



Published in final edited form as:

Air Qual Atmos Health. 2019 May ; 12(5): 597–611. doi:10.1007/s11869-019-00680-1.

Artificial turf: chemical flux and development of silicone wristband partitioning coefficients

Carey E Donald^{1,2}, Richard P Scott¹, Glenn Wilson¹, Peter D Hoffman¹, Kim A Anderson^{1,*}

¹Food Safety and Environmental Stewardship Program, Department of Environmental and Molecular Toxicology, 1007c Agricultural and Life Sciences Building, Oregon State University, Corvallis, OR 97330, USA

²Present address: Institute of Marine Research, Nordnesgaten 50, 5005 Bergen, Norway

Abstract

This work provides the first quantitative measure of *in situ* flux of semi-volatile contaminants on artificial turf fields. Passive samplers were used to identify gas-phase PAHs and OPAHs not previously reported associated with artificial turf. Utilizing a broad and targeted screen, we assess both artificial turf and from crumb rubber for 1,529 chemicals, including several with known health effects including benzo[c]fluorene. We also report the presence of 25 chemicals that have not yet been reported in artificial turf literature, including some with known effects on human health. This is the first report of bioavailable gas-phase PAH and OPAH concentrations on an outdoor field, to date gas-phase concentrations have only been reported from indoor facilities. Turf air and air were highly correlated at all three sites, and particularly at the recently-installed indoor site. Finally, thermal extraction and silicone passive samplers are highly suitable for larger-scale sampling campaigns that aim for less solvent and sample processing. We demonstrate for the first time that silicone passive samplers can be used to quantify volatile and semi-volatile organic chemicals from artificial turf. Co-deploying silicone passive samplers and conventional low density polyethylene, we develop partitioning coefficients that can be used for silicone passive air sampling environmental assessment.

Keywords

Polycyclic aromatic hydrocarbons; oxygenated polycyclic aromatic hydrocarbons; semi-volatile organic contaminants; LDPE; silicone; flux; partition coefficients

Introduction

Professional and amateur athletes commonly compete and practice on artificial turf. The latest generation of artificial turf is composed of several layers to mimic the look and feel of grass, often including plastic “grass” fibers and infill made of crumb rubber and/or sand.¹ Crumb rubber is ~90% of field material by weight, and is made primarily of recycled tires.^{1, 2} Components of the recycled tires have been considered as potential toxicants, including

*corresponding author.

lead, zinc, particulate matter, and volatile and semi-volatile organic chemicals.³⁻⁵ Potential exposure routes from crumb rubber include inhalation of particles or gas-phase contaminants, dermal contact, and inadvertent ingestion of crumb rubber. Risk estimates to date have yielded mixed results, concluding either that a) artificial turf components meet or do not exceed levels that would contribute to health risks,^{2, 5-12} or b) that some exposures are above levels that may contribute to risk.¹³⁻¹⁷ Refining these conclusions is the subject of recent and ongoing investigations by the U.S. Environmental Protection Agency, Centers for Disease Control and Prevention and Agency for Toxic Substances and Disease Registry^{3, 4} and the European Chemicals Agency⁵.

Semi-volatile organic chemicals, *e.g.* phthalates, benzothiazole, and polycyclic aromatic hydrocarbons (PAHs), are used in tire production and are commonly detected in crumb rubber analyses.^{1, 2, 14-16, 18, 19} Other toxicologically-relevant chemicals are also present, but crumb rubber has not yet been fully characterized and these unknown components remain as an uncertainties in risk evaluations.⁵ Oxygenated PAHs (OPAHs), like PAHs, derive from numerous natural and anthropogenic sources. OPAHs are also formed as photo-oxidation products of PAHs,²⁰ and formation of OPAHs is likely in the high-sun environment typical on outdoor sports field. For other contaminants not descended of recycled tires, artificial turf could act as an initial sink with gradual release over time. Kanematsu, et al.²¹ and Nilsson, Malmgren-Hansen and Thomsen¹² used mass spectra libraries and identified potential, previously unreported toxicants in rubber mulch leachate. To the authors' knowledge only targeted approaches have been used when characterizing crumb rubber. Non-specific sampling and analytical methods are still needed to fully characterize artificial turf fields.

PAHs are a subgroup of VOCs known as *semi-volatile* organic compounds (SVOCs) and generally have higher molecular weights and boiling points (bp), nominally between 250C and 400C.²² However, despite high bps, SVOCs do vaporize and are typically present partly in the gaseous phase and partly absorbed onto surfaces and particulates.²³ SVOCs can be released from solids as they are not bound to the material. As such, contaminants can off-gas from crumb rubber infill, making chemicals available for inhalation by athletes and field users. Li, et al.²⁴ and Zhang, Han, Zhang and Crain¹⁷ report that chemical off-gassing rates generally decrease as the field ages. Under most conditions, lower molecular weight PAHs are primarily in the gaseous phase, but importantly, PAHs with higher molecular weights are also present in the gaseous phase^{25, 26} and are often the largest contributor to PAH-associated health risks.²⁷ Researchers have observed that gas-phase PAHs can contribute heavily to the carcinogenic potency of PAH mixtures.^{25, 27, 28} Thus measuring PAHs in the gaseous phase is relevant when assessing personal PAH exposure.

Of environmental chemical transport processes, diffusion is the only continuously active process and has been used as a baseline for total flux.²⁹ Flux between soil and air is the subject of current research, but *in situ* flux on the unique artificial turf environment has not yet been measured. Artificial turf may be an important source of semi-volatile chemicals, including PAHs, to air.

Passive sampling is an established method for measuring trace levels of contaminants and researchers often use passive samplers to detect chemicals in air environments.^{30, 31} The silicone samplers described in this work are identical to silicone wristbands in previous publications that measure personal exposure.^{32–37} Partition coefficients are necessary to convert from concentrations in the passive sampling material to environmental concentrations. To determine partition coefficients a new material or technique may be deployed with a well-understood and established sampling technique. Partitioning coefficients have been previously estimated for numerous types of silicone materials in water^{38, 39} and air.^{40, 41} In this work, we co-deploy well-established low-density polyethylene (LDPE) samplers with more recently-described silicone passive samplers configured as wristbands to allow the calculation of silicone-wristband-specific partitioning coefficients.

Our objectives in this study were to use LDPE passive samplers to identify gas-phase PAHs and OPAHs not previously reported associated with artificial turf. Utilizing a broad and targeted screen, we assess both artificial turf and crumb rubber for 1,529 chemicals, including several with known health effects, including benzo[c]fluorene, a PAH with an EPA-determined relative potency factor (RPF) of 20. We quantify PAH and OPAH flux between turf and the overlying air. Additionally, we demonstrate for the first time that silicone passive samplers can be used to quantify volatile and semi-volatile organic chemicals from artificial turf. We develop partitioning coefficients that can be used for silicone passive air sampling environmental assessment. This work will aid in future risk assessments by advancing and broadening the characterization of organic chemicals associated with artificial turf and this study is the first quantitative measure of *in situ* flux rates characteristic of artificial turf.

Materials and Methods

Chemicals

Target PAH analytes, deuterium-labeled internal standards, and extraction surrogates (Table 1) with purity 97% or greater; were purchased from distributors as detailed previously.^{42, 43} PAHs fluorene-D10, pyrene-D10, benzo[b]fluoranthene-D12 (C/D/N Isotope Inc.; Quebec, Canada) and the OPAH anthraquinone-D8 (Sigma-Aldrich; St. Louis, Missouri, USA) were used as performance reference compounds (PRCs) for determining *in situ* sampling rates. Low-density polyethylene (LDPE) passive samplers were constructed from lay-flat tubing purchased from Brentwood Plastics, Inc. (St. Louis, Missouri, USA). Silicone passive samplers (width: 1.3 cm; inner diameter: 5.8 cm) were purchased from 24hourwristbands.com (Houston, Texas, USA). LDPE and silicone samplers were transported and stored in individual polytetrafluorethylene (PTFE) bags from Welch Fluorocarbon, (Dover, New Hampshire, USA).

Site descriptions and sampling design

We collected samples at 3 artificial turf fields in western Oregon, United States: indoor, an indoor facility (turf field approximately 2 months old), outdoor A, an outdoor field surrounded by a rubberized track (approximately 2 years old); and outdoor B, an outdoor

multi-use field (approximately 5 years old). Crumb rubber is added to fields on an as-needed bases.

Passive sampling devices were used to measure two matrices: *air* at an approximate height of 1.5 m; and *turf air*; air immediately above and in close contact with turf (analogous to soil pore air). Paired *air* and *turf air* boxes, as described in Donald and Anderson⁴⁴ were deployed at the locations with triplicate equipment at *outdoor A*. Additional site details including weather conditions, photographs and figures are provided in SI. All sampling equipment was set up concurrently and remained for 27 days in August and early September 2016.

Sample preparation and extraction

Low-density polyethylene (LDPE) passive samplers—Passive samplers were prepared using strips of LDPE tubing as in Anderson, et al.⁴⁵ The strips were pre-conditioned in multiple solvent baths, and once dry, a solution containing performance reference compounds (PRCs) infused into each before heat-sealing. Infusion with PRCs allows calculation of *in situ* air sampling rates and time-integrated air concentrations, as described in Sower and Anderson and references therein.⁴⁶ Post deployment, strips were cleaned in isopropanol and extracted with *n*-hexane after addition of surrogate extraction standards as in Donald and Anderson⁴⁴. Five LDPE strips from each sampling box were composited for extraction. Final volume was quantitatively reduced to 1.0 mL. Internal standards were added to aliquots prior to instrumental analysis.

Silicone passive samplers—Silicone passive samplers were pre-conditioned in a vacuum oven, and 20uL of a PRC solution applied directly to the surface and air dried as in Anderson et al.³⁷ Silicone samplers were thermally extracted onto Markes sorbent tubes (C3-AAXX-5304) using a Markes micro-chamber/thermal extractor. The tubes were fitted with Markes diffusion lock caps (difflock C-DL100) during analysis, and with Swagelok caps (B-400-C) with Teflon ferrules (T-400-SET) for storage. Tubes used a Markes Unity 2/ Ultra 2 Thermal Desorption System for introduction into the GC/MS. Conditions for thermal desorption are presented in SI, Table S5.

Crumb rubber—Deployed crumb rubber collected from 4 locations of each field was composited into single sample for each field. Additional crumb rubber sample was taken from “fresh” stock that had yet to be applied. Samples were analyzed using the identical parameters as silicone passive samplers. Approximately 50 mg of crumb rubber was used, and extraction and analysis performed in triplicate. Concentrations were normalized for crumb rubber mass.

Instrumental analysis

LDPE passive samplers—Extracts were analyzed using previously described methods for 62 PAHs and 19 OPAHs (Table 1).^{42, 43} PAH analysis was conducted using gas chromatography electron-impact/triple quadrupole mass spectrometry (GC/MS-MS, Agilent 7000C) with an Agilent PAH-select column.⁴² Analysis for OPAHs was performed with gas-chromatography electron impact mass spectrometry (GC/MS, Agilent 7890A and 5975C)

with a DB5-MS column.⁴³ Presence or absence of 1529 chemicals was determined also using GC/MS with a DB5-MS column.³⁶ Over 100 additional chemicals were added to an existing presence/absence method, including several related to recycled tires and artificial turf, *e.g.* benzothiazole. This presence/absence screen, hereafter referred as the “1529 screen,” uses mass spectral deconvolution software, and the complete list of analytes is included in SI. Chemical concentrations in the 1529 screen are not quantified against calibration curves, however responses from blanks and quality control samples are compared to infer relative concentrations.

GC-MS 1529 screen method parameters—Data was acquired using an Agilent 7890A GC and Agilent 5975C MS operated in full scan mode with electron ionization using an Agilent DB-5MS column (30 m × 0.25 mm). Inlet pressure was locked to the retention time of chlorpyrifos at 19.23 (± 0.20) minutes. Full details are provided in Tables S3 and S4.

Deconvolution—AMDIS version 2.66 (NIST), as part of the Deconvolution Reporting Software (DRS, Agilent) was used to de-convolute and identify peaks. AMDIS software parameters are given in Table S4. AMDIS integrated the identified peaks which were used for some general comparisons.

Silicone passive samplers and crumb rubber—Silicone samplers and crumb rubber were analyzed for 77 compounds, including PAHs, OPAHs, volatile organic compounds (VOCs), flame retardants, tri-R-phosphates, polybrominated diphenyl ethers (PBDEs), pesticides, pharmacological chemicals and consumer products, via GC/MS following thermal extraction as per supplemental information Table S5. Silicone and crumb rubber samples were thermally extracted with a Markes micro-chamber/thermal extractor. Extraction chambers were wiped with isopropanol and dried between extractions. Samples were loaded into the extraction chamber and spiked with 2uL of a 50ng/uL extraction surrogate solution. A sorbent tube packed with quartz wool, Tenex TA, and carbograph 5TD was secured to the extraction chamber. Before starting the thermal desorption extraction carrier gas (nitrogen 99.999%) was allowed to flow through the chamber for approximately 2 mins.

Thermal desorption GS-MS method—Samplers were thermally extracted by heating from an initial temperature of 25°C to 50°C at the maximum heating rate, held for 30 mins, then heated at the maximum heating rate to 250°C and held for 1.5 hrs. Nitrogen was used as carrier gas at a flow rate of 40–50mL/min. After extraction tubes were fitted with difflok caps, and were analyzed with an Agilent 6890N GC with an Agilent 5975B with triple axis detector MS equipped with a Markes series 2 Ultra auto sampler and Markes Unity 2 cold trap sample introduction system. Markes systems were controlled using Markes Maverick thermal desorption system control program, version 5.1.0. Agilent Chemstation E.02.00.493 was used to control Agilent components and for sample analysis. Settings for sample acquisition can be viewed in supplemental information Table S5 and S6. Where overlap of PAH and OPAH compounds occur in two analysis methods, the value for the triple-quadrupole instrument is reported.

Calculations

Gas-phase concentrations of PAHs and OPAHs in air (C_{air}) and turf air ($C_{turf\ air}$) were determined from LDPE passive samplers using an empirical uptake model with PRCs as *in situ* calibration standards.^{44, 47, 48} Details are provided in SI. Method detection limits (Table S1) were calculated separately for air and turf air, using average PRC retention per matrix and average temperature of deployment. Generally, detection limits increase from air to turf air, and increase with chemical volatility.

Quantitative flux ($\text{ng m}^{-2} \text{h}^{-1}$) between air and turf air was calculated for PAHs and OPAHs at each site when concentrations were above limits of quantitation in both matrices:

$$flux = \frac{D^T}{\delta_L} (C_{turf\ air} - C_{air}) \quad \text{Eq. 1}$$

where $C_{turf\ air}$ is the concentration of a target chemical in air immediately at the turf surface (ng m^{-3}) and C_{air} is the concentration of a target chemical in air (ng m^{-3}). The height of the boundary layer (δ_L) was estimated at 0.001 m. Temperature-corrected mass transfer coefficients (D^T) were estimated from the D^T of pyrene at 298 K as a reference (Table S1).⁴⁴

Statistical analysis

Mean temperature and relative humidity comparisons were made using two-sided t-tests with serial correlation corrections. Uncertainty of flux calculations was estimated via propagation of error,^{49, 50} following the methods described in SI. Logarithms of air and turf air concentrations were compared using simple linear regression. Statistical analyses were performed in Microsoft Excel 2016 and JMP Pro 13.0.0.

Quality control

QC samples represented over 50% of all samples analyzed as part of the turf study. Details of quality control are provided in SI. Initial target compound retention time and reference library spectrum were obtained from single analyte solutions (Accustandard, New Haven CT) directly injected through a Markes calibration solution loading rig (CSLR). Additional details of the quality assurance are provided in SI. Instrumental limits of quantitation (LOQs) were calculated in accordance with other methods in our laboratory^{42, 51} and as described by the U.S. EPA.⁵² LOQs values and additional QC details are described in SI.

Results and Discussion

Environmental concentrations of PAHs and OPAHs in Turf

Among ten turf air and pore-air LDPE samples we detected 44 PAHs, and 7 OPAHs (Figure 1). Higher-molecular weight chemicals were more frequently detected in air, the matrix with the lowest detection limits. The *indoor site*, also the newest field sampled, had the highest concentrations, with average levels 20- and 13-fold greater than *outdoor A* and *outdoor B*, respectively. Indoor fields, particularly those with poor ventilation, have documented higher levels of air contaminants.⁵ While consistent with previous work, with limited sampling locations, we cannot differentiate the effects of indoor/outdoor facility or field age.

Samples at *outdoor A* were collected in triplicate, and variance across target analytes present in both matrices was similar between air (average RSD 26%) and turf air (average RSD 21%). This contrasts with the initial demonstration of the flux passive sampling equipment in which variance in soil air (RSD 40%) far exceeded the variance in air (RSD 8%)⁴⁴. These differences in variance may reflect the relative homogeneity of an artificial turf field versus natural settings.

Twelve detected PAHs had not been reported previously in work related to artificial turf⁴ (Table 1), including many alkyl-naphthalenes. The presences of these alkylated-naphthalenes is noteworthy for risk assessment considerations. Baird et al⁵³ and others⁵⁴ have previously identified the lack of exposure data for alkylated PAHs to adequately assess human PAH risk. In aquatic studies, mounting evidence suggests alkylated PAHs may be more toxic than parent PAHs, perhaps due to bioavailability and toxic potency of alkylated PAHs.⁵⁵ Han (and references therein, Calbet et al⁵⁶) illustrated an 18-fold increase in toxicity for alkylated-naphthalenes over naphthalene in copepod *P.grani*. While more studies are needed [to assess human toxicity] these results demonstrate the importance of analyzing large numbers of chemicals simultaneously in human exposure scenarios.

One PAH not previously reported was benzo[c]fluorene, with an estimated carcinogenic potency 20 times greater than benzo[a]pyrene.⁵⁷ Benzo[c]fluorene was detected in all LDPE samplers at all sites. In all cases turf air concentrations were higher than air concentrations, indicating the analyte to be volatilizing from turf. Independent of turf, Yagishita found benzo[c]fluorene in the gas phase in a recent atmospheric study in Japan. Yagishita, reported that benzo[c]fluorene was 44% in the gas phase and a large contributor to the atmospheric carcinogenic risk of PAHs.⁵⁸

Many PAHs in tires are from the addition of highly-aromatic oils (HA-oils) during manufacturing.^{2, 59} HA-oils formerly contained between 10 and 30% PAHs by weight, but high-PAH HA-oils have been phased out of European Union (EU) countries after directive 2005/69/EC beginning in 2010. It is expected that tire producers worldwide will increasingly use alternative, low-PAH HA-oils.¹ Tires are also a documented source of carcinogenic, 6-ringed dibenzopyrene PAHs to the environment, but levels are expected to decline as high-PAH HA-oils are phased out.⁵⁹ Pyrene and benzo[ghi]perylene are major PAH components in tires, and have been documented as major components in artificial turf crumb rubber as well.⁵⁹ Pyrene was present in all samples, while the less-volatile benzo[ghi]perylene was below limits of detection in turf air, but detected in all air samples.

This experimental design sampled gas-phase volatile and semi-volatile contaminants exclusively, and most PAHs observed were the more volatile lower-MW PAHs. We did not detect the carcinogenic dibenzopyrenes described in Sadiqsis, Bergvall, Johansson and Westerholm⁵⁹ which analyzed crumb from tires containing HA-oils. If present, such 6-ringed dibenzopyrenes would be highly associated with particles and are only likely to be present in the gas-phase at low levels. The lack of dibenzopyrenes in the present study does not necessarily indicate that tires sourced for this crumb rubber did not contain HA oils, rather the levels are below limits of detection. PAHs are pervasive environmental

contaminants with multiple sources, and it is likely that other sources contributed to the measurements, *e.g.* traffic on adjacent roads or regional wildfires.

We detected 6 OPAHs not previously reported at artificial turf fields. (Table 1). Previous reports are limited to three OPAHs: 6H-benzo[cd]pyren-6-one, 4H-cyclopenta[def]phenanthrene-4-one, and 2-ethyl-9,10-anthraquinone.^{4, 21} Two of these were included in our analysis, and we detected 4H-cyclopenta[def]phenanthrene-4-one, but not 6H-benzo[cd]pyren-6-one. Compared to the PAHs, the toxicity of OPAHs is less well-studied.²⁰ OPAHs may have more mutagenic potential than their corresponding unsubstituted parent PAHs, and some OPAHs need not be metabolically activated to induce toxicity.²⁰ Knecht, et al.⁶⁰ screened 38 OPAHs for morphological malformations using the embryonic zebrafish bioanalytical model, and found 9,10-phenanthraquinone to be one of the most toxic OPAHs, followed closely by benzofluorenone. Benzofluorenone is also a potent inhibitor of the CYP1A1 enzyme, indicating that this OPAH is as toxicologically relevant as the more studied PAHs.⁶¹ These newly-reported PAHs and OPAHs should be considered as potential toxicants in future human risk assessments of artificial turf field users.

Numerous previous studies report concentrations of PAHs associated with particles, however to the authors' knowledge only one report gives gas-phase concentrations on an artificial turf field.¹⁸ Dye, Bjerke, Schmidbauer and Mano¹⁸ used active samplers to collect the gas-phase concentration in three indoor facilities with artificial turf. Air data from *indoor* agree well with their results (Figure S14), demonstrated with values from a representative site, Valhall. Their report also includes particle-phase (PM10) PAH concentrations. Comparing these two phases (Figure S15), PM10-bound and gas-phase, we infer that over 97% of measured PAHs were in the gas-phase. Generally, the low-molecular weight, more volatile chemicals were predominantly present in the gas-phase, while PAHs with log K_{oa} approximately 9 or larger were mostly associated with particles. Gas-phase contaminants are bioavailable and can enter biological membranes when inhaled or contacted. Contaminants adsorbed to particles are less bioavailable, and particle size affects penetration into the lungs.⁵ The present experimental design sampled the bioavailable, gas-phase chemicals, therefore low concentrations of high-molecular weight chemicals were expected. The current work gives the first gas-phase concentrations around outdoor artificial turf fields to date.⁴

Concentrations in crumb rubber

Crumb rubber stock and the 2 month old indoor field crumb rubber samples were quite similar both for VOC/SVOC detections and concentrations (Figure 2). Crumb rubber stock had more chemicals than either indoor air sample A or B, 35 versus 31 and 19 chemicals respectively. The *Outdoor A* and *B* samples were mostly missing the decanes (*e.g.* tetradecane, pentadecane, heptadecane) and the naphthalenes compared with the stock crumb rubber. *Outdoor B* crumb rubber had the fewest chemicals detected and was also missing phenanthrene and substituted phenanthrenes. While we do not have an exact age on the last addition of crumb rubber to *Outdoor B*, it is the oldest field. We found that *Outdoor B* crumb rubber had fewer detections of many higher molecular weight SVOCs, specifically we did not detect benz[b or c]fluorene, chrysene, triphenylene, or benzo[a]pyrene to name a

few (see Figure 3). Both benzo[b]fluorene and benzo[a]pyrene have hazard concerns as discussed above. Crumb rubber is an important contribution to the chemicals measured and could pose a *potential* inhalation exposure hazard.

Presence/absence of 1529 chemicals

Additionally, the LDPE samplers were screened for the presence or absence of 1529 additional compounds. Nineteen chemicals were detected beyond the PAHs and OPAHs (Figure 3). Seven of these chemicals have not been previously reported in literature pertaining to artificial turf, recycled tires, or crumb rubber (Table 1).⁴ Two phthalates were present in procedural blanks and are included in Figure 3 nonetheless, because responses were more than 500-fold greater in field samples than in procedural blanks, and we report them as positive detects: bis(2-ethylhexyl)phthalate and di-n-butylphthalate (Table S9).

Phthalates detected in the present work have been reported in previous analyses of crumb rubber,¹⁵ playground material,¹⁴ and air at playing fields.^{4, 5} Four are recognized as reproductive toxicants by the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) directive. A recent risk analysis of these four (bis(2-ethylhexyl)phthalate, di-n-butylphthalate, butyl benzyl phthalate, and diisobutylphthalate) concluded that concentrations are below levels that would lead to health problems in players and workers.⁵ The present work confirms the presence of these phthalates but not absolute concentrations. Therefore, we cannot compare risk estimates to previous reports.

Several personal care products were detected using the 1529 screen in both air and turf air samplers. The chemical *b*-citronellol is a component of perfumes and essential oils of various plants.⁶² Benzyl salicylate, a scent compound,⁶³ was present in all air samples, but in no turf air samples. Drometrizole, an ultraviolet light absorber used in sunscreen products⁶⁴ and plastic polymers,⁶⁵ was found in one turf air sampler. This chemical has been previously been detected in leachate,¹² and we cannot distinguish whether our detection is due to personal care product usage or as an antioxidant additive in sourced tires. The common insect repellent N,N-diethyl-m-toluamide (DEET) was found in turf air samplers. With the possible exception of drometrizole, personal care products such as these are unlikely to be present in fresh crumb rubber, therefore their detections likely stem from field users rather than the artificial turf. Personal care products in turf air support the theory that turf can act an initial sink to naive chemicals, with gradual off-gassing over time.

In addition, we observed several other chemicals, seven of which have not been reported previously to be associated with artificial turf, tires, or crumb rubber (Table 4). Ethiolate, a dithiocarbamate herbicide believed to be obsolete or no longer in use,⁶⁶ has not been previously associated. However, dithiocarbamates are used as vulcanizing agents in tire production,⁶⁷ and we hypothesize this detection represents a structurally-similar dithiocarbamate constituent of tires. Pentachlorobenzene is a persistent organic pollutant included in the Stockholm Convention.⁶⁸ This chemical was seen in two samples: in turf air from the indoor, newest field and in turf air from the outdoor, oldest field. These detections do not suggest a pattern related to field age or indoor/facility. Pentachlorobenzene can also be emitted from biomass burning,⁶⁸ and regional wildfires around the sampling period are a potential source. Finally, triphenyl phosphate is an organophosphate flame retardant, an

emerging class of chemicals used as alternative to phased-out brominated flame retardants.⁶⁹ Triphenyl phosphate detections only in air, and only at the older and outdoor fields, suggest that artificial turf is not a source of this chemical.

At the outdoor locations, we detected benzothiazole only in turf air, as in previous findings where samples were collected 6 inches above turf.^{6, 8} Benzothiazole levels were substantially higher indoors than outside in those studies. Similarly, in our work, benzothiazole was above detection limits in both matrices at *indoor*, but only detectable in turf air at the outdoor fields, generally suggesting lower levels outdoors. Phthalimide, another chemical associated with rubber vulcanization, was detected in one turf air sampler and has been reported previously in leachate from artificial turf.⁴ Preservatives and antioxidants like butylate hydroxy toluene and diphenylamine are known components of tires, although benzyl benzoate has not previously been reported in artificial turf literature.⁴

Flux of PAHs and OPAHs

Flux varied substantially among the three fields (Figure 4) and was evaluated for 35 PAHs and OPAHs at sites in which both air and turf air measurements were above limit of detection. Complete flux values with uncertainty determined via propagation of error are given in Table S10. Naphthalene the highest measured rate of volatilization (*indoor* site, 38,000 ng m⁻² h⁻¹), and the highest rate of deposition (*outdoor B*, -2000 ng m⁻² h⁻¹). All flux values at the *indoor* site were positive, indicating volatilization, with an average rate of 3000 ng m⁻² h⁻¹. In comparison, only higher molecular-weight, less-volatile chemicals were volatilizing at the outdoor sites. The more volatile chemicals naphthalene and 1- and 2-methylnaphthalene were depositing at both *outdoor A* and *outdoor B*, while the slightly-heavier dimethylnaphthalenes were generally depositing only at the oldest of the three sites, *outdoor B*. When measurable, OPAHs were volatilizing, however only chromone was significantly volatilizing.

Profiles of PAH/OPAH flux agrees with previous evidence that off-gassing relates to the age of the field.^{17, 24} Due to the small sampling design, we cannot discern effects of indoor/outdoor facility or field age, and any observed trends relating to field age may be complicated by the occasional addition of new crumb rubber, though the magnitude of these effect remain unclear.¹⁷ (https://www.health.ny.gov/environmental/outdoors/synthetic_turf/crumb-rubber_infilled/docs/fact_sheet.pdf) Compared to the newest field, *indoor*, the two older fields appear to be acting as a sink for the more volatile chemicals.

The relationship between turf and overlying air can also be represented by a simple correlation (Figure 5). We observed correlations (p-value < 0.05) at each field, although the strength of correlation varied. The newest field, *indoor*, had the strongest correlation (R² = 0.964), indicating that volatilization from turf strongly affects concentrations in the overlying air at this site. Slightly less-strong correlations were observed at *outdoor A* (R² = 0.717) and *outdoor B* (R² = 0.670), providing evidence that the contribution of volatilization at the two older, outdoor sites is likely convoluted by additional outdoor sources and potentially greater air movement. Similar correlation analyses have been conducted, albeit sparingly. Cabrerizo, et al.⁷⁰ report high correlations (R² = 0.63 and 0.76) between air fugacity and soil fugacity where volatilization of organochlorine pesticides occurs at

background sites, but weaker correlations ($R^2 = 0.32$ and insignificant) at sites with deposition signatures. In a similar approach, Bidleman and Leone⁷¹ point to good correlations between soil concentrations and overlying air concentrations (R^2 up to 0.73) as evidence of volatilization. The strength of correlation observed at the *indoor* site exceeds these previous reports of volatilization from soil, and we hypothesize that the strength of this correlation will decrease over time as the field ages.

Silicone-air partitioning coefficient

Commonly, new techniques are calibrated against existing technologies. Khairy and Lohmann⁷² co-deployed LDPE passive samplers with established active samplers to, in part, determine sampler-air partition coefficients. Similarly, we co-deployed silicone samplers alongside the more established LDPE. Numerous types of silicone polymer have been used in organic pollutant research.³⁸ O'Connell, et al.⁷³ co-deployed LDPE and silicone to illustrate that the properties of target compounds should be considered when selecting a polymer in passive sampling studies. Co-deployment of conventional and new samplers is considered a gold standard. Further, previous reports (Dye, Bjerke et al 2006) using active samplers are very similar to our LDPE results, providing additional support of LDPE values used in the paired approach for assessing silicone-air partitioning coefficients.

Side-by-side deployment of passive samplers of two materials allowed for calculation of silicone-air partition coefficients ($K_{silicone-air}$):

$$K_{silicone - air} = \frac{C_{silicone}}{C}$$

where $C_{silicone}$ is the concentration in silicone and C is the concentration in air or turf air determined with LDPE samplers. Values for $K_{silicone-air}$ of chemicals were only determined for chemicals at equilibrium, as inferred from PRC loss data.

Our determinations are similar to previous reports of silicone-air partitioning in Anderson et al 2017, albeit with greater spread and prediction intervals. The silicone material in this work is identical to wristbands in previous studies³²⁻³⁵. In that work, the silicone was worn on participants' wrists, so sampling occurred at near-constant temperatures. In contrast, average temperatures in this turf study ranged between 20.5 and 25.2 °C, and though this is a small range, even small differences in temperature can result in large changes in partitioning. A 10 °C increase in temperature is expected to decrease $K_{silicone-air}$ by 2-fold.³⁰ We propose that the high variability in our prediction of $K_{silicone-air}$ can be attributed to the differences in environmental conditions. In future work, this information can be combined to understand the contribution of vapor-phase contaminants in environmental and personal exposure.

Limitations

This study has a small sample size and does not incorporate fields with a range of ages, adjacent contaminant sources, geographic location, artificial turf manufacturers, use patterns, *etc.* With the sample size, we cannot distinguish the effects of field age or indoor/outdoor facility on chemical detections or flux. We sampled only during the warmest days of

the year. As chemical volatility increases with temperature, we expect lower volatilization rates in cooler temperatures, all else constant. Data were not compared to samples from adjacent background or natural turf fields, and the detection of a chemical in an air sample does not necessarily indicate it derives from artificial turf. Detections in the self-contained turf air sampling boxes are more likely associated with artificial turf and infill. Method detection limits vary depending on the matrix being sampled and the rate of air exchange or wind across the samplers, as indicated with PRC data. Detection limits must be carefully considered when comparing between the air and turf air matrices. Further work is necessary to determine what risk these chemicals may contribute to adverse health outcomes. The described sampling scheme is a candidate for large-scale assessment of artificial turf field flux. Thermal extraction and silicone passive samplers are highly suitable for larger-scale sampling campaigns that aim for less solvent and sample processing.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

The authors thank Gary Points for increasing number of the chemicals in the 1529 screen. Holly Dixon, Jessica Scotten, Lane Tidwell, and Amber Barnard provided additional field and laboratory support. We greatly appreciate the permission of the field managers and their assistance in field sampling.

References

1. Cheng H; Hu Y; Reinhard M, Environmental and health impacts of artificial turf: a review. *Environ. Sci. Technol* 2014, 48, (4), 2114–29 [PubMed: 24467230]
2. Schihiro T; Traversi D; Degan R; Pignata C; Alessandria L; Scozia D; Bono R; Gilli G, Artificial turf football fields: environmental and mutagenicity assessment. *Arch. Environ. Contam. Toxicol.* 2013, 64, (1), 1–11. [PubMed: 23007896]
3. U.S. Environmental Protection Agency; Centers for Disease Control and Prevention; Agency for Toxic Substances and Disease Registry Research Protocol: Collections Related to Synthetic Turf Fields with Crumb Rubber Infill; 2016.
4. U.S. Environmental Protection Agency Federal Research Action Plan on Recycled Tire Crumb Used on Playing Fields and Playgrounds STATUS REPORT; 2016.
5. European Chemicals Agency An evaluation of the possible health risks of recycled rubber granules used as infill in synthetic turf sports fields; 2017.
6. Connecticut Department of Public Health Human Health Risk Assessment of Artificial Turf Fields Based Upon Results from Five Fields in Connecticut; Program in Environmental and Occupational Health Assessment 2010.
7. California Environmental Protection Agency Evaluation of Health Effects of Recycled Waste Tires in Playground and Track Products; Office of Environmental Health Hazard Assessment,; 2007.
8. Ginsberg G; Toal B; Simcox N; Bracker A; Golembiewski B; Kurland T; Hedman C, Human health risk assessment of synthetic turf fields based upon investigation of five fields in Connecticut. *J. Toxicol. Environ. Health A* 2011, 74, (17), 1150–74. [PubMed: 21797769]
9. Menichini E; Abate V; Attias L; De Luca S; di Domenico A; Fochi I; Forte G; Iacovella N; Iamiceli AL; Izzo P; Merli F; Bocca B, Artificial-turf playing fields: contents of metals, PAHs, PCBs, PCDDs and PCDFs, inhalation exposure to PAHs and related preliminary risk assessment. *Sci. Total Environ.* 2011, 409, (23), 4950–7. [PubMed: 21907387]
10. Norwegian Institute of Public Health and the Radium Hospital Artificial turf pitches – an assessment of the health risks for football players; 2006.

11. Pavilonis BT; Weisel CP; Buckley B; Liroy PJ, Bioaccessibility and Risk of Exposure to Metals and SVOCs in Artificial Turf Field Fill Materials and Fibers. *Risk Anal.* 2014, 34, (1), 44–55. [PubMed: 23758133]
12. Nilsson NH; Malmgren-Hansen B; Thomsen US Mapping, emissions and environmental and health assessment of chemical substances in artificial turf; Danish Ministry of the Environment: 2008.
13. Bocca B; Forte G; Petrucci F; Costantini S; Izzo P, Metals contained and leached from rubber granulates used in synthetic turf areas. *Sci. Total Environ.* 2009, 407, (7), 2183–90. [PubMed: 19155051]
14. Celeiro M; Lamas JP; Garcia-Jares C; Dagnac T; Ramos L; Llompart M, Investigation of PAH and other hazardous contaminant occurrence in recycled tyre rubber surfaces. Case-study: restaurant playground in an indoor shopping centre. *Int. J. Environ. Anal. Chem.* 2014, 94, (12), 1264–1271.
15. Llompart M; Sanchez-Prado L; Pablo Lamas J; Garcia-Jares C; Roca E; Dagnac T, Hazardous organic chemicals in rubber recycled tire playgrounds and pavers. *Chemosphere* 2013, 90, (2), 423–31. [PubMed: 22921644]
16. Marsili L; Coppola D; Bianchi N; Maltese S; Bianchi M; Fossi MC, Release of Polycyclic Aromatic Hydrocarbons and Heavy Metals from Rubber Crumb in Synthetic Turf Fields: Preliminary Hazard Assessment for Athletes. *Journal of Environmental & Analytical Toxicology* 2015, 5, 265.
17. Zhang JJ; Han IK; Zhang L; Crain W, Hazardous chemicals in synthetic turf materials and their bioaccessibility in digestive fluids. *J. Expo. Sci. Environ. Epidemiol* 2008, 18, (6), 600–7. [PubMed: 18728695]
18. Dye C; Bjerke A; Schmidbauer N; Mano S Measurement of air pollution in indoor artificial turf halls NILU OR 03/2006; Norwegian Institute for Air Pollution: 2006.
19. Johns DM Initial evaluation of potential human health risks associated with playing on synthetic turf fields on Bainbridge Island; Windward Environmental, LLC: 2008.
20. Lundstedt S; White PA; Lemieux CL; Lynes KD; Lambert IB; Öberg L; Haglund P; Tysklind M, Sources, Fate, and Toxic Hazards of Oxygenated Polycyclic Aromatic Hydrocarbons (PAHs) at PAH- contaminated Sites. *AMBIO: A Journal of the Human Environment* 2007, 36, (6), 475–485.
21. Kanematsu M; Hayashi A; Denison MS; Young TM, Characterization and potential environmental risks of leachate from shredded rubber mulches. *Chemosphere* 2009, 76, (7), 952–8. [PubMed: 19450864]
22. Weschler CJ; Nazaroff W, SVOC exposure indoors: fresh look at dermal pathways. *Indoor air* 2012, 22, (5), 356–377. [PubMed: 22313149]
23. Xu Y, Z. J, Understanding SVOCs. *ASHRAE Journal*, 2011, 53, (12), 121–125.
24. Li X; Berger W; Musante C; Mattina MI, Characterization of substances released from crumb rubber material used on artificial turf fields. *Chemosphere* 2010, 80, (3), 279–85. [PubMed: 20435333]
25. Ramírez N; Cuadras A; Rovira E; Marcé RM; Borrull F, Risk assessment related to atmospheric polycyclic aromatic hydrocarbons in gas and particle phases near industrial sites. *Environ. Health Perspect.* 2011, 119, (8), 1110. [PubMed: 21478082]
26. Khairy MA; Lohmann R, Field validation of polyethylene passive air samplers for parent and alkylated PAHs in Alexandria, Egypt. *Environ. Sci. Technol.* 2012, 46, (7), 3990–3998. [PubMed: 22397460]
27. Samburova V; Zielinska B; Khlystov A, Do 16 Polycyclic Aromatic Hydrocarbons Represent PAH Air Toxicity? *Toxics* 2017, 5, (3), 17.
28. Tsai P-J; Shieh H-Y; Lee W-J; Lai S-O, Characterization of PAHs in the atmosphere of carbon black manufacturing workplaces. *Journal of hazardous materials* 2002, 91, (1), 25–42. [PubMed: 11900904]
29. Fernandez LA; Lao W; Maruya KA; Burgess RM, Calculating the diffusive flux of persistent organic pollutants between sediments and the water column on the Palos Verdes shelf superfund site using polymeric passive samplers. *Environmental Science & Technology* 2014, 48, (7), 3925–34. [PubMed: 24564763]

30. Huckins JN; Petty JD; Booij K, Monitors of organic chemicals in the environment: semipermeable membrane devices. Springer Science & Business Media: 2006.
31. Paulik LB; Smith BW; Bergmann AJ; Sower GJ; Forsberg ND; Teeguarden JG; Anderson KA, Passive samplers accurately predict PAH levels in resident crayfish. *Sci. Total Environ.* 2016, 544, 782–791. [PubMed: 26674706]
32. Donald CE; Scott RP; Blaustein KL; Halbleib ML; Sarr M; Jepson PC; Anderson KA, Silicone wristbands detect individuals' pesticide exposures in West Africa. *Royal Society Open Science* 2016, 3, (8), 160433. [PubMed: 27853621]
33. Hammel SC; Hoffman K; Webster TF; Anderson KA; Stapleton HM, Measuring Personal Exposure to Organophosphate Flame Retardants Using Silicone Wristbands and Hand Wipes. *Environ. Sci. Technol.* 2016, 50, (8), 4483–91. [PubMed: 26975559]
34. Kile ML; Scott RP; O'Connell SG; Lipscomb S; MacDonald M; McClelland M; Anderson KA, Using silicone wristbands to evaluate preschool children's exposure to flame retardants. *Environ. Res.* 2016, 147, 365–72. [PubMed: 26945619]
35. O'Connell SG; Kincl LD; Anderson KA, Silicone Wristbands as Personal Passive Samplers. *Environ. Sci. Technol.* 2014, 48, (6), 3327–3335. [PubMed: 24548134]
36. Bergmann AJ; North PE; Vasquez L; Bello H; Del Carmen Gastanaga Ruiz M; Anderson KA, Multi-class chemical exposure in rural Peru using silicone wristbands. *J. Expo. Sci. Environ. Epidemiol* 2017, 27, (6), 560–568. [PubMed: 28745304]
37. Anderson KA; Points Iii GL; Donald CE; Dixon HM; Scott RP; Wilson G; Tidwell LG; Hoffman PD; Herbstman JB; O'Connell SG, Preparation and performance features of wristband samplers and considerations for chemical exposure assessment. *J Expos Sci Environ Epidemiol* 2017.
38. Smedes F; Geertsma RW; Zande T. v. d.; Booij K, Polymer–Water Partition Coefficients of Hydrophobic Compounds for Passive Sampling: Application of Cosolvent Models for Validation. *Environ. Sci. Technol.* 2009, 43, (18), 7047–7054. [PubMed: 19806740]
39. Jonker MTO; van der Heijden SA; Kotte M; Smedes F, Quantifying the Effects of Temperature and Salinity on Partitioning of Hydrophobic Organic Chemicals to Silicone Rubber Passive Samplers. *Environ. Sci. Technol.* 2015, 150515094105006.
40. Reppas-Chrysovitsinos E; Sobek A; MacLeod M, Screening-level models to estimate partition ratios of organic chemicals between polymeric materials, air and water. *Environ Sci Process Impacts* 2016, 18, (6), 667–76. [PubMed: 27158699]
41. Okeme JO; Parnis JM; Poole J; Diamond ML; Jantunen LM, Polydimethylsiloxane-air partition ratios for semi-volatile organic compounds by GC-based measurement and COSMO-RS estimation: Rapid measurements and accurate modelling. *Chemosphere* 2016, 156, 204–11. [PubMed: 27179237]
42. Anderson KA; Szelewski MJ; Wilson G; Quimby BD; Hoffman PD, Modified ion source triple quadrupole mass spectrometer gas chromatograph for polycyclic aromatic hydrocarbon analyses. *J. Chromatogr. A* 2015, 1419, 89–98. [PubMed: 26454790]
43. O'Connell SG; Haigh T; Wilson G; Anderson KA, An analytical investigation of 24 oxygenated-PAHs (OPAHs) using liquid and gas chromatography–mass spectrometry. *Anal. Bioanal. Chem.* 2013, 405, 8885–8896. [PubMed: 24005604]
44. Donald CE; Anderson KA, Assessing soil-air partitioning of PAHs and PCBs with a new fugacity passive sampler. *Sci. Total Environ.* 2017, 596–597, 293–302. [PubMed: 29272828]
45. Anderson KA; Sethajintanin D; Sower GJ; Quarles L, Field trial and modeling of uptake rates of in situ lipid-free polyethylene membrane passive sampler. *Environ. Sci. Technol.* 2008, 42, (12), 4486–93. [PubMed: 18605575]
46. Sower GJ; Anderson KA, Spatial and Temporal Variation of Freely Dissolved Polycyclic Aromatic Hydrocarbons in an Urban River Undergoing Superfund Remediation. *Environmental Science & Technology* 2008, 42, (24), 9065–9071. [PubMed: 19174872]
47. Huckins JN; Petty JD; Lebo JA; Almeida FV; Booij K; Alvarez DA; Cranor WL; Clark RC; Mogensen BB, Development of the permeability/performance reference compound approach for in situ calibration of semipermeable membrane devices. *Environ. Sci. Technol.* 2002, 36, (1), 85–91. [PubMed: 11811495]

48. Lohmann R, Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. *Environ. Sci. Technol.* 2012, 46, (2), 606–18. [PubMed: 22122117]
49. Liu Y; Wang S; McDonough CA; Khairy M; Muir D; Lohmann R, Estimation of Uncertainty in Air-Water Exchange Flux and Gross Volatilization Loss of PCBs: A Case Study Based on Passive Sampling in the Lower Great Lakes. *Environ. Sci. Technol.* 2016, 50, (20), 10894–10902. [PubMed: 27623269]
50. Minick D; Anderson KA, Diffusive flux of PAHs across sediment-water and water-air interfaces at urban Superfund sites. *Environ. Toxicol. Chem.* 2017, In Press.
51. Donald CE; Scott RP; Blaustein KL; Halbleib ML; Sarr M; Jepson PC; Anderson KA, Silicone wristbands detect individuals' pesticide exposures in West Africa. *Royal Society Open Science* 2016, 3, (8), 160433. [PubMed: 27853621]
52. EPA, U. S., EPA 821-R-16-006 Definition and procedure for the determination of the method detection limit, revision 2. In *Water O. o.*, Ed. Washington, D.C., 2016.
53. Baird SJS; Bailey EA; Vorhees DJ, Evaluating Human Risk from Exposure to Alkylated PAHs in an Aquatic System. *Human and Ecological Risk Assessment: An International Journal* 2007, 13, (2), 322–338.
54. Agency, U. S. E. P., U.S. EPA. PEER CONSULTATION WORKSHOP ON APPROACHES TO POLYCYCLIC AROMATIC HYDROCARBON (PAH) HEALTH ASSESSMENT. Office of Research and Development, National Center for Environmental Assessment 2002.
55. Han J; Won E-J; Hwang D-S; Shin K-H; Lee YS; Leung KM-Y; Lee S-J; Lee J-S, Crude oil exposure results in oxidative stress-mediated dysfunctional development and reproduction in the copepod *Tigriopus japonicus* and modulates expression of cytochrome P450 (CYP) genes. *Aquatic Toxicology* 2014, 152, 308–317. [PubMed: 24813263]
56. Calbet A; Saiz E; Barata C, Lethal and sublethal effects of naphthalene and 1,2-dimethylnaphthalene on the marine copepod *Paracartia grani*. *Marine Biology* 2007, 151, (1), 195–204.
57. U.S. Environmental Protection Agency, Development of a relative potency factor approach for PAH mixtures. 2010.
58. Yagishita M; Kageyama S; Ohshima S; Matsumoto M; Aoki Y; Goto S; Nakajima D, Atmospheric concentration and carcinogenic risk of polycyclic aromatic hydrocarbons including benzo[c]fluorene, cyclopenta[c,d]pyrene, and benzo[j]fluoranthene in Japan. *Atmospheric Environment* 2015, 115, 263–268.
59. Sadiqtsis I; Bergvall C; Johansson C; Westerholm R, Automobile tires--a potential source of highly carcinogenic dibenzopyrenes to the environment. *Environ. Sci. Technol.* 2012, 46, (6), 3326–34. [PubMed: 22352997]
60. Knecht AL; Goodale BC; Truong L; Simonich MT; Swanson AJ; Matzke MM; Anderson KA; Waters KM; Tanguay RL, Comparative developmental toxicity of environmentally relevant oxygenated PAHs. *Toxicol. Appl. Pharmacol.* 2013, 271, 266–275. [PubMed: 23684558]
61. Wincent E; Le Bihanic F; Dreij K, Induction and inhibition of human cytochrome P4501 by oxygenated polycyclic aromatic hydrocarbons. *Toxicol. Res.* 2016, 5, (3), 788–799.
62. Ribeiro-Filho HV; de Souza Silva CM; de Siqueira RJ; Lahlou S; dos Santos AA; Magalhaes PJ, Biphasic cardiovascular and respiratory effects induced by beta-citronellol. *Eur. J. Pharmacol.* 2016, 775, 96–105. [PubMed: 26872991]
63. Lapczynski A; McGinty D; Jones L; Bhatia S; Letizia CS; Api AM, Fragrance material review on benzyl salicylate. *Food Chem. Toxicol.* 2007, 45 Suppl 1, S362–80. [PubMed: 18035470]
64. Antoniou C; Kosmadaki MG; Stratigos AJ; Katsambas AD, Sunscreens - what's important to know. *J. Eur. Acad. Dermatol. Venereol.* 2008, 22, (9), 1110–1119. [PubMed: 18482317]
65. Lygre H; Hol PJ; Solheim E; Moe G, Organic leachables from polymer-based dental filling materials. *Eur. J. Oral Sci.* 1999, 107, 378–383. [PubMed: 10515203]
66. World Health Organization, The WHO Recommended Classification of Pesticides by Hazard. In Geneva, Switzerland, 2009.
67. ChemRisk Inc.; DIK Inc. State of knowledge report for tire materials and tire wear particles; 2008.

68. Bailey RE; van Wijk D; Thomas PC, Sources and prevalence of pentachlorobenzene in the environment. *Chemosphere* 2009, 75, (5), 555–64. [PubMed: 19298997]
69. Hou R; Xu Y; Wang Z, Review of OPFRs in animals and humans: Absorption, bioaccumulation, metabolism, and internal exposure research. *Chemosphere* 2016, 153, 78–90. [PubMed: 27010170]
70. Cabrerizo A; Dachs J; Jones KC; Barceló D, Soil-Air exchange controls on background atmospheric concentrations of organochlorine pesticides. *Atmospheric Chemistry and Physics* 2011, 11, (24), 12799–12811.
71. Bidleman TF; Leone AD, Soil–air exchange of organochlorine pesticides in the Southern United States. *Environ. Pollut.* 2004, 128, (1–2), 49–57. [PubMed: 14667719]
72. Khairy M; Lohmann R, Field calibration of low-density polyethylene passive samplers for gaseous POPs. *Environmental Science Processes & Impacts* 2014, 16, 414–421. [PubMed: 24270460]
73. O’Connell SG; McCartney MA; Paulik LB; Allan SE; Tidwell LG; Wilson G; Anderson KA, Improvements in pollutant monitoring: optimizing silicone for co-deployment with polyethylene passive sampling devices. *Environ. Pollut.* 2014, 193, 71–8. [PubMed: 25009960]

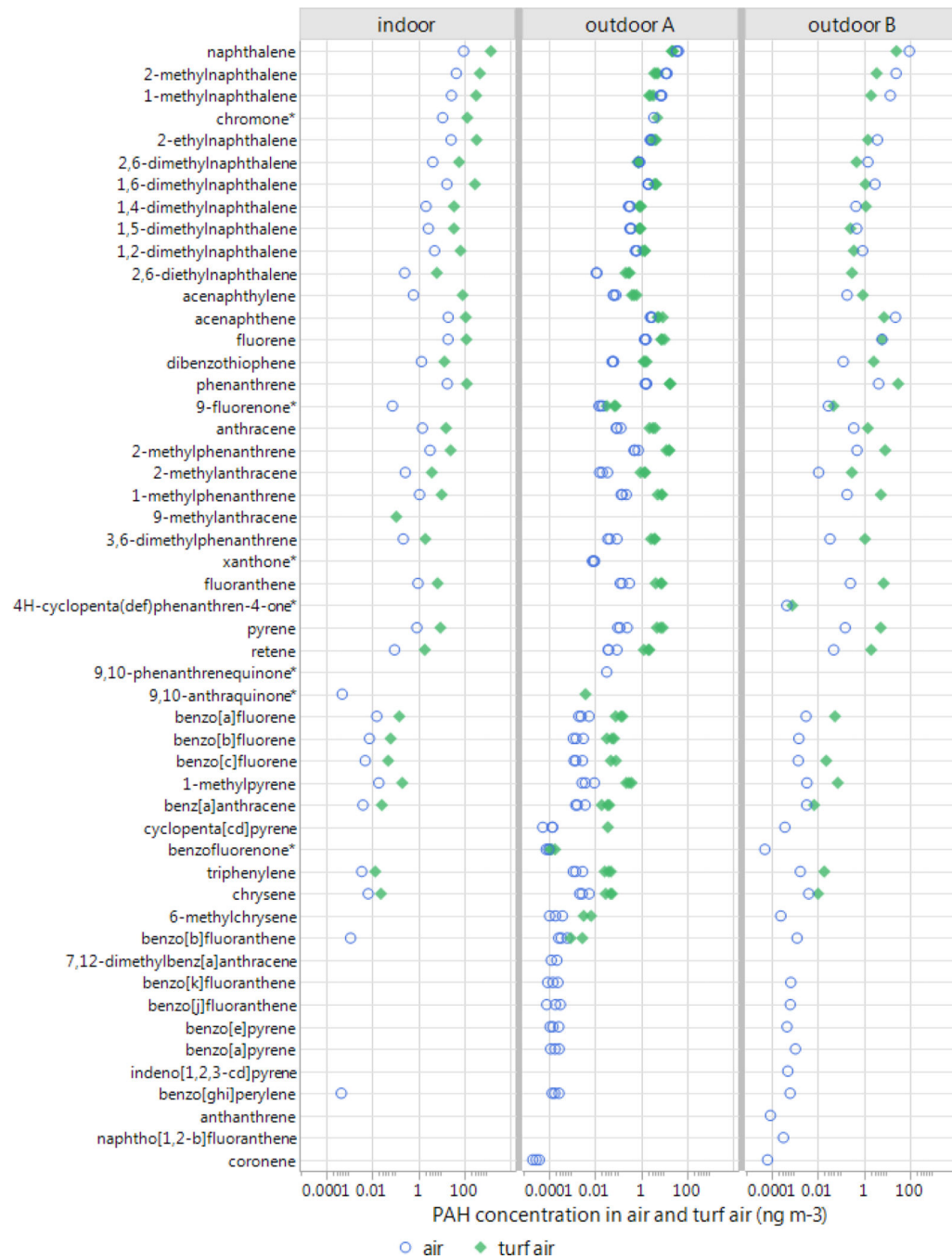


Figure 1. Concentrations of PAHs and OPAHs in air and turf air. OPAHs are indicated with asterisks. Triplicate samples were collected at *outdoor A*.

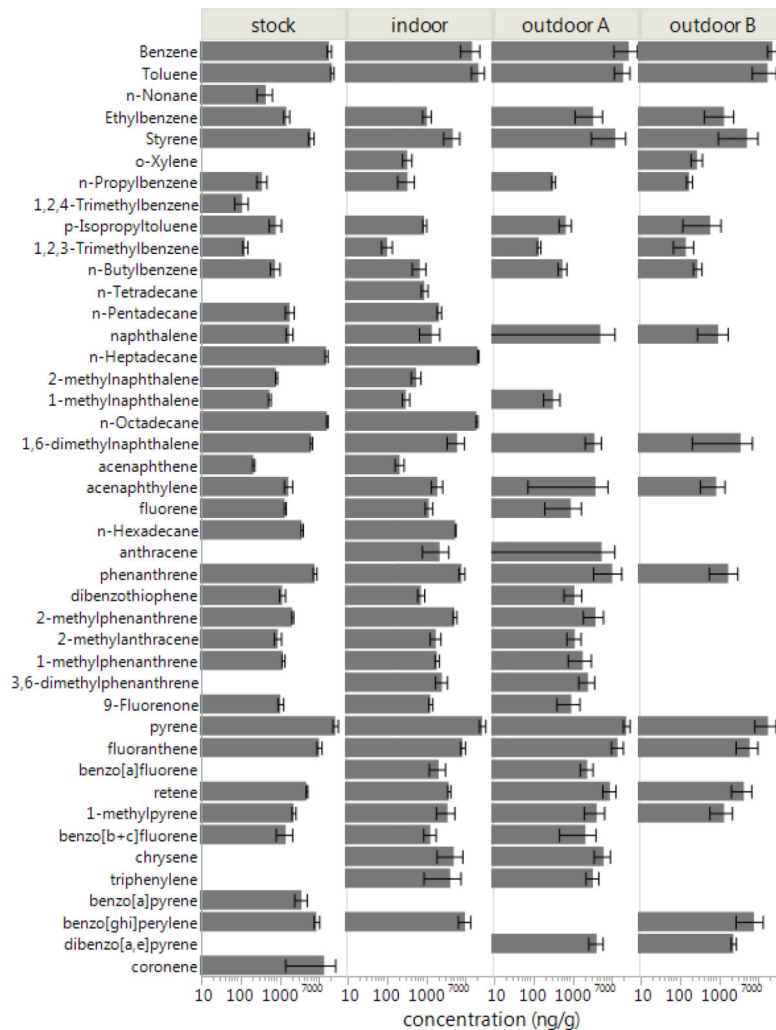


Figure 2.

Average concentrations ($n=3$) in crumb rubber samples. Each sample was composited from 4 locations per field, and analyzed in triplicate. Stock crumb rubber was pulled from stock and has never been applied to fields. It is important to note that with construction application of crumb rubber at a typical rate of 10 – 15 kg/m², a full-sized artificial turf soccer field will contain between 75,000 and 112,500 kg of crumb rubber at time of installation. (Calculated from https://www.health.ny.gov/environmental/outdoors/synthetic_turf/crumb-rubber_infilled/docs/fact_sheet.pdf) Post-installation “refill” often involves 5 gallon buckets of material manually added to high-traffic areas. Each bucket will add only fractions of a percent of the total crumb rubber mass. More often facilities will use “top-dresser” machinery intended to redistribute existing infill and only add sparingly. It is unlikely that addition of small amounts of never-deployed crumb will significantly change the chemical emission profile of an existing field.

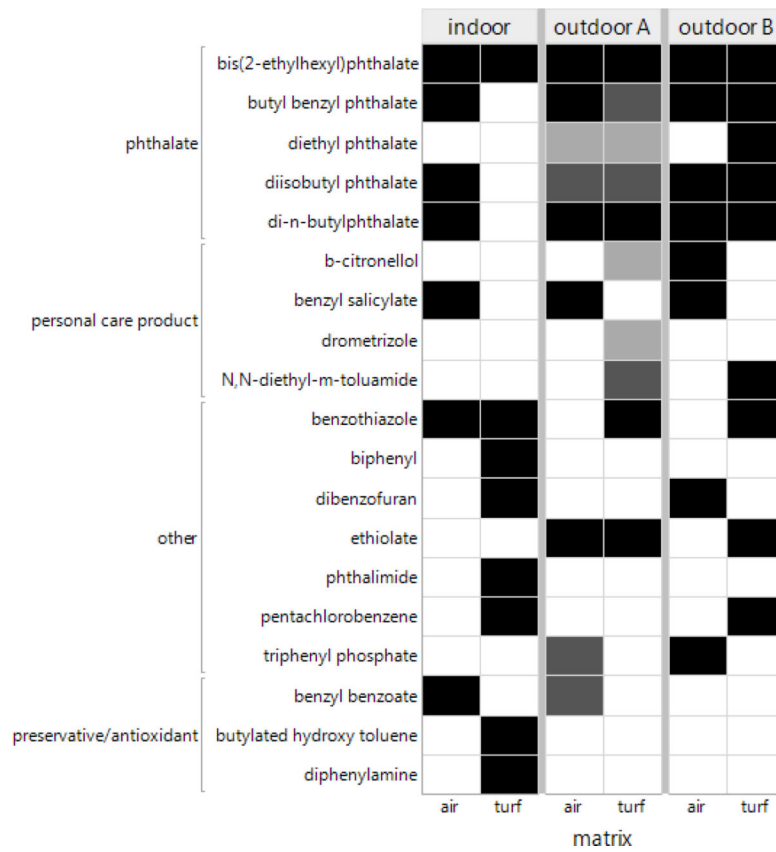


Figure 3. Detections in the presence/absence (1529) screen, where a shading indicates the chemical is present. At *indoor* and *outdoor B*, black indicates presence. Samples at *outdoor A* were collected in triplicate; the greyscale corresponds to the frequency of detection from 1 to 3.

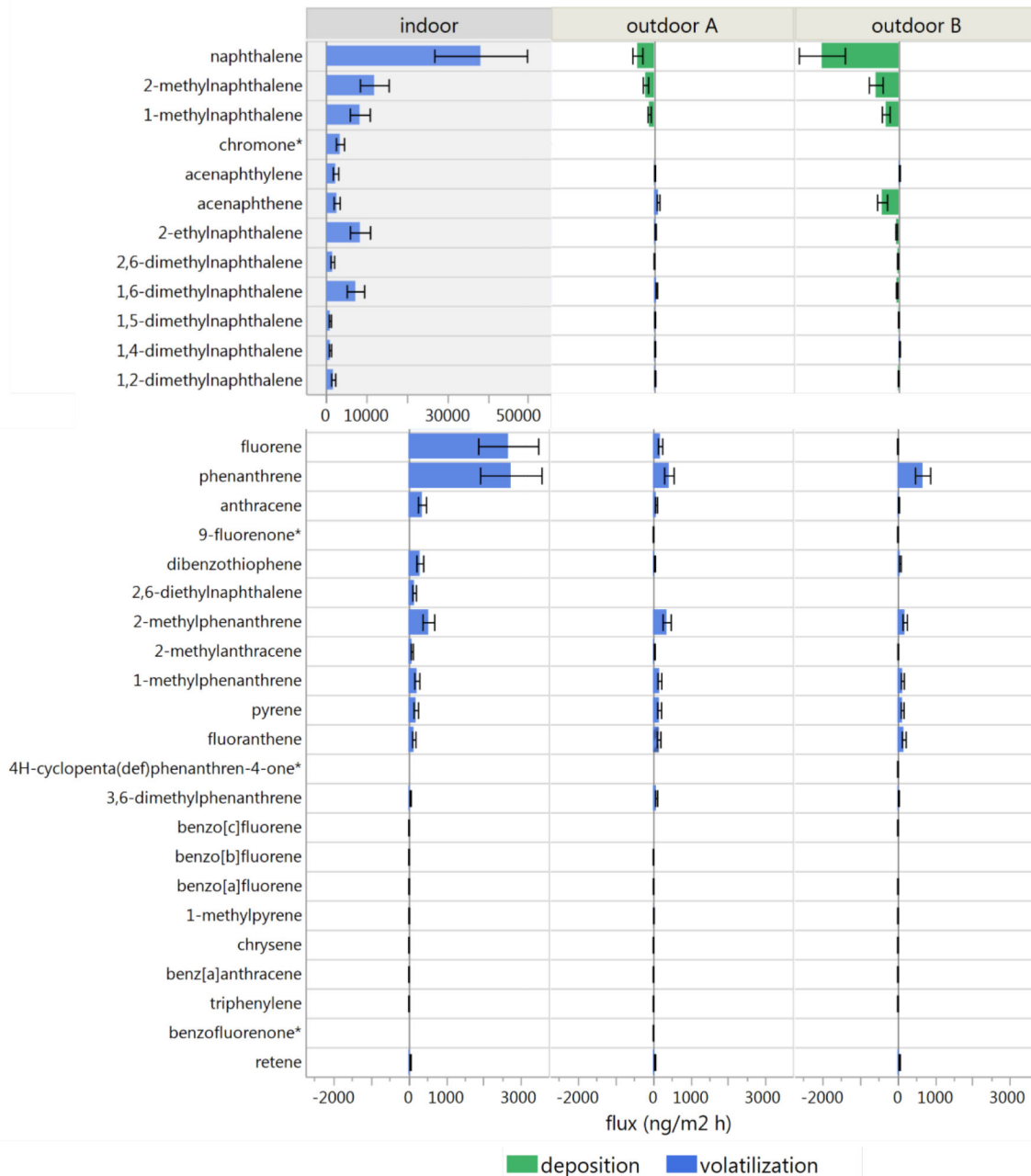


Figure 4. Magnitude and direction of PAH and OPAH flux. Error bars show uncertainty determined via propagation of error. The scale in the top left is reduced to larger values. Chemicals are listed in order of molecular weight, from low to high. OPAHs are indicated with asterisks. Flux was not determined if a chemical was below limit of detection in either air or turf air.

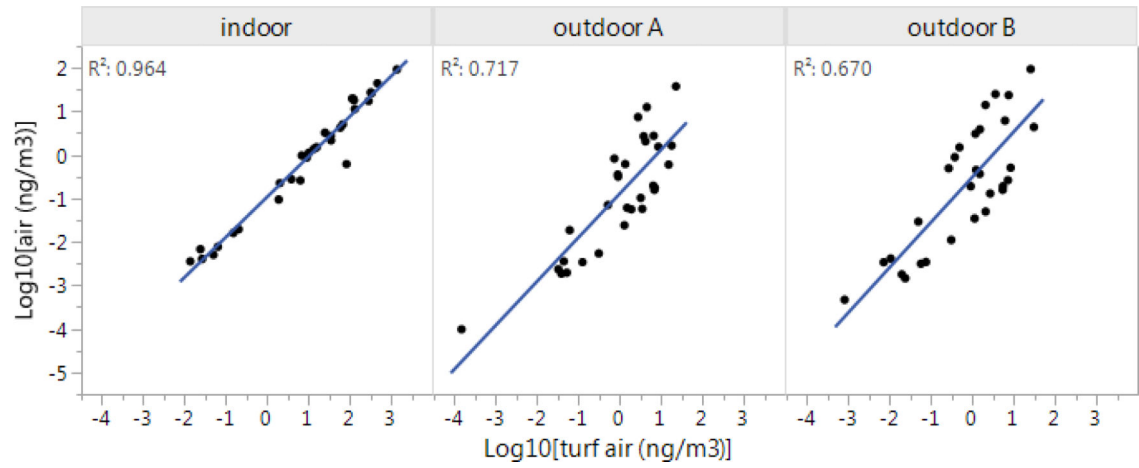


Figure 5.

Turf air concentrations correlated with air concentrations fit is greatest at *indoor*, the location with more volatilization and likely less convection from air movement and temperature extremes.

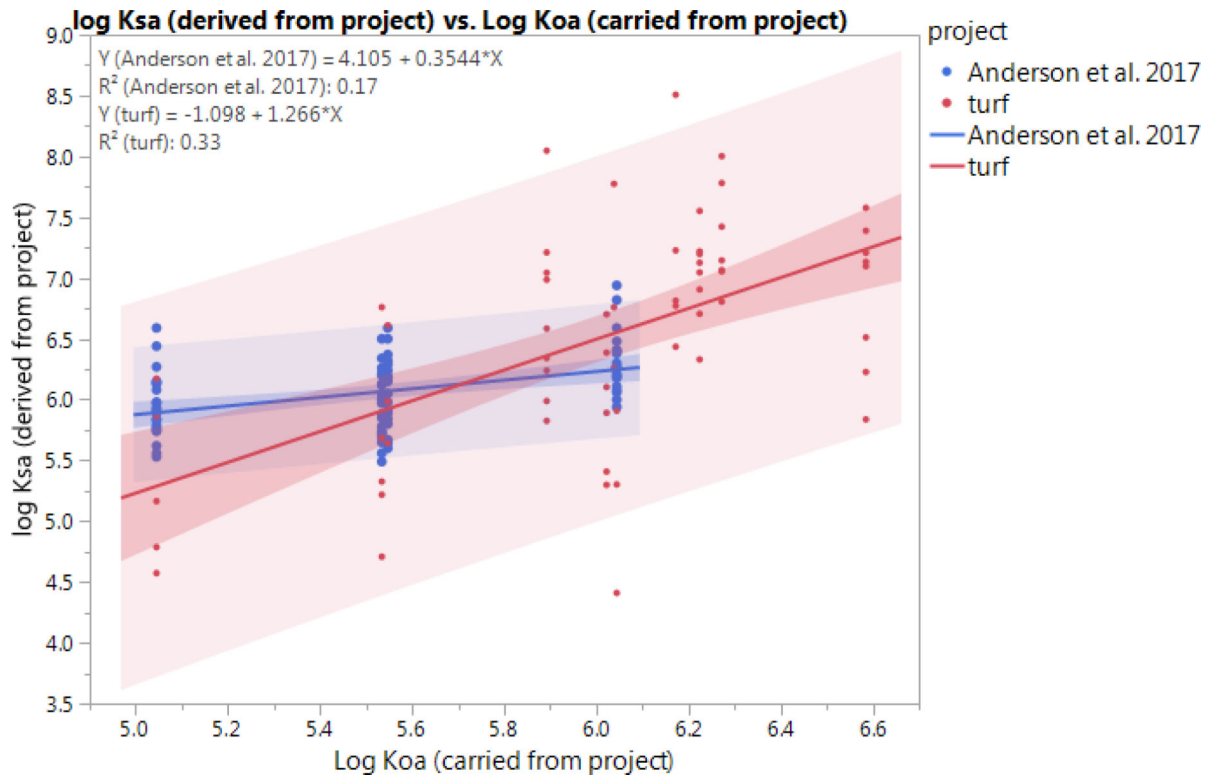


Figure 6. K_{sa} determination as determined in the present study (red line) and the foundations manuscript (blue line).

Table 1.

Detected artificial turf-associated chemicals that are previously unreported in a 2016 literature survey conducted by U.S. Environmental Protection Agency ⁴

PAH method	
2-ethylnaphthalene	2,6-diethylnaphthalene
1,6-dimethylnaphthalene	3,6-dimethylphenanthrene
1,4-dimethylnaphthalene	<i>benzo[c]fluorene</i>
2,4-dimethylnaphthalene	triphenylene
1,5-dimethylnaphthalene	6-methylchrysene
1,2-dimethylnaphthalene	naphtho[1,2-b]fluoranthene
OPAH method	1529 screen
chromone	b-citronellol
9-fluorenone	benzyl salicylate
xanthone	N,N-diethyl-m-toluamide
9,10-phenanthrenequinone	ethiolate
9,10-anthraquinone	pentachlorobenzene
benzofluorenone	triphenyl phosphate
	benzyl benzoate