanone	78-93-3	3.86E+01	1.37E+02	ALD	ALD	NA
2-Butoxyethanol	111-76-2	3.23E+02	9.68E+02	VOC	VOC	NA
2-Hexanone, 5-methyl	110-12-3	3.62E+02	1.09E+03	VOC	VOC	NA
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	5.64E+01	1.69E+02	SVOC	SVOC	NA
3-Carene	13466-78-9	1.08E+02	3.24E+02	VOC	VOC	NA
4-tert-Octylphenol	140-66-9	8.84E-01	2.65E+00	SVOC	SVOC	NA
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	4.12E+00	1.24E+01	SVOC	SVOC	NA
7H-Benzo[c]fluorene	205-12-9	9.36E-02	2.81E-01	SVOC	SVOC	NA
Acenaphthylene	208-96-8	1.72E+00	5.15E+00	SVOC	SVOC	NA
Acetaldehyde	75-07-0	6.04E+01	2.14E+02	ALD	ALD and VOC	Unstable in sorbent tube samples and required DNPH-coated cartridge sampler
Acetone	67-64-1	4.76E+01	1.69E+02	ALD	ALD	NA
Acrolein	107-02-8	5.39E+01	1.91E+02	ALD	ALD	NA
Aniline	62-53-3	1.68E+01	5.04E+01	SVOC	SVOC and VOC	Higher analytical sensitivity in HES-GC-MS analysis of extracts from SVOC samples than TD-GC-MS analysis of VOC samples
Anthracene	120-12-7	5.99E-01	1.80E+00	SVOC	SVOC	NA
Anthracene, 2-methyl-	613-12-7	4.47E-02	1.34E-01	SVOC	SVOC	NA
Anthracene, 9,10-dimethyl	781-43-1	9.09E-02	2.73E-01	SVOC	SVOC	NA
Anthracene, 9,10-diphenyl-	1499-10-1	2.01E-01	6.03E-01	SVOC	SVOC	NA
Anthracene, 9-phenyl	602-55-1	4.09E-01	1.23E+00	SVOC	SVOC	NA
a-Pinene	7785-70-8	9.96E+01	2.99E+02	VOC	VOC	NA
a-Terpineol	98-55-5	1.26E+02	3.79E+02	VOC	VOC	NA
Azulene	275-51-4	9.68E+01	2.91E+02	VOC	VOC	NA
Benz[a]anthracene	56-55-3	2.23E-01	6.70E-01	SVOC	SVOC	NA
Benzaldehyde	100-52-7	1.29E+02	3.88E+02	VOC	ALD and VOC	Stable in sorbent tube samples, which have comprehensive sampling scheme
Benzene	71-43-2	1.80E+02	5.41E+02	VOC	VOC	NA
Benzene, 1,2,3-trimethyl-	526-73-8	1.01E+02	3.03E+02	VOC	VOC	NA

Targeted Chemical	CASRN	MDL[a]	LOQ[b]	Source of MDL[c]	Quantifiable in Sample Type[d]	Note
Benzene, 1,2,4,5-tetramethyl-	95-93-2	2.69E+01	8.07E+01	VOC	VOC	NA
Benzene, 1,2,4-trimethyl-	95-63-6	1.33E+02	4.00E+02	VOC	VOC	NA
Benzene, 1,4-dichloro	106-46-7	7.89E+01	2.37E+02	VOC	VOC	NA
Benzene, 1-chloro-4-(trifluoromethyl)-	98-56-6	3.34E+01	1.00E+02	VOC	VOC	NA
Benzene, 1-ethyl-2,4-dimethyl-	874-41-9	2.50E+01	7.51E+01	VOC	VOC	NA
Benzene, 2-ethyl-1,4-dimethyl-	1758-88-9	1.65E+01	4.96E+01	VOC	VOC	NA
Benzene, n-butyl-	104-51-8	7.34E+01	2.20E+02	VOC	SVOC and VOC	Highly volatile chemical is better sampled with sorbent tube and analyzed with TD-GC-MS, than the SVOC sample trains
Benzo[a]pyrene	50-32-8	5.37E-02	1.61E-01	SVOC	SVOC	NA
Benzo[b]fluoranthene	205-99-2	2.79E-01	8.37E-01	SVOC	SVOC	NA
Benzo[e]pyrene	192-97-2	8.48E-02	2.54E-01	SVOC	SVOC	NA
Benzo[g,h,i]perylene	191-24-2	6.64E-02	1.99E-01	SVOC	SVOC	NA
Benzo[k]fluoranthene	207-08-9	2.31E-01	6.94E-01	SVOC	SVOC	NA
Benzothiazole	95-16-9	8.21E+01	2.46E+02	VOC	SVOC and VOC	Highly volatile chemical is better sampled with sorbent tube and analyzed with TD-GC-MS, than the SVOC sample trains. Higher analytical sensitivity in TD-GC-MS analysis than the SVOC samples
Benzothiazole, 2-mercapto	149-30-4	2.56E+02	7.67E+02	VOC	VOC	NA
Benzothiazole, 2-methylthio-	615-22-5	3.81E+01	1.14E+02	VOC	VOC	NA
Benzothiazole, 2-phenyl-	883-93-2	3.89E-01	1.17E+00	SVOC	SVOC	NA
Benzyl butyl phthalate	85-68-7	1.55E+01	4.66E+01	SVOC	SVOC	NA
Biphenyl	92-52-4	6.19E+01	1.86E+02	VOC	VOC	NA
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	52829-07-9	8.41E+01	2.52E+02	SVOC	SVOC	NA
Bis(2-Ethylhexyl)adipate	103-23-1	1.88E+02	5.63E+02	SVOC	SVOC	NA
Butanal	123-72-8	3.21E+02	9.63E+02	VOC	ALD and VOC	Stable in VOC samples, which have comprehensive sampling scheme

Targeted Chemical	CASRN	MDL[a]	LOQ[b]	Source of MDL[c]	Quantifiable in Sample Type[d]	Note
Butylated Hydroxytoluene	128-37-0	2.48E+02	7.43E+02	VOC	SVOC and VOC	Highly volatile chemical is better sampled with sorbent tube and analyzed with TD-GC-MS, than the SVOC sample trains. Higher analytical sensitivity in TD-GC-MS analysis than the SVOC samples
Chrysene	218-01-9	2.82E-01	8.45E-01	SVOC	SVOC	NA
Coronene	191-07-1	1.70E-01	5.09E-01	SVOC	SVOC	NA
Crotonaldehyde	123-73-9	6.71E+01	2.38E+02	ALD	ALD	NA
Cyclohexanamine, N-cyclohexyl-	101-83-7	3.08E-01	9.23E-01	SVOC	SVOC	NA
Cyclohexanone	108-94-1	2.50E+02	7.49E+02	VOC	VOC	NA
Cyclohexylamine	108-91-8	2.06E+01	6.18E+01	SVOC	SVOC	NA
Cyclopenta[cd]pyrene	27208-37-3	1.81E-02	5.42E-02	SVOC	SVOC	NA
Cyclopentasiloxane, decamethyl-	541-02-6	9.88E+01	2.96E+02	VOC	VOC	NA
Cyclotetrasiloxane, octamethyl-	556-67-2	1.01E+02	3.03E+02	VOC	VOC	NA
Cyclotrisiloxane, hexamethyl-	541-05-9	1.05E+03	3.16E+03	VOC	VOC	NA
Decanal	112-31-2	1.71E+02	5.14E+02	VOC	VOC	NA
Decane	124-18-5	1.08E+02	3.24E+02	VOC	VOC	NA
Demecolcine	477-30-5	4.28E+00	1.28E+01	SVOC	SVOC	NA
Dibenz[a,h]anthracene	53-70-3	4.74E-02	1.42E-01	SVOC	SVOC	NA
Dibenzothiophene	132-65-0	1.37E+00	4.10E+00	SVOC	SVOC	NA
Dibutyl phthalate	84-74-2	5.54E+02	1.66E+03	SVOC	SVOC and VOC	High adhesion to particles. Higher analytical sensitivity in HES-GC-MS analysis of extracts from SVOC samples than TD-GC-MS analysis of VOC samples
Diethyl phthalate	84-66-2	1.19E+02	3.57E+02	SVOC	SVOC and VOC	Higher analytical sensitivity in HES-GC-MS analysis of extracts from SVOC sample trains than the TD-GC-MS analysis of VOC samples.
Diisobutyl phthalate	84-69-5	7.97E+00	2.39E+01	SVOC	SVOC	NA
Diisooctylphthalate	27554-26-3	5.41E+01	1.62E+02	SVOC	SVOC	NA
Dimethyl phthalate	131-11-3	1.62E+01	4.87E+01	SVOC	SVOC and VOC	High adhesion to particles. Higher analytical sensitivity in HES-GC-MS analysis of extracts from SVOC samples than TD-GC-MS analysis of VOC samples

Targeted Chemical	CASRN	MDL[a]	LOQ[b]	Source of MDL[c]	Quantifiable in Sample Type[d]	Note
Di-n-octyl phthalate	117-84-0	7.27E-01	2.18E+00	SVOC	SVOC	NA
D-Limonene	5989-27-5	1.34E+02	4.02E+02	VOC	VOC	NA
Dodecane	112-40-3	1.18E+02	3.54E+02	VOC	VOC	NA
Ethylbenzene	100-41-4	2.36E+02	7.08E+02	VOC	VOC	NA
Fluoranthene	206-44-0	9.03E-01	2.71E+00	SVOC	SVOC	NA
Fluorene	86-73-7	4.57E+00	1.37E+01	SVOC	SVOC	NA
Formaldehyde	50-00-0	2.91E+01	1.03E+02	ALD	ALD	Unstable in sorbent tube samples and required DNPH-coated cartridge sampler
Formamide, N-(1,1-dimethylethyl)-	2425-74-3	1.21E+02	3.62E+02	VOC	VOC	NA
Furan, 2-methyl	534-22-5	2.97E+01	8.90E+01	VOC	VOC	NA
g-Terpinene	99-85-4	1.40E+02	4.19E+02	VOC	VOC	NA
Heptanal	111-71-7	1.29E+02	3.86E+02	VOC	VOC	NA
Heptane	142-82-5	1.77E+02	5.32E+02	VOC	VOC	NA
Hexadecane	544-76-3	4.23E+01	1.27E+02	SVOC	SVOC and VOC	Higher analytical sensitivity in HES-GC-MS analysis of extracts from SVOC samples than TD-GC-MS analysis of VOC samples
Hexanal	66-25-1	2.45E+02	7.35E+02	VOC	ALD and VOC	Stable in VOC samples, which have comprehensive sampling scheme
Hexane	110-54-3	2.67E+02	8.02E+02	VOC	VOC	NA
Indan	496-11-7	2.59E+01	7.78E+01	VOC	VOC	NA
Indeno[1,2,3-cd]pyrene	193-39-5	8.12E-01	2.44E+00	SVOC	SVOC	NA
Limonene	138-86-3	3.24E+01	9.71E+01	SVOC	SVOC	NA
m/p-Xylene	106-42-3	2.35E+02	7.04E+02	VOC	VOC	NA
Mesitylene	108-67-8	2.55E+01	7.65E+01	VOC	VOC	NA
methacrolein	78-85-3	1.03E+02	3.08E+02	VOC	ALD and VOC	Stable in VOC samples, which have comprehensive sampling scheme
Methyl Isobutyl Ketone	108-10-1	2.43E+02	7.29E+02	VOC	VOC	NA
Methyl stearate	112-61-8	7.00E+00	2.10E+01	SVOC	SVOC	NA
m-Tolualdehyde	620-23-5	6.90E-02	2.45E+02	ALD	ALD	NA
N,N-Dicyclohexylmethyl amine	7560-83-0	3.35E-01	1.00E+00	SVOC	SVOC	NA

Targeted Chemical	CASRN	MDL[a]	LOQ[b]	Source of MDL[c]	Quantifiable in Sample Type[d]	Note
Naphthalene	91-20-3	8.65E+01	2.60E+02	VOC	SVOC and VOC	Highly volatile chemical is better sampled with sorbent tube and analyzed with TD-GC-MS, than the SVOC sample trains. Higher analytical sensitivity in TD-GC-MS analysis than the SVOC samples
Naphthalene, 1,2-dimethyl-	573-98-8	2.40E+00	7.20E+00	SVOC	SVOC	NA
Naphthalene, 1,6-dimethyl-	575-43-9	3.13E+00	9.40E+00	SVOC	SVOC	NA
Naphthalene, 1-methyl-	90-12-0	1.41E+01	4.22E+01	SVOC	SVOC and VOC	Higher analytical sensitivity in HES-GC-MS analysis of extracts from SVOC samples than TD-GC-MS analysis of VOC samples
Naphthalene, 2-(bromomethyl)-	939-26-4	1.67E+00	5.01E+00	SVOC	SVOC	NA
Naphthalene, 2,3-dimethyl-	581-40-8	2.47E+00	7.40E+00	SVOC	SVOC	NA
Naphthalene, 2-methyl-	91-57-6	2.50E+01	7.50E+01	SVOC	SVOC and VOC	Higher analytical sensitivity in HES-GC-MS analysis of extracts from SVOC samples than TD-GC-MS analysis of VOC samples
n-Caproic acid vinyl ester	3050-69-9	4.65E+01	1.39E+02	SVOC	SVOC	NA
Nonanal	124-19-6	5.44E+02	1.63E+03	VOC	VOC	NA
N-Phenylbenzamide	93-98-1	3.69E+01	1.11E+02	SVOC	SVOC	NA
Octanal	124-13-0	5.53E+01	1.66E+02	VOC	VOC	NA
Octane	111-65-9	2.33E+02	7.00E+02	VOC	VOC	NA
o-Xylene	95-47-6	2.67E+02	8.02E+02	VOC	VOC	NA
p-Cymene	99-87-6	3.17E+01	9.51E+01	VOC	VOC	NA
Phenanthrene	85-01-8	9.27E+00	2.78E+01	SVOC	SVOC	NA
Phenanthrene, 1-methyl	832-69-9	4.93E-01	1.48E+00	SVOC	SVOC	NA
Phenanthrene, 2-methyl-	2531-84-2	6.73E-01	2.02E+00	SVOC	SVOC	NA
Phenanthrene, 3-methyl	832-71-3	8.55E-01	2.57E+00	SVOC	SVOC	NA
Phenol	108-95-2	1.38E+02	4.14E+02	VOC	VOC	NA
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	2772-45-4	4.02E-01	1.21E+00	SVOC	SVOC	NA
Phenol, 4-(1-phenylethyl)-	1988-89-2	7.20E-01	2.16E+00	SVOC	SVOC	NA
Propionaldehyde	123-38-6	5.01E+01	1.78E+02	ALD	ALD	NA

Targeted Chemical	CASRN	MDL[a]	LOQ[b]	Source of MDL[c]	Quantifiable in Sample Type[d]	Note
Pyrene	129-00-0	6.49E-01	1.95E+00	SVOC	SVOC	NA
Pyridine, 2-(4-methylphenyl)-	4467-06-5	1.18E-01	3.55E-01	SVOC	SVOC	NA
Resorcinol	108-46-3	1.01E+01	3.03E+01	SVOC	SVOC	NA
Styrene	100-42-5	9.10E+01	2.73E+02	VOC	VOC	NA
Tetrachloroethylene	127-18-4	2.78E+02	8.35E+02	VOC	VOC	NA
Tetradecane	629-59-4	1.42E+02	4.26E+02	VOC	VOC	NA
Texanol, TXIB (mono-isomer)	25265-77-4	4.38E+01	1.31E+02	VOC	VOC	NA
Toluene	108-88-3	2.00E+02	6.00E+02	VOC	VOC	NA
Trichloroethylene	79-01-6	1.86E+01	5.59E+01	VOC	VOC	NA
Trichloromethane	67-66-3	1.56E+02	4.69E+02	VOC	VOC	NA
TXIB "Kodaflex"	6846-50-0	1.38E+02	4.15E+02	VOC	VOC	NA
Undecane	1120-21-4	1.01E+02	3.04E+02	VOC	VOC	NA
Valeraldehyde	110-62-3	4.73E+01	1.68E+02	ALD	ALD	NA

[a]Values of MDL selected from Table D-14, Table D-15, or Table D-16 according to the quantifiable sample types and notes in this table.

[b]Values of LOQ for VOC and SVOC samples were calculated as three times of MDL of each chemical. Values of LOQ for carbonyl analysis of the ALD samples were determined as 10 times the standard deviation of the 10 replicate analyses of the low calibration standard, which was 3.54 times of MDL for each carbonyl.

[c]Source of MDL indicates the selected type of sample used to derive concentration of a chemical in air.

[d]Chemicals were considered as quantifiable in a sample type when the chemicals were detected by the corresponding instrumental analyses and with established MDL presented in Table D-14, Table D-15, or Table D-16.

ALD: 2,4-dinitrophenylhydrazine coated silica gel cartridge samples of low molecular weight carbonyls; CASRN: CASRN: Chemical Abstracts Service Registry Number; HES-GC-MS: high efficiency source coupled with gas chromatography mass spectrometry; LOQ: limit of quantification; MDL: method detection limit; NA: not applicable; SVOC: semi-volatile organic sample train for SVOC vapor and airborne fine particulate matters with diameter 2.5 µm and below in air; TD-GC-MS: thermal desorption coupled with gas chromatography mass spectrometry; VOC: sorbent tube samples for volatile organic chemicals

All values rounded to three significant figures.

D.3.6.1.5. Determination of MDL for HES-GC-MS Analysis Organic Chemicals in the Oral (Gastrointestinal, GI) and Dermal Bioaccessibility Measurements

Table D-18 and Table D-19, respectively, provide the values of method detection limit of the Sink and SBSE (stir bar sorptive extraction) stir bars for each targeted chemical in the HES-GC-MS analysis of the artificial GI fluid extracts of crumb rubber samples (see Sections D.4.1.3 and D.4.1.4). Table D-20 and Table D-21, respectively, provide the values of method detection limit of the Sink and SBSE stir bars for each targeted chemical in the HES-GC-MS analysis of the artificial sweat extracts of crumb rubber samples. LBNL determined the values of MDL for HES-GC-MS of the targeted organic

chemicals in the oral and dermal bioaccessibility tests using the blank and the spiked samples with following the steps below:

1. Preparation of Blank Samples: To determine MDL_b, a minimum of five blanks bioaccessibility tests were conducted for each the oral (using artificial GI fluids) and dermal (using artificial sweat) pathways. These tests used the same method as described in the SOPs for both the Sink and SBSE reactions (Sections D.4.1.3.2 and D.4.1.4.2), but no crumb rubber samples were added to the tests. The Sink and SBSE stir bars were analyzed in the same manner as the samples including addition of the internal standards.
2. Preparation of Spiked Samples: To determine the MDLs for the Sink, the lowest calibration standards (including the internal standard) were injected directly onto the surface of the Sink stir bar, then purged with helium for two minutes to remove the solvent. A minimum of seven stir bars were prepared and analyzed by HES GC-MS. To determine the MDLs for the SBSE stir bar, the SOPs for bioaccessibility test (Sections D.4.1.3.2 and D.4.1.4.2) were followed but a clean working artificial GI biofluids or artificial sweat with no crumb rubber added was used for the test. The lowest calibration standards detectable, including the internal standards, were added to the test.

Table D-1. Method Detection Limits (MDL_s, MDL_b, and MDL, ng) of the Sink Stir Bar for HES-GC-MS Analysis of Organic Chemicals in the Artificial Gastrointestinal Fluid Extracts of Crumb Rubber Samples

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=8)	Selected MDL[b]
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	793-24-8	0.113	0.0790	46.0	46.0
1,4-Benzenediamine, N,N'-diphenyl-	74-31-7	9.10	not determined	not detected	9.10
1,4-Benzenediol, 2,5-bis(1,1-dimethylethyl)-	88-58-4	9.90	not determined	not detected	9.90
17-Pentatriacontene	6971-40-0	5.00	not determined	not detected	5.00
1-Hydroxypyrene	5315-79-7	26.2	not determined	not detected	26.2
1-Octadecene	112-88-9	0.0494	0.0190	0.154	0.154
2,5-di-tert-Butyl-1,4-benzoquinone	2460-77-7	0.0552	0.0290	0.299	0.299
2,5-Hexanedione	110-13-4	5.46	not determined	not detected	5.46
2-Benzothiazolone	934-34-9	52.2	not determined	0.459	52.2

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=8)	Selected MDL^b
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	0.145	0.0650	8.490	8.49
4-tert-Octylphenol	140-66-9	0.0784	0.0700	1.890	1.89
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	0.347	0.269	0.813	0.813
7H-Benzo[c]fluorene	205-12-9	0.0960	0.0720	0.0220	0.0717
Acenaphthylene	208-96-8	0.0821	0.0250	0.122	0.122
Aniline	62-53-3	1.24	0.967	0.347	0.967
Anthracene	120-12-7	0.0737	0.0230	0.110	0.110
Anthracene, 2-methyl-	613-12-7	0.0677	0.226	0.0790	0.226
Anthracene, 9,10-dimethyl	781-43-1	0.201	0.230	not detected	0.230
Anthracene, 9,10-diphenyl-	1499-10-1	0.220	not determined	not detected	0.220
Anthracene, 9-phenyl	602-55-1	0.244	0.197	0.0140	0.197
Benz[a]anthracene	56-55-3	0.230	0.0630	0.0480	0.0633
Benzene, n-butyl-	104-51-8	0.552	0.193	2.29	2.29
Benzo[a]pyrene	50-32-8	0.144	0.121	not detected	0.121
Benzo[b]fluoranthene	205-99-2	0.265	0.112	0.0680	0.112
Benzo[e]pyrene	192-97-2	0.268	0.143	0.0930	0.143
Benzo[g,h,i]perylene	191-24-2	0.237	0.115	0.392	0.392
Benzo[k]fluoranthene	207-08-9	0.229	0.138	0.019	0.138
Benzothiazole	95-16-9	0.540	0.345	4.72	4.72
Benzothiazole, 2-phenyl-	883-93-2	0.521	not determined	0.0410	0.521
Benzyl butyl phthalate	85-68-7	0.242	0.240	20.1	20.1
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	52829-07-9	52.4	not determined	not detected	52.4
Bis(2-Ethylhexyl)adipate	103-23-1	0.0862	0.0430	2.40	2.40
Butylated Hydroxytoluene	128-37-0	0.213	0.102	0.334	0.334
Chrysene	218-01-9	0.0626	0.025	0.033	0.0334
Coronene	191-07-1	5.17	not determined	not detected	5.17
Cyclohexanamine, N-cyclohexyl-	101-83-7	52.4	not determined	not detected	52.4
Cyclohexyl isothiocyanate	1122-82-3	0.334	0.402	66.6	66.6
Cyclohexylamine[c]	108-91-8	0	not determined	not detected	not determined

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=8)	Selected MDL^b
Cyclopenta[cd]pyrene	27208-37-3	0.172	0.130	1.260	1.26
Demecolcine[c]	477-30-5	0	not determined	not detected	not determined
Dibenz[a,h]anthracene	53-70-3	0.209	not determined	0.00900	0.209
Dibenzothiophene	132-65-0	0.386	0.226	0.197	0.226
Dibutyl phthalate	84-74-2	0.157	0.077	1620.000	1620
Diethyl Phthalate	84-66-2	0.285	0.119	2.960	2.96
Diisobutyl Phthalate	84-69-5	0.0497	0.015	9.310	9.31
Diisooctylphthalate	27554-26-3	0.0493	0.012	90.500	90.5
Dimethyl phthalate	131-11-3	0.267	0.123	0.060	0.123
Di-n-octyl phthalate	117-84-0	0.237	0.212	0.600	0.6
Fluoranthene	206-44-0	0.102	0.018	0.194	0.194
Fluorene	86-73-7	0.103	0.017	0.269	0.269
Hexadecane	544-76-3	0.093	0.032	0.518	0.518
Hexanoic Acid, 2-ethyl	149-57-5	2.26	not determined	not detected	2.26
Indeno[1,2,3-cd]pyrene	193-39-5	0.493	1.52	not detected	1.52
Limonene	138-86-3	0.189	0.140	7.69	7.69
Methyl stearate	112-61-8	0.227	0.243	3.63	3.63
N,N-Dicyclohexylmethylamine	7560-83-0	157	not determined	0.559	157
Naphthalene	91-20-3	0.158	0.0530	3.64	3.64
Naphthalene, 1,2-dimethyl-	573-98-8	0.0701	0.0190	0.0570	0.0567
Naphthalene, 1,6-dimethyl-	575-43-9	0.349	0.179	0.116	0.179
Naphthalene, 1-methyl-	90-12-0	0.117	0.0290	0.276	0.276
Naphthalene, 2-(bromomethyl)-	939-26-4	5.25	not determined	0.916	0.916
Naphthalene, 2,3-dimethyl-*	581-40-8	0.68	0.416	0.113	0.416
Naphthalene, 2-methyl	91-57-6	0.150	0.0400	0.427	0.427
n-Caproic acid vinyl ester	3050-69-9	5.51	not determined	not detected	5.51
N-Phenylbenzamide	93-98-1	0.288	0.174	4.26	4.26
Phenanthrene	85-01-8	0.0999	0.020	0.582	0.582
Phenanthrene, 1-methyl	832-69-9	0.197	0.169	0.014	0.169

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=8)	Selected MDL[b]
Phenanthrene, 2-methyl-	2531-84-2	0.233	0.223	not detected	0.223
Phenanthrene, 3-methyl	832-71-3	0.279	0.184	0.572	0.572
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	2772-45-4	0.255	0.288	0.211	0.288
Phenol, 4-(1-phenylethyl)-	1988-89-2	0.542	not determined	2.880	2.88
Phthalimide	85-41-6	52.2	not determined	not detected	52.2
Pyrene	129-00-0	0.114	0.022	1.230	1.23
Pyridine, 2-(4-methylphenyl)-	4467-06-5	0.703	0.245	0.005	0.245
Resorcinol	108-46-3	306	not determined	not detected	306

[a]Spiked samples had the same amounts as the lowest detected calibration standards.
[b]MDL: method detected limit; selected the greater of MDL_s (or spike amount) or MDL_b as the MDL. MDL_b were not determined for chemicals not detected in the blank samples. MDL_s were selected as the MDL for those chemicals. When both MDL_s was not determined and MDL_b was not detected (or with intermittent detects with highest blank value<lower limit of the calibration curve), selected MDL = lower limit of the calibration curve.
[c]Cyclohexylamine (CASRN 108-91-8, matrix interference) and demecolcine (CASRN 477-30-5, no response) could not be analyzed by the HES-GC-MS. Their MDL were not calculated.
CASRN: Chemical Abstracts Service Registry Number; MDL_b: MDL based on method blanks, calculated using Equation D-2. For chemicals that were not detected in the blanks, MDL_b equaled to 0 or not detected. For chemicals with intermittent detects (count<5), MDL_b = the highest detected blank value; and MDL_s: MDL based on spiked samples, calculated using Equation D-1. Spiked amount equaled to 0 and MDL_s were not determined for chemicals with poor responses or not detected in the spike samples.
All values shown are rounded to three significant figures.

Table D-2. Method Detection Limits (MDL_s, MDL_b, and MDL, ng) of the Stir Bar Sorptive Extraction (SBSE) Stir Bar for HES-GC-MS Analysis of Organic Chemicals in the Artificial Gastrointestinal Fluid Extracts of Crumb Rubber Samples

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=9)	Selected MDL[b]
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	793-24-8	8.26	not determined	21.1	21.1
1,4-Benzenediamine, N,N'-diphenyl-	74-31-7	1.36	not determined	not detected	1.36
1,4-Benzenediol, 2,5-bis(1,1-dimethylethyl)-	88-58-4	0.706	not determined	not detected	0.706

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=9)	Selected MDL[b]
17-Pentatriacontene	6971-40-0	0.143	not determined	not detected	0.143
1-Hydroxypyrene	5315-79-7	15.7	not determined	not detected	15.7
1-Octadecene	112-88-9	1.59	not determined	5.8	5.8
2,5-di-tert-Butyl-1,4-benzoquinone	2460-77-7	0.114	0.383	0.201	0.383
2,5-Hexanedione[c]	110-13-4	0	not determined	not detected	not determined
2-Benzothiazolone	934-34-9	261	not determined	1.61	261
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	0.332	0.137	0.0936	0.137
4-tert-Octylphenol	140-66-9	0.259	0.189	2.01	2.01
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	0.177	0.0791	0.134	0.134
7H-Benzo[c]fluorene	205-12-9	0.0964	0.0251	0.001	0.0251
Acenaphthylene	208-96-8	0.0834	0.0252	0.0605	0.0605
Aniline[c]	62-53-3	0	not determined	not detected	not determined
Anthracene	120-12-7	0.107	0.0331	0.515	0.515
Anthracene, 2-methyl-	613-12-7	0.174	0.0587	0.279	0.279
Anthracene, 9,10-dimethyl	781-43-1	0.0623	0.0523	not detected	0.0523
Anthracene, 9,10-diphenyl-	1499-10-1	1.65	not determined	not detected	1.65
Anthracene, 9-phenyl	602-55-1	0.0563	0.0214	0.0356	0.0356
Benz[a]anthracene	56-55-3	0.115	0.054	0.108	0.108
Benzene, n-butyl-	104-51-8	0.095	0.0254	0.126	0.126
Benzo[a]pyrene	50-32-8	0.279	0.118	0.125	0.125
Benzo[b]fluoranthene	205-99-2	0.148	0.14	0.224	0.224
Benzo[e]pyrene	192-97-2	0.104	0.119	0.334	0.334

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=9)	Selected MDL[b]
Benzo[g,h,i]perylene	191-24-2	0.327	0.155	2.43	2.43
Benzo[k]fluoranthene	207-08-9	0.113	0.109	0.16	0.16
Benzothiazole	95-16-9	15.8	41.4	91.2	91.2
Benzothiazole, 2-phenyl-	883-93-2	0.0684	0.0532	0.142	0.142
Benzyl butyl phthalate	85-68-7	0.766	1.04	2.54	2.54
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	52829-07-9	60.8	not determined	not detected	60.8
Bis(2-Ethylhexyl) adipate	103-23-1	1.28	1.64	5.78	5.78
Butylated Hydroxytoluene	128-37-0	0.133	0.154	1.01	1.01
Chrysene	218-01-9	0.0732	0.0475	0.136	0.136
Coronene	191-07-1	7.44	not determined	not detected	7.44
Cyclohexanamine, N-cyclohexyl-	101-83-7	7.55	not determined	0.139	7.55
Cyclohexyl isothiocyanate	1122-82-3	6.13	7.2	151	151
Cyclohexylamine[c]	108-91-8	0	not determined	not detected	not determined
Cyclopenta[cd]pyrene	27208-37-3	0.0595	0.027	0.0602	0.0602
Demecolcine[c]	477-30-5	0	not determined	not detected	not determined
Dibenz[a,h]anthracene	53-70-3	0.326	0.23	1.81	1.81
Dibenzothiophene	132-65-0	0.134	0.0858	0.434	0.434
Dibutyl phthalate	84-74-2	105	36.5	44.4	44.4
Diethyl Phthalate	84-66-2	1.6	2.31	7.32	7.32
Diisobutyl Phthalate	84-69-5	0.419	0.319	1.27	1.27
Diisooctylphthalate	27554-26-3	24.1	27.7	68.6	68.6
Dimethyl phthalate	131-11-3	1.12	1.91	11.8	11.8
Di-n-octyl phthalate	117-84-0	2.06	5.25	1.93	5.25

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=9)	Selected MDL[b]
Fluoranthene	206-44-0	0.128	0.0414	0.256	0.256
Fluorene	86-73-7	0.0979	0.0319	0.124	0.124
Hexadecane	544-76-3	2	1.43	3.6	3.6
Hexanoic Acid, 2-ethyl	149-57-5	283	not determined	not detected	283
Indeno[1,2,3-cd]pyrene	193-39-5	0.964	0.385	2.07	2.07
Limonene	138-86-3	0.0805	0.28	0.0382	0.28
Methyl stearate	112-61-8	1.91	2.17	6.45	6.45
N,N-Dicyclo-hexylmethylamine[c]	7560-83-0	0	not determined	not detected	not determined
Naphthalene	91-20-3	0.15	0.632	2.11	2.11
Naphthalene, 1,2-dimethyl-	573-98-8	0.0776	0.0184	0.0723	0.0723
Naphthalene, 1,6-dimethyl-	575-43-9	0.0697	0.0126	0.0462	0.0462
Naphthalene, 1-methyl-	90-12-0	0.0835	0.0286	0.0235	0.0286
Naphthalene, 2-(bromomethyl)-	939-26-4	0.51	0.386	0.133	0.386
Naphthalene, 2,3-dimethyl-	581-40-8	0.116	0.0341	0.097	0.097
Naphthalene, 2-methyl	91-57-6	0.0976	0.0639	0.032	0.0639
n-Caproic acid vinyl ester	3050-69-9	0.078	not determined	1.14	1.14
N-Phenylbenzamide	93-98-1	1.47	not determined	16.9	16.9
Phenanthrene	85-01-8	0.233	0.085	0.489	0.489
Phenanthrene, 1-methyl	832-69-9	0.0932	0.0337	0.351	0.351
Phenanthrene, 2-methyl-	2531-84-2	0.2	0.0681	0.369	0.369
Phenanthrene, 3-methyl	832-71-3	0.162	0.0382	0.634	0.634
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	2772-45-4	0.239	0.0889	0.142	0.142

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=9)	Selected MDL[b]
Phenol, 4-(1-phenylethyl)-	1988-89-2	0.774	not determined	0.25	0.774
Phthalimide	85-41-6	0.074	not determined	1.48	1.48
Pyrene	129-00-0	0.236	0.109	0.639	0.639
Pyridine, 2-(4-methylphenyl)-	4467-06-5	9.82	1.6	9.76	9.76
Resorcinol[c]	108-46-3	0	not determined	not detected	not determined

[a]Spiked samples had the same amounts as the lowest detected calibration standards.
[b]MDL: method detected limit; selected the greater of MDL_s (or spike amount) or MDL_b as the MDL. MDL_b were not determined for chemicals not detected in the blank samples. MDL_s were selected as the MDL for those chemicals. When both MDL_s was not determined and MDL_b was not detected (or with intermittent detects with highest blank value<lower limit of the calibration curve), selected MDL = lower limit of the calibration curve.
[c]2,5-Hexanedione (CASRN 110-13-4, poor response), aniline (CASRN 62-53-3, not detected), cyclohexylamine (CASRN 108-91-8, matrix interference), demecolcine (CASRN 477-30-5, not detected), N,N-dicyclohexylmethylamine (CASRN 7560-83-0, not detected), and resorcinol (CASRN 108-46-3, not detected) could not be analyzed by the HES-GC-MS. Their MDL were not calculated.
CASRN: Chemical Abstracts Service Registry Number; MDL_b: MDL based on method blanks, calculated using Equation D-2. For chemicals that were not detected in the blanks, MDL_b equaled to 0 or not detected. For chemicals with intermittent detects (count<5), MDL_b = the highest detected blank value; and MDL_s : MDL based on spiked samples, calculated using Equation D-1. Spiked amount equaled to 0 and MDL_s were not determined for chemicals with poor responses or not detected in the spike samples.
All values shown are rounded to three significant figures.

Table D-3. Method Detection Limits (MDL_s, MDL_b, and MDL, ng) of the Sink Stir Bar for HES-GC-MS Analysis of Organic Chemicals in the Artificial Sweat Extracts Crumb Ruber Samples

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=5)	Selected MDL[b]
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	793-24-8	0.113	0.079	4.23	4.23
1,4-Benzenediamine, N,N'-diphenyl-	74-31-7	9.1	not determined	not detected	9.1
1,4-Benzenediol, 2,5-bis(1,1-dimethylethyl)-	88-58-4	9.9	not determined	not detected	9.9
17-Pentatriacontene	6971-40-0	5	not determined	not detected	5
1-Hydroxypyrene	5315-79-7	26.2	not determined	not detected	26.2

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=5)	Selected MDL[b]
1-Octadecene	112-88-9	0.25	0.193	0.212	0.212
2,5-di-tert-Butyl-1,4-benzoquinone	2460-77-7	0.252	0.118	0.123	0.123
2,5-Hexanedione	110-13-4	5.46	not determined	not detected	5.46
2-Benzothiazolone	934-34-9	0	not determined	0.152	0.152
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	0.363	0.182	0.863	0.863
4-tert-Octylphenol	140-66-9	0.0784	0.0697	2.81	2.81
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	0.347	0.269	0.83	0.83
7H-Benzo[c]fluorene	205-12-9	0.096	0.0717	not detected	0.0717
Acenaphthylene	208-96-8	0.305	0.125	0.0281	0.125
Aniline	62-53-3	1.24	0.967	6	6
Anthracene	120-12-7	0.345	0.166	0.0429	0.166
Anthracene, 2-methyl-	613-12-7	0.35	0.213	0.00085	0.213
Anthracene, 9,10-dimethyl	781-43-1	0.221	0.177	not detected	0.177
Anthracene, 9,10-diphenyl-	1499-10-1	0.22	not determined	not detected	0.22
Anthracene, 9-phenyl	602-55-1	0.172	0.13	0.0686	0.13
Benz[a]anthracene	56-55-3	0.619	0.222	0.286	0.286
Benzene, n-butyl-	104-51-8	0.552	0.193	0.777	0.777
Benzo[a]pyrene	50-32-8	0.144	0.121	not detected	0.121
Benzo[b]fluoranthene	205-99-2	0.611	0.268	not detected	0.268
Benzo[e]pyrene	192-97-2	0.952	0.297	0.388	0.388
Benzo[g,h,i]perylene	191-24-2	0.706	0.189	1.21	1.21
Benzo[k]fluoranthene	207-08-9	0.674	0.188	not detected	0.188

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=5)	Selected MDL[b]
Benzothiazole	95-16-9	0.769	0.511	3.3	3.3
Benzothiazole, 2-phenyl-	883-93-2	0.521	not determined	not detected	0.521
Benzyl butyl phthalate	85-68-7	0.865	0.547	0.416	0.547
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate[c]	52829-07-9	0	not determined	not detected	not determined
Bis(2-Ethylhexyl)adipate	103-23-1	0.244	0.197	0.146	0.197
Butylated Hydroxytoluene	128-37-0	0.391	0.13	2.93	2.93
Chrysene	218-01-9	0.449	0.234	0.131	0.234
Coronene	191-07-1	5.17	not determined	not detected	5.17
Cyclohexanamine, N-cyclohexyl-	101-83-7	0	not determined	0.0104	0.0104
Cyclohexyl isothiocyanate	1122-82-3	2.09	not determined	not detected	2.09
Cyclohexylamine[c]	108-91-8	0	not determined	not detected	not determined
Cyclopenta[cd]pyrene	27208-37-3	0.395	0.271	0.11	0.271
Demecolcine[c]	477-30-5	0	not determined	not detected	not determined
Dibenz[a,h]anthracene	53-70-3	0.209	not determined	not detected	0.209
Dibenzothiophene	132-65-0	0.386	0.226	0.13	0.226
Dibutyl phthalate	84-74-2	0.338	0.285	13.1	13.1
Diethyl Phthalate	84-66-2	0.285	0.119	1.92	1.92
Diisobutyl Phthalate	84-69-5	0.537	0.187	1.96	1.96
Diisooctylphthalate*	27554-26-3	0.644	0.435	0.375	0.435
Dimethyl phthalate	131-11-3	0.288	0.258	0.117	0.258
Di-n-octyl phthalate	117-84-0	0.237	0.212	0.188	0.212
Fluoranthene	206-44-0	0.592	0.186	0.108	0.186
Fluorene	86-73-7	0.539	0.221	0.121	0.221

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=5)	Selected MDL[b]
Hexadecane	544-76-3	0.467	0.18	0.275	0.275
Hexanoic Acid, 2-ethyl	149-57-5	2.26	not determined	not detected	2.26
Indeno[1,2,3-cd]pyrene	193-39-5	0.207	not determined	not detected	0.207
Limonene	138-86-3	0.189	0.14	0.21	0.21
Methyl stearate	112-61-8	0.299	0.161	0.0557	0.161
N,N-Dicyclohexylmethylamine	7560-83-0	0	not determined	0.0932	0.0932
Naphthalene	91-20-3	0.493	0.282	4.43	4.43
Naphthalene, 1,2-dimethyl-	573-98-8	0.361	0.142	0.0528	0.142
Naphthalene, 1,6-dimethyl-	575-43-9	0.349	0.179	0.0506	0.179
Naphthalene, 1-methyl-	90-12-0	0.323	0.234	0.143	0.234
Naphthalene, 2-(bromomethyl)-	939-26-4	0	not determined	0.144	0.144
Naphthalene, 2,3-dimethyl-	581-40-8	0.68	0.416	15.6	15.6
Naphthalene, 2-methyl	91-57-6	0.346	0.148	0.291	0.291
n-Caproic acid vinyl ester	3050-69-9	5.51	not determined	not detected	5.51
N-Phenylbenzamide	93-98-1	0.288	0.174	0.675	0.675
Phenanthrene	85-01-8	0.546	0.228	0.49	0.49
Phenanthrene, 1-methyl	832-69-9	0.197	0.169	0.00111	0.169
Phenanthrene, 2-methyl-	2531-84-2	0.233	0.223	1.13	1.13
Phenanthrene, 3-methyl	832-71-3	0.279	0.184	1.83	1.83
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	2772-45-4	0.563	0.366	0.0594	0.366
Phenol, 4-(1-phenylethyl)-	1988-89-2	0.542	not determined	not detected	0.542
Phthalimide	85-41-6	0	not determined	0.0674	0.0674
Pyrene	129-00-0	0.65	0.223	0.264	0.264

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=5)	Selected MDL[b]
Pyridine, 2-(4-methylphenyl)-	4467-06-5	0.703	0.245	0.013	0.245
Resorcinol[c]	108-46-3	0	not determined	not detected	not determined

[a]Spiked samples had the same amounts as the lowest detected calibration standards.
[b]MDL: Method Detected Limit; selected the greater of MDL_s (or spike amount) or MDL_b as the MDL. MDL_s were selected as the MDL for those chemicals. When both MDL_s was not determined and MDL_b was not detected (or with intermittent detects with highest blank value<lower limit of the calibration curve), selected MDL = lower limit of the calibration curve.
[c]bis(2,2,6,6-Tetramethyl-4-piperidyl) sebacate (CASRN 52829-07-9, poor response), cyclohexylamine (CASRN 108-91-8, matrix interference), demecolcine (CASRN 477-30-5, not detected), and resorcinol (CASRD 108-46-3, not detected) could not be analyzed by the HES-GC-MS. Their MDL were not calculated.
CASRN: Chemical Abstracts Service Registry Number; MDL_b: MDL based on method blanks, calculated using Equation D-2. For chemicals that were not detected in the blanks, MDL_b equaled to 0 or not detected. For chemicals with intermittent detects (count<5), MDL_b = the highest detected blank value; MDL_s: MDL based on spiked samples, calculated using Equation D-1. Spiked amount equaled to 0 and MDL_s were not determined for chemicals with poor responses or not detected in the spike samples.
All values shown are rounded to three significant figures.

Table D-4. Method Detection Limit (ng) of the Stir Bar Sorptive Extraction (SBSE) Stir Bar for HES-GC-MS Analysis of Organic Chemicals in the Artificial Sweat Extracts of Crumb Rubber Samples

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=5)	Selected MDL[b]
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	793-24-8	0	not determined	1.58	1.58
1,4-Benzenediamine, N,N'-diphenyl-	74-31-7	1.36	not determined	not detected	1.36
1,4-Benzenediol, 2,5-bis(1,1-dimethylethyl)-	88-58-4	0.706	not determined	not detected	0.706
17-Pentatriacontene	6971-40-0	0.143	not determined	not detected	0.143
1-Hydroxypyrene	5315-79-7	15.7	not determined	not detected	15.7
1-Octadecene	112-88-9	0	not determined	0.817	0.817
2,5-di-tert-Butyl-1,4-benzoquinone	2460-77-7	0.167	0.0789	0.0718	0.0789
2,5-Hexanedione[c]	110-13-4	0	not determined	not detected	not determined

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=5)	Selected MDL[b]
2-Benzothiazolone[c]	934-34-9	0	not determined	not detected	not determined
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	0.439	0.169	0.438	0.438
4-tert-Octylphenol	140-66-9	0.282	0.189	0.298	0.298
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	0.177	0.0791	0.0716	0.0791
7H-Benzo[c]fluorene	205-12-9	0.0964	0.0251	0.0019	0.0251
Acenaphthylene	208-96-8	0.323	0.0782	0.049	0.0782
Aniline[c]	62-53-3	0	not determined	not detected	not determined
Anthracene	120-12-7	0.321	0.0997	0.237	0.237
Anthracene, 2-methyl-	613-12-7	0.174	0.0587	not detected	0.0587
Anthracene, 9,10-dimethyl	781-43-1	0.323	0.221	not detected	0.221
Anthracene, 9,10-diphenyl-	1499-10-1	1.65	not determined	0.245	0.245
Anthracene, 9-phenyl	602-55-1	0.276	0.123	not detected	0.123
Benz[a]anthracene	56-55-3	0.365	0.159	0.139	0.159
Benzene, n-butyl-	104-51-8	0.209	0.0675	0.0254	0.0675
Benzo[a]pyrene	50-32-8	0.279	0.118	0.0914	0.118
Benzo[b]fluoranthene	205-99-2	0.39	0.14	0.148	0.148
Benzo[e]pyrene	192-97-2	0.331	0.14	0.058	0.14
Benzo[g,h,i]perylene	191-24-2	0.327	0.155	0.0999	0.155
Benzo[k]fluoranthene	207-08-9	0.393	0.229	0.0992	0.229
Benzothiazole	95-16-9	15.8	not determined	18.3	18.3
Benzothiazole, 2-phenyl-	883-93-2	0.263	0.114	0.00325	0.114
Benzyl butyl phthalate	85-68-7	0.996	not determined	0.29	0.29
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate[c]	52829-07-9	0	not determined	not detected	not determined
Bis(2-Ethylhexyl)adipate	103-23-1	1.28	not determined	0.498	0.498
Butylated Hydroxytoluene	128-37-0	0.124	not determined	7.54	7.54
Chrysene	218-01-9	0.29	0.0941	0.0926	0.0941
Coronene	191-07-1	7.44	not determined	not detected	7.44

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=5)	Selected MDL^b
Cyclohexanamine, N-cyclohexyl-	101-83-7	7.55	not determined	2.05	7.55
Cyclohexyl isothiocyanate	1122-82-3	0.149	not determined	not detected	0.149
Cyclohexylamine[c]	108-91-8	0	not determined	not detected	not determined
Cyclopenta[cd]pyrene	27208-37-3	0.195	0.0791	0.0449	0.0791
Demecolcine[c]	477-30-5	0	not determined	not detected	not determined
Dibenz[a,h]anthracene	53-70-3	0.326	0.23	0.0625	0.23
Dibenzothiophene	132-65-0	0.362	0.0914	0.212	0.212
Dibutyl phthalate	84-74-2	108	51.6	10	51.6
Diethyl Phthalate	84-66-2	1.79	not determined	8.57	8.57
Diisobutyl Phthalate	84-69-5	0.456	0.319	0.699	0.699
Diisooctylphthalate	27554-26-3	21.5	6.11	7.83	7.83
Dimethyl phthalate	131-11-3	1.85	not determined	17	17
Di-n-octyl phthalate	117-84-0	1.22	0.648	0.0301	0.648
Fluoranthene	206-44-0	0.368	0.144	0.123	0.144
Fluorene	86-73-7	0.282	0.0543	0.13	0.13
Hexadecane	544-76-3	1.82	1.43	3.6	3.6
Hexanoic Acid, 2-ethyl[c]	149-57-5	0	not determined	not detected	not determined
Indeno[1,2,3-cd]pyrene	193-39-5	0.964	0.385	0.0241	0.385
Limonene	138-86-3	0.0706	0.0248	0.0199	0.0248
Methyl stearate	112-61-8	1.88	1.88	0.704	1.88
N,N-Dicyclohexylmethylamine[c]	7560-83-0	0	not determined	not detected	not determined
Naphthalene	91-20-3	0.221	not determined	1.13	1.13
Naphthalene, 1,2-dimethyl-	573-98-8	0.32	0.106	0.0657	0.106
Naphthalene, 1,6-dimethyl-	575-43-9	0.252	0.0892	0.0338	0.0892
Naphthalene, 1-methyl-	90-12-0	0.275	0.0922	0.0796	0.0922
Naphthalene, 2-(bromomethyl)-	939-26-4	0.51	0.386	0.14	0.386

Targeted Chemical	CASRN	Spiked Amount (ng)[a]	MDL_s (n=7)	MDL_b (n=5)	Selected MDL[b]
Naphthalene, 2,3-dimethyl-*	581-40-8	0.552	0.151	0.0672	0.151
Naphthalene, 2-methyl	91-57-6	0.27	0.12	0.139	0.139
n-Caproic acid vinyl ester	3050-69-9	0.078	not determined	not detected	0.078
N-Phenylbenzamide	93-98-1	0	not determined	10.8	10.8
Phenanthrene	85-01-8	0.422	0.131	0.553	0.553
Phenanthrene, 1-methyl	832-69-9	0.302	0.119	0.0364	0.119
Phenanthrene, 2-methyl-	2531-84-2	0.395	0.195	not detected	0.195
Phenanthrene, 3-methyl	832-71-3	0.447	0.18	4.22	4.22
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	2772-45-4	0.239	0.0889	0.0744	0.0889
Phenol, 4-(1-phenylethyl)-	1988-89-2	0.774	not determined	not detected	0.774
Phthalimide	85-41-6	0.074	not determined	12.6	12.6
Pyrene	129-00-0	0.51	0.317	0.0704	0.317
Pyridine, 2-(4-methylphenyl)-	4467-06-5	9.83	1.6	0.992	1.6
Resorcinol[c]	108-46-3	0	not determined	not detected	not determined

[a]Spiked samples had the same amounts as the lowest detected calibration standards.

[b]MDL: Method Detected Limit; selected the greater of MDL_s (or spike amount) or MDL_b as the MDL. MDL_s were selected as the MDL for those chemicals. When both MDL_s was not determined and MDL_b was not detected (or with intermittent detects with highest blank value<lower limit of the calibration curve), selected MDL = lower limit of the calibration curve.

[c]2,5-Hexanedione (CASRN 110-13-4, poor response), 2-benzothiazolone (CASRN 934-34-9, poor response), aniline (CASRN 62-53-3, not detected) bis(2,2,6,6-Tetramethyl-4-piperidyl) sebacate (CASRN 52829-07-9, poor response), cyclohexylamine (CASRN 108-91-8, matrix interference), demecolcine (CASRN 477-30-5, not detected), hexanoic Acid, 2-ethyl (CASRN 149-57-5, poor response), N,N-dicyclohexylmethylamine (CASRN 7560-83-0, not detected), and resorcinol (CASRN 108-46-3, not detected) could not be analyzed by the HES-GC-MS. Their MDL were not calculated.

CASRN: Chemical Abstracts Service Registry Number; MDL_b: MDL based on method blanks, calculated using Equation D-2. For chemicals that were not detected in the blanks, MDL_b equaled to 0 or not detected. For chemicals with intermittent detects (count<5), MDL_b = the highest detected blank value; and MDL_s: MDL based on spiked samples, calculated using Equation D-1. Spiked amount equaled to 0 and MDL_s were not determined for chemicals with poor responses or not detected in the spike samples.

All values shown are rounded to three significant figures.

D.3.6.1.6. Determination of MDL for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Analysis of Metals and Metalloids (except Mercury) in the Oral Bioaccessibility Measurements

Table D-22 and Table D-23, respectively, shows the values of MDL for each metal or metalloid in acid extracts of crumb rubber using the USEPA 3051A and ASMT F3188-16 methods. LBNL determined the values of MDL using the blanks and the spiked samples prepared below for each method:

1. USEPA 3051A: Prepared seven blanks and seven spiked samples. Blank samples were initially prepared with a 1:3 (v/v) of concentrated ultrapure hydrochloric acid and nitric acid, and then diluted 25 times with 2 percent (v/v) nitric acid. The spiked samples were prepared with the same procedure, but additionally spiked with elements with the same concentrations as the lowest calibration standard.
2. American Society for Testing and Materials Method (ASTM F3188-16): Prepared seven blanks and seven spiked samples. Blank samples were initially prepared with a concentration of 0.08 M ultrapure hydrochloric acid, and then diluted 10 times with 2 percent (v/v) nitric acid. The spiked samples were prepared with the same procedure, but additionally spiked with elements with the same concentrations as the lowest calibration standard.

The values of LOQ were determined as three times of the MDL for each metal or metalloid in an extract. Prior to analysis, the instrumentation was optimized and passed daily performance checks. The calibration was conducted with eight calibration standards with excellent QC agreement.

Table D-1. Method Detection Limit (MDL, part per billion, ppb) for Metals and Metalloids in USEPA 3051A Method Extracts of Curmb Rubber Samples

Symbol of Metal or Metalloid	Spiked Concentration[a]	MDL_s	MDL_b	Selected MDL	MDL (Corrected)[b]
Li	0.0063	0.0070	0.0701	0.0701	1.7515
Be	0.0503	0.0051	0.0205	0.0205	0.5114
B	0.0126	0.0920	0.7806	0.7806	19.5162
Na	2.5136	0.0773	0.7195	0.7195	17.9879
Mg	2.5136	0.0497	0.5568	0.5568	13.9210
Al	2.5141	0.0373	0.3669	0.3669	9.1724
Si	1.2830	0.2414	6.4572	6.4572	161.4310
K	2.5136	0.0447	0.4906	0.4906	12.2647
V	0.0503	0.0020	0.2295	0.2295	5.7368
Cr	0.0503	0.0009	0.0152	0.0152	0.3802
Mn	0.0503	0.0026	0.0093	0.0093	0.2321
Ca	2.5136	2.6857	2.6835	2.6835	67.0866
Fe	2.5125	0.0457	0.4098	0.4098	10.2446

Symbol of Metal or Metalloid	Spiked Concentration[a]	MDL_s	MDL_b	Selected MDL	MDL (Corrected)[b]
Se	0.0251	0.0419	0.1108	0.1108	2.7707
Ti	0.0257	0.0078	0.7103	0.7103	17.7565
Ni	0.0503	0.0006	0.0500	0.0500	1.2511
Co	0.0503	0.0024	0.0006	0.0006	0.0161
Cu	0.0503	0.0147	0.0310	0.0310	0.7758
Zn	0.0503	0.0586	0.3205	0.3205	8.0137
As	0.0503	0.0020	0.0005	0.0020	0.0494
Rb	0.0126	0.0008	0.0006	0.0008	0.0199
Sr	1.2568	0.0129	not detected	0.0129	0.3233
Mo	0.0257	0.0003	0.0027	0.0027	0.0667
Ag	0.0251	0.0011	0.0603	0.0603	1.5080
Cd	0.0251	0.0031	0.0040	0.0040	0.1010
Sn	0.0257	0.0061	0.0421	0.0421	1.0523
Sb	0.0257	0.0026	0.0047	0.0047	0.1185
Ba	0.0503	0.0055	0.0033	0.0055	0.1379
Tl	0.0251	0.0009	0.0003	0.0009	0.0215
Pb	0.0503	0.0017	0.0012	0.0017	0.0431

[a]Spiked samples have the same concentrations as the lowest calibration standard (in ppb).
[b]The corrected MDL = selected MDL x dilution factor (DF = 25).
MDL: Method Detected Limit ; select the greater of MDL_s or MDL_b as the MDL; MDL_b: MDL based on method blanks, calculated using Equation D-2; and MDL_s: MDL based on spiked samples, calculated using Equation D-1.
All values shown are rounded to four decimal places.

Table D-2. Method Detection Limits (MDL, part per billion, ppb) for Metals and Metalloids in American Society for Testing and Materials (ASTM) Method F3188-16 Extracts of Crumb Samples

Symbol of Metal or Metalloid	Spiked Concentration[a]	MDL_s	MDL_b	Selected MDL	MDL (Corrected)[b]
Li	0.0063	0.0175	0.0641	0.0641	0.6413
Be	0.0503	0.0025	0.0047	0.0047	0.0468
B	0.0126	0.0182	0.5531	0.5531	5.5312
Na	2.5136	0.3734	0.2385	0.3734	3.7340
Mg	2.5136	0.1210	0.1679	0.1679	1.6786
Al	2.5141	0.0590	0.1320	0.1320	1.3203
Si	1.2830	0.1662	1.8789	1.8789	18.7889
K	2.5136	0.1463	0.2084	0.2084	2.0838
V	0.0503	0.0003	0.2282	0.2282	2.2820
Cr	0.0503	0.0028	0.0040	0.0040	0.0399
Mn	0.0503	0.0015	0.0103	0.0103	0.1034

Symbol of Metal or Metalloid	Spiked Concentration[a]	MDL_s	MDL_b	Selected MDL	MDL (Corrected)[b]
Ca	2.5136	0.9991	2.2871	2.2871	22.8710
Fe	2.5125	0.0333	0.7852	0.7852	7.8522
Se	0.0251	0.0007	0.1199	0.1199	1.1987
Ti	0.0257	0.0366	0.2410	0.2410	2.4099
Ni	0.0503	0.0001	0.0055	0.0055	0.0550
Co	0.0503	0.0004	0.0000	0.0004	0.0039
Cu	0.0503	0.0158	0.0088	0.0158	0.1579
Zn	0.0503	0.0049	0.1403	0.1403	1.4035
As	0.0503	0.0016	not detected	0.0016	0.0164
Rb	0.0126	0.0004	not detected	0.0004	0.0037
Sr	1.2568	0.0189	not detected	0.0189	0.1894
Mo	0.0257	0.0005	0.0076	0.0076	0.0763
Ag	0.0251	0.0083	0.0196	0.0196	0.1956
Cd	0.0251	0.0063	0.0018	0.0063	0.0630
Sn	0.0257	0.0012	not detected	0.0012	0.0120
Sb	0.0257	0.0011	not detected	0.0011	0.0114
Ba	0.0503	0.0019	0.0021	0.0021	0.0213
Tl	0.0251	0.0002	0.0003	0.0003	0.0027
Pb	0.0503	0.0016	0.0060	0.0060	0.0602

[a]Spiked samples have the same concentrations as the lowest calibration standard (in ppb).
[b]The corrected MDL = selected MDL x dilution factor (DF = 10).
MDL: Method Detected Limit ; select the greater of MDL_s or MDL_b as the MDL; MDL_b: MDL based on method blanks, calculated using Equation D-2; and MDL_s: MDL based on spiked samples, calculated using Equation D-1.

D.3.6.1.7. Determination of MDL for ICP-MS Analysis of Mercury in the USEPA 3051A and ASTM F3188-16 Extracts of Crumb Rubber Samples

LBNL determined the MDL for mercury (Hg) with a spiked Hg concentration of 25 parts per trillion (ppt, initial estimated MDL ~10 ppt based on the region of calibration). The spiked samples and blanks (2 percent nitric acid) were prepared and analyzed on three separate calendar dates (three batches) within six months. Gold (in the form of $AuCl_3$) was added (200 ppb) to all samples (mercury samples, standard solutions, and blanks) and the ICP-MS rinse solutions. All instrumentation and calibration conditions were the same as described in a PerkinElmer ICP-MS application note: Determination of mercury in wastewater by inductively coupled plasma-mass spectrometry (PerkinElmer Inc, 2011).

The analyzed results are provided in Table D-24 and Table D-25 for the mercury-spiked samples and the blank samples, respectively.

Table D-1. Inductively Coupled Plasma Mass Spectrometry Analysis of Mercury in Mercury Spiked Samples (25 part per trillion, ppt) Containing 200 ppb Gold in Two Percent Nitric Acid Matrix

Replicates (n)	Mercury Concentration (ppt)	Note
#1	25.50	Batch-1
#2	27.62	Batch-1
#3	19.27	Batch-2
#4	18.90	Batch-2
#5	28.05	Batch-3
#6	26.62	Batch-3
#7	27.97	Batch-3
#8	19.73	Batch-3
#9	27.62	Batch-3
#10	27.93	Batch-3
#11	27.92	Batch-3
Mean value	25.18	NA
S_s (standard deviation)	3.68	NA
MDL_s	10.17	from Equation D-1[a]

[a] $t_{(n-1,1-\alpha=0.99)}$ = 2.764 at degree of freedom = 11-1 = 10

MDL_s: method detection limit based on spiked samples and NA: not applicable

Table D-2. Inductively Coupled Plasma Mass Spectrometry Analysis of Mercury in Blank Samples Containing 200 ppb Gold in Two Percent Nitric Acid Matrix

Replicates (n)	Mercury Concentration (ppt)	Note
#1	9.3	Batch-1
#2	4.79	Batch-1
#3	2.98	Batch-1
#4	1.63	Batch-1
#5	-1.46	Batch-1
#6	-1.4	Batch-1
#7	4.97	Batch-1
#8	1	Batch-1
#9	4.97	Batch-1
#10	2.36	Batch-1
#11	9.15	Batch-2
#12	6.28	Batch-2
#13	7.03	Batch-2
#14	8.45	Batch-2
#15	12.40	Batch-2
#16	9.75	Batch-2
#17	8.13	Batch-2
#18	11.15	Batch-2

Replicates (n)	Mercury Concentration (ppt)	Note
#19	8.59	Batch-2
#20	6.77	Batch-2
#21	5.19	Batch-3
#22	11.54	Batch-3
#23	8.05	Batch-3
#24	4.41	Batch-3
#25	8.51	Batch-3
#26	8.33	Batch-3
#27	11.17	Batch-3
#28	8.92	Batch-3
#29	9.64	Batch-3
#30	8.27	Batch-3
#31	9.10	Batch-3
#32	9.75	Batch-3
#33	9.04	Batch-3
#34	7.80	Batch-3
#35	9.15	Batch-3
#36	6.28	Batch-3
#37	7.03	Batch-3
#38	8.45	Batch-3
#39	9.75	Batch-3
#40	11.15	Batch-3
#41	8.59	Batch-3
#42	4.85	Batch-3
#43	6.77	Batch-3
#44	5.19	Batch-3
#45	11.54	Batch-3
#46	8.05	Batch-3
#47	4.41	Batch-3
#48	4.95	Batch-3
Mean value	7.14	NA
S_b (standard deviation)	3.18	NA
MDL_b	14.80	from Equation D-2[a]

[a] $t_{(n-1,1-\alpha=0.99)}$ = 2.408 at degree of freedom = 48 – 1 = 47
MDL_b: method detection limit based on blank samples and NA: not applicable

Since the determined MDL_b is greater than MDL_s, the determined MDL for mercury is 14.8 ppt (0.0148 ppb or 0.0148 µg per L) with a confidence level of 99%. It is comparable with the value determined using the similar ICP-MS method (Allibone *et al.*, 1999). Allibone and coworkers reported a LOD (limit of detection) of 0.032 µg per L (32 ppt).

For the extracts of ASTM (F3188-16) (ASTM International, 2016), the original samples have been diluted with a dilution factor (DF) of 10, so the MDL for the original extract using ASTM (F3188-16) method should be approximately 148 ppt.

For the extracts of USEPA 3051A (USEPA, 2007a), the original samples have been diluted with a DF of 25, so the MDL for the original extract using USEPA 3051A method should be approximately 370 ppt.

D.3.6.2. Determination of Limits of Quantification (LOQ) for Analyses of Samples Collected in The Phase 3 Field Work and Quality Control

The USEPA (USEPA, 2007b) defines the limit of quantification (LOQ) as: "The smallest detectable concentration of analyte greater than the Detection Limit (DL) where the accuracy (precision & bias) achieves the objectives of the intended purpose." Although USEPA does not provide a simple formula for calculation of LOQ, a review in the literature (Lister, 2005) suggested the determination of LOQ by a signal to noise ratio of 10:1 or an estimation of 3.3 times of the MDL. OEHHA determined the MDL and LOQ for each chemical targeted in an instrumental analysis of a sample. We estimated the value of LOQ of a chemical as three times of the MDL for most of the instrumental analyses performed in the Synthetic Turf Study, with two exceptions:

- HPLC Analysis of the ALD Samples: LBML calculated values of LOQ of the seven carbonyls (2-butanone, CASRN 78-93-3; acetaldehyde, CASRN 75-07-0; acetone, CASRN 67-64-1; acrolein, CASRN 107-02-8; crotonaldehyde, CASRN 123-73-9; formaldehyde, CASRN 50-00-0; m-tolualdehyde, CASRN 620-23-5; propionaldehyde, CASRN 123-38-6; and valeraldehyde, CASRN110-62-3) analyzed by HPLC as 10 times of the standard deviation of the 10 repeated low calibration spike analysis. The LOQ of these carbonyls were 3.54 times of their MDL (see values in Table D-17).
- High Resolution Accurate Mass Liquid Chromatography Mass Spectrometry (HRAM LC-MS) Analysis of the Oral and Dermal Bioaccessibility Measurements: values of MDL or LOQ were not determined for the analysis. Due to limitation on the availability of the instrument, LBNL was unable to determine the MDL of chemical analyses using the HRAM LC-MS. However, the sensitivity of this instrument has been reported to be at the sub-femtomole level (UWPR, 2007). Research on the literature revealed the detection limit of this instrument was 5 pg in 1 microliter (microliter) volume of injection (Cheng *et al.*, 2017) which were well below the amounts detected in the sample extracts (range from ng to µg per microliter).

D.3.6.3. Quality Control (QC) Analysis and Validation of Analytical Data Based on MDL

OEHHA performed QC analysis on the raw analytical data of samples collected during the Phase 3 Field Work and validated the chemical results by following the steps below:

1. Inspected and confirmed or invalidated irregular data for irregularity:
    - Removed negative data
    - Requested LBNL to check and confirm against instrumental output of the outliers (e.g., compared with data within a time series or duplicated samples from a field)
2. Removed raw data of invalid chemicals:
    - Removed raw data of chemicals that failed calibration (e.g., instrument failed to detect the chemical standard, matrix interference rendered the calibration process to fail, unsatisfied calibration curve fitting due to poor instrumental response to the chemical standard)
    - Raw data of values above the maximum curve fitted level of the chemical standard calibration
    - Raw data from samples that could not be tracked according to the field logs or from invalidated samples (e.g., due to equipment failure) as noted in field logs
3. Applied MDL and LOQ to modify raw data:
    - Detected amount or concentration a chemical in a sample was below the MDL, modified the value to zero and counted as not detected in the sample
    - Detected amount or concentration of a chemical in a sample was between the MDL and less than the LOQ, modified the value to half of the LOQ of the chemical
    - Detected amount or concentration a chemical in a sample equaled to or above the LOQ, did not modify the value

OEHHA used the validated chemical results to determine the concentrations of each chemical (organic chemical) in the air or bioaccessible from the crumb rubber (organic chemical, metal, or metalloid) for each field (Section 2).

D.4. Analyses of Field Samples

D.4.1. Analyses of Crumb Rubber Samples

D.4.1.1. American Society for Testing and Materials (ASTM) Method F3188-16 Metals and Metalloids Extraction of Crumb Rubber

SAFETY: Workers need to have WPC approval for work in Room 70-258 at LBNL. Corrosive solutions are used. All work is to be performed while wearing nitrile gloves and safety glasses.

D.4.1.1.1. ASTM Method F3188-16

This is the summary of the ASTM method F3188-16 (ASTM International, 2016) used to extract metal by leaching at 37 °C in 0.08 M HCl.

Table D-1. Equipment and Supplies

EnviroGenie Incubator	Erlenmeyer flasks
Micro balance	Graduated cylinder
pH meter	Serological pipets
Vortex mixer	Glass pipet
Crumb Rubber samples	Pipet aid
Google tracking sheet	Syringe filter, 0.45 µm, PVDF, (Acrodisc, 13 mm #28143-997)
Teflon spatula	Plastic syringe, 10 mL, Luer (#66064-754)
Weighing paper	Bench paper
15 mL polypropylene tubes (Sarstedt #62.554.205)	Nitrile gloves
1 L plastic bottles #16125-876	Timer
Ion chromatography (IC) grade water (RICCA)	Kimwipes™
37 percent hydrochloric acid (HCl), (BDH Aristor Ultra, #87003-220)	Labeling tape

D.4.1.1.2. Preparation

1. Preparation of 2 M HCl solution
   a Clean glassware with citrate cleaning solution: 1 L graduated cylinder and 1 L Erlenmeyer flask and 1 L glass bottle.
   b Prepare fume hood for work with concentrated acid. Remove all organic solvents before opening the acid.
   c Transfer about 700 mL of RICCA (IC grade) water to the 1 L Erlenmeyer.
   d Carefully transfer 160 mL of 37 percent Ultrapure HCl to a graduated cylinder.
   e Slowly add the acid to the water in the Erlenmeyer flask **(Never the other way!!)**. The flask will become warm.
   f Use a glass 10 mL pipet to add 6.7 mL more of the acid to this Erlenmeyer flask.
   g Mix and allow the solution to cool to room temperature.
   h Transfer to the 1 L graduated cylinder and dilute to 1 L.
   i Store in a glass bottle and label using a corrosive label.
2. Preparation of the 0.08 M HCl solution
   a Transfer about 300 mL of RICCA water to a 500 mL Erlenmeyer.

b Use a serological pipet to add 20 mL of 2M HCl to the Erlenmeyer.

c Mix and let the solution cool.

d Transfer to a 500 mL graduated cylinder.

e Dilute to 500 mL with RICCA water.

f Store in a glass bottle and label using a corrosive label.

3. Prepare High Impact (HI) Area composite samples (see details in Section D.1.8.1)

a Record in notebook or google sheet Sample ID numbers to mix.

b Label 120 mL plastic bottle using the following naming convention:

Composite: F19-A,B (Field ID-Sample Location(s))

Prepared: 7/16/2018 (Date)

c Mix bottles well by shaking 30 seconds, rolling 15 seconds, and shaking again for 15 seconds.

d Weigh ~9 g of each of HI area crumb samples and add to 120 mL labelled bottle. Record weight in notebook.

4. Prepare Rest of Field (RoF) composite samples (see details in Section D.1.8.1)

a Record in notebook or google sheet Sample ID numbers to mix.

b Label 1 L plastic bottle using the following naming convention:

Composite: F19-C,D,E,F,G (Field ID-Sample Location(s))

Prepared: 7/22/2018 (Date)

c Mix bottles well by shaking 30 seconds, rolling 15 seconds, and shaking again for 15 seconds.

d Weigh ~9 g of each of RoF area crumb samples and add to 1 L labelled bottle. Record weight in notebook.

D.4.1.1.3. Crumb Rubber Digestion

1. Turn on EnviroGenie (with rocking platform installed) and set the temperature to 37 °C.
2. Calibrate pH meter for acid measurement (<7.0).
3. Label 15 mL tubes with ID number. Record in notebook.
4. Mix composite bottles well by shaking 30 seconds, rolling 15 seconds, and shaking again for 15 seconds.
5. Weigh 0.2 g turf composite samples and record actual amount.
6. Transfer to a 15 mL Sarstedt tube.
7. Add 10 mL 0.08 M HCl using serological pipet.

8. Cover EnviroGenie window with aluminum foil or protect from light.
9. Rock 1 minute at 37 °C.
10. Measure pH.
    a If pH > 1.5, add 2 M HCl, dropwise until pH is between 1.0 and 1.5.
    b If pH < 1.5 continue to Step 11.
11. Rock at 37 °C for 1 hour.
12. Prepare a second 15 mL labeled tube.
13. Cool extracted samples to room temperature.
14. Use a 10 mL Luer syringe and remove about 4 to 5 mL of extract.
15. Place an Acrodisc syringe filter onto the syringe.
16. Dispense the extract into the new tube through the syringe filter.
17. The syringe and filter may be discarded into the regular trash.
18. Use a new syringe and filter for each sample.
19. Be sure to prepare one blank sample.

D.4.1.1.4. ICP-MS Analysis

a. Filter with 0.45 µm PVDF membrane (Acrodisc LC 13 mm syringe filter, PALL Life Science).
b. Filtrates are diluted for ICP-MS analysis.
c. Sample filtrates were first diluted with a dilution factor (DF) = 10 and run ICP-MS analysis.
d. Mercury analysis: analyzed separately (see Section D.2.7).

D.4.1.1.5. Result of Gastric Bioaccessibility Measurements of Metals and Metalloids in Artificial Gastric Fluid Extracts

Table D-27 summarizes the 35 individual-field gastric bioaccessible concentrations of metals and metalloids in crumb rubber samples ($C_{GI\text{-}crumb\ rubber\text{-}field}$, micrograms per gram of crumb rubber) extracted using the ASTM Method. The mean values represent the mean of the 35 individual-field average concentrations of the metals and metalloids ($C_{ing\text{-}crumb\ rubber}$, micrograms per gram of crumb rubber).

Table D-1. Individual-Field Gastric Bioaccessilbe Concentrations of Metals and Metalloids in Crumb Rubber Samples ($C_{GI\text{-}crumb\ rubber\text{-}field}$, micrograms per gram of crumb rubber) Collected from the 35 Fields During the State-Wide Study

Metals and Metalloids	Detection[a]	$C_{ing\text{-}crumb\ rubber\text{-}field}$					
		Minimum	Mean ($C_{ing\text{-}crumb\ rubber}$)	Standard Deviation	Median	95th Percentile	Maximum
Aluminum	35	7	22	11	20	40	52
Antimony	35	0.0015	0.024	0.021	0.02	0.055	0.1
Arsenic	35	0.0012	0.01	0.0072	0.0092	0.018	0.039
Barium	35	0.4	1.5	1	1.5	2.9	5.7
Beryllium	11	0	0.00063	0.001	0	0.0022	0.0035
Boron	25	0	0.45	0.51	0.2	1.3	1.8
Cadmium	34	0	0.017	0.01	0.015	0.036	0.04
Calcium	35	13	460	1500	99	1800	7900
Chromium	35	0.0088	0.047	0.046	0.031	0.1	0.26
Cobalt	35	0.2	1.1	0.74	1	2.1	3.8
Copper	35	0.84	2.1	1.1	1.9	3.5	6.7
Iron	35	8.1	23	8.1	22	35	38
Lead	35	0.19	1	0.86	0.75	2.5	4.5
Lithium	3	0	0.0033	0.011	0	0.03	0.047
Magnesium	35	3.2	19	22	15	48	130
Manganese	35	0.18	0.99	0.58	1	1.6	3.1
Molybdenum	14	0	0.0018	0.0025	0	0.0056	0.009
Nickel	35	0.021	0.097	0.079	0.067	0.27	0.37
Potassium	35	2.9	13	8	13	25	40
Rubidium	35	0.016	0.05	0.028	0.049	0.08	0.17
Selenium	4	0	0.006	0.018	0	0.042	0.088
Silicon	35	5.3	16	10	15	33	50
Silver	2	0	0.0006	0.0026	0	0.0022	0.014
Sodium	35	0.9	21	22	14	61	110
Strontium	35	0.081	0.85	1.6	0.45	2.5	9.6
Thallium	21	0	0.00024	0.0004	0.00019	0.00073	0.0022
Tin	30	0	0.0093	0.0093	0.0069	0.025	0.037
Titanium	35	0.16	0.36	0.19	0.32	0.66	0.69
Vanadium	2	0	0.0048	0.02	0	0.025	0.085
Zinc	35	46	210	110	200	370	600

[a] Detection value is the number of fields with concentration in extracts above the method of detection for a metal or metalloid.
Values are rounded to two significant figures.

D.4.1.2. USEPA 3051A Method Microwave Assisted Acid Digestion of Crumb Rubber for Extraction of Metals and Metalloids

D.4.1.2.1. Method 3051A Acid Digestion

This is the summary of the USEPA Method 3051A (USEPA, 2007c) used to extract metals and metalloids by microwave digestion at 175 °C in concentrated nitric acid (HNO_3) and concentrated hydrochloric acid (HCl).

Table D-1. Equipment and Supplies

EnviroGenie Incubator	Microwave system (Multiwave 3000, Anton Paar)
Micro balance	Erlenmeyer flasks
pH meter	Graduated cylinder
Vortex mixer	Serological pipets
Crumb Rubber samples	Glass pipet
Google tracking sheet	Pipet aid
Teflon spatula	Syringe filter, 0.45 µm, PVDF, (Acrodisc, 13 mm #28143-997)
Weighing paper	Plastic syringe, 10 mL, Luer (#66064-754)
15 mL polypropylene tubes (Sarstedt #62.554.205)	Bench paper
1 L plastic bottles #16125-876	Nitrile gloves
Ultrapure concentrated nitric acid, HNO_3	Timer
Ultrapure concentrated, hydrochloric acid HCl	Kimwipes™
Not applicable	Labeling tape

D.4.1.2.2. Sample Preparation

1. Prepare High Impact (HI) Area composite samples (see details in Section D.1.8.1)
   a. Record in notebook or google sheet Sample ID numbers to mix.
   b. Label 120 mL plastic bottle using the following naming convention:

      Composite: F19-A,B (Field ID-Sample Location(s))

      Prepared: 7/16/2018 (Date)

   c. Mix bottles well by shaking 30 seconds, rolling 15 seconds, and shaking again for 15 seconds.
   d. Weigh ~9 g of each of HI area crumb samples and add to 120 mL labelled bottle. Record weight in notebook.
2. Prepare Rest of Field (RoF) composite samples (see details in Section D.1.8.1)

a. Record in notebook or google sheet Sample ID numbers to mix.

b. Label 1 L plastic bottle using the following naming convention:

   Composite: F19-C,D,E,F,G (Field ID-Sample Location(s))

   Prepared: 7/22/2018 (Date)

c. Mix bottles well by shaking 30 seconds, rolling 15 seconds, and shaking again for 15 seconds.

d. Weigh ~9 g of each of RoF area crumb samples and add to 1 L labelled bottle. Record weight in notebook.

D.4.1.2.3. Analytical Method

Follow the following steps to conduct the acid digestion of crumb rubber sample for ICP-MS analysis:

1. Microwave Calibrations
   - Calibrate the power, pressure and temperature (follow the manual standard procedures).

2. Cleaning Extraction Vessels
   a. Prepare the acids for cleaning the vessels (particularly clean the fluoropolymer microwave vessels for sample extraction).
   b. Conduct cleaning procedures.

3. Microwave Extraction
   a. Weigh turf samples (~ 0.2 g) into the fluoropolymer microwave vessels (pre-cleaned).
   b. Add 9 mL ultrapure concentrated nitric acid (HNO_3) and 3 mL ultrapure hydrochloric acid (HCl), then cap with fluoropolymer seals and safety holders.
   c. Put into the microwave rotor (Rotor 8SXF100) following the manual procedures.
   d. Set up digestion method (temperature rise to 175 °C in approximately 5.5 minutes and remain at 175 °C for 10 minutes digestion period).
   e. Test to pass initial power, temperature, pressure, and exhaust checks etc.
   f. Start digestion method.
   g. After cooling down, let the sample vessels stand overnight.

4. ICP-MS Analysis
   a. Filter with 0.45 µm PVDF membrane (Acrodisc LC 13 mm syringe filter, PALL Life Science).

b. Filtrates are diluted for ICP-MS analysis.

c. Sample filtrates were first diluted with a dilution factor (DF) = 100 and run ICP-MS analysis.

d. The filtrates are then prepared for two types of samples: DF = 5000 for zinc analysis and DF = 25 for other metals and metalloids analysis.

e. Mercury analysis: analyzed separately (see Section D.2.7).

Notes:

1. Before sample analysis: first check instrument daily performance, calibrations for each metal and metalloid, run quality control (QC) check standards and blanks.
2. During and after sample analysis: run QC check standards and blanks.
3. After instrument analysis:
   a Conduct data review, enter dilution factor correction, edit and report.
   b Clean the fluoropolymer vessels.
   c Neutralize waste.

D.4.1.2.4. Result of Total Metals and Metalloids Extraction

Table D-29 summarizes the 35 individual-field total concentrations of metals and metalloids in crumb rubber samples (Total $C_{GI\text{-}crumb\ rubber\text{-}field}$, micrograms per gram of crumb rubber) extracted using the USEPA Method. The mean values represent the mean of the 35 individual-field average total concentrations of the metals and metalloids in crumb rubber (Total $C_{ing\text{-}crumb\ rubber}$, micrograms per gram of crumb rubber).

Table D-1. Individual-Field Total Concentrations of Metals and Metalloids in Crumb Rubber Samples ($C_{GI\text{-}crumb\ rubber\text{-}field}$, micrograms per gram of crumb rubber) Collected from the 35 Fields During the State-Wide Study

Metals and Metalloids	Detection[a]	Total $C_{ing\text{-}crumb\ rubber\text{-}field}$					
		Minimum	Mean (Total $C_{ing\text{-}crumb\ rubber}$)	Standard Deviation	Median	95th Percentile	Maximum
Aluminum	35	380	860	390	790	1500	2300
Antimony	35	0.18	0.82	0.42	0.78	1.5	2.5
Arsenic	35	0.25	0.75	0.45	0.59	1.6	2.1
Barium	35	4	11	12	7.9	19	75
Beryllium	4	0	0.0021	0.0081	0	0.011	0.045
Boron	31	0	5.2	7.6	1.9	18	39
Cadmium	35	0.22	0.96	0.81	0.74	2.3	4.5
Calcium	35	920	8300	26000	1700	36000	120000
Chromium	35	0.72	5.2	19	1.9	3.4	120
Cobalt	35	48	150	72	140	290	360

Metals and Metalloids	Detection[a]	Total $C_{ing\text{-}crumb\ rubber\text{-}field}$					
		Minimum	Mean (Total $C_{ing\text{-}crumb\ rubber}$)	Standard Deviation	Median	95th Percentile	Maximum
Copper	35	8.3	21	7.4	18	34	35
Iron	35	270	720	500	560	1600	2600
Lead	35	3.6	23	20	15	65	91
Lithium	35	0.76	1.7	0.62	1.6	2.9	3.1
Magnesium	35	170	430	720	290	450	4600
Manganese	35	4.5	8.8	4.6	7.1	18	25
Molybdenum	35	0.0059	0.15	0.077	0.14	0.23	0.51
Nickel	35	1.1	3.7	2.5	3.2	5.8	17
Potassium	35	250	490	230	440	570	1700
Rubidium	35	1	2	1.3	1.8	2.5	9.4
Selenium	35	1.4	2.6	0.74	2.5	4	4.4
Silicon	35	61	600	260	550	1000	1100
Silver	11	0	0.65	2.3	0	3.8	11
Sodium	35	140	370	120	360	560	650
Strontium	35	1.9	6.8	10	3.7	28	49
Thallium	35	0.026	0.046	0.017	0.039	0.084	0.1
Tin	35	0.44	1.9	1.6	1.5	3.9	9.8
Titanium	35	20	57	42	44	130	220
Vanadium	35	0.51	2.3	0.96	2.2	3	6.9
Zinc	35	7600	16000	4500	17000	23000	25000

[a] Detection value is the number of fields with concentration in extracts above the method of detection for a metal or metalloid.
Values are rounded to two significant figures.

D.4.1.3. Dermal Bioaccessibility Extraction of Organic Chemicals in Crumb Rubber Using a Stir Bar Sorptive Extraction System

D.4.1.3.1. Artificial Sweat Preparation

SAFETY: Workers need to have WPC (EE-0103) approval for work in 70-258 at LBNL. All work is to be performed while wearing nitrile gloves, safety glasses and lab coat.

1. Summary

Prepare 1 L of an artificial biofluid designed to simulate human sweat. This will be used to model dermal exposure to crumb rubber in an extraction process. Note: Corrosive acids are used in this buffer.

Table D-1. Equipment and Supplies

Micro Balance	Pipet aid
pH Meter	1 L glass storage bottle (or 2 amber bottles)

Stir plate (Gerstel, Twister 20)	Sodium chloride, NaCl
Metal spatula	Ammonium chloride, NH_4Cl
Weighing paper	Urea
Water (HPLC Grade glass bottle)	Lactic Acid, 85 percent
1 M Hydrochloric acid, HCl	Acetic Acid, 1M
Sodium hydroxide, NaOH, pellets or beads	Bench paper
Stir bar	Nitrile gloves
1 L Erlenmeyer flask	Timer
1 L Graduated cylinder	Kimwipes™
50 mL Graduated Cylinder	Labeling tape
10 mL Glass pipet	Not applicable

2. Preparation of Artificial Sweat Buffer Solutions

   a Prepare solvent clean glassware, pipets and bottles. Air dry glassware to remove any traces of solvent (use oven). Dedicate this glassware to the preparation of the artificial sweat. Once the glassware is solvent clean, it can be re-used after rinsing with the high performance liquid chromatography (HPLC) grade water.

   b Make all solutions in HPLC grade water stored in a glass bottle.

   c Add a large stir and about 600 to 700 mL HPLC grade water to the 1 L Erlenmeyer flask.

   d While stirring, add the following salts:

   - 19.87 g NaCl
   - 17.65 g NH_4Cl
   - 4.98 g Urea

   e Stir until dissolved (30 minutes). If the salts are not dissolved, add 50 mL of water at a time and record how much extra is added (if necessary) until all the salts are dissolved.

   f Move to a fume hood before adding the acids.

   g Use the glass 10 mL pipet to add 12.7 mL of 85 percent lactic acid. (This can be done in two additions and you can use a 5 mL pipet for the 2.7 mL second addition if you like.)

   h Stir until dissolved (5 minutes).

   i Use the graduated cylinder to add 42 mL of 1 M acetic acid. You might also need a funnel for this step.

   j Stir until dissolved (5 to 10 minutes). At this point, the flask can be removed from

the fume hood.

k Check the pH and adjust the pH to 5.4.

l Use a graduated cylinder to dilute the buffer (with water) to a final volume of 1000 mL.

m Return to Erlenmeyer flask to mix.

n Store in a solvent clean bottle and label with the name, pH and date.

D.4.1.3.2. Dermal Biofluid Extraction of Crumb Rubber with Stir Bar Sorptive Extraction (SBSE) Analysis

SAFETY: Workers need to have WPC (EE-0103) approval for work in 70-258 at LBNL. All work is to be performed while wearing nitrile gloves, safety glasses and lab coat.

1. Summary

Artificial biofluids designed to simulate human sweat are used to extract composite samples of crumb rubber (CR). This will be a two-step process using a large polydimethylsiloxane (PDMS) stir bar in the "Sink" extraction with the CR present. The second step will be the Stir Bar Sorptive Extraction (SBSE) using a small PDMS stir bar for the extraction of just the supernatant, "SBSE" extraction.

Table D-1. Equipment and Supplies

Incubator (Forma Scientific)	HPLC Water (BDH 23595)
Micro Balance	Methanol
pH Meter	Acetonitrile
Stir plate (Gerstel, Twister 20)	Erlenmeyer flasks
Teflon spatula	Graduated cylinder
"Twister" large PDMS stir bars (Gerstel, 011555-001-00)	Glass pipets
"Twister" small PDMS stir bars (Gerstel, 011222-001-00)	Pipet aid
"Twister" Ethylene Glycol-Silicone (EG) stir bars (Gerstel, 016904-001-00)	Pasteur pipets, muffle baked
Thermal desorption tubes (Gerstel, 012518)	Metal forceps
Composite Crumb Field samples	Bench paper
Tracking sheets	Nitrile gloves
Volatile organic analysis (VOA) vials, 60 and 40 mL	Timer
Teflon-coated micro stir bar	Kimwipes™
2 mL autosampler vials	Labeling tape
Teflon lined screw caps for vials	Enviro-Genie Shaker, model SI-1200

2. Crumb Rubber Dermal Digestion Sink Stir Bar for Gas Chromatography Mass Spectrometry (GC-MS) Analysis

   a Condition large, 20 mm, 1 mm film PDMS stir bars (P/N 011555-001-00), “Sink” stir bars, under a 75 c.c. per minute helium flow at 300 °C for 2 hours. Cool to room temperature under helium flow and store in sealed glass thermal desorption tubes.

   b Solvent wash all vials, caps and glassware.

   c Bring composite sample to room temperature.

   d Mix the sample in the Enviro-Genie Shaker for 10 minutes.

   e Prepare tracking sheets and sample labels.

   f Turn on the Forma incubator and set to 37 °C.

   g Place the Twister 20 stir plate inside the incubator and plug it into the power strip.

   h Place the artificial sweat (Section D.4.1.3.1) into the incubator and bring to 37 °C (about 1 hour).

   i Label a 60 mL VOA vial for every sample to be digested.

   j Record the tare weight of the labeled vial on the tracking sheet.

   k Transfer 5 mL of composite crumb sample to the vial. (This was on average about 4 g of crumb.)

      i Use a Teflon spatula or metal spatula cleaned with methanol.

      ii Shake and roll the bottle of field crumb rubber to get a uniform sample.

   l Weigh the vial again. Record the final weight of the vial with crumb sample on the tracking sheet.

   m Add a Teflon micro stir bar to each vial.

   n Place a magnetic sleeve on the vial then carefully add the Sink stir bar to the vial so it catches on the magnet thus positioning it on the side of the vial.

   o Record the ID# of the stir bar on the tracking sheet.

   p Use a glass pipet to add 30 mL of warm artificial sweat to each sample. Seal tightly and begin stirring at 37 °C setting of 500 rpm for 120 minutes.

   q While digesting, prepare a 40 mL labeled VOA vial for the SBSE step (described below).

   r Remove the samples from the incubator after 120 minutes.

   s Clean the metal forceps with methanol.

   t Immediately remove the Sink stir bar using the clean metal forceps. Rinse the Sink stir bar with high performance liquid chromatography (HPLC) grade water

then pat dry with a Kimwipe™. Place the Sink stir bar back in its glass thermal desorption tube. Clean the forceps before harvesting the next Sink stir bar. Record the ID# in the tracking sheet.

u Sink stir bars were not stored but prepared for analysis the same day. Before analysis, 50 ng of a deuterium labeled polyaromatic hydrocarbon (d-PAH) internal standards (see Table D-3) was added to the surface of the stir bar. The stir bar was dried under a stream of helium for 2 minutes.

v Analyze the Sink stir bars on the TD-HES-GCMS using method HES SBSE SVOC SIM_Scan.m with a 50:1 split (see bullet 6 below and Section D.2.5).

3. Crumb Rubber Dermal SBSE Stir Bar for GC-MS Analysis

a Condition small, 10 mm, 1 mm film PDMS stir bars (P/N 011555-001-00), "SBSE" stir bars, under a 75 c.c. per minute helium flow at 300 °C for 1 hour. Cool to room temperature under helium flow and store in sealed glass thermal desorption tubes.

b Solvent wash all vials, caps and glassware.

c Using a clean glass pipet for each sample, transfer 30 mL of the supernatant from the digestion step to a clean labeled 40 mL vial using an 100 mesh metal screen to filter out crumb particles. Be careful not to include any crumb particles.

d Add 3 mL of methanol and record on tracking sheet.

e Add 50 µL of 1 ng per µL d-PAH internal standard (50 ng total, see Table D-3). Use a dedicated glass syringe.

f Carefully add a small (10 mm) SBSE stir bar.

g Immediately begin stirring at room temperature (1500 rpm) for 60 minutes.

h After 60 minutes, harvest the SBSE stir bar using clean metal forceps.

i Rinse the SBSE stir bar with HPLC grade water then pat dry with a Kimwipe™. Place the stir bar back in its glass thermal desorption tube. Clean the forceps before harvesting the next stir bar. Record the ID# in the tracking sheet.

j The SBSE stir bar was analyzed the same day. Before analysis, the stir bar was dried under a stream of helium for 2 minutes.

k Analyze the SBSE stir bars from the SBSE reaction on the TD-HES-GCMS using method HES SBSE SVOC SIM_Scan.m with a 10:1 split (see bullet 6 below and Section D.2.5.

4. Crumb Rubber Dermal Digestion for Liquid Chromatography Mass Spectrometry (LC-MS) Analysis

a Repeat the extraction for each composite sample with modifications for LC-MS analysis.

b Solvent wash all vials, caps and glassware.

c Mix and use the same composite sample as above.

d Prepare tracking sheets and sample labels.

e Turn on the Forma incubator and set to 37 °C.

f Place the Twister 20 stir plate inside the incubator and plug it into the power strip.

g Place the artificial sweat (see Section D.4.1.3.1) into the incubator and bring to 37 °C (about 1 hour.)

h Label a 60 mL VOA vial for every sample to be digested.

i Record the tare weight of the labeled vial on the tracking sheet.

j Transfer 5 mL of composite crumb sample to the vial. (This was on average about 4 g of crumb rubber).

i Use a Teflon spatula or metal spatula cleaned with methanol.

ii Shake and roll the bottle of field crumb rubber to get a uniform sample.

k Weigh the vial again. Record the final weight of the vial with crumb sample on the tracking sheet.

l Add a Teflon micro stir bar to each vial.

m Do not add any PDMS stir bar to this digestion.

n Use a glass pipet to add 30 mL of warm artificial sweat to each sample. Seal tightly and begin stirring at 37 °C setting 500 rpm for 120 minutes.

o While digesting, prepare a 40 mL labeled VOA vial for the SBSE step (described below).

p Remove the samples from the incubator after 120 minutes.

q Immediately transfer the supernatant to the SBSE step described below.

5. Crumb Rubber Dermal SBSE for LC-MS Analysis

a Condition ethylene glycol-silicone (EG) stir bars (P/N 011555-001-00) under a 75 c.c. per min helium flow at 240 ℃ for 2 hours. Cool to room temperature under helium flow and store in sealed glass thermal desorption tubes.

b Solvent wash all vials, caps and glassware.

c Using a clean glass pipet for each sample, transfer 30 mL of the supernatant from the digestion step to a clean labeled 40 mL vial using an 100 mesh metal screen to filter out crumb particles. Be careful not to include any crumb particles.

d Add 3 mL of methanol and record on tracking sheet.

e Carefully add an EG stir bar and record on the tracking sheet.

f Immediately begin stirring at room temperature (1500 rpm) for 60 minutes.

g While stirring label a 2 mL autosampler vial and add 1 mL of acetonitrile to each vial.

h After 60 minutes harvest the stir bar using clean metal forceps.

i Rinse the stir bar with HPLC grade water then pat dry with a Kimwipe™. Place the stir bar in the labeled 2 mL auto-sampler vial containing acetonitrile.

j Clean the forceps before harvesting the next stir bar. Record the ID# in the tracking sheet.

k After 18 hours, remove the stir bar from the 2 mL autosampler vial and save the acetonitrile extract for high resolution accurate mass liquid chromatography mass spectrometry (HRAM LC-MS) analysis (see Section D.2.6). Store the extracts in the freezer until analysis.

l Before HRAM LC-MS analysis, d4-bis(2-ethylhexyl)phthalate (final concentration of 0.1 ng per µL internal standard) was added to the extracts.

6. SBSE Analysis for Semi-Volatile Organic Compounds (SVOCs) by Thermal Desorption Gas Chromatography Mass Spectrometry (GC-MS)

Polydimethylsiloxane (PMDS) coated stir bars were analyzed using the following thermal desorption injection system: a ThermoDesorption Autosampler (Model TDSA2; Gerstel), a thermal desorption oven (Model TDS3, Gerstel) and a cryogenically cooled injection system (Model CIS4; Gerstel). The cooled injection system contained a deactivated glass bead liner (P/N 011714-005-00; Gerstel). The samples were desorbed at 60 c.c. per minute (splitless) using the following temperature profile: 25 °C followed by a 60 °C per minute ramp to 280 °C with a 5-minute hold time followed by a 1-minute hold at 300 °C and a transfer line temperature of 320 °C. The cooled inlet was held at -120 °C and then heated after 0.1 minutes to 300 °C at a rate of 12 °C per second, followed by a 3-minute hold time.

The GC (Series 7890 Plus; Agilent Technologies) was operated in the solvent vent mode with a 10:1 split injection for small (10 mm) PDMS stir bars and a 50:1 injection for large (20 mm) PDMS stir bars. The oven was held at 30 °C for 2 minutes followed by a 25 °C per minute ramp to 150 °C held for 2 minutes, then ramped slowly at 3 °C per minute to 200 °C, ramped at 8 °C per minute to 250 °C then increased at 3 °C per minute to 310 °C with an 8 minutes hold time. Compounds were resolved on a 30 meter by 0.25-mm diameter DB-UI8270D column (Agilent, P/N 122-9732) with 2.5 micron film thickness. The helium flow through the column was held constant at 1.0 mL per minute. The resolved analytes were detected on a high efficiency source MS detector (5977B; Agilent Technologies) using simultaneous full scan and SIM (selected ion monitoring) mode. The MS temperature settings were 300 °C, 300 °C, and 150 °C for the transfer line, MS source, and MS quad, respectively.

D.4.1.3.3. Result of Dermal Bioaccessibility Measurements of Organic Chemicals in Artificial Sweat Extracts

Table D-32 summarizes the 35 individual-field dermal bioaccessible concentrations of organic chemicals in crumb rubber samples ($C_{der\text{-}crumb\ rubber\text{-}field}$, nanograms per gram of crumb rubber) extracted in artificial sweat using SBSE methods. The mean values represent the mean of the 35 individual-field average concentrations of the organic chemicals ($C_{der\text{-}crumb\ rubber}$, nanograms per gram of crumb rubber).

Table D-1. Individual-Field Dermal Bioaccessilbe Concentrations of Organic Chemicals in Crumb Rubber Samples ($C_{der\text{-}crumb\ rubber\text{-}field}$, nanograms per gram of crumb rubber) Collected from the 35 Fields During the State-Wide Study

Chemical	CASRN	Detection[a]	$C_{der\text{-}crumb\ rubber\text{-}field}$					
			Minimum	Mean ($C_{der\text{-}crumb\ rubber}$)	Standard Deviation	Median	95th Percentile	Maximum
Acenaphthylene	208-96-8	10	0	0.0056	0.0096	0	0.023	0.035
Aniline	62-53-3	4	0	0.18	0.56	0	1.4	2.7
Anthracene	120-12-7	20	0	0.062	0.081	0.042	0.15	0.41
Anthracene, 2-methyl-	613-12-7	35	0.022	0.089	0.073	0.059	0.21	0.35
Anthracene, 9,10-diphenyl-	1499-10-1	5	0	0.012	0.034	0	0.074	0.17
Anthracene, 9-phenyl	602-55-1	9	0	0.03	0.069	0	0.17	0.3
2-Azacyclotridecanone	947-04-6	2	0	0.24	1.1	0	0.75	6
Benz[a]anthracene	56-55-3	31	0	0.25	0.28	0.13	0.69	1.3
Benzene, n-butyl-	104-51-8	1	0	0.00037	0.0022	0	0	0.013
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	793-24-8	32	0	17	27	6.9	51	140
1,4-Benzenediamine, N,N'-diphenyl-	74-31-7	9	0	3.5	15	0	13	86
Benzo[a]pyrene	50-32-8	32	0	0.19	0.18	0.12	0.48	0.76
Benzo[b]fluoranthene	205-99-2	34	0	0.35	0.31	0.28	0.87	1.4
7H-Benzo[c]fluorene	205-12-9	26	0	0.03	0.038	0.016	0.098	0.16
Benzo[e]pyrene	192-97-2	35	0.053	0.55	0.4	0.52	1.3	1.5
Benzo[g,h,i]perylene	191-24-2	35	0.051	0.42	0.27	0.38	0.92	1.1
Benzo[k]fluoranthene	207-08-9	29	0	0.15	0.16	0.092	0.5	0.62
Benzothiazole	95-16-9	35	46	200	100	170	390	450
Benzothiazole, 2-phenyl-	883-93-2	35	1.4	4.8	3.8	3.4	13	19
1,3-Benzothiazole-2-thiol	149-30-4	1	0	1.3	7.8	0	0	46
Benzothiazolone	934-34-9	35	120	560	180	630	780	790
Benzyl butyl phthalate	85-68-7	35	0.15	2.3	1.6	1.9	5.6	6.5
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	52829-07-9	1	0	0.52	3.1	0	0	18
Bis(2-Ethylhexyl)adipate	103-23-1	35	0.18	2.5	4	1.3	5.7	23
Chrysene	218-01-9	35	0.17	1.6	1	1.6	3.2	3.6

Chemical	CASRN	Detection[a]	$C_{der\text{-}crumb\ rubber\text{-}field}$					
			Minimum	Mean ($C_{der\text{-}crumb\ rubber}$)	Standard Deviation	Median	95th Percentile	Maximum
Coronene	191-07-1	1	0	0.13	0.74	0	0	4.4
Cyclohexyl isothiocyanate	1122-82-3	1	0	0.0084	0.05	0	0	0.29
Cyclopenta[cd]pyrene	27208-37-3	35	0.029	0.28	0.17	0.27	0.54	0.65
Dibenz[a,h]anthracene	53-70-3	14	0	0.091	0.17	0	0.44	0.69
Dibenzothiophene	132-65-0	20	0	0.054	0.067	0.046	0.15	0.32
N,N-Dicyclohexylmethylamine	7560-83-0	28	0	0.084	0.17	0.039	0.35	0.88
N,N'-Dicyclohexylurea	2387-23-7	18	0	25	66	4.1	110	360
Diethyl Phthalate	84-66-2	5	0	0.41	1.2	0	2.3	6.2
Diisobutyl Phthalate	84-69-5	28	0	0.35	0.58	0.23	0.91	3.4
Diisooctylphthalate	27554-26-3	35	0.098	11	7.9	9.8	28	33
Dimethyl phthalate	131-11-3	3	0	0.25	0.83	0	2.7	3.2
Di-n-octyl phthalate	117-84-0	33	0	2.4	3.4	1.4	8.3	16
1,3-Diphenylguanidine	102-06-7	2	0	0.72	3.2	0	2.3	18
Diphenylurea	102-07-8	32	0	61	68	34	210	220
2,5-di-tert-Butyl-1,4-benzoquinone	2460-77-7	4	0	0.0021	0.0063	0	0.017	0.028
3,5-Di-tert-butyl-4-hydroxybenzaldehyde	1620-98-0	25	0	11	27	2.5	29	160
Fluoranthene	206-44-0	35	0.31	1.9	1.5	1.3	4.9	5.2
Fluorene	86-73-7	6	0	0.008	0.025	0	0.034	0.14
Hexanoic Acid, 2-ethyl	149-57-5	1	0	0.0092	0.054	0	0	0.32
1-Hydroxypyrene	5315-79-7	1	0	0.53	3.1	0	0	19
Indeno[1,2,3-cd]pyrene	193-39-5	28	0	0.18	0.15	0.16	0.42	0.66
Limonene	138-86-3	35	0.077	0.34	0.32	0.24	0.81	1.8
Linoleic acid	60-33-3	1	0	1.1	6.3	0	0	37
2-(Methylthio)benzothiazole	615-22-5	9	0	7.3	16	0	34	73
Methyl stearate	112-61-8	28	0	1.1	1.5	0.58	2.8	8.1
Naphthalene	91-20-3	2	0	0.012	0.048	0	0.059	0.21
Naphthalene, 1,2-dimethyl-	573-98-8	1	0	0.00083	0.0049	0	0	0.029
Naphthalene, 1,6-dimethyl-	575-43-9	6	0	0.0087	0.021	0	0.063	0.065
Naphthalene, 1-methyl-	90-12-0	1	0	0.0019	0.011	0	0	0.065
Naphthalene, 2-(bromomethyl)-	939-26-4	33	0	0.34	0.28	0.21	0.82	1.1
Naphthalene, 2,3-dimethyl-	581-40-8	33	0	0.1	0.09	0.061	0.29	0.41
Naphthalene, 2-methyl	91-57-6	1	0	0.0018	0.011	0	0	0.063
1-Octadecene	112-88-9	27	0	0.59	1.6	0.16	1	9.7

Chemical	CASRN	Detection[a]	$C_{der\text{-}crumb\ rubber\text{-}field}$					
			Minimum	Mean ($C_{der\text{-}crumb\ rubber}$)	Standard Deviation	Median	95th Percentile	Maximum
Oleic acid	112-80-1	3	0	5.5	22	0	30	110
Phenanthrene	85-01-8	29	0	0.4	0.55	0.2	1.3	2.5
Phenanthrene, 1-methyl	832-69-9	35	0.04	0.21	0.16	0.17	0.51	0.65
Phenanthrene, 2-methyl-	2531-84-2	34	0	0.26	0.24	0.2	0.72	0.96
Phenanthrene, 3-methyl	832-71-3	3	0	0.093	0.35	0	0.67	1.9
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	2772-45-4	35	0.11	1.4	1.1	0.98	3.4	5.2
Phenol, 4-(1-phenylethyl)-	1988-89-2	35	0.13	1.5	1.7	0.84	5.5	7.3
Phenoxazine	135-67-1	2	0	4.3	19	0	14	100
N-Phenylbenzamide	93-98-1	8	0	0.58	1.2	0	2.8	4.2
Phthalimide	85-41-6	26	0	3.8	8.8	0.052	22	38
Pyrene	129-00-0	35	0.94	5.1	3.3	4.5	12	14
Pyridine, 2-(4-methylphenyl)-	4467-06-5	14	0	0.19	0.36	0	0.8	1.6
Ricinoleic acid	141-22-0	3	0	3.8	14	0	33	67
4-tert-Octylphenol	140-66-9	34	0	4.6	9.7	1.2	22	43
TRIETHYLENE GLYCOL MONOBUTYL ETHER	143-22-6	7	0	0.98	2.4	0	6.2	11
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	32	0	0.13	0.16	0.047	0.39	0.63
Dicyclohexylamine	#N/A	30	0	48	79	37	89	480

[a] Detection value is the number of fields with concentration in extracts above the method of detection for an organic chemical.
Values are rounded to two significant figures.

D.4.1.4. Oral Bioaccessibility Extraction of Organic Chemicals in Crumb Rubber Using a Stir Bar Sorptive Extraction System

D.4.1.4.1. Oral Biofluids Preparation

SAFETY: Workers need to have WPC (EE-0103) approval for work in 70-258 at LBNL. All work is to be performed while wearing nitrile gloves, safety glasses and lab coat.

1. Summary

Artificial biofluids designed to simulate the human oral digestive pathway are used in the extract process of crumb rubber samples. The oral biofluids digestion of crumb rubber (see Section D.4.1.4.2) will use the fasted and fed state of the oral pathway including artificial saliva, gastric and intestinal fluids.

Table D-1. Equipment and Supplies

Micro Balance	Glass pipets
pH Meter	Pipet aid

Stir plate (Gerstel, Twister 20)	Amylase (Sigma A3176)
Metal spatula	Mucin (Alpha Aesar J63859)
Weighing paper	BioRelevant® powders (FaSSGF, FeSSIF-v2, FaSSIF-v2)
HPLC Water (BDH 23595)	Ultra-heat treated (UHT) milk, reduced fat
1M hydrochloric acid HCl	Bench paper
Sodium hydroxide, NaOH, pellets or beads	Nitrile gloves
Stir bar, acid washed	Timer
Erlenmeyer flasks	Kimwipes™
Graduated cylinder	Labeling tape

2. Preparation of Stock Buffer Solutions

a 10x Artificial Saliva Buffer (10x AS)

i Add about 400 mL of high performance liquid chromatography (HPLC) grade water to a 500 mL Erlenmeyer containing a stir bar.

ii While stirring, add the following salts:

- 2.98 g NaCl
- 8.96 g KCl
- 8.88 g NaH_2PO_4 x $2H_2O$
- 5.70 g Na_2SO_4
- 2.00 g Urea
- 2.00 g KSCN

iii Stir for 1 hour.

iv Adjust the pH to 6.8 with NaOH beads. (The starting pH should be about 4.0.)

v Use a graduated cylinder to dilute the buffer to a final volume of 500 mL.

vi Store in a bottle and label with the name, pH and date.

b Fasted State Simulated Gastric Fluid Buffer (1x and 2x FaSSGF)

i Transfer about 400 mL of HPLC grade water to a 500 mL Erlenmeyer flask containing a stir bar.

ii Add 2.0 g NaCl.

iii Stir until dissolved, about 1 hour.

iv Adjust the pH to 1.6 with 1 M HCl.

v Use a 1 L graduated cylinder to dilute the solution to 1 L.

vi Re-check final pH and adjust if necessary.

vii Transfer to a 1 L bottle and label with name, pH and date.

viii Repeat the process to make a second buffer but dilute only to 250 mL final volume of HPLC water to create a 2x stock buffer of FaSSGF. Label and store in a sealed bottle.

c *4x Fasted State Simulated Intestinal Fluid Buffer (4x FaSSIF-v2)*

i Transfer 200 mL of HPLC grade water to a 250 mL Erlenmeyer flask.

ii While stirring add:

- 1.44 g NaOH beads
- 2.22 g Maleic acid
- 4.00 g NaCl

iii Stir until dissolved, about 1 hour.

iv Adjust the pH to 6.5 with NaOH beads. The stating pH should be about 6.1.

v Use a graduated cylinder to dilute the buffer to 250 mL.

vi Store in a bottle and label with name, pH and date.

d *2x Fed State Simulated Intestinal Fluid Buffer (2x FeSSIF-v2)*

i Transfer 400 mL of HPLC grade water to a 500 mL Erlenmeyer flask.

ii While stirring add:

- 3.27 g NaOH beads
- 6.39 g Maleic acid
- 7.35 g NaCl

iii Stir until dissolved, about 1 hour.

iv Adjust the pH to 5.8 with NaOH beads.

v Use a graduated cylinder to dilute the buffer to 500 mL.

vi Store in a bottle and label with name, pH and date.

3. Preparation of Working Simulated Biofluids

a *Prepare 100 mL of Artificial Saliva (AS) biofluid*

i Dispense 10 mL of 10x AS buffer to a flask using a serological pipet.

ii Add about 50 mL HPLC water and a stir bar.

- Add 333 mg $NaHCO_3$
- Add 250 mg Amylase (stored in the refrigerator)
- Add 49 mg Mucin (stored in the refrigerator)

iii Stir until dissolved about 1 hour.

iv Use a graduated cylinder and dilute to 100 mL with HPLC water.

v Store in Erlenmeyer flask at room temperature.

vi The solution is only good for 2 days.

b *Prepare 500 mL of Gastric biofluid in the fasted state using FaSSGF powder from BioRelevant (Stored in the refrigerator).*

i Dissolve 29.8 mg of BioRelevant power in about 400 mL of 1x FaSSGF buffer.

ii Stir until dissolved about 15 minutes.

iii Dilute to 500 mL in a graduated cylinder with the 1x FaSSGF buffer.

iv Label with name and date. The solution is only good for 2 days.

c *Prepare 500 mL of Fed State Gastric biofluid (FeSSGF)*

i Use a graduated cylinder to transfer 250 mL of 2x FaSSGF stock buffer to an Erlenmeyer flask.

ii Add 250 mL of ultra-heat treated (UHT) milk, reduced fat.

iii Stir to mix, label and seal. Prepare immediately before use.

d *Prepare 500 mL of Fasted State Intestinal fluid using FaSSIF-v2 powder from BioRelevant (Stored in the refrigerator).*

i Use a graduated cylinder to transfer 125 mL of 4x FaSSIF Buffer to a 500 mL Erlenmeyer flask.

ii Add about 300 mL HPLC water and a stir bar.

iii Add 0.895 g of FaSSIF-v2 powder from BioRelevant.

iv Stir until dissolved.

v Use a graduated cylinder to bring the final volume to 500 mL with HPLC water.

vi Store in an amber bottle or the flask until use.

vii Wait 1 hour before using.

e *Prepare 500 mL of Fed State Intestinal fluid using FeSSIF-v2 powder from BioRelevant (found in the refrigerator)*

i Use a graduated cylinder to transfer 250 mL of 2x FeSSIF Buffer to a 500 mL Erlenmeyer flask.

ii Add about 200 mL HPLC water and a stir bar.

iii Add 4.9 g of FeSSIF-v2 powder from BioRelevant.

iv Stir a couple minutes, then let stand 10 minutes to soften crystals, stir until dissolved.

v Let stand 1 hour before use.

f *Place these working buffers in the incubator to bring them to 37 °C before use.*

D.4.1.4.2. Oral Biofluids Extraction of Crumb Rubber with SBSE Analysis

SAFETY: Workers need to have WPC (EE-0103) approval for work in 70-258 at LBNL. All work is to be performed while wearing nitrile gloves, safety glasses and lab coat.

1. Summary

Artificial gastrointestinal (GI) biofluids designed to simulate the human oral digestive pathway are used to extract samples of crumb rubber. This procedure will use the fasted and fed states of the oral pathway including artificial saliva, gastric and intestinal fluids. The digestion will take place at 37 °C with rocking.

Table D-1. Equipment and Supplies

Incubator (Forma Scientific)	Sodium hydroxide, NaOH, pellets or beads
Micro Balance	2 mL autosampler vials
pH Meter	Stir bar, micro teflon
stir plate (Gerstel, Twister 20)	Erlenmeyer flasks
Composite Crumb rubber field samples	Graduated cylinder
Teflon spatula	Glass pipets
Weighing paper	Pipet aid
“Twister” large stir bars (Gerstel, 011555-001-00)	Pasteur pipets, muffle baked
“Twister” small stir bars (Gerstel, 011222-001-00)	Amylase (Sigma A3176)

"Twister" Ethylene Glycol-Silicone (EG) stir bars (Gerstel, 016904-001-00)	Mucin (Alpha Aesar J63859)
Thermal desorption tubes (Gerstel, 012518)	BioRelevant powders (FaSSGF, FeSSIF-v2 FaSSIF-v2)
250 mL glass jars	Metal forceps
Teflon lined screw caps for jars	Bench paper
HPLC Water (BDH 23595)	Nitrile gloves
Methanol	Timer
Acetonitrile	Kimwipe™
Volatile organic analysis (VOA) vials, 60 and 40 mL	Labeling tape
1M hydrochloric acid HCl	Enviro-Genie Shaker, model SI-1200

2. Crumb Rubber Oral Digestion for Gas Chromatography Mass Spectrometry (GC-MS) and Liquid Chromatography Mass Spectrometry (LC-MS)

   a Condition large, 20 mm 1 mm film polydimethylsiloxane (PDMS) stir bars (P/N 011555-001-00), "Sink" stir bars, under a 75 c.c. per minute helium flow at 300 °C for 2 hours. Cool to room temperature under helium flow and store in sealed glass thermal desorption tubes.

   b Solvent wash all vials, caps and glassware.

   c Bring composite sample to room temperature.

   d Mix the sample in the Enviro-Genie Shaker for 10 minutes.

   e Prepare tracking sheets and sample labels.

   f Turn on the Forma incubator and set to 37 °C.

   g Place the Twister 20 stir plate inside the incubator and plug it into the power strip.

   h Place the working oral biofluids (see Section D.4.1.4.1) into the incubator and bring to 37 °C (about 1 hour).

   i Label two 60 mL VOA vial for every sample to be digested. One will contain the Sink stir bars for the GC-MS analysis. The other vial will NOT use Sink stir bars and will be used for LC-MS analysis.

   j Record the tare weight of each labeled vial on the tracking sheet.

   k Transfer 2.5 mL of composite crumb sample to each vial. (This was on average about 1.5 g of crumb rubber.)

      i Use a Teflon spatula or metal spatula cleaned with methanol.

      ii Shake and roll the bottle of field crumb rubber to get a uniform sample.

   l Weigh the vials again. Record the final weight of each vial with crumb sample on

the tracking sheet.

m Add a Teflon micro stir bar to each vial.

n Place a magnetic sleeve on the vial of the GC-MS sample then carefully add the Sink stir bar to the vial so it catches on the magnet thus positioning it on the side of the vial. The LC-MS vial does not use a Sink stir bar, only the Teflon micro stir bar.

o Record the ID# of the Sink stir bar on the tracking sheet.

p Use a glass pipet to add 5 mL of warm artificial saliva biofluid (see Section D.4.1.4.1) to each sample. Swirl and seal vial with aluminum foil and incubate at 37 °C for 5 minutes.

q Add 40 mL warm gastric fluid (see Section D.4.1.4.1) to each vial, cap and place on stir plate in incubator. Stir for 1500 rpm for 120 minutes.

r Remove the samples from the incubator after 120 minutes.

s Clean the metal forceps with methanol.

t Immediately remove the Sink stir bar using the clean metal forceps. Rinse the Sink stir bar with HPLC grade water then pat dry with a Kimwipe™. Place the Sink stir bar back in its glass thermal desorption tube. Clean the forceps before harvesting the next stir bar. Record the ID# in the tracking sheet.

u Use an 80 mesh screen cap to decant the spent gastric fluid into a 120 mL clean jar while retaining all the crumb in the 60 mL vial. Repeat for the LC-MS vial and store the reserved gastric fluid in another, separate 120 mL jar.

v Add a fresh Sink stir bar to the magnetic sleeve on the side of the GC-MS vial.

w Add 40 mL of warm working Intestinal Fluid (see SOP in Section D.4.1.4.1) to each vial and stir for 18 hours at 37 °C, 1500 rpm.

x Clean the metal forceps with methanol.

y Immediately remove the Sink stir bar using the clean metal forceps. Rinse the stir bar with HPLC grade water then pat dry with a Kimwipe™. Place the second Sink stir bar in the same glass thermal desorption tube containing the gastric Sink stir bar. Clean the forceps before harvesting the next stir bar. Record the ID# in the tracking sheet.

z Use an 80 mesh screen cap to decant the spent intestinal fluid into the 120 mL jar containing the gastric fluid while retaining all the crumb in the 60 mL vial. Save this for the SBSE reaction described below. Repeat for the LC-MS vial.

aa Sink Stir bars were not stored but prepared for analysis the same day. Before analysis, 50 ng of a d-PAH IS (see Table D-3) was added to the surface of the stir bar. The stir bar was dried under a stream of helium for 2 minutes.

bb Analyze the stir bars on the TD-HES-GCMS using method HES SBSE SVOC SIM_Scan.m with a 50:1 split (see Section D.2.5).

3. Crumb Rubber Oral SBSE for GC-MS

   a Condition small, 10 mm, 1 mm film PDMS stir bars (P/N 011555-001-00), “SBSE” stir bars, under a 75 c.c. per minute helium flow at 300 °C for 1 hour. Cool to room temperature under helium flow and store in sealed glass thermal desorption tubes.

   b Solvent wash all vials, caps and glassware.

   c Using a clean glass pipet for each sample, transfer 30 mL of the combined gastric/intestinal fluid supernatant from the GC-MS digestion step to a clean labeled 40 mL vial using an 100 mesh metal screen to filter out any remaining crumb particles. Be careful not to include any crumb particles.

   d Add 3 mL of methanol and record on tracking sheet.

   e Add 50 µL of 1 ng per µL d-PAH IS (50 ng total). Use a dedicated glass syringe.

   f Carefully add a small (10 mm) PDMS stir bar.

   g Immediately begin stirring at room temperature (1500 rpm) for 60 minutes.

   h After 60 minutes, harvest the PDMS stir bar using clean metal forceps.

   i Rinse the stir bar with HPLC grade water then pat dry with a Kimwipe™. Place the stir bar back in its glass thermal desorption tube. Clean the forceps before harvesting the next stir bar. Record the ID# in the tracking sheet.

   j The SBSE stir bar was analyzed the same day. Before analysis the stir bar was dried under a stream of helium for 2 minutes.

   k Analyze the PDMS stir bars from the SBSE on the TD-HES-GCMS using method HES SBSE SVOC SIM_Scan.m with a 10:1 split (see bullet 5 below and in Section D.2.5).

4. Crumb Rubber Oral SBSE for LC-MS

   a Condition ethylene glycol-silicone (EG) stir bars (P/N 011555-001-00) under a 75 c.c. per minute helium flow at 240 °C for 2 hours. Cool to room temperature under helium flow and store in sealed glass thermal desorption tubes.

   b Solvent wash all vials, caps and glassware.

   c Using a clean glass pipet for each sample, transfer 30 mL of the combined gastric/intestinal fluid supernatant from the LC-MS digestion step to a clean labeled 40 mL vial using an 100 mesh metal screen to filter out crumb particles. Be careful not to include any crumb particles.

   d Add 3 mL of methanol and record on tracking sheet.

   e Carefully add an EG stir bar and record on the tracking sheet.

f Immediately begin stirring at room temperature (1500 rpm) for 60 minutes.

g While stirring, label a 2 mL autosampler vial and add 1 mL of acetonitrile to each vial.

h After 60 min, harvest the EG stir bar using clean metal forceps.

i Rinse the EG stir bar with HPLC grade water then pat dry with a Kimwipe™. Place the stir bar in the labeled 2 mL autosampler vial containing acetonitrile.

j Clean the forceps before harvesting the next EG stir bar. Record the ID# in the tracking sheet.

k After 18 hours, remove the EG stir bar from the 2 mL autosampler vial and save the acetonitrile extract for high resolution accurate mass liquid chromatography mass spectrometry (HRAM LC-MS) analysis (see Section D.2.6). Store the extracts in the freezer until analysis.

l Before HRAM LC-MS analysis, add d4-bis(2-ethylhexyl)phthalate (final concentration of 0.1 ng per µL, internal standard) to the extracts.

5. SBSE Analysis for Semi-Volatile Organic Compounds (SVOCs) by Thermal Desorption Gas Chromatography Mass Spectrometry (GC-MS)

Polydimethylsiloxane (PDMS) coated stir bars were analyzed using the following thermal desorption injection system: a ThermoDesorption Autosampler (Model TDSA2; Gerstel), a thermal desorption oven (Model TDS3, Gerstel) and a cryogenically cooled injection system (Model CIS4; Gerstel). The cooled injection system contained a deactivated glass bead liner (P/N 011714-005-00; Gerstel). The samples were desorbed at 60 c.c. per minute (splitless) using the following temperature profile: 25 °C followed by a 60 °C per minute ramp to 280 °C with a 5.0 minute hold time followed by a 1.0 minute hold at 300 °C and a transfer line temperature of 320 °C. The cooled inlet was held at -120 °C and then heated after 0.1 minute to 300 °C at a rate of 12 °C per second, followed by a 3 minute hold time.

The GC (Series 7890 Plus; Agilent Technologies) was operated in the solvent vent mode with a 10:1 split injection for small (10mm) PDMS stir bars and a 50:1 injection for large (20mm) PDMS stir bars. The oven was held at 30 °C for 2 minutes followed by a 25 °C per minute ramp to 150 °C held for 2 minutes, then ramped slowly at 3 °C per minute to 200 °C, ramped at 8 °C per minute to 250 °C then increased at 3 °C per minute to 310 °C with an 8-minute hold time. Compounds were resolved on a 30 m by 0.25-mm diameter DB-UI8270D column (Agilent, P/N 122-9732) with 2.5 micron film thickness. The helium flow through the column was held constant at 1.0 mL per minute. The resolved analytes were detected on a high efficiency source MS detector (5977B; Agilent Technologies) using simultaneous full scan and SIM (selected ion monitoring) mode (see Section D.2.5). The MS temperature settings were 300 °C, 300 °C, and 150 °C for the transfer line, MS source, and MS quad, respectively.

D.4.1.4.3. Variations in Chemical Composition of Crumb Rubber

Crumb rubber particles, of a wide range of particle sizes and installed as infill on synthetic fields, were produced from a wide variety of automobile waste tires (different tire types, models, brands, production years, age in traffic). To assess variation in chemical composition of this heterogenous infill field material, OEHHA calculated percent variances in the concentration of each detected chemical in gastrointestinal (GI) biofluid extracts of field crumb rubber samples. This section focuses the analyses of variance on concentrations of organic chemicals among the field samples. We used the amount of organic chemicals obtained in GI bioaccessibility measurements of crumb rubber to illustrate the variation in chemical composition: percent variance within a composite sample (Table D-35) and among individual samples of a field (Table D-36), as well as the relative difference between two composite samples (one from the high impact area of the field, HI, and one from the rest of the field, ROF) for each of the individual fields (Table D-37). For a chemical being not detected (or at concentrations below the method of detections) in a sample, this may be due to age of a field, local climate of a field, environment of a field, and/or heterogeneity within a sample or a field. We, therefore, only included detected chemical concentrations in the analyses of composition variances in this section.

Within-Sample Variation. The Study detected 40 organic chemicals in the GI bioaccessibility measurements of three repeated samples prepared from a single randomly selected composite crumb rubber sample of a synthetic turf field. Table D-35 summarizes the values of within-sample percent variance in GI bioaccessible concentrations of these chemicals. The percent variance describes the absolute percent difference between the chemical concentrations detected in a crumb rubber aliquot divided by the mean concentration across all the aliquots (excluding non-detected samples). For a chemical, a small percent variance value indicates that the chemical concentration in the aliquot is similar to the mean chemical concentration. A percent variance of 100 percent indicates that an aliquot might contain a concentration twice or one-half of the mean concentration for a chemical, whereas a zero percent indicating the concentration of a chemical in the aliquot equals to the mean concentration of all the aliquots analyzed.

As shown in Table D-35, the minimum percent variances for all detected organic chemicals were well below 100 percent (1 to 83 percent). Similarly, the mean percent variances and maximum variances were of all the detected chemicals below 100 percent, except for phthalimide. Phthalimide had the highest mean percent variance of 83 percent and maximum percent variance of 199 percent (an aliquot containing nearly 3-fold of the mean phthalimide concentration). This chemical is neither a non-cancer hazard driver, nor a carcinogen. OEHHA determined that the observed within-sample variation of phthalimide had minimal impact on the risk assessment results.

The within-sample variance data suggested a low variation in chemical composition within this single composite crumb rubber sample. Assuming a similar within-sample

variance presence in the composite samples, OEHHA believed that it was appropriate to use chemical concentrations obtained from composite samples to evaluate the exposure to chemicals at a field, despite the intrinsic heterogeneous nature of the infill material (described above).

Table D-1. Within-Sample Percent Variance[a] (Percent) for Gastrointestinal Bioaccessibility Analysis of a Randomly Selected Composite Field Crumb Rubber Sample[b]

Chemical	CASRN	Detection[c]	Within-Sample Percent Variance		
			Minimum	Mean	Maximum
Acenaphthylene	208-96-8	6	2%	5%	7%
Anthracene	120-12-7	4	29%	32%	36%
Anthracene, 2-methyl-	613-12-7	6	0%	7%	15%
Anthracene, 9-phenyl	602-55-1	5	23%	45%	76%
Benzene, n-butyl-	104-51-8	3	1%	2%	3%
Benz[a]anthracene	56-55-3	3	1%	2%	3%
Benzo[a]pyrene	50-32-8	3	1%	2%	3%
Benzo[b]fluoranthene	205-99-2	6	1%	33%	75%
Benzo[e]pyrene	192-97-2	6	7%	26%	57%
Benzo[k]fluoranthene	207-08-9	4	32%	51%	69%
Benzothiazole	95-16-9	6	1%	4%	9%
Benzothiazole, 2-phenyl-	883-93-2	6	2%	6%	13%
Benzyl butyl phthalate	85-68-7	5	15%	36%	56%
Bis(2-Ethylhexyl)adipate	103-23-1	3	7%	42%	63%
Chrysene	218-01-9	6	4%	19%	42%
Cyclohexyl isothiocyanate	1122-82-3	6	1%	22%	44%
Cyclopenta[cd]pyrene	27208-37-3	6	8%	29%	74%
Dibenzothiophene	132-65-0	4	30%	39%	48%
Diisobutyl Phthalate	84-69-5	4	20%	34%	68%
Diisooctylphthalate	27554-26-3	3	1%	2%	3%
Dimethyl phthalate	131-11-3	4	32%	34%	37%
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	5	2%	24%	58%
Fluoranthene	206-44-0	6	1%	8%	15%
Fluorene	86-73-7	3	1%	2%	3%
Limonene	138-86-3	3	1%	2%	3%
Naphthalene, 1-methyl-	90-12-0	3	1%	2%	3%
Naphthalene, 1,2-dimethyl-	573-98-8	5	24%	32%	41%
Naphthalene, 1,6-dimethyl-	575-43-9	5	2%	6%	14%
Naphthalene, 2-(bromomethyl)-	939-26-4	3	1%	2%	3%
Naphthalene, 2,3-dimethyl-	581-40-8	3	1%	2%	3%
4-tert-Octylphenol	140-66-9	6	3%	17%	47%
Phenanthrene	85-01-8	6	1%	4%	7%

Chemical	CASRN	Detection[c]	Within-Sample Percent Variance		
			Minimum	Mean	Maximum
Phenanthrene, 1-methyl	832-69-9	6	1%	16%	31%
Phenanthrene, 2-methyl-	2531-84-2	6	4%	14%	33%
Phenanthrene, 3-methyl	832-71-3	6	8%	33%	51%
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	2772-45-4	6	5%	20%	39%
Phenol, 4-(1-phenylethyl)-	1988-89-2	6	4%	21%	40%
Phthalimide	85-41-6	5	8%	83%	199%
Pyrene	129-00-0	6	1%	11%	22%
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	6	0%	1%	3%

[a] Percent Variance of a chemical = absolute value (concentration of a chemical in an aliquot – mean concentration of a chemical in all aliquots) ÷ mean detected concentration of a chemical in all aliquots. Aliquots with concentrations of a chemical below its method of detection (non-detected aliquots) were excluded in the variance and mean concentration calculations.
[b] For a randomly selected composite crumb rubber sample, three replicates of crumb rubber samples were prepared and extracted following the gastrointestinal bioaccessibility analysis protocol (three extracts, Section D.4.1.4). Two aliquots from each extract were analyzed using gas chromatography mass spectrometry (GC-MS).
[c] Detection: number of aliquots with detected concentrations above its method detection limit of a chemical (total of six aliquots from the single sample analyzed by GC-MS)

Within-Field Variation. The Study detected 55 organic chemicals in 10 individual crumb rubber samples collected from a randomly selected synthetic turf field. Table D-36 shows the values of within-field percent variance in GI bioaccessible concentrations of these organic chemicals. A percent variance of 100 percent indicates that an individual sample might contain twice or one-half of the mean concentration of a chemical, whereas a zero percent indicating the concentration of a chemical in the sample equals the mean concentration of all the samples in the selected field.

As shown in Table D-36, the minimum percent variances were below 100 percent (0 to 68 percent) for all chemicals. Ten chemicals had mean percent variances above 100 percent (109 to 160 percent) and 28 chemicals (21 general chemicals, 7 DARTs, 1 carcinogen among the 7 DARTs) had maximum percent variances above 100 percent (106 to 799 percent). The highest maximum percent variance of 799 percent (nearly 9 folds of the mean concentration) was noted in naphthalene, 2-methyl.

The sum of chronic hazard quotients for ingestion exposure to the 21 general chemicals (Chronic HQ_{ing}) were 0.017 for 0<2 years old spectators (the receptor category and age group with the highest Chronic HQ_{ing}).

The sum of one-day hazard quotients for the group of seven DARTs (One-Day $HQ_{ing\text{-}DARTs}$) was 0.002 for 0<2 years old spectators (the receptor category and age group with the highest One-Day $HQ_{ing\text{-}DARTs}$ for these 7 DARTs, for a single field).

The maximum life-time cancer risk for the carcinogen, cyclopenta[cd]pyrene, was 1.2E-06 at a field, for the spectators (the receptor category with the highest cancer risk via ingestion). Cyclopenta[cd]pyrene had a maximum percent variance of 134 percent,

indicating that the maximum concentration might be less than three-fold the mean concentration among samples collected at a field.

Taken together, OEHHA considers that the observed within-field variances of these highly variable chemicals probably have minimal impact on the risk assessment results. We, therefore, believe that the chemical concentrations in composite samples can be used to represent the chemical compositions of crumb rubber on an individual field. Based on observed activity patterns and self-reported survey data on participation history of soccer athletes at synthetic turf fields, athletes participated in sport activities across the whole field (discussed in Section 5.3). We, therefore, determined that the concentration of chemicals detected in composite samples represented the level of chemical exposures at the field. The Laboratory, therefore, prepared 2 composite samples from high impact areas (HI) and rest of the field (ROF) for each field for bioaccessibility measurements (GI and dermal) and chemical analyses. One of the 35 fields is a baseball field with no crumb rubber at the four bases. The Laboratory composited the 10 samples to one sample (ROF) for chemical analyses.

Table D-2. Within-Field Percent Variance[a] (Percent) for Gastrointestinal Bioaccessibility Analysis of Individual Crumb Rubber Samples from a Randomly Selected Field[b]

Chemical	CASRN	Chemical Group	Detection[c]	Within-Field Percent Variance		
				Minimum	Mean	Maximum
Naphthalene, 2-methyl	91-57-6	General	10	35%	160%	799%
Naphthalene, 1-methyl-	90-12-0	General	10	30%	158%	788%
Naphthalene, 1,6-dimethyl-	575-43-9	General	10	2%	127%	631%
Dimethyl phthalate	131-11-3	DART	9	68%	153%	620%
Butylated Hydroxytoluene	128-37-0	General	9	42%	120%	496%
Phthalimide	85-41-6	General	10	21%	110%	465%
Fluorene	86-73-7	General	9	14%	93%	404%
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	General	10	3%	79%	340%
Naphthalene, 2,3-dimethyl-	581-40-8	General	10	0%	65%	311%
Naphthalene, 1,2-dimethyl-	573-98-8	General	5	43%	121%	304%
Di-n-octyl phthalate	117-84-0	General	10	17%	63%	271%
Phenol, 4-(1-phenylethyl-	1988-89-2	DART	10	8%	72%	264%
Acenaphthylene	208-96-8	General	10	4%	52%	262%
N-Phenylbenzamide	93-98-1	General	10	6%	79%	255%
2,5-di-tert-Butyl-1,4-benzoquinone	2460-77-7	General	4	60%	120%	241%
Diethyl Phthalate	84-66-2	General	10	15%	64%	223%
1,4-Benzenediamine, N,N'-diphenyl-	74-31-7	DART	4	40%	109%	219%
1-Octadecene	112-88-9	General	10	38%	109%	218%
Bis(2-Ethylhexyladipate	103-23-1	DART	10	8%	40%	175%
Pyrene	129-00-0	General	10	19%	52%	165%
1,4-Benzenediamine, N-(1,3-dimethylbutyl-N'-phenyl-	793-24-8	General	9	19%	76%	162%
4-tert-Octylphenol	140-66-9	DART	10	27%	69%	156%

Diisooctylphthalate	27554-26-3	General	8	25%	52%	142%
Cyclopenta[cd]pyrene	27208-37-3	DART / Carcinogen	10	3%	34%	134%
Benzothiazole	95-16-9	General	9	5%	39%	132%
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	General	10	0%	34%	122%
Methyl stearate	112-61-8	DART	10	8%	48%	115%
7H-Benzo[c]fluorene	205-12-9	General	10	3%	27%	106%
Limonene	138-86-3	General	10	0%	50%	100%
Dibenzothiophene	132-65-0	General	10	1%	41%	93%
Benzene, n-butyl-	104-51-8	General	10	7%	21%	85%
Cyclohexyl isothiocyanate	1122-82-3	General	7	13%	41%	85%
Benzothiazole, 2-phenyl-	883-93-2	General	10	0%	24%	84%
Anthracene	120-12-7	General	10	4%	24%	83%
Naphthalene, 2-(bromomethyl-	939-26-4	General	10	2%	45%	81%
Benzo[k]fluoranthene	207-08-9	General / Carcinogen	10	8%	40%	73%
Anthracene, 9-phenyl	602-55-1	General	10	2%	26%	70%
Phenanthrene	85-01-8	DART	10	19%	41%	70%
Benzo[g,h,i]perylene	191-24-2	DART	10	36%	49%	66%
Benzo[e]pyrene	192-97-2	DART	10	1%	26%	65%
Phenanthrene, 3-methyl	832-71-3	General	10	4%	33%	65%
Benzyl butyl phthalate	85-68-7	General	10	6%	32%	63%
Dibutyl phthalate	84-74-2	General	10	5%	26%	62%
Phenanthrene, 2-methyl-	2531-84-2	General	10	12%	38%	62%
Chrysene	218-01-9	DART / Carcinogen	10	1%	24%	59%
Diisobutyl Phthalate	84-69-5	General	10	4%	21%	58%
Phenanthrene, 1-methyl	832-69-9	General	10	10%	34%	57%
Anthracene, 2-methyl-	613-12-7	General	10	9%	31%	56%
Benzo[b]fluoranthene	205-99-2	General / Carcinogen	10	6%	30%	55%
Phenol, 2,4-bis(1-methyl-1-phenylethyl-	2772-45-4	DART	10	4%	23%	51%
Fluoranthene	206-44-0	General	10	1%	28%	50%
Benzo[a]pyrene	50-32-8	DART / Carcinogen	10	8%	27%	47%
Benz[a]anthracene	56-55-3	General / Carcinogen	10	1%	23%	44%
Cyclohexanamine, N-cyclohexyl-	101-83-7	DART	9	2%	10%	24%
Hexadecane	544-76-3	General	5	3%	7%	14%

[a] Percent Variance of a chemical = (detected concentration of a chemical in an individual sample – mean detected concentration of a chemical in all samples collected from the randomly selected field) ÷ mean detected concentration of a chemical in all samples collected from the randomly selected field. Samples with detected concentrations of a chemical below its method of detection (non-detected samples) were excluded in the variance and mean concentration calculations.

[b] Ten individual crumb rubber samples from a randomly selected field were extracted using the gastrointestinal bioaccessibility analysis protocol (Appendix D) and analyzed using gas chromatography

mass spectrometry (GC-MS).
[c] Detection: number of samples with detected concentrations above its method detection limit of a chemical (for a total of 10 samples from the selected field).

Relative Difference Between Composite Samples. The Study detected 62 organic chemicals in composite samples of the 34 fields. Two composite samples were prepared from individual crumb rubber samples collected at 10 locations at each field (HI: samples from high impact area and RoF: samples from the rest of field). Table D-37 and Table D-38 illustrate the ratio and relative differences, respectively, between the HI and RoF sample GI bioaccessible concentrations of these chemicals. Ratio of HI to RoF represents the relative GI bioaccessible chemical concentrations between the pair of composite samples of an individual field. For a chemical, a ratio of one indicates that the HI and RoF composite samples contain the same chemical concentrations. Relative percent difference describes the absolute difference in chemical concentrations between the HI and RoF composite samples for an individual field relative to the average value of the composite samples of the same field. A relative percent difference of 100 percent suggests that one of the composite samples contains three-fold concentration of the other composite sample. The maximum value of percent difference could not equal to or exceed 200 percent for a chemical, as 200 percent represents the chemical is not detected in one of the composite samples and we excluded samples with detected chemical concentration below the method of detection (non-detected samples) from this variation analyses.

The mean ratio of chemical concentrations in the composite samples for the 35 individual fields ranged from 0.55 to 2.65 for all but two chemicals (anthracene, 9,10-dimethyl and limonene). Anthracene, 9,10-dimethyl was detected in both HI and RoF composite sample from only one field. OEHHA determined that the concentration ratio obtained from the single field was highly uncertain and excluded this chemical from further discussion of chemical variation.

The mean relative differences were below 100 percent. The maximum relative differences ranged from 10 to 199 percent. Dimethyl phthalate and limonene had maximum relative differences of 199. For the two fields reflecting the highest maximum relative difference, the ratios of HI to RoF were 0.00226 and 710 for dimethyl phthalate and limonene, respectively. The Study did not assess the human health risk from exposure to limonene (details in Section 4.4.4 and Section 4.5) and therefore, we excluded limonene from further discussion of chemical variation. Dimethyl phthalate was detected in both HI and RoF composite samples of six fields. Two of these fields had very low concentration ratios of HI to RoF (<0.01) and hence resulting high relative differences (198 and 199 percent). The other four fields had similar dimethyl phthalate concentrations between the HI and RoF composite samples (ratio 0.47 to 1.02 and relative differences of 2 to 73 percent). For the field with the highest relative difference of 199 percent, the ratio of HI to RoF was 0.00226 (or ratio of RoF to HI was 443) and the ratio of HI to the average of the composite was 0.005 (or ratio of HI to average of

composite was 2). OEHHA derived the One-Day $HQ_{ing\text{-}DART}$ of dimethyl phthalate as 4.4E-08 for 16<30 years old athletes (the age group with highest One-Day HI_{DART}) based on the mean of the 35 One-Day $HQ_{ing\text{-}DART\text{-}field}$ for dimethyl phthalate. If we assumed the maximum relative difference between composite samples of the 35 fields, we estimated a high-end One-Day $HQ_{ing\text{-}DART}$ of dimethyl phthalate might be 2.0E-05 for the 16<30 years old athletes.

Taken together, despite the noted large difference in concentrations between the two composite samples for a few chemicals, they were not driving chemicals in assessing the non-cancer hazards or cancer risk in the Study. Data on ratios and relative difference between the composite samples among the 35 fields demonstrated low variation in chemical composite within a field for many of the detected chemicals. OEHHA, therefore, considered that it is appropriate to use average concentration of composite samples for a field to represent the chemical exposure on the field.

Table D-3. Ratio[a] of High Impact (HI) and Rest of Field (RoF) (unitless) Gastrointestinal Biaccessibilty Concentrations by Chemical for the 34 Individual Field

Chemical	CASRN	Detection[b]	HI:ROF Ratio		
			Minimum	Mean	Maximum
Acenaphthylene	208-96-8	14	0.13	1.51	5.88
Aniline	62-53-3	5	0.15	1.36	2.98
Anthracene	120-12-7	2	0.91	0.97	1.03
Anthracene, 2-methyl-	613-12-7	25	0.03	1.67	11.42
Anthracene, 9,10-dimethyl	781-43-1	2	0.57	0.83	1.09
Anthracene, 9-phenyl	602-55-1	3	1.01	1.84	3.07
Benzene, n-butyl-	104-51-8	31	0.07	2.21	21.34
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	793-24-8	34	0.43	1.07	2.38
1,4-Benzenediamine, N,N'-diphenyl-	74-31-7	34	0.36	0.98	1.29
Benz[a]anthracene	56-55-3	25	0.30	0.93	1.90
Benzo[a]pyrene	50-32-8	34	0.33	1.04	2.79
Benzo[b]fluoranthene	205-99-2	8	0.42	0.98	1.27
7H-Benzo[c]fluorene	205-12-9	27	0.27	1.15	4.12
Benzo[e]pyrene	192-97-2	34	0.30	1.15	4.03
Benzo[g,h,i]perylene	191-24-2	1	7.29	7.29	7.29
Benzo[k]fluoranthene	207-08-9	26	0.64	1.30	4.44
Benzothiazole	95-16-9	34	0.37	1.03	2.09
Benzothiazole, 2-phenyl-	883-93-2	24	0.26	0.99	1.93
Benzothiazolone	934-34-9	34	0.32	1.24	9.96
Benzyl butyl phthalate	85-68-7	34	0.40	1.00	2.80
Bis(2-Ethylhexyl)adipate	103-23-1	34	0.53	1.03	3.27
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	52829-07-9	33	0.06	1.11	3.21
Butylated Hydroxytoluene	128-37-0	34	0.21	1.27	8.30
Chrysene	218-01-9	34	0.13	1.45	9.70

Chemical	CASRN	Detection[b]	HI:ROF Ratio		
			Minimum	Mean	Maximum
Coronene	191-07-1	34	0.39	1.04	2.15
Cyclohexyl isothiocyanate	1122-82-3	33	0.48	1.08	2.73
Cyclopenta[cd]pyrene	27208-37-3	34	0.25	1.54	6.11
Dibenzothiophene	132-65-0	3	0.91	1.01	1.08
Dibutyl phthalate	84-74-2	31	0.20	1.58	8.23
Dicyclohexylamine	101-83-7	13	0.49	1.88	6.96
N,N'-Dicyclohexylurea	2387-23-7	34	0.41	0.96	2.59
Diethyl Phthalate	84-66-2	4	0.47	0.82	1.09
Diisobutyl Phthalate	84-69-5	24	0.27	1.12	6.72
Diisooctylphthalate	27554-26-3	34	0.37	1.06	4.32
Dimethyl phthalate	131-11-3	23	0.15	1.16	4.60
Di-n-octyl phthalate	117-84-0	24	0.27	0.98	2.73
Diphenylurea	102-07-8	14	0.57	1.04	2.16
2,5-di-tert-Butyl-1,4-benzoquinone	2460-77-7	16	0.32	1.13	2.69
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	28	0.28	1.70	9.39
Fluoranthene	206-44-0	27	0.14	1.31	4.10
Fluorene	86-73-7	6	0.00	0.55	1.02
Hexadecane	544-76-3	17	0.05	1.67	10.58
Indeno[1,2,3-cd]pyrene	193-39-5	30	0.35	1.73	16.83
Limonene	138-86-3	34	0.32	0.97	1.86
Linoleic acid	60-33-3	6	0.32	1.57	3.11
Methyl stearate	112-61-8	18	0.41	1.05	2.54
2-(Methylthio)benzothiazole	615-22-5	5	0.90	1.29	2.46
Naphthalene, 1-methyl-	90-12-0	30	0.04	25.57	709.64
Naphthalene, 1,2-dimethyl-	573-98-8	33	0.50	0.98	1.59
Naphthalene, 1,6-dimethyl-	575-43-9	28	0.25	1.54	5.95
Naphthalene, 2-(bromomethyl)-	939-26-4	9	0.31	1.12	2.05
Naphthalene, 2,3-dimethyl-	581-40-8	8	0.49	1.15	2.18
Naphthalene, 2-methyl	91-57-6	34	0.18	1.11	4.31
1-Octadecene	112-88-9	27	0.09	1.36	13.07
4-tert-Octylphenol	140-66-9	34	0.30	0.92	1.47
17-Pentatriacontene	6971-40-0	33	0.29	0.97	2.33
Phenanthrene	85-01-8	13	0.77	1.47	7.78
Phenanthrene, 1-methyl	832-69-9	20	0.22	1.96	18.27
Phenanthrene, 2-methyl-	2531-84-2	34	0.30	0.93	1.97
Phenanthrene, 3-methyl	832-71-3	34	0.24	1.07	2.72
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	2772-45-4	33	0.24	1.02	2.84
Phenol, 4-(1-phenylethyl)-	1988-89-2	34	0.28	1.01	2.15
Phenoxazine	135-67-1	34	0.39	1.01	2.97
N-Phenylbenzamide	93-98-1	33	0.43	1.84	25.86

Chemical	CASRN	Detection[b]	HI:ROF Ratio		
			Minimum	Mean	Maximum
Phthalimide	85-41-6	1	1.00	1.00	1.00
Pyrene	129-00-0	13	0.30	1.32	3.18
Ricinoleic acid	141-22-0	34	0.18	0.99	2.03
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	28	0.29	1.22	5.30

[a] Ratio of gastrointestinal (GI) bioaccessible chemical concentration in HI to RoF = GI bioaccessible chemical concentration in the HI composite sample ÷ GI bioaccessible chemical concentration in the RoF sample of an individual field. For a chemical, the mean ratio is the average the 34 individual-field ratios. Fields with detected concentration of a chemical below its method of detection in either HI or RoF sample (non-detected samples) were excluded in calculating the ratio.
[b] Detection: Number of fields with detected concentration of a chemical above its method of detection in both the HI and RoF samples.

Table D-4. Relative Percent Difference[a] between Gastrointestinal (GI) Biaccessibilty (BA) Chemical Concentrations of High Impact and Rest of Field Composite Samples Within Each of the 34 Studied Fields[b]

Chemical	CASRN	Detection[c]	Relative Precent Difference, %		
			Minimum	Mean	Maximum
Limonene	138-86-3	30	1	60	199
Dimethyl phthalate	131-11-3	6	2	82	199
1-Octadecene	112-88-9	25	2	62	187
Phenol, 4-(1-phenylethyl)-	1988-89-2	33	2	37	185
Di-n-octyl phthalate	117-84-0	17	1	53	183
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	31	0	55	182
N-Phenylbenzamide	93-98-1	20	0	29	179
Diphenylurea	102-07-8	30	12	55	178
Benzo[g,h,i]perylene	191-24-2	33	0	42	177
Naphthalene, 1-methyl-	90-12-0	27	1	33	172
Benzo[a]pyrene	50-32-8	34	3	41	164
Benzothiazole	95-16-9	34	1	34	163
Diisobutyl Phthalate	84-69-5	28	0	45	161
Benzo[k]fluoranthene	207-08-9	34	1	48	157
Bis(2-Ethylhexyl)adipate	103-23-1	31	2	74	157
Naphthalene, 2-methyl	91-57-6	13	0	20	154
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	793-24-8	14	6	62	154
Anthracene, 9,10-dimethyl	781-43-1	1	152	152	152
Diisooctylphthalate	27554-26-3	27	0	35	150
Butylated Hydroxytoluene	128-37-0	13	0	48	150
1,4-Benzenediamine, N,N'-diphenyl-	74-31-7	5	15	71	148
Cyclohexyl isothiocyanate	1122-82-3	24	2	30	148
Dibenzothiophene	132-65-0	23	0	51	147
Benzyl butyl phthalate	85-68-7	34	0	51	144
Methyl stearate	112-61-8	28	0	50	142

Chemical	CASRN	Detection[c]	Relative Precent Difference, %		
			Minimum	Mean	Maximum
Pyrene	129-00-0	34	2	28	138
Naphthalene, 1,6-dimethyl-	575-43-9	34	0	33	138
Ricinoleic acid	141-22-0	28	2	54	137
Anthracene, 9-phenyl	602-55-1	26	0	28	126
Cyclopenta[cd]pyrene	27208-37-3	34	5	33	125
Phenanthrene, 1-methyl	832-69-9	34	2	36	123
Phenanthrene, 2-methyl-	2531-84-2	33	1	37	123
Anthracene	120-12-7	27	1	38	122
Anthracene, 2-methyl-	613-12-7	34	2	35	120
Benzene, n-butyl-	104-51-8	24	0	22	117
Dibutyl phthalate	84-74-2	24	1	28	115
Phenanthrene, 3-methyl	832-71-3	34	0	37	112
Naphthalene, 2,3-dimethyl-	581-40-8	33	1	29	109
7H-Benzo[c]fluorene	205-12-9	25	1	34	108
Naphthalene, 2-(bromomethyl)-	939-26-4	34	2	21	108
Phthalimide	85-41-6	13	5	67	108
Phenanthrene	85-01-8	34	1	26	107
Benzo[e]pyrene	192-97-2	34	0	24	106
N,N'-Dicyclohexylurea	2387-23-7	9	2	35	104
Diethyl Phthalate	84-66-2	16	1	29	104
Fluorene	86-73-7	6	17	67	103
Fluoranthene	206-44-0	34	0	26	102
2,5-di-tert-Butyl-1,4-benzoquinone	2460-77-7	3	1	46	102
Acenaphthylene	208-96-8	34	0	32	100
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	2772-45-4	34	0	28	99
Benzo[b]fluoranthene	205-99-2	34	0	29	95
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	34	1	15	95
Benzothiazolone	934-34-9	33	1	22	93
Benz[a]anthracene	56-55-3	34	1	34	91
Chrysene	218-01-9	34	0	26	88
Benzothiazole, 2-phenyl-	883-93-2	34	1	22	88
Hexadecane	544-76-3	18	0	24	87
Indeno[1,2,3-cd]pyrene	193-39-5	5	0	21	84
4-tert-Octylphenol	140-66-9	34	1	28	82
Aniline	62-53-3	8	1	17	81
Naphthalene, 1,2-dimethyl-	573-98-8	8	5	31	74
Dicyclohexylamine	101-83-7	14	2	22	73
Coronene	191-07-1	4	6	27	73
Linoleic acid	60-33-3	33	0	14	66
2-(Methylthio)benzothiazole	615-22-5	2	8	31	54

Chemical	CASRN	Detection[c]	Relative Precent Difference, %		
			Minimum	Mean	Maximum
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	52829-07-9	3	3	7	10
17-Pentatriacontene	6971-40-0	2	3	6	10
Phenoxazine	135-67-1	1	0	0	0

[a] Relative percent difference describes the relative difference in chemical concentration between the pair of HI and RoF composite samples of individual fields. Relative Percent Difference = absolute value of (chemical concentration in HI composite sample – chemical concentration in RoF composite sample) / the average chemical concentration of the HI and RoF composite of an individual field. Fields with non-detected samples were excluded in calculating the relative percent difference.
[b] Two composite crumb rubber samples were prepared from each of the individual fields by compositing individual samples collected at high impact area (HI sample) or rest of the field (RoF sample) of a field.
[c] Detection: Number of fields with detected concentration of a chemical above its method of detection in both the HI and RoF samples (total number of fields with samples analyzed by gas chromatography-mass spectrometry

Calculation of Chemical Exposure Concentrations. Despite of the complex and highly heterogeneous nature of crumb rubber particles, OEHHA considered that variations in chemical composition within a sample, within a field, and between pair of composite samples from the 35 individual fields were low. In addition, results from the TAS (observed activity pattern of soccer players and the self-reported survey data from soccer athletes) suggested athletes often played multiple positions in the team and the athletes frequently traveled across the whole field during practices and games. Also, soccer athletes participated in sports on multiple fields during their soccer tenure (practices and games). Taken together, we determined that the use of chemical concentration data from composite samples to characterize the chemical composition of crumb rubber, average chemical concentrations of the composite samples from an individual field to represent the chemical composition of a field, and a mean of the 35 individual-field average concentrations of each chemical as an exposure chemical concentration in exposure and risk assessments were appropriate. In addition, we incorporated conservative approaches in the calculation of exposure concentration of chemicals, thus assessing the human health from chemical exposure, by assuming all chemicals detected in at least one field sample were present at the field and excluding all the non-detected samples in the calculation of average chemical concentrations.

D.4.1.4.4. Gastrointestinal Bioaccessibility Fraction of Organic Chemicals in Crumb Rubber

There were very few studies in the literature regarding bioaccessibility or bioavailability of organic chemicals in tire products, including crumb rubber. The USEPA Risk Assessment for Superfund Sites, RAGs (USEPA, 1989) provided details on evaluating exposure of contaminants in environmental matrices like soil and water. Multiple chemical components, high temperature, and high pressure used in the tire manufacturing processes plus post-manufacturing weathering and aging of tires on the road greatly contributed to the difficulties to evaluate human exposure to chemicals released from tire products. Organic chemicals (especially PAHs) in crumb rubber are

adhered, bound, or embedded in the rubber polymer matrix that may not be readily released into GI fluids following ingestion or sweat following dermal contact to crumb rubber. To address the uncertainties in accessibility of organic chemicals following ingestion or dermal contact to crumb rubber at synthetic turf fields, OEHHA conducted GI and dermal bioaccessibility measurements of chemicals using artificial biofluids and artificial sweat, respectively, to measure GI and dermal bioaccessible concentrations of organic chemicals from field crumb rubber samples. We adopted a stir bar sorptive extraction system in the extraction setups to mimic the gut linings or the lipid layer on skin to enhance the solubility of lipophilic chemicals like PAHs to the artificial fluids (Main Report Section 3.2.2). In this section, we employ chemical data from GI bioaccessibility measurements of the pre-installed crumb rubber samples to understand the GI bioaccessibility fraction of organic chemicals in crumb rubber. Since ingestion exposure to metals and metalloids were not major concerns for non-cancer hazard or cancer risk (Section 6), the GI bioaccessibility discussion here focused on organic chemicals. Our Study did not measure the total organic chemical contents in the crumb rubber samples, but the USEPA (USEPA and CDC/ATSDR, 2019) performed solvent extraction (1:1 acetone:hexane by volume) on 27 pre-installed crumb rubber samples collected from tire recycling facilities in the United States, including some of the California facilities which OEHHA collected our pre-installed samples. The OEHHA GI bioaccessibility measurements and the USEPA solvent extraction measurements of pre-installed samples shared 18 common organic chemicals. To estimate the GI bioaccessibility fraction of these organic chemicals, we compared the GI bioaccessible concentrations of these chemicals in our nine pre-installed samples obtained from tire recycling facilities in California with the chemical concentrations in the solvent extracts reported in the USEPA study (Table D-40).

Table D-1.Gastrointestinal (GI) Bioaccessibility Fraction[a] of SVOC Chemicals Detected in Manufacturing Crumb Rubber Samples Calculated using OEHHA GI Bioaccessible Chemical Concentrations and USEPA (2019) Total Solvent Extraction Concentrations

Chemical (Chemical Abstracts Service Registry Number)	Mean	Minimum	Maximum
4-tert-Octylphenol (140-66-9)	0.022	0.017	0.030
Acenaphthylene (208-96-8)	0.043	0.026	0.068
Aniline (62-53-3)	0.014	0.010	0.016
Anthracene (120-12-7)	0.028	0.002	0.090
Benzo[a]pyrene (50-32-8)	0.018	0.005	0.062
Benzyl butyl phthalate (85-68-7)	0.053	0.012	0.120
Chrysene (218-01-9)	0.008	0.004	0.021
Dibenzothiophene (132-65-0)	0.035	0.012	0.082
Dibutyl phthalate (84-74-2)	0.086	0.066	0.150
Diethyl Phthalate (84-66-2)	0.652	0.352	1.006
Diisobutyl Phthalate (84-69-5)	0.025	0.009	0.054
Dimethyl phthalate (131-11-3)	0.203	0.003	0.443
Di-n-octyl phthalate (117-84-0)	0.147	0.064	0.316
Fluoranthene (206-44-0)	0.013	0.008	0.026
Fluorene (86-73-7)	0.058	0.010	0.200
Naphthalene (91-20-3)	0.060	0.021	0.109
Phenanthrene (85-01-8)	0.022	0.009	0.059
Pyrene (129-00-0)	0.006	0.003	0.009

[a] The gastrointestinal (GI) bioaccessibility fraction for each manufacturing sample was calculated as the GI bioaccessible concentration of a chemical (nanogram per gram crumb rubber) in nine manufacturing samples collected in the OEHHA Synthetic Turf Study divided by the mean concentration of a chemical in solvent extracts [(milligram per kilogram crumb rubber) * 1000 nanogram per milligram] of the 23 tire crumb samples collected from recycling plants as reported in Table 4-36 of USEPA 2019.
Values are rounded to three decimal places.

The mean GI bioaccessibility fraction of aromatic hydrocarbons (including PAHs) were low, ranging from 0.0055 to 0.0597 (or 0.55 to 5.97 percent). However, the mean fractions were higher for phthalates (range from 0.0253 to 0.652), with higher values for lower-molecular-weight phthalates like dimethyl phthalate and diethyl phthalate. The data demonstrated that PAHs in crumb rubber probably were tightly bound and not readily released into artificial GI fluids, even with incorporating the SBSE system in the extraction to enhance the solubility of these chemicals in the artificial biofluid system. OEHHA believed that PAHs were generally low in bioaccessibility following ingestion of crumb rubber. The low molecular phthalates are generally more soluble in aqueous solution and hence more readily released into the artificial GI biofluids.

The Study did not measure the dermal bioaccessibility concentration of chemicals in pre-installed crumb rubber samples. Considering the dermal bioaccessibility extraction was less vigorous (shorter incubation duration and a simple artificial sweat) than the GI bioaccessibility extraction (longer incubation duration and an artificial GI fluid system of different pHs: artificial saliva, artificial gastric fluid, and artificial intestinal fluid), OEHHA anticipated the dermal bioaccessibility fraction of these chemicals in crumb rubber

would probably be lower than the GI bioaccessibility fraction.

D.4.1.4.5. Bioavailability of Organic Chemicals in Crumb Rubber

The USEPA RAGs Part E (USEPA, 2004) reported dermal absorption fractions of 0.13 and 0.1 respectively, for PAHs and SVOCs in soil. Meanwhile, the guidelines cited gastrointestinal absorption fractions of 58 and 89 percent for PAHs in starch solution and diet respectively. These GI and dermal absorption fractions, together with concentrations of chemicals in extracts of environmental samples like soil or groundwater, may be applied to estimate the bioavailability of chemicals (amount of chemicals entering the circulation system of human body) upon ingestion or dermal contacts with the sources of contamination. Because of the highly complex structure of crumb rubber, OEHHA considered these empirically measured gastrointestinal and dermal absorption fractions of organic chemicals from soil or diets not applicable to estimate the bioavailability fraction of chemicals from crumb rubber on this Study. In the absence of measured GI and dermal absorption fractions, OEHHA applied a conservative approach in our risk assessment by assuming a 100 percent GI and dermal absorption fraction of the GI or dermal bioaccessible concentrations of chemicals in the GI artificial fluids or the artificial sweat, respectively.

D.4.1.4.6. Result of Gastrointestinal Bioaccessibility Measurements of Organic Chemicals in Artificial Gastrointestinal Fluid Extracts

Table D-35 summarizes the 35 individual-field GI bioaccessible concentrations of organic chemicals in crumb rubber samples ($C_{GI\text{-}crumb\ rubber\text{-}field}$, nanograms per gram of crumb rubber) extracted in artificial GI fluids using SBSE methods. The mean values represent the mean of the 35 individual-field average concentrations of the organic chemicals ($C_{GI\text{-}crumb\ rubber}$, nanograms per gram of crumb rubber).

Table D-1. Individual-Field Gastrointestinal Bioaccessilbe Concentrations of Organic Chemicals in Crumb Rubber Samples ($C_{GI\text{-}crumb\ rubber\text{-}field}$, nanograms per gram of crumb rubber) Collected from the 35 Fields During the State-Wide Study

Chemical	CASRN	Detection[a]	$C_{ing\text{-}crumb\ rubber\text{-}field}$					
			Minimum	Mean ($C_{ing\text{-}crumb\ rubber}$)	Standard Deviation	Median	95th Percentile	Maximum
Anthracene	6971-40-0	20	0	48	66	18	180	230
Anthracene, 2-methyl-	5315-79-7	7	0	5.5	22	0	21	120
Anthracene, 9,10-dimethyl	112-88-9	9	0	4	9.3	0	22	42
Anthracene, 9,10-diphenyl-	615-22-5	1	0	1.1	6.8	0	0	40
Anthracene, 9-phenyl	2460-77-7	32	0	4.7	4.1	3.6	13	14
Benzene, n-butyl-	1620-98-0	5	0	15	54	0	84	300
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	140-66-9	4	0	0.082	0.26	0	0.64	1.2
1,4-Benzenediamine, N,N'-diphenyl-	689-67-8	35	0.049	18	36	1.1	73	180

Chemical	CASRN	Detection[a]	$C_{ing\text{-}crumb\ rubber\text{-}field}$					
			Minimum	Mean ($C_{ing\text{-}crumb\ rubber}$)	Standard Deviation	Median	95th Percentile	Maximum
Benz[a]anthracene	205-12-9	35	5.3	69	94	30	270	430
Benzo[a]pyrene	208-96-8	35	2	3.4	1.1	3.2	5.3	6.5
Benzo[b]fluoranthene	62-53-3	31	0	0.77	1.3	0.25	3.1	6.2
7H-Benzo[c]fluorene	120-12-7	35	0.041	0.32	0.29	0.19	0.92	1.2
Benzo[e]pyrene	613-12-7	12	0	1.8	4	0	9.8	18
Benzo[g,h,i]perylene	781-43-1	28	0	0.83	1.5	0.32	3.1	6.8
Benzo[k]fluoranthene	1499-10-1	35	0.48	3.3	2.9	2.4	7.6	15
Benzothiazole	602-55-1	2	0	0.027	0.15	0	0.017	0.88
Benzothiazole, 2-phenyl-	56-55-3	2	0	0.21	0.94	0	0.59	5.3
Benzothiazolone	104-51-8	30	0	0.31	0.33	0.19	0.98	1.4
Benzyl butyl phthalate	50-32-8	35	0.19	2.9	3.2	1.4	9	13
Bis(2-Ethylhexyl)adipate	205-99-2	29	0	0.18	0.45	0.099	0.27	2.7
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	192-97-2	35	0.47	2.4	2	1.7	6.6	7
Butylated Hydroxytoluene	191-24-2	35	0.81	4	2.9	2.7	9.7	12
n-Caproic acid vinyl ester	207-08-9	35	2.1	7.1	4.2	5.5	15	16
Chrysene	95-16-9	35	0.33	4.8	3	4.3	9.7	13
Coronene	883-93-2	35	0.11	1.3	1.2	0.82	3.8	4.8
Cyclohexyl isothiocyanate	934-34-9	35	110	490	340	360	1000	1200
Cyclopenta[cd]pyrene	85-68-7	35	15	53	49	38	120	280
Dibenz[a,h]anthracene	52829-07-9	35	790	1200	240	1200	1600	1700
Dibenzothiophene	103-23-1	35	1.3	25	21	22	56	100
Dibutyl phthalate	128-37-0	4	0	12	36	0	110	130
Dicyclohexylamine	218-01-9	33	0	16	14	11	46	57
N,N'-Dicyclohexylurea	191-07-1	19	0	0.67	1.2	0.23	3.4	5.6
Diethyl Phthalate	1122-82-3	35	3.2	13	6.9	13	22	35
Diisobutyl Phthalate	27208-37-3	7	0	1.8	5.1	0	7.5	28
Diisooctylphthalate	53-70-3	29	0	160	110	160	370	410
Dimethyl phthalate	132-65-0	35	0.49	2.8	2.6	2.4	7.3	13
Diphenylurea	101-83-7	7	0	0.17	0.43	0	0.78	2.1
2,5-di-tert-Butyl-1,4-benzoquinone	84-66-2	27	0	0.67	1	0.2	2.7	4.1
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	84-69-5	31	0	48	36	38	120	140
Fluoranthene	27554-26-3	25	0	41	34	39	94	110
Fluorene	131-11-3	23	0	4	3.5	4.4	9.5	12
Hexadecane	117-84-0	32	0	4.8	12	1.1	13	73
1-Hydroxypyrene	102-07-8	33	0	100	75	74	260	270
Indeno[1,2,3-cd]pyrene	206-44-0	9	0	0.93	3.1	0	8.3	15

Chemical	CASRN	Detection[a]	$C_{ing\text{-}crumb\ rubber\text{-}field}$					
			Minimum	Mean ($C_{ing\text{-}crumb\ rubber}$)	Standard Deviation	Median	95th Percentile	Maximum
Limonene	86-73-7	26	0	9.9	24	2.6	48	110
Linoleic acid	544-76-3	35	5.6	130	170	65	520	770
Methyl stearate	193-39-5	35	3.1	22	22	13	57	110
2-(Methylthio)benzothiazole	138-86-3	11	0	0.29	0.7	0	1.5	3.5
Naphthalene	60-33-3	28	0	2.1	1.8	2.2	5	8.2
Naphthalene, 1-methyl-	112-61-8	12	0	0.48	0.85	0	2.1	3.3
Naphthalene, 1,2-dimethyl-	2387-23-7	34	0	4.2	13	0.68	12	76
Naphthalene, 1,6-dimethyl-	91-20-3	35	630	1000	190	1100	1300	1300
Naphthalene, 2-(bromomethyl)-	573-98-8	35	2.5	10	8.8	7.7	24	47
Naphthalene, 2,3-dimethyl-	575-43-9	17	0	23	45	0	110	220
Naphthalene, 2-methyl	90-12-0	1	0	0.053	0.31	0	0	1.8
1-Octadecene	939-26-4	12	0	0.032	0.071	0	0.16	0.36
Oleic acid	581-40-8	35	0.083	0.21	0.1	0.18	0.42	0.59
17-Pentatriacontene	91-57-6	31	0	0.14	0.47	0.023	0.28	2.8
Phenanthrene	3050-69-9	35	0.19	5.5	2.6	5.4	9.6	12
Phenanthrene, 1-methyl	93-98-1	35	0.041	1.6	1.6	1.1	4.8	7
Phenanthrene, 2-methyl-	112-80-1	19	0	0.12	0.51	0.022	0.28	3
Phenanthrene, 3-methyl	85-01-8	1	0	0.13	0.8	0	0	4.7
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	832-69-9	22	0	22	42	3.4	130	150
Phenol, 4-(1-phenylethyl)-	2531-84-2	3	0	54	180	0	530	760
Phenoxazine	832-71-3	35	1.7	9.8	12	5.5	28	63
N-Phenylbenzamide	2772-45-4	35	0.23	2.6	2.5	1.9	6.5	11
Phthalimide	1988-89-2	35	0.071	3.4	3.9	2	9.5	18
Pyrene	135-67-1	35	0.43	5.6	6	3.6	15	28
Pyridine, 2-(4-methylphenyl)-	85-41-6	35	3.1	26	16	23	52	70
Ricinoleic acid	129-00-0	34	0	14	19	8.1	49	94
4-tert-Octylphenol	4467-06-5	3	0	13	52	0	75	250
Triethylene glycol monobutyl ether	141-22-0	16	0	3.9	9.1	0	20	42
5,9-Undecadien-2-one, 6,10-dimethyl-	143-22-6	35	8.8	47	31	39	99	140

[a] Detection value is the number of fields with concentration in extracts above the method of detection for an organic chemical.
Values are rounded to two significant figures.

D.4.2. Analyses of Samples Collected from the Air

D.4.2.1. Extraction of Semi-Volatile Chemicals (SVOCs) from Sample Trains

SAFETY: This procedure uses flammable solvents and a high pressure extraction system located in B70-217 at LBNL. Workers need to have WPC approval for work on this system. All work is to be performed in the fume hood while wearing nitrile gloves, safety glasses and lab coat.

D.4.2.1.1. Extracting Polyurethane Foam (PUF), XAD™, and Glass Fiber Filter (GFF) Samples

PUF, XAD™ and GFF air sample media are placed in accelerate solvent extraction (ASE) cells and then extracted with DCM or a mixture of 50:50 acetone and hexanes using an ASE system at 1500 psi. The SVOC extracts are combined into a 250 mL amber bottle for storage.

Table D-1. Equipment and Supplies

Dionex ASE 200 Extraction system	Spatula
Micro Balance	Large forceps
SVOC Sample	Filter insertion tool (P/N 049495; Dionex)
Tracking sheet	ASE glass fiber filter (P/N 047017; Dionex)
N_2 cylinder	Sand, baked 450 °C for 6 hours
Acetone	250 mL amber bottle (Qorpak)
Hexanes	Green PTFE lined cap
Dichloromethane	Solvent clean filter
Glass syringe, 250 µL	Solvent clean Kimwipe™
ASE cells, 33 mL (P/N 048763; Dionex)	Pasteur pipets, baked
Caps for ASE cells	Bench paper
60 ml amber vials (IChem S246-0060)	Nitrile gloves
Open cap for 60 mL vials	Timer
Septa, (P/N 288-7222; Thermo)	Kimwipes™
ASE funnel (049288; Dionex)	Aluminum foil
Not applicable	Labeling tape

D.4.2.1.2. Procedure

1. Preparation
    a. Muffle bake (450 °C) pipets, 2 mL autosampler vials, and sand.
    b. Solvent clean (3 times hexanes, 3 times DCM, and 3 tiles acetone) all 60 mL vials, 250 mL jars, caps and septa, and the baked autosampler vials along with its caps and septa.
    c. Wash stainless steel cells in hot soapy water, rinse and air-dry overnight. Just

before use, solvent clean with 3 times rinses of acetone, DCM and hexanes.

d. Inspect ASE cell caps and replace any worn or dirty seals and frits. Clean the cells before use with 3 times rinses of acetone, DCM and hexanes using the vacuum flask in the Room 260 hood.

e. For each paired PUF/XAD™ sample you will need one 33 mL ASE cell, two 11 mL cells, six caps, three 60 mL amber vials with open caps and septa, and a 250 mL amber jar, all solvent cleaned.

f. On a clean benchtop put down a new Kimwipe™ for each sample.

g. Bring the PUF/XAD™/GFF sample train to room temperature before use.

h. Rinse funnel, forceps, and spatula with DCM.

i. Print out tracking sheet and fill out sample name and extraction date.

j. Label 60 mL collection vials. Place the label near the bottom of the tube so it does not interfere with the ASE sensor.

k. Prepare ASE for use:

   i. Check N_2 cylinder.

   ii. Fill carousel with clean, labeled amber 60 mL collection vials capped with new septa.

   iii. Fill ASE solvent reservoirs with acetone, hexanes and DCM.

2. PUF Extraction

a. Record the number on an 11 mL ASE cell. Assemble bottom cap and insert a cleaned filter.

b. Place the PUF sample on a solvent clean Kimwipe™. Roll up PUF tightly and insert into ASE cell.

c. Seal the ASE cell tightly with the top cap.

d. Place cell in ASE. Record position in carousel.

e. Place one labeled 60 mL collection vial with open cap/septa in the bottom carousel.

f. Run ASE Method 2 for each PUF cell (Table D-41). Expected volume of extract is 51 mL.

Table D-1. ASE Program: Method 2. PUF Extraction in 11 mL Cell

Oven temp: 100 °C	Pressure: 1500 psi
Preheat: 0 minutes	Static: 5 minutes
Heat: 5 minutes	Solvent: 50:50 (v/v) Hexanes and Acetone
Cycles: 3	Purge: 120 seconds

Flush: 120 percent	Elapsed time: 25 minutes

3. XAD™ Extraction

   a. Prepare a 33 mL ASE cell with bottom cap and filter. Record the cell number on the tracking sheet.

   b. Transfer XAD™ to the cell using a clean funnel and spatula.

   c. Top off the remaining empty space with baked sand.

   d. Seal the ASE cell tightly with the top cap.

   e. Place cell in ASE. Record position in carousel.

   f. Place a labeled 60 mL collection vial with open cap/septa in the bottom carousel.

   g. Run ASE Method 4 for each XAD cell (Table D-42). Expected extract volume is 43 mL.

Table D-2. ASE Program: Method 4. XAD Extraction in 33 mL Cell

Oven temp: 75 °C	Pressure: 1500 psi
Preheat: 0 minute	Static: 5 minutes
Heat: 5 minutes	Solvent: Dichloromethane
Cycles: 3	Purge: 120 second
Flush: 50 percent	Elapsed time: 25 minutes

4. GFF Extraction

   a. Record the number on an 11 mL ASE cell. Assemble bottom cap and insert a cleaned filter.

   b. Add 2 teaspoon (tsp) baked sand to the cell.

   c. Place the GFF sample on a solvent clean Kimwipe™. Use 2 forceps to fold the filter and slide it into the cell.

   d. Fill the remaining space in the cell with baked sand.

   e. Seal the ASE cell tightly with the top cap.

   f. Place cell in ASE. Record position in carousel.

   g. Place one labeled 40 mL collection vial with open cap/septa in the bottom carousel.

   h. Run ASE Method 19 for each GFF cell (Table D-43). Expected volume of extract is 18 mL.

Table D-3. ASE Program: Method 19. GFF Extraction in 11 mL cell

Oven temp: 100 °C	Pressure: 1500 psi
Preheat: 0 minutes	Static: 5 minutes
Heat: 5 minutes	Solvent: Dichloromethane

Cycles: 3	Purge: 120 seconds
Flush: 120 percent	Elapsed time: 25 minutes

D.4.2.2. Concentration of Semi-Volatile Chemical Extracts for Analysis by Gas Chromatography Mass Spectrometry (GC-MS)

SAFETY: This procedure uses flammable solvents and an evaporation system located in B70-260 at LBNL. Workers need to have WPC approval for work on this system. All work is to be performed in the fume hood while wearing nitrile gloves, safety glasses and lab coat.

D.4.2.2.1. Concentrating SVOC Extracts for Analysis by GC-MS

PUF, XAD™ and GFF air sample extract is concentrated in the TurboVap concentration system and stored in an autosampler vial with a final nominal volume of 1 mL.

Table D-1. Equipment and Supplies

TurboVap II (P/N 46343, Biotage)	Glass syringe, 250 µL and 100 µL
Evaporation tube (P/N C128507, Biotage)	TurboVap tubes
Micro balance	2 mL autosampler vial, baked
Semi-volatile organic chemical (SVOC) accelerate solvent extraction (ASE) Sample Extracts	Cap with septa
Tracking sheet	Pasteur pipets, baked
N_2 cylinder	Bench paper
Acetone	Nitrile gloves
Hexanes	Timer
Dichloromethane (DCM)	Kimwipes™
Internal standard (IS, 1 ng per µL)	Aluminum foil
Recovery standard (RS, 1 ng per µL)	Labeling tape

D.4.2.2.2. Procedure

1. Preparation
   a. Bake 9 inches glass pipettes and 2 mL autosampler vials in the muffle furnace at 450 °C for 6 hours.
   b. Solvent clean (3 times hexanes, 3 times DCM, and 3 times acetone) each baked autosampler vial along with its cap and septa.
   c. Clean TurboVap tubes in a chem-solve bath for at least 1 hour. Do not scrub these tubes with any brush. Rinse 5 times in warm water followed by 5 times in deionized (DI) water. Air dry overnight.
   d. Solvent clean dry TurboVap tubes (3 times hexanes, 3 times DCM, and 3 times acetone).
   e. Clean a 250 µL and a 100 µL glass syringe with using 3 clean wash vials of DCM

(7 times rinses each vial).

f. Bring the deuterated-polycyclic aromatic hydrocarbons (d-PAHs) internal standard (IS, 1 ng per µL) to room temperature.

g. For each field gather the following:

i. ASE extracts in their 250 mL bottles

ii. Corresponding tracking sheets

iii. 2 mL solvent clean autosampler vials

iv. Pre-printed labels

2. Sample Concentration

a. Turn on the TurboVap and set the temperature to 39 °C. Fill the bath with water if needed. Select manual endpoint and set the display reading to pressure.

b. Connect the copper line from the TurboVap to the N_2 cylinder. Open the N_2 cylinder and set the second stage pressure to 30 psi.

c. Adjust the pressure at the TurboVap to about 21 psi by turning on one of the positions in order to test the flow.

d. Apply labels to the 2 mL autosampler vials. Weigh the vials and record the tare weight on the tracking sheet.

e. Label one TurboVap tube for each ASE extract. Place the label near the top of the tube.

f. Use the 100 µL syringe (blue tape) to add 100 µL of 1 ng per µL d-PAHs IS (100 ng) to each TurboVap tube (Table D-45). Dispense to the side of the glass and below the 100 mL line. Continue to add 100 ng d-PAHs IS to each TurboVap tube.

g. Transfer the ASE extract into the TurboVap tube. Pour the extract down the side of the tube where you added the d-PAH IS.

h. Rinse each extract jar two times with 5 mL each DCM and add the rinse to the TurboVap tube (a total volume of 10 mL).

i. Place the TurboVap tube into the TurboVap bath. Record the TurboVap position of each tube. Concentrate to the shoulder of the TurboVap tube (about 1.0 to 0.7 mL) at 39 °C and 21 to 20 psi. If the TurboVap tube is full to the 200 mL line start with the pressure at 10 psi and slowly increase to 21 psi to prevent splashing. The concentration takes about 25 minutes.

j. Set an alarm for 22 minutes. At this point, you will need to watch the evaporation in order to remove the tubes when the level just reaches the top of the nipple.

k. Immediately remove the TurboVap tube and cover with a foil cap. Be careful not

to drip water into the tubes.

l. Note the color of the extract on the tracking sheet. Note if any precipitate forms.

3. Transfer Sample

   a. Before the transfer, rinse down the tapered part of the tube 3 times. Carefully transfer the concentrated sample to the pre-weighed, labeled autosampler vial using a muffle baked glass pipet. Leave the pipet in the TurboVap tube.

   b. Use the 250 µL syringe to add 250 µL of DCM to the TurboVap tube. Swirl the rinse around the shoulder of the TurboVap tube, re-pipet down the sides to clean any extract off the glass. Transfer to the autosampler vial.

   c. Repeat the rinse with another 250 µL of DCM.

   d. Weigh the vial and record the final weight of sample (about 1.3 g).

   e. Store the sample in the Room 70-223 refrigerator in the designated box.

   f. Place the tracking sheet in the project binder.

4. Prepare Sample for Analysis: Adding Recovery Standard

   a. Bring the sample to room temperature.

   b. Use a clean syringe to add 100 µL of 1 ng per µL recovery standard to the sample (Table D-45).

   c. Weigh the sample and record the new weight on the tracking sheet and in the "Turf SVOC Sample Tracking" spreadsheet.

   d. Calculate the volume needed to bring the sample to 1.0 mL using the density of DCM (1.33 g per mL). Record the make-up volume on the tracking sheet.

   e. Add the makeup volume of DCM required using a baked pipette or clean syringe.

   f. Weigh the vial again and record the final weight of sample (about 1.3 g).

   g. If the sample is over a 1 mL final volume, use a stream of dry UHP N_2 gas to reduce the volume. Use an evaporation rate of 53 µL per minute with the N_2 flow set at 40 c.c. per minute with the flow controller in the Room 260 hood. Weigh the vial again and adjust the volume as necessary to get a final volume of 1.0 mL.

   h. Store the sample in the Room 70-223 refrigerator in the designated box.

   i. Place the tracking sheet in the "Done" section of the project binder.

Table D-1. List of Polyaromatic Hydrocarbon Standards Used in Preparing the Extracts of the Semi-Volatile Organic Chemical (SVOC) Sample Trains for Instrumental Analysis

Internal Standards	Recovery Standards
Naphthalene-d8	2-Methylnaphthalene-d10

Acenaphthylene-d8	p-Terphenyl-d14
Acenaphthene-d10	Perylene-d12
Fluorene-d10	Not applicable
Phenanthrene-d10	Not applicable
Anthracene-d10	Not applicable
Fluoranthene-d10	Not applicable
Pyrene-d10	Not applicable
Benz[a]anthracene-d12	Not applicable
Chrysene-d12	Not applicable
Benzo[b]fluoranthene-d12	Not applicable
Benzo[k]fluoranthene-d12	Not applicable
Benzo[a]pyrene-d12	Not applicable
Indeno[1,2,3-cd]pyrene-d12	Not applicable
Dibenz[a,h]anthracene-d14	Not applicable
Benzo[g,h,i]perylene-d12	Not applicable

D.4.2.3. Result of Chemical Analyses for Volatile and Semi-Volatile Organic Chemicals in Air

Table D-46 and Table D-47, respectively, summarize the average concentrations of VOCs and SVOCs detected in air on and off the 35 individual field ($C_{air\text{-}field}$, nanograms per gram of crumb rubber). The mean values represent the mean of the 35 individual-field average concentrations of VOCs and SVOCs in the air ($C_{air\text{-}avg}$, nanograms per gram of crumb rubber).

Table D-1. Individual-Field On-Field Concentrations of Organic Chemicals in Samples Collected from the Air ($C_{air\text{-}field}$, nanograms per gram of crumb rubber) of 35 Fields During the State-Wide Study

Chemical	CASRN	Detection[a]	$C_{air\text{-}field}$					
			Minimum	Mean ($C_{GI\text{-}avg}$)	Standard Deviation	Median	95th Percentile	Maximum
Acenaphthylene	208-96-8	11 (34)	0	1	2	0	4.2	8.7
Acetaldehyde	75-07-0	34 (34)	260	2500	1900	1900	4800	9600
Acetone	67-64-1	34 (34)	1600	20000	22000	11000	64000	69000
Aniline	62-53-3	10 (34)	0	6.5	11	0	25	44
Anthracene	120-12-7	12 (34)	0	0.33	0.61	0	1.4	2.4
Anthracene, 2-methyl-	613-12-7	15 (34)	0	0.085	0.12	0	0.33	0.42
Anthracene, 9,10-dimethyl	781-43-1	16 (34)	0	0.097	0.17	0	0.27	0.94
Anthracene, 9-phenyl	602-55-1	1 (34)	0	0.009	0.053	0	0	0.31
Benz[a]anthracene	56-55-3	1 (34)	0	0.0049	0.029	0	0	0.17
Benzaldehyde	100-52-7	15 (35)	0	89	140	0	320	540
Benzene	71-43-2	35 (35)	90	600	490	430	1500	2500
Benzene, 1,2,3-trimethyl-	526-73-8	6 (35)	0	13	39	0	58	210

Chemical	CASRN	Detection[a]	$C_{air\text{-}field}$					
			Minimum	Mean ($C_{GI\text{-}avg}$)	Standard Deviation	Median	95th Percentile	Maximum
Benzene, 1,2,4,5-tetramethyl-	95-93-2	5 (35)	0	2.5	6.5	0	15	27
Benzene, 1,2,4-trimethyl-	95-63-6	13 (35)	0	120	210	0	420	970
Benzene, 1,4-dichloro	106-46-7	7 (35)	0	19	42	0	120	120
Benzene, 1-chloro-4-(trifluoromethyl)-	98-56-6	34 (35)	0	570	600	380	1700	2100
Benzene, 1-ethyl-2,4-dimethyl-	874-41-9	7 (35)	0	5.3	14	0	27	71
Benzene, 2-ethyl-1,4-dimethyl-	1758-88-9	12 (35)	0	7.5	15	0	33	68
Benzene, butyl-	104-51-8	2 (35)	0	2.6	13	0	5.5	73
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	793-24-8	26 (34)	0	3.7	4.4	2.2	12	15
Benzo[a]pyrene	50-32-8	28 (34)	0	1.1	1.2	0.61	3.1	4.7
Benzo[b]fluoranthene	205-99-2	2 (34)	0	0.025	0.1	0	0.15	0.42
7H-Benzo[c]fluorene	205-12-9	13 (34)	0	0.054	0.082	0	0.14	0.36
Benzo[e]pyrene	192-97-2	6 (34)	0	0.019	0.043	0	0.13	0.13
Benzo[g,h,i]perylene	191-24-2	19 (34)	0	0.13	0.19	0.05	0.52	0.76
Benzo[k]fluoranthene	207-08-9	4 (34)	0	0.031	0.09	0	0.23	0.35
Benzothiazole	95-16-9	19 (35)	0	37	42	21	120	120
Benzothiazole, 2-phenyl-	883-93-2	27 (34)	0	2.9	3.9	1.5	10	17
2-Benzothiazolone	934-34-9	5 (34)	0	4.6	12	0	30	45
Benzyl butyl phthalate	85-68-7	7 (34)	0	3.4	7.3	0	23	23
Bis(2-Ethylhexyl)adipate	103-23-1	1 (34)	0	22	130	0	0	730
Butanal	123-72-8	13 (35)	0	310	750	0	1800	3800
Butanal	123-72-8	9 (34)	0	41	86	0	220	370
2-Butanone	78-93-3	30 (34)	0	570	410	460	1200	1400
2-Butoxyethanol	111-76-2	1 (35)	0	4.9	29	0	0	170
n-Caproic acid vinyl ester	3050-69-9	1 (34)	0	6.8	40	0	0	230
3-Carene	13466-78-9	1 (35)	0	0.77	4.6	0	0	27
Chrysene	218-01-9	13 (34)	0	0.2	0.32	0	0.77	1.3
Coronene	191-07-1	10 (34)	0	0.085	0.16	0	0.3	0.73
Cyclohexanamine, N-cyclohexyl-	101-83-7	19 (34)	0	0.34	0.57	0.23	1	3.1
Cyclohexylamine	108-91-8	4 (34)	0	2.3	6.7	0	15	31
Cyclopenta[cd]pyrene	27208-37-3	28 (34)	0	0.073	0.088	0.027	0.21	0.41
Cyclopentasiloxane, decamethyl-	541-02-6	18 (35)	0	160	270	49	570	1300
Cyclotetrasiloxane, octamethyl-	556-67-2	13 (35)	0	58	92	0	230	330
Cyclotrisiloxane, hexamethyl-	541-05-9	1 (35)	0	73	430	0	0	2600

Chemical	CASRN	Detection[a]	$C_{air\text{-}field}$					
			Minimum	Mean ($C_{GI\text{-}avg}$)	Standard Deviation	Median	95th Percentile	Maximum
p-Cymene	99-87-6	21 (35)	0	25	30	16	84	120
Decanal	112-31-2	7 (35)	0	28	96	0	110	550
Decane	124-18-5	11 (35)	0	54	97	0	300	310
Dibenz[a,h]anthracene	53-70-3	14 (34)	0	0.14	0.29	0	0.71	1.2
Dibenzothiophene	132-65-0	14 (34)	0	1.2	1.9	0	5.3	6.8
Dibutyl phthalate	84-74-2	7 (34)	0	380	960	0	1700	4900
N,N-Dicyclohexylmethylamine	7560-83-0	18 (34)	0	0.33	0.47	0.25	1.4	2
Diethyl phthalate	84-66-2	1 (34)	0	2.6	15	0	0	89
Diisobutyl phthalate	84-69-5	15 (34)	0	14	28	0	45	150
Diisooctylphthalate	27554-26-3	9 (34)	0	49	160	0	130	950
Dimethyl phthalate	131-11-3	4 (34)	0	3.6	12	0	24	62
Di-n-octyl phthalate	117-84-0	5 (34)	0	0.096	0.25	0	0.55	1.1
2,5-di-tert-Butyl-1,4-benzoquinone	2460-77-7	26 (34)	0	32	44	17	130	140
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	8 (34)	0	17	33	0	85	110
Dodecane	112-40-3	4 (35)	0	6.7	23	0	38	120
Ethylbenzene	100-41-4	13 (35)	0	170	290	0	700	1200
Fluoranthene	206-44-0	21 (34)	0	3.8	4.8	1.4	13	17
Fluorene	86-73-7	15 (34)	0	6	12	0	21	61
Formaldehyde	50-00-0	34 (34)	810	3800	2900	3200	6400	16000
Furan, 2-methyl	534-22-5	34 (35)	0	110	89	78	250	410
Heptanal	111-71-7	7 (35)	0	15	37	0	130	130
Heptane	142-82-5	20 (35)	0	230	340	44	950	1500
Hexadecane	544-76-3	11 (34)	0	32	58	0	170	230
2,5-Hexanedione	110-13-4	5 (34)	0	27	71	0	180	260
Hexanal	66-25-1	30 (35)	0	790	1000	370	3000	4000
Hexane	110-54-3	26 (35)	0	670	1500	300	1800	8700
1-Hexanol, 2-ethyl-	104-76-7	6 (35)	0	7.8	20	0	39	91
Indan	496-11-7	12 (35)	0	14	25	0	59	110
Indeno[1,2,3-cd]pyrene	193-39-5	3 (34)	0	0.11	0.35	0	1.2	1.2
D-Limonene	5989-27-5	4 (35)	0	7.7	22	0	67	67
Limonene	138-86-3	14 (34)	0	29	40	0	100	160
Mesitylene	108-67-8	15 (35)	0	28	49	0	110	230
Methacrolein	78-85-3	20 (35)	0	76	97	43	220	430
Methyl Isobutyl Ketone	108-10-1	5 (35)	0	16	43	0	120	180
Methyl stearate	112-61-8	10 (34)	0	5.5	12	0	37	44
Naphthalene	91-20-3	9 (35)	0	27	55	0	110	260
Naphthalene, 1,2-dimethyl-	573-98-8	4 (34)	0	0.37	1.1	0	3.6	3.6

Chemical	CASRN	Detection[a]	$C_{air\text{-}field}$					
			Minimum	Mean ($C_{GI\text{-}avg}$)	Standard Deviation	Median	95th Percentile	Maximum
Naphthalene, 1,6-dimethyl-	575-43-9	14 (34)	0	2.7	4.1	0	13	15
Naphthalene, 1-methyl-	90-12-0	15 (34)	0	22	37	0	97	150
Naphthalene, 2-(bromomethyl)-	939-26-4	11 (34)	0	0.74	1.1	0	2.5	2.5
Naphthalene, 2,3-dimethyl-	581-40-8	14 (34)	0	2	3	0	9.1	10
Naphthalene, 2-methyl-	91-57-6	10 (34)	0	33	70	0	160	320
Nonanal	124-19-6	2 (35)	0	7.8	32	0	41	140
1-Octadecene	112-88-9	16 (34)	0	4.4	5.7	0	15	18
Octanal	124-13-0	24 (35)	0	45	52	28	130	210
Octane	111-65-9	10 (35)	0	60	110	0	250	420
4-tert-Octylphenol	140-66-9	10 (34)	0	1.8	3.8	0	10	14
17-Pentatriacontene	6971-40-0	2 (34)	0	0.73	3.1	0	2.9	17
a-Pinene	7785-70-8	12 (35)	0	37	82	0	170	380
N-Phenylbenzamide	93-98-1	6 (34)	0	9	20	0	55	55
Phenanthrene	85-01-8	17 (34)	0	13	20	7	57	84
Phenanthrene, 1-methyl	832-69-9	17 (34)	0	0.82	1.1	0.37	3	3.4
Phenanthrene, 2-methyl-	2531-84-2	18 (34)	0	1.5	1.9	1	5.5	6.3
Phenanthrene, 3-methyl	832-71-3	18 (34)	0	1.8	2.3	0.96	6.6	7.5
Phenol	108-95-2	18 (35)	0	58	74	34	210	210
Phenol, 2,4-bis(1-methyl-1-phenylethyl)-	2772-45-4	2 (34)	0	0.018	0.072	0	0.11	0.3
Phenol, 4-(1-phenylethyl)-	1988-89-2	9 (34)	0	0.44	1.2	0	2.1	6.3
Propionaldehyde	123-38-6	12 (34)	0	180	370	0	730	1800
Pyrene	129-00-0	20 (34)	0	3.2	4.1	1.3	11	14
Pyridine, 2-(4-methylphenyl)-	4467-06-5	2 (34)	0	0.035	0.18	0	0.062	1
Resorcinol	108-46-3	18 (34)	0	19	27	7.6	61	120
Styrene	100-42-5	17 (35)	0	59	120	0	200	660
Tetrachloroethylene	127-18-4	7 (35)	0	48	110	0	320	420
Tetradecane	629-59-4	3 (35)	0	8.1	29	0	71	140
Texanol, TXIB (mono-isomer)	25265-77-4	15 (35)	0	100	320	0	480	1600
m-Tolualdehyde	620-23-5	19 (34)	0	270	280	220	740	900
Toluene	108-88-3	35 (35)	200	1400	1600	600	3700	7700
Trichloroethylene	79-01-6	12 (35)	0	9.7	19	0	33	94
Trichloromethane	67-66-3	10 (35)	0	38	82	0	230	350
TXIB "Kodaflex"	6846-50-0	1 (35)	0	2	12	0	0	69
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	14 (34)	0	3.8	5.3	0	13	19
Undecane	1120-21-4	5 (35)	0	13	34	0	100	130
Valeraldehyde	110-62-3	11 (34)	0	930	1600	0	4200	4600

Chemical	CASRN	Detection[a]	$C_{air\text{-}field}$					
			Minimum	Mean ($C_{GI\text{-}avg}$)	Standard Deviation	Median	95th Percentile	Maximum
m/p-Xylene	106-42-3	25 (35)	0	580	830	230	2000	3500
o-Xylene	95-47-6	13 (35)	0	190	320	0	770	1300

[a] Detection value is the number of fields with concentration in extracts above the method of detection for an organic chemical. The total number of fields with samples collected are shown in the parathenesis. Values are rounded to two significant figures.

Table D-2. Individual-Field Off-Field Concentrations of Organic Chemicals in Samples Collected from the Air ($C_{air\text{-}field}$, nanograms per gram of crumb rubber) of 35 Fields During the State-Wide Study

Chemical	CASRN	Detection[a]	$C_{air\text{-}field}$					
			Minimum	Mean ($C_{ing\text{-}avgr}$)	Standard Deviation	Median	95th Percentile	Maximum
Acenaphthylene	208-96-8	8 (33)	0	1.1	2.3	0	6.1	9.4
Aniline	62-53-3	8 (33)	0	7.2	14	0	25	60
Anthracene	120-12-7	4 (33)	0	0.2	0.62	0	1.4	2.8
Anthracene, 2-methyl-	613-12-7	11 (33)	0	0.052	0.097	0	0.26	0.37
Anthracene, 9,10-dimethyl	781-43-1	12 (33)	0	0.084	0.15	0	0.35	0.67
Anthracene, 9-phenyl	602-55-1	2 (33)	0	0.037	0.15	0	0.25	0.61
Benzaldehyde	100-52-7	14 (34)	0	97	150	0	390	580
Benzene	71-43-2	34 (34)	180	640	530	400	1500	2700
Benzene, 1,2,3-trimethyl-	526-73-8	6 (34)	0	17	40	0	100	160
Benzene, 1,2,4,5-tetramethyl-	95-93-2	5 (34)	0	3.2	8.9	0	18	41
Benzene, 1,2,4-trimethyl-	95-63-6	12 (34)	0	130	220	0	540	890
Benzene, 1,4-dichloro	106-46-7	6 (34)	0	17	40	0	120	120
Benzene, 1-chloro-4-(trifluoromethyl)-	98-56-6	33 (34)	0	580	630	230	1900	2000
Benzene, 1-ethyl-2,4-dimethyl-	874-41-9	7 (34)	0	6	14	0	34	52
Benzene, 2-ethyl-1,4-dimethyl-	1758-88-9	11 (34)	0	8.4	17	0	35	77
Benzene, butyl-	104-51-8	3 (34)	0	4.3	15	0	37	73
1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-	793-24-8	19 (33)	0	4.2	5.5	1.8	14	16
Benzo[a]pyrene	50-32-8	24 (33)	0	1.4	2.2	0.58	5	9.9
Benzo[b]fluoranthene	205-99-2	3 (33)	0	0.038	0.12	0	0.42	0.42
7H-Benzo[c]fluorene	205-12-9	6 (33)	0	0.031	0.074	0	0.14	0.33
Benzo[e]pyrene	192-97-2	6 (33)	0	0.027	0.062	0	0.13	0.26
Benzo[g,h,i]perylene	191-24-2	16 (33)	0	0.13	0.22	0	0.48	0.99
Benzo[k]fluoranthene	207-08-9	3 (33)	0	0.032	0.1	0	0.35	0.35
Benzothiazole	95-16-9	2 (34)	0	4.8	20	0	29	82
Benzothiazole, 2-phenyl-	883-93-2	15 (33)	0	0.43	0.59	0	1.7	1.8

Chemical	CASRN	Detection[a]	$C_{air\text{-}field}$					
			Minimum	Mean ($C_{ing\text{-}avgr}$)	Standard Deviation	Median	95th Percentile	Maximum
2-Benzothiazolone	934-34-9	3 (33)	0	4.1	13	0	45	45
Benzyl butyl phthalate	85-68-7	5 (33)	0	4.4	11	0	23	51
Bis(2-Ethylhexyl)adipate	103-23-1	2 (33)	0	17	68	0	110	280
Butanal	123-72-8	12 (34)	0	280	750	0	2000	3400
2-Butoxyethanol	111-76-2	1 (34)	0	4.7	28	0	0	160
n-Caproic acid vinyl ester	3050-69-9	3 (33)	0	13	54	0	70	300
3-Carene	13466-78-9	1 (34)	0	1.6	9.3	0	0	54
Chrysene	218-01-9	7 (33)	0	0.1	0.22	0	0.42	0.93
Coronene	191-07-1	7 (33)	0	0.068	0.15	0	0.25	0.7
Cyclohexanamine, N-cyclohexyl-	101-83-7	10 (33)	0	0.2	0.35	0	1.1	1.2
Cyclohexylamine	108-91-8	1 (33)	0	0.94	5.4	0	0	31
Cyclopenta[cd]pyrene	27208-37-3	22 (33)	0	0.064	0.082	0.027	0.23	0.26
Cyclopentasiloxane, decamethyl-	541-02-6	14 (34)	0	150	260	0	600	1200
Cyclotetrasiloxane, octamethyl-	556-67-2	13 (34)	0	52	83	0	220	320
Cyclotrisiloxane, hexamethyl-	541-05-9	3 (34)	0	77	290	0	530	1600
p-Cymene	99-87-6	18 (34)	0	26	33	16	92	120
Decanal	112-31-2	1 (34)	0	17	100	0	0	580
Decane	124-18-5	12 (34)	0	60	98	0	240	350
Dibenz[a,h]anthracene	53-70-3	9 (33)	0	0.09	0.2	0	0.58	0.73
Dibenzothiophene	132-65-0	12 (33)	0	1.2	2.1	0	5.7	8.5
Dibutyl phthalate	84-74-2	5 (33)	0	300	1100	0	1200	5800
N,N-Dicyclohexylmethylamine	7560-83-0	12 (33)	0	0.35	0.54	0	1.3	1.8
Diethyl phthalate	84-66-2	2 (33)	0	11	43	0	71	180
Diisobutyl phthalate	84-69-5	14 (33)	0	15	25	0	74	91
Diisooctylphthalate	27554-26-3	6 (33)	0	15	32	0	81	81
Dimethyl phthalate	131-11-3	3 (33)	0	3.3	12	0	24	60
Di-n-octyl phthalate	117-84-0	3 (33)	0	0.099	0.32	0	1.1	1.1
2,5-di-tert-Butyl-1,4-benzoquinone	2460-77-7	26 (33)	0	39	66	14	150	310
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	3 (33)	0	11	39	0	85	190
Dodecane	112-40-3	3 (34)	0	8.7	30	0	80	120
Ethylbenzene	100-41-4	13 (34)	0	180	310	0	800	1300
Fluoranthene	206-44-0	14 (33)	0	2.2	4.1	0	10	19
Fluorene	86-73-7	11 (33)	0	5	11	0	22	53
Furan, 2-methyl	534-22-5	21 (34)	0	38	60	30	140	270

Chemical	CASRN	Detection[a]	$C_{air\text{-}field}$					
			Minimum	Mean ($C_{ing\text{-}avgr}$)	Standard Deviation	Median	95th Percentile	Maximum
Heptanal	111-71-7	5 (34)	0	15	39	0	130	130
Heptane	142-82-5	17 (34)	0	230	360	44	900	1700
Hexadecane	544-76-3	9 (33)	0	46	93	0	200	420
2,5-Hexanedione	110-13-4	3 (33)	0	35	130	0	260	640
Hexanal	66-25-1	27 (34)	0	870	1200	430	2900	5800
Hexane	110-54-3	28 (34)	0	460	510	270	1400	2000
1-Hexanol, 2-ethyl-	104-76-7	7 (34)	0	18	45	0	61	230
Indan	496-11-7	12 (34)	0	13	26	0	63	110
Indeno[1,2,3-cd]pyrene	193-39-5	2 (33)	0	0.074	0.3	0	0.49	1.2
D-Limonene	5989-27-5	5 (34)	0	9.9	24	0	67	67
Limonene	138-86-3	10 (33)	0	22	47	0	74	240
Mesitylene	108-67-8	13 (34)	0	28	50	0	130	200
Methacrolein	78-85-3	16 (34)	0	70	94	0	220	400
Methyl Isobutyl Ketone	108-10-1	1 (34)	0	3.6	21	0	0	120
Methyl stearate	112-61-8	8 (33)	0	5.5	12	0	35	44
Naphthalene	91-20-3	9 (34)	0	29	59	0	130	260
Naphthalene, 1,2-dimethyl-	573-98-8	6 (33)	0	0.78	1.8	0	3.6	7.6
Naphthalene, 1,6-dimethyl-	575-43-9	12 (33)	0	2.8	5	0	14	20
Naphthalene, 1-methyl-	90-12-0	12 (33)	0	22	35	0	97	120
Naphthalene, 2-(bromomethyl)-	939-26-4	8 (33)	0	0.77	1.6	0	2.5	7.8
Naphthalene, 2,3-dimethyl-	581-40-8	12 (33)	0	2.1	3.6	0	10	15
Naphthalene, 2-methyl-	91-57-6	12 (33)	0	35	59	0	170	190
1-Octadecene	112-88-9	14 (33)	0	4.1	6.1	0	18	19
Octanal	124-13-0	16 (34)	0	44	63	0	170	240
Octane	111-65-9	9 (34)	0	73	130	0	350	480
4-tert-Octylphenol	140-66-9	7 (33)	0	0.53	1.3	0	3.1	5.8
17-Pentatriacontene	6971-40-0	1 (33)	0	0.5	2.9	0	0	17
a-Pinene	7785-70-8	9 (34)	0	46	100	0	290	450
N-Phenylbenzamide	93-98-1	4 (33)	0	8.9	27	0	55	130
Phenanthrene	85-01-8	12 (33)	0	11	22	0	67	92
Phenanthrene, 1-methyl	832-69-9	13 (33)	0	0.49	0.83	0	2.2	3.4
Phenanthrene, 2-methyl-	2531-84-2	13 (33)	0	0.96	1.7	0	4.8	6.3
Phenanthrene, 3-methyl	832-71-3	13 (33)	0	1.1	1.9	0	5.2	7.7
Phenol	108-95-2	12 (34)	0	53	82	0	210	210
Phenol, 4-(1-phenylethyl)-	1988-89-2	9 (33)	0	0.64	1.4	0	2.7	7
Pyrene	129-00-0	14 (33)	0	1.6	2.7	0	7.7	10
Pyridine, 2-(4-methylphenyl)-	4467-06-5	1 (33)	0	0.0054	0.031	0	0	0.18

Chemical	CASRN	Detection[a]	$C_{air\text{-}field}$					
			Minimum	Mean ($C_{ing\text{-}avgr}$)	Standard Deviation	Median	95th Percentile	Maximum
Resorcinol	108-46-3	18 (33)	0	32	55	15	120	260
Styrene	100-42-5	13 (34)	0	60	130	0	220	670
Tetrachloroethylene	127-18-4	7 (34)	0	49	110	0	330	420
Tetradecane	629-59-4	2 (34)	0	6.3	27	0	25	140
Texanol, TXIB (mono-isomer)	25265-77-4	11 (34)	0	100	400	0	330	2300
Toluene	108-88-3	34 (34)	200	1400	1600	710	4000	7100
Trichloroethylene	79-01-6	11 (34)	0	9.8	19	0	38	84
Trichloromethane	67-66-3	7 (34)	0	37	80	0	230	230
TXIB "Kodaflex"	6846-50-0	2 (34)	0	4.1	17	0	24	69
5,9-Undecadien-2-one, 6,10-dimethyl-	689-67-8	13 (33)	0	2.7	3.7	0	6.2	15
Undecane	1120-21-4	7 (34)	0	18	40	0	100	160
m/p-Xylene	106-42-3	24 (34)	0	610	880	230	2200	3400
o-Xylene	95-47-6	11 (34)	0	190	350	0	850	1400

[a] Detection value is the number of fields with concentration in extracts above the method of detection for an organic chemical. The total number of fields with samples collected are shown in the parathenesis.

D.4.3. Source Designations of Volatile Organic Chemicals (VOCs) Detected in Air Based on Statistical Analysis of Stratified VOC Data

Linear mixed-effect model analysis was performed on stratified volatile organic chemical (VOC) sample, or tower sample, data (Table D-48 and Table D-49). These data are one-hour VOC vapor samples collected in air on each field at four levels above the field surface as described in Appendix Sections D.1.2.4 and D1.2.5. This type of analysis models the detected concentrations in tower samples as a function of position height (a fixed effect that has a predictable impact on the chemical concentration) and field (a random effect that has an unpredictable impact on the impact) for each chemical. Values of P1, P2, P3, and P4 were used for position number to represent sample heights of 0.1, 0.5, 1.07, and 1.63 meters above field surface, respectively. OEHHA performed the analysis using RStudio (RStudio Team, 2018) with R (version 3.6.0) using the *lme4* package (Bates *et al.*, 2015). We used the *lmerTest* package (Kuznetsova *et al.*, 2017) to determine p-values for the significance of position number in regards to chemical concentration with analysis of variance (ANOVA) via Satterthwaite's degrees of freedom method. Table D-48 and Table D-49 detail the intercepts (nanograms per cubic meter air), change in concentration change per height at P2 (nanograms per cubic meter per meter), slope estimates, and model p-values for the 61 VOCs identified in tower samples. For chemical models that show position number to have a significant effect (model p-value <0.05) and show a trend of decreasing concentrations as sample height increases (negative slope estimates at P2 to P4) are presumed to have the turf field as the primary exposure source. These

chemicals are designated as “field-related chemicals” for the purposes of risk assessment in the Synthetic Turf Study. All other tower VOCs are designated to as “Non-Field-Related Chemicals”. Table D-50 and Table D-51 show the mean air concentration and range (minimum to maximum) at each height level for field-related and non-field-related chemicals, respectively.

While this method boasts the benefit of incorporating both fixed and random effects on the concentration data, one limitation is our use of a single random effect. There are undoubtedly additional variables, apart from the field, that could have an effect on the chemical concentration that our study measurements did not capture and are not included in the model. Another limitation is that our study’s data collection was limited. For each field, data collection was for a single day only. A larger dataset including, for example, data from more fields or encompassing more sampling dates and locations could provide more information about the relationship between concentration and position height.

Table D-1. Linear Mixed-Effect Model Analysis Results for Stratified Volatile Organic Chemical Samples (Tower Samples)—Field-Related Chemicals

Chemical (CASRN)	Detection[a]	Intercept Estimate[b], ng per cubic meter	Concentration Change per Height at P2, ng per cubic meter per meter	P3 Slope Estimate[b], ng per cubic meter	P4 Slope Estimate[b], ng per cubic meter	Linear Mixed-Effect Model with Position Number Anova p-value[b]
Benzaldehyde (100-52-7)	33-35	190***	-28**	-47***	-37***	<0.001
Benzene, 1,2,3-trimethyl- (526-73-8)	32-34	37***	-3.8*	-6***	-5.5***	<0.01
Benzene, 1,2,4,5-tetramethyl- (95-93-2)	18-19	15***	-3.2**	-4.3***	-4.5***	<0.001
Benzene, 1,2,4-trimethyl- (95-63-6)	33-35	160***	-14*	-24***	-23***	<0.01
Benzene, 1-ethyl-2,4-dimethyl- (874-41-9)	20-22	17***	-2.6**	-4***	-3.6***	<0.001
Benzene, 2-ethyl-1,4-dimethyl- (1758-88-9)	20-22	17***	-1.7	-3.2***	-2.8**	<0.01
Benzene, butyl- (104-51-8)	27-28	19***	-2.7**	-4.6***	-3.5***	<0.001
Benzothiazole (95-16-9)	33-35	350***	-210***	-250***	-270***	<0.001
Benzothiazole, 2-methylthio- (615-22-5)	11	22***	-19***	-20***	-21***	<0.001
Biphenyl (92-52-4)	26-27	5.3***	-1.1*	-1.8***	-1.9***	<0.001
Butanal (123-72-8)	33-35	400***	-130**	-92	-120*	<0.05
Butylated Hydroxytoluene (128-37-0)	7-8	19***	-15***	-19***	-19***	<0.001
3-Carene (13466-78-9)	8	17**	-6*	-13***	-6.6*	<0.001
Cyclohexanone (108-94-1)	25-27	140***	-75***	-110***	-110***	<0.001
Cyclopentasiloxane, decamethyl- (541-02-6)	33-35	190***	-19	-44*	-66***	<0.01
Cyclotetrasiloxane, octamethyl- (556-67-2)	33-35	110***	-5.6	-15**	-21***	<0.001
p-Cymene (99-87-6)	33-35	40***	-5.8**	-7.2***	-6.2***	<0.001
Decane (124-18-5)	26-28	120***	-12	-23***	-24***	<0.001
Dibutyl phthalate (84-74-2)	30-31	160**	-19	-97*	-130**	<0.01
Diethyl phthalate (84-66-2)	30-31	28***	-4.2	-10***	-11***	<0.001
D-Limonene (5989-27-5)	27-28	42***	-17***	-23***	-20***	<0.001

Chemical (CASRN)	Detection[a]	Intercept Estimate[b], ng per cubic meter	Concentration Change per Height at P2, ng per cubic meter per meter	P3 Slope Estimate[b], ng per cubic meter	P4 Slope Estimate[b], ng per cubic meter	Linear Mixed-Effect Model with Position Number Anova p-value[b]
Dodecane (112-40-3)	19	39***	-7.1	-17***	-13**	<0.01
Formamide, N-(1,1-dimethylethyl)- (2425-74-3)	5-6	27***	-27**	-27**	-22*	<0.05
Furan, 2-methyl (534-22-5)	33-35	460***	-240***	-310***	-330***	<0.001
Heptanal (111-71-7)	28-29	120***	-50***	-55***	-51***	<0.001
2-Hexanone, 5-methyl (110-12-3)	18-19	42***	-18**	-26***	-24***	<0.001
Indan (496-11-7)	26-27	25***	-3.1*	-4.2***	-4.3***	<0.01
Mesitylene (108-67-8)	31-33	34***	-3.9*	-5.2**	-4.7**	<0.01
Methacrolein (78-85-3)	29-31	220***	-56***	-72***	-67***	<0.001
Methyl Isobutyl Ketone (108-10-1)	28-30	430***	-220***	-280***	-280***	<0.001
Naphthalene (91-20-3)	33-35	53***	-6.1**	-9.5***	-8.3***	<0.001
Naphthalene, 1-methyl- (90-12-0)	17-18	11***	-2.1**	-3.5***	-3.6***	<0.001
Naphthalene, 2-methyl- (91-57-6)	25-26	15***	-3**	-5.1***	-5.5***	<0.001
Octanal (124-13-0)	25	150***	-62**	-84***	-72***	<0.001
Octane (111-65-9)	33-35	150***	-13	-19**	-15*	<0.05
a-Pinene (7785-70-8)	19-20	110***	-30**	-46***	-35***	<0.001
Styrene (100-42-5)	33-35	100***	-15***	-19***	-16***	<0.001
g-Terpinene (99-85-4)	1	560***	-38	69	-39	<0.01
TXIB "Kodaflex" (6846-50-0)	29-30	38***	0.4	-7.9**	-8.4**	<0.01
Undecane (1120-21-4)	25	63***	-5.6	-17***	-17***	<0.001

[a]Number of detections of a chemical at each position (P1 to P4) on the 35 fields.
[b] Linear mixed-effect model analysis, p-values: *** <0.001, **<0.01, *<0.05. A chemical is designated as "Field-Related Chemical" if slope estimates at all positions are mostly negative and model p-value<0.05, otherwise it is designated as "Non-Field-Related Chemical".
CASRN: Chemical Abstracts Service Registry Number; P2: Position 2 at 0.5 meters above field surface; P3: Position 3 at 1.07 meters above field surface; and P4: Position 4: 1.63 meters above field surface. Value of estimates are rounded to two significant figures. p-Values are rounded to one significant figure.

Table D-2. Linear Mixed-Effect Model Analysis Results for Stratified Volatile Organic Chemical Samples (Tower Samples)—Non-Field-Related Chemicals

Chemical (CASRN)	Detection[a]	Intercept Estimate[b], ng per cubic meter	Concentration Change per Height at P2, ng per cubic meter per meter	P3 Slope Estimate[b], ng per cubic meter	P4 Slope Estimate[b], ng per cubic meter	Linear Mixed-Effect Model with Position Number Anova p-value[b]
Benzene (71-43-2)	33-35	750***	-38	-30	3.5	≥0.05
Benzene, 1,4-dichloro (106-46-7)	33-34	49***	-3.9	-4.1	-3.5	≥0.05
Benzene, 1-chloro-4-(trifluoromethyl)- (98-56-6)	33-35	750***	-39	-41	-36	≥0.05
2-Butoxyethanol (111-76-2)	5	41	18	46	140	≥0.05
Cyclotrisiloxane, hexamethyl- (541-05-9)	33-35	440***	-14	-39	-41	≥0.05
Decanal (112-31-2)	19	180*	-130	-150	-33	≥0.05
Ethylbenzene (100-41-4)	33-35	270***	-17	-23*	-17	≥0.05
Heptane (142-82-5)	33-35	300***	-1.7	0.94	30	≥0.05
Hexanal (66-25-1)	30-32	810***	-230	-110	-200	≥0.05
Hexane (110-54-3)	33-35	560***	-38	69	-39	≥0.05
1-Hexanol, 2-ethyl- (104-76-7)	31-33	130***	-55	-34	-63	≥0.05
Nonanal (124-19-6)	33-35	260***	-88*	-87*	-79*	≥0.05
Phenol (108-95-2)	33-35	330***	-150	-170	-170	≥0.05
Tetrachloro-ethylene (127-18-4)	33-35	120***	-4.2	-5.9	-4.2	≥0.05
Tetradecane (629-59-4)	22	42***	1.3	-6.7	-3.2	≥0.05
Texanol, TXIB (mono-isomer) (25265-77-4)	14	740	-160	-630	-140	≥0.05
Toluene (108-88-3)	33-35	750***	-38	-30	3.5	≥0.05
Trichloroethylene (79-01-6)	13	29***	-0.72	2.1	-1.2	≥0.05
Trichloromethane (67-66-3)	33-35	120***	12	13	16*	≥0.05
m/p-Xylene (106-42-3)	33-35	680***	-41	-69*	-56	≥0.05
o-Xylene (95-47-6)	33-35	290***	-17	-27*	-22	≥0.05

[a] Number of detections of a chemical at each position (P1 to P4) on the 35 fields.

[b] Linear mixed-effect model analysis, p-values: *** <0.001, **<0.01, *<0.05. A chemical is designated as

"Field-Related Chemical" if slope estimates at all positions are mostly negative and model p-value<0.05, otherwise it is designated as "Non-Field-Related Chemical".
CASRN: Chemical Abstracts Service Registry Number; P2: Position 2 at 0.5 meters above field surface; P3: Position 3 at 1.07 meters above field surface; and P4: Position 4: 1.63 meters above field surface. Value of estimates are rounded to two significant figures. p-Values are rounded to one significant figure.

Table D-3. Designated Stratified Field-Related Volatile Organic Chemicals (Stratified VOCs) Concentrations in Air (nanograms per cubic meter air)

Chemical (CASRN)	P1 Mean (Stdev)	P1 Range (Detection Frequency)	P2 Mean (Stdev)	P2 Range (Detection Frequency)	P3 Mean (Stdev)	P3 Range (Detection Frequency)	P4 Mean (Stdev)	P4 Range (Detection Frequency)
Benzaldehyde (100-52-7)	190 (160)	26-610 (35/35)	170 (170)	27-700 (33/33)	140 (130)	19-540 (35/35)	150 (150)	16-610 (35/35)
Benzene, 1,2,3-trimethyl- (526-73-8)	36 (39)	0-130 (34/35)	34 (39)	0-130 (29/33)	31 (36)	0-120 (30/35)	31 (35)	0-120 (30/35)
Benzene, 1,2,4,5-tetramethyl- (95-93-2)	8.4	0-37 (18/35)	7 (9.6)	0-40 (16/33)	6 (8.5)	0-30 (17/35)	5.9 (9.3)	0-37 (14/35)
Benzene, 1,2,4-trimethyl- (95-63-6)	160 (180)	9.8-580 (35/35)	150 (180)	6.7-570 (33/33)	140 (170)	4.7-640 (35/35)	140 (160)	0-550 (34/35)
Benzene, 1-ethyl-2,4-dimethyl- (874-41-9)	11 (13)	0-39 (22/35)	9.5 (12)	0-38 (17/33)	8.1 (12)	0-43 (17/35)	8.3 (12)	0-36 (18/35)
Benzene, 2-ethyl-1,4-dimethyl- (1758-88-9)	10 (12)	0-35 (22/35)	9.8 (12)	0-39 (18/33)	8.4 (12)	0-48 (17/35)	8.6 (12)	0-38 (18/35)
Benzene, butyl- (104-51-8)	16 (16)	0-50 (27/35)	14 (16)	0-51 (23/33)	12 (15)	0-54 (20/35)	13 (15)	0-50 (23/35)
Benzothiazole (95-16-9)	350 (280)	3.5-1100 (35/35)	130 (100)	3.4-450 (33/33)	93 (77)	5.2-380 (35/35)	77 (56)	0-260 (34/35)
Benzothiazole, 2-methylthio- (615-22-5)	6.9 (16)	0-77 (11/35)	0.86 (4)	0-22 (2/33)	0.5 (3)	0-18 (1/35)	0.32 (1.9)	0-11 (1/35)
Biphenyl (92-52-4)	4.1 (3.7)	0-14 (25/35)	3.4 (3.6)	0-13 (20/33)	2.7 (3.1)	0-12 (21/35)	2.6 (2.7)	0-9.8 (20/35)
Butanal (123-72-8)	400 (270)	76-1100 (35/35)	280 (180)	20-690 (33/33)	310 (350)	54-1800 (35/35)	280 (250)	0-1400 (34/35)
Butylated Hydroxytoluene (128-37-0)	4.4 (11)	0-55 (8/35)	0.91 (3.8)	0-19 (2/33)	0 (0)	0-0 (0/35)	0 (0)	0-0 (0/35)
3-Carene (13466-78-9)	4 (9.2)	0-42 (8/35)	2.8 (8.3)	0-39 (5/33)	0.99 (5.9)	0-35 (1/35)	2.5 (8.2)	0-41 (5/35)
Cyclohexanone (108-94-1)	110 (110)	0-350 (26/35)	53 (52)	0-210 (20/33)	28 (43)	0-150 (13/35)	26 (42)	0-150 (13/35)
Cyclopentasiloxane, decamethyl- (541-02-6)	190 (210)	5.2-730 (35/35)	180 (210)	9.7-700 (33/33)	150 (180)	11-770 (35/35)	120 (140)	0-570 (33/35)
Cyclotetrasiloxane, octamethyl- (556-67-2)	110 (110)	8.6-540 (35/35)	110 (100)	5.1-410 (33/33)	98 (96)	8.4-410 (35/35)	93 (88)	6.6-400 (35/35)
p-Cymene (99-87-6)	40 (30)	3.5-110 (35/35)	36 (28)	3.3-110 (33/33)	33 (29)	0-100 (34/35)	34 (28)	0-120 (34/35)

Chemical (CASRN)	P1 Mean (Stdev)	P1 Range (Detection Frequency)	P2 Mean (Stdev)	P2 Range (Detection Frequency)	P3 Mean (Stdev)	P3 Range (Detection Frequency)	P4 Mean (Stdev)	P4 Range (Detection Frequency)
Decane (124-18-5)	97 (160)	0-780 (27/35)	92 (160)	0-690 (23/33)	78 (140)	0-660 (23/35)	77 (140)	0-590 (22/35)
Dibutyl phthalate (84-74-2)	150 (370)	0-2000 (30/35)	140 (340)	0-1900 (28/33)	60 (150)	0-850 (30/35)	35 (74)	0-420 (29/35)
Diethyl phthalate (84-66-2)	25 (20)	0-70 (29/35)	22 (17)	0-68 (28/33)	16 (14)	0-68 (28/35)	15 (11)	0-41 (28/35)
D-Limonene (5989-27-5)	34 (33)	0-120 (27/35)	21 (28)	0-110 (17/33)	15 (29)	0-110 (13/35)	18 (28)	0-120 (17/35)
Dodecane (112-40-3)	21 (28)	0-110 (17/35)	18 (26)	0-77 (14/33)	12 (22)	0-79 (11/35)	14 (21)	0-72 (16/35)
Formamide, N-(1,1-dimethylethyl)- (2425-74-3)	4.7 (15)	0-78 (4/35)	0 (0)	0-0 (0/33)	0 (0)	0-0 (0/35)	0.93 (4)	0-21 (2/35)
Furan, 2-methyl (534-22-5)	460 (390)	21-1400 (35/35)	230 (170)	24-590 (33/33)	150 (100)	17-440 (35/35)	130 (84)	15-330 (35/35)
Heptanal (111-71-7)	100 (100)	0-400 (28/35)	61 (78)	0-270 (19/33)	54 (73)	0-290 (20/35)	57 (72)	0-330 (22/35)
2-Hexanone, 5-methyl (110-12-3)	23 (34)	0-150 (17/35)	14 (26)	0-110 (11/33)	8.9 (21)	0-98 (8/35)	10 (21)	0-78 (8/35)
Indan (496-11-7)	19 (23)	0-99 (26/35)	18 (21)	0-76 (24/33)	16 (21)	0-96 (26/35)	16 (20)	0-77 (26/35)
Mesitylene (108-67-8)	32 (36)	0-130 (32/35)	29 (35)	0-120 (25/33)	27 (34)	0-150 (27/35)	27 (33)	0-120 (28/35)
Methacrolein (78-85-3)	220 (180)	0-680 (29/35)	170 (150)	0-610 (25/33)	140 (140)	0-600 (26/35)	150 (160)	0-590 (24/35)
Methyl Isobutyl Ketone (108-10-1)	370 (310)	0-1200 (30/35)	170 (140)	0-520 (26/33)	130 (98)	0-310 (27/35)	120 (100)	0-370 (27/35)
Naphthalene (91-20-3)	53 (48)	5.2-150 (35/35)	49 (48)	5-150 (33/33)	44 (43)	3.2-160 (35/35)	45 (41)	3.2-160 (35/35)
Naphthalene, 1-methyl- (90-12-0)	5.5 (6.9)	0-26 (18/35)	4.7 (6.4)	0-17 (14/33)	3.8 (5.8)	0-19 (13/35)	3.7 (5.4)	0-15 (13/35)
Naphthalene, 2-methyl- (91-57-6)	11 (13)	0-58 (26/35)	9.2 (12)	0-36 (18/33)	7.3 (11)	0-43 (18/35)	6.9 (9.2)	0-28 (17/35)
Octanal (124-13-0)	110 (130)	0-520 (22/35)	69 (81)	0-290 (18/33)	50 (70)	0-220 (15/35)	58 (96)	0-450 (16/35)
Octane (111-65-9)	150 (130)	26-440 (35/35)	140 (140)	0-470 (31/33)	130 (130)	0-490 (34/35)	130 (130)	0-500 (34/35)
a-Pinene (7785-70-8)	65 (90)	0-340 (19/35)	50 (77)	0-340 (18/33)	39 (63)	0-230 (19/35)	46 (76)	0-320 (19/35)
Styrene (100-42-5)	100 (81)	16-340 (35/35)	86 (78)	18-350 (33/33)	84 (66)	16-270 (35/35)	86 (77)	16-340 (35/35)
g-Terpinene (99-85-4)	0 (0)	0-0 (0/35)	0 (0)	0-0 (0/33)	0 (0)	0-0 (0/35)	0.18 (1.1)	0-6.5 (1/35)
TXIB "Kodaflex" (6846-50-0)	32 (31)	0-150 (28/35)	34 (36)	0-190 (28/33)	25 (29)	0-130 (26/35)	25 (30)	0-110 (25/35)
Undecane (1120-21-4)	45 (49)	0-190 (24/35)	43 (54)	0-200 (18/33)	33 (43)	0-140 (18/35)	33 (44)	0-180 (19/35)

CASRN: Chemical Abstracts Service Registry Number; P2: Position 2 at 0.5 meters above field surface; P3: Position 3 at 1.07 meters above field surface; P4: Position 4: 1.63 meters above field surface; and Range: Minimum – Maximum.

Table D-4. Designated Non-Field-Related Volatile Organic Chemicals (Stratified VOCs) Concentrations in Air (nanograms per cubic meter air)

Chemical (CASRN)	P1 Mean (Stdev)	P1 Range (Detection Frequency)	P2 Mean (Stdev)	P2 Range (Detection Frequency)	P3 Mean (Stdev)	P3 Range (Detection Frequency)	P4 Mean (Stdev)	P4 Range (Detection Frequency)
Benzene (71-43-2)	750 (490)	200-2300 (35/35)	740 (450)	190-2100 (33/33)	720 (490)	180-2500 (35/35)	750 (460)	220-2100 (35/35)
Benzene, 1,4-dichloro (106-46-7)	48 (47)	0-130 (33/35)	47 (46)	0-140 (29/33)	44 (43)	0-140 (33/35)	45 (44)	0-150 (32/35)
2-Butoxyethanol (111-76-2)	5.8 (24)	0-100 (2/35)	8.8 (38)	0-210 (2/33)	12 (73)	0-430 (1/35)	25 (100)	0-440 (2/35)
Cyclotrisiloxane, hexamethyl- (541-05-9)	440 (700)	46-4300 (35/35)	450 (460)	42-2700 (33/33)	400 (460)	55-2800 (35/35)	400 (440)	56-2700 (35/35)
Decanal (112-31-2)	97 (340)	0-2000 (15/35)	27 (40)	0-120 (12/33)	17 (36)	0-150 (8/35)	79 (390)	0-2300 (6/35)
Ethylbenzene (100-41-4)	270 (270)	30-1000 (35/35)	270 (260)	15-950 (33/33)	250 (250)	22-1100 (35/35)	250 (250)	21-920 (35/35)
Heptane (142-82-5)	300 (310)	23-1400 (35/35)	310 (320)	0-1300 (32/33)	300 (350)	18-1500 (35/35)	330 (440)	21-2300 (35/35)
Hexanal (66-25-1)	740 (840)	0-4100 (29/35)	540 (610)	0-2700 (25/33)	640 (890)	0-3700 (26/35)	560 (890)	0-3900 (27/35)
Hexane (110-54-3)	560 (520)	46-1900 (35/35)	550 (470)	35-1600 (33/33)	630 (800)	43-4400 (35/35)	520 (450)	50-1500 (35/35)
1-Hexanol, 2-ethyl- (104-76-7)	120 (370)	0-2200 (28/35)	71 (100)	0-530 (26/33)	91 (160)	0-770 (27/35)	63 (100)	0-550 (25/35)
Nonanal (124-19-6)	260 (310)	0-1700 (34/35)	180 (160)	52-950 (33/33)	180 (120)	0-500 (33/35)	180 (230)	0-1400 (31/35)
Phenol (108-95-2)	330 (890)	21-5400 (35/35)	180 (150)	22-800 (33/33)	160 (120)	25-580 (35/35)	150 (110)	19-600 (35/35)
Tetrachloro-ethylene (127-18-4)	120 (130)	11-440 (35/35)	120 (130)	0-450 (32/33)	110 (130)	9.6-470 (35/35)	110 (130)	11-450 (35/35)
Tetradecane (629-59-4)	26 (32)	0-100 (17/35)	29 (35)	0-100 (17/33)	22 (32)	0-130 (15/35)	24 (30)	0-110 (17/35)
Texanol, TXIB (mono-isomer) (25265-77-4)	300 (1200)	0-6900 (11/35)	250 (1200)	0-6700 (10/33)	44 (89)	0-410 (10/35)	240 (1200)	0-7000 (9/35)
Toluene (108-88-3)	1400 (1300)	160-4300 (35/35)	1400 (1300)	94-4200 (33/33)	1300 (1200)	140-4700 (35/35)	1300 (1200)	170-4400 (35/35)
Trichloroethylene (79-01-6)	11 (17)	0-56 (12/35)	11 (17)	0-61 (12/33)	11 (19)	0-74 (13/35)	10 (16)	0-65 (12/35)
Trichloromethane (67-66-3)	120 (84)	36-460 (35/35)	140 (130)	38-770 (33/33)	130 (120)	32-700 (35/35)	140 (130)	34-780 (35/35)
m/p-Xylene (106-42-3)	680 (720)	57-2600 (35/35)	670 (710)	27-2500 (33/33)	610 (670)	34-2900 (35/35)	630 (660)	42-2400 (35/35)
o-Xylene (95-47-6)	290 (300)	23-1100 (35/35)	290 (300)	12-1000 (33/33)	260 (280)	18-1200 (35/35)	270 (280)	18-980 (35/35)

CASRN: Chemical Abstracts Service Registry Number; P2: Position 2 at 0.5 meters above field surface; P3: Position 3 at 1.07 meters above field surface; ;P4: Position 4: 1.63 meters above field surface; and Range: Minimum – Maximum.

D.5. Analysis of Meteorological Data

D.5.1. Introduction

At every field, meteorological data describe the climate and weather conditions during each sampling event. Temperature, relative humidity (RH), ozone, and wind data were collected on and off the field. This appendix section describes the protocols used to collect and present some of these data.

D.5.2. Ambient Temperature on the field

D.5.2.1. Data Collection

Temperature was monitored for five hours on and off the field. Data were collected for one hour before any field activity, for three hours during field activity, and for one hour following field activity. On the sampling tower, temperature data were collected at heights of 8, 24, 45, and 65 inches above the field surface. Thermocouples mounted inside solar radiation shields were used at each height. At 8, 24, and 45 inches, data were continuously collected and logged with a HOBO model UX120 data logger. At 65 inches, data were continuously collected and logged with a HOBO model HU23 data logger. Temperature data were recorded every minute at each height and then averaged over the five hour study period for each height.

Temperature data were also collected at a height of 50 inches above the ground surface on the cart behind the goal frame and on the off field cart. Data were continuously recorded and logged with a HOBO model HU23 mounted inside solar radiation shields.

D.5.2.2. Results

The fields studied were distributed throughout California and placed into five climatic regions, as described in Section 2.3.1.1. These regions were reduced to four regions when Region 4 and Region 5 were combined, because of the low number of fields in these regions, to Region 4/5. The fields were further divided into newer fields, less than nine years of age, and older fields, nine years of age and older, see Section 2.3.1.2. The fields were studied from June through December 2017. Because temperatures vary significantly during the year and California does not have distinct seasons, for this discussion sampling was divided between warmer months, June and October, and colder months, November and December.

Figure D-8 shows the single day average ambient field temperatures at 45 inches above the field for the 35 fields studied over the study period.

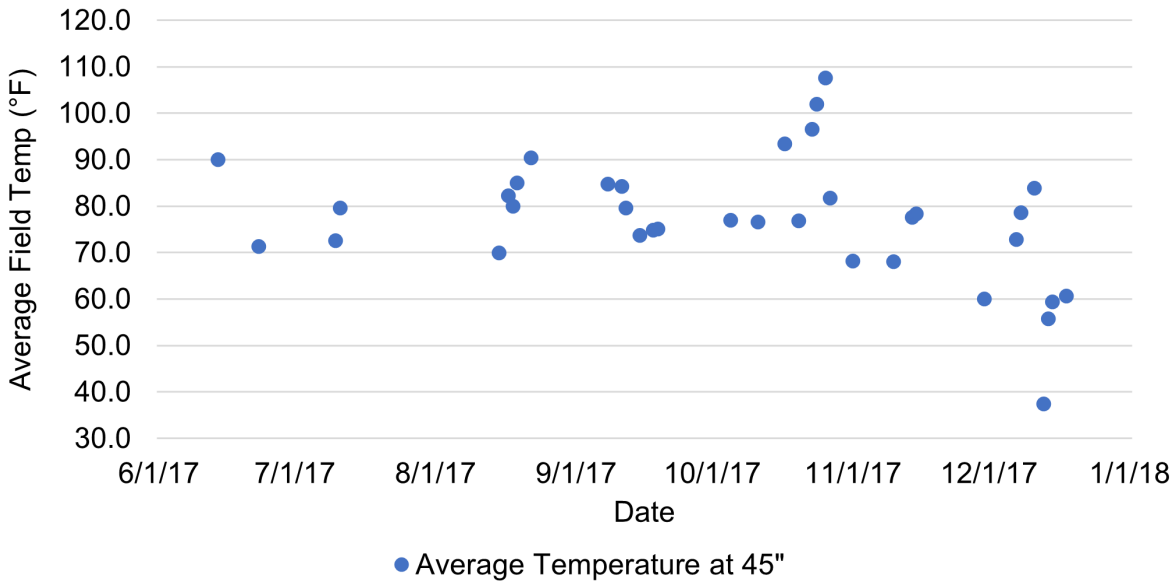


Figure D-1. Average Ambient Field Temperature at 45 inches above the field

In separating the fields into regions, Table D-53 shows the average temperatures measured at each height. The temperatures generally decreased as the height of the measurement increased.

Table D-1. Average Temperature[a] and Standard Deviation (SD), in degrees Fahrenheit, at Different Heights above the Surface of the Fields Studied in the Different Regions

Region (No. Fields)	Temperature	8"	24"	45"	65"
1(13)	Ave. Temp (SD)	83.1 (9.47)	82.1 (10.3)	82.4 (12.3)	79.6 (8.71)
2(9)	Ave. Temp (SD)	75.4 (8.37)	75.7 (7.88)	74.6 (6.94)	70.9 (9.30)
3(11)	Ave. Temp (SD)	80.7 (12.2)	79.2 (11.2)	79.1 (11.7)	76.8 (12.8)
4/5(2)	Ave. Temp (SD)	48.2 (12.2)	46.4 (12.7)	46.6 (13.0)	45.5 (11.6)

[a] The value used for each height was the average of average temperatures of the fields in the region measured for the five hours during the study and the standard deviation (SD) of the average temperatures, although on some fields the temperatures were not measured for the full five hours.

Separating the fields studied by their age and time of the year they were studied, Table D-54 and Table D-55 show how these factors affected the measured temperatures. As seen previously, the temperatures were lower as the height at which the temperature was measured increased. No real differences in temperature between old and new

fields that could be determined. There is an obvious difference between average temperatures in the warmer months and colder months, but not affecting temperatures between field age. Of course, there are other factors that could hide the appearance of any difference between field age including weather conditions when the fields were studied.

Table D-2. Average Temperature[a] and Standard Deviation, in degrees Fahrenheit, at Different Heights above the Surface of the Fields During the Warmer Months[b] of Newer and Older Fields Studied

Age of Field Category[c]	8"	24"	45"	65"
Newer Fields (14) Average Temperature	79.5	83.6	83.1	75.1
Newer Fields (14) Standard Deviation	16.7	9.3	11.3	16.1
Older Fields (9) Average Temperature	83.7	81.7	82.3	75.2
Older Fields (9) Standard Deviation	8.16	7.75	7.73	18.5

[a] The value used for each height was the average of average temperatures measured for the five hours during the study and the standard deviation of the average temperatures, although on some fields the temperatures were not measured for the full five hours.
[b] Warm months are June through October
[c] Newer Fields are < 9 years old and Older Fields are ≥ 9 years old. Numbers in parentheses are the number of fields studied in each region.

Table D-3. Average Temperature[a] and Standard Deviation, in degrees Fahrenheit, at Different Heights above the Surface of the Fields During the Colder Months[b], of Newer and Older Fields Studied

Age of Field Category[c]	8"	24"	45"	65"
Newer Fields (6) Average Temperature	69.8	67.7	67.1	66.8
Newer Fields (6) Standard Deviation	15.4	15.5	15.2	15.0
Older Fields (6) Average Temperature	67.5	66.7	66.3	65.0
Older Fields (6) Standard Deviation	12.3	11.9	11.7	12.0

[a] The value used for each height was the average of average temperatures measured for the five hours during the study and the standard deviation of the average temperatures, although on some fields the temperatures were not measured for the full five hours.
[b] Cold months are November through December
[c] Newer Fields are < 9 years old and Older Fields are ≥ 9 years old. Numbers in parentheses are the number of fields studied in each region.

The temperature values provided are from above the studied fields. To compare these temperatures with ambient temperatures, ambient temperatures were obtained from Weather Underground stations located near the fields and recorded at the same time the studies were taking place. The Weather Underground is a commercial service providing weather information from the internet. Its information comes from the National Weather Service and a network of over 250,000 personal weather stations. It is from these personal weather stations our ambient area information was obtained. Table D-56 compares the average ambient field temperatures in each region with the average area ambient temperatures. The ambient field temperatures are higher than the ambient area

temperatures as would be expected since the ambient temperatures are generally taken at a higher elevation. Figure D-9 shows this comparison over the entire study period.

Table D-4. Ambient Field Temperature and Standard Deviation (SD), in degrees Fahrenheit, at a Height of 65" Compared to Ambient Area Temperature in the Different Regions

Field and Area Temperature	1 (13)[a]	2 (6)	3 (8)	4/5 (1)
Average Ambient Field Temperature	79.6	70.9	76.8	53.7
Ambient Field Temperature SD	8.71	9.3	13.5	
Average Ambient Area Temperature[b]	78.1	70.6	74.8	43.7
Ambient Area Temperatures SD	10.6	10.2	11.3	

[a] Region number with the number of fields in parentheses. Because not all area temperatures were available, only fields temperatures where ambient field and ambient area temperatures were available are used in the calculations.
[b] The ambient area temperature was from a Weather Underground station located near a field.

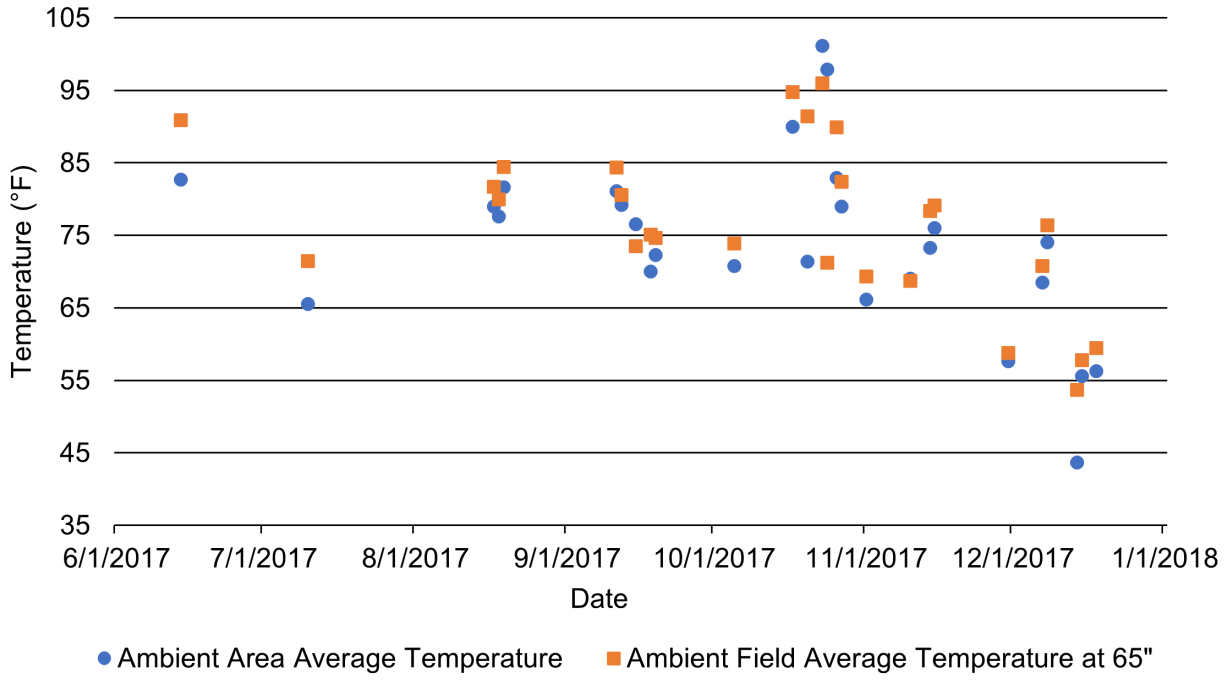


Figure D-2. Field Temperature at 65" and Ambient Temperature

D.5.3. Synthetic Turf Temperatures

To address how hot synthetic turf gets while it is being used, temperature sensors were placed deep and shallow into the crumb rubber on each field as well as on the surface.

D.5.3.1. Data Collection

Temperature probes were used to monitor the temperature of deep and shallow crumb rubber for the five-hour sampling period on and off the field. Surface temperature was recorded using infrared (IR) temperature probes aimed at the field surface mounted on three carts surrounding the goal frame, on one cart at each off-field location, and on an on-field sampling tower as described in Section D.1.2.5. Two on-field carts were located on either side of the goal frame. The third cart and sampling tower were located behind the goal frame. Deep crumb rubber, shallow crumb rubber, and surface temperature data were continuously recorded and logged with a HOBO model UX120 data logger.

D.5.3.2. Results

In Figure D-10, the average surface temperature is compared to the average ambient temperature at 45 inches above the field for each field in the study. The average surface temperature of the fields rise as the average ambient temperature above the fields increase. At around 85 degrees Fahrenheit ambient field temperature, the surface temperatures leveled off between 100 and 130 degrees Fahrenheit as ambient field temperatures continued to rise.

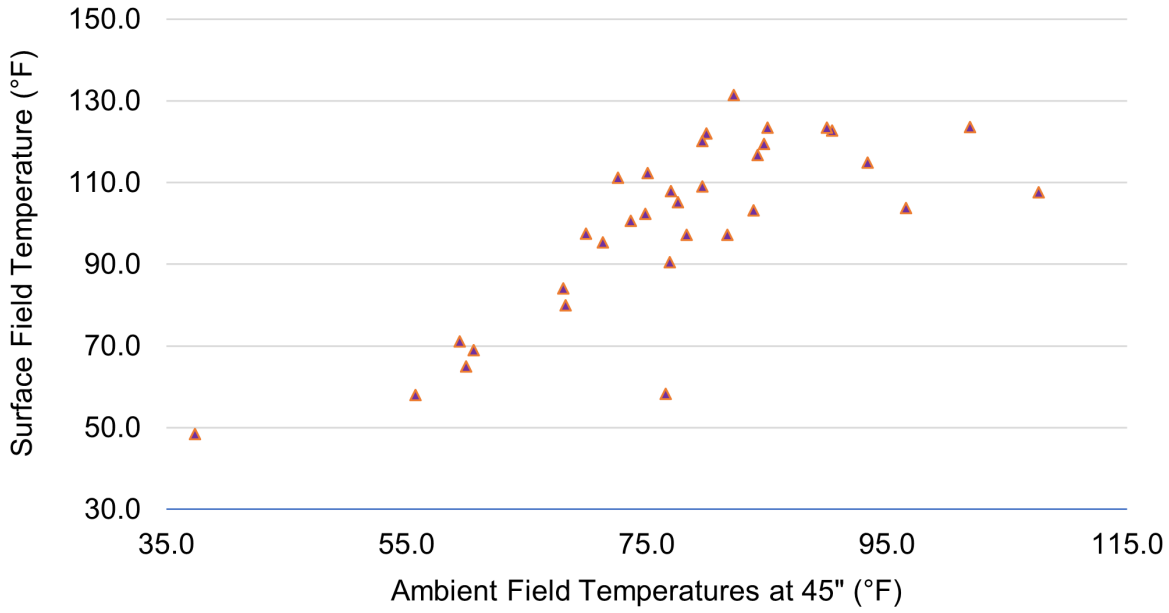


Figure D-1. Average Surface Field Temperature vs Average Ambient Field Temperature of each Field

The temperatures at the deep, shallow and surface levels on the fields in the four regions studied can be seen in Table D-57. The average temperatures and the average

of the field maximum temperatures (average maximum) all seemed to follow the same pattern with the deeper the probe, the cooler the temperature. The surface temperatures were the hottest and were more than 20 degrees higher than ambient temperatures except in Region 4/5 where the two fields studied had cold ambient temperatures. The highest average surface temperature measured on a single field was 131 degrees Fahrenheit.

Table D-1. Average and Average Maximum Temperature[a], in degrees Fahrenheit, at Different Depths in the Crumb Rubber and the Surface of the Fields and Average Ambient Temperature 45 Inches above the Fields Studied in the Different Regions

Region[b], Temperature	Deep	Shallow	Surface	Ambient Temp. at 45"
Region 1 (13), Average Temperature	86.6	93.7	104	82.4
Region 1 (13), Average Max. Temperature	95.8	106	120	89.2
Region 2 (9), Average Temperature	95.4	97.1.	98.3	74.6
Region 2 (9), Average Max. Temperature	113	113	116	81.6
Region 3 (11), Average Temperature	92.5	105	105	79.1
Region 3 (11), Average Max. Temperature	105	119	123	85.8
Region 4/5 (2), Average Temperature	36.7	49.9	53.2	46.6
Region 4/5 (2), Average Max. Temperature	41.4	61.8	67.6	55.3

[a] The value used for each depth was the average of average temperature and the average maximum temperatures for each field measured for the five hours during the study and the standard deviation, although on some fields the temperatures were not measured for the full five hours.
[b] Numbers in parentheses are the number of fields studied in each region.

The data were analyzed to see whether newer and older fields behaved differently. Table D-58 and Table D-59 show the differences between newer and older fields during warmer and colder months. While in warmer months there were higher temperatures observed in older fields, the differences were not significant. In colder months the differences observed were not very large. Table D-60 shows there were no differences in temperatures observed at any depth when all newer fields were combined and compared to all older fields combined.

Table D-2. Average Temperature[a] and Standard Deviation, in degrees Fahrenheit, at Different Depths Below the Surface of the Fields and Average Ambient Temperature at

45 Inches above the Fields During the Warm Months[b], on Newer and Older Fields Studied

Field Category[c], Temperature	Deep	Shallow	Surface	Ambient Temp. at 45"
Newer Fields (14), Average Temperature	94.6	105	106	83.1
Newer Fields Standard Deviation	14.9	18.8	17.2	11.3
Older Fields (9), Average Temperature	105	111	114	82.3
Older Fields Standard Deviation	11.2	16.1	12.1	7.73

[a] The value used for each depth was the average of average temperature for each field measured for the five hours during the study and the standard deviation, although on some fields the temperatures were not measured for the full five hours.
[b] Warm months are June through October.
[c] Newer Fields are < 9 years old and Older Fields are ≥ 9 years old. Numbers in parentheses are the number of fields studied in each region.

Table D-3. Average Temperature[a] and Standard Deviation, in degrees Fahrenheit, at Different Depths Below the Surface of the Fields and Average Ambient Temperature at 45 Inches above the Fields During the Cold Months[b], on Newer and Older Fields Studied

Field Category[c], Temperature	Deep	Shallow	Surface	Ambient Temp. at 45"
Newer Fields (6), Average Temperature	70.6	74.8	79.4	67.1
Newer Fields Standard Deviation	17.2	15.0	23.4	15.2
Older Fields (6), Average Temperature	63.8	71.0	77.2	66.3
Older Fields Standard Deviation	17.6	14.6	18.4	11.7

[a] The value used for each depth was the average of average temperature for each field measured for the five hours during the study and the standard deviation, although on some fields the temperatures were not measured for the full five hours.
[b] Cold months are November through December.
[c] Newer Fields are < 9 years old and Older Fields are ≥ 9 years old. Numbers in parentheses are the number of fields studied in each region.

Table D-4. Average Temperature[a] and Standard Deviation, in degrees Fahrenheit, at Different Depths Below the Surface of the Fields and Average Ambient Temperature at 45 Inches above the Fields Studied

Field Category[b], Temperature	Deep	Shallow	Surface	Ambient Temp. at 45"
Newer Fields (20), Average Temperature	87.4	96.1	100	78.3
Newer Fields Standard Deviation	18.9	22.5	21.3	14.3
Older Fields (15), Average Temperature	88.4	95.1	99.2	75.9
Older Fields Standard Deviation	24.8	25.2	23.5	12.2

[a] The value used for each depth was the average of average temperature for each field measured for the five hours during the study and the standard deviation, although on some fields the temperatures were not measured for the full five hours.
[b] Newer Fields are < 9 years old and Older Fields are ≥ 9 years old. Numbers in parentheses are the number of fields studied in each region.

While the ambient temperatures above the fields likely have some effect on the field surface and below surface temperatures, there is no clear pattern as seen in Table D-61, which shows the surface and below surface average temperatures when the ambient temperature is divided into categories of 10 degrees from 60 degrees to 100 degrees and above. The surface temperatures stayed high down to the 70 to 80 degree category, while the shallow and deep field temperatures varied. The below surface temperatures may be more dependent on longer term ambient temperatures than a one-day measurement as done in this study.

Table D-5. Average Temperature[a], in degrees Fahrenheit, at Different Depths in the Crumb Rubber and the Surface of the Fields for Different Average Ambient Field Temperature Ranges at 45 Inches above the Fields Studied

Temperature Range[b], Temperature	Deep	Shallow	Surface	Ambient Temp. at 45"
≥100 (2), Average Temperature	88.8	98.9	116	105
≥90 <100 (4), Average Temperature	94.8	110	116	92.6
≥80 <90 (7), Average Temperature	104	118	116	83.1
≥70 <80 (14), Average Temperature	91.8	94.0	109	76.0
≥60 <70 (5), Average Temperature	74.5	81.5	79.1	65.4
<60 (3), Average Temperature	43.9	54.2	59.2	50.8

[a] The value used for each depth was the average of average temperature for each field measured for the five hours during the study and the standard deviation, although on some fields the temperatures were not measured for the full five hours.
[b] Numbers in parentheses is number of fields in that temperature range.

D.5.4. Ozone

Ozone is a molecule made up of three oxygen atoms (O_3). It occurs naturally in the

stratosphere above the earth but is also formed troposphere near the ground surface from the photochemical reaction between air pollutants of volatile organic compounds (VOCs) and nitrogen oxides. As discussed in Section 2.3.1, ozone has been known to affect the aging and degradation of crumb rubber on synthetic turf fields. It is also known to be harmful to human health. Ozone is most likely to reach unhealthy levels on hot sunny days in urban environments but can still reach high levels during colder months. The California ambient ozone air standard is 90 parts per billion (ppb) for a 1-hour exposure and the National and the California ambient ozone air standard is 70 ppb for an 8-hour exposure.

D.5.4.1. Data Collection

Concentration of ozone was measured on the cart behind the goal frame and on the cart off-field with Ozone Dual Beam Monitors. The Ozone Monitor gives measurements of ozone concentration ranging from low ppb (precision of ~1.5 ppb) up to 250,000 ppb (0-250 parts per million, ppm) based on the well-established technique of absorption of UV light at 254 nanometers (nm). The equipment makes use of two detection cells to improve precision, baseline stability, and response time. In the Dual Beam instrument, UV light intensity measurements Io (ozone-scrubbed air) and I (unscrubbed air) are made simultaneously.

D.5.4.2. Results

During field sampling, ozone values were lowest in the morning and tended to peak around midday. Figure D-11 shows the average ozone levels measured during the study hours for the fields monitored during the months of June through December 2017. The highest concentrations were found during the hotter months of the year.

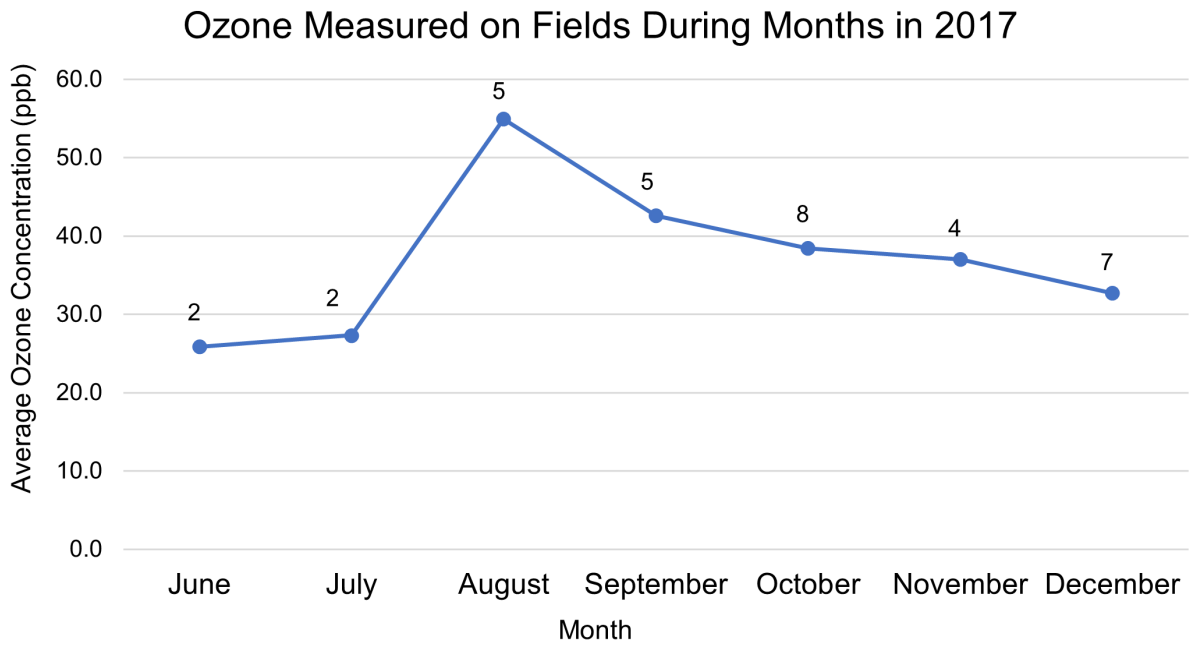


Figure D-1. The average ozone concentrations, in parts per billion (ppb), measured on fields studied during the months of 2017. The number above each point is the number of fields monitored during the month.

Table D-62 and Table D-63 show the average, average minimum and average maximum ozone concentrations measured on the fields in the different climatic regions of California. In the warmer months, no fields in Region 4/5 were studied. During these warmer months, ozone levels were found to be highest in Region 3. During the colder months the highest average concentration was found in Region 1, but Region 2 was found to have the highest average maximum concentration. These values are from snapshot measurements throughout the regions and time periods. They only represent the current conditions during the study sampling period and may not represent the ozone levels that are expected within each region on an everyday basis.

Table D-1. Average, Average Minimum, and Average Maximum[a] for Ozone Concentration Levels (parts per billion, ppb) on Fields in Region 1, Region 2 and Region 3 During the Warmer Months[b]

Region[c]	Average Ozone (ppb)	Average Minimum Ozone (ppb)	Average Maximum Ozone (ppb)
Region 1 (6)	39.2	21.4	60.3
Region 2 (8)	36.2	21.9	51.4
Region 3 (8)	48.3	36.0	66.9

[a] The value used for each field was the average ozone concentrations measured for the five hours during the study, although the ozone concentrations were not measured for the full five hours on some fields.
[b] Warmer months are June through October.
[c] Numbers in parentheses are the number of fields studied in each region.

Table D-2. Average, Average Minimum, Average Maximum[a] for Ozone Concentration Levels (parts per billion, ppb) on Fields in Region 1, Region 2, Region 3 and Region 4-5 During the Colder Months[b]

Region[c]	Average Ozone (ppb)	Average Minimum Ozone (ppb)	Average Maximum Ozone (ppb)
Region 1 (5)	37.9	19.1	57.9
Region 2 (1)	23.0	8.4	62.4
Region 3 (3)	34.1	25.4	48.1
Region 4/5 (2)	31.1	13.8	39.2

[a] The value used for each field was the ozone concentrations measured for the five hours during the study, although the ozone concentrations were not measured for the full five hours on some fields.
[b] Cold months are November through December.
[c] Numbers in parentheses are the number of fields studied in each region.

Ozone in our environment at ground level is primarily formed from the photochemical interaction of VOCs and nitrogen oxides pollutants and occurs most readily in the warmer summer months. The relationship between ozone levels and ambient temperature or sun light intensity are shown in Table D-64 and Table D-65, respectively. Sun light intensity was measure during the study period on each field as solar energy in watts per square meter (W/m^2).

Table D-64 compares the average, average minimum and average maximum ozone levels on fields when the average ambient temperature at 45 inches above the field is above or below 84.2 degrees Fahrenheit in Regions 1 and 3. The cut off at 84.2 degrees Fahrenheit was the 75th percentile of the distribution of all the average temperatures measured at 45” above the fields. Data from the other regions were not compatible for this comparison. Ozone levels in Region 1 were higher at lower temperatures while they were higher at higher temperature in Region 3. Average light intensity also did correlate with temperature.

Table D-3. Average, Average Minimum, and Average Maximum[a] for Ozone Concentration Levels (parts per billion, ppb) on Fields in Region 1 and Region 3 at Average Ambient Field Temperatures Above or Below 84.2 °F at 45 inches and the Average Light Intensity Measured During the Study Period

Region (No. Fields), Temperature Range °F	Average Ozone (ppb)	Minimum Ozone (ppb)	Maximum Ozone (ppb)	Average Ambient Temp (°F)	Light Intensity (W/m^2)
Region 1 (3), ≥ 84.2 °F	36.7	22.0	57.4	102	549
Region 1 (10), < 84.2 °F	39.3	20.0	55.3	76.4	466
Region 3 (5), ≥ 84.2 °F	49.8	37.0	63.0	88.7	596
Region 3 (5), < 84.2 °F	38.2	28.7	51.7	70.4	460

[a] The value used for each field was the ozone concentrations measured for the five hours during the study, although the ozone concentrations were not measured for the full five hours on some fields.

Table D-65 compares the average, average minimum and average maximum ozone levels on fields when the average light intensity on the field is above or below 611 watts per square meter in Regions 1, 2 and 3. The cut off at 611 watts per square meter was the 75th percentile of the distribution of all the average light intensities measured on the fields. Data from Region 4/5 were not compatible for this comparison. In all three regions ozone concentrations were higher in the groups above 611 watts per square meter. The average temperatures were also higher in these groups.

Table D-4. Average, Average Minimum, and Average Maximum[a] for Ozone Concentration Levels (parts per billion, ppb)[b] on Fields in Region 1 and Region 3 at Above or Below Average Light Intensity 611 watts per square meter and the Average Ambient Field Temperatures at 45 inches Measured During the Study Period

Region (No. Fields), Light Intensity (W/m^2)	Average Ozone (ppb)	Maximum Ozone (ppb)	Minimum Ozone (ppb)	Average Ambient Temp (°F)	Light Intensity (W/M^2)
Region 1 (2), ≥ 611 W/m^2	54.1	67.1	31.3	81.1	750
Region 1 (10), < 611 W/m^2	35.6	53.6	18.3	84.0	434
Region 2 (2), ≥ 611 W/m^2	45.5	59.9	28.3	77.1	711
Region 2 (3), < 611 W/m^2	36.5	63.5	19.2	72.3	527
Region 3 (3), ≥ 611 W/m^2	51.4	68.7	35.0	81.2	694
Region 3 (6), < 611 W/m^2	42.8	55.6	33.5	77.0	441

[a] The value used for each field was the ozone concentrations measured for the five hours during the study, although the ozone concentrations were not measured for the full five hours on some fields.

The data in Table D-65 and Figure D-12 show ozone levels increasing with light intensity. This suggests that the ozone concentrations measured are related to photochemical reactions to create ozone. The high variability seen in Figure D-12 suggest there are other factors contributing to the formation of ozone, such as the levels of VOCs and nitrogen oxides that are present at the time.

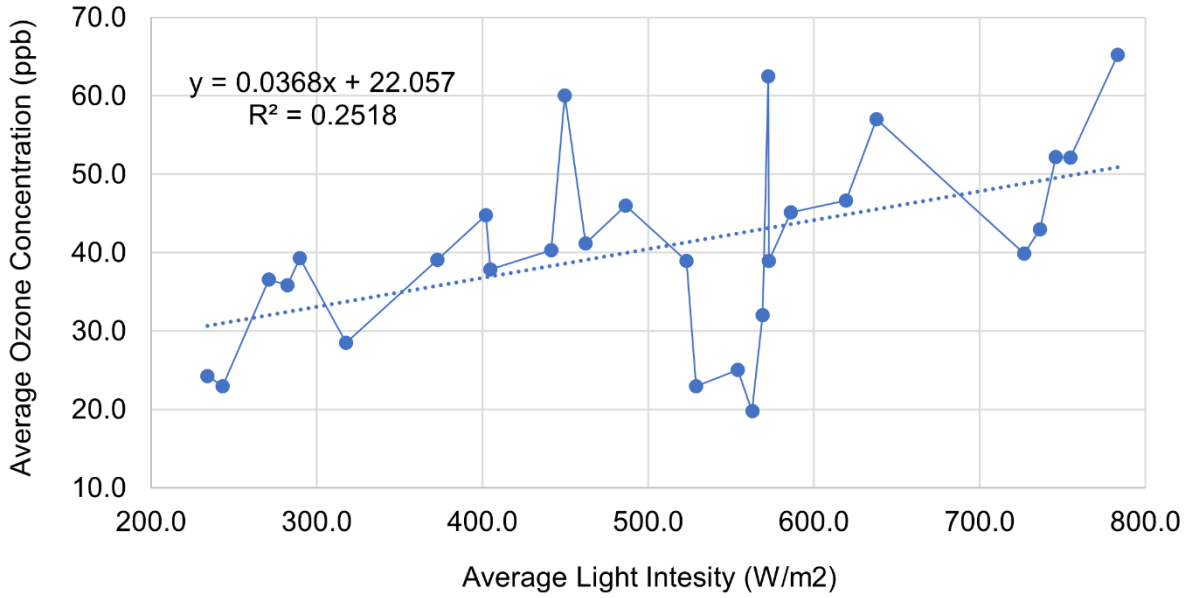


Figure D-2. Graph of the correlation between the average ozone concentration at the fields and the average light intensity measured at the same time. A regression line runs through the data and the regression coefficient is provided.

As mentioned earlier, the California ambient ozone air standard is 90 ppb for a 1-hour exposure and the California and the National ambient ozone air standard is 70 ppb for an 8-hour exposure. During the study period, three fields exceeded the 8-hour ozone standard with the highest measured concentration at 87.0 ppb. These higher concentrations occurred in the early afternoon, typically when the study period was concluding.

D.5.5. Particles, $PM_{2.5}$

Pollutants may adhere to particles in the air. To see if particulate matter increased over the fields during activity, filters were used to trap the particulates and weighed before and after to determine the change in weight.

D.5.5.1. Data Collection

$PM_{2.5}$ was collected on Teflon filters from 1.8 meters cubed (m^3) of air sampled at 10 liters per minute (L/min) size specific impaction sampler (Personal Environmental Monitor [PEM], SKC, Eighty Four, PA). Individual filters were stored at room temperature in dedicated Petri dishes (i.e., each filter has its own dish) wrapped in foil. The filters were conditioned in the balance chamber for at least 24 hours with the Petri dish lid set in place loosely. Conditioned filters were weighed prior to loading in PEMs to get pre-weights and then again after use to get post-weights. Particulate collectors were

place on Carts 1 and 3 to measure on-field particulate levels and on Cart 4 to measure off-field particulate levels.

D.5.5.2. Results

Unless there is a large difference between on-field and off-fields levels, it is difficult to determine if there is a significant difference using this data collection method because the necessity of so much handling and weighing of the filters brings in the likelihood of increased variability between samples. In addition, a number of samples were compromised because at least one of the three filters used on each field did not provide useable information. In the end, only $PM_{2.5}$ levels from 19 fields were useable. The calculated average $PM_{2.5}$ concentration, in micrograms per cubic meter of air, from on the field was 13.4 micrograms per cubic meter of air and from off the field the average $PM_{2.5}$ was 14.1 micrograms per cubic meter of air. When the off-field filter $PM_{2.5}$ weight was first subtracted from the on-field $PM_{2.5}$ weight the average difference seen for the 19 fields was -0.63 micrograms per cubic meter. This suggests activity on the fields did not increase $PM_{2.5}$ concentrations. A pairwise t-test of these data also suggests that there was not a significant difference between on-field and off-field $PM_{2.5}$ concentrations. As previously mentioned, because of technical difficulties and methodology, these results are uncertain.

D.5.6. Effect of Environmental Factors on Chemical Air Concentrations on the Fields

It is assumed that environmental factors may have an influence on the volatilization of chemicals from the crumb rubber on the fields. To do a preliminary investigation of this assumption, three chemicals found at detectable concentrations on many of the fields studied (see Section 3.4.6, Table 3-10) were chosen to compare to how three different environmental factors affected the measured concentrations. The chemicals chosen were two volatile chemicals, 2-methly furan and benzene and one semi-volatile chemical, 2-phenyl benzothiazole. The environmental factors chosen were artificial turf surface temperature, age of the field, and wind speed at the time of the field study. 2-methly furan and 2-phenyl benzothiazole are considered field-related chemicals and benzene is considered an air pollutant.

D.5.6.1. Data Collection

The chemicals chosen for this evaluation were found on many fields, were identified as volatile or semi-volatile, and were considered to have an origin from the field, environmental or other sources as described in the introduction. The average on-field concentration, in nanograms per cubic meter was used. Section 2.3.2.3 describes the protocols and methods used to collect and analysis field air samples.

The average surface temperatures were taken as described in Section 3 above. The age of the fields were determined as described before in Section D.5.2.2. Wind speed was measured on Cart 1, 2, and 3 at one-minute increments. The wind speed measured

at each cart was averaged over the five-hour study duration and then the three cart averages were averaged. On some fields, not all the instruments worked on each cart, so the average may be of just one or two instrument readings.

D.5.6.2. Statistical Analysis

To see if any of the environmental factors influenced the air concentrations measured above the fields, we used the Chi-square test of independence, which is used to determine if a difference between observed data and expected data is due to chance, or if it is due to a relationship between the variables being studied. In this analysis, the data used were the number of fields which had chemical concentrations, surface temperatures, and windspeeds above and below the median value of those measurements from all the fields and the age of the fields above and below the age deemed to be newer or older in age. The Chi-square analysis compares two actual sets of data, such as the number of fields with air concentrations of a chemical above or below the median concentrations on all fields and the number of fields with surface temperature that is above or below the median surface temperature of all fields, to the theoretical expected number in each category if the two sets of data were independent of each other. Table D-66 and Table D-67 present the median chemical concentrations, surface temperature and wind speed and the total number of fields above and below those values. For age of field, the actual number of newer and older fields was used (Table D-67). Table D-68, Table D-69, and Table D-70 present the observed and expected number of fields for 2-methyl furan, 2-phenylbenzothiazole, and benzene above or below the median air concentration, surface temperature, field age, and wind speed. In this case, an environmental factor may affect the air concentration of the chemical over the field. In doing the Chi-square test, only fields where both the concentration of the chemical and the environmental factor were measured were used. Therefore, in many cases the numbers in Table D-66 and Table D-67 may differ than the numbers used in Table D-68, Table D-69, and Table D-70.

Table D-1. Number of Fields Above and Below the Median Chemical Concentration Value Used in Chi-Square Analysis

Chemical	Median Conc. (ng per cubic meter)	Number Above the Median	Number Below the Median
Furan, 2-methyl	85.6	17	17
Benzothiazole, 2-phenyl-	2.4	14	13
Benzene	440	18	17

Table D-2. Number of Fields Above and Below the Median Environmental Factors Used in Chi-Square Analysis

Environmental Factor	Median Value	Number above the Median	Number below the Median
Surface Temperature	104 °F	17	16
Newer / Older[a]	n/a	20 Newer	15 Older
Wind Speed	2.8 mph	18	17

[a] Newer Fields are < 9 years old and Older Fields are ≥ 9 years old. Numbers in parentheses are the number of fields studied in each region.

Table D-3. Observed and Expected Number of Fields Above or Below the Median Air Concentration and Above or Below the Median Surface Temperature for Selected Chemicals

Chemical	Air Concentration Level[a]	Observed Number of Fields with Hotter Surface Temperatures[b]	Observed Number of Fields with Colder Surface Temperatures	Expected Number of Fields with Hotter Surface Temperatures	Expected Number of Fields with Colder Surface Temperatures
2 Methyl Furan	Higher	14	3	8.8	8.2
	Lower	3	13	8.2	7.8
2-Phenyl-Benzothiazole	Higher	11	3	8.4	5.6
	Lower	4	7	6.6	4.4
Benzene	Higher	11	7	9.3	8.7
	Lower	6	9	7.7	7.3

[a] Higher or lower air concentration were those levels that were greater or lesser, respectively, of the median air concentrations of the chemicals in Table 14.

[b] Hotter or colder surface temperature level were those level that were greater or lower, respectively, of the median surface temperature level of 104 °F.

Table D-4. Observed and Expected Number of Newer and Older Fields With Air Concentrations Above or Below the Median Value

Chemical	Air Concentration Level[a]	Observed Number of Newer Fields[b]	Observed Number of Older Fields	Expected Number of Newer Fields	Expected Number of Older Fields
2 Methyl Furan	Higher	7	10	9.5	7.5
	Lower	12	5	9.5	7.5
2-Phenyl-Benzothiazole	Higher	8	6	8.8	5.2
	Lower	9	4	8.2	4.8
Benzene	Higher	9	9	10.3	5.2
	Lower	11	6	9.7	7.3

[a] Higher or lower air concentration were those levels that were greater or lesser, respectively, of the median air concentrations of the chemicals in Table 14.

[b] Newer Fields are < 9 years old and Older Fields are ≥ 9 years old.

Table D-5. Observed and Expected Number of Fields Above or Below the Median Air Concentration and Above or Below the Median Wind Speed for Selected Chemicals

Chemical	Air Concentration Level[a]	Observed Number of Fields with Higher Wind Speeds[b]	Observed Number of Fields with Lower Wind Speeds	Expected Number of Fields with Higher Wind Speeds	Expected Number of Fields with Lower Wind Speeds
2 Methyl Furan	Higher	6	11	8.5	8.5
	Lower	11	6	8.5	8.5
2-Phenyl-Benzothiazole	Higher	7	7	6.2	6.2
	Lower	8	5	7.2	5.8
Benzene	Higher	5	7	9.3	8.7
	Lower	12	9	8.7	8.3

[a] Higher or lower air concentration were those levels that were greater or lesser, respectively, of the median air concentrations of the chemicals in Table 14.

[b] Higher or lower wind speeds were those speeds that were greater or lesser, respectively, of the median wind speed of 2.8 mph.

Table D-6. Observed and Expected Number of Newer and Older Fields With Surface Temperatures Above or Below the Median Value

Surface Temperature Level	Observed Number of Newer Fields[b]	Observed Number of Older Fields	Expected Number of Newer Fields	Expected Number of Older Fields
Hotter	10	7	9.3	7.7
Colder	8	8	8.7	7.3

[a] Hotter or colder surface temperature level were those level that were greater or lower, respectively, of the median surface temperature level of 104 °F.

[b] Newer Fields are < 9 years old and Older Fields are ≥ 9 years old.

Table D-7. Observed and Expected Number of Fields With Hotter and Colder Surface Temperatures and Above or Below the Median Wind Speed for Selected Chemicals

Surface Temperature Level	Observed Number of Fields with Higher Wind Speeds[b]	Observed Number of Fields with Lower Wind Speeds	Expected Number of Fields with Higher Wind Speeds	Expected Number of Fields with Lower Wind Speeds
Hotter	8	9	8.2	8.8
Colder	8	8	7.8	8.2

[a] Hotter or colder surface temperature level were those level that were greater or lower, respectively, of the median surface temperature level of 104 °F.

[b] Higher or lower wind speeds were those speeds that were greater or lesser, respectively, of the median wind speed of 2.8 mph.

D.5.6.3. Summary of the Environmental Factors influence on the Chemical Air Concentrations

Using Microsoft Excel's CHISQ.TEST formula, which calculates the probability, p-value, that two sets of data are independent, we consider a p-value of less than 0.05 to indicate the two sets of data are not independent and therefore, one factor may influence the other one. We also provide the Chi-square (X^2) value, the degrees of freedom (df) for each analysis and the combined number of variables (N) in each analysis.

In this evaluation, the air concentrations of 2-methyl furan and 2-phenyl-benzothiazole and surface temperatures are shown to be dependent (Table D-73). Both 2-methyl furan and 2-phenyl-benzothiazole are field related chemicals, with one being a volatile organic chemical and the other being a semi-volatile organic chemical. Thus, air concentration being dependent on ambient temperature makes sense. All other chemical air concentrations and environmental conditions evaluated are statistically independent of each other, but the data are not conclusive because of the small number of chemicals and fields analyzed.

A comparison of the environmental factors (i.e. surface temperature, field age and wind speed) was also done and showed they were independent of each other (Table D-74).

Table D-1. Chi-Square Test of Independence Results Between Chemical Air Concentrations and Environmental Factors for Selected Chemicals

Chemical	Variable Relationship	X^2	df	N	P-value
2 Methyl Furan	Air Concentration:Surface Temperature	13.4	1	33	>0.001
	Air Concentration:Field Age	2.98	1	34	0.084
	Air Concentration:Wind Speed	2.94	1	34	0.086
2-Phenyl-Benzothiazole	Air Concentration:Surface Temperature	4.57	1	25	0.032
	Air Concentration:Field Age	0.422	1	27	0.52
	Air Concentration:Wind Speed	0.363	1	27	0.54
Benzene	Air Concentration:Surface Temperature	1.46	1	33	0.22
	Air Concentration:Field Age	0.772	1	35	0.38
	Air Concentration:Wind Speed	2.33	1	35	0.058

Table D-2. Chi-Square Test of Independence Results For Environmental Factors

Environmental Factor Relationship	X^2	df	N	P-value
Surface Temperature:Field Age	0.259	1	33	0.61
Surface Temperature:Wind Speed	0.029	1	33	0.87

D.6. References

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