AN ABSTRACT OF THE DISSERTATION OF

Carey E. Donald for the degree of Doctor of Philosophy in Toxicology presented on April 17, 2017

Title: Advances in Passive Sampling: Measuring Chemical Transport and Human Exposures

Abstract approved:

Kim A. Anderson

Passive sampling devices have been used for decades to measure complex mixtures of bioavailable organic chemicals in a variety of environmental media. More recently passive sampler applications have expanded beyond monitoring chemical concentrations, and this dissertation continues to advance methods of passive sampling on many fronts. Despite their growing use, no practical, evidence-based guidelines exist to ensure concentrations of chemicals sequestered in passive samplers are stable in transport and storage. We demonstrated that concentrations of semivolatile chemicals sequestered within passive samplers would be stable with low-cost shipping from isolated locales by simulating in the laboratory a worst-case scenario at 35 °C for two weeks. Quantitative measures of the flux of semivolatile chemicals between soil and air have been limited by the challenges of collecting soil and estimating chemical fugacity from soil. We avoided these pitfalls by adapting passive sampling equipment to directly sample gas-phase chemicals in air above the soil. The sensitivity of the novel technique was demonstrated at three disparate sites, where volatilization was measured at a site with historically contaminated soil, and deposition was measured at another site with a recent oil spill and fire. In a related study, we deployed the same equipment on artificial turf fields to provide the first quantitative measure of semivolatile flux between artificial turf and overlying air. We detected an additional 26 compounds that have not been previously associated with artificial turf, including some that have known human health impacts. Finally, passive sampling principles were applied to measure chemicals in the human personal environment, using a newly-developed silicone passive sampler wristband. Nineteen pesticides were detected that were not reportedly used among 35 rural farmer participants, demonstrating the utility of the wristband in measuring personal exposures to pesticides. Pesticide concentrations in multiple wristbands, worn by a

participant over time, were more similar to each other than to other participants, signifying the uniqueness of personal environments and the importance of taking personalized measurements when assessing risk. The advancements in this dissertation capitalize on the features of passive sampling techniques: easy, yet robust, transport capabilities were demonstrated to provide evidence-based transport criteria; ability to directly measure gas-phase chemicals led to quantitative flux measurements from soil and artificial turf; non-selective organic chemical sequestration allowed for identification of unexpected, or previously unreported chemicals; and the polymer qualities that mimic biological membranes sampled the bioavailable fraction for comparing human exposures. The advancements herein provide logistical solutions and sensitive measures of chemical transport and human exposures, and contribute to the expanding range of possibilities for passive sampling.

Advances in Passive Sampling: Measuring Chemical Transport and Human Exposures

by
Carey E. Donald

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Approved:

Major Professor, representing Toxicology

Head of the Department of Environmental and Molecular Toxicology

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Dean of the Graduate School

I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Carey E. Donald, Author

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CONTRIBUTION OF AUTHORS

In Chapter 2, Marc R. Elie provided experimental design, and performed instrumental analysis. Brian W. Smith performed and advised in statistical analysis. Peter D. Hoffman acquired UV transmittance data. Kim A. Anderson assisted in experimental design and manuscript preparation.

In Chapter 3, Kim A. Anderson assisted in experimental design and manuscript preparation.

In Chapter 4, Kim A. Anderson assisted in experimental design and manuscript preparation.

In Chapter 5, Richard P. Scott performed GC-ECD method enhancement. Kathy L. Blaustein and Mary L. Halbleib coordinated the study in Senegal and Institutional Review Board approval, and communicated with volunteer. Makhfousse Sarr participated in study design and coordinated support staff and volunteer participants. Paul C. Jepson participated in study design, coordinated the study in Senegal, and communicated results to volunteer participants. Kim A. Anderson participated in study design and manuscript preparation.

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CHAPTER 1 – INTRODUCTION

Chemical mixtures

The environment inherently contains complex chemical mixtures. For example, crude oil is a hydrocarbon mixture that changes its character further when it enters the surface environment, whether through a natural seep or an oil spill. Human technology combusts, refines, and plasticizes components, while the environment oxidizes, partitions, and dilutes the original crude oil. Pesticides applied to a crop enter and affect the target organism although portions may drift with wind currents, sorb to soil particles, or be inhaled by humans. Diverse environmental conditions first create and then continuously change the mixtures. An easily defined formulation of an industrial product is harder to define when it is detected decades later in organisms worldwide. As analytical methods improve, so does our ability to characterize complex environmental mixtures and better understand exposures.

In an effort to simplify, complex mixtures are frequently characterized by the classes of chemical they include. Classes of environmental contaminants can be defined by their source, as with polycyclic aromatic hydrocarbons (PAHs) that are associated with either natural or anthropogenic sources like oil seeps or diesel truck emissions, or with metals in mine waste. Chemicals with common molecular structures are grouped together, like the 209 polychlorinated biphenyl (PCB) congeners. Classes might be characterized by their function, as with pesticides or flame retardants. Their physicochemical properties might also lead to groupings, like volatile chemicals. Subsets of chemicals might be recognized for their effects on ecological or human health, as with carcinogenic ortho-PCBs or endocrine-disrupting chemicals.

A mixture must be thoroughly characterized to best understand any adverse effects. The archetypal carcinogenic PAH, benzo[a]pyrene, is rarely present without numerous other PAHs. The toxicity of the mixture can be simplified by comparing the carcinogenic potency of each component PAH to that of benzo[a]pyrene,[1] and a similar toxic equivalence factor approach is used with mixtures of polychlorinated dioxins and furans.[2] A risk analysis that excludes an unidentified component may understate potentail toxic effects. Many non-cancer effects can also result from exposures, *e.g.* cardiac toxicity from oil exposure,[3] reproductive toxicity from pesticide exposure,[4] and respiratory stress from exposure to volatile organic compounds.[5] In addition to understanding any toxic interactions within the mixture, the most robust risk

assessment should incorporate all relevant toxicants and adverse outcomes. Combined with increasing sensitivity of analytical instruments, developments in sampling techniques are improving our ability to characterize complex environmental mixtures.

Passive sampling techniques

To assess the movement, potential exposure, or toxicity of environmental mixtures, we first need a useful means of measuring them. Passive sampling techniques were developed decades ago as effective and sensitive metric for environmental monitoring, and such techniques continue to be refined today.[6] Passive samplers are particularly useful when characterizing complex mixtures because they non-selectively sequester hydrophobic organic chemicals. The passive sampling material, often a polymer, acts as a chemical sponge by mimicking the physicochemical properties of biological membranes. In the manner of like-dissolves-like, lipophilic compounds preferentially sorb into the passive sampling material from the environment being sampled. By sequestering and concentrating only the freely dissolved fraction in water or the gas-phase fraction in air, passive samplers accumulate the bioavailable fraction. The samplers are placed in the environment for a period ranging from hours to months and require no pumps or electricity to operate. Following deployment, the lightweight samplers are collected and returned or easily shipped to the laboratory for analysis with high sensitivity.

Passive sampling devices were first used to sample freely-dissolved, bioavailable contaminants in rivers, oceans, and estuaries.[6] In emerging applications however, researchers have begun using passive samplers to better understand how chemicals move throughout the environment, *e.g.* chemical flux between sediment porewater and overlying water.[7] Passive sampling principles have also expanded beyond more traditional environmental applications and been applied to human exposure assessments.[8] The uses of passive sampling in measuring complex mixtures are only limited by the creativity of the researcher.

Dissertation outline

In this dissertation, I aimed to advance methods of passive sampling on many fronts: by providing evidence-based **guidelines for practical passive sampler transport**; by developing novel **field-sampling techniques** to measure contaminant movement between environmental matrices and applying the techniques to sites with diverse contamination sources; by providing the first

quantitative measure of contaminant flux from artificial turf fields; and finally by demonstrating the sensitivity of the newly-developed passive sampler wristband in **measuring personal exposures to pesticides**.

We begin in Chapter 2 by establishing principles in passive sampling technology that allow for data-based decisions in guidelines for using passive samplers in field studies. Chapter 2 asks the question, do LDPE passive samplers need to be transported frozen? And are the compounds stable in storage? We answered these questions by simulating a worst-case shipping scenario of two weeks at 35°C. Along with low material costs, relaxed transport guidelines make passive sampling advantageous over other sampling techniques, particularly in isolated locales.

In Chapter 3, we adapt current passive sampling techniques to measure partitioning between soil and air at three locations, each with unique contamination sources. This method used a novel sampling configuration to sample soil air, that is, air in close contact and equilibrium with surface soil. Combining measurements of chemicals in soil air with the overlying air, we demonstrated a new way to measure magnitude and direction of soil-air flux.

In Chapter 4, we use the novel sampling techniques developed in the previous chapter to understand movement of semivolatile contaminants in a unique man-made environment—artificial turf fields. In addition to reporting the first quantitative measure of flux from artificial turf fields, we also report the presence of 26 chemicals that have not been previously associated with turf fields. Some of these compounds are toxicologically-relevant, and their inclusion in future risk assessments will provide better estimates of potential health effects.

Finally, in Chapter 5, we apply the analytical capabilities of passive sampling to exposure science with the recently-developed passive sampler wristbands. After its initial demonstration,[9] the silicone wristband was used to compare exposures of pesticides among farmers in rural areas. We detected between 2 and 10 pesticides in every participant wristband. Two wristbands worn by the same farmer were similar, indicating that differences among personal environments can have more variation than repeated measures of one personal environment. Surprisingly, we detected 19 more pesticides than the volunteers reported using, demonstrating both the sensitivity of the wristband and the complexity of the participants' personal environments. Concluding thoughts are given in Chapter 6.

CHAPTER 2 – TRANSPORT STABILITY OF PESTICIDES AND PAHS SEQUESTERED IN POLYETHYLENE PASSIVE SAMPLING DEVICES

Carey E. Donald, Marc R. Elie, Brian W. Smith, Peter D. Hoffman, and Kim A. Anderson

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14197 Berlin, Germany

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Abstract

Research using low-density polyethylene (LDPE) passive samplers has steadily increased over the past two decades. However such research efforts remain hampered because of strict guidelines, requiring that these samplers be quickly transported in airtight metal or glass containers, or foil-wrapped on ice. We investigate the transport stability of model pesticides and polycyclic aromatic hydrocarbons (PAHs) with varying physicochemical properties using polytetrafluoroethylene (PTFE) bags instead. Transport scenarios were simulated with transport times up to 14 days with temperatures ranging between -20 and 35 degrees Celsius. Our findings show that concentrations of all model compounds examined were stable for all transport conditions tested, with mean recoveries ranging from 88% to 113%. Furthermore, PTFE bags proved beneficial as reusable, lightweight, low-volume, low-cost alternatives to conventional containers. This documentation of stability will allow for more flexible transportation of LDPE passive samplers in an expanding range of research applications while maintaining experimental rigor.

Introduction

Passive sampling devices made from low-density polyethylene (LDPE) or other polymers have been used for over two decades to sample the freely-dissolved fraction of organic contaminants in numerous environmental media.[6; 10] LDPE passive samplers have been used to sample non-polar and semi-polar compounds in air,[11; 12] water,[13; 14] and sediment porewater.[15; 16] Contaminants diffuse into passive samplers, and concentrations increase until equilibrium is reached with the sampled matrix. The first generation of samplers, called semipermeable membrane devices (SPMDs), consisted of LDPE strips containing a volume of triolein to retain sequestered hydrophobic contaminants. [17] Recent single-phase variations without triolein afford simpler extraction and analytical clean-up.[10; 18; 19] LDPE passive samplers are constructed from low-cost materials and are often more cost effective compared to active sampling methods.[20; 21] Additionally, performance reference compounds (PRCs), also called depuration compounds, are infused into the passive sampler material before deployment The rate at which PRCs diffuse from the material into the surrounding environment, either air or aqueous, corresponds to the rate at which compounds are sequestered from that surrounding environment.[20; 22] The use of these PRCs, along with solvent extraction and instrumental analysis allows for determination of time-weighted averages of bioavailable freely-dissolved or vapor-phase environmental concentrations.

Guidelines proposed by the U.S. Environmental Protection Agency[21] and the US Geological Society[23] indicate that field-deployed LDPE passive samplers or SPMDs should be stored immediately in airtight cans or jars and transported frozen or near frozen via overnight courier, or as soon as possible. Overnight frozen shipping can be expensive or logistically unattainable from some locations[24]. Moreover, airtight canisters are suggested for passive sampler transport to and from the study site as a means to suspend sampling and to prevent loss of compounds by volatilization. Recommended canister materials are either glass or metal to limit compound absorption to canister surfaces.[6] Rigid canisters add volume and weight that may increase shipping costs. Other transportation guidelines propose wrapping passive samplers in clean aluminum foil and subsequently placing them in plastic bags.[21] While plastic bags are more amenable to shipping, a barrier of pre-cleaned aluminum foil is needed to prevent direct exchange of compound between the passive sampling material and the polymer of the transport bag, often polyethylene. Additionally, polyethylene bags are neither airtight nor chemically impervious, and vapor-phase chemicals can potentially diffuse through the polyethylene bag and be captured by the LDPE passive sampler during transport. The polyethylene bag itself may also sequester contaminants that volatilize from the passive sampler. Alternatively, bags made of polytetrafluoroethylene (PTFE) would provide an airtight, lightweight, low-volume, and chemically inert solution for cost-effective shipping. The use of such PTFE bags is only supported by limited data regarding silicone, rather than LDPE passive samplers.[25] To the authors' knowledge, there are no studies of transport of LDPE passive samplers in PTFE bags. Data-based criteria for transport conditions will increase the utility of passive sampling techniques in an expanding range of applications.

Transportation at ambient temperatures in lightweight, durable bags would allow more cost-effective shipping or transport compared to airtight metal cans or glass jars shipped overnight on ice. In contrast to samples wrapped in aluminum foil and enclosed in polyethylene bags, the PTFE bags are air-tight and chemically inert, eliminating the need for foil. We hypothesize that less stringent transport conditions will have no effect on concentrations of commonly studied contaminants sequestered in LDPE passive samplers. The aim of this work is to demonstrate the stability of model pollutants in LDPE passive samplers under simulated transport in PTFE bags, with temperatures between -20^0 and 35°C and for durations between 10 hours and 14 days. These conditions were chosen to mimic a worst-case scenario of a 14-day transport from a hot climate.

Model compounds include organochlorine and organophosphate pesticides and polycyclic aromatic hydrocarbons (PAHs).

Materials and Methods

Standards, solvents, and materials

Pesticide (alachlor, alpha-BHC, chlorpyrifos, and endrin ketone) and PAH (anthracene, benzo[ghi]perylene, chrysene, and fluoranthene) compounds were selected to represent a range physicochemical properties (Table 2.1). All were of purity ≥ 98% (Accustandard, USA). Tetrachloro-meta-xylene and PCB-209 (Accustandard, USA) were used as extraction surrogate standards for pesticides, and phenanthrene-d10, fluoranthene-d10, chrysene-d12, and benzo[ghi]perylene-d12 were used for PAHs (CDN Isotopes, Canada). Internal standards 4,4'-dibromooctafluorobiphenyl (Supelco Analytical, USA) and perylene-d12 (Chemservice, USA) were added immediately before instrumental analysis to correct for instrument variation (Table 2.2). Hexane solvents were Optima™ grade or better (Fisher Chemical, USA). PTFE transport/storage bags and Clip N Seal closures were purchased from Welch Fluorocarbon, Inc. (USA). LDPE lay-flat tubing used to make passive samplers was purchased from Brentwood Plastics, Inc. (USA). Average width of tubing is 2.7 cm, average membrane thickness is 75-95 μm, and average transient polymer cavity size is 10 Å.[18]

Sample preparation

Passive samplers were constructed from LDPE tubing cut into 100 cm lengths. Each LDPE strip was pre-cleaned to remove potential chemical interferences with three successive conditioning washes in 100 mL of hexanes, each for 24 hours. After drying, each strip of tubing was heat-sealed at one end, infused with <100 μL of target compound solution in *n*-hexane (200-600 ng of each compound per strip), and then heat-sealed at the remaining end. Pressure was applied lengthwise between (gloved) thumb and index finger to uniformly disperse target compound solution throughout the sealed LDPE sampler. The same target compound solution was used in all LDPE strips, and all were constructed in one batch. This method of infusion and heat-sealing was chosen because it requires less solvent than equilibration techniques as in Booij *et al.*[26] Unlike SPMDs which can contain 1 mL of triolein in each strip of tubing,[17] the constructed strips contained only a small volume and are considered single-phase samplers. Each passive sampler strip was placed in an individual PTFE bag (Figure 2.1). Samples were immediately moved to

dark, temperature-controlled environments at -20, 4, 20, or 35^{0}C. Ambient light was minimized during laboratory preparation steps. The PTFE bags used in this study are translucent, and attenuate UVA and UVB transmittance by 49% (Figure A1). UV degradation of chemicals was not examined in this study, but is expected to be minimal based on previous findings of reduced rates of photodecomposition of PAHs when adsorbed to coal ash[27] and silicone passive sampling devices.[9]

Eight samplers were extracted immediately following preparation to represent the t=0 treatment. Four samplers from each temperature treatment were extracted at 10 h, 1.5 days, 3 days, and 7 days. An additional 4 samplers at 35^{0}C were extracted after 14 days. Passive samplers were extracted with two 40 mL *n*-hexane dialyses following the addition of extraction surrogate standards. Dialysates were combined and quantitatively reduced to a volume of 1 mL. Extracts were stored in the dark in amber glass vials at -20°C until analyzed.

Instrumental analysis

Instrumental analysis for each of the model compounds was performed on two methods (Table 2.2). Pesticides were quantified with gas chromatography with electron capture detectors (GC-ECD). PAHs were quantified with gas chromatography with mass spectrometry (GC-MS). All concentrations were quantified by the relative response of the internal standard to target compounds in a 5-8 point calibration curve (all $R^2 > 0.99$). Instrument detection limits are given in Table 2.1, and analytical parameters are given in Table 2.2.

Statistical analysis

Treatment recoveries were scaled as a percentage of the mean control (t=0) treatments. Mean percent recoveries were analyzed by one-sided Dunnett's tests. Significance for all tests was set at $\alpha = 5\%$. Statistical analyses were performed with JMP Pro 11.2.0 and Microsoft Excel 2013.

Quality control

Over 30% of the samples analyzed were quality control samples. Blank LDPE samples were pulled during the pre-cleaning and construction phases and retained as quality control samples. The extraction process was performed without LDPE for a solvent extraction blank. Injections of *n*-hexane solvent, instrument reagent blanks, were included in all analytical batches, and were

used to demonstrate that the instruments had low background responses. All target compounds were below detection limits in all blank quality control samples. Continuing calibration verifications consist of a solution of known concentration of all target compounds to monitor instrument performance and were within 20% of known value for all target compounds. Extraction surrogate standards were added to passive samplers prior to extraction in order to quantify procedural recoveries. Pesticide surrogate recoveries averaged 92% (standard deviation = 10%) and concentrations were not corrected for procedural losses. Recoveries of PAH surrogate standards averaged 65% (standard deviation = 11%), and PAH concentrations *were* corrected for losses.

Results and Discussion

Overall mean recovery was 101% (standard deviation = 6%) of t=0 across all time and temperature treatments for all pesticides (Figure 2.2) and PAHs (Figure 2.3). The lowest mean recovery among all time/temperature treatment groups was endrin ketone at 88% (95% confidence interval (CI) = 77-98) for the 7 day, 4°C treatment, and the highest mean recovery was for alpha-BHC at 113% (95% CI = 106-119) for the 1.5 day, 35°C treatment. Mean recoveries and standard deviations for these and other compounds and treatment conditions and are given in Table A1. Average relative standard deviation (RSD) for pesticides was 7.4%. Average RSD was lower for PAHs at 4.9%, likely because PAH concentrations were corrected for sample preparation losses while pesticide concentrations were not. No mean recovery was less than mean t=0 treatment (one-sided Dunnett's test, all p-values < 0.05) and therefore, there was no effect of transport on target compound concentrations for any condition tested.

The model pesticides and PAHs in this transport study exhibited no decrease in recovery after 14 days of simulated transport conditions in temperatures as high as 35°C. As the selected model compounds span a range of physicochemical properties, these data suggest that similar compounds would also exhibit no decrease in concentration. Care should be taken in extending the inferences to more extreme conditions, as effects may exist that were not detectable within the given experimental design. The transport stability findings presented here suggest that researchers performing targeted analysis on PAHs and pesticides can do so using more flexible transport conditions. However, if the intended chemical analysis is non-targeted, then expedient transport at or near freezing is a conservative approach to ensure recovery. Huckins *et al.*[6] caution that in

SPMDs, high-fugacity compounds such as naphthalene can be lost if samplers are not kept under freezing conditions within hours of retrieval. The compounds selected for this study (log K_{oa} range: 7.55-12.0, Table 2.1) are comparatively less volatile than naphthalene (log K_{oa}: 5.19).[28] We did not observe any trend between compound volatility and recovery loss, because no recovery loss was observed for any compound in any treatment. If compound loss *were* to occur under the conditions mimicked in this study, it would be limited to compounds more volatile than the pesticide alpha-BHC, the three-ringed PAH anthracene, or compounds that have lower thermal stability, a chemical characteristic not examined in this study. Biodegradation was also not examined in the present study. LDPE that are deployed in water can develop a biofilm[6; 24] that might favor biodegradation. Passive samplers deployed in air are unlikely to develop a biofilm. Booij *et al.*[29] demonstrated that biofouling does not drastically affect target compound uptake while the passive samplers are deployed in water, but biodegradation resulting from biofouling is not well described. Careful selection of PRCs allows researchers to estimate potential effects from biofilms, including biodegradation.[30] During retrieval, the LDPE passive samplers can be cleaned in water from the sampling location to remove biofouling and limit biodegradation during transport. In addition to thermal stability and biodegradation, the effects of more extreme transport durations or temperatures for other classes of semi-volatile organic compounds in passive samplers are also worthy of future study.

The LDPE tubing strips selected for this study have an average thickness of 75-95 μm, a thickness that has been used previously in passive sampling techniques.[18; 19; 26; 31] However, LDPE sheets nominally 50 μm[15; 32; 33] or 20-30 μm[34; 35] are also used. Equilibrium partition coefficients are not affected by LDPE polymer thickness,[36] but it is expected that thinner polymers reach equilibrium faster. We conclude that compounds in the present study reached equilibrium quickly with the small volume of air in the airtight PTFE bag because concentrations did not change across temperature or time. Similarly, we hypothesize concentrations of compounds sequestered in thinner LDPE to also exhibit stability, because equilibrium is expected to be reached quickly.

Accelerated stability tests have been used in chemical standard and pharmaceutical industries as a means to estimate long-term storage stability albeit on a shorter time scale. In such studies, the storage temperature is increased by at least 20°C and recoveries are evaluated at standard time intervals.[37] Deviations from acceptable stability in accelerated tests give an early indication of shorter shelf life and inform study design in subsequent long-term studies.[38] Typically, for every

10°C increase, the rate of degradation doubles.[37; 39] The design of the present study represents accelerated stability tests across a temperature range of 55 degrees Celsius, or the equivalent of about 634 days (14 days x $2^{5.5}$). Using the principles of accelerated stability tests, the present study suggests that these compound concentrations are expected to be stable in cold storage for about two years.

The compound stabilities tested herein support the use of PTFE bags as a reliable alternative to glass jars, metal canisters, or aluminum foil and plastic bags when transporting LDPE passive samplers. The burden of cost in passive sampling campaigns is in extraction and analysis, while the materials and preparation of an LDPE passive sampler is comparatively inexpensive. In one cost analysis for polychlorinated biphenyl analysis, the U.S. Environmental Protection Agency[21] reported that an LDPE passive sampler costs only $5 USD to prepare, but costs about $375 USD for extraction and analysis. The PTFE bags used in the present study cost approximately $5 USD each. Similarly, pre-cleaned glass jars with PTFE liners cost $3-8 USD each, depending on the volume. Both PTFE bags and glass jars may be solvent-cleaned and re-used, and therefore have similar costs for repeated uses. The PTFE bags have lower risk of breakage during transport or shipment and cost less to ship because they weigh less. Another transport option is to wrap the passive sampler in aluminum foil and transport on ice, optionally stored in a plastic bag. While this method is more cost-effective than jars or PTFE bags, it does not prevent analytes from partitioning out of the sampling material into or through the plastic bag, if used. As demonstrated in this work, PTFE bags allow for lower cost, chemically-inert transport at ambient temperature without increasing material costs.

Passive samplers have been gaining utility in recent decades as a cost-effective means of detecting low concentrations of hydrophobic contaminants in a variety of environments. The present study documents an additional benefit of LDPE passive samplers when studying environmental contaminants represented by the chosen model pesticides and PAHs—that they may be transported in the dark in lightweight PTFE bags at ambient temperature up to 14 days at 35°C.

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Conflict of interest

The authors declare no conflict of interest.

Figure 2.1. LDPE passive sampling strip in PTFE bag.

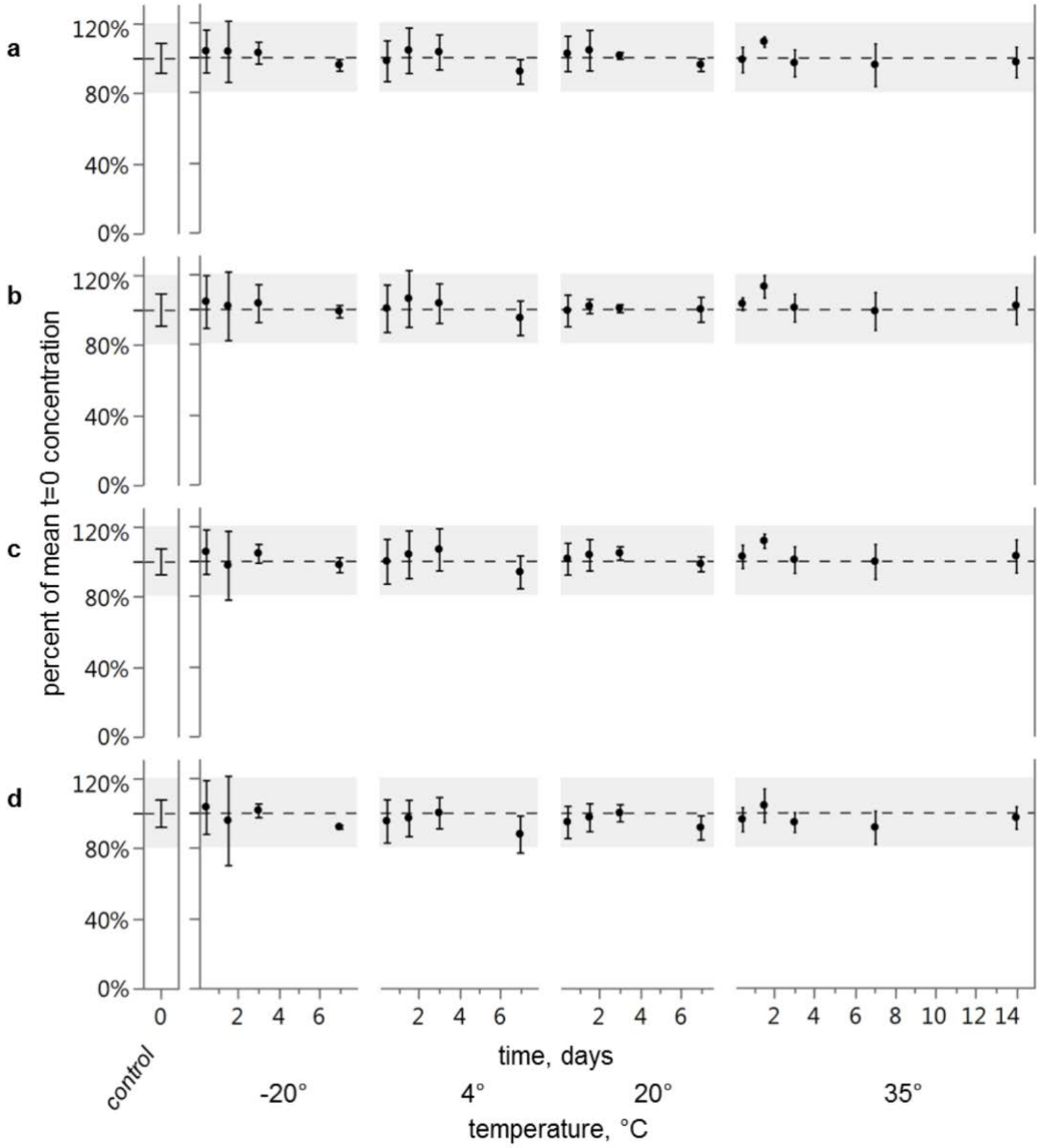

Figure 2.2. Mean recoveries of pesticides a) alachlor, b) alpha-BHC, c) chlorpyrifos, and d) endrin ketone. Concentrations are represented as a percent of control treatment (t=0). No recovery is less than control (one-sided Dunnett's test). Grey area highlights ±20% of control. Error bars represent 95% confidence intervals of the means (n=8 for t=0 control, and n=4 for all other treatments)

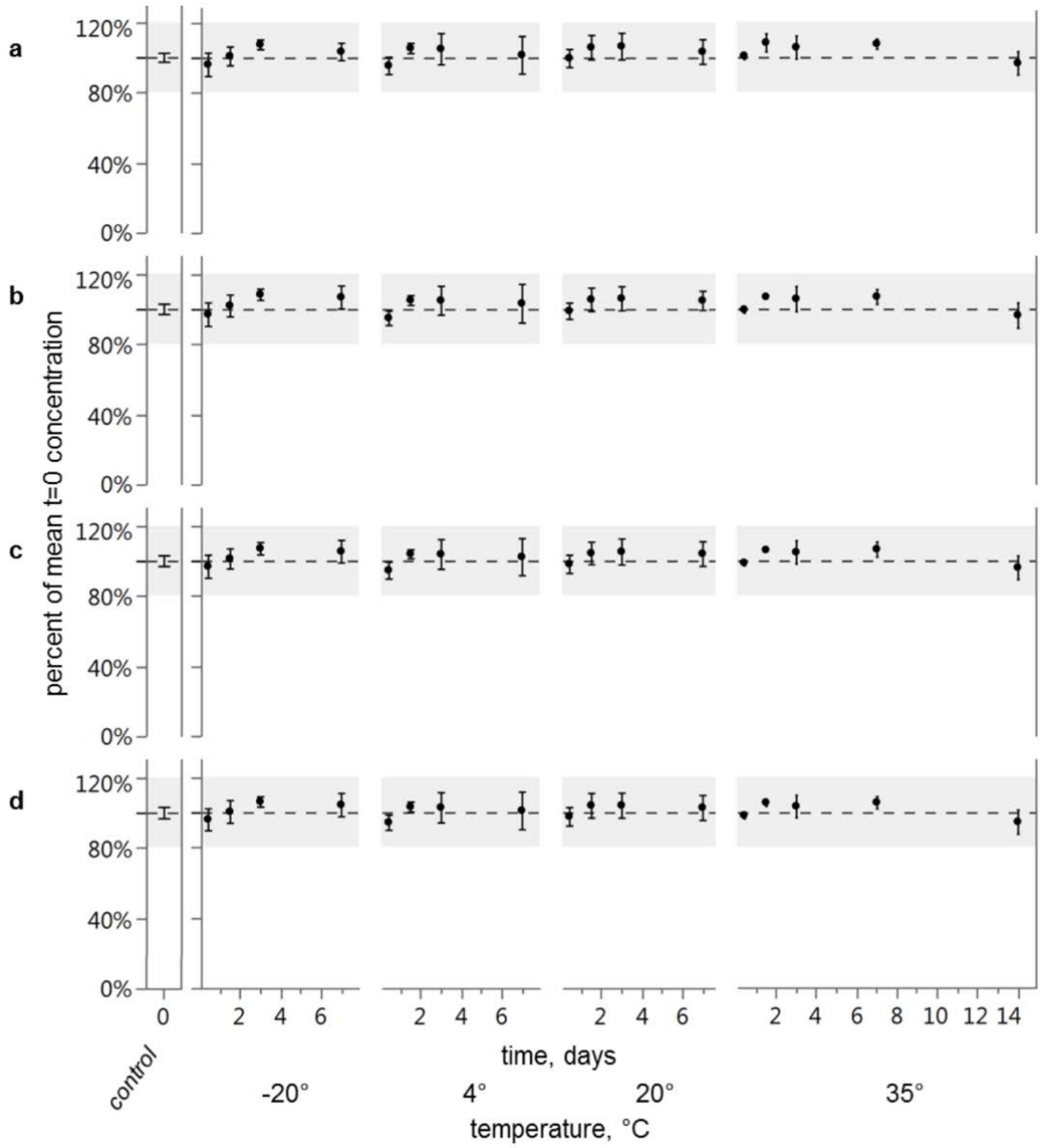

Figure 2.3. Mean recoveries of PAHs a) anthracene, b) benzo[ghi]perylene, c) chrysene, d) fluoranthene. Concentrations are represented as a percent of control treatment (t=0). No recovery is less than control (one-sided Dunnett's test). Grey area highlights ±20% of control. Error bars represent 95% confidence intervals of the means (n=8 for t=0 control, and n=4 for all other treatments)

Table 2.1. Model compounds used in transport stability analysis

		CAS Number	Molecular weight ($g\ mol^{-1}$)[28]	Log K_{ow}[28]	Log K_{oa}[28]	IDL (ng/ml)[b]
Pesticide	alachlor	15972-60-8	269.77	3.52	10.0b	0.5
	alpha-BHC	319-84-6	290.83	3.72	8.84	2.0
	chlorpyrifos	2921-88-2	350.59	4.66	8.88	0.5
	endrin ketone	53494-70-5	380.91	4.99b	11.1[a]	1.0
PAH	anthracene	1719-06-8	178.23	4.45	7.55	1.7
	benzo[ghi]perylene	191-24-2	276.33	6.70b	12.0	1.7
	chrysene	218-01-9	228.29	5.81	9.48[a]	1.7
	fluoranthene	206-44-0	202.25	5.16	8.88	1.7

[a] estimated value

[b] Instrument detection limits (IDL) for extracts of LDPE are determined as 3 times the standard deviation of 7 runs of the lowest standard, expressed as concentration.

Table 2.2. Analytical parameters

	Pesticide method	PAH method
Extraction Surrogate Standards	tetrachloro-meta-xylene, PCB-209	phenanthrene-d10, fluoranthene-d10, chrysene-d12, benzo[a]pyrene-d12
Internal Standard	4,4'-dibromooctafluorobiphenyl	perylene-d12
Gas Chromatograph	6890N (Agilent)	7890A (Agilent)
Detector(s)	2x micro-electron capture detectors	5975C mass spectrometer (Agilent)
Column(s)	DB-XLB and DB-17MS (both Agilent)	DB5-MS (Agilent)
No. of calibration points (R2>0.98)	5	6 or 7
Temperature program	110°C, 1 min. 4°C/min to 300°C, hold 10 min.	60°C, 1 min. 30°C/min. to 180°C 3°C/ min. to 230°C, hold 5 min. 28°C/ min. to 280°C, hold 10 min. 8°C/ min. to 310°C 16°C / min. to 350°C, hold 5 min.
Reference	Anderson *et al.*[24]	Allan *et al.*[14]

CHAPTER 3 – ASSESSING SOIL-AIR PARTITIONING OF PAHS AND PCBS WITH A NEW FUGACITY PASSIVE SAMPLER

Carey E. Donald and Kim A. Anderson

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Radarweg 29

1043 NX Amsterdam, The Netherlands

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Abstract

Soil-air fluxes of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were determined using a novel application of passive samplers to measure air and soil air, which is air in close proximity and in equilibrium with soil. Existing methods to measure flux of semi-volatile compounds between soil and air require collecting samples from the top soil layer. Yet, the top soil layer is hard to define and oversampling may misrepresent the exchangeable fraction. Alternatively, modified active samplers can measure soil air *in situ*, but require electricity while deployed. We present a new method to measure time-weighted averages of soil air concentrations *in situ* using passive sampling and requiring no electricity: a box is placed over low-density polyethylene passive samplers deployed 1 cm above the soil. Passive air samplers were also co-deployed 1.5 m above the soil to measure ambient air concentrations in three U.S. locations: near a former PCB manufacturing facility in Anniston, Alabama; on a former creosoting and the current Wyckoff/Eagle Superfund site near Seattle, Washington; and near the site of a recent oil-train derailment and fire in Mosier, Oregon. Following *n*-hexane extraction, sampler extracts were analyzed for PAHs with gas chromatography-tandem mass spectrometry and PCBs with dual gas chromatography-electron capture detectors. PAHs were generally depositing at Anniston and Mosier sites, but volatilizing from soil in Wyckoff, the site with historically-contaminated soil. PCBs were detected most frequently at the Anniston site, although levels were lower than previous reports. Variability in concentration measurements was greater among soil air samplers than air samplers, likely due to soil heterogeneity. Environmental conditions under the novel soil air box did not substantially change soil-air partitioning behavior. This method of measuring soil air *in situ* will allow for understanding of source-sink dynamics at sites with recent and historical contamination, and where conventional sampling is challenging.

Introduction

Soil is an important reservoir of persistent pollutants. Initially, soil can be a sink for hydrophobic chemicals such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), and can remain a lingering source after the point source is removed.[40] Remediation efforts can be hampered if cleaned soils act as a sink for new contaminants. Effective tools are necessary to understand the direction and magnitude of soil-air partitioning. Previous methods of determining soil-air partitioning involve sampling the soil directly.[41; 42] Soil concentrations are converted to a measure of fugacity with temperature and soil-air partitioning coefficients.

Comparing fugacity between ambient air and soil air allows for determination of the magnitude and direction of soil-air partitioning. The top 0.1 to 1 cm of soil is the exchange layer, and it responds quickly to fluctuations in air concentrations.[43; 44] However, this exchange layer is hard to define and can be challenging to collect.[45] Soil concentrations vary with depth and sampling more than the exchange layer may skew interpretation. For example, a soil sample including not only the soil-air exchangeable layer, but also a portion of the non-exchangeable layer below may misrepresent partitioning between soil and air. Furthermore, levels of compounds extracted with organic solvents exceed the levels that freely exchange with air.[45]

Alternative *in situ* techniques have been developed more recently to directly sample the soil air, *i.e.* air that is in close proximity and equilibrium with the soil.[44-48] *In situ* techniques are particularly useful in multi-compartment systems, *e.g.* where compounds may partition between air and ground vegetation.[45; 48] Low-volume active air samplers draw air slowly across the soil surface for nominally 48 hours to ideally ensure that sampled air is in equilibrium with soil. As with other active sampling methods, these devices are bulky, require electricity, care must be taken to ensure sufficient equilibrium time. Alternatively, passive samplers are increasingly used to measure freely-dissolved or gas-phase concentrations of semi-volatile compounds in water and air. Compared to active sampling methods, passive samplers are deployed for weeks at a time, require no electricity, and yield time-weighted averages.[49] Previously, passive samplers have been employed to measure *in situ* flux of hydrophobic organic contaminants between environmental compartments such as air and water[50; 51] and water and sediment porewater.[15; 16] The few passive sampling studies that have measured soil air or soil-air partitioning *in situ* profiled concentration gradients using polyurethane foam passive samplers near the soil surface.[47; 49] We present an alternative method by collecting two concentrations measurements—in ambient air and at the soil surface.

The objective of this work is to demonstrate a new design for a soil air passive sampler that can be used to evaluate volatilization or deposition of hydrophobic organic contaminants. We compare the sensitivity of this novel sampling design among dissimilar sampling locations, both on and near sites of historical contamination, and at a site of recent contamination. Repeatability is measured within and among sampler boxes. Environmental conditions under the soil air sampling boxes are also monitored to ensure the sampling equipment does not substantially alter

the environment being measured. Two measures of soil-air partitioning are presented: fugacity ratio and flux.

Materials and Methods

Site descriptions and sampling

Identical sampling schemes were deployed at three locations: Anniston, Wyckoff, and Mosier. We sampled diverse locations that would demonstrate the technology's ability to measure both volatilization and deposition for multiple chemical classes. The Anniston PCB Superfund site consists of downstream waterways, surrounding residential properties, and a facility that manufactured PCBs from 1929 until 1979 in Anniston, Alabama. Anniston samplers were deployed on adjacent wooded property approximately 0.7 km south of the facility, with the permission of Forever Wild Land Trust. The Wyckoff/Eagle Harbor site on Bainbridge Island, Washington is the location of a former wood treatment facility. Wyckoff samplers were deployed centrally on soil that was historically contaminated with creosote and pentachlorophenol. The third sampling site was in Mosier, Oregon, near the site of a recent oil train derailment, spill, and fire. Cleanup was underway at the time the samplers were deployed in Mosier, three weeks after the accident occurred on 3 June 2016.

A total of 3 air boxes and 4 soil air boxes were co-deployed at each of the three locations for a duration of 14 days (Figure 3.1a). Each box contained 5 LDPE passive samplers (Figure 3.1b). All deployments occurred in May, June, or July of 2016. Five LDPE strips were hung inside metal, T-shaped air sampling boxes that protect from UV radiation but allow airflow, as used previously.[52] The LDPE strips are contained within the upright portion (55 x 14 x 9 cm) positioned under the top portion (5 x 25 x 9 cm). Air boxes were hung on trees in Anniston and Mosier, and on cleaned metal fence posts at Wyckoff, approximately 1.5 m above the soil at a height used commonly in studies using high-volume active air samplers.[44]

Four soil air sampling boxes were deployed on soil immediately adjacent to the air boxes. Five LDPE strips were strung on carriers and placed on a grate immediately above the soil (Figure 3.1b). The soil air sampling box was placed over the LDPE passive samplers. The soil air box (50 x 30 x 8 cm) is open on the soil side, but impermeable on the other surfaces to reduce free exchange with ambient air. Air diffuses into the soil air box by permeating through the soil near

where the lip is placed on the soil surface; it is assumed this air has reached equilibrium with soil air. Cabrerizo *et al.*[44] report that the soil air reaches equilibrium with PAHs and PCBs in soil within 4 minutes. Care was taken at all sites to deploy in shaded locations. Temperature and relative humidity (RH) loggers were placed inside one air box and one soil air sampling box at each site and recorded at thirty minute intervals for the duration of deployment. A soil sample (top 15 cm) was taken at each site from outside a soil air box at time of deployment. Soil samples were analyzed for texture, organic matter, and moisture content at the Central Analytical Laboratory at Oregon State University.

Standards, solvents, and materials

Native PAH and PCB compounds of purity 97% or greater were purchased from Accustandard (New Haven, Conn., USA). Complete lists of target PAH and PCB compounds are given in Table 3.1; CAS numbers and physicochemical properties are given in Tables B.1 and B.2. Deuterium-labeled compounds used as performance reference compounds (PRCs, Tables B.1 and B.2) and extraction surrogates and internal standards (Table B3) were purchased from Cambridge Isotope Laboratories (Tewksbury, Mass., USA) and C/D/N Isotopes (Pointe-Claire, Quebec, Canada). Extraction solvent *n*-hexane and solvents used for rinsing, isopropanol, hexanes, and acetone, were Optima™ grade or better (Fischer Chemical, USA). Passive samplers were transported in polytetrafluoroethylene (PTFE) bags with Clip N Seal closures purchased from Welch Fluorocarbon, Inc. (Dover, New Hampshire, USA). Temperature and RH data loggers were purchased from Onset Computer Corporation (Bourne, Mass., USA). Passive samplers were constructed from LDPE lay-flat tubing purchased from Brentwood Plastics, Inc. (St. Louis, Missouri, USA). Average membrane thickness is 75‑95 μm, average width of tubing is 2.7 cm, and average transient polymer cavity size is 10 Å.[18]

Sample preparation

Each passive sampling strip was constructed from 1.1 m lengths of lay-flat LDPE tubing after Anderson *et al.*[18] Strips were cleaned with three successive 24-hour washes in hexanes to remove potential chemical interferences. Once dry, one end was heat-sealed, a 50 μL PRC solution in isooctane was added, and the other end was heat-sealed. This method of infusion and heat-sealing was chosen because it requires less solvent than other equilibration techniques. Strips were immediately placed in individual PTFE bags with airtight closures for transport to and from

sampling locations and up to 3 weeks' storage at -20°C. We do not expect PAH degradation following previous work showing concentrations of representative PAHs sequestered in LDPE passive samplers are stable out to 14 days at 35°C.[53] Each strip was infused with nominally 2 μg fluorene-d10, 1 μg pyrene-d10, 1 μg benzo[b]fluoranthene-d12, 0.2 μg PCB-116-d5, and 0.2 μg PCB-65-d5. The average of three blank infused LDPE strips was used to determine initial t=0 PRC concentrations (Table B4).

Following field deployment and upon receipt in the laboratory, all samplers were cleaned briefly in two washes of isopropanol to remove particulate matter and superficial fouling. Five LDPE replicates from one soil air box from each site were analyzed initially to ensure PAHs were sufficiently above detection limits. Remaining Anniston samples were composited and extracted by combining the five LDPE strips within each sampling box to achieve greater sensitivity, while remaining Wyckoff and Mosier samplers were extracted as individual strips. For extraction, samplers were placed in two successive solutions of 50 mL hexane containing extraction surrogate standards. Dialysates were combined and reduced to 0.5 mL. Exposure to ambient light was minimized during all laboratory steps.

Instrumental analysis

Analysis for 62 PAHs was performed with an Agilent 7890A gas chromatograph (GC) with an Agilent 7000 GS/MS-MS mass spectrometer.[54] Select samples were also analyzed for 52 PCBs on a dual-column Agilent 6890N GC equipped with dual electron capture detectors. Instrument parameters are detailed in Table B3. Detection and quantitation limits for all compounds at the instrument and in both air and soil air are included in Tables B.1 and B.2. Instrument concentrations were quantitatively corrected for loss during laboratory processing steps using extraction surrogate compound recoveries. Average extraction surrogate recovery was 73% (range 29-114) where recoveries were generally lower for relatively more volatile compounds, *e.g.* naphthalene-d8.

Environmental concentrations

Time-weighted average gas-phase air and soil air concentrations were determined using an empirical uptake model. Sampling rates were derived using performance reference compounds

(PRCs) as in situ calibration standards. Sampler-air partition coefficients are adjusted using the average temperature while deployed. Detailed equations are given in Appendix B.

Fugacity ratio and flux calculations

The unitless fugacity ratio (f_{ratio}) indicates the net direction of exchange of a compound between the air and soil surface:[42-45; 50; 55]

$$f_{ratio} = \frac{f_{soil\ air}}{f_{air}} \quad \text{Eq. 3.1}$$

where $f_{ratio} > 1$ indicates volatilization out of the soil and $f_{ratio} < 1$ indicates deposition. Fugacity of soil air ($f_{soil\ air}$, atm) and air (f_{air}, atm) are calculated using the same equation:

$$f_{(soil)air} = \frac{C_{(soil)air} RT}{MW * 10^{15}} \quad \text{Eq. 3.2}$$

where $C_{(soil)air}$ (ng m^{-3}) is the concentration of analyte in soil air or air, R (cm^3 atm K^{-1} mol^{-1}) is the gas constant, T (K) is the temperature measured within soil air or air box, MW (g mol^{-1}) is molecular weight of the analyte, and 10^{15} is a unit conversion factor.[44; 45; 55] Alternatively, Eq. 3.1 might be represented more simply as the ratio of two concentrations, but we present fugacity ratios to allow incorporation of small temperature differences. Uncertainty of f_{ratio} was estimated at 45% after incorporating all error ranges in air concentrations, soil air concentrations, and log K_{oa};[43; 56] more details are provided in Appendix B. This range of uncertainty is similar to previous reports measuring soil-air partitioning: 43%[55] and 30-40%[57]. In this work, values of f_{ratio} outside 0.55—1.45 ($\log_{10} f_{ratio}$: -0.26—0.19) indicate significant deviations from equilibrium (Appendix B).

Flux was calculated following Fick's law of diffusion:[7; 16; 58]

$$flux = \frac{D^T}{\delta_L} * (C_{soil\ air} - C_{air}) \quad \text{Eq. 3.3}$$

where positive values of flux indicate volatilization from soil to air (ng m^{-2} h^{-1}). $C_{soil\ air}$ and C_{air} are concentrations in soil air and air (ng m^{-3}). The boundary layer (δ_L, m), is set at 0.001, the value used in the Pesticide Leaching Model (PELMO) simulation.[58; 59] D^T (m^2 h^{-1}) is the temperature-corrected diffusivity in air using D^T of pyrene at 298 K as a reference.[58; 60; 61] Calculations and values for D^T for target compounds are given in SI. Values of flux >1 indicate

volatilization, and flux <1 indicates deposition from air to soil. Uncertainty for flux measurements using propagation of error are detailed in Appendix B.[57; 62]

Statistical analysis

Mean temperature and RH in air and soil air sampling boxes were compared using two-sided t-tests with serial correlation corrections. Mean air and soil air concentrations were compared using two-sided t-tests assuming unequal variance. Paired t-tests were used to compare relative standard deviation (RSD) of air and soil air measurements to assess differences in within- and between-box variability. Significance for all tests was set at $\alpha = 5$ %. Average PAH concentrations, fugacity ratio, and flux calculations were only calculated at each location for compounds that were above quantitation limit in all replicates in both air and soil air. Environmental concentrations of PCBs were calculated for all analyzed samples when detected, but fugacity and flux were not determined for PCBs because of low detection frequencies. Statistical analyses were performed with JMP Pro 12.0.1 and Microsoft Excel 2016.

Quality control

Quality control samples comprised 21% of all samples. Blank LDPE passive samplers that served as procedural blanks were prepared, sent without opening to and from the field sites, cleaned following deployment, and extracted. These procedural blanks ($n = 3$) were below limit of quantitation for all compounds, except 9 PAHs (Table B5). Average instrument concentrations for these 9 compounds were subtracted from all samples before environmental concentrations were calculated. The sum of these background-subtracted compounds comprised an average of 2% (range 2-23%) of the sum instrument concentrations of 62 PAHs. Blank solvent runs were included in each analytical batch of 20 samples. Continuing calibration verifications were included in each analytical batch to ensure a minimum of 80% of compounds were within ± 25% of true value for PAHs and ± 40% of true value for PCBs.

Results

Estimates of the soil-air partitioning, measured with the novel passive sampling design, suggest that PAHs are partitioning from air to soil in Anniston and Mosier, but the majority of PAHs were volatilizing from soil at Wyckoff. Mean air and soil air levels were different in all but three instances (Figure 3.2 and Table B6, two-sample t-test assuming unequal variance, $\alpha = 0.05$).

When statistically different, concentrations of detected PAHs at Anniston and Mosier were greater in air than soil air. All but four PAHs at Wyckoff had greater concentrations in soil air: naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, and 2-ethylnaphthalene. Soil-air partitioning for PCBs was not calculated because PCBs were not detected consistently at levels above quantitation limits. Four PCB congeners were detected in Anniston samples: PCB 4, 17, 77, and 118; and PCB 4 and 17 were also detected in some Wyckoff samples (Table 3.2). PCBs were below detection limit in all samples from Mosier. Complete PCB results for all analyzed samples are given in Table B7.

Temperature and relative humidity

Conditions within the air and soil air boxes were measured to evaluate if the sampling equipment was altering the *in situ* environment. No significant differences in mean temperature were found between the soil air boxes and air boxes at each site (Table 3.3). Mean RH was greater in the soil air box for all sites. Generally, diurnal fluctuations for temperature and RH were muted inside the soil air box (Figure B2-B3). Environmental conditions recorded at local weather stations agreed with temperature and RH measurements from within air boxes, indicating the micro-environment inside the air boxes is similar to ambient air.

Fugacity ratio (f_{ratio}) and flux

Numerous PAHs were in a state of deposition at both Anniston and Mosier, and none were observed to be volatilizing (Figure 3.3). The magnitude of deposition, measured by flux, was an average of 10 times greater in Mosier than in Anniston for all PAHs detected. The highest degree of flux, in either direction, was measured for naphthalene at -844 ng m^{-2} h^{-1} in Mosier, the site of the oil train fire in close proximity to a major highway. Our analysis also suggests volatilization from soil to air for many detected PAHs at Wyckoff, the site with substantial historical soil contamination, however f_{ratio} and *flux* data indicate different levels of significance. By both metrics, lower-molecular weight PAHs are in equilibrium between air and soil air.

Replicate analysis

Variability of PAH levels, measured by relative standard deviation (RSD), was greater in soil air than air (Figure 3.4). *Between*-box variability for PAH compounds was significantly greater in soil air than air (paired t-test, two-sided p-value < 0.001). Average *within*-box variability was also

assessed by analyzing five separate LDPE strips within each air or soil air box. Average within-box variability for PAHs was also significantly greater for soil air than air across all detected PAHs at Wyckoff and Mosier (paired t-test, two-sided p-value < 0.001). The majority of Anniston samples were analyzed as composites, and thus, within-box variability was not assessed for this site.

Soil moisture and organic content

Soil samples were collected from the top 15 cm and analyzed for descriptive qualities (Table 3.3). Moisture and organic carbon content are estimated, because the soil samples included approximately 1-5 cm duff that was excluded in analysis. Fraction of organic (f_{oc}) was estimated by dividing fraction of organic matter by 2.[60] Moisture content ranged between 2-50%, and f_{oc} was between 5-30%.

Discussion

Sensitivity of passive fugacity sampler at three unique locations

Direction of soil-air partitioning of semi-volatile organic contaminants can be represented both by fugacity and flux. Regardless of the metric used, partitioning measured with the novel sampling equipment design suggests that the direction and magnitude of soil-air partitioning varies by site. PAHs were either volatilizing or at equilibrium at the historically contaminated soil at the Wyckoff Superfund, while PAHs were in deposition near the Anniston Superfund site and the site of a recent oil train fire in Mosier.

The objective of this work was to demonstrate a novel sampling device for measuring soil to air flux. While our aim was not to characterize or monitor the sites, comparisons of contaminant profiles among the three sites provide interesting insights. Diagnostic ratios are often used to assess potential sources of PAHs.[63] A discussion of numerous sourcing ratios in included in Appendix B, with inconclusive results between pyrogenic/petrogenic sources as well as contributions of creosote, paving materials, and tire dust.

Anniston

Of the three selected sites, PCBs were expected to be detected at Anniston near the site of historical PCB contamination. Anniston also had the lowest measured PAH concentrations. This

site was in a wooded recreation area with trails, approximately 0.7 km slightly uphill from the main facility and 200 m from the on-site south landfill. Large machinery could be heard, but not seen from the deployment location. Average sum of 52 PCBs at the Anniston site in the present work was 0.35 and 0.55 ng/m^3 for air and soil air, respectively. For the two PCBs that were detected in all analyzed samples at this site, PCB 4 and PCB 17, levels were not different between soil air and air ($p = 0.15$ and 0.24 respectively, t-test assuming unequal variance). These results suggest PCB equilibrium between air and soil air, or more likely, that more data is needed to conclude the direction of soil-air flux. Previous research at the Anniston site suggests that the source of atmospheric gas-phase PCBs is material buried in the landfill, while volatilization from surface soil is a minor contributor.[64] Hermanson *et al.*[64] report sum air concentrations of 120 PCB congeners between ~5 and 12 ng m^{-3}. A more recent report found sum PCB concentrations between 3 and 19 ng m^{-3}.[65] Sampling in an undisturbed, wooded area and/or analyzing for fewer target PCBs may have led to lower sum PCBs levels in this work than previous reports.

Wyckoff

The samplers were placed in a location within the Superfund site with the known highest contaminations based on historical data (pers. comm. Helen Bottcher 2016). Samples from this site also had the highest PAH levels compared to Mosier and Anniston, as well as the heaviest, least-volatile PAHs up to the 6-ring PAH indeno[1,2,3-cd]pyrene. Adjacent to the samplers was an active remediation well that pumps contaminated groundwater to the surface before treatment at the on-site plant. A storage tank by the well head contains product with an obvious odor that may have impacted measured PAH concentrations in air. The Wyckoff site is not close to any major roads, but is adjacent to the ferry route that runs > 20 times daily between Seattle and Bainbridge Island. Regardless of potential current PAH sources in the area that might lead to deposition, many detected PAHs were volatilizing from the soil, while none were significantly depositing. The major PAH constituents of the creosote NAPL (non-aqueous phase liquid) at the Wyckoff site are, in order, phenanthrene, fluoranthene, pyrene, acenaphthalene, and naphthalene.[66] These PAHs were found in all Wyckoff samples, although not in the same ratios likely because of weathering and differential volatilization.

Mosier

This site was anticipated to have the most diverse PAH sources. A railroad and a large highway run parallel to the Columbia River through the town of Mosier. Samplers were intentionally placed in a shaded, calm location in close proximity to the site of oil train derailment and fire. The sampling location was approximately 60 m north of the railroad, and 60 m south of the highway. Charred brush could be seen from the deployment location. Post-spill clean-up operations included repaving a short section of road approximately 100 m south of the samplers. Finally, a brush fire covering >2800 acres occurred 25 km east of Mosier while samplers were in place. The dominant wind direction during summer months and this deployment is from the west, so this brush fire would be expected to have only small, if any, effects on measured PAH concentrations in air. Numerous diagnostic ratios yielded conflicting evidence of pyrogenic or petrogenic sources that may reflect the diverse PAH sources, including most notably crude oil (petrogenic) and the fire resulting from the derailment (pyrogenic) (Appendix B). More information is needed to understand the relative contribution of these and other likely sources including exhaust and tire dust from the adjacent highway.

Previous reports of PAH soil-air partitioning

In the Northeastern region of the United States, total flux for ten PAHs was estimated to be -82 ng m^{-2} h^{-1}.[67] Approximately 10% of flux rate for these PAHs, -8.2 ng m^{-2} h^{-1}, is directly partitioning to soil, while the majority is sequestered in vegetation before falling and decaying. For this subset of ten PAHs in the present work, average soil-air flux in Anniston and Mosier was -12 and -290 ng m^{-2} h^{-1} respectively. At Wyckoff, these PAHs were volatilizing at an average of 52 ng m^{-2} h^{-1}. Flux of PAHs in Anniston is consistent with Simonich and Hites[67], and Anniston is likely most representative of a regional average because it is undeveloped but in proximity to a city. Flux at Mosier may be greater than a regional average because of the recent oil train spill and fire, as well as its proximity to a major highway and railway. Finally, flux at the Wyckoff Superfund site has substantial contamination and represents a highly contaminated site.

Previous researchers have reported volatilization or deposition trends based on physicochemical properties. Wang *et al.*[42] found that low-molecular weight PAHs were volatilizing, and high-molecular weight PAHs were depositing to soil on “pristine” pastureland of the Tibetan Plateau. In contrast, Degrendele *et al.*[55] measured numerous semivolatile contaminants at background sites

in Hungary, and found that the more volatile, less-chlorinated PCB congeners were depositing, while the heavier, less-volatile PCBs were volatilizing. Similarly, our data suggest that the most-volatile, lightweight compounds were either depositing or were at equilibrium during our study period. General trends regarding the direction of soil-air partitioning are not expected to be dependent on chemical volatility alone, as trends are the result of multiple site parameters including, for example, age and type of contamination, climate, and soil characteristics.

Replicate analysis

Variability in PAH levels, measured by relative standard deviation (RSD), was greater in soil air than air (Figure 3.4). The differences between the two sampled matrices are likely attributable to the non-homogenous nature of soil, while air is comparatively more mixed. These results suggest that multiple air boxes may serve as replicates, but adjacent soil air samplers are pseudo-replicates that also incorporate the soil heterogeneity. Such heterogeneity is important to measure in future applications for accurate site characterization. Even *within* sampling boxes, we found more variability with soil air samplers. This result suggests that air diffusion is slow under the soil air box and that individual passive sampling strips are strongly influenced by the soil directly over which they are deployed.

Cabrerizo *et al.*[44] assessed repeatability of soil fugacity measurements by collecting samples on consecutive days, and found agreement within 10% in similar weather conditions. In comparison to the active sampling methods of Cabrerizo *et al.*[44], passive samplers like those described in the present work are deployed for weeks at a time. Day-to-day variability is incorporated into the resulting time-weighted averages and it cannot be quantified for a direct comparison between active and passive sampling. Instead of repeating measurements in time, we repeated samples in close proximity and found higher variability in samples that incorporate the heterogeneity of the soil.

One set of within-box replicate (n=5) soil air samples from each site were analyzed initially to check for instrument sensitivity. The least-volatile PAH detected in these individual samples from Anniston was triphenylene (log K_{ow} = 5.49, log K_{oa} = 10.69). Remaining Anniston soil air samplers were composited, and PAHs up to benzo[b]fluoranthene (log K_{ow} = 5.78, log K_{oa} = 10.35) were then above detection limit. Resulting environmental concentrations of individual and composited sampled were nominally the same. In this case, compositing multiple passive

sampling strips allowed for the detection of less volatile compounds that were previously below detection limits. The mass of passive sampling material per analyzed sample can be adjusted in future applications to optimize sensitivity.

Environmental conditions

The design of the soil air box affects $K_{soil\text{-}air}$ by lowering the temperature and increasing RH, relative to the air cage. The effects of temperature and RH offset each other, which is a result of the soil air box design providing shade but limiting the exchange of water vapor with ambient air. Together, these effects can change the environment slightly during sampling. Notably, active air sampling methods also change the soil air microenvironment when drawing air slowly across soil surface. Further, both active and passive *in situ* sampling methods change the environmental conditions less than *ex situ* soil sample collection methods.

Even small changes in temperature and RH can correspond to large changes in partitioning behavior between air, the passive sampling material,[17] and soil.[68] Field measurements of temperature are incorporated into partition coefficients between air and the sampling material ($K_{sample\text{-}air}$) using a modified van 't Hoff equation (Appendix B). Soil-air partition coefficients, $K_{soil\text{-}air}$, are also affected, and artificially high temperature or high humidity can increase partitioning from soil to air. In previous work that samples soil directly rather than with active or passive sampling, $K_{soil\text{-}air}$ is incorporated in estimating $f_{soil\ air}$ from the concentration in soil (C_{soil}):[44; 45]

$$f_{soil\ air} = \frac{C_{soil}RT}{K_{soil-air}*MW} \qquad \text{Eq. 3.4}$$

$K_{soil\text{-}air}$ is an additional term in the denominator in this expression that is analogous to Eq. 3.2. Following Eq. 3.4 and Eq. 3.1 above, a change in $K_{soil\text{-}air}$ is inversely related to both $f_{soil\ air}$ and f_{ratio}.

Davie-Martin *et al.*[68] developed an equation that predicts $K_{soil\text{-}air}$ of individual compounds using 22 pesticide compounds in varying conditions:

$$\log K_{soil-air} = -26.2 + 0.714\ logK_{oa} + 8291\frac{1}{T} - 0.0218\ RH + 0.121\ logf_{oc} \qquad \text{Eq. 3.5}$$

where $log\ K_{oa}$ is the logarithm of the octanol-air partition coefficient, T (K) is the mean environment temperature during deployment, RH (%) is relative humidity, and $log\ f_{oc}$ (%) is the logarithm of soil organic carbon content. The pesticides used in the Davie-Martin model have similar physicochemical properties (log K_{oa} range 6.4-10.4) as the PAHs in the present study (log K_{oa} range 5.0-13.7). For a compound in a given environment, $log\ K_{oa}$ and $log\ f_{oc}$ are unchanged by the sampling equipment. In this present study, relative humidity was significantly different between soil air and air, while temperatures were not significantly different. Using Eq. 3.5, the temperature and RH differences observed in the soil air boxes are expected to correspond to $K_{soil\text{-}air}$ decreases of 1.5-fold (0.17 log units) for both Anniston and Wyckoff, and 1.8-fold (0.26 log units) for Mosier. These fold differences by location were constant across compounds for all molecular weights. As a conservative estimate, the expected differences in $K_{soil\text{-}air}$ would correspond to, at most, a 1.8-fold increase in both $f_{soil\ air}$ and f_{ratio}. For any compounds close to equilibrium, the effect of the sampling equipment altering soil-air partitioning may change the direction of flux. Under the conditions measured in the present work, volatilization may be underestimated. Additionally, a 1.8-fold change is likely an overestimate because temperature and RH were not measured on the exterior of the soil air box at ground level, where conditions are expected to be more similar to the soil air box's interior, but at 1.5m above the soil air box. We recommend monitoring temperature and RH in future applications.

Organic carbon content correlates with a soil's capacity to sorb semi-volatile contaminants.[60; 68; 69] It might therefore be expected that soils rich in organic matter would favor partitioning to soil through deposition. Among our sampling locations, Mosier had the highest organic carbon content as well as the highest rates of deposition. Wykcoff had the lowest organic carbon content and no evidence of deposition. We predict that these associations are coincidences in this study, as there are other important variables that lead to deposition or volatilization, such as the time elapsed since contamination events.

Detection limits and relative PRC diffusion rates

Performance reference compounds (PRCs) are used to estimate how compounds are approaching equilibrium. Lighter, more volatile compounds generally reach equilibrium more quickly and are estimated using PRCs with similar physicochemical properties. Greater amounts of PRCs diffused from air samplers than from soil air samplers suggesting that, in comparison, compounds

in air samplers are closer to equilibrium with the environment. On average, only 2% of fluorene-d10 remained in air samplers across all sites, while 36% remained in soil air samplers (Figure B1). Similar but less dramatic differences in dissipation occurred with the remaining PRCs. Accordingly, the air boxes sampled a larger volume of air than the soil air, and this discrepancy is expected because the design of the soil air box allows only limited exchange with ambient air. The different sampling rates do not affect air and soil air concentrations, because the calculations incorporate PRC loss on a per sample basis.

The volume of air sampled, however, does affect the environmental detection limit. Lower-molecular weight PAHs have similar limits in both air and soil air, but the quantitation limit for the heaviest PAHs is about 6 times greater in soil air (Table B1). As an example, consider a compound at equilibrium has the same concentration in both air and soil air. The passive samplers must have sequestered a concentration at least equal to the detection limit for it to be measured at the instrument. Because more air passes over the air sampler than the soil air sampler (inferred from PRC loss), it is possible that the soil air sampler has not accumulated enough of the compound for it to be above detection limit. For this reason, we only calculated fugacity ratios and flux if compounds were above quantitation limit in all air and soil air samplers, on a site-by-site basis. This ensures that we are not falsely assuming that air concentration is greater than soil air when sampling rates may be affecting detection limits.

Limitations and advantages

Passive sampling is advantageous because the technique does not require electricity or maintenance while deployed. The novel soil air sampler and previous adaptations of passive sampling yield time-weighted average concentrations that are measured *in situ*. Compared to active samplers which can be deployed for hours to days at a time, passive samplers must often be deployed longer. The heaviest and least volatile compound detected in any sample was dibenzo[e,l]pyrene (log K_{ow} = 7.28, log K_{oa} = 12.77), which was found in approximately half of the samplers from Wyckoff. The detection of this compound indicates that the 2-week deployment period was sufficient for appreciable accumulation above detection limits at the most contaminated site. This PAH or other heavier compounds may also be present at the other sites, but require longer than two weeks to appreciably accumulate in the passive sampler material in

lower environmental concentrations. The length of deployment and mass of passive sampling material should be tailored for the site of interest.

Previous soil-air partitioning research has revealed diurnal fluctuations.[55] Measurements made with passive samplers are time-weighted averages over the scale of weeks and are not suitable for discerning variation within a day. Seasonal variations have also been reported, where volatilization of semi-volatile contaminants is greater in warmer temperatures.[47; 56; 70] Wyckoff had the lowest average temperature yet had the highest PAH concentrations of all three sites. Direction and magnitude of soil-air partitioning is likely affected seasonally, and the results presented do not represent an annual average. Repeated measures at a site are necessary to determine seasonal variation. Results provided herein are an estimate of average flux over the duration of deployment only.

We present two metrics of soil-air partitioning: fugacity ratio and flux. Comparing these two metrics highlights an important difference, particularly with the Wyckoff data (Figure 3.3). Flux compares the *difference* between two concentrations (Eq. 3.3), while f_{ratio} is a ratio of two concentrations (Eq. 3.1). For example, at Wyckoff, indeno[1,2,3-cd]pyrene levels in air (0.000739 ng m^{-3}) and soil air (0.00464 ng m^{-3}) were both low, but significantly different. The soil air level is ~6 times greater than air, although the difference in these values is only 0.00390 ng m^{-3}. These data yield high f_{ratio}, but low magnitude of flux. A weight-of-evidence approach should be considered when concluding direction and magnitude of soil-air partitioning.

The height of boundary layer was estimated as 0.001 m and used in flux calculations across all three sites. In windier locations, the boundary layer might be expected to be smaller, thereby increasing the magnitude of flux. Importantly, however, the samplers in the present study were each deployed in areas without large influence of wind. If another value were used in flux calculations, the profile and relative trends of flux among the three sites would be unchanged, and only the magnitude would be different. Computing the fugacity ratio does not require an estimated value for boundary layer.

A major advantage of the recent *in situ* methods for measure soil-air partitioning is that they use the same sampling technique for measuring both air and soil air. Traditional method of measuring soil-air flux requires the measurement of several soil parameters and the estimation of compound-

specific physicochemical properties including f_{oc} and $K_{soil\text{-}air}$. The overlying air samplers, whether active or passive must also be effectively calibrated. Numerous estimated values are also used in the present work, however the sampling equipment and calculations for both environmental matrices are nearly identical. Any input parameters for the environmental concentration calculations that are over- or under-estimated would affect both matrices in the same manner.

Conclusions

The passive soil air sampler described here is suitable for measuring concentrations of semi-volatile organic contaminants in air that are in equilibrium with soil. When co-deployed with ambient air passive samplers, direction and magnitude of soil-air partitioning can be measured. Along with the advantages of *in situ* sampling, the described passive sampling method requires no electricity and allows for longer, maintenance-free deployment periods. We have demonstrated its performance in three unique environments where compounds were found to be differentially partitioning between air and soil. Variability among soil air samplers is predictably greater than air samplers, and sensitivity can be adjusted with length of deployment and mass of passive sampling material. Environmental conditions under the novel soil air box do not substantially change soil-air partitioning behavior and should be monitored in future uses. The passive soil-air fugacity sampler is a candidate for use in numerous sites with new or historical contamination, or in locations where conventional soil sampling techniques are challenging.

Acknowledgements

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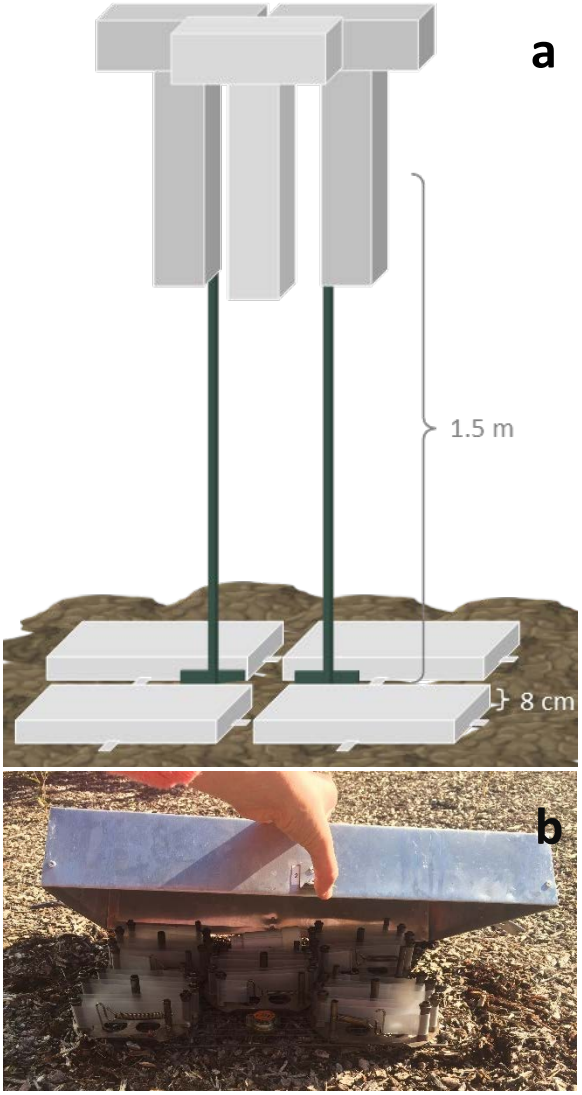

Figure 3.1. Schematic of air and soil air sampling design (a) and arrangement of LDPE passive sampling strips under the soil air box (b).

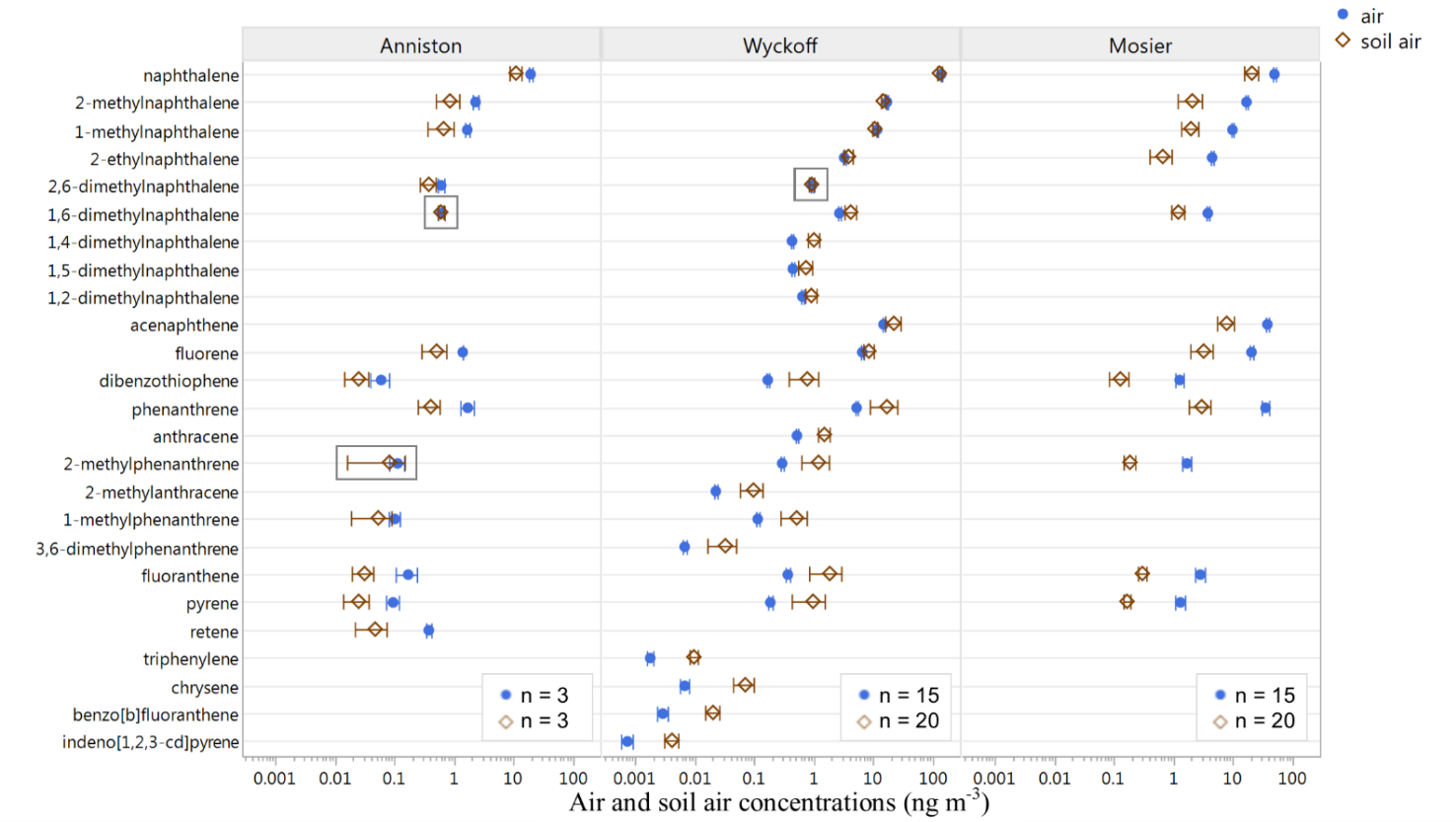

Figure 3.2. Air and soil air PAH concentrations at three sampling locations. Data are omitted for a site if below quantitation limit in any air or soil air replicate. The 25 PAHs shown were above quantitation limit for all replicates at one or more sites. Error bars represent 95% confidence interval. Boxes indicate instances where levels were not different between air and soil air (two-sample t-test assuming unequal variance, $\alpha = 0.05$). Anniston samples were composited before analysis and thus have smaller n.

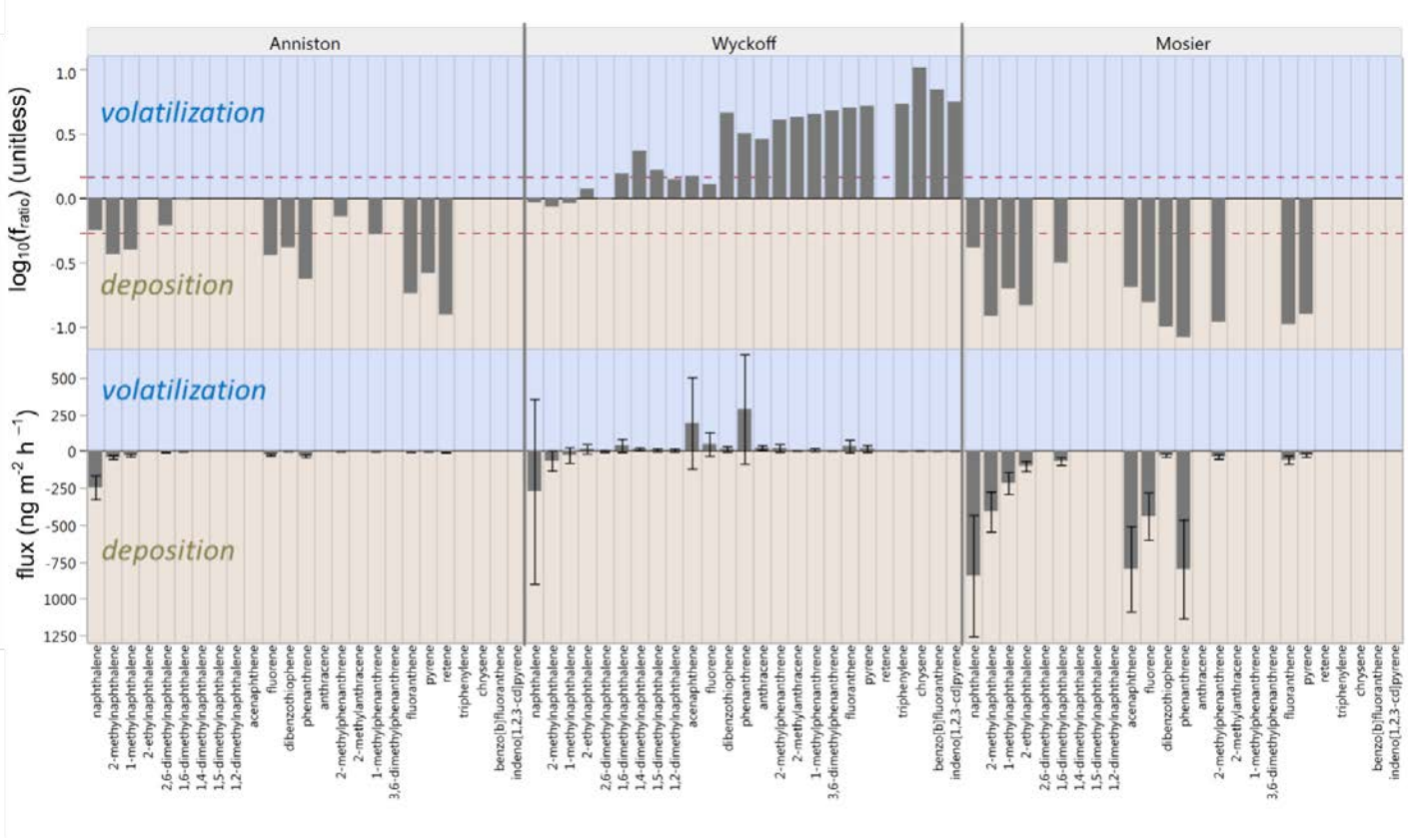

Figure 3.3. Soil-air partitioning at three sampling locations represented by fugacity ratio (f_{ratio}) and flux. Bars in the positive direction indicate volatilization, and bars in the negative direction indicate deposition. Bars (f_{ratio}) outside the red dashed line indicate significant deviations from equilibrium between soil and air. Error bars for flux measurements show propagation of error (Appendix C). Data are omitted for a site if below quantitation limit in any air or soil air replicate. PAHs are only shown if above quantitation limit for all replicates at one or more site.

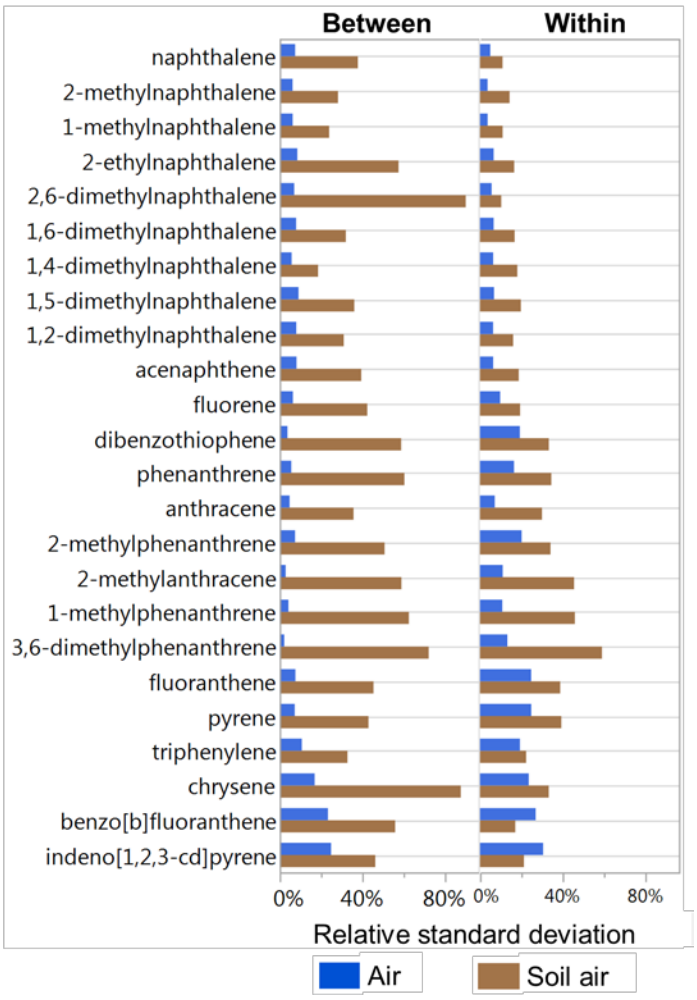

Figure 3.4. Average relative standard deviation for between-box and within-box air and soil air samplers. Between-box variability for PAH compounds was significantly greater in soil air (average 40%) than air (average 8%; paired t-test, two-sided p-value < 0.001). Average within-box variability for PAHs was also greater for soil air (average 23%) than air (average 13%) across all detected PAHs at Wyckoff and Mosier (paired t-test, two-sided p-value < 0.001).

Table 3.1. Target analytes. PAHs are listed in order of GC retention time. CAS numbers and physicochemical properties are provided in Tables B.1 and B.2.

PAHs	naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, 2-ethylnaphthalene, 2,6-dimethylnaphthalene, 1,6-dimethylnaphthalene, 1,4-dimethylnaphthalene, 1,5-dimethylnaphthalene, 1,2-dimethylnaphthalene, 1,8-dimethylnaphthalene, 2,6-diethylnaphthalene, acenaphthylene, acenaphthene, fluorene, dibenzothiophene, phenanthrene, anthracene, 2-methylphenanthrene, 2-methylanthracene, 1-methylphenanthrene, 9-methylanthracene, 3,6-dimethylphenanthrene, 2,3-dimethylanthracene, fluoranthene, 9,10-dimethylanthracene, pyrene, retene, benzo[a]fluorene, benzo[b]fluorene, benzo[c]fluorene, 1-methylpyrene, benz[a]anthracene, cyclopenta[cd]pyrene, triphenylene, chrysene, 6-methylchrysene, 5-methylchrysene, benzo[b]fluoranthene, 7,12-dimethylbenz[a]anthracene, benzo[k]fluoranthene, benzo[j]fluoranthene, benz[j]aceanthrylene & benz[e]aceanthrylene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, benzo[a]chrysene, benzo[ghi]perylene, anthanthrene, naphtho[1,2-b]fluoranthene, naphtho[2,3-j]fluoranthene, dibenzo[a,e]fluoranthene, dibenzo[a,l]pyrene, naphtho[2,3-k]fluoranthene, naphtho[2,3-e]pyrene, dibenzo[a,e]pyrene, coronene, dibenzo[e,l]pyrene, naphtho[2,3-a]pyrene, benzo[b]perylene, dibenzo[a,i]pyrene, dibenzo[a,h]pyrene
PCB congeners	1, 4, 5, 8, 10, 11, 16, 17, 18, 21, 28, 31, 33, 37, 44, 49, 50, 52, 60, 66, 70, 74, 77, 81, 82, 87, 99, 101, 104, 105, 110, 114, 118, 123, 126, 128, 138, 145, 153, 156, 157, 158, 166, 167, 169, 170, 179, 180, 183, 187, 189, 204

Table 3.2. Mean concentrations of PCBs in air and soil air for data above limits of detection.

Sampling location		Air			Soil air		
		Mean (ng/m^3)	RSD[a]	Frequency of detections (n=3)	Mean (ng/m^3)	RSD[a]	Number of detections (n=3)
Anniston	PCB 4	0.31	45%	3	0.49	26%	3
	PCB 17	0.034	2%	3	0.046	114%	3
	PCB 77	0.0033	8%	2	0.010	28%	2
	PCB 118	0.0038	[c]	1	[b]	[c]	0
Wyckoff	PCB 17	0.0079	[c]	1	0.029	9%	2
Mosier	*no PCBs detected*	[b]	[c]	0	[b]	[c]	0

[a] r*elative standard deviation*
[b] *not detected*
[c] *not calculated because of low detection frequency*

Table 3.3. Estimated soil characteristics and environmental parameters. Mean temperature and relative humidity (RH) were compared with t-test adjusted for serial correlation. Asterisks denote significant differences between air and soil air boxes.

Sampling location	Soil type	f_{oc} (%)	Moisture content (%)		Temp. (°C)		RH (%)	
					Mean	p-value	Mean	p-value
Anniston	sandy loam	8	20	Air	22.2	0.429	70.0	0.002*
				Soil air	20.4		97.3	
Wyckoff	sandy loam	5	2	Air	16.9	0.841	67.5	0.026*
				Soil air	16.5		84.0	
Mosier	organic	30	50	Air	21.0	0.336	59.0	<0.001*
				Soil air	19.0		94.7	

CHAPTER 4 – CONTAMINANT FLUX FROM ARTIFICIAL TURF

Abstract

Characterization of artificial turf fields and the health risks they may pose are the subjects of ongoing research. The rates of chemical off-gassing, or deposition, are expected to decline over time, but have not been previously measured *in situ*. Furthermore, unidentified and undetected chemicals may be contributing to risk for field users and athletes. We analyzed for 62 PAHs, 19 OPAHs, and 1533 compounds of various classes present in air and turf air, that is, air immediately above the artificial turf surface. Volatilization and deposition were measured with quantitative flux between air and turf air. Low-density passive sampling devices were deployed in air and turf air at three artificial turf fields: a new indoor facility and two outdoor fields installed 2 and 5 years previously. Following extraction in *n*-hexane, extracts were analyzed with gas-chromatography/mass spectrometry (GC/MS) and GC/triple-quadrupole MS. We detected 26 chemicals not previously associated with artificial turf, including some that are known to have adverse effects on human health. All PAHs and OPAHs at the indoor, newest field were volatilizing. At the older, outdoor fields only the higher-molecular weight PAHs were volatilizing, while the more-volatile PAHs were depositing from ambient air. This sampling scheme provides the first quantitative measure of flux from artificial turf fields, and is a candidate for large-scale sampling to better characterize organic chemical content and turf-air partitioning.

Introduction

Professional and amateur athletes commonly practice on artificial turf. The latest generation of artificial turf fields are composed of several layers to mimic the look and feel or grass, including plastic “grass” fibers and infill made of crumb rubber and/or sand.[71] Crumb rubber, is ~90% of field material by weight, and is made primarily of recycled tires.[71; 72] Numerous components of the recycled tires have been considered as potential toxicants, including lead, zinc, particulate matter, and volatile and semi-volatile organic chemicals.[5; 73; 74] Potential exposure routes from crumb rubber include inadvertent ingestion of crumb rubber, dermal contact, and inhalation of particles or gas-phase contaminants. 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,[5; 72; 75-81] or b) that some exposures are above levels that may contribute

to risk.[82-86] Refining these conclusions is the subject of recent and ongoing investigations by the U.S. Environmental Protection Agency *et al.*[73; 74] and the European Chemicals Agency[5].

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.[71; 72; 83-85; 87; 88] Much of the PAHs in tires are from the addition of highly-aromatic oils (HA-oils) during tire manufacturing.[72; 89] HA-oils formerly contained between 10 and 30% PAHs by weight, but these 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.[71] Automobile 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.[89] 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.[89]

Other toxicologically-relevant chemicals may be present, but have not been identified and remain an uncertainty in risk evaluations.[5] Oxygenated PAHs (OPAHs), like PAHs, derive from numerous natural and anthropogenic sources, although the toxicity of OPAHs is less well-understood. OPAHs are also formed as oxidation products of PAHs,[90] and formation of OPAHs is likely in the high sun environment typical on outdoor sports field. For other contaminants not directly related to recycled tires, artificial turf could act as an initial sink with gradual release over time. Kanematsu *et al.*[91] and Nilsson *et al.*[81] used mass spectra libraries and identified potential, previously unreported toxicants in rubber mulch leachate. Otherwise, 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.

Semi-volatile contaminants can off-gas from crumb rubber in fields with artificial turf, making such chemicals available for inhalation by athletes and field users. Li *et al.*[92] and Zhang *et al.*[86] report that chemical off-gassing rates generally decrease as the field ages. 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.

In this work, we apply a recently-demonstrated passive sampling design[93] to non-selectively sample gas-phase organic chemicals and measure flux *in situ* between turf and overlying air. Our objectives in this study were to 1) identify novel gas-phase PAHs, OPAH, and various other chemicals associated with artificial turf, and 2) to quantify PAH and OPAH flux between turf and overlying air. This work will aide in future risk assessments by further characterizing organic chemicals associated with artificial turf. It is also the first to measure quantitative *in situ* flux rates from artificial turf.

Materials and Methods

Chemicals

Target PAH analytes, internal standards, and deuterium-labeled extraction surrogates (Table C1) were purity 97% or greater, and were purchased from distributers as detailed previously.[25; 54] 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).

Site descriptions and sampling design

We collected samples at 3 artificial turf fields in western Oregon: *indoor*, an indoor facility (field approximately 2 months old), *outdoor A*, an outdoor field surrounded by a rubberized track (field approximately 2 years old); and *outdoor B*, an outdoor multi-use field (field approximately 5 years old). Crumb rubber is likely to have been added to outdoor fields since first installation.

Passive sampling devices were used to measure two matrices: air at an approximate height of 1.5 m; and turf air, or air immediately above and in close contact with turf. Paired air and turf air boxes, as described in Donald and Anderson[93], were deployed at the three locations with triplicate equipment at *outdoor A*. Each box contained 5 LDPE strips and a temperature logger. A relative humidity logger was also placed in each an air and turf air box at *outdoor A*. Sampling equipment was set up and remained for 27 days in August and early September 2016. Average temperature in the region during sampling duration was 26 °C (range 14-39). Temperatures on the fields varied more, averaging 21°C (range 6-46), whether measured within or outside the air box.

Temperature was not different between air and turf air at any site (two-sample t-test p-values > 0.05), and relative humidity was not different (p-value > 0.05) where measured at *outdoor A*. Temperature and relativity humidity profiles over time are included in Figure C1 and C2.

LDPE sample preparation

Passive samplers were prepared using meter-long strips of LDPE lay-flat tubing as in Anderson *et al.*[18] Briefly, the strips were pre-conditioned in multiple solvent bathes, and, once dry, a solution containing PRCs was infused inside each strip of LDPE lay-flat tubing before heat-sealing on both ends. Following deployment, passive sampling strips were cleaned in isopropanol and extracted with surrogate standards in *n*-hexane as in Donald and Anderson[93]. Five LDPE strips from each sampling box were composited for extraction. Final extract volume was quantitatively reduced to 1.0 mL. Internal standards were added to extract aliquots prior to instrumental analysis.

Instrumental analysis

Extracts of LDPE were analyzed using previously described methods for 62 PAHs and 19 OPAHs (Table C1). PAH analysis was conducted using gas chromatography electron-impact/triple quadrupole mass spectrometry (GC/MS-MS, Agilent 7000C) with an Agilent PAH-select column.[54] Analysis for OPAHs was performed with gas-chromatography electron impact mass spectrometry (GC/MS, Agilent 7890A and 5975C) with a DB5-MS column.[25] Presence or absence of 1533 chemicals was determined also using GC/MS with a DB5-MS column as described in Anderson *et al.*[24] and Bergmann *et al.*[94] Over 100 additional chemicals were added to the present method, including several related to recycled tires and artificial turf, *e.g.* benzothiazole. This presence/absence screen, hereafter referred as the "1533 screen," uses mass spectral deconvolution software, and the complete list of analytes is included in List C1 (Appendix C). Chemical concentrations in the 1533 screen are not quantified against a calibration curve, however responses among blanks and samples can be compared to infer relative concentrations.

Calculations

Gas-phase concentrations of PAHs and OPAHs in air (C_{air}) and turf air ($C_{turf\ air}$) were determined from passive samplers using an empirical uptake model with PRCs as *in situ*

calibration standards.[22; 36; 93] More details are given in Appendix B, where turf air is calculated in the same manner as soil air. Method detection limits (Table C1) 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 with chemical volatility.

Quantitative flux (ng m^{-2} 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:

$$flux = \frac{D^T}{\delta_L}(C_{turf\ air} - C_{air}) \quad \text{Eq. 4.1}$$

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) is 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 (Appendix B and Table C1).[93]

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,[57; 62] following the methods described in Appendix B. Uncertainties of air, turf air, and mass transfer coefficients used were 33%, 21%, and 30%, respectively. 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

Procedural blanks of each LDPE (n=3) were included and used as the basis for background-subtraction and determination of initial PRC concentrations. These samples were pre-conditioned, infused with PRCs, transported to field locations, extracted, and analyzed alongside field-deployed samples. Concentrations of PAHs and OPAHs in these procedural blanks were subtracted from field-deployed samples before calculating environmental concentrations. Subtracted concentrations accounted for 0.1 to 1.1% of sum concentrations in the field-deployed air and turf air samples. We detected the presence of 4 chemicals in the 1533 screen of the procedural blanks. Two had substantially smaller responses in procedural blanks than in field samples: bis(2-ethylhexyl)phthalate and di-n-butylphthalate. One, 2,4-di-tert-butylphenol, had similar responses in both procedural blanks and field samples and was thus removed from further

analyses. The fourth dicyclohexyl phthalate was not seen in any field samples. More information on procedural blanks is provided in Table C2 and C3. Instrument blanks, aliquots of *n*-hexane, were included before each analytical batch of no more than 20 samples. Surrogate recoveries averaged 69% (range 24 to 109%). Continuing calibration verifications were included before, after, and at least every ten samples in PAH and OPAH methods to ensure 80% of target analytes were within 20% of true value.

Results and Discussion

Environmental concentrations of PAHs and OPAHs

Among ten LDPE samples we detected 31 of 62 PAHs, and 7 of 19 OPAHs (Figure 4.1). Higher-molecular weight chemicals were more frequently detected in air, the matrix with lower detection limits. The *indoor site* has 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, are documented as having higher levels of air contaminants than outdoor fields,[5] however, in the present study design 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%). Generally, standard deviation was greater with lower mean PAH concentration. Accordingly, the overall RSD for air increased to 33% when also including chemicals found only in air, which were typically at low levels.

Thirteen of the detected PAHs have not previously been reported in work related to artificial turf[74] (Table 4.1). Over half of these novel artificial turf PAHs are alkyl-naphthalenes. Notably this list also includes benzo[c]fluorene, which has an estimated carcinogenic potency 20 times greater than benzo[a]pyrene.[1] The present experimental design sampled gas-phase contaminants exclusively, and the dominant PAHs observed were the more volatile PAHs. Pyrene and benzo[ghi]perylene are major PAH components of tires,[89] and pyrene was present in all samples. The less-volatile benzo[ghi]perylene was below limits of detection in turf air, but detected in all air samples. We did not detect the carcinogenic dibenzopyrenenes described in Sadiktsis *et al.*[89] Importantly, the tires in Sadiktsis *et al.*[89] were analyzed before HA-oils were phased out of tires. If present at the fields sampled in the present work, the 6-ringed dibenzopyrenenes would be highly associated with particles and are only likely to be present in the gas-phase in low levels

and below limits of detection. However, the lack of dibenzopyrenenes in the present study may indicate that tires sourced for the crumb rubber did not contain HA oils. 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 4.1). Previous reports of turf-associated OPAHs are limited to three OPAHs: 6H-benzo[cd]pyren-6-one and 4H-cyclopenta[def]phenanthrene-4-one, and 2-ethyl-9,10-anthraquinone.[74; 91] 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.[90] OPAHs can have more mutagenic potential than their corresponding unsubstituted parent PAHs, and OPAHs need not be metabolically activated to induce toxicity.[90] Knecht *et al.*[95] 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.[96] 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.[87] Dye *et al.*[87] 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 4.2), demonstrated with values from a representative site, Valhall. Comparisons with the other sites sampled by Dye *et al.*[87] are similar to Valhall. Their report also includes particle-phase (PM10) PAH concentrations. Comparing these two phases (Figure C3), 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 majorly present in 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. In contrast, contaminants adsorbed to particle are less bioavailable, and particle size affects how far contaminants can penetrate into the lungs.[5] The present experimental design sampled only the bioavailable, gas-phase chemicals, therefore low

concentrations of high-molecular weight chemicals were expected. The current work gives the only gas-phase concentrations around outdoor artificial turf fields to date.[74]

Presence/absence (1533) screen

The results of our 1533 screen revealed the presence of an additional 19 chemicals beyond the PAHs and OPAHs (Figure 4.3). Seven of these chemicals have not been previously reported in literature pertaining to artificial turf, recycled tires, or crumb rubber (Table 4.1).[74] Two phthalates were present in procedural blanks and are included in Figure 4.3 nonetheless, because responses were substantially greater in field samples than in procedural blanks: bis(2-ethylhexyl)phthalate and di-n-butylphthalate (Table C3).

The phthalates detected in the present work have been reported in previous analyses of crumb rubber,[84] playground material,[83] and air at playing fields.[5; 74] Four of these phthalates are recognized as reproductive toxicants by the Registration, Evaluation, Authorisation 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 does not measure absolute concentrations. Therefore, we cannot compare risk estimates to previous reports.

Several personal care products were detected using the 1533 screen in both air and turf air samplers. The chemical *b*-citronellol is a component of perfumes and essential oils of various plants.[97] Benzyl salicylate, a scent compound,[98] was present in all air samples, but in no turf air samples. Drometrizole, an ultraviolet light absorber used in sunscreen products[99] and plastic polymers,[100] was found in one turf air sampler. This chemical has been previously been detected in leachate,[81] 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 itself. Personal care products in turf air samplers support the theory that turf can act an initial sink to naive chemicals, with gradual off-gassing over time.

In addition to the personal care products and phthalates, we observed several other chemicals, 7 of which have not been reported previously to be associated with artificial turf, tires, or crumb rubber (Table 4.1). Ethiolate, a dithiocarbamate herbicide believed to be obsolete or no longer in use,[101] has not been previously associated with artificial turf fields. However, dithiocarbamates are used as vulcanizing agents in tire production,[102] and we hypothesize this detection represents a structurally-similar dithiocarbamate constituent of tires. Pentachlorobenzene is a persistent organic pollutant included in the Stockholm Convention that formerly had a variety of industrial uses.[103] 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,[103] and regional wildfires around the sampling period are a potential source. Finally, triphenyl phosphate is a organophosphate flame retardant, an emerging class of chemicals used as alternative to phased-out brominated flame retardants.[104] 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, like in previous findings where samples were collected 6 inches above turf.[75; 77] 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.[74] 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.[74]

Flux of PAHs and OPAHs

Flux varied substantially among the three sampled fields (Figure 4.4). We evaluated flux 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 are given in Table C4. Naphthalene had both 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 measured flux values at the *indoor* site were positive indicating volatilization, with an average rate of 3000 ng m^{-2} h^{-1}. In comparison, only the 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, we determined that OPAHs were volatilizing, however only chromone was significantly volatilizing.

Profiles of PAH/OPAH flux across the three selected fields agrees with previous evidence that off-gassing relates to the age of the field.[86; 92] 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 to compensate for depletion in high traffic areas.[86] 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 4.5). We observed significant correlations (p-value < 0.05) at each of the sampled fields, although the strength of correlation varied. The newest field, *indoor*, had the strongest correlation ($R^2 = 0.964$), indicating that volatilization from turf strongly affects concentrations in the overlying air at this site. Slightly less-strong correlations were observed at, *outdoor A* ($R^2 = 0.717$) and *outdoor B* ($R^2 = 0.670$), providing evidence that volatilization at the two older, outdoor sites is comparatively less substantial. Similar correlation analyses have been conducted, albeit sparingly. Cabrerizo *et al.*[105] report high correlations ($R^2 = 0.63$ 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 Leone[41] 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.

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*. The fields sampled herein do not represent all artificial turfs, and any inferences to other fields are limited. With the small sample size, we cannot distinguish the effects of field age or

indoor/outdoor facility on chemical detections or flux. We collected samples only during the warmest days of the year. As chemical volatility increases with temperature, we would expect lower volatilization rates in cooler temperatures, holding all other variables constant. Data were not compared to samples from adjacent background or natural turf fields, and the detection of a chemical does not necessarily indicate it derives from artificial turf. 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. Finally, the semi-enclosed turf air box has the potential to affect temperature and relative humidity, which can in turn affect crumb rubber-air or passive sampler-air partitioning. We detected no differences in temperature or relative humidity between the air and turf air boxes, so subsequent effects on partitioning are unlikey.

Data from the 1533 screen provides MS response data, while absolute air concentrations, turf air concentrations, and sensitivity are not currently determined. Theoretically we could infer the direction of flux if the response is substantially different when detected in both air and turf air, but this would assume sensitivity is equal between the two matrices. With the use of PRCs, we conclude that air samplers have lower detection limits and are quicker to approach equilibrium. The detection limit for each matrix also varies by chemical, as demonstrated by a 1.8 order of magnitude increase in detection limits from turf air to air for the least-volatile PAHs (Table C1). Flux direction cannot be inferred from 1533 screen because of the differences in sensitivity between air and turf air. Current efforts are being directed towards collecting quantitative data from the 1533 screen to enable calculation of environmental concentrations and flux. A brief comparison of data between the 1533 screen and quantitative PAH method is included in Figure C4.

Future directions: comparing LDPE and silicone passive samplers

New sampling techniques are commonly calibrated against existing technologies. Khairy and Lohmann[106] co-deployed LDPE passive samplers with more conventional active samplers to, in part, determine sampler-air partition coefficients. In a similar fashion, we included silicone passive samplers alongside the more established LDPE within the air and turf air sampler boxes used herein. Numerous types of silicone polymer have been used in organic pollutant research.[107] O'Connell *et al.*[108] co-deployed LDPE and silicone rubber sheets to illustrate that the properties of

target analytes should be considered when selecting a polymer in passive sampling studies. The silicone material included in this experimental design is identical to silicone wristbands in previous studies in human exposure,[9; 109-112] and silicone samplers will be analyzed following validation of a solvent-free, thermal extraction technique. The side-by-side analysis will establish silicone-air partition coefficients and yield important insight into the contribution of gas-phase contaminants in environmental and personal exposures, particularly with the developing silicone wristband technology.

Conclusions

This work provides the first quantitative measure of *in situ* flux of semi-volatile contaminants on artificial turf fields. We also report the presence of 26 chemicals that have not yet been reported in artificial literature, including some with known effects on human health. Further work is necessary to determine what risk, if any, these chemicals may contribute to adverse health outcomes. Gas-phase concentrations in ambient air agree with previous reports, and flux measurements generally align with evidence that compound volatilization decreases with field age, although that hypothesis was not specifically tested. This is the first report of bioavailable gas-phase PAH and OPAH concentrations on an outdoor field, as such gas-phase concentrations have only yet been reported from indoor facilities. Turf air and air were highly correlated at all three sites, and particularly at the recently-installed indoor site. The described sampling scheme is a candidate for large-scale assessment of artificial turf field flux.

Acknowledgements

The authors thank Pete Hoffman for assistance in study design and Gary Points for extending the chemicals in the 1533 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.

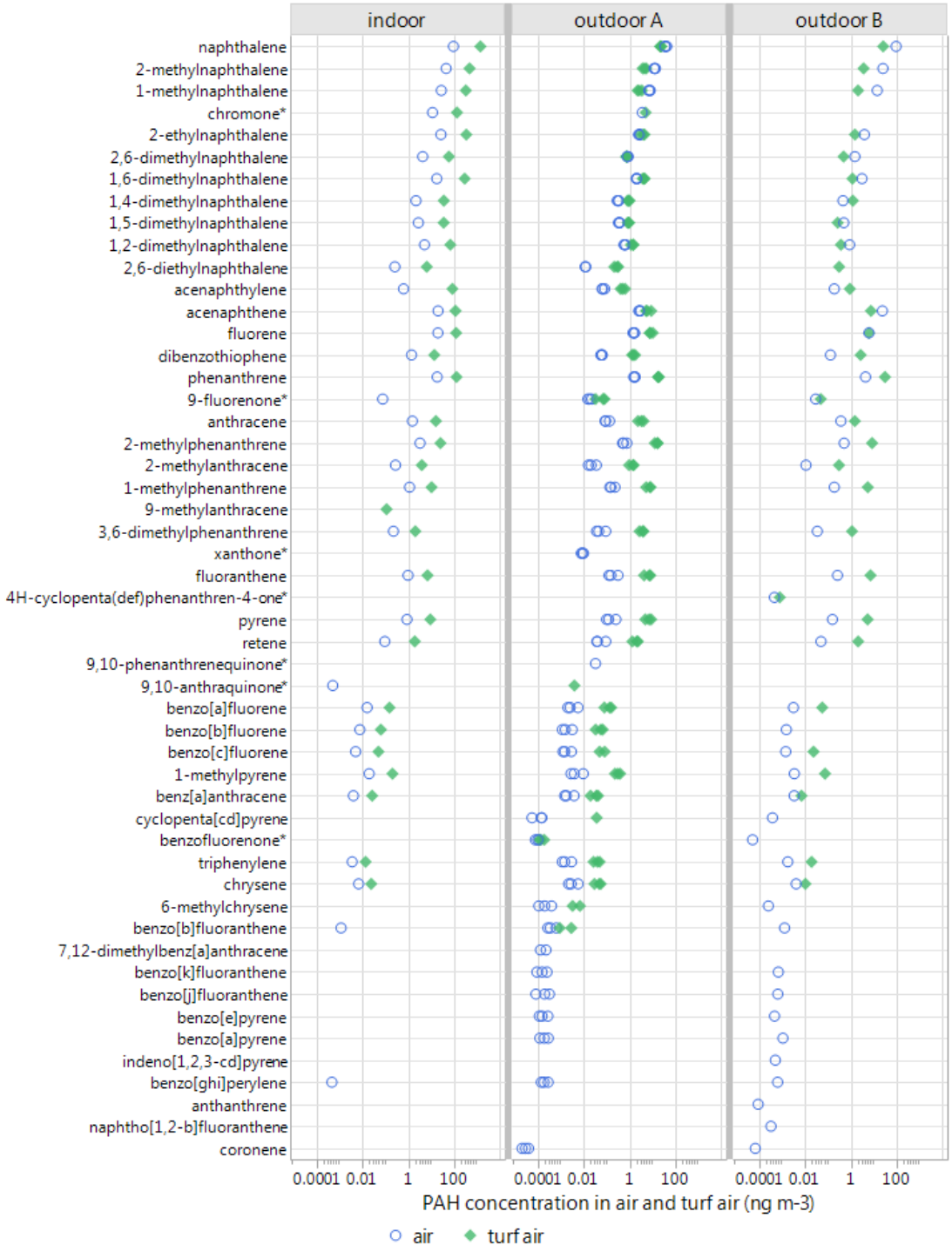

Figure 4.1 Concentrations of PAHs and OPAHs in air and turf air. OPAHs are indicated by dashed, grey horizontal lines. Triplicate samples were collected at *outdoor A*.

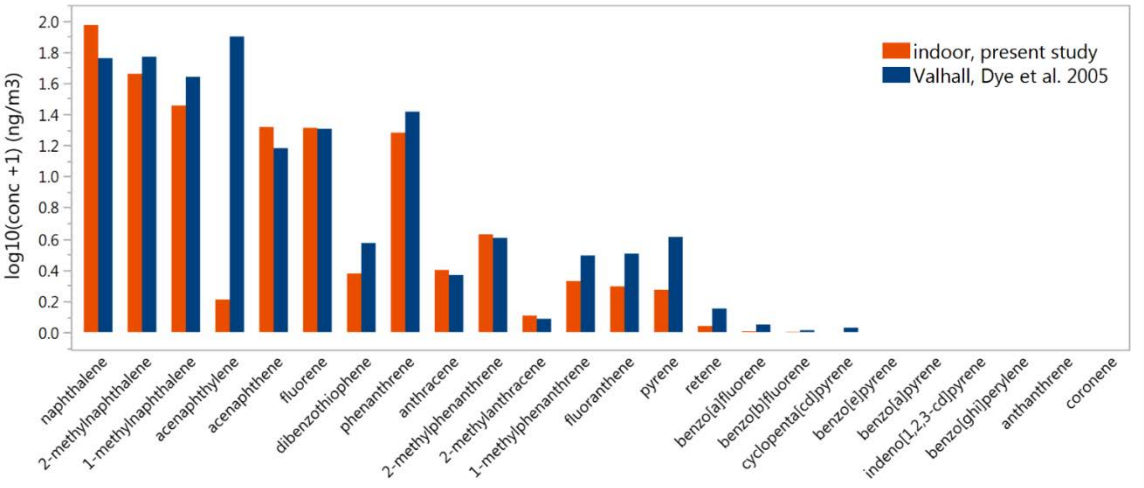

Figure 4.2. Comparison to gas-phase concentrations as reported in Dye *et al.*[87]

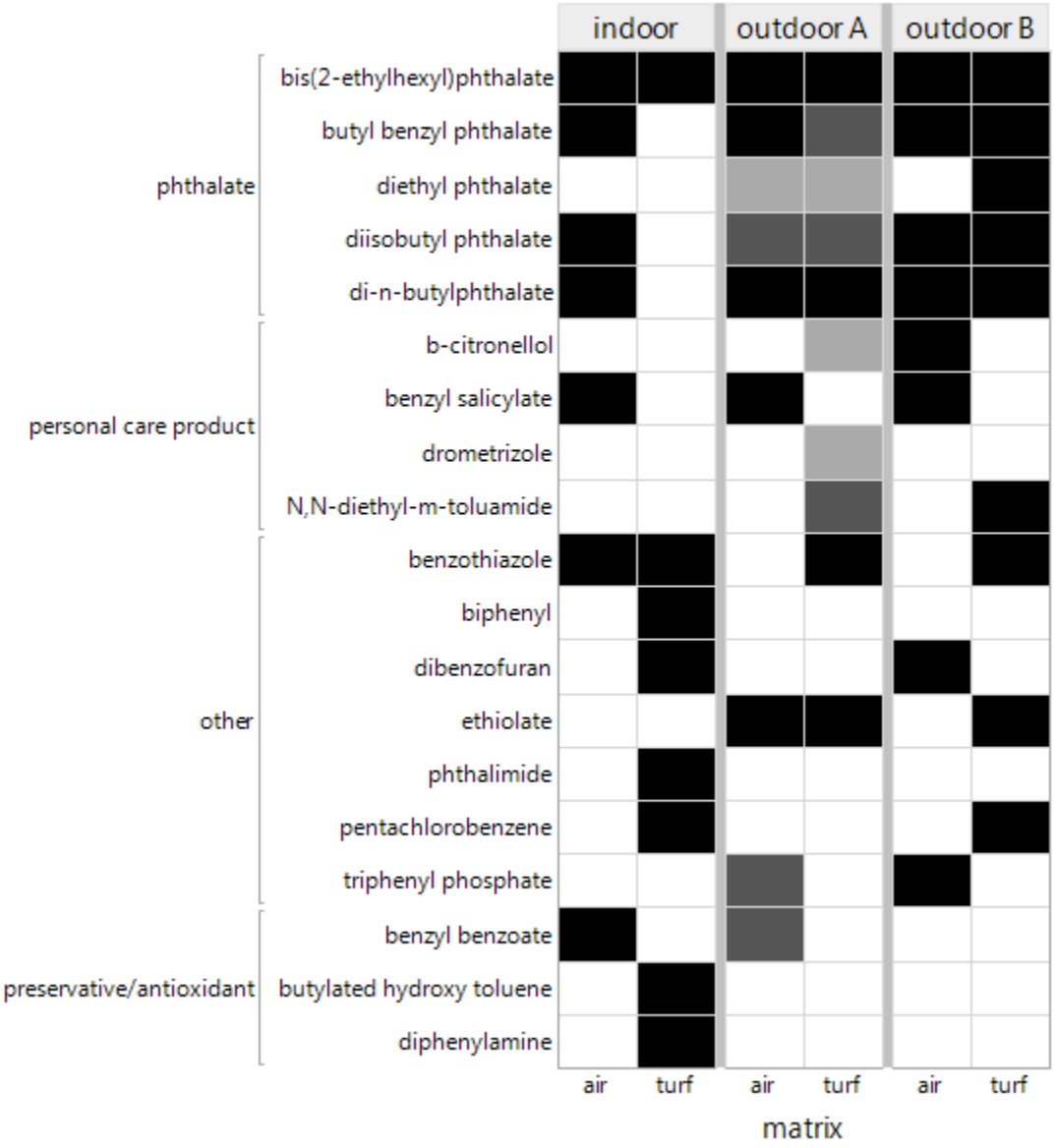

Figure 4.3 Detections in the presence/absence (1533) screen, where a shading indicates the chemical is present. At *indoor* and *outdoor B*, black indicates presence. Samples at *outdoor A* were collected in triplicate; the greyscale corresponds to the frequency of detection from 1 to 3.

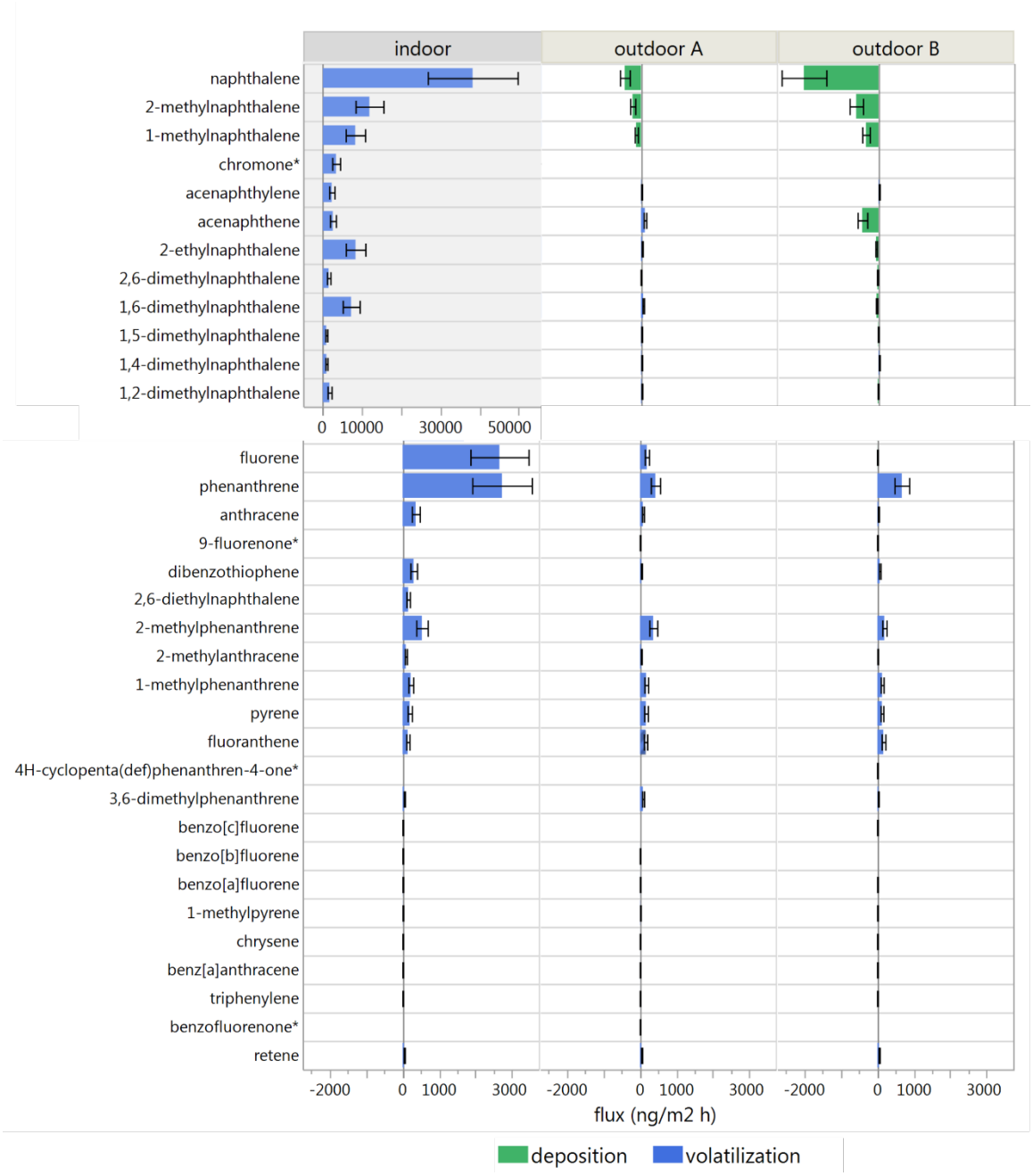

Figure 4.4. Magnitude and direction of PAH and OPAH flux. Error bars show uncertainty determined via propagation of error. The scale in the top left is reduced to larger values. Chemicals are listed in order of molecular weight, from low to high. OPAHs are indicated with asterisks. Flux was not determined if a chemical was below limit of detection in either air or turf air.

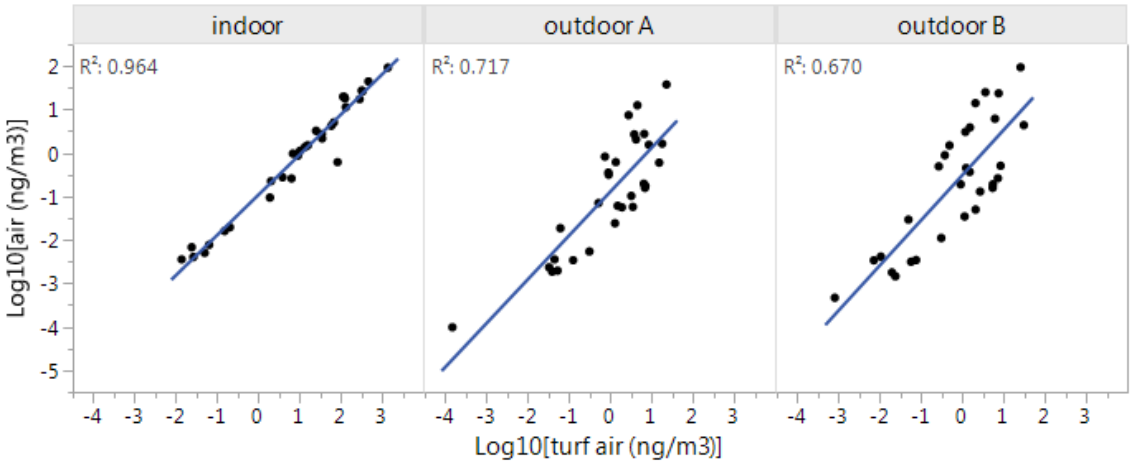

Figure 4.5. Turf air concentrations correlated with air concentrations. Linear fit is greatest at *indoor*, the location with more volatilization.

Table 4.1. Detected artificial turf-associated chemicals that are previously unreported in a 2016 literature survey conducted by U.S. Environmental Protection Agency[74].

PAH method	
2-ethylnaphthalene	9-methylanthracene
1,6-dimethylnaphthalene	3,6-dimethylphenanthrene
1,4-dimethylnaphthalene	benzo[c]fluorene
2,4-dimethylnaphthalene	triphenylene
1,5-dimethylnaphthalene	6-methylchrysene
1,2-dimethylnaphthalene	naphtho[1,2-b]fluoranthene
2,6-diethylnaphthalene	

OPAH method	**1533 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

CHAPTER 5 – SILICONE WRISTBANDS DETECT INDIVIDUALS' PESTICIDE EXPOSURES IN WEST AFRICA

Carey E. Donald, Richard P. Scott, Kathy L. Blaustein, Mary L.Halbleib, Makhfousse Sarr, Paul C. Jepson, and Kim A. Anderson

Royal Society Open Science

Royal Society

6-9 Carlton House Terrace

London SW1Y 5AG United Kingdom

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Abstract

We detected between 2 and 10 pesticides per person with novel sampling devices worn by thirty-five participants who were actively engaged in farming in Diender, Senegal. Participants were recruited to wear silicone wristbands for each of two separate periods of up to 5 days. Pesticide exposure profiles were highly individualized with only limited associations to demographic data. Using a 63-pesticide dual-column gas chromatography-electron capture detector (GC-ECD) method, we detected pyrethoid insecticides most frequently, followed by organophosphate pesticides which have been linked to adverse health outcomes. This work provides the first report of individualized exposure profiles among smallholder farmers in West Africa, where logistical and practical constraints have prevented use of more traditional approaches to exposure assessment in the past. The wristbands and associated analytical method enabled detection of a broad range of agricultural, domestic, legacy and current-use pesticides, including esfenvalerate, cypermethrin, lindane, DDT, and chlorpyrifos. Participants reported the use of 13 pesticide active ingredients while wearing wristbands. All 6 of the pesticides that were both reportedly used and included in the analytical method were detected in at least one wristband. An additional 19 pesticide compounds were detected beyond those that were reported to be in use, highlighting the importance of measuring exposure in addition to collecting surveys and self-reported use records. The wristband method is a candidate for more widespread use in pesticide exposure and health monitoring, and in the development of evidence-based policies for human health protection in an area where food security concerns are likely to intensify agricultural production and pesticide use in the near future.

Introduction

Increases in both global population and *per capita* food consumption require sustainable intensification of agricultural production in order to increase the food supply while minimizing additional impacts on the environment.[113; 114] Global pesticide production is estimated to increase 1.7 fold between 2001 and 2020 in response to this anticipated expansion in production.[115] Climate change is also expected to contribute to the food shortage burden and exacerbate pesticide use, particularly in the developing world.[116] While only 2-5% of global pesticide use is in Africa, health risks to African farmers are disproportionately high because of poor handling practices, uneconomical use patterns, lack of knowledge about pesticide toxicity and exposure pathways, and the availability of pesticides banned or unauthorized in developed countries.[117-119]

Given the high mammalian toxicity of many of the pesticides used in Africa, effective strategies are necessary to quantify individual risks to farmers. Using data from surveys administered to 1704 farming family members in 19 villages across five West African countries, Jepson *et al.*[118] modeled pesticide use practices, and identified substantial human and ecological health risks. Levels of risk varied considerably among villages within the five studied countries. Although there is very low residual uncertainty associated with these pesticide risks to human health and the environment throughout West Africa,[120] direct measurements of personal exposure have not yet been published. The lack of direct analysis of human and environmental exposures is a result of low capacity for chemical analysis in the region, and the limited suitability of many of the available methods of monitoring.[24; 118]

Anderson *et al.*[24] employed passive sampling devices to determine the freely-dissolved fraction of pesticides in West African irrigation water used not only for agriculture, but also for drinking, bathing, and washing. Passive sampling methods have been used extensively in recent decades and mimic the passive uptake of freely-dissolved or vapor-phase organic contaminants in water or air.[6; 24; 36; 121] Human occupational exposure profiles for pesticides have traditionally been obtained through obtrusive active sampling methods, including urine collection, [122; 123] hand-wash samples,[123-125] breathing zone air pumps,[125-127] or whole body dosimetry.[126; 127] Passive sampling approaches are less burdensome for participants, and commonly consist of dermal patches.[124; 128]

Recently, O'Connell *et al.*[9] demonstrated an adaption of passive sampling technology with an easy-to-wear silicone wristband, allowing individualized exposure characterization. Because the wristband material nonspecifically sequesters non-polar and semi-polar contaminants, we hypothesized that wristbands could also be used to assess pesticide exposure in farm workers. This investigation represents a first use of this technology in Africa, and also the first case of direct measurement of the pesticide residues to which these farmers may be exposed. We expanded an existing semi-quantitative chemical screening analysis[9] to accommodate quantitative analysis of 63 pesticides with an optimized method for gas chromatography using electron capture detection (GC-ECD) that achieved detection limits as low as 0.046 ng/g wristband.

This work was undertaken in Diender, a rural farming community in the Niayes region of Western Senegal. Farming in this and other similar areas is a family task in which men, women, children, and even infants are present in the field.[118] Community members demonstrated interest

in decreasing the risks associated with pesticide use following a farmer education program in early 2014[120] and agreed to participate in this investigation.

The objectives of this work were to examine the utility of passive sampling technology to detect and measure a wide range of pesticides, to quantify pesticide exposure profiles among individual members of a farming community, and to identify potential demographic risk factors. Individual pesticide exposure information provides valuable feedback to Diender farmers; it is intended to enable more informed decision making about pesticide use, and contribute evidence of the degree to which farmers are directly exposed to toxic chemicals. This evidence has the potential to inform policy, and the methodology reported here could serve as the basis for widespread long-term monitoring of pesticide exposure, which could help to underpin sound chemical management.[129]

Materials and Methods

Materials

Sixty-three target pesticides and related compounds were analysed in wristbands (Table D1). Three extraction surrogate standards; tetrachloro-meta-xylene (TCMX), PCB-100 and PCB-209; and an internal standard *p,p'*-dibromooctofluorobiphenyl were used. All standards were of purity 97% or greater and purchased from Accustandard (New Haven, Conn., USA). Ethyl acetate solvent was Optima grade or equivalent. Glassware and other laboratory equipment were solvent-rinsed and baked before use. Two sizes of silicone wristbands were purchased from an online distributer (24hourwristbands.com; large: 4.8 ± 0.1g; small: 4.3 ± 0.1g; both sizes width = 0.5 inch).

Population sample and data collection

Thirty-five men and women from farming families in Diender, Senegal were recruited in November 2014. All research activities were granted prior approval by Oregon State University's Institutional Review Board (No. 6479). Children who are active in the field, or accompanied parents could be included with parental consent, as long they also consented. After providing verbal consent, participants were given two wristbands to wear for two separate periods of up to 5 days and asked to provide their gender, and age. Verbal consent scripts for recruitment of adult and child volunteers are included in Appendix D. Additionally, we received pesticide use records

from 21 participants. Participants in this study were actively working with crops where pesticides are applied. Participants were instructed to seal the wristbands in an individual polytetrafluoroethylene (PTFE) bag with the participant's identification and the dates worn recorded on the bags. Wristbands were returned to the study coordinator (M. Sarr) and shipped to Oregon State University for analysis. Following analysis, results were communicated back to participants via the study coordinators. A second follow up is planned for 2017 to share further results and implications. An example of that draft report is included in Appendix D.

Wristband preparation

Prior to shipment to Diender, Senegal, wristbands were conditioned at 280-300 °C for 48 hours to remove impurities, then individually packaged in durable, air-tight PTFE bags. Several wristbands from each batch were extracted and analysed by gas chromatography-mass spectrometry before inclusion in the study to ensure they were free of impurities (see *Quality Control* below). Following deployment and return to Oregon State University, wristbands were cleaned in sequential baths of 18 mega-ohm/cm water and isopropanol to remove superficial fouling or particles. Wristbands were stored in amber glass jars at −20 °C for up to one month until extraction. Extraction surrogates were added immediately before extraction, then, wristbands were extracted twice in 100 mL ethyl acetate. Extracts were combined and quantitatively reduced to 1 mL.

Chemical analysis

A novel, fast GC-ECD method was developed and validated for analysis of pesticides in passive sampler wristbands. The list of target analytes from a previously described method [24] was expanded and analysis time was shortened, without sacrificing detection limits. Hydrogen was used as carrier gas instead of helium to improve chromatographic resolution. The use of H_2 reduced analytical cost, increased analytical sensitivity, and allowed for decreased analysis time. The current method provides good chromatographic separation in less than 22 minutes. Further modification of the temperature profile and a 33% reduction of nitrogen makeup gas flow-rate resulted in approximately 5-fold increase in sensitivity. In comparison, recently published pesticide GC-ECD methods using helium as the carrier gas,[24; 125; 130] are over 55 minutes long,[24; 130; 131] or have costlier make-up gases like methane and argon.[130] A less resource-intensive methodology is better adapted to West African laboratories.[24]

An internal standard was added to correct for instrument variability, and extracts were analysed using an Agilent 6890N gas chromatograph (GC) with dual 7683 injectors, dual DB-XLB and DB-17MS columns (Agilent, Santa Clara, Cal., USA), and dual micro-electron capture detectors (μ-ECD). Detection limits, quantitation limits, and chromatographic conditions are given in Tables D1 and D2. Identification and quantitation was typically made with the DB-17MS column, and the DB-XLB column was used for confirmation. Target compounds were quantified by the relative response of the internal standard to target compound in a 4 to 6 point calibration curve ($R^2 > 0.98$, Table D1). Two compounds, fenitrothion and malathion were not chromatographically resolved, and thus are reported as a sum. Instrument concentrations were corrected for extraction surrogate recovery and normalized for the mass of the wristband. Examples of standard and wristband extract over-spike chromatograms are shown in Figure D1 and Figure D2, illustrating the high degree of separation. Final concentrations are given as ng/g wristband.

Statistical analysis

Compounds with concentrations above detection limit in at least 2 wristbands were subjected to statistical analysis. For these analyses, any compounds that were below the detection limit were assigned a value equal to one-half of the detection limit. Compounds between detection and quantitation limits were assigned a value of one-half the quantitation limit. Spearman correlation coefficients were computed to evaluate the relationship between individual compounds. One pair was highly correlated with each other (*cis*- and *trans*-permethrin, $\rho = 0.81$; Table D3), and these isomers were summed for subsequent analyses. Spearman correlation analysis was also performed to compare concentrations in wristbands worn by each participant in two sequential, 5-day periods. Fisher's exact test and odds ratio analysis was used to compare counts of detected and non-detected, reported and non-reported pesticides. Signed rank tests were used to compare concentrations and number of detections between wristbands worn by each participant in both periods. Rank-sum tests were used to compare pesticide concentrations in wristbands worn by male and female participants. These non-parametric alternatives to paired and two-sample t-tests allow incorporation of left-censored data present in this dataset as values below detection and quantitation limits. Bonferroni adjustments were used to correct for family-wise error rates. Exploratory principal component analysis was also used to evaluate associations between

pesticides and selected demographic data to identify risk factors. Statistical analyses were performed with JMP 12.0.1 (SAS Institute, Inc., Cary, NC, USA).

Quality control

To ensure data quality objectives were met, over 40% of samples analysed in this study were quality control (QC) samples. QC samples included pre-deployed wristband conditioning batch verification (n=2), instrument solvent blanks (n=10), sample matrix overspikes (n=6), sample duplicates (n=2), and continuing calibration verifications (CCVs, n=28). Trip blanks (unopened wristband samples in individual PTFE bags that are shipped to and from the study site alongside the samples) were not returned for analysis. However, in an analogous project in which samples travelled between Oregon and Peru, all wristband trip blank samples were below detection limit for all compounds.[94] Field blanks were not collected in the study. All target pesticide compounds were below detection limit in all blank QC samples. Sample matrix overspikes were within 20% of expected value, and duplicate samples were within 50% relative percent difference for all detected compounds. Quantitation of CCVs were within data quality objectives of ± 30% of true value for 70% of compounds.

Results

Seventy wristbands were analysed, with 100% compliance among the 35 participants. Thirty participants were male, and 5 were female. Participants reported the use of 13 pesticide active ingredients during wristband wear, including 6 that were included in the 63-analyte method (Table 5.1). All 6 of the pesticides that were both reportedly used and included in the analytical method were detected in at least one wristband. Nineteen pesticide active ingredients were detected beyond those reportedly in use. Participant ages ranged between 15 and 63, averaging 38.

Of the 63 pesticide compounds included in the analytical method, 26 were detected in one or more wristbands. Deltamethrin and cypermethrin were the most frequently detected compounds, found in 69 and 66 of 70 wristbands respectively (Figure 5.1). An analogous figure showing the frequency of detection by participant is included as Figure D3. Each wristband provided between 2 and 10 pesticide detections. Extraction recoveries averaged 66% (range = 11-124%, median = 68%). Such extraction recoveries have been seen previously in silicone wristbands (surrogate

PAH recovery 53-122%[9]) and silicone rubber (surrogate pesticide recovery 13-113%[108]). Log octanol-air partition coefficient (log K_{oa}) of detected pesticides ranged from 5.84 (endosulfan sulfate) to 12.5 (bifenthrin). Log octanol-water partition coefficient (log K_{ow}) values ranged from 0.78 (dimethoate) to 8.15 (bifenthrin) (Table D1).[28] Of the 383 total pesticide detections in the 70 wristbands, 97% were insecticide or insecticide degradation products or metabolites, and 63% of the insecticide detections were synthetic pyrethroids. The remaining 3% of total detections were herbicide and fungicide active ingredients.

Detection of a pesticide sequestered within a silicone wristband represents an individualized, composite dermal and inhalation exposure that is suitable for comparison among participants. Relative concentrations from below detection limit to maximum amount are depicted as a heat map (Figure 5.2). Comparisons of concentrations *within* one wristband should be made with caution, as greater concentrations of different pesticides may be the result of several factors beyond personal exposure, including uptake kinetics (*i.e.* sampling rate) and partition coefficients (*e.g.* log K_{ow}), which have been shown to be inversely correlated.[132] For example, we expect dimethoate to have a higher sampling rate than bifenthrin, based on their relative K_{ow} values. Specific sampling rates are not determined in this study, so comparing bifenthrin concentrations to dimethoate concentrations is inappropriate. Concentrations on an absolute scale are depicted in Figure D4. Conversely, the uptake rate of bifenthrin will be the approximately equivalent for all participants, and comparisons of bifenthrin between study participants are reasonable. The highest concentration of any pesticide measured was deltamethrin at 4200 ng/g wristband (Figure 5.1).

Each participant wore a wristband for two separate periods. Wristbands were worn for up to 5 days in each period, with 94% worn for either 4 or 5 days. Concentrations were not adjusted for the duration of wear because the vast majority were worn for a similar length of time. Neither the number of positive detections nor the concentrations of individual pesticides sequestered in a participant's wristband were different between the two periods (signed-rank test, no significant p-values after Bonferroni adjustment < 0.003). Concentrations between the two periods were correlated for five pesticides: deltamethrin, cypermethrin, λ-cyhalothrin, chlorpyrifos, and dimethoate (Figure 5.3, Spearman's rho correlation, significant p-value after Bonferroni adjustment <0.003). Pesticides with fewer overall detections were less strongly-correlated. This

analysis yielded similar results when repeated with omitting data below detection limit (Table D4).

For the 42 wristbands worn by the participants with pesticide use data, there were a total of 2016 possible detections in the analytical method: 42 samples x 48 analytes (after combining isomers, degradation products, and metabolites). Counts of reported and non-reported, and detected and non-detected data are summarized in Table 5.2. The odds of a pesticide being detected are 4.3 times greater if it was reportedly used (95% CI: 2.5-7.3; Fisher's exact 2-tailed p-value < 0.001). Quantitative analysis comparing the magnitude of concentrations against use reports were not possible because of little overlap of pesticides both detected and reported. Approximately 10% of positive detections were also reported to be in use by participants during wristband wear. Nineteen pesticide active ingredients were detected beyond those reportedly in use.

Rank-sum tests were used to compare pesticide concentrations in wristbands worn by male (n=60) and female (n=10) participants. Two pesticides showed significant p-values after Bonferroni adjustment ($p < 0.003$, Figure D5). Deltamethrin and λ-cyhalothrin had higher concentrations in male participants' wristbands than females. Identical significance conclusions are obtained when this analysis is repeated with concentrations that have been normalized to (divided by) the number of days the wristbands were worn.

Exploratory principal component analysis results did not reveal any strong demographic groupings among the detected pesticides (Figure D6). Wristbands worn by female participants are clustered slightly, however principal components 1 and 2 cumulatively explained only 22.1% of the variance. No other clusters were present that would represent either participant age or the number of days that wristbands were worn (data not shown).

Discussion

The majority of analytes in the instrument method were insecticides because they were expected to be used most frequently. The 63-analyte method included 38 insecticides, 10 herbicides, 7 fungicides, and 8 other chemicals, *e.g.* degradation products. Williamson *et al.*[117] determined that insecticides made up 55% of reported active ingredients through surveys in Senegal and three other African countries. They suggest this is attributable both to the greater severity of insects compared to other pests, and that insecticides are more available and less expensive than other

pesticides. The bias towards insecticides in the present study aligns with the expectation that pesticides targeting insect pests are the most commonly used. Furthermore, the wristband and analytical methods of the present study detected 7 of the top 9 active ingredients in Williamson *et al.*[117], suggesting that the methods are effective at determining exposure to relevant pesticides. Williamson *et al.*[117] also found that 33-60% of villagers in a cowpea and cotton-farming village in Ghana reported ill health effects each season associated with exposure to endosulfan, chlorpyifos, and λ-cyhalothrin. Though the geographic location described differ from the present study, all three of these pesticides were detected in one or more wristband. The wristbands sequestered the pesticides that are most likely to have effects on human health. Ideally, the 63-pesticide method would include all pesticides sold in the West African market, *e.g.* methamidophos which is believed to be a major driver of risk in similar communities,[118] but was not included in the method because it was not amenable to detection via GC-ECD.

We detected in at least one wristband, all 6 of the pesticides that were both reportedly used and included in the analytical method. The most frequently reported pesticide, dimethoate is the least hydrophobic analyte in the method. In comparison to the more hydrophobic analytes, it is expected that a higher level of exposure is required for appreciable accumulation in the wristband polymer. Dimethoate was detected in only 4 wristbands despite being used by 15 of 21 reporting participants. Similarly, acetamiprid was frequently used, but only detected above quantitation limit in one wristband. The electron capture detector is less sensitive to acetamiprid, whose quantitation limit is more than 10 times higher than the average limit for the other compounds. For these two compounds, exposures are likely to have occurred without detection. Both of these examples highlight that the passive sampling wristband polymer as well as the chosen analytical method play a role in the resulting exposure profiles in this study.

Beyond those reported by participants for use in agriculture, an additional 19 pesticide active ingredients were detected, notably cypermethrin and chlorpyrifos. These and other pesticides may not have been reported because they are not used in food crops, but rather for pest control within the home, on domestic animals, or in forage crops intended for animal consumption. Additional exposures may be the result of improper pesticide storage, contaminated equipment, or unknown use in neighbors' crops. Finally, the farmers may not always know what they have applied because of illiteracy or improper/missing labels[118; 133] (M. Halbleib, pers. obs.).

Overall, variation in exposure profiles was highly individualized with only small effects that suggest participant gender may be a risk factor for increased exposure. Only one demographic trend was identified in which two pesticides, deltamethrin and λ-cyhalothrin, were detected in greater amounts in wristbands worn by men, however small sample size and unbalanced gender distribution may limit inferences. The number of pesticide detections as a function of number of days worn was also greater among male participants. A focus group with six women (ages 23-40) was conducted in March 2015 within the study area to gain understanding of the role women play in farming and pesticide management. This revealed that some women routinely apply pesticides on the part of the family farm they manage [M. Halbleib, pers. comm.]. This information suggests both genders may have the same chance for exposure, but actual exposure can vary by the identity of crops managed by men and women.

The wristband technology allowed us to detect highly individualized exposure profiles for the participants in the study. Neither the number of pesticides detected nor the concentrations differed between the two sampling periods. Periods of wear were chosen at the discretion of the participants, however all had completed the first period by the midpoint of the study on 25 November 2014. With no temporal overlap between the first and second periods by any participants, these findings reveal that no distinct trend in pesticide profiles occurred before or after the midpoint of the study. Exposure profiles for both periods were therefore averaged for each participant, and the individualized results depicted in Figure 5.2 corroborate the finding that the presence of one pesticide does not correlate with the presence of another. Results from both signed-rank and Spearman correlation analyses (Figure 5.3) reveal two wristbands worn by any one individual yield similar results. Additionally, the limited results of PCA highlight the highly individualized profiles among participants. Despite being worn by the same individuals, the paired wristband samples are not true replicates because the dates worn do not coincide. Regardless, multiple analyses reveal that the greatest variability in exposure profiles is among individuals, not between wristbands worn by the same individual.

Pesticide detections in the present investigation could be compared with three other studies (Figure 5.4): Jepson *et al.*[118] administered surveys to village farmers in 5 West Africa countries in 2007 and 2010; Murphy *et al.*[133] analyzed vector control pesticides collected from markets in the Gambia in 2005; and Anderson *et al.*[24] deployed passive samplers in water near agriculture in 5 West Africa countries. Isomers, degradation products, and metabolites are combined to better

enable comparisons. Only the 63 pesticides in the described analytical method are included in Figure 5.4: a list of compounds found in those studies but not included in the present analysis can be found in Appendix D. Three pesticides were detected only in the present study and not reported in the three comparator studies: esfenvalerate, heptachlor, and fipronil. Esfenvalerate was detected in 27 wristbands, and although it was not reported to be used in this study or recent surveys,[118] it is known to be available in the region (M. Sarr, pers. obs.). The presence of heptachlor in a single wristband may be attributable to its environmental persistence, supported by a recent report of heptachlor detections in Senegal estuary sediments.[134] Fipronil was also detected in a single wristband and has been used to control locusts, grasshoppers, and animal parasites in this region (P. Jepson, pers. obs.).

Surveys administered by Jepson *et al.*[118] provide details of regional pesticide use practices. Compounds that were detected in wristbands but absent in Jepson *et al.*[118] highlight legacy contaminants or pesticides that farmers are unaware are being used, *e.g.* esfenvalerate, bifenthrin, and DDT and its breakdown products. We also include a comparison with Murphy *et al.*[133] as the best available analysis of pesticides in the regional markets. Active ingredients identified in Murphy *et al.*[133] are intended for vector control, rather than a focus on agricultural pesticides as in the present study. However, the vector control pesticides were purchased in an informal market, and therefore represent what may be available for purchase by village farmers. Murphy *et al.*[133] were unlikely to be hampered by analytical detection limits because they were analyzing a packaged product, whereas compounds sequestered in the wristband have been subjected to varying degrees of dilution and degradation. Finally, a small percentage of collected samples were not identifiable in the GC/MS analysis used by Murphy *et al.*[133]

The analytical method used is an expansion of that used in Anderson *et al.*[24] In addition to an extended list of analytes, further differences in detected compounds between Anderson *et al.*[24] and the present work may be a result of several factors: duration of deployment ($\leq$ 5 days versus 14 days), dates of deployment (2014 versus 2012), identity of the sampled matrix (air/dermal versus water), material of the passive sampler (silicone versus low-density polyethylene), different study location (Senegal alone, versus greater West Africa including Senegal), and different analytical parameters. Nevertheless, almost half of the pesticides detected in wristbands were also found using stationary environmental passive sampling. The three most-frequently

detected pesticides, deltamethrin, cypermethrin, and λ-cyhalothrin, were not included in chemical analysis methods of Anderson *et al.*[24]

Certain pesticide active ingredients with increased potential for human or environmental harm are subject to international negotiations and restriction. Countries or parties adhering to the Rotterdam Convention may only export a listed chemical with the prior informed consent of the importing country or party.[101; 135] The Stockholm Convention compels countries to phase out the production, trade and use of several chlorinated persistent organic pollutants.[135] The wristbands sequestered three pesticides that are subject to both the Rotterdam and Stockholm conventions: DDT, heptachlor, and lindane (Table D5). Senegal, under the Rotterdam Convention, does not consent to allow imports of DDT or heptachlor but does consent lindane to be imported conditionally.[136] Under the Stockholm Convention lindane use is permissible for human pharmaceutical treatment of head lice and scabies.[137] The detection of lindane in wristbands worn in Senegal is not therefore unexpected because use is permitted, although environmental persistence from past applications may also explain our detections. No exemptions in Senegal are permitted for heptachlor under either convention, but it is a legacy contaminant that has been detected as recently as 2008 in environmental samples in Senegal.[134] It is likely that the single detection of heptachlor in a wristband is the result of historic use.

DDT was not found in survey data from West African farmers,[118] or in analysis of vector control pesticides available in adjacent Gambian markets,[133] and it is our understanding that DDT is no longer used in Senegal (M. Sarr, pers. obs.). Under the Stockholm Convention, DDT may be used in the event of a plague,[137] and an estimated 0.3 tonnes of DDT are stockpiled in the event of malaria outbreaks.[138] Whether or not DDT has been used in recent decades, the presence of DDT and its degradation products was expected because of its environmental persistence. Diagnostic ratios such as DDT/(DDE+DDD) are frequently calculated in environmental sampling campaigns in order to estimate the relative age of DDT applications, where values >1 suggest more recent DDT applications.[139-141] In this dataset, comparisons of concentrations within one wristband sample must be made with caution because pesticide compounds have different sampling rates that cannot be estimated without the use of *in situ* calibration standards (performance reference compounds, PRCs). Relative sampling rates were approximated from previous research that found the sampling rate of DDT by passive sampling devices to be 10-20% less than that of DDE or DDD.[6; 142] When the above ratio is calculated for the 36 wristbands that contained one or more

of DDT, DDE, or DDD, 16 had a ratio that suggests recent DDT application. This count increases to 17 when the DDT concentration is mathematically increased by 20%. Both the ratios of the absolute values and the adjusted values give an evenly mixed distribution of old and new signatures.

The analytical method included 9 "active ingredients believed to be obsolete or discontinued for use as pesticides" by the World Health Organization[101] (Table D5). Of these, two pesticides chloroneb and heptachlor were detected in 4 and 1 wristbands, respectively. Neither were reportedly used, but the presence of heptachlor may be expected due to its long environmental half-life.[134] In total, legacy and obsolete pesticides (DDT, heptachlor, lindane , and chloroneb) comprised 18% of total detections among all wristband samples.

Three pesticides included in instrumental analysis are classified by the WHO as Class Ia (extrememly hazardous), however none were detected in any samples: captafol, prophos (ethoprophos), and hexachlorobenzene. The majority of target analyte pesticides are Class II (moderately hazardous), while others were Class III (slightly hazardous) (Table D1). Of the reportedly used pesticides (Table 5.1), methamidophos and methomyl are Class Ib (highly hazardous), while the remainder are either Class II or Class III.

Pyrethroid insecticides comprised the majority of detections in wristbands samples. These compounds are widely used because they have low toxicity to humans but are highly toxic to insects. Common uses include insect repellents in clothes and mosquito nets, topical treatment for head lice, and agricultural use as replacement for some organophosphate pesticides. Type II pyrethroids (*e.g.* cypermethrin, deltamethrin, λ-cyhalothrin, and esfenvalerate) are generally more toxic to insects and mammals than Type I (*e.g.* bifenthrin and permethrin).[4; 143; 144] The silicone wristbands incorporate both inhalation and dermal exposures by sequestering compounds in air and in direct contact with skin or materials/solutions that touched the skin that contain lipophilic compounds. Inhalation and dermal exposure to pyrethroids are linked to respiratory, neurological, and skin effects,[4; 143; 144] while more recent reports investigate male reproductive effects or exposures during pregnancy.[4] The high frequency of pyrethroid pesticides detected among participants clearly indicate a pervasive presence in the participants' immediate environment.

Organophosphate (OP) pesticides, predominantly chlorpyrifos, were detected in over half of the wristband samples. Higher levels of urinary OP metabolites in pregnant mothers have been linked to impaired cognitive development,[145; 146] and remain the subject of ongoing epidemiological research.[147] Frequently, organophosphate pesticide exposure is estimated in epidemiological studies by urinary dialkyl phosphate concentrations. The use of these metabolites as biomarkers has limitations, in particular, that dialkyl phosphates are not specific to individual OP pesticide compounds from which they are derived.[148] Furthermore, dialkyl phosphates can be formed directly on food products, and cannot be differentiated from those formed during metabolism.[147] Parent OP pesticide compounds can be identified using the silicone wristband, and they represent opportunity for both dermal and inhalation exposure.

The ease-of-use of the wristbands by the participants resulted in 100% compliance. Participant training was accomplished quickly, and the wristbands were worn for days, indicating a relative ease of compliance and incorporating agricultural, domestic, and other exposure sources. Ease-of-use of passive samplers has been described previously,[12; 149] although not at the personal level. Easy training and high compliance rates suggest that the silicone wristbands represent a promising tool for establishing baseline data in pesticide risk management education, a necessary, yet often missing piece of information when evaluating for example, the effectiveness of farmer field schools.[150] They may also be used to verify risk management decisions that farmers make following education, and also determine the degree to which farmers and their families can reduce pesticide exposure through their own decisions.[120]

A further benefit of this method is ease of sample transportation to and from the study location. O'Connell *et al.*[9] demonstrated the stability of 5 model compounds sequestered in wristbands under simulated transport conditions in PTFE bags at 35°C for up to 72 hours, mimicking conditions of overseas shipment, and also representing common conditions of transport in West Africa.[9] In comparison, handwash and patch samples are transported and stored in glass containers under refrigeration, or on ice.[125] Biological samples including blood and urine also need to be transported quickly on ice.[151] The lightweight, easily transportable wristband passive samplers are better-suited for human exposure assessments in remote locations where expedient transport on ice is costly or even impossible.

The chosen analytical method and silicone wristband material have limitations that influence which pesticides can be detected. Chemicals measured by gas chromatography must be have thermal stability and be at least partially volatilized at a nominal 300-350°C. The selected detector further constrains analysis. In this study, electron capture detectors (ECD) were used because they have greater sensitivity to electronegative elements and functional groups that are common in many organic pesticides,[152] and simultaneous analysis with confirmation on two columns minimizes the possibility of false positives. The silicone material of the wristband is intended for sequestration of lipophilic compounds, though it may sequester compounds with lower K_{ow} values through splashing or direct contact with skin. For instance, caffeine (log K_{ow} = -0.07) which is not very lipophilic, was detected in the initial demonstration of the silicone wristband as a personal passive sampler.[9] In the present study, the detected compound with the lowest log K_{ow} was dimethoate (log K_{ow} = 0.78), found in a single wristband.

This is the first direct measure of individualized pesticide exposure in West Africa, but there are limitations to consider when drawing inferences. First, the limited sample size may not be representative of a wider population as participants were recruited as volunteers and do not represent a random sample. Statistical power in comparisons between genders is limited because male participants outnumbered female 6 to 1. Analysis of a trip blank was not included in this study, but we expect blank results as measured in a similar study.[94] The wristband is a proxy for exposure that incorporates both dermal and vapor-phase inhalation routes, and it does not consider oral and dietary pathways of exposure. Additionally, wristbands were cleaned to remove particles that adhered to the wristband surface. This excludes pesticides that may be toxicologically relevant when inhaled while adsorbed to airborne particles. It is intrinsically difficult to interpret what portion of the pesticide load in a wristband aligns with different routes of exposure. Performance reference compounds (PRCs, or depuration compounds) are often used as *in situ* calibration standards in environmental passive sampling campaigns. PRCs are infused into the passive sampler before deployment, and the rate at which PRCs diffuse out is correlated to the rate at which environmental compounds are sequestered.[6] Because the wristbands sample multiple media, PRC loss, and thus compound uptake, cannot be linked definitively to either air for an inhalation exposure or to skin for a dermal exposure. Finally, chemical uptake into a wristband is anticipated to be affected by differing environmental conditions among participants that were not measured in this study, *e.g.* temperature and wind/air speed. However, the

hydrophobic silicone material of the wristband mimics biological membranes, and factors that increase uptake into the wristband should coincide with increased exposure for participants.

Conclusions

Silicone wristbands sampled personal exposure to a broad range of agricultural, domestic, legacy and current-use pesticides and provided the first report of individualized exposure profiles among smallholder farmers in West Africa. Reports of personal pesticide exposure in West Africa have been lacking because of difficulties in sampling logistics, *e.g.* participant compliance with invasive methods, the difficulties of sample shipment, and the lack of analytical capacity in the region. Every wristband sequestered 2 or more pesticides, demonstrating both the individualized nature of pesticide exposure in the sampled population, and the sensitivity of the wristbands and analytical method. An additional 19 pesticide compounds were detected beyond those that were reported to be in use, highlighting the importance of measuring exposure in additional to collecting surveys and self-reported use records. Future surveillance systems for pesticide exposure and health effects in West Africa will require reliable and standardized methods that are within the capacity of local institutions and which support decision makers including regulators, policy makers, educators and medical practitioners.[129] The methodology that we outline here represents the first practical solution to these challenges in West Africa.

Ethics

All research activities were granted prior approval by Oregon State University's Institutional Review Board (No. 6479). Participants provided verbal consent prior to data collection.

Data accessibility statement

The dataset supporting this chapter has been loaded as supplementary material to the online article. Gender and age data are not included to maintain anonymity. The following information is also available in the Appendix D: pesticide identities and physiochemical properties, chromatographic conditions, Spearman's rho correlation coefficients, a list of analyzed pesticides subject to international treaties, example chromatograms, individualized pesticide concentrations, concentration distributions by gender, results of principal component analysis, and verbal consent scripts.

Competing interests statement

KA discloses a financial interest in MyExposome, Inc. which is marketing products related to the research being reported. The terms of this arrangement have been reviewed and approved by Oregon State University in accordance with its policy on research

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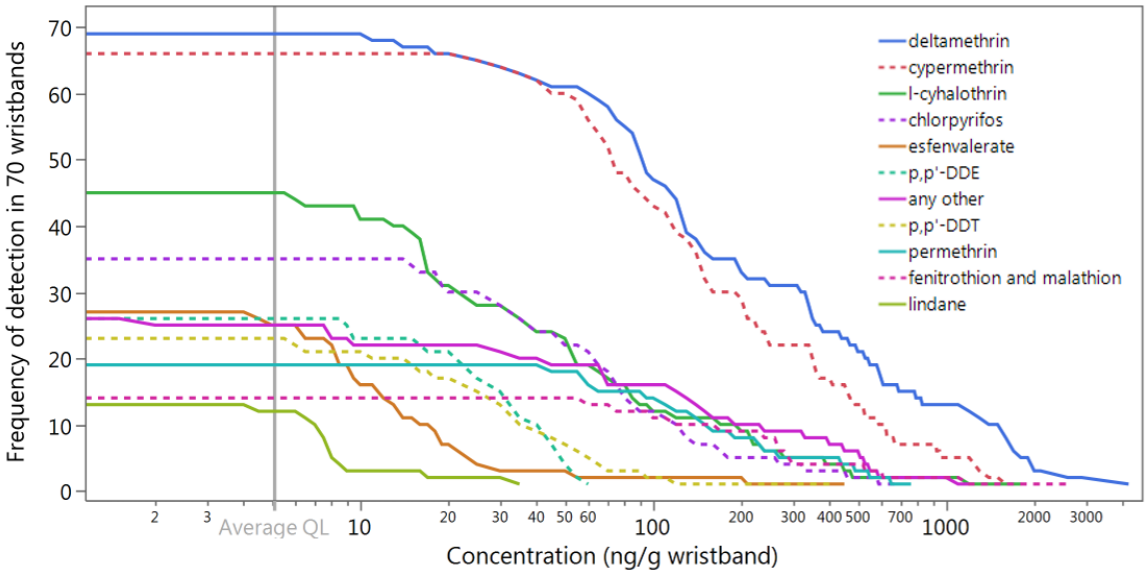

Figure 5.1. Frequencies of detected pesticides by concentration. Each line represents the frequency that met or exceed a given concentration threshold. Cypermethrin and deltamethrin were above quantitation limit in 69 and 66 of 70 wristbands, respectively. The highest detected concentration was deltamethrin at 4200 ng g^{-1} wristband. Average quantitation limit (QL) for these 10 most frequently detected pesticides, 5.1 ng/g wristband is highlighted.

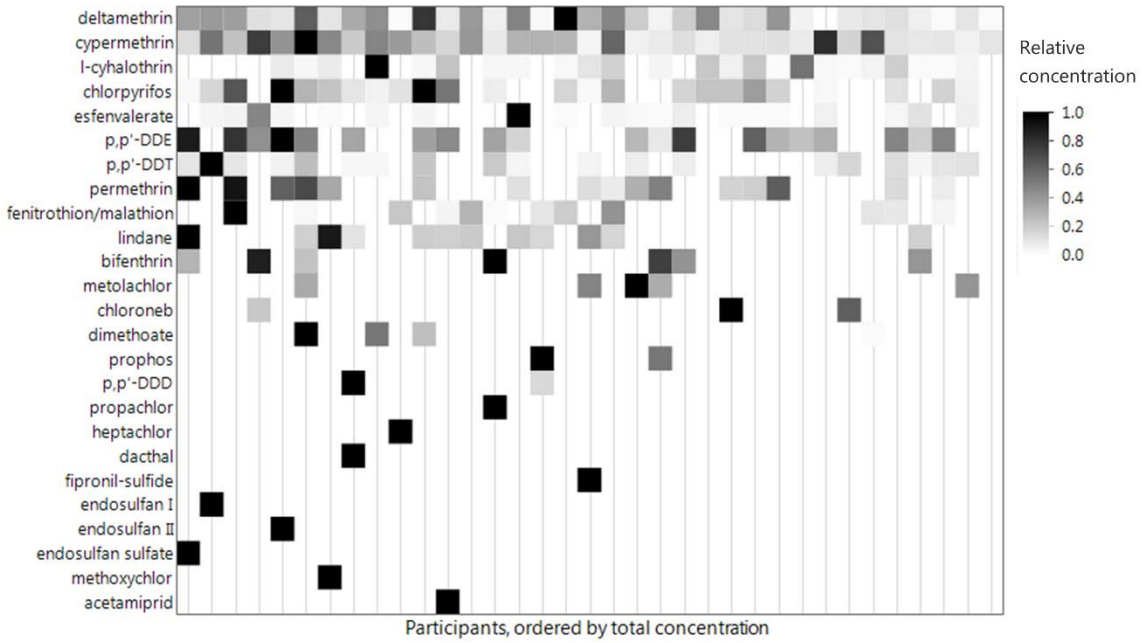

Figure 5.2. Concentrations of the detected pesticides, each on a relative scale. Boxes from palest to darkest indicate the concentration range of pesticides detected above quantitation limit. Pesticide concentrations in wristbands worn in two periods are averaged for each participant. Participant order was arbitrarily assigned, and gender is not given in order to maintain participant anonymity.

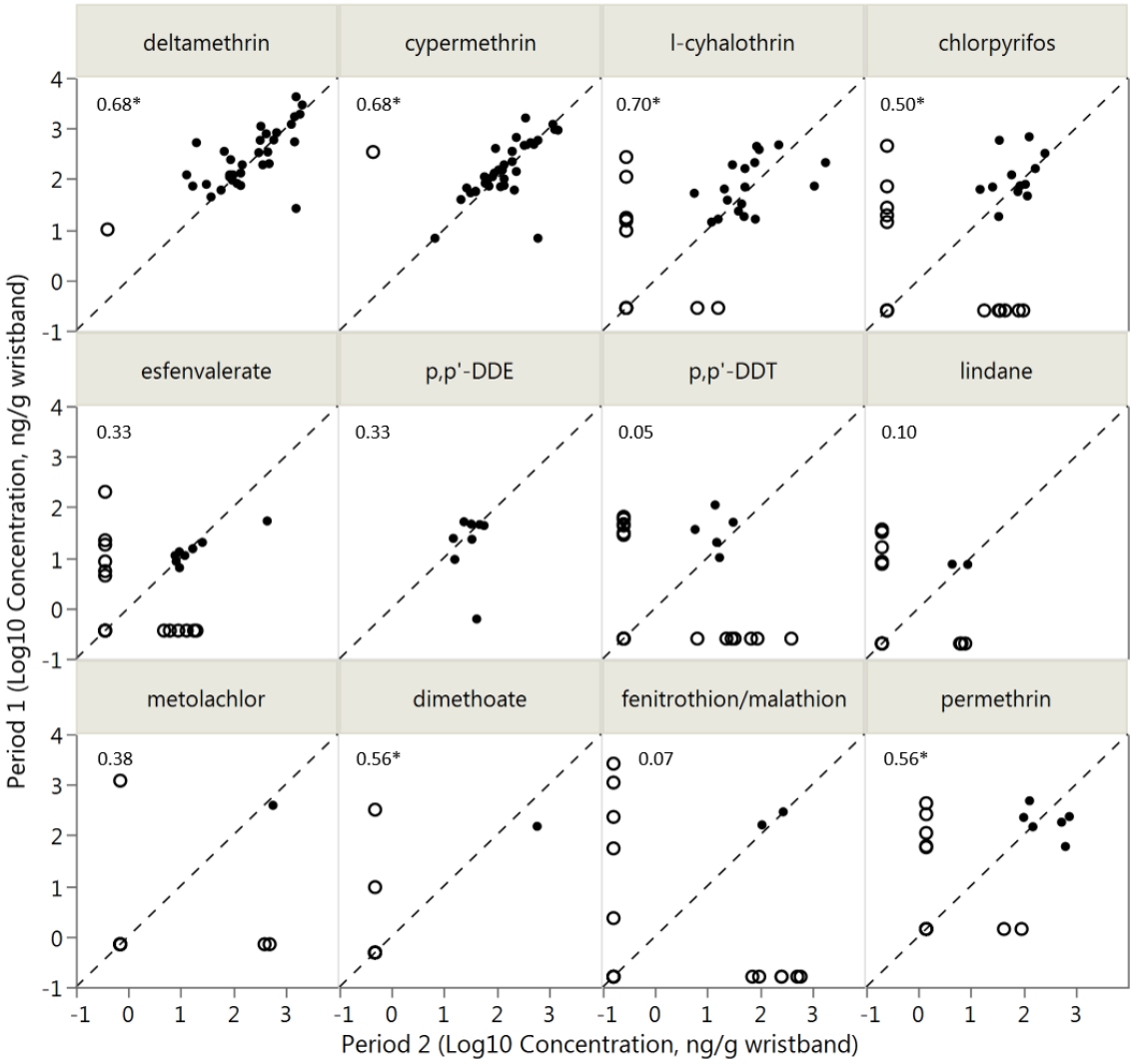

Figure 5.3. Comparison of concentrations in wristbands worn by participants in two sequential periods of up to 5 days. Dashed line represents 1 : 1 relationship, and open circles indicate when pesticide was detected in only one wristband. Spearman correlation coefficients are given, where asterisks indicate significant p-values after Bonferroni adjustment <0.003. Data are not shown if below limit of detection in both wristbands.

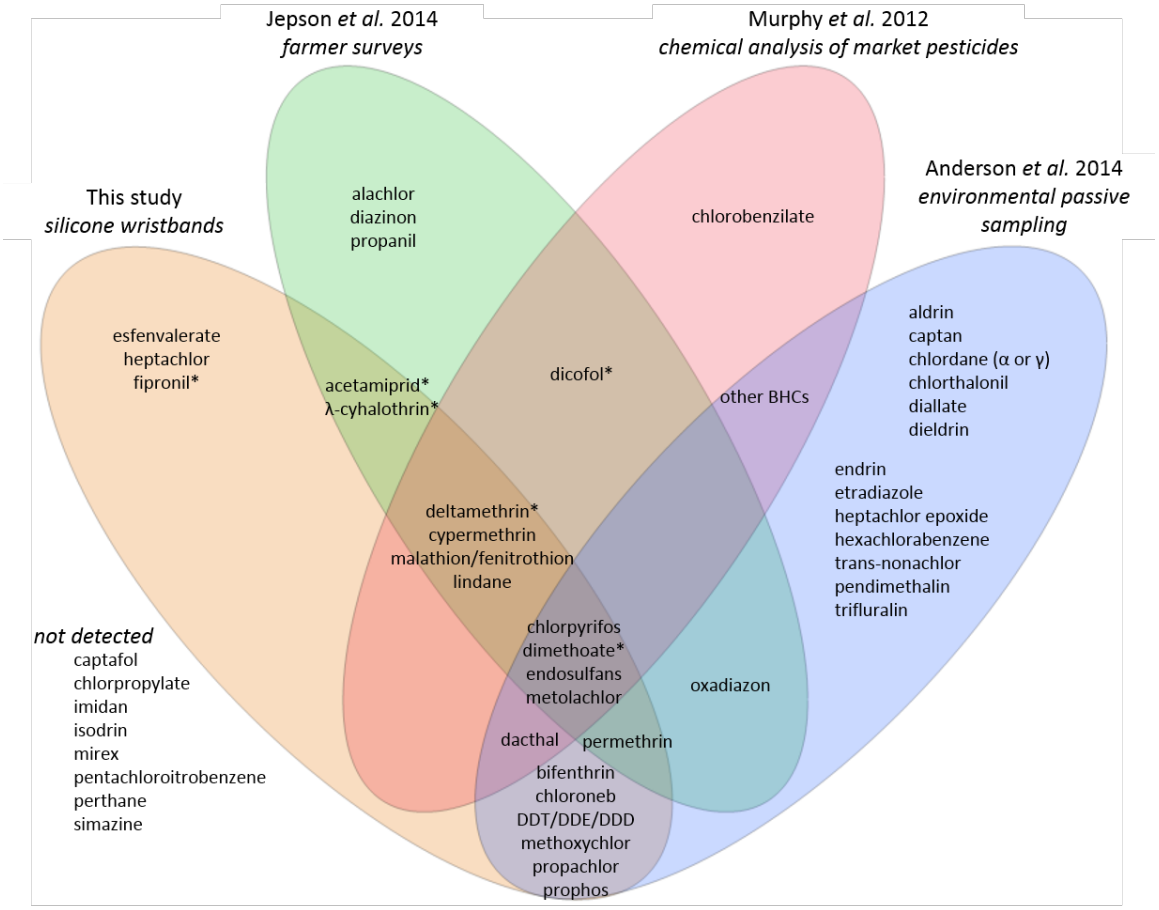

Figure 5.4. Comparison of pesticides detected in this study to previous pesticide use studies in West Africa, with survey data of village farmers, 2007 and 2010 (Jepson *et al.*[118]); analysis of vector control pesticides sold in markets in the Gambia, 2005 (Murphy *et al.*[133]); and environmental water sampling with passive samplers, 2012 (Anderson *et al.*[24]). Only pesticides included in the 63-pesticide method are included here, and lists of further pesticide detections in comparable studies are given in Appendix D. Asterisks indicate compounds that were reported in use by participants as listed in Table 5.1.

Table 5.1. Counts of pesticide ingredients used by participants. Use data were obtained from 21 of 35 participants, for a total of 42 wristbands. Asterisks indicate compounds that were included in the analytical method.

Pesticide active ingredient	**Times reported (of 42)**
dimethoate*	20
acetamiprid*	16
λ-cyhalothrin*	16
imazapyr	14
profenofos	13
Bacillus thuringiensis	9
fipronil*	7
dicofol*	5
methomyl	5
methamidophos	3
sulfur	3
azadirachtin	2
deltamethrin*	2

Table 5.2. Contingency table of counts and total percentages for the 42 wristband samples worn by 21 participants with pesticide use reports. Total sum is 2016; 42 samples×48 analytes, after combining isomers, degradation products and metabolites.

	Reported	**Not reported**
Detected	21 (1%)	192 (10%)
Not detected	45 (2%)	1758 (87%)

CHAPTER 6 – CONCLUSION

Passive sampling methods for organic chemicals have advanced considerably since their first uses in measuring chemical concentrations in water. The advancements described in this dissertation capitalize on several facets of passive sampling technology, from their lightweight, inexpensive construction to their ability to non-selectively sequester the gas-phase, bioavailable fraction of organic chemicals.

Compared to existing active sampling technology, passive samplers are constructed from cheap, lightweight materials. They are suitable for use in isolated locales where overnight, refrigerated transport is impossible or unlikely, as we demonstrate that concentrations of sequestered compounds are stable in warm transport conditions for up to 2 weeks. The polymer in passive samplers absorbs gas-phase or freely-dissolved chemicals. Taking advantage of this, we collected measurements of air in equilibrium with soil, rather than the soil itself, to determine diffusive flux between soil and overlying air. This technique revealed three different flux profiles at three disparate sites, and it is an excellent candidate for quantitative flux determination at other sites of contamination. One location of recent interest is artificial turf fields, as concerns have arisen about the potential for long-term health effects associated with chemical constituents of crumb rubber infill. Again at these field sites we measured air in equilibrium with turf to determine the first measurements of chemical volatilization and deposition on artificial turf fields. Volatilization was substantially greater at the newest, indoor field compared to the older, outdoor fields sampled. Capitalizing on the non-selectivity of the passive sampling material, we screened the sample extracts for 1533 contaminants of multiple classes, and detected 26 chemicals not previously associated with artificial turf. Similarly, among passive sampling wristbands worn by farmers in rural West Africa, we detected 19 pesticides beyond those reportedly used during the sampling period. Finally, by mimicking biological membranes, the passive sampling wristbands served as an easy-to-wear means of determining relative human exposures.

Future and ongoing efforts will continue to advance passive sampling. In this work, we adapted passive sampling and demonstrated a new means of measuring flux and fugacity ratios between air and terrestrial environments. This method can be applied to monitor chemical movement at contaminated sites. Alternately, repeated measures could be collected to understand how chemical movement changes with seasons or over years. Future developments in LDPE and

silicone passive sampler extractions aim to embody green chemistry by reducing solvents needed in analysis. Lastly, ongoing work with silicone passive samples aims to link air concentrations, dermal exposures, and health outcomes to exposures represented by detections in wristbands. The advancements herein provide logistical solutions and sensitive measures of chemical transport and human exposures and contribute to the expanding range of possibilities for passive sampling.

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APPENDICES

Appendix A: Supporting Information to Chapter 2 - Transport stability of pesticides and PAHs sequestered in polyethylene passive sampling devices

UV Transmittance Test: The irradiation system consisted of a 1000 W xenon arc lamp housed in an Oriel model 6140 lamp housing, driven by an Oriel model 8540 arc lamp power supply. The quasi-collimated UV beam passes through a water-cooled 10 cm aqueous filter to remove infrared radiation and two layers of 4 mm Solarphire PV annealed glass (Pittsburg Paint and Glass, Pittsburg PA) to remove UVC and modulate UVB and UVA wavelengths. Intensity of the UV region of the resultant spectrum (290 – 400 nm) is tuned to 68 W/m2, equivalent to the OECD standard dose rate, and has a UVA:UVB ratio of approximately 20. The spectrum closely resembles the solar spectrum for mid-July at Corvallis OR, 44.5667°N latitude, 123.2833°W longitude. Spectral output was measured with a Black-Comet C-50 UV-Vis spectrometer (StellarNet Inc, Tampa FL, USA) running SpectraWiz™ software.

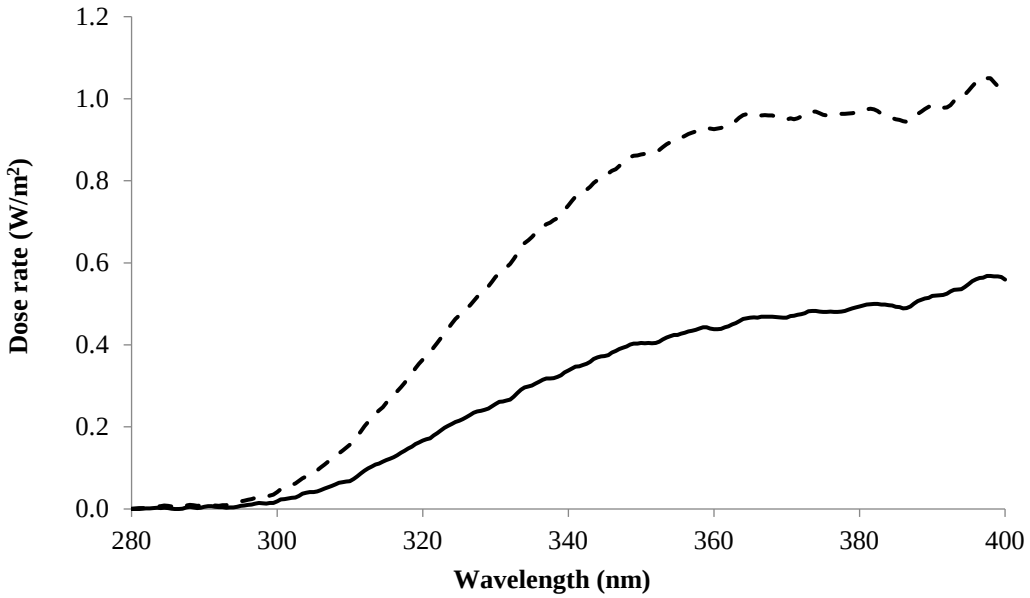

Figure A1. UV transmittance through PTFE bags. Presented data represent a reference spectrum with the sensor uncovered (dashed line) and the test spectrum collected through one-layer of PTFE bag material (solid line). PTFE bag attenuates UVA and UVB transmittance by 49%.

Table A1. Transport stability mean recovery (μg/L), standard deviation, and sample size. No values were significantly less than control (one-sided Dunnett's test)

	control, t = 0			t = 10 hours			t = 1.5 days			t = 3 days			t = 7 days			t = 14 days		
-20° C				Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n			
alachlor				467	35	4	466	49	4	463	18	4	431	10	4			
α-bhc				256	23	4	250	30	4	254	17	4	243	5	4			
chlorpyrifos				412	31	4	382	48	4	408	13	4	383	11	4			
endrin ketone				350	33	4	324	54	4	343	8	4	311	2	4			
anthracene				550	24	4	577	19	4	615	10	4	592	18	4			
fluoranthene				498	20	4	521	21	4	551	9	4	541	22	4			
chrysene				524	22	4	548	19	4	579	12	4	570	22	4			
benzo[ghi]-perylene				506	22	4	532	20	4	565	11	4	557	21	4			
4° C				Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n			
alachlor				442	33	4	469	37	4	465	28	4	415	20	4			
α-bhc				247	21	4	260	25	4	254	17	4	233	15	4			
chlorpyrifos				391	31	4	406	33	4	417	29	4	367	23	4			
endrin ketone				323	26	4	328	22	4	339	19	4	297	22	4			
anthracene				546	18	4	603	10	4	601	32	4	581	38	4			
fluoranthene				489	14	4	535	9	4	533	28	4	524	35	4			
chrysene				512	16	4	562	9	4	561	29	4	553	36	4			
benzo[ghi]-perylene				495	14	4	548	9	4	547	27	4	538	36	4			
20° C	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n			
alachlor	452	46	8	461	29	4	469	33	4	456	5	4	432	10	4			
α-bhc	246	27	8	244	14	4	250	6	4	247	4	4	245	11	4			
chlorpyrifos	392	35	8	396	22	4	405	22	4	409	9	4	385	11	4			
endrin ketone	339	31	8	321	19	4	330	17	4	338	10	4	310	15	4			
anthracene	572	17	8	571	19	4	606	25	4	609	27	4	592	25	4			
fluoranthene	519	20	8	507	17	4	539	23	4	540	23	4	533	23	4			
chrysene	541	20	8	531	18	4	565	22	4	569	25	4	563	24	4			
benzo[ghi]-perylene	521	18	8	516	15	4	550	22	4	553	22	4	547	18	4			
35° C				Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n
alachlor				446	21	4	492	8	4	438	22	4	433	34	4	440	25	4

Table A1. Transport stability mean recovery (μg/L), standard deviation, and sample size (Continued)

	control, t = 0	t = 10 hours			t = 1.5 days			t = 3 days			t = 7 days			t = 14 days		
α-bhc		253	6	4	278	10	4	248	12	4	243	17	4	251	16	4
chlorpyrifos		401	16	4	436	10	4	394	19	4	390	25	4	402	23	4
endrin ketone		325	15	4	352	20	4	320	12	4	310	20	4	329	14	4
anthracene		577	7	4	620	19	4	605	24	4	616	10	4	553	24	4
fluoranthene		510	6	4	548	7	4	537	21	4	548	11	4	491	22	4
chrysene		534	5	4	574	2	4	567	22	4	576	15	4	520	23	4
benzo[ghi]-perylene		519	6	4	557	2	4	551	23	4	558	14	4	503	24	4

Appendix B: Supporting Information to Chapter 3 - Assessing soil-air partitioning of PAHs and PCBs with a new fugacity passive sampler

PAH environmental concentration calculations

Time-weighted average gas-phase air and soil air concentrations were determined using an empirical uptake model using performance reference compounds (PRCs) to predict sampling rates.[6] PRCs have representative physicochemical properties. The model makes no assumptions about whether compounds have reached equilibrium between the air and the sampler material. We have calculated the equilibrium-corrected concentrations using PRCs to determine *in situ* sampling rates, rather than waiting for the LDPE to reach complete equilibrium with the soil air.

Soil air and air concentrations ($C_{(soil)air}$, ng m^{-3}) were calculated

$$C_{(soil)air} = \frac{N_{PAH}}{V_s K_{sa}^T \left[1 - e^{\left(\frac{-R_s t}{V_s K_{sa}^T}\right)}\right]} \quad \text{Eq. B1}$$

where N_{PAH} (ng) is the mass of a target PAH in LDPE extract, V_s (m^3) is the volume of sampler, K_{sa}^T is the sampler-air partition coefficient (See *Explanation 1* below), R_s is the sampling rate (m^3 day^{-1}, see *Explanation 2* below), and t (days) is the duration of deployment.

Explanation 1: K_{sa}^T

K_{sa}^T is calculated in several steps. First, K_{sw}, the sampler-water partition coefficient is estimated from an empirical relationship[6]

$$\log K_{sw} = -2.61 + 2.321 * \log K_{ow} - 0.1618 * (\log K_{ow})^2 \quad \text{Eq. B2}$$

Next, K_{sa}^{298} is determined[36]

$$K_{sa}^{298} = \frac{K_{sw}}{H'_{298}} \quad \text{Eq. B3}$$

where H'_{298} is the unitless Henry's law constant at 298 K. It is computed[153]

$$H'_{298} = \frac{H_{298}}{RT} \quad \text{Eq. B4}$$

where R is the gas constant (8.206 x 10^{-5} atm m^3 mol^{-1} K^{-1}), T is temperature (K), and H_{298} is Henry's law constant with units (atm m^3 mol^{-1}). Finally, K_{sa}^{298} is temperature-corrected to K_{sa}^{T} using a modified van 't Hoff equation [154]

$$K_{sa}^{T} = K_{sa}^{298} * e^{\left[\frac{\Delta H_{vap}}{R} * \left(\frac{1}{T} - \frac{1}{298}\right)\right]} \quad \text{Eq. B5}$$

where R is the gas constant (8.31 x 10^{-3} kJ mol^{-1} K^{-1}), T is the mean temperature (K) of air or soil air over the length of deployment, and ΔH_{vap} is the enthalpy of vaporization (kJ mol^{-1}). ΔH_{vap} is calculated for each PAH using the relationship developed by Khairy and Lohmann[154] using 15 model PAHs

$$\Delta H_{vap} = -9.3891 * \log P_L + 69.354 \quad \text{Eq. B6}$$

where $\log P_L$ is the logarithm of the vapor pressure (Pa). ΔH_{vap} inputs for the 15 model PAHs are given in Roux *et al.*[155]. Vapor pressures for all PAHs are estimated from molecular weight (MW, g mol^{-1}) [156]

$$\log P_L = -0.054 * MW + 8.52 \quad \text{Eq. B7}$$

Explanation 2: R_s

R_s is estimated with performance reference compounds that are added in known amounts to each sampler before field deployment using Eq. B8-10. First, the PRC exchange rate constant, k_e (d^{-1}) is estimated using[6]

$$k_e = \frac{-\ln\left(\frac{N_{PRC}}{N_{0,PRC}}\right)}{t} \quad \text{Eq. B8}$$

where N_{PRC} is the mass of PRC remaining in the strip after field deployment (ng), $N_{0,PRC}$ was the mass of PRC in the strip before field deployment (ng), and *t* was the length of deployment (days). Fluorene-d10 was the PRC used in soil air calculations, and pyrene-d10 was used for air. Second, the PRC sampling rate, $R_{s,PRC}$, was estimated[6]

$$R_{s,PRC} = V_s \, K_{sa}^{T} \, k_e \quad \text{Eq. B9}$$

Next, $R_{s,PRC}$, was related to R_s, the sampling rate for each PAH, using

$$R_s = R_{s,PRC} * \frac{\beta}{\beta_{PRC}} \quad \text{Eq. B10}$$

where β values are based on an empirical relationship with log K_{oa}[6]

$$\log \beta = 0.154 * \log K_{oa} - 0.80 \quad \text{Eq. B11}$$

PCB environmental concentration calculations

Soil air and air calculations for PCBs were performed similarly to PAHs, with the following exceptions:

Estimation of K_{sw} (Eq. B2) is replaced by:[36]

$$\log K_{sw} = 1.14 * \log K_{ow} - 1.14 \quad \text{Eq. B12}$$

where K_{sw} has units of kg L^{-1}. The K_{sw} value is divided by the density of LDPE (0.91 kg L^{-1}) to yield K_{sw} in units of kg kg^{-1}.[36]

Estimation of ΔH_{vap} (Eq. B6 and Eq. B7) is replaced by regressing $\log K_{ow}$ against ΔH_{vap} values reported for several PCBs in Puri *et al.*[157]:

$$\Delta H_{vap} = 9.61 * \log K_{ow} - 28.5 \quad (R^2 = 0.98) \quad \text{Eq. B13}$$

Both literature values and interpolated values of ΔH_{vap} are given in Table B2.

PCB 65-d5 was used as PRC in PCB environmental concentration calculations.

Diffusivity in air calculations

Diffusivity in air at 25°C for all PAHs, D^{298} (m^2 h^{-1}) was estimated using the diffusivity of pyrene in air at 25°C D^{298}_{pyrene} (m^2 h^{-1}), as a reference:[60]:

$$D^{298} = D^{298}_{pyrene} * \left(\frac{MW}{MW_{pyrene}}\right)^{-0.5} \quad \text{Eq. B14}$$

where MW is the molecular weight of a PAH, and MW_{pyrene} is the molecular weight of pyrene. D^{298} is the temperature-corrected using the mean temperature over deployment, T:[58]

$$D^T = D^{298} * \left(\frac{T}{298}\right)^{1.75} \quad \text{Eq. B15}$$

Values for pyrene reference and target PAHs are given in Table B1. D^{298}_{pyrene} from Gustafson and Dickhut[61] was chosen as the reference PAH with the closest temperature to the deployment, and pyrene has intermediate physicochemical properties for the PAHs included in analysis.

Estimate of uncertainty in f_{ratio}

Uncertainty of f_{ratio}, unc (%), was estimated at 45% after incorporating error ranges in air concentrations, soil air concentrations, and log K_{oa}[43; 56]

$$unc = \sqrt{unc^2_{air} + unc^2_{soil\ air} + unc^2_{K_{oa}}} \quad \text{Eq. B16}$$

where unc^2_{air} (8%) is the relative standard error of between-box air measurements, $unc^2_{pore\ air}$ (40%) is the relative standard error of between-box soil air measurements, and $unc^2_{K_{oa}}$ (20%) is an estimate of uncertainty of log octanol-air partition coefficients. This range is similar to previous reports [55; 57]. Values of f_{ratio} outside 0.55-1.45 ($\log_{10} f_{ratio}$: -0.26—0.19) were considered to be significant deviations from equilibrium.

Estimate of uncertainty in flux

Uncertainty of flux, unc_{flux} (%), was calculated after Liu *et al.*[57] and Minick and Anderson[62]

$$unc_{flux} = \sqrt{unc^2_{mass\ transfer} + \left(\frac{mass\ transfer}{flux} * s_{C_{air}}\right)^2 + \left(\frac{mass\ transfer}{flux} * s_{C_{soil\ air}}\right)^2}$$

where $mass\ transfer$ is the mass transfer coefficient (equivalent to D^T/δ_L); $unc_{mass\ transfer}$ is the relative standard deviation of the mass transfer coefficient estimated at 30% [57]; $s_{C_{air}}$ is the standard deviation of air replicates; and $s_{C_{soil\ air}}$ is the standard deviation of soil air replicates.

Environmental conditions

Temperatures inside the soil air box were slightly lower but similar to the air cage. Diurnal fluctuations were muted inside the soil air box. Relative humidity inside the soil air was higher than air. RH and temperature measurements inside the air cages were similar to local weather station data, indicating the micro-environment inside the air cages is similar to ambient air. See also Figures B.2 – B.4.

Anniston

Notes/observations/general weather: Weather was clear on most days. From West Anniston weather station on wunderground.com: average temp: 23 ℃, range 11-33 ℃. Sum of rain 1.1 cm, range 0-0.58 cm/day. Humidity range was 26-93%.

Wyckoff

Notes/observations/general weather: Weather was generally mild. From Seattle weather station on wunderground.com: average temp: 16 ℃, range 7-30 ℃. Sum of rain 2.3 cm, range 0-0.74 cm/day. Humidity range was 31-96%.

Mosier

Notes/observations/general weather: From Dallesport, WA weather station on wunderground.com: average temp: 22 ℃, range 13-36 ℃. Sum of rain 0.4 cm, range 0-0.4 cm/day. Humidity range was 12-90%.

Diagnostic sourcing ratios

Potential sources of PAHs in LDPE passive samplers were examined using numerous diagnostic sourcing ratios. Mean concentrations of PAHs were compared for both matrices (air and soil air) at each of the three sites. Results overall were mixed and inconclusive, but the results below are included nonetheless.

1. Four ratios are presented in Paulik *et al.*[52] and references therein:
    a. Fluoranthene/Pyrene >1 suggests pyrogenic. Both matrices at all sites yielded a pyrogenic signature.
    b. Phenanthrene/Anthracene < ~15 suggests pyrogenic source. Air and soil air at Wyckoff gave a pyrogenic signature, while Anniston and Mosier gave a petrogenic signature.
    c. Fluoranthene/(Fluoranthene+Pyrene) > 0.5 suggest wood/coal combustion. Both matrices at all sites yielded this wood/coal combustion signature.
    d. Anthracene/(Anthracene+Phenanthrene) < 0.01 suggests petrogenic. Both matrices at all sites yielded a petrogenic signature.
2. The ratio of alkylated PAHs to their parent, *e.g. mono*-, *di*-methylnaphthalenes, and ethylnaphthalenes to naphthalene, can also indicate pyrogenic or petrogenic sources.[63] Only naphthalenes and phenanthrenes were detected consistently enough to make these comparisons. In both cases, the parent PAH dominates, suggesting pyrogenic sources for both matrices and all sites.
3. The ratio of monomethylnaphthalenes/naphthalene < 0.2 can be used to differentiate creosote and coal tar from other sources .[63] All but Anniston soil air point to creosote. Mosier has a stronger signal than the site of known creosote contamination, Wyckoff.
4. PAHs heavier than fluoranthene and pyrene dominate in paving materials,[63] like those that might have been used when repaving the damaged road in Mosier. Fluoranthene and pyrene were the heaviest that we saw regularly in Mosier samples, although a few heavier ones were present in low levels in Mosier air. Heavier PAHs that might be from paving materials are near the detection limits.
5. Similarly, indeno[1,2,3-cd]pyrene is a dominant PAH in tire dust[63] that might be expected at the Mosier site adjacent to a large highway This PAH is also near limits of detection, and was only consistently found at Wyckoff. Although the passive samplers do not sample dust or particulate matter, a portion of this PAH could partition into the vapor phase.

Table B1. PAH physicochemical properties and detection limits.

PAH (in order of retention time)	*CAS*	*MW (g mol^{-1})*	*log K_{ow}[a]*	*log K_{oa}[b]*	*H_{298} (atm m^3 mol^{-1})[c]*	*D^{298} (m^2 h^{-1})[d]*	*IDL (ng/mL)[e]*	*IQL (ng/mL)[f]*	*DL in air (ng/m^3)[g]*	*QL in air (ng/m^3)[h]*	*DL in soil air (ng/m^3)[g]*	*QL in soil air (ng/m^3)[h]*
fluorene-d10 (PRC)	81103-79- 9	176.18	4.18	6.59	6.83E-03	n/a	0.52	2.965	n/a	n/a	n/a	n/a
pyrene-d10 (PRC)	1718-52-1	212.12	4.88	8.19	3.39E-04	n/a	0.35	2.35	n/a	n/a	n/a	n/a
benzo[b]fluoranthene-d12 (PRC)	205-99-2	264.15	5.78	10.35	3.31E-05	n/a	0.14	2.075	n/a	n/a	n/a	n/a
naphthalene	91-20-3	128.17	3.30	5.045	5.26E-04	0.0302	0.485	2.6	0.72	3.61	0.72	3.61
2-methylnaphthalene	91-57-6	142.20	3.86	5.534	5.80E-04	0.0287	0.445	1.75	0.11	0.56	0.11	0.56
1-methylnaphthalene	90-12-0	142.20	3.87	5.547	5.80E-04	0.0287	0.405	0.695	4.4E-02	0.22	4.4E-02	0.22
2-ethylnaphthalene	939-27-5	156.09	4.38	6.038	7.71E-04	0.0274	0.62	2.42	6.0E-02	0.30	6.4E-02	0.32
2,6-dimethylnaphthalene	581-42-0	156.22	4.31	5.892	6.41E-04	0.0274	0.595	2.215	5.3E-02	0.26	5.7E-02	0.29
1,6-dimethylnaphthalene	575-43-9	156.22	4.44	6.022	6.41E-04	0.0274	0.47	2.025	3.7E-02	0.18	4.2E-02	0.21
1,4-dimethylnaphthalene	571-58-4	156.22	4.37	6.172	6.41E-04	0.0274	0.415	3.11	6.5E-02	0.32	7.1E-02	0.36
1,5-dimethylnaphthalene	571-61-9	156.22	4.38	6.224	6.41E-04	0.0274	0.405	2.965	6.1E-02	0.30	6.7E-02	0.33
1,2-dimethylnaphthalene	573-98-8	156.22	4.31	5.892	6.41E-04	0.0274	1.165	2.35	5.6E-02	0.28	6.1E-02	0.30
1,8-dimethylnaphthalene	569-41-5	156.22	4.26	6.224	6.41E-04	0.0274	0.535	2.075	5.5E-02	0.27	5.7E-02	0.29
2,6-diethylnaphthalene	59919-41-4	184.27	**5.25**	6.585	1.13E-03	0.0252	0.395	2.03	1.4E-02	7.0E-02	2.3E-02	0.12
acenaphthylene	208-96-8	152.19	3.94	6.272	5.48E-05	0.0277	0.12	5.825	2.8E-02	0.14	6.3E-02	0.32
acenaphthene	83-32-9	154.20	3.92	6.044	2.82E-04	0.0275	0.23	2.675	6.8E-02	0.34	7.3E-02	0.36
fluorene	86-73-7	166.22	4.18	6.585	1.67E-04	0.0265	0.525	1.985	1.6E-02	7.8E-02	2.4E-02	0.12
dibenzothiophene	132-65-0	184.26	4.38	7.240	2.79E-05	0.0252	0.195	0.6	8.0E-04	4.0E-03	3.7E-03	1.9E-02
phenanthrene	85-01-8	178.23	4.46	7.222	5.13E-05	0.0256	0.235	1.155	1.9E-03	9.6E-03	7.5E-03	3.8E-02
anthracene	120-12-7	178.23	4.45	7.093	5.13E-05	0.0256	0.53	2.615	4.5E-03	2.2E-02	1.8E-02	8.9E-02
2-methylphenanthrene	2531-84-2	192.25	4.86	7.495	5.67E-05	0.0247	0.435	0.965	1.1E-03	5.6E-03	5.5E-03	2.7E-02
2-methylanthracene	613-12-7	192.25	5.00	7.635	5.67E-05	0.0247	0.21	1.18	1.2E-03	6.1E-03	6.2E-03	3.1E-02
1-methylphenanthrene	832-69-9	192.25	5.08	7.776	5.67E-05	0.0247	0.27	2.66	2.6E-03	1.3E-02	1.3E-02	6.7E-02
9-methylanthracene	779-02-2	192.25	5.07	7.870	5.67E-05	0.0247	0.17	2.185	2.1E-03	1.0E-02	1.1E-02	5.3E-02
3,6-dimethylphenanthrene	1576-67-6	206.28	**5.44**	8.033	6.25E-05	0.0238	0.425	1.04	8.5E-04	4.2E-03	4.8E-03	2.4E-02
2,3-dimethylanthracene	613-06-9	206.28	**5.44**	8.033	6.25E-05	0.0238	0.21	0.855	7.7E-04	2.4E-03	4.9E-03	1.5E-02
fluoranthene	206-44-0	202.26	5.16	8.601	8.30E-06	0.0240	0.42	1.36	6.9E-04	5.5E-03	3.9E-03	3.1E-02
9,10-dimethylanthracene	781-43-1	206.28	5.69	8.283	6.25E-05	0.0238	0.835	2.115	1.5E-03	7.5E-03	8.8E-03	4.4E-02
pyrene	129-00-0	202.25	4.88	8.193	8.30E-06	0.0240 [i]	0.835	1.045	7.1E-04	3.5E-03	4.4E-03	2.2E-02
retene	483-65-8	234.33	**6.35**	8.697	1.10E-04	0.0223	0.15	2.095	1.3E-03	6.5E-03	7.5E-03	3.7E-02
benzo[a]fluorene	238-84-6	216.23	5.40	8.364	1.63E-05	0.0233	0.19	2.5	2.6E-03	7.8E-03	1.6E-02	4.9E-02
benzo[b]fluorene	243-17-4	216.23	5.77	9.566	1.63E-05	0.0233	0.375	2.5	1.7E-03	5.1E-03	1.1E-02	3.2E-02

Table B1. PAH physicochemical properties and detection limits (Continured)

PAH (in order of retention time)	*CAS*	*MW (g mol^{-1})*	*log K_{ow}[a]*	*log K_{oa}[b]*	*H_{298} (atm m^3 mol^{-1})[c]*	*D^{298} (m^2 h^{-1})[d]*	*IDL (ng/mL)[e]*	*IQL (ng/mL)[f]*	*DL in air (ng/m^3)[g]*	*QL in air (ng/m^3)[h]*	*DL in soil air (ng/m^3)[g]*	*QL in soil air (ng/m^3)[h]*
benzo[c]fluorene	205-12-9	216.23	**5.19**	8.366	1.63E-05	0.0233	0.265	0.75	4.8E-04	2.4E-03	3.0E-03	1.5E-02
1-methylpyrene	2381-21-7	216.28	**5.48**	8.907	9.16E-06	0.0233	0.205	0.95	4.8E-04	2.4E-03	3.1E-03	1.5E-02
benz[a]anthracene	56-55-3	228.29	5.76	9.069	5.01E-06	0.0226	0.25	1.885	8.8E-04	4.4E-03	5.7E-03	2.9E-02
cyclopenta[cd]pyrene	27208-37-3	226.27	**5.70**	10.151	8.65E-07	0.0227	0.445	1.335	4.2E-04	2.1E-03	2.8E-03	1.4E-02
triphenylene	217-59-4	228.29	5.49	10.691	5.01E-06	0.0226	0.835	1.02	2.8E-04	1.4E-03	1.8E-03	8.8E-03
chrysene	218-01-9	228.28	5.81	9.480	5.01E-06	0.0226	0.185	1.245	5.1E-04	2.5E-03	3.3E-03	1.6E-02
6-methylchrysene	1705-85-7	242.31	**6.07**	9.716	5.53E-06	0.0220	0.47	2.22	8.3E-04	4.1E-03	5.4E-03	2.7E-02
5-methylchrysene	3697-24-3	242.31	**6.07**	9.716	5.53E-06	0.0220	0.265	2.5	1.6E-03	4.6E-03	1.0E-02	3.0E-02
benzo[b]fluoranthene	205-99-2	252.30	5.78	10.351	8.10E-07	0.0215	0.28	0.925	2.7E-04	1.4E-03	1.8E-03	8.9E-03
7,12-dimethylbenz[a]anthracene	57-97-6	256.34	5.80	9.613	6.10E-06	0.0214	0.355	2.355	9.1E-04	4.6E-03	5.9E-03	3.0E-02
benzo[k]fluoranthene	207-08-9	252.30	6.11	10.732	8.10E-07	0.0215	0.59	1.315	3.4E-04	1.7E-03	2.2E-03	1.1E-02
benzo[j]fluoranthene	205-82-3	252.30	**6.11**	10.590	8.10E-07	0.0215	0.13	1.395	3.8E-04	1.9E-03	2.5E-03	1.2E-02
benz[j]aceanthrylene & *benz[e]aceanthrylene*	202-33-5 & 199-54-2	252.30 252.30	**6.29** **6.14**	10.960 9.716	5.23E-07 6.49E-06	[j]	0.835	1.765	[j]	[j]	[j]	[j]
benzo[e]pyrene	192-97-2	252.30	6.44	11.351	8.10E-07	0.0215	0.51	2.95	3.7E-04	1.8E-03	2.4E-03	1.2E-02
benzo[a]pyrene	50-32-8	252.30	6.13	10.859	8.10E-07	0.0215	0.37	0.66	7.2E-04	3.6E-03	4.8E-03	2.4E-02
indeno[1,2,3-cd]pyrene	193-39-5	276.33	**6.70**	11.547	1.31E-07	0.0206	0.17	2.555	1.2E-04	6.3E-04	8.2E-04	4.2E-03
dibenzo[a,h]anthracene	53-70-3	278.35	6.75	11.779	4.89E-07	0.0205	0.165	1.86	4.5E-04	2.3E-03	3.0E-03	1.5E-02
benzo[a]chrysene	213-46-7	278.35	7.11	11.809	4.89E-07	0.0205	0.835	0.855	3.2E-04	1.6E-03	2.1E-03	1.1E-02
benzo[ghi]perylene	191-24-2	276.33	6.63	11.499	1.31E-07	0.0206	0.835	0.825	1.7E-04	8.3E-04	1.1E-03	5.5E-03
anthanthrene	191-26-4	276.33	7.04	12.311	1.31E-07	0.0206	0.235	0.835	1.2E-04	6.0E-04	8.0E-04	4.0E-03
naphtho[1,2-b]fluoranthene	111189-32-3	302.36	**7.28**	12.770	7.91E-08	0.0197	0.24	0.835	5.2E-04	5.2E-04	3.4E-03	3.4E-03
naphtho[2,3-j]fluoranthene	205-83-4	302.36	**7.28**	12.770	7.91E-08	0.0197	0.835	1.18	5.2E-04	5.2E-04	3.4E-03	3.4E-03
dibenzo[a,e]fluoranthene	5385-75-1	302.27	**7.28**	12.771	7.91E-08	0.0197	0.835	1.205	1.5E-04	7.3E-04	9.6E-04	4.8E-03
dibenzo[a,l]pyrene	191-30-0	302.27	7.71	13.20	7.91E-08	0.0197	3.22	0.835	1.3E-04	6.4E-04	8.5E-04	4.2E-03
naphtho[2,3-k]fluoranthene	207-18-1	302.37	**7.28**	12.770	7.91E-08	0.0197	0.35	0.835	5.2E-04	5.2E-04	3.4E-03	3.4E-03
naphtho[2,3-e]pyrene	193-09-9	302.37	**7.28**	12.770	7.91E-08	0.0197	0.835	16.11	5.2E-04	5.2E-04	3.4E-03	3.4E-03
dibenzo[a,e]pyrene	192-65-4	302.37	7.71	13.200	7.91E-08	0.0197	0.835	1.745	1.7E-03	8.6E-03	1.1E-02	5.7E-02
coronene	191-07-1	300.35	7.64	13.702	2.12E-08	0.0197	0.835	0.835	1.6E-04	7.8E-04	1.0E-03	5.1E-03
dibenzo[e,l]pyrene	192-51-8	302.36	**7.28**	12.770	7.91E-08	0.0197	0.71	0.835	5.2E-04	5.2E-04	3.4E-03	3.4E-03
naphtho[2,3-a]pyrene	196-42-9	302.36	**7.28**	12.770	7.91E-08	0.0197	0.26	0.835	5.2E-04	5.2E-04	3.4E-03	3.4E-03
benzo[b]perylene	197-70-6	302.36	**7.28**	12.770	7.91E-08	0.0197	0.52	3.55	5.2E-04	5.2E-04	3.4E-03	3.4E-03

Table B1. PAH physicochemical properties and detection limits (Continued)

PAH (in order of retention time)	*CAS*	*MW (g mol^{-1})*	*log K_{ow}*[a]	*log K_{oa}*[b]	*H_{298} (atm m^3 mol^{-1})*[c]	*D^{298} (m^2 h^{-1})*[d]	*IDL (ng/mL)*[e]	*IQL (ng/mL)*[f]	*DL in air (ng/m^3)*[g]	*QL in air (ng/m^3)*[h]	*DL in soil air (ng/m^3)*[g]	*QL in soil air (ng/m^3)*[h]
dibenzo[a,i]pyrene	189-55-9	302.37	**7.28**	12.770	7.91E-08	0.0197	0.35	1.3	4.4E-04	2.2E-03	2.9E-03	1.5E-02
dibenzo[a,h]pyrene	189-64-0	302.37	**7.28**	12.770	7.91E-08	0.0197	0.14	2.6	1.6E-04	8.1E-04	1.1E-03	5.3E-03

[a] bold values are KOWWIN v1.67, others are experimental values reported in [28]

[b] all values are KOAWIN v1.10 [28]

[c] Henry's law constant at 298: estimated via the bond method [28]

[d] Diffusivity in air at 298 K: estimated using Eq. B14

[e] Instrument detection limit: determined as 3X the standard deviation of seven runs of the lowest calibration standard

[f] Instrument quantitation limit: equivalent to 3 or 5X the IDL

[g] Detection limit, determined by calculating the environmental concentration of the IDL at 18.6°C, the mean temperature of all sites

[h] Quantitation limit, determined by calculating the environmental concentration of the IQL at 18.6°C, the mean temperature of all sites

[i] Gustafson and Dickhut[61]

[j] compounds co-elute: no environmental concentrations, fugacity ratios, or flux vales were determined

Table B2. PCB physicochemical properties and detection limits.

PCB congener	*CAS*	*MW* (g mol^{-1})	log K_{ow}[a]	log K_{oa}[b]	H_{298} (atm m^3 mol^{-1})[c]	ΔH_{vap} (kJ mol^{-1})[d]	*IDL* (ng/mL)[e]	*IQL* (ng/mL)[f]	*DL in air* (ng/m^3)[g]	*QL in air*[e] (ng/m^3)[h]	*DL in soil air*[d] (ng/m^3)[g]	*QL in soil air*[e] (ng/m^3)[h]
PCB 65-d5 (PRC)	1219794-80-5	297.02	**6.34**	**8.376**	1.25E-04	72.1	na	na	na	na	na	na
PCB 116-d5 (PRC)	1219798-92-1	331.43	6.75	**9.173**	9.34E-05	73.1	na	na	na	na	na	na
PCB 1	2051-60-7	186.65	**4.53**	6.561	3.07E-04	**72.1**	0.3	7.5	3.5E-02	0.87	3.8E-02	0.96
PCB 10	33146-45-1	223.10	**4.98**	7.007	2.27E-04	76.3	0.35	2.5	8.9E-03	6.3E-02	1.9E-02	0.14
PCB 4	13029-08-8	223.10	4.97	7.180	2.27E-04	76.2	0.9	25	2.3E-02	0.65	4.8E-02	1.34
PCB 8	34883-43-7	223.10	**4.98**	7.007	2.27E-04	76.3	0.25	7.5	6.3E-03	0.19	1.4E-02	0.42
PCB 5	16605-91-7	223.10	**5.02**	7.047	2.27E-04	76.7	0.35	2.5	8.0E-03	5.7E-02	1.9E-02	0.13
PCB 11	2050-67-1	223.10	**5.27**	7.291	2.27E-04	**81.0**	0.4	5.0	4.7E-03	5.9E-02	1.7E-02	0.22
PCB 18	37680-65-2	257.54	5.55	7.600	1.68E-04	**80.2**	0.8	5.0	4.4E-03	2.7E-02	2.9E-02	0.18
PCB 17	37680-66-3	257.54	**5.76**	7.923	1.68E-04	83.8	0.4	2.5	1.6E-03	9.9E-03	1.3E-02	7.8E-02
PCB 16	38444-78-9	257.54	**5.31**	7.397	1.68E-04	79.5	0.55	2.5	4.6E-03	2.1E-02	2.2E-02	0.10
PCB 50	62796-65-0	295.00	**6.34**	**8.632**	1.68E-04	89.4	0.55	2.5	1.3E-03	5.8E-03	1.3E-02	5.9E-02
PCB 31	16606-02-3	257.54	5.69	7.920	1.68E-04	83.2	0.35	0.5	1.5E-03	2.1E-03	1.1E-02	1.6E-02
PCB 28	7012-37-5	257.54	**5.62**	7.707	1.68E-04	82.5	0.4	0.5	1.9E-03	2.4E-03	1.4E-02	1.7E-02
PCB 33	38444-86-9	257.54	**5.87**	8.054	1.68E-04	84.9	0.45	5.0	1.6E-03	1.7E-02	1.3E-02	0.15
PCB 21	55702-46-0	257.54	**5.86**	8.023	1.68E-04	84.8	0.25	5.0	8.8E-04	1.8E-02	7.5E-03	0.15
PCB 52	35693-99-3	292.00	6.09	8.470	1.25E-04	87.0	0.55	5.0	1.4E-03	1.3E-02	1.4E-02	0.13
PCB 49	41464-40-8	292.00	6.22	8.390	1.25E-04	**87.4**	0.55	5.0	1.4E-03	1.2E-02	1.4E-02	0.13
PCB 104	56558-16-8	326.43	**6.98**	**9.403**	9.24E-05	95.6	0.5	1.5	7.9E-04	2.4E-03	8.9E-03	2.7E-02
PCB 44	41464-39-5	292.00	5.81	8.360	1.25E-04	84.3	0.4	0.5	1.2E-03	1.5E-03	1.1E-02	1.3E-02
PCB 37	38444-90-5	257.54	**5.90**	8.288	1.68E-04	85.2	0.35	2.5	1.1E-03	8.0E-03	9.5E-03	6.8E-02
PCB 74	32690-93-0	292.00	**6.67**	9.058	1.25E-04	92.6	0.65	2.5	1.2E-03	4.6E-03	1.3E-02	5.1E-02
PCB 70	32598-11-1	292.00	**6.23**	8.618	1.25E-04	88.4	0.4	0.5	9.3E-04	1.2E-03	9.5E-03	1.2E-02
PCB 66	32598-10-0	292.00	6.31	9.020	1.25E-04	89.1	0.15	0.5	3.0E-04	1.0E-03	3.1E-03	1.0E-02
PCB 101	37680-73-2	326.43	6.80	9.060	9.24E-05	93.8	0.15	1.5	2.7E-04	2.7E-03	3.0E-03	3.0E-02
PCB 60	33025-41-1	292.00	**5.84**	8.132	1.25E-04	84.6	0.25	1.5	8.0E-04	4.8E-03	7.2E-03	4.3E-02
PCB 99	38380-01-7	326.43	**7.21**	9.706	9.24E-05	97.8	0.25	1.5	3.5E-04	2.1E-03	4.0E-03	2.4E-02
PCB 145	74472-40-5	360.88	**7.62**	**10.173**	6.85E-05	101.7	0.35	25	4.2E-04	3.0E-02	4.8E-03	0.34
PCB 81	70362-50-4	292.00	**6.34**	**8.632**	1.25E-04	89.4	0.3	5.0	6.7E-04	1.1E-02	7.1E-03	0.12
PCB 87	38380-02-8	326.43	**6.85**	9.369	9.24E-05	94.3	0.2	2.0	3.2E-04	3.2E-03	3.6E-03	3.6E-02
PCB 110	38380-03-9	326.43	6.22	9.060	9.24E-05	88.3	0.15	0.5	2.9E-04	9.8E-04	3.0E-03	1.0E-02

Table B2. PCB physicochemical properties and detection limits (Continued)

PCB congener	*CAS*	*MW* (g mol^{-1})	*log* K_{ow}[a]	*log* K_{oa}[b]	H_{298} (atm m^3 mol^{-1})[c]	ΔH_{vap} (kJ mol^{-1})[d]	*IDL* (ng/mL)[e]	*IQL* (ng/mL)[f]	*DL in air* (ng/m^3)[g]	*QL in air*[e] (ng/m^3)[h]	*DL in soil air*[d] (ng/m^3)[g]	*QL in soil air*[e] (ng/m^3)[h]
PCB 77	32598-13-3	292.00	6.63	9.700	1.25E-04	92.2	0.3	5.0	4.5E-04	7.5E-03	4.8E-03	8.1E-02
PCB 123	65510-44-3	326.43	**6.98**	**9.403**	9.24E-05	95.6	0.35	5.0	5.6E-04	7.9E-03	6.3E-03	8.9E-02
PCB 118	31508-00-6	326.43	7.12	9.820	9.24E-05	96.9	0.95	5.0	1.3E-03	6.8E-03	1.5E-02	7.7E-02
PCB 82	52663-62-4	326.43	**6.98**	**9.403**	9.24E-05	95.6	0.35	2.5	5.6E-04	4.0E-03	6.3E-03	4.5E-02
PCB 153	35065-27-1	360.88	7.75	9.730	6.85E-05	**103.5**	0.25	0.5	3.5E-04	7.0E-04	4.0E-03	7.9E-03
PCB 114	74472-37-0	326.43	**6.98**	**9.403**	9.24E-05	95.6	0.45	1.5	7.2E-04	2.4E-03	8.0E-03	2.7E-02
PCB 179	52663-64-6	395.32	**8.27**	**11.278**	5.07E-05	108.0	0.3	5.0	2.4E-04	4.0E-03	2.8E-03	4.6E-02
PCB 105	32598-14-4	326.43	6.79	10.000	9.24E-05	93.7	0.5	5.0	6.5E-04	6.5E-03	7.2E-03	7.2E-02
PCB 138	35065-28-2	360.88	7.44	9.510	6.85E-05	100.0	0.35	2.0	5.3E-04	3.0E-03	6.0E-03	3.4E-02
PCB 158	74472-42-7	360.88	**7.62**	**10.173**	6.85E-05	101.7	0.4	2.5	4.8E-04	3.0E-03	5.4E-03	3.4E-02
PCB 187	52663-68-0	395.32	8.27	**9.870**	5.07E-05	108.0	0.4	2.5	5.3E-04	3.3E-03	6.0E-03	3.8E-02
PCB 126	57465-28-8	326.43	6.98	**10.350**	9.24E-05	95.6	0.3	4	3.4E-04	4.6E-03	3.8E-03	5.1E-02
PCB 183	52663-69-1	395.32	**8.27**	**10.953**	5.07E-05	108.0	0.4	1	3.6E-04	9.0E-04	4.1E-03	1.0E-02
PCB 166	41411-63-6	360.88	**7.31**	9.627	6.85E-05	98.7	0.2	3	2.9E-04	4.4E-03	3.3E-03	4.9E-02
PCB 167	52663-72-6	360.88	**7.50**	10.053	6.85E-05	100.6	0.5	1.5	6.2E-04	1.9E-03	7.1E-03	2.1E-02
PCB 128	38380-07-3	360.88	**7.31**	10.585	6.85E-05	98.7	0.3	2	3.1E-04	2.1E-03	3.5E-03	2.3E-02
PCB 204	74472-52-9	429.77	**8.97**	**11.723**	3.76E-05	114.7	0.55	2.5	3.8E-04	1.7E-03	4.3E-03	2.0E-02
PCB 156	38380-08-4	360.88	**7.60**	9.833	6.85E-05	101.5	0.3	1.5	4.0E-04	2.0E-03	4.6E-03	2.3E-02
PCB 180	35065-29-3	395.32	8.27	**9.880**	5.07E-05	108.0	0.5	2	6.6E-04	2.6E-03	7.5E-03	3.0E-02
PCB 157	69782-90-7	360.88	**7.62**	**10.173**	6.85E-05	101.7	0.25	15	3.0E-04	1.8E-02	3.4E-03	0.20
PCB 169	32774-16-6	360.88	**7.41**	9.963	6.85E-05	99.7	0.3	7.5	3.9E-04	9.7E-03	4.4E-03	0.11
PCB 170	35065-30-6	395.32	**8.27**	**11.704**	5.07E-05	108.0	0.3	1.5	2.1E-04	1.0E-03	2.4E-03	1.2E-02
PCB 189	39635-31-9	395.32	**8.27**	**10.953**	5.07E-05	108.0	0.5	2	4.5E-04	1.8E-03	5.1E-03	2.1E-02

[a] bold values are KOWWIN v1.67, others are experimental values reported in [28]

[b] bold values are KOAWIN v1.10, others are experimental values reported in [28]

[c] Henry's law constant at 298: estimated via the bond method [28]

[d] Enthalpy of vaporization: Bold values are from [157] and other values estimated with Eq. B13

[e] Instrument detection limit: determined as 3X the standard deviation of seven runs of the lowest calibration standard

[f] Instrument quantitation limit: equivalent to 3 or 5X the IDL

[g] Detection limit, determined by calculating the environmental concentration of the IDL at 18.6°C, the mean temperature of all sites

[h] Quantitation limit, determined by calculating the environmental concentration of the IQL at 18.6°C, the mean temperature of all site

Table B3. Instrument parameters.

	PAH method	PCB method
Internal standard	perylene-d12	PBDE-18
Extraction surrogates	naphthalene-d8, acenaphthylene-d8, phenanthrene-d10, fluoranthene-d10, chrysene-d12, benzo[a]pyrene-d12, benzo[ghi]perylene-d12	tetrachlorometaxylene, PCB 100, PCB 209
Gas chromatograph	Agilent 7809/7000C GC-MS/MS	6890 N (Agilent)
Detector(s)		2 x µ-electron capture detector
Column(s)	PAH select (Agilent)	DB-17MS (Agilent) & DB-XLB (Agilent)
No. of calibration points	5-9	5
Temperature program	hold 60°C for 1 min, ramp 40°C/min to 180°C, 3°C/min to 230°C, 1.5°C/min to 280°C, hold for 10 min, ramp 6°C/min to 298°C ramp 16°C/min to 350°C, hold at 350°C for 4 min Total time = 47.25 min	hold 100°C for 0.1 min, ramp 25°C/min to 200°C, hold for 0.5 min, ramp 10°C/min to 240°C hold for 0.5 min, ramp 30°C/min to 320°C, hold for 1.5 min, Total time =12.87 min
Reference	Anderson *et al.*[54]	n/a

Table B4. Mass (ng) of t = 0 performance reference compound per LDPE sampler strip.

PRC compound	*Log K_{oa} estimated* [28]	*Mean t=0 (ng, n=3)*	*standard deviation (relative standard dev.)*
fluorene-d10	6.585	2520	82 (3.3%)
pyrene-d10	8.193	790	5.4 (0.8%)
benzo[b]fluoranthene-d12	10.351	1003	1.7 (0.2%)
PCB 65-d5	8.376	127	9.9 (7.8%)
PCB 116-d5	9.173	149	20 (13%)

Table B5. Mean PAH detections in procedural blanks, n=3. Blank LDPE passive samplers that serve as procedural blanks were prepared, sent to and from the field sites, cleaned following deployment, and extracted. PCBs were below limit of detection in procedural blanks.

	Mean concentration in procedural blanks (ng/mL)
naphthalene	9.55
2-methylnaphthalene	4.24
1-methylnaphthalene	2.62
2-ethylnaphthalene	3.57
1,6-dimethylnaphthalene	3.92
1,5-dimethylnaphthalene	0.64
fluorene	2.32
phenanthrene	3.09
2-methylphenanthrene	0.94

Table B6. Mean air and soil air PAH concentrations (ng m^{-3}). Data are omitted (-) for a site if below quantitation limit in any replicate. The 25 PAHs shown were above quantitation limit for all replicates at one or more sites. All concentrations are different between air and soil air, except the three designated with bold text (two-sample t-test assuming unequal variance, $\alpha = 0.05$)

	Anniston						***Wyckoff***						***Mosier***					
	Air			*Soil air*			*Air*			*Soil air*			*Air*			*Soil air*		
PAH	*Mean*	*N*	*SD*	*Mean*	*N*	*SD*	*Mean*	*N*	*SD*	*Mean*	*N*	*SD*	*Mean*	*N*	*SD*	*Mean*	*N*	*SD*
naphthalene	19.3	3	0.577	11.0	3	1.00	139	15	8.00	128	20	20.2	49.7	15	5.13	19.6	20	8.81
2-methylnaphthalene	2.30	3	0.100	0.853	3	0.146	17.0	15	0.845	14.3	20	2.18	16.9	15	1.32	2.44	20	1.59
1-methylnaphthalene	1.67	3	0.0577	0.667	3	0.125	11.6	15	0.635	10.5	20	1.65	9.81	15	0.725	2.11	20	1.02
2-ethylnaphthalene	-			-			3.25	15	0.320	3.05	20	1.72	4.47	15	0.417	0.750	20	0.450
2,6-dimethylnaphthalene	0.607	3	0.0306	0.377	3	0.0451	0.931	15	0.0740	1.71	20	1.43	-			-		
1,6-dimethylnaphthalene	0.613	3	0.0321	0.600	3	0.0265	2.70	15	0.258	4.27	20	1.45	3.78	15	0.350	1.23	20	0.467
1,4-dimethylnaphthalene	-			-			0.431	15	0.0333	1.04	20	0.345	-			-		
1,5-dimethylnaphthalene	-			-			0.445	15	0.0448	0.770	20	0.311	-			-		
1,2-dimethylnaphthalene	-			-			0.645	15	0.059	0.929	20	0.311	-			-		
acenaphthene	-			-			14.9	15	1.22	22.8	20	10.1	37.9	15	4.10	8.95	20	4.46
fluorene	1.40	3	0.000	0.510	3	0.0917	6.54	15	0.656	8.68	20	2.70	20.4	15	2.64	3.96	20	2.52
dibenzothiophene	0.0597	3	0.00839	0.0250	3	0.00436	0.169	15	0.0150	0.768	20	0.632	1.27	15	0.365	0.150	20	0.0827
phenanthrene	1.700	3	0.173	0.407	3	0.0651	5.25	15	0.414	16.9	20	13.1	35.3	15	9.17	3.68	20	2.29
anthracene	-			-			0.522	15	0.0446	1.38	20	0.577	-			-		
2-methylphenanthrene	0.113	3	0.0127	0.0820	3	0.0266	0.295	15	0.0306	1.16	20	0.933	1.68	15	0.514	0.202	20	0.0736
2-methylanthracene	-			-			0.0226	15	0.00250	0.0864	20	0.0645	-			-		
1-methylphenanthrene	0.101	3	0.00854	0.0533	3	0.0140	0.114	15	0.0126	0.498	20	0.385	-			-		
3,6-dimethylphenanthrene	-			-			0.00679	15	0.000900	0.0299	20	0.0266	-			-		
fluoranthene	0.170	3	0.0265	0.0313	3	0.00493	0.367	15	0.0568	1.75	20	1.63	2.82	15	0.962	0.302	20	0.0793
pyrene	0.0947	3	0.00924	0.0250	3	0.00458	0.187	15	0.0288	0.899	20	0.873	1.31	15	0.445	0.164	20	0.0361
retene	0.377	3	0.0153	0.0473	3	0.0104	-			-			-			-		
triphenylene	-			-			0.00179	15	0.000393	0.00899	20	0.00278	-			-		
chrysene	-			-			0.00680	15	0.00212	0.0602	20	0.0459	-			-		
benzo[b]fluoranthene	-			-			0.00291	15	0.00107	0.0195	20	0.00886	-			-		
indeno[1,2,3-cd]pyrene	-			-			0.000739	15	0.000293	0.00464	20	0.00201	-			-		
SUM	28.5			14.7			204			219			185			43.6		

Table B7. Mean air and soil air PCBs concentrations (ng m^{-3}). Only the 4 PCBs shown were above detection limit in at least one sample. Data are omitted (-) for a site if below quantitation limit in any replicate.

Site	*Sample ID*	*PCB 4*	*PCB 17*	*PCB 77*	*PCB 118*	***Sum***
Anniston	soil air 1	0.432	0.0173	0.00829	-	**0.456**
	soil air 2	0.395	0.0142	0.0124	-	**0.422**
	soil air 3	0.628	0.106	-	-	**0.734**
	air 1	0.462	0.0336	0.00346	0.00378	**0.467**
	air 2	0.176 [a]	0.0328	-	-	**0.209**
	air 3	0.304 [a]	0.0341	0.0031	-	**0.341**
Wyckoff	soil air 1	-	0.0268 [a]	-	-	**0.0268**
	soil air 2	-	-	-	-	**-**
	soil air 3	-	0.0305 [a]	-	-	**0.0305**
	air 1	-	0.00785 [a]	-	-	**0.00785**
	air 2	-	-	-	-	**-**
	air 3	-	-	-	-	**-**
Mosier	soil air 1	-	-	-	-	**-**
	soil air 2	-	-	-	-	**-**
	soil air 3	-	-	-	-	**-**
	air 1	-	-	-	-	**-**
	air 2	-	-	-	-	**-**
	air 3	-	-	-	-	**-**

[a] estimated value: below limit of quantitation

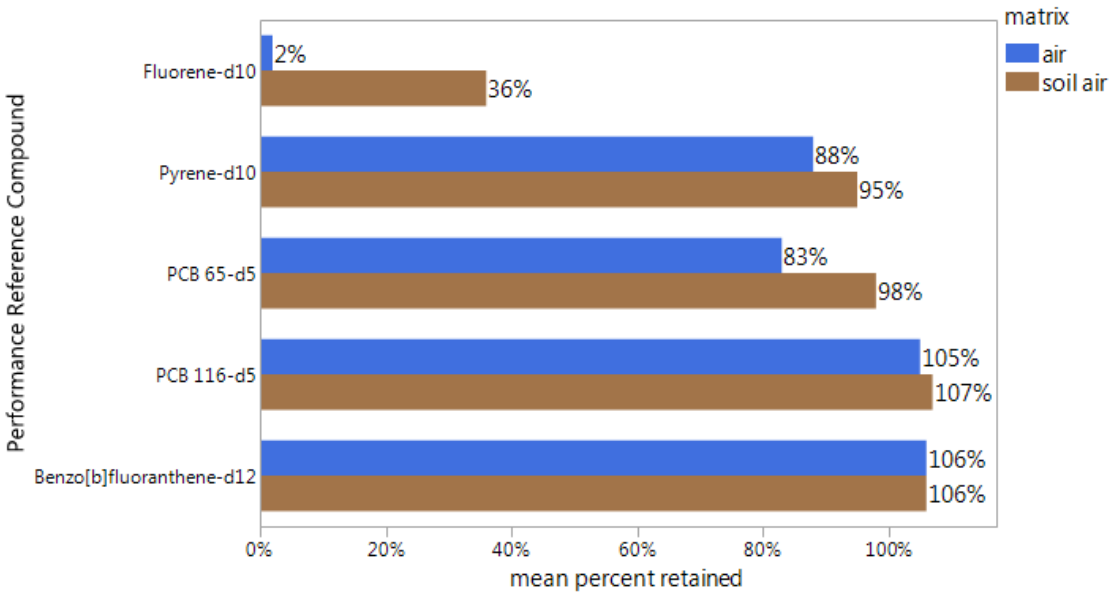

Figure B1. Mean performance reference compound retained after 14 day deployment for air and soil air. PRC are listed in order of K_{oa}, where fluorene-d10 has the lowest K_{oa}.

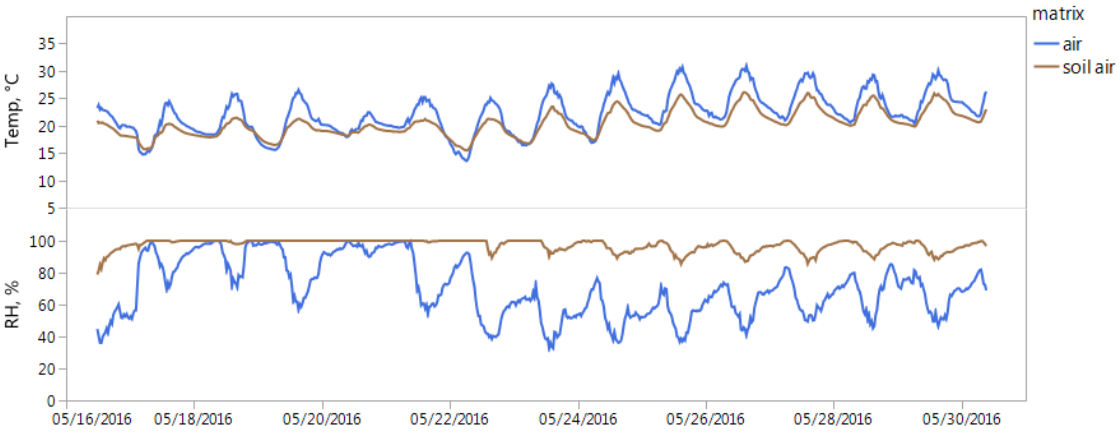

Figure B2. Temperature and relative humidity at Anniston site.

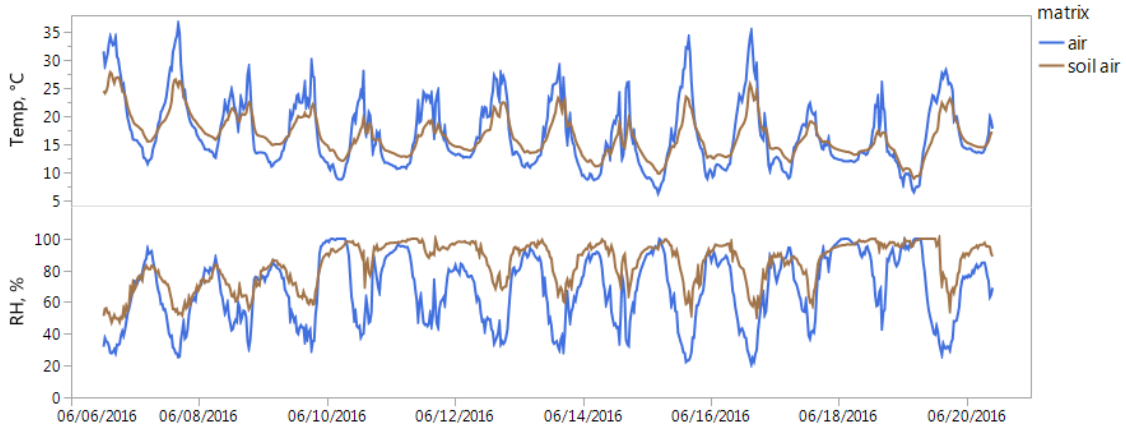

Figure B3. Temperature and relative humidity at Wyckoff site.

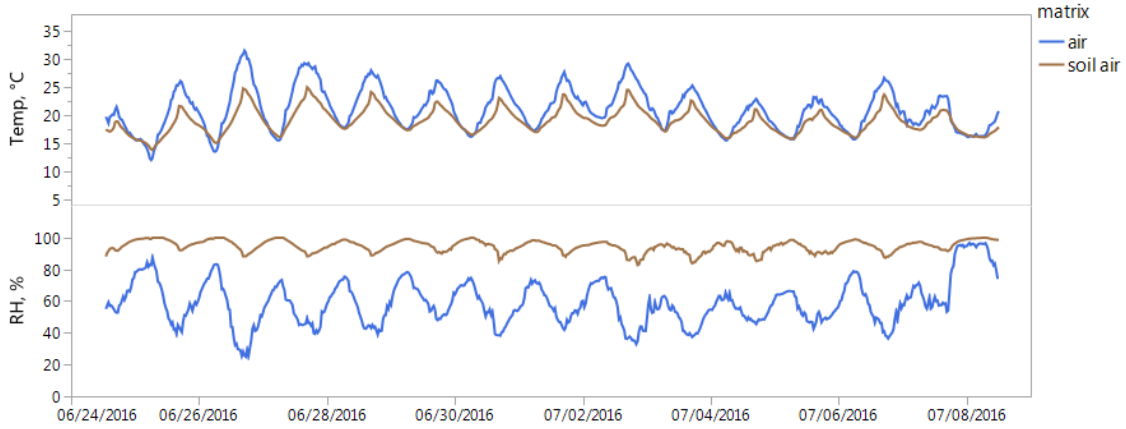

Figure B4. Temperature and relative humidity at Mosier site.

Appendix C: Supporting Information to Chapter 4 - Contaminant flux from artificial turf

Table C1. Physicochemical properties and detection limits of target PAHs and OPAHs.

analyte (in order of retention time for each method)	*CAS*	*MW (g mol^{-1})*	*log K_{ow}[a]*	*log K_{oa}[b]*	*H_{298} (atm m^3 mol^{-1})[c]*	*D^{298} (m^2 h^{-1})[d]*	*IDL (pg µL^{-1})[e]*	*IQL (pg/µL^{-1})[f]*	*DL in air (ng m^{-3})[g]*	*QL in air (ng m^{-3})[h]*	*DL in turf air (ng m^{-3})[g]*	*QL in turf air (ng m^{-3})[h]*
naphthalene	91-20-3	128.17	3.30	5.045	5.26E-04	0.0274	1.0	5.2	1.0	5.1	1.0	5.1
2-methylnaphthalene	91-57-6	142.20	3.86	5.534	5.80E-04	0.0274	0.70	3.5	0.15	0.77	0.15	0.77
1-methylnaphthalene	90-12-0	142.20	3.87	5.547	5.80E-04	0.0274	0.28	1.4	0.060	0.30	0.060	0.30
2-ethylnaphthalene	939-27-5	156.09	4.38	6.038	7.71E-04	0.0274	0.97	4.8	0.064	0.32	0.064	0.32
2,6-dimethylnaphthalene	581-42-0	156.22	4.31	5.892	6.41E-04	0.0274	0.89	4.4	0.060	0.30	0.060	0.30
1,6-dimethylnaphthalene	575-43-9	156.22	4.44	6.022	6.41E-04	0.0274	0.81	4.1	0.038	0.19	0.038	0.19
1,4-dimethylnaphthalene	571-58-4	156.22	4.37	6.172	6.41E-04	0.0274	1.2	6.2	0.070	0.35	0.070	0.35
1,5-dimethylnaphthalene	571-61-9	156.22	4.38	6.224	6.41E-04	0.0252	1.2	5.9	0.065	0.33	0.066	0.33
1,2-dimethylnaphthalene	573-98-8	156.22	4.31	5.892	6.41E-04	0.0277	0.94	4.7	0.063	0.31	0.063	0.31
1,8-dimethylnaphthalene	569-41-5	156.22	4.26	6.224	6.41E-04	0.0275	0.83	4.2	0.064	0.32	0.064	0.32
2,6-diethylnaphthalene	59919-41-4	184.27	**5.25**	6.585	1.13E-03	0.0265	0.81	4.1	0.0064	0.032	0.010	0.050
acenaphthylene	208-96-8	152.19	3.94	6.272	5.48E-05	0.0252	2.3	12	0.038	0.19	0.045	0.22
acenaphthene	83-32-9	154.20	3.92	6.044	2.82E-04	0.0256	1.1	5.4	0.095	0.47	0.095	0.47
fluorene	86-73-7	166.22	4.18	6.585	1.67E-04	0.0256	0.79	4.0	0.019	0.098	0.020	0.10
dibenzothiophene	132-65-0	184.26	4.38	7.240	2.79E-05	0.0247	0.24	1.2	0.00054	0.0027	0.0018	0.0088
phenanthrene	85-01-8	178.23	4.46	7.222	5.13E-05	0.0247	0.46	2.3	0.0015	0.0078	0.0037	0.018
anthracene	120-12-7	178.23	4.45	7.093	5.13E-05	0.0247	1.1	5.2	0.0036	0.018	0.0088	0.044
2-methylphenanthrene	2531-84-2	192.25	4.86	7.495	5.67E-05	0.0247	0.39	1.9	0.00046	0.0023	0.0024	0.012
2-methylanthracene	613-12-7	192.25	5.00	7.635	5.67E-05	0.0238	0.47	2.4	0.00037	0.0019	0.0027	0.014
1-methylphenanthrene	832-69-9	192.25	5.08	7.776	5.67E-05	0.0238	1.1	5.3	0.00067	0.0034	0.0057	0.029
9-methylanthracene	779-02-2	192.25	5.07	7.870	5.67E-05	0.0240	0.87	4.4	0.00057	0.0028	0.0046	0.023
3,6-dimethylphenanthrene	1576-67-6	206.28	**5.44**	8.033	6.25E-05	0.0238	0.42	2.1	0.00011	0.00054	0.0020	0.0099
2,3-dimethylanthracene	613-06-9	206.28	**5.44**	8.033	6.25E-05	0.0240[i]	0.54	1.7	5.9E-05	0.00019	0.0021	0.0065
fluoranthene	206-44-0	202.26	5.16	8.601	8.30E-06	0.0223	0.34	2.7	8.8E-05	0.00071	0.0016	0.013
9,10-dimethylanthracene	781-43-1	206.28	5.69	8.283	6.25E-05	0.0233	0.85	4.2	0.00013	0.00064	0.0036	0.018
pyrene	129-00-0	202.25	4.88	8.193	8.30E-06	0.0233	0.42	2.1	7.7E-05	0.00038	0.0019	0.0093
retene	483-65-8	234.33	**6.35**	8.697	1.10E-04	0.0233	0.84	4.2	6.9E-05	0.00034	0.0031	0.015
benzo[a]fluorene	238-84-6	216.23	5.40	8.364	1.63E-05	0.0233	1.7	5.0	0.00019	0.00057	0.0069	0.021
benzo[b]fluorene	243-17-4	216.23	5.77	9.566	1.63E-05	0.0226	1.7	5.0	0.00010	0.00031	0.0045	0.013

Table C1. Physicochemical properties and detection limits of target PAHs and OPAHs (Continued)

analyte (in order of retention time for each method)	*CAS*	*MW (g mol^{-1})*	*log K_{ow}[a]*	*log K_{oa}[b]*	*H_{298} (atm m^3 mol^{-1})[c]*	*D^{298} (m^2 h^{-1})[d]*	*IDL (pg µL^{-1})[e]*	*IQL (pg/µL^{-1})[f]*	*DL in air (ng m^{-3})[g]*	*QL in air (ng m^{-3})[h]*	*DL in turf air (ng m^{-3})[g]*	*QL in turf air (ng m^{-3})[h]*
benzo[c]fluorene	205-12-9	216.23	**5.19**	8.366	1.63E-05	0.0227	0.3	1.5	4.6E-05	0.00023	0.0013	0.0063
1-methylpyrene	2381-21-7	216.28	**5.48**	8.907	9.16E-06	0.0226	0.38	1.9	2.9E-05	0.00015	0.0013	0.0065
benz[a]anthracene	56-55-3	228.29	5.76	9.069	5.01E-06	0.0226	0.75	3.8	4.5E-05	0.00023	0.0024	0.012
cyclopenta[cd]pyrene	27208-37-3	226.27	**5.70**	10.151	8.65E-07	0.0220	0.53	2.7	2.1E-05	0.00011	0.0012	0.0058
triphenylene	217-59-4	228.29	5.49	10.691	5.01E-06	0.0220	0.41	2.0	1.7E-05	8.3E-05	0.00074	0.0037
chrysene	218-01-9	228.28	5.81	9.480	5.01E-06	0.0215	0.5	2.5	2.6E-05	0.00013	0.0014	0.0069
6-methylchrysene	1705-85-7	242.31	**6.07**	9.716	5.53E-06	0.0214	0.89	4.4	4.2E-05	0.00021	0.0023	0.011
5-methylchrysene	3697-24-3	242.31	**6.07**	9.716	5.53E-06	0.0215	1.7	5.0	7.8E-05	0.00023	0.0043	0.013
benzo[b]fluoranthene	205-99-2	252.30	5.78	10.351	8.10E-07	0.0215	0.37	1.9	1.4E-05	6.8E-05	0.00075	0.0038
7,12-dimethylbenz[a]anthracene	57-97-6	256.34	5.80	9.613	6.10E-06		0.94	4.7	4.8E-05	0.00023	0.0025	0.012
benzo[k]fluoranthene	207-08-9	252.30	6.11	10.732	8.10E-07	0.0215	0.53	2.6	1.7E-05	8.3E-05	0.00094	0.0047
benzo[j]fluoranthene	205-82-3	252.30	**6.11**	10.590	8.10E-07	0.0215	0.56	2.8	1.9E-05	9.3E-05	0.0010	0.0052
benz[j]aceanthrylene & benz[e]aceanthrylene	202-33-5 & 199-54-2	252.30 252.30	**6.29** **6.14**	10.960 9.716	5.23E-07 6.49E-06	0.0206	1.7	5.0	j	j	j	j
benzo[e]pyrene	192-97-2	252.30	6.44	11.351	8.10E-07	0.0205	0.71	3.5	1.8E-05	8.9E-05	0.0010	0.0050
benzo[a]pyrene	50-32-8	252.30	6.13	10.859	8.10E-07	0.0205	1.2	5.9	3.6E-05	0.00018	0.0020	0.010
indeno[1,2,3-cd]pyrene	193-39-5	276.33	**6.70**	11.547	1.31E-07	0.0206	0.26	1.3	6.1E-06	3.1E-05	0.00035	0.0018
dibenzo[a,h]anthracene	53-70-3	278.35	6.75	11.779	4.89E-07	0.0206	1.0	5.1	2.2E-05	0.00011	0.0012	0.0063
benzo[a]chrysene	213-46-7	278.35	7.11	11.809	4.89E-07	0.0197	0.74	3.7	1.6E-05	8.0E-05	0.00090	0.0045
benzo[ghi]perylene	191-24-2	276.33	6.63	11.499	1.31E-07	0.0197	0.34	1.7	8.1E-06	4.1E-05	0.00046	0.0023
anthanthrene	191-26-4	276.33	7.04	12.311	1.31E-07	0.0197	0.33	1.7	5.9E-06	3.0E-05	0.00034	0.0017
naphtho[1,2-b]fluoranthene	111189-32-3	302.36	**7.28**	12.770	7.91E-08	0.0197	1.7	1.7	2.5E-05	2.5E-05	0.0014	0.0014
naphtho[2,3-j]fluoranthene	205-83-4	302.36	**7.28**	12.770	7.91E-08	0.0197	1.7	1.7	2.5E-05	2.5E-05	0.0014	0.0014
dibenzo[a,e]fluoranthene	5385-75-1	302.27	**7.28**	12.771	7.91E-08	0.0197	0.47	2.4	7.2E-06	3.6E-05	0.00041	0.0020
dibenzo[a,l]pyrene	191-30-0	302.27	7.71	13.20	7.91E-08	0.0197	0.48	2.4	6.3E-06	3.2E-05	0.00036	0.0018
naphtho[2,3-k]fluoranthene	207-18-1	302.37	**7.28**	12.770	7.91E-08	0.0197	1.7	1.7	2.5E-05	2.5E-05	0.0014	0.0014
naphtho[2,3-e]pyrene	193-09-9	302.37	**7.28**	12.770	7.91E-08	0.0197	1.7	1.7	2.5E-05	2.5E-05	0.0014	0.0014
dibenzo[a,e]pyrene	192-65-4	302.37	7.71	13.200	7.91E-08	0.0197	6.4	32	8.4E-05	0.00042	0.0048	0.024
coronene	191-07-1	300.35	7.64	13.702	2.12E-08	0.0197	0.7	3.5	7.7E-06	3.8E-05	0.00043	0.0022
dibenzo[e,l]pyrene	192-51-8	302.36	**7.28**	12.770	7.91E-08	0.0197	1.7	1.7	2.5E-05	2.5E-05	0.0014	0.0014
naphtho[2,3-a]pyrene	196-42-9	302.36	**7.28**	12.770	7.91E-08	0.0197	1.7	1.7	2.5E-05	2.5E-05	0.0014	0.0014
benzo[b]perylene	197-70-6	302.36	**7.28**	12.770	7.91E-08	0.0302	1.7	1.7	2.5E-05	2.5E-05	0.0014	0.0014

Table C1. Physicochemical properties and detection limits of target PAHs and OPAHs (Continued)

analyte (in order of retention time for each method)	*CAS*	*MW (g mol^{-1})*	*log K_{ow}[a]*	*log K_{oa}[b]*	*H_{298} (atm m^3 mol^{-1})[c]*	*D^{298} (m^2 h^{-1})[d]*	*IDL (pg µL^{-1})[e]*	*IQL (pg/µL^{-1})[f]*	*DL in air (ng m^{-3})[g]*	*QL in air (ng m^{-3})[h]*	*DL in turf air (ng m^{-3})[g]*	*QL in turf air (ng m^{-3})[h]*
dibenzo[a,i]pyrene	189-55-9	302.37	**7.28**	12.770	7.91E-08	0.0287	1.4	7.1	2.2E-05	0.00011	0.0012	0.0061
dibenzo[a,h]pyrene	189-64-0	302.37	**7.28**	12.770	7.91E-08	0.0287	0.52	2.6	7.9E-06	4.0E-05	0.00045	0.0022
1,4-benzoquinone	106-51-4	108.095	0.2	1.908	1.22E-09	0.0329	0.49	2.4	0.0086	0.042	0.0086	0.042
chromone	491-38-3	146.143	1.38	5.862	8.07E-07	0.0283	0.89	4.4	0.35	1.7	0.35	1.7
1,4-naphthoquinone	130-15-4	158.153	1.71	8.804	1.97E-09	0.0272	0.45	2.3	0.00017	0.00085	0.00017	0.00085
1,2-naphthoquinone	524-42-5	158.153	2.11	8.876	4.19E-09	0.0272	2500	5000	0.64	1.3	0.64	1.3
9-fluorenone	486-25-9	180.202	3.58	8.138	6.77E-07	0.0255	0.20	0.99	0.00013	0.00063	0.00013	0.00063
xanthone	90-47-1	196.201	3.39	8.493	1.93E-07	0.0244	0.38	1.9	0.00011	0.00057	0.00011	0.00057
perinaphthenone	548-39-0	180.202	3.39	8.766	1.03E-07	0.0255	0.89	4.4	0.00015	0.00072	0.00015	0.00072
phenanthrene-1,4-dione	569-15-3	208.212	2.84	10.945	1.82E-10	0.0237	0.86	4.3	1.3E-06	6.6E-06	1.9E-06	9.6E-06
9,10-anthraquinone	84-65-1	208.212	3.39	9.407	3.18E-09	0.0237	1.5	7.7	7.3E-06	3.8E-05	8.5E-06	4.4E-05
1,4-anthraquinone	635-12-1	208.212	2.84	10.945	1.92E-10	0.0237	5.6	28	8.9E-06	4.5E-05	1.3E-05	6.4E-05
4h-cyclopenta(def)-phenanthren-4-one	5737-13-3	204.223	4.14	9.604	8.4E-08	0.0239	0.21	1.0	3.3E-06	1.6E-05	3.3E-06	1.6E-05
9,10-phenanthrenequinone	84-11-7	208.212	2.52	9.477	2.7E-09	0.0237	250	500	0.012	0.023	0.012	0.023
2-ethylanthraquinone	84-51-5	236.265	4.37	11.09	4.66E-09	0.0222	0.35	1.8	3.2E-07	1.6E-06	5.8E-07	3.0E-06
benzofluorenone	76723-60-9	230.261	4.73	10.298	6.61E-08	0.0225	0.45	2.3	1.1E-06	5.6E-06	1.4E-06	7.4E-06
benzanthrone	82-05-3	230.261	4.81	10.378	6.61E-08	0.0225	0.78	3.9	1.6E-06	7.9E-06	2.2E-06	1.1E-05
benz[a]anthracene-7,12-dione	2498-66-0	258.06	4.4	12.297	3.1E-10	0.0213	0.85	4.2	3.8E-07	1.9E-06	8.0E-07	4.0E-06
benzo(c)phenanthrene-(1,4)-quinone	109699-80-1	258.06	4.01	13.124	1.88E-11	0.0213	1.7	8.5	5.6E-07	2.8E-06	1.2E-06	5.9E-06
5,12-naphthacene-quinone	1090-13-7	258.271	4.52	12.417	3.1E-10	0.0213	1.3	6.3	5.6E-07	2.7E-06	1.2E-06	5.7E-06
6H-benzo(cd)pyrenone	3074-00-8	274.331	5.31	11.785	8.2E-09	0.0206	1.1	5.7	6.1E-07	3.2E-06	1.3E-06	6.5E-06

[a] bold values are KOWWIN v1.67, others are experimental values reported in [28]

[b] all values are KOAWIN v1.10 [28]

[c] Henry's law constant at 298: estimated via the bond method [28]

[d] Diffusivity in air at 298 K: estimated using Eq. B14

[e] Instrument detection limit: determined as 3X the standard deviation of seven runs of the lowest calibration standard

[f] Instrument quantitation limit: equivalent to 3 or 5X the IDL

[g] Detection limit, determined by calculating the environmental concentration of the IDL at 22°C, the mean temperature of all sites

[h] Quantitation limit, determined by calculating the environmental concentration of the IQL at 22°C, the mean temperature of all sites

Table C1. Physicochemical properties and detection limits of target PAHs and OPAHs (Continued)

[i] Gustafson and Dickhut[61]
[j] analytes co-elute: no environmental concentrations or flux vales were determined

Table C2. Mean concentrations of target analytes detected in procedural blanks (n=3).

Target analyte	Mean extract concentration (pg/µL)	Frequency of detection
naphthalene	16	3
2-methylnaphthalene	4.1	3
1-methylnaphthalene	2.6	3
2-ethylnaphthalene	3.1	3
1,6-dimethylnaphthalene	3.2	3
fluorene	0.94	2
phenanthrene	3.5	3
2-methylphenanthrene	1.1	3
retene	2.5	3

Table C3. Comparative responses in 1533 analyte screen of chemicals present in procedural blanks (n=3) and field samples (n=10). Dicyclohexyl phthalate was not detected in any field samples, thus comparisons between blanks and field samples are not applicable (na).

	Procedural blanks (n=3)		Field samples (n=10)		range of fold-increase over mean procedural blank response		
chemical	**frequency of detection**	**mean response (range)**	**frequency of detections**	**mean response (range)**	**min.**	**average**	**max.**
2,4-di-tert-butylphenol	3	830 (200-1000)	9	1180 (300-2000)	0.4	1.4	2.4
bis(2-ethylhexyl)phthalate	2	250 (200-300)	10	25400 (2000-80000)	8.0	102	320
dicyclohexyl phthalate	1	40	0	na	na	na	na
di-n-butylphthalate	1	700	9	11700 (3000-30000)	4.3	17	43

Table C4. Flux between turf and air, with uncertainty (unc.). Data are not included (-) when either air or turf air values were below limit of detection, and flux values were not calculated. OPAHs are designated by italicized font. Replicates (n=3) from *outdoor A* are reported as averages.

analyte (in order of retention time for each method)	**flux (ng m-2 h-1)**	**unc. (%)**	**mean flux (ng m-2 h-1)**	**mean unc. (%)**	**flux (ng m-2 h-1)**	**unc. (%)**
	indoor	*indoor*	*outdoor A*	*outdoor A*	*outdoor B*	*outdoor B*
naphthalene	38000	30%	-450	30%	-2000	30%
2-methylnaphthalene	12000	30%	-230	30%	-610	30%
1-methylnaphthalene	8300	30%	-130	31%	-340	30%
2-ethylnaphthalene	8300	30%	30	46%	-64	34%
2,6-dimethylnaphthalene	1500	30%	-2.4	430%	-27	48%
1,6-dimethylnaphthalene	7200	30%	59	35%	-51	36%
1,4-dimethylnaphthalene	890	30%	16	71%	21	58%
1,5-dimethylnaphthalene	860	30%	15	77%	-6.1	170%
1,2-dimethylnaphthalene	1780	30%	20	60%	-14	80%
acenaphthylene	2300	30%	12	92%	20	62%
acenaphthene	2500	30%	110	32%	-440	30%
2,6-diethylnaphthalene	150	31%	-	-	-	-
fluorene	2700	30%	190	30%	-0.26	3900%
dibenzothiophene	300	30%	36	40%	64	34%
phenanthrene	2700	30%	420	30%	670	30%
anthracene	360	30%	80	32%	29	45%
2-methylphenanthrene	530	30%	360	30%	190	30%
2-methylanthracene	87	32%	31	43%	7.2	130%
1-methylphenanthrene	220	30%	170	31%	130	31%
3,6-dimethylphenanthrene	42	37%	82	32%	26	46%
fluoranthene	140	31%	150	31%	170	31%
pyrene	190	30%	160	31%	130	31%
retene	40	37%	41	37%	45	35%
benzo[a]fluorene	3.1	290%	2.8	320%	1.2	720%
benzo[b]fluorene	1.3	690%	1.2	770%	-	-
benzo[c]fluorene	1.0	860%	-	-	0.51	1700%
1-methylpyrene	4	210%	7.1	130%	1.6	540%
benz[a]anthracene	0.50	1700%	0.69	1300%	0.083	10000%
triphenylene	0.23	3700%	0.83	1000%	0.40	2200%
chrysene	0.38	2200%	0.92	950%	0.14	6100%
4H-cyclopenta(def)-phenanthren-4-one	-	-	-	-	0.0080	120000%
9-fluorenone	-	-	1.1	900%	0.49	2000%
benzofluorenone	-	-	0.0010	780000%	-	-
chromone	3400	30%	-	-	-	-

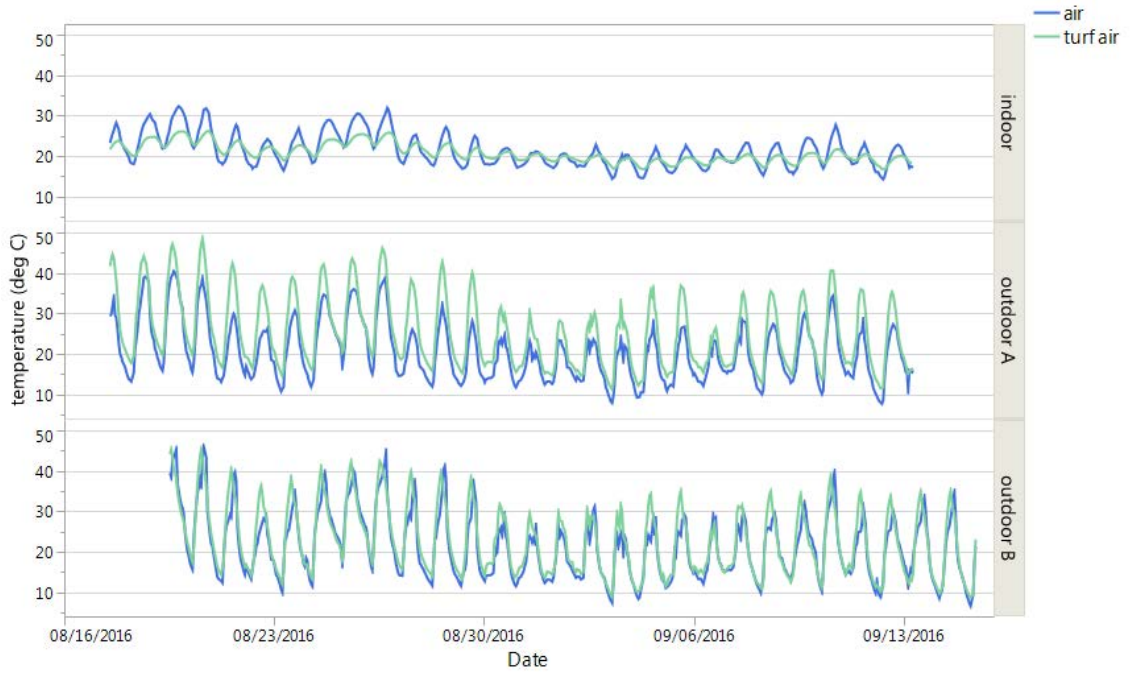

Figure C1. Temperatures recorded within air and turf air boxes.

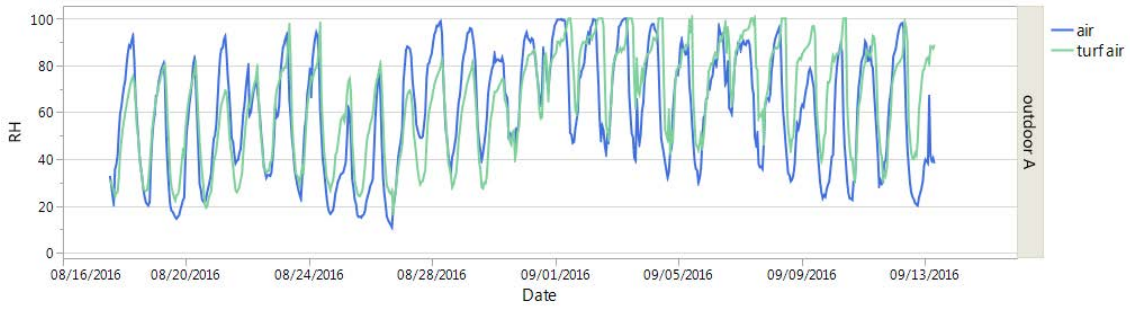

Figure C2. Relative humidity (RH, %) recorded within air and turf boxes at the *outdoor A* site.

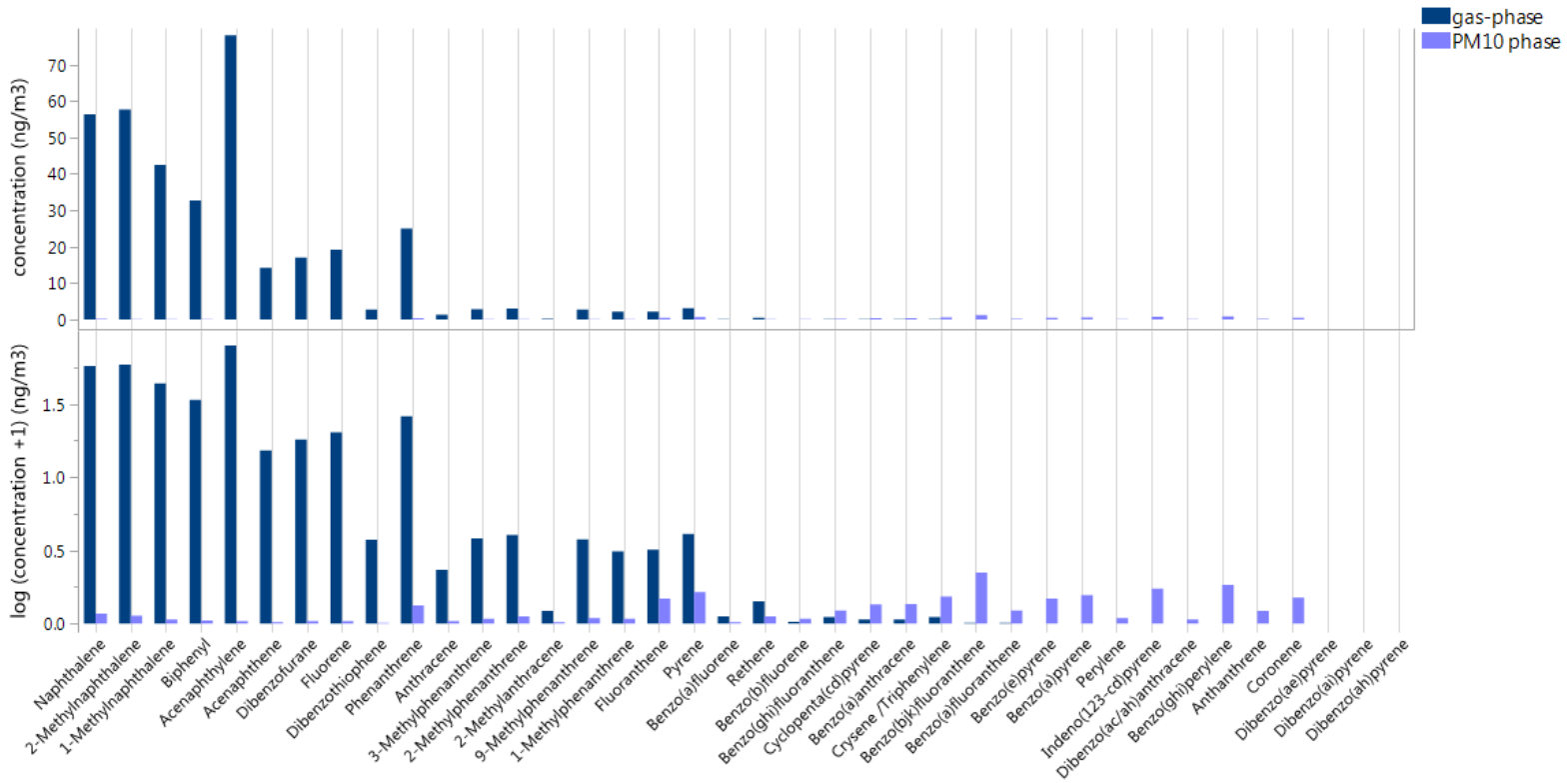

Figure C3. Distribution of PAHs in gas- and particle-phase: data from Valhall site, Dye *et al.*[87] The x-axis in the top plot is on an absolute scale, while the x-axis on the bottom plot is on a $\log_{10}$ scale. Ninety-seven percent of measured PAHs are in gas-phase.

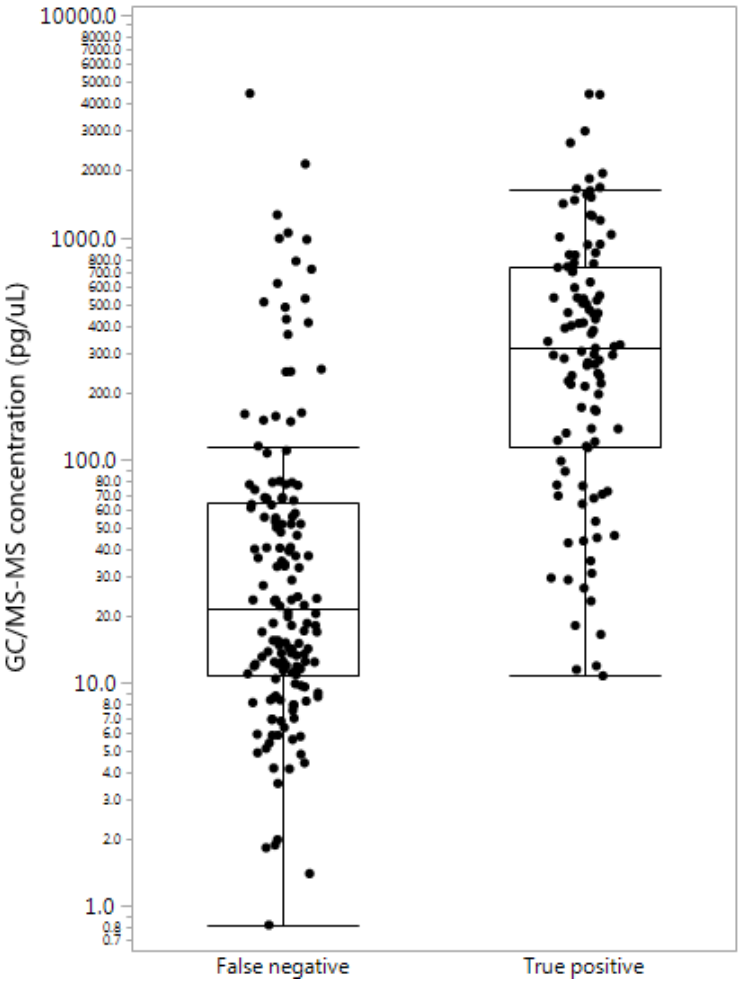

Figure C4. Comparison of PAHs detected in quantitative analysis and 1533 screen. True positives were detected in both methods. False negatives were detected in the more sensitive quantitative analysis but not in the 1533 screen. As with the quantitative analysis, detection limits must be carefully considered in the 1533 screen. Although absolute detection limits are not defined for the 1533 screen, we expect a similar trend as in the quantitative screen, where air samplers likely have lower method detection limits than turf air samplers. All PAHs in the quantitative GC/MS-MS analysis are included in the 1533 screen. No PAHs were detected in the 1533 screen that were not also seen in the quantitative analysis, *i.e.*, there were no false positives. Conversely, only 40% of the PAHs detections in the quantitative screen were also seen in the 1533 screen. Comparing the concentrations of true positives and false negatives, we infer the approximate detection limit for PAHs in the 1533 screen is nominally between 10 and 100 pg/µL, although there are many cases in which the 1533 screen missed detections well above 100 pg/µL. By comparison, the detection limit for the quantitative screen varies by PAH between 0.2 and 6 pg/µL. Although it includes drastically more analytes, the 1533 screen is less sensitive than more targeted methods

List C1. Analytes in the 1533 screen

PCB 1
PCB 2
PCB 3
PCB 4
PCB 5
PCB 6
PCB 7
PCB 8
PCB 9
PCB 10
PCB 11
PCB 12
PCB 13
PCB 14
PCB 15
PCB 16
PCB 17
PCB 18
PCB 19
PCB 20
PCB 21
PCB 22
PCB 23
PCB 24
PCB 25
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PCB 126
PCB 127
PCB 128
PCB 129
PCB 130
PCB 131
PCB 132
PCB 133
PCB 134
PCB 135
PCB 136
PCB 137
PCB 138

List C1. Analytes in the 1533 screen (Continued)

PCB 139
PCB 140
PCB 141
PCB 142
PCB 143
PCB 144
PCB 145
PCB 146
PCB 147
PCB 148
PCB 149
PCB 150
PCB 151
PCB 152
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PCB 198
PCB 199
PCB 200
PCB 201
PCB 202
PCB 203
PCB 204
PCB 205
PCB 206
PCB 207
PCB 208
PCB 209
Diethylene glycol
Aniline
p-Dichlorobenzene
Dicyclopentadiene
Dimefox
o-Dichlorobenzene
2-Methylphenol
4-Methylphenol
m-Cresol
1,2-Dibromo-3-chloropropane
2,4-Dimethylaniline
2,6-Dimethylaniline
1,2,4-Trichlorobenzene
Ethiolate
3-Chloroaniline
4-Chloroaniline
2-Ethyl-1,3-hexanediol
p-Nitrotoluene
Methamidophos
Dichlorvos
Allidochlor
2,3,5-Trichlorophenol
2,6-Dichlorobenzonitrile
Nicotine
EPTC
Dichlormid
Phenoxyacetic acid
Biphenyl
Propamocarb
2-Phenoxypropionic acid
3,5-Dichloroaniline
Mevinphos
Butylate
3,4-Dichloroaniline
Acephate
Chlormefos
Vernolate
Dimethylphthalate
Propham
Nitrapyrin
Etridiazole
Pebulate
Metolcarb
Trichlorfon
Butylated hydroxyanisole
Methacrifos
Chloroneb
o-Phenylphenol
Crimidine
Dicamba methyl ester
2-(2-Butoxyethoxy)ethyl thi...
Pentachlorobenzene
2-(Octylthio)ethanol
Molinate
Isoprocarb
Demephion
2,3,5,6-Tetrachlorophenol
Mecoprop methyl ester
Ethylenethiourea
2,3,4,5-Tetrachlorophenol
Methomyl
MCPA methyl ester
Tetraethylpyrophosphate (TEPP)
Heptenophos
N,N-Diethyl-m-toluamide
Chlorfenprop-methyl

List C1. Analytes in the 1533 screen (Continued)

Omethoate
Diethyl phthalate
Tecnazene
Thionazin
Propachlor
4,6-Dinitro-o-cresol (DNOC)
Dichlorprop methyl ester
Demeton-S-methyl
Diphenylamine
Azobenzene
Benzophenone
Cycloate
Ethoprophos
2,4-D methyl ester
Fenuron
Tributyl phosphate
Dicamba
Chlorpropham
2-[3-Chlorophenoxy]propiona...
Chlordimeform
2,3,5-Trimethacarb
Ethalfluralin
Dicrotophos
Thiofanox
Bromoxynil
Bendiocarb
Trifluralin
Benfluralin
Monocrotophos
Sulfotep
Tebutam
Desbromo-bromobutide
Promecarb
Di-allate I
Phorate
Triclopyr methyl ester
BHC alpha isomer
Methyl-1-naphthalene acetate
Di-allate II
Thiometon
Hexachlorobenzene
Desmedipham
Dazomet
Dicloran
Pentachloroanisole
Demeton-S
Diethyl dithiobis(thionofor...
Dimethoate
Atraton
Dichlorprop
3,4,5-Trimethacarb
Ethoxyquin
Simazine
Prometon
Carbofuran
Swep
Chlorbufam
Dimethipin
Atrazine
BHC beta isomer
Clomazone
Fenoprop methyl ester
Propazine
Cyromazine
Lindane
Terbumeton
Chloramben methyl ester
N-Methyl-N-1-naphthyl aceta...
Isocarbamide
Aminocarb
Cycluron
Di-n-propyl phthalate
Pentachloronitrobenzene
Cyanophos
Terbufos
Pyroquilon
Terbuthylazine
Trietazine
Fonofos
Propetamphos
Propyzamide
2,4,5-T methyl ester
MCPB methyl ester
Profluralin
Dinoterb
Pyrimethanil
Pindone
Dichlone
Phosphamidon I
Diazinon
BHC delta isomer
Disulfoton
Dinoseb
Methyl paraoxon
Fenfuram
Fluchloralin
2,4-D sec-butyl ester
Secbumeton
Terbacil
Chlorothalonil
Dinitramine
Tri-allate
Isazophos
Carbofuran-3-keto
Etrimfos
Bromocyclen
Isobornyl thiocyanoacetate
Sebuthylazine
Oxabetrinil
Endosulfan ether
Iprobenfos
Monalide
Metobromuron
Pentachloroaniline
Formothion
2,4-DB methyl ester
Ethiofencarb
Furmecyclox
Pirimicarb
Dinoseb methyl ether
Butoxycarboxim
N-1-Naphthylacetamide
Dioxacarb
Benfuresate
Desmetryn
Chlorthiamid
Propanil
Dichlofenthion
Dimethachlor
Cyprazine
Phosphamidon II
Bromobutide
Metribuzin
Prothoate
Bentazone methyl derivative
Acetochlor
Fuberidazole
Methyl parathion

List C1. Analytes in the 1533 screen (Continued)

Chlorpyrifos Methyl
Vinclozolin
Plifenat
Terbucarb
Chloranocryl
3-Hydroxycarbofuran
Heptachlor
Carbaryl
Tolclofos-methyl
Simetryn
Fenoprop
Malathion-o-analog
Alachlor
Isoproturon
Ametryn
Flurenol-methylester
Dimetilan
Tridiphane
Fenchlorphos
Oxydemeton-methyl
Metalaxyl
Paraoxon
Prometryn
Dinoseb acetate
2-(1-naphthyl)acetamide
Demeton-S-methylsulfon
Tycor (SMY 1500)
Picloram methyl ester
Ioxynil
Dinoterb acetate
Terbutryn
Methiocarb
Fenitrothion
Dithiopyr
Quinoclamine
Linuron
Pentanochlor
Esprocarb
Pirimiphos-methyl
Ethofumesate
Probenazole
Bromacil
Chlorotoluron
Dichlofluanid
Di-n-butylphthalate
9,10-Anthraquinone

Aldrin
Amidithion
Benthiocarb
Dipropetryn
Oxamyl
Malathion
Metolachlor
Kinoprene
Fenthion
Diethofencarb
Dimethylvinphos(Z)
4,4'-Dichlorobenzophenone
Tetrapropyl thiodiphosphate
Chlorpyrifos
Fepropimorph
Parathion
Isomethiozin
Cyanazine
Triadimefon
Dicapthon
Isobenzan
Chlorthal-dimethyl
Methfuroxam
Carbetamide
Tiocarbazil I
Fenson
Tiocarbazil II
Bentazone
Chlorthion
Phthalide
Trichloronat
Nitrothal-isopropyl
Drazoxolon
Crufomate
Dodemorph I
Flurochloridone I
Sulfur (S8)
Pyracarbolid
Isodrin
Bromophos
Flurochloridone II
Naphthalic anhydride
Diphenamid
Butralin
Endosulfan lactone
Octachlorostyrene

Pirimiphos-ethyl
Heptachlor exo-epoxide isom...
Isopropalin
Oxychlordane
Dodemorph II
Metazachlor
Methoprene I
Mefluidide
Thiabendazole
Benazolin-ethyl
Anilazine
Chlorbromuron
Pendimethalin
Penconazole
Dimethametryn
Tributyl phosphorotrithioite
Phosfolan
Captan
Tolylfluanid
Pyrifenox I
Methyldymron
Diuron
Mephosfolan
Chlozolinate
Chlorfenvinphos
Folpet
Isofenphos
Pyridinitril
Quinalphos
Triadimenol
Phenthoate
Mecarbam
Bioallethrin S-cyclopenteny...
Chlorbenside
Bioallethrin
Chinomethionat
Furalaxyl
Procymidone
Dinobuton
trans-Chlordane
Chlorflurecol-methyl ester
Flurenol-butyl ester
Crotoxyphos
Methidathion
Methoprene II
Triflumizole

List C1. Analytes in the 1533 screen (Continued)

o,p'-DDE
Bromophos-ethyl
Paclobutrazol
Endosulfan (alpha isomer)
Pyrifenox II...
Vamidothion
cis-Chlordane
Tetrachlorvinphos
2,4-Dichlorophenyl benzenes...
TCMTB
Flutriafol
Ditalimfos
Butachlor
Chlorfenson
Flumetralin
Napropamide
Diamyl phthalate
Hexaconazole
Jodfenphos
Butamifos
Tricyclazole
Fenamiphos
Diethatyl ethyl
Fluorodifen
Prothiofos
Imazalil
Flutolanil
Bisphenol A
Dieldrin
Isoprothiolane
Profenofos
Uniconizole-P
p,p'-DDE
Barban
S,S,S-Tributylphosphorotrit...
Pretilachlor
Carboxin
o,p'-DDD
Flubenzimine
Diclobutrazol
Myclobutanil
Oxadiazon
Metamitron
Azaconazole
Flamprop-methyl
Buprofezin
Flusilazole
Methoprotryne
Tryclopyrbutoxyethyl
Nitrofen
Erbon
Isoxathion
Ancymidol
Endosulfan (beta isomer)
Perthane
Binapacryl
Fluazifop-p-butyl
Acifluorfen methyl ester
Chlorobenzilate
Chloropropylate
Fensulfothion
Fenthion sulfoxide
Diniconazole
Cyprofuram
p,p'-DDD
Methiocarb sulfoxide
Etaconazole
o,p'-DDT
Flamprop-isopropyl
Oxadixyl
Endrin aldehyde
Methiocarb sulfone
Triamiphos
Benodanil
Ethion
Chlordecone
Tetrasul
Chlorthiophos
Fenazaflor
Mepronil
Sulprofos
Triazophos
Chlornitrofen
2,3,7,8-Tetrachlorodibenzof...
Carbophenothion
Famphur
Benalaxyl
Edifenphos
Endosulfan sulfate
Cyanofenphos
Bromoxynil octanoic acid ester
Lenacil
Propiconazole-I
Diethylstilbestrol
Norflurazon
Hexestrol
p,p'-DDT
Butyl benzyl phthalate
Pyrazon
2,3,7,8-Tetrachlorodibenzo-...
Propiconazole-II
Piperalin
Hexazinone
Tebuconazole
Nuarimol
Thenylchlor
Captafol
Diclofop methyl
Fluroxypyr-1-methylheptyl e...
Propargite
Diflufenican
Oxycarboxin
Dinocap I
Piperonyl butoxide
Resmethrin
Bioresmethrin
Epoxiconazole
Fluotrimazole
Nitralin
Endrin ketone
Dinocap II
Pyributicarb
Benzoylprop ethyl
Iprodione
Dichlorophen
Hexabromobenzene
Phosmet
Pyridaphenthion
Leptophos oxon
Chlorthiophos sulfoxide
Menazon
Tetramethrin I
Bromopropylate
Dinocap III
EPN
Carbosulfan
Fenoxycarb
Tetramethrin II

List C1. Analytes in the 1533 screen (Continued)

Bifenthrin
Piperophos
Methoxychlor
Phenkapton
Dinocap IV
Fenpropathrin
Bifenox
Dicyclohexyl phthalate
Chlorthiophos sulfone
Tetradifon
d-(cis-trans)-Phenothrin-I
d-(cis-trans)-Phenothrin-II...
Furathiocarb
Bis(2-ethylhexyl)phthalate
Azinphos-methyl
Phosalone
Leptophos
Mirex
Mefenacet
Amitraz
Cyhalothrin I (lambda)
Fenarimol
Azinphos-ethyl
Pyrazophos
b-Estradiol
Isoxaben
Dialifos
Bitertanol I
Oryzalin
Bitertanol II...
Permethrin I
Pyridaben
Permethrin II
17a-Ethynylestradiol
Coumaphos
Prochloraz
Tamoxifen
Dioxathion
Fenbuconazole
Cyfluthrin I
Cyfluthrin II
Cyfluthrin III
Cyfluthrin IV
Cypermethrin I
Cypermethrin II.
Quizalofop-ethyl
Cypermethrin III
Cypermethrin IV
Flucythrinate I
Benzo(a)pyrene
Hexachlorophene
5,7-Dihydroxy-4'-methoxyiso...
Flucythrinate II.
Fluridone
2-Hydroxyestradiol
Pyridate
Fenvalerate I
Fenvalerate II
Esfenvalerate
Fluvalinate-tau-I
Fluvalinate-tau-II
Difenoconazol I
Difenoconazol II
Deltamethrin
Temephos
Phenol
2-Chlorophenol
1,3-Dichlorbenzene
3-Trifluormethylaniline
Triethylphosphate
2-Nitrophenol
4-Chlorophenyl isocyanate
2,4-Dimethylphenol
Naphthalene
3-Chloro-4-fluoroaniline
4-Isopropylaniline
Carvone
2-ethyl-6-methylaniline
Profenofos metabolite (4-Br...
3-Aminophenol
4-Chloro-3-methylphenol
Thymol
4-Chloro-2-methylaniline
2,4,5-Trimethylaniline
4-Bromoaniline
Carbofuran-7-phenol
Diuron Metabolite [3,4-Dich...
Promecarb artifact [5-isopr...
2,4,6-Trichloroanisole
Eugenol
2,3,6-Trichloroanisole
Indoxacarb and Dioxacarb de...
1,3,5-Tribromobenzene
3-Chloro-4-methoxyaniline
Acenaphthylene
Phthalimide
Tetrahydrophthalimide, cis-...
Acenaphthene
Cashmeran
1-naphthalenol
Tebuthiuron
4-Nitrophenol
XMC (3,4-Dimethylphenyl N-m...
Amitraz metabolite [Methani...
2,4,5-Trichloroaniline
Benzenesulfonamide
Benzene, 1,3-bis(bromomethyl)-
XMC (3,5-Dimethylphenyl N-m...
Tolyltriazole [1H-Benzotria...
Benzoximate metabolite
Fluorene
2-Methyl-4,6-dinitrophenol
Phorate-oxon
2,4,6-Tribromoanisole
2,4,5,6-Tetrachloro-m-xylene
Chlorethoxyfos
Dichlofluanid metabolite (D...
Naled
Methabenzthiazuron [decompo...
Atrazine-desethyl
2,3,4,5-Tertrachloronitrobe...
Dioxabenzofos
2,6-Dichlorobenzamide
Terbuthylazine-desethyl
Cadusafos
Sulfallate
Fenclorim
Celestolide
Fluoroimide
Empenthrin IV
Empenthrin V
Schradan
Fenazaflor metabolite
4-Aminodiphenyl

List C1. Analytes in the 1533 screen (Continued)

Sebuthylazine-desethyl
Tolylfluanid metabolite (DMST)
Tris(2-chloroethyl) phosphate
Phantolide
Benzyl benzoate
Bufencarb
Phenanthrene-d10
Phenanthrene
Diazinon-oxon
Anthracene
Chlordene, trans-
3-Indolylacetonitrile
Cyclopentadecanone
Aziprotryn metabolite [2-Am...
BHC epsilon isomer
Tefluthrin, cis-
Exaltolide [15-Pentadecanol...
Azoxybenzene
Musk amberette
Methyl (2-naphthoxy)acetate
Cyclafuramid
Caffeine
Tebupirimifos
Benoxacor
Traseolide
Tridemorph , 4-tridecyl-
p,p'-DDM [bis(4-chloropheny...
Fenchlorphos-oxon
Silthiopham
Theobromine
Diisobutyl phthalate
4-Nonylphenol
Musk xylene
Tonalide
Hydroprene
Fenitrothion-oxon
Ethofumesate, 2-Keto
Dimethenamid
Flurprimidol
Spiroxamine I
Musk Moskene
Dipropyl isocinchomeronate
Azibenzolar-S-methyl
Simeconazole
Cymiazole
Flurochloridone, deschloro-
Transfluthrin
Propisochlor
Propargite metabolite [Cycl...
Bis(2,3,3,3-tetrachloroprop...
Fipronil, Desulfinyl-
Prosulfocarb
2,4'-Dichlorobenzophenone (...
Fenpropidin
Orbencarb
Musk Tibetene (Moschustibeten)
Spiroxamine II
Quintozene metabolite (pent...
Bifenazate metabolite (5-Ph...
Triapenthenol
Prodiamine
Phorate sulfoxide
Terbufos-oxon-sulfone
Difenoxuron
Phorate sulfone
Sulfanilamide
Musk Ketone
Thiazopyr
Rabenzazole
Isocarbophos
Flufenacet
Isofenphos-oxon
Isoxaflutole
Tetraconazole
Fosthiazate I
Ethidimuron
Fosthiazate II
Cyprodinil
Phenothiazine
Chlorbicyclen
Fluoranthene
Terbufos-sulfone
Chlorfenvinphos, cis-
Fipronil-sulfide
Dimepiperate
Irgarol
Chlorfenvinphos, trans-
Fluazinam
MCPA-butoxyethyl ester
Fipronil
Zoxamide decomposition product
Beflubutamid
Triclosan
Pyrene
DDMU [1-Chloro-2,2-bis(4'-c...
4,4'-Oxydianiline
Prallethrin, cis-
Benzidine
Propaphos
Prallethrin, trans
Fenothiocarb
Trichlamide
Haloxyfop-methyl
Triclosan-methyl
Disulfoton sulfone
Nonachlor, trans-
Mepanipyrim
Bromfenvinphos-(E)
Triazamate
Bromfenvinphos-(Z)
Picoxystrobin
Fluazolate
Metominostrobin (E)
Fludioxonil
Fensulfothion-oxon
Prothioconazole-desthio
Iprovalicarb I
Aramite I
p,p'-Dibromobenzophenone
Toxaphene Parlar 26
Imazamethabenz-methyl I
Endrin
Fipronil-sulfone
Bupirimate
Thifluzamide
Metominostrobin (Z)
Cyproconazole
Kresoxim-methyl
Iprovalicarb II
Fensulfothion-oxon -sulfone
Aramite II
Imazamethabenz-methyl II
Carpropamid
Chlorfenapyr
Cyflufenamid

List C1. Analytes in the 1533 screen (Continued)

Fenoxanil
ortho-Aminoazotoluene
Nonachlor, cis-
Fenthion-sulfone
Aclonifen
Pyriminobac-methyl (Z)
fensulfothion-sulfone
Chlorbenside sulfone
Isoxadifen-ethyl
Ofurace
Pyrethrin I
Quinoxyfen
Methoxychlor olefin
Diofenolan I
Fenhexamid
Di-n-hexyl phthalate
Carfentrazone-ethyl
Diofenolan II -...
Clodinafop-propargyl
Trifloxystrobin
Pyraflufen-ethyl
Pyriminobac-methyl (E)
Triphenyl phosphate
Toxaphene Parlar 50
Tris(2-butoxyethyl) phosphate
Resmethrine II
Zoxamide
Mefenpyr-diethyl
Fenpiclonil
Spiromesifen
Benzo(a)anthracene
Fenamiphos sulfoxide
Bromuconazole I
Sudan I
Chrysene
Fenamiphos-sulfone
Ethoxyfen-ethyl
Dimoxystrobin
Tris(2-ethylhexyl) posphate
Bis(2-butoxyethyl) phthalate
Picolinafen
Cloquintocet-mexyl
o-Dianisidine
Etoxazole
Sulfentrazone
Metconazole I

Fenamidone
Fenazaquin
Tebufenpyrad
Bromuconazole II..
Anilofos
Fenchlorazole-ethyl
Phenothrin I
Toxaphene Parlar 62
Phenothrin II
Diphenyl phthalate
Potasan
Flurtamone
Pyriproxyfen
Cyhalofop-butyl
Naproanilide
Ioxynil octanoate
Trifenmorph
Lactofen
Pyriftalid
Acrinathrin
Fluoroglycofen-ethyl
Benfuracarb
Tricresylphosphate, ortho-
Pyraclofos
Metrafenone
Fenoxaprop-ethyl
Tricresylphosphate, meta-
Spirodiclofen
Sudan II
Tricresylphosphate, para
Fluquinconazole
Di-n-octyl phthalate
2,4,5-Trichloro-p-terphenyl
Butafenacil
Benzo[b]fluoranthene
Cafenstrole
2,3,5,6-Tetrachloro-p-terph..
Fluoxastrobin cis-
Boscalid (Nicobifen)
Halfenprox
Cekafix
Ethofenprox
Acequinocyl
Silafluofen
Pyrimidifen
Di-n-nonyl phthalate

Flumiclorac-pentyl
Azoxystrobin
Famoxadon
Dimethomorph-(Z)
Tolfenpyrad
Dimethomorph-(E)
Indeno[1,2,3-cd]pyrene
Dibenz[a,h]anthracene
Cinidon-ethyl
Benzo[g,h,i]perylene
Rotenone
Spiroxamine metabolite (4-t..
Tolyltriazole [1H-Benzotria..
Benzo[k]fluoranthene
Ipconazole
Triticonazole
Metconazole II
Norflurazon, Desmethyl-
Empenthrin I
Empenthrin II
Empenthrin III
Diphacinone
Pyrazoxyfen
Fenobucarb
Propoxur
Cymoxanil
Fluometuron
Monolinuron
Aziprotryne
Chlorfenethol
Oxyfluorfen
Azamethiphos
acetamiprid
Cyphenothrin cis-
Cyphenothrin trans-
Sudan Red
Fluthiacet-methyl
Diclocymet I
Diclocymet II
p,p'-Dicofol
Fluacrypyrim
Flumioxazin
Furilazole
Cyhalothrin (Gamma)
Imibenconazole
Imibenconazole-desbenzyl

List C1. Analytes in the 1533 screen (Continued)

Prohydrojasmon I
Prohydrojasmon II
Jasmolin I
Cinerin I
Cinerin II
Jasmolin II
Pyrethrin II
Heptachlor epoxide isomer A
Dimethylvinphos(E)
5,12-Napthacenequinone
9-Fluorenone-D8
1,4-Anthraquinone
Benzanthrone
9-Fluorenone
Acenapthenequinone
4H-cyclopenta[def]phenanthr..
9,10-phenthrenequinone
Phenanthrene-1,4-dione
9,10-Anthraquinone-d8
Benzofluorenone
7,12-benz[a]anthracenquinone
Chrysene-d12
Benzo[c]phenanthrene-[1,4]q..
1,6-Benzo(a)pyrene-quionone
Benzo(cd)pyrenone
Aceanthracenequinone
Naphthalene-D8
2-Methylnaphthalene
1-Methylnaphthalene
1,6-Dimethylnaphthalene
Acenaphthylene-D8
1,2-Dimethylnaphthalene
Dibenzothiophene
Retene
1-Methylpyrene
6-Methylchrysene
Dibenzo(a,l)pyrene
Fluoranthene-D10
Pyrene-D10
Benzo(a)pyrene-D12
Benzo[ghi]perylene-D12
Perylene-D12
1-Nitronaphthalene
2-Nitronaphthalene
3-Nitrobiphenyl
4-Nitrobiphenyl
5-Nitroacenaphthene
2-Nitrofluorene
9-Nitroanthracene
9-Nitrophenanthrene
3-Nitrophenanthrene
2-Nitroanthracene
3-Nitrofluoranthene
1-Nitropyrene
2-Nitropyrene
7-Nitrobenz[a]anthracene
6-Nitrochrysene
3-Nitrobenzanthrone
1,3-Dinitropyrene
1,6-Dinitropyrene
1,8-Dinitropyrene
6-Nitrobenzo[a]pyrene
5-Nitroacenaphthene-D9
2-Nitrofluorene-D9
1-Nitropyrene-D9
6-Nitrochrysene-D11
2-Nitrobiphenyl
2-Methylanthracene
1-Methylphenanthrene
p,p' DDE-D8
PCB 77-D6
Acenaphthene-D10
2-Ethylnaphthalene
2,6-Dimethylnaphthalene
1,4-Dimethylnaphthalene
1,5-Dimethylnaphthalene
1,8-Dimethylnaphthalene
2,6-Diethylnaphthalene
2-Methylphenanthrene
9-Methylanthracene
3,6-Dimethylphenanthrene
2,3-Dimethylanthracene
9,10-Dimethylanthracene
Benzo(c)fluorene
Cyclopenta(c,d)pyrene
7,12-Dimethylbenz(a)anthracen
Benzo(j)fluoranthene
Benzo(e)pyrene
Picene
Anthanthrene
Dibenzo(a,e)fluoranthene
Coronene
Dibenzo(a,e)pyrene
Dibenzo(a,i)pyrene
Dibenzo(a,h)pyrene
Triphenylene
Benzo(a)fluorene
Benzo(b)fluorene
5-Methylchrysene
Benz[j]+[e]aceanthrylene
Naphtho[1,2-b]fluoranthene
Naphtho[2,3-j]fluoranthene
Naphtho[2,3-k]fluoranthene
Naphtho[2,3-e]pyrene
Dibenzo(e,l)pyrene
Naphtho[2,3-a]pyrene
Benzo(b)perylene
PBB-001
PBB-002
PBB-003
PBB-004
PBB-007
PBB-009
PBB-010
PBB-015
PBB-018
PBB-026
PBB-029
PBB-030
PBB-031
PBB-049
PBB-052
PBB-053
PBB-077
PBB-080
PBB-101
PBB-103
PBB-114
PBB-137
PBB-141
PBB-153
PBB-155
PBB-156
PBB-159
PBB-169
PBB-180
PBB-189
PBB-200

List C1. Analytes in the 1533 screen (Continued)

PBDE-001	PBDE-088	1,2,5,6,9,10-Hexabromocyclo..
PBDE-002	PBDE-089	1,2-Bis(2,4,6-tribromopheno..
PBDE-003	PBDE-103	Dibenzo-p-dioxin
PBDE-10	PBDE-108	1,4-Dioxino(2,3,b,5,6,b')di..
PBDE-007	PBDE-115	2-Chlorodibenzo-p-dioxin
PBDE-011	PBDE-127	1-Chlorodibenzo-p-dioxin
PBDE-008	PBDE-128	1,3-Dichlorodibenzo-p-dioxin
PBDE-012	PBDE-142	1,4-Dichlorodibenzo-p-dioxin
PBDE-013	PBDE-144	1,6-Dichlorodibenzo-p-dioxin
PBDE-015	PBDE-155	2,7-Dichlorodibenzo-p-dioxin
PBDE-030	PBDE-160	2,8-Dichlorodibenzo-p-dioxin
PBDE-032	PBDE-185	2,3-Dichlorodibenzo-p-dioxin
PBDE-017	PBDE-201	1,2-Dichlorodibenzo-p-dioxin
PBDE-025	2'-Hydroxy-4-	1,2,4-Trichlorodibenzo-p-di..
PBDE-028	monobromodiphe..	1,2,3-Trichlorodibenzo-p-di..
PBDE-033	2'-Hydroxy-2,4,4'-tribromod..	1,7,8-Trichlorodibenzo-p-di..
PBDE-035	2'-Methoxy-2,4,4'-tribromod..	2,3,7-Trichlorodibenzo-p-di..
PBDE-037	3-Methoxy-2,2',4,4',6-penta..	1,3,6,8-Tetrachlorodibenzo-..
PBDE-075	2-Bromoanisole	1,3,7,9-Tetrachlorodibenzo-..
PBDE-049	3-Bromoanisole	1,3,7,8-Tetrachlorodibenzo-..
PBDE-071	4-Bromoanisole	1,2,6,8-Tetrachlorodibenzo-..
PBDE-047	2,5-Dibromoanisole	1,2,3,4-Tetrachlorodibenzo-..
PBDE-066	2,4-Dibromoanisole	1,2,6,7-Tetrachlorodibenzo-..
PBDE-077	2,3-Dibromoanisole	1,2,7,8-Tetrachlorodibenzo-..
PBDE-100	2,6-Dibromoanisole	1,2,8,9-Tetrachlorodibenzo-..
PBDE-119	3,5-Dibromoanisole	1,2,4,6,8-pentachlorodibenz..
PBDE-118	2,4,5-Tribromoanisole	1,2,4,7,8-Pentachlorodibenz..
PBDE-154	4-Bromophenol	1,2,3,4,7-Pentachlorodibenz..
PBDE-153	3-Bromophenol	1,2,3,7,8-Pentachlorodibenz..
PBDE-099	2,4-Dibromophenol	1,2,3,8,9-Pentachlorodibenz..
PBDE-138	2,5-Dibromophenol	1,2,4,6,8,9-Hexachlorodiben..
PBDE-166	2,6-Dibromophenol	1,2,3,4,7,8-Hexachlorodiben..
PBDE 116	3,5-Dibromophenol	1,2,3,6,7,8-Hexachlorodiben..
PBDE-004	2,3-Dibromophenol	1,2,3,4,6,7-Hexachlorodiben..
PBDE-006	2,4,6-Tribromophenol	1,2,3,7,8,9-Hexachlorodiben..
PBDE-009	2,3,4-Tribromophenol	2,3,7,8-Tetrabromodibenzo-p..
PBDE-019	3-Bromostyrene	1,2,3,4,6,7,9-Heptachlorodi..
PBDE-021	4-Bromostyrene	1,2,3,4,6,7,8-Heptachlorodi..
PBDE-026	Tribromoneopentyl alcohol	1,2,3,4,6,7,8,9-Octachlorod..
PBDE-027	2,4,6-Tribromophenyt allyl ..	Dibenzofuran
PBDE-031	1,2-Dibromo-4-(1,2-dibromoe..	2-Chlorodibenzofuran
PBDE-050	Tetrabromo-o-chlorotoluene	4-Chlorodibenzofuran
PBDE-051	Pentabromotoluene	2,8-Dichlorodibenzofuran
PBDE-062	Pentabromoethylbenzene	3-Nitrodibenzofuran
PBDE-069	1,3,5-Tribromo-2-(2,3-dibro..	2,4,8-Trichlorodibenzofuran
PBDE-085	Tetrabromophthalate diol	1,3,6,8-Tetrachlorodibenzof..

List C1. Analytes in the 1533 screen (Continued)

1,2,3,4-Tetrachlorodibenzof..
1,2,3,7,8-Pentachlorodibenz..
2,3,4,7,8-Pentachlorodibenz..
1,2,3,4,7,8-Hexachlorodiben..
1,2,3,4,6,7,8-Heptachlorodi..
1,2,3,4,6,7,8,9-Octachlorod..
4-Chlorophenyl phenyl ether
4-nitrophenyl phenyl ether
2-chlorophenyl-4-nitropheny..
3-chlorophenyl-4-nitropheny..
4-chlorophenyl-4-nitropheny..
2,6-dichlorophenyl-4-nitrop..
2,5-dichlorophenyl-4-nitrop..
3,5-Dichlorophenyl-4-nitrop..
2,3-Dichlorophenyl-4-nitrop..
3,4-dichlorophenyl-4-nitrop..
2,3,6-Trichlorophenyl-4-nit..
2,3,5-Trichlorophenyl-4-nit..
2,4,5-Trichlorophenyl-4-nit..
2,4-Dibromophenyl-4-nitroph..
3,4,5-Trichlorophenyl-4-nit..
2,3,4-Trichlorophenyl-4-nit..
2,4-Dichlorophenol
4-Chlorophenol
2,6-Dichlorophenol
4-Chloroguaiacol
2,4,6-Trichlorophenol
2,4,5-Trichlorophenol
3,4-Dichlorocatechol
3,4-Dichloroguaiacol
4-Chlorocatechol
4,6-Dichloroguaiacol
4,5-Dichloroguaiacol
6-Chlorovanillin
2,3,4,6-Tetrachlorophenol
3,4,6-Trichloroguaiacol
5-Chlorovanillin
Pentachlorophenol
2-Chlorosyringaldehyde
5,6-Dichlorovanillin
Tetrachloroguaiacol
Trichlorosyringol
2,6-Dichlorosyringaldehyde
Tri(2-chloroisopropyl)phosp..
Galaxolide
Zinc diethyldithiocarbamate
Nickel dibutyl dithiocarbamat
1-naphthylamine
linalool
benzothiazole
2-(4-chlorophenyl)benzothia..
2-benzothiazolyl sulfide
indole
benzotriazole
2-methyl-9,10-anthraquinone
N-cyclohexyl-2-benzothazoly..
butylated hydroxy toluene
2-mercaptobenzothiazole
2-(morpholinothio)benzothia..
4-(2-benzothiazolyldithio)m..
2-ethylphenol
2,3,5-trimethylphenol
3-ethylphenol
2,6-di-tert-butyl-methoxyph..
3,5-dimethylphenol
propenyl guaethol
4-isopropylphenol
3-tert-butylphenol
2,6-dimethoxyphenol
2-naphthylamine
carbazole
2,4,6-tri-tert-butylphenol
4-hydroxybiphenyl
drometrizole
n-phenyl-2-naphthylamine
2,4-dinitroaniline
3-nitroaniline
2-nitroaniline
2-bromo-4,6-dinitroaniline
4-nitroaniline
2-chloro-4-nitroaniline
2-chloroaniline
2-chloro-4,6-dinitroaniline
4-chloro-2-nitroaniline
2,6-dibromo-4-nitroaniline
2-isopropylaniline
2,5-dichloroaniline
p-toluidine
m-toluidine
3,5-dimethylaniline
2,4-dichloroaniline
3,4-dimethylaniline
2,4,6-trichloroaniline
2,6-diisopropylaniline
N-phenyl-1-naphthylamine
4,4'-methylenedianiline
o-toluidine
2-ethylaniline
2,6-diethylaniline
2,5-dimethylaniline
2,3-dimethylaniline
2,5-dichlorophenol
2-bromophenol
d-limonene
citral B
citral A
b-citronellol
hydroxy citronellal
b-ionone
geraniol
farnesol I
farnesol II
farnesol III
farnesol IV
amylcinnamyl alcohol
amyl cinnamal
methyl eugenol
coumarin
benzyl salicilate
isoeugenol
anisyl alcohol
cinnamyl alcohol
a-ionone
benzyl cinnamate
benzyl alcohol
Ethylene brassylate
Lyral
lilial
cinnamal
Methyl 2-octynoate
4-ethoxyphenol
4-n-octylphenol
bisphenol Z
4-hydroxy-3-chlorobiphenyl
bisphenol E
4-chloro-2-methylphenol
bisphenol AF
3,4,5-trichlorophenol

List C1. Analytes in the 1533 screen (Continued)

3-nitrophenol	4-aminophenol	2,4,6-triiodophenol
2,5-dimethylphenol	N,N-diethyl-3-aminophenol	2,4-dichloro-3,5-dimethylph..
2-(1-methylbutyl)phenol	4-methoxyphenol	4-chloro-3,5-dimethylphenol
3,4-dimethylphenol	4-ethylphenol	2,4-bis(alpha,alpha-dimethy..
2,6-di-tert-butylphenol	4-tert-butylphenol	4-amino-2,6-dichlorophenol
2,3,6-trimethylphenol	2-chloro-5-methylphenol	2-nitro-p-cresol
2-propylphenol	2,3-dimethylphenol	2-sec-butylphenol
2,6-dimethylphenol	2,4-di-tert-amylphenol	2,6-di-t-butyl-4-dimethylam..
3-methoxyphenol	2-methoxy-4-methylphenol	2-aminophenol
4-butylphenol	2,4-di-tert-butylphenol	2,4,6-trimethylphenol
2-isopropylphenol	2,6-di-tert-butyl-4-ethylph..	3-hydroxybiphenyl
2-ethoxyphenol	4-benzylphenol	3-chlorophenol
4-alpha-cumylphenol	2-amino-4-chlorophenol	guaiacol
3-(dimethylamino)phenol	2-amino-p-cresol	

Appendix D: Supporting Information to Chapter 5 - Silicone wristbands detect individuals' pesticide exposures in West Africa

Table D1. Pesticide identities and physiochemical properties. Compounds were quantified against a 6-point calibration curve unless otherwise noted.

Pesticide compound	*CAS*	*DL*[e] *(ng/g WB)*	*QL*[f] *(ng/g WB)*	*log* K_{oa} [28]	*log* K_{ow} [28]	*MW (Da)*	*WHO Class*[g] [101]
Insecticides							
acetamiprid	135410-20-7	49	730 [b]	8.10 [c]	2.55 [c]	222.7	[d]
aldrin	206-215-8	0.75	11	8.08	6.50	364.9	O
α-BHC	119911-70-5	0.046	0.69	8.84	3.72	290.8	II
β-BHC	319-85-7	0.19	2.9	8.84	3.80	290.8	II
δ-BHC	319-86-8	0.48	7.2	8.84	3.78	290.8	II
bifenthrin	82657-04-3	0.84	13	12.54 [c]	8.15 [c]	422.9	II
chlorobenzilate	510-15-6	2.1	32	10.27 [c]	4.72	325.2	O
α -chlordane	5103-71-9	0.10	1.5	8.92	6.16	409.8	II
γ-chlordane	5566-34-7	0.20	3.0	8.92	6.22	409.8	II
chloropropylate	1437871	3.3	49	10.89 [c]	4.41 [c]	339.2	O
chlorpyrifos	2921-88-2	0.51	7.6	8.88 [c]	4.96	250.6	II
λ-cyhalothrin	91465-08-6	0.55	8.3	11.22 [c]	6.80	449.9	II
cypermethrin	52315-07-8	0.89	13	10.83 [c]	6.60	416.3	II
p,p'-DDT	50-29-3	0.50	7.4	9.82	6.91	354.5	II
deltamethrin	52918-63-5	0.81	12	9.90 [c]	6.20	505.2	II
diazinon	333-41-5	3.5	52	9.15 [c]	3.81	304.3	II
o,p'-dicofol	10606-76-9	0.64	9.6	13.45 [c]	5.81 [c]	370.5	II
p,p'-dicofol	115-32-2	2.6	39	10.03 [c]	5.02	370.5	II
dieldrin	60.57-1	0.16	2.3	8.13	5.40	380.9	O
dimethoate	60-51-5	0.94	14	9.15 [c]	0.78	229.3	II
endosulfan I	959-98-9	0.077	1.2	[d]	3.59 [c]	406.9	II
endosulfan II	33213-65-9	0.18	2.7	8.64	3.83	406.9	II
endrin	72-20-8	0.34	5.0	8.13	5.40	380.9	O
esfenvalerate	66230-04-4	0.72	11	10.97 [c]	6.20	419.9	II
fipronil	120068-37-3	1.2	19	11.46 [c]	4.00	437.1	II
heptachlor	76-44-8	0.71	11	7.64	5.47	373.3	O
imidan (phosmet)	732-11-6	0.24	3.6	9.25 [c]	2.78	317.3	II
isodrin	370-14-9	0.14	2.1	9.74 [c]	1.74 [c]	165.2	O
lindane (γ-BHC)	58-89-9	0.40	6.0	8.84	4.14	290.8	II
malathion/ fenitrothion	121-75-5/ 122-14-5	0.31	4.7	9.06/ 7.72 [c]	2.63/ 3.30	330.4/ 277.2	III/ II
methoxychlor	72-43-5	0.70	11	10.16 [c]	5.08	345.6	U
mirex	2385-85-5	0.51	7.6	8.37 [c]	6.89	545.5	O
trans-nonachlor	39765-80-5	0.056	0.84	9.66	6.35	444.2	[d]
cis-permethrin	61949-76-6	1.7	26	10.17 [c]	6.50	391.3	II
trans-permethrin	51877-74-8	1.1	16	10.62 [c]	6.50	391.3	II
perthane (perthan)	72-56-0	11	161 [a]	8.19 [c]	6.66 [c]	307.3	[d]

Table D1. Pesticide identities and physiochemical properties (Continued)

Pesticide compound	*CAS*	*DL*[e] *(ng/g WB)*	*QL*[f] *(ng/g WB)*	*log* K_{oa} [28]	*log* K_{ow} [28]	*MW (Da)*	*WHO Class*[g] [101]
prophos (ethoprophos)	13194-48-4	2.3	35	8.77 [c]	3.59	242.3	Ia
Herbicides							
alachlor	15972-60-8	0.60	9.0	9.99 [c]	3.52	269.8	II
dacthal (chlorthal-dimethyl)	1861-32-1	0.38	5.7	8.33 [c]	4.28	332.0	III
diallate	2303-16-4	2.2	33 [a]	8.23 [c]	4.49	270.2	O
metolachlor	51218-45-2	1.4	21 [a]	9.33 [c]	3.13	283.8	III
oxadiazon	19666-30-9	5.0	75	10.33 [c]	4.80	345.2	U
pendimethalin	40487-42-1	1.4	20 [a]	18.84 [c]	2.62 [c]	281.3	II
propachlor	1918-16-7	2.4	37	7.61 [c]	2.18	211.7	II
propanil	709-98-8	0.70	10	9.23 [c]	3.07	218.1	II
simazine	122-34-9	4.4	66	9.59 [c]	2.18	201.7	U
trifluralin	1582-09-8	0.63	9.4	7.72 [c]	5.34	335.3	U
Fungicides							
captafol	2425-06-1	49	730 [b]	10.87 [c]	3.80	349.1	Ia
captan	133-06-2	0.26	3.9	9.34 [c]	2.80	300.6	U
chloroneb	2675-77-6	2.2	33	6.81 [c]	3.44 [c]	207.1	O
chlorothalonil	1897-45-6	0.43	6.5	7.14 [c]	3.05	265.9	U
etridiazole	2593-15-9	0.36	5.4	8.31 [c]	3.37	247.5	III
hexachlorobenzene	118-74-1	0.23	3.4	7.38	5.73	284.8	Ia
pentachloronitrobenzene (quintozene)	82-68-8	0.74	11	7.38 [c]	4.64	295.3	U
By-products							
endosulfan sulfate	1031-07-8	0.22	3.2	5.84 [c]	3.66	422.9	[d]
endrin aldehyde	7421-93-4	0.45	6.7	11.20 [c]	5.73 [c]	382.9	[d]
endrin ketone	53494-70-5	2.3	35	11.07 [c]	4.99 [c]	380.9	[d]
heptachlor epoxide	1024-57-3	0.44	6.7	8.05 [c]	4.98	389.3	[d]
p,p'-DDD	72-54-8	0.27	4.0	10.10	6.02	320.0	[d]
p,p'-DDE	72-55-9	0.081	1.2	9.86	6.51	318.0	[d]
Metabolites							
fipronil sulfide	120067-83-6	0.75	11	16.51 [c]	4.82 [c]	421.1	[d]
fipronil sulfone	120068-36-2	0.80	12	18.21 [c]	4.42 [c]	453.1	[d]

[a] 5-point calibration
[b] 4-point calibration
[c] estimate
[d] data not available
[e] Detection limit, determined as described in Table D2
[f] Quantitation limit, determined as described in Table D2
[g] U: unlikely to present acute hazard in normal use. O: believed to be obsolete or discontinued for use as a pesticide. Ia, II, and III: defined as in World Health Organization[101].

Table D2. Chromatographic conditions and methodology.

Injectors	Each 10 µL injector needle was washed with three alternating hexane and acetone aliquots, before and after each sample in order to remove sample carry-over. Injector needles were both set for fast plunger speed.
Inlets	Inlet temperature set at 250°C, and inlets were equipped with 4mm ID liners with a single taper. Inlets were purged after injection at 40 mL/min for 0.75 min.
Carrier gas	Hydrogen carrier gas was used, with a linear flow rate of 72 mL/min.
Columns	Both Agilent DB-XLB and Agilent DB-17MS capillary columns were 30 m in length, 0.25 mm diameter, and a 0.25µm film thickness.
Oven	Hold at 110°C for 0.5 minute, ramp to 150°C at 25°C/min, ramp to 229°C at 6°C/min, ramp to 320°C at 20°C/min, and hold at 320°C for 2.5 minutes.
Detectors	µ-ECDs set to 320 °C with combined column flow and detector make-up gas set to 40 mL/min, where make-up gas was 99.999% nitrogen.
Software	Data analysis was performed using Agilent Chemstation version E.02.00.493.
Confirmation process	The process of confirmation includes identifying the target analyte by comparing the retention time of the peak on both the DB-17MS chromatogram with those peaks in the standard and sample on the second DB-XLB column chromatogram. A confirmed target analyte that has a value above the quantitation level and comparable area (and shape) on both chromatographic columns and appropriate retention times was considered confirmed. By comparing these additional data elements, peak size, shape and retention time for both columns, false identification can be reduced.
Determination of detection and quantitation limits	A low standard, 10 ug/L, was analyzed a minimum of 7 times. Detection limits were calculated as 3 X standard deviation. Quantitation limits were then determined to be 15 X detection limit, reported in Table D1.

Table D3. Spearman's rho coefficients among concentrations of pesticides detected above quantitation limits in at least 2 wristbands. Bold-face values are significant ($p < 0.05$).

	cypermethrin	*λ-cyhalothrin*	*chlorpyrifos*	*esfenvalerate*	*p,p'-DDE*	*p,p'-DDT*	*trans-permethrin*	*malathion/ fenitrothion*	*lindane (γ-BHC)*	*cis-permethrin*	*bifenthrin*	*metolachlor*	*chloroneb*	*dimethoate*	*prophos*	*p,p'-DDD*
deltamethrin	-0.09	0.16	**0.28**	-0.05	-0.03	0.06	0.17	-0.23	0.21	0.22	0.04	0.02	-0.11	**0.24**	-0.19	-0.06
cypermethrin		-0.08	0.15	-0.07	-0.09	-0.13	0.05	**0.38**	0.02	0.02	-0.18	-0.17	-0.07	0.20	0.00	0.17
λ-cyhalothrin			**0.32**	0.01	-0.04	-0.10	**0.25**	-0.09	0.16	0.14	-0.07	-0.05	0.06	0.23	-0.07	-0.14
chlorpyrifos				-0.13	0.16	0.02	0.10	-0.02	0.10	-0.03	-0.04	-0.05	0.02	0.09	-0.16	-0.05
esfenvalerate					0.17	0.21	0.17	-0.05	-0.18	0.03	0.03	-0.02	0.03	-0.05	-0.13	-0.13
p,p'-DDE						**0.37**	0.16	-0.19	0.14	0.03	**0.29**	-0.14	-0.19	-0.19	-0.02	0.05
p,p'-DDT							0.02	-0.18	0.19	**-0.25**	0.01	-0.19	0.00	-0.02	-0.12	0.02
trans-permethrin								-0.01	0.10	**0.81**	0.12	**0.34**	-0.02	0.17	0.09	-0.10
malathion/ fenitrothion									-0.08	-0.15	-0.10	-0.03	-0.13	0.01	0.12	0.12
lindane (γ-BHC)										0.01	0.04	-0.13	-0.12	0.04	0.11	**0.29**
cis-permethrin											0.22	**0.45**	0.03	0.07	0.15	-0.08
bifenthrin												0.23	-0.09	0.10	0.21	-0.06
metolachlor													-0.07	0.17	**0.26**	-0.05
chloroneb														-0.06	-0.04	-0.04
dimethoate															-0.04	-0.04
prophos																**0.49**

Table D4. Spearman correlation analysis of concentrations worn by participants in two sequential periods of up to 5 days. Asterisks indicate significant p-values after Bonferroni adjustment.

	excluding pairs where 1 or both are below detection limit			**including all data**		
	rho	**p-value[a]**	**n**	**rho**	**p-value[b]**	**n**
deltamethrin	0.65*	<0.001	34	0.68*	<0.001	35
cypermethrin	0.74*	<0.001	34	0.68*	<0.001	35
λ-cyhalothrin	0.65*	0.0038	18	0.70*	<0.001	35
chlorpyrifos	0.47	0.1245	12	0.50*	0.0021	35
esfenvalerate	0.74	0.0349	8	0.33	0.0530	35
p,p'-DDE	0.02	0.9554	8	0.33	0.0495	35
p,p'-DDT	-0.20	0.7471	5	0.05	0.7639	35
permethrin	-0.25	0.6228	2	0.56*	0.0004	35
malathion/ fenitrothion	n/a	n/a	2	0.07	0.6962	35
lindane (γ-BHC)	n/a	n/a	1	0.10	0.5782	35
bifenthrin	n/a	n/a	0	-0.12	0.4765	35
metolachlor	n/a	n/a	1	0.38	0.0262	35
chloroneb	n/a	n/a	0	-0.05	0.7648	35
dimethoate	n/a	n/a	1	0.56*	0.0005	35
prophos	n/a	n/a	0	-0.03	0.8668	35

[a] significant after Bonferroni correction at the level $p < 0.006$
[b] significant after Bonferroni correction at the level $p < 0.003$

Table D5. Active ingredients included in the 63-analyte GC-ECD method that are believed to be obsolete or discontinued for use as pesticides, or subject to the Rotterdam or Stockholm Conventions[136; 137].

	Frequency of detection in 70 wristbands	**believed to be obsolete or discontinued for use as pesticides**	**pesticides subject to the Rotterdam Convention**	**prohibited or severely restricted by the Stockholm Convention**
aldrin	0	*	*	*
captafol	0		*	
chlordane	0		*	*
chlorobenzilate	0	*	*	
chloroneb	4	*		
chlorpropylate	0	*		
diallate	0	*		
DDT	23		*	*
dieldrin	0	*	*	*
endrin	0	*		
endosulfan (or by-products)	3		*	*
heptachlor	1	*	*	*
hexachlorobenzene	0		*	*
HCH (mixed isomers)	0		*	*
isodrin	0	*		
lindane	13		*	*
mirex	0	*		

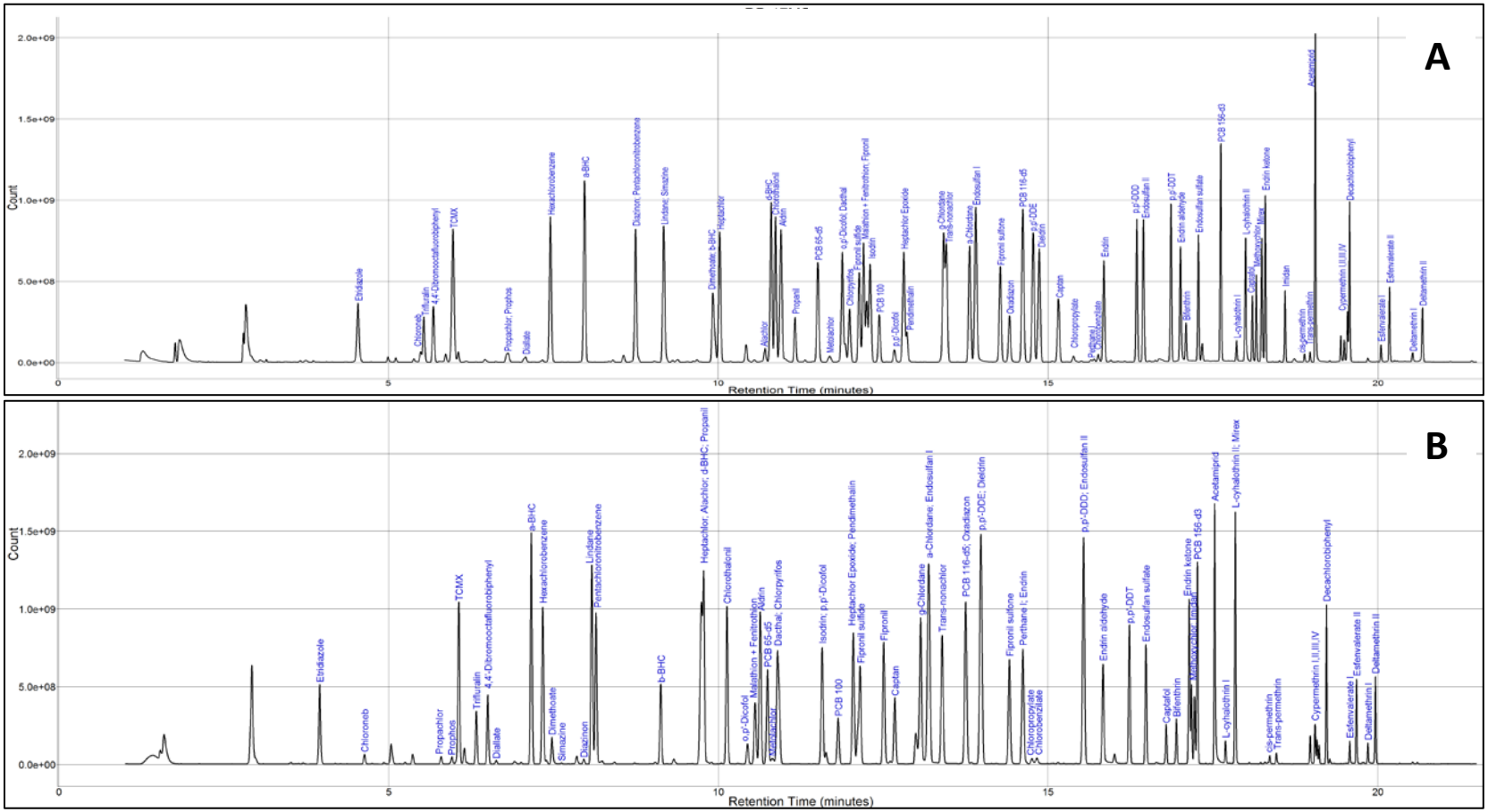

Figure D1. Example 250 µg/L standard chromatograms on 17-MS (A) and XLB (B) columns.

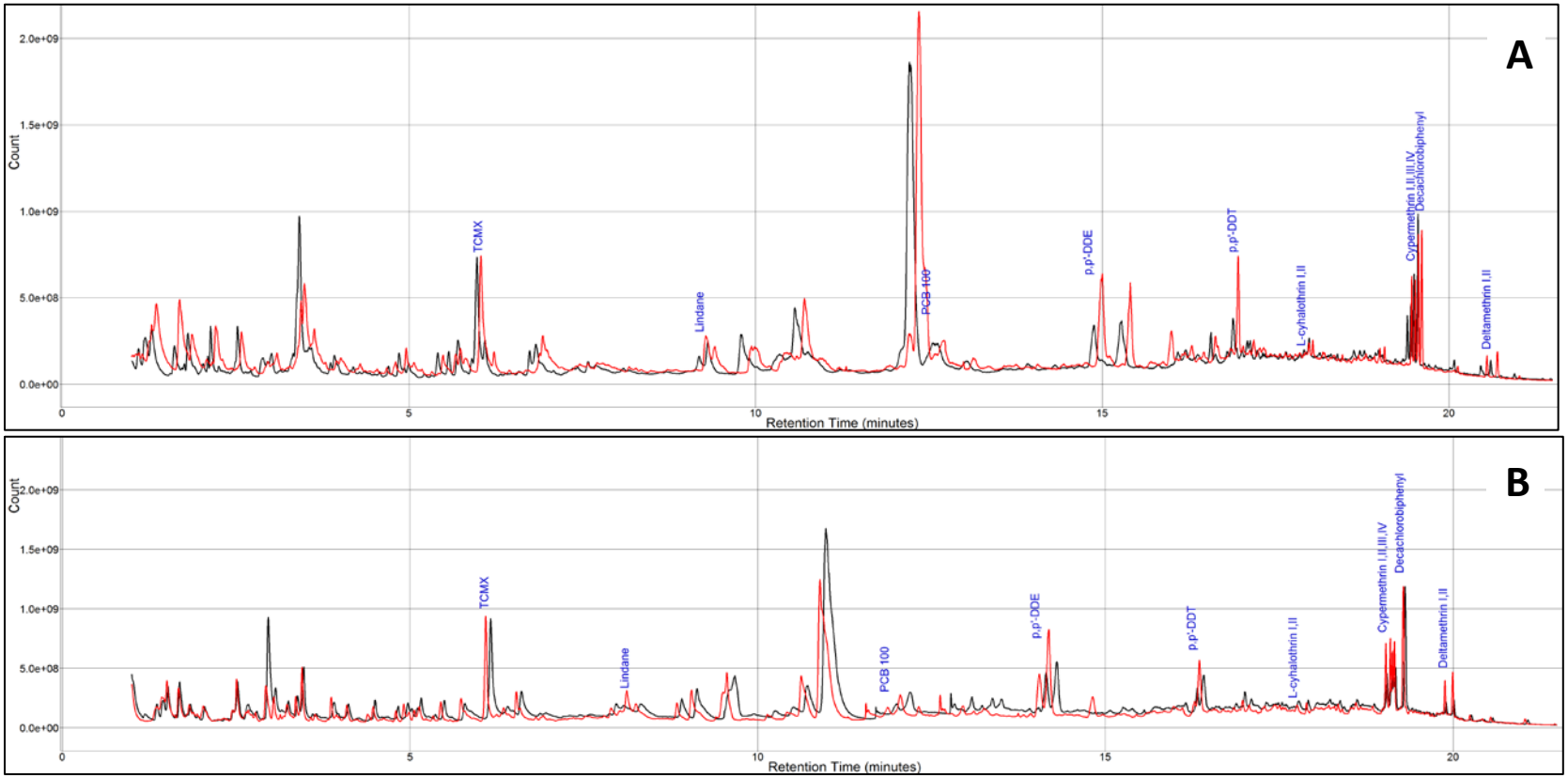

Figure D2. Example wristband sample extracts on 17-MS (A) and XLB (B) columns. The black chromatograms are a wristband sample extracted with TCMX, PCB 100, and decachlorobiphenyl as extraction surrogate standards. The red chromatogram is the sample extract that includes extraction surrogates and standard overspike of lindane, p,p'-DDE, p,p'- DDT, λ-cyhalothrin, cypermethrin, and deltamethrin (800-4,000 µg/L).

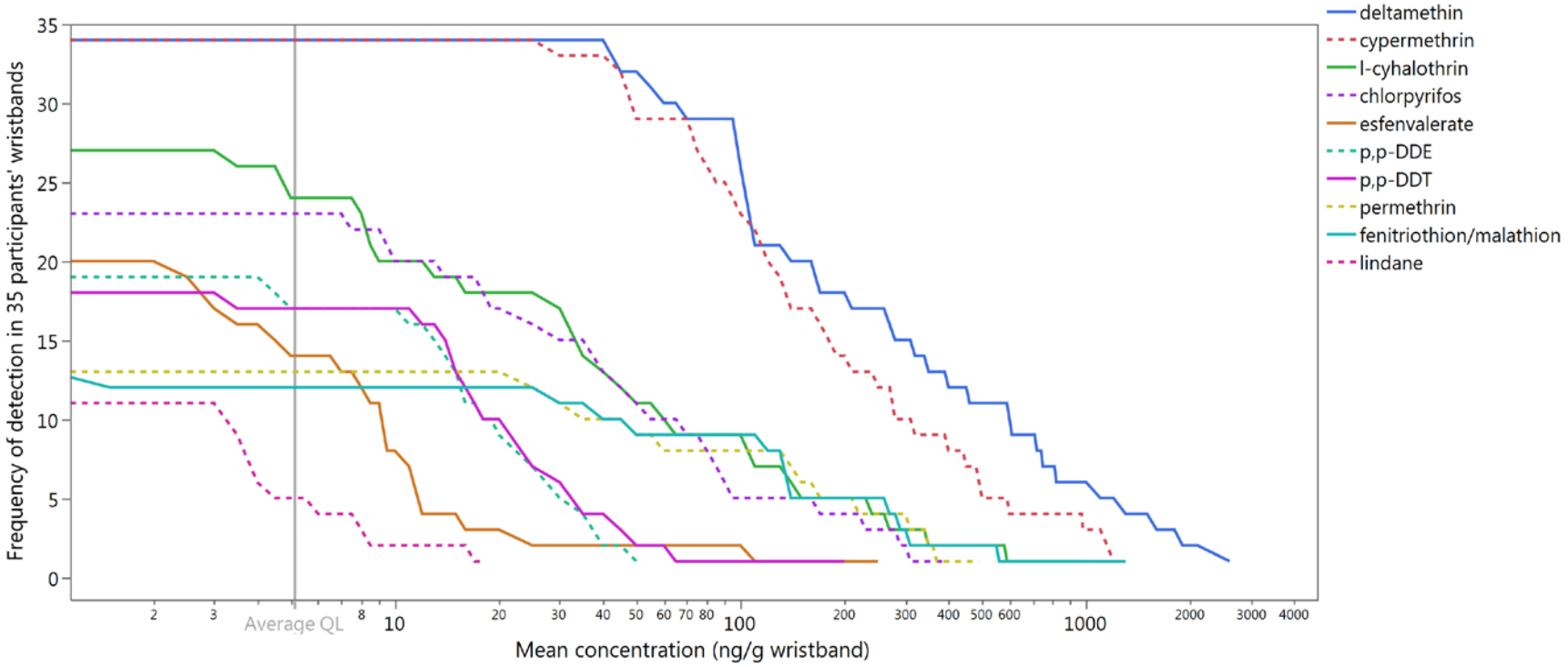

Figure D3. Frequencies of detected pesticides in 35 participants' wristbands by average concentration. Each line represents the frequency that met or exceed a given concentration threshold. Positive detections are counted if detected in at least one of the two wristbands worn. Mean concentration is the average concentration between of 1 and 2. Cypermethrin and deltamethrin were above quantitation limit in at least one wristband for every participant. Average quantitation limit (QL) for these 10 most frequently detected pesticides, 5.1 ng/g wristband is highlighted.

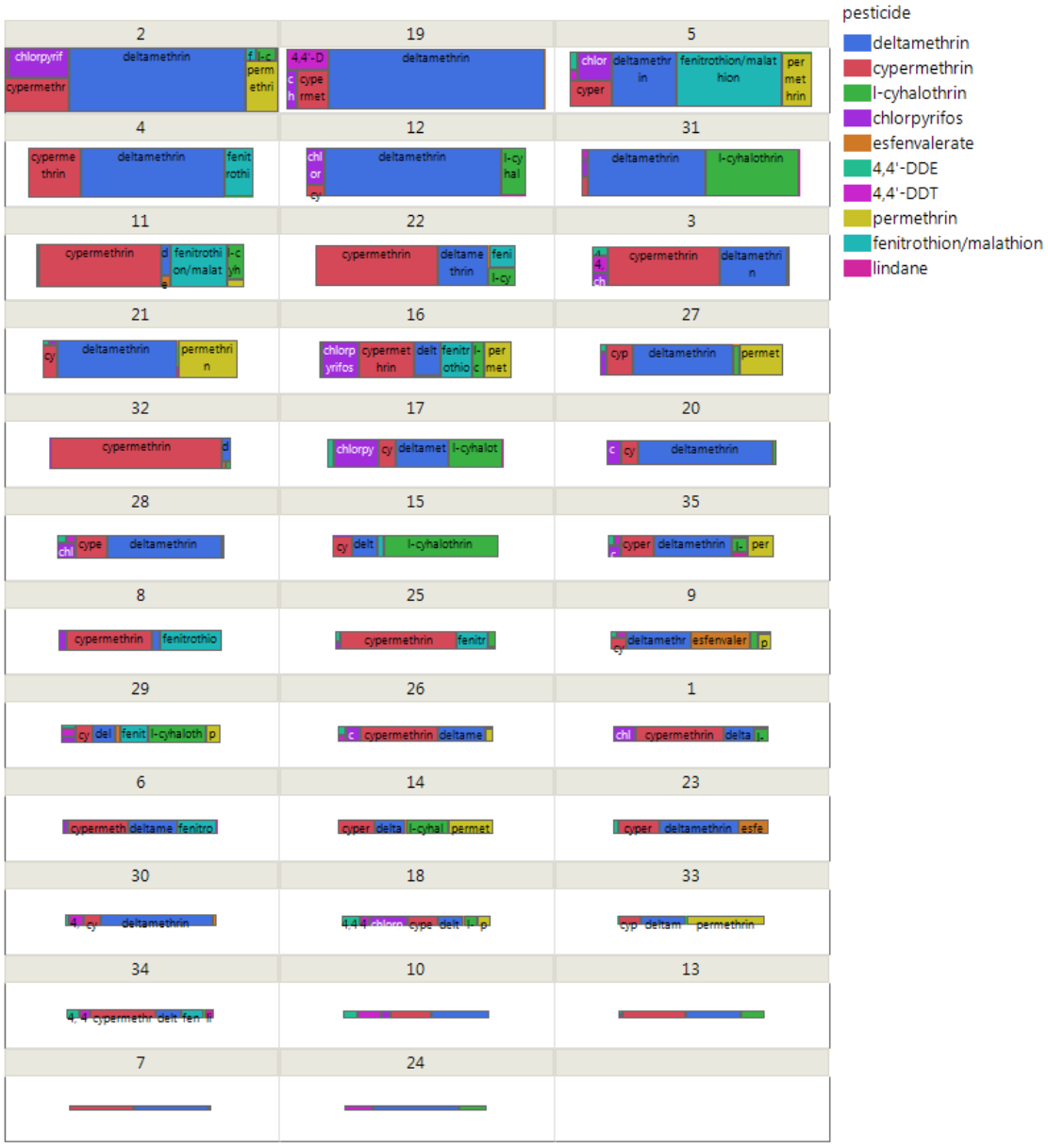

Figure D4. Average concentration of 10 most-frequently detected pesticides by participant. Area is proportional to concentration of pesticides above limit of detection. Participants are ordered by total concentration.

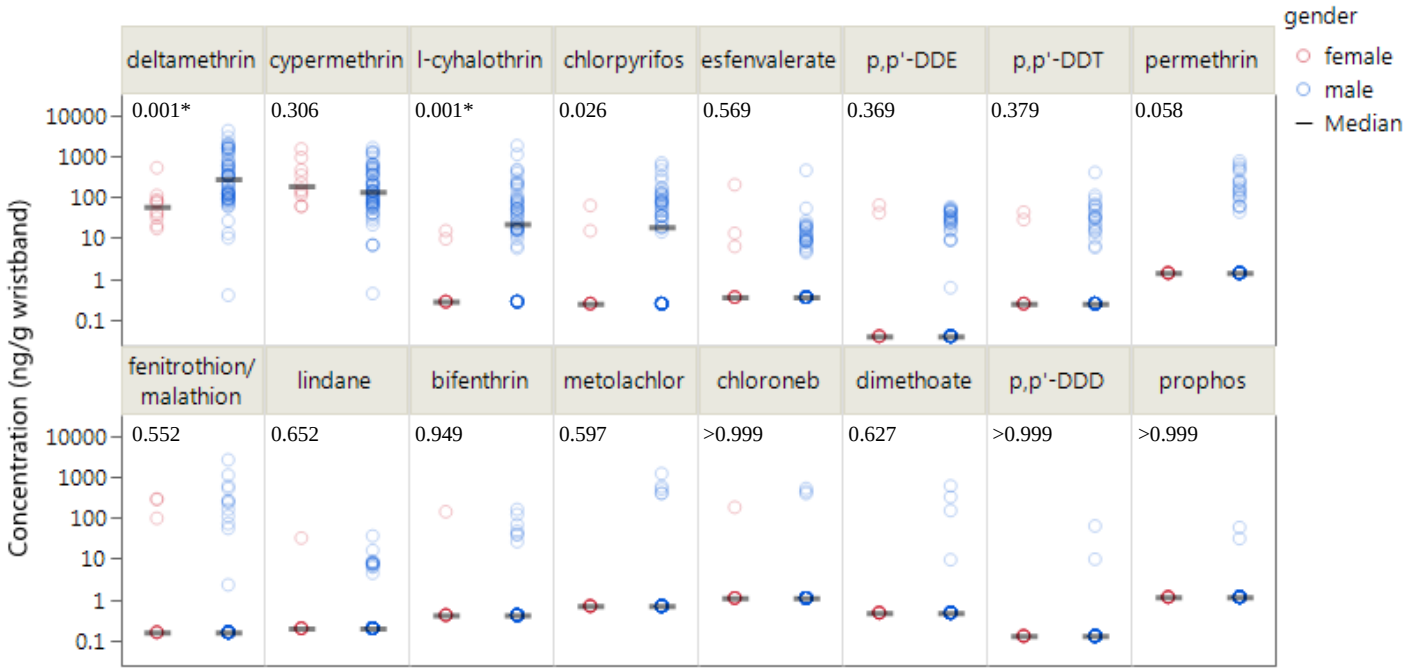

Figure D5. Distribution of pesticide concentrations in 70 wristbands by participant gender. Rank-sum test p-values are given, where * indicates a significant effect of gender on wristband concentration after Bonferroni adjustment (two-sided p-value < 0.003). Compounds are ordered by frequency of detection.

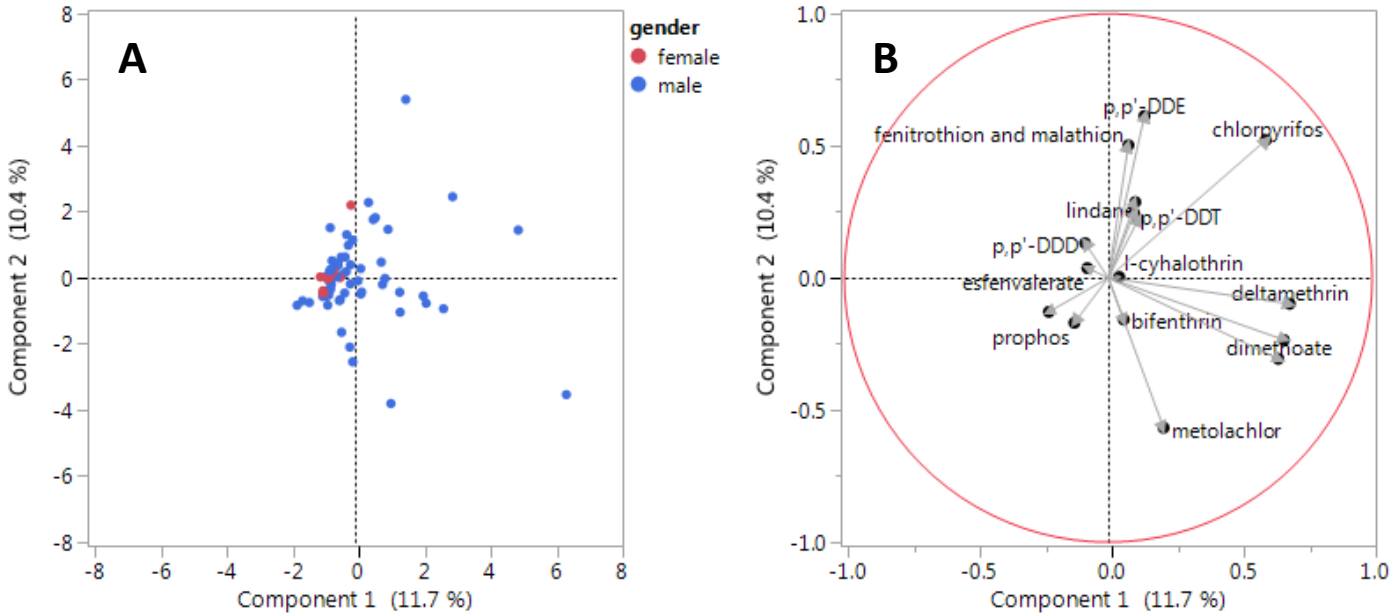

Figure D6. Principal component analysis scatterplot with participant gender designated (A) and pesticide loading plot (B).

Additional pesticides detected in comparison studies in Figure 5.4.

Other pesticides reported in Jepson *et al.*[118], but not in the present GC-ECD method: 2,4-D, acephate, atrazine, azadirachtin, bensulfuron methyl, carbofuran, copper oxychloride, diazinon, dichlorprop, glyphosate, imadacloprid, malathion, maneb, methamidophos, paraquat dichloride, profenofos, sulfur, thiophanate methyl, thiram, and triazophos.

Other pesticides reported in Murphy *et al.*[133], but not in the present GC-ECD method: benzyl benzoate, diallate, N,N-diethyl-meta-toluamide, diphenylamine, ethiolate, and hexachloracyclopentadiene.

Other pesticides reported in Anderson *et al.*[24], but not in the present GC-ECD method: carbaryl, carbofuran, chlorfenson, methylparathion, monocrotophos, naphthalene, pirimiphos methyl, profenofos, propoxur, sulfur, tetrafidon, and tetramethrin.

Verbal consent script for recruitment of an adult volunteer. This script was translated to French prior to approval by Oregon State University Institutional Review Board.

1. Purpose. The purpose of this research study, A Pilot Project to Evaluate the Utility of Wristbands for Evaluating Personal Exposure to Pesticides, is to help us understand possible human exposure to the pesticides applied to agricultural crops in Diender, Senegal.

2. Activities. At the beginning of the study you will be asked to complete a brief survey about your family farm, the crops grown, and pesticides applied. During the growing season you will be asked to wear a wristband that will provide information about pesticides you may be exposed to. A wristband will be worn for two separate five-day long periods. You will be asked to keep a checklist during the time you wear the wristband and record the time spent and activities conducted on the days that the wristband is worn. The wristband may not pick up certain pesticides even if they are present. If a pesticide does not show up on a wristband it does not mean it is safe to use or present in only small amounts.

3. Time. The survey will take ~15 minutes. The wristband part of the study will take a total of 10 days, divided into two five-day periods. You will be asked to maintain a checklist during the days you wear the wristband. The checklist should take no more than 10 minutes per day to complete. If your child is participating in this study you will be asked to keep a separate checklist for your child to record her/his activities and the hours worked.

4. Risks. There are no physical risks from wearing the wristband. People will be able to see the wristband and know you are part of the study. However your survey responses and the checklist information will be identified only with a code, not your name, and will be confidential. People will not be able to link your name with any of the information you provide. The results of your exposure, as determined from the analysis of the wristbands, will also be coded and remain confidential. Benefits. The information gathered from this research project will increase our understanding of pesticide exposure from farm work. The results will be provided to your community to assist you in reducing exposure by changing practices and personal behaviors but your name will not be linked to any of the information.

5. Confidentiality. All of the information you provide during this study will remain confidential. Your survey answers, checklist and the results from the wristbands you wear will carry a code instead of your name. Your survey answers, checklist, wristband information and the confidential document with your name and code will be kept in a secure, locked location and destroyed seven years after this study ends.

6. Contact Information. The research is being led by Oregon State University in cooperation with the UNFAO. If you have questions please contact Dr. Makhfousse Sarr during the study or in Dakar, Senegal at +221 33889164.

7. Voluntariness. Your participation in this study is voluntary. You may refuse to participate and you may discontinue participation at any time. You may refuse to answer any questions. Whether you decide to participate or not participate in this study, it will not affect your relationship with the researchers or UNFAO."

8. Funding. This study is being paid for by the United Nations Food and Agriculture Organization (UNFAO).

9. Comprehension. I want to be sure that you understand what the study involves. Would you please tell me what you think we are asking you to do?

10. Enrollment of Minor Child (0-17 years). Do we have your permission to enroll your child in this study? If you answer yes we will provide this information to your child and ask if he/she would like to participate in this study. If your child says "No" we will not enroll him/her.

Verbal consent script for recruitment of a child (0-17 years) volunteer. This script was translated to French prior to approval by Oregon State University Institutional Review Board.

1. We are asking you whether you want to be in a research study. Research is a way to test new ideas and learn new things. You do not have to be in the study if you do not want to. You can say Yes or No. If you say yes now, you can change your mind later.

2. Ask questions if you don't understand something. After all of your questions have been answered, you can decide if you want to be in this study or not.

3. This study is about the pesticides that are sprayed on your family farm and whether anyone in your family gets them on their skin.

4. We are asking you if you want to be in this study because sometimes you go in the field to help your family work on the crops.

5. If you take part in this study, we will ask you to wear a wristband for five days. Your parents will tell you when to wear the wristband and they will record what kinds of activities you do.

6. It is important for you to wear the wristband when your parents tell you to. The wristband will not be uncomfortable to wear.

7. We might learn things that will help other children someday. We are not sure that this will happen.

8. We will write a report when the study is over, but we will not use your name in the report.

9. I want to be sure you understand. Can you tell me what you think you will do during the study? Do you have any questions?

10. If you want to be in the study, say Yes. If you do not want to be in the study say No.

Text of the second follow-up results and implications report for participants

Wristband Project Summary
Diender, Senegal

The goal of this project was to better understand pesticide exposure, and reduce risks associated with exposure to pesticides. We also wanted to see how well the new wristband technology worked in detecting pesticides.

In November of 2014, 35 volunteer participants wore wristbands for two separate periods of up to 5 days each. The wristband absorbs many types of chemicals, including pesticides, in a similar way that skin does. We looked for 63 agricultural pesticides in the wristbands.

What did we find?

- Every wristband had between 2 and 10 different pesticides. We found a total of 23 different pesticides.
- The participants reported using 13 different pesticide active ingredients while wearing the wristbands. We were able to test for 6 of these, and all 6 were detected in at least one wristband.
- We found 19 more pesticides that no participants reported using.
- The most frequently found pesticides were deltamethrin (Decis), cypermethrin (Cypermet, Conquest, Phoenix, Tersen, Terpride), l-cyhalothrin (K-optimal, Lampride, Paschami), chlorpyrifos (Dursban), and esfenvalerate.
- The second page of this report shows your individual and community results. We cannot link health effects to the presence of any pesticide found in the wristbands, but if a pesticide was detected in your wristband it could indicate the potential for a health effect.

What do the results mean? We learned that exposure to pesticides is widespread. We need to understand how pesticide exposures happen in order to reduce risks because some pesticides are associated with negative health effects. We did not analyze for all the pesticides that you might be exposed to, so you are likely exposed more pesticides than this report shows.

What to do next? We will follow this research with a continuing pesticide risk management education program in Senegal, possibly including additional monitoring with wristbands. Goals for follow-up will be to better understand pathways of exposure of pesticides, and to work together on education and policy that will lead to reduced exposure, and reduced potential for health effects.

The more exposure you have to pesticides, the higher the likelihood of health effects. Pesticide exposure can happen through your skin, by inhaling vapor, through handling cigarettes and through your diet. You can reduce your exposure by:

- Thinking carefully about whether a pesticide is needed, and if so, which one is best to apply.
- Taking caution opening pesticide containers and fitting sprayers. This is where a high level of exposure can happen.
- Wearing protective clothing and use safety equipment, if available, when applying pesticides.
- Knowing and following application rates and re-entry intervals for the pesticides you are using. Do not enter fields immediately after pesticide applications.

Text of the second follow-up results and implications report for participants (Continued)

- Communicating with your neighbors—be aware of which products your neighbors use on fields near you and avoid fields that have been treated recently.
- Washing exposed skin and rinse your gloves and shoes after handling pesticides. Change clothes and wash separately.
- Storing pesticides in a safe place away from children. Dispose of unused pesticides properly, and never re-use pesticide containers for any purpose.
- Children and pregnant women should stay away from areas where pesticides are mixed and applied

Thank you for volunteering to help us learn more about the wristbands and understand pesticide exposure risks. If you have any questions, contact Makhfousse Sarr via [contact information withheld].

Text of the second follow-up results and implications report for participants (Continued)

This list below includes all of the 23 detected pesticides (left column) among all of the 35 participants (across the bottom). The pesticides are listed in order of those found most frequently, with those most frequently detected at the top of the list. Nineteen of these pesticides were not reported to be in use by any participant. These are marked with an asterisk. Gray shaded cells show the pesticides found in either of the wristbands worn by any of the participants.

You are participant number ____. The gray shaded squares in the column above your number show the pesticides found in either of your wristbands.